Optoelectronic processes at polymer-fullerene heterojunctions: charge transfer states in organic solar cells

Citation for published version (APA):

DOI:
10.6100/IR740136

Document status and date:
Published: 01/01/2012

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

Please check the document version of this publication:
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Optoelectronic Processes at Polymer - Fullerene Heterojunctions

Charge Transfer States in Organic Solar Cells

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen
op dinsdag 11 december 2012 om 16.00 uur

door

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geboren te Sesto San Giovanni, Italië
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This research forms part of the research programme of the Dutch Polymer Institute (DPI), Technology Area Functional Polymer Systems, DPI project #631

A catalogue record is available from the Eindhoven University of Technology Library

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Printed by: Wöhrmann Print Service
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Abstract

The importance of research on photovoltaic devices is motivated in view of the global energy problem and in relation to other more established energy sources. A description of the working principles of organic solar cells is then presented, with focus on the open scientific questions regarding the processes of charge generation and recombination. Finally, the outline of the thesis is described.
Chapter 1

1.1 The energy challenge

Mankind makes heavy use of energy in its daily activities. In 2011 the primary energy consumption was estimated at ~ 500 ExaJoules,\(^1\) corresponding to an average power of more than 16 TW. This corresponds to almost 2.5 kW for each of the 7 billion inhabitants of the planet. Human population is growing and is expected to reach 8-11 billion (depending on different growth scenarios) by 2050.\(^2\) Furthermore, the actual average consumption per inhabitant does not reflect the huge differences between areas of the world: in the USA the average consumption per person is ~10 kW, while in China it is ~2.5 kW and in Africa it is as low as ~0.5 kW.\(^1,2\) If every country would increase its average consumption to the levels of the USA, the energy needs would increase greatly in the future. Most estimates foresee that by 2050 the total primary energy consumption will have grown to a value between 600 and 1000 EJ per year, corresponding to a power between 20 and 30 TW.\(^3,4\) Here we will assume the lower limit of 20 TW; the energy challenge is to match this demand and its rapid growth with sources that are abundant, durable, and do not irreversibly affect the environment.

Nowadays the sources of primary energy are fossil fuels (87%), nuclear fission (5%), and renewables (8%, of which hydroelectric 6.5%). Fossil fuels include oil (33%), coal (24%) and natural gas (30%).\(^1\) A strong dependence on fossil fuels presents several disadvantages: first of all the reserves are not unlimited and the supply of fuels is destined to not cope with the increase in demand.\(^4,5\) Additionally, they are not available in every geographical area, creating interdependence between regions of the world. Finally, the combustion of fossil fuels generates greenhouse gases that have been identified to be causing climate changes that could reach uncontrollable levels already in the next 2-3 decades.\(^6\)

Nuclear power is an energy source that would not contribute to the climate change. However present technologies are based on uranium fission, which share some of the same disadvantages of fossil fuels (limitedness and geographical localization) together with high environmental risks and difficulties in the treatment of the radioactive waste. Most importantly, the construction of a nuclear power plant requires a remarkable amount of time and economic investments. To provide 20 TW of power with nuclear sources by 2050, would require the construction of one plant per day during the next 40 years, globally.

The main advantage of renewable sources is their very low or negligible impact on the environment. The main renewable sources can be listed as hydroelectric, solar, wind, geothermal, biomass, and ocean tidal energy. Among these options, the most abundant is solar energy\(^7\): one face of the Earth’s atmosphere is constantly irradiated
with $\sim 2 \cdot 10^5$ TW of sunlight power. The average power at the whole Earth’s surface is on the order of $10^4$ TW, which is still $10^3$ times the present global consumption. Besides abundance, an advantage of solar energy is the availability in every area of the planet. Solar energy can be converted into usable energy in two ways: converting it into heat (“thermal”) or into electricity (“photovoltaic”). The most used is photovoltaic, with a worldwide cumulative installed power capacity that has been growing rapidly in the last years and now amounts to 70 GW peak, mainly provided by crystalline silicon solar cells.$^8$ However this amount of generated power is still marginal compared to the global consumption of primary energy. A difficulty in increasing the photovoltaic power production is related to the main drawback of solar energy, which is its low area density: large areas need to be covered to harvest the required amount of solar energy.

### 1.2 Motivation and challenges for organic photovoltaic solar cells

One can roughly estimate the production rate of photovoltaic active layer required to provide the amount of power that may be needed in the next decades. Assuming a module lifetime of 20 years and a power conversion efficiency of 15% at an average irradiance of 200 W/m$^2$, an area of 1.3 million km$^2$ would need to be covered to provide 20 TW average power by 2050. This corresponds to a production and installation rate of 90 km$^2$ per day for 40 years. To achieve this rate of production, fast and low energy consuming fabrication processes are a strict requirement. It is difficult to achieve this rate of production with traditional silicon solar cells. The use of a thick (hundreds of micrometers) and defect-free high-purity crystalline silicon layer in the cells requires a considerable amount of energy in the fabrication. This results in a typical energy payback time of 2-3 years. Polycrystalline silicon solar cells have a lower energy payback time, which nevertheless does not go below 1 year.$^9$

In this sense an ideal candidate for high production rate is represented by organic photovoltaic solar cells: in these devices the active layer consists of organic semiconductors which can be processed at high rates, using printing techniques. The active layer thickness is reduced in this case to $\sim 100$ nm. The production of organic photovoltaic modules with an energy payback time in the order of days is in principle possible.$^9$ In addition organic solar cells are potentially cheap, again because of to the low amount of material and energy required to produce them. Finally, they can be fabricated on flexible modules and thus can be more easily integrated in buildings.
These possibilities have in recent years stimulated a lot of interest, making organic photovoltaics (OPV) one of the fastest growing sectors in the research on photovoltaics. Efficiencies exceeding 10% on the lab scale have recently been reached. However, several steps have still to be made in order to achieve high efficiencies on large module areas and to realize large scale production as prospected in the estimation made above. Another important point is to achieve high stability of these devices, in order to ensure a long operational lifetime. Substantial progress still needs to be made to reach the requirements for large scale production.

Many of the technological challenges are also scientific challenges: the fundamental mechanisms taking place in a working organic solar cell are not fully understood yet. To fully optimize materials and processes for large scale production they should be understood in as much detail as possible. In the next paragraphs the basic working principles of organic solar cells will be explained and some of the main scientific questions will be treated in detail.

1.3 Basic working principles of organic photovoltaic solar cells

Absorption of a photon in an organic semiconductor results in a tightly (0.3-0.4 eV) bound electron-hole pair called exciton residing on the same molecule (Figure 1.1). The dissociation of the photogenerated exciton into free charges at room temperature is highly unlikely, explaining why the first organic solar cells in the 1970s had rather low power conversion efficiencies (< 1%). Later it became clear that to efficiently transform the photogenerated excitons into free collectable charges, a heterojunction between an electron donating material (D) and an electron accepting material (A) must be used. At the D-A heterojunction the photogenerated exciton can be split into an electron residing on A and a hole residing on D thanks to the energy offset between the lowest unoccupied molecular orbitals (LUMOs) and between highest occupied molecular orbitals (HOMOs) of donor and acceptor. If the exciton is created far from the heterojunction, it has to diffuse towards the active interface in the limited time interval between its creation and recombination to the ground state.

Once the exciton has been split, the electron on A and the hole on D are in principle still close enough to be electrostatically bound across the heterojunction, forming a charge transfer (CT) state. Again, due to the low dielectric constant of the materials used, the CT state may still have a considerable (0.1-0.2 eV) binding energy and may not be dissociated easily by thermal energy at room temperature (0.025 eV). This aspect will be discussed in detail in a following paragraph of this chapter. Free
charges that result from the dissociation of the CT state have to drift or diffuse to the collecting electrodes and be extracted.

All the steps of light-to-electricity conversion in an organic solar cell are shown in Figure 1.1 and are summarized in the following list:

1) absorption of a photon, resulting in the creation of a bound exciton, either on D or A;
2) migration of the exciton to the D-A interface;
3) charge transfer resulting in an electron residing on A and a hole residing on D still bound through the interface to form the CT state;
4) dissociation of the CT state into free charges;
5) transport and collection of the free charges at the electrodes.

The basic characterization of a solar cell is the measurement of the current it can deliver as function of the voltage difference applied to the extracting contacts. Such a measurement results in a current-voltage (I-V) curve (Figure 1.1). In dark the solar cell acts as a diode, with low (ideally zero) current at negative voltage bias and positive current above a certain threshold positive voltage bias. The threshold voltage is the bias at which electrons can be injected into the electron LUMO of the acceptor and holes into the HOMO of the donor. Under illumination, photocurrent is induced in the 3rd and 4th quadrants of the I-V plot. The open-circuit voltage ($V_{oc}$) is defined as the condition at which the total current under illumination ($I_{light}$) is zero. The short-circuit current $I_{sc}$ is defined as $I_{light}$ at zero applied bias, that is when the two electrodes are shorted. The 4th quadrant is where the solar cell under illumination delivers power. The point in the 4th quadrant where the product $I \cdot V$ is maximum is called maximum power point (MPP) and defines the maximum power $P_{max}$ that the cell can deliver to an external circuit. Ideally $P_{max}$ should be close to the product $I_{sc} \cdot V_{oc}$, resulting in a fill factor ($FF$) close to 1, where $FF = P_{max} / I_{sc} \cdot V_{oc}$. The fill factor is a useful number to quantify the extent to which generation and extraction of charges depend on the electric field present across the device. The power conversion efficiency ($PCE$) of a solar cell is defined as

$$PCE = \frac{P_{max}}{P_{in}} = \frac{FF \cdot I_{sc} \cdot V_{oc}}{P_{in}}$$

where $P_{in}$ is the power of the incoming light. For solar cells standard test conditions have been defined. Under these conditions the cell is illuminated by the AM 1.5 G (AM: air mass) global reference spectrum at an intensity of $P_{in} = 1000$ W/m$^2$.

The best reported organic solar cells show fill factors between 60% and 70%. These numbers are rather low compared to inorganic solar cells, which can reach
values above 80%\textsuperscript{[18]} This is probably due to low charge mobility (compared to inorganic semiconductors) combined with recombination of free charges before extraction (see next paragraph), resulting in a rather strong field dependence of the photo-generated current. Paragraph 1.5 discusses how a field dependence of CT state dissociation can contribute to a low fill factor.
Figure 1.1: (Top) Energy diagram that shows the steps involved in the light-to-electricity conversion in an organic donor-acceptor solar cell. For convenience, only the case of photon absorption in the donor is represented. The Fermi energies of the electrodes used to extract photogenerated holes (1) and electrons (2) are also schematically shown. (Bottom) I-V characteristic of a 0.091 cm$^2$ active layer organic solar cell in dark (black line) and under 100 mW/cm$^2$ illumination (red line). The blue line represents the power delivered by the cell as function of voltage bias. The rectangle in the I-V plot indicates the maximum output power, $P_{\text{max}}$, at the maximum power point condition. The numbering of the quadrants is indicated.
In a conventional organic solar cell, the active layer is sandwiched between two electrodes with different workfunctions (Figure 1.1). A transparent conductive oxide is used as front contact on top of which a hole conductive layer such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is deposited. In lab devices the transparent electrode is typically ITO (indium tin oxide) deposited on a glass substrate. On top of the active layer the second, electron collecting, electrode is deposited (e.g. lithium fluoride/aluminum). The difference in workfunctions creates the internal electric field that makes that free photogenerated electron and holes move in opposite directions and create a photovoltage.

An important characteristic of new materials for the active layer of organic solar cells is the overlap of their absorption with the solar light spectrum, which extends roughly over the wavelength region from 300 to 2000 nm. To collect as many solar photons as possible, many new types of molecules with small optical band gaps (down to the near infrared photon energies) are being synthesized.\textsuperscript{[19]}

For organic solar cells with single layer architecture a practical limit efficiency of ~10-12\% has been predicted\textsuperscript{[20,21]}, although this is not a fundamental limit. In a single active layer, all the photon energy in excess of the optical band gap energy is lost in form of heat. To better manage the photon energies of solar light, multi-junction architectures are used, where various layers are optimized, each one converting a different part of the spectrum. In this way the efficiency limit is raised.\textsuperscript{[22]} Both evaporated and solution processed double junction (tandem) solar cells with efficiencies around or above 10\% have been reported recently.\textsuperscript{[10,23]}

**Figure 1.2:** An example of conventional lab device structure with a zoom in on the active layer to show the bulk hetero-junction. Under illumination photogenerated electrons are extracted from the aluminum electrode and holes from the ITO electrode.
1.4 The bulk heterojunction

The donor-acceptor bilayer structure presents a limitation: at room temperature excitons in organic semiconductors have typical diffusion lengths of 5-20 nm,\cite{24-26} while a layer thickness of \textasciitilde100 nm is needed to efficiently absorb light. Therefore, in thick cells many excitations are not converted into charges because they are created too far from the heterojunction. On the other hand in thin cells, where exciton dissociation is efficient, not all the photons are absorbed. To overcome this limitation the bulk heterojunction was introduced in 1995.\cite{27,28} In the bulk heterojunction, donor and acceptor materials are blended with a dimension of the phase separation that is on the order of tens of nanometers (Figure 1.2): in this way most of the excitons are created at a distance from the heterojunction that is in the order of or shorter than the diffusion length.

Furthermore, the bulk heterojunction blend can be deposited from solution, where the blend is already prepared. Today, the most efficient organic solar cells employ the bulk heterojunction architecture in their active layer. However, to reach optimal efficiency with the bulk heterojunctions requires careful tuning of the length scale of phase segregation, as will be discussed later.

The bulk heterojunction architecture can allow essentially each exciton to reach the active D-A interface. However, going from two pure stacked layers to an intimately mixed blend possibly introduces complications related to the transport of charges: first of all a percolation path must be present to allow charges to reach the collecting electrodes. Secondly, increasing the internal D-A interface area increases the chance for electron and hole to meet and recombine before being extracted (bimolecular recombination). Due to the presence of the heterojunction all over the active layer, bimolecular recombination can be in strong competition with collection (drift to the electrodes) at high illumination intensities and low effective electric field strengths. Note that close to the open-circuit voltage low electric fields are expected and the high rate of recombination will result in a poor fill factor.\cite{29,30} Finally, also the dissociation of the CT state may be affected by the degree of phase separation. These aspects will be discussed in more detail in paragraphs 1.5 and 1.6.

The materials used in the active layer of organic solar cells can be divided in two classes: polymers and small molecules. Polymers are typically used as electron donating material in combination with fullerene derivatives based on C_{60} or C_{70} fullerene, e.g. [60]PCBM ([6,6]-phenyl-C_{61}-butyric acid methyl ester) or [70]PCBM ([6,6]-phenyl-C_{71}-butyric acid methyl ester). [70]PCBM has the same electronic levels as [60]PCBM, but due to the different symmetry has a stronger optical absorption in the visible range. This commonly results in higher photo-generated
current compared to [60]PCBM.\textsuperscript{[31]} These kind of active layers are usually processed from solution. Presently the highest reported power conversion efficiencies for single layer organic solar cells are obtained in polymer:[70]PCBM bulk heterojunction devices, with efficiencies between 8 and 10%.\textsuperscript{[10,32,33]} These values approach the predicted efficiency limit and imply internal quantum efficiencies of essentially unity. So far no electron accepting materials performing as well as C\textsubscript{60}/C\textsubscript{70} derivatives have been found.

Small molecule based active layers can be deposited either from solution or by thermal evaporation. Historically polymers have shown better efficiencies compared to small molecules in solution processing of the active layer. However small molecules solution processed solar cells are recently filling the gap.\textsuperscript{[34]}

### 1.5 Charge transfer state

As mentioned in paragraph 1.3 the process of charge transfer at the donor-acceptor heterojunction in organic solar cells results in the population of the so called charge transfer (CT) state. The CT state consists of an electron-hole pair electrostatically bound across the heterojunction, with the electron residing on the acceptor and the hole on the donor. In the following paragraphs it will be argued that the properties of the CT state determine many crucial aspects of the operation of organic solar cells.

#### 1.5.1 Charge transfer, energy of the CT state, and open-circuit voltage

Charge transfer involves electron transfer from the LUMO of the donor to the LUMO of the acceptor, in case the photon is absorbed in the donor (Figure 1.1). If the photon is absorbed by the acceptor, an electron from the HOMO of the donor is transferred to semi-filled HOMO of the acceptor. The latter process is often referred to as hole transfer. The minimum of the LUMO-LUMO and HOMO-HOMO energy offsets between donor and acceptor materials provides the energy necessary to overcome the increase in Coulomb energy for the electron transfer from donor to acceptor to occur. This implies that both offsets must be present to create the charge transfer state. This condition is represented by the CT state having the lowest available energy at the heterojunction. The required energy offset was estimated experimentally by Veldman et al. as 0.1 eV.\textsuperscript{[35]} Let $E_g$ denote the lowest value of the optical gaps (corresponding to the transition from ground state to lowest excited singlet state) of the pure donor and acceptor material. The required energy loss in the charge transfer step to reach the CT state with energy $E_{CT}$ can then be expressed as $E_g - E_{CT} \geq 0.1$ eV (Figure 1.3).
The CT state can also be directly populated from the ground state via an optical transition. The oscillator strength of these transitions is usually quite low, but nevertheless optical detection with sensitive techniques is possible: luminescence (photo and electro, steady-state and time-resolved) from the CT state has been observed in many systems, as well as absorption on thin film and via photo-current measurements on devices. This provides a convenient way to carefully determine $E_{CT}$ and to investigate the process of charge generation and recombination.\[^{36-43}\]

Being the first state populated after charge transfer, the CT state also sets an upper limit to the attainable open-circuit voltage. It was estimated that under ~1 sun illumination conditions the CT state energy relates linearly to the open-circuit voltage as $E_{CT} \sim q \cdot V_{oc} + 0.5\,\text{eV}$, with $q$ the elementary charge.\[^{35,38,40}\] The 0.5 eV loss is often interpreted as the energy associated with relaxation of the free charge carriers, including energetic relaxation near the electrodes due to band bending. Maximizing the open-circuit voltage corresponds to maximizing the energy of the CT state and for a chosen optical band gap $E_g$, the maximum attainable $V_{oc}$ in efficient devices is estimated at $E_g/q - 0.6\,\text{V}$.\[^{35}\]

1.5.2 Charge transfer state dissociation and recombination

One of the most intriguing questions in organic photovoltaics regards the process of free charge generation at the donor-acceptor interface. Several devices showing high internal quantum efficiency (above 80%) at short circuit have been demonstrated.\[^{32,33,44,45}\] Assuming small polaronic carriers it is not immediately clear how the carriers overcome the barrier for dissociation of the CT state (0.1-0.2 eV) within the limited lifetime of the CT state itself (~ns). Knowing the mechanisms involved in dissociation of the CT state would allow one to rationally design materials with optimized quantum efficiencies.

Evidence for CT state binding energies as high as 0.1-0.2 eV have been reported.\[^{46-49}\] Given this considerable Coulombic barrier, dissociation at room temperature without the aid of any external force seems unlikely, since thermal vibrations provide only 0.025 eV. Furthermore the CT state has a finite lifetime since, as mentioned in Paragraph 1.5.1, the probability for recombination to the ground state is significant. This implies that the overall dissociation probability is the result of a competition between dissociation and recombination (Figure 1.3). CT state luminescence lifetimes in the order of nanoseconds are typically observed in organic donor-acceptor systems, corresponding to a decay rate of $\sim 10^8 - 10^9\,\text{s}^{-1}$.\[^{39,50}\]

Another important question is how strongly CT dissociation depends on the electric field.\[^{51,52}\] It is expected that all the CT electron-hole pairs will dissociated in
the limit of a high electric field strength in the active layer. In the 4th quadrant of the I-V curve the effective electric field present across the active layer goes from \(~\text{zero} (\text{close to } V_{\text{oc}})\) to \(~10^5-10^6 \text{ V/cm}\) at short circuit. For efficient solar cells the condition of high probability of CT dissociation should be reached already at low fields. This requirement minimizes the detrimental impact of field assisted free carrier generation on the fill factor of the I-V curve and therefore on the power conversion efficiency.

The Onsager-Braun model is often used to describe the probability of CT dissociation as function of applied electric field \(E\) and temperature \(T\):\(^{[53-55]}\) The dissociation probability is expressed as 

\[
P(E,T) = \frac{k_d(E,T)}{k_d(E,T) + k_f},
\]

where \(k_d(E,T)\) is the rate of dissociation into free charges and \(k_f\) is the rate of CT recombination (Figure 1.3). The rate constant \(k_f\) may be assumed to be independent of field and temperature; the dependence of \(k_d\) on \(T\) and \(E\) contains several physical parameters and is expressed as:

\[
k_d(E,T) = k_R \frac{3}{4\pi R_{cc}^3} e^{-E_B/k_B T}\frac{J_1(2\sqrt{-2b(E,T)})}{\sqrt{-2b(E,T)}}
\]

where \(R_{cc}\) is the electron-hole separation distance in the CT state and \(E_B\) is the binding energy. The binding energy is considered as originating from the electrostatic interaction between two point charges in a continuous medium with relative permittivity \(\varepsilon\), and therefore is expressed as \(E_B = q^2/4\pi\varepsilon_0\varepsilon R_{cc}\). A distribution of separation distances \(R_{cc}\) can be included to account for the disorder in the blends.\(^{[56,39]}\) \(J_1\) is the Bessel function of order 1 and \(b\) is given by

\[
b(E,T) = q^3/8\pi\varepsilon_0\varepsilon R_{cc}^2 T^2.
\]

Finally, \(k_R = q\langle\mu\rangle/\varepsilon_0\varepsilon\) is a Langevin type bimolecular recombination rate, with \(\langle\mu\rangle\) the average charge mobility. According to the Onsager-Braun model high probability of CT dissociation at the low electric fields in the 4th quadrant of the I-V curve is possible for materials with high carrier mobility, CT states with large \(R_{cc}\) and low recombination rate \(k_f\).

Numerical simulations taking into account the transport and extraction of charges at the electrodes together with a field dependent charge generation based on the Onsager-Braun model have successfully reproduced experimental I-V characteristics of organic solar cells, including systems with high short-circuit EQE, such as P3HT:PCBM,\(^{[57,58]}\) using the values of mobilities obtained from transport measurements. However, to do so \(k_f\) in the order of \(10^5-10^6 \text{ s}^{-1}\) need to be used, in contrast with the above mentioned optical measurements showing much higher values. To try to solve this discrepancy, it has been proposed that the local charge mobilities at the nanoscale are orders of magnitude higher than the bulk measured ones.\(^{[39]}\)
The discussion above on the implementation of the Onsager-Braun model to describe photo-currents illustrates the difficulty in determining values for the parameters describing processes on the molecular scale. These complications make the experimental test of models for CT dissociation difficult.

A number of mechanisms for dissociation of the CT state taking into account the properties of the donor-acceptor systems at the molecular scale have been proposed. Models describing CT dissociation by hopping motion indicate that dissociation of the CT state is favored by energetic disorder. By Monte Carlo simulations \cite{59-61} and analytical modeling \cite{62} it has been shown that high efficiency of CT dissociation at low electric field can be achieved in an energetically disordered landscape. Because of the presence of molecular sites with low carrier energy, charge separated states with energy lower than that of the CT state are available close to the hetero-junction, assisting the dissociation.

An important aspect to take into account is that charged states in organic π-conjugated systems have a certain degree of delocalization. In conjugated polymers it is known that the charge can extend over ~10 polymer units.\cite{63} This could help to reduce the net Coulombic binding energy between opposite charged delocalized polarons, facilitating separation of the charge pair.\cite{64-66} Bakulin et al.\cite{65} have proposed that the hole wave-function on donating polymers has an increased delocalization in higher excited CT states compared to the thermalized bottom of the CT band. Atomistic details of the donor-acceptor interface (electronic structure and orientation) may furthermore influence the CT dissociation process influencing the binding energy of the electron-hole pair via static dipoles\cite{67} and multipoles.\cite{68} Finally, CT dissociation may be aided by the photon excess energy (i.e. the difference between the energy of the absorbed photon and that of the CT state).\cite{69,70} In this picture the photogenerated exciton first populates a so called ‘hot’ CT state. The ‘hot’ CT state is a state in the upper part of the vibronic manifold of the CT band. If the dissociation happens faster than the thermal relaxation of the ‘hot’ CT state, the Coulombic barrier may be overcome and free charges would be formed directly without passing through a strongly bound CT state. The relevance of this mechanism is currently under investigation. Yet accord on its importance has not been reached. On the one hand experimental evidence for a correlation between available excess energy and efficiency of charge generation has been obtained.\cite{66,71,72} On the other hand efficient CT dissociation with no dependence on excess energy has been also reported.\cite{65,66,73} It is important to realize the consequences for the optimization of solar cells: a mechanism of charge generation requiring excess energy would imply a necessary energy loss in the carrier separation.
Importantly, the ‘hot’ CT mechanism implies that thermalized CT states that are typically probed by luminescence techniques are not intermediates in the process of free charge generation in solar cells. Therefore experimental parameters obtained for the thermalized CT state may not be relevant.\textsuperscript{[61]}

### 1.5.3 Charge transfer state recombination to the triplet state

A possible loss mechanism in organic solar cells is recombination of the CT state to the triplet state localized on one of the two materials (Figure 1.3). The total recombination rate $k_f$ for the CT state including this process is given by $k_{\text{CT0}} + k_{\text{CTT}}$. Here $k_{\text{CT0}}$ represents the rate of recombination to the ground state and $k_{\text{CTT}}$ the rate of recombination to the triplet state. Organic materials have typically a high $S_1$ to $T_1$ energy gap (0.6-1 eV)\textsuperscript{[74]}, where $S_1$ and $T_1$ are the lowest singlet and triplet excited state respectively. If the energy of the CT state is higher than that of the triplet, the recombination process is energetically allowed. This condition is often encountered in systems in which the $V_{oc}$ has been optimized by raising the CT state energy.

CT states could be classified as singlet and triplet according to the spin character of the electron and hole. For the CT states a much smaller $S_1$ to $T_1$ energy gap may be expected because of the limited spatial overlap of the electron and hole wave-functions, resulting in small exchange energy. As a consequence, efficient singlet-triplet mixing in the CT state can be expected.\textsuperscript{[75]} This opens the way for $S_1$ to $T_1$ inter-conversion, in the case of charge back-transfer populating an intramolecular triplet state.

Recombination of the CT state to the triplet state has been observed in various systems.\textsuperscript{[76-81]} Veldman et al.\textsuperscript{[39]} have argued that the energy of the CT state needs to be at least 0.1 eV above the energy of the triplet state for the recombination to happen efficiently.

One of the few studies aiming at a quantitative determination of the efficiency of recombination of the CT state into triples is by Westenhoff et al. It was shown that in thin films of a polymer:polymer blend up to 75\% of CT states recombine into intrachain triplet states.\textsuperscript{[79]} A way to minimize the loss mechanism represented by recombination to triplet excited states would be the design of materials with low singlet-triplet energy splitting.\textsuperscript{[82,83]}

Finally, a non-negligible density of populated triplet states may have a negative influence on the photostability of the active layer. If the triplet energy is above $\sim$1 eV, energy transfer to molecular oxygen present in the film will result in the production of oxygen in its singlet excited state $^1$O$_2$, the energy of which is 0.98 eV. Singlet oxygen
is chemically highly reactive and has been shown to participate to the degradation of polymers.\textsuperscript{[11,84]}

In Chapter 5 we show evidence for a correlation between photogeneration of triplets and photostability in thin solid films of conjugated polymers blended with PCBM.

\begin{center}
\textbf{Figure 1.3:} Jablonski diagram showing the transitions involved in the generation of free charges. Indicated in green are the steps of charge transfer to form the CT state and CT dissociation, with rate $k_d$. In red are shown the possible recombination processes of the CT state with the respective rates: recombination to the triplet state ($k_{CTT}$) and to the ground state ($k_{CT0}$), with the total recombination rate given by $k_f = k_{CT0} + k_{CTT}$. The relation between $V_{oc}$ and $E_{CT}$ is also displayed.
\end{center}

\section*{1.6 Relation between the bulk heterojunction nanomorphology and the performance of solar cell devices}

The nanomorphology of the bulk heterojunction plays a crucial role in the optimization of device performances. In solution processing of bulk heterojunctions, the morphology can be influenced through the choice of the solvent\textsuperscript{[85]} and the degree of phase segregation can be optimized using cosolvents\textsuperscript{[86,87]} Another option to optimize the morphology is represented by thermal annealing, as has been demonstrated for P3HT:PCBM blends.\textsuperscript{[88,89]}
The general criteria that the bulk heterojunction should satisfy in order to obtain high efficiencies of charge photogeneration and collection can be summarized as follows: first the mixing of the donor and acceptor phases should be intimate enough to result in efficient photogenerated exciton splitting. Second, the phase segregation should be such that fast and efficient transport towards the electrodes is possible. This second requirement is to ensure low losses due to bimolecular recombination of photogenerated carriers. Third, the local mobility of charge carriers near the donor-acceptor interface should be high, so that losses due to geminate recombination are minimized. It has been proposed that the degree of phase separation and PCBM domain crystallinity in polymer:PCBM blends can influence the local charge mobility resulting in higher CT dissociation efficiency.\textsuperscript{[39,64]}

Figure 1.4 summarizes the two extreme cases of blends having too high or too low level of mixing. The crystallinity of the phases will likely influence the charge generation and transport properties.

\textbf{Figure 1.4: }Cartoons of archetype morphologies of polymer:fullerene bulk heterojunction morphologies: very finely dispersed (left) and very coarse phase separation (right).
1.7 Aim and outline of this thesis

This thesis focuses on the role of the charge transfer state in charge generation and recombination in organic solar cells comprising polymer:fullerene bulk heterojunction as active layer. The mechanisms of CT state formation, dissociation and recombination are investigated. The aim is to understand the rates and efficiencies of these steps in terms of excited state properties of the materials and of the nanomorphology of the active layer blend.

In Chapter 2 the effect of the thermodynamic driving force on the efficiency of photoinduced charge transfer between a semiconducting polymer and various fullerene derivatives is investigated. Blends comprising a polyfluorene copolymer mixed with a variety of fullerene mono- and bisadducts with different acceptor levels are studied. By spectroscopic characterization of bulk heterojunction thin films and corresponding photovoltaic devices it is found that the charge transfer state needs to be at least 0.1 eV lower in energy than the singlet excited state of the fullerene to be formed efficiently.

Chapters 3 and 4 treat the relation between nanoscale morphology of the polymer-fullerene heterojunction and the efficiency of CT state dissociation. Blends composed of a small band gap semiconducting polymer mixed with fullerene are studied. The nanoscale phase separation of these blends can be controlled by adding high-boiling point cosolvents to the solutions used to process the thin films. Without cosolvent the blends are very finely mixed and the addition of cosolvents increases the phase separation. In blends that are too finely mixed the CT state does not dissociate efficiently into free charge carriers and recombines to the triplet state of the polymer. The recombination to the triplet state constitutes a loss mechanism and here is identified using near steady state photoinduced absorption (PIA) spectroscopy on thin films. This process is reduced in favor of dissociation into free charges when the phase separation is increased. The increased phase separation correlates with the increased device performance via increase of fill factor and short-circuit current. These results show that photophysical processes of the CT state are largely controlled by the nanoscale morphology. Efficient recombination in blends with too fine morphologies is confirmed by charge extraction experiments on solar cells. It is shown that fast CT recombination (to the triplet and to the ground state) is largely responsible for the poor device performances of non-optimized blends. It may be expected that formation of triplet excited states in large quantities has a detrimental effect on the photostability of the blend. Indications for such a destabilization in polymer:fullerene blends are put forward in Chapter 5.
In Chapters 6 and 7 the influence of excess photon energy on the dissociation of the CT state is investigated by means of charge extraction and spectral response measurements. It is found that excess energy is not necessary for CT dissociation; this result shows that the energy loss in converting a photon to free charges can in principle be minimized to 0.1 eV, which was indicated in Chapter 2 as the requirement for efficient charge transfer.

Chapter 8 investigates factors limiting the photocurrent of solar cells close to open-circuit voltage. It is found that under these conditions photocurrents show an intensity dependence expected for space-charge limited current, indicating that the CT dissociation step is efficient enough to generate the limiting densities of free charge carriers. Impedance spectroscopy is the technique used here. The experimental results are supported by an analytical model and by drift diffusion simulations.

Finally, Chapter 9 is an epilogue giving an overview of the thesis and linking together the results of the different chapters.
1.8 References and notes

[1] *BP Statistical Review of World Energy, June 2012*. Consumption of energy is reported here in units of TOE (Tons of Oil Equivalent), with 1 TOE = 41.87 GJ and assuming that a 38% average conversion efficiency in electrical power stations. This equivalence overestimates the consumption in form of electricity produced from sources with highly efficient (e.g. hydroelectric) or direct conversion (e.g. photovoltaic). For more information on the different possible equivalences see reference [7].


Chapter 1


Simultaneous open-circuit voltage enhancement and short-circuit current loss in polymer:fullerene solar cells correlated by reduced quantum efficiency for photoinduced electron transfer

Abstract

The limits of maximizing the open-circuit voltage $V_{oc}$ in solar cells based on poly[2,7-(9,9-didecylfluorene)-alt-5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)] (PF10TBT) as a donor using different fullerene derivatives as acceptor are investigated. Bulk heterojunction solar cells with PF10TBT and [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PCBM) give a $V_{oc}$ over 1 V and a power conversion efficiency of 4.2%. Devices in which PF10TBT is blended with fullerene bisadduct derivatives give an even higher $V_{oc}$, but also a strong decrease in short-circuit current ($J_{sc}$). The higher $V_{oc}$ is attributed to the higher LUMO of the acceptors in comparison to PCBM. By investigating the photophysics of PF10TBT:fullerene blends using near-IR photo- and electroluminescence, time-resolved photoluminescence, and photoinduced absorption we find that the charge transfer (CT) state is not formed efficiently when using fullerene bisadducts. Hence, engineering acceptor materials with a LUMO level that is as high as possible can increase $V_{oc}$, but will only provide a higher power conversion efficiency, when the quantum efficiency for charge transfer is preserved. To quantify this, we determine the CT energy ($E_{CT}$) and optical band gap ($E_g$), defined as the lowest first singlet state energy $E_{S1}$ of either the donor or acceptor, for each of the blends and find a clear correlation between the free energy for photoinduced electron transfer and $J_{sc}$. We find that $E_g - qV_{oc} > 0.6$ eV is a simple, but general criterion for efficient charge generation in donor-acceptor blends.

This work has been published:
2.1 Introduction

Polymer solar cells will contribute to future renewable energy production when high efficiencies can be combined with low-cost large-area production and long lifetimes. The most efficient polymer solar cells to date use an active layer that consists of a bulk heterojunction in which electron donor and electron acceptor materials are mixed on a nanometer scale. In recent years, a myriad of semiconducting donor polymers has been developed that have provided polymer solar cells with power-conversion efficiencies (PCEs) exceeding 9% in single and tandem junctions.\[1−6\] Virtually all polymer solar cells employ a fullerene derivative, [6,6]-phenyl-C$_{61}$-butyric acid methyl (PC$_{61}$BM) or its C$_{70}$ analogue (PC$_{71}$BM), as the electron acceptor.

