Synthesis and application of pi-conjugated polymers for organic solar cells

Citation for published version (APA):

DOI:
10.6100/IR691445

Document status and date:
Published: 01/01/2010

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.
Synthesis and Application of \(\pi\)-Conjugated Polymers for Organic Solar Cells

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op donderdag 9 december 2010 om 16.00 uur

door

Johannes Cornelis Bijleveld

egen te Rhenen
Dit proefschrift is goedgekeurd door de promotor:

prof.dr.ir. R.A.J. Janssen

Omslagontwerp: Johan Bijleveld, TEM afbeeldingen van lagen PDPPTPT:-[70]PCBM (zie Chapter 6) door Veronique Gevaerts.

Druk: Wöhrmann Print Service, Zutphen

A catalogue record is available from the Eindhoven University of Technicology Library.


The research was supported by a TOP grant of the Chemical Sciences (CW) division of The Netherlands Organisation of Scientific Research (NWO) and is part of the Joint Solar Programme (JSP). The JSP is cofinanced by the Foundation for Fundamental Research on Matter (FOM), Chemical Sciences of NWO, and the Foundation Shell Research.
# Table of contents

**Chapter 1. Introduction**

1.1 Background 2
1.2 Organic photovoltaic cells 3
1.3 Working principle of an organic solar cell 5
1.4 Device layout and performance parameters 6
1.5 Aim and scope 9
1.6 Designing polymers 9
1.7 Recent developments 12
1.8 Optimizing morphology 14
1.9 Outline 15
1.10 References 16

**Chapter 2. Copolymers of cyclopentadithiophene and electron-deficient aromatic units designed for photovoltaic applications**

2.1 Introduction 20
2.2 Results 22
   2.2.1 Synthesis 22
   2.2.2 Molecular weights 25
   2.2.3 Optical properties 25
   2.2.4 Redox properties 26
   2.2.5 Photovoltaic devices 28
2.3 Conclusions 31
2.4 Experimental 32
2.5 References 37

**Chapter 3. Controlling morphology and photovoltaic properties by chemical structure in copolymers of cyclopentadithiophene and thiophene segments**

3.1 Introduction 40
3.2 Results 41
   3.2.1 Synthesis 41
   3.2.2 Optical and electrochemical properties 42
   3.2.3 Photovoltaic devices 43
3.3 Conclusions 45
3.4 Experimental 46
3.5 References 48
# Chapter 7. Copolymers of diketopyrrolopyrrole and thienothiophene for photovoltaic applications

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1 Introduction</td>
<td>90</td>
</tr>
<tr>
<td>7.2 Results</td>
<td>91</td>
</tr>
<tr>
<td>7.2.1 Synthesis</td>
<td>91</td>
</tr>
<tr>
<td>7.2.2 Optical, electrochemical and electrical properties</td>
<td>93</td>
</tr>
<tr>
<td>7.2.3 Photovoltaic devices</td>
<td>95</td>
</tr>
<tr>
<td>7.3 Conclusions</td>
<td>98</td>
</tr>
<tr>
<td>7.4 Experimental</td>
<td>99</td>
</tr>
<tr>
<td>7.5 References</td>
<td>103</td>
</tr>
</tbody>
</table>

# Chapter 8. Furan and thiophene containing diketopyrrolopyrrole copolymers

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1 Introduction</td>
<td>106</td>
</tr>
<tr>
<td>8.2 Results</td>
<td>107</td>
</tr>
<tr>
<td>8.2.1 Synthesis</td>
<td>107</td>
</tr>
<tr>
<td>8.2.2 Optical, electrochemical and electric properties</td>
<td>109</td>
</tr>
<tr>
<td>8.2.3 Photovoltaic devices</td>
<td>111</td>
</tr>
<tr>
<td>8.3 Conclusions</td>
<td>115</td>
</tr>
<tr>
<td>8.4 Experimental</td>
<td>115</td>
</tr>
<tr>
<td>8.5 References</td>
<td>119</td>
</tr>
</tbody>
</table>

# Chapter 9. Epilogue

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1 Epilogue</td>
<td>122</td>
</tr>
<tr>
<td>9.2 References</td>
<td>126</td>
</tr>
</tbody>
</table>

# Summary

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summary</td>
<td>127</td>
</tr>
</tbody>
</table>

# Samenvatting

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samenvatting</td>
<td>130</td>
</tr>
</tbody>
</table>

# Curriculum vitae

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curriculum vitae</td>
<td>134</td>
</tr>
</tbody>
</table>

# List of publications

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of publications</td>
<td>135</td>
</tr>
</tbody>
</table>

# Dankwoord

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dankwoord</td>
<td>137</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction
1.1 Background

At present, most of the energy the population of the world consumes originates from fossil resources. Apart from the social awareness of the environmental impact caused by the burning fossil fuels, these sources will become increasingly shorter in supply. Eventually our global society has to convert to renewable forms of energy to maintain our wealth and life standards. Of all traditional and alternative energy resources like gas, oil, coal, wind, hydropower, and biomass, solar energy is most abundant.\(^1\) The power of the sunlight that reaches the earth’s surface amounts to 120,000 TW and vastly exceeds the world’s energy demand (~15 TW). The AM1.5G spectrum shown in Figure 1.1 shows the energy flux of the sunlight recorded on the ground passed through a mass of air that is 1.5 times as large as under normal incidence. This spectrum is referred to as the solar spectrum and it contains light with photon energies varying roughly from 4 down to 0.5 eV, with a broad peak around 2 eV. The total power of the AM1.5G spectrum is 1000 W m\(^{-2}\).

![Figure 1.1. The AM1.5G spectrum](image.png)

Already in 1839, the photovoltaic effect was demonstrated by Becquerel, who found an electrical current when illuminating a silver chloride covered platinum electrode in a liquid electrolyte.\(^2\) It took, however, more than one century before the first demonstration of an efficient photovoltaic device by Chapin et al., who built a 6% silicon-based solar cell in 1954.\(^3\) This landmark discovery has resulted in the large scale production of silicon solar cells, growing at an annual rate of ~40% lately and with an installed capacity of 7.5 GW in 2010. Silicon solar cells dominate the photovoltaic market and have reached maximum efficiencies of 25% on a lab scale and ~15% in commercial modules. Over the last decades
several technologies have emerged, such as those based on multicrystalline, microcrystalline, or amorphous silicon with record efficiencies of ~20%, ~10%, and ~10% respectively.\textsuperscript{4} Because crystalline silicon has an indirect band gap, crystalline silicon solar cells require relatively thick layers to absorb all the light. Combined with the high purity that is required for collecting the charges, semiconductor materials costs for modules are significant.

To reduce materials costs, there is a search for thin film solar cell materials with direct absorbers. Apart from amorphous silicon, this has resulted in cells that use thin films of e.g. copper-indium-gallium-diselenide (CIGS)\textsuperscript{5} or cadmium telluride (CdTe)\textsuperscript{6} as the active layer and still provide high efficiencies. However, for these materials abundance of feedstock and issues with toxicity remain.

An alternative option for solar cell applications that has emerged during the last two decades is the use of organic or polymer, i.e. carbon-based, materials. Dye-sensitized solar cells\textsuperscript{7} and bulk-heterojunction organic solar cells are at present the two most promising examples of this technology. Although progress has been enormous, both options still require further progress in terms of efficiency and stability.

Eventually, however, organic solar cells may offer the desired combination of being based on low cost, abundant, non-toxic materials together with high efficiencies and good stability. The impact for society would be gigantic. In this thesis new materials for bulk-heterojunction organic solar cells are explored to bring this goal closer to reality.

1.2 Organic photovoltaic cells

The discovery of electrical conductivity of polyacetylene after doping with iodine by Heeger, Macdiarmid, and Shirakawa\textsuperscript{8,9} was key to a new class of materials that is able to combine conducting and semiconducting properties with solubility and ease of processing. Conducting and semiconducting polymers use alternating single and double bonds to create π-conjugation in which high energy electrons are delocalized over large parts of the molecules or polymers chains. Such π-conjugated polymers exhibit semiconducting properties; they are able to transport charges and absorb light. Importantly, through the use of synthetic organic chemistry, the optoelectronic and physical properties of these conjugated polymers can be varied to an almost unlimited extent. Nowadays, applications of organic semiconductors are found in light-emitting diodes,\textsuperscript{10} field-effect transistors,\textsuperscript{11} and photovoltaic cells. The main advantage of organic polymer semiconductors over their inorganic counterparts is that they
can be processed from solution onto flexible substrates at low temperatures. In this way thin films can be made over large areas with very little material at a high speed.\textsuperscript{12} For solar cells in general, one of the challenges is the fast production of modules with minimal resources in terms of materials and power. This is potentially achievable with organic semiconductors.

In most inorganic semiconductors, absorbed photons give rise to electron-hole pairs, that are only weakly bound compared to the thermal energy ($kT$). By applying a field in these materials, for instance by creating a depletion zone at the interface of $n$-doped and $p$-doped layers, these charges can be spatially separated and collected at two electrodes to provide a photovoltage and a photocurrent, and hence convert light into electrical power.

The use of organic materials in solar cells complicates their operation because photoexcitation results in formation of excitons. Excitons are coulombically bound electron-hole pairs that can only be separated at energies much larger than $kT$,\textsuperscript{13} or in the presence of large electric fields. An elegant solution to this problem, inspired by natural photosynthesis, is using a combination of two materials with offset energy levels to split the hole and the electron. In the photoexcited state, charge separation is easily achieved at the interface of two materials because an electron can gain energy by a transfer from a material with a low electron affinity to another with a larger electron affinity, as illustrated in Figure 1.2b.

The first organic photovoltaic cell (OPC) that featured a considerable power conversion efficiency (PCE $\sim$1\%) consisted of a layer of copper phthalocyanine as $p$-type material covered with a layer of a perylene tetracarboxylic acid derivative as $n$-type material, sandwiched between two electrodes.\textsuperscript{14} Both layers were deposited by thermal evaporation and the flat interface between $p$-type and $n$-type material limited the interfacial area. This reduces the performance of the cell, because only excitons that are generated close to the interface can lead to charges, while excitons created at larger distances will decay via intrinsic processes and cannot contribute to charge formation. In this respect it is important to note that the diffusion length of excitons is often limited to 10 nm or less, such that only very thin layers next to the interface contribute to current generation. As these very thin layers are not optically dense, the efficiency of bilayer cells is often limited

A major breakthrough that can alleviate this problem, was accomplished by creating a bulk-heterojunction (BHJ) in which both materials are intimately mixed to create a large interface throughout the bulk of the active layer. The first OPCs with an photoactive BHJ layer that was processed from solution, used $p$-type polymers for their film forming abilities together with a $n$-type fullerene or second polymer.\textsuperscript{15,16} The BHJ layer is deposited from
solution, e.g. by spin coating or ink jet printing, where the quick evaporation of solvents secures a mixed morphology. The phases will undergo partial segregation due to the difference in surface energy with domains of (relatively) pure materials. In this way the area of the interface between $p$-type and $n$-type is much larger than in bilayer cells. At present, BHJ organic solar cells reach PCEs close to 7.5% in simulated AM1.5G light.\textsuperscript{17}

### 1.3 Working principle of an organic solar cell

To make rational improvements of organic solar cells it is instructive to have a more detailed insight into the operational principles of BHJ organic solar cells. The four elemental processes in an organic solar cell are illustrated in Figure 1.2.

![Figure 1.2. Working principle of an organic solar cell in a thin film device (a) and in a schematic energy diagram (b), where filled circles represent electrons, and open circles represent holes. 1. Exciton generation, 2. Diffusion of an exciton towards the interface, 3. Electron transfer, 4. Diffusion of charges to the electrodes.](image)

The first step, absorption of light by one of the two components, requires a photon that has enough energy to promote an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The minimum energy for excitation is called the optical band gap energy $E_g$. Absorbed photons with an energy larger than $E_g$ will create a ‘hot exciton’ that will thermalize via non-radiative decay processes to the HOMO and LUMO band edges. The extra energy of these photons is lost to heat. Once an electron is promoted to the LUMO it leaves a positively charged hole, in the HOMO. Because of the low dielectric constant in organic materials the electron and hole often remain coulombically bound as an exciton. The formed exciton can diffuse to the interface between $p$-type material and $n$-type material where exciton dissociation can take place by transferring the electron from the LUMO of the photoexcited $p$-type material to the energetically more favorable state in the LUMO of the $n$-type material.\textsuperscript{18} Note that the alternative process is also possible: a hole in the HOMO of the photoexcited $n$-type material can be transferred to the HOMO of the $p$-type material. In practice both routes will take place. The transfer of charges
at the donor-acceptor interface occurs on the femtosecond timescale\textsuperscript{19} and is much faster than the competing intrinsic processes such as photoluminescence, intersystem crossing, or thermal decay.\textsuperscript{20} Hence the quantum yield for charge generation can be essentially unity. The lifetime of an exciton, however, is very limited and so is the distance it can travel to reach an interface, which is typically found less than 10 nm.\textsuperscript{21-23} Once the charges are created, they have to separate and overcome their mutual coulomb attraction before they can be transported through the respective phases towards the electrodes where they are collected. In the separation and transport the charges are assisted by the built-in electric field in the device that is created by the different work functions of the electrode materials. As a consequence, the low work function electrode will collect the electrons and the high work function electrode will collect the holes. All the above processes have to occur with high quantum efficiencies to have an optimal performance of a solar cell.

Three types of \textit{n}-type materials are used in combination with organic \textit{p}-type material, being small molecules, polymers, and inorganic nanoparticles. The best performing devices are made with the small molecules based on fullerenes, [60]PCBM (Scheme 1.1), first synthesized in 1995.\textsuperscript{24} This thesis the focus on cells based on [60]PCBM and [70]PCBM as \textit{n}-type materials because they combine good solubility with a high electron mobility, both in devices\textsuperscript{25} and in FETs.\textsuperscript{26} The advantage of using [70]PCBM is the extra absorption in the visible range of the solar spectrum, caused by the lower symmetry of C\textsubscript{70}, and hence more allowed optical transitions compared to [60]PCBM, without significantly compromising in electron mobility.\textsuperscript{27}

\begin{itemize}
\item Three types of \textit{n}-type materials are used in combination with organic \textit{p}-type material, being small molecules, polymers, and inorganic nanoparticles.
\item The best performing devices are made with the small molecules based on fullerenes, [60]PCBM (Scheme 1.1), first synthesized in 1995.\textsuperscript{24}
\item This thesis focus on cells based on [60]PCBM and [70]PCBM as \textit{n}-type materials because they combine good solubility with a high electron mobility, both in devices\textsuperscript{25} and in FETs.\textsuperscript{26}
\item The advantage of using [70]PCBM is the extra absorption in the visible range of the solar spectrum, caused by the lower symmetry of C\textsubscript{70}, and hence more allowed optical transitions compared to [60]PCBM, without significantly compromising in electron mobility.\textsuperscript{27}
\end{itemize}

\textbf{Scheme 1.1.} Structure of [6,6]-phenyl-C\textsubscript{61}-butyric acid methyl ester [60]PCBM and [6,6]-phenyl-C\textsubscript{71}-butyric acid methyl ester [70]PCBM
1.4 Device layout and performance parameters

An OPC is schematically depicted in Figure 1.3. It is generally built on a transparent substrate, being glass or polymer like PET, with a pattern of a transparent, high work function electrode like indium tin oxide (ITO). The electrode is most often covered with a layer of poly(ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (Figure 1.3b) which serves as a hole conducting layer (HCL), smoothening the surface of the electrode and providing a good wettability for the active layer. The work function of the electrode is then pinned at the work function of the PEDOT:PSS layer which is 5.1 eV ± 0.2 eV. More recently metal oxides like NiO and MoO₃ have also been used as HCL. The active layer can be deposited from solution, e.g. by spin coating, spray coating, blade coating, gravure printing or ink jet printing which offers cheap and rapid processing. On top of the active layer, a low work function electrode, often consisting of calcium and aluminum or lithium fluoride and aluminum is applied by thermal evaporation.

Figure 1.3. Schematic picture of an OPC (a) and the molecular structure of PEDOT:PSS (b).

The performance of a solar cell is measured using voltage sweeps and recording the current density through a cell in dark and under illumination. Without illumination, OPCs behave like a diode, exhibiting a very low current density in reverse bias and a high current density in forward bias. Under illumination the solar cell is generating power in the fourth quadrant of a $J-V$ curve, a typical example is given in Figure 1.4.
The open circuit voltage ($V_{oc}$) and short circuit current density ($J_{sc}$) are obtained from the intersection of the graph with the axes in the $J$-$V$ diagram (Figure 1.4). The output power of the cell ($P_{out}$) is given by the product of $J$ with $V$ for any point on the curve. In the maximum power point (MPP) this product maximizes and $P_{out}$ is given by:

$$P_{out} = J_{MPP}V_{MPP}$$

Where $J_{MPP}$ is the current density in the MPP and $V_{MPP}$ is the voltage in the MPP. The ratio of $J_{MPP}V_{MPP}$ and $V_{oc}J_{sc}$ is called the fill factor (FF) (see also Figure 1.4):

$$FF = \frac{J_{MPP}V_{MPP}}{J_{sc}V_{oc}}$$

Typically, the $J$-$V$ curves are measured under simulated solar light and provide an estimate of the performance of the cell. The spectrum of a white light lamp is not exactly the same as the AM1.5G spectrum and causes that the measured $J$-$V$ curve is different from what is expected in solar light. Provided the lamp spectrum is close to the AM1.5G spectrum, the most significant difference is in $J_{sc}$. Alternatively, the $J_{sc}$ that is expected for AM1.5G illumination can also be estimated by measuring the monochromatic external quantum efficiency (EQE($\lambda$)), which is defined as the number of charges collected at short circuit per incident photon when monochromatic light is used. By convoluting the EQE with the AM1.5G spectrum and integrating over all wavelengths, a more precise estimate for the $J_{sc}$
can be obtained. With this extra correction the power conversion efficiency (PCE) of an OPC is given by:

\[
PCE = \frac{P_{\text{out}}}{P_{\text{in}}} = \frac{FFJ_{\text{oc}}V_{\text{oc}}}{P_{\text{in}}} = \frac{FFV_{\text{oc}}}{P_{\text{in}}} \frac{e}{h\lambda} \int \text{EQE}(\lambda)E_{\text{AM1.5G}}(\lambda)\lambda d\lambda
\]

Where \( P_{\text{in}} \) is the power density of the incident light, \( e \) the elementary charge, \( h \) Planck’s constant, \( c \) the speed of light, \( \lambda \) the wavelength of the light, and \( E_{\text{AM1.5G}}(\lambda) \) is the power of the AM1.5G spectrum per wavelength of light. Because the EQE is measured with low monochromatic light intensity, EQE measurements have to be done with appropriate bias light to bring the cell to illumination conditions that are equivalent to AM1.5G.

### 1.5 Aim and scope

The research described in this thesis has the purpose to explore the possibilities to improve the performance of polymer:fullerene BHJ solar cells. This is primarily achieved by changing the molecular structure of polymers to optimize the optical band gap, the HOMO and LUMO levels, and the charge carrier mobility. It also involves addressing issues like molecular weight, solubility, miscibility with fullerenes and exploring processing conditions to reach the optimum degree of phase separation and morphology in the blend.

### 1.6 Designing polymers

During initial stages of the developing the field of polymer solar cells in the 90s, the most used material combination is a poly(p-phenylenevinylene),\(^{29}\) with poly[2-methoxy-5-(3',7'-dimethyl-octyloxy)-2,4-phenylene vinylene] (MDMO-PPV, 1 Scheme 1.2) as prime example, blended with [60]PCBM. MDMO-PPV:[60]PCBM blends have reached efficiencies of 2.5%.\(^{27,30,31}\) Using [70]PCBM the efficiency of these devices was further enhanced to 3%.\(^{27}\) The second work horse of OPC research is poly(3-hexylthiophene) (P3HT, 2 Scheme 1.2). P3HT blended with [60]PCBM has reached an PCE of 4-5%.\(^{32-35}\)

Design rules for efficient electron donor and acceptor material combinations were early recognized\(^{36}\) and have been outlined in more detail by Scharber et al.\(^{42}\) for PCBM. Here a similar, but more general, approach is followed. We assume that the energy levels of the
HOMO and LUMO for the donor:acceptor blend are as shown in Figure 1.5a. Within this approximation, photoinduced charge transfer will occur if there is a net gain in energy $\alpha$ (or $\alpha'$) for electron (or hole) transfer, upon excitation of the donor (or acceptor). Note that $\alpha$ (or $\alpha'$) actually represents an energy loss in the operation of the device. The open-circuit voltage of a bulk heterojunction solar cell is related to energy difference $\beta$ between the HOMO of the electron donor and the LUMO of the acceptor.\textsuperscript{37-39} In practice, the actual value is about 0.4 V less than $\beta$.\textsuperscript{37} The smallest optical gap of donor ($\alpha + \beta$) or acceptor ($\alpha' + \beta$) determines the onset of absorption of the materials. Within this simplified energy level diagram it is then straightforward to calculate the maximum attainable current of an organic donor:acceptor solar cell with $\alpha$ (or $\alpha'$) as a parameter by integrating photons of the AM1.5G spectrum above the optical gap $\alpha + \beta$ (or $\alpha' + \beta$) that are absorbed, which is the upper limit for the $J_{sc}$. An estimate of the maximum PCE (Figure 1.5b) is obtained by arbitrarily assuming an external quantum efficiency (EQE) of 0.65 over the whole absorption range, assigning an energy equal to $\beta - 0.4$ eV to all generated charges, and assuming a FF = 0.65. Deviations from these values of FF and EQE will linearly influence the performance of a cell. Optimization of the FF involves tuning of the charge carrier mobilities of both donor and acceptor phase. For conjugated polymers, optimizing the $\pi$-stacking of the chains, and hence the orbital overlap and interchain charge transport are essential to optimize the FF.

Figure 1b clearly identifies $\alpha$ (or $\alpha'$) as a crucial parameter and shows that ultimately the efficiency drops at low and high values of the optical gap, because of a loss in voltage or a loss in current, respectively. In general it is assumed that a substantial offset $\alpha$ (or $\alpha'$) = 0.3-0.4 eV\textsuperscript{40-42} is required to provide quantitative charge transfer. This would place the optimum band gap of conjugated polymers for bulk heterojunction solar cells in a broad range between 1.35 and 1.8 eV. With some materials, working polymer solar cells are claimed with $\alpha$ as low as 0.1 eV\textsuperscript{43} but only very few of these devices are known and none of them display a high PCE. In principle, Figure 1.5b can be used to gauge achievable power conversion efficiencies for any donor:acceptor materials combination when $\alpha$, $\alpha'$, and $\beta$ are known.
Figure 1.5. Simplified presentation of the frontier orbital energy levels in a bulk heterojunction solar cell, defining the offset energies $\alpha$, $\alpha'$, and $\beta$. (b) AM1.5G energy conversion efficiency of bulk heterojunction solar cells as function of $\alpha$ (or $\alpha'$) and $\beta$, assuming that EQE = 0.65 for energies larger than the optical band gap, FF = 0.65 and $eV_{oc} = \beta - 0.4$ eV.

The position of P3HT ($E_g \sim 1.9$ eV, $\alpha \sim 0.9$ eV) in the Figure 1.5 predicts a maximum efficiency of $\sim 5\%$, close to what has been achieved.$^{34,35}$

Figure 1.5 also shows that with polymers with a smaller band gap in the range of 1.5 eV and lower values for $\alpha$ (or $\alpha'$) much higher efficiencies can be expected. One way of accomplishing a smaller band gap energy is to decrease the bond length alternation between monomers in a chain. This can be achieved by stabilizing the so-called quinoidal structure, the first excited state, decreasing the energy difference between ground state and excited state. An example of a small band gap polymer is polyisothianaphthene$^{44}$ (PITN, Figure 1.6a) displaying a band gap of $\sim 1$ eV, where the quinoid structure is stabilized by the benzene ring fused to the thiophene ring.

Another way to accomplish lower $E_g$ in organic materials is incorporating electron rich (donor) and electron poor (acceptor) moieties in one molecule or repeating those in a polymer chain.$^{45}$ The principle of using electron rich and electron poor units to decrease the band gap is depicted in Figure 1.6. By making use of the HOMO and LUMO of the respective units, the resulting HOMO and LUMO of the material lay closer together, decreasing the effective band gap.
Figure 1.6. Resonance structures of PITN where the band gap is lowered by the lowering of the bond length alternation (a) and simplified energy level diagram in a donor acceptor molecule, where the effective band gap is lowered compared to these of the separate molecules (b).

1.7 Recent developments

One of the first polymers used for solar cells that successfully used the approach depicted in Figure 1.6b was poly[2,5-bis(-2-thienyl)-N-dodecylpyrrole-alt-4,7-dibromo-[2,1,3]-benzothiadiazole] (PTPTB, 3 Scheme 1.2),\(^3\) displaying a band gap of 1.6 eV, and when applied in an OPC reaching an efficiency of \(~1\%)\).

The same approach used in PTPTB, was also applied in the closely related poly[2,7-(9,9-dioctylfluorene)-alt-5,5-(4\(^`\),7\(^`\)-di-2-thienyl-2\(^`\),1\(^`\),3\(^`\)-benzothiadiazole)] (APFO-3, 4 Scheme 1.2)\(^3\) and poly[2,7-(9,9-didecylfluorene)-alt-5,5-(4\(^`\),7\(^`\)-di-2-thienyl-2\(^`\),1\(^`\),3\(^`\)-benzothiadiazole)] (PFTBT, 5 Scheme 1.2)\(^4\), which both have a similar band gap energy \(E_g\) as P3HT, but display a significantly different oxidation potential. The value of \(\alpha \sim 0.5\ eV\) for APFO-3 and PFTBT predicts a maximum value of PCE = 6.5\%. Despite the fact that the best efficiencies for these polymers are limited to maximum 4.2% with PFTBT\(^4\), this was the first successful approach to improve the cells made with P3HT.
The first new specifically designed polymer that exceeds the 5% power conversion efficiency that can be reached with P3HT, is poly(4,4-di(2-ethylhexyl)-4H-cyclopenta-[2,1-b:3,4-b’]dithiophene-alt-[2,1,3]-benzothiadiazole)\textsuperscript{49} (PCPDTBT, Scheme 1.2). When blended with [70]PCBM it provides a power conversion efficiency of PCE = 5.5%\textsuperscript{50} With an optical band gap of \(E_g = 1.40\) eV in the film and an offset between the LUMOs corresponding to \(\alpha = 0.55\) eV, the maximum efficiency that can be expected for PCPDTBT:PCBM from Figure 1.5 is about PCE = 6.2%. Figure 1.5 shows, however, that higher efficiencies can be expected for materials with slightly wider band gaps and that further gain may be expected when \(\alpha\) becomes smaller, to further reduce the difference of \(~0.75\) eV between \(E_g\) (1.40 eV) and \(E_{V_{oc}}\) (0.65 eV) for PCPDTBT:PCBM.

Another polymer that displays a similar band gap energy as P3HT (\(E_g \sim 1.9\) eV) is poly[N-9′′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)]\textsuperscript{51} (PCDTBT, Scheme 1.2). PCDTBT has a lower value of \(\alpha \sim 0.6\) eV compared to P3HT when combined with PCBM, which can result in a higher efficiency. The improved energy levels compared to P3HT lead to maximum expected efficiency PCE = \(~6.5\)%, similar to PFTBT and APFO-3, but higher than for P3HT and PCPDTBT. A PCE = 6.1\% for PCDTBT:PCBM has been reported\textsuperscript{52}.

Recently, a polymer based on diketopyrrolopyrrole (DPP) was reported, poly[3,6-bis-(4′-dodecyl-[2,2′]bithiophenyl-5-yl)-2,5-bis-(2-ethylhexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione] (PBBTDPP2, Scheme 1.2) exhibiting \(E_g = 1.4\) eV and \(\alpha \sim 0.3\) eV, which would place this polymer close to the optimal position in Figure 1.5. The predicted maximum PCE of 9.5\% has not yet been reached, with a reported PCE = 4.0\%.\textsuperscript{53} The difference is due to a low (~40\% in the maximum) EQE of the device.

The highest published PCE =7.4\% for a polymer:PCBM OPC has been obtained for poly[4,6-(octyl-3-fluorothieno[3,4-b]thiophene-2-carboxylate)-alt-2,6-(4,8-dioctylbenzo[1,2-b:4,5-b′]dithiophene)] (PTB7, Scheme 1.2) and [70]PCBM.\textsuperscript{17} With \(E_g \sim 1.65\) eV and \(\alpha \sim 0.35\) eV an efficiency of PCE = 9\% would be feasible.
1.8 Optimizing morphology

The morphology of the BHJ layer has a very large effect on the performance of the solar cell. After deposition, the morphology of the active layer is usually not in a thermodynamically stable state and very often not optimal in terms of solar cell performance. Careful optimization of the processing conditions (concentration, solvent, temperature, donor acceptor ratio) of the layers is crucial to obtain the best cell. Moreover, even for the same polymer, properties like molecular weight, polydispersity, regiochemistry, and end groups can be determining factors for the efficiency of BHJ solar cells. The morphology of the active layer can also be modified by post-deposition methods like thermal or solvent annealing. Recently, the use of solvent mixtures, slow drying of the active layer, and addition of co-solvents like oleic acid or nitrobenzene have shown significant effects.

All the above treatments improve the performance of the P3HT:PCBM OPCs, but this does not hold for other material combinations in general. As a consequence, for each polymer:PCBM combination, deposition conditions and post production treatments have to be optimized independently.

The method of influencing the morphology of the active layer by adding a co-solvent, which is a good solvent for PCBM and a bad solvent for the polymer used, was discovered to work not only for P3HT, but also for PCPDTBT. This method of changing the morphology was explained by the fact that the co-solvent remains in the drying layer longer than the main solvent, forcing the polymer to form semi-crystalline domains, while the PCBM stays mobile for a longer time, inducing larger crystals. The effect of the co-solvent was a net increase in the domain size of both polymer and PCBM. Later, the same processing technique was applied to a close structural analog of PCPDTBT and here the effect was reversed: the domains were decreased in size upon addition of co-solvent to the spin coating mixture.

From these two examples it is clear that creating a morphology during spin coating is the result of a complex interplay between two processes: solidification of the polymer into a gel or semicrystalline state and crystallization of the PCBM. The timescales at which both processes occur will ultimately determine the morphology of the active layer. Co-solvents can have a major influence on the eventual morphology of the active layer and on the performance of an OPC.
1.9 Outline

This thesis describes the results of exploring and synthesizing new conjugated donor polymers for use in organic solar cells in combination with PCBM.

In Chapter 2 the electron poor unit in CPDT based copolymers is changed to increase the efficiency using predictions based on Figure 1.5. Several copolymers of CPDT and different acceptors were synthesized and evaluated. This resulted in materials that reach higher performance than PCPDTBT when compared under identical conditions. The new copolymers in Chapter 3 are also based on CPDT and by introducing un-substituted oligothiophene units of different lengths, it is shown that it is possible to influence the film formation of these materials, mixed with PCBM. Based on AFM images we conclude that by reducing the amount of side chains on the conjugated polymer, the sequence of polymer solidification and PCBM crystallization can be reversed.

In Chapter 4, the limits of the $V_{oc}$ are explored with a polymer that exhibits a very high oxidation potential. This polymer features a benzothiadiazole unit, alternating with a substituted thieno[3,2-b]thiophene (TT), where the twist in the backbone is causing the high oxidation potential. Despite a moderate PCE, the obtained $V_{oc}$ of 1.15 V compares to the highest reported for polymer:PCBM films, and approaches the limits of what seems possible with solar cells based on PCBM.

The research presented in Chapters 5 and 6 aims at improving OPCs with DPP-based polymers. In Chapter 5 the importance of molecular weight is demonstrated for a polymer in which DPP is alternating with terthiophene (PDPP3T), together with using 1,8-diiodooctane (DIO) as a co-solvent during processing a PCE of 4.7% is obtained for PDPP3T:[70]PCBM. Furthermore, the photophysical processes occurring within PDPP3T:PCBM films processed with and without the co-solvent are compared. Because of the high ambipolar mobilities measured in a FET, it was possible to construct a CMOS like inverter with PDPP3T. Chapter 5 deals with a similar polymer as PDPP3T, in which the middle thiophene unit is replaced by phenylene (PDPPTPT). PDPPTPT displays a higher voltage and higher PCE than PDPP3T. Here the effect of DIO is even more clearly illustrated with TEM images of layers. Solar cell performance of up to 5.5% efficiency has been achieved.

