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Morphology control and device optimization for efficient organic solar cells

PROEFSCHRIFT

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Abstract

Organic solar cells hold the promise to provide renewable solar energy at low cost from abundant and environmentally benign materials. This chapter provides a brief introduction to the field of organic solar cells, covering the basic working principles and the most important device architectures that are used to convert sunlight into electrical power with organic semiconductors. Presently the most successful organic solar cells are using active layers that are based on two complementary materials with electron donating and electron accepting properties. The actual choice of the two organic semiconductors and the way these are distributed in the photoactive layer, e.g. in a layered or blended fashion, are crucial to achieve efficient power conversion. Increased performance can be achieved when the morphology of the donor and acceptor in the active layer is tuned to enhance charge generation, separation, and transport. Further, by using advanced cell architectures such as tandem configurations, it is possible to simultaneously reduce losses that arise from thermalization of charge carriers and the transmission of light. The different topics discussed in this introduction define the goal and title of this thesis as “Morphology Control and Device Optimization for Efficient Organic Solar Cells”.
1.1 Solar cells

Renewable energy sources, including solar energy are considered to be of major importance to be able to meet the energy demand in the future. Solar energy is available worldwide and on a daily basis enough energy reaches the earth to power the entire planet. The development of photovoltaic devices that can convert solar energy into electricity is therefore one of the most promising long-term solutions for clean, renewable energy. The conversion was first observed by Becquerel in 1839.\(^1\) In 1953 Chapin \textit{et al.} developed the very first silicon solar cell, employing a $p$-$n$ junction.\(^2\) Due to their favorable efficiency and use in aerospace, industrial research and large scale fabrication developed quickly. Crystalline silicon is currently the most frequently used material in solar cells and has reached a maximum efficiency of 25.0\% for converting solar light into electricity in cells and 22.9\% in modules.\(^3,4\) The photovoltaic industry is growing annually by more than 30\% in the last decade, and worldwide solar cell production reached 29.5 GW in 2011, with crystalline silicon accounting for about 90\% of total production. A drawback of crystalline silicon solar cells is their time- and energy consuming and hence expensive production process due to the high quality and thick layers of crystalline silicon that are required for high performance. These disadvantages have created a search for new thin film technologies. Rather than using thick crystalline silicon layers, the new technologies use thin layers of semiconductor materials like amorphous silicon (a-Si), copper indium gallium diselenide (CIGS), or cadmium telluride (CdTe). Although the production of these thin-film devices is less expensive than of crystalline silicon devices, scarcity of elements and possible environmental impact will restrict commercialization on large scale. Furthermore their power conversion efficiency is less (a-Si: 10.1\%; CIGS 19.6\%; and CdTe 17.3\%).\(^4\)

In the search for alternative solar cell technologies, organic materials are attracting increasing interest. This development was motivated by the pioneering work of Tang who first demonstrated thin-film, bilayer organic photovoltaic cells fabricated from vacuum evaporated copper phthalocyanine and a perylene tetracarboxylic derivative and by the pioneering work of O’Reagan and Grätzel who introduced dye-sensitized organic solar cells, employing mesoporous titanium dioxide covered with a ruthenium-bipyridine dye in a liquid electrolyte. Presently organic solar cells have reached certified efficiencies of 10.0\% (Mitsubishi Chemical) while for dye-sensitized solar cells a certified efficiency of 11.0\% (Sharp) has been reported.\(^4\)

Following the discovery by Shirakawa, MacDiarmid, and Heeger that the prototype conducting polymer, polyacetylene, can be doped to reach a metallic conduction level\(^7,8\) research on $\pi$-conjugated organic conducting and semiconducting materials has expanded enormously in the last decades. One of the prime advantages of $\pi$-conjugated polymers is that they can be made soluble in a wide range of solvents,
by adding solubilizing side chains. Hence semiconductor inks can be made such that devices can be printed. Applications are foreseen in a wide range of opto-electronic devices like field-effect transistors, light-emitting diodes, memories, sensors, and solar cells. Owing to their high absorption coefficients, exceeding $10^5 \text{ cm}^{-1}$, only thin layers in the order of a few hundred nanometers are needed to absorb light. The first reports on efficient conjugated polymer solar cells based on donor-acceptor blends were published in 1995 independently by Halls et al. and Yu et al. The latter employed the ultrafast photoinduced charge transfer between a $\pi$-conjugated polymer as donor and a fullerene derivative as acceptor as discovered by Sariciftci et al. in the photoactive layer. Since then, these polymer-fullerene bulk heterojunction solar cells have advanced considerably, reaching 9.2% efficiency in 2012.

Combined with simple and scalable processing techniques, such as printing on flexible substrates, organic semiconductors are a very appealing alternative for use in solar cells. The efficiencies of bulk heterojunction organic solar cells have increased tremendously over the last few years, attracting considerable attention from industry. Mainly due to strategic design of new materials, optimization of processing and increasing insight in the physical processes in organic solar cells, record efficiencies exceeding 10% have been certified for undisclosed materials. Commercialization of organic solar cells only just started and more research is needed in all areas to be able to reach efficiencies exceeding 11% for single layer solar cells that are needed for successful competition with inorganic solar cells.

The work in this thesis explores novel strategies to increase efficiency of solution processed bulk heterojunction organic solar cells by changing the morphology or composition of the photoactive layer or improving the device architecture. Combining the successful approaches that have been briefly outlined above, new solar cells are presented that use $\pi$-conjugated polymers in blends with TiO$_2$ and in graded bilayers with fullerenes. Further small $\pi$-conjugated molecules are used to create solution processed bulk heterojunction solar cells as an alternative to vacuum processed small molecule cells. Finally tandem cell configurations will be presented for solution processed small molecules and conjugated polymers. In all of the solar cells presented, the morphology of the photoactive layer is studied in detail using a variety of techniques and shown to be a crucial factor in determining the performance.

The remainder of this chapter provides an introduction to the operation principles of organic solar cells followed by a brief overview of device architectures and choice of materials. Finally a brief outline of the contents of the thesis is given.
1.2 Organic solar cells

In a typical semiconductor photons with energy ($E_{\text{photon}}$) equal to or higher than the bandgap ($E_g$) of the material can be absorbed by promoting an electron from the valence to the conduction band. In most inorganic semiconductors this results in a weakly bound electron-hole pair that can easily be spatially separated by thermal energy ($kT$). If the photon energy exceeds the bandgap ($E_{\text{photon}} > E_g$), the excess of energy is lost via rapid thermalization to the band edges. When an internal electric field is created in the semiconductor, for example by introducing a junction between p- and n-type doped regions, the charges can be spatially separated and transported to two opposite electrodes. By connecting the electrodes a photocurrent and photovoltage can be extracted, hence the incident light is converted to electrical power.

![Diagram of organic solar cell](image)

**Figure 1.** The working principle of an organic solar cell under $V_{oc}$ conditions; (a) creation of an exciton in the donor phase, (b) diffusion to the interface, (c) charge transfer, (d) charge separation, (e) charge transport, (f) collection at the respective electrodes. Charge transport and collection under $J_{sc}$ conditions are shown in (e') and (f'). Alternative to (a) and (b) the exciton can also be created in the acceptor, followed by diffusion to the interface in the acceptor.

The working principle of an organic solar cell is fundamentally different from that of an inorganic solar cell. Due to low dielectric constant of organic semiconductors a strongly bound electron-hole pair is formed when an electron is promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). This bound electron-hole pair is commonly referred to as exciton and can be considered as a localized excitation (Figure 1a). Excitons generally have a lifetime of 1 ns or less and hence have limited diffusion length. To dissociate the exciton into free charges a second semiconducting material is needed with an offset
in the energy levels (Figure 1b). The energy offset between the HOMO and LUMO levels makes that the complementary organic semiconducting materials can act as an electron donor and electron acceptor, respectively. At the donor-acceptor interface excitons are dissociated into charges, resulting in an electron in the material with the highest electron affinity (acceptor) and a hole in the material with the lowest ionization potential (donor). Initially the electron and hole are still bound across the donor-acceptor interface by a Coulombic attraction (Figure 1c). However, by the increased spatial separation induced by the transfer across the interface, the carriers can be separated in the internal electric field in the cell that is created by the difference in work function of the collecting electrodes (Figure 1d). Once separated, the electrons are transported through the acceptor material to the low work function electrode and the holes travel through the donor phase to the high work function electrode (Figure 1e). In the last step the carriers are collected at the respective electrodes (Figure 1f) and a photocurrent and photovoltage can be extracted from the solar cell.

1.3 Characterization of solar cells

The performance of a solar cell is determined by measuring a current density-voltage ($J-V$) curve in dark and under illumination at 25 °C. The standard for illumination is the AM1.5G solar spectrum with an intensity of 1000 W/m² (Figure 2a). The AM1.5G (air mass 1.5 global) solar spectrum is the light that reaches the earth’s surface on a clear, cloudless day when the sun is at a 48.2° angle with the zenith such that the light travels through 1.5 times the thickness of the earth atmosphere. Typically the $J-V$ curves are measured using a lamp and appropriate filters to simulate the AM1.5G solar spectrum.

![Figure 2](image_url)

**Figure 2.** (a) AM1.5G solar spectrum (b) Typical $J-V$ curves of a solar cell in dark and under illumination. The symbols indicate the important characteristics, the open circuit voltage ($V_{oc}$), the short circuit current density ($J_{sc}$), the maximum power point ($P_{MPP}$) and the corresponding voltage ($V_{MPP}$) and current density ($J_{MPP}$).
In the dark a solar cell behaves like a diode. Ideally the dark J-V curve exhibits a low leakage current in reverse bias and high current density in the forward bias regime. Under illumination an additional photocurrent is created (Figure 2b). In the voltage region between short circuit (\(V = 0\)) and open circuit (\(V = V_{oc}\)) the solar cell delivers power under illumination. The point on the J-V curve where the product of \(J\) and \(V\) maximizes is referred to as the maximum power point (MPP) and defines the maximum extractable power density \(P_{MPP} = J_{MPP} \cdot V_{MPP}\). It is convenient to define the fill factor (FF) which is the ratio of the maximum power density (\(P_{MPP}\)) to the product of the open circuit voltage and short circuit current density.

\[
\text{FF} = \frac{P_{MPP}}{J_{sc} \cdot V_{oc}} = \frac{J_{MPP} \cdot V_{MPP}}{J_{sc} \cdot V_{oc}}
\]

The fill factor is influenced by the leakage current and the efficiency of charge collection in the cell. The power conversion efficiency (\(\eta\)) of a solar cell is defined by the ratio of \(P_{MPP}\) and the power density of the incident light (\(P_{in}\)).

\[
\eta = \frac{P_{MPP}}{P_{in}} = \frac{J_{sc} \cdot V_{oc} \cdot \text{FF}}{P_{in}}
\]

This equation shows that enhancing the power conversion efficiency involves enhancing three parameters simultaneously: the short circuit density, open circuit voltage, and fill factor.

In general the power conversion efficiency of a solar cell depends on both the spectrum and intensity of the incident light. In reporting the power conversion efficiency solar cells it is customary to use the AM1.5G spectrum at an intensity of 1000 W/m². Usually simulated solar light is used to obtain the J-V characteristics and estimate the efficiency of the solar cell. The simulated spectrum obtained from a white light source and filters is not exactly the same as the AM1.5G spectrum; hence the obtained J-V curve differs from what is expected in solar light. The current density that is extracted from the cell is most sensitive to the spectrum and intensity of the incident light, and primarily affects \(J_{sc}\).

A more precise estimate for \(J_{sc}\) can be measured using the spectrally resolved external quantum efficiency (EQE), which is the fraction of incident photons that is converted to electrons in the external circuit at short circuit conditions at a certain wavelength (\(\lambda\)). \(J_{sc}\) can be calculated by convolution of the spectrally resolved measurement with the AM1.5G spectral irradiance (\(E_{AM1.5G}\)) at 1000 W/m².

\[
J_{sc} \text{ (SR)} = \int \text{EQE}(\lambda) \cdot E_{AM1.5G}(\lambda) \cdot \frac{e \cdot \lambda}{h \cdot c} \, d\lambda
\]
In which \( e \) represents the elementary charge, \( h \) is the Planck constant, and \( c \) the speed of light. The EQE of organic solar cells is preferably determined under continuous bias illumination that enables to measure EQE at one-sun operating conditions. This is necessary due to the sub-linear light intensity dependence of some organic solar cells. At low light intensity carrier concentrations are low and recombination is limited. At one-sun intensity recombination increases and carrier transport is less efficient due to space-charge build up in the solar cells,\(^{19}\) and measurements are carried out using bias illumination to prevent overestimation of the \( J_{sc} \).

1.4 Solar cell architectures

A typical organic solar cell contains a photoactive layer sandwiched between two electrodes with different work functions (Figure 3a). For the operation of the cells the morphology of the photoactive layer, \textit{i.e.} spatial distribution of the complementary donor and acceptor semiconductors, and the device architecture, \textit{i.e.} the choice of electrodes and charge transport layers, are important.

Active layer morphology

The active layer of an organic solar cell consists of a combination of a donor and an acceptor semiconductor. The morphology of this active layer varies from a stacked bilayer of pure materials to an intimately mixed bulk heterojunction configuration (Figure 3b).\(^{9,20}\) In the very first days of research on organic photovoltaics, single layers of organic materials were sandwiched between two electrodes with different work functions. This pioneering work was inspired by the working principle of silicon solar cells. The excitons that are created in organic semiconductors, however, are strongly bound and in general efficiencies remained very low. The first organic solar cell that reached an efficiency of 1\% was published by Tang in 1986 who introduced the bilayer heterojunction of \( n \)-type and \( p \)-type organic semiconductor materials.\(^{5}\) In this bilayer configuration the excitons created diffuse to the interface between the layers, where exciton dissociation can take place and charges are created that can be extracted from the device at the respective electrodes. The number of excitons that can reach the interface in this bilayer structure is limited due to the short diffusion length of the excitons in organic semiconductor materials, which is typically estimated to be below 10 nm.\(^ {21,22}\) When the exciton diffusion length is less than the absorption depth, it is not possible to convert all incoming light.

To alleviate this drawback the bulk heterojunction was introduced by blending a donor and an acceptor material.\(^{9-11}\) In this configuration the interface area is increased and becomes virtually infinite to maximize the number of excitons that can reach the interface. Bulk heterojunctions can be made \textit{via} solution processing, such as spin casting or printing from a mixture of the donor and acceptor in a single solvent or
by co-evaporation of two small molecule organic semiconductors. The drawback of this bulk heterojunction is that the charges that are created at the interface need to be transported to the electrodes for which percolating pathways through both materials are needed. Optimizing the morphology of these bulk heterojunction solar cells is of major importance to find a balance between maximizing the interface while preserving efficient charge transport through the layer. The morphology can be influenced by thermal or solvent annealing of the layer after deposition, or by changing the solvent or making use of additives or co-solvents to directly change the morphology that is obtained during deposition.23

In addition to planar bilayer and bulk heterojunctions, more advanced morphologies such as hybrid bilayer-bulk molecular heterojunctions have also been considered to increase the interface between the two materials and charge transport. In these systems a three layer donor/donor-acceptor/acceptor configuration or a concentration gradient in a mixed absorber layer with increasing content of donor (acceptor) towards the hole (electron) collecting contact is used to improve the charge carrier collection.24,25 These structures are readily obtained by vacuum deposition. The equivalent in solution processing is the creation of a diffuse interface between the p- and n-type materials by lamination, sequential spin coating, or controlled diffusion by annealing.

**Device structure**

In an organic solar cell the active layer is sandwiched in between two electrodes with different work functions (Figure 3a). One of the electrodes needs to be transparent to be able to absorb light in the active layer of the solar cell. The transparent electrode is often a conductive oxide that can be sputtered or solution
processed from a precursor material. The other electrode is a metal that can easily be evaporated on top of the active layer. This metal contact reflects the light that was not absorbed, which increases the exciton generation in the active layer. Traditionally the organic solar cells are fabricated on a glass substrate with patterned indium tin oxide (ITO) electrodes.

In normal architecture organic photovoltaic devices the ITO electrode acts as the hole collecting contact. A hole transporting layer (HTL) is often used in between ITO and the photoactive layer. Poly(3,4-ethylendioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) is often used for this purpose. The HTL has several functions; it smoothen the rough ITO bottom contact layer which is necessary because the active layer is in the order of 100 nm thick. It further allows to adjust the work function to increase hole collection and maximize open circuit voltage. On top of the photoactive layer a thin (~1 nm) layer of lithium fluoride or calcium is evaporated through a shadow mask followed by thicker layer of aluminum (~100 nm) as electron collecting contact. The origin of the effect of the LiF is still unclear, but it effectively increases the efficiency of the organic solar cells with respect to an Al electrode, by increasing FF and $V_{oc}$.\textsuperscript{26-28}

In inverted solar cells the polarity of the devices is reversed, the bottom contact now collects the electrons while the metal on top collects the holes. This is achieved by using an electron transport layer (ETL, e.g. ZnO) on ITO and using a HTL (e.g. PEDOT:PSS or MoO$_3$) between the photoactive layer and the metal top electrode. In Figure 3a an example is given for a typical inverted device architecture that is also used in this thesis. The inverted device structures have shown to be more stable and resistant to ambient conditions due to the higher work function of the top metal electrode that can be used.\textsuperscript{29} On the other hand the reproducibility of the inverted device structure can still be a challenge with respect to the application of the metal oxide layers. The exact work function of the ZnO layer can be different depending on processing conditions and the use of different precursor solutions, while small differences in thickness of the transparent oxide in front of the metal back contact can change the optical field and efficiency of the solar cell.\textsuperscript{30-32} It is noted that going from normal to inverted device structures or vice versa using the same active layer often renewed optimization of the processing conditions needs to be done, mostly due to different wetting of the solution on the bottom contact which can change the obtained morphology.

**Tandem solar cells**

The first organic solar cells only used a small part of the solar spectrum, because the optical bandgap of most organic semiconducting materials was around 2 eV. The highest intensity of the solar photon flux is between 600 and 800 nm, while the most commonly used polymer donor materials were poly[2-methoxy-5-
(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) and poly(3-
hexylthiophene) (P3HT) that absorb only up to a wavelength of 600 and 650 nm,
respectively. To increase the absorption in the red region a huge effort has been
made in the last decade to make low bandgap materials with absorption up to and
beyond 1000 nm and now there are examples galore. There is, however, a principal
relation between the optical bandgap and the maximum open circuit voltage of the
cell. Presently it is estimated that for organic solar cells $V_{oc} \leq E_g/e – 0.6 \text{ V}$\(^{33}\). To make
optimal use of the full solar spectrum while preserving the open circuit voltage,
photoactive layers with complementary absorption spectra can be combined in a
series connected tandem junction solar cell. In a tandem configuration high energy
photons are absorbed in a wide bandgap cell, while the low energy photons are
absorbed in a small bandgap cell. Compared to single junctions, the use of a tandem
solar cell allows reduction of transmission and thermalization losses (Figure 4).

The active layers in a tandem solar cell are stacked and separated by an intermediate
contact resulting in a series connection. For series connection Kirchhoff’s law
determines that equal currents must flow through the subcells and the voltage of
the tandem is a summation of the voltages of the subcells. The intermediate contact
consists of an ETL that collects electrons from one subcell and a HTL that collects
the holes from the other subcell. At the interface between these layers the opposite
charges recombine, ideally at the same energy level to avoid voltage losses. The
HTL and ETL must make ohmic contacts to the respective subcells and should be
transparent to avoid both voltage and current losses in the tandem configuration.
Like single junction solar cells the tandem junctions can have normal or inverted
architectures. The schematic energy band diagram of a normal architecture tandem
solar cell under $V_{oc}$ conditions is shown in Figure 4.

![Figure 4. Schematic energy band diagram of a tandem solar cell under illumination at $V_{oc}$ conditions showing frontier energy levels.](image-url)
The first organic tandem solar cell was reported by Hiramoto et al. in 1990. This tandem consisted of two series connected subcells based on evaporated small molecules and an intermediate contact of evaporated gold. The advantage of evaporating a stack of layers is that the control over the exact composition is very high and interfaces are sharp. By evaporating small molecules it is possible to create very thin, well defined layers and by co-evaporation graded or bulk heterojunction or doped layers can be produced. This high degree of control has resulted in the current record certified efficiency for an organic solar cell of 10.7% by Heliatek.

In 2006 the first examples emerged for tandem solar cell fabricated using solution processed polymer based active layers. For solution processing of the second active layer an additional requirement is that the ETL and HTL should prevent damage of the first active layer during deposition of the second active layer. The intermediate contacts that were used by Kawano et al. and Hadipour et al. were sputtered or evaporated, which implies the mixing of different techniques during processing. The first fully solution processed tandem solar cell was demonstrated by Gilot et al., who showed that ZnO nanoparticles and PEDOT:PSS could make up a robust and well working intermediate contact. Kim et al. subsequently used TiO$_2$ and PEDOT:PSS in a similar approach to create 6.5% tandem polymer solar cells. Solution processed tandem solar cells have now reached certified efficiencies of 10.6% which is very close to the current world record of Heliatek’s evaporated tandem.

