Infrared Absorber Materials in Organic Small Molecule Solar Cells

Dissertation
zur Erlangung des
akademischen Grades
Doctor rerum naturalium,
(Dr. rer. nat.)

vorgelegt von
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geboren am 14. August 1979 in Dresden

Dresden 24.08.2015
Eingereicht am 23.04.2015

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Verteidigt am 24.08.2015
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Abstract

Broadening the spectrum available to solar cells towards infrared wavelengths is one way to increase efficiency of organic solar devices. This thesis explores the possibilities of these organic heterojunction devices and two different material classes in thin films and organic solar devices: tin phthalocyanines (SnPcs) and aza-bodipys.

To estimate the efficiency reachable under sunlight, model calculations are done for single and tandem cells. These calculations include a distinction between the optical gap and the electrical gap and the splitting of the quasi-Fermi levels. With a number of assumptions, e.g. a fill factor (FF) and an external quantum efficiency (EQE) within the absorption range of 65%, the resulting efficiencies are 15% in a single cell and of 21% in a tandem cell.

Halogenation is known to lower the energy levels of molecules without changing the optical band gap. Three different fluorinated and chlorinated SnPcs are investigated and compared to the neat SnPc. While chlorination of SnPc worsens the transport properties of the active layer leading to a lowered FF, the fluorination of SnPc results in the intended increase in $V_{OC}$ and, consequently, efficiency for planar heterojunctions. In bulk heterojunction, however, fluorination does not change the efficiency probably due to the unstably bound fluorine.

One method to modify the ionization potential (IP) and the absorption of the second material class, the aza-bodipys, is the annulation of the benzene ring. The energy levels determined by CV and UPS measurement and DFT-calculation show very good agreement and can be linked to a decrease in $V_{OC}$: The Ph$_4$-bodipy (not benzannulated) device has an efficiency of 1.2% with an EQE reaching up to 800 nm and a $V_{OC}$ of almost 1 V. The Ph$_2$-benz-bodipy device shows a $V_{OC}$ of 0.65 V and an efficiency of 1.1%, the EQE reaching up to 860 nm.

The variation of the molecule’s end groups to vary their IP is successfully employed for three different benz-bodipys: The variation results in a decrease of the optical gap from 1.5 eV for the phenyl group, to 1.4 eV for the MeO group, and 1.3 eV for the thiophene group with the effective gap and the $V_{OC}$ following this trend. Efficiencies of 1.1% and 0.6% in combination with C$_{60}$ can be reached in nip-type devices. Ph$_2$-benz-bodipy is then optimized into a single cell with an efficiency of 2.9%. In a tandem cell with DCV6T-Bu4:C$_{60}$, a $V_{OC}$ of 1.7 V, a FF of 57% and an efficiency of 5% is reached.
Die Erweiterung des verfügbaren Spektrums in den Infrarotbereich ist eine Möglichkeit, die Effizienz organischer Solarzellen zu erhöhen. Diese Arbeit erkundet das Potential dieser Heteroübergänge und zwei Materialklassen in dünnten Schichten und Bauelementen: Zinphthalocyanine (SnPc) und aza-Bodips.

Um die potentielle Effizienz abzuschätzen, werden Modellberechnungen für Einzel- und Tandemzellen durchgeführt, unter Berücksichtigung des Unterschieds von optischer und elektrischer Bandlücke und der Quasiferminiveauaufspaltung. Mithilfe einiger Annahmen (z.B. Füllfaktor (FF) und externe Quanteneffizienz (EQE) gleich 65 %) lässt sich die Einzelzelleffizienz auf 15 %, die Tandemzelleffizienz auf 21 % abschätzen.

Halogenierung kann die Energieniveaus organischer Moleküle herabsetzen, ohne die optische Bandlücke zu verändern. Drei verschiedene chlorierte und fluorierte SnPcs werden mit dem reinen SnPc verglichen. Während die Chlorierung die Transporteigenschaften der aktiven Schicht und den FF verschlechtert, erhöht die Fluorierung wie erwartet Leerlaufspannung ($V_{OC}$) und Effizienz im flachen Übergang, nicht jedoch in der Mischschicht, vermutlich aufgrund des nicht stabil gebundenen Fluors.

Ein Weg, Ionisationspotential (IP) und Absorption der aza-Bodips zu verändern, ist die Anelierung des Benzenrings. Die durch CV und UPS ermittelten und mittels DFT errechneten Energieniveaus stimmen gut überein und führen zu einer Verringerung der $V_{OC}$: Die Zelle mit nichtaniliertem Ph$_4$-bodipy zeigt eine Effizienz von 1.2 %; das EQE reicht bis 800 nm, die $V_{OC}$ beträgt fast 1 V. Die Ph$_2$-benz-bodipy-Zelle zeigt eine $V_{OC}$ von 0.65 V und eine Effizienz von 1.1 %, das EQE reicht bis 860 nm.

Der Austausch der Endgruppen zur Vergrößerung des IP, erfolgreich angewandt auf drei Benz-Bodip-verbindungen, führt zu einer Verringerung der optischen Bandlücke: von 1.5 eV (Phenyl) über 1.4 eV (MeO) zu 1.3 eV (Thiophen); effektive Bandlücke und $V_{OC}$ folgen diesem Trend. Effizienzen von 1.1 % und 0.6 % in Kombination mit C$_{60}$ werden in nip-Zellen erreicht. Ph$_2$-benz-bodipy zeigt in einer optimierten nip-Zelle sogar eine Effizienz von 2.9 %. Eine Tandemzelle mit DCV6T-Bu4:C$_{60}$ zeigt eine $V_{OC}$ von 1.7 V, einen FF von 57 % und eine Effizienz von 5 %.
Also in a long term, sun, water, and wind cannot satisfy more than 4% of our electricity demand.
– Angela Merkel, German minister for the environment, 1994

In total, the renewable energies solar, wind, water, and biomass [...] produced ca. 30% of the public net electricity production in 2014 in Germany.
– Fraunhofer ISE Freiburg, January 2015.
1 Introduction

Ever since the start of the discussion on climate change the question of how our energy needs should be met has been raised. Not least for that reason, the renewable energy have taken an increasing part in energy production: From 2004 to 2013 the total renewable power capacity worldwide has almost doubled from 800 GW to 1560 GW [1] From a physical point of view, photovoltaic power generation appears to be the most elegant for electricity supply: the abundant solar energy is converted directly into an electric current. Yet, only 31 TWh of the 632 TWh electricity produced in Germany in 2013 was produced by solar cells [2].

Germany has an estimated area of roofs and facades of about 2300 m$^2$ available for PV installations with a reasonable output [3]. Though not all these surface have an optimal angle, with a yearly solar energy intake of about 1 TWh/km$^2$ a, a higher share could be envisaged. One reason is, naturally, the still high price of solar installations, partly compensated by feed-in tariffs.

Another reason is the difficulty of access of these roofs. Silicon modules are heavy, about 20 kg/m$^2$, which makes installation cost a considerable share of the overall cost. This may be one reason why, in 2012, only 35 out of about 4300 buildings belonging to the Saxon state had photovoltaic modules installed on their roofs [5]. On the other hand, many building surfaces are not included in the estimation above, as they do not support the weight of solar installation or are shaped in ways not suitable for the rigid silicon technology, e.g. lightweight constructions and airhouses.

Flexible and light weight solar cells on foils in general and organic photovoltaics (OPV) in particular can help address this issue. Organic solar cells are very thin; thicknesses of a few hundred nanometers including the contacts make it lighter and much less brittle than silicon single crystal solar cells. They can be printed

Figure 1.1: Design study: Building integrated OPV; from [4].
or evaporated onto PET or PEN substrates in a roll-to-roll reducing the overall weight by a factor of 20 while enabling customized dimensions. Hence, they can be used on glass facades, tents or even lorry covers.

Furthermore, film thicknesses are easily adaptable, allowing for the fabrication of transparent solar cells. This further broadens the range of applications to the actual window area. Here, it can extend the functionality of already existing tinted windows to electricity generation.

Being an emerging technology, many issues remain to be solved: PET and other foils materials have a considerably higher water vapor transition rate, hence, powerful, yet, flexible encapsulation has to be developed. For transparent bottom contact, OPV like all other photovoltaic technologies relies on indium tin oxide (ITO), which is brittle and expensive. Additionally, with power conversion efficiencies (PCE) of about 12% in the lab, there is room and need for improvement as every increase in efficiency also means a decrease in price.

One approach is the broadening of the solar spectrum available to the solar cell. As ultraviolet (UV) light is potentially harmful to organic compounds, this broadening has to take place towards absorbers utilizing infrared (IR) light. These infrared absorbers can be further beneficial for transparent OPV: with the human eye having its maximum sensitivity at about 550 nm, introducing an IR absorber into the cell’s stack can result in an increase in PCE without the corresponding decrease in transparency in the visible (VIS).

These IR absorbers are the focus of this work. After introducing the basic physics of organic semiconductors in general in Chapter 2 and of organic photovoltaics in particular in Chapter 3, Chapter 4 outlines the materials and methods used in this study. In Chapter 5, an estimation of the efficiency potential of organic single and tandem cells aims to outline what is necessary in terms of harvesting a wider spectrum. In Chapter 6 the performance of halogenated, IR absorbing tin phthalocyanines is investigated and discussed.

Chapters 7 and 8 examine two different ways to modify aza-bodipy compounds in order to tune electrical and optical properties for an absorption increase in the IR: benzannulation (Chapter 7) and end group variation (Chapter 8). In Chapter 9 solar cells incorporating one particular aza-bodipy compound, Ph$_2$-benz-bodipy, are optimized for an increased efficiency. The material, finally, is combined with the green absorber DCV6T-Bu$_4$ in a series of tandem solar devices.
2 Physics of Organic Solids

The following chapter starts with a short introduction to the physics of organic and especially aromatic solids in comparison to inorganic solids. The next part addresses the $\pi$-electron system of organic semiconductors and their excited states. Then, the generation and transport of excitons is explained. The final part will focus on charge carriers in a molecular solid and the intentional doping of organic semiconductors.

2.1 Organic Molecular Crystals

Organic molecules form solid crystals that differ strongly from their inorganic counterparts, in mechanical and optical as well as in electrical properties. They tend to have lower densities and melting temperatures as well as much lower concentrations and mobilities of charge carriers.

The dominating forces governing the intermolecular interactions are the main reason for this behavior. In inorganic solids the rather strong covalent and ionic bonds (in the region of several electron volts) lead to high densities and melting temperatures. The electronic states are highly delocalized. The description via Bloch states takes into account the high periodicity of the solid’s lattice. Thus, the physics of an inorganic crystal is largely determined by its structure.

In organic solids, however, the free, unpaired valence electrons needed for covalent bonding between the molecules are usually not available. Consequently, Vander-Waals forces\(^1\) are dominating the crystal structures. These forces are based on fluctuating multipole moments and only reach magnitudes of 0.01 eV and lower [6]. It follows that intramolecular forces are much higher than forces between molecules; the molecules exist separately. The delocalization of the electronic wave function and the electron density between the molecules are comparatively low, leading to low charge carrier mobilities and permittivities. The small intermolecular forces lead, furthermore, to a large influence of pressure, temperature, and electric field when forming an organic molecular crystal.

Additionally, polarization constitutes an important factor in organic solids. While negligible in inorganic materials, the polarization energy in organic solids

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\(^1\)Johannes Diderik van der Waals (1837 - 1923)
Figure 2.1: When two carbon atoms approach each other the sp$_2$-orbitals form $\sigma$-bonds within the plane, the remaining p$_z$-orbitals form $\pi$-bonds perpendicular to the plane, resulting in an ethene molecule. As the p$_z$-orbitals overlap less the $\pi$-orbitals of ethene are split less than the $\sigma$-orbitals. Adapted from [7].

may exceed 1 − 2 eV. Hence, the model of energy bands is no longer applicable straightforward; organic semiconductors are considered to have levels that are still reflecting the single molecule orbitals. This is described in more detail in Section 2.3. The physics of organic molecular solids are determined by the properties of the molecules it consists of.

2.1.1 Delocalization in Conjugated Systems

The materials employed in this work are organic semiconductors. The cause of their high conductivity compared to the otherwise often insulating organic solids is the sp$_2$-hybridization: the s-, p$_x$ and p$_y$-orbitals of the carbon valence electrons combine to create mixed orbitals, the so-called sp$_2$-orbitals. These are lying within a plane and form $\sigma$-bonds with neighboring sp$_2$-orbitals (see Figure 2.1).
Perpendicular to this plane, the remaining $p_z$-orbitals form $\pi$-bonds. This covalent bonding of atoms within a molecule with alternating single and double bonds is called conjugation. It results in a delocalization of electrons which in turn not only increases the stability of the molecule, but also the materials conductivity as there exists a strong $\pi-\pi$-coupling between molecules. The properties of these organic materials are largely defined by their $\pi$-electrons.

### 2.2 Energies and Excitations

#### 2.2.1 Organic Molecules

The Coulomb\(^2\) interaction between atoms and electrons lifts the degeneracy in orbital energy when these atoms approach each other. Two new orbitals are the result. One, usually denoted $\Phi_+$, is called the bonding orbital, as it is non-zero everywhere between the two nuclei (see Figure 2.2). Hence, the electron density is non-zero as well, which allows the bonding of the two atoms. The other one $\Phi_-$ is zero at one point between the two nuclei and along with it the electron density. Bonding is not possible, the orbital is, thus, called antibonding. The bonding $\Phi_+$ has a lower energy than $\Phi_-$, both electrons, consequently, occupy $\Phi_+$. As the Pauli principle\(^3\) demands, both electrons have to have different spins. For more complex molecules it becomes increasingly complicated to analytically calculate the orbitals, but the formation of bonding and antibonding orbitals as well as the appearance of energy gaps remains a general principle.

As the $p_z$-orbitals overlap less than the $sp_2$-orbitals, they also lead to the smaller splitting of the intramolecular orbitals (see Figure 2.1). Thus, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are formed by the $\pi$-orbitals of the molecule, which are denoted $\pi$ and $\pi^*$. Considering excitations of the electrons, the $\pi-\pi^*$-transition also translates into the lowest electrical excitation possible and is called the electrical gap of a molecule.

The larger the $\pi$-conjugation is made by adding more contributing $p_z$-orbitals, the smaller the gap between $\pi$ and $\pi^*$ becomes, as the additional electronic states increase the splitting within the $\pi$- Orbitals. The decreased difference between HOMO and LUMO can be observed for series of simple arenes [9]. Upon adding benzene rings to a benzene molecule, the gap is reduced from 4.88 eV to 2.13 eV in pentacene. This shows the importance of the existence and size of $\pi$-conjugated systems: As the $\pi$-conjugation clearly determines the electrical properties of a molecule, it also determines its behavior upon optical excitation.

\(^2\)Charles-Augustin de Coulomb (1736 - 1806)

\(^3\)Wolfgang Pauli (1900 - 1958)
Figure 2.2: The wavefunctions of two atoms form two new wavefunctions when combined to form a molecule: a bonding one ($\Phi_+$) and an anti-bonding one ($\Phi_-$). Adapted from [8].

When a molecule absorbs a photon it gets excited. This generally means an electronic excitation where an electron is excited into a higher state ($S_1, S_2...$). As organic materials usually have an even number of electrons, obeying the Pauli-principle leads to an overall spin of zero; the ground state of these molecules is, therefore, a singlet state ($S_0$). Additionally, the photonic energy can be converted into vibrations of the nucleus, so-called vibronic states of this electronic state. Their energy differs from $0.06 \text{ eV}$ to $0.25 \text{ eV}$ [10].

The probabilities of the transitions are determined by the overlap of the orbitals of the initial and the final state. The larger the overlap the larger the probability of a transition. This so-called Franck-Condon principle$^4$ is illustrated in Figure 2.3. The overlap of wavefunctions allows the nucleus to best adapt its motion to the new electronic potential. The Jablonski scheme$^5$ in Figure 2.4 illustrates some of the transitions possible in a molecule. Each transition has its own characteristic rate. While electronic excitations have a typical duration of $10^{-15}$ s, the subsequent relaxation into the lowest vibronic state of the excited electronic

$^4$James Franck (1888 - 1946) and Edward Condon (1902 - 1974)
$^5$Aleksander Jablonski (1898 - 1980)
state takes place in the range of picoseconds [9] and is called internal conversion (IC). There, the electrons have a typical lifetime of nano- to microseconds.

The subsequent relaxation again not necessarily ends in the vibronic and electronic ground state of the molecule, but can also end in a higher vibronic state. This transition is usually accompanied by the emission of a photon and followed by the thermal relaxation into the ground state $S_0$ but can also take place entirely non-radiatively.

The emission is called fluorescence when the electron relaxes from an excited singlet state. It is mainly governed by the $S_0$-$S_1$ transitions. This is very common and known as Kasha’s rule\(^6\) [13]. It states that the molecule reaches the lowest excited state much faster than it can fluoresce, when the involved energy levels are close to each other, which is usually the case for all singlet states but $S_0$ and $S_1$. Hence, the emission wavelength is independent of the energy of the exciting photon.

\(^6\)Michael Kasha (1920 - 2013)
A direct excitation into a triplet state, i.e. a state with both electrons having the same spin is forbidden, as it would require excitation and a spin-flip at the same time. However, a weak spin-orbit coupling allows the spin of the excited molecule to flip when a vibrational mode of an excited triplet state with compatible energy is available. This \textit{intersystem crossing (ISC)} is facilitated when heavy atoms (e.g. bromine, iridium) are incorporated into the molecule, which enhances the spin-orbit coupling. The radiative relaxation into the ground state is called phosphorescence. As this process requires the spin of the electron to turn again, the lifetimes of triplet states are much higher than the lifetimes of singlet states and can approach several seconds \cite{9}. The phosphorescence usually occurs at smaller wavelengths than the fluorescence. The lower energy of the triplet state owing to the smaller repulsion of same-spin electrons causes this bathochromic shift.

Figure 2.5 shows the absorption and the emission of MePTCDI\textsuperscript{7} dissolved in chloroform. The energetic difference between the maximum of absorption and the maximum of emission, called Stokes shift\textsuperscript{8}, is very small. This means only little energy is lost to internal conversion. Both spectra are mirror symmetrical because of the similarity of vibronic states in electronic ground and excited state.

\footnote{MePTCDI: N,N'-dimethylperylene-3,4,9,10-dicarboximid}

\footnote{Sir George Stokes (1819 - 1903)}
2.2 Energies and Excitations

Figure 2.5: Absorption and emission of MePTCDI: The absorption of energy-rich photons, internal conversion and the subsequent emission of photons of smaller energy into different vibronic states of $S_0$ as well as the similarity of the vibronic states of $S_1$ and $S_0$ lead to the mirror symmetry of absorption and emission spectra. Measurements were done in chloroform. From [14].

2.2.2 Organic Solids

As already explained in Section 2.1, intermolecular forces are small for organic molecules since they lack the unpaired valence electrons needed for covalent bonding. Molecular properties will, therefore, remain important for their solid counterparts. Consequently, the absorption and emission properties are only slightly modified.

Figure 2.6 shows the changes in energy levels when going from a single molecule to a solid governed by Van-der-Waals forces. The interaction with the surrounding solid leads to the broadening of the energy levels. As it is smaller than the interactions in inorganic solids, also the broadening remains comparatively small.

The HOMO corresponds to the hole transport level $E_h$ in the solid. Its energy is the energy needed to extract an electron, the ionization potential (IP). The hole is able to polarize its surrounding solid. Consequently, $E_h$ is shifted upwards by the polarization energy $P_h$ compared to the HOMO. While in inorganics this
Figure 2.6: The overlap of many wavefunctions in a solid leads to a broadening of the energy levels. These are also stabilized owing to polarization of the surrounding solid by the charge carrier; adapted from [16].

polarization energy can be neglected, it is usually high compared to the broadening of the energy levels in organic materials\(^9\) [15]. Polarization of charge carriers is further discussed in Section 2.3.

The HOMO eigenstate of a molecule charged once, HOMO(M\(^-\)), is often also called “LUMO for additional electrons” as the LUMO is obviously the first orbital to be occupied by an added electron. It is, however, slightly changed by the additional charge. In the solid, this HOMO(M\(^-\)) becomes the electron transport level \(E_h\). Its energy is determined by the electron affinity (EA). This energy as well is stabilized by the polarization energy \(P_e\) originating from the polarization of the surrounding solid by the electron. The difference between \(E_h\) and \(E_e\) is called the electrical gap \(E_g\) of an organic solid. EA, \(E_e\) and LUMO are sometimes used synonymously for organic solids. This is likewise true for IP, \(E_h\) and HOMO. In this work, mainly the terms EA and IP are used.

### 2.2.3 Excitons

An electron can be excited by absorbing a photon. Together with the vacancy created in the valence level, this electron-hole pair can be regarded as an electrically

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\(^9\)Therefore, the term “level” is also used for solid instead of the otherwise common “band”
2.2 Energies and Excitations

Figure 2.7: Exciton formation: The screening of excited electrons depends on the dielectric constant of the material. Therefore, in inorganic solids, usually, Wannier excitons with low binding energies are formed; in organics Frenkel excitons with high binding energies are found. Excitons spreading over neighboring molecules are called charge transfer excitons. After [12].

neutral quasi-particle, also called exciton [17]. The Coulombic bonding between electron and hole determines its size. In inorganic semiconductors with their highly delocalized electrons and large dielectric constant, the electric field screening is high. Thus, the binding energy of the exciton is typically on the order of 0.01 eV and can easily be overcome thermally. Considering them as hydrogen-like bound electrons with an effective mass leads to exciton radii of several nanometers (Figure 2.7). These excitons were first described by Wannier and Mott\textsuperscript{10} and are called Wannier excitons [18, 19]. In contrast, as described in Section 2.1, the overlap of the electronic wavefunctions of different molecules within an organic solid is small as well as the dielectric constant. The excitons are of the size of one molecule leading to exciton binding energies of 0.2 eV - 1.5 eV [12, 20]. As these energies are much larger than the thermal energy\textsuperscript{11}, this so-called Frenkel-exciton\textsuperscript{12} is not as easily dissociated.

Additionally, charge transfer excitons are known [21]: Here, the exciton only extends over a few adjacent molecules and electron and hole remain Coulombically bound.\textsuperscript{13}

Transport

The diffusion of excitons in an isotropic medium obeys the diffusion equation:

\[ \frac{p(\vec{r})}{\tau_0} - D \frac{d^2p(\vec{r})}{d\vec{r}^2} = G(\vec{r}), \]  

\textsuperscript{10}Gregory Hugh Wannier (1911 - 1983), Sir Nevill Francis Mott (1905 - 1996)
\textsuperscript{11}kT, at 300 K about 25meV
\textsuperscript{12}Yakov Il’ich Frenkel (1894 - 1952)
\textsuperscript{13}For polymers this can be further divided into intrachain excitons and interchain excitons
with the generation rate \( G(\vec{r}) \), the exciton density \( p(\vec{r}) \), the diffusion constant \( D \) and the exciton lifetime \( \tau_0 \). With \( D \) and \( \tau_0 \) an exciton diffusion length \( L_e \) can be defined:

\[
L_e = \sqrt{D\tau_0}
\]  

(2.2)

This diffusion length is a measure for the distance excitons can travel before they decay, an important value for organic solar cells where these excitons have to travel to an interface to be split into separate free charges (more on this in Section 3.2.1).

The transport of the exciton quasi-particle can mainly take place in three different ways:

**Emission-Absorption** This is the most important process over ranges larger than 10 nm: the excitonic energy is emitted as a photon by the first molecule; the second molecule reabsorbs it, a new exciton is created.

**Förster resonance electron transfer (FRET)**  
This transfer is due to a dipole-dipole interaction of the electron-donating molecule and the electron-accepting molecule: The former induces an oscillation in the latter, thereby, transferring the energy. As the FRET does not change the spin of both donor and acceptor, it is a singlet-singlet transfer. Despite sometimes being called fluorescence resonance energy transfer, it is a radiationless process as only virtual photons are exchanged. As it rapidly decreases with distance \( r \) \((\propto r^{-6})\) it occurs only for distances of up to 10 nm [22, 23].

**Dexter energy transfer (DET)**  
The DET occurs via actual transfer of electrons. As this requires the overlap of the electronic wavefunction of the donating and the accepting molecule, its rate decreases exponentially with distance. The DET is, therefore, only relevant on scales of about 1 nm. As the spin of the electron is also transferred it is the dominant mechanism in triplet-triplet energy transfer [24].

All these processes crucially depend on the spectral overlap of the emission of the electron donor and the absorption of the electron acceptor.

### 2.3 Charge Carriers

For the description of charge carrier transport in inorganic semiconductors, the band model introduced by Bloch\(^\text{16}\) in 1928 can be used [25]. The periodicity of
the lattice and the overlap of orbitals lead to broad transport bands; the charge carriers move quasi-free with an effective mass through the lattice, their wave function is modulated by the ionized atoms. In an electric field $\vec{E}$ they can reach relatively high velocities $\vec{v}$. As the mobility $\mu$ of a material is defined as

$$\vec{v} = \mu \vec{E}$$

it is tantamount to say inorganic semiconductors have comparatively high mobilities for electrons and holes. Silicon, for example, has a hole mobility of $450 \text{ cm}^2/\text{Vs}$ [26]. For band transport the mobility is decreasing with increasing temperature due to the interaction with phonons; e.g. for acoustic phonons $\mu$ is proportional to $T^{-3/2}$. Only for very low temperatures, the mobility increases for increasing temperatures due to scattering on ionized trap sites in the solid.

As described in Section 2.2.2 the bandwidth B of the transport levels is decreased in organic semiconductors. If it is small compared to the polarization energy $E_{pol}$

$$B \ll E_{pol},$$

quasi-particles called polarons are formed. As the electronic polarization of the surrounding molecules is the fastest and strongest effect, it commonly governs the polarization of charge carriers resulting in an electronic polaron: The time for this dipole-dipole interaction to occur is usually smaller than the charge carrier localization time; the charge carrier travels with its polarization cloud. Therefore, the charge carrier transport levels $E_h$ and $E_e$ introduced in Section 2.2.2 are actually polaron transport levels [27].

For carriers with very low mobilities, also interactions with the intramolecular vibrations can occur, leading to so-called vibronic polarons. For very large localization times as for trapped carriers, even the comparatively slow interaction with the lattice becomes important.

These polarons usually no longer travel within a band but via a hopping process: the polarization and the small intermolecular overlap owing to the high disorder in the usually amorphous or polycrystalline organic solids lead to the localization of the charge carriers at molecular sites. These localized charge carriers will move from one molecule to the next with a certain probability - they hop. However, this probability is low which leads to charge carrier mobilities that are orders of magnitudes lower than mobilities in inorganics and can vary greatly. For example, metal phthalocyanines display mobilities between $10^{-5} \text{ cm}^2/\text{Vs}$ and $10^9 \text{ cm}^2/\text{Vs}$ depending on the substituted metal atom, morphology, and packing [28].

As this hopping process is thermally activated, the mobility increases with temperature. The energies of the transport levels are statistically distributed and several models have been suggested to explain this temperature dependence [12,
one being the so-called Bäsler model\textsuperscript{17} \cite{bassler}. This model considers the density of states (DOS) of the transport levels to be a Gaussian distribution. Hopping processes to neighboring states of lower energy are thought to be independent of the energetic difference, hopping to neighbors of higher energy depend on the energetic difference, field and temperature. The resulting mobility $\mu$ is

$$\mu = \mu_0 \exp \left[ - \left( \frac{T_0}{T} \right)^2 \right], \quad (2.5)$$

with $T_0 = \frac{2\sigma}{3k}$, $\mu_0$ as the mobility for an infinite temperature, and $\sigma$ as the distribution width of the Gaussian DOS.

