Numerical simulation and optimisation of organic light emitting diodes and photovoltaic cells

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1. Introduction and motivation

In recent years, the investigation of Organic Light Emitting Diode (OLED) and photovoltaic devices based on small organic molecules and polymers has attracted growing interest, mainly due to the promising aspect of lower costs compared to existing technology and the possibility of preparing flexible large area devices at low process temperatures on polymer foils. Organic semiconductors have unique physical properties, which offer many advantages: Many fluorescence dyes emit strongly red shifted to their absorption. Thus, there are almost no reabsorption losses in OLED [1]. The extremely high absorption coefficients in the visible range of some dyes offer the possibility to prepare very thin photodetectors and photovoltaic cells [2]. Due to the small thicknesses of the layers, the requirements on chemical and structural perfection are reduced since the excitation energy does not have to travel a long way. The electronic structure of organic semiconductors is largely determined by the individual molecules and only weakly modified by solid state effects. Therefore, interface states play a minor role and also amorphous layers grown on cheap, amorphous substrates exhibit attractive electrical properties and sufficiently low densities of deep traps. There are a nearly unlimited number of chemical compounds available, and it is possible to tailor materials for the various sample structures and characterization techniques. Although a complete understanding of the doping process is still a challenge for organic semiconductors [3-13], the technique of p-type doping by coevaporation with strong organic acceptor molecules has already been successfully employed for organic LEDs [3]. More recently, a technique of n-type doping using a salt or the leuco form of organic cationic dyes as a precursor for an efficient n-dopant [13] has been developed in our institute.

Organic light-emitting diodes (OLED) have been investigated intensively [1,14-16] due to their promising applications in large-area, flat and ultra-thin displays. Up to now, fluorescence based organic electroluminescent devices have reached the commercial level. In the future, OLED displays have the potential to be brighter than a conventional TV screen with much higher efficiency, brilliant colors, large viewing angle, switching times fast enough for video frequency and lifetimes well above 10 000 hours.

To gain better insight into the interplay of the various critical parameters of the organic light emitting diodes, we propose here a numerical simulation routine presented in the Sections 3.1 and 4.1 that can model the current voltage characteristics and the luminance. The first single heterojunction light emitting device was described by C.W. Tang from Kodak in 1987 [1]. This device consisted of a hole transport layer (HTL) and an emitting layer (EML), sandwiched between ITO and Al (Section 4.2). The EML serves
simultaneously as an electron transport layer. In the heterojunction device, the energy levels are chosen such that there is only a small barrier for hole injection from the HTL into the EML, while electrons from the EML meet a very high barrier so they can hardly penetrate into the HTL. For such an architecture, the main recombination region will be around the center of the device in the EML, close to the internal interface if electron injection into the EML is reasonably efficient and the electron mobility is much higher than the hole mobility in the EML. In contrast, single layer devices require that the injection of holes from the anode and electrons from the cathode into the organic material are equally efficient and the mobilities are the same for both types of carriers.

The light emission is the result of radiative decay of singlet excitons formed by recombination of charge carriers. However, not all charge carriers which recombine contribute to the generation of light: a part of the excitons may decay non-radiatively or may be quenched in the bulk or at interfaces. Because the ratio of triplet exciton formation to singlet exciton formation under electrical excitation is approximately 3:1 due to spin-statistics, organic fluorescent emitters are limited to 25% internal quantum efficiency whereas phosphorescent emitters can in principle reach a quantum efficiency of 100% if the intersystem crossing process is efficient. Recently, highly efficient organic electrophosphorescent devices have been demonstrated [12,18]. Many studies also focus on using highly fluorescent dye molecules as the emissive dopant in the emitter layer of OLED [14,20,74,115]. As described in Section 4.3, these OLED are based on energy transfer from host to guest molecules. Hereby, the emission wavelength can be tuned in the desired way and the efficiency and stability of devices have been improved by separate optimization of the properties of the guest and host molecules [19-30]. The control of doping in the transport layers also plays a crucial role for the OLED, decreasing the operation voltage to values as low as 2.5 V for 100 cd/m² [10]. This topic is discussed in Section 4.2, where the results of numerical simulations show the advantage of doping.

Although the efficiency of organic solar cells (OSC) [31-37] is not yet high enough to be competitive with inorganic solar cells, organic cells based on blend and multi-layered structures have increased significantly in power conversion efficiency to reach around >5% at present. Most of the future work will probably concentrate on the development of highly absorbing materials with reduced band gap, compared to typical polymers used so far. However, the diode architectures also leave room to further improve the efficiency of the power conversion process.

In Chapter 5, we report about p-i-n type bulk heterojunction and p-i-i-n heterojunction solar cells with a photoactive donor-acceptor blend layer or photoactive intrinsic bilayers, respectively, embedded between doped wide-gap transport layers. To
gain better insight into the critical parameters of the cells, we present here a numerical simulation routine in the Sections 3.1 and 5.1 that can model the photocurrent of such p-i-n and p-i-i-n types heterojunction solar cells. The model comprises a simulation of both the optical and electrical properties. The optical calculation yields the distribution of the electromagnetic field in the multilayer system. This allows to predict the absorption profile to be used as an input for electrical modeling, and thus accounts for the origin of the photocurrent. By numerical modeling, we are able to show the variation of the photocurrent, when parameters such as thickness, mobility of charge carriers, and recombination conditions in the active layer are varied. These calculations help for the optimization of cells and illustrate which parameters are critical (Section 5.2). Using the numerical model, we also compare two solar cell structures, bulk heterojunction and heterojunction, and summarize the advantages and disadvantages of the simulated devices in Section 5.2 [37,38]. Fits to experimental data using two alternative models of losses in the active layer (geminate and non-geminate recombination) are given in Sections 5.3. Herein, the focus is on the modelling of current-voltage characteristics under different illumination of solar cell with one common set of parameters.

The mechanism of photocurrent generation can be understood by a two step process: First, the creation of excitons by absorption of light in the active region of the device (blend layer or intrinsic bilayers) and second, the charge generation by dissociation of excitons at the interface between two molecular compounds in the blended film or at the interface between two photoactive layers. However, quenching of excitons at the contacts or losses caused by recombination of charge carriers reduce the internal quantum efficiency. With carrier mobilities being generally rather low in organic materials, such non-geminate recombination losses become even more pronounced with thicker layers, thus limiting the range of active layer thicknesses that can be used. One of the benefits of the p-i-n architecture with highly doped conductive wide-gap transport layers is that the thickness of the transport layers can be chosen arbitrarily. Thus, the total thickness of the device that determines the optical microcavity effects and the thickness of the photoactive blend layer can be optimized separately [37].

Since the first reports of organic light-emitting diodes [1] and photovoltaic cells [2], almost all current knowledge of physical processes occurring in OLED and solar cell has essentially come from experiment. Indeed, numerous experiments have provided an insight into mechanisms and processes such as the injection processes, charge transport, the effect of doping, recombination and exciton diffusion, quenching and decay. However, even with a relatively good knowledge of these particular processes, it is still not an easy task to predict the properties of a multilayer organic device. For this reason, a number of
OLED device models [39-60] and number of photovoltaic cell models [61-64] have been developed, aimed at a comprehensive description of these devices. These are limited by the state of knowledge about the materials and have to be adapted to real experimental measurements. Nevertheless, as the theoretical description of various processes becomes more established, modeling will begin to have greater importance. Ultimately, it is hoped that device modeling will significantly reduce the experimental work necessary to get insight into device architectures and their behavior. This should help with avoiding the problems and accelerate the progress towards the development of optimized devices by study of crucial parameter variations. Detailed pictures of the charge, field and recombination distribution, and of the current in the devices have been obtained by using the experimental data as input to our model. This combination of experimental data and numerical device modeling for multilayer organic devices is the essence of the present study. It also demonstrates the straightforward applicability of our device models (Sections 4.2, 4.3 and 5.3) to multilayer organic structures.

The numerical models mentioned, describing either organic light emitting diodes or photovoltaic cells are restricted for particular cases by simplification of boundary conditions, e.g. omission of trapping processes, quenching processes of excitons, allowing the use of the special numerical methods by accelerating the time of calculation. Basically, our model is based on the work of Staudigel at. al. [58], using especially the self consistent mechanism for simulation of the injection and transport of charge carriers (space charge limiting current SCLC for OLED, Section 3). Solving the rate equations with temporal and spatial discretisations by implementation of an iterative method [65] to obtain the solution of nonlinear equations system (convergence of variables to steady state) is not the fastest method. However, the time of calculation depends strongly on the number of implemented processes and mainly on the relaxation time of particular mechanisms. The advantage of this numerical method is the possibility to implement in an easy way additional processes describing the behavior inside the organic materials and decreasing the number of required initial parameters to a minimum. Thus, we were able to introduce in the model new mechanisms describing acceptor or donor molecules in transport layers, emissive dopants in the emitting layer of OLED and a geminate recombination process in the absorption layer of organic solar cells. These new effects are crucial for the correct description of more advanced devices.
2. General remarks about organic multilayer devices and physical processes

In this section, we will discuss the structure of OLED and OSC together with their working principles and the physical mechanisms of charge carrier and exciton creation, transport, annihilation and recombination. Moreover, the transport of free charges through metal/organic and organic/organic interfaces will be covered with special emphasis on the implementation problems in the numerical model.

2.1. Organic Light Emitting Diodes and Photovoltaic Cells: Basics and Characterization

2.1.1. Organic Light Emitting Diodes

The basic organic light emitting diode is a Metal-Insulator-Metal (Figure 2.1) diode working in the double injection regime with a hole injecting and electron injecting anode and cathode, respectively. For efficient fluorescent OLED, the injected electrons and holes should initially form molecular excited states, so called excitons, which should recombine radiatively, and the generated photon should leave the organic layer through a transparent electrode. However, as a result of this very simple device and a number of different loss mechanisms, not all injected carriers contribute to fluorescence. Some of them may leave the organic layer instead of recombining with charges of opposite sign. These losses are summarized in the charge balance factor $\gamma$, the ratio between the number of formed excitons and the number of electrons flowing in the external circuit. Only a fraction $r_{st}$ of the excitons are singlet excitons according to spin statistics. Furthermore, the probability $\Phi_r$ that an exciton decays radiatively is below unity due to quenching processes and intrinsic non-radiative decay channels (e.g. via exciton-phonon coupling). The others losses result from non-perfect light outcoupling $\Phi_{out}$. Accordingly, the total external power efficiency an OLED is given by

$$\eta_p = \gamma \cdot r_{st} \Phi_r \Phi_{out} \frac{h\nu}{eV},$$

(2.1)

where $h\nu$ denotes the average energy of the emitted photons, $V$ the applied bias and $e$ the elementary charge.
Figure 2.1  Energy level diagram for OLED structure based on a single organic layer with an applied bias voltage $V$. The scheme shows the required steps to obtain fluorescence from the organic layer. First the holes and electrons are injected from the opposite anode and cathode, next they are transported through the organic layer and recombination occurs close to the right electrode (the mobility of holes is assumed to be higher than for electrons).

Figure 2.2  Energy level scheme for a double heterojunction OLED with applied bias. The mechanism for the creation of light is similar to a single organic layer. However, the additional hole and electron transport layers (HTL and ETL) improve the charge carrier injection into the organic multilayer system and efficiency of transport to the emitting layer (EML). Moreover, the transport layers should prevent the electrons and holes from drifting to the anode and cathode, respectively.

The quenching processes, which significantly reduce the efficiency, occur close to the electrodes and are the result of either the interaction between the exciton and the
metal, organic defects or diffusion of the excitons to the electrode resulting in non-radiative recombination. Thus, creation of excitons in the center of the organic layer gives the highest radiative yield. However, the realization of this task is not easy because in pure small molecule organic materials, one of the charge carriers is usually more mobile than the other. Organic layers with similar mobilities of holes and electrons can be achieved by blending two materials, but here the mobilities tend to be lower than for the individual organic materials, thus affecting the efficiency. Therefore, OLED typically consist of at least two or three-layer of different organic materials to overcome these loss problems. Improvement of injection and recombination efficiency is obtained by the implementation of additional hole and electron transport layers (ETL and HTL, respectively).

\[
\text{Alq}_3 + \text{QAD} + \text{PtOEP} + \text{Spiro-ANTH}
\]

**Figure 2.3** Examples of organic emitter materials with good efficiency:

(i) green - Alq\textsubscript{3} (tris (8-hydroxy-quinolinato)-aluminium) and Alq\textsubscript{3} doped by N,N'-diphenyl-quinacridone (QAD)

(ii) red or red-orange – Alq\textsubscript{3} doped by PtOEP-(2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphine platinum (II))

(iii) blue – Spiro-ANTH - Spiro-Anthracene.

In Figure 2.2, we show the case with undoped charge transport layers. Here, the motion of charge carriers in the transport layers is ensured by correctly choosing the organic materials with mobilities of the order of $10^{-4}$ to $10^{-6}$ cm\textsuperscript{2}/(V*s) [58]. However, by controlled evaporation of dopants together with the matrix material, an additional improvement of transport properties is obtained, together with ohmic injection [3]. These innovations result
in lower operating voltage of OLED, allowing them to reach 100 cd/m$^2$ (a typical brightness for display application) at 2.5 V [10].

![Fluorescence spectra for Alq$_3$ doped by emissive dopants (QAD) (dashed line) and pure Alq$_3$.](image)

**Figure 2.4** Fluorescence spectra for Alq$_3$ doped by emissive dopants (QAD) (dashed line) and pure Alq$_3$.

The transport layers should have wider gaps than the EML. The ETL has a larger ionization potential than the EML and the HTL has smaller electron affinity than the EML. Hence, neither excitons nor holes or electrons from EML can penetrate into the ETL and HTL, respectively [67], when the diode is operated at forward applied bias.

When we consider the preparation of OLED structures, most conjugated polymer OLED consist of a single layer [69]. If one considers the usual Pedot layer to be a doped HTL, such devices can also be considered as two layer devices. For large area applications, polymer thin films have the advantage of easy deposition by spin coating, printing or dipping. However, this makes multilayer structures difficult to prepare since there are stringent conditions on solubilities of the successively deposited polymers and also the interfaces are not sharp. Conversely, using small molecules allows physical vapour deposition in vacuum by sublimation, and multilayers with sharp interfaces are easily prepared [10]. The use of shadow masks, however, imposes limitations to the possible panel size for vacuum deposited OLED displays.

The device architectures above introduced allow us to obtain an efficient yield of fluorescence or phosphorescence from the EML. The desired wavelength of light can be
changed by using different materials as the emitter, or shifted by co-evaporation of the matrix material with emissive dopants. Examples for emitters in the green, blue and red or red-orange are illustrated in Figure 2.3. Here, green light is obtained by implementation of pure Alq$_3$ [10]. If dopants of the phosphorescent molecule PtOEP are added, by controlling the concentration of dopants, the spectrum can be shifted to red or red-orange [70]. Also a slight change of color occurs when the dopant material is QAD [14,20,74,115], see Figure 2.4. This material is a fluorescent dye, which is primarily added to improve the efficiency and lifetime of green emission. To obtain blue light, fluorescent dyes such as Spiro-Anthracene can be used [41].

2.1.2. Photovoltaic cells

The conversion of solar light into electric power requires efficient generation of both negative and positive charges as well as a driving force that can easily push these charges through an external electric circuit. The heterojunction and bulk heterojunction structures based on organic materials seem to be a promising way to create efficient photovoltaic devices [31-37]. The variety of organic compounds can deliver specific materials, which can meet the requirements. The main components in both heterojunction and bulk heterojunction devices are the photoactive materials responsible for efficient generation and transport of created carriers. Figure 2.5 shows device designs used for cells comprising two components, an electron donor (D) and an electron acceptor material (A). Charge separation occurs at the interface between these two. To improve the transport from the photoactive layers to the contacts, for the heterojunction cell (ii), the donor material is in contact with a p-doped transport layer, which is deposited on the top of an electrode material with high workfunction (typically ITO, transparent electrode). Similarly, the photoactive acceptor material adjoins the n-doped transport layer, which is contacted by the electrode with the lower workfunction (typically Al). This double layer cell (heterojunction) benefits from the separated charge transport layers that give the charge carriers photogenerated at the D-A-interface only little chance to recombine with their counterparts. The drawback is the small interface area that allows only excitons from a thin layer to reach it and get dissociated, i.e. the main loss path is recombination of excitons before they reach the active interface. The strong point of blended photoactive layers (bulk heterojunctions), which can again be embedded between doped wide gap transport materials, is the large interface area. Here, the molecular mixing should occur on a scale that allows good contact between alike molecules (closed percolation paths) and allows most excitons to reach the D/A interface. The main problem with this approach is that carrier mobilities are reduced and charge-trap densities are typically increased in
blended materials, where crystalline order is difficult to achieve. This may lead to severe losses by charge carrier recombination as – in contrast to flat heterojunction cells – the clouds of photogenerated holes and electrons interpenetrate throughout the active layer. Research in this area has therefore focused on improving the charge transport properties of the blends by controlling the film morphology [68].

![Schematic of p-i-n cell based on a bulk heterojunction (i) and a p-i-i-n cell with a flat heterojunction (ii): the active region is sandwiched between two wide-gap layers. The black arrows indicate the light going through the sample structure, taking account of the reflecting cathode.](image)

Figure 2.5  Schematic illustration of a p-i-n cell based on a bulk heterojunction (i) and a p-i-i-n cell with a flat heterojunction (ii): the active region is sandwiched between two wide-gap layers. The black arrows indicate the light going through the sample structure, taking account of the reflecting cathode.

The power conversion efficiency of a photovoltaic cell under standard illumination conditions depends on the following three parameters: (i) The current density under zero bias, i.e., the short-circuit current density $J_{SC}$, (ii) the photovoltage under open circuit conditions, i.e., the open-circuit voltage $V_{OC}$, and (iii) the fill factor

$$FF = \frac{\max(J_p V_p)}{J_{sc} V_{oc}},$$  \hspace{1cm} (2.2)

which characterizes the shape of the current density versus voltage curve in the power-generating fourth quadrant (Figure 2.6). The power conversion efficiency is then

$$\eta_p = \frac{J_{sc} V_{oc} FF}{P_{inc}},$$  \hspace{1cm} (2.3)

where $P_{inc}$ is the incident flux of optical power density (typically the AM1.5 solar spectrum (2.7) is used at an intensity of $P_{inc}=100 \text{ mW/cm}^2$).


Figure 2.6 Current versus applied voltage of a solar cell with the characteristic parameters describing the photovoltaic cell.

Figure 2.7 AM1.5 solar spectrum at an intensity of $P_{\text{inc}}=100 \text{ mW/cm}^2$ in the absorption range of the organic molecules ZnPc and $C_{60}$.

All photovoltaic cells should be optimized for maximum electrical power generation under standard illumination condition, the AM1.5 spectral illumination (see Figure 2.7). For organic heterojunction solar cells, this requires that the two components should absorb in different spectral ranges to cover as much as possible of the sun spectrum.
Figure 2.8 Organic materials responsible for:

(i) efficient absorption of light (a blend of fullerene $C_{60}$ (acceptor) and zinc phthalocyanine (ZnPc) (donor) or a heterojunction ZnPc / $C_{60}$),

(ii) transport of holes (p-type layer of (4,4',4''-tris(3-methylphenylphenylamino)-triphenylamine (m-MTDATA) or $N,N,N',N'$-Tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD) doped by the strong acceptor tetrafluoro-tetracyano-quinodimethane ($F_4$-TCNQ))

(iii) transport of electrons (n-type layer of $C_{60}$ doped by Rhodamine B)

The simulation result presented in this work refer to a number of materials which have been typically used in our labs in the recent years: For the absorption of white light in our photovoltaic devices, two materials are responsible, namely phthalocyanine zinc (ZnPc) as the donor molecule and fullerene ($C_{60}$) as the acceptor. Their chemical structures are shown in Figure 2.8. The spectrum of $k$ values, which characterizes the absorption, is shown in Figure 2.9. The maximum of absorption for ZnPc lies close to 630 nm, whereas $C_{60}$ mainly collects the photons at shorter wavelengths in the order of 300 nm, with a long tail of weak absorption into the visible range. Both photoactive materials do not overlap in their absorption, but only the absorption of ZnPc coincides with a strong region of the solar spectrum. The contribution of $C_{60}$ is significantly lower due to weaker photon flux in the range from 300 nm to 450 nm and due to the fact that the absorption coefficient of $C_{60}$ at the 450nm peak is by about a factor of two smaller than the peak absorption coefficient of ZnPc. These two materials are used both for the blended layer (bulk heterojunction) and the double layer (flat heterojunction) solar cells. To allow efficient transport of the electrons from the photoactive layer to the cathode, we use $C_{60}$
doped with rhodamine B, which has a conductivity of the order of $10^{-4}$ S/cm (the organic salt rhodamine B is a precursor of a strong donor formed upon evaporation in vacuum, as pointed out by Werner and Li in references [7,13,71,72]). The holes are transported through the hole transport layer made of MeO-TPD doped by F$_4$-TCNQ with a conductivity about one order of magnitude lower, i.e., $\sim 10^{-5}$ S/cm [7,13,71,72]. Using doped m-MTDATA instead, the conductivity is only $3 \times 10^{-7}$ S/cm and thus represents a severe current limiting factor.

![Figure 2.9](image)

*Figure 2.9  Dependence of $k$ versus the wavelength for neat ZnPc and $C_{60}$ and blends of the two materials with mass-ratio 1:1 and 1:2.*
2.2. Bulk behavior of excitons and charge carriers

2.2.1. Mechanisms governing the exciton dynamics

Excitons are very important for both OSC and OLED devices, which aim at the creation of free charge carriers and the emission of photons, respectively. An exciton is a bound state of an electron and a hole in an insulator (or semiconductor), or in other words, a Coulomb correlated electron/hole pair. It is an elementary excitation of a solid. In organic materials, excitons can be separated into two groups: Frenkel excitons and charge-transfer excitons. The Frenkel exciton is looked upon as a correlated hole and electron pair that is located in the same molecular site, i.e. an excited state of a molecule that can move through the organic material. Its size corresponds to the molecular size (0.5-1 nm) and its binding energy is on the order of 0.3 to 1 eV. Excitons with the negative and the positive charge centered on different neighbouring molecules with the radius of one or two times the nearest-neighbor intermolecular distance are called charge transfer excitons. Due to the low dielectric constant and the essentially localized nature of charge carriers, Mott–Wannier excitons with hydrogen-type orbitals as in inorganic semiconductors have not been observed in organic semiconductors.

Excitons can be generated in any of the ways in which an excited state can be generated, e.g., direct optical excitation, carrier recombination, indirect optical excitation, thermal and chemical activation, or generation by other excitons. Only the first two are specifically important for the operation of organic light emitting diodes and photovoltaic cells. If the single excitons are generated in the higher-lying molecular states or Davydov bands [73], they generally decay with a characteristic time of picoseconds to the lowest-lying state. The lifetime of an exciton in this lowest-state is of the order of nanoseconds and the exciton may decay radiatively or non-radiatively to the ground state or pass over to the triplet manifold. The most convenient way to generate the excitons is by direct optical excitation being maximized by choosing the appropriate frequency and polarization for incident light. The distribution of excitons in the organic layer is only concentrated to a region close to the interface when the penetration depth is low due to the high absorption coefficient of the material. In order to obtain a uniform spatial distribution of excitons, weakly absorbed light can be used, greatly reducing the concentration of excited state. A high absorption coefficient is desired for photoactive layers in the range of the solar spectrum. However, the organic materials only efficiently absorb light in absorption bands with a width of 100-200 nm, while the solar spectrum is significantly broader. Therefore, to collect as much light as possible even in the spectral regions of weak absorption, the active layers should be as thick as possible, whether blended layers or intrinsic bilayers
are used. The challenge is to create a stacked solar cell with different photoactive materials that allow absorption of light from as much of the solar spectrum as possible.

The second method of exciton generation, by formation from charge carriers, is especially important for organic light emitting diodes. Here, the process of electroluminescence takes place because the injected electrons and holes from opposite electrodes are driven by an electric field to form a bound state in the bulk of the organic material, generating the excitons. The number of triplet and singlet excited states agree with spin statistics, i.e. three of the four possible exciton states are triplet states. This rate has been confirmed experimentally for the first time by Helfrich at. al. [66] for small molecules. However, Wohlgenannt at al. [18] found that for some polymers this ratio could take values as low as 1:1.

The recombination of charge carriers results in an electrically excited state. If at least one of the charges of the pair is mobile, then recombination can take place via the process

\[
\begin{align*}
p^+ + n^- & \rightarrow S_n^* \rightarrow S_1, \\
& \rightarrow T_n^* \rightarrow T_1, \\
\end{align*}
\]

where \(S_n^*\) and \(T_n^*\) are highly excited singlet and triplet exciton states and \(S_1\) and \(T_1\) denote lowest singlet and triplet exciton states.

For solar cells, recombination is an undesirable mechanism which results in lowering of the photocurrent, and can result from geminate and non-geminate processes. Upon dissociation of excitons, when the positive charge carrier and the separated electron are still relatively close to each other, the probability that hole and electron will recombine can be substantial (geminate recombination, see Section 5.3). The second path of losses in the photoactive layer is the non-geminate direct or indirect recombination. In OLED, only non-geminate recombination takes place, where the injected charge carriers can recombine either directly or indirectly via trap states. Recombination can lead to the creation of an exciton that decays to the ground state by the emission of a photon plus some phonons, or purely by phonon emission. These processes are referred to as radiative and non-radiative recombination. If the oppositely charged carriers are produced in a statistically independent manner from each other, then carrier recombination is a random process and is kinetically bimolecular. Langevin [73] was the first to consider this
treatment of recombination. The important initial assumption is that the mean free path of the carriers is lower than the capture radius of one carrier by another.

A possible loss path for OLED is reabsorption of the emitted photon by the organic layers. However, the reabsorption process in many fluorescent dyes is negligible since organic materials typically emit strongly red shifted to their absorption.

![Diagram of Föster and Dexter transfer](image)

**Figure 2.10** Föster and Dexter transfer as transport mechanisms for excitons in organic materials.

It is generally assumed that the excitons are more or less mobile in organic crystals. It follows from the existence of the exciton bandwidth that crystal excitations are somewhat delocalized immediately after excitation. After self-trapping by exciton-phonon-coupling, excitons can still move by incoherent hopping processes. The transport of excitons between different organic molecules will be called energy transfer, while between the same type of molecules is named energy migration. In literature, we can find two mechanisms of energy transfer or migration, named Föster and Dexter transfer. The first, the Föster transfer (Figure 2.10) is based on resonant dipole-dipole coupling and the energy transfer rate $K$ depends on the overlap between the absorption of the acceptor and the emission spectra of the donor. Between Alq$_3$ and QAD molecules, e.g., $K$ is in the order $10^{-8}$–$10^{-10}$ s [74]. Being mediated by the electromagnetic field, resonant Förster transfer does not require an orbital overlap and is only efficient for transfer between singlet states (or for transfer of a triplet on a phosphorescent molecule to a singlet on a different molecule). However, it is to be distinguished from the process of real emission
and reabsorption of a photon, which is much less efficient and only important at long distances, typically more than 10 nm from the side of excitation. Dexter transfer occurs only with overlapping molecular orbitals and is therefore only relevant for neighbouring molecules with transfer occurring by higher multiple interactions or by electron exchange (Figure 2.10). The transfer is allowed between triplet-triplet and singlet-singlet states. The four general methods used to measure diffusion of excitons are bulk quenching, surface quenching, bimolecular recombination and photoconduction.

In accordance with a theory first given by Einstein [73], there is rigorous connection between the processes of absorption and emission of radiation. However, the true lifetime of the excited state is often different from the radiative lifetime, because of the additional channels for decay of excitons. These involve the interaction of the mobile exciton with phonons, others excitons, with foreign molecules or structural defects. As a result of these additional processes, it is possible for the mobile excitons to be trapped and decay with the emission of light at longer wavelengths. Excitons can also be quenched by charge carriers: ionized molecules often feature low energy transitions, i.e. red shifted absorption as compared to the neutral state. Accordingly, excitons can transfer their energy to ionized molecules via Förster transfer leading to red shifted emission or more likely to radiationless decay. These two processes – exciton-exciton annihilation and exciton-quenching by free or trapped carriers - play an especially important role in decreasing the efficiency of OLED at high brightness.

At interfaces or surfaces, excitons can either be reflected back into the organic layer, or they can be quenched when they reach the surface of the crystal after diffusing through the bulk material. One process of quenching can be by a reaction with impurity molecules whose energy levels lie below those of the host. Another important process is the transfer of the exciton energy to the free electrons in the metal at the metal-organic-interface, which covers the surface of the OLED.

