CHAPTER ONE

INTRODUCTION TO POLYMER LIGHT-EMITTING DIODES

1.1 Introduction

Our daily life is strongly influenced by solid-state electronic products. Nowadays, a life without electronic products like computers, mobile phones, displays, solar energy harvesting systems, artificial intelligence, and so on is hard to imagine. All of these products are assembled from solid-state electronic devices like transistors, diodes and sensors. Transistors are a key component of modern electronics, processors and chip sets are composed of a huge amount of this element that acts as a switch to generate and process electronic signals. On the other hand, optoelectronic devices are another branch from solid-state electronics that can produce, harvest and detect light. Light harvesting systems absorb sun light and convert it to electricity, also called photovoltaics. For these systems, there is a big demand in the entire world due to growing energy demand. Solar energy harvesting systems are very advantageous since solar energy is a free, clean and available energy source. Light producing systems, which opposite to photovoltaics convert electricity to light, are used in lighting and displays. Unlike silicon (Si), for light-emitting diodes (LEDs) semiconductors with a direct band gap like gallium arsenide (GaAs) are being used. LEDs made of III-V semiconducting materials are very efficient and have very low energy consumption. Beside these advantages, highly sophisticated deposition systems are required to fabricate LEDs and this makes the final product rather expensive. An emerging new class of semiconducting materials are conducting polymers, in 1977 it was discovered that polyacetylene can be made conductive upon doping. This discovery opened a new field for electronic device fabrication. Although polyacetylene is not a stable chemical and also not easy to work with, but it still attracted a big attention from the scientific community to explore more stable forms of conducting organic materials. From that time, many conducting organics have
been investigated and synthesized for electronic applications. Generally, polymers are flexible as well as mechanically strong, which opens up new options for flexible and lightweight (opto)electronic devices. Compared to inorganic semiconductors these devices can be produced more cheaply. Polymers can be processed from solution, enabling roll-to-roll technologies similar to newspaper printing systems that allow for a high production speed. This makes them attractive especially for large-area devices as solar cells and lighting panels, resulting in a new emerging field, plastic electronics.

1.2 Polymeric Semiconductors

A polymer is a large molecule composed of a repeating molecular unit called monomer. A wide variety of polymers exists, from synthetic plastics to DNA and proteins, which all play a crucial role in our daily life. A small group from the wide range of polymers or plastics has conducting properties that can be used as active material in electronic devices. The first conducting polymer was $\text{AsF}_5$ and iodine doped polyacetylene, for which the 2000 Nobel Prize in chemistry was awarded.$^1$ Most well-known polymers in daily life are good insulators and are used to insulate electrical elements. Now the basic question is what makes a polymer or plastic an insulator or a conductor. The feature that gives (semi)conducting properties to a polymer is the so-called bond conjugation, in other words an alternation of double and single bond between carbon atoms. Carbon has 4 electrons in its outer shell that can form different hybrid orbital structures as $sp^3$, $sp^2$ and $sp$. In the insulating polymers, carbon atoms are hybridized in four $sp^3$ orbitals that all are identical and called $\sigma$ bonds. While in the conducting polymers carbon atoms are hybridized in three in-plane $sp^2$ orbitals that make $\sigma$ bonds with adjacent atoms (making the backbone of the polymer) and a non-hybridized $p_z$ orbital that is perpendicular to the $\sigma$ bonds. The $p_z$ orbitals of two adjacent atoms overlap and form $\pi$ bonds in which electrons are delocalized. Figure 1.1 shows delocalized $p_z$ orbitals on a segment of polyacetylene that overlap from two neighboring carbon atoms and form $\pi$ bond. The bonding level $\pi$, still occupied with electrons, is known in chemistry as the highest occupied molecular orbital (HOMO). The anti-bonding level, $\pi^*$, being the first empty energy level, is called the lowest unoccupied molecular orbital (LUMO). These energy levels in a conjugated polymer, which consist of a repetition of molecular units, can be explained with one-dimensional periodic Bloch wave functions. Figure 1.2 (left) shows the energy diagram for such a system and the corresponding energy-momentum ($E - k$) plot. It is also illustrated how $\pi$ bonds (HOMO) and $\pi^*$ anti-bonds (LUMO) form by superposition of wave functions from adjacent atomic orbitals. Bonding and anti-bonding levels, according to the $p_z$ orbital configuration/phase are schematically shown in Figure 1.2 (right). The more nodes the orbitals have, the higher the corresponding energy level is. Figure 1.2 shows the most stable superposition to the energetically most unstable superposition in accordance with $p_z$ orbitals and their phase.