The most commonly used materials for the HTL and ETL in single junction and tandem solar cells include PEDOT:PSS and various metal oxides. Amongst others NiO, MoO$_3$, and V$_2$O$_5$ are used in solution processed HTL, while other metal oxides like ZnO and TiO$_2$ are applied as solution processed ETL. These metal oxides are solution processed by the use of sol-gel precursor solutions or dispersions of pre-synthesized nanoparticles and have shown to be good candidates for fully solution processed tandem solar cells.

1.5 Organic solar cell materials

The active layer of an organic solar cell consists of a combination of a donor and an acceptor $\pi$-conjugated organic semiconductor, which can either be a small and well-defined molecule or a polymer. In hybrid organic solar cells, one of the two semiconductors is organic and the other inorganic, such as a metal oxide. Traditionally the photoactive layers of organic solar cells are deposited via solution processing or vacuum deposition. Solution processing is quite versatile and can be used for polymers, small molecules, and hybrid cells. Vacuum deposition has so far mainly been used for depositing small molecule layers. In the sections below the current state of the art is briefly addressed for the three types of materials.
Polymers

Most $\pi$-conjugated polymers that are used in solution processed organic solar cells are hole conducting donor polymers, that are combined with either an acceptor polymer or acceptor small molecule. It has proven to be rather challenging to create well performing acceptor or $n$-type polymers and hence polymer:polymer solar cells have not contributed to the field as much until now.\textsuperscript{50-53} The most used electron acceptors for donor polymers are the small molecule soluble derivatives of the C$_{60}$ and C$_{70}$ fullerenes, such as [6,6] phenyl-C$_{61}$-butyric acid methyl ester ([60]PCBM)\textsuperscript{54} and [6,6] phenyl-C$_{71}$-butyric acid methyl ester ([70]PCBM). Especially the latter is increasingly used because it has a higher absorption in the visible part of the spectrum due to its lower symmetry.\textsuperscript{55} Major advancements have been made in the synthesis of donor polymers, especially towards small bandgap materials. This resulted in the record efficiency of polymer:fullerene single junction organic solar cells going from $\sim$6\% at the start of this thesis\textsuperscript{56-59} to 9.2\% at this moment.\textsuperscript{12} Creation of small bandgap polymers is based on combining electron donating and electron accepting moieties in the polymer backbone. One of the new contributors to these so-called donor-acceptor polymers is the diketopyrrolopyrrole (DPP) unit that has shown high efficiencies when copolymerized with thiophenes and other electron rich conjugated materials.\textsuperscript{41,59-63} Some of the recent highly efficient polymers in polymer:fullerene bulk heterojunction solar cells, including the best performing DPP-containing polymer (PDPP2FT), are given in Figure 5.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure5.png}
\caption{Molecular structure of some highly efficient donor polymers: PTB7,\textsuperscript{12} PDTSTPD,\textsuperscript{64} PCDTBT,\textsuperscript{59} PDPP2FT,\textsuperscript{61} PDPPTPT,\textsuperscript{63}}
\end{figure}
Introduction

Small molecules

Though historically small molecules were exclusively used to make organic solar cells via vacuum evaporation, solution processable small molecule donor materials combined with fullerene acceptors are attracting considerable attention in the last years. Now both deposition techniques have reached efficiencies up to 7.1% for single junction devices.

Solution processed small molecule solar cells were first described by Roncali et al. for oligothiophenes and by Würthner and Meerholz for merocyanine and squaraine dyes. Recently research in small molecules has also advanced in the direction of creating small bandgap materials like for the conjugated polymers, also using electron rich and electron poor moieties; some key examples are given in Figure 6.

Solution processable small molecules have some important advantages over polymers. They have a well-defined molecular structure considering end groups and position of side chains and have a precise molecular weight. Because of the absence of a molecular weight distribution, batch to batch variations that are frequently observed for polymers are minimized, while preserving the solution processability, which is interesting for scaling up. Furthermore small molecules are amenable to rigorous purification.

Figure 6. Molecular structure of some important solution processed small molecule donor materials: DPP(TBFu)₂, ᵇ DR₃TBDT, ᵇ DTS(PTTh₂)₂, ᵇ DERHD7T. ᵇ

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Solution processed small molecule solar cells were first described by Roncali et al. for oligothiophenes and by Würthner and Meerholz for merocyanine and squaraine dyes. Recently research in small molecules has also advanced in the direction of creating small bandgap materials like for the conjugated polymers, also using electron rich and electron poor moieties; some key examples are given in Figure 6. Solution processable small molecules have some important advantages over polymers. They have a well-defined molecular structure considering end groups and position of side chains and have a precise molecular weight. Because of the absence of a molecular weight distribution, batch to batch variations that are frequently observed for polymers are minimized, while preserving the solution processability, which is interesting for scaling up. Furthermore small molecules are amenable to rigorous purification.
Hybrid materials

Alternative to fully organic active layers, an organic semiconductor can be combined with an inorganic material creating a hybrid solar cell.\(^7\) In these hybrid solar cells the well studied and commercially available π-conjugated polymer P3HT is mostly used. Since this polymer has a relatively wide bandgap inorganic materials are used that broaden the absorption range of the active layer, for example by using nanoparticles of CdSe.\(^7\) Other hybrid solar cells use transparent metal oxides as acceptors such as TiO\(_2\)\(^7\) or ZnO\(^7\) to potentially combine the light-absorbing properties and processability of the organic donor material with high electron mobility and stability of the inorganic semiconductor. Due to the poor miscibility of the materials and surface traps on the interface between the materials, the overall obtained efficiencies of these hybrid solar cells remain low (~3%) in comparison to fully organic devices.\(^7\),\(^8\)-\(^10\)

1.6 Outline of the thesis

All of the more efficient solar cells reported in this introduction make use of a bulk heterojunction morphology of the active layer. The work in this thesis explores different options to increase efficiency of solution processed bulk heterojunction organic solar cells by controlling the morphology and optimizing the device architecture. Organic polymers, small molecules, and hybrid materials have been used to achieve this goal.

A start was made exploring the options to blend TiO\(_2\) nanocrystals and P3HT in a hybrid organic solar cell, with the goal to make use of the advantages of both types of materials. In Chapter 2 it is shown that creating an efficient bulk heterojunction of these two materials is challenging because of poor miscibility. The miscibility of the materials can be enhanced by the use of capping ligands on the TiO\(_2\), but the insulating properties of these ligands then hinder charge separation and charge transport.

An alternative way of producing a more efficient bulk heterojunction is described in Chapter 3 and involves the sequential processing of a P3HT layer and a fullerene layer that are mixed upon annealing of the completed active layers. The extent of intermixing is crucial to the operation of the solar cell, but difficult to access. Optical modeling and one-dimensional exciton diffusion calculations are used to demonstrate that the EQE of the active layer can be used to differentiate between bilayer, annealed bilayer, and bulk heterojunction morphologies.

DPP-based materials have shown to be quite efficient as building blocks for conjugated polymers in organic solar cells and can similarly be used in small molecules. In Chapters 4 to 6 DPP-based small molecules, a star-shaped molecule, and a polymer are used in single junction and tandem junction solar cells. The
influence of the position of solubilizing side chains on the small molecules was investigated. Changing the position of the side alters the aggregation of the molecules and the opto-electronic properties, which was studied in detail using a wide range of techniques. In these molecules the stacking, crystallization kinetics, and the obtained morphology upon use in bulk heterojunctions is different for different side chain positions, which all influences the behavior of the solar cells.

Morphology was also studied for bulk heterojunction solar cells made from a star-shaped DPP molecule and PCBM when using a solvent-additive during processing of the active layer. A remarkable difference in morphology evolution and solar cell efficiency was found between the use of [60]PCBM and [70]PCBM, which shows that for small molecules the difference in solubility between the components in the solvent mixture is of crucial importance. Tandem junctions were prepared using a complementary dendritic thiophene:fullerene active layer. The performance of the inverted tandem junction exceeded that of the single junctions of the separate active layers.

In the last chapter an efficient DPP-based polymer:fullerene active layer was optimized in single junction devices and combined with an efficient optimized polymeric wide bandgap active layer with complementary absorption in tandem solar cells. Optical and electrical modeling was used to determine the optimal layer thicknesses of these active layers in a tandem configuration and the tandems were fabricated and characterized. The experimental tandem solar cell reached high efficiencies that were an improvement over the best single junction devices.
Chapter 1

1.7 References

Introduction

Chapter 1


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Abstract

Crystalline titanium dioxide nanorods were synthesized with an organic capping layer of oleic acid. The removal and exchange of bound oleic acid ligands on the surface of the nanorods was investigated. Nanorods with different surface ligands were applied as electron acceptor in hybrid organic solar cells with poly(3-hexylthiophene) as a donor. Removing part of the oleic acid ligands resulted in improved performance of the solar cells, providing a higher photocurrent. Exchange of oleic acid by 2-thiophenecarboxylic acid also lead to a higher solar cell efficiency. The improved solar cells performance indicates that the oleic acid ligands act as a barrier for charge separation and charge transport in hybrid solar cells.
2.1 Introduction

In hybrid organic solar cells a \( \pi \)-conjugated polymer is combined with an inorganic semiconductor like ZnO^{1,2} TiO\(_2\)^{3,4} or CdSe^{5,6} Using an inorganic semiconductor instead of a fullerene derivative is expected to lead to more stable morphologies and hence longer lifetimes of the solar cells. Hybrid solar cells potentially combine the light-absorbing properties and the processability of the polymer with the high electron mobility and stability of the inorganic semiconductor. Like in fully organic solar cells, the hybrid bulk heterojunction needs to consist of a nanometer-scale interpenetrating network of the two materials to create efficient solar cells.\(^7\) The intimate mixing of the two components ensures efficient charge generation, which predominantly occurs at the interface between the two materials. After charge generation, the charges need to be separated and transported to the respective electrodes. The charge transport through the layer takes place in the two respective materials; holes are transported by the polymer while the electrons are transported by the inorganic material. For efficient charge transport in the blend efficient percolation pathways should exist in the blend.

Previously ZnO has been successfully applied as acceptor material in bulk heterojunction solar cells using ZnO nanoparticles or a ZnO precursor in a blend with \( \pi \)-conjugated polymers.\(^1,8-10\) ZnO and TiO\(_2\) have similar electronic properties and have demonstrated good electron accepting and transporting properties. Hybrid solar cells with TiO\(_2\) from precursor materials have been investigated, but only very moderate efficiencies have been reported.\(^11-14\) The most extensively studied hybrid solar cells are obtained by mixing conjugated polymers with presynthesized inorganic semiconductor (nano)particles.\(^15-17\) In this case the electron transport takes place through the inorganic particles that need to make good contact to enable efficient transport. High efficiencies reaching over 3\% have been obtained using dye molecules on the interface between TiO\(_2\) nanoparticles and P3HT.\(^18,19\)

In the hybrid solar cells presented here, the well-known conjugated polymer poly(3-hexylthiophene) (P3HT) was blended with titanium dioxide (TiO\(_2\)) nanoparticles. For the fabrication of these devices, TiO\(_2\) nanoparticles are synthesized, purified, and subsequently mixed with P3HT in a common organic solvent that is used to cast a blend film. TiO\(_2\) nanoparticle synthesis can generally be divided into two different routes. The synthesis can be performed in aqueous media, which often leads to non-crystalline particles that need additional heat treatment. There is little control over the synthesis and the obtained particles cannot be dissolved in organic media. Alternatively, the particles can be synthesized in organic media, resulting in well defined crystalline particles that can be dissolved in common solvents for P3HT.\(^20,21\) These particles, however, are capped with ligands having insulating long alkyl chains that provide solubility and prevent aggregation and conglomeration. These capping
ligands are necessary for synthesis but can act as a barrier for charge separation and charge transport, which will be investigated here.

2.2 TiO$_2$ nanoparticle synthesis

TiO$_2$ nanoparticles were synthesized from titanium tetraisopropoxide in oleic acid ((9Z)-octadecenoic acid) at 90 °C and extracted using precipitation.$^{22}$ This procedure provides TiO$_2$ nanorods. The size of the TiO$_2$ nanorods was estimated using transmission electron microscopy (TEM) (Figure 1a). These were estimated to be 4 nm in diameter and up to 50 nm in length. Of the small cluster of nanorods in the image a selected area electron diffraction (SAED) pattern was taken, which is shown in Figure 1b. This diffraction pattern shows incomplete rings consistent with the anisotropic growth of the crystals.$^{22}$

In Figure 2a the electron diffraction pattern of a large amount of TiO$_2$ nanorods is given. Comparing the radial integrated intensity of this pattern with the Miller indices of anatase TiO$_2$ (Figure 2b),$^{23}$ the crystal structure of the particles can be identified as being mainly anatase. The other peaks cannot be identified as one of the other TiO$_2$ crystal structures (rutile, brookite). The intensity and the sharpness of the (004) peak indicate that the particles are elongated in one direction, which is consistent with the observation that the particles have a high aspect ratio.

2.3 Ligand removal

Due to the synthesis in oleic acid, the as-synthesized TiO$_2$ nanocrystals are capped with oleic acid ligands. These ligands make that the nanocrystals are soluble in chloroform and other organic solvents. The as-synthesized particles are isolated from the reaction product by precipitation in ethanol. Using this technique, most of the
unbound oleic acid is removed. There is, however, still a small fraction of unbound oleic acid present, as shown by the infrared (FT-IR) measurement of a drop cast sample of the TiO$_2$ particle stock solution (Figure 3a, upper graph) in which a narrow band at a wavenumber of 1710 cm$^{-1}$ is present, which is specific for C=O vibrations in the oleic acid dimer.$^{24,25}$ The oleic acid forms a bidentate complex on the surface of the nanorods (Figure 3b). This bidentate binding results in the disappearance of the typical vibration at 1710 cm$^{-1}$ and the appearance of two bands around at 1525 and 1430 cm$^{-1}$, which are indicative for asymmetric and symmetric COO$^-$ vibrations.$^{24-26}$

The oleic acid binds strongly to the surface, but by repeated washing, oleic acid can be removed from the TiO$_2$ surface as is evidenced by the FT-IR measurements in Figure 3a. The removal is indicated by the change in intensity of the COO$^-$ and $-\text{CH}_2$ vibrations at around 1500 and 2800 cm$^{-1}$ respectively. The solubility becomes less after each washing step, also indicating the removal of part of the oleic acid capping. But even after washing the particles five times with ethanol, enough oleic acid remains present on the particles to be soluble in chloroform.

![Figure 2. Electron diffraction of TiO$_2$ nanoparticles; (a) full diffraction pattern (b) radial integration of the diffraction intensity with Miller indices of the anatase crystal structure.](image)

![Figure 3. Infrared measurements of drop cast samples of the TiO$_2$ particles as isolated and after repeated washing (data is shifted for clarity). (b) Bidentate binding of oleic acid ligands on TiO$_2$.](image)
2.4 Ligand exchange

Washing the particles with ethanol can only partly remove the oleic acid, because the oleic acid binds to the surface stronger than ethanol. A way to remove the oleic acid completely without clustering the particles is to exchange them with a better suitable ligand. This direct ligand exchange was carried out on the fully oleic acid capped particles (one time washed) using different ligands, with functional groups that are known to bind well to the surface of TiO₂ such as 2-thiophenecarboxylic acid (TCA) and phenylphosphonic acid (PPA).

To verify the exchange of the ligands ¹H NMR spectra of the supernatant after exchange were recorded. Figure 4 shows the ¹H NMR spectrum of the supernatant of the TCA exchange as an example. In this spectrum the characteristic peaks of TCA and oleic acid are present and the ratio between these molecules is determined. The relative efficacy of the exchanges can be calculated using this ratio, the amount of new ligand added, and assuming that one new ligand molecule replaces one molecule of oleic acid which results in the estimated amount of oleic acid that was removed.

![Figure 4. ¹H NMR spectrum of the supernatant from the thiophene-2-carboxylic acid ligand exchange.](image)

Figure 5 shows the IR spectra of the once washed oleic acid capped particles together with the spectra of the particles after ligand exchange. In the spectra after ligand exchange only very small peaks of –CH₂ vibrations (2800 cm⁻¹) remain, indicating that most of the oleic acid is removed. In the spectrum of the PPA exchanged particles the strong COO⁻ vibrations of the oleic acid at around 1500 cm⁻¹ are replaced by the phosphonic acid vibrations at about 1100 cm⁻¹.²²,²⁷ For the TCA exchanged particles the COO⁻ vibrations change slightly. The vibrations of the acid group in TCA are different from the oleic acid, because of the difference in the
environment of the acid groups. Both groups of vibrations indicate that the ligand exchange was successful.

The TiO₂ particles with TCA capping could be dissolved in chloroform and were used to make hybrid solar cells with P3HT. The PPA-capped particles, however, do not dissolve in chloroform or chlorobenzene, hence no hybrid solar cells could be prepared.

2.5 Devices

The large oleic acid ligands on the TiO₂ surface can act as an insulating barrier in charge separation and charge transport. The oleic acid capping of the TiO₂ nanorods is therefore expected to limit the current that can be obtained in a hybrid solar cell. Removal of a part of the oleic acid from the surface of the nanorods should therefore enhance the current. This is indeed observed for the hybrid solar cells made with these washed TiO₂ nanorods and P3HT, as shown by the current density-voltage (J-V) curves in Figure 6.

The short circuit current of the devices (J_{sc}) increases with decreasing oleic acid on the nanoparticle surface, from 0.2 mA/cm² for once to 1.4 mA/cm² for five times washed particles. Due to this increase the maximum power obtained from these cells increases from 0.03 mW/cm² to 0.29 mW/cm². As the amount of oleic acid decreases the solar cell performance improves. This indicates that the oleic acid ligands act as an insulating barrier in charge separation and charge transport.

![Infrared measurements of the TiO₂ particles before and after direct ligand exchange](image)
The effect of organic capping of TiO$_2$ nanorods on the performance of hybrid solar cells

Also solar cells were prepared using TiO$_2$ nanoparticles after TCA exchange and compared to the one time washed particles before exchange. The exchange of the insulating oleic acid by this better suitable ligand is expected to improve efficiency of the solar cells. The $J$-$V$ curves that were obtained can be found in Figure 7. The short circuit current ($J_{sc}$) and the open circuit voltage ($V_{oc}$) are higher for the devices with the TCA capped particles. For the devices with the TCA capped particles $J_{sc}$ is 0.7 mA/cm$^2$ and $V_{oc}$ is 0.7 V, while for the devices with oleic acid capped particles $J_{sc}$ is 0.2 mA/cm$^2$ and $V_{oc}$ is 0.4 V. Though the fill factor is a bit smaller, the total efficiency increases upon using TCA as a ligand.

In Table 1 the characteristics of all hybrid solar cells are given for better comparison. The performance of the solar cells improved upon removal of the oleic acid or exchange with TCA, which indicates that the oleic acid acts as a barrier in charge separation and charge transport in these devices. The charge separation taking place at the interface between the P3HT and the TiO$_2$ particles is influenced by both the insulating nature of the oleic acid ligand, as well as the effect of the dipole moment of the capping layer. This last effect is clear from the large difference in $V_{oc}$ between
the cells with oleic acid and TCA capped particles. Simultaneously the charge transport is affected by the contact between the TiO₂ particles, which improves upon the use of less ligands or smaller, less insulating ligands. Maximum power conversion efficiency (PCE) obtained from these hybrid solar cells is 0.29 mW/cm² with partial oleic acid capping and 0.17 mW/cm² with TCA capping. The increase in efficiency by replacing the alkyl chain of the oleic acid with the conjugated moiety of the TCA is not as large as was expected. The highest efficiency was obtained using washed particles with a partial oleic acid capping.

Table 1. Solar cell characteristics of hybrid solar cells with P3HT and TiO₂ particles. The TiO₂ particles were capped with oleic acid which were washed one, three, or five times or capped with thiophene-2-carboxylic acid.