2.2.2. Transport in organic materials

Since most polymeric or small molecular materials used in OLED or OSC form disordered amorphous films without long-range translational symmetry, it is not possible to simply adopt mechanisms developed for molecular crystals. Because of the absence of extended delocalized states, charge transport is usually not a coherent motion in well-defined bands, but rather a stochastic process of hopping between localized states, which leads to the low carrier mobilities typically observed, being are strongly dependent on temperature and electric field [13,58,80,81]. Thus, most studies make use of arguments
based on the disorder formalism by Bässler and co-workers [82,83]. The formalism is based on the assumption that transport occurs through a manifold of localized states. The key element of the assumption is the method used to compute the jump rates. Kenkre and Dunlap [84] have reviewed the validity of this approach. Also, the problem of hopping in disordered molecular solids has been considered by Garstein and Conwell [85,86], Novikov and Vannikov [87].

In disordered organic materials, charge carriers are transported by hopping, characterized by incoherent jumps between isolated molecular sites (Figure 2.11). Some of the hopping steps will be easy and some will be difficult, depending on the distance between site and the site energies. Even if there are no trapping sites, there will be times where the distance between available sites is so large that a step will require a much higher activation energy as if the carrier was in a conventional trap. In fact, it has been shown that for certain measurements, dispersive transport based on the continuous time random walk model [82,88], which deals with a system devoid of conventional traps, but in which the distance between sites is distributed randomly, is mathematically equivalent to a system in which the sites are uniformly distributed, but contain traps that are distributed in energy, forcing the carriers to undergo multiple trapping and reemission. Specifically, the hopping rates between sites should not change with T if they are affected only by the distances between sites (off diagonal disorder). If the hopping rates depend on the energetic differences between sites (i.e., diagonal disorder), the rate will change with temperature.

Figure 2.11 Hopping transport of carriers through a disordered organic material. $E_n$ and $E_m$ denote the individual energy levels, $E$ is the center of the density of states (DOS) and $\sigma$ is the width of the DOS.
Bässler disorder model

The Monte Carlo techniques were used to solve the transport problem in organic materials by Bässler, who achieved a quite good fit to the field and temperature dependence of the mobility obtained e.g. by transient electroluminescence experiments [82,83]. The Gaussian shape of the density of states is assumed since the polarisation energy is determined by a large number of internal coordinates, each varying randomly by small amounts [82]. Thus the proposed function, implying that all states are localised, reads

\[
\Gamma(E) = \frac{N_{\text{HOMO}}}{\sigma\sqrt{2\pi}} \exp\left(-\frac{E^2}{2\sigma^2}\right),
\]

(2.5)

where the energy \(E\) is measured relative to the centre of the DOS and \(\sigma\) denotes the standard deviation of the distribution function of the sites (width of DOS). The diameter of the molecules and therefore the spacing between the molecules has been approximated to 1 nm for all materials involved, thus yielding densities of state \(N_{\text{HOMO}}\) and \(N_{\text{LUMO}}\) of \(10^{21}\) cm\(^{-3}\).

The jump rate among sites \(n\) and \(m\) is supposed to be of the Miller–Abrams type: jumps to higher site energies scale by Boltzmann factors with neglecting the polaronic effect, while the respective factor is unity for hops to lower energies

\[
\nu_{nm} = v_0 \exp\left(-2\gamma_d \cdot a \frac{\Delta R_{nm}}{a}\right) \left[\exp\left(-\frac{E_n - E_m}{kT}\right); \quad E_n > E_m, \right.
\]

\[
\left.\exp\left(1; \quad E_n < E_m\right)\right],
\]

(2.6)

where \(v_0\) is the prefactor, \(a\) is the average lattice constant, \(\gamma_d\) denotes the dimensionless random variable describing the off diagonal disorder effects and \(\Delta R\) is the intersite distance between transports sites located at lattice site \(R_n\) and \(R_m\).

The key parameters of the analytical expression of \(\mu\) from the Monte Carlo simulation of the Gaussian formulation are \(\sigma, \Sigma\) and \(\mu_0\), characterizing disorder on an energetic scale, the spatial disorder parameter, and a pre-exponential factor, respectively. The equation is of the form

\[
\mu(\sigma, E, \Sigma) = \mu_0 \exp\left(-\left(\frac{2\sigma^2 \beta}{3}\right)\right) \cdot \exp\left(C\left(\sigma^2 - \Sigma^2\right)E^{\frac{1}{2}}\right); \quad \Sigma \geq 1.5,
\]

(2.7)
or
\[
\mu(\sigma, E, \Sigma) = \mu_0 \exp\left(-\frac{2\sigma^2\beta_3}{3}\right) \cdot \exp\left(C\left(\sigma^2 - 2.25^2\right)E^{1/2}\right); \quad \Sigma < 1.5, \quad (2.8)
\]

where \(\beta = (k^T T)^{-1}\) and the constant \(C\) depends on the distance between adjacent hopping sites. Accordingly, the interplay between the Boltzmann factors and the Gaussian distribution of states can determine the equilibrium energetic distribution of the charge carriers and the average transport energy.

**Poole-Frenkel formula**

The field dependence mobility can also be described with a Poole-Frenkel-like formula. It describes the field-assisted ionisation of a carrier trapped in a Coulombic well, in which charge separation takes place exclusively in the field-assisted direction. The effect is analogous to the Schottky effect [91], which refers to the lowering of the metal-insulator barrier arising from the image force interaction between the carrier and the electrode. These processes can be expressed by the formulas

\[
\mu(E, T) = \mu_0 \exp\left(-\frac{\beta_{PF} F^{1/2}}{kT}\right) \quad (2.9)
\]

and

\[
\mu(E, T) = \mu_0 \exp\left(-\frac{F}{F_0}\right) \quad (2.10)
\]

where \(\mu_0\) is the low-field mobility and both characteristic parameters \(\beta_{PF}\) and \(F_0\) can be obtained from a plot log \(\mu\) versus \(F\) at constant temperature \(T\). The parameters \(\mu_0, \beta_{PF}\) and \(F_0\) depend on temperature with different activation energies. Thus the whole field dependence and temperature dependence is given by

\[
\mu(E, T) = \mu_0 \exp\left(-\frac{\Delta_0}{kT_{\text{eff}}}\right) \cdot \exp\left(-\frac{\beta_{PF} F^{1/2}}{kT_{\text{eff}}}\right) \quad (2.11)
\]

with
\[
\frac{1}{T_{\text{eff}}} = \frac{1}{T} - \frac{1}{T_0},
\]  

(2.12)

which was proposed by Gill [92] to describe the temperature and field dependence of the mobility in poly(N-vinylcarbazole). Herein, the occurring factor \( T_0 \) is equivalent with the Meyer-Neldel law [93].

In the study of hole transport by Shein et. al. [94], it is suggested to factorize the field and temperature dependence of the hole mobility as

\[
\mu(E, T) = \mu_0 \exp \left( \frac{T_0}{T} \right)^2 \exp \left( \frac{\beta}{T} \right) \exp \left( \gamma \right),
\]  

(2.13)

The constant \( \beta \) was found to agree within a factor of 2 with the Poole-Frenkel coefficient, while \( \delta \) was an empirical parameter. Borsenberger investigated tri-p-toylamine-doped polycarbonate and confirmed the validity of Equation 2.13 if replacing the term \( 1/T \) by \( 1/T^2 \).

The mobility of disordered materials can be determined by several methods. One of the most popular ones is the time-of-flight method (TOF), i.e. to measure the transit time of a sheet of carriers created by a transient light pulse [75,76-78,95-99]. If an anomalous broadening of TOF current pulses occurs, the information about diffusivities can be obtained as well. An alternative experimental method to determine the transport properties is to examine the transient current response [58,100,101] when the injection contacts are ohmic. Abkowitz at al [102-105] were the first to successfully apply this method. Another approach is to measure field effect mobilities [6,79] in an organic field effect transistor setup. The field effect mobility should differ from mobilities derived from the above mentioned methods [106], as it is a steady-state method where thermalized carriers are observed. However, each method has certain problems, which need to be taken into account. The transient SCL method requires that the contacts are ohmic, since injection limited currents can give the same voltage dependence as a field-dependent mobility [107] due to the Schottky barrier lowering effect. The transient time-of-flight measurements often yield too high values of the mobilities since the transport does not take place in the equilibrium energetic charge carrier distribution, except for large layer thicknesses. It is well known from time-of-flight measurements and simulations that the deep sites in the tail of the distribution [82] dominate hopping transport through a Gaussian density of states (DOS).
Transport in doped organic materials

In most doped organic materials, the carrier mobility depends on the applied electric field and temperature, and can be described by Equations 2.9 and 2.10. To determine the conductivity or mobility for such a system, the percolation theory regarding the system as a random resistor network has been used [6]. The values of individual factors are dependent on the donor or acceptor concentration. Using strong donor or acceptor molecules that introduce basically shallow dopant states, a superlinear increase of conductivity with the doping ratio [106] has been observed. This increase can be explained by the saturation of the energetic states in the tail of the distribution, while states close to the center of the DOS are occupied. Here, the density of states is high, the mean hopping distance is accordingly low and the hopping rate is high. The whole material is electrically neutral with the concentration of electrons \( n \) and holes \( p \) corresponding to the density of negatively charged acceptors \( N_A^- \) or donors \( N_D^+ \), respectively. For instance, p-type doping occurs when strongly acceptor-type molecules are evaporated together with the matrix molecules. The dopants introduce unoccupied states, the LUMO of the acceptors, close to the HOMO of the matrix material. An electron transferred from matrix to the acceptor leads to a negatively charged acceptor and a positively charged matrix molecule, i.e. a hole that can move freely among the matrix molecules.
2.3. Charge carrier transport across interfaces

2.3.1. Interface between metal electrode and organic material

The current density flowing through organic light emitting diodes or photovoltaic cells can be limited in two regimes, namely space-charge limitation in the bulk and injection limitation next to the contacts. For multilayer devices, the limitation zone can also include the internal interfaces between the organic materials. The injection limitation occurs if the injection barrier is so large that the injection current from the contact into the organic is insufficient to deliver the maximum possible SCLC. Therefore, the occurrence of space-charge limited currents (SCLC) requires that the contact has good injection properties to provide an inexhaustible carrier reservoir. The injection barrier has to be small enough \[57,108\] to guarantee efficient injection without the assistance of an external electric field.

Injection limited transport through metal/organic interface

If the injection limitation occurs, two models of carrier injection into a semiconductor are usually used: carrier injection is treated either in terms of Fowler-Nordheim (FN) tunnelling or Richardson-Schottky (RS) thermionic emission \[91\] (see Figure 2.12). The thermionic emission is based on lowering of the image charge potential by the external field. The current density as a function of the field \(F\) is then given by

\[
J_{th} = A \cdot T^2 \exp \left( \frac{-\Delta E - B \sqrt{F}}{k_b T} \right),
\]

(2.14)

\[
A = 4\pi q m^* k^2_b / h^3, \quad B = \sqrt{q^3 / 4\pi \varepsilon \varepsilon_0}
\]

(2.15)

with the Richardson constant \(A\) and the zero field injection barrier \(\Delta E\). Additionally, the individual signs denote: \(q\) - elementary charge, \(h\) - Planck’s constant, \(\varepsilon\) - permittivity of material, \(\varepsilon_0\) - vacuum permittivity, \(m^*\) - effective mass of free electrons in the material and \(k_b\) - the Boltzmann constant.
The FN model ignores image charge effects and describes the tunneling of electrons from the metal through a triangular barrier into unbound continuum states. It predicts a temperature independent current injection following

\[
J_{FN} = \frac{Aq^2F^2}{\Delta E C^2 k_b^2} \exp \left( -\frac{2C\Delta E^{3/2}}{3qF} \right) \tag{2.16}
\]

with

\[
C = \frac{4\pi \sqrt{2m^*}}{h}. \tag{2.17}
\]

Both concepts are appropriate under certain conditions for use in organic semiconductors with extended band states and large mean free path, yet one cannot expect that they hold for organic semiconductors where the average mean path is of the order of the molecular distances. The existence of disorder in organic semiconductors poses an additional obstacle to be overcome by the injected carrier: to move away from the contact into the bulk, the carriers have to overcome random energy barriers caused by disorder. This leads to an enhanced backflow of injected carriers into the electrode. However, in some cases, disorder may even enhance current injection under applied bias because it may provide favourable tunnelling sites in the triangular barrier [111]. The process of injection into a disordered hopping system has been studied analytically [42] and by Monte-Carlo simulation [113]. Abkowitz et al. [110] and Gartstein and Cowan [112] used a transfer rate
that depends on the distance of the target site from the interface. This rate was taken to be similar to that for site-to-site hopping, as previously used in the bulk transport simulations of Bassler et al. [82]. It can therefore be obtained, in principle, by comparison with experimental mobility data or by quantum-mechanical calculations of molecule-to-molecule charge transfer matrix elements.

Within our model, the spatial boundary conditions are given by the concentration of carriers or the current density at the contacts. The model assumes electron injection at the left contact (x=0), and hole injection at the right contact (x=L). If the height of the energetic barrier at the contact exceeds 0.3 eV, the injection of free carries from electrode can be a bottleneck that determines the forward current density. However, this special value is dependent on the transport properties of the organic material. At low mobilities, an even higher value than 0.3 eV can guarantee sufficient injection, but for typical mobilities in order $10^{-5}$ cm$^2$/V·s, we suppose that this is the border value being similar to the values reported in [57,108]. For higher differences between the work function of the metal and the particular level of the organic layer, the contacts are treated by assuming that thermionic emission dominates tunnelling. We have not introduced tunneling injection, which will add an additional component to the current at high electric fields and may become only dominant for large values of electric field or low temperature. Especially for high voltage, the contact will inject a high enough number of free carries allowing that the bulk material will become the main current limiting factor. Thus, the thermionic emission process establishes quasi-equilibrium carrier densities at the injecting contacts (first organic monolayer) for electrons or holes,

\[
n_0 = N_0 \cdot \exp\left(\frac{\Delta E'}{k_B T}\right),
\]

where $k_B$ is Boltzmann constant, $T$ is the temperature, $N_0$ is the density of states for the organic material adjacent to the contact, $\Delta E'$ is the field-dependent energy barrier for injection at the right contact. It includes image force lowering of the barrier $\Delta E' = \Delta E - B\sqrt{F}$ if the electric field $F$ at the energetic barrier $\Delta E$ has the correct sign for barrier lowering. The recombination of minority carriers at the metal/organic interface can be neglected in all heterojunction devices discussed in this work due to high internal barriers which prevent minority carrier injection into the transport layers.
**Space charge limitation in the bulk (Ohmic contacts)**

The injection can be also depend on charge transport in the organic layer controlled by space charge accumulation close to the injection electrode. This case requires the electrode to be ohmic, i.e. it must be able to supply more charge carriers per unit time than the sample can transport. Under this condition, the electric field $F$ at the injecting contact vanishes. In this situation, the current density is proportional to the mobility and the square of the applied bias and inversely proportional to the cube of the thickness. This effect will be described in Section 3.2, where the simulation for a single organic layer is shown. Here, the appropriate modeling of ohmic injection is presented.

An ohmic contact is defined as a metal/organic layer contact that has a negligible contact resistance relative to the bulk or spreading resistance of the organic layer. A satisfactory ohmic contact should not significantly perturb device performance, and it can supply the required current with a voltage drop that is sufficiently small compared to the drop across the active region of the device. An ideally injecting ohmic contact can be implemented by assuming a huge amount of charge carriers at the electrode–organic interfaces. One possible description has been presented by Staudigel at. al. [58]. The change of the free hole density in the monolayer adjacent to the electrode is assumed as

$$\frac{\Delta p_0}{\Delta t} = \frac{\mu F p_{\text{anode}}}{d_n},$$

(2.19)

where $\mu$ is the carrier mobility in the organic material, $F$ the electric field between the electrode and the first organic monolayer, $d_n$ is the thickness of the monolayer in agreement with discretisation criteria and $p_{\text{anode}}$ should be at least one order of magnitude larger than the maximum hole density in the bulk of the organic layer system. This equation implies that we treat the contact as a reservoir of high charge density where carriers can enter the organic layer system with their bulk mobility and without any further barrier. The actual amount of injected holes is governed by the electric field $F$, which will be decreased due to space charges and limit further charge injection.

To reach high power efficiency and low driving voltage for organic light emitting diodes and a high fill factor for organic photovoltaic cells, non-limiting contacts at the interfaces and low ohmic losses in transport layers are required. These conditions for both kinds of devices can be fulfilled by using highly doped transport layers, which guarantee a negligible voltage drop in the bulk [3,8,114,115]. A further advantage of doped transport layers is that they can enable efficient charge injection from contacts even over high energy barriers: For very high doping levels, the depletion region becomes sufficiently thin.
that carriers can tunnel through the barrier. It has been shown by thickness dependent photoelectron spectroscopy that good quasi-ohmic contacts are guaranteed by high doping levels. In that case, the overall behavior becomes almost independent of the actual work function of the contacts due to easy tunneling injection [3]. The thin depletion layer close to the metal contact in the doped layer produces a negligible potential drop compared to the intrinsic parts of the electronic devices. Thus ohmic contacts between doped transport layers and metals can be implemented in our model simply by assuming identical numbers of free carriers and dopants [91] in the monolayer next to the contact. More precisely, for the case of n-doping, we suppose as the boundary condition for free carriers at the cathode

$$n = \frac{1}{2} \left[ (N_D^+ - N_A^-) + \sqrt{(N_D^+ - N_A^-)^2 + 4n_i^2} \right]$$

and

$$p = \frac{n_i^2}{n},$$

where $N_A$ and $N_D$ are the concentration of dopants, $n$ and $p$ denote the concentration of free carriers at the interfaces of the organic material and $n_i$ is the intrinsic concentration which is negligible in wide gap materials $n_i < 10^{10}$ cm$^{-3}$ [73] compared to typical dopant concentrations of $10^{16}$-10$^{19}$ cm$^{-3}$. The equations for the p-doped layer next to the anode read similarly, with $N_D$ and $N_A$ being exchanged. Thus, the concentration next to the particular electrodes can be approximated as $n=N_A$, $p=0$ for the anode and $p=N_D$, $n=0$ for the cathode.

### 2.3.2. Internal interface between two adjacent organic materials

In multilayer device structures, one of the important factors influencing current flow is the transition across interfaces of organic materials with different molecular energy levels and charge carrier mobilities. For OLEDs, these internal barriers are an additional obstacle for the injected carriers to reach the recombination zone [8,9,116]. In case of photovoltaic heterojunction devices, high energetic barriers ensure that the positive current is determined by recombination processes [7,37,117], whereas the design is such that the negative photocurrent is not hindered by any barriers. Discontinuities of both the molecular energy levels and of charge carrier mobility can result in charge accumulation and thus redistribution of the electric field.
**Crossing of internal interfaces by free charge carriers**

Free carriers can overcome energetic barriers due to thermally assisted hopping. The height of such barriers ($\Delta E_p$, $\Delta E_n$) is given by the difference between the HOMO levels for holes or LUMO levels for electrons, respectively, which may be modified by electric fields as illustrated in Figure 2.13. Here, we assume for simplicity that no dipole layers are formed at organic heterointerfaces, i.e. particular surface states or charge-transfer complex formation are not considered. The assumption that interface reactions do not occur for most relevant material combinations is confirmed by UPS/XPS investigations on organic/organic heterojunctions [118]. It has been shown that the probability that free carriers can cross an energetic barrier takes advantage of an extended density of states (DOS) with a Gaussian shape equivalent to the energetic bulk disorder proposed by Bässler [82],

$$\Gamma(E) = \frac{N_{\text{HOMO}}}{\sigma \sqrt{2 \cdot \pi}} \exp\left(-\frac{E^2}{2\sigma^2}\right),$$  \hspace{1cm} (2.22)

where $\sigma$ is the energetic width of the DOS, $E$ denotes the energetic distance to the position of the maximum of the DOS and $N_{\text{HOMO}}$ denotes the density of states. However, the transport of free carriers through an interface with an energetic barrier is not the only possible process. Another possibility is that a pair of free carriers recombines directly at the interface. This effect is described in the next section in the context of the creation of charge-transfer (CT) excitons (interface excitons or exciplexes).

The electric field is responsible for a decrease of the effective barrier height to $\Delta E'$, which is proposed to be of the form

$$\Delta E' = \Delta E - e \cdot d_n \cdot F,$$  \hspace{1cm} (2.23)

where $d_n$ is the thickness of a monolayer. Here, $F$ denotes the electric field at the interface. It depends weakly on the chosen discretisation, because $F$ is the average of the electric fields from two adjacent monolayers. However, the choice of monolayer thicknesses close to real size of organic molecules allows this problem to be overcome and well explains the physical behavior not only at interfaces, but also through the whole device.
Interface between two organic materials with the energetic barriers $\Delta E_p$ and $\Delta E_n$ lowered by the electric field $F$ by $\Delta E'_p$ and $\Delta E'_n$). The hopping of electrons (i) and holes (ii) to another organic layer is reduced by the energetic barriers. The flow of electrons and holes in the other direction takes place without limitation. The $d_n$ denotes the thickness of a molecule or monolayer.

To express the probability of energetic barriers being crossed by free carriers, the Miller–Abrahams [109] form is used, in which the rate is activated for hops that increase the carrier energy (uphill, Boltzmann term) and is constant for hops that decrease the carrier energy (downhill, 1). Herein, the occupation of proposed DOS is assumed to be uniform, due to insufficient relaxation of free carriers at the given electric field, as has been proposed by Staudigel at al. [58]. Given these assumptions, the total probability for charge carriers to enter the neighboring DOS is express by the equation

$$G(\Delta E) = a_{DOS} \int_{-\infty}^{\infty} dE \int_{-\infty}^{\infty} dE' T(E') \left\{ \exp \left( -\frac{E' + \Delta E + E}{k_B T} \right), E' + \Delta E \leq E \right\}, \quad (2.24)$$

with $E$ and $E'$ denoting the energetic distance to the maximum of the DOS for materials before and after the interface. The constant $a_{DOS}$ is deduced from the condition $G(0)=1$, when the transport of electrons or holes is not limited by the energetic barrier (second case of Equation 2.24). The current flowing through the internal interfaces are calculated by modification of the usual drift and diffusion terms by $G(\Delta E)$.
The description of the hopping rates between two sites differing in energy according to Miller–Abrahams [109] (see Equation 2.24) neglects polaron effects. Therefore, Holstein and Emin [119] and previously Marcus [120] and Levich [121] proposed an alternative formula where the hopping rate is proportional to

\[ G(\Delta E) = \exp\left(\frac{-\left(\Delta E + E_p\right)}{4k_bTE_p}\right), \]  

(2.25)

where \( E_p \) denotes the polaron binding energy. However, we do not use this formula, due to the introduction of an additional (and frequently unknown) parameter. Moreover, this model does not satisfy the condition of detailed balance, as argued by Ruhstaller [40].

**Crossing of internal interfaces by excitons and interface recombination**

As in the case of free carriers, the diffusion of bulk Frenkel excitons through an organic heterointerface is corrected by a factor \( G(\Delta E) \), given by Equation 2.24. Here, the energetic barrier \( \Delta E \) is assumed to be the difference between the gap energies (energetic distances between the HOMO and the LUMO) on both sides of the interface (Figure 2.14), i.e. \( \Delta E = E_{II} - E_I \). We assume that the exciton binding energy is similar for both materials. It is thus assumed to be irrelevant whether we use the difference between the optical or the electrical gap energies to calculate \( \Delta E \). For diffusion across an interface in a direction with decreasing gap (from left side of interface to right side of interface, \( E_{II} > E_I \)), no limitation is expected, whereas diffusion in the reverse direction is supposed to require thermal activation expressed by a Boltzmann factor \( G_{ex}(\Delta E) = \exp(-\Delta E/(k_bT)) \). Here, excitons are not affected by the electric field and relax into their equilibrium distribution rather rapidly.
Figure 2.14 Diffusion of exciton through an interface between two organic materials for two different case: (i) $E_I > E_{II}$: no limitation for transport of Frenkel excitons through the interface, (ii) energetic barrier $\Delta E = E_I - E_{II}$ where $E_I$ and $E_{II}$ are the exciton energies of the respective materials, estimated from the difference between the respective HOMO and LUMO levels.

The number of bulk Frenkel exciton in the monolayers adjacent to the interface can be increased by transformation of interface CT excitons into Frenkel excitons. The CT excitons (exciplexes) are created from recombination between the free electrons and holes accumulated at both sides of the interface (Figure 2.15). Naturally, the ratio of singlet to triplet excitons (3:1) has to be considered for interface creation as well. Similar to the recombination in the bulk (Section 3.1), the recombination at the interface is assumed to be in agreement with Langevin theory [122,123,124], i.e.

\[ R(x,t) = \gamma_{n-p} n_f(x+1,t) p_f(x,t) \]  \hspace{1cm} (2.26)

with

\[ \gamma_{n-p} = \frac{q\mu_p(F,T,x)\mu_n(F,T,x+1)}{\varepsilon\varepsilon_0} , \]  \hspace{1cm} (2.27)

where $x$ and $x+1$ denote the monolayers in front and behind the interface, respectively, and $\gamma_{n-p}$ is the recombination rate. Thus, due to this recombination at the interface, CT excitons (exciplexes) are created, which can relax to the ground state non-radiatively or they can be transformed into bulk Frenkel excitons. Direct radiative recombination of exciplexes is not included into the simulation, as a red shifted exciplex emission is not found experimentally for the systems to be described in this thesis. The transformation of
an interface CT exciton into a Frenkel exciton requires that one of the carriers crosses the interface barrier.

![Diagram of recombination of a free hole with a free electron waiting at opposite sides of an interface. (i) formation of a bulk Frenkel exciton in organic layer II from an interface CT exciton (ii) formation of a bulk Frenkel exciton in organic layer I and (iii) recombination.](image)

The respective effective barrier heights $\Delta E_n'$ and $\Delta E_p'$ are once again affected by electric fields according to Equation 2.23. The probability for transformation into bulk Frenkel excitons on the left (electron) side or the right (hole) side of the interface is then derived using the factors $G(\Delta E_n')$ and $G(\Delta E_p')$, respectively, calculated from Equation 2.24. To ensure that the correct number of bulk excitons is produced, the generation probability for interface CT excitons has to be multiplied by the factor $1 - G(\Delta E_p') \cdot G(\Delta E_n') / 2$. Otherwise, e.g., in the case of small barriers with $G(\Delta E_p') \approx 1$ and $G(\Delta E_n') \approx 1$, the number of generated bulk excitons would become twice the number of the formed interface excitons.

**Width of DOS and probability of crossing the internal interface**

The probability that free carriers or Frenkel excitons can cross the energetic barriers can be calculated with the above model. The main parameters deciding about the rate are the height of energetic barrier and the width $\sigma$ of the DOS. In disordered molecular materials, $\sigma$ typically lies between 0.07 and 0.13 eV [82]. For the field dependence of the barrier height, also the average thickness of the monolayers, i.e. the
size of the organic molecules plays a role, which is assumed as ~1 nm [73]. In agreement with this, the total density states is set to $10^{21}$ cm$^{-3}$. However, due to the normalization condition $G(0)=1$, the total density of states does not affect the transition probabilities.

\[ \text{Figure 2.16} \quad \text{Probability that free carriers cross an energetic barrier of height } \Delta E \text{ for identical values of DOS width for both organic layers.} \]

To illustrate the different influences on the transition probability $G$, Figure 2.16 shows calculated values of $G$ as a function of $\Delta E$ for different DOS widths between 20 and 200 meV. Making the assumption that the DOS occupation is uniform due to insufficient relaxation of free carriers at the given electric field, the highest transition probability is found for the largest width ($\sigma=200$ meV). For instance, at the barrier height of 0.4 eV, the difference between the case with 20 meV and 200 meV is about six orders of magnitude. For the typical range of 80 to 120 meV, the difference is still above one order of magnitude. The reason for this critical influence of the DOS width is that the transition probability increases together with a reduced energetic distance between the levels with the highest energy in the DOS in front of interface and the lowest level in the DOS to be entered.
Figure 2.17  Probability that free carriers cross an energetic barrier of height $\Delta E$ for different DOS widths for the two organic materials. Widths of 80 meV, 100 meV and 120 meV are considered for the density of state for the organic material in front of energetic barrier, while the width of the DOS to be entered is kept constant.

Figure 2.17 illustrates the transition probability for free carriers when the DOS widths for the two organic materials are not identical. The variation is chosen in the range of typical values from 80 meV to 120 meV, while the DOS behind the energetic barrier remains unchanged (120 meV). The difference between the particular curves in Figure 2.17 is only a factor of about two, while for the above mentioned two identical widths, the probability varies by a factor of ten with $\sigma$ being reduced from 120 meV to 80 meV.
3. Basics of the numerical model for organic multilayer devices

In this chapter, we present a numerical model for the electrical properties for organic light emitting diodes (OLED) and organic photovoltaic cells (OSC). The electrical part is based on solving the one-dimensional continuity equations for holes and electrons. The electric field is obtained from the Poisson equation. The model accounts for drift- and diffusion transport, recombination, trapping and re-emission processes. To show compatibility between our numerical model and theory, we simulate unipolar and bipolar transport in the space charge limited current (SCLC) regime for single organic layers with ohmic contacts. The numerical data are fitted to an analytical equation at different regimes of applied bias with and without traps. Moreover, we show that our model is able to reproduce the time-evolution of space charge limited currents after a bias is applied, which represents a powerful tool to obtain information about the mobility of organic materials.

