THE APPLICATION OF WIDE BAND GAP CONJUGATED POLYMERS IN SINGLE JUNCTION POLYMER SOLAR CELLS

Chemical Engineering and Chemistry
Molecular Systems and Materials Chemistry
Eindhoven University of Technology
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Abstract

In this research, a new phenanthroline derivative was synthesized and characterized on purpose to polymerize the monomer via a Stille-polymerization with different electron donating moieties leading to a range of new wide band gap polymers. The novelty in this monomer would be the long side chains in order to ensure the solubility of the entire polymer. Hence there would be no necessity for the donor moiety to have sidechains in order to make the polymer soluble. Beside this phenanthroline synthesis two new benzothiadiazole based wide bandgap polymers were synthesized characterized and implemented in photovoltaic devices. These wide bandgap polymers are normally used in the front cell of tandem photovoltaic devices, however, in this research the application of wide bandgap materials in single junction photovoltaic devices is investigated.

Chapter one starts with an outline of the concerns about global warming and climate change. In order to address the consequences of these phenomena, a gradual replacement of the conventional resources by renewable energy resources is necessary. Solar radiation is a free and globally available energy resource and hence solar energy appears to be a good candidate as renewable energy resource. A small history is outlined for photovoltaic devices in general and organic photovoltaic in particular. This chapter also includes the working principle, device layout and characterization methods of organic photovoltaic devices.

Chapter two describes the synthesis of a phenanthroline derivative containing decyltetradecyl side chains at the 4 and 7 positions. Three different synthesis routes were performed to synthesize 2,9-dibromo-4,7-di(tricosan-11-yl)dithieno[3,2-c:2',3'-i] [1,10]-phenanthroline on purpose to polymerize this monomer afterwards. The purification of this monomer was the drawback leading to the inability of performing a Stille-polymerization. Also a direct(hetero)arylation polymerization did not result in high molecular weight polymers. In order to ease the purification of the phenanthroline derivative, the length of the side chains was reduced to hexyldecyl. The bromination of the hexyldecyl-phenanthroline derivative was unsuccessful, implying that the length of the side chains is not the bottleneck in this synthesis.

Chapter three includes the synthesis of two wide band gap polymers via a Stille-polymerization. The polymers differ in their side chains as one contain octyldodecyl carboxylate side chains (PDCDTBT-OD) and the other polymer is the hexyldecyl analogue (PDCDTBT-HD) Both polymers were characterized and implemented in both conventional and inverted geometry photovoltaic devices. The photovoltaic properties corresponds to the expectations that the devices containing the hexyldecyl derivative in its active layer reaches higher efficiencies with a maximum PCE of 6.2%. However, these results were not reproducible. The photovoltaic devices were optimized for solvent system, thickness and
donor:acceptor (D:A) ratio. The best results obtained for the PDCDTBT-OD was a PCE of 4.82% for the photovoltaic devices which were processed from 2% DPE in chloroform in a 1:1.5 donor:acceptor ratio. On the other hand, an efficiency of 6.2% was reached for the PDCDTBT-HD processed from a 1% DIO in chlorobenzene solvent system with a 1:1.5 D:A ratio. The inverted device processed from the same solvent system and donor acceptor ratio resulted in a PCE of 5.26%
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Abstract

Global warming and climate change has tremendous consequences for human population resulting in the necessity to gradually replace the conventional energy resources by renewable energy. Solar cells are addressed as a viable successor due to the long term availability of solar energy. An overview of the existing photovoltaics is given and specifically focused on organic photovoltaics. Furthermore the working principles of organic photovoltaic devices are described followed by an overview of their layout and characterization. Finally the research purpose of this graduation project is described in detail.
1.1 Why solar energy?

Global warming and climate change are now the greatest threats facing the planet. According to a temperature analysis of NASA’s Goddard Institute for Space Studies (GISS), the global temperature on Earth has increased by 0.8°C between 1880 and 2013.¹ This increase in temperature is mainly a consequence of greenhouse gases in the atmosphere, such as carbon dioxide (CO$_2$), which traps heat and therefore play an important role in the control of changing Earth’s climate.¹

CO$_2$ is a naturally occurring greenhouse gas and is emitted by the burning of fossil fuels. According to BP’s Energy outlook (2016), the global energy consumption has risen sharply by about 30% since 2000 and they expect an increase of 34% percent from 2014 to 2035.² Up to now, fossil fuels are mainly used as energy resource, resulting in increased levels of CO$_2$. These levels recently passed the ominous boundary of 400 parts per million (ppm) and are predicted to reach about 600 ppm by 2100.¹³⁴ In turn, the temperature would rise about 1.9°C, which may have disastrous consequences. One example is the fast rising sea level as a result of ice melting at the Earth’s poles.³⁴ Therefore, to minimize this effect and guarantee a sustainable development of human population, a reduction of CO$_2$-emission is required. Lower CO$_2$-emissions can be achieved by a gradual replacement of fossil fuels by renewable energy resources.

Renewable energy resources are inexhaustible, clean and can sometimes be applied by the local population. The two major renewable energy resources that contribute most to the world’s energy demand are hydropower and wind energy.⁵ However, a global growth in new hydropower capacity is unlikely, as the most efficient sites for hydropower have already been developed.⁶ In addition, a disadvantage of wind energy is its horizon pollution due to the dimensions of the wind turbines. These wind turbines also create noise pollution proportional to the wind speed. On the other hand, solar irradiation is present in large abundance, free and globally available and is therefore probably the most promising candidate to replace conventional energy resources.
1.2 Evolution of solar cells

The origin of solar cells as we know them today traces back to the 19th century. In 1839, A.E. Becquerel discovered the photovoltaic effect -or Becquerel effect- describing the development of a current while a material, in this case a platina electrode, is exposed to light. Despite this early breakthrough, it lasted until 1954 before the first efficient crystalline silicon solar cell with a power conversion efficiency of 6% was developed by Chapin and coworkers (1954). A p-n junction was used to convert sunlight into electricity. The first practical application of this type of solar cells was the generation of electricity in space on the orbiting satellite Vanguard I in 1958. For years, this was the only application of solar cells since manufacturing costs were too high for large scale applications. In the 70's, the oil crisis raised the interest for new energy resources for terrestrial applications and solar energy in particular. Now, the solar cell market is strongly dominated by silicon solar cells, which already reached power conversion efficiencies above 25%. Despite their high efficiency and their domination on the solar cell market, the necessity for highly pure and thick silicon wafers raises the manufacturing costs. These types of cells, i.e. with high efficiency and high production costs, were introduced as first generation solar cells by M. A. Green.

In order to lower the production costs, more research has been done in thin-film solar cells. However, this type of cells does not only reduce the cost, but also show a lower power conversion efficiency. These flexible, lower-cost solar cells are referred to as the second generation solar cells, mainly consisting of amorphous silicon (a-Si:H), cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) solar cells. These cells respectively reached efficiencies of 10.1%, 16.5% and 19.9 %.

Among these well-established thin film solar cells, there are several emerging photovoltaic technologies -the third generation- lacking the scarce gallium (Ga) and toxic cadmium (Cd). One of the most promising technologies are organic photovoltaics. Due to the ability of processing the organic layers from solution, organic solar cells can be produced via roll-to-roll processing which significantly lower the production costs compared to silicon solar cells. Furthermore, this allows the active layers to be implemented in flexible devices. Despite these promising properties, one big disadvantage of organic photovoltaics is their low efficiency compared to their inorganic counterparts. Although efficiencies of organic photovoltaics have raised sharply the last decade, a similar increase in efficiency is required in the near future to fulfill the requirements for a successful commercialization of organic-based devices. Techniques for improvement can only be developed with a proper understanding of the working principles and limitations of organic photovoltaics.
1.3 Organic photovoltaics

1.3.1 Evolution of organic photovoltaics

Pochettino (1906) and Volmer (1913) discovered the first aromatic organic compound, anthracene, which showed photoconductivity.\(^{16}\) Despite this early breakthrough, the investigation of other photoconductive organic materials lasted until the 1960's. During the 1960's the semiconducting properties of organic dyes and biological pigments were discovered.\(^{16}\) However, the field of organic semiconducting materials only arose in 1977, when Heeger, Macdiarmid and Shikrawa discovered the effect of doping on the conductivity of polyacetylene.\(^{17}\) These new insights raised the interest in other semiconducting polymers leading to the discovery of the electroluminescent behavior of poly(p-phenylene-vinylene) (PPV), and the first polymer light emitting diodes (LED's)\(^{18}\)

![Chemical structure of antracene, polyacetylene and PPV](image)

Weinberger and coworkers were the first researchers who made a solar cell using polyacetylene as a sandwiched layer between two dissimilar electrodes.\(^{19}\) A photovoltaic effect was observed, although circuit voltages (\(V_{oc}\)'s) of around 0.3 V and low power conversion efficiencies (PCE's) were reached.\(^{16}\) In 1985, Tang made a major breakthrough by investigating solar cells consisting of an active layer in bilayer morphology. Copper phthalocyanine was used as electron donating material and a perylene derivative as an electron acceptor between two electrodes.\(^{16,19}\) Using this two-layer morphology (Figure 2a), a PCE around 1% was achieved under simulated AM2 illumination.\(^{19}\) Even though the achieved efficiency was a major breakthrough, there was room for improvement since the bilayered structure imposes certain limitations.

When an organic photovoltaic device is exposed to sunlight, the photons can be absorbed. If the photon energy is high enough, one of the two semi conducting materials in the active blend -mostly the donor material- can excite an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (Figure 2a).\(^{20,21,22}\) The minimum energy to excite an electron from the HOMO to the LUMO is the band gap energy (\(E_g\)) of the material, which is defined by the energy difference between the HOMO and the LUMO energy levels.\(^{21}\) When the photon has a higher energy than \(E_g\), the energy excess is rapidly thermalized.\(^{23}\) The promotion of an electron to the LUMO results in an electron and...
hole pair, called an exciton (Figure 2b). In an exciton, the electron and hole are tightly bound by coulombic interactions as a result of the low dielectric constant of the organic material in which the exciton is formed.\textsuperscript{24,25} Therefore the electron and hole diffuse as an exciton towards the donor-acceptor interface. To overcome the coulombic interaction between the electron and hole, the acceptor material plays an important role.\textsuperscript{26} The acceptor has a higher electron affinity and ionization potential than the donor material and thus the HOMO and LUMO are lower in energy. Once the exciton reaches the interface the electron can move from the donor LUMO to the lower lying LUMO of the acceptor material as this is energetically favored (Figure 2c).\textsuperscript{21,27} Under influence of the built-in electric field or $V_{BI}$, these separated charges will drift via a hopping mechanism towards their respective electrodes where charge collection takes place (Figure 2d).\textsuperscript{25}

As the hopping mechanism limits the electron and hole mobility, the distance from exciton regeneration towards the donor-acceptor interface needs to be minimalized in order to overcome recombination of the electron and hole.\textsuperscript{28} Due to the limited lifetime of an exciton, the maximum distance which an exciton can travel without recombination is approximately 10 nm. In the case of a bilayered morphology, the donor and acceptor layer can only be 10 nm
each meaning that the active layer has a maximum thickness of 20 nm. This results in a lack of absorption and consequently a low current is generated.\textsuperscript{29}

This problem was solved by Yu and coworkers in 1995 with the introduction of a bulk heterojunction (BHJ) (Figure 3b), in which the active layer is a bicontinuous network of a donor and acceptor material.\textsuperscript{29} An intimate mixing of the donor and acceptor reduces the diffusion length in order to ensure that most excitons can reach the donor-acceptor interface before recombining. However, very small domain sizes are undesirable to ensure both charge dissociation and transport.

