Strategies for Optimizing Organic Solar Cells:
Correlation Between Morphology and Performance in DCV6T - C60 Heterojunctions

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David Wynands
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1. Gutachter: Prof. Dr. K. Leo
2. Gutachter: Prof. Dr. C. Brabec

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Contents

1 Introduction ......................................................... 9

2 Physical Properties of Organic Semiconductors ...................... 11
   2.1 Organic Solids .................................................. 11
   2.2 Molecules with Conjugated $\pi$-Electron Systems ................ 12
      2.2.1 Energy Splitting in Molecular Orbital Theory ............... 12
      2.2.2 Extended $\pi$-Conjugated Systems .......................... 14
   2.3 Optical Excitations in Organic Molecules ....................... 16
   2.4 From Molecules to Solids ....................................... 19
      2.4.1 Self-Polarization in Organic Solids ....................... 19
      2.4.2 Excitations in Organic Solids ............................. 21
      2.4.3 Charge Carriers and Transport ............................ 23

3 Organic Photovoltaics ............................................. 27
   3.1 Solar Cell Physics ............................................. 27
      3.1.1 Conversion of Radiation into Chemical Energy .......... 28
      3.1.2 Conversion of Chemical Energy into Electrical Energy .. 32
      3.1.3 Conventional pn-Junction as Photodiode ................. 35
      3.1.4 Simple Equivalent Circuit ................................ 39
   3.2 Organic Solar Cells ............................................ 40
      3.2.1 Donor-Acceptor Heterojunction .......................... 40
      3.2.2 Recombination Processes ................................. 46
      3.2.3 Transport Layers – The p-i-n Concept ................... 48

4 Experimental ................................................................ 49
   4.1 Materials ......................................................... 49
      4.1.1 C60 .......................................................... 49
      4.1.2 Transport Materials ....................................... 50
   4.2 Sample Preparation ............................................... 52
   4.3 Experimental Methods ........................................... 54
      4.3.1 X-Ray Diffraction ......................................... 54
      4.3.2 Optical Characterization .................................. 55
      4.3.3 Topography Characterization .............................. 55
Abstract

This work investigates organic solar cells made of small molecules. Using the material system α,ω-bis(dicyanovinylene)-sexithiophene (DCV6T) - C60 as model, the correlation between the photovoltaic active layer morphology and performance of the solar cell is studied. The chosen method for controlling the layer morphology is applying different substrate temperatures (T_{sub}) during the deposition of the layer.

In neat DCV6T layers, substrate heating induces higher crystallinity as is shown by X-ray diffraction and atomic force microscopy (AFM). The absorption spectrum displays a more distinct fine structure, a redshift of the absorption peaks by up to 11 nm and a significant increase of the low energy absorption band at T_{sub} = 120 °C compared to T_{sub} = 30 °C. Contrary to general expectations, the hole mobility as measured in field effect transistors and with the method of charge extraction by linearly increasing voltage (CELIV) does not increase in samples with higher crystallinity. In mixed layers, investigations by AFM and UV-Vis spectroscopy reveal a stronger phase separation induced by substrate heating, leading to larger domains of DCV6T. This is indicated by an increased grain size and roughness of the topography, the increase of the DCV6T luminescence signal, and the more distinct fine structure of the DCV6T related absorption.

Based on the results of the morphology analysis, the effect of different substrate temperatures on the performance of solar cells with flat and mixed DCV6T - C60 heterojunctions is investigated. In flat heterojunction solar cells, a slight increase of the photocurrent by about 10 % is observed upon substrate heating, attributed to the increase of DCV6T absorption. In mixed DCV6T : C60 heterojunction solar cells, much more pronounced enhancements are achieved. By varying the substrate temperature from -7 °C to 120 °C, it is shown that the stronger phase separation upon substrate heating facilitates the charge transport, leading to a significant increase of the internal quantum efficiency (IQE), photocurrent, and fill factor. Consequently, the power conversion efficiency (PCE) increases from 0.5 % at T_{sub} = -7 °C to about 3.0 % at T_{sub} ≥ 77 °C. Subsequent optimization of the DCV6T : C60 mixing ratio and the stack design of the solar cell lead to devices with PCE of 4.9±0.2 %. Using optical simulations, the IQE of these devices is studied in more detail to identify major remaining loss mechanisms. The evaluation of the absorption pattern in the wavelength range from 300 to 750 nm shows that only 77 % of the absorbed photons contribute to the exciton generation in photovoltaic active layers, while the rest is lost in passive layers. Furthermore, the IQE of the photovoltaic active layers, consisting of an intrinsic C60 layer and a mixed DCV6T : C60 layer, exhibits a lower exciton diffusion efficiency for C60 excitons compared to DCV6T excitons, attributed to exciton migration into the adjacent electron transport layer.
Kurzfassung

Diese Arbeit befasst sich mit organischen Solarzellen aus kleinen Molekülen. Anhand des Materialsystems $\alpha,\omega$-bis(Dicyanovinyl)-Sexithiophen (DCV6T) - C60 wird der Zusammenhang zwischen Morphologie der photovoltaisch aktiven Schicht und dem Leistungverhalten der Solarzellen untersucht. Zur Beeinflussung der Morphologie werden unterschiedliche Substrattemperaturen ($T_{\text{sub}}$) während des Schichtwachstums der aktiven Schicht eingestellt.


Ausgehend von den Ergebnissen der Morphologieuntersuchung werden die Auswirkungen von verschiedenen Substrattemperaturen auf das Leistungsverhalten von DCV6T - C60 Solarzellen mit planarem und Volumen-Heteroübergang analysiert. Solarzellen mit planarem Heteroübergang weisen eine geringe Verbesserung des Photostromes von etwa 10 % beim Heizen des Substrates auf. Diese wird durch die Erhöhung der DCV6T Absorption verursacht. In Volumen-Heteroübergängen führt die stärkere Phasentrennung bei steigender Substrattemperatur im untersuchten Temperaturbereich von -7 °C bis 120 °C zu einer Verbesserung des Ladungsträgertransports. Dadurch verbessern sich die interne Quanteneffizienz (IQE), der Photostrom und der Füllfaktor. Der Wirkungsgrad der Solarzellen erhöht sich von 0.5 % bei $T_{\text{sub}} = -7$ °C auf 3.0 % bei $T_{\text{sub}} \geq 77$ °C.

Eine weitere Optimierung des DCV6T : C60 Mischverhältnisses und des Schichtaufbaus ermöglicht Solarzellen mit Wirkungsgraden von 4.9±0.2 %. Mittels optischer Simulationen wird die IQE dieser Solarzellen näher untersucht, um verbleibende Verlustmechanismen zu identifizieren. Es ergibt sich, dass innerhalb des Wellenlängenbereichs von 300 bis 750 nm nur 77 % der absorbierten Photonen tatsächlich in den photovoltaisch aktiven Schichten absorbiert werden, während der Rest in nicht aktiven Schichten verloren geht. Des Weiteren kann nachgewiesen werden, dass C60 Exzitonen aus der aktiven Schicht, bestehend als einer intrinsischen C60 Schicht und einer DCV6T : C60 Mischschicht, durch Diffusion in die angrenzende Elektronentransport schicht verloren gehen.
Publications

Articles


Conference Contributions


Patents

1 Introduction

Our daily life needs energy. Energy is mainly used for heating, transportation, and as electricity. The primary energy consumption in Germany in the year 2009 amounts to the hardly imaginable number of 13 341 PJ or 3 694 TWh [1]. Only 9% of this huge amount are coming from renewable sources, the rest is mainly provided by oil, natural gas, and coal. In the same year, the gross electricity generation, which is only a small fraction of the primary energy consumption, was 596 TWh. So, the averaged electricity generation per capita in Germany (2009) amounts to 7 250 kWh\(^1\), which is equivalent to the energy released by burning of 0.62 tons of oil, but also equivalent to the energy of one year sun irradiation onto 7.25\(^2\) m\(^2\) in Germany\(^2\). The fraction of renewable sources in electricity generation has already been increased to 15.6%. But still, the major part is generated from non-sustainable sources like coal (42.9%), uranium (22.6%), and natural gas (12.9%).

Clearly, this way of meeting our energy demand implies several severe problems. First, the usage of fossil fuel releases greenhouse gases, especially CO\(_2\), into the atmosphere, causing a rise of the world’s average temperature leading to a fundamental climate change [2]. Secondly, the usage of nuclear power is still lacking a satisfactory solution for the storage of the nuclear waste, and furthermore the possible misuse of nuclear material for weapons is a very precarious matter. Finally, these resources exploited since the beginning of industrialization are limited. Considering these thoughts, we obviously need to enforce a change in technology towards more sustainable and environmentally friendly energy sources.

One technology that is able to contribute to the future energy generation is photovoltaics. There are several photovoltaic technologies, using different types of solar cells to convert solar radiation into electrical power. This work addresses the investigation and development of a quite new class of photovoltaics: organic solar cells. Organic materials offer very high extinction coefficients (>5·10\(^4\) cm\(^-1\)), allowing for very thin active layers and consequently very low material consumption in solar cell devices. Furthermore, they can be processed on flexible substrates with low energy-consuming techniques. Thus, organic solar cells have the potential to provide a low cost alternative

\(^1\)The value of 7250 kWh per capita not only includes the electricity consumption of the households, but is the total sum of electricity consumption in Germany divided by the number of citizens and thus also contains electricity consumed by industry and transportation.

\(^2\)The German average of solar power is 1000 kWh/m\(^2\)/a.
for the present solar cell types, which are all together too expensive to compete with the price conventional energy is currently sold at. Today, organic solar cells are at the very beginning of real commercial applications. Since Tang [3] introduced in 1986 the key concept of organic donor-acceptor heterojunctions, research of the basic organic solar cell function and development of new absorber materials have lead to steadily increasing power conversion efficiencies, approaching values up to 8% now [4–7]. Although technological improvements are progressing fast, the microscopic understanding of organic solar cells is still incomplete, since many aspects of solar energy conversion in organic photovoltaics are based on very complex processes. One interesting and also very important aspect is the correlation between active layer morphology and performance. For many polymer heterojunction systems, it was found that morphology has a significant influence on the device efficiency, leading to dramatic variations within one material system just by changing the preparation conditions [8–11]. Numerous investigations have addressed this correlation in the field of polymer solar cells, where the solution based preparation techniques offer a large diversity of methods to affect the morphology. In small molecule solar cells, such studies are still rare because the possibilities for morphology control are rather limited. To bridge this gap, this work focuses on the investigation of morphology-performance relations in small molecule solar cells by using the model system $\alpha,\omega$-bis(dicyanovinylene)-sexithiophene (DCV6T) – C60. With the related material $\alpha,\alpha$-bis(dicyanovinylene)-quinqueathiophene (DCV5T) solar cells reaching an efficiency of 3.4% were already shown [12, 13]. However, in these works, the actual layer morphology was not addressed, disregarding the great potential for performance optimization. The aim of this work is thus to provide a detailed investigation of morphological effects in DCV6T – C60 heterojunctions, to identify their impact on solar cell performance, and subsequently combine the obtained results into a small molecule solar cell with optimized performance.

In Chapter 2 the basic physics of organic semiconductors is introduced. The function of solar cells in general and specifically of organic solar cells is then discussed in Chapter 3. The concept of p-i-n solar cells, which sets the basis for the solar cells presented in this work, is briefly introduced. Chapter 4 gives an overview about the preparation methods, materials, and characterization techniques, including a short discussion of standard reporting conditions and how they are implemented in this work. In Chapter 5 the material system DCV6T - C60 is investigated. In particular, the morphology of neat DCV6T and mixed DCV6T : C60 layers is studied for different substrate temperatures applied during the layer deposition. The resulting effects on important properties like absorption or charge mobility are discussed. The effect of the morphology change on solar cells is addressed in Chapter 6. Implications on the solar cell characteristics like current-voltage curve, quantum efficiency, and charge carrier recombination behavior are discussed. The optimized preparation conditions giving the maximal performance are determined and finally incorporated into a solar cell with subsequently optimized device design.
2 Physical Properties of Organic Semiconductors

In this chapter the basic physical properties of organic solids are introduced. In the beginning, a quantum physical description of molecules with conjugated $\pi$-electron systems is given in accordance with molecular orbital theory. Subsequently, the character of optical excitations in organic molecules is discussed. The next section deals with properties of organic solids and will start with a description of several polarization effects that may appear. After that, the characteristics of excitations and charge carriers in organic solids are discussed and a brief introduction into aspects of charge transport is given.

2.1 Organic Solids

Organic solids are made of molecules prepared by organic chemistry, i.e. molecules with carbon atoms as their essential structural elements. They can form single crystals, polycrystals, or glasses. The fundamental aspects, which determine all main properties of organic solids, are that the molecules are neutral and that their molecular orbitals are fully occupied. Therefore, they cannot form ionic or covalent bonds to their neighbouring molecules, but are bound together by van der Waals forces. These forces originate from the instantaneous induced dipole-dipole interaction, also called London dispersion force. This intermolecular force is very weak ($\approx 0.1 \text{ eV}$ [14]) compared to intramolecular forces and has a very short range (binding forces have a $\sim r^{-6}$ dependency on the distance [14]). Consequently, molecules as such remain intact within organic crystals and exhibit a well separated arrangement. This results in some typical properties of organic solids. Most organic compounds are characterized by low melting points, small dielectric constants, and low charge carrier mobilities. As another consequence of the very low intermolecular interactions compared to intramolecular interactions, the electronic structure of organic solids is mainly determined by the electronic levels of the individual molecule, rather than resulting from electronic interactions with a periodic crystal lattice structure like in inorganic semiconductors or metals.
2.2 Molecules with Conjugated \( \pi \)-Electron Systems

Many organic materials have a very large energy gap and are thus insulators. A precondition for semiconducting properties is that the molecules have an extended \( \pi \)-electron system, i.e. by overlapping \( p_z \)-orbitals between neighbouring atoms \( \pi \)-bonds are formed. We will here use molecular orbital theory to understand the quantum chemical origin of such \( \pi \)-electron systems.

2.2.1 Energy Splitting in Molecular Orbital Theory

Generally, the quantum physical wave function \( \Psi \) of a molecule is described by the time independent Schrödinger equation:

\[
H \Psi = E \Psi. \tag{2.1}
\]

Here, \( \Psi \) contains coordinates of all electrons and atomic nuclei, and \( H \) is the Hamiltonian containing all kinetic and potential energies that are assigned to them. The first simplification to solve this problem is the Born-Oppenheimer approximation. Comparing the mass of an electron to that of an atomic nucleus (\( m_{\text{proton}} = 1836 \cdot m_{\text{electron}} \)), it can be assumed that electrons move much faster than the nuclei. We can therefore treat nuclear and electronic motions independently. That means that the nuclear kinetic energy is neglected and the wavefunction of the electrons is now solved for fixed positions of the nuclei. This is still a many particle problem where each electron interacts with all other electrons. Therefore, an additional approximation is made, the independent electron approximation. Assuming that for each electron the electron interaction with other electrons can be accounted for in an averaged potential \( v_{\text{eff}}^i \), the electronic Hamiltonian can be separated into individual parts:

\[
H_{\text{el}} = H_{\text{el}}^1 + H_{\text{el}}^2 + H_{\text{el}}^3 + ..., \tag{2.2}
\]

where \( H_{\text{el}}^i \) is only dependent on the properties of the \( i \)-th electron. The problem is then reduced to the one-electron Schrödinger equation:

\[
H_i \Psi_i = \epsilon_i \Psi_i, \tag{2.3}
\]

\[
H_i = T_i + v_{\text{eff}}^i, \tag{2.4}
\]

where \( T_i \) is the kinetic energy of electron \( i \), \( \Psi_i \) is the one-electron wavefunction, or a so-called molecular orbital and \( \epsilon_i \) is the respective energy. To determine these molecular orbitals, we use the Linear Combination of Atomic Orbitals (LCAO) - method. In this method, molecular orbitals are constructed by a linear combination of atomic orbitals \( \Phi_j \), centered on individual atoms:

\[
\Psi_i = \sum_{j=1}^{n} c_{ij} \Phi_j. \tag{2.5}
\]
Coefficients $c_{ij}$ may be numerically determined by insertion of Equation (2.5) into the Schrödinger equation (2.3) and by applying the variational principle, e.g. using the Hartree-Fock method. For computational reasons, the number of orbitals $\Phi_j$ used for the calculation is finite and thus forms a finite set of basis functions. Therefore, the result cannot be an exact solution to Equation (2.3) but is only approximate. For a qualitative understanding, we can now consider a diatomic molecule as the simplest case, where each atom has one electron and only the atomic orbital with the lowest energy $\Phi_{1,2}$ (e.g. 1s state of atom 1 and atom 2) is considered for LCAO:

$$\Psi = c_1 \Phi_1 + c_2 \Phi_2. \quad (2.6)$$

When the atoms are brought together, their atomic orbitals overlap and the Coulomb interactions between atom cores and electrons will induce a splitting of the corresponding energy of $\Psi$, given by:

$$\epsilon = \frac{c_1^2 \alpha_1 + 2 c_1 c_2 \beta_{12} + c_2^2 \alpha_2}{c_1^2 + c_2^2 + 2 c_1 c_2 S}, \quad (2.7)$$

where $\alpha_j$ is the Coulomb integral which determines the energy of an electron in the orbital $\Phi_j$, and $\beta_{jk}$ is the resonance integral, which is a measure for the strength of bonding interaction as a result of overlap between $\Phi_j$ and $\Phi_k$. $S$ represents the overlap integral, determining the amount of overlap between the orbitals themselves. Given that the two atoms are of the same type, i.e. $\alpha_1 = \alpha_2 = \alpha$, the two solutions of Equation (2.7) can be written as:

$$\epsilon_{\pm} = \frac{\alpha \pm \beta}{1 \pm S}. \quad (2.8)$$

The energy splitting is sketched in Figure 2.1 together with a schematical representation of the shape of the respective orbitals $\Psi_{\pm}$. It can be seen that the electron density between the atoms and thus the screening of the positive charge of the nuclei by the electrons is higher in $\Psi_+$ than in $\Psi_-$. Correspondingly, $\Psi_+$ is lower in energy and is therefore called bonding orbital, while $\Psi_-$ is called antibonding orbital. The splitting between them is mainly determined by the resonance integral $\beta$ as $S$ can be neglected, since it is usually very small ($S \ll 1$). This splitting is a general consequence whenever there is considerable overlap between the original atomic orbitals. Beginning with the lowest energy the electrons are now assigned to the molecular orbitals. According to the Pauli exclusion principle, two electrons can occupy one molecular orbital when they differ in their spin quantum number. Thus, we find both electrons with different spins in the bonding molecular orbital $\Psi_+$.

From this example, we already see that bonding is a consequence of overlapping orbitals between two (or more) atomic sites and that new molecular orbitals are formed which are bonding and antibonding. Although more complex molecules cannot be solved analytically, we can use this knowledge to understand the molecules of interest qualitatively.
2.2.2 Extended \(\pi\)-Conjugated Systems

Let us now consider complex organic molecules with \(\pi\)-conjugated electron systems. Such systems are found in aromatic hydrocarbons, conjugated heterocyclic compounds, or in alkenes like ethene. A simple example of a \(\pi\)-conjugated molecule is benzene. Figure 2.2 shows a schematic representation of this aromatic molecule, which indicates shape and direction of the bonding orbitals. Carbon has six electrons in the configuration \(1s^2\ 2s^2\ 2p^2\) providing four valence electrons for bonding. Looking at the arrangement of atoms in benzene we see that all carbons as well as hydrogens are located in a plane and that their connecting lines, i.e. the direction of the bonds, are forming angles of 120°. In the calculation of molecular orbitals, this is regarded by use of the so-called \(sp^2\) hybridization. For this, the \(2s^2\) orbitals are mixed together with \(p_x\) and \(p_y\) orbitals to form three \(sp^2\) orbitals pointing into the 120° directions of the plane, while the \(p_z\) orbital is standing out of the plane. This new set of basis functions enables an easy qualitative description of the energy splitting in the molecules of interest. As can be seen in Figure 2.2, the \(sp^2\) orbitals of adjacent atoms have a very large overlap and therefore they form strong bonds, the so-called \(\sigma\)-bonds. Accordingly, the energy splitting between \(\sigma\) (bonding) and \(\sigma^*\) (antibonding) molecular orbitals is very wide. The six \(p_z\) orbitals are each overlapping with the \(p_z\) orbitals of neighbouring atoms, thus forming six molecular orbitals that are delocalized over the whole carbon ring (simultaneously below and above the plane). These molecular orbitals constitute so-called \(\pi\)-bonds. Consequently, the six electrons originating from the \(p_z\) orbitals now occupy three bonding \(\pi\) orbitals and may be found anywhere within the ring. They form a
2.2 Molecules with Conjugated π-Electron Systems

so-called π-conjugated system. The energy splitting between π (bonding) and π* (anti-bonding) orbitals is small compared to the σ-bonds, because there is only small overlap of the p_z orbitals. In the ground state, the electrons will occupy the bonding σ and π orbitals leaving the antibonding σ* and π* orbitals empty. Therefore, the Highest Occupied Molecular Orbital (HOMO) is generally a π orbital, while the Lowest Unoccupied Molecular Orbital (LUMO) is a π* orbital. Because of the small energy splitting of π orbitals the lowest energetic transitions are π-π* transitions.

From this example, we can understand the importance of the π-conjugated system. It determines the main energetic transitions and therefore properties like absorption and emission of light. As a general rule the energetic gap between the π orbitals, i.e. the gap between HOMO and LUMO, is decreasing with increasing number of p_z orbitals that constitute the π-conjugation. For example, this can be seen by adding more and more rings to benzene, which gives naphthalene, anthracene, tetracene, pentacene, and so on. In this series the optical gap is steadily reduced from 4.88 eV for benzene to 2.13 eV for pentacene [16]. Furthermore, π-conjugated systems are a prerequisite for electrical transport, since the delocalization enables the electrons to move freely within the molecule. Additionally, the density of states near HOMO and LUMO states increases with the size of the π-conjugated system. Polymers with long extended π-conjugation have quasi-continuous bands and can correspondingly show good conductivities.

The above mentioned intuitive considerations are based on the simple model of molecular orbital theory using LCAO, which only gives approximate solutions and does not yield quantitative results. To calculate orbital energies for a molecule with n electrons, the effective potential \( v_i^{eff} \) for every electron has to be determined by a self-consistent-field (SCF) approach like the Hartree-Fock method. This assures that the resulting one-electron orbitals of all n electrons are consistent with the mean field by all other

![Figure 2.2: Schematic representation of the orbitals and resulting orbital energies of benzene and the formation of a delocalized π-conjugated electron system. Picture is taken from www.orgworld.de.](image-url)
n-1 electrons. Those equations are almost universally solved by means of iterative algorithms. However, to obtain a realistic total energy of the molecule, configuration interactions have to be additionally taken into account. These are neglected in the independent electron approach. Details of these quantum chemical calculations are beyond the scope of the present work. In this context, we only want to point out that there is a difference between the orbital energies of a neutral molecule and of an ionized molecule. In the first case, the orbitals refer to the energy of the n-th electron of the molecule, e.g. upon excitation in higher orbitals, that is consistent to the interaction with all other n-1 electrons. In the second case, an additional charge, e.g. an electron, is brought into the molecule. It occupies a higher orbital with an energy consistent to all other n electrons of the molecule. Therefore, the respective energies differ by the additional shielding effect of one electron.

2.3 Optical Excitations in Organic Molecules

A molecule can be excited by absorption of light. The energy $h\nu$ of the incoming photon is thereby used to change from the electronic state $\Psi_n$ into a higher energy state $\Psi_m$. This interaction is usually described by the transition dipole moment $\mu_{n\rightarrow m}$, whose direction determines the polarization of the interaction with the electromagnetic wave, while the square of the magnitude gives the strength of the interaction. Using the dipole operator, which sums over all electron coordinates, $\mu_{n\rightarrow m}$ can be written as:

$$\mu_{n\rightarrow m} = \langle \Psi_m | -e \sum_i \hat{r}_i | \Psi_n \rangle.$$  \hspace{1cm} (2.9)

As already stated above, in the Born-Oppenheimer approximation the wavefunction $\Psi$ is separated into an electronic wavefunction $\Psi^e$ and a vibronic wavefunction $\Psi^\nu$ that accounts for intramolecular vibrations between the nuclei. Furthermore, the spin contribution is accounted for in the term $\Psi^s$, such that the overall wavefunction can be written as:

$$\Psi = \Psi^e \Psi^\nu \Psi^s.$$ \hspace{1cm} (2.10)

By inserting this into Equation (2.9), the transition dipole moment results in:

$$\mu_{n\rightarrow m} = \langle \Psi^e_m \Psi^\nu_m \Psi^s_m | -e \sum_i \hat{r}_i | \Psi^e_n \Psi^\nu_n \Psi^s_n \rangle$$

$$= \langle \Psi^e_m | -e \sum_i \hat{r}_i | \Psi^e_n \rangle \cdot \langle \Psi^\nu_m | \Psi^\nu_n \rangle \cdot \langle \Psi^s_m | \Psi^s_n \rangle,$$  \hspace{1cm} (2.11)

where the transition probability is determined by different selection rules for the orbital configuration, the vibrational wavefunctions, and the spin state. The selection term of
2.3 Optical Excitations in Organic Molecules

Figure 2.3: Left: Illustration of the Franck-Condon principle in case of a diatomic molecule: transition into $v' = 3$ is favored, due to higher overlap with the ground vibrionic state $v = 0$. Right: Photoluminescence and absorption spectra of N,N’-dimethyl-3,4,9,10-perylenetetracarboxylic diimide (MePTCDI), showing a typical mirror symmetry of emission and absorption. Taken from [17].

the vibrational wavefunctions is called Franck-Condon factor, because this term represents the Franck-Condon principle. It states that the probability of an electronic transition scales with the overlap between the vibrational wavefunctions of initial and final state. A schematic representation of this principle is given in Figure 2.3. In a semiclassical interpretation we can explain this by considering that electronic transitions are essentially instantaneous compared to the time scale of nuclear motions. Therefore, a transition will more likely happen if the positions and momenta of the nuclei in the final state are compatible to those of the initial state.

Let us now discuss some typical excitations by considering the energy terms of an organic molecule. Figure 2.4 schematically shows several energies of excited states compared to the energy of the ground state. With only few exceptions, organic molecules have even numbers of electrons and therefore the ground state $S_0$ is a singlet state (total spin is zero). By absorption of a photon, electrons can be excited into higher energy singlet states ($S_1, S_2...$) or into their vibrational sublevels, according to the Franck-Condon principle. Vibrational energies can typically achieve values of 0.06 to 0.25 eV which are much lower than the energy of the electronic states [18]. However, the large number of vibrational degrees of freedom in a molecule results in many such vibrational sublevels, as is depicted in Figure 2.4. Excitations into these sublevels will very rapidly give up their excess energy to relax into the corresponding vibrationless state. This process is called Internal Conversion (IC) and typically has time constants of the order of picoseconds [16]. After a certain lifetime, usually between $10^{-9}$ and $10^{-6}$ s for $S_1$, the excited electron will relax into the ground state $S_0$. This can either happen by emis-
Excitation of a photon with respective energy, i.e. fluorescence, or non-radiative. As shown in Figure 2.3, it is often found that absorption spectra and emission spectra of organic molecules show a mirror symmetry. This can be understood by the similarity of the vibrational levels of ground state and excited state, when applying the Franck-Condon principle to both absorption and emission transitions.

On the right side of Figure 2.4 excited triplet states are shown (total spin is one). Transitions from $S_0$ into these states are normally forbidden by spin selection rules. Nevertheless, this is partially lifted by weak spin-orbit-coupling, thereby allowing Intersystem Crossing of an electron from singlet to the triplet state. The rate constant of this process is usually very small and also absorption coefficients for $S_0 \rightarrow T_1$ are typically extremely low ($10^{-4}$ to $10^{-5}$ cm$^{-1}$ [16]). However, by use of molecules containing heavy atoms like iridium, bromine, or iodine, the spin-orbit interaction can be increased and transitions into triplet states are thus significantly enhanced. The radiative relaxation from a triplet state into the ground state is called phosphorescence. Typical lifetimes of triplet states are higher than singlet state lifetimes ($10^{-4}$ to 20 s for $T_1$, [16]), again by the argument of spin-selection. Another general aspect of triplet states is their lower energy compared to corresponding singlet states. This is a result of Pauli’s principle and can be understood qualitatively in the following way: Two electrons in a triplet state must have a spatially antisymmetric wave function and therefore cannot approach each other closely, i.e. their spatial wave functions do not overlap. Accordingly, the Coulomb repulsion between those triplet electrons is lower than that between singlet electrons resulting in a lower energy for the triplet states.

**Figure 2.4:** Jablonski diagram illustrating various possible radiative and non-radiative transitions in a molecule. ISC: intersystem crossing. IC: internal conversion.
Now that we know the basic properties of a molecule and its transitions, we want to consider the properties of an organic solid made from such molecules. As already stated above, intermolecular interactions are very weak compared to intramolecular interactions. This is due to the weak and short ranged van der Waals forces. Therefore, individual properties of molecules such as molecular dimension or intramolecular vibrational frequencies remain intact in the solid and are only slightly changed. Also, the electronic structure of the molecule, which determines the electronic transitions and therefore the optical properties, does not get lost but is only modified. Other properties like charge and energy transport within the solid particularly depend on intermolecular interactions and are governed by them as well as by the regularity of the crystal structure.

2.4.1 Self-Polarization in Organic Solids

When organic molecules condense to form a solid phase, charge carriers are not solely subject to the energy levels of the molecule itself. They will also interact with the surrounding by polarizing neighbour molecules and thereby reduce their energy. Particularly in highly polarizable compounds such as aromatic and heterocyclic molecules, this energy relaxation is not negligible. Measurements of anthracene show a change of the ionization potential by 1.5 eV between gas phase and crystal, which is attributed to the energy gain $P_h$ caused by electronic polarization of the solid during the ionization process [19]. In Figure 2.5 the evolution of HOMO and HOMO ($M^-$) upon formation of the solid is depicted schematically. HOMO ($M^-$) is the energy eigenstate of a molecular anion and thus determines the electron affinity $EA_G$ of an isolated molecule. As can be seen from the diagram, the energy of an electron in the solid is stabilized by the polarization energy $P_e$, thus enhancing the electron affinity $EA_S$ with respect to an isolated molecule. Correspondingly, the energy of a hole is stabilized by the polarization energy $P_h$ and therefore the ionization potential of the solid is decreased with respect to the isolated molecule. The resulting energies $E_e$ and $E_h$ are referred to as conduction levels of the solid, because they determine the self energy of charge carriers in the solid. Nevertheless, these levels should not be confused with conduction bands of traditional semiconductor physics, since here they are mainly determined by polarization of the molecule environment and the corresponding states are thus rather localized. Consequently, direct optical transitions from $E_h$ to $E_e$ cannot occur. Optical excitations are of molecular nature (see Section 2.4.2) and free charge carriers are usually created via secondary processes (see Section 3.2.1). Due to small overlap of $\pi$-orbitals between neighbouring molecules, $E_e$ and $E_h$ are only slightly broadened. The energy gap $E_{\text{gap}} = E_h - E_e$ is called electronic gap.

\footnote{Often there is a misuse of the terms HOMO and LUMO to refer to the solid state levels $E_h$ and $E_e$. In this work this shall be avoided.}
**Figure 2.5:** Schematic energy diagram of an isolated molecule versus the corresponding solid state. $IP_G$ and $EA_G$ denote ionization potential and electron affinity in the molecular gas phase, respectively. $IP_s$ and $EA_s$ are those for the solid state.

**Polarons**

Polarization phenomena of quasilocalized charge carriers in organic solids are categorized in terms of their different interaction types, i.e. phononic, vibronic, and electronic polarization. They are characterized by a specific relaxation time needed to build up the polarized state and by a specific quasi-static relaxation energy that is gained by the polarization. Typical values for relaxation time and energy are summarized in Table 2.1. Whether the different polarization processes will take place or not is depending on the actual mobility, or in other words on the localization time of the charge carrier. The most prominent type is the electronic polarization which denotes polarization of electronic orbitals of surrounding molecules. The time needed for this induced dipole formation is very short and usually faster than the charge carrier localization time. Therefore charge carriers appear to move together with their electronic polarization cloud. This quasistatic formation is called an *electronic polaron*. Interactions with intramolecular vibrations have slower relaxation times because they require a reconfiguration of the nuclei from the equilibrium configuration of a neutral molecule to the equilibrium configuration of an ionized molecule. In disordered materials where charge carriers move slowly, it is still expected that vibronic polarization takes place thus forming a dynamic state called *vibronic polaron*. Another type of polaron is due to interaction with phonons. Lattice relaxation times are in general very large and well below typical localization times of charge carriers. However, this interaction can play a role whenever a charge carrier is trapped and therefore its mean capture time exceeds the lattice relaxation time.
Table 2.1: Typical relaxation times and energies for the three different types of polaronic interactions [20].

<table>
<thead>
<tr>
<th>Interaction type</th>
<th>Relaxation time scale (s)</th>
<th>Interaction energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic polarization</td>
<td>$10^{-16} \sim 10^{-15}$</td>
<td>$1.0 \sim 1.5$</td>
</tr>
<tr>
<td>Vibronic relaxation</td>
<td>$10^{-15} \sim 10^{-14}$</td>
<td>$\approx 0.15$</td>
</tr>
<tr>
<td>Lattice relaxation</td>
<td>$10^{-12} \sim 10^{-11}$</td>
<td>$\approx 0.03$</td>
</tr>
</tbody>
</table>

2.4.2 Excitations in Organic Solids

Excitations in organic solids can be created through a large number of processes, e.g. absorption of electromagnetic radiation such as light or X-ray, electron irradiation, or through charge injection. Here, we briefly want to describe how the character of optical transitions that was introduced for individual molecules in Section 2.3 is changed in the ensemble of an organic solid and discuss possible types of the created excitons. Due to the weak intermolecular interaction by van der Waals forces, the structure of the energy levels of a molecule is not lost in the solid but only modified. Optical transitions are therefore only slightly changed in the solid and certain new features appear: (1) A general shift in the transitions occurs, mostly to lower energies. This so-called solvent shift is due to weak van der Waals interaction between neighbouring molecules. It has different magnitudes for different excited states and is molecule specific. (2) In crystals, a splitting of each molecular term into $Z$ terms appears, where $Z$ equals the number of molecules in the unit cell. This so-called Davydov splitting is due to interactions between translationally non-equivalent molecules. The resulting transitions also differ in their polarization. (3) Selection rules may be varied and degeneracies may be lifted, because they are now determined by the crystal symmetry and not by the symmetry of a free molecule. Accordingly, the oscillator strength of affected transitions will change.

Excitons

By excitation of a molecule, an electron hole pair is formed on the molecular site. This pair is still bound by Coulomb attraction. Frenkel proposed a model which describes such an excitation as a neutral quasi-particle called Frenkel exciton [21]. The radius of an exciton can be defined as the average distance between electron and hole. Due to the low dielectric constant in organic compounds, the Coulomb attraction is rather large and therefore Frenkel excitons have a small radius of typically 0.5 - 1 nm. In contrast inorganic semiconductors have higher dielectric constants. Therefore, excitons in inorganic semiconductors, as first introduced by Mott and Wannier [22], have a larger radius of 4 - 10 nm and correspondingly weak Coulomb attraction. This allows for an easy dissociation of such Wannier excitons into free charge carriers, because the small binding energy can be overcome thermally. In organic solids, binding energies of Frenkel excitons are 0.2 to 1.5 eV [23, 24]. Accordingly, dissociation into free charge
**Figure 2.6:** Representation of an exciton in an energy diagram of the organic semiconductor. Left: The exciton energy is considered as energy of the electron with respect to the hole which is set at the energy of the hole transport level. The potential of the electron is determined by the Coulomb attraction. $E_B$ denotes the binding energy of the exciton. The role of electron and hole might also be swapped around, i.e. the hole can also be accounted as being in the coulomb potential of the electron. Right: Schematic picture of the exciton as a bound state between the transport levels. This picture is often drawn to indicate the presence of this excited state in the semiconductor, but one has to keep in mind that the exciton is itself neutral and electron and hole may only be related to the semiconductor energy levels after they are dissociated into free charge carriers.