An electron from HOMO can be excited to the LUMO by absorbing energy/light, leaving behind a hole in the HOMO. The opposite interaction may also occur by recom-
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Figure 1.1: The chemical structure of polyacetylene which have double and single bond alternation. Blue and red lobes show the overlap between $p_z - p_z$ orbitals (wave-functions) making $\pi$ bond; color difference shows the phase of wave-function.

The combination of an electron in the LUMO with a hole in the HOMO thereby generating light. The HOMO-LUMO levels are equivalent to the valance and conduction band in solid-state physics, respectively and the energy difference between them can be compared to the energy band gap.

The energy level for the LUMO (HOMO) of conjugated organic materials is in the range of $-1$ eV to $-4$ eV ($-4.5$ eV to $-6.5$ eV) below vacuum. The band gap of organic materials covers the ultraviolet to the visible light range. This makes them suitable materials to be used in optoelectronic devices.
1.3 Polymers as Light Source

As discussed, conjugation is the key feature that makes one-dimensional polymer molecules (semi)conductive. Since these materials can be synthesized chemically, their solubility, absorption/emission spectrum, and charge transporting properties can be adjusted by changing the conjugated main chain and the side chains. A set of conjugated polymers are listed in Figure 1.3 that we study in this dissertation. Poly(p-phenylene vinylene) (PPV) is a greenish yellow emitting polymer, which has very poor solubility in organic solvents. Hence, it is functionalized with different kind of side chains that increase the solubility and cause a red-shift in the emission. Of the PPV family, we specifically mention two well known polymers which have been investigated widely; poly (2-[3’-(3,7-dimethyloctyloxy)] 5-methoxy-p-phenylenvinylene)co(2-[3’-(3,7-dimethyloctyloxy)]-phenyl-p-phenylenevinylene), also known as super-yellow PPV (SY-PPV), and poly[2-methoxy-5-(20-ethylhexyloxy)-p-phenylene vinylene (MEH-PPV). SY-PPV, developed by Covion Semiconductors GmbH is commercially available (Figure 1.3(a)). MEH-PPV is probably the most studied PPV derivative, being functionalized with ethoxy and methoxy side groups emitting orange light. This polymer has served as a work-horse for two decades to investigate the charge transport and photo-physical properties of conjugated polymers.

Figure 1.2: Schematic $E - k$ plot for different $p_z$ molecular orbital orientation (perpendicular to the polymer backbone) in polyacetylene, that makes $\pi$ and $\pi^*$ bonds or HOMO-LUMO energy levels. (right) Schematically $p_z$ orbitals and their phase in blue and red colors are shown; according to the degree of being in-phase of $p_z$ orbitals, energy levels can have different energies.
The discovery of another solution processable polymer, poly(9,9-dialkylfluorene) (PFO)\textsuperscript{[5,6]} (Figure 1.3(c)), opened the door to fabricate blue emitting diodes. Upon addition of benzothiadiazole (BT) moiety in the PFO backbone (Figure 1.3(d)), its band gap decreases and the emission shifts to the green. Polyalkoxyspirofluorene (PSF) is another PFO derivative that is widely investigated as blue emitting material and in combination with red and green dyes can be used to fabricate white light-emitting diodes (Figure 1.3(e)).

Poly(9-vinylcarbazole) (PVK) is a large band gap polymer with a non-conjugated backbone, that has also been studied for application in OLEDs (Figure 1.3(f)). This polymer was already extensively studied in the past because it has been used as photoreceptor in xerography. We have used this polymer not only as a host but also as electron-blocking layer in this dissertation. In PVK, conduction occurs through the conjugated carbazole parts that are attached to the non-conjugated polymer chain.