<table>
<thead>
<tr>
<th>Capping on TiO₂</th>
<th>J_{sc} (mA/cm²)</th>
<th>V_{oc} (V)</th>
<th>FF</th>
<th>PCE (mW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic acid, washed one time</td>
<td>0.20</td>
<td>0.42</td>
<td>0.40</td>
<td>0.03</td>
</tr>
<tr>
<td>Oleic acid, washed three times</td>
<td>0.69</td>
<td>0.51</td>
<td>0.45</td>
<td>0.16</td>
</tr>
<tr>
<td>Oleic acid, washed five times</td>
<td>1.43</td>
<td>0.48</td>
<td>0.42</td>
<td>0.29</td>
</tr>
<tr>
<td>Thiophene-2-carboxylic acid</td>
<td>0.73</td>
<td>0.70</td>
<td>0.33</td>
<td>0.17</td>
</tr>
</tbody>
</table>

2.6 Discussion

By partial removal of the oleic acid capping the highest power conversion efficiency obtained was rather low with an estimated efficiency of 0.3%. Similar low efficiencies were published using TiO₂ nanotubes, linear and branched nanorods and P3HT with dyes as interface modifiers. Higher efficiencies for hybrid solar cells using organic capped TiO₂ nanocrystals were reported by Chen, Su and co-workers. They used a similar method exchanging oleic acid ligands by ligands such as anthracene acid or a ruthenium dye, and obtained efficiencies up to 2.20% in solar cells with P3HT. It should be noted that Zhu et al. were able to achieve an efficiency of 2.63% using a layer of TiO₂ nanocrystals, that was impregnated with the same ruthenium dye and covered by a layer of P3HT. In ligand exchange towards the ruthenium dye coated nanocrystals an intermediate step is used where the oleic acid is exchanged with pyridine, which binds weakly to the TiO₂ surface. Also other interface modifiers and control over morphology of the hybrid layers have been investigated. Remarkably this group seems to be the only one being able to obtain rather efficient devices. The large differences in obtained efficiencies using similar preparation methods have not been elucidated yet.
The effect of organic capping of TiO$_2$ nanorods on the performance of hybrid solar cells

2.7 Conclusion

The synthesis of TiO$_2$ nanocrystals in oleic acid leads to high-aspect-ratio, crystalline nanorods that are soluble in organic solvents such as chloroform. The as-synthesized particles are surface capped with oleic acid ligands, which can be partly removed by washing the particles with ethanol. Hybrid solar cells were made with the washed TiO$_2$ nanorods and P3HT. The performance of these solar cells improved upon removal of the oleic acid, which indicates that the oleic acid acts as a barrier in charge separation and charge transport in these devices.

Direct exchange of the oleic acid on the TiO$_2$ particles was successful and hybrid solar cells were prepared. This direct exchange seems to be a promising method to exchange the oleic acid ligands for ligands that are better suited for making hybrid solar cells. The highest efficiency for the hybrid solar cells, however, was obtained with the five times washed oleic acid capped TiO$_2$ nanocrystals. From both experiments we can conclude that a partly covered surface and a better suited ligand are beneficial for obtaining higher efficiencies in hybrid solar cells.

2.8 Experimental

TiO$_2$ synthesis
Crystalline TiO$_2$ nanoparticles were synthesized by hydrolysis of titanium tetraisopropoxide in oleic acid as described by Cozolli et al.$^{22}$ In a three-necked round bottom flask connected to a reflux cooler 25 g oleic acid (90%, Aldrich) was dried at 120 °C under vacuum for one hour. The temperature was reduced to 90 °C and 1.0 g of titanium isopropoxide (97%, Aldrich) was added under slight argon flow. The solution was stirred for 5 minutes. A solution of 0.786 g trimethylamine-N-oxide dihydrate (purum, Fluka) in 3.57 mL demineralized water was prepared and injected into the oleic acid solution using a syringe. The reaction mixture was kept stirring at 90 °C for eight hours.

The TiO$_2$ nanoparticles were extracted by precipitation using ethanol (technical grade, Aldrich) at room temperature. The precipitate was isolated by centrifugation using a Heraeus Megafuge 1.0 centrifuge. After centrifugation the supernatant was removed. The particles were dissolved in chloroform (Chromasolv®) and again precipitated using ethanol to remove the excess of oleic acid. After isolation the particles were dissolved in chloroform. This solution will be referred to as the stock solution.

Removal and exchange of oleic acid capping
The nanoparticles in the stock solution are surface capped with oleic acid. To remove a part of this capping the particles were washed one, three or five times using the following method. The particles in the stock solution were isolated by precipitation using an excess of ethanol, centrifugation and removal of the supernatant. Subsequently the particles were dispersed in ethanol and isolated again by centrifuging and removal of the ethanol, with which part of
the oleic acid was removed. After washing and isolation, the nanoparticles were dissolved in chloroform for further use. The nanoparticle solubility in chloroform became less after each washing step, which indicates the removal of part of the oleic acid capping.

Alternatively oleic acid was removed by direct exchange with another ligand. Direct ligand exchange was performed by precipitation of the oleic acid capped particles from the stock solution using ethanol, the resulting particles are identical to the one time washed particles as described before. The isolated particles were dispersed in ethanol and the desired new ligand was added in excess. The mixture was heated to 50 °C and stirred overnight. Then the mixture was cooled to room temperature and the particles were isolated using heptane. The removed supernatant contained the excess of new ligand and the exchanged oleic acid. To visualize the efficacy of the exchange, the ligands that remain in the solvent after reaction were analyzed using NMR.

Solar cell devices
To prepare solar cells the TiO$_2$ nanoparticle solution was added to a solution of P3HT (Plexcore® OS 2100) in chlorobenzene (Aldrich) in a 1:1 weight ratio. The concentration of the particles and the P3HT was 20 mg/mL in total. The devices were made on pre-cleaned indium tin oxide (ITO) patterned glass substrates (Naranjo), covered with poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) (Clevios P, VP Al4083). The active layers were prepared by spin casting the solution of the TiO$_2$ nanoparticles and P3HT at 2500 rpm. Finally, an aluminum electrode was deposited on top of the hybrid film as a back contact.

Characterization
Solar cell characteristics were measured under ~100 mW/cm$^2$ white light from a tungsten halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter, using a Keithley 2400 source meter. Infrared measurements were acquired by drop casting the TiO$_2$ nanoparticle solution on the ATR crystal of a PerkinElmer Spectrum One Fourier Transform Infrared spectrometer. Transmission electron microscopy was performed on a Tecnai G$^2$ Sphera (FEI) operated at 200 kV, samples were prepared by drying a diluted droplet of particle solution on a carbon coated copper grid (Agar Scientific). Electron diffraction patterns were integrated using ImageJ (1.43u) software with the Radial Profile plugin. $^1$H NMR spectra were recorded in deuterated ethanol (Cambridge Laboratories) on a 400 MHz Varian Mercury NMR. Proton chemical shifts are reported in ppm downfield from tetramethylsilane.
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Chapter 2

Chapter 3

Discriminating between bilayer and bulk heterojunction polymer:fullerene solar cells using the external quantum efficiency

Abstract

The morphology of the active layer in polymer:fullerene solar cells is a key parameter for the performance. We compare bilayer poly(3-hexylthiophene)/[6,6]-phenyl-C_{61}-butyric acid methyl ester (P3HT/PCBM) solar cell devices produced from orthogonal solvents before and after thermal annealing with P3HT:PCBM bulk heterojunction solar cells produced from a single solvent. Additionally, bilayer solar cells of P3HT and evaporated C_{60} were fabricated and characterized. By comparing the spectral shape and magnitude of the experimental and theoretically modeled EQEs for both bilayers, we show that P3HT/PCBM bilayers made via orthogonal solution processing do not lead to bilayers with a sharp interface but that intermixing has occurred. Thermal annealing of these diffusive P3HT/PCBM bilayers leads to increased mixing and/or crystallization of PCBM but does not result in the same mixed bulk heterojunction morphology that is obtained when P3HT and PCBM are cast simultaneously from single solution. For thicker layers, the annealed bilayers significantly outperform the bulk heterojunction devices with the same nominal composition and the same total thickness.

Part of this chapter has been published:
3.1 Introduction

Efficient organic photovoltaic cells can be made by mixing a semiconducting π-conjugated polymer with fullerene derivative into a bulk heterojunction photoactive layer.\(^1,2\) Such a bulk heterojunction consists of a nanometer scale interpenetrating network of the two materials, formed spontaneously during layer deposition, sometimes assisted by thermal or solvent annealing. Because of the nanometer size exciton diffusion lengths in organic semiconductors, a large interface area between the two components, and hence intimate mixing, is beneficial for dissociating excitons formed under illumination and generating charges. At the same time, the components must form percolating pathways to transport the charges to the electrodes. Charge transport benefits from larger domains. The effects of mixing vs. phase separation on performance have been studied in some detail for bulk heterojunction solar cells based on poly(3-hexylthiophene) (P3HT) and \([6,6\)]-phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM).\(^2,3\)

Interestingly, Ayzner et al.\(^4\) recently reported that solution processed thermally annealed P3HT/PCBM bilayer solar cells can be almost as efficient as bulk heterojunction cells. In their work an orthogonal solvent combination (\(o\)-dichlorobenzene and dichloromethane) was used to process a PCBM layer on top of a P3HT layer. Although evidence was presented that this procedure results in real bilayers with a sharp interface,\(^4\) several recent more detailed investigations, using transmission electron microscopy, X-ray photon electron spectroscopy, time-of-flight secondary-ion mass spectrometry, X-ray scattering, and time-resolved microwave conductivity provide evidence of interdiffusion of PCBM into P3HT producing an intermixed heterojunction directly after deposition.\(^5-11,12\) The partial mixing of P3HT and PCBM during deposition of PCBM is caused by swelling of the P3HT in the solvent used to deposit the PCBM. Thermal annealing drives the interdiffusion of P3HT and PCBM to completion.\(^10,11\) During thermal annealing PCBM becomes mobile and miscible in disordered and amorphous P3HT regions, without disrupting the ordered domains with lamellar stacking of P3HT chains.\(^7,11\)

Here we show that the spectrally resolved external quantum efficiency (EQE) of the solar cells can be used as an indicator of bilayer interfacial mixing. For the bilayers that are made by evaporation of C\(_{60}\) on top of a P3HT layer, the EQE can be modeled quite accurately, assuming a perfect bilayer with a sharp interface. We reveal that the EQE of P3HT/PCBM bilayer devices cast from orthogonal solvents is not compatible with a discrete P3HT/PCBM interface and that some intermixing occurs at the interface when depositing the PCBM layer.\(^5-11\) We further demonstrate that annealing of the diffusive P3HT/PCBM bilayers does not result in the same mixed bulk heterojunction morphology that is obtained when P3HT and PCBM are cast simultaneously from single solution. These results are consistent with a
recent morphological study of Russell et al. showing that after annealing PCBM is distributed in the amorphous P3HT regions that separate the crystalline P3HT domains in the film.11

### 3.2 Bilayer and bulk heterojunction solar cells

Three sets of bilayer and bulk heterojunction solar cells were prepared and characterized. The device layout of the bilayer solar cells is given in Figure 1a, for the bulk heterojunctions the P3HT and PCBM layers are replaced by a mixed active layer. Figure 1b compares the current density-voltage ($J-V$) curves of P3HT(80 nm)/PCBM(20 nm) bilayer devices made using dichloromethane as an orthogonal solvent before and after annealing with the performance of an equally thick (100 nm) P3HT:PCBM bulk heterojunction made in a volume ratio of 4:1 (weight ratio of 8:3) that corresponds to relative thickness of the P3HT and PCBM layers in the bilayers. The annealed bilayer device outperforms both other devices. The relevant solar cell parameters collected in Table 1 show that the same conclusion holds for devices with thinner (40 nm) and thicker (120 nm) P3HT layers, although the differences are small for the thin films. EQE measurements for the as-cast bilayer, annealed bilayer, and bulk heterojunction solar cells reveal similar differences (Figure 2).

![Figure 1](image_url)

**Figure 1.** (a) Device layout of the bilayer solar cells. (b) Current density-voltage characteristics of as-cast bilayer, annealed bilayer, and bulk heterojunction cells using 20 nm of PCBM and 80 nm of P3HT.
The EQE of the 40/20 bilayer increases slightly after annealing and the contribution at short wavelength (likely due to PCBM) becomes more important (Figure 2a). After annealing the EQE resembles that of the bulk heterojunction. For the thicker active layers with volume ratios of 4:1 (b) and 6:1 (c) the changes are more dramatic. Annealed bilayers and bulk heterojunctions show strikingly different performance. In both cases, the annealed bilayer reaches a much higher EQE and shows different

Table 1. Short-circuit current ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF), and maximum power point (MPP) for as-cast bilayer (BL), annealed bilayer (A-BL), and bulk heterojunction (BHJ) solar cells with different layer thicknesses (d) and volume ratios of P3HT and PCBM.

<table>
<thead>
<tr>
<th>Type</th>
<th>d (nm)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>MPP (mW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BL</td>
<td>40/20</td>
<td>4.00</td>
<td>0.47</td>
<td>0.49</td>
<td>0.93</td>
</tr>
<tr>
<td>A-BL</td>
<td>40/20</td>
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Figure 2. EQEs of as-cast bilayer, annealed bilayer, and bulk heterojunction configurations having 20 nm of PCBM and (a) 40, (b) 80, and (c) 120 nm of P3HT.
Discriminating between bilayer and bulk heterojunctions using the external quantum efficiency wavelength dependence. Because the layers have the same composition (P3HT/PCBM ratio) and thickness this demonstrates that thermal annealing of the as-cast bilayers produces composite layers that differ from the bulk heterojunction obtained from casting the same mixture from solution.

Figure 2c shows that the EQE of the annealed P3HT(120 nm)/PCBM(20 nm) bilayer cell is almost three times higher than the corresponding as-cast bilayer and bulk heterojunction cells and does not show a minimum in the EQE at ~500 nm. For the as-cast bilayer the minimum is directly explained by the reduced amount of light that reaches the P3HT/PCBM interface through the thicker layer of P3HT (see also Figure 6 and 7 later this chapter). Also for the bulk heterojunction the minimum in EQE is due to an internal filter effect. In the (6:1 v/v) bulk heterojunction the concentration of PCBM is low, which causes poor percolation pathways for electron transport to the LiF/Al electrode. Electrons generated close to the PEDOT:PSS electrode are therefore likely to recombine before being collected. In contrast, the annealed bilayer shows no obvious filter effects. The large increase in EQE and the change in spectral shape leave no doubt that by annealing intermixing occurs at the P3HT/PCBM interface and PCBM crystallizes ensuring good electron transport. We conjecture that the annealed morphology is neither a real bilayer and nor an intimately mixed bulk heterojunction, but rather a morphology in which PCBM is dispersed throughout the P3HT layer in a continuous manner to explain the absence of a filter effect in the EQE and the excellent percolation pathways for electrons. This result is consistent with recent morphological studies that imply that fullerene derivatives rapidly diffuse into the amorphous P3HT regions that separate the crystalline P3HT domains.11,12

Bright field TEM images of the annealed bilayers and the solution cast bulk heterojunctions confirm that the morphologies are not the same (Figure 3). For the annealed bilayers (Figure 3a-c) the phase separation produced appears to be finer than for the bulk heterojunctions (Figure 3d-f). Especially in Figure 3e and d a rather large phase separation between P3HT and PCBM is visible with domain sizes of circa 100 nm. The differences are more evident for the thinner films, because in the thicker films the volume concentration of PCBM is small (14%).
To investigate the origin of the EQE differences in more detail, optical modeling was performed assuming perfect bilayers with a sharp interface. The transfer matrix method was used to calculate exciton generation profiles from the wavelength dependent refractive index ($n$) and extinction coefficient ($k$) of P3HT and PCBM (Figure 4a). The $n$ and $k$ values of PCBM were measured using ellipsometry. Obtaining the $n$ and $k$ values for P3HT is more difficult, because they vary with degree of aggregation, molecular weight, regioregularity, and processing conditions.

**3.3 Optical constants**

Figure 3. Bright field TEM images of annealed P3HT/PCBM bilayers (a) 40/20 nm, (b) 80/20 nm, (c) 120/20 nm and of solution cast P3HT:PCBM bulk heterojunctions (d) 60 nm (2:1 v/v), (e) 80 nm (4:1 v/v), and (f) 140 nm (6:1 v/v).

Figure 4. (a) Optical constants for P3HT and PCBM. (b) Measured and simulated transmission of a thick and a thin layer of P3HT cast from ODCB on a glass slide.
Also anisotropy in the films complicates the measurements. Germack et al. used variable angle spectroscopic ellipsometry on three P3HT films with different degrees of aggregation to obtain three sets of optical constants.\(^\text{13}\) Here we used a linear combination of these functions that accurately reproduced the transmission of both thick and thin P3HT layers cast from ODCB (Figure 4b).

![Figure 5](image.png)

**Figure 5.** Measured and calculated reflection of the as-cast bilayer devices with 20 nm of PCBM and (a) 40, (b) 80 and (c) 120 nm P3HT layer.

Optical modeling of the solar cells was verified by comparing calculated and measured reflection of the as-cast bilayer devices used in this study. Due to the geometry of the devices and the beam inside the spectrometer that was used, reflection was measured of an area on which only a small part of the patterned ITO was present. The optical modeling for this comparison was therefore done on the device stack without ITO. As can be seen in Figure 5 the overlap between modeling and measurement is good down to a wavelength of about 450 nm. Below this wavelength the ITO has a large influence on the reflection, which was not included in the modeling.

### 3.4 Modeling the external quantum efficiency

As was shown for all three as-cast bilayer devices the experimental reflection spectrum accurately matches with the results from the optical modeling when a discrete interface is assumed. This shows that the optical absorption is not very sensitive to the intermixing at the interface and that we can use the optical modeling to determine the number of absorbed photons. Figure 6 shows the calculated exciton generation rate in a P3HT/PCBM bilayer for three selected wavelengths.
Combining the exciton generation rate profiles with one-dimensional exciton diffusion we calculated the wavelength dependent EQE for perfect bilayers with a sharp interface. The diffusion of excitons in each layer is described by

$$\frac{dn(x)}{dt} = g(x) - \frac{n(x)}{\tau} + D \frac{d^2n(x)}{dx^2}$$

(1)

where $g(x)$ is the exciton generation rate, $D$ the exciton diffusion constant, $\tau$ the exciton lifetime, and $n(x)$ the exciton density. The exciton lifetime and diffusion constant in PCBM were taken from the literature: $\tau = 1.25$ ns and $D = 2.0 \times 10^{-8}$ m$^2$/s, giving a diffusion length in the $x$-direction of $L = (D \cdot \tau)^{1/2} = 5$ nm. For P3HT different exciton diffusion lengths were considered; the largest value found in literature was $L \approx 25$ nm, with $\tau = 0.60$ ns and $D = 1.0 \times 10^{-6}$ m$^2$/s. We assume that all P3HT and PCBM excitons are quenched when they reach the P3HT/PCBM interface and at the LiF/Al electrode, such that $n(t) = 0$ at these positions. At the PEDOT:PSS electrode either full (model A) or no (model B) quenching of excitons was considered. Equation 1 is solved numerically for steady state ($dn(x)/dt = 0$) and from the steady state exciton density profile the number of excitons quenched at the interfaces is determined. The excitons quenched at the P3HT/PCBM interface are assumed to generate charges that contribute to the photocurrent in the solar cell at short circuit without further losses. Because of the short diffusion length in PCBM and the high P3HT/PCBM ratio, excitons generated in P3HT give the main contribution to the current and, hence, the EQE (Figure 7).

The calculations show that even for a relatively large value of $L \approx 25$ nm for P3HT, the calculated EQEs of perfect bilayers remain well below the experimental values (Figure 7), irrespective of assuming full (A) and no (B) quenching at the PEDOT:PSS interface. Higher values for $L$ also do not reproduce the experimental data (not shown).
Discriminating between bilayer and bulk heterojunctions using the external quantum efficiency

The EQE calculations reproduce the minimum at 500 nm for the 80/20 and 120/20 bilayers (Figure 7b,c). This is a direct consequence of the reduced exciton generation rate near the P3HT/PCBM interface for photons of 500 nm (Figure 6) because only few photons reach the interface with PCBM as they are attenuated by the absorbing P3HT. This optical filtering does not occur to the same extent at 400 and 600 nm, where P3HT absorbs less strongly. Though the magnitude of the EQE cannot be reproduced by modeling, the shape of the modeled curves resembles the measured data. Therefore we conclude that the use of orthogonal solvents does not produce perfect bilayers and that some intermixing at the P3HT/PCBM interface occurs before annealing, likely caused by swelling of P3HT in the dichloromethane used to cast PCBM.10,12 Because the performance of the 40/20 as-cast bilayer changes only slightly upon annealing (Figure 2a), the diffusion of PCBM into P3HT during deposition is at least 40 nm.

3.5 P3HT/C$_{60}$ bilayers

To confirm that our optical modeling can accurately describe a true bilayer, P3HT/ C$_{60}$ bilayer solar cells were made and characterized. These bilayers were obtained by slow evaporation of C$_{60}$ onto a layer of P3HT. The P3HT layers were identical to the ones used for the P3HT/PCBM bilayer solar cells. On top of the C$_{60}$ a 10 nm layer

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**Figure 7.** Measured (symbols) and calculated (lines) EQEs for as-cast bilayer solar cells having 20 nm PCBM and (a) 40 nm, (b) 80 nm, and (c) 120 nm P3HT. The calculations include (model-A) or exclude (model-B) quenching of P3HT excitons at the PEDOT:PSS electrode.
of bathocuprine (BCP) was evaporated as an exciton blocking and protective layer before evaporation of the Al back contact.18

Figure 8a shows the current density-voltage ($J-V$) curve for a bilayer with 82 nm of P3HT and 23 nm of $C_{60}$. As expected for true bilayer solar cells, the short circuit current is rather low due to limited exciton diffusion lengths in organic materials. In comparison, the as-cast bilayer with 80 nm of P3HT and 20 nm of PCBM gives over three times more current. Figure 9 shows the spectrally resolved EQE spectra for four different layer thickness combinations of P3HT/$C_{60}$ bilayer cells. Comparing Figure 2a (40 nm P3HT/20 nm PCBM) with Figure 9a (45 nm P3HT/25 nm $C_{60}$) shows that EQEs spectra differ significantly.