Excitons can travel through the lattice by diffusion and are thereby transporting their excitation energy. There are two processes describing this transport: Förster transfer [25, 26] and Dexter transfer [27]. Förster transfer is based on dipole-dipole interaction. Typical distances for this type of transport can be up to 10 nm. Dexter transfer is based on orbital overlap of neighbouring molecules. Accordingly, the transfer range is limited to the distance between two molecules, i.e. 1 - 1.5 nm. In contrast to Förster transfer that only allows for transport of singlet excitons, Dexter transfer also includes transport of triplet excitons.
2.4 From Molecules to Solids

Figure 2.7: (a) Frenkel exciton with tightly bound electron hole pair. (b) Wannier exciton with large radius compared to the lattice constant $a_0$. (c) Charge transfer exciton with electron and hole located on neighbouring molecules. Adapted from [23].

An important parameter for the operation of organic solar cells, where excitation energy needs to be transported to a so-called donor-acceptor interface (see Section 3.2.1) is the exciton diffusion length:

$$L = \sqrt{\tau_0 D},$$  \hspace{1cm} (2.12)

which is defined by the lifetime $\tau_0$ and the diffusion coefficient $D$ of the exciton.

2.4.3 Charge Carriers and Transport

Charge carrier transport in presence of an electric field $\vec{F}$ is determined by the conductivity $\sigma$ as:

$$\vec{j} = \sigma \vec{F},$$  \hspace{1cm} (2.13)

where $\vec{j}$ is the current density and $\vec{F}$ is the electric field strength. Assuming the current would only be sustained by one carrier type, e.g. electrons, it can be written as:

$$\vec{j} = -e n_e \vec{v}_D^e,$$  \hspace{1cm} (2.14)

where $e$ is the electric charge, $n_e$ the charge carrier density (i.e. density of free electrons), and $\vec{v}_D^e$ is the drift velocity. This way, a more decisive parameter for the description of electric current, the mobility $\mu$, can be defined as:

$$\vec{v}_D^e = \mu \vec{F}.$$  \hspace{1cm} (2.15)

Mobilities of organic materials are usually by far lower than those of conventional semiconductors. Only in ultrapure organic crystals and at very low temperature, band like transport with high mobilities up to 400 cm$^2$/Vs was observed [28]. These mobilities exhibit an inverse power law $\mu \propto T^{-n}$ which is typical for band transport with inelastic scattering of the charge carriers with acoustic phonons. At room temperature mobilities
of ultrapure polyacene crystals were measured around 1 cm$^2$/Vs both for electrons and holes [16]. However, charge transport in most organic solids can hardly be described by band theories. This is mainly due to the weak van der Waals interaction that allows only for small bandwidths. For example, calculations by a one-electron tight-binding method for polyacene crystals yield bandwidths in the order of 300 meV to 700 meV [29]. A second reason for the inadequacy of band models is the strong polarization effect in organic semiconductors (Section 2.4.1) that leads to energetic stabilization and therefore localization of the charge carrier. Furthermore, most organic solids are amorphous or polycrystalline and do not exhibit a crystal lattice with long range symmetry but are rather disordered. This causes an energetically and spatially inhomogeneous distribution of the localized transport states. Because of these features charge carriers in organic solids generally exhibit a rather small mean free path which is in the range of the lattice constant as well as short mean scattering times. Therefore, application of band conduction theories is not possible for most organic solids but can only be used in particular cases of ultrapure crystals at low temperatures.

In fact, transport in disordered molecular systems like present in organic thin films must be treated in terms of a hopping mechanism, meaning that the charge carrier which is usually localized at a molecular site will eventually be transported to another molecular site by performing a hopping step. The mobilities associated with this process are typically by some orders of magnitude smaller than in crystals. The hopping process is thermally activated and therefore mobilities increase with increasing temperature. Since hopping times are by a factor of 100 slower than the relaxation time of electronic polarization, charge carriers appear to move together with their electronic polarization cloud and can therefore be treated as polarons with an energy corresponding to the transport levels $E_e$ and $E_h$ (Section 2.4.1). Due to molecular disorder these transport levels are not distinct in energy but statistically distributed. Numerous models have been introduced to describe hopping mechanisms in organic solids (see e.g. [20, 23]). At this point we only want to mention the model of Bässler [30]. In this model the energetic distribution of transport states is considered as a Gaussian distribution function with one state per molecule or per segment of a polymer chain (sites). It is assumed that hopping probabilities to neighbouring sites with lower energies only depend on the overlap of the wavefunctions between two sites, while hopping probabilities to sites with higher energy additionally depend on a Boltzmann factor which takes field and temperature dependence into account. By simulating charge transport with a Monte-Carlo method, Bässler found the following result for the mobility at low fields:

$$\mu = \mu_0 \cdot \exp \left[ - \left( \frac{T_0}{T} \right)^2 \right] \quad (2.16)$$

with

$$T_0 = \frac{2\sigma}{3k} \quad (2.17)$$
where $\mu_0$ is the mobility of the hypothetical disorder free system at temperature $T \to \infty$, and $\sigma$ is the width of the Gaussian distribution of states. Besides the temperature dependence of $\mu$, mobilities in disordered organic materials also exhibit a characteristic dependence on the electric field. From experimental results for a large number of organic compounds the following correlation can generally be assumed [16]:

$$\mu(F) = \mu_{F,0} \cdot \exp \left( \beta \sqrt{F} \right).$$

(2.18)

Here $\mu_{F,0}$ is the mobility under zero field conditions, and $\beta$ is called field amplification factor.
3 Organic Photovoltaics

In this chapter an introduction into organic photovoltaics is given. In the beginning, general processes for conversion of radiation into electrical energy are discussed. The ideal layout of a solar cell is presented thereafter, while general photovoltaic characteristics are introduced using the common inorganic pn-junction as example. The second part of this chapter deals with organic solar cells. The concept of donor-acceptor heterojunctions is discussed and important aspects of exciton separation, influence of architecture on quantum efficiency as well as the origin of the open circuit voltage are addressed. This is followed by an introduction into relevant recombination processes in such solar cells. Finally, advantages of the p-i-n concept are presented to motivate its use in this work and in general.

3.1 Solar Cell Physics

Solar cells harvest the energy of the sun to convert it into electrical energy. The spectrum of solar radiation observed in space agrees well with a blackbody spectrum at $T_s=5800\,\text{K}$, which is approximately the surface temperature of the sun. The thermal radiation is absorbed by an absorber and will excite electrons into higher energy states. Neglecting impact ionization effects, the excitation of one electron requires one absorbed photon. The excitation energy is thus determined by the photon energy $h\nu$. Before any interactions with the lattice occur, the excitations have the same energy spectrum and therefore the same high temperature $T_s$ as photons from the sun. That means heat from the sun has been transferred into heat of these excitations. To make use of this energy, a special quality of the absorber is needed, which is usually fulfilled by semiconductors: It must have an energy gap ($E_{\text{gap}}$), in which no states for electrons exist. Otherwise the energy of the excitation would be consecutively transferred to phonons (i.e. lattice vibrations) in many small portions, and therefore all excitation energy would be lost as heat. Semiconductors only provide energy levels above and below the energy gap, which are normally denoted as conduction and valence band, respectively. Without loss of generality these terms are in the following used for description of the basic physics of the photovoltaic energy conversion. Excited electrons will lose energy by interacting with phonons only until they relax to the conduction
band edge. There, they have a considerably long lifetime before they recombine with the respective hole in the valence band. This enables the conversion of the electron energy into chemical energy and subsequently into electrical energy.

### 3.1.1 Conversion of Radiation into Chemical Energy

To discuss how the heat of the excitations is converted into chemical energy, we now consider a simple two-band system with conduction and valence band energies \( E_C \) and \( E_V \), respectively. The occupation of the energy band states shall be in equilibrium with the surrounding blackbody radiation (300 K). By applying Fermi statistics, the equilibrium density of charge carriers in the conduction band is given by

\[
 n = \int_{E_C}^{\infty} f(E_e) D(E_e) dE_e,
\]

where \( f(E_e) \) is the Fermi distribution and \( D(E_e) \) is the density of states. If \( E_C \) exceeds the Fermi energy \( E_F \) by at least a few \( kT \), only states in the lower part of the conduction band contribute to the integral in Equation (3.1) and the Fermi distribution can be approximated by the Maxwell-Boltzmann distribution. The total number of electrons is then given by

\[
 n = N_C \cdot \exp \left( -\frac{E_C - E_F}{kT} \right),
\]

where \( N_C \) is the effective density of states, and \( k \) is the Boltzmann constant. For ideal semiconductors \( N_C \) can be expressed by using the effective mass \( m_e^* \):

\[
 N_C = 2 \left( \frac{2\pi m_e^* kT}{\hbar^2} \right)^{3/2}.
\]

The density of holes in the valence band (\( p \)) is derived likewise. With the product of \( n \) and \( p \) the so-called intrinsic density \( n_i \) can be introduced:

\[
 np = N_C N_V \cdot \exp \left( -\frac{E_C - E_V}{kT} \right) = n_i^2.
\]

The value of \( n_i \) is not only valid in intrinsic semiconductors but stays constant upon doping, i.e. \( n_i \) is independent of doping.

**Quasi-Fermi Distribution**

In Figure 3.1 (left) the energy diagram under dark conditions with respective Fermi energy and charge densities is presented schematically. When the solar cell is illuminated with sunlight, excitations are created and electron as well as hole densities are significantly increased. Their distribution is then characterized by a higher temperature according to the temperature of the radiation (Figure 3.1, middle).
Figure 3.1: Conversion of solar heat into chemical energy. Left: Energy diagram for the solar cell under dark condition. Charge carrier densities are determined by thermal equilibrium with the environment. Center: After absorption of photons a hot electron-hole gas at a temperature corresponding to the temperature $T_s$ of the radiation exists. Right: By interaction with vibrations, the electron-hole gas is cooled down to ambient temperature. Since the electron and hole densities remain unchanged during the cooling process, two separate Fermi distributions with Fermi energies $E_{FC}$ and $E_{FV}$ evolve. $\mu_{chem}^{\mu_{chem}}$ is the chemical energy of the electron-hole gas. Adapted from [31].

By interaction of the excitations with phonons, electrons and holes will lose some energy and converge towards the band edges. Due to this cooling process they achieve equilibrium with the lattice vibrations and will consequently have the same temperature, i.e. the temperature of the lattice. Although electrons and holes are in equilibrium within their respective band, they are not in equilibrium with each other. This leads to a splitting of the corresponding Fermi distributions for electrons and holes as is presented in Figure 3.1 (right). Electrons are characterized by a quasi-Fermi distribution referring to $E_{FC}$, which is only valid in the conduction band, while holes are characterized by a quasi-Fermi distribution referring to $E_{FV}$, which is only valid in the valence band:

$$n = N_C \cdot \exp \left( -\frac{E_C - E_{FC}}{kT} \right),$$

(3.5)

$$p = N_V \cdot \exp \left( \frac{E_V - E_{FV}}{kT} \right).$$

(3.6)

Here, $T$ equals the ambient temperature. The product of electron and hole densities can now be written as

$$np = n_i^2 \cdot \exp \left( \frac{E_{FC} - E_{FV}}{kT} \right).$$

(3.7)
Since the chemical potential of electrons and holes is identified by their respective Fermi energies, the amount of quasi-Fermi energy splitting $E_{FC} - E_{FV}$ is the chemical energy per electron hole pair: $\mu_{\text{chem}}^{\text{eh}}$. In particular, this is the energy that can be gained by extraction of an electron hole pair as free energy, i.e. this energy is free of entropy. Thus, we may hope to convert this energy into electrical energy when we extract electrons and holes at separate contacts. It shall be emphasized that high charge carrier densities are preferable for an efficient conversion of solar energy, as Equation (3.7) indicates a logarithmic increase of the achievable energy per electron hole pair with the product of the charge carrier densities. These densities result from the balance between generation and recombination processes that occur before the electron hole pair can be extracted. Therefore, every process that leads to recombination will not only reduce the amount of current that can be gained, but will also reduce the amount of free energy that is gained per extracted pair.

**Radiative Limit for Solar Cell Efficiency**

The previous considerations demonstrate that an ideal solar cell has to accomplish maximum absorption and minimum recombination at the same time. Absorption is primarily limited by the energy gap, because only photons with energies $\hbar \nu$ higher than $E_{\text{gap}}$ can be absorbed while the semiconductor is transparent for photons with lower energies. Recombination of charge carriers can either result from radiative or from non-radiative processes. In non-radiative recombination processes, electrons and holes recombine by interaction with lattice vibrations. The energy is thereby transferred to phonons. This happens in many steps since typical phonon energies are much smaller than the energy of the electron hole pair. Accordingly, the probability for this process is comparably small and only significant when the recombination is mediated by states within the energy gap such as traps. Thus, non-radiative recombination can in principle be avoided in an ideal solar cell. In radiative recombination processes, electrons and holes recombine by emission of a photon with the exact energy of the electron hole pair. The probability of this spontaneous emission depends on the transition moment and the population densities of excited and ground state. Radiative recombination is therewith tied to the same properties which also determine the absorption. Moreover, it will increase concomitantly with the increase of quasi-Fermi energy splitting, and is thus unavoidable.

In consequence, the solar cell efficiency is limited by the amount of absorbed photons and the amount of energy gain per extracted electron hole pair. This energy is determined by the quasi-Fermi energy splitting. It results from the value of the energy gap and the obtained charge carrier densities, which in turn result from the balance between generation, charge extraction, and recombination.

By this, we can estimate the maximum obtainable efficiency for an ideal solar cell, by assuming an absorption probability of one for photon energies $\hbar \nu$ equal or above the energy gap and furthermore allowing only radiative recombination. Without illumin-
3.1 Solar Cell Physics

Figure 3.2: Power conversion efficiency as a function of the energy gap for an ideal solar cell at temperature $T_c = 300$ K exposed to the black body spectrum of the sun with $T_s = 5800$ K. The solar cell is assumed to absorb all photons with energy $h\nu$ higher than the band gap and to exhibit no recombination other than radiative recombination. The efficiency limit is calculated according to the detailed balance limit presented by Shockley and Queisser [32].

In equilibrium, the solar cell is in equilibrium with the surrounding, meaning that the emitted radiation of the cell $R_{rad}^0$ equals the absorbed radiation of the surrounding. When the solar cell is illuminated with light, the charge carrier densities increase due to absorption, and quasi-Fermi energy splitting occurs (according to Equation (3.7)). Evidently, the recombination current by emission of photons is now given by

$$ j_{rad} = R_{rad}^0 \cdot \frac{n_p}{n_i} = R_{rad}^0 \cdot \exp \left( \frac{E_{FC} - E_{FV}}{kT} \right). $$

(3.8)

On the other hand, the current of absorbed photons can be expressed by

$$ j_{abs} = R_{rad}^0 + \Delta G, $$

(3.9)

where $\Delta G$ is the generation rate in excess of the generation in the dark. If we now accomplish to contact the solar cell in a way that electrons are extracted without energy loss exclusively at one side, while holes are exclusively extracted at the other side, the voltage between the contacts will be determined by $e(E_{FC} - E_{FV})$, i.e. by the quasi-Fermi energy splitting. The resulting charge current is given by the balance between generation and recombination:

$$ j_Q = e (j_{rad} - j_{abs}). $$

(3.10)
Inserting Equations (3.8) and (3.9) results in the current-voltage (IV) characteristics:

\[ j_Q = eR_{\text{rad}}^0 \left[ \exp\left( \frac{eV}{kT} \right) - 1 \right] - e\Delta G. \]  

(3.11)

The generation rate \( \Delta G \) can be calculated from the given illumination. In Figure 3.2 the resulting maximum efficiency for an ideal solar cell illuminated by black body radiation from the sun (\( T_s = 5800 \) K) is illustrated. The temperature of the solar cell is set to 300 K. This efficiency limit for solar cells with a single bandgap was first derived by Shockley and Queisser [32]. It is valid for standard sun radiation, i.e. not concentrated radiation. The maximum achievable efficiency is found to be 29.9% at an energy gap of 1.3 eV. In multi-junction solar cells, this limit can be overcome by using different bandgap materials in series [33].

### 3.1.2 Conversion of Chemical Energy into Electrical Energy

We will now discuss how charges can be extracted from the solar cell to convert the chemical energy of each electron hole pair into electrical energy. For this we will briefly go into the details of the two driving forces for electrical current [34]. These are the electric field \( (F) \) which causes the drift current and charge density gradients which cause the diffusion current. For convenience, we will only consider the current of electrons, knowing that the current of holes can be discussed likewise. When current is solely caused by an electric field, it is given by

\[ j_{QF,e} = en\mu_e F = \sigma_e F \]  

(3.12)

where \( \sigma_e \) is the electron conductivity. Using \( F = -\text{grad}(\phi) \) this converts into

\[ j_{QF,e} = \frac{\sigma_e}{e} \cdot \text{grad}(-e\phi). \]  

(3.13)

If no electrical field is present, i.e. \( \text{grad}(\phi) = 0 \), then current is only driven by diffusion and therefore only dependent on spatial differences of charge carrier concentration. Following Fick’s law the diffusion current is

\[ j_{QD,e} = eD_e \cdot \text{grad}(n), \]  

(3.14)

where \( D_e \) is the diffusion constant. With

\[ \frac{\text{grad}(n)}{n} = \text{grad} \left[ \ln \left( \frac{n}{N_C} \right) \right] \]  

(3.15)

and the chemical potential

\[ \mu_{e,\text{chem}} = \mu_{e,0} + kT \cdot \ln \left( \frac{n}{N_C} \right), \]  

(3.16)
this transforms into [34]

\[ j_{QD,e} = \frac{enD_e}{kT} \cdot \text{grad}(\mu_{chem}^e). \]  

(3.17)

Assuming the validity of the Einstein relation

\[ \frac{D_e}{\mu_e} = \frac{kT}{e} \]  

(3.18)

to correlate \( D_e \) with the mobility \( \mu_e \) the diffusion current can be written as

\[ j_{QD,e} = n\mu_e \cdot \text{grad}(\mu_{chem}^e) = \frac{\sigma_e}{e} \cdot \text{grad}(\mu_{chem}^e). \]  

(3.19)

With both driving forces present, electric field and diffusion influence the electrons at the same time and are thus superimposing each other. Since Equation (3.13) and Equation (3.19) are both derived from a potential, this can be regarded by summarizing them into

\[ j_Q = \frac{\sigma_e}{e} \cdot \text{grad}(E_{EC}) + \frac{\sigma_h}{e} \cdot \text{grad}(E_{EV}). \]  

(3.21)

Thus, we find that charges are driven by the gradient of their respective quasi-Fermi energies and that the extent of current scales with the conductivity.

**The Ideal Solar Cell Structure**

Coming back to the problem of extracting charges from a solar cell, we need a structure which drives electrons and holes in opposite directions, to extract them at different contacts. This is ideally done with a minimal loss of quasi-Fermi energy splitting. In this section, an ideal solar cell structure as introduced by Würfel [34] will be presented to discuss how solar cells work in principle. In Section 3.1.1 we have studied how radiation energy is converted into chemical energy by virtue of a semiconducting absorber with a certain energy gap. To achieve charge extraction of electrons and holes at different contacts, i.e. at different sides of the absorber, special contacts are needed. Ideally, the contacts act like semipermeable membranes only allowing one type of charge carrier to pass, while rejecting the other. Figure 3.3 shows how this is accomplished by the use of additional p-type and n-type layers adjacent to the absorber. Electron affinity and energy gap of the contact layers are chosen in a way that the p-layer on
Figure 3.3: Ideal solar cell structure as discussed by Würfel [31]. In the absorber layer electrons and holes are generated by photon absorption. Electrons can leave the absorber to the right without energy loss, but cannot move into the p-type layer at the left due to a step in the electron affinities (EA). Correspondingly, holes do not move into the n-type material on the right due to the energy barrier. Holes will leave the absorber to the left where they move into the p-type layer without energy loss. The interfaces therefore act as semipermeable membranes, which spatially separate electrons and holes. Small gradients of the quasi-Fermi energies $E_{F,C}$ and $E_{F,V}$ drive electrons to the right and holes to the left generating an electric current.

The left side transmits holes and blocks electrons, while the n-layer on the right side acts the other way around. Transfer of holes into the p-layer occurs without energy loss, as can be seen from the constant value of $E_{F,V}$ at the interface. The p-layer must therefore be a good hole conductor and has to match the Fermi energy $E_{F,V}$ of the illuminated absorber. This applies vice versa to the n-layer. Usually, such properties are achieved by doping. Consequently, only a very small gradient of quasi-Fermi energies is needed to transport holes to the left and electrons to the right. In Figure 3.3 those gradients are considered negligible to exemplify the ideal case. At the contacts, the quasi-Fermi energies $E_{F,V}$ and $E_{F,C}$ will inevitably align, because of the high recombination probability at metal interfaces. Accordingly, large gradients of $E_{F,C}$ and $E_{F,V}$ appear in the p-layer and n-layer, respectively. This causes a current of minority carriers to flow into the wrong direction, i.e. electrons in the p-layer flow towards the hole contact and holes in the n-layer towards the electron contact. In the ideal case this unwanted recombination current can be neglected, because the wide gap character of the contact layers guarantees that the minority carrier density is sufficiently low. However, in real solar
cells, e.g. in case of the conventional pn-junction that is discussed in the next section, these recombination currents have to be considered and play a significant role for solar cell efficiency.

The voltage at which charges are extracted is given by the difference of the Fermi energies at the contacts \((E_{F_{\text{right}}} - E_{F_{\text{left}}})/e\). Under open circuit conditions, when no current is flowing, this is equal to the quasi-Fermi energy splitting within the absorber. Thus, we find for the open circuit voltage:

\[
V_{oc} = \frac{1}{e}(E_{F_{\text{C}}} - E_{F_{\text{V}}}).
\]  

(3.22)

Regarding Equation (3.5) and (3.6), \(E_{F_{\text{C}}}\) and \(E_{F_{\text{V}}}\) can be obtained by

\[
E_{F_{\text{C}}} = E_C + kT \cdot \ln \left( \frac{n}{N_C} \right) \tag{3.23}
\]

\[
E_{F_{\text{V}}} = E_V - kT \cdot \ln \left( \frac{p}{N_V} \right) \tag{3.24}
\]

Insertion into Equation (3.22) yields:

\[
eV_{oc} = E_{\text{gap}} - kT \cdot \ln \left( \frac{N_C N_V}{n p} \right) \tag{3.25}
\]

Obviously, \(V_{oc}\) depends on the energy gap and increases with the product of charge carrier densities \(np\).

It should be emphasized that Equation (3.22) is only valid when charge recombination in the transport layers can be neglected. As stated above, a current of minority charge carriers can cause recombination. Furthermore, additional recombination occurs when nonideal contact layers are used. This happens when charge carriers of the wrong type are not sufficiently blocked or when energy levels between absorber and contact layer do not match. Further recombination might occur at interface states. These processes will decrease the achievable \(V_{oc}\) below the limit given by the quasi-Fermi energy splitting in the absorber (Equation (3.22)). Nevertheless, if ideal contact layers (perfectly blocking one carrier, while perfectly conducting the other) could be realized, the chemical energy of each electron hole pair would be converted into electric energy without losses.

### 3.1.3 Conventional pn-Junction as Photodiode

For inorganic semiconductors, the most common realization of a solar cell is a pn-junction. This type of solar cell shall now be discussed exemplarily in its most simple form to introduce the basic solar cell characteristics.

When bringing a p-doped and an n-doped semiconductor into contact, free charge carriers adjacent to the interface diffuse into the neighbouring part and recombine with
their counter charges. By this, a depletion region will be formed in proximity of the interface. Due to the remaining charges of immobile dopant atoms, a space charge develops within the depletion region. The associated electric field has opposite direction to diffusion, therefore counterbalancing the diffusion current in equilibrium.

In Figure 3.4 (left) the energy diagram of a pn-junction is presented under dark condition without applied voltage, i.e. in equilibrium. The built-in potential, which compensates for diffusion, is denoted as $eV_{bi}$. It actually results from the difference in Fermi energies of the n-doped ($E_{Fn}^p$) and p-doped side ($E_{Fp}^n$), which can be derived from the corresponding doping concentrations $N_D$ and $N_A$:

$$E_C - E_{Fn}^p = kT \cdot \ln \left( \frac{N_C}{N_D} \right)$$  \hspace{1cm} (3.26)

$$E_{Fp}^n - E_V = kT \cdot \ln \left( \frac{N_V}{N_A} \right)$$  \hspace{1cm} (3.27)

where $N_C$ and $N_V$ are the effective densities of states in conduction and valence band, respectively. The built-in potential then becomes

$$eV_{bi} = E_{Fn}^p - E_{Fp}^n = E_{gap} - kT \cdot \ln \left( \frac{N_C N_V}{N_D N_A} \right).$$  \hspace{1cm} (3.28)

When a positive voltage is applied, i.e. the n-contact potential is lifted, charge carriers are driven into the depletion layer, where they meet their counter charges coming from the other contact. A recombination current occurs. When the voltage is reversed, i.e. the n-contact potential is lowered, charge carriers are extracted at both sides. The total current is then limited by the rate of charge generation within the device, also denoted as dark saturation current ($j_s$). In this situation, the device is blocking, because $j_s$ is very small compared to the forward current. For low recombination rates and small injected currents, the IV-characteristic of a pn-junction is given by the Shockley diode equation:

$$j = j_s \left[ \exp \left( \frac{eV}{kT} \right) - 1 \right].$$  \hspace{1cm} (3.29)

When the pn-junction is illuminated, photons are absorbed and a splitting of quasi-Fermi energies occurs. By virtue of the asymmetric doping and the resulting built-in field, electrons and holes are directed towards opposite contacts. In this respect the n- and p-doped regions act as semipermeable membranes, allowing electrons to be extracted on the n-doped side and vice versa for holes. A photocurrent $j_{ph}$ develops.

Figure 3.4 (right) shows the energy diagram of an illuminated pn-junction under open circuit condition. It looks similar to what was discussed to be an ideal solar cell (Figure 3.3), apart from two aspects. First, there is no barrier in the energy bands which would block the charge carriers from going into the wrong direction. This gives rise to a recombination current of electrons which flow towards the p-contact and holes which flow towards the n-contact. This problem can partially be overcome by the introduction
of a so-called back-surface field (not drawn here) [35]. Second, the Fermi energies at the contacts are (in this example) slightly lower than the amount of quasi-Fermi energy splitting within the device. A higher difference of $E_{F, \text{left}}$ and $E_{F, \text{right}}$ would be preferable to make better use of the contained energy. Yet, the Fermi energies at the contacts are inevitably restricted to the equilibrium value of the respective contact layers, which results from the very high recombination probabilities at the metal interface. This problem can be amended by a higher doping concentration as is evident from Equation (3.28). By this, the built-in potential increases and may then match the quasi-Fermi splitting under illumination. Accordingly, a higher $V_{oc}$ can be obtained, indicating a higher energy content of the extracted charge pairs. These considerations point out that the $V_{oc}$ of the pn-junction is necessarily limited by the built-in potential, which is not the case for the ideal solar cell that was discussed above.

Assuming that photocurrent ($j_{ph}$) is independent of the applied voltage, Equation (3.29) can be extended to
\[
    j = j_s \left[ \exp \left( \frac{eV}{kT} \right) - 1 \right] - j_{ph}. \tag{3.30}
\]
Figure 3.5: IV-characteristics of a pn-junction according to Equations (3.29) (dark) and (3.30) (illuminated). The current at zero voltage is denoted as short circuit current $j_{sc}$. The voltage at a current of zero is called open circuit voltage $V_{oc}$. MPP stands for maximum power point. At this point of the IV-characteristic, maximum power is delivered by the solar cell. Current and voltage at the MPP are denoted as $j_{MPP}$ and $V_{MPP}$, respectively.

Figure 3.5 presents these IV-characteristics of an illuminated pn-junction. Several characteristic parameters used to evaluate solar cell performance are depicted. The current at zero voltage is denoted as short circuit current $j_{sc}$. $V_{oc}$ is the open circuit voltage. There is exactly one point of the IV-characteristic, where the solar cell delivers maximum power. This point is not surprisingly called the maximum power point (MPP). From current and voltage at the MPP, the fill factor (FF) is derived:

$$FF = \frac{V_{MPP} \cdot j_{MPP}}{V_{oc} \cdot j_{sc}}.$$  \hspace{1cm} (3.31)

This parameter is a figure of merit indicating how close the IV-characteristic under illumination is to an ideal rectangular shape. Finally, the power conversion efficiency ($\eta_{PCE}$) is calculated by dividing the maximum electric power by the power of the incoming light $P_{light}$:

$$\eta_{PCE} = \frac{V_{MPP} \cdot j_{MPP}}{P_{light}} = \frac{V_{oc} \cdot j_{sc} \cdot FF}{P_{light}}.$$  \hspace{1cm} (3.32)
3.1 Solar Cell Physics

Figure 3.6: IV-characteristics of solar cells according to an equivalent circuit as presented in the inset. Parameters used to calculate the characteristics are $J_{ph}=45$ mA and $J_s=1 \cdot 10^{-8}$ mA. 1) $R_S=0 \Omega$, $R_P=\infty$, 2) $R_S=0 \Omega$, $R_P=40 \Omega$, 3) $R_S=8 \Omega$, $R_P=\infty$.

3.1.4 Simple Equivalent Circuit

IV-characteristics of real solar cells will always differ slightly from the curve given by the Shockley ideal diode equation (3.30). One reason are inevitable electrical resistances of the devices. To account for these effects, an equivalent circuit as shown in the inset of Figure 3.6 can be used. It introduces a parallel resistance $R_P$ and a series resistance $R_S$ in addition to the photodiode. $R_P$ represents shunt paths in the device by-passing the diode. This resistance should therefore be infinite in an ideal device. $R_S$ represents resistances of contacts and the materials themselves. It should ideally be zero. By extending Equation (3.30) with $R_S$ and $R_P$ we derive

$$J = J_s \left[ \exp \left( \frac{e(V - R_S J)}{kT} \right) - 1 \right] + \frac{V - R_S J}{R_P} - J_{ph} \quad (3.33)$$

as the IV-characteristics of the equivalent circuit.

In Figure 3.6 corresponding curves are presented for different combinations of $R_S$ and $R_P$. A pure series resistance limits the forward current behavior and primarily lowers the FF. If $R_S$ is comparatively high, it can also effect $j_{sc}$. Nevertheless, $R_S$ has no influence on $V_{oc}$ because the current through the contacts is zero (per definition) at this point. On the other hand, a non-ideal parallel resistance has only little effect on the forward current, but lowers FF and $V_{oc}$. This is due to the additional shunt path that introduces a recombination current parallel to the photodiode.
3.2 Organic Solar Cells

There are three types of organic solar cells: dye sensitized solar cells, polymer solar cells, and small molecule solar cells. Dye sensitized solar cells are using organic molecules only for absorption of light while charge transport is typically achieved by a liquid electrolyte and an inorganic semiconductor. This type of solar cells shall not be discussed here. Polymer and small molecule solar cells are mainly distinguished by their different production processes. Polymer solar cells are solution processed, which means layers are usually made by spin coating or printing techniques. Small molecule solar cells typically use vacuum based evaporation processes like vacuum thermal evaporation. However, the functional principle of both is the same.

Although basic principles of solar cell function were already discussed in the previous section, there are some peculiarities for organic solar cells that need to be addressed. Compared to inorganic semiconductors, organic materials are characterized by high exciton binding energies, low mobilities, and low diffusion coefficients [36]. On the other hand they offer high absorption coefficients in the range of \(10^5\) cm\(^{-1}\). A layer thickness of approximately hundred nm is therefore sufficient to absorb nearly all incoming light. Organic solar cells are consequently very thin, which attenuates the problem of limited transport properties. Nevertheless, absorption of photons does not create free charge carriers but excitons that have typical binding energies of hundreds of meV (Section 2.4.2). To dissociate these excitons an electrical field as high as \(10^6\) Vcm\(^{-1}\) would be necessary [37]. Such high fields are not present in solar cells under operating conditions. However, it was found by Tang that efficient dissociation of excitons can also be achieved at a so-called donor-acceptor (D-A) heterojunction [3]. Shortly after the first publication of this concept, it became the key principle for organic solar cells.

3.2.1 Donor-Acceptor Heterojunction

The process of photocurrent generation in an organic solar cell with a D-A heterojunction is schematically presented in Figure 3.7. The D-A heterojunction is developed by contacting a donor material with low ionization potential (IP) to an acceptor material with high electron affinity (EA). By this, an energetic step occurs at the interface that facilitates the separation of excitons into free charge carriers.

When illuminating the solar cell, photons are absorbed depending on a certain absorption probability \(\eta_A\) and excitons are created. These excitons cannot be dissociated within the pristine material itself but have to travel to the D-A interface by diffusion. Depending on their lifetime and the distance to travel, they reach the D-A interface with a certain probability \(\eta_{ED}\). Exciton separation takes place at the interface via a charge transfer process. The probability for this process is denoted as \(\eta_{CT}\). Finally, the created charge carriers, i.e. holes on the donor and electrons on the acceptor, are transported to their respective contacts by means of the electric field and charge carrier density gradients. The probability for this charge collection process is \(\eta_{CC}\). All these efficiencies
The EQE determines the ratio of extracted charge pairs per incident photon at a certain wavelength $\lambda$. It is dependent on material properties like absorbance, exciton diffusion length, and charge carrier mobility as well as on the actual device architecture. IQE is the internal quantum efficiency, combining the efficiencies of all processes that happen after photon absorption. Understanding of EQE and IQE is particularly important, because they determine the $j_{sc}$, which is a key parameter for solar cell efficiency (Equation (3.32)), by

$$j_{sc} = e \int_{\lambda_1}^{\lambda_2} \Phi_{\text{flux}}(\lambda) \cdot \text{EQE}(\lambda, V=0 \text{V}) \ d\lambda.$$  

(3.35)

$\Phi_{\text{flux}}$ is the illumination photon flux (see Section 4.4 for the standard sun spectrum). In the following section we will briefly discuss limitations to the EQE and analyze how device architecture can amend those limitations. We will furthermore address the issue of $V_{oc}$ in D-A heterojunction solar cells, since this is as well a key parameter for solar cell performance.
Charge Separation

As already stated, excitons can efficiently be separated at a D-A interface. The concept of this heterojunction is to provide an energetic step in the corresponding transport levels for electrons and holes. If this step exceeds the exciton binding energy, charge transfer from one material to the other will occur with high probability as soon as the exciton reaches the interface. In systems consisting of donor type polymers and fullerene acceptors, such charge transfer processes were found to be ultrafast, i.e. the electron is transferred to the polymer on a femtosecond time scale [39–42].

The charge separation process converts an exciton, which is typically described as Frenkel exciton, into a free pair of electron and hole, which are typically described within the energy diagram of the transport levels. Without going into details of charge separation, we can discuss this process based on Figure 3.8, in which two typically drawn representations are shown. The scheme on the left side shows the energy diagram regarding to the excitonic picture as is for example discussed in [20, 23, 43]. The initial charge transfer leads to formation of a CT-exciton with the electron placed on an acceptor molecule and the hole on a neighbouring donor molecule. This geminate pair, which is still coulombically bound, can subsequently be dissociated via several steps of increasing distance between electron and hole ($r$). This process may be driven by thermal energy and be assisted by the electric field. Also the direct transition from the exciton into a charge transfer exciton at higher $r$ may be postulated, so that some excess energy is used to overcome the Coulomb attraction. The second scheme on the right side of Figure 3.8 presents the charge separation process in the semiconductor energy diagram as proposed by Würfel [31]. In this picture the charge separation is explained as follows. The energy is drawn from the perspective of an electron that is coulombically bound to a hole on the donor, thus representing the exciton. In this view, exciton energy is regarded as energy of the bound electron with respect to the free hole and is therefore counted upwards from the level $E_{h,D}$. Consequently, the energy of the electron is smaller by the value of the exciton binding energy than the energy of a free electron in level $E_{e,D}$. According to the principles of the D-A heterojunction, the acceptor material on the right side of the contact has a lower lying level $E_{e,A}$ due to its higher EA. Far away from the hole, the electron at this level has an energy less or equal to the energy of the excitonic state. This enables the electron to be transferred to the acceptor by tunneling through the Coulomb barrier into the donor. In vicinity of the interface, the electron on the acceptor is still subject to Coulomb attraction. However, its initial energy is larger than the potential energy, thus it has sufficient kinetic energy to overcome this Coulomb attraction and to finally be free. In the separated state of free electron and hole, the sum of their energies is ideally equal or little less than the exciton energy. Otherwise energy would be lost. If the electron loses part of its kinetic energy by scattering while it is still in the range of Coulomb attraction, it might not be able to reach a separated state. This would decrease the separation efficiency $\eta_{\text{CT}}$. Therefore, the level $E_{e,A}$ should be somewhat lower (50 - 100 meV) than the exciton
3.2 Organic Solar Cells

Figure 3.8: Schematic representations of the charge separation process. a) The excitonic picture, visualizing the initial charge transfer process ($k_f$) of the exciton into a charge transfer (CT) exciton at the D-A interface. A geminate electron hole pair is formed, which can subsequently be separated ($k_{diss}$) via several steps of increasing distance between the two charge carriers ($r$). A more detailed discussion of the rate constants can for example be found in [43] b) Energy scheme for the separation of an exciton as proposed by Würfel [31]. The electron in the donor material is coulombically bound to the hole. However, it is considered to be able to tunnel into a free state in the acceptor material on the right, where it has sufficient kinetic energy to overcome the Coulomb attraction.

energy to achieve efficient separation. An analogous description can be made for the dissociation of excitons which are created in the acceptor.