In a PLED, a conjugated polymer is sandwiched between two electrodes, the cathode and anode. Due to the very low mobility of organic semiconductors ($< 10^{-7}$ m$^2$/Vs),
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the thickness of the emissive layer must be limited in the order of 100 nm to keep the operating voltage low. Upon application of a voltage higher than the band gap of the polymer the cathode and anode inject electrons and holes into the polymer, respectively. Due to Coulombic attraction between electrons and holes they form a bound electron-hole pair that is called exciton.

Since the electrical charges play the main role inside an electronic device, it is crucial to study the charge transport and recombination processes in these devices. Organic and inorganic LEDs are bipolar devices, which means that electrons and holes simultaneously flow in the semiconductor. In these bipolar devices, electrons flow through conduction band or LUMO and holes through valence band or HOMO. For a better understanding, it is important to study the transport of the electrons and holes individually. To investigate the transport properties of conjugated polymers, we therefore need to fabricate three types of devices: hole-only and electron-only devices, which each measure the hole or electron current separately and bipolar LEDs where also recombination takes place. In order to measure the bulk properties of the polymer in the hole-only (electron-only) device the injection electrode needs to be Ohmic. The collecting contact on the other hand should block injection of the opposite carrier into the device. For a bipolar LED both the contacts for electron and hole injection need to be Ohmic. Figure 1.4 shows a schematic structure of hole-only and electron-only devices. For hole-only device the polymer is typically sandwiched between a spin-coated poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) (Clevios™ PV Al 4083) bottom contact and an evaporated MoO$_3$/Al top electrode. Both electrodes are well-known hole injecting materials that have sufficiently high work functions for Ohmic hole injection, while blocking the injection of electrons. For polymers with a very deep HOMO like PFO and F8BT, with a HOMO around $-5.8$ eV, PEDOT:PSS with a work function of $-5.1$ eV cannot form an Ohmic hole contact. For these polymers only MoO$_3$ insures Ohmic hole injection due to its very high work function of $-6.7$ eV. To measure the electron transport, the polymer layer is sandwiched between thermally evaporated Al (which blocks injection of holes and electrons into the device) as bottom contact and an evaporated Ba/Al (5/100nm) contact on a glass substrate, resulting in an electron-only device.

For double-carrier devices, ITO/PEDOT:PSS is used as the anode and Ba/Al as the cathode, as shown schematically in Figure 1.5. In such a PLED generated excitons might transfer their energy to the electrodes instead of emission of a photon, which is an important loss process in PLEDs. To prevent these losses additional layers are being placed between the emissive layer and the electrodes. By tuning of the HOMO and LUMO levels the injected carriers are then confined inside the active emitting polymer, as schematically shown in Figure 1.5. As a result, efficiency of the PLED will be enhanced. In the following chapters, we will discuss the applicability of such a multilayer device from solution processing in detail.

All PLEDs and single-carrier devices were fabricated on glass substrates with a patterned indium-tin oxide (ITO) layer. The substrates were cleaned, dried, and treated with UV-ozone. The emissive polymer and blocking polymer layers were spin-coated in
1.4. Physical Structure of Polymer Diodes and Fabrication

Figure 1.4: Schematically shown the hole-only (left) and electron-only (right) devices which each measures only hole and only electron current respectively.

a nitrogen atmosphere from toluene and chlorobenzene solutions. To avoid side-effects from pollutants like dusts and so on, we carried out all the experimental procedures for fabrication of devices in a cleanroom. After device preparation, steady state electrical measurements were carried out in a controlled N₂ ambient using a computer-controlled Keithley 2400 source meter. Device light-output was simultaneously recorded with a Hamamatsu S1336 silicon photodiode.
1.5 Charge Transport in Polymer Semiconductors

Conduction and charge carrier density in non-doped organic semiconductors are very low. Therefore, injected charges into the organic device are not neutralized with counter charges, as is the case in a conductive medium. As a result upon injection of charges a space-charge region is being formed. These space charges produce an electrostatic field that limits the amount of the charges that can be injected into the device. This type of conduction that occurs in dielectric media is called space-charge limited (SCL) conduction and the measured current from such a device is called space-charge limited current (SCLC). Mott and Gurney formulated the SCL transport with accordance to the applied voltage and device thickness

\[ J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3}, \]  

where \( \varepsilon_0, \varepsilon_r \) is the vacuum permittivity and dielectric constant of the semiconductor, respectively. \( \mu \) is the charge mobility in the material and shows how quickly a charge carrier can move under an applied electric field; by definition where \( \bar{v} = \mu E \) is the average drift velocity of the carriers. The mobility is an important material parameter that determines the performance of electronic devices. The conductivity of a materials is proportional to the mobility and the amount of charge carriers; \( \sigma = ne\mu \), where \( n \) is the carrier density and \( e \) is the elementary charge value.
1.5. Charge Transport in Polymer Semiconductors

