ORGANIC SOLAR CELLS:
NOVEL MATERIALS, CHARGE TRANSPORT AND PLASMONIC STUDIES

Bernd Ebenhoch

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Organic solar cells
- Novel materials, charge transport and plasmonic studies

A thesis submitted to the School of Physics and Astronomy, University of St Andrews, for the degree of Doctor of Philosophy

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This thesis was developed under the guidance of Prof. Ifor D.W. Samuel at the University of St Andrews (UK),

and was examined on the 18/06/2015 by Prof. Niyazi Serdar Sarıçiftçi from the Linz Institute for Organic Solar Cells (Austria) and Dr. Andrea Di Falco from the University of St Andrews (UK).

If you have questions or comments about this work, please contact me at bernd.ebenhoch@t-online.de
Abstract

Organic solar cells have great potential for cost-effective and large area electricity production, but their applicability is limited by the relatively low efficiency. In this dissertation I report investigations of novel materials and the underlying principles of organic solar cells, carried out at the University of St Andrews between 2011 and 2015.

Key results of this investigation:

- The charge carrier mobility of organic semiconductors in the active layer of polymer solar cells has a rather small influence on the power conversion efficiency. Cooling solar cells of the polymer:fullerene blend PTB7:PC71BM from room temperature to 77 K decreased the hole mobility by a factor of thousand but the device efficiency only halved.

- Subphthalocyanine molecules, which are commonly used as electron donor materials in vacuum-deposited active layers of organic solar cells, can, by a slight structural modification, also be used as efficient electron acceptor materials in solution-deposited active layers. Additionally these acceptors offer, compared to standard fullerene acceptors, advantages of a stronger light absorption at the peak of the solar spectrum.

- A low band-gap polymer donor material requires a careful selection of the acceptor material in order to achieve efficient charge separation and a maximum open circuit voltage.

- Metal structures in nanometer-size can efficiently enhance the electric field and light absorption in organic semiconductors by plasmonic resonance. The fluorescence of a P3HT polymer film above silver nanowires, separated by PEDOT:PSS, increased by factor of two. This could be clearly assigned to an enhanced absorption as the radiative transition of P3HT was identical beside the nanowires.

- The use of a processing additive in the casting solution for the active layer of organic solar cells of PTB7:PC71BM strongly influences the morphology, which leads not only to an optimum of charge separation but also to optimal charge collection.
Declarations

Candidate's declarations:
I, Bernd Ebenhoch, hereby certify that this thesis, which is approximately 50,000 words in length, has been written by me, and that it is the record of work carried out by me or principally by myself in collaboration with others as acknowledged, and that it has not been submitted in any previous application for a higher degree.
I was admitted as a research student in April 2011 and as a candidate for the degree of Doctor of Philosophy in April 2011; the higher study for which this is a record was carried out in the University of St Andrews between 2011 and 2015.

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Publications from this project


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Introduction

1.1 Solar energy for world peace

I want to start this PhD thesis with the experience I had at the conference “Solar Energy for World Peace”. The conference was held in Istanbul in August 2013 and was organized by the well known Professor Sarıçiftçi who pioneered organic solar cells. The place, Istanbul, was chosen on purpose as it symbolizes the bridge of the Western World with the Middle East and Africa and the aim was to promote knowledge transfer between these. In the opening speech, the President of Turkey, at the time Abdullah Gül, made an appeal “to make peace with nature for the sake of our own wellbeing and that of next generations” and proposed that solar power was a way to achieve this. The conference was a great success, discussing all aspects of solar technology as a secure and environmentally friendly way of energy production. My hope is that the work presented here contributes a little to achieve a more environmentally friendly technology.

As we all are aware not only from the debates of politicians but also from the weather news and experience, the climate is changing. Since 1980, within just 35 years, the earth’s temperature has increased by about 0.6 °C, reported by the NASA in a global study. Many factors are contributing to this global warming, the sun-activity, volcanic activity, clouds and dust particles in the atmosphere and many more, however most reports now come to the conclusion that global warming is mainly driven by the emission of carbon dioxide (CO₂) due to the green house effect. The fraction of CO₂ in the atmosphere has increased from 318 ppm in 1960 to its current value of 400 ppm as measured at the Mauna Lao Observatory in Hawaii. This dramatic increase of CO₂ proposes a further accelerated increase of the earth's temperature and can lead to a turning point of uncontrolled warming. It is of vital importance to limit global warming to a maximum of 1.5 °C to 2 °C compared to the pre-industrial value, and it was proposed that the fraction of CO₂ in the atmosphere has to be decreased to at least 350 ppm to achieve this.

The emission of carbon dioxide arises from multiple sources, like agriculture, forest fires, cement production, and burning fossil fuels for human transport, heating and electricity. These aspects however are vital for the well-being of the growing and developing human population. Therefore new technologies are needed in all of these sectors which allow to maintain a high standard of living but reduce the emission of greenhouse gases. Indeed in recent years environmentally friendly technologies are emerging, in electrically powered human transport, in solar- and geothermal heating of buildings and the electricity generation from renewable sources. The fraction of renewable energies in global electricity production
increased from an estimated 18 % in 2008 to 22.1 % in 2013. This shows that good progress has been made to come to a cleaner energy production, however resources like hydropower, which contributed to 16.4 % out of the 22.1 %, are already exhausting and a further expansion becomes challenging in some countries. Solar power on the other hand, contributes with only 0.7 %, although it is the most direct and abundant renewable energy resource and has the highest acceptance in the population. Figure 1.1 shows the average solar flux on the earth’s surface. In the Sahara desert the highest irradiance reaches up to 2700 kWh/m² per year. The US Energy Information Administration estimated the worldwide energy consumption of $1.5 \times 10^{14}$ kWh for 2012. In order to produce this entire amount of energy by solar panels of, let’s say 10 % efficiency, in the Sahara desert an area of two times the UK land area would have to be covered. This demonstrates the worldwide sheer enormous energy supply by the sun, but also shows that very large areas are required to capture it. There lies the great advantage of organic photovoltaic, which allows a large-area and cost-effective production of solar panels.

![Figure 1.1: Global map of the solar energy flux on the earth’s surface of a long-term average. Reproduced from SolarGIS © 2015 GeoModel Solar.](image)

### 1.2 Potential for organic solar cells

Photovoltaic solar panels convert the solar flux directly into electricity, which is the most convenient energy form to be transported and used – for lighting, for cooling and heating buildings and for electronic applications. Conventional photovoltaic panels on the market most commonly consist of ultrapure silicon solar cells, which require a comparably high energy and costs for fabrication. For silicon solar panels costs have been estimated between 0.50 and 0.75 US$ per watt excluding subsidies from governments and excluding installation costs. As organic solar cells are just entering the market a detailed cost analysis is not possible, but early estimates reach as low as 0.05 € per watt. What is the reason for these lower costs? Organic solar cells consist of plastic-like semiconductors which are amorphous and do not require high temperature steps for their fabrication. Due to the high absorption
coefficient of such materials the active layer can be very thin, on the order of 100 nm and the production can therefore be material effective. Furthermore these properties allow the active layer to be deposited from a solution, like paint, and solar cells can indeed be screen- or inkjet printed. This offers the great advantage of high-speed roll-to-roll fabrication, as solar panels could be produced on a single substrate in a continuous process. This can be imagined like processes in the packaging industry, as plastic solar cells will be based on a flexible conducting substrate, with a solution coated active layer, laminated top-electrodes and an encapsulation. The high-speed fabrication with avoidance of high temperature steps gives prospects to such low-costs. Additionally it reduces the energy payback time, which is the duration the solar panels have to be installed to produce the same energy that was needed for their fabrication, to about one day, compared to more than a year for conventional solar cells. The mechanical flexibility and low weight additionally gives potential to lower installation costs compared to inorganic solar cells.

Companies that produce organic solar panels are on the market now, however a few disadvantages limit widespread applications. These are the generally lower efficiency compared to conventional solar cells, technological issues and the fact that a few cost-limiting factors have not been eliminated yet. However, costs for the synthesis of the organic compounds are believed to drop, once it is scaled up to mass production. Technological aspects, like an effective encapsulation to protect the oxygen and water sensitive organic, can be solved once further experience is gained. The efficiency of about 2 to 5 % for commercial devices and 9 to 11 % for upper-end research devices is however fundamentally lower compared to silicon solar cells of about 15 % (polycrystalline) to 19 % (monocrystalline) of commercial devices and 25 % of research devices. The lower device performance of organic solar cells stems from multiple aspects, which are issues of fundamental research.

1.3 My contribution

This thesis is contributing to a broader understanding of the limiting factors and further developments of new materials of state of the art, solution-processed, organic solar cells. For example the band gap of the organic semiconductors used for the active layer is of great importance as it influences how much of the solar spectrum can be captured. By reducing the band gap in novel materials, photons in the near infrared can be absorbed and theoretically a higher short circuit current of the solar cell is achievable. In organic semiconductors absorbed photons do not directly generate free charge carriers, but excitons, which are bound electron-holes pairs. In order to split these excitons the active layer of organic bulk-heterojunction solar cells consists of two components a donor and an acceptor material. After describing the theory and methods in chapters 2 and 3, in chapter 4 I will show that reducing the band gap of the donor component to absorb more photons has direct implications on the choice of the acceptor component as both should have a similar band gap and an appropriate offset of the energy levels.
During the development of organic solar cells it emerged that a wide range of donor components was synthesized leading to promising efficiencies. However for the acceptor components only a very small selection of materials, like fullerenes, is available. In chapter 5 I explore new acceptor components based on the subphthalocyanine structure. With blends of PTB7, a commercial donor material, I demonstrate 3.5 % efficient solar cells which is lower compared to fullerene acceptors, but shows high potential due to additional light absorption by the acceptor. I thoroughly analyse the loss mechanism of recombination and charge trapping and propose a route for further improvements.

Organic semiconductors have due to their amorphous structure a much lower charge carrier mobility compared to inorganic crystals. In chapter 6 I analyse the mobility of common organic photovoltaic materials and investigate how it influences the solar cell performance. I make use of the temperature dependence of the charge carrier mobility in organic semiconductors and show that even a drastic reduction by a factor of thousand changes the efficiency only by a factor of two. This result will be explained by a thorough analysis of the underlying physical principles of organic solar cells.

A crucial aspect to generate free charge carriers and to avoid recombination is the morphology of the donor and acceptor blend of bulk-heterojunction solar cells. An additive, which is used in the casting solution, changes the morphology from a coarsely intermixed nano-structure to a finely intermixed blend. Can the device efficiency be explained by just the charge separation efficiency? In chapter 7 I will present an attempt to link properties of the morphology to the electronic properties of the solar cells.

The reduced mobility of organic semiconductors often leads to very thin active layers of the solar cells, which are required to efficiently extract the charge carriers faster than they recombine. In such thin active layers some photons are lost due to transmission and reflection and thus cannot contribute to the photocurrent. In chapter 8 I will investigate if light scattering and a plasmonic enhancement of the electric field near metallic nanostructures can improve the absorption and give a higher photocurrent.

1.4 Readers benefit

You, as the reader of this thesis will learn about the working principles of organic solar cells. You will learn how to characterise novel materials, their device optimisation and how to investigate prominent loss mechanisms and to eliminate them. In an outlook, future directions will be given, as promising ways to drive the progress in this field.
2 Theory of organic solar cells

2.1 General picture of an organic solar cell

This chapter describes the structure of an organic solar cell and the general working principle. In the following sections a detailed description of the function of each layer and their most recent developments will be given.

An organic solar cell belongs to the class of thin film photovoltaics, which requires only a thin active layer to absorb most of the light. In order to achieve rigidity, the solar cells are thus processed on a supporting substrate like sheets of glass or plastic films. In principle an organic solar cell is a diode, consisting of a layer of organic semiconductors placed between two electrodes. In photovoltaic operation the electrode at which electrons are extracted is called the cathode and the electrode at which holes are extracted is called the anode. Whereas in silicon solar cells the front contact consists of a metal grid, organic solar cells typically have both electrodes covering the entire device area. Therefore the front contact must be transparent in order to let light pass into the active layer.

Between the electrodes and the active layer additional charge selecting layers can be used to avoid that charge carriers are leaking to the wrong electrode. At the anode these are hole transporting (or electron blocking) layers and at the cathode electron transporting layers. The general configuration of an organic solar cell uses a transparent conductor as the anode and the so-called inverted device structure uses a transparent conductor as the cathode where the charge transporting layers act to modify the work function.

The difference of the work function of the materials on either side of the active layer induces an electrical potential and an electric field arises in the active layer. At the anode a high work function and at the cathode a low work function is thus required. This provides a Schottky junction and gives rise to the diode like behaviour of the devices.

The basic working principle of an organic solar cell is illustrated in Figure 2.1. Upon absorption of a photon in the active layer, a molecule is placed in an excited state. In organic semiconductors this means that an exciton is formed, consisting of a Coulombically bound pair of an electron in the lowest unoccupied molecular orbital (LUMO) and a hole in the highest occupied molecular orbital (HOMO). The most common way to split the exciton is to introduce a donor/acceptor heterojunction. An energy offset of the HOMO and LUMO between donor and acceptor at this heterojunction helps to dissociate the exciton. A free
electron in the acceptor phase and a free hole in the donor phase is thus generated, which then drift to the electrodes within the electric field.

To make use of a solar cell, an external circuit is required and the external connections influence the behaviour within the device.\(^{33}\)

- If the external circuit between the anode and cathode is shorted, photo-generated charge carriers are quickly extracted and the short circuit current can be measured. This photo-current is approximately proportional to the number of absorbed photons and is thus often normalised by the device area to give a more comparable figure of the short circuit current density \(\text{J}_\text{SC}\).

- If the external connection is open, charges are building up at the electrodes until the open circuit voltage \(\text{V}_{\text{OC}}\) is reached. At this point the field, due to accumulated charges, balances with the built-in field due to the electrodes and the photo-generated charge carriers recombine or are extracted equally to both electrodes.

- If an external voltage is applied to the solar cell in forward direction, additional charge carriers are injected from the electrodes and a high current can flow through the solar cell in forward direction.

Between the points of \(\text{J}_\text{SC}\) and \(\text{V}_{\text{OC}}\) the maximum power, \(\text{P}_{\text{MPP}}\) is generated. This power divided by the optical power per area, \(\text{P}_{\text{in}}\), gives the power conversion efficiency (PCE) of the device.

\[
\text{PCE} = \frac{\text{P}_{\text{MPP}}}{\text{P}_{\text{in}}} = \frac{\text{V}_{\text{OC}} \cdot \text{J}_\text{SC} \cdot \text{FF}}{\text{P}_{\text{in}}}
\]

(2.1)

The fill factor (FF) is a performance parameter which states how rectangular the JV-curve is.

---

**Figure 2.1:**

a) General device structure (non-inverted) of an organic solar. The transparent conduction layer functions as hole collecting anode and a metal layer as electron collecting cathode.

b) The work function difference of cathode and anode creates a strong electric field at short circuit (SC) and photo-generated charges are efficiently extracted. At the open circuit (OC) the electric field cancels and no charges are extracted. At high forward voltages additional charge carriers are injected from the electrodes giving a current in the opposite direction.\(^{33}\)

c) This gives rise to the current-voltage characteristics. At the maximum power point (MPP) most power is generated by the solar cell.
2.2 Substrates used for organic solar cells

Not much research has been focused on the supporting substrate of organic solar cells and mostly glass slides are used as the support for the transparent conductor. However, a great advantage of organic solar cells is the mechanical flexibility of the active layer which can lead to flexible solar cells. Simple roll-to-roll fabrication of solar cells is desirable as it allows a fast production of large area solar cells. For this technique to gain its full potential, flexible substrates are required. Polyethylene terephthalate (PET) is a common plastic material, used for example to make water bottles, it is durable and heat resistant in the temperature range required for organic solar cells. This makes it an often used choice as the substrate for flexible organic solar cells. Kaltenbrunner and co-workers showed flexibility of organic solar cells in the extreme, with curvature radii of under 10 µm, using ultrathin (1.4 µm) PET foils and device efficiencies of 4.2% were achieved. Other interesting directions are the use of paper, either as the opaque back electrode, or as novel transparent paper based on oxidized cellulose fibres with 5.88% power conversion efficiency achieved in the laboratory. To reduce reflections on the transparent substrate and to couple more light into the active layer, nanostructured substrates have recently been developed with a great enhancement of the external quantum efficiency.

2.3 Transparent conductors

Transparent conductors are a very popular research field in their own right and strongly impact on organic solar cells. Metals have a good conductivity but are far from transparent because of the high density of free electrons. As the conductivity, $\sigma$, is given by

$$\sigma = n e \mu$$

where $n$ is the charge density, $e$ is the elemental charge and $\mu$ is the mobility of electrons. The electrons interact with the electromagnetic field of photons, causing a high reflectivity and absorption. A few routes are thus conceivable to achieve a transparent conductor:

- Using a thin metallic layer. This reduces the amount of electrons in the pathway of photons and the interaction is reduced.
- Using a doped semiconductor with a large band gap. This is the basis for most transparent conductive oxides, such as indium tin oxide (ITO), where typically a tin amount of 10% acts as doping component, which introduces electrons into the conduction band. The large band gap prevents a direct absorption of photons in the visible region and only intra band absorption is the major loss mechanism in the infrared region.

The quality of a transparent conductor is given by the ratio of conductivity and absorption coefficient. Theoretical calculations show that the efficiency of thin film solar cells reaches above 90%, compared to the maximum achievable, if the transparent conductor has at least 90% transparency and and a sheet resistance of 10 $\Omega/\square$.

For organic solar cells ITO is the most common transparent conductive electrode. However, ITO has the disadvantage of relatively high costs and a high embodied energy. The costs of
ITO have been estimated to make about 35% to 42% of the total costs of an organic solar cell.\textsuperscript{15} Two reasons amount for the costs, the first is the high temperature required to deposit ITO and the second is the scarcity of indium.\textsuperscript{23} Therefore new materials as transparent electrodes are required to make organic solar cells more commercially attractive.

Progress has been made in various directions. A promising route is to use highly conductive PEDOT:PSS as electrode material. PEDOT:PSS is a conductive polymer blend consisting of PEDOT and PSS with typically a concentration of 1:6 by weight.\textsuperscript{42,43} PEDOT:PSS is synthesized by polymerisation of EDOT in an aqueous PSS solution, during this process PEDOT becomes oxidized and PSS reduced to form a stable polyelectrolyte (PEDOT$^+$:PSS$^-\!$).\textsuperscript{44} The conductivity of PEDOT:PSS can be tuned in an enormous range from $10^6$ to $10^3$ S cm$^{-1}$ can be obtained by changing the phase separation of the blend.\textsuperscript{45,44} For a layer thickness of 30 nm the transparency is about 88% and the sheet resistance 450 $\Omega/\square$.\textsuperscript{46} Thus the sheet resistance is relatively high compared to ITO of about 10 $\Omega/\square$ and often the conductivity is additionally supported by a metal grid or embedded metal nanowires.\textsuperscript{23} The rapid progress on the forefront of graphene research has made this material another candidate as a transparent conductor. Graphene is based on single sheets of carbon and as such has a minimum thickness to interact with light, but still provides a high conductivity. It has been found that a four layer graphene electrode had a promising sheet resistance of about 30 $\Omega/\square$ and a transparency of more than 90%.\textsuperscript{47} however the fabrication process of graphene electrodes was considered energy and time consuming and not viable for large scale processing, at least at present.\textsuperscript{23}

### 2.4 The active layer

The organic active layer plays the key role of the function of an organic solar cell. It is responsible for light absorption, exciton dissociation, charge transport and charge extraction.

#### 2.4.1 Organic semiconductors

For the active layer of organic solar cells a variety of organic semiconductors can be used. These can be loosely categorized in the following classes:

- Small molecules describe covalently bound structures in the size of about 1,000 g/mol. Due to the small size, these can be thermally sublimed without decomposition, but also processing from solution is possible.
- Fullerenes are special small molecules based on a closed cage of carbon atoms in a three dimensional shape e.g. C$_{60}$ or C$_{70}$.
- Conjugated polymers are based on repetitive units of monomers bound in a linear chain. The molecular weight is typically between 5,000 and 100,000 g/mol.
Figure 2.2: Examples of organic semiconductors, small molecules, fullerenes and conjugated polymers, used in this thesis.

Organic semiconductors have in common that a part of the molecule consists of alternating single and double bonds of carbon, giving rise to a conjugated system. In this configuration carbon atoms form sp²-hybridised orbitals with three equivalent sp²-orbitals in a plane and one perpendicular sp²-orbital. In a conjugated segment the sp²-orbitals form σ-bonds on the axis of a C-C bond, whereas the sp²-orbitals form π-bonds beside this axis. The π-bonds can thus overlap for many conjugated atoms, which strongly weakens the binding energy of electrons residing in this orbital. In the ground-state the π-orbital is completely filled with electrons and is thus called highest occupied molecular orbital (HOMO). The next higher orbital in energy is the π*-orbital, which is completely empty and thus called lowest unoccupied molecular orbital (LUMO). Between HOMO and LUMO of organic semiconductors a small energy gap arises. Photons with an energy larger than the energy gap can be absorbed and an electron is promoted from the HOMO to the LUMO, placing the molecule in an excited state called an exciton, a bound pair of an electron in the LUMO and a hole in the HOMO.

The energy gap between HOMO and LUMO is thus a very important characteristic of an organic semiconductor and one of its biggest advantage is that it can be tuned easily by altering the molecular structure. In order to absorb most of the solar flux, a low energy gap would be desired and a great effort has been directed to reduce the band gap of organic semiconductors. Organic materials can have a high absorption coefficient in the visible region, on the order of $1 \times 10^5$ cm$^{-1}$ at the peak. This corresponds to an absorption of 63% of the photons in a 100 nm thick film and allows the use of thin active layers for organic semiconductors.

2.4.2 Dissociation of the exciton

Photon absorption in organic semiconductors leads to Coulombically bound excitons, consisting of an electron in the LUMO and a hole in the HOMO. In organic semiconductors a high binding energy of these Frenkel-type excitons arises, because of the molecular nature of the materials, where both holes and electrons reside on the same molecule. The low dielectric constant of about 3 to 4, compared to inorganic semiconductors of around 20, leads to a strong Coulombic interaction of the electron and hole. The exciton binding energy for a
dielectric constant of 4 and a charge separation of 1 nm within the exciton gives a binding energy of 0.35 eV. Therefore thermal energy is not sufficient to dissociate excitons in organic semiconductors. A charge separation of about 14 nm would be required to overcome the Coulombic attraction and create free charge carriers (see Figure 2.3). For an organic solar cell free charge carriers are required to reach opposite electrodes in order to create a photovoltage and photocurrent. Thus the exciton needs to be dissociated.

![Figure 2.3](image)

*Figure 2.3: Electron-hole binding energy potential as a function of the charge separation distance for a material with a dielectric constant of 4. At a separation of approximately 14 nm the binding energy is equal to the thermal energy (kT) and charge carriers can be considered unbound. Calculated according to ref. 54.*

The general concept to dissociate excitons is to use a donor/acceptor interface consisting of two materials with an offset of the energy levels. In Figure 2.4 a schematic of exciton dissociation at such an interface is shown. After light absorption in the donor phase, the exciton is formed and has to reach a donor/acceptor interface. The acceptor has a deeper lying LUMO level than the donor. If the LUMO offset is higher than the exciton binding energy, it is energetically favourable for the electron to transfer to the acceptor phase and dissociate into free charge carriers, with the hole remaining in the donor phase. The process occurs similarly if the exciton was initially formed in the acceptor phase, then it can be dissociated by hole transfer to the donor phase, where the HOMO offset is the critical driving force. From either process a free hole in the HOMO of the donor and a free electron in the LUMO of the acceptor is generated. The effective band gap between these transport levels determines the open circuit voltage of organic solar cells.

To overcome the exciton binding energy a sufficient offset of the energy levels is required but as a high open circuit voltage is desirable, the HOMO and LUMO offset should be close to the exciton binding energy, which might be different in the donor and acceptor phase. Thereby research has been directed to accurately measure the exciton binding energy. Together with Dr. Alex Ward I contributed to the understanding how the driving force influences the exciton dissociation. The ideal energy offset strongly depends on the reorganisation energy of the material in which the exciton resides, which for a typical donor material (PTB7) was found to
The active layer

be about 0.4 eV ± 0.2 eV. Exciton splitting was found to be governed by Marcus theory which describes that the electron transfer rate depends on the energetic barrier between the initial and destination state\(^{62}\). This barrier will be a minimum if the energy offset between these two states is equal to the reorganisation energy. For an energy offset higher than the reorganisation energy the electron transfer rate reduces, because by the Marcus theory an inverted regime with a higher energy barrier is reached\(^ {61}\).

The exciton itself is metastable and can spontaneously recombine within an associated lifetime. This geminate recombination of the electron and hole created by the same photon can occur via a radiative or non-radiative transition both with an associated decay rate. The excited state lifetime of typical organic semiconductors is on the order of several 100 ps\(^ {63}\). During this period the energy of the exciton can transfer to other molecules by a random-walk diffusion process. The diffusion length until the exciton recombines is a critical parameter as it determines if the exciton is able to reach a donor/acceptor interface\(^ {64}\). Charge separation is therefore dependent on the charge carrier mobility and the charge transfer state lifetime which for P3HT:PC\(_{61}\)BM was found to be about 3 ns\(^ {56,68}\). Charge separation can additionally be aided by thermal activation and an electric field according to Onsager Braun theory\(^ {69,70}\). Thus in organic solar cells a higher electric field than the built-in field can be necessary to effectively dissociate excitons\(^ {71}\). Currently there is an ongoing debate if exciton diffusion can be influenced by an energetic potential towards lower band-gap\(^ {72,73}\).

After charge transfer, the exciton can still be bound and form a charge transfer state. Monte Carlo simulations have shown that many hopping steps are required to separate the charge carriers, until the exciton finally dissociates into free charge carriers\(^ {56}\). Charge separation is therefore dependent on the charge carrier mobility and the charge transfer state lifetime which for P3HT:PC\(_{61}\)BM was found to be about 3 ns\(^ {56,68}\). Charge separation can additionally be aided by thermal activation and an electric field according to Onsager Braun theory\(^ {69,70}\). Thus in organic solar cells a higher electric field than the built-in field can be necessary to effectively dissociate excitons\(^ {71}\). Currently there is an ongoing debate if exciton diffusion can be influenced by an energetic potential towards lower band-gap\(^ {72,73}\).

The exciton diffusion length of organic semiconductors is often found is to be about 10 nm\(^ {64,74}\). This has a strong influence on the architecture of the active layer. A planar
heterojunction as shown in Figure 2.5 has a limited region, where the exciton can dissociate. With absorption coefficients on the order of $10^5 \text{cm}^{-1}$, a film thickness of about 100 nm is required to absorb most of the light. Thus exciton harvesting would be quite limited if only excitons within the diffusion length were dissociated. Therefore the concept of the bulk-heterojunction has been developed on an early stage of organic solar cell research.$^{75,76,77}$ This concept makes use of the self assembly of the donor and acceptor compounds in a blend film. Solution processed bulk-heterojunction devices can thus be prepared from a single solution with both components dissolved. During the drying process or by an additional thermal treatment, a separation of the donor and acceptor phase leads to the formation of an interpenetrating network with dimensions on the nanometer scale.$^{78}$ Within the bulk structure therefore a large interface between the donor and acceptor phase is formed leading to efficient exciton dissociation.

**Figure 2.5:**

- **a)** Device structure with a planar donor/acceptor heterojunction. Only excitons close to the interface are dissociated.
- **b)** Device structure with a bulk-heterojunction active layer allowing exciton dissociation in the entire bulk of the active layer and charges are then transported through percolated pathways.

### 2.4.3 Charge transport

After exciton dissociation the next step is to get the charge carriers out of the device, aided by the built-in field due to the work function difference of the electrodes. In bulk-heterojunction devices the charge carriers are required to follow percolation pathways in the blend morphology as the offset of the energy levels of donor and acceptor acts as a barrier for the mobile charge carriers. Thus the electron will be extracted in the acceptor phase and the hole in the donor phase. The interpenetrating network has to provide continuous pathways of the acceptor phase to the cathode and of the donor phase to the anode. Therefore the concept of the ordered heterojunction has been developed which consists of nanopillars in the width of the exciton diffusion length and straight connections to the electrodes. However the realisation of such ordered heterojunctions thus far has not reached the predicted performance, mainly due to fabrication issues and a low mobility of charge carriers within the nanopillars.$^{79}$
In organic semiconductors, charge transport can be described by a hopping process, where the charge carriers are transferred from one molecule or conjugated segment of a polymer to a nearest neighbour. The spatial distance between these transport sites provides an energetic barrier which has to be overcome by thermal energy. Therefore the mobility of organic semiconductors is strongly influenced and reduces with temperature. A few very successful models for charge transport in organic disordered media were developed based on different approaches and a comparison is given by Coehoorn et al.\textsuperscript{80} The Gaussian disorder model, based on a Monte Carlo simulation, is one of the most applicable and will be described here in more detail, following the descriptions by Bässler et al.\textsuperscript{81,82} It assumes that the transport sites have an energy distribution with a Gaussian disorder, $\sigma$. The energy of each transport site arises mainly from its interaction with neighbour molecules, due to a varying orientation and due to the geometrical conformation of the molecule or polymer.\textsuperscript{83} Accordingly, the stiffness of the backbone of polymers plays a major role in the energetic disorder of the transport sites.\textsuperscript{83}

Charge transfer from one site to another depends on the overlap of the adjacent orbitals, \textit{i.e.} the HOMOs for holes and the LUMOs for electrons. The hopping rate $\nu$ from one site of energy $E_i$ to a further site $E_j$ was given by Miller and Abrahams\textsuperscript{84} by

$$
\nu_{ij} = \nu_0 \exp \left( -2 \gamma \Delta r_{ij} \right) \begin{cases} 
\exp \left( \frac{-E_j - E_i}{kT} \right) ; & E_j > E_i \\
1 ; & E_j < E_i
\end{cases}
$$

where $\nu_0$ is a proportionality factor, $\gamma$ is a factor which describes the form of the wavefunction of the orbitals, $\Delta r_{ij}$ is the distance between the two hopping sites, $k$ is the Boltzmann constant and $T$ is temperature. Charge transfer to a hopping site with higher energy must be thermally activated by the Boltzmann factor, whereas hops towards lower energy occur with a probability of unity. An electric field pointing from $r_i$ to $r_j$ lowers for electrons the energy between the hopping sites in this direction. Monte Carlo simulations based on such a system show that charge carriers over time relax in energy and tend to thermal equilibrium. Therefore sites with lower energy get occupied more over time and the mobility can decrease.

![Figure 2.6: Illustration of electron transport states of the LUMO with a Gaussian energetic disorder and spatial disorder without electric field. Over time charge carriers can decay in energy into the tail states (red) of the distribution.](image)
In disordered organic materials the hopping site distance is not constant as it would be in a crystalline lattice. Therefore a spatial disorder parameter, \( \Sigma \), was introduced which allows the spatial overlap \( \gamma \Delta r_{ij} \) to vary statistically with a Gaussian distribution. The Monte Carlo simulation with these conditions revealed a mobility dependence on the parameters \( \sigma \) and \( \Sigma \) by

\[
\mu(\sigma, \Sigma) = \mu_0 \exp\left(-\frac{4 \hat{\sigma}^2}{9}\right) \exp\left(\psi(\hat{\sigma}^2 - \Sigma^2)\sqrt{F}\right) \quad \Sigma \geq 1.5
\]

and

\[
\mu(\sigma, \Sigma) = \mu_0 \exp\left(-\frac{4 \hat{\sigma}^2}{9}\right) \exp\left(\psi(\hat{\sigma}^2 - 1.5^2)\sqrt{F}\right) \quad \Sigma \leq 1.5
\]

where \( \mu \) is the charge carrier mobility, \( \hat{\sigma} = \sigma/kT \) is the energetic disorder, \( F \) is the electric field and \( \psi \) is an empirical constant. The strong temperature dependence of the mobility on the temperature by \( \exp(-1/T^2) \) arises from the thermally activated hopping rate. This temperature dependence is additionally influenced by the charge carrier density. A low charge carrier density leads to lower thermal equilibrium within the Gaussian energetic disorder, where the density of transport sites is lower and a \( \exp(-1/T^2) \) dependence arises. For a high charge carrier density the Gaussian band is filled to a higher level and the mobility tends to a \( \exp(-1/T^1) \) dependence. A higher charge carrier density thereby also can give a higher mobility.

The spatial disorder parameter has a lower limit of 1.5, from where it has no influence on the mobility. If the spatial disorder parameter exceeds the energetic disorder parameter (\( \Sigma > \hat{\sigma} \)) the electric field dependence becomes negative and the mobility decreases with increasing electric field. For a high spatial disorder a high barrier can be considered between the hopping sites and the migration of charge carriers becomes more diffusion dominated, such that hops against the electric field become more likely. For a diffusion dominated hopping mechanism the mobility thus would scale proportional to \( F^{-1} \).

For the mechanism of a solar cell the mobility of the charge carriers is an important parameter as it determines how quickly they are extracted from the active layer. Charge collection competes with recombination processes which are important loss mechanisms of solar cells.

### Charge recombination

During charge transport to the electrodes charge carriers can be lost due to recombination of electrons and holes. Two processes can be distinguished, bimolecular recombination and monomolecular recombination. Both reduce the charge carrier density within the active layer which can be described by

\[
\frac{dn}{dt} = G - \zeta n - \beta n^2 - f_{\text{extract}} n
\]

where \( n \) is the density of charge carriers (electrons in the LUMO or holes in the HOMO) of the active layer, \( G \) is the generation rate of free electrons and holes, \( \zeta \) is the rate constant of
monomolecular recombination, $\beta$ is the rate constant of bimolecular recombination and $f_{\text{extract}}$ is the rate constant at which charge carriers are extracted to the electrodes.

Bimolecular recombination describes the encounter of an electron in the acceptor phase and a hole in the donor phase randomly in space. The probability of electrons and holes to encounter and recombine depends on their charge density. The generation of charge carriers by light absorption and exciton dissociation, produces equal amounts of electrons and holes, therefore the dependence of bimolecular recombination is proportional to the square of the total charge density. The rate constant of bimolecular recombination of organic semiconductor devices is often compared with the theory by Langevin, where the recombination of electrons and holes is limited by the diffusion of charge carriers and is thus dependent on their mobility.\(^{86}\)

$$\beta_L = e \frac{\mu_n + \mu_p}{\epsilon_0 \epsilon_r} \left(2.6\right)$$  \hspace{1cm} (2.6)

Where $\mu_n$ is the electron mobility, $\mu_p$ is the hole mobility and $\epsilon_0$ and $\epsilon_r$ are the dielectric permittivity of the vacuum and active layer respectively. In bulk-heterojunction organic solar cells however a much lower recombination rate is generally found compared to the Langevin rate. A Langevin reduction factor $\beta / \beta_L$ was found to reach down to $10^{-4}\,^{87,88,89,90}$ This can be explained by the fact that bulk-heterojunction blends consist of two phases which spatially separate electron and hole transport, therefore the probability to encounter the charge carriers with the opposite sign is reduced compared to a homogeneous film. Additionally it was speculated that the interface between donor and acceptor decreases the Coulomb attraction, which could also lead to a reduction of bimolecular recombination.\(^{87,91}\) Contrary to Langevin theory, the recombination rate constant was often found to depend on the charge carrier density, $\beta(n)$,\(^{92,93}\) A charge carrier density dependent $\beta$ can arise from state filling of tail states in the Gaussian distribution which indirectly influences the mobility.\(^{94}\) Relaxation of the charge carriers to the tail states also leads to a time dependent mobility and a time dependent bimolecular recombination rate.\(^{95,96}\)

Monomolecular recombination involves recombination via trap states or at an interface. A trap state is a hopping site with a low energy. This low energy prevents a charge carrier in this state escaping by a thermally activated hop. The charge carriers can be trapped for times of microseconds such that a significant number of charge carriers is lost during the time needed for charge extraction.\(^{97}\) An occupied trap state can act as a recombination centre for charge carriers of the opposite sign. As this trap-assisted recombination depends only on the density of one type of mobile charge carrier, the recombination rate is proportional to $n$. The recombination rate can be described by a Shockley Read Hall (SRH) process and the rate is given by\(^{98,99,100}\)

$$R_{\text{SRH}} = \frac{n p - n_i^2}{\tau_e (n + n_{\text{trap}}) + \tau_p (p + p_{\text{trap}})}$$  \hspace{1cm} (2.7)

where $\tau_e$ is the trapping time for electrons, $\tau_p$ is the trapping time for holes, $n_{\text{trap}}$ the trap density for electrons, $p_{\text{trap}}$ is the trap density for holes and $n_i$ is the density of intrinsic charge
Charge recombination
carriers. Generally the density of photo-generated charge carriers highly exceeds the density of intrinsic charge carriers, so that these can be neglected. In most experimental approaches recombination via electron or hole traps cannot be differentiated, thus an average of both trapping processes is measured, under the assumption that the density of trap states is much smaller than the density of transport states, equation 2.7 simplifies to
\[ R_{SRH} = \frac{n}{t_{\text{trap}}}. \] (2.8)
Therefore \( \zeta \) from equation 2.5 is identical to the inverse of the trapping time, \( t_{\text{trap}}^{-1} \).

In order to minimize recombination losses the charge extraction rate \( f_{\text{extract}} \) must be higher than the rate of bimolecular and trap-assisted recombination. The maximum time needed for charge carriers to drift through the active layer is given by
\[ t_{\text{extract}} = \frac{d}{\mu F}, \] (2.9)
where \( d \) is the film thickness, \( \mu \) is the minimum charge carrier mobility and \( F \) is the electric field. Additionally there is a chance that charge carriers are extracted at the wrong electrode against the electric field. Especially if the charge transport is trap dominated the leakage of charge carriers can be significant. Diffusion to the wrong electrode can be described by the Einstein relation of \( \text{E} \)
\[ f_{\text{wrong}} = \frac{8 \mu k T}{e d^2}, \] (2.10)
and \( f_{\text{extract}} = 1/t_{\text{extract}} - f_{\text{wrong}} \). The leakage current of organic solar cells can be reduced by the incorporation of additional electron and hole blocking layers between the active layer and the electrodes.

2.4.5 Charge extraction

Charge extraction is the next important step in the function of an organic solar cell. The cathode and the anode for electron and hole extraction typically consist of a metal or metal-like material. In this context I use the term metal-like for a strongly doped material with free charge carriers. Thereby materials like ITO and PEDOT:PSS can be considered metal-like.\( ^{101,44} \)

In a metal electrons occupy states up to the Fermi level and the work function is the difference between this level and the vacuum. The work function of different types of elemental metals varies between about 2.1 eV for caesium and 5.6 eV for platinum.\( ^{102} \) Generally the materials become more noble (less reactive) with increasing work function. In an (undoped) organic semiconductor the Fermi level is between the HOMO and the LUMO. After contact formation with a metal electrode the Fermi level will equalize throughout the device by the flow of mobile charge carriers. Depending on the alignment of the work function of the electrode and the energy levels of the semiconductor either an Ohmic contact or a Schottky barrier can form. As an example the hole extraction from an organic bulk-heterojunction solar cell at \( i.e. \) a PEDOT:PSS electrode will now be described, see Figure 2.7.
Hole extraction will occur from the hole transport level, which is the HOMO of the donor. If the Fermi level of the anode is lower than this level, holes will diffuse into the semiconductor in order to equalize the Fermi level on both sides of the contact. The so-generated holes in the HOMO cause a local electric field and stop further holes diffusing into the semiconductor. The electric field also induces a local band bending, such that the HOMO aligns with the metal Fermi level. In such a configuration an Ohmic contact is formed and no barrier exists for hole injection and extraction. The formation of the Ohmic contact leads to a Fermi level pinning of the contact such that the potential of the electrode adjusts to the HOMO level of the donor component.\(^{57}\)

If the Fermi level of the metal electrode is higher than the HOMO of the donor, an interface dipole will form, because in order to equalize the Fermi level, a high number of holes would have to diffuse from the semiconductor to the metal. As the charge density of holes in the semiconductor is much lower compared to the charge density in a metal, in a wide layer all the holes will be removed, forming a wide depletion region. In this depletion region an electric field is created which prevents the extraction of further charge carriers. Therefore a Schottky barrier is formed, which shows a rectifying behaviour. If the electrode is on negative bias the depletion region increases even further and no current flows. At positive bias the depletion region reduces and vanishes above a threshold, then a high current can flow.