Mobilities in organic solids also depend on the electric field, unlike their inorganic counterparts. Experimentally, the following dependency has been established for a large number of materials:

$$\mu(\left| \vec{E} \right|) = \mu_{E_0} \exp (\beta \sqrt{\left| \vec{E} \right|}), \quad (2.6)$$

with $\mu_{E_0}$ as the mobility without field and $\beta$ as the field amplification factor \cite{9}.

Furthermore, a dependency on the charge carrier density has been suggested to explain the mobilities measured in organic field effect transistors (OFETs) and hole-only devices, which sometimes differ up to three orders of magnitude for the same material \cite{30}.

It remains to be mentioned that band-like transport is not impossible in organics: in very pure and highly ordered organic solids, charge carrier transport is limited by scattering processes with phonons leading to mobilities of up to $400 \text{ cm}^2/\text{Vs}$. Additionally, it has been observed that organic crystals showing band-like transport for low temperatures appear to shift to transport via hopping at higher temperatures \cite{31, 32}.

### 2.3.1 Doping of Organic Semiconductors

The current density $\vec{j}$ in a solid depends both on the mobility of a charge carrier in this solid and the number of charge carriers $n$ present, which together define the conductivity $\sigma$ of the solid:

$$\vec{j} = -en\mu \vec{E} = \sigma \vec{E}, \quad (2.7)$$

with the elementary charge $e$. When the free electrons and holes in a semiconductor are created only thermally, it is referred to as intrinsic. As these intrinsic charge carrier densities are rather small at room temperature, even in inorganic solids, the materials are often doped: the matrix semiconductor is mixed with a

\textsuperscript{17}Heinz Bäsler (1938)
2.3 Charge Carriers

dopant. For better hole conduction the matrix is p-doped using an electron accepting material (acceptor, e.g. for silicon boron is often used); n-doping with an electron donating material leads to better electron conduction (donor, for silicon e.g. phosphor).

The Fermi level $E_F$ is the electrochemical potential at which a state has a probability of 0.5 to be occupied by an electron. In intrinsic semiconductors, the Fermi level is in the center of the band gap. As the electron of a donor is easily ionized, i.e. the ionization potential is low, the Fermi level of an n-doped layer is shifted towards the conduction band or electron transport level. In turn, the Fermi level is shifted towards the valence band or hole transport level by the increased electron affinity of the p-doping acceptor; this will be discussed in more detail in Section 3.1.1.

Likewise, organic semiconductors are dopable. p-Doping, for example, can be described as a reaction of a matrix molecule $M$ with an acceptor molecule $A$:

$$M + M + M + A \rightleftharpoons M + M + [M^+A^-] \rightleftharpoons M + M^+ + [MA^-] \rightleftharpoons \ldots \ (2.8)$$

This process is also illustrated in Figure 2.8: Firstly, an electron is transferred from the ground state of the matrix molecule to the electron transport level of the dopant $E_{E_{dopant}}$ of the neighboring dopant molecule. For this process to be sufficiently probable, the ground state should not lie deeper than $E_{E_{dopant}}$. The electron transfer leaves behind a hole on the matrix molecule, a so-called charge transfer state $[M^+A^-]$ is formed. To now form free holes ($M^+ + [MA^-]$) the Coulombic attraction between hole and electron has to be overcome. As this Coulomb energy is in the range of $0.5 \ldots 1\text{eV}$, again due to the weak electrical screening, thermal energy is not sufficient (similar to the dissociation of excitons created upon illumination, see Section 2.2.3). The creation of polarons lowering the energy of the system of transferred hole and localized electron is needed to split the charge transfer state [16].

For p-doping molecules with very deep lying energy levels are needed. These p-dopants can be inorganic such as tungsten oxide (WO$_3$) or lithium fluoride (LiF) as well as organic like small and reactive molecules such as F4TCNQ$^{19}$ [34, 35, 36]. Analogously, n-dopants have to have very shallow energy levels. Therefore, these n-dopants can easily be oxidized and are harder to find and difficult to process. However, e.g. acridine orange base (AOB) has proven to successfully n-dope the buckminster fullerene C$_{60}$ [37].

---

$^{18}$Enrico Fermi (1901 - 1954)

$^{19}$F4TCNQ: tetrafluorotetracyanoquinodimethane
Figure 2.8: Above: The matrix transfers an electron to the acceptor dopant resulting in p-doping. Below: The donor dopant transfers an electron to the matrix molecule leading to n-doping. The charge carriers have, then, to overcome the Coulombic binding energy. See e.g. [33].
3 Physics of Photovoltaics

The following chapter describes the principles of photovoltaic devices after introducing current techniques used in photovoltaics. The discussion of the pn-junction and the diode law will lead to the definition of characteristic values in solar cells and the idea of an ideal solar cell structure. After discussing general limits for the efficiency of this device, the organic solar cell in particular is described. The focus here lies on heterojunction (HJ) cells and the advantages of the pin-concept which is used e.g. in tandem devices.

3.1 Photovoltaics in General

Techniques in Photovoltaics

In 1839, the photovoltaic effect was published by Alexandre Becquerel\(^1\) for the first time [38]. Upon illuminating different liquids with immersed platinum rods he measured a small electric current in some of them. In 1876, Adams\(^2\) discovered that illuminating a junction between crystalline selenium and platinum also has a photovoltaic effect [39].

Though attempts to produce a photovoltaic cell soon followed, it was not until 1954 that commercial applications became possible: Chapin et al. [40] from the Bell Laboratories produced a silicon based solar cell with an efficiency of 6\%. However, high production costs limited the use of photovoltaics to space and satellite applications. Only after the first oil crisis of the 1970s research increased to make solar cell usage both efficient and less costly. As a result the price of photovoltaic modules has dropped almost by a factor of 100 over the last forty years (see Figure 3.1). Today, the price for crystalline silicon solar cells is at about 0.60\$/wp\(^3\) [42]. Grid parity, i.e. that electricity from PV modules can be produced at the average energy consumer prices, was reached in beginning of 2012 for Germany [43]. However, this grid parity price neglects extrinsic cost, e.g. grid stabilization but also fluctuating energy prices.

\(^1\)Alexandre Edmond Becquerel (1820 - 1891), father of the discoverer of radio activity and Nobel laureate Antoine Henri Becquerel

\(^2\)William Grylls Adams (1836 - 1915)

\(^3\)Wattpeak (1 Wp) is the power generated at standard reporting conditions (SRC)
Figure 3.1: New materials, concepts, and production techniques but also the tremendously increased output have led to a decrease in price from more than 60 $ in 1976 to about 0.60 $ in 2014 [41, 42]. From [42].

The crystalline silicon cell is the most common module type with a market share of about 85%. It reaches efficiencies of about 20.8% (multicrystalline, see Figure 3.2) and 25.6% (monocrystalline) in the laboratory and about 18.5% and 22.9%, respectively, in a module [44]. As the active Si layer of these cells is rather thick (200 - 300 μm, mainly owing to process limitations) the production of the bulk silicon substrate accounts for more than 50% of the module price. One approach to reduce production costs is therefore to decrease this layer thickness. For the layer transfer technique a thin silicon layer (a few microns) is electrochemically split from a wafer. It is then transferred to a low-cost substrate for further manipulation. Efficiencies of 21.2% have been reached with this process [44].

Thin film technologies additionally allow for flexible and semi-transparent devices. Amorphous silicon (a-Si) and hydrogenated silicon (a-Si:H) have been under investigation for quite some time. Typical thicknesses are about 1 μm. Devices are mainly used in indoor low-efficiency low-cost applications, though in the laboratory more than 13% have been measured. However, attempts to increase stability in turn increase the complexity of fabrication and, consequently, the price.
3.1 Photovoltaics in General

Besides silicon, also other materials are investigated to be used in thin film solar cells. Ternary compound semiconductors and their alloys like CuInSe (CIS) and Cu(In,Ga)(S,Se)$_2$ (CIGS) are used as active materials of a CdS window layer. They also have thicknesses of several microns. Laboratory efficiencies of about 20.5% have been reported [45]. Modules have shown efficiencies of about 17.5% [44]. However, two disadvantages hinder the wide success for these thin film devices: On the one hand, some of the materials used are rather scarce. For example, indium and gallium are not only rare but also used in other electronic devices, especially in light emitting diodes. On the other hand, cadmium is toxic. While stable in compounds, cadmium needs special attention during production and recycling of modules.

Another approach to decrease the costs of solar cells is to increase the efficiency. Multijunction devices, e.g. tandem cells of different materials are used to harvest a larger spectral part of the incoming light. However, the materials investigated like the III-V semiconductors GaAs and InP again face the problem of rareness and, thus, high price. To decrease material usage concentrators are used to collect light from an area much larger than the actual cell. By hundredfold concentrating the sun light onto multijunction cells, efficiencies of about 46% have been reported [46].

This overview clearly illustrates that quite a few different concepts are currently under investigation, none of which is without difficulties at some point. The threefold of efficiency, production costs, and stability is to be considered for every technique that sets out to make photovoltaic energy competitive.

3.1.1 pn-Junction

The working principle of photovoltaics is the transformation of solar photonic energy into electric energy, i.e. the conversion of photons into free electrons and holes. As explained in Section 2.2.1 the photon creates an excited electron upon its absorption. To ensure sufficient lifetimes of the excited state, a semiconductor is used whose band gap prevents fast, thermal relaxation. Electron and hole now have to be transferred out of the absorbing material at different positions. The most common way to realize this in inorganic semiconductors is the pn-junction: a p- and an n-doped semiconductor are brought together. Free electrons diffuse from the n-doped into the p-doped region to fill the holes driven by the concentration differences of free charge carriers in both sides. Thus, they create negatively charged ions and leave behind positively charged ions. As the ionized atom cores are left behind, an electric field develops and the resulting drift force eventually stops the diffusion (see Figure 3.3). The zone around the interface which is now depleted of free charge carriers is called depletion layer or space charge region (SCR).

4One can equally say, free electrons and holes diffuse to the interface to recombine there.
Figure 3.2: The efficiencies of photovoltaic devices have increased significantly in the last decades. While multijunction concentrators reach very high efficiencies but are too costly for large market shares, the thin film technologies already show efficiencies of more than 20% (Graph from [47]).
3.1 Photovoltaics in General

Energy Levels

Electrons are fermions. Consequently, Fermi statistics can be used to determine the electron density \( n \) in the conduction band. In the thermodynamic equilibrium including a surrounding black body radiation, the density depends on the Fermi distribution \( f(E) \) and the density of states \( D(E) \):

\[
n = \int_{E_C}^{\infty} f(E)D(E)dE, \tag{3.1}
\]

with conduction band energy \( E_C \). For Fermi levels \( E_F \) lower than \( E_C \) by more than a few \( kT \), only the lowest states in the conduction band are occupied and the Maxwell-Boltzmann approximation\(^5\) can be used to calculate the integral:

\[
n = 2 \left( \frac{2\pi m^*_e kT}{\hbar^2} \right)^{3/2} \exp \left( -\frac{E_C - E_F}{kT} \right), \tag{3.2}
\]

\[
= N_C \exp \left( -\frac{E_C - E_F}{kT} \right), \tag{3.3}
\]

where \( N_C \) is called the effective density of states in the conduction band and \( m^*_e \) is the effective mass in an ideal semiconductor. Equation 3.2 also explains the increase in charge carrier density upon doping the semiconductor which brings the Fermi level closer to the conduction level (see Section 2.3.1). The hole density \( h \) can be calculated analogously, using the valence band energy \( E_V \) and its effective density \( N_V \).

\[
p = N_V \exp \left( -\frac{E_F - E_V}{kT} \right). \tag{3.4}
\]

When an n-doped layer is now combined with a p-doped layer, the energies have to rearrange along with the charge carrier densities. By definition, there is only one constant Fermi level in a semiconductor at thermodynamic equilibrium. As shown in Figure 3.3 the bands have to change at the interface; this band bending introduces an electrical potential between the two layers, called built-in potential \( E_{bi} \). It represents the field formed by the diffused charge carriers. It can be calculated:

\[
E_{bi} = E_g - kT \ln \left( \frac{N_CN_V}{N_AN_D} \right), \tag{3.5}
\]

with the concentrations of ionized acceptors and donors, \( N_A \) and \( N_D \), respectively.

\(^5\)Ludwig Boltzmann (1844 - 1906) and James Clerk Maxwell (1831 - 1879)
Figure 3.3: Before the p-doped material and the n-doped material are brought into contact (left side), the densities of the majority charge carriers in each layer are higher than the density of the minority charge carriers by orders of magnitudes. Fermi levels are close to the transport band of the majority charge carriers. Upon contact (right side) the density gradient causes free charge carriers to diffuse into the opposite layer. That results in a field developing that eventually stops the diffusion when the Fermi energies are evened out. The region depleted with free charge carrier is called space charge region.

Diode Law

At equilibrium without any applied bias $V$ or illumination, energy conservation laws demand the current density $j$ to be zero. However, when a negative bias\(^6\) is applied to an ideal pn-junction, electrons and holes are drawn from the interface and the space charge region expands. New electrons and holes are created only by the black body radiation resulting in a saturation current $j_S$. As this process is bias-independent the current in reverse direction is limited to $j_S$. The behavior in forward direction is very different. The positive bias pushes electrons into the n-doped and holes into the p-doped layer, the space charge region is reduced.

---

\(^6\)A negative bias is defined such that the positive pole is connected to the n-doped layer and vice versa.
3.1 Photovoltaics in General

The electrons and holes recombine at the interface. The current density increases exponentially with increasing voltage. This diode-like behavior can, hence, be described by the diode law

\[ j = j_s \left[ \exp \left( \frac{eV}{kT} \right) - 1 \right]. \tag{3.6} \]

Upon illumination photons are absorbed creating electrons and holes within the bulk of the semiconductor. These charge carriers diffuse and are separated by the field when reaching the space charge region; a photocurrent \( j_{Ph} \) is generated, flowing in backward direction. When it is taken to be field independent, the diode law can be modified to:

\[ j = j_s \left[ \exp \left( \frac{eV}{kT} \right) - 1 \right] - j_{Ph}. \tag{3.7} \]

Solar Cell Parameters

Figure 3.4 schematically shows the J-V-characteristics resulting from the diode law both in dark and upon illumination. From it, also the main characteristic parameters of a solar cell can be deduced:

**Short-circuit current density \( j_{SC} \):** The current density without any bias applied. For an ideal pn-junction this is equal to the photocurrent \( j_{Ph} \).

**Open-circuit voltage \( V_{OC} \):** The bias voltage that has to be applied to achieve zero current. As the name suggests this is equal to the terminal voltage of the pn-junction. In an ideal pn-junction it depends logarithmically on the photocurrent:

\[ V_{OC} \propto \ln \left( \frac{j_{Ph}}{j_s} \right) \text{ for } j_{Ph} \gg j_s. \]

**Maximum power point MPP:** The point in the J-V-characteristics where the product of current and bias voltage is maximal, hence, where the solar cell can deliver the highest power density \( p_{MPP} \).

**Fill factor FF:** The ratio of the power density at the MPP and the product of \( j_{SC} \cdot V_{OC} \). In Figure 3.4 the fill factor can be considered being the ratio of areas of the hatched and the unhatched rectangle.

The power conversion efficiency \( \eta \) of a solar cell for a given illumination power density \( p_{Light} \) can, therefore, be determined:

\[ \eta = \frac{p_{MPP}}{p_{Light}} = \frac{FF V_{OC} J_{SC}}{p_{Light}}. \tag{3.8} \]
Figure 3.4: The current density-voltage characteristics (J-V-curve) of an ideal heterojunction diode in the dark saturate in the backward direction of voltage and increases exponentially in forward direction. Upon illumination the J-V-curve is shifted by the photocurrent which, thus, forms the short-circuit current density $j_{SC}$. At the open-circuit voltage $V_{OC}$ no current is flowing. The power density, derived from the product of current density and voltage, is maximal at the maximum power point MPP. Inset: Logarithmic representation of the J-V-curves.

The maximum efficiency of a solar cell is discussed further in Section 3.1.4.

To describe real solar cells the diode law (Equation 3.7) has to be extended to incorporate parasitic influences. Electrically this can be done by introducing additional resistances. The inset in Figure 3.5 shows the equivalent circuit diagram that has been extended by an additional series resistance $R_S$ and an additional parallel resistance $R_P$. The extended diode law is now:

$$j = j_S \left[ \exp \left( \frac{e(V - j R_S)}{kT} \right) - 1 \right] + \frac{V - j R_S}{R_P} - j_{Ph}. \quad (3.9)$$

Figure 3.5 shows the influence of both types of resistances. The introduction of a parallel path for the current impedes the saturation of the current density in backward direction. Additionally, it lowers $V_{OC}$ where photocurrent and external current balance, as the latter is now increasing faster. The series resistance, in
3.1 Photovoltaics in General

3.1.2 Quasi-Fermi Levels

As described in Section 3.1.1 the current of electrons or holes is governed mainly by two effects: drift and diffusion. The first is a result of an electric field, hence, the gradient of an electrical potential coupling with the charge

$$\vec{E}(\vec{r}) = -\text{grad}\phi(\vec{r})$$

For the diffusion the gradient of the concentration is the driving force. For electrons, this is grad $n$. Using Fick’s law of diffusion\(^7\) and the definition of the conductivity $\sigma$ (Equation 2.7), the current density is:

$$j = \sigma \text{grad} \phi + e D \text{grad} n,$$

\(^7\)Adolf Eugen Fick (1829 - 1901)
with the electron diffusivity $D$. Considering Equation 3.2 for $n$, this can be rewritten as:

$$j = \sigma \text{grad} \phi + e D n \text{grad} \ln \left( \frac{n}{N_C} \right).$$

(3.11)

Since the position of the Fermi level depends on the electron density, the chemical potential $\mu_{\text{chem}}$ of an electron can be divided into a density-dependent part and a density independent part $\mu_{\text{chem},0}$ [48]

$$\mu_{\text{chem}} = \mu_{\text{chem},0} + kT \ln \left( \frac{n}{N_C} \right).$$

Hence, Equation 3.11 can be rewritten as

$$j = \sigma \text{grad} \phi + \frac{e D n}{kT} \text{grad} \mu_{\text{chem}},$$

(3.12)

and employing the Einstein-Smoluchowski relation\(^8\) about the diffusion of charged particles $\mu = eD/kT$ with the mobility $\mu$:

$$j = \sigma \text{grad} \phi + \mu n \text{grad} \mu_{\text{chem}}.$$  

(3.13)

Again using Equation 2.7 for the conductivity, this can be changed to

$$j = \sigma \text{grad} \phi + \frac{\sigma}{e} \text{grad} \mu_{\text{chem}} = \frac{\sigma}{e} \text{grad} \left( \frac{\phi}{e} + \mu \right).$$

(3.14)

Electrical and chemical potential of an electron can be combined to the electrochemical potential $\eta$. As explained in Section 2.3.1, this electrochemical potential is the Fermi level $E_F$:

$$j = \frac{\sigma}{e} \text{grad} \eta = \frac{\sigma}{e} \text{grad} E_F \equiv j_e.$$  

(3.15)

The current density of a semiconductor is governed by the local change of its Fermi level. For holes, the current density $j_h$ can be calculated analogously using the hole conductivity $j_h$:

$$j_h = -\frac{\sigma_h}{e} \text{grad} E_F.$$  

(3.16)

The overall current density $j_{\text{total}}$ is the sum of both, $j_e$ and $j_h$. Quite obviously, no current is flowing through the device at equilibrium without illumination since the contribution of both types of charge carriers cancel each other out.

\(^8\)Albert Einstein (1879 - 1955) and Marian von Smoluchowski (1872 - 1917)
3.1 Photovoltaics in General

Figure 3.6: Left: Within the illuminated space charge region (SCR) the Fermi level splits into a quasi-Fermi level for electrons \( E_{F,e} \) and one for holes \( E_{F,h} \), as both charge carrier densities increase upon illumination. The current density is determined by the gradient of the Fermi levels; however, in the highly conductive parts outside the SCR only a very small gradient is needed. The difference between the Fermi levels outside the SCR is determined by the applied voltage \( V_{ap} \). Right: When \( eV_{ap} \) reaches the built-in field, the Fermi level gradient disappears, and the current stops.

Illumination

The situation is entirely different for an illuminated semiconductor. The absorption of photons leads to an increased electron density, which is equivalent to a shift of the Fermi level towards the electron transport level (see Section 2.3.1). On the other hand, the hole density is increased, too, which is equivalent to a Fermi level shift towards the hole transport level. This, as well as the existence of a current density \( j_{total} > 0 \) results in the distinction of two so-called quasi-Fermi levels, one level \( (E_{F,e}) \) linked to the electrons and their density and one level \( (E_{F,h}) \) linked to the holes and their density. The current density is then no longer zero:

\[
j_{total} = j_{e} + j_{h} = \frac{\sigma_{e}}{e} \text{grad} E_{F,e} - \frac{\sigma_{h}}{e} \text{grad} E_{F,h}. \tag{3.17}
\]

Figure 3.6 a) shows the energy scheme of an illuminated pn-junction including the quasi-Fermi levels. Their gradient is (according to Equation 3.17) determining the charge carrier density. The applied voltage \( V_{ap} \) is translated into the difference of quasi-Fermi levels outside the space charge region. It is smaller than the built-in potential. Decreasing this voltage increases the level gradients leading to a higher current density. Increasing the voltage decreases the current density until the
3.1.3 pin-Concept - Semipermeable Membranes

To consequently use the whole chemical energy of the electrons and holes, recombination of electrons and holes outside the space charge region has to be prevented. One way to do this is to allow only one sort of charge carrier to exit the space charge region at each side. This leads to the concept of semipermeable membranes described by Peter Würfel [48]. This concept is depicted in Figure 3.7. The active absorber layer is placed between two doped wide-gap membrane layers. One layer is n-doped having, therefore, a large conductivity for electrons and a low conductivity for holes. The other layer is p-doped resulting in a large hole conductivity and a low electron conductivity.

Since both materials have a wide gap, they do not absorb but transmit all incoming photons and no charge carriers are generated. Additionally, the levels are chosen such that the n-doped layer is transporting electrons well without any
energy barrier but is blocking holes; the p-doped layer is designed analogously. The current is driven by a small gradient of $E_{F,e}$ and $E_{F,h}$, respectively.

As doped materials with high conductivities are used, only a very small Fermi energy gradient is needed to transport the majority charge carriers, the minority charge carriers flowing in the “wrong” direction are negligible. The entropy does not change substantially while the charge carriers are transported to the contacts and the whole chemical energy can be used. Thus, the maximum voltage $V_{OC}$ is equal to the difference of quasi-Fermi levels:

$$eV_{OC} = E_{F,e} - E_{F,h}. \quad (3.18)$$

Using Equations 3.2 and 3.4 the quasi-Fermi levels can be calculated:

$$E_{F,e} = E_C + kT \ln \left( \frac{n}{N_C} \right), \quad (3.19)$$

and

$$E_{F,h} = E_V - kT \ln \left( \frac{p}{N_V} \right). \quad (3.20)$$

The open-circuit voltage, hence, depends on the gap energy $E_g$:

$$eV_{OC} = E_g - kT \ln \frac{N_C N_V}{np}. \quad (3.21)$$

Using the concept of semipermeable membranes, the open-circuit voltage can, thus, be larger than the built-in potential would actually allow. It has to be pointed out that a built-in electric field, though it supports the charge carrier separation, is not even intrinsically necessary using this ideal solar cell. In reality, it is of course impossible to completely avoid recombination. Not only the small minority charge carrier current but also non-ideal contacts give rise to recombination, when the membranes do not fully block.

### 3.1.4 Efficiency Limits

Section 3.1 illustrates that the question which efficiencies can be reached with photovoltaic devices is interesting not only academically but also economically. As the name suggests, solar cells convert the energy of the sun’s photons into electrical energy via the chemical energy of exited charge carriers. All these processes impose limitations to the efficiency.
Thermodynamic Limits

A heat engine transfers energy from a warm region to a cool region of space. The solar cell is converting the heat of solar photons into excited electrons. It has to obey Carnot’s theorem\(^9\), the most basic theorem for heat engines [49]:

$$\eta = 1 - \frac{T_{sc}}{T_{sun}}.$$ \hspace{1cm} (3.22)

The sun has a surface temperature \(T_{sun}\) of about 5800 K. Since the cell has itself a temperature \(T_{sc}\) of roughly 300 K the maximum Carnot efficiency is about 95%.

As the solar energy is transferred via radiation, the Stefan–Boltzmann law \(^{10}\) [50, 51] has to be obeyed:

$$j^* = \sigma_B T^4 = 5.67 \times 10^{-8} \text{W/m}^2\text{K}^4 \ T^4.$$ \hspace{1cm} (3.23)

It links the energy flux density \(j^*\) radiated by a black body with its temperature \(T\). As the solar cell is also an absorber and emitter at a temperature \(T_{abs}\) the net power flux \(j_{net}^*\) is

$$j_{net}^* = \sigma_B (T_{sun}^4 - T_{abs}^4).$$ \hspace{1cm} (3.24)

Only this energy can be used in the Carnot process:

$$\eta = \left(1 - \frac{T_{sc}}{T_{abs}}\right) \left(1 - \frac{T_{abs}^4}{T_{sun}^4}\right).$$ \hspace{1cm} (3.25)

This \(\eta\) has a maximum of 85% for an absorber temperature of 2500 K [52].

Shockley-Queisser limit

Obviously, the thermodynamic limits are just an upper limit for the power conversion efficiency. For more realistic values using Equation 3.8 for the efficiency maximum, the spectral shape of the sunlight has to be taken into account. It resembles the radiation of a black body spectrum [48], but is altered, for example, by absorption in the atmosphere. Since the intensity and the spectral shape depend on several circumstances, e.g. angle above the horizon, a standard power spectrum \(p_{AM1.5}(\lambda)\) is defined for an angle above the horizon of 45 degrees. It is called AM1.5 as the light has to travel 1.5 times the thickness of the atmosphere at this angle. Using this spectrum the current density can be calculated.

$$j = \frac{e}{h c} \int_{E_G}^{\infty} \lambda p(\lambda) d\lambda$$ \hspace{1cm} (3.26)

---

\(^9\)Nicolas Léonard Sadi Carnot (1796 - 1832)

\(^{10}\)Jožef Stefan (1835 - 1893)
3.2 Organic Solar Cells

$V_{OC}$ can be derived from Equation 3.21. This calculation was done by Shockley and Queisser [53]. They used a general diode law (see Section 3.1.1) to determine the maximum fill factor possible for a given $V_{OC}$, considering also the ratio of radiative and non-radiative recombination. For a solar cell without non-radiative recombination, the maximum efficiency is 33.7 $\%$ for a band gap of 1.34 eV.

This is much lower than the thermodynamic limit stated above. The major reason is the difference between the energy of the absorbed photon and the energy of the collected charge carriers: A semiconductor theoretically absorbs all photons with an energy equal or higher than its band gap. However, as these excited electrons are quickly relaxing into the lowest excitation level, the electrons collected at the contact always have a lower energy $E_e = eV_{ap}$.

One way to use some of that energy lost due to thermalization is the stacking of two diodes with materials with different band gaps. Thus, the two diodes have different open-circuit voltages and are able to collect electrons at two different energies. The light first has to pass the subcell with the larger band gap to minimize absorption of high energy photons by the subcell with the lower band gap. This device is called a tandem solar cell (see also Section 3.2.3). The efficiency limit for these tandem cells is 42 $\%$ [54].