3.1. Numerical modelling of electrical properties

3.1.1. Introduction

The electrical behaviour of organic light emitting diodes can be predicted by solving a self-consistent numerical model. The model consists of three elements: calculation of the spatial distribution of electric field (Poisson equation), solving the rate equations for charge carriers and solving the rate equation for singlet Frenkel excitons. The introduced numerical model is solved by spatial and temporal discretisation using the appropriate boundary conditions and electrical parameters. The numerical simulation requires as an initial step some contact boundary conditions and an initial spatial distribution of the electric field. The injection of free carriers is specified by a self-regulation mechanism independent of the chosen discretisation, which was proposed by Staudigel [58]. Additionally, if the height of the contact barrier is significant, thermionic injection is introduced into the model (Section 2.3). Due to the use of organic materials with rather wide gap of at least 2 eV, the concentrations of intrinsic carriers are negligible. For undoped systems, we therefore start the simulation with the assumption that there are no existing charges in the whole multilayer diode. Therefore, a uniform distribution of electric field is received from the applied bias, the built-in potential and the organic multilayer thickness. During the time of simulation, the free carriers, which were injected from anode and cathode can move, be trapped, or recombine with each other in the organic materials following terms included in the rate equation. Simultaneously, the rate
equation is solved for the singlet excitons, which are created, diffuse, decay, or may be quenched at electrodes or by free carriers. The luminescence of OLED can then be obtained from the radiative part of the decay. The solution of the numerical model is found when a steady state is reached, as indicated by a constant value of current density. The simulation provides a detailed look into the distribution of electric field and concentration of free and trapped carriers at a particular applied voltage.

### 3.1.2. Self-consistent calculation of charge transport and electric field distribution

The derivative of the electric field $F$ inside the organic diode is proportional to the density of free $p_f, n_f$ and trapped $p_t, n_t$ charge carriers, according to the Poisson equation

$$\frac{\partial F}{\partial x} = \frac{q}{\varepsilon \varepsilon_0} \left( p_f(x,t) + p_t(x,t) - n_f(x,t) - n_t(x,t) - N_A(x) + N_D(x) \right),$$  \hspace{1cm} (3.1)

where the constant parameters denote the elementary charge $q$, the relative permittivity of the vacuum $\varepsilon_0$ and the material $\varepsilon$, which typically takes a value around 3 for small molecular systems [73]. $N_A$ and $N_D$ denote the densities of ionised acceptors and donors, respectively. The electric field distribution is obtained through integration of the Poisson equation across the layers of total thickness $L$ using the effective bias

$$V_{\text{eff}} = (V - V_{\text{bi}}) = \int_0^L F(x) \, dx.$$  \hspace{1cm} (3.2)

Herein, neglecting energy level shifts due to interface dipoles, the built-in voltage equals the contact-potential difference of the two electrode materials. For p-i-n type devices with highly doped charge transport layers and thus quasi-ohmic contacts, the built-in potential is determined by the work-function difference between the two doped transport layers.

The variation of free charge carrier density in organic multilayer diodes is described by the time dependent continuity equation. The drift-diffusion current $J$, direct and indirect recombination rate $R$, and trapping rate $T$ determine the rate of change inside each monolayer. Taking into account the sign and direction of movement of free carriers in the electric field, Equation 3.3 is adequate to describe the case of holes and electrons. For electrons, the continuity equation reads
\[ \frac{\partial n_f(x,t)}{\partial t} = \frac{1}{q} \frac{\partial J_{nf}(x,t)}{\partial x} - R_{nf-pf}(x,t) - R_{nf-pt}(x,t) - T_{nf}(x,t). \]  

(3.3)

Here, \( R_{nf-pf} \) denotes the recombination rate between free electrons and free holes while \( R_{nf-pt} \) refers to recombination between free electrons and trapped holes. The changes resulting from the drift and diffusion of holes and electrons are included in first part of Equation 3.3. The current density is determined by a drift term, a diffusion term and a displacement term, which must be only considered as long as the steady state is not reached. For the equilibrium case, the steady state current can therefore be describe by

\[ J_{nf}(x,t) = q\mu_n(F,T)\left( n_f(x,t)F(x,t) + \frac{kT}{q} \frac{\partial n_f(x,t)}{\partial x} \right), \]  

(3.4)

where \( k \) is the Boltzmann constant and \( \mu \) the mobility of carriers in the organic material.

The mobilities are taken to be dependent on the field \( F \) with the Poole–Frenkel-type form

\[ \mu_n(E,T) = \mu_0(T)\exp(-\beta_{PF}\sqrt{F(x,t)}), \]  

(3.5)

where the factor \( \mu_0 \) describes the value of mobility without electric field and \( \beta_{PF} \) defines its field dependence. In organic media, transport phenomena are commonly presented as a hopping process, which occurs randomly. However, statistics allow using average parameters such as charge carrier mobilities [82] for a huge number of hopping processes.

### 3.1.3. Influence of traps and recombination of carrier pairs

The trap states assumed in our model can have various origins, for instance, structural disorders or impurities [48]. The traps are considered as discrete levels for electrons and holes with an energetic position within the forbidden gap. The trapping rate \( T_{nf} \) for electrons is given by

\[ T_{nf}(x,t) = v(x,t)\sigma \left[ n_f(x,t)(N_{nv}(x,t)-n_i(x,t))-n_i(x,t)(N_{LUMO}-n_f(x,t))\exp\left(\frac{-E_{nc}(x,t)}{k_BT}\right)\right], \]  

(3.6)
where $N_t$ is the density of electron traps, $N_{LUMO}$ is the density of states at the energy of the lowest unoccupied molecular orbital (LUMO), $\nu$ is the velocity of mobile carriers and $\sigma_t$ is the cross section for electron capture which is estimated from the geometric area occupied by a single molecule [58]. The rate for electron capture by traps is determined by the density of unoccupied electron traps ($N_t(x,t) - n_f(x,t)$) and the density $n_f$ of free electrons, while the detrapping rate is thermally activated with the trap depth $E_{nt}$ as an activation energy and is related to the density of free states in the LUMO ($N_{LUMO} - n_f(x,t)$) and the density of trapped carriers $n_t$. The rate equation for hole trapping reads similarly to Equation 3.6 using the respective quantities for holes $p_t$, $p_f$, $N_{HOMO}$, $N_p$ and $E_{tp}$. The uncharged, empty trap states are non-degenerated. The influence of shallow traps on the transport is included in the value of mobility for electrons or holes.

The other effects that affect the number of free and trapped carriers are direct and indirect recombination due to attractive Coulombic interaction. The recombination rate is determined by both electron $n$ and hole $p$ concentration multiplied by the recombination coefficient $\gamma$:

$$R_{nf\rightarrow pf\;or\;pn\rightarrow pt}(x,t) = \gamma \cdot n_f(x,t)p_f(x,t)$$

(3.7)

with

$$\gamma_{nf\rightarrow pf} = \frac{q \cdot (\mu_p(F,T) + \mu_n(F,T))}{\varepsilon \varepsilon_0}$$

(3.8)

and

$$\gamma_{nf\rightarrow pt} = \frac{q \mu_n(F,T)}{\varepsilon \varepsilon_0}$$

(3.9)

where $\gamma$ is assumed in accordance with Langevin theory [122,127], (Equation 3.8 and 3.9).

3.1.4. Organic heterointerfaces

The recombination is also included in processes describing the interface between two adjacent organic materials. Here, the recombination of the accumulated free carriers at both sides of the interface is described by Equations 2.26 and 2.27. Alternatively, the free carriers can overcome the energetic barrier due to thermally assisted hopping. The height of such a barrier $\Delta E$ is given as the difference between the energetic levels HOMOs for holes and LUMOs for electrons reduced by the electric field. The probability of barrier crossing by free carriers is calculated assuming a density of states (DOS) with Gaussian shape (Section 2.3.2).
3.1.5. Numerical routines

The introduced numerical problem is solved by spatial and temporal discretisation using appropriate boundary conditions. The multilayer system is described as a stack of discrete layers with thickness close to the typical size of molecules. We will choose an approach which partly reflects the discrete nature of amorphous molecular organic thin films, since the diameters of commonly used organic molecules are only between one and two orders of magnitude smaller than actual layer thickness. The set of Equations from 3.3 to 3.9 is solved iteratively, assuring that the time step is smaller than the fastest transit time across a cell in the device at any given iteration step. The system is considered to be in equilibrium and the iteration is terminated when the average local deviation is a small fraction, typically $10^{-4}$, of the total current.

A simple discretisation in time is given by $x' = x + f(x,y)\cdot dt$ where $y$ represents a set of extrinsic parameters, which influence the system behaviour. Variables $x$ and $x'$ denote the variables of state of concern in all monolayers before and after the time step $dt$. However, this simple approach forces unacceptable small time steps because of an under- or overestimation of the actual change during the time step. This is due to the fact that the transformation of $f(x,y)$ in $f(x',y)$ during the time step is neglected. This effect can be compensated in first order approximation by an iterative calculation of the time steps, with an iteration given by [65], $x'_{n+1} = x + 0.5[f(x,y) + f(x'_n,y)]dt$. The iteration starts at $x_0 = x$, and for practical calculations the iteration can be stopped at $n = 3$. The value of $dt$ is adjusted after each time step in a way that the expected maximum relative change during the next time step in any of the variables of state remains small. The value of the time step thus depends on the velocities of changes in the variables of state and has to be determined for the fastest process (variable of state). When this condition is not met, the system does not reach convergence. Sometimes, a long calculation time can be the result of differences between the relaxation times of the various processes.

As an example, we present the fluctuation of current versus time for p-i-n solar cell (see Figure 3.1). The steady state current for this structure is reached after $10^{-4}$ s. After this time, the current is only determined by diffusion and drift terms while the displacement current converges to zero. Thus, the electric field distribution and the number of free and trapped carriers are constant in time. However, this time dependence from Figure 3.1 does not correspond to any observable process, but reflects the transition from an artificial initial charge carrier distribution to a realistic steady state of the system.
Figure 3.1  Evolution of short circuit current in time for p-i-n solar cell from Section 5.3.1 under constant illumination
3.2. Numerical simulation of space charge limited currents

3.2.1. Introduction

Space charge limiting currents (SCLC) in an organic layer can occur if at least one contact is able to inject higher carrier densities than the bulk material has in thermal equilibrium and if the injected charges are not too rapidly shielded by equilibrium carriers. The equilibrium concentration of charge carriers in insulators is very small because of the dependence of carrier density on the band gap $E_g$. With an energy gap of 4 eV, the fraction of electrons excited across the gap at room temperature is of the order $10^{-35}$ for an intrinsic semiconductor. Since the charge carriers cannot be thermally generated, the current through the insulator can be determined by the concentration of charge carriers injected from the contacts. These are transported in the applied field towards the counter electrode.

Due to the disorder, charge carrier transport in organic materials is described by hopping between sites with different energy and distance. Additionally, carriers can be intermittently trapped in gap states originating from impurities or structural disorder. These results in low effective carrier mobilities, which are typically between $10^{-3}$ and $10^{-8}$ cm$^2$/V at room temperature. In many cases, they depend strongly on temperature and the magnitude of the applied electric field [95,172]. With low carrier mobilities and negligible free carrier concentration, even in the presence of non-vanishing injection barriers, the metal organic contacts are able to inject carriers faster than the organic bulk material can carry away. This will then lead to the formation of a space charge, which reduces the electric field at the injecting contact and thus impedes further charge carrier injection. The problem of SCLC in insulators has been treated by Lampert and Mark [125]. Therefore, we will list only the main basic equations and compare these analytical approaches with the numerical simulation described in Section 3.2.

3.2.2. Space charge limited unipolar currents

Our considerations begins with the discussion of the current-voltage characteristics for the simplest possible situation, namely the perfect insulator with two symmetric, ohmic contacts, free of traps, without additional dopants and with negligible number of free carriers in thermal equilibrium. In this case, all injected electrons remain free and contribute to the formation of space charge. The quantitative description of carrier transport through an insulator is obtained using the Mott and Gurney formula [175]
where \( L \) is the cathode-anode spacing and \( \varepsilon \) is the permittivity of the material. Equation 3.10 is useful for both low and high applied bias \( V \), but for high voltages one has to take into account a possible field dependence of the mobility.

The analytical Equation 3.10 is reproduced by the numerical model when only free carrier drift is implemented. The diffusion process is neglected. In our simulation, we used as a model structure an organic insulator with thickness 50, 100 and 200 nm, respectively. The permittivity of the organic layer is assumed to be 3, which is in the range of typical values for organic materials [73]. The zero field hole mobility is assumed to be \( \mu_p=10^6 \text{cm}^2/(\text{V} \cdot \text{s}) \) and the field dependence is characterized by the constant \( C=2 \times 10^{-3} \text{(cm/V)^0.5} \), which allows us to calculate the field-dependent mobility in accordance with Equation 3.5 (a value close to realistic mobilities of Alq3 [58,95,145]). Using the self-regulation mechanism from reference [58], an ohmic contact needed to simulate the SCLC is obtained. These electrical parameters will be used for all numerical calculations concerning unipolar currents for single organic layers.

![Simulated current density versus voltage curves for two different thickness of organic layer 50 (triangular dots) and 100 (circular dots) nm, respectively, with (closed dots) field-dependent mobility and with constant mobility (open dots). Curves with square dots are obtained from the analytical Equation 3.10.](image)

\[
J = \frac{9}{8} \varepsilon \mu \frac{V^2}{L^3},
\]  

(3.10)
In Figure 3.2, the current is plotted as a function of applied bias for two samples with different thickness. For the case of field independent mobility, the current is proportional to the square of applied bias and fits very well to Equation 3.10. The discrepancy between the numerical calculation and the analytical equation for field-dependent mobilities occurs due to the use of an averaged electric field in the analytical calculations. Similar results are presented in Figure 3.3, which illustrates the current density versus total sample thickness. Here, a perfect fit is obtained for the calculation with the mobility independent of electric field and small discrepancies occur for the field-dependent mobility, similar to the results shown in Figure 3.2.

Although a perfect organic insulator is not a realistic object, the result of Equation 3.10 is still quite useful, since it is the limiting form of the current–voltage characteristics for real organic materials when the applied voltages are high enough for the total number of injected holes to exceed substantially the total number of initially empty traps in the material.

The presence of hole traps in the organic layer will generally result in a greatly reduced current at lower injection levels, since those initially empty traps will capture and thereby immobilize most of the free carriers. The following equation describes the case of shallow-traps and is identical to the Mott-Gurney solution, except for the addition of the trapping factor $\theta$. 

Figure 3.3 Current density versus total thickness of organic layers obtained from the numerical simulation (open dots) and equation (closed dots) at applied bias of 7 V. Triangular dots present a calculation with field-dependent mobility and circular ones without.
\[ J = \frac{9}{8} \varepsilon \mu \cdot \frac{V^2}{L} \cdot \Theta . \] (3.11)

Here, hole traps at \( E_{tp} \) are called shallow if the quasi Fermi level for holes \( E_{QF, h} \) lies well above \( E_{tp} \) throughout the device. The predicted trapping factor found by the familiar Fermi-Dirac formula assuming discrete trap levels reflects the ratio between free and trapped carriers as

\[ \Theta = \frac{N_{Homo}}{N_{tp}} \exp \left( -\frac{E_{tp}}{kT} \right) = \frac{n_{pf}}{n_{pt}} , \] (3.12)

where \( N_{Homo} \) is the density of states for the highest occupied molecular orbital, \( N_{tp} \) describes the total density of traps uniformly distributed in the material, and \( E_{pt} \) is a positive quantity that expresses the trap depth with respect to the transport band.

As the current flow grows with applied bias, the quasi-Fermi level moves closer to the valence band and may eventually cross the energy level of the trap at \( E_{tp} \). At this point, the traps will become essentially filled and further injected free carriers cannot be trapped.

The equilibrium trap occupancy results from a balance between capture of holes into the traps and their thermal re-emission into the transport states. As long as the applied electric field is not high enough to substantially heat up the free holes, the presence of the electric field will not affect the elementary microscopic processes of hole capture and thermal re-emission. Thus, the balance between free and trapped electrons is altered only through the change in injected free-hole density. This effect is reached in the simulation by implementation of the statistical equations described in Section 3.1, where the capture and re-emission processes depend on thermal and drift velocity. Thus, in the whole range of applied voltage, three regions can be distinguished: (i) square law in the presence of shallow trapping, (ii) trap-filled limit and (iii) trap-free square law for deep energetic trap level \( E_{tp} \) with occupation of all traps states, see Figure 3.4. The first and last intervals can be calculated from Equations 3.11 and 3.10, respectively, for shallow (circles) and deep (triangular dots) trap states. Nevertheless, the analytical calculation can only offer a limit for the current, which corresponds to the value of trapping factor \( \Theta \) calculated from Equation 3.12 by conditions (\( \Theta<1 \) and \( \Theta=1 \)). The numerical simulation is able to reproduce the current for a whole range of voltages (square dots), where the current density is limited by the different occupation of trap states as a result of injection of different amounts of free carriers (Equation 3.6). For numerical and analytical calculation,
one level of traps with energetic depth equal to 0.4 eV at a concentration of $5 \times 10^{17} \text{ cm}^{-3}$ has been assumed.

\[ \text{Figure 3.4} \quad \text{Current density versus applied bias including a discrete level of trap states for holes. Three ranges can be distinguished: (ii) square law in the presence of shallow trapping, (iii) trap-filled limit, (iv) trap-free square law when all traps states are occupied. Lines with circles and triangles are calculated from the analytical Equations 3.10 and 3.11, respectively.} \]

The characteristic range of voltage where the current abruptly increases is called the trap-filled limit, and $V_{TFL}$ is the characteristic voltage to reach trap filling (Figure 3.4). The position of this crossover for discrete levels of traps at energy $E_{pt}$ is roughly estimated from the formula

\[ V_{TFL} = \frac{Q_{TFL}}{C} = \frac{qN_{pt}L}{C} = \frac{qN_{pt}L^2}{2\varepsilon}, \quad (3.13) \]

assuming a capacitance $C$ per unit area $C = 2\varepsilon/L$, where all trapping states $N_{pt}$ are occupied. The correctness of this assumption can be confirmed by the numerical model with the possibility to observe the distribution of free and trapped charge concentration (Figure 3.5). At $V_{TFL} = 3.7 \text{ V}$, the occupation of a trap state (line with closed dots) is nearly complete and much higher than the number of free carriers (open dots).
Figure 3.5  Distribution of free and trapped carriers at external bias equaled 3.7 V (Trap-Filled limit).

For a system with only one discrete trap level, it is possible to determine the concentration of traps $N_{pt}$ at the energetic position $E_{pt}$ from the experimental curve using Equation 3.13. If there is more than one discrete trap level, then there will be several sharply rising regions in the current as the quasi Fermi level sweeps through each trap energy.

The next step is the inclusion of thermally generated or doping induced free holes, which influences the current at low voltages and overrides the square law in the presence of shallow traps. Here, it is expected that Ohm's law

$$J = q\rho_0 \mu \frac{V}{L}$$  \hspace{1cm} (3.14)

will be observed. Although we expect at any applied voltage charge injection in the insulator, there cannot be a significant departure from Ohms law until the average density of injected excess free holes becomes comparable with the thermally generated one ($\rho_0=N_A$). If trap states occur, the Equation 3.14 needs to be multiplied by factor $\theta<1$, when the concentration of dopants is below the trap concentration.
A plot of the current-voltage characteristics for ohmic conduction is the curve labelled (i) in Figure 3.6 (line with triangular dots). The square dots in Figure 3.6 represent a numerical simulation including the drift process and a discrete level of traps without doping, while, for the line with circle dots, a density of dopants of $10^{17}$ cm$^{-3}$ is assumed which is five times lower than the trap concentration. Due to the high concentration of injected carriers, the additional dopants do not affect the current at large voltage (iv). However, they shift the position of the trap-filled limit to about 3 V (iii), because a lower number of injected carriers is needed to completely fill the remaining empty trap states. When the density of injected carriers becomes comparable to the density of dopants, the square law (ii) starts to modulate the current component given by Ohm’s law. The density of free and trapped carriers for voltages corresponding to this range of applied bias is shown in Figure 3.7. with and without dopants. As expected, the simulation with dopants (triangular dots) shows a higher density of trapped and free carriers. Almost all thermally activated free carriers are caught by the trap states and their charge is compensated by the ionised dopant molecules and thus does not contribute to the change in electric field (Figure 3.8). Therefore, only the injected free carriers close to the electrode modulate the profile of electric field and space charges hardly hinder further injection. In the absence of additional thermally activated carriers, the trap states capture injected holes, and similarly
shaped profiles of free and trapped carriers are obtained. In this situation, the distribution of the electric field strongly depends on the number of trapped carriers, resulting in a low value of electric field close to the electrode.

Figure 3.7  Distribution of trapped and free carriers in an organic thin film at 0.04 V (in the square law-shallow trap region (i)) with and without dopants.

Figure 3.8  Electric field in an organic thin film at 0.04 V (in the square law shallow trap region (i)): undoped and doped organic layer with dopant density of $10^{17}$ cm$^{-3}$.
The electrical behavior can be reproduced in the simulation and agrees well with the simple analytical equation. However, to fit our numerical calculation to real data, other electrical processes such as diffusion and field-dependent mobility must be introduced. So far, this second effect has been implemented only for a perfect insulator. The current with and without field-dependent mobilities is presented in Figure 3.9, with implementation of a discrete level of traps. The curve with circular dots corresponds to the simulation with field-dependent mobility from low bias to the trap-filled limit, where the influence is insignificant. The discrepancy starts to be considerable for voltages higher than 10 V. The triangular dots calculated by Equation 3.10 (as in Figure 3.2) have somewhat lower values, since the average field is used for the field-dependent mobility in the analytical calculation. The spatial distribution of injected carriers at 70 V applied voltage is presented in Figure 3.10. Due to the high injection rate of free carriers, all trap states are occupied and the Fermi level is between the trap level $E_{tp}$ and the conduction band $E_{LUMO}$. The predominantly free carriers modulate the profile of electric field in organic materials (see Figure 3.11). A decreasing concentration of carriers in the whole sample is found for a field-dependent mobility. The carriers leave the organic layer more quickly and do not limit the injection of free carries by reducing the local electric field close to the injecting contact. Thus, the distribution of the electric field at the same applied voltage is more uniform for the case of field-dependent mobility.

Figure 3.9  Current density vs applied bias with discrete level of trap states for holes and hole mobility being either field-dependent (circles) or field independent (squares). The three ranges are the same as in Figure 3.4. The curve with triangular dots is calculated from the analytical Equation 3.10 including the field-dependent mobility.
Figure 3.10 Spatial distribution of the charges in the organic layer at 70 V applied bias (square law region (iv)). The lines with closed dots show that the traps states are fully occupied. The concentration of free carriers injected from the electrode for field-dependent and field-independent mobility determines the electric field distribution (Figure 3.11).

Figure 3.11 Electric field versus position in the organic layer for two cases: mobility dependent and independent of electric field at 70 V (square Law region (iv)).
Figure 3.12  Current density versus voltage with implementation of one discrete level of shallow traps, accounting for drift and diffusion motion of charges (closed dots) and accounting for drift only (line with open dots).

Figure 3.13  Spatial distributions of free (open dots) and trapped (close dots) charges in the organic layer at 0.02 V (square law-shallow trap region (ii)): Simulations accounting for either drift only or both drift and diffusion of charge carriers in the organic layer are shown with square and circle dots, respectively.

The inclusion of the diffusion term into the analytical calculation is very difficult. Only for the case of a perfect insulator without traps and thermal free carriers, it is analytically
solvable. Here, we propose a numerical model which allows us to include diffusion and compare to results without it (see Figure 3.12).

This thermal motion has a strong influence on the current-voltage characteristics at low electric fields (i) due to the fact that diffusion of free carriers makes the distribution of trapped and free carriers more smooth (close to logarithmic) than without diffusion (Figure 3.13). The shapes of free and trapped carrier concentrations are obviously caused by the boundary conditions: We suggest that the charge carriers are only able to overcome the image potential in the presence of an electric field. Thus, the diffusion of charge carriers from the right electrode into the organic bulk material is not significant [42]. The same assumption is made for the left electrode; here, however, drift injection occurs. Diffusion significantly increases the current for low applied bias by providing a logarithmic distribution of free and trapped carriers with high concentrations close to the injecting electrode.

3.2.3. Transient unipolar space charge limited currents

The numerical simulation also gives the possibility of modeling the quasi one-dimensional flow of space charge limited current versus time after switching the voltage from zero to a constant value. The analytical fitting to the measured characteristics was first used by Many, Helfrich and Mark [170,171] to determine the free-carrier drift mobility in low-mobility molecular crystals. For simplicity, it is assumed that the RC-time of the outer circuit is negligible as compared to the transit time in the organic material. The mobility is then obtain from the formula [170,171]

$$\mu = \frac{0.786L^2}{t_1V}, \quad (3.15)$$

where $t_1$ is the time at which a current peak occurs, and other symbols have the same definition as given in the above text. The current flowing through the organic material is determined by drift-diffusion movement and a displacement current proportional to the change of electric field in time. This second effect vanishes in the equilibrium case as a result of the constant distribution of the electric field. Figure 3.14 shows the space charge limited current against time with the dashed curve including the effect of trapping of injected carriers. The solid curve does not include this effect. Additionally, the diffusion term is implemented for the case without traps. Current begins to flow at constant voltage. The main features of the transient current for the case of drift movement are the monotonic rise to the maximum current occurring after a time interval $t_1$ and an overshoot.
of the steady-state current. The initial current equals about half of the steady-state current and, after the decay with a slight undershoot, the steady-state current is reached after approximately $3t_1$. An important theoretical result is that the current overshoot persists in the presence of trapping, provided that the trapping is not too fast. Furthermore, the peak in the current occurs at the same time $t_1$. Likewise, the initial current density is independent of the trapping time. The diffusion process accelerates the movement of free holes and influences the value of the current at low voltage, but the peak position occurs at the same time as before. Calculation of the mobility from the position of the peak (Equation 3.15) gives the mobility value $1.034 \times 10^{-6}$ cm$^2$/V·s, which fits very well with the assumed value used in the numerical calculation $10^{-6}$ cm$^2$/V·s. This method can be useful for investigation of the properties of organic materials [58, 172, 174], where mobility values are input parameters for calculations of multilayer structures such as organic light emitting diodes and solar cells.

![Figure 3.14](image.png)

**Figure 3.14** Transient Space-charge-limited current with time normalized to $t_0 = 0.786L^2/\mu V$: Simulation accounting for drift only in presence of trap states (dashed line), and without traps (solid line) and simulation accounting for both drift and diffusion without traps (dash-dotted line).

### 3.2.4. Space charge limited bipolar currents

The situation becomes more complicated with double carrier injection due to the recombination effect. It is assumed to be a bimolecular process following the Langevin theory based on diffusive motion of positive and negative carriers in the attractive mutual
Coulomb field, according to Equation 3.7. Therefore, an analytical solution for the electron, hole and recombination currents as a function of voltage are only possible under simplifying assumption of field-independent mobility and in absence of diffusion and trapping [123,125]. To find a solution including all effects, the problem is solved numerically for special electrical parameters characterizing the organic layer. Because of the injection of two-types of charge, the current is higher than for single injection and it is proportional to the direct recombination.

\[
\begin{align*}
\text{position from electrode (nm)} & \quad 0 & \quad 10 & \quad 20 & \quad 30 & \quad 40 & \quad 50 \\
\text{electric field (V/cm)} & \quad 0.0 & \quad 3.0 \times 10^5 & \quad 6.0 \times 10^5 & \quad 9.0 \times 10^5 & \quad 1.2 \times 10^6 & \quad 1.5 \times 10^6 \\
\text{Applied bias } V=4 \text{ V} & \quad \square & \quad \bigcirc & \quad \triangle & \quad \bigtriangleup \\
\mu_n=10^{-6} \text{ cm}^2/(V\text{s}) & \quad \square & \quad \bigcirc & \quad \triangle & \quad \bigtriangleup \\
\mu_n=10^{-7} \text{ cm}^2/(V\text{s}) & \quad \square & \quad \bigcirc & \quad \triangle & \quad \bigtriangleup \\
\mu_n=10^{-8} \text{ cm}^2/(V\text{s}) & \quad \square & \quad \bigcirc & \quad \triangle & \quad \bigtriangleup 
\end{align*}
\]

Figure 3.15 Spatial distribution of electric field for bipolar charge injection into a 50 nm thick organic layer. Three cases are considered at constant mobility of holes: (i) \( \mu_n=10^{-6} \text{ cm}^2/(V\text{s}) \), (ii) \( \mu_n=10^{-7} \text{ cm}^2/(V\text{s}) \) and (iii) \( \mu_n=10^{-8} \text{ cm}^2/(V\text{s}) \).