The spectrally resolved EQEs of the P3HT/$C_{60}$ bilayer solar cells were calculated by optical modeling of the device stack given in Figure 8b and solving Equation 1, as was done for the P3HT/PCBM bilayers. The modeling assumes perfectly flat and sharp interfaces between all layers, though the interface between the P3HT and $C_{60}$ is rather rough due to the crystallinity of the P3HT layer.

![Figure 8.](image-url)

**Figure 8.** (a) Current density-voltage characteristics of a bilayer with 82 nm of P3HT and 23 nm of evaporated $C_{60}$ and (b) the complete device stack of these P3HT/$C_{60}$ bilayer solar cells.

In the exciton diffusion calculations full exciton quenching was assumed at all interfaces and only excitons that are quenched at the interface between P3HT and $C_{60}$ contribute to the current at short circuit without any losses. The exciton lifetime and diffusion constant of $C_{60}$ were obtained from literature: $\tau = 1.2$ ns$^{19}$ and $D = 3.0 \times 10^{-7}$ m$^2$/s, which was calculated using a diffusion length of 19 nm.$^{20}$ For P3HT initially the same exciton lifetime and diffusion constant were used as before in modeling the P3HT/PCBM as-cast bilayers. In Figure 9 measured and modeled wavelength dependent EQE spectra are shown for the four different layer thickness combinations. Using an exciton diffusion length of $L \sim 25$ nm for P3HT, which is the largest value reported in literature, leads to large overestimation of the EQE (dashed lines in Figure 9). Moreover, the spectral shape of the modeled EQE does not resemble the measurements for bilayers with thin P3HT layers.
Discriminating between bilayer and bulk heterojunctions using the external quantum efficiency

The solid lines in Figure 9 are the results of modeling the EQE when the P3HT diffusion constant and lifetime were taken to be $D = 1.8 \times 10^{-7} \text{ m}^2/\text{s}$ and $\tau = 0.4 \text{ ns}$ respectively, combined giving a diffusion length of a more realistic value of $L = 8.5 \text{ nm}$. These modeling results quite accurately describe the measured data, both in spectral shape as well as magnitude, especially considering that the modeling assumes perfectly smooth surfaces and does not take into account any recombination mechanisms.

3.6 XPS of bilayers

Depth profiling X-ray photoelectron spectroscopy (XPS) was used to verify that evaporating C$_{60}$ on top of a crystalline P3HT layer actually produces a bilayer. For comparison also an as-cast P3HT/PCBM bilayer was measured using this depth profiling XPS. Figure 10 shows the XPS spectra of three binding energy regions for both bilayer samples. The carbon 1s and silicon 2p peaks are plotted next to the sulfur 2p region to determine where the bilayers are situated and where the silicon wafer starts to be probed. The first line on the bottom of the graphs is the XPS spectrum of the surface of the samples. For depth profiling the samples were etched with an ion beam and measured after each etching step. The measurements are plotted with

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**Figure 9.** EQE measurements and simulations of bilayers with (a) 45 nm P3HT and 25 nm C$_{60}$, (b) 45 nm P3HT and 34 nm C$_{60}$, (c) 82 nm P3HT and 23 nm C$_{60}$, (d) 123 nm P3HT and 34 nm C$_{60}$. Simulations are based on an exciton diffusion length ($L$) of 25 nm or 8.5 nm.

The solid lines in Figure 9 are the results of modeling the EQE when the P3HT diffusion constant and lifetime were taken to be $D = 1.8 \times 10^{-7} \text{ m}^2/\text{s}$ and $\tau = 0.4 \text{ ns}$ respectively, combined giving a diffusion length of a more realistic value of $L = 8.5 \text{ nm}$. These modeling results quite accurately describe the measured data, both in spectral shape as well as magnitude, especially considering that the modeling assumes perfectly smooth surfaces and does not take into account any recombination mechanisms.
a small offset in intensity. When comparing both samples, the surface of the P3HT/PCBM as-cast bilayer shows a clear signature of the sulfur 2p whereas this signal is absent in the P3HT/C60 bilayer. In the P3HT/PCBM as-cast bilayer (Figure 10a) the sulfur 2p peak is visible throughout the entire sample indicating that indeed the PCBM intermixes with the P3HT upon deposition.7,11,12,22 The XPS depth profiling spectra show that in the P3HT/C60 bilayer sample the sulfur 2p peak only becomes visible after the top part of the sample, the C60 layer, is etched away (Figure 10b). There seems to be a diffusive transition going from the C60 layer to the P3HT layer. This could be a result of the etching, which is never perfectly homogeneous and causes a bit of mixing of the materials on the nanometer scale. This mixing is also observed at the P3HT/Si wafer interface in the sulfur binding energy region scan, where a broad Si peak at 168 eV becomes visible, while the small S 2p peak at 164 eV is still present. Also the interface between P3HT and C60 is not expected to be perfectly flat, due to the crystallinity of the P3HT layer. In conclusion these XPS measurements confirm that evaporation of C60 on top of a P3HT layer results in a discrete bilayer and that intermixing of PCBM into the underlying P3HT layer is already present in the as-cast P3HT/PCBM bilayer films.

3.7 Conclusions

EQE measurements in combination with optical modeling can be used as an indicator of bilayer interfacial mixing. The EQE of perfect bilayer solar cells was calculated by combining the exciton generation profile in the cell with one dimensional exciton diffusion. The measured EQE data for P3HT and evaporated C60 bilayers were accurately modeled using this technique. However, the spectral shape of the calculated EQE of P3HT/PCBM bilayers resembles the experimental data of the as-cast bilayer but does not reproduce its magnitude. This indicates that P3HT/PCBM bilayers made using regioregular P3HT via orthogonal solution processing
lead to bilayer-like morphologies that are partly intermixed at the interface. Thermal annealing crystallizes the PCBM and enhances the depth of PCBM segregation and hence percolation and converts the layer into a bulk heterojunction. For thick (≥ 80 nm) P3HT films the performance of the annealed P3HT/PCBM bilayers is significantly better that of corresponding solution cast bulk heterojunctions. This is consistent with the recent result that annealing of bilayers provides a morphology that has a percolating PCBM network throughout the P3HT layer.\textsuperscript{11}

\section*{3.8 Experimental}

\textbf{Solar cell devices}

P3HT (Plexcore OS 2100, > 98\% regioregular) was spun slowly from \textit{o}-dichlorobenzene (ODCB) and dried for at least 20 min. On top, PCBM (Solenne BV) was spun from dichloromethane.\textsuperscript{4} Three different P3HT layer thicknesses (40, 80, and 120 nm) were used, keeping the thickness of the PCBM layer (20 nm) constant. The thickness of the PCBM layer was limited by the solubility of PCBM in dichloromethane that is used as an orthogonal solvent for the underlying P3HT layers. These bilayers were studied as cast and after annealing at 150 °C in a nitrogen atmosphere for 20 min.

Bulk heterojunctions of P3HT:PCBM were made using volume ratios (2:1, 4:1, and 6:1) and layer thickness (60, 100, and 140 nm) that allow direct comparison with the P3HT/PCBM bilayers because they nominally have the same thickness and composition. These blends were spun cast from ODCB which evaporates slowly such that a phase-segregated morphology with semicrystalline P3HT and PCBM domains was obtained without annealing. All layers were deposited on glass covered with patterned indium tin oxide (ITO) and poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS). Devices were completed by evaporating LiF (1 nm) and Al (100 nm) as back contact in vacuum.

Bilayers of P3HT and C\textsubscript{60} were made by evaporating C\textsubscript{60} on top of P3HT films cast from ODCB as was used for the P3HT/PCBM bilayers. C\textsubscript{60} was evaporated in a high vacuum chamber at an average rate of 0.5 Å/s. On top of the C\textsubscript{60} a 10 nm layer of bathocuproine (BCP) was evaporated at the same rate. Finally 100 nm of aluminum was evaporated as a top contact.

\textbf{Characterization}

Solar cell characteristics were measured under ~100 mW/cm\textsuperscript{2} white light from a tungsten halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter, using a Keithley 2400 source meter. The external quantum efficiency was measured using monochromatic light from a 50 W tungsten halogen lamp (Philips focusline) in combination with monochromator (Oriel, Cornerstone 130). The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Stanford research Systems SR830). A calibrated Si cell was used as reference to obtain external quantum efficiencies. The device was measured in a nitrogen filled box. The thicknesses of the layers in the solar cells were measured on a Veeco Dektak 150 profilometer.
Chapter 3

Transmission electron microscopy (TEM) was performed on a Tecnai G2 Sphera TEM (FEI) operated at 200 kV. Thin films for TEM were processed on PEDOT:PSS, which was dissolved in water to create a free standing film that was transferred onto a copper TEM grid. Bright field TEM images were acquired under slight defocusing conditions.

Depth profiling X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha, equipped with a monochromatic small-spot X-ray source and a 180° double focusing hemispherical analyzer with a 128-channel detector. Spectra were obtained using an aluminum anode (Al Kα = 1486.6 eV) operating at 72W and a spot size of 400 μm. Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. The background pressure was $2 \times 10^{-9}$ mbar and during measurement $3 \times 10^{-7}$ mbar Argon because of the charge compensation dual beam source. Sputtering was done with a beam energy of 2000 eV at high current. XPS samples were prepared by application of the bilayers (as described for solar cell devices) on a piece of Si wafer that was covered with a naturally grown oxide layer.

Optical modeling

Absorption and reflection spectra were measured using a Perkin-Elmer Lambda 900 spectrometer equipped with an integrating sphere. Calculations of the optical electric field were performed with Setfos 3 (Fluxim AG, Switzerland). In the program the following layers are used for the P3HT/PCBM bilayer solar cells: air (infinite), glass (incoherent), SiO₂ (20 nm), ITO (132 nm), PEDOT:PSS (43 nm), P3HT (different thicknesses), PCBM (20 nm), Al (100 nm) and air (infinite). The device stack of the P3HT/C₆₀ bilayers consisted of the following layers: air (infinite), glass (incoherent), SiO₂ (20 nm), ITO (132 nm), PEDOT:PSS (43 nm), P3HT (different thicknesses), C₆₀ (different thicknesses), BCP (10 nm), Al (100 nm) and air (infinite). Optical constants of glass, ITO, BCP and Al were provided with the Setfos 3 software package. The optical constants of PCBM were measured by the Energy research Centre of the Netherlands. The other optical constants were obtained from variable angle ellipsometry or literature.²³,²⁴,²⁵
Discriminating between bilayer and bulk heterojunctions using the external quantum efficiency

3.8 References

5. Wang, D. H.; Choi, D-G; Lee, K.-J.; Im, S. H.; Park, O. O.; Park, J. H. Organic Electronics 2010, 11, 1376
Abstract

Small molecules based on diketopyrrolopyrrole (DPP) and thiophenes with solubilizing side chains on different positions were investigated for use in solution processed organic solar cells. The position of the side chains on these π-conjugated molecules is of major influence on their optical properties in film. Moreover, aggregation, and crystallization behavior are different when these different molecules are combined with a fullerene derivative in a thin film. The position of the side chain affects the morphology and hence the efficiency when these films are used as the photoactive layer in a solar cell. Efficiencies over 3% were obtained when a mild annealing step was used. It is demonstrated that changing the side chain position is an additional tool to influence behavior of conjugated molecules in organic photovoltaics. A first example of a solution processed small molecule tandem solar cell is demonstrated.
4.1 Introduction

Solution processed organic photovoltaic cells are considered to be a viable option in meeting the future global energy demand as they can be produced using fast roll-to-roll printing production techniques. Most solution processed organic solar cells are made by blending $\pi$-conjugated polymers with a fullerene derivative, usually [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM), in a so called bulk heterojunction.\textsuperscript{1,2} The efficiency obtained using a specific polymer does not only depend on the chemical composition, it also strongly depends on molecular weight, regioregularity, and end groups.\textsuperscript{3-5} Due to the polymerization techniques used to obtain $\pi$-conjugated polymers, there are often significant batch to batch variations in exact composition and properties. These variations often lead to irreproducibility in solar cell performance.

Instead of a polymer small molecules can be used in solution processed bulk heterojunction solar cells.\textsuperscript{6} Recently, several examples of efficient solar cells containing $\pi$-conjugated small molecules processed from solution have been reported.\textsuperscript{7-12} Efficiencies of 7.1\% have been achieved,\textsuperscript{13} which approaches the highest efficiencies of about 9\% reported for polymer solar cells.\textsuperscript{14} Even higher efficiencies have been reported for undisclosed solution processed small molecules.\textsuperscript{15} With respect to polymers the synthesis of small molecules is more reproducible and hence gives the opportunity to investigate a well defined system. Side chains are needed on conjugated molecules and polymers to make them solution processable, but are insulating in nature which can hamper charge transport. It has been shown that the number and size of the side chains can be of influence on the solar cell performance.\textsuperscript{10,16-19} Here, we show that also the position of the side chains on a conjugated molecule can be of major influence on the aggregation behavior and hence the morphology and efficiency of the photoactive layer. The synthesized molecules consist of a diketopyrrolopyrrole (DPP) core flanked by two thiophene rings of which the outer rings carry a hexyl chain on the 3, 4 or 5 position (Figure 1). DPP is a planar bicyclic structure that provides strong $\pi-\pi$ stacking and is widely used to make small band gap polymers for photovoltaics.\textsuperscript{4,17,20,21} By changing the position of the side chain the $\pi-\pi$ stacking and aggregation behavior of the DPP can be influenced, which in turn changes its optical and electrical properties in thin films.

### 4.2 Optical properties of pure DPPs

DPP(3), DPP(4), and DPP(5) were synthesized using a Suzuki reaction from 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione and thiophene boronic esters with hexyl side chains on the 3, 4 or 5 position. Figure 2 shows the normalized UV-vis absorption spectra of the
Influence of the side chain position on aggregation and solar cell performance of DPPs

different molecules in chloroform solution and in film. The films were spin cast from chloroform and thermally annealed to reach equilibrium conditions. Only small differences were observed before and after annealing. The position of the hexyl chain has little influence on the band gap of the molecule and absorption spectra in solution are very similar (Figure 2a). The molar absorption coefficient of the three DPP molecules was identical within experimental error. The absorption spectra of DPP(4) and DPP(5) overlap perfectly, while a small blue shift can be seen for DPP(3). This shift might be a result of a minor difference in planarity caused by steric hindrance of the side chain which is very close to the $\pi$-conjugated core.

Similar to other $\pi$-conjugated molecules the DPPs stack upon aggregation in film, which induces a change in electronic structure and hence the optical absorption. Depending on the position of the side chain, the absorption in film is quite different (Figure 2b). The maximum of absorption significantly shifts to the blue for DPP(4), while a less intense absorption peak is found at higher wavelengths when compared to the spectrum in solution. These changes indicate that DDP(4) forms an $H$-type aggregate. In contrast, DPP(3) shows a clear red shift of the absorption maximum when going from solution to film. This suggests a $J$-type aggregate. For DDP(5) the
changes are in between those of DPP(3) and DPP(4). The formation of different types of aggregates in film is supported by the photoluminescence spectra and lifetimes shown in Figure 3. The photoluminescence maximum is found at much lower energy for DPP(4) and the lifetime is much longer compared to DPP(3) and DPP(5). For all DPPs identical lifetimes were observed for the emission at 840 nm (Figure 3b) and at 725 nm, indicating that emission at both wavelengths originates from the same species. The photoluminescence intensity of DPP(3) is a factor 10 higher than of both other molecules and its fluorescence spectrum has as fairly small Stokes’ shift. The longer lifetime of DPP(4) is consistent with the fact that emission from the low energy exciton coupled state in a H-type aggregate has a reduced probability and shows that the reduced fluorescence intensity is not due to quenching. Likewise, the higher photoluminescence intensity and shorter lifetime of DPP(3) is consistent with a dipole-allowed low energy transition, characteristic for a J-type aggregate. In J-type aggregates exciton diffusion is faster than in H-type aggregates, because the lowest energy excitation is stronger, and hence the Förster transfer is enhanced.\(^\text{22}\) The situation for DPP(5) seems to be more complex. Compared to DPP(3) the fluorescence intensity is less and the lifetime is shorter, but also the Stokes’ shift is much larger. It cannot be excluded that the reduced intensity and shorter lifetime of DPP(5) is due to quenching by an impurity.

4.3 Solar cells

The active layers of the solar cells were made by spin casting a 2:1 mixture of the DPP molecule with [6,6]-phenyl-C\(_{71}\)-butyric acid methyl ester ([70]PCBM). When [6,6]-phenyl-C\(_{61}\)-butyric acid methyl ester ([60]PCBM) was used, similar results were obtained. Here only the results obtained with [70]PCBM are shown. The active layers were deposited from chloroform and thermally annealed for 1 minute at 100 °C after evaporation of the back contact. The use of different donor-acceptor ratios, solvents, and solvent additives was investigated, but did not lead to improved solar

\[\text{Figure 3.} \quad \text{(a) Photoluminescence spectra and (b) Time-resolved photoluminescence intensity recorded at 840 nm and fitted lifetimes for DPP(3), DPP(4), and DPP(5) thin films.}\]
Influence of the side chain position on aggregation and solar cell performance of DPPs

cell efficiencies. Longer annealing times or higher temperatures did not improve the overall device efficiencies. The $J-V$ curves of the best solar cells made are shown in Figure 4 before and after thermal annealing. In Table 1 the device characteristics of these cells are given. For all solar cells the fill factor (FF) and current density ($J$) through the active layer in forward bias increases upon annealing, both observations are indicative of improved charge transport through the active layers. The short circuit current ($J_{sc}$), however, increases twofold for DPP(3), 1.4 times for DPP(4), while it decreases for DPP(5) active layers. These changes relate to the different type of aggregation and morphology of the photoactive layers for the three DPP molecules. This will be further investigated in paragraph 4.5 and 4.6 by characterization of the blend films.

**Figure 4.** $J-V$ curves of the best solar cells of DPP(3), DPP(4), and DPP(5) blended with [70]PCBM in a 2:1 weight ratio, as-cast and after 1 minute annealing at 100 °C (open symbols in dark and closed symbols under illumination).

**Table 1.** Solar cell characteristics of the best solar cells of DPP(3), DPP(4), and DPP(5) blended with [70]PCBM in a 2:1 weight ratio, as cast and after 1 minute annealing at 100 °C.

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<td>5.30</td>
<td>0.79</td>
<td>0.45</td>
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</tr>
</tbody>
</table>
Chapter 4

The external quantum efficiency (EQE) of the cells (Figure 5) shows several characteristics that can directly be related to the optical absorption of the DPP molecules in thin films (Figure 2b). The EQEs change only slightly after annealing (Figure 5). This indicates that the molecules are already in an aggregated state in the as-cast active layers and that upon annealing morphology changes, for example due to growth of the aggregates.

4.4 Optical properties of the blend films

To investigate aggregation, crystallization, and morphology evolution in the blend films absorption and photoluminescence measurements are used, complemented with atomic force microscopy (AFM), transmission electron microscopy (TEM) and diffraction. Absorption and photoluminescence spectra were measured for mixed films of the DPPs with [70]PCBM on a PEDOT:PSS covered glass slide (Figure 6 and 7). The layer of PEDOT:PSS was approximately 30 nm thick and was used to ensure identical film formation as for the solar cells.

Figure 5. EQE curves of the best solar cells of DPP(3), DPP(4), and DPP(5) blended with [70]PCBM in a 2:1 weight ratio, as-cast (open symbols) and after 1 minute annealing at 100 °C (closed symbols).

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Figure 6. Absorption spectra of DPP:[70]PCBM blend films in a 2:1 weight ratio, as-cast, after 24 hours at room temperature and after 1 minute annealing at 100 °C.
For each DPP:[70]PCBM blend two identical films were prepared, for one absorption was measured directly after spin casting (as-cast) and again after annealing at 100 °C. The other films were kept at room temperature (RT) in dark and measured several times to investigate the kinetics of aggregation of the DPPs. Figure 6 shows the absorption of the films as-cast, after annealing at 100 °C and after 24 hours ageing at RT for the three blends. In the blend of DPP(5):[70]PCBM only small changes are observed in absorption spectra, indicating that DPP(5) readily crystallizes during film formation and the aggregation only changes slightly upon ageing or heating of the film. For the DPP(4):[70]PCBM blend film changes in the absorption spectra are larger, but some aggregation is already observed in the as-cast samples. This is in sharp contrast to the DPP(3):[70]PCBM blend, which seems to be in an amorphous state directly after casting and changes are significant upon annealing. The kinetics at room temperature is very slow for DPP(3); the absorption only shows significant changes after 24 hours. After three days the absorption of DPP(3):[70]PCBM blend was still not the same as the annealed film, whereas after 7 hours of RT aging in dark the absorption of the DPP(4):[70]PCBM shows little difference to the 24 hours aged film. From these absorption measurements it can be concluded that the stacking of the DPPs in presence of [70]PCBM has different kinetics depending on the position of the side chain.