At the cathode the situation for electron extraction is very similar. Electrons are transported in the LUMO of the acceptor and an electrode with a lower work function is required to form an...
Ohmic contact and to allow efficient charge extraction. If an Ohmic contact is formed on either side of the active layer for respectively hole and electron extraction, the open circuit voltage is mainly determined by the effective band gap.\textsuperscript{57}

Thus far HOMO and LUMO were treated as inorganic valence and conduction bands. However due to the molecular nature of organic semiconductors the situation is slightly different as the HOMO and LUMO are strictly speaking the energy values of the completely occupied and completely empty orbitals. If the orbital is occupied by a single electron or hole, the energy levels shift slightly. Due to the pinning of the electrode potentials to the energy levels of charge transport, the open circuit voltage can be described as the energy difference between the quasi Fermi level of electrons and holes. The quasi Fermi level describes the energy at which electrons in the LUMO (and holes in the HOMO) are in thermal equilibrium. For increasing light intensity, and therefore increasing charge carrier densities, the quasi Fermi levels shift away from the band gap and give rise to a higher open circuit voltage.\textsuperscript{103}

The $V_{OC}$ is then given by

$$V_{OC} = \frac{E_{\text{gap}}}{e} - \frac{kT}{e} \ln \left( \frac{N^2}{n p} \right)$$

(2.11)

where $E_{\text{gap}}$ is the energy gap between HOMO and LUMO and $N$ is the effective density of states. The charge densities $n$ and $p$, again can be assumed to be equal so that we count them as $n^2$ which is proportional to the intensity. Koster \textit{et al.} have shown that if bimolecular recombination is the only loss process in the solar cell the slope of the open circuit voltage versus the natural logarithm of light intensity equals $kT/e$ rather than $f kT/e$, as it is found for pn-junction solar cells, where $f$ is the diode ideality factor.\textsuperscript{103} The dependence of the open circuit voltage on light intensity which deviates from a slope of $kT/e$ has thereafter been attributed to trap-assisted recombination.\textsuperscript{104}

If the electrodes are non-Ohmic then charge extraction will be hindered and the charge carriers accumulate at the Schottky barrier. This leads to the formation of a space charge and increased monomolecular recombination.\textsuperscript{105} Severe space charge effects can lead to an $s$-shaped JV-curve with a strongly reduced fill factor.\textsuperscript{106}

After charge extraction the charge carriers will be stored at the electrodes. Therefore the solar cell contains a geometric capacitance which arises directly from the electrodes and is given by

$$C_{\text{el}} = \varepsilon_0 \varepsilon_i \frac{A}{d},$$

(2.12)

where $\varepsilon_0 \varepsilon_i$ is the dielectric constant, $A$ is the solar cell area and $d$ is the active layer thickness. Additional charge carriers are stored in the bulk of the active layer such that a total capacitance is the given by the sum $C = C_{\text{bulk}} + C_{\text{el}}$. The charge stored in the device is thus generally given by $Q = C V_{OC}$. However the capacitance is sometimes described as voltage dependent, as the charge density stored in the device scales non-linearly with the voltage.\textsuperscript{92,107}
2.5 Equivalent circuit diagram

Based on the description given above an organic solar cell can be modelled by simplifying its electrical properties. This model based on an equivalent circuit takes only macroscopic effects into account but is not suitable to describe recombination effects or the fill factor with all their details. However it is a useful approach to describe the general behaviour of the solar cells. As shown in Figure 2.8, the solar cell is basically represented by a diode and a current source in parallel, such that the current would flow through the diode in forward direction. The photo current would depend on the device area, light intensity and exciton dissociation efficiency. The series resistance of the bulk (R_{s(B)}) and the contacts (R_{s(C)}) accounts for voltage losses in the device when a current is flowing. The capacitance arises from the contacts and the bulk and associates the storage of charge carriers. The shunt resistance accounts for internal charge carrier losses, like recombination and diffusion of charge carriers to the wrong electrode. The measurement of the resistive losses will be described in chapter 3.4.2.

Figure 2.8:  a) Equivalent circuit diagram of a solar cell. The solar cell produces a photocurrent in reverse direction to the Schottky diode. Resistive losses occur in the bulk of the active layer (R_{s(B)}) and due to the outer connection (R_{s(C)}). Due to the electrodes a capacitor is created and charged over the bulk resistance. The shunt resistance (R_{sh}) accounts for current losses due to internal leakage.

b) Illustration how series and shunt resistance influence the JV-curve. A high series resistance reduces the slope at high forward voltage and a low shunt resistance increases the slope at short circuit. Both effects reduce the fill factor.
Experimental Methods

3.1 Introduction

This chapter has the purpose to define standard sample fabrication and measurement techniques which were used repeatedly. It serves to provide the reader with a detailed description of the equipment used and typical parameter settings. A couple of measurement techniques have been developed new in the group and another purpose of this chapter is to pass them on to the next generation.

3.2 Commercial materials for the active layer

A wide range of organic semiconductors is commercially available and was used in this thesis in combination with novel materials for solar cells. Typical acceptor materials are based on the soluble derivatives of fullerenes, PC_{61}BM ([6,6]-phenyl-C_{61}-butyric acid methyl ester) and PC_{71}BM ([6,6]-phenyl-C_{71}-butyric acid methyl ester) and were purchased from Solenne. Typical donor materials used in this thesis were MEH-PPV, P3HT and PTB7. Chemical structures are shown in Figure 3.1. MEH-PPV (Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]) is a common donor polymer with a relatively large band gap and is used for light emitting diodes and solar cells. It was purchased from Sigma Aldrich with a molecular weight of 150-200 kg/mol.

P3HT (Poly(3-hexylthiophene)) is a rather simple polymer, consisting of a thiophene unit and a hexyl chain on the third position. The polymerisation of this unit can lead to different orientations of the hexyl chain in respect to the polymer chain. It can be distinguished between the head-to-head (HH) or tail-to-tail (TT) coupling where the hexyl chains are facing or opposing each other and head-to-tail (HT) coupling (shown) where the hexyl chains are both on the same side of the thiophene.\textsuperscript{108} For the HT coupling the repeat unit within the polymer backbone consists of just two thiophenes, whereas for other couplings the smallest repeat unit consist of at least four isomers (...HT-HH-TT-HT...). The consistency of these repeat units is described by the regioregularity. For P3HT it turned out that a high regioregularity of HT-couplings is advantageous for the molecular order of the polymer chains.\textsuperscript{108,109} P3HT was purchased from Rieke Metals (4002-EE) and had a specified regioregularity of 91-94% and a molecular weight of 50-70 kg/mol.

PTB7 (poly[[4,8-bis[(2-ethylhexyl) oxy]benzo[1,2-b:4,5-b0]dithiophene-2,6-diyl][3-fluoro-2-(2-ethylhexy)carbonyl]thieno[3,4-b]thiophenediyl]]) is a low band gap donor material based on an electron rich benzodithiophene (BDT) unit and an electron deficient thienothiophene
Commercial materials for the active layer

(TT) unit within the backbone. This combination of donor and acceptor units reduces the band gap and will be discussed in detail in section 4.2. PTB7 was purchased from 1-Material with a molecular weight of about 100 kg/mol.

3.3 Characterising the properties of an organic semiconductor

Throughout this Ph.D. we were collaborating with other research groups who supplied an enormous range of organic semiconductors, with each being a viable candidate to boost the solar cell efficiencies. However for the chemists to design a molecule from scratch is a challenging task as many parameters are influencing the device performance. Characterising the properties of the materials serves the purpose to understand limiting factors and to give feedback to optimise the chemical structures. This chapter presents typical methods used to characterise an organic semiconductor for its potential use in solar cells.

3.3.1 Preparing solutions and the solubility

The solubility of an organic material is a crucial aspect for the formation of bulk-heterojunction blends and homogeneous films. For the fabrication of thin films and blends a wide range of organic solvents were used. Typical solvents were chlorobenzene, 1,2-dichlorobenzene, chloroform, dichloromethane and tetrachloroethane. Solutions were prepared by weighing the powder material on a laboratory scale (with an estimated error of 0.05 mg), transferring it into a nitrogen glove box, in order to keep out oxygen and water, and then adding the equivalent amount of solvent to achieve the desired concentration. The solution was then stirred for at least six hours on a hotplate of typically 50 °C. A concentration of 20 mg/ml gave for most materials an appropriate film thickness between 50 and 150 nm.

The solubility can be measured as the dissolved concentration of a saturated solution. Inspecting the solution or spin-coated films, reveals undissolved particles and gives so a qualitative estimate of the solubility.

Figure 3.1: Chemical structures of commercial organic solar cell materials. P3HT is shown as a structure with head-to-tail coupling. PTB7 consists of the electron rich BDT unit (red) and the electron deficient TT unit (blue).
3.3.2 Film fabrication, thickness and quality

Organic thin films were prepared by spin-coating or solution-casting on various substrates. For absorption and fluorescence measurements quartz discs with a size of 12 mm in diameter have been used. Because of the high crystallinity, quartz has a wide transparency even down to a wavelength of 200 nm and up to about 2 µm (specified by the supplier: uqg optics111), allowing absorption measurements in the same region. Other substrates used are indium tin oxide, which is a transparent conductor used for solar cells, and mono-crystalline silicon used for electron beam microscopy.

All substrates were thoroughly cleaned by wiping with acetone, ultrasonication in acetone for 5 minutes and ultrasonication in isopropanol for 5 minutes. The substrates were then blow-dried with nitrogen and afterwards plasma ashed at 80 W for 2 minutes with a Flecto-Mini from Gala Instruments. The plasma oxidises any carbon based contamination into carbon dioxide and creates an almost atomically clean surface. This step greatly improves the wettability of the surface with a typical contact angle below 3°.

The substrates were then transferred into a nitrogen glove box. Organic thin films up to 400 nm thickness were spin-coated and films with larger thickness were solution-cast. In the method of solution-casting a thin layer of solution was spread onto the substrate and let dry for several hours. In the spin-coating process the sample is hold by a vacuum chuck, the solution evenly dripped onto the substrate and then accelerated up to a variable speed and for variable duration. The equilibrium of the centrifugal force and surface tension causes that the solution flattens on the substrate, forming a thin layer, excess solution is spread-off at the edge. During the spinning the solvent quickly evaporates and leaves a smooth solid film after about 60 s. The resulting film thickness depends on a couple of parameters such as the spin speed, the evaporation rate of the solvent and the concentration of the solution.

The film thickness was measured with a Dektak surface profiler. This instrument uses a thin needle (tip size about 15 µm) which is moved in contact over the surface. The film was removed from the sample by scratching it with a blunt razor blade (back side) on a few positions and the film thickness was detected by scanning over the scratch. The tip was pressed on the substrate with a force of 1 mg, which is low enough to prevent sinking in the organic layer. The film thickness was averaged over at least three measurements per film and the error is typically about 5 nm. Thus, especially for very thin films this method is not very accurate.

It is always recommended to observe the film quality after a layer is spin-coated. This was most conveniently done by the use of an optical microscope. Several defects in spin-coated films can be identified as shown in Figure 3.2:

- Particles in films are often observed because of low solubility of the material. Particles in the solution typically form a comet-like halo around them which points away from the centre of the spin-coating chuck. Smaller particles often do not cause much
influence on the solar cell performance, but larger particles can lead to pinholes in the film.

- Many organic materials especially small molecules, but also polymers tend to aggregate and stack in a specific orientation. This can lead to well defined crystal structures. Large aggregates and crystals are detrimental for bulk-heterojunction solar cells because they enforce a large phase separation.

- Striations are film thickness variations with a typical pattern where small features are found in the centre of the chuck and elongated features towards the edges of the substrate. Striations often occur by spin-coating from low boiling point solvents such as chloroform. Due to fast evaporation of the solvent, the film formation is strongly disturbed and folded in this particular pattern.\textsuperscript{112}

<table>
<thead>
<tr>
<th>Undissolved particles</th>
<th>Crystallisation</th>
<th>Striations</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Undissolved particles" /></td>
<td><img src="image2.png" alt="Crystallisation" /></td>
<td><img src="image3.png" alt="Striations" /></td>
</tr>
</tbody>
</table>

\textit{Figure 3.2: Film defects in spin-coated organic films.}

### 3.3.3 Absorption

The absorption spectrum of a photovoltaic material is a very important characteristic, because it determines the fraction of the sunlight that can be converted into electricity. The absorption spectrum is not only determined by the molecular structure of the molecule or polymer, but also by the way the molecules order in the film. A comparison of the absorption in solution and films can reveal such \( \pi \)-stacking interactions as these lead to a (typically red-) shift of the absorption spectrum.\textsuperscript{113}

Absorption spectra were measured with a Cary 300 spectrometer from Varian. This spectrometer had a UV and a visible lamp to cover a range of 190 to 850 nm. The 850 nm detection limit is due to a decay of the sensitivity of the photomultiplier tube. Absorption measurements were taken on films spin-coated onto quartz substrates or solutions filled into quartz cuvettes with 1 cm pathlength. All spectra were corrected for the absorption of the substrate or the cuvette with only the solvent. The reading from the spectrometer was absorbance \((A)\) which is equal to \(\log(I_0/I)\), where \(I_0\) is the light intensity transmitted through the substrates or cuvette without the sample material and \(I\) is the intensity transmitted through the substrate and sample material. Absorbance is by Beer's law directly related to the film thickness \((d)\) or the concentration \((c)\) of the solution by

\[ A = \log\left(\frac{I_0}{I}\right) = \log\left(\frac{1}{I/d}\right) = \log\left(\frac{1}{c}\right) \]
Absorption

\[
\frac{I_0}{I} = T_a^{-1} = 10^4 = 10^{0.4 \epsilon_a} = e^{\alpha_a d}
\]

with the absorption coefficient \(\alpha_a\) and the molar decadic extinction coefficient \(\epsilon_a\). In this thesis mostly the absorbance or the absorption coefficient is stated. The absorption coefficient allows to compare different materials, whereas absorbance gives an idea how much light is absorbed by a particular film. The transmittance (\(T_a\)) is an expression for the percentage of light transmitted and \(1-T_a\) is often used as an approximation for the total absorption.

The energy gap between HOMO and LUMO can be estimated from the absorption onset, which is at the longest absorption wavelength (furthest to the red) where the absorption starts to rise. At this point the photon energy is just sufficient to promote an electron from the edge of the HOMO to the edge of the LUMO. Higher photon energies lead to a vibronic excitation of the molecule.

3.3.4 Fluorescence

Many organic semiconductors are fairly fluorescent. The emission of light after exciton generation can provide a tool to study the dynamics of the excited state. Especially the charge transfer process in donor:acceptor blends can be probed by fluorescence quenching, which gives a good indication of losses by geminate recombination.

During this Ph.D. three different fluorescence spectrometers were used in the lab (from Gilden, Fluoromax and Edinburgh Instruments). In principle all these spectrometers work in the same way where the main application is to measure the emission spectrum of a sample (film or solution). The sample is excited at a wavelength slightly shorter than the absorption maximum and generally emits light of lower energy than the HOMO-LUMO gap because the exciton, created by absorption of a photon, quickly relaxes to its minimum energy, which is equal to the band gap energy.

The photoluminescence quantum yield (PLQY) is defined as the total number of photons emitted divided by the number of photons absorbed. It has been measured on films with an Hamamatsu U6039-05 integrating sphere and a CCD spectrometer. The measurement involves two steps:

1. Taking a reference measurement without the sample: The software sums all the counts of the CDD spectrometer in the region (can be specified) of the exciton source.
2. Taking a sample measurement: The software again sums all counts in the same region and calculates the number of absorbed photons and the fraction of absorption. Additionally it sums the number of emitted photons in a second region. From the number of photons emitted and number of photons absorbed the PLQY is calculated.

In fluorescent materials a certain delay between absorption and emission of a photon occurs. As fluorescence is a spontaneous process, the rate of emission is proportional to the number of excited states, leading to an exponential decay of the fluorescence. This decay is associated with a lifetime at which the number of emitted photons drops to 1/e of the initial value and its
decay rate \( (k_r) \) is given by the inverse of the lifetime. Additionally excited states, \( \Phi \), can relax non-radiatively to the ground-state without emission of a photon. This process is associated with a non-radiative decay rate \( (k_{nr}) \).

\[
\frac{d \Phi}{dt} = -k_r \Phi - k_{nr} \Phi .
\]  
(3.2)

The PLQY is based on these decay rates and given by

\[
PLQY = \frac{k_r}{k_r + k_{nr}}.
\]  
(3.3)

Hence knowing the excited state lifetime gives another access to study the dynamics of the excited state, which has a lifetime of

\[
\tau = \frac{1}{k_r + k_{nr}}.
\]  
(3.4)

Besides the intrinsic non-radiative decay, additional losses of the excited state, which is a singlet exciton, such as charge transfer can be examined. If we assume we have an exciton in the donor phase of a bulk-heterojunction solar cell, the excited state will be quickly depopulated by electron transfer to the acceptor phase. Hence the non-radiative decay rate increases and the PLQY decreases. Measuring the PLQY or radiative lifetime for different concentrations of the acceptor in a blend thus gives a good estimate of the efficiency of charge transfer.

The radiative lifetime was measured with a technique called time correlated single photon counting. In this method the fluorescent sample is excited with an electronically controlled laser pulse which simultaneously triggers a time-to-amplitude converter, which internally charges a capacitor. After a certain delay the sample will emit a photon, which passes through a monochromator and is detected by a photomultiplier tube. This creates a voltage pulse and stops the charging of the capacitor. The accumulated charge is then measured by a multi-channel analyser and a histogram is generated by adding one count to a channel defined by the time delay. The window in which the decay is monitored can be selected, but due to the electrical response of the circuitry the minimum is limited to about 500 ps. As the first photon emitted is counted in this method, the count rate must be low enough in order to give slower photons a chance to be counted. For all measurements the count rate was adjusted by the laser intensity to give less than 5 % of the pulse rate (about 100 kHz). The measurement is stopped once a number of 10000 counts is reached at the peak in one channel. In order to extract the lifetime, the histogram is fitted with a mono- or multi-exponential decay function. As the system has a limited response time, a response function, obtained without a sample, was convoluted with the data for a more accurate fitting. An example of a typical fluorescence decay is shown in Figure 3.3.
3.3.5 The blend morphology

The blend morphology plays a very important role in the device performance of bulk-heterojunction solar cells. On one hand the donor and acceptor should be finely intermixed in order to achieve a large interface between the two phases for efficient exciton dissociation, on the other hand the interpenetrating network must form continuous pathways to allow charge carriers being extracted.

Tapping mode atomic force microscopy (AFM), based on a Bruker Caliber Head, offers a convenient way to explore this morphology. AFM is based on a sharp tip (a tip-diameter of 8 mm was used, model Bruker TESP-MT) which was positioned close to the surface of a sample such that the atomic forces of the Lennard-Jones potential act on it. In tapping mode the tip is driven in a continuous oscillation at resonance frequency (for the tips used about 300 to 400 kHz). This oscillation is influenced by the morphology and the composite of the surface. A piezo-positioner moves the tip over the surface in a specified area and a feedback control keeps the distance to the surface constant, thus the topography can be observed. The area of about 5 by 5 µm is typically scanned with 512 lines of 512 points and a scan rate lower than 1 Hz per line. The image of the tapping phase can provide information about the composite of the surface, which is very useful to distinguish between the donor and acceptor phase. However the phase image is generally also influenced by the topography which makes a clear distinction often difficult.

In order to achieve a crisp image the laser, which provides the feedback, must be carefully aligned on the tip and the feedback parameters (setpoint, gain and the integral component) adjusted. A reference sample (shown in Figure 3.4) is used to ensure that sufficient image quality is achieved.

Figure 3.3: Illustration of a fluorescence decay measurement by TCSPC. For simplicity only 64 channels are shown with each resembling a 1 ns time slot. The decay is mono-exponential with 5 ns lifetime. Typically the small background noise is negligible.
In a few circumstances scanning electron microscopy (SEM) was also used to image the topography of a sample. An SEM uses a focussed electron beam scanned over a sample surface. Depending on the morphology the secondary electrons created at the surface (in a few nanometers depth) are emitted in various directions and can be observed from various angles, where typically a combination of an upper and lower detector was used.

SEM imaging was done with a Hitachi S4800 on silicon substrates, as silicon has a higher conductivity than glass and prevents charging of the surface. SEM has the advantage over AFM that a larger field of view is provided and a complete image is visible within less than a second. This allows to zoom in at the point of interest. Additionally an advantage of SEM is that the cross-section of a structure can be examined by tilting the sample at an angle. This for example was used to investigate the morphology of solution-cast thick layers of a donor:acceptor blend. Besides the investigation of bulk-heterojunction blends SEM was mainly used to study plasmonic structures as described in chapter 8. Typical settings for SEM imaging are a relatively low flow of electrons of about 2 µA and a voltage of 1 to 5 kV. Especially on organic layers the voltage and current was kept low in order to avoid charging and damage.

Figure 3.4: AFM image of a reference sample used to optimize the scanning properties. The field of view is 5 × 5 µm

Figure 3.5: Example of an SEM image. Shown is a silicon nano-imprint master with 100 nm square pillars and 150 nm spacing, viewed at an angle of 30°.
3.4 Preparation of organic solar cells and device characterisation

The main subject of this thesis is the investigation of novel photovoltaic devices based on new materials and device structures. In this chapter a typical device fabrication process, the methods for determining the efficiency and further device attributes will be presented. Some details are provided about the calibration of the measurements.

3.4.1 A typical solar cell fabrication procedure

During the progress of the Ph.D. of course not all parameters of the procedure could be kept constant and a few steps changed during the course. Individual process parameters are thus given in the following research chapters and here a general schematic is drawn.

Fabrication of organic solar cells starts with the preparation of indium tin oxide (ITO) substrates. ITO is a transparent conductor and acts as the anode in classic organic solar cells. The ITO is a thin layer of about 155 nm on a glass substrate, purchased from XinYan technology. The sheet resistance is specified between $10 \, \Omega/\square$ and $13 \, \Omega/\square$ and the transparency higher than 85 % at 550 nm. The size of the substrates was 12 mm by 12 mm and the ITO layer was patterned as a central stripe of 4 mm width. Patterning was initially done manually by covering the stripe with adhesive tape and then etching the ITO in hydrochloric acid. As this process is rather time consuming and can lead to a slight inaccuracy of the size, we switched to purchasing pre-patterned substrates of the same dimension and from the same company. The substrates were first wiped with an acetone damped clean-room tissue in order to remove residual glue or photo-resist from the patterning process. They were then sonicated first in acetone and afterwards in isopropanol for 5 minutes, as described above and finally plasma treated (where it was ensured that the ITO side of the substrate is exposed to the plasma) to gain perfectly clean substrates. From the literature it is known that the cleaning procedure and especially the process of plasma ashing is a critical step to achieve high solar cell performance.

After cleaning, the substrates were labelled at the back with a marker pen. The samples were labelled with a batch and a sample number and this scheme was continued throughout the Ph.D. Together with a data sheet for each batch this allowed to clearly identify the process conditions for each sample. If I would have to start a Ph.D. again, I probably would use a database system to manage device properties and fabrication conditions considering that over 100 batches were produced. The next step then was to spin-coat PEDOT:PSS, which is a conductive polymer with a high work function of about 5.2 eV, which allows the formation of an Ohmic contact to the HOMO of typical donor polymers. PEDOT:PSS comes in a water based solution, purchased from Heraeus (CLEVIOS P VP AI 4083) and was first passed through a syringe filter of 400 nm pore size, then spin-coated at 4000 rpm in a wetdeck. The resulting film thickness was about 35 nm, which is sufficient to smooth the etches of the ITO stripe and hence serves additionally to prevent shorts when only a thin active layer is used. The PEDOT:PSS film was baked at 120 °C on a hotplate for 10 minutes to cure and remove the residual water.
Afterwards the samples were transferred into a nitrogen filled glove box, where the active layer was spin-coated. Solutions of donor:acceptor blends, which as described above were prepared a few hours before, were then spin-coated at a generally quite low speed of about 700 to 1500 rpm. The film dries slowly with this procedure and gives the bulk-heterojunction a bit of time to self-assemble. Also for a few materials slow drying was found beneficial to allow a higher degree of crystallisation and the devices thus feature from better charge transport.\textsuperscript{115,116}

As the next step for many materials it was beneficial to heat the active layer after spin-coating. This again can give a higher degree of crystallisation and can modify the blend microstructure. Annealing was done in the glove box on a hotplate. The hotplate was set to warm up for a few minutes and the samples were placed once the final temperature was reached. For P3HT:PC\textsubscript{61}BM a typical annealing condition was 130 °C for 20 minutes.

To complete the solar cells, top-contacts of aluminium or calcium/aluminium were thermally evaporated. In this device structure the top contact has a low work function and forms an Ohmic contact to the LUMO of the acceptor, it thus works as the cathode to extract the electrons. The calcium layer had a thickness of 20 nm and to avoid oxidation was covered with an aluminium layer of more than 100 nm thickness. The cathode was defined by a shadow mask of three stripes of 2 mm width, perpendicular to the ITO stripe. During the project, the device structure was changed from initially four stripes of 1.5 mm width, because the pixel size needed to be increased in order to have all light of an optical fibre with a diameter of 1 mm absorbed, as needed for an accurate measurement of the external quantum efficiency (see below). The devices were finally completed by encapsulation with a UV-epoxy and a glass slide placed over the active area. An illustration of the device structure is shown in Figure 3.6.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{device_structure.png}
\caption{a) Three dimensional representation of the typical device structure. To make contact at the ITO the active layer is removed with a blade.
\hspace{1cm} b) Layers of the organic solar cell from bottom to top: Glass substrate, ITO layer, PEDOT:PSS, Active layer, Ca/Al electrodes and a glass slide for encapsulation.}
\end{figure}
3.4.2 Measurement of the performance of a solar cell – the JV-curve

Solar cells are generally measured under simulated sunlight. A solar simulator is a lamp which provides a spectrum close to the spectrum of the sunlight on the earth’s surface. As the atmosphere scatters and absorbs some parts of the spectrum more strongly than others, the pathway through the atmosphere influences not only the brightness but also the shape of the spectrum. To allow that solar cells from different laboratories and manufacturers can be compared, the testing conditions must be unified. Thus they are regulated by international norms. The generalised spectrum, which has to be used for testing solar cells, is published by the National Renewable Energy Laboratory of the United States of America and shown in Figure 3.7. This spectrum is representative for a pass of 1.5 times through the atmosphere, equivalent to an angle of 48° to the normal. The integral of the irradiance gives the intensity, which is in total 1 kW/m², which is equal to 100 mW/cm². The photon flux, however is a more representative figure, as in conventional solar cells every photon absorbed can create maximum one electron in the solar cell circuit (a few techniques have shown to overcome this limitation, like singlet-exciton fission and multi-exciton generation with more than 100 % external quantum efficiency). The photon flux has a maximum at 680 nm and this region is therefore of great interest to obtain a high short circuit current.

Thus a solar simulator should provide a spectrum close to the AM1.5G spectrum. Because of the strong absorption bands, a perfect match however is impossible. The solar simulator used in this thesis is of class A, which means that the spectral match must be within 25 % in each spectral range of 100 nm (400-500 nm, 500-600 nm …). Additionally the uniformity of the illumination is within ±2 % for an area of 4 cm in diameter and the temporal stability within ±2 % in a time of 10 minutes.

Every time before measuring a batch of solar cells, the intensity of the solar simulator was calibrated with a silicon reference cell and a KG5 filter. The lamp power was adjusted to reach one sun intensity. Further details on calibration are given in the section 3.4.4. The most important characteristic of a solar cell is its current-voltage (JV) curve. In order to obtain it, a
voltage, typically between -1 V and +1 V is applied, where the positive bias is at the ITO electrode (anode), and the current through the cell measured. This measurement was done with a Keithley 2400 sourcemeter controlled by a LabVIEW interface. The current was normalised by the device area (overlap of the ITO and Ca/Al electrodes) to give a current density ($J$), which can be compared with solar cells of other dimensions. The devices were masked with a black metal cover with three windows, exactly matching the pixel size and position in order to avoid light, absorbed outside the active area, contributing to the photocurrent.

A typical JV-characteristic is shown in Figure 3.8 for an example solar cell of P3HT:PC$_{61}$BM. The short circuit current density ($J_{SC}$) was determined from the point where the voltage is zero. The Keithley 2400 accurately applies a voltage which cancels all potentials in the circuit such that the voltage is zero. In contrast, due to the fixed step size of the applied voltage no data point would coincide with the open circuit voltage ($V_{OC}$) thus a linear interpolation between the last point with negative current and the first point with positive current was implemented in the LabVIEW program to accurately obtain the $V_{OC}$ value. The maximum power point (MPP) was determined by the minimum (as $J$ is recorded as a negative value) of $J$ times $V$. Due to the step size of typically 0.05 V there is slight underestimate of $P_{MPP}$ of typically less than 2 % deviation. The power density obtained at the MPP was divided by the light intensity of fixed 100 mW/cm$^2$ to yield the power conversion efficiency ($PCE$). The fill factor ($FF$) is given by $P_{MPP}$ divided by $V_{OC}$ and $J_{SC}$. For the device shown, the $PCE$ is 2.34 % and the $FF$ 58 %.

![Figure 3.8: Example of a P3HT:PC$_{61}$BM JV-curve measured in dark and under the solar simulator with the characteristic points of $J_{SC}$, $V_{OC}$ and MPP highlighted. Also shown is the determination of the shunt resistance ($R_{sh}$) and series resistance ($R_{s}$) from the slope at short circuit and high voltage.](image)

Other insightful parameters of the JV-characteristic are the shunt resistance ($R_{sh}$) and series resistance ($R_{s}$). The shunt resistance was obtained from the inverse of the slope at short circuit. For the series resistance the correct determination is discussed in the literature, where either numerical approaches or the determination from more than one JV-curves are
considered most accurate\textsuperscript{120,121}. In this thesis the series resistance in most cases refers to the slope at high voltage. Thus the determination from the inverse of the slope at high forward voltage gives only an estimate. Only in a few occasions the quantitatively more accurate value according to the procedure of the IEC 60891 standard\textsuperscript{121} in which the characterisation of solar cells is defined, was applied.

3.4.3 Measurement of the spectral response – the external quantum efficiency

A few factors influence the spectral response of an organic solar cell. The major influence comes from the absorption spectrum of the donor acceptor blend, which is additionally modified by thin film interference effects and reflections of the metal electrode. Also the exciton dissociation efficiency could be wavelength dependent. Either because of a better dissociation of excitons excited in high vibronic modes (so-called hot excitons)\textsuperscript{56,122} or different dissociation channels from the donor or acceptor.\textsuperscript{123} In terms of a plasmonic enhancement also the spectral resonance of the plasmon contributes. The external quantum efficiency (EQE) is a measure of the spectral dependent contributions to the short circuit current.

To obtain the EQE spectrum, a solar cell was illuminated with a monochromatic light source and the short circuit current measured. For illumination a xenon lamp attached to a monochromator was used. The spectral width was less than one nanometer and the wavelength can be set with high accuracy (less than one nanometer deviation) via a GPIB interface. The light from the monochromator is coupled into an optical fibre of 1 mm diameter and pointed onto the larger device pixel. All outcoupled light thus falls onto the active area, which is an important required for this measurement. The short circuit current of the test cell $\text{ISC}_{\text{Test-Cell}}$ is measured and afterwards compared with a reference cell $\text{ISC}_{\text{Reference-Cell}}$ of known EQE. The EQE spectrum of the reference cell was calibrated by the National Physics Laboratory (NPL) of the UK. The reference was measured every time when an EQE measurement was performed in order to correct for changes of the lamp power or transmittance of the optical fibre. The EQE is then given by

$$
\text{EQE}_{\text{Test-Cell}} = \text{EQE}_{\text{Reference-Cell}} \frac{\text{ISC}_{\text{Test-Cell}}}{\text{ISC}_{\text{Reference-Cell}}}
$$

(3.5)

3.4.4 Calibration of solar cell measurements

The accurate determination of the efficiency is of great importance. During this Ph.D. major aspects have been modified in order to perform the measurements according to the standards in the literature. The spectrum of the solar simulator will always have a mismatch compared to the AM1.5G spectrum. Thus it is of importance to know about the accuracy. To measure the spectrum of the solar simulator, the monochromator was equipped with a photodiode at the exit slit and light from the solar simulator coupled in through a fibre at the entrance slit. The current of the photodiode was compared with the current produced by a calibrated tungsten
lamp. Using the monochromator had a couple of advantages compared to using just a spectrometer: High spectral resolution, high linearity and a selective filter wheel to cancel the second order diffraction. The reference lamp was calibrated by Bentham shortly before the use.

The measurement of the spectrum, shown in Figure 3.9 (black curve), reveals a good agreement with the AM1.5G spectrum from 400 nm to 800 nm. Between 800 nm and 1000 nm a few spikes occur from the xenon lamp and are not well compensated by the AM1.5G filter within the simulator.

The intensity of the solar simulator was initially calibrated with a thermopile sensor. This provided a few issues: The thermopile detects light far into the infrared region and is thus strongly influenced by thermal radiation and the detector was buried deeply in its housing giving rise to a partial shading. Thus we switched to the commonly accepted method of using a reference solar cell. This reference solar cell should have an EQE spectrum similar in shape to the measured solar cell. A silicon solar cell with a KG5 short pass filter, calibrated by ORIEL was selected. A holder in front of the solar simulator is used in order to place the reference and test cell at exactly the same position. The holder and the simulator are fixed at an optical table.

The spectral mismatch factor $M$ can be calculated by

\[
M = \frac{\int I_{AM1.5G}(\lambda)EQE_{Reference Cell}(\lambda)d\lambda}{\int I_{AM1.5G}(\lambda)EQE_{Test Cell}(\lambda)d\lambda} \times \frac{\int I_{Simulator}(\lambda)EQE_{Reference Cell}(\lambda)d\lambda}{\int I_{Simulator}(\lambda)EQE_{Test Cell}(\lambda)d\lambda} \ .
\]

where $I_{AM1.5G}$ and $I_{Simulator}$ denote the spectral irradiance shown above. If these spectra are completely identical $M$ becomes unity and additionally if the EQE of the reference cell has the same shape as the EQE of the test cell $M$ also becomes unity. The spectrum of the reference solar cell is compared to the EQE spectra of P3HT:PC$_{61}$BM and PTB7:PC$_{71}$BM devices in Figure 3.10. The spectra are not identical but a close similarity is obvious. The calculated
spectral mismatch factor is 0.995 for the PTB7 device and 1.057 for the P3HT device. Thus the short circuit current and the efficiency would have to be corrected by

\[ J_{SC(AM1.5G)} = \frac{J_{SC(AM1.5G)}}{M}, \quad PCE_{AM1.5G} = \frac{PCE_{AM1.5G}}{M}. \] (3.7)

As this adjustment is within the experimental error it was omitted for these types of solar cells. However for other material combinations corrections are stated in the individual chapters.

Another control experiment is provided by the integral of the EQE spectrum times the number of photons of the solar spectrum, given by

\[ J_{SC} = e \int EQE \cdot \frac{I_{AM1.5G}}{h \cdot c} \, d \lambda, \] (3.8)

where \( e \) is the elemental charge, \( h \) is Planck’s constant and \( c \) is the speed of light. The equation was solved numerically and gave identical results as an online tool. Due to the lower intensity of the EQE measurement bimolecular recombination losses are reduced and a slightly higher value than the \( J_{SC} \) can be expected. However in a recent literature survey it has been found that often a great mismatch occurs between these two measurements with the \( J_{SC} \) obtained from EQE being often more than 20% lower. This was attributed to a too high light intensity of the solar simulator or invalid masking. With the carefully calibrated conditions and masked pixels as described here generally a good agreement between the \( J_{SC} \) and integrated EQE was achieved. Thus I am confident that the calibration gives accurate results.

\[ J_{SC} = e \int EQE \cdot \frac{I_{AM1.5G}}{h \cdot c} \, d \lambda, \] (3.8)

where \( e \) is the elemental charge, \( h \) is Planck’s constant and \( c \) is the speed of light. The equation was solved numerically and gave identical results as an online tool. Due to the lower intensity of the EQE measurement bimolecular recombination losses are reduced and a slightly higher value than the \( J_{SC} \) can be expected. However in a recent literature survey it has been found that often a great mismatch occurs between these two measurements with the \( J_{SC} \) obtained from EQE being often more than 20% lower. This was attributed to a too high light intensity of the solar simulator or invalid masking. With the carefully calibrated conditions and masked pixels as described here generally a good agreement between the \( J_{SC} \) and integrated EQE was achieved. Thus I am confident that the calibration gives accurate results.

\[ J_{SC} = e \int EQE \cdot \frac{I_{AM1.5G}}{h \cdot c} \, d \lambda, \] (3.8)

Figure 3.10: EQE spectrum of the reference solar cell compared to a P3HT:PC_{71}BM and a PTB7:PC_{71}BM device.

### 3.5 Methods for investigating the charge carrier mobility and recombination

To understand the limitations of an organic solar cell and the influencing parameters, further measurements were performed on the devices. I developed a few new set-ups in the group for measuring the charge mobility by CELIV, charge extraction measurements, transient photovoltage and transient photocurrent. I will describe these measurements in detail in order to let them be continued by other members of the group.
3.5.1 Equipment for optoelectronic measurements

The methods described in the following sections were performed with a set of equipment used repeatedly but in different configurations. Table 3.1 gives a description of the equipment used.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Supplier</th>
<th>Important parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen laser</td>
<td>Photon Technology International GL-3300</td>
<td>337 nm, 500 ps pulse width, 1 mJ/pulse</td>
</tr>
<tr>
<td>Dye laser</td>
<td>Photon Technology International GL-302</td>
<td>Tuneable wavelength, 500 ps pulse width, ~100 µJ/pulse</td>
</tr>
<tr>
<td>LED</td>
<td>Cree XML T6, Controller homebuilt</td>
<td>White light, 1600 lm, 1 sun intensity, &lt;2 µs response time</td>
</tr>
<tr>
<td>Function generator</td>
<td>Keithley 3390</td>
<td>-10 to 10 V, Ramp and Pulse function, 50 Ω output resistance, GPIB controlled</td>
</tr>
<tr>
<td>Delay generator</td>
<td>Stanford DG645</td>
<td>&lt;30 ps delay on external trigger, 5 ps resolution, GPIB controlled</td>
</tr>
<tr>
<td>Microsecond switch</td>
<td>Homebuilt</td>
<td>&lt;200 ns response time, open circuit 1 GΩ, short circuit 9 Ω</td>
</tr>
<tr>
<td>Transimpedance amplifier</td>
<td>Homebuilt</td>
<td>Video amplifier, ~27 Ω input resistance, 1 V per 100 µA</td>
</tr>
<tr>
<td>Oscilloscope</td>
<td>Tektronix TDS 3032</td>
<td>Digital storage, 2.5 GS/s, GPIB controlled</td>
</tr>
</tbody>
</table>

3.5.2 Intensity dependent JV-curve

Varying the light intensity of current-voltage characteristics allows the identification of a couple of loss mechanisms of the solar cell. Especially bimolecular recombination strongly depends on the density of charge carriers in the active layer, which can be tuned by the intensity. From the dependence of the $V_{oc}$ on the light intensity additional mechanisms like charge trapping can be investigated.