The organized bulkheterojunction is the ideal morphology which is optimal for all processes occurring in a solar cell. (Figure 3c). In this heterojunction both charge separation and transport are ensured over the entire active layer as the interface between donor and acceptor molecule is maximized. Although this configuration is the most promising, the practical fabrication is a challenge. Therefore, the regular bulkheterojunction is widely used as a reasonable alternative.\textsuperscript{30}

**Figure 3:** Overview of three donor-acceptor morphologies as active layer in organic photovoltaic devices. a) a bilayer morphology, b) a bulk heterojunction, c) an ideal bulkheterojunction.

### 1.3.2 Organic photovoltaic device layout

An organic photovoltaic device consists of stacks of (semi-)conductive layers deposited on a transparent substrate, which in this case is glass. The device is built-up of two electrodes, an anode and a cathode, a hole transport layer, an active layer and an electron transport layer, as depicted in Figure 4.\textsuperscript{24}

**Figure 4:** Schematic overview of the configuration of a regular organic photovoltaic device: The layered structure consists of an anode, a hole transporting layer (HTL), an active layer, an electron transporting layer (ETL) and a cathode. The arrows at the right shows the transporting direction of the electrons and holes.
Both electrodes are typically conductive materials which serve as electron or hole collectors. The anode is the electrode which collects holes, where the cathode is the electron collecting electrode. The difference in workfunction between the anode and the cathode creates a built-in potential ($V_{IB}$).\textsuperscript{20,31} This potential is the driving force for the diffusion of electrons and holes to their respective electrode. One of the electrodes is deposited on the substrate. In order to ensure light penetrating towards the active layer, this electrode is a transparent conducting material as for example indium tin oxide (ITO).\textsuperscript{20,24} The other electrode, the top electrode, is a reflective metal electrode such as aluminium (Al) or silver (Ag).

The organic active layer is composed of two intimately mixed semiconducting materials: a electron donating small molecule or polymer and an electron acceptor which is in most cases a fullerene derivative such as phenyl-C$_{61}$-butyric acid methyl ester (PCBM). This blend of semiconductors perform various functions starting from absorbing photons to converting excitons into charges and the transport towards their respective electrodes.\textsuperscript{20}

The hole transporting layer (HTL) is a high workfunction material, such as poly(3,4-ethylenedioxythiophene):poly(styrene sulfanate) (PEDOT:PSS) (Figure 5), which facilitates the transport of holes by forming an ohmic contact with the ITO.\textsuperscript{30} In addition, this layer smoothen the ITO surface in order to avoid leakage current.\textsuperscript{20,24} Various metal oxides, such as molibdenum oxide (MoO$_3$) form a reasonable alternative as hole transporting layer.\textsuperscript{24}

![Figure 5: Molecular structure of the high work-function hole transporting material PEDOT:PSS](image)

The electron transporting layer (ETL) is a low workfunction material inserted between the active layer and the electrode. This layer serves as a protecting layer which enhances electron extraction and improves the device performance.\textsuperscript{16,20,32} Commonly used electron transporting layers are metal oxides such as zinc oxide (ZnO) or lithium fluoride (LiF).\textsuperscript{20}

Two types of device layouts are commonly known for organic photovoltaics (Figure 6). Depending on the processing order and the composition of the layers, a conventional or inverted solar cell is obtained.\textsuperscript{20} These different configurations cause electron and hole transport in opposite directions. In literature, commonly the conventional device layout is described. However, the inverted structure recently gained more interest due to its higher air-stability.\textsuperscript{33,34} In this graduation report, both configurations have been used.
1.3.3 Characterization of a photovoltaic device

The sun is a powerful energy resource and essential for life on earth. Sunlight is a form of electromagnetic radiation travelling through the atmosphere and the magnitude of its energetic output on earth varies depending on the weather conditions and the angle with respect to the earth’s surface. Globally, the solar emission spectrum is simulated via a AM1.5 reference spectrum (Figure 4). The air mass coefficient defines the path length of the direct solar beam through the atmosphere. An AM 1.5 spectrum gives the energy flux per photon on a path length which is 1.5 time longer than under normal incidence, i.e. at the zenith (AM 1). Upon increasing the angle to the zenith, the air mass coefficient increases; for the AM 1.5 spectrum the angle of incidence is 48.2° relative to the zenith, i.e. when the sun is directly overhead. The AM 1.5 spectrum is used for characterizing organic photovoltaic devices.

The performance of a photovoltaic device is investigated by two standard characterization techniques: current density-voltage measurements (J-V curves) and spectral response measurements.
J-V measurements are carried out in dark and under illuminated conditions. In dark, an ideal cell should behave like a diode whereas under illumination (AM 1.5) it should produce a photocurrent. This photocurrent results in a shifted J-V curve. From the J-V graph (Figure 8) different parameters can be derived: maximal power point (MPP), open-circuit voltage (\(V_{oc}\)), short-circuit current (\(J_{sc}\)) and the fill factor (FF)

![Figure 8: A typical J-V curve.](image)

The \(V_{oc}\) is the maximum voltage that is available within the solar cell, which is the available voltage under illumination without a current flow (\(J=0\)). When assuming ohmic contacts between the active layer and the electrodes, this energy difference is approximately equal to the energy difference between the HOMO of the donor material and the LUMO of the acceptor. By lowering the LUMO-LUMO or HOMO-HOMO offset between donor and acceptor, the \(V_{oc}\) can be increased. However, the LUMO-LUMO offset needs to be high enough to ensure charge separation. Theoretically the \(V_{oc}\) can be calculated using equation 1.1.

\[
V_{oc} = \frac{1}{e} \cdot \left( |E_{donor\,HOMO}| - |E_{acceptor\,LUMO}| \right) - 0.3 V
\]  
\text{(eq. 1.1)}

![Figure 9: A schematic overview of the energy level alignment of a donor and acceptor material.](image)
When considering the empirical equation 1.1, another energy loss of 0.3 eV next to the minimal LUMO-LUMO offset between donor and acceptor of 0.3 eV is observed. This extra energy loss is related to different physical factors such as reorganization energy or recombination. Combination of both energy losses sets a minimal energy loss of 0.6 eV. The energy loss in turn is defined as the energy difference between the band gap energy and the $V_{oc}$ (equation 1.2)\(^\text{38}\)

$$E_{\text{loss}} = E_g - qV_{oc} \quad \text{(eq 1.2)}$$

The $J_{sc}$ is the current generated under illumination at zero voltage and thus without external resistance. This parameter is also influenced by the incoming photon flux, which can be different for a lamp simulating AM 1.5 light compared to the solar spectrum.\(^\text{16,20}\) When the active layer’s absorption spectrum has a large overlap with the solar emission spectrum, more light can be absorbed and hence more current can be generated since more excitons are formed. However, the presence of more excitons also increases the chance for recombination of charges. The occurrence of recombination can lower the $J_{sc}$ again.

Another factor which can be derived from the I-V curve is the maximum power point. The MPP is defined as the point at which maximal power can be extracted from the device.\(^\text{21}\) Power is defined as the product of current density and the voltage which implies that the MPP is defined as as the product between the $J_{MPP}$ and the $V_{MPP}$.\(^\text{37}\)

$$MPP = J_{MPP} \cdot V_{MPP} \quad \text{(eq. 1.3)}$$

The fill factor (FF) can be derived from the MPP and is defined as the ratio between the maximal extractable power from the device and the theoretically achievable maximum in power for a given $J_{sc}$ and $V_{oc}$ (equation 1.4).\(^\text{26}\) Illustratively, it is defined as the ratio between the two rectangles shown in Figure 8.\(^\text{16}\) This parameter is an ideality factor which qualifies the charge transport. When the fill factor is close to one, the J-V curve adapts a rectangular shape and the $J_{MPP}$ and $V_{MPP}$ are almost equal to the $J_{sc}$ and $V_{oc}$ respectively. However, mainly lower fill factors are obtained, as this parameter is influenced by different factors such as morphology, recombination and carrier mobility.\(^\text{20}\)

$$FF = \frac{P_{MPP}}{J_{sc}V_{oc}} \quad \text{(eq. 1.4)}$$

The final parameter which can be derived is the power conversion efficiency (PCE). The PCE is the ratio between the maximal extractable power and the power from the incoming light (equation 1.5). The measurements under illumination are performed using standard AM 1.5 conditions with an incoming power of 100 mW/cm².
\[
PCE = \frac{V_{oc} \cdot J_{sc} \cdot FF}{P_{in}}
\]  
(eq. 1.5)

In order to get a high PCE of an organic photovoltaic device, the \(V_{oc}\), \(J_{sc}\) and the FF needs to be maximized.\(^{38}\)

When measurements are carried out under illumination with a solar simulator with a spectrum close to the sunlight spectrum, \(J_{sc}\) is the only main difference between the simulated J-V outcome and the real characteristics. Spectral response measurements are used to determine the \(J_{sc}\) more accurately. The spectral response \(S(\lambda)\) is related to the external quantum efficiency (EQE) via equation \(1.6\).\(^{21,39}\) Both the donor and acceptor have a contribution to the spectral response and hence the EQE is dependent on both molecules.

\[
S(\lambda) = EQE(\lambda) \cdot \frac{e \lambda}{hc}
\]  
(eq. 1.6)

The spectral response \((S(\lambda))\) is equal to the EQE at a certain wavelength multiplied by the ratio between the elementary charge \((e)\) and the wavelength \((\lambda)\) and Planck’s constant \((h)\) and the speed of light \((c)\). The EQE is defined as the ratio between the collected electrons per incident photon at short circuit conditions at a certain wavelength. EQE measurements are always performed under different light conditions: biased and non-biased. Biased light is used in order to check whether the photovoltaic device is bias-dependent, i.e. when recombination dominates the current generation. Integration of the light biased EQE-spectrum and convolution with the AM 1.5 spectrum results in a more reliable \(J_{sc}\) (equation \(1.7\)).\(^{21,24,39}\)

\[
J_{sc} = \int S(\lambda) \cdot E_{AM1.5}(\lambda) d\lambda
\]  
(eq. 1.7)

### 1.3.4 Polymer photovoltaic devices

The active layer of an organic photovoltaic device consists of a donor and acceptor polymer material. In order to reach higher efficiencies, the material needs to fulfill some properties. The three most important factors determining the device performance are the energy level alignment, morphology and the device structure.

#### 1.3.4.1 Molecular optimization

One of the important factors is the alignment of energy levels in order to efficiently convert sunlight into electricity. Fortunately, most molecules used in solar cells are highly tunable, making the fine-tuning of the energy levels of the material possible.
As the device needs to harvest as much light as possible, a good overlap in absorption with the solar spectrum is required. Fine-tuning of the energy levels can drastically improve the organic photovoltaic device performance, as the absorbed fraction of the emission spectrum of the sun is determined by the band gap of the material. In order to absorb as much as photons as possible, the band gap needs to be as small as possible.\textsuperscript{40}

**Figure 10:** a) General representation of the energy level alignment of the donor and acceptor. b) when the HOMO of the donor is raised, the $V_{oc}$ decreases. c) When the LUMO of the donor is lowered, there is not enough driving force for charge separation.

A narrow band gap can be achieved by raising the HOMO or lowering the LUMO of the donor material. Increasing the HOMO level of the donor material results in a smaller band gap.\textsuperscript{,} Since the open circuit voltage is determined by the difference in HOMO and LUMO of the donor material, the $V_{oc}$ will decrease and hence the device performance can drop (Figure 10b). On the other hand, lowering the LUMO level can prevent electron transfer between donor and acceptor, as the driving force on the exciton is lowered and hence charge separation is limited (Figure 10c). This would result in lower current generation. A balance between both should be found.