3.2 Organic Solar Cells

Organic solar cells (OSCs) can be distinguished by several criteria: their way of preparation, the design of their active layers, or the number of solar cells stacked. Most commonly they are divided into three different groups.

The so-called dye-sensitized solar cells (DSSCs), also known as Grätzel cells, is the first group. In DSSCs, organic dyes e.g. ruthenium complexes are used as absorber material. They are cast on porous titanium dioxide (TiO) nanoparticles. The TiO is immersed in an electrolyte solution held between two glass electrodes [55].

The second group consists of the polymer-based solar cells. In these cells, polymers provide at least one of the absorber materials. Polymer solar cells are usually cast from solution, qualifying them for printing techniques.

Solar cells based on small molecules form the third group of OSCs. They are made of monomers and oligomers and they are usually processed via physical vapor deposition (PVD) such as high temperature vacuum evaporation. Small molecules are sometimes used, however, in solution-cast devices [56]. Though small molecules tend to have lower mobilities, the PVD allows for easy stacking of different layers fulfilling different functions in the solar cell. This thesis will only address these small-molecule based devices.

---

$^{11}$Michael Grätzel (1944)
The first organic molecule to show photoconductivity was anthracene, discovered in the beginning of the 20th century [57, 58]. It was, however, not until 1959 that the first anthracene-based organic solar cell was described by Kallmann and Pope [59]. It had a photovoltage of 0.2 V but an extremely low efficiency. Additionally porphyrins and phthalocyanines like magnesium phthalocyanine were investigated, leading to similar results [60]. The first cell showing the enhancing effect of different contact materials was based on copper phthalocyanine (CuPc) and was prepared in 1964 [61].

Upon the description of conductivity in polymers, devices incorporating single layers of polyacetylene and polythiophenes were produced [62, 63, 64]. First used in light emitting devices, layers of poly(phenylene vinylene)(PPV) were placed between indium tin oxide (ITO) and different metal back contacts [65]. They showed voltages of more than 1 V but efficiency remained low, at about 0.1% at white light illumination [66].

An important breakthrough was made by Tang et al. [67] in 1986: Using a planar junction of CuPc and a perylene tetracarboxylic derivative in a solar cell improved the generation of free charges at the interface and lead to a current density of 2.3 mA/cm². Together with a very good fill factor of 65% and a $V_{OC}$ of 0.45 V, an energy conversion efficiency of almost 1% was achieved. The working principle of heterojunctions will be explained in Section 3.2.1.

In 1990 the first tandem cell was produced by Hiramoto et al. [68]. By inserting a thin gold layer between two identical subcells made of phthalocyanine (H$_2$Pc) and a perylene tetracarboxylic derivative, the open-circuit voltage could be increased from 0.44 V to 0.78 V (see Section 3.2.3).

In 1993 Sariciftci et al. [69] reported a polymer cell based on MEH-PPV$^{13}$ and evaporated C$_{60}$. The cell showed a $V_{OC}$ of 0.44 V employing the ultrafast charge transfer from the conjugated polymer onto the fullerene. The stacking of solution-cast layers is difficult as the application of the second subcell often influences the first. Therefore, polymer-based tandem cells were reported only in 2006 [70, 71, 72]: Shrotriya et al. [70] used a combination of lithium fluoride, aluminum and gold inserted as a layer between two subcells of MEH-PVV and PCBM$^{14}$. This almost doubled the cell’s $V_{OC}$ from 0.86 V to 1.64 V, yielding an efficiency of 2.6%.

Today, dye-sensitized solar cells reach efficiencies of about 11.6% [73]. Toshiba has reported 11.0% for polymer-based solar cells [74]; Heliatek GmbH holds the record for solar cells based on small molecules with an efficiency of 12.0% on an area of 1.1 cm$^2$ [75].

---

$^{12}$Ching W. Tang (1947)
$^{13}$MEH-PPV: poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene)
$^{14}$PCBM: phenyl C61-butyric acid methylester (PCBM)
3.2 Organic Solar Cells

3.2.1 Organic Heterojunctions

As described in Section 2.2.2, organic semiconductors behave quite differently from their organic counterparts. Very high absorption coefficients of up to $10^5$ $\text{cm}^{-1}$ in organic materials necessitate layer thicknesses of much less than 1 $\mu\text{m}$, which softens the restrictions imposed by the low charge carrier mobilities. Additionally, the excitons formed upon absorption of a photon for the major part do not dissociate spontaneously into free charge carriers. Fields of more than $10^6$ V/cm are needed, which translate into a necessary voltage of more than 10 V for a typical OSC of 100 nm. As this is not possible, a heterojunction is often used to overcome the exciton binding energy. The most simple way to prepare such a heterojunction is the bilayer device depicted in Figure 3.8 as it was also used by Tang et al. [67].

A layer of an acceptor material having a high electron affinity and possibly a high electron mobility is placed next to a layer of a donor material with a comparatively low ionization potential and possibly a high electron mobility. The conversion of a photon flux into an electrical current now mainly takes place in four steps:

Figure 3.8: Top: In a bilayer or flat heterojunction, donor and acceptor layer are stacked upon each other and placed between the contacts. Bottom: After absorption ($\eta_A$) the created exciton has to diffuse to the heterojunction interface ($\eta_{ED}$). There it is separated into free charge carriers with the help of the heterojunction ($\eta_{CT}$). Then the charge carriers have to be collected at the contacts ($\eta_{CC}$).
1 – Absorption: The photon is absorbed by the organic semiconductor and an exciton is formed. The probability of an incident photon to be absorbed is governed by the absorption coefficient of the materials and their thickness.

2 – Exciton diffusion: The exciton diffuses through the layer. Whether it reaches the interface between donor and acceptor is governed by the exciton diffusion length $L_e$. It is typically in the region of 10 nm [76].

3 – Exciton dissociation: When reaching the interface from the bulk of the donor layer, the exciton is separated and the electron is transferred to the acceptor. Analogously the hole is transferred to the donor when the exciton is coming from the bulk of the acceptor layer. This takes place via the formation of a charge transfer state. The offset between the donor and the acceptor transport levels ensure the separation of the exciton.

4 – Charge collection: The separated holes and electrons have to reach the contacts to form a current within the circuit. On the one hand, this transport can be driven by a built-in field, induced e.g. by different contact materials. On the other hand, as free charge carriers are mainly created at the heterojunction interface, the transport is also diffusion-driven. Hence, the diffusion length and the mobility of the charge carriers are the constraining parameters for charge collection.

The probability for a photon to be converted into an electron in the electric circuit is called external quantum efficiency ($\eta_{EQE}$ or EQE). It can be expressed as a product of the probabilities of the four processes stated above [77]:

$$\eta_{EQE}(\lambda, V, d) = \eta_A(\lambda, d) \eta_{ED}(d) \eta_{CT}(\lambda, V) \eta_{CC}(V, d).$$

(3.27)

The absorption efficiency $\eta_A$ is increasing with increasing thickness, while charge collection efficiency $\eta_{CC}$ and, more importantly, the exciton diffusion efficiency $\eta_{ED}$ decrease for higher layer thicknesses. While the charge transfer efficiency $\eta_{CT}$ and $\eta_{CC}$ can approach unity [77, 76, 78], the opposing thickness dependences of $\eta_A$ and $\eta_{ED}$ usually prevent both of them being high at the same time. Therefore, the highest reported maximum EQEs do not surpass 80% at one wavelength [79].

As already explained above, the interfacial energy level offset of the heterojunction is crucial for the separation of excitons. This difference in energy is needed between the electron transport levels and between the hole transport levels alike. It is to provide the energy needed to split the exciton. Hence, when the exciton binding is smaller than this step, charge transfer can occur when the exciton reaches the interface, as it allows for a gain in energy. Depending on the mobility and the delocalization of the charge carriers but also on the electric field, [80] this process can take place within a few hundred femtoseconds [81, 82].
The process of charge separation is discussed in two different ways, both depicted in Figure 3.9, leading to the same constraints for the heterojunction interface. In Figure 3.9 a) the Frenkel exciton has diffused to an interface molecule (Frenkel excitons, see Section 2.2.3). A charge is transferred to a neighboring molecule of the opposite type. A so-called charge transfer exciton (CTE) is formed as this electron hole pair is still Coulombically bound. Depending on the exact position of the energy levels this process can also occur into higher states. Thereupon, driven by the excess energy of the Frenkel exciton, thermal energy and possibly an electric field, the charge carriers decrease their Coulombic bond by increasing their distance to the interface [27, 84, 85].

Another scheme is proposed by Würfel et al [83]. It is depicted in Figure 3.9 b). Here, the energy of an electron bound in an exciton is considered as the combination of the energy of a free electron in combination with a Coulombic potential in relation to a free hole. If the electron transport level of the acceptor is in the bulk equal to or lower than the energy of the excitonic state, the electron can tunnel through the Coulombic barrier into the acceptor. Since there is still Coulombic attraction close to the interface, it is the surplus energy from the
excitonic state compared to this interface energy level that provides the kinetic energy to overcome the barrier. This description can, of course, be adapted for a hole transferred.

For both schemes described, the energy stored in the exciton has to be as high as the effective gap of the heterojunction, i.e. the energy difference between the electron transport level of the acceptor and the hole transport layer of the donor. Only then the exciton can be dissociated into free charge carriers. Furthermore, an additional energy stored in the exciton helps to increase $\eta_{CT}$. While the exact working principle of a heterojunction is still under discussion, the necessity of an interface offset between the electron transport levels of donor and acceptor layers and likewise between the hole transport levels is generally accepted.

This means, however, that the effective electrical gap is lower than each of the two electrical gaps of donor and acceptor. Any increase of the offsets to ensure better exciton dissociation without changing these electrical gaps automatically decreases the effective gap of the heterojunction.

**Open-circuit Voltage**

In most inorganic solar cells, free electrons and holes are created throughout the device upon the absorption of photons; the diffusion of these charge carriers does not lead to a photocurrent. The internal field in the space charge region is the dominant driving force of the separation of charge carriers. The open-circuit voltage is limited to the built-in potential as explained in Section 3.1.1. For the first organic cells which had undoped, active layers, it was, therefore, assumed that the potential difference of the work functions of the contacts was limiting the possible $V_{OC}$. However, this is not true for a device based on a heterojunction. Experiments have shown that the open-circuit voltage can exceed the contact potential difference and that even a solar cell with a negative difference is possible. The reason is simply that the free charge carriers are primarily created at the heterojunction interface. Thus, a large concentration gradient is produced; furthermore, the heterojunction with its energy level offsets forms a blocking membrane for electrons into one direction and for holes in the other direction, similar to the semipermeable membranes of the ideal solar cell (see Section 3.1.3). As laid out this is a device which does not need an internal field at all to function as a solar cell.

However, it is not the electrical gap of the layers that directly limits the open-circuit voltage as is the case for the ideal pin-device. As the quasi-Fermi levels cannot be split beyond any of the electrical gaps of the absorber layers, it is rather the effective electrical gap $E_{g,eff}$, i.e. the difference between the electron transport level of the acceptor $E_{e,A}$ and the hole transport level of the donor $E_{h,D}$ that sets the limit for the $V_{OC}$. In accordance with the derivation of Section 3.1.3, the $V_{OC}$ can be calculated:
\[ e V_{OC} = E_{F,e} - E_{F,h} = E_{e,A} - E_{h,D} - kT \ln \frac{N_e N_h}{n_p} \]

\[ = E_{\text{g,eff}} - kT \ln \frac{N_e N_p}{n_p} \]  

(3.28)

with the effective density of states \( N_e \) in \( E_{e,A} \) and \( N_h \) in \( E_{h,D} \). As explained above recombination of photogenerated charge carriers outside the active layers reduces the splitting of the quasi-Fermi levels and, consequently, the \( V_{OC} \) available.

Additionally, the disorder in an amorphous layer with molecules of different orientation leads to the broadening of the density of states into a Gaussian distribution [86]. Equation 3.28, however, is based on the Maxwell-Boltzmann approximation which is valid only when the quasi-Fermi levels are distant from the transport levels by a few \( kT \). Nonetheless, the relation between \( V_{OC} \) and the effective gap has been observed experimentally and is important for the right choice of materials [87, 88, 89, 78, 90, 91]. Choosing an effective gap too large eventually reduces the interface offsets, and, in consequence, the charge transfer and the power conversion efficiency. Choosing an unnecessary low gap reduces \( V_{OC} \), also leading to a decreased cell efficiency. How the efficiency of heterojunction solar cells depends on the choice of energy levels is further discussed in Chapter 5.

**Bulk Heterojunctions**

In the previous section it was pointed out that the thickness of the active layer is limited by the exciton diffusion, more specifically the exciton diffusion length \( L_e \), which is often 10 nm or less [33, 77, 92, 93, 94].

Therefore, heterojunction bilayer or flat heterojunction cells following the design proposed by Tang et al. [67] have a maximum thickness. It is usually not large enough to absorb all incident photons. Hence, materials with a sufficiently high \( L_e \) to ensure optimally absorbing layers cannot always be found.

Alternatively, the distance from the bulk to the interface can be lowered when the interface surface is increased by forming interpenetrating layers. The most common way to do this are so-called bulk heterojunctions (see Figure 3.10). Here, donor and acceptor are both present in one mixed layer. Especially in solution-cast devices where the subsequent application of layers is often difficult, mixed layers are frequently used.

The excitons have to diffuse only a short distance; the transport of the subsequently created free charge carriers takes place within their respective donor and acceptor material. This, however, makes direct connections to the adjacent layers necessary, so called percolation paths. Obviously, for high thicknesses these closed paths become less and less probable, resulting again in a maximum thickness, which is, however, much larger than for flat heterojunctions. Great efforts are
made both for solution-cast and evaporated solar cells to increase the likelihood of closed paths, e.g. by a greater phase separation of the two materials. Thermal and solvent annealing, processing on heated substrates, using different solvents and material ratios are often used to manipulate and increase $\eta_{ED}$. With increasing phase separation also the non-geminate recombination, i.e. the quenching of free electrons and holes at the interface is reduced (recombination mechanisms see Section 3.2.2).

Phase separation is, of course, limited. When the distance to the next interface approaches $L_e$, exciton diffusion efficiency drops again. Therefore, the reproducible control of the morphology of the mixed heterojunction layer to achieve the best phase separation is necessary.

### 3.2.2 Recombination Processes

In any semiconductor material, the electrons excited by absorbed photons eventually have to relax back into their ground state. This recombination with a hole can either occur radiatively, i.e. emitting a photon or non-radiatively converting the energy stored in the electron into heat. Obviously, this basic thermodynamic
requirement is also valid for photovoltaic devices. The purpose of a solar cell is to ensure that, while the excitation takes place in the device itself, the recombination occurs within the loads of the electric circuit. However, recombination is always present in the device as well, where it constitutes a loss mechanism reducing the efficiency of the solar cell.

Recombination can be geminate or non-geminate. Geminate means that both electron and hole originate from the same exciton. In contrast, non-geminate refers to the electron and the hole being independent prior to recombination. Furthermore, linear and quadratic recombination is distinguished, depending on whether the recombination depends linearly or quadratically on the density of the recombining species\textsuperscript{15}.

Excitons in an organic heterojunction can recombine geminately before they reach the separating interface. For low light intensities this recombination is predominantly depending linearly on the exciton density. As the intensity increases, this dependence becomes more and more quadratic, as the quenching of excitons upon contact with other excitons dominates the recombination. When reaching the interface the excitons are transformed into a charge transfer exciton constituting a geminate pair. When the separation cannot take place because the kinetic and thermal energy is not sufficient, the pair is trapped and eventually recombines.

When the exciton is dissociated, electron and hole are free. These charge carriers can recombine non-geminately. As a free hole and a free electron is needed, the recombination rate \( R \) is depending on both the hole density \( p \) and the electron density \( n \); it is, hence, a quadratic recombination and it corresponds to the time rate of change when the generation is turned off \((\dot{n}_G=0)\):

\[
R = \beta np \dot{\equiv} \dot{n}_G=0, \tag{3.29}
\]

\( \beta \) is called the recombination constant and it has the dimension of \([cm^3/s]\). For species recombining quadratically no average lifetime can be determined.

The Coulomb radius is the distance below which the Coulomb binding energy is too large to be overcome thermally. When the charge carrier densities are small enough, the distances between the electron and the hole are larger than this radius. Additionally, for pristine materials, the mean free path of the charge carriers usually is smaller than this radius. Their recombination is then governed mainly by their drift velocity and the so-called Langevin theory\textsuperscript{16} can be adopted \([95]\): the recombination rate is determined by the mobilities of the carriers \( \mu_e \) and \( \mu_h \) and their densities. Furthermore, the dielectric constant \( \epsilon \) of the surrounding material influences their attraction:

\textsuperscript{15}The linear recombination is often also called monomolecular or indirect, the quadratic recombination is also called binmolecular or direct

\textsuperscript{16}Paul Langevin (1872 - 1946)
\[ R = e \varepsilon_0 e (\mu_e + \mu_h) np =: \beta_L np \quad (3.30) \]

While the Langevin model and recombination constant \( \beta_L \) is well defined in pure organic layers, the situation in organic heterojunctions is more complex: Here, the recombination only partially takes place within the bulk. As the heterojunction separates the holes and the electrons, the main recombination occurs at the interface. How to incorporate this is still under debate [96, 97]. Koster et al. [97], for example suggest that the more mobile carrier has to wait for the less mobile one at the interface. Consequently, the recombination rate is determined by the lower mobility: \( R \propto \min(\mu_e, \mu_h) \).

Free charge carriers can also recombine linearly. In doped layers, illumination only significantly changes the carrier density of the minority charges \( n_{min} \):

\[ R = \beta n_{min} =: \frac{1}{\tau} n_{min} \quad (3.31) \]

Usually, organic active layers in solar cells are undoped. Therefore, another process becomes more important: the recombination at trap states. When a free electron encounters a trapped hole or vice versa they recombine. If the number of trap sites can be considered static for a given layer, this also is a linear recombination process.

As the quadratic recombination increases faster with increasing species density and consequently with increasing illumination than the linear recombination, the current density \( j \) is influenced differently by both processes. While for linear recombination \( j \) is thought to increase also linearly with the intensity \( I \), it is considered to be proportional to the square root of \( I \) for quadratic recombination [98, 99]. Yet, as also the space charge limitation of the photocurrent may be the reason of a square root dependency on \( I \), the two mechanisms are sometimes difficult to distinguish [100, 101].

### 3.2.3 Transport Layers – pin-Concept in OSC

The pin-cell proposed by Würfel (Section 3.1.3) combines an intrinsic active layer with two doped layers of wide gap materials. These layers have to effectively transport one sort of charge carrier while blocking the other.

This principle can be adapted very well to organic solar cells [33, 98]. Especially cells prepared by physical vapor deposition are fit as this technique allows for easy stacking and controlled mixing of layers. In Section 2.3.1 it is described how organic materials can be doped mixing different organic or inorganic molecules into the desired matrix material. This leads to conductivities above \( 10^{-5} \, \text{S/cm} \). It also shifts the Fermi energies towards the transport levels. Using doped transport layers has several advantages [16, 86, 102, 103, 104]:
- The high conductivity ensures good transport of the majority charge carriers, the charge carriers hardly loss any energy.

- In materials with a high doping ratio, level bending at the interface occurs over very short ranges. Hence, ohmic contact between the electrodes and the doped layers is possible as the charge carriers can tunnel through the thin energy barrier at the interface.

- This also decouples the energy levels of the active layers from the contact work function. In consequence, the built-in field is determined by the doped layers.

- The shift of the Fermi-levels towards the transport levels in doped layers creates a large built-in field.

- Using materials with a large energy gap (usually about 3 eV) prevents parasitic absorption within the transport layers. This means, more photons reach the active layers. Additionally the active layers can be made thin enough for all generated excitons to reach the interface.

- As the transport layers are highly conductive and not or weakly absorbing, they can be made thick enough to place the active layers into the maximum of the optical field: When the incoming optical field is reflected at the back electrode a standing wave develops. Therefore, the maxima of the optical field are spatially separated from the back electrode depending on the wavelength of the incoming light.

- By choosing a wide-gap material with the “right” energy levels, the minority charge carriers are blocked while the majority carriers can be transported. This results in reduced recombination in the transport layers as described in Section 3.1.3.

- Additionally, this energy design also blocks the excitons and prevents them from being quenched at the contacts.

Obviously, the multiple requirements to transport layer materials concerning dopability, energy gap, and energy levels but also more general concerning stability and processability makes finding suitable materials difficult. Especially, good n-type transport materials are still sought. Nonetheless, the concept of transparent, highly conductive transport layers is a good way to increase solar cell efficiencies [33, 105, 106].
Figure 3.11: Top: In the stack of an organic tandem solar cell using the pin concept, doped wide-gap materials are used not only to efficiently collect the charge carriers, but also to place the active layers where the optical field is high. Between the two subcells a recombination layer consisting of two very highly doped transport layers is used as recombination or interlayer to connect the two subcells ohmically. Bottom: This is also illustrated by the energy levels. When the electron reaches the recombination layer it can recombine with a hole created in the adjacent subcell. As this recombination layers are highly doped, the difference between the energy levels is low and only very little energy is lost.

Tandem Cells

As explained in Section 3.2.1 flat heterojunction layers have a maximum thickness limited by the exciton diffusion length. Consequently, not all incoming photons can be absorbed. To overcome this limitation mixed heterojunctions can be used. However, they have a limited thickness, too, as closed percolation paths are needed to transport the charge carriers created.

One idea to increase the absorption of solar cells is the concept of multijunction solar cells. In those devices, several cells are stacked upon each other and the light has to pass several absorbing heterojunctions. These subcells are connected either in parallel or in series. In both cases, a thin interlayer is needed between the contacts. In a parallel setup, this interlayer is needed to separately address the subcells and it has to be guided out of the active device to get hold of the different currents.
As this is difficult to control, the serial setup is more commonly used. There, the interlayer is needed to ohmically contact the different subcells and to allow the electrons to pass from one subcell to the other without a loss of energy. In consequence, the current density generated in all subcells has to be equal, as is the case for all serial circuits. The voltage is the sum of the voltages created by the subcells.

The requirement of equal current density also means matching the absorption in each subcell. Usually, in thin OSCs thin film effects of the optical fields have to be considered (see Section 3.2.1). This complicates the design of the stack. Thus, only two subcells are usually used in organic devices. They are called tandem solar cells. Figure 3.11 shows the stack of a pin tandem solar cell. For the interlayer a thin film or even clusters of metal can be used [68]. It has been shown recently that also very highly doped widegap materials can be used in organic solar cells. This has the advantage of avoiding parasitic absorption of the interlayer (see Figure 3.11).

The electron created at the heterojunction interface of the first subcell reaches the electron transport layer (ETL) and approaches the interlayer. As this is highly conductive the Fermi levels are very close to the transport levels. The electron can, therefore, tunnel through and recombine with a hole in the hole transport layer (HTL) generated in the second subcells without a considerable energy loss.

An additional idea, also employed in inorganic photovoltaics, is the usage of different materials with an absorption in different spectral regions. This has two advantages. Firstly, the subcells do not “steal” photons, i.e. intensity from each other anymore. Especially organic materials, which usually only absorb in spectral regions of a few hundred nanometers are very well adapted to this approach. In single heterojunction solar cells these narrow absorption bands are a disadvantage. In tandem cells, their different electrical gaps can be used to increase the efficiency.

The second advantage is the following: As the voltage depends on the electrical gap of the donor and the acceptor of each heterojunction, using different materials means different voltages supplied from each subcell which then add up to the overall voltage in a tandem cell. In contrast, the losses caused by the thermalization of the excited electrons are reduced as the photons are absorbed by the “appropriate” gap. While in inorganic materials with their broad absorption ranges, the material with the largest gap has to be put first (see Section 3.1.4). Organic materials with their absorption overlapping only little can be stacked as the optical field distribution in the stack calls for. In consequence, the concept of tandem cells is especially suited to increase the absorption and the efficiency of organic solar cells [107, 108, 109].
4 Materials and Experimental Setups

The following chapter serves two purposes: Firstly, the organic materials used in this work (besides the investigated infrared absorber materials) are introduced. Secondly, the experimental setups used for the preparation and characterization both of single layers and entire devices are described. Within the scope of the latter, the conditions for measurement are discussed.

4.1 Materials

As described in Chapter 3.2 this work deals with so-called small molecules. They are processed by physical vapor evaporation. In addition to the infrared absorber materials under investigation, other materials are used as absorbers, transport and contact materials.

4.1.1 Buckminsterfullerene $C_{60}$

The molecule $C_{60}$, also known as bucky ball is the best known of the fullerenes. It was first theoretically predicted in 1970 and synthesized by Kroto et al. in 1985 [110].

Its structure is displayed in Figure 4.1. The molecule consists of 20 hexagons and 12 pentagons forming a so-called truncated icosahedron. All 90 edges, representing the chemical bonds, have the same length; the carbon molecules sit at the 60 vertices. This high symmetry causes a very high delocalization of the electrons, and, consequently, high mobilities of up to $6 \text{cm}^2/\text{Vs}$ in organic field effect transistors [111, 112]. Additionally, the rate for intersystem crossing is very high, created singlet excitons are quickly converted to triplet excitons [12]. Their long lifetime leads to exciton diffusion lengths of about 40 nm [76]. It is for these properties and for its high electron affinity of 4.0 eV [113] that $C_{60}$ and its derivatives like PCBM are often used as acceptor materials in organic solar cells.

---

1A molecule with a molar mass of up to 1000 g/cm$^3$
2Richard Buckminster Fuller (1895 - 1983)
Figure 4.1: Most of the materials shown are used as HTLs: MeO-TPD, PV-TPD, Di-NPB, BPAPF and ZnPc; C_{60} is used both as acceptor and as ETL. The transparent BPhen is employed in an exciton blocking layer.
### 4.1 Materials

<table>
<thead>
<tr>
<th>Name</th>
<th>IP / eV</th>
<th>(\lambda_{\text{onset}}) / nm</th>
<th>(\rho) / g/cm(^3)</th>
<th>(T_{\text{evap}}) / °C</th>
<th>Supplier</th>
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</thead>
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<tr>
<td>C(_{60})</td>
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<td>570</td>
<td>1.56</td>
<td>400</td>
<td>ABCR</td>
</tr>
<tr>
<td>ZnPc</td>
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<td>830</td>
<td>1.34</td>
<td>380</td>
<td>ABCR</td>
</tr>
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<td>1.46</td>
<td>180</td>
<td>Sensient</td>
</tr>
<tr>
<td>PV-TPD</td>
<td>5.2</td>
<td>440</td>
<td>1.15</td>
<td>240</td>
<td>Sensient</td>
</tr>
<tr>
<td>Di-NPB</td>
<td>5.3</td>
<td>420</td>
<td>1.14</td>
<td>220</td>
<td>Sensient</td>
</tr>
<tr>
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<td>390</td>
<td>1.2</td>
<td>280</td>
<td>Lumtec</td>
</tr>
<tr>
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<td>350</td>
<td>1.24</td>
<td>120</td>
<td>ABCR</td>
</tr>
</tbody>
</table>

**Table 4.1:** Overview over the material properties: Ionization potential (IP, measured by UPS at the IAPP), onset of absorption \(\lambda_{\text{onset}}\), density \(\rho\), evaporation temperature \(T_{\text{evap}}\) and the main material supplier.