In summary, the concept of the D-A heterojunction provides a suitable energy step at the interface so that the energy difference between two separated charge carriers $E_{DA} = E_{e,A} - E_{h,D}$, i.e. the electron in the acceptor and the hole in the donor, is lower than the exciton energy. This facilitates the charge separation process. The lower $E_{DA}$ the more this process is supported, but also the lower is the resulting energy of the separated electron hole pair.

Usually, solar cells with reasonable power conversion efficiencies exhibit very high charge separation efficiencies close to unity [5, 38, 44, 45]. This demonstrates the practicability of the D-A heterojunction concept. However, this should not hide the fact that some physical details of the charge separation process are still under debate and not sufficiently understood [46–48]. However, optimization of the tradeoff between low $E_{DA}$ in favor for an easy charge transfer versus a high $E_{DA}$ for minimized energy losses has become a general principle for organic solar cell design [49, 50].
Organic Photovoltaics

Figure 3.9: Different device architectures for organic solar cells. a) Simple flat heterojunction solar cell without transport layers as used by Tang [3]. Only excitons that are generated within reach of the exciton diffusion length from the interface contribute to photocurrent. Dashed lines indicate the photoactive part according to this limitation by $\eta_{ED}$. b) Flat heterojunction solar cell with transparent electron and hole transport layers (ETL, HTL) as introduced by the IAPP [51]. The absorber thickness is reduced to the photoactive thickness to minimize parasitic absorption. Dashed lines indicate the optical field density, that is zero at the reflecting electrode and maximized within the absorber layers by careful choice of HTL and ETL thickness. c) Mixed heterojunction solar cell with transparent transport layers. Donor and acceptor material are mixed in one layer to form an interpenetrating network. Thereby, the interface area between donor and acceptor is largely increased and excitons only have to travel a few nm to reach an interface. This enhances $\eta_{ED}$. In return, charges have to be transported on percolation paths of the respective materials. Thus, the charge transport capability ($\eta_{CC}$) is typically reduced compared to neat layers.

Flat and Mixed Heterojunction Concepts

There are different concepts for realizing a D-A heterojunction: It can either be achieved by a planar structure, as it was the case in Tang’s solar cell, or it can be made in the form of an interpenetrating network or a so-called mixed heterojunction [3, 38, 52–54]. Figure 3.9 depicts layer stacks of both concepts. In a planar structure, donor and acceptor layers are just stacked on top of each other and form a so-called flat heterojunction. In a mixed heterojunction, donor and acceptor materials are mixed in one layer and ideally form separated domains. Thereby, the dissociating D-A interface area is largely increased compared to a flat heterojunction.

The major challenge in optimizing these heterojunctions is to achieve an efficient collection of excitons that are separated at the D-A interface and at the same time provide
efficient transport of created charges. Furthermore, for optimizing the EQE, a high absorption is desirable, which means the layer should be sufficiently thick to absorb all incoming light. In flat heterojunctions, only excitons that are created within the distance of the exciton diffusion lengths ($L_d$) from the D-A interface can be separated. Typical exciton diffusion lengths are as low as 5 - 30 nm [38, 55–59]. Despite the fact that absorption coefficients can be very high, this is well below the light penetration depth. Flat heterojunctions are therefore usually limited by $\eta_{ED}$ and it is difficult to reach optimized efficiencies with this architecture.

Mixed heterojunctions are more promising, because in a mixed layer of donor and acceptor the distance to a dissociating interface can be only a few nm, which ensures that nearly every exciton gets separated into charges within its lifetime. Nevertheless, a perfect homogeneous mixing is not favorable because this would impede charge transport. To achieve efficient charge transport from the mixed heterojunction layer to the contacts, a phase separation between donor and acceptor is needed to form percolation pathways. By this, electrons are transported on percolation paths in the acceptor while holes use percolation paths in the donor. On the one hand, transport capabilities of the mixed layer increase if strong phase separation between both materials is achieved, because percolation pathways are more likely to be continuous. Furthermore, there is lower contact area between both phases, where charges can recombine with their counterparts. On the other hand, however, strong phase separation also increases the distance for excitons to reach a D-A interface and therefore reduces $\eta_{ED}$. It is mainly this tradeoff between large and small phase separation that makes control of the nanoscale morphology of mixed heterojunctions a crucial prerequisite for the optimization of mixed heterojunction solar cells. In polymer solar cells a large number of studies have addressed the characterization and control of morphology. Especially the use of thermal and solvent annealing as well as different composition ratios and solvents turned out to significantly improve solar cell performance by achieving heterojunctions with higher crystallinity of the donor and a better phase separation [8, 9, 11, 60–62].

$V_{oc}$ in Organic Solar Cells

For inorganic solar cells, it is well accepted that $V_{oc}$ is mainly limited by the built-in voltage $V_{bi}$ (see Section 3.1.3). Therefore, the application of a so-called metal-insulator-metal model, where $V_{bi}$ is regarded as the difference of the workfunctions between anode and cathode, seemed reasonable to explain $V_{oc}$ in first organic solar cell results [63–65]. However, in subsequent investigations this approach was not applicable and deviations from the model were reported [66, 67]. The simple reason is that the assumption $V_{bi}$ would exclusively limit $V_{oc}$ is not generally true and particularly not true for organic solar cells [34, 68]. It is only valid when diffusion forces that separate charge carriers can be neglected and hence the internal field is the only driving force for photocurrent. This is the case in most inorganic solar cells. In organic solar cells, however, charges are generated at a D-A interface and are, therefore, also spatially sep-
arated. Consequently, a large driving force is introduced by charge density gradients from the interface to the contacts and, thus, the internal field is no longer an exclusive requirement for charge separation. Organic solar cells with $V_{oc}$ exceeding $V_{bi}$ have been shown [68, 69].

The actual limit of $V_{oc}$ in organic solar cells can be determined by calculating the quasi-Fermi energy splitting within the absorber layer. According to Equations (3.23) and (3.24) this can be achieved by using the Maxwell-Boltzmann approximation and effective densities of states $N_C$ and $N_V$ to determine the quasi-Fermi energies with respect to the transport level of electrons and holes. This approach can in general be adopted for organic semiconductors. For this we use the electron transport levels of the acceptor ($E_{e,A}$) and the hole transport level of the donor ($E_{h,D}$) to calculate the quasi-Fermi energies within the D-A heterojunction. Using Equations (3.23) and (3.24) we get

$$V_{oc} = E_{e,A} - E_{h,D} - kT \cdot \ln \left(\frac{N_C N_V}{n_p}\right) = E_{DA} - kT \cdot \ln \left(\frac{N_C N_V}{n_p}\right),$$  

(3.36)

where $E_{DA}$ is the energy gap of a photogenerated electron hole pair, i.e. an electron on the acceptor and an hole on the donor, and $n_p$ is the product of electron and hole densities. Apparently, the maximum achievable $V_{oc}$ is limited by the energies $E_{e,A}$ and $E_{h,D}$ and therefore by $E_A$ of the acceptor and $IP$ of the donor. Of course, a rather ideal device architecture without recombination losses in the transport layers or at the contacts is still required to really realize this limit (see Section 3.1.2). It should also be mentioned that a broad Gaussian density of states, as assumed in disordered organic layers, will affect the practicability of the Maxwell-Boltzmann approximation as soon as the Fermi energy approaches the tail states. In this case the exact Fermi distribution has rather to be used to determine the Fermi energies. Nevertheless, the general correlation of $V_{oc}$ to $E_{DA}$ has been confirmed by many studies and optimization of $V_{oc}$ by energy level tuning of donor and acceptor has become a major design rule for organic solar cells [50, 70–76].

### 3.2.2 Recombination Processes

The solar cell functionality is affected by many recombination processes that may occur. All of them are loss mechanisms and will reduce the EQE.

Excitons can recombine before they reach a dissociating D-A interface either radiatively or non radiatively. This effect is usually accounted for by evaluating the exciton diffusion length.

When the exciton reaches a D-A interface, recombination of the electron with its geminate hole might occur instead of charge separation. Directly after charge transfer across the D-A interface, electron and hole constitute a so-called geminate pair with the electron placed on an acceptor molecule and the hole placed on a neighbouring donor

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1 Often the terms LUMO of the acceptor and HOMO of the donor are also used to refer to $E_{e,A}$ and $E_{h,D}$.
molecule. If the transferred carrier has not sufficient energy (kinetic or thermal) to overcome Coulomb attraction, it will be trapped in this charge transfer state and finally recombine. This process is then called geminate recombination. Charge carriers can also recombine when they are free (after exciton dissociation). This process is called non-geminate recombination and usually a distinction between two types is made. The first type is direct non-geminate recombination, where a free electron recombines directly with a free hole by a band-to-band like capture process. The corresponding recombination rate can be calculated by

\[ R_{\text{direct}}^{\text{ng}} = \gamma \cdot n_f \cdot p_f, \]  

(3.37)

where \( n_f \) and \( p_f \) are densities of free electrons and holes, respectively and \( \gamma \) is the recombination constant. For pristine materials \( \gamma \) is usually adopted from the Langevin theory [23, 77, 78]:

\[ \gamma = \frac{e}{\varepsilon_0 \varepsilon} \left( \mu_n + \mu_p \right), \]  

(3.38)

where \( \mu_n \) and \( \mu_p \) are electron and hole mobility, respectively. In pure organic crystals \( \gamma \) has been measured by Karl [79]. However, in organic solar cells with a D-A heterojunction, electrons and holes populate different material phases and are consequently spatially separated from each other. Direct geminate recombination thus requires both charge carriers to meet at an interface and, consequently, the recombination constant in such devices can differ from Equation (3.38). Modified expressions for \( \gamma \) are currently under debate [80, 81].

The second non-geminate recombination process occurs via trap states, i.e. a free electron is captured by a trapped hole or vice versa. This process is called indirect non-geminate recombination. For inorganic semiconductors, it is described by the Shockley-Read-Hall theory with a recombination rate given by

\[ R_{\text{indirect}}^{\text{ng}} = \sigma_{e,\text{trap}} \cdot \nu_e \cdot n_e \cdot n_{h,\text{trap}}, \]  

(3.39)

where \( \sigma_{e,\text{trap}} \) is the cross section, \( \nu_e \) is the velocity of electrons, \( n_e \) is the electron density, and \( n_{h,\text{trap}} \) is the density of hole populated traps. Recombination of holes is calculated accordingly.

Due to their different dependence on charge carrier densities, it is assumed that the effect of direct and indirect non-geminate recombination on the correlation between photocurrent and illumination intensity is different. Generally, the photocurrent density is proportional to the illumination intensity: \( j_{\text{ph}} \sim I^\alpha \) [23]. For direct non-geminate recombination Equation (3.37) postulates \( \alpha \approx 0.5 \), while in case of indirect non-geminate recombination \( \alpha \approx 1 \) is expected [45, 82]. However, \( \alpha \approx 0.5 \) may also be caused by space charge limited photocurrents [83, 84].
3.2.3 Transport Layers – The p-i-n Concept

In Section 3.1.2 we discussed an ideal solar cell structure as first proposed by Würfel (see Figure 3.3) [34]. It has been demonstrated that transport layers which act as semipermeable membranes facilitate charge transport to the respective contacts and are therefore essential for the functioning of a solar cell. The IAPP is aiming for such transport layers by using doped wide-gap materials. As shown in Figure 3.9, the absorber layers are embedded between a p-doped hole transport layer (HTL) and an n-doped electron transport layer (ETL). Following the sequence of the layer stack, such solar cell architectures are called p-i-n structure (p-doped - intrinsic - n-doped) [51]. However, the concept also applies to solar cells with the inverted sequence, which is then denoted as n-i-p structure.

Doping is achieved by mixing dopant molecules into the matrix layer. It is a key concept for p-i-n solar cells and fulfills several requirements necessary for good transport layers [85–90]. First, it enables high conductivities above $10^5 \text{ S cm}^{-1}$ and thereby avoids energy loss during charge transport to the contacts. It also shifts the Fermi energy towards the respective transport level. This provides a high built-in field in the device, aiding efficient charge extraction from the absorber without energy loss. Doping furthermore enables ohmic contact to cathode and anode for a variety of metals with different workfunctions [91, 92].

The reason for using wide gap materials is twofold. First of all, it ensures that no or little light is absorbed in the transport layers. Moreover a large energy gap of the HTL results into an energy barrier for electrons, which is desired to prevent them from reaching the hole contact (anode). The same applies for the ETL, that shall reject holes. Also excitons are blocked at the transport layers, since their energy is usually lower than those of excited states in wide gap materials.

Another benefit of using transport layers with high conductivities is the freedom of choosing their thicknesses to optimize the thin film optics within the device. To increase absorption, the absorber layers need to be placed in the optical field maximum between incident light and light reflected from the back contact. This can easily be realized with adjusting the transport layer thickness.

Finally, the p-i-n concept allows for an easy upgrade of single solar cells to tandem or even triple solar cells. This is particularly beneficial when several absorber materials covering different spectral regions become available [93, 94].

Of course, the correct choice of suitable transport materials, which match the absorber energy levels and are dopable, processable, thermally stable, and last but not least transparent is not easy to accomplish. Especially the search for n-type transport layers remains a challenge. However, the use of transparent transport layers that are either doped or by other means highly conductive is a general design concept to improve organic solar cell efficiencies [51, 95–97].

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2For a conductivity of $10^5 \text{ S cm}^{-1}$, a current of $10 \text{ mA cm}^{-2}$, and a transport layer thickness of 100 nm, the voltage loss for charge transport amounts to 10 mV.
4 Experimental

This chapter introduces the materials and experimental methods. First, basic properties of the utilized materials are presented. Then, the sample preparation by vacuum thermal evaporation is explained and the different preparation tools are specified. Subsequently, an overview about all characterization methods is given and the approach of mismatch correction is discussed.

4.1 Materials

The chemical structures of the materials used in this work are presented in Figure 4.1. All of them are processed by vacuum thermal evaporation. Their ionization potential (IP) as well as their electron affinity (EA) in thin films is summarized in Table 4.1. Basic properties are introduced in the following. The DCV6T molecules which are investigated in this work are introduced in Chapter 5.

4.1.1 C60

The chemical structure of fullerene C60 is presented in Figure 4.1. It is a well known organic semiconductor having an extended $\pi$-conjugated electron system with a very high symmetry. The molecule forms a truncated icosahedron consisting of 12 pentagons and 20 hexagons with the carbon atoms placed at the 60 vertices. This gives C60 a nearly spherical shape. Because of the electron delocalization over the whole molecule, electron mobilities are very high and can reach up to 6 cm$^2$/Vs in organic field effect transistors (OFETs) [98]. Furthermore, C60 exhibits a high electron affinity of 4.0 eV as measured in thin films via inverse photoelectron spectroscopy (IPES) [99]. Due to these properties C60 and its derivatives such as [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) are often utilized as electron acceptor materials in organic solar cells.

The thin film absorption spectrum of C60 is presented in Figure 4.2. The absorption onset is at 635 nm, which corresponds to an optical gap of 1.95 eV [100]. However, the lowest transition is dipole forbidden because of the symmetry of the molecule and thus the absorption above 600 nm is very low [101, 102]. The main absorption features are
Figure 4.1: Chemical structures of the materials used in this work.

found at 270 nm (4.59 eV), 350 nm (3.54 eV), and 448 nm (2.77 eV). Therefore, C60 can only contribute to absorption of the high energy edge of the sun spectrum when used in solar cells.

Because of the large spin-orbit interaction in the nearly spherical molecule, C60 exhibits intersystem crossing quantum yields close to unity [103, 104]. The major presence of triplet excitons might explain the comparatively long exciton diffusion length of $40 \pm 10$ nm that is reported for C60 [38].

In this work C60 is utilized in two ways. First, it is used as acceptor material in the photoactive layers. That means that the investigated D-A heterojunctions are comprised of the DCV6T donor materials (see Section 5.2) and C60. C60 is secondly used as electron transport material because of its high electron transport capability. For this purpose, C60 is doped with the n-dopant NDN1 from Novaled AG (Dresden, Germany) providing a conductivity of $0.05 \text{Scm}^{-1}$. This dopant is used for stability reasons. Similar conductivities are achievable for example with acridine orange base (AOB). The density of vacuum deposited thin film layers of C60 is $1.54 \text{gcm}^{-3}$. The material is purified four times by thermal gradient sublimation.

4.1.2 Transport Materials

**BPAPF**: 9,9-bis{4-(N,N-bis-biphenyl-4-yl-amino)phenyl}-9H-fluorene is used as hole transport material. As such, it was first introduced by Ko et al. in organic light emitting diodes (OLEDs) [105]. It has a high glass transition temperature ($T_g$) of 167 °C and therefore provides better thermal stability than other typically used transport materials. Here, it is used due to its high IP of 5.6 eV which matches the high IP of the DCV6T
4.1 Materials

**Figure 4.2:** Thin film absorbance spectra of the materials used in this work. The sun spectrum AM 1.5 G (see Section 4.4) is given for comparison.

Donor materials.

**Di-NPB:** *N,N'-diphenyl-N,N'-bis(4'-(N,N-bis(naphth-1-yl)-amino)-biphenyl-4-yl)-benzidine* is also a hole transport material. It has already been incorporated in organic p-i-n solar cells reported in [12, 69], where it was chosen due to its IP of 5.3 eV. It has a high $T_g$ of 157°C and showed good stability in solar cell devices [106]. The optical gap of Di-NPB in thin films is 2.9 eV as determined from the onset of absorption.

**ZnPc:** *zinc-phthalocyanine* is a well known material in the area of small molecule organic solar cells and mainly used as donor in heterojunctions with C60 [51, 53, 107]. It has an optical gap of 1.54 eV and absorption coefficients above $10^5$ cm$^{-1}$ [108, 109]. Besides of this application, it also became a standard material for investigation of organic doping, because it is easily p-type dopable with many known organic dopants, e.g. with 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) [110]. Due to shifting of the Fermi level towards the hole transport level, p-doped ZnPc layers provide very low hole injection barriers to metal electrodes of indium tin oxide (ITO) or Au [91]. Therefore, p-doped ZnPc ensures good ohmic contacts. This was shown for OLEDs as well as for solar cells [107, 111]. In this work, ZnPc is solely used in form of such a doped contact layer.

**Bphen:** *4,7-diphenyl-1,10-phenanthroline* is a wide gap electron transport layer. It is similar to 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP). Bphen is used as inter-layer between C60 and the metal back contact. In principle, the high EA of 2.9 eV does not suggest good electron transport from C60 to Bphen. However, it is assumed that the electron transport occurs mainly through cathode induced defect states, as was reported for BCP by Peumans et al. [38].
Table 4.1: Ionization potential (IP), electron affinity (EA), density, and supplier of the transport materials and C60. a) the IP of these materials is measured via UPS at the IAPP. b) the EA of Di-NPB is estimated from the optical gap using the phenomenological correlation between optical gap and transport gap given in [24].

<table>
<thead>
<tr>
<th>material</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>density (gcm$^{-3}$)</th>
<th>supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPAPF</td>
<td>5.6 a)</td>
<td>2.2 [112]</td>
<td>1.2</td>
<td>Lumtec (Hsin-Chu, Taiwan)</td>
</tr>
<tr>
<td>Di-NPB</td>
<td>5.3 a)</td>
<td>1.7±0.8 b)</td>
<td>1.14</td>
<td>Sensient (Milwaukee, USA)</td>
</tr>
<tr>
<td>ZnPc</td>
<td>5.1 a)</td>
<td>3.34 [113]</td>
<td>1.34</td>
<td>ABCR GmbH (Karlsruhe, Germany)</td>
</tr>
<tr>
<td>Bphen</td>
<td>6.4 [114]</td>
<td>2.9 [114]</td>
<td>1.24</td>
<td>ABCR GmbH (Karlsruhe, Germany)</td>
</tr>
<tr>
<td>C60</td>
<td>6.4 a)</td>
<td>4.0 [99]</td>
<td>1.54</td>
<td>BuckyUSA (Houston, USA)</td>
</tr>
</tbody>
</table>

The absorbance of all presented materials is depicted in Figure 4.2. BPAPF, Di-NPB, and ZnPc are doped with the p-dopant NDP9 from Novaled AG and a ratio of 10 wt%, 5 wt%, and 3 wt%, respectively. In all cases the achieved conductivity of the HTLs is above $10^{-5}$ Scm$^{-1}$. NDP9 is chosen for stability reasons, similar electrical properties can be achieved with dopants described e.g. in [89, 115]. All materials except of the dopants are purified at least twice by thermal gradient sublimation. The density in thin films and the suppliers are summarized in Table 4.1.

4.2 Sample Preparation

In this work the organic thin films are processed by vacuum thermal evaporation. A schematic picture of this method is given in Figure 4.3. The material is placed in a ceramic crucible which can be heated by surrounding heating wires. The temperature is measured by a type K (alumel-chromel) thermocouple and is adjusted by a controller from the company Eurotherm (Modell 2416). When the material is heated up to the sublimation temperature it evaporates and is deposited on the sample, forming a thin layer. Typical sublimation temperatures vary between 100 to 500 $^\circ$C, depending on size and shape of the molecules. The area to be coated is defined by a shadow mask. The metal layers are evaporated using a boron nitride crucible for aluminum and a molybdenum boat for gold. The thicknesses of the deposited layers are controlled by quartz crystal microbalance (QCM) sensors (Leybold Inficon Inc.).

Two different ultra high vacuum tools are used for device preparation. The one is a multi-chamber tool (UFO-tool) from the company Bestec GmbH. It has separate chambers for intrinsic materials, p-doping, n-doping, and metal evaporation. The samples can be transferred between the chambers without leaving vacuum. Only single samples (size: $2.5 \times 2.5$ cm$^2$) can be processed with this tool. The second is a single chamber tool (Lesker B) from the Kurt J. Lesker Company. Lesker B is used for production of large wafers (size: $15 \times 15$ cm$^2$) containing 36 samples (6 rows $\times$ 6 columns). The
4.2 Sample Preparation

Figure 4.3: Material deposition via thermal evaporation.

material and the thicknesses of individual layers can be varied independently in rows and columns, providing a very convenient way for investigating variations in the stack design. The base pressure in both vacuum systems is below $10^{-6}$ mbar.

Substrate heating during the layer deposition is realized in different ways. Figure 4.4 shows the method used in the UFO-tool. On the back side the substrate is connected to an ITO covered glass plate, which is used for heating. The temperature is measured with a type K thermocouple at the surface of the sample with an accuracy of $\Delta T=2.5$ K. Considering that the temperature is not measured directly at the place of the active area an additional uncertainty of 2.5 K is taken into account, i.e. the accuracy of $T_{\text{sub}}$ is $\Delta T_{\text{sub}}=5$ K. Substrate cooling is done by connecting the substrate to a copper block in the chamber which can be cooled by liquid nitrogen. In Lesker B the sample is heated via halogen lamps. The substrate temperature cannot be measured directly but is calibrated by temperature indicating stripes and furthermore checked by comparing the results of a reference material deposited in Lesker B and another chamber, where the temperature is known. This leads to the quite high inaccuracy of $T_{\text{sub}}$ of $\Delta T_{\text{sub}}=10$ K.

The maximal error of the absolute layer thickness, resulting from the errors of the quartz monitor measurement ($\Delta d_{\text{QCM}}=3.5\%$), the accuracy of the material density ($\Delta \rho =3\%$), and the error of the QCM calibration ($\Delta d_{\text{cal}}=5\%$), is estimated to be 11.5 %. Note that $\Delta \rho$ is a systematic error. Furthermore, the QCM calibration for deposition of the active layers is done more frequently, resulting in reduced $\Delta d_{\text{cal}}$ of only 2 %. So, the maximal thickness deviations between the investigated layers are 5.5 %. For samples prepared in Lesker B another thickness error of $\Delta d_{\text{hom}}=3\%$ results from the inhomogeneous deposition across the large substrate. However, in this tool $\Delta d_{\text{cal}}$ and $\Delta d_{\text{QCM}}$ can be considered as systematic error, because all samples are prepared in one run. Thus, maximal thickness deviations between samples from the same run are
Figure 4.4: Schematic sample layout with heating substrate on top. a) Layout of the sample as seen from below, i.e. as seen from the position of the source. There are 4 pixels each with an active area of $6.4\pm0.2 \text{ mm}^2$. b) Side view of sample and heating substrate. c) Top view of the heating substrate layout. A current is driven through the ITO of the heating substrate to heat the sample. The temperature of the sample surface is measured with a type K thermocouple (chromel-alumel), that is pinned on the sample with a small drop of silver paste.

3 %. A list of all devices of this work with their respective run number and preparation tool is given in the appendix.

The ITO covered glass substrates (Thin Film Devices Inc.) are prestructured for solar cells and exhibit a sheet resistance of $30 \Omega/sq$. A single sample comprises four pixels, i.e. four equal solar cells (see Figure 4.4). All substrates are cleaned using aqueous detergent, acetone, ethanol, and isopropanol in an ultrasonic bath.

Solar cell devices are encapsulated with a cover glass that is glued onto the substrate using UV resin (Nagase ChemteX). For samples made in Lesker B a moisture getter (Dynic) is additionally introduced into the encapsulation.

The active area of the solar cells, defined by the overlap between the ITO ground contact and the metal top contact, is $6.4\pm0.2 \text{ mm}^2$. A control experiment with aperture masks of different sizes showed that edge effects as reported in [116] can be excluded.

4.3 Experimental Methods

4.3.1 X-Ray Diffraction

The nanostructure of the samples is investigated by wide-angle X-ray diffraction (WAXRD) on the instrument URD-6 (Seifert FPM) using monochromatic Cu-$K\alpha$ radiation ($\lambda=1.5406\text{Å}$). The measurements are carried out in Bragg-Brentano geometry applying the symmetrically coupled $\omega-2\theta$ specular scan mode where $2\theta$ is the diffraction angle and $\omega=\theta$ is the angle of incidence of the X-rays, i.e. $\theta-2\theta$ scan mode. Only
4.3 Experimental Methods

Bragg reflections from lattice planes parallel to the substrate surface can be detected. The XRD patterns are measured with $2\theta$ steps of 0.01° to 0.05° and a sampling time of 60 to 180 s according to intensity and width of the reflections. XRD patterns are analyzed using the program ANALYZE to extract the parameters peak position ($2\theta$), interplane distance ($d$), peak width at half maximum intensity (FWHM), and crystallite size ($D$). The interplane distance is determined by Bragg’s law

$$n\lambda = 2\sin(\theta) \cdot d,$$

(4.1)

where $\lambda$ is the radiation wavelength and $\theta$ the Bragg reflection angle. The crystallite size $D$ is a measure for the vertical extend of the crystallites and is determined using the Scherrer equation

$$D = \frac{K\lambda}{\beta\cos \theta},$$

(4.2)

where $K$ is the shape factor ($K=0.94$ is used here), and $\beta$ is the line broadening at half the maximum intensity in radians. The line broadening component of the FWHM is determined by subtracting the corresponding components of instrumental broadening and microstrain.

The measurements are carried out by Dr. Rosina Rentenberger (Universität Ilmenau) and Dr. Alexander Levin (IAPP). All measurements are performed at room temperature on either Si or glass substrates, which are cleaned following the same procedure as for solar cell substrates.

4.3.2 Optical Characterization

Absorbance spectra of the organic layers are recorded with a two-beam spectrometer UV 3100 (Shimadzu Corporation) in transmission geometry. The accuracy of this measurement is 1%. Absorption spectra of the solar cells are determined using the same instrument in reflection geometry with an incident angle of 5°. An aperture mask with four pinholes of 4.5 mm² each is utilized to measure the absorption of the active area. The accuracy of the reflection measurement is 4%. Additionally, the errors by using the aperture mask can add up to 5%-points as is determined from a reference sample. The luminescence spectra are recorded using the spectrometer Fluoromax (Spex).

4.3.3 Topography Characterization

The surface topography is analyzed by atomic force microscopy (AFM) using a Digital Instrument Nanoscope IIIa in tapping mode. Measurements are done at room temperature in air, and are carried out by Dr. Marieta Levichkova (IAPP). Furthermore, scanning electron microscopy (SEM) pictures are taken by Ellen Kern (Universität Dresden) with a Zeiss Gemini DSM 982 instrument, measuring the signal of secondary electrons with the in-lens detector.
Figure 4.5: Illustrations of opening regimes of field-effect transistors with their respective IV-characteristics: a) linear regime; b) start of saturation regime; c) saturation regime. Adapted from [117].

4.3.4 Mobility Measurements

Two methods are used to determine the hole mobility of the investigated DCV6T donor materials. The first is an OFET measurement and the second is the charge carrier extraction by linearly increasing voltage (CELIV) method.

OFET

OFETs are based on the principle of thin film transistors and are therefore well adapted to low conductivity materials. The schematic layout and the working principle of an OFET are depicted in Figure 4.5. The bottom electrode is the gate electrode. The probed layer on top is separated from this gate electrode by an insulating gate dielectric, thus forming a capacitor, and is contacted by the source and drain contacts. By applying a gate voltage ($V_G$) charge carriers are induced in the probed layer at the interface to the dielectric. Deep traps have to be filled first before the additionally induced charges can be mobile. That means the applied $V_G$ has to be higher than a certain threshold voltage ($V_{th}$) in order to induce free charge carriers, which then create a conducting channel. The number of accumulated charges is proportional to the capacitance ($C_i$) and $V_G$. A current ($I_{SD}$) can be driven through the channel by applying a voltage between source and drain ($V_{SD}$). Depending on $V_{SD}$ there are different operating regimes of the transistor, which are presented in Figure 4.5. At small voltages ($V_{SD} \ll V_G$) the current is proportional to $V_{SD}$. This is the linear regime. When $V_{SD}$ is further increased, reaching $V_{SD}=V_G-V_{th}$, a depletion region develops at the drain contact and the channel is “pinched off”. By applying higher $V_{SD}$ the current does not increase any more but
is constant, signifying the saturation regime. The IV-characteristic of OFETs in both regimes can be described analytically \[117, 118\] by

\[ I_{SD, \text{linear}} = \frac{W}{L} \mu C_i \left( (V_G - V_{th})V_{SD} - \frac{1}{2} V_{SD}^2 \right), \]

(4.3)

and

\[ I_{SD, \text{saturation}} = \frac{W}{2L} \mu C_i (V_G - V_{th})^2, \]

(4.4)

where \( W \) is the channel width, \( L \) the channel length, and \( \mu \) the mobility. With these equations the mobility can either be determined from the slope of \( I_{SD} \) with \( V_{SD} \) in the linear regime or from the development of \( I_{SD} \) with the square of \( (V_G - V_{th}) \) in the saturation regime. A more detailed description of OFETs is found in \[117, 118\].

In this work OFET chips of the 4th generation from Fraunhofer IPMS are used. The chips are prestructured with four transistors for each channel length of 2.5, 5, 10, and 20 \( \mu \)m, respectively (16 transistors in total). The gate electrode consists of n-doped Si and a 230 nm thick layer of SiO\(_2\) forms the dielectric. Gold is used for the source and drain contacts. The substrates are cleaned in an ultrasonic bath by subsequently using aqueous detergent, acetone, ethanol, and isopropanol. Additionally, the substrates are plasma cleaned using oxygen plasma. Heating of the substrate during the layer deposition is done in the same way as for solar cell devices (see Figure 4.4). The IV-curves are measured under nitrogen atmosphere in a glovebox that is directly connected to the vacuum preparation chamber. To minimize charging effects during the measurements the IV-characteristics are recorded with a refresh time of 10 s between the data points. Further information on the measurement method and the utilized OFET chips can be found in \[119\]. The OFET measurements are carried out by Moritz Hein (IAPP).

**CELIV**

The CELIV method was first reported by Juška et al. \[120, 121\] to measure the mobility in \textit{poly(3-hexyl thiophene)} (P3HT) and in microcrystalline silicon. The working principle is presented in Figure 4.6. The samples are of sandwich type with a blocking contact. Two consecutive pulses of linearly increasing voltage \( V(t) = A \cdot t \) are applied to the sample and the resulting current transient is measured. The time between the two pulses is the so-called delay time \( t_d \). The peak voltage of the triangle pulse is \( V_{max} \). The initial current step

\[ j_0 = \frac{\epsilon \epsilon_0 A}{d}, \]

(4.5)

is caused by the geometric capacitance of the sample, i.e. it represents the displacement current, and is present in both sweeps. From \( j_0 \), either the dielectric constant or the thickness \( d \) of the active material can be measured. Additionally, a current peak of extracted charges is observed in the first sweep. It has the height \( \Delta j \), is maximal at the characteristic time \( t_{max} \), and develops until the sample is depleted after the so-called
**Figure 4.6:** Schematic illustration of the CELIV method. Two linearly increasing voltage pulses (1 and 2) are applied to the sample. $t_d$ is the delay time between both pulses. The transient current is measured ($j$), exhibiting a peak of extracted charge carriers during the first pulse additionally to $j_0$, which is caused by the geometric capacitance of the sample. From the peak position ($t_{\text{max}}$) the mobility of the extracted charges can be determined. The dotted curve indicates a partial recovery of charge carriers in the sample, e.g. by imperfect blocking or by thermal generation of charges. Adapted from [120].

transit time ($t_u$). Usually only the equilibrium charges are extracted, but it is also possible to increase the initial charge density by photoexcitation under illumination of the sample. For evaluation of the charge extraction peak, a good blocking behavior of the sample is important, to prevent recovering of the charge density in the sample. At sufficiently small delay times the sample is still depleted during the second sweep, which therefore does not exhibit an extraction peak. The amount of extracted charges is then equal to the difference of the two transients. By varying the delay time, the recovery of equilibrium charges can be investigated. The second pulse is therefore also important for identification of non ideal conditions like imperfect blocking.

The current transient can be analytically described [120] by

$$j(t) = \frac{\varepsilon \varepsilon_0 A}{d} + \sigma \left( 1 - \frac{l(t)}{d} \right) \left( \frac{\mu A t}{d} - \frac{\sigma}{2 \varepsilon \varepsilon_0 d} l^2(t) \right),$$  \hspace{1cm} (4.6)$$

where $l(t)$ is the depletion depth given by a Riccati differential equation in the form:

$$\frac{dl(t)}{dt} + \frac{\sigma}{2 \varepsilon \varepsilon_0 d} l^2(t) = \frac{\mu A t}{d}.$$  \hspace{1cm} (4.7)$$

$\sigma$ and $\mu$ are the conductivity and the mobility, respectively. For low conductivity materials, where the transit time is low against the dielectric relaxation time of the material
(\(t_u \ll \tau_{\sigma} = \frac{\mu_{\sigma}}{\sigma}\)), the mobility can be directly determined from the maximum current time [120]

\[
t_{\text{max}} = d \sqrt{\frac{2}{3 \mu A}}.
\]  

(4.8)

The CELIV measurements and evaluations are carried out by Prof. Kažukauskas and his students Mindaugas Pranaitis and Andrius Arlauskas (Semiconductor Physics Department, Institute of Applied Research of Vilnius University).

A cryostat, cooled with liquid nitrogen, is used to measure the mobility at different temperatures varying from 190 to 320°C. To increase the charge extraction signal the samples are illuminated with a light pulse from a blue LED prior to the voltage sweep. The samples are prepared in the Lesker-B tool using the standard device layout for solar cells, i.e. the samples comprise 4 pixels each with an active area of 6.4±0.2 mm². The devices are encapsulated with the same method like the solar cells.