The combination of TT and DPP units in one polymer is evaluated in Chapter 7. Different substitution patterns of side chains are presented, which are reflected in charge
carrier mobility and photovoltaic performance. Also a comparison is presented with a polymer that contains more un-substituted thiophenes in the backbone.

The effect of replacing thiophene rings for furan in a DPP-based polymer is presented in Chapter 8. Despite lower molecular weights these polymers show significant PCEs. The performance of these materials is not yet on the level of the thiophene-based polymers, but the absorption, energy levels and charge carrier mobility are putting furan forward as a good alternative for thiophene.

At the end of the thesis a short epilogue is presented that relates the most important findings reported in this thesis to recent developments in the fields and identifies possible new directions for polymer design.

1.10 References

(2) A. E. Becquerel, Comptes Rendus, 1839, 9, 561.
Introduction


Chapter 1


Abstract

Alternating copolymers based on cyclopentadithiophene (CPDT) and five different electron deficient aromatic units with reduced optical band gaps have been synthesized via Suzuki coupling. All polymers show a significant photovoltaic response when mixed with a fullerene acceptor. The frontier orbital levels of the new polymers are designed to minimize energy losses by increasing the open-circuit voltage with respect to the optical band gap, while maintaining a high coverage of the absorption with the solar spectrum. The best cells are obtained for a copolymer of CPDT and benzooxadiazole (BO) with a band gap of 1.47 eV. This cell gives a short-circuit current of 5.4 mA cm$^2$, an open-circuit voltage of 0.78 V, and a fill factor of 0.6 resulting in a power conversion efficiency of about 2.5%.

* This work has been published:
2.1 Introduction

Thin film bulk-heterojunction polymer solar cells offer an opportunity for low-cost renewable energy production. These devices use a phase separated blend of two organic semiconductors with offset energy levels that lead to an intermolecular charge transfer between the two components after photoexcitation.\(^1\) Blends of conjugated polymers as donor and fullerene derivatives as acceptor have emerged as a very successful combination. The power conversion efficiency (PCE) of these devices depends on the quantum and energy efficiency by which photons from the sun can be converted into charges in an external circuit. To be efficient, absorption of light, as well as charge generation, transport and collection all have to occur with high quantum efficiency (i.e. converting all photons into electrons) and with minimal losses in energy (i.e. keeping the photovoltage close to the photon energy). This complex sequence of events is controlled by several material and device parameters of which optical absorption, relative position of energy levels, charge carrier mobility, and nanoscale morphology are probably most important. The PCE of these devices has recently reached levels exceeding 7% in single junctions.\(^2,3\)

New materials that are able to convert a large fraction of solar spectrum have contributed significantly to improving the energy conversion efficiency.\(^4-14\) The main strategy to control the band gap of conjugated polymers is incorporating electron rich (donors) and electron poor groups (acceptors) in an alternating fashion in the main chain of the polymer.\(^15\)

The energy conversion efficiency of a photovoltaic cell is set by the product of short-circuit current density (\(J_{sc}\)), fill factor (FF), and open-circuit voltage (\(V_{oc}\)) relative to the light intensity. Design rules for electron donor and acceptor materials with higher performance have been outlined by Scharber et al.\(^16\) and in Chapter 1 of this thesis.

One of the best bulk heterojunction solar cells up to now, with a reported PCE of 5.5%,\(^2\) has an active layer that consists of poly(4,4-di(2-ethylhexyl)-4H-cyclopenta-[2,1-b:3,4-b']dithiophene-alt-[2,1,3]-benzothiadiazole) (PCPDT-BT, Scheme 2.1) and [6,6]-phenyl-C\(_{71}\)-butyric acid methyl ester ([70]PCBM). With an optical band gap of \(E_g = 1.40\) eV in the film and an offset between the LUMOs of the polymer and PCBM corresponding to \(\sim 0.55\) eV,\(^11\) the efficiency that can be expected determined for PCPDT-BT:PCBM is about 6.2%. From Figure 1.5 of Chapter 1, however, we know that higher efficiencies can be expected for materials with slightly wider band gaps and that further gain may be expected when the
difference between the LUMOs becomes less to reduce the difference of ~0.75 eV between $E_g$ (1.40 eV) and $eV_{oc}$ (0.65 eV) for PCPDT-BT:PCBM.

Recently, a significant number of new alternating copolymers with CPDT and an electron poor moiety displaying a small band gap (<1.6 eV) have been reported. Moulé et al.\textsuperscript{17} have described copolymers of CPDT alternating with thiophene-benzothiadiazole-thiophene (PCPDT-TBTT) and with bis(ethylhexyl)-quinoxaline (PCPDT-Q') that both have higher band gaps ($E_g = 1.57$ eV) but unfortunately do not improve $V_{oc}$ (0.60 and 0.64 V, respectively) when combined with [60]PCBM. You et al.\textsuperscript{18} have synthesized polymers of CPDT alternating with benzodithiophene (BDT), naphthodithiophene (NDT), and dithienoquinoxaline (QDT) with optical band gaps in the range from 1.9–2.0 eV, but also here the $V_{oc}$ (0.47–0.53 V) of cells with [60]PCBM decreased rather than increased compared to PCPDT-BT. Furthermore, Yang et al.\textsuperscript{19} combined CPDT with benzoselenadiazole (BSe) to achieve a reduced band gap ($E_g = 1.35$ eV) polymer that gave $V_{oc} = 0.53$ V and PCE = 0.89\% in combination with [70]PCBM. Finally, Chen et al.\textsuperscript{20} synthesized copolymers of CPDT with thiophene-acceptor-thiophene units, the acceptor being thienopyrazine, benzothiadiazole, quinoxaline and dithienoquinoxaline, but the $V_{oc}$ (<0.64 V) in combination with [70]PCBM was not increased. Each of these examples shows that substantial changes in materials properties can be achieved, but that improving $V_{oc}$ with respect to $E_g$ has not been achieved.

In this chapter a series of alternating co-polymers is presented based on a CPDT as electron rich unit and different electron poor units (Scheme 2.1), designed to control the band gap $E_g$ and the LUMO - LUMO offset.

Scheme 2.1. Alternating copolymers of cyclopenta-[2,1-b:3,4-b']dithiophene (CPDT) with quinoxaline (Q), benzooxadiazole (BO), benzothiadiazole (BT), bis(benzothiadiazole) (BBT), and thienopyrazine (TP).
The polymers, including PCPDT-BT, were synthesized via a palladium catalyzed Suzuki polymerization and have been analyzed for their optical, electrochemical, and photovoltaic properties. In the following we demonstrate that out of the series of CPDT-X polymers shown in Scheme 2.1, two materials, PCPDT-BO and PCPDT-BBT, have more favorable energy levels and show promising photovoltaic response when mixed with [60]PCBM, equivalent or better than that of PCPDT-BT, when prepared under similar conditions.

2.2 Results

2.2.1. Synthesis

To obtain the alternating copolymers we employed a Suzuki polycondensation reaction using the bisboronic ester of CPDT that was synthesized as shown in Scheme 2.2.

First, 3-bromothiophene (1) was lithiated and subsequently coupled with 3-thiophenecarboxaldehyde (2) to yield di-3-thienylmethanol (3). Without further purification 3 was reduced with LiAlH₄ to yield di-3-thienylmethane 4, which could be isolated more easily than 3. The overall yield of the first two steps is about 88%. Direct bromination of 4 with N-bromosuccinimide (NBS) proceeded selectively at the 2 and 2' positions to yield the dibrominated dithienomethane 5. The subsequent intramolecular Ullmann coupling to 4H-cyclopenta[2,1-b:3,4-b']dithiophene (CPDT, 6) proceeded with microwave irradiation within
three hours at moderate yield (~40%). Recrystallization from methanol gave 6 as off-white flakes. Alkylation of 6 was achieved in the presence of a base and 2-ethylhexylbromide to give 7. Bromination of 7 with NBS in DMF gave 8. Finally, monomer 9 was obtained by reacting 8 with \( n \)-butyllithium and 2-isopropoxy[1,3,2]dioxaboralane in dry conditions. Bisboronic ester 9 was subjected to preparative recycling GPC in chloroform to remove traces of the corresponding monoboronic ester and enable high molecular weights in the Suzuki polymerization reactions.

The electron poor moieties to be copolymerized with 9 were synthesized according to Scheme 2.3.

\[
\begin{align*}
\text{Scheme 2.3. Synthesis of electron deficient co-monomers 12, 14, 18 and 21.}
\end{align*}
\]

Reduction of dibromobenzothiadiazole 10 with LiAlH yielded diamine 11, which was used without purification in a condensation reaction with aqueous glyoxal solution to yield monomer 12 as white needles. Bromination of benzooxadiazole 13 was carried out with elemental bromine according to a literature procedure without solvent in a melt of 13,\(^{13}\) catalyzed by iron powder to yield monomer 14 as yellow crystals after recrystallization. Monobromination of benzothiadiazole 15 had only moderate yields (~30%). The monobrominated product 16 was used in a copper and zinc mediated coupling to yield dibenzothiadiazole 17. Subsequent iodination with iodine in the presence of AgSO\(_4\) yielded a yellow powder that was recrystallized from toluene to give monomer 18. This compound was only sparingly soluble in common organic solvents such as chloroform and THF. The
commercial available diamine 19 was directly converted via a condensation coupling to thienopyrazine 20. The product was brominated with NBS to yield monomer 21 as a yellow solid, which had a limited stability.

All the dihalogenated monomers 10, 12, 14, 18 and 21 were copolymerized with 9 in a Suzuki type polycondensation to yield the desired copolymers, depicted in Scheme 2.1. The polymerizations were carried out for three days in degassed toluene with K₂CO₃ as base. As a consequence, water and a phase transfer catalyst, Aliquat 336, were needed. After workup, soxhlet fractionation with hexane and chloroform yielded the chloroform soluble fractions of the polymers PCPDT-Q, PCPDT-BO, PCPDT-BT, and PCPDT-BBT as dark blue powders. PCPDT-TP was obtained as a dark green powder. The typical yield of the polymerizations was in the range of 30-70%. The molecular structure of the polymers was verified by ¹H-NMR.

### 2.2.2. Molecular weights

Molecular weights of the polymers have been determined with GPC in ortho-dichlorobenzene (o-DCB) at 80 °C relative to polystyrene standards, except for PCPDT-TP which adsorbed to the column material in o-DCB and was therefore measured in THF at room temperature. The number averaged molecular weights (Mₙ) of the polymers range from 4300 to 21000 g mol⁻¹ (Table 2.1), with polydispersity indices in the range of 1.4, except PCPDT-BO which had a broader molecular weight distribution (PDI = 1.95). The molecular weight of PCPDT-BBT is substantially lower, the Mₙ being 4300 g mol⁻¹, which is probably due to the limited solubility of longer polymer chains in the reaction mixture. All the synthesized polymers were very soluble in chlorobenzene (>5 mg ml⁻¹).

<table>
<thead>
<tr>
<th></th>
<th>Mₙ (g mol⁻¹)</th>
<th>Mₘ (g mol⁻¹)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCPDT-Q</td>
<td>10400</td>
<td>15000</td>
<td>1.44</td>
</tr>
<tr>
<td>PCPDT-BO</td>
<td>21000</td>
<td>41000</td>
<td>1.95</td>
</tr>
<tr>
<td>PCPDT-BT</td>
<td>15000</td>
<td>22000</td>
<td>1.47</td>
</tr>
<tr>
<td>PCPDT-BBT</td>
<td>4300</td>
<td>5900</td>
<td>1.37</td>
</tr>
<tr>
<td>PCPDT-TP</td>
<td>8900</td>
<td>12200</td>
<td>1.38</td>
</tr>
</tbody>
</table>
2.2.3. Optical properties

Normalized optical absorption spectra of the CPDT-X polymers in \(\nu\)-DCB solution and as thin films on glass (Figure 2.1) clearly show that these materials exhibit a strong absorption band in the long wavelength region extending beyond 1000 nm for PCPDT-TP. The optical gaps \(E_g\) in solution and film have been determined from the crossing of the tangent in the inflection point with wavelength axis (Table 2.2). In thin films all polymers, except PCPDT-TP, exhibit optical gaps close to the ideal value of 1.5 eV (c.f. Figure 1.5 of Chapter 1), with gaps of Q and BBT being slightly larger than with BO and BT. The fact that the optical gap of PCPDT-BBT with the bis-BT moiety between the CPDT units is higher than that of PCPDT-BT, which has a single BT is tentatively attributed to an unfavorable steric interactions between the neighboring BT units in BBT that leads to twisting around their interring bonds, causing reduced conjugation. The thienopyrazine extends the absorption of PCPDT-BT well beyond 1 µm and creates an optical gap that is smaller than other CPDT-X polymers.17-20

![Figure 2.1](image-url). Normalized optical absorption spectra of CPDTS-X in solution (a) and as thin film on glass (b).
2.2.4. Redox properties

The electrochemical properties of the polymers were determined with cyclic voltammetry in o-DCB using TBAPF₆ as electrolyte under an inert atmosphere. The onsets of the electrochemical reduction ($E_{\text{red}}^{\text{sol}}$) and oxidation ($E_{\text{ox}}^{\text{sol}}$) waves of the CPDT-X polymers are listed in Table 2.2 and shown in Figure 2.2.

There is quite some spread between the oxidation potentials among the five polymers. PCPDT-TP is most readily oxidized. The oxidation potentials of PCPDT-BO and PCPDT-BBT are found at more positive values than for PCPDT-BT or PCPDT-Q, which is beneficial for reaching a higher open-circuit voltage in photovoltaic devices (vide infra). The reduction potentials vary less. For PCPDT-BBT the reduction potential is only slightly less than for PCPDT-BT, showing that the neighboring electron deficient units do lead to better accepting properties but that the effect is small because of the steric hindrance between the two BT units (vide supra).

For a copolymer with alternating electron rich (CPDT) and electron deficient units (X), one might expect that by changing X, only the LUMO would be affected. However, Figure 2.2 clearly shows that the X unit in PCPDT-X can have an equally large effect on the HOMO ($E_{\text{ox}}^{\text{sol}}$) level of the polymer as on the LUMO ($E_{\text{red}}^{\text{sol}}$) level. For X = TP the effect on the HOMO level is even much more pronounced. Apparently, TP is both a better donor and a better acceptor than CPDT. The reduction of the band gap of PCPDT-TP seems primarily caused by introducing TP units, and less by the alternation of CPDT and TP. This is in accordance with the fact that the band gap of polythienopyrazine (poly-TP)²¹,²² is lower than that of PCPDT-TP. Similar arguments, although less evident, will apply to the other PCPDT-
X polymers. This shows that naming these materials alternating electron rich and deficient monomers is maybe less appropriate.

| Table 2.2. Optical and redox potentials of PCPDT-X |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------|
|                | $E_g^{sol}$      | $E_{ox}^{sol,a}$| $E_{red}^{sol,a}$| $E_{cv}^{sol,a}$| $\Delta E^{sol}$| $E_{\text{film}}$| $\alpha^b$| $\beta^b$ |
|                | (eV)             | (V)             | (V)             | (V)             | (V)             | (eV)        | (eV)       | (eV)       |
| PCPDT-Q        | 1.66             | -0.06           | -1.80           | 1.74            | 0.08            | 1.54        | 0.73       | 1.01       |
| PCPDT-BO       | 1.54             | +0.16           | -1.52           | 1.68            | 0.14            | 1.47        | 0.45       | 1.23       |
| PCPDT-BT       | 1.55             | -0.07           | -1.67           | 1.60            | 0.05            | 1.43        | 0.60       | 1.00       |
| PCPDT-BBT      | 1.69             | +0.22           | -1.60           | 1.82            | 0.13            | 1.53        | 0.53       | 1.29       |
| PCPDT-TP       | 1.24             | -0.39           | -1.73           | 1.34            | 0.10            | 1.18        | 0.66       | 0.68       |
| PCBM           | -1.07            |                |                |                |                |            |            |            |

$^a$) Electrochemical potentials are vs. Fe/Fe$^+$. $^b$) As defined in Chapter 1

The electrochemical gap defined as $E_{cv}^{sol} = e(E_{red}^{sol} - E_{ox}^{sol})$ (with e the charge of the electron) follows the same trend as the optical gap ($E_g^{sol}$) measured in the same solvent but is consistently somewhat larger by $\Delta E^{sol} = 0.08-0.14$ eV (see Table 2.1). Such small difference is not unexpected because for determining $E_{ox}$ and $E_{red}$ electrons are extracted or added, whereas the optical gap provides the energetic difference for an intramolecular, excitonic state, with the hole and the electron stabilized by Coulomb attraction.

Taking the onsets of the oxidation and reduction potentials as a measure for the HOMO and LUMO levels, it is possible to estimate the LUMO- LUMO offset ($\alpha$) and the difference between HOMO of the polymer and LUMO of the PCBM ($\beta$) values for these polymers as defined in Chapter 1 (see Table 2.2), by comparing with the reduction of [60]PCBM (-1.07 V vs. Fe/Fe$^+$). The resulting values for $\alpha = e(E_{red} - 1.07)$ and $\beta = e(-1.07 - E_{ox})$ are collected in Table 2.2 and reveal that for each CPDT-X polymer photoinduced electron transfer can be expected ($\alpha > 0.4$ eV) and that the open-circuit voltage should increase from X = TP via Q, BT, and BO, to BBT. More interestingly, using $\alpha$ and $\beta$ and the optical gap in the film and the assumptions outlined in the introduction to this thesis, we can make some predictions with respect to efficiencies that can be expected using the diagram in Chapter 1. The resulting values 4.7% (Q), 7.9% (BO), 5.7% (BT), 7.0% (BBT), < 2.2% (TP) indicate that PCPDT-BO and PCPDT-BBT are promising materials for photovoltaics, considering their frontier orbital energies.
2.2.5. Photovoltaic devices

Solar cells were fabricated on glass substrates with a transparent ITO/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT: PSS) front electrode and a reflecting LiF/Al back electrode. The active layers were spin coated from chlorobenzene solutions of the polymer and [60]PCBM. The weight ratio PCPDT-X:[60]PCBM in the solution was 1:3 and for each polymer and the layer thickness was optimized for optimal performance by varying the spin speed. The current density vs. voltage ($J-V$) curves, measured under simulated solar light (100 mW cm$^{-2}$), are depicted in Figure 2.3a. The monochromatic external quantum efficiency (EQE) (Figure 2.3b) was measured under bias light corresponding to approximately 1 sun intensity. The relevant parameters are summarized in Table 2.3, together with an overview of literature data on related CPDT based polymers. We note that the difference in molecular weights of the polymers hampers a direct comparison of the device parameters, especially because short-circuit current and fill factor are often negatively affected by too low molecular weights.\cite{Mühlbacher2011, Schlor2012} For PCPDT-BT the molecular weight has been found critical for attaining the desired morphology and efficiency.\cite{Mühlbacher2011, Schlor2012}

For PCPDT-BT:[60]PCBM we obtain a very similar response as found by Mühlbacher et al.,\cite{Mühlbacher2011} with nearly identical $V_{oc}$, FF, and an EQE that maximizes at 31%. The estimate of the short circuit current of $J_{sc}(SR) = 6.5$ mA cm$^{-2}$ is, however, lower than the 9 mA cm$^{-2}$ previously reported, which results in a lower estimated efficiency of PCE = 1.9% compared to PCE = 2.67%.\cite{Mühlbacher2011} The difference is most likely due to a difference in white light spectra used in the two studies.

Each of the other four polymers also shows a significant photovoltaic effect. As expected from the oxidation potentials, the $V_{oc}$ for cells with PCPDT-BO and PCPDT-BBT is higher than that of PCPDT-BT. For both polymers the energy loss from $E_g$ to $eV_{oc}$ is 0.7 eV, which places these two polymers closer to the energy conversion optimum as set in Chapter 1 than PCPDT-BT. In fact the 0.7 eV difference approaches the 0.6 eV that was recently predicted as being the minimum loss in bulk heterojunction solar cells.\cite{Kopp2013} The maximum EQE values for the two polymers (27 and 29%, for BO and BBT, respectively) are slightly lower than that of PCPDT-BT. The good FF and the increased $V_{oc}$ of the PCPDT-BO:[60]PCBM cell makes its power conversion efficiency superior to that of the others polymers. The performance of PCPDT-Q is significantly less than that of PCPDT-BT, mainly due to a loss in
short-circuit current. Finally, PCPDT-TP shows the most red-shifted response of all polymers, beyond 1 µm (Figure 2.3b), but since the EQE remains small the photocurrent is low. The high HOMO level of PCPDT-TP, causes a loss of $V_{oc}$ and with PCE = 0.1%, the overall performance is low.

Table 2.3. Characteristics of PCPDT-X:[60]PCBM photovoltaic cells
<table>
<thead>
<tr>
<th>Material</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$J_{sc}$(SR) (mA cm$^{-2}$)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>d (nm)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCPDT-Q</td>
<td>0.61</td>
<td>5.2</td>
<td>4.6</td>
<td>0.39</td>
<td>1.1$^d$</td>
<td>79</td>
<td>This work</td>
</tr>
<tr>
<td>PCPDT-BO</td>
<td>0.78</td>
<td>5.2</td>
<td>5.4</td>
<td>0.60</td>
<td>2.5$^d$</td>
<td>94</td>
<td>This work</td>
</tr>
<tr>
<td>PCPDT-BT</td>
<td>0.66</td>
<td>7.0</td>
<td>6.5</td>
<td>0.44</td>
<td>1.9$^d$</td>
<td>98</td>
<td>This work</td>
</tr>
<tr>
<td>PCPDT-BT$^a$</td>
<td>0.65</td>
<td>9.0</td>
<td>2.7</td>
<td>150-250</td>
<td></td>
<td>[11]</td>
<td></td>
</tr>
<tr>
<td>PCPDT-BT$^{a,b}$</td>
<td>0.62</td>
<td>11.0</td>
<td>3.2</td>
<td>150-250</td>
<td></td>
<td>[11]</td>
<td></td>
</tr>
<tr>
<td>PCPDT-BBT</td>
<td>0.62</td>
<td>16.2</td>
<td>5.5</td>
<td>110</td>
<td></td>
<td></td>
<td>[2]</td>
</tr>
<tr>
<td>PCPDT-BBT$^*$</td>
<td>0.83</td>
<td>6.4</td>
<td>6.1</td>
<td>0.39</td>
<td>2.0$^d$</td>
<td>71</td>
<td>This work</td>
</tr>
<tr>
<td>PCPDT-TP</td>
<td>0.18</td>
<td>0.9</td>
<td>1.0</td>
<td>0.38</td>
<td>0.1$^d$</td>
<td>74</td>
<td>This work</td>
</tr>
<tr>
<td>PCPDT-TBTT</td>
<td>0.60</td>
<td>8.3</td>
<td>4.2</td>
<td>70</td>
<td></td>
<td></td>
<td>[18]</td>
</tr>
<tr>
<td>PCPDT-Q$^*$</td>
<td>0.64</td>
<td>2.4</td>
<td>0.48</td>
<td>70</td>
<td></td>
<td></td>
<td>[18]</td>
</tr>
<tr>
<td>PCPDT-BDT</td>
<td>0.47</td>
<td>2.5</td>
<td>0.32</td>
<td>90</td>
<td></td>
<td></td>
<td>[19]</td>
</tr>
<tr>
<td>PCPDT-NDT</td>
<td>0.47</td>
<td>3.6</td>
<td>0.33</td>
<td>90</td>
<td></td>
<td></td>
<td>[19]</td>
</tr>
<tr>
<td>PCPDT-QDT</td>
<td>0.53</td>
<td>4.6</td>
<td>0.47</td>
<td>100</td>
<td></td>
<td></td>
<td>[19]</td>
</tr>
<tr>
<td>PCPDT-BSe$^a$</td>
<td>0.52</td>
<td>5.0</td>
<td>0.34</td>
<td>60</td>
<td></td>
<td></td>
<td>[20]</td>
</tr>
</tbody>
</table>

$^a$) Using [70]PCBM. $^b$) Using octanedithiol as a processing agent during film formation. $^c$) Using convolution of the spectral response with the AM1.5G emission. $^d$) Based on $J_{sc}$(SR).

Comparing $eV_{oc}$ for the five polymers with the $\beta$ values in Table 2.2 reveals a similar trend with an offset of $0.42 \pm 0.08$ eV. This demonstrates that the oxidation potential of the donor and the reduction potential of the acceptor as determined in solution can be used to obtain a fairly accurate estimate of $V_{oc}$. The offset of $0.42 \pm 0.08$ V is close to the value of 0.4 eV predicted by Blom et al.$^{29}$ and the value of 0.43 eV found by Manca et al.$^{30}$ for the difference between $eV_{oc}$ and the absorption band to charge transfer state.

The fill factor for the solar cells are in the range FF = 0.38-0.44 for these polymers, except for PCPDT-BO where FF = 0.60. A low fill factor is often associated with strongly unbalanced charge transport that leads to space charge limited photocurrents. However, for PCPDT-BT:[60]PCBM, the origin of the low fill factor has recently been studied in more detail by Blom et al.$^{31}$ They showed that the low FF (= 0.40 in Ref 35) was due to the short lifetime of the bound electron-hole pairs at the donor/acceptor interface. Although we cannot speculate on the reasons for the low FF for the other three polymers, it is clear that for
PCPDT-BO, that gives FF = 0.60, neither charge transport or electron-hole pair lifetime seem to limit the performance.

From Table 2.3, PCPDT-BT, PCPDT-BBT, and PCPDT-BO clearly identify as providing the best efficiencies. Detailed studies for PCPDT-BT have revealed that a high molecular weight for obtaining a high hole mobility and the addition of processing agents are key parameters for further improving the efficiency of these solar cells, in addition to the use of [70]PCBM to enhance the absorption in the visible spectral region. This study reveals that PCPDT-BBT and PCPDT-BO are interesting leads for such further optimization of molecular weight and processing conditions. Their initial performance is good and their energy levels are positioned more favorable than that of PCPDT-BT with respect to PCBM.

2.3 Conclusions

Alternating copolymers using an electron rich CPDT unit and five different electron deficient aromatic units (Scheme 2.1) have been synthesized via a Suzuki polymerization reaction. The optical absorption and electrochemical potentials were used to determine the relevant energy levels of these CPDT-X polymers. The photovoltaic devices of the corresponding PCPDT-X:[60]PCBM donor:acceptor blends revealed that the open-circuit voltages of the cells corresponds to the expected values based on the redox potentials. The best solar cells were made with polymers based on CPDT with benzooxadiazole (BO) or bisbenzothiadiazole (BBT) as electron deficient unit. Mixed with PCBM these polymers showed an open-circuit voltage that is significantly higher than that of PCPDT-BT. The best device was based on a PCPDT-BO:PCBM blend and gave $J_{sc} = 5.4$ mA cm$^{-2}$, FF = 0.6, $V_{oc} = 0.78$ V, resulting in a maximum PCE of over 2.5% at an optical band gap of $E_g = 1.47$ eV. The energy loss from $E_g$ to $eV_{oc}$ is 0.69 V and one of the lowest values reported for bulk-heterojunction solar cells, close to the expected minimum loss of 0.6 V.
2.4 Experimental

All synthetic procedures were performed under an argon atmosphere. Commercial chemicals were used as received. Dry solvents were distilled over 4 Å molecular sieves.

$^1$H-NMR and $^{13}$C-NMR spectra were recorded at 400 MHz and 100 MHz respectively on a VARIAN mercury spectrometer with CDCl$_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. The peaks are given in ppm, relative to TMS (0 ppm). Molecular weights were determined with GPC at 80 °C on a PL-GPC 120 system using a PL-GEL 5µ MIXED-C column and o-DCB as the eluent. For PCPDT-TP a PLgel MIXED-C in series with a PLgel MIXED-D column at room temperature was used with THF as the eluent.

UV/vis spectra were recorded on a Perkin Elmer Lambda 900 Uv/vis/nearIR spectrophotometer. Cyclic voltammograms were recorded with a scan rate of 0.1 V/s under an inert atmosphere with 1M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in o-DCB as the electrolyte. The working electrode was a platinum disk and the counter electrode was a silver electrode. The concentration of the samples in the electrolyte was approximately 2 mM, based on monomers. Fe/Fe$^+$ was used as internal standard.

Recycling GPC was performed with a JAIGEL 2H and a 2.5H column attached to a LC system equipped with a UV detector with a path of 0.5 mm and a switch for recycling and collecting the eluent. The eluent was chloroform at 3.5 ml min$^{-1}$ and the injection volume was 1 ml.

Photovoltaic devices were processed on cleaned patterned ITO glass substrates. A mixed solution of polymer and [60]PCBM (Solenne BV) in a 1:3 weight ratio was spin coated from chlorobenzene on 50 nm of PEDOT:PSS (Clevios P VP AI 4083, H.C. Starck). The devices were transported into a glovebox with nitrogen atmosphere. LiF (1 nm) and aluminum (100 nm) were thermally evaporated on top of the active layer at a pressure of 10$^{-7}$ mbar. The devices had an active area of 0.091 cm$^2$ which is determined by the overlap of the ITO and the evaporated aluminum. Current-voltage curves were measured with a Keithley 2400 source meter under illumination of simulated solar light in nitrogen atmosphere. Spectral response curves were measured with a Stanford Research Systems Model SR830 DSP lock-in-amplifier by using modulated monochromatic light from a tungsten halogen lamp in combination with a monochromator (Oriel, Cornerstone 130). During the measurement the device was operating at 1 equivalent sun intensity by use of a bias laser (532 nm). A calibrated Si cell was used as a reference. The device was kept behind a quartz window in a nitrogen filled container. The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak150 profilometer.
Di-3-thienylmethanol (3). n-Butyllithium in hexanes (15.7 ml, 2.5 M) was slowly added to a solution of 3-bromothiophene 1 (3.3 mL, 5.7 g, 3.5 mmol) in dry diethyl ether (100 ml) at -75 °C. The mixture was stirred for 30 min. at -78 °C. Then 3-thiophencarboxaldehyde 2 (3.13 ml, 4.0 g, 3.6 mmol) was added dropwise. This mixture was allowed to reach room temperature overnight. The reaction mixture was washed with acid, base, and brine. The organic layer was dried on sodium sulfate and the solvent was evaporated under reduced pressure. The crude product, which was 90% pure, was taken to the next reaction without further purification.

Di-3-thienylmethane (4). AlCl₃ (4.70 g, 35 mmol) was added to a solution of LiAlH₄ (1.32 g, 35 mmol) in dry diethyl ether (100 ml) at room temperature. To this mixture crude 3 (6.68 g) was added dropwise. This mixture was refluxed for 3 h after which the reaction mixture was washed with hydrochloric acid (150 ml, ~1M), NaOH solution (150 ml, ~1M), and twice with brine (150 ml). All water layers were once extracted with diethyl ether. The combined organic layers were dried on sodium sulfate and subjected to column chromatography (silica, heptane). This resulted in 4.56 g (25 mmol, 88%) of 4 as a colorless oil. 1H-NMR: 7.26 (dd, J = 3.6 Hz, 2H), 6.95 (dd, J = 4.2 Hz, 2H), 6.94 (t, J = 4.8 Hz, 2H), 3.99 (s, 2H). 13C-NMR: 140.99 (q), 128.40 (t), 125.61 (t), 121.17 (t), 31.11 (s).

Bis(2-bromothien-3-yl)methane (5). N-bromosuccinimide (9.01 g, 51 mmol) was slowly added to an ice-cooled and stirred solution of di-3-thienylmethane 4 (4.56 g, 25 mmol) in DMF (200 ml). The mixture was allowed to reach room temperature overnight and then extracted with diluted hydrochloric acid and diethyl ether. The diethyl ether layer was washed with water and brine. The organic solvent layers were evaporated under reduced pressure and column chromatography (silica, eluent heptane) yielded 5 (7.31 g, 21.6 mmol, 86%) of a colorless oil. 1H-NMR: 7.18 (d, J = 5.2 Hz, 2H), 6.73 (d, J = 6.0 Hz, 2H), 3.86 (s, 2H). 13C-NMR: 138.79 (q), 128.46 (t), 125.70 (t), 109.80 (q), 29.47 (s).