However, as can be seen in Figure 4.2, C\(_{60}\) only absorbs up to about 550 nm. Furthermore, the peak at 448 nm is rather low as the lowest transition in C\(_{60}\) is dipole forbidden due to its high symmetry. The other peaks at 270 nm and 350 nm are already at a wavelength where the energetic contribution of the sun is small. Therefore, layers of C\(_{60}\) have to have a rather large thickness when used as absorber, somewhat neutralizing the advantage of high mobilities and diffusion lengths [114]. Table 4.1 summarizes the ionization potential, the absorption onset, the density, evaporation temperature and supplier of C\(_{60}\) and the other organic materials used.

The material is mainly used as acceptor material in the active heterojunction. However, as good transparent electron transport layers (ETLs) are still under investigation, C\(_{60}\) is also used as ETL (see also Chapter 3.2.3). To achieve good electron transport, the material is then doped with NDN1 (Novaled AG, Dresden, Germany). This leads to a conductivity of about 0.05 S/cm. The proprietary material NDN1 is used for better stability; similar conductivities, however, can be achieved by using acridine orange base (AOB). The C\(_{60}\), purchased from Bucky (Houston, USA), is purified four times by thermal gradient sublimation to filter impurities remaining from the synthesis.

**4.1.2 Transport Materials**

As explained in Section 3.2.3 the choice of transport layer materials depends on the energy levels of the active layers. Therefore, different transport materials are used, both, in hole transport layers (HTLs) and in electron transport layers. Their absorption is depicted in Figure 4.2. Their most important properties are summarized in Table 4.1. All organic materials except the dopants are also purified by thermal gradient sublimation.
Figure 4.2: The graph illustrates why ZnPc and C$_{60}$ are only used in thin transport layers. While the other materials absorb mainly below 400 nm where the solar contribution is still small, ZnPc and C$_{60}$ also strongly absorb above 400 nm.

Hole Transport

ZnPc: *zinc-phthalocyanine* is a material very often used as an absorbing donor material in organic solar cells [33, 93, 115] having an extinction coefficient of the order of $10^5$ cm$^{-1}$ for wavelengths between about 550 nm and 750 nm. In this work it is, however, mainly used for its dopability with F4-TCNQ\(^3\) and NDP2. As the Fermi level is shifted towards the ionization potential (IP) of 5.1 eV, the hole injection barrier between p-doped ZnPc and metal electrode materials like indium tin oxide (ITO) and gold is decreased. This ensures good ohmic contact. However, photons absorbed in the HTL are no longer available for absorption in the active layer. Hence, only thin layers are usually used as HTL. [102]

MeO-TPD: *N,N',N'-tetrakis(4-methoxyphenyl)-benzidine* has been used as a hole transport material, both, for organic solar cells [33, 116] and organic light emitting diodes [117, 118]. As it also has an ionization potential of 5.1 eV it can be combined well with ZnPc.

\(^3\)F4-TCNQ: 2,3,4,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane
PV-TPD: \(N,N'-\text{di}(4-(2,2\text{-diphenyl-ethen-1-yl})\text{-phenyl} )\text{-}\text{N,N'-di}(4\text{-methylphenyl-phenyl})\text{-benzidine}\) is an HTL also used in OSC \([119]\). The ionization potential is 5.2 eV, somewhat higher than the IP of MeO-TPD.

Di-NPB: \(N,N'\text{-diphenyl-N,N'bis(4'-(N,N\text{-bis(naphth-1-yl)-amino})\text{-biphenyl-4-yl})\text{-benzidine}\)} has an IP of about 5.3 eV and is considered more stable due to its higher glass transition temperature which makes it possible to use in solar cells heated during or after processing.

BPAPF: \(9,9\text{-bis}\{4-(N,N\text{-bis-biphenyl-4-yl-amino})\text{-phenyl}\}\text{-9H-fluorene}\) was first employed as a HTL in a light emitting diode. The glass transition temperature of 167°C allows for usage in heated solar cells. With an IP of 5.6 eV it can be used for donors with lower lying hole transport levels \([120]\).

BPAPF is doped using NDP9, for all others, NDP2 is usually used. Both dopants are proprietary materials of the Novaled AG and are chosen for their high stability. Similar electrical properties can be obtained with other dopants (e.g. \([104, 121]\)).

Electron Transport

\(\text{C}_{60}\): The \textit{buckminsterfullerene} is mainly used as an active acceptor, as explained in Section 4.1.1. Yet, owing to its good n-dopability, it is also used as electron transport material. Again, due to the parasitic absorption within a doped \(\text{C}_{60}\)-layer, only small thicknesses are used. As it is not a wide gap material, it does not act as an exciton blocking layer (see Chapter 3.2.3).

\(\text{BPhen}\): \(4,7\text{-diphenyl-1,10-phenanthroline}\) is a phenanthroline similar to BCP\(^4\). It is used as an exciton blocking layer between the acceptor layer and the back contact (usually aluminum). Though the electron affinity of 2.9 eV does not fit that of \(\text{C}_{60}\) (EA: 4.1 eV \([113]\)), electrons are transported well. It is assumed that cathode induced defect states are responsible for this transport behavior, as was reported for BCP \([76]\).

4.2 Sample Preparation

The preparation of solar cells but also of the single layers, needed e.g. for absorption and morphology measurements, involves several steps: treatment of the substrate, production of the actual stack by thermal evaporation in vacuum, and, if necessary, the encapsulation of the finished device.

\(^4\text{2,9-dimethyl-4,7-diphenyl-1,10-phenantroline}\)
4 Materials and Experimental Setups

**Organic layers**

**Metal top electrode**

**Four ITO bottom electrodes**

**Four devices or pixels**

**ITO enforcing for top electrode**

**Figure 4.3:** Left: The overlap of the prestructured ITO bottom contacts and the evaporated metal top contact constitutes four identical devices, that can be addressed and measured separately. The top contact is additionally reinforced by an ITO strip to protect it against scratches during measurement. Right: Photo of a finished sample.

**Substrates**

The single layers and the stacks, that do not need electric contacting, are prepared on regular boron-crown glass (BK7) or quartz substrates. When electrodes are needed, pre-structured glass substrates are used. They are partially covered with indium tin oxide (ITO), an oxide that is both transparent in thin layers and conductive (see Figure 4.3). The sheet resistance of the substrates used is $30 \, \Omega / \text{sq.}$ They are purchased from Thin Film Devices (Anaheim, USA). All substrates are cleaned using aqueous detergent, acetone, ethanol and isopropanol in ultrasonic bath.

Each substrate has a size of $25 \text{ mm} \times 25 \text{ mm}$, but may be cut into smaller sizes e.g. for morphology measurements. When processed it is referred to as one sample. Each sample with structured ITO sample features four identical devices also called pixels. They are defined by the overlap of the four ITO fingers and the metal top electrode and they have an area of $6.4 \pm 0.2 \, \text{cm}^2$. The structure of an ITO sample is also depicted in Figure 4.3.

**Thermal Evaporation**

The organic layers have been produced by thermal evaporation in ultra-high vacuum (UHV; $p < 10^{-6} \, \text{Pa}$): The materials are placed into ceramic crucibles and are heated by surrounding tungsten heating wires. The evaporation temperature varies from about $100^\circ \text{C}$ to $500^\circ \text{C}$ and depends on size and shape of the molecules. These evaporators are supplied by the Creaphys GmbH (Dresden, Germany). The metals are evaporated from crucibles or boron nitride (for alu-
4.2 Sample Preparation

Figure 4.4: Left: The materials are evaporated by heating the crucible. The material shield avoids cross contamination and crosstalk of the QCMs monitoring the thickness. The setup allows for the coevaporation of two materials onto a substrate. The deposition area is further defined by different shadow masks. Right: The multi-chamber tool has five different chambers for separately evaporation of different materials. For example, the n-doping is prepared separate from the p-doping to avoid them canceling each other.

minum) and molybdenum (for silver and gold). The temperatures are monitored by temperature controllers from Eurotherm GmbH (Limburg, Germany) using a type K (alumel/chromel) thermocouple.

The evaporated amounts and, consequently, the thicknesses are determined using a quartz crystal microbalance (QCM) sensor of Leybold Inficon Inc. (Pfäffikon, Switzerland). The ratio between the amount reaching the sensor and the position of the substrate is determined after each manipulation of the evaporator or the entire chamber; this is referred to as tooling of the QCM. Shadow masks are used to refine the area of the substrate covered with the organic materials or metal (see Figure 4.4, left).

Two different devices can be used for the preparation of layers and devices:

**Multi-chamber tool:** This tool from Bestec GmbH (Berlin, Germany) consists of five different chambers for active, intrinsic materials, doped layers, and metal contacts and is referred to as “UFO” (see Figure 4.4, right). Thus, the different layers can be processed spatially separated, but without leaving the UHV, allowing for less impurities during preparation. The substrates can be heated using heated copper blocks in contact with the sample.

**Lesker tools:** In these two single-chamber tools, it is possible to process wafers consisting of 6×6 samples at once, also called runs. Different masks allow for the processing of particular rows or columns of samples. This makes variation of layer thicknesses but also differing stack designs possible. Both single-chamber tools are supplied by Kurt J. Lesker Company (Hastings, Great Britain). They are referred to as Lesker A and B. In the latter heating of wafers during processing is possible.
<table>
<thead>
<tr>
<th>Error</th>
<th>Type</th>
<th>Value</th>
<th>Within one run</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \rho$</td>
<td>systematic</td>
<td>3%</td>
<td>not important</td>
</tr>
<tr>
<td>$\Delta d_{QCM}$</td>
<td>random</td>
<td>3.5%</td>
<td>important</td>
</tr>
<tr>
<td>$\Delta d_{cal}$</td>
<td>random</td>
<td>2.5%</td>
<td>not important</td>
</tr>
<tr>
<td>$\Delta d_{homo}$</td>
<td>random</td>
<td>0% (UFO)</td>
<td>important</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3% (Lesker)</td>
<td></td>
</tr>
<tr>
<td>$\Delta d_{total}$</td>
<td></td>
<td>8.5-14.5%</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: The accuracy of the thickness is influenced by several errors. While $\Delta d_{QCM}$ has always to be taken into account, $\Delta d_{homo}$ is only relevant for samples produced in the Lesker. $\Delta \rho$ and $\Delta d_{cal}$ always reflect upon the absolute thickness value, but when comparing samples within one Lesker run or samples processed shortly after each other.

Both tools have a base pressure below $10^{-6}$ Pa. In the chambers of both tools, co-evaporation of two or more materials at the same time is possible using several QCMs. This is necessary to produce doped layers and mixed heterojunctions.

After evaporation all substrates can be encapsulated using a cover glass that is glued at the substrate using UV resin from Nagase Chemtex (Osaka, Japan). Additionally, for the substrates produced in the Lesker tools, a moisture getter can be introduced into the encapsulation.

**Thickness**

The layer thicknesses in this work are all given in nanometers unless otherwise stated. As it is difficult to determine the error of a single thickness within a device no error margins are given. However, some estimations can be made for the maximal thickness error. Mainly, it consists of four errors: accuracy of the density ($\Delta \rho$), accuracy of the QCM measurement ($\Delta d_{QCM}$), error of the QCM calibration($\Delta d_{cal}$), and the thickness inhomogeneity across the wafer ($\Delta d_{homo}$, only relevant for the Lesker tools). All errors are summarized in Table 4.2. As the accuracy of the calibration decreases with changing fill level of the crucibles, active materials are toolied more often. For the comparison of substrates on one wafer or for substrates produced shortly after each other only $\Delta d_{QCM}$ and $\Delta d_{homo}$ are relevant. Thus, the thickness error of maximally 14.5% is usually much lower, when comparing these substrates.

**Stack Notation**

The stacks mentioned in this work are labeled as follows:

- Different layers are separated by a slash (/), starting with the one closest to the substrate.
• The layer thickness is given in parentheses.

• Materials in mixed layers are separated with a colon (:). The thickness ratio
and the overall thickness are given in parentheses.

• Doped layers start with a “p”- or an “n”- for p-doped and n-doped layers, re-
spectively. Dopant, doping ratio in wt% and overall thickness in nanometers
are given in parentheses.

An example of a combination of a mixed and a doped layer could be:
C$_{60}$:ZnPc(1:1,20)/n-C$_{60}$(NDN1,10 wt%,10)

4.3 Experimental Methods

4.3.1 Characterization of Thin Layers

Optical Characterization

Transmission spectra have been measured using two different devices: The UV3100
from Shimadzu Corporation (Kyoto, Japan) has a range of about 250-900 nm. The
Lambda900 from Perkin Elmer Inc. (Waltham, USA) can measure absorption and
diffuse reflection between 200 nm and 3500 nm. The latter has also been used to
determine the refractivity of the thin films. Software developed at the IAPP is
used to calculate these wavelength dependent values (i.e. the real part and the
imaginary part k) from the reflectivity $R$ and the transmission $T$. The expressions
absorbance $A_\lambda$, optical density $OD$, transmission $T$, and extinction coefficient $\alpha$
are all linked to the incident intensity $I_0$ and the transmitted intensity $I$:

$$ \frac{I}{I_0} = T = 10^{-OD} = 10^{-A_\lambda} = e^{-\alpha d}. \quad (4.1) $$

Only $\alpha$ is independent of the thickness $d$ of the film (except for effects of dispersion
and reflection at the interface).

The luminescence of the thin films is measured using the fluorescence spec-
trometer FLS from Edinburg Instruments Ltd. (Livingston, Great Britain) with
a range of 200 nm to 1010 nm. To block the exciting beam reflected from the
sample from being recorded, edge filters are used between sample and analyzer of
the instrument.

Density

The density is determined indirectly: a thin film of the material in question is
evaporated on a glass substrate using a recent tooling. A nominal density and a
Figure 4.5: Left: A voltage $V_{SD}$ is applied to source and drain, and a small current flows between them. Upon application of a gate voltage $V_G$, charge carriers are induced in the evaporated organic material which fill the traps and increase the conductivity and, thus, the current. This current depends on the voltages applied, but also on the mobility within the organic material. Right: The typical IV characteristics of an OFET can be split into three different regimes: linear (I), intermediate (II), and saturating (III).

nominal thickness\(^5\) are assumed for the QCM. Then the real thickness is determined using a Dektak 150 profilometer from Veeco (Plainview, USA) and the real density calculated.

**Topography**

Scanning probe microscopic images of the topography of thin films are obtained using two different atomic force microscopes (AFM): the Nanoscope IIIa from Digital Instrument (now Veeco) and the Combiscope from AIST-NT (Moscow, Russia). Both instruments are used in tapping mode.

**Mobility**

The charge carrier mobility of the materials is measured using an organic field effect transistor (OFET). The gate electrode made of silicon is at the bottom covered with silicon oxide as a dielectric insulator. On top, the organic material investigated is evaporated between two gold electrodes (see Figure 4.5).

The organic material, hence, acts as a capacitor between the two electrodes, which are called source and drain. Only a very small current is flowing when a voltage between source and drain $V_{SD}$ is applied, because of the low conductivity of intrinsic organic materials. When a voltage $V_G$ is applied to the gate, charge

\(^5\)usually 50 nm and 1.2 g/cm\(^3\)
4.3 Experimental Methods

carriers are induced at the interface between the silicon oxide and the organic material. After all traps are filled, i.e. above a certain threshold voltage $V_{\text{th}}$ free charge carriers allow for a current to flow between source and drain. At small voltages (i.e. $V_{SD} \ll V_G - V_{\text{th}}$) it is proportional to $V_{SD}$. For higher voltages ($V_{SD} \geq V_G - V_{\text{th}}$) the region at the drain electrode depletes and the current saturates. The mobility $\mu$ can be determined in both regimes, provided that length $L$ and width $W$ of the current channel as well as the capacitance of the dielectric $C_{\text{die}}$ are known:

$$I_{SD,\text{linear}} = \mu \frac{W C_{\text{die}}}{L} \left( (V_G - V_{\text{th}}) V_{SD} - \frac{1}{2} V_{SD}^2 \right)$$ (4.2)

$$I_{SD,\text{saturation}} = \mu \frac{W C_{\text{die}}}{2L} (V_G - V_{\text{th}})^2$$ (4.3)

The principles of the OFET are described in more detail in [122, 123]. The current-voltage measurements are done in nitrogen atmosphere directly after preparation without exposing the sample to air. The OFET chips of the 4th generation from Fraunhofer-Institut für Photonische Mikrosysteme (Dresden, Germany) are used with different channel length. They are cleaned using the procedure explained in Section 4.2. More details on the measurement setup can be found in [124].

**X-Ray Diffraction**

X-ray diffraction can be used to determine the nanostructure, namely the inter-plane distance within a crystal $d$. Monochromatic radiation of the wavelength $\lambda$ is diffracted by the sample and the reflected radiation recorded as a function of the diffraction angle $\theta$. The calculation of $d$ makes use of Bragg’s law:

$$d = \frac{2 \sin \theta}{n\lambda}$$ (4.4)

with $n$ the number of the observed intensity maximum.

The measurements are done using wide-angle X-ray diffraction (WAXRD) at a diffractometer URD-6 from Seifert FPM (Freiberg, Germany). The monochromatized Cu-K$_{\alpha}$ radiation has a wavelength $\lambda$ of 1.5406 Å. All measurements are done at room temperature. The layers are evaporated on glass substrates.

**Photoelectron Spectroscopy**

Photoelectron spectroscopy is based on the photoelectric effect, i.e. the emission of electrons from matter upon the absorption of photons. It was first described by

---

6Sir William Lawrence Bragg (1890 - 1971)
Heinrich Hertz in 1887 and explained by Albert Einstein in 1905. If the photonic energy $h \nu$ is larger than the energy needed for ionization, electrons are emitted with certain kinetic energy. The wavelength employed defines the binding energy which can be probed. Ultraviolet photoelectron spectroscopy (UPS) can be used to determine the energetics of the weakly bound valence electrons, with a photonic energy between 10 eV and 40 eV. The energy of X-ray photoelectron spectroscopy (XPS) lies between 1 keV and 2 keV; it is able to ionize the electrons of the core. Hence, it is possible to investigate the chemical environment and composition of the analyzed material. As the mean free path of electrons is only a few monolayers, UPS and XPS are surface sensitive measurements [125].

Figure 4.6 introduces the energies important for UPS: The He I excitation used in the setup from Specs (Berlin, Germany) of has an energy $h \nu$ of 21.22 eV. This energy is used to ionize atoms, i.e. transfer the electron to the vacuum level $E_{\text{vac}}$, the excess energy is converted into kinetic energy $E_k$. The electrons with the highest kinetic energy are originating in the highest orbital. This edge of the spectrum measured by the UPS-analyzer is, therefore, called HOMO cutoff. On the other hand, the electrons with almost no kinetic energy, i.e. that barely reach
the vacuum level owing to their high binding energy, mark the so-called high binding energy cutoff (HBEC). The spectrum next to the HBEC is dominated by secondary electrons created by inelastic scattering below the material surface. Consequently, the ionization potential (IP) can be calculated

\[ IP = h\nu - |E_{\text{HBEC}} - E_{\text{HOMO cutoff}}| \]  

(4.5)

The difference between the Fermi level \( E_F \) and \( E_{\text{vac}} \) is called work function (WF). For metals this equals the IP, as the highest occupied electron states are situated at the Fermi level. In organic materials, an additional injection barrier \( E_{\text{inj}} \) has to be overcome to ionize the HOMO electrons. Additionally, an interface dipole \( \Delta \) often occurs at the interface between metals and organic materials, that changes the vacuum level \( E_{\text{vac}} \):

\[ \Delta \equiv \Delta E_{\text{vac}} = E_{\text{metal \ HBEC}} - E_{\text{organic \ HBEC}} \]  

(4.6)

The XPS measurements are done using a XR-50 X-ray source from Specs (Berlin, Germany). The twin anode offers the energies of Al K\( \alpha_{1/2} \) of 1486.61 eV and Mg K\( \alpha_{1/2} \) of 1253.64 eV. As it probes the core electrons of the atoms of the first 8 - 10 monolayers, the peak position can be identified with specific elements. Small peak shifts can be attributed to bonds between these atoms depending on the electronegativities involved. The relative peak heights are a measure for the elemental composition of the sample taking into account the cross section between the photon and the respective transition.

All organic materials measured in this work have been evaporated on gold foils. The positions in the spectrum are considered to be the intersection of a line approximating the edge and the background. The values determined for the IP have an error of about 50 meV. More details about the measurement setup can be found in [86].

### 4.3.2 Characterization of Solar Cells

#### Electrical Characterization

Two different measurement setups are used for the electrical characterization of solar cells, mainly depending on the preparation tool. The samples prepared in the UFO multi chamber are measured in the nitrogen atmosphere of the glovebox directly attached to the UFO. This has the advantage of being able to measure without having to encapsulate the device, making immediate measurements after processing possible. The devices are illuminated by the sun simulator SoCo 1200 MGH from Steuernagel GmbH (Mörfelden-Walldorf, Germany).\(^7\) The intensity

\(^7\)Some samples are illuminated using a SOL1200 from Dr. Hönle AG (Gräfelfing, Germany). It is explicitly pointed out, when this is the case.
Figure 4.7: While the sun simulator SoCo from Steuernagel has a considerably higher contribution than the sun (AM1.5) in the UV and the blue spectral region, the sun simulator Solar Light uses special filters to minimize the spectral mismatch. However, the high peaks above 800nm, stemming from the Xenon lamp used in the Solar Light, are difficult to filter. This increases the mismatch especially for IR-absorbing solar cells. Adapted from [126].

is referenced by a calibrated silicon photodiode from the Fraunhofer Institut für Solare Energiesysteme (Freiburg, Germany). The current-voltage characteristic is recorded using a source measurement unit SMU236 from Keithley Instruments (Solon, USA).

For the samples produced with the Lesker tools an automated setup is used. The sun simulator 16S-003-300 from Solar Light Company Inc. (Glenside, USA) illuminates the wafer through an optical fiber. The intensity is referenced to a silicon photodiode S1337-33BQ from Hamamatsu Photonics K.K. (Hamamatsu, Japan). J-V-characteristics are recorded using a SMU2400, also from Keithley. Only encapsulated samples can be measured as the measurements are done in air. The spectra of the two sun simulators are depicted in Figure 4.7.

Spectral Response

The wavelength dependent spectral response $SR(\lambda)$ is the current density produced by a solar cell or photo diode for a given intensity of monochromatic light. For the measurements in this work, an Apex Monochromator Illuminator from Newport (Irvine, USA) is used, consisting of a xenon arc lamp and a Corner-
4.3 Experimental Methods

The monochromatic light is chopped with a chopper and the cells current density recorded with a lock-in amplifier SR7265 from Signal Recovery (Wokingham, Great Britain).

The external quantum efficiency (EQE), i.e. the number of electrons collected at the contact per incident photon can be derived from the $SR$:

$$\text{EQE}(\lambda) = \frac{hc}{e\lambda} \frac{SR(\lambda)}{SR(\lambda)} \approx \frac{\lambda \text{[in nm]}}{1240 \text{ nm}} \frac{SR(\lambda)}{SR(\lambda)}.$$ (4.7)

In order to calculate the internal quantum efficiency (IQE), i.e. the number of electrons collected at the contact per absorbed photon, the absorption of the entire sample has to be measured. This can be done for samples produced with the Lesker tools in the setup also used for electrical characterization.

Device Lifetime

For any commercial use, not only the efficiency but also the lifetime of the photovoltaic device is important. As the measurement in real outdoor environment is slow and prone to instabilities of setup and environment, the cells are, therefore, measured in a closed environment. These measurement boxes are a development of the IAPP and Heliatek GmbH (Dresden, Germany). Light emitting diodes illuminate the sample with different intensities. Both, white-light and colored diodes can be used. The intensity is monitored using two different monitor photo diodes.

The temperature can be measured and controlled as well. For that a PT1000 resistance thermometer combined with cooling elements and a ventilation system on the one hand and electrical heating on the other is used. The accuracy of the temperature control is $1{\degree}\text{C}$.

The electronics needed to measure the device are placed in an external box to avoid unnecessary heating of the box. The measurement is done automatically using a SMU 2400 from Keithley Instruments (Solon, USA). For more details on the lifetime measurement of solar cells see [127].

Standard Reporting Conditions

The interest in organic photovoltaic has been growing considerably over the last years. However, as power conversion efficiencies approach values considered sufficient for commercial applications (see Chapter 3.1) it is important that the methods used to determine this efficiencies follow a more standardized procedure [70, 128]. Such standards have already been developed for inorganic photovoltaic devices describing standard reporting conditions (SRC) (see e.g. [129, 130]) The main demands are:

- a measurement temperature of $25{\degree}\text{C}$
• a sun simulator with certified spectrum and stability, and referencing to a standardized sun spectrum, called AM1.5

• an AM1.5 light intensity of 1000 W/m² (or 100 mW/cm²)

This AM1.5 spectrum is a sun spectrum considered to have passed 1.5 atmosphere thicknesses. This number corresponds to a solar zenith angle of 48.2°; it is chosen as it represents mid-latitudes where photovoltaic panels are most common.

Mismatch

The intensity of the solar simulator $I_{\text{sim}}(\lambda)$ is monitored by a reference solar cell having a spectral response $SR_{\text{ref}}(\lambda)$. The current density $j_{\text{ref}}^{\text{sim}}$, the reference solar cell delivers, can be calculated [70]:

$$j_{\text{ref}}^{\text{sim}} = \int I_{\text{sim}}(\lambda) SR_{\text{ref}}(\lambda) \, d\lambda. \quad (4.8)$$

However, as can be seen in Figure 4.7 the simulated spectrum always differs from the standard AM1.5 spectrum. Hence, even if both spectra have the same overall intensity, the current density of the reference cell under AM1.5 illumination $j_{\text{ref}}^{\text{AM1.5}}$ can differ:

$$j_{\text{ref}}^{\text{AM1.5}} = \int I_{\text{AM1.5}}(\lambda) SR_{\text{ref}}(\lambda) \, d\lambda, \quad (4.9)$$

and the part of the mismatch caused by the reference, $M_{\text{ref}}$, is

$$M_{\text{ref}} = \frac{j_{\text{ref}}^{\text{AM1.5}}}{j_{\text{ref}}^{\text{sim}}} = \frac{\int I_{\text{AM1.5}}(\lambda) SR_{\text{ref}}(\lambda) \, d\lambda}{\int I_{\text{sim}}(\lambda) SR_{\text{ref}}(\lambda) \, d\lambda}. \quad (4.10)$$

$M_{\text{ref}}$ can be considered as the factor by which the reference device misjudges the overall intensity of the simulator.

Likewise, the current density $j_{\text{test}}^{\text{sim}}$ produced by the solar cell to be tested with $I_{\text{sim}}(\lambda)$ can be determined using the spectral response of the tested cell $SR_{\text{test}}(\lambda)$:

$$j_{\text{test}}^{\text{sim}} = \int I_{\text{sim}}(\lambda) SR_{\text{test}}(\lambda) \, d\lambda, \quad (4.11)$$

and may once more differ from the current density obtained for an AM1.5 sun of equal overall intensity

$$j_{\text{test}}^{\text{AM1.5}} = \int I_{\text{AM1.5}}(\lambda) SR_{\text{test}}(\lambda) \, d\lambda, \quad (4.12)$$
4.3 Experimental Methods

with the part of the mismatch caused directly by the measurement of the tested cell $M_{test}$ given by:

\[
M_{test} = \frac{j_{sim}}{j_{AM1.5}} = \frac{\int I_{sim}(\lambda) \cdot SR_{test}(\lambda) \, d\lambda}{\int I_{AM1.5}(\lambda) \cdot SR_{test}(\lambda) \, d\lambda}.
\] (4.13)

The overall mismatch $M$ is the product of both:

\[
M = M_{ref} \cdot M_{test} = \frac{\int I_{sim}(\lambda) \cdot SR_{test}(\lambda) \, d\lambda}{\int I_{AM1.5}(\lambda) \cdot SR_{test}(\lambda) \, d\lambda} \cdot \frac{\int I_{AM1.5}(\lambda) \cdot SR_{ref}(\lambda) \, d\lambda}{\int I_{AM1.5}(\lambda) \cdot SR_{ref}(\lambda) \, d\lambda}.
\] (4.14)

This mismatch is an individual number for each device tested. However, it is not necessary for the overall intensity with which both, monitoring and tested cell, are illuminated, to be 100 mW/cm$^2$, given the spectral shape is not a function of intensity.