It has been demonstrated that Equation 1.1 can describe the trap-free hole transport in polymers like MEH-PPV, but only at low applied voltages and room temperature. When the applied voltage is higher, the current rises more rapidly with voltage than what Equation 1.1 predicts. Initially, to explain this deviation, contrary to Mott-Gurney law that assumes a constant value for mobility, an empirical field-and temperature dependent mobility with a Poole-Frenkel like field dependence was proposed\[8\]

\[ \mu = \mu_0 \exp \left( -\frac{\Delta}{kT} \right) \exp \left( \gamma \sqrt{E} \right), \tag{1.2} \]

where \( \mu_0 \) is the mobility when the temperature is infinite and electric field is zero, \( \Delta \) the activation energy, \( k \) the Boltzmann constant, \( T \) the absolute temperature, \( E \) the electric field, and \( \gamma \) is a field activation parameter. This equation was applied successfully to describe the transport in PVK and other molecularly doped polymers.\[9,10\] However, a scientific justification for this empirical model was missing.

Conventional inorganic semiconductors like silicon (Si) and gallium arsenide (GaAs) exhibit a periodic crystal structure, where electrons and holes flow through delocalized energy bands. In contrast to inorganic semiconductors, conjugated polymers lack the 3D crystal order and band transport. Polymers are highly disordered materials and often form amorphous structures. Besides their structural disorder, polymer chains also contain defects and kinks where the conjugation is broken. As a result a polymer chain consists of conjugated segments that might have different length and therefore also slightly different energy. As schematically shown in Figure 1.6, shorter conjugated segments have a wider energy gap than longer segments (quantum size effect), which can lead to spreading in site energies, also termed energetic disorder, of about 0.1 \(- 0.2 \text{ eV.}\) The energy offset leads to localization of the conjugated sites. To transfer a charge from one site to another, electrons need to gain energy to hop. The energy to make a hop can be provided by the absorbance and emission of phonons. Therefore, conjugated organics have better conduction at higher temperatures. Conwell and Mott suggested this kind of thermally assisted conduction for the first time in 1956, for impurity conduction in inorganic semiconductors.\[11,12\] Miller and Abrahams suggested a hopping rate, \( W_{ij} \), which considers the probability of a carrier hopping from an occupied state, \( i \), to an unoccupied one, \( j.\)\[13\] The hopping rate depends on the difference in energy of each state, \( \varepsilon_j - \varepsilon_i \), and on the distance between those states, \( R_{ij} \), as

\[ W_{ij} = v_0 \exp \left( -2\alpha |\vec{R}_{ij}| \right) \begin{cases} \exp \left( -\frac{\varepsilon_j - \varepsilon_i}{kT} \right), & \varepsilon_j > \varepsilon_i, \\ 1, & \varepsilon_j \leq \varepsilon_i \end{cases}, \tag{1.3} \]

where \( v_0 \) is the attempt-to-jump frequency, \( \alpha \) the inverse localization length and \( k \) the Boltzmann constant. The first exponential term represents the wave function overlap for state \( i \) and \( j \) that determines the tunneling probability between the states. The second term describes the phonon distribution as a function of energy and temperature. In 1993, Bässler by using Miller-Abrahams hopping rates, Equation 1.3, proposed a model
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to explain the transport in positionally and energetically disordered polymers.\textsuperscript{[14]} He assumed that the energy distribution of the localized states may be approximated by a Gaussian distribution (as shown in Figure 1.6) with a standard deviation;

\[ DOS = \frac{N}{2\pi \sigma^2} \exp \left( -\frac{\epsilon^2}{2\sigma^2} \right), \quad (1.4) \]