If trapping states are implemented in the calculation, consideration of two paths of recombination is needed: (a) direct recombination between free carriers and (b) indirect recombination between free and trapped charges. Thus, at steady state, the current density might be equal to the recombination processes. This assumption is more appropriate for low applied bias; with increase of electric field, carriers have a larger probability to reach the opposite electrodes. However, due to the high concentration of free carriers, the recombination is still the dominant path of current flow. The profile of the recombination rate inside the organic layer strongly depends on the spatial distribution of free and trapped carriers, which will be contingent on the ratio of carrier mobilities.
Figure 3.16  Spatial profile of the recombination rate, including direct and indirect paths in a 50 nm thick organic layer. Three different electron mobilities are considered for a constant mobility of holes.

For instance, for pure organic layers of Alq₃, the electron mobility was measured to be two magnitudes higher than for holes [58]. On the other hand, one has to consider the situation where holes and electrons have similar mobilities, found, e.g., for blend layers of C₆₀ and ZnPc used in organic solar cells. To show the behavior for different mobilities, a set of numerical simulations has been prepared with a constant value of hole mobility, a constant density, $5 \times 10^{17}$ cm⁻³, of hole traps of depth 0.4eV and different values of electron mobility. The diffusion process and a built-in potential of 1V are implemented as well. In Figure 3.15, the distribution of electric field at 4 V is considered for three cases: (i) $\mu_n = 10^{-6}$ cm²/(V·s), (ii) $\mu_n = 10^{-7}$ cm²/(V·s) and (iii) $\mu_n = 10^{-8}$ cm²/(V·s). For all cases, the electric field vanishes close to the electrodes due to space charges. It is symmetrical for equal values of mobilities for holes and electrons, because of negligible trap concentrations compared to free carrier densities. For lower electron mobilities, an accumulation of negative charges is created close to the electron injecting electrode leading to a higher recombination rate with mobile holes close to the cathode (Figure 3.16, circular and triangular dots).
The recombination profile in the case of identical mobilities is not symmetrical as it is the case for the electric field due to indirect recombination of electrons with the non-uniformly distributed trapped holes. This recombination profile is also modified with a change of applied voltage: for low voltage, the recombination occurs in the center of the organic layer, with increasing applied bias, the maximum shifts closer to the electrodes (Figure 3.16 square dots). The current-voltage characteristics are presented in Figure 3.17 for the set of simulations mentioned above. The factor of two increase of current is a result of field-dependent mobility and the bipolar current is given as the sum of the recombination current and the leakage of free carriers to the electrode. Moreover, in case of double injection, the trap-filled limit vanishes as the steady state carrier densities are generally lower due to recombination. Finally, we note that the simulations confirm that a large enhancement of current by bipolar injection is only observed if both mobilities are similar, resulting in a wide recombination profile (see Figure 3.16).
4. Organic light emitting diodes

In this chapter, we present simulations for organic light emitting diodes (OLED). The electrical part of the simulation is based on solving the one-dimensional continuity equation for the rates of holes and electrons, described in the Section 3.1. Here, the description of the model is focused on the exciton dynamics and the calculation of luminance. In the next sections, we present the results of numerical calculations. First, we compare simulations of OLED consisting of two- or three-layer with experimental data showing the advantages of more complex structures. The set of numerical simulations has been made for doped and undoped HTL to prove that the implementation of controlling doping of the transport layers can significantly improve the device performance. Also, the simulation results can be adapted to experimental data when the transport layers have different thickness. A successful method to improve the performance of OLED can be the introduction of emissive dopants to the emitting layer. The advantage of fluorescent molecules is presented by comparison of experimental and simulated results in the last part this chapter.

4.1. Numerical model of organic light emitting diodes

4.1.1. Introduction

Several theoretical models for OLED have been proposed in the past, each starting from different assumptions to simplify the complex interplay of mechanisms involved. Due to the large variety of known OLED structures, suitable materials, and mechanisms governing their behaviour, various models were developed to explain the experimental findings [39-60]. The proposed models comprise injection limited current flow [43,44,52], the transition from injection to bulk limitation [39-42,45] and purely space charge limited current (SCLC) flow, [47-50,58] either in monolayers [43,48,49,50,52] or multilayer [40,44-47,58] devices.

The present work comprises the numerical modelling of multilayer vapour-deposited OLED based on small molecules. For this purpose, we chose a numerical rather than an analytical model for an adequate implementation of the discrete nature of the amorphous molecular organic solids. The free carriers are injected into the organic material where they are transported in the applied field towards the counter electrode.

4.1.2. Exciton generation, diffusion and recombination

Excitons are supposed to be Frenkel excitons rather than charge-transfer excitons or Mott–Wannier excitons, which mean that they are spatially limited to one excited molecule. In absence of phosphorescent emitters, we take into account only singlet
excitons, as triplet excitons due not contribute to the light emission, but rather decay radiationless. In rate Equation 4.1, effects such as singlet exciton creation, diffusion, decay, quenching at electrodes $R_{q-el}$, and recombination with free carriers $R_{s-nf}$, $R_{s-pf}$ and trapped carriers $R_{s-nt}$, $R_{s-pt}$ are included.

$$\frac{\delta s(x,t)}{\delta t} = \frac{1}{4} (R_{s-pf} + R_{s-pf}) + D_s \frac{\delta s(x,t)}{\delta x} - \frac{s(x,t)}{\tau_s} - R_{s-pf} - R_{s-nf} - R_{s-pf} - R_{s-nt} - R_{q-el} \quad (4.1)$$

Exciton and therefore excitation energy transport is supposed to occur only due to exciton hopping processes to nearest neighbour molecules, where the diffusion constant $D_s$ can be derived from the average number of hopping processes during the lifetime $\tau_s$. The migration process of singlet excitons can be explained by a Förster type interaction [128]. The pre-factor $1/4$ accounts for the singlet/triplet spin statistics and is a first order approximation [18]. The singlet excitons have also the possibility to be quenched by free and trapped carriers [129], as described by the expression

$$R_{s-nf} = (v_s + v_n) \delta_q s(x,t)n_f(x,t) \quad (4.2)$$

with $v_s$ as the velocity of excitons, $v_n$ as the velocity of free carriers, and $\delta_q$ as the reaction cross section. For quenching of excitons by trapped carriers, the carrier velocity vanishes in the formula. Moreover, excitons can decay at electrodes due to the diffusion of electrode material into the organic layer (Equation 4.3), which considerably reduces the photoluminescence yield. As proposed by Staudigel [58], this phenomenon is described by

$$R_{q-el} = \exp \left( -\frac{z}{L_q} \right) + \exp \left( -\frac{L - z}{L_q} \right) \frac{s(x,t)}{\tau_q} \quad (4.3)$$

with $L_q$ denoting the length of the interdiffusion zone of the electrode material, $t_q$ representing a reduced lifetime proposed to be about one order of magnitude shorter than the actual lifetime in the bulk, and $z$ denoting the position of the monolayer. The quenching of excitons close to the electrode can also be implemented by a special boundary condition for diffusion. Here, it is assumed that all neutral pairs can diffuse to the electrode and are immediately quenched. This assumption is in agreement with experimental findings, for instance in Alq$_3$ [132].
Similar to the case of free carriers, the rate equation for exciton diffusion is changed at organic heterointerfaces. The energetic barrier for interface crossing by singlet excitons is assumed to be the difference between the energetic distances between the HOMO and the LUMO on both sides of the interface. For diffusion across an interface in a direction with decreasing energetic distance between HOMO and LUMO, no limitation is expected, whereas diffusion in reverse direction is supposed to occur similarly to the charge carrier interface barrier crossing, i.e., the probability is given according to Equation 2.24. The other possible effect, namely the formation of exciplexes, is described in Section 2.3.2.

4.1.3. Optical modelling of emission intensity

The number of photons internally generated per area and time in an OLED is given as an integral over the total device thickness

\[
S = \eta_{\text{bulk}} \int_0^L \frac{s(x)}{\tau_s} \, dx
\]

(4.4)

with \( \eta_{\text{bulk}} \) denoting the quantum efficiency of singlet exciton radiative decay in the solid state.

To obtain the external emission, several loss mechanisms have to be considered, such as waveguiding and absorption. For the waveguiding losses in the glass substrate, we assume the photons to be isotropically emitted from the functional layers into the glass substrate, thus a Lambertian emission characteristic inside the substrate can be expected [131]. The losses due to waveguiding in the glass substrate can then be easily estimated under the assumption of a totally reflecting cathode, the absence of absorption and microcavity effects in the functional layers, and a diode area diameter much larger than the substrate thickness. In this case, all forward and backward emitted photons with angles relative to the normal of the substrate surface smaller than the total reflection angle \( \theta_1 \) between substrate and air will leave the interface.

Assuming the material to be homogeneous and having no interface, the internal emission from the recombination zone is isotropic. The ratio between total emitted flux \( \phi_{\text{Int}} \) into the forward half space and the flux \( \phi_{\text{ie}} \) from the interior towards the exterior can be written in the form [133]
where the critical angle \( \theta_i \) imposes a restriction on the emitted rays. Given that \( \sin(\theta_i) = 1/n \), the term \( (1 - \cos(\theta_i)) \) can be approximated as follows

\[
 n_{\text{out}} = (1 - \cos(\theta_i)) = (1 - (\sin 2(\theta_i))) = \left(1 - \left(1 - \frac{1}{n^2}\right)^{\frac{1}{2}}\right) \approx \left(1 - \left(1 - \frac{1}{2n^2}\right)\right) = \frac{1}{2n^2}, \tag{4.6}
\]

with \( n \) denoting the refractive index of the glass substrate.

For a calculation of the conversion factor between the total emission and the emission per solid angle in the forward direction, we follow reference [58], where the factor \( 1/\pi \) in Equation 4.8 results from the transition from lumen (lm, total emission) to candela (cd, emission per solid angle, here in the forward direction) for Lambertian emission.

The optical characteristics of OLED are commonly presented in photometric units. Variables in energetic units can be transformed using the formula [130]

\[
 X_{\text{photo}} = k_m \cdot \int_0^\infty X_{\text{energetic}}(\lambda) \cdot V(\lambda) \cdot d\lambda \tag{4.7}
\]

with the constant for a daylight-adopted human eye \( k_m = 683 \text{ lm/W} \), and \( V(\lambda) \) denoting the relative spectral sensitivity of the human eye. For actual calculations, we assume a monochromatic green OLED with \( V = 0.65 \), so that Equation 4.7 can be modified to yield the luminance [130]

\[
 L = \eta_{\text{out}} \cdot k_m \cdot V \cdot S \cdot h \nu \cdot \frac{1}{\pi}, \tag{4.8}
\]

where \( h \nu \) is the average energy per emitted photon. More information about microcavity effects and outcoupling can be found in references [135-138].
4.2. Simulation for various OLED device architectures

4.2.1. Performance improvement of OLED by implementation of a blocking layer

*Introduction*

The pioneering work in the field of organic light emitting diodes (OLED) has been performed by Tang and VanSlyke [1] who reported a low-voltage, high-efficiency OLED consisting of two organic layers. However, to reach even higher efficiencies, three-layer structures have been proposed and investigated, e.g., by Shirota at. al. [162]. The advantage of the new structure including transport and blocking layers can be confirmed by comparing the experimental results (see [8, 58] or [114]). The new concept implements a layer between the hole transport layer (HTL) and the electron transport or emission layer (ETL or EML). The layer should fulfill two requirements to work properly (i) hole injection from the HTL and hole transport should be efficient and (ii) the difference between its LUMO and the LUMO of the EML should be high enough to efficiently block injection of electrons from the EML into this additional layer. Thus, this interlayer is often called electron blocking layer (EBL). However, this is not the only advantage of the EBL. The additional layer also separates the accumulations of free holes and electrons, thus preventing creation of exciplexes at organic interface. This is crucial since exciplexes mostly decay non-radiatively at interface if interface barriers are too high.

In order to achieve a high efficiency for two- or three-layer OLED, the layers have to fulfill certain requirements. The anode, indium-tin-oxide (ITO) has to easily inject holes into the hole transport layer (HTL). This might be achieved by choosing an organic material the HOMO of which is close to the energetic position of the Fermi level of the anode. The hole transport layer and the blocking layer should efficiently transport holes to the EML and have to efficiently block the electrons from leaving the EML. Moreover, the leakage of holes into the cathode should be avoided by using an EML material with high ratio of electron to hole mobility. The HOMO and LUMO levels of the EML have to allow for hole and electron injection from the neighboring layers. The properties of the electron transport (ETL) layer should be complementary to those of the HTL. The anode should have a high ionization potential to inject holes into the HOMO of the HTL. Accordingly, the cathode should be a low work function metal like magnesium or calcium. Finally, the optical transmission of all organic layers has to be high in the emission wavelength region, and at least one electrode must be at least semi-transparent.
In the simple picture of an OLED given in Figure 4.1, the HOMO and LUMO levels of two- and three-layer devices fulfilling the above mentioned requirement are drawn. By comparison of the experimental data reported by Staudigel [58], and our numerical model described in Sections 3.1 and 4.1, we show the advantage the additional blocking layer.

![Energy levels diagram](image)

**Figure 4.1** Energetic levels of organic materials [163] and ionization potentials of contact materials for two different OLED. For the diode consisting of two layers, the blocking layer (EBL) is replaced by additional 10 nm of the HTL material, thus the 1-NAPHDATA is 50 nm thick.

**Parameters**

The main parameters required as an input for the simulation of charge carrier transport are the mobilities including their dependence on electric field and temperature, the concentration of trap states at certain energy levels, the energy levels for organic layers, and the effective work function of electrode materials in contact with the respective organic material, i.e. the energetic barriers at the contact interfaces. For the simulation, the mobilities for three materials are needed, namely Alq3, NPB and 1-Naphdata. In the simulation, the supposed field-dependent mobility of Alq3 is similar to values found in literatures [58,95,145], see Table 4.2. Moreover, we assume a hole mobility being two orders of magnitude lower than the electron mobility, which is in agreement with the work of Kepler et. al.[145] or Naka et. al.[95]. Since the blocking layer should properly transport the holes to the emissive region and block the electrons, we choose the N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4-diamine (NPB or α-NPD) values, which fulfil the transporting and blocking conditions (Table 4.2). The hole mobility of α-NPD has been investigated by Naka et. al. [95]. Alternatively, we can also choose the values of N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) [58,80], which yields identical OLED
performance. Similarly, the electron mobility is assumed to be two orders of magnitude lower than the hole mobility. The starburst material 1-Naphdata plays the role of a hole transport layer (HTL), thus the predominant transport of holes is governed by the mobility on the order of $10^{-5}$ cm$^2$/V*s [58], about one order of magnitude lower than the hole mobility of TPD. Similarly to the other materials, the electron mobility has been estimated to be two orders of magnitude lower. However, it is obvious from the high barrier for electron injection from Alq$_3$ into NPB or 1-Naphdata that the electron mobility in these materials is basically irrelevant for device performance.

<table>
<thead>
<tr>
<th>Organic material</th>
<th>$\mu_p$ cm$^2$/V*s</th>
<th>$\mu_n$ cm$^2$/V*s</th>
<th>$\beta_{PF}$ (cm/V)$^{0.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-NAPHDATA</td>
<td>1.2$\times$10$^5$</td>
<td>1.2$\times$10$^7$</td>
<td>2.1$\times$10$^{-3}$</td>
</tr>
<tr>
<td>NBP</td>
<td>6.1$\times$10$^4$</td>
<td>6.1$\times$10$^6$</td>
<td>1.5$\times$10$^{-3}$</td>
</tr>
<tr>
<td>Alq$_3$</td>
<td>1.8$\times$10$^8$</td>
<td>1.8$\times$10$^6$</td>
<td>3.1$\times$10$^{-3}$</td>
</tr>
</tbody>
</table>

Table 4.2 Hole and electron mobilities with factor $\beta_{PF}$ describing the field–dependence for particular materials at room temperature.

The particular energy levels are presented in Figure 4.1, where the alignment of the ITO work function (4.8 eV) with the ionization energy of 1-Naphdata (5.1eV) [146] allows us to assume ohmic contact behaviour. The second contact between Alq$_3$ and Al is also known as being efficient for electron injection when a thin layer of LiF is introduced between the Alq$_3$ and the Al contact [159,160]. The energetic levels of NPB which decide about the energetic barriers for the two internal interfaces are assumed in agreement with work of Hosokawa et. al.[148]. The thermally assisted crossing of the energetic barriers by free electrons and holes is calculated by assuming a Gaussian shape of the density of states distribution (DOS) with widths 81 meV and 120 meV [58] at the interfaces between 1-Naphdata/NPB and NPB/Alq$_3$, respectively.

The diameter of the molecules and therefore the spacing between the molecules has been approximated to 1 nm for all materials involved, thus yielding total densities of states $N_{HOMO}$ and $N_{LUMO}$ of 10$^{21}$ cm$^{-3}$.

The diffusion and decay of singlet excitons depend on the lifetime and are proposed to adopt a typical value for amorphous organic singlet emitter materials, 10 ns [73], this value being also valid for Alq$_3$ [144]. The crucial parameter that determines the transport of singlet excitons in Alq$_3$ is the diffusion length, which is found in literature to be 10 nm [144,161]. Also the quenching processes have an influence on the luminescence: The cross section for recombination between singlet excitons and free carriers is supposed to be $\delta_q=10^{-14}$ cm$^2$. The width $L_q$ of the quenching zone at the electrodes, a
parameter of minor importance, was estimated to be 2 nm. The total outcoupling efficiency of the internally emitted photons, considering waveguiding losses and absorption has been estimated to 20% and the quantum efficiency of radiative decay of singlet excitons was set to 30% [150].

The built-in potential, the concentration of trap states and the energetic alignment is chosen as free parameter and is discussed when the fits to experimental curves are presented.

**Results and discussion**

The simulations and the experimental characteristics obtained for two- and three-layer devices are presented in Figure 4.3 (current-voltage) and Figure 4.7 (luminance-voltage). The experimental data have been taken from an investigation of these two structures by Staudigel et. al [58]. The built-in potential, trap densities and trap depths have been adjusted to fit the simulation results to the experimental data. The built-in potential is supposed to equal 2 V. Trap densities for holes in 1-Naphdata, NPB and for electrons in Alq$_3$ of $4 \times 10^{17}$ cm$^{-3}$ with trap depths of 0.25 eV are supposed. Here, the value of 0.25 eV is comparable to reported trap depths derived from thermally stimulated luminescence (TSL) [164]. This amount of discrete shallow traps ($4 \times 10^{17}$ cm$^{-3}$) can be associated with structural defects in the disordered amorphous films or impurities. For holes in the ETL and electrons in the HTL, no trapping was considered, since the mobilities are assumed to be two orders of magnitude smaller anyway. The traps states in transport and blocking layers decrease the current which can be, with the above mentioned assumptions, reproduced over three orders of magnitude, namely in the typical range of applied bias (4-12 V) under operation (see Figure 4.3). Introducing the additional blocking layer does not significantly influence the current, which is not surprising since the mobility of the majority carriers in NPB is one order of magnitude higher than in the transport layers. Additionally, transport of electrons does not take place in this layer due to the high energetic barrier at the interface NPB/Alq$_3$, which similarly occurs in the double layers structure at the interface 1-Naphdata/Alq$_3$. A confirmation can be found in the distribution of free carriers and electric field at applied bias of 10 V. Figure 4.4 and 4.5 show the profiles when steady state is reached for two (Figure 4.4) and three-layer (Figure 4.5) devices. The low concentration of free and trapped charges in NPB layer can witness its very high hole mobility. Also, the low concentration of charge does not significantly affect the electric field, which is constant and high in the NPB layer due to the high injection barrier for holes from 1-Naphdata into NPB.
Figure 4.3  Current-voltage characteristics for two- and three-layer organic light emitting diodes. The simulation results (full dots) are fitted to experimental curves (open dots).

The specific shape of the electric field in the transport layers for both two- and three-layer devices is resulting from space charge limited regimes (free and trapped charges) close to the injecting electrodes. Here, the injection is decreased by the low value of electric field, as discussed in Section 3.2 for unipolar and bipolar current. Moreover, the current strongly depends on the energetic interface barriers, which govern the transport of free holes to the recombination zone and the confinement of electrons in Alq$_3$. Thus, the dominant current path is via recombination of free carriers near and at the internal interface of NPB and Alq$_3$. As shown in Figure 4.5, only a small amount of free holes crosses the Alq$_3$ by diffusion or drift to the cathode while drift of electrons to the anode is hindered by the high heterojunction barrier. Also, leakage through pin-holes seems to play only a minor role as evidenced by the high rectification factor for the experimental data [58].
Figure 4.4  Distribution of free and trapped charge carriers and electric field in the steady state for an OLED consisting of two organic layers. The applied bias is 10 V.

Figure 4.5  Distribution of free and trapped charge carriers and electric field for a diode with additional blocking layer (EBL). The applied bias is 10 V.
Figure 4.6 Concentration profiles for singlet excitons for two- and three-layer OLED, respectively. The main creation and decay takes place in the Alq$_3$ layer close to the heterointerface.

Figure 4.7 Luminance as a function of bias for two- and three-layer devices. Similar to Figure 4.3, the full dots denote the simulation results and the open dots show the experimental data.

Implementation of the thin blocking layer only slightly reduced the current. However, we can find the main reason why this layer is used when we compare the two profiles of singlet exciton density (Figure 4.6). The explanation for the higher creation...
efficiency for singlet excitons in the three-layer structure is found in the separation of free holes and electrons accumulating close the internal interface 1-Naphdata/Alq₃. If the free carriers accumulate at the same interface on both sides, interface recombination takes place. The result of this process is the formation a charge transfer state (exciplex). The probability that such an exciplex can be transformed into a bulk singlet exciton is determined by the lower of the two offset energies for HOMO and LUMO levels, i.e. here the HOMO offset: This offset energy should be lower than the difference in exciton binding energy between the interface CT-exciton and the bulk singlet exciton in the EML to make this transformation energetically favourable (Section 2.3.2). For the interface of 1-Naphdata and Alq₃, this criterion is not fulfilled due to the high HOMO offset. Thus, the efficiency for generation of bulk excitons in Alq₃ is here significantly lower, as compared to the efficiency obtained when electrons and holes recombine directly or indirectly in the bulk material. On the other hand, the HOMO offset between Alq₃ and NPB is very low which has two effects (i) holes can more easily be injected into Alq₃, followed by bulk generation of excitons (ii) the probability that interface CT-excitons are transformed into bulk excitons in Alq₃ is much higher as in the case of the 1-Naphdata/Alq₃ interface. Altogether, this results in a higher exciton concentration close to the internal interface EBL/EML, and due to singlet exciton diffusion, also 20 nm away from the interface. Close to both electrodes, a strong impact of the quenching effect on the exciton profile can be observed, originating from the non-radiative recombination induced by diluted electrode material being diffused into the organic layers.

The difference between the luminance obtained experimentally can be explained by this effect. Two luminance-voltage characteristics are depicted in Figure 4.7. Here, the implementation of the additional layer increases the luminance by a factor of about 2. However, the increase of luminance depends on the thickness of the blocking layer. The results of simulations with variation of NPB thickness from 5 to 20 nm are presented in Figures 4.8 and 4.9. Here, the luminance is reduced with increasing thickness of the EBL, which also significantly lowers the current density. Since the NBP has a high mobility for holes, we should expect that it introduces only small changes with variation of thickness. However, the highest electric field occurs in this layer by accumulation of holes and electrons at its interfaces. Thus, with rising thickness of NBP, the drop of potential increases significantly. For instance at V=10V, the potential drop in the 5nm thick NPB is 0.75 V, with 10nm rises to 1.42 V, while for 20nm the potential drop reaches 2.54V (see Figure 4.10). This effect influences the transport through the HTL and EML, and thus reduces the current density.
Figure 4.8  Current as a function of bias for three-layer devices with different thickness of NPB.

Figure 4.9  Luminance as a function of bias for three-layer devices with different thickness of NPB.
Figure 4.10 Electric field distribution for three-layer devices with different thickness of NPB.

Figure 4.11 Current as a function of bias for three-layer devices with different electron mobility in Alq3.

The layer of Alq3 plays here a double role as electron transport layer and emitting layer. Thus, the mobility of electrons is the most important parameter, which decides directly about the transport of free carriers and the recombination (see Equations 3.4 and 3.7). A series of current-voltage characteristics are shown in Figures 4.11 and 4.12, where the electron mobility varies from $1.86 \times 10^{-6}$ cm$^2$/V*s to $1 \times 10^{-5}$ cm$^2$/V*s. The hole mobility is
always assumed two order of magnitude lower than the electron mobility. The increase of mobility significantly modifies the current and also the luminance by more efficient transport and injection of electrons from the cathode to the recombination zone at the interface between NPB and Alq₃.

![Graph showing luminance as a function of bias for three-layer devices with different electron mobility for Alq₃.](image)

**Figure 4.12** Luminance as a function of bias for three-layer devices with different electron mobility for Alq₃.

### 4.2.2. Doping of hole transport layers

**Introduction**

The improvement of transport for organic materials is one of the crucial topics, since carrier mobilities are typically low in amorphous organic materials (10⁻³–10⁻⁹ cm²/Vs), which leads to space charge limited currents and a considerable voltage drop over the transport layers. Therefore, a key technique to realize more efficient devices with low operating voltage is controlled doping of the organic material, which increases significantly the equilibrium concentration of free carriers. However, the principle of such doping is not as simple as for inorganic semiconductors where dopants can be the atoms with one more or one less valence electron than the matrix for donor and acceptor dopants, respectively. In organic semiconductors, the host molecules are more complex and one has to develop new strategies for efficient doping [6,13,106].

A second important effect of doping is that it facilitates carrier injection even with nominally very high barriers: When the density of dopants is high, thin space charge layers are created, allowing for efficient tunneling from the anode to the HTL with quasi-
ohmic contact behaviour. Thus, an adequate concentration of dopants can be crucial for the performance of light emitting devices [5,23,114,165].

Improved hole transport and hole injection is only beneficial for the device performance when efficient injection of electrons to the EML is ensured by good ohmic contacts. Otherwise, the high concentration of holes injected into the EML will not recombine with electrons, but they will be transported through the whole ETL and reach the cathode before recombination. However, this case would require extremely bad electron injection for Alq₃ based OLED because the electron mobility is higher by about two orders of magnitude than the hole mobility in Alq₃. Therefore, a penetration of holes through the complete EML is unlikely.

<table>
<thead>
<tr>
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<th>HTL</th>
<th>BL</th>
<th>EL and ETL</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO</td>
<td>-2.3</td>
<td>-2.4</td>
<td>65 nm</td>
</tr>
<tr>
<td>TDATA: F₄-TCNQ</td>
<td></td>
<td></td>
<td>10 nm</td>
</tr>
<tr>
<td>NBP</td>
<td></td>
<td></td>
<td>100 nm</td>
</tr>
<tr>
<td>Alq₃</td>
<td></td>
<td></td>
<td>10 nm</td>
</tr>
<tr>
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<td></td>
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</tr>
<tr>
<td>Al</td>
<td></td>
<td></td>
<td>65 nm</td>
</tr>
</tbody>
</table>

Figure 4.13 Alignment of energetic levels (HOMO and LUMO) for organic materials and Fermi level of electrodes for an OLED structure with doped HTL.

**Parameters**

The electrical parameters for the blocking layer (NPB) and the emission layer (Alq₃) are assumed similar as in the last section (compare Table 4.14 and Table 4.2). The hole transport layer, here based on m-MTDATA as a matrix, is assumed to have a mobility of $4.8 \times 10^{-6}$ cm²/(V·s) [58]. The density of trap states is assumed to be $10^{18}$ cm⁻³ with a depth of 0.25 eV for holes in the HTL and EBL, and for electrons in the ETL. The doping ratio is chosen to be 0.2-1 mol % yielding concentrations of $2 \times 10^{18}$-10¹⁹ cm⁻³. For this doping density, ohmic contact behaviour is assumed between the ITO and the MTDATA layer. The validity of this assumption has been proven by Blochwitz et al. [3]. The method of simulating Ohmic contact behaviour for doped layers is discussed in Section 2.3.1. The
properties of formation, transport, quenching and decay for singlet excitons are identical to those in the last section. The total outcoupling efficiency of the internally generated photons, considering waveguiding losses and absorption has been estimated to be 18% (ray calculation) and the fraction of radiative decay of singlet excitons was set to be 30%.