In polymers, these low band gaps can be achieved by combing an electron donating and electron withdrawing moiety. This type of polymers are called push-pull polymers and the band gap is lowered by the orbital mixing of both molecules incorporated in the polymer. The HOMO and LUMO level of the polymer are mainly determined by the HOMO level of the electron donating molecule and the LUMO level of the electron accepting material incorporated in the polymer respectively (Figure 11).\textsuperscript{40,41} Not to be confuse with the fullerene acceptor in the active layer.
1.3.4.2 Single junction versus tandem organic photovoltaic devices

The device structure also plays an important role in increasing the efficiency of the photovoltaic device. Single junction solar cells are built up as a single active layer sandwiched between two electrodes deposited on a substrate (Figure 4). This type of solar cells exist in two different configurations as shown in Figure 6. In order to maximize photon absorption, low-band gap materials are preferred. However, in this case thermalization and transmission losses are present. On the other hand, wide band gap materials, being the scope of this research, can also be used in photovoltaic devices since these polymers show lower thermalization losses.

In order to maximize the absorption of photons and to minimize the thermalization and transmission losses, a tandem organic photovoltaic device was developed. A tandem photovoltaic device consists of two active layers, a wide-band gap and a low band gap material, put on top of each other (Figure 12a). These two different layers are separated by an intermediate contact existing of a hole transporting layer and an electron transporting layer. This results in the formation of a wide-band gap front-cell and a low-band gap back-cell. High energy photons are absorbed by the wide-band gap front-cell. All photons which have an energy lower than the band gap of the front-cell material are transmitted. These photons can subsequently be absorbed by the low-band gap back-cell (Figure 12). At the interface between both cells, the holes from the back cell recombine with the electrons from the front cell. The cells are connected in series and the \( V_{oc} \)'s for both cells add up while the current for both cells remains the same.
Figure 12 The architecture (a) and working principle (b) of tandem solar cells.
1.4 Research purpose

Currently organic photovoltaics have passed the barrier of 10 percent in PCE.\textsuperscript{43} This improvement in PCE is influenced by different factors, including the molecular engineering of organic semiconductors with the design and development of a variety of conjugated polymers in particular.\textsuperscript{44} Low band gap materials have gained a lot of interest since their absorption range is higher which improves the device performance of a photovoltaic cell. Also wide band gap polymers are interesting for use in organic photovoltaic cells since these materials can absorb high energy photons which reduces the thermalization losses.\textsuperscript{42} A variety of wide band gap materials are already investigated, however, new materials are still discovered.

Previous research has shown that fused-ring systems have been a promising material as electron acceptor block in polymers used as donor block in polymer organic photovoltaics. They have a large π-conjugation due to its co-planarity and small π-stacking distances, which increases the charge carrier mobility. In addition, these fused-ring systems are thought to decrease the energy loss of the solar cell due to its rigidity.\textsuperscript{44-46} This rigidity reduces the reorganization energy upon excitation, which in turn lowers the energy loss. According to Chen and coworkers (2016), one of these promising fused-ring systems is 1,10-phenanthroline, which is a rigid structure containing three coplanar aromatic rings.\textsuperscript{47} Different properties of this molecule, as for example solubility, can extensively be tuned by variable functionalization of the different rings.

In this research thiophene-fused 1,10-phenanthroline acceptor monomer functionalized with different alkyl chains varying from hexyldecyl to decyltetradecyl on the 4 and 7-positions is synthesized. By changing the length of the side chains, solubility can be tuned. Polymerization of this monomer together with a bithiophene donor moiety would result in a wide band gap polymer which could be implemented in a photovoltaic device.

Two other benzothiadiazole based wide band gap polymers were synthesized. Bis(2-octyldodecyl) 5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarboxylate and 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole, were already synthesized by Ruurd. Heuvel. These monomers are polymerized via a Stille-polymerization leading to two wide bangap polymers which are characterized for power conversion efficiency, external quantum efficiency and morphology in polymer/fullerene solar cells. The obtained results are compared to the characteristics of the hexyldexyl derivative, a less soluble polymer, which could increase the performance of the photovoltaic device since the polymer is more crystalline and hence the charge mobility is increased.
1.5 References


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Introduction

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Abstract

2,9-Dibromo-4,7-di(tricosan-11-yl)dithieno[3,2-c:2’,3’-i]-[1,10]-phenanthroline is introduced as a promising material for use in organic photovoltaic devices due to its large π-conjugation and its rigidity. In chapter 2 the synthesis towards this phenanthroline derivative is extensively described. Different synthesis routes towards the monomer are proposed. However, the desired monomer was not obtained in a pure form which in turn hinders the Stille-polymerization. To address the problem, an alternative polymerization route was proposed. 4,7-Di(tricosan-11-yl)dithieno[3,2-c:2’,3’-i][1,10]phenanthroline was polymerized via a direct (hetero)arylation polymerization with 5,5’-dibromo-2,2’-bithiophene, yielding a copper-colored low molecular weight compound with a metallic luster.
2.1 Introduction

Even though polymer photovoltaics have promising properties such as flexibility, light-weight and low-cost, it remains a challenge to push their efficiencies and make them economically viable.\(^1\) The active layer in a polymer photovoltaic device consist of a donor polymer intimately mixed with a fullerene acceptor, such as \([6,6]\)-phenyl-\(C_{71}\)-butyric acid methyl ester (\([70]\)PCBM). Although the variety of existing polymer donors is rather high, new promising materials are still being discovered and reported in literature. Over years, many different building blocks such as diketopyrroloporrole (DPP) and benzothiadiazole (BT) were used in donor polymers for organic photovoltaic devices. However, improvement in efficiency can be reached by the molecular engineering of organic semiconductors with the design and development of a variety of conjugated polymers in particular.\(^2\) There are many different ways to tune these materials focusing on different functionalities.

Fused ring systems are promising materials regarding to the electronic properties of the donor polymer. They have a large \(\pi\)-conjugation due to its co-planarity and small \(\pi\)-stacking distances, which increases the charge carrier mobility. In addition, these fused-ring systems are thought to decrease the energy loss of the solar cell due to its rigidity.\(^2\phantom{}^4\) This rigidity reduces the reorganization energy upon excitation, which in turn lowers the energy loss. According to Chen and coworkers (2016) one of these promising fused-ring systems is 1,10-phenanthroline (Figure 13)\(^5\), which is a rigid structure containing three coplanar aromatic rings. Different properties of this molecule, i.e. solubility and electronic properties, can extensively be tuned by variable functionalization of the different rings.

In this chapter three synthesis routes towards 2,9-dibromo-4,7-di(tricosan-11-yl)dithieno[3,2-c:2',3'-i][1,10]phenanthroline are extensively described. Also two different polymerization routes are proposed.

![Figure 13: Molecular structures of a) 1,10-phenanthroline and b) 2,9-dibromo-4,7-di(R)dithieno[3,2-c:2',3'-i][1,10]phenanthroline with R representing a decyltetradecyl or hexyldecyl side chain](image-url)
2.2 Results and discussion

2.2.1. Synthesis

The synthesis towards 2,9-dibromo-4,7-di(tricosan-11-yl)dithieno[3,2-c:2',3'-i] [1,10]-phenanthroline was based on work by Wang and coworkers (2016) in which they started from 4,7-Dibromobenzo[c]-1,2,5-thiadiazole to synthesize a thiophene-fused-1,10-phenanthroline functionalized with a tert-butyl solubilizing side chains at the 4- and 7-positions.6

2.2.2 Monomer synthesis

The synthesis of the phenanthroline monomer started with the desired side chains. Starting from 2-decyl-tetradecanol (1), decyl-tetradecanoic acid (2) was obtained as a pale yellow solid in a 68% yield via an oxidation reaction with periodic acid (H5IO6) as oxidizing agent and pyridinium chlorochromate (PCC) as catalyst. The crude material was purified by column chromatography, which was followed by a full conversion into decyl-tetradecanoyl chloride (3) using oxalylchloride (Scheme 1). Infrared spectroscopy was used to verified the full conversion, showing a shift in C-O vibration from 1703 cm\(^{-1}\) to 1792 cm\(^{-1}\), representing a carboxylic acid and an acid chloride respectively. These long alkyl side chains were chosen in order to ensure a good solubility of the fused ring system afterwards.

![Scheme 1](image)

Scheme 1: Synthesis route towards the decyltetradecyl side chains. i) H5IO5, PCC, MeCN, r.t., overnight, ii) C2O2Cl2, dry DCM, dry DMF, 0°C, 3h.

The synthesis of the central [1,10]-phenantroline core (Scheme 2) was initiated with the reduction of 4,7-dibromobenzo[c]-1,2,5-thiadiazole (4) resulting in 3,6-dibromobenzene-1,2-diamine (5). Due to the air sensitivity of the diamine, diamine (5) was directly coupled with acid chloride (3) via a nucleophilic addition/elimination to obtain N,N’-(3,6-dibromo-1,2-phenylene)bis(2-hexyldecanamide) (6) as a pale yellow solid in 69% yield. After purification by column chromatography, both bromines were substituted with thiophenes via a Stille-coupling using 2-(tributylstannyl)thiophene resulting in a diamide (7). However, this diamide (7) was not obtained in a pure form, even after a three-step purification procedure. The product was purified by two column purification steps and a recrystallization from ethanol. Even though compound 7 was not obtained in a pure form, the synthesis pathway towards
the desired [1,10]-phenanthroline was continued by performing a Bischer-Napieralski cyclization. The reaction was monitored with thin layer chromatography (TLC) and nuclear magnetic resonance (NMR). After stirring overnight different spots on TLC were observed and the color of the expected product spot on TLC changed to blue. In the aromatic range of the NMR-spectrum two doublets at 7.72 ppm and 7.58 ppm and one singlet at 8.12 ppm had appeared. The doublets represent the two protons on each thiophene functionality and the singlet represents the two protons on the central benzene. After a total of 18 hours a brown sticky solid was obtained. Wang and coworkers (2016) reported an alkaline work up for the Bischer-Napieralski cyclization and column chromatography for purification. When the proposed work-up was applied on the crude mixture of the phenanthroline (8), the peaks at 7.58, 7.72 and 8.12 ppm in the NMR-spectrum were exchanged for one broad peak around 7.5 ppm. In contrast, the results from the matrix-assisted laser desorption/ionization (MALDI)-spectrum showed the presence of the phenanthroline core (8). A plausible explanation could be found in the stacking ability of the molecule because of its planar nature, however, high temperature NMR at 100 °C showed similar spectra. Further purification was attempted by recycling gel permeation chromatography (GPC). However, this effort was unsuccessful as only one peak was observed in the chromatogram, hence it was impossible to resolve the purification by recycle GPC.