To further enhance the performance of polymer solar cells, judicious design of new materials in terms of frontier energy levels, charge-carrier mobility, and morphology is becoming increasingly important. For this purpose, design rules are required. It is by now well established that the maximum open-circuit voltage ($V_{oc}$) delivered by bulk heterojunction polymer:fullerene solar cells is determined by the difference between the energy of the lowest unoccupied molecular orbital (LUMO) of the electron acceptor and the energy of the highest occupied molecular orbital (HOMO) of the electron donor.\[7-9\] Hence, a strategy to increase power-conversion efficiency is to engineer acceptors with a LUMO energy that is as high as possible, since this would result in higher a $V_{oc}$. This approach has been successfully applied to solar cells containing poly(3-hexylthiophene) (P3HT) as electron donor by using fullerene bisadducts as acceptors.\[10-13\]

In a HOMO-LUMO band diagram the intuitive limit of raising the acceptor LUMO level would be the case where the difference between the LUMO levels and HOMO levels of the donor and acceptor would become less than the exciton binding energy on donor or acceptor, which for many organic materials would be typically around 0.4 eV. However, this design criterion is oversimplified: increasing the acceptor LUMO also increases the donor-acceptor HOMO-LUMO offset that in turn determines the energy ($E_{CT}$) of the charge transfer (CT) state that should be formed in the photoinduced electron transfer reaction between electron donor and acceptor.\[9,14\] The CT state has an important role in organic solar cells because it is a precursor state in forming free charges. Energetically, the CT state must be below the singlet exciton ($S_1$) energies ($E_{S1}$) of both the donor and the acceptor to be formed in appreciable yield under illumination. By increasing the donor-acceptor HOMO-LUMO offset, the $E_{CT}$ will eventually be above the $E_{S1}$ states, inhibiting charge formation. $E_{CT}$ has been identified in various donor-acceptor blends via photoluminescence (PL), electroluminescence (EL), photothermal-deflection absorption spectroscopy, and by
Simultaneous open-circuit voltage enhancement and short-circuit current loss... measuring the wavelength dependence of the photocurrent. From these studies, it has become clear that $V_{oc}$ and $E_{CT}$ are directly related.

To investigate the limits of increasing the $V_{oc}$ versus efficiency of charge formation, we consider polymer solar cells based on poly[2,7-(9,9-didecylfluorene)-alt-5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)] (PF10TBT) (Figure 2.1). PF10TBT is a copolymer with a wide band gap ($E_g = 1.95$ eV) that, combined with PCBM, gives a PCE of 4.2% and a high $V_{oc}$ of 1 V under 1 sun illumination. Optimized PF10TBT:PCBM solar cells have an internal quantum efficiency (IQE) of 75%. We investigate PF10TBT blended with PCBM and fullerene derivatives having higher LUMO energies, namely bis-PCBMs and indene-C$_{60}$-bisadduct (ICBA) (Figure 2.1). For bis-PCBM the LUMO is about 100 mV higher than that of PCBM and for ICBA the increase is about 190 mV. Bis-PCBM, like all fullerene bisadducts, is commonly obtained as a mixture of regio- and stereoisomers and in this study we compare three samples of bis-PCBM that differ in the number of isomers. We blend these different fullerene derivatives with PF10TBT to gain information on the efficiency of charge transfer relative to the free energy for photoinduced charge transfer by means of steady state near-IR PL and EL, time-resolved PL, and photoinduced absorption (PIA) spectroscopy, and compare the results with the performance of the PF10TBT:fullerene solar cells. The similarity in chemical structure between the various acceptors allows us to establish a clear correlation between photogenerated current and energy of the $S_1$ and CT states. When using the optical band gap ($E_g$), defined as the lowest first singlet state energy $E_{S1}$ of either the donor or acceptor, as a measure for the lowest optically accessible state, we find that for an $E_g - E_{CT}$ energy difference of less than +100 meV, CT-state formation and generation of free charge carriers are significantly reduced.

### 2.2 Results and Discussion

#### 2.2.1 Materials

In this study we compare PCBM, bis-PCBM, and ICBA (Figure 2.1). HPLC analysis shows that synthesized bis-PCBM consists of at least 15 different isomers out of the 22 possible regio- and stereoisomers. A smaller selection of isomers is the mixture $t_2$-bis-PCBM that was synthesized using a ethylene tether between the 4-phenylbutyric acid moieties to control their mutual position on the fullerene. After transesterification with methanol, $t_2$-bis-PCBM was found to contain 7 different isomers. Finally, a small sample of a single isomer, $s_i$-bis-PCBM, was obtained by...
separation from the standard bis-PCBM isomer mixture using preparative HPLC.\textsuperscript{[21]} Compared to PCBM the reduction potentials of the bis-PCBM\textsubscript{s} and ICBA are more negative and, hence, their higher LUMO levels are expected to increase the $V_{oc}$ of the solar cell. The reduction potentials vs. Fc/Fc$^+$ are collected in Table 2.1.

![PF10TBT](image1)

\textbf{Figure 2.1: Structure of PF10TBT and the fullerene derivatives used. For bis-PCBM three different regio- and stereoisomer mixtures ($t_2$-bis-PCBM, bis-PCBM, and si-bis-PCBM) were used (see text).}

\subsection*{2.2.2 Solar cells}

The $J$--$V$ curves of the solar cells made from the five different PF10TBT:fullerene blends in 1:4 weight ratio with ITO/PEDOT:PSS and LiF/Al electrodes are shown in Figure 2.2 and the device parameters are summarized in Table 2.1. For PF10TBT:PCBM, a PCE of 4.1\% was obtained, which is close to optimal for this system.\textsuperscript{[18]} The $V_{oc}$ of 1.005 V for the PF10TBT:PCBM cell is high. Interestingly, Figure 2.2 shows that $V_{oc}$ can be further increased by using bis-PCBM or ICBA. The highest $V_{oc}$ of 1.173 V was obtained for PF10TBT:ICBA, \textit{i.e.} for the bulk heterojunction incorporating the acceptor with the highest LUMO level. As can be seen in Figure 2.2, the increase in $V_{oc}$ for the PF10TBT cells based on the fullerene bisadducts is accompanied by a dramatic decrease of the short-circuit current density ($J_{sc}$) and, hence, a strong decrease in PCE. We note that for all samples the increase in
current density under illumination going from 0 to −2 V is very similar. This indicates that the loss in current is not primarily due to stronger field dependence in charge generation or transport in this bias regime. Further the intrinsic electron mobilities of bis-PCBM and ICBA are not limiting the performance of their cells with PF10TBT either, as very efficient operation of these derivatives was reported with P3HT.\textsuperscript{[10,12]}

To investigate if morphology differences of the PF10TBT:fullerene blends can rationalize the observed differences in current density, we studied the phase separation in the photoactive blends with bright-field transmission electron microscopy (TEM). Figure 2.3 illustrates that the morphology of all layers is very similar. The darker areas in the TEM correspond to fullerene rich areas and suggest that fullerene domains of 50-100 nm are present for PF10TBT:PCBM and the PF10TBT:bis-PCBM. The morphologies of the blends of PF10TBT with PCBM and three bis-PCBM blends are virtually indistinguishable (Figure 2.3). From this we conclude that differences in morphology are unlikely the main cause of the differences in performance of the solar cells. Only for PF10TBT:ICBA the fullerene domains appear to be larger (100-150 nm). Although we have no detailed information on the composition of the darker domains, we consider it unlikely that these are pure in fullerene.

Because the differences in morphology are relative small, we consider that factors such as exciton migration to the donor-acceptor interface and percolation of photogenerated charges to the electrodes are unlikely to be strongly different for the blends.
Figure 2.2: Current density – voltage (J−V) characteristics of solar cells based on PF10TBT as electron donor blended with the different fullerene acceptors (see legend). The PF10TBT:fullerene weight ratio is 1:4 for all cells.

Table 2.1: Characteristics of PF10TBT:fullerene solar cells

<table>
<thead>
<tr>
<th>Fullerene</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (A/m$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>$E_{red}^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBM</td>
<td>1.005</td>
<td>68.6</td>
<td>0.60</td>
<td>4.14</td>
<td>-1.09</td>
</tr>
<tr>
<td>t$_2$-bis-PCBM</td>
<td>1.114</td>
<td>29.6</td>
<td>0.46</td>
<td>1.51</td>
<td>-1.18</td>
</tr>
<tr>
<td>bis-PCBM</td>
<td>1.127</td>
<td>25.3</td>
<td>0.45</td>
<td>1.27</td>
<td>-1.19</td>
</tr>
<tr>
<td>si-bis-PCBM</td>
<td>1.163</td>
<td>20.3</td>
<td>0.47</td>
<td>1.11</td>
<td>-1.15</td>
</tr>
<tr>
<td>ICBA</td>
<td>1.173</td>
<td>4.0</td>
<td>0.42</td>
<td>0.20</td>
<td>-1.28</td>
</tr>
</tbody>
</table>

$^a$ Reduction potential vs. Fc/Fc$^+$
Simultaneous open-circuit voltage enhancement and short-circuit current loss…

Figure 2.3: Bright field TEM images of layers containing PF10TBT mixed with (a) PCBM, (b) t₂-bis-PCBM, (c) bis-PCBM, (d) si-bis-PCBM, and (e) ICBA. The bar represents 0.2 µm.

2.2.3 Steady state near-IR luminescence

A possible reason for the decrease in photocurrent for PF10TBT:bis-PCBM and PF10TBT:ICBA is a reduction of the quantum yield of formation of the CT state under illumination. For PF10TBT:PCBM, a clear signature of formation of the CT state is the detectable CT luminescence in which the CT state recombines radiatively to the ground state.\textsuperscript{15,22} We use this property to investigate the charge transfer step in all the blends under study.

Figure 2.4a shows the normalized PL spectra of a pristine PF10TBT film (green line), of PCBM in toluene solution (blue line), and of a PF10TBT:PCBM blend (black line). The films were excited using 2.21 eV photons, exciting both the polymer and the fullerene. The PL of pristine PF10TBT is characterized by a spectrum peaked at 1.79 eV. PCBM has a PL spectrum with two vibronically coupled peaks at 1.75 and 1.58 eV. When PF10TBT and PCBM are blended, the polymer luminescence is quenched by a factor of \(~10^3\). The remaining PL is completely different from the emission of the single compounds and is characterized by a broad spectrum, peaked at
1.52 eV, that can be attributed to CT emission. The PL spectrum of the blend shows a small residual, blue-shifted, fluorescence of PF10TBT at ~1.9 eV.

Figure 2.4b shows the results of the same experiments using PF10TBT:t$_2$-bis-PCBM. The PL of the blend film has two peaks respectively at 1.65 and 1.50 eV, with a spectral shape and position that is very similar to the emission of the acceptor t$_2$-bis-PCBM in toluene. For blends of PF10TBT with bis-PCBM, si-bis-PCBM, or ICBA, photoluminescence spectra with a band shape very similar to PF10TBT:t$_2$-bis-PCBM are obtained (Figures 2.4c-e). For none of the PF10TBT:fullerene bisadduct films CT luminescence is clearly distinguishable. For the PF10TBT blends with fullerene bisadducts, we attribute the PL to fluorescence from the S$_1$ excited state of the fullerene acceptor. In the series t$_2$-bis-PCBMs, bis-PCBM, si-bis-PCBM, and ICBA the relative amount of residual polymer fluorescence increases, with the intensity rising from $\sim 10^{-3}$ to $\sim 10^{-2}$ relative to fluorescence of pristine PF10TBT.

These observations suggest that only the blend containing PCBM has an efficient photoinduced charge transfer between PF10TBT and the polymer, whereas with the other acceptors the charge-transfer efficiency is significantly reduced. By raising the LUMO of the fullerene, the CT state energy increases and approaches the fullerene S$_1$ energy, reducing the overall exciton dissociation efficiency and creating exergonic pathways for charge recombination of holes in PF10TBT and electrons in the fullerene, to form the fullerene S$_1$ state. Similar results were recently shown in literature.$^{[23]}$ Of course we cannot rule out that the CT is formed initially, but that (back) electron transfer from CT state to pure fullerene bisadduct excited state is fast as compared to dissociation of the CT state into free charge carriers.

To study the energy difference between CT and fullerene S$_1$ states in more detail, we recorded electroluminescence of the PF10TBT:fullerene blends sandwiched between ITO/PEDOT:PSS and LiF/Al electrodes. Because of lack of material it was not possible to fabricate PF10TBT:si-bis-PCBM additional devices for this experiment. Figure 2.5 shows the dark $J$–$V$ and light output–$V$ characteristics for four PF10TBT:fullerene blends. The onset of light emission at ~1.2 V roughly matches with a sharp rise in dark current density (0.9-1.1 V). For pure PF10TBT layers, the onset of current and light output occurs at higher potentials (~1.8 V).$^{[22]}$ The voltage at which the dark current density increases, scales with the $V_{oc}$ of the cells and hence corresponds to injection of holes in the HOMO of PF10TBT and of electrons in the LUMO of the fullerene. Recombination of holes and electrons at the PF10TBT-fullerene interface is therefore expected to form primarily, and certainly initially, the CT state.
Figures 2.4a-e show the normalized electroluminescence (EL) spectra recorded at forward bias (+3 V) (red lines). In each case, the EL spectrum closely matches the PL spectrum. With PCBM, luminescence from the PF10TBT:PCBM CT state is indeed observed (redshifted compared to the PL). This suggests that the CT state has the lowest energy among all excited states in that blend. For all bisadducts, however, the EL spectrum of the blends is dominated by fullerene bisadduct emission. Apparently, electron-hole recombination does not give rise to CT emission, but rather emission from the fullerene singlet $S_1$ state, which has been rapidly formed from the initial CT state. The small differences observed between the EL and the PL spectra in Figure 2.4 can be due to the different way the states are populated compared to the PL and to different out-coupling of light.
Figure 2.4: Comparison between the photoluminescence (PL) spectra of thin films (black lines) and electroluminescence (EL) spectra (3 V forward bias) of solar cells (red lines) of blends of PF10TBT with different fullerene acceptors (see legends). In each panel the PL of the fullerene acceptor in toluene solution is shown (blue lines). Thin films were excited at $E_{\text{exc}} = 2.21$ eV, solutions at $E_{\text{exc}} = 2.38$ eV. For si-bis-PCBM the EL spectrum could not be recorded because of lack of material. Panel (a) also shows the photoluminescence spectrum of a pristine PF10TBT film (green line).
Simultaneous open-circuit voltage enhancement and short-circuit current loss…

Figure 2.5: Semi-logarithmic plot of the dark J–V characteristics of PF10TBT:fullerene devices (open symbols) and the electroluminescence (EL) intensities (closed symbols) under forward bias obtained by integrating over the emission spectrum.

2.2.4 Time-resolved photoluminescence

To further investigate the differences in the photophysics of the blends, we performed time-resolved PL experiments that may reveal individual contributions from PF10TBT and PCBM S\textsubscript{1} states and their CT state via different lifetimes. Figure 2.6 shows the decay traces of the PL from a PF10TBT pristine film and from PF10TBT:fullerene blends, using 3.06 eV as excitation photon energy. The instrument response function (IRF) is also plotted. The emission was recorded at 1.97 eV, where the steady-state spectra show some polymer residual fluorescence in the blends (Figure 2.4). The PL decay of the pristine PF10TBT film is characterized by a distribution of lifetimes.

In the PF10TBT:fullerene blends the fluorescence from the polymer is significantly quenched. The fluorescence decay generally occurs on a very fast time scale, close to the IRF, which precludes a quantitative analysis. Only for the PF10TBT:ICBA blend we find a decay that is slower than the IRF and contains a long-lived component that resembles the decay observed in the PF10TBT pristine film. This indicates that in PF10TBT:ICBA blends, some excitations on the polymer
are not quenched. Likely, this is a consequence of a somewhat stronger phase separation (Figure 2.3).

Figure 2.7 depicts the PL decay traces of the PF10TBT:fullerene blends with excitation at 3.06 eV and detection at 1.65 eV and compares these with the decay traces of pristine fullerene films at the same photon energies. At 1.65 eV emission from both the fullerene $S_1$ state and the CT state can be expected. The traces were fitted to multi-exponential functions and the parameters extracted from the fits are summarized in Table 2.2. The pristine fullerenes show single exponential fluorescence decays in thin films with lifetimes between 0.77 and 1.52 ns.

Blending PCBM with PF10TBT changes the dynamics of the fluorescence completely (Figure 2.7a). The blend shows a three-component decay: a fast component (80 ps, in the order of the instrument time resolution), a second one of 0.5 ns and a relatively long-lived third one (3 ns). The first component is assignable to residual polymer fluorescence, consistent with the emission observed at 1.97 eV (Figure 2.6). The two latter components are assignable to the $S_1$ decay of PCBM and the CT-state decay.[15,22]

The $t_2$-bis-PCBM and bis-PCBM acceptors show a different behavior, with fluorescence decays that do not change as strongly as for PCBM when going from the pristine film to the blend. This is not unexpected because the steady state PL spectra are dominated by fullerene fluorescence. Again, three components appear: a first one below the instrument response time (< 80 ps), a second one between 1 and 1.5 ns, and a longer lived one above 3 ns. As with PCBM, the first short component is coming from some residual polymer fluorescence, but in these cases its lifetime weighted fractional intensity ($\alpha < \sim 0.1$) is lower than for PCBM ($\alpha \sim 0.2$). An exception is the blend containing si-bis-PCBM, where the first fast component has $\alpha \sim 0.25$, comparable with to the PF10TBT:PCBM blend. The second component, however, is similar in all the cases to the pristine films lifetimes (1 - 1.5 ns) and we assign it to the decay of the fluorescence from the acceptors. The third longer component is in the same range (3 ns) as the one observed in PF10TBT:PCBM and we interpret it to originate from CT emission.

The time-resolved PL of the pristine ICBA acceptor and the PF10TBT:ICBA film show the strongest resemblance. Also in this case the curve was best fitted with a three-exponential decay, which resulted in a fast component (50 ps) having a very small $\alpha$ and two longer components, respectively 0.88 and 1.78 ns, that we can attribute to the decay of fluorescence from the acceptor itself (1.09 ns mono-exponential in the pristine film). The 3 ns long-lived decay time associated with CT emission and observed in all other blends is not present in this case.
The time-resolved PL results show that some long-lived CT emission occurs in the blends of PF10TBT with the three bis-PCBM isomer mixtures, but less compared to PCBM. Likely, also in the steady state PL spectra, emission from the CT state is present, but buried under the emission of the acceptors. For PF10TBT:ICBA, instead, there is no evidence for charge transfer from either steady state or time-resolved PL.

Figure 2.6: Time-resolved photoluminescence of PF10TBT in pristine film and in PF10TBT:fullerene films recorded for $E_{em} = 1.97$ eV with $E_{exc} = 3.06$ eV at room temperature. The instrument response function (IRF) is shown. The emission of pristine PF10TBT can be fitted with a three-exponential curve with lifetimes $\tau = 0.3$, 0.8, and 1.6 ns, accounting for 25%, 50%, and 25% of the emission, respectively.
Figure 2.7: Time-resolved photoluminescence of fullerenes in pristine films (black lines) (a) PCBM, (b) $t_2$-bis-PCBM, (c) bis-PCBM, (d) si-bis-PCBM, and (e) ICBA compared to the photoluminescence of the same fullerene acceptors when blended with PF10TBT (gray lines). Spectra were recorded for $E_{\text{em}} = 1.65$ eV with $E_{\text{exc}} = 3.06$ eV at room temperature.
Table 2.2: *Fit parameters of the time-resolved PL decay traces.*

<table>
<thead>
<tr>
<th></th>
<th>$\tau_1$ (ns)</th>
<th>$\alpha_1^b$</th>
<th>$\tau_2$ (ns)</th>
<th>$\alpha_2^b$</th>
<th>$\tau_3$ (ns)</th>
<th>$\alpha_3^b$</th>
<th>$\chi^2$</th>
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<td>0.726</td>
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<td>3.32</td>
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<td>PF10TBT: si-bis-PCBM</td>
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<td>0.593</td>
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<td>0.617</td>
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<td>PF10TBT: ICBA</td>
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<td>0.072</td>
<td>0.88</td>
<td>0.650</td>
<td>1.78</td>
<td>0.278</td>
<td>0.447</td>
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*a* Recorded at $E_{em} = 1.65$ eV with $E_{exc} = 3.06$ eV. $b\alpha_i$ is the lifetime weighted fractional intensity of each component of the multi-exponential fit.

### 2.2.5 Photoinduced absorption

Photoinduced absorption (PIA) spectroscopy can be used to probe the formation of free charges or excited states and provide additional information on the photophysical processes occurring in the blends. We recorded PIA spectra for films of pristine PF10TBT and mixed PF10TBT:fullerene blends at room temperature and 80 K (Figure 2.8). The PIA spectrum of the pristine PF10TBT film at room temperature shows a broad band between 1.0 and 1.8 eV with a broad maximum centered at 1.5 eV (Figure 2.8a). This band is attributed to the $T_n \leftarrow T_1$ transition of PF10TBT, where $T_1$ is the lowest triplet state in the polymer.\textsuperscript{[22,24]} When PF10TBT is blended with PCBM, the PIA spectrum exhibits two new bands at 1.25 and at ~0.5 eV. These two bands are comparable in intensity and are a signature of long-lived charges on PF10TBT.\textsuperscript{[22,25]}
At 80 K, the spectrum of pure PF10TBT (Figure 2.8b) has increased in intensity because the lifetime of the T$_1$ state has increased. For the PF10TBT:PCBM blend, the PIA spectrum is now dominated by a strong T$_n$←T$_1$ transition, although the signal at ~0.5 eV of charges remains clearly visible. In the near-steady state PIA technique, the signal intensity is proportional to the lifetime (as one probes a steady state concentration) and the increase of the T$_n$←T$_1$ transition for pristine PF10TBT is due to a longer lifetime.$^{[22]}$ The fact that the T$_1$ signal intensity in the PF10TBT:PCBM blend is about twice that of the pristine film, indicates that recombination of (some) CT states into the PF10TBT T$_1$ state occurs at the interface. The recombination to the triplet state is consistent with triplet state energy of PF10TBT of ~1.4 eV$^{[22]}$ being less than that of the CT state (1.48 eV, Table 2.3). Charge recombination to the triplet state represents an additional loss mechanism, and has been indentified in various material combinations.$^{[26-30]}$

For the three bis-PCBM samples, the PIA spectra of blends with PF10TBT are virtually identical to that of PF10TBT:PCBM. The triplet signal is between 20 and 30 times higher than at room temperature and in all cases it is stronger than in the pristine PF10TBT film. This shows that also with bis-PCBM's recombination of the CT state to the PF10TBT T$_1$ state competes with dissociation in long-lived charge carriers. In contrast, the PF10TBT:ICBA blend shows almost no signatures from charges at ~0.5 eV, consistent with very limited photocurrent extracted from the devices and in agreement with the luminescence experiments.

The triplets observed in the PIA spectrum of PF10TBT:ICBA likely originate via triplet energy transfer from the triplet state of ICBA, formed via intersystem crossing from the singlet state. The same process likely also occurs in the blends containing the different bis-PCBM isomeric mixtures, where the singlet state of the acceptor is not completely depopulated by charge transfer.
Figure 2.8: Near steady state PIA spectra of pristine PF10TBT and mixed PF10TBT:fullerene films (see legend). (a) Recorded at 290 K. (b) Recorded at 80 K. Excitation at $E_{exc} = 2.41$ eV.

2.2.6 Energy of the CT and $S_1$ states in PF10TBT:fullerene blends

To explain the increase in $V_{oc}$ and the concomitant loss in $J_{sc}$, and to rationalize the outcome of the photophysical experiments, it is useful to consider the energetics of the PF10TBT:fullerene blends in more detail. We will follow the approach of
Veldman et al., who developed an empirical relation to estimate the CT energy at room temperature: \[ E_{\text{CT}} = qV_{\text{oc}} + 0.47 \text{ eV}, \] (1)
in which \( V_{\text{oc}} \) is the value at room temperature and 1 sun illumination and \( q \) the elementary charge. Relations similar to Eq. (1) have been described by Vandewal et al.\[9,16\]

Table 2.3 summarizes the \( E_g \) and CT \((E_{\text{CT}})\) energies of the blends containing PF10TBT and the different fullerene acceptors, estimated using Eq. (1). We note that in each case \( E_g \) equals \( E_{S1} \) of the acceptor. Table 2.3 reveals that while the \( S_1 \) energy of the different fullerene derivatives is almost invariant around 1.65 eV and significantly less than that of PF10TBT at 1.95 eV, the CT energy increases from PCBM, via the bis-PCBMs, to ICBA. The rise in CT energy is a consequence of the more negative reduction potential and, hence, higher LUMO energy of the higher adducts. As a consequence of these effects, the free energy for photoinduced electron transfer (\( \Delta G_{\text{CT}} \)), approximated as \( \Delta G_{\text{CT}} = E_{\text{CT}} - E_g \), decreases from about \(-0.2\) eV for PF10TBT:PCBM, via \(-0.1\) eV for the three bis-PCBM blends with PF10TBT, to almost \(0\) eV for PFT10TBT:ICBA (Table 2.3). The increase of \( \Delta G_{\text{CT}} \) eventually inhibits the photoinduced electron transfer between PF10TBT and the fullerene bisadducts and explains the loss in \( J_{\text{sc}} \). It is remarkable to see that the trend in \( \Delta G_{\text{CT}} \) accurately follows the trend in \( J_{\text{sc}} \) for all five acceptors. The Jablonski diagrams in Figure 2.9 summarize the transitions taking place in the blends containing the different acceptors after photoexcitation.

Interestingly, the present results are in accurate agreement with the empirical predictions previously made by Veldman et al. based on the study of a broad range of donor-acceptor blends, where photoinduced charge transfer was found to be efficient when \( \Delta G_{\text{CT}} = E_{\text{CT}} - E_g < -0.1 \)\[14\] Vandewal et al. recently described a similar result.\[31\] This energetic estimate also explains the observations made in photoluminescence and electroluminescence. CT emission was clearly identified for PF10TBT:PCBM, but was less evident for the three PF10TBT:bis-PCBM blends, and virtually absent for PF10TBT:ICBA. The fact that the electroluminescence spectra of the PF10TBT:fullerene bisadduct blends mainly show fullerene emission, evidences that a CT state, initially formed by capturing an electron and hole at the PF10TBT:fullerene bisadduct interface, can populate the fullerene bisadduct \( S_1 \) state, which emits radiatively or intersystem crosses to its \( T_1 \) state.

Finally, we note that the offset \( E_g - E_{\text{CT}} \) follows the same trend as the short-circuit currents observed in the devices and of the charge transfer efficiency as suggested by the time resolved PL measurements. This correlation indicates the
importance of the population of bound CT states as a first step in the generation of free charges in these blends.

Table 2.3: Open-circuit voltage and CT state energies of PF10TBT:fullerene blends.

<table>
<thead>
<tr>
<th>Fullerene</th>
<th>$V_{oc}$ (V)</th>
<th>$E_{CT}$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$E_g - E_{CT}$ (eV)</th>
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<tr>
<td>PCBM</td>
<td>1.005</td>
<td>1.48</td>
<td>1.66</td>
<td>0.18</td>
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<tr>
<td>t$_2$-bis-PCBM</td>
<td>1.114</td>
<td>1.58</td>
<td>1.66</td>
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<td>bis-PCBM</td>
<td>1.127</td>
<td>1.60</td>
<td>1.65</td>
<td>0.05</td>
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<tr>
<td>si-bis-PCBM</td>
<td>1.163</td>
<td>1.63</td>
<td>1.66</td>
<td>0.03</td>
</tr>
<tr>
<td>ICBA</td>
<td>1.173</td>
<td>1.64</td>
<td>1.63</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

$^a$ From Eq. (1), $^b$ $E_g$ in the blend.

Figure 2.9: Jablonski diagram of the transitions that occur after photoexcitation in the PF10TBT:fullerene blends for (a) PCBM, (b) bis-PCBM isomeric mixtures, and (c) ICBA. Note that the CT energy rises from (a) to (c). Solid lines represent dominant processes, dashed lines represent minor processes.
2.3 Conclusions

When PF10TBT is blended with C_{60} bisadducts (bis-PCBM in three different isomeric selections and ICBA) in bulk heterojunction solar cells the open-circuit voltage ($V_{oc}$) is increased compared to PCBM as electron acceptor. A simultaneous dramatic loss in short-circuit current ($J_{sc}$), however, results in a reduced power-conversion efficiency. By using photoluminescence and photoinduced absorption spectroscopy, we have identified that the principal reason for the loss in $J_{sc}$ is the fact that photoinduced charge transfer becomes increasingly more impeded when going from PCBM, via the bis-PCBMs, to ICBA. Electroluminescence experiments revealed that the $S_1$ states of bis-PCBM and ICBA can be formed subsequent to electron-hole recombination at the PF10TBT-bisfullerene interface.

We have found a clear correlation between the efficiency of charge transfer and the free energy for photoinduced charge generation $\Delta G_{CT} = E_{CT} - E_g$, where $E_g$ is the lowest optical band gap among donor and acceptor. In fact, in our experiments $\Delta G_{CT}$ correlates with $J_{sc}$. Triplet formation is an additional loss channel for all PF10TBT:fullerene blends. PF10TBT $T_1$ states can be formed from the CT state by charge recombination as observed in PF10TBT:PCBM or via intersystem crossing ($S_1 \rightarrow T_1$) of the fullerene $S_1$ state and subsequent triplet energy transfer to PF10TBT, which prevails in the PF10TBT:ICBA blend.

In this work we have obtained a clear confirmation of the measure for efficient photoinduced electron transfer in donor-acceptor bulk heterojunctions in terms of the free energy: $\Delta G_{CT} = E_{CT} - E_g < -0.1$. Because $E_{CT}$ directly relates to $V_{oc}$ via Eq. (1) (at 1 sun and room temperature), a very simple general, albeit mainly empirical, criterion for an efficient donor-acceptor blend is: $E_g - qV_{oc} > 0.6$ eV. Any attempt to bring $V_{oc}$ closer to $E_g$ will likely result in a loss of quantum efficiency for photoinduced electron transfer.\[14,23\] To the best of our knowledge, no efficient organic solar cells have been described to date that violate this criterion, giving further credence to the validity of this design criterion. Of course it is important to find ways to lift this limitation, which is mainly governed by the large loss between $E_{CT}$ and $V_{oc}$.\[16\] Suggestions for materials design that achieve high charge separation with less energetic losses have been proposed recently.\[32,33\] These include increasing the dielectric constant of the active layer materials or reducing the energetic disorder to enhance the charge carrier mobilities.
2.4 Experimental section

Materials. PCBM, bis-PCBM, and ICBA were obtained from Solenne BV. The synthesis of PF10TBT \cite{34}, t$_2$-bis-PCBM\cite{19} and si-bis-PCBM\cite{21} have been described previously.

Devices preparation and characterization. Photovoltaic devices were made by spin-coating PEDOT:PSS (Clevios P Al 4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates. The photoactive layer was deposited by spin coating from chlorobenzene solutions. The top electrode consisting of LiF (1 nm) and Al (80 nm) was deposited by vacuum evaporation at 1 × 10$^{-6}$ mbar. Device characterization was performed under N$_2$ atmosphere. Current density-voltage measurements were carried out under illumination of a Steuernagel SolarConstant 1200 metal halide lamp, which was set to 1 sun intensity using a silicon reference cell and correcting for spectral mismatch. A computer-controlled Keithley 2400 was used as source meter.

Microscopy. Transmission electron microscopy was performed on a Tecnai G$^2$ Sphera TEM (FEI) operated at 200 kV. Bright field TEM images were acquired under slight defocusing conditions (see also Ref.17).

Photoluminescence and electroluminescence. Steady state photoluminescence and electroluminescence spectra were recorded at room temperature using an Edinburgh Instruments FLSP920 double-monochromator luminescence spectrometer equipped with a nitrogen-cooled near-IR sensitive photomultiplier (Hamamatsu). All spectra were corrected for the spectral response of the monochromators and photomultiplier. Fullerene solutions were prepared in toluene at 50 µg/mL and measured in 10 mm near-IR grade quartz cells at room temperature, with an optical density ~0.1 at the excitation wavelength. Thin films for PL were prepared by spin coating on quartz substrates using the same condition as for solar cell preparation. Electroluminescence was measured driving the solar cell in forward bias in a sealed box with a quartz window.

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

\[ I(t) = \sum_{i=1}^{n} A_i e^{-t/\tau_i} dt, \]

where $A_i$ is the amplitude of the $i^{th}$ component with a lifetime $\tau_i$. The lifetime weighted fractional amplitude $a_i$ corresponding to the lifetime $\tau_i$ is given by $a_i = \frac{A_i \tau_i}{\sum_i A_i \tau_i}$.

Photoinduced absorption. Near steady-state photoinduced absorption (PIA) spectra were recorded between 0.35 and 2.4 eV by excitation with a mechanically modulated (275 Hz) laser source and by measuring the change in transmission of a tungsten-halogen probe beam through the sample ($\Delta T$) with a phase sensitive lock-in amplifier after dispersion with a monochromator and detection using Si, InGaAs, and cooled InSb detectors. The pump wavelength used was 514 nm (2.41 eV, Ar ion laser) with a pump power of 25 mW and a beam diameter of 2 mm. The PIA signal ($\Delta T/T$) was corrected for the photoluminescence, which was recorded in a separate experiment. All the spectra were corrected for the optical density at the pump wavelength. Thin films were prepared
by spin coating from chlorobenzene solution and samples were held in an inert nitrogen atmosphere using an Oxford Optistat continuous flow cryostat during PIA measurements. Experiments were recorded at 290 and 80 K.

### 2.5 References


Simultaneous open-circuit voltage enhancement and short-circuit current loss...


Improved film morphology reduces charge carrier recombination into the triplet excited state in a small band gap polymer-fullerene photovoltaic cell

Abstract

We study PCPDTBT:PCBM blends with photoinduced absorption (PIA) spectroscopy to unravel charge formation and recombination. PCPDTBT is a small band gap polymer which, in combination with PCBM in solar cells, gives power conversion efficiencies up to 5.5%. We demonstrate that in this blend the charge transfer (CT) state, formed after illumination, has a high tendency to recombine into the triplet state on the PCPDTBT polymer. Energetically this process is favorable because the energy of the CT state (~0.9-1.0 eV) is higher than that of $T_1$ (~0.6-0.8 eV). The same loss mechanism has previously been observed in several polymer:polymer and polymer:fullerene blends. For PCPDTBT:PCBM blends a strong increase in PCE is obtained when high-boiling processing additives are used during layer deposition. We investigated the role of processing additives on the charge recombination process to the PCPDTBT triplet state. In blends processed with diiodooctane that provide a higher PCE in solar cells, the triplet recombination is strongly reduced in favor of charge formation, as evidenced by the clear disappearance and appearance of the corresponding PIA signals. The reason for the improved charge generation is that diiodooctane dramatically increases aggregation and order within the polymer domains. This leads to a high hole mobility, which facilitates charge separation. In addition, changes in morphology induced by the additive may lower the energy of the CT state below that of $T_1$, making the triplet recombination energetically disadvantageous. The lowering of the open-circuit voltage upon treatment with additive provides experimental evidence for this energy shift. The results demonstrate that triplet recombination can play an important role in determining the efficiency of polymer solar cells in cases were charge separation from the donor-acceptor interface is sluggish.