4H-Cyclopenta[2,1-b:3,4-b’]dithiophene (6). Bis(2-bromothien-3-yl)methane 5 (3.01 g 8.9 mmol) was added to activated copper bronze (6.1 g, 96 mmol) in dry DMF (200 ml). This mixture was stirred in a Milestone MicroSYNTH microwave reactor at 140 W at an internal temperature of 145 °C for 3 h. The reaction mixture was repeatedly extracted with water and heptane and the organic layers were combined. The solids that resulted after evaporation of the organic solvent were recrystallized from methanol to yield 6 (0.73 g, 4.1 mmol, 47%) as off-white flakes. 1H-NMR: 7.18 (d, J = 5.2 Hz, 2H), 7.09 (d, J = 4.8 Hz, 2H), 3.54 (s, 2H). 13C-NMR: 149.65 (q), 138.64 (q), 124.45 (t), 122.94 (t), 31.81 (s).
Chapter 2

4,4-Di(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (7). To a solution of 6 (4.23 g, 24 mmol) in DMSO, powdered KOH (4.80 g, 86 mmol), and KI (30 mg, 0.2 mmol) were added, followed by 2-ethylhexylbromide (10.67 g, 55 mmol). This mixture was stirred at room temperature overnight and then poured out in water and heptane. The organic layer was washed two times with water and one time with brine. The heptane was evaporated in vacuo and the resulting light yellow oil was subjected to column chromatography (silica, eluent heptane) to yield 7 as a light-yellow oil (8.49 g, 21 mmol, 89%). 

\[ \text{H-NMR: } 7.10 (d, J = 4.4 \text{ Hz}, 2H), 6.91 (m, 2H), 1.85 (m, 2H), 0.90 (m, 18H), 0.75 (t, 2H), 0.58 (t, 2H). \]

\[ \text{C-NMR: } 157.59 (q), 136.77 (q), 123.92 (t), 122.30 (t), 53.22 (q), 43.21 (s), 34.97 (s), 34.11 (s), 28.57 (s), 27.24 (s), 22.74 (s), 14.07 (p), 10.63 (p). \]

2,6-Dibromo-4,4-di(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (8). NBS (380 mg, 2.13 mmol) was added in small portions to a solution of 7 (390 mg, 0.97 mmol) in DMF (25 ml). This mixture was stirred overnight, after which of water (50 ml) was added and the water layer was extracted with diethyl ether. The organic layer was dried on MgSO\(_4\) and the solvents from the organic layer were evaporated. The resulting yellow oil was subjected to column chromatography (silica, eluent heptane) to yield 8 (480 mg, 0.86 mmol, 88%) as a light yellow oil. 

\[ \text{H-NMR: } 6.93 (t, J = 3.2 \text{ Hz}, 2H), 1.80 (m, 4H), 1.26 (m, 2H), 0.9 (m, 16H), 0.78 (m, 6H), 0.62 (m, 6H). \]

\[ \text{C-NMR: } 155.56 (q), 136.60 (q), 125.21 (q), 110.68 (q), 54.95 (q), 43.03 (s), 35.09 (s), 34.02 (t), 28.53 (s), 27.28 (s), 22.76 (s), 14.06 (p), 10.64 (p). \]

2,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-4,4-di(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (9). An n-butyllitium solution in hexanes (1.1 ml, 2.5 M) was added at -70 °C to a solution of 8 (260 mg, 0.46 mmol) in dry THF (20 ml). The mixture was stirred for 30 min. at -70 °C, after which 2-isopropoxy-(1,3,2)-dioxaboralane (0.5 ml, 0.46 g, 2.4 mmol) was added at -70 °C. This mixture was allowed to reach room temperature overnight. The reaction mixture was poured out in water and diisopropyl ether, and the organic layer was washed with brine. The solvents were evaporated from the organic layer and the resulting oil was subjected to column chromatography (eluent heptane/ethyl acetate 97/3). This yielded a light-green oil which was then subjected to recycling GPC in CHCl\(_3\). This result in 9 (185 mg, 0.28 mmol, 61%) as a slight yellow sticky oil. 

\[ \text{H-NMR: } 7.44 (t, 2H), 1.83 (m, 4H), 1.3 (s, 24H), 0.9(m, 18H), 0.73 (m, 6H), 0.58 (m, 6H). \]

\[ \text{C-NMR: } 160.99 (q), 144.10 (q), 131.90 (q), 83.94 (t), 52.68 (q), 43.21 (s), 35.14 (s), 33.85 (s), 29.72 (q), 28.33 (s), 27.43 (s), 24.75 (p), 22.79(s), 14.10 (p), 10.59 (p). \]
Copolymers of CPDT with different electron deficient units for photovoltaics

5,8-Dibromoquinoxaline (12). NaBH₄ (2.18 g, 58 mmol) was added in small portions to dibromobenzothiadiazole (10) (1.0 g, 3.40 mmol) dissolved in ethanol (25 ml) at room temperature. This mixture was stirred overnight, after which diethyl ether and water were added. The organic layer was washed three times with water, and one time with brine. The solvents from the organic layer were evaporated and the resulting white solid 11 was used without further purification. To a solution of 11 in ethanol (30 ml) 40 wt% glyoxal in water (1.5 ml) was added, followed by 2 drops of dry triethylamine. This mixture was stirred at room temperature overnight. The white crystals that had formed were filtered off and recrystallized from ethanol to give 12 as white needles (760 mg, 2.64 mmol, 76%). ¹H-NMR: 9.01 (s, 2H), 8.00 (s, 2H). ¹³C-NMR: 146.04 (t), 141.57 (q), 133.72 (t), 123.98 (q).

4,7-Dibromobenzooxadiazole (14). Bromine (15.2 g, 95 mmol) was added dropwise to a melt of benzooxadiazole (13) (4.86 g, 40.4 mmol) at 90 °C containing iron dust (93 mg, 1.6 mmol). After stirring 2 h at 90 °C the mixture was poured out in water. A solution of sodium bisulfite was added until no gas evolution was observed. The solid was filtered off and impregnated on silica. This was subjected to column chromatography (silica, eluent heptane). The resulting yellow solid was recrystallized in ethanol to yield 14 (8.40 g, 30 mmol, 75%) as yellow crystals. ¹H-NMR: 7.51 (s, 2H). ¹³C-NMR: 149.38 (q), 134.17 (q), 108.70 (q).

4-Bromo-2,1,3-benzothiadiazole (16). 2,1,3-Benzothiadiazole 15 (14.3 g, 105 mmol) was dissolved in aqueous 48 wt% HBr (125 ml) at 150 °C and bromine (5.9 ml, 18 g, 115 mmol) was added slowly. This mixture was stirred for 2 h at 150 °C, after which GC-MS analysis showed that there was about 40% nonbrominated product. Then an additional amount of bromine (6 g, 38 mmol) was added. The resulting mixture was refluxed for another 3 h. The reaction mixture was cooled down to room temperature poured out in of ice water (800 ml), after which saturated Na₂S₂O₅ solution was added until the water was colorless. The water layer was extracted with diethyl ether. The solvent of the organic layer was evaporated and the solid was subjected to column chromatography (silica, eluent ethyl acetate and heptane) to yield 16 (7.41 g, 34 mmol, 32%) as a white solid. ¹H-NMR: 7.97 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.48 (t, J = 8.8 Hz, 1H). ¹³C-NMR: 154.61 (q), 153.37 (q), 131.99 (t), 129.93 (t), 120.90 (t), 114.43 (q).

4,4'-Bis(2,1,3-benzothiadiazole) (17). To a solution of tetraethylammonium iodide (2.93 g, 1.14 mmol), zinc powder (1.14 g, 17 mmol) and di(triphenylphosphine)nickel dibromide (2.46 g, 3.36 mmol) in THF (20 ml), a solution of 16 (2.50 g, 11.6 mmol) was added slowly. The resulting mixture was heated to 55 °C for 8 h, after which it was poured out in CHCl₃ (50 ml). The solvents were evaporated and the crude product was impregnated on silica and subjected to column chromatography.
silica, dichloromethane). The resulting white product was recrystallized from ethanol to yield 17 (804 mg, 2.97 mmol, 51%) as a yellow powder. $^1$H-NMR: 8.27 (d, $J = 6.8$ Hz, 2H), 8.12 (d, $J = 8.8$ Hz, 2H), 7.81 (t, $J = 7.2$ Hz, 2H). $^{13}$C-NMR: 155.47 (q), 153.59 (q), 130.77 (t), 129.99 (q), 129.44 (t), 121.64 (t).

7,7'-Diiodo-4,4'-bis(2,1,3-benzothiadiazole) (18). AgSO$_4$ (1.06 g, 3.40 mmol) in sulfuric acid (2.5 ml) was stirred until the solid was dissolved. Iodine (278 mg, 1.10 mmol) was added and the solution was stirred for 3 h at room temperature until all the iodine had dissolved. The mixture was then added to 17 (100 mg, 0.37 mmol) at 110 ºC. The resulting mixture was stirred at 110 ºC for 1 h after which it was poured out in water (100 ml). The yellow water layer was extracted repeatedly with chloroform until the extracts were colorless. The solvents were evaporated from the organic layer and the yellow substance was recrystallized from toluene to yield 18 (132 mg, 0.25 mmol, 69%) as a yellow powder. $^1$H-NMR: 8.30 (d, $J = 8.0$ Hz, 2H), 8.06 (d, $J = 8.0$ Hz, 2H). The product was not soluble enough to perform $^{13}$C NMR.

2,3-Di-n-octylthieno[3,4-b]pyrazine (20). To a solution of 3,4-diaminothiophene dihydrochloride 19 (325 mg, 1.72 mmol) and octadeca-9,10-dione (800 mg, 2.84 mmol) in ethanol (20 ml), triethylamine (1 ml) was added. The mixture was stirred for two hours at room temperature after which the solvents were evaporated and the solid extracted with heptane. The heptane was evaporated and the resulting whitish solid was subjected to column chromatography (silica, heptane and ethyl acetate) to yield 20 (412 mg, 1.14 mmol, 67%) as a yellow solid. $^1$H-NMR: 7.79 (s, 2H), 2.88 (t, $J = 8.0$ Hz, 4H), 1.78 (t, $J = 8.0$ Hz, 4H), 1.45 (m, 4H), 1.3 (m, 16H), 0.87 (t, $J = 6.8$ Hz, 6H). $^{13}$C-NMR: 156.39 (q), 141.64 (q), 11.79 (t), 35.75 (s), 31.85 (s), 29.72 (s), 29.44 (s), 29.23(s), 28.39 (s), 22.67 (s), 14.10 (p).

5,7-Dibromo-2,3-di-n-octylthieno[3,4-b]pyrazine (21). NBS (148 mg 0.91 mmol) in DMF (3 ml) was slowly added to a solution of 2,3-di-n-octylthieno[3,4-b]pyrazine (153 mg, 0.42 mmol) in DMF (10 ml) at -15 ºC. This mixture was stirred in dark at room temperature overnight. The reaction mixture was poured out in water (50 ml) and diethyl ether (50 ml). The water layer was extracted until the extracts were colorless. The solvents of the organic layers were evaporated without heat. The solid was subjected to column chromatography (silica, pentane and dichloromethane) to yield 21 (130 mg, 0.25 mmol, 60%) as a yellow solid. $^1$H-NMR: 2.89 (t, $J = 8.0$ Hz, 4H), 1.80 (q, $J = 7.6$ Hz, 4H), 1.45 (m, 4H), 1.3 (m, 16H), 0.89 (t, $J = 6.4$ Hz, 6H). $^{13}$C-NMR: 158.16 (q) 139.34 (q), 103.09 (q), 35.33 (s), 31.84 (s), 29.56 (s), 29.42 (s), 29.22 (s), 27.93 (s), 22.66 (s), 14.10 (p).
Copolymers of CPDT with different electron deficient units for photovoltaics

*PCPDT-Q.* To a degassed solution of 9 (65 mg, 0.10 mmol), 12 (28 mg, 0.10 mmol), 1 drop of Aliquat 336, and 2M K₂CO₃ in degassed water (0.2 ml) in toluene (3 ml), tetrakis(triphenylphosphine)palladium(0) (2 mg, 1.7 μmol) was added. This mixture was stirred at 115 ºC for three days, after which it was precipitated in methanol. The solids were filtered off, redissolved in CHCl₃ (75 ml) and refluxed with 28% NH₃ solution in water (75 ml) for 3 h. The layers were separated and the organic layer was stirred with EDTA (250 mg) overnight, after which water (100 ml) was added and the liquids were stirred for 1 h. The layers were separated and the organic layer was reduced in volume by evaporating most of the chloroform. The polymer was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was extracted with methanol, after which the thimble was allowed to dry in ambient conditions. Then the polymer was extracted with hexane and chloroform. The solvent from the chloroform fraction was evaporated and the solid was precipitated in methanol. The polymer was collected by filtering over a 0.45 μm PTFE membrane filter and dried in a vacuum oven to yield PCPDT-Q (15 mg, 29%) as a dark blue powder. ¹H-NMR: 9.00 (b, 2H), 8.15 (b, 2H), 7.80 (b, 2H), 2.05 (b, 4H), 1.00 (b, 18H), 0.65 (b, 12H).

*PCPDT-BO.* Identical procedure as for PCPDT-Q, using 9 and 14, yield: 68% as a dark blue powder. ¹H-NMR: 8.05 (b, 2H), 7.55 (b, 2H), 2.10 (b, 4H), 1.00 (b, 18H), 0.65 (b, 12H).

*PCPDT-BT.* Identical procedure as for PCPDT-Q except at 80 ºC, using 9 and 10, yield: 72% as a dark blue powder. ¹H-NMR: 8.13 (b, 2H), 7.88 (b, 2H), 2.05 (b, 4H), 1.0 (b, 18H), 0.80 (b, 6H), 0.65 (b, 6H).

*PCPDT-BBT.* Identical procedure as for PCPDT-Q, using 9 and 18, yield: 40% as a dark blue powder. ¹H-NMR: 8.45 (b, 2H), 8.30 (b, 2H), 8.00 (b, 2H), 2.05 (b, 4H), 1.05 (b, 18H), 0.65 (b, 12H).

*PCPDT-TP.* Identical procedure as for PCPDT-Q, using 9 and 21, yield: 32% as a dark green powder. ¹H-NMR: 7.45 (b, 2H), 3.00 (b, 4H), 2.00 (b, 8H), 1.36, (b, 14H), 1.00 (b, 24H), 0.70 (b, 18H).

### 2.5 References


(25) See Chapter 5 of this thesis


(34) See Chapter 6 of this thesis
Chapter 3

Controlling morphology and photovoltaic properties by chemical structure in copolymers of cyclopentadithiophene and thiophene segments *

Abstract

A series of polythiophenes (PT\textsubscript{n}) based on dialkyl-cyclopentadithiophene (CPDT) units alternating with short un-substituted thiophene segments of length \textit{n} (\textit{n} being the number of thiophenes) along the chain has been synthesized to control the morphology of PT\textsubscript{n}:PCBM blends for solar cell applications via the chemical structure of the polymer, rather than via (post) processing conditions. The degree of phase separation in PT\textsubscript{n}:PCBM blends can be controlled via \textit{n}, because with increasing \textit{n} the number of solubilizing side chains per thiophene is reduced. For the most soluble derivative, PT0, we find that PCBM crystallizes first, while for the least soluble version, PT3, polymer aggregation prevails. The most intimately mixed morphology and best solar cells were obtained for PT2 that exhibits a PCE of about 1.5\% under AM1.5G conditions when mixed with PCBM. Although the final PCE is moderate, the study represents an example of a rational approach towards morphology control via chemical structure, rather than via processing.


3.1 Introduction

Organic photovoltaic cells attract attention for future low-cost, large-area conversion of sunlight into electrical energy. Although very encouraging progress has been made recently, reaching a power conversion efficiency (PCE) in these devices of above 7% in AM1.5G solar light, further improvement and understanding of structure-property relations are required. One crucial issue is the morphology of the photo-active layer that consists of a nanoscale phase-separated blend of two complementary organic semiconductors with donor and acceptor character, respectively.

Poly(3-hexylthiophene) (P3HT) is presently possibly the most deeply investigated semiconducting donor polymer for solar cell applications. Blends of P3HT and the fullerene derivative [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM) as acceptor have reached PCEs of 5% in optimized devices. The morphology of the P3HT:PCBM blend, as well as other polymer:PCBM blends, is crucial to the performance of the cells, and such morphology can be affected by external stimuli, such as thermal annealing of as cast films, and through the use of high boiling solvents, processing additives, or poor solvents during spin coating.

Recently, copolymers of cyclopentadithiophene (CPDT) have been reported displaying PCEs up to 5.5% in a solar cell and high charge carrier mobility. Following these reports, several CPDT based polymers have been developed for application in solar cells. The CPDT unit features two thiophene units, bridged by an sp$^3$ hybridized carbon atom that locks the two thiophene units in a coplanar configuration. Solubilizing alkyl chains are attached to the bridging carbon atom to ensure good solubility, but do not prevent the polymers of obtaining a planar configuration at the inter ring bonds between two CPDT units. Also for CPDT co-polymers the use of processing additives has been shown to be advantageous for the performance of solar cells when blended with [6,6]-phenyl-C$_{71}$-butyric acid methyl ester ([70]PCBM).

We were interested in controlling the morphology of conjugated polymer blends via the chemical structure of the polymer, rather than via (post) processing conditions. To achieve this objective we have synthesized a series of CPDT based polythiophenes (PT$_n$, Scheme 3.1) that have CPDT units alternating with short un-substituted thiophene segments of length $n$ ($n$ being the number of thiophenes) along the chain. The branched alkyl chains on the CPDT units in the PT$_n$ polymers improve the solubility, while the un-substituted thiophene segments provide a tendency for the polymer to aggregate. It is exactly this balance between solubility
and tendency to aggregate that has to be controlled when creating the optimal morphology in phase-separated blends with commonly used fullerene derivatives such as PCBM. Here is shown that by increasing \( n \), the number of un-substituted thiophenes relative to the number of CPDT units in the chain, it is possible control the morphology and thereby the photovoltaic performance of the devices. For the most soluble derivative, PT0, we see that PCBM crystallizes first, while for the least soluble version, PT3, polymer aggregation prevails. Consequently, the best cells are made for PT2 that exhibits a PCE of about 1.5% under AM1.5G conditions when mixed with PCBM. Although the final PCE is moderate, the study represents an example of a rational approach towards morphology control via chemical structure, rather than via processing.

### 3.2 Results

#### 3.2.1. Synthesis

The synthesis of the polymers is depicted in Scheme 3.1. 4,4-Di(2’-ethylhexyl)-4H-cyclopenta[2,1-\(b\):3,4-\(b’\)]dithiophene (CPDT) and the corresponding 2,6-dibromo-CPDT were synthesized according to literature procedures.\(^{17}\) For PT0, oxidative polymerization was performed using CPDT and FeCl\(_3\) as the oxidant.\(^{20}\) Polymers PT1, PT2, and PT3 were synthesized via Suzuki co-polymerization from 2,6-dibromo-CPDT and the appropriate end substituted bis(boronic ester)oligothiophene using Pd(PPh\(_3\))\(_4\) as a catalyst. For \( n = 1 \) and 2, the bis(boronic esters) were commercially available and recrystallized before use. For \( n = 3 \), the bis(boronic ester) was synthesized using from 5,5''-dibromo-2,2':5',2''-terthiophene-dibromoterthiophene via deprotonation and subsequent reaction with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaboralane.
The polymers were obtained as dark powders with molecular weights ($M_n$) between 2700 and 13000 g mol$^{-1}$ (Table 3.1). The molecular weights of PT1 and PT3 are lower than those of PT0 and PT2, which might hinder proper comparison of the polymers. However, based on the $M_n$ of PT1 and PT3, the number of repeating thiophene rings is around 40 and 30, respectively, which would be enough to reach the conjugation length, where the optical\textsuperscript{21} and electrochemical\textsuperscript{22} properties of an infinitely long polymer are reached. For PT3, the low number of side chains apparently hampers dissolving the polymer in later stages of the polymerization reaction. For use in organic solar cells the differences in molecular weight can be important, due to the differences in film forming properties.\textsuperscript{23} Polymer PT2 has previously also been synthesized by via Stille polymerization, giving similar values for $M_n$.\textsuperscript{24,25}

**3.2.2. Optical and electrochemical properties**

The absorption spectra of the polymers are shown in Figure 3.1 for ortho-dichlorobenzene ($o$-DCB) solution and thin films. The polymers show an absorption in the visible region. The optical band gap ($E_g$) estimated from the onset of absorption in thin film (1.81-1.94 eV) is only slightly red shifted compared to the corresponding spectra in solution (1.86-1.99 eV) (Table 3.1), indicating that there are no strong interchain interactions affecting the electronic structure in thin films. The optical band gap in the solid state increases monotonously with the number of un-substituted thiophene rings, i.e. going from PT0 to PT3.
The onsets of the oxidation potentials of the polymers (Table 3.1) were determined by cyclic voltammetry in o-DCB solution. Going from PT0 to PT3, the HOMO energy level is lowered (higher oxidation potential), consistent with the reducing number of electron donating alkyl chains per thiophene in the polymer chain. This leads to the expectation that in a photovoltaic cell the open circuit voltage $V_{oc}$ will increase going from PT0 to PT3, when combined with PCBM.

### Table 3.1. Physical properties of the PT$n$

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ kg mol$^{-1}$</th>
<th>$M_w$ kg mol$^{-1}$</th>
<th>$E_g^{\text{film}}$ (eV)</th>
<th>$E_g^{\text{sol}}$ (eV)</th>
<th>$E_{ox}$ a (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT0</td>
<td>13</td>
<td>20</td>
<td>1.81</td>
<td>1.86</td>
<td>-0.18</td>
</tr>
<tr>
<td>PT1</td>
<td>6.3</td>
<td>11</td>
<td>1.87</td>
<td>1.89</td>
<td>-0.19</td>
</tr>
<tr>
<td>PT2</td>
<td>11</td>
<td>19</td>
<td>1.89</td>
<td>1.99</td>
<td>0.00</td>
</tr>
<tr>
<td>PT3</td>
<td>2.7</td>
<td>6.7</td>
<td>1.94</td>
<td>1.99</td>
<td>+0.03</td>
</tr>
</tbody>
</table>

a) Oxidation potential is vs. Fe/Fe$^\text{2+}$.

### 3.2.3. Photovoltaic devices

Solar cells were fabricated by spin coating mixed PT$n$:PCBM solutions from chlorobenzene into thin films onto a glass|ITO|PEDOT:PSS front electrode and subsequent evaporation of LiF and Al as back electrode. The PT$n$:PCBM weight ratio and layer thickness were optimized for each polymer. All the polymers require an excess (by weight) of PCBM for optimal performance. The current density versus voltage ($J$-$V$) characteristics under illumination with simulated solar light (100 mW/cm$^2$) are depicted in Figure 3.2 for the
optimized cells, together with the monochromatic external quantum efficiency (EQE), measured under a light bias of approximately one sun. The parameters that characterize the solar cells under simulated AM1.5G conditions are summarized in Table 3.2. The open-circuit voltage is consistent with the empirical relation $eV_{oc} = |E_{ox}(PTn) - E_{red}(PCBM)| - 0.4$ eV$^{19,26}$ ($E_{red}(PCBM) = -1.07$ V vs. Fe/Fe$^+$) within 80 mV. The highest short circuit current density ($J_{sc}$) is found for PT2:PCBM and this is reflected in the EQE measurements, where the maximum is above 35%. The fill factors (FF) of the cells are moderate (0.4-0.5), possibly resulting from an imbalance in electron and hole carrier mobility between the PCBM and the polymer. The best solar cells were made with PT2 and provide an estimated AM1.5 PCE of over 1.5%. In another study, where PT2 was combined with [70]PCBM, a PCE of 2.2% was obtained$^{25}$ due to the additional absorption of light by [70]PCBM$^{27}$ and, hence, photocurrent, while $V_{oc}$ and FF are very similar. Thermal annealing of the completed devices, as commonly done for P3HT:PCBM solar cells to improve the performance by generating a more phase separated and semi-crystalline morphology, did not result in better cells for the PT$n$:PCBM blends.

![Figure 3.2](image-url)  
*Figure 3.2. J-V curves (a) and monochromatic EQE (b) of the best cells made with PT$n$ and [60]PCBM.*
Controlling morphology and photovoltaic properties in CPDT-based copolymers

Table 3.2. Characteristics of the best cells made with PTn.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>PTn:PCBM ratio</th>
<th>d (nm)</th>
<th>$J_{sc}(SR)^a$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (-)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PT0</td>
<td>1:2</td>
<td>90</td>
<td>1.54</td>
<td>0.48</td>
<td>0.48</td>
<td>0.36</td>
</tr>
<tr>
<td>PT1</td>
<td>1:3</td>
<td>64</td>
<td>3.33</td>
<td>0.51</td>
<td>0.41</td>
<td>0.72</td>
</tr>
<tr>
<td>PT2</td>
<td>1:3</td>
<td>70</td>
<td>5.06</td>
<td>0.62</td>
<td>0.50</td>
<td>1.56</td>
</tr>
<tr>
<td>PT3</td>
<td>1:2</td>
<td>74</td>
<td>3.41</td>
<td>0.62</td>
<td>0.39</td>
<td>0.82</td>
</tr>
</tbody>
</table>

$^a$) Current densities derived from spectral response measurements with the AM1.5G spectrum.

To investigate the morphology of the PTn:PCBM blends we used AFM (Figure 3.3). The AFM image of the surface of the PT0:PCBM blend shows bright features of several hundred nanometers that have previously been identified as of large PCBM clusters,\textsuperscript{28,29} that have phase separated from the blend during film formation due to aggregation and crystallization of PCBM from solution, while the polymer is still dissolved. The PT1:PCBM and PT2:PCBM films, however, are very smooth, as evidenced by their low RMS roughness (<2 nm for PT1:PCBM and <1 nm for PT2:PCBM). Finally, the PT3:PCBM film shows larger features and more surface roughness, with height differences over 10 nm. This is a direct consequence of the reduced solubility of PT3 compared to the other polymers. The AFM images correlate well with the EQE data, in the sense that smoothest film correlates with most charges being collected.

![AFM images](image)

Figure 3.3. AFM images of layers consisting of the optimal PTn:PCBM mixtures (Table 3.2) PT0 (a), PT1 (b), PT2 (c), PT3 (d). Area 1 µm × 1 µm, height scale is 15 nm (a, d) and 3 nm (b, c).

3.3 Conclusions

Four CPDT-based polythiophenes, PTn, containing a variable number ($n = 0$-3) of unsubstituted thiophene units were synthesized to control the morphology and performance in solar cells of PTn:PCBM blends via changing the chemical structure. The differences in chemical structure among the four PTn’s have a relatively small effect on the optical band
gap, which increases with \( n \), and the position of the HOMO level, which decreases with \( n \), but largely affects the performance of the photovoltaic device when mixed with PCBM. AFM studies show that for PT0, large PCBM clusters are formed. With increasing \( n \) the mixing becomes more intimate, reaches a maximum performance for \( n = 2 \), and then decreases again because the polymer becomes increasingly less soluble starts to phase separate before PCBM clusters can form. The best cells, obtained with PT2:PCBM, have a PCE of just over 1.5%. The study represents an example of a rational morphology control via chemical structure, rather than via processing. Such control need not be restricted to changes in the polymer main chain as shown here, but can likely also be affected by the changing the size, branching, and number of solubilizing side chains.

### 3.4 Experimental

All reactions were performed under an argon atmosphere. Commercial chemicals were used as received, but the bisboronic esters were recrystallized from methyl-t-butyl ether prior to use. Dry solvents were distilled over 4 Å molecular sieves. 2,6-Dibromo-4,4-di(2’-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene and 2,6-dibromo-4,4-di(hexadecyl)-4H-cyclopenta[2,1-b:3,4-b’]dithiophene were prepared according to literature procedures\(^{19}\).

\(^1\)H-NMR and \(^{13}\)C-NMR spectra were recorded at 400 MHz and 100 MHz respectively on a VARIAN mercury spectrometer with CDCl\(_3\) as the solvent and tetramethylsilane (TMS) as the internal standard. The peaks are given in ppm, relative to TMS (0 ppm) and denoted as singlets (s) and doublets (d) or broad (b) for \(^1\)H-NMR and primary (p), tertiary (t) or quaternary (q) for \(^{13}\)C-NMR. Matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a PerSeptive Biosystems Voyager-DE PRO spectrometer. Molecular weights were determined with GPC at 80 ºC on a PL-GPC 120 system using a PL-GEL 5\(\mu\) MIXED-C column and o-DCB as the eluent.

UV/vis/nearIR spectra were recorded on a Perkin Elmer Lambda 900 Uv/vis/nearIR spectrophotometer. Cyclic voltammograms were recorded with a scan rate of 0.1 V/s under an inert atmosphere with 1M tetrabutylammonium hexafluorophosphate in o-DCB as the electrolyte. The working electrode was a platinum disk and the counter electrode was a silver electrode. The concentration of the samples in the electrolyte was approximately 2 M, based on monomers. Fe/Fe\(^+\) was used as an internal standard.

Photovoltaic devices were processed on cleaned patterned ITO glass substrates. A mixed solution of polymer and [60]PCBM (Solenne BV) was spin coated from chlorobenzene on 50 nm of PEDOT:PSS (Clevios P VP AI 4083, H.C. Starck). The devices were transported into a glovebox with
Controlling morphology and photovoltaic properties in CPDT-based copolymers

nitrogen atmosphere. LiF (1 nm) and Al (100 nm) were thermally evaporated on top of the active layer at a pressure of 10⁻⁷ mbar. The devices had an active area of 0.091 cm² which is determined by the overlap of the ITO and the evaporated aluminum. Current-voltage curves were measured with a Keithley 2400 source meter under illumination of simulated solar light in nitrogen atmosphere. Spectral response curve were measured with a Stanford Research Systems Model SR830 DSP lock-in-amplifier by using monochromatic light from a tungsten halogen lamp in combination with a monochromator (Oriel, Cornerstone 130). During the measurement the device was kept operating at 1 equivalent sun intensity by use of a bias laser (532 nm). A calibrated Si cell was used as a reference. The device was kept behind a quartz window in a nitrogen filled container. The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak150 profilometer. Tapping mode AFM was measured on a MFP-3D (Asylum research) using PPP-NCHR probes (Nanosensors).

5,5'′-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-2,2′:5′,2′′-terthiophene. To a solution of 5,5′-dibromo-2,2′:5′,2′′-terthiophene (250 mg, 0.62 mmol) in dry THF a butyllithium solution (0.9 ml of a 1.6 M) was added at -78 ºC. This mixture was stirred for 2 h at 78 ºC, after which 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaboralone (0.4 ml, 1.9 mmol) was added. The resulting mixture was allowed to reach room temperature overnight and poured out in dichloromethane (25 ml) and water (25 ml). The organic layer was washed with water three times and the solvents were removed in vacuo. The resulting green solid was recrystallized in methyl-t-butyl ether yielding the title compound (145 mg, 45%) as green crystals. 1H-NMR: 7.53 (d, 2H, J = 3.9 Hz), 7.24 (d, 2H, J = 2.7 Hz), 7.15 (s, 2H), 1.36 (s, 24H). 13C-NMR: 143.64 (q), 138.97 (t), 136.66 (q), 125.13 (t), 124.98 (t), 84.23 (q), 24.76 (p). MALDI-TOF MS: (Mw = 500.21), 500.15 (M+).