<table>
<thead>
<tr>
<th>Organic material</th>
<th>$\mu_p \text{ cm}^2/(V\cdot s)$</th>
<th>$\mu_n \text{ cm}^2/(V\cdot s)$</th>
<th>$\beta_{PF} \text{ cm/V}^{0.5}$</th>
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<td>NBP</td>
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<td>$6.1 \times 10^{-5}$</td>
<td>$1.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>Alq$_3$</td>
<td>$1.66 \times 10^{-8}$</td>
<td>$1.66 \times 10^{-6}$</td>
<td>$3.6 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Table 4.14 Parameters used in the simulation: zero field hole and electron mobilities and factor $\beta_{PF}$, describing the field–dependence for particular materials at room temperature.

**Results and discussion**

The effect of a doped hole transport layer on the distribution of the electric field is shown in Figure 4.15. In case of layers without doping, all free and trapped carriers are injected non-equilibrium carriers and directly affects the distribution of the electric field (dashed line Figure 4.15). Here, a positive space charge formed close to the anode and holes accumulated in front of the interface of HTL/EBL increase the electric field in the hole transport layer. Due to the high mobility of holes in the blocking layer, there is a low and uniform concentration of holes and thus an almost constant electric field in the EBL. In the EML, the field decreases due to the presence of injected electrons, see Figure 4.16. When dopants are introduced into the HTL, the electric field in the HTL almost vanishes. This low value of the field is a result of the charge compensation between positive free and trapped holes and the immobile negative acceptors. Moreover, the concentration of mobile holes is that high that the voltage drop at typical current densities associated with the Ohmic resistance of the doped layer is almost negligible. Because the contact is Ohmic, the drop of potential close to it is negligible.
Figure 4.15  Distribution of electric field in diodes consisting of three organic layers with either doped or undoped MTDATA as a hole transport layer at identical applied bias of 8 V.

Figure 4.16  Spatial distribution of free holes and electrons for a three-layer OLED with doped and undoped hole transport layer, respectively.

Only at the opposite side of the hole transport layer, the field dramatically rises due to the accumulation of holes in front of the blocking layer: the transport of free holes is limited by the interface energetic barrier of 0.5 eV. However, efficient transport and injection of holes is ensured by the high electric field in the EBL and the large concentration of free charges.
Even the trap states do not significantly influence the transport due to the higher number of dopants as trap states. The shape of the electric field in the EBL and EML is similar to the undoped diode. Nevertheless, the value of field in the EML is higher for the doped device than for the undoped device at a given applied bias. The reason is the lower voltage drop in the HTL for the doped device. The increased electric field in the EML comes enhanced injection of free electrons, and thus an enhanced recombination rate and a new distribution of excitons, see Figure 4.17.

![Profile of singlet excitons](image)

**Figure 4.17** Profiles of singlet excitons as a result of direct and indirect recombination, decay and quenching processes at 8 V.

The difference is first of all a result of the higher concentration of holes and electrons, but also the quenching processes and especially the quenching with free carriers rise. However, the average number of singlet excitons grows when the electric field and the concentration increase in the EML. The controlled doping significantly changes the current voltage characteristics (see Figure 4.18). From the above discussion, it is to be expected that also the current-voltage-characteristics (Figure 4.18) and the luminance voltage characteristics (Figure 4.19) are considerably steeper for the OLED with doped HTL, where most of the applied voltage can be used to drive the electrons through the Alq₃ layer.
Figure 4.18  Current voltage characteristics for three-layer light emitting diodes with undoped and doped hole transport layer ($N_A=2\times10^{18} \text{ cm}^{-3}$), respectively.

Figure 4.19  Luminance voltage characteristics for the OLED with undoped and doped HTL.
Figure 4.20 Efficiency of two organic light emitting diodes with and without dopants in the hole transport layer. For the sample with doped HTL, results for various values of cross section $\delta_q$ are also shown.

The efficiency for both the OLED with doped and undoped transport layer is voltage-dependent, with a gradual increase of efficiency observed with growing applied bias (Figure 4.20). Quenching processes between carriers and excitons can also reduce the efficiency of OLED. These mechanisms occur when a high concentration of free charge carriers is found close to the generation region for excitons in the EML. The influence of this quenching effect on the efficiency is illustrated by calculating the efficiency for the OLED with doped HTL. The cross section $\delta_q$ (see Equation 4.2) for the quenching processes between free and trapped charge carriers with the excitons has been set to values of $10^{-14}$ cm$^2$, $5 \times 10^{-13}$ cm$^2$ and $10^{-13}$ cm$^2$ (Figure 4.20). Here, together with increasing the factor $\delta_q$, the quenching process becomes more likely. This effect changes both the value and the shape of the efficiency-voltage curve, which drops with rising applied bias for larger values of $\delta_q$. However, if one uses a value of $10^{-14}$ cm$^2$ for $\delta_q$, which is on the order of the size of a molecule, it is obvious from the increasing curve for the doped sample that this quenching process hardly plays any role. On the other hand, quenching can occur via long range Förster transfer of the excitation energy from the neutral singlet to an excited state of a charged molecule. Therefore, scattering cross sections that significantly exceed the molecular size may be realistic. However, the data observed from experimental work in our laboratory show that quenching effects play only a minor role [115].
Figure 4.21  Efficiency of organic light emitting diodes with dopants in the hole transport layers, when the transport of carriers and distribution of electric field are changed by different DOS widths (\(\sigma=0.06 \text{ eV}-0.07 \text{ eV}\)) at the HTL/EBL interface.

The increase of efficiency with rising applied bias is a result of an increasing probability that holes can penetrate into the Alq\(_3\) to recombine there. The effect is illustrated in Figure 4.21, which presents the efficiency of OLED with doped HTL at different probability of hole hopping through HTL/EBL interface. Simulations have been made for three widths of DOS, varying from 0.06 eV to 0.07 eV. Here, together with decreasing width, the transport process for holes becomes less likely, due to the large height of barrier (for holes 0.5 eV). The different interface condition changes both the value and the shape of the efficiency-voltage curve, which shows low values at low bias if transport of holes into the Alq\(_3\) is difficult. At low bias, more holes are accumulated at the first organic interface, while electrons are efficiently blocked by a high 0.7 eV barrier between EBL/EML. Thus, the electric field is highest in the EBL compared to transport layers. This effect allows that a higher number of holes can overcome the barrier at HTL/EBL and reach the recombination zone. However, also the energetic barrier for electrons is lowered and some electrons can be injected into the EBL, where they recombine with holes, but do not contribute to luminance. Therefore, this effect leads to a decreasing efficiency. Together with applying higher voltage, the ratio between the injected holes from HTL and electrons from EML into the EBL grows. In other words, much more holes can reach the recombination zone in Alq\(_3\) than electrons the EBL. The higher concentration of holes accumulated at the interface in the doped layer and the
lower barrier for hole injection than for electron injection favours the hole transport to $\text{Alq}_3$ as compared to recombination in the EBL.

A similar conclusion can be drawn for the OLED with undoped HTL. Here, the current efficiency also grows with the applied bias. The current efficiency is significantly higher for the OLED with doped HTL, especially at low applied voltages (Figure 4.20), because of more efficient hole transport to the recombination zone.
4.3. Fitting simulation results to experimental data

4.3.1. OLED with undoped hole transport layer

Introduction

The thickness of the transport layers has a crucial impact on the current-voltage characteristics. To obtain a luminance of above 100 cd/m² at a low operating bias, the thickness of the transport layer should not be too large to avoid a significant potential drop. Another possibility to overcome the problem of the thickness of the transport layer is controlled doping, which improves the transport properties and allows the device to reach high luminance at lower voltages (Section 4.2). It is also important to ensure easy injection of electrons from the metal electrode into the EML. The LUMO of Alq₃, which plays a role in both the emitting and electron transport layers, is at about -3.1 eV below the vacuum level. Accordingly, reasonable electron injection can be obtained by application of magnesium (Mg) as the cathode, as it has a low ionization potential of around 3.6 eV, or alternatively a magnesium–silver alloy (Mg:Ag) with ionization energy around 3.7 eV can be used [147]. An even better, quasi-Ohmic contact can be obtained when aluminum (Al) is used together with an ultrathin interlayer of lithium fluoride (LiF) between the metal and the electron transport layer. Aluminum by itself has an ionization potential of 4.3 eV, which is too high to allow for efficient injection. However, when Al is deposited onto the LiF layer, some atomic Li is set free and can diffuse into the organic layer and act as a donor dopant, which enables quasi-Ohmic injection [159,160].

However, the electrons in OLED that use Alq₃ both as EML and ETL material not only have to overcome the mentioned contact barrier, but also must travel through most of the Alq₃ layer to accumulate as close to the interface with NPB as possible. As to the holes, they have to overcome the contact barrier between ITO and the HTL, cross the hole transport layer and two barriers between HTL and EBL and between EBL and EML. Thus, ensuring a good hole transport and injection in the HTL-EBL system and ensuring good electron transport in the Alq₃ in spite of its rather low electron mobility are the two key requirements. Low voltage operation can be obtained when all layers are prepared with low thickness, but then quantum efficiency and production yield may suffer.

In the following, we show the fits of numerical data to the experimental results for different thicknesses of hole and electron transport layers in order to show the influence of transport properties on luminance and efficiency. The series of samples using TNATA for the hole transport layer was prepared in a vertical in-line manufacturing set-up (VES 400, developed by Applied Films, [166], by Dr Manfred Schreil in Fraunhofer-Institute for Photonic Microsystems, Dresden.
Figure 4.22 Alignment of HOMO and LUMO levels for the particular organic layers in a three-layer OLED structure. In experiment and simulation, the hole transport layer (HTL) and emissive layer (EML) thickness are varied from 60 to 90 nm with step of 15 nm, while the blocking layer (EBL) remains 10 nm thick.

Parameters

To simulate the whole OLED structure, the mobilities for the three materials Alq$_3$, NPB and TNATA are needed. Field-dependent mobilities for Alq$_3$ and NBP are supposed to be similar as in Section 4.2 (see Table 4.14 and Table 4.23). The starburst material 4,4',4''-tris[N-(1-naphthyl)-N-phenylamino]-triphenylamine (TNATA) is used for the hole transport layer (HTL). The mobility of this material is predicted from the current-voltage characteristics for different thickness of HTL and ETL (Figure 4.24 and Figure 4.25): The current changes are similar with changes in both layer thicknesses. We therefore conclude that the hole mobility in the HTL (Table 4.23) should be in the same order as the electron mobility in the ETL.

The particular energy levels are presented in Figure 4.22, where the close alignment of ITO work function (4.8 eV) with the ionization energy of TNATA (5.1 eV) [146] allows us to assume ohmic contact behaviour. The second contact between Alq$_3$ and Mg is also assumed as ohmic, which may be justified according to reference [147]. However, there remain some doubts about this assumption as it is known that lower operating voltages can be obtained for Alq$_3$ based OLED using the LiF/Al contact system as compared to Mg.

Similar to Section 4.2.2, the concentration of trap states at a particular energy is chosen as a free parameter. We assumed $10^{18}$ cm$^{-3}$ as concentration of hole traps in
TNATA and NPB and the some for electron traps in Alq₃. Here, the depth of all traps is assumed as 0.25 eV. Identical assumptions are supported from Section 4.2.2. The traps influence the drift, diffusion and quenching processes.

The total outcoupling efficiency of the internally generated photons, considering waveguiding losses and absorption has been estimated to be 18% and the fraction of radiative decay of singlet excitons has been set to 30% [150].

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<th>Organic material</th>
<th>$\mu_p \text{ cm}^2/(\text{V*s})$</th>
<th>$\mu_n \text{ cm}^2/(\text{V*s})$</th>
<th>$\beta_{PF} \text{ (cm/V)}^{0.5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNATA</td>
<td>$1.35 \times 10^{-6}$</td>
<td>$1.35 \times 10^{-8}$</td>
<td>$2.67 \times 10^{-3}$</td>
</tr>
<tr>
<td>NPB</td>
<td>$6.1 \times 10^{-4}$</td>
<td>$6.1 \times 10^{-6}$</td>
<td>$1.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>Alq₃</td>
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<td>$1.66 \times 10^{-6}$</td>
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</tbody>
</table>

Table 4.23  Hole and electron mobilities, with factor $\beta_{PF}$ describing the field–dependence for particular materials at room temperature as used for the simulation.

**Discussion**

Assuming the above parameters, we are able to simulate the current-voltage and current-luminescence characteristics for OLED with different thickness of hole transport layer (TNATA), see Figure 4.22. As mentioned, we are forced to set the hole mobility of TNATA to about $10^{-6}$ cm²/(V*s) due to the significant influence of the different thickness on the current. Alternatively, we tried to reproduce the experimental data assuming a higher hole mobility, but a non-ohmic contact between ITO and TNATA. Here, one observes also a strong thickness dependence, but we have not been able to obtain a reasonable fit to the IV-curves with this assumption. This is thus a hint that the boundary condition for hole injection has been correctly supposed. The interface between Alq₃ and Mg seems to fulfil ohmic injection as well, since there is a good fit to the experimental results with the thickness of Alq₃ varied from 60 nm to 90 nm (Figure 4.25), using literature values for the electron mobility (Table 4.23). Thus, the fits suggests that the mobilities in the transport layers rather than the contacts represent the main bottleneck for the transport of free carriers to the recombination zone. However, as long as there is a lack of reliable input parameters for the individual carrier mobilities and trap densities, this conclusion cannot be finally unambiguous. The small deviation between the experimental and calculated curves for 60 nm TNATA, 10 nm NBP and 60 nm Alq₃ can be explained by a small error in thickness (about 3 nm) for one of the layers. Altogether, the fits between simulations and experimental curves is quite good for the series of devices with a different thickness of transport layers.
Another parameter which can influence the transport of holes is the internal interface between TNATA and NPB. A barrier height of 0.4 eV has been obtained from the HOMOs of the two organic materials. However, the thermal hopping through the barrier is assisted by the electric field, which is high in the center of the diode, whereas the electric field vanishes close to the injection contacts when currents are space charge limited. Since high fields are needed for hole injection into NPB, it is obvious that the NPB layer should be thin in order avoid a high potential drop over this layer. However, for the present structure with only 10 nm NPB, this potential drop is below 1 V at a brightness of 100 cd/m² and 1.4 V at 1000 cd/m². Thus the holes can be transported through the NPB and afterwards, they can easily hop into the Alq₃ (barrier only 0.2 eV) where they recombine with electrons blocked by the energetic barrier on the NBP/Alq₃ interface. Also for this energetic barrier, the electric field increases the injection rate for electrons. However, the influence is very low as the barrier is as high as 0.7 eV.

Solving the rate equation describing the exciton processes allows us to obtain the concentration profile for singlet excitons, which can decay radiatively and contribute to the luminance. The simulation results do not suggest a strong influence of the layer thicknesses on the internal quantum yield. This agrees nicely with the experimental finding for the series of samples with different HTL thickness. Here, also the current efficiency is obviously independent of HTL thickness as shown in Figure 4.26. However, one would expect from a simple consideration of the optical interference pattern inside the OLED that the thickness of the Alq₃ layer, which determines the distance between the reflecting electrode and the main exciton generation zone, should have a significant influence on the outcoupling efficiency. However, the available experimental data do not show a clear trend but rather some scattering. This is most obvious from the lower luminance for the sample with 75 nm Alq₃ shown in Figure 4.27, even though the current at a given voltage agrees well with the other diodes (see Figure 4.26). Accordingly, we can only conclude here that we have been able to account for the influence of layer thickness on the IV-characteristics with reasonable parameters within our model. As to the voltage-luminance characteristics, we also obtain a qualitative agreement and we can roughly account for the quantum efficiency. However, a more detailed analysis of the influence of layer thickness due to optical or electrical effects still suffers from a lack of reliable and systematic experimental data. Such data will soon be available with the new masking system in one of the OLED preparation tools recently being installed at our institute, which allows to prepare a complete series of OLED with different layer thickness on a large substrate in one run.
Figure 4.24  Current-voltage characteristics for OLED with various HTL thickness (TNATA: 60 nm, 75 nm and 90 nm), while the thickness of NPB and Alq3 are kept constant at 10 and 60 nm, respectively.

Figure 4.25  Current-voltage characteristics for OLED with various EML thickness (Alq3: 60 nm, 75 nm and 90 nm), while the thickness of TNATA and NPB are kept constant at 60 and 10 nm, respectively.
Figure 4.26  Luminance of OLED with different thickness of TNATA (HTL) layer. Thicknesses are identical as for the current-voltage characteristics (Figure 4.24).

Figure 4.27  Luminance of OLED with different thickness of emissive layer (Alq3). Thicknesses are identical as for the current-voltage characteristic (Figure 4.25).
### 4.3.2. OLED with doped hole transport layer

**Parameters and results**

The main parameters are assumed to be similar to the previous part of this section. Here, however, p-doped MTDATA is used as the hole transport layer instead of TNATA. For the mobility of holes in this layer, we assumed a zero-field value of about $5 \times 10^{-6} \text{cm}^2/(\text{V}\cdot\text{s})$, corresponding to values reported by Staudigel et. al. [58]. The two sets of samples with TNATA and MTDATA have been prepared by two different vacuum systems. The first series of undoped samples using TNATA was prepared in a vertical in-line manufacturing set-up, while the series of doped samples discussed in the following stems from a the multi-chamber system at our institute. This might partly explain the slightly different mobilities we had to use to obtain a good fit (see Table 4.23 and Table 4.28).

<table>
<thead>
<tr>
<th>Organic materials</th>
<th>$\mu_p \text{cm}^2/(\text{V}\cdot\text{s})$</th>
<th>$\mu_n \text{cm}^2/(\text{V}\cdot\text{s})$</th>
<th>$\beta_{PF} \text{(cm/V)}^{0.5}$</th>
</tr>
</thead>
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<tr>
<td>MTDATA</td>
<td>$4.78 \times 10^{-6}$</td>
<td>$4.78 \times 10^{-8}$</td>
<td>$2.67 \times 10^{-3}$</td>
</tr>
<tr>
<td>NPB</td>
<td>$6.1 \times 10^{-4}$</td>
<td>$6.1 \times 10^{-6}$</td>
<td>$1.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>Alq$_3$</td>
<td>$1 \times 10^{-3}$</td>
<td>$1 \times 10^{-8}$</td>
<td>$3.6 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

*Table 4.28*  Hole and electron mobilities with factor $\beta_{PF}$ describing the field–dependence for particular materials at room temperature as used in the simulations presented in the following graphs

The contact between ITO and the doped layer is assumed to be Ohmic, similar to the last sections [3]. Here, however, the opposite contact seemingly does not fulfil the Ohmic condition for these diodes. The difference between the LUMO of Alq$_3$ and the ionization potential of Al corresponds to a value of 1 eV. By inserting an interlayer of LiF, this difference can be lowered by about 0.7 eV [160]. Nevertheless, we found that the simulation result only fits well to experimental results when we assume thermionic injection (see Section 2.3.1) for the contact of Alq$_3$/LiF/Al with a barrier height of 0.52 eV. The reason for this may be that this series of diodes has been measured in air where the ambient oxygen is expected to compensate the n-doping effect of Li. Moreover, the different contacts can have a slight influence on the optical modelling of the structure. Thus, for this diode, an outcoupling factor of 20% is assumed instead of 18% corresponding to a slightly higher current efficiency. All other parameters have been chosen in agreement with the assumptions made in the previous sections.
Figure 4.29  Current-voltage characteristics for different thickness of emitting layer (Alq$_3$), changing from 65 nm to 200 nm. The 100 nm thick MTDATA later (HTL) is p-doped with 1mol% $F_4$-TCNQ which leads to a conductivity of 3*10$^{-7}$ S/cm.

Figure 4.30  Luminance at different thickness of Alq$_3$ layer obtained from the experimental measurement and numerical simulation.

The initial adjustment of parameters has been made for the sample with 65 nm of Alq$_3$. To get agreement between experimental and simulation data, a lower mobility of Alq$_3$ was assumed $\mu_p=10^{-6}$ cm$^2$/V*s(Table 4.28). However, this value only departs
insignificantly from reported values [58,95,145]. Simulations for other diodes with different thickness of emitting layer are calculated using the same set of initial parameters. A good agreement of current voltage dependence is achieved for diodes with a thickness of the emitting layer ranging from 65 nm to 200 nm even under a high applied bias as shown in Figure 4.29.

Also for the luminescence, the calculated results agree with the experimental data in the whole range of thicknesses (see Figure 4.30). Similar to Section 4.2, the best OLED is the one with the thinnest emitting layer, which allows for the highest electron current at given voltage from the non-Ohmic contact to the recombination zone.

4.3.3. Emissive dopants in the emission layer

Introduction

Another improvement of OLED efficiency can be obtained by use of controlled molecular doping of organic solid thin films with highly fluorescent guest molecules, e.g., laser dyes [14,74,115, 141,154,157,158]. Using this approach, one can take advantage of the large molecular quantum yield of the dopant molecules and achieve high quantum yields in the composite materials. This results from efficient Förster energy transfer from host to guest molecules [73]. In this process, the exciton is created either after absorption of a higher energy photon, in case of photoluminescence, or after an electron and a hole recombine at a host site, in case of electroluminescence, and transfer their energy to a guest molecule. In case of electroluminescence, exciton generation on the guest can also occur by subsequent capture of a charge carrier pair. The use of a host-guest-system reduces the degree of exciton quenching often observed in neat solid films of either guest or host [157] (aggregate quenching), and together with the high probability that excitons on guest molecules can decay radiatively for particular doped systems, even a photoluminescence quantum yield of 80% is found [154]. The improved efficiency of such OLED due to an efficient energy transfer from the host to the guest molecules with a higher photoluminescence quantum yield in solution has been demonstrated first by Tang [14]. A successful and frequently used example for such a system is the coevaporation of around 1% of quinacridone (QAD) with Alq$_3$ as a matrix. However, this method has also disadvantages; the operating voltages rapidly increase with increasing thickness of the QAD doped layer. This is due to the fact that QAD seemingly acts as a trap in Alq$_3$ for electrons and probably also for holes.

In this section, we show a comparison of the experimental and simulated structure with and without doping of the emitting layer. For the doped structure, the Alq$_3$ layer, which serves as EML and ETL in the undoped structure, is replaced by an EML of Alq$_3$
doped with approx. 1 mol% of the emitter molecule N,N'-diphenyl-quinacridone (QAD) next to the TPD layer and an ETL of neat Alq₃. The OLED emit bright green light with a spectrum shown in Figure 3.4, which can be attributed to the emission from the QAD guest molecules [115].

**Theory**

Emitter dopants are carrier traps and degrade the transport properties of carriers, leading to an increase of the operation voltage of devices [50,142]. To reduce the effect of carrier trapping, the admixture of emissive dopants can be confined to the essential region, i.e., the carrier recombination zone [14].

There are two possible ways to create an exciton on an emitter dopant: (i) the recombination of a trapped charge with a free carrier and (ii) the energy transfer from a host molecule to the guest molecule. Process (i) is modeled in accordance to Equations 3.6 and Equation 3.7 (indirect recombination) with the same singlet/triplet spin statistics as for host molecules. The process of resonant singlet exciton transfer (ii) can be described within the dipole-dipole interaction mechanism as originally proposed by Förster [140]. The energy transfer rate $K$ induced via dipole-dipole interactions between a single pair of organic molecules is given by [73]

$$K = \frac{1}{\tau_H} \left( \frac{R_0}{R_{H-G}} \right)^6$$

(4.9)

and

$$R_0 = \left( \frac{3}{4\pi} \int \frac{c^4}{\omega^4 n^4} F_H(\omega) \sigma_D(\omega) d\omega \right)^{\frac{1}{6}},$$

(4.10)

where $\tau_H$ denotes the radiative lifetime of the singlet excitons of the host materials, $c$ is the light velocity, $R_{H-G}$ is the mean distance between host and guest molecules and $R_0$ is the effective Förster radius, $F_H(\omega)$ is the normalized fluorescence spectrum of the host material, $\sigma(\omega)$ the normalized optical absorption cross-section of the emitter dopant, $\omega$ the light frequency and $n$ the refractive index of the host. As a competing process to the intrinsic recombination of excitons on the guest molecules, quenching between these excitons and free carriers on the host material is implemented in our model.
The structure of the OLED with doped emitter layer is shown in Figure 4.31. To obtain an efficient device, the doping has been introduced only in a 35 nm layer of Alq₃ close to the interface between EBL and EML, i.e., in the main recombination zone between the charge carriers where the excitons are created. The concentration of dopants in the emissive layer is derived from the doping ratio 1 mol-% and the depth of dopant states is assumed as 0.15 eV for holes and 0.28 eV for electrons. The energetic position of the QAD LUMO has been adjusted to get an optimum fit to the current-voltage characteristics. Since the energetic position of QAD HOMO does not significantly influence the current, we can not draw any conclusions on the hole trap depth from the fitting. Huang at al. [167] obtains from experimental results the same conclusions. The other parameters are chosen identical to the previous simulations for undoped structures (compare Table 4.14 and Table 4.32). An efficient energy transfer is reached when the overlap between the emission spectra of the host and the absorption spectra of the guest is large. This overlap determines the value of effective Förster radius $R_0$, for which a typical value for disordered organic materials is $R_0=3$ nm [74]. The mean distance $R_{H-G}$ between the host and the guest molecules is supposed to be 2 nm or 1 nm, which enables an efficient transfer from host to guest molecules [74]. The cross section for recombination between the free carriers and the excitons formed in QAD are supposed to be similar to the host materials, $\delta_q=10^{-14}$ cm$^2$. The excitons formed on QAD are not expected to diffuse due to the large distances between dopant molecules. Therefore, quenching processes between occupied
trap states and immobile excitons do not take place. This is reflected in the lower influence of the exciton concentration on quenching effects [144]. The next advantage of using dopant molecules in the recombination zone is the higher fraction of radiative decay of singlet excitons as compared to undoped materials. For our system, the fraction of excitons which decay radiatively is assumed to be 36%.

<table>
<thead>
<tr>
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<td>2.67*10^3</td>
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<tr>
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</tr>
<tr>
<td>Alq₃</td>
<td>1.66*10^8</td>
<td>1.66*10^6</td>
<td>3.6*10^3</td>
</tr>
</tbody>
</table>

Table 4.32 Hole and electron mobilities with factor $\beta_{PF}$ describing the field–dependence for particular materials at room temperature used in the simulations shown in the following graphs

**OLED with doped and undoped emitting layer**

A good agreement between simulation and experiment is achieved for diodes with a 35 nm layer of Alq$_3$ doped with QAD: Figure 4.33 shows experimental and simulated current-voltage characteristics for structures consisting of 60 nm TNATA, 10 nm NPB, 35 nm Alq$_3$:QAD and 25 nm Alq$_3$ sandwiched between ITO and Mg. For comparison, we add the corresponding characteristics for an OLED with identical layer thicknesses (HTL – 60 nm, EBL – 10 nm and EML – 60 nm), but without QAD doping in the EML. The doping of the EML with QAD significantly reduces the slope of the current-voltage characteristics and thus increases the operating bias. The emissive dopants obviously reduce the effective carrier mobility of at least one type of carrier by forming trap states in Alq$_3$. As the main recombination zone is close to the EBL without emitter doping, we conclude that doping hinders the transport of electrons to the EBL. Here, the two crucial parameters are the LUMO position of QAD with respect to Alq$_3$, i.e. the effective electron trap depth, and the concentration of emissive dopants. The strong influence of the electron trap depth on the current is shown in Figure 4.34, where the current increases together with decreasing trap depth. On the other hand, the HOMO of QAD, i.e. the trap depth for holes, hardly influences the current–voltage characteristics as the penetration depth of holes into the EML is anyway small due to the low mobility of holes in Alq$_3$. Also for QAD-doped EML, the recombination zone is thus close to the NBP/Alq$_3$ interface and holes only have to overcome the small energetic barrier at the interface and then drift or diffuse until they may be trapped or recombine. On the other side, the electrons have to move through the doped Alq$_3$ before they can recombine close to the interface.
Figure 4.33  Current-voltage characteristics for the sample with 35nm QAD-doped Alq$_3$ (1mol%) and 25nm undoped Alq$_3$ and for an otherwise identical sample without QAD doping, i.e. 60nm of undoped Alq$_3$. The numbers in the inset refer to the thickness of TNATA, NPB, QAD-doped Alq$_3$ and undoped Alq$_3$.

Figure 4.34  Simulated current-voltage characteristics for the QAD-doped structure from the previous figure with different electron trap depths for QAD in Alq$_3$. 

Figure 4.35  Simulated distribution of electric field for an OLED with 35 nm doped Alq$_3$, compared to the undoped device at applied bias of 10 V.

Figure 4.36  Occupied electron trap states in the EML with emissive dopants (QAD). The dopants act as traps states, thus we show the concentration of carriers trapped by these states.