This work has been published:
3.1 Introduction

Detailed studies on the bulk heterojunction (BHJ) involving the small band gap polymer poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b0]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole) (PCPDTBT) and the fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) illustrate the extreme importance of processing conditions when making these junctions from solution.\textsuperscript{[1-5]} The use of processing additives was found to boost the power conversion efficiency by a factor of 2 \textsuperscript{[1,3]} by influencing the morphology of the blend. In principle, the change in morphology can enhance the performance in several ways. The optimized morphology may allow for faster and therefore more efficient transport of photogenerated free charge carriers. In addition, the efficiency for free charge carrier generation out of the primary photoexcitations may be enhanced in the optimized morphology.

In this study we focus on the efficiency of carrier generation and show that for the non-optimized morphology obtained from processing PCPDTBT and PCBM from a solution without additives, the generation of free charge carriers is reduced because of recombination of the photogenerated hole and electron to a long-lived, low lying electronic state with triplet spin signature.\textsuperscript{[6-10]} Using processing additives, the formation of these triplet excitations can be suppressed, favoring the formation of free charge carriers out of the charge transfer (CT) state resulting from the photoinduced electron transfer in the BHJ.

3.2 Results and discussion

In Figure 3.1 we illustrate the influence of the processing additive diiodooctane (DIO) on the performance of a solar cell with PCPDTDBT:PCBM in a 1:2 weight ratio as active layer. As can be seen, use of the additive during film formation leads to substantial increase in short-circuit current $J_{sc}$ and an improvement in fill factor from 0.41 to 0.52. In contrast, the open-circuit voltage $V_{oc}$ decreases from 0.69 to 0.62 V.
Figure 3.1: Current density as a function of bias voltage for PCPDTBT: PCBM (1:2 weight ratio) solar cells made by spin coating from chlorobenzene using diiodooctane as processing with additive (solid markers) and without (open markers). The structure of PCPDTBT is shown in the inset.

The charge generation process in the active layers prepared with and without processing agent was studied using near steady state photoinduced absorption (PIA) spectroscopy. This technique provides a sensitive probe for the long-lived excitations in films. In Figure 3.2a we compare the PIA spectra for the two films on quartz substrate. We notice three striking differences between the two PIA spectra. First, after processing with DIO, the PIA intensity at 0.3 eV is much higher. Second, DIO induces an intense PIA band with a maximum at 0.88 eV, while without DIO, a band with a maximum at 0.95 eV is obtained. Third, the magnitude of the bleaching signal relative to the 0.9 eV absorption band is much higher upon processing with DIO. These differences indicate that the long-lived excitations in the films with and without processing additive are actually different. As will be detailed below, use of the additive during spin coating leads to long-lived photoinduced charges in the film, whereas without additive neutral photoexcitations on the small band gap polymer with triplet spin character are responsible for the PIA.

To support this assignment we have first studied PCPDTBT mixed with PCBM in toluene solution. For this mixture, we observe an intense PIA band at 1.0 eV, but essentially no signal below 0.5 eV (Figure 3.2b). For only PCPDTBT in toluene
solution, we observe the same bandshape, but with a 20 times lower intensity. We assign the 1.0 eV PIA signal to a triplet-triplet absorption originating from the lowest excited triplet state on the polymer ($T_n \leftarrow T_1$). In neat film of PCPDTBT at low temperature we also observe this triplet signal but here the $T_n \leftarrow T_1$ PIA band has shifted slightly to lower photon energies (0.95 eV). We attribute this shift to aggregation effects of the polymer chain and the reduced temperature.

In PIA experiments, this triplet excitation can be distinguished from the charge carrier absorption by looking at signals in the 0.3 eV energy range. Chemical oxidation of the polymer to the corresponding radical cation in solution and in solid film shows that the polaronic, positive charges on the PCPDTBT polymer are characterized by two absorption bands, one at 0.9 eV and one at ~0.3 eV (Figure 3.2c) that are attributed to the dipole allowed $D_1 \leftarrow D_0$ and $D_2 \leftarrow D_0$ transitions of the doublet state radical cation of PCPDTBT. In contrast the lowest triplet excited state shows only one PIA band in the mid infrared. These optical features of the charged and triplet states of PCPDTBT are characteristic for \(\pi\)-conjugated polymers.\[11,12\]

An important parameter determining the outcome of photoinduced processes in donor acceptor blends, is the difference between the energy of the lowest triplet excited state, $E_T$, and that of the charge transfer state, $E_{CT}$. The energy for the triplet state of PCPDTBT, $E_T$, is not known exactly, but can be estimated from the following experiments. In the presence of PCBM, the signal for the $T_1$ state on the polymer in solution is much more intense, while at the same time any $T_n \leftarrow T_1$ absorption from PCBM at 1.73 eV\[13\] is absent (Figure 3.2b). This indicates that the $T_1$ state on the polymer can be populated by transfer of energy from the $T_1$ state of PCBM. The latter is formed efficiently via intersystem crossing from the singlet excited state of the fullerene and has an energy of 1.5 eV. Hence $E_T$ of PCPDTBT must be below 1.5 eV. Additional experiments on triplet-triplet energy transfer in solution showed that energy can be transferred from rubrene ($E_T = 1.14$ eV \[14\]) to the polymer, while transfer of triplet energy occurs from the polymer to bis(trihexylsiloxy)silicon-2,3-naphthalocyanine ($E_T = 0.93$ eV\[15\]). Furthermore, in solution the $T_1$ excited state on the polymer is quenched by molecular oxygen through a process that generates $^1\text{O}_2$ ($E = 0.98$ eV). From this we deduce that for PCPDTBT $E_T \approx 1.0$ eV. Empirically, it has been found that $E_{CT}$ is approx. 0.45-0.47 eV higher than $qV_{oc}$ in polymer fullerene heterojunctions, with $q$ the elementary charge\[8,16\] and hence we estimate $E_{CT} \approx 1.1$ eV for PCPDTBT:PCBM. This estimate correlates well with the observation of the CT emission in PCPDTBT:PCBM blends which maximizes at ~1.20 eV.\[17\] From this we conclude that the triplet excited state is equal or lower in energy than the CT state.
Improved film morphology reduces charge carrier recombination into the triplet…

![Graphical representation of PIA spectra](image)

**Figure 3.2:** (a) PIA spectra of films of PCPDTBT:PCBM (1:2 weight ratio) processed by spin coating from chlorobenzene with (solid squares) and without diiodooctane (open circles). Excitation photon energy $E_{\text{exc}} = 1.49 \text{ eV, } T = 80 \text{ K}$. The inset shows a zoom-in on the low photon energy region of the PIA spectra. (b) PIA spectra of PCPDTBT:PCBM (1:1) (solid triangles) and PCPDTBT (open triangles) in toluene solution, $E_{\text{exc}} = 2.54 \text{ eV, } T = 293 \text{ K}$. PIA spectrum of a pristine PCPDTBT film (solid diamonds). $E_{\text{exc}} = 1.49 \text{ eV, } T = 80 \text{ K}$. (c) Differential absorbance for PCPDTBT induced upon slight oxidation in solution (open squares) with thianthrenium hexafluorophosphate (solid triangles) and in a solid film with chloranil (circles) at $T = 293 \text{ K}$. 

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We now address the question of how the triplet excitations in the films without additive are formed, see also Figure 3.3. Measurements of the photoluminescence from the PCPDTBT polymer in solid film, show a dramatic reduction of the intensity of this signal of more than a hundredfold upon inclusion of PCBM in the films. This implies that the lifetime of the singlet excited state from which the luminescence originates, is reduced at least a hundred times. In consequence, also the yield for formation of the $T_1$ from the $S_1$ state by direct intersystem crossing must be strongly reduced. Combined with the high intensity of the PIA signal in the mixed film, this indicates that the $T_1$ excited state in the blend is populated via recombination of geminate charge carriers in the charge transfer state at the donor acceptor interface.\textsuperscript{[6-10]} In order for this recombination to the $T_1$ state to be an efficient process, the energy of the CT and charge separated states of the polymer:PCBM heterojunction should be positioned above $E_T$. For efficient population of the triplet state from the CT state the energy difference $E_{CT} - E_T$ should be $> 0.1 \text{ eV}$,\textsuperscript{[10]} consistent with the estimates of the energy levels involved. The recombination to the triplet state from the CT level can be spin allowed, provided that the CT level lives sufficiently long for spin dephasing to occur.\textsuperscript{[7]} Formation of triplet excitations is also observed in films of PCPBTBT:[70]PCBM. Incidentally, in previous spectroscopic studies on PCPDTBT:PCBM blends, photoinduced absorption near 1 eV was assigned exclusively to photogenerated charge carriers on PCPDTBT.\textsuperscript{[18-20]} However, it now appears that conclusive evidence on charge carrier dynamics also requires the PIA in the 0.5-0.3 eV range to be probed. This is because both photoinduced charges and triplet photoexcitations contribute to PIA at 1 eV, displaying even a very similar bandshape.
Improved film morphology reduces charge carrier recombination into the triplet...

Figure 3.3: Jablonski diagram illustrating formation of triplet and charge transfer excitations as well as free charges in PCPDTBT:PCBM blends. Important transitions in photoinduced absorption for these excitations are indicated with solid arrows. Dashed arrows represent non-radiative processes.

Finally we discuss the influence of the processing additive on the morphology of the films and relate it to photophysics. Previous studies have shown that the additive induces aggregation of polymer chains into more ordered supramolecular polymer structures prior to complete drying.\cite{2,21} Optical spectroscopy on the $S_1 \leftarrow S_0$ transition of the polymer in our films, fully supports this view (Figure 3.4a). The red shift of the onset of absorption observed, is typical for aggregation of $\pi$-conjugated polymers. Additionally, transmission electron microscopy (TEM) (Figure 3.4b and 3.4c) shows more pronounced contrast in the mixed film when using DIO. In agreement with earlier reports.\cite{2,21} TEM shows that the use of DIO induces formation of fullerene clusters that appear dark in the TEM and of polymer fibrils with a diameter on the order of a few nanometer.\cite{3} These changes indicate phase separation of the two components on a larger length scale into polymer and PCBM domains with higher purity. Such a morphology enhances carrier mobility in each of the subphases. In the Onsager-Braun model for charge generation,\cite{22} the higher mobility allows geminate charge carriers to escape from their mutual attraction more efficiently. At the same time it allows carriers to reach the lower energy levels in their inhomogenously broadened density of states, through rapid diffusional motion. This effectively lowers
the energy of the charge separated states, allowing the CT state to dissociate more efficiently into free carriers. If the effective energy of charge separated states drops below $E_T$, recombination into the triplet state is further suppressed. An experimental indication for the lowering of the energy of the charge transfer states upon using additive is the reduction of $V_{oc}$.

**Figure 3.4:** (a) Absorption spectra of PCPDTBT:PCBM (1:2 weight ratio) thin films prepared by spin coating from chlorobenzene without (open circles) and with (solid squares) diiodooctane. (b) and (c) TEM images of PCPDTBT:PCBM films processed without and with diiodooctane. The white bar represents 100 nm.
3.3 Conclusions

In conclusion, we find that the use of processing additive for deposition of small band gap polymer:fullerene bulk heterojunctions can raise the yield of photoinduced free carrier formation by suppressing the recombination of photogenerated carrier into the lowest triplet excited state of the polymer. This can, at least partly, explain the enhanced energy conversion efficiency induced by the use of processing additives. The results illustrate that for efficient polymer solar cells, the energy of the lowest triplet state of the polymer must be properly adjusted with respect to the energy of the charge transfer and charge separated states. This may be achievable through control over the morphology.
3.4 Experimental section

Device preparation and optoelectronic characterization. Photovoltaic devices were made by spin coating poly(ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP Al4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). The photoactive layer was deposited by spin casting in air at 2000 rpm, using a chlorobenzene solution containing 10 mg/mL PCPDTBT \( (M_n = 27700 \text{ g mol}^{-1}, \text{PDI} 1.9) \), 20 mg/mL \( [6,6]\)-phenyl-C_{61}-butyric acid methyl ester (PCBM) (Selenne) and, optionally, 50 mg/mL of 1,8-diiodooctane (DIO). The metal electrode, consisting of LiF (1 nm) and Al (100 nm), was deposited by vacuum evaporation at \( \sim 3 \times 10^{-7} \text{ mbar} \). The active area of the cells was 0.162 cm\(^2\). J-V characteristics were measured under \( \sim 100 \text{ mW/cm}^2 \) white light from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter, using a Keithley 2400 source meter. The mismatch factor of this lamp to the AM1.5 (100 mW/cm\(^2\)) spectrum was not determined for the PCPDTBT:PCBM devices.

Thin film preparation. Films for PIA were prepared on quartz substrates using the same condition as for solar cell preparation. Film thicknesses were between 60 and 70 nm as measured using profilometry.

Microscopy. Transmission electron microscopy was performed on a Tecnai G\(^2\) Sphera TEM (FEI) operated at 200 kV. Bright field TEM images were acquired under slight defocusing conditions (see also Ref. [21]).

Spectroscopic measurements. Near steady state photoinduced absorption (PIA) spectra were recorded between 0.35 and 2 eV by excitation with a mechanically modulated (275 Hz) laser source and by measuring the change in transmission of a tungsten-halogen probe beam through the sample \( (\Delta T) \) with a phase sensitive lock-in amplifier after dispersion with a monochromator and detection using Si, InGaAs, and cooled InSb detectors. Pump wavelengths used: 488 nm (2.54 eV, Ar\(^+\) laser) or 830 nm (1.49 eV, laser diode). The pump power was typically 50 mW with a beam diameter of 2 mm for the argon laser and 130 mW and 1 mm for the diode laser. The PIA signal \( (\Delta T/T) \) was corrected for the photoluminescence, which was recorded in a separate experiment. Solutions for PIA were prepared in oxygen free toluene at 300 μg/mL in an inert atmosphere (H\(_2\)O, O\(_2\) < 10 ppm). The measurements were carried out in 1 mm near-IR grade quartz cell at room temperature. The maximal optical density was between 2 and 2.5. Thin films samples were held in an inert nitrogen atmosphere using an Oxford Optistat continuous flow cryostat during PIA measurements. Chemical oxidation of the polymer in \( o \)-dichlorobenzene solution was induced using thianthrenium hexafluorophosphate\(^{[23]}\) as oxidizing agent. Partial oxidation in solid film was induced by adding \( \sim 10 \text{ wt.}\% \) of chloranil.
3.5 References

Charge generation and recombination at open-circuit voltage conditions in a small band gap polymer solar cell: influence of the morphology of the bulk heterojunction

Abstract

We investigate charge generation and recombination processes in bulk heterojunction (BHJ) PCPDTBT:PCBM blends at low or zero electric field by means of photo-CELIV on solar cells and near steady state photoinduced absorption (PIA) on thin films. We compare finely and coarser mixed active layer morphologies by including the cosolvent diiodooctane (DIO) in the solution from which the active layer is spin coated. Solar cells processed with DIO show an improved power conversion efficiency compared to the as-cast samples in which no DIO was used, mainly due to improved fill factor (FF). Photo-CELIV measurements show that in the finer BHJ morphology sub-microsecond recombination is more extensive than in the improved morphology. PIA measurements on the corresponding thin films show that nearly all photogenerated charge carriers recombine on a sub-microsecond time scale. Apart from recombination to the ground state, the charge transfer (CT) state in finely mixed blends also recombines to the PCPDTBT triplet state. The improved efficiency of CT dissociation is the main cause for the improved FF of the DIO processed solar cells compared to the as-cast cells. Bimolecular recombination of free charge carriers, remains significant in both morphologies and limits the ultimate performance of the cells.
4.1 Introduction

The power conversion efficiency of organic solar cells is strongly influenced by the nanomorphology of the active layer’s donor-acceptor bulk heterojunction (BHJ). Often the optimization of organic solar cells goes through the optimization of the BHJ morphology. In polymer solar cells the morphology of the BHJ can be controlled via the solvent used in the deposition of the active layer or via thermal annealing steps.\(^1\)\(^-\)\(^4\)

The degree of phase separation between donor and acceptor can in principle impact the efficiency of collection of free charges. The efficiency of free charge collection is limited by the bimolecular charge recombination. Intuitively, increasing the phase separation decreases the extension of donor-acceptor interface area through the bulk, thus reducing the chance for free electrons and holes to meet and recombine via bimolecular processes. It has been argued that the efficiency of charge transfer (CT) state dissociation into free charges might be influenced by the degree of phase separation as well.\(^5\),\(^6\) Both efficiency of CT dissociation and of free charge collection can be field dependent and therefore can affect the shape of the current-voltage (J-V) characteristic, especially at low electric fields close to open-circuit voltage. To predict the J-V characteristic of an organic solar cell one would need to determine the overall rates for CT dissociation and for charge collection at a given applied voltage bias. Figure 4.1 summarizes the competing processes during charge generation.

An intensively studied system is the blend composed by the small band-gap polymer (poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b0]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole) (PCPDTBT) mixed with [6,6]-phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM), acting respectively as electron donor and acceptor (Figure 4.1). It has been shown that the inclusion of the cosolvent diiodooctane (DIO) in the spin coating solution of this blend results in improved power conversion efficiency of the solar cell compared to as-cast devices.\(^7\) The devices processed with DIO show higher fill factor under one sun illumination. The improved performance correlates with an increased degree of phase separation in the bulk heterojunction processed using DIO.\(^8\)

Previous studies have indicated that the coarser morphology results in improved efficiency of free charge generation at the heterojunction\(^9\)\(^-\)\(^12\) However, it has also been shown that in the coarser morphology bimolecular recombination is increased compared to as-cast devices.\(^11\)\(^-\)\(^13\) This may explain the rather low fill factors that are obtained in optimized devices.
Figure 4.1: (Left) Jablonski diagram showing the steps involved in photoinduced charge generation and indicating the possible recombination mechanisms. \( k_{CTT}, k_{CT0} \) and \( k_d \) represent the rate of recombination of the CT state to the triplet and to the ground state and the CT dissociation rate, respectively. \( k_{BR} \) and \( k_{extr} \) represent the rates of bimolecular recombination and of extraction. (Right) Chemical structure of the materials studied.

In Chapter 3 we have used near steady state photoinduced absorption (PIA) spectroscopy to show that in as-cast blend films the CT state recombines to the triplet state of PCPD TBT. In coarser morphologies this recombination is suppressed and a significantly larger amount of longlived photogenerated charges was observed.

Because the formation of triplets is a recombination process and hence a loss mechanism for photovoltaic performance, it may be argued that the improvement of the power conversion efficiencies in optimized blends is, at least in part, due to a reduction of the recombination of photogenerated charge carriers. This efficiency loss mechanism involving formation of triplet excited states has been identified in other systems \cite{14-16} and is an issue involving any system where the open-circuit voltage \( (V_{oc}) \) is maximized. Increasing the \( V_{oc} \) involves maximizing the energy of the CT state to a level just below the lowest excited singlet state energy of D and A \cite{17,18}. Because the exchange energy in \( \pi \)-conjugated materials is substantial, the CT state energy will be above the triplet energy, enabling the triplet formation as an effective recombination pathway.

Being a quasi steady state technique, however, PIA cannot give information on the time scales of free charge formation and recombination. In particular, one cannot
discern between the formation of triplets as recombination of geminate CT pairs or of CT pairs formed in a later stage via bimolecular recombination (Figure 4.1).

In this chapter we investigate charge recombination close to $V_{oc}$ conditions in PCPDTBT:PCBM blends with as-cast and optimized nanoscale morphology using DIO as cosolvent. We use photo-CELIV on complete photovoltaic cells and correlate the results to PIA spectroscopy on bulk heterojunction films that are prepared under identical conditions as the active layer in the solar cells investigated by CELIV.

In photo-CELIV free charges are photogenerated with a laser pulse and extracted with a linear voltage ramp after a variable delay time. We measure the amount of extracted photogenerated charges as function of the delay time. During the delay, a compensating voltage bias is applied to the device in order to minimize the drift of photogenerated charges to the electrode before the extracting ramp is applied. In this way the recombination processes during the delay time take place at $\sim V_{oc}$ conditions. The amount of charges extracted in these conditions is normalized to the amount of charges extracted applying a constant $-2$ V bias to the device under pulsed illumination. In this way we obtain the “fraction of extractable charges” as function of delay time, which depends on the recombination processes occurring in the blend.

We find that in as-cast PCPDTBT:PCBM blends, over $97\%$ of the photogenerated charges recombine within $1 \mu s$ at $V_{oc}$ and at room temperature. In the devices with optimized power conversion efficiency through use of cosolvent, the yield of longlived charges is at least three times higher. This further supports the conjecture that recombination of charges to form triplet excited states can be an efficient loss mechanism that needs to be minimized for optimal device performance. Furthermore, in accordance with previous studies, we find that bimolecular recombination of free photogenerated charges is important in both morphologies.

### 4.2 Results and discussion

#### 4.2.1 Photo-CELIV

Figures 4.2(a,c,e) show the fraction of extractable charges versus delay time between the laser pulse and the voltage ramp in the photo-CELIV experiment on PCPDTBT:PCBM solar cells processed from chlorobenzene without cosolvent, which we refer to as as-cast. In these layers the BHJ morphology is not optimized for high power conversion efficiency. The experiments were performed at three different temperatures: 290, 185, and 80 K. At each temperature the CELIV experiments were
performed using two different fluences: \(2 \times 10^{-5}I_0\) and \(4 \times 10^{-5}I_0\), with \(I_0 = 3.7\) mJ cm\(^{-2}\) per pulse, with photon energy 1.55 eV. Results for solar cells processed with DIO as cosolvent to optimize the BHJ morphology are shown in Figures 4.2(b,d,f).

In Figure 4.2a the fraction of extractable charges \(f_{\text{as-cast}}\) at 290 K for a PCPDTBT:PCBM solar cell with the active layer spin coated from chlorobenzene is shown. Using a pulse fluence of \(4 \times 10^{-5}I_0\), the fraction of extractable charges \(f_{\text{as-cast}}\) after 1 µs from the laser pulse amounts to 0.03, corresponding to a density of charges \(n_{\text{avg}}\) of \((2.90 \pm 0.63) \times 10^{14}\) cm\(^{-3}\). The signal rapidly decays and becomes undetectable around 100 µs delay. The fraction of extractable charges is very low compared to P3HT:PCBM blends, for which we observed fractions as high as 0.4 (Chapter 6).

The inset in Figure 4.2a shows the average density of extracted charges \(n_{\text{avg}}\) at constant applied bias of 0 V as function of the pulse fluence. The pulse fluences used in the photo-CELIV experiments are indicated in the graph and fall in the range where \(n_{\text{avg}}\) increases linearly. With this choice of the pulse fluence we excluded the influence of non-linear processes on the photogenerated charge dynamics that can appear at high excitation densities. The same linearity check was performed at every temperature and for both as-cast and DIO processed cells.

Processing the PCPDTBT:PCBM layer using DIO as cosolvent, we find an improvement in the solar cell \(J-V\) characteristic under white light illumination of 100 mW/cm\(^2\) compared to the as-cast blend. The fill factor \(FF = 0.45\) and short-circuit current \(J_{\text{sc}} = 8.4\) mA/cm\(^2\) are both higher than those of the as-cast layer for which \(FF = 0.33\) and \(J_{\text{sc}} = 6.5\) mA/cm\(^2\). Subjecting the improved cells to the photo-CELIV measurement with a laser pulse fluence of \(4 \times 10^{-5}I_0\), we find that the fraction of charges extractable after a 1µs delay time equals \(f_{\text{DIO}} = 0.11\) at 290 K (Figure 4.2b). This is almost 4 times higher than in the as-cast sample. In this case the corresponding density of extracted charges is \((1.06 \pm 0.17) \times 10^{15}\) charges/cm\(^3\), that is 3.7 times higher than in the as-cast sample, resulting in a higher signal to noise ratio compared to the as-cast sample. For this sample the decay of the fraction could be followed in time. After 10 µs that fraction has reduced to 0.01, which is close to the detection limit of the current setup.

Figures 4.2(c,e) show the fraction of extractable charges for as-cast cells \((f_{\text{as-cast}})\) at 185 and 80 K. \(f_{\text{as-cast}}\) increases with decreasing temperature and the decay slows down. At 80 K and at 1 µs \(f_{\text{as-cast}}\) reaches 0.05, with \(n_{\text{avg}} = 2.50 \pm 0.24 \times 10^{14}\) cm\(^{-3}\). Figures 4.2(d,f) show the fractions for DIO processed cells at 185 and 80 K. Also \(f_{\text{DIO}}\) increases with decreasing temperature and the decay becomes slower. Using a fluence of \(4 \times 10^{-5}I_0\), a value of 0.19 for \(f_{\text{DIO}}\) at 1 µs is reached, which is ~4 times higher than \(f_{\text{as-cast}}\) (1 µs) at 80 K at the same pulse fluence. The corresponding density \(n_{\text{avg}}\) of
extracted charges is \((6.64 \pm 0.43) \times 10^{14} \text{ cm}^{-3}\). We note that at 80 K the charges were too slow to be all extracted during the 12.5 \(\mu\text{s}\) voltage ramp for both as-cast and DIO films, resulting in measured \(f\) being less than the total fraction of extractable charges. The same problem was encountered at 185 K, but less than at 80 K.

Figure 4.2a reveals that the values of \(f_{\text{as-cast}}\) at each delay time do not change when the laser pulse fluence is decreased to \(2 \times 10^{-5}I_0\). This indicates that, on this time scale, bimolecular recombination between photogenerated carriers is not an important recombination mechanism. For the as-cast sample, the independence of the charge dynamics on the laser pulse fluence is observed also at 185 and 80 K (Figures 4.2(c,e)).

In the DIO processed cell at 185 and 80 K, the decay of the fraction in time exhibits a dependence on the excitation intensity (Figures 4.2(d,f)). This suggests that bimolecular recombination of the long-lived carriers is occurring at low temperature. At room temperature the DIO processed cell does not show any dependence of the long-lived free charge dynamics on the laser pulse fluence.

To summarize, the fractions of extractable charges show that in as-cast and in DIO processed samples massive recombination takes place before 1 \(\mu\text{s}\). At 290 K, 97\% of the charges that are extractable at −2 V recombine before 1\(\mu\text{s}\) when the as-cast device is held at \(V_{oc}\). This 97\% is only a lower limit for the amount of charges undergoing recombination, since at −2 V the photocurrent of PCPDTBT:PCBM as-cast cells is not saturated. The amount of extractable charges beyond 1 \(\mu\text{s}\) is 4 times higher in the DIO processed sample than in the as-cast device. This evidences that at \(V_{oc}\) significantly more recombination takes place in the sub-microsecond regime in the as-cast sample compared to the DIO processed solar cell.
Figure 4.2: Semi-logarithmic plot of the fraction of extractable charges $f$ measured on as-cast (a, c, e) and DIO processed (b, d, f) cells at different temperatures (see legend) comparing excitation fluencies of $2 \times 10^{-5} I_0$ (open triangles) and $4 \times 10^{-5} I_0$ (filled circles), where $I_0 = 3.7 \text{ mJ/cm}^2$ per pulse. The inset in panel (a) shows the dependence on laser pulse fluence of the density $n_{\text{avg}}$ of extracted charges when a constant 0 V bias is applied to the as-cast solar cell at 290 K.
Temperature can influence both the efficiency of CT dissociation into free charges and the efficiency of bimolecular recombination. Assuming that CT dissociation is an endothermic process, the dissociation of bound CT pairs is expected to become less efficient with decreasing temperature. Langevin type bimolecular recombination is linearly dependent on the mobility of free charges, which in turn is expected to decrease with decreasing temperature in organic semiconductors. Therefore bimolecular recombination can be expected to decrease with decreasing temperature, contributing to an increase in efficiency of charge collection.

For both the as-cast and optimized samples, the fraction of extractable charges at time delays beyond 1 µs increases with decreasing temperature. From this observation we infer that at times < 1 µs bimolecular recombination is occurring in both morphologies at $V_{oc}$. Moreover we conclude that the decrease in temperature results in an increase in efficiency of delayed charge collection (consequence of decreased bimolecular recombination efficiency) which is stronger than an eventual decrease in free charge formation in the CT dissociation step.

The dependence of the fraction of extractable charges at varying delay time on the laser pulse fluence indicates that in the as-cast morphology bimolecular recombination is not relevant beyond ~1 µs after charge photogeneration at every temperature. In contrast, in the coarser morphology, a dependence of the free charge dynamics on the laser pulse fluence is observed at 185 and 80 K. This indicates that bimolecular recombination of free charges is still active at those temperatures at times > 1µs after the photogeneration.

### 4.2.2 Near steady state photoinduced absorption

We performed near steady state PIA on as-cast and DIO processed PCPDTBT:PCBM thin films to investigate the dynamics of photogenerated species in more detail and correlate them with the observed charge dynamics in photo-CELIV. An advantage of PIA is that it can also detect neutral photoexcitations such as long-lived excitons, which are not directly detected by photo-CELIV. PIA and photo-CELIV cover approximately the same time scales; with photo-CELIV we look at the 1−100 µs range and with the PIA at the 10 µs − 1 ms range. Furthermore, in both cases the signals are compared in absence of an electric field.

Figure 4.3a shows the PIA spectrum of the as-cast PCPDTBT:PCBM blend at room temperature and at 80 K. The 80 K spectrum shows two PIA bands at 0.95 eV and below 0.5 eV with the first having a higher intensity than the second. We attribute the PIA band at 0.95 eV to the $T_{n*}$←$T_1$ transitions from the lowest excited triplet state.
in PCPDTBT. This assignment is based on the PIA spectrum relative to pristine polymer PCPDTBT films (Chapter 3). In that case we attribute the 0.95 eV band to absorption from triplets generated via intersystem crossing from the polymer $S_1$ singlet state. In the blend, the PCPDTBT singlet state $S_1$ is efficiently depopulated by charge transfer, as confirmed by the complete quenching of polymer photoluminescence by PCBM (Chapters 3 and 5). Therefore triplet formation cannot proceed via intersystem crossing from the $S_1$ state. We conclude that the formation of triplets in PCPDTBT:PCBM blends is the result of the recombination of the CT state.

The other band below 0.5 eV photon energies is attributed to absorption from photogenerated positive charges (radical cations or polarons) residing on the PCPDTBT. In Chapter 3 we have shown that positive charges on PCPDTBT give rise to two absorption bands with similar intensities at ~0.9-0.95 eV and below 0.5 eV. We conclude that at 80 K the PIA spectrum of the PCPDTBT:PCBM as-cast blend is given by a superposition of the triplets and the polaron spectra. This indicates that both charges and triplets are photogenerated in this blend.

![Figure 4.3: Photoinduced absorption spectra at 80 K (line) and 290 K (line plus circle) of PCPDTBT:PCBM blends processed without (a) and with (b) diiodooctane. $E_{exc} = 1.55$ eV. The pump modulation frequency was 275 Hz.](image)

At room temperature the lifetime of the triplets becomes too short to give a measurable PIA signal and the spectrum that remains has two bands of similar intensity that we attribute to positive charges on the polymer: at 0.95 eV and below 0.5 eV. We stress that this does not imply that triplets are not formed via CT
recombination at room temperature. It rather signifies that, even if formed, they are not detectable in the near steady-state PIA measurements as result of reduced lifetime.

The corresponding results on films processed using DIO are shown in Figure 4.3b. Both at room temperature and 80 K we observe two bands with equal intensities at 0.95 eV and below 0.5 eV. These spectra indicate that mainly charges and no triplets are generated in the film, both at room temperature and at 80K. We notice that the signal from charges at 0.35 eV in films processed with DIO is ~2 times higher than in as-cast films at room temperature and 1.5 times at 80 K.

In summary, by means of PIA we observe that in as-cast thin film blends, both long-lived charges and triplets are formed. The triplets are formed via recombination of the CT state. In the DIO processed blend no recombination to the triplet state is observed.

Both at room temperature and at 80 K, the DIO processed blend shows an increased amount of photogenerated charges. The increased amount of long-lived charges observed in PIA in the coarser BHJ morphology is consistent with the higher fractions of extractable charges observed in photo-CELIV experiments. In PIA and photo-CELIV we investigate formation and recombination of photogenerated charges on the same time scale (> 1µs). Furthermore, in both experiments the blends are in low or zero field conditions. Therefore the two experiments are complementary and investigate the same set of long-lived charges.

Combining the photo-CELIV and PIA results we obtain information on the time scale of the CT to triplet recombination process. We observe that, compared to the coarser morphology, the increase of triplet formation in as-cast films correlates with the decrease in extracted charges after 1 µs from the pulse. This observation suggests that recombination to triplets must be happening on time scales shorter than 1 µs. Therefore we argue that geminate CT states, rather than CT states formed via bimolecular recombination of free and electrons and holes, are the intermediates in triplet formation. As a consequence, recombination to triplets must be regarded as an independent recombination process additional to the bimolecular recombination.

The assignment of the PCPDTBT:PCBM PIA spectrum at 0.95 eV to absorption from triplets is complicated by the overlap with the absorption from charges at the same photon energy. Incidentally, the fact that a lower amount of extracted charges in photo-CELIV correlates with a higher PIA signal at 0.95 eV supports the assignment of the PIA band at 0.95 eV to a neutral species, viz. triplets.

Figures 4.4(a,c) show the modulation frequency dependence of the normalized PIA signal at 0.35 eV, which we attribute to charges for as-cast and DIO processed films. The measurements were performed at 290, 185, and 80 K. The as-cast and DIO
processed films show a similar decay of the PIA signal with increasing modulation frequency.

**Figure 4.4:** Log-log plots of normalized PIA intensities of PCPDTBT:PCBM blends processed without (a) and with (c) DIO as function of the modulation frequency at different temperatures (see legend). The data for as-cast (b) and DIO (d) blends at 80 K are re-plotted in together with the curves obtained by fitting with (iv-vi).

$E_{\text{probe}} = 0.35 \text{ eV}$. $E_{\text{exc}} = 1.55 \text{ eV}$. 
In the PIA experiment the intensity of the signal is given by the steady-state concentration of photogenerated species, which is in turn determined by their lifetime and generation rate. Monitoring the change in signal intensity with increasing modulation frequency allows to measure the lifetime of the probed photogenerated species. Therefore the fact that charges in the as-cast and DIO processed films have similar frequency dependence, indicates that they have similar lifetimes.

The PIA triplet signal at 0.95 eV showed a negligible roll-off with increasing frequency at 80 K, indicative of a much shorter lifetime for the triplets than for the charges. Assuming that the absorption cross sections for triplet state and radical cation of PCPDTBT are similar, this would imply that the ratio in PIA signal intensities at 0.95 and 0.35 eV underestimates the ratio between the densities of triplets and charges in the as-cast film.