Since the Bischer-Napieralski was only reported with moderated yields (40 %), this might imply that the reaction is strongly dependent on the reaction conditions. In this case the impurity of the diamide (7) might influence the Bischer-Napieralski cyclisation. In order to overcome the purification problems of the diamide (7), the synthesis pathway towards the phenanthroline product was changed (Scheme 3). Since the purification of the thiophene-substituted diamide (7) was challenging as a consequence of the long side chains, the
synthesis order represented in Scheme 3 was chosen. In this synthesis route the bromine-thiophene substitution already occurs in the first reaction step. The purification of the bithiophene-benzothiadiazole is less challenging compared to the purification of the diamide (7). The synthesis route started by substituting both bromines on the benzothiadiazole (4) with two thiophenes via a Stille-coupling, resulting in 4,7-di(thiophen-2-yl)benzo[c][1,2,5]-thiadiazole (10). This was followed by a similar reduction of the thiophene substituted benzothiadiazole (10) as in the first synthesis pathway using sodium borohydride ($\text{NaBH}_4$) as reducing agent. Also this 3,6-di(thiophen-2-yl)cyclohexa-3,5-diene-1,2-diamine (11) was directly reacted with the acid chloride (3) resulting in the diamide (12), which is structurally similar to the diamide (7) in Scheme 1. The crude product was purified via column chromatography to obtain the diamide (12) as a pale yellow solid in 46.3 % yield. A Bischer-Napieralski cyclisation was performed on the diamide (12) to obtain the phenanthroline derivative. A similar problem arose as for the cyclization of the diamide (7) obtained via the first proposed synthesis route represented in Scheme 1. After a basic work-up, the product peaks disappeared in the NMR. The alkaline work-up could be reversed by an acidic treatment resulting in the phenanthroline core (13), verified by MALDI and NMR. Hence, a neutral work-up was chosen leading to a successful synthesis of The phenanthroline derivative (13) in a 92% yield. In order to allow a Stille-polymerization, two bromines were introduced on the thiophenes. Since the phenanthroline was obtained as a waxy solid stannyl functionalities could not be introduced. Stannyl-functional groups have a poor stability and can only be purified via recrystallization, which is challenging for waxy solids. A variety of reaction conditions were tested in order to functionalize the phenanthroline core with a two bromines. However, only one reaction condition appeared to be promising. Approximately 70% conversion was obtained in using an excess of n-butyl lithium and tetrabromomethane (1:1). Although bis-brominated adduct was formed, its separation from mono-brominated adduct remains a challenge. The difficulty originates from the long side chains making the change in polarity upon bromination too low to result in a significant difference in retention factor in column chromatography. GPC was employed in an attempt to separate mono- and bis-adduct via recycling GPC. Unfortunately, the difference between both molecules was too small to resolve the purification by recycling GPC.

Although, the synthesis of the bis-adduct was proven by NMR, the mixture was unable to be purified. In order to address the impossible separation, the reaction needed to be pushed to full conversion. Unfortunately, pushing the reaction to full conversion failed; the maximum reached conversion point was the above mentioned 70%. Again the steric hindrance of the long side chains could be an explanation for this difficulty.
Scheme 3: Overview of the adapted synthesis pathway towards the desired phenanthroline derivative in order to ease the Bischer-Napieralski cyclisation. vii) 2-trisbutylstannyl, Pd$_2$(dba)$_3$, PPh$_3$, Toluene/DMF (9:1), 110 °C, overnight, ix) NaBH$_4$, EtOH, r.t., 3h, xi) Et$_3$N, THF, r.t., overnight, xi) P$_2$O$_5$, POCl$_3$, 110°, overnight, xii) BuLi, THF, -78°- r.t. 6u; 2. CBr$_4$, THF, -78°- r.t., overnight.

To address the problems with the bromination of the phenanthroline core (13), bromination was attempted in an earlier stage of the synthesis (Scheme 4). In this case the purification of the mono- and bis-adduct would be easier and there would be less steric hindrance to hinder the bromination. In this synthesis route the thiophene substituted benzothiadiazole (10) was synthesized via a Stille-coupling using dibromo-benzothiadiazolide (4) and 2-(tributylstannyl)thiophene. The bromination of dithiophene benzothiadiazole (10), resulted in an insoluble -dithiophene-benzothiadiazole derivative 15 hindering characterization of the molecule and further reactions towards the desired phenanthroline derivative.

Scheme 4: Overview of the further adapted synthesis route towards the desired phenanthroline in order to address the problems with bromination of compound 13. Xiii) 2-(trisbutyl)stannyl, Pd$_2$(dba)$_3$, PPh$_3$, toluene/DMF (9:1), 110 °C, overnight. xix) NBS, CHCl$_3$, 0°- r.t., overnight, xx) NaBH$_4$, EtOH, r.t., 3h.

In order to ease the synthesis and purification of compound 7 and 8 the same synthesis was performed in parallel with 2-hexyldecanoyl chloride instead of 2-decyltetradecanoyl chloride. The shorter side chains provide less steric hindrance and eases purification. This shorter side-chain containing acid chloride was synthesized via an analogous synthesis route as illustrated in Scheme 1. All intermediate molecules were obtained in moderate yields and the Bischer-Napieralski-cyclisation was successful. However, for the bromination of the hexyldecyl-phenanthroline derivative even less conversion was observed.
2.2.3 Polymer synthesis

The aim of the project was to polymerize 2,9-dibromo-4,7-di(pentadecan-7-yl)dithieno[3,2-c:2',3'-i][1,10]phenanthroline with a range of donor molecules via a Stille-polymerization. Stille-polymerization requires that one of both monomers possesses a dibromide functionality, whereas the other monomer bears two stannyl functional groups. In this case the bromination of phenanthroline (13) failed, excluding the possibility to continue the polymer synthesis via a Stille-polymerization. A solution to this problem was found in polymerizing the phenanthroline derivative (13) with a donor monomer via a direct (hetero)arylation polymerization (DHAP) as illustrated in Scheme 5. This direct-(hetero)arylation is advantageous over the Stille-polymerization as there is no necessity for a stannyl functionalized monomer which excludes the necessity to brominate the phenanthroline monomer (13). Thereby, this monomer (13) could be directly polymerized with a 5,5′-dibromo-2,2′-bithiophene. Although there is a wide variety of reaction conditions known for this type of polymerizations, only one condition was selected. The chosen reaction conditions were in literature used for the polymerization of a benzothiadiazole derivative. This reported derivative was the most similar compound to the phenanthroline derivative in this research. The reaction was performed in presence of an acid/base mixture of pivalic acid (PivOH) and potassium carbonate (K2CO3) with palladium acetate (Pd(OAc)2) as catalytic system in dimethylacetamide (DMAc). The reaction mixture became viscous after two days of stirring at 110°C and was precipitated in methanol. The palladium residue was removed from the polymer by an ethylenediaminetetraacetic acid (EDTA) treatment. The reaction mixture was cooled to room temperature and extracted with water and chloroform to remove the EDTA-residue. The organic layer was concentrated and precipitated in methanol to yield a copper-colored material with a metallic luster. This precipitate was purified by a soxhlet extraction using acetone, hexane, CH2Cl2 and CHCl3. Hexane was the most concentrated fraction, implying that low molecular weight molecules are mainly formed. This was verified by GPC as the molecular weight of the material was too low to be measured by GPC.

![Scheme 5: Overview of the DHAP reaction xiii) K2CO3, PivOH, Pd(OAc)2, DMAc, 110°C, 2 days.](image)
2.3 Conclusion and outlook

The synthesis of the bis-brominated phenanthroline monomer (14) was completed. Spectral data (NMR) and MALDI results indicated the formation of this monomer (14). However, due to the presence of the mono-adduct and the inability to separate both molecules using column chromatography or recycling GPC, the monomer was not obtained in a pure form. The monomer needs to be as pure as possible in order to get high molecular weights via a Stille-polymerization. The fabrication of photovoltaic devices was omitted as no high molecular weight polymers were obtained.

The obtained non-brominated phenanthroline derivative was used in a DHAP. This did not afford any polymer material. Consequently no photovoltaic devices have been made using the 4,7-di(tricosan-11-yl)dithieno[3,2-c:2′,3′-i][1,10]-phenanthroline monomer.

Next steps for this research could be the synthesis of a bis-brominated phenanthroline derivative with shorter side-chains, which could improve the purification. This monomer can afterwards be polymerized with a donor containing longer side chains in order to ensure good solubility. Another effort could be made, elongating the synthesis route proposed in Scheme 4 by synthesizing first a bis-TMS-adduct. This compound is soluble and hence allows further synthesis of the diamide and the phenanthroline derivative. These TMS functional groups can afterwards be substituted by bromines using N-Bromosuccinimide (NBS).
2.4 Materials and methods

2.3.1. General

Air-sensitive synthetic procedures were performed under an argon atmosphere, except for the synthesis of the carboxylic acid of the desired side chains. If not specified, commercial available solvents and reagents were used without extra purification. 4,7-dibromo-2,1,3-bezothiadiazole was purchased from TCI Europe N.V. Decyltetradecan-2-ol and oxalylchloride were purchased from Sigma Aldrich co.

$^1$H-NMR and $^{13}$C-NMR spectra were recorded on a Bruker 400MHz ($^1$H 400 MHz, $^{13}$C 100 MHz) and a high temperature 500 MHz Varian Unit Inova ($^1$H 500 MHz). Deuterated chloroform (CDCl$_3$) and deuterated TCE were used as solvent with tetramethylsilane (TMS) as internal standard. Chemical shift are expressed in ppm with respect to TMS at 0 ppm.

UV/vis absorption spectra were recorded on a Perkin Elmer Lambda 1050 spectrophotometer. Optical absorption spectra in solution were measured from chloroform in a quartz cuvet, while spectra in solid state film were measured from a spin coated sample layer (6mg/mL chloroform) at 1500 rpm on a glass substrate. The glass substrates were cleaned with acetone and isopropanol after which they were treated with UV-ozone for 30 min in a UV-ozone photoreactor PR-100. Infrared spectroscopy was performed on a Perkin Elmer Two spectrometer. Matrix assisted laser desorption ionization time of flight (MALDI-TOF) was measured on a Bruker Autoflex Speed spectrometer. Gas-chromatography mass-spectroscopy (GC-MS) was measured on a Shimadzu gas chromatograph fitted with a Phenomenex Zebron column (30m, 0.25 mm internal diameter, 0.25 μm film thickness).

2.3.2 Monomer synthesis

2-decyltetradecanoic acid (2): a mixture of periodic acid (H$_5$IO$_6$) (14.06 g, 6.17 mmol) in acetonitrile (221 mL) was stirred vigorously at room temperature for 15 minutes. 2-decyltetradecan-1-ol (10.00 g, 2.82 mmol) was added at 0°C followed by a two-step addition of a solution of pyridinium chlorochromate (PCC) (0.12 g, 0.56 mmol) in acetonitrile (2 x 13 mL). After overnight stirring at room temperature, the mixture was diluted with ethyl acetate, washed with brine, aqueous NaHSO$_3$ solution and brine and dried over magnesium sulfate (MgSO$_4$). After filtration and removal of the solvent, the crude product was purified by flash chromatography (silica, 50-100% CH$_2$Cl$_2$/heptane), yielding 3 as a white solid (2.05 g, 19.7%). $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm): 0.88 (t, 8.0 Hz, 6H, CH$_3$), 1.26 (s, 36H), 1.46 (m, 2H), 1.61 (m, 2H), 2.33 (m, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz), δ (ppm): 14.08, 22.70, 27.39, 29.36, 31.94, 32.19, 45.66, 183.27.
2-decyltetradecanoyl chloride (3): Oxalylchloride (1.4 mL, 19.5 mmol) was added to a solution of decyltetradecanoic acid (2) (2.00 g, 6.7 mmol) in dry dichloromethane (8.7 mL) at 0°C followed by addition of 2 drops of dry N,N-dimethylformamide (DMF). After stirring for 3 h at room temperature the mixture was evaporated to dryness yielding 3 as a yellow-brown oil (1.53 g, quantitative). Infrared spectroscopy: 1792 cm⁻¹ (C=O Stretch).