As mentioned, the current through the active layer of the solar cells in forward bias increases upon annealing (Figure 4). After annealing the injection currents through the layer are about equal, but when looking more carefully Figure 4 reveals that the change is smallest for DPP(5), larger for DPP(4), and the largest difference is found for DPP(3). This directly correlates to the initial crystallization of the DPPs in the blend films that is observed in the absorption measurements (as-cast samples in Figure 6).

It should be noted that for the DPP(3):[70]PCBM solar cells the EQE of the as-cast sample already shows aggregation of the DPP (Figure 5), this is due to the fact that there is some time in between the spin casting of the sample and the measurements of the finished solar cells. Also some aggregation can be caused by warming-up of the device by the lamp or current going through the active layer during J-V measurements.

Aggregation of the DPPs was also investigated using near-infrared photoluminescence for the as-cast and annealed blend films (Figure 7). For the as-cast films most of the luminescence which was observed for the pristine films was quenched. When annealed, the luminescence increases significantly for all blends. The shape of the luminescence spectrum after annealing is identical to that of the pure films of the DPPs (Figure 3a). This indicates that the initial morphology is very fine mixed and phase separation into pure phases occurs upon annealing.
4.5 Crystallization in the blend films

Phase separation can sometimes also be observed by measuring the surface topology using atomic force microscopy (AFM) on the active layers (Figure 8). The as-cast films are relatively smooth and show little surface features. For all samples the surface roughness increases upon thermal annealing and, especially for DPP(3):[70]PCBM and DPP(5):[70]PCBM blends, formation of crystallites on the surface are clearly visible. Similar behavior has also been observed in pristine films.

Figure 7. Photoluminescence spectra of the photo-active layers as-cast (lines) and after annealing (symbols).

Figure 8. AFM height images for as-cast (a,b,c) and annealed (d,e,f) blends of DPP(3):[70]PCBM (a,d), DPP(4):[70]PCBM (b,e) and DPP(5):[70]PCBM (c,f). Size of the images is 1 by 1 μm, height scales are 10 nm (a,b,c,e,f) and 30 nm (d).
of DPP-based oligophenylenethiophenes. The surface of the DPP(4):[70]PCBM blend shows similar features as-cast and after annealing, which is due to changes in the as-cast sample during the AFM measurement, confirmed by a color change of the film during the measurement. Again this indicates that the kinetics of aggregation of DPP(4) is very fast compared to the other DPPs. The formation of crystals on the surface is not expected for the solar cell active layers, since for solar cell fabrication the annealing step is applied after the metal back contact is deposited on top of the active layer which alters the surface energy significantly.

Absorption, photoluminescence, and AFM measurements show that the DPPs aggregate upon aging and annealing. Next to that it is known that PCBM crystallizes upon heating, which can improve the performance of a polymer solar cell. Using small molecules instead of polymers in the active layer introduces additional crystallization of the donor component. The crystallization behavior of both components in the blend films can be visualized using diffraction techniques such as electron diffraction.

![Figure 9. Integrated electron diffraction spectra of DPP(3), DPP(4), and DPP(5) films, pristine and blends with [70]PCBM, as-cast and after 1 minute annealing at 100 °C. The asterisk indicates diffraction of the [70]PCBM.](image)

Electron diffraction patterns were measured for pure films of the DPP small molecules and for the blend films with [70]PCBM as-cast and after annealing. The diffraction patterns were radially integrated to obtain diffraction spectra (Figure 9). Increase in both DPP and [70]PCBM crystallinity upon annealing is observed in these spectra. Again it is observed that DPP(3) initially is not crystalline when cast with [70]PCBM, while for DPP(4) and DPP(5) some weak reflections can be seen. After thermal annealing the reflections corresponding to the pure crystalline DPPs are observed in the diffraction spectra for all blends. Simultaneous crystallization of [70]PCBM is most clear from the blend with DPP(3), indicated by reduction of the width of the [70]PCBM diffraction ring. In the other spectra the [70]PCBM diffraction overlaps with diffraction of the DPPs, making it more difficult to see.
Lattice fringes of nanoscopic crystals have been visualized in bright-field TEM for \( \pi \)-conjugated small molecules.\(^{12}\) Lattice fringes were successfully imaged for DPP(5) in the blend films, with a d-spacing of about 1.9 nm (Figure 10). These large \( d \)-spacings in crystallites are found in the small \( q \)-range in diffraction mode. Figure 11 shows the electron diffraction in the small \( q \)-range for all pure DPP samples. The peak that corresponds to the observed crystal fringes is located at \( q \approx 0.49 \text{ nm}^{-1} \). This value does not correspond exactly to the distance observed in bright field, possibly because the analysis of the electron diffraction patterns is less accurate for small \( q \)-values. The diffraction patterns in Figure 11 show that the lattice spacing is largest for DPP(5), while the typical distance between the lattice planes is much smaller for DPP(3) and DPP(4) with \( q = 0.66 \text{ nm}^{-1} \) and \( 0.69 \text{ nm}^{-1} \) respectively. The smaller distance and the fact that these samples are very sensitive to the electron beam\(^{26,27}\) preclude imaging lattice fringes for DPP(3) and DPP(4). Direct evidence for phase separation upon annealing is found in the TEM images in Figure 10, which show small crystallites of DPP(5) in the as-cast DPP(5):[70]PCBM blend film, that grow significantly when the film is annealed.

Figure 10. Bright-field TEM images and diffraction patterns of active layers consisting of DPP(5) and [70] PCBM in a 2:1 weight ratio, as cast and after 1 minute annealing at 100 °C.

Figure 11. Integrated electron diffraction spectra of pristine DPP(3), DPP(4), and DPP(5) films in the lower \( q \)-range.
Additional to TEM and electron diffraction measurements, grazing incidence wide angle X-ray scattering (GIWAXS) was measured on the pristine films and annealed DPP:[70]PCBM blends (not shown). In general these measurement show that the stacking of the DPPs is less ordered when mixed with [70]PCBM. Further the GIWAXS data shows numerous reflections that, however, are difficult to analyze in detail without knowing the crystal structure of the DPP molecules. The extent of crystallization of the DPP molecules in the blends with [70]PCBM is difficult to determine. Looking at the intensities of the reflections in Figure 9 crystallization of the annealed blend films seems to decrease going from DPP(3) and DPP(4) to DPP(5). Since crystallinity, ordering and charge mobility are related, the higher crystallization of DPP(3) and DPP(4) compared to DPP(5) is consistent with the higher FF in the solar cells (Table 1). It is surprising to note that in the blend films the kinetics of aggregation of the DPPs seems to be inversely related to the amount of ordered crystallization that is found in the final annealed films.

4.6 Influence of aggregation on solar cell behavior

Combining all techniques used to characterize the blend films, a correlation between solar cell performance and crystallization behavior was found. For the as-cast samples, the difference in charge transport through the active layers for the different DPPs can be related to the crystallinity of the DPP molecules. The performance in solar cells of the as-cast blends also depends on the amount of crystallization of the DPPs. The efficiency of the as-cast solar cells is the highest for the DPP(5):[70]PCBM, lower for DPP(4):[70]PCBM and lowest for DPP(3):[70]PCBM, which is in the same order as the degree of DPP crystallinity in the as-cast blend films.

Upon thermal annealing of all DPP:[70]PCBM films, both components crystallize, phase separation increases and morphology coarsens, which increases charge transport through the active layers and thereby the fill factor of the solar cells increases. Crystallite growth of DPP(5) has a negative influence on the short-circuit current, which decreases as a consequence of less interface area between donor and acceptor. The increase in short-circuit current for both other DPPs can be related to improved charge transport and the higher efficiency of charge generation from the charge transfer state at the interface, due to enhancement of dissociation in coarser morphologies.28,29

4.7 Tandem solar cells using DPP small molecules

Most organic tandem solar cells are made by either using solution processed polymer:fullerene active layers or by the evaporation of thin layers of small molecules. The advantage of the evaporated tandem solar cells is that there is precise control
over the exact composition of the active layers and the intermediate contact.\textsuperscript{30,31} In solution processed polymer tandem solar cells the layers are deposited from viscous solutions that have good film forming properties and are relatively forgiving in the processing of a large amount of layers on top of each other.\textsuperscript{21,32}

The use of the DPP small molecules in solution processed tandem solar cells was tested, to investigate the possibilities of processing layers of these small molecules from a low viscous, fast drying solution in a tandem device. In the tandem solar cell active layers of DPP(3) and DPP(4) with [70]PCBM are used, because these material combinations both benefit in performance from a mild annealing step and have the largest difference in absorption spectra (Figure 12).

![Figure 12. (a) EQE measurements of the DPP(3):[70]PCBM and DPP(4):[70]PCBM single junction cells and (b) the lay-out of the tandem solar cell.](image)

Tandem cells were made using a recombination layer that consists of a 30 nm thick layer of 4-5 nm ZnO nanoparticles, processed from isopropanol and a 20 nm layer of pH neutral PEDOT:PSS spin coated from water. A pH neutral PEDOT:PSS formulation needs to be used on top of the ZnO nanoparticles to prevent dissolution of the ZnO. Due to this pH neutrality, however, the work function of the obtained PEDOT:PSS layer is lower. This causes a loss in open circuit voltage ($V_{oc}$) of the active layer that is used on top if materials with a high ionization potential are used, such as these DPPs. To reduce this loss a very thin layer of Naion is applied between the pH neutral PEDOT:PSS and the DPP(3):[70]PCBM layer, by which the work function and hence the $V_{oc}$ that can be obtained increase.\textsuperscript{33,34} To be able to correctly compare the single junction solar cells with the tandem solar cell the DPP(3):[70]PCBM single junction cells are also prepared on pH neutral PEDOT:PSS and Naion. The results of all solar cells are given in Table 2.

The tandem solar cells show a high $V_{oc}$ of 1.57 V and a reasonable fill factor, indicating that the subcells are indeed series connected in this tandem solar cell. The total efficiency of the tandem is not higher than each of the single junctions though, due to the low current that can be extracted from the device which is caused by the
large overlap in absorption of the active layers. The $V_{oc}$ is not an exact summation of the voltages of the two subcells, indicating that there might be some losses in the recombination contact, the results show that working tandem solar cells can successfully be prepared using DPP-based small molecule active layers.

4.8 Conclusions

In this work we show that changing the position of a side chain is a means to control the aggregation and solar cell performance of $\pi$-conjugated molecules. The effect of the side chain position was studied using DPP-based small molecules with hexyl side chains on different positions of the outer thiophene ring. Though the side chain position has little influence on the absorption in solution, it changes the optical properties of the molecules in film. Using absorption, photoluminescence, and lifetime measurements it was shown that the molecules form an $H$-type aggregate when the side chain is on the 4-position, a $J$-type aggregate for the 3-position, while an intermediate orientation is found for the molecule with the alkyl chain in the 5-position.

Power conversion efficiencies up to 3.3% were obtained when the DPPs were blended with [70]PCBM in a bulk heterojunction solar cell. Large differences were observed in solar cell characteristics for the different DPPs. Especially the current that can be extracted from an active layer of DPP with [70]PCBM is differs with position of the side chain. Absorption, photoluminescence, diffraction, and electron microscopy show that the side chain position affects the molecular packing in the crystallites, varying from $H$-type to $J$-type, as well as the kinetics and ordering of DPP crystallinity in the blend films. These differences affect morphology and in the end efficiency and behavior of solar cells made with these DPP-based molecules. It was also shown that these small molecules can be used as active layers in solution processed tandem solar cells, obtaining a $V_{oc}$ of 1.57 V.

The fact that the small donor molecules tend to crystallize, sometimes in identifiable small domains, creates a new question with respect to the optimized morphology and its consequences for charge generation and charge transport in solution-processed molecule:fullerene cells as compared to polymer:fullerene

Table 2. Solar cell characteristics of the tandem and single junction devices, for the DPP(3):[70]PCBM cells, pH neutral PEDOT:PSS and Nafton were used as hole contact.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (mW/cm²)</th>
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</thead>
<tbody>
<tr>
<td>DPP(4):[70]PCBM</td>
<td>6.04</td>
<td>0.83</td>
<td>0.52</td>
<td>2.59</td>
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<tr>
<td>DPP(3):[70]PCBM</td>
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<td>Tandem Measured</td>
<td>2.62</td>
<td>1.57</td>
<td>0.42</td>
<td>1.72</td>
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</table>
cells in which the fullerenes intercalate in the polymer domains. The morphology reflected in the type of self-organization and crystallization of the molecules and the effect of that on the electronic properties (H- or J-type aggregate), the introduction of grain boundaries, and the interconnectivity of crystalline domains were shown to have profound effects on the optical and electrical properties of these materials that directly translate into performance of the corresponding solar cells. For future design and optimization of new small molecule materials for organic solar cells, detailed insights in the relation between molecular structure, processing, morphology, and performance for solution-processed small molecule solar cells will be required.

4.9 Experimental

Solar cell devices
Solar cells were prepared by spin casting PEDOT:PSS (Clevios P, VP Al4083) on pre-cleaned ITO patterned glass substrates (Naranjo substrates). The PEDOT:PSS layer was dried by heating at 120 °C for 20 minutes before deposition of the active layer. On top of the dried PEDOT:PSS the active layers were deposited by spin casting a mixture of the DPP small molecule with [70]PCBM (Solenne BV) in a 2:1 ratio from chloroform. A back contact of 1 nm LiF and 100 nm Al was evaporated in vacuum.

Tandem solar cells were obtained by solution processing an intermediate contact consisting of ZnO nanoparticles and PEDOT:PSS on the DPP(4):[70]PCBM active layer. The ZnO layer was spun from a solution of 10 mg/mL ZnO nanoparticles from isopropanol. The pH neutral PEDOT:PSS (Orgacon, Agfa) was diluted 1:1 with ultrapure water after which 0.2 mL/mL isopropanol was added to improve the wetting on the ZnO nanoparticles. Prior to spin casting the solution was filtered using a 5.0 μm Whatman Puradisc FP30 syringe filter.

A very thin layer of Nafluorinated ion-exchange resin, Aldrich) was applied by spin casting a 1:200 v/v diluted solution in ethanol. The DPP(3):[70]PCBM active layer was spun on top of that and the back contact was evaporated. Processing of the tandem solar cells was fully carried out in nitrogen atmosphere.

Annealing was performed on the finished devices after evaporation of the back contact in a nitrogen environment. Tandem cells were illuminated for one minute with UV light with a Spectroline EN-160 L/F 365 nm hand lamp from Spectronics Corporation. Device areas of 0.09 and 0.16 cm² were used, which provided similar results.

Characterization
Current-density versus voltage curves (J-V) were measured under simulated solar light (100 mW/cm²) from a tungsten–halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight using a Keithley 2400 source meter. The J-V curves of the tandem solar cells and the simultaneously prepared single junction cells were measured under illumination through a mask of smaller dimensions (0.0676 cm² for the 0.09 cm² cell and 0.1296 cm² for the 0.16 cm² cell) to the device area determined by the overlap of the ITO and Al electrodes, to avoid extra current generation due to the high lateral conductivity of the pH neutral PEDOT.
During EQE measurements the devices were contacted in a nitrogen filled box with a quartz window and illuminated through an aperture of 2 mm. Mechanically modulated (Stanford Research, SR 540) monochromatic (Oriel, Cornerstone 130) light from a 50 W tungsten halogen lamp (Osram 64610) was used as probe light, in combination with continuous bias light from a solid state laser (B&W Tek Inc. 532 nm, 30 mW). The intensity of the bias laser light was adjusted until short circuit current was obtained using a variable-neutral density filter. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Stanford Research Systems SR830).

Steady state photoluminescence spectra were recorded at room temperature using an Edinburgh Instruments FLSP920 double-monochromator luminescence spectrometer equipped with a nitrogen-cooled near-IR sensitive photomultiplier (Hamamatsu). All spectra were corrected for the spectral response of the monochromators and photomultiplier.

Time-resolved photo-luminescence measurements were performed on an Edinburgh Instruments LifeSpec-PS spectrometer using a 405 nm (3.06 eV) pulsed laser (PicoQuant PDL 800B) operated at 2.5 MHz with a pulse duration of 59 ps. For detection a Peltier-cooled Hamamatsu microchannel plate photomultiplier (R3809U-50) was used. Each intensity decay curve was fitted by a multi-exponential fit by convoluation of the instrument response function (IRF) using

\[ I(t) = \int_{-\infty}^{t} IRF(t') \sum_{i=1}^{n} A_i e^{-\frac{t-t'}{\tau_i}} \, dt' \]

where \( A_i \) is the amplitude of the \( i \)th component with a lifetime \( \tau_i \).

Transmission electron microscopy (TEM) and electron diffraction was performed on a Tecnai G² Sphera TEM (FEI) operated at 200 kV. Bright field TEM images were acquired under slight defocusing conditions (see also Ref 37). Electron diffraction patterns were integrated using ImageJ (1.43u) software with the Radial Profile plugin.

Thin films for absorption, photoluminescence, and AFM were prepared by spin coating on PEDOT:PSS coated glass substrates using the same conditions as for solar cell preparation. For TEM the films were processed on PEDOT:PSS, which was dissolved in water to create a free standing film that was transferred onto a TEM grid. Layer thicknesses were measured using a Veeco Dektak 150 Surface Profiler.
4.10 References

8. Loser, S.; Bruns, C. J.; Miyauchi, H.; Ortiz, R.C.; Facchetti, A.; Stupp, S. I.; Marks, T. J. Journal of the American Chemical Society 2011, 21, 8142
15. Press release Mitsubishi Chemical, June 2011
Influence of the side chain position on aggregation and solar cell performance of DPPs


Abstract

Solution processed small molecule solar cells combine the reproducibility of organic synthesis and purification with potentially cheap and fast solution processing of polymer solar cells. A new star-shaped molecule, TPADPP, consisting of a triphenylamine core with three diketopyrrolopyrrole-oligothiophene branches was found to reach power conversion efficiencies over 3% when combined with [60]PCBM or [70]PCBM. Compared to blends of TPADPP with [60]PCBM the light absorption and extracted current increases when [70]PCBM is used, but voltage and fill factor are significantly lower resulting in similar optimized efficiencies. The morphology of the active layer critically depends on the concentration of co-solvent that is used for the processing and large differences were found for layers with [60]PCBM and [70]PCBM. The TPADPP:[60]PCBM layer was used as a small bandgap subcell and combined with a complementary photoactive thiophene dendrimer blended with [70]PCBM as a wide bandgap subcell to fabricate a fully solution processed dendritic small molecule tandem solar cell in an inverted configuration. The performance of the tandem configuration exceeded that of the corresponding inverted single junction cells.
5.1 Introduction

In the past decade the synthesis of small bandgap $\pi$-conjugated polymers has attracted strong interest to increase the use of the solar spectrum in organic photovoltaics.$^{1,2}$ Appealing power conversion efficiencies (PCEs) up to $\sim$10% have been achieved by combing these novel small bandgap materials with complementary absorbing [70]PCBM in single junction bulk heterojunction solar cells or using these with [60]PCBM in tandem junction solar cells as the small bandgap subcell.$^{3-5}$ Small bandgap polymers generally consist of alternating electron donating and electron accepting units in the $\pi$-conjugated backbone.$^2$ Here the donor-acceptor approach is used in a star-shaped $\pi$-conjugated molecule (TPADPP, Figure 1) containing thiophenes as the donating and diketopyrrolopyrrole (DPP) as the accepting moieties and triphenylamine as a core. DPP is a planar bicyclic structure that provides strong $\pi-\pi$ stacking and is widely used to make efficient small bandgap polymers.$^6-8$ Solar cell active layers based on these DPP polymers are often processed from a solvent mixture containing chloroform and an additive such as 1,8-diiodooctane (DIO).$^9-11$ Without the additive, many solution processed DPP polymer:PCBM blends give rise to very coarse morphologies having large (>100 nm) PCBM domains in a polymer matrix, due to demixing that occurs during spin coating. This can be prevented by the use of an additive in which the PCBM and the donor material have a different solubility.$^{12,13}$ The amount of additive that is needed to produce a good morphology leading to the highest power conversion efficiencies is often between 1 to 5% DIO in chloroform.$^{14}$ The use of an additive to improve the morphology has been applied to a large variety of systems. Striking is the behavior of smaller molecules, that can be very different to that of polymers as shown by Sun et al. for the DTS(PTTh$_2$)$_2$ molecule, where an optimum morphology was found at 0.25% of DIO additive, reaching power conversion efficiencies of almost 7%.$^{15}$ In solution processed small molecule solar cells the choice of fullerene derivative, solvent, and additive play an important role in the morphology that is obtained by spin coating and with that the solar cell efficiency.