The introduction of dopants is also reflected in the different distribution of electric field and charge carriers in the three-layer OLED. The electric field for devices with undoped and doped emitting layer is shown in Figure 4.35. Here, the additional dopants lead to a slightly higher electric field in doped Alq$_3$, corresponding to the reduced effective
electron mobility while, for a given applied bias, the field in the other layers is reduced. The distribution of occupied trap states in the emitted layers is shown in Figure 4.36. The number of holes and electrons captured by the guest molecules is comparable close to the interface between EBL and EML. With increasing distance from the interface in direction of the cathode, the occupation of guest molecules by holes is decreased due to their low mobility. In case of electrons, the concentration gradient has a reverse direction according to the typical profile for space charge limited electron currents, taking into account recombination processes with free and trapped holes.

The additional dopants lead to a higher operating voltage, but also increases the current efficiency (see Figure 4.37). The both effects are the results of the high trapping of electrons by emissive dopants in EML. Trapped electron can easily recombined together with hole and created higher fraction of excitons which decay radiatively.

![Figure 4.37 Experimental and simulated luminance-voltage characteristics for the diodes with undoped and QAD-doped emissive layer, respectively.](image)

Finally, we discuss the distribution of singlet excitons on Alq3 and QAD for a QAD-doped OLED (Figure 4.38) and the dominant mechanism of exciton generation on QAD. There are two possible ways of exciton creation on QAD, namely (i) exciton generation on Alq3 followed by Förster transfer to QAD (ii) and direct generation on QAD by subsequent capture of an electron and a hole – or vice versa. A comparison of the rates for these two paths shows that both rates are similar close to the interface of NBP with Alq3:QAD. However, with increasing distance from the interface, direct recombination on QAD becomes more and more dominant. If we compare the QAD doped and the undoped
OLED, the total exciton concentration is similar for both structures close to the interface with NPB, but it is higher for the QAD-doped OLED in the center of the emitting layer (Figure 4.39).

Efficient Förster transfer as assumed above is witnessed by the exciton profiles of QAD and Alq$_3$ shown in Figure 4.38. Here, the concentration of singlet Frenkel excitons on Alq$_3$ is lower by almost two orders of magnitude than the exciton concentration on QAD throughout the whole doped layer. The narrow region close to the interface NPB/Alq$_3$ is the place where holes injected from the EBL into the EML meet the accumulated electrons, leading to a high local exciton concentration. However, this exciton density decreases rapidly by a factor about ten with increasing distance from the interface. The high concentration of excitons close to the interface can be explained by efficient Förster energy transfer to QAD molecules, which precludes the diffusion of excitons formed in Alq$_3$ inside the doped layer. The exciton generation on QAD mainly results from direct formation of excitons in QAD by recombination between trapped charge carriers on QAD and free carriers (80%), while only 20% are from generation on Alq$_3$ and subsequent Förster transfer. The exciton concentration in the guest molecules first decreases together with increasing distance from the interface between EBL and EML due to a decreasing density of free or trapped charge carriers. However, close to the interface between the doped and undoped EML, the exciton density on QAD even increases slightly due to diffusing of excitons formed in the undoped part of the emitting layer, followed by Förster transfer to QAD. However, this influence is rather small because the penetration depth of holes into the EML is rather low and the generation rate in the undoped part of the EML is accordingly low. Moreover, the excitons formed in the undoped part of the emitting layer can either decay inside the layer or, if they diffuse towards the cathode, may be quenched at metal atoms that have diffused into the organic layer.
The concentration profiles for excitons are compared for diodes with undoped and doped Alq₃ layer in Figure 4.39. Here, the curve for the undoped case decays exponentially with the distance from the NBP/Alq₃ interface. The slope is a result of the diffusion of mobile excitons, which are created close to the interface. When emissive dopants are introduced, the profile is more uniform. The reason for this is that we assumed that QAD forms more deep traps for electrons than for holes. Therefore, the ratio of mobilities is changed in favour of the hole mobility, leading to a larger penetration depth of holes into the EML and a correspondingly higher probability for exciton creation directly on QAD deep in the EML. The fact that we observed a decrease in efficiency when we reduced the thickness of the QAD doped region below 35nm is an experimental hint that this assumption about relative trap depths is qualitatively correct: With a ratio of electron and hole mobility as in undoped Alq₃ and the exciton diffusion length being low due to the doping, we would end up with a very sharp exciton profile, and 5 to 10 nm of QAD doping would be enough to get the full efficiency.
Figure 4.39  Distribution of the total concentration of excitons on either Alq₃ or QAD for diodes with and without QAD doping in the 35 nm of the emission layer next to the interface of NPB and Alq₃.
5. Organic solar cells

In this chapter, we introduce a numerical model to simulate optical and electrical properties of organic photovoltaic devices. The optical field distribution is calculated using a matrix method in terms of the complex index of refraction. The current generation is calculated by solving two rate equations for excitons and charge carriers. We present results of the numerical simulation for solar cells with various types of P-I-N structures. The influence of critical parameters on the photovoltaic conversion is shown, with particular attention on the interface recombination of dissociated charge carriers in cells based on flat heterojunctions and recombination processes in the blend layer of bulk heterojunction cells. The comparison of simulations with experimental results is described in the Section 5.3. We show that the linear dependence of short circuit current on illumination intensity can be reproduced by our numerical model either by introducing trap mediated non-geminate recombination or field-dependent geminate recombination.

5.1. Numerical model of organic solar cells

The photoresponse of vacuum-deposited heterojunction or bulk-heterojunction devices can be accurately modelled by including the optical properties of the thin-film multilayer structure while simultaneously solving the equations governing exciton and free carrier transport. The primary process for generation of photocurrent in an organic photovoltaic device is the generation of excitons by absorption of photon energy from the optical electric field. Once created, the excitons have a lifetime determined by recombination through radiative or non-radiative decay or by dissociation into free charge carriers. The desired process, to make charge collection possible, is the dissociation of the exciton into free charge carriers. The dissociation can be forced by an electric field or by interaction of the excitons with molecular interfaces, impurities, or defects where charge transfer can occur. Since the diffusion range of the excitons is limited, only those excitons within the diffusion range of the dissociation sites will contribute to the photocurrent. In case of a bulk-heterojunction, all excitons are assumed to reach the dissociation centers, as the typical diameter of single-component domains in the blend material is considered to be shorter than the diffusion length of excitons. However, losses occur during the transport of free electrons and holes, which move within the mixed organic layer in opposite directions and can recombine. On the other hand, for cells based on flat donor-acceptor-heterojunctions as introduced by Tang [2], the generation and recombination of carrier pairs takes place only at the interface, thus the recombination losses are considerably lower compared to bulk-heterojunctions. Here, however, the
limiting factor is the diffusion length of excitons, which must reach the interface in order to
dissociate into free carriers. When short circuited, the main driving force for transport in
both devices is drift in the electric field of the heterojunction. The diffusion process starts
to play a more important role only close to the open circuit voltage.

5.1.1. Optical modeling of exciton generation profile

A number of studies have employed different models to describe photovoltaic
action spectra [168-179]. Harrison, Grüner, and Spencer give a thorough description of
some of these models. A common feature of the models is the assumption that the
intensity of the optical electric field is assumed to decrease exponentially along the
direction of propagation inside the device structure. Given this assumption, reflection at
the front surface of the device and the optical mode structure inside the device are
neglected. Such models will therefore only give an appropriate description in the case of a
single layer that is thick compared to the penetration depth of light. However, interference
effects become important for thin film structures where layers are thin compared to the
penetration depth of the incident light and where a highly reflecting interface such as a
metal electrode is present in the device.

Many different approaches are possible in order to obtain the distribution of the
electromagnetic field for multilayer systems. An elegant model is to employ the transfer
matrix formalism [61,62,181-184] in a one-dimensional system, in which the amplitude of
the electromagnetic field vector is calculated by taking into account the optical constants \( n \)
and \( k \). In the following brief introduction into the theory, we largely follow reference [62].
The solar cell structure is described by 2 x 2 matrices, where both the forward and
backward propagation of the electric field vector are included assuming isotropic and
homogeneous media and plane parallel interfaces. The absorption of light waves inside
the multilayer structure can be obtained from the calculation of the amplitude of the
electric field. The propagation of a plane wave incident from the left at a multilayer
structure having \( m \) monolayers between a semi-infinite transparent ambient and a semi-
infinite substrate is described in Figure 5.1. The optical properties of each monolayer are
described by the complex index of refraction \( n' = n + ik \), which is a function the wavelength of
the incident beam. At any monolayer with thickness \( d_j \), the optical field consists of two
components of the optical wave: propagation in the positive direction \( x \), and in the
opposite one, denoted by \( E_j^+(x) \) and \( E_j^-(x) \), respectively.
The changes of electric field in the organic system are described by two matrices corresponding to the propagation of the optical waves through the interface between two adjacent layers and the changes upon propagation through the layer. The phase matrix $L_j$ describing the absorption and the phase shift inside layer $j$ reads

$$L_j = \begin{bmatrix} e^{-i\xi_j d_j} & 0 \\ 0 & e^{i\xi_j d_j} \end{bmatrix},$$

(5.1)

where

$$\xi_j = \frac{2\pi}{\lambda} q_j$$

(5.2)

is the phase thickness of a certain layer corresponding to the phase change for wavelength $\lambda$. At an interface between layer $j$ and $k$, the interface matrix $I_{jk}$ describing the propagation of the optical field reads

$$I_{jk} = \frac{1}{t_{jk}} \begin{bmatrix} 1 & r_{jk} \\ r_{jk} & 1 \end{bmatrix},$$

(5.3)
where \( r_{jk} \) and \( t_{jk} \) are the complex Fresnel coefficients for refraction and transmission at the interface \( jk \). The complex reflection and transmission coefficients for light with normal incidence are given by

\[
\begin{align*}
    r_{jk} &= \frac{n_j - n_k}{n_j + n_k}, \\
    t_{jk} &= \frac{2n_j}{n_j + n_k}.
\end{align*}
\]  

(5.4)

(5.5)

The transfer matrix \( S \) for the total system, which relates the electric field at the ambient side with the field at the substrate side

\[
\begin{bmatrix}
E_0^+ \\
E_0^-
\end{bmatrix}
= \begin{bmatrix}
E_{m+1}^+ \\
E_{m+1}^-
\end{bmatrix},
\]

(5.6)

is calculated by using the interface and phase matrix

\[
S = \begin{bmatrix}
S_{11} & S_{12} \\
S_{21} & S_{22}
\end{bmatrix} = \left( \prod_{v=1}^{m} I_{(v-1),L_v} \right) I_{m(m+1)},
\]

(5.7)

By using the matrix elements of \( S \) and plugging \( E_{m+1}=0 \) into equation (5.9) (i.e. no light incident from the backside), one can express the complex reflection and transmission coefficients as

\[
R = \frac{E_0^-}{E_0^+} = \frac{S_{21}}{S_{11}},
\]

(5.8)

\[
T = \frac{E_{m+1}^+}{E_0^+} = \frac{1}{S_{11}}.
\]

(5.9)

To determine the electric field within layer \( j \), we note that the total multilayer transfer matrix can be expressed as

\[
S = S_j' L_j S_j^*,
\]

(5.10)
where $S'_j$ is the transfer matrix for the system on the left of layer $j$ (see Figure 5.1), defined as

$$
\begin{bmatrix}
E^+_0 \\
E^-_0
\end{bmatrix} = S'_j \begin{bmatrix}
E'^+_j \\
E'^-_j
\end{bmatrix}
$$

(5.11)

with

$$
S'_j = \begin{bmatrix}
S'_{j11} & S'_{j12} \\
S'_{j21} & S'_{j22}
\end{bmatrix} = \left( \prod_{r=3}^{j-1} I_{(r-1)} \right) I_{(j-1)j},
$$

(5.12)

where $E'^+_j$ and $E'^-_j$ refer to the left interface $(j-1)/j$ of layer $j$ and $S''_j$ is the transfer matrix for the system on the right of layer $j$, defined as

$$
\begin{bmatrix}
E''^+_j \\
E''^-_j
\end{bmatrix} = S''_j \begin{bmatrix}
E''^+_{m+1} \\
E''^-_{m+1}
\end{bmatrix}
$$

(5.13)

with

$$
S''_j = \begin{bmatrix}
S''_{j11} & S''_{j12} \\
S''_{j21} & S''_{j22}
\end{bmatrix} = \left( \prod_{r=1}^{m} I_{(r-1)} \right) I_{(m+1)},
$$

(5.14)

where $E''^+_j$ and $E''^-_j$ refer to the right interface $j/(j+1)$ of layer $j$. Also for the partial systems $S''_j$ and $S'_j$, it is possible to define complex reflection and transmission coefficients for layer $j$ in terms of the matrix elements

$$
r'_j = \frac{S'_{j21}}{S'_{j11}}, \quad t'_j = \frac{1}{S'_{j11}}, \quad r''_j = \frac{S''_{j21}}{S''_{j11}}, \quad t''_j = \frac{1}{S''_{j11}}
$$

(5.15)

Combining Equations 5.8-5.15, an internal transfer coefficient which relates the incident plane wave to the internal electric field propagating in the positive $x$ direction in layer $j$ at interface $(j-1)/j$ can be derived as

$$
t'_j = \frac{E'_j}{E'_0} = \frac{t'_j}{1 - r'_j r''_j e^{i2\phi_j}},
$$

(5.16)
where $r_j^- = \frac{S_{ji2}^*}{S_{ji1}^*}$. An internal transfer coefficient which relates the incident plane wave to the internal electric field propagating in the negative $x$ direction in layer $j$ at interface $(j-1)/j$ can also be derived as

$$
t_j^- = \frac{E_j^-}{E_0^+} = \frac{t_j^* r_j e^{i2\xi_d j}}{1 - r_j^* r_j e^{i2\xi_d j}} = t_j^* r_j e^{i2\xi_d j}.
$$  \hspace{1cm} (5.17)

Using the two above equations, the total electric field in an arbitrary plane in layer $j$ at a distance $x$ to the right of boundary $(j-1)/j$ in terms of the incident plane wave $E_0^+$ is given by

$$
E_j(x) = E_j^+(x) + E_j^-(x) = \left( t_j^* e^{i\xi_d j} + t_j e^{-i\xi_d j} \right) E_0^+ = t_j^* \left( e^{i2\xi_d j} + r_j e^{-i2\xi_d (j-1)} \right)
$$  \hspace{1cm} (5.18)

for $0 < x < d_j$. The expression in Equation 5.18 can also be expressed in terms of the matrix elements of the partial system transfer matrices as

$$
E_j(x) = \frac{S_{ji1}^* e^{-i\xi_j (d_j - x)}}{S_{ji1}^* S_{ji2}^* e^{i2\xi_d j} + S_{ji2}^* S_{ji3}^* e^{i2\xi_d j}} E_0^+.
$$  \hspace{1cm} (5.19)

The time average of the energy absorbed per second and position interval in layer $j$ at the position $x$ at normal incidence is proportional to the modulus square of the electric field, the absorption coefficient $\alpha$ and the refractive index

$$
Q_j(x) = \frac{1}{2} c \varepsilon_0 \alpha_j n_j |E_j(x)|^2
$$  \hspace{1cm} (5.20)

with

$$
\alpha_j = \frac{4\pi \cdot k_j}{\lambda}.
$$  \hspace{1cm} (5.21)

The transparent glass substrate must be treated with special care in the model calculations of our device structure. This was accomplished by calculating the resultant transmission through the glass substrate by summation of the transmitted intensities at various wavelengths instead of dealing with the complex amplitudes.
For comparison, the absorption profile in the whole solar cell structure can also be calculated with a crude approximation using the Lambert-Beer’s law

\[ Q(x) = \alpha \cdot I_0 \exp(-\alpha \cdot x), \]  

(5.22)

where \( I_0 \) is the initial intensity of light and \( x \) denotes the position in the layer structure. To account for the light which is reflected at the metal electrode and propagates once again through the active layer, we add a second term similar to Equation 5.22, where \( I_0 \) is replaced by the reflected light intensity and \( x \) is replaced by \( d-x \). However, in this approximation, the optical mode structure inside the photovoltaic cell is neglected.

### 5.1.2. Charge carrier generation from excitons in heterojunction and bulk-heterojunction solar cells

The generation of excitons directly depends on the photon absorption profile, which consequently influences the photocurrent of the devices. Light absorption in organic materials almost always results in the production of a mobile excited state rather than a free electron-hole pair [185]. This occurs for two reasons: (i) the dielectric constant of organic materials is usually low, the attractive Coulomb potential between electrons and holes is stronger and (ii) the non-covalent electronic interactions between organic molecules are weak (narrow band width), the electron wave functions are spatially restricted, allowing it to be localised in the potential well of its conjugate hole (and vice versa). Therefore, a tightly bound so-called Frenkel exciton is the usual product of light absorption in organic materials [73]. It is a mobile, electrically neutral quasi particle, the motion of which is unaffected by electric fields.

A general mechanism for efficient photoconversion is the interfacial dissociation of excitons at the interface between different molecules (molecular heterointerface) into a free electron on the acceptor-type material and a free hole on the donor-type material. Excitons must first move to the heterointerface, usually via diffusion (Föster transfer) or relaxation to lower-energy states in disordered materials, and then dissociate. An efficient dissociation of neutral excitons into geminate pairs of charge carriers can take place at the interface between two kinds of molecules, if the energy of local Frenkel excitons is higher for both materials than the energy of a charge transfer (CT) exciton comprising a hole on the donor and an electron on the neighbouring acceptor molecule. In this case, the charge separated state is the excited state with the lowest energy of all possible excited states in vicinity of the interface. This implies that the offset of both the highest occupied and lowest unoccupied molecular levels (HOMO and the LUMO levels) of the two materials is higher
than the difference in exciton binding energy between Frenkel and CT excitons. For the blend system ZnPc / fullerene C\textsubscript{60} chosen for the following studies, this criterion is fulfilled.

In agreement with the almost complete quenching of luminescence that is mostly observed in such blend layers (compare, e.g., the work of Loi et al. and Hope et. al. [186,187] on films of covalently linked ZnPc-fullerene dyads), we assume that the quantum yield for the generation of geminate charge carrier pairs from excitons at the donor-acceptor-heterointerface is unity.

**Figure 5.2** Processes leading to the creation of free carrier pairs in bulk-heterojunction cells:

(i) absorption of photons and creation of excitons,
(ii) dissociation of exciton into geminate carrier pair at molecular interface
(iii) drift of charge carriers in the field of the junction, competing with recombination

For both bulk-heterojunction and heterojunction cells, the generation of excitons is predicted from the above mentioned one-dimensional optical model or by the Lambert-Beer law. In the case of bulk-heterojunctions, the main absorption of electromagnetic waves occurs in the blend-layer and contributes more or less efficiently to the generation of photocurrent (Figure 5.2). The doped wide gap materials absorb some photons too, but the lifetime of formed excitons is very short due to the quenching mechanism between excitons and a high concentration of dopants and free holes or electrons. In the blend-layer, due to the diffusion length of excitons being longer than the typical distance to the nearest molecular heterointerface, the favoured mechanism is the dissociation of excitons into geminate carrier pairs and not the quenching or decay processes. The question
whether or not these *geminate* pairs can be efficiently dissociated into *free* carrier pairs will be discussed later.

For bulk-heterojunctions, the generation profile for electron-hole pairs can be deduced directly from the generation profile of excitons assuming that the lifetime and thus the diffusion length of Frenkel excitons in blend layers is very low. Consequently, we have assumed that there is no exciton diffusion.

For a flat heterojunction, however, the main absorption which governs the photocurrent takes place in two pure layers, which may be embedded between p- and n-doped wide gap layers (p-i-i-n junction). Similar to the bulk-heterojunction, the creation of excitons in these two layers with dopants does not have a significant impact on photocurrent and it is not considered. Excitons formed in the pure layers only contribute to the efficiency of the solar cell if they can reach the interface by diffusion motion and dissociate into free carriers, see Figure 5.3. Since the organic heterointerface is not a sharp borderline between two molecularly flat layers, we assume that a thin blend layer of about 3 nm thickness exists, where, similar to the bulk-heterojunction case, the generation of free carriers corresponds to the absorption profile and field-dependent recombination losses may occur.

*Figure 5.3*  
*The processes leading to the creation of free carrier pairs in flat heterojunction cells:*

(i) absorption and formation of excitons,
(ii) diffusion of excitons,
(iii) reflection at the interface of the wide gap material,
(iv) charge separation at the heterojunction, and
(v) drift in the field of the junction (recombination only at interface).
Our model in principle follows the model of Ghosh and Feng [168] where exciton diffusion is described by the standard diffusion equation. However, in our case, the model is extended to take into account the distribution of the total exciting optical electric field inside the thin film structure, including interference effects. Also, quenching effects and dissociation of excitons in the 3nm thick interface layer are implemented in the rate equation. The rate equation for excitons formed in pure layers amounts to

\[
\frac{\partial s(x,t)}{\partial t} = G(x) - \frac{s(x,t)}{\tau_s} + D_s \frac{\partial^2 s(x,t)}{\partial x^2} - R_q
\]

(5.23)

where \(s\) is the exciton density and \(G(x)\) is the generation profile calculated from the optical model. The decay of excitons is represented by the second term of Equation 5.23 and it is determined by a lifetime \(\tau_s\) of excitons and by quenching processes with free electrons or holes characterized by a rate constant \(R_q\). It turns out, however, that none of these non-linear quenching processes involving two excited species plays a significant role for light intensities on the order of the sun or lower. Finally, the diffusion coefficient \(D_s\) decides about the diffusion velocity of the excitons. In the one-dimensional model examined here, this coefficient equals \(D_s = \frac{L^2}{\tau_s}\), where \(L\) denotes the average free path of excitons; the diffusion range of excitons is not dependent on excitation energy (wavelength) because all higher excited states rapidly relax into the lowest singlet exciton state. The creation of free carriers at the interface between two organic materials is described in mathematical calculations by the boundary conditions for the diffusion process. For instance (see Figure 2.3), the excitons reaching the interface from left side will dissociate into free electrons on the right side (inside the interfacial blend layer) and holes will stay on left side, where the generation rate for free carriers equals the rate for excitons reaching the interface by diffusion from the left side. Because all excitons are assumed to dissociate, a diffusion of excitons through the interface is not taken into consideration. For the case of interfaces of intrinsic photoactive layers with doped organic materials, one can distinguish two situations: (i) if the exciton energy of the transport material is greater than the exciton energy in the photoactive layer, the excitons are reflected from the interface until equilibrium is reached, and (ii) if the opposite is true, the excitons can diffuse inside the doped material where they are rapidly quenched by free carriers or dopants.

In our laboratory, bulk-heterojunction cells are prepared including an additional thin intrinsic layer of \(C_{60}\) between the blend layer and the electron transport layer to avoid diffusion of dopant molecules into the blend layer. As this layer can also contribute to the
photocurrent generation, the rate equation for exciton diffusion (Equation 5.23) is also implemented into the numerical model for these diodes. The creation of additional free carriers takes place at the interface of the blend layer and the thin pure layer.

5.1.3. Transport and recombination of carriers in photovoltaic devices

As mentioned above, the generation occurs in the blend layer while the p- and n-doped layers have a wide band gap, i.e., they are almost transparent for visible light. They serve as an optical spacer layer between the active layer and the contacts and, due to their high conductivity; they can transport the carriers to the contacts with low ohmic losses. Furthermore, the high doping level guarantees good quasi ohmic contact behaviour, almost independently of the actual work function of the contacts by tunneling [3].

The electrical properties of such diodes can be modelled using a self-consistent numerical solution of the Poisson and the continuity equations. The numerical simulation is based on a quasi-one-dimensional iteration algorithm, which was used to analyse the electrical effects in organic light emitting diodes in Chapter 4, where the organic multilayer is described as a stack of discrete monolayers between an anode and a cathode (Figure 2.2 and 2.3). Assuming an initial distribution of carriers, the field distribution is calculated according to Poisson’s equation. Then, the carrier transport is calculated for a given time step making use of the continuity equation, which yields a new carrier concentration profile after the time step. This procedure is repeated until a steady state is reached. The numerical routines described in Section 3.1 also allow the simulation of photoelectrical properties of bulk-heterojunction and heterojunction structures.

The creation of charge carriers $G(x)$ is calculated from the above mentioned optical model for the special structure of solar cells, including the rate equation for excitons. For the bulk-heterojunction, the main dissociation of excitons occurs within the whole blend layer, for the heterojunction only at the interface. Both electrons and holes coexist close to the interface and in the active blend-layer: Only there, they are able to recombine, favoured by the attractive Coulombic interaction between oppositely charged carriers. The magnitude of recombination is proportional to the concentration of recombining charges. Because electrons as well as holes can be trapped, there exists another path of recombination between free and trapped carriers. The rates of both direct recombination (between free electrons and holes) and indirect recombination (between trapped and free carriers) is proportional to the concentrations of the respective types of carriers.
\[ R_{n-p}(x,t) = \gamma_{n-p} n_f(x,t) p_{f,or,x}(x,t), \quad (5.24) \]

\[ \gamma_{n-p} = \frac{q\mu_n(F,T)}{\varepsilon\varepsilon_0}. \quad (5.25) \]

For indirect recombination, we assume that the factor \( \gamma_{n-p} \) follows Equation 5.25, which is based on the Langevin theory [122]. For direct recombination, we cannot use the Langevin theory because it assumes that carriers recombine whenever they meet. This, however, is not the case in photoactive blend layers where recombination seems to be at least partly suppressed. One approach to understanding this phenomenon was recently put forward by Arkhipov, and is based on assuming an interplay of hole delocalisation and ground state interface dipoles [188]. The details of the mechanism are not yet well understood. We therefore treat the cross section for direct recombination as a free parameter.
5.2. Model calculations for various device architectures

Several approaches to designing organic solar cells have been proposed in the last few years. One may split them in two basic concepts for realization. As a first basic concept, the so-called bulk heterojunctions were successfully developed for various systems for both small molecules and polymers [7,33,37,36,61]. Here bulk-generated charge carriers need to percolate within the bulk blend towards their specific electrodes. Typically mixing of the two compounds reduces the charge carrier mobility and raises the risk of recombination especially for thick blend layers. Accordingly, blend layers with low thickness are typically used which suffer from incomplete optical absorption. In the second case, highly purified more or less ordered layers of donor-type and acceptor-type materials are stacked on each other and create basically a heterojunction device [31,35,61]. The dissociation of excitons into free carriers takes place at the interface between two organic materials. Here, the limitation factor is the exciton diffusion and interface recombination, which allows only a small part of the excitons to be converted into pairs of free carriers. Both systems can be simulated by the optical and the electrical model, which is described in Sections 3.1 and 5.1. The model calculations presented in the following will give more information about the critical processes and parameters, and may serve as a tool for a future improvement of devices.

5.2.1. Bulk-heterojunction cells

The first modelled structure is the bulk-heterojunction, the working principle of which has been introduced above (cp. Figure 5.2). The energy levels of the material used for the following model calculations are summarized in Figure 5.4. Here, the individual layer thicknesses are 50 nm for the n- and p-doped transport layers and 30 nm for the active blend layer. Optionally, a 10nm thick layer of pure C$_{60}$ is inserted between the blend layer and the n-doped layer. Because the transport layers are doped, the contact with both electrodes can be assumed as ohmic [3]. Thus the boundary conditions are supposed as in Section 2.3.1. For the electron mobility in the n-layer and the hole mobility in the p–layer, we assume $2 \times 10^{-5}$ cm$^2$/V*s and $8 \times 10^{-5}$ cm$^2$/V*s, respectively, together with an assumed number of dopants in both layers of $10^{18}$ cm$^{-3}$. Here, the conductivities are that high that the voltage drop over these layers is almost negligible and they are not the main limiting factor for the current flow.
For the active blend layer, we assume mobility values of $2.5 \times 10^{-6}$ cm$^2$/Vs for holes on ZnPc and $5 \times 10^{-6}$ cm$^2$/Vs for electrons on C$_{60}$. For every mobility, a dependence on electric field is assumed according to Equation 3.5 with the parameter $\beta_{PF} = 2 \times 10^{-3}$ (cm/V)$^{1/2}$. However, this field dependence hardly influences the current density due to the low electric field. In the photoactive blend layer, we calculate the generation profile of charges resulting from the absorption of white light with an intensity of 127 mW/cm$^2$ using the optical model (see Figure 5.5). The other parameters describing the active layer properties, such as concentrations of traps and recombination rates, are varied in certain ranges.