3,6-dibromobenzene-1,2-diamine (5): Sodium borohydride (1.54 g, 40.80 mmol) was added portion-wise to a stirred solution of 4,7-dibromo-2,1,3-benzothiadiazole (4) (1.2 g, 4.08 mmol) in ethanol (70.0 mL) at 0°C under argon. After stirring for 10 minutes at 0°C, the reaction mixture was warmed to room temperature and left overnight. After being cooled to 0°C, the reaction mixture was poured into water, extracted with diethylether and washed with brine and dried over anhydrous MgSO₄ respectively. After evaporation to dryness, the crude product was purified by flash chromatography (silica, 4:1 CH₂Cl₂:heptane), yielding 5 as a white solid (0.99 g, 91%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 3.89 (s, 4H, NH₂), 6.84 (s, 2H, ArH). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): 109.63, 123.27, 133.73. MALDI-TOF, m/z: calcd, 265.9; found, 266.12.

N,N’-(3,6-dibromo-1,2-phenylene)bis(2-decyltetradecanamide) (6): A solution of 3 (1.40 g, 3.62 mmol) in dry tetrahydrofuran (THF) (8.7 mL) was added dropwise to a solution of 5 (0.44 g, 1.65 mmol) in a dry THF/Et₃N (4 mL/0.26 mL) solution at 0°C. After stirring for 16 h, the reaction mixture was poured into water (25 mL) and extracted with CH₂Cl₂. Afterwards, the organic extracts were dried over anhydrous MgSO₄ and evaporated to dryness. The crude product was then purified by column chromatography (silica, 2:3 heptane:CH₂Cl₂), yielding 6 as a pale yellow wax-like solid (1.1 g, 69%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 0.86 (t, 16H, CH₃), 2.27 (m, 2H), 1.26 (m, 65H), 1.58 (m, 4H), 1.68 (m, 8H) 7.41 (s, 2H, ArH), 7.78 (s, 2H, NH). ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): 14.11, 22.68, 27.54, 29.35, 29.8, 31.89, 32.35, 45.35, 120.74, 131.60, 132.93, 174.86. MALDI-TOF, m/z: calcd, 967.2; found, 644.0, 989.6 [M + Na⁺].
4,7-substituted-1,10-phenantroline derivatives as acceptor in copolymer donors

N,N’-(3,6-di(thiophen-2-yl)-1,2-phenylene)bis(2-decyltetradecanamide) (7): A schlenk tube was charged with 6 (0.20 g, 2.07 mmol), tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$) (2.84 mg, 3.10 µmol) and triphenylphosphine (PPh$_3$) (3.30 mg, 12.40 µmol) and degassed followed by the addition of 2-(tributylstannyl)thiophene. A solvent mixture toluene:DMF (9:1) (4 mL) was added and the reaction mixture was degassed by bubbling with argon for 15 minutes. The mixture was heated up to 115°C and stirred overnight. After cooling to room temperature, the mixture was diluted with CH$_2$Cl$_2$, washed with brine, dried over MgSO$_4$ and evaporated to dryness. The crude product was then purified by column chromatography (silica, 1:3 heptane:CH$_2$Cl$_2$) and recrystallized from ethanol followed by a second column chromatography (silica, 1:6 heptane:ethylacetate) for purification yielding a slightly contaminated compound 7 as a white solid. $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm): 7.07, (m, 2H, ArH), 7.14 (dd, 2H, ArH), 7.35 (dd, 2H, ArH), 7.37 (s, 2H, ArH), 7.81 (s, 2H, NH). $^{13}$C NMR (CDCl$_3$, 100 MHz), δ (ppm): 14.13, 22.70, 27.45, 29.38, 29.89, 31.94, 47.65, 126.22, 126.92, 127.24, 130.75, 131.97, 139.78, 174.82. MALDI-TOF, m/z: calcd, 973.6; found, 995.7 [M + Na$^+$], 1011 [M + K$^+$], 623.4.

MALDI-TOF, m/z: calcd, 973.65; found, 605.40, 623.42, 995.6 [M + Na$^+$], 1011.7 [M + K$^+$], 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (10): A schlenk flask was charged with 4,7-dibromo-2,1,3-bezothiadiazole (4) (2 g, 6.8 mmol), Pd$_2$(dba)$_3$ (185 mg, 0.20 mmol) and PPh$_3$ (217 mg, 0.81 mmol) was degassed followed by the addition of 2-(tributylstannyl)thiophene. A solvent mixture toluene:DMF (9:1) (40mL) was added and the reaction mixture was degassed by bubbling with argon. The reaction mixture was heated up to 115°C and stirred overnight. After cooling to room temperature the crude was passed over a silica plug, followed by a recrystallization from ethanol to yield compound 10 as orange crystals (2.03 g, 99%). $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm): 7.22 (m, 2H, ArH), 7.46 (dd, 2H, ArH), 7.88 (s, 2H, ArH), 8.12 (dd, 2H, ArH). $^{13}$C NMR (CDCl$_3$, 100 MHz), δ (ppm): 125.79, 126.02, 126.80, 127.51, 128.01, 139.35, 152.65.

N,N’-(3,6-di(thiophen-2-yl)-1,2-phenylene)bis(2-decyltetradecanamide) (12): Sodium borohydride (2.52 g, 6.66 mmol) was added portion-wise to a stirred solution of 10 (2.00 g, 66.60 mmol) in ethanol (114.20 mL) at 0°C under an argon atmosphere. After stirring for 10 minutes at 0°C, warmed to room
temperature and stirred for 15 minutes and cobalt(II)chloride (CoCl$_2$) (0.39 g, 1.33 mmol) was added. After stirring for 30 minutes at room temperature, the black precipitate was filtered off. The filtrate was then poured into water, extracted with diethylether and washed with brine and dried over anhydrous MgSO$_4$. After evaporation to dryness, the pale yellow solid (11) (1.5g, 83%) was dissolved in dry THF (25 mL) and Et$_3$N (3.25 mL) followed by the addition of a dry solution of the acid chloride (3) in dry THF (50 mL) at 0°C. The obtained mixture was poured into water and extracted with CH$_2$Cl$_2$, and brine and dried over anhydrous Mg$_2$SO$_4$. The organic layers were evaporated to dryness and purified by a two-step column chromatography (silica, 4:2 CH$_2$Cl$_2$:heptane and 6:1 heptane:EtOAc) to yield compound 12 as a pale yellow solid (2.48g, 46.3%). $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm): 0.88 (m, 12H, CH$_3$), 1.26 (s, 36H, CH$_2$), 1.54 (m, 4H, CH$_2$), 2.11 (m, 2H, CH), 7.05 (m, 2H, ArH), 7.14 (dd, 2H, ArH), 7.35 (dd, 2H, ArH), 7.37 (s, 2H, ArH), 7.83 (s, 2H, NH). $^{13}$C NMR (CDCl$_3$, 100 MHz), δ (ppm): 14.13, 22.73, 27.48, 29.77, 29.07, 31.97, 47.66, 126.23, 126.95, 127.25, 129.12, 130.83, 132.03, 139.81, 174.84. MALDI-TOF, m/z: calcd, 973,65; found, 973,7 [M], 995,6 [M + Na$^+$], 1011 [M + K$^+$].

4,7-di(tricosan-11-yl)dithieno[3,2-c:2',3'-i][1,10]phenanthroline (13): A solution of 7 (0.14 g, 1.48 mmol), phosphorous pentoxide (P$_2$O$_5$) (0.43 g, 3.04 mmol) and phosphorous(V)oxychloride (POCl$_3$) (4.1 ml) was overnight stirred at 100°C. Afterwards, the reaction mixture was concentrated and the crude product was diluted with CH$_2$Cl$_2$ followed by a dropwise addition of water. This mixture was then extracted with CH$_2$Cl$_2$, water and dried over Mg$_2$SO$_4$. After this extraction, the product was purified by column chromatography (silica, CH$_2$Cl$_2$:5%Et$_3$N) resulting in compound 13 as a brown sticky solid (2.50 g, 90%). $^1$H NMR (400 MHz, CDCl$_3$), δ (ppm): 0.84 (m, 16H, CH$_3$), 1.18 (m, 18H, CH$_2$), 1.87 (m, 4H, CH$_2$), 2.28 (m, 4H, CH$_2$), 3.47 (m, 2H, CH), 7.58, (d, 2H, ArH), 7.72 (d, 2H, ArH), 8.12 (s, 2H, ArH). $^{13}$C NMR (CDCl$_3$, 100 MHz), δ (ppm): 14.12, 22.70, 28.00, 29.65, 31.92, 35.16, 45.84, 121.83, 122.53, 123.47, 125.78, 134.25, 141.60, 145.26, 161.31. MALDI-TOF, m/z: calcd, 937, 6; found, 937,7 [M].
Synthesis pathways towards the hexyldecyl derivatives are analogous to the pathways described in this chapter:

**2-hexyldecanoic chloride**: The same procedure as for 2-decyltetradecanoyl chloride (3) was used but with oxalylchloride (2.15 g, 17.00 mmol), a solution of 2-hexyldecanoic acid (1.50 g, 5.85 mmol) in dry dichloromethane (8.7 mL). The product was obtained as a yellow oil (1.5 g, 66%).

**N,N’-(3,6-dibromo-1,2-phenylene)bis(2-hexyldecanamide)**: The same procedure as for the N,N’-(3,6-dibromo-1,2-phenylene)bis(2-decyltetradecanamide) (6) was used but with a solution of 2-hexyldecanoic chloride (1.50 g, 3.87 mmol) in dry THF (9 mL) and a solution of 3,6-dibromobenzene-1,2-diamine (0.41 g, 1.55 mmol) in a dry THF/Et₃N (4 mL/0.68 mL). The product was obtained as a colorless waxy solid (60.0 mg, 16%).

**N,N’-(3,6-di(thiophen-2-yl)-1,2-phenylene)bis(2-hexyldecanamide)**: The same procedure as for the N,N’-(3,6-di(thiophen-2-yl)-1,2-phenylene)bis(2-decyl-tetradecanamide) (7) was used but with N,N’-(3,6-dibromo-1,2-phenylene)bis(2-hexyldecanamide) (0.17 g, 2.28 mmol), 2-(tributylstannyl)thiophene (0.18 g, 0.50 mmol) and tris(dibenzylideneacetone)-dipalladium(0) (3.14 mg, 3.43 µmol) and triphenylphosphine (3.60 mg, 1.37 µmol) as catalyst. A solvent mixture toluene:DMF (9:1) (4 mL).