### 4.3.5 Electrical Characterization of Solar Cells

There are two measurement systems for electrical characterization of the solar cells. The first is placed at the UFO-tool to measure the devices under nitrogen atmosphere in the glovebox which is directly connected to the vacuum system. The devices are illuminated with the sun simulator SOL 1200 (Hoene AG) or, after an upgrade, with SoCo 1200 MGH (Steuernagel). In both cases the intensity is monitored by an outdoor reference diode (Fraunhofer Institute for Solar Energy Systems). The intensity can be varied by applying different metal gray filters. The current-voltage (IV) characteristics are recorded with a source measure unit SMU 236 (Keithley). The second measurement system is used for characterization of the Lesker B substrates. There, the sun simulator 16S-003-300 (Solarlight Company Inc.) is utilized to illuminate the devices via an optical fiber, and the IV-characteristics are recorded with a source measure unit 2400 Sourcemeter (Keithley). The intensity is monitored by the calibrated reference diode S1337-33BQ (Hamamatsu). Because this measurement is done in air, only encapsulated samples are measured.

The measurement errors of the FF and \(V_{oc}\) depend on the step width of the IV measurement. Here, a step width of 0.025 V is used, providing a small error below 1 % for both parameters. The accuracy of the \(j_{sc}\) is mainly limited by the accuracy of the device area. The efficiencies in this work are always given with their corresponding error.

In addition to the typical performance parameters of solar cells, the so-called saturation factor (\(S\)) is determined from the measured IV-characteristics. This factor is defined as ratio between the current at -1 V and \(j_{sc}\):

\[
S = \frac{j(-1V)}{j_{sc}},
\]  

(4.9)

and thus measures how close the \(j_{sc}\) is to a saturated photocurrent. It can also be considered as parameter for the dependency of the photocurrent on the electric field and
therefore as a figure of merit for charge transport in the solar cell.
For the EQE measurement, a home made setup based on a xenon arc lamp, a monochromator (Cornerstone 260), and a Lock-In amplifier (Signal Recovery SR 7265) is used. The EQE and hence also the resulting IQE spectra are all recorded under short circuit conditions.

4.3.6 Optical Simulation

To investigate and optimize the thin film optics, the devices are optically modeled using the program OSOLEMIO (programmed by Mauro Furno, IAPP). This program is based on a transfer-matrix-formalism [122]. Values of the optical constants $n$ and $k$ are derived by fitting transmission and reflection spectra of thin film layers of the respective materials [123]. However, the accuracy of these values is limited, in that they do not account for the effect of dopant admixture into Di-NPB and C60. Optical constants of BPAPF are measured with dopant, although a thin neat layer of BPAPF is also used in the devices. The mixed layer (DCV6T-Bu : C60) optical constants are determined on a heated quartz glass substrate. That means that the influence of a C60 underlayer or a possible vertical-dependence of the mixed layer optical constants can not be accounted for by this method.

For determining the absorption spectra of individual layers, e.g. of the active layers, the absorption spectrum of the device is modeled first and then matched to the measured absorption by varying the layer thicknesses according to the thickness error. Following the report of Burkhard et al. [124], the absorption spectrum of active layers is then determined by subtracting the modeled absorption of passive layers from the measured device absorption.

4.3.7 Ultraviolet Photoelectron Spectroscopy

Ultraviolet photoelectron spectroscopy (UPS) is used to measure the molecular energy levels in the valence region. It is based on the photoelectric effect that was explained by Einstein in 1905. The schematic working principle is depicted in Figure 4.7. By excitation of the sample with photons of the energy $h\nu$, photoelectrons with a maximum kinetic energy of

$$E_{\text{kin}}^{\text{max}} = h\nu - IE,$$

are emitted, where IE is the ionization energy. UPS is particularly sensitive to the surface region (up to 10 nm depth), because the emitted photoelectrons have a very small mean free path in solids. The kinetic energy spectrum of the photoelectrons directly resembles the density of states of the bound electrons in the sample. In Figure 4.7 the first graph (left) represents the measurement of a metal substrate, while the right spectra represent the second measurement of an organic layer on top. Typical photon energies are in the range of 10 to 40 eV. Therefore UPS probes the valence levels of the molecules (or the metal), where the electrons are rather weakly bound.
Figure 4.7: Schematic illustration of the working principle of photoelectron spectroscopy. By excitation with photons of energy \( h\nu \) photoelectrons are emitted from the sample. The spectrum of their kinetic energy directly resembles the density of states of the valence levels. The dotted lines indicate the signal from scattered electrons.

The additional signal at low kinetic energies indicated by the dotted lines in Figure 4.7 comes from scattered electrons. The spectrum is cut off at the lowest possible kinetic energy that can be detected, i.e. where electrons have just sufficient energy to overcome the ionization energy. This edge is the so-called high binding energy cutoff (HBEC) and determines the position of the vacuum level.

In metals the spectrum at high kinetic energies extends up to the Fermi edge, denoting the position of the Fermi energy \( (E_F) \). In case of organics the spectrum extends up to the first HOMO peak. From the width of the spectrum given as \( E_{\text{kin}}^{\text{max}} - E_{\text{kin}}^{\text{min}} \) the ionization potential (IP) can be determined by

\[
\text{IP} = h\nu - (E_{\text{kin}}^{\text{max}} - E_{\text{kin}}^{\text{min}}).
\] (4.11)

The IP of a metal is equal to its work function \( (\Phi_M) \). It is assumed that the Fermi energy is constant throughout both measurements, i.e. constant throughout the sample. The work function of the organic \( (\Phi_{\text{org}}) \) is then determined by

\[
\Phi_{\text{org}} = \Phi_M - (E_{\text{HBEC}}^{\text{org}} - E_{\text{HBEC}}^M).
\] (4.12)

where \( E_{\text{HBEC}}^M \) and \( E_{\text{HBEC}}^{\text{org}} \) are the HBEC energies of metal and organic, respectively. Their difference denotes a step in the vacuum level at the interface, representing a so-called interface dipole given as

\[
\Delta = (E_{\text{org}}^{\text{HBEC}} - E_{\text{M}}^{\text{HBEC}}).
\] (4.13)
UPS measurements are carried out by Dr. Selina Olthof (IAPP). The investigations are performed using a helium discharge lamp UV210/35 (Specs) with the main excitation line (He I) at 21.22 eV. The photoelectron mean free path at this energy can be estimated to be 2 to 3 monolayers. The UPS detector is directly connected to the UFO-tool, which enables preparation and measurement of the samples without leaving vacuum. The base pressure in the UPS chamber is $10^{-9}$ mbar. A more detailed description of the measurement setup and method can be found in [90].

4.4 Standard Reporting Conditions and Mismatch

As a result of the continuing research efforts, organic solar cells are by now reaching efficiencies that make them attractive for some first commercial applications. With this success comes increased attention from many other research fields and more and more laboratories as well as companies are entering the field of organic solar cells. To ensure the healthy development of this technology and to enable a fair comparison between the reported results, it is crucial to adhere to the generally accepted standards for solar cell characterization [125, 126]. These so-called standard reporting conditions (SRC), which were developed for inorganic solar cells, are described in the standards IEC 60904-3, IEC 60904-1, IEC 60904-7, and other related thereon. They define the following main specifications:

- Solar cell characteristics are determined in regard to the spectrum AM 1.5 G. This spectrum represents the sun spectrum after passing 1.5 times the thickness of the atmosphere (“AM” stands for “air mass”).
- The light intensity is $100 \text{ mWcm}^{-2}$.
- The sample temperature is $25^\circ \text{C}$.

Figure 4.8 shows the AM 1.5 G spectrum in comparison to the spectra of the two sun simulators which are mainly used in this work. The simulator spectra significantly deviate from the designated spectrum, which can apparently cause large discrepancies between the obtained results. On account of the SRC, the reference diode, which is used to monitor the intensity, is calibrated to the spectrum of the sun (AM 1.5 G). Thus, the intensity is determined from the photocurrent of the diode $j_{\text{ref}}^{\text{sun}}$ multiplied by the calibration factor $c$:

$$I_{\text{sun}} = c \cdot j_{\text{sun}}^{\text{ref}} = c \cdot \int_{\lambda_1}^{\lambda_2} E_{\text{sun}}(\lambda) S_{\text{ref}}^{\text{ref}}(\lambda) \, d\lambda.$$  \hspace{1cm} (4.14)

$E_{\text{sun}}$ denotes the spectral irradiance of the sun (AM 1.5 G) and $S_{\text{ref}}^{\text{ref}}$ is the spectral response of the reference diode. The limits of integration $\lambda_1$ and $\lambda_2$ encompass the range
Figure 4.8: Illumination spectra of the sun simulators that are used for solar cell characterization compared to the sun spectrum (AM 1.5 G). The simulator spectra are normalized to an intensity of 1000 Wm$^{-2}$ within the given wavelength range of 300 to 1100 nm.

of $S^{\text{ref}}$. Consequently, the nominal intensity $I^*$ as displayed by the reference diode at illumination with the sun simulator

$$I^* = c \cdot j_{\text{sim}}^{\text{ref}} = c \cdot \int_{\lambda_1}^{\lambda_2} E_{\text{sim}}(\lambda) S^{\text{ref}}(\lambda) \, d\lambda$$

(4.15)

is wrong by means of the spectral mismatch. Here, $E_{\text{sim}}$ denotes the spectral irradiance of the sun simulator. When the spectral response of the test cell ($S^{\text{TC}}$), which shall be measured, is known, this spectral mismatch can be accounted for in the measurement [125]. This correction procedure is performed in the following way. An intensity $I_{\text{eff}}$ can be evaluated, which measures the effective intensity for the test cell in regard to the sun spectrum (AM 1.5 G), so as to relate the photocurrent under sun ($j_{\text{sun}}^{\text{TC}}$) and under simulator ($j_{\text{sim}}^{\text{TC}}$) like

$$I_{\text{eff}} = j_{\text{sim}}^{\text{TC}} \cdot j_{\text{sun}}^{\text{TC}} \cdot I_{\text{sun}}.$$
With the given spectrum of the sun simulator, the photocurrent of the test cell can be identified with

\[
j_{TC}^{\text{sim}} = j_{\text{ref}}^{\text{sim}} \frac{\int_{\lambda_1}^{\lambda_2} E_{\text{sim}}(\lambda) S_{TC}(\lambda) \, d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{\text{sim}}(\lambda) S_{\text{ref}}(\lambda) \, d\lambda}, \tag{4.17}\]

The photocurrent under sun irradiance can be written as

\[
j_{TC}^{\text{sun}} = \int_{\lambda_1}^{\lambda_2} E_{\text{sun}}(\lambda) S_{TC}(\lambda) \, d\lambda. \tag{4.18}\]

Finally, insertion of Equations (4.14), (4.17), and (4.18) into Equation (4.16) results in

\[
I_{\text{eff}} = c \cdot j_{\text{ref}}^{\text{sim}} \frac{\int_{\lambda_1}^{\lambda_2} E_{\text{sim}}(\lambda) S_{TC}(\lambda) \, d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{\text{sim}}(\lambda) S_{\text{ref}}(\lambda) \, d\lambda} \frac{\int_{\lambda_1}^{\lambda_2} E_{\text{sun}}(\lambda) S_{\text{ref}}(\lambda) \, d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{\text{sun}}(\lambda) S_{TC}(\lambda) \, d\lambda}, \tag{4.19}\]

where the last term is the so-called mismatch factor

\[
M = \frac{\int_{\lambda_1}^{\lambda_2} E_{\text{sim}}(\lambda) S_{TC}(\lambda) \, d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{\text{sim}}(\lambda) S_{\text{ref}}(\lambda) \, d\lambda} \frac{\int_{\lambda_1}^{\lambda_2} E_{\text{sun}}(\lambda) S_{\text{ref}}(\lambda) \, d\lambda}{\int_{\lambda_1}^{\lambda_2} E_{\text{sun}}(\lambda) S_{TC}(\lambda) \, d\lambda}. \tag{4.20}\]

This factor is an individual number for every test cell measured at a certain sun simulator with a certain reference diode. As can be seen from Equation (4.19), the mismatch factor enables to evaluate the mismatch corrected intensity \(I_{\text{eff}}\) from the measured nominal intensity \(I^*\):

\[
I_{\text{eff}} = I^* \cdot M, \tag{4.21}\]

and thus ensures that the determined power conversion efficiency refers to the spectral irradiance of \(E_{\text{sun}}\) (AM 1.5 G) as is requested by the SRC. Only the relative spectra of \(E_{\text{sim}}, E_{\text{sun}}, S_{TC}, \) and \(S_{\text{ref}}\) are needed for determination of \(M\). The integration limits \(\lambda_1\) and \(\lambda_2\) have to encompass the spectral responses of both test cell and reference diode.

If the sun simulator is adjustable in intensity, then the second requirement of the SRC, i.e. measuring of the IV-characteristics at \(I_{\text{eff}}=I_{\text{sun}}=100\, \text{mWcm}^{-2}\), can be fulfilled by matching the nominal intensity to the value given by \(M\). According to Equation (4.16) the measured photocurrent at the sun simulator is then equal to the photocurrent obtained under sun irradiance (AM 1.5 G):

\[
I^* = \frac{I_{\text{sun}}}{M} = \frac{100\, \text{mWcm}^{-2}}{M} \iff j_{\text{TC}}^{\text{sim}} = j_{\text{TC}}^{\text{sun}}. \tag{4.22}\]
In this work, the reported intensity generally denotes the effective intensity as corrected by the mismatch factor, apart from a few examples where the intensity is explicitly denoted as nominal intensity. That means all power conversion efficiencies given in this work account for the first requirement of the SRC, i.e. they refer to the irradiance spectrum AM 1.5 G. The second requirement, i.e. using an intensity of 100 mWcm$^2$, could not be fulfilled throughout this work. Only in some cases the measurements are done at the adjusted intensity of 100 mWcm$^2$. For measurements at the sun simulator SoCo 1200 MGH, a possible spectral change of $E_{\text{sim}}$ upon adjusting the intensity is not accounted for in the evaluations (concerns devices T1 – T7). Measurements at the sun simulator 16S-003-300 include possible changes, since there the spectrum is measured individually for every measurement run (concerns devices M1 – M4). The third requirement of the SCR, i.e. measuring at a sample temperature of 25°C, is not fulfilled due to technical reasons. The sample temperature during the measurements varies between 28°C to 35°C depending on the chosen intensity and measurement system.

Some of the presented solar cells, which reach promising efficiencies and therefore require the highest possible efforts to accurately determine the $\eta_{\text{PCE}}$, are additionally tested under outdoor conditions to verify their efficiency. Independently certified efficiency values of organic tandem cells, which are based on solar cells as presented in this work, can be found in [7, 33].
5 The Material System DCV6T - C60

In this chapter the properties of DCV6T and DCV6T - C60 heterojunctions are investigated. In the beginning, the function of oligothiophenes as donor materials in solar cells is briefly reviewed, in particular affirming the suitability of DCV6T. Basic optical and electronic properties of the two DCV6T derivatives which are investigated in this work are presented thereafter. Subsequently, the influence of substrate temperature during the deposition on the morphology of neat and mixed layers is investigated. Neat layers of the DCV6T derivatives show increased crystallinity when grown on heated substrates. In mixed layers, high substrate temperatures lead to higher phase separation between DCV6T and C60. These effects are studied by UV-Vis absorption and luminescence spectroscopy, X-ray diffraction (XRD), and atomic force microscopy (AFM). Finally, the hole mobility in DCV6T neat layers is investigated by OFET and CELIV measurements.

5.1 Oligothiophenes as Donors in Heterojunctions with C60

Oligothiophenes are widely used in organic electronic devices because they offer a large variety of possible chemical modifications as well as a relatively straightforward synthesis [133]. They have particularly been reported as efficient semiconducting layers in OFETs exhibiting high hole mobilities. Depending on the chemical purity and structural order, unsubstituted oligothiophenes as for example α-sexithiophene (6T) can reach mobilities up to 0.08 cm²/Vs [134]. Many studies have shown that a high order which provides good stacking of the thiophene π-electron systems is essential for high mobilities. This can be achieved by facilitating the self organization during the
Figure 5.1: Chemical structures and schematic energy diagrams of DCVnT donor molecules combined with C60 in D-A heterojunctions. Characteristic values of the ionization potential (IP), the electron affinity (EA), the optical gap ($E_{\text{opt}}$) of the donor, and $E_{\text{DA}}$ are taken from references below. Furthermore, typical $V_{\text{oc}}$ values as received from solar cells with these material combinations are displayed. EA values of the oligothiophenes were determined by cyclic voltammetry (from 1st reduction potential vs. $\text{Fc}^+/\text{Fc}$) [50]. The EA value of C60 was determined by IPES [99]. The presented IP values were all determined by UPS at the IAPP, besides that of DCV6T, which was estimated from comparison of cyclic voltammetry HOMO energies and the open circuit voltage of solar cells [127]. The optical gaps were determined from the onset of absorption [13, 128, 129]. $V_{\text{oc}}$ of typical solar cells are taken from references [12, 127, 128, 130, 131].
5.1 Oligothiophenes as Donors in Heterojunctions with C60

Figure 5.2: Chemical structures and schematic energy diagrams of $\alpha$-sexithiophene (6T) and ZnPc combined with C60 in D-A heterojunctions. Both materials are widely used as standard materials for organic devices and are well known in literature. The EA value of 6T was determined by cyclic voltammetry (from 1st reduction potential vs. $\text{Fc}^+/\text{Fc}$) [24] and is thus directly comparable to the values given for the DCVnT materials in Figure 5.1. The EA values of C60 and ZnPc were measured by IPES [99, 113]. The IP values were determined by UPS at the IAPP, apart from the value for 6T, which is taken from [24]. The optical gaps were determined from the onset of absorption [108, 132]. $V_{oc}$ of typical solar cells with these heterojunctions can be found in [130, 131].

film growth, for example with high substrate temperatures or by using alkyl substituted oligothiophenes, promoting a standing up orientation [134–137].

Figure 5.1 shows a series of dicyanovinylene substituted oligothiophenes (DCVnTs) which were synthesized by the group of Prof. Bäuerle (Universität Ulm) for application as donor materials in organic solar cells. The number of thiophene units of the molecule backbone is varied from 3 (DCV3T) to 6 (DCV6T) to systematically investigate the relationship between molecular structure and electrical performance.

To achieve good photovoltaic performance, the position of energy levels relative to those of the acceptor C60 are particularly important (see Section 3.2.1). In this regard, unsubstituted oligothiophenes like for example 6T (Figure 5.2) are not suitable, because their electron affinity is too low and they can not absorb much sunlight due to their large optical gap. In the DCVnTs, strong electron withdrawing dicyanovinylene endgroups are introduced which increase the electron affinity [138, 139]. The electron density in the excited state (LUMO) is then mainly localized on these endgroups. Therefore, the LUMO energy is stabilized and nearly independent of the backbone conjugation. In Figure 5.1 the electron affinities as measured by cyclic voltammetry are given. All
DCV\textsubscript{n}Ts exhibit values around 3.5 eV, providing an energetic step of approximately 0.5 eV to the respective value of C60, which is considered as a favorable offset for the function of solar cells.

In contrast to the LUMO, the electron density in the ground state (HOMO) is mainly localized on the molecule backbone, and thus the HOMO energy can be tuned by varying the backbone conjugation length. In general, an enhancement of the $\pi$-conjugated system leads to a decrease of the energy gap [136, 140]. Accordingly, the ionization potential is systematically decreased with increasing number of thiophene units and also the optical gap decreases. This is presented in Figure 5.1. It can be seen that the energetic difference $E_{\text{DA}}$ between the ionization potential of DCV\textsubscript{n}T and the electron affinity of C60 is reduced with increasing number of thiophene units. By reduction of $E_{\text{DA}}$, a larger driving force for exciton separation is provided, but at the same time the resulting energy of separated charge carriers is lowered (see Section 3.2.1).

In fact, it was shown in the work of Schüppel [141] that in D-A heterojunctions of DCV\textsubscript{3}T - C60, a too high $E_{\text{DA}}$ prevents efficient exciton separation. An energy exchange process, finally leading to a higher triplet population of DCV\textsubscript{3}T, was observed instead. In DCV\textsubscript{4}T to DCV\textsubscript{6}T exciton separation takes place at the D-A heterojunction with C60. Nevertheless, it was shown by photo-induced absorption measurements (PIA) at low temperatures that exciton separation competes with the relaxation of the charge transfer state into the DCV\textsubscript{n}T triplet exciton. By decreasing $E_{\text{DA}}$ (with increasing the number of thiophenes), the probability of this process is reduced while the probability for exciton separation increases. In solar cells measured at room temperature, efficient exciton separation was proven for DCV\textsubscript{5}T and DCV\textsubscript{6}T. The $V_{\text{oc}}$ was shown to depend linearly on $E_{\text{DA}}$ (Figure 5.1) [50].

In these studies, DCV\textsubscript{6}T proved to be a very promising donor material in heterojunctions with C60. Compared to other widely used donor materials like 6T and ZnPc, which are presented in Figure 5.2, DCV\textsubscript{6}T provides a higher energy difference $E_{\text{DA}}$ while still exhibiting efficient exciton separation. Thus, it achieves higher photovoltages in solar cells. Furthermore, DCV\textsubscript{6}T has an optical gap of 1.77 eV and a high absorption coefficient of $2.9 \cdot 10^5$ cm\textsuperscript{-1}, leading to high absorption in the green part of the sun spectrum. In former works, a power conversion efficiency of $2.1 \pm 0.2$ % and $V_{\text{oc}}$ up to 0.9 V was shown for DCV\textsubscript{6}T - C60 solar cells [50, 127]. However, the layer morphology was not further addressed in these works, albeit it is known to have a large influence on the performance. Especially in mixed heterojunction solar cells, morphology is very important (see Section 3.2.1) and carries a great potential for further improvement of DCV\textsubscript{6}T - C60 solar cells.
5.2 Basic Material Properties of DCV6T

In this work, two derivatives of $\alpha,\omega$-bis(dicyanovinylene)-sexithiophene (DCV6T) are studied. The chemical structures of these molecules are presented in Figure 5.3. Both derivatives are differing in position and length of the alkyl side-chains which are attached to the thiophene backbone. The first one has butyl side-chains attached to thiophenes number 1, 2, 5, and 6, and is from here on denoted as DCV6T-Bu. The second DCV6T derivative has two ethyl side-chains attached to thiophenes number 2 and 5 each. It is from here on denoted as DCV6T-Et.

The alkyl side-chains do not contribute to the $\pi$-conjugated electron system, but have a weak electron-releasing character. The corresponding inductive effect rather scales with the number of side-chains than with the substitution pattern. Therefore, the basic electronic properties of the molecule should be independent of the actual substitution pattern and it can be assumed that the investigated DCV6T derivatives exhibit properties similar to those of the formerly studied DCV6T-Bu(2,2,5,5) (Figure 5.1) comprising two butyl side-chains at thiophenes number 2 and 5 each. However, side chain variation
can have significant influence on the solid state morphology giving rise to preferential molecular orientations or even inducing a distinct molecular order. Important properties like absorption or charge transport can be affected and may thus lead to significant changes in device performance.

DCV6T-Bu is purchased from Heliatek GmbH (Dresden, Germany), while DCV6T-Et is delivered by the group of Prof. Bäuerle (Universität Ulm). Both materials are outgased in vacuum prior to use (below sublimation temperature).

5.2.1 Optical Properties

Figure 5.4 shows absorption and photoluminescence spectra of DCV6T-Bu and DCV6T-Et measured in thin film and in solution. The thin films have a thickness of 30 nm and 20 nm, respectively, and are deposited on quartz glass substrates. Solution spectra are measured using dichloromethane as solvent.

Both DCV6T derivatives show similar absorption behavior in solution with the main peak at 513 nm (2.42 eV) and a second peak at 392 nm (3.16 eV). From comparison with quantum-chemical calculations, performing density functional theory on DCV6T without any side-chains, the main absorbance peak can be related to the $S_0 \rightarrow S_1$ transition, while the second peak corresponds to the $S_0 \rightarrow S_4$ transition [50]. The spectra do not show a distinct vibronic structure but are rather broad and featureless. This can be attributed to a loss of planarity and rigidity related to rotational disorder of the thiophene units, which limits the effective conjugation length. Furthermore, the corresponding luminescence spectra exhibit a rather large Stokes shift. The peak to peak distance between absorption and luminescence is 0.72 eV for DCV6T-Bu and 0.69 eV for DCV6T-Et. Regarding the energy scale, the luminescence spectra are also narrower than the absorption spectra and do not have a clear mirror symmetry to those. This behavior indicates a planarization of the molecule upon excitation, whereas in the ground state the thiophene rings are free to rotate around the inter-ring $\sigma$-bonds [142].

The thin film absorption spectra of both DCV6T derivatives are broadened and red-shifted compared to the solution spectra. Also, the thin film luminescence shifts to lower energies. This shift of transition energies is typical for aggregation into the solid state and results from the molecular interactions. Furthermore, the thin film absorption spectra are more structured as compared to solution, which indicates a higher planarity of the individual molecules and a preferential ordering within the solid. However, there are differences in some spectral features between both materials. DCV6T-Bu exhibits a stronger red-shift with the maximum peak at 594 nm whereas the DCV6T-Et thin film peak is at 574 nm. Furthermore, the absorption spectrum of DCV6T-Bu is more structured with a distinct absorption feature at 655 nm appearing as shoulder in the
Figure 5.4: Absorbance and photoluminescence of DCV6T-Bu and DCV6T-Et. Thin film spectra are measured using 30 nm and 20 nm thick layers on quartz glass, respectively. Positions of maxima are indicated. The maximum absorption coefficients are given in the insets. Solution spectra are measured in dichloromethane. The photoluminescence spectra are measured with excitation at the respective wavelengths of maximum absorption.
spectrum. This feature is also present in DCV6T-Et but much less pronounced. These results indicate that DCV6T-Bu has a higher molecular order compared to DCV6T-Et, which could be a consequence of the different side-chain pattern.

In some other oligothiophenes like \(\alpha\)-quinqethiophene or \(\alpha\)-sexithiophene, a blue-shift of absorption is reported for the thin film spectra [136, 143]. In such cases, which are denoted as H-aggregation, the molecules are oriented with their long-axes parallel to each other and are typically standing upright on the substrate. This results from self organization by strong interactions between the thiophene backbones. Due to the excitonic coupling between the molecules, the lowest energy transition is forbidden and thereby the absorption is blue-shifted. Furthermore, the fluorescence yield is very low because the excitons relax into the lower energy state, which is optically forbidden, and therefore recombine mainly non-radiatively. Although the molecular structure of DCV6T-Bu and DCV6T-Et comprises a sexithiophene backbone, the substitution with rather bulky dicyanovinylene endgroups and alkyl side-chains introduces steric hindrances, which prevent such H-aggregation.

The absorption properties of the DC6V6T derivatives are very promising for application in solar cells. The optical gaps of DCV6T-Bu and DCV6T-Et are 1.70±0.02 eV and 1.72±0.2 eV, respectively. The maximum absorption coefficient is 3.2±0.3·10^5 cm\(^{-1}\) for both and the spectra cover the wavelength range from approximately 400 to 680 nm. Thus, much of the sunlight in the visible range can be absorbed.

### 5.2.2 Electronic Properties

In Table 5.1 energy levels and the optical gaps of DCV6T-Bu and DCV6T-Et are presented. The IP is measured by UPS on thin films on gold substrate. The presented HOMO and LUMO energies \(E_H^{CV}\) and \(E_L^{CV}\) are determined by cyclic voltammetry (CV) and are calculated using the standard expression \(E_{H,L}^{CV} = -qE_{onset}^{ox,red} + E_{ref}\), with \(E_{ref} = -4.8\) eV as ionization energy of ferrocene and \(q\) as elementary charge. \(E_{onset}^{ox}\) and \(E_{onset}^{red}\) are the onset voltages of the first oxidation and the first reduction potential, respectively. The optical gap is determined from the onset of the thin film absorption spectrum (Figure 5.4).

The HOMO energies determined by CV are equal for both DC6V6T derivatives but are higher (in energy) by approximately 0.2 eV than the corresponding ionization levels which are measured by UPS. This difference generally results from the different measurement methods and is thus inherent. Cyclic voltammetry measures the oxidation and reduction potentials of molecules in solution, while UPS measures the surface ionization energy of thin films. Nevertheless, D’Andrade et al. [144] showed that the ionization level determined by UPS (\(E_{HOMO}\)) can phenomenologically be related to the
Table 5.1: Energy levels and the optical gap of DCV6T-Bu and DCV6T-Et. The ionization potential (IP) is determined by UPS. HOMO ($E_{CV}^H$) and LUMO ($E_{CV}^L$) energies are determined by cyclic voltammetry (CV) and are calculated from the onset energies of the first oxidation and first reduction potential versus the ferrocene reference potential ($E_{ref} = -4.8$ eV), respectively. The optical gap is determined from the onset of the thin film absorption spectrum.

<table>
<thead>
<tr>
<th>material</th>
<th>IP (eV)</th>
<th>$E_{CV}^H$ (eV)</th>
<th>$E_{CV}^L$ (eV)</th>
<th>optical gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCV6T-Bu</td>
<td>5.42±0.05</td>
<td>-5.25</td>
<td>-3.58</td>
<td>1.70±0.02</td>
</tr>
<tr>
<td>DCV6T-Et</td>
<td>5.44±0.05</td>
<td>-5.24</td>
<td>-3.22</td>
<td>1.72±0.02</td>
</tr>
</tbody>
</table>

HOMO energy measured as first reduction potential ($V_{CV}$) in cyclic voltammetry by

$$E_{HOMO} = -(1.4 \pm 0.1) \cdot (qV_{CV}) - (4.6 \pm 0.08) \text{ eV.} \quad (5.1)$$

Calculating the corresponding values of $E_{HOMO}$ for DCV6T-Bu and DCV6T-Et gives -5.23±0.13 eV and -5.22±0.12 eV, respectively. This, however, still does not match the ionization energy as determined by UPS. Equation (5.1), therefore, seems not to be applicable to the materials investigated in this work. It might be applied for the estimation of $E_{HOMO}$ when no UPS measurement is possible, but can lead to deviations.

In the following, only the ionization energy as determined by UPS will be used for discussion, since it is the more relevant value with respect to solar cell application. The IP of both DCV6T derivatives are equal and fit well into the series found for DCVnT materials (Figure 5.1), where the IP of DCV6T-Bu(2,2,5,5) was estimated at 5.5 eV. Considering an electron affinity of 4.0 eV for C60 [99], the energy difference $E_{DA}$ between the respective transport levels of DCV6T and C60 is 1.4 eV. This is well below the measured optical gap in the DCV6Ts of 1.7 eV, and hence provides a sufficient driving force for exciton separation. According to the solar cell results of the DCVnT series, $V_{oc}$ up to 0.9 V under standard measurement conditions can be achieved with the given $E_{DA}$. This is confirmed by the solar cells presented in this work in Chapter 6.

5.3 Effect of Substrate Heating on Layer Morphology

Investigation and control of layer morphology have become key principles for the optimization of organic devices. In neat layers, study of morphology is mainly aiming for the control of crystallinity and molecular orientation. This is particularly important to achieve high charge carrier mobilities [134], but can as well influence the absorption spectrum [110, 145] or the energetic alignment at interfaces [146]. All of these aspects
have to be considered for the optimization of solar cells, especially when utilizing flat heterojunctions. In mixed heterojunction solar cells, the control of phase separation between donor and acceptor material plays the dominant role [11, 147, 148].

In this work, the effects on morphology by applying different substrate temperatures ($T_{\text{sub}}$) during the deposition of the layers are studied. From the methods available for vacuum deposited devices, it is the most promising way to control the morphology of both neat and mixed layers. Since the temperature can be adjusted continuously, assembly of the molecules can easily be facilitated by heating or even prevented if the substrate is cooled down. The effect of different substrates or organic underlayers is studied to the extent necessary for solar cell application. Thus, only organic underlayers which are used in a solar cell stack, i.e. C60, BPAPF and Di-NPB, are investigated.

In the following, the morphology of DCV6T-Bu and DCV6T-Et layers is studied by X-ray diffraction (XRD), UV-Vis absorption spectroscopy, and atomic force microscopy (AFM). The effect of different applied substrate temperatures during the film growth is discussed. Relations between morphology and performance of the solar cells are addressed in Chapter 6.

### 5.3.1 Neat DCV6T Layers

**X-Ray Diffraction**

In Figure 5.5 XRD patterns of neat DCV6T-Bu and DCV6T-Et layers deposited on silicon substrates are presented. The substrate temperature during the evaporation is varied from 30 °C to 90 °C. In the chosen $\theta$–$2\theta$ scan mode, only Bragg reflections from lattice planes oriented parallel to the sample surface can be detected. Values of the central-angle peak positions $2\theta$, the corresponding interplane distances $d$, the FWHM of the peaks, and the related crystallite sizes $D$ are summarized in Table 5.2. The crystallite size is a measure for the vertical extent of crystalline domains. The lateral extent or orientation of crystallites can not be determined with this method. The feature at $2\theta=10.5^\circ$ in the measurements of DCV6T-Bu (Figure 5.5, left) is caused by the instrument.

All samples, especially those with substrate heating, exhibit clear Bragg reflection peaks. Only the DCV6T-Et layer grown on the room temperature substrate ($T_{\text{sub}} = 30^\circ C$, 64 nm) exhibits a relatively weak and very broad feature around 8.7 °, indicating a rather amorphous structure. In comparison, the unheated DCV6T-Bu layer (50 nm) shows a more distinct peak at 7.83 °, corresponding to an interplane distance of 11.29 Å and a crystallite size of 13.4±0.2 nm. Obviously, DCV6T-Bu has a higher tendency for
5.3 Effect of Substrate Heating on Layer Morphology

Figure 5.5: XRD patterns of DCV6T-Bu and DCV6T-Et layers grown at different substrate temperatures on silicon substrate. The first and second order peaks are designated with arrows. The patterns of different samples are shifted vertically for easier comparison. The feature at $2\theta = 10.5^\circ$ in the measurement of DCV6T-Bu (left) is caused by the instrument. Heated samples show well resolved peaks indicating crystalline phases. The corresponding values for interplane distance and crystallite size are summarized in Table 5.2.

molecular ordering than DCV6T-Et, when grown at room temperature. This confirms the previous assumption from the comparison of thin film absorption spectra, which already suggested a higher molecular order for DCV6T-Bu.

The XRD patterns of the heated samples are characterized by clear Bragg reflection peaks at 8.2° and 10.4° for DCV6T-Bu and DCV6T-Et, respectively. These signals are much more pronounced than those in the room temperature samples, even featuring the second order peak (indicated by arrows in Figure 5.5). The corresponding interplane distance for the heated DCV6T-Bu layer ($T_{\text{sub}} = 90^\circ \text{C}, 50 \text{ nm}$) is 10.78 Å and the crystallite size is 49 nm. The heated DCV6T-Et layer ($T_{\text{sub}} = 90^\circ \text{C}, 71 \text{ nm}$) exhibits an interplane distance of 8.5 Å and the crystallite size is 56.1 nm. Thus, the interplane distance is smaller and the crystallites are larger than in the case of the room temperature deposited films. In both DCV6T derivatives a distinct molecular order is present, with the vertical crystallite size approaching the nominal layer thickness. These results confirm that a crystalline nature of DCV6T films can be achieved by substrate heating.

The lower interplane distance for DCV6T-Et as compared to DCV6T-Bu might be related to the shorter side-chains, which generally allow for a closer packing of the molecules. Thus, both DCV6T derivatives might crystallize in different structures.
Table 5.2: Central-angle peak positions $2\theta$, interplane distances $d$, and crystallite sizes $D$ of DCV6T-Bu and DCV6T-Et layers grown at different substrate temperatures on Si substrate. Values are determined from the XRD patterns presented in Figure 5.5 and Figure 5.6.