For the as-cast sample, the roll-off of the normalized PIA at 0.35 eV with increasing frequency becomes stronger with decreasing temperature, indicating an increase in lifetime. The same occurs for the DIO processed sample, but showing a smaller change when going from 80 K to 185 K. Comparing Figures 4.4a and c, shows that the lifetime of charges in the DIO-processed blend is longer than in the as-cast blend. The frequency dependence of the PIA signal can be modeled to estimate a lifetime if the recombination mechanism of the probed species is known. In Figure 4.4b and 4.4d we show the fitting of the data at 80K for the two samples using models accounting for different recombination mechanisms. For the comparison between samples we use the data at 80 K because at higher temperature (especially at 290 K) the as-cast sample shows a decay that is too small to give a meaningful fit.

For both morphologies, a monomolecular decay model fails to provide a good fit to the data. For monomolecular decay, the frequency dependence can be expressed as:

\[ \Delta T \propto \frac{g \tau}{\sqrt{1 + \omega^2 \tau^2}} \]  

where \( \tau \) is the monomolecular decay lifetime, \( g \) the generation rate, with \( g = I \phi \), with \( \phi \) the charge generation efficiency and \( I \) the light intensity. \( \omega = 2 \pi \nu \), with \( \nu \) the modulation frequency. For pure bimolecular recombination the frequency dependence of the PIA signal can be described by the following expression:

\[ \Delta T \propto \sqrt{g / \beta} \cdot \frac{\alpha \cdot \tanh \alpha}{\alpha + \tanh \alpha} \]  

For both morphologies, a monomolecular decay model fails to provide a good fit to the data. For monomolecular decay, the frequency dependence can be expressed as:

\[ \Delta T \propto \frac{g \tau}{\sqrt{1 + \omega^2 \tau^2}} \]  

where \( \tau \) is the monomolecular decay lifetime, \( g \) the generation rate, with \( g = I \phi \), with \( \phi \) the charge generation efficiency and \( I \) the light intensity. \( \omega = 2 \pi \nu \), with \( \nu \) the modulation frequency. For pure bimolecular recombination the frequency dependence of the PIA signal can be described by the following expression:

\[ \Delta T \propto \sqrt{g / \beta} \cdot \frac{\alpha \cdot \tanh \alpha}{\alpha + \tanh \alpha} \]
where $\alpha = \frac{\pi}{\omega \tau}$, $\tau = \frac{1}{\sqrt{\beta}}$ is the lifetime of the probed species and $\beta$ the rate constant for bimolecular decay. This model gives a reasonably good fit for both samples, resulting in a lifetime of $\tau = 83 \pm 3 \, \mu s$ and $\tau = 166 \pm 6 \, \mu s$ for as-cast and DIO processed films respectively. Table 4.1 summarizes the lifetimes obtained fitting the data with Equation (2) at the other temperatures.

**Table 4.1:** Lifetimes $\tau$ and adjusted R-square values $\bar{R}^2$ obtained fitting the PIA signals at 0.35 eV as function of modulation frequency to the bimolecular recombination model expressed by Equation (2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fit parameter $\tau$ ($\mu s$)</th>
<th>$T = 80$ K</th>
<th>$T = 185$ K</th>
<th>$T = 290$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-cast</td>
<td>$\tau$ ($\mu s$)</td>
<td>83 ± 3</td>
<td>43 ± 2</td>
<td>17 ± 2</td>
</tr>
<tr>
<td></td>
<td>$\bar{R}^2$</td>
<td>0.95</td>
<td>0.8</td>
<td>-0.74</td>
</tr>
<tr>
<td>with DIO</td>
<td>$\tau$ ($\mu s$)</td>
<td>166 ± 6</td>
<td>141 ± 6</td>
<td>45 ± 2</td>
</tr>
<tr>
<td></td>
<td>$\bar{R}^2$</td>
<td>0.95</td>
<td>0.91</td>
<td>0.8</td>
</tr>
</tbody>
</table>

The better fit of the PIA versus modulation frequency with Equation (2) indicates that the main recombination mechanism of the long-lived charges in the thin films is bimolecular, which is supported by the observation of a square root dependence of the PIA signal at 0.35 eV on pump intensity.

We notice that the lifetimes observed in PIA are consistent with the decays observed in photo-CELIV, as well as their evolution with temperature. At 80 K the lifetime is around 100 $\mu s$ in both cases, consistent with the very slow decay shown in Figure 4.2. Going to 185 K we observe a different behavior for the as-cast and DIO processed samples. In the DIO processed sample the lifetime does not decrease significantly, while in the as-cast blend it does, going below 100 $\mu s$. Finally, at 290 K both samples show a lifetime below 100 $\mu s$. The consistency between the dynamics observed with the PIA and photo-CELIV confirms the assignment of the PIA signal at 0.35 eV to charges.

The lifetime extracted from the PIA frequency dependence is consistent with the excitation fluence dependence observed in photo-CELIV (Figure 4.2). At all temperatures for the as-cast samples and at room temperature for the DIO processed sample, the bimolecular recombination lifetime of the long-lived charges is in the 1-100 $\mu s$ range. Being in its last stage, the recombination process does not show a dependence on excitation intensity in photo-CELIV. For DIO processed samples at
185 and 80 K, instead, the density of long-lived charges decays after the 1-100 µs range, therefore a change in initial density still gives a measurable change in recombination dynamics.

Finally in Figures 4.4b and 4.4d we show that another model for the interpretation of the frequency dependent PIA signal can be used, taking into account bimolecular recombination in a disordered system, where excitations can have a distribution of lifetimes. Such a model results in the following expression for the PIA signal versus pump modulation frequency:[21]

$$\Delta T \propto \frac{1}{1 + (\omega \tau)^\delta}$$

(3)

where $\delta$ is a factor expressing the width of such a distribution, getting closer to 1 as the distribution gets narrower. The dispersion of the lifetimes can be the result of energetical and/or morphological traps in the blend.[22,23] Figure 4.4d shows that a better fit of the data could be obtained using Equation (3) rather than with Equation (2), resulting in a lifetime of $56.5 \pm 1.4$ µs and a $\delta$ of 0.89 at 80 K. In Table 4.2 the parameters obtained by fitting Equation (3) to the data are summarized for different temperatures. The fits result in values of $\delta$ between 0.9 and 0.6, decreasing with increasing temperature. Values for the as-cast film at 290 K are not reported because of the extremely small roll-off of the PIA signal, not resulting in meaningful fits.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fit parameter</th>
<th>$T = 80$ K</th>
<th>$T = 185$ K</th>
<th>$T = 290$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-cast</td>
<td>$\tau$ (µs)</td>
<td>24.7 ± 0.8</td>
<td>5.6 ± 1.1</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\delta$</td>
<td>0.89 ± 0.04</td>
<td>0.66 ± 0.04</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$\bar{R}$</td>
<td>0.99</td>
<td>0.89</td>
<td>-</td>
</tr>
<tr>
<td>with DIO</td>
<td>$\tau$ (µs)</td>
<td>56.5 ± 1.4</td>
<td>42.2 ± 1.4</td>
<td>4.8 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>$\delta$</td>
<td>0.89 ± 0.04</td>
<td>0.79 ± 0.02</td>
<td>0.61 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>$\bar{R}$</td>
<td>0.99</td>
<td>0.99</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Table 4.2: Lifetime $\tau$, dispersion parameter $\delta$, and adjusted R-square value $\bar{R}^2$ obtained by fitting the PIA signal at 0.35 eV as function of modulation frequency to Equation (3).
In conclusion, bimolecular recombination was observed in both morphologies by means of PIA. A model taking into account a distribution of the lifetimes introduced by disorder successfully reproduces the dependence of the charges PIA absorption on pump modulation frequency. The degree of disorder in lifetimes, as inferred from the dispersion parameter $\delta$, does not decrease in the coarser morphology. The lifetimes of photogenerated charges measured with PIA are consistent with the dynamics observed for the extractable charges in photo-CELIV. We cannot exclude that a difference in the values of lifetimes measured with photo-CELIV and PIA might be introduced by the diffusion of charges to the contacts in photo-CELIV as additional decay mechanism. Being performed on contactless thin films, in PIA the only process determining the lifetime can be recombination at the donor-acceptor interface. The small range of delay times used in photo-CELIV prevented us to fit the charge vs. time traces with analytical formulas taking into account the different decay mechanisms (recombination and diffusion to the contacts).

### 4.3 Conclusions

Solar cells based on the PCPDTBT:PCBM blend show a poor fill factor of the $J-V$ curve under illumination, resulting from a strong field dependence of the photogenerated current. The introduction of diiodooctane in the solvent mixture for the spin coating of the active layer results in solar cells with improved fill factor, resulting in an improvement in the overall power conversion efficiency. The morphology of the DIO processed PCPDTBT:PCBM bulk heterojunction shows a higher degree of phase separation compared to the as-cast blends, which are very finely mixed.

In this work we have investigated the charge recombination processes that may be responsible for the poor fill factor of PCPDTBT:PCBM cells. We have tried to find the factors that determine the improvement of fill factor obtained with coarser morphologies, focusing on the distinct processes of CT geminate recombination and bimolecular recombination. For this purpose we have investigated solar cells at open-circuit voltage conditions, where the recombination processes are expected to have the strongest influence on the field dependence of the photogenerated current.

With photo-CELIV we observed that in PCPDTBT:PCBM solar cells at $V_{oc}$ photogenerated charges recombine almost completely on a sub-microsecond timescale. For as-cast PCPDTBT:PCBM devices, at least 97% of the photogenerated charges recombine within 1 $\mu$s at room temperature. For solar cells processed with
diiodooctane the yield of extractable charges beyond 1 µs is 4 times higher. These results indicate that the improvement in device performance associated with coarser bulk heterojunction morphology is mainly due to the enhanced dissociation of the charge transfer state into free charges.

Furthermore, the lower efficiency of CT dissociation in the as-cast PCPDTBT:PCBM blends correlates with a higher population of the triplet state on the PCPDTBT, as described in Chapter 3, but we now have the additional information that this process cannot happen on a time-scale longer than one microsecond. This result further supports the idea that recombination of the geminate CT pair to the PCPDTBT triplet state is a loss mechanism which is suppressed in the optimized morphology.

In agreement with previous studies\cite{11-13} we find significant bimolecular recombination of free photogenerated charges in both as-cast and optimized morphologies. This might explain the moderate fill factor of the devices, even after optimizing the morphology for charge generation. The bimolecular recombination in the coarser morphology is then understandable in terms of increased density of photogenerated free charges due to the improved CT dissociation, which is apparently not counteracted by a more efficient transport of the charges. Moet et al. have been able to numerically simulate the $J-V$ curves of as-cast and optimized morphologies for PCPDTBT:PCBM solar cell with a 1-D drift-diffusion model assuming the same hole and electron mobilities for both blends. We note that the rate constant for geminate recombination is then the only fit variable that can accommodate for differences in charge carrier dynamics in finely dispersed and coarser morphologies.\cite{10} We point out that 2-D numerical drift-diffusion simulations as proposed by Maturova et al.\cite{24} provide a more realistic description of the influence of morphology on charge carrier dynamics in blends with coarse morphology.

In sum, the experimental results described in this chapter support the idea that tweaking the morphology of the PCPDTBT:PCBM blend succeeds in enhancing the charge generation step, but fails in improving the transport properties. This suggest that optimization of the extent of phase separation is not sufficient to obtain high efficiencies of charge extraction. More order inside the phase separated domains should be introduced to facilitate the transport of charges to the electrodes.
4.4 Experimental section

Solar cells and thin films. Photovoltaic devices were made by spin coating poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (Clevios P, VP Al4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). The photoactive layer was deposited by spin casting in air at 2000 rpm, using a chlorobenzene solution containing 10 mg mL\(^{-1}\) PCPDTBT (\(M_w = 55.7\) kg mol\(^{-1}\); PDI = 2.28, Konarka), 20 mg mL\(^{-1}\) [6,6]-phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM) (Solenne) and, optionally, 37.5 mg/mL 1,8-diiodooctane (DIO). The metal electrode, consisting of LiF (1 nm) and Al (100 nm), was deposited by vacuum evaporation at ~ 3 \(\times\) 10\(^{-7}\) mbar. The active area of the cells was 0.091 cm\(^2\) and the thickness of the active layer was ~ 70 nm. Under ~1 sun white light illumination (tungsten-halogen lamp with a Schott GG385 UV filter and a Hoya LB120 daylight filter at 100 mW cm\(^{-2}\)) as-cast devices showed a short-circuit current \((J_{sc})\) of 6.5 mA cm\(^{-2}\), a fill factor (FF) of 0.33 and an open-circuit voltage \((V_{oc})\) of 0.67 V, resulting in a maximum power point (MPP) of 1.43 mW cm\(^{-2}\). With the use of DIO as cosolvent, the \(J_{sc}\) increased to 8.4 mA cm\(^{-2}\), the FF to 0.45 and the \(V_{oc}\) decreased to 0.61 V, resulting in a MPP of 2.33 mW cm\(^{-2}\). The corresponding thin films for PIA were prepared on quartz substrates by spin coating using the same solutions.

Photo-CELIV. For photo-CELIV with direct excitation of PCPDTBT, short pulses from an amplified Ti:sapphire laser were used (photon energy 1.55 eV, pulse duration 10\(^2\) fs, fluence \(I_0 = 3.7\) mJ cm\(^{-2}\) per pulse, spot size 0.07 cm\(^2\)). The fluence was varied using neutral density filters. Voltage ramps were generated using an Agilent 33250A arbitrary wave generator. A compensating voltage \((V_{bias},\) see Chapter 6 or Ref.[19]) was applied to minimize charge extraction before the start of the voltage ramp. The length \(τ\) of the voltage ramp was 12.5 \(\mu\)s. The collection voltage \(V_{coll}\) equals: \(V_{coll} = V_{bias} - 2.0\ V \equiv -1.4\text{--}1.5\ V\). A 50 Ω probe resistor was used to record the transient photocurrent through the solar cell using an oscilloscope. The number of photogenerated charge carriers extracted was calculated by integrating the difference between the extraction currents upon application of the voltage ramp in dark and after pulsed illumination. Transient currents were determined averaging over 10\(^3\) laser pulses and the statistical error of measurement was estimated by triplicating each transient current experiment.

Photoinduced absorption. Near steady-state photoinduced absorption (PIA) spectra were recorded between 0.35 and 2 eV by excitation with a mechanically modulated (275 Hz) laser source and by measuring the change in transmission of a tungsten-halogen probe beam through the sample \((ΔT)\) with a phase sensitive lock-in amplifier after dispersion with a monochromator and detection using Si, InGaAs, and cooled InSb detectors. Pump wavelengths used: 830 nm (1.49 eV) from a laser diode with 130 mW power and a beam diameter of 1 mm. The PIA signal \((-ΔTT)\) was corrected for the photoluminescence, which was recorded in a separate experiment. During the measurements the thin film samples were held in an inert nitrogen atmosphere using an Oxford Optistat continuous flow cryostat equipped with a temperature controller.
4.5 References


Abstract

The photo-oxidation behavior of three different polymers, namely poly(3-hexylthiophene) (P3HT), poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b’]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (C-PCPDTBT), and poly[2,6-(4,4-bis(2-ethylhexyl)dithieno[3,2-b:2′,3′-d]silole)-alt-4,7-(2,1,3-benzothiadiazole)] (Si-PCPDTBT) is investigated in neat polymer films and in blends with [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) for different polymer:PCBM ratios. PCBM is shown to have both stabilizing and destabilizing effects, whose extent depends on the type of polymer. Screening of the polymer from incident light by PCBM turns out to play an only minor role in the stabilization of P3HT. Quenching of the polymer excited states is also not a significant stabilization mechanism, as demonstrated by the comparison of the reduction of photo-oxidation rates to the extent of photoluminescence quenching by PCBM and 2,7-dinitrofluorenone (DNF). Photoinduced absorption spectroscopy reveals that the enhanced degradation of C-PCPDTBT in blend films with PCBM correlates with the population of the polymer triplet state via the polymer:PCBM charge transfer state.

This work is part of:

A. Distler, P. Kutka, and T. Sauermann performed the measurements of degradation (Figures 5.2-5.4).
D. Di Nuzzo performed the photoluminescence and PIA measurements (Figures 5.5 - 5.6).
5.1 Introduction

PCBM ([6,6]-phenyl-C_{61}-butyric acid methyl ester) has been observed to stabilize many \(\pi\)-conjugated polymers used in the active layer of organic photovoltaic (OPV) cells by reducing the degradation rate under different conditions, such as photo-oxidation\(^{[1–3]}\) and thermolysis.\(^{[4]}\) Two mechanisms are usually invoked for the stabilizing effect of PCBM: exciton quenching and radical scavenging. Polymer exciton quenching by electron transfer to PCBM reduces the lifetime of the excited singlet state and thus reduces the population of all reaction-inducing states which are populated via the singlet manifold, e.g., triplet states. Triplet states are notorious for their reactivity, due to their relatively long lifetime, which favors bimolecular reactions such as singlet oxygen sensitization. They have been proposed recently as reactive intermediates in the photo-oxidation of poly(3-hexylthiophene) (P3HT) films.\(^{[5]}\) However, the fact that PCBM also drastically reduces the reaction rate of thermolysis of polymers in the dark proves that excited state quenching is not the only mechanism of stabilization. Chambon et al.\(^{[4]}\) have suggested that at least part of the stabilizing effect of fullerenes is due to their ability to scavenge oxygen centered radicals.

On the other hand, PCBM may as well accelerate the degradation of some \(\pi\)-conjugated polymers. Due to its high intersystem crossing (ISC) yield, which is around 50% in solution,\(^{[6–8]}\) electronically excited PCBM in the presence of oxygen is well known for its ability to generate singlet oxygen.\(^{[9]}\) In the solid state the ISC efficiency is much less,\(^{[10]}\) but depending on the degree of crystallinity, it might still be high enough to cause significant degradation. Also superoxide anions have been shown to form by electron transfer from fullerene anions to molecular oxygen.\(^{[11]}\)

Actually, the increasing degradation rate of a series of polymers in blends with fullerenes of decreasing electron affinity has been interpreted as a result of enhanced formation of superoxide anions via the fullerene anions.\(^{[12]}\) As a further mechanism, triplet energy transfer from the PCBM triplet at 1.57 eV to the polymer triplet state should be possible for most polymers with an optical band gap (\(S_0-S_1\)) of less than about 2.2 eV (the singlet-triplet energy gap (2\(K\)) is about 0.6–1 eV for most OPV polymers).\(^{[13]}\) The polymer triplet (T\(_1\)) may also be populated via recombination of the charge transfer (CT) state that is formed in the photoinduced electron transfer reaction at the interface of the polymer and PCBM.\(^{[14–19]}\) This triplet recombination will only occur when the CT state is > 0.1 eV higher in energy than the polymer T\(_1\) state.\(^{[16,20]}\)

The goal of this work is to give more insight into the role which PCBM plays in the degradation of OPV polymers. To this end, the photo-oxidation rates of three different polymers (Figure 5.1) were determined as a function of PCBM concentration.
The effect of PCBM on the photodegradation kinetics of polymers for OPV

in the polymer films. In order to quantify the effect of excited state quenching on the stabilization of polymers, the photo-oxidation rates were also determined as a function of the concentration of 2,7-dinitrofluorenone (DNF) which quenches the fluorescence of polymer films to a similar extent as PCBM does. Finally, in order to evaluate the role of triplet population of the polymer via the CT state, the population of the polymer triplet state was determined by photoinduced absorption spectroscopy in the presence and in the absence of PCBM.

![Chemical structures of the polymers under investigation.](image)

5.2 Results

5.2.1 The Effect of PCBM on the Degradation Rate

Pristine polymer and polymer:PCBM blend films were exposed to the light of a metal halide lamp (AM 1.5, 1000 W m⁻²) in ambient air at a temperature of 45 °C and 10% relative humidity. The degradation of the films with time was monitored by UV/vis spectroscopy as the loss of absorbance of the polymer. Figure 5.2 shows that the stability of neat polymer films under these conditions increases in the series P3HT < Si-PCPDTBT < C-PCPDTBT. Upon addition of PCBM (polymer:PCBM weight ratio 2:1), this order is reversed. P3HT is stabilized by PCBM, whereas the degradation of C-PCPDTBT is accelerated by almost a factor of two (Figure 5.2). In the case of Si-PCPDTBT, the effect of PCBM is less pronounced: during the first two hours of degradation, there is no significant effect on the degradation rates. At later
times, the degradation in the presence of PCBM is slightly slower than in the neat polymer.

The use of processing agents such as diiodooctane (DIO) is known to affect the film morphology of C-PCPDTBT:PCBM films, leading to a more phase-separated blend and improved photovoltaic performance.\cite{22,23} For Si-PCPDTBT:PCBM, processing agents have little effect on film morphology or device performance.\cite{24} Figure 5.2 shows that the use of DIO as processing agent in C-PCPDTBT:PCBM film formation leads to a reduction of the degradation rate by about 40%. However, the degradation is still slightly accelerated with respect to the pristine polymer. For Si-PCPDTBT, the addition of DIO does not significantly affect the degradation process.

**Figure 5.2:** Temporal development of absorbance (in the respective absorption maxima, normalized to the initial values) during the degradation of polymer films with different additives under a solar simulator in air. Circles: pure polymers, Triangles: polymer:PCBM (2:1 w/w) blends, Open squares: polymer:PCBM (2:1 w/w) blends processed with 3 vol% DIO added to the casting solution.
The extent of both effects, namely stabilization and destabilization, increases with increasing PCBM content (Figure 5.3). In Figure 5.3 we plot the normalized degradation rate, $D/D_0$, where $D$ is the relative change in absorbance after 16 hours of the blend and $D_0$ the corresponding relative change in the pristine film. At a polymer:PCBM ratio of 1:1, the normalized degradation rate of C-PCPDTBT reaches a maximum value of slightly more than twice the rate observed without PCBM. At the same polymer:PCBM ratio, the degradation rate of P3HT is reduced to about 25% of its original value and that of Si-PCPDTBT is reduced by about 75%.

PCBM quenches the fluorescence of all three polymers, however, to different extents (Figure 5.3). The fluorescence quenching by PCBM is more pronounced in the case of the PCPDTBT polymers that for P3HT. Whereas the extent of fluorescence quenching, expressed as $(F_0/F) - 1$, does not exceed a value of ten in P3HT, even for large PCBM contents, it reaches values of more than 400 in the case of C-PCPDTBT (Figure 5.3, right panel). The use of DIO as processing agent in film formation leads to a reduction of fluorescence quenching by 50% in the case of C-PCPDTBT:PCBM, whereas quenching is only slightly reduced in Si-PCPDTBT:PCBM films. These observations are in accordance with previous results obtained on these polymers, and the increased phase separation in C-PCPDTBT:PCBM films when processed with DIO.
Figure 5.3: (Left) Normalized degradation rates \(D/D_0\), squares) and fluorescence intensities \(F/F_0\), triangles) of three different polymer films processed with (open symbols) and without DIO (full symbols) as a function of PCBM content. The degradation rates are calculated from the absorbance changes after 16 h as displayed in Figure 5.2. (Right) The fluorescence quenching of the left panel presented in a Stern-Volmer plot.

5.2.2 The Effect of DNF on the Degradation Rate

The effects of DNF on the normalized degradation rates \(D/D_0\) and normalized fluorescence \(F/F_0\) of the three investigated polymers are shown in Figure 5.4. DNF and PCBM show very much the same behavior with respect to fluorescence quenching. At 5% (w/w) concentration, both dopants quench the fluorescence intensities of C- and Si-PCPDTBT by more than 90% and that of P3HT by about 60%. However, the effect of DNF on the degradation rate of the polymer is significantly different from the effect of PCBM. Upon admixture of 5% DNF to C-PCPDTBT, P3HT and Si-PCPDTBT, the degradation rates are reduced by about 15%, 5% and 10%, respectively. At the same concentration, PCBM increases the
degradation rate of C-PCPDTBT by 15%, while it reduces the rates for P3HT and Si-PCPDTBT by 30% and 5%, respectively.

![Figure 5.4: Normalized degradation rates (D/D₀, circles) and fluorescence intensities (F/F₀, triangles) of films of the three different polymers blended with additives (full symbols: DNF, open symbols: PCBM) as a function of dopant concentration.](image)

**5.2.3 Photogenerated Species in the Different Blends**

To obtain more information about photogenerated species formed in the polymers and the polymer:fullerene blends, their films were studied using photoluminescence (PL) and near steady state photoinduced absorption (PIA) spectroscopy.

The PL spectra of pristine films of C-PCPDTBT (Figure 5.5a) show a band peaking at 1.45 eV. Upon mixing with PCBM in 1:1 weight ratio, the polymer fluorescence is quenched by a factor of more than 150 and a new band arises, peaking at 1.22 eV, which we attribute to emission from the CT state. When P3HT is mixed with PCBM (1:1 weight ratio), the fluorescence is quenched only by a factor of four and no CT emission is observed (Figure 5.5b). Likewise, mixing of Si-PCPDTBT with PCBM results in an 85-fold quenching of the Si-PCPDTBT fluorescence and without giving luminescence from the CT state (Figure 5.5c).
Near steady state photoinduced absorption (PIA) measurements were performed on the pristine films and on the blends with PCBM at low temperature \((T = 80 \text{ K})\) in inert atmosphere. Figure 5.5d shows the PIA spectra of a pristine C-PCPDTBT film and of a C-PCPDTBT:PCBM blend film (1:1 weight ratio). In the pristine film the PIA spectrum consists of a single band at 0.95 eV that we attribute to the \(T_n \rightarrow T_1\) transition from the lowest excited triplet state on the polymer, which is populated via intersystem crossing from the \(S_1\) state after excitation. The same spectrum (blueshifted) was observed in pristine polymer solution in toluene (Chapter 3).\(^{[27]}\) A band with very similar shape and position in energy appears also when PCBM is added to the polymer. In transient absorption experiments on C-PCPDTBT:PCBM blends this band has been attributed by various authors to the transition of polymer polarons (radical cations).\(^{[28–30]}\) However, we previously demonstrated that C-PCPDTBT radical cations are characterized by the simultaneous presence in the PIA spectrum of a low-energy band at 0.35 eV and a high-energy band at 0.95 eV with similar intensities (Chapter 3).\(^{[27]}\) The occurrence of two bands (\(D_1 \rightarrow D_0\) at low energy and \(D_2 \rightarrow D_0\) at higher energy) in the PIA spectrum of C-PCPDTBT radical cations is a characteristic feature of the optical signatures of radical cations of \(\pi\)-conjugated polymers.\(^{[31,32]}\) Therefore, in C-PCPDTBT:PCBM blends, the 0.95 eV band can only be unambiguously assigned, when the intensity of the low-energy band at 0.35 eV is also known.

In the present case, the C-PCPDTBT:PCBM blend PIA spectrum shows both the 0.95 and 0.35 eV bands, with the latter being about 4 times less intense. Based on the above considerations, we interpret this spectrum as originating from C-PCPDTBT radical cations together with triplets, the latter contributing only to the signal at 0.95 eV and making it substantially higher than the signal at 0.35 eV.

Figure 5.5e shows the PIA spectra of P3HT thin films. The pristine P3HT film shows a PIA peak at 1.06 eV and a shoulder at 1.2 eV. The 1.06 eV peak is typically assigned to the \(T_n \rightarrow T_1\) transition on P3HT.\(^{[19,33–35]}\) When P3HT is mixed with PCBM, the PIA spectrum shows three bands: below 0.5 eV, at 1.22 eV and at 1.8 eV. Such a spectrum is attributed to absorption from P3HT radical cations, with a possible contribution from the radical anion on PCBM at 1.22 eV.

Figure 5.5f shows the PIA spectrum of a pristine Si-PCPDTBT film and of a Si-PCPDTBT:PCBM blend in a 1:1 weight ratio. The pristine material shows a single PIA band at 0.92 eV, which we attribute to the \(T_n \rightarrow T_1\) transition. Given the close resemblance in electronic structure, it is not surprising that the pristine films of the C- and Si-PCPDTBT show very similar PIA spectra. When blended with PCBM, the PIA spectrum shows three bands: at 0.35 eV, 0.94 and 1.21 eV. In analogy with the PIA on
the C-PCPDTBT:PCBM blend, we attribute the band at 0.35 eV to the $D_1 \leftarrow D_0$ transition of positive Si-PCPDTBT radical cations. The band at 1.21 eV is assignable to the radical anion on PCBM.\cite{36} Again, the band at 0.94 eV may comprise absorption of polymer triplets ($T_n \leftarrow T_1$) and polymer radical cations ($D_2 \leftarrow D_0$). However, compared C-PCPDTBT:PCBM, the ratio between the PIA signal at 0.92 eV and at 0.35 eV is now much lower (~1.5), suggesting that fewer triplets are generated in the Si-PCPDTBT:PCBM.

Figure 5.5: (Left) Normalized PL spectra of (a) C-PCPDTBT, (b) P3HT and (c) Si-PCPDTBT. Pristine films (circles) and blended with PCBM in 1:1 weight ratios (red lines). Measurements performed in air at room temperature. $E_{\text{exc}} = 2.06$ eV. (Right) PIA spectra of (d) C-PCPDTBT, (e) P3HT and (f) Si-PCPDTBT. Pristine films (circles) and blends with PCBM in 1:1 weight ratio (red lines). Measurements in inert atmosphere at $T = 80$ K. $E_{\text{exc}} = 1.49$ eV for (d) and (f), $E_{\text{exc}} = 2.41$ eV for (e).
To further support the assignment of the PIA bands in C-PCPDTBT:PCBM and Si-PCPDTBT:PCBM blends and to obtain additional information about the contributions of triplet and charges to the PIA spectra, the temperature dependence of the PIA spectra was investigated. The signal intensity of a photogenerated species measured with the near steady state PIA technique is proportional to the yield of formation and the lifetime of the species itself.\[^{37}\] When we induce a change in lifetime of two photogenerated species, namely triplets and radical cations of the polymer, by changing the temperature of the sample we can vary their relative signal intensities. At 290 K, we are not able to detect the $T_n \leftarrow T_1$ triplet signal that we observed at 80 K in pristine C-PCPDTBT films. This indicates that the lifetime of the triplet state of C-PCPDTBT strongly decreases with increasing temperature. In Figure 5.6 we compare the PIA spectra recorded at 80 and 290 K on C-PCPDTBT and Si-PCPDTBT, both blended with PCBM in 1:1 weight ratio (Figure 5.6). The results for the C-PCPDTBT:PCBM are shown in Figure 5.6a; the spectra are normalized to the maximum at 0.95 eV. At 80 K the band at 0.95 eV is about 4 times more intense than the 0.35 eV, but at 290 K both bands have almost the same intensity. The absolute intensity of the signal at 0.95 eV increases 11.2 times on going from 290 to 80 K. Because the reduced lifetime of C-PCPDTBT triplet states in pristine films caused it to be undetectable with PIA at 290 K, we conclude that at room temperature the PIA spectra measured on C-PCPDTBT:PCBM blends only consists of the absorption features of radical cations. Triplets, even if present transiently, have a lifetime that is too short to give a steady-state signal.

This result confirms that the PIA spectrum of radical cations in the C-PCPDTBT:PCBM blend is given by two bands having approximately the same intensity. At 80 K the band at 0.95 eV is prominent, indicating the additional contribution from triplets. To further support this interpretation, in Figure 5.6c we normalize the spectrum measured at 80 K to the PIA maximum (0.95 eV), obtaining $\text{PIA}_{\text{norm}}(80 \text{ K})$. Subsequently we equalize the PIA spectrum measured at 290 K to the value of $\text{PIA}_{\text{norm}}(80 \text{ K})$ at 0.35 eV and we subtract it from $\text{PIA}_{\text{norm}}(80 \text{ K})$. As a result, we find a spectrum that has the same shape as the PIA on pristine C-PCPDTBT films. This supports our conclusion that the PIA spectrum of the C-PCPDTBT:PCBM blend recorded at 80 K contains two separate components: one from the triplets (at 0.95 eV) and one from the radical cations (at 0.35 and 0.95 eV). For the Si-PCPDTBT:PCBM film the changes in the PIA spectrum with temperature are different (Figure 5.6b): the normalized spectra at 80 and 290 K show approximately the same shape. The intensity of the band at 0.94 eV increases 3 times at 80 K compared to 290 K. Again, we consider that at 290 K the PIA spectrum stems purely from radical cations and has
no contribution of Si-PCPDTBT triplet states. The fact that the spectral shape is not modified going to 80 K (where triplets, if generated, would be detectable) indicates that for this blend at 80 K the dominant photogenerated species are radical cations and triplets are not formed. Confirmation of this is given in Figure 5.6d, where we show the same manipulations performed for C-PCPDTBT. Subtracting the equalized 290 K spectrum from the 80 K normalized one results in a small signal only. The subtracted spectrum shows bands at 0.94 and 1.21 eV and differs from the pristine polymer spectrum, which has only one band at 0.92 eV.

We note that the fact that at 290 K no triplets are observed in the PIA spectra of C-PCPDTBT or C-PCPDTBT:PCBM but only at 80 K, does not imply that they are not formed at 290 K, but rather that their lifetime is too small to be detected with PIA. Although we do not exclude differences in the photophysical pathways between 80 and 290 K, we consider that the low temperature primarily causes these processes to be observed.
Figure 5.6: Normalized PIA spectra of films of (a) C-PCPDTBT and (b) Si-PCPDTBT mixed with PCBM (1:1 w/w) at 80 K (red lines) and 290 K (diamonds) in inert atmosphere. In (c) and (d) the grey lines represent $\text{PIA}_{\text{norm}}(80 \text{ K}) - \text{PIA}_{\text{eq}}(290 \text{ K})$, where $\text{PIA}_{\text{norm}}(80 \text{ K})$ are the spectra measured at 80 K and normalized to the PIA maximum (0.95 eV) and $\text{PIA}_{\text{eq}}(290 \text{ K})$ are the spectra measured at 290 K and equalized to $\text{PIA}_{\text{norm}}(80 \text{ K})$ at the polaron signal (0.35 eV). The result is compared with the PIA on pristine films at 80 K (circles). $E_{\text{exc}} = 1.49 \text{ eV}$.