**4,7-di(pentadecan-7-yl)dithieno[3,2-c:2’,3’-i][1,10]phenanthroline**: The same procedure as for the 4,7-di(tricosan-11-yl)dithieno[3,2-c:2’,3’-i][1,10]phenanthroline was used but with a solution of N,N’-(3,6-di(thiophen-2-yl)-1,2-phenylene)bis(2-hexyldecanamide) (0.1 g, 0.13 mmol), phosphorous pentoxide (P₂O₅) (0.39 g, 2.76 mmol) and phosphorous(V)oxychloride (POCl₃) (3 ml).
2.3.3 Polymer Synthesis

5,5′-dibromo-2,2′-bithiophene (18) was recrystallized from methanol prior to use. A schlenk tube was charged with 13 (0.1 g, 1.0 mmol), 18 (34.6 mg, 1.0 mmol), Pd(OAc)$_2$ (1.1 mg, 5.0 mol%), PivOH (0.3 mg, 3.2 mol%), K$_2$CO$_3$ (2.9 mg, 0.21 mol%) and degassed with argon. DMAc (2 mL) was added and the mixture was degassed by bubbling with argon. The reaction mixture was heated to 110° and left stirring for two days. Next, the viscous mixture was cooled down to room temperature and precipitated in methanol. The precipitate was filtered off and diluted with chloroform. EDTA (1 g) was added and the mixture was refluxed for 1 h. After cooling down to room temperature, the mixture was poured into water and extracted with chloroform. The organic layers were concentrated and precipitated in methanol and the precipitate was purified via a soxhlet extraction (acetone, hexane, CH$_2$Cl$_2$ and chloroform). The hexane fraction yielded a copper colored product with a metallic luster. (0.02 mmol, 30 mg, 27% Mn: undefined).
2.5 References


Abstract

Two wide band gap polymers, PDCDTBT-OD and PDCDTBT-HD were synthesized, characterized and implemented in photovoltaic devices. Only single junction devices were fabricated in this chapter, however, wide band gap polymers are especially applicable in tandem photovoltaic devices. The less soluble polymer, PDCDTBT-HD, lead to the highest performance in photovoltaic devices, however, the results were irreproducible since the active layers were de-wetted and thus the performance of the device was dependent on the local wetting of the active layer. Devices processed from 1% DIO in chloroform lead to a maximal efficiency of 6.2%. Inverted devices were also fabricated, however no higher performances were obtained although the results were more reproducible than for the conventional devices.
3.1 Introduction

Polymer photovoltaics have attracted great interest due to their flexibility, light-weight and low-cost characteristics.\(^1\) Properly use of molecular engineering and device optimization can tremendously improve the device performance.\(^2\) Mostly, donor-acceptor conjugated polymers are used as donor polymer in the active layer. This type of polymers has the advantage of being highly tunable with respect to the energy levels of the polymer. The tunability of the energy levels eases device optimization as the LUMO-LUMO offset and \(V_{oc}\) can indirectly be controlled.\(^3,4\)

Benzothiadiazole is one of the most widely used acceptor monomers in conjugated polymers. Benzothiadiazole is a strong acceptor which was firstly used in a polymersynthesis by Yamamoto and coworkers (1993) in order to synthesize an accepting polymer.\(^5\) Two years later, in 1995, this benzothiadiazole was coupled with two thiophenes by Yamashita and coworkers, resulting in benzothiadiazole- bithiophene.\(^6\) This monomer unit was afterwards widely used as acceptor monomer in conjugated donor-acceptor molecules.

Already many different polymers have been investigated containing benzothiadiazole-bithiophene in the backbone of the polymer, however, still new polymers are discovered and optimized. In combination with a bithiophene donor moiety the BT-bithiophene results in narrow band gap polymer.\(^7\) Upon modification of the side chains on the bithiophene donor moiety, the band gap of the conjugated polymer can be tuned.

In this chapter the polymerization of poly(dicarboxylic)bithiophene-dithiophene benzothiadiazole was described. The synthesis was performed using the octyldecyl carboxylate and hexyldecyl carboylate resulting in two polymers which were characterized for physical and electrochemical properties as well as for photovoltaic properties.
3.2 Results and discussion

3.2.1 Synthesis
PDCDTBT-OD was synthesized by polymerizing bis(2-octyldodecyl) 5,5’-dibromo-[2,2’-bithiophene]-4,4’-dicarboxylate as electron donating monomer with 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c]-[1,2,5]thiadiazole as electron acceptor via a Stille-polymerization. The same reaction is performed using the hexyldecyl derivative of the donor moiety resulting in PDCDTBT-HD. Both monomers were synthesized by Ruurd Heuvel.

![Figure 14: Schematic representation of the PDCDTBT polymer. R represents the alkyl chain which can either represent octyldodecyl (PDCDTBT-OD) or hexyldecyl (PDCDTBT-HD).](image)

3.2.2 Polymer synthesis
PDCDTBT-OD and PDCDTBT-HD are synthesized via the same polymerization route. Equimolar amounts of the monomers are polymerized via a Stille-polymerization to obtain a copolymer of an electron donating and electron accepting moiety.

Both reaction mixtures became viscous overnight, indicating the presence of higher molecular weight materials showing a lower solubility. After two days of polymerization the reaction mixture was precipitated in methanol after which the blue precipitate was treated with EDTA. The EDTA treatment was performed in chloroform and TCE solutions for PDCDTBT-OD and PDCDTBT-HD respectively. The EDTA mixture was subsequently poured into water and extracted with chloroform followed by a volume reduction and precipitation in methanol. Soxhlet extraction resulted in a concentrated CH$_2$Cl$_2$ fraction for the polymer containing long side chains and a concentrated chloroform fraction was obtained for its hexyldecyl derivative. The concentrated solutions were precipitated in methanol and two blue colored solids were obtained. However, PDCDTBT-OD becomes purple in solution while PDCDTBT-HD retains its blue color. This implies that, since the polymers appears to be blue in an aggregated film, PDCDTBT-HD shows aggregation in solution as well.
3.2.3 Physical properties

The UV-vis absorption spectra of PDCDTBT-OD and PDCDTBT-HD from chloroform solution and as thin film on a glass substrate were investigated as illustrated in Figure 15.

![Absorption spectra](image)

**Figure 15:** Absorption spectra of the PDCDTBT-OD and PDCDTBT-HD in a) chloroform solution and b) solid state films spin coated on a glass substrate.

In chloroform solution, both polymers show an intense absorption in the range of 400-700 nm with maximal absorption around 560 nm and 630 nm for the PDCDTBT-OD and PDCDTBT-HD respectively. This red-shift can be attributed to the lower solubility of the hexyldecyl derivative and its tendency to aggregate in solution. In film, both polymers show a red-shifted absorption with respect to the solution spectra, corresponding to aggregation of the molecules. Since both polymers aggregate similarly in film, the spectra measured from thin film are almost superimposed. For each polymer a shoulder in the absorption spectrum is observed, which can be attributed to the aggregation of the polymer chains. The optical band gap can be calculated from the absorption onset in film, indicating a similar band gap of 1.64 eV. The results are summarized in Table 1.

**Table 1:** Optical properties of PDCDTBT-OD and PDCDTBT-HD.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Chloroform solution</th>
<th>Thin film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\lambda_{\text{onset}}$ (nm)</td>
</tr>
<tr>
<td>PDCDTBT-OD</td>
<td>560</td>
<td>715</td>
</tr>
<tr>
<td>PDCDTBT-HD</td>
<td>640</td>
<td>720</td>
</tr>
</tbody>
</table>

3.2.4 Electrochemical properties

The electrochemical properties of both polymers were investigated by cyclic voltammetry (Figure 16).
The polymers were measured as a film on full ITO glass substrates in a tetrabutylammonium hexafluorophosphate acetonitrile solution at a scan rate of 0.2 V/s. Both polymers produced a similar oxidation and reduction potential and hence the driving force for charge separation based on the LUMO-LUMO offset between the polymers and [70]PCBM is equal. The HOMO and LUMO energy levels are calculated using equation 3.1 and 3.2 respectively. The results are shown in Table 2. The band gaps are slightly different than the optical band gap in chloroform (Table 1). This difference can be attributed to the fact that in UV-vis spectroscopy one electron is excited whereas in cyclic voltammetry the molecule is charged.

\[
E_{HOMO} = -e(E_{ox} + 5.23) \quad \text{(eq. 3.1)}
\]

\[
E_{LUMO} = -e(E_{red} + 5.23) \quad \text{(eq. 3.2)}
\]

**Table 2: Electrochemical properties of PDCDTBT-OD and PDCDTBT-HD.**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(E_{red} \text{ (V)}^a)</th>
<th>(E_{ox} \text{ (V)}^a)</th>
<th>(E^\text{CV} \text{ (eV)})</th>
<th>(E_{LUMO} \text{ (eV)}^b)</th>
<th>(E_{HOMO} \text{ (eV)}^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDCDTBT-OD</td>
<td>-1.67</td>
<td>0.367</td>
<td>2.03</td>
<td>-3.56</td>
<td>-5.59</td>
</tr>
<tr>
<td>PDCDTBT-HD</td>
<td>-1.67</td>
<td>0.363</td>
<td>2.04</td>
<td>-3.56</td>
<td>-5.60</td>
</tr>
</tbody>
</table>

\(a) \text{ versus Fc/Fc}^+ \text{ b) determined using a work-function value of -5.23 eV for Fc/Fc}^+

### 3.2.5 Photovoltaic properties

The photovoltaic properties were investigated by using the conventional structure glass/ITO/PEDOT:PSS/polymer/[70]PCBM/LiF/Al, unless stated differently. The polymers are both readily soluble in common solvents like chloroform. Active layers were optimized for different solvent-co-solvent systems and donor:acceptor ratios. For PDCDTBT-HD also a concentration dependence was tested and the morphology of the optimized cells were investigated using TEM.
3.2.5.1 PDCDTBT-OD

Solvent optimization

The photovoltaic performance was first investigated by testing a polymer blend with [70]PCBM in a 1:1.5 \( w_{\text{donor}}:w_{\text{acceptor}} \) ratio, unless stated otherwise. Different solvent systems were used going from pure chloroform and chlorobenzene to a combination with 10 v/v% diphenyl ether or 1,8-diodo-octane as co-solvent. A total concentration of 15mg/mL, i.e. 6 mg/mL polymer and 9 mg/mL [70]PCBM, was used for all systems. Uniform layers of approximately 80 nm thickness were obtained for all solvent systems. The J-V characteristic are shown in Figure 17.

![Figure 17](image1)

Figure 17: J-V curves for PDCDTBT-OD devices processed from a) pure solvents and b) solvent-co-solvent mixtures.

PDCDTBT-OD is highly soluble in chloroform which enhances the device processing, however, high solubility of the polymer can result in large polymer:PCBM domains in the active layer. This hinders the charge separation and transport which lowers the \( J_{\text{sc}} \) and hence the device performance. Upon addition of a co-solvent the solubility of the polymer is lowered and hence smaller domains are obtained resulting in a better device performance. The solubility of PDCDTBT-OD is lower in chlorobenzene. However, upon changing the solvent from chloroform to chlorobenzene the current decreased approximately 40% (Figure 17a). This decrease could be attributed to the fact that the solubility in chlorobenzene is too low in order to form the ideal size of polymer/PCBM domain sizes. The \( V_{\text{oc}} \) only slightly changes since it is mainly dependent on the energy levels of the polymer-PCBM blend and the blend is similar for all measurements. Also the FF does not change significantly upon changing the solvent. As expected, the addition of a co-solvent results in a \( J_{\text{sc}} \) which is more than double of the \( J_{\text{sc}} \) given for the active layer processed from a pure solvent (Figure 17b).

A decrease in current leading to a lower PCE was observed when the solvent-co-solvent ratio was varied (Figure 18a). An optimum in photovoltaic characteristics was found for the
device processed from 2% DPE in chloroform resulting in a PCE of 4.84%. As can be seen from Figure 18b, the maximum reached EQE is 51%. Both the polymer and [70]PCBM have a contribution to the EQE.

**Table 3:** Photovoltaic characteristics of PDCDTBT-OD processed from different solutions and a 1:1.5 donor – acceptor ratio.