Now, the effective overall intensity $I_{eff}$, the tested cell actually “sees”, can be calculated from the current density of the monitor cell $j_{sim}^{ref}$, when the simulator’s calibration factor $C$ between $j_{sim}^{ref}$ and the overall simulator intensity $I_{sim}$ is known:

\[
I_{eff} = I_{sim} \cdot M = C \cdot j_{sim}^{ref} \cdot M.
\] (4.15)

The power conversion efficiency calculated from the J-V-characteristics (see Chapter 3.1.1) always refers to this effective overall intensity of an AM1.5 sun. Hence, for the solar cell to be measured at an effective intensity of 100 mW/cm$^2$, the monitor current has to be adjusted:

\[
j_{sim}^{ref} = \frac{j_{AM1.5}^{ref}}{M} \iff j_{test}^{AM1.5} = j_{test}^{sim}.
\] (4.16)

Only now, the current density of the test cell is the same for simulator and AM1.5 sun and the J-V-characteristics are comparable. However, this mismatch correction can only be done when the spectral response and, consequently, the mismatch are known before the J-V-measurement. In this work, due to technical difficulties, this is not possible for most measurements. Additionally, the temperature cannot be fixed to 25 °C, but it is about 8-10 °C higher during the measurement. All intensities given here, however, are AM1.5 intensities corrected for mismatch using Equation 4.15.
5 Efficiency of an Organic Solar Cell

The following chapter investigates the question of the efficiency organic photovoltaics can possibly reach and the spectral range of sunlight that has to be harvested to attain that efficiency. This maximum efficiency is calculated taking into account the difference between optical and electrical gap of organic semiconductors and the heterojunction characteristic for organic solar cells. Both, single heterojunction and tandem heterojunction cells are discussed.

5.1 Introduction

Today, heterojunction devices reach a certified power conversion efficiency in the laboratory of about 11 to 12% [44, 75] on an area of above 1 cm². However, to compete with existing technologies especially in the power generation market, an efficiency of well beyond 10% in production is usually considered necessary for the low material costs of organic materials to be of advantage. Hence, the question of the maximum efficiency of organic heterojunction devices is not merely an academic one, but it is also important for the economic estimation of price development.

The maximum power conversion efficiency which can be obtained has already been studied by several authors [131, 132]. Usually, these calculations were carried out for heterojunctions using PC₆₀BM, without taking the influence of temperature and charge carrier densities on the open-circuit voltage into account. Additionally, most studies do not distinguish between the electrical gap and the onset of absorption. It is remarkable that the ideal efficiency of a single junction solar cell is about 30% [53] and 15% for a two-junction tandem cell [54], which is much higher than the values of about 10% and 15%, respectively, predicted so far for organic solar cells [131, 132, 133].

Here, the power conversion efficiency of idealized single and tandem heterojunction devices is calculated taking into account the existence of a quasi-Fermi level splitting under illumination, a concept well known in inorganic semiconductor physics [134] (see Chapter 3.1.2). Furthermore, the difference between optical
and electrical gap of an organic material due to direct creation of excitons is incorporated in the calculations.

5.2 Theoretical Model

5.2.1 The Power Conversion Efficiency

As explained in Chapter 3.1.1, the power conversion efficiency $\eta$ for the standard AM1.5g spectrum [70, 135] with an intensity of 100 mW/cm$^2$ is defined as

$$\eta = \frac{FF V_{OC} j_{SC}}{100 \text{ mW/cm}^2},$$

(5.1)

with $FF$ as fill factor, $V_{OC}$ as open-circuit voltage, and $j_{SC}$ as the short-circuit current density.

5.2.2 Optical Gap and Short-Circuit Current Density

The electrical gap $E_{eg}$ or $E_g$ of an organic semiconductor is defined by the difference between its ionization potential (IP) and its electron affinity (EA). In organic materials, the fraction of free charge carriers generated upon absorption of a photon is small, around 1% to 10% [136, 137]. Thus, absorption primarily leads to the creation of bound electron-hole pairs, i.e. excitons. Having a lower energy than free charge carriers, these excitons can also be created by photons of lower energy than the electrical gap [20]. Hence, the optical gap $E_{og}$, i.e. the onset of absorption in a material can be calculated as

$$E_{og} = E_{eg} - E_B = EA - IP - E_B,$$

(5.2)

with the exciton binding energy $E_B$. In this work, $E_B$ is set to 0.3 eV which is a typical value for organic compounds [12, 20]. The short-circuit current density can be calculated for the Standard Reporting Conditions (SRC) [129, 135] by

$$j_{SC} = e \int \Phi(\lambda) EQE(\lambda) d\lambda,$$

(5.3)

for the photon flux (i.e. photons per area and time) of an AM 1.5 sun, here denoted $\Phi(\lambda)$. $e$ is the elementary charge and EQE is the external quantum efficiency at SRC (see Chapter 3.1.2). The latter is assumed to be 65% throughout the respective absorption range ($E_{\text{photon}} > E_{og}$). In reality, it will be difficult to find materials with an EQE that high for the whole absorption region. However,
5.2 Theoretical Model

Figure 5.1: The external quantum efficiency is considered to be a constant 65% over the whole range from the lowest optical gap up to 4.14 eV (300 nm). Left: In a single cell the photons are absorbed both by the donor and acceptor. Right: In a tandem cell, the absorption is affected by both donors and both acceptors, with the additional condition that the currents produced by both subcells are equal.

organic solar cells with an EQE of 80% and higher between 350 nm and 650 nm have been reported [138]. Hence, these 65% are in reach at least on average. The same applies for tandem cells, as long as the currents of the two subcells match.

5.2.3 Open-Circuit Voltage and Splitting of Quasi-Fermi Levels

Many studies have argued that the open-circuit voltage ($V_{OC}$) of an organic solar cell is proportional to the difference between the electron affinity of the acceptor ($E_A$) and the ionization potential of the donor ($I_P$), without ever reaching this difference at operating conditions. In the description introduced e.g. by Würfel [134], it is the splitting of the quasi-Fermi levels upon illumination that is limiting the open-circuit voltage. In this model, assuming that the difference from the Fermi energy to the gap is much larger than $kT$, $V_{OC}$ can be calculated as follows:

$$
e V_{OC} = \epsilon_{F,C} - \epsilon_{F,V} = E_A - I_P - kT \ln \frac{N_A N_D}{n p}, \quad (5.4)$$

where $\epsilon_{F,C}$ and $\epsilon_{F,V}$ are the quasi-Fermi levels, $T$ is the temperature, $n$ and $p$ the charge carrier densities of electrons in the acceptor and holes in the donor, respectively, and $N_A$ and $N_D$ the effective densities of states in the acceptor and donor, respectively. The third term describes the difference between the effective
electrical energy gap of the heterojunction and the splitting of the quasi-Fermi levels. This difference is denoted here as quasi-Fermi splitting loss.

As the solar cell is itself an emitting black body, recombination at room temperature will never be zero. In simple terms, this difference is caused by the fact that the electrochemical potential of the Boltzmann-distributed electrons and holes is not at the electrical energy levels, but at a lower energy, depending on charge carrier density and temperature. The difference was found to be 0.3 eV for several polymers in combination with PC_{60}BM at room temperature and an intensity of one sun [131]. Such values are expected for photogenerated carrier densities of approx. 10^{16} \text{1/cm}^3 at SRC.

A minimum energy offset $\Delta E$ between the EAs of donor and acceptor is considered necessary to efficiently separate the excitons [139], likewise for the offset between the IPs. Consequently, $\Delta E$ is here considered to be equal to $E_B$. The fill factor is set to 65%, which represents a realistic value for advanced organic devices [87, 120]. The absorption of both materials is assumed to start at the lower of the two materials’ optical gaps and to reach up to 4.14 eV (300 nm) above which the number of photons arriving from the sun is very small (see Figure 5.1). For the idealized calculation, it does not matter whether the donor or the acceptor has the lower gap and what the absolute values for the IPs and the EAs are. The acceptor is chosen to have the lower gap. Therefore, the $E_{A_A}$ defines both $V_{OC}$ and the onset of absorption, with the $E_{A_D}$ being at least the minimal offset of 0.3 eV above the $E_{A_A}$ (see Figure 5.2).
5.3 Calculation

5.3.1 Single Heterojunction Solar Cells

In Figure 5.3, the maximum power conversion efficiency of a single heterojunction device is plotted as a function of the minimum electrical gap of the materials and the loss occurring with the quasi-Fermi level splitting. As the $V_{OC}$ increases with decreasing quasi-Fermi splitting loss (see Equation 5.4), the performance of the device increases. For an electrical gap of 1.7 eV and a loss of 0.3 eV, the $\eta$ is 15.3%. Yet, even at a higher loss of 0.5 eV and an electrical gap of 1.95 eV (resulting in absorption only in the visible range of 300 nm to 750 nm), the calculated efficiency is larger than 11.5%. When calculating the efficiency assuming that the $V_{OC}$ is 0.6 V smaller than the lowest optical gap as done by Veldman et al. [133], the maximum efficiency of 11% stated there is reproduced here. The large difference to literature values is caused by the distinction between optical and electrical gap.

Figure 5.3: The power conversion efficiency of a single heterojunction device is depicted as a function of the minimum electrical gap and the quasi-Fermi splitting loss. It has a maximum of 15.3% for a quasi-Fermi splitting loss of 0.3 eV and decreases for higher losses.
Figure 5.4: The power conversion efficiency of a tandem heterojunction device is depicted as a function of the minimum electrical gap of each of the two subcells. Additionally, the electrical gap of the first subcell is considered to be always the higher one.

If the $E_{og}$ is also considered the limit of absorption, the optimum gap shifts to 1.4 eV (890 nm) and the efficiency drops to 11.1%.

5.3.2 Tandem Heterojunction Solar Cells

In tandem solar cells, all four active materials contribute to the absorption (see Figure 5.1). For the calculation, the first subcell is assumed to absorb from 4.14 eV (300 nm) down to the larger optical gap of the two materials, where the absorption of the second subcell starts and reaches down to the smaller optical gap. Given the same fill factor of 65%, the current density delivered by the device is always limited by the lower current of the two subcells:

$$j_{SC} = \min(j_{SC, 1st \ subcell}, j_{SC, 2nd \ subcell}).$$  \hfill (5.5)
The \( V_{OC} \) of the entire device is determined by adding the open-circuit voltages of the two subcells:

\[
V_{OC} = V_{OC, \text{1st subcell}} + V_{OC, \text{2nd subcell}}.
\]

Each \( V_{OC, \text{subcell}} \) is calculated using Equation (5.4). It was shown by Timmreck et al. [108] that this addition is possible for real organic tandem devices.

Figure 5.4 shows the power conversion efficiency of a tandem solar cell plotted against the electrical gaps of its subcells with a constant quasi-Fermi splitting loss of 0.3 eV. The maximum \( \eta \) that can be reached with a tandem cell is as high as 21\% with electrical gaps of 1.25 eV and 1.9 eV, corresponding to optical gaps of 1300 nm and 770 nm. However, this means that practically all visible light absorbed has to be absorbed by the first subcell, and good organic semiconductors absorbing up to 1300 nm need to be found. Yet, assuming electrical gaps of a more easily reachable 2.23 eV and 1.7 eV (i.e. optical gaps of 645 nm and 890 nm), one could still obtain an efficiency of 19\%. Again, only using one value for electrical and optical gap would lead to an optimal efficiency of 15.2\% with gaps of about 1.75 eV (710 nm) and 1.15 eV (1080 nm).

### 5.3.3 Summary

By combining absorbers with suitable energy levels for an organic solar cell, a power conversion efficiency of about 15\% in a single cell and of 21\% in a tandem cell should be feasible. More importantly, by using materials in a tandem cell whose absorption covers a spectral region from 300 nm to 890 nm, an efficiency of about 19\% could be reached. Thus, even without absorbers reaching very far in the infrared, it should be possible to produce competitive organic devices employing the approach of tandem solar devices. For these calculations, the fill factor and the EQE within the absorption range are set to 65\%. The exciton binding energy as well as the energy level offset between IPs (EAs) are assumed to be 0.3 eV, both of which are often higher in today’s photovoltaic devices. Hence, to find good absorbers with suitable energy levels is one major challenge on the route to a broad application of organic photovoltaics.
6 Tin Phthalocyanines in Organic Solar Cells

This chapter is dedicated to the investigation of fluorinated tin phthalocyanines as absorber materials in organic solar cells. Both material and thin film properties are described. Then, these materials are tested in simple photovoltaic devices.

6.1 Introduction

Phthalocyanines have been under investigation as absorber materials in OSC for some time now (e.g. [33, 107, 140, 141]). The molecules consist of four pyrrolic connected by nitrogen atoms with a metal or nitrogen center atom. They are almost flat and can pack very well in a thin film. This leads to absorption coefficients in the region of $10^{-5}\text{cm}^{-1}$ [142]. They are arenes which makes them usually both chemically and thermally stable [143]. Especially copper phthalocyanine (CuPc) and zinc phthalocyanine (ZnPc) have been successfully used in all kinds of solar cell devices.

However, these materials absorb well below 800 nm. When looking for a material that absorbs above that threshold and can thus be considered an infrared absorber, other phthalocyanines are better suited. Lead Phthalocyanine, for example, is known to absorb in the infrared. Tin phthalocyanine (SnPc) is another molecule absorbing in the infrared; it has successfully been employed in organic solar cells. Yet, due to its ionization potential (IP) of about 5.1 eV, the $V_{OC}$ when combined with C$_{60}$ in flat heterojunction cells is only about 0.45 V.

An approach to changing the IP of metal phthalocyanines is fluorination, i.e. the reaction of the molecule with fluorine to F$_x$-MePc. This method has been used on ZnPc with success; it has led to an increase of the IP of more than 0.3 eV [144] to more than 5.4 eV. Consequently, solar cell devices with a bulk heterojunction consisting of an F$_x$-ZnPc:C$_{60}$ attain a $V_{OC}$ of 0.66 V, about 0.15V higher than devices using a non-fluorinated ZnPc [145, 146]. Hence, the fluorination of SnPc could be a way to obtain an organic solar cell using C$_{60}$ where light from the infrared region is contributing to the current, and where the $V_{OC}$ exceeds the 0.45 V of unsubstituted SnPc:C$_{60}$ heterojunctions.
Figure 6.1: The different halogenated tin phthalocyanines (B-D) and the neat SnPc (A) are investigated. The halogenation with fluorine and chlorine is done, both, at the outer R position and the center M position indicated in the structural formula on the right.

For this investigation, four different molecules are examined, both fluorinated and chlorinated. The molecular structures of the materials studied here are depicted in Figure 6.1. Molecule A is the neat SnPc molecule, which is investigated for comparison. Molecule B is fluorinated, the center group is F$_2$Sn. Molecule C is chlorinated, the two chlorine atoms also being attached to the centered tin atom. Finally, molecule D, is both fluorinated and chlorinated, with two chlorine atoms attached the center position and four flour atoms being bound to the outer benzene rings (for full names see Table 6.1).

All halogenated materials were synthesized by the group of Prof. Währle at the IOMC, University of Bremen. Mass spectroscopy and absorption measurements in solution were done in Bremen by Dr. Schnurpfeil from the same group.

6.2 Material Analysis

Evaporation

All materials have been gradient sublimated three times to achieve the necessary purity. From the mass spectrometry, done by the group of Prof. Währle in Bremen, it is known that the fluorine in molecule B is only weakly bound to the center atom. In contrast, the fluorines attached as side groups of molecule D are bound much stronger and the mass spectroscopy shows only little loss of fluorine. Both results are reinforced by the sublimation results. The materials A and C can be stably sublimated. During sublimation of molecule D, only little corrosion
6.2 Material Analysis

Table 6.1: Sum formulae and names: Both fluorinated and chlorinated tin phthalocyanines are investigated.

<table>
<thead>
<tr>
<th>Sum formula</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>A SnPc</td>
<td>tin(II) phthalocyanine</td>
</tr>
<tr>
<td>B F₂SnPc</td>
<td>tin(IV)-38,38-difluoro-phthalocyanine</td>
</tr>
<tr>
<td>C Cl₂SnPc</td>
<td>tin(IV)-38,38-dichloro-phthalocyanine</td>
</tr>
<tr>
<td>D F₄Cl₂SnPc</td>
<td>tin(IV)-38,38-dichloro-4,13,22,30-tetrafluoro-phthalocyanine</td>
</tr>
</tbody>
</table>

Table 6.2: Overview over the material properties: All materials have a similar thin film density \( \rho \) and an almost identical maximum absorption wavelength \( \lambda_{Max(\text{liq})} \) when dissolved in chloronaphthalene.

<table>
<thead>
<tr>
<th>Sum formula</th>
<th>Density / g/cm(^3)</th>
<th>( \lambda_{Max(\text{liq})} / \text{nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A SnPc</td>
<td>1.59</td>
<td>700</td>
</tr>
<tr>
<td>B F₂SnPc</td>
<td>1.47</td>
<td>699</td>
</tr>
<tr>
<td>C Cl₂SnPc</td>
<td>1.45</td>
<td>702</td>
</tr>
<tr>
<td>D F₄Cl₂SnPc</td>
<td>1.77</td>
<td>698</td>
</tr>
</tbody>
</table>

by hydrofluoric acid occurs inside the sublimation tubes and only during the first of the three sublimation steps. This may also be due to prior impurities.

For material B, however, heavy corrosion occurs in the glass tubes, and not only during the first sublimation, but during all three sublimation steps. This shows that at least part of the bound fluorine is lost during sublimation.

The mass densities of all materials are determined via a thickness measurement with the profilometer (for details see Chapter 4.3.1). They are comparable to other organic thin films (e.g. C\(_{60}\): 1.56 \( g/cm^3 \)), ranging from 1.45 \( g/cm^3 \) for molecule C to 1.77 \( g/cm^3 \) for molecule D.

Absorption

Figure 6.2 shows the wavelength dependence of the extinction coefficient in thin film for the four materials, derived from transmission measurements. All four materials exhibit a very similar contribution below 400 nm. This peak is also known for other phthalocyanines (e.g. [147]) though not always as high. In the spectral region between 400 nm and 600 nm, the absorption of all SnPcs is very low. Between 600 nm and 1000 nm, the absorption of all four materials has two maxima. The first always occurs at about 735 nm, but with differing intensity. While materials C and D containing chlorine show a higher intensity, the chlorine free substances have a lower and practically identical intensity of about 1.5\( \times 10^5 \) cm\(^{-1} \). This peak is not only bathochromically shifted as compared to e.g. CuPc, but is also considerably higher than the CuPc peak at 620 nm with an extinction of 1.3\( \times 10^5 \) cm\(^{-1} \) [148].
Figure 6.2: Besides a strong absorption below 400 nm the extinction coefficients of the SnPcs are particularly high for wavelength from 600 nm to almost 1000 nm. The first peak at 740 nm is especially prominent for the Cl$_2$SnPc; SnPc and F$_2$SnPc show their highest absorption at 890 nm.

The situation is inverse for the second peak at about 890 nm. The absorption spectra of the chlorine free molecules A and B show a high peak with an extinction coefficient of almost $2.0 \times 10^5 \text{ cm}^{-1}$, again both being very similar and much higher than the peak at 740 nm. For molecule C, however, this second peak is much lower than the peak at 740 nm and higher than the second peak of molecules A and B. For molecule D, this second peak is lowered to a shoulder of the 740 nm peak.

In literature ([147, 149]) this second peak of SnPc is often attributed to the absorption of the SnPc dimer. According to this, the dimer forms upon aggregation in thin films. The dimerization increases with increasing size of the crystallites formed in the aggregate. As the crystallite size depends upon the thickness of the layer, the dimer signal also increases with growing film thickness. At the same time, the monomer contribution at 740 nm is known to decrease for higher film thickness. The absorption peak at 890 nm originating in a dimer also explains its absence in the solution absorption spectrum. This inversion of peak heights for SnPc on crystallization points to a lower crystallization in the
thin films of materials containing chlorine. The chlorine possibly presents a steric obstacle for the phthalocyanine molecules to dimerize.

When comparing the absorption of molecules A and B, one can see that both are practically the same for wavelengths above 600 nm. Partially, this is to be expected as the fluorination usually does not change the optical gap but only shifts the HOMO and the LUMO of the molecule towards deeper energy levels. This leads to the absorption onset in the infrared being the same at 1000 nm. Additionally, the wavelength of maximum absorption in solution ($\lambda_{\text{Max}}(\text{liq})$) is virtually the same for all four molecules (see Table 6.2).

**Morphology**

![Morphology images](image-url)

*Figure 6.3:* The morphologies of halogenated SnPc layers on C$_{60}$ are measured using a Nanoscope AFM. They are of a grain-like structure, with different but generally small grain sizes.

The morphology of the materials is investigated with the AFM from Digital Instruments. The resulting topography images are shown in Figure 6.3. All thin films are prepared on glass with the layer combination also used in the solar cells:
Table 6.3: All root mean square roughnesses (RMS) of this table are determined using the Nanoscope from Digital Instruments. Halogenating SnPc at the center position appears to somewhat increase the roughness, yet, adding fluorine at the outer position even allows for smoother layers.

<table>
<thead>
<tr>
<th>Sum formula</th>
<th>Roughness RMS / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A SnPc</td>
<td>2.7</td>
</tr>
<tr>
<td>B F₂SnPc</td>
<td>5.4</td>
</tr>
<tr>
<td>C Cl₂SnPc</td>
<td>6.2</td>
</tr>
<tr>
<td>D F₄Cl₂SnPc</td>
<td>1.1</td>
</tr>
</tbody>
</table>

All materials show a grain-like structure. Layers composed of molecule A (the neat SnPc) and molecule D (containing both fluorine and chlorine) form small grains. Materials B and C, however, result in the formation of larger grains. This also translates into a larger mean square roughness for the latter two. All the values are displayed in Table 6.3. All roughnesses should be small enough for working solar cells.

6.3 Solar Cells

Solar cells are manufactured to investigate the photovoltaic properties of the materials in question. The so-called mip-structure is used: The intrinsic absorber materials are evaporated onto the ITO followed by the hole transporter, in this case BPAPF (for the names and properties of all materials see Chapter 4.1). A first thin layer of the hole transport remains undoped to protect the photoactive layers from unintentional doping, which could lead to trap states for the charge carriers. Usually such thin layers pose no barrier for the charge transport even when undoped. Then, a thicker hole transport layer (HTL) follows which is doped to permit a good carrier conductivity. This layer is used to decrease shorts, increase absorption in the active layers and allow for good extraction of the holes (see also Chapter 4.1). The latter is further promoted by a thin layer of the dopant, which is here NDP9 from Novaled AG (Dresden). Gold is used as cathode material.

No electron transport layer is used to make processing easier. This is possible because electron extraction from the C₆₀ to ITO is working well enough without tuning energy levels at the interface by doping. This may lead to losses in current density due to a non-optimized cavity. The HTL thickness also is not optimized to yield the best current density, but kept constant to allow for better comparability.
6.3 Solar Cells

Figure 6.4: The J-V-characteristics of the planar heterojunction cells show that all devices display a good blocking behavior in backward direction in the dark (open symbols; illuminated: filled symbols) as well as a low series resistance. Right: Zoom of J-V-characteristics

<table>
<thead>
<tr>
<th>Sum formula</th>
<th>$V_{OC}$ / V</th>
<th>$J_{SC}$ / mA/cm²</th>
<th>FF / %</th>
<th>Sat</th>
<th>$\eta$ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A SnPc</td>
<td>0.46</td>
<td>2.2</td>
<td>43.7</td>
<td>1.60</td>
<td>0.4</td>
</tr>
<tr>
<td>B F₂SnPc</td>
<td>0.49</td>
<td>2.8</td>
<td>48.3</td>
<td>1.43</td>
<td>0.6</td>
</tr>
<tr>
<td>C Cl₂SnPc</td>
<td>0.41</td>
<td>2.9</td>
<td>27.1</td>
<td>2.57</td>
<td>0.3</td>
</tr>
<tr>
<td>D F₄Cl₂SnPc</td>
<td>0.53</td>
<td>1.0</td>
<td>29.7</td>
<td>2.67</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 6.4: The fingerprints of the planar heterojunction reflect that the fluorination leads to a higher $V_{OC}$, though the effect is not very large for material B. The chlorination does not show this effect, but rather decreases the overall efficiency.

6.3.1 Planar Heterojunctions

To evaluate the photovoltaic properties of the phthalocyanines, planar heterojunction OSCs are prepared, using the following stack:

ITO/C₆₀(15)/X-SnPc(10)/BPAPF(5)/p-BPAPF(50;5%)/NDP9(1)/Au(40)

The J-V-characteristics are depicted in Figure 6.4. An overview over the fingerprints of the devices can be found in Table 6.4. It can be seen that the fluorination, as expected, increases the $V_{OC}$. The effect is small for the molecules without the chlorine: from 0.46 V (molecule A) to 0.49 V (molecule B) where the fluorine atoms are attached to the center.

For the chlorinated molecules where the fluorine atoms are attached to the outer benzene rings, the effect is larger: from 0.41 V (molecule C) to 0.53 V
(molecule D). This can be explained by the expected lowering of the IP. It cannot be determined from this experiment, whether the EA is lowered as well. However, as the absorption of $F_2SnPc$ shows an unchanged optical band gap, this may well be the case. The absorption of $F_4Cl_2SnPc$ rather suggests an enlarged band gap with the IP lowered more than the EA. As the increase in $V_{OC}$ is larger for the chlorinated molecules, possibly, only the IP is lowered from a certain point. On the other hand, the smaller increase in $V_{OC}$ going from A to B can also be attributed to fluorine losses that occur during sublimation.

Figure 6.5: Up to 800 nm the spectral shape of the EQE (determined using filtered light of a Steuernagel sun simulator) resembles the extinction coefficient shown in Figure 6.2. The dimer absorption at 890 nm, however, can hardly be seen, probably due to a low optical field of the infrared light close to the top contact.

The heavily decreased absorption of material D is reflected by a low $j_{SC}$ and a very low external quantum efficiency (EQE; see Figure 6.5). The fill factor of both chlorinated materials C and D are very low as well. One reason could be a hindered separation of the excitons. However, as the $V_{OC}$ does not differ greatly from materials A and B and the band gap is not altered either, this is not likely. A more likely explanation is the impairment of the charge carrier transport. Then, already a small bias in forward direction can prevent the charge carriers from reaching the contacts.

On the other hand a bias in backward direction increases the current density, which translates into a large saturation value. This can be seen for both solar cells
with the two chlorinated materials. The J-V-characteristics without illumination show a very flat behavior, ruling out parallel shunts as cause of the high saturation.