In this chapter the influence of the amount of DIO as processing additive in chloroform was investigated for TPADPP combined with the fullerene derivatives [70]PCBM and [60]PCBM in solar cells. It is found that the morphology and solar cell performance are strongly dependent on the DIO concentration, with important changes in short-circuit current, open-circuit voltage and fill factor. The TPADPP:[60]PCBM blends were further tested as photoactive layer in the small bandgap subcell of a solution processed small molecule tandem solar cell that uses a photoactive layer based on a thiophene dendrimer blended with [70]PCBM$^{16,17}$ in the wide bandgap subcell. The tandem cell was fabricated in an inverted device configuration and represents a first example of a small dendritic molecule solution processed tandem
cell featuring two different absorber layers. The inverted tandem devices showed an increased performance compared to the corresponding single junction cells.

5.2 Solar cells of TPADPP with [70]PCBM

TPADPP has a relatively small bandgap and has a maximum in UV-vis absorption at 662 nm in solution, which is red shifted to 687 nm in thin films (Figure 1). In the visible and UV region the absorption is small. To be able to use a larger part of the solar spectrum in the solar cells [70]PCBM is used as an acceptor, which has a higher absorption in the 400-600 nm wavelength region than [60]PCBM and complements the absorption of TPADPP. The active layers of the solar cells were made by spin casting a 1:2 mixture of TPADPP with [70]PCBM from chloroform. As mentioned DPP based materials often show coarse phase separation when processed from a solution of pure chloroform. This can be circumvented by adding DIO as a co-solvent.6,12,14,15 The effect of different amounts of DIO in the spin casting mixture on solar cell performance was tested for the TPADPP molecule (Table 1 and Figure 2).

The behavior of the active layer in the solar cells is very similar to what has been observed for different DPP polymers, such as PDPPTPT.6 The J-V curves in Figure 2b clearly show extremely high bias dependent current extraction for the

Table 1. Solar cell characteristics of active layers of TPADPP and [70]PCBM in a 1:2 weight ratio processed from different solvent mixtures.

<table>
<thead>
<tr>
<th>Solvent mixture</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (mW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure chloroform (CF)</td>
<td>3.81</td>
<td>0.71</td>
<td>0.36</td>
<td>0.96</td>
</tr>
<tr>
<td>15 μL/mL DIO in CF</td>
<td>6.22</td>
<td>0.64</td>
<td>0.49</td>
<td>1.94</td>
</tr>
<tr>
<td>50 μL/mL DIO in CF</td>
<td>10.10</td>
<td>0.61</td>
<td>0.51</td>
<td>3.16</td>
</tr>
<tr>
<td>250 μL/mL DIO in CF</td>
<td>10.50</td>
<td>0.60</td>
<td>0.51</td>
<td>3.15</td>
</tr>
</tbody>
</table>
solar cell processed without DIO, resulting in low short circuit current ($J_{sc}$) and fill factor (FF). Upon addition of more DIO the bias dependence decreases, resulting in an increase in $J_{sc}$ and FF until a plateau is reached. The open circuit voltage ($V_{oc}$) drops with addition of DIO and levels off at a $V_{oc}$ of about 0.60 V. As a consequence relatively high amounts of DIO are required to reach the highest efficiencies. The best PCE is about 3.1% when using more than 5 vol% DIO. EQE measurements (Figure 2c) clearly show the contribution of TPADPP in the 600-700 nm region and of [70]PCBM in the 400-600 nm region to the photocurrent. The maximum of the EQE shows a blue shift with increasing DIO concentration in the processing solvent. The blue shift suggests that in the DIO-processed films less aggregation of TPADPP occurs.

Bright field TEM images show large differences in morphology of the active layers. Figure 3a shows that the morphology obtained from pure chloroform solution is very coarse and has large domains that are rich in [70]PCBM. In these coarse phase separated morphologies only a small amount of the photogenerated excitons reach the donor-acceptor interface and, hence, the current that can be extracted is low resulting in poor device performances. The morphology and with that the performance can be improved by the addition of DIO. DIO is a better solvent for fullerenes than it
Morphology control in star-shaped DPP-based small molecule solar cells

is for DPP-based materials and evaporates slower than chloroform. By adding DIO to the spin casting mixture phase separation is strongly suppressed and finer mixed morphologies are obtained. The TEM images in Figure 3 show that already at 1.5 vol.% of DIO the morphology has changed dramatically and that 5 vol.% of DIO, a fibrilar structure is formed that is likely associated with TPADPP. The finer mixed morphology leads to an increase in the number of excitons that dissociate in charge carriers, increasing the photocurrent. The fact that there is a simultaneous increase in fill factor indicates that also charge transport is improved. As a tentative explanation it can be argued that the concentration of TPADPP and [70]PCBM in each other’s phases is probably small in the coarse morphology (Figure 3a) such that one type of charge carrier becomes trapped and cannot easily be collected. For a better mixed morphology percolation of charges is easier. We note that the change in morphology that governs the change in solar cell performance for TPADPP:[70]PCBM is very similar to what was previously found for PDPPTPT:[70]PCBM.6

5.3 Solar cells of TPADPP with [60]PCBM

In a tandem solar cell two spectrally complementary absorber layers are combined to reduce thermalization and transmission losses by absorbing the high energy photons in a wide bandgap front cell and low energy photons in a small bandgap back cell.3,5,7,19 TPADPP has a relatively small bandgap and could be used for making the small bandgap back subcell. For a tandem configuration, however, it is not advantageous to combine TPADPP with [70]PCBM as one would rather absorb the high energy photons in the wide bandgap front cell. To develop a small bandgap subcell for a solution processed tandem solar cell TPADPP was combined with the less absorbing [60]PCBM derivative.

Single junction cells of TPADPP with [60]PCBM were newly optimized varying the amount of DIO that is used in the spin coating mixture. This is necessary because
the morphology of the active layer depends on the relative solubility of the materials and the solvent mixture used and hence can be different when using a different fullerene derivative. The active layers of the solar cells were made by spin casting a 1:2 mixture of TPADPP with [60]PCBM from chloroform and DIO. Interestingly, the maximum power conversion efficiency of 3.2% that is reached for TPADPP:[60]PCBM after optimization is slightly higher than that of TPADPP:[70]PCBM, despite the fact that [60]PCBM contributes less to the charge generation due to its lower absorption coefficient.

Table 2 lists the characteristics of the solar cells prepared using different amounts of DIO as an additive to the chloroform solution. By increasing the amount of DIO the $V_{oc}$ of the solar cell decreases. This was also observed for the cells with [70]PCBM and for other DPP molecules and polymers. Interestingly the trend in short circuit current density ($J_{sc}$) and fill factor (FF) is not the same as observed for the active layer with [70]PCBM. Here $J_{sc}$ first shows a very fast decrease after which it slowly increases again with the amount of DIO, a plateau was not observed in this series. The FF reaches a value of 0.62 at a DIO concentration of ~0.5%, which is high compared to many small molecule solar cells, but not exceptional. The general trend in FF is opposite to the trend in current, suggesting that there is an inverse relation between these characteristics (Figure 4a). Combined the $V_{oc}$, $J_{sc}$ and FF result in two solvent composition regions where the power conversion efficiency (PCE) is the highest.

The shape of the EQE vs. wavelength of the different solar cells is similar for all photoactive TPADPP:[60]PCBM layers (Figure 4c). It is likely that the variation in solar cell efficiency is related to the morphology and bright field TEM was performed on the different active layers (Figure 5). TEM shows that the coarse phase separation that occurs when TPADPP and [70]PCBM (Figure 3a) are cast from pure chloroform.

<table>
<thead>
<tr>
<th>Solvent mixture</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (mW/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure chloroform (CF)</td>
<td>8.1</td>
<td>0.75</td>
<td>0.53</td>
<td>3.19</td>
</tr>
<tr>
<td>2 μL/mL DIO in CF</td>
<td>8.2</td>
<td>0.75</td>
<td>0.53</td>
<td>3.25</td>
</tr>
<tr>
<td>3 μL/mL DIO in CF</td>
<td>8.0</td>
<td>0.72</td>
<td>0.57</td>
<td>3.23</td>
</tr>
<tr>
<td>4 μL/mL DIO in CF</td>
<td>6.8</td>
<td>0.70</td>
<td>0.62</td>
<td>2.91</td>
</tr>
<tr>
<td>5 μL/mL DIO in CF</td>
<td>4.7</td>
<td>0.69</td>
<td>0.62</td>
<td>2.03</td>
</tr>
<tr>
<td>10 μL/mL DIO in CF</td>
<td>5.0</td>
<td>0.66</td>
<td>0.57</td>
<td>1.89</td>
</tr>
<tr>
<td>20 μL/mL DIO in CF</td>
<td>7.0</td>
<td>0.64</td>
<td>0.56</td>
<td>2.50</td>
</tr>
<tr>
<td>50 μL/mL DIO in CF</td>
<td>8.3</td>
<td>0.63</td>
<td>0.53</td>
<td>2.78</td>
</tr>
</tbody>
</table>
Morphology control in star-shaped DPP-based small molecule solar cells

Figure 4. (a) Short circuit current and fill factor (FF) versus the amount of DIO in chloroform in the solution used for spin casting. (b) J-V curves and (c) experimental EQE of the TPADPP:[60]PCBM (1:2 w/w) active layer solar cells processed using different amounts of DIO in chloroform.

Figure 5. Bright field TEM images of the active layer of TPADPP:[60]PCBM (1:2 w/w) solar cells cast from a) pure chloroform, and different DIO concentrations in chloroform being: b) 4 μL/mL, c) 5 μL/mL, d) 10 μL/mL, e) 20 μL/mL and f) 50 μL/mL.
does not occur for TPADPP and [60]PCBM (Figure 5a). The dramatic differences between the morphologies obtained for TPADPP blended with [60]PCBM and [70] PCBM is not unique, and shows that subtleties in processing are important. We note that the solubility of [70]PCBM is higher than that of [60]PCBM and that solubility, alone, is not the explanation for this phenomenon.

From Figure 5a-c it becomes clear that the initial morphology from pure chloroform is very fine and more phase separation occurs when a small amount of DIO is added to the mixture. This leads to a smaller interface area between the two materials, yielding lower $J_{sc}$ and higher FF. Upon addition of even more DIO (Figure 5d-f) also here fibrillar structures start to be formed and eventually again a very fine phase separation is obtained giving a high $J_{sc}$ but a lower FF. These fibrils were also found in TPADPP:[70]PCBM, but this change in morphology and the influence of the small amounts (below or equal to 5 μL/mL) was not observed before.

5.4 Solution processed small molecule tandem solar cell

In tandem solar cells two active layers are combined that have complementary absorption spectra. The TPADPP molecule combined with [60]PCBM is a good candidate for a small molecule tandem solar cell, since it has a specific absorption in the high wavelength region of the solar spectrum and reaches efficiencies of around 3%. The choice in solution processable wide bandgap small molecules for organic solar cells, however, is rather limited since most of the recent more efficient materials have small bandgaps and absorb in the same region as the TPADPP. One of the more efficient materials with the desired absorption is the third generation thiophene dendrimer 42T (Figure 6), which can reach efficiencies of 2.8% when it is combined with [70]PCBM having a high $V_{oc}$ of 0.96 V, FF up to 0.49, and $J_{sc}$ around 6.0 mA/cm$^2$.

![Molecular structure of 42T and EQE measurement of a solar cell using an active layer of 42T and [70]PCBM.](image-url)
The absorption spectra of the TPADPP:[60]PCBM and 42T:[70]PCBM active layers are shown in Figure 7a and show reasonable spectral complementarity. These active layers were combined to make a solution processed tandem solar cell in a regular device architecture as shown in Figure 7b. The two subcells in the tandem must be connected by an intermediate contact in which the electrons of the front subcell recombine with the holes from the back subcell without energy loss. The voltage of a series connected tandem cell is the sum of the voltages of the subcells and, in first approximation, the current through the subcells equals the lowest current of the two subcells. To fabricate a solution processable intermediate contact a layer of ZnO nanoparticles can be combined with a PEDOT:PSS layer. To fabricate such cell in the normal device configuration a pH neutral PEDOT:PSS formulation must be used on top of ZnO nanoparticle layer to prevent dissolution of the ZnO. Due to this pH neutrality, however, the work function of the PEDOT:PSS layer is reduced. This causes a loss in $V_{oc}$ of the active layer that is used on top if materials with a high ionization potential are used, such as TPADPP. To reduce this loss a very thin layer of Nafion can be applied between the pH neutral PEDOT:PSS and the second active layer. Upon application of a thin layer of Nafion the work function of the underlying anode is increased and by this the $V_{oc}$ that can be obtained from the second subcell also increases.

Following this strategy, normal configuration tandem cells were made using a recombination layer that consists of a 30 nm thick layer of 4-5 nm ZnO nanoparticles, processed from isopropanol or acetone and a 20 nm layer of pH neutral PEDOT:PSS spin coated from water. To reduce the loss in $V_{oc}$ of the TPADPP:[60]PCBM active layer caused by the use of pH neutral PEDOT:PSS a very thin layer of Nafion is applied on top of the PEDOT:PSS.

The TPADPP:[60]PCBM subcell was processed from 0.4 vol% DIO in chloroform, which has the highest fill factor and still provides a relatively high short circuit current (Table 2). The 42T:[70]PCBM active layers were spin cast from chlorobenzene in a weight ratio of 1:2, resulting in very smooth layers with a thickness of 120 nm.
Although the surface of the 42T:[70]PCBM layer was very smooth, processing the intermediate contact of ZnO nanoparticles and pH neutral PEDOT:PSS on top resulted in very rough and only partly covered layers. This was caused by poor wetting behavior of the ZnO nanoparticle solution. The nanoparticle solution is very hydrophilic, whereas the front cell is hydrophobic and clustering of the nanoparticles occurred. The wetting of the ZnO nanoparticles on the surface of the 42T:[70]PCBM layer did not improve by using a mild plasma treatment, using a different solvent, or applying a very thin layer of PFN on the front cell. Due to the roughness of the ZnO layer, the integrity of the intermediate contact was not optimal and in all tandem devices the PEDOT:PSS layer in the recombination layer made contact with the front cell resulting in bad performance. In Figure 8 typical $J-V$ and EQE curves are shown for the single junction reference devices and tandem solar cell. The characteristics of all normal architecture tandem devices resemble those of the TPADPP:[60]PCBM back cell, indicating that the front cell merely acts as a hole transport layer due to contact between the front cell and the pH neutral PEDOT:PSS layer. In the tandem device the 42T:[60]PCBM layer acts as an optical filter which reduces the short circuit current of the back cell in the low wavelength region (Figure 8b). In total this tandem can be seen as a single junction solar cell with a hole contact consisting of PEDOT:PSS, 42T:[70]PCBM, and PEDOT:PSS, which leads to suboptimal charge collection and low current in forward bias as evidenced by the S-shape in the $J-V$ curve of the tandem (Figure 8a). Due to the effects of the bad wetting of the ZnO nanoparticles the total efficiency of the tandem is lower than that of both reference cells.

### 5.5 Inverted solution processed small molecule tandem

To circumvent the problems encountered in making a closed and smooth ZnO layers in normal architecture cells, it is possible to use an inverted configuration.
In an inverted tandem device structure, the polarity is switched and the order of the layers in the intermediate contact is reversed. Since ZnO can be processed also on acidic PEDOT:PSS, the use of a pH neutral PEDOT:PSS layer is not needed. In the inverted configuration the polarity of the devices is reversed. This can be accomplished by using a low work function bottom contact and a high work function top contact. To switch the polarity ITO/ZnO was used as the bottom contact and MoO$_3$/Ag was evaporated as top contact. First inverted single junction solar cells were prepared using the 42T:[70]PCBM and TPADPP:[60]PCBM active layers from chlorobenzene and 4 $\mu$L/mL DIO in chloroform respectively. The solar cell characteristics and the EQEs of the inverted single junction solar cells are shown in Table 3 and Figure 9b. A significant difference in efficiency was observed for the TPADPP:[60]PCBM layer compared to the normal architecture devices, especially the $J_{sc}$ and FF of the cells were lower. As was shown in the first part of this chapter, the morphology of the layer is very critical for the performance and since the wetting of the solution will be different on different substrates this is possibly a reason of the lower performance but of course the charge transport layers and electrodes (ZnO/ITO vs. LiF/Al for electrons and MoO$_3$/Ag vs. PEDOT:PSS/ITO for holes) have also changed. Inverted tandem solar cells were made using these active layers without further optimization of the single junctions.

![Figure 9.](a) Device layout of the inverted tandem solar cell. (b) Experimental EQE of the single junction inverted solar cells.

In the inverted tandem devices the intermediate contact consists of a 45 nm layer of PEDOT:PSS and a 30 nm layer of ZnO nanoparticles, which are applied in reversed order compared to the normal architecture (Figure 9a). The PEDOT:PSS is spin cast on top of the smooth 42T:[70]PCBM layer and the wetting of the ZnO nanoparticles on this layer is good. This approach resulted in a well defined intermediate contact producing tandem devices with a $V_{oc}$ of up to 1.44 V after UV illumination for 1 minute (Figure 10a, Table 3). In Figure 10b the EQE measurements are given for this inverted tandem solar cell. When the EQE of the tandem is measured without bias illumination only the overlapping absorption of the two subcells is visible.
(diamond symbols), since the cells are series connected and the current through the subcells is equal. In the low wavelength region the TPADPP:[60]PCBM subcell is current limiting, while in the high wavelength region the 42T:[70]PCBM subcell determines the measured current. To be able to measure the subcells, continuous bias illumination is used to increase charge generation in one of the subcells in such a way that the other subcell is current limiting over the entire spectrum and can be measured.\textsuperscript{30} Green or red flood light was used as bias illumination and by convolution of the measured EQE with the solar spectrum the current generated by the subcells was determined.

The $J$-$V$ curves of the two single junction cells were measured under appropriate reduced light intensity such that the $J_{sc}$ matched the current generated in the tandem by the subcells as inferred from integrating the EQE spectra of the subcells. With these the $J$-$V$ of the tandem can be mathematically constructed assuming a loss free intermediate contact and compared to the experimental curve of the real tandem (Figure 10a and Table 3, Tandem constructed).

Table 3 shows the solar cell characteristics of the constructed tandem and the measured tandem and the single junction devices. A large difference is found in the $J_{sc}$ of the tandems. This can be explained by the method used to determine the

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>42T:[70]PCBM</td>
<td>6.24</td>
<td>0.89</td>
<td>0.39</td>
<td>2.14</td>
</tr>
<tr>
<td>TPADPP:[60]PCBM</td>
<td>4.86</td>
<td>0.66</td>
<td>0.48</td>
<td>1.54</td>
</tr>
<tr>
<td>Tandem Measured</td>
<td>3.79</td>
<td>1.44</td>
<td>0.41</td>
<td>2.25</td>
</tr>
<tr>
<td>Tandem Constructed</td>
<td>4.30</td>
<td>1.50</td>
<td>0.42</td>
<td>2.72</td>
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</table>
$J_{sc}$ of the subcells, which overestimates the current since it is measured at low light intensity and without correction for the voltage over the subcells. This electrical bias correction was not possible due to large variations that were observed in the $V_{oc}$ of the single junction reference devices. The $V_{oc}$ is not as high as could be expected from the reference cells. In the $J-V$ of the measured tandem a slight S-shape can be observed and the dark EQE measurement (Figure 10b) of the tandem shows some leakage through the front cell. These observations indicate that some losses exist in the recombination contact.

It should be noted, however, that the TPADPP:[60]PCBM active layer shows a significantly lower performance in inverted geometry, dropping from almost 3% in normal devices to 1.5% in inverted. Together with the 42T:[70]PCBM layer, which is also less efficient, it leads to inverted tandem solar cells with only moderate performance. Though it is possible to make a tandem solar cells combining the 42T:[70]PCBM and TPADPP:[60]PCBM active layers, the results show that there is ample room for improvement which should predominantly be found in restoring the efficiencies of the inverted subcells to the level of the regular device configurations.

### 5.6 Conclusion

A new star-shaped DPP-based molecule (TPADPP) was combined with [60] or [70]PCBM in single junction solar cells, reaching efficiencies of more than 3%. The active layers of TPADPP with [70]PCBM show a dramatic change in morphology and increase in performance by the use of the co-solvent DIO. For TPADPP with [60]PCBM, on the other hand, rather efficient cells are already obtained without the use of co-solvent. Nevertheless, also for TPADPP with [60]PCBM small amounts of DIO in chloroform cause significant changes in the morphology of the active layer. Concomitantly, the short circuit current and the fill factor of the solar cells are influenced directly by the amount of phase separation that is obtained by adding DIO to the spin coating mixture.