A simple way to vary the intensity of illumination is to use a combination of neutral density filters in front of the test solar cells. The neutral density filters do not alter the spectrum and the good temporal stability provided by the solar simulator is maintained. However changing the filters manually is rather time consuming. Thus a dimmable LED was used instead of the simulator. This LED from Cree provides a light intensity of about 1 sun (100 mW/cm²) at a current of 1.17 A. There is a slight roll-off of the light intensity at high driving current...
because of Joules heating. With the help of the Electronics Workshop a driver for the LED was developed which converts an input of 0 V to 10 V to the drive current of the LED between 0 A and 1.5 A and was then calibrated for linearity. A third order polynomial function was used to fit the light intensity versus driving voltage on double logarithmic scales shown in Figure 3.11 (a). The fit parameters where then used by a LabVIEW program and the driving voltage was applied by a function generator.

The spectrum of the LED, shown in Figure 3.11 (b), of course differs strongly from the solar spectrum. Thus every solar cell was first measured in front of the solar simulator in order to obtain the accurate characteristics ($J_{SC (Simulator)}$) and then the $J_{SC}$ was measured with the LED set at one sun intensity and the short circuit current ($J_{SC (LED)}$) was measured. The real light intensity of the LED ($I_{LED}$) was then taken as the ratio of the short circuit currents, by

$$I_{LED} = I_{Set} \frac{J_{SC (LED)}}{J_{SC (Simulator)}}$$

where $I_{set}$ is the intensity set by the program. This method is valid as the spectrum itself does not influence the device parameters as long as the generation rate of carriers is the same.

![Figure 3.11: a) Emission intensity of a white light LED from Cree as a function of driving voltage. Squares are obtained with the ORIEL reference cell in steady state and are fitted with a polynomial function shown as the red line. The grey line shows a measurement of a fast-response detector to a ramped voltage of 800 µs period. Due to heating, the roll-off at high intensity is slightly stronger for the steady state measurement. b) Emission spectrum of the LED, normalised to 1 sun intensity.](image)

### 3.5.3 Photocurrent and photovoltage transients

The time dependence of the photocurrent and the photovoltage of solar cells provides insight into the dynamics of the devices. How quickly the solar cell responds to a light pulse can qualitatively provide an estimate of the charge carrier mobility and charge trapping. A photocurrent transient was measured by connecting the solar cell to a 50 Ω impedance input of an oscilloscope, whereas photovoltage transients were measured at 1 MΩ impedance. Both measurements can be performed with a light offset, meaning that the solar cell is illuminated continuously with a first light source and a pulsed illumination from a second light source.
Methods for investigating the charge carrier mobility and recombination

The charge carriers from the pulsed illumination interact and recombine with charge carriers generated by continuous illumination. Thus recombination processes can be studied in dependence of the charge carrier density in the active layer and the charge carrier lifetime can be deduced.\textsuperscript{92,128}

For measurements with a light offset, the white-light LED was used for constant illumination and a laser was used for pulsed illumination. For measurements without offset, the LED was used to provide pulsed illumination. Therefore first the performance of the LED as a pulsed light source was investigated. The LED illuminated a fast PIN-photodiode and the photocurrent was measured with an oscilloscope. Figure 3.12 (a) shows the response to a rectangular pulse of 8 V peak to peak, applied to the controller of the LED. A delay time of about 0.5 µs arises before the LED turns on and a slight overshoot is observed at about 2 µs before reaching steady state illumination. The frequency response to a sine wave of 8 V peak-to-peak and 4 V offset had a cut-off frequency at 540 kHz as the amplitude dropped to $\sqrt{1/2}$ of the initial, as shown in Figure 3.12 (b). Thus the LED is a viable toolkit to measure responses longer than 2 µs.

![Figure 3.12](image)

\textit{Figure 3.12: a) Light output of the Cree LED. At a driving voltage of 8 V a delay of about 0.5 µs arises and 90 % of the steady state value is reached after 1.6 µs. b) Frequency response of the LED to a sine function with 8 V amplitude of the driving voltage. The cut-off frequency at 70 % of the amplitude is at 540 kHz.}

3.5.4 Charge extraction by linearly increasing voltage (CELIV)

Charge extraction by linearly increasing voltage is a quite popular technique to derive the mobility of a material. This technique was developed by Juška \textit{et al.}\textsuperscript{129,130} who I visited during this PhD for a detailed introduction. The technique allows to quantitatively estimate the charge carrier mobility in an organic solar cell. CELIV is based on the extraction of intrinsic or photo-generated (Photo-CELIV) charge carriers by a voltage ramp. An illustration is given in Figure 3.13. Applying a voltage ramp to a capacitor (which arises due to the electrodes of the device) leads to a rectangular current, as
Charge extraction by linearly increasing voltage (CELIV)

\[ J = \frac{C}{A} \frac{dV}{dt} \]  \hspace{1cm} (3.10)

with the current density \( J \), the device area \( A \), the capacitance \( C \) and the voltage ramp slope \( dV/dt \). Thus the current during the ramp period is constant and scales linearly with the slope. As the organic material between the electrodes is not a dielectric, but a semiconductor, additional charge carriers can reside there. The increasing voltage sweeps these charge carriers out to the electrodes, giving an additional current. As the charge carriers speed up with increasing electric field the extraction current rises, but at some point most charge carriers are extracted and the extraction current decays. This gives rise to a peak, with the peak time depending on the charge carrier mobility. Note, however, that due to the indifferent extraction of electrons and holes from the active layer a distinction between their mobility is generally not possible. It is thus referred to the mobility of majority charge carriers. The mobility from a CELIV experiment is given by

\[ \mu = \frac{2d^2 \Delta t}{3t_{\text{max}} \Delta V} \]  \hspace{1cm} (3.11)

where \( d \) is the device thickness, \( \Delta V/\Delta t \) is the slope of the voltage ramp and \( t_{\text{max}} \) is the time when the extraction current forms the maximum.

In many cases no intrinsic charges are observed in organic semiconductors, thus the method is only applicable if charge carriers are created before the voltage ramp is applied. This is generally done by excitation with a short laser pulse. In photo-CELIV a positive bias is applied (in forward direction of the diode) in order to cancel the built-in field. This allows the created charge carriers to reside much longer in the film. A delay of a few microseconds between the laser pulse and the voltage ramp ensures that the charge carriers have relaxed in energy to the lowest state and distributed across the sample.

After the laser pulse the charge carriers will start to recombine during the delay time. By measuring the extracted charge as a function of delay, recombination and charge extraction can be investigated. The offset voltage plays a crucial role for these measurements as it determines how quickly the charge carriers leak out from the active layer or additional charge carriers are injected. As charge extraction and injection can never be completely compensated additional measurements based on a microsecond switch were developed and will be discussed in the following section.
3.5.5 Charge extraction (CE)

The charge extraction method (CE) was initially used in the field of dye sensitized solar cells and was established in the organic solar cell research by Shuttle et al. The method makes use of a fast switch which reacts to an external trigger signal to change from open circuit to short circuit. The circuit used in this project was developed on a suggestion by Dr. Kristijonas Genevičius at Vilnius University and is based on an integrated circuit multiplexer (ADG202). The open circuit resistance is about one GΩ and the short circuit resistance about 9 Ω, which is small compared to the series resistance of the solar cell. In this project it was found that the internal electric field is sufficient to extract the charge carriers, although it could be combined with an additional external voltage or voltage ramp.

![Figure 3.13](image1.png)

**Figure 3.13:** Schematic of a Photo-CELIV signal without applied voltage offset. A laser pulse creates free charge carriers which, after a delay, are extracted by a voltage ramp. The extraction current adds to the capacitive response and forms a maximum at \( t_{max} \). From this maximum the mobility can be estimated. The dependence of the extracted charge \( Q \) on the delay allows to study the recombination dynamics.

![Figure 3.14](image2.png)

**Figure 3.14:** a) Time response of the microsecond switch used for CE measurements. The trigger signal (red line) connects the switch to short circuit which allows a current (shown for a constant bias of 1 V - black line) being measured at the 50 Ω impedance of the oscilloscope. The current measured without the switch (grey line) is about 19 % higher because of the voltage drop at the switch, which has a resistance of 9 Ω.  

b) The extracted charge \( Q \) obtained as the time-integrated current of an organic solar cell at different illumination intensities. The voltage of the device is in equilibrium before charge extraction then charge carriers are extracted after 80 µs by switching to short-circuit.
Figure 3.14 gives an illustration of the switch behaviour. Upon applying the trigger pulse, a short delay of about 120 ns arises before the switch completely connects. A few oscillations occur in the first microsecond, but are not considered important because these do not affect the actual amount of the extracted charge. CE measurements were performed on standard organic solar cells. The sample was first illuminated by a pulse of the dye laser or a pulsed LED, then the illumination was turned off and the switch connected to short circuit. The internal electric field of the solar cell quickly drives out the charge carriers and the extracted charge was measured by the time-integrated current. The extracted charge can be converted to the charge carrier density $n$ by

$$n = \frac{e}{A d} Q, \quad Q = \int I_{sc}(t) dt$$  \hspace{1cm} (3.12)

where $A$ is the device area (geometrical overlap of the anode and cathode) and $e$ is the elemental charge. The charge carrier density derived from CE measurements however can be a misleading figure as a significant amount of charge carriers is stored at the electrodes rather than in the bulk of the active layer.

CE was used in different configurations to investigate the turn-off, steady-state and turn-on behaviour of a solar cell:

- Turn-off CE was performed with a variable delay between the illumination pulse and the extraction of the charge carriers. During the delay charge carriers in the film recombine and leak to the opposite electrode, thus the amount of extracted charge decays over time and the dynamics can give insight of the loss mechanisms involved.

- Steady-state CE was performed at variable light intensities provided by a pulsed LED. The period of illumination was chosen such that the open circuit voltage of the solar cell reached saturation. Immediately after the LED turned off, the extracted charge was measured (illustrated in Figure 3.14 b). This method allows to relate the extracted charge to the JV characteristics of the solar cell.

- Turn-on CE was performed at varying illumination periods of the LED. The extracted charge was measured immediately after the LED turned off. The measurement combined with measurements of the open circuit voltage allows to investigate how quickly the charge carriers are extracted to the electrodes.

### 3.5.6 Time of flight mobility measurements

Time of flight is a technique to measure the mobility of charge carriers. It is based on the simple idea of measuring the time the charge carriers need to pass through a certain distance, filled with the test material, in an applied electric field. Thus it requires two electrodes on either side of a film, to apply the electric field and to collect the charge carriers. Holes will propagate in the direction of the field whereas electrons will propagate against it. To accurately determine the transit time, the charge carriers must be generated on one electrode in a depth much shorter than the film thickness. This is generally achieved by a short laser pulse absorbed in roughly the absorption depth $(1/\alpha_{a})$ and a thick active layer. The electrodes
must be chosen so that charge carriers are well extracted, thus an Ohmic contact with the HOMO and an Ohmic contact with the LUMO on either side is preferred, as will be explained in more detail later.

The device fabrication is thus based on ITO substrates with a PEDOT:PSS or MoO$_3$ layer, which acts as the hole extraction contact and a calcium/aluminium electrode which acts as the electron extraction contact. MoO$_3$ has a high work function of 6.8 eV and thus can form an Ohmic contact even to deep HOMO levels.\textsuperscript{132} Due to the selective contacts, the electric field can only be applied positively at the Ca/Al electrode in order to avoid injection of charges. The consequence is that the laser pulse must generate charge carriers at the ITO electrode for the electron mobility and at the Ca/Al electrode for the hole mobility. Typically a thin Ca/Al layer of about 20 nm / 20 nm is therefore used as a semi-transparent electrode.

Figure 3.15: a) Circuit diagram of the TOF set-up. The voltage (left) is applied to the sample (represented as a diode) and the current recorded with the oscilloscope over a resistor. The (switch) left allows to discharge the sample and the polarity of the bias can be selected. 

b) Illustration of a TOF measurement in temporal sequence: charge generation, propagation through the active layer and charge extraction, shown with the corresponding current.

The thick active layer was created by solution-casting. In this method the organic solution was spread evenly onto a cleaned ITO substrate coated with PEDOT:PSS or MoO$_3$ and let drying for several hours. The device design is otherwise identical to a solar cell except that for the active layer also neat materials were used. The devices were not encapsulated because the film thickness was measured individually for each pixel after the measurement.

The electrical measurement was performed under vacuum in a cryostat which also allows cooling to 77 K and heating to about 375 K and avoids degradation of the films. The voltage was applied with a stabilized power supply and the current recorded with a digital storage oscilloscope at a resistor or a transimpedance amplifier in series. The electrical circuit is shown in Figure 3.15. The set-up created by the former group member Dr. Salvatore Gambino allows to connect to four pixels of the sample and easily invert the bias and discharge the sample. I developed a LabVIEW interface to simplify data gathering from the oscilloscope.
A typical TOF sequence is shown in Figure 3.15 (b). After excitation with a laser pulse a spike of the photocurrent arises, this occurs as the charge carriers close to the electrode will be quickly extracted, followed by a plateau of the current, when one type of charge carrier drifts through the sample and finally a drop of the current when the carriers are extracted on the counter electrode. The transit time is thus signified by the kink, when the photocurrent goes from the plateau into the tail. In non-dispersive media all charge carriers created reach the counter electrode at the same time giving rise to a sharp kink. In organic materials however, often dispersive transport is observed with the kink not very pronounced. This arises when some charge carriers are faster and some are slower or can also also arise when some charge carriers are lost due to trap states such that fewer carriers reach the counter electrode.\textsuperscript{81,133} Dispersive transport is traditionally analysed on double-logarithmic plots, which makes the kink much more distinct due to the strong difference of the slope at the plateau and tail.\textsuperscript{134} The mobility, $\mu$, is then derived from the transit time, $t_{\text{Tr}}$, by

$$
\mu = \frac{d^2}{V t_{\text{Tr}}},
$$

(3.13)

where $d$ is the layer thickness and $V$ is the applied voltage.
4 A low band gap DPP/BBT polymer

4.1 Motivation

An attractive feature of organic semiconductors is the tuneability of the energy gap between the HOMO and LUMO by chemical design. In order to harvest most sunlight, small energy gaps are required. In standard single-junction solar cells the optimum band gap of about 1.1 eV, corresponding to an efficiency of 30 %, as has been theoretically calculated. However the situation in organic bulk-heterojunction solar cells is different, because of the need for a donor/acceptor offset of the energy levels, to dissociate the exciton. This additional dissociation energy is lost in the device and reduces the maximum achievable efficiency. Various calculations have come to different conclusions about the ideal energy gap of organic semiconductors as summarized by Scharber et al., the optimum values found are between 1.45 and 1.9 eV with maximum efficiencies reaching up to 15 %. Since the first development of bulk-heterojunction solar cells most improvements in the device efficiency were introduced by donor materials with lower energy gap. Whereas for acceptors fullerene derivatives are still mainly used. Table 4.1 shows the significant developments of donor materials used in organic solar cells which caused considerable interest.

<table>
<thead>
<tr>
<th>Donor</th>
<th>Ref.</th>
<th>Year</th>
<th>PCE</th>
<th>Absorption onset</th>
<th>$E_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MDMO-PPV</td>
<td>137</td>
<td>2001</td>
<td>2.5 %</td>
<td>575 nm</td>
<td>2.14 eV</td>
</tr>
<tr>
<td>P3HT (with PC$_6$BM)</td>
<td>138</td>
<td>2002</td>
<td>2.80%</td>
<td>650 nm</td>
<td>1.90 eV</td>
</tr>
<tr>
<td>P3HT (with ICBA)</td>
<td>139</td>
<td>2010</td>
<td>6.5 %</td>
<td>650 nm</td>
<td>1.90 eV</td>
</tr>
<tr>
<td>PCPDTPT</td>
<td>140</td>
<td>2007</td>
<td>6.5 %</td>
<td>850 nm</td>
<td>1.45 eV</td>
</tr>
<tr>
<td>PCDTBT</td>
<td>141</td>
<td>2012</td>
<td>6.9 %</td>
<td>680 nm</td>
<td>1.81 eV</td>
</tr>
<tr>
<td>PTB7</td>
<td>30,142</td>
<td>2010</td>
<td>7.4 - 9.2 %</td>
<td>750 nm</td>
<td>1.64 eV</td>
</tr>
</tbody>
</table>

Reducing the energy gap allows to harvest more photons from the solar spectrum, where especially the region of 700 to 800 nm, the maximum of the solar photon flux, is of interest. Different concepts have been applied in organic chemistry to lower the energy gap of a material which include:

- Increase the conjugation length
- Increase of molecular weight of polymers
- Use of a combination of donor and acceptor moieties
- Increase the planarity of the polymer backbone
- Use electron donating or withdrawing side groups
Besides the energy gap, also the position of the LUMO and HOMO levels from the vacuum is of great importance in order to provide enough energy offset from the LUMO of the donor to the LUMO of the acceptor and enough offset of the HOMO of the acceptor to the HOMO of the donor for efficient exciton dissociation. Too high offset on the other hand will reduce the \( V_{OC} \).

In this chapter a new polymer based on a DPP (diketopyrrolopyrrole) and BBT (4,8-benzobisthiazole) unit with a low energy gap will be presented. This material was synthesized by Gary Conboy in the group of Professor Peter Skabara at Strathclyde University in Glasgow. The polymer was the first of this class of materials and the results of investigations of the photophysical properties, photovoltaic devices, the thin film morphology and mobility by time of flight led to further improvements in following materials. Particularly the position of the energy levels from the vacuum could be further improved as was identified by the JV-Characteristics and EQE spectra.

### 4.2 Chemical background

One of the most often applied concepts to reduce the energy gap of a polymer is by a push-pull mechanism of an electron rich (donor) and electron deficient (acceptor) unit in the polymer backbone.144 Through intramolecular charge transfer the effective energy gap is reduced to roughly the difference of the LUMO of the acceptor unit and the HOMO of the donor unit.

<table>
<thead>
<tr>
<th>Electron donating units</th>
<th>Electron withdrawing units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorene</td>
<td>Carbazole</td>
</tr>
</tbody>
</table>

![Figure 4.1](https://example.com/figure4.1.png)

*Figure 4.1: Typical donor and acceptor building blocks for low energy gap organic semiconductors.*150,144 *Full chemical names are given in the list at end of this thesis.*

Figure 4.1 presents typical electron donating and withdrawing units used for the molecular design of low band gap polymers. Covalent bonding between electron donating and withdrawing groups leads to intramolecular charge transfer, which stabilises the molecular structure and gives rise to the low band gap.144 The position of the HOMO and LUMO level can be controlled by carefully choosing the strength of electron donating and withdrawing units.145 Combining a strong donor with a weak acceptor gives a high LUMO level whereas a
combination of a strong acceptor with a weak donor gives a deeper LUMO level. Additionally, side chains play an important role in the design of a conjugated polymer as they can donate and withdraw electrons from the polymer backbone and allow to adjust the energy level position. Side chains are also important to promote solubility and influence the packing behaviour of the polymers.

4.3 Synthesis and chemical characterisation of P(DPPThBBT)

The synthesis and chemical characterisation of P(DPPThBBT) was performed by Gary Conboy at Strathclyde University in Glasgow. The copolymer consisting of a DPP and a BBT unit was synthesized by an alternating Suzuki coupling procedure. Benzobisthiazole (BBT) is a fairly common building block for low band gap polymers and small molecules. Gopal et al. obtained an efficiency of 6.5 % with a co-polymer of thiophene and BBT as a weak donor unit and BT as acceptor unit. Most commonly, BBT units are connected at the 2- and 6-positions on the thiazole rings in the polymer backbone (e.g. horizontally). To increase the solubility of the polymers the BBT unit was connected at the core benzene ring (e.g. vertically) into the conjugated backbone and the 2- and 6- positions were capped with alkyl chains (see Figure 4.2). This allowed concentrations up to 70 mg/ml in 1,2-dichlorobenzene. The molecular weight was 28,000 g/mol and the polydispersity was with 2.2 reasonably low.

The energy gap is about 1.39 eV estimated from cyclic voltammetry in chloroform solution with the HOMO at -4.90 eV and the LUMO at -3.51 eV measured against a ferrocene standard with the redox couple taken at -4.8 eV. The LUMO is hence between classic donor materials (e.g. P3HT of -3.0 eV) and acceptor materials (e.g. PC\textsubscript{61}BM and PC\textsubscript{71}BM of -3.7 eV). P(DPPThBBT) can therefore potentially be used either as donor or acceptor.

Differential scanning calorimetry revealed great stability of the polymer up to 250 °C without endothermic or exothermic phase changes. The material was considered highly amorphous and field effect transistors revealed a hole mobility of $4.8 \times 10^{-5} \text{cm}^2/\text{Vs}$, independent on annealing conditions.
4.4 Photophysical characterisation

P(DPPThBBT) has a major absorption peak at 690 nm and extends up to 900 nm (beyond the limit of the spectrometer used). In films spin-coated from 1,2-dichlorobenzene a slight red shift of about 20 nm of the spectrum is observed. This bathochromic shift is an indication of π-π stacking interactions which can facilitate charge transport. However the shift is relatively small, for example in P3HT the bathochromic shift is 80 nm. Thus π-π stacking is considered not to play an important role in film formation, which is consistent with a high degree of an amorphous phase.

![Absorption spectra of P(DPPThBBT) in 1,2-dichlorobenzene and of a spin-coated film.](image)

The fluorescence of P(DPPThBBT) was investigated in solution and films with a photomultiplier detector (range up to 900 nm) and a CDD (charge coupled device) spectrometer (range up to 1100 nm) but no fluorescence was detected.

4.5 Using P(DPPThBBT) as an acceptor

Because of the mixture of donor and acceptor moieties and the low lying LUMO of P(DPPThBBT) it can potentially be used as donor or acceptor and was investigated as such. To use P(DPPThBBT) as acceptor it was blended with P3HT in a device structure of ITO/PEDOT:PSS/P3HT:P(DPPThBBT)/Ca/Al. The blend ratio was 1:1.3 and the concentration in chlorobenzene 20 mg/ml. The active layer was annealed at 140 °C for 20 minutes before evaporation of the cathode.

The device characteristics are shown in Figure 4.4 and reveal poor performance with a $J_{SC}$ of only 0.03 mA/cm$^2$. The current in forward bias is very low with only 0.5 mA/cm$^2$ at 1 V indicating poor charge injection and conduction in the active layer. For comparison also a device of neat P3HT in an ITO/MoO$_3$/P3HT/Ca/Al device structure is also shown (blue). This clearly reveals the disadvantage of using P(DPPThBBT) as acceptor as devices containing it give an even lower short circuit current. It is likely that P(DPPThBBT) has poor electron transport properties, as in organic field effect transistor no electron current was found and thus prevents efficient electron extraction.
Another issue in blends with P3HT is that although the LUMO offset is sufficient, the HOMO offset is only marginal (see Figure 4.5 a). This can promote energy transfer from P3HT to P(DPPThBBT) by Förster resonance rather than exciton dissociation. The Förster resonance transfer occurs via a long range (typically 5 nm) dipole-dipole interactions. The transfer rate is proportional to the spectral overlap of the sensitizer emission and the acceptor absorption. As shown in Figure 4.5 (b) the emission of P3HT lies within the absorption peak of P(DPPThBBT) what implies a high energy transfer rate. The exciton in P(DPPThBBT) is then expected to recombine non-radiatively as no fluorescence was observed from the neat material. To allow efficient charge separation, a donor material with a smaller energy gap would be required, but has not been further investigated in this study.

![Figure 4.4: Solar cell device characteristics of P(DPPThBBT) used as acceptor with P3HT as donor. J-V-characteristics in dark (black line) and under one sun illumination (red line). For comparison a device of neat P3HT as active layer is shown (blue line).](image)

![Figure 4.5: a) Energy level alignment of an ITO/PEDOT:PSS/P3HT:P(DPPThBBT)/Ca/Al device structure. b) Overlap of the emission of P3HT with the absorption of P(DPPThBBT).](image)
4.6 Using P(DPPTThBBT) as donor

4.6.1 Selection of acceptors

For high efficiency solar cells only a small selection of acceptor materials is commonly available, all based on fullerenes and their derivatives. In the optimisation of P(DPPTThBBT) solar cells, the commercially available fullerenes $C_{60}$, PC$_{71}$BM and PC$_{84}$BM were used as acceptors. PC$_{71}$BM is the most commonly used acceptor for low gap polymer solar cells. $C_{60}$ and PC$_{84}$BM in this investigation were additionally chosen because of their deeper lying LUMO level to provide more offset for exciton dissociation.\textsuperscript{151} With increasing size of the fullerene core the energy gap reduces, a broader light absorption is provided and the LUMO shifts away from the vacuum.\textsuperscript{152} The PCBM derivatives of the fullerenes generally have a higher LUMO level by about 0.2 eV compared to neat fullerenes.\textsuperscript{153} This provides us with $C_{60}$ as an alternative to the PCBM acceptors with a deeper LUMO. $C_{60}$ is commonly used by vacuum processing for organic solar cells because of its limited solubility. Although it is often known as insoluble in organic solvents, a solubility of 23 mg/ml in 1,2-dichlorobenzene has been measured,\textsuperscript{154} which is a reasonable concentration for the fabrication of solution-processed bulk-heterojunction blends. In Figure 4.6 the energy levels of the used acceptors in relation to P(DPPTThBBT) are shown.

In the literature quoted values of the HOMO and LUMO strongly deviate between different reports with a variation of about $\pm$ 0.2 eV. Hence the literature data contain a high uncertainty for both the electrical properties of the materials, as well as the required energy offset to efficiently split the exciton. In order to accurately determine the LUMO offset, the energy levels of PC$_{71}$BM have been measured by Gary Conboy according to the same protocol as for P(DPPTThBBT) and a LUMO offset of 0.1 eV was confirmed. For $C_{60}$ the LUMO offset is about 0.3 eV and for PC$_{84}$BM about 0.4 eV as shown in Figure 4.6.

![Energy level alignment of P(DPPTThBBT) with different fullerene acceptors and the electrode materials.](image)

4.6.2 Device fabrication

Solar cells of the three acceptors were fabricated in the standard device structure (ITO/PEDOT:PSS/Active layer/Ca/Al) or the inverted structure (ITO/C$_{2}$CO$_{3}$/Active layer/MoO$_{3}$/Ag). For the inverted structure C$_{2}$CO$_{3}$ was spin-coated on ITO substrates from 2-
methoxyethanol solution of 2 mg/ml concentration at a spin speed of 5000 rpm to yield a film thickness of less than 5 nm. The film was annealed at 150 °C for 10 minutes. The layer of MoO$_3$ which acts as the anode in the inverted structure was thermally evaporated followed by a metal contact of more than 150 nm of silver.

4.6.3 P(DPPThBBT):PC$_{71}$BM

First solar cells of P(DPPThBBT) were fabricated with PC$_{71}$BM in the standard architecture, based on a solution of 17.5 mg/ml of chlorobenzene and a blend ratio of 1:1.8. To the solution 3 vol% of 1,8-diiodooctane (DIO) were added in order to achieve uniform dispersion of PC$_{71}$BM. No annealing of the active layer was performed because previous investigations by the chemists at Strathclyde University have shown detrimental effects by thermal annealing. The device characteristics under simulated AM1.5G illumination revealed a power conversion efficiency of 0.4 %, which is a promising starting point. The device characteristic is shown in Figure 4.7. The most prominent feature of the JV-curve is the kink at about 0.5 V, which dramatically reduces the fill factor to only 23 %. Such a kink in the JV-curve has been attributed to unbalanced electron and hole mobilities or space charge limited currents due to a Schottky barrier at the electrodes.$^{155,156}$

![Figure 4.7: Device characteristic of P(DPPThBBT):PC$_{71}$BM (1:1.8).](image)

The solar cell performance is additionally limited by the low short circuit current density of only 2.5 mA/cm$^2$. This is partly due to the active layer not absorbing much light. The absorbance of the active layer is shown in the upper panel of Figure 4.8 and covers nicely the region between 300 and 800 nm with a relatively flat spectrum. However the absorbance reaches only a low value of 0.15 at a reasonable film thickness of 70 nm and is due to a low absorption coefficient of P(DPPThBBT). The absorption coefficient shown in the lower panel of Figure 4.8 has a maximum of $0.95 \times 10^5$ cm$^{-1}$, which is about a factor of two lower than for P3HT or PTB7 (both about $1.8 \times 10^5$ cm$^{-1}$). The low absorption coefficient of a material might arise from various origins including the molecular weight of the polymer,$^{157}$ intramolecular charge transfer,$^{158}$ film homogeneity$^{159}$ and conformation of side chains.$^{160}$ I expect the bulky
side chains to be the main reason for the low absorption coefficient as they contribute to 45% of the molecular weight of the polymer but not to the absorption.

To improve the solar cell characteristics, the next step was to increase the active layer thickness and to optimize the device architecture. Increasing the concentration of the solution to about 70 mg/ml was necessary in order to achieve a film thickness between 90 and 130 nm at a spin speed of 1000 rpm. To investigate interactions of the electrodes with the active layer, which can prevent efficient charge extraction, two other types were explored: the inverted architecture with Cs$_2$CO$_3$ as electron transporting layer at the ITO electrode. Details of the device fabrication and JV-characteristics are shown in Figure 4.9 and Table 4.2. The regular device structure had a poor electrical performance due to a pronounced kink in the JV characteristics. The inverted structure gave better performance with an efficiency of maximum 0.5% for a blend ratio of 1:3 (P(DPPThBBT):PC$_{71}$BM). Although the kink in the JV-curve has reduced in the inverted structure, the current still is fairly limited in forward direction, such that the series resistance obtained from the slope at 1 V is between 200 and 600 $\Omega$ cm$^2$.

From the work function of the electrodes no Schottky barrier should arise and the fact that the behaviour slightly depends on the blend ratio points towards unbalanced electron and hole mobilities of the active layer which causes the S-shape. Additionally, the morphology plays an important role for efficient charge transport and can be influenced by the work function of the substrate. This gives a potential explanation why the solar cells slightly improve in the inverted cell structure.
Using P(DPThBBT) as donor

Besides the blend ratio, the morphology can be altered by the choice of the casting solvent. Especially the boiling point and the evaporation rate of the solvent play an important role in the drying dynamics of the active layer and its tendency to phase separate and crystallise. Due to the different crystallisation behaviour, of for example P3HT, also the mobility can be significantly influenced by the casting solvent, which would change the charge transport dynamics of bulk-heterojunction solar cells.

Figure 4.10 shows the JV-characteristic of P(DPThBBT):PC$_7$BM devices, in the standard architecture, spin-coated from chloroform (CF), chlorobenzene (CB) and tetrachloroethane (TCE) solutions with and without 3 vol% of DIO. With DIO the s-shape of the JV-characteristics vanished, whereas it is very pronounced in devices prepared without DIO. This suggests that the morphology plays an important role for obtaining a reasonable fill factor. The short circuit current of these devices however still remained fairly low and increased
from CB (0.89 mA/cm²), and CF (1.05 mA/cm²) to TCE (1.22 mA/cm²). This can suggest there is an improvement of the morphology with TCE.

![Graph showing JV characteristics of P(DPPThBBT):PC71BM devices prepared from different solvents.](image)

**Figure 4.10:** JV-characteristics of P(DPPThBBT):PC71BM devices prepared from different solvents (CF = chloroform, CB = chlorobenzene, TCE = tetrachloroethane, DIO = 1,8-diiodooctane).

Figure 4.11 displays AFM images of the blends prepared with DIO. A quite high surface roughness is visible for all blends prepared by the three different solvents. The surface roughness (RMS) for blends prepared from CF is 21.4 nm, from CB it is 9.7 nm and from TCE it is 8.2 nm. For a well intermixed blend, a surface roughness of about 1 nm to 2 nm typically gives a high power conversion efficiency. However also the texture of the film must be considered. The blend spin-coated from CB appears very coarse and grainy, but the features more and more disappear when using CF and TCE. This can give rise to the improvement of the short circuit current. The coarse blend structure is expected to prevent efficient exciton dissociation which limits the short circuit current.

![AFM images of P(DPPThBBT):PC71BM spin-coated from different solvents.](image)

**Figure 4.11:** AFM images of P(DPPThBBT):PC71BM spin-coated from different solvents.

Studies of fluorescence quenching as described in chapter 3.3.4 provide another valuable tool to investigate exciton dissociation. Unfortunately P(DPPThBBT) has no fluorescence emission itself and thus can not be investigated by this method, however PC71BM has a weak fluorescence which is strong enough to be observed in a streak camera. A streak camera provides the ability to investigate the fluorescence decay in a very short time range, down to about 2 ps. With the help of Dr Gordon Hedley the fluorescence decay of
P(DPPTbBBT):PC$_{71}$BM was investigated. As shown in Figure 4.12, the decay of neat PC$_{71}$BM has an associated lifetime of about 750 ps and is strongly reduced in the blend with P(DPPTbBBT) to about 300 ps. This associates that the population of excitons of PC$_{71}$BM is quickly depopulated because of charge transfer to the polymer. However this measurement does not guarantee that free charge carriers are generated after exciton dissociation and still a pathway of non-radiative decay via charge transfer states is possible. Comparing the blend of P(DPPTbBBT) with the highly efficient blend of PTB7:PC$_{71}$BM shows that exciton dissociation is still less efficient, potentially due to a large phase separation. This is in agreement with the value of the external quantum efficiency of only 16% in the PC$_{71}$BM dominated part of the spectrum (shown in Figure 4.13).

![Fluorescence decay of neat PC$_{71}$BM, P(DPPTbBBT):PC$_{71}$BM and PTB7:PC$_{71}$BM.](image)

Figure 4.12: Fluorescence decay of neat PC$_{71}$BM, P(DPPTbBBT):PC$_{71}$BM and PTB7:PC$_{71}$BM.

In order to further evaluate the contribution to the short circuit, an EQE measurement was performed on a 1:1 blend from 1,2-dichlorobenzene, which gave the best device performance. The EQE spectrum in Figure 4.13 is compared with the absorption spectrum of the blend and a typical absorption spectrum of PC$_{71}$BM. The EQE has the major contribution in the region up to 600 nm and is very low beyond 700 nm. The absorption peak of P(DPPTbBBT) at 710 nm is not strongly resembled in the EQE spectrum, which is completely dominated by the absorption spectrum of PC$_{71}$BM. This means that excitons created in the donor phase of P(DPPTbBBT) only weakly contribute to the photocurrent, whereas excitons from PC$_{71}$BM have the major contribution. This behaviour can be explained by the relatively low offset of the LUMO of P(DPPTbBBT) to the LUMO of PC$_{71}$BM of 0.1 eV. This offset plays a crucial role and is typically estimated to be in the range of 0.3 eV for efficient exciton dissociation.$^{61,136}$ Excitons from PC$_{71}$BM are dissociated by a hole transfer to the polymer. The HOMO offset of 0.7 eV means that excitons can be dissociated efficiently.
The recombination of free charge carriers can be studied from the analysis of the current/voltage characteristics for various light intensities. For a device of 0.2 % PCE and a FF of 36 % of the standard device structure, Figure 4.14 shows the $J_{SC}$ and $V_{OC}$ as a function of light intensity. The intensity dependent recombination effects, such as bimolecular recombination, have an impact on the short circuit current, as it depends sub-linearly on the intensity. $J_{SC}$ was fitted to a power law by fitting a straight line to data on log-log scale. This obtained an exponent of 0.92, which is in a region where recombination plays a significant but not entirely dominating role.$^{168,169}$ Additionally, the $V_{OC}$ dependence on light intensity gives an indication of trap-assisted recombination or limited charge extraction.$^{103,105}$ Surprisingly the slope of the $V_{OC}$ on light intensity is with 1.15 kT/e relatively low, such that this recombination mechanism does not play a significant role. The solar cells of P(DPPTBBT) thus seem to be limited by the exciton dissociation efficiency which is very low for excitons created in the polymer phase because of the low LUMO offset and limited by the morphology for excitons in the fullerene phase. The low LUMO offset can be potentially improved by the use of other fullerene acceptors.

![Figure 4.13: EQE spectrum of a P(DPPTBBT):PC$_{71}$BM solar cell (black) and the absorption spectrum of the blend (red) and PC$_{71}$BM (blue). The absorption peak at 750 nm of the blend is not resembled in the EQE spectrum because of poor exciton dissociation.](image)

![Figure 4.14: a) Short circuit current density of P(DPPTBBT):PC$_{71}$BM devices as a function of light intensity. b) Open circuit voltage as function light intensity.](image)
4.6.4 P(DPPThBBT):PC\textsubscript{84}BM and P(DPPThBBT):C\textsubscript{60}

As illustrated in Figure 4.6, PC\textsubscript{84}BM and C\textsubscript{60} have deeper LUMO levels compared to PC\textsubscript{71}BM. Because of the low solubility of C\textsubscript{60}, a concentration of in total 30 mg/ml was chosen for the solution and a blend ratio of 1:1.5. Figure 4.15 shows the JV-characteristics of P(DPPThBBT) blended with C\textsubscript{60}. The device performance had about 0.3 % efficiency in the standard architecture. The short circuit current density was 2.5 mA/cm\textsuperscript{2} and no improvement of exciton harvesting from P(DPPThBBT) was thus observed. The FF of 29 % was again rather low, but no s-shape was present. A reference device based on P3HT had a power conversion efficiency of 0.9 %, which is higher than in previous reports\textsuperscript{170,171} and had a good FF of 52 %.

![Figure 4.15: JV-characteristics of P(DPPThBBT):C\textsubscript{60} compared to P3HT:C\textsubscript{60} at 1 sun illumination and in dark.](image)

PC\textsubscript{84}BM has a very small band gap of 1.3 eV and the HOMO and LUMO offset appear very promising with P(DPPThBBT).\textsuperscript{152} It is a material not commonly used in organic photovoltaics, because of the large LUMO offset to common donor materials, the $V_{OC}$ would be rather low. The mobility of PC\textsubscript{84}BM is comparable to the C\textsubscript{60} and C\textsubscript{70} analogs, but a lower solubility has been reported.\textsuperscript{152} With MDMO-PPV as donor, a maximum power conversion efficiency of 0.25 % was reached.\textsuperscript{152} Solar cells of P(DPPThBBT):PC\textsubscript{84}BM prepared from 1,2-dichlorobenzene revealed no power conversion efficiency. A possible explanation is strong charge trapping and space charge accumulation, as was reported in previous studies,\textsuperscript{172,152} combined with a large phase separation with P(DPPThBBT).