<table>
<thead>
<tr>
<th>Solvent system</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>2.81</td>
<td>0.82</td>
<td>0.56</td>
<td>1.28</td>
</tr>
<tr>
<td>CB</td>
<td>1.96</td>
<td>0.71</td>
<td>0.53</td>
<td>0.74</td>
</tr>
<tr>
<td>CF 2% DIO</td>
<td>7.17</td>
<td>0.79</td>
<td>0.69</td>
<td>3.89</td>
</tr>
<tr>
<td>CF 2% DPE</td>
<td>8.12</td>
<td>0.79</td>
<td>0.69</td>
<td>4.43</td>
</tr>
<tr>
<td>CB 10% DIO</td>
<td>5.26</td>
<td>0.74</td>
<td>0.65</td>
<td>2.52</td>
</tr>
</tbody>
</table>

**Figure 18:** a) $J$-$V$ curves for PDCDTBT-OD processed from chloroform with different co-solvent concentrations b) EQE for the photovoltaic device processed from 2% DPE in chloroform.

**Thickness optimization**

For the photovoltaic device processed from 2% DPE in chloroform a FF of around 0.7 was obtained. The FF is lowered upon increasing the thickness of the active layer, however, more light can be absorbed and hence a higher current can be generated which result in a better device performance. For the cells processed from 2% DPE in chloroform, the thickness of the active layer was varied from around 95 nm to around 190 nm.

The 190 nm thick active layer showed a sharp decrease in current, implying that charge recombination was the dominating factor. In contrast, the devices fabricated with active layers of 95 nm or 120 nm showed an increase in $J_{sc}$ compared to the 80 nm reference device. Despite this increase in current, no increase in PCE was observed. The performance of the device was limited by the FF, which was lowered upon increasing the layer thickness. Hence, the best photovoltaic characteristics were obtained for the device processed from 2%
DPE in chloroform. The J-V curves are shown in Figure 19 and photovoltaic device characteristics are summarized in Table 4.

**Table 4**: Photovoltaic characteristics of PDCDTBT-OD processed from a 2% DPE in chloroform solution with different active layer thicknesses and a 1:1.5 donor-acceptor ratio.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>7.90</td>
<td>0.73</td>
<td>0.61</td>
<td>3.50</td>
</tr>
<tr>
<td>120</td>
<td>8.57</td>
<td>0.74</td>
<td>0.64</td>
<td>3.97</td>
</tr>
<tr>
<td>95</td>
<td>8.78</td>
<td>0.74</td>
<td>0.66</td>
<td>4.26</td>
</tr>
<tr>
<td>80</td>
<td>8.12</td>
<td>0.79</td>
<td>0.69</td>
<td>4.43</td>
</tr>
</tbody>
</table>

**Figure 19**: J-V curves for PDCDTBT-OD processed from a 2% DPE in chloroform solution with different thicknesses.

*Donor-acceptor ratio optimization*

Also the donor:acceptor ratio has an influence on the device performance. A higher amount of PCBM in the active layer result in an increase the FF since carrier transport is enhanced. On the other hand, the absorption coefficient of PCBM is way lower than for the donor polymer, which limits the absorption of photons and hence lowers the current generation. The donor:acceptor ratio was varied between 1:1 and 1:2 for a photovoltaic device processed from 2% DPE in chloroform. The results were also compared to the 1:2.5 donor:acceptor ratio and are illustrated in Table 5. No clear trend was observed. However, compared to 1:2.5 ratio the current is significantly larger. This can be attributed to the loss in absorption due to the lower absorption coefficient of PCBM.
Table 5: Photovoltaic characteristics for PDCDTBT-OD processed from a 2% DPE in chloroform solution with different donor:acceptor ratios.

<table>
<thead>
<tr>
<th>D:A ratio</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>6.88</td>
<td>0.74</td>
<td>0.59</td>
<td>3.01</td>
</tr>
<tr>
<td>1:1.25</td>
<td>6.87</td>
<td>0.75</td>
<td>0.59</td>
<td>3.07</td>
</tr>
<tr>
<td>1:1.5</td>
<td>6.9</td>
<td>0.75</td>
<td>0.59</td>
<td>3.05</td>
</tr>
<tr>
<td>1:1.75</td>
<td>6.31</td>
<td>0.74</td>
<td>0.51</td>
<td>2.39</td>
</tr>
<tr>
<td>1:2</td>
<td>6.64</td>
<td>0.76</td>
<td>0.58</td>
<td>2.93</td>
</tr>
<tr>
<td>1:2.5</td>
<td>4.23</td>
<td>0.77</td>
<td>0.61</td>
<td>1.98</td>
</tr>
</tbody>
</table>

3.2.5.1 PDCDTBT-HD

Solvent optimization

The photovoltaic performance was investigated for PDCDTBT-HD by testing a polymer blend with [70]PCBM in a 1:1.5 w\textsubscript{donor}/w\textsubscript{acceptor} ratio. The same solvent-co-solvent mixtures were tested and significantly different results were obtained. This polymer was expected to be more crystalline as a result of the shorter side chains and hence a lower solubility. Higher crystalline materials usually show higher carrier mobility, resulting in higher J\textsubscript{sc}’s and hence higher PCE’s. Comparison of the photovoltaic characteristics of both PDCDTBT-OD and PDCDTBT-HD processed from chloroform confirmed the increased current generation, which was 21% higher for PDCDTBT-HD.

For the photovoltaic devices processed from chloroform as main solvent, uniform active layers were obtained except for layers processed from solvent systems containing 10% co-solvent. De-wetting of the layers was observed. This resulted in a flower-like structure (Figure 20). As a consequence of the irregularity the devices showed a poor performance.

Figure 20 non-uniform layer spin coated from a 10% co-solvent mixture with chloroform.

Chloroform was used in combination with DPE or DIO as co-solvent in different ratios. DPE turned out to be the best co-solvent in combination with chloroform. The best results were obtained for the device processed from a 1% DPE in chloroform solvent-co-solvent mixture with a PCE of 4.76%. Upon changing the amount of co-solvent, an optimum in Jsc was
obtained for a 1% DPE in chloroform solvent system. The J-V curve for the devices are shown in Figure 21 and the photovoltaic characteristics are summarized in Table 6.

![Figure 21: J-V curves for the photovoltaic devices processed from PDCDTBT-HD different solvent-co-solvent mixtures. a) the results obtained for chloroform as main solvent in combination with different co-solvents, b) different ratios of chloroform and DPE resulted in the best performance for 2% DPE in chloroform.](image)

**Table 6**: Photovoltaic characteristics of PDCDTBT-HD processed from different solvent systems and a 1:1.5 donor-acceptor ratio.

<table>
<thead>
<tr>
<th>Solvent system</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>3.36</td>
<td>0.81</td>
<td>0.53</td>
<td>1.56</td>
</tr>
<tr>
<td>CF 1% DIO</td>
<td>9.40</td>
<td>0.76</td>
<td>0.63</td>
<td>4.47</td>
</tr>
<tr>
<td>CF 1% DPE</td>
<td>9.92</td>
<td>0.76</td>
<td>0.63</td>
<td>4.76</td>
</tr>
<tr>
<td>CF 2% DPE</td>
<td>10.30</td>
<td>0.74</td>
<td>0.62</td>
<td>4.75</td>
</tr>
<tr>
<td>CF 5% DPE</td>
<td>8.55</td>
<td>0.71</td>
<td>0.54</td>
<td>3.29</td>
</tr>
</tbody>
</table>

Upon changing the main solvent from chloroform to chlorobenzene, all layers appeared to be de-wetted. Even with hot spin coating at 90°C of the active layer non-uniform layers were obtained, except for the layers spin coated from 10% DPE of DIO in chlorobenzene. As a consequence, the obtained photovoltaic characteristics were not reproducible. Despite the irreproducibility, the obtained result has shown that there is a potential to reach higher efficiencies than 6%. In order to overcome the problems with spin coating, the concentration was lowered from 15 mg/mL to 10 mg/mL, i.e. 4 mg/mL PDCDTBT-HD and 6 mg/mL [70]PCBM. The obtained active layers were still de-wetted. Another attempt was made to avoid de-wetting by exchanging the PEDOT:PSS layer for molybdenum oxide ($\text{MoO}_3$). Unfortunately, de-wetting of the layers was still observed.

Ortho-dichlorobenzene was also tested as main solvent for the PDCDTBT-HD in combination with DIO, since DIO showed the most reasonable results in combination with chlorobenzene.
Uniform layers were obtained by spin coating a hot solution (90°C) onto a cold substrate using a cold pipet. Despite the uniformity of the layers low PCE’s were obtained. This can be attributed to the thickness which was only 60 nm.

Inverted geometry combined with donor:acceptor ratio optimization

Inverted geometry photovoltaic devices were fabricated for the PDCDTBT-HD using three main solvents: chloroform, chlorobenzene and ortho-dichlorobenzene. 1% of DPE was used as co-solvent in combination with chloroform whereas 1% DIO and 5 % DIO were combined with chlorobenzene and ortho-dichlorobenzene respectively. For each solvent, three different donor:acceptor ratios were tested. A 1:1.5 donor acceptor ratio resulted for all solvent systems in an optimum in device performance. For chlorobenzene the J-V curves are illustrated in Figure 22b. Although non-uniform layer were obtained for active layers processed from chlorobenzene, these devices showed the best photovoltaic characteristics. The non-uniformity of the layers can also result in high leakage when the active area is located on a locally thinner layer, which is the case for the devices processed from chlorobenzene with a 1:1.5 donor: acceptor ratio. Even in the conventional geometry, it was observed that chlorobenzene resulted in the best photovoltaic characteristics. However, the results obtained with the inverted geometry showed to be more reproducible as the characteristics were similar for each cell measured from one substrate despite the non-uniformity of the layers. The photovoltaic characteristics for all solvent systems are summarized in Table 7.

Figure 22: Photovoltaic characteristics for inverted configuration solar cells with a 1:1.5 PDCDTBT-HD: PCBM ratio processed from different solvent systems.
Table 7: Photovoltaic characteristics of PDCDTBT-HD processed from different solvent systems and different donor:acceptor ratios (D:A).

<table>
<thead>
<tr>
<th>Solvent system</th>
<th>D:A</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF 1% DPE</td>
<td>1:1</td>
<td>10.40</td>
<td>0.65</td>
<td>0.44</td>
<td>2.98</td>
</tr>
<tr>
<td>CF 1% DPE</td>
<td>1:1.5</td>
<td>10.1</td>
<td>0.72</td>
<td>0.57</td>
<td>4.16</td>
</tr>
<tr>
<td>CF 1% DPE</td>
<td>1:2</td>
<td>9.62</td>
<td>0.71</td>
<td>0.56</td>
<td>3.82</td>
</tr>
<tr>
<td>CB 1% DIO</td>
<td>1:1.5</td>
<td>9.62</td>
<td>0.71</td>
<td>0.68</td>
<td>4.62</td>
</tr>
<tr>
<td>o-DBC 5% DIO</td>
<td>1:1.5</td>
<td>6.52</td>
<td>0.68</td>
<td>0.68</td>
<td>3.02</td>
</tr>
</tbody>
</table>

Morphology

The morphology of the active layers for both polymers PDCDTBT-OD and PDCDTBT-HD was studied using transmission electron microscopy (TEM). The morphology study can explain some trends observed in the characteristics. The morphology of the best performing active layer, except for the inverted cells, are illustrated in Figure 23.