<table>
<thead>
<tr>
<th>DCV6T-Bu on Si</th>
<th>$2\theta$ ($^\circ$)</th>
<th>$d$ (Å)</th>
<th>FWHM ($^\circ$)</th>
<th>$D$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 °C; 50 nm</td>
<td>7.83</td>
<td>11.29</td>
<td>0.71</td>
<td>13.4±0.2</td>
</tr>
<tr>
<td>90 °C; 50 nm</td>
<td>8.19</td>
<td>10.78</td>
<td>0.22</td>
<td>49±4</td>
</tr>
<tr>
<td>90 °C; 20 nm</td>
<td>8.17</td>
<td>10.82</td>
<td>0.45</td>
<td>23.0±0.9</td>
</tr>
<tr>
<td>90 °C; 10 nm</td>
<td>8.09</td>
<td>10.92</td>
<td>1.03</td>
<td>8.1±0.1</td>
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<table>
<thead>
<tr>
<th>DCV6T-Et on Si</th>
<th>$2\theta$ ($^\circ$)</th>
<th>$d$ (Å)</th>
<th>FWHM ($^\circ$)</th>
<th>$D$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 °C; 64 nm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>90 °C; 71 nm</td>
<td>10.4</td>
<td>8.5</td>
<td>0.17</td>
<td>56.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DCV6T-Bu on C60</th>
<th>$2\theta$ ($^\circ$)</th>
<th>$d$ (Å)</th>
<th>FWHM ($^\circ$)</th>
<th>$D$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 °C; 6 nm</td>
<td>8.15</td>
<td>10.84</td>
<td>1.58</td>
<td>5.5±0.1</td>
</tr>
<tr>
<td>90 °C; 10 nm</td>
<td>8.20</td>
<td>10.78</td>
<td>1.28</td>
<td>7.0±0.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DCV6T-Bu on BPAPF</th>
<th>$2\theta$ ($^\circ$)</th>
<th>$d$ (Å)</th>
<th>FWHM ($^\circ$)</th>
<th>$D$ (Å)</th>
</tr>
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<td>11.23</td>
<td>1.80</td>
<td>4.6±0.1</td>
</tr>
<tr>
<td>90 °C; 10 nm</td>
<td>8.12</td>
<td>10.88</td>
<td>1.00</td>
<td>8.4±0.2</td>
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</tbody>
</table>

However, only the spacing parallel to the substrate is probed, and therefore, the lower interplane distance can also be a result of a different orientation of the unit cell. The actual spacing between the molecules and their real configuration cannot be given, since the crystal structures have not been resolved yet. Nevertheless, the observed interplane distances for both DCV6T derivatives are well below the length of the molecules, suggesting that they are not standing upright with respect to the substrate plane, but rather adopt a tilted orientation.

The presence of one clear reflection feature, denoted by first and second order peaks, without any further signals, implies the dominance of one crystalline phase. In case of DCV6T-Bu, also heated samples with lower layer thickness of 20 nm and 10 nm are investigated (Figure 5.5). Equally to the results of the heated sample with 50 nm thickness, these samples exhibit reflection peaks at 8.2° and 8.1°, respectively, and their crystallite sizes are approaching the layer thickness (Table 5.2). Apparently, the layer thickness has no influence on the preferential crystalline growth.

Investigation of the influence of different substrates is done by using different organic underlayers. Figure 5.6 presents XRD patterns of 6 nm and 10 nm thick DCV6T-Bu layers grown on silicon substrates precovered with 15 nm of C60 or BPAPF. The DCV6T-Bu layer is grown at a substrate temperature of 90 °C, while C60 and BPAPF are deposited at room temperature ($T_{\text{sub}} = 30 ^\circ \text{C}$). For comparison, samples with 50 nm thick
5.3 Effect of Substrate Heating on Layer Morphology

Figure 5.6: XRD patterns of 6 nm and 10 nm thick DCV6T-Bu layers grown on top of 15 nm thick layers of C60 and BPAPF (red lines). The substrate temperature during the deposition of DCV6T-Bu is 90 °C, whereas the underlayers are deposited at room temperature. For comparison, samples with 50 nm thick neat layers of C60 and BPAPF grown at room temperature are also presented (blue lines). The corresponding values for interplane distance and crystallite size are summarized in Table 5.2.

neat layers of C60 and BPAPF grown at room temperature are also presented. Evidenced by their featureless XRD patterns without any significant reflections, both C60 and BPAPF appear to be amorphous in XRD. In contrast, the samples with DCV6T-Bu grown on top of C60 and BPAPF underlayers exhibit reflection peaks at 8.2 ° and 8.1 °, respectively. Thus, these samples have exactly the same peak positions as found on silicon substrate, suggesting the presence of the same crystalline phase. These results confirm the dominance of one crystalline phase, which is growing independently of substrate or layer thickness, at least to the extent investigated here. Of course, other substrates might cause a different behavior, but in this work only systems relevant for typical solar cell stacks are relevant.

Optical Properties

Figure 5.7 presents UV-Vis absorption and luminescence spectra of DCV6T-Bu and DCV6T-Et layers grown at different substrate temperatures varying from 30 °C to 120 °C. The layer thickness is 20 nm and quartz glass is used as substrate. In case of DCV6T-Et, the substrate is precovered with an organic underlayer of 15 nm Di-NPB, which is deposited at room temperature. This wide-gap material causes an absorption
feature at 385 nm, but has no considerable absorption above 450 nm. Further absorption spectra of DCV6T-Et layers grown directly on quartz glass are depicted in Figure 5.8.

By increasing the substrate temperature, the main absorption band of both DCV6T derivatives shifts to lower energies and a higher structuring of the spectra with well resolved features evolves. In DCV6T-Et the main peak shifts by 5 nm, while it shifts by 11 nm in DCV6T-Bu. The most striking alteration in the spectral structure is the development of the low energy absorption band. In DCV6T-Et, this absorption band is positioned at 640 nm. It is rather weak at $T_{\text{sub}} = 30^\circ C$, but increases with higher substrate temperatures featuring a distinct shoulder at $T_{\text{sub}} = 100^\circ C$. In DCV6T-Bu, this absorption band is also increasing with higher substrate temperatures, developing from a pronounced shoulder at $T_{\text{sub}} = 30^\circ C$ into a clearly distinguishable second peak at $T_{\text{sub}} = 105^\circ C$. At the same time the position shifts towards lower energies by approximately 11 nm, resulting in a peak at 667 nm for $T_{\text{sub}} = 120^\circ C$. These results can be attributed to a better aggregation of the molecules, induced by substrate heating. Thus, the results are consistent to the findings of the previous XRD investigations, which already revealed a higher crystallinity when using elevated substrate temperatures. By reduction of disorder of the molecular configurations, i.e. their actual shape, the optical transitions become more distinct, resulting in a better resolved vibronic fine structure of the spectrum. Additionally, a closer packing of the molecules also increases the intermolecular interactions, which is suggested to cause the observed red-shifts. In this respect, the effect of heating exhibits the same trends as were observed for the development of the solution spectra, characterized by high configurational disorder and no intermolecular interaction, into the thin film spectra, which already showed more distinct spectral features and a shift to lower excitation energies by introduction of higher rigidity and intermolecular interactions (see Section 5.2.1). Substrate heating even more supports this effect because it facilitates a higher molecular order.

The observed evolution of the absorption spectra is similar to the changes reported for regioregular P3HT [149, 150]. There, the low energy absorption feature located at approximately 2.09 eV is attributed to an interchain transition, which is enhanced as the interchain order is increasing. In case of the DCV6T derivatives, the low energy absorption feature is as well strongly enhanced by the increase of molecular order. However, it remains uncertain whether it originates from an intramolecular (Frenkel type) or an intermolecular (charge transfer type) transition band. In case of DCV6T-Bu, with increasing substrate temperature the respective peak shifts to lower energies in the same way as the higher energy features are shifted. This suggests a correlation between these features, which implies that they are just different vibronic features of the same excitation. It is therefore assumed that the low energy transition is rather of intramolecular nature, but is, however, strongly dependent on the degree of order.
5.3 Effect of Substrate Heating on Layer Morphology

Figure 5.7: Absorbance and photoluminescence of DCV6T-Bu and DCV6T-Et layers of 20 nm thickness grown at different substrate temperatures. Quartz glass is used as substrate. For DCV6T-Et the substrate is additionally precovered with a 15 nm thick layer of Di-NPB to imitate a situation closer to a real solar cell stack. This wide gap material causes an absorption feature at 385 nm, but has no significant absorption above 450 nm. The photoluminescence spectra are measured with excitation at the respective wavelengths of maximum absorption.
Comparing the DCV6T-Et results observed with the Di-NPB underlayer (Figure 5.7) and without (Figure 5.8), no significant difference can be seen. This indicates that the substrate has no influence on the preferential growth mode, as it is the case in the XRD measurements. However, different substrates or organic underlayers might show other results. For example, it was shown for phthalocyanine (H$_2$Pc) thin films that molecular orientation and hence thin film absorption properties can be influenced by the introduction of an organic underlayer of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) [145].

The development of the photoluminescence spectra is different between both DCV6T derivatives. In DCV6T-Et, the luminescence spectrum shifts to higher energies with increasing substrate temperature, whereas the spectrum of DCV6T-Bu is just slightly broadened. Additionally, upon substrate heating, the absorbance itself is increasing for DCV6T-Et, but decreasing for DCV6T-Bu. The increase found for DCV6T-Et is present on Di-NPB precovered substrates (Figure 5.7) as well as on clean quartz glass substrates (Figure 5.8). These differences might result from different crystalline structures of both DCV6T derivatives, that can well be caused by the different side-chain lengths and substitution patterns.

Figure 5.8: Absorbance of DCV6T-Et layers with 20 nm thickness grown at different substrate temperatures on quartz glass.
5.3 Effect of Substrate Heating on Layer Morphology

Atomic Force Microscopy

The influence of substrate temperature on the topography of DCV6T-Bu and DCV6T-Et thin films is analyzed by AFM using the same samples as for investigation of the optical properties. Figure 5.9 presents AFM pictures of 20 nm thick films of DCV6T-Et grown on quartz glass precovered with 15 nm Di-NPB. The substrate temperature during the deposition of DCV6T-Et is varied from 30°C to 100°C. For comparison, Figure 5.9 additionally comprises an AFM picture of a DCV6T-Et layer grown directly on quartz glass at $T_{\text{sub}} = 100$ °C (bottom, right).

The room temperature sample ($T_{\text{sub}} = 30$ °C) exhibits a rather smooth topography with small granular structure. The root mean square (rms-) roughness is 1.3 nm. Upon increasing the substrate temperature to 100°C, the rms-roughness increases to 5.3 nm and the grains are growing larger, reaching long axis sizes exceeding 200 nm. This indicates a more crystalline growth mode and is thus consistent with the results of XRD and UV-Vis absorption. The higher crystallinity can be explained by a higher mobility of the molecules when adsorbed on the surface during the deposition process. Due to the higher surface temperature, the molecules have more freedom to reach energetically favorable configurations by more regular and closer packing. The nucleation rate decreases at higher temperatures whereas the lateral growth rate increases because of the higher mobility. This gives rise to the growth of larger grains. Thus, the higher substrate temperature supports the self ordering and consequently leads to crystallite growth. Comparing the topography of heated DCV6T-Et layers grown on Di-NPB and grown directly on quartz glass (Figure 5.9, bottom), no significant difference of grain size and shape is detected. It can therefore be assumed that the growth mode of DCV6T-Et is the same on both surfaces.

Figure 5.10 depicts the effect of substrate heating on the topography of a 20 nm thick DCV6T-Bu layer grown on quartz glass at different substrate temperatures varying from 30°C to 120°C. Similar to the results for DCV6T-Et layers on Di-NPB, the room temperature sample shows a rather smooth surface with an rms-roughness of 1.4 nm and a granular structure. Since a rapid nucleation takes place at this temperature, condensation results in larger number of small grains, leading to a uniform surface and low tendency for crystallite aggregation. At higher substrate temperatures up to 105°C, larger grains are observed and also the rms-roughness increases up to 2.0 nm. More massive clusters are formed reaching lateral sizes up to 200 nm. In contrast to the room temperature sample, the surface looks very rugged and exhibits some deep valleys in the order of 10 to 15 nm. Apparently, the high substrate temperature induces a three-dimensional growth mechanism with stronger crystallite aggregation. Thus, the layer does not grow homogeneously anymore. When further increasing the substrate temperature to 120°C, the topography changes to even larger clusters of about 12 to 20 nm height and size of 500 to 800 nm (Figure 5.10, bottom, right). The high substrate tem-
Figure 5.9: AFM pictures of neat DCV6T-Et layers with 20 nm thickness grown on Di-NPB. The substrate temperature during the deposition of DCV6T-Et is varied. For comparison, the AFM picture of the same layer grown on quartz glass at $T_{\text{sub}} = 100^\circ \text{C}$ is also presented. Note that the bottom pictures have a smaller lateral scale.
5.3 Effect of Substrate Heating on Layer Morphology

Figure 5.10: AFM pictures of neat DCV6T-Bu layers with 20 nm thickness grown on quartz glass. The substrate temperature during the deposition is varied.

Temperature induces a cellular growth, forming a discontinuous surface. Consequently, the roughness is significantly increased, reaching an rms value exceeding 6 nm. An interesting feature is the development of distinct terraces on the surface of the clusters. This clearly demonstrates a crystalline aggregation of the molecules and thus underlines the findings of XRD and UV-Vis investigations. The step height of several terraces varies between 1.0 to 1.5 nm, thereby corresponding well to the interplane distance $d=1.1$ nm of heated DCV6T-Bu layers determined by XRD. Compared to the maximum length of a DCV6T-Bu molecule, the step height suggests a tilted orientation of the molecule long axis with respect to the substrate plane.

The very rough topography with large voids between the crystallites might be a reason for the decrease in absorption that is observed for the heated DCV6T-Bu samples. However, this influence can hardly be distinguished from the effect of changed molecular orientation. In fact DCV6T-Et does not show a decrease of absorption up to a substrate
temperature of 100°C, although it exhibits similar topography changes.

In summary, upon substrate heating a transition from homogeneous and smooth layer growth towards a three-dimensional growth mechanism with strong crystallite aggregation has been proven by XRD, UV-Vis, and AFM investigations for both DCV6T-Bu and DCV6T-Et layers.

5.3.2 Mixed DCV6T : C60 Layers

The investigation of mixed layer morphology is particularly important for solar cells comprising mixed D-A heterojunctions. Especially, the degree of phase separation between donor and acceptor plays a crucial role for optimizing the performance (see Section 3.2.1). In the following, the morphology of mixed DCV6T-Bu : C60 and DCV6T-Et : C60 layers are studied by UV-Vis absorbance and luminescence spectroscopy, AFM, and scanning electron microscopy (SEM).

Optical Properties

Figure 5.11 depicts absorbance and photoluminescence spectra of 20 nm mixed DCV6T-Bu : C60 layers grown directly on quartz glass. The respective mixing ratio is 2:1 by volume. The substrate temperature during deposition of the mixed layer is varied from 30°C to 110°C. Luminescence spectra are measured using an excitation wavelength corresponding to the maximum absorption of DCV6T-Bu, i.e. 594 nm. C60 is hardly absorbing at this wavelength and furthermore has a very low luminescence quantum yield [151]. Therefore, only the luminescence signal of DCV6T-Bu is observed.

The absorption spectra show a peak at 340 nm, attributed to C60. Between 400 nm and 500 nm both materials contribute to the absorption and above 500 nm the absorption of DCV6T-Bu is dominating. Apparently, the room temperature sample \((T_{\text{sub}} = 30\, ^\circ\text{C})\) exhibits a loss of fine structure in the DCV6T-Bu absorption when compared to spectra of neat layers (see e.g. Figure 5.4). Moreover, the peak position is shifted to lower wavelengths, resulting in a maximum at 580 nm instead of the expected value of 594 nm. This indicates a lower self organization of the DCV6T-Bu molecules, which can be attributed to the presence of C60. Due to the mixing with C60, the aggregation of DCV6T-Bu molecules among themselves is hindered.

However, when higher substrate temperatures are applied, the self aggregation of DCV6T-Bu is recovered, as can be seen from the development of the respective absorption spectra. With increasing substrate temperature the maximum shifts to lower energies and
5.3 Effect of Substrate Heating on Layer Morphology

Figure 5.11: Absorbance and photoluminescence spectra of 20 nm thick mixed DCV6T-Bu : C60 layers on quartz glass. The mixing ratio is 2:1 by volume. The substrate temperature during the deposition of the mixed layers is varied. Luminescence spectra are measured using an excitation wavelength of 594 nm, corresponding to the maximum absorption of DCV6T-Bu.

also the characteristic low energy absorption band develops. That means that aggregation of DCV6T-Bu in mixed layers can be achieved by substrate heating despite of the steric hindrance by C60 molecules.

A clear indication for the presence of aggregated clusters of DCV6T-Bu is given by the development of the luminescence signal. While no significant luminescence is present in the sample prepared at room temperature ($T_{\text{sub}} = 30 \degree C$), a clear signal evolves in the heated samples, evidently increasing with substrate temperature. This can be explained by reduced quenching of excitons. The mixed DCV6T-Bu : C60 layer forms a D-A heterojunction, where excitons are separated at the D-A interface. Therefore, a close mixture between both materials, with domain sizes below the exciton diffusion length, leads to quenching of the excitons because they are always in proximity to such an interface. This is why the room temperature sample does not exhibit luminescence. However, when phase separation between donor and acceptor is enhanced, the D-A interface area decreases and the excitons need to diffuse over longer distances in order to reach an interface site. Consequently, they have a higher probability to recombine before they reach the interface, resulting in an observable luminescence signal. Therefore, it can be concluded that the increase of luminescence with increasing substrate...
**Figure 5.12:** Absorbance and photoluminescence spectra of mixed DCV6T-Bu : C60 and DCV6T-Et : C60 layers with 20 nm thickness. The layers are grown on glass/ITO substrates that are precovered with 15 nm C60. Mixing ratio is 2:1 by volume. The substrate temperature during the deposition of the mixed layers is varied. The photoluminescence spectra are measured with excitation at the wavelengths of maximum absorption in DCV6T-Bu and DCV6T-Et, i.e. at 594 nm and 554 nm, respectively.
5.3 Effect of Substrate Heating on Layer Morphology

Temperature is a sign for better phase separation between DCV6T-Bu and C60.

Using the luminescence measurement of neat DCV6T-Bu layers on quartz glass (Figure 5.4) as reference, the ratio of excitons that are quenched in the mixed layers can be estimated. Since the luminescence measurements of both neat and mixed layers are carried out in the same geometry and with the same illumination, one can directly relate the luminescence signal heights of mixed ($L_{\text{mix}}$) and neat ($L_{\text{neat}}$) layers, and further multiply a factor that corrects for the different absorption probabilities ($A_{\text{mix}}$, $A_{\text{neat}}$) at the chosen excitation wavelength. By this, a ratio $r_{\text{Lum}}$ can be defined as the ratio between the luminescence signals of a neat layer and that of a mixed layer:

\[
r_{\text{Lum}} = \frac{L_{\text{mix}} \cdot A_{\text{neat}}}{L_{\text{neat}} \cdot A_{\text{mix}}}.
\]

This ratio is related to the probability for exciton diffusion to a D-A interface ($\eta_{\text{ED}}$), which is an essential parameter for the external quantum efficiency of solar cells (Equation (3.34)). In fact, if non-radiative decay of excitons was absent or if the ratio between non-radiative decay and fluorescence efficiency could be considered equal in both neat and mixed layers, then the calculated ratio $r_{\text{Lum}}$ would be identified with $1 - \eta_{\text{ED}}$. However, the dynamics of non-radiative decay mechanisms have not been addressed in this work. Without knowledge of the recombination probabilities, only the upper limit of $\eta_{\text{ED}}$ can be given.

For the different substrate temperatures of 30°C, 90°C, and 110°C the ratio $r_{\text{Lum}}$ of luminescence of the mixed layer over the luminescence of a neat layer is 1.2±0.4%, 3.6±1.1%, and 12±4%, respectively. This means that at room temperature nearly all excitons are quenched, while only 96.4±1.1% of the excitons are quenched at $T_{\text{sub}} = 90°C$ and 88±4% are quenched at $T_{\text{sub}} = 110°C$. Here, the luminescence value at the peak, i.e. at 777 nm, is used to determine $L_{\text{mix}}$ and $L_{\text{neat}}$. In principle, it is better to determine $L_{\text{mix}}$ and $L_{\text{neat}}$ by integration of the whole luminescence spectrum, to take eventual broadening of the spectrum into account. This is not possible, because the instrument accuracy is not sufficient at wavelengths above 820 nm. Therefore, the peak value is taken as a first approximation. The measurement errors for determining absorption and luminescence as well as the uncertainty about the intensity variations between the measurements give rise to the large errors of $r_{\text{Lum}}$.

In summary, the results show that higher substrate temperatures facilitate a higher ordering of the DCV6T-Bu molecules such that larger domains of DCV6T-Bu are achieved, leading to higher phase separation. The resulting quenching ratios suggest that the domains of DCV6T-Bu are approaching sizes corresponding to the exciton diffusion length, i.e. sizes of 10 to 20 nm [127, 129]. From comparison of the absorption spectra with the findings in neat layers, a crystalline nature of these domains is plausible. However, it is not clear how pure these domains are. The locally self organized DCV6T-Bu domains might still contain defect sites introduced by C60. These defects
would also lead to quenching of excitons, albeit leaving the separated charges trapped on the C60 site. In this case, the domain size could well exceed the diffusion length by several times, still exhibiting the observed amount of exciton quenching.

To verify whether the same effect can be achieved in typical solar cell stacks, mixed layers grown on glass/ITO substrates are investigated. An organic underlayer of 15 nm C60 is used to represent a typical electron transport layer as will be used in Chapter 6. Figure 5.12 shows the corresponding absorbance and luminescence spectra for DCV6T-Et : C60 and DCV6T-Bu : C60 on C60. The layer thickness is 20 nm, the mixing ratio is 2:1, and two substrate temperatures of 30 °C and 90 °C are compared. The results are analog to the previous findings. At elevated substrate temperature the luminescence signal increases, and the absorption spectra are more structured and red-shifted. A higher phase separation is thus also present on typical solar cell substrates, and it may already be assumed that this will enhance the solar cell performance. Interestingly, the absorption itself increases with substrate temperature and hence may also lead to better solar cell performance by higher photocurrent generation.

**Topography**

Figure 5.13 shows the topography of mixed DCV6T-Bu : C60 layers measured by AFM and SEM. The layers are grown on glass / ITO / C60 substrates, their thickness is 20 nm, and the mixing ratio is 2:1. The substrate temperature during deposition of the mixed layer is varied from 30 °C to 90 °C. The C60 underlayer is deposited at room temperature ($T_{\text{sub}} = 30 \degree C$) and has a thickness of 15 nm. To increase the contrast of the SEM pictures and also to prevent the samples from charging, a thin gold layer is sputtered onto the SEM samples.

The room temperature sample ($T_{\text{sub}} = 30 \degree C$) shows a rather flat surface with small grains. The rms-roughness is 0.5 nm. No structure can be seen in the SEM picture. With increasing substrate temperature, the surface is getting rougher and the grains become larger. At $T_{\text{sub}} = 90 \degree C$ the rms-roughness is 3.6 nm and the grain size reaches 40 to 60 nm. The SEM pictures show the same trend. These results confirm that a larger phase separation by stronger self-organization is achieved with substrate heating. However, it can not be distinguished whether the grains are DCV6T-Bu or C60. Also, the crystalline nature of these clusters remains an open question. The increase of roughness typically indicates higher crystallinity, but does not give sufficient evidence. XRD investigations of 20 nm thick mixed layers grown at $T_{\text{sub}} = 90 \degree C$ (samples M1a – M4a from Section 6.2) do not reveal any crystal reflections. Nevertheless, the probed thickness might just be too low to detect small crystallites in the mixed layers. Also a disorder in orientation of crystallites can hinder their detection by XRD. For future XRD measurements, samples with higher layer thickness should therefore be used.
5.3  Effect of Substrate Heating on Layer Morphology

Figure 5.13: Topography of mixed DCV6T-Bu : C60 layers with 20 nm thickness deposited at different substrate temperatures. The layers are grown on glass/ITO substrates that are precovered with 15 nm C60. The mixing ratio is 2:1 by volume. Left: AFM pictures with corresponding rms-roughness. Right: SEM pictures. To increase the contrast of the SEM pictures and also to prevent the samples from charging, a thin gold layer is sputtered onto the SEM samples.
5.4 Effect of Substrate Heating on Mobility

In the previously presented investigations it has been shown that the morphology of neat DCV6T and mixed DCV6T:C60 layers is considerably dependent on the substrate temperature during the deposition of the layer. It was seen that substrate heating leads to better self aggregation of the DCV6T molecules resulting in a higher crystallinity. Besides the change of absorption that was already shown in Section 5.3.1, it is also expected that the charge transport properties change upon this modification of morphology. Therefore, the hole mobility ($\mu_h$) of neat DCV6T-Bu layers is in the following investigated by OFET measurements and with the CELIV method.

The layout of the respective devices is depicted in Figure 5.15. In the OFET devices a 30 nm thick layer of DCV6T-Bu is used, which is either deposited at room temperature
5.4 Effect of Substrate Heating on Mobility

Figure 5.15: Layout of the OFET-devices I and II (left) and the CELIV-devices I and II (right). The DCV6T-Bu layer is either deposited at room temperature (devices I) or at an elevated substrate temperature (devices II). The OFET-devices comprise several transistors with different channel lengths $L$ varying from 2.5 to 20 $\mu$m. Also for the CELIV measurement several devices of the type I are prepared.

The IV-curves of the OFET devices I and II are presented in Figure 5.16. Only one transistor with a channel length of 20 $\mu$m is exemplarily shown. The results of all measured transistors of device I and II are summarized in Table 5.3.

In device I ($T_{\text{sub}} = 30 ^\circ \text{C}$) transistors with channel length of 2.5 and 5 $\mu$m are not eval-
Figure 5.16: IV-characteristics of the OFET-devices I and II at different gate voltage ($V_G$). Transistors with 20 µm channel length are exemplarily shown. The corresponding mobility values are summarized in Table 5.3.

The IV-curves of the OFET-devices I and II show the typical OFET behavior. The linear regime extends up to a $V_{SD}$ of -20 V at $V_G$ below -30 V. At $V_{SD}$ below -30 V, the current saturates. The small decrease of current in the saturation regime is an artefact, presumably caused by partial charging. The presented hole mobility values (Table 5.3) are determined in the saturation regime at $V_{SD}=-40$ V according to Equation (4.4). Averaging over all measured transistors gives a DCV6T-Bu hole mobility of $\mu_h=2.43 \times 10^{-5}$ cm$^2$/Vs with a standard deviation of $0.22 \times 10^{-5}$ cm$^2$/Vs. This is a rather low value compared to mobilities of other frequently used donor materials like for example copper-phthalocyanine (CuPc) or 6T, which exhibit mobilities up to $7 \pm 1 \times 10^{-4}$ cm$^2$/Vs and 0.08 cm$^2$/Vs, respectively [134, 152].

In device II the saturation regime develops at higher $V_{SD}$ than in device I. Also the observed current is lower, as can be seen from the IV-curve of transistor 5 with 20 µm channel length (Figure 5.16, right). The linear regime at high gate voltages (i.e. at $V_G=50$ V) extends up to $V_{SD}$ of -30 V and complete saturation is not achieved up to the lowest measured $V_{SD}$. Therefore, the mobility is determined from evaluation of the linear regime according to Equation (4.3). As in device I only transistors with channel length of 10 µm and 20 µm are evaluated. The mean value of all measured mobilities is $\mu_h=0.76 \times 10^{-5}$ cm$^2$/Vs with a standard deviation of $0.26 \times 10^{-5}$ cm$^2$/Vs. Obviously, the mobility is slightly lower than in the room temperature device. This is an intriguing result, since in most cases the mobility is expected to increase when a higher crys-
Table 5.3: Hole mobilities ($\mu_h$) in the measured transistors of OFET-devices I and II. $L$ is the channel length of the respective transistor. In device I the mobility is determined from the saturation regime according to Equation (4.4). In device II the mobility is determined from the slope in the linear regime according to Equation (4.3).

<table>
<thead>
<tr>
<th>Transistor</th>
<th>$L$ (µm)</th>
<th>$\mu$ ($\text{cm}^2/\text{Vs}$)</th>
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<td></td>
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<tr>
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</tr>
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<td>8</td>
<td>10</td>
<td>2.54·10^{-5}</td>
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<tr>
<td><strong>OFET-device II ($T_{sub} = 98^\circ$C)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 (see Figure 5.16)</td>
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<td>20</td>
<td>0.67·10^{-5}</td>
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<td>0.95·10^{-5}</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>1.34·10^{-5}</td>
</tr>
</tbody>
</table>

tallinity of the material is achieved [132, 134, 153]. However, this increase of mobility is usually attributed to a better stacking of the $\pi$-electron systems related to the better ordering. Although observed for many oligothiophenes, this needs not necessarily to be the case for DCV6T-Bu, since the substitution pattern with dicyanovinylene endgroups and butyl side groups may lead to a different stacking mode.

**CELIV**

Figure 5.17 presents the hole mobility data of CELIV devices I and II measured at different temperatures varying from 180 to 320 K. Clearly, a typical field and temperature dependent behavior of mobility is observed as is typical for hopping transport in organic semiconductors (see Section 2.4.3).

The two nominally equal devices a and b of device type I ($T_{sub} = 30^\circ$C) exhibit differences in both mobility value (at 300 K) and field dependency. This might be caused by different degradation between the devices, due to different storing times prior to the measurement or differing quality of the encapsulation. Also some inhomogeneities between the devices might play role. Consequently, in general many experiments with
Figure 5.17: Mobility values from CELIV-devices I and II measured at different temperatures. Two nominally equal devices of the type I ($T_{\text{sub}} = 30^\circ\text{C}$), denoted as (a) and (b), are measured. Lines are fits to the data according to Equation (2.18).
the same sample type are necessary to achieve statistically sound results. Nevertheless, the data shows some interesting features concerning the hole mobility of DCV6T-Bu on heated and not heated substrates.

Apparently, the mobility in device II ($T_{\text{sub}} \approx 90^\circ \text{C}$) is lower than in the devices prepared at room temperature. This confirms the results of the OFET measurements, where the same trend is observed. However, the respective mobility values differ strongly between both methods. At room temperature and at an electric field of 900 V/m (i.e. $E_{1/2}=300 \sqrt{\text{V/cm}}$ or 0.9 V applied over 100 nm) the determined CELIV mobilities are $2.4 \cdot 10^{-7}$ cm$^2$/Vs, $1.0 \cdot 10^{-6}$ cm$^2$/Vs, and $3.1 \cdot 10^{-7}$ cm$^2$/Vs for device I(a), I(b), and device II, respectively. This is much lower than compared to the OFET mobility, being in the range of $10^{-5}$ cm$^2$/Vs. Possible reasons for this discrepancy may lie in the completely different approaches of the two methods. In OFET the conduction lateral to the substrate in a very thin channel of accumulated charge carriers is measured, while CELIV probes the extraction of carriers perpendicular to the substrate, depleting the layer with a linearly increasing voltage pulse. Thus, measuring conditions like charge density, electric field, and direction of the current are quite different and can therefore give rise to significant deviations.

Following Equation (2.18) to express the field dependent mobility by a zero field mobility $\mu_{F0}$ and the so-called field amplification factor $\beta$, gives $\mu_{F0}=1.74 \cdot 10^{-8}$ cm$^2$/Vs and $\beta=8.77 \cdot 10^3 \sqrt{\text{cm/V}}$ in device I(a) and $\mu_{F0}=7.19 \cdot 10^{-8}$ cm$^2$/Vs and $\beta=4.89 \cdot 10^3 \sqrt{\text{cm/V}}$ in device II. The corresponding fit, performed at the 300 K data, is presented in Figure
5.17. It can be seen from these values that the heated device exhibits a lower field dependence (lower \( \beta \)), which could be explained by a higher molecular order in the DCV6T-Bu layer deposited at elevated substrate temperature. However, the significance of this result is questionable, since device I(b) on the other hand exhibits nearly no field dependence.

In Figure 5.18 the mobility data measured at \( V_{\text{max}} = 2.5 \, \text{V} \) in dependence of the inverse temperature is drawn. Both devices I(b) and II exhibit an increase of mobility with increasing temperature, typical for hopping transport in organic semiconductors. From the slope in Figure 5.18 (lines) the activation energy \( (E_A) \) is determined, resulting in 186 meV and 87 meV for device I(b) and II, respectively. Obviously, the activation energy is lower in the DCV6T-Bu layer prepared at elevated substrate temperature, which is certainly a result of the higher molecular order of DCV6T-Bu in device II.

In summary, the OFET as well as the CELIV measurements show a slightly decreased mobility for the heated DCV6T-Bu layers, contrary to the expectations. The highest observed mobility of DCV6T-Bu is measured in the OFET device made at room temperature, resulting in \( \mu_h = 2.43 \pm 0.22 \cdot 10^{-5} \, \text{cm}^2/\text{Vs} \). The investigations by CELIV exhibit a temperature and field dependent behavior of the mobility, which is typical for hopping transport. The activation energy in the device made at room temperature is 186 meV, while it is 87 meV in the device using substrate heating for deposition of DCV6T-Bu. This is attributed to the higher molecular order, achieved by the higher substrate temperature.
6 DCV6T - C60 Solar Cells

In this chapter DCV6T - C60 solar cells in n-i-p structure are studied. These solar cells are based on the p-i-n concept, only they have an inverted layer sequence, i.e. the ITO serves as electron collecting contact and the metal top layer is the hole collecting contact. At first, the effects of morphology tuning by applying different substrate temperatures during the active layer growth are presented. Especially, in mixed heterojunction solar cells large improvements in performance are obtained upon substrate heating. Furthermore, mixed heterojunction solar cells with different composition ratios of DCV6T : C60 are compared and the ratio giving the best performance is identified. In the subsequent section the layer design of the presented solar cells is further optimized by investigation of their thin film optics and by comparing different mixed layer thicknesses. All these steps finally lead to a device efficiency of 4.9±0.2%. The quantum efficiency of this optimized device is then investigated in more detail by using optical simulations and the major loss mechanisms are discussed. In the end, performance changes upon thermal annealing of finished devices are presented. This method shows similar effects like the results obtained with substrate heating during the layer deposition, but needs long time scales.

6.1 Effect of Substrate Heating in DCV6T - C60 Solar Cells

In Chapter 5 it was shown that the morphology of single DCV6T layers and mixed DCV6T : C60 layers is influenced by substrate heating during the deposition. Single layers of DCV6T exhibit crystalline features in X-ray diffraction and UV-Vis absorption when grown on a heated substrate. Investigations of DCV6T : C60 mixed layers revealed that elevated substrate temperatures induce an increased phase separation between the two materials with increasing domain size of DCV6T and a higher surface roughness. These effects have been also demonstrated on underlayers which resem-
Figure 6.1: Schematic layer design of flat heterojunction m-i-p solar cells for investigation of the effect of applying different substrate temperatures during the active layer growth.

In the following, substrate heating (and cooling) is applied during the active layer growth of DCV6T-C60 solar cells. Based on the previous observations, the effects of the related morphology changes on solar cell performance are discussed, showing that morphology is significantly influencing the solar cell performance.

6.1.1 Flat Heterojunction Solar Cells

Figure 6.1 shows the layer design of devices F1–F3, which comprise flat heterojunctions of DCV6T-Et/C60. The layer thickness of DCV6T-Et is 10 nm and the substrate temperatures during the deposition of this layer are 30°C, 80°C, and 100°C, respectively. The C60 layer fulfills two functions. It is the acceptor layer and furthermore provides the n-contact. It is not doped because doping could introduce sites for exciton quenching. Moreover, doping sites at the interface to DCV6T-Et would constitute recombination centers which hinder efficient charge separation. Although undoped, the C60 layer provides ohmic contact to ITO. According to its layer sequence, this device layout is also often called m-i-p (metal-intrinsic-p-doped) structure.

The current density-voltage (JV) characteristics of devices F1–F3, measured under
6.1 Effect of Substrate Heating in DCV6T-C60 Solar Cells

Figure 6.2: JV-characteristics of devices F1–F3 measured under illumination with the sun simulator SOL 1200 at a nominal intensity of 127 mW/cm² as given by the outdoor reference diode. The mismatch corrected intensities (I) are given in the inset. Performance parameters are presented in Table 6.1.

Table 6.1: Performance parameters of devices F1–F3. The corresponding JV-characteristics are presented in Figure 6.2.