PT0. 4,4-di(2′-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene (269 mg, 0.73 mmol) in degassed chloroform (1 ml) was added to a degassed suspension of FeCl₃ (452 mg, 2.8 mmol) in chloroform (3 ml). The mixture was stirred at 50 ºC for 72 h, after which it was precipitated in methanol. The solids were filtered off, re-dissolved in CHCl₃ (100 ml) and refluxed with 28% NH₃ solution in water (100 ml) for 3 h. The organic layer was washed three times with water, after which the organic layer was reduced in volume by evaporating most of the chloroform. The polymer was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was extracted with methanol, after which the thimble was allowed to dry in ambient conditions. Then the polymer was extracted with hexane and chloroform. The solvent from the chloroform fraction was evaporated and the solid was precipitated in methanol. The polymer was collected by filtering over a 0.45 µm PTFE membrane filter and dried in a vacuum oven to yield PT1 (57 mg, 21%) as a dark powder. 1H-NMR: 6.95 (b, 2H), 1.9 (b, 4H), 1.0 (b, 18H), 0.8 (b, 6H), 0.6 (b, 6H)
**PT1.** Tetrakis(triphenylphosphine)palladium(0) (8 mg, 6.9 μmol) was added to a degassed mixture of 2,6-dibromo-4,4-di(2'-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (196 mg, 0.39 mmol), 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)thiophene (130 mg, 0.39 mmol), 1 drop of Aliquat 336, and degassed 2M K₂CO₃ (aq) (0.5 ml) in toluene (3 ml). This mixture was stirred at 115 °C for three days, after which it was precipitated in methanol. The solids were filtered off, re-dissolved in CHCl₃ (75 ml) and refluxed with 28% NH₃ solution in water (75 ml) for 3 h. The layers were separated and the organic layer was stirred with EDTA (250 mg) overnight, after which water (100 ml) was added and the liquids were vigorously stirred for 1 h. The layers were separated and the organic layer was reduced in volume by evaporating most of the chloroform. The polymer was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was extracted with methanol, after which the thimble was allowed to dry in ambient conditions. Then the polymer was extracted with hexane and chloroform. The solvent from the chloroform fraction was evaporated and the solid was precipitated in methanol. The polymer was collected by filtering over a 0.45 μm PTFE membrane filter and dried in a vacuum oven to yield PT1 (54 mg, 29%) as a dark powder. ¹H-NMR: 7.03 (b, 2H), 7.02 (b, 2H), 1.9 (b, 4H), 1.3-1.0 (b, 18H), 0.8 (b, 6H), 0.7 (b, 6H)

**PT2.** Similar procedure as for PT1, using 2,6-dibromo-4,4-di(2'-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (75 mg, 0.13 mmol) and 5,5'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-2,2'-bithiophene (56 mg, 0.13 mmol). Yield: 54 mg (73%). ¹H-NMR: 7.07 (b, 4H), 7.04 (b, 2H), 1.9 (b, 4H), 1.3-1.0 (b, 18H), 0.8 (b, 6H), 0.7 (b, 6H)

**PT3.** Similar procedure as for PT1, using 2,6-dibromo-4,4-di(2'-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (67 mg, 0.12 mmol) and 5,5'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-2,2':5',2''-terthiophene (60 mg, 0.12 mmol). Yield: 13 mg (17%). ¹H-NMR: 7.12 (b, 2H), 7.08 (b, 2H), 7.05 (b, 4H), 1.9 (b, 4H), 1.3-1.0 (b, 18H), 0.8 (b, 6H), 0.6 (b, 6H)

### 3.5 References

Controlling morphology and photovoltaic properties in CPDT-based copolymers


Chapter 4
Maximizing the open-circuit voltage of polymer:fullerene solar cells*

Abstract

The open-circuit voltage ($V_{oc}$) of bulk heterojunction solar cells based on polymers and fullerene derivatives is limited to $\sim$1.15 V by the optical band gap of the fullerene of $\sim$1.75 eV and the required 0.6 eV offset for efficient charge generation. In practice this limit has not yet been reached. We present a semiconducting polymer, PTTBT, based on alternating thienothiophene and benzothiadiazole units that gives $V_{oc} = 1.15$ V with [70]PCBM as acceptor. To reach this $V_{oc}$ the surface of the PEDOT:PSS hole collecting electrode is modified by UV-ozone. This increases the work function and creates an Ohmic contact. Under simulated AM1.5G conditions optimized PTTBT:[70]PCBM cells provide a short circuit current density ($J_{sc}$) of 2.8 mA cm$^{-2}$ and a power conversion efficiency of $\sim$1%. The performance is limited by a low hole mobility of the polymer.

* This work has been published:
4.1 Introduction

Organic photovoltaic cells based on polymers hold the promise of low cost large area energy production. In recent years the focus in this area shifted towards designing and creating materials with decreased optical band gap energy ($E_g$) to enhance optical absorption in sunlight.\(^1\) As a result of these efforts, power conversion efficiencies, (PCE), up to 7.4\% have been reported for bulk heterojunction solar cells comprising blends of a conjugated polymer and a fullerene derivative.\(^2\)

Higher PCEs can be obtained with multi-junction devices such as tandem cells that employ sub cells with $V_{oc}$’s that are more closely matched to $E_g$ of the active layer to minimize photon energy losses.\(^3\)-\(^6\) Recently it was shown that in practice (295 K, solar light) the maximum attainable $V_{oc}$ for single junction cells is limited by the optical gap energy via $eV_{oc} \leq E_g - 0.6\ eV$.\(^7\) This limit is controlled by the free energy needed for efficient charge transfer and by a loss in $V_{oc}$ relative to the energy of the charge separated state.\(^7\) Commonly used acceptor materials in bulk heterojunction solar cells such as the fullerene derivatives such as [6,6]-phenyl-C$_{61}$-butyric acid methyl ester [60]PCBM and [6,6]-phenyl-C$_{71}$-butyric acid methyl ester [70]PCBM feature a high electron mobility and have $E_g = 1.75\ eV$. This limits the $V_{oc}$ of any polymer:PCBM solar cell to $V_{oc} \leq 1.15\ V$. So far the highest reported $V_{oc}$’s for PCBM-based cells are <1.05 V,\(^8\)-\(^12\) which leaves room for further optimization.

Increasing the $V_{oc}$ for PCBM-based solar cells requires a lowering of the HOMO energy of the polymer with respect to the vacuum level. This can be effective as long as the polymer semiconductor can form an Ohmic contact with the hole collecting electrode by aligning its HOMO level with the Fermi level of the electrode. Hence, for the commonly used poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) electrode the work function of 5.1±0.2 eV\(^13\) will limit the $V_{oc}$, when the HOMO level of the semiconducting polymer becomes less than -5.3 eV vs. vacuum. Fortunately, the work function of PEDOT:PSS can be increased via treatment with UV-ozone or by mixing or covering with Nafion\(^\circledR\).\(^14\)-\(^18\) The changes in work function are reported to be 0.13 to 0.25 eV for UV-ozone treated films,\(^14\)-\(^16\) up to 0.65 eV for the films with Nafion\(^\circledR\).\(^17\)-\(^18\)

Here we present poly[3,6-di(4’ethyloctyl)-thieno[3,4-c]thiophene-2,5-diy-alt-[2,1,3]benzothiadiazole-4,7-diy]- PTTBT (Scheme 4.1), a polymer with a low HOMO energy that provides $V_{oc} = 1.15\ V$ in solar cells when combined with [70]PCBM and using an UV-ozone
treated PEDOT:PSS electrode. This $V_{oc}$ is approaching the limit of what seems possible in PCBM-based solar cells.\(^7\)

### 4.2 Results

#### 4.2.1. Synthesis

To obtain PTTBT, Suzuki polymerization was chosen as the polymerization method. The thienothiophene monomer was synthesized as depicted in Scheme 4.1. Synthesis of an alkylated version of thienothiophene via Kumada coupling with a Grignard reagent proved to be unsuccessful in our hands. Trimethylsilylacetylene 1 was deprotonated with butyllithium and the resulting anion was reacted with 2-ethylhexylbromide, to yield the protected alkyne 2. Deprotection with tetrabutylammonium fluoride of the 2 yielded the primary alkyne 3, which was reacted with 3,6-dibromothieno[3,2-b]thiophene via a Sonogashira reaction to produce 4. The unsaturated side chains were hydrogenated via a reduction using palladium on coal under a hydrogen atmosphere to yield 5. Bromination gave the desired monomer 6 which could then be used in the Suzuki polymerization with 7 to form PTTBT. PTTBT was obtained as an orange powder with a number average molecular weight $M_n = 15$ kg mol\(^{-1}\) and a polydispersity of 3.2 as determined by GPC in o-DCB at 80 °C.

![Scheme 4.1. Synthesis and structure of PTTBT](image-url)
4.2.2. Physical properties

UV/vis absorption (Figure 4.1a) reveals that PTTBT has an optical band gap of 2.31 eV in solution and of 2.20 eV in thin films. This relatively wide band gap is most probably due to a non-planar configuration of the chain caused by steric hindrance between the 4-ethyloctyl side chains and the benzothiadiazole unit. The absorption of PTTBT is slightly blue shifted compared to the related poly[4,7-bis(3-octyl-2-thienyl)-2,1,3-benzothiadiazole] (PB3TB) that incorporates a bithiophene unit instead of a thienothiophene.19

![Figure 4.1](image)

**Figure 4.1.** Optical absorptions (a) of PTTBT in o-DCB solution (closed squares) and as a solid (open circles) and cyclic voltammogram of PTTBT in o-DCB containing 2 M of TBAHPF₆ as the electrolyte (b)

The HOMO and LUMO levels of PTTBT were estimated using cyclic voltammetry (Figure 4.1b) in o-DCB to be +0.54 and −1.80 V vs. ferrocene/ferrocinium (Fc/Fc⁺) or -5.64 and -3.3 eV vs. vacuum. The difference matches with the optical band gap in solution. The $V_{oc}$ for donor (D) – acceptor (A) bulk heterojunction cells can be estimated from $eV_{oc} = |E_{HOMO(D)} - E_{LUMO(A)}| - 0.4$ eV.20 Applying this experimental rule to PTTBT and [70]PCBM ($E_{LUMO(A)} = -1.07$ V vs. Fc/Fc⁺, -4.03 V vs. vacuum)21 provides 1.2 V as the estimate $V_{oc}$ for a PTTBT:[70]PCBM solar cell, which is larger than the maximum value of 1.15 V, predicted for PCBM-based solar cells. As a consequence incomplete charge generation is expected.

4.2.3. Photovoltaic properties

Solar cells were made by spin casting PEDOT:PSS (Clevios P, VP Al4083) directly followed by a mixture of PTTBT and [70]PCBM from chlorobenzene onto a pre-cleaned glass slide with a pattern of ITO. The devices were completed by evaporating 1 nm LiF and 100 nm Al onto the active layer in vacuum, which is known to form an Ohmic contact with PCBM.20 The use of pristine PEDOT:PSS resulted in rather irreproducible and poor performance (PCE
< 0.1%) and a significant dark current at reverse bias. The operation was limited by a low photocurrent and a low \( V_{oc} \) of 0.4 V on average (see Figure 4.2a). A short treatment of the freshly spin coated PEDOT:PSS layer in a UV-ozone reactor before deposition of the active layer results in a dramatic increase in the performance. Figure 4.2a shows the \( V_{oc} \) obtained as a function of UV-ozone exposure.

\[
\begin{align*}
\text{Figure 4.2.} \quad \text{The} \quad V_{oc} \quad \text{of cells made with PTTBT and [70]PCBM as a function of PEDOT treatment time (a) and RMS roughness, PCE and} \quad V_{oc} \quad \text{as a function of the composition of the spincoating mixture (b).}
\end{align*}
\]

The optimal exposure time of 3 min. results in a \( V_{oc} \) of 1.15 V with little variation. The effect is already very strong after 30 s and longer treatment times than 3 min. do not further improve \( V_{oc} \). The short circuit current density (\( J_{sc} \)) also showed a dramatic increase, from \(<1 \) to over 2.5 mA cm\(^{-2}\). The treatment mainly affects the surface of the PEDOT:PSS and lowers the work function to 5.4 eV\(^{15}\), but also seems to affect the photoactive layer, increasing the photocurrent. The fill factor (FF) however, remained low, possibly due to the low hole mobility (\( \mu_h \)) of PTTBT, which was \( \sim10^{-6} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\) as measured in a FET bottom gate bottom contact structure. This value is significantly lower than the values which can be obtained for hole mobilities in semi crystalline thieno[3,2-\(b\)]thiophene-based polymers, probably due to decreased orbital overlap in the chains caused by the twisting in the backbone of PTTBT. Another cause for the low \( \mu_h \) is the low crystallinity due to the branched alkyl chains.\(^{22}\)

The ideal blend layer for an organic solar cell has a large interface area between the two components to effectively split the excitons and at the same time comprises large enough phase-separated domains of PCBM or polymer to form effective percolating pathways for collecting the charges at the electrodes. To optimize the performance the PTTBT:[70]PCBM blend was spin coated from different solvent mixtures onto UV-ozone treated PEDOT:PSS layers. The solvents tested consisted of mixtures of chloroform (CHCl\(_3\)) and chlorobenzene...
(CB); other solvents tested gave inferior results. From either of the two pure solvents, the thin films featured low performance, whereas layers spin coated using a mixture of the two yielded improved solar cells. Figure 4.2b shows the efficiency vs. composition of the solvent mixture. Using 15–20 vol.% CHCl₃ in CB, solar cells with an estimated efficiency of just over 1% were obtained. The voltage does not vary significantly with the chloroform:CB ratio as shown in Figure 4.2b.

Atomic force microscopy (AFM) studies revealed that the composition of the solvent mixture affects the morphology of the active layer. Figure 4.2b also shows that the efficiency of the cells inversely correlates with the rms-roughness of the films as measured with AFM over a 1 μm² area (Figure 4.3). At the optimal performance the rms-roughness is in a (local) minimum. Since films from pure CB appear more corrugated than films from pure CHCl₃, we assume that the 15–20 vol.% CHCl₃ serves to reduce the extent of phase separation obtained with pure CB. This view is consistent with the fact that layers obtained from pure CHCl₃ have the overall lowest rms-roughness. The lower performance for films made from pure CHCl₃ is then likely due to a lack of phase separation.

The J-V curve and external quantum efficiency recorded with the equivalent of 1 sun light bias of an optimized cell with layer thicknesses typically between 70 and 80 nm and a PFTBT:[70]PCBM weight ratio of 1:4 are shown in Figure 4.4. In the spectral region from 350–500 nm, more than 20% of the photons are converted in electrons. From convolution of the external quantum efficiency (EQE) with the AM1.5G spectrum a $J_{sc}$ of 2.81 mA cm⁻² is obtained. Combined with FF = 0.32 and $V_{oc} = 1.15$ V this results in PCE ≈ 1.0%. Under reverse bias the photocurrent is strongly enhanced, which suggests that the generation of free charge carriers is assisted by the electric field.
4.3 Conclusions

In conclusion, PTTBT is a semiconducting polymer that exhibits a high oxidation potential and $V_{oc} = 1.15$ V when combined with [70]PCBM in bulk heterojunction solar cells. To reach the high $V_{oc}$ the PEDOT:PSS electrode was treated with UV-ozone to increase the work function and create an Ohmic contact with PTTBT. The overall PCE of the optimized cells (1%) is moderate and limited by a low hole mobility and the incomplete generation of free carriers close in the maximum power point. With $V_{oc} = 1.15$ the practical limit thought to be possible for PCBM-containing polymer solar cells has been reached.7

4.4 Experimental

Polymerization reactions were conducted under an argon atmosphere. Commercial chemicals were used as received. [70]PCBM was purchased from Solenne BV. 1H-NMR and 13C-NMR spectra were recorded at 400 MHz and 75 MHz, respectively on a VARIAN mercury spectrometer with CDCl3 as the solvent and tetramethylsilane (TMS) as the internal standard. The peaks are given in ppm, relative to TMS (0 ppm). Molecular weights were determined with GPC at 80 ºC on a PL-GPC 120 system using a PL-GEL 5µ MIXED-C column and o-dichlorobenzene (o-DCB) as the eluent and against polystyrene standards. UV/vis spectra were recorded on a Perkin Elmer Lambda 900 Uv/vis/nearIR spectrophotometer. Cyclic voltammetry was conducted with a scan rate of 0.1 V s$^{-1}$ under an inert atmosphere with 1 M tetrabutylammonium hexafluorophosphate in o-DCB as the electrolyte. The working electrode was a platinum disk and the counter electrode was a silver electrode. The concentration of the sample in the electrolyte was approximately 2 mM, based on monomers. Fc/Fc$^+$ was used as an internal standard.
Chapter 4

Photovoltaic devices were made by spin coating poly(ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP Al4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). Optional treatment of the PEDOT:PSS layer happened on the freshly spincast PEDOT:PSS layer, by laying the substrates in a UV-ozone photoreactor PR-100 from Ultra violet Products for a measured time. The photoactive layer was deposited by spin coating from the appropriate solvent. The counter electrode, consisting of LiF (1 nm) and aluminum (100 nm), was deposited by vacuum evaporation at 3 · 10^{-7} mbar. The active area of the cells was 0.091 cm² or 0.16 cm². J-V characteristics were measured under ~100 mW/cm² white light from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter, using a Keithley 2400 source meter. Short-circuit currents under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The spectral response was measured under simulated 1 sun operation conditions using bias light from a 532 nm solid state laser (Edmund Optics). Monochromatic light from a 50 W tungsten halogen lamp (Philips focusline) in combination with monochromator (Oriel, Cornerstone 130) was modulated with a mechanical chopper. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Stanford research Systems SR830). A calibrated Si cell was used as reference. The device was kept behind a quartz window in a nitrogen filled container. The thickness of the active layers in the photovoltaic devices were measured on a Veeco Dektak150 profilometer. Field-effect transistors were fabricated using heavily doped silicon wafers as the common gate electrode with a 20 nm thermally oxidized SiO₂ layer as the gate dielectric. Using conventional photolithography, gold source and drain electrodes were defined in a bottom contact device configuration with channel width and length of 2500 µm and 10 µm, respectively. A 10 nm layer of titanium was used acting as an adhesion layer for the gold on SiO₂. The SiO₂ layer was exposed to the vapor of the primer hexamethyldisilazane for 60 min. prior to semiconductor deposition in order to passivate the surface of the dielectric. PTTBT films were spun form a chloroform solution at 1500 rpm for 30 s. Freshly prepared devices were annealed in a dynamic vacuum for 10^{-5} bar at 100 °C for 72 h to remove traces of solvent. All electrical measurements were performed in a vacuum using an HP 4155C semiconductor parameter analyzer. Tapping mode AFM was performed on a MFP-3D atomic force microscope (Asylum research) using PPP-NCHR probes (Nanosensors).

1-(trimethylsilyl)-4-ethyl-1-octyne (2). To a solution of trimethylsilylacetylene (1) (1.85 g, 19 mmol) in dry THF (50 ml), 1.6 M n-butyllithium (13 ml, 21 mmol) in hexanes was added at -78 °C. This mixture was stirred for one hour at low temperature, after which 2-ethylhexylbromide (3.0 ml, 16 mmol) was added followed by hexamethylphosphoramide (3.4 ml, 19 mmol). The reaction mixture was allowed to reach RT overnight, after which it was heated to reflux for 3 hours. The reaction mixture was cooled down and quenched using saturated ammonium chloride solution (5 ml), after
which it was extracted with heptane and water. The organic layer was subjected to column chromatography (silica, eluent: heptane) and yielded 1.44 mg (6.9 mmol) of a colorless oil (38 %). $^1\text{H-NMR}$: 2.19 (d, 2H), 1.2 (m, 9H), 0.89 (m, 6H), 0.14 (s, 9H). $^{13}\text{C-NMR}$: 106.55 (q), 85.18 (q), 38.60 (t), 32.64 (s), 28.92 (s), 26.02 (s), 23.78 (s), 22.91 (s), 14.07 (p), 11.10 (p), 0.18 (p). MS (EI): 123.4 (0.5%), 109.15 (5%), 57.05 (100%) M$^+$ was not detected.

$4\text{-ethyl-1-octyne}$ (3). To a mixture of 1-(trimethylsilyl)-4-ethyl-1-octyne (1.44 g, 6.9 mmol) in THF (15 ml), tetrabutylammonium fluoride on silica was added (5.0 mg). This mixture was stirred at room temperature for 30 min, after which the reaction mixture was filtered to remove the silica. The solvents from the resulting mixture were evaporated and the concentrate was subjected to column chromatography (silica, eluent: pentane) to yield 0.61 g (4.4 mmol) of a colorless oil (64%). $^1\text{H-NMR}$: 2.18 (m, 2H), 1.91 (t, 1H), 1.2 (m, 9H), 0.89 (m, 6H). $^{13}\text{C-NMR}$: 83.36 (q), 68.81 (t), 38.42 (t), 32.62 (s), 28.99 (s), 25.83 (s), 22.91 (s), 0.18 (p). MS (EI): 195.15 (25%), 73.05 (100%), M$^+$ was not detected.

$3,6\text{-di(4\text{-ethyl-1-octyne})thieno[3,2-b]thiophene}$ (4). To a degassed mixture of 4-ethyl-1-octyne (600 mg, 4.3 mmol), copper(I) iodide (13 mg, 68 µmol) and tetrakis(triphenylphosphine)palladium(0) (32 mg, 27 µmol) in triethylamine (5 ml), 3,6-dibromo[3,2-b]thienothiophene (524 mg, 1.76 mmol) was added. This mixture was stirred overnight at 130 ºC, after which heptane (50 ml) was added. The resulting mixture was filtered, and the filtrate was washed with diluted hydrochloric acid (50 ml) and brine. The organic layer was subjected to column chromatography (silica, eluent: pentane), yielding 699 mg (1.69 mmol) of a slightly yellow oil (96%). $^1\text{H-NMR}$: 7.1, (s, 2H), 2.28 (d, 4H), 1.2 (m, 18H), 0.75 (m, 12H). $^{13}\text{C-NMR}$: 139.87 (q), 129.04 (t), 116.14 (q), 91.63 (q), 74.10 (q), 38.58 (t), 32.73 (s), 28.92 (s), 26.03 (s), 23.12 (s), 22.82 (s), 13.96 (p). MS (MALDI): 412.27, calculated: 412.23 (M$^+$)

$3,6\text{-di(4\text{-ethyloctyl})thieno[3,2-b]thiophene}$ (5). To a solution of 3,6-di(4’-ethyl-1-octyne)-thieno[3,2-b]thiophene (699 mg, 1.69mmol) in ethylacetate (10 ml), which was bubbled with nitrogen for 30 min., 10% palladium on coal (180 mg) was added under an hydrogen atmosphere. This mixture was stirred overnight, after which it was filtered over celite. The celite was flushed thoroughly with ethylacetate. The solvent was evaporated and the resulting oil was subjected to column chromatography (silica, eluent: heptane) to yield 593 mg (1.41 mmol) of a colorless oil (83%). $^1\text{H-NMR}$: 6.96 (s, 2H), 2.69 (t, 4H, J = 7.6 Hz), 1.72 (m, 4H), 1.2 (m, 22H), 0.8 (m, 12H). $^{13}\text{C-NMR}$: 139.23 (q), 135.47 (q), 120.83 (t), 38.64 (s), 32.94 (s), 32.77 (s), 30.22 (t), 28.93 (s), 25.88 (s), 25.86 (s), 23.14 (s), 14.15 (p), 10.87 (p)/ MS (EI): 420.05 (16%) M$^+$, 294.15 (100%), 167.90 (40%)
2,5-dibromo-3,6-di(4’-ethyloctyl)thieno[3,2-b]thiophene (6). To a mixture of 3,6-di(4’-ethyloctyl)thieno[3,2-b]thiophene (500 mg, 1.11 mmol) in DMF (30 ml), of N-bromosuccinimide (435 mg, 2.44 mmol) dissolved in DMF (5 ml) was added. This mixture was stirred overnight in dark, after which it was poured out in water and heptane. The organic layer was washed with brine and the solvents were evaporated. The resulting oil was subjected to column chromatography which yielded 580 mg (1.00 mmol) of a colorless oil (83%). ¹H-NMR: 2.65 (t, 4H, J 7.6), 1.64 (m, 4H), 1.2 (m, 22H), 0.88 (t, 6H, J = 6.8 Hz), 0.82 (t, 6H, J = 6.4 Hz). ¹³C-NMR: 136.06 (q), 134.42 (q), 109.40 (q), 38.49 (s), 32.76 (s), 32.69 (s), 29.33 (t), 28.89 (s), 25.79 (s), 25.19 (s), 23.11 (s), 14.15 (p), 10.82 (p). MS (MALDI): calculated: 578.11, found: 578.04 (M⁺).

PTTBT. A mixture of 2,5-dibromo-3,6-di(4’-ethyloctyl)thieno[3,2-b]thiophene (126 mg, 0.22 mmol) and 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (85 mg, 0.22 mol), 50 wt.% aliquat 336 solution in toluene (0.5 ml) and K₂CO₃ (61 mg, 0.44 mmol) and water (0.4 ml) in toluene (4 ml) was degassed for 20 min. by bubbling Ar through. After this Pd(PPh₃)₄ (7.0 mg, 6 μmol) was added and the reaction mixture was stirred at 120 ºC for 6 h. The reaction mixture was precipitated in methanol (70 ml). After filtration on a Buchner funnel, the crude polymer was redissolved in 50 ml chloroform and stirred with 100 ml ammonia (25% aq. sol.) under reflux for 30 min. The layers were separated and the organic layer was stirred overnight with EDTA (250 mg). Water was added and the layers were separated and the organic layer was washed twice with water. The organic layer was concentrated under reduced pressure and precipitated in methanol (70 ml), filtered through a Soxhlet thimble and fractionated by Soxhlet extraction using methanol, hexane and CHCl₃, respectively. The chloroform soluble fraction was reduced in volume in vacuo and precipitated in methanol, after which the polymer was collected after filtering over a 4.5 μm PTFE filter. After drying in a vacuum oven, the polymer was obtained in 97 mg as an orange solid (80% yield). ¹H-NMR: 7.79 (b, 2H), 2.83 (b, 4H), 1.84 (b, 4H), 1.19 (b, 22H), 0.86 (b, 12H). $M_n$: 15000 g/mol, PDI: 3.1
4.5 References

Chapter 5
Poly(diketopyrrolopyrrole-terthiophene) for ambipolar logic and photovoltaics*

Abstract

A new semiconducting polymer with alternating diketopyrrolopyrrole and terthiophene units, PDPP3T is presented. PDPP3T has a small optical band gap of 1.3 eV and exhibits nearly balanced hole and electron mobilities of 0.04 cm$^2$ V$^{-1}$ s$^{-1}$ and 0.01 cm$^2$ V$^{-1}$ s$^{-1}$ respectively in field-effect transistors. By combining two identical ambipolar transistors an inverter was constructed that exhibits a gain of about 30. When PDPP3T was combined with [60]PCBM or [70]PCBM in a 1:2 weight ratio, photovoltaic cells were made that provide a photoresponse up to 900 nm and AM1.5G power conversion efficiencies of 3.8 and 4.7%, respectively. In contrast to the almost constant FET mobility, the efficiency of the photovoltaic cells was found to be strongly dependent on the molecular weight of PDPP3T and the use of diiodooctane as a processing agent.

* This work has been published:

5.1 Introduction

Polymers based on diketopyrrolopyrrole (DPP) have been known for a relatively long time\textsuperscript{1,2} but are only recently emerging as a promising candidate for use in optoelectronic applications, particularly in field-effect transistors (FETs)\textsuperscript{3,4} and organic photovoltaic cells (OPCs).\textsuperscript{5-14} OPC efficiencies up to 4.45% have been reached with DPP polymers and oligomers.\textsuperscript{5,13} For DPP-based polymers, the highest power conversion efficiency (PCE) is reached with the highest molecular weight polymers \textsuperscript{9,10,14} identifying molecular weight as a crucial parameter for photovoltaic performance. Here we present a new DPP based polymer, PDPP3T (Scheme 5.1), that features high, almost balanced charge carrier mobilities for both electrons and holes in combination with an extended optical absorption towards the infrared region. These favorable characteristics allow PDPP3T to be used for the construction of a FET-based inverter and to further enhance the power conversion efficiency of DPP based materials for OPCs.

PDPP3T was designed to have an un-substituted terthiophene unit in between the DPP units along the chain.\textsuperscript{8} Compared to other DPP polymers that generally have more extended and complex conjugated segments and carry solubilizing chains,\textsuperscript{5-10} terthiophene induces additional planarity, which enhances packing and charge carrier mobility. By using extended side chains, i.e. 2-hexyldecyl (HD) on DPP, the expected loss in solubility is compensated. This allows obtaining PDPP3T in high molecular weight, which is a crucial factor for its photovoltaic performance (vide infra).

5.2 Results

5.2.1 Synthesis

PDPP3T was synthesized by Suzuki polymerization from the dibromo-DPP monomer\textsuperscript{3} and 2,5-thiophenebis(boronic ester) (Scheme 5.1). The use of Pd\textsubscript{2}(dba)\textsubscript{3}/PPh\textsubscript{3} as catalyst and potassium phosphate as base yielded PDPP3T with $M_n = 54,000$ g mol\textsuperscript{-1} (PDI = 3.15). At higher concentrations (>1 mg ml\textsuperscript{-1}) PDPP3T only dissolves in chloroform. A much lower $M_n = 10,000$ g mol\textsuperscript{-1} (PDI = 2.4) was obtained when Pd(PPh\textsubscript{3})\textsubscript{4} was used as a catalyst together with potassium carbonate. The details of synthesis and characterization are given in the experimental section.
5.2.2 Optical and electrochemical properties

The absorption profiles of the different batches of polymer at varying temperatures in ortho-dichlorobenzene (o-DCB) are shown in Figure 5.1. Both spectra at 20 °C show a broad peak with two maxima, of which the one at lower energy is decreasing in intensity with temperature, indicating that this peak is probably due to aggregation of the polymer. The fact that the peak not fully disappears in the spectrum of the high $M_n$ batch indicates that this polymer is not molecularly dissolved even at 100 °C.

![Figure 5.1](image_url)
The absorption spectra in the solid state are not significantly different, pointing to a similar packing of the polymer when cast onto a glass slide. From the onset of absorption a band gap of 1.36 eV in \( o\)-DCB solution and at 1.30 eV in a thin film is derived, which classifies PDPP3T as a small band gap polymer.

The cyclic voltammogram of PDPP3T was recorded in \( o\)-DCB and is shown in Figure 5.2. The onsets of oxidation and reduction, which are used to determine HOMO and LUMO levels, do not differ significantly for the different batches, predicting a similar value for the open circuit voltage \( V_{oc} \) when combined with an acceptor in an OPC. The HOMO and LUMO levels were determined from the onset of the large peak in the cyclic voltammogram and are estimated at +0.07 and -1.49 V vs. Fc/Fc\(^+\) or -5.17 and -3.61 eV vs. vacuum. The electrochemical band gap is significantly larger (1.58 eV) than the optical band gap. The difference relates, at least in part to the fact that in cyclic voltammetry charged species are formed, whereas in optical measurements, coulombically bound excitons exist.

![Figure 5.2. Cyclic voltammetry of PDPP3T.](image)

5.2.3 Electronic properties

FETs with PDPP3T as semiconductor were fabricated on a heavily doped silicon wafer covered by 200 nm thermally grown silicon dioxide, which acted as common gate electrode and gate dielectric, respectively. Gold electrodes were defined by standard photolithography. The polymer was applied by spin coating a solution of PDPP3T and subsequent drying in vacuum at 110 °C for 72 h to remove traces of solvent. Charge transport was studied as a function of gate bias at room temperature. Typical ambipolar transfer characteristics are presented in Figure 5.3 for negative and positive drain biases. The electron and hole mobilities were extracted from the slope of \( (|I_D|)^{1/2} \) versus \( V_G \) in the saturation region. The
transistors made with the high molecular weight version ($M_n = 54000 \text{ g mol}^{-1}$) exhibited nearly balanced hole and electron mobilities of 0.04 cm$^2$ V$^{-1}$ s$^{-1}$ and 0.01 cm$^2$ V$^{-1}$ s$^{-1}$ respectively. These values are among the highest reported for single-component ambipolar transistors.$^3$ Just like the solid state absorption profile and the electrochemical behavior, these mobilities were found to be almost independent of molecular weight; the $M_n = 10,000 \text{ g mol}^{-1}$ version of PDPP3T gave $\mu_h = 0.05 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_e = 0.008 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

![Figure 5.3](image)

**Figure 5.3.** Semi-logarithmic plots of the drain current $I_D$ versus gate voltage $V_G$ (right axis) and plot of ($I_D$)$^{1/2}$ versus $V_G$ (left axis) from a bottom contact FET, consisting of PDPP3T ($M_n = 54,000 \text{ g mol}^{-1}$) (a) and PDPP3T ($M_n = 10,000 \text{ g mol}^{-1}$) (b).

Two identical ambipolar transistors were combined into an inverter, with the common gate as the input voltage (inset Figure 5.4).$^{16}$ Figure 5.4 shows the output voltage ($V_{OUT}$) as a function of the input voltage ($V_{IN}$) at constant supply bias ($V_{DD}$). From the steepness of the inverter curve, a gain of about 30 is deduced, which is comparable to state-of-the-art CMOS-like inverters$^{17}$ and much higher than usually obtained for unipolar logic.$^{18}$

![Figure 5.4](image)

**Figure 5.4.** Inverter characteristics of an inverter based on two identical FETs. Channel length and width were 10 and 2500 µm, respectively, inset shows schematic layout of the inverter.
5.2.4 Photovoltaic devices

Photovoltaic cells containing PDPP3T (\(M_n = 54,000\) g/mol) and [60]PCBM ([6,6]phenyl-C_{61}-butyric acid methyl ester) were fabricated by spin coating on a PEDOT:PSS/ITO transparent front electrode. The LiF/Al back electrode was evaporated in vacuum. Cells with an active layer spin coated from chloroform had a relatively low performance, due to formation of larger [60]PCBM clusters, vide infra. Control over the morphology is crucial for bulk heterojunction solar cells and several strategies to accomplish a more favorable morphology such as thermal treatment and the use processing additives have been developed. Adding a small amount (~25 mg ml\(^{-1}\)) of diiodooctane (DIO) to the mixture before spin coating, improved the efficiency of cells significantly, mainly due to an increase in photocurrent. The best cells were obtained for PDPP3T:[60]PCBM in a 1:2 weight ratio and gave an open circuit voltage of \(V_{oc} = 0.68\) V, a fill factor of \(FF = 0.67\), and a short circuit current density of \(J_{sc} = 8.3\) mA cm\(^{-2}\) under simulated AM1.5 (100 mW cm\(^{-2}\)) conditions, which was derived from convolution of the monochromatic external quantum efficiency (EQE) spectrum (Figure 5.5b) with the AM1.5G spectrum. These characteristics resulted in an estimated power conversion efficiency of \(PCE = 3.8\%\) (Figure 5.5a and Table 5.1). The EQE shows a very sharp onset at the optical band gap and rises to ~33% in 750-850 nm region (Figure 5.5b).