Tandem solar cells were made combining TPADPP:[60]PCBM as the small bandgap subcell with 42T:[70]PCBM as the wide bandgap subcell in normal and inverted architecture. In the normal device architecture the wetting of the ZnO in the intermediate contact was not good enough to obtain a working tandem solar cell and the efficiency stayed below that of the individual subcells. Inverted tandem solar cells were made and in this case a $V_{oc}$ of 1.44 V was obtained and the total efficiency of the tandem was higher than that of the individual subcells. Electrical characterization showed that there was a small leakage over the front 42T:[70]PCBM subcell and that the intermediate contact induced small losses.
Chapter 5

5.7 Experimental

Materials
TPADPP was synthesized by M. Kirkus using a palladium catalyzed Suzuki reaction from triphenyl amine trisboronic ester and mono bromo TDPP(EH)TT(C_{12}).^{31} 42T was generously provided by Dr. C.-Q. Ma of the group of prof. dr. P. Bäuerle, Institute of Organic Chemistry II and Advanced Materials, Ulm University.^{16,17} [6,6]phenyl-C_{61}-butyric acid methyl ester ([60]PCBM) and [6,6]phenyl-C_{71}-butyric acid methyl ester ([70]PCBM) were obtained from Solenne BV. ZnO nanoparticles were obtained using the synthesis method described by Beek et al.^{32}

Solar cell devices
All solar cells were prepared using pre-cleaned ITO patterned glass substrates (Naranjo substrates). Normal architecture devices start with the application of a layer of PEDOT:PSS (Clevios P, VP Al4083). On top of this the different active layers were deposited by spin casting and finally 1 nm LiF and 100 nm Al were evaporated in vacuum as back contact. For inverted solar cells a ZnO layer was prepared on top of the ITO substrates from a precursor solution containing 0.5 M ethanolamine (ReagentPlus grade, Sigma-Aldrich) and 0.5 M zinc acetate dehydrate (98+, Aldrich) in anhydrous 2-methoxyethanol (99.8+, Sigma-Aldrich) that was annealed at 150 °C for 5 minutes. After application of the active layers 10 nm of MoO_{3} and 100 nm of Ag were thermally evaporated under vacuum as back contact. TPADPP:[70]PCBM and TPADPP:[60]PCBM active layers were obtained by spin casting a 1:2 ratio of TPADPP (8 mg/mL) and [70]PCBM or [60]PCBM from chloroform solvent mixture. The solvent mixtures were prepared in advance by filtering the 1,8-diodooctane (98%, Aldrich) using a 0.22 μm PTFE syringe filter and adding the appropriate volume to the chloroform. 42T:[70]PCBM active layers were prepared by spin casting a 1:2 ratio of 42T (8.5 mg/mL) and [70]PCBM from chlorobenzene. Normal architecture tandem solar cells were obtained by solution processing an intermediate contact consisting of ZnO nanoparticles^{32} and PEDOT:PSS on the 42T:[70]PCBM active layer. The ZnO layer was spun from a solution of 10 mg/mL ZnO nanoparticles from isopropanol or acetone. The pH neutral PEDOT:PSS (Orgacon, Agfa) was diluted 1:1 with ultrapure water after which 0.2 mL/mL isopropanol was added to improve the wetting on the ZnO nanoparticles. Prior to spin casting the solution was filtered using a 5.0 μm Whatman Puradisc FP30 syringe filter. A very thin layer of Nafion (perfluorinated ion-exchange resin, Aldrich) was applied by spin casting a 1:200 v/v diluted solution in ethanol. The TPADPP:[60]PCBM active layer was spun on top of that and the back contact was evaporated. Inverted architecture tandem solar cells were obtained by solution processing an intermediate contact consisting of PEDOT:PSS (Clevio P, VP Al4083) and ZnO nanoparticles^{32} on the 42T:[70]PCBM active layer. The ZnO layer was spun from a solution of 10 mg/mL in isopropanol in a nitrogen-filled glovebox on top of the PEDOT:PSS layer that was allowed to dry for about 15 minutes. We found that in nitrogen environment the wetting of the ZnO nanoparticles was improved. All other layers were processed in ambient conditions.
Device areas of 0.09 and 0.16 cm\(^2\) were used, which provided similar results. Tandem cells were illuminated for one minute with UV light with a Spectroline EN-160 L/F 365 nm hand lamp from Spectronics Corporation.

**Characterization**

EQE measurements were done in a homebuilt set-up, with the devices kept in a nitrogen filled box with a quartz window and illuminated through an aperture of 2 mm. Mechanically modulated (Stanford Research, SR 540) monochromatic (Oriel, Cornerstone 130) light from a 50 W tungsten halogen lamp (Osram 64610) was used as probe light, in combination with continuous bias light from a solid state laser (B&W Tek Inc. 532 nm, 30 mW) or a focused 50W Philips brilliantine halogen 12V lamp with dichroic reflector. The intensity of the bias laser light was adjusted using a variable-neutral density filter. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Stanford Research Systems SR830). For all the single junction devices, the measurement was carried out under representative illumination intensity (AM1.5G equivalent, provided by the 532 nm-laser).

Current-density versus voltage curves \( (J-V) \) were measured under simulated solar light (100mW/cm\(^2\)) from a tungsten–halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight using a Keithley 2400 source meter. No mismatch correction was done. For the single junction cells the accurate short-circuit current density \( (J_{sc}) \) was determined from the EQE by convolution with the AM1.5G solar spectrum.\(^9\) For the tandem solar cell measurements, the simulated solar light spectrum was tuned to provide appropriate illumination to each subcell. This was achieved by adjusting the voltage over the tungsten halogen lamp in such a way that both the wide bandgap and the narrow bandgap single junction reference cell gave the \( J_{sc} \) as determined from the EQE measurement. The \( J-V \) curves of the tandem solar cells and the inverted single junction cells were measured under illumination through a mask of smaller dimensions (0.0676 cm\(^2\) for the 0.09 cm\(^2\) cell and 0.1296 cm\(^2\) for the 0.16 cm\(^2\) cell) to the device area determined by the overlap of the ITO and Al electrodes, to avoid extra current generation due to the high lateral conductivity of the pH neutral PEDOT.\(^33\)

Transmission electron microscopy was performed on a Tecnai G\(^2\) Sphera TEM (FEI) operated at 200 kV. Bright field TEM images were acquired under slight defocusing conditions (see also Ref 34). To measure the active layers of the solar cells, the layer of PEDOT:PSS underneath was dissolved in water creating a free standing film of the active layer, which was transferred onto a TEM grid and allowed to dry. The absorption of the active layers was determined by spin casting on glass and measuring with a Perkin-Elmer Lambda 900 UV-Vis spectrometer. Layer thicknesses were measured using a Veeco Dektak 150 Surface Profiler.
5.8 References

23. Lin, Y.; Li, Y.; Zhan, X. Chemical Society Reviews 2012, 41, 4245
Morphology control in star-shaped DPP-based small molecule solar cells

Chapter 6
Solution processed polymer tandem solar cells using efficient small and wide bandgap polymer:fullerene solar cells

Abstract
Efficient complementary small and wide bandgap polymer:fullerene blends are used as subcells in a fully solution processed organic tandem solar cell. In single junction solar cells the PDPP5T:[60]PCBM and PCDTBT:[70]PCBM absorber layers reach power conversion efficiencies of 5.3 and 5.8%, respectively. Optimal layer thicknesses of these complimentary layers in a tandem configuration were determined using optical and electrical modeling. In the experimental tandem cell an efficiency of 7.0% was reached, while still a small resistive loss over the recombination layer is observed.

This chapter has been published:
6.1 Introduction

Solution processed organic photovoltaic cells are expected to contribute to the global energy problem by enabling potentially cheap roll-to-roll processing. By combining design and synthesis of new materials with advanced processing procedures the power conversion efficiency ($\eta$) that has been obtained in single junction polymer:fullerene bulk heterojunction solar cells increased to more than 9%.\(^1\) Even higher efficiencies have been reported for undisclosed materials.\(^2\) The efficiency that can be obtained in a solar cell with a single absorber layer is a tradeoff between the amount of photons that can be converted into current and the voltage that can be extracted. Realistic estimates of the maximum reachable efficiency for single junction organic solar cells devices are 10-12%,\(^3\) but this is not considered a fundamental limit.\(^4\) Many of the highest efficiency materials published have an optical bandgap of 1.55-1.75 eV and convert only part of the solar spectrum.\(^5\) The performance can be improved by using a tandem configuration, in which two different active layers with complementary absorption spectra work in concert.\(^6,7\) Compared to single junctions, tandem cells allow reduction of thermalization losses by absorbing high energy photons in a wide bandgap cell, and reduction of transmission losses by absorbing low energy photons in a small bandgap cell as was explained in Chapter 1.4. Proper material combinations for polymer tandem cells are, however, scarce, mainly because of a lack of small bandgap materials (1.2-1.5 eV) with very good performance.\(^8\) On top, most high-efficiency small bandgap polymer solar cells use [70]PCBM to enhance the absorption in the visible region,\(^9\) but for a tandem subcell the much weaker absorbing [60]PCBM is preferred in the small bandgap active layer, because it does not compete for the visible photons that should be absorbed in the wide bandgap cell. Here we demonstrate that a 7.0% efficient tandem solar cell can be made using an efficient small bandgap polymer:[60]PCBM layer with a complementary wide bandgap:[70]PCBM absorbing layer.

6.2 Materials and device structure

The top subcell contains a small bandgap diketopyrrolopyrrole-oligothiophene copolymer (PDPP5T, Figure 1) that provides 5.3% efficient solar cells in single junction cells with [60]PCBM, which is one of the best performing small bandgap polymers to date. PDPP5T has an optical bandgap of $E_g = 1.46$ eV and $M_n = 48$ kg/mol with polydispersity of 1.75. The PDPP5T:[60]PCBM layer is used to make a tandem cell that employs PCDTBT:[70]PCBM\(^10,11\) as the complementary wide bandgap absorber (Figure 1).
Solution processed polymer tandem solar cells using efficient small and wide bandgap cells

Tandem cells were made using an intermediate charge recombination layer that consists of a 30 nm thick layer of 4-5 nm ZnO nanoparticles, processed from isopropanol and a 20 nm layer of pH neutral PEDOT:PSS spin coated from water. The complete device stack is shown in Figure 1. The layers in this stack can be spin coated on top of each other without dissolving underlying layers. The schematic energy band diagram in Figure 1 is drawn using frontier energy levels of the polymers and fullerenes, and the quasi Fermi energy levels (dashed lines) to illustrate the working principle of a series connected tandem construction. The quasi Fermi energy levels align due to high doping of the intermediate contact.

6.3 Optimization of subcells

The performance of PDPP5T:[60]PCBM layers in solar cells was optimized for the composition and the processing conditions by using different mixing ratios and solvent mixtures. We found that PDPP5T:[60]PCBM layers with a 1:2 weight ratio, processed from chloroform with o-dichlorobenzene as co-solvent in a 9:1 volume ratio gave the best performance. The current density-voltage characteristics ($J-V$) and external quantum efficiency (EQE) of the optimized solar cells are shown in Figure 2.
and the characteristic parameters are collected in Table 1. PDPP5T:[60]PCBM cells reach $\eta = 5.3\%$ in simulated AM1.5G (100 mW/cm$^2$) solar light using 120 nm thin films. The EQE has an onset at 870 nm (1.42 eV) and reaches a maximum of 64% at 710 nm.

For the complementary wide bandgap ($E_g = 1.88$ eV) PCDTBT:[70]PCBM cells optimal performance was found for a 1:4 weight ratio and spin coating from o-dichlorobenzene with chlorobenzene as co-solvent in a 7:3 volume ratio.$^{11}$ Two different optimal layer thicknesses (80 and 210 nm) were identified, providing power conversion efficiencies of $\eta = 5.6$-5.8% (Figure 2 and Table 1). In these PCDTBT:[70] PCBM cells there is a tradeoff between fill factor (FF) and short circuit current ($J_{sc}$), while the open circuit voltage ($V_{oc}$) is constant.

Transmission electron microscopy (TEM) revealed a rather intimate mixing in both active layers (Figure 3). Phase separation was slightly more pronounced for the PDPP5T:[60]PCBM layer.

### 6.4 Optical modeling of tandem solar cell

To determine the layer thicknesses that give the best performance in a tandem cell, a series of single junction solar cells with different layer thickness was made using the optimized processing conditions and the cells were characterized in detail. For each thickness, the spectrally averaged internal quantum efficiency (IQE) was determined

**Table 1.** Characteristics of the best performing single junction solar cells.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120 nm PDPP5T:[60]PCBM</td>
<td>14.0</td>
<td>0.58</td>
<td>0.65</td>
<td>5.3</td>
</tr>
<tr>
<td>210 nm PCDTBT:[70]PCBM</td>
<td>12.3</td>
<td>0.90</td>
<td>0.52</td>
<td>5.8</td>
</tr>
<tr>
<td>80 nm PCDTBT:[70]PCBM</td>
<td>9.4</td>
<td>0.90</td>
<td>0.66</td>
<td>5.6</td>
</tr>
</tbody>
</table>
Solution processed polymer tandem solar cells using efficient small and wide bandgap cells

as the ratio between the experimental short circuit current and the absorbed photon flux. The short circuit current was determined by convolution the solar spectrum with the EQE of the solar cell, while the absorbed photon flux was calculated via optical modeling of the entire layer stack using the wavelength dependent refractive index ($n$) and extinction coefficient ($k$) (Figure 4a). The $n$ and $k$ of the DPP5T:[60] PCBM layer were determined using absorption and reflection spectra. The optical constants of PCDTBT:[70]PCBM were obtained from reference 14. The spectrally averaged IQEs are 70% for PCDTBT:[70]PCBM and 76% for PDPP5T:[60]PCBM with standard deviations of 3% and 5% respectively. The variations in IQE with layer thickness are less than the experimental error (Figure 4b).

![Figure 3](image1.png)

**Figure 3.** Bright field TEM images of the optimized active layers of PDPP5T:[60]PCBM (left) and PCDTBT:[70]PCBM (right).

![Figure 4](image2.png)

**Figure 4.** (a) Optical constants and (b) spectrally averaged IQE vs. layer thickness for PCDTBT:[70]PCBM and PDPP5T:[60]PCBM. The lines in (b) represent the values used for modeling.

The $n$ and $k$ values were used together with the thickness dependent $J$-$V$ and the IQE of the single junction devices in a combined electrical and optical model that calculates the $J$-$V$ curve of the tandem solar cell as function of the layer thickness of both cells, assuming no losses in the intermediate ZnO/PEDOT:PSS charge recombination layer. The modeling accounts for the electrical and optical interactions
between the individual subcells in the tandem configuration and accounts for the thickness dependence of the light absorption and charge collection. The calculations assume smooth interfaces between all layers and a recombination contact that is free of resistive losses. The modeling predicts that in a tandem cell $\eta$ can reach 7.1% when a 170 nm PCDTBT:[70]PCBM front cell is combined with a 120 nm PDPP5T:[60]PCBM back cell (Figure 5).

### 6.5 Tandem solar cell with optimal layer thicknesses

A series of tandem solar cells were made using the optimal thicknesses of the active layers that were determined using the optical and electrical model. The average efficiency over 20 different tandem devices was $\eta = 6.75 \pm 0.3\%$, with a maximum close to the predicted value of $\eta = 7.1\%$. The $J$-$V$ curve of a tandem cell with an efficiency of $\eta = 7.0\%$ is shown in Figure 6a.

When the simulated cell parameters are compared to experimental results (Table 2), we see that the actual device has a lower $FF$ and $V_{oc}$, which are compensated by a higher $J_{sc}$. These differences in $V_{oc}$ and $J_{sc}$ are related to the day-to-day variations.

Table 2. Characteristics of the tandem and single junction solar cells. The single junction cells were made in the same run as the actual tandem, in brackets the characteristics of the cells used for the simulation are given.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120 nm PDPP5T:[60]PCBM</td>
<td>14.0 (13.3)</td>
<td>0.58</td>
<td>0.65</td>
<td>5.3 (5.0)</td>
</tr>
<tr>
<td>170 nm PCDTBT:[70]PCBM</td>
<td>10.2 (10.7)</td>
<td>0.87 (0.89)</td>
<td>0.51 (0.53)</td>
<td>4.5 (5.0)</td>
</tr>
<tr>
<td>Tandem Measured</td>
<td>9.0</td>
<td>1.44</td>
<td>0.54</td>
<td>7.0</td>
</tr>
<tr>
<td>Tandem Simulated</td>
<td>8.1</td>
<td>1.47</td>
<td>0.59</td>
<td>7.1</td>
</tr>
<tr>
<td>Tandem Constructed</td>
<td>8.8</td>
<td>1.44</td>
<td>0.59</td>
<td>7.5</td>
</tr>
</tbody>
</table>
Solution processed polymer tandem solar cells using efficient small and wide bandgap cells

in the performance of the single junction cells. For the modeling of the tandem solar cells a series of single junction PDPP5T:[60]PCBM and PCDTBT:[70]PCBM cells with different thickness were made to be able to identify the layer thickness combination for the optimal performance of the tandem cell. At the time of making the actual tandem cells, new single junction cells with the same layer thickness were processed. The performance of the series of cells used in the simulation and those made along with the tandem deviated slightly for the same layer thickness, as shown in Table 2.

The EQE of the tandem cell (Figure 6b) was measured using appropriate illumination bias and electrical bias conditions, and convoluted with the AM1.5G (100 mW/cm²) solar spectrum to estimate the current generated in each subcell when it is in short circuit. We find that 8.6 mA/cm² is generated in the PDPP5T:[60]PCBM back cell and 9.5 mA/cm² in the PCDTBT:[70]PCBM front cell. Both currents are higher than predicted for these subcells (8.0 and 8.5 mA/cm², respectively), rationalizing the measured $J_{sc}$ of the tandem device, which is 9.0 mA/cm².

The $J$-$V$ curves of the two single junction cells made in the same run as the tandem cells were also measured under reduced light intensity such that their $J_{sc}$ matches the current generated in the subcells of the tandem. When assuming a loss free recombination layer the $J$-$V$ curve of the tandem can be constructed (Figure 6c).
measured, simulated, and constructed $J-V$ curves are compared in Figure 6a and reveal good agreement between the experimental and constructed curves. The excellent agreement between the $J_{sc}$ of the measured (9.0 mA/cm$^2$) and the constructed (8.8 mA/cm$^2$) $J-V$ curves demonstrates that the white light source accurately simulates AM1.5G light for this tandem solar cell. The measured and constructed cells have the same $V_{oc}$ (1.44 V). This demonstrates that the recombination contact does not cause a significant voltage loss. The fact that the $V_{oc}$ of the simulated cell (1.47 V) is slightly higher than that of the measured is due to small day-to-day variations in the $V_{oc}$ of the PCDTBT:[70]PCBM subcell, which varies between 0.87 and 0.89 V (Table 2). The main difference between the measured and constructed $J-V$ is found in the FF, which is lower for the measured device (Table 2), indicating that in the actual tandem cell small resistive losses exist in the recombination layer. Without these losses the efficiency of a PCDTBT:[70]PCBM / PDPP5T:[60]PCBM tandem cell can further increase to $\eta = 7.5\%$.

6.6 Conclusions

In summary we have demonstrated 7.0% efficient solution processed tandem solar cell made using efficient small bandgap PDPP5T:[60]PCBM and wide bandgap PCDTBT:[70]PCBM active layers and a ZnO/PEDOT:PSS recombination layer. With $\eta = 7.0\%$, the tandem polymer solar cell performs 20% better than each of the best single junction solar cells that give 5.3% and 5.8%, respectively, and a further increase to 30% can be expected when the present losses in FF can be alleviated. This demonstrates that the tailored development of wide and small bandgap absorbers for tandem polymer solar cells is a relevant new area in materials research that allows increasing the performance of organic solar cells.
Solution processed polymer tandem solar cells using efficient small and wide bandgap cells

6.7 Experimental

Materials
PDPP5T was synthesized using a palladium catalyzed Suzuki reaction from 3,6-bis(5'-bromo-4'-dodecyl[2,2':bithiophen]-5-yl)-2,5-bis(3-hexyldecyl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione17 and 2,5-di(4,4,5,5-tetramethyl-1,3-dioxaborolane)thiophene, following standard procedures.8b,18 Poly[[9-(1-octynonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT)10a was generously provided by Konarka Technologies. [6,6]phenyl-C$_{61}$-butyric acid methyl ester ([60]PCBM) and [6,6]phenyl-C$_{71}$-butyric acid methyl ester ([70]PCBM) were obtained from Solenne BV. ZnO nanoparticles were obtained using the synthesis method described by Beek et al.19

Solar cell devices
Solar cells were prepared by covering pre-cleaned ITO patterned glass substrates (Naranjo substrates) with PEDOT: PSS (Clevios P, VP Al4083). On top of this the different active layers were deposited by spin casting. Single junction PDPP5T devices were obtained by spin casting a 1:2 ratio of PDPP5T (8 mg/mL) and [60]PCBM from chloroform with 10% o-dichlorobenzene (ODCB) in air. For application of the PCDTBT active layer the PEDOT:PSS layer was dried by heating at 140 °C for 10 minutes. On top of the dried PEDOT:PSS a mixture of PCDTBT and [70]PCBM in a 1:4 ratio was cast in nitrogen atmosphere for both the single junction as well as the tandem devices. Processing in nitrogen atmosphere was found to be advantageous for the wetting of the PCDTBT:[70]PCBM layer. The solvent mixture was optimized and found to be 30% chlorobenzene in ODCB using a polymer concentration of 7 mg/mL. The PCDTBT active layer was dried on a hotplate for 10 minutes at 70 °C.