The sublimation of the two materials has gone well. This makes it unlikely that impurities forming trap states are the reason for the decreased charge carrier transport. Another reason for bad transport is often an unfavorable packing of the molecules in the thin layer: phthalocyanines are known to form a 1D-stack of molecules lying flat on top of each other with their orbitals overlapping well [150]. Possibly, the chlorine attached to the center Sn atom prevents the molecules from stacking leading to a decreased mobility and, consequently, a decreased fill factor.

As can be seen in Figure 6.2 the fluorination of A to form B leads to higher absorption. This is echoed in both, the EQE and the $j_{SC}$ of the solar cell with material B. The fill factor as well is somewhat higher. This, however, is not necessarily due to a problematic charge transport in material A: the solar cell of material A exhibits a small shunt that produces the little bit higher backward current density observed in the dark curve. It leads to an additional leakage current through the cell, increasing the backward current density and decreasing the forward current in the fourth quadrant, for increasing bias. This explains the increased saturation and the decreased fill factor of the OSC with material A.

In the absorption (see Figure 6.2) all materials exhibit a second peak at about 890 nm attributed to dimer absorption. Neither of the EQEs (Figure 6.5) reflects this very well; their peak at this wavelength is developed only weakly. While the flat layer of the SnPc should still absorb at this region, it apparently does not lead to a current. One explanation might be that the C$_{60}$-layer changes the morphology of the phthalocyanine evaporated on top of it. This may inhibit the dimerization, e.g. by forming a partially mixed layer. However, C$_{60}$ is known to form a smooth thin film layer. Additionally the effect also occurs for material A for which the dimer peak has been observed also in literature. It is, therefore, far more likely that the intensity of the optical field of a wavelength as large as 890 nm close to the opaque contact is too small to lead to a considerable contribution to the current.

### 6.3.2 Bulk Heterojunctions

To further test the materials, they are employed in bulk heterojunction solar cells. In bulk heterojunctions, the distance from the photon-created exciton and the closest donor-acceptor interface is usually much smaller than in a flat heterojunction device. The exciton diffusion length, therefore, is usually not a limiting factor. On the other hand, the transport is no longer necessarily parallel to the built-in electric field, so a good transport of the respective charges is crucial (electrons in the acceptor, holes in the donor; see Chapter 3.2.1). The following bulk heterojunction devices are made, using C$_{60}$ as acceptor material:
Figure 6.6: The J-V-characteristics of the bulk heterojunction devices again show a good blocking behavior suggesting that no morphological problems impair the solar cell performance. All SnPc-based devices, however, have a low FF and a low \( j_{SC} \), as can be seen in the zoomed-in graph on the right; it is much lower than the FF and \( j_{SC} \) of the ZnPc reference cell.

Additionally, a bulk heterojunction in mip structure using zinc phthalocyanine (ZnPc) as donor material\(^1\) is made for comparison. ZnPc is not absorbing in the infrared spectral region having an optical gap of about 750nm.

Figure 6.6 shows the J-V-characteristics of these cells. The overview over all fingerprints is given by Table 6.5. Most noticeably, the \( V_{OC} \) is increased by about 0.1 V compared to the respective flat heterojunction devices, more in case of material C. This effect is known also for ZnPc and can possibly be attributed to interface dipoles. These can form at the interface between \( C_{60} \) and the donor and change the effective band gap of the heterojunction. Consequently, the energy of the separated charge carriers, and, hence, the \( V_{OC} \) is altered.

Additionally, all materials show now roughly the same \( V_{OC} \) of about 0.6 V. The neat SnPc (material A) had the second lowest \( V_{OC} \) in the flat heterojunction; it now exhibits the highest \( V_{OC} \) though only by a small margin that may well be attributed to statistical variation. This means that the idea that the fluorination or chlorination of SnPc leads to higher \( V_{OC} \) is not confirmed for bulk heterojunction solar cells.

Both, material A and material B show higher current densities than their flat heterojunction counterparts. As the absorber layer has a bulk volume ratio of 2:1 (\( C_{60} \) to X-SnPc) the number of donor molecules in a 20 nm thick mixed layer is only 67% of a 10 nm flat donor layer. That means that more of the excitons

\(^1\)The active bulk layer is 30 nm thick, which has an impact mainly on the current density observed and to a lesser extent the FF. The \( V_{OC} \) should only vary slightly.
Table 6.5: The fingerprints of the bulk heterojunction devices show that the $V_{OC}$ is generally higher than in the planar devices. Yet, due to the low FF the overall efficiency is not increased.

<table>
<thead>
<tr>
<th>Sum formula</th>
<th>$V_{OC}$ / V</th>
<th>$j_{SC}$ / mA/cm²</th>
<th>FF / %</th>
<th>Sat</th>
<th>$\eta$ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A SnPc</td>
<td>0.62</td>
<td>2.9</td>
<td>35.1</td>
<td>1.60</td>
<td>0.6</td>
</tr>
<tr>
<td>B F₂SnPc</td>
<td>0.58</td>
<td>3.0</td>
<td>37.2</td>
<td>1.59</td>
<td>0.6</td>
</tr>
<tr>
<td>C Cl₂SnPc</td>
<td>0.59</td>
<td>2.4</td>
<td>34.4</td>
<td>1.81</td>
<td>0.5</td>
</tr>
<tr>
<td>D F₄Cl₂SnPc</td>
<td>0.60</td>
<td>0.6</td>
<td>27.6</td>
<td>2.80</td>
<td>0.1</td>
</tr>
<tr>
<td>E ZnPc</td>
<td>0.58</td>
<td>6.9</td>
<td>53.2</td>
<td>1.09</td>
<td>2.0</td>
</tr>
</tbody>
</table>

created also reach the electrodes, i.e. the internal quantum efficiency is increased as expected by using a mixed layer. Obviously, the exciton diffusion length is so low that even in a thin donor layer of 10 nm in a flat device, not all of the excitons reach the separating interface. In contrast, the $j_{SC}$ of the devices using the chlorinated materials C and D drops by 20-40 %, the internal efficiencies are not increased.

Without the assistance of a built-in field that supports the transport of the charge carriers to their respective electrodes in a flat device, the fill factor of the bulk heterojunction devices drops considerably (materials A, B, and D) or remains low (material C). Furthermore, the saturation remains high for all materials. As all diodes show a very good blocking behavior in the dark, saturation and FF cannot be explained by shunts through the cell leading to parasitic currents at higher biases. The most likely explanation is a low charge carrier mobility in the active layer. When assisted by the applied bias, i.e. in backward direction more carriers can reach the transport layers and, consequently, the electrodes. When hindered by a forward bias, many electrons and holes recombine before reaching the transport layer.

Figure 6.7 shows the external quantum efficiencies of the bulk heterojunction devices as a function of wavelength. Materials A, B, and C all show a similar EQE; the EQE for B is slightly higher and the EQE of C is slightly lower than the EQE of the neat SnPc, material A. This is very much in accordance with their $j_{SC}$. The dimer peak observed in the absorption of A and B again only contributes marginally to the current, as is the case for flat heterojunctions. The bulk heterojunction device of material D has a much lower EQE, also in accordance with its low $j_{SC}$. The EQEs of materials C and D again show that without negative bias, the cells cannot produce the current density that the absorption of these two materials suggests (see Figure 6.2).

The height of the peak at about 450 nm that can be attributed to $C_{60}$ has remained comparable to the same peak in the flat device. However, the amount of $C_{60}$ has decreased in the bulk layer to about 90 %; this shows that it is beneficial or at least not detrimental to use a material with a very high diffusion length like
Figure 6.7: The external quantum efficiencies of the bulk heterojunction devices with C₆₀ (measured with filtered light from a Steuernagel sun simulator) extends further into the infrared than the EQE of the reference bulk device based on ZnPc. However, corresponding well to the low $j_{SC}$ the integral EQE is considerably lower. Furthermore, dimer peak has entirely vanished in the bulk heterojunctions.

C₆₀ in a bulk heterojunction. For the donor materials A and B the effect is definitely positive: the peak height at 750 nm is increasing from 11% and 13% to about 17% and 20% respectively despite the smaller amount used in the bulk layers. The same peak decreases for materials C and D. It is, therefore, clearly the donor that is responsible for the change in $j_{SC}$.

Nonetheless, the integral quantum efficiency remains low, when compared to the EQE of the ZnPc bulk heterojunction device. Above 750 nm the SnPcs (also taking into account the different thicknesses), show a higher quantum efficiency than the ZnPc.²

²The small contribution of light above 800 nm to the EQE of the ZnPc:C₆₀ device is sometimes attributed to the absorption of an exciplex at the heterojunction interface, but can also be explained partially as an artifact originating in light of other wavelengths going around the bandpass filters and through filter scratches/imperfections.
6.3 Solar Cells

Figure 6.8: As the UPS signal of thin film layers of the materials A and B on the left shows the energetic difference between the two is small leading to almost identical IPs. Additionally, as can be seen on the right, there is no detectable XPS signal of fluorine on either of the two thin film samples making it probable that hardly any fluorine is present in the layer.

6.3.3 Photoelectron Spectroscopy

Both, in flat and in bulk heterojunctions, the neat and the fluorinated SnPc (material A and B) show very similar results. Furthermore, the absorption of both materials is very similar above 600 nm. Since there is evidence of unbound fluorine during sublimation, the question arises, whether and to what degree material B is still fluorinated. To investigate this question a combined XPS/UPS scan is done (see Chapter 4.3.1). The results of this measurement are depicted in Figure 6.8.

The graph on the left shows the UPS measurement giving information on the energy levels of the layers. Each layer has a thickness of 10 nm and is evaporated on a gold substrate. The resulting measurement of material B only slightly differs from the data of material A. The ionization potentials derived from these data are 5.17 eV for the fluorinated material B and 5.14 eV of the neat material A. Hence, the attached fluorine that is left only allows for a minor increase in IP.

This finding is further supported by the XPS measurement (Figure 6.8 right): the difference between the fluorine peaks in materials A and B is below detection level. If material B were still fluorinated for a large part, at least a qualitative signal should be detectable. One can, therefore, conclude that the fluorine attached to the center atom is not bound strong enough to withstand evaporation reliably.
6.3.4 Summary

Halogenation of phthalocyanines is a known way to increase the efficiency of organic solar cells by lowering the donor’s IP. For the materials under investigation, however, this is observed only partially. While chlorination of SnPc considerably worsens the transport properties of the active layer leading to a lowered FF, the fluorination of SnPc results as expected in an increase in $V_{OC}$ and, consequently, efficiency for planar heterojunctions.

Transferring this increase to bulk heterojunction, however, is not possible; both efficiency and spectral behavior of F$_2$SnPc-based devices remain unchanged. Additionally, evaporation and XPS analysis suggest that F$_2$SnPc cannot be stably evaporated without losing the fluorine atoms. One way to reduce this instability would be to attach the fluorine outside the core molecule, i.e. at the R position, yet, without the chlorination of the centered Sn atom. This can lead to a material that is stably evaporable and has the lowered IP intended without the draw back of a decreased fill factor of the material F$_4$Cl$_2$SnPc.
7 Benzannulation of Aza-Bodipy Dyes

This chapter treats the effect of benzannulation of aza-bodipy materials on their thin film properties, amongst others absorption and energy levels. The two materials are then used in comparison as donor materials in organic solar cells [151].

7.1 Introduction

For organic solar cells prepared from solution, approaches for NIR absorption range from the use of low band gap polymers like PCPDTBT [152] over the use of solution processable small molecules [56] to the incorporation of colloidal quantum dots like PbSe [153]. In photovoltaic devices based on vacuum evaporation of small molecules, metal phthalocyanines have shown good performance [154, 149, 155]. However, in order to fully use the chemical flexibility and to tailor the optical and electronic properties, the material class has to be improved. This is usually done by peripheral substitution of the phthalocyanines with bulky groups or hydrocarbon chains to enhance their solubility [156, 157]. Those functionalized phthalocyanines show promising properties but are in turn difficult to evaporate due to their side chains and have low volatility [158, 159, 160]. Additionally, in combination with the fullerene C_{60} they often deliver open-circuit voltages (V_{OC}) considerably lower than the heterojunction’s effective energy gap (e.g. a V_{OC} of 0.5V for zinc phthalocyanine:C_{60}) [33].

The bodipy 4,4′-difluoro-4-bora-3a,4a-diaza-s-indacene and especially the aza-bodipy 4,4′-difluoro-4-bora-3a,4a,8-triaza-s-indacene [161, 162, 163] have shown an intense absorption up to the NIR region despite the rather small π-conjugated system [164, 165]. The convenient synthesis allows an easy introduction of functional groups, therefore, bodipy derivatives are currently investigated for all types of organic solar cell applications such as solution processed organic [166, 167] and Grätzel [168] type solar cells. For the former cells, bodipys as donor materials in combination with PCBM as acceptor showed an efficiency of up to 2.0 %, for the latter one an efficiency of around 1.7 % was reported.
Since the robust molecule core (Figure 7.1) usually offers an enhanced thermal stability, bodipys are particularly interesting for applications using vacuum sublimation. It has been shown that benzannulated aza-bodipys are readily accessible by the addition of aryl Grignards to phthalodinitrile and a subsequent in-situ reduction-condensation mechanism with formamide [169]. These structures showed a bathochromic shift of the absorption maximum, compared to the non-benzannulated aza-bodipys.

In this chapter, the material class of aza-bodipys for application in vacuum-deposited organic photovoltaics is investigated, by comparing the 1,3,5,7-Tetraphenyl-borondifluoride-azadipyrromethene (Ph₄-bodipy) with the benzannulated Bis-(phenyl)-borondifluoride-azamethene (Ph₂-benz-bodipy) (see Figure 7.1). The focus is on the solution and thin film properties of the molecules. Organic heterojunction solar cells based on both materials are prepared to study the impact of the planarized bodipy core on the optical and electronic properties and the solar cell performance.
7.2 Properties of Bodipys

7.2.1 Chemical Preparation

Synthesis of the 1,3,5,7-Tetraphenyl-borondifluoride-azadipyrromethene (Ph$_4$-bodipy) is done according to the procedure reported in literature [170, 161, 162]. Synthesis of the Bis-(phenyl)-borondifluoride-azamethene (Ph$_2$-benz-bodipy) is carried out according to the process described in Gresser et al. [169]. The crude product is purified by flash chromatography (dichloromethane/hexane) yielding the borondifluoride complex of the Ph$_2$-benz-bodipy (4.37 g, 78%), with physical characteristics identical to those already described in Ref. [169].

For both the cyclic voltammetry (CV) and the absorption measurements of solutions, HPLC grade dichloromethane is used. The UV/VIS spectra in solution are recorded on the SHIMADZU UV-VIS-NIR recording spectrometer. The cyclic voltammetry scans are performed with a three-electrode setup (Pt-working, Pt-counter electrode, and an Ag/AgCl secondary reference electrode) in degassed dichloromethane and tetrabutylammonium hexafluorophosphate (TBAHFP, 0.1M) under inert gas (N$_2$) atmosphere at a scan rate of 100mV/s. All stated potentials denote the half wave potentials of the reduction and oxidation, respectively, and are internally referenced to the half wave potential of the ferrocene/ferrocenium couple (Fc/Fc$^+ = 4.78$ eV).

For the quantum chemical calculations, density functional theory with the b3lyp functional and the 6-31+g** basis set is used without symmetry constraints, as implemented in the Gaussian03 program package [171]. All optimized structures are confirmed with a subsequent frequency calculation to make sure that a true minimum is reached.

7.2.2 Solution and Thin Film Properties

The benzene ring annulation in the Ph$_2$-benz-bodipy system has a strong impact on the molecular as well as on the electronic structure of the system. The consequence for the molecular structure is a planarized core consisting of five fused rings whereas in the Ph$_4$-bodipy the core spans only three rings (see Figure 7.1). That way, the annulation significantly reduces the rotational degree of freedom since in the Ph$_4$-bodipy all phenyl rings can tilt relative to the planar core, whereas in the Ph$_2$-benz-bodipy only two rings have the ability to twist. Accordingly, the electronic structure of the Ph$_2$-benz-bodipy is also affected by the extended π-electron system.

Figure 7.2 depicts the distribution of the highest occupied and the lowest unoccupied electron orbitals for both molecules. They are calculated using time dependent density functional theory and Gaussian03 (see 7.2.1). The colored
The benzannulation leads to the distribution of both, the HOMO and the LUMO to the benzene rings as can be determined from the DFT calculation illustrated here. Areas represent the spatial distribution of the amplitude of the orbital over the molecule; large areas indicate high electron density.

Though calculated for the molecule, the low intermolecular interactions outlined in Chapter 2.1 allow for the conclusions to be transferred also to the thin film at least qualitatively. Figure 7.2 shows that upon benzannulation, the HOMO distribution is spread from the core of the molecule to the upper benzene rings. The same is true for the effect of benzannulation on the LUMOs, though to a lesser extent: The orbital distribution is spread over the benzene rings. This leads to a larger conjugated system as mentioned.

The resulting bathochromic shift in absorption can be seen in Figure 7.3. In solution with dichloromethane, the absorption maximum is moved from 650 nm (Ph₄-bodipy) to 710 nm (Ph₂-benz-bodipy), a change of 60 nm. This shift found in solution upon modification of the molecules can also be observed in thin films. The wavelength dependence of the attenuation coefficient α of both materials is also plotted in Figure 7.3.

The absorption maximum shifts from 702 nm for the Ph₄-bodipy to 773 nm for the Ph₂-benz-bodipy. Additionally, the absorption maxima of the materials in thin films are bathochromically shifted compared to their solution absorption (Figure 7.3). This effect is well known and often attributed to the close packing in films.
This increases the intermolecular interaction, which lifts degeneracies in energy levels and often leads to smaller energy gaps by the formation of J-aggregates [12].

The onset of absorption on the bathochromic side is used to find the optical gap. It has a value of 1.62 eV cm\(^2\) for the Ph\(_4\)-bodipy and 1.48 eV for the Ph\(_2\)-benz-bodipy, respectively. As can be seen in Figure 7.3, the attenuation coefficients of the materials reach 3.2 \(\times 10^5\) 1/cm and 3.3\(\times 10^5\) 1/cm. They are almost twice as large as those of ZnPc at 700 nm, a material frequently used in small molecule OSC as absorber [172]. Hence, the absorption suits the needs for organic solar cell absorbers well.

To analyze the performance in organic solar cells, the energy levels of these materials have to be known. In cyclic voltammetry, Ph\(_2\)-benz-bodipy and Ph\(_4\)-bodipy show completely reversible redox waves for the one electron reduction and one electron oxidation. These results indicate the formation of stable radical anions and cations in solution for both compounds (see Figure 7.4).
The HOMO energies are determined to be 5.68 eV for the Ph₄-bodipy and 5.22 eV for Ph₂-benz-bodipy. The LUMO energies are measured to be 4.01 eV and 3.65 eV, respectively.

From the UPS measurements the thin film ionization potential (IP) is determined: The IPs are found to be 5.62 eV for the Ph₄-bodipy and 5.29 eV for the Ph₂-benz-bodipy. Considering the optical gaps as lower limits for the electrical gaps, the electron affinities (EAs) are at most 4.0 eV (Ph₄-bodipy) and 3.7 eV (Ph₂-benz-bodipy) or most likely smaller, depending on the exciton binding energies [20]. Hence, the thin film energy levels are consistent with their molecular counterparts measured in solution.¹

The DFT calculations on the b3lyp/6-31+g** level of theory on both relaxed structures result in HOMO energies of 5.67 eV for Ph₄-bodipy and 5.21 eV for the Ph₂-benz-bodipy which are very close to the experimentally determined values.

¹While being molecular properties, the expressions HOMO and LUMO are often used for the IP and the EA of thin films.
The calculated LUMO energies of 3.47 eV for Ph$_4$-bodipy and 3.20 eV for the Ph$_2$-benz-bodipy deviate from the LUMO energies measured by CV. The deviation results to some extent from the calculation in gas phase, which might be improved slightly by applying an appropriate solvation model. However, it is known to be a difficulty of DFT in general to accurately predict virtual orbital energies [173]. Nonetheless, the calculations still reflect the trends correctly and support the concurring values measured. Table 7.1 gives an overview over the values determined by CV, UPS, and DFT calculations.

The enlarged electronic system in Ph$_2$-benz-bodipy with the energetic destabilization of the frontier orbitals explained above leads to a more pronounced increase of the HOMO energy (460 meV) than of the LUMO energy (360 meV). Accordingly, the HOMO-LUMO gap is reduced for the benzannulated bodipy.

Measuring the emission, no photoluminescence signal is detected below 1000 nm. Mass density values of 1.21 $g/cm^3$ for the Ph$_4$-bodipy and 1.09 $g/cm^3$ for the Ph$_2$-benz-bodipy are found by profilometer measurement.

The evaporation temperatures are 230 °C for the Ph$_4$-bodipy and 200 °C for Ph$_2$-benz-bodipy when evaporated at a pressure of $10^{-6}$ mbar or lower. The thermogravimetric analysis shows that both materials are stable for temperatures above that: Ph$_4$-bodipy is stable up to 260 °C and has lost about 11% of its mass at 340 °C. Ph$_2$-benz-bodipy is very stable up to 260 °C and loses less than 2% at 340 °C (see Figure 7.5).
7.3 Solar Cells

The solar cells comprising the IR absorbing materials are prepared in a mip-architecture (metal–intrinsic–p-doped [33, 172]) with a planar heterojunction. Figure 7.6 shows the chemical structure of the acceptor and the HTLs used, the device stacks, and the according energy levels.

A layer of C_{60} with a thickness of 15 nm is used as acceptor, followed by 10 nm of either Ph_{4}-bodipy (devices A and B) or Ph_{2}-benz-bodipy (device C) as donor layer. As hole transport layer (HTL) either PV-TPD (devices A and C) or BPAPF (device B) are used. A 5 nm intrinsic layer of the HTL is evaporated between the active layers and the p-doped HTL (25 nm) to reduce dopant diffusion into the
active layers. In all solar cells, a 10 nm thick layer of p-doped ZnPc is used to ensure good contact to the top electrode of 40 nm gold.

An overview of the J-V-characterization of the devices (including the light intensities used) is given in Table 7.2. The J-V-characteristics are shown in Figure 7.7. Device A exhibits a large s-kink. This can be explained considering the energy levels of donor and HTL: As the IP of PV-TPD is 0.4 eV smaller than the IP of Ph₄-bodipy, holes in forward direction see an injection barrier [174, 175]. Analogously, holes extracted from the active layers lose free energy when they enter the PV-TPD. Being a planar heterojunction, this does not affect the $V_{OC}$, but reduces the fill factor $FF$ [134, 174]. Therefore, device B is prepared with BPAPF as HTL, whose IP allows for a good transport through the interface. For Ph₂-benz-bodipy with its smaller IP, PV-TPD suits well as an HTL (Device C).

The short-circuit current densities ($j_{SC}$) of all three cells are in the same range. However, the stacks are not optimized in terms of optical interference pattern [109].
Benzannulation of Aza-Bodipy Dyes

Device Donor/HTL I V OC jSC FF Sat η
mW/cm² V mA/cm² % %
A Ph₄-bodipy/PV-TPD 121 0.92 3.0 33 1.369 0.8
B Ph₄-bodipy/BPAPF 122 0.96 3.15 48 1.275 1.2
C Ph₂-benz-bodipy /PV-TPD 91 0.65 2.4 65 1.16 1.1

Table 7.2: The fingerprints of the nip solar devices show that the energy shift as a result of the benzannulation naturally leads to a lower V OC but also to a better transport leading to a FF of 65%. The intensities I and consequently η are corrected for spectral mismatch.

The FF of the Ph₄-bodipy device (device B) is 48%, which is considerably smaller than the FF of 65% of the Ph₂-benz-bodipy device (device C). A decrease in FF can either indicate a problem in exciton dissociation or in the collection of charge carriers. The latter depends on the charge carrier mobility. However, the hole mobilities of both materials are measured to be of the order of 10⁻⁵ cm²/Vs. This leaves as explanation the dissociation of excitons which depends crucially on the energy levels at the heterojunction. A certain offset both between the EAs and between the IPs of donor and acceptor is considered necessary to overcome the exciton binding energy [139].

As this exciton binding energy is the main difference between optical and electrical gap, the optical gaps of both donor and acceptor have to be at least as large as the effective gap, i.e. the difference between the EA of the acceptor and the IP of the donor. With the effective gap of device B being about 1.6eV, the acceptor C₆₀ clearly fulfills this requirement. However, the optical gap of the Ph₄-bodipy barely fulfills this requirement, not allowing for measurement uncertainties. Consequently, the lower FF in device B may be attributed to unfavorable energy level alignment leading to inefficient exciton dissociation.

The relevance of the energy levels can also be observed from the V OC of the devices. The Ph₄-bodipy device has a V OC of 0.96V and the difference to the effective gap is hence 640meV. Generally, this difference is explained with the splitting of the quasi-Fermi levels as a limit to the V OC of photovoltaic devices [134].

As the IP of the Ph₂-benz-bodipy is about 0.3eV smaller, the effective gap is decreased by this amount to about 1.3eV. The J-V-characteristics of device C show that this directly affects the V OC: it is also lowered by about 0.3 eV to 0.65 V. A solar cell using both, Ph₄-bodipy as acceptor and a Ph₂-benz-bodipy as donor shows a voltage of 0.78 eV with the effective gap being at least 1.3 eV.

Figure 7.8 shows the morphology of a 20 nm pristine layer of Ph₄-bodipy and Ph₂-benz-bodipy on glass and the morphology of 10 nm of both of the two materials on 15 nm C₆₀. It can clearly be seen that the growth of both investigated materials on C₆₀ greatly differs from the growth on glass: the layers are much
The topography images obtained by atomic force spectroscopy of 20 nm thick films on glass display a rather large roughness (RMS) of 18 nm (Ph₄-bodipy) and 16 nm (Ph₂-benz-bodipy). When evaporated on C₆₀, a 10 nm thick film, however, has a roughness of 1.3 nm (Ph₄-bodipy) and 0.7 nm (Ph₂-benz-bodipy) and a considerably less insular growth.

Figure 7.8: The topography images obtained by atomic force spectroscopy of 20 nm thick films on glass display a rather large roughness (RMS) of 18 nm (Ph₄-bodipy) and 16 nm (Ph₂-benz-bodipy). When evaporated on C₆₀, a 10 nm thick film, however, has a roughness of 1.3 nm (Ph₄-bodipy) and 0.7 nm (Ph₂-benz-bodipy) and a considerably less insular growth.

The external quantum efficiencies (EQEs) for the devices B and C are shown in Figure 7.9 together with the absorbance of the active materials. Both materials contribute to the short-circuit current. However, though the Ph₄-bodipy and Ph₂-benz-bodipy have a much higher absorption than C₆₀, their contribution is in the same range as that of C₆₀. The main reason is again the distribution of the optical field: The thickness of the HTL of about 40 nm favors the C₆₀ layer with its absorption maximum at 450 nm over the donor materials with their absorption at and above 700 nm [109].

The spectral mismatch of the solar cells [135, 176] in the setup is found to be 1.17 for device B and 1.08 for device C. For the Ph₄-bodipy device (device B) the mismatch corrected efficiency is 1.2 % for an intensity of 122 mW/cm² of AM1.5.
Figure 7.9: The external quantum efficiency (EQE) spectrum of device B and device C reproduce the red shift visible in the absorbance of the two materials. The decrease in peak height for the EQE of device C is probably due to the less favorable optical field distribution as thicknesses are kept constant. The absorbance of 20 nm of C$_{60}$ (line), Ph$_4$-bodipy (open triangles) and Ph$_2$-benz-bodipy (open circles) is also displayed for comparison (right axis).

sun illumination; for the Ph$_2$-benz-bodipy device (device C) an $\eta$ of 1.1% can be calculated for an intensity of 91 mW/cm$^2$.