4.7 Hole transport of P(DPPThBBT)

To find out about the charge carrier mobility of P(DPPThBBT), I employed time of flight studies on thick, solution-cast samples, employing the procedure for TOF described in chapter 3.5.6. The samples were prepared on ITO substrates covered with a layer of 9 nm MoO\textsubscript{3}, deposited by thermal evaporation. MoO\textsubscript{3} acts as the hole collection electrode, as it turned out during this PhD that the efficient charge extraction provided by an Ohmic contact is required for reliable TOF measurements. The active layer was solution-cast from a 62 mg/ml solution
of 1,2-dichlorobenzene and dried for more than 24 hours in a nitrogen glove box. The active layer had a film thickness of 7.37 µm ± 5% and was measured at the specific pixel individually after the measurement. The cathode consisted of 20 nm of Ca and 20 nm of Al to give a semi-transparent contact. The sample was excited with the nitrogen laser of 337 nm wavelength from the Al side, where the positive bias was applied to measure the mobility of holes. The current was recorded with a trans-impedance amplifier.

Figure 4.16: a) Typical hole photocurrent transient of P(DPPTbBBT) at an applied voltage of 70 V (95 kV/cm).

b) The hole mobility as a function of electric field.

Figure 4.16 (a) shows a typical hole photocurrent transient at an applied electric field of 95 kV/cm. The photocurrent resembles the hole transport through the active layer. An initial spike is followed by a weak plateau when the holes drift to the opposite electrode and followed by a decay when the holes are extracted at the counter electrode. The small kink between the plateau and tail as illustrated by the red fitting lines gives the transit time. From this transit time the mobility is determined by equation 3.13. The hole mobility shown in Figure 4.16 (b) is between $7 \times 10^{-5}$ and $7 \times 10^{-4}$ cm²/Vs. The mobility decreases with increasing electric field which is generally attributed to a large amount of charge trapping and a high spatial disorder. The strong field dependence is caused by the transit kink being almost independent of the electric field. This arises when the charge trapping time is much longer than the transit time and the hopping rate in the direction of the electric field and against the electric field are equally likely. The mobility is similar to that of P3HT of about $2 \times 10^{-4}$ cm²/Vs, however the negative field dependence makes it a bit difficult to compare. A detailed investigation of the charge carrier mobility of other photovoltaic materials will be given in chapter 6.

4.8 Conclusions

In this chapter a new low band gap material was investigated as an acceptor and donor material for organic photovoltaics. Devices with P3HT as donor failed, potentially because of Förster energy transfer from P3HT to P(DPPTbBBT) dominating over exciton separation.
Devices with PC$_{71}$BM as acceptor gave promising results of about 0.4 to 0.6 % PCE and a rather low exciton dissociation efficiency, especially for excitons of the P(DPPThBBT) phase were determined as the limiting factors. The use of acceptors with a deeper LUMO could provide a larger offset to split the exciton and devices with C$_{60}$ showed working devices, however the performance was not improved compared to PC$_{71}$BM. Using PC$_{84}$BM however, resulted in devices without photovoltaic response. Using C$_{60}$ however, resulted in devices without photovoltaic response. Finally the hole mobility of P(DPPThBBT) was explored and a value between $7 \times 10^{-5}$ and $7 \times 10^{-4}$ cm$^2$/Vs was found. The negative field dependence of the mobility gives an indication of large spatial disorder and charge trapping in this material.

Identifying these issues greatly helped to design new polymers of the same building blocks (DPP and BBT) with a shallower LUMO and improved hole mobility. This second step of development of the polymers improved the solar cell performance to over 4 % efficiency, which is a great step forward and demonstrates the potential of such DPP/BBT donor/acceptor polymers.
Solution-processed subphthalocyanine acceptors

5.1 Motivation

Organic solar cells have greatly evolved in the obtained device efficiency in recent years and the major improvement comes from the development of new materials for the active layer. A few polymers and small molecules now exhibit close to 10 % power conversion efficiency.\(^27,28,29\) This development however mainly arises from the development of new donor materials whereas as the acceptor only a handful of fullerene derivatives is used in the high performance solar cells. Fullerenes have a couple of outstanding properties, which make them so attractive as electron acceptors in organic solar cells. These are the high electron mobility\(^175,176,177\) and a well favoured electron affinity, as the fullerene core can accept up to six electrons.\(^178,179\) Fullerenes however are also associated with certain drawbacks for example a low tuneability of the electronic properties\(^110,151\) and a low absorption coefficient in the visible region.\(^152\) The synthesis costs of fullerene derivatives are unusually high compared to other organic materials and the synthesis involves high temperature steps, which raise the embedded energy.\(^180\) This embedded energy increases the energy pay back time of the resulting solar cells, as a solar cell has to work for a longer time to produce the energy it consumed for its own the manufacturing.

The limited tuneability of the electronic properties is probably one of the most important issues. It has led to the development of new donor materials, which are highly adopted to the properties of fullerene derivatives but reduces the synthetic flexibility. For example fullerene derivatives are inherently unstable materials under illumination and will cause solar cells to degrade in a certain period of time.\(^181\) Other materials can be photochemically stable but would not match the required energy levels. For these reasons great research has been directed towards the development of non-fullerene acceptors, but their success is still to come.\(^182,183,184\) Although the efficiency of fullerene-free solar cells is catching up with an efficiency of 6.8 % reported for a solution processed\(^185\) and 8.4 % for a vacuum deposited device,\(^186\) the majority still is between 2 and 4 %.\(^182,183,184\) The high planarity of small molecular and polymeric acceptors was identified as one of the key issues associated with these structures, as it leads to a strong aggregation behaviour by \(\pi\)-stacking.\(^187\) Thus recent research has focussed its attention on three-dimensional structures, which can prevent the aggregation.\(^188\)

Subphthalocyanines (SubPcs) are such three-dimensional molecules which are often based on a boron core and an axial linker.\(^189\) SubPcs have been successfully used in vacuum-processed solar cells mainly with \(C_{60}\)\(^190,191,192\) or \(C_{70}\)\(^193,194\) as acceptors. However also their electron accepting properties have been investigated and a high electron mobility was
Motivation

Depositing the active layer by thermal evaporation however has a few disadvantages. A strong vacuum pump system is required and it is generally not a continues process, although progress has been made to incorporate roll-to-roll manufacturing in such systems.\textsuperscript{200} The processability from solution instead offers the advantage that the active layer can be formed by spray-coating, inkjet-printing, screen printing and similar techniques.\textsuperscript{34} These systems provide a continuous and high speed manufacturing with low energy consumption and are therefore highly desired.\textsuperscript{15}

As discussed earlier to allow the fabrication of organic solar cells from solution, a high solubility of the organic compounds is required. The solubility of SubPcs can be easily altered by the outer atoms of the molecules.\textsuperscript{201,202} Halogen atoms such as fluorine and chlorine and a phenol linker have shown to improve the solubility of SubPc molecules by more than a factor of hundred, which makes them viable candidates for solution processed organic solar cells.\textsuperscript{203}

In this chapter SubPc derivatives were investigated as donor and acceptor materials for organic solar cells. These molecules were supplied by Prof. Graeme Cooke at the University of Glasgow and synthesized by Nor Prasetya. The results of this investigation were published in the \textit{Journal of Materials Chemistry}.\textsuperscript{204}

5.2 \textbf{Synthesis of subphthalocyanine acceptors}

The synthesis and chemical characterisation was performed by Nor Prasetya at the University of Glasgow. The synthesis of these materials was based on a two step reaction from commercial compounds. Compound 3 and 4 were synthesized according to the procedure by Sullivan \textit{et al}.\textsuperscript{205} and are based on the precursors of 4,5-difluorophthalonitrile (5) and 4,5-dichlorophthalonitrile (6) which react under reflux with BCl\textsubscript{3} to a boronsubphthalocyanine (3, 4) with a chlorine linker (see Figure 5.1).

\textbf{Figure 5.1: First reaction step. Synthesis of halogenated boron-subphthalocyanine.}

In the second reaction step the chlorine linker is replaced by a phenol or pentafluorophenol under reflux of toluene for 24 hours. The product was cooled to room temperature and then purified by column chromatography. The end-products (1 and 2) were extracted as a purple solid. Compound 1 is thus based on a fluorinated subphthalocyanine with a fluorinated phenol
as linker and compound 2 on a chlorinated subphthalocyanine with a non-halogenated phenol linker (see Figure 5.2)

![Reaction Diagram]

Figure 5.2: Second reaction step. Replacing the chlorine linker with a phenol. Reproduced from ref. 204 with permission from The Royal Society of Chemistry.

5.3 Electrochemical characterisation

For every organic semiconductor the HOMO and LUMO energy levels are of great importance. For the given compounds these were measured by cyclic and square wave voltammetry, performed by the chemists in Glasgow. The compounds were dissolved in dichloromethane at a concentration of $1 \times 10^{-3}$ M. Ferrocene was used as an internal reference with the redox couple estimated at an energy of -4.8 eV from the vacuum. Three electrodes, a platinum disc working electrode, a platinum wire counter electrode and a silver wire pseudo-reference electrode were used, with positive bias applied to the counter electrode.

Figure 5.3 shows the square wave and cyclic voltammogram of the two compounds. The oxidation and reduction potentials are both clearly visible. The cyclic voltammogram shows that the reduction wave (at negative bias) completely recovers in the backward sweep, whereas the oxidation has no pronounced recovery wave, which can indicate a permanent transition to a new compound. In Table 5.1 the HOMO and LUMO levels of compound 1 and 2 are listed. The LUMO level of both compounds is identical at an energy of -3.5 eV. This level is between typical donor materials used for organic solar cells such as P3HT, MEH-PPV or PTB7 and typical acceptor materials like PC$_{61}$BM or PC$_{71}$BM. Thus a large enough energy offset could arise to use them either as donors or acceptors. Strong research efforts have been directed to design materials in this region of the LUMO, as it could provide an increased open circuit voltage and has been successful with the development of ICBA, a fullerene derivative with a raised LUMO level. The HOMO level of compound 1 is with -5.7 eV slightly lower than of compound 2 with -5.6 eV giving a larger band gap.
The orbital distribution of the HOMO and LUMO over the molecule has been calculated by DFT using the Spartan ‘14 software suite and were performed by Prof. Graeme Cooke.

The optimized structures were obtained as the energetic minima by the hybrid functional B3LYP/6-31G*. As illustrated in Figure 5.4 the HOMO is evenly distributed across the SubPc core, whereas the LUMO is less evenly distributed. Only a small contribution of the HOMO and LUMO arises from the peripheral halogens, whereas the axial phenoxy and the boron linker unit appear to provide no contributions whatsoever. The calculated energy levels of Table 5.1 are in good agreement with the experimentally obtained values.

Table 5.1: HOMO and LUMO energy levels of compound 1 and 2 by square wave voltammetry (SWV) and theoretical predictions by density functional theory (DFT) provided by Prof. Graeme Cooke.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{\text{ox}}$ (V)</th>
<th>$E_{\text{red}}$ (V)</th>
<th>HOMO$_{\text{(SWV)}}$ (eV)</th>
<th>LUMO$_{\text{(SWV)}}$ (eV)</th>
<th>HOMO$_{\text{(DFT)}}$ (eV)</th>
<th>LUMO$_{\text{(DFT)}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.85</td>
<td>-1.29</td>
<td>-5.7</td>
<td>-3.5</td>
<td>-5.8</td>
<td>-3</td>
</tr>
<tr>
<td>2</td>
<td>0.81</td>
<td>-1.27</td>
<td>-5.6</td>
<td>-3.5</td>
<td>-5.8</td>
<td>-3.1</td>
</tr>
</tbody>
</table>

The orbital distribution of the HOMO and LUMO over the molecule has been calculated by DFT using the Spartan ‘14 software suite and were performed by Prof. Graeme Cooke. The optimized structures were obtained as the energetic minima by the hybrid functional B3LYP/6-31G*. As illustrated in Figure 5.4 the HOMO is evenly distributed across the SubPc core, whereas the LUMO is less evenly distributed. Only a small contribution of the HOMO and LUMO arises from the peripheral halogens, whereas the axial phenoxy and the boron linker unit appear to provide no contributions whatsoever. The calculated energy levels of Table 5.1 are in good agreement with the experimentally obtained values.

Figure 5.3: Square wave (top) and cyclic (bottom) voltammetry of compound 1 and 2. Data provided by Nor Prasetya. Adapted from ref. 204 with permission from The Royal Society of Chemistry.

Figure 5.4: DFT modelled structures of compound 1 and 2 showing the distribution of LUMO (top) and HOMO (bottom). Picture provided by Prof. Graeme Cooke. Adapted from ref. 204 with permission from The Royal Society of Chemistry.
5.4 Optical characterisation

The absorption spectra of the derivatives 1 and 2 was measured in solutions and films and are compared in Figure 5.5. In chlorobenzene solutions compound 1 has a strong absorption peak at 553 nm and compound 2 at 571 nm, which is red-shifted to 560 nm and 582 nm, respectively, in films. This bathochromic shift is typically an indicator for the nature of π-stacking and molecular order of the molecules.\textsuperscript{148} As this shift is rather small these interactions are assumed not to be dominant in film formation. However aggregations were seen to form in compound 1, although they did not lead to a significant red-shift. Both compounds have a high peak absorption coefficient of $1.5 \times 10^5$ for compound 1 and $3.5 \times 10^5$ for compound 2. Such high absorption coefficients are typical for subphthalocyanne molecules.\textsuperscript{207}

An interesting aspect of these compounds is the complete transparency in the region between 400 and 425 nm as seen in the solution absorption spectra and by studying the fluorescence emission for a variable excitation wavelength. By excitation in this region no absorption and fluorescence was detected, which is rather unusual for organic compounds. Typically a molecule can be excited into higher vibronic states by more energetic wavelengths. For an energy of 3 eV (410 nm) above the HOMO obviously no vibronic states exist and the photons thus cannot be absorbed. This behaviour can be interesting for the fabrication of low-cost optical band-pass filters, or to study the dynamics of the excited state of bulk-heterojunction blends by techniques like transient absorption where it is very useful to excite only one component of the blend.

![Figure 5.5](image)

*Figure 5.5: a) Absorption spectra of compounds 1 and 2 in chlorobenzene solution (solid lines) compared to fluorescence excitation spectra (symbols).
   b) The absorption coefficient of spin-coated films.
   Both graphs reproduced from ref. 204 with permission from The Royal Society of Chemistry.*

Both materials are also fairly emissive with a fluorescence quantum yield of about 14 % (1) to 16 % (2) in chlorobenzene solutions and similar in polystyrene blends (13 % to 15 %). The quantum yield in solution thereby was measured according to procedures described in the literature with a quinine sulphate reference.\textsuperscript{208} The fabrication of polystyrene blends has the advantage that the PLQY of films can be easily measured with the Hamamatsu integrating
sphere (section 3.3.4). The dilution of the chromophores in a matrix strongly reduces the interaction of dipoles and gives the natural quantum yield. In neat films these interactions are much more significant due to the close packing. In neat films therefore a red-shift of the fluorescence and a reduced quantum yield to about 2.5% was observed.

5.5 Solubility and film formation

The solubility of the component materials is a crucial parameter for solution-processed bulk-heterojunction solar cells as it strongly influences the blend morphology and phase separation. The solubility can be quantitatively measured by determining the concentration of a completely dissolved solution. An initial concentration of 100 mg/ml of the compounds was prepared in 1,2-dichlorobenzene. Compound 2 readily went into complete solution and a spin-coated film gave a particle free film of 136 nm ± 18 nm thickness.

![Figure 5.6: Fluorescence emission spectra of solutions and films of compounds 1 and 2 at 360 nm excitation. Reproduced from ref. 204 with permission from The Royal Society of Chemistry.](image)

500 600 700 800
0.0 0.2 0.4 0.6 0.8 1.0
Solution Film
Wavelength (nm)

a) Optical microscope image of compound 2, spin-coated from 100 mg/ml in 1,2-dichlorobenzene.

b) Image showing crystalline structures of compound 1, which grew in about 2 days. The inset shows an undissolved mono-crystalline particle of 15 µm size. Reproduced from ref. 204 with permission from The Royal Society of Chemistry.

![Figure 5.7: a) Optical microscope image of compound 2, spin-coated from 100 mg/ml in 1,2-dichlorobenzene. b) Image showing crystalline structures of compound 1, which grew in about 2 days. The inset shows an undissolved mono-crystalline particle of 15 µm size. Reproduced from ref. 204 with permission from The Royal Society of Chemistry.](image)
Optical images are shown in Figure 5.7. In films from compound 1, however, well defined crystallites were found with a size of 15 µm. These particles dissolved when the concentration was reduced to 45 mg/ml. In spin-coated films from compound 1, left for two days in air or the nitrogen glove box, large crystalline structures were found, especially on the edges of the substrate but also in the main area of the film. These aggregates might originate from the interaction of the outer fluorine atoms of this compound and form non-covalent C—F···H and C—F···π bonds.209

5.6 Using SubPcs as donor materials for solution-processed solar cells

The first test of solar cells with these materials was done by using them as donor materials in blends with PC71BM as acceptor. In this combination the LUMO level has an offset of 0.2 eV, which can be sufficient to dissociate excitons. Solar cells were prepared in the standard device structure of ITO/PEDOT:PSS/Active layer/Ca/Al, where the active layer was spin-coated from chlorobenzene, 20 mg/ml and a ratio SubPc:PC71BM of 1:1. Devices were fabricated without thermal annealing.

Figure 5.8 shows the solar cell characteristics of the compounds with a rather poor device performance of less than $8 \times 10^{-3} \%$. The short circuit current density was only 0.025 mA/cm², but still a clearly distinguishable from the JV-curve in dark. The EQE spectra are rather noisy because of the small current, but a clear contribution from the absorption of the SubPc is visible in the spectra by the strong peaks at 560 nm for compound 1 and 580 nm for compound 2. Beyond this region the EQE tails off towards 700 nm. This part comes from the absorption of PC71BM. Recently a couple of small molecular donors have become very popular and achieved high power conversion efficiencies approaching 10 %,28,29 where often the blend microstructure was tuned by different additives or annealing. The low efficiency of the compounds shown here however is not promising for device optimisation and the next step was to use these materials as the acceptor component rather than the donor.

![Figure 5.8: a) JV-characteristics of solar cells based on compound 1 and 2 blended with PC71BM. Dashed lines show the characteristics without illumination. b) The corresponding EQE spectra.](image-url)
5.7 P3HT:SubPc solar cells

5.7.1 Quenching studies

P3HT is still the most commonly used donor material for organic solar cells, in spite of its limited performance, which arises from the rather large band gap,. The relatively low cost, wide availability and the high degree of information available for P3HT makes it the most obvious choice to investigate the performance of new acceptor compounds. P3HT is fairly emissive which makes it a very good candidate for studies of fluorescence quenching and electron transfer. Introducing an acceptor into the polymer matrix of P3HT allows excitons to be dissociated at the acceptor site. This reduces the number of emitted photons and therefore reduces (quenches) the fluorescence. This method can be used to probe how efficiently excitons are dissociated by electron transfer to an acceptor site.

Samples for quenching measurements were prepared from 20 mg/ml of P3HT in 1,2-dichlorobenzene and the acceptor concentration varied between 0 and 6 wt%. The spin-coated films were excited at 500 nm and the fluorescence was detected between 600 and 900 nm in an integrating sphere. As shown in Figure 5.9 neat P3HT films had a PLQY of 12 %, which decreased very rapidly by introducing only 0.3 wt% of either compound 1 or 2 to about 6.5 %. The fluorescence spectra maintained a similar shape for increasing amount of acceptor up to about 4 wt%, then an additional emission peak as shown for compound 2 at 600 nm is visible in Figure 5.9 (a). At 2 wt% no further decrease of the PLQY is observed and a plateau is reached (Figure 5.9 (b)). This flattening for higher concentrations of acceptors is typically ascribed to aggregation of the molecules.\(^{210}\)

\[\text{Figure 5.9: a) Fluorescence spectra of P3HT with variable concentration of compound 2 increasing from 0 to 6 wt%}.\]

\[\text{b) Photoluminescence quantum yield of P3HT with variable concentration of compound 1 and 2.}\]

In a similar way also the lifetime of the exciton can be measured by the fluorescence decay. The samples were excited with a pulsed laser at a wavelength of 393 nm and the emission detected at 650 nm by time correlated single photon counting. For neat P3HT a mono-
exponential decay was found with a lifetime of 670 ps, which rapidly decreases when small concentrations of the acceptor compound 2 were introduced. In Figure 5.10 (b) the decrease of PLQY is compared with the decrease of the mono-exponential fluorescence lifetime and the integral of the normalised fluorescence decay curve. Electron transfer to the acceptor introduces an additional pathway to depopulate the excitons with a rate initially proportional to the concentration, at low concentration thus the inverse of the lifetime and PLQY gives a linear increase with an offset of 1. The quenching efficiency by one minus the normalised quenching ratio reaches a value of 75 % obtained from the PLQY measurement and about 65 % from the lifetime measurements. Differences might arise from degradation of the fluorescence between PLQY and lifetime measurements. The high degree of quenching, even at low concentrations of the acceptor, suggests efficient electron transfer from P3HT to the acceptor. Alternative Förster energy transfer by dipole-dipole interactions can be neglected because of the minor overlap of the emission of P3HT with the absorption of the acceptors.

![Figure 5.10: a) TCSPC fluorescence decay of P3HT blends with compound 2. b) Comparison of the quenching efficiency by three different methods.](image)

5.7.2 Devices

As the previous paragraph has shown, efficient electron transfer from P3HT to the SubPc molecules can be expected. This is an important criterion to prepare efficient photovoltaic devices. From P3HT:PC_{60}BM it is known that the device performance is strongly influenced by the crystallinity of P3HT, which can be tuned by the choice of the casting solvent, thermal annealing and a couple of other methods. This influence has to be considered in the optimisation of solar cells. Therefore the devices were prepared with thermal annealing of the active layer at 120 °C for 20 minutes. The blend ratio of the devices was varied between 1:1 and 1:4 by weight and the active layer was spin-coated from 20 mg/ml of 1,2-dichlorobenzene. This solvent was chosen because of its high boiling point and low evaporation rate. During spin-coating this gives a slow formation of the film and higher crystallinity can be obtained.

Figure 5.11 shows the performance of photovoltaic devices of P3HT blended with compound 1 and 2. Solar cells with compound 1 as the acceptor strongly depend on the blend ratio and
the performance has a maximum at the ratio of 1:2 with an efficiency of 0.15%. Compound 2 however performed much better with a quite similar performance for all blend ratios and a maximum efficiency of 1.1% for the 1:3 blend ratio. Annealing at a higher temperature of 150 °C had no strong influence on the performance, but the series resistance increased slightly. Devices from compound 2 had a good fill factor of 43% to 50%, whereas the fill factor of P3HT:1 is only about 30%. The device parameters are summarized in Table 5.2. The spectral mismatch factor as described in section 3.4.4 was calculated from the EQE spectra presented in Figure 5.16 and gave about 1.002 for P3HT:1 (1:2) and 0.982 for P3HT:2 (1:3). As these are close to unity corrections of the efficiency were neglected.

5.7.3 Analysis of the morphology

In order to investigate the origin of the lower performance of compound 1 in these blends, I analysed the quality of the spin-coat coated films illustrated in Figure 5.12. The blend films with compound 1 showed a rather coarse microstructure on the order of a few micrometers. The area of the darker regions seem to decrease with increasing concentration of the acceptor therefore might be assigned to P3HT. Especially the blend film of 1:3 ratio looks strongly phase separated and coincides with the low device performance. The 1:2 ratio appears more

Table 5.2: Device parameters of P3HT solar cells with compounds 1 and 2 as acceptors.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>P3HT:1</th>
<th>P3HT:2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1:1</td>
<td>1:2</td>
</tr>
<tr>
<td>Efficiency (%)</td>
<td>0.04</td>
<td>0.15</td>
</tr>
<tr>
<td>J_SC (mA/cm²)</td>
<td>0.94</td>
<td>1.67</td>
</tr>
<tr>
<td>V_OC (V)</td>
<td>0.14</td>
<td>0.28</td>
</tr>
<tr>
<td>FF (%)</td>
<td>29.9</td>
<td>32.1</td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>70 ± 3</td>
<td>55 ± 4</td>
</tr>
</tbody>
</table>
homogeneously intermixed, which is consistent with the higher short circuit current density. In the lower panel, blends with compound 2 are shown, where no microstructure morphology is observed except for the 1:4 blend ratio, which appears slightly phase separated. Again this coincides with a slightly lower device performance. As discussed above, compound 1 tends to form large crystals even in neat films, thus it is very likely that aggregation of these molecules leads to coarse blend formation and reduced device performance.

The AFM provides us with a closer look at some details of the blend morphology and images are shown in Figure 5.13. For compound 1 of a blend ratio of 1:2 the height morphology is relatively coarse with a variation of 40 nm in an area of 5 × 5 µm and the phase image shows a well-defined phase separation with high contrast. This can provide the origin of the rather low short circuit current as excitons are not well dissociated in such coarse structures. The images of P3HT:2 show that the variation in height is much lower with about 11 nm and the phase images seem much less defined. Therefore I speculate that on the nanometer scale the films with compound 2 are more finely intermixed, which gives rise to the better performance.

5.7.4 Mobility and recombination

After exciton dissociation in organic cells free charge carriers are generated, which have to reach the electrodes before they have recombined. The charge carrier mobility is an important
parameter, which describes how quickly the charges drift in the electric field of the device. For one of the devices I applied the simple charge extraction by linearly increasing voltage technique (CELIV). This technique, works well with P3HT blends because of intrinsic charge carriers, which arise from oxygen or moisture in P3HT films.\textsuperscript{218,219,220} These intrinsic charge carriers are extracted by an applied voltage ramp and from the peak extraction time an estimate of the charge carrier mobility is given. For an applied voltage ramp of 33 kV/s the peak extraction time was at 5.7 µs, which relates to a mobility of $9 \times 10^{-6}$ cm$^2$/Vs by a given film thickness of 38 nm. This value is quite a bit lower compared to P3HT:PC$_{61}$BM of about $8 \times 10^{-5}$ cm$^2$/Vs (see chapter 6). In CELIV measurements the type of charge carrier mobility is undefined.

![CELIV current transient of P3HT:2 (1:3) for a voltage ramp of 33 kV/s.](image)

Lower mobility can lead to a slower extraction of charge carriers and increased bimolecular or trap-assisted recombination. The simplest way to probe these processes is by intensity dependent JV-curves. Figure 5.15 shows the short circuit current density and open circuit voltage as a function of illumination intensity. The $J_{SC}$ could be nicely fitted with a power law of exponent 0.94, which is typical for some losses due to bimolecular recombination. The $V_{OC}$ showed two regimes with a different slope as a function on the logarithm of the intensity. The low intensity part, where trapping is more dominant, was fitted with a slope of 3.0 kT/e, which indicates severe losses due to monomolecular recombination. At higher light intensity $V_{OC}$ increases slower with a slope of 1.7 kT/e. This roll-off can reduce the $V_{OC}$ at 1 sun intensity and limit the device performance.
5.7.5 External quantum efficiency

The external quantum efficiency is shown in Figure 5.16 and gives insight into the spectral dependence of charge generation. The peak EQE of P3HT:2 is about 33 % and the spectra appear all very similar, only the dip at 400 nm becomes more pronounced with increasing concentration of the acceptor. This is due to lack of absorption of the SubPcs in this region. Compared to a standard P3HT:PC$_{61}$BM device, the response region is slightly extended with the additional peak at 580 nm. Figure 5.16 (b) clearly shows the contribution from P3HT and compound 2 to the photocurrent. The absorption spectra were converted to 1 – Transmission as this gives a better estimate than absorbance of the amount of absorbed photons.

Figure 5.15: a) Short circuit current density as a function of light intensity of P3HT:2. The red line is a fit to a power law as a linear fit on logarithmic scales.

b) Open circuit voltage as a function of light intensity. The red line is a linear fit on semi-logarithmic scales.

Figure 5.16: a) The EQE spectra of P3HT:2 for varying blend ratios.

b) Contribution to the EQE spectrum of P3HT:2 (1:3) from absorption of P3HT (red line) and absorption of compound 2 (blue line).
5.7.6 Conclusions

The EQE spectra of P3HT:2 reached a value of about 30 % in the region of 500 to 600 nm and was comparably lower for compound 1. By the integral of the EQE times the number of photons in the solar spectrum we get the short circuit current of 3.62 mA/cm$^2$ for P3HT:2 (1:1) which is in reasonable agreement with the measured $J_{SC}$ of 3.82 mA/cm$^2$. This slightly lower value can be attributed to degradation effects of the solar cells between the measurement of the JV-characteristic and the EQE spectrum. To estimate the potential for optimisation of these devices we can roughly estimate that the EQE will be limited at about 70 %, as for organic solar cells rarely higher values are reported, and the fill factor could also increase to about 70 %. This brings us to an approximate power conversion efficiency of maximum 4 %. This limitation basically arises from the relatively poor coverage of the sun spectrum, as P3HT and the acceptor compound absorb in the same region. In order to broaden the spectral response the next step was to use other donor components.

5.8 MEH-PPV:SubPc solar cells

5.8.1 Introduction

In order to achieve a better coverage of the solar spectrum and to observe the benefit of absorbing acceptor compounds, MEH-PPV, a donor with a relatively large band gap, was chosen next. MEH-PPV absorbs strongly in the region of 430 nm to 570 nm and thus provides absorption complementary to the blue part of the spectrum of the SubPc acceptors. As shown in Figure 5.17 the acceptor compounds in this case absorb at longer wavelength than the donor component, which can nicely broaden the spectral response. MEH-PPV was used in early stages of the research of organic solar cells and efficiencies around 2 % were obtained (at 0.8 sun illumination). Typically high concentrations of acceptors with blend ratios of 1:4 are required in order to obtain high solar cell performance. MEH-PPV is generally considered rather amorphous and thermal annealing is not required for solar cells with PC$_{61}$BM as acceptor.

![Figure 5.17: Absorption spectra of MEH-PPV and compared to compounds 1 and 2.](image-url)
5.8.2 Devices

Solar cells of MEH-PPV and the SubPc derivatives were prepared from toluene with a total concentration of 13 mg/ml and 11 mg/ml and a blend ratio of 1:5 and 1:3 for compounds 1 and 2, respectively. The device architecture was ITO/PEDOT:PSS/Active layer/Ca/Al. Although thermal annealing is rather unusual for MEH-PPV solar cells, its effect was investigated on a selection of solar cells with a condition of 160 °C and 10 minutes, on a hot plate before deposition of the cathode.

The JV-characteristics of MEH-PPV solar cells, provided in Figure 5.18, show devices with compound 1 of 0.07 % power conversion efficiency, with only a marginal effect of thermal annealing and with compound 2 of 0.3 % PCE without thermal annealing and 0.4 % with thermal annealing. With compound 2 thermal annealing had a positive effect with the short circuit current almost doubled. The spectral mismatch factor was 0.950 for MEH-PPV:1 and 0.952 for MEH-PPV:2 but the efficiency uncorrected. The EQE spectra clearly show the broadening of the response of these solar cells beyond the absorption region of MEH-PPV. With compound 1 the response reaches up to 590 nm and with compound 2 up to 615 nm. This demonstrates the benefit of absorbing acceptor components in organic solar cells, where efficient hole transfer to the donor can provide complementary response of the solar cell. The solar cell performance and EQE with MEH-PPV, however, is lower compared to the devices with P3HT, which might arise from a rather poor intermixing of donor and acceptor.

Figure 5.18: a) JV-characteristics of MEH-PPV blended with compound 1 and 2 with and without (n.a.) thermal annealing of the active layer.
b) EQE spectra for the same solar cells.

5.8.3 Morphology

Under the optical microscope blend films of MEH-PPV:SubPc revealed a rather coarse film with some undissolved particles. Under the AFM MEH-PPV:1 and MEH-PPV:2 revealed a very similar morphology where MEH-PPV:1 had a slightly larger surface roughness of 0.81 nm compared to 0.46 nm for MEH-PPV:2. The Phase images show a fine network with grain sizes of 23 nm and 33 nm respectively. The smaller grain size with MEH-PPV:1 would
suggest a better device performance and higher short circuit current, but is in contrast to the measured solar cells. As AFM only images the surface morphology a different morphology and mixed phases cannot be resolved. The general problem of AFM images being a non-quantitative measure of the morphology is thus a subject of current investigations.\textsuperscript{224}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{afm_images.png}
\caption{AFM images of MEH-PPV:SubPc.}
\end{figure}

### 5.8.4 Conclusions

The EQE spectra have clearly shown a contribution to the solar cell response beyond the absorption range of MEH-PPV which demonstrates the benefits of absorbing acceptor compounds. The solar cells can probably be further optimised and reached a maximum power conversion efficiency of 0.4 \%. As the next step, the low band gap polymer PTB7 was used as donor component and a full device optimisation performed.

### 5.9 PTB7:SubPc solar cells

#### 5.9.1 Device optimisation

PTB7 is a low band gap donor material which has among the highest efficiencies reported for organic solar cells.\textsuperscript{27,30,142} It absorbs up to about 750 nm, which corresponds to a band gap of 1.6 eV. PTB7 is generally considered highly amorphous and no annealing is required for solar cells.\textsuperscript{225} However the film morphology can be strongly modified by the solvent additive 1,8-diiodooctane. In chapter 7 a detailed investigation of the influence of this additive DIO is given, which revealed an optimum concentration of 3 vol\% in PTB7:PC\textsubscript{71}BM solar cells to achieve an efficiency above 7 \%. Similar conditions were thus used for the investigation of the SubPc derivatives followed by a detailed device optimisation.

From the previous sections we have seen that the solar cell efficiency of these acceptor compounds depends on the annealing conditions and by experience this often has a stronger effect than, for example, the blend ratio. Thus the device optimisation of PTB7:SubPc solar cells was performed by investigation of annealing conditions first and solar cells were prepared in the standard architecture from a 1:1.5 blend ratio with 3 vol\% of DIO. The annealing duration was kept constant at 10 minutes and the temperature was varied.

In Figure 5.20 the performance of the solar cells is shown. The JV-characteristics reveal a $J_{SC}$ of PTB7:2 of about 7.0 mA/cm\textsuperscript{2} which increases to 7.9 mA/cm\textsuperscript{2} upon thermal annealing at
160 °C. The $J_{SC}$ of PTB7:1 of about 6.1 mA/cm$^2$ however is not strongly influenced by thermal annealing and rather decreases when annealed at 160 °C. Solar cells from compound 2 had a higher $V_{OC}$ of 0.9 V compared to 0.74 V with compound 1. The fill factor increases with annealing temperature in both types of solar cells, for PTB7:1 from 33 to 37 % and for PTB7:2 from 39 to 44 %. The improvement of FF is attributed to improvements of shunt and series resistance as the shunt resistance trends towards higher values and the series resistance towards lower values. This gives rise to a very promising power conversion efficiency up to 3.2 % for PTB7:2 and 1.3 % for PTB7:1. All device parameters are listed in Table 5.3.

![Figure 5.20: a) JV-characteristics of PTB7:1 (dashed lines) and PTB7:2 (solid lines) without active layer annealing (n.a.) and annealing at 100 °C, 130 °C and 160 °C for 10 minutes. b) The corresponding EQE graphs.](image)

Table 5.3: Device parameters of PTB7:SubPc solar cells with variable annealing conditions. Error margins are given by the standard deviation of functioning devices.

<table>
<thead>
<tr>
<th></th>
<th>PTB7:1 n. a.</th>
<th>PTB7:1 100 °C</th>
<th>PTB7:1 160 °C</th>
<th>PTB7:2 n. a.</th>
<th>PTB7:2 100 °C</th>
<th>PTB7:2 130 °C</th>
<th>PTB7:2 160 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency (%)</td>
<td>1.23 ± 0.03</td>
<td>1.35 ± 0.11</td>
<td>1.28 ± 0.12</td>
<td>2.49 ± 0.20</td>
<td>2.48 ± 0.10</td>
<td>2.66 ± 0.02</td>
<td>3.20 ± 0.07</td>
</tr>
<tr>
<td>$J_{SC}$ (mA/cm$^2$)</td>
<td>-5.1 ± 0.1</td>
<td>-5.2 ± 0.4</td>
<td>-4.6 ± 0.0</td>
<td>-7.0 ± 0.6</td>
<td>-7.1 ± 0.2</td>
<td>-7.1 ± 0.2</td>
<td>-7.9 ± 0.2</td>
</tr>
<tr>
<td>$V_{OC}$ (V)</td>
<td>0.73 ± 0.00</td>
<td>0.73 ± 0.00</td>
<td>0.75 ± 0.02</td>
<td>0.91 ± 0.01</td>
<td>0.88 ± 0.00</td>
<td>0.89 ± 0.00</td>
<td>0.92 ± 0.00</td>
</tr>
<tr>
<td>FF (%)</td>
<td>33 ± 0</td>
<td>35 ± 0</td>
<td>37 ± 3</td>
<td>39 ± 0</td>
<td>40 ± 1</td>
<td>42 ± 1</td>
<td>44 ± 1</td>
</tr>
<tr>
<td>$R_{sh}$ (Ohm cm$^2$)</td>
<td>238 ± 9</td>
<td>235 ± 48</td>
<td>331 ± 47</td>
<td>368 ± 19</td>
<td>325 ± 24</td>
<td>351 ± 26</td>
<td>369 ± 22</td>
</tr>
<tr>
<td>$R_s$ (Ohm cm$^2$)</td>
<td>26.2 ± 3.8</td>
<td>14.9 ± 0.6</td>
<td>13.0 ± 2.0</td>
<td>49.7 ± 0.3</td>
<td>22.1 ± 1.5</td>
<td>15.0 ± 0.9</td>
<td>18.1 ± 1.1</td>
</tr>
</tbody>
</table>

The EQE spectra shown in Figure 5.20 reveal a response of these solar cells up to 750 nm, corresponding to the absorption edge of PTB7 and have a pronounced peak at 570 nm for PTB7:1 and 590 nm for PTB7:2. These peaks again clearly identify that photons absorbed in the acceptor phase efficiently contribute to the photocurrent. The EQE reaches about 39 % for PTB7:1 and 44 % with PTB7:2 and follows the trend of the $J_{SC}$. All results will be thoroughly discussed in the next paragraph after the device optimisation is presented.
For the next step of device optimisation I kept the temperature at 160 °C constant, as this was found to give the best results for PTB7:2 and varied the duration of thermal annealing. The device performance of this batch was slightly lower compared to the previous with a maximum efficiency of 2.7 % obtained for an annealing duration of 10 minutes. As Figure 5.21 illustrates, the efficiency has a relative improvement of 25 % compared to the non-annealed device and forms a clear maximum at a duration of 10 minutes. This maximum corresponds to the trend of the device parameters. Especially $V_{OC}$, FF and shunt resistance form the trend of a maximum for the 10 to 15 minutes duration, whereas the series resistance has a minimum. The $J_{SC}$ potentially further increases for longer duration times as it has the maximum at 20 minutes duration, however an outlier at 15 minutes slightly disturbs the trend.

Next we will look at the solvent additive 1,8-diiodooctane and its influence on the device performance. Up to now a concentration of 3 vol% DIO was used as this is the standard for PTB7:PC$_7$BM solar cells. However in other systems the optimum content of the additive can vary significantly and thus needs to be optimized. Because of the large range of reported values for the concentration of DIO, it was varied in steps of factor two between 0.5 vol% and 8 vol% to find the optimum condition for the PTB7:SubPc solar cells.