The distribution of free and trapped carriers as a function of position within the device is presented in Figure 5.6. Since ohmic contacts are assumed, the number of free carriers in the doped wide gap materials is uniform and equal to the number of dopants. However, close to the heterojunction interfaces with the intrinsic active layer, depletion zones are formed due to diffusion of free majority carriers from the doped layers into the intrinsic layer. The profile of free carrier concentration within the active layer is established from the balance of recombination, generation, trapping and transport. In short circuit conditions, the flow of free carrier out of the active layer is mainly field driven. The observed difference between hole and electron distribution in Figure 5.6 is a consequence of the different hole and electron mobilities.
Figure 5.5  Generation profile of free carriers calculated by the optical model for a bulk heterojunction cell without pure C$_{60}$ interlayer. The excitons formed in the 50 nm thick doped transport layer do not contribute to the photocurrent; only in the 30 nm thick blend layer, carriers are created.

Figure 5.6  Distribution of free and trapped charges without external voltage for photodiode under illumination. The transport layers are 50 nm thick and have concentration of dopants of $10^{18}$ cm$^{-3}$. The intrinsic layer absorbing the light is 30 nm thick and comprises hole and electron traps with a concentration of $10^{18}$ cm$^{-3}$ each.

For the active layer, the traps are described by two discrete levels for holes and electrons, respectively, with trap concentrations equal to $10^{18}$ cm$^{-3}$ and energetic depth of 0.45 eV.
Despite of the lower free carrier concentration in the active layer due to drift under short circuit condition, the concentration of occupied trap states close to the n-layer and p-layer, respectively, is large for the respective carrier type. In these regions, the probability that a trap captures a carrier is high due to the high number of electrons and holes, which move to the respective transport layers. These trapped charges and the uncompensated dopant ions in the depletion zones lead to the electric field distribution shown in Figure 5.7. The electric field in the bulk of the transport layers and at the electrodes is close to zero due to the implementation of dopants and the accordingly high ohmic conductivity in the wide gap transport layers.

The concentration of traps also strongly influences the value of the current density at both positive and negative bias. This dependence is shown in Figure 5.8 at trap densities ranging from $10^{16}$ to $10^{19}$ cm$^{-3}$. At the lowest trap concentrations, the current density rapidly reaches saturation due to low losses in the active layer. For the forward current characteristics, the observed current is unchanged up to trap concentrations of $10^{18}$ cm$^{-3}$. However, in this range of trap concentrations, the current in the reverse direction is limited by indirect recombination, while at forward bias, direct and indirect recombination rates are comparable. For the highest concentrations, the current is limited in the whole range of bias. Here, the forward current suffers from space charge limitation associated with low effective mobilities in the blend layer.

![Figure 5.7](image)

*Figure 5.7*  Spatial distribution of electric field calculated for a solar cell under illumination of 127 mW/cm$^2$ at short circuit condition. The simulation was made with the electrical parameters for the structure in Figure 5.4.
Figure 5.8 IV-characteristics with two discrete levels of traps for electrons and holes with energetic depth of 0.45 eV. The concentration of trapping states varies from $10^{16}$ to $10^{19}$ cm$^{-3}$.

For most cells prepared in our labs, we find that the short circuit photocurrent scales linearly with light intensity. We can therefore rule out direct non-geminate recombination as a relevant process under short circuit conditions as this would lead to a sublinear scaling. Now the question arises if this already means that the mechanism is insignificant for the complete IV-characteristics. In Figure 5.9, we show a set of simulations, which includes once again a trap density of $10^{18}$ cm$^{-3}$ and varying cross sections $\gamma_{nf-pf}$ for direct non-geminate recombination (cp. Equations 5.24 and 5.25). It is obvious from the graph that in a certain range of $\gamma_{nf-pf}$ values, the fill factor already suffers from direct recombination losses, while open circuit voltage and short circuit current are hardly affected. Consequently, one has to check not only the scaling of short circuit current, but also the evolution of the fill factor with light intensity, if one wants to decide whether or not direct non-geminate recombination plays a role in a given solar cell. It is interesting to note that the different recombination conditions also influence the forward part of the IV-characteristics by varying the steady state carrier concentration in the blend layer: Fast indirect non-geminate recombination, e.g., will reduce the free carrier concentration and thus the space-charge limited current density at a given forward bias. A similar influence can be expected from the indirect non-geminate recombination. Nevertheless, this influence is noticeable only when concentrations of injected free carriers are comparable with trap concentrations. With increasing injection of free carriers, both recombination rates increase, but the indirect recombination starts to become
dominant. When all trap states are occupied, the indirect recombination increases linearly with injection, while direct recombination changes according to a square law, depending on both free electron and holes concentrations. Therefore, for positive current, the direct non-geminate recombination begins to become dominant. This is demonstrated by comparing the rates for direct and indirect non-geminate recombination with the generation of free carriers by light within the whole blend layer (Figure 5.10). This simulation corresponds to the IV-characteristics from Figure 5.9 for the cross section $\gamma_{nr} = 10^{-12} \text{ cm}^3/\text{s}$. In addition, at positive currents, the low generation rate compared to both recombination rates proves that the number of injected free carriers exceeds that of generated free carriers. For voltages closer to short circuit conditions, the direct non-geminate recombination becomes negligible compared to indirect processes and the reverse part of IV-characteristic is modulated only by indirect non-geminate recombination. Therefore, the proper trap concentration can be found by fitting the results of numerical simulations to experimental IV-characteristics.

![Figure 5.9](image)

**Figure 5.9**  
Current density as function of voltage assuming different cross sections for direct recombination of carriers inside the blend-layer. The concentration of traps, i.e. centers for indirect recombination, is kept constant at $10^{18} \text{ cm}^3$. 

The $\gamma$ factor

- $\gamma = 10^{-12} \text{ cm}^3/\text{s}$, FF=41
- $\gamma = 10^{-13} \text{ cm}^3/\text{s}$, FF=45.5
- $\gamma = 10^{-14} \text{ cm}^3/\text{s}$, FF=46
5.2.2. Heterojunction cells

The operation principle of p-i-i-n diodes with a flat heterojunction between the two intrinsic layers has been introduced above (compare Figure 5.3). For the simulation, we assume the energy level alignment summarized in Figure 5.11. Here, the creation of free carriers takes place at the interface between the intrinsic layers I and II. The transport of photogenerated electrons from the active interface to intrinsic I layer is forbidden by a high energetic barrier of 0.7 eV. Similarly, transport of holes in the right direction is hindered by a barrier of 0.9 eV. Thus, current density in forward direction is determined mainly by direct and indirect recombination processes at the interfaces. The free charge carriers created by dissociation of excitons at the interface drift in the electric field of the heterojunction, which is proportional to the built-in potential, and contribute to the current in reverse direction of the diode. Due to low energetic barriers at electrodes, the contacts are assumed to be Ohmic. The simulation is performed for a dopant concentration of $10^{18}$ cm$^{-3}$ and mobilities of $2\times10^{-5}$ cm$^2$/V*s and $8\times10^{-5}$ cm$^2$/V*s for holes in the p-layer and electrons in the n-layer, respectively. These mobility values are used for holes in the intrinsic layers I and electrons in the intrinsic layer II, as well. However, the conductivity of these layers is lower than for the transport layers due to the rather wide gap (>1.5eV) of the used materials and the absence of doping. This assumption is in agreement with experimental observation [71], where the pure materials have considerably higher mobility.

Figure 5.10  Rates for direct and indirect recombination at different applied bias, compared to the generation rate for excitons generated by light in the blend using the parameters $\gamma_{nf\text{-}pf} = 10^{-12}$ cm$^3$/s and $N_t=10^{18}$ cm$^{-3}$. 
than the mixture. As introduced in Section 5.1.2, the interface between the two intrinsic layers is assumed not to be molecularly flat and it is therefore implemented as a thin blend layer with the mobilities of $2.5 \times 10^{-6}$ cm/V*s for holes and $5 \times 10^{-6}$ cm/V*s for electrons as for bulk heterojunction cells. The thickness of the particular layers is assumed to be 50 nm for the p- and n-layer and 20 nm for both intrinsic layers. The interfacial blend layer is assumed to be 3 nm thick. The optical absorption profile in the active part of the solar cell is drawn in Figure 5.12, where we have used the $n$ and $k$ values from MeO-TPD as p-wide gap material, ZnPc as intrinsic layer I, ZnPc:C$_{60}$(1:1) as interfacial blend layer, C$_{60}$ as intrinsic layer II and n-wide gap material and Al as a reflective anode [37]. For this structure, the highest absorption occurs in intrinsic layer I and in the interface layer, while the generation rate for excitons in intrinsic layer II is about 2.5 times lower. The transport of excitons in the active parts of the cell is defined by diffusion lengths of 10 nm for both materials and the life time is supposed as 10 ns [73], which allows only a portion of the excitons to reach the dissociation interface.

Figure 5.11 Schematic diagram of energy levels for the different layers used in electrical simulation of p-i-i-n cells with a flat photoactive heterojunction between the intrinsic layers. The values of HOMO and LUMO and work function refer to the same materials used in bulk-heterojunction cells (see Figure 5.4): cathode: ITO, p-layer: p-doped MeO-TPD, intrinsic layer I: ZnPc, intrinsic layer II: C$_{60}$, n-layer: n-doped C$_{60}$ and anode: Al.
Figure 5.12  Absorption profile of photons in a p-i-i-n diode under illumination by 127 mW/cm² white light. The particular layers correlate with the materials in Figure 5.11.

The low generation of free carriers from exciton generation in intrinsic layer II has two origins, namely the low absorption coefficient of C₆₀ in the visible range and the possibility that excitons can diffuse to the n-doped layer where they are rapidly quenched by free carriers or dopants. On the other hand, the interface between the p-layer and intrinsic I layer is supposed to reflect the excitons due to the wide gap of the p-layer (see Figure 5.11). The electric field and distribution of free carriers are presented in Figure 5.14 and Figure 5.13, respectively, under short circuit conditions. Trap states are supposed only in the thin interfacial blend layer and are omitted in Figure 5.13. Only in this layer, all absorbed photons can immediately dissociate into free holes and electrons, but both mobilities are lower than for the pure materials, which is reflected in higher charge carrier concentrations in the center of the heterojunction. The low concentration of holes on the right hand side of the interface and of electrons on the left hand side result from energetic barriers. Additionally, the negative electric field favours a drift of the photogenerated carriers in the respective opposite direction. The electric field at the heterojunction in the absence of applied bias changes only insignificantly between the two intrinsic layers (see Figure 5.14). The reason is the fact that the high mobility in the active layers, excluding thin interfacial layer, prevents the accumulation of free carriers.
Figure 5.13  Distribution of free holes and electrons in a p-i-i-n diode without applied bias.

Figure 5.14  Electric field distribution under identical conditions.

The influence of the cross section for direct recombination on the properties of heterojunction cells ($FF$, $I_{sc}$ and $V_{oc}$) is displayed in Figure 5.15. With increasing recombination losses in the interfacial blend layer, all variables are reduced as in the case of the bulk-heterojunction cells (Figure 5.9). The most pronounced reduction of 28% is observed for the fill factor when the factor $\gamma_{nf-pf}$ is increased by two orders of magnitude while $J_{sc}$ as $V_{oc}$ only vary by approximately 8% and 15%, respectively.
Figure 5.16 presents the absorption of photons within the heterojunction diodes with varying thickness of intrinsic layer I. The changing thickness is reflected by changing current density as shown in Figure 5.17: By implementation of a narrower active layer (intrinsic I), the photodiode becomes optically thinner, which reduces filtering losses of the light on its way to the active interface, leading to a higher differential absorption directly at the active interface (Figure 5.16). Moreover, for low thickness of the intrinsic layer I, excitons which are reflected at the interface to the p-doped wide gap layer have a higher probability to reach the active interface before recombination. This process leads to the maximum photocurrent for approximately 5nm thickness, since the diffusion length for the excitons is assumed to be 10 nm.

Figure 5.15 FF, $V_{oc}$ and $J_{sc}$ for different scattering cross sections of the direct recombination between free charge carriers in the interfacial blend layer.
Figure 5.16 Absorption profiles at different thickness of intrinsic layer I, varied from 5 nm to 30 nm, using identical parameters for material properties and residual thicknesses, under illumination with 130 mW/cm$^2$ white light.

Figure 5.17 Current-voltage characteristics for four different thicknesses of the intrinsic layer I.

This trend is true both for the short circuit photocurrent and the saturation photocurrent at negative bias. In fact, the photocurrent is already close to saturation for all thicknesses, i.e. recombination losses at zero bias are negligible and the differences in photocurrent are exclusively associated with a different flux of excitons reaching the active interface. However, changes in thickness are reflected in changing $FF$ values (Figure 5.18) where the favoured thickness is about 10 nm. For larger thicknesses, we
find lower values for the FF because the electric field at given bias is reduced, leading to more pronounced recombination losses at bias values close to $V_{oc}$. As expected, the value of $V_{oc}$ remains nearly constant for all thicknesses of the intrinsic layer I.

![Figure 5.18](image)

**Figure 5.18** FF, $V_{oc}$ and $J_{sc}$ for heterojunction devices with different thickness of intrinsic layer I.

### 5.2.3. Comparison of heterojunction and bulk-heterojunction cells

Photovoltaic diodes based on the two basic concepts introduced above are compared, both with 43 nm thick active layers. For the bulk heterojunction cell, this thickness refers to the thickness of the blend layer. In case of the heterojunction, the thickness of the two intrinsic absorption layers are 20 nm each and the interfacial blend layer is assumed to be 3 nm thick. Similarly to the above discussion, we use about one order of magnitude higher carrier mobilities for pure layers as compared to the blend layer, which is expected to be more disordered. Moreover, similar absorption profiles are guaranteed by placing the centres of the blend layer (for the bulk-heterojunction cell) and the photoactive interface (for the heterojunction cell) in the same position with respect to the reflecting electrode (Figure 5.19). In both simulations of bulk-heterojunction and heterojunction, we assume the same conductivity values and the same thicknesses of transport layers, and we assume ohmic contact behaviour. The cross sections for recombination processes are assumed to be identical in the blended parts of the solar cells. The factor $\gamma_{0-0}$ for direct recombination is set to $10^{-12}$ cm$^3$/s and the density of deep traps (centers for indirect recombination) is assumed to be $10^{18}$ cm$^{-3}$. 

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Figure 5.19 Comparison of exciton generation profiles for a bulk heterojunction (p-i-n) and a heterojunction (p-i-i-n) cell calculated using the optical simulation described in Section 5.1.

Both exciton generation profiles for bulk-heterojunction and for heterojunction are shown in Figure 5.19 for illumination with 127 mW/cm² white light. Here, we also show the absorption inside the doped transport layers. In the simulation, it is assumed that all
excitons created in these layers are immediately quenched and do not contribute to the photocurrent.

The first difference between these two structures is the photocurrent created in the bulk of the blend layer and at the interface, respectively. Under identical illumination, the absorption for both structures is comparable, but the short circuit photocurrent is about five times larger for the bulk heterojunction than for the heterojunction (Figure 5.20). The reason for the high difference is that the excitons in the bulk-heterojunction can efficiently dissociate in the whole blend layer, while for the heterojunction, the excitons can only dissociate when they reach the interface by diffusion. As the model assumes only 10nm diffusion length for excitons, only a small portion of the excitons can dissociate into free carriers at the interface between active materials. Even if the diffusion length and lifetime of excitons were higher values, this would not guarantee comparable photocurrents because a transfer of excitons can also occur in the direction away from the active interface. The second process affecting the photocurrent is the recombination. Here, the situation is reversed: there is a higher probability that free charge carriers can recombine by indirect or direct processes for the bulk-heterojunction cell because holes and electrons meet in the whole blended layer before they reach the transport layers. This significantly influences the $FF$, which is better for the heterojunction where electrons and holes can recombine only in the assumed 3 nm thick interfacial blend layer. The recombination processes also influence the saturation current density: For the heterojunction structure, saturation is already attained at positive applied bias (0.3 V, Figure 5.20). For the bulk-heterojunction cell, however, the negative photocurrent still rises at –1V. Since the pure materials have a higher mobility than the blend layer, a higher forward current is observed for the heterojunction cell. $V_{oc}$ is lower than the built-in potential of 0.64 V for both bulk-heterojunction (0.44 V) and heterojunction (0.52 V). The fact that for the heterojunction, $V_{oc}$ exceeds the value of the bulk-heterojunction can be rationalized as follows: The value of $V_{oc}$ is directly linked to the splitting of quasi Fermi levels in the blend layer. In the case of the simple heterojunction, the assumed interfacial blend layer is additionally fed with excitons generated in the pure layers, which leads to a higher local generation rate in the blend and thus to a higher local charge carrier density. Moreover, high charge carrier densities can exist in the pure layers close to the active interface for the heterojunction cell under open circuit conditions in a region where they cannot recombine.

According to the general solar cell model introduced by Würfel [201], it should be possible that $V_{oc}$ exceeds the built-in potential $V_{bi}$ if the splitting of quasi Fermi levels exceeds $V_{bi}$ and the generated charge carrier pairs face asymmetric conditions for their diffusion (so called selective membranes). This condition of selectivity is fulfilled for the
heterojunction solar cell by the fact that holes can leave the interfacial blend layer only towards the intrinsic layer I and electrons only towards the intrinsic layer II (compare also the heterojunction model proposed by Gregg et al [63]). In this case, the diffusion can lead to a negative current under flat band conditions (applied bias equal to $V_{bi}$) and zero current ($V_{oc}$) is found at a voltage exceeding $V_{bi}$. For the parameters used above, the diffusion effect has a minor influence on $V_{oc}$ due to the high electric field of the heterojunction which favours drift. Roughly spoken, diffusion plays a minor role and $V_{oc}$ is lower than $V_{bi}$ if the doping induced carrier density in the transport layers which determines $V_{bi}$ is higher than the photoinduced carrier density close to the active interface under open circuit conditions.

In order to create conditions where the diffusion process at the photoactive interface can compete with drift in a positive field, we suppose a thinner interfacial blend layer of 1 nm with lower losses, i.e. we assume a lower trap density of only $10^{17}$ cm$^{-3}$ and low cross section for direct recombination $\gamma_{nf-pf}=10^{-13}$ cm$^3$/s to get adequately high accumulation close to the dissociation interface. Moreover, the dopant concentration in the transport layers is reduced to $2\times10^{17}$ cm$^{-3}$, which lowers the built-in potential to 0.55 V. In Figure 5.21, the results of a numerical calculation with the above mentioned parameters and using the optical profile identical as in Figure 5.19 are presented, however an illumination level of 3 suns is assumed. Here, the achieved $V_{oc}$ is about 0.05 V higher than $V_{bi}$ which demonstrates that this, at least in principle, is possible. The distribution of free carriers and electric field at $V_{oc}$ voltage is shown in Figure 5.22 and Figure 5.23, respectively. It can be seen that the diffusion of accumulated free carriers on both sides of the generation interface is equal to the drift in the positive field. Similar balances occur at both interfaces between the transport layers and pure active layers where the drift towards the transport layer in the negative field is compensated by diffusion from the doped transport layers. The situation is characterized by a photogenerated charge carrier density being higher close to the active interface than the doping induced charge carrier density in the transport layers (Figure 5.23).

In a structure where $V_{bi}$ is reduced by energetic offsets between the active layers and the respective transport layers, a similar situation could occur also for higher doping levels in the transport layers. With such offsets, photogenerated carriers lose energy when they pass from the active layer to the respective transport layer. However, the disadvantage of the structure with higher $V_{oc}$ and lower $V_{bi}$ is obvious the lower $FF$ of the voltage–current characteristics shown in Figure 5.21: The lower built-in field and the extremely high local concentration of photogenerated carriers close to the interface favour recombination losses at applied voltages above $-0.6V$. 

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Figure 5.21  Current-voltage characteristics for a p-i-i-n heterojunction with $V_{oc}$ being higher than $V_{bi}$.

Figure 5.22  Electric field distribution for open circuit conditions (applied voltage 0.6 V) for the structure from Figure 5.21.
Figure 5.23 Free electron and hole distribution at open circuit voltage (0.6 V) for the structure from Figure 5.21.
5.3. Comparison of simulation and experimental results

5.3.1. Fits assuming only direct and indirect non-geminate recombination

The model structure for our simulation has the layer sequence cathode/p-layer/photoactive blend-layer/i-layer/n-layer/anode. A typical realization of this general concept comprises ITO as cathode, N,N,N',N'-Tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD) doped by tetrafluoro-tetracyano-quinodimethane (F₄-TCNQ) as p-layer, phthalocyanine zinc (ZnPc) and C₆₀ as photoactive blend-layer, C₆₀ doped by Rhodamine B as n-layer and Al as anode. The energy level scheme of such a p-i-n solar cell is depicted in Figure 5.24. As mentioned above, the generation occurs in the blend layer while the p- and n-doped layers have a wide band gap, i.e. they are almost transparent for visible light. They serve as an optical spacer layer between the active layer and the contacts, provide the internal electric field by Fermi level adjustment over the undoped active layer, and transport the carriers to the contacts with low ohmic losses. Furthermore, the high doping level guarantees good quasi ohmic contact behaviour by tunneling [3], almost independently of the actual work function of the contacts. The additional thin i-layer consists of the same matrix material as the n-layer. It is introduced to make sure that dopants from the n-layer do not quench excitons in the blend layer.

The electrical parameters, which are used for the numerical calculations, are chosen such that they are consistent with accessible experimental values for the individual organic materials. For the electron mobility of the n-layer and the hole mobility of the p-layer, we assume 2*10⁻⁵ cm²/V*s and 8*10⁻⁵ cm²/V*s, respectively. Together with the assumed number of dopants in both layers of 10¹⁸ cm⁻³, the mobility values agree with the experimentally obtained ohmic conductivities of these layers. Except for a weak (logarithmic) influence of the dopant density on the built-in potential, the crucial property of the doped transport layers is only the conductivity and not the mobility, as they only serve for majority carrier transport. Here, the conductivities are that high that the voltage drop over these layers is almost negligible and they are not the main limiting factor for the current flow. The critical point for the solar cell performance is the carrier dynamics in the blend layer, consisting of a mixture of two organic materials that both have high values of mobility in single layers with polycrystalline structure. However, in case of a blend of two materials, layers are rather amorphous and mobilities are lower [71]. For the simulation, we used 2.5*10⁻⁶ and 5*10⁻⁶ cm²/Vs for the electron and hole mobility in the mixed layer with ratio 1:1, respectively. First attempts to measure the mobility values of the blend layer by field effect yield rather lower values between 10⁻⁸ and 10⁻⁷ cm²/Vs for both electrons and holes [71]. However, with such low values, we could not reproduce the high fill factors
of the experimentally obtained solar cell characteristics. For every mobility, we assumed a dependence on electric field according to Equation 3.5 with $\beta_{PF}=2 \times 10^{-3} \text{ (cm/V)}^{1/2}$. However, this field dependence hardly influences the current density due to the low electric field. In the photoactive blend layer, we calculate the generation profile of charges resulting from the absorption of white light with an intensity of 127 mW/cm$^2$ by the optical model.

![Figure 5.24](image)

**Figure 5.24** Energy level diagram for the p-i-n bulk-heterojunction cell discussed in this section.

The calculation of optical constants used in the determination of the optical field is based on simultaneous analysis of reflectance and transparency at normal light incidence of similar samples with various known relative layer thicknesses, see Ref. [189]. This method additionally yields a correction factor for the accurate layer thicknesses. The simulated photodiode has an optically thin active layer 32 nm which means that only part of the incident light is absorbed. Another parameter that influences the external efficiency is the position of the blend layer with respect to the reflecting contact. The distance is equal to the sum of the thicknesses of the thin pure layer C$_{60}$ that blocks the diffusion of dopants (10 nm) and the electron transport layer of C$_{60}$ doped by Rhodamine B (48nm), see Figure 5.24. The wide gap hole transport layer is 55nm thick and has only a minor impact on the distribution of the optical field in our solar cell [37]. The creation of free carriers at the interface between the blend layer and the neat, intrinsic C$_{60}$ layer is predicted assuming a diffusion length of 10 nm and an exciton lifetime of 10 ns, in agreement with reference [73]. For the initial generation step of exciton dissociation at ZnPc/C$_{60}$ interfaces, we suppose 100% efficiency. However, recombination losses, traps and the resistance of ITO can still limit the current density.
The energetic positions of the carrier transport states are taken from literature (Figure 5.24). Here, the only critical parameters are the HOMO of MeO-TPD and ZnPc and the LUMO of C\textsubscript{60}. They have to be adjusted to account for the measured open circuit voltage. However, the assumed values of 5.1 eV and 4.1 eV, respectively, are well within the range of literature values [36,190,191]. The energetic barriers appearing in the structure are deduced from energetic levels of HOMO and LUMO of the used materials. For the reverse current, holes and electrons are not expected to face energetic barriers due to similar HOMO values of ZnPc and MeO-TPD (5.1 eV) and the use of the C\textsubscript{60} with LUMO at 4.1 eV for both the electron transport layer and the acceptor component in the active layer. However, this is not the case for current flow in forward direction. Here, the charges injected from transport layer to the active layer accumulate and recombine rather than crossing the high energetic barriers for hole injection into C\textsubscript{60} (0.9 eV) and electron injection into MeOTPD (1.5 eV). For the charge transport layers p-MeO-TPD and n-C\textsubscript{60}, the mobility values for holes and electrons and the effective dopant density were chosen such that they agree with the measured conductivity of the doped layers [7,13,72]. To get an optimum agreement between the simulated and experimental current-voltage-characteristics, we adjust the recombination rates, the trap density in the active layer and the resistance of ITO.

In order to obtain information about the critical parameters for the losses in the blend layer, we performed a set of simulations. From the experiment, it is expected that the recombination process considerably influence the fill factor of the solar cells and also the change of current density with negative bias. On the other hand, we found in experiment that the short circuit current depends linearly on illumination intensity [37], which is not expected in presence of direct non-geminate recombination. To check if the appropriate assumptions are made, we carried out simulations with and without deep traps as centers for indirect recombination under two different illumination levels. The calculations made assuming only losses due to direct recombination yield completely different curves for low and high illumination, respectively. Under low illumination, the low concentration of generated free carriers leads to a low probability of direct recombination. Therefore, the current rapidly reaches the saturation value. At high illumination levels, direct recombination losses close to short circuit conditions are significant and one needs to apply a reverse bias in order to reach saturation. Accordingly, the short circuit photocurrent increases less than linearly with light intensity. By the implementation of recombination between free and trapped carriers, the shape of the reverse characteristics obtained by the calculation is similar under low and high illumination (Figure 5.25).
Figure 5.25  Reverse current with and without discrete trap levels that serve as recombination centers under illumination by white light with an intensity of 0.08 suns and 1.27 suns, respectively. The lack of saturation at negative field observed in experiment for both high and low illumination levels can be reproduced by the implementation of traps.

Figure 5.26  IV-characteristics of a photovoltaic cell consisting of ITO/ p-MeO-TPD/ ZnPc:C₆₀ / C₆₀ / n-C₆₀ / Al under illumination with 70 and 127 mW/cm². The empty symbols describes the simulation results, the full symbols represent the measured data.

The model thus allows to reproduce the slope of the IV-characteristics under negative bias typically observed for solar cells with photoactive blend layers [37], together with the linear
dependence of short circuit current on illumination. Such a behaviour can be described at an empirical level as a light dependent shunt resistance. However, the physical concept behind this so called photoshunt is quite unclear, and we suggest here that the description as a field-dependent recombination phenomenon is much more meaningful.

![Graph](image)

**Figure 5.27** Linear dependence of short circuit current vs. illumination for the cell corresponds to Figure 5.26. The line with empty squares describes the simulation.

The scenario can be summarized as follows: A striking feature of the experimental curves is the slope of the IV-curves at reverse bias, which cannot be interpreted in terms of a shunt resistance as they show very low reverse currents in the dark. Therefore, this is a hint for field-dependent recombination losses: At high fields, the carriers have a higher probability to leave the blend layer before recombination. This recombination affects both the short circuit photocurrent and the fill factor. However, the probability for direct bimolecular recombination of free carriers should increase with the illumination level, i.e. the concentration of photogenerated charges, which is in contradiction to our finding that the short circuit photocurrent scales exactly linearly with illumination. Consequently, we had to introduce deep trap states that mediate recombination and provide the dominant recombination path. One might as well account for the observed behaviour by assuming a field depending geminate recombination, as discussed in the following section. However, the assumption of trap-induced recombination agrees better with the empirical finding that the slope of the reverse characteristics under illumination depends sensitively on the purity of the used materials. As shown in Figure 5.26, good agreement between
experiment and simulation for different illumination levels was obtained assuming discrete levels of traps with concentration about $8.5 \times 10^{17}$ cm$^{-3}$. Here, the main limitations for the forward current are from ITO with a resistance of about 150 Ohm for the given contact geometry and from the photoactive blend layer, while the doped transport layers hardly play any role. Figure 5.27 shows the linear dependence of a short circuit current on illumination in the range from 8 mW/cm$^2$ to 127 mW/cm$^2$ both in experiment and simulation and confirms the good agreement.