5.3 Discussion

5.3.1 Stabilizing Effects of PCBM

For the stabilization of polymers against photo-oxidation by additives three basic mechanisms are usually discussed: screening from UV light, excited state quenching and chemical effects (radical scavenging, hydroperoxide cleavage).\textsuperscript{[1–4]}

The UV light screening mechanism is a purely optical effect that arises from PCBM absorbing short wavelength photons (< 400 nm) and preventing them to initiate photodegradation reactions in the polymer.\textsuperscript{[38]} In separate experiments, which involved placing a PCBM film in front of a P3HT film, it was established that light
filtering by PCBM cannot account for more than 30% of the stabilization of P3HT in P3HT:PCBM (1:1) blends.\(^{39}\)

The role of excited state quenching has been elucidated by comparing photoluminescence quenching and stabilization. The results show clearly that the extent of fluorescence quenching by an additive is not correlated to its capability of stabilizing the polymer. In all cases investigated here (i.e., for all polymers and both additives), fluorescence quenching is by far stronger than the reduction of the photochemical reaction rate. At a PCBM content of 13% (w/w), fluorescence is quenched by factors of 50 and 5 for the PCPDTBTs and P3HT, respectively, whereas the reaction rates are enhanced by 50% in the case of C-PCPDTBT and reduced by 10% and 50% in the cases of Si-PCPDTBT and P3HT, respectively. While the dependence of fluorescence quenching on quencher concentration is in accordance with a quenching mechanism based on exciton diffusion over distances of several nanometers,\(^{40–42}\) the dependence of the reaction rates on PCBM concentration rather points to a short range stabilizing/destabilizing effect of PCBM. The comparison between the two additives, PCBM and DNF, is most instructive. While they quench the fluorescence of all three polymers by about the same extent (another evidence for the rate of fluorescence quenching being controlled by exciton diffusion), DNF has only a small stabilizing effect on all the polymers.

These observations have two important implications. First of all, degradation by photo-oxidation does not proceed from the fluorescent excited state (\(S_1\)) of the polymer or any of the states which are involved in exciton diffusion. This also excludes the population of the polymer triplet excited states (\(T_1\)) formed by intersystem crossing (ISC) from \(S_1\). Otherwise, fluorescence intensity and degradation rate would show the same, more or less Stern-Volmer-like dependence on quencher concentration. Our conclusion that the polymer \(S_1\) state and its intrinsic decay processes are not primarily involved in the photodegradation is in line with the observation that the action spectrum of photo-oxidation of P3HT does not coincide with the P3HT absorption spectrum.\(^{38}\) The fact that with DNF and PCBM the degradation is unaffected or reduced (except for C-PCPDTBT:PCBM), also implies that charges formed on the polymer (radical ions) are not the primary intermediates in photo-oxidation reactions.

The second implication concerns the stabilizing effect of PCBM. As it is neither based on quenching of the polymer \(S_1\) excited state nor on light screening, at least not to a significant extent, the stabilizing effect of PCBM is likely due to some ground state property of PCBM which it does not share with DNF. PCBM has been reported to stabilize MDMO-PPV against thermal oxidation in the dark, which the
authors ascribed to its radical scavenging ability.\cite{4} The radical scavenging ability of fullerenes, mainly due to the stabilization of radicals by their addition to the extended \(\pi\)-system of the fullerenes, is well documented in the literature.\cite{43-45}

The possibility that the stabilizing effect of PCBM is based on radical scavenging rather than on excited state quenching also explains the observed effects of DIO on both fluorescence intensity and degradation rates of C- and Si-PCPDTBT. For C-PCPDTBT:PCBM, DIO enhances the phase separation of polymer and fullerene and thus reduces the interface area between them.\cite{22,23} This effect is very pronounced in the case of C-PCPDTBT whereas it is rather minute for the Si analogue. Phase separation leads to longer average distances between polymer and fullerene, which in turn leads to the reduction of fluorescence quenching (by more than 50% in the case of C-PCPDTBT:PCBM (2:1 w/w)).\cite{24} Enhanced phase separation does not only increase the diffusion distances of excitons, but also those of radicals, which leads to the diminution of the stabilizing effect of PCBM on Si-PCPDTBT in the presence of DIO. In the case of C-PCPDTBT, enhanced phase separation in the presence of DIO leads to decreased destabilization of the polymer by PCBM. We ascribe this effect to the reduced population of polymer-fullerene charge transfer states which in turn leads to the reduced formation of polymer triplet states. This mechanism will be described in more detail in the next section.

5.3.2 Destabilizing Effect of PCBM

PCBM has been shown to stabilize many different conjugated polymers towards photo-oxidation, among them P3HT, Si-PCPDTBT and MDMO-PPV.\cite{1-4} However, in combination with C-PCPDTBT it accelerates polymer degradation. Destabilizing effects have already been reported for other fullerenes, especially for those with small electron affinities.\cite{12} On the basis of the results of our PL and PIA experiments we attempt to provide an explanation for this unusual behavior.

The PIA spectra of all three neat polymer films exhibit a weak triplet signal. While this signal is quenched upon addition of PCBM in the cases of Si-PCPDTBT and P3HT, it is enhanced by up to 50% in the case of C-PCPDTBT. The increase in triplet formation in C-PCPDTBT:PCBM blends compared to neat C-PCPDTBT correlates with the enhanced degradation rate of C-PCPDTBT upon addition of PCBM. This experimental correlation between degradation rate and presence of polymer triplet states is further substantiated by the changes that occur in C-PCPDTBT:PCBM blends when they are processed with DIO. The use of DIO in processing films of C-PCPDTBT:PCBM blends results in significantly less
destabilization (see Figures 5.1 and 5.2) and also reduces the formation of triplets as observed with PIA as shown previously (Chapter 3 and 4).\textsuperscript{[27]}

We can exclude that the triplets observed in PIA of the C-PCPDTBT:PCBM blend originate from intersystem crossing from the $S_1$ state of the polymer, since charge transfer from C-PCPDTBT to PCBM happens on a faster timescale, as indicated by the almost complete polymer fluorescence quenching. However, the presence of the red-shifted structure-less emission in the photoluminescence spectrum of C-PCPDTBT:PCBM indicates the population of a charge transfer (CT) state,\textsuperscript{[26,46]} which can recombine to the polymer triplet state.\textsuperscript{[14,27]} For the other two polymer:PCBM blends no CT state emission is observed.

The population of the polymer triplet state could be the initial step of a well known degradation mechanism involving singlet oxygen. If the energy of the polymer triplet state is higher than that of the oxygen singlet state (0.98 eV), it is able to transfer its energy to the oxygen molecule, thus producing singlet oxygen, which is highly reactive and participates in chemical reactions that damage the polymer itself (e.g. [4+2]cycloaddition to the thiophene ring).\textsuperscript{[47–49]} Considering a typical $S_1$-$T_1$ energy gap of $\sim$0.7 eV in conjugated polymers,\textsuperscript{[13]} the $T_1$ energy should lie around 1.1-1.2 eV for P3HT and around 1 eV for C-PCPDTBT and Si-PCPDTBT.\textsuperscript{[27]} Consequently, population of the polymer triplet state could lead to the formation of singlet oxygen for all of the investigated polymers.

Our PIA measurements show that C-PCPDTBT:PCBM is the only blend film where polymer triplet is formed. This observation may be explained by a more efficient dissociation of the excited states of P3HT:PCBM and Si-PCPDBT:PCBM into free charges due to a higher degree of crystallinity and phase separation compared to the C-PCPDTBT:PCBM blend.\textsuperscript{[24]} Another possible explanation for this phenomenon could be the relative position of the energy level of the respective charge transfer state with respect to the polymer triplet level. The CT state energy ($E_{CT}$) of C-PCPDTBT:PCBM can be extracted from the PL spectrum of the blend film, which shows a maximum at 1.22 eV that was ascribed to the CT state emission. The energy of the CT state of Si-PCPDTBT:PCBM cannot be extracted from the photoluminescence spectrum, since no measurable CT state emission occurs. However, an estimate is possible from the value of the open-circuit voltage ($V_{oc}$) under 1 sun illumination in solar cells using the relationship $E_{CT} = q \cdot V_{oc} + 0.47$ eV, where $q$ is the elementary charge.\textsuperscript{[20]} Devices fabricated using the same active layer coating conditions as in the thin films for optical spectroscopy delivered a $V_{oc}$ of 0.56 V. Therefore for these blends the CT state energy is estimated to be $E_{CT} = 1.03$ eV. In good agreement with this estimation, \textit{Faist et al.} have shown that the CT state
electroluminescence from Si-PCPDTBT:PCBM devices has a maximum occurring at 0.97 eV photon energy.\textsuperscript{[50]} Note that on C-PCPDTBT:PCBM (1:2 weight ratio) devices we measured a considerably higher \( V_{oc} \) (0.69 V), from which \( E_{CT} = 1.16 \) eV can be estimated. On the same devices we measured CT electroluminescence peaked at 1.18 eV. These values are very close to the CT emission maximum observed in photoluminescence on thin films (Figure 5.5a). For P3HT:PCBM solar cells, the \( V_{oc} \) was measured to 0.55 V, resulting in an estimated CT state energy of \( E_{CT} = 1.02 \) eV. Also in this case the estimation of \( E_{CT} \) is in agreement with the electroluminescence signal at 1.05 eV reported by Tvingstedt et al.\textsuperscript{[51]}

Figure 5.7 gives an overview of the different states in the three blends including the involved transitions. As one can see, the energy of the charge transfer state lies above the polymer \( T_1 \) state in the case of C-PCPDTBT:PCBM, which enables population of the polymer triplet state via the CT state. However, the CT state of Si-PCPDTBT:PCBM has approximately the same energy as the Si-PCPDTBT triplet and the P3HT:PCBM state even lies below the respective polymer triplet energy, which impedes polymer triplet population via the CT state in those systems. Thus, this energetic scheme could give an explanation for the formation of polymer triplet exclusively in the case of C-PCPDTBT leading to an enhanced degradation rate in this blend, which correlates with our experimental results.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{state_diagram}
\caption{State diagram of the three investigated polymer:PCBM blends (CT state – charge transfer state between polymer and PCBM; FC – free charge carriers state). The oxygen singlet state energy is indicated by the dashed red line across the graphs.}
\end{figure}
5.4 Conclusions

We investigated the effects of PCBM on the photodegradation of polymers and established at least three mechanisms that are active simultaneously. Two of them stabilize the polymer (excited state quenching, and chemical effects, i.e., radical scavenging and hydroperoxide cleavage). In the case of P3HT, the stabilization is clear, while in Si-PCPDTBT it is less strong. We propose that the stabilization of these two polymers by PCBM can be mainly ascribed to chemical effects while the exciton quenching does not seem to play a significant role. The third, but destabilizing, effect by PCBM is related to the enhanced generation of triplets in these blends via the charge transfer state. In the presence of oxygen, the triplet state may sensitize the formation of chemically active oxygen species (e.g., singlet oxygen), which then would act as oxidants for the polymer. For P3HT and Si-PCPDTBT the triplet populations are reduced in the presence of PCBM. This effect likely contributes to the stabilization of the polymers, although we note that for P3HT it has been reported that singlet oxygen does not play a significant role in the photo-oxidation of P3HT under white light conditions.\textsuperscript{[12,52,53]}

In C-PCPDTBT:PCBM, where the CT state energy is above the polymer triplet state energy, the triplet state may be populated by the deactivation of the CT state. By means of photoinduced absorption we showed that the triplet population in C-PCPDTBT is enhanced upon blending with PCBM. Interestingly, the increased triplet generation correlates with increased photodegradation, suggesting that this CT state deactivation mechanism, when present, plays a role in the photostability of polymer solar cells.
5.5 Experimental section

Materials. P3HT (Mw = 59.5 kg mol⁻¹, PD = 1.49) was purchased from Merck. C-PCPDTBT (Mw = 55.7 kg mol⁻¹, PD = 2.28) was synthesized according to the published route. The preparation of Si-PCPDTBT (Mw = 52.8 kg mol⁻¹, PD = 2.85) has been described in a patent. 1,8-Diiodooctane (DIO) and 2,7-dinitrofluorenone (DNF) were purchased from Aldrich. [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) was purchased from Solenne.

Film Preparation. Thin films of P3HT, C-PCPDTBT and Si-PCPDTBT with optical densities of around 0.75 were prepared under ambient conditions by doctor blading on soda lime glass. P3HT films were prepared from 1% (w/v) polymer solutions in o-xylene, while C-PCPDTBT and Si-PCPDTBT films were prepared from 1% (w/v) and 0.7% (w/v) polymer solutions in chlorobenzene, respectively. Blend films were processed from analogous solutions (same solvents and polymer concentrations) containing different contents of PCBM, DIO or DNF. Prior to polymer deposition, the substrates were cleaned for 15 minutes in acetone and 15 minutes in 2-propanol using an ultrasonic bath. After deposition, the samples were annealed in a nitrogen atmosphere. The P3HT samples were annealed at 140 °C for 1 minute and the C/Si-PCPDTBT samples were annealed at 140 °C for 5 minutes.

Degradation and Absorption Spectroscopy. The samples were degraded by exposing them to the light of a metal halide lamp (AM 1.5, 1000 W m⁻²) in ambient air at a temperature of 45 °C and 10% relative humidity. After certain times of degradation, absorption spectra were recorded with a Perkin Elmer Lambda 35 UV/vis spectrometer. The progress of degradation refers to the loss of absorbance in the absorption maximum of the polymer.

Emission Spectroscopy. To quantify quenching of the excited states of the polymers in dependence of the PCBM and DNF content, photoluminescence (PL) measurements were performed with an Andor Shamrock SR 303i Spectrometer. The P3HT samples were excited with a 405 nm laser with an intensity of 0.95 mW for 10 s and the C/Si-PCPDTBT samples with a 637 nm laser with an intensity of 0.6 mW. In order to exclude contributions of the lasers in the fluorescence spectra, a 550 nm high pass cut-off filter was used for the 405 nm laser and a 700 nm filter for the 637 nm laser.

Near-IR PL spectra were recorded using an Edinburgh Instruments FLSP920 double-monochromator luminescence spectrometer equipped with a nitrogen-cooled near-infrared sensitive photomultiplier (Hamamatsu). All samples for PL studies were encapsulated in nitrogen atmosphere with glass and sealed with Torr Seal (Varian) to avoid degradation of the films during the measurements under ambient air conditions at room temperature. All spectra were corrected for the detection sensitivity of the photomultiplier and for the absorption at the excitation wavelength.

Photoinduced Absorption Spectroscopy. Steady state photoinduced absorption (PIA) spectra were recorded between 0.35 and 2.1 eV (2.5 eV for P3HT based samples) by excitation with a mechanically modulated (275 Hz) laser source and by measuring the change in transmission of a tungsten-halogen probe beam through the sample (ΔT) with a phase sensitive lock-in amplifier after dispersion with a monochromator and detection using Si, InGaAs and cooled InSb detectors. For the C/Si-PCPDTBT based films, the pump photon energy was 1.49 eV (diode laser) with a pump power of 130 mW and a beam diameter of 1 mm. For the P3HT based films, the pump photon energy was 2.41 eV (Ar⁺ laser) with a pump power of 50 mW and a beam diameter of 2 mm. During PIA measurements, the samples were held at low temperature (T = 80 K) and in an inert nitrogen
atmosphere using an Oxford Optistat continuous flow cryostat. The PIA signal (-$\Delta T/T$) was corrected for the photoluminescence, which was recorded in a separate experiment. All spectra were corrected for the absorption at the excitation energy.

### 5.6 References and notes


In this chapter and in chapter 7 C-PCPDTBT is the same material as PCPDTBT described in Chapters 3 and 4. The notation C-PCPDTBT is used to distinguish it from the silicon bridged Si-PCPDTBT.
The effect of PCBM on the photodegradation kinetics of polymers for OPV

Influence of photon excess energy on charge carrier dynamics in a polythiophene:fullerene solar cell

Abstract

We study the influence of photon excess energy, i.e. the difference between photon energy and the energy of the charge transfer (CT) state, on the generation of free extractable charges in bulk heterojunction solar cells. We investigate solar cells comprising poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as electron donor and electron acceptor respectively in the active layer, both as-cast and thermally annealed. To investigate the dynamics of photogenerated charges we use the charge extraction by linearly increasing voltage (CELIV) technique. We find that charges created via excitation of the CT transition at the donor-acceptor interface display dynamics that are indistinguishable from the dynamics of charges generated by excitation of the conjugated polymer at higher photon energy. We support these results by measuring the spectral response of solar cells as function of applied voltage bias. We find that the spectral response related to the direct CT excitation and that related to the above band-gap excitation of P3HT and PCBM have the same dependence on voltage bias. From these results we conclude that excess energy liberated in the photoinduced electron transfer between polymer and fullerene has no influence on the efficiency of free charge generation in P3HT:PCBM blends.

This work has been published:
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6.1 Introduction

An important question in research on polymer solar cells is the mechanism of free charge carrier generation. In organic bulk heterojunction solar cells, photoinduced electron transfer between the donor and acceptor molecules leads to population of a charge transfer (CT) state at the donor-acceptor interface. The residual electrostatic binding energy between electron and hole in the CT state may be considerable; experimental studies indicate a binding energy of 0.1-0.2 eV which is much higher than the thermal energy \( k_B T = 0.025 \) eV.\(^{[1-4]} \) Given the low dielectric constant of organic materials \( (\varepsilon_r = 3-4) \) charges need to be separated over a large distance (10-15 nm) before their electrostatic interaction energy becomes comparable to \( k_B T \). Even though the lifetime of the CT state can be as short as only a few ns,\(^{[5,6]} \) the efficiency of free charge carrier generation can be very high. In optimized polymer solar cells, charge carrier generation occurs with an efficiency close to unity.\(^{[7,8]} \)

The mechanism by which the large energy barrier for charge separation from the CT state is overcome within the short lifetime is not known. Several explanations have been proposed, but no consensus on this issue has yet been reached.\(^{[9,10]} \)

One particular explanation for the efficient charge generation involves the excess energy liberated in the photoinduced electron transfer step leading to the formation of the CT state.\(^{[11-13]} \) In polymer-methanofullerene solar cells containing poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM), there is a large difference in energy between the lowest singlet excited states \( S_1 \) on P3HT (1.9 eV) and on PCBM (1.7 eV) relative to the CT state (1.1 eV).\(^{[14,15]} \) Photoinduced electron transfer from the \( S_1 \) state on PCBM or from the higher lying \( S_1 \) state on P3HT, leads to formation of a ‘hot’ CT state and the 0.6 eV energy dissipated in the electron transfer step may still be available to drive apart the positive and negative charge in the CT state to yield a charge separated state. For this mechanism to be efficient, charge separation needs to be much faster than vibrational relaxation within the manifold of CT states. This mechanism is illustrated in Figure 6.1.

It has been shown that the CT state in the P3HT:PCBM junction can be populated directly from the ground state by illumination with 1.2-1.6 eV photons.\(^{[14,16,17]} \) This opens the possibility to generate ‘cold’ CT states with much less excess energy and to test the abovementioned hypothesis on the importance of the excess energy for charge separation.

By comparing the internal quantum efficiency and the open-circuit voltage (\( V_{oc} \)) for P3HT:PCBM solar cells upon excitation of the lowest excited singlet state of P3HT and under direct excitation of the CT state, Lee et al. conclude that the
Influence of photon excess energy

Influence of excess energy liberated in the electron transfer process is negligible for the formation of free charges.\textsuperscript{[17]}

Here we investigate the influence of excess energy on charge recombination process and on the presence of long-lived, photogenerated charge carriers in P3HT:PCBM photovoltaic cells employing the charge extraction by linearly increasing voltage (CELIV) method.\textsuperscript{[18-20]} In the photo-CELIV experiment, a short light pulse is used to generate carriers (Figure 6.2) and by applying a voltage ramp at a variable delay after the excitation pulse, charge carriers are extracted. During illumination, a compensating bias voltage $V_{\text{bias}}$ comparable in magnitude to $V_{oc}$ is applied to minimize extraction of charge carriers due to built-in electric fields in the cell. During the ramp, the applied bias is lowered to extract long-lived charge carriers by $\Delta V = -2.0$ V, starting from $V_{\text{bias}}$ and reaching a reverse bias voltage $V_{\text{coll}}$ of $\sim -1.5$ V.

![Figure 6.1](image)

**Figure 6.1:** Schematic Jablonski diagram illustrating the formation of free charges in the charge separated state (CSS) via $S_1 \leftarrow S_0$ excitation or via the charge transfer transition directly populating the charge transfer (CT) state. The dashed lines indicate the vibrational manifold of the CT band.

![Figure 6.2](image)

**Figure 6.2:** (a) Schematic diagram of the photo-CELIV method showing timing of the laser pulse and voltage ramp. $V_{\text{bias}}$ indicates the compensating bias that is applied to the solar cell and $V_{\text{coll}}$ indicates the minimum of the voltage ramp. (b) The electrical circuit used to determine the current and voltage through the solar cell.
6.2 Results and discussion

Results from photo-CELIV measurements for as-cast P3HT:PCBM solar cells are shown in Figure 6.3. In as-cast P3HT:PCBM films the mixing of the donor and acceptor is relatively intimate and large semi-crystalline domains of P3HT and PCBM have not yet been formed.[21] Figure 6.3a shows results for direct excitation of the CT state in P3HT:PCBM using 1.55 eV excitation. An average number density of light induced extractable charge carriers, \( n_{\text{avg}} \), is determined by integrating the photoinduced excess current during the extraction pulse over time and dividing by the volume of the bulk heterojunction. \( n_{\text{avg}} \) is plotted as a function of delay time between illumination pulse and the onset of the charge extraction ramp. As can be seen, 5 µs after the light pulse the cell holds around \( 10^{15} \) extractable carriers per cm\(^3\). With increasing delay time, \( n_{\text{avg}} \) decays following a power-law. Upon lowering the fluence \( I \) of the laser pulse used to illuminate the cell, fewer photoinduced charge carriers can be extracted. Figure 6.3a shows results for three different fluencies by attenuating the primary beam with fluence \( I_0 = 4 \text{ mJ cm}^{-2} \) per pulse.

The range of fluences used for each measurement, was chosen such that the deviations in linearity of the magnitude of the spontaneous photocurrent with light intensity under short-circuit conditions were less then <5%. To illustrate the linearity, we show in the inset of Figure 6.3c the dependence of the spontaneous, time-integrated photocurrent as a function of fluence. For the low fluences used in the CELIV experiment, the number of extracted carriers varies linearly with fluence. This excludes two-photon absorption by either P3HT or PCBM as excitation mechanism in the charge generation process. Moreover, insertion of additional low-pass cut-off filter to eliminate any high energy photons with energy > 1.59 eV did not result in any detectable change in the signal for either spontaneous photocurrent or delayed extraction current.

The dynamics of the charge carriers created by sub-gap excitation can be compared to the case of above-gap excitation, where 2.14 eV photons are used. The results are shown in Figure 6.3b,d. Also for excitation with 2.14 eV photons we observe a power-law type decay for the extractable charge carriers, with an exponent that is very similar to the case of sub-gap excitation via the CT transition.

In order to compare carrier dynamics for direct and indirect population of the CT states more quantitatively, we have determined the fraction of the total number of extractable carriers which can still be extracted after a delay time (\( \tau_{\text{delay}} \), Figure 6.2). To obtain this surviving fraction, first the total number of extractable photogenerated carriers was determined by integrating the photocurrent upon application of a constant
−2 V bias during pulsed illumination. Dividing the number of charge carriers after a delay time by this total number of extractable carriers then yields the fraction. For the two photon energies used, 1.55 eV (Figure 6.3c) and 2.14 eV (Figure 6.3d), and a delay of 5 µs we find a fraction of extractable carriers of 0.12. The similarity in the fraction for sub-gap and above-gap excitation shows that the excess energy liberated during photoinduced electron transfer from the excited singlet state has a negligible influence on the recombination dynamics of the charge carriers. By comparing the fraction determined for different excitation fluencies, we observe that for long delay times, the probability for survival of charge carriers becomes higher at lower light intensity (Figure 6.3c). This provides direct evidence for bimolecular recombination kinetics of the long-lived carriers, implying that a significant fraction of the directly created CT states has dissociated into free carriers. The observation of bimolecular recombination of photo-generated charges in P3HT:PCBM films is consistent with previous observations. \[22-25\]

We note that the intensity of the 1.55 eV beam is $10^2$ higher than for the 2.14 eV light. Lee et al. report that the absorption at 1.55 and 2.14 eV differs by $10^2$. Hence, the density of primary photoexcitations should be similar for the two different excitation beams. The experimental observation of a similar density and fraction of extracted carriers for the two excitation photon energies, indicates that the charge carrier dynamics for the sub-gap and above-gap excitation are very similar.

The fraction of charges extractable after a delay determined from the experiments contains information on the efficiency of charge generation. To explain this we write the overall efficiency of charge collection $\eta$ in a solar cell as the product of efficiencies for absorption ($\eta_{\text{abs}}$), diffusion of excitations to the donor-acceptor interface and formation of a CT state ($\eta_{\text{CT}}$), dissociation of the CT state into free carriers ($\eta_{\text{dis}}$), and collection of the charges ($\eta_{\text{coll}}$): $\eta = \eta_{\text{abs}} \eta_{\text{CT}} \eta_{\text{dis}} \eta_{\text{coll}}$. We assume that $\eta_{\text{abs}}$ and $\eta_{\text{CT}}$ are independent of electric bias ($V_{\text{bias}}$) and charge carrier density ($\rho$), but that $\eta_{\text{dis}}$ may depend on photon energy ($h\nu$), the magnitude of $V_{\text{bias}}$ at which the device is held during the delay $\Delta t$, and the voltage $V_{\text{coll}}$ used for collecting the charges, hence, $\eta_{\text{dis}} = \eta_{\text{dis}}(h\nu, V_{\text{bias}}, \Delta t, V_{\text{coll}})$. Further, $\eta_{\text{coll}}$ will depend on $\rho$ (in case of bimolecular recombination) and $V_{\text{coll}}$ such that $\eta_{\text{coll}} = \eta_{\text{coll}}(\rho, V_{\text{coll}})$. The ratio $f$ of the number of charges extracted using the $V_{\text{coll}}$ (−2 V) pulse after a delay $\Delta t$, at which the cell was kept at $V_{\text{bias}}$ and the number of charges extracted under constant $V_{\text{coll}}$ (−2 V) bias can then be expressed as:

$$f = \frac{\eta_{\text{dis}}(h\nu, V_{\text{bias}}, \Delta t, V_{\text{coll}}) \eta_{\text{coll}}(\rho, V_{\text{coll}})}{\eta_{\text{dis}}(h\nu, V_{\text{coll}}, 0, V_{\text{coll}}) \eta_{\text{coll}}(\rho', V_{\text{coll}})},$$

(1)
In Eq. (1) the term $\eta_{\text{dis}}(h\nu, V_{\text{coll}}, 0, V_{\text{coll}})$ in the denominator signifies that $V_{\text{bias}} = V_{\text{coll}}$ and $\Delta t = 0$ under constant collection bias. From Eq. (1) the ratio of the fractions of extractable carriers after a delay $\Delta t$ for sub-gap ($h\nu_{sg}$) and above-gap ($h\nu_{ag}$) excitation equals:

$$\frac{f(h\nu_{sg}, \Delta t)}{f(h\nu_{ag}, \Delta t)} = \frac{\eta_{\text{dis}}(h\nu_{sg}, V_{\text{bias}}, \Delta t, V_{\text{coll}})}{\eta_{\text{dis}}(h\nu_{ag}, V_{\text{bias}}, \Delta t, V_{\text{coll}})} \cdot \frac{\eta_{\text{dis}}(h\nu_{ag}, V_{\text{coll}}, 0, V_{\text{coll}})}{\eta_{\text{dis}}(h\nu_{sg}, V_{\text{coll}}, 0, V_{\text{coll}})}$$

(2)

In Eq. (2) we assume that $\eta_{\text{coll}}$ is independent of the small difference between the charge carrier densities $\rho_{ag}$ and $\rho_{sg}$ that exist for above-gap excitation and sub-gap excitation. Figures 6.3a and 6.3b confirm that the carrier density and dynamics in the two CELIV experiments with $h\nu_{sg} = 1.55$ eV and $h\nu_{ag} = 2.14$ eV are virtually identical. At sufficiently negative $V_{\text{coll}}$ it can be expected that virtually all interfacial CT states will dissociate into free carriers, independent of how they were generated. In that case the rightmost term in Eq. (2) cancels and we find that:

$$\frac{f(h\nu_{sg}, \Delta t)}{f(h\nu_{ag}, \Delta t)} = \frac{\eta_{\text{dis}}(h\nu_{sg}, V_{\text{bias}}, \Delta t, V_{\text{coll}})}{\eta_{\text{dis}}(h\nu_{ag}, V_{\text{bias}}, \Delta t, V_{\text{coll}})}$$

(3)

Eq. (3) suggests that the ratio of the fractions reflects the dissociation ratio for sub-gap and above-gap excitation. Figure 6.3c and 3d show that $f(h\nu_{sg}, \Delta t) \approx f(h\nu_{ag}, \Delta t)$ and, hence, we find that $\eta_{\text{dis}}(h\nu_{sg}, V_{\text{bias}}, \Delta t, V_{\text{coll}}) = \eta_{\text{dis}}(h\nu_{ag}, V_{\text{bias}}, \Delta t, V_{\text{coll}})$.
Influence of photon excess energy on charge carrier dynamics…

To find support for this conclusion, we performed external quantum efficiency (EQE) measurements as function of photon energy and applied bias voltage (Figure 6.4). As expected, the EQE has three main spectral components. Below 1.65 eV, the contribution of the CT absorption is visible. Above 1.7 eV, charge generation via the S_1 ← S_0 for PCBM and P3HT can be seen. When normalizing the EQE to unity at 2.53 eV, we notice that the applied bias, ranging from V_{bias} ≈ V_{oc} to -2 V, has no significant effect on the EQE under direct excitation of the CT transition. This implies

Figure 6.3: Extracted photoinduced charge carriers in an as-cast P3HT:PCBM bulk heterojunction cell as function of delay time between pulsed illumination and bias ramp. (a) The average number density of extracted charges (n_{avg}) upon excitation via the charge transfer transition at 1.55 eV and V_{bias} = 0.52 V. (b) n_{avg} upon excitation of the polymer S_1 ← S_0 transition at 2.14 eV and V_{bias} = 0.44 V. In the inset, the black squares show n_{avg} at constant zero applied bias and the red circles n_{avg} at a constant applied bias of -2 V. (c), (d) fraction of the total number of extractable carriers at constant −2 V bias which can still be extracted after a delay for 1.55 and 2.14 eV, respectively, plotted versus delay time.
that the electric field $V_{\text{bias}}$ does not change the ratio between charge formation for above-gap and sub-gap excitation. In the EQE experiment a special condition of Eq. (3) occurs, namely $\Delta t = 0$ and $V_{\text{bias}} = V_{\text{coll}}$. As the ratio of the EQE for above-gap and sub-gap excitation is found to be independent of $V_{\text{bias}}$, it follows that the relation between excitation photon energy and dissociation of charges from the interface must be such that: \[ \eta_{\text{dis}}(h\nu_{\text{sg}}) = \eta_{\text{dis}}(h\nu_{\text{ag}}). \] This conclusion is the same as the one inferred from the CELIV experiments.

We note that for excitation photon energies of 2.0 eV there is a relatively small variation of normalized EQE with applied bias. We tentatively attribute this to a variation in the collection efficiency. Near 2.0 eV crystalline domains of P3HT can be selectively excited and in these ordered domains hole transport is expected to be faster than in the disordered phase. This interpretation is supported by EQE measurements on thermally annealed cells (Figure 6.4 b). After annealing, most of the P3HT will be in crystalline phase and transport limitations should be lifted. Indeed the measurements now show a complete independence of the normalized EQE value with respect to applied bias.

From the similarity of the fraction of carriers extractable after a delay for sub-gap and above-gap excitation we conclude, making use of Eq. (3), that the efficiency of dissociation of the CT state under open-circuit conditions is virtually independent of the excitation photon energy used. The hypothesis mentioned in the introduction that ‘cold’ CT state lacking excess energy can only give rise to strongly bound geminate charge pairs has to be dismissed for P3HT:PCBM films.
Figure 6.4: Normalized external quantum efficiency (EQE) for (a) as-cast and (b) thermally annealed P3HT:PCBM cells as function of excitation photon energy and applied bias.

Photo-CELIV characterization of thermally annealed P3HT:PCBM cells are shown in Figure 6.5. Thermal annealing results in a considerably enhanced performance of the solar cell as a result of more coarse phase separation and enhanced crystallinity of both P3HT and PCBM.\[21\] Comparing the photo-CELIV results at 1.55 and 2.14 eV excitation, we find that also for annealed cells, the excess energy dissipated in the carrier generation process has negligible influence on the fraction of long-lived charge carriers. In contrast to the as-cast heterojunctions, charge carrier dynamics in annealed P3HT:PCBM films results in an approximately exponential decay of the number of extractable carriers with delay time. The decay rate is virtually independent of the excitation fluence. This rapid, monomolecular decay may be rationalized by rapid diffusion of carriers during the delay followed by recombination at the electrodes. The occurrence of this particular lifetime limiting process in annealed cells, is consistent with the known fact that thermal annealing significantly improves the transport properties,\[26\] and that bimolecular recombination in thermally...
annealed P3HT:PCBM films is significantly suppressed as compared to as-cast films.\cite{24, 25} In as-cast films, diffusion to the contacts would be slower, resulting in carrier lifetimes limited by bimolecular recombination.

**Figure 6.5:** Extracted photoinduced charge carriers in a thermally annealed P3HT:PCBM bulk heterojunction cell as function of delay time. (a) $n_{\text{avg}}$ after CT excitation at 1.55 eV photon energy. $V_{\text{bias}}=0.48$ V. (b) $n_{\text{avg}}$ after $S_1 \leftrightarrow S_0$ excitation at 2.14 eV. $V_{\text{bias}}=0.44$ V. (c), (d) fraction of the total number of extractable carriers at constant $-2$ V bias which can still be extracted after a delay, plotted versus delay time.
6.3 Conclusions

In conclusion, photo-CELIV measurements provide a means to compare the recombination dynamics in polymer solar cells. In combination with EQE measurements, we find that excess energy liberated in photocarrier generation by photons with energy far above the energy of the CT state, has no significant effect on the charge generation and recombination process. This indicates that in P3HT:PCBM blends a large excess energy in the electron transfer step, is not a strict requirement for free carrier generation.
6.4 Experimental section

Solar cells. Photovoltaic devices were made by spin coating poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (Clevios P, VP Al4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). The photoactive layer was deposited by spin casting in air at 1000 rpm, using a 1:1 (v:v) chloroform: chlorobenzene solution containing 15 mg mL\(^{-1}\) P3HT (Rieke, \(M_n < 50\) kg mol\(^{-1}\), 98% regioregular) and 15 mg mL\(^{-1}\) [6,6]-phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM) (Solenne). The metal electrode, consisting of LiF (1 nm) and Al (100 nm), was deposited by vacuum evaporation at \(\sim 3 \times 10^{-7}\) mbar. Thermal annealing of cells was done at 120 °C for 15 minutes after deposition of the top metal contact. The active area of the cells was 0.091 cm\(^2\) and the thickness of the active layer was 200 nm. Under \(~1\) sun white light illumination (tungsten-halogen lamp with a Schott GG385 UV filter and a Hoya LB120 daylight filter at 100 mW cm\(^{-2}\)) the pristine devices showed a short-circuit current (\(J_{sc}\)) of 5.8 mA cm\(^{-2}\), a fill factor (FF) of 0.51 and an open-circuit voltage (\(V_{oc}\)) of 0.58 V, resulting in a maximum power point (MPP) of 1.7 mW cm\(^{-2}\). After thermal annealing, the \(J_{sc}\) increased to 7.2 mA cm\(^{-2}\), the FF to 0.68 and the \(V_{oc}\) decreased to 0.51 V, resulting in an MPP of 2.5 mW cm\(^{-2}\).