Figure 5.22 shows the device results where for PTB7:2 a strong dependence of the performance on the concentration of DIO is found and for PTB7:1 only a minor dependence. For PTB7:2 a sharp maximum of the power conversion efficiency is obtained at a concentration of 1 vol% DIO. The maximum efficiency is 3.5 % which is a two-fold increase compared to devices without DIO. Increasing the content of DIO beyond 1 vol% leads to a continuous decrease of the efficiency. For PTB7:1 the maximum occurs at 2 vol% of DIO with an efficiency of 1.9 % which compares to 1.6 % without DIO. The improvement with the additive mainly arises from an increase of $J_{SC}$ and a slight increase of the FF and $V_{OC}$.
Device optimisation

Finally the blend ratio can be optimized, where also a wide range was chosen from 1:0.5 to 1:4. The blend ratio can have an influence on the charge transport properties and exciton dissociation efficiency. So far a blend ratio of 1:1.5 was used as this corresponds to the optimum of PTB7:PC$_{71}$BM devices.

Figure 5.23 shows the EQE spectra of PTB7:SubPc blends for varying ratio. As mentioned before the peak at 570 nm arises from compound 1 and the peak at 590 nm from compound 2 shown in the figures (a) and (b) respectively. Increasing the concentration of the acceptor component changes the ratio between the absorption of the SubPc and PTB7 and gives a relative increase of the acceptor peak. In both blends a maximum of the EQE is observed for the 1:1.5 blend ratio. At this blend ratio not only the EQE at the peak has a maximum but also in the entire spectrum, which suggests that the best trade-off between donor and acceptor absorption, exciton dissociation efficiency and charge transport is reached. Surprisingly the blend ratio found optimal is the same as for PTB7:PC$_{71}$BM devices and the previously used value.

5.9.2 Summary of results

The device optimisation let to a maximum device efficiency of 3.5 % with compound 2 and 1.9 % with compound 1. A strong correlation of the device parameters was found, which
indicates that these are global optima. However the device performance was influenced by a higher batch to batch variation of solar cell fabrication, such that PTB7:2 solar cells have an efficiency of about 3.3 % ± 0.2 % for conditions close to the optimum. The spectral mismatch factor for the optimised conditions was 0.917 for PTB7:1 and 0.901 for PTB7:2 which was uncorrected and if applied would lead to a slightly larger efficiency of a factor of 1.1 increase. Within each device batch these variations appear much lower and typically consistent trends were found. The most obvious observation after the device optimisation is that compound 1 has a much lower performance compared to compound 2. The origin of this difference is multifold and can be assigned to following parameters:

1. Compound 1 has a slightly larger band gap, which leads to a smaller amount of harvested photons, although the maximum EQE for both compounds is similar (∼ 43 %). Taking the integral of the sun-spectrum multiplied with the normalised EQE of the 1:1.5 blend ratio gives a 14 % higher short circuit current with compound 2.

2. Compound 1 has obtained a drastically lower $V_{OC}$ of 0.75 V compared to 0.90 V with compound 2. This difference is quite surprising, as both materials have the same LUMO levels also the same $V_{OC}$ would be expected. However the $V_{OC}$ can additionally be influenced by recombination losses which will be investigated further below.

3. Devices from compound 1 had a slightly reduced FF of 40 % in the optimized condition which compares to 48 % of compound 2.

During the optimisation, devices with compound 1 were less strongly influenced by the variation of process parameters. Adjusting annealing conditions, the concentration of DIO and the blend ratio gave only small changes in the device efficiency. This is an indication that the morphology of the active layer is more determined by other parameters such as the intrinsic crystallisation behaviour of compound 1 (See section 5.5).

In Figure 5.24 the JV-characteristics of the optimised solar cells are compared with the performance of PTB7:PC$_{71}$BM. The higher open circuit voltage with compound 2 as acceptor is very positive and gives hope to reach a new regime for higher device efficiency. However it
is obvious that the $J_{sc}$ and FF have to be further improved to obtain a comparable performance. In the next paragraphs the limiting factors will be further investigated.

5.9.3 Losses of exciton dissociation

As explained previously, exciton dissociation can be explored by investigations of the fluorescence of the components. In this study I looked at the fluorescence emitted from PTB7 blends with the SubPc derivatives for varying blend ratio. The samples were based on the same solutions as used for the solar cell studies, but spin-coated on quartz substrates as they were commonly prepared as references to obtain the film thickness. The fluorescence was studied at an excitation wavelength of 280 nm which is absorbed by PTB7 and the acceptor.

![Figure 5.25](image)

Figure 5.25: a) Fluorescence emission spectra of PTB7:2 for varying blend ratio. b) Comparison of the excitation spectrum at 800 nm emission with the absorption of PTB7 and comparison of the excitation spectrum at 650 nm with the absorption of compound 2. Both graphs reproduced from ref. 204 with permission from The Royal Society of Chemistry.

Figure 5.25 shows the emission spectra of PTB7:2, obtained with a full excitation band-width of 16 nm and the iris completely open. Thus the sensitivity of the instrument is far below 1% photoluminescence quantum yield and the count rate of $10^6$ indicates that only a tiny fraction of the absorbed photons are emitted by fluorescence. The region at 800 nm can be clearly attributed to emission from PTB7 as seen by the good agreement of the absorption and excitation spectra and the region at 650 nm can be attributed to emission from compound 2. At a blend ratio of 1:0.5 all emission from the acceptor is completely quenched but steadily increases with increasing content of the SubPc acceptor. The PTB7 emission however initially is high for the blend ratio of 1:0.5 and fall to a minimum for the blend ratio of 1:1.5 and then increases again. In the entire spectrum the blend ratio of 1:1.5 has a minimum of fluorescence, which is in good agreement with the device performance having a maximum. However at none of the blend ratios PTB7 is completely quenched. This might arise from the rather low LUMO offset of PTB7 and the SubPc acceptors. As PTB7 has the LUMO energy level at -3.18 eV (See Figure 6.14) and the SubPc acceptors at -3.5 eV the driving force to split the excitons is only 0.32 eV. This might be slightly insufficient for complete exciton harvesting as for example in blends with PC$_{71}$BM no fluorescence from PTB7 was detected.
5.9.4 Electrical losses

In order to investigate losses of charge carriers after exciton dissociation. The solar cells were investigated under variable light intensity and the change of the JV-curve was analysed. Especially the lower open circuit voltage obtained with compound 1 was quite surprising and potentially originates from higher recombination losses.\textsuperscript{126,227,228} Figure 5.26 shows the \( J_{SC} \) and \( V_{OC} \) as a function of light intensity for the optimized solar cells compared to the reference of PTB7:PC\textsubscript{71}BM. The short circuit current density depends on the light intensity with an exponent slightly below unity of 0.92 with compound 1, 0.95 with compound 2 and 0.97 with PC\textsubscript{71}BM. This shows that losses like bimolecular recombination are more pronounced in solar cells prepared from compound 1 as acceptor as the short circuit levels off at high intensities. The \( V_{OC} \) of PTB7:2 is much higher compared to PTB7:1 and PTB7:PC\textsubscript{71}BM for all light intensities, though a similar slope of 1.48 kT/e and 1.55 kT/e is found respectively. For PTB7:1 additionally a kink at 0.15 sun is observed, separating two logarithmic regimes. The fit was taken in the region with the higher slope. In the literature the observation of a similar kink has been reported and attributed to a low shunt resistance of such devices.\textsuperscript{229} However electrical simulations, as discussed in chapter 6, could not directly verify this behaviour. Thus the origin of the strongly reduced \( V_{OC} \) of compound 1 is unclear. Compared to PC\textsubscript{71}BM, with a slope of only 1.16 kT/e, drastically higher losses of monomolecular recombination are thus evident. These monomolecular losses are mainly attributed to charge trapping in the bulk or at interfaces in the device.\textsuperscript{105} Thus potentially impurities remaining from the synthesis or defects in the interpenetrating network of the blend are potential origins, as charge trapping at the interfaces should be similar in devices of both compounds.

Looking at the collapsed JV-curves provides another way of investigating bimolecular and monomolecular recombination losses. By normalizing the JV-curves, obtained for different light intensities, it is possible to directly observe how the curves change. The spread at short circuit was attributed to monomolecular recombination and the spread at open circuit to bimolecular recombination.\textsuperscript{100,105} Figure 5.27 shows collapsed JV-curves of the optimized

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure526.png}
\caption{a) \( J_{SC} \) of the optimized solar cells as a function of light intensity (I) fitted by a power law on exponential scales.\newline
b) \( V_{OC} \) as a function of light intensity, fitted with a linear dependence on a logarithmic x-axis.}
\end{figure}
PTB7:1 and PTB7:2 devices, normalised at -0.5 V to a value of -1. For PTB7:1 clearly a larger spread at short circuit is visible, the curves then follow a cross-over point and spread again at open circuit. This can be attributed to a transition from trap-assisted recombination to bimolecular recombination. For PTB7:2 the trap-assisted recombination appears less pronounced and no such cross-over point of the JV-curves arises.

5.10 Conclusions

In this chapter I investigated novel subphthalocyanine derivatives as donor and acceptor components. Using SubPcs as solution processed donors with PC71BM as acceptor an efficiency of $8 \times 10^{-3} \%$ was obtained. But using the SubPcs as acceptor gave good efficiencies up to 3.5 % with PTB7, 1.1 % with P3HT and 0.4 % with MEH-PPV as donors. In all cases a clear contribution to the photocurrent from absorption in the acceptor phase was manifested from the EQE spectra. In the case of MEH-PPV devices this could even extend the spectral response beyond the absorption edge of MEH-PPV. Generally a lower performance was observed with the fluorinated compound 1 which can be attributed to its stronger aggregation behaviour. Three potential limits were identified with these materials which can be overcome by the following suggestion:

1. Adjustments of the band gap of the compounds: The absorption spectrum of the compounds strongly overlaps with common donor materials, which limits the spectral response. Further reduction of the band gap can be very promising to provide complementary absorption. A smaller band gap can be provided by similar subnaphthalocyanines$^{186,230,231}$ and it would be interesting to explore these structures as solution processable acceptors.

2. Adjustments to the aggregation behaviour: Especially compound 1 has shown aggregation which can cause charge trapping and lead to the observed effects of increased recombination. Aggregation can be altered by the choice of additional solubilising side groups or modifications to the phenol group.

![Figure 5.27: a) Collapsed JV-curves of PTB7:SubPc normalised at a voltage of -0.5 V to a value of -1. Reproduced from ref. 204 with permission from The Royal Society of Chemistry.](image-url)
3. Reduction of traps: Further origins of traps might be residues from the synthesis, oxygen or moisture within the compounds. Potentially the synthetic procedure can be further optimized to obtain compounds with higher purity. But also the formation of the bulk-heterojunction can lead to charge traps, which can be reduced by further optimisation steps.

Figure 5.28 provides a graphical summary of this investigation, illustrating the contribution of the SubPc components to the EQE of PTB7:2 devices.

![Graphical summary of the investigation showing EQE and absorption spectra of PTB7:SubPc compound 2 with a power conversion efficiency of 3.5 %. Reproduced from ref. 204 with permission from The Royal Society of Chemistry.](image)
6 Charge transport of donor:acceptor blends

6.1 Introduction

In this chapter the charge carrier mobility and its effect on organic solar cells will be described. The charge carrier mobility plays an important role for solar cells to allow high conductance in forward direction, which allows a low series resistance and high fill factor. Also due to bimolecular recombination it is of great importance to quickly extract charge carriers from the active layer, faster than they recombine. In this chapter the mobility of commercial solar cell materials is investigated by time of flight and CELIV measurements and other techniques also are briefly discussed. In order to achieve a full understanding of the electrical properties of organic solar cells, the relation of the charge carrier mobility to recombination and the JV-characteristics is discussed. The measurements are aided by electrical modelling to compare the behaviour with standard inorganic solar cells. Additionally studies at different operational temperature are included which allow to observe the influence of a temperature dependent mobility on the device characteristics and find the intrinsic charge transport properties of the materials like the energetic Gaussian disorder.

The materials of this study are common for organic solar cells and commercially available, the donors are P3HT and PTB7 and the acceptors are PC$_{61}$BM and PC$_{71}$BM. Their blends are well studied for solar cells and achieve high power conversion efficiencies of about 3 % for P3HT:PC$_{61}$BM and 7 % for PTB7:PC$_{71}$BM in standard device architectures in our laboratories. Further details about the materials and molecular structures were provided in section 3.2. Parts of this investigation were recently published in the journal Organic Electronics.\(^{232}\)

6.2 Charge carrier mobility of neat materials

In this section measurements of the charge carrier mobility of neat donor and acceptor materials typically used for bulk-heterojunction organic solar cells will be presented. For donor materials the hole mobility is of importance and for acceptor materials the electron mobility, because after exciton dissociation electrons and holes are transported in these separate phases.

6.2.1 Hole mobility of P3HT by time of flight measurements

Time of flight is the most direct way to measure the mobility of a material and is considered very accurate.\(^{233}\) Compared to other methods it provides the great advantage that the
dependence of the electric field of the charge carrier mobility can be studied, as well as the
time dependence of the mobility and dependence of the charge carrier concentration. As
discussed in the theory part of this thesis, the hopping of charge carriers between transport
states is preferred in the direction of the electric field and thus provides the directionality of
charge carrier drift. At higher electric fields statistically more charge carriers are driven in
field direction giving rise to faster motion.

For this study, samples of P3HT were prepared from chlorobenzene solutions of 20 mg/ml
concentration and solution-casting onto ITO/PEDOT:PSS substrates. The active layer was
thermally annealed at 140 °C for 20 minutes and had a thickness of 3.5 µm ± 0.3 µm standard
deviation. The cathode was provided by a thin Ca/Al electrode of 20 nm/20 nm thickness to
provide a semi-transparent contact. The hole photocurrents were obtained by exciting the
sample with 480 nm laser pulses through the Ca/Al electrode. In Figure 6.1 the hole
photocurrent transients are shown for three electric fields. At +5 V bias, applied to the Ca/Al
electrode, the holes are propagating through the film rather slowly, with a transit time of 250
µs observed from the transition of the plateau of the photocurrent and the tail, where charge
carriers drift in the film and are extracted respectively. Increasing the applied bias to 25 V
reduces the transit time to 41 µs. Thus the mobility, given by the film thickness divided by the
transit time and electric field, is constant with respect to electric field, as shown in Figure 6.2.

The mobility of P3HT was about $1.0 \times 10^{-4}$ cm$^2$/Vs with an error range of $\pm 5 \times 10^{-5}$ cm$^2$/Vs. Further discussions on the accuracy of the TOF technique is provided in the section of
PC$_{71}$BM (Figure 6.8). The hole mobility of P3HT found here is very similar to literature
values from $10^{-5}$ to $10^{-4}$ cm$^2$/Vs, where it has been shown that the mobility depends on the
molecular weight of the polymer. Baumann et al. found a value of about $3 \times 10^{-4}$ cm$^2$/Vs for
neat P3HT and studied the effect of introducing PC$_{61}$BM into the blend. P3HT is also a
typical material to compare different techniques of charge transport measurements. By
comparing time of flight with CELIV a good agreement was found and the mobility between
$10^{-4}$ and $10^{-3}$ cm$^2$/Vs with a slightly negative field dependence at room temperature. A
comparison of TOF and dark-injection space charge limited current also gave a good
agreement and values from 3 to $6 \times 10^{-4}$ cm$^2$/Vs.
6.2.2 Mobility of P3HT by the CELIV technique

CELIV has a few advantages compared to TOF, namely it can measure the mobility of charge carriers in thin films as they are typically used for solar cells. But standard CELIV cannot distinguish between electrons and holes and provides only the mobility of the majority charge carrier. Additionally CELIV requires free charge carriers in the active layer which can be extracted by the applied voltage ramp. P3HT is a very convenient material to work with, because it has an intrinsic oxygen doping which provides these charge carriers.\textsuperscript{218,219,220}

P3HT samples were prepared in the typical device structure by 20 mg/ml of chlorobenzene, spin-coated at 900 rpm and annealed at 130 °C for 20 minutes. This gave a film thickness of 115 nm. Figure 6.3 (a) shows a typical current transient for an applied voltage ramp of 11 kV/s. A clear extraction peak is visible with a peak extraction time of 3.7 µs, determined by a polynomial fit. This is related to a mobility of $5.6 \times 10^{-5}$ cm$^2$/Vs. Increasing the ramp speed gives a faster extraction of the charge carriers and a higher mobility, as shown in (b). The electric field for different ramps is generally estimated at the peak extraction time\textsuperscript{130} and the field dependence is shown in (c). The mobility increases from 3 to $6 \times 10^{-5}$ cm$^2$/Vs with increasing electric field and is slightly lower compared to TOF, where a reason can be the higher crystallinity of P3HT from solution cast films.\textsuperscript{162,164}

![Figure 6.2: Hole mobility of P3HT as a function of electric field.](image)

![Figure 6.3: a) CELIV current transient of P3HT with a thickness of 115 nm. The linearly increasing voltage has a ramp of 11 kV/s. The extraction maximum is obtained by a polynomial fit (red line). b) Mobility as a function of ramp speed. c) Mobility as a function of electric field at the time corresponding to the maximum of charge extraction.](image)
6.2.3 Hole mobility of PTB7 by the time of flight technique

Next we want to look into the hole mobility of PTB7, where not so much is known about the charge transport properties. The samples for TOF were again prepared in the same device structure by ITO/PEDOT:PSS/PTB7/Ca/Al. Samples were excited at 640 nm, which is in the strong absorbing regime of PTB7, where the absorption depth is 65 nm, taken from the absorption coefficient as the intensity drops to 1/e. This absorption depth is much smaller than the film thickness of 8.3 µm ± 20 %, thus the requirement that charge carriers must be generated in a thin sheet much smaller than the layer thickness, is clearly fulfilled.

Mobility measurements of PTB7 were performed by Stuart Thomson, a project I have supervised. Figure 6.4 (a) shows the hole photocurrent transient of PTB7 at an electric field of $F = 1.2 \times 10^5$ V/cm. A clear transit kink is visible on logarithmic and linear scales (inset). The transit time is taken from the intersection of two linear fits and comes to 6.3 µs. This corresponds to a mobility of $1.1 \times 10^{-3}$ cm$^2$/Vs. The mobility as a function of electric field shown in (b) initially has a negative slope, which can be explained by the built-in field, which arises from the work function difference of the electrodes and is not accounted for by the calculation. At higher applied fields this effect is negligible and the mobility becomes independent of the field strength. The scattering of the data gives an indication of the error margins. In the literature only values obtained by other techniques such as space charge limited current exist for PTB7. The value of about $1 \times 10^{-3}$ cm$^2$/Vs is slightly higher compared to the value found by Liang et al. of $5.8 \times 10^{-4}$ cm$^2$/Vs$^{142}$ and Foster et al. of $2 \times 10^{-4}$ cm$^2$/Vs, who argued the low mobility of PTB7 influences the fill factor of solar cells with thick active layers.$^{176}$ Other measurements are also in that regime.$^{236,237}$ In comparison to P3HT however we found the hole mobility an order of magnitude higher, which can give rise to faster hole extraction from the active layer. The high mobility of PTB7 in our measurement agrees with the high fill factor of PTB7 solar cells of 70 % (see chapter 5.9.2). However in the solar cell blend with PC$_7$BM the morphology plays an additional role on the charge carrier mobility.

![Figure 6.4](image_url)

**Figure 6.4:** a) Hole photocurrent transient of PTB7 by conventional TOF at an applied bias of 100 V, $F = 1.2 \times 10^5$ V/cm. The inset shows the transient on linear scales.

b) The hole mobility of PTB7 as a function of electric field. Data obtained by Stuart Thomson. Both graphs reprinted from ref.232 Copyright (2015), with permission from Elsevier.
6.2.4 Mobility of PTB7 by the photo-CELIV technique

Although CELIV offers the great opportunity to determine the mobility of thin samples as they are used in solar cells, for PTB7 it turned out that the charge extraction is on an inaccessibly short time scale and the response is limited by resistive effects as reported in the literature. Therefore the measurements were performed on thick active layers prepared by solution-casting. Without optical pumping no charge carriers were extracted from neat PTB7 films, thus no intrinsic doping is present. Photo-CELIV however combines the generation of charge carriers by a short laser pulse with the extraction voltage ramp. Between the laser pulse and the voltage ramp a variable delay can be applied, which allows the charge carriers to settle and potentially recombine.

Figure 6.5 shows photo-CELIV transients of PTB7 with a delay from 10 µs to 90 µs. The sharp spikes arise from the fast extraction of charge carriers during the laser pulse. However, a few charge carriers reside in the film and are extracted by the ramped voltage, which is applied after a variable delay. For short delays a pronounced charge extraction peak is visible, which steadily decreases for longer delay times. One disadvantage of photo-CELIV is that the peak extraction time depends on the delay and a potential offset voltage used to compensate the built-in field. Thus only a range of the mobility can be given. For the data presented, the mobility is between 3.2 and $6.9 \times 10^{-4}$ cm$^2$/Vs for an active layer thickness of about 1.3 µm and a voltage ramp speed of 140 kV/s. As, exceptionally, the sample was measured in air at the laboratory of Prof. Juška, degradation of the film is also visible by the decreasing current from the laser excitation which could also cause a change of mobility.

![Figure 6.5: Photo-CELIV transients of PTB7 for different delay times between laser excitation and charge extraction by an applied voltage ramp of 14 V in 100 µs.](image)

6.2.5 Electron mobility of PC$_{71}$BM by the time of flight technique

The next material we want to investigate is the most common electron acceptor PC$_{71}$BM. This fullerene is used in almost all high efficiency organic solar cells but relatively little is known about its charge transport properties. Previous measurements of the electron mobility of
PC$_{71}$BM include techniques like space charge limited current (SCLC), with reported mobilities from $8 \times 10^{-4}$ to $1 \times 10^{-2}$ cm$^2$/V$\cdot$s. The cage size of the fullerene has little impact on the mobility, thus for PC$_{61}$BM, PC$_{71}$BM and PC$_{84}$BM the mobility is rather similar, whereas the solubilising groups can influence the electron transport more strongly. SCLC measurements provide an estimate of the mobility at zero electric field only, as the entire voltage dependent current is fitted with a single mobility in this technique. TOF is able to provide the electric field dependence, but due to the rather poor film quality only one attempt of these measurements is reported by Tuladhar et al., who blended PC$_{61}$BM into a polystyrene matrix and found relatively non-dispersive electron transport.

In order to obtain TOF measurements on PC$_{71}$BM I chose tetrachloroethane as the casting solvent. This provides a high solubility of the fullerenes and the solvent has a high boiling point to allow slowly drying films with good homogeneity. A high concentration of 39 mg/ml was required in order to get a reasonable thickness of 2.8 µm with a standard deviation of ± 3%. Figure 6.6 shows images of the PC$_{71}$BM device for TOF measurements. A film with good homogeneity was obtained, providing a very smooth surface with a roughness of only 0.77 nm (RMS).

The typical device structure of ITO/PEDOT:PSS/PC$_{71}$BM/Ca/Al was used initially. In order to obtain the electron mobility, the samples were excited through the ITO contact by a laser pulse of 337 nm wavelength and a positive bias was applied at the Ca/Al electrode. After excitation with the laser pulse, a current was observed with the oscilloscope, measured at a resistor of 2 kΩ, in series with the device. Figure 6.7 (a) shows the current as function of time on a linear scale at a bias of 20 V. Surprisingly the signal was found to decrease over time within a few seconds from an initial high current (black curve) of 80 µA to an initially negative current (blue curve) of -10 µA, which then turns into the positive at 0.3 µs and decays. By discharging the device through an external short, the signal recovers to the black curve. Thus it is obvious that charge carriers reside in the film and cause a local charging. This distracts the electric field and an accurate determination of a time of flight measurement is prevented. To avoid charging, instead of a continuous voltage, a pulse can be applied, during which the TOF measurement is performed, this ensures discharging of the device before every laser pulse.
In order to investigate this charging effect, the sample was investigated without external voltage to extract the charge carriers only within the built-in field. The sample was connected to the oscilloscope in four different configurations as illustrated in Figure 3.15.

1. ITO electrode on the input terminal, Ca/Al electrode on ground
2. ITO electrode on the input terminal, Ca/Al electrode floating
3. Ca/Al electrode on the input terminal, ITO electrode on ground
4. Ca/Al electrode on the input terminal, ITO electrode floating

If one electrode is floating no current can flow and the oscilloscope is used to measure the potential at the connected electrode versus ground. As shown in Figure 6.7 (b) the current measured at the Ca/Al electrode is identical with and without the connection on the ITO electrode (3,4) and is negative. Additionally the magnitude of the signal on the Ca/Al electrode is much higher compared to the signal measured on the ITO electrode, where the charge carriers are generated close to. This implies that the charge carriers close to the ITO interface are not well extracted at this electrode and rather are compensated through a current at the Ca/Al electrode. This might arise from a fast polarisation effect. Therefore it appears that the extraction of holes on the ITO interface is very limited and causes this space charge effect. A plausible explanation is the formation of a Schottky barrier at the interface between ITO/PEDOT:PSS and the HOMO of PC$_{71}$BM. The Fermi level of PEDOT:PSS is at about -5.2 eV and the HOMO level of PC$_{71}$BM at about -5.9 eV. This is a strong mismatch due to the deep HOMO of PC$_{71}$BM and is likely the origin of a barrier formation. Just to explain, for standard solar cells, the holes are extracted from the donor component, which typically has a much higher HOMO level (ca. 5.0 eV) and allows the formation of an Ohmic contact with PEDOT:PSS.

In order to overcome this problem, an alternative electrode is required. As mentioned before molybdenum oxide is another typical interlayer material for hole extraction with a high work function. The work function of MoO$_3$ has been reported as 6.8 eV$^{132}$ and the formation of an Ohmic contact with the deep HOMO level of a polyfluorene polymer (ca. 6 eV) has been
shown.\textsuperscript{244} Thus for the next device structure, first MoO$_3$ was evaporated onto ITO substrates with a film thickness of 8 nm. Special care was required by the evaporation of MoO$_3$ to completely cover the entire substrate, thus no shadow mask was used for the evaporation. Any contamination of the top surface would cause the solution-cast active layer to dry non-uniformly. Figure 6.8 illustrates the photocurrent of the devices of ITO/MoO$_3$/PC$_{71}$BM/Ca/Al at an applied voltage of 20 V. A clear transition from the plateau to the tail is observed with the transit time of the electrons given by the intersection at 3.8 $\mu$s. The mobility increases with electric field. This positive trend indicates a low spatial disorder according to the Poole Frenkel type charge transport.\textsuperscript{245} At a field strength of $9 \times 10^4$ V/cm the mobility is $1 \times 10^{-3}$ cm$^2$/Vs with an experimental error of $\pm 2 \times 10^{-4}$ cm$^2$/Vs obtained from two different samples and two different pixels each. This shows a very good agreement between different samples and is consistent with previous measurements by space charge limited current reported in the literature,\textsuperscript{176,239-243} but with the advantage that the electric field dependence could be determined.

In order to evaluate the charge transport properties of PC$_{71}$BM, the temperature of the sample was varied by cooling with liquid nitrogen in the cryostat. Upon reducing the temperature from 295 K to 215 K, the mobility decreased by about one order of magnitude as shown in Figure 6.9 (a). The data of electron mobility vs. electric field could be well fitted exponentially as straight lines for all temperatures. According to the Gaussian disorder model described in chapter 2.4.3, from the y-axis offset of these fits, the zero field mobility is obtained. This is at about $1 \times 10^{-4}$ cm$^2$/Vs at room temperature, due to the high slope. By plotting the zero field mobility, $\mu_0$, as a function of the inverse temperature, $1/T^2$, the energetic disorder parameter, $\sigma$, can be determined. From the inverse of the slope in Figure 6.9 (b) we obtain a value of 525 K for the characteristic temperature $T_0$. Using $\sigma = 3kT_0/2$, gives a value of 68 meV for the energetic disorder. This agrees with values obtained by the SCLC method by Mihailetchi of 73 meV.\textsuperscript{241} As shown, the fits agree well with the data points, however the trends and the zero field mobility contain significant error margins.
Electron mobility of PC71BM by the time of flight technique

Especially the slopes of the fits in Figure 6.9 (a) strongly vary for different temperatures, whereas from the Gaussian disorder model a continuous increase would be expected. In (c) these slopes are plotted as a function of the energetic disorder. From this graph, in principle, the spatial disorder parameter, , could be obtained, however due to the variations, no trend could be fitted. The dashed line shows a trend through the origin of the graph which would represent a spatial disorder of zero. The data would point towards negative spatial disorder, which is non-physical.

The energetic disorder parameter was found to have a direct influence on the solar cell performance, especially on and and can cause charge trapping as charge carriers over time drop in energy within the Gaussian band of charge transport. At the low energetic states the intersite distance is large, due to the low density of states. Thus a large hopping distance is required to reach the next transport site of similar energy. This means that charge carriers in the low energetic states are rather immobile and act as recombination centres for charges of the opposite sign. In the next section we will have a closer look at this charge trapping behaviour in blends of PTB7:PC71BM.

6.3 The mobility of bulk-heterojunction blends and its relation to device performance

6.3.1 Hole mobility of PTB7:PC71BM

In the previous section I have shown investigations of the hole and electron mobility of PTB7 and PC71BM as separate materials. Their mobilities turned out to be very similar to each other of about \(1 \times 10^{-3} \text{ cm}^2/\text{Vs}\), which could provide nicely balanced electron and hole transport in the photovoltaic devices. However in bulk-heterojunction blends the morphology plays an additional role in maintaining this high mobility as continuous percolation pathways are required for efficient charge transport.

I chose again the well established TOF method to measure the charge carrier mobilities of PTB7:PC71BM blends. The devices were prepared in the typical structure of
ITO/PEDOT:PSS/PTB7:PC_{71}BM/Ca/Al with the active layer solution-cast from a 40 mg/ml solution of 1,2-dichlorobenzene with 3 vol% of DIO and a blend ratio of 1:1.5. The active layer had a thickness of 7.35 ± 0.3 µm. The device was placed in the cryostat under vacuum and excited with a nitrogen laser of 337 nm wavelength and the current recorded at a variable resistor. The temperature was controlled by the evaporation of liquid nitrogen and an electrical heat source within the cryostat.

Figure 6.10 shows the temperature dependence of the hole photocurrent transients of TOF measurements. A pronounced kink is observed which strongly shifts towards longer time scales upon reducing the temperature and can be attributed to the extraction of holes on the counter electrode. However in the high temperature regime an additional first kink is observed at a shorter time. The origin of this transition is rather unclear, but has been observed in P3HT:PC_{61}BM blends and attributed to a high degree of phase separation. The hole mobility obtained from the second kink at longer times, decreases exponentially by almost three orders of magnitude when the sample was cooled from room temperature to 115 K (see Figure 6.11). The hole mobility has a slightly negative field dependence which is typical for bulk-heterojunction blends due to the high spatial disorder. The average mobility at a field strength of 2.2 × 10^4 V/cm is about 2 × 10^{-4} cm^2/Vs. The hole mobility in the blend is thus a factor of five lower than that of neat PTB7 due to the enhanced disorder. A similar reduction was also observed by SCLC measurements, which are between 5.4 × 10^{-5} cm^2/Vs and 3.2 × 10^{-4} cm^2/Vs for the blend. In Figure 6.11 (b) the hole mobility is plotted as a function of the inverse square of the temperature, which shows a fast initial drop and a slower decrease at low temperature. In the high temperature regime the data could be nicely fitted with the Gaussian disorder model in which, as discussed above, the slope is related to the energetic disorder. From the fit an energetic disorder of 70 meV and µ_0 of 2.0 × 10^{-3} cm^2/Vs was derived. The energetic disorder thus compares similarly with the value obtained above for PC_{71}BM and with P3HT where it is between 56 meV and 71 meV.

![Figure 6.10](image-url)  
*Figure 6.10: a) Hole photocurrent transients of PTB7:PC_{71}BM for varying temperature. The arrows indicate characteristic kinks.  
b) The electric field dependence of the hole mobility at room temperature. Both graphs reprinted from ref. 232 Copyright (2015), with permission from Elsevier.*
Hole mobility of PTB7:PC71BM

The temperature dependence was also analyzed with an effective medium approach (EMA) including trap states according to Fishchuk et al.\textsuperscript{254} In this approach the distribution of the density of states (DOS) is provided by the sum of a Gaussian function for charge transport sites with a width of $\sigma_0$ and a Gaussian function for trap states, with a width of $\sigma_1$, at lower energy, offset by $E_t$. Although the condition of high energetic disorder ($\sigma/kT >> 1$) is not clearly fulfilled, fits according to equations 6.2 and 6.3 were applied. Where $c$ is the concentration of trap states compared to conduction states, $T_{Cr}$ is the critical temperature at which charge transport via trap states becomes dominant and $\mu_0$ is the trap free mobility.

\begin{equation}
T_{Cr} = \frac{-E_t}{2k \ln(c)}
\end{equation}

\begin{equation}
T > T_{Cr}: \mu = \mu_0 c \frac{\alpha_0}{kT} \exp\left(-\frac{E_t}{2kT} \left(\frac{\alpha_1}{kT}\right)^2\right)
\end{equation}

\begin{equation}
T < T_{Cr}: \mu = \mu_0 c \frac{\alpha_0}{kT} \exp\left(-0.5\left(\frac{\alpha_1}{kT}\right)^2\right)
\end{equation}

The fits are shown as dashed lines in Figure 6.11 (b) and show a good agreement with the experimental data. Parameters of the trap energy of 0.1 eV and the trap concentration of 8 % were obtained. The inset shows a representation of the two Gaussian functions and shows that the distribution of trap states is partly within the tail of the charge transport sites, which implies that the charge trapping originates from these tail states. The distribution of the tail states and how it can be influenced by material parameters is currently a subject of interest.\textsuperscript{258,259} Nelson et al. recently presented molecular dynamic calculations based on P3HT, which suggest that the tail states of the density of states mainly arise from intra-chain coupling and proposed that a stiffer polymer backbone would lead to a sharper decay of the tail states.\textsuperscript{256} As the tail states reach from the HOMO and LUMO into the band gap, the EQE spectrum in the sub-gap regime can reveal absorption from the tail states, however there is an ongoing debate if these states are best expressed by a Gaussian or exponential decay,\textsuperscript{257,258,259} but as Nelson explained the implications of both functional forms are rather similar.\textsuperscript{256} We will

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure6_11.png}
\caption{a) The hole mobility as a function of temperature.\newline
b) The hole mobility as a function of the inverse square of the temperature, fitted with the Gaussian disorder model (GDM) in the high temperature range and with an effective medium approach (EMA) including trap states. The inset shows the two Gaussian functions obtained by the EMA for the density of states (DOS) as a function of energy (E).\newline
Both graphs reprinted / adapted from ref. 232 Copyright (2015), with permission from Elsevier.}
\end{figure}
come back to the effect of charge trapping later and next consider the influence of tuning the mobility by temperature on the solar cell performance.

6.3.2 Device performance of PTB7:PC_{71}BM as a function of temperature

In the previous section we have seen that the hole mobility of PTB7:PC_{71}BM is strongly influenced by the temperature and decreases by almost three orders of magnitude when the samples were cooled from room temperature to 115 K. This effect will now be used to tune the mobility of bulk-heterojunction solar cells. In the research of organic solar cells the charge carrier mobility plays a very important role and is commonly reported within publications of high efficiency solar cells. However, about the actual role of the charge carrier on the device performance relatively little is known. Theoretical calculations have been used to study the influence of the mobility on the device efficiency and an optimum electron and hole mobility of about $10^{-2}$ to $10^{-3}$ cm^2/Vs with a relatively flat maximum was predicted.$^{260,261,262,263}$ A direct experimental relation of the mobility and device efficiency has not been deeply studied. Until recently Proctor et al. observed the dependence of the fill factor on the mobility of various small molecule materials and found a relation between them.$^{264}$ Tuning the mobility by varying the temperature should provide a widely accessible range of mobilities and would provide at least a lower limit for the device performance at lower mobility, as other parameters changed by lowering the temperature would also be detrimental rather than beneficial for the solar cells.

Devices of this investigation were prepared in the standard device configuration of ITO/PEDOT:PSS/PTB7:PC_{71}BM/Ca/Al. Where the active layer was prepared by spin-coating from a solution of 20 mg/ml of 1,2-dichlorobenzene and 3 vol% DIO. No thermal annealing was applied. The JV-characteristics and device parameters as a function of temperature are shown in Figure 6.12. At room temperature the device had an efficiency of 6.9 % with a $J_{SC}$ of 12.9 mA/cm^2, $V_{OC}$ of 0.78 V and a FF of 65 %. Upon reducing the temperature, a decrease of the $J_{SC}$ and FF was observed, but the $V_{OC}$ linearly increased. At 77 K the $J_{SC}$ dropped to 8.1 mA/cm^2 and the FF to 33 % whereas the $V_{OC}$ increased to 0.92 V, this led to a reduced device efficiency of 2.5 %. When we see this result in context with the previously observed decrease of the hole mobility (of $10^{-7}$ cm^2/Vs) at this low temperature, it is astonishing that the devices still work reasonably well. The device performance completely recovered upon warming up to room temperature. In Figure 6.12 (b) the device parameters are presented as a function of temperature and the hole mobility, which are related exponentially in this regime by $\mu_h = ae^{b/T}$. The fit parameters $a = 2.75 \times 10^9$ cm^2/Vs and $b = 29.2$ K were obtained from the mobility as a function of temperature presented above. Interestingly the power conversion efficiency is forming a flat maximum in the regime of 260 to 295 K and decreases upon further increasing the temperature due to the drop of the $V_{OC}$, whereas the FF and $J_{SC}$ reach into a plateau. These results show a good qualitative agreement with the theoretical trend,$^{260-263}$ although the maximum PCE occurs at a lower hole mobility of $3 \times 10^{-5}$ cm^2/Vs.
Device performance of PTB7:PC71BM as a function of temperature

6.3.3 The temperature dependence of the $V_{OC}$

Here we observed a linear decrease of the $V_{OC}$ with increasing temperature from 0.92 V to 0.78 V. We will now have a detailed look at the parameters influencing the $V_{OC}$ in order to compare different models and assumptions.