<table>
<thead>
<tr>
<th>device</th>
<th>$V_{oc}$ (V)</th>
<th>$j_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>$S$</th>
<th>$I$ (mW/cm²)</th>
<th>$\eta_{PCE}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1 ($T_{sub} = 30^\circ$C)</td>
<td>0.88</td>
<td>6.1</td>
<td>58.5</td>
<td>1.14</td>
<td>179</td>
<td>1.8±0.1</td>
</tr>
<tr>
<td>F2 ($T_{sub} = 80^\circ$C)</td>
<td>0.91</td>
<td>6.7</td>
<td>58.2</td>
<td>1.17</td>
<td>175</td>
<td>2.0±0.1</td>
</tr>
<tr>
<td>F3 ($T_{sub} = 100^\circ$C)</td>
<td>0.85</td>
<td>6.6</td>
<td>58.0</td>
<td>1.17</td>
<td>174</td>
<td>1.9±0.1</td>
</tr>
</tbody>
</table>

illumination with the sun simulator SOL 1200, are presented in Figure 6.2. The performance parameters are summarized in Table 6.1. The heated samples F2 and F3 exhibit the same FF, same $S$, and similar $V_{oc}$ as the room temperature device F1. Only the photocurrent is increased upon heating, with $j_{sc}$ rising by approximately 10% from 6.1 mA/cm² at $T_{sub} = 30^\circ$C to 6.7 mA/cm² at $T_{sub} = 80^\circ$C. In Figure 6.3 the corresponding EQE spectra of devices F1–F3 are presented. It can be seen that the EQE generally follows the development of the absorption spectra of C60 and DCV6T-Et. In the wavelength range of C60 absorption (300 nm to 400 nm) the EQE is nearly equal for all devices. In contrast, in the wavelength range of DCV6T-Et absorption (500 nm to 700 nm) the EQE increases with substrate heating. The EQE peak value at 577 nm rises from 28% at $T_{sub} = 30^\circ$C to 32% at $T_{sub} = 80^\circ$C. This shows that the observed
increase of photocurrent with substrate heating is related to higher quantum efficiency of the DCV6T-Et layer, meaning that either the absorption probability ($\eta_A$) or the exciton diffusion efficiency ($\eta_{ED}$) is increased by substrate heating. In fact, an increase of absorption of neat DCV6T-Et layers, using heated quartz glass substrates as well as Di-NPB covered quartz glass, was already shown in the previous chapter (see Section 5.3.1). Thus, the increased photocurrent can be attributed to the enhancement of absorption in DCV6T-Et. However, an increase of exciton diffusion efficiency may not be excluded, since heated layers also exhibited higher crystallinity, which generally suggests a higher diffusion length due to lower disorder in the film.

Although a higher hole mobility in the heated DCV6T-Et layers compared to layers grown at room temperature could be expected from the increase of crystallinity, there is no indication for better charge transport in the corresponding devices. The FF as well as the saturation factor $S$ remain unchanged upon heating, only showing minor variations. This is consistent to the previously presented results of OFET and CELIV measurements at heated DCV6T-Bu layers, which did not exhibit an improved hole
mobility. Thus, it has to be expected that neat DCV6T-Et layers as well do not reach higher hole mobilities upon heating and, hence, the flat heterojunction solar cells do not improve in regard of charge transport.

The change of $V_{oc}$ is not systematic. Especially the rather low value of 0.85 V in device F3 ($T_{\text{sub}} = 100 \, ^\circ\text{C}$) is below the expected value of 0.90 V usually observed in DCV6T-Et-C60 heterojunctions. This might be explained by the very rough surface of the heated layer, leading to more recombination sites at the DCV6T-Et/BPAPF interface.

In summary, substrate heating in the investigated devices with flat DCV6T-Et/C60 heterojunctions leads to a slight increase of photocurrent, mainly caused by higher absorption in the DCV6T-Et layer. Beside this effect, no further improvement is achieved by means of substrate heating.

### 6.1.2 Mixed Heterojunction Solar Cells

It is well known for many mixed heterojunction solar cells that tuning of the phase separation can lead to significant changes in the performance. Especially, in polymer solar cells this effect is intensely studied by different methods as for example thermal annealing, choice of solvent, or solvent annealing [8–11]. In the field of small molecules, the correlation between morphology and performance was studied in phthalocyanine : C60 heterojunction solar cells using substrate heating or current treatment [131, 154, 155]. The variations in performance upon changing the degree of phase separation between donor and acceptor are mainly caused by the tradeoff between efficient exciton dissociation and ease of charge transport. Little phase separation leading to a high interface area facilitates efficient exciton diffusion ($\eta_{\text{ED}}$), while strong phase separation leading to formation of more continuous percolation paths for charge transport increases the charge collection probability ($\eta_{\text{CC}}$). Consequently, by tuning of the phase separation the internal quantum efficiency (Equation (3.34)) can be optimized [156].

Here, the phase separation in mixed DCV6T : C60 heterojunctions is varied by applying different substrate temperatures during the deposition of the mixed layer. Figure 6.4 shows the layer stack of devices T1 – T5, comprising mixed DCV6T-Bu : C60 heterojunctions and of devices T6 and T7 comprising mixed DCV6T-Et : C60 heterojunctions. The mixed layer thickness is 20 nm and the mixing ratio is 2:1 by volume. The n-doped C60 layer, which is incorporated beneath the active mixed layer, is stable at temperatures up to 160 °C (manufacturer information by Novaled AG). Thus, substrate heating has no effect on the electrical properties of this n-contact layer. Usually, the typically observed increase of surface roughness upon substrate heating is reported to cause problems with shortcuts in the solar cells [157, 158]. This effect is not relevant here, because the active layers are covered by rather smooth and thick HTLs.
Mixed DCV6T-Bu : C60 Solar Cells

In device T1, the substrate is cooled down to -7°C during the deposition of the mixed layer. By this, a more intimate mixing than in the room temperature device T2 is achieved, due to the rapid condensation of the molecules on the cool substrate. In devices T3 to T5, the applied substrate temperatures are 77°C, 92°C, and 120°C, respectively.

The JV-characteristics of devices T1–T5, measured under illumination with the sun simulator SoCo 1200 MGH, are presented in Figure 6.5. The corresponding performance parameters are given in Table 6.2 and are also depicted in Figure 6.7 for better comparison. The JV-characteristics are differing significantly, especially between $T_{sub} = -7°C$ to $T_{sub} = 77°C$. The most prominent changes are observed for the FF and $j_{sc}$ which increase from 34.2% and 1.8 mAcm$^{-2}$ in device T1 ($T_{sub} = -7°C$) to 63.1% and 6.2 mAcm$^{-2}$ in device T3 ($T_{sub} = 77°C$), respectively. $V_{oc}$ shows only slight variations, approaching values of 0.88 V. Consequently, the efficiency is substantially increased from 0.5±0.1 % in device T1 to 3.4±0.2 % in device T3 and then saturates, achieving values of about 3.0 % at higher substrate temperatures.
6.1 Effect of Substrate Heating in DCV6T-C60 Solar Cells

Figure 6.5: JV-characteristics of devices T1–T5 measured at mismatch corrected intensities around 100 mWcm\(^{-2}\). The performance parameters are given in Table 6.2 and are depicted in Figure 6.7.

Table 6.2: Performance parameters of devices T1–T5. The corresponding JV-characteristics are given in Figure 6.7.

<table>
<thead>
<tr>
<th>device</th>
<th>(V_{oc}) (V)</th>
<th>(j_{sc}) (mAcm(^{-2}))</th>
<th>FF (%)</th>
<th>(S) (mWcm(^{-2}))</th>
<th>(I) (mWcm(^{-2}))</th>
<th>(\eta_{PCE}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1 ((T_{sub} = -7^\circ C))</td>
<td>0.84</td>
<td>1.8</td>
<td>34.2</td>
<td>1.72</td>
<td>99.8</td>
<td>0.5±0.1</td>
</tr>
<tr>
<td>T2 ((T_{sub} = 30^\circ C))</td>
<td>0.85</td>
<td>3.6</td>
<td>42.7</td>
<td>1.34</td>
<td>99.1</td>
<td>1.3±0.1</td>
</tr>
<tr>
<td>T3 ((T_{sub} = 77^\circ C))</td>
<td>0.86</td>
<td>6.2</td>
<td>63.1</td>
<td>1.07</td>
<td>99.9</td>
<td>3.4±0.2</td>
</tr>
<tr>
<td>T4 ((T_{sub} = 92^\circ C))</td>
<td>0.88</td>
<td>5.6</td>
<td>57.9</td>
<td>1.11</td>
<td>99.4</td>
<td>2.9±0.2</td>
</tr>
<tr>
<td>T5 ((T_{sub} = 120^\circ C))</td>
<td>0.86</td>
<td>6.2</td>
<td>62.5</td>
<td>1.05</td>
<td>100.9</td>
<td>3.3±0.2</td>
</tr>
</tbody>
</table>
Figure 6.6: Absorption, EQE and IQE of devices T1 – T5. The performance parameters are given in Table 6.2 and are depicted in Figure 6.7.
6.1 Effect of Substrate Heating in DCV6T - C60 Solar Cells

The EQE and IQE spectra as well as the absorption spectra of devices T1 – T5 are presented in Figure 6.6. In accordance with the observed increase of $j_{sc}$, the EQE spectra are increasing with rising substrate temperature up to 77 °C. This effect is present over the whole investigated spectrum, but is particularly pronounced in the absorption range of DCV6T-Bu. Indeed, the absorption in this region is enhanced upon substrate heating, which accounts partially for the increase of the EQE. Thus, the effect of increasing absorption at elevated substrate temperatures as found in previous investigations (see Section 5.3.2) is also present here. At very high substrate temperatures of 120 °C (device T5) even the low energy absorption band, which is typically observed in DCV6T-Bu layers grown on heated substrates, evolves and subsequently results in a shoulder at 660 nm in the respective EQE spectrum.

However, the main reason for the increase of the EQE is the development of the IQE, which is itself significantly increased when enhancing the substrate temperature from -7 °C to 77 °C. Considering the individual efficiencies for exciton diffusion ($\eta_{ED}$), charge transfer ($\eta_{CT}$), and charge collection ($\eta_{CC}$) that are constituting the IQE, the main reasons for this increase can be deduced. As already stated in Section 5.1, the energy levels of DCV6T-Bu generally allow for a high exciton separation efficiency in the heterojunctions with C60, which is close to unity. This was proven by PIA measurements [50] and is furthermore evident in formerly reported flat heterojunction solar cells that typically show high FF and low saturation ratios [127, 129]. The development of the exciton diffusion probability in heated mixed layers of DCV6T-Bu : C60 was discussed in Section 5.3.2 and $\eta_{ED}$ was found to be rather decreasing with increasing the substrate temperature. That means, both $\eta_{CT}$ and $\eta_{ED}$ may not account for the observed increase of the IQE in devices T1 – T5. Consequently, it has to be attributed to the enhancement of the collection probability of the generated charges ($\eta_{CC}$) and, hence, to the increased charge transport capability of the mixed layer. This effect is directly understandable by considering the observed morphology changes. The enhanced phase separation upon substrate heating provides more continuous percolation pathways for charge transport and leads to reduced dead ends. Thus, the IQE and therewith $j_{sc}$ increase by applying substrate heating during the mixed layer growth. Also the FF, which is directly related to the charge transport capability, increases significantly.

The effect of enhanced charge transport is as well evident from the development of the series resistance ($R_s$) and the saturation ratio ($S$) of the investigated devices. Determining $R_s$ from the linear slope of the JV-characteristics in the range from 1.3 V to 1.4 V, gives 22.4 Ωcm$^2$, 10.8 Ωcm$^2$, 3.6 Ωcm$^2$, 8.0 Ωcm$^2$, and 7.6 Ωcm$^2$ for devices T1 – T5, respectively. Certainly, $R_s$ is not only depending on the resistance of the active layer, but also of the transport layers, the metal contacts, and the ITO, and thus some variations between the individual devices are always present. Nonetheless, these results show that the charge transport in the heated devices is more efficient, i.e. has a lower resistance. Therefore a lower resistance of the active mixed layer is assumed. However,
Figure 6.7: Performance parameters of devices T1–T5 in dependence of the substrate temperature. The corresponding JV-characteristics are measured at mismatch corrected intensities of $100\pm1\text{mWcm}^{-2}$ and can be seen in Figure 6.5. Dashed lines are guides to the eye.
for an investigation of the voltage dependence of the photocurrent the parameter $S$ is more meaningful, since it relates $j_{sc}$ with the current density at $-1.0\,\text{V}$. As can be seen in Figure 6.7, $S$ is decreasing from $S=1.72$ in device T1 ($T_{\text{sub}}= -7\,\degree\text{C}$) to $S=1.07$ in device T3 ($T_{\text{sub}}= 77\,\degree\text{C}$) and subsequently stays at a very low level for higher temperatures. This demonstrates the poor charge collection in devices T1 and T2, implying that the photocurrent in those devices depends much stronger on the applied voltage than in devices T3 – T5.

Device T1 exhibits a small kink in the JV-characteristic leading to a slightly S-shaped curve. The reason for this behavior has not been clearly identified up to now. The reason might be that a small energetic extraction barrier for charge transport is present at the mixed layer interface, leading to charges piling up as soon as the applied voltage is close to $V_{oc}$ and hence the electric field within the device is very low. This accumulation of charges, which are remaining in the mixed layer, would cause enhanced recombination and therefore results in a loss of photocurrent [159]. This effect might be particularly significant in device T1, because it exhibits the worst charge transport capability among the investigated devices, resulting in a stronger pronounced kink.

A bad charge collection probability can generally be compensated by applying large backward voltages in order to create a high electric field that is driving the carriers towards the contacts. If the voltage is high enough, $\eta_{CC}$ close to unity can be reached and the photocurrent is then only controlled by the voltage independent quantum efficiencies $\eta_A$ and $\eta_{ED}$. To demonstrate this effect, the JV-characteristics of devices T1 – T5 at negative bias voltages up to $-3\,\text{V}$ are presented in Figure 6.8 (left). These curves are measured using a constant nominal intensity of 104 mWcm$^{-2}$ as given by the outdoor reference diode. In the right graph of Figure 6.8 the photocurrent $j_{ph} = j_{\text{light}} - j_{\text{dark}}$ at $-3\,\text{V}$ and the $j_{sc}$ resulting from the presented JV-characteristics are presented in dependence on the respective substrate temperatures used for the preparation of devices T1 – T5. Furthermore, the saturation ratio $S_{ph,-3V}$ calculated by

$$S_{ph,-3V} = \frac{j_{ph}(-3\,\text{V})}{j_{sc}} \quad (6.1)$$

is given. It has to be mentioned that the saturation regime, with the photocurrent being independent of voltage, is not completely reached at the lowest chosen voltage of $-3\,\text{V}$. Due to a photoshunt effect, which is currently under investigation elsewhere (see work of Wolfgang Tress, IAPP), this saturation regime can hardly be identified. Furthermore, the samples tend to break down at higher backward voltages, and so a moderate voltage of $-3\,\text{V}$ is chosen as limit. Nevertheless, the development of $j_{ph,-3V}$ already shows that the photocurrents of devices T1 and T2 are closer to those of the heated devices, meaning the limitation by $\eta_{CC}$ is partly compensated by the backward voltage. $j_{ph,-3V}$ rises from 6.3 mAcm$^{-2}$ in device T1 ($T_{\text{sub}}= -7\,\degree\text{C}$) to 8.7 mAcm$^{-2}$ in device T3 ($T_{\text{sub}}= 77\,\degree\text{C}$) and is then decreasing to 8.2 mAcm$^{-2}$ in device T5 ($T_{\text{sub}}= 120\,\degree\text{C}$). Apparently, at very
Figure 6.8: Devices T1 – T5 measured at high negative bias voltages up to -3 V. All measurements are done under illumination with the sun simulator SoCo 1200 MGH at a constant nominal intensity of 104 mWcm⁻² as given by the outdoor reference diode. Left: JV-characteristics. Right: Development of the $j_{sc}$ and the photocurrent $j_{ph} = j_{light} - j_{dark}$ at -3 V with different substrate temperatures as used in devices T1 – T5. Lines are guides to the eye. The saturation ratio $S_{ph,-3V}$ calculated according to Equation (6.1) is given in the legend.

High substrate temperatures as in device T5 the photocurrent cannot further be supported by high backward voltages but is already limited by the voltage independent quantum efficiencies. This is also evident in the development of the saturation ratio $S_{ph,-3V}$, which is close to unity in the heated devices. In particular, the lower resulting $j_{ph,-3V}$ for device T5 compared to the other devices indicates that the performance of device T5 is probably limited by the exciton diffusion efficiency ($\eta_{ED}$). The effect of decreasing $\eta_{ED}$ with increasing substrate temperature was already observed in Section 5.3.2. Because of the increasing phase separation upon substrate heating and the correspondingly large domains of DCV6T-Bu some excitons are not reaching a D–A interface, and can therefore not contribute to the photocurrent. This leads to the reduced $j_{ph,-3V}$ of device T5 compared to T3 and T4.

In summary, substrate temperatures varying between -7 °C and 120 °C are shown to have significant effects on the device performance of mixed DCV6T-Bu:C60 heterojunction solar cells. In particular, by achieving stronger phase separation in the mixed layer, the charge transport capability is significantly improved upon heating. This leads to a large increase of the IQE, $j_{sc}$, and FF. Hence, a major increase of power conversion efficiency from 0.5 % at $T_{sub} = -7$ °C to about 3.0 % for $T_{sub} \geq 77$ °C is observed. The effect of decreasing exciton diffusion efficiency upon substrate heating, which was ob-
6.1 Effect of Substrate Heating in DCV6T - C60 Solar Cells

served in the former chapter, is completely outweighed by the gain in charge collection probability. It is only relevant at very high substrate temperatures of 120 °C, where it limits the photocurrent.

These results are in agreement with reports about morphology-performance correlations in polymer as well as phthalocyanine:C60 solar cells [8, 10, 11, 131, 154, 155]. Here, the optimized morphology is found for substrate temperatures between 70 °C and 100 °C. At lower temperatures the charge transport is limiting the performance, while at higher temperatures limitation by $\eta_{ED}$ becomes relevant.

Intensity Dependence of Photocurrent and $V_{oc}$

As discussed above, the investigation of the JV-characteristics of devices T1 – T5 reveals that devices T1 and T2, which are made at low substrate temperatures, need higher electric fields to drive the photocurrent and therefore deliver lower photocurrent at a certain voltage, e.g. lower $j_{sc}$, than the devices with substrate heating. This means that in those devices more charge carriers are lost due to recombination. In the following, a closer look onto these recombination processes shall be given by investigation of the intensity dependence of the photocurrent and $V_{oc}$.

In Section 3.2.2 the basic recombination processes have already been introduced. Due to their different dependences on the charge carrier density the relation between photocurrent ($j_{ph}$) and illumination intensity ($I$) is given in form of a power law

$$j_{ph} \sim I^\alpha. \quad (6.2)$$

By an evaluation of the exponent $\alpha$ two cases can be distinguished. In case of direct recombination of charge carriers, e.g. by Langevin type recombination, $\alpha$ approaches 0.5. On the contrary, $\alpha$ is approaching unity when indirect recombination, e.g. of Shockley-Read-Hall type, dominates the photocurrent. However, the same value of $\alpha$ is also expected for geminate recombination, i.e. recombination of the original electron hole pair directly after charge transfer but before complete dissociation. These two latter processes can not be distinguished in the investigations presented here. Nevertheless, it is expected that the charge separation process is very efficient due to the appropriate design of donor and acceptor energy levels (see Section 5.1). Geminate recombination is therefore considered to play a minor role. Only in heterojunctions with high intermixing of donor and acceptor it is to be supposed that separated molecular sites give rise to geminate recombination, because one of the transferred charges can not escape, lowering the chance of dissociation for both. However, such a situation also gives rise to trapping sites and thus enhanced indirect recombination.
Figure 6.9: Development of the exponent $\alpha$ with voltage. The values for $\alpha$ are determined by fitting the corresponding curves $j_{ph}(V_{appl})$ according to Equation (6.2). Left: The applied voltage is varied. Right: For determining the photocurrent, which is used to fit $\alpha$, not the voltage itself is set constant but the difference between $V_{oc}$ and the applied voltage. By this, the photocurrent is determined with a constant offset $V_x = V_{oc} - V_{appl}$ to $V_{oc}$. Since $V_{oc}$ is depending on intensity, the development of $\alpha$ differs from the characteristic for constant applied voltage (left). The error bars are resulting from the quality of the fit.

In Figure 6.9 (left) the exponents $\alpha$, characterizing the intensity dependence of $j_{ph}$, are presented for different applied voltages. The values for $\alpha$ are determined by fitting the corresponding curves $j_{ph}(V_{appl})$ at intensities from 2 mWcm$^{-2}$ to 140 mWcm$^{-2}$ according to Equation (6.2). For the case of zero voltage, i.e. in short circuit, the corresponding curves are depicted in Figure 6.10. At zero voltage devices T1 ($T_{sub} = -7^\circ$C) and T2 ($T_{sub} = 30^\circ$C) have $\alpha = 0.952$ and $\alpha = 0.958$, respectively, which is close to unity. This shows that in this voltage regime recombination in these devices is mainly due to indirect processes. For the heated devices T3 – T5 $\alpha$ around 0.99 is found. However, it must be considered that $j_{sc}$ is hardly attenuated by losses in these devices, as can be seen from their good saturation ratios $S_{ph,-3V}$ (Figure 6.8). Therefore, the interpretation of $\alpha$ with regard to determine recombination processes is not reasonable in this case. When increasing the voltage up to values near $V_{oc}$, $\alpha$ is decreasing. Devices T1 and T2 exhibit the strongest decrease, with $\alpha$ reaching 0.896 and 0.925 at 0.5 V, respectively, while devices T3 – T5 still show an $\alpha$ above 0.97. At voltages close to $V_{oc}$, the evaluation of $j_{ph}$ at a fixed applied voltage does not yield meaningful results for $\alpha$ anymore, because $V_{oc}$ is itself dependent on intensity. To overcome this problem, $j_{ph}$ is determined at voltages with fixed offset $V_x$ to $V_{oc}$, such that $V_{appl} = V_{oc} - V_x$. In Figure 6.9 (right) the results for the exponent $\alpha$ are given for different values of $V_x$. The unusual development of $\alpha$ in
device T1 seems to be affected by the S-shaped JV-characteristics of this device. In particular, the presence of the maximum is not considered to be an effect of changing recombination processes. However, the graphs generally show a decrease of $\alpha$ when $V_x$ approaches zero, i.e. at voltages close to $V_{oc}$. This means that direct recombination becomes more and more significant when approaching $V_{oc}$. Considering that at $V_{oc}$ by definition all generated charges in the device have to recombine, this result is reasonable, because the photo-generated charge carrier density is highest at this point and therefore direct recombination is enhanced. Interestingly, devices T1 ($T_{sub} = -7$ °C) and T2 ($T_{sub} = 30$ °C) show the decrease of $\alpha$ already at higher $V_x$, i.e. further away from $V_{oc}$, while devices T3 – T5 still exhibit values above 0.95 at $V_x = 0.3$ V. This indicates that T1 and T2 reach higher photo-generated charge carrier densities already at lower voltages due to their low charge collection efficiency. So, by increasing the voltage up to $V_{oc}$ the photocurrent in devices T1 and T2 changes from being preferentially controlled by indirect recombination towards being dominated by direct recombination. Also, the heated devices T3 – T5 are dominated by direct recombination when approaching $V_{oc}$.

In the following, the intensity dependence of $V_{oc}$ shall be investigated. As already stated above, in this distinct point of the JV-characteristic all photo-generated charge carriers recombine within the device, resulting in an external current of zero. In Section 3.2.1, $V_{oc}$ of organic solar cells was already discussed and found to be

$$eV_{oc} = E_{DA} - kT \ln \left( \frac{N_D N_A}{n p} \right)$$  \hspace{1cm} (6.3)

in the ideal case. $E_{DA}$ can be considered as fixed in the investigated devices. Hence, $V_{oc}$ is only determined by the development of the product $n p$, which results from the balance between generation and recombination of charge carriers. The generation of charge carriers results from the generation of excitons that are separated into geminate pairs at the D-A interface and subsequently dissociated into free charge carriers. Therefore, $n p$ is dependent on intensity $(I)$ and can be expressed by

$$p n = b \cdot I^\beta,$$  \hspace{1cm} (6.4)

where $b$ and $\beta$ account for the actual balance between recombination and dissociation. Inserting Equation (6.4) into Equation (6.3) gives

$$eV_{oc} = E_{DA} - kT \ln \left( \frac{N_D N_A}{n p} \right) = E_{DA} + \beta \cdot kT \ln \left( \frac{I}{I_0} \right),$$  \hspace{1cm} (6.5)

where $I_0$ is introduced to account for the parameters $N_A$, $N_D$, and $b$ that are not known at this point, but can only be extracted from additional temperature dependent measurements. Here, only the development of $\beta$ shall be considered, since it already enables to distinguish between the basic recombination processes [76]. In case of direct recombination of charge carriers, e.g. by Langevin type, $\beta$ approaches unity. On the contrary, $\beta$
approaches 2 when indirect recombination, e.g. Shockley-Read-Hall type, is prevailing. When geminate recombination is limiting \( n_p \), i.e. recombination of the charge transfer pairs before dissociation into free charge carriers, \( \beta \) is also approaching 2. These latter two cases can therefore not be distinguished by the investigations presented here.

Figure 6.10 (right) presents the development of \( V_{oc} \) with intensity for devices T1 – T5. The predicted logarithmic behavior is observed for an intensity range of at least one order of magnitude, i.e. from 10 mWcm\(^{-2}\) to 100 mWcm\(^{-2}\). At lower intensities \( V_{oc} \) exhibits a stronger decrease. Generally, the slope depends on intensity, because a transition from a behavior dominated by indirect recombination at low intensities towards direct recombination dominated behavior at high intensities is expected. For the evaluation of \( \beta \), only intensities above 5 mWcm\(^{-2}\) are considered when fitting \( V_{oc} \), since this is the region relevant for solar cells. The resulting values for \( \beta \) are given in the legend of Figure 6.10 (right). Apparently, there is a systematic decrease of \( \beta \) from 1.678 in device T1 (\( T_{sub} = -7 \) °C) to 1.036 in device T5 (\( T_{sub} = 120 \) °C). This means that recombination in the heated devices T3 – T5 is mainly dominated by direct recombination, and indirect as well as geminate recombination play a minor role. In contrast, in devices T1 (\( \beta = 1.678 \)) and T2 (\( \beta = 1.250 \)) this is not the case. Indirect recombination or geminate recombination are not negligible there, but play a significant role although not solely dominating the development of charge carrier density \( (n_p) \) at \( V_{oc} \). This is consistent with the above presented investigations of the intensity dependence of the photocurrent, which showed that indirect recombination is prevailing at zero bias voltage.
In summary, the heated devices T3 – T5 have only little recombination losses at low voltages ($V_{\text{appl}} < 0.4$ V) and are dominated by direct recombination, e.g. Langevin type, at voltages approaching $V_{\text{oc}}$. On the other hand, the devices T1 ($T_{\text{sub}} = -7^\circ$C) and T2 ($T_{\text{sub}} = 30^\circ$C) exhibit a significant loss of photocurrent at low voltages ($-3 < V_{\text{appl}} < 0.4$ V) which is mainly attributed to indirect recombination, e.g. Shockley-Read-Hall type. For voltages approaching $V_{\text{oc}}$ a transition to direct recombination dominated behavior is found. However, at $V_{\text{oc}}$ recombination via indirect processes is still relevant leading to $\beta$ higher than one. Considering the respective change of morphology at different substrate temperatures, these results are very reasonable. For increasing substrate temperature, the phase separation between DCV6T-Bu and C60 increases, the domain size is enhanced, and the DCV6T-Bu molecules are better ordered. Consequently, the percolation pathways are more continuous and there are less dead ends. By this, the probability of indirect recombination by trapping of charges in deep tail states, separated molecules, or in dead ends is reduced and the charges can be extracted faster and more efficiently.

Mixed DCV6T-Et : C60 Solar Cells

Devices T6 and T7 have the same layer design as the above presented devices T1 – T5 (Figure 6.4), but are made with DCV6T-Et instead of DCV6T-Bu. The substrate temperatures during the deposition of the mixed layer are 30$^\circ$C and 90$^\circ$C, respectively.

The J-V-characteristics of devices T6 and T7, measured under illumination with the sun simulator SoCo 1200 MGH, are presented in Figure 6.11. The corresponding performance parameters are given in Table 6.3. Apparently, the change of performance with substrate heating is equal to the results of the DCV6T-Bu : C60 devices (T1 – T5) that are presented above. The FF as well as $j_{\text{sc}}$ are increasing from 43.7 % and 4.1 mAcm$^{-2}$ in device T6 ($T_{\text{sub}} = 30^\circ$C) to 64.0 % and 6.5 mAcm$^{-2}$ in device T7 ($T_{\text{sub}} = 90^\circ$C), respectively. The EQE and absorption spectra of devices T6 and T7 are depicted in Figure 6.12. As already observed for the DCV6T-Bu : C60 solar cells, the EQE is significantly increased upon substrate heating. In the range from 550 nm to 700 nm also the absorption increases slightly, exhibiting values that are by 1–4 % higher in device T7 than in device T6. This increase reproduces the results of the morphology investigations on heated mixed layers (see Section 5.3.2). However, as already explained for the DCV6T-Bu : C60 solar cells, the main effect of increased performance can be attributed to the improved charge transport. This improvement results from the change of morphology upon substrate heating, characterized by stronger phase separation, larger domains of DCV6T-Et, and higher molecular order.

Although the presented devices with DCV6T-Et (T6, T7) have the same layer structure as the devices with DCV6T-Bu (T1 – T5), an unambiguous conclusion about which
Figure 6.11: JV-characteristics of devices T6 and T7. The performance parameters are given in Table 6.3.

Table 6.3: Performance parameters of devices T6 and T7. The corresponding JV-characteristics are depicted in Figure 6.11.

<table>
<thead>
<tr>
<th>Device</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>S</th>
<th>PCE (mW/cm$^2$)</th>
<th>$\eta_{PCE}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T6 ($T_{sub} = 30^\circ C$)</td>
<td>0.86</td>
<td>4.1</td>
<td>43.7</td>
<td>1.37</td>
<td>101.8</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>T7 ($T_{sub} = 90^\circ C$)</td>
<td>0.90</td>
<td>6.5</td>
<td>64.0</td>
<td>1.09</td>
<td>101.1</td>
<td>3.7 ± 0.2</td>
</tr>
</tbody>
</table>

Material gives better solar cells is not possible. Both materials are nearly equal in their basic electronic and optical properties (see Section 5.2) and show analogous behavior upon substrate heating when mixed with C60 (see Section 5.3.2). Not surprisingly, they achieve a similar performance in the investigated solar cells. The observed variations between respective devices fabricated at comparable substrate temperatures, e.g. between T2 and T6 ($T_{sub} = 30^\circ C$), are rather resulting from inevitable variations of the preparation conditions like for example differences in the batches used for C60 and BPAPF.

In summary, also in mixed DCV6T-Et: C60 heterojunction solar cells substrate heating leads to significant improvement of the performance, showing that the control of the nanoscale morphology plays a crucial role for the optimization of organic solar cells.
6.2 Influence of the Mixing Ratio

Besides the effects of different substrate temperatures, another important parameter is also substantially controlling the nanoscale morphology: the mixing ratio between donor and acceptor material. For many different material systems, regardless whether polymers or small molecules, morphology is found to be strongly dependent on the composition ratio [152, 160–162]. Different properties, like for example strong crystallization of one material or nanoscale intercalation of one material into the other, significantly affect the morphology, and are especially defining the degree of phase separation [130, 163]. Such effects can be controlled by the composition ratio. Furthermore, the composition ratio determines the balance between the charge transport of holes and electrons in the mixed layer, which is essential for a high charge collection probability in the corresponding solar cells [152, 164]. Consequently, for every single material system there is a certain ratio which leads to the optimal degree of phase separation giving the best solar cell performance. Yet, this quantity usually also depends on the actual preparation conditions, e.g. substrate temperature.

In the following, the influence of different composition ratios on the performance of mixed DCV6T-Bu:C60 heterojunction solar cells is investigated. The mixed layer thickness is set to 20 nm. The substrate temperature during the deposition of the mixed layer is chosen to be approximately 90 °C in order to facilitate phase separation, and,
Figure 6.13: Schematic layer design of mixed heterojunction p-i-n solar cells for investigation of the influence of mixing ratio. a) Devices M1–M4 with mixing ratios DCV6T-Bu : C60 varying from 1:1 to 1:4. b) Samples M1a–M4a of the same production-run without hole transport layers. These samples serve for the investigation of topography, absorption, and luminescence of the different mixed layers.

thus, to determine the influence of different mixing ratios at optimized preparation conditions (see Section 6.1.2). The different mixing ratios between DCV6T-Bu : C60 in devices M1 – M4 are 1:1, 2:1, 3:1, and 4:1, respectively. This translates to volume ratios of DCV6T-Bu of 0.5, 0.66, 0.75, and 0.8, respectively. Apart from the solar cells themselves, additional samples M1a – M4a (Figure 6.13, right) are prepared, which only comprise the two first layers up to the mixed layer. All samples are produced in the Lesker B tool. Thus, the additional samples M1a – M4a are prepared at the same time and at the very same preparation conditions as their solar cell counterparts M1 – M4. This allows to investigate the mixed layer morphology by UV-Vis absorption and luminescence spectroscopy as well as AFM measurements on the samples M1a – M4a, while determining the corresponding solar cell performances from M1 – M4.

Figure 6.14 presents the JV-characteristics of devices M1 – M4 as measured under illumination with the sun simulator 16S-003-300. The corresponding performance parameters are given in Table 6.4 and are furthermore depicted in Figure 6.15 in dependence on the DCV6T-Bu ratio. The curves are mainly differing in $j_{sc}$ and FF. $V_{oc}$ is constant over the investigated range of mixing ratios, and reaches values of 0.91 V. $j_{sc}$ increases
6.2 Influence of the Mixing Ratio

Figure 6.14: JV-characteristics of devices M1 – M4. The performance parameters are given in Table 6.4 and are depicted in Figure 6.15.

from 5.2 mAcm⁻² at a DCV6T-Bu ratio of 0.5 (M1) to 7.2 mAcm⁻² at a ratio of 0.75 (M3). Subsequently, it decreases slightly to 7.1 mAcm⁻² at a ratio of 0.8 (M4). Figure 6.16 shows the absorption, EQE, and IQE spectra of the respective devices. There, it can be seen that the increase of $j_{sc}$ is mainly caused by the increase of absorption from DCV6T-Bu concomitant to the growing fraction of this material in the mixture. In accordance to the development of $j_{sc}$, the EQE spectra principally follow the trend of the absorption. The spectra are mainly differing in the range of DCV6T-Bu absorption, where the lowest EQE is found for a DCV6T-Bu ratio of 0.5 (M1). This low EQE in device M1 is not solely caused by the lower absorption but also the IQE in this device appears to be significantly lower compared to the other devices. This may be attributed to both the lower charge transport capability and the effect of parasitic absorption (see Section 6.3.3), which generally becomes more relevant when the active layer absorption is low. The best IQE values are reached for a DCV6T-Bu ratio of 0.66 (M2), indicating that this mixture is the optimum for reaching high charge collection efficiency and efficient exciton diffusion to the D-A interface at the same time. For higher ratios the IQE is slightly lower. Indeed, also the highest FF and the best saturation ratio $S$ are achieved for this DCV6T-Bu ratio of 0.66 (M2) reaching 67.1 % and 1.06, respectively. Thus, it confirms that this ratio exhibits the best transport capability, i.e. it provides the optimal balance between continuous hole and electron percolation pathways.
Table 6.4: Performance parameters of devices M1–M4. The corresponding JV-characteristics are given in Figure 6.14.