Photo-CELIV. For photo-CELIV with direct excitation of the CT states, short pulses from an amplified Ti:sapphire laser were used (photon energy 1.55 eV, pulse duration 10\(^2\) fs, fluence \(I_0\) 4 mJ cm\(^{-2}\) per pulse, spot size 0.07 cm\(^2\)). To excite into the S\(_1\) state of P3HT, the second harmonic of the output of an OPA pumped by the Ti:sapphire laser was used (photon energy 2.14 eV, fluence \(I_0\) of 0.68 \(\mu\)J cm\(^{-2}\) per pulse and spot size 0.03 cm\(^2\)). The fluence was varied using neutral density filters. Voltage ramps were generated using an Agilent 33250 A arbitrary wave generator. A compensating voltage (\(V_{bias}\), See Figure 6.2) was applied to minimize charge extraction before the start of the voltage ramp. The length \(\tau\) of the voltage ramp was 12.5 \(\mu\)s. The extraction voltage \(V_{min}\) equals: \(V_{bias} - \Delta V = V_{bias} - 2.0\) V\(\equiv -1.5\) V. A 50 Ω probe resistor was used to record the transient photocurrent through the solar cell using an oscilloscope. The number of photogenerated charge carriers extracted was calculated by integrating the difference between the extraction currents upon application of the voltage ramp in dark and after pulsed illumination. Transient currents were determined averaging over \(10^3\) laser pulses and the statistical error of measurement was estimated by triplicating each transient current experiment.

EQE measurements. EQE measurements were done in a homebuilt setup, with the devices kept in a nitrogen filled box with a quartz window and illuminated through an aperture of 2 mm. Mechanically modulated (Stanford Research, SR 540) monochromatic (Oriel, Cornerstone 130) light from a 50 W tungsten halogen lamp (Osram 64610) was used as probe light, in combination with continuous bias light from a solid state laser (B&W Tek Inc. 532 nm) to create a representative illumination intensity for 1 sun conditions. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Stanford Research Systems SR830). Variable voltage bias over the cell was applied by the lock-in amplifier.
6.5 References

Abstract

We investigate the role of photon energy on the generation efficiency of free charges at the donor-acceptor interface in bulk heterojunction solar cells. The bias voltage dependence of photocurrent was probed for excitation with different photon energies below and above the optical band gap. In C-PCPDTSBT:PCBM solar cells charges generated via excitation of the low energy charge transfer (CT) state that is situated below the optical band gap need more voltage to be extracted than charges generated with excitation above the optical band gap. We interpret these experiments in terms of a lower effective binding energy of the electron and hole in the CT state when the excitation is above the band gap. Compared to C-PCPDTSBT, the silicon analogue Si-PCPDTSBT shows improved performance in photovoltaic cells with PCBM, providing higher fill factor and short-circuit current. C-PCPDTSBT:PCBM and Si-PCPDTSBT:PCBM blends differ in the nanoscale phase separation, which increases in Si-PCPDTSBT based blends. In the Si-PCPDTSBT:PCBM solar cells we see no effect of the photon energy on the electric field dependence of the dissociation efficiency of the charge transfer state. Given the very similar electronic properties of C-PCPDTSBT:PCBM and Si-PCPDTSBT:PCBM, these results suggest that the nanomorphological properties of the bulk heterojunction is crucial element in the generation of free charges from lower energy CT states.
7.1 Introduction

The dissociation of Coulombically bound charge transfer (CT) states into free electrons and holes at an organic donor-acceptor (D–A) interface is a critical process in the operational mechanism of efficient organic solar cells. At present the mechanistic details of this process are only partly understood: the electron and hole in the CT state can be expected to be strongly bound across the heterojunction,\cite{1,2} making the dissociation into free charges problematic. However many devices displaying high quantum efficiency of charge generation at short circuit have been demonstrated.\cite{3-6} A number of mechanisms have been invoked to explain the high efficiency of free charge generation at the hetero-junction, including disorder, ‘hot’ CT states, permanent dipoles, and delocalization of the excitations.\cite{7} Here we investigate the influence of excess photon energy on the dissociation of CT states into free charges. The excess photon energy is defined as the difference between the energy of the incoming photons ($h\nu$) and the energy of the bottom of the CT band ($E_{\text{CT}}$).

Evidence of a correlation between available excess energy and charge generation efficiency has been reported in literature.\cite{8,9} On the other hand, in Chapter 6 we have shown that the availability of photon excess energy does not influence the efficiency of CT dissociation into free charges in P3HT:PCBM blends. Similar conclusions on P3HT:PCBM and other blends were reached recently by other authors.\cite{10-12} To explain the discrepancy between these observations a better understanding of the mechanism of free charge generation at the donor-acceptor heterojunction is needed. Such an improved understanding would be beneficial for the optimization of device power conversion efficiencies. In fact, the need of excess energy for efficient CT dissociation would impose a limit to the maximum attainable open-circuit voltage ($V_{\text{oc}}$), since the latter scales with the energy of the CT state.

By studying the electric field dependence of the yield of free charges generated with different photon energies, the role of the photon excess energy on the charge generation mechanism can be investigated. An appreciable change in the field dependence of the yield of current generated with different photon energies has been observed in diodes consisting of a pure polymer active layer.\cite{13-15}

In this work we use the electrical field dependence of charge generation to investigate the influence of the photon excess energy on CT state dissociation in D-A bulk heterojunction solar cells. Specifically we measure the external quantum efficiency (EQE) of solar cells as function of photon energy ($h\nu$) for different bias voltages ($V \leq V_{\text{oc}}$) applied to the solar cell. The EQE is scanned over a wide range of photon energies, corresponding to sub band gap (CT$\rightarrow$S$_0$) and above band gap
We also determine the energy of the bottom of the CT state band \( (E_{CT}) \) from the CT electroluminescence spectrum. If the (excess) photon energy has an effect on the efficiency of CT dissociation, the yield of free charges as measured via the EQE with sub band gap excitation \( (E_{CT} < h\nu < E_{S1}) \) should display a stronger field dependence compared to the EQE with above band gap excitation \( (h\nu > E_{S1}) \). The implicit assumption in this experiment is that the transport and collection of free charge carriers are independent of the photon excitation energy and that only the generation efficiency of free carriers varies with photoenergy.

The system we investigate is the C-PCPDTBT:PCBM blend. The photocurrent of C-PCPDTBT:PCBM solar cells shows a strong field dependence, resulting in a rather low fill factor in the \( J-V \) curve. Lenes et al.\textsuperscript{[16]} have reproduced the \( J-V \) characteristic of C-PCPDTBT:PCBM solar cells by means of numerical drift-diffusion simulations, using an Onsager-Braun like field dependence of charge generation. They explained the low fill factor of C-PCPDTBT:PCBM solar cells by arguing that the photocurrent in these cells is limited by the strong recombination of the CT state. Experimental evidence for strong CT recombination was given by the CT photoluminescence observed in C-PCPDTBT:PCBM blends, as well by the observation that the CT state recombines to triplet states on C-PCPDTBT (Chapter 3).

Here we show that the bias voltage dependence of the photocurrent exhibited by C-PCPDTBT:PCBM solar cells differs for different photon energies, and becomes stronger when \( E_{CT} < h\nu < E_{S1} \). We numerically simulate the experiments using the separation distance between electron and hole in the CT pair as a pure fitting parameter and estimate an effective binding energy of the CT state precursor of free charges as function of the available excess energy. We find that this effective binding energy decreases as the photon energy increases for \( E_{CT} < h\nu \approx E_{S1} \) and is practically constant for \( h\nu > E_{S1} \). These results indicate that, depending on the energy of the exciting photon, free charges are generated from different intermediate CT states.

We also investigate Si-PCPDTBT:PCBM solar cells, which show improved power conversion efficiency due to a considerably higher fill factor. The only difference in chemical structure between the two systems is the nature of the bridging atom in the CPDT unit, which is either a carbon or a silicon atom (Figure 7.1). This small structural change induces an interesting difference in the behavior of the polymers in the bulk heterojunction with PCBM. The nanoscale morphology of the C-PCPDTBT:PCBM or Si-PCPDTBT:PCBM blends differs, going from very finely mixed (carbon) to coarser phase separation (silicon).\textsuperscript{[17]} In Si-PCPDTBT:PCBM blends the CT state photoluminescence is reduced compared to C-PCPDTBT:PCBM blends.
and no generation of triplets is observed (Chapter 5), suggesting a higher efficiency of CT dissociation.

![Chemical structure of X-PCPDTBT and PCBM](image)

**Figure 7.1:** chemical structure of the materials used and J-V characteristics under white light 1000 W/m² for C-PCPDTBT:PCBM (grey dots) and Si-PCPDTBT:PCBM (black dots) solar cells. The red line represents the numerical simulation of the illumination J-V curve of the C-PCPDTBT:PCBM solar cell.

By determining the bias voltage dependence of photocurrents generated with different photon energies in Si-PCPDTBT:PCBM, we find that photocurrents generated with vanishing small excess energy display the same voltage dependence as those generated with excess energies of 1-2 eV. A stronger field dependence for photocurrent generated via the direct CT absorption is observed only close to $V_{oc}$. We
concluded that the amount of excess energy available to the system has no influence on the generation of free charges at the Si-PCPDTBT:PCBM heterojunction, if not at very low electric fields such those present close to $V_{oc}$.

7.2 Results and discussion

7.2.1 Measurements of current density and spectral response as function of voltage bias

Figure 7.1 shows the $J$-$V$ characteristics under 1000 W/m$^2$ white light illumination of C-PCPDTBT:PCBM and Si-PCPDTBT:PCBM solar cells. Both cells were prepared in a 1:2 polymer:PCBM weight ratio. Comparing C-PCPDTBT to Si-PCPDTBT, the fill factor ($FF$) and short-circuit current ($J_{sc}$) improve considerably, going from 0.39 to 0.62 and from 7 to 12 mA/cm$^2$ respectively, resulting in a maximum extractable power improving from 1.9 to 4.2 mW/cm$^2$.

Figure 7.2a shows the normalized EQE of a C-PCPDTBT:PCBM solar cell for photon energies ranging from 1.24 to 3.1 eV and an applied bias voltage between $-3$ and $+0.65$ V. For this cell $V = +0.65$ V corresponds to a value slightly lower than $V_{oc}$ under ~1 sun illumination. The EQE was measured with modulated monochromatic light using lock-in detection. To create conditions representative for ~1 sun operational illumination intensity, the measurements were performed with a constant background illumination (see Experimental section). The curves in Figure 7.2a are normalized to the maximum of EQE, which always occurs at the same photon energy ($\sim 1.75$ eV) and coincides with the maximum of optical absorption of the blend. In Figure 7.2a only a small selection of the complete set of measurements is displayed, namely the normalized EQE spectra recorded at $+0.65$, 0, and $-3$V. The maximum of EQE increased from 9% at 0.65 V to 53% at $-3$ V, passing from 28% at 0 V.

The EQE spectra are shown in a semilogarithmic plot to better visualize the different absorption bands. The low energy absorption is attributed to the CT$\leftarrow S_0$ transition.$^{[18,19]}$ The $S_n$$\leftarrow S_0$ of C-PCPDTBT transitions give rise to the absorption band with onset at $\sim 1.4$ eV, as measured on thin films. The contribution of the absorption by C-PCPDTBT to the EQE extends to the UV. Around 2.5 eV also a contribution from PCBM becomes appreciable. The EQE for excitations via the C-PCPDTBT and PCBM absorption bands is between 10 and 100 times higher than for the CT band.
Figure 7.2: (a) Normalized EQE spectra of a C-PCPDTBT:PCBM solar cell at three different applied voltage biases. The inset shows the normalized EQEs in the low energy band. The blue curve represents the electroluminescence from the same device obtained running the device at 3 V forward bias. (b) EQE recorded at $\hbar \nu = 1.31$ eV photon energy as function of applied bias, normalized to the EQE at $\hbar \nu = 1.75$ eV.
Figure 7.2a shows no significant change in spectral shape with applied bias for photon energies above ~1.5 eV that correspond to excitation above the optical band gap. In contrast, for photon energies below 1.5 eV, \textit{i.e.} sub optical band gap excitation, the normalized EQEs at reveal a small, but significant, monotonous increase going to reverse bias. The inset in Figure 7.2a illustrates that the increase is higher at the lower photon energies. Figure 7.2b depicts the normalized EQE recorded at \( h\nu = 1.31 \) eV as function of applied voltage bias. The change in the normalized EQE amounts to ~30% going from 0.65 to –3 V bias.

Figure 7.2a also shows the electroluminescence from the same device measured by applying a forward bias of \( V = +3 \) V. We attribute the observed emission to the radiative recombination of the CT state,\(^{[20]}\) which is formed by injected electrons and holes that meet at the heterojunction. We use the photon energy of the maximum of electroluminescence intensity as a measure of the energy of the bottom of the CT band: \( E_{CT} = 1.18 \) eV.

Figure 7.3a shows the corresponding EQE measurements for a Si-PCPDTBT:PCBM solar cell at \( V = +0.5, 0, \) and –2.2 V, normalized at the maximum of polymer absorption \( (h\nu = 1.77 \) eV). In this solar cell \( V_{oc} = 0.56 \) V. At \( V = +0.5 \) V the EQE signal became undetectable for photon energies below 1.25 eV. The maximum of EQE has an absolute value of 29% at \( V = +0.5 \) V, increasing to 50% at short circuit, and to 0.58% at –2.2 V. The assignment of the EQE bands to CT\( \leftarrow \)\( S_0 \) and S\( _1\leftarrow S_0 \) excitations is indicated in Figure 7.3a and does not differ significantly from the assignment for C-PCPDTBT:PCBM (Figure 7.2a). Given the very similar chemical structure of the two polymers, the optical properties are expected to be also similar. The Si-PCPDTBT:PCBM did not show any detectable electroluminescence from the CT state, in accordance with previous results.\(^{[17]}\) Hence we use the linear relation between \( E_{CT} \) and \( V_{oc} \) \((E_{CT} \sim q \cdot V_{oc} + 0.5 \) eV,\(^{[21]}\)) to estimate that \( E_{CT} \) in the Si-PCPDTBT:PCBM blend is ~0.1 eV less than in the C-PCPDTBT:PCBM blend.

Figure 7.3a reveals that for the Si-PCPDTBT:PCBM solar cell there is no measurable change in the shape of the EQE in the bias range \(-2.2 < V < 0 \) V. A change in spectral shape of the EQE is only observed in the bias range \(0 < V < +0.5 \) V, at photon energies between 2.5 and 3 eV, and below 1.5 eV. In these two regions of the EQE spectrum more bias is required to extract charges compared to those created by exciting between 1.5 and 2.5 eV. The inset in Figure 7.3a shows the normalized spectra at three different biases in the low energy region below 1.5 eV. The normalized spectra recorded at –2.2 and 0 V are virtually identical. The normalized EQE recorded at +0.5 V deviates from the other two spectra.
Figure 7.3: (a) Normalized EQE spectra of a Si-PCPDTBT:PCBM solar cell with varying applied electrical bias. The inset shows the normalized EQEs in the low energy band. (b) EQE recorded at 1.31 eV photon energy as function of applied bias, normalized to the EQE at 1.77eV.
The behavior of the EQE as function of bias at low photon energy is shown in Figure 7.3b. Here the EQE recorded at $h\nu = 1.31$ eV and normalized to the values at $h\nu = 1.77$ eV is shown as function of applied voltage bias. Between $-2.2$ and $+0.3$ V the normalized EQE values are essentially constant with bias. The normalized EQE reduces substantially only above 0.4 V.

The Si-PCPDTBT polymer is known to aggregate more strongly than C-PCPDTBT. The spectral response related to Si-PCPDTBT falls in the ~1.6-2.1 eV region. Regions in the bulk with lower degree of order could be present. In these regions the transport of photogenerated charges is expected to be more problematic and therefore more field dependent than in the more ordered domains. We tentatively attribute the stronger field dependence observed between 2.5 and 3 eV to lower collection efficiency of charges created in less ordered regions of the bulk. We observed a similar behavior on the EQE spectral dependence on bias of P3HT:PCBM solar cells (Chapter 6).

Summarizing, the spectral shape of the EQE changes with applied bias for C-PCPDTBT:PCBM solar cells in the low energy part of the spectrum, corresponding to direct absorption to the CT state. Charges created via excitations in this part of the spectrum require more bias voltage to be dissociated compared to charges created via excitations of C-PCPDTBT or PCBM. Compared to C-PCDPTBT:PCBM cells, the bias voltage dependence of the EQE spectral shape is much smaller in Si-PCPDTBT:PCBM solar cells. A barely detectable change of the low energy part of the spectrum appears only for bias voltages between short circuit and open circuit. Si-PCPDTBT:PCBM devices do not give any measurable electroluminescence in forward bias. For C-PCPDTBT:PCBM devices, instead, a clear CT electroluminescence is observed.

### 7.2.2 Numerical modeling of photocurrents on C-PCPDTBT:PCBM

We now make the assumption that the transport properties of free carriers are independent of the energy of the primary photo-excitations. With this assumption, the comparison of the bias dependence of extracting charges generated with different photon energies reduces to a comparison of the bias dependence of the separation of the CT state into free charges at the heterojunction. At this point one might argue that with different photon energies free charges are generated which have different CT states as precursors.

To investigate the nature of the CT states as precursor states to free charges, we analyzed the results by means of numerical simulations. We used numerical one-dimensional drift-diffusion simulations to reproduce the dependence of the EQE on
the applied bias at each photon energy $h\nu$. In the numerical simulations, the field dependence of charge generation is treated using the Onsager-Braun model for the dissociation of the CT state.\textsuperscript{[22-24]} In the Onsager-Braun model the field dependent rate of CT dissociation $k_d$ is described as

\begin{equation}
    k_d(E,T) = k_R \frac{3}{4\pi R_{cc}^3} e^{-E_B/k_B T} \frac{J_1(2\sqrt{-2b(E,T)})}{\sqrt{-2b(E,T)}}
\end{equation}

where $R_{cc}$ is the electron-hole separation distance in the CT state and $E_B$ is the binding energy, expressed as $E_B = q^2/4\pi\varepsilon_0\varepsilon_r R_{cc}$, with $\varepsilon_r$ the dielectric constant of the medium. $J_1$ is the Bessel function of order 1 and $b$ is given by $b(E,T)=q^3E/8\pi\varepsilon_0\varepsilon_r k_B^2T^2$. Finally, $k_R = q<\mu>/\varepsilon_0\varepsilon_r$ is a Langevin type bimolecular recombination rate, with $<\mu>$ the average charge mobility. In the model, the field and temperature dependent probability $P(E,T)$ of CT dissociation is calculated as $P(E,T) = k_d(E,T) / [k_d(E,T) + k_f]$, where $k_d(E,T)$ is the rate of dissociation into free charges and $k_f$ is the rate of CT recombination.

To account for disorder in the blend, a distribution of CT states having different separation distances was incorporated into the numerical simulations. To this purpose a normalized distribution function $f(R_{cc},y)$ was used as proposed by Mihailetchi et al.:\textsuperscript{[25]}

\begin{equation}
    f(R_{cc},y) = \frac{4}{R_{cc}^3\sqrt{\pi}} y^2 e^{-y^2/R_{cc}^2}
\end{equation}

The dissociation probability $P$ is calculated as the integrated probability over the distribution of separation distances, so that:

\begin{equation}
    P(E,T) = \int_0^\infty p(E,T,y) f(R_{cc},y) dy
\end{equation}

where $p(E,T,y)$ is the dissociation probability at a specific distance $y$. The procedure used for the numerical simulations has been described in detail by Koster et al.\textsuperscript{[26]} (see also Experimental section).

We are aware of the fact that the Onsager-Braun model might not correctly capture all the microscopic physical details of the complex kinetics of the CT dissociation process.\textsuperscript{[27,28]} However, here we use this model as a tool to describe the bias dependence of the EQE($h\nu$) data in terms of a field dependent dissociation of the CT state and parameterize the experimental data in terms of an effective electron-hole separation distance and an effective binding energy. We simulate the photocurrent recorded at different photon energies as function of the bias voltage and we fit the results to the experimental data using $R_{cc}$ as fit parameter. The correlation between $R_{cc}$ and the energy of the exciting photons can then be evaluated. This analysis was
possible for the C-PCPD-TBT:PCBM cells. For the Si-PCPD-TBT:PCBM cells the change in dependence on field at different photon energies was too minute to obtain meaningful information.

The procedure used is the following: first the $J-V$ characteristic of the C-PCPD-TBT:PCBM cell under constant white light illumination (Figure 7.1) was simulated. The best fit was obtained using $R_{cc} = 1.9$ nm as separation distance of the electron and hole in the CT state. The relevant parameters used in the simulation are shown in Table 7.1 and are similar to the ones used by Lenes et al.\textsuperscript{[16]} The EQE of a solar cell is given by $\text{EQE}(h\nu) = \eta_{abs}(h\nu) \cdot \text{IQE}(h\nu)$, where $\eta_{abs}(h\nu)$ is the efficiency of photon absorption at a given wavelength and IQE is the internal quantum efficiency. $\eta_{abs}(h\nu)$ is considered to be independent on the applied bias in our model. Conceptually, the IQE can be considered as being determined by three consecutive processes, photoinduced charge transfer to produce a CT state, dissociation of the CT state into free charges, and the transport and collection of free charges. Transport and collection are in competition with recombination, which may reduce the IQE. For the present discussion we assume that all absorbed photons create CT states. For C-PCPD-TBT:PCBM blends this assumption is justified by the virtually complete quenching of the polymer photoluminescence together with the appearance of CT luminescence. In our model, the IQE approaches unity in the limit of high reverse bias. We normalized the simulated photocurrent to the saturation value at high reverse voltage, obtaining the simulated IQE of the solar cell as function of bias. We fitted the simulated IQE vs. bias to the experimental EQE vs. bias data divided by $\eta_{abs}$ defined above, which in this case is an additional free fitting parameter. To fit the field dependence at different excitation photon energies, only $\eta_{abs}$ and $R_{cc}$ were changed. All the other parameters were kept fixed in the simulations, corresponding to the assumption that the transport of charges is independent of the properties of the intermediate CT state from which they were generated. Hence we interpret differences in the field dependence of the photocurrent for different photon energies as being solely caused by differences in dissociation efficiency of CT states.

The results of the simulations on a reduced set of photon energies are shown in Figure 7.4. The data are plotted versus effective voltage bias $V_{\text{eff}}$, which corresponds to the absolute values of the difference between the applied voltage and the voltage $V^*$ at which $J_{\text{photo}}(V^*) = 0$. Here $J_{\text{photo}}$ is the photocurrent density, defined as the difference in current density under illumination and in dark. For each photon energy the IQE vs. $V_{\text{eff}}$ can be reproduced by changing only $R_{cc}$. The curve recorded at 1.24 eV photon energy was fitted using $R_{cc} = 1.47$ nm. Increasing the photon energy results in an increase of $R_{cc}$, which reaches values around 1.9 nm at ~1.7 eV photon energy.
For higher photon energies, the $R_{cc}$ needed to fit the curves does not change sensibly. $R_{cc}$ is 1.98 nm for excitations at 3.02 eV. $R_{cc}$ values of ~ 1.9 nm for above band gap excitations are in agreement with the value of 1.9 nm used to fit the white light $J$-$V$ curve. This is not surprising, since the main part of the current under white light illumination is generated via above band gap excitations.

**Figure 7.4:** IQE at different photon energies as function of the effective voltage bias on the solar cell (circles), fitted with the simulated IQE (lines). The experimental curves have been fitted changing only the separation distance ($R_{cc}$) of electron and hole in the geminate pair. In the legend some of the photon energies $h\nu$ used in the experiments and the corresponding $R_{cc}$ are indicated.
Table 7.1: Values of the parameters used in the numerical simulation of the J-V curve under white light illumination and for the voltage dependence of the EQE.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>295</td>
<td>K</td>
</tr>
<tr>
<td>$L$</td>
<td>Thickness of the active layer</td>
<td>80</td>
<td>nm</td>
</tr>
<tr>
<td>$N_C$</td>
<td>DOS of conduction and valence band</td>
<td>$2.5 \times 10^{25}$</td>
<td>m$^{-3}$</td>
</tr>
<tr>
<td>$\mu_n$</td>
<td>Electron mobility</td>
<td>$7 \times 10^{-8}$</td>
<td>m$^2$ V$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$\mu_p$</td>
<td>Hole mobility</td>
<td>$1.5 \times 10^{-8}$</td>
<td>m$^2$ V$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$g_{\text{max}}$</td>
<td>Maximum charge generation rate</td>
<td>$11.6 \times 10^{27}$</td>
<td>m$^{-3}$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_f$</td>
<td>CT recombination rate</td>
<td>$6.25 \times 10^{6}$</td>
<td>s$^{-1}$</td>
</tr>
<tr>
<td>$\varepsilon_i$</td>
<td>Relative dielectric constant</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>$R$</td>
<td>Langevin recombination prefactor</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>$R_{\text{cc}}$</td>
<td>Electron-hole separation distance in the CT state</td>
<td>1.9</td>
<td>nm</td>
</tr>
</tbody>
</table>

To fit the IQE vs. voltage bias at different excitation photon energies only $R_{\text{cc}}$ was varied.

Figure 7.5 shows the $R_{\text{cc}}$ values obtained for several of the used photon energies as function of the excess photon energy $E_{\text{excess}} = \hbar \nu - E_{\text{CT}}$ (with $E_{\text{CT}} = 1.18$ eV). Two regions in the dependence of $R_{\text{cc}}$ on the available excess energy can be discerned. First $R_{\text{cc}}$ rises steeply with increasing photon excess energy. Then it reaches a value of $\sim 1.9$ nm at around $E_{\text{excess}} = 0.5$ eV and does not increase sensibly for higher excess energies. As stated above, $R_{\text{cc}}$ is used as measure of the effective binding energy of the CT pair, calculated as $E_B = q^2/4\pi \varepsilon_0 \varepsilon R_{\text{cc}}$, where we use $\varepsilon = 3$. The values of $E_B$ as function of excess energy are simultaneously shown in Figure 7.5. The calculated binding energy amounts to $\sim 0.35$ eV for the lowest excited CT states and decreases to a stable value of $\sim 0.25$ eV for photons carrying more excess energy. The saturation value of $R_{\text{cc}}$ and $E_B$ is reached at a photon energy of $\sim 1.7$ eV, that is for excitations fully in the C-PCPDTCB absorption band.
Figure 7.5: Values of $R_{cc}$ (full symbols) obtained from the simulations plotted versus the available excess energy $E_{\text{excess}}$, defined as $\hbar \nu - E_{\text{CT}}$. The photon energy $\hbar \nu$ is also shown on the top axis. The corresponding effective binding energies $E_B$ of the CT pairs calculated using $E_B = q^2/4\pi\varepsilon_0\varepsilon_r R_{cc}$ and $\varepsilon_r = 3$ are shown (empty symbols).

Our results suggest that in C-PCPDTBT:PCBM blends free charges are generated via intermediate CT states which have different effective binding energy depending on the energy of the exciting photon. In particular, photo-excitations above the optical band gap result in free charge generation via intermediate CT states with effective binding energy lower than for CT states populated through optical excitation in the tail of the CT absorption band. CT states populated with higher photon energy are the most relevant precursors to free charges in the solar cell under standard white light illumination (~1 sun), since most of the photo-responsivity is above the optical band gap.

Our analysis cannot provide an exact insight into the microscopic nature of these differences. However we note that our results are consistent with recent studies providing a microscopic interpretation of charge generation at the donor-acceptor heterojunction. Using Monte Carlo simulations van Eersel et al.\[28\] have suggested that CT dissociation in bulk heterojunctions proceeds via states which are in the low energy tail of a disorder-broadened density of states. Depending on the initial energies
of the electron and hole, the energy the charges can gain by further relaxation in the
DOS may, or may not be small as compared to the Coulomb barrier to be overcome.
In the former case the electron and hole have high probability for dissociation into
free charges at low electric fields. In the latter case, which is likely to coincide with
excitation in the lower energy part of the CT band, the simulations showed lower
probability of CT dissociation and a stronger dependence on electric field. This
picture could explain our results on C-PCPDTBT:PCBM.

7.3 Conclusions

We measured the electrical field dependence of the EQE spectra of C-
PCPDTBT:PCBM and Si-PCPDTBT:PCBM solar cells to investigate the influence of
the photon energy ($h\nu$) on the process of charge generation in organic solar cells. In
C-PCPDTBT:PCBM blends we found that the extraction of charges generated with
sub band gap excitations in the CT band have a stronger dependence on applied
voltage bias than the extraction of charges generated with above band gap excitations.
Considering that charge transport is unlikely to be affected by the photon energy used
we attributed the field dependent EQE spectra to a bias dependence of the dissociation
of the interfacial CT state. We analyzed the measured photocurrents by numerical
drift-diffusion simulations in terms of the Onsager-Braun model for field dependent
CT state dissociation. For each excitation photon energy used, we could extract an
effective binding energy of the corresponding CT state that acts as precursor of free
charges. In C-PCPDTBT:PCBM solar cells we find that the effective binding energy
of the charge transfer state precursor of free charges decreases with increasing photon
excess energy for photon energies below the optical band gap. For excitations above
the optical band gap the effective binding energy is lower than for sub band gap
excitations and is practically independent on the amount of available excess energy.
Under white illumination the vast majority of extracted charges are generated via
above band gap excitations. Therefore our results suggest that, in solar cells working
under standard conditions, the relevant intermediate states in charge generation are a
reduced set of CT states with energies higher than the completely relaxed state at the
bottom of the CT band. The microscopic nature of the different CT states that might
be involved in charge generation when sub band gap or above band gap excitations
are used is beyond the reach of our analysis. As a consequence we presently cannot
unravel the exact mechanism of CT dissociation in the studied blend. However a
possible interpretation is CT dissociation in an energetically disordered landscape.\[28\]

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For Si-PCPDTBT:PCBM solar cells the excess energy does not enhance the CT dissociation efficiency, if not at very small effective fields corresponding to \( \sim V_{oc} \) conditions. This suggests that relaxed CT states have the same dissociation efficiency as higher energy CT states. C-PCPDTBT:PCBM and Si-PCPDTBT:PCBM blends differ in their nanoscale morphology. The Si-PCPDTBT:PCBM blend shows a higher degree of phase separation and of aggregation in the polymer domains. It has been argued \([29,30]\) that such a blend morphology can result in higher local charge mobility and thus facilitate the CT dissociation at low electric fields. In agreement with this suggestion Si-PCPDTBT:PCBM blends exhibit less geminate recombination to the ground state and to the triplet state of the polymer compared to C-PCPDTBT:PCBM (Chapter 5). In systems showing similar nano-morphology properties as those of Si-PCPDTBT:PCBM, such as P3HT:PCBM or MDMO-PPV:PCBM, other authors have also concluded that excess energy is not a necessary requirement for CT dissociation.\([10,12]\) In Chapter 6 we reached the same conclusion on P3HT:PCBM using photo-CELIV techniques.

In conclusion, our results suggest that, to achieve high charge generation efficiency, large energy offsets between the donor and acceptor materials in the bulk heterojunction are not needed. Rather, the morphological properties of the donor-acceptor interface should be tuned to optimize the efficiency of CT dissociation. The recombination of the CT state to a lower triplet states might also play an important role on the final efficiency of free charge formation.
7.4 Experimental section

Solar cells fabrication. Photovoltaic devices were made by spin coating poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (Clevios P, VP Al4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). The photoactive layer was deposited by spin casting in air at 1500 rpm, using a chlorobenzene solution containing 10 mg mL\(^{-1}\) C-PCPDTBT (\(M_w = 55.7\) kg mol\(^{-1}\), PD = 2.28, Konarka) or Si-PCPDTBT (\(M_w = 52.8\) kg mol\(^{-1}\), PD = 2.85, Konarka), blended with 20 mg mL\(^{-1}\) [6,6]-phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM) (Solenne). The metal electrode, consisting of LiF (1 nm) and Al (100 nm), was deposited by vacuum evaporation at ~ 3 × 10\(^{-7}\) mbar. The active area of the cells was 0.091 cm\(^2\) and the thickness of the active layer was ~80 nm for both C-PCPDTBT and Si-PCPDTBT cells.

J-V and External Quantum Efficiency measurements. J-V curves were recorded using a Keithley 2400 source meter. White light 1000 W/m\(^2\) illumination was provided by a tungsten-halogen lamp corrected with a Schott GG385 UV filter and a Hoya LB120 daylight filter. Under these conditions C-PCPDTBT based devices showed a short-circuit current (\(J_{sc}\)) of 7.0 mA cm\(^{-2}\), a fill factor (FF) of 0.39 and an open-circuit voltage (\(V_{oc}\)) of 0.69 V, resulting in a maximum power point (MPP) of 1.91 mW cm\(^{-2}\). Si-PCPDTBT based devices showed a short-circuit current (\(J_{sc}\)) of 12 mA cm\(^{-2}\), a fill factor (FF) of 0.62 and an open-circuit voltage (\(V_{oc}\)) of 0.56 V, resulting in a maximum power point (MPP) of 4.20 mW cm\(^{-2}\).

EQE measurements were performed with the devices kept in a nitrogen filled box with a quartz window and illuminated through an aperture of 2 mm. Mechanically modulated (Stanford Research, SR 540) monochromatic (Oriel, Cornerstone 130) light from a 50 W tungsten halogen lamp (Osram 64610) was used as probe light, in combination with continuous bias light from a solid state laser (B&W Tek Inc. 532 nm) to create representative illumination intensity for 1 sun conditions, which were set matching \(J_{sc}\) with the \(J_{sc}\) obtained under 1000 W/m\(^2\) white light. The response was recorded as the voltage over a 50 Ω resistance, using a lock-in amplifier (Stanford Research Systems SR830). Variable voltage bias over the cell was applied by the lock-in-amplifier. The measurement in the low energy EQE band was also repeated placing a lowpass cutoff filter (\(h\nu > 1.59\) eV) in front of the device, to rule out contributions from higher energy stray photons coming out of the monochromator.

Photoluminescence and electroluminescence. To measure steady state electro-luminescence the solar cell was driven in forward bias (+3V) in a sealed box with a quartz window. The experiment was performed at room temperature using an Edinburgh Instruments FLSP920 double-monochromator luminescence spectrometer equipped with a nitrogen-cooled near-IR sensitive photomultiplier (Hamamatsu). The luminescence signal was corrected for the spectral response of the monochromators and photomultiplier.