**Model 1, shift of the quasi-Fermi levels:** As proposed by Koster et al.\textsuperscript{103} the $V_{OC}$ is given by the quasi-Fermi level splitting by equation 2.11,

$$V_{OC} = \frac{E_{gap}}{e} - \frac{kT}{e} \ln \left( \frac{N^2}{n \cdot p} \right)$$ (2.11)

where the $V_{OC}$ is given as a function of charge density, density of states ($N$), energy gap and temperature. As the $V_{OC}$ depends about linearly on the temperature we observe from equation 2.11 that the term $k/e \ln(N^2/np)$ must be constant. From a fit of the $V_{OC}$ vs. temperature the slope is $-7.5 \times 10^{-4}$ V/K and thus the charge densities $n$ and $p$ compared to density of charge transport sites gives a population of $np/N^2$ of $1.7 \times 10^{-4}$. Additionally the $V_{OC}$ is influenced by the light intensity, which was also varied between 0.01 to 1 sun. In these solar cells the $V_{OC}$ depends fairly linearly on the light intensity and the population density scales according to a power law with an exponent of 0.85 as shown in Figure 6.13, indicating bimolecular recombination losses.\textsuperscript{127}

---

**Figure 6.12:**

*a) The JV-characteristics of PTB7:PC71BM as a function of temperature (T) strongly influenced by the charge carrier mobility ($\mu$).* 

*b) The device parameters as a function of temperature and hole mobility.* 

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From equation 2.11 it is also evident that the $V_{OC}$ at 0 K is only determined by the effective band gap of the blend. Accordingly extrapolations of the $V_{OC}$ to zero Kelvin are shown in Figure 6.13 (a) and the intersection of the curves at higher intensity indeed meet at a single point at a value of 1.0 eV, for lower intensities, however there is a slight mismatch. In order to compare this with the electronic properties of the compounds PTB7 and PCB$_{71}$BM, I have obtained cyclic and square wave voltammetry measurements. These measurements were performed in dichloromethane solution by a concentration of 0.5 mM and ferrocene as a reference, shown in Figure 6.14. The reduction potentials for PC$_{71}$BM and PTB7 amount to LUMO levels of -3.71 eV and -3.18 eV respectively, with the redox couple of ferrocene taken at -4.8 eV. As the HOMO of PTB7 is not visible in the voltammogram, the absorption onset is taken for the energy gap of PTB7 of 1.64 eV and thus the HOMO is approximately at -4.82 eV. The energy difference of the LUMO of PC$_{71}$BM and the HOMO of PTB7 then gives an effective band gap of 1.12 eV, which agrees fairly well with the $V_{OC}$ at 0 K.

At low temperature a slight deviation from the linear dependence of the $V_{OC}$ is observed. Rauh et al. found a similar, but more pronounced effect in PTB7:PC$_{71}$BM devices and attributed this
to non-Ohmic contacts with the active layer.\textsuperscript{265} This indicates that the contacts also play an important role determining the $V_{OC}$.

**Model 2, reduced dark injection**\textsuperscript{266,267}: This more inorganic approach starts from the classical Shockley equation where the current generated by the solar cell is in the opposite direction to the forward current of the diode, given by

$$J(V) = J_s \left[ \exp \left( \frac{eV}{f k T} \right) - 1 \right] - J_{\text{Photo}}(V)$$  \hspace{1cm} (6.4)

where $J$ is the total current, $J_s$ is the reverse saturation current, $f$ is the ideality factor and $J_{\text{Photo}}$ is the photo generated current. The equation 6.4 can be extended to include parasitic resistances to include the effects of series and shunt resistance, but is not necessary for the discussion here. The open circuit voltage is obtained when the forward current is equal to the photocurrent.

$$V_{OC} = \frac{f k T}{e} \ln \left( \frac{J_{\text{Photo}}}{J_s} + 1 \right)$$  \hspace{1cm} (6.5)

On the first view this looks like the $V_{OC}$ is increasing with temperature in this scenario, however as it is known from inorganic diodes the reverse saturation current is also strongly dependent on temperature. $J_s$ generally decreases sharply with reducing temperatures such that the $V_{OC}$ increases. In order to compare the concepts, the open circuit voltage has been modelled based on an electrical simulation using PSpice. A simple diode (D14148) with an ideality factor of 2.0 was chosen as the model solar cell. The photocurrent was varied between 0.12 and 12 mA and the temperature as above from 77 K to 325 K. The modelled $V_{OC}$ shown in Figure 6.15 (a) shows a strikingly similar behaviour than the measured organic solar cell shown above. The increase of the $V_{OC}$ of the silicon diode originates from a drastic reduction of the reverse saturation current which decreases by 18 orders of magnitude, as shown in (b), which results in a change of factor 4 after the logarithm is taken. Figure 6.15 (c) shows a measurement of the dark current of PTB7:PC$_{71}$BM devices at room temperature and 77 K. It is also observed that the dark current reduces at low temperature, but only by a factor of 3. The dark current, however, is strongly influenced by the shunt resistance, which is neglected in the simulation, therefore a direct observation is difficult without a deeper analysis.

![Figure 6.15: a) Modelled open circuit voltage as a function of temperature. Simulation with PSpice based on a commercial diode. b) The corresponding reverse saturation current for the same diode by the PSpice model. c) Measured dark current of PTB7:PC$_{71}$BM devices at room temperature and 77 K.](image-url)
**Model 3, reduced recombination:** This model is based on the assumption that at open circuit all charge carriers have to recombine and no charge leakage to the wrong electrodes is taking place. This leads to the interpretation that in forward direction the current is solely dominated by bimolecular recombination processes, meaning that all injected charge carriers recombine. The open circuit voltage is then determined by

\[
V_{OC} = \frac{f k T}{e} \ln \left( \frac{J_{\text{photo}}}{J_{\text{Rec}}} \right), \quad \text{with} \quad J_{\text{Rec}} = \frac{e d n_0^{\kappa+1}}{\tau_0}
\]

where \(J_{\text{Rec}}\) is the rate of bimolecular recombination, which is thought to be depending on the charge density \((n_0)\) by a reaction order of \(\kappa+1\) and the charge carrier lifetime \(\tau_0\). The index 0 expresses the variables at short circuit. The authors studied a range of materials systems where the recombination current was determined by transient photovoltage and found a good agreement of the calculated and experimentally obtained \(V_{OC}\). However they restrict their argumentation to room temperature operation. Vandewal *et al.* used a similar approach and determined the recombination current from the charge transfer state emission. They argue the spectral position of charge transfer state emission is directly related to the effective band gap and in this way relates back to the recombination rate. Applying the model of equation 6.6 to explain the temperature dependence of the \(V_{OC}\) gives rise to incredibly low recombination currents as it can be easily compared with the reverse saturation current of model 2. In order to fit the experimental data of the PTB7:PC\(_{71}\)BM solar cells a reduction of the recombination current by 22 orders of magnitude would be required, which is not realistic, especially as the \(J_{SC}\) of these devices is decreasing with temperature and not increasing as it would be required for a reduced recombination.

**Model 4, increased charge density:** This argument by Mandoc *et al.* is based on the reduced electron and hole mobility at lower temperature which leads to a slower sweep-out of charge carriers and thus to a higher density in the active layer. However, Tress *et al.* argued that charge extraction is not important at open circuit conditions and found a constant \(V_{OC}\) as a function of mobility if the bimolecular recombination is mobility independent. For a Langevin type bimolecular recombination where the recombination rate is mobility dependent (equation 2.6), however, an increase of the charge density would be observed, which in turn increases the \(V_{OC}\) according to equation 2.11.

In order to investigate the influence of the charge carrier density, I performed charge extraction measurements on similar PTB7:PC\(_{71}\)BM devices. Charge extraction measurements were performed as described in section 3.5.5 with a microsecond switch. The sample was illuminated at open circuit conditions for a variable duration provided by a pulsed LED. After the LED turned off, the switch connected to short circuit. The charge carriers were extracted by the built-in field and the total charge was given by the time integral of the current. The extracted charge is additionally compared to the time integral of the photocurrent, when the sample is held at short circuit conditions during illumination and with the open circuit voltage measured at the 1 MΩ impedance input of the oscilloscope.
The temperature dependence of the VOC

As Figure 6.16 shows, the extracted charge, the integral of the photocurrent and the open circuit voltage start from the origin and increase simultaneously with the same slope, which is proportional to the light intensity. As the \( \text{V}_{\text{OC}} \) initially is zero this implies that the built-in field is literally identical if the device has an external short circuit or open circuit connection. This means that only the electrodes are required to create the built-in field. Whereas one could think that without any external connection no built-in field arises. Studies of the charge carrier recombination for example have shown to be identical on samples with and without electrodes. At longer times the \( \text{V}_{\text{OC}} \) levels-off and reaches the steady state value and similarly the extracted charge levels-off.

By comparing the two different temperatures of Figure 6.16 a slower initial rise is observed at 77 K, which corresponds to the reduced short circuit current. Additionally the extracted charge at low temperature is quite a bit higher compared to room temperature with an increase of the steady state value by a factor of 2.4 at 0.93 sun intensity. As in equation 2.11 the \( \text{V}_{\text{OC}} \) is depending on the logarithm of the charge carrier density, its increase by factor 2.4 has only a marginal influence, as also Rauh et al. pointed out. Another representation of the same data is provided in Figure 6.17 where the extracted charge is plotted as a function of voltage. At room temperature this gives a straight line for all light intensities, where the slope can be assigned to a capacitance of 3.3 - 3.4 nF, which is very close to geometric capacitance. At 77 K the extracted charge is much more strongly influenced by the light intensity. For 0.12 sun the associated capacitance is 5.5 nF and for 0.93 sun the capacitance is 7.0 nF. This dependence can be explained by the higher density of charge carriers stored in the active layer, which is a function of intensity, whereas at 295 K most charge carriers are stored at the electrodes, which is not intensity dependent. The extracted charge as a function of intensity shown in (c) can be fitted by a power law dependence, \( Q = a I^b \). At room temperature the exponent \( b \) is only 0.02 whereas at 77 K it is increased to 0.11. This emphasizes that more charge carriers at 77 K are stored in the active layer as a function of intensity.

Figure 6.16: The extracted charge (symbols), the integrated photocurrent (solid lines) and the open circuit voltage (dashed lines) as a function of illumination duration of an LED at 295 K and 77 K. Both graphs reprinted from ref. 232 Copyright (2015), with permission from Elsevier.
The charge carrier density and the capacitance can also be investigated by the decay of the open circuit voltage at the 1 MΩ impedance input of an oscilloscope. Figure 6.18 shows the open circuit voltage of PTB7:PC71BM devices after the LED was turned off at $t=0$. The curve for 295 K shows an initial rapid decrease, which can be attributed to charge carrier leakage to the opposite electrode as the solar cell is biased in forward direction. Once the voltage has reduced below the turn-on voltage, the decay slows down and is dominated by charge extraction through the 1 MΩ resistor. Thus the exponential decay can be assigned to a capacitance of 3.93 nF, which is quite similar to the value obtained above. At 77 K the curve looks slightly different: After turning-off the $V_{OC}$ initially decreases less rapidly, which I attribute to additional charge carriers being extracted from the active layer, then also turns into an exponential decay with an associated capacitance of 4.86 nF. Both curves are compared with an electrical simulation using the equivalent circuit shown in (b). At 295 K a perfect agreement with the simulation is observed for an ideality factor of 1.5. Keeping all diode parameters the same but programatically changing the temperature shows a deviation at 77 K between simulation and experiment. Where the difference is ascribed to the slower extraction of charge carriers.

The charge carrier density and the capacitance can also be investigated by the decay of the open circuit voltage at the 1 MΩ impedance input of a solar cell. Figure 6.18 shows the open circuit voltage of PTB7:PC71BM devices after the LED was turned off at $t=0$. The curve for 295 K shows an initial rapid decrease, which can be attributed to charge carrier leakage to the opposite electrode as the solar cell is biased in forward direction. Once the voltage has reduced below the turn-on voltage, the decay slows down and is dominated by charge extraction through the 1 MΩ resistor. Thus the exponential decay can be assigned to a capacitance of 3.93 nF, which is quite similar to the value obtained above. At 77 K the curve looks slightly different: After turning-off the $V_{OC}$ initially decreases less rapidly, which I attribute to additional charge carriers being extracted from the active layer, then also turns into an exponential decay with an associated capacitance of 4.86 nF. Both curves are compared with an electrical simulation using the equivalent circuit shown in (b). At 295 K a perfect agreement with the simulation is observed for an ideality factor of 1.5. Keeping all diode parameters the same but programatically changing the temperature shows a deviation at 77 K between simulation and experiment. Where the difference is ascribed to the slower extraction of charge carriers.

Figure 6.17: a, b) Extracted charge vs. the open circuit voltage of data from Figure 6.16 at 77 K and 295 K respectively. The grey line is a linear fit which gives approximately the capacitance of the device. c) The extracted charge after long illumination as a function of intensity. At low temperature the extracted charge depends much more strongly on the light intensity.

Figure 6.18: a) Decay of the open circuit voltage at a 1MΩ resistor. The sample was illuminated with 0.93 sun intensity until $t=0$. Dashed lines show the $V_{OC}$ modelled with an equivalent circuit approach. b) The model circuit in PSpice using a diode of type D1N4148 with an adjusted ideality factor of 1.5 and reverse saturation current of 0.47 pA which changes with temperature as controlled by the program. The capacitance was chosen in order to fit the slope of the voltage decay.
Conclusions: In conclusion, upon reducing the temperature of PTB7:PC\textsubscript{71}BM devices a linear increase of the $V_{OC}$ was observed. This can be best described by model 1 which proposes a temperature dependent quasi-Fermi level splitting provided in equation 2.11. Additionally an increase of the charge carrier density by about a factor of two was observed when the sample is cooled to 77 K. This was attributed to a slower extraction from the active layer, but the additional charge carriers have only a minor influence on the $V_{OC}$.

6.3.4 The temperature dependence of the $J_{SC}$ and recombination

In Figure 6.12 it is seen that the $J_{SC}$ reduces by about one third when the solar cells are cooled to 77 K. This could potentially have various origins which will now be discussed. The short circuit current is influenced by the following parameters: The absorption spectrum, the exciton dissociation efficiency, recombination losses and charge leakage to the wrong electrode.

Influences of charge generation: The first aspect to look at, is the absorption spectrum of PTB7:PC\textsubscript{71}BM at low temperature. As shown in Figure 6.19 the absorption spectrum is rather independent on the temperature. Upon cooling only a minor change is observed by a more pronounced valley between the vibronic peaks as seen for example at 650 nm. At low temperature thus the number of absorbed photons is unchanged, but the EQE is gradually decreasing with temperature. The EQE spectra also show no spectral change which could potentially arise if the exciton dissociation efficiency in the polymer and fullerene phase becomes asymmetric as a function of temperature and agrees with observations of P3HT:PC\textsubscript{61}BM.\textsuperscript{273} Because of reflection losses on the cryostat windows and the illumination beam being larger than the pixel size, the EQE is given in arbitrary units, normalised to the spectrum at 295 K. The integrals of the EQE spectra resemble the trend of the $J_{SC}$.

![Figure 6.19: a) Absorption spectrum of PTB7:PC\textsubscript{71}BM at room temperature and 77 K. b) EQE spectra as function of temperature. Both graphs reprinted / adapted from ref. 232 Copyright (2015), with permission from Elsevier.](image)

To investigate changes of exciton dissociation, the fluorescence of the blend was measured as a function of temperature. Figure 6.20 shows an increase of the emission of PTB7:PC\textsubscript{71}BM
blends with reducing temperature. The region of the spectrum around 715 nm can be attributed mainly to the emission of PC₇₁BM and the peak at 790 nm mainly to the emission of PTB7 as observed by excitation spectra. Again I want to point out that the total emission of these blends is very low and only detectable with a wide slit and completely opened iris. Thus most excitons are efficiently quenched. To analyse these data, three mechanisms have to be considered which depopulate the excited state excitons: radiative recombination and nonradiative recombination and the dissociation of excitons due to charge transfer. The non-radiative decay can generally be temperature dependent as it depends on the thermally activated collisions of excited molecules. In neat films of PC₇₁BM the excited state lifetime is 600 ps, which reduces drastically to 100 fs (in which 80 % of excitons have decayed) for the blend with PTB7 as shown in Figure 4.12. Therefore the decay due to charge transfer can be considered the dominant quenching mechanism and the enhanced emission with reducing temperature can be attributed to a reduction of the charge transfer efficiency, however only a marginal change of the quenching efficiency is observed and its relation to the \( J_{SC} \) is still unclear.

Mauer et al. used the transient absorption technique to study the generation of charge carriers of P3HT:PC₆₁BM and found it temperature-independent. According to the general theory of charge separation by Braun and Onsager, the exciton dissociation efficiency is temperature and electric field dependent, and a good agreement has been found in early solar cells. However in high performance bulk-heterojunction devices geminate recombination of the exciton before charge separation is mainly believed to have minor impact.

**Losses by bimolecular recombination.** As Figure 6.16 shows, the charge density in the solar cell increases at a reduced temperature, which can be ascribed to the slower charge extraction because of the reduced mobility. Bimolecular recombination depends strongly on the density of charge by a reaction order, \( \kappa \), of two or even higher orders and potentially also on the mobility according to the theory by Langevin. As both effects are contributing oppositely, the recombination rate can increase or decrease.
To study bimolecular recombination we can look at the intensity dependence of the $J_{SC}$ as a function of temperature as shown in Figure 6.21. The $J_{SC}$ scales with the light intensity according to a power law, $J_{SC} = a I^b$, where the exponent is an indicator for bimolecular recombination losses. The exponent is found to be approximately constant for temperatures above 200 K at a value of 0.965. For lower temperatures the exponent decreases and reaches 0.917 at 77 K. The trend looks qualitatively similar to the $J_{SC}$ as a function of temperature. However a direct relation between the two is thus far not established. Applying the approach by Koster et al. to quantify the bimolecular recombination losses by the fraction of recombined charge carriers, $\eta_{Br} = 1/b - 1$, obtained no better matching relation. Accordingly the charge carrier losses would increase from $\eta_{Br} = 3.5 \%$ to 9.1 \% upon cooling to 77 K whereas the $J_{SC}$ reduces by 37 \%.

**Figure 6.21:** a) The short circuit current density as function of light intensity for varying temperature. Solid lines are fits according to a power law of $J_{SC} = a I^b$. Adapted from ref. 232 Copyright (2015), with permission from Elsevier.

b) The exponent, $b$, as a function of temperature compared to the $J_{SC}$.

Besides the steady state photocurrent, also its time dependence can provide good insight of the charge recombination and extraction dynamics. By probing the photocurrent response of these devices, we can observe how quickly the charge carriers are extracted to the electrodes. This measurement was performed on a different sample. It was illuminated with a rectangular light pulse, provided by an LED and the photocurrent was measured at the 50 \( \Omega \) impedance of the oscilloscope. Figure 6.22 shows the photocurrent response at room temperature and 77 K normalised by the light intensity of the LED. As the photocurrent is almost proportional to the intensity at room temperature all traces almost overlap and follow the rectangular shape of the light pulse. At early times a slight overshoot of the photocurrent is observed, especially for low light intensities. As the lamp reaches steady-state conditions within 3 \( \mu s \) (Figure 3.12) this overshoot can be attributed to a slight charge trapping effect. At 77 K however the behaviour is quite different as the current increases very slowly with time until it reaches steady state conditions. At high intensity also a slight overshoot is visible until it reaches steady state conditions at about 30 \( \mu s \). At low light intensity the current is still slightly increasing at the end of the light pulse of 57 \( \mu s \). After turning off the LED, the current decreases rapidly at room temperature and very slowly at 77 K. The slowly decaying current
The mobility of bulk-heterojunction blends and its relation to device performance

at 77 K can be attributed to charge carriers which are still extracted from the active layer. This slow extraction arises from the higher accumulation of trap states and the strongly reduced charge carrier mobility. This strongly reduced charge extraction time can increase the bimolecular recombination, because the charge carriers are given more time to interact in the active layer.

Bimolecular recombination was additionally investigated by transient photovoltage measurements, where the samples were illuminated with a continuous light source of variable intensity provided by an LED and a pulsed illumination from a laser. The voltage was traced with the oscilloscope at an input impedance of 1 MΩ. The high impedance prevents charge carriers flowing in the external circuit and it is assumed that all charge carriers in the film have to recombine. By increasing the background illumination, the steady state density of charge carriers increases, which is measured as an offset voltage, and the additional charge carriers from the laser pulse would recombine faster. The laser pulse was attenuated such that the voltage change $\Delta V$ is about 10 mV without background illumination, this ensures the small perturbation regime where an exponential decay can be expected.

![Figure 6.22: The photocurrent transient of PTB7:PC$_{71}$BM at room temperature and 77 K. The device was illuminated with a 57 µs long light pulse of variable intensity. The photocurrent is normalised to the light intensity.](image)

![Figure 6.23: Transient photovoltage measurements of PTB7:PC$_{71}$BM at room temperature and 77 K after subtraction of the offset voltage. The photovoltage decays reduce for increasing offset intensity (I) from dark to one sun, which causes the increasing offset voltage (V).](image)
Figure 6.23 shows the raw photovoltage transients after subtraction of the offset voltage. The photovoltage change, created by the laser pulse, decreases exponentially with time and becomes shorter with increasing background illumination. At 77 K it is also observed that the peak maximum is shifted to a longer time scale compared to room temperature. The red line shows a maximum at about 100 µs and corresponds to 0.09 sun background illumination, creating an offset voltage of 0.65 V, whereas at room temperature the peak is almost instantaneous, < 1 µs. This difference can be explained by the slower extraction of charge carriers due to the reduced mobility. In fact a similar technique has recently been applied to determine the mobility, when the photovoltage transients were observed for a variable resistance.\(^\text{97}\)

Another obvious difference of the photovoltage transients is the decrease of magnitude compared to the curve without background illumination. This decrease is caused by a variation of the bulk capacitance compared to the electrode capacitance. The capacitance can thus be estimated from a technique called differential charging, by extrapolating the voltage change \(\Delta V\) to \(t = 0\) divided by the charge created by the laser pulse, \(Q\).\(^\text{92}\) Therefore \(Q\) is simply measured by the integral of the photocurrent response through a 50 \(\Omega\) resistance, for the same laser intensity and without background illumination.

\[
C = \frac{Q}{\Delta V}
\]

The capacitance shown in Figure 6.24 (a) can be approximated by an exponential increase of \(C = a \exp(bV)\) in the high voltage range and the density of charge carriers generated by the offset illumination is then given by the integral of \(C\) with respect to \(V\).

\[
n = \int_0^V C \, dV, \quad n = \frac{a \left[ \exp(bV) - 1 \right]}{b}
\]

The charge carrier density then has the form \(n = n_0 \exp(\phi V)\), which combined with the decay lifetime \(\tau = \tau_0 \exp(\rho V)\) gives the bimolecular recombination coefficient of

\[
\beta = \frac{n^{k-1}}{(k+1)\tau_0 n_0^k}, \quad \kappa = \frac{\rho}{\phi
\]

Figure 6.24 shows the derivation of the bimolecular recombination coefficient from the transient photovoltage technique. The capacitance seems to have two slopes a slower one in the low voltage range and a faster slope in the high voltage range, with the latter ascribed to the storage of charge carriers in the active layer. The capacitance at 77 K shows a very rapid increase in the region of 0.9 V. This is because in the low temperature regime the open circuit voltage tends towards the effective band gap and thus all intensities give more or less the same voltage, as shown in Figure 6.13. The lifetime of the voltage decay, which is generally thought to be directly related to lifetime of free charge carriers,\(^\text{92}\) is increased at 77 K which leads to a reduced bimolecular recombination coefficient by about one order of magnitude. The bimolecular recombination coefficient has a similar dependence on \(n\) and is on the order of \(10^{-12}\) cm\(^3\)/s at room temperature and \(10^{-13}\) cm\(^3\)/s at 77 K. The decrease of the bimolecular recombination coefficient, cannot be directly translated to an absolute reduction of the recombination as at lower temperature the charge carrier density and the sweep-out time of charge carriers are increased. At short circuit it is quite difficult to estimate the equilibrium charge density in the active layer.
Critical discussion on TPV: Finally on this subject I want to raise a critical discussion on the technique of transient photovoltage, used to provide an estimate of the charge carrier lifetime and recombination. As explained above the technique basically relies on the assumption that all photogenerated charge carriers have to recombine in the active layer at open circuit conditions. However from the diode response we observe that the $V_{OC}$ arises in the region where the current is rising quickly with increasing voltage as the diode is basically biased in forward direction. Thus the charge carriers at the electrode almost cancel the built-in field and the directionality for charge carriers is reduced. Thus if no effective blocking layers are used at the electrodes, the charge carriers can easily leak to the wrong electrodes. In the typical device structure, in principle no such blocking layers are used as both electrodes ITO/PEDOT:PSS and Ca/Al can be considered as metals. Thus by comparing the transient photovoltage decays with an electrical simulation with just a diode in parallel with a capacitor gave a quite a good agreement as shown in Figure 6.25. The electrical simulation shows a reasonable agreement with the photovoltage response at room temperature in the dark and at 0.08 sun. However for higher offset voltages the decay of the simulations appear faster even after adjustments of the diodes ideality factor and junction capacitance. Ideally the photovoltage response should be corrected for the diode leakage but no such concept has been
The temperature dependence of the JSC and recombination proposed yet. Although these issues with transient photovoltage measurements have been raised in the literature\textsuperscript{277,278} it is still a very common technique and its results mostly agree with other methods.\textsuperscript{92,93,229}

Losses by trap-assisted recombination: At short circuit conditions losses due to trap-assisted recombination are often considered more severe than bimolecular recombination, as the charge carriers trapped in the film have a much longer reaction time than the charge carriers which are efficiently swept out.\textsuperscript{100,105} The trap-assisted recombination can be studied by the voltage dependence of the light intensity. As Koster and Mandoc et al. have shown, the ideality factor in organic solar cells can be understood as a factor determined by trap-assisted recombination.\textsuperscript{103,104} This factor, as shown in

![Diagram of an electrical model of the transient photovoltage technique using PSpice.](image)

**Figure 6.25:** a) Diagram of an electrical model of the transient photovoltage technique using PSpice based on a D14148 diode, a 2.5 nF capacitor which corresponds to the geometrical capacitance and a combination of a pulsed and offset photocurrent. b) Comparison of the simulation (black lines) with the voltage decay from above at room temperature.

![Graph showing the voltage change over time.](image)

**Figure 6.26:** a) The $V_{oc}$ as a function of light intensity for varying temperature fitted with a logarithmic dependence (solid lines) according to $V_{oc}=a+b \ln (I)$. b) The slope $b$ divided by $kT/e$ as a function of temperature. Both graphs adapted from ref. 232 Copyright (2015), with permission from Elsevier.
Figure 6.26, increases strongly with reducing temperature from the minimum of 1.03 kT/e at 325 K to 1.93 at 77 K. This increase can be attributed to a strong increase of trap-assisted recombination at low temperature. The trap states or tail states of the Gaussian distribution of transport sites are stronger occupied at lower temperature, because the thermal energy to escape these states is reduced. This leads to an increase of the monomolecular recombination and can also reduce the $J_{SC}$.

Another way to look at this subject is by investigating the collapsed JV-characteristics of different light intensities, which were normalised at a voltage of -0.5 V to a value of -1. As Figure 6.27 shows the spread at short circuit conditions, which is attributed to trap-assisted recombination, is strongly enhanced at 77 K and reduces with increasing temperature. At 77 K the curves have a cross-over point close to the open circuit voltage, where the distribution is assigned to bimolecular recombination.

**Figure 6.27:** Collapsed JV-curves, normalised at -0.5 V to a value of -1. The spread at short circuit is an indication of trap-assisted recombination and the spread at open circuit for bimolecular recombination.

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**Conclusions:** In conclusion the short circuit current as a function of temperature decreased by about one third when the devices where cooled from room temperature to 77 K. The losses arose from a potential reduction of the exciton dissociation efficiency, increased bimolecular recombination due to the enhanced charge carrier density and reduced sweep-out time but mainly enhanced trap-assisted recombination due to stronger occupation of traps.

### 6.3.5 The temperature dependence of the fill factor

For the data shown in Figure 6.12 the FF decreases from 65 % at room temperature to 33 % at 77 K. This is a dramatic reduction and strongly contributes to the reduced power conversion efficiency. The fill factor has again multiple origins as obviously all device parameters are linked in certain ways. In principle the FF can be understood as a change of extraction current of the solar cell as a function of voltage. We have already seen that the charge extraction and recombination processes are voltage dependent, additionally exciton dissociation can be field activated, reducing with decreasing electric field as discussed above and other parameters are the parasitic resistances.
Influence of the bimolecular recombination: Monomolecular and bimolecular recombination both influence the fill factor. Monomolecular recombination has an influence on the shunt resistance and will be discussed below. Bimolecular recombination influences the fill factor because the recombination rate depends on the voltage applied to the device. At short circuit, bimolecular recombination losses are low, because the charge carriers are extracted quickly from the active layer. Increasing the voltage towards open circuit conditions reduces the built-in electric field and charge carriers are extracted slower. This gives rise to higher recombination losses and the photocurrent is reduced. Figure 6.28 shows the FF as a function of light intensity and temperature. For all curves a decrease of the FF at high intensities is observed, which arises from bimolecular recombination increasing with the density of charge carriers in the film. As was shown in Figure 6.16 at low temperature the density of charge carriers in the film increases more rapidly with light intensity compared to at room temperature and thus explains the faster decrease of the FF shown here.

Influence of series resistance: The series resistance of a solar cells mainly arises from the bulk conductivity and the contact with the electrodes. As the conductivity is directly linked to the mobility and charge density by equation 2.2, the series resistance can be expected proportional to \(1/n\mu\). The simplest estimate for the series resistance is the inverse slope of the current at a high forward voltage. In this regime the diode is in forward direction and the current is limited only by the series resistance. According to model 3 in section 6.3.3, the forward current is limited by recombination, in the other models also charge leakage to the opposite electrode contributes to the current in forward direction. From the curves in Figure 6.12 a clear increase of the series resistance was observed with reducing temperature and is displayed in Figure 6.29. The series resistance was additionally obtained by the inverse slope at the open circuit voltage and by a method using two JV-curves of different light intensity.
The method using two JV-curves and the slope at the open circuit voltage show a good agreement, whereas the slope at the high forward voltage gives slightly lower values. The series resistance at the high voltage increases from $7 \Omega \text{cm}^2$ at room temperature to $15 \Omega \text{cm}^2$ at 77 K and $R_s$ of the two JV-curves from $10 \Omega \text{cm}^2$ to $71 \Omega \text{cm}^2$. The series resistance from two JV-curves and obtained at the $V_{OC}$ are strongly dependent on the light intensity and increase by more than order of magnitude for intensities from 0.08 sun to 1 sun. The series resistance from the high voltage slope in contrast is almost independent of light intensity. This difference likely arises from the charge carrier density dependence of the conductivity. In high forward bias the charge density is dominated by injected charge carriers, whereas close to open circuit voltage it is dominated by photo-generated carriers. Interestingly the series resistance of the two matching methods can be approximated with a straight line on double logarithmic scales. Accordingly the series resistance depends on the hole mobility by a power law with $R_s \sim \mu_h^{-1/4}$. This shows that the series resistance depends on the bulk conductivity in a more complex way, as the conductivity according to 2.2 would drop with the mobility by three orders of magnitude whereas the charge density only doubles.

**Influence of the shunt resistance:** The shunt resistance is a parameter which describes leakage of charge carriers to the wrong electrode, monomolecular recombination and electric field activated exciton dissociation. The shunt resistance can simply be measured by the slope of the JV curve at short circuit and also depends on the illumination intensity. The temperature dependence shown in Figure 6.30 reveals a strong decrease of $R_{sh}$ from about 1000 $\Omega \text{cm}^2$ at room temperature to 250 $\Omega \text{cm}^2$ at 77 K. Reducing the light intensity from one sun to 0.08 sun gave a strong increase of $R_{sh}$ by about 2 orders of magnitude. This intensity dependence must be seen in context with the $J_{SC}$ which also strongly depends on the intensity. Calculating the change of the photocurrent near short circuit by $\Delta J = \Delta V / R_{sh}$ normalised by $J_{SC}$ gives a value almost independent on the light intensity, in the high temperature range. Thus it shows that the leakage of charge carriers is proportional to the short circuit current. At
low temperatures the leakage of charge is generally slightly higher and increases with intensity. This can be an effect of increased charge trapping, when the hopping probability against the electric field increases. In this way more charge carriers reach the wrong electrode and annihilate there.

How strongly the series and shunt resistance influence the FF can be estimated from an approximate empirical formula

\[
FF = FF_0 \left(1 - \frac{R_S J_{SC}}{V_{OC}}\right), \quad FF = FF_0 \left(1 - \frac{V_{OC}}{R_{SH} J_{SC}}\right)
\]

(6.10)

where FF is the fill factor influenced by the parasitic resistance and FF₀ is the fill factor without resistive effects. The calculated FF₀, corrected for the series and shunt resistance, is plotted in Figure 6.31. The series resistance, taken from the double-JV curve analysis, has a strong influence on the fill factor, which would improve to over 80 % if the series resistance would be zero, whereas the shunt resistance has a smaller effect. Correcting for both gives values above 100 % in the low temperature regime, which is non-physical and general issues have been raised which question the applicability of methods determining the FF from other JV-curve parameters.
Conclusions: The fill factor is strongly influenced by three factors: The series resistance increases with reducing temperature due to reduced conductivity. The shunt resistance contains leakage of charge carriers to the wrong electrode which increases at low temperature due to hopping of charge carriers against the electric field and due to trap-assisted recombination. Bimolecular recombination influences the FF due to the voltage dependent sweep-out dynamics.

6.4 Conclusions of this chapter

In this chapter I studied the electron and hole mobility of commercially available materials PTB7, P3HT and PC_{71}BM by the accurate time of flight technique and CELIV. The hole mobility of PTB7 was found approximately $1 \times 10^{-3}$ cm$^2$/Vs which is about one order of magnitude larger than the hole mobility of P3HT. For the first time the electron mobility of neat fullerene layers was determined by time of flight and a value of $1 \times 10^{-3}$ cm$^2$/Vs found. From the temperature dependence a Gaussian disorder parameter of about 68 meV was found which very is similar to the blend of PTB7:PC_{71}BM of 70 meV. For the blend, additionally, the mobility was analysed by an effective medium approach which identified trap states influencing the mobility. Fits to the mobility gave a trap concentration of 8 % and a trap energy of 0.1 eV which clearly showed that trapping originates from tail states reaching from the HOMO into the band gap of PTB7. The hole mobility of the blend decreased by three orders of magnitude upon cooling to 77 K which was then used to relate to the solar cell performance in the same temperature range.

The device efficiency of PTB7:PC_{71}BM devices dropped from 6.9 % to 2.5 % upon cooling from room temperature to 77 K. Thus the question arose, can we link the mobility measurements and the solar cell performance by changing the temperature? I found that most parameters like recombination, series and shunt resistance, the $J_{SC}$ and FF indeed depend mainly on the mobility. The $V_{OC}$ however is influenced by the temperature itself by the shift of the quasi-Fermi levels. At low temperature the charge extraction time is strongly reduced, which leads to a higher density of charge carriers in the active layer and although the bimolecular recombination coefficient potentially decreases, the combination of these factors gives rise to a higher net-loss of charge carriers. Additionally trap-assisted recombination recombination is increased at low temperature due to the reduced thermal energy to escape trap or band tail states, which directly reflects the mobility. Finally the conductivity depends on the charge carrier density and the mobility and was assumed to be directly linked to the series resistance. However it turned out that the series resistance depends on the mobility to the power of -1/4, which needs further explanation.
Influence of DIO on PTB7:PC$_{71}$BM solar cells

7.1 Introduction

The active layer morphology of organic bulk-heterojunction devices is of great importance for the device performance as it serves two aspects: It has to provide finely intermixed regions of the donor and acceptor phase in order to obtain efficient exciton dissociation, and it has to provide continuous pathways for efficient electron and hole transport. A wide range of techniques have become available to influence the active layer morphology such as thermal annealing, the choice of the casting solvent, solvent mixtures, solvent additives, solid additives and so forth. Since the first use of solvent additives, which are relatively small quantities of solvents added to the casting solution before spin-coating, they have rapidly become very popular. As we have already seen in previous chapters PTB7:PC$_{71}$BM is one typical material combination which strongly benefits from the solvent additive 1,8-diiodooactone. The effect of the additive on the morphology and on the electrical properties has already been studied in great detail, but a conclusive theory has not been established. In previous reports only two concentrations of the DIO have been compared 0 vol% and 3 vol%, but no specific justification for the 3 vol% concentration was given. Thus in this chapter I varied the concentration of DIO in a wide range from 0 vol% to 20 vol% which provides a better resolution of the underlying processes and allows to identify an optimum concentration.

7.2 Literature background

PTB7 was first mentioned as a photovoltaic material in 2010 and obtained a record efficiency of 7.4 % in a blend ratio of 1:1.5 with PC$_{71}$BM and the solvent additive DIO of 3 vol%. One year later the efficiency could be strongly improved by inserting a water soluble tertiary-aminesubstituted polyfluorene (PFN) interlayer, at the electron collecting electrode to 8.37 % PCE. This interlayer was again used in 2012 in an inverted device structure and achieved 9.2 %. The latest state on a very similar material was a nanostructured device, which reduces reflection and transmission losses, and achieved 10.1 % PCE in 2014. PTB7 has thus been the benchmark for high efficiency solar cells for about 5 years and its research has boosted since the material was commercially available. The long intervals between each innovation step can be attributed to the rather difficult fabrication procedure of the PFN cathode interlayer for which still only a few publications are available. Due to the difficulties of device fabrication with PFN, it was also not used in the studies presented in this thesis. Its effect on the performance was attributed to an improved charge extraction by a better contact selectivity due to the formation of an interface dipole and an enhanced electric field.
The use of solvent additives to influence the active layer morphology was discovered in 2006, where the authors intended to use gold particles in the active layer of P3HT:PC$_{61}$BM. However instead of the particles they found that the solvent residues had a dramatic effect on the photoconductivity and thus compared different alkane additives of a few vol% and a variety of solvents. One year later the same method was applied to PCPDTBT:PC$_{71}$BM which gave a dramatic improvement of the device performance from 2.8 to 5.5 % by adding 24 mg of octanedithiol in 1 ml chlorobenzene solution. DIO was introduced in 2008 and gave the best performance of PCPDTBT:PC$_{71}$BM of 5.1 % by adding 2.5 vol% to chlorobenzene solutions and the improvement was attributed to a finer domain size and fibril like structure. 3 vol% DIO was thereafter used in devices of PBDTTT–CF with a certified efficiency of 6.77 %. Then came the application in PTB7 devices, again with a concentration of 3 vol% and later on the use in small molecule devices where strangely quite different concentrations of DIO are required of typically less than 1 vol%.

### 7.3 Photovoltaic devices

To study the influence of the DIO content on the solar cell performance the typical device structure of ITO/PEDOT:PSS/PTB7:PC$_{71}$BM/Ca/Al was chosen. For the active layer a single solution of in total 25 mg/ml of chlorobenzene and a blend ratio of 1:1.5 (PTB7:PC$_{71}$BM) was prepared. This solution was then separated into six volumes and a concentration of 0, 0.7, 1.6, 3.0, 8.0 and 20.0 vol% of DIO was added. This provided a large range of concentrations and ensured that the blend ratio and the solution concentration was the same for each content of DIO and strongly reduces the influence from these factors. In batch 1 the spin-coating speed of the active layer was kept constant at 1000 rpm. No thermal annealing of the active layer was performed.