<table>
<thead>
<tr>
<th>device (DCV6T-Bu : C60)</th>
<th>$V_{oc}$ (V)</th>
<th>$j_{sc}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>$S$ (%)</th>
<th>$I$ (mW cm$^{-2}$)</th>
<th>η_{PCE} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1 (1:1)</td>
<td>0.89</td>
<td>5.2</td>
<td>59.4</td>
<td>1.07</td>
<td>98.6</td>
<td>2.8±0.1</td>
</tr>
<tr>
<td>M2 (2:1)</td>
<td>0.91</td>
<td>6.9</td>
<td>67.1</td>
<td>1.06</td>
<td>100.2</td>
<td>4.2±0.2</td>
</tr>
<tr>
<td>M3 (3:1)</td>
<td>0.91</td>
<td>7.2</td>
<td>60.8</td>
<td>1.08</td>
<td>98.5</td>
<td>4.1±0.2</td>
</tr>
<tr>
<td>M4 (4:1)</td>
<td>0.91</td>
<td>7.1</td>
<td>57.7</td>
<td>1.10</td>
<td>100.1</td>
<td>3.7±0.2</td>
</tr>
</tbody>
</table>

Figure 6.15: Performance parameters of devices M1–M4 in dependence on the DCV6T-Bu ratio (by volume) of the mixed layer. The corresponding JV-characteristics are given in Figure 6.14 and are measured at mismatch corrected illumination intensities about 100 mW cm$^{-2}$. Dashed lines are guides to the eye. The DCV6T-Bu : C60 ratio showing the highest value in each case of $j_{sc}$, FF, and η_{PCE}, respectively, is indicated.
6.2 Influence of the Mixing Ratio

![Graph showing absorption, EQE, and IQE of devices M1-M4.](image)

**Figure 6.16**: Absorption, EQE and IQE of devices M1-M4. Performance parameters are given in Table 6.4.
The observed decrease in the IQE upon increasing the DCV6T-Bu ratio above 0.66 might also be related to a loss in $\eta_{\text{ED}}$, because of the higher amount and therefore larger domains of DCV6T-Bu. This effect is now investigated by measuring the luminescence of the samples M1a–M4a. Figure 6.17 (right) presents the respective spectra, which are measured at an excitation wavelength of 594 nm. The shown spectra are weighted by the corresponding absorption at this wavelength to correct for the influence of different absorption probabilities on the luminescence signal intensity. The absorption spectra are given in Figure 6.17 (left). Generally, the luminescence signal is very low, similar to the results presented in Section 5.3.2, where more than 95% of the excitons were found to be quenched when using a substrate temperature of 90°C and a DCV6T-Bu:C60 mixing ratio of 2:1. In sample M1a with a DCV6T-Bu ratio of 0.5, no clear luminescence signal is observed, which indicates complete quenching of excitons at this ratio. However, the absorption in this sample is very low, which additionally impairs the detection. For DCV6T-Bu ratios of 0.66 to 0.8 (M2a–M4a) the luminescence signals (after correction for different absorption) are nearly equal. This implies that there is no considerable difference in the exciton diffusion efficiency ($\eta_{\text{ED}}$) between these mixing ratios.

Figure 6.18 shows AFM pictures of the surface of samples M1a–M4a. These pictures give information about the topography of the mixed active layer and its dependence
Figure 6.18: AFM pictures of samples M1a to M4a, showing the surface of mixed layers of DCV6T-Bu : C60 grown on top of a C60 layer on Glass/ITO substrates. The mixed layer thickness is 20 nm and it is grown at a substrate temperature of 90 °C. The ratio of DCV6T-Bu is varied from 0.5 to 0.8. These samples resemble the layer stack of devices M1 to M4, allowing the investigation of the active layer surface.
on varying mixing ratios. All pictures exhibit a granular topography, with increasing grain size for higher ratios of DCV6T-Bu. The low grain size at a DCV6T-Bu ratio of 0.5 (M1a) supports the conclusion that excitons are efficiently quenched at this ratio, as was seen above from the small luminescence signal. The rms-roughness is only slightly differing, and shows the highest value of 1.6 nm at a DCV6T-Bu ratio of 0.66 (M2a), while it is between 1.2 and 1.3 nm in the other cases. These results are different to reports about mixtures of 6T with C60, where a very high surface roughness at 6T ratios of 0.5 was reported [130]. Due to the strong crystallization of 6T, phase separation could only be suppressed by using an excess amount of C60 and consequently the best solar cell performance was observed at extremely low 6T ratios of 0.17. Here, the rather low roughness which is observed in the samples M1a – M4a implies that the crystallization effect must be much weaker for DCV6T-Bu as compared to 6T.

In summary, the highest power conversion efficiency is found for a DCV6T-Bu ratio of 0.66 (M2), closely followed by the ratio of 0.75 (M3). Although the absorption can be further increased with higher content of DCV6T-Bu, this is detrimental for the charge transport and leads to a drop in FF, and consequently to lower efficiency. The surface roughness of the mixed active layer is highest at the optimal DCV6T-Bu ratio of 0.66 (M2a) where it reaches a value of 1.6 nm. Concomitant to the increase of the DCV6T-Bu ratio the grain size in the AFM pictures rises. The sample with the lowest investigated DCV6T-Bu ratio of 0.5 (M1a) and therefore the lowest grain size exhibits nearly complete exciton quenching. However, the luminescence signals of the other samples give no indication of enhanced loss of excitons upon increasing the DCV6T-Bu ratio from 0.66 to 0.8, but are nearly equal.

6.3 Optimizing the Layer Stack

The previous sections focused on the correlation between active layer morphology and performance of the solar cell. By tuning of different preparation conditions like substrate temperature and mixing ratio an optimal morphology was found which provides the best compromise between efficient collection of excitons and good charge transport capabilities and thus leads to good performances. Now, the next step will be taken towards a solar cell with high power conversion efficiency, i.e. the optimization of the layer design. In particular, the influence of the layer thicknesses of the wide gap transport layers and the active layer are investigated, to find the layer design with maximum efficiency. Here, only mixed heterojunction solar cells are considered because they are the most promising concept, showing superior results compared to the flat heterojunction devices especially when an optimum mixed layer morphology is achieved. Comprehensive reports about flat DCV6T/C60 heterojunction solar cells were given in [127, 129]. In these studies, the limitation by $\eta_{ED}$ was found to be a critical bottleneck.
6.3 Optimizing the Layer Stack

As already introduced in Section 3.2.3, the application of doped transport layers allows the tuning of thin film optics in a very convenient way, because their thickness can be freely chosen. Therewith, the absorption of the active layer can be increased by placing it into the maximum of the optical field distribution [51, 96, 165]. This is especially important since the thickness of the mixed active layer is usually limited to lower values than the thickness necessary for complete absorption of all incoming light. Generally, the optimum mixed layer thickness is determined by the tradeoff between efficient charge extraction, which is supported by a small thickness, and high absorption, which would require a large thickness [11, 127, 166]. Again, thin film optics has to be taken into account, when the absorption shall be increased by the increase of the mixed layer thickness [167]. To provide a comprehensive understanding of the interplay between the thin film optics and the performance of the solar cells presented here, optical simulations based on the transfer-matrix-formalism are performed [122].

In Figure 6.19 the layout of devices O1–O6 for the investigation of the influence of the hole transport layer (HTL) thickness ($d_{D_i-NPB}$), and of devices H1–H3, C1, and C2 with varying active layer thickness. In devices H1–H3, the substrate is heated to approximately 90°C during the deposition of the mixed layer. Devices C1 and C2 are prepared without substrate heating.

Figure 6.19: Schematic layer design of solar cells with a mixed $\text{DCV6T-Bu : C60}$ heterojunction. a) Devices O1–O6 for the investigation of the influence of the transport layer thickness ($d_{\text{Di-NPB}}$) on the thin film optics. b) Devices H1–H3, C1, and C2 with varying active layer thickness. In devices H1–H3, the substrate is heated to approximately 90°C during the deposition of the mixed layer. Devices C1 and C2 are prepared without substrate heating.
C2 for the investigation of the influence of the mixed active layer thickness ($d_{\text{mix}}$), are presented. According to the results of the previous sections, a DCV6T-Bu : C60 ratio of 2:1 is chosen in all devices. Devices O1 – O6 are prepared with substrate heating at approximately 90 °C during the deposition of the mixed active layer. The top contact is realized by incorporating a recombination interface between the top p-doped hole transport layer and another layer of n-doped C60 [168]. This sequence provides good ohmic contact to the Al anode, which is used here instead of gold due to its better reflectivity. The thickness of the HTL ($d_{\text{Di-NPB}}$) is varied between 10 to 35 nm. Devices H1 – H3 are prepared at a substrate temperature of approximately 90 °C and have mixed layer thicknesses of 20 nm, 30 nm, and 40 nm, respectively. In comparison, the devices C1 and C2 are prepared without substrate heating ($T_{\text{sub}} = 30 \degree C$) and have a mixed layer thickness of 20 nm and 30 nm, respectively. Here, the n-doped C60 contact layer is replaced by highly doped Di-NPB followed by 1 nm NDP9, since it was found to provide an ohmic contact as well and furthermore reduces parasitic absorption.

### 6.3.1 Influence of the Transport Layer Thickness

To understand the influence of the transport layer thickness on the thin film optics and subsequently to find the optimal thickness, the optics of devices O1 – O6 are simulated by using a transfer-matrix-formalism method (see Section 4.3.6). The corresponding absorption patterns are presented in Figure 6.20, showing the absorbed photon flux depending on the position $x$ within the layer stack ($x$-axis is perpendicular to the substrate). The HTL thickness $d_{\text{Di-NPB}}$ is varied from 0 to 40 nm comprising the respective thicknesses of devices O1 – O6 (black curves). Apparently, absorption mainly occurs in the active layers, i.e. in the mixed DCV6T-Bu : C60 layer (20 nm) and in the adjacent intrinsic C60 layer (15 nm). The HTLs Di-NPB and BPAPF do not absorb much light due to their wide optical gap. However, the n-doped C60 transport layers and the Al anode apparently absorb some light that is lost for photocurrent generation (see also Section 6.3.3). From the profiles of the absorption pattern it can be seen that the mixed layer is shifted into the maximum of the optical field distribution for $d_{\text{Di-NPB}}$ of approximately 25 nm, where the absorbed photon flux is highest. For smaller and higher Di-NPB thicknesses the mixed layer is shifted away from this maximum. In contrast, the C60 layer exhibits the highest absorbed photon flux already at $d_{\text{Di-NPB}}=0$ nm and is shifted out of this maximum from there on. This is explained by the different wavelength regions of the respective absorption spectra. The C60 layer is preferentially absorbing in the blue wavelength region (300 – 450 nm) while the mixed layer is preferentially absorbing in the green wavelength region (450 – 650 nm) because it mainly contains DCV6T-Bu. Due to the shorter wavelength, the interference maximum of the blue light is closer to the reflecting electrode than that of the green light. Consequently, the C60 layer should ideally be placed closer to the electrode than the mixed layer, in order to
achieve maximum absorption in both layers. This is unfortunately not possible with the actual layer sequence. The optimum HTL thickness is therefore in between the ideal values for both layers and is found where the sum of both contributions is maximized.

The overall amounts of the absorbed photon fluxes in the active layers are compared in Figure 6.21. There, the equivalent current of each active layer and their sum are presented depending on $d_{Di-NPB}$. The equivalent current is the photocurrent for the case that all absorbed photons in the layer are converted into current, i.e. IQE is unity. It can directly be extracted from the absorption pattern of the layer stack by integrating over the respective coordinates $x$ of the layer. Figure 6.21 also depicts the development of the measured $j_{sc}$ of devices O1 – O6. All other performance parameters are summarized in Table 6.5. The corresponding JV-characteristics are measured under illumination with the sun simulator 16S-003-300. For better comparison, i.e. to exclude the effects of spectral mismatch, the equivalent currents (Figure 6.21) are calculated by using the illumination spectrum of the sun simulator in the optical simulation. Again, it can be seen that the total absorption of the C60 layer is decreasing with increasing $d_{Di-NPB}$.
Figure 6.21: Simulated equivalent currents of the total absorbed photon flux in the active layers of devices O1 – O6 depending on $d_{\text{Di-NPB}}$. The measured $j_{\text{sc}}$ values are also presented. The total absorbed photon flux is calculated by integrating the absorption profile over the respective coordinates $x$ of the layer. Subsequently, the equivalent current is determined by assuming that every absorbed photon contributes to the photocurrent (IQE is unity). To have comparable results to the measurement, the illumination spectrum of the sun simulator (16S-003-300) is used in the simulation. The nominal illumination intensity is 143 mWcm$^{-2}$ as given by the reference diode S1337-33BQ.

while the mixed layer absorption increases up to $d_{\text{Di-NPB}}=25$ nm. The sum of both is maximal at $d_{\text{Di-NPB}}=15$ nm. The measured performance parameters show nearly equal $V_{\text{oc}}$, FF, and $S$ for the devices O1 – O6. That means that the variations in thickness of the p-Di-NPB layer do not affect these properties, which is of course expected since the layer is doped and therefore has a high conductivity (see Section 3.2.3). Thus, the development of $j_{\text{sc}}$ with varying $d_{\text{Di-NPB}}$ can be attributed solely to the change of the absorption properties. Apparently, the measured $j_{\text{sc}}$ exhibits the maximum at the same thickness as predicted from the simulation, i.e. at $d_{\text{Di-NPB}}=15$ nm, and generally follows the trend of the sum of the calculated equivalent currents. However, the variations over the investigated HTL thicknesses are rather small.

In summary, the variation of the transport layer thickness enables to place the active layer in the maximum of the optical field distribution without impairing the electrical transport, as can be seen from the performance parameters of the devices O1 – O6. By this, the achieved $j_{\text{sc}}$ is enhanced due to the increased absorption of photons in the
6.3 Optimizing the Layer Stack

Table 6.5: Performance parameters of devices O1 – O6. The illumination intensity $I^*$ is not corrected for spectral mismatch, but is the nominal intensity as displayed by the reference diode S1337-33BQ. The sun simulator 16S-003-300 is used for illumination.

<table>
<thead>
<tr>
<th>device</th>
<th>$V_{oc}$ (V)</th>
<th>$j_{sc}$ (mAcm$^{-2}$)</th>
<th>FF (%)</th>
<th>$S$</th>
<th>$I^*$ (mWcm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1 (d$_{Di\text{-}NPB}$=10 nm)</td>
<td>0.90</td>
<td>7.6</td>
<td>60.7</td>
<td>1.10</td>
<td>143</td>
</tr>
<tr>
<td>O2 (d$_{Di\text{-}NPB}$=15 nm)</td>
<td>0.90</td>
<td>8.0</td>
<td>61.3</td>
<td>1.09</td>
<td>143</td>
</tr>
<tr>
<td>O3 (d$_{Di\text{-}NPB}$=20 nm)</td>
<td>0.90</td>
<td>7.8</td>
<td>60.8</td>
<td>1.10</td>
<td>143</td>
</tr>
<tr>
<td>O4 (d$_{Di\text{-}NPB}$=25 nm)</td>
<td>0.90</td>
<td>7.7</td>
<td>61.2</td>
<td>1.10</td>
<td>143</td>
</tr>
<tr>
<td>O5 (d$_{Di\text{-}NPB}$=30 nm)</td>
<td>0.90</td>
<td>7.7</td>
<td>62.1</td>
<td>1.09</td>
<td>143</td>
</tr>
<tr>
<td>O6 (d$_{Di\text{-}NPB}$=35 nm)</td>
<td>0.90</td>
<td>7.2</td>
<td>62.0</td>
<td>1.09</td>
<td>143</td>
</tr>
</tbody>
</table>

active layers. The optimal thickness predicted by optical simulations is consistent with the measured results and found to be at $d_{Di\text{-}NPB}$=15 nm for the investigated devices. This translates into an overall thickness of all transport layers of 45 nm. The simulated absorption patterns show that it is not possible to place both active layers into their ideal optical position at the same time, because the C60 layer has to be closer to the electrode than the mixed DCV6T-Bu : C60 layer, since it is preferentially absorbing at lower wavelengths. However, the main contribution to the photocurrent comes from the mixed layer.

### 6.3.2 Influence of the Mixed Layer Thickness

The mixed active layer thickness plays an important role for the resulting efficiency of the solar cell. Very thick layers give rise to high absorption but are on the other hand detrimental for efficient charge collection, because the charges have to travel a longer distance. The optimum thickness is therefore determined by the balance between gain in absorption against loss in charge collection efficiency. Consequently, this optimum value is depending on the actual charge transport capability of the mixed layer and therewith on the morphology, i.e. the phase separation and the continuity of the percolation pathways. Here, the optimum thickness shall be determined by investigating the devices H1 – H3 which combine all optimization steps that were presented so far, so as to accomplish a solar cell with high power conversion efficiency. That means, in devices H1 – H3 substrate heating to approximately 90 °C and a DCV6T-Bu : C60 mixing ratio of 2 : 1 are used. The mixed layer thickness ($d_{mix}$) is varied from 20 nm to 40 nm. The simulated absorption profiles of devices H1 – H3 are presented in Figure 6.22. The overall HTL thickness amounts to 45 nm, which corresponds to $d_{Di\text{-}NPB}$=15 nm in devices O1 – O6, where this value was found to be optimal for a mixed layer thickness of 20 nm. However, also in the devices H2 ($d_{mix}$=30 nm) and H3 ($d_{mix}$=40 nm) the
Figure 6.22: Simulated absorption profiles of devices H1 – H3. These profiles show the absorbed photon flux within the layer stack, depending on the position x. Position x=0 is set at the surface of the reflecting metal layer (Al). The sun spectrum AM 1.5 G is used as illumination spectrum.

active layers are positioned close to the optimal position, as can be seen from the maxima of the absorption profiles in Figure 6.22. For further comparison, the devices C1 (d_{mix}=20 nm) and C2 (d_{mix}=30 nm) are presented additionally. They are prepared at room temperature (T_{sub} = 30 °C), but are equal to the devices H1 and H2 in all other aspects.

Figure 6.23 presents the JV-characteristics of devices H1 – H3, C1, and C2 as measured under illumination with the sun simulator SoCo 1200 MGH. The corresponding performance parameters are summarized in Table 6.6. As already expected from the results in Section 6.1.2, the heated devices H1 – H3 are superior to the not heated devices C1 and C2, showing better j_{sc}, FF, and S. V_{oc} is comparatively constant among the investigated devices, reaching typical values of 0.90 V. Generally, upon increasing the mixed layer thickness j_{sc} is increasing, while the FF drops and also the saturation factor S gets worse. This is seen for both the heated and not heated devices, however to very different degrees. For the devices prepared at room temperature the increase of d_{mix} from 20 nm to 30 nm (C1 to C2) causes an increase of j_{sc} from 7.1 mAcm^{-2} to only 7.3 mAcm^{-2}, but a large drop in FF from 50.3 % to 42.2 %. In contrast, the same increase of d_{mix} in the heated devices (H1 to H2) results in an increase of j_{sc} from 9.7 mAcm^{-2} to 10.9 mAcm^{-2}, while the FF decreases only slightly from 64.0 % to 60.7 %. Consequently, the power conversion efficiency drops for the not heated devices, but rises for the heated ones. This means that the optimal thickness for d_{mix} in devices prepared at room temperature
Figure 6.23: JV-characteristics of devices H1 – H3, C1, and C2 measured under illumination with the sun simulator SoCo 1200 MGH at a nominal intensity $I^*$ of $99.4 \pm 1.5 \text{mWcm}^{-2}$ as given by the outdoor reference diode. The mismatch corrected intensities ($I$) are given in the legend. The performance parameters are presented in Table 6.6.

<table>
<thead>
<tr>
<th>device</th>
<th>$V_{oc}$ (V)</th>
<th>$j_{sc}$ (mAcm$^{-2}$)</th>
<th>$FF$ (%)</th>
<th>$S$</th>
<th>$I$ (mWcm$^{-2}$)</th>
<th>$\eta_{PCE}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1 ($d_{mix}=20 \text{ nm}$)</td>
<td>0.89</td>
<td>7.1</td>
<td>50.3</td>
<td>1.22</td>
<td>128.2</td>
<td>2.5±0.1</td>
</tr>
<tr>
<td>C2 ($d_{mix}=30 \text{ nm}$)</td>
<td>0.88</td>
<td>7.3</td>
<td>42.2</td>
<td>1.30</td>
<td>126.0</td>
<td>2.1±0.1</td>
</tr>
<tr>
<td>H1 ($d_{mix}=20 \text{ nm}$)</td>
<td>0.90</td>
<td>9.7</td>
<td>64.0</td>
<td>1.07</td>
<td>125.9</td>
<td>4.4±0.2</td>
</tr>
<tr>
<td>H2 ($d_{mix}=30 \text{ nm}$)</td>
<td>0.89</td>
<td>10.9</td>
<td>60.7</td>
<td>1.08</td>
<td>119.3</td>
<td>4.9±0.2</td>
</tr>
<tr>
<td>H3 ($d_{mix}=40 \text{ nm}$)</td>
<td>0.88</td>
<td>11.6</td>
<td>57.0</td>
<td>1.09</td>
<td>117.7</td>
<td>4.9±0.2</td>
</tr>
</tbody>
</table>
is already at approximately 20 nm, because the drop in charge collection efficiency and hence in FF cannot be compensated by the gain in absorption. This finding is consistent with previous reports on DCV6T:C60 mixed heterojunction solar cells, where also lower thicknesses than 20 nm were investigated [127]. In the heated devices with optimized morphology, the optimal thickness is considerably higher, because the charge transport is better and therefore the charge collection efficiency is not as susceptible to an increase of the thickness. From the results of the investigated devices H1–H3 showing \( \eta_{PCE} \) of 4.4±0.2 %, 4.9±0.2 %, and 4.9±0.2 %, respectively, the optimal thickness \( d_{\text{mix}} \) is found between 30 nm and 40 nm.

The EQE, \( \eta_A \), and IQE spectra of devices H1–H3 are presented in Figure 6.24. It can be seen that the absorption rises with increasing mixed layer thickness. Interestingly, the IQE spectra are nearly equal among the devices H1–H3. As a consequence, the EQE completely follows the development of rising \( \eta_A \), and hence the gain of absorption with increasing \( d_{\text{mix}} \) results in a direct increase of \( j_{\text{sc}} \). However, a slight drop in IQE due to a reduced charge collection probability (\( \eta_{CC} \)) at higher mixed layer thickness should be expected. In fact, the decrease in FF and the slight increase of \( S \) (see Table 6.6) indicate a drop in \( \eta_{CC} \). Here, an additional effect of the increase of \( d_{\text{mix}} \) is proposed, which is attributed to compensate for this drop. That is the effect of lower parasitic absorption in the passive layers like the metal electrode or the HTLs. By increasing \( d_{\text{mix}} \) the absorption in the active layers increases and so the absorption in passive layers decreases. This results in a better exploitation of the absorbed photons, so to say in an increase of \( \eta_{ED} \). The finding that the IQE seems to be nearly unaffected by \( d_{\text{mix}} \) is considered as a result of this interplay between both effects. A comprehensive discussion of the parasitic absorption in the devices H1–H3 will be given in the next Section 6.3.3.

In summary, the optimal mixed layer thickness is found to be at 30 to 40 nm for the investigated devices H1–H3. The devices prepared at room temperature C1 and C2 show that the limitations due to the lower charge collection necessitate a lower thickness, i.e. in their case approximately 20 nm are found to be optimal. A maximum power conversion efficiency of 4.9±0.2 % is found in both optimized devices H3 and H4. This is a substantial improvement compared to the best oligothiophene-C60 solar cells that were reported so far [12]. It is mainly the result of an improved morphology of the mixed layer, giving rise to an enhanced charge transport capability by better phase separation and hence more continuous percolation pathways. By this, not only the basic performance parameters like \( j_{\text{sc}} \) and FF increase but also the mixed layer thickness for obtaining the optimal results is higher and therefore more light can be converted.
Figure 6.24: Absorption, EQE and IQE of devices H1-H3. Performance parameters are given in Table 6.6.
In comparison to other small molecule solar cells, the obtained power conversion efficiency of 4.9±0.2 % is among the highest results that are reported in literature. Xue et al. [169] reported an efficiency of 5.0 % for CuPc - C60 solar cells, however, without commenting on the mismatch correction. For ZnPc - C60 solar cells an efficiency of 2.6 % was reported by Pfützner et al. [131]. In this study, substrate heating was used to achieve an optimized morphology of the mixed heterojunction but the device stack has not been optimized accordingly. The same author reported an efficiency of 2.9 % for solar cells utilizing ZnPc - C70 heterojunctions [170]. With the material DCV5T, which is related to the DCV6T presented here, Schulze et al. achieved an efficiency of 3.4 %, using flat heterojunctions. For other small molecule solar cells, e.g. with tetracene - C60 or 6T - C70 heterojunctions, the reported efficiencies are between 2 and 3 % [171, 172].

**Efficiency Verification in Outdoor Measurements**

To confirm the reported power conversion efficiencies of devices H1 – H3, an outdoor measurement was conducted on the balcony of the IAPP (51° 3’N, 13° 44’ 24”E) on the 9th of August in 2009. An aperture of 2.985 mm² is used. The intensity of the sun irradiation is determined with the outdoor reference diode. In Fig. 6.25 the corresponding JV-characteristics are presented. The performance parameters are given in Table 6.7. The temperature of the assembly platform is 32.8 °C. Nevertheless, a higher temperature of the devices during the measurement has to be expected. The real device temperature is estimated to be around 45 °C because the devices could not be cooled.
6.3 Optimizing the Layer Stack

Table 6.7: Performance parameters of devices H1 – H3 obtained by outdoor measurement. The corresponding JV-characteristics are given in Figure 6.25.

<table>
<thead>
<tr>
<th>device</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mAcm$^{-2}$)</th>
<th>FF (%)</th>
<th>$S$ (%)</th>
<th>$I$ (mWcm$^{-2}$)</th>
<th>$\eta_{PCE}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1 ($d_{mix}$=20 nm)</td>
<td>0.87</td>
<td>7.1</td>
<td>67.3</td>
<td>1.07</td>
<td>98.0</td>
<td>4.2±0.2</td>
</tr>
<tr>
<td>H2 ($d_{mix}$=30 nm)</td>
<td>0.86</td>
<td>8.3</td>
<td>65.8</td>
<td>1.08</td>
<td>98.3</td>
<td>4.8±0.2</td>
</tr>
<tr>
<td>H3 ($d_{mix}$=40 nm)</td>
<td>0.86</td>
<td>9.2</td>
<td>62.2</td>
<td>1.08</td>
<td>98.9</td>
<td>5.0±0.2</td>
</tr>
</tbody>
</table>

directly. Due to this reason a higher FF and a lower $V_{oc}$ are observed as compared to the above reported measurements at the sun simulator. However, $\eta_{PCE}$ of 4.2±0.2 %, 4.8±0.2 %, and 5.0±0.2 % are determined for devices H1 – H3, respectively. Thus, the reported efficiencies are confirmed and the devices are proven to provide high efficiencies up to 5.0 % under real working conditions.

6.3.3 Discussion of Quantum Efficiency and Loss Mechanisms

The power conversion efficiencies that were reported in the previous section for the devices H1 – H3 are very promising. As has been explained in this work so far, this is a result of careful optimization of several aspects like phase separation, mixing ratio, and layer stack design. Now, the IQE of these devices shall be discussed in more detail, in order to get a deeper insight into the quantum efficiency of these devices. By this, major loss mechanisms can be identified, offering new starting points for further improvement.

The absorption, EQE, and IQE of devices H1 – H3 were already presented above in Figure 6.24. These devices are prepared with substrate heating and therefore achieve higher quantum efficiencies compared to the devices C1, and C2 which are prepared at room temperature. This is mainly due to the effect of increased charge collection ($\eta_{CC}$) as is explained in Section 6.1.2. With increasing mixed layer thickness in the devices H1 – H3, the absorption and the EQE are rising. The IQE spectra of devices H1 – H3 exhibit values above 70 % in the wavelength range of the DCV6T-Bu absorption (500 to 650 nm). As denoted earlier, it is very remarkable that the IQE spectra of these devices are nearly equal, because it is expected that $\eta_{CC}$ decreases with increasing mixed layer thickness, while $\eta_{ED}$ and $\eta_{CT}$ should be unaffected. Another interesting feature of the IQE spectra is their strong dependence on the wavelength, showing significantly lower values at wavelengths beneath 450 nm than at higher wavelengths. These characteristics shall be discussed now by considering the results of optical simulations. The optical modeling of devices H1 – H3 provides detailed insight into the absorption pat-
Figure 6.26: IQE, EQE and absorption spectra of device H3. Next to the measured total absorption of the device, the absorption of active layers, i.e. the mixed DCV6T-Bu : C60 layer (40 nm) and the adjacent intrinsic C60 layer (15 nm), as well as the absorption of passive layers (all other) are presented. The absorption of passive layers is calculated using optical simulation and is subsequently subtracted from the total absorption to achieve the absorption of the active layers [124]. The internal quantum efficiency of the active layers (IQE_{act}) is then determined according to Equation (6.6).
terns within their layer stacks (see Figure 6.22). This enables to distinguish between absorption in the active layers, i.e. the mixed DCV6T-Bu : C60 layer ($d_{\text{mix}}=20-40$ nm) and the adjacent intrinsic C60 layer (15 nm), and absorption in passive layers, i.e. the HTLs, the metal contacts (ITO and Al), and the doped C60 layer as well as the glass substrate. Following the study of Burkhard et al. [124], the absorption spectrum of the active layers ($\eta_{A}^{\text{act}}$) is calculated by subtracting the simulated absorption of passive layers ($\eta_{A}^{\text{pas}}$) from the measured total absorption of the device ($\eta_{A}$), in order to reduce errors by inadequacies of the simulation.

In Figure 6.26 the several absorption spectra are exemplarily presented for the device H3, since it exhibits the highest $\eta_{\text{PCE}}$. Below 400 nm, the absorption of passive layers dominates the total absorption. This is mainly caused by absorption of the transport layers like Di-NPB. Above 400 nm, the absorption in passive layers is only between 10 to 20% and mainly caused by the metal layer. Accordingly, the IQE is significantly decreased in the lower wavelength region, because there the majority of absorbed photons does not contribute to the photocurrent. This explains the strong variations of the IQE with different wavelengths. The IQE spectrum is following the development of active absorption versus total absorption and is thus influenced by parasitic absorption.

With the given $\eta_{A}^{\text{act}}$ a modified IQE$^{\text{act}}$ can be established which is only accounting for the absorption of photons within active layers:

$$\text{IQE}^{\text{act}} = \frac{\text{EQE}}{\eta_{A}^{\text{act}}}. \quad (6.6)$$

It is only dependent on processes within the active layers and is no more influenced by parasitic absorption. IQE$^{\text{act}}$ of device H3 is also presented in Figure 6.26. Due to the large errors, it is only plotted in the wavelength range where $\eta_{A}^{\text{act}}$ is the dominating part. Apparently, high IQE$^{\text{act}}$ values up to 83% are achieved at a wavelength of 610 nm, decreasing to 67% at a wavelength of 420 nm. The reason for this decline can be found in the different exciton diffusion efficiency ($\eta_{\text{ED}}$) for C60 and DCV6T-Bu excitons. In particular, excitons created in the intrinsic C60 layer which is adjacent to the mixed layer have a lower probability to reach a D-A interface since they might also migrate into the n-doped C60 layer and recombine there. Therefore, IQE$^{\text{act}}$ is lower in the wavelength range dominated by C60 absorption. Besides this effect, the mixed DCV6T-Bu : C60 layer itself exhibits a very high IQE$^{\text{act}}$, which confirms that the mixed layer morphology in the heated device is considerably optimized. The reduced exploitation of C60 excitons that is found here, could be amended by the use of exciton blocking wide gap electron transport materials instead of n-doped C60.

Apparently, the absorption of photons in passive layers is a considerable loss mechanism. The amount of losses that are attributed to this effect can be estimated in the following way. By assuming that every absorbed photon in the device would contribute
Table 6.8: Equivalent currents of the total absorbed photon fluxes in the device \( (j_{\text{max}}) \) and in the respective active layers \( (j_{\text{max}}^{\text{act}}) \) compared to the photocurrent calculated from the EQE \( (j_{\text{sc}}^{\text{EQE}}) \). These quantities are calculated according to Equations (6.7) and (3.35), respectively. The integration limits are set from 300 to 750 nm and the sun spectrum AM 1.5 G is used as illumination. The ratio of \( j_{\text{max}}^{\text{act}} \) and \( j_{\text{sc}}^{\text{EQE}} \) with respect to \( j_{\text{max}}^{\text{total}} \) is given in brackets.

<table>
<thead>
<tr>
<th>device</th>
<th>( j_{\text{max}} ) (mAcm(^{-2}))</th>
<th>( j_{\text{max}}^{\text{act}} ) (mAcm(^{-2}))</th>
<th>( j_{\text{sc}}^{\text{EQE}} ) (mAcm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1 ((d_{\text{mix}}=20 \text{ nm}))</td>
<td>14.2</td>
<td>9.8 (69%)</td>
<td>7.9 (56%)</td>
</tr>
<tr>
<td>H2 ((d_{\text{mix}}=30 \text{ nm}))</td>
<td>15.6</td>
<td>11.5 (74%)</td>
<td>8.9 (57%)</td>
</tr>
<tr>
<td>H3 ((d_{\text{mix}}=40 \text{ nm}))</td>
<td>16.4</td>
<td>12.6 (77%)</td>
<td>9.7 (59%)</td>
</tr>
</tbody>
</table>

to the photocurrent (IQE is unity), the maximum current \( j_{\text{max}} \) given by

\[
j_{\text{max}} = e \int_{\lambda_1}^{\lambda_2} \Phi_{\text{flux}}(\lambda) \cdot \eta_A(\lambda) \, d\lambda
\]

is calculated. In the same form, a maximal current \( j_{\text{max}}^{\text{act}} \) is obtained which only accounts for absorption in the active layers \( (\eta_A^{\text{act}}) \). In Table 6.8 these maximal currents are compared to \( j_{\text{sc}} \) as calculated from the EQE by Equation (3.35). The integration limits are set from 300 to 750 nm and the sun spectrum AM 1.5 G is used as illumination photon flux \( \Phi_{\text{flux}}(\lambda) \). In device H1 the current according to the total absorption is 14.2 mAcm\(^{-2}\), while the current according to absorption in active layers is 9.8 mAcm\(^{-2}\). This means that a photon current equivalent to 4.4 mAcm\(^{-2}\) is lost to parasitic absorption. For devices H2 and H3 this loss amounts to 4.1 mAcm\(^{-2}\) and 3.8 mAcm\(^{-2}\), respectively. Therefore, the ratio of photons that can really be used for conversion, i.e. the ratio of photons absorbed in active layers, is 69 %, 74 %, and 77 %, respectively. These values show that parasitic absorption is a prominent effect significantly limiting the IQE. The development of this ratio from device H1 to H3 furthermore shows that there is indeed a gain in IQE upon increasing the mixed layer thickness. For higher \( d_{\text{mix}} \) this ratio becomes larger, which means that a higher amount of the absorbed photons can be utilized for photocurrent generation. This improves the IQE and can nominally be considered as increase in \( \eta_{\text{ED}} \). However, \( \eta_{\text{ED}} \) is originally defined to address the exciton diffusion efficiency within the active layer and not meant to account for parasitic absorption. Nevertheless, this effect explains why the IQE of the devices H1–H3 appears to be rather independent on the mixed layer thickness. In fact, it is assumed that the negative effect of decreasing \( \eta_{\text{CC}} \) with rising \( d_{\text{max}} \) is compensated by the positive effect of a higher ratio of photons that are absorbed in active layers.

Comparing the \( j_{\text{sc}} \) values which are calculated from the EQE spectra \( (j_{\text{sc}}^{\text{EQE}}) \) to \( j_{\text{max}} \) shows how much of the absorbed photon flux is really converted into photocurrent in the end. The ratio between both currents (given in brackets in Table 6.8) can be
6.3 Optimizing the Layer Stack

Figure 6.27: Individual absorption spectra of all passive layers of device H3 as obtained from optical simulation. In the inset, the equivalent current of these absorption spectra is given. This is the current that would be gained, when all absorbed photons in this layer were converted into photocurrent instead of being lost. It is calculated according to Equation (6.7) using a wavelength range of 300 to 750 nm and the sun spectrum AM 1.5 G as illumination.

considered as the total IQE of the device, i.e. an IQE averaged over all wavelength, and amounts to about 59 %. Summarizing the numbers for device H3, this means that only a $j_{sc}$ of 9.7 mA/cm$^2$ is extracted from a total absorbed photon current which is equivalent to 16.4 mA/cm$^2$. 6.7 mA/cm$^2$ are lost, 3.8 mA/cm$^2$ of them due to parasitic absorption and another 2.9 mA/cm$^2$ due to internal conversion processes which are accounted for by IQE$^{act}$. In other words, only 77 % of the absorbed photons are absorbed in active layers, where they are subsequently converted into photocurrent with an averaged IQE of 77 %. This results in a total averaged IQE of device H3 of 59 %. One should keep in mind that these numbers are determined for the wavelength range of 300 nm to 750 nm and will differ with another choice of integration limits. Nevertheless, these numbers point out that parasitic absorption is a prominent loss mechanism.