Tandem solar cells were obtained solution processing an intermediate contact consisting of ZnO nanoparticles19 and PEDOT:PSS on the PCDTBT:[70]PCBM active layer. The ZnO layer was spun from a solution of 10 mg/mL ZnO nanoparticles from isopropanol. The pH neutral PEDOT:PSS (Orgacon, Agfa) was diluted 1:1 with ultrapure water after which 0.2 mL/mL isopropanol was added to improve the wetting on the ZnO nanoparticles. Prior to spin casting the solution was filtered using a 5.0 μm Whatman Puradisc FP30 syringe filter. The PDPP5T:[60]PCBM active layer was spun on top of that. Finally a back contact of 1 nm LiF and 100 nm Al was evaporated in vacuum for all devices. Device areas of 0.09 and 0.16 cm$^2$ were used, which provided similar results.

Characterization
EQE measurements were done in a homebuilt set-up, with the devices kept in a nitrogen filled box with a quartz window and illuminated through an aperture of 2 mm. Mechanically modulated (Stanford Research, SR 540) monochromatic (Oriel, Cornerstone 130) light from a 50 W tungsten halogen lamp (Osram 64610) was used as probe light, in combination with continuous bias light from a solid state laser (B&W Tek Inc. 532 nm, 30 mW and 780 nm, 21 mW). The intensity of the bias laser light was adjusted using a variable-neutral density filter. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier.
(Stanford Research Systems SR830). For all the single junction devices and the PDPP5T:60 PCBM subcell, the measurement was carried out under representative illumination intensity (AM1.5G equivalent, provided by the 532 nm-laser). For the PCDTBT:70PCBM subcell, the measured EQE was mathematically corrected for the intensity difference between the monochromatic light and AM1.5G.15 For the tandem subcells, a compensating electrical bias was applied by the lock-in-amplifier to ensure short-circuit conditions in the respective subcells during the spectral response measurements.

Current-density versus voltage curves (J-V) were measured under simulated solar light (100mW/cm²) from a tungsten–halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight using a Keithley 2400 source meter. No mismatch correction was done. For the single junction cells the accurate short-circuit current density (Jsc) was determined from the EQE by convolution with the AM1.5G solar spectrum.20 For the tandem solar cell measurements, the simulated solar light spectrum was tuned to provide appropriate illumination to each subcell. This was achieved by adjusting the voltage over the tungsten halogen lamp in such a way that both the wide bandgap and the narrow bandgap single junction reference cell gave the exact Jsc as determined from the EQE measurement. The J-V curves of the tandem solar cells were measured under illumination through a mask of identical dimensions to the device area determined by the overlap of the ITO and Al electrodes, to avoid extra current generation due to the high lateral conductivity of the pH neutral PEDOT.6e Transmission electron microscopy was performed on a Tecnai G² Sphera TEM (FEI) operated at 200 kV. Bright field TEM images were acquired under slight defocusing conditions (see also ref 21). Layer thicknesses were measured using a Veeco Dektak 150 Surface Profiler.

**Optical modeling**

Absorption and reflection spectra of DPP5T:60PCBM layers having different thicknesses were measured using a Perkin-Elmer Lambda 900 spectrometer equipped with an integrating sphere. The refractive index was calculated making use of the Kramers-Kronig transformation. Calculations of the optical electric field were performed with Setfos 3 (Fluxim AG, Switzerland).
6.8 References


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5. For a recent review see: Boudreault, P. T.; Najari, A.; Leclerc, M. Chemistry of Materials 2011, 23, 456


Summary

Morphology control and device optimization for efficient organic solar cells

Renewable energy is paramount for a sustainable global future. Solar cells convert solar light directly into electricity and are therefore of great interest in meeting the world’s energy demand. Currently crystalline silicon solar cells dominate the market. Solution processed organic solar cells can potentially be made on large scale using fast and easy roll-to-roll processing, which will make them an attractive alternative for crystalline silicon solar cells that are fabricated using a time- and energy consuming production process.

The photoactive layer in an organic solar cell consists of a combination of an electron donating and an electron accepting material. Light is absorbed, creating an exciton that is split into charges at the interface of these materials. The charges are transported through the layer and collected at the electrodes. Efficient exciton generation, dissociation, and charge transport are key to obtain the highest efficiencies from these active layers. All these are affected by the morphology of the layer. The morphology of the active layer depends critically on different material parameters, such as solubility, miscibility, and tendency to crystallize and it can be influenced and optimized by changing the processing conditions. In this thesis control over the morphology of the photoactive layer is described for different material combinations. Higher efficiencies can be obtained when two complementary photoactive layers are combined in a tandem solar cell. The tandem construction alleviates losses that arise from thermalization of charge carriers and the transmission of light by absorbing high energy photons in a wide bandgap front cell and low energy photons in a small bandgap back cell. Device optimization of two different layer combinations into a tandem architecture is also described in this thesis.

Hybrid organic solar cells combine a conjugated polymer with an inorganic semiconductor to potentially make use of the light-absorbing properties and the processability of the polymer, and high electron mobility and morphological stability of the inorganic semiconductor. These materials are very different in nature and therefore morphology control in a hybrid organic solar cell is a challenge. In Chapter 2 the synthesis of titanium dioxide nanocrystals capped with oleic acid ligands and their mixing with poly (3-hexylthiophene) (P3HT) into an active layer is described. The effect of the oleic acid capping on the solar cell performance was investigated by partial removal or replacement by less insulating ligands. Higher solar cell efficiencies were obtained when the amount of oleic acid on titanium dioxide was
reduced, mainly as a result of an increase in photocurrent. This indicates that the oleic acid ligands act as a barrier for charge separation and charge transport in hybrid solar cells. Full removal of the ligands was not possible as they are needed to provide solubility to the titanium dioxide. Maximum solar cell efficiencies remained very low.

Chapter 3 describes an investigation into bilayer organic solar cells of P3HT and a C$_{60}$ fullerene derivative ([60]PCBM). Photoactive layers of P3HT and [60]PCBM were sequentially deposited from orthogonal solvents. The solar cells made from these layers were studied before and after thermal annealing and compared to mixed P3HT:[60]PCBM bulk heterojunction solar cells produced from a single solvent and bilayers of P3HT with vacuum evaporated C$_{60}$ on top. Comparison of the spectral shape and magnitude of the experimental and theoretically modeled external quantum efficiencies showed that P3HT/[60]PCBM stacks made via orthogonal solution processing do not lead to bilayers with a sharp interface. A sharp interface was only obtained for P3HT/C$_{60}$ bilayers. Thermal annealing of the diffuse-interface P3HT/[60]PCBM bilayers led to increased mixing, and with that increased efficiencies. Remarkably annealing of the solution processed bilayers did not result in the same mixed bulk heterojunction morphology that was obtained when P3HT and [60]PCBM were cast simultaneously from single solution and the efficiency in solar cells was higher.

In small molecule organic solar cells different parameters can be used to control the morphology of the active layer. The effect of the side chain position was studied using diketopyrrolopyrrole (DPP)-based small molecules in Chapter 4. Efficiencies up to 3.3% were obtained when the DPPs were blended with a C$_{70}$ derivative ([70]PCBM) in a bulk heterojunction solar cell. A variety of characterization techniques was used to study the behavior of these molecules in pristine films and mixed films with [70]PCBM, such as absorption, photoluminescence, electron and X-ray diffraction, and electron microscopy. The side chain position affects the molecular packing, varying from $H$-type to $J$-type, as well as the kinetics and ordering of DPP crystallinity in the mixed films. These differences affect the morphology of the active layer blends and in the end efficiency and behavior of solar cells made with these DPP-based molecules. Finally, also the use of these DPP small molecules in solution processed tandem solar cells was tested, to investigate the possibilities of processing layers of these small molecules from a low viscous, fast drying solution in a tandem device. The results showed that working tandem solar cells can successfully be prepared using these DPP-based small molecule active layers.
In Chapter 5 a novel small bandgap DPP-based dendritic small molecule was investigated in active layer blends with [60]PCBM and [70]PCBM fullerene derivatives. The morphology that was obtained upon spin casting the blend strongly depends on the fullerene used. This morphology could be influenced by the addition of very small amounts of a processing additive to the spin casting mixture. While the short circuit current increased when using the [70]PCBM, the fill factor was significantly lower due to the differences in morphology evolution. In the end this resulted in similar efficiencies that could be obtained using either of the fullerene derivatives.

Next an effort was made to produce a small molecule tandem solar cell with this small bandgap DPP-based dendritic molecule and a wide bandgap thiophene dendrimer. In the conventional architecture the integrity of the intermediate contact was not good enough to obtain a working tandem solar cell. An inverted architecture was needed to successfully process all the necessary layers on top of each other from orthogonal solvents. The efficiency of the inverted tandem solar cell was higher than that of the individual inverted single junction solar cells.

In the last chapter polymer tandem solar cells with a power conversion efficiency of 7.0% were obtained using efficient complementary absorbing small and wide bandgap layers. The small bandgap layer consisted of a DPP-based polymer and [60]PCBM, while the wide bandgap material was the very efficient PCDTBT polymer with [70]PCBM. The morphology of the individual layers was optimized using solvent additives and thickness series were made. With the solar cell performance of the small and wide bandgap layers and optical modeling of the complete device stack the best tandem configuration was calculated. With 7.0% the tandem polymer solar cell performed 20% better than each of the best single junction solar cells that gave efficiencies of 5.3% and 5.8%.
Samenvatting

Het beheersen van de morfologie en het optimaliseren van de laagopbouw voor efficiënte organische zonnecellen


De fotoactieve laag in een organische zonnecel bestaat uit twee materialen, namelijk een elektrondonerend en een elektronaccepterend materiaal. In deze laag wordt het licht geabsorbeerd en omgezet naar een elektron-gatpaar, een exciton genaamd. Dit exciton wordt gesplitst in de respectievelijke ladingen op het grensvlak tussen de twee materialen. De ladingen worden door de laag getransporteerd en verzameld aan de elektrodes, waarna een elektrische stroom ontstaat door de elektrodes met elkaar te verbinden. De efficiëntie van excitongeneratie, het opsplitsen van de ladingen en het transport naar de elektrodes zijn de sleutel tot het verkrijgen van een hoge efficiëntie uit deze fotoactieve lagen. Deze processen worden allen beïnvloed door de manier waarop de twee materialen zich in deze laag bevinden, de zogenaamde morfologie van de actieve laag. De oplosbaarheid, mengbaarheid en het kristallisatiegedrag van de gebruikte materialen is hierop van grote invloed, waardoor de uiteindelijke morfologie beïnvloed en geoptimaliseerd kan worden door het aanpassen van de procesomstandigheden. De controle over de morfologie van de fotoactieve laag wordt in dit proefschrift beschreven voor verschillende materiaalcombinaties.

In een zonnecel met een enkele actieve laag wordt de hoogst haalbare efficiëntie beperkt door een wisselwerking tussen stroom en spanning. Dit komt doordat fotonen met een energie groter dan de bandafstand hun extra energie verliezen door thermalisatie en doordat fotonen met een energie die kleiner is dan de bandafstand niet geabsorbeerd kunnen worden. Een hogere efficiëntie kan behaald worden wanneer twee fotoactieve lagen met complementaire absorptie worden gecombineerd in een zogenaamde tandemzonnecel. Het gebruik van een tandem minimaliseert deze verliezen door het absorberen van hoogenergetische fotonen in een subcel met grote bandafstand en laagenergetische fotonen in een subcel met een kleine bandafstand. De optimalisatie van de lagen in verschillende tandemzonnecellen staat ook beschreven in dit proefschrift.
In hybride organische zonnecellen wordt een geconjugeerd polymeer gecombineerd met een anorganische halfgeleider om mogelijk gebruik te maken van de lichtabsorberende eigenschappen en de verwerkbaarheid van het polymeer, in combinatie met de hoge elektronenmobiliteit en morphologische stabilititeit van de anorganische halfgeleider. Deze materialen zijn zeer verschillend van aard en van nature niet mengbaar. Het beheersen van de morfologie in een hybride organische zonnecel is daarom een uitdaging. De synthese van titaniumdioxide nanokristallen met oliezuurliganden wordt beschreven in Hoofdstuk 2. Door de oliezuurliganden kan de titaniumdioxide gemengd worden met poly(3-hexylthiofeen) (P3HT) om een actieve laag te maken in een zonnecel. Het effect van de oliezuurliganden is onderzocht door het gedeeltelijk verwijderen van de liganden of door deze te vervangen door minder isolerende moleculen. Hogere efficiëntie in zonnecellen werd behaald wanneer de hoeveelheid oliezuur werd verminderd, voornamelijk als gevolg van een toename in kortsluitstroom. Dit resultaat laat zien dat de oliezuurliganden een barrière vormen voor ladingsscheiding en ladingstransport in deze hybride zonnecellen. Het was niet mogelijk om alle oliezuurliganden te verwijderen, omdat deze nodig voor de oplosbaarheid van de titaniumdioxide. De maximale efficiënties van de zonnecellen bleef hierdoor erg laag.

Het onderzoek aan dubbellaag organische zonnecellen van P3HT en een C_{60} fullerereenderivaat ([60]PCBM) staat beschreven in Hoofdstuk 3. Fotoactieve lagen van P3HT en [60]PCBM werden achtereenvolgens aangebracht uit orthogonale oplosmiddelen. De zonnecellen met deze lagen werden bestudeerd voor en na verwarmen en vergeleken met gemengde P3HT:[60]PCBM bulkheterojunctie zonnecellen, welke werden verkregen uit een enkele oplossing, en dubbellagen van P3HT en opgedampte C_{60}. Door vergelijking van de experimentele en theoretisch gemodelleerde externe kwantumeficiëntie bleek dat P3HT/[60]PCBM dubbellagen gemaakt uit orthogonale oplosmiddelen geen scherp grensvlak hebben. Een scherp grensvlak werd wel verkregen in de P3HT/C_{60} dubbellagen. Het verwarmen van de P3HT/[60]PCBM dubbellagen met een diffuus grensvlak leidde tot nog grotere menging van de materialen en daarmee een hogere efficiëntie in de zonnecellen. Opmerkelijk genoeg resulteerde het verwarmen van de dubbellagen vanuit orthogonale oplosmiddelen niet in dezelfde morfologie die verkregen werd bij het gelijktijdig aanbrengen van de P3HT en [60]PCBM uit één oplossing en was de behaalde efficiëntie in zonnecellen hoger voor deze verwarmde dubbellagen.
De morfologie van de actieve laag in kleine molecuul zonnecellen kan beïnvloed worden door gebruik te maken van verschillende variabelen. Het effect van de positie van de zijketen op een molecuul gebaseerd op diketopyrrolopyrrool (DPP) is onderzocht in Hoofdstuk 4. Efficiënties tot 3,3% werden behaald wanneer deze DPP’s werden gemengd met een C70 derivaat ([70]PCBM) in een bulkheterojunctie zonnecel. Een breed scala aan karakterisatietechnieken werd gebruikt om het gedrag van deze moleculen te bestuderen in pure en gemengde lagen met [70]PCBM, zoals absorptie, fotoluminescentie, elektron- en röntgendiffractie en elektronenmicroscopie. De positie van de zijketen op de DPP’s is van invloed op de moleculaire stapelingen, die variëren van $H$- tot $J$-type aggregaten, alsook op de kinetiek en organisatie van de kristalliniteit in de gemengde lagen. Deze verschillen hebben een effect op de morfologie van de actieve lagen en daarmee ook op de efficiëntie en het gedrag van de zonnecellen die met de DPPs gemaakt werden. Tot slot werden deze kleine DPP’s getest in tandemzonnecellen waarbij alle lagen uit oplossing zijn aangebracht. De resultaten lieten zien dat het mogelijk was om werkende tandemzonnecellen te maken met de snel drogende DPP-oplossingen met lage viscositeit.

Hoofdstuk 5 beschrijft het onderzoek naar een nieuw DPP-gebaseerd dendritisch klein molecuul in bulkheterojunctie actieve lagen met [60]PCBM en [70]PCBM fullereenderivaten. De verkregen morfologie kon worden beïnvloed door toevoeging van kleine hoeveelheden additief aan de oplossing waaruit de laag werd aangebracht. Bij het gebruik van [70]PCBM in plaats van [60]PCBM nam de kortsluitstroom toe, maar tegelijk was de valfactor significant lager door verschillen in morfologie. Het resultaat hiervan was dat de efficiëntie die verkregen werd met elk van de fullereenderivat gelijk was.

Vervolgens werd geprobeerd om een klein molecuul tandemzonnecel te produceren met dit dendritische DPP-molecuul met kleine bandafstand en een thiofeendendrimer met een grote bandafstand. In de conventionele laagopbouw van de tandem was de integriteit van het tussenliggende contact niet goed genoeg om een werkende tandemzonnecel te maken. Een geïnverteerde opbouw was nodig om met succes alle lagen op elkaar aan te brengen vanuit orthogonale oplosmiddelen. De efficiëntie van de geïnverteerde tandemzonnecel was hoger dan die van de geïnverteerde zonnecellen gemaakt met de afzonderlijke actieve lagen.

In het laatste hoofdstuk werden polymere tandemzonnecellen gemaakt met een efficiëntie van 7,0% gebruik makende van efficiënte fotoactieve lagen met kleine- en grote bandafstand met complementaire absorptie. De fotoactieve laag met de kleine bandafstand bestond uit een DPP-gebaseerd polymer en [60]PCBM, waar voor de fotoactieve laag met grote bandafstand gebruik werd gemaakt van het efficiënte polymer PCDTBT in combinatie met [70]PCBM. De morfologie
van de afzonderlijke actieve lagen werd geoptimaliseerd door gebruik te maken van additieven. Van deze geoptimaliseerde fotoactieve lagen met grote- en kleine bandafstand werden diktereeksen gemaakt in zonnecellen. Door het combineren van de elektrische karakterisatie van deze enkellaagszonnecellen en de optische modellering van de complete laagopbouw, werd de beste tandemconfiguratie berekend. De beste enkellaagszonnecellen hadden efficiënties van 5,3% en 5,8% en met een efficiëntie van 7,0% voor de tandemzonnecel werd dat met 20% verbeterd.
Curriculum Vitae

Veronique Gevaerts was born on the 20th of May 1983 in Rotterdam. After finishing her pre-university education at the “RSG Lingecollege” in Tiel she studied Chemistry at Utrecht University from 2002. During the Masters Program Chemistry & Physics she conducted research on synthesis and characterization of CdTe/CdSe quantum dots within the group of Condensed Matter and Interfaces. She did an internship on enhancing the spectral response of silicon solar cells in the infrared at the School of Photovoltaic and Renewable Energy Engineering of the University of New South Wales, Sydney, Australia in the group of prof. Martin Green and dr. Gavin Conibeer. After she graduated in 2008, she started a PhD project in the group of Molecular Materials and Nanosystems of the Eindhoven University of Technology under supervision of dr. Martijn Wienk and prof. René Janssen. The results of this research are presented in this dissertation.
List of publications

Publications related to this thesis

*Discriminating between Bilayer and Bulk Heterojunction Polymer:Fullerene Solar Cells Using the External Quantum Efficiency*
*ACS Applied Materials & Interfaces* **2011**, *3*, 3252-3255

*Solution processed polymer tandem solar cell using efficient small and wide band gap polymer:fullerene blends*
*Advanced Materials* **2012**, *24*, (16), 2130-2134

*Influence of the position of the side chain on aggregation and solar cell performance of DPP-based small molecules*
*In preparation*

Other publications

*Efficient Solar Cells Based on an Easily Accessible Diketopyrrolopyrrole Polymer*
*Advanced Materials* **2010**, *22*, (35), E242-E246

*Improved Film Morphology Reduces Charge Carrier Recombination into the Triplet Excited State in a Small Bandgap Polymer-Fullerene Photovoltaic Cell*
*Advanced Materials* **2010**, *22*, (38), 4321-4324

*Simultaneous open-circuit voltage enhancement and short-circuit current loss in polymer: fullerene solar cells correlated by reduced quantum efficiency for photoinduced electron transfer*
*Advanced Energy Materials, 2012* DOI: 10.1002/aenm.201200426
Biofunctional Silicon Nanoparticles by Means of Thiol-Ene Click Chemistry
Chemistry – An Asian Journal 2011, 6, 2776-2786

Preparation, Characterization, and Surface Modification of Trifluoroethyl Ester-Terminated Silicon Nanoparticles
Chemistry of Materials 2012, 24, (22), 4311-4318
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