### 5.3.2. Geminate recombination as an alternative model

For both organic and inorganic semiconductors, recombination can be divided in two processes, taking into account the origin of the recombining charge carriers: If a photoexcited charge carrier pair recombines without ever leaving the mutual Coulomb potential, i.e. the excited carrier recombines with its initial counterpart, we call this process geminate recombination; if the hole and electron can be separated, leave their mutual Coulomb potential and afterwards recombine with other free carriers (direct recombination) or trapped carriers (indirect recombination), this is called non-geminate recombination [73]. So far, we have assumed in our simulations that the geminate recombination is forbidden and the losses of charge carriers in the blend layer mainly result from indirect recombination, while direct recombination plays a minor role due to the low value supposed for the cross section $\gamma_{pf-nf}$. With this assumption, the photocurrent at negative applied bias can be fitted well, see Section 5.3.1. However, we will show in the following that an equally good agreement between simulation and experimental results can be achieved by accounting for field-dependent geminate recombination losses. In this case, trap mediated, indirect non-geminate recombination does not have to be included.

**Theory**

Having calculated the generation profile for geminate electron hole pairs from the optical model, the generation profile for free carriers follows via a probability $P(F, T)$ that the pair can escape from geminate recombination. An adequate model to describe the geminate pair kinetics was proposed by Braun [192]. Herein, the nearest neighbour charge-transfer state (CT) is assumed to be formed from the initial excitation. This CT state can either be separated into free carriers with an electric field-dependent rate constant $k_d(F, T)$, or it can decay to the ground state with a rate constant $k_f$. On the other hand, one can calculate the equilibrium constant $K(F, T)$ for dissociation of a geminate carrier pair according to Onsager’s theory [192]: This equilibrium constant translates into the rate constant for dissociation by multiplication with a Langevin type rate constant for
bimolecular hole-electron recombination $\gamma_{pl,re}$. Altogether, we have

$$k_d(F,T) = \gamma_{n,-p} \cdot K(F,T)$$

(5.26)

with

$$\gamma_{n,-p} = \frac{q\left(\mu_n(F,T) + \mu_p(F,T)\right)}{\varepsilon \varepsilon_0}$$

(5.27)

and

$$K(F,T) = \left[\frac{3}{4\pi \cdot r_0^3} \exp\left(-\frac{q^2}{4\pi \varepsilon \varepsilon_0 r_0 kT}\right)\right] \left[1 + \left(\frac{q^3}{8\pi \varepsilon \varepsilon_0 k^2 T^2}\right)^F\right].$$

(5.28)

Here, $r_0$ is the distance between the hole and electron in the nearest neighbour charge-transfer state. The field dependence and temperature dependence of the mobilities ($\mu_n$ and $\mu_p$) are described by a Poole-Frenkel term (Equation 3.4). Thus, the probability $P(F,T)$ that the charge carrier pair can escape from each other to prevent geminate recombination is

$$P(F,T) = k_d(F,T) l(k_f + k_d(F,T)).$$

(5.29)

This theory has been developed by Braun to describe free carrier generation in organic mixed donor-acceptor crystals where the lowest excited state has charge transfer character. Instead of assuming a large thermalization distance to account for large quantum yields, the reason for efficient photocarrier generation within this theory is the slow recombination rate constant $k_f$ for the nearest neighbour pair.

To get a self-consistent description of organic solar cells with the above introduced set of equations, one has to account for the field-dependent probability of re-dissociation (according to Equation 5.29) also then calculating the direct recombination processes.

**Does geminate recombination play a role?**

In principle, one should expect that the initial charge transfer step leads to a carrier pair with a distance on the order of the intermolecular distance. As the energy gain in the transfer step could be transformed into a kinetic energy, this distance could also become somewhat higher, i.e. on the order of the mean free path of a carrier, which is generally considered as being low in disordered organic materials. Therefore, the carrier pair should
still be strongly bound by mutual Coulomb attraction. The probability to escape \( P_{\text{Ons}} \) should follow Onsager’s theory [73] that predicts

\[
P_{\text{Ons}}(F,T) = \exp\left( -\frac{q^2}{4 \pi \varepsilon_0 k_B T} \left( 1 + \frac{q^3}{8 \pi \varepsilon_0 k_B T^2} F \right) \right),
\]

(5.30)

where the all variables and constants are defined as for the previous equations.

However, even if we assume an initial distance of 3 nm, a typical electric field of \( 10^5 \) V/cm and a permittivity of the organic material of 3, the escape probability calculated from Equation 5.30 is below 3%. This is in sharp contrast to the high internal quantum yields of 60-80% observed in experiment for p-i-n cells based on ZnPc*C60 blends as an active layer [37].

As pointed out in Section 2.3, Braun [192] proposed a modified form of Onsager’s theory which introduces a field independent rate constant \( k_f \) for the recombination of nearest neighbour CT-states to the ground state. Let us now estimate the order of magnitude of \( k_f \) with a realistic set of parameters: With a distance between hole and electron in a nearest neighbour CT state of 1 nm, an electric field of \( 10^5 \) V/cm and carrier mobilities of \( 2.5 \times 10^{-5} \) cm²/Vs for holes and \( 5 \times 10^{-5} \) cm²/Vs for electrons in the blend layer, the escape rate constant \( k_d(F,T) \) at room temperature is about \( 10^4 \) s⁻¹. To ensure an efficiency on the order of 90% for the creation of free carriers from geminate pairs, the rate constant for recombination to the ground state \( k_f \) would have to be about a factor of ten lower than the escape rate constant \( k_d(F,T) \), i.e. around \( 10^3 \) s⁻¹. When the distance between the electron and holes is raised to 2 nm, the particular constant rates, \( k_d(F,T) \) and \( k_f \), are about \( 10^7 \) s⁻¹ and \( 10^6 \) s⁻¹, respectively. These second values are only one order of magnitude lower than the value of \( 10^8 \) s⁻¹ used by Braun to account for the photoconductivity of a mixed crystal of anthracene and pyromelliticdianhydride (PMDA). The reason why we have to assume such a low value for \( k_f \) is that we find a very high quantum yield in spite of the low mobility values in our disordered system. Moreover, we note that even for distance of 2 nm between the electron and hole, value of \( k_f \) is also much lower than the rate constant of \( 3 \times 10^8 \) s⁻¹ found by Guldi et al. [193] for recombination of excited CT states in covalently linked dyads of ZnPc and C60 measured in dilute solution. Obviously, there are some specific solid state effects that hinder recombination in the active blend systems used for solar cells [186]. The reason for the low recombination losses may be found in a complex interplay of the following factors: (i) Due to the small reorganisation energy for the fullerene molecule, recombination occurs with a low rate constant according to the Marcus-inverted regime [194] (ii) As proposed by Arkhipov
recombination may be hindered in presence of a ground state interface dipole by an
effective barrier arising due to increased zero point oscillations directly at the interface, (iii)
The statistical scattering of site energies in disordered materials may dominate over the
Coulomb attraction.

**Fitting of experimental IV curves**

![Experimental and simulated current voltage characteristics for the same solar cell which has been used in Section 5.3.1 for the fits based on indirect, non-geminate recombination. The fit presented here neglects indirect recombination, but takes into account geminate recombination losses assuming an initial distance between photoexcited holes and electrons of 1nm.](image.png)

It is possible to fit the experimental IV curves at a given temperature for our cells
taking into account only field-dependent geminate recombination losses according to
Equation 5.29 and non-geminate recombination according to a Langevin term (Equation
5.27) leading to CT states as an intermediate step, which can either decay to the ground
state or be separated again with a probability following Equation 5.29. Here, trap
mediated, indirect non-geminate recombination does not have to be included. Such a
model may be appropriate for certain photoactive material combinations. We fitted the
simulation data to the experimental data from Section 5.3.2. Figure 5.28 and Figure 5.29
show the agreement between experiment and simulation under different illumination
levels. The parameters describing the transport layers are the same as used in previous
sections. Only the particular values of the mobility have been slightly changed to $2.5 \times 10^{-5}$
cm²/Vs for holes and 5*10⁻⁵ cm²/Vs for electrons in the photoactive layer to compensate for the absence of trapping states.

![Graph](image)

**Figure 5.29**  Simulation results and experimental data for the short circuit current as a function of illuminating intensity. The parameters are the same used in Figure 5.28 showing excellent agreement.

**Influence of decay rate constant and mobilities**

The decay rate constant \( k_f \) which decides about both geminate and non-geminate recombination has a crucial influence on the photocurrent. As mentioned above, \( k_f \) must be about one order of magnitude lower than the escape rate constant \( k_d(F,T) \) to account for the high quantum yields observed in experiment. If the value of \( k_f \) increases, the geminate and non-geminate recombination losses rise as well (see Figure 5.30). Thus, the short circuit current decreases by a factor of two when \( k_f \) increases by a factor of six. However, the impact of decay rate constant on the open circuit voltage is insignificant and also the forward currents remain similar due to the high rate of non-geminate recombination that occurs when high concentrations of free charge carriers are injected into the blend layer.

The mobilities of the photoactive materials also significantly influence the current density. These values are not only crucial for the transport in the blend layer, but also influence the geminate and non-geminate recombination due to the implementation of the Langevin theory in the model. Thus the different mobilities, which can be the result of the mixing ratio of the two materials, significantly change the photocurrent. If both electron and hole mobilities are high, the probability that they can escape from geminate recombination increases (for a given value of \( k_i \)) and the charge carriers can easily arrive...
at the transport layers. On the other hand, we find higher losses both by geminate and non-geminate recombination then assuming lower mobilities. Non-geminate recombination losses are favoured due to the accumulation of free charge carriers in the blend layer.

![Graph showing current-voltage characteristics for different decay rate constants](image)

**Figure 5.30** Current-voltage characteristics for different decay rate constants $k_f$ ranging from $10^3 \text{ s}^{-1}$ to $6 \times 10^3 \text{ s}^{-1}$, when the distance between the charge carriers is 1 nm.

These dependencies are shown in the next two graphs. In Figure 5.31, the values for both electron and hole mobility are raised from $4 \times 10^{-6} \text{ cm}^2/(\text{V} \cdot \text{s})$ to $2.5 \times 10^{-5} \text{ cm}^2/(\text{V} \cdot \text{s})$ for holes and from $8 \times 10^{-6} \text{ cm}^2/(\text{V} \cdot \text{s})$ to $5 \times 10^{-5} \text{ cm}^2/(\text{V} \cdot \text{s})$ for electrons, respectively. On the other hand, results are shown in Figure 5.32 when only the hole mobility is varied from $10^{-7} \text{ cm}^2/(\text{V} \cdot \text{s})$ to $2.5 \times 10^{-5} \text{ cm}^2/(\text{V} \cdot \text{s})$. If the hole and electron mobilities are reduced, the short circuit current $J_{sc}$ is decreased significantly. However, the values of $V_{oc}$ remain almost constant.
Figure 5.31  Current-voltage characteristics when both mobilities of photoactive layer are changed. The ratio between the hole and electron mobility is kept constant (factor of 2).

Figure 5.32  Change of the current by implementation of different hole mobilities for a constant electron mobility of $5 \times 10^{-5}$ cm$^2$/Vs in the photoactive layer.

The forward parts of the current-voltage characteristics change with decreasing mobilities due to more pronounced space charge limitation of the current flow (Figure 5.31). This effect is not visible when one of the mobilities is kept at a high value (Figure 5.32). In this case, the forward current remains almost the same, but a reduction of the hole mobility is
reflected in increasing recombination losses because the electrons can easily recombine with a high number of accumulated holes.

**Which model is more appropriate?**

Finally, the question arises, which of the above introduced models that are both able to reproduce the experimental IV characteristics are closer to the physical reality. A strong hint in favour of the model based on trap mediated recombination is the fact that we have found that ZnPcC₆₀ based cells with an active layer thickness of 30-50nm show a temperature independent short circuit current density \( J_{sc} \) in a wide temperature range around room temperature [195]. This is in contrast to geminate recombination losses following Equation 5.29, which is therefore obviously not an appropriate description of the observed behaviour. From the lack of temperature dependence in \( J_{sc} \) in our cells, we can conclude that geminate recombination does not play a significant role. This assumption is in agreement with recent spectroscopic studies for a polymeric photoactive blend system [196] that seem to rule out geminate pair recombination losses. A final answer to this question, however, can only be given for a specific system when more systematic experimental data including spectroscopic results, temperature dependent IV characteristics, and a reliable determination of the charge carrier mobilities in the blend layer are made available.
5. Summary and Outlook

In this work, we have shown that the simulation is a powerful tool which can yield important information about the physical mechanisms in organic devices. However, to get unambiguous results, reliable parameters such as mobilities, concentration of trap states and energy levels are needed for the particular organic materials, which are often not available. Thus, much work has still to be done to obtain consistent parameters describing the individual layers and interfaces in the organic light emitting diodes (OLED) and organic solar cells (OSC). Such knowledge can be used as input for the proposed numerical model. New information about the validity of parameters or the proposed model can be obtained by comparison of the simulation and the experimental results, e.g. current-voltage characteristics. This process is illustrated in Figure 5.1.

Figure 5.1 Scheme of teamwork when utilizing the numerical model to create efficient organic devices.

We have shown the applicability of our two models for quantitative simulations of multilayer solar cell architectures and organic light emitting diodes. For organic light emitting diodes, the numerical model helps to analyze the problems of different structures...
and provides deeper insight into the relevant physical mechanism involved in device operation. Moreover, it is possible to identify technological problems for certain sets of devices. For instance, we could show that – in contrast to literature reports - the contact between Alq₃ and LiF/Al did not show ohmic behaviour for the series of devices discussed in Section 4.3.2. The role of additional organic layer between HTL and EML was presented in section 4.2.1. The explanation for the higher creation efficiency for singlet excitons in the three-layer structure is found in the separation of free holes and electrons accumulating close the internal interface 1-Naphdata/Alq₃.

The numerical calculation has demonstrated the importance of controlled doping of the organic materials, which is a way to obtain efficient light emitting diodes with low operating voltage (Section 4.2.2). The proper operation of the first vertical In-Line manufacturing set-up (VES 400, developed by Applied Films) has been confirmed by agreement of numerical and experimental results for a series of OLEDs with different thicknesses of the hole transport layer and emitting layer (Section 4.3.1) and for doped emitting layers (Section 4.3.3).

The advantages and drawbacks of solar cells based on flat heterojunctions and bulk heterojunctions are analyzed in Section 5.2. From the simulations, it can be understood why bulk-heterojunctions typically yield higher photocurrents while flat heterojunctions typically feature higher fill factors. The performance of the organic bulk-heterojunction solar cells under different illumination conditions could be reproduced with two alternative assumptions about the main recombination path: It is found that by introducing trap states, the simulation is able to reproduce the linear dependence of short circuit currents on the light intensity. The apparent light-induced shunt resistance often observed in organic solar cells can also be explained by losses due to trapping and indirect recombination of photogenerated carriers (Section 5.3.1), which we consider a crucial point of our work. However, these two effects, the linear scaling of the photocurrent with light intensity and the apparent photoshunt, could also be reproduced when field-dependent geminate recombination is assumed to play a dominant role (Section 5.3.2). A final answer to the question about the dominant recombination path can be expected from the simulation of temperature dependent measurements. First results that show a temperature independent short circuit photocurrent favour the model based on trap-mediated indirect recombination. Consequently, further improvements of device performance can be expected with more thorough material purification. Moreover, our model calculations emphasize the importance of equally high mobilities for both carrier types in the photoactive blend layer since low or unbalanced mobilities impose serious restrictions on the accessible thickness of the photoactive layer.
An attractive way to get efficient devices in spite of low carrier mobilities is the preparation of tandem cells. First simulations of tandem cells consisting of two bulk heterojunction sub-cells based on the same photoactive material system have already been carried out (they are not included in the thesis in order to stick to an acceptable length). They confirm that the open circuit current can be doubled compared to a single cell, whereas the short circuit current slightly decreases. We expect that the numerical simulations will become particularly useful for a future development and optimization of tandem cells including two different photoactive material systems where the two sub-cells absorb the light of the sun from different parts of the spectrum. The challenge here is to balance the photocurrent generation of the two cells, since a tandem cell is essentially a stack of two cells connected in series. To simulate such tandem cells, the exciton generation profile from the optical calculation is needed, which can also answer the question of the optimum thickness of the particular organic layers to ensure that the photoactive layers are placed in their respective interference maximum.

The numerical model can also be applied to a large variety of other materials and different multilayer photovoltaic solar cell architectures, where charge carriers are created in blend layers and at interfaces, or organic diodes, which emit light by phosphorescence or fluorescence. The model can easily be modified to include e.g. spatial variations in trap densities and extra layers. Moreover, it also allows to simulate light emitting devices that consist of more than one emission layer. Thus, OLED with a so-called double emission layer, a concept recently developed at our Institute to realize ultrahigh efficiency green phosphorescent OLED, or even white OLED can be modeled. Especially for white OLED, the light is emitted from up to three different layers which further increases the number of unknown parameters even further. At the same time, however, the analysis of the emission spectrum of white OLED also yields additional information on the distribution of carriers and excitons at different bias and thus provides another self-consistency test. Still, the simulation results depend strongly on the parameters used, so that the determination of unknown parameters remains a crucial point to further ensure the physical relevance.

An alternative to this bottom-up approach – from determination of individual parameters to the simulation of a complex device – can be a kind of top-down approach. The latter recently became accessible in our institute with the installation of a new preparation tool that enables the preparation of a complete set of devices with several parameters being systematically varied in one run. If we are able to reproduce the performance data for a high numer of more or less complex devices with one common set of parameters, we gain confidence in the validity of the assumptions and the accuracy of the used parameters.
6. Acknowledgements

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Finally, I would like to thank my wife and son for their love.
List of reference


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List of the most important mathematical symbols and abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>acceptor or Richardson constant</td>
</tr>
<tr>
<td>a</td>
<td>average lattice constant</td>
</tr>
<tr>
<td>ANTH</td>
<td>anthracene</td>
</tr>
<tr>
<td>Al</td>
<td>aluminium</td>
</tr>
<tr>
<td>Alq₃</td>
<td>aluminium-tris-(8-hydroxy-quinolate), emitter and electron transport material</td>
</tr>
<tr>
<td>α</td>
<td>emission angle relative to the substrate normal and absorption coefficient</td>
</tr>
<tr>
<td>BL</td>
<td>blocking layer</td>
</tr>
<tr>
<td>c</td>
<td>speed of light (3*10⁸ m/s)</td>
</tr>
<tr>
<td>C₆₀</td>
<td>fullerene, donor</td>
</tr>
<tr>
<td>CT</td>
<td>charge transfer</td>
</tr>
<tr>
<td>D</td>
<td>donor</td>
</tr>
<tr>
<td>d₀</td>
<td>hopping distance or intermolecular distance in an organic layer</td>
</tr>
<tr>
<td>DOS</td>
<td>distribution of states</td>
</tr>
<tr>
<td>Dₛ</td>
<td>diffusion constant for excitons</td>
</tr>
<tr>
<td>dt</td>
<td>time step</td>
</tr>
<tr>
<td>d</td>
<td>thickness of organic material absorbed the light</td>
</tr>
<tr>
<td>Δ₀</td>
<td>energetic barrier</td>
</tr>
<tr>
<td>ΔR</td>
<td>intersite distance between transports sites located at lattice site Rᵣ and Rₘ</td>
</tr>
<tr>
<td>Eᵥ</td>
<td>vacuum energy level</td>
</tr>
<tr>
<td>Eᵣ, Eₘ</td>
<td>individual energy levels</td>
</tr>
<tr>
<td>E</td>
<td>center of the density of states (DOS)</td>
</tr>
<tr>
<td>ΔE, ΔEₚ, ΔEₙ</td>
<td>potential barrier for charge injection at the interface for holes and electrons</td>
</tr>
<tr>
<td>ΔE', ΔEₚ', ΔEₙ'</td>
<td>field-dependent energy barrier for holes and electrons</td>
</tr>
<tr>
<td>E, E'</td>
<td>energetic distance to the maximum of the DOS for materials before and after the interface</td>
</tr>
<tr>
<td>Eₚ</td>
<td>polaron binding energy</td>
</tr>
<tr>
<td>Eₙt, Eₚₙt</td>
<td>trap depth for holes and electrons</td>
</tr>
<tr>
<td>Eᵢ(x), Eᵢ'(x)</td>
<td>two components optical wave: propagation in the positive direction x, and in the opposite direction</td>
</tr>
<tr>
<td>Eᵣ</td>
<td>electric field of the incident wave in layer j</td>
</tr>
<tr>
<td>EL</td>
<td>emission layer</td>
</tr>
<tr>
<td>ETL</td>
<td>electron transport layer</td>
</tr>
<tr>
<td>ε₀</td>
<td>dielectric constant of vacuum (8.85*10¹² As/Vm)</td>
</tr>
<tr>
<td>ε</td>
<td>relative dielectric constant of a material</td>
</tr>
<tr>
<td>F</td>
<td>electric field</td>
</tr>
<tr>
<td>FF</td>
<td>fill factor</td>
</tr>
<tr>
<td>FN</td>
<td>Fowler-Nordheim (tunneling)</td>
</tr>
<tr>
<td>F4-TCNQ</td>
<td>2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane, acceptor molecule</td>
</tr>
<tr>
<td>Fₙ(ω)</td>
<td>normalized fluorescence spectrum of the host material</td>
</tr>
<tr>
<td>G</td>
<td>generation of charge carriers</td>
</tr>
<tr>
<td>φ(λ)</td>
<td>emission spectra of an OLED</td>
</tr>
<tr>
<td>Φᵣ</td>
<td>number of excitons which decay radiatively</td>
</tr>
</tbody>
</table>
$\Phi_{\text{out}}$ light outcoupling

$\gamma$ Langevin recombination rate

$\gamma_d$ dimensionless random variable describing the off-diagonal disorder effects

$h$ Planck constant ($h = 6.626\times 10^{-34}$ Js)

$h\nu$ average energy of the emitted photons

HTL hole transport layer

HOMO highest occupied molecular orbital

ITO indium tin oxide, transparent anode material

$\eta_{\text{abs}}$ losses due to absorption and waveguiding

$\eta_{\text{wk}}$ fraction of photons leaving the substrate

$\eta_{\text{bulk}}$ efficiency of singlet exciton radiative decay

$\eta$ power conversion efficiency

$I_0$ initial intensity of light

$J$ current density

$J_{\text{SC}}$ short-circuit current density

$J_p, V_p$ value describing the maximum power in the power-generating fourth quadrant (SC)

$\varphi$ work function of metal

$I_k$ matrix describes the propagation of the optical field

$K$ Förster energy transfer rate

$k_m$ radiometric-photometric conversion constant ($683\text{ lm/W}$)

$k_l$ decay rate constant (geminate recombination)

$k_d$ escaping rate constant (geminate recombination)

$k_B$ Boltzmann constant ($1.381\times 10^{-23}$ J/K and $8.62\times 10^{-5}$ eV/K)

$L$ total organic layer thickness of an OLED of OSC

$L_q$ length of the interdiffusion zone of the electrode materials

$L_j$ phase matrix (describing the absorption and the phase shift inside j layer)

$\Gamma(E)$ function describing the localization of energetic states (DOS)

$\lambda$ wavelength

OLED organic light emitting diode

OSC organic solar cell

LiF lithium-fluoride

$m^*$ effective mass of free electron

MTDATA 4,4',4''-tris(3-methylphenylphenylamino)-triphenylamine, hole transport material

MeO-TPD N,N,N',N'-Tetrakis(4-methoxyphenyl)-benzidine, hole transport material

Mg magnesium

Mg:Ag magnesium-silver alloy

$N_{\text{HOMO}}, N_{\text{LUMO}}$ densities of state for LUMO and HOMO

$N_0$ density of state for organic material advancement the contact

NPB or $\alpha$-NPD N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'' diamine, hole transport material

LUMO lowest unoccupied molecular orbital

$\mu_p, \mu_n$ mobility of charge carriers (holes or electrons)

$\mu_0$ low-field mobility, pre-exponential factor in the formula for the mobility of a charge carrier

$n$ density of electrons or index of refraction

$n_f, n_t$ free and trapped electron density

$\eta_f, \eta_t$ intrinsic density of electrons and of holes

$n_r, n_i$ optical constants
\( n_{\text{sub}} \) refractive index of the glass substrate
\( N_{A,D} \) density of acceptor/donator molecules
\( N_{\text{tp}} \) density of hole traps
\( N_{\text{tn}} \) density of electron traps
\( \rho \) charge balance factor: ratio between the number of formed excitons and the number of electrons flowing in the external circuit
\( q \) elementary charge \((1.602 \times 10^{-19} \text{ C})\)
\( Q \) quantum efficiency of an OLED in %
LED light emitting diode
\( \rho \) density of holes
\( P \) probability that the charge carrier pair can escape from each other to prevent geminate recombination
\( \rho_0, n_0 \) density of charge carriers activated thermally
\( p_r, p_h \) free and trapped hole density
\( P_{\text{inc}} \) incident optical power density
PMMA Poly(methyl methacrylate)
PMDA Pyromellitic dianhydride
\( p-i-n \) bulk heterojunction solar cell, n and p are doped transport layers
\( p-\text{ii-n} \) heterojunction solar cell, n and p are doped transport layers
\( P_{\text{Ons}} \) probability of the escape of charge carriers to prevent geminate recombination, calculated from Onsager’s theory
PPV poly(phenylene vinylene)
PtOEP \((2,3,7,8,12,13,17,18\text{-Octaethyl}-21H,23H\text{-porphine platinum (II)})\)
\( q_j \) value proportional to the refractive index of the transparent ambient
\( Q_j(x) \) energy dissipated per second in layer \( j \)
QAD quinacridone, an emitter dopant molecule
\( \Theta \) trapping factor found by the Fermi-Dirac formula
\( R_{\text{nf-pf}} \) recombination of free holes with free electrons
\( R_{\text{nf-pt}, R_{\text{pf-nt}}} \) recombination of free holes with trapped electrons and vice versa
\( R_{\text{f-t}} \) sum of recombinations of free holes with trapped electrons and vice versa
\( R_{\text{s-pf}}, R_{\text{s-nf}} \) quenching of excitons by recombination with free charge carriers
\( R_{\text{s-pf}}, R_{\text{s-nt}} \) quenching of excitons by recombination with trapped charge carriers
\( r_s \) fraction of excitons formed as singlet (spin statistic)
RS Richardson-Schottky (injection)
\( R_{\text{G-H}} \) mean distance between host and guest molecules
\( R_{\text{T}} \) complex reflection and transmission
\( R_0 \) effective Förster radius
\( r_0 \) distance between the hole and electron in the nearest neighbour charge-transfer state
\( r_{jk}, t_{jk} \) Fresnel complex refraction and transmission coefficients at interface \( jk \)
\( s \) singlet exciton density
\( \sigma_t \) cross section for electron capture (trapping)
\( \sigma \) width of DOS
\( S \) number of photons emitted per surface or total system transfer matrix
SC solar cell
SCL space charge limited (current)
\( S_n, T_n \) highly excited singlet and triplet exciton states
\( S_1 \) and \( T_1 \) lowest singlet and triplet exciton states
\( \sigma_{\text{Do}}(\omega) \) normalized optical absorption cross-section of the emitter dopant
\( T_n, T_p \) trapping, detrapping holes and electrons rate
\( \beta_{\text{PF}}, F_0 \) constants obtain from a plot \( \mu \) versus \( F \) at constant temperature \( T \)
t time
\( t_1 \) time at which the current peak occurs (SCLC)
$T$  absolute temperature
$T_{\text{eff}}$  effective temperature $T_{\text{eff}}^{-1} = T^{-1} - T_0^{-1}$
$T_0$  constant
$T_{\text{CL}}$  trap charge limited (current)
$T_{\text{FL}}$  trap filled limit
$\text{TPD}$  N,N8-bis(3-methylphenyl)-N,N8-diphenylbenzidine
$\tau_h$  radiative lifetime of the singlet excitons of the host materials
$\tau_s$  singlet exciton lifetime
$\text{TNATA}$  4,4',4''-tris[N-(1-naphthyl)-N-phenylamino]-triphenylamine
$\text{TSL}$  thermally stimulated luminescence
$V, V_{\text{bi}}, V_{\text{eff}}$  voltage, built-in voltage of a diode, and effective bias
$V_{\text{OC}}$  open-circuit voltage
$\nu_{\text{nm}}, \nu_0$  rate among energetic sites n and m, prefactor
$\nu_s$  velocity of exciton
$\nu_n, \nu_n$  velocities of mobile charge carriers
$V(\lambda)$  relative spectral sensitivity of the human eye
$\sigma_q$  reaction cross section for quenching processes
$x$  position from electrode in OLED and OSC
$x, x'$  variables of state
$\text{ZnPc}$  zinc-phthalocyanine
$\zeta d_j$  layer phase thickness corresponding to the phase change for wavelength $\lambda$
$\Sigma$  spatial disorder parameter
$\Phi_r$  number of excitons decayed radiatively