![Figure 5.5](image_url)

**Figure 5.5.** \(J-V\) curves (a) and monochromatic EQE curves (b) of PDPP3T:PCBM bulk heterojunction solar cells high \(M_n\) (54000 g mol\(^{-1}\)).

To increase the photocurrent in the visible region, we changed the electron acceptor to [70]PCBM, which possesses an increased absorption coefficient in that part of the spectrum. Because [70]PCBM probably has different crystallization behavior in chloroform than [60]PCBM an increase of the DIO concentration to ~100 mg ml\(^{-1}\) was required to reach
optimum device performance. The optimized cells had PDPP3T:[70]PCBM in a 1:2 weight ratio and provided $V_{oc} = 0.65 \text{ V}$, $J_{sc} = 11.8 \text{ mA cm}^{-2}$, and FF = 0.60, resulting in PCE = 4.7% (Figure 5.5a and Table 5.1). The need for DIO strengthens the view of Lee et al.\textsuperscript{21} that the role of the processing additive is to keep the fullerene in solution longer, giving the polymer more time to aggregate. This hinders the formation of large PCBM crystals and realizes a superior morphology of the active layer. The EQE of the cell with [70]PCBM is similar to that of the [60]PCBM cell in the long wavelength region but much higher in the visible region, accounting for the higher short-circuit current.

In contrast to the constant FET mobility, a dramatic reduction of OPC performance was observed when the lower $M_n = 10,000 \text{ g mol}^{-1}$ version of PDPP3T was used in combination with [60]PCBM or [70]PCBM (Fig 5.6). Under identical processing conditions, the PCEs did not exceed 1.3 and 2.7%, respectively (Figure 5.6a and Table 5.1). The reduced PCE is mainly caused by a decreased photocurrent and this is reflected in the EQE curve in Figure 5.6b. The voltage and fill factor are comparable for the cells with high and low $M_n$, reflecting the similar behavior in the cyclic voltammetry measurements and the similar values for $\mu_e$ and $\mu_h$.

**Figure 5.6.** $J$-$V$ curves (a) and monochromatic EQE curves (b) of PDPP3T:PCBM bulk heterojunction solar cells made with low $M_n$ (10,000 g mol$^{-1}$).
Table 5.1. Characteristics of photovoltaic cells made with high and low molecular weight versions of PDPP3T and different acceptors

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>$M_n = 54,000$ g mol$^{-1}$</th>
<th>$M_n = 10,000$ g mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[60]PCBM</td>
<td>[70]PCBM</td>
</tr>
<tr>
<td>$J_{sc}$ (mA cm$^{-2}$)</td>
<td>8.9</td>
<td>11.4</td>
</tr>
<tr>
<td>$J_{sc,sr}$ (mA cm$^{-2}$)</td>
<td>8.3</td>
<td>11.8</td>
</tr>
<tr>
<td>$V_{oc}$ (V)</td>
<td>0.68</td>
<td>0.66</td>
</tr>
<tr>
<td>FF</td>
<td>0.67</td>
<td>0.60</td>
</tr>
<tr>
<td>PCE (%)</td>
<td>3.83</td>
<td>4.69</td>
</tr>
</tbody>
</table>

The fact that two molecular weight fractions of PDPP3T that have the same electronic levels and virtually the same FET-mobility give distinctly different performance in solar cells when mixed with PCBM, suggests that a difference in morphology of the active layer is present. The AFM images recorded for the active layers of PDPP3T:[60]PCBM and PDPP3T:[70]PCBM (Figure 5.7) give a first indication that such difference in morphology indeed exists.

![AFM images](https://example.com/afm_images.png)

Figure 5.7. AFM height images of the surface of the PDPP3T:PCBM (1:2) bulk heterojunction layers (lateral dimensions: 5 μm × 5μm) processed from chloroform/diiodooctane for the high (a and c) and low (b and d) $M_n$ versions of the polymer with [60]PCBM (a and b) and [70]PCBM (c and d). Height scales are 25 nm (a), 60nm (b), 20 nm (c) and 50 nm (c). Films with low $M_n$ have higher roughness, indicative of more extended phase separation.

The layers made with the lower $M_n$ fraction of PDPP3T are clearly more corrugated than those with the high $M_n$ fraction. Especially the surface corrugation seen in the upper right panel is reminiscent of larger PCBM clusters in the film, which are known to result in
lower device performance than smaller clusters.\textsuperscript{24,25} The other films are smoother, an indication for smaller phase separation.

With a $V_{oc}$ of 0.65-0.68 V and an optical band gap of $E_g = 1.30$ eV, the PDPP3T:PCBM combination approaches the minimum offset of $eV_{oc} = E_g - 0.6$ eV that was recently put forward as being a threshold for bulk heterojunction solar cells.\textsuperscript{26} The fact that PDPP3T is approaching the minimum offset required for electron transfer to occur, could be the reason that the quantum efficiency is less than found in the more efficient, 7\%, cells published lately.\textsuperscript{27,28}

\section*{5.3 Conclusions}

Two versions of PDPP3T were synthesized showing significantly different $M_n$. The two versions have similar optical absorption in films and both exhibit ambipolar transport in FETs, with high, nearly balanced electron and hole mobilities in the $10^{-2}$ cm$^2$/Vs range. By combining two identical FETs an inverter exhibiting a gain of about 30 was obtained. The influence of the molecular weight is expressed clearly in the formation of films with PCBM as the acceptor. For the lower $M_n$ version the surface roughness is higher and all the resulting solar cell results are inferior to the cells made with the high $M_n$ version. In combination with [70]PCBM the high $M_n$ version of PDPP3T reaches an estimated PCE of 4.7\% in photovoltaic cells and has a photoresponse up to 900 nm.

\section*{5.4 Experimental}

Polymerization reactions were conducted under an argon atmosphere. Commercial chemicals were used as received. [60]PCBM and [70]PCBM were purchased from Solenne BV. $^1$H-NMR spectra were recorded at 400 MHz on a VARIAN mercury spectrometer with CDCl$_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. The peaks are given in ppm, relative to TMS (0 ppm). Molecular weights were determined with GPC at 80 °C on a PL-GPC 120 system using a PL-GEL 5μ MIXED-C column and o-DCB as the eluent and against polystyrene standards. UV/vis spectra were recorded on a Perkin Elmer Lambda 900 Uv/vis/nearIR spectrophotometer. Cyclic voltammetry was conducted with a scan rate of 0.1 V s$^{-1}$ under an inert atmosphere with 1 M tetrabutylammonium hexafluorophosphate in o-DCB as the electrolyte. The working electrode was a platinum disk and the counter electrode was a silver electrode. The concentration of the sample in the electrolyte was approximately 2 mM, based on monomers. Fc/Fc$^+$ was used as an internal standard.
Field-effect transistors were fabricated using heavily doped silicon wafers as the common gate electrode with a 200 nm thermally oxidized SiO$_2$ layer as the gate dielectric. Using conventional photolithography, gold source and drain electrodes were defined in a bottom contact device configuration with channel width and length of 2500 μm and 10 μm, respectively. A 10 nm layer of titanium was used, acting as an adhesion layer for the gold on SiO$_2$. The SiO$_2$ layer was exposed to the vapor of the primer hexamethyldisilazane for 60 min. prior to semiconductor deposition in order to passivate the surface of the dielectric. PDPP3T films were spun from a chloroform solution at 1500 rpm for 30 s. Freshly prepared devices were annealed in a dynamic vacuum of $10^{-5}$ mbar at 110 °C for 72 h to remove traces of solvent. All electrical measurements were performed in vacuum using an HP 4155C semiconductor parameter analyzer.

Photovoltaic devices were made by spin coating poly(ethylene dioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP Al4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). The photoactive layer was deposited by spin coating from the appropriate solvent. The counter electrode, consisting of LiF (1 nm) and aluminum (100 nm), was deposited by vacuum evaporation at $3 \times 10^{-7}$ mbar. The active area of the cells was 0.091 cm$^2$ or 0.16 cm$^2$. $J$-$V$ characteristics were measured under ~100 mW cm$^{-2}$ white light from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya L B120 daylight filter, using a Keithley 2400 source meter. Short-circuit currents under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The spectral response was measured under simulated 1 sun operation conditions using bias light from a 532 nm solid state laser (Edmund Optics). Monochromatic light from a 50 W tungsten halogen lamp (Philips focusline) in combination with monochromator (Oriel, Cornerstone 130) was modulated with a mechanical chopper. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Stanford Research Systems SR830). A calibrated Si cell was used as reference. The device was kept behind a quartz window in a nitrogen filled container. The thickness of the active layers in the photovoltaic devices were measured on a Veeco Dektak150 profilometer.

**PDPP3T Higher $M_n$ version.** To an argon bubbled solution of 3,6-bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-di(2'-hexyldecyl)-pyrrolo[3,4c]pyrrolo-1,4-dione (242 mg, 266 μmol), 2,5-di-(4,4,5,5-tetramethyl-1,3-dioxaboralane)-thiophene (90 mg, 267 μmol), a 50% Aliquat solution in toluene (0.5 ml), triphenylphosphine (7 mg, 26 μmol) and K$_3$PO$_4$ (286 mg, 1.34 mmol) in toluene (4.5 ml) with demineralised water (0.5 ml), was added tris(dibenzylideneacetone)dipalladium (10 mg, 11 μmol). This mixture was stirred for 3 days at 115 °C after which the crude polymer was precipitated in methanol. The solids were filtered over a Büchner funnel and re-dissolved in chloroform (80 ml) and stirred under reflux with ammonia (80 ml of 25% aq. sol.) for 3 h. The layers were separated and the organic phase was stirred with ethylenediaminetetraacetate (EDTA) (300 mg) for 3 h. Then
demineralised water (100 ml) was added, and the mixture was stirred for another hour. The organic layer was washed with demineralised water (2 × 100 ml), reduced in volume in vacuum and precipitated in methanol. The precipitate was collected in a Soxhlet thimble and was extracted with methanol, hexane, and chloroform until the extracts were colorless. The chloroform fraction was reduced in volume and precipitated in methanol and filtered over a 4.5 μm PTFE filter. The polymer was collected and dried in a vacuum oven at 60 ºC overnight, resulting in 189 mg (84%) of a dark green powder. 1H-NMR: 8.92 (b, 2H), 7.32 (b, 2H), 7.01 (b, 2H), 4.03 (b, 4H), 1.89 (b, 2H), 1.20-1.00 (b, 48H), 0.80-0.70 (b, 12H). GPC: $M_n = 54,000$ g mol$^{-1}$, PDI = 3.15.

**PDPP3T Lower $M_n$ version.** To a solution of 3,6-bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-di(2′-hexyldecyl)-pyrrolo[3,4c]pyrrolo-1,4-dione (227 mg, 250 μmol) and bis(4,4,5,5-tetramethyl-1,3-dioxaborolane)-2,5-thiophene (84 mg, 250 μmol) in toluene (5 ml, degassed for 30 min), aliquat 336 (3 drops) and tetrakis(triphenylphosphine)palladium (6.7 mg, 5.8 μmol) were added. The reaction mixture was heated to 120 ºC, after which degassed (30 min) 2 M aqueous K$_2$CO$_3$ (0.6 ml, 1.2 mmol) was added. After 3 days water (10 ml) was added, followed by an extraction with chloroform (200 ml). Ammonia (100 ml of 25% aq. sol.) was added to the organic phase and the mixture was refluxed for 2 h. After washing with water (2 × 100 mL) and stirring in presence of an excess EDTA in chloroform for at least 3 h, the mixture was washed again with water (3 × 100 ml). The organic phase was concentrated under reduced pressure. The polymer was precipitated in methanol, filtered through a Soxhlet thimble and fractionated by Soxhlet extraction using methanol, hexane and CHCl$_3$, respectively. The polymer was obtained in 170 mg as a green solid (69% yield). 1H-NMR: δ 8.90 (br, 2H), 7.32 (br, 2H), 7.07 (br, 2H), 4.04 (br, 4H), 1.96 (br, 2H), 1.64-1.00 (m, 48H), 0.98-0.61 (m, 12H). $M_n = 10,000$ g mol$^{-1}$, PDI = 2.4.
5.5 References


Chapter 6
Efficient solar cells based on an easily accessible diketopyrrolopyrrole polymer*

Abstract
A new easily accessible, high molecular weight, alternating dithieno-
diketopyrrolopyrrolophenylene co-polymer provides high electron and hole mobilities exceeding 0.02 cm$^2$ V$^{-1}$ s$^{-1}$ in FETs and AM1.5G power conversion efficiencies of 4.6 and 5.5% in solar cells when combined with [60]PCBM and [70]PCBM. The performance of the solar cells strongly depends on the use of a co-solvent.

* Part of this work has been published:
6.1 Introduction

Semiconducting co-polymers with diketopyrrolopyrrole (DPP) units are emerging as interesting materials for optoelectronic applications in field-effect transistors (FETs)\(^1\) and organic photovoltaic cells (OPCs).\(^2\)-\(^9\) Most DPP co-polymers used in efficient organic photovoltaic cells contain synthetically elaborate co-monomers, such as dibenzosilole, benzothiophene, dithienosilole, or substituted bithiophenes. In Chapter 5, PDPP3T has been described which has electron rich terthiophene segments alternating with electron deficient DPP units along the chain, to reach a small optical band gap. In high molecular weights PDPP3T provided a power conversion efficiency (PCE) up to 4.7% in an OPC. Here we present PDPPTPT (Scheme 6.1) as new member of the DPP-based co-polymer family with favorable semiconducting properties that can be synthesized in four simple steps from commercial products. Introduction of the phenyl ring between two thiophene rings adjacent to the DPP unit in the main chain lowers the HOMO level of the polymer compared to PDPP3T and increases the open circuit voltage. In combination with [6,6]phenyl-C\(_{71}\)-butyric acid methyl ester ([70]PCBM) PCEs of 5.5% are obtained under simulated AM1.5G (100 mW cm\(^{-2}\)) conditions.

6.2 Results

6.2.1. Synthesis and properties

PDPPTPT was synthesized by a Suzuki cross coupling reaction between a commercially available benzenediboronic ester and a DPP monomer that can be obtained in three steps (Scheme 6.1).\(^1\) The use of Pd\(_2\)(dba)\(_3\)/PPh\(_3\) as a catalyst yielded a polymer that exhibits a limited solubility (<1 mg ml\(^{-1}\)) in all organic solvents tested, except in chloroform. The optical band gap of a solid film of PDPPTPT was determined from the onset of absorption at 1.53 eV, see Figure 6.1.

Scheme 6.1. Synthesis and Structure of PDPPTPT. i: Pd\(_2\)(dba)\(_3\), PPh\(_3\), K\(_3\)PO\(_4\), Aliquat 336, H\(_2\)O, toluene.
Efficient solar cells based on easily accessible DPP polymer

Figure 6.1. Optical absorption spectra of PDPPTPT in CHCl₃ solution (a) and in the solid state as a thin film (b).

The optical band gap is virtually identical in chloroform solution, indicating that even at low concentration in the best solvent known to us, PDPPTPT is in an aggregated state. Heating the solution to 60 °C causes minor changes in the spectrum. As a consequence of the tendency to aggregate, accurate molecular weight determination was not possible and GPC traces, obtained for different PDPPTPT concentrations in chloroform, were significantly dissimilar, caused by an increased aggregate content or aggregate size at higher concentration.

The energy levels of the frontier orbitals were estimated by cyclic voltammetry (Figure 6.2), which provided the onsets of oxidation and reduction at 0.25 and -1.57 V vs. Fe/Fe⁺, respectively (i.e., -5.35 and -3.53 eV vs. vacuum). This indicates a sufficiently large LUMO level offset (~0.5 eV) for electron transfer from PDPPTPT to [60]PCBM or [70]PCBM that have an onset of reduction at -1.07 V vs. Fe/Fe⁺. Compared to PDPP3T (with a HOMO at -5.17 eV and LUMO at -3.61 V vs. Fe/Fe⁺), the HOMO level is lower while the LUMO is higher.

Figure 6.2. Cyclic voltammogram of PDPPTPT
6.2.2. FETs

Field-effect transistors were fabricated in a bottom-gate bottom-contact geometry. Typical transfer curves are presented in Figure 6.3a and 6.3b for positive and negative drain biases. PDPPTPT clearly exhibits ambipolar behavior. Charge carrier mobilities of PDPPTPT were extracted in the saturated region and amount to 0.02 ± 0.01 and 0.04 ± 0.01 cm² V⁻¹ s⁻¹ for electrons and holes, respectively. These characteristics enabled fabricating CMOS-like inverters by combining two identical ambipolar transistors with a common gate (inset of Figure 6.3c). Figure 6.3c shows the output voltage ($V_{\text{OUT}}$) of such inverter as a function of the input voltage ($V_{\text{IN}}$) at constant supply bias ($V_{\text{DD}}$). From the steepness of the inverter curve a gain of 15 is obtained, which is comparable to state-of-the-art CMOS-like inverters.

![Typical ambipolar transfer characteristics of a field-effect transistor with PDPPTPT as the semiconductor (a and b). Channel length and width were 10 and 10000 μm, respectively. Static input-output characteristics of an inverter based on two identical ambipolar FETs (c). Channel length and width were 10 and 2500 μm, respectively.](image)

6.2.3. Photovoltaic devices

Photovoltaic cells were fabricated by spin coating a mixed layer of PDPPTPT and PCBM onto a glass/ITO/PEDOT:PSS electrode and evaporation of LiF/Al as a back contact, using an optimized 1:2 PDPPTPT:PCBM weight ratio and layer thickness of 80-90 nm. Using pure chloroform for processing the blends, only modest PCEs of ca. 2% were obtained for cells with [60]PCBM and [70]PCBM, due to low photocurrents. Losses in these devices are mainly related to the coarse de-mixing of the polymer:fullerene blend as evidenced by transmission electron microscopy (TEM, Figure 6.4a and d) and atomic force microscopy (AFM, Figure 6.5 a and d).
Efficient solar cells based on easily accessible DPP polymer

Figure 6.4. TEM images of layers consisting of PDPPTPT and [60]PCBM (a-c) and [70]PCBM (d-f) processed from CHCl₃ (a,d), with 25 mg mL⁻¹ DIO (b,e) and with 200 mg mL⁻¹ DIO (c,f). The scale bar is 200 nm.

Figure 6.5. AFM height images (1 x 1 µm) of layers consisting of PDPPTPT and [60]PCBM (a-c) and [70]PCBM (d-f) processed from CHCl₃ (a,d), with 25 mg ml⁻¹ DIO (b,e) and with 200 mg ml⁻¹ DIO (c,f). Height scales are 10 nm (a), 15 nm (b,c,f), 20 nm (e) and 35 nm (d).

The morphology of the blend can greatly be improved by addition of a co-solvent during processing.²,¹³-¹⁵ Here 1,8-diiodooctane (DIO) is used, affording a much finer phase separation. The effect of DIO is most clearly visualized by TEM (Figure 6.4). Mixed films, processed from chloroform without DIO contain large (>200 nm wide) fullerene clusters that show up as dark regions in the bright-field TEM image, owing to the crystallinity and the relatively high density of PCBM (~1.5 g cm⁻³).¹⁶ These coarse morphologies are known to result in poor device performance.²,¹⁷ In films, processed with DIO, large fullerene domains are absent. Instead, elongated structures are observed, which are brighter than the background and therefore attributed to polymer fibers. Despite the fibrillar nature of the polymer in these blends, electron diffraction did not reveal any reflections, besides those of PCBM crystallites,
suggesting that the polymer remains essentially amorphous. DIO is a good solvent for fullerenes and is much less volatile than chloroform. As such, it prevents the formation of large PCBM domains during spin coating.

Figure 6.6. Power conversion efficiency of PDPPTPT:PCBM cells vs. DIO content in coating solution.

Figure 6.6 shows that addition of 25 mg ml$^{-1}$ DIO results in optimal performing cells, both with [60]PCBM and [70]PCBM as the electron acceptor. The $J-V$ curves of the best cells are shown in Figure 6.7a. Under simulated AM1.5G conditions, cells fabricated with [60]PCBM exhibit an open circuit voltage ($V_{oc}$) of 0.79 V, a short circuit current density ($J_{sc}$) of 9.3 mA cm$^{-2}$, and a fill factor (FF) of 0.63, resulting in a PCE of 4.6% (Table 6.1) (values are averaged for 8 cells, ranging from 4.5-4.7%). Changing the acceptor to [70]PCBM, which has an increased absorption in the visible part of the spectrum, improved the $J_{sc}$ to 10.8 mA cm$^{-2}$, as derived from convolution of the external quantum efficiencies (EQE, Figure 6.7b). The $V_{oc}$ remains at 0.80 V and also the FF is preserved at 0.65, resulting in a PCE of 5.5% (Table 6.1) (values are averaged for 8 cells, ranging from 5.5-5.6%). The EQE (Figure 6.7b) display a very sharp onset at the optical band gap of the polymer. Cells with [70]PCBM display an EQE above 40% over a broad spectral range (770-440 nm). Cells made with [60]PCBM exhibit an even higher response (~45%) in the 600-750 nm region, but due to a lower response below 600 nm, these are outperformed by the [70]PCBM devices.
In a comparison to two related small band gap DPP-based polymers which were reported recently,²⁸ PDPPTPT provides an improved efficiency in a solar cell (5.5% vs. 4.0% for PBBTDPP² and 4.7% for PDPP3³⁸). The main reason for the enhanced performance of PDPPTPT is an increase $V_{oc}$, which is induced by a lowering of the HOMO level combined with somewhat higher optical band gap to prevent reducing the driving force for electron transfer.

### 6.2.4. Nature of co-solvent

To obtain more insight in the effect and prerequisites of co-solvents, other co-solvents were tested for their effect on layers and photovoltaic behavior of layers consisting of PDPPTPT and [60]PCBM. In the parent view, the spincoating process is a balance between crystallization of the PCBM and solidification of the polymer. The role of the co-solvent is then to delay the crystallization of PCBM, while at the same time precipitation of the polymer is taking place, so the growth of large agglomerates visible in Figure 6.4a and 6.4d is avoided. A suitable co-solvent that can do this, should be miscible with chloroform, show a higher solubility for [60]PCBM than for PDPPTPT and have a higher boiling point than chloroform. Three co-solvents were selected that show this behavior: 1,8-dibromooctane (DBO), ortho-dichlorobenzene (o-DCB) and ortho-dibromobenzene (o-DBB) (Scheme 6.2).

![Scheme 6.2. Structure of the selected co-solvents](image-url)
With all of the selected co-solvents, OPCs based on PDPPTPT and [60]PCBM were optimized for the layer thickness, amount of co-solvent in the spincoating mixture and the ratio of PDPPTPT to [60]PCBM. The optimal ratio turned out to be 1:2 in weight. The best performing layers displayed thicknesses between 90 and 100 nm for each of the co-solvents. The amount of co-solvent needed for optimal performance of the layer was varied. For the alkane derivatives, approximately half the amount is needed compared to the aromatic co-solvents. This is remarkable, because one of the prerequisites is the higher PCBM solubility in the co-solvent, which is higher for the aromatic co-solvents. Apparently solubility alone does not explain these differences.

**Figure 6.8.** MPP (not corrected with EQE) vs. The amount of co-solvent in OPCs based on PDPPTPT and [60]PCBM

A striking feature of Figure 6.8 is that, within a small margin, all the co-solvents lead to a similar performance. This similarity in performance obtained with different co-solvents suggests that, when using the optimal amounts, they all lead to the same morphology and domain sizes. To verify this hypothesis, the internal structure of the layers with different co-solvents was studied with TEM and the images (Figure 6.9 and 6.5b) reveal that qualitatively very similar morphologies are obtained.

**Figure 6.9.** TEM images of layer optimized with DBO (a), \(o\)-DCB (b) and \(o\)-DBB (c). Scale bar is 100 nm

This raises the question if this performance is the maximum attainable with this material combination and this processing method. Other methods of optimizing layer which have
proven to work for other polymer:PCBM layers,\textsuperscript{18} like heating or solvent annealing, i.e. exposing the layer to a saturated vapor of (co-)solvent did not improve performance.

\section*{6.2.5. Photophysics}

To investigate the effect of DIO on the photophysics of the polymer:fullerene blends we used photoinduced absorption (PIA). The PIA spectrum of the blend (Figure 6.10a) shows two distinct peaks at 0.9 and 1.1 eV and a bleaching signal between 1.5 and 2 eV. In the pure polymer only the PIA signal at 1.1 eV of the triplet state is detected. The 0.9 eV peak is assigned to polymer radical cations because it corresponds to the absorption band of chemically oxidized PDPPTPT (Figure 6.10b). Radical cations (polarons) of conjugated polymers generally give two absorption bands,\textsuperscript{19} but in case of PDPPTPT the low energy band appears to be shifted below the low energy limit of our PIA setup and only the onset of this band can be detected below 0.5 eV. The presence of both triplets and radical cations in the PIA spectrum of PDPPTPT:PCBM can be rationalized in two ways: either not all excitons created in the polymer are quenched, eventually leading to intersystem crossing and triplets, or part of the initially charge separated states recombine to the triplet state.\textsuperscript{20,21} Because the intensity of the triplet absorption in the pristine film is significantly lower than in the blend, the triplets in the blend most likely result from charge recombination rather than from direct intersystem crossing from the excitons.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure610.png}
\caption{Photoinduced absorption spectra of recorded at $T = 80 \text{ K}$ ($\lambda_{\text{ex}} = 780 \text{ nm}$) layers made with PDPPTPT and [70]PCBM processed with and without 25 mg ml$^{-1}$ DIO (a). Absorption difference between oxidized and pristine PDPPTPT (closed squares) and PIA of a pristine PDPPTPT (open circles) (b).}
\end{figure}

Comparing the PIA spectra of mixed films deposited with and without DIO, we learn that DIO affords larger radical cation and triplet signals, whereas their ratio remains essentially constant. This can be caused by a higher initial charge generation efficiency and/or by a longer lifetime for the photoinduced species.
6.3 Conclusions

In conclusion, we have synthesized PDPPTPT in one step from two easily accessible monomers. PDPPTPT has high charge carrier mobilities for electrons and holes and the absorption spectrum has good overlap with the solar spectrum. These characteristics lead to photovoltaic cells with a PCE of 5.5%, when using [70]PCBM as electron acceptor. The performance of the solar cells strongly depends on the morphology of the active layer of the cell, which was optimized by varying the amount of DIO used in the processing. This is in remarkable correspondence with recent results of high efficiency solar cells based on alternating co-polymers using benzothiadiazole or thieno[3,4-b]thiophene as electron deficient units in the main chains.\textsuperscript{13-15}

6.4 Experimental

Polymerization reactions were conducted under an argon atmosphere. Commercial chemicals were used as received. [60]PCBM (purity >99%) and [70]PCBM (purity >95%) were purchased from Solenne BV. \textsuperscript{1}H-NMR spectra were recorded at 400 MHz on a VARIAN mercury spectrometer with CDCl\textsubscript{3} as the solvent and tetramethylsilane (TMS) as the internal standard. The peaks are given in ppm, relative to TMS (0 ppm). Molecular weights were determined with GPC on a Shimadzu LC-10AD using a Polymer Laboratories Resipore column (length 300 mm, diameter 7.5 mm), a Shimadzu SPD-M20A photodiode array detector from 250-700 nm and chloroform as the eluens with a flow rate of 1 mg min\textsuperscript{-1}. (T= 293 K). Polystyrene standards were used.

UV-vis-near IR spectra were recorded on a Perkin Elmer Lambda 900 spectrophotometer. Oxidation experiments were performed under an inert atmosphere with thianthrenium hexafluorophosphate\textsuperscript{22} as the oxidant. Cyclic voltammetry was conducted under an inert atmosphere with a scan rate of 0.1 V s\textsuperscript{-1}, using 1 M tetrabutylammonium hexafluorophosphate in o-DCB as the electrolyte. The solution was stirred for 72 h at room temperature to ensure enough PDPPTPT was dissolved. The working electrode was a platinum disk and the counter electrode was a silver rod electrode. A silver wire coated with silver chloride (Ag/AgCl) was used as quasi-reference electrode in combination with Fe/Fe\textsuperscript{2+} as an internal standard. The vacuum level of Fe/Fe\textsuperscript{2+} is assumed at –5.1 eV. Tapping mode AFM was measured on a MFP-3D (Asylum research) using PPP-NCHR probes (Nanosensors). Transmission electron microscopy was performed on a Tecnai G\textsuperscript{2} Sphera TEM (FEI) operated at 200 kV.
Field-effect transistors were fabricated using heavily doped silicon wafers as the common gate electrode with a 200 nm thermally oxidized SiO$_2$ layer as the gate dielectric. Using conventional photolithography, gold source and drain electrodes were defined in a bottom contact device configuration with channel width and length of 10000 μm and 10 μm, respectively. A 10 nm layer of titanium was used acting as an adhesion layer for the gold on SiO$_2$. The SiO$_2$ layer was exposed to the vapor of the primer hexamethyldisilazane for 60 min. prior to semiconductor deposition in order to passivate the surface of the dielectric. PDPPTPT films were spun from a chloroform solution at 1500 rpm for 30 s. Freshly prepared devices were annealed in a dynamic vacuum of $10^{-5}$ mbar at 100 ºC for 72 h to remove traces of solvent. All electrical measurements were performed in a vacuum using an HP 4155C semiconductor parameter analyzer. The reported values are average values over five different devices.

Photovoltaic devices were made by spin coating poly(ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP Al4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). The photoactive layer was deposited by spin coating a chloroform solution containing 6 mg ml$^{-1}$ PDPPTPT and 12 mg ml$^{-1}$ PCBM and the appropriate amount of 1,8-diiodooctane. The counter electrode, consisting of LiF (1 nm) and Al (100 nm), was deposited by vacuum evaporation at $\sim 3 \times 10^{-7}$ mbar. The active area of the cells was 0.091 or 0.162 cm$^2$ and no size dependence was found between these two dimensions. For larger areas, starting at 0.36 cm$^2$, resistive losses in the ITO lead to a reduction of FF. J-V characteristics were measured under $\sim 100$ mW cm$^{-2}$ white light from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter, using a Keithley 2400 source meter. Short-circuit currents under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The spectral response was measured under simulated 1 sun operation conditions using bias light from a 532 nm solid state laser (Edmund Optics). Monochromatic light from a 50 W tungsten halogen lamp (Philips focusline) in combination with monochromator (Oriel, Cornerstone 130) was modulated with a mechanical chopper. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Stanford research Systems SR830). A calibrated Si cell was used as reference. The device was kept behind a quartz window in a nitrogen filled container. This method has shown to give PCEs that are in close correspondence with those obtained using a WXS-300S-50 solar simulator and using spectral mismatch correction. In the J-V measurements made with the white light set up described above, the measured $J_{sc}$ differed on average by 3-4% from the value obtained by convoluting the spectral response with AM1.5G (see Table 6.1). The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak150 profilometer.

Photoinduced absorption (PIA) samples were prepared by spin coating the appropriate mixture on quartz substrates. PIA spectra were recorded by exciting with a mechanically modulated B&W, Tek Inc. laser ($\lambda = 780$ nm) pump beam and monitoring the resulting change in transmission of a
tungsten-halogen probe light through the sample (ΔT) with a phase-sensitive lock-in amplifier after
dispersion by a grating monochromator and detection, using Si, InGaAs, and cooled InSb detectors.
The pump power incident on the sample was typically 21 mW with a beam diameter of 1 mm. The
PIA (ΔT/T) was corrected for the photoluminescence, which was recorded in a separate experiment.
Photoinduced absorption spectra and photoluminescence spectra were recorded with the pump beam in
a direction almost parallel to the direction of the probe beam. Temperature of the substrates was
controlled by using an Oxford Optistat continuous flow cryostat.