Drift-diffusion simulations. The software used for the numerical drift-diffusion simulations was developed by Jan Anton Koster and Paul Blom. The description of the model and of the algorithm implemented in the software are in ref.[26]. In the present work constant electron and hole mobilities were used. No electron and hole traps were included. The Onsager-Braun field dependence of charge generation was implemented with a distribution of electron-hole separation distances in the CT state as given by Equation (3). The generation rate was assumed to be constant in space through the active layer. Ohmic collecting electrodes were used in the simulation.
7.5 References


Evidence for space-charge limited conduction in organic photovoltaic cells at open-circuit conditions

Abstract
The ac admittance of solar cells under illumination is investigated under open-circuit conditions. Open-circuit conditions are imposed by inserting a probe capacitor into the circuit. The capacitance and conductance of the cells are investigated as function of frequency and continuous illumination intensity. Results are compared with numerical and analytical modeling of charge recombination and transport. In bulk heterojunction solar cells with PCBM as acceptor and poly(3-hexylthiophene)(P3HT) or poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene](MDMO-PPV) as electron donor, the high frequency capacitance $C$ and conductance $G$ follow a power-law dependence on intensity of white light $I$, with $G(I) \propto I^{3/4}$ and $C(I) \propto I^{1/4}$. The modeling shows that these dependencies can be explained in terms of space-charge limited current in combination with Langevin type recombination of carriers. For poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl]](PCPDTBT) the capacitance shows a weaker dependence on intensity, indicating fast recombination of photogenerated carriers. Results indicate that the fill factor of relatively well performing polymer solar cells can still be limited by space charge effects and can be improved by enhancing the charge carrier mobility or by reducing the bimolecular Langevin recombination.
8.1 Introduction

Compared to cells made of inorganic semiconductors, polymer solar cells show lower efficiencies (≤ 10 %). Part of the lower efficiency is due to a relatively poor fill factor (FF), defined as the ratio of the maximum extractable power and the product of short-circuit current ($J_{sc}$) and open-circuit voltage ($V_{oc}$). In solar cells with high fill factors the photocurrent |$J$| shows a step-like, sharp drop for voltages approaching the open-circuit potential $V_{oc}$. This implies a large value of the conductance $G = dJ/dV$ at voltages near $V_{oc}$ for solar cells with high fill factor.

In order to improve the fill factor in a rational way, it is mandatory to have an understanding of which processes limit the current densities in polymer solar cells near open-circuit conditions and thus control the conductance and fill factor of the cell. In scientific literature on polymer solar cells, various possible limiting factors on the photocurrent near $V_{oc}$ have been discussed.

First, the current may be limited by the rate of charge generation. In polymer solar cells efficient generation of extractable charge carriers from primary photoexcitations can be realized, but is found to be strongly dependent on materials and processing conditions used. Near $V_{oc}$, where the internal electric field in the cell is small, charge generation may be low because of a field dependence of the generation process of mobile carriers out of the primary photoexcitations. Furthermore, primary photoexcitations may decay rapidly due to the close proximity of charge carriers in the material (exciton-charge annihilation). Exciton-charge annihilation is likely to reduce the overall generation efficiency near $V_{oc}$, because carrier densities increase when going from short circuit to open-circuit conditions.

Second, currents may be limited due to rapid recombination of photogenerated charge carriers. This recombination may be of Langevin type, but could also be effected by the metal contacts. Third, currents may also be limited by space charge considerations. The net amount of charge that can be accumulated in a certain volume of semiconducting material is restricted because of the electrostatic energy needed to build up such a space charge and generally depends on the potential difference over the semiconducting layer. It is important to realize that the possible sources of current limitation discussed above are not mutually exclusive. For instance, a space charge limitation on current densities automatically implies some sort of recombination in the bulk of the device.

Here we investigate the (photo-)admittance of polymer–fullerene bulk heterojunction solar cells in order to develop an understanding of the limiting processes in the photocurrent generation in the solar cells near open-circuit
Evidence for space-charge limited conduction in organic photovoltaic cells at \( V_{oc} \) conditions. The polymers P3HT, PCPDTBT and MDMO-PPV (Figure 8.1) are used as electron donors in the bulk heterojunctions with either [60]PCBM or [70]PCBM as electron acceptor. Achieving open-circuit conditions can be experimentally complicated. We overcome this difficulty by inserting a probe capacitor in the analysis circuit. In this way one can automatically ensure open-circuit conditions under all continuous, white light illumination intensities (Figure 8.2). Since no dc signals can be present in this configuration, ac analysis is necessary: applying a small oscillating ac bias voltage, the conductance and capacitance of the cell can be probed as function of frequency and illumination intensity.\(^{[13-15]}\)

Experimental investigations are combined with numerical and analytical modeling of photocurrents under open-circuit conditions considering drift and diffusion transport in combination with Langevin type bimolecular recombination of charge carriers. We find that the dependence of photoconductance \( G \) on illumination intensity \( I \) can be described by \( G(I) \propto I^{3/4} \) while the photocapacitance \( C \) follows \( C(I) \propto I^{1/4} \). We attribute this common behavior to a space charge limitation on the magnitude of the photocurrent in the polymer–fullerene bulk heterojunction layer of the cells.

\[
\begin{align*}
\text{P3HT} & & \text{PCPDTBT} & & \text{MDMO-PPV} \\
\text{[60]PCBM} & & \text{[70]PCBM}
\end{align*}
\]

**Figure 8.1:** Chemical structure of the materials used.
8.2 Modeling

8.2.1 Analytical model of charge transport with bimolecular recombination at open circuit

In this section we derive analytical expressions for the capacitance and conductance of a solar cell under open-circuit conditions. To simplify the modeling as much as possible, we assume that the $p$ and $n$ charge carriers have the same mobility $\mu$ and diffusion constant $D$ (i.e. $\mu_n = \mu_p$ and $D_n = D_p$) and that these are related via the Einstein relation $D = \mu kT/q$. We model the bulk heterojunction as a single homogenous material with effective bands for electron and hole transport. Furthermore we assume spatially homogeneous charge carrier generation with rate $g$ and a homogenous recombination via the Langevin mechanism with recombination rate $\gamma np$, in which $\gamma$ is a constant and $n$ and $p$ are the density of electrons and holes. The generation $g$ is assumed to be independent of the local electric field strength. We restrict ourselves to one-dimensional transport of charges in the $x$ direction and include drift and diffusion contributions to the transport. The origin $x = 0$ is chosen in the middle of the bulk heterojunction layer with thickness $L$. 
Under these approximations the following differential equations for the electron \((n)\) and hole \((p)\) carrier density apply in the bulk of the material:

\[
\begin{align*}
p'' - \frac{F}{V_T} p' - \frac{F'}{V_T} p - \frac{\gamma}{D} np + \frac{g}{D} &= \frac{1}{D} \frac{\partial p}{\partial t} \\
n'' + \frac{F}{V_T} n' + \frac{F'}{V_T} n - \frac{\gamma}{D} np + \frac{g}{D} &= \frac{1}{D} \frac{\partial n}{\partial t}
\end{align*}
\]

Where the prime indicates \(\partial / \partial x\) and the double prime \(\partial^2 / \partial x^2\). Further \(V_T = kT/q\) is the thermal voltage and \(F\) the electric field strength. \(F\) is a scalar related to the electrostatic potential \(\varphi(x): F(x) = -\frac{d\varphi(x)}{dx}\). To make optimal use of the symmetry relation in charge carrier transport we introduce the total carrier density \(Q = p + n\) and the net charge density \(M = p - n\) as alternatives for \(p\) and \(n\). Making use of symmetry, it suffices to solve the second order differential equation for \(M\):

\[
M'' - \frac{F}{V_T} Q' - \frac{F'}{V_T} Q = \frac{1}{D} \frac{\partial M}{\partial t}
\]

(3)

This equation can be simplified by neglecting the term containing \(Q'\). This approximation can be related to an approximation that is often used in charge transport: the linearization of the Poisson-Boltzmann equation. This linearization is used in e.g. Debye-Hückel theory for conduction in electrolytes and the second derivative of the potential is expressed in terms of the potential itself: \(^{[16]}\)

\[
\varphi' = \kappa^2 \varphi = \frac{\tilde{q}}{V_T} Q \varphi
\]

(4)

Where \(\tilde{q} = q / \varepsilon_0 \varepsilon_r\). To show how the linearization of the Poisson Boltzmann equation relates to the magnitude of the \((F/V_T)Q'\) term in (3) we first combine (4) with the Poisson equation \(F' = -\varphi'' = \tilde{q} M\). This gives:

\[
Q(x) \frac{\varphi(x)}{V_T} = -M(x)
\]

(5)

Considering that the diode is under open-circuit condition \((J_p + J_n = 0\) in steady state) gives:

\[
M' - \frac{F}{V_T} Q = 0
\]

(6)
So that:

\[ M' = -Q' \frac{\phi}{V_T} - Q \frac{\phi'}{V_T} = Q' \frac{\phi}{V_T} + Q \frac{F}{V_T} = \frac{F}{V_T} Q \quad (7) \]

It follows thus that \( Q'(\phi/V_T) = 0 \). In the case that \( \phi \) is not constant and not equal to zero, we find that \( Q' = 0 \), so that the second term in (3) vanishes.

Next we introduce the small signal approximation. In impedance spectroscopy, a small alternating voltage is applied around the constant open-circuit voltage \( \phi_0 \) so:

\[ \phi(t) = \phi_0 + \phi_1(t) = \phi_0 + \phi_0 e^{i\omega t} \quad (8) \]

Adopting the usual small signal analysis we get:

\[ M = M_0 + M_1(t) = M_0 + M_1 e^{i\omega t} \quad (9) \]

and a corresponding relation for \( Q \). The admittance of the diode can now be evaluated by calculating the ac current density \( J_1 \) exactly in the middle of the diode at \( x = 0 \) where \( M_0 = 0 \). From (3) this gives the following second order differential equation for \( M_1 \):

\[ M_1'' = -\frac{\bar{q}}{V_T} Q_0 M_1 - \frac{\omega}{D} M_1 = 0 \quad (10) \]

At \( x = 0 \) the derivative of \( Q_0 \) with respect to \( x \) vanishes and \( Q_0 \) is approximately constant along \( x \) with a magnitude depending on the carrier generation rate \( g \). Taking into account the boundary condition \( M_1 = 0 \) at \( x = 0 \), the solution to (10) is:

\[ M_1(x) = a_1 \sinh\left(\sqrt{\left(f(g, \omega)\right)}x\right) \quad (11) \]

Where

\[ f(g, \omega) = \frac{\bar{q}Q_0(g)}{V_T} + \frac{i\omega}{D} \quad (12) \]

Using the identity \( np = (1/4)(Q^2 - M^2) \) and the fact that in the bulk at open circuit, the rate of recombination has to match the rate of generation \( \gamma np = g \), we get at \( x = 0 \)

\[ Q_0(g) = \sqrt{\frac{4g}{\gamma} + M_0^2(x)} \cong \sqrt{\frac{4g}{\gamma}} \quad (13) \]

The ‘amplitude’ \( a_1 \) in Equation (11) depends on the applied voltage because:
Evidence for space-charge limited conduction in organic photovoltaic cells at $V_{oc}$

\[- \varphi_i = F_i' = \tilde{q} \int M_1 \]

(14)

using (11) we get

\[ a_1 = \frac{- \varphi_i f(g, \omega)}{\sinh \left( \frac{\sqrt{f(g, \omega) L}}{2} \right)} \]

(15)

So that the final expression for $M_1$ near $x = 0$ is:

\[ M_1 = \frac{- \varphi_i f(g, \omega)}{\sinh \left( \frac{\sqrt{f(g, \omega) L}}{2} \right)} \sinh \left( \sqrt{f(g, \omega)} x \right) \]

(16)

The measured current density in an ac impedance measurement includes a contribution from the displacement current. The measured current density $J_{\text{meas}}$ is related to the particle current density and the displacement term in the following way

\[ J_{\text{meas}} = J + \frac{1}{q_e} \frac{\partial D}{\partial t} = J + \frac{\epsilon_0 \epsilon_r}{q_e} \frac{\partial F}{\partial t} = J + \frac{1}{\tilde{q}} \frac{\partial F}{\partial t} \]

(17)

This follows from the Ampère-Maxwell law.

The measured current density that is constant throughout the diode and hence the admittance derived at $x = 0$ should hold for the diode as a whole. The measured ac current density in the diode can now be expressed as:

\[ J_{\text{meas},1} / D = J_1 / D + \frac{i \omega}{\tilde{q} D} F_1 = \left( n' + \frac{F}{V_T} \right) n - \left( p' + \frac{F}{V_T} \right) p + \frac{i \omega}{\tilde{q} D} F_1 \]

(18)

\[ J_{\text{meas},1} / D = -M_1' + \frac{F_0 Q_0}{V_T} + \frac{F_0 Q_1}{V_T} + \frac{i \omega}{\tilde{q} D} F_1 = -M_1' + f(g, \omega) F_1 + \frac{F_0 Q_1}{V_T} \]

(19)

From small signal analysis of $np = (1/4)(Q^2 - M^2)$ it follows that

\[ Q_0 Q_1 - M_1 M_0 = 0 \]

(20)

At $x = 0$, $M_1 = 0$ because of symmetry so that at $x = 0$, $Q_1 = 0$.

\[ J_{\text{meas},1} (x = 0) / D = -M_1'(0) + f(g, \omega) \int M_1 \]

(21)

The ac admittance of the diode becomes:
\[ Y(\omega) \equiv G(\omega) + i\omega C(\omega) = \frac{J_{\text{meas},1}(x = 0)}{\varphi_1} = \frac{D(-M'_1(0) + f(g, \omega) \int M_1)}{\varphi_1} \]  
\[ (22) \]

We need \( M'_1(x=0) \) and \( f(g, \omega) \int_{-L/2}^{x=0} M_1 \) to obtain \( Y(\omega) \). From (16):

\[ M'_1(x = 0) = -\frac{\varphi_1 f^{3/2}(g, \omega) \cosh(0)}{\sinh\left(\sqrt{f(g, \omega)} \frac{L}{2}\right)} = -\frac{\varphi_1 f^{3/2}(g, \omega)}{\sinh\left(\sqrt{f(g, \omega)} \frac{L}{2}\right)} \]  
\[ (23) \]

\[ f(g, \omega) \int_{-L/2}^{x=0} M_1 = -\frac{\varphi_1 f^{3/2}(g, \omega) - \cosh(\sqrt{f(g, \omega)} x)}{\sinh\left(\sqrt{f(g, \omega)} \frac{L}{2}\right)} \bigg|_{x=0}^{x=-L/2} = -\frac{\varphi_1 f^{3/2}(g, \omega)}{\sinh\left(\sqrt{f(g, \omega)} \frac{L}{2}\right)} + \frac{\varphi_1 f^{3/2}(g, \omega)}{\tanh\left(\sqrt{f(g, \omega)} \frac{L}{2}\right)} \]  
\[ (24) \]

Inserting (23) and (24) into (22), we get

\[ Y(g, \omega) = \frac{D f^{3/2}(g, \omega)}{\tanh\left(\sqrt{f(g, \omega)} \frac{L}{2}\right)} \]  
\[ (25) \]

At sufficiently high light intensity, the denominator in (25) containing the hyperbolic tangent approaches unity so that at low frequency:

\[ G(g) = D \left( \frac{\bar{q}}{V_T} \right)^{3/2} \left( \frac{g}{\gamma} \right)^{3/4} \]  
\[ (26) \]

\[ C(g) = \left( \frac{\bar{q}}{V_T} \right)^{1/2} \left( \frac{g}{\gamma} \right)^{1/4} \]  
\[ (27) \]

Finally, by taking the ratio between capacitance and conductance one obtains a characteristic time \( \tau \) (often interpreted as minority carrier lifetime). Using the Langevin-type expression (28) for \( \gamma \) with adjustable prefactor \( R \)

\[ \gamma = R\bar{q}2\mu \]  
\[ (28) \]

One finds:

\[ \frac{C(g)}{G(g)} = \tau(g) = \left( \frac{V_T}{\bar{q}D} \right)^{1/2} \left( \frac{g}{\gamma} \right)^{-1/2} = \sqrt{\frac{R}{\bar{q}\mu}} \frac{1}{\sqrt{g}} \]  
\[ (29) \]
Interestingly, provided that the mobility $\mu$ is known from e.g. transport measurements, relation (29) offers a possibility to evaluate the recombination prefactor $R$ from an admittance measurement.

### 8.2.2 Space-charge limited current in photovoltaic diodes

The results obtained in the previous section can qualitatively be related to the better known behavior under static conditions. Photovoltaic diodes may, under certain conditions, generate a photocurrent that is limited by the maximum allowed space charge inside the diode.\[11,12\] In this space-charge limited operating condition, the dependence of photocurrent on the generation rate $g$ follows a power law with exponent $3/4$:

$$J_{\text{photo}} = q\left(\frac{9e_0\varepsilon_r\mu}{8q}\right)^{1/4} g^{3/4}V^{1/2} \tag{30}$$

The similarity in the dependence on generation rate in the expressions (26) for the conductance and (30) for the steady-state photocurrent, suggests that the intensity dependence of the conductance expressed by relation (26) may be understood in terms of a space charge limitation on the ac photocurrent. Because in the derivation of (26) electrodes were not taken into account explicitly, charge extraction or injection cannot be limiting the current in (26). Also charge generation was assumed to occur with unit efficiency after photon absorption. As mentioned in the introduction, the concept of space-charge limited photocurrents presupposes a bulk recombination mechanism. Hence the ac currents near open-circuit conditions as considered in the derivation of (26), must be limited by a combination of restrictions on the built-up of space charge and kinetic limitations imposed by the bimolecular Langevin-type recombination of charge carriers.

As pointed out by Goodman and Rose\[11\] the thickness $d$ of the space charge region that limits the current scales with the generation rate to the inverse $1/4$ power:

$$d = \left(\frac{9e_0\varepsilon_r\mu}{8qg}\right)^{1/4} V^{1/2} \tag{31}$$

If we assume that the capacitance scales with the inverse thickness of the current limiting layer, it follows that space-charge limited photocapacitance varies with generation rate to the $1/4$ power,\[17\] consistently with the finding of Equation (27).

As an alternative but equivalent reasoning we can consider that in open-circuit conditions all charge carriers recombine, either in the bulk or, after diffusion, at the
electrodes. Under conditions of high illumination intensity and negligible electrode- and trap-mediated recombination, the bimolecular Langevin recombination mechanism predicts a lifetime \( \tau \) for photogenerated carriers that varies as \( g^{-1/2} \).\[18\] Using the relation \( C = \tau G \) it follows from (30) that photocapacitance should vary as \( g^{1/4} \), consistent with (27) and (31).

### 8.2.3 Equivalent circuit analysis

The two types of devices under investigation in this study are represented schematically in Figure 8.2. Both types of devices may be represented by the equivalent circuit shown on the left of Figure 8.2. With the help of this equivalent circuit we now analyze the influence of the probe capacitor \( C_{\text{probe}} \) on the total admittance. We derive expressions relating the admittance of the bulk heterojunction layer in the solar cell to the total admittance of the photovoltaic diode - probe capacitor combination. The photovoltaic cell is connected in series with a probe capacitor (see Figure 8.2). This gives a total admittance:

\[
\frac{1}{Y_{\text{total}}(\omega)} = \frac{1}{Y_d(\omega)} + \frac{1}{Y_{\text{probe}}(\omega)}
\]

Using \( Y_{\text{total}}(\omega) = G_{\text{total}}(\omega) + i \omega C_{\text{total}}(\omega) \), \( Y_{\text{probe}}(\omega) = +i \omega C_{\text{probe}}(\omega) \), and \( Y_d(\omega) = G_d(\omega) + i \omega C_d(\omega) \), \( C_{\text{total}} \) and can \( G_{\text{total}} \) be re-written as:

\[
C_{\text{total}}(\omega) = C_{\text{probe}} \frac{1 + \omega^2 \frac{C_d}{G_d} \left( \frac{C_d + C_{\text{probe}}}{G_d} \right)}{1 + \omega^2 \left( \frac{C_d + C_{\text{probe}}}{G_d} \right)^2}
\]

and

\[
G_{\text{total}}(\omega) = \frac{\omega^2 C_{\text{probe}}^2 G_d}{G_d^2 + \omega^2 (C_{\text{probe}} + C_d)^2}
\]

which goes from 0 at \( \omega = 0 \) to \( G_d \) in the high frequency limit, when \( C_{\text{probe}} >> C_d \). Defining:

\[\tau_d \equiv \frac{C_d}{G_d} \quad \text{and} \quad \tau_{\text{probe}} \equiv \frac{C_{\text{probe}}}{G_d}\]

(29) can be rewritten as
Evidence for space-charge limited conduction in organic photovoltaic cells at $V_{oc}$

\[
C_{total}(\omega) = C_{probe} \frac{1}{1 + \omega^2 (\tau_d + \tau_{probe})^2} + C_{probe} \frac{\omega^2 \tau_d (\tau_d + \tau_{probe})}{1 + \omega^2 (\tau_d + \tau_{probe})^2}
\]

(35)

Provided that $C_{probe} \gg C_d$, in the high frequency limit this expression reduces to:

\[
C_{total}(\omega) \equiv C_{probe} \frac{\tau_d}{\tau_d + \tau_{probe}} \equiv C_d(\omega)
\]

(36)

While in the low frequency limit one obtains

\[
C_{total}(\omega) \equiv C_{probe}
\]

(37)

The characteristic frequency at which the crossover between high and low frequency behavior occurs is:

\[
\nu_{cross}(g) = \frac{\omega_{cross}(g)}{2\pi} \equiv \frac{\sqrt{3}}{6\pi(\tau_d + \tau_{probe})} \equiv \frac{G_d(g)}{2\sqrt{3}\pi C_{probe}}
\]

(38)

where we used $\tau_{probe} \gg \tau_d$ which follows directly from the assumption $C_{probe} \gg C_d$. The crossover frequency is defined as the frequency at which the derivative of the capacitance with respect to frequency reaches a maximum.

8.3 Results and discussion

8.3.1 P3HT:[60]PCBM diodes with internal probe capacitor

In Figures 8.3a and 8.3b the capacitance and conductance for P3HT:[60]PCBM bulk heterojunction diode incorporating a 30 nm thick Al$_2$O$_3$ blocking layer are plotted versus ac frequency for different illumination intensities. The layout of the diode is shown in Figure 8.2 top left. The blocking Al$_2$O$_3$ layer is placed in between the transparent conducting oxide and PEDOT:PSS polymer electrode of the photovoltaic cell. The Al$_2$O$_3$ layer is thus sandwiched between quasi-metallic layers and not directly in contact with the active bulk heterojunction layer. The geometric capacitance associated with the Al$_2$O$_3$ dielectric ($\epsilon = 9$) in between metallic contacts is ~20 nF. This is considerably larger that the capacitance estimated for the organic bulk heterojunction layer (3 nF). The Al$_2$O$_3$ dielectric incorporated in the photovoltaic diode may therefore be considered as a probe capacitor as discussed in section 8.3.2.

We first discuss the response in the dark. In agreement with Equations (34) and (35), the capacitance versus ac frequency plots for the diode incorporating the
Al$_2$O$_3$ layer show three distinct regions. At low frequency the oxide capacitance is dominating (~20 nF). This is because the half period of the ac voltage perturbation is long enough to generate and accumulate the amount of charge $Q = C_{\text{probe}} \phi_1$ needed to fully charge the probe capacitor. At high frequency (~100 kHz), the half period of the ac modulation is too short in comparison with the carrier transport and generation to fully charge the probe capacitor. In the high frequency limit, the total capacitance becomes dominated by the active layer geometrical capacitance $C_{\text{geom}}$. The two regions are connected by a transition region centered on the crossover frequency ($\nu_{\text{cross}}$) where the capacitance shows a crossover from probe to bulk heterojunction capacitance. At very high frequencies (> 500 kHz) the signal is limited by instrumental $RC$ times.

Upon increasing the illumination intensity, the crossover frequency shifts to higher values. As anticipated, the 20 nF probe capacitance, observable at low frequency, remains constant with increasing intensity. In contrast, the high frequency capacitance increases with light intensity. We attribute this to a contribution of photogenerated carriers to the capacitance of the bulk heterojunction layer. The shift of $\nu_{\text{cross}}$ to higher frequencies with increasing light intensity indicates that the amount of carriers needed to charge the probe capacitor can be generated in a shorter period of time at higher illumination intensity. This indicates significant generation of free charge carriers out of photoexcitations even though the applied potential differs only 50 mV from the open-circuit voltage under this illumination intensity.

Measurements of the conductance also show the same three different frequency regions. At low frequency the conductance is essentially zero due to the blocking of the current by the Al$_2$O$_3$ layer. In the transition region, the conductance rises with frequency and reaches a plateau. The plateau we assign to the (photo-)conductance of the bulk heterojunction. At very high frequency the conductance rises, which is common for disordered materials and amorphous semiconductors.$^{[19,20]}$

The magnitude of the photoconductance contains information on the efficiency of charge carrier generation. Looking at the highest light intensities, which corresponds roughly to 1 sun intensity, we find $G = 10^{-3}$ S at the plateau near $\nu_{\text{cross}} = 5 \times 10^4$ Hz. The magnitude of $G$ at this frequency combined with the amplitude of the voltage modulation implies a current density on the order of 1 mA/cm$^2$, which is the same order of magnitude as the short-circuit current density in unannealed P3HT:[60]PCBM cells under AM 1.5 illumination conditions. In addition the $\nu_{\text{cross}} = 5 \times 10^4$ Hz and $C_{\text{probe}} = 20$ nF also yield current densities on the order of 1 mA/cm$^2$. Hence the efficiency of charge carrier generation near open-circuit conditions is high.
This a posteriori justifies the choice for a field-independent charge generation rate $g$ for this device.

The ratio of capacitance and conductance contains information of the recombination prefactor $R$. From the measurements in Figures 8.3a and 8.3b at $2 \times 10^4$ Hz and relative intensity 0.08, corresponding to $0.8 \text{ nm}^{-3}\text{s}^{-1}$, we take a photocapacitance $C = 4 \text{ nF}$ and a photoconductance $G = 5 \times 10^4 \text{ S}$. Using Equation (29) assuming a mobility $\mu$ on the order of $10^{-4} \text{ cm}^2/\text{Vs}$, we find a recombination prefactor $R$ on the order of unity.

### 8.3.2 P3HT:[60]PCBM photovoltaic cell with external probe capacitor

Results for as-cast P3HT:[60]PCBM solar cells connected to an external capacitor (40 nF) are shown in Figures 8.3c and 8.3d. Taking into account the higher probe capacitance, results are in good agreement with those for the diodes incorporating the Al$_2$O$_3$ dielectric current blocking layer. We conclude that the method of incorporating the probe capacitor into the circuit (external or internal) does not significantly influence the results. The method based on the external probe capacitor can be used on standard devices and is therefore preferred.

### 8.3.3 Numerical drift-diffusion modeling of P3HT:[60]PCBM cells

Figures 8.3e,f show the capacitance and conductance versus ac frequency as predicted from numerical modeling of drift-diffusion processes in the P3HT:[60]PCBM device incorporating the Al$_2$O$_3$ and PEDOT:PSS layers. In the simulation, equal electron and hole mobilities were assumed (Table 8.1) and recombination was included using a homogenous Langevin type mechanism with an adjustable recombination prefactor $R$. Metallic contacts were taken into account explicitly; relevant band offsets and densities of states are listed in Table 8.1. Figures 8.3e and 8.3f show results for $R = 0.1$ at different generation rates $g$. For the P3HT:[60]PCBM cells, $g = 10 \text{ nm}^{-3}\text{s}^{-1}$ corresponds approximately to 1 sun illumination intensity. In Figures 8.3g and 8.3h the photocapacitance and photoconductance are calculated varying the recombination prefactor $R$ at a fixed generation rate $g = 10 \text{ nm}^{-3}\text{s}^{-1}$ (~0.1 sun).
Figure 8.3: (a, b) Capacitance and conductance versus ac frequency at different light intensity of P3HT:[60]PCBM devices containing an Al$_2$O$_3$ layer. (c, d) Same measurements on as-cast P3HT:[60]PCBM devices connected in series to a capacitor. (e, f) Simulation of the capacitance and conductance response as a function of AC frequency of a P3HT:[60]PCBM devices containing an Al$_2$O$_3$ layer at different generation rates and using a Langevin recombination prefactor $R$ equal to 0.1. (g, h) Capacitance and conductance were also simulated varying the recombination prefactor for a fixed generation rate $g = 1 \text{ nm}^{-3} \text{s}^{-1}$. 
Table 8.1: An overview of the parameters that were used in the model to simulate the P3HT:[60]PCBM cell.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO energy</td>
<td>4.1</td>
<td>eV</td>
</tr>
<tr>
<td>HOMO energy</td>
<td>5.2</td>
<td>eV</td>
</tr>
<tr>
<td>LUMO DOS</td>
<td>0.3</td>
<td>nm(^{-3})</td>
</tr>
<tr>
<td>HOMO DOS</td>
<td>0.3</td>
<td>nm(^{-3})</td>
</tr>
<tr>
<td>Electron mobility</td>
<td>1×10(^{-7})</td>
<td>m(^2)/Vs</td>
</tr>
<tr>
<td>Hole mobility</td>
<td>1×10(^{-7})</td>
<td>m(^2)/Vs</td>
</tr>
<tr>
<td>Relative dielectric constant</td>
<td>3.6</td>
<td>-</td>
</tr>
<tr>
<td>Generation rate</td>
<td>10</td>
<td>nm(^3)/s</td>
</tr>
<tr>
<td>Injection barrier</td>
<td>0.2</td>
<td>eV</td>
</tr>
<tr>
<td>Recombination prefactor $R$</td>
<td>0.1</td>
<td>-</td>
</tr>
</tbody>
</table>

The simulations support the assignment of the low frequency plateau to the oxide capacitance and the high frequency plateau to the bulk heterojunction response. The simulations also confirm the rise of the high frequency capacitance plateau with increasing generation rate. Comparison of Figures 8.3g and 8.3c leads to an estimate for the recombination prefactor $R$ of about 0.01. The estimation is done identifying the curves that in Figure 8.3g,h best match the curves in Figures 8.3c,d at 0.1 sun. The shift of crossover frequency with increasing rate of carrier generation is also born out.

8.3.4 Light intensity dependence of the photoadmittance

We now investigate the dependence of the photocapacitance $C$ on illumination intensity in more detail. Values for $C$ are taken from admittance spectra at 100 kHz of the diodes with external capacitor (see Figures 8.3c and 8.3d) and the capacitance in dark is subtracted. Values for $C$ are plotted in Figure 8.4 as function of light intensity (normalized to 1 sun). Data for as-cast P3HT:[60]PCBM active layers and for three solar cells with other active layers (thermally annealed P3HT:[60]PCBM, MDMO-PPV[70]PCBM, and PCPDTBT:[70]PCBM) are shown.

As can be seen in Figure 8.4a, the dependence of capacitance on intensity $I$ follows a power law $I^{\alpha_C}$. The exponent $\alpha_C$ obtained from fitting $I^{\alpha_C}$ to the experimental data points amounts to 0.24 for P3HT:[60]PCBM as-cast solar cells. The value $\alpha_C = 0.24$ is in close agreement with the prediction from Equation (27) $\alpha_C = \frac{1}{4}$. In Table 8.2 values for $\alpha_C$ obtained for different solar cells are listed. Drift-diffusion
numerical modeling indicates a power-law dependence and predicts $\alpha_C = 0.4$ for the P3HT:[60]PCBM device incorporating the $\text{Al}_2\text{O}_3$ layer, while the experimental value amounts to $\alpha_C = 0.28$.

The $\alpha_C = 0.13$ for the PCPDTBT:[70]PCBM bulk heterojunction shows the largest deviation from the predicted $1/4$. Note that field dependent charge generation is not taken into account in the analytical and numerical models presented above. For MDMO-PPV and P3HT based solar cells this assumption is supported by experimental indication of weak field dependence of charge generation.$^{[21,22]}$ In PCPDTBT:[70]PCBM cells, however, strong geminate recombination has been observed and may cause a stronger field dependence in the charge generation.$^{[23-26]}$ For a diode which is recombination limited one expects at high light intensities current densities $\propto \sqrt{g}$ and carrier lifetimes $\tau \propto 1/\sqrt{g}$ Hence photocapacitance is expected to be small and insensitive to light intensity.
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Figure 8.4: (a) High frequency capacitance (100 kHz), (b) conductance \( G_{\text{plateau}} \) and (c) crossover frequency measured as a function of light intensity (normalized to 1 sun) on the different solar cells connected in series with the external probe capacitor. The data (symbols) are fitted with a power law \( I^\alpha \) (lines) in order to extract \( \alpha_C \), \( \alpha_G \) and \( \alpha_{\text{cross}} \) (see Table 8.2).
Table 8.2: Values for $\alpha_C$, $\alpha_G$ and $\alpha_{cross}$ relative to the solar cells connected in series with the probe capacitor and to the device containing the Al$_2$O$_3$ insulating layer (both measured and simulated).

<table>
<thead>
<tr>
<th>Solar cell</th>
<th>$\alpha_C$</th>
<th>$\alpha_G$</th>
<th>$\alpha_{cross}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P3HT:[60]PCBM + oxide as-cast</td>
<td>0.28 ± 0.01</td>
<td>0.81 ± 0.03</td>
<td>0.99 ± 0.03</td>
</tr>
<tr>
<td>P3HT:[60]PCBM as-cast</td>
<td>0.24 ± 0.03</td>
<td>0.80 ± 0.03</td>
<td>0.86 ± 0.04</td>
</tr>
<tr>
<td>P3HT:[60]PCBM annealed</td>
<td>0.27 ± 0.01</td>
<td>0.71 ± 0.03</td>
<td>0.82 ± 0.01</td>
</tr>
<tr>
<td>MDMO-PPV:[70]PCBM</td>
<td>0.24 ± 0.01</td>
<td>0.87 ± 0.02</td>
<td>0.83 ± 0.02</td>
</tr>
<tr>
<td>PCPDTBT:[70]PCBM</td>
<td>0.13 ± 0.01</td>
<td>0.85 ± 0.02</td>
<td>0.83 ± 0.01</td>
</tr>
<tr>
<td>Simulated a</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P3HT:[60]PCBM + oxide, $R=0.1$</td>
<td>0.42 ± 0.04</td>
<td>0.84 ± 0.02</td>
<td>0.87 ± 0.02</td>
</tr>
</tbody>
</table>

a) Capacitance evaluated at 950 kHz

Figure 8.5: Real and imaginary part of the admittance measured on the P3HT:[60]PCBM device incorporating the Al$_2$O$_3$ layer as function of the amplitude of the ac voltage at a modulation frequency of 250 kHz. Measurements in dark and at different light intensities are shown.
The dependence of the admittance $Y = G + i\omega C$ on the voltage amplitude has been investigated. Results for the P3HT:[60]PCBM cell with internal capacitor are shown in Figure 8.5. The conductance $G$ in dark probed at 250 kHz (Figure 8.5), does not show any significant dependence on ac voltage amplitude; under illumination the conductance decreases with increasing ac amplitude as expected for space-charge limited admittance (see Equation (30)). The imaginary part of the admittance, $\omega C$, shows a similar dependence of ac voltage amplitude.