7.3.1 Summary

It is demonstrated that aza-bodipys can successfully be used as an active absorber material in evaporated small molecule solar cells. Upon annulation of the benzene ring, the $\pi$-conjugation is increased which leads to a shift in absorption up to 860 nm for the Ph$_2$-benz-bodipy. The energy levels investigated by CV and UPS measurement and DFT-calculation show very good agreement.

The materials used as donor in combination with C$_{60}$ form a working planar heterojunction device. The Ph$_4$-bodipy device has a power conversion efficiency of 1.2% with an EQE reaching up to 800 nm and a $V_{OC}$ of almost 1 V. The Ph$_2$-benz-bodipy device shows a $V_{OC}$ of 0.65 V. This loss in voltage compared to the device with Ph$_4$-bodipy is due to a lower IP and the smaller gap. It is partly
compensated by a higher FF which can be ascribed to a better energy level design. Consequently, this Ph₂-benz-bodipy solar cell displays an efficiency of 1.1%, the EQE showing a considerable contribution of far red and near infrared absorption.
8 Effect of End Group Variation on Aza-Bodipy Dyes

The effect the variation of the end groups of aza-bodipy materials has on its properties is the topic of this chapter. Three different compounds are studied in respect to their thin film properties and their usability in mip-type solar cells. As has been shown in the previous chapter, benznannulation of aza-bodipy molecules leads to a more planar and rigid core and, consequently, to a larger conjugational system. This is an effective way to shift the absorption of the molecules and, particularly their films towards the red. A further method to alter the electrical properties of these benznannulated bodipys or azadiisoindomethenes and, consequently, their optical properties is the variation of the molecules’ end groups. This possibly allows the conjugational system to extend onto the end groups as well, which often results in a red shift in absorption [12].

The effect of end group variation on the semiconductor’s properties is studied here for three different benznannulated bodipy: Ph$_2$-benz-bodipy (A), Ph$_2$-benz-bodipy-MeO (B) and Ph$_2$-benz-bodipy-Thio (C). Their full names can be found in Table 8.1, the chemical structures are depicted in Figure 8.1. They were synthesized by Roland Gresser at the TU Dresden as described in [177]. All materials are purified both by column chromatography and gradient sublimation.

8.1 Thin Film Properties

When tested all three materials proved to be evaporable in ultra-high vacuum, with their evaporation temperature between 200°C and 230°C, well below their

<table>
<thead>
<tr>
<th>Material</th>
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<tr>
<td>A</td>
<td>Ph$_2$-benz-bodipy</td>
<td>Bis-(phenyl)-borondifluoride-ADIM</td>
</tr>
<tr>
<td>B</td>
<td>Ph$_2$-benz-bodipy-MeO</td>
<td>Bis-(p-methoxy-phenyl)-borondifluoride-ADIM</td>
</tr>
<tr>
<td>C</td>
<td>Ph$_2$-benz-bodipy-Thio</td>
<td>Bis-(5-methyl-thienyl)-borondifluoride-ADIM</td>
</tr>
</tbody>
</table>

Table 8.1: Three azadiisoindomethanes (ADIM) or benz-bodipy with three different end groups are compared in this chapter.
Effect of End Group Variation on Aza-Bodipy Dyes

Figure 8.1: Chemical structures of the benz-bodipy materials compared: the end group is varied from phenyl to methoxy-phenyl (MeO) to methyl-thiophene (Thio).

<table>
<thead>
<tr>
<th>Material</th>
<th>T_{evap}</th>
<th>T_{decomp}</th>
<th>ρ</th>
<th>μ_{hole}</th>
<th>μ_{electron}</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>230 °C</td>
<td>350 °C</td>
<td>1.09</td>
<td>6.9</td>
<td>3.7</td>
</tr>
<tr>
<td>B</td>
<td>200 °C</td>
<td>320 °C</td>
<td>1.36</td>
<td>2.6</td>
<td>–</td>
</tr>
<tr>
<td>C</td>
<td>230 °C</td>
<td>330 °C</td>
<td>1.04</td>
<td>23</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table 8.2: Material properties of the compared materials: all three materials evaporate 100 K or more below their decomposition temperature $T_{decomp}$. They all display common density $ρ$ and mobility values $μ_{hole}$ and $μ_{electron}$.

decomposition temperatures derived from thermogravimetric analysis (see Table 8.2 for exact values). The density is determined using a nominally 50 nm thick film measured by the Dektak profilometer (see Chapter 4.3.1). The values are between 1.04 $g/cm^3$ and 1.36 $g/cm^3$ – typical values for organic thin films.

The charge carrier mobilities are measured using an OFET setup (as described in Chapter 4.3.1). Most values are of the order of $10^{-5}cm^2/Vs$, a low, but not unusual value for organic semiconductors. The electron mobility of Ph$_2$-benz-bodipy-MeO is not measurable; on the other hand, the hole mobility of Ph$_2$-benz-bodipy-Thio reached a high $23 \times 10^{-5}cm^2/Vs$ (see Table 8.2).

8.1.1 Optical Properties

Figure 8.2 shows the absorption of a thin film of 20 nm thickness for all three materials and for zinc phthalocyanine (ZnPc) in comparison. It can be seen that all three compounds not only absorb much farther in the infrared spectral region. They also have a higher relative absorption when compared with ZnPc – the absorption integrals of the red/infra-red peaks being 41, 55 and 52 as compared
8.1 Thin Film Properties

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda_{\text{max, solv}}$ nm</th>
<th>$\epsilon_{\text{solv}}$ $10^5$L cm$^{-1}$ mol$^{-1}$</th>
<th>$\lambda_{\text{max, film}}$ nm</th>
<th>OD integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>715</td>
<td>1.06</td>
<td>773</td>
<td>0.27</td>
</tr>
<tr>
<td>B</td>
<td>729</td>
<td>0.91</td>
<td>792</td>
<td>0.35</td>
</tr>
<tr>
<td>C</td>
<td>793</td>
<td>0.95</td>
<td>868</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Table 8.3: While the absorption maximum $\lambda_{\text{max}}$, both in solvent and thin film, for MeO-compound B is less than 20 nm larger, the thiophene compound C exhibits a strong shift to the infrared with comparable absorbances OD.

to 35 for ZnPc$^1$. The addition of the MeO group shifts the maximum wavelength from 773 nm of A to 792 nm. Using thiophene as an end group leads to an even larger shift to 868 nm which places the major part of the absorption peak into the infrared region (see also Table 8.3).

This nicely reproduces the behavior of the materials in solution: When dissolved in DCM Ph$_2$-benz-bodipy has a maximum peak at 715 nm, Ph$_2$-benz-bodipy-MeO at 729 and Ph$_2$-benz-bodipy-Thio at 793 nm with extinction coefficients $\epsilon_{\text{solv}}$ of about $1 \times 10^5$ L/mol cm for all three materials.

While the methoxy group only leads to a change of less than 20 nm compared to the phenyl compound both in thin film and solution, adding the thiophene to the molecular core results in a large bathochromic shift. Electron density calculations show that the donor-acceptor character of material C and, hence, the charge transfer character of the excitation is greatly increased. This can possibly be attributed to the smaller dihedral angle in material C, found in these calculations [177].

8.1.2 Energetic Properties

To investigate the origin of this absorption behavior, energy values, both, from solution and thin film measurements can be compared. Dissolved in DCM cyclovoltai measurements yield a good estimate of the HOMO and the LUMO of the molecules (for exact values see Figure 8.3). It turns out that the change of the end groups changes the LUMO of the molecules only to a minor extent. All values are between 3.60 eV and 3.70 eV. The HOMO on the other hand is decreased from 5.22 eV for Ph$_2$-benz-bodipy to 5.05 eV for Ph$_2$-benz-bodipy-MeO to 4.96 eV for Ph$_2$-benz-bodipy-Thio. That is a difference of 0.26 eV. Consequently, the electric gap between HOMO and LUMO decreases from 1.57 eV (A) to 1.45 eV (B) and 1.26 eV (C).

$^1$The integration over the red peak in the absorbance spectra is done from the minimum on the hypsochromic side to the wavelength on the bathochromic side, where the absorbance decreases to values lower than 0.01 again. The unit $1 \times$ nm is left out to avoid confusion.
Figure 8.2: The three absorbance curves in this graph display a peak in the red to infrared region, which is both larger and bathochromically shifted compared to the common red absorber zinc phthalocyanine.

These values can now be compared to thin film values. The ionization potentials measured by UPS (see Chapter 4.3.1) follow the trend of the molecular measurements very nicely: From 5.3 eV (Ph$_2$-benz-bodipy) to 5.1 eV (Ph$_2$-benz-bodipy-MeO) and 5.0 eV (Ph$_2$-benz-bodipy-Thio). To complete the picture the optical gaps derived from the bathochromic side of the thin film absorption in the red/IR follow the same trend as the molecular electrical gap: 1.5 eV for A, 1.4 eV for B, and 1.3 eV for C.

Figure 8.3 gives a graphic representation of all values collectively. It can be concluded that the variation of end groups can be used effectively to tune the energetic configuration, and consequently, the absorption of these materials.

8.1.3 Morphology

Figure 8.4 shows the morphology of Ph$_2$-benz-bodipy and Ph$_2$-benz-bodipy-MeO, measured by AFM. As in Chapter 7.2.2, both, a pristine layer of 20 nm thickness directly on quartz glass and a layer of 10 nm of the materials on a 15 nm thick C$_{60}$ layer on glass are compared. The pristine materials form large islands which leads to a root-mean-square roughness of 16 nm (A) and 11 nm (B), with peak
8.2 Solar Cells

In Section 8.1.2 it has been shown that end group variation in aza-bodipy can lead to energetic changes. As the core of the molecules remains unaltered the conjugation stays intact. Hence, their usability as semiconductors in organic solar cells should be unimpaired. To test this, the materials are incorporated in planar heterojunction devices of the following general mnp-type stack:

\[
\text{ITO/C}_{60}(15)/\text{bodipy(10)}/\text{HTL(5)}/p-\text{HTL(25)}/p-\text{ZnPc(10)}/\text{Au(40)}
\]

The exact stack with the materials used and their energetic values can be found in Figure 8.5. Different HTLs are chosen to ensure matching energy levels between HTL and donor. The Novaled dopant NDP2 is used as p-dopant for all HTLs. p-ZnPc is used for a good electric contact to the gold top layer.

Figure 8.6 shows the J-V-characteristics of the three devices, their fingerprints being summarized in Table 8.4. The \(V_{OC}\) behavior is certainly the most important: Just like for the benzannulation (see Chapter 7.3) the decrease in electrical gap
Figure 8.4: Independent of the end group, the materials grow very rough on a glass substrate. An underlayer of $C_{60}$ decreases the roughness dramatically allowing for smooth layers that can be used in planar heterojunction solar cells.

<table>
<thead>
<tr>
<th>Device</th>
<th>$I$ (mW/cm²)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>SAT (%)</th>
<th>$J_{SC,AM1.5}$ (mA/cm²)</th>
<th>$η_{AM1.5}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>91</td>
<td>0.65</td>
<td>2.6</td>
<td>64.9</td>
<td>1.16</td>
<td>1.08</td>
<td>2.5</td>
</tr>
<tr>
<td>B</td>
<td>99</td>
<td>0.56</td>
<td>3.3</td>
<td>61.0</td>
<td>1.21</td>
<td>1.01</td>
<td>3.2</td>
</tr>
<tr>
<td>C</td>
<td>125</td>
<td>0.37</td>
<td>2.9</td>
<td>53.8</td>
<td>1.39</td>
<td>1.23</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Table 8.4: The fingerprints of the mip solar devices show that the energy shift as a result of the end group variation naturally leads to a lower $V_{OC}$. The intensities $I$ and consequently $J_{SC}$ and $η$ are corrected for spectral mismatch.
translates into a decrease in voltage. It changes from 0.65 V for Ph$_2$-benz-bodipy to 0.56 V for Ph$_2$-benz-bodipy-MeO and 0.37 V for Ph$_2$-benz-bodipy-Thio. Hence, the differences between the optical gaps of the thin layers and also the electrical gaps of the molecules can be translated into the $V_{OC}$. Though this is detrimental to the overall efficiency of the device, it illustrates nicely the physical restriction when looking for absorbers in the infrared: the conjunction of the electrical gap determining the $V_{OC}$ and the optical gap determining the EQE onset which was used as a basic principle in Chapter 5.

When calculating the difference between the effective gap (determined by the EA of the C$_{60}$ layer and the IP of the bodipy layer) and the $V_{OC}$, values of about 0.6 eV are found for all three materials, a common value for the energetic loss in organic solar cells [178].

The EQE measurements of the three devices are depicted in Figure 8.7. Their bathochromic onset follows the absorption behavior: about 1.5 eV for A, 1.4 eV for B, 1.3 eV for C, exactly the values of the optical gap. The Ph$_2$-benz-bodipy-MeO
Figure 8.6: These J-V-characteristics of the mip devices show that the serial resistance is low and no shunts occur, as can be seen from the dark curves (filled symbols). The illuminated curves (open symbols) are measured at nominally 1 sun according to the Si reference cell and are not mismatch corrected. Inset: Enlargement of fourth quadrant.

Device A: Ph₂-benz-bodipy
Device B: Ph₂-benz-bodipy-MeO
Device C: Ph₂-benz-bodipy-Thio

device has the highest EQE maximum of 18.7% at 775 nm. On the other hand, unlike their absorption, the maximum peak height in EQE for Ph₂-benz-bodipy and Ph₂-benz-bodipy-Thio decreases from 14.9% at 770 nm to 13.3% at 885 nm. This can easily be understood by looking at the stack. All layers have been kept constant in thickness for all three devices to ensure comparability, e.g. of series resistance. This, however, leads to a lower, and consequently, less favorable optical field for longer wavelengths, as it is reflected hard at the opaque top contact.

This principle is illustrated in Figure 8.8. It shows the absorption of the donor within the mip solar cell, as derived from optical matrix simulation [179], and how it changes with varying HTL thickness. Clearly, as the distance of the active donor layer from the back contact increases this absorption increases as well as the layer is placed in a higher intensity of the optical field. The 25 nm layer thickness used in the test are still considerably away from the optimum.

²Due to the lack of optical refraction index values for PV-TPD needed for the simulation, the optically similar DiNPB is used for this calculation (see Chapter 4.1.2).
8.2 Solar Cells

Figure 8.7: The external quantum efficiency (EQE) spectra of the devices reproduce nicely the absorption peaks of the benz-bodipy compared with one exception: as the stacks are not optically optimized, the EQE peak of IR absorber C is lowered compared to the material A. For layer sequence see Figure 8.5.

The decrease of the fullerene absorption due to the decreasing intensity at smaller wavelengths can only partially compensate this, as C₆₀ is a weaker absorber. As material B and especially C absorb at significantly higher wavelengths, an even larger distance to the Au back contact would be needed to optimize their performance as donors.

Because of its broad peak the Ph₂-benz-bodipy-Thio based cell has, nonetheless, a $J_{SC}$ of 2.9 mA/cm² after mismatch correction and normalization to 100 mW/cm², despite the outlined non-optimized stack architecture. This is more than the $J_{SC}$ of Ph₂-benz-bodipy of 2.6 mA/cm². It is, however, less than the $J_{SC}$ of the Ph₂-benz-bodipy-MeO device, the latter yielding a $J_{SC}$ of 3.3 mA/cm² as expected considering the substantially larger absorption.³

These measured short-circuit currents normalized to AM1.5 intensity can be compared with the currents $J_{SC,EQE}^{AM1.5}$ derived from the convolution of the defined AM1.5 spectrum with the measured EQE. It emerges that both are approximately

³The J-V-characteristics in Figure 8.6 are neither normalized nor mismatch corrected. As the sun simulator spectrum used has an IR contribution significantly higher than AM1.5, the Ph₂-benz-bodipy-Thio device is, in truth, illuminated with a higher intensity and, consequently, yields a higher current in the actual measurement.
Figure 8.8: For these simulated thin film absorbance spectra of the Ph$_2$-benz-bodipy layer in a mip solar cell the p-HTL thickness has been varied. Clearly, the thickness of 25 nm used in the experiment does not perfectly suit the cell as the higher C$_{60}$ contribution (dashed lines) at lower thicknesses cannot compensate the low bodipy contribution (continuous lines). This effect is even graver for materials absorbing further in the IR.

The fill factors of cells A and B amount to good values of 64.9% and 61% and the saturation values are 1.16 and 1.21, respectively. For device C using Ph$_2$-benz-bodipy-Thio as donor the fill factor drops to 53.8%, while the saturation increases to 1.39. As both, the reverse blocking behavior of the dark curve (filled symbols in Figure 8.6) and the current density slope in forward direction indicate no problem with either serial or parallel resistance of the device, this decrease in performance is likely to be an intrinsic voltage dependent effect.

The energy steps of at least 0.3 eV at the separating interface should be sufficient to separate the excitons. Possibly, a layer thickness of 10 nm for Ph$_2$-benz-bodipy-Thio is already too large to allow separated charge carriers to be transported to the contacts without the help of an additional electric field, which would result in the voltage dependence observed.

The efficiency $\eta$, normalized and corrected for mismatch to a 1 sun AM1.5 spectrum, is 1.1% for the device with Ph$_2$-benz-bodipy. As the absorption and, hence, EQE increases, Ph$_2$-benz-bodipy-MeO yields the same efficiency of 1.1%, despite its decreased voltage. Material C, Ph$_2$-benz-bodipy-Thio, however, is
absorbing further in the infrared region of the spectrum. Despite having about the same absorption integral as Ph$_2$-benz-bodipy-MeO, when held against the AM1.5, it is bound to deliver less current, as the intensity of AM1.5 decreases towards the infrared. With the decreased voltage the device shows an efficiency of 0.6%. As explained this could be increased to a certain extent by optimizing the stack architecture.

8.2.1 Summary

The way to influence a molecule’s conjugation system, and hence its energetics, by varying its end groups is successfully tested on three different benz-bodipys: Ph$_2$-benz-bodipy (A), Ph$_2$-benz-bodipy-MeO (B), and Ph$_2$-benz-bodipy-Thio (C). The change in end group leads to altered molecular orbital energies, resulting in a decrease of the optical gap from $1.5\,\text{eV}$ for A, to $1.4\,\text{eV}$ for B, and $1.3\,\text{eV}$ for C. In consequence, the thiophene compound C becomes a true IR absorber with a maximum at 868 nm. All three materials can be used in solar cell devices. The mip-type cells produce efficiencies of $1.1\%$ (A and B) and only $0.6\%$ (C). Not only does the smaller electrical gap cause a smaller $V_{OC}$, the sun’s decreased intensity in the IR also limits the current that can be harvested in such a cell.

Though energetic alignment to the acceptor can be further optimized to increase the $V_{OC}$, and though optical matrix simulation can help optimizing the stack layout, this restricts all attempts to push absorption limits of solar cells towards the infrared region. One way out are multi-junction cells, like tandem or even triple cells, where currents are purposefully lowered in favor of increased voltages, but here, current matching and mismatch correction have to be done carefully.
9 Optimization of Infrared Absorbing Organic Solar Cells

The following chapter is dedicated to the optimization of a single heterojunction device using Ph$_2$-benz-bodipy and C$_{60}$. After several methods are tested, an optimized stack is presented. The knowledge thus attained is then used to prepare and discuss a series of tandem cells employing DCV6T-Bu$_4$ as complementary absorber in the second subcell.

One of the advantages of vacuum sublimation of small molecule solar cells is that the processing conditions and the stack configurations can be employed in a very versatile and reproducible manner to change the device’s energetics, optics, and morphology (e.g. [109, 119, 120, 126, 180]). This creates "screws and levers" to optimize the overall device efficiency by increasing one of the three fingerprints determining this efficiency – $V_{OC}$, $j_{SC}$, and FF – or combinations thereof.

In this chapter the Ph$_2$-benz-bodipy is investigated with the aim of increasing its performance in a heterojunction (HJ) device. Different changes in the mentioned production process are tested to find out whether the efficiency of 1.1 %, the material obtained in a simple mip device can be raised.

9.1 Optimization of the Single Cell

As starting point a pii-type device with a flat heterojunction of Ph$_2$-benz-bodipy and C$_{60}$ is made with Di-NPB and BPhen as hole transport material (HTM) and electron blocker. The principle stack of this device (Device A) and of all single heterojunction devices discussed in this chapter can be seen in Figure 9.1. The fingerprints of this and all other single devices are summarized in Table 9.1; the J-V-characteristics of Devices A – H are depicted in Figure 9.2.

When compared to the mip device A of Chapter 8, it can be seen that the FF is much lower, while the $j_{SC}$ is increased by about 1 mA/cm$^2$. The latter can be

\footnote{The efficiencies have not been corrected for mismatch with the exception of Devices I and J, as the primary purpose of this section is to study the qualitative effect of different processing conditions etc. on the fingerprints. The Solarlight sun simulator used for these Lesker samples reproduces the AM1.5 spectrum well, slightly underestimating the region from 300 – 500 nm and overestimating the region from 500 – 700 nm (see also Figure 4.7).}
Figure 9.1: To investigate the possibilities of optimization for the Ph\(_2\)-benz-bodipy, two different general stack types are used and depicted above: a pii-type structure (left; Devices A – E and H) and a nip-type structure (left; Devices F, G, I, J)

explained as the order of the absorber materials within the stack is more favorable: the C\(_{60}\) absorbing at shorter wavelengths is closer to the reflecting back contact, the Ph\(_2\)-benz-bodipy absorbing at higher wavelengths is farther away (for more details see Chapter 8.2). Even more importantly, the amount of C\(_{60}\) used here is higher. Thus, not surprisingly, the EQE contribution of the C\(_{60}\) peaks at 32 % at a wavelength of 450 nm, while the Ph\(_2\)-benz-bodipy peak is a much lower 15 % at 760 nm (EQEs not shown).

Why the FF decreases is not perfectly clear, this heterojunction being essentially the one used in the mip device. There is one difference, however: here, the Ph\(_2\)-benz-bodipy is grown on Di-NPB. As it is known from the morphology measurement described in Chapters 7.2.2 and 8.1.3, the bodipy are very sensitive to the underlying layer. Hence, it is possible that the Ph\(_2\)-benz-bodipy layer is not entirely closed. This is further supported by the increase in \(V_{OC}\) from 0.65 V in the mip cell to 0.8 V in the pii device which suggests a change in separating interface. However, the Di-NPB:C\(_{60}\) heterojunction has about the same or even a slightly smaller effective gap. Thus, the \(V_{OC}\) should be similar.

As a next step a bulk heterojunction with a mixing ratio of 1:2 (Ph\(_2\)-benz-bodipy:C\(_{60}\)) is used in Device B in order to increase the number of created excitons that can indeed reach the separating interface, thus increasing the current density. The \(j_{SC}\) does increase, though only to a small extent. The EQE contribution of Ph\(_2\)-benz-bodipy at 760 nm increases to 17 %, while the C\(_{60}\) peak does not change. As the C\(_{60}\) has a very high exciton diffusion length [181], using a mixed layer in
9.1 Optimization of the Single Cell

<table>
<thead>
<tr>
<th>Device</th>
<th>Step</th>
<th>$V_{OC}$</th>
<th>$j_{SC}$</th>
<th>FF</th>
<th>Sat</th>
<th>$\eta^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>initial pii with flat HJ</td>
<td>0.79</td>
<td>3.6</td>
<td>39.6</td>
<td>1.30</td>
<td>1.14</td>
</tr>
<tr>
<td>B</td>
<td>pii with bulk HJ</td>
<td>0.81</td>
<td>3.8</td>
<td>37.7</td>
<td>1.45</td>
<td>1.17</td>
</tr>
<tr>
<td>C</td>
<td>heated pii</td>
<td>0.72</td>
<td>4.3</td>
<td>44.7</td>
<td>1.34</td>
<td>1.39</td>
</tr>
<tr>
<td>D</td>
<td>heated hybrid pii</td>
<td>0.76</td>
<td>4.4</td>
<td>43.0</td>
<td>1.34</td>
<td>1.45</td>
</tr>
<tr>
<td>E</td>
<td>heated hybrid pii with BPAPF</td>
<td>0.78</td>
<td>4.5</td>
<td>49.8</td>
<td>1.22</td>
<td>1.73</td>
</tr>
<tr>
<td>F</td>
<td>nip with flat HJ</td>
<td>0.64</td>
<td>4.2</td>
<td>60.4</td>
<td>1.18</td>
<td>1.59</td>
</tr>
<tr>
<td>G</td>
<td>hybrid nip</td>
<td>0.80</td>
<td>5.2</td>
<td>35.7</td>
<td>1.42</td>
<td>1.49</td>
</tr>
<tr>
<td>H</td>
<td>pii with ratio 1:1</td>
<td>0.84</td>
<td>5.0</td>
<td>45.0</td>
<td>1.31</td>
<td>1.90</td>
</tr>
<tr>
<td>I</td>
<td>optimized nip with 55 nm p-BPAPF</td>
<td>0.81</td>
<td>6.2</td>
<td>56.4</td>
<td>1.17</td>
<td>2.81</td>
</tr>
<tr>
<td>J</td>
<td>optimized nip with 35 nm p-BPAPF</td>
<td>0.80</td>
<td>6.5</td>
<td>56.0</td>
<td>1.18</td>
<td>2.92</td>
</tr>
</tbody>
</table>

*Table 9.1: In total, ten different samples are discussed to illustrate the different optimization approaches. The fingerprints above, namely $j_{SC}$ and efficiency are not corrected for mismatch, but those of Device I and J. All samples have an area of 6.2 mm$^2$. *not corrected for mismatch

addition to a flat 35 nm C$_{60}$ layer is not beneficent to the fullerene’s contribution. $V_{OC}$ and FF of Device B do not change much compared to Device A, hence, the overall power is also practically the same.

One way to address the low FF is to sublimate especially the bulk layer onto a substrate of elevated temperature. This can lead to a better phase separation between C$_{60}$ and the absorber allowing for a better transport of the separated charge carriers. Temperatures of 60, 80, and 100°C are tested with Device C at 80°C substrate temperature showing the best results: the FF of the bulk heterojunction device increases to almost 45% and the short-circuit current density increases to 4.3 mA/cm$^2$.

According to the EQE measurement, this $j_{SC}$ increase is mainly caused by an increase of the Ph$_2$-benz-bodipy maximum to 20% with the C$_{60}$ peak remaining at 29% at 450 nm. The $V_{OC}$ drops to 0.72 V; perhaps the ameliorated phase separation shifts the exciton separation back to the Ph$_2$-benz-bodipy:C$_{60}$ interface. This, however, cannot explain the $V_{OC}$ increase occurring upon adding a (likewise heated) neat layer of Ph$_2$-benz-bodipy below the bulk layer. This hybrid device (Device D) also sees a slight increase in $j_{SC}$ and a slight drop in FF not uncommon in hybrid cells.

According to the ionization potentials (IP), depicted for example in Figure 8.5, Di-NPB works well as an HTL to Ph$_2$-benz-bodipy, though its IP of 5.1 eV may be a bit too low. For efficient transport, it would be helpful to use a deeper lying HTL.