PDPPTPT. Tris(dibenzylideneacetone)dipalladium (10 mg, 11 μmol) was added to an argon
bubbled mixture of 3,6-bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-di(2′-hexyldecyl)-pyrrolo[3,4-c]pyrrolo-1,4-dione (221 mg, 244 μmol), 1,4-di-(4,4,5,5-tetramethyl-1,3-dioxaboralane)-benzene (80.5 mg, 244 μmol), 50% Aliquat solution (v/v) in toluene (0.5 ml), triphenylphosphine (7 mg, 26 μmol), and K3PO4 (221 mg, 1.04 mmol) in toluene (4 ml) with demineralised water (0.5 ml).
This mixture was stirred for 3 h at 115 ºC in a Schlenk flask after which the crude polymer was
precipitated in methanol. The solids were filtered over a Büchner funnel and redissolved in chloroform
(80 ml) and stirred under reflux with ammonia (50 ml of 25% aq. sol.) for 2 h. The layers were
separated and the organic phase was stirred with ethylenediaminetetraacetate (300 mg) for 3 h. Then
demineralised water (50 ml) was added, and the mixture was stirred for 2 h. The layers were separated
and the organic layer was reduced in volume in vacuum and precipitated in methanol. The precipitate
was collected in a Soxhlet thimble and was extracted with methanol, hexane, and chloroform until
the extracts were colorless. The chloroform fraction was reduced in volume and precipitated in methanol
and filtered over a 4.5 μm PTFE filter. The polymer was collected and dried in a vacuum oven at 60 ℃
overnight, resulting in 141 mg (69%) of a dark powder.

1H-NMR: 9.0 (b, 2H), 7.5 (b, 4H), 7.1 (b, 2H), 4.0 (b, 4H), 1.9 (b, 2H), 1.20-1.00 (b, 48H),
0.80-0.70 (b, 12H).
6.5 References

(8) See Chapter 4 of this thesis
Chapter 7
Copolymers of diketopyrrolopyrrole and thienothiophene for photovoltaic applications*

Abstract

Three new copolymers of thieno[3,2-b]thiophene and diketopyrrolo[3,4-c]pyrrole with a varying number of connecting thiophene units were synthesized by Suzuki coupling. The polymers displayed optical band gaps in the range of 1.33 to 1.52 eV and showed ambipolar charge transport when applied in a field-effect transistor (FET) with hole and electron mobilities up to $3 \times 10^{-2}$ and $2 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively. Organic solar cells based on the new polymers as donor and [60]PCBM as acceptor achieved power conversion efficiencies up to 3.4% when the layer was deposited with the use of a co-solvent. The co-solvent was shown to strongly affect the morphology of the active layer. For these polymers the LUMO-LUMO offset with [60]PCBM correlates with the photocurrent and the maximum external quantum efficiency.

* This work will be submitted for publication:
7.1 Introduction

Solar cells are rapidly developing as a prime application of organic semiconductors.\textsuperscript{1} Published power conversion efficiencies (PCEs) are as high as 7.4\% at present.\textsuperscript{2} Apart from having a large overlap of the absorption spectrum with the solar emission and suitable HOMO and LUMO levels, many additional prerequisites have to be met for a polymer to act as successful donor in organic photovoltaic cells (OPCs). In addition to suitable physical properties, such as molecular weight, solubility, and ability to form a nanoscale phase separated blend with acceptor materials, a high charge carrier mobility is required to optimize the fill factor and transport of photogenerated charges to the electrodes.

Tuning of absorption and frontier orbital levels is mostly done by combining electron rich and electron poor moieties in the main chain of the polymer,\textsuperscript{3} following strategies as described in Chapter 1, but the design of materials with high charge carrier mobility is less well controlled. Increasing the tendency of the conjugated polymers to aggregate and crystallize, as well as increasing the size of π-conjugated segments, often leads to more π-stacking and improved interchain charge transfer. Consequently, fusing of aromatic rings and optimizing thin film processing has resulted in field-effect transistors (FET) structures in which conjugated polymers display charge carrier mobilities in the order of 0.1 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} for electrons\textsuperscript{4} and 1 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} for holes.\textsuperscript{5} Polymers based on the fused ring system thieno[3,2-\textit{b}]thiophene (TT) have displayed high charge carrier mobility in FET devices.\textsuperscript{6} Moreover, in OPCs high voltages were obtained with TT-based polymers,\textsuperscript{7} making it an interesting building block for incorporating in conjugated polymers.

In the two previous chapters, polymers based on 3,6-di-2-thienyl-1,4-diketopyrrolo[3,4-\textit{c}]pyrrole (T-DPP-T) alternating with intermediate 2,5-thienylene and 1,4-phenylene units were shown to provide PCEs in OPCs exceeding 5\% together with an ambipolar charge transport in FETs, with electron and hole mobilities exceeding 10\textsuperscript{-2} cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}. High performance of PCE = 4\% was also obtained when T-DDP-T was alternating with 3,3\textsuperscript{′}-didodecyl-2,2\textsuperscript{′}-bithiophene-5,5\textsuperscript{′}-diyl as in PBBTDPP.\textsuperscript{8} On the other hand, for the T-DPP-T homopolymer photoinduced electron transfer to PCBM is inhibited by a small LUMO-LUMO offset.\textsuperscript{9} From these examples it is clear that by controlling the aromatic segment alternating with the T-DPP-T segment, polymers with high efficiencies can be obtained. This justifies further exploring these structures to increase performance.
Here we present three new polymers (I-III) based on T-DPP-T alternating with TT or T-TT-T (Scheme 7.1) and vary the alkyl side chains to control the optical band gap, HOMO and LUMO levels, and charge transport characteristics. It will be shown that the polymers reach charge carrier mobilities in the $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ regime in FETs and that in OPCs they provide a PCE up to 3.4% with [60]PCBM as acceptor.

![Scheme 7.1. Structures of the three TT based polymers](image)

### 7.2 Results

#### 7.2.1 Synthesis

The synthesis of the TT and T-TT-T monomers is shown in Scheme 7.2. The synthesis of 2,5-dibromo-3,6-di(4′-ethyloctyl)thieno[3,2-b]thiophene (1) has already been described in Chapter 5, while 2,5-dibromothieno[3,2-b]thiophene (3) was obtained from TCI. The corresponding boronic esters 2 and 4 were obtained via debromination with $n$-butyllithium and subsequent borylation of the formed anions. The conversion occurred with reasonable yield for 2, but the yield for 4 was poor due to a difficult purification and the high purity required for the polymerization reaction. The first step in the synthesis of monomer 7 was a Stille coupling of 1 with 2-(tributylstannyl)thiophene to yield 5. Bromination with NBS led to 6, which was borylated in the same way as 1 and 3 to give monomer 7 in high yield. The T-DDP-T monomers, 3,6-bis(5-bromothien-2-yl)-2,5-dihydro-2,5-di(dialkyl)-pyrrolo[3,4-c]pyrrolo-1,4-dione 8 and 9 (Scheme 7.3) were synthesized according to literature procedures.$^{10,11}$
Polymers I-III were synthesized as described in Scheme 7.3 using a Suzuki reaction with Pd$_2$(dba)$_3$ as the catalyst. The polymers were obtained with number average molecular weights ($M_n$) in the range of 9,000 – 15,000 g mol$^{-1}$ and polydispersity indices varying from 2 to 4 (Table 7.1).

**Scheme 7.2.** Synthesis of the TT and T-TT-T monomers.

**Scheme 7.3.** Synthesis and structures of the polymers I - III: i: Pd$_2$(dba)$_3$, PPh$_3$, aliquat 336, K$_3$PO$_4$, water, toluene, 105 ºC.
7.2.2 Optical, electrochemical and electrical properties

The absorption spectra of the polymers are shown in Figure 7.1 for solutions in chloroform and for thin films on glass. Going from solution to the solid state there is a small red shift of the absorption, signifying aggregation of chains. The optical band gaps in the solid state were determined from the onsets of absorption (Table 7.1). The optical band gaps of I and II (1.31-1.33 eV) are very similar to that of PDPP3T (1.36 eV, Chapter 5), showing that the effect of the thieno[3,2-b]thiophene-2,5-diyl unit (TT) on the optical gap is similar to that of thiophene-2,5-diyl (T). The similar band gap is somewhat unexpected because the higher aromatic stabilization energy of thieno[3,2-b]thiophene compared to a single thiophene, would result in an increased the gap between the aromatic and quinoid states. The optical band gap of III is much larger (1.52 eV), also compared to PBBTDPP2 (1.40 eV),\(^9\) and resembles that of PDPPTPT (1.53 eV, Chapter 6). This shows that the extending the number of thiophene units between the DPP units can be used to widen the optical band gap.

![Figure 7.1. Optical absorption spectra of I-III in chloroform solution (a) and in the solid state (b).](image)

The HOMO and LUMO levels of the polymers were determined by cyclic voltammetry (CV) in \(\sigma\)-DCB solution (Table 7.1). I and II have very similar HOMO levels but their LUMO levels differ by 80 mV. This difference is also reflected in the optical band gap in solution, which is a little larger for I. The reason for the higher band gap could be that the alkyl chains on the thieno[3,2-b]thiophene induce twisting between adjacent units, decreasing the orbital overlap and conjugation. For III, the low solubility in pure \(\sigma\)-DCB required a CV measurement in a mixture of \(\sigma\)-DCB and chloroform. Due to reduction of chloroform at negative potentials, only the HOMO level of III could be obtained from the CV experiments. The LUMO of III was estimated at -1.54 \pm 0.03 V vs. Fe/Fe\(^+\) from the optical band gap and
the HOMO level, correcting for the average difference between $E_{g, \text{sol}}$ and $eE_{g, \text{CV}}$ for the other two polymers ($\Delta E_g = 0.06 \pm 0.03 \text{ eV}$) (Table 7.1), to give $eE_{\text{LUMO}} \approx eE_{\text{HOMO}} - E_{g, \text{sol}} - \Delta E_g$.

Table 7.1. Physical properties of the polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (kg mol$^{-1}$)</th>
<th>PDI</th>
<th>$E_{g, \text{sol}}$ (eV)</th>
<th>$E_{g, \text{film}}$ (eV)</th>
<th>HOMO (V)$^a$</th>
<th>LUMO (V)$^a$</th>
<th>$E_{g, \text{CV}}$ (V)</th>
<th>$\Delta E_g$ (eV)</th>
<th>$\alpha$ (eV)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>13</td>
<td>2.0</td>
<td>1.39</td>
<td>1.33</td>
<td>0.08</td>
<td>-1.39</td>
<td>1.47</td>
<td>0.08</td>
<td>0.32</td>
</tr>
<tr>
<td>II</td>
<td>9</td>
<td>3.9</td>
<td>1.34</td>
<td>1.31</td>
<td>0.10</td>
<td>-1.31</td>
<td>1.41</td>
<td>0.03</td>
<td>0.24</td>
</tr>
<tr>
<td>III</td>
<td>15</td>
<td>4.0</td>
<td>1.58</td>
<td>1.52</td>
<td>0.10</td>
<td>$\sim-1.54^b$</td>
<td>$\sim0.47$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBBTDPP2</td>
<td>20</td>
<td>3.4</td>
<td>1.70</td>
<td>1.40</td>
<td>0.30</td>
<td>-1.40</td>
<td>1.70</td>
<td>0.00</td>
<td>0.33</td>
</tr>
<tr>
<td>PDPP3T</td>
<td>54</td>
<td>3.2</td>
<td>1.36</td>
<td>1.30</td>
<td>0.07</td>
<td>-1.49</td>
<td>1.56</td>
<td>0.20</td>
<td>0.42</td>
</tr>
<tr>
<td>PDPPTPT</td>
<td>-</td>
<td>-</td>
<td>1.53</td>
<td>1.53</td>
<td>0.25</td>
<td>-1.57</td>
<td>1.82</td>
<td>0.29</td>
<td>0.50</td>
</tr>
</tbody>
</table>

$^a$ vs. Fc/Fc$^+$; $^b$ Estimated, see text. $^c$ $\alpha = E_{\text{LUMO(PCBM)}} - E_{\text{LUMO}}$, with $E_{\text{LUMO(PCBM)}} = -1.07$ vs. Fc/Fc$^+$.  

The pristine polymers were applied in a FET structure to measure their charge carrier mobility. All polymers show ambipolar behavior, see Figure 7.2. The transfer curves of I and II are similar and the hole and electron mobilities ($\mu_h$ and $\mu_e$, Table 7.2) determined from the slope of the square root of source-drain current ($|I_{DS}|^{1/2}$) vs. the gate voltage ($V_G$) in the saturation regime$^{13}$ and are within one order of magnitude. Apparently, the presence of the alkyl side chains does not significantly affect the charge transport properties. The transfer curves of III are notably different from the other two because both $\mu_h$ and $\mu_e$ are lower. The low $\mu_e$ results in a larger on/off ratio at negative gate voltages. The hole mobility of I-III is less than for TT-based polymers that have been optimized for use in FETs,$^6$ but similar to those achieved with other DPP based polymers such as PBBTDPP2, PDPP3T, and PDPPTPT. For I and II $\mu_h$ and $\mu_e$ are fairly balanced.
Copolymers of DPP and thienothiophene for photovoltaics

Figure 7.2. Transfer curves of FETs (channel width and length are 10 μm and 2500 μm, respectively) made with the pristine polymers.

Table 7.2. Electron and hole mobilities of the pristine polymers in a FET.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\mu_h$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_e$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$1 \times 10^{-2}$</td>
<td>$2 \times 10^{-3}$</td>
</tr>
<tr>
<td>II</td>
<td>$3 \times 10^{-2}$</td>
<td>$9 \times 10^{-3}$</td>
</tr>
<tr>
<td>III</td>
<td>$5 \times 10^{-3}$</td>
<td>$2 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

7.2.3. Photovoltaic devices

Solar cells were built by spin coating the active layer from a solution of [60]PCBM and the polymer on a sheet of glass, covered with ITO and a layer of PEDOT:PSS. LiF and aluminum were evaporated in vacuum and served as the reflecting second electrode. The active layer was optimized for the polymer:[60]PCBM ratio. Optimal photovoltaic behavior was found for an excess of [60]PCBM (by weight) (Table 7.3). Similar to previous reports,$^{14,15}$ the use of 1,8-diiodooctane (DIO) as a co-solvent was found to be beneficial in creating a morphology of the active layer that leads to improved performance of the cells.
Figure 7.3. Tapping mode AFM images (lateral dimensions 5 µm) of layers consisting of [60]PCBM and I (a, d), II (b, e) and III (c, f) in the ratios mentioned in Table 7.3, without DIO (a-c) and with the optimal amount of DIO (d-f). Height scales are 10 nm (a, c, d, f), 15 nm (e) and 20 nm (b).

Tapping mode AFM showed that layers processed without DIO contain large (100-200 nm) globular domains of semicrystalline [60]PCBM (Figure 7.3(a-c)), but when a small amount of DIO was added to the mixture of polymer and [60]PCBM in chloroform before the spin coating, the large [60]PCBM clusters disappeared and the length scale of phase separation decreased (Figure 7.3(d-f)). Simultaneously, the photovoltaic behavior of the cells increased significantly (Figure 7.4). For cells made with II and III an optimal performance was found when 25 mg ml\(^{-1}\) DIO was added to the chloroform and cells with I needed even less of the co-solvent (10 mg ml\(^{-1}\)). The marked change in performance is a consequence of the change in morphology. The increase in performance when using DIO is mainly due to an increase in photocurrent (Figure 7.4b), while the \(V_{oc}\) and the fill factor remain relatively constant. The variation on \(V_{oc}\) was less than 5% and the fill factors were within 20% of the best value. Addition of extra DIO in the spin coating mixture resulted in a reduced performance of the cells as a result of a lower photocurrent.
The $J$-$V$ curves and the monochromatic external quantum efficiencies of the best cells are shown in Figure 7.5. The relevant parameters are listed in Table 7.3. For all cells, the FFs are in the same range, despite the fact that hole mobility of III was less than for I and II. The onsets of the EQEs correspond to the optical band gaps of the polymers, extending up to 900 nm for the cells made with I and II. Figure 7.5b shows, however that for II the EQE reaches only 5% in the region where the polymer absorbs, while for II and III the EQE is reaching much higher values of 20% and 35%, respectively. The increase in EQE going from II, via I, to III correlates with the LUMO-LUMO offset energy $\alpha$ (Table 7.1). The very low EQE for II is consistent with the notion that its $\alpha$ of 0.24 eV is less than the minimal value of 0.3-0.4 eV that is generally considered to be required for efficient exciton separation.\textsuperscript{16,17} This conclusion is supported for three other high efficiency DPP derivatives, for which relevant parameters are collected in Tables 7.2 and 7.3. We note that for polymers I-III listed in Table 7.3 the molecular weight ($M_n$) is less than for the three previously reported DPP polymers (Table 7.1). Especially for PDPP3T, the influence of $M_n$ on the PCE has been found to be very significant and this possibly hampers a straightforward correlation between EQE and $\alpha$.
### Table 7.3. Characteristics of the best cells based on [60]PCBM and DPP polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ratio polymer:</th>
<th>$J_{sc}^a$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Max EQE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1:2</td>
<td>6.0</td>
<td>0.68</td>
<td>0.59</td>
<td>2.3</td>
<td>0.20</td>
</tr>
<tr>
<td>II</td>
<td>1:1.5</td>
<td>2.8</td>
<td>0.63</td>
<td>0.61</td>
<td>1.2</td>
<td>0.05</td>
</tr>
<tr>
<td>III</td>
<td>1:1.5</td>
<td>8.2</td>
<td>0.65</td>
<td>0.63</td>
<td>3.4</td>
<td>0.35</td>
</tr>
<tr>
<td>PBBTDPP2^B</td>
<td>1:2</td>
<td>9.0</td>
<td>0.63</td>
<td>0.54</td>
<td>3.2</td>
<td>0.42</td>
</tr>
<tr>
<td>PDPP3T</td>
<td>1:2</td>
<td>8.3</td>
<td>0.68</td>
<td>0.67</td>
<td>3.8</td>
<td>0.33</td>
</tr>
<tr>
<td>PDPPTPT</td>
<td>1:2</td>
<td>9.3</td>
<td>0.79</td>
<td>0.63</td>
<td>4.6</td>
<td>0.45</td>
</tr>
</tbody>
</table>

^a$J_{sc}$ was derived from spectral response measurements under the bias of approximately one sun. The data of PDPP3T and PDPPTPT are taken from chapter 5 and 6, respectively.

![Figure 7.5](image)

**Figure 7.5.** $J-V$ curves (a) and external quantum efficiency (b) of the best cells with [60]PCBM and polymers I-III.

### 7.3 Conclusions

Three new polymers based on thieno[3,2-$b$]thiophene and diketopyrrolo[3,4-$c$]pyrrole with a varying number of connecting thiophene units have been synthesized and characterized. The polymers exhibit suitable absorption spectra and energy levels for use as a donor in OPCs. All polymers show ambipolar charge transport with hole mobilities in the $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ range. The morphology of the active layers and the photovoltaic performance of the resulting OPCs with [60]PCBM as acceptor strongly depend on the use of a co-solvent. The best solar cells exhibited a PCE of 3.4%.
7.4 Experimental

All synthetic procedures were performed under an argon atmosphere. Commercial chemicals were used as received. Dry solvents were distilled over 4 Å molecular sieves. 2,5-Dibromo-3,6-di(4′-ethyoctyl)thieno[3,2-b]thiophene (1) and 3,6-bis(5-bromothien-2-yl)-2,5-dihydro-2,5-dialkylpyrrolo[3,4-c]pyrrolo-1,4-diones (8 and 9) were synthesized according to literature procedures.7,11,12

\(^1\)H-NMR and \(^{13}\)C-NMR spectra were recorded at 400 MHz and 100 MHz respectively on a VARIAN mercury spectrometer with CDCl3 as the solvent and tetramethylsilane (TMS) as the internal standard. The peaks are given in ppm, relative to TMS (0 ppm). Molecular weights were determined with GPC at 80 ºC on a PL-GPC 120 system using a PL-GEL 5 \(\mu\text{MIXED-C}\) column and \(\alpha\)-DCB as the eluent.

UV/vis spectra were recorded on a Perkin Elmer Lambda 900 Uv/vis/nearIR spectrophotometer. Cyclic voltammograms were recorded with a scan rate of 0.1 V s\(^{-1}\) under an inert atmosphere with 1M tetrabutylammonium hexafluorophosphate (TBAPF\(_6\)) in \(\alpha\)-DCB as the electrolyte. The working electrode was a platinum disk and the counter electrode was silver rod. The concentration of the samples in the electrolyte was approximately 2 mM, based on monomers. Fe/Fe\(^+\) was used as internal standard.

Field-effect transistors were fabricated using heavily doped silicon wafers as the common gate electrode with a 200 nm thermally oxidized SiO\(_2\) layer as the gate dielectric. Using conventional photolithography, gold source and drain electrodes were defined in a bottom contact device configuration with channel length and width of 10 \(\mu\)m and 2500 \(\mu\)m, respectively. A 10 nm layer of titanium was used acting as an adhesion layer for the gold on SiO\(_2\). The SiO\(_2\) layer was exposed to the vapor of the primer hexamethyldisilazane for 60 min. prior to semiconductor deposition in order to passivate the surface of the dielectric. Polymer films were spun from a chloroform solution at 1500 rpm for 30 s. Freshly prepared devices were annealed in a dynamic vacuum of 10\(^{-5}\) mbar at 100 ºC for 72 h to remove traces of solvent. All electrical measurements were performed in a vacuum using an HP 4155C semiconductor parameter analyzer.

Photovoltaic devices were processed on cleaned patterned ITO glass substrates. A mixed solution of polymer and [60]PCBM (Sollenne BV) in a weight ratio as indicated in Table 7.3 was spin coated from chloroform with the appropriate amount of DIO on 50 nm of PEDOT:PSS (Clevios P VP AI 4083, H.C. Starck). The devices were transported into a glovebox with nitrogen atmosphere. LiF (1 nm) and aluminum (100 nm) were thermally evaporated on top of the active layer at a pressure of 10\(^{-7}\) mbar. The devices had an active area of 0.091 cm\(^2\) which is determined by the overlap of the ITO and the evaporated aluminum. Current-voltage curves were measured with a Keithley 2400 source meter under nitrogen in the dark and under simulated solar illumination of 100 mW cm\(^{-2}\) created by white
light from a tungsten-halogen lamp, filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter. The EQE was measured with a Stanford Research Systems Model SR830 DSP lock-in-amplifier by using modulated monochromatic light from a tungsten halogen lamp in combination with a monochromator (Oriel, Cornerstone 130). During the measurement the device was operating at 1 equivalent sun intensity by use of a bias laser (532 nm). A calibrated Si cell was used as a reference. The device was kept behind a quartz window in a nitrogen filled container. The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak150 profilometer. Tapping mode AFM was measured on a MFP-3D (Asylum research) using PPP-NCHR probes (Nanosensors).

2,5-di(4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-3,6-di(4′-ethyloctyl)thieno[3,2-b]thiophene (2). To a solution 2,5-dibromo-3,6-di(4′-ethyloctyl)thieno[3,2-b]thiophene (1) (141 mg, 0.24 mmol) in of dry THF (6 ml), 1.6 M n-butyllithium (0.8 ml, 1.28 mmol) solution in hexanes was added at -70 °C. This was stirred for 30 min. at -70 °C, after which 2-isopropoxy-(1,3,2)-dioxaboralane (0.3 ml, 1.47 mmol) was added at -70 °C. This mixture was allowed to reach room temperature overnight. The reaction mixture was poured out in water and heptane, and the organic layer was washed with brine. The solvents were evaporated from the organic layer and the resulting oil was subjected to column chromatography (eluent heptane/ethyl acetate). The result of this was 89 mg (51%) of a white solid. ¹H-NMR: 2.96 (t, 2H, J = 6.0 Hz), 1.67 (m, 2H), 1.34 (s, 24H), 1.2 (m, 22H), 0.88 (m, 6H), 0.82 (m, 6H). ¹³C-NMR: 146.22 (q), 146.06 (q), 83.77 (q), 83.68, (q), 38.52 (s), 32.94 (s), 32.82 (s), 30.11 (t), 28.93 (s), 27.01 (s), 25, 80 (s), 24.78 (p), 23.14 (s), 14.17 (p), 10.85 (p). MS (MALDI): calculated: 672.46, found: 672.46 (M⁺)

2,5-di(4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-thieno[3,2-b]thiophene (4). To a solution of 2,5-dibromothieno[3,2-b]thiophene (3) (0.51 g, 1.71 mmol) in 12 ml of dry THF, 1.6 M n-butyllithium (5.4 ml, 8.6 mmol) solution in hexanes was added at -70 °C. This was stirred for 60 min. at -70 °C, after which 2-isopropoxy-(1,3,2)-dioxaboralane (2.1 ml, 10.3 mmol) was added at -70 °C. This mixture was allowed to reach room temperature overnight. The reaction mixture was poured out in water and heptane, and the organic layer was washed with brine. The solvents were evaporated from the organic layer and the resulting solid was recrystallized multiple times from heptanes to yield 43 mg (5%) of a white solid. ¹H-NMR: 7.75 (s, 2H), 1.24 (s, 24H). ¹³C-NMR: 146.57 (q), 128.80 (t), 84.46 (q), 77.2 (q), 24.83 (p). MS (MALDI): calculated: 392.15, found: 392.06 (M⁺)

2,5-di(thien-2-yl)-3,6-di(4′-ethyloctyl)thieno[3,2-b]thiophene (5). To a solution of 2,5-dibromo-3,6-di(4′-ethyloctyl)thieno[3,2-b]thiophene (1) (0.45 g, 0.78 mmol) and 2-(tributylstannyl)thiophene (0.55 ml, 1.8 mmol) in toluene (5 ml), tetrakis(triphenylphosphine)palladium(0) (25 mg, 21 µmol) was
added. The resulting mixture was stirred at 130 °C overnight and diluted with 10 ml heptane. This suspension was filtered over a Buchner funnel and the solvents of the filtrate were evaporated in vacuum. The resulting solid was subjected to kugelröhr distillation to remove traces of bithiophene. This yielded 250 mg (0.43 mmol, 55%) of a yellow solid. \(^1\)H-NMR: 7.36 (d, 1H), 7.18 (d, 1H), 7.1 (t, 1H), 2.86 (t, 2H), 1.75 (q, 2H), 1.28 (m, 22H), 0.89 (m, 12H). \(^{13}\)C-NMR: 138.47 (q), 136.57 (q), 132.0 (q), 131.29 (q), 127.46 (t), 126.15 (t), 125.72 (t), 38.56 (s), 33.18 (s), 32.71 (s), 29.18 (s), 28.92 (s), 26.22 (s), 25.87 (s), 23.15 (s), 14.19 (p), 10.88 (p). MS (MALDI): calculated: 584.26, found: 584.16 (M\(^+\))

\(2,5\)-di(5-bromothien-2-yl)-3,6-di(4'-ethyloctyl)thieno[3,2-b]thiophene (6). To a solution of 2,5-di(thien-2-yl)-3,6-di(4'-ethyloctyl)thienothiophene (5) (250 mg, 0.43 mmol) in DMF (30 ml), N-bromosuccinimide (0.17 g, 0.95 mmol) was added and the reaction mixture was stirred overnight. After this the mixture was poured out in water/heptane and the heptane layer was washed with water and brine. The solvents were evaporated and the resulting yellow solid was subjected to column chromatography (silica, eluent heptane) to yield 270 mg (0.36 mmol, 85%) of a yellow solid. \(^1\)H-NMR: 7.04 (d, 2H, \(J = 4.0 \text{ Hz}\)), 6.90 (d, 2H, \(J = 4.0 \text{ Hz}\)), 2.80 (t, 4H, \(J = 4.0 \text{ Hz}\)), 1.71 (m, 4H), 1.35-1.2 (m, 22H), 0.82 (m, 6H). \(^{13}\)C-NMR: 138.60 (q), 137.91 (q), 132.54 (t), 130.64 (q), 130.33 (q), 126.51 (t), 112, 43 (t), 38.54 (s), 33.12 (s), 32.69 (s), 29.13 (t), 28.92 (s), 26.21 (s), 25.87 (s), 23.16 (s), 14.21 (p), 10.89 (p). MS (MALDI): calculated: 742.08, found: 741.98 (M\(^+\))

\(2,5\)-di(5-(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)thien-2-yl)-3,6-di(4'-ethyloctyl)thieno[3,2-b]thiophene (7). To a solution of 2,5-di(5-bromothien-2-yl)-3,6-di(4'-ethyloctyl)thienothiophene (6) (205 mg, 0.28 mmol) in dry THF (20 ml) at -78 °C, 1.6 M butyllithium (0.8 ml, 1.28 mmol) solution was added. The reaction mixture was stirred for 30 min. after which 2-isopropoxy-(1,3,2)-dioxaboralane (0.5 ml, 2.9 mmol) was added. The resulting mixture was allowed to reach room temperature after which it was poured out in heptane, which was washed with water and brine. The resulting solid was subjected to column chromatography (silica, eluent heptanes/ethyl acetate). This yielded 231 mg (0.28 mmol, 97%) of a yellow-brown solid. \(^1\)H-NMR: 7.58 (d, 2H, \(J = 3.2 \text{ Hz}\)), 7.23 (d, 2H, \(J = 3.2 \text{ Hz}\)), 2.88 (t, 4H, \(J = 7.6 \text{ Hz}\)), 1.72 (m, 4H), 1.30-1.2 (m, 22H), 0.82 (m, 6H). \(^{13}\)C-NMR: 143.51 (q), 138.93 (q), 137.55 (t), 132.36 (q), 131.69 (q), 128.27 (t), 113.87 (t), 84.17 (q), 38.55 (s), 33.12 (s), 32.70 (s), 29.26 (s), 28.89 (s), 26.45 (s), 25.82 (s), 24.79 (s), 24.75 (p), 23.13 (s), 14.18 (p), 10.86 (p). MS (MALDI): calculated: 836.43, found: 836.29 (M\(^+\))

**Polymer I.** To a degassed solution of 2,5-di(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-3,6-di(4'-ethyloctyl)thieno[3,2-b]thiophene (2) (27 mg, 40 µmol), 3,6-bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-di(2'-hexyldecyl)-pyrrolo[3,4-c]pyrrolo-1,4-dione (8) (28 mg, 40 µmol), 50% Aliquat solution
(v/v) in toluene (0.3 ml), K$_3$PO$_4$ (18 mg, 84 µmol), of triphenlyphosphine (2.0 mg, 2.1 µmol) and water (0.1 ml) in toluene (2 ml), tris(dibenzylideneacetone)dipalladium(0) (2 mg, 1.7 µmol) was added. This mixture was stirred at 105 °C for three days, after which it was precipitated in methanol. The solids were filtered off, redissolved in CHCl$_3$ (75 ml) and refluxed with 28% NH$_3$ solution in water (75 ml) for 3 h. The layers were separated and the organic layer was stirred with EDTA (250 mg) overnight, after which water (100 ml) was added and the liquids were stirred for 1 h. The layers were separated and the organic layer was reduced in volume by evaporating most of the chloroform. The polymer was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was extracted with methanol, after which the thimble was allowed to dry in ambient conditions. Then the polymer was extracted with hexane and chloroform. The solvent from the chloroform fraction was evaporated and the solid was precipitated in methanol. The polymer was collected by filtering over a 0.45 µm PTFE membrane filter and dried in a vacuum oven to yield I (21 mg, 56%) as a dark green powder. $^1$H-NMR: 9.15 (b, 2H), 7.26 (b, 2H), 4.08 (b, 4H), 2.95 (b, 4H), 2.70 (b, 2H), 1.97 (b, 4H), 1.75 (b, 4H), 1.5-1.1 (b, 34H), 0.95-0.8 (b, 24H). GPC: $M_n = 13,000$ g mol$^{-1}$, PDI = 2.5.

**Polymer II.** Same procedure as for I was used, but now 2,5-di(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-thieno[3,2-b]thiophene (43 mg, 0.11 mmol) and of 3,6-bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-di(2-hexyldecyl)-pyrrolo[3,4-c]pyrrolo-1,4-dione (9) (100 mg, 0.11 mmol) were used as the monomers. Reaction time was 16 h. Yield: 71 mg (67%). $^1$H-NMR: 9.12 (b, 2H), 7.13 (b, 4H), 4.03 (b, 4H), 1.93 (b, 2H), 1.5-1.1 (b, 48H), 1.0-0.6 (b, 12H). GPC: $M_n = 9,000$ g mol$^{-1}$, PDI = 3.9.