The domains sizes for the PDCDTBT-OD are much larger than those for PDCDTBT-HD derivative. The difference can be attributed to the higher solubility of the PDCDTBT-OD compared to the PDCDTBT-HD as a consequence of its larger side chains. A Higher solubility can result in larger domains. Also liquid-liquid phase separation can occur. Smaller domain sizes lead to an increase in current since the donor acceptor interface increases and hence there is more room for charge separation. For PDCDTBT-OD a maximal current of 7.17 mA/cm² was measured whereas for the PDCDTBT-HD a Jsc of 10.30 mA/cm² was obtained. Considering the morphology of both layers, the outcome entirely corresponds to the expectations.
However, not only domains size is an important factor. Also the interconnectivity of the domains plays an important role in order to reach high device performances. As can be seen from Figure 23 b and c, the domains sizes in in the active layer processed from 1% DIO in chlorobenzene (Figure 23c) are slightly bigger than the layer processed from 1% DPE in chloroform (Figure 23b). Although the domain sizes are bigger, the current increased to 10.30 mA/cm² compared to the photovoltaic device processed with PDCDTBT-HD from chloroform (Table 6). This increase in current for bigger domains can be attributed to the higher interconnectivity between the domains (Figure 23c). When the domains are more interconnected, charge transport towards the electrode is facilitated resulting in a higher current generation.
3.3 Conclusion and outlook

Both wide band gap polymers PDCDTBT-OD and PDCDTBT-HD were synthesized in moderate yields. The solubility is tuned by the length of the carboxylate side chains. PDCDTBT-OD is more soluble than PDCDTBT-HD. This is also verified by UV-vis where the \( \lambda_{\text{max}} \) in solution for the shorter-side chain containing polymer is red shifted and similar to the \( \lambda_{\text{max}} \) measured in an aggregated film, which implies that PDCDTBT-HD also show some aggregation in solution.

The band gap of both polymers was determined using the on-set of the absorption spectra of the polymer resulting in thin film band gaps of 1.64 eV. This wide band gap makes the polymer applicable for tandem photovoltaic devices. Cyclic voltammetry measurements showed that the driving force for charge separation, i.e. the LUMO-LUMO and HOMO-HOMO offset between the donor polymer and [70]PCBM, is high enough to use both polymers in photovoltaic devices.

Photovoltaic devices were fabricated and optimized for both polymers. The best results for PDCDTBT-OD were obtained for a photovoltaic device with a 1:1.5 polymer/PCBM ratio processed from 2% DPE chloroform leading to an efficiency of 4.84%. For PDCDTBT-HD a PCE of 6.2% was reached with a photovoltaic device processed from a 1:1.5 polymer PCBM ratio in 1% DIO in chlorobenzene. However, non-uniformity of the layers make the results irreproducible. Inversion of the configuration resulted in non-uniform layers but with more reproducible characteristics for the photovoltaic cells measured on the same substrate. A maximum efficiency of 5.26% was reached for a photovoltaic device processed from 1% DIO in chloroform with a 1:1.5 donor acceptor ratio.

In order to improve the performance of the photovoltaic devices, annealing of the active layers could improve the crystallinity of the layers which could result in higher charge mobility and hence an improved current. Also the fill factor can be influenced by annealing. In addition more research needs to be done in order to avoid de-wetting of the layers. A solvent system consisting of chloroform and chlorobenzene could help the wetting of the layers. Since processing from chloroform lead to uniform layers and chlorobenzene to higher performances. The photovoltaic devices processed from ortho-dichlorobenzene needs to be further optimized since the layers were too thin to improve the efficiency compared to the devices fabricated using chlorobenzene or chloroform.
3.4 Experimental

3.4.1 General

The synthetic procedures were performed under an argon atmosphere. Both monomers were synthesized by Ruurd Heuvel and purified by recrystallization or column chromatography prior to polymerization. Solvents were used without extra purification. [70]-PCBM (90-95 % purity) was purchased from Solenne BV.

UV/vis absorptions were recorded on a Perkin Elmer Lambda 1050 spectrophotometer. Optical absorption spectra in solution were measured from chloroform in a quartz cuvet, while spectra in solid state film were measured from a spin coated sample layer (6mg/mL chloroform) at 1500 rpm on a glass substrate. The glass substrates were cleaned with acetone and isopropanol after which they were treated with UV-ozone for 30 min. Infrared spectroscopy was performed on a Perking Elmer Two spectrometer. Molecular weight distributions of the polymers were measured by GPC at 140°C. These measurements were performed on a PL-GPC 120 system using a PLGEL 10 mm MIXED-C column with ortho-dichlorobenzene (o-DCB) as the eluent and polystyrene external standard. Samples were prepared as a solution in o-DCB stirred for 1h at 140°C. Cyclic voltammetry was performed at a scan speed of 0.2 V/s in a 1M tetrabutylammonium hexafluorophosphate acetonitrile solution. A polymer spin coated ITO-substrate was used as work-electrode, a silver rod as counter-electrode and a silver-silverchloride rod as quasi-reference-electrode. Ferrocene (Fc/Fc⁺) was used as external standard. Transmission electron microscopy was performed on a Tecnai G2 sphere using 200 square mesh copper grids. The measurements were performed at high tension (200 kV).

ABAB ITO-patterned substrates are used to fabricate photovoltaic devices. A-cells have an active area of 9 mm² as B-cells have one of 16 mm². All devices are fabricated in air. The substrates were cleaned by sonication in acetone for 15 minutes followed by a sodium dodecyl sulfate solution scrub and rinsing with ultra-pure water. To finalize, the substrates were sonicated in 2-propanol for 15 more minutes. Prior to the deposition of the hole/electron transporting layer the substrates are treated with UV-ozone for 30 minutes. Next, PEDOT:PSS (Clevois P.VP Al 4083, November 2016) was spin coated at 3000 rpm resulting in a 40 nm layer. ZnO was spin coated at 4000 rpm. Molibdenum oxide (MoO₃) was deposited from a crucible using thermal evaporation under high vacuum (~3.10⁻⁷ mbar). The polymer:[70]-PCBM active layer was spin coated from different solutions and at various speeds (specified in chapter 3). The active layer thickness was determined on a Veeco Dektak150 profilometer. The 1 nm LiF and 100 nm Al-back electrode layers were deposited by thermal evaporation from a boat-holder under high vacuum (~3.10⁻⁷ mbar) in a nitrogen
filled glovebox. J-V characterization was performed in the nitrogen filled glovebox using a Keithley 2400 source under white light illumination from a tungsten halogen lamp filtered by a AM1.5 daylight filter. A silicium cell is used as reference. External quantum efficiency measurements were performed using a setup consisting of a tungsten-halogen lamp, an optical chopper, a monochromator a preamplifier and a lock-in amplifier. A 730 nm LED is used in order to provide the 1 sun conditions. A calibrated silicon cell was used as reference cell and the photovoltaic devices were encapsulated in a nitrogen-filled box with a quartz window. The alignment of the cell is performed under illumination at 500 nm prior to the measurement.

3.4.2 Polymer synthesis

**PDCDTBT-OD**

A degassed schlenk tube was loaded with bis(2-octyldodecyl) 5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarboxylate (100 mg, 0.103 mmol), with 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c]-[1,2,5]thiadiazole (64.5 mg, 0.103 mmol), Pd$_2$(dba)$_3$ (2.83 mg, 0.003 mmol) and PPh$_3$ (3.24 mg, 0.012 mmol) and degassed again. A solvent mixture of toluene:DMF (9:1) (2mL) was added and the mixture was bubbled with argon for 15 minutes. After bubbling, the reaction mixture was heated to 110°C and stirred for 2 days. The obtained reaction mixture was precipitated in methanol, followed by resoluation with chloroform. EDTA (1g) was added and the mixture was refluxed for 1h. After cooling down to room temperature, the mixture was poured into water and extracted with chloroform. The obtained reaction mixture was precipitated in methanol and the precipitate was purified via a soxhlet extraction using acetone, hexane, CH$_2$Cl$_2$ and chloroform. The CH$_2$Cl$_2$ fraction yielded a blue polymer (100mg, 0.8 mmol, 85%, Mn: 13000).

**PDCDTBT-HD**

This polymerization reaction was performed in the same way as the PDCDTBT-OD using bis(2-hexyldodecyl) 5,5'-dibromo-[2,2'-bithiophene]-4,4'-dicarboxylate (100 mg, 0.116 mmol), with 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c]-[1,2,5]thiadiazole (72.8 mg, 0.116 mmol), Pd$_2$(dba)$_3$ (3.18 mg, 0.003 mmol) and PPh$_3$ (3.65 mg, 0.013 mmol). Also the work up was performed in the same way. The chloroform fraction of the soxhlet extraction yielded a blue polymer (80mg, 0.07mmol, 55%, Mn: 40000).
3.5 References


Abstract

In this chapter, the main conclusions of this research were outlined. This includes the drawbacks in the synthesis of 4,7-substituted phenanthroline and the main characteristics of the wide band gap PDCDTBT-OD or PDCDTBT-HD polymers. Also the photovoltaic properties of both polymers are outlined.
4.1 Conclusion

2,9-Dibromo-4,7-di(tricosan-11-yl)dithieno[3,2-c:2',3'-i]-[1,10]-phenanthroline was successfully synthesized as NMR spectral data and MALDI indicated the formation of the monomer. Even though, the monomer is unable to be separated from the mono- and bis-adduct mixture using chromatography of recycling GPC. The necessity for a pure monomer relies on the limitation to reach high molecular weight polymers when a polymerization is performed using impure monomers. In addition, the fabrication of well performing photovoltaic devices is limited by the molecular weight of the polymer.

Since purification of the dibromo-phenanthroline derivative was unsuccessful, 4,7-di(tricosan-11-yl)dithieno[3,2-c:2',3'-i]-[1,10]-phenanthroline was polymerized via a DHAP, which, unfortunately, did not afford any polymer material. Hence, no photovoltaic devices has been made using the unbrominated monomer.

The synthesis of both blue colored wide band gap polymers PDCDTBT-OD and PDCDTBT-HD was successful. As expected the hexyldexyl derivative appears to have a lower solubility than the octyldodecyl derivative, which was verified by a red-shifted $\lambda_{\text{max}}$ in the absorption spectrum from PDCDTBT-HD in solution. This is also qualitatively confirmed by the color of the polymer in solution, since the PDCDTBT-HD remains blue in solutions where PDCDTBT-OD changes its color to purple. The blue color indicates the aggregation of the molecules in solution and hence a lower solubility.

Cyclic voltammetry measurements have shown a high enough driving force for charge separation, making both polymer usable in photovoltaic devices. Both polymers have a wider band gap of 1.64 eV for PDCDTBT-HD and PDCDTBT-OD respectively and therefore these polymers can be implemented in the front cell of tandem photovoltaic devices.

Photovoltaic devices were fabricated and optimized for both polymers using different solvent systems, D:A ratios and thicknesses. For the photovoltaic devices containing PDCDTBT-OD the best result were obtained for the one with a 1:1.5 polymer/PCBM ratio and processed from 2% DPE chloroform leading to an efficiency of 4.84%. A PCE of 6.2% was reached with a photovoltaic device processed from a 1:1.5 PDCDTBT-HD:PCBM ratio in 1% DIO in chlorobenzene. Since the active layers processed from chlorobenzene were non-uniform, the results were irreproducible. Inversion of the configuration resulted in non-uniform layers showing reproducible characteristics per substrate. No higher PCE’s were obtained for the inverted configurations, however, a maximum efficiency of 5.26% was reached for a photovoltaic device processed from 1% DIO in chloroform with a 1:1.5 PDCDTBT-HD:70]PCBM acceptor ratio.
4.2 Acknowledgements

I truly enjoyed working on my graduation project and I learned a lot on organic photovoltaics and on good research in general. It has been an inspiring 7 month and I decided that I want to start a PhD after graduation. However this project wouldn’t be possible without the support of many people. My gratitude goes out to everyone who supported me during the last 7 month and helped me to finalize my graduation report.

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