Consequently, Device E is prepared like Device D but with BPAPF as a hole transport material, which has an IP of 5.6 eV. This not only results in a further
increase of $V_{OC}$ to 0.78 V but also in a boost in FF which increases from 43% to almost 50%. The EQEs of Device D and E are similar to Device C with 20% at 770 nm and 27% and 33% respectively at 450 nm. The fact that the $V_{OC}$ is only slightly increased makes the explanation less likely that the HTL-C$_{60}$ interface is involved in the charge carrier separation, as the BPAPF increases the effective gap of this interface by about 0.5 eV.

The problems in FF even in the flat heterojunction pii (Device A) and the still low contribution of Ph$_2$-benz-bodipy in the EQE of around 20% suggest to investigate the inverted stack, a nip device: here, the Ph$_2$-benz-bodipy or the bulk layer is grown onto C$_{60}$, which should form a smooth layer (see Chapter 8.1.3). Furthermore, this allows for more freedom in the optical design as the p-HTL is the layer that, being transparent, can be varied most easily to place the absorber layers at their best possible position.

Device F is a flat heterojunction much like the mip cell in Chapter 7, with the difference of an additional, transport assisting n-C$_{60}$ layer on the ITO layer and a thicker intrinsic, absorbing C$_{60}$ layer of 35 nm to ensure comparability to the other samples discussed here. Also, BPAPF is used as an HTM here and in all further single devices of this chapter. The fingerprints also fit well to those measured for the mip device: the $V_{OC}$ is 0.64 V, the FF is a good 60.4%. The $j_{SC}$ is increased to 4.2 mA/cm$^2$ which, as the EQE of 19% at 450 nm and 19% at 770 nm makes clear, is mainly a consequence of the thicker C$_{60}$ layer.$^2$

However, when adding a bulk layer of 20 nm in Device G, the $V_{OC}$ and FF behavior of the pii device is reproduced: a low FF of about 36% and a $V_{OC}$ of 0.8 V$^3$. On the other hand, the $j_{SC}$ is increased to 5.2 mA/cm$^2$ by increasing the Ph$_2$-benz-bodipy contribution to the EQE to 27% at 770 nm, while at the same time reducing the C$_{60}$ peak to 15%.

Before further exploring the possibilities of optically tuning the stack and combining the findings so far, one more way to influence the morphology remains to be tested: so far, all bulk layers had a mixing ratio of 1:2 (Ph$_2$-benz-bodipy:C$_{60}$). The FF along with the somewhat high saturation values of these devices indicate problems in charge carrier transport. Therefore, other ratios may facilitate the transport, especially on the Ph$_2$-benz-bodipy side.

$^2$Note, that the current densities are only comparable to a certain extent as different sun simulators are used.

$^3$This further weakens the argument that the HTL:C$_{60}$ heterojunction may be involved, as adding a bulk layer should not increase the influence of this heterojunction.
Figure 9.2: The J-V-characteristics of the first eight single heterojunction devices are split into two graphs: Devices A-D above and Devices E-H below. Open symbols are used for illuminated measurement; filled symbols denote dark measurements. It can be seen that all samples block well in backward direction and have a low series resistance.
Device B is manufactured again as Device H, but with a ratio of 1:1 (and BPAPF as HTM). This leads to a significant increase in all three fingerprints: the $V_{OC}$ is a very good 0.84 V; the FF increases to 45% (though part of this is probably a result of the BPAPF used). As the amount of the Ph$_2$-benz-bodipy within the bulk is increased, not surprisingly, the $j_{SC}$ increases as well to 5 mA/cm$^2$. Again, the EQE confirms this: 22% at 770 nm and 24% at 460 nm.

Other ratios with an even higher content in Ph$_2$-benz-bodipy have been tested but do not exhibit any further $j_{SC}$ increase but just a lowered FF again.

### 9.1.1 Optimized Single Device

In the previous section several devices were used to test and discuss different approaches to optimizing a solar cell comprising the infrared absorbing Ph$_2$-benz-bodipy:

- a bulk heterojunction with a mixing ratio of 1:1 proves to yield the best FF;
- heating the bulk to 80 °C increases phase separation and, thus, FF as well;
- BPAPF works well as hole transport material;
- using a nip type structure allows for optical tuning.

Combining all this, a series of devices is made with the p-BPAPF layer thickness ranging from 25-65 nm and the n-C$_{60}$ layer is varied from 30-10 nm to keep the overall stack thickness constant to a certain extent. The two best working solar cells of this variation are added to Table 9.1 as Devices I and J. Their J-V-characteristics are depicted in Figure 9.3. The first device, Device I, has a p-BPAPF thickness of 55 nm and a C$_{60}$ thickness of 10 nm, hence, concentrating absorption on the longer wavelengths. At a $V_{OC}$ of 0.81 V and a FF of 56.4% it delivers a much increased current density of 6.2 mA/cm$^2$ (after mismatch correction).

The second device, Device J, has a transport layer combination of 35/20 nm. The $V_{OC}$ of 0.80 V and the FF of 56.0% are practically the same, illustrating that neither $V_{OC}$ nor FF and consequently, energetics and charge carrier transport within the stack depend on the HTL/ETL thicknesses. The $j_{SC}$ of this device is further increased to 6.5 mA/cm$^2$. The reason can be found in the EQE shown in Figure 9.4. While the Ph$_2$-benz-bodipy peak at 770 nm is slightly reduced from 43% to 41% the C$_{60}$ peak almost doubles from 12% to almost 21%. These values lead to mismatch corrected efficiencies of 2.8 and 2.9% for the Devices I and J, respectively. Depending on whether the C$_{60}$ absorption is desirable or not, e.g. in combination with other heterojunctions in a tandem cell, transport layer thicknesses can be chosen without much changing the good efficiencies for this material absorbing partially in the infrared.
9.1 Optimization of the Single Cell

Figure 9.3: The J-V-characteristics of the two optimized single devices are very similar with a small difference in current density caused by the change in HTL/ETL thickness. Again, the illumination and the dark curves display a low series resistance (open symbols: dark; filled: illumination) and a very good blocking behavior.

9.1.2 Device Lifetime

When it comes to commercialization, the cost of energy is, naturally, an important parameter. This is determined by the price and the electric power per area, but also by the lifetime of the device that determines how long and to what extent the device efficiency can be used to harvest energy. While the price per area is beyond the scope of this work and the efficiency is discussed in previous chapters, this section is dedicated to a first test of the materials lifetime.

To this end, Device E is aged at the following conditions for 2500 h: the temperature is kept constant at about 50 °C; all four pixels of the device are monitored separately and illuminated with white light LEDs at four different intensities (P1: 101 mW/cm², P2: 22 mW/cm², P3: 73 mW/cm², P4: 809 mW/cm²). Figure 9.5 shows the development of $V_{OC}$, $J_{SC}$, FF and, consequently, efficiency over aging time. After an initial swift rise in FF and $V_{OC}$, possibly caused by some further phase separation all pixels degrade continuously in all parameters, though the $J_{SC}$ is harder to monitor due to the fluctuation of the LEDs. The $V_{OC}$ decreases only by the fraction of a percent. FF and $J_{SC}$ show a slightly faster degradation.
Figure 9.4: The EQEs of the optimized single heterojunction devices (symbols and lines) show that it is mainly the Ph$_2$-benz-bodipy that contributes to the cells’ current. However, with changes in HTL and ETL thicknesses, the C$_{60}$ contribution at 450 nm can be much increased. The neat layer absorbance characteristics (lines) are well preserved in the bulk layer EQEs.

The two pixels aged at lower intensities, P2 and P3, degrade very similarly. This suggests that the device degradation is not purely light intensity based but that already the temperature of 50 °C causes some degradation. Less surprisingly, the sample kept at more than 8 suns, P4, degrades most quickly, though far less quickly than eight times the speed of the pixels kept at lower intensities. P1, illuminated with one sun intensity, degrades relatively the fastest, mainly owing to the $j_{SC}$ degrading. Though this and the shape of the $j_{SC}$ degradation indicate that this increased degradation can at least partially be attributed to an unstable LED, the resulting efficiency after 2500 h of 95 % of its initial value means already a stable device.

The parameter most commonly used to describe lifetime is T80, the time when the efficiency has dropped to 80 % of its initial value. Linear extrapolation of the aging measurement leads to a T80 of 10,000 h at an intensity of approximately 1
Figure 9.5: After 2500h of aging with white light LEDs, all four pixels of Device E are degraded in all three fingerprints though only resulting in an efficiency degradation of up to 10%.

The single cells I and J of the previous section yield a very good $V_{OC}$ of 0.8 V and a $j_{SC}$ of 6.5 mA/cm². Yet, the overall efficiency of 2.9% is not a competitive number for solar modules of any kind. On the other hand, with an EQE mainly limited to the wavelength region of 600-850 nm it is ideally suited to be combined in a tandem configuration.

4It has to be kept in mind though that this is not directly comparable to a lifetime under operational conditions, as these testing conditions do not, for example, include high UV, humidity or sudden temperature changes.
Tandem devices

Figure 9.6: The absorber heterojunction \( \text{Ph}_2\text{-benz-bodipy:}C_{60} \) (see molecular structure on the right above) is combined with a heterojunction of DCV6T-Bu4:C \(_{60}\) (molecular structure left above) to a series of nipnip-type tandem devices (for details on wedge thicknesses see Figure 9.7).

tandem cell with absorbers that use the more hypsochromic wavelength regions of the solar spectrum.

DCV6T-Bu4 is a derivative of \( \alpha,\omega\text{-bis(dicyanovinylene)-sexithiophene} \) comprising four butyl side groups. Its chemical structures can be found in Figure 9.6. The material has successfully been used as a donor in organic bulk heterojunction solar cells in combination with \( C_{60} \)\cite{126}. With its IP of 5.4 eV and its optical gap of 1.7 eV it can yield open-circuit voltages of up to 0.9 V and fill factors above 65% in optimized photovoltaic devices. The contribution of DCV6T-Bu4 to the EQE of these devices lies between 500-700 nm with the maximum around 600 nm. This complements the absorption of \( \text{Ph}_2\text{-benz-bodipy} \) very well.

Therefore, a series of tandem cells is prepared with DCV6T-Bu4:C \(_{60}\) (mixing ratio 2:1) as an active bulk layer of the first subcell and \( \text{Ph}_2\text{-benz-bodipy:}C_{60} \) (1:1) of the second, both with varying thicknesses. The general stack is depicted in Figure 9.6. As a third wedge the thickness of the HTL Di-NPB used as spacer is varied to adjust the optical field distribution between the two subcells. The specific thicknesses used for all three wedges are given in Figure 9.7 alongside with the fingerprints of the tandem devices.
These fingerprints are shown each in their own matrix plot, with the values also color-coded: red meaning higher (except for saturation) and better values. Additionally, the \( j_{SC} \) obtained from an optical simulation is displayed: For this, the optics within the stack are simulated using the matrix formalism (e.g. [107]) and the photons absorbed in the active layers are converted into a current density. The subcell with the lower \( j_{SC} \) is considered to be the limiting one and this \( j_{SC} \) is taken to be the tandem cell \( j_{SC} \). In this series, the DCV6T-Bu4 cell is always the limiting subcell according to the simulation.

The intrinsic layers are considered to be contributing with an average internal quantum efficiency (IQE) of 50\%, as not all excitons created here will reach the separating interface. The IQE of the bulk layers are set to be 100\%. Though organic materials with such a high IQE have been observed, this does not necessarily have to be the case here, making this calculation an upper estimate. This probably explains the quantitative differences between the simulated and the measured \( j_{SC} \). On the other hand, qualitatively, the simulation predicts the trend in the measured \( j_{SC} \) quite accurately: thicker active layers lead to higher absorption and, thus, higher currents as long as the layers are not shifted out of the optical field maximum suited to their absorption.

As the DCV6T-Bu4 is not well positioned within the optical field for HTL thicknesses of 0 and 5 nm, current densities created are much smaller. The best HTL thickness is 100 nm, with the simulation predicting it at 90 nm, the slight difference probably being due to an underestimated thickness in the n&k-value determination of Di-NPB.

The FF, unsurprisingly, is best for thinner bulk heterojunctions, as thicker layers can impede charge carrier transport due to an insufficient amount of percolation paths [182]. Furthermore, according to simulation, in the devices with a thicker DCV6T-Bu4:C\(_{60}\) layer of 40 nm, currents of both subcells are very similar. Without the thiophene subcell being the clearly limiting one, it is known that also the FF of the bodipy subcell is becoming more influential. Since the single cell experiments suggest that this is also the lower value, the tandem cell FF can be expected to decrease.

The \( V_{OC} \) and the saturation value show a nicely uniform behavior throughout the series, only worsening for the devices with lower FF. The maximum \( V_{OC} \) of 1.71 V shows that the open-circuit voltages of the single cells of 0.8 V and 0.9 V can be conserved in a tandem cell.

Combining all this, the devices with medium thickness absorber layers and a spacer of about 100 nm have the highest efficiencies. The combination of 30 nm thickness for each bulk layer and 100 nm thick spacer shows the best efficiency of 5.87\%. This value, however, has to be treated with caution as mismatch correction cannot be straightforwardly done for multijunction devices. As an approximation the mismatch of the limiting subcell can be used if it is limiting under both light
spectra. Since this is the case for the DCV6T-Bu4 subcell, its mismatch of 1.11 can be used to alter the efficiency to 5.3%.
Figure 9.7: The different measured fingerprints of the series of tandem devices are each collected in a separate matrix table to color code their values: red values are better, green are worse. The $J_{SC}$ derived from optical simulation is also listed. On the right and lower borders the thicknesses chosen for the wedges are displayed.
Properly determining the efficiency involves the usage of a multi-source sun simulator. This has been carried out by Timmreck et al. [183]. By carefully varying the intensities of the different light sources and by thorough determination of the EQEs of the subcells and in cooperation with the imec (Leuven, Belgium) and the Fraunhofer ISE (Freiburg, Germany) the efficiency of the sample with the absorber combination of 25/30 nm was determined to be 5.0%, whereas the single light source measurement used here resulted in an efficiency of 5.2%.

Furthermore, the study confirmed the prediction done by the optical simulation: the DCV6T-Bu4 is the limiting cell and the current matching between the subcells under AM1.5g can be optimized. Moreover, the study shows that with changing the limiting cell by modification of the light spectrum the fill factor changes as it is dominated by the limiting subcell.

Figure 9.8 depicts the EQEs of the two subcells of the 30/30 nm device. They are measured using colored LEDs to flood the subcell not under investigation. Additionally, the wavelength dependent absorption within the active layers (intrinsic layers weighted with 50%) as calculated by the optical simulation is shown. Clearly, not all absorbed photons are actually converted into free charge carriers, but the general wavelength dependence is predicted well.

With a maximum of 38% at 550 nm for the thiophene subcell and 53% at 770 nm for the bodipy subcell, these measurements illustrate nicely how complementary absorbing materials can be used in tandem cells to harvest the sunlight over a large wavelength range, yet, at the same time at high open-circuit voltages.

9.2.1 Summary and Outlook

Different methods of optimization are investigated like substrate heating, variation of mixing ratios and changing the optical field distribution by HTL thickness variation. This results in an optimized nip-type single cell comprising a heated bulk layer of Ph2-benz-bodipy and C60 that can utilize light of wavelengths up to 850 nm, hence, partially in the infrared, and that has an efficiency of 2.9%. By combining this device with a solar cell based on the oligothiophene DCV6T-Bu4:C60 in a series of tandem cells, a VOC of 1.7 V, a FF of 57% and an efficiency of 5% can be reached.

When it comes to further increasing these values, different ways can be conceived: Firstly, both, simulation and EQE measurements show that current matching is not yet ideal. Here, further variations in thicknesses may be advantageous. Secondly, further process optimization also within the tandem cell, e.g. of the absorber heating that is not adjusted when combining the single cells, possibly increases the FF and the maximum absorber thickness that can be used. The latter would also increase the EQE which, though already a good value, can still be improved. Thirdly, the spectral region of 300-500 nm is yet only partially used. Here, a material absorbing this blue light, either as an acceptor or as a third donor
Figure 9.8: Both, the EQEs (symbols and lines) and active layer absorption calculated from optical simulation (lines) show that the thiophene subcell (green) is generally the limiting one.

in a triple cell can further increase the portion of the solar energy converted into electricity.
10 Summary and Outlook

Broadening the spectrum available to solar cells towards infrared wavelengths is one way to increase the power conversion efficiencies of these devices. While silicon-based solar cells start to absorb at 1100 nm, typical organic devices are still often limited to the visible spectrum. This thesis explores two different material classes in thin film and organic solar devices: tin phthalocyanines and bodipys.

Efficiency Estimation

To estimate which efficiency is reached absorbing sunlight from a varying wavelength interval model calculations are done for single and tandem cells. These calculations include a distinction between the optical gap and the electrical gap and the splitting of the quasi-Fermi levels. The absorption is considered to be shared among the different absorbers. For the tandem cell the effective gap of each subcell is used to calculate the open-circuit voltage of this subcell.

A number of assumptions have to be made: The fill factor and the external quantum efficiency (EQE) within the absorption range are set to 65%. The exciton binding energy as well as the energy level offset between ionization potentials (IP) and between electron affinities (EA) are assumed to be 0.3 eV. The resulting efficiencies are 15% in a single cell and of 21% in a tandem cell with absorption reaching far into the infrared. But even with a less demanding 890 nm as upper absorption limit, an efficiency of 19% is possible when good absorbers with suitable energy levels can be found.

Tin Phthalocyanines

As the $V_{OC}$ is determined by the effective band gap it is favorable for the donor to have a higher ionization potential as long as charge separation is not impaired. One known way to increase the IP without changing the optical band gap is halogenation. Therefore, three different fluorinated and chlorinated tin phthalocyanines (SnPc) are investigated and compared to the neat SnPc. While chlorination of SnPc seems to worsen the transport properties of the active layer leading to a lowered FF, the fluorination of SnPc results in the intended increase in $V_{OC}$ and, consequently, efficiency for planar heterojunctions.
In bulk heterojunction, however, this is not observed. Fluorination does not change either efficiency or spectral behavior of the SnPc. Additionally, sublimation and XPS analysis suggest that when the fluorine is attached to the molecule’s center position, the compound cannot be stably evaporated without losing the fluorine atoms. One way to reduce this instability would be to attach the fluorine outside the core molecule. This can lead to a material that is stably evaporable and has the lowered IP intended.

**Aza-Bodipys**

Two different methods are investigated to modify the IP of several aza-bodipys and, consequently, shift their absorption towards infrared wavelength.

The first method is the annulation of the benzene ring. This increases the $\pi$-conjugation which leads to a shift in absorption up to 860 nm for the Ph$_2$-benz-bodipy. The energy levels determined by CV and UPS measurement and DFT-calculation show very good agreement and can be linked to a decrease in $V_{OC}$: The Ph$_4$-bodipy (without benzannulation) device has a power conversion efficiency of 1.2% with an EQE reaching up to 800 nm and a $V_{OC}$ of almost 1 V. The Ph$_2$-benz-bodipy device shows a $V_{OC}$ of 0.65 V. This decrease is partly compensated by a higher FF which can be ascribed to a better energy level design. Consequently, this Ph$_2$-benz-bodipy solar cell displays an efficiency of 1.1%, the EQE showing a considerable contribution of far red and near infrared absorption.

The second method to influence a molecule’s conjugation system, and, hence, its energetics is the variation of the molecule’s end groups. This is successfully employed for three different benz-bodipys: The change in end group leads to altered molecular orbital energies, resulting in a decrease of the optical gap from 1.5 eV for the phenyl group, to 1.4 eV for the MeO group, and 1.3 eV for the thiophene group (see Table 10.1). As the IP of the compounds is changed, the effective gap and the $V_{OC}$ follow the trend of the optical gap.

In consequence, the thiophene compound becomes a true IR absorber with a maximum at 868 nm. Like all three materials, it produces smooth layers on C$_{60}$ and can be used in nip-type devices with an efficiency of only 0.6%, while the other two donor materials produce efficiencies of 1.1% in combination with C$_{60}$. Though optimization of stack layout and energy alignment can help to increase this number, this trade-off between a broad wavelength range and a high $V_{OC}$ remains fundamental.

After testing its basic properties, Ph$_2$-benz-bodipy is then optimized towards a high efficiency. Methods investigated are e.g. substrate heating, variation of mixing ratios and changing the optical field distribution by HTL thickness variation. The resulting optimized nip-type single cell comprises a heated bulk layer of Ph$_2$-benz-bodipy and C$_{60}$ with a mixing ratio of 1:1. It absorbs light of wavelengths up to 850 nm, hence, partially in the infrared and has an efficiency of 2.9%.
<table>
<thead>
<tr>
<th>Name</th>
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<th>Effective gap / eV</th>
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<td>1.3</td>
<td>0.65/0.8*</td>
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<tr>
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<td>1.1</td>
<td>0.56</td>
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<tr>
<td>Ph$_2$-benz-bodipy-Thio</td>
<td>1.3</td>
<td>1.0</td>
<td>0.37</td>
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Table 10.1: Overview over the gap values of the aza-bodipy investigated in Chapter 8. The optical gap is derived from the EQE and absorption onset, the effective gap is calculated with respect to the electron affinity of C$_{60}$ of 4.0 eV. The $V_{OC}$ is measured in mip-type flat heterojunction devices (except for: *bulk heterojunction nip).

By combining this device with a solar cell based on the oligothiophene DCV6T-Bu4:C$_{60}$ in a series of tandem cells, a $V_{OC}$ of 1.7 V, a FF of 57 % and an efficiency of 5 % can be reached, despite the two subcells not being optimally matched. The EQEs have their maximum at 550 nm (DCV6T-Bu4) and 780 nm (Ph$_2$-benz-bodipy).

**Outlook**

The aza-bodipys have shown themselves to be a promising class of materials for use as donors in organic solar cells. Yet, the EQE maximum of about 50 % of Ph$_2$-benz-bodipy in the tandem cell with DCV6T-Bu4 is still considerably lower than the 65 % average assumed for the estimations. Furthermore, the subcell-$V_{OC}$ of 0.8 V is high in comparison to other absorbers like SnPc but the effective gap is 0.5 eV larger instead of the 0.3 eV assumed. And pushing the absorption further into the infrared will not only increase the available amount of photons but also decrease the attainable open-circuit voltage. As the series of halogenated SnPcs illustrates, energy level tuning is also not always straightforward. Hence, the estimated 19 % for a tandem cell absorbing up to 890 nm probably requires a lot of material development and screening.

It is, on the other hand, one of the strengths of OPV that it can choose from millions of compounds. Already, the 12 % cell published by Heliatek is a triple cell. This allows for the absorption to be divided among six possible absorbers. Certainly, cells with four or more subcells are still in an early academic stage as matching the subcells’ currents and determining the exact overall efficiency becomes increasingly complex. But thermal evaporation allows for the easy stacking of the layers needed. And each additional subcell would lead to a lower total $j_{SC}$. This would not only increase the possible cell area as series resistance decreases, thus, increasing the module efficiency. It would also bring into play materials whose absorption is not large enough to fulfill the requirements stated in the tandem cell estimation but whose energy levels are well suited to yield – eventually – efficient, lightweight, flexible and possibly transparent solar modules.
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<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>AM1.5g</td>
<td>global spectrum of 1.5 air mass</td>
</tr>
<tr>
<td>CT</td>
<td>charge transfer</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>D-A</td>
<td>donor-acceptor</td>
</tr>
<tr>
<td>EA</td>
<td>electron affinity</td>
</tr>
<tr>
<td>ETL</td>
<td>electron transport layer</td>
</tr>
<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>HBEC</td>
<td>high binding energy cutoff</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HJ</td>
<td>heterojunction</td>
</tr>
<tr>
<td>HTL</td>
<td>hole transport layer</td>
</tr>
<tr>
<td>HTM</td>
<td>hole transport material</td>
</tr>
<tr>
<td>IAPP</td>
<td>Institut für Angewandte Photophysik</td>
</tr>
<tr>
<td>IC</td>
<td>internal conversion</td>
</tr>
<tr>
<td>IE</td>
<td>ionization energy</td>
</tr>
<tr>
<td>IP</td>
<td>ionization potential</td>
</tr>
<tr>
<td>IQE</td>
<td>internal quantum efficiency</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
</tr>
<tr>
<td>IV</td>
<td>current-voltage</td>
</tr>
<tr>
<td>JV</td>
<td>current density-voltage</td>
</tr>
<tr>
<td>LCAO</td>
<td>linear combination of atomic orbitals</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>mip</td>
<td>metal–intrinsic–p-doped</td>
</tr>
<tr>
<td>nip</td>
<td>n-doped–intrinsic–p-doped</td>
</tr>
<tr>
<td>OPV</td>
<td>organic photovoltaics</td>
</tr>
<tr>
<td>OSC</td>
<td>organic solar cell</td>
</tr>
<tr>
<td>PCE</td>
<td>power conversion efficiency</td>
</tr>
<tr>
<td>pin</td>
<td>p-doped–intrinsic–intrinsic</td>
</tr>
<tr>
<td>pin</td>
<td>p-doped–intrinsic–n-doped</td>
</tr>
<tr>
<td>QCM</td>
<td>quartz crystal monitor</td>
</tr>
<tr>
<td>rms</td>
<td>root mean square (-roughness)</td>
</tr>
<tr>
<td>SRC</td>
<td>standard reporting conditions</td>
</tr>
<tr>
<td>UFO</td>
<td>unidentified flying object</td>
</tr>
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<td>UV</td>
<td>ultraviolet</td>
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<td>ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
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</table>
Acknowledgments

Being part of the OSOL group of the IAPP has been a wonderful experience. I would like to thank Professor Dr. Leo for this opportunity and the help, guidance, and patience he has given me over the years as my supervisor. This thesis on the exciting field of organic solar cells would not exist without him.

I also would like to thank Professor Dr. Wöhrle for his review on this thesis and him and Dr. Schnurpfeil for supplying some of the interesting materials I could investigate. Great thanks also are in order for Dr. Riede and Dr. Männig who, as group leaders, always gave their support and established a tremendously helpful working environment – to which belongs ensuring the funding of this work by the BMBF Innoprofile grant "Organische p-i-n Bauelemente".

My thanks also go to all members of the OSOL group, the Institute of Applied Photophysics, and all inhabitants of the vibrating microcosm also known as Bey95. In particular, working together with Dr. Gresser both on the theory of how organic materials in solar cells should work and making sure they do so nicely, has been a privilege. Furthermore, the help and insight I got from my colleagues Dr. Wynands and Dr. Falkenberg cannot be overestimated.

Others also have shown great support with measurements and interpretation such as the long living Dr. Hermenau, the well tempered Dr. Widmer, the foresightful Dr. Tress, the energetic Dr. Olthoff, the mobile Dr. Hein, the absorbing Dr. Schüppel, the spectral Mr. Timmreck, and the forceful Mrs. Röttinger. Priceless technical support has come and was very much appreciated from Mrs. Petrich, Mr. Wolf, Mr. Schmidt, and Mr. Kunze, but also the whole Lesker team. Mrs. Petrich in particular has helped greatly with her skills in sublimation and device fabrication. Support with administrative issues and pitfalls was given by Mrs. Hunger, Mrs. Wolf, and, of course, the one and only Mrs. Schmidt. Many more have helped who will hopefully forgive me for not mentioning them by name.

Friends have to be thanked sincerely, firstly for being true friends and, in the case of Anne, Bine, Christiane, and Michael, secondly for being proofreaders. Last but most assuredly not least, thank and love go to my family and my partner Iris without whom all this would not be (and have become) anything.

Toni Müller
Dresden, den 24.04.2015