**Polymer III.** Same procedure as for I was used, but now 2,5-di(5-(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)thien-2-yl)-3,6-di(4′-ethyloctyl)thieno-thiophene (7) (102.25 mg, 0.12 mmol) and of 3,6-bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-di(2-hexyldecyl)-pyrrolo[3,4-c]pyrrolo-1,4-dione (9) (111 mg, 0.12 mmol) were used as the monomers. Reaction time was 40 min. Yield: 70 mg (44%). $^1$H-NMR: 8.95 (b, 2H), 7.31 (b, 2H), 7.16 (b, 2H), 7.01 (b, 2H), 4.06 (b, 4H), 2.91 (b, 4H), 2.71 (b, 2H), 1.92 (b, 4H), 1.5-1.1 (b, 66H), 1.0-0.6 (b, 24H). GPC: $M_n = 15,000$ g mol$^{-1}$, PDI = 4.0.
7.5 References

(7) See Chapter 4 of this thesis
Chapter 8

Furan and thiophene containing DPP copolymers*

Abstract

Four small band gap copolymers based on electron deficient diketopyrrolopyrrole alternating with electron rich trimers of benzene, furan, and thiophene have been synthesized via Suzuki polymerization. The polymers show optical band gaps between 1.4 and 1.6 eV, optimized for solar energy conversion, and exhibit ambipolar charge transport in field-effect transistors with hole and electron mobilities higher than $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. In solar cells the polymers are used as electron donor and provide power conversion efficiencies up to of 3.7% in simulated solar light when mixed with [70]PCBM as acceptor.

* This work has been submitted for publication:
8.1 Introduction

Polymers containing five-membered heterocyclic rings, such as thiophene and pyrrole, are frequently used in organic semiconductors for organic photovoltaic cells (OPCs) owing to their favorable electronic properties.\textsuperscript{1} Although thiophene is a well-explored and versatile building block, its oxygen analog, furan, has received much less attention.\textsuperscript{2-4} Furan derivatives can be obtained from natural sources,\textsuperscript{5} and hence polymers based on furan have been considered as a step towards renewable polymers. Although the optical absorption of oligofurans is somewhat blue shifted compared to oligothiophenes,\textsuperscript{6} copolymers based on zinc porphyrin and furan or thiophene display similar optical band gaps.\textsuperscript{7} Furan units were also incorporated into other conjugated polymers and their photophysical and electrochemical properties were found to be similar to their thiophene analogs.\textsuperscript{8} By comparing the packing and charge transport in oligofurans and oligothiophenes no difference in charge carrier mobility between thiophene and furan units is expected,\textsuperscript{9} making furan a potentially good replacement for thiophene in OPCs.

We have recently shown that with easily accessible polymers based on 3,6-di-2-thienyl-1,4-diketopyrrolo[3,4-c]pyrrole (T-DPP-T) (DPP) copolymerized with 2,5-thienylene or 1,4-phenylene power conversion efficiencies (PCEs) up to 5.5% can be obtained in OPCs.\textsuperscript{10} In exploring the DPP structural motif for photovoltaic polymers, we were interested in assessing furan as a building block in the main chain and synthesized four new copolymers (PDPP-XYX) that have DPP units alternating along the chain with conjugated segments that consist of three aromatic rings (XYX) consisting of 2,5-furanylene (F) with 2,5-thienylene (T) or 1,4-phenylene (P) (Scheme 8.1). The new polymers are compared to PDPP-TTT and PDPP-TPT that were described in Chapters 5 and 6. It will be shown that furan based polymers exhibit ambipolar charge transport in field-effect transistors (FET) with almost balanced electron and hole mobilities that can exceed 10\textsuperscript{-2} cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}. Solar cells made with the furan polymers gave a PCE up to 3.7% with [70]PCBM as acceptor. Comparison with PDPP-TTT, suggests that the PCE is limited by the molecular weight that has been obtained.
8.2 Results

8.2.1. Synthesis

In the remainder of the text the PDPP-XYX notation will be abbreviated as XYX, with \( X = F \) or \( T \) and \( Y = F, T, \) or \( P \) (Scheme 8.1). The synthesis of the new XYX polymers was accomplished via a Suzuki polymerization as outlined in Scheme 8.2. This procedure required access to 3,6-bis(5-bromo-2-furanyl)-2,5-bis(2’-hexyldecyl)-2,5-dihydro-pyrrolo[3,4-c]pyrrolo-1,4-dione (1) and 3,6-bis(5-bromo-2-thienyl)-2,5-bis(2’-hexyldecyl)-2,5-dihydro-pyrrolo[3,4-c]pyrrolo-1,4-dione (2) as well as 2,2’-(2,5-furandiyl)bis[4,4,5,5-tetramethyl-1,3,2-dioxaborolane] (3), 2,2’-(2,5-thiophenediyl)bis[4,4,5,5-tetramethyl-1,3,2-dioxaborolane] (4), and 2,2’-(1,4-phenylene)bis[4,4,5,5-tetramethyl-1,3,2-dioxaborolane] (5).

The synthesis of 1 is depicted in Scheme 8.3. In the first step 2-furonitril and diethylsuccinate were condensed to form 6 in a one pot reaction. DPP derivative 6 was then alkylated using potassium carbonate as the base yielding the better soluble DPP derivative 7.
Subsequent bromination yielded the desired monomer 1. The other monomers were synthesized as described before (2\textsuperscript{11}) or were commercially available (3-5).

Scheme 8.3. Synthesis of 1.

The polymers were obtained via Suzuki polymerization in yields varying from 44% to 69% after purification by Soxhlet extraction. Only the chloroform fraction was used and the hexane fraction and insoluble material were discarded. The reaction conditions for the polymerizations have been optimized to provide the highest possible molecular weight. All polymers are very soluble in chloroform (> 5 mg ml\textsuperscript{-1}) at room temperature. Molecular weights were estimated at 80 °C in o-DCB. The number average molecular weight (\(M_n\)) ranges from 13,000 to 17,000 g mol\textsuperscript{-1} (Table 8.2). Although all polymers were subjected to Soxhlet fractionation, the polydispersity index (PDI) varies over a broad range, being the highest (> 5) for FPF. The similar \(M_n\) and PDI for TFT, FTF and FFF allow a direct comparison of these three polymers for optoelectronic applications.

Table 8.1. Molecular weight, optical and electrochemical data of the XYX polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(M_n) (kg mol\textsuperscript{-1})</th>
<th>PDI</th>
<th>(E_g), solid (eV)</th>
<th>(E_g), solution (eV)</th>
<th>(E_g), CV (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPF</td>
<td>17</td>
<td>5.5</td>
<td>1.59</td>
<td>1.55</td>
<td>1.66</td>
</tr>
<tr>
<td>TPT\textsuperscript{a}</td>
<td>-</td>
<td>-</td>
<td>1.53</td>
<td>1.53</td>
<td>1.82</td>
</tr>
<tr>
<td>FFF</td>
<td>13</td>
<td>2.8</td>
<td>1.48</td>
<td>1.48</td>
<td>1.47</td>
</tr>
<tr>
<td>FTF</td>
<td>15</td>
<td>3.5</td>
<td>1.44</td>
<td>1.46</td>
<td>1.45</td>
</tr>
<tr>
<td>TFT</td>
<td>16</td>
<td>2.6</td>
<td>1.40</td>
<td>1.44</td>
<td>1.42</td>
</tr>
<tr>
<td>TTT\textsuperscript{b}</td>
<td>10</td>
<td>2.4</td>
<td>1.33</td>
<td>1.39</td>
<td>1.58</td>
</tr>
<tr>
<td></td>
<td>54</td>
<td>3.2</td>
<td>1.30</td>
<td>1.36</td>
<td>1.56</td>
</tr>
</tbody>
</table>

\textsuperscript{a}) Chapter 6. \textsuperscript{b}) Chapter 5.
8.2.2. Optical, electrochemical and electrical properties

The absorption spectra of the polymers are shown in Figure 8.1 and the optical band gaps determined from the onsets of absorption are collected in Table 8.1 and compared to the TTT and TPT polymers reported in Chapters 5 and 6. The shape of the absorption spectra in solution and in solid state show remarkable similarities, indicating that the polymers are not fully molecularly dissolved. This is confirmed by the fact that for all polymers the maximum at higher wavelengths of the absorption spectrum in solution is decreasing in intensity upon heating. The optical band gap is significantly larger for FPF and TPT than for the other materials. Steric hindrance will cause the phenylene ring to partly twist out of the plane defined by the furan or thiophene rings, which reduces the orbital overlap and conjugation in the electron rich part of the polymer chain. For the furan/thiophene trimers there is a clear increase of the optical band gap with increasing number of furan units.

![Figure 8.1](image)

*Figure 8.1*. Normalized optical absorption spectra of the different polymers in o-DCB solution (a) and in solid state (b). The curves are offset vertically for clarity.

The energy levels of the polymers have been determined with cyclic voltammetry, in o-DCB solution, using TBAPF$_6$ as the electrolyte. For the new furan-based polymers, the band gap derived from electrochemical measurements is generally in good agreement with the optical band gap (Table 8.1). We tentatively assign the band gaps in both experiments to that of aggregated species. In contrast, the electrochemical and optical band gaps of TPT and TTT differ substantially, obstructing a quantitative comparison between these polymers and their furan containing analogs. The ambiguity of the cyclic voltammetry data could possibly originate from the difference in size of polymer aggregates in the o-DCB solution, causing the charging of the polymer particles to be different. The oxidation and reduction potentials can be translated to HOMO and LUMO energy levels which are schematically depicted in Figure
8.2. Compared to the other polymers, FPF and TPT that have a phenylene ring in the main chain, are somewhat more difficult to oxidize and therefore the open circuit voltage in a cell with PCBM is expected to be higher than for the other polymers (FFF, FTF, TFT, and TTT) for which the HOMO levels are rather similar.

![Simplified energy diagram of the different polymers.](image)

The charge carrier mobilities of the polymers were measured in a bottom gate, bottom contact FET. From the transfer curves (Figure 8.3) it is evident that the polymers show ambipolar behavior. The electron and hole mobilities ($\mu_e$ and $\mu_h$) determined from the slope of the square root of the source drain current ($I_{DS}$)\(^{12}\) in the saturation regime are listed in Table 8.2. Mobilities are in the range of $10^{-3}$ - $10^{-2}$ cm\(^2\) V\(^{-1}\) s\(^{-1}\) for both polarities, except for FFF where $\mu_e$ is significantly smaller (Figure 8.3b). As a general trend, replacing thiophene by furan results in a reduced mobility. In the comparison, we note that although it is known that $M_n$ can affect the mobility of charge carriers,\(^{13}\) this was previously not observed for PDPP-TTT.\(^{14}\) Since differences in $M_n$ among the new polymers are small, we think that these are not the primary cause for the observed differences the mobility. The charge carrier mobilities are in the same range as described in Chapter 7 for copolymers of DPP and thienothiophene and generally higher than those found for DPP polymers with more extended aromatic structures in the chain.\(^{15}\)
Figure 8.3. p-type (a) and n-type(b) transfer curves of FETs made with the different polymers. $I_{DS}$ is normalized with respect to the channel length for fair comparison of the polymers.

Table 8.2. FET mobilities of the PDPP-XYX polymers.

<table>
<thead>
<tr>
<th>PDPP-XYX</th>
<th>$\mu_h$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_e$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPF</td>
<td>$3 \times 10^{-3}$</td>
<td>$7 \times 10^{-3}$</td>
</tr>
<tr>
<td>TPT$^a$</td>
<td>$4 \times 10^{-2}$</td>
<td>$2 \times 10^{-2}$</td>
</tr>
<tr>
<td>FFF</td>
<td>$3 \times 10^{-3}$</td>
<td>$8 \times 10^{-5}$</td>
</tr>
<tr>
<td>FTF</td>
<td>$1 \times 10^{-3}$</td>
<td>$2 \times 10^{-3}$</td>
</tr>
<tr>
<td>TFT</td>
<td>$2 \times 10^{-2}$</td>
<td>$4 \times 10^{-2}$</td>
</tr>
<tr>
<td>TTT$^b$</td>
<td>$4 \times 10^{-2}$</td>
<td>$1 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

$^a$) Chapter 6. $^b$) Chapter 5 (independent of $M_n$).

8.2.3. Photovoltaic devices

Solar cells, consisting of XYX:[70]PCBM thin films on a pre-cleaned, patterned ITO substrate covered with a thin layer of PEDOT:PSS were made via spin coating. The devices were completed by thermal evaporation of the back contact made of 1 nm of LiF and 100 nm aluminum. The composition of the active layers was optimized and it was found that the best performance was reached at a XYX:[70]PCBM weight ratio of 1:2, except for FFF where a 1:1 ratio gave higher power conversion. When the active layers were spin coated from pure chloroform, the devices showed moderate PCEs in the range of 0.5 – 1.3% (see Figure 8.4). However, addition of 1,8-diiodooctane (DIO) as co-solvent to the solution gave rise to a significantly (factor of 2 – 4) enhanced performance (Figure 8.4). For all polymers, a good performance can be obtained for a relatively wide range of concentrations of DIO, but a
relatively large amount had to be added to reach the highest PCE (100 mg ml\(^{-1}\) for FPF and TFT, 200 mg ml\(^{-1}\) for FTF and FFF).

Figure 8.4. Dependence of estimated efficiency on the amount of DIO used during spin coating.

Figure 8.5 shows the tapping mode AFM surface topology for the active layers processed from pure chloroform and after addition of the optimal amount of DIO. For pure chloroform the layers show relatively large (150-300 nm) globular clusters that can be attributed to [70]PCBM domains.\(^{17}\) The large [70]PCBM clusters originate from the fact that during the drying of the film [70]PCBM crystallizes before the polymer is solidifying. This results in a very coarse phase separation and high RMS roughness (11.6 – 13.4 nm). In layers where the co-solvent is used, a much finer intermixing of [70]PCBM and polymer domains is found and the RMS roughness of the layers is less (Table 8.3). For layers with TFT and FFF the final RMS roughness is still somewhat higher than for layers with FPF and FTF, but this is not reflected in the photovoltaic performance (Table 8.3).
The current density – voltage ($J$-$V$) curves of the best cells are shown in Figure 8.6, together with the monochromatic external quantum efficiency. The short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF), and PCE that characterize the cells are collected in Table 8.3. For the furan containing polymers the PCE = 1.9 – 3.8% is less than for TTT (4.7%) and TPT (5.5%), described in Chapters 5 and 6. The $V_{oc}$ of the cells of the phenylene polymers (FPF and TPT) is higher than for those only based on thiophene or furan, consistent with their somewhat higher oxidation potentials. The fill factors (FF) of all the cells are relatively high (> 0.6, except for FFF), indicative of high and balanced charge carrier mobility. It is tempting to relate the reduced fill factor of the FFF cell to its lower intrinsic hole mobility (Table 8.2), but we note that FTF, which has similar mobility, gives rise to a higher FF. The differences can possibly originate from a less optimal morphology for FFF.
Figure 8.6. $J-V$ curves (a) and monochromatic spectral response (b) of the optimized cells made with the polymers and [70]PCBM.

Table 8.3. Characteristics of the best cells made with PDPP-XYX:[70]PCBM.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ratio</th>
<th>$M_n$ (kg mol$^{-1}$)</th>
<th>$J_{sc, sr}$ (mA cm$^{-2}$)$^c$</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
<th>RMS roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPF$^a$</td>
<td>1:2</td>
<td>17</td>
<td>7.0</td>
<td>0.82</td>
<td>0.63</td>
<td>3.8</td>
<td>2.6</td>
</tr>
<tr>
<td>TPT$^{a,b}$</td>
<td>1:2</td>
<td>-</td>
<td>10.8</td>
<td>0.80</td>
<td>0.65</td>
<td>5.5</td>
<td>2.1</td>
</tr>
<tr>
<td>FFF$^c$</td>
<td>1:1</td>
<td>13</td>
<td>5.4</td>
<td>0.66</td>
<td>0.54</td>
<td>1.9</td>
<td>9.6</td>
</tr>
<tr>
<td>FTF$^c$</td>
<td>1:2</td>
<td>15</td>
<td>4.3</td>
<td>0.73</td>
<td>0.63</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>TFT$^a$</td>
<td>1:2</td>
<td>16</td>
<td>6.4</td>
<td>0.64</td>
<td>0.63</td>
<td>2.6</td>
<td>12.9</td>
</tr>
<tr>
<td>TTT$^{a,d}$</td>
<td>1:2</td>
<td>10</td>
<td>6.3</td>
<td>0.68</td>
<td>0.63</td>
<td>2.7</td>
<td>12.1</td>
</tr>
<tr>
<td>TTT$^{a,d}$</td>
<td>1:2</td>
<td>54</td>
<td>11.8</td>
<td>0.65</td>
<td>0.60</td>
<td>4.7</td>
<td>2.4</td>
</tr>
</tbody>
</table>

$^a$) Made with 100 ml ml$^{-1}$ DIO in CHCl$_3$. $^b$) Chapter 6. $^c$) Made with 200 mg ml$^{-1}$ DIO in CHCl$_3$. $^d$) Chapter 5. $^e$) From convolution of the EQE spectrum with the AM1.5G spectrum.

The molecular weight of the polymer has proven to be a crucial parameter in film formation and photovoltaic performance in an OPC made with TTT. Films of similar molecular weight FTF or FFF-based polymer display a similar surface profile and roughness as films made with lower molecular weight ($M_n = 10,000$ g mol$^{-1}$) TTT. For the low $M_n$ version of TTT, the maximum PCE of 2.7% is similar to the FFF, FTF, and TFT polymers that have comparable $M_n$ (Table 8.3). This strongly suggests that for the furan based polymers the performance of the solar cells can be further increased when higher molecular weight materials can be obtained in the polymerization. If this can be accomplished furan-based polymers would likely become a suitable alternative to their thiophene-based analogs.
8.3 Conclusions

Four new DPP-based small optical band gap co-polymers with different number of furan rings in the repeating unit have been synthesized and optimized with respect to their molecular weight. The polymers have an optical gap between 1.4 and 1.6 eV. In combination with [70]PCBM the polymers give power conversion efficiencies up to 3.7% in solar cells. Although this clearly shows that furan based conjugated polymers do provide good performance in solar cells, their efficiency is somewhat less than that for the corresponding thiophene based materials. The reduction can, at least in part, be ascribed to the lower molecular weights that have been obtained in the polymerization reactions. Higher molecular weight materials often give better performance in bulk heterojunction solar cells due to improved film forming properties and morphology.18,19

8.4 Experimental

All reactions were conducted under an argon atmosphere. Commercial chemicals were used as received. [70]PCBM was purchased from Solenne BV. 1H-NMR and 13C-NMR spectra were recorded at 400 MHz and 100 MHz, respectively on a VARIAN mercury spectrometer with CDCl3 as the solvent and tetramethylsilane (TMS) as the internal standard unless specified otherwise. The peaks are given in ppm, relative to TMS (0 ppm). Molecular weights were determined with GPC at 80 ºC on a PL-GPC 120 system using a PL-GEL 5µ MIXED-C column and o-DCB as the eluent. Polystyrene standards were used.

UV-vis-nearIR spectra were recorded on a Perkin Elmer Lambda 900 spectrophotometer. Cyclic voltammetry was conducted under an inert atmosphere with a scan rate of 0.1 V s⁻¹, using 1 M tetrabutylammonium hexafluorophosphate in o-DCB as the electrolyte. The working electrode was a platinum disk and the counter electrode was a silver rod electrode. Fc/Fc⁺ was used as an internal standard. Tapping mode AFM was measured on a MFP-3D (Asylum research) using PPP-NCHR probes (Nanosensors).

Field-effect transistors were fabricated using heavily doped silicon wafers as the common gate electrode with a 200 nm thermally oxidized SiO₂ layer as the gate dielectric. Using conventional photolithography, gold source and drain electrodes were defined in a bottom contact device configuration with channel length of 10 μm and different widths. A 10 nm layer of titanium was used acting as an adhesion layer for the gold on SiO₂. The SiO₂ layer was exposed to the vapor of the primer hexamethyldisilazane for 60 min. prior to semiconductor deposition in order to passivate the surface of the dielectric. PDPPTPT films were spun from a chloroform solution at 1500 rpm for 30 s.
Freshly prepared devices were annealed in a dynamic vacuum of $10^{-5}$ mbar at 100 °C for 72 h to remove traces of solvent. All electrical measurements were performed in a vacuum using an HP 4155C semiconductor parameter analyzer.

Photovoltaic devices were made by spin coating poly(ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP A14083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). The photoactive layer was deposited by spin coating a chloroform solution containing 6 mg/ml polymer and 12 mg ml$^{-1}$ [70]PCBM (9 and 9 mg ml$^{-1}$ for FFF) and the appropriate amount of 1,8-diiodooctane. The counter electrode, consisting of LiF (1 nm) and Al (100 nm), was deposited by vacuum evaporation at ~3 · 10$^{-7}$ mbar. The active area of the cells was 0.091 cm$^2$. J-V characteristics were measured under ~100 mW cm$^{-2}$ white light from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter, using a Keithley 2400 source meter. Short-circuit currents under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The spectral response was measured under simulated 1 sun operation conditions using bias light from a 532 nm solid state laser (Edmund Optics). Monochromatic light from a 50 W tungsten halogen lamp (Philips focusline) in combination with monochromator (Oriel, Cornerstone 130) was modulated with a mechanical chopper. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Stanford research Systems SR830). A calibrated Si cell was used as reference. The device was kept behind a quartz window in a nitrogen filled container. The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak150 profilometer. Tapping mode AFM was measured on a MFP-3D (Asylum research) using PPP-NCHR probes (Nanosensors).

$$3,6\text{-bis}(\text{furan-2-yI})\text{-2,5-dihydropyrrolo[3,4-c]pyrrolo-1,4-dione} \ (6). \ 2\text{-Furonitrile} \ (5.1 \ g, \ 55 \ mmol) \ and \ K\text{OrBu} \ (7.9 \ g, \ 70 \ mmol) \ were \ dissolved \ in \ t\text{-amyl \ alcohol} \ (80 \ ml) \ and \ heated \ to \ reflux. \ At \ reflux, \ a \ solution \ of \ diethyl \ succinate \ (4.6 \ ml, \ 27 \ mmol) \ was \ added \ dropwise, \ in \ t\text{-amyl \ alcohol} \ (15ml) \ over \ 2 \ h. \ The \ mixture \ was \ stirred \ at \ reflux \ overnight. \ Methanol \ (300 \ ml) \ and \ acetic \ acid \ (20 \ ml) \ were \ added \ and \ the \ mixture \ was \ stirred \ at \ reflux \ for \ 0.5 \ h. \ Solids \ were \ filtered \ and \ washed \ with \ water \ and \ methanol \ and \ dried \ in \ vacuo. \ Yield: \ 4.5 \ g \ (61\%\). \ ^1\text{H-NMR} \ (400 MHz, \ DMSO): \ \delta \ 11.75 \ (s, \ 2H), \ 8.05 \ (d, \ J = 1.4 \ Hz, \ 2H), \ 7.67 \ (d, \ J = 3.5 \ Hz, \ 2H), \ 6.84 \ (dd, \ J = 1.6 \ Hz, \ 3.5 \ Hz, \ 2H). \ ^{13}\text{C-NMR} \ (100 MHz, \ DMSO): \ \delta \ 161.17, \ 146.90, \ 143.77, \ 131.28, \ 116.79, \ 113.71, \ 107.58. \ MALDI-TOF-MS: \ m/z \ 268.14 \ (100\%), \ 269.14 \ (25), \ 270.14 \ (5).$$

$$3,6\text{-bis(furan-2-yI)}\text{-2,5-dihydro-2,5-bis(2'-hexyldecyl)pyrrolo[3,4-c]pyrrolo-1,4-dione} \ (7). \ Compound \ 6 \ (2.75 \ g, \ 10 \ mmol), \ 2\text{-hexyl-1-bromodecane} \ (8.4 \ g, \ 26 \ mmol) \ and \ K\text{CO}_3 \ (4.3 \ g, \ 31 \ mmol) \ were \ dissolved \ in \ DMF \ (40 \ ml) \ and \ heated \ at \ 120 \ °C \ overnight. \ Diethyl \ ether \ (300 \ ml) \ was \ added \ and \ the \ mixture \ was \ washed \ with \ 0.1 \ M \ HCl \ (3\times100 \ ml). \ The \ organic \ phase \ was \ dried \ over
MgSO$_4$ and the solvent was evaporated. The crude product was purified by flash chromatography on silica, using dichloromethane/heptane as the eluent. Yield: 3.8 g (52%). $^1$H-NMR (400 MHz, CDCl$_3$): δ 8.33 (d, $J$ = 3.6 Hz, 2H), 7.60 (d, $J$ = 1.2 Hz, 2H), 6.69 (dd, $J$ = 1.6 Hz, 3.6 Hz, 2H), 4.02 (d, $J$ = 7.4 Hz, 4H), 1.80 (m, 2H), 1.38-1.17 (m, 48H), 0.91-0.81 (m, 12H). $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 161.22, 144.78, 144.66, 133.91, 120.14, 113.44, 106.45, 46.51, 38.48, 31.86, 31.80, 31.47, 29.99, 29.65, 29.53, 29.29, 26.47, 26.44, 22.67, 22.63, 22.62, 14.08, 14.06. MALDI-TOF-MS: m/z 716.47 (100%), 717.48 (65), 718.48 (25), 719.49 (5).

3,6-bis(5-bromofuran-2-yl)-2,5-dihydro-2,5-bis(2’-hexyldecyl)pyrrolo[3,4-c]pyrrolo-1,4-dione (1). Compound 7 (1.8 g, 2.5 mmol) was dissolved in chloroform (50 ml). NBS (0.96, 5.4 mmol) was added at 0 °C in a few portions and the mixture was stirred overnight while warming to room temperature. Chloroform (100 ml) was added and the solution was washed with water (3×50 ml). The organic phase was dried over MgSO$_4$ and the solvent was evaporated. The crude product was purified by flash chromatography on silica, using chloroform/heptane as the eluent. Yield: 1.62 g (72%). $^1$H-NMR (400 MHz, CDC$_3$): δ 8.30 (d, $J$ = 3.4 Hz, 2H), 6.62 (d, $J$ = 3.5 Hz, 2H), 3.98 (d, $J$ = 7.4 Hz, 4H), 1.78 (m, 2H), 1.40-1.18 (m, 48H), 0.89-0.82 (m, 12H). $^{13}$C-NMR (100 MHz, CDCl$_3$): δ 160.89, 146.21, 132.78, 126.20, 122.21, 115.50, 106.29, 46.59, 38.81, 31.89, 31.78, 31.44, 30.11, 29.78, 29.52, 29.30, 26.47, 26.45, 22.66, 22.63, 14.11, 14.08. MALDI-TOF-MS: m/z 872.46 (50%), 873.46 (25), 874.46 (100), 875.46 (55), 876.46 (60), 877.46 (60), 877.46 (25), 878.47 (5).

**FPF.** To a argon bubbled solution of 3,6-bis(5-bromofuran-2-yl)-2,5-dihydro-2,5-bis(2’-hexyldecyl)pyrrolo[3,4-c]pyrrolo-1,4-dione (1) (112 mg, 128 μmol), 2,2’-(1,4-phenylene)bis[4,4,5,5-tetramethyl-1,3,2-dioxaborolane] (5) (42 mg, 127 μmol), a 50% Aliquat solution in toluene (0.3 ml), triphenylphosphine (4.1 mg, 15 μmol), K$_3$PO$_4$ (60 mg, 0.28 mmol) in of toluene (3.5 ml) with demineralised water (0.4 ml), tris(dibenzylidene)di palladium(0) (7.0 mg, 7.6 μmol) was added. This mixture was stirred for 3 days at 115 °C after which the crude polymer was precipitated in methanol. The solids were filtered over a Büchner funnel and redissolved in chloroform (80 ml) and stirred under reflux with 28% aqueous ammonium hydroxide (80 ml) solution for 3 h. The layers were separated and the organic phase was stirred with ethylenediaminetetraacetate (300 mg) for 3 h. Then demineralised water (100 ml) was added, and the mixture was stirred for another hour. The layers were separated and the organic layer was washed with demineralised water and reduced in volume in vacuum and precipitated in methanol. The precipitate was collected in a Soxhlet thimble and was extracted with methanol, hexane and chloroform until the extracts were colorless. The chloroform fraction was reduced in volume and precipitated in methanol and filtered over a 4.5 μm PTFE filter. The polymer was collected and dried in a vacuum oven at 60 °C overnight, resulting in 70 mg (69%)
of a dark blue powder. $^1$H-NMR: 8.6 (b, 2H), 7.4 (b, 4H), 7.1 (b, 2H), 4.0 (b, 4H), 1.9 (b, 2H), 1.20-1.00 (b, 48H), 0.8-0.7 (b, 12H) GPC: $M_n = 17,000$ g mol$^{-1}$, PDI = 5.5.

**FFF.** The same procedure was employed as for FPF, but using 3,6-bis(5-bromofuran-2-yl)-2,5-dihydro-2,5-bis(2’-hexyldecyl)pyrrolo[3,4-c]pyrrolo-1,4-dione (1) (141 mg, 161 μmol) and 2,2’-(2,5-furandiyl)bis[4,4,5,5-tetramethyl-1,3,2-dioxaborolane] (3) (52 mg, 162 μmol). FFF was obtained as a dark blue powder, 55 mg (44%). $^1$H-NMR: 8.5 (b, 2H), 6.8 (b, 4H), 6.7 (b, 2H), 4.1 (b, 2H), 3.8 (b, 2H), 1.9 (b, 2H), 1.20-1.00 (b, 48H), 0.80-0.70 (b, 12H) GPC: $M_n = 13,000$ g mol$^{-1}$, PDI = 2.8.

**FTF.** The same procedure was employed as for FPF, but using 3,6-bis(5-bromofuran-2-yl)-2,5-dihydro-2,5-bis(2’-hexyldecyl)pyrrolo[3,4-c]pyrrolo-1,4-dione (1) (105 mg, 120 μmol) (1) and 2,2’-(2,5-thiophenediyl)bis[4,4,5,5-tetramethyl-1,3,2-dioxaborolane] (4) (40 mg, 119 μmol). FTF was obtained as a dark blue powder, 44 mg (46%). $^1$H-NMR: 9.0 (b, 2H), 7.5 (b, 4H), 7.1 (b, 2H), 4.0 (b, 4H), 1.89 (b, 2H), 1.20-1.00 (b, 48H), 0.80-0.70 (b, 12H) GPC: $M_n = 15,000$ g mol$^{-1}$, PDI = 3.5.

**TFT.** The same procedure was employed as for FPF, but using 3,6-bis(5-bromothien-2-yl)-2,5-dihydro-2,5-bis(2’-hexyldecyl)pyrrolo[3,4-c]pyrrolo-1,4-dione (2) (108 mg, 119 μmol) and 2,2’-(2,5-furandiyl)bis[4,4,5,5-tetramethyl-1,3,2-dioxaborolane] (3) (39 mg, 120 μmol). TFT was obtained as a dark blue powder, 56 mg (58%). $^1$H-NMR: 8.9 (b, 2H), 7.1 (b, 2H), 6.9 (b, 2H), 4.1 (b, 4H), 1.9 (b, 2H), 1.2-1.0 (b, 48H), 0.8-0.7 (b, 12H) GPC: $M_n = 16,000$ g mol$^{-1}$, PDI = 2.6.
8.5 References

(10) See Chapter 6 of this thesis.
(14) See Chapter 5 of this thesis.
Chapter 9

Epilogue


9.1 Epilogue

The research described in this thesis was targeted at designing, synthesizing, and testing new polymers as \( p \)-type materials in organic photovoltaic cells (OPCs). The polymer needs to absorb a large fraction of the solar spectrum and display electron affinity smaller than the acceptor to be successful as \( p \)-type material. Both requirements can be accomplished by judicious alternating electron deficient and electron rich moieties in a conjugated polymer chain. By changing electron deficient groups in conjugated polymers with cyclopentadithiophene as electron rich unit, the frontier orbital levels and optical absorption can be tuned as illustrated in Chapter 2. A simplified approximation of the energy levels in Chapter 1, led to the prediction that the exchange of a single sulfur atom in benzothiadiazole for an oxygen in benzooxadiazole in an alternating co-polymer with cyclopentadithiophene would yield a material with higher efficiency in an OPC. These predictions were confirmed by making the actual solar cells and give credence to the fact that, at least in part, materials can be rationally designed. The best efficiency obtained did, however, not exceed the value of the benzothiadiazole-based copolymer reported in literature.\(^1\) This can be ascribed to the lower molecular weight of the polymers obtained and the processing of the layers without co-solvents. These two factors proved to be crucial in forming films with optimal morphologies for photovoltaic energy conversion.\(^2,3\)

The important role of the polymer molecular weight in the deposition of the active layers is illustrated in Chapter 5 where high performances are reached with a polymer based on diketopyrrolo[3,4-\(c\)]pyrrole and terthiophene (PDPP3T). The difference in power conversion efficiency of 4.7% vs. 2.7% for cells made with high (\( M_n = 54,000 \text{ g mol}^{-1} \)) and low (\( M_n = 10,000 \text{ g mol}^{-1} \)) molecular weight fractions of PDPP3T is striking and exclusively caused by different film and morphology forming properties.