Figure 7.1 shows the JV-characteristics of the solar cells and the device parameters are given in Table 7.1. Evident from the JV-characteristics is the strong influence of the concentration of DIO on the $J_{SC}$, which increases from 4.6 mA/cm$^2$ for 0 vol% of DIO to 15.5 mA/cm$^2$ for 8 vol% and then decreases slightly to 13.7 mA/cm$^2$ for 20 vol%. This directly influences the power conversion efficiency which increases from 1.7 % for 0 vol% to 6.7 % for 8 vol% and decreases as well to 6.01 % for 20 vol% of DIO. The $V_{OC}$ and FF are not strongly influenced by the content of DIO and are in the region of 0.73 to 0.76 V and 43 % to 59 % respectively. The spectral mismatch factor of PTB7:PC$_{71}$BM devices was with 0.995 close to unity and not corrected for. From the JV-curves additionally a strong influence on the series resistance is evident from the slope at high forward bias. The $R_S$ is similar for the concentrations from 3 vol% to 20 vol%, but steadily decreases in the range from 0 vol% to 3 vol%. After the full device characterisation, it turned out that for this batch of devices the film thickness was strongly influenced by the content of DIO, as adding DIO to the solutions reduced the overall mass to liquid ratio and gave a thinner film, decreasing from 227 nm (0 vol%) to 130 nm (20 vol%). The higher film thickness thus caused an increase of the series resistance of the devices with low DIO concentrations.
Photovoltaic devices

In order to get a similar active layer thickness for all concentrations of DIO a second device batch was prepared, where the spin speed was adjusted for each concentration of DIO in order to get a similar active layer thickness. A few of the following measurements were only performed on batch 1 (will be indicated) and thus the performance was given here to compare these. Batch 2 was prepared from a reduced concentration of in total 20 mg/ml of chlorobenzene because the devices in batch 1 had a rather low FF, which might arise from a too high film thickness, as discussed in the literature. To control the film thickness the spin-coating speed was adjusted between 800 rpm (20 vol %) and 2500 rpm (0 vol%) and a quite uniform film thickness was obtained. As PTB7 blends are considered highly amorphous, the faster evaporation rate of the casting solvent, when the spin speed is increased, would not lead to a detrimental phase separation, as it could arise for example in P3HT:PC$_{61}$BM.

The JV-characteristics and the device performance parameters of batch 2 are given in Figure 7.2 and Table 7.2. For this batch the active layer thickness was reduced to about 59 nm to 73 nm. This in turn resulted in a very similar series resistance, obtained from the slope at +1.5 V and varies only between 3.6 $\Omega$cm$^2$ and 4.9 $\Omega$cm$^2$. The series resistance was

![Figure 7.1: a) JV-characteristics of PTB7:PC$_{71}$BM devices prepared from chlorobenzene with a variable content of DIO additive. Batch 1. b) The corresponding EQE spectra.](image)

Table 7.1: Device parameters of PTB7:PC$_{71}$BM with varying content of DIO. Batch 1. Error margins represent the standard deviation of up to three working pixels.

<table>
<thead>
<tr>
<th>DIO (vol%)</th>
<th>0</th>
<th>0.7</th>
<th>1.6</th>
<th>3</th>
<th>8</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency (%)</td>
<td>1.71 ± 0.03</td>
<td>2.8 ± 0.05</td>
<td>3.77 ± 0.10</td>
<td>6.22 ± 0.22</td>
<td>6.7 ± 0.04</td>
<td>6.01 ± 0.10</td>
</tr>
<tr>
<td>$J_{SC}$ (mA/cm$^2$)</td>
<td>4.56 ± 0.12</td>
<td>8.58 ± 0.21</td>
<td>11.47 ± 0.36</td>
<td>15.06 ± 0.32</td>
<td>15.47 ± 0.42</td>
<td>13.66 ± 0.30</td>
</tr>
<tr>
<td>$V_{OC}$ (V)</td>
<td>0.76 ± 0</td>
<td>0.76 ± 0</td>
<td>0.76 ± 0</td>
<td>0.73 ± 0.01</td>
<td>0.74 ± 0</td>
<td>0.74 ± 0.01</td>
</tr>
<tr>
<td>FF (%)</td>
<td>49.0 ± 0.4</td>
<td>43.1 ± 0.6</td>
<td>43.4 ± 0.5</td>
<td>56.8 ± 2.1</td>
<td>58.4 ± 1.8</td>
<td>59.5 ± 1.9</td>
</tr>
<tr>
<td>$R_{sh}$ (Ω cm$^2$)</td>
<td>403 ± 21</td>
<td>177 ± 8</td>
<td>171 ± 8</td>
<td>1707 ± 1623</td>
<td>858 ± 95</td>
<td>768 ± 181</td>
</tr>
<tr>
<td>$R_s$ at 1.5 V (Ω cm$^2$)</td>
<td>63 ± 5.0</td>
<td>58.5 ± 0.1</td>
<td>38.9 ± 0.9</td>
<td>12.8 ± 1.0</td>
<td>10.3 ± 0.8</td>
<td>10.6 ± 0.8</td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>227 ± 2.0 %</td>
<td>205 ± 1.4 %</td>
<td>199 ± 2.9 %</td>
<td>191 ± 0.7 %</td>
<td>155 ± 10.8 %</td>
<td>130 ± 7.7 %</td>
</tr>
</tbody>
</table>
additionally determined by the method using two JV-curves of different intensity, which gives values that are more strongly influenced by the shape of the curve in the fourth quadrant and thus are depending on the fill factor. The FF has a minimum of 52 % for 0 vol% of DIO and forms a maximum of 67 % for 3 vol%. Similarly follows the $J_{SC}$, also with a minimum of 8.5 mA/cm$^2$ for 0 vol% and a maximum of 14.5 mA/cm$^2$ for 3 vol%. For higher concentrations of DIO the FF and $J_{SC}$ are both decreasing slightly. The $V_{OC}$ has a trend towards lower values for increasing content of DIO, decreasing from 783 mV (0 vol%) to 755 mV (20 vol%). The combination of these factors gives the device efficiency of 3.44 % for 0 vol% of DIO, increasing to 7.39 % for 3 vol% and is then decreasing again towards 6.17 % for 20 vol%. Thus in agreement with previous investigations this device batch gave the best performance for 3 vol% of DIO and the efficiency is identical to the literature value of 7.4 % PCE. But what are the underlying principles of this improvement with DIO content and why does 3 vol% give the best result? In the following, I employed a range of methods to investigate the origin of these.

![Figure 7.2: a) JV-characteristics of PTB7:PC$_{71}$BM devices prepared from chlorobenzene with a variable content of DIO additive. Batch 2. b) The corresponding EQE spectra.](image)

<table>
<thead>
<tr>
<th>DIO (vol%)</th>
<th>0</th>
<th>0.7</th>
<th>1.6</th>
<th>3</th>
<th>8</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency (%)</td>
<td>3.44 ± 0.11</td>
<td>4.89 ± 0.09</td>
<td>6.62 ± 0.17</td>
<td>7.39 ± 0.00</td>
<td>7.17 ± 0.09</td>
<td>6.17 ± 0.13</td>
</tr>
<tr>
<td>$J_{SC}$ (mA/cm$^2$)</td>
<td>8.5 ± 0.3</td>
<td>11.1 ± 0.3</td>
<td>13.6 ± 0.3</td>
<td>14.5 ± 0.2</td>
<td>14.4 ± 0.3</td>
<td>12.6 ± 0.2</td>
</tr>
<tr>
<td>$V_{OC}$ (mV)</td>
<td>783 ± 5</td>
<td>762 ± 5</td>
<td>756 ± 6</td>
<td>759 ± 4</td>
<td>753 ± 2</td>
<td>755 ± 3</td>
</tr>
<tr>
<td>FF (%)</td>
<td>52.1 ± 0.4</td>
<td>58.1 ± 0.7</td>
<td>64.4 ± 0.7</td>
<td>67.2 ± 0.9</td>
<td>66.2 ± 0.9</td>
<td>64.9 ± 1.2</td>
</tr>
<tr>
<td>$R_{sh}$ (Ω cm$^2$)</td>
<td>390 ± 18</td>
<td>568 ± 10</td>
<td>879 ± 217</td>
<td>1414 ± 615</td>
<td>1017 ± 105</td>
<td>814 ± 20</td>
</tr>
<tr>
<td>$R_{sc}$, 2 curves (Ω cm$^2$)</td>
<td>36.3 ± 1.5</td>
<td>13.5 ± 0.0</td>
<td>6.3 ± 0.2</td>
<td>5.3 ± 0.0</td>
<td>6.5 ± 0.5</td>
<td>6.7 ± 0.5</td>
</tr>
<tr>
<td>$R_s$ at 1.5 V (Ω cm$^2$)</td>
<td>3.7 ± 0.9</td>
<td>3.6 ± 0.8</td>
<td>4.9 ± 1.2</td>
<td>4.2 ± 0.8</td>
<td>4.1 ± 0.6</td>
<td>4.1 ± 0.9</td>
</tr>
<tr>
<td>Spin speed (rpm)</td>
<td>2500</td>
<td>2000</td>
<td>1700</td>
<td>1400</td>
<td>1100</td>
<td>800</td>
</tr>
<tr>
<td>Thickness (nm)</td>
<td>59 ± 3.2 %</td>
<td>63 ± 7.1 %</td>
<td>73 ± 9.4 %</td>
<td>72 ± 8.7 %</td>
<td>69 ± 6.4 %</td>
<td>59 ± 3.8 %</td>
</tr>
</tbody>
</table>
7.4 Influence of film thickness

As discussed above, the film thickness of the second batch had a slight variation between 59 nm and 73 nm (Table 7.2). This is not a strong variation and is considered to have no influence on the charge extraction properties which could influence the fill factor. However for such thin films, the thickness can have an influence on the number of absorbed photons. Therefore the internal quantum efficiency (IQE), which is given by the number of collected electrons per absorbed photon, would provide the most accurate figure about the processes of the solar cell influenced by the content of DIO and would provide a fair comparison of the devices. However obtaining the internal quantum yield is a rather difficult task as all optical losses like reflection, transmission and scattering of photons have to be determined in order to obtain the total number of absorbed photons.\textsuperscript{297} These losses can be estimated by the measurement of the spectral reflectivity of solar cell devices but additionally parasitic absorption of the substrate, interlayers and the metal electrode has to be considered, which can in sum only be accounted for by a combination of various measurements and optical modelling.\textsuperscript{298} When these effects are correctly determined the IQE is spectrally flat, even below the absorption edge for conventional organic solar cells.\textsuperscript{299} However the photon absorption by the donor and by the acceptor are generally associated by different internal processes as electron and hole transfer which can have a different efficiency,\textsuperscript{123} as we have seen in the investigation of P(DPPTBBT) and the SubPcs.

In order to observe the influence of the film thickness variations I thus just compared the EQE spectra, which are shown above, with the absorption of reference films. As the effects of reflection, transmission, scattering and interference were not taken into account, therefore this gives only a rough estimate. Figure 7.3 shows a comparison of the EQE spectra of the second batch of solar cells for 0, 3 and 20 vol% of DIO. The absorption spectra of all films are similar and have about 50 % photon absorption between 350 nm and 700 nm. Obvious differences of the absorption and EQE spectra are prominent for the concentrations of 3 vol% and 20 vol% of DIO, whereas the blend with 0 vol% of DIO has a strong similarity between 450 nm and 750 nm. This difference might arise from reduced thin film interference in the blend with 0 vol% of DIO because of a higher surface roughness, leading to scattering of this film as observed by the reduced transmission above the absorption edge (at 800 nm). In the main part of the spectrum, for 0 vol% of DIO the EQE is in magnitude lower than the absorption spectrum, whereas for 3 vol% it is markedly higher and for 20 vol% slightly higher. The drop of EQE below 350 nm can be attributed to absorption losses of the glass/ITO substrate. Higher EQE than the absorption arises from reflections on the metal electrode in these devices which allows a double pass through the active layer as well as interference effects which are not present in the films used for absorption measurements. Overall the results indicate that the EQE spectra and hence the $J_{sc}$ for these solar cells are not strongly influenced by the film thickness but rather by internal processes, which will be further investigated in the following paragraphs.
Influence of film thickness

7.5 Morphology

The blend morphology of PTB7:PC$_{71}$BM without and with 3 vol% of DIO has already been deeply studied. However nothing was reported for intermediate values. I will try to quantify the influence on the morphology by several statistical parameters obtained by atomic force microscopy to then relate it to the device performance, which is possible by studying a range of concentrations of DIO. It is known that in PTB7:PC$_{71}$BM blends, fabricated without DIO, large clusters appear in the active layer film with a size on the order of about 200 nm. Hedley et al. observed that these clusters contained even smaller neat fullerene spheres of about 20 to 60 nm in diameter which are covered by a skin layer of PTB7.

The topography of the films with varying content of DIO is shown in Figure 7.4 and 7.5. To get quantitative values from the images, the surface roughness, the grain size and the grain boundary length were determined by the analysing software Gwyddion, applying a method described by Otsu which has the advantage that no free parameters are required to determine the grain threshold. Gao et al. have found a direct correlation of the grain boundary length with the $J_{SC}$ and PCE of P3HT:PC$_{61}$BM devices. The surface roughness of the blends shown is strongly influenced by the content of DIO and decreases from 17.5 nm for 0 vol% to 1.1 nm for 3 vol%, then increases again slightly to 2.5 nm for 20 vol%. The grain size is also
forming a minimum for 1.6 vol% to 3 vol% of DIO decreasing from 483 nm (0 vol%) to 73 nm (3 vol%) and then increasing again for higher concentrations. The grain boundary length however steadily increases from 94 µm (0 vol%) to 284 µm (20 vol%). Thus the grain size and the surface roughness qualitatively have a similarity with the $J_{SC}$ and the device efficiency whereas the grain boundary length shows no such correlation. However it should be noted that the analysis here was done on the topography of the AFM measurements rather than the phase profile, because of a rather poor quality of the phase images. The origin of the grains cannot be dissolved by simple AFM measurements, but from the similarity with previous observations we could speculate that the grains mainly consist of PC$_{71}$BM.$^{63}$

<table>
<thead>
<tr>
<th>DIO Concentration</th>
<th>Grain Size</th>
<th>Grain Boundary Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 vol% DIO</td>
<td>483 nm</td>
<td>94 µm</td>
</tr>
<tr>
<td>0.7 vol% DIO</td>
<td>325 nm</td>
<td>146 µm</td>
</tr>
<tr>
<td>1.6 vol% DIO</td>
<td>68 nm</td>
<td>182 µm</td>
</tr>
<tr>
<td>3 vol% DIO</td>
<td>73 nm</td>
<td>186 µm</td>
</tr>
<tr>
<td>8 vol% DIO</td>
<td>193 nm</td>
<td>199 µm</td>
</tr>
<tr>
<td>20 vol% DIO</td>
<td>90 nm</td>
<td>284 µm</td>
</tr>
</tbody>
</table>

Figure 7.6: AFM images of the PTB7:PC$_{71}$BM blend topography with varying content of DIO. The field of view is 5 × 5 µm.

### 7.6 Exciton dissociation

We have just seen that the blend morphology is strongly affected by the concentration of DIO. In order to observe if this blend morphology influences the exciton dissociation efficiency we studied the fluorescence emission from similar blends. My colleague Iain Robertson performed lifetime measurements using a streak camera to obtain the fast decay of the fluorescence emission, which is on the order of a few hundred picoseconds. Figure 7.6 shows the fluorescence decay of PTB7:PC$_{71}$BM detected in the range of 710 nm to 840 nm at an excitation of 515 nm. The data has been obtained for two batches with each sample averaged over a couple of measurements. The samples of these measurements were prepared from
Exciton dissociation

different solutions compared to the solar cells discussed above, thus these are not directly related. The traces of time-resolved fluorescence show a fast initial decay, which is limited by the instrument’s response and a longer tail. This multi-exponential behaviour arises from different processes leading to quenching of the excited state, such as resonant energy transfer, direct charge transfer and diffusion of exciton to the donor/acceptor interface.\(^\text{63}\) The long tail of the fluorescence decay is more strongly influenced by the concentration of DIO than the fast initial decay and the lifetime of it can be estimated by the slope on a logarithmic scale. For both batches the fluorescence lifetime strongly decreased from the blend of 0 vol% of DIO to the blend of 3 vol% of DIO and stayed low with only a slight increase for higher concentrations of 8 vol% and 20 vol% of DIO. These results show that 3 vol% of DIO gives the fastest decay of fluorescence, which is in good agreement with reported observations.\(^\text{303}\) The shorter lifetime can be attributed to a high quenching efficiency as discussed in section 5.7.1 and might originate from a better intermixing of the PTB7 and PC\(_{71}\)BM phase, giving a better \(J_{\text{SC}}\) compared to 0 vol% of DIO. Between both batches however occurs a quantitative difference of the fluorescence lifetime which is longer in batch 2 and both are compared in Table 7.3. This difference can arise from varying fabrication conditions as is commonly observed in the fabrication of organic solar cells. Additionally compared is the quenching efficiency which was deduced by\(^\text{63}\)

\[
\eta = \frac{\tau_{\text{blend}}}{\tau_{\text{PC71BM}}} ,
\]

where \(\tau_{\text{PC71BM}}\) is the lifetime of neat PC\(_{71}\)BM of 752 ps.

Batch 1  Batch 2

<table>
<thead>
<tr>
<th>DIO (vol%)</th>
<th>0</th>
<th>0.7</th>
<th>1.6</th>
<th>3</th>
<th>8</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\tau), batch 1 (ps)</td>
<td>350</td>
<td>210</td>
<td>179</td>
<td>173</td>
<td>219</td>
<td></td>
</tr>
<tr>
<td>(\tau), batch 2 (ps)</td>
<td>637</td>
<td>289</td>
<td>265</td>
<td>204</td>
<td>216</td>
<td>238</td>
</tr>
<tr>
<td>(\eta), batch 1 (%)</td>
<td>53.5</td>
<td>72.1</td>
<td>76.2</td>
<td>77.0</td>
<td>70.9</td>
<td></td>
</tr>
<tr>
<td>(\eta), batch 2 (%)</td>
<td>15.3</td>
<td>61.6</td>
<td>64.8</td>
<td>72.9</td>
<td>71.3</td>
<td>68.4</td>
</tr>
</tbody>
</table>

\(\text{Figure 7.6:}\) Normalised fluorescence decay attributed to the emission of PC\(_{71}\)BM from blends with PTB7 of varying concentration of DIO. Data provided by Iain Robertson, University of St Andrews.

\(\text{Table 7.3:}\) The long-tail fluorescence lifetime (\(\tau\)) of the PC\(_{71}\)BM emission in PTB7:PC\(_{71}\)BM blends. Data analysed from Figure 7.6 by straight lines on a logarithmic scales. The quenching efficiency (\(\eta\)) is obtained with the lifetime of PC\(_{71}\)BM of 752 ps by \(\eta = 1 - \tau/\tau_{\text{PC71BM}}\).
7.7 Bimolecular recombination

As bimolecular recombination depends on the probability of electrons and holes to encounter each other within the blend, it also depends on the bulk-heterojunction nano-structure.\(^{85,304,305}\) Recombination of solar cells of batch 2 (Figure 7.2) with varying concentration of DIO was investigated by the intensity dependent short circuit current method. The \(J_{SC}\) was found to depend on the light intensity sub-linearly. The exponent of a power law \((J_{SC} \sim I^b)\) of 0.945 for 0 vol\% of DIO increases to 0.961 for 3 vol\% of DIO then decreases again slightly to 0.955 for 20 vol\% of DIO. The loss due to recombination can be estimated from the inverse of the exponent\(^{85}\) \((1/b - 1)\) which amounts to a maximum of 5.8 % for 0 vol\% of DIO and a minimum of 4.1 % for 3 vol\% of DIO. All extracted parameters are shown in Table 7.4. This shows that the bimolecular recombination losses are only partially responsible for to the trend of the \(J_{SC}\).

![Figure 7.7: The \(J_{SC}\) of PTB7:PC\(_{71}\)BM with varying content of DIO as a function of light intensity (I). Straight lines are fits according to \(J_{SC} = a I^b\).

Table 7.4: The fit-parameters of Figure 7.7 and the obtained bimolecular recombination loss according to ref. 85.

<table>
<thead>
<tr>
<th>DIO (vol%)</th>
<th>0</th>
<th>0.7</th>
<th>1.6</th>
<th>3</th>
<th>8</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor (a) (mA/cm(^2))</td>
<td>8.2</td>
<td>10.5</td>
<td>13.0</td>
<td>13.8</td>
<td>13.6</td>
<td>12.0</td>
</tr>
<tr>
<td>Exponent (b)</td>
<td>0.945</td>
<td>0.959</td>
<td>0.960</td>
<td>0.961</td>
<td>0.957</td>
<td>0.955</td>
</tr>
<tr>
<td>Loss, (1/b - 1) (%)</td>
<td>5.8</td>
<td>4.3</td>
<td>4.2</td>
<td>4.1</td>
<td>4.5</td>
<td>4.7</td>
</tr>
</tbody>
</table>

7.8 Charge extraction measurements

In order to get further insight of the recombination dynamics, time-resolved charge extraction measurements were performed on the samples of batch 1. In this measurement the sample was excited by an LED with a light pulse of 30 µs duration, which is long enough to reach steady state conditions. The solar cells were held at open circuit during illumination and for a variable delay time after the LED turned off. Then a microsecond switch connected to short
circuit and the remaining charge carriers were extracted by the built-in field. During the delay, the charge carriers can recombine or leak to the opposite electrode. By fitting the extracted charge density as a function of delay, the recombination dynamics can be explored as demonstrated by Clarke and co-workers.\textsuperscript{88,93} In this way they observed a biphasic decay behaviour which was attributed to either a charge density dependent or a time dependent bimolecular recombination rate and the method was considered most accurate compared to other optoelectronic techniques as it provided a good agreement with transient absorption studies.

Figure 7.8 (a) shows the extracted charge carrier density as a function of delay time. The minimum delay time was 1 µs, which is the limit given by the fall-time of the LED and the response of the microsecond switch. The initial charge density is of about 10\textsuperscript{16} cm\textsuperscript{-3} and depends on the light intensity. During a delay of about 25 to 40 µs the charge density drops quickly until it becomes equal for all light intensities. Remaining charge carriers then reside in the devices for delays up to seconds. Multiplying the extracted charge with the capacitance of the device gives an estimate of the open circuit voltage the charge would create. This can be compared with a measurement of the open circuit voltage shown in Figure 7.8 (b). The open circuit voltage, measured by holding the device at open circuit with the high impedance switch for varying delays, gives a good agreement at long time scales. This shows that at longer time scales the extracted charge originates mainly from charge stored at the electrodes. At short time scales (<30 µs) however the extracted charge is higher than the open circuit voltage. Therefore these charge carriers likely originate from the bulk of the active layer, which are extracted by the built-in field when the switch connects to short circuit. To estimate the bimolecular recombination from these measurements thus the fast part of the charge density as a function of time is of relevance. Comparing the experimental data with an electrical simulation, as described in the previous chapter and in the literature,\textsuperscript{306} shows a good agreement for a resistance of 0.6 GΩ for the switch at open circuit. If however the voltage trace is measured with the oscilloscope directly, at the 1 MΩ impedance, a much faster decay of the voltage is observed due to faster leakage of charge carriers through the external connection.
Figure 7.9 shows the extracted charge density as a function of delay time with fits according to Clarke et al.\textsuperscript{88,93}

\[ n = n_0 \left[ 1 + \frac{\kappa n^\kappa t}{1 + \kappa a b^\kappa} \right]^{-1/\kappa}, \]

(7.2)

where \(a\), \(b\), \(n_0\) and \(\kappa\) are fit parameters. The bimolecular recombination coefficient is then given by

\[ \beta = \frac{n^{\kappa-1}}{|\kappa| a b^\kappa}, \]

(7.3)

which is identical to equation 6.9 when the parameter \(a\) can be assigned to the lifetime of charge carriers and \(b\) to the initial charge density. A good agreement of the fitting equation with the experimental data is observed at early time scales. But for the higher concentrations of DIO (3 vol\% and 8 vol\%) a slight deviation appears for time scales larger than 100 \(\mu\)s. Thus the data has to be limited to a short region in order to obtain a reasonable fit. The bimolecular recombination coefficient obtained by this method is strongly dependent on the charge density, by the reaction order \(\kappa\), and thus decreases by about one order of magnitude from 1 \(\mu\)s to 10 \(\mu\)s. This dependence makes it difficult to compare the different blend films. Thus I chose a constant charge density of \(1 \times 10^{16}\) cm\(^{-3}\) for the comparison in Figure 7.9 (bottom right). For varying light intensity a slightly different coefficient arises, but the overall trend shows a decreasing bimolecular recombination coefficient with increasing concentration of DIO which would agree with the trend of the device performance of batch 1. The recombination coefficient is compared in Table 7.5 with the analysis of \(J_{SC}\) as a function of light intensity of the same batch (these data were obtained in the same way as shown for batch 2 in section 7.7). The recombination coefficient in this way decreases from \(1.1 \times 10^{10}\) cm\(^3\)/s for 0 vol\% of DIO to \(5.1 \times 10^{12}\) cm\(^3\)/s for 8 vol\% of DIO which is a factor of 20, whereas the total losses of bimolecular recombination at short circuit decrease only by a factor of 2.5. This implies that the relation between these is not linear, as proposed by Koster et al.\textsuperscript{85}
Due to the accumulation of charge carriers at the electrodes I have a few concerns about these measurements, although in other work they have been shown to agree well with other techniques. Supposedly the charge carriers at the electrode do not contribute to bimolecular recombination, for these charge carriers should be subtracted from the total charge density. However, as Figure 7.8 (b) shows, the voltage of the cell has to be carefully measured with a high-impedance switch to prevent charge carriers being extracted through the external circuit and has to be obtained with low noise. As the graph shows there is a slight discrepancy between the measurement of the charge and the $V_{oc}$, which can amount to quite a large difference after subtraction. This makes the analysis rather difficult. However, if both data could be obtained more consistently, subtracting the charge at the electrodes will give more accurate results and might resolve the rather large reaction orders, $\kappa$, found by this measurement technique.
7.9 Trap-assisted recombination

Trap-assisted recombination can be explored by the dependence of the $V_{OC}$ on the light intensity and the results for the solar cells of batch 2 are shown in Figure 7.10 and Table 7.6. The $V_{OC}$ of the devices shown here has a higher noise than previous measurements shown in the other chapters. The origin of this is unknown. However the $V_{OC}$ vs. the logarithm of intensity still could be approximated with a single straight line of which the slope is a measure of monomolecular recombination. The slope for these samples varies between 1.10 and 1.19 $kT/e$, where 3 vol% and 0 vol% have minimum values and 0.7 vol% and 20 vol% have maximum values. This shows a rather small contribution from mono-molecular recombination in all devices.

![Figure 7.10: The $V_{OC}$ of PTB7:PC71BM with varying content of DIO as a function of light intensity (I). Straight lines are fits according to $V_{OC} = a + b \ln(I)$.](image)

<table>
<thead>
<tr>
<th>DIO (vol%)</th>
<th>0</th>
<th>0.7</th>
<th>1.6</th>
<th>3</th>
<th>8</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Offset $a$ (mV)</td>
<td>767</td>
<td>772</td>
<td>768</td>
<td>767</td>
<td>762</td>
<td>768</td>
</tr>
<tr>
<td>Slope $b$ (kT/e)</td>
<td>1.10</td>
<td>1.18</td>
<td>1.12</td>
<td>1.11</td>
<td>1.12</td>
<td>1.19</td>
</tr>
</tbody>
</table>

7.10 Photocurrent traces

Li et al. investigated the effect of DIO on PTB7 devices by light intensity and voltage dependent photocurrent transients. They found that photocurrent transients contained an overshoot in the beginning of the light pulse, which was more pronounced in devices fabricated without DIO and was attributed to a higher degree of trap-assisted recombination. In order to compare these observations, the devices of batch 2 were illuminated with a 100 µs LED pulse of variable light intensity. Figure 7.11 shows the photocurrent transient at an intensity of about 0.8 sun measured at the 50 Ω impedance input of the oscilloscope. The traces of 0 vol%, 3 vol% and 8 vol% of DIO have a rather rectangular shape without an initial photocurrent overshoot. The traces of 0.7 vol% 1.6 vol% and 20 vol% of DIO have a short
overshoot which decays after about 8 µs. This overshoot can be explained by charge trapping, which creates a space charge region with a disturbed electric field.\textsuperscript{307,308} As described in ref. 127 this effect can also be observed from the current decay after the LED turned off and this region is highlighted in Figure 7.11 (b). Compared to their result, a faster decay is observed for all blends, but the blends with 0 vol% and 20 vol% show markedly longer tails of the photocurrent transients. These tails can be attributed to charge carriers extracted after they have been released from trap states or a reduced charge carrier mobility. Compared to Table 7.6 these observations are not well in agreement as 0 vol% previously revealed rather low trap-assisted recombination by the intensity dependent open circuit voltage. It should be noted that these measurements were quite sensitive to degradation effects as the samples, even when kept in the cryostat under vacuum, showed quite a different behaviour after a few hours. Additionally the slower extraction of charge carriers from traps or due to reduced mobility does not necessarily contribute to stronger trap-assisted recombination.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7_11.png}
\caption{a) Photocurrent response to a 96 µs long LED pulse as a function of DIO concentration. 
b) Normalised photocurrent decay after the LED turned off, shown on logarithmic scales.}
\end{figure}

### 7.11 Photovoltage traces

Like photocurrent transients, photovoltage transients also provide information about how quickly the charge carriers are extracted, but as a function of the electric field. Figure 7.12 shows the photovoltage response of devices from batch 2, during illumination with a 97 µs long light pulse provided by an LED. For 0 vol% of DIO the photovoltage rises much slower compared to devices with higher concentrations of DIO and reaches the saturation level in about 15 µs whereas 3 vol% of DIO reached the saturation level in 7 µs. This shows that the charge carriers generated in devices with 3 vol% of DIO are quickly extracted. After turning off the LED the behaviour is the opposite – the photovoltage of 0 vol% decreases slowly whereas blends of 3 vol% show a faster decay. This indicates that charge carriers stored at the electrode are more quickly extracted when discharged over the 1 MΩ of the oscilloscope.
As the electrodes are associated with a capacitance, the open circuit voltage can be described as

$$V = \int \frac{A}{C(V)} J(V) \, dt,$$

(7.4)

where $A$ is the solar cell area and $C$ is the capacitance. Thus from the time derivative of the voltage trace we should be able to obtain the internal current flowing to the electrodes if the capacitance is constant. This is illustrated in Figure 7.13 where an external capacitor of 1 µF was used in parallel to the solar cell to measure the photovoltage. The inset of (a) shows the time derivative of the photovoltage trace divided by the cell area and the capacitance. Plotting this curve against the photovoltage resembles nicely the JV-curve in the fourth quadrant of the same solar cell measured conventionally (b). If the photovoltage however is measured directly on the solar cell, a deviation between the conventional JV-curve and the derivative appears due to the changing capacitance of the solar cell and due to a delayed interaction of the electric field with charge carries in the active layer. Thus the faster rise time of the photovoltage for 3 vol% of DIO compared to 0 vol% of DIO can also arise from a higher internal photocurrent.

Figure 7.12: Photovoltage transients of PTB7:PC$_{71}$BM devices, batch 2. For better comparison the voltage is normalized at the saturated value.

Figure 7.13: a) Photovoltage trace of an organic solar cell measured at an external capacitor in parallel to the cell. The inset shows its time derivation divided by the cell area and the capacitance.
b) The derivative ($y$) of the photovoltage plotted as a function of the original photovoltage ($x$), compared to a standard JV-curve of the same cell – showing good agreement.
c) Derivative of the photovoltage directly measured on the solar cell compared to a standard JV-curve shows a disagreement.
7.12 Charge leakage

As we have observed in the beginning of this investigation the concentration of DIO strongly affects the morphology of the PTB7:PC_{71}BM blends. Especially the formation of skin layer of neat PTB7 observed for 0 vol% of DIO could be quite detrimental to charge extraction. In the typical device structure this skin layer would arise on top of the blend film, which is at the cathode where electrons are extracted. To study the leakage current of the solar cells of batch 2, the shunt resistance was investigated as a function of light intensity. In order to express the loss due to charge leakage, the change of the current close to short circuit is calculated by \( \Delta J_{RSH} = \Delta V / R_{SH} \), where \( \Delta V \) is taken as 0.1 V. \( \Delta J_{RSH} \) is then divided by the \( J_{SC} \), which gives a value almost independent on the light intensity and is shown in Figure 7.14 (a). The leakage of charge carriers to the wrong electrode is about a factor of three higher for 0 vol% of DIO compared to 3 vol% of DIO, where it is minimal. The photocurrent in the dark, however does not resemble this trend and shows a very similar reverse saturation current for all blends except 1.6 vol% of DIO, which is about a factor hundred increased. However, this increase seems to have no impact on the JV-curve under illumination. Thus the shunt resistance under illumination probably provides the more accurate figure and shows another aspect which influences the device efficiency.

\[ \Delta J_{RSH} / J_{SC} \]

\( \Delta J_{RSH} / J_{SC} \) normalized to the \( J_{SC} \).

Figure 7.14: a) Change of the current density near the short circuit, \( \Delta J_{RSH} = \Delta V / R_{SH} \), with \( \Delta V \) of 0.1 V, normalised to the \( J_{SC} \).

b) Comparison of the dark (lines) and light (lines + symbols) photocurrent of PTB7:PC_{71}BM devices from batch 2. Shown is the absolute current density on logarithmic scales.

7.13 Discussion

Figure 7.15 shows the device parameters and properties of the bulk-heterojunction blend of PTB7:PC_{71}BM as a function of DIO. Comparing the device efficiency with the other device properties potentially allows to see more clearly which factors are determining the efficiency. The strong correlation of device parameters indicates that more than one factor is influencing the efficiency.
The power conversion efficiency of batch 2 was mainly influenced by the $J_{SC}$ and increases from 3.44 % for 0 vol% of DIO to 7.39 for 3 vol% of DIO then decreases again slightly towards 6.17 % for 20 vol%. The surface roughness obtained by the AFM measurements and the grain size decreases in the region of 0 vol% to 1.6 vol% then forms a maximum followed by slight decrease towards 20 vol%. The grain boundary length however continuously increases with increasing concentration of DIO. The quenching efficiency was measured for two batches of samples and shows a minimum for 0 vol% in either case and stays about

Figure 7.15: Correlation of device parameters of PTB7:PC$_7$BM as a function of DIO content.
constant for concentrations of DIO larger than 0.7 vol%. These results are consistent with the theory that DIO helps to dissolve PC$_{71}$BM clusters to form a homogenous blend with PTB7. This in turn reduces the surface roughness and grain size and thus increases the interfacial area between donor and acceptor domains and leads to the observed decrease of the exciton lifetime. The quenching efficiency calculated from the lifetime thus increases from 0 vol% to 3 vol% of DIO which is in agreement with the observed geminate recombination losses for 0 vol% reported in comparable studies.$^{176,309,310,311,312}$

Considering the processes after charge separation we found that bimolecular and trap-assisted recombination losses are minimal for 3 vol% of DIO which originates from the fast charge extraction observed in transient photocurrent measurements. Surprisingly from the intensity dependent open circuit voltage also the blends with 0 vol% of DIO show low trap-assisted recombination although a slow charge extraction was observed and trap-assisted is reported as a dominant loss mechanism for these devices.$^{127,312}$ For concentrations of DIO larger than the optimum, the blend microstructure starts to become coarser as the surface roughness and grain size increases slightly and which reduces the quenching efficiency. Also trap-assisted and bimolecular recombination increases as generally a higher degree of traps is observed for blends with excess DIO.$^{311}$

### 7.14 Conclusions

In this chapter we explored the influence of the solvent additive DIO on the device performance of PTB7:PC$_{71}$BM fabricated from chlorobenzene solutions. The DIO had a strong impact on the active layer morphology transforming the blend from a coarse microstructure to a well intermixed blend. We found quantitative values to describe this morphology by three parameters, the surface roughness, grain size and grain boundary length from AFM images. A direct relationship of the grain boundary length to the short circuit current density has been reported in the literature, but could not be directly confirmed by the values obtained here. The grain size and surface roughness however showed similar trends as the $J_{SC}$ and the efficiency of the devices. Strongly related was also the exciton lifetime of PC$_{71}$BM which decreased for better performing blends with a finer intermixed morphology, which is assigned to improved charge transfer between the donor and acceptor component. The optimized blend morphology to generate free charge carriers coincided with an optimum structure for charge collection as bimolecular and trap-assisted recombination had a minimum. This agreement of an optimized morphology for charge separation and collection is likely the cause for the high efficiency of PTB7:PC$_{71}$BM devices for the optimal concentration of additive of 3 vol% of DIO.
Enhanced absorption by plasmonic structures

8.1 Motivation

In the active layer of organic solar cells, aspects of the morphology, electronic properties, and optical properties are combined. As we have seen, organic semiconductors have a low charge carrier mobility compared to inorganic semiconductors and due to the amorphous bulk-heterojunction structure, they can contain a considerable number of traps. Both of these effects limit the transport of charge carriers and can induce trap-assisted and bimolecular recombination. In general, both of these effects become more severe for thicker active layers due to the longer interaction pathway. On the other hand, thick active layers are desirable to absorb more photons. As we have seen in the previous chapter, for devices of PTB7:PC$_7$BM with 3 vol% of DIO with an active layer thickness of 191 nm, a higher $J_{SC}$ of 15.06 mA/cm$^2$ could be obtained compared to 14.5 mA/cm$^2$ for 72 a nm thick active layer. However, the thinner active layer resulted in a much higher fill factor of 67% compared to 57%, resulting in a higher power conversion efficiency.

In order to improve the relation of photon absorption and charge collection, a range of techniques have been applied to organic solar cells.

- The inclusion of interlayers, acting as optical spacers, can redistribute the interference pattern of the incoming light wave with the reflection from the metal electrode to achieve a stronger absorption in the active layer.$^{313,314,315}$
- Patterned substrates or interlayers can induce light scattering, which enhances the pathway of photons in the active layer and thus gives an increased absorption.$^{27,39}$
- The use of a semitransparent front-metal layer can induce a cavity mode in the active layer to increase light absorption.$^{316,317,318,319}$
- The use of metallic nanostructures and particles for plasmonic light scattering and electric field enhancement can increase the absorption.$^{320,321}$

Enhancement of light absorption by plasmonic structures has been achieved by structured electrodes,$^{318,319,322,323}$ incorporating metal nanoparticles in the active layer,$^{324,325,326}$ and in interlayers.$^{327,328,329,330,331}$ Most research articles report an enhanced power conversion efficiency in solar devices with plasmonic structures by about 10 to 20%. However, the enhancement of the power conversion efficiency should be regarded with special care as sample to sample variations are of similar magnitude.$^{332}$ In this context, the EQE spectrum provides better insights into the origin of efficiency enhancements as the plasmonic resonance is typically wavelength dependent and thus provides an absorption enhancement, only in a limited wavelength region.$^{320}$ Besides the absorption, introducing metallic nanostructures in
Motivation

Organic bulk-heterojunction solar cells can alter additional aspects influencing the device performance like the active layer morphology and the conductivity. In order to disentangle electrical and optical properties in this chapter I will show how light absorption of P3HT is increased near silver nanowires. Additionally the effect of gold nanospheres and nanorods in the active layer of PTB7:PCBM devices will be explored.

8.2 Theory of the plasmonic resonance

The underlying principle of the plasmonic resonance in metallic structures is the collective oscillation of free electrons and an electromagnetic wave. Due to the skin-effect, the oscillation of electrons is strongly confined to the surface of the metallic structure and couples with the electric field in the surrounding medium. This coupled oscillation is called a surface plasmon polariton and depending on the size of the metal structure it can have a resonance in the visible part of the electromagnetic wave spectrum. The coupling of electron motion and the electric field in the surrounding medium gives rise to a strong interaction and leads to three effects:

1. Strong light scattering at the resonance frequency.
2. Strong light absorption by the metal structure due to damping of the electron motion.
3. An electric field enhancement in the surrounding medium near the metal structure.