Also the intensity dependence of photoconductance has been investigated in more detail. Figure 8.4b shows $G_{\text{plateau}}$, the conductance measured on the plateau occurring at the ac frequencies where the capacitance shows a crossover. For example, in P3HT:[60]PCBM devices under 0.01 sun illumination (Figures 8.3c, d), this plateau occurs between $\sim10^3$ and $10^4$ Hz ac frequencies. We find for the as-cast P3HT:[60]PCBM cell with external capacitor that $G$ follows a power law dependence on intensity with exponent $\alpha_G = 0.80$ (see Table 8.2). Equation (26) predicts $\alpha_G = \frac{3}{4}$. For the other bulk heterojunctions we find $\alpha_G$ values close to 0.8 while numerical modeling yields $\alpha_G = 0.84$.

The crossover frequency $\nu_{\text{cross}}$ is expected to show the same dependence on light intensity as the high frequency conductance $G$ according to Equation (38). Indeed for $\nu_{\text{cross}}$ we also find a power-law dependence with an exponent $\alpha_{\text{cross}}$ that is similar in magnitude to $\alpha_G$ (See Figure 8.3c, Table 8.2). For the P3HT:[60]PCBM bulk heterojunction with internal probe capacitor we find a slightly larger value for $\alpha_{\text{cross}}$. We expect that in this case non-ideal behavior of the thin dielectric in the form of a frequency dependent leakage and/or $C_{\text{probe}}$ may affect the measurement.

Earlier reports on photoadmittance spectroscopy on polymer fullerene bulk heterojunction solar cells [27,28] report values for $\alpha_C$ and $\alpha_G$ very similar to ours. In these studies open-circuit conditions were imposed by applying a compensating dc bias voltage. In these studies, values for the exponents $\alpha_C$ and $\alpha_G$ were related to trapping of charges in a disorder broadened density of states (DOS) resulting in filling of the DOS at high light intensity. Our results do not exclude trapping of charges in a broadened DOS, but indicate the values $\alpha_C$ close to $\frac{1}{4}$ combined with $\alpha_G$ around $\frac{3}{4}$ may be the result of a more general transport phenomenon: space-charge limited photocurrents in combination with bimolecular recombination.

Curiously, the intensity dependence of photoadmittance of silver chloride layers can also be described by power laws with exponents $\alpha_C \cong \frac{1}{4}$ and $\alpha_G \cong \frac{3}{4}$, as reported 50 year ago.[29] In contrast, photocapacitance in inorganic silicon solar cells
shows a much more pronounced intensity dependence with $\alpha_C = 1$ at low light intensities.$^{30,31}$ At high light intensity $\alpha_C$ can rise above 1 and up to 2.$^{32}$

### 8.4 Conclusions

We measured the ac (photo-)admittance of polymer-fullerene bulk heterojunction solar cells under conditions close to open-circuit voltage, as function of oscillating bias voltage frequency and illumination intensity for a devices comprising different electron donating polymers blended with PCBM as acceptor. Open-circuit voltage conditions were imposed by incorporating an insulating layer in the solar cell layers stack or, equivalently, by connecting the devices in series with an external capacitor. In the case of the internal oxide layer, the experimental results were reproduced by numerical drift-diffusion simulations including Langevin type bimolecular recombination of charge carriers. By reproducing the experimental results with the numerical simulations it was possible to estimate the Langevin recombination prefactor $R$.

We further developed an analytical description of the ac admittance of organic solar cells at open-circuit voltage conditions. We found that at low modulation frequency and at $V_{oc}$ conditions, the capacitance and conductance are expected to vary with illumination intensity $I$ as $C(I) \propto I^{1/4}$ and $G(I) \propto I^{3/4}$ respectively, when bimolecular recombination is taken into account. These dependences are interpreted in terms of space charge limitation of the photogenerated current. We investigated the dependence of capacitance and admittance of our devices on light intensity and established a power-law type dependency near open-circuit conditions. The exponents observed are consistent with predictions for space-charge limited photocurrent in the bulk heterojunction layers. Only PCPDTBT:[70]PCBM based devices showed a weaker dependence of capacitance on the light intensity, indicating that space charge limitation was not reached in that case.

To conclude we suggest that, close $V_{oc}$ conditions, the photocurrent in organic solar cells can be limited by the buildup of space charge. Space-charge limited conditions are more likely to be reached by solar cells having high efficiency of free charge generation, weakly depending on electric field. For active layers in which the photogeneration of current is strongly limited by geminate recombination, such as in PCPDTBT:[70]PCBM, the space charge limit might not be reached.

Our results indicate that relatively well performing polymer solar cells can still be limited in fill factor by space charge effects. In this case, an option to increase
Evidence for space-charge limited conduction in organic photovoltaic cells at $V_{oc}$

the fill factor would be the enhancement of the charge carrier mobility or a reduction of the extent of Langevin recombination.
8.5 Experimental section

Materials and device fabrication. Photovoltaic devices were made by spin coating poly(ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP Al4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). [6,6]-Phenyl-C_{61}(C_{71})-butyric acid methyl ester ([60]([70])PCBM) (Solenne) was used as electron acceptor in spin-coated bulk heterojunction active layers in combination with a π-conjugated polymer as electron donors. The bulk heterojunction layers were deposited by spin coated in air at room temperature. Below the specific fabrication procedure for each conjugated polymer used is listed.

Poly[3-hexylthiophene] (P3HT) ($M_n < 50$ kg/mol, 98% regioregular, Rieke) was spin coated at 5000 rpm from chloroform:chlorobenzene (1:1 volume) solution containing 15 mg P3HT per mL and [60]PCBM in a 1:1 polymer: [60]PCBM weight ratio. Both as-cast and thermally annealed devices were fabricated. Annealing was performed at 140°C for 60 s in inert atmosphere prior to the metal electrode evaporation. Active layer thickness = 70 nm. Modified P3HT:[60]PCBM devices were also fabricated, incorporating a 30 nm Al$_2$O$_3$ layer deposited by means of atomic layer deposition (ALD) on top of ITO and before spin coating PEDOT:PSS and the active layer. The devices incorporating Al$_2$O$_3$ combined with an active bulk heterojunction layer of 70 nm thick were not annealed.

Poly[2-methoxy-5-(3’,7’-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) ($M_w = \sim 10^3$ kg/mol, PDI = 7) was spin coated at 1000 rpm using a chlorobenzene solution containing 3 mg MDMO-PPV per mL and [60]PCBM in a 1:4 polymer: [70]PCBM weight ratio. Active layer thickness = 175 nm.

Poly[2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b0]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole (PCPDTBT) ($M_n = 27.7$ kg/mol, PDI =1.9) was spin coated at 2000 rpm using a chlorobenzene solution containing 10 mg of PCPDTBT per mL and [60]PCBM in a 1:2 polymer: [70]PCBM weight ratio. Active layer thickness = 80 nm.

Solar cells were completed with a top contact consisting of LiF (1 nm) and Al (100 nm) deposited by vacuum evaporation at $\sim 3 \times 10^{-7}$ mbar. The active area of the cells was 0.091 cm$^2$. J-V characteristics were measured under $\sim 100$ mW/cm$^2$ white light from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter, using a Keithley 2400 source meter. The mismatch factor of this lamp to the AM1.5 (100 mW/cm$^2$) spectrum was not determined (see Table 8.3 for the device parameters).

Table 8.3: Solar cells characteristics: short-circuit current ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF) and maximum power point (MPP) under 100 mW/cm$^2$ illumination

<table>
<thead>
<tr>
<th>Solar cell</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>MPP (mW/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT:[60]PCBM as-cast</td>
<td>4.13</td>
<td>0.62</td>
<td>0.6</td>
<td>1.53</td>
</tr>
<tr>
<td>P3HT:[60]PCBM annealed</td>
<td>7.94</td>
<td>0.54</td>
<td>0.69</td>
<td>2.96</td>
</tr>
<tr>
<td>MDMO-PPV:[70]PCBM</td>
<td>3.11</td>
<td>0.84</td>
<td>0.55</td>
<td>1.44</td>
</tr>
<tr>
<td>PCPDTBT:[70]PCBM</td>
<td>9.06</td>
<td>0.67</td>
<td>0.42</td>
<td>2.55</td>
</tr>
</tbody>
</table>
Evidence for space-charge limited conduction in organic photovoltaic cells at \( V_{oc} \)

**Impedance spectroscopy measurements.** Impedance spectroscopy was performed using a Solartron 1260 impedance analyzer. White light steady-state illumination was obtained from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter, achieving \( \sim 100 \text{ mW/cm}^2 \).

**Numerical modeling.** A 1-dimensional numerical model was used to reproduce the experimental results of the structure containing the insulating Al\(_2\)O\(_3\) layer. An active layer of length \( L = 70 \text{ nm} \) was divided in \( N = 36 \) discrete points that represented the P3HT:[60]PCBM layer. The relative dielectric constant was set at 3.6. The insulating layer with thickness of 50 nm and a dielectric constant of 9.5 was placed next to the active layer. The numerical model solves the drift-diffusion equations and Poisson’s equation on this grid by forward integration in time. A detailed description of the numerical model can be found in Ref. [33]. Electrons and holes were injected from metal contacts described by a Boltzmann factor \( \sim \exp(-E_{\text{inj}}/kT) \). The hole and electron injection barriers \( E_{\text{inj}} \) were set at 0.2 eV. Carriers were generated with a rate \( g \) at each grid point in the active layer. In the simulation, only bimolecular Langevin type recombination was considered. In the simulations the rate of recombination \( \gamma \)is taken as \( R \gamma_0 \) with \( R \) an adjustable recombination prefactor and \( \gamma_0 \) the Langevin expression: \( \gamma_0 = (q/\varepsilon_0 \varepsilon_r) (\mu_p + \mu_n) \). The temperature \( T \) was set at 300 K. Table 8.1 lists the parameters used in the simulations.

To compute the admittance spectrum, the currents through the diode were first allowed to reach steady-state in the modeling procedure. After this, a voltage step of 0.01 V was applied and the resulting step response of the current was calculated. The complex admittance spectra can then be derived by a Fast Fourier Transform of the derivative of the conductance.

### 8.6 References and notes

Under these conditions, $j \propto n$, $p \propto \sqrt{g}$ and hence $dn/dt \propto -\gamma np \propto -\gamma n \sqrt{g}$ which leads to an exponential decay for $n$ with time constant $\tau^{-1} \propto \gamma \sqrt{g}$.
Epilogue
One of the principal questions in organic photovoltaics is the mechanism of generation of free, extractable charge carriers near the donor-acceptor heterojunction. The research described in this thesis dealt with this question in polymer:fullerene based solar cells.

The first step in charge generation is the dissociation of the photogenerated excitons at the donor-acceptor interface, which results in the population of an interfacial charge transfer (CT) state. In Chapter 2 we have shown that a minimum energy loss of \( \sim 0.1 \) eV between the energy of the lowest excited singlet exciton \( E_{S1} \) and the energy of the interfacial CT state \( E_{CT} \) is necessary to have a yield of charge transfer states close to unity. Empirically one finds that the open-circuit voltage expressed in electron volt \( (qV_{oc}) \) is 0.5 eV lower than \( E_{CT} \). This implies a maximum value for the open-circuit voltage in cells with high quantum efficiency at \( \sim 0.6 \) eV below the optical band gap of the donor-acceptor blend.

Once formed, the CT state must dissociate into free charges. This critical step in charge generation is also one of the least understood. Thermalized CT states are expected to represent strongly bound electron-hole pairs positioned across the heterojunction interface. The binding energy of electron and hole in the CT state may be estimated at \( \sim 0.5 \) eV, assuming that the charges are small polarons and that classical electrostatics applies.

The geminate electron hole pair at the heterojunction comprising the CT state pair has a finite lifetime because of electron-hole recombination, either to the ground state or to a lower lying triplet state on either of the two components. For efficient dissociation of the CT state, a dissociation rate exceeding the rate of recombination \( (\sim \text{ns}^{-1}) \) is required. In this picture, it is problematic to explain the experimental observations of high yields of free charge formation, given the high Coulombic barrier that has to be overcome. The high rate of dissociation in combination with the high expected barrier has been the enigma of organic solar cells.

It is important to note that a high yield of free carrier formation and a large electron-hole binding do not exclude each other on the basis of energy conservation. The experimentally observed difference between \( E_{CT} \) and \( qV_{oc} \) of about 0.5 eV shows that, on the whole, carrier generation and collection is exothermic. The Coulombic attraction between electron and hole would only lead to an energetically unfavorable transition state.

In this respect it may be instructive to express the rate for charge carrier dissociation in terms of transition state theory: \( k_d = \exp(-\Delta G^{\ddagger}/k_b T) = \exp(-\Delta H^{\ddagger}/k_b T) \times \exp(\Delta S^{\ddagger}/k_b) \). Here the Coulombic attraction leads to an unfavorable enthalpy of activation \( (\Delta H^{\ddagger}) \). The height of \( \Delta H^{\ddagger} \) and the location of this maximum are expected to
depend on the charge distribution in the diode including bound and trapped charges. Furthermore $\Delta H^{\ddagger}$ will also depend on the applied electrostatic potential. The unfavorable enthalpy $\Delta H^{\ddagger}$ may be compensated by a favorable entropy of activation ($\Delta S^{\ddagger}$). The activation entropy relates to the number of ways the transition state can be realized and depends on the densities of CT and polaron states. The local densities of these states depend on the distribution of donor and acceptor molecules. Note that also the attempt frequency for dissociation of the CT pair may formally be included in $\Delta S^{\ddagger}$. As put forward by Veldman et al. \cite{1} for polarons diffusing in a Coulombic potential well, a higher mobility raises the attempt frequency for escape from the well.

The CT state can recombine radiatively to the ground state, resulting in detectable luminescence signal. The luminescence signal was used in Chapter 2 to investigate the formation of the CT state. In addition to the radiative decay pathway of the CT state, also recombination to a lower lying triplet state (either on the donor or the acceptor) can take place. \cite{2,3} In Chapters 3 and 4 we have observed the formation of triplets via the CT state in the PCPDTBT:PCBM blend combining optical (PIA) and electro-optical (photo-CELIV) techniques. When the dimension of the nanoscale domains and, hence, the phase separation of the bulk heterojunction was increased, we observed a reduction of recombination to triplets in favor of free charge formation. The reduction in recombination correlates with an improved fill factor and short-circuit current in devices under illumination. We explain the reduced recombination to triplet states by proposing that the dissociation rate of the CT state into free charges is enhanced in morphologies having a higher degree of phase separation. This results in a decreased number of CT states available for recombination to triplets. Consistent with this explanation, CT photoluminescence is almost completely quenched in the optimized morphology, indicating that the CT state is more efficiently depopulated via dissociation. The higher dissociation rate can be due to an enhancement of local carrier mobilities, when larger donor and acceptor domains are available. \cite{1}

Additionally, increased phase separation and interchain order in the polymer domains could result in larger delocalization of the charged states at the heterojunction, giving reduced effective Coulombic barrier to be overcome in order to dissociate the CT state. \cite{4,5} Furthermore, in Chapter 5 we have suggested that preventing the population of triplet states can enhance the photochemical stability of polymer:PCBM blends.

The probability of CT dissociation depends on the electric field acting on the electron-hole pair. A strong dependence of the dissociation probability on the electric field will result in a low fill factor of the $J-V$ curve under illumination. Ideally, one would like to achieve the maximum probability of dissociation at electric fields as low as possible, close to those present at open-circuit voltage. The dependence on electric
field of the probability of CT dissociation is in principle influenced by the details of the CT dissociation mechanism itself. In Chapters 6 and 7 we used the voltage dependence of photocurrents to get more insight into this mechanism, considering that the voltage applied is related to the electric field inside the active layer. In as-cast PCPDTBT:PCBM blends (Chapter 7) we showed that CT states created with no excess energy via the CT $\leftarrow S_0$ transition necessitate more field to be dissociated compared to CT states created with above band gap excitations, where more excess energy is available. Empirical evidences of a correlation between excess energy and increased yield of free charge formation have been reported.$^{[6,7]}$ This would indicate that a certain amount of photon energy needs to be lost in order to achieve high internal quantum efficiency.

However we also observed that the efficiency of CT dissociation does not necessarily depend on the excess energy. No influence of excess energy on CT dissociation was observed in Si-PCPDTBT:PCBM blends. The chemical structure of Si-PCPDTBT is almost identical to the one of PCPDTBT; only with a bridging carbon atom being substituted by a silicon atom in the CPDT unit. When blended with PCBM, the Si-PCPDTBT results in coarse nanomorphologies, similarly to those obtained by the addition of cosolvents in casting PCPDTBT:PCBM blends. The effect on device performance is also similar. In particular, the fill factor is strongly increased compared to as-cast PCPDTBT:PCBM (from $\sim$40% to $\sim$60%). We obtained similar results on P3HT:PCBM solar cells, both annealed and as-cast (Chapter 6). Other authors also reported on the independence of CT dissociation efficiency on photon excess energy in P3HT:PCBM solar cells.$^{[8,9]}$ Both Si-PCPDTBT:PCBM and annealed P3HT:PCBM blends show large nanoscale phase segregation together with aggregation of the polymer chains. Consistently with what concluded on the recombination to triplets, our results suggest that these morphological properties allow efficient CT dissociation at low electric fields.

It is interesting to note that also not annealed P3HT:PCBM blends show no influence of excess energy on CT dissociation (Chapter 6). In this case the nanoscale morphology is expected to be quite finely mixed. Therefore the morphology related explanation given above for efficient CT dissociation cannot hold in this case. However it must be noted that in this system recombination of the CT state to a lower triplet state is not possible, because the CT state is the lowest excited state. The results on the independence of CT dissociation on excess energy in as-cast P3HT:PCBM blends seem to suggest that, in absence of recombination to triplets, the total CT recombination rate might become low enough to have high probability of CT dissociation at low electric fields even with not particularly high dissociation rates. A
similar conclusion was reached recently by Murthy et al. by measuring the yield of free charge generation in blends consisting of P3HT mixed with different fullerene derivatives.\cite{9}

For a solar cell under illumination one may expect that under open-circuit conditions the internal electric fields are minimized. If the charge carrier generation process would depend critically on the electric field strength then close to open-circuit conditions it may be expected that the photocurrent becomes limited by the net generation rate. In Chapter 8, impedance spectroscopy was used to investigate photocurrents around open circuit. We find that the dependence of the photocurrent on light and applied bias are conform to the expectation for space-charge limited currents combined with bimolecular recombination of free charge carriers in blends not affected by strong geminate recombination such as P3HT:PCBM and PPV:PCBM. This indicates that field dependent generation of free charge carriers is not limiting the photocurrent under these conditions in these systems.

In summary, for efficient organic solar cells the chemical structure of donor and acceptor the materials used in the active layer should be such that the charge transfer state can be formed from neutral excited states with minimal energy dissipation ($E_{S1} - E_{CT} = \sim 0.1$ eV). Once the CT state is formed, recombination of the CT state to triplet excited states should be minimized to ensure high efficiency and photochemical stability. Efficient dissociation of the CT state into free carriers is possible without large excess energies or strong electric fields provided that the nanoscale morphology of organic bulk heterojunction near the donor-acceptor interface is sufficiently coarse. Coarse morphologies with extended phase segregation on the length scale of $\sim$10 nm result in low geminate recombination (both to ground and triplet state) and efficient CT dissociation.


Summary

Optoelectronic Processes at Polymer - Fullerene Heterojunctions

Charge Transfer States in Organic Solar Cells

Polymer photovoltaic cells currently achieve power conversion efficiencies (PCE) above 10% on lab scale. To compete with the efficiencies above 20% of inorganic solar cells, understanding and elimination of all the loss channels is necessary. This thesis investigates charge generation and recombination processes in polymer-fullerene solar cells with the aim of elucidating the nature of such losses.

Chapter 1 provides a general introduction to the subject of the thesis and an overview of the most relevant literature. In Chapter 2 the effect of the thermodynamic driving force on the efficiency of photoinduced charge transfer between semiconducting polymers and fullerene is investigated. A polyfluorene copolymer is mixed with a variety of fullerene mono- and bisadducts having different LUMO energy levels. The difference in LUMO energy of the acceptors results in different energies of the charge transfer (CT) states in the blends. By spectroscopic characterization of bulk heterojunction thin films and photovoltaic devices it is found that the CT state needs to be at least 0.1 eV lower in energy than the singlet excited state of the fullerene to be formed efficiently.

The central finding of Chapters 3 to 5 is that the nanoscale morphology of the polymer-fullerene heterojunction strongly influences the CT state dissociation and recombination. Blends composed of a small optical band gap semiconducting polymer (PCPDTBT) mixed with fullerene are studied with various techniques. The nanoscale phase separation of these blends is controlled by adding high-boiling point cosolvents to the solutions used to process the thin films. Without cosolvent the blends are very finely mixed and the addition of cosolvents increases the phase separation. In blends that are too finely mixed we observe recombination of the CT state to the triplet state of the polymer (Chapter 3). We monitor the formation of triplets and charges in the thin films by means of photoinduced absorption (PIA). The recombination to the triplet state is a loss mechanism, in competition with the dissociation of the CT state into free charges. This process is reduced in favor of free charge formation when the phase separation is increased, correlating with the increased device performance. Specifically, increased fill factor and short-circuit current are observed in the devices with optimized morphology. These results show that photophysical processes are controlled by the nanoscale morphology. In Chapter 4 we perform charge extraction experiments on solar cells having different nanoscale phase separation and we support
the results with PIA experiments on corresponding thin films. In the charge extraction and PIA experiments we study the same set of long-lived charges. We confirm that CT recombination (to the triplet and to the ground state) is largely responsible for the poor device performances of non-optimized blends. Finally, in Chapter 5 we show a correlation between population of triplet excited states and decreased photostability of the blends. We suggest that triplet states can lead to the formation of singlet oxygen, which in turn can initiate destructive chemical reactions involving the polymer chains.

In Chapters 6 and 7 the influence of excess photon energy (i.e. the difference between the energy of the absorbed photon and that of the CT state) in the CT state dissociation is investigated by means of charge extraction and spectral response measurements in different polymer:fullerene blends. We find that excess energy is not necessary for CT dissociation in blends with coarse phase separation. A measurable influence of the excess photon energy on CT dissociation is observed only in PCPDTBT:PCBM finely dispersed blends, which were shown in the previous chapters to be strongly affected by CT state recombination.

Chapter 8 investigates what is limiting the photocurrent of solar cells close to the open-circuit voltage. It is found that under these conditions space charge can build up, so that the photocurrent becomes space-charge limited. This condition is reached only in blends where CT dissociation is efficient at low electric fields. Impedance spectroscopy is the technique used here. The experimental results are supported by an analytical model and by drift diffusion simulations.

Summarizing, in this thesis it is shown that the CT state is a critical intermediate state in the charge generation process in polymer solar cells. The energy of the CT state needs to be low enough to convert neutral excitations into charges. The blend morphology is a crucial factor determining the branching ratio between dissociation into free carriers and recombination to the ground state or to the triplet state of the polymer.
Samenvatting

Opto-elektronische processen in polymeer–fullereen bulk-heterojuncties

Ladingsoverdrachttoestanden in organische zonnecellen

Plastic zonnecellen kunnen zonne-energie omzetten in elektrische energie met een efficiëntie van meer dan 10% op laboratoriumschaal. Om te kunnen concurreren met anorganische zonnecellen met efficiënties van meer dan 20%, is het nodig om alle verlieskanalen in kaart te brengen en te elimineren. Dit proefschrift beschrijft ladingsgeneratie en ladingsrecombinatie in polymeer-fullereen zonnecellen met als doel verliesmechanismes op te helderen.

Hoofdstuk 1 geeft een algemene inleiding over het onderwerp van dit proefschrift en geeft een overzicht van de meest relevante literatuur. Hoofdstuk 2 beschrijft het effect van de thermodynamische drijvende kracht op de efficiëntie van fotogei induceerde ladingsoverdracht tussen halfgeleidend polymeer en fullereen. Polyfluoreencopolymeer wordt gemengd met een scala van fullereen mono- en bisadducten waarvan de LUMO energieën onderling verschillen. Verschillen in de energie van de LUMO van de fullerenen resulteren in verschillen in energie van de ladingsoverdrachttoestand in de verschillende mengsels. Door middel van spectroscopische analyse aan de dunne-film bulk-het erojuncties en corresponderende zonnecellen wordt gevonden dat de ladingsoverdrachttoestand minstens 0.1 eV lager in energie moet liggen dan de singlet-aangeslagen toestand van de fullereen om efficiënte ladingsscheiding mogelijk te maken.

De algemene constatering in Hoofdstuk 3 t/m 5 is dat de morfologie van de polymeer-fullereen heterojunctie een grote invloed heeft op het dissociëren van de ladingsoverdrachttoestand in losse ladingen en het terugvallen van de ladingsoverdrachttoestand naar de grondtoestand of triplettoestand. Mengsels van halfgeleidend polymeer met kleine bandafstand en fullereen worden met verschillende technieken onderzocht. De fasescheiding op nanometer lengteschaal van deze mengsels wordt gecontroleerd door kleine hoeveelheden hoogkoken oplosmiddel bij te mengen in de oplossingen die gebruikt worden voor maken van de heterojuncties. Zonder dit co-oplosmiddel zijn de mengsels goed gemengd; de toevoeging van co-oplosmiddel induceert een fasescheiding. Voor mengsels die zeer fijn gemengd zijn, nemen we waar dat de ladingsoverdrachttoestand kan vervallen naar de triplet-aangeslagen toestand van het polymeer (Hoofdstuk 3). We detecteren de vorming van triplettoestanden en geladen toestanden in de dunne film door middel van
fotogeïnduceerde absorptiemetingen (PIA). Het terugvallen van de ladingsoverdracht naar de triplettoestand is een verliesmechanisme, dat optreedt in competitie met de dissociatie van de ladingsoverdrachttoestand in vrije elektrische ladingsdragers. In bulk-heterojuncties met een grovere fasescheiding is het verval naar de triplettoestand onderdrukt ten gunste van vorming van vrije ladingsdragers. De onderdrukking van tripletvorming blijkt gecorreleerd aan de toename in de efficiëntie van de zonnecel. In meer detail, het optimaliseren van de morfologie leidt tot een toename in vulfactor en kortsluitstroom van de zonnecel. Deze resultaten laten zien dat fotofysische processen worden gecontroleerd door de morfologie op nanometerschaal. In Hoofdstuk 4 wordt ladingsextractie in zonnecellen met verschillende morfologie gecorreleerd aan het optreden van fotogeïnduceerde absorptie in dunne films met dezelfde samenstelling en morfologie als de actieve laag in de zonnecel. Met de ladingsextractie en PIA experimenten kan dezelfde verzameling van langlevene ladingsdragers bestudeerd worden. Dit levert een bevestiging van de bewering dat de matige efficiëntie voor de niet-geoptimaliseerde morfologie te wijten is aan terugval van de ladingsoverdrachttoestand naar ofwel de triplet- of wel de grondtoestand, voordat de ladingsoverdrachttoestand kan dissociëren in vrije ladingsdragers. In Hoofdstuk 5 laten we, als slot van dit deelonderzoek, zien dat er een anticorrelatie bestaat tussen de bevolking van de triplettoestand door terugval van de ladingsoverdrachttoestand en de fotochemische stabiliteit van de actieve polymeerlaag in de zonnecel. We vermoeden dat de triplettoestand aanleiding geeft tot vorming van het uiterst reactieve singlet zuurstof. Dit singlet zuurstof kan op haar beurt aanvallen op de polymeren en ze afbreken.

Hoofdstuk 6 belicht de invloed van de overmaat aan fotonnergie op het proces van ladingsscheiding in de zonnecel. Met overmaat aan fotonnergie bedoelen we het verschil tussen de fotonnergie en de energie van de ladingsoverdrachttoestand. Door de efficiëntie van de zonnecel voor de verschillende kleuren van het zonlicht apart te bepalen vinden we dat een overmaat aan fotonnergie niet noodzakelijk is voor efficiënte ladingsscheiding, mits de polymeerfase en fullereenfase in the actieve laag voldoende gescheiden zijn. Een waarnembare invloed van de overmaat aan fotonnergie werd alleen gevonden voor zeer fijn gedispergeerde PCPDTBT:PCBM mengsels. Zoals in de voorafgaande hoofdstukken is besproken vinden we juist voor deze mengsels dat de terugval van de ladingsoverdrachttoestand naar triplettoestand of grondtoestand een belangrijke beperkende factor in de energieconversie is.

Hoofdstuk 8 behelst de vraag wat de fotostroom van een plastic zonnecel eigenlijk beperkt onder elektrische spanningen vlakbij de openklemspanning. We vinden dat zich onder deze condities een ruimtelading vormt die een beperking oplegt
aan de grootte van de stroom. Deze toestand kan alleen verwacht worden voor mengsels waarin het uiteenvallen van de ladingsoverdrachttoestand al bij zeer lage elektrische veldsterktes met een zeker efficiëntie verloopt. Impedantiespectroscopie is hier de te gebruiken techniek. De experimentele resultaten worden onderbouwd met zowel een analytisch als een numeriek model voor drift-diffusie transport in de actieve organische laag.

Samenvattend, in dit proefschrift wordt duidelijk gemaakt dat de ladingsoverdrachttoestand, een kritieke overgangstoestand is in het proces van fotogeïnduceerde ladingsscheiding in zonnecellen op basis van halfgeleidende polymeren. De energie van de ladingsoverdrachttoestand moet laag genoeg zijn om ongeladen excitaties om te kunnen zetten in ladingsdragers. De morfologie van de gemengde polymer-fullereen laag is een cruciale factor in de omzetting van de ladingsoverdrachttoestand en bepaalt in belangrijke mate de uiteindelijke uitkomst van de door licht geïnduceerde excitatie: terugval naar de grondtoestand met volledige omzetting van de fotonenergie in nutteloze warmte of vorming van vrije energetische ladingsdragers.
Daniele Di Nuzzo was born on July 27th 1982 in Sesto San Giovanni, Italy. After obtaining his high school degree from Liceo Scientifico “Giulio Casiraghi” in Cinisello Balsamo, he studied physics at the University of Milano-Bicocca. In 2008 he obtained his Master of Science degree with specialization in solid state physics. His master thesis project involved the study of the photophysics of organic lanthanide complexes. The thesis research was performed in the group of prof. Riccardo Tubino (University of Milano-Bicocca).

In November 2008 he started his PhD project at the Eindhoven University of Technology in the group “Molecular Materials and Nanosystems”, under the supervision of prof. René Janssen and dr. Stefan Meskers. The most important results of his PhD are presented in this thesis. His work forms part of the research program of the Dutch Polymer Institute (DPI).
**List of publications**

*Efficient solar cells based on an easily accessible diketopyrrolopyrrole polymer.*

*Improved film morphology reduces charge carrier recombination into the triplet excited state in a small bandgap polymer-fullerene photovoltaic cell.*

*Influence of cathode oxidation via the hole extraction layer in polymer:fullerene solar cells.*

*Influence of photon excess energy on charge carrier dynamics in a polymer-fullerene solar cell.*

*Simultaneous open-circuit voltage enhancement and short-circuit current loss in polymer:fullerene solar cells correlated by reduced quantum efficiency for photoinduced electron transfer.*

*The effect of PCBM on the photo-degradation kinetics of polymers for organic photovoltaics.*
List of publications

*Carrier recombination in polymer fullerene solar cells probed by reversible exchange of charge between active layer and electrodes induced by a linearly varying voltage.*

*Evidence for space-charge limited conduction in organic photovoltaic cells at open-circuit conditions.*
Acknowledgements

At the end of my PhD there are many people that I would like to thank. First of all my supervisors René Janssen and Stefan Meskers. It was a great opportunity to work with you. In both of you I always appreciated your knowledge on a broad range of topics, from synthetic chemistry to device physics, without losing contact with the experimental and practical sides of making science. Besides, you were always very present to help and guide me. Thank you.

Here I would also like to thank Vladimir Dyakonov, Maria Antonietta Loi and Martijn Kemerink for accepting to be in the reading committee and for the review of my thesis. Particularly useful was the discussion on Chapter 7 with Martijn Kemerink. I am also thankful to Enrico Da Como for taking part in my defense.

Many of the results that I have obtained during these four years would not have been possible without the help of others. In chronological order, I would like to start thanking Arantxa Aguirre, with whom I performed my first experiments in Eindhoven, which finally led to Chapter 3. Many thanks also to Munazza Shahid for providing me with the polymer I used in those experiments.

Veronique Gevaerts is kindly acknowledged for the TEM images that are shown in Chapters 2 and 3. Concerning Chapter 2, I would like to mention the nice collaboration with Gert-Jan Wetzelaer, who provided the samples and was always ready to give feedback and Ricardo Bouwer, who synthesized the fullerene derivatives.

Special thanks go to Tom van der Hofstad, whom I supervised in his bachelor and master projects. During your master project you obtained what I consider as a remarkable amount of results: without your work Chapters 4 and 6 would not be there. Thank you and good luck with your PhD.

I also want to acknowledge Mauricio van den Berg, who made a nice contribution during his internship under my supervision, including the first voltage dependent EQE measurements that are shown in Chapter 6.

I had a good time in the lab with Andreas Distler when he came to visit Eindhoven for a few days. Especially I want to thank him and Hans-Joachim Egelhaaf for the collaboration in the study on photo-stability presented in Chapter 5 and the work on the manuscript.
Chapter 8 greatly profited from the numerical simulations performed by Stephan van Reenen. Thanks a lot to you and Martijn Kemerink, also for the discussion on the manuscript. Here I also take the opportunity to thank Pablo Perez Boix, with whom I made my first impedance spectroscopy measurements when he was visiting, also having good times.

The latest in time is Chapter 7. For this I have to thank Dominique Wehenkel for his precious help in discussions and with the numerical simulations, together with Jan Anton Koster for providing the simulation software and for the discussions as well.

The Dutch Polymer Institute (DPI) is acknowledged for funding. In the many DPI review meetings I could always appreciate the discussions on my results with the chairmen Frans De Schryver and John van Haare.

Not every experiment or ever day of work ends up in something written down. However I believe that every day contributes to professional and human growth if it is spent in a good working environment. The Molecular Science and Technology group provided such an environment. Here in these years I could enjoy the presence of many people from all around the world and always learn something from them, in the lab, in the group meetings, in the DPI meetings, in the office or in the coffee room. For this I would like to mention the ones that were the most present in my daily life at work: Martijn Wienk, Benjamin Bory, Mindaugas Kirkus, Veronique Gevaerts, Isabelle Monnaie, Henk Eding, Arjan Zoombelt, Johan Bijleveld, and Jan Gilot in the first two years. Rafael Juarez during his few-months visit. Finally, my present and past officemates always contributed to an enjoyable atmosphere, often with interesting discussions, either on science or other topics: Dominique Wehenkel, Dhritiman Gupta, Weiwei Li, Ratheesh Kunnathodi, Gijs van Pruissen, Alice Furlan, Girish Lakhwani, Martin Wolffs, Arantxa Aguirre, Stefan Oosterhout, Marie-France Falzon, Bram Karsten, Jan Anton Koster. Thank you all.