The origin of the parasitic absorption shall be discussed in more detail for device H3. In Figure 6.27 the individual absorption spectra of all passive layers are depicted. Furthermore, the losses that are attributed to the individual layers are given in the inset as equivalent current. This is the current that would be gained, when all absorbed photons in this layer were converted into photocurrent instead of being lost. It is calculated according to Equation (6.7) using a wavelength range of 300 to 750 nm and the sun spectrum AM 1.5 G as illumination. In other words, this is the current which is lost between $j_{max}$ and $\eta_{max}^{act}$. Apparently, the main losses are due to absorption in the metal
contact layer (2.0 mAcm$^{-2}$) and the HTLs (1.0 mAcm$^{-2}$). Although very thin (5 nm), the n-doped C60 layer gives rise to another loss of 0.3 mAcm$^{-2}$. While the metal layer is absorbing in the complete wavelength range, the HTLs mainly absorb below 400 nm and show only a small absorption tail from 400 to 550 nm, which might partly be caused by the dopant. In principle, the absorption of the metal can hardly be overcome. It may only be reduced by stronger absorption of the active layers, so that a lower amount of photons needs to be reflected at the metal contact. The absorption of the HTLs could be reduced by a further increase of their optical gap, ideally above 4.1 eV because this is the onset of sun irradiation. Additional improvements can be made by reducing the amount of dopants that are used and by replacing the n-doped C60 with a true wide gap electron transport material.

In summary, it is shown that absorption in passive layers plays an important role and is significantly limiting the IQE. For example, in the wavelength range from 300 to 750 nm only 77% of the absorbed photons in device H3 are absorbed in active layers. The main part of this parasitic absorption is due to the metal layer and the HTLs. The investigation of devices H1–H3 with increasing mixed layer thickness reveals that the ratio of absorption in active layers increases with $d_{\text{max}}$. From this point of view, polymer solar cells, which usually utilize very thick active layers and do not apply thick HTLs, have an advantage and were already shown to provide IQEs close to unity [5]. Generally, the IQE spectra of all devices are strongly influenced by the effect of parasitic absorption. Since this effect is not covered by the original definition of the IQE (see Equation (3.34)), a modified quantity $\text{IQE}^{\text{act}}$ (Equation (6.6)), which only accounts for photons that are absorbed in the active layers, is introduced. The development of this $\text{IQE}^{\text{act}}$ in device H3 shows a maximum of 83% at a wavelength of 610 nm and decreases to 67% at a wavelength of 420 nm. This discloses another loss mechanism that is attributed to a lower exciton diffusion probability of C60 excitons. Similar findings were reported recently for P3HT:PCBM solar cells [173]. However, the reason there was the large domain size of PCBM. Here, the lower $\eta_{\text{ED}}$ is attributed, to migration of C60 excitons into the n-doped C60 layer where they are lost for photocurrent generation, because they do not reach a D-A interface. This effect can be amended by use of wide gap electron transport materials currently under investigation at the IAPP [97].

### 6.4 Thermal Annealing

The previous investigations showed that morphology control is one of the main concerns for achieving solar cells with high power conversion efficiencies. Besides the possibility of substrate heating during the layer growth, which was presented in Section 6.1 and finally lead to $\eta_{\text{PCE}}$ of 4.9 ± 0.2% (device H2, H3), there are also other means to affect the morphology. One of these is the so-called thermal annealing or post
annealing, which means heating the finished solar cells to a certain temperature and for a specific time. In polymer solar cells this is a well known and widely used method [9, 174–176]. Also in small molecule solar cells thermal annealing was reported to improve the performance [38, 38, 148]. In this Section, it shall be shown that thermal annealing also affects mixed DCV6T-Bu : C60 heterojunction devices.

Here, the previously introduced devices C1 and C2 (Figure 6.19) are annealed at a temperature of approximately 85 °C and furthermore illuminated by white light LEDs at intensities corresponding to approximately 4 suns, to continuously test their stability and measure the JV-characteristics. Both devices are prepared at room substrate temperature, but are equal to the devices H2 and H3 in all other aspects, i.e. they comprise mixed DCV6T-Bu : C60 heterojunction layers of 20 nm and 30 nm thickness, respectively.

In Figure 6.28 the JV-characteristics of devices C1 and C2 are shown before (1st measurement) and after (2nd measurement) a heat-light treatment of 2000 h. The corresponding performance parameters are given in Table 6.9. The $j_{sc}$ increases and also $S$ is improved, showing the same trend as has been achieved with substrate heating during the mixed layer deposition. The development of the EQE and the absorption (Figure

Figure 6.28: JV-characteristics of devices C1 and C2 measured before (1st) and after the heat-light treatment (2nd). The nominal intensity $I^*$ of the sun simulator 16S-003-300 is 145 mWcm$^{-2}$ as measured by the reference diode S1337-33BQ. The performance parameters are given in Table 6.9.
Table 6.9: Performance parameters of devices C1 and C2 measured before (1st) and after the heat-light treatment (2nd). The nominal intensity $I^*$ of the sun simulator 16S-003-300 is measured by the reference diode S1337-33BQ. The corresponding JV-characteristics are given in Figure 6.28.

<table>
<thead>
<tr>
<th>device</th>
<th>$V_{oc}$ (V)</th>
<th>$j_{sc}$ (mAcm$^{-2}$)</th>
<th>FF (%)</th>
<th>$S$ (mWcm$^{-2}$)</th>
<th>$I^*$ (mWcm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1 (1st)</td>
<td>0.88</td>
<td>5.7</td>
<td>50.8</td>
<td>1.22</td>
<td>145</td>
</tr>
<tr>
<td>C2 (1st)</td>
<td>0.88</td>
<td>6.2</td>
<td>43.0</td>
<td>1.29</td>
<td>145</td>
</tr>
<tr>
<td>C1 (2nd)</td>
<td>0.90</td>
<td>7.6</td>
<td>51.2</td>
<td>1.10</td>
<td>145</td>
</tr>
<tr>
<td>C2 (2nd)</td>
<td>0.90</td>
<td>9.0</td>
<td>44.2</td>
<td>1.12</td>
<td>145</td>
</tr>
</tbody>
</table>

6.29) show that the same changes like in the devices with substrate heating are present: The absorption exhibits a slight enhancement at the low energy edge, even indicating the presence of the low energy absorption band, which is typically observed upon substrate heating of DCV6T-Bu layers (Section 5.3.1). Moreover, the EQE itself is significantly improved, showing an increase of the maximum EQE value by approximately 15 %-points and 22 %-points in device C1 and C2, respectively. Consequently, this reveals a substantial enhancement of the IQE. These effects are attributed to a similar change of morphology like that obtained for substrate heating during the layer deposition. That means a better ordering and stronger phase separation can also be achieved by thermal annealing and thus lead to an increase of $j_{sc}$, especially by improving $\eta_{CC}$ due to the presence of more continuous percolation pathways for charge transport. $V_{oc}$ is not significantly altered. Also the FF seems not to be changed. This is attributed to the opposite effects of annealing, which improves the FF, and degradation of the device, which reduces the FF. This is illustrated in Figure 6.30, where the time dependent development of $j_{sc}$ and FF of devices C1 and C2 during the heat-light treatment is presented. This graph allows for the determination of relevant times for the annealing process. Note that these characteristics are measured during the annealing, i.e. at a sample temperature of approximately 85 °C and with a light intensity of approximately 4 suns. Therefore the values can not directly be compared to the values given in Table 6.9. FF and $j_{sc}$ show a strong increase during the first 10 to 60 h. Here, the FF reaches its maximum and subsequently declines. In contrast, $j_{sc}$ increases further and reaches its maximum between 200 to 400 h. This shows that rather long time scales are needed to achieve a considerable morphology change with this method.

In summary, a positive thermal annealing effect can be shown for devices C1 and C2 using a sample temperature of approximately 85 °C. The findings are similar to the results obtained for substrate heating, i.e. FF, $j_{sc}$ and $S$ are improving while the $V_{oc}$ stays constant. The absorption shows features that are typical for DCV6T-Bu layers grown at elevated substrate temperatures and furthermore the EQE is increased. This is attributed to a change in morphology equivalent to the results with substrate heating, meaning that
6.4 Thermal Annealing

**Figure 6.29:** Absorption and EQE of devices C1 and C2 measured before (1st) and after the heat-light treatment (2nd).

**Figure 6.30:** Development of $j_{sc}$ and FF of devices C1 and C2 during the first 800 h of the heat-light treatment. The measurements are done at a sample temperature of $85\pm1{}^\circ\text{C}$ under illumination by a white light LED with an intensity corresponding to approximately 4 suns.
the molecules rearrange to achieve stronger phase separation and consequently the percolation pathways for charge transport are improved. In the presented investigation, the annealing effect takes place on a time scale up to 200 to 400 h, which is rather slow, and therefore competes with degradation. It is suggested that a faster progression can be achieved with higher temperatures. However, it is apparent that the method of substrate heating during the evaporation of the active layer is advantageous compared to thermal annealing, due to several aspects. First, it is faster because it achieves the optimized morphology directly during the sample preparation. Moreover, only layers up to the active layer are heated, meaning lower thermal stress for the top wide gap layers. And last but not least, it can be used selectively, e.g. in multicell structures every active layer can be produced using its own optimized temperature conditions.
7 Conclusions and Outlook

7.1 Conclusions

In this thesis, the effect of the active layer morphology on the performance of small molecule solar cells is studied. It is investigated how morphology can be controlled by substrate heating during the active layer deposition and how this influences the properties, which are relevant for solar cells. Using the material system \(\alpha, \omega\text{-bis(dicyanovinylene)}\)-sexithiophene (DCV6T) - C60, it is the first aim to provide a deeper understanding of morphology-performance relations, and second to achieve an optimized solar cell with high power conversion efficiency.

Two DCV6T derivatives, DCV6T-Et and DCV6T-Bu, differing only by length and substitution pattern of the side chains, are investigated. These materials exhibit high absorption with the optical gap at 1.7 eV and a maximum absorption coefficient of \(3.2 \pm 0.3 \cdot 10^5 \text{cm}^{-1}\). Furthermore, they provide a high IP of 5.4 eV sufficient for good charge separation in heterojunctions with C60, while still enabling high photovoltages up to 0.9 V.

In neat layers, substrate heating leads to a transition from homogeneous and smooth layer growth towards a three-dimensional growth mechanism with strong crystallite aggregation. This is proven by XRD, and AFM investigations for both DCV6T-Bu and DCV6T-Et layers and can be attributed to a higher molecule mobility on the hot surface, which facilitates self ordering. Concomitantly, the absorption spectra display a more distinct fine structure, a redshift of the absorption peaks by up to 11 nm, and a significant increase of the low energy absorption band, when substrate temperatures up to 120 °C are applied. The hole mobility of DCV6T-Bu is measured by OFET and with the CELIV method, showing a temperature and field dependence typical for hopping transport. Both investigations reveal a slight decrease of mobility for the heated DCV6T-Bu layers, contrary to the general expectations. It can be concluded that the self ordering effect does not provide a better stacking of the \(\pi\)-electron systems, as is for example the case in \(\alpha\text{-sexithiophene}\). However, a lower activation energy of the hole
mobility is found in the heated sample, consistent to the higher molecular order. The highest mobility is observed in OFET devices prepared at room substrate temperature, reaching $\mu_h=2.43\pm0.22\cdot10^5 \text{cm}^2/\text{Vs}$.

In mixed layers, investigations by AFM and UV-Vis spectroscopy reveal that substrate heating induces a stronger phase separation, leading to larger domains of DCV6T in the mix, proven by a more pronounced fine structure of the DCV6T related absorption and an increase in grain size and roughness of the topography. Furthermore, the luminescence signal of DCV6T is shown to increase upon substrate heating, indicating that less excitons reach an D-A interface. Consequently, a lower exciton diffusion efficiency is expected in the heated layers. The upper limit for the exciton diffusion efficiency in mixed DCV6T-Bu : C60 heterojunctions is determined by comparison with the luminescence signal heights of neat layers, resulting in $88\pm4\%$ at a substrate temperature of $110^\circ\text{C}$. These results are quite promising in respect of solar cells, because the phase separation between donor and acceptor is a decisive parameter for the tradeoff between efficient exciton collection on the one hand and loss-free charge transport on the other hand. It is demonstrated that the variation of substrate temperature is a very convenient technique to control the degree of phase separation, and therefore is a well suited method for morphology optimization.

Based on the results of the morphology analysis, solar cells prepared at different substrate temperatures are investigated. In DCV6T-Et/C60 solar cells with a flat heterojunction, substrate heating leads to a slight increase of photocurrent by about 10%, mainly caused by higher absorption in the DCV6T-Et layer. Besides this effect, no further improvement is achieved. This is in accordance to the observation that the hole mobility does not increase upon substrate heating, as measured for DCV6T-Bu layers.

In mixed DCV6T : C60 heterojunctions substrate temperatures varying between -7°C and 120°C are investigated and significant effects on the solar cell performance are observed. In particular, by inducing a stronger phase separation the charge transport in the mixed layer is significantly improved upon heating. This leads to a large increase of the IQE, $j_{sc}$, and FF. Hence, a major increase of power conversion efficiency from 0.5% at $T_{\text{sub}}=-7^\circ\text{C}$ to about 3.0% for $T_{\text{sub}}\geq 77^\circ\text{C}$ is achieved. The effect of decreasing exciton diffusion efficiency upon substrate heating is completely outweighed by the gain in charge collection probability. It is only relevant at very high substrate temperatures of 120°C, where it limits the photocurrent.

By evaluating the intensity dependence of photocurrent and $V_{\text{oc}}$, the development of recombination behavior in the mixed heterojunction solar cells is studied for varying substrate temperatures. Heated devices exhibit only little recombination losses at high backward up to low forward voltages and are dominated by direct recombination, e.g. Langevin type, at voltages approaching $V_{\text{oc}}$. On the other hand, devices prepared at $T_{\text{sub}}=-7^\circ\text{C}$ and $T_{\text{sub}}=30^\circ\text{C}$ exhibit a significant loss of photocurrent at voltages near
7.1 Conclusions

0 V (e.g. at \( j_{sc} \)) which is mainly attributed to indirect recombination, e.g. Shockley-Read-Hall type. For voltages approaching \( V_{oc} \) a transition to direct recombination dominated behavior is found. However, at \( V_{oc} \) recombination via indirect processes is still relevant in these solar cells. These results are attributed to the higher degree of phase separation and the higher molecular order which are achieved upon substrate heating. By this, the probability of indirect recombination by trapping of charges in deep tail states, on separated molecules, or in dead ends is reduced and therefore charges can be extracted faster and more efficiently in heated devices.

Additionally to the choice of substrate temperature during the deposition of the active mixed layer, also the mixing ratio itself plays an important role. The comparison of different composition ratios of DCV6T-Bu : C60 heterojunctions displays an increasing grain size in the AFM pictures for an increasing amount of DCV6T-Bu. The corresponding solar cells show the best performance at a DCV6T-Bu : C60 mixing ratio of 2 : 1. Although higher ratios of DCV6T-Bu are found to increase the absorption further, the drop in FF causes an overall efficiency decrease.

While the first part of the work is focusing on the correlation between active layer morphology and performance, the second part of the work addresses the optimization of whole working solar cells incorporating the mixed DCV6T-Bu : C60 heterojunction which showed the best results in the previous studies. Therefore, a mixing ratio of 2:1 and a substrate temperature of 90 °C during the deposition of the mixed layer is chosen. Using an n-i-p structure, the influence of the thicknesses of the hole transport layer and the active layer are investigated, so as to find the layer design with maximum efficiency.

An appropriate thickness of the hole transport layer is particularly important for placing the active layer in the maximum of the optical field distribution. By performing optical simulations based on the transfer-matrix-formalism this optimum is determined at an overall thickness of all transport layers of 45 nm and has been subsequently confirmed with solar cell measurements.

For the mixed layer thickness the optimum is found at 30 to 40 nm, and the respective devices reach a power conversion efficiency of 4.9 ± 0.2 %. This value is further verified in an outdoor measurement. In contrast, devices prepared at room temperature showed the maximum efficiency already at a mixed layer thickness of approximately 20 nm, which is attributed to the lower charge collection probability in these heterojunctions.

Based on the optimized devices showing a high efficiency, the role of IQE is investigated in detail, in order to get a deeper insight into the quantum efficiency within the active layers and to identify major loss mechanisms. It is shown that absorption in passive layers plays an important role and is significantly limiting the IQE. For example, in the wavelength range from 300 to 750 nm, only 77 % of the absorbed photons in the device are absorbed in active layers. The main part of the parasitic absorption is due to
the metal layer and the HTLs. Using optical simulations the IQE of the active layers, consisting of an intrinsic C60 layer (15 nm) and a mixed DCV6T : C60 layer (40 nm), is determined and can be analyzed free of the effects of parasitic absorption. The IQE spectrum shows a maximum of 83 % in the absorption range of DCV6T-Bu but declines when going towards lower wavelengths. It is concluded that the exciton diffusion efficiency of C60 excitons is lower, due to the possible migration into the adjacent electron transport layer of n-doped C60, where they are lost.

Finally, thermal annealing of a DCV6T-Bu : C60 heterojunction solar cell after preparation is tested and found to induce similar improvements in solar cell performance like obtained for substrate heating. However, the annealing effect using a temperature of approximately 85 °C takes place on a time scale of 200 to 400 h. Accordingly, this method seems not to be applicable regarding large scale production and needs further investigation, which should firstly address the acceleration of the annealing process.

7.2 Outlook

In this work, a power conversion efficiency of 4.9±0.2 % is shown in a small molecule single heterojunction solar cell. This is among the highest reported efficiencies for this type of solar cells and a very promising result for the future success of organic photovoltaics. More than the result itself, the findings that made this result possible are important for upcoming research and development efforts.

With the information given in this work, the material system DCV6T - C60 not only provides high efficiency solar cells, but can also serve as a model system for the investigation of morphology-performance relations. There are several aspects that should be addressed in further works, in order to gain a more complete and detailed understanding of the influence of morphological parameters on the solar cell performance. The determination of the crystal structure of the DCV6T material would shine light on remaining questions. With this information a deeper understanding of the optical transitions and their variations with substrate temperature, e.g. the origin of the low energy absorption edge in heated layers, could be clarified. Moreover, the reason that the mobility is not increasing with a higher molecular order can be addressed by this. Another open question is the development of hole and electron mobilities in the mixed layers with varying substrate temperatures. Although the increase of pure DCV6T domain size by higher phase separation and a better charge collection probability are demonstrated in this work, it has still to be investigated whether this improvement is related to the better carrier mobility of electrons or holes, or even both on equal scales. Furthermore, the crystallinity of DCV6T in mixed layers should be investigated more deeply, e.g. by X-ray diffraction or transmission electron microscopy, because crystalline domains can
be expected from the results of this work but still lack their discovery. At the same time the effect of substrate heating on the crystallinity of C60, which could not be addressed in this work, should be checked.

Concerning device optimization, this work discusses some loss mechanisms in the optimized solar cell that need to be addressed in future works. Such a problem is parasitic absorption, which is shown to cause considerable losses, in particular in the metal anode layer and in the hole transport layer. These losses could be amended by transport materials with larger optical gaps. In this respect, also the absorption fraction of the dopant has to be considered. A general possibility to reduce the parasitic absorption, especially in the reflecting metal layer, is the application of a thicker active layer. However, this thickness is mainly limited by the electrical properties of the active material and therefore a real reduction of this loss will only come with implementation of new higher absorbing materials or by using multiple-junction structures. The second loss mechanism is the decreased exciton collection efficiency in C60 compared to DCV6T, which is caused by exciton migration into the adjacent n-C60 layer. Here, the use of a real wide gap n-type transport layer would be beneficial, because the excitons would then be blocked and therefore a higher quantum efficiency could be achieved.

Based on the presented optimized solar cells, which only utilize photons of energies higher than 1.7 eV, the incorporation into tandem cells seems very promising. By using infrared absorber materials which are currently under investigation, power conversion efficiencies of 7% or higher might be approached.

Clearly, an optimized performance is not possible without control of the active layer morphology. The author wants to encourage the transfer of the experience gained from the model system DCV6T-C60 towards any other small molecule heterojunction system. In particular substrate heating appears to be a very convenient method for providing morphology control, and on basis of the p-i-n concept the successive optimization of all morphological parameters and layer thicknesses, is generally adoptable to any other small molecule material. Combined with the increasing efforts in organic chemistry and the development of new absorber materials, the ultimate goal of flexible, lightweight, low-cost, and long-living organic photovoltaics seems a bit closer.
In Chapter 6 only solar cells in n-i-p structure were discussed, i.e. the ITO electrode provides the electron collecting contact and the metal electrode on top provides the hole collecting contact. This sequence can also be inverted and is then called p-i-n structure. Such structures, where the ITO is the hole collecting contact and the metal electrode is the electron collecting contact, are for example reported in [12, 51]. In terms of optimization of the thin film optics a p-i-n structure is favorable compared to the n-i-p structure. The reason is that the acceptor material C60 is mainly absorbing in the blue wavelength range and therefore at lower wavelength than the DCV6T donor materials. The optical interference maximum of the blue light is closer to the reflecting electrode, and so C60 has to be placed closer to the electrode in order to achieve its maximum absorption. In Section 6.3.1 it was shown that this is not possible in the presented n-i-p structures. In p-i-n structures, however, this is easily possible, because there the electrons are collected at the metal electrode and therefore C60 is automatically placed adjacent to it. So, why is the p-i-n design not the structure of choice for an optimized DCV6T - C60 solar cell? It appeared that the substrate heating, which is used to achieve an optimized morphology of the active layers, leads to a negative effect in p-i-n solar cells: S-shaped JV-characteristics. Although this effect is not sufficiently understood at the moment, these results shall be presented in the following to set the basis for further research and to show why p-i-n devices are not considered for the development of an DCV6T - C60 solar cell with optimized efficiency.

In Figure 7.1 the layout of the investigated p-i-n devices S1 – S7 is presented. They comprise either flat DCV6-Et / C60 (S3, S4) or mixed DCV6-Et : C60 (S5 – S7) heterojunctions. BPAPF is utilized as HTL as has been the case in the n-i-p devices. The n-contact is provided by a thin layer of Bphen on top of C60 followed by the 100 nm Al layer. Devices S1 and S2 are reference samples without the DCV6T-Et layer, but with a flat BPAPF / C60 heterojunction. Devices S1, S3 and S5 are prepared without substrate heating ($T_{\text{sub}} = 30$ °C). In device S4 a substrate temperature of 100 °C is applied during
Figure 7.1: Schematic layer design of devices S1–S7 with p-i-n structure. S1 and S2 are reference samples without the DCV6T-Et layer, but with a flat BPAPF/C60 heterojunction. S3 and S4 comprise flat DCV6T-Et/C60 heterojunctions. S3 is done without substrate heating \(T_{\text{sub}}=30^\circ \text{C}\), while in S4 the substrate is heated up to 100\(^\circ\)C during the deposition of the DCV6T-Et layer. Device S1 is annealed for approximately 15 minutes at 100\(^\circ\)C after deposition of BPAPF and before the deposition of C60, in order to investigate the effects of substrate heating on the transport layers. S5–S7 comprise mixed DCV6T-Et:C60 heterojunctions. The substrate temperature during deposition of the mixed layer is varied from 30\(^\circ\)C (S5) to 80\(^\circ\)C (S6) and 90\(^\circ\)C (S7).

The JV-characteristics of the flat heterojunction devices S1–S4 as measured under the sun simulator SOL 1200 are presented in Figure 7.2. The corresponding performance parameters are given in Table 7.1. The device without substrate heating (S3) exhibits reasonable parameters with \(V_{\text{oc}}=0.92\) V and \(\text{FF}=53.2\%\). In contrast, the heated device S4 shows an S-shaped curve with strongly decreased FF of 36.6\%. Also the \(V_{\text{oc}}\) and the \(j_{\text{sc}}\) are decreased. The reference samples without DCV6T-Et (S1, S2) show equal results despite of the annealing of device S2. Only \(V_{\text{oc}}\) in device S2 is slightly increased compared to S1.

the deposition of the DCV6T-Et layer. In devices S6 and S7 substrate temperatures of 80\(^\circ\)C and 90\(^\circ\)C, respectively, are used during the growth of the mixed DCV6-ET:C60 layer. To study the effects of substrate heating on the underlying BPAPF layers, the reference device S2 is annealed for approximately 15 minutes at 100\(^\circ\)C after deposition of BPAPF and before the deposition of C60.
Figure 7.2: JV-characteristics of devices S1 – S3 measured under illumination with the sun simulator SOL 1200. Performance parameters are presented in Table 7.1.

Figure 7.3: JV-characteristics of devices S5 – S7 measured under illumination with the sun simulator SOL 1200. Performance parameters are presented in Table 7.1.
Table 7.1: Performance parameters of devices S1–S7. The corresponding JV-characteristics are presented in Figure 7.2 and Figure 7.3.

<table>
<thead>
<tr>
<th>device</th>
<th>$V_{oc}$ (V)</th>
<th>$j_{sc}$ (mAcm$^{-2}$)</th>
<th>FF (%)</th>
<th>$S$</th>
<th>$I^*$ (mWcm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d$_{DCV6T-Et}=$0 nm</td>
<td>0.94</td>
<td>2.7</td>
<td>56.2</td>
<td>1.28</td>
<td>105</td>
</tr>
<tr>
<td>S1 ($T_{sub} =$30°C)</td>
<td>0.97</td>
<td>2.5</td>
<td>57.25</td>
<td>1.17</td>
<td>102</td>
</tr>
<tr>
<td>d$_{DCV6T-Et}=$10 nm</td>
<td>0.92</td>
<td>5.2</td>
<td>53.2</td>
<td>1.16</td>
<td>104</td>
</tr>
<tr>
<td>S3 ($T_{sub} =$30°C)</td>
<td>0.81</td>
<td>4.2</td>
<td>36.6</td>
<td>1.19</td>
<td>102</td>
</tr>
<tr>
<td>d$_{mix}=$20 nm</td>
<td>0.90</td>
<td>9.8</td>
<td>43.8</td>
<td>1.20</td>
<td>129</td>
</tr>
<tr>
<td>S5 ($T_{sub} =$30°C)</td>
<td>0.91</td>
<td>11.0</td>
<td>39.0</td>
<td>1.14</td>
<td>118</td>
</tr>
<tr>
<td>S6 ($T_{sub} =$80°C)</td>
<td>0.91</td>
<td>11.2</td>
<td>35.6</td>
<td>1.12</td>
<td>128</td>
</tr>
<tr>
<td>S7 ($T_{sub} =$100°C)</td>
<td>0.91</td>
<td>11.2</td>
<td>35.6</td>
<td>1.12</td>
<td>128</td>
</tr>
</tbody>
</table>

The JV-characteristics of the mixed heterojunction devices S5–S7 are given in Figure 7.3. They are also measured under the sun simulator SOL 1200. The corresponding performance parameters are summarized in Table 7.1. The device without substrate heating (S5) exhibits $j_{sc}$, $V_{oc}$, $S$, and FF of 9.8 mAcm$^{-2}$, 0.90 V, 1.20, and 43.8 %, respectively. Again, with substrate heating during the deposition of the active mixed layer (S6, S7) an S-shape occurs and therefore the FF is significantly reduced to 39.0 % (S6) and 35.6 % (S7). However, $V_{oc}$ is not affected. Moreover, the $j_{sc}$ increases with substrate heating and also the saturation factor $S$ is improved, reaching values of 11.0 mAcm$^{-2}$ and $S=1.14$ in device S6 ($T_{sub} =$80°C) and 11.2 mAcm$^{-2}$ and $S=1.12$ in device S7 ($T_{sub} =$90°C). This indicates that the same morphology effects upon substrate heating, i.e. better absorption and charge transport due to higher molecular order of DCV6T-Et and stronger phase separation, are also present in these p-i-n solar cells. Nevertheless, the performance is impaired by the additional effect causing the S-shape.

Although S-shaped JV-characteristics are often observed in different kinds of organic solar cells, it is not comprehensively understood how they evolve [177–180]. Different reasons are possible. The most common observation is that the contacts to the metal electrodes are not ohmic. As can be seen from the performance of the reference devices and the not heated devices (S1, S2, S3), this can be excluded for the chosen contacts. The Bphen/Al contact is in any case prepared at room temperature and therefore not affected by the substrate heating during the active layer deposition. A non-ohmic contact between ITO and p-BPAPF, which may be caused by the substrate heating, e.g. by degradation of the doping, can also be excluded, since the annealed reference device (S2) shows the same performance as its counterpart (S1). In another device of the same structure like device S3, the in situ measurement of the lateral conductivity of the
p-doped BPAPF showed a decrease by only 10% during annealing for 30 min. at 90°C.

In former studies of oligothiophene-C60 and 4,4’-Bis-(N,N-diphenylamino)-quaterphenyl (4P-TPD)-C60 solar cells, S-shapes were reported to be caused by injection barriers between the HTL and the donor [12, 69, 127]. An injection barrier means that the transport level of the HTL is lying higher in energy than that of the donor. In flat heterojunction solar cells, this situation caused an S-shaped JV-characteristic, while in mixed heterojunction solar cells a reduction of the $V_{oc}$ was observed instead. Recently, Tress et al. reported that the opposite situation, i.e. an extraction barrier with the transport level of the HTL lying lower in energy than that of the donor, may also lead to an S-shape, which is then present in both flat and mixed heterojunction solar cells [159].

In order to reveal transport barriers, UPS measurements of DCV6T-Et layers on top of BPAPF are conducted. Figure 7.4 shows the layout of the respective samples. The layer sequence is equal to the p-side of the investigated solar cells. Only Ag is used as substrate instead of ITO and the thin layer of gold is omitted. Sample I is prepared without substrate heating, while in sample II the substrate is heated to 90±10°C during the deposition of the DCV6T-Et layer. UPS spectra are recorded on the BPAPF layer and on the DCV6T-Et layer, respectively. During the measurements a charging effect appeared, which seemed to be caused by the p-doped BPAPF, since it is not present with other hole transport materials. This effect leads to a shift of the spectra to higher binding energies when measured several times. The shift between two measurements, e.g. between the first scan and the second detailed measurement of the HBEC amounts to approximately 100 meV and has to be considered as error. For comparison, solely the first detailed measurements of the HBEC and the HOMO region are chosen from every measurement series. The resulting spectra are presented in Figure 7.5. The corresponding energy values for the HOMO onset, the HBEC and the workfunction ($\Phi$) are summarized in Table 7.2.
Appendix

Figure 7.5: UPS spectra of samples I and II with DCV6T-Et on top of BPAPF. The left graph shows the HBEC region. The right graph shows the HOMO region. In sample I the DCV6T-Et is deposited at room temperature, while in sample II a substrate temperature of 90 ± 10 °C is used during the deposition. The corresponding energies of HBEC, HOMO onset, and the workfunction are summarized in Table 7.2.

Table 7.2: Energies of the HBEC, the HOMO onset, and the workfunction (Φ) of samples I and II. The corresponding UPS spectra are given in Figure 7.5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>HBEC (eV)</th>
<th>HOMO (eV)</th>
<th>Φ (eV)</th>
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<td>BPAPF</td>
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<td>0.55</td>
<td>5.1</td>
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<td>4.87</td>
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<tr>
<td>sample II</td>
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<tr>
<td>BPAPF</td>
<td>16.09</td>
<td>0.57</td>
<td>5.13</td>
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<tr>
<td>DCV6T-Et (T_{sub} = 90 °C)</td>
<td>16.20</td>
<td>0.65</td>
<td>5.02</td>
</tr>
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</table>
It can be seen that the DCV6T-Et HOMO onset of the heated sample (II) is equal to
that of the sample prepared at room temperature (I). Only the HOMO peak position and
the HBEC are shifted by approximately 100 meV and 150 meV, respectively, towards
lower binding energies. The HOMO position of the BPAPF is equal in both samples.
Although the slight shift of the HBEC and the HOMO peak indicate a change in the
energy alignment of DCV6T-Et upon substrate heating, the measurements do not reveal
any development of transport barriers, which might explain the S-shape. However, the
presented measurements only compare the energy levels of the surface of the 5 nm thick
DCV6T-Et layer. The band bending cannot be resolved from these data and therefore
the measurement is not able to detect changes of the energy alignment within the first
monolayers at the BPAPF/DCV6T-Et interface. Anyway, for closer investigations the
technical problems of the shifting spectra have to be solved first.

In summary, the p-i-n solar cells with substrate heating suffer from a reduced FF, caused
by an S-shaped JV-characteristic. This effect is present in both flat and mixed DCV6T-
C60 heterojunction solar cells. The reason for this effect is not resolved yet. A degra-
dation of the p-doped BPAPF layer or non-ohmic contacts can be excluded. The UPS
investigation of the energy alignment of a 5 nm thick DCV6T-Et layer on top of BPAPF
did not reveal any transport barriers that evolve upon substrate heating. However, a
more detailed study of the band bending directly at the interface, like for example
reported in [181] for ZnPc : C60 or in [182] for 6T, is suggested for further investiga-
tions. Also other reasons like an imbalance of electron and hole mobilities could be
considered. Although this effect largely impairs the device performance, the increase
of $j_{sc}$ and the improvement of the saturation factor $S$ in the mixed heterojunction de-
vices using substrate heating show that the positive effect of improved morphology is
nonetheless present. Therefore, it will be possible to achieve optimized efficiencies
also with p-i-n devices as soon as the S-shape effect is overcome, e.g. by other material
combinations.
# List of Materials

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<thead>
<tr>
<th>Material</th>
<th>Description</th>
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</tr>
<tr>
<td>6T</td>
<td>α-sexithiophene</td>
</tr>
<tr>
<td>BCP</td>
<td>2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline</td>
</tr>
<tr>
<td>BPAPF</td>
<td>9,9-bis[4-(N,N-bis-biphenyl-4-yl-amino)phenyl]-9H-fluorene</td>
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<tr>
<td>Bphen</td>
<td>4,7-diphenyl-1,10-phenanthroline</td>
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<tr>
<td>C60</td>
<td>Buckminster fullerene</td>
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<tr>
<td>CuPc</td>
<td>copper-phthalocyanine</td>
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<tr>
<td>DCV6T</td>
<td>α,ω-bis(dicyanovinylene)-sexithiophene</td>
</tr>
<tr>
<td>DCV5T</td>
<td>α,α-bis(dicyanovinylene)-quinqueithiophene</td>
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<td>Di-NPB</td>
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<td>F4-TCNQ</td>
<td>2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane</td>
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<td>H₂Pc</td>
<td>phthalocyanine</td>
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<td>MePTCDI</td>
<td>N,N′-dimethyl-3,4,9,10-perylenetetracarboxylic diimide</td>
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<tr>
<td>P3HT</td>
<td>poly(3-hexyl thiophene)</td>
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<tr>
<td>PCBM</td>
<td>[6,6]-phenyl-C61-butyric acid methyl ester</td>
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<tr>
<td>PTCDA</td>
<td>3,4,9,10-perylene tetracarboxylic dianhydride</td>
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<tr>
<td>ZnPc</td>
<td>zinc-phthalocyanine</td>
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List of Abbreviations

<table>
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<th>Abbreviation</th>
<th>Description</th>
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<td>AFM</td>
<td>atomic force microscopy</td>
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<tr>
<td>CT</td>
<td>charge transfer</td>
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<td>CV</td>
<td>cyclic voltammetry</td>
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<td>D-A</td>
<td>donor-acceptor</td>
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<tr>
<td>EA</td>
<td>electron affinity</td>
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<td>ETL</td>
<td>electron transport layer</td>
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<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
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<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
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<tr>
<td>HBEC</td>
<td>high binding energy cutoff</td>
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<td>HOMO</td>
<td>highest occupied molecular orbital</td>
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<td>HTL</td>
<td>hole transport layer</td>
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<td>IAPP</td>
<td>Institut für Angewandte Photophysik</td>
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<tr>
<td>IC</td>
<td>internal conversion</td>
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<tr>
<td>IE</td>
<td>ionization energy</td>
</tr>
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<td>IPES</td>
<td>inverse photoelectron spectroscopy</td>
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<td>ITO</td>
<td>indium tin oxide</td>
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<td>IV</td>
<td>current-voltage</td>
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<td>JV</td>
<td>current density-voltage</td>
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<td>LCAO</td>
<td>linear combination of atomic orbitals</td>
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<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
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<td>organic light-emitting diode</td>
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<td>PIA</td>
<td>photo-induced absorption</td>
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<td>quartz crystal monitor</td>
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<td>rms</td>
<td>root mean square (-roughness)</td>
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<td>SEM</td>
<td>scanning electron microscopy</td>
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<td>standard reporting conditions</td>
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<td>unidentified flying object</td>
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<td>ultraviolet photoelectron spectroscopy</td>
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## Appendix

### Assignment of Solar Cells to Database Data

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Bibliography


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Erklärung

Diese Dissertation wurde am Institut für Angewandte Physik/Photophysik der Fakultät Mathematik und Naturwissenschaften an der Technischen Universität Dresden unter wissenschaftlicher Betreuung von Prof. Dr. Karl Leo angefertigt.

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David Wynands
Dresden, den 08.02.2011