The first and the third effect are desirable for enhanced photon absorption in the surrounding medium, whereas the second is a parasitic effect, reducing the available photons for current generation in solar cells.

In order to get a more quantitative description of the effects, we consider a spherical metal particle of a few nanometers in diameter. The dipole moment, \( p_d \), induced by an electric field, \( F \), is given by

\[
p_d = \varepsilon_m \varepsilon_0 \text{Vol} \chi F,
\]

where \( \varepsilon_m \) is the complex dielectric permittivity of the metal, \( \varepsilon_0 \) is the vacuum permittivity, \( \text{Vol} \) is the volume of the particle and \( \chi \) is the polarisability. The polarisability, which in the general case is a tensor, is the key parameter in describing the plasmon resonance. It depends on the wavelength of the electric field and the size and material parameters of the particle. For a spherical particle of a diameter much smaller than the wavelength of the electric field, the polarisability is given by

\[
\chi = 3 \text{Vol} \frac{\varepsilon_m - \varepsilon_s}{\varepsilon_m + \varepsilon_s},
\]

where \( \varepsilon_s \) is the permittivity of the surrounding material. From the imaginary part of the complex permittivity follows the absorption cross-section \( \sigma_a \) of the nanoparticle

\[
\sigma_a = \frac{2 \pi}{\lambda} \text{Im} |\chi|.
\]
Theory of the plasmonic resonance

\[ \alpha_s = \frac{1}{6\pi} \left( \frac{2\pi}{\lambda} \right)^4 |\chi|^2. \]  

(8.4)

Figure 8.1 shows the complex permittivity of gold, obtained from Johnson et al.\textsuperscript{333} The imaginary part of the dielectric permittivity of gold is high in the spectral region below 500 nm and rises again slightly above 650 nm. This behaviour give the typical colour of gold. The real part of the permittivity is negative as is typical for metals and decreases for increasing wavelengths. The plasmon resonance which is shown as a clear peak of the absorption cross-section in (b) is at about 500 nm. The magnitude and position of this peak agrees well with calculations using an online tool.\textsuperscript{334} From equation 8.2 it is obvious that the plasmon resonance appears at the wavelength where \(|\varepsilon_m + \varepsilon_s|\) has a minimum and is thus strongly affected by the dielectric permittivity of the surrounding material. For a surrounding material with a higher permittivity, the plasmon resonance shifts towards longer wavelength due to the decreasing real part of the permittivity of gold. This in turn leads to a higher amplitude of the resonance as the imaginary part, which induces damping on the resonance, reduces. For gold nanoparticles of 6 nm diameter, the scattering cross-section is a factor of a thousand smaller than the absorption cross-section but the ratio reduces strongly with increasing size.

For larger or non-spherical sizes of particles the plasmonic resonance is more complex and can involve multiple contributions from higher modes and a dependence on the light polarisation.\textsuperscript{335,336,337} A few approaches of numerical modelling of more complex shapes have become popular such as finite difference time domain simulations based on Maxwell’s equations. This approach can also be used to study the local electric field enhancement near the metal nanoparticles. Figure 8.2 shows a simulation of the electric field distribution around a gold nanosphere embedded in PEDOT:PSS, performed by Yang et al. adapted with permission from ACS Nano, vol. 5, no. 8, pp. 6210–6217, Copyright (2011) American
Chemical Society. The figure shows a simulation of gold particles of 80 nm in diameter embedded in PEDOT:PSS. Light of 577 nm wavelength is propagating in the positive z-direction and the electric field vector is polarised in the x-direction. Figure (a) shows the light intensity enhancement due to light scattering on the particle. Significant intensity enhancement by more than a factor of three, is confined to a region of about 15 nm from the particle’s surface. The electric field enhancement shown in (b) extends slightly further out from the particle to about 20 nm, where the enhancement decreased to a factor of three. Both contributions are located on the x-axis of the particle, in parallel to the polarisation direction of the incident light wave. This shows that the enhancement of absorption in the medium surrounding plasmonic nano-structures is quite localised, but due to the thin active layers of organic solar cells a significant enhancement could arise.

8.3 Using silver nanowires to enhance the absorption in P3HT

8.3.1 Introduction

This section reports an investigation of using silver nanowires to explore the effect on the absorption of a P3HT film. This investigation was performed in collaboration with Prof. Sebastian Mackowski at the Nicolaus Copernicus University in Torun, Poland. The experiments were carried out at his research labs during a visit in September 2012. The results of this investigation were published in Applied Physics Letters and a summary will be given here. As explained in the introduction to this chapter, a plasmonic field enhancement or light scattering has been applied in several organic solar cells. However the small size of typically used metal particles makes them difficult to observe. Silver nanowires are relatively large.
sized particles and can be easily observed in a wide-field microscope. This allows to locally investigate the enhancement of absorption of P3HT near such metal structures.

8.3.2 Silver nanowires

Silver nanowires (AgNWs) are elongated particles of tens of micrometers in length and a few hundred nanometers in diameter. They have been synthesized by the group of Prof. Sebastian Mackowski according to a polyol process. The synthesis was performed in ethylene glycol solution with CuCl\(_2\) reaction seeds, thoroughly stirred and heated at 160 °C. AgNO\(_3\) and poly(vinyl-pyrrolidone) were added drop-wise simultaneously. The polymer acts as a stabilisation agent and is adsorbed on the surface of the forming AgNWs, which makes them dispersible in the solution and prevents aggregation. The resulting nanowires were diluted in isopropanol and centrifuged at 2000 rpm for 20 minutes. The supernatant containing small silver particles and other reaction products was disposed and the nanowires were re-dispersed in water.

To measure the dimensions of the AgNWs, the water solution was spin-coated onto cleaned silicon substrates and annealed at 120 °C for 10 minutes to remove any residual water. The sample was then investigated by scanning electron microscopy (performed afterwards in our laboratories with the help of Dr. Emiliano Rezende-Martins) and typical images are shown in Figure 8.3. Figure (a) shows a single nanowire with dimensions of 397 nm in width and 9.7 µm in length. Figure (b) shows other particles found in the same solution, containing small fractions of nanocubes, nanotriangles and nanorods.

![Figure 8.3](image1.png)

**Figure 8.3:** a) Scanning electron microscopy image of a single silver nanowire with 397 nm in width and 9.7 µm in length. b) SEM image of silver nanoparticles, cubes, triangles and nanorods located at a nanowire.

In order to investigate the plasmonic behaviour of the AgNWs, the extinction (absorbance) spectrum of a water solution was measured. The extinction is given by the sum of absorption and scattering losses and thus provides good insight of the plasmonic resonance, occurring in these structures. Figure 8.4 shows the extinction spectrum of an AgNW solution. The shoulder at 350 nm can be assigned to the longitudinal resonance which is identical to bulk silver and
the shoulder at 380 nm to the transversal resonance. Additionally peaks from nanoparticles at 420 nm and nanorods at 500 nm are visible. After purification, these smaller particles can be reduced.

8.3.3 PEDOT:PSS as an optical spacer

As the next step we want to explore the plasmonic field enhancement or the effect of light scattering on a P3HT film. We will make use of the fluorescence properties of P3HT to observe an increase of absorption. This side step to explore the fluorescence rather than the absorption directly is convenient because it allows to assign a change of light absorption directly to the polymer phase, whereas measuring the absorption by transmission gives a difficulty to disentangle the contributions of absorption and scattering from the AgNWs. As we have discussed above, the electric field and intensity enhancement of metallic structures is highest at the surface of the metal and decays rapidly with distance. Thus it would be most convenient to embed the nanowires in a P3HT film to achieve the strongest effect. However charge transfer from P3HT to the silver nanowires and mirror charges induced in P3HT can reduce the photo-luminescence quantum yield in such a configuration. We therefore explored PEDOT:PSS as an optical spacer to separate the AgNWs from P3HT chromophores. Two configurations were explored, in the first AgNWs were spin-coated on glass substrates and covered with PEDOT:PSS, spin-coated over them, and in the second configuration AgNWs were mixed with PEDOT:PSS and spin-coated as a single film. The PEDOT:PSS films were then annealed at 130 °C for 10 minutes and P3HT was spin-coated on top. The spin speed for all layers was 3600 rpm and the thickness of P3HT was 30 nm and of undiluted PEDOT:PSS was 40 nm. I made these films at the Nicolaus Copernicus University in Torun, Poland and the deposition was carried out in air.

The samples were then investigated by a wide-field optical microscope with LED illumination of 405 nm and 485 nm. The wavelength of 405 nm is close to the major plasmonic resonance of the AgNWs, whereas 485 nm is close to the peak absorption of P3HT. The samples were
illuminated from the side of PEDOT:PSS containing nanowires and the fluorescence was imaged from the P3HT side onto a CCD camera. The excitation wavelength was blocked by a dichroic beam splitter and a band pass filter. An illustration of the microscope is provided in Figure 8.5 (b).

**Figure 8.5:** a) Sample configuration of glass/silver nanowires covered or embedded in PEDOT:PSS/P3HT. Dimensions not true to scale.  
b) Schematic of the Nikon Eclipse wide-field microscope. The fluorescence of the P3HT film was observed with a CCD camera from the top whilst illuminated from the bottom.  
c) A typical fluorescence image with clearly visible nanowires as bright regions in a P3HT film. (The colour of the image was adjusted to make the background fluorescence more representative).

In Figure 8.5 (c) a typical fluorescence image of a P3HT film is shown. The silver nanowires below the P3HT film, separated by PEDOT:PSS, are clearly visible as brighter regions of enhanced fluorescence. In order to quantify this fluorescence enhancement, several images were taken and the intensity of pixels on nanowires and beside nanowires obtained. The intensities were then added to a statistic, creating the histograms of Figure 8.6. The background intensity of the P3HT film besides the AgNWs has a very narrow distribution of about 470 counts per second (cps) for 405 nm excitation and 500 cps for 485 nm excitation and is similar for both device configurations. In the configuration of AgNWs mixed into PEDOT:PSS a clear enhancement of 880 cps (405 nm) and 1050 cps (485 nm) is observed.

**Figure 8.6:** Histograms of the fluorescence intensity divided into channels of 100 counts per second (cps) for an excitation wavelength of 405 nm (blue) and 485 nm (red).  
a) The histogram of samples of silver nanowires and PEDOT:PSS spin-coated simultaneously.  
b) The histogram of samples of silver nanowires and PEDOT:PSS spin-coated consecutively.  
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Using silver nanowires to enhance the absorption in P3HT

This amounts to an enhancement factor of 1.9 for 405 nm excitation and 2.1 for 485 nm excitation, respectively. In the case of AgNWs covered with PEDOT:PSS the enhancement factor is slightly lower of approximately 1.4 for both wavelengths. However when the nanowires are covered with PEDOT:PSS the histograms have a narrower distribution which indicates that the thickness of PEDOT:PSS covering the AgNWs is more uniform. This shows that there is room for further improvements to obtain a uniform enhancement and an optimum spacing distance. The enhancement up to a factor of two is highly promising for implementing such structures into organic solar cells and PEDOT:PSS has proven to be an effective optical spacer. The difference between the two sample geometries indicates that the fluorescence enhancement originates from a plasmodium field enhancement rather than just light scattering which would give similar results for either geometry.

8.3.4 Increased absorption

We have just seen, the fluorescence near the nanowires was strongly increased, but can this in fact be assigned to an increase of absorption? Plasmonic structures can generally enhance the coupling of matter with electromagnetic waves. Thus also an increase of the fluorescence due to the electric field enhancement is possible.\textsuperscript{342,343} In order to investigate if the fluorescence enhancement originates from a modified radiative rate, we performed time-resolved fluorescence measurements in a home-built set-up at the labs of Prof. Sebastian Mackowski. The samples were therefore mounted on a piezo-driven XY-stage which allowed to position an excitation laser on and beside the nanowires. The fluorescence was collected into a time-correlated single photon counting module (Becker & Hickl) equipped with a fast photodiode which provided a time resolution of 100 ps. Figure 8.7 shows the fluorescence decay of P3HT on and beside the nanowires for the two sample configurations. In all configurations the fluorescence decay was identical. This clearly shows that the mechanism of fluorescence is not influenced by the presence of silver nanowires and thus the increased fluorescence intensity can be solely attributed to increased absorption.

![Figure 8.7: Fluorescence decay of a P3HT film excited at 485 nm and probed by time-correlated single photon counting.](image)

a) Silver nanowires mixed into PEDOT:PSS and spin coated simultaneously.

b) Silver nanowires and PEDOT:PSS spin-coated consecutively.

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8.3.5 Section conclusions

By investigating the fluorescence of a P3HT film fabricated on top of silver nanowires covered with PEDOT:PSS or embedded in PEDOT:PSS, an enhancement of the absorption by a factor of 1.4 to 2.1 was found, depending on the sample configuration. Embedding the AgNWs in PEDOT:PSS gave a higher but more varying enhancement which can be attributed to a higher variation of the distance of P3HT chromophores to the surface of the nanowires. This distance dependence indicates that the fluorescence enhancement arises from an plasmonic field enhancement rather than light scattering. The increased fluorescence could be clearly assigned to an increase of absorption as the time-resolved fluorescence decay was identical for all sample configurations near and beside the AgNWs. This enhancement is very promising for organic bulk-heterojunction solar cells and has been successfully demonstrated by other groups.\textsuperscript{344,345} I have also attempted the fabrication of solar cells in the configuration of ITO/AgNWs/PEDOT:PSS/P3HT:PC\textsubscript{61}BM/Ca/Al but due to the large size of the nanowires the active layer was shorted. Therefore AgNWs are due to their large size not the ideal candidates for incorporation in devices. As an alternative the incorporation of gold nanospheres and nanorods was investigated and is described in the next paragraphs.

8.4 Gold nanospheres and nanorods in PTB7:PC\textsubscript{71}BM solar cells

In this section I describe the incorporation of gold nanospheres (AuNS) and nanorods (AuRods) in the active layer of PTB7:PC\textsubscript{71}BM solar cells.

8.4.1 Materials

AuNS were synthesized and supplied by Ryan Landis from the group of Prof. Vincent Rotello at the University of Massachusetts Amherst and AuRods were supplied by Dr. Laura Fabris at the Rutgers State University of New Jersey. Although the investigation of both materials was performed consecutively the results are combined in a single report for a direct comparison. Both materials had a high amount of non-conductive capping ligands. For the nanospheres this was an alkane with 12 carbon atoms (dodecane) and for the nanorods a polystyrene ligand of 57 kg/Mol (ca. 550 monomers). In both cases the capping ligands were covalently bound to the gold surface. These ligands made both materials dispersible in chlorinated solvents, which are used to deposit the active layer of organic solar cells, and additionally could act as the optical spacer to prevent charge transfer, as discussed above. The AuNS had a size of 6 nm in a diameter and the AuRods a longitudinal length of about 45 nm and a width of about 16 nm, which gives an aspect ratio of 2.8. The aspect ratio of the gold nanorods has a strong influence on the plasmon resonance, which red-shifts with increasing ratio.\textsuperscript{325} Extinction spectra of AuNS and AuRods are shown in Figure 8.8. AuRods in chlorobenzene solution show two maxima of the extinction at 520 nm and 765 nm which can be assigned to the lateral and longitudinal modes of the plasmon resonance.\textsuperscript{325} The peak at 765 nm is stronger as the imaginary part of the dielectric function in this spectral region is lower as discussed in section 8.2.
Gold nanospheres and nanorods in PTB7:PC71BM solar cells

The AuNS have, due to the spherical symmetry, only one plasmon resonance at about 525 nm, in 1,2-dichlorobenzene solutions. A good agreement of the extinction for two different concentrations of the AuNS is shown, which indicates that aggregation at higher concentrations is effectively prevented by the alkane ligand. As the plasmon resonance is strongly influenced by the dielectric function of the surrounding material, the extinction spectrum was compared with a sample, where the nanospheres were blended in a polystyrene matrix. The refractive index is related to the real part of the dielectric function by $\varepsilon^{0.5}$. Polystyrene has a refractive index of 1.60, slightly higher than 1,2-dichlorobenzene of 1.55, at the peak of the plasmon resonance. This leads to a red-shift of the plasmon resonance of 30 nm to 555 nm. This shift is clear signature of the plasmonic nature of this extinction peak.

As the AuNS and AuRods both were very sticky materials and it is difficult to measure the weight required to determine the concentration of solutions, quantitative extinction spectra were used in further solutions to estimate the concentration. This was valid as the extinction spectra were of similar shape for varying concentrations.

8.4.2 Increased absorption of PTB7 films

To explore the plasmon induced absorption enhancement, I used a similar method to that for the AgNWs and measured the fluorescence excitation spectra of PTB7 films incorporating AuNS or AuRods and compared them to neat PTB7. As we have seen in previous investigations the excitation spectrum typically resembles the absorption spectrum, although depending on the test geometry, it can be influenced by interference effects. As the plasmon...
resonance of these materials is very sharp, the enhancement of absorption should arise in only a part of the spectrum and could thus be detected in the excitation spectra.

For the investigation of gold nanorods, solutions of 10 mg/ml of PTB7 in chlorobenzene were prepared and 0.2 mg/ml of AuRods (2 wt%) were added, calculated from the concentration of a solution in chlorobenzene. The solution was spin-coated at 1000 rpm to give a film thickness of about 50 nm, which was similar with and without the addition of nanorods. For the investigation of gold nanospheres a solution of PTB7 of 16 mg/ml in 1,2-dichlorobenzene was prepared and concentrations between 10 wt% and 74 wt% of AuNS were added. Figure 8.9 shows the fluorescence excitation spectra of PTB7:AuRods and PTB7:AuNS. The fluorescence of PTB7 was detected at 760 nm. All spectra were normalised at 400 nm to allow a direct comparison with neat PTB7.

The comparison of the excitation spectrum of PTB7 containing AuRods with neat PTB7 reveals a significant change of the spectrum for wavelengths longer than 550 nm. At 700 nm the fluorescence is increased by a factor of 1.3. As no spectral change of the excitation spectrum below 550 nm is observed, a contribution in the region of 550 to 650 nm can only arise from the lateral plasmon resonance of the nanorods as in chlorobenzene solutions the AuRods had two resonant peaks at 520 nm (lateral) and 765 nm (longitudinal). In order to compare the resonance of the AuRods in PTB7 films we have to consider the refractive index, which is about 2.3 at 700 nm. This higher refractive index compared to chlorobenzene generally leads to a red-shift of the plasmon resonance, however due to the large capping ligands the shift might be less pronounced than expected as the ligands separate the core of the nanorod from the environment. Additionally Chen et al. showed theoretically that the lateral plasmon resonance of gold nanorods is less strongly dependent on the refractive index of the environment and is thus almost constant at 520 nm. This shows that the enhancement of fluorescence falls in a region where no plasmonic resonance is present and we might rather consider other effects, like thin film interference, which caused the spectral change of the excitation spectrum. A measurement of the photoluminescence quantum yield, with an excitation at 650 nm, gave an identical result for both films, with and without AuRods, of 4.9%. This shows that no contribution of enhanced emission or fluorescence quenching is induced.

As shown in Figure 8.9 (b), the excitation spectra of PTB7 films containing AuNS all have the same shape except the film with a very high fraction of 74 wt%. From the previous investigation and the illustration of Figure 8.2, we could expect a rather substantial increase of the absorption, whereas the change of the excitation spectra presented here is only marginal. This also raises doubts, about whether this increase is due to a plasmonic resonance.
Gold nanospheres and nanorods in PTB7:PC71BM solar cells

To investigate the origins of this low enhancement, the films of PTB7:AuNS were investigated with an optical microscope which clearly show increasing clusters of gold particles in the films with increasing concentration. For the 1:0.1 weight ratio, smaller clusters of particles were relatively well dispersed, however for the higher concentrations increased lumps of particles were found. These aggregates could be the reason for the rather low improvement of absorption, as only a small fraction of the film could benefit from the plasmonic absorption enhancement.

8.4.3 Gold spheres incorporated in the active layer of PTB7:PC71BM solar cells

Besides the fluorescence, the spectrally resolved photocurrent of solar cells also gives a direct measure of a plasmonic enhanced absorption. Solar cells were prepared in the typical device configuration of ITO/PEDOT:PSS/PTB7:PC71BM:AuRods or AuNS/Ca/Al. The active layer was prepared from PTB7:PC71BM either from a 25 mg/ml solution in chlorobenzene containing 3.3 wt% of AuRods or 20 mg/ml in 1,2-dichlorobenzene containing variable concentrations of AuNS, both with 3 vol% of the solvent additive DIO.
Gold spheres incorporated in the active layer of PTB7:PC71BM solar cells

Figure 8.11 shows the EQE of the devices. In both cases the standard solar cells had the best performance. In case of the AuRods the EQE spectra strongly vary in shape but a contribution from a plasmonic induced absorption cannot be identified. The different shape of the spectra are rather due to thin film interference as the thickness of the active layer strongly reduced upon adding the AuRod solution. The thickness of neat PTB7:PC$_{71}$BM was 72 nm, spin coated at 1400 rpm and the thickness with AuRods was 44 nm spin coated at 800 rpm. Reducing the spin speed from 1400 rpm to 800 rpm for blends containing AuRods strongly improved the photocurrent and clearly shows the change of the spectrum with varying thickness. In the case of the gold nanospheres, however the active layer thickness was found relatively constant and all EQE spectra for devices of varying concentration of the AuNS have an almost identical shape. Only a concentration of 1:1.5:0.28 (PTB7:PC$_{71}$BM:AuNS) shows a slight deviation of the spectrum in the region above 570 nm.

Figure 8.12 shows the corresponding JV-characteristics of the solar cells. Due to the film thickness variation of solar cells containing AuRods a decrease of the short circuit current is observed. However the FF and the open circuit voltage are not strongly affected by the addition of the nanorods, which is an interesting result. For a small concentration of gold nanospheres of 1:1.5:0.14 concentration, a slight increase of the $J_{SC}$ compared to the reference device without AuNS is observed however this increase is within the sample to sample variations and as seen from the EQE spectrum cannot be attributed to a plasmonic enhanced absorption. Higher concentrations revealed a strongly reduced FF and $V_{OC}$ which can be attributed to partly conductive pathways of the AuNS in the active layer as the series resistance and the shunt resistance both are decreased. This itself might originate from the stronger tendency of the gold nanoparticles to aggregate.
Section conclusions

In this section we investigated if gold nanorods and gold nanospheres can be used to increase the light absorption of PTB7 films and PTB7:PC_{71}BM active layers of solar cells. As the plasmonic resonance of these structures is spectrally well defined, the fluorescence excitation spectra and EQE spectra were used to explore an increase of absorption. In the study of gold nanospheres almost no spectral change was observed although a relatively high concentration of the particles was used. The incorporation of gold nanorods gave a substantial change of the spectra, however no spectral correlation to the plasmonic resonance was evident. The spectral change of these samples was rather attributed to thin film interference as the thickness of the films varied.

Conclusions of this chapter

In this chapter the benefits of plasmonic structures to increase the light absorption whilst maintaining good electrical properties were introduced. The theory of plasmonics showed that metallic structures can provide a substantial electric field enhancement to locally increase the absorption and light scattering to increase the pathlength of photons in the active layer. A study of silver nanowires embedded in PEDOT:PSS gave a locally increased fluorescence of a P3HT film on top. This increase of fluorescence by about a factor of two, could be clearly assigned to a plasmonic enhancement of the absorption by a comparison of the fluorescence lifetime near and beside the nanowires. This is a very promising result and demonstrates that a locally enhanced electric field can indeed give stronger absorption.

In order to apply this method to organic solar cell devices, the active layer material PTB7:PC_{71}BM was chosen as it is known that increasing the active layer thickness, to harvest more photons, leads to a degradation of electronic properties. Directly applying the silver nanowires in solar cells proved difficult because of the large diameter of these structures,
causing electrical shorts in the devices. Thus smaller gold nanorods and nanospheres were studied instead. The nanorods had two distinct plasmonic resonances and the nanospheres one resonance which overlapped nicely with the absorption spectrum of PTB7:PC$_{71}$BM. Incorporating these structures into PTB7 and PTB7:PC$_{71}$BM layers to study an increased absorption by fluorescence excitation spectra and the EQE of solar cells gave no clear result. The solar cell performance however could be almost maintained by incorporating gold nanorods which is promising for future investigations. The results are in agreement with some published articles giving warnings that the incorporation of metallic particles often leads to side effects like changes of the morphology and conductivity rather than a plasmonic enhancement and special care should be taken.
Conclusions

This dissertation focussed on solution-processed organic bulk-heterojunction solar cells and presented thorough investigations of novel donor and acceptor materials, how charge transport and recombination affect the device performance, and how plasmonic effects can be used to enhance the absorption of the active layer. This dissertation thus presents a selection of the research conducted within the EPSRC project (EP/100243X). The investigations presented, have revealed that the efficiency of organic solar cells is determined by a complex interplay of optical, morphological and electronic properties of the active layer blend. The combination of a wide variety of methods was required to disentangle the parameters influencing the device performance.

The active layer morphology is such a parameter which as shown in section 7.5 strongly influences the exciton dissociation efficiency and also the collection of free charge carriers. Based on the topography of the active layer, obtained by atomic force microscopy, three parameters of the morphology could be determined: the surface roughness, the grain size and the grain boundary length. These parameters could be used to describe the morphology in a more quantitative way and a correlation with the device performance was found.

Measurements of the JV-characteristics for variable light intensity was another method that proved very useful in this thesis as it quickly gives insight of bimolecular and trap-assisted recombination. A new measurement technique was presented by combining the time dependent $V_{oc}$, charge carrier density and integrated short circuit current density for variable illumination times of an LED (section 6.3.3 and 7.11). This technique allowed to observe the internal photocurrent to the electrodes and how quickly charge carriers are extracted. Combined with photocurrent traces, charge trapping could be investigated. The measurement also showed that the built-in field arises due to the different work function electrodes and applies even without external connection until the electrodes are charged.

To examine the exciton dissociation efficiency, the fluorescence of donor:acceptor blends was investigated by steady-state and time-resolved measurements. Both measurements showed a good agreement (section 5.7.1) and also showed that the device efficiency is strongly related to the quenching of fluorescence. Two aspects play a role in achieving a high exciton dissociation efficiency, the morphology and the offset of energy levels between donor and acceptor. Both aspects were found important in all material investigations of this thesis.

A selection of these techniques combined with the well established measurements of the JV-characteristics and EQE-spectra allowed to identify key limitations in organic solar cells. In
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chapter 4 a novel low band gap donor polymer was investigated. The efficiency reached a maximum of 0.6 % in blends with PC71BM. The EQE spectrum revealed that mainly absorption of the PC71BM phase was contributing to the photocurrent whereas photon absorption in the donor phase gave only a small contribution. This difference could be explained by the rather low LUMO offset of the polymer to PC71BM which provided little driving force to split excitons in the polymer phase, whereas the HOMO offset was sufficient to split excitons in the acceptor phase. In the standard device architecture an s-shape of the JV-curve was found, which strongly reduced the fill factor. This could be overcome by an inverted device architecture with caesium carbonate as electron transporting layer and molybdenum trioxide as hole transporting layer. The polymer could be further optimised by increasing the LUMO energy level to provide a higher driving force with common acceptors and a reduction of the bulky side chains to allow a higher absorption coefficient.

The limitations of fullerene acceptors were discussed in chapter 5 and novel subphthalocyanine derivatives as promising alternatives were suggested. The SubPcs provided a high absorption in the spectral region of high solar flux, which manifested in an improved EQE in this region. The device efficiency in blends with PTB7 reached up to 3.5 % for the chlorinated compound and 1.9 % for the fluorinated compound. The fluorinated compound had a lower solubility and a higher tendency to aggregate which led to a higher phase separation. The fluorescence emission of the blend indicated losses due to geminate recombination, which were minimal for the optimized blend ratio of 1:1.5. Both compounds had a high degree of traps which led to a reduced efficiency compared to fullerene acceptors. Reducing the number of traps in these materials would be a good way to further improve the devices. This could potentially be achieved by a thorough purification of the compounds and further optimisation of the blend morphology. Reducing the band gap to provide complementary absorption with common donor materials and a slight down-shift of the LUMO level to provide better exciton dissociation from the donor phase can also help to improve the device performance.

In chapter 6 the charge carrier mobility of organic semiconductors was investigated and a high hole mobility of PTB7 and electron mobility of PC71BM of each \(1 \times 10^{-3}\) cm²/Vs was observed. For PC71BM for the first time the time of flight technique was used to determine the electron mobility and it was found that a modified device architecture with a MoO₃ hole transporting layer was required to efficiently extract the charge carriers. The hole mobility for PTB7 was almost one order of magnitude higher than for P3HT of \(1 \times 10^{-4}\) cm²/Vs and the question arose how strongly this mobility difference might influence the device performance. The hole mobility of a PTB7:PC71BM blend could be tuned by three orders of magnitude by varying the temperature. This was then related to the device efficiency and clearly showed that the mobility has only a small influence on the performance. Decreasing the mobility by a factor of thousand led to a decrease of the efficiency from 6.9 % to 2.5 %, which is less dramatic than commonly expected. Upon reducing the mobility, trap-assisted and bimolecular recombination increased as well as the series resistance, leading to this lower performance.
In chapter 7 the morphology of PTB7:PC$_{71}$BM blends was modified by the content of a solvent additive and its effect on the device performance was observed. To allow a fair comparison for different ratios of additive, it was important to adjust the spin-coating speed in order to obtain a similar film thickness. The maximum efficiency of 7.4 % for 3 vol% of DIO originated from a minimum of trap-assisted and bimolecular recombination, a minimal surface roughness and a maximum exciton dissociation efficiency.

Motivated by a reduction of the fill factor for thick active layers, in chapter 8 it was explored if the absorption of the active layer can be increased by a plasmonic electric field enhancement. In a study of silver nanowires embedded in PEDOT:PSS it was shown that the absorption is enhanced near such metal structures by about a factor of two. Blending nanoparticles in the active layer, however gave no conclusive enhancement of the absorption as spectral changes of the external quantum efficiency or fluorescence excitation spectra were in a region were no plasmonic resonance of the nanoparticles was present. This emphasizes that an efficiency enhancement in such device structures should be proven by other additional measurements.

The development of solution-processed organic solar cells has progressed for almost 20 years now and a great improvement of the efficiency has been achieved. However as this thesis has shown some details of the working principle and technological aspects are still unclear. The limit of the power conversion efficiency of organic solar cells, which arises from the need to dissociate excitons, is by theoretical calculations lower than efficiencies already achieved by competing technologies, such as perovskite solar cells. This challenges the future of organic photovoltaics unless the current limitations are overcome or niche applications of the technology are found. In a broader context, the fundamental research of organic semiconductors such as the recombination and the charge carrier mobility also helps for a deeper understanding of other applications, like organic light emitting diodes and organic electronics.
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Gwyddion is an open source project. The software is available from http://gwyddion.net/.


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Value obtained by Dr. Emiliano Rezende-Martins for neat PTB7. Value agrees with the PTB7:PC71BM blend published in ref. 63


Symbols and abbreviations

Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Solar cell area</td>
</tr>
<tr>
<td>$A_a$</td>
<td>Absorbance, optical density</td>
</tr>
<tr>
<td>$a$</td>
<td>General constant describing offsets or proportionality factors</td>
</tr>
<tr>
<td>$b$</td>
<td>General constant describing slopes or exponents</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Bimolecular recombination rate constant</td>
</tr>
<tr>
<td>$C$</td>
<td>Capacitance</td>
</tr>
<tr>
<td>$c$</td>
<td>Concentration</td>
</tr>
<tr>
<td>$d$</td>
<td>Film thickness</td>
</tr>
<tr>
<td>$E$</td>
<td>Energy</td>
</tr>
<tr>
<td>$e$</td>
<td>Elemental charge</td>
</tr>
<tr>
<td>$\varepsilon_a$</td>
<td>Molar decadic extinction coefficient</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Vacuum permittivity</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>Material specific permittivity</td>
</tr>
<tr>
<td>EQE</td>
<td>External Quantum efficiency</td>
</tr>
<tr>
<td>$F$</td>
<td>Electric field</td>
</tr>
<tr>
<td>$f$</td>
<td>Diode ideality factor</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>$G$</td>
<td>Charge generation rate</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Conductivity</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Gaussian energy disorder, width of the density of states</td>
</tr>
<tr>
<td>$\sigma_a$</td>
<td>Absorption cross section</td>
</tr>
<tr>
<td>$\sigma_s$</td>
<td>Scattering cross section</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>Spatial disorder parameter</td>
</tr>
<tr>
<td>$I$</td>
<td>Light intensity</td>
</tr>
<tr>
<td>$I_{SC}$</td>
<td>Short circuit current</td>
</tr>
<tr>
<td>$J_{SC}$</td>
<td>Short circuit current density</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$k_r, k_{nr}$</td>
<td>Radiative and non-radiative decay rates of an exciton</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Order of the bimolecular recombination constant ($\beta - n^*$)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$M$</td>
<td>Spectral mismatch factor</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>$\mu_e$</td>
<td>Electron mobility</td>
</tr>
<tr>
<td>$\mu_h$</td>
<td>Hole mobility</td>
</tr>
<tr>
<td>$N$</td>
<td>Density of states</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of electrons per volume</td>
</tr>
<tr>
<td>$\eta_{br}$</td>
<td>Loss of bimolecular recombination</td>
</tr>
<tr>
<td>$P$</td>
<td>Electrical power</td>
</tr>
<tr>
<td>$P_{Light}$</td>
<td>Optical power</td>
</tr>
<tr>
<td>$P_{max}$</td>
<td>Maximal output power of a solar cell</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$p$</td>
<td>Number of holes per volume</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
</tr>
<tr>
<td>$P_d$</td>
<td>Dipole moment</td>
</tr>
<tr>
<td>PLQY</td>
<td>Photoluminescence quantum yield</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>Density of excitons</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>Constant describing the charge carrier density as a function of voltage</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Constant describing the charge carrier lifetime as a function of voltage</td>
</tr>
<tr>
<td>$Q$</td>
<td>Electric charge</td>
</tr>
<tr>
<td>$r$</td>
<td>Position vector</td>
</tr>
<tr>
<td>$R_{sh}$</td>
<td>Shunt resistance</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Series resistance</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Lifetime of an excited state or charge carriers</td>
</tr>
<tr>
<td>$T_a$</td>
<td>Transmission</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Hopping rate</td>
</tr>
<tr>
<td>$V$</td>
<td>Voltage</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>Vol</td>
<td>Volume</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Polarisability</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Monomolecular recombination constant</td>
</tr>
</tbody>
</table>

### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM</td>
<td>Air mass</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
</tr>
<tr>
<td>CE</td>
<td>Charge Extraction (Method)</td>
</tr>
<tr>
<td>CELIV</td>
<td>Charge Extraction by Linearly Increasing Voltage (Method)</td>
</tr>
<tr>
<td>cps</td>
<td>Counts per second</td>
</tr>
<tr>
<td>DOS</td>
<td>Density Of States</td>
</tr>
<tr>
<td>EMA</td>
<td>Effective Medium Approach</td>
</tr>
<tr>
<td>EPSRC</td>
<td>Engineering and Physical Science Research Council of the United Kingdom</td>
</tr>
<tr>
<td>GDM</td>
<td>Gaussian Disorder Model</td>
</tr>
<tr>
<td>GPIB</td>
<td>General Purpose Interface Bus, IEEE-488</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
</tr>
<tr>
<td>IQE</td>
<td>Internal Quantum Efficiency</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest Unoccupied Molecular Orbital</td>
</tr>
<tr>
<td>MPP</td>
<td>Maximum Power Point</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration (of the United States of America)</td>
</tr>
<tr>
<td>rms</td>
<td>Root mean square</td>
</tr>
<tr>
<td>rpm</td>
<td>Rotations per minute</td>
</tr>
<tr>
<td>PSpice</td>
<td>A software for modelling electrical circuits</td>
</tr>
<tr>
<td>SCLC</td>
<td>Space Charge Limited Current (Method)</td>
</tr>
</tbody>
</table>

### Chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>AgNW</td>
<td>Silver nanowire</td>
</tr>
<tr>
<td>Symbol</td>
<td>Abbreviation</td>
</tr>
<tr>
<td>------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>AuNS</td>
<td>Gold nanosphere</td>
</tr>
<tr>
<td>AuRod</td>
<td>Gold nanorod</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminium</td>
</tr>
<tr>
<td>BBT</td>
<td>Benzobisthiadiazole</td>
</tr>
<tr>
<td>BDT</td>
<td>Benzodithiophene</td>
</tr>
<tr>
<td>BT</td>
<td>Benzothiadiazole</td>
</tr>
<tr>
<td>C₆₀</td>
<td>C60-Fullerene</td>
</tr>
<tr>
<td>Ca</td>
<td>Calcium</td>
</tr>
<tr>
<td>CB</td>
<td>Chlorobenzene</td>
</tr>
<tr>
<td>CF</td>
<td>Chloroform</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>Compound 1</td>
<td>Pentfluorophenoxy-[2,3,9,10,16,17-hexafluorosubphthalocyaninato]-boron (III)</td>
</tr>
<tr>
<td>Compound 2</td>
<td>Phenoxy-[2,3,9,10,16,17-hexafluorosubphthalocyaninato]-boron (III)</td>
</tr>
<tr>
<td>CPDT</td>
<td>Cyclopenta[2,1-b;3,4-b]dithiophene</td>
</tr>
<tr>
<td>Cs₂CO₃</td>
<td>Caesium carbonate</td>
</tr>
<tr>
<td>DCB</td>
<td>1,2-Dichlorobenzene</td>
</tr>
<tr>
<td>DIO</td>
<td>1,8-Diodooctane</td>
</tr>
<tr>
<td>DPP</td>
<td>Diketopyrrolopyrrole</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]</td>
</tr>
<tr>
<td>MoO₃</td>
<td>Molybdenum trioxide</td>
</tr>
<tr>
<td>NDI</td>
<td>Naphthalene diimide</td>
</tr>
<tr>
<td>P(DPPThbBBT)</td>
<td>Poly-3-(5-(2,6-diundecylbenzo[1,2-d:4,5-d']bis(thiazole)-4-yl)thiophen-2-yl)-2,5-bis(2-octyldodecyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexythiophene)</td>
</tr>
<tr>
<td>PC₆₁BM</td>
<td>[6,6]-phenyl-C61-butryc acid methyl ester</td>
</tr>
<tr>
<td>PC₇₁BM</td>
<td>[6,6]-phenyl-C71-butryc acid methyl ester</td>
</tr>
<tr>
<td>PC₈₅BM</td>
<td>[6,6]-phenyl-C85-butryc acid methyl ester</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)</td>
</tr>
<tr>
<td>PFN</td>
<td>Poly ([9,9-bis(3′-(N,N-dimethylamino) propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctyllfluorene)]</td>
</tr>
<tr>
<td>PTB7</td>
<td>Poly[[4,8-bis([2-ethylhexyl oxy]benzo[1,2-b:4,5-b0]dithiophene-2,6-diyl][3-fluoro-2-(2-ethylhexy)carbonyl]thieno[3,4-b]thiophenediyl]]</td>
</tr>
<tr>
<td>SubPc</td>
<td>Subphthalocyanine</td>
</tr>
<tr>
<td>TCE</td>
<td>Tetrachloroethane</td>
</tr>
<tr>
<td>TT</td>
<td>Thienothiophen</td>
</tr>
</tbody>
</table>