Co-solvents also prove to be significant in obtaining the optimal morphology and performance. Their importance was most clearly established in Chapter 6 where the addition of a co-solvent greatly enhances the photovoltaic behavior of the cells for PDPPTPT:[70]PCBM from 2.0 to 5.5%, setting a new record efficiency for DPP-based solar cells.\(^4\) Remarkably, we find that the use of different co-solvents leads, after optimization, to virtually identical cell performance and morphology. This is in contrast to reports where the efficiency was found to dependent on the choice of the co-solvent.\(^5\) Because the TEM images
of the optimized layers show no differences for the different co-solvents, the question arises if the achieved performance is indeed an absolute maximum for this material combination.

For all DPP-based polymers explored in this thesis, blend films with PCBM cast from solutions in pure chloroform show relatively large PCBM crystals (>100 nm) in AFM and TEM images. These clusters disappear upon using a suitable co-solvent. The influence of the co-solvent can be explained if the solidification of a layer is considered as a balance between two processes: the gelation or aggregation of the polymer and the crystallization of the fullerene. When no co-solvent is added, the polymer remains in solution and PCBM is crystallizing first, allowing formation of large fullerene domains. When a co-solvent is used, the solubility of the fullerene is enhanced, while the polymer, which is less soluble in the co-solvent, is forming a gel or aggregate before the PCBM starts to crystallize. A suitable co-solvent should therefore exhibit (1) a higher boiling point than the main solvent, (2) a higher solubility for the PCBM than the main solvent, (3) a lower solubility for the polymer than the main solvent, and (4) be miscible with the main solvent.

For the well known and well explored P3HT:PCBM system, the approach of using co-solvents also works, but here the effect is opposite in the sense that without the co-solvent a very intimately mixed blend is obtained and the co-solvent leads to more phase separation. For P3HT:PCBM this has been ascribed to a more rapid formation of PCBM crystals by the co-solvent, while the effect on the crystallization kinetics of pure P3HT is rather small compared to its effect on PCBM.6

For PCPDTBT, a copolymer also described in this thesis, the positive effect of the co-solvent on the performance of the cells was shown similar to that of P3HT:PCBM in the sense that it led to an increased phase separation. However in this case, it was found to originate from an aggregation of the polymer.7 These authors found that the polymer is in a more aggregated state before spin coating when a co-solvent is added, increasing the domain size of the polymer. With the DPP-based polymers described in this thesis, the results suggest a strong aggregation, even in the best solvents known, indicating that this effect is negligible in the solar cells described in this thesis. This may be the result of a change of the main solvent as chloroform, which is used for the DPP polymers, is a worse solvent for PCBM compared to chlorobenzene and o-dichlorobenzene, used for P3HT and PCPDTBT.

For poly[(4,4-didodecylthieno[3,2-b:2’,3’-d]silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl], a Si bridged analog of PCPDTBT, it was shown that addition of a co-solvent also smoothened the layers and decreases phase separation in mixtures with PCBM,8 similar to
results obtained in this thesis. Because the co-solvent had a similar preferential solubility for PCBM compared to Si-PCPDTBT as the main solvent, the main effect of the co-solvent here seems to be the slower drying of the layer. In contrast, in the examples described in this thesis, the co-solvent exhibited negligible solubility for the polymer and much higher solubility for PCBM.

Also for the best performing polymer published to date, PTB7, a processing additive is needed to reach efficiencies above 7%, proving the wide applicability of co-solvents. In this case, as for the DPP polymers, phase separation is reduced.

From these examples it is clear that co-solvents can improve the performance of solar cells for a wide variety of polymers, but the effect is complicated and may be different for different families of polymers. The formation of the internal phase separation of a layer can only be understood and improved when the formation of layers is studied in detail, by for instance doing real time measurements on a drying layer that give information on the sequence of events or by exploring the four above mentioned boundaries of prerequisites for co-solvents.

A relatively unexplored way of influencing the degree of mixing between polymer and acceptor material without the use of a co-solvent is by changing the chemical structure of the polymers used. In Chapter 3 polymers with different solubilities are used, influencing the order of solidification of the components of the active layer, which yielded different patterns of the top layer. These polymers, however, have band gaps that are too wide to yield high efficiency devices according to the predictions from Chapter 1. In addition, it should be mentioned that the almost unlimited choice of co-solvents and possible compositions, probably offers a more versatile way of controlling the film forming process, than synthesizing series of polymers with small modifications.

The limits of the maximum open-circuit voltage for PCBM based devices are explored in Chapter 4, where an open-circuit voltage of 1.15 V is reached for PTTBT:PCBM, improving the highest literature value by ~0.1 V. As the optical band gap of PCBM is $E_g = 1.75$ eV and the minimum offset between $E_g - eV_{oc}$ has been predicted to be 0.6 eV, this obtained $V_{oc}$ might be the ultimate limit for PCBM containing cells. The PTTBT:PCBM cells suffer from a relatively low fill factor, possibly caused by the low hole mobility, and a photocurrent that is strongly field dependent, signifying a bound charge-transfer state at the PTTBT:PCBM interface and a correspondingly modest external quantum efficiency of ~20% at short circuit.
The same minimum offset of $E_g - eV_{oc} \geq 0.6$ eV, is also approached for PDPP3T:PCBM as described in Chapter 5, but then with the polymer instead of PCBM has the lowest band gap. The band gap of PDPP3T is 1.3 eV and with a $V_{oc}$ up to 0.68 V, the threshold has been effectively reached. As for PTTBT:PCBM, the external quantum efficiency of the PDPP3T:PCBM is modest (~35%) but there is no sign of a strong field assisted charge collection. Geminate recombination of the charge transfer state to the lower lying triplet state is one of the reasons for this loss in quantum efficiency.

In Chapter 7 thienothiophene units and DPP units are combined in one polymer in an attempt to produce materials with high charge carrier mobility. The resulting polymers display ambipolar behavior, but no higher mobilities than other DPP-based polymers reported in this thesis or other thienothiophene-based polymers\textsuperscript{12} were obtained. The lower mobility and the moderate photovoltaic performance could in part be due to the moderate molecular weights of the polymers.

In the DPP-based polymers presented in Chapter 8, an example of the use of furan rings in conjugated polymers is presented. The efficiencies obtained with these polymers are significant, but lower than for the corresponding high performance thiophene analogs presented in Chapters 5 and 6. This is probably due to less favorable film forming abilities of the furan polymers compared to the higher molecular weight thiophene analogs. If the furan chemistry is better understood and controlled, polymers with molecular weights exceeding >50,000 g mol\textsuperscript{-1}, like the polymers in Chapters 5 and 6, maybe feasible. It is only then that we can really judge if furan is a promising substitution for thiophene or not.

An important and often underestimated parameter in research for an efficient OPC, is the lifetime of efficient operation. This includes both chemical stability of the polymer as well as the physical stability of the optimized morphology and the device integrity, including electrodes and interface layers. These factors were not studied in this thesis, but should be examined in order to produce commercially viable OPCs.

In conclusion, the thesis shows that knowledge of optical band gap and frontier orbital energies can be used to rationally control several of the characteristics of bulk-heterojunction solar cells, such as the open-circuit voltage and the efficiency. However, none of the materials made so far, has reached its intrinsic limits of performance that can be expected from its electronic energy levels. The origin for that is not clear at present, but it is clearly established that control over morphology, dimension and extend of phase separation are crucial. While thermal annealing, solvent annealing, and the use of co-solvents can be useful to achieve this
goal, predictive quantitative methods for morphology control are virtually absent and progress is hence obtained by careful optimization and exploration of the processing parameters, guided by simple principles. Using this approach, PDPPTPT, has emerged as a material with high 5.5% performance in solar cells, better than DPP materials reported to date, and approaching that of the best cells in general.

The missing link to high performing solar cells is knowledge of the processes that control the formation of the morphology of the active layer. Such knowledge will be essential to establish the full potential of new materials and approach the intrinsic performance as predicted by the simple guidelines explained in Chapter 1.

9.2 References

Synthesis and Application of $\pi$-Conjugated Polymers for Organic Solar Cells

Summary

Organic photovoltaic cells (OPCs) hold the promise of being a cheap and environmentally benign large scale renewable energy resource. The photoactive layer in OPCs is based on a blend, or bulk heterojunction, of an electron donor ($p$-type) and an electron acceptor ($n$-type) material. The operational principle involves the absorption of light to create an exciton that diffuses to the $p$-$n$ interface and is split into charges that are subsequently transported to the electrodes and collected. All of these processes have to occur with high quantum efficiencies and minimal energy losses to make a high efficiency solar cell. In this thesis new materials have been developed by means of synthetic chemistry to improve the efficiency of existing materials in OPCs by absorbing a larger part of the solar spectrum and minimizing energy losses in the conversion process. The morphologies of the new donor-acceptor bulk heterojunction layers have been optimized for high efficiency by influencing the degree of mixing of the two materials.

In designing new small band gap polymers for bulk heterojunctions that can absorb and convert a large part of the solar spectrum various aspects need to be considered. The frontier energy levels of the new polymers must be designed to minimize energy losses by increasing the open-circuit voltage with respect to the optical band gap, while maintaining a high coverage of the absorption with the solar spectrum. Another balance is the amount of interface between the two materials that should be large to create free charge carriers, while maintaining percolating domains of pure material to transfer these charges to the electrodes. To prevent recombination during the transport, free charge carrier mobility in the two materials should be high.

In a first approach, alternating copolymers based on cyclopentadithiophene (CPDT) and five different electron deficient aromatic units with reduced optical band gaps have been synthesized via palladium catalyzed coupling. All polymers showed a significant photovoltaic response when mixed with a fullerene (PCBM) as acceptor. The best cells have been obtained for a copolymer of CPDT and benzooxadiazole with a band gap of 1.5 eV. This cell gives a power conversion efficiency (PCE) of about 2.5%.

Next, a series of polythiophenes (PT$n$) based on CPDT units alternating with short oligothiophenes of different length $n$ along the chain has been synthesized to control the
morphology of PT$n$:PCBM blends via the chemical structure of the polymer, rather than via processing conditions. The degree of phase separation in PT$n$:PCBM blends can be controlled via $n$, because with increasing $n$ the number of solubilizing side chains per thiophene is reduced. The best cells and most intimately mixed morphology were obtained for PT2 that exhibits a PCE of about 1.5% when mixed with PCBM. Although the final efficiency is moderate, the study represents an example of a rational approach towards morphology control via chemical structure.

To maximize the open-circuit voltage of polymer:PCBM cells, a new polymer has been synthesized based on benzothiadiazole and a substituted thienothiophene, to create a material with a relatively deep lying level of the highest occupied molecular orbital. To obtain working and reproducible devices, the poly(ethylenedioxythiophene):poly(styrenesulfonate) hole conducting layer was treated with UV-ozone. This treatment increased the work function of the electrode, facilitating an Ohmic contact with the polymer in the active layer. The open-circuit voltage of 1.15 V corresponds to the highest value obtained for any polymer:PCBM cell to date and matches with the previously predicted ultimate limit for PCBM-based OPCs.

In a new approach a semiconducting polymer with alternating diketopyrrolopyrrole (DPP) and terthiophene units has been developed with a small band gap of 1.3 eV. This polymer exhibits high, nearly balanced hole and electron mobilities of 0.04 cm² V⁻¹ s⁻¹ and 0.01 cm² V⁻¹ s⁻¹, respectively in field-effect transistors (FETs). When the polymer was combined with [60]PCBM or [70]PCBM, photovoltaic cells were made that provide a photoresponse up to 900 nm and a PCE of 3.8 and 4.7% in sunlight, respectively. The efficiency of the photovoltaic cells was found to be strongly dependent on the molecular weight of the polymer and the use of processing agents during film formation.

In a further development, a new easily accessible, alternating DPP and dithienylphenylene co-polymer has been developed, again with high electron and hole mobilities, exceeding 0.01 cm² V⁻¹ s⁻¹. PCEs of 4.6 and 5.5% were obtained with [60]PCBM and [70]PCBM. The performance of these cells strongly depends on the use of a processing agent, 1,8-diiodooctane (DIO), during film formation. The active layers have been studied with atomic force microscopy and transmission electron microscopy and show vast variations in size of the PCBM clusters upon application of DIO, together with appearance of fiber-like structures. Photoinduced absorption measurements support the generation of more charges in the optimized morphology.
The use of thienothiophene (TT) as a co-monomer was further explored by alternation with DPP units in an attempt to combine the successful strategies for improved performance described above. Two polymers, with substituted and unsubstituted thienothiophenes were prepared. No significant difference was observed in charge carrier mobility, but the photovoltaic behavior was better for the polymer with more and shorter side chains (2.3% vs. 1.2%). A further co-polymer with extra thiophene units between TT and DPP in the chain was also synthesized. This polymer has a lower charge carrier mobility in an FET, but outperformed the other polymers in an OPC, with the best cell exhibiting a PCE of 3.4%. One reason for the overall lower PCE in the TT-DPP copolymers is the moderate molecular weight of the materials obtained.

In further exploring the electron deficient DPP structural motif for photovoltaic polymers, furan rings were considered as a building block in the main chain. Four small band gap copolymers based on DPP alternating with electron rich trimers of benzene, furan, and thiophene have been synthesized via Suzuki polymerization. The polymers show optical band gaps between 1.4 and 1.6 eV, optimized for solar energy conversion, and exhibit ambipolar charge transport in field-effect transistors with hole and electron mobilities higher than $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$. In solar cells the polymers are used as electron donor and provide power conversion efficiencies up to of 3.7% in simulated solar light when mixed with [70]PCBM as acceptor. Again the reduced molecular weight of the new materials is possibly limiting the PCE compared to higher efficiencies reached earlier.

With the development of DPP type polymers a new, highly successful, class of promising materials for OPCs has been created. The final efficiencies obtained, compare favorably to the state of the art in the field. Several of the materials made have close to optimal energy levels for very efficient OPCs. Hence further improvements can be expected when improved control over molecular weight, morphology, and charge carrier mobility can be obtained.
Synthese en Toepassing van π-Geconjugeerde Polymeren voor Organische Zonnecellen

Samenvatting

Van alle alternatieve energiebronnen is zonne-energie het meest beschikbaar op aarde. De zon levert ongeveer 8000 keer meer energie aan de aarde dan we als samenleving nodig hebben. Om de zonne-energie efficiënt te kunnen gebruiken, zijn zonnecellen nodig die goedkoop en snel te produceren zijn. Zonnecellen opgebouwd uit organische polymeren kunnen mogelijk voldoen aan deze eisen, maar zijn nog niet efficiënt genoeg in het omzetten van licht in elektriciteit. De licht absorberende laag in deze cellen is gebaseerd op een mengsel, of bulk heterojunctie, van twee organische halfgeleidermaterialen: een p-type materiaal en een n-type materiaal. Het p-type materiaal dat gebruikt is in het onderzoek beschreven in dit proefschrift, is een geconjugeerd polymeer, het n-type materiaal een C_{60} of C_{70} fullerenderivaat ([60]PCBM of [70]PCBM). Als licht geabsorbeerd wordt in een van de materialen, kan de aangeslagen toestand (exciton) van dit materiaal diffunderen naar het grensvlak waar een elektron overgedragen kan worden. De daarbij gecreëerde ladingen worden aan het grensvlak gescheiden en vervoerd naar de corresponderende elektrodes. Alle processen die hiermee samenhangen, moeten plaatsvinden met een hoge kwantumefficiëntie en met geringe energieverliezen om een goed conversierendement uit het zonlicht te halen.

In het onderzoek dat beschreven is in dit proefschrift zijn nieuwe p-type polymeren ontworpen, gesynthetiseerd en getest om de efficiëntie van organische zonnecellen te verbeteren. Een aantal aspecten speelt een belangrijke rol bij het ontwerp van een polymeer dat geschikt is voor organische zonnecellen. De energieniveaus van de hoogst bezette en laagst onbezette orbitalen moeten zo ontworpen worden dat er weinig energieverlies is om de open-klemspanning zo hoog mogelijk te laten zijn terwijl tegelijkertijd een groot deel van het zonlichtspectrum geabsorbeerd moet kunnen worden. De ladingsmobiliteit in beide materialen moet ook hoog zijn om het transport van gevormde ladingen te faciliteren en recombinatie van ladingsdragers te voorkomen. Voorts is de menging van de twee materialen in de actieve laag (de morfologie) een zeer belangrijke parameter. Doordat een aangeslagen toestand van een molecuul slechts een beperkte levensduur heeft, moet er een grensvlak dichtbij zijn om de kans op ladingsscheiding te optimaliseren, maar tegelijkertijd moeten er pure fases van de beide materialen zijn om de gevormde ladingen te vervoeren. De balans tussen goede
menging en pure fases blijkt heel nauw te luisteren en is ook onderzocht en geoptimaliseerd in het onderzoek beschreven in dit proefschrift.

In eerste instantie zijn alternerende copolymeren op basis van cyclopentadieneen (CPDT) en verschillende elektrondeficiënte groepen gemaakt door middel van palladium gekatalyseerde polymerisatiereacties in Hoofdstuk 2. Alle gesynthetiseerde polymeren vertonen een fotovoltaïsch effect in combinatie met een [60]PCBM als n-type materiaal. De beste cellen zijn gemaakt met een polymer gebaseerd op benzooxadiazool als comonomeer naast CPDT dat een bandafstand heeft van 1.5 eV. Deze cel heeft een efficiëntie van ongeveer 2.5%.

Als vervolg is in Hoofdstuk 3, op basis van CPDT een serie gemaakt van polythiofenen (PTn) die verschillende aantallen n ongesubstitueerde thiofeeneenheden hebben. Deze zijn gemaakt met als doel de morfologie van de polymer:PCBM laag te beïnvloeden door de chemische structuur van het polymer. De morfologie wordt beïnvloed door n, doordat het verhogen van aantal thiofeeneenheden de oplosbaarheid van het polymer verlaagt. De beste cellen zijn gemaakt met PT2, die de meest fijne morfologie geeft in combinatie met [60]PCBM, en een efficiëntie bereikt van 1.5%. Ondanks dat de efficiëntie matig is, is dit wel een goed voorbeeld van het beïnvloeden van de morfologie door de chemische structuur van het polymer en niet via het beïnvloeden van de morfologie door de procescondities.

In Hoofdstuk 4 is een verhoging van de open-klemspanning van de polymer:PCBM cellen bereikt met een polymer dat gebaseerd is op een afwisseling van thienothiofeen en benzothiadiazool in een keten, resulterend in een polymer dat een relatief hoge oxidatiepotentiaal heeft. Om werkende zonnecellen te verkrijgen, moet de poly(ethylendioxythiofeen):poly(styreensulfonaat) elektrode behandeld worden met UV-ozon omdat daarmee een Ohms contact verkregen kan worden met de actieve laag. De open-klemspanning van 1.15 V voor de cellen komt overeen met de hoogste waarde ooit beschreven voor polymer:PCBM zonnecellen en correspondeert met de eerder voorspelde maximale waarde voor dit type cellen.

Hoofdstuk 5 beschrijft een polymer gebaseerd op een diketopyrrolopyrrool (DPP) en drie thiofeeneenheden dat een bandafstand heeft van 1.3 eV. Het polymer heeft bijna gelijke mobiliteiten voor elektronen en gaten van 0.04 cm² V⁻¹ s⁻¹ en 0.01 cm² V⁻¹ s⁻¹ in veld-effecttransistoren. In combinatie met [60]PCBM en [70]PCBM zijn zonnecellen gemaakt met een respons tot 900 nm en met een efficiëntie van 3.8% en 4.7%. De efficiëntie van de
zonnecellen is erg afhankelijk van het molecuulgewicht van het polymeer en het gebruik van co-oplosmiddelen tijden de depositie van de laag vanuit oplossing.

Een vervolg hierop staat beschreven in Hoofdstuk 6, waar de synthese van een eenvoudig toegankelijk polymeer gebaseerd op DPP en dithienylbenzeen is beschreven. Dit polymeer heeft weer een heel hoge, en bijna identieke, mobiliteit voor elektronen en gaten van meer dan 0.01 cm² V⁻¹ s⁻¹ in een veld-effecttransistor. De efficiënties in zonnecellen met [60]PCBM en [70]PCBM zijn 4.6% en 5.5%. Deze hoge efficiënties worden alleen gehaald als er een co-oplosmiddel gebruikt wordt, in dit geval 1,8-dijoodoctaan. Deze manier van verwerken heeft tot gevolg dat in de actieve laag van de cel, een veel fijnere fasescheiding ontstaat met een fiberachtige polymeerfase, terwijl zonder co-oplosmiddel er relatief grote PCBM clusters aanwezig zijn. Er zijn verschillende co-oplosmiddelen getest en voor alle co-oplosmiddelen kon er een vergelijkbare cel verkregen worden met vergelijkbare morfologie. Lichtgeïnduceerde absorptiemetingen laten zien dat er met co-oplosmiddel meer ladingen gevormd werden.

De thienothiofeen (TT) eenheid is ook toegepast in DPP gebaseerde polymeren in een poging om de succesvolle aanpak geïntegreerd in Hoofdstukken 4 en 5 te combineren. Twee polymeren met een gesubstitueerde en ongesubstitueerde thienothiofeen zijn gemaakt. Het ladingstransport verschilt niet significant voor deze twee polymeren, maar de efficiëntie van de resulterende cellen wel (1.2 vs. 2.3%). Een derde copolymeer met extra thiofeeneenheden tussen TT en DPP in de keten is ook gesynthetiseerd. Dit polymeer heeft een lagere ladingstransport in een veld-effecttransistor, maar leidde tot een betere efficiëntie in zonnecellen, met een maximaal rendement van 3.4%. Een mogelijke reden voor het toch wat lage rendement in de TT-DPP copolymeren is het gelimiteerde molecuulgewicht van deze materialen.

In het gebruik van elektrondeficiënte DPP eenheden voor fotovoltaïsche polymeren zijn furaaneenheden onderzocht als bouwsteen in de polymeerketen. Vier polymeren met een kleine bandafstand gebaseerd op DPP alternerend met elektronrijke trimeren van benzeen, furaan, en thiofeen zijn gesynthetiseerd via Suzuki polymerisatie. De polymeren hebben een optische bandafstand tussen 1.4 and 1.6 eV, een optimale waarde voor zonnecellen, en vertonen ambipolaire ladingstransport in veld-effect transistoren met gaten- en elektronenmobiliteiten van meer dan 10⁻² cm² V⁻¹ s⁻¹. Zonnecellen waarin deze polymeren gebruikt worden als elektronendonor geven efficiënties tot 3.7% in zonlicht als ze gemengd worden met[70]PCBM als acceptor. Wederom is het relatief lage molecuulgewicht van de
nieuwe materialen de limiterende factor voor het rendement in vergelijking met de waarden bereikt in Hoofdstuk 5 en 6.

Concluderend hebben de hier beschreven polymeren geleid tot een verhoging van de efficiëntie van organische zonnecellen gebaseerd op DPP polymeren. De rendementen die behaald zijn, zijn goed in vergelijking met de beste waarden gepubliceerd voor dit type zonnecellen. Verschillende van de nieuwe materialen hebben vrijwel optimale energieniveaus voor hoogefficiënte zonnecellen. Daarom kunnen verdere verbeteringen mogelijk worden als er een betere controle kan worden verkregen over molecuulgewicht, morfologie, en ladingmobiliteit.
Curriculum Vitae

Johan Bijleveld was born on Wednesday, December 3rd, 1980 in Rhenen. After obtaining the athenaeum diploma at the ‘Christelijk Lyceum Veenendaal’ he studied chemistry at the University of Utrecht. After a graduation project in the group of Leo Jenneskens, on the topic of polycyclic aromatic hydrocarbons, he did an internship at the laboratories of Mats Andersson at Chalmers University of Technology in Gothenburg, Sweden on polymers for organic solar cells. In 2006 he became a PhD student at the Eindhoven University of Technology in the Molecular Materials and Nanosystems group, under supervision of René Janssen. The results of his PhD research on the synthesis and application of π-conjugated polymers for organic solar cells are collected in this thesis.
List of publications

High photovoltage achieved in low band gap polymer solar cells by adjusting energy levels of a polymer with the LUMOs of fullerene derivatives

Copolymers of cyclopentadithiophene and electron deficient aromatic units designed for photovoltaic applications

Electronic structure of small band gap oligomers based on cyclopentadithiophenes and acceptor units

Nanomorphology of bulk heterojunction organic solar cells in 2D and 3D correlated to photovoltaic performance

Poly(diketopyrrolopyrrole-terthiophene) for ambipolar logic and photovoltaics

Maximizing the open-circuit voltage of polymer:fullerene solar cells
Diketopyrrolopyrroles as acceptor materials in organic photovoltaics

Efficient solar cells based on easily accessible diketopyrrolopyrrole polymer

Controlling morphology and photovoltaic properties by chemical structure in copolymers of cyclopentadithiophene and thiophene segments

Small band gap copolymers based on furan and diketopyrrolopyrrole for field effect transistors and photovoltaic cells

Copolymers of diketopyrrolopyrrole and thienothiophene for photovoltaic applications
Dankwoord

Punt.
Zo, dat was vier jaar promoveren met als resultaat dit proefschrift, maar dat had ik nooit alleen kunnen schrijven, ik heb van enorm veel mensen heel veel hulp gehad en die wil ik hier bedanken.

Allereerst natuurlijk mijn promotor René Janssen, waarvan ik de kans kreeg in Eindhoven aan dit geweldig mooie onderzoek te werken. Rene, ik bewonder je vermogen om een probleem tot essentie terug te brengen en vrijwel direct te begrijpen waar iemand heen wil. In jouw groep zijn zoveel aspecten van organische elektronica vertegenwoordigd, dat op iedere vraag wel een zinnig antwoord komt. Ik heb heel veel van je geleerd niet alleen over de organische elektronica, maar ook over het schrijven van een goed stuk tekst.

Martijn, ondanks dat je soms wat ondankbaar en onzichtbaar werk verricht, wordt dat door mij wel enorm gewaardeerd. Je inzichten zijn voor mij vaak heel verhelderend geweest en je weet met op het oog simpele vragen met de juiste antwoorden uit te lokken. Ook van jou heb ik de afgelopen vier jaar heel veel geleerd. Bedankt voor het lezen van alle aparte hoofdstukken en voor het zitting nemen in de oppositie.

Ullrich Scherff, many thanks for taking part in the reading committee and taking part in the defense. Mats Andersson, I want to thank you again for the time I spent in Göteborg and suggesting Eindhoven as a place to do my PhD. Of course also for reading the manuscript of my thesis and being present at the defense, tack så mycket. Rint Sijbesma en Albert Schenning hartelijk dank voor het lezen en becommentariëren van dit boekwerk en het zitting nemen in de commissie tijdens de verdediging. Dirk Vanderzande, hartelijk dank voor de deelname aan de oppositie van dit proefschrift.

Ik heb tijdens mijn promotie het genoegen gehad twee studenten te mogen begeleiden tijdens hun afstuderen. Sandra en Melanie, ik heb van jullie allebei erg veel geleerd en ook veel lol met jullie gehad. Sandra, zonder jou zou hoofdstuk 6 niet zo mooi zijn geworden als het nu geworden is en ik denk dat we nu een beetje meer begrijpen van de wereld achter de co-oplosmiddelen. Melanie, jouw synthese vaardigheden hebben bijgedragen aan hoofdstukken 4 en 7, waar je jouw mooie resultaten terug kan zien.

Ook wil ik de rest van mijn collega’s en labgenoten bedanken voor de goede sfeer en het geouwehoer op de gang of in het lab. Het voert te ver om iedereen op te noemen, maar een paar licht ik er graag uit: Arjan (zuurkast-buurman en pionier in de DPP polymeren), Jan G
(meester van de (tandem)zonnecellen), Simon (expert in het maken van FETs en het meten van nano- of zelfs picoampères), Martha (expert in AFM and making cells with my First polymers), Veronique (voor alle TEM plaatjes en natuurlijk in het speciaal die op de voorkant van dit boekje), Bram (synthese van DPP monomeren en synthese discussies), Michel (labführer), Martin (zuurkast-buurman), Daniele (master of the PIA) en Karthik and Jian Bin (fumehood-neighbours).

Ik ben ook enorm veel dank verschuldigd aan het analytische team bestaande uit Joost, Mr. Lou en Ralf voor het meten van alle sampletjes en alle analyse oplossingen. Ook alle secretaressen, die er velen zijn geweest, hartelijk dank voor alle antwoorden op praktische vragen, net als Hans voor alle bestellingen van chemicaliën. The rest of my colleagues and lab mates at SMO / MST / M2N, I won’t forget you, but there are just too many of you to mention everyone separately. I had a lot of fun working in your presence.

Een speciaal woord van dank voor mijn kamergenoten die ik door de jaren heen op STO 4.81 en later op STO 4.30 versleten heb. Jos, Karthik, Frank, Wiljan, Arjan, Veronique, Dominique and Mindaugas bedankt voor het delen van de droppot en het aanhoren van mijn eeuwige geklaag over besturingssystemen ontwikkeld door Bill Gates.

Mijn nieuwe collega’s op de Hogeschool Leiden wil ik bedanken voor de flexibiliteit en de mogelijkheid dit boekje op een mooie manier af te ronden.

De ontspanning naast het werk is minstens zo belangrijk als een goede werksfeer en ik wil op deze plaats graag stilstaan bij de mensen die mijn leven de afgelopen vier jaar van een andere kant hebben meegemaakt. Volkert, (alle) Vierhouters, Tom, Tania, Sipke, Sander van Thillo, Sander Engels, Rudy, René, Peter, Martin, Martijn, Marleen, Marije, Loes, Linda, Lai Mei, Judith, Jochem, Jan, Irene, Hanneke, Frederik, Floor, Elles, Edwin, Edo, Dirk, Christina en Chantal, bedankt voor alle weekendjes, stapavonden, biertjes, diepe gesprekken, voetbalavonden, terrassen, (stijl)dansavonden, theetjes, fietsrond(j)es, spelletjes, feestjes, etentjes, kortom voor alles buiten de scheikunde.

Mijn beide paranimfen, Irene en Hanneke wil ik speciaal bedanken. Irene, ik vind onze danslessen heel leuk en dat is echt een mooie uitlaatklep als je in de stress van het promoveren zit. Hanneke, ik waardeer het enorm dat we af en toe onze harten even kunnen luchten bij elkaar over werk en privé onder het genot van een hapje en een biertje, ik hoop dat er nog vele volgen.

Ik heb enorm veel mazzel gehad met mensen die ik niet voor het uitkiezen had. Hans, Wilma, Jasper, Laura en Mark, ondanks dat jullie misschien niet helemaal begrepen waar ik
me die vier jaar nou zo druk mee heb gehouden, hebben jullie wel altijd interesse getoond. Dankjewel.

Henny, heel veel succes met het afronden van je eigen promotie en je leven samen met Tjeerd, al twijfel ik er niet aan dat dat helemaal goed gaat komen. Pieter, succes met je werk in Brabant en al je andere bezigheden waar je zo gedreven mee bezig bent. Papa en mama, zonder jullie als inspiratiebron had ik nooit kunnen komen waar ik nu ben. Jullie hebben me altijd geholpen waar mogelijk en hebben mij onvoorwaardelijk gesteund in mijn keuzes, al waren die soms wat last-minute. Dank voor alles.

De laatste alinea is voor jou, lieve Merel. Jij kunt me optillen met je lach maar ook zo heerlijk nuchter zijn dat je mij weer met beide voetjes op aarde zet. Het kan niet anders dan dat wij ons gelukkige bestaan van nu een supermooi vervolg gaan geven, met jou heb ik zin in de rest van mijn leven. Ik hou van je!

Johan