where \( N \) is the total transporting sites and \( \epsilon \) is the energy of a single state relative to the center of the DOS. Such a formalism with Equation 1.3 is not analytically solvable. Therefore, Bässler used Monte Carlo method to calculate the charge transport in disordered semiconductors, presently known as the Gaussian Disorder Model (GDM). The outcome of his numerical simulations for the charge carrier mobility could be approximated with an analytical formula of the form

\[ \mu = \mu_\infty \exp \left[ -\left( \frac{2\sigma}{3kT} \right)^2 \right] \times \begin{cases} \exp \left( C[(\sigma/kT)^2 - \Sigma^2]\sqrt{E} \right); & \Sigma \geq 1.5 \\ \exp \left( C[(\sigma/kT)^2 - 2.25^2]\sqrt{E} \right); & \Sigma < 1.5 \end{cases}, \quad (1.5) \]

where \( \mu_\infty \) is the mobility at infinite temperature and amounts to interval \( 10^{-6} \) to \( 10^{-5} \text{m}^2/\text{Vs} \), \( C \) is a constant depending on lattice spacing, and \( \Sigma \) is a scale for positional disorder. The GDM model showed that the mobility depends on inverse square root of temperature, which is non-Arrhenius. However, the predicted field dependence of the GDM is in agreement with experimental results only at high electric field (> \( 10^8 \text{V/m} \)). Gartstein and Conwell proposed the correlated disorder model (CDM), which takes the spatial energetic correlation between neighboring sites into account\textsuperscript{[15]}. This model could improve the agreement with experiment at low electric fields.

Studies conducted in the 80’s and mid-90’s considered mainly electric field and temperature dependence of the mobility. In 2003 also the dependence of the mobility on charge carrier density was experimentally addressed. Since the density of carriers is relatively low in diodes and with increasing voltage both the electric field and charge carrier density are simultaneously enhanced, it is not straightforward to study the effect of carrier density on the mobility in a diode structure. However, by combining diode measurements with field-effect transistor (FET) measurements Tanase et al. showed that the measured mobility in FET device structure is much higher (orders of magnitude) than that in diode while the applied electric field between source and drain is much smaller.\textsuperscript{[16]} Therefore, the enhancement of the mobility in a FET can be solely attributed to the enhancement of charge carrier density in the conductive channel due to applied gate voltage, which controls the carrier density.\textsuperscript{[17,18]} In diodes, hopping occurs through the sites in the tail of the DOS where the density of sites is low. While in a FET structure, upon application of a gate bias the tail of the DOS is filled and the Fermi-level approaches the center of Gaussian DOS. Here there are more sites available for transport; and due to this filling effect an enhanced mobility is measured. Model calculations by Pasveer et al.
Figure 1.6: Schematically shown disordered polymer; red lines show conjugation length and short blue lines conjugation break on chains. Short conjugation parts result in a wider band gap and long conjugation narrower one.

showed that the field- and density dependence of the mobility depend both on temperature in a way that at room temperature the density dependence is dominant whereas at low temperature field dependence is dominant.

This model that includes the temperature, density and field dependence of the mobility is now known as the extended Gaussian disorder model (EGDM). The model assumes that a charge can only occupy one state (due to high Coulombic repulsion in presence of more than one carrier in a state) and the hopping process occurs through Miller-Abrahams transition rate, Equation 1.3. To account for the effect of an applied electric field the term $-eER_{ijx}$ is implemented in Equation 1.3. The mobility is determined from a numerical solution of the three-dimensional Pauli’s master equation

$$\sum_{i \neq j} [W_{ij}n_i(1 - n_j) - W_{ji}n_j(1 - n_i)] = 0. \quad (1.6)$$

From the solution of Equation 1.6 the mobility is obtained

$$\mu = \sum_{i,j} W_{ij}n_i(1 - n_j)R_{ijx}/nEV, \quad n = \langle n_i \rangle / a^3, \quad (1.7)$$

where $V$ is the system volume and $a$ is the lattice constant or hopping parameter. It was found that the obtained numerical results can be parametrized by separating the
mobility dependence on carrier density and electric field, given by:

\[ \mu(T, n, E) \approx \mu(T, n) f(T, E), \]  

(1.8)

where the individual density and field dependent parametrization is given by:

\[ \mu(T, n) \approx \mu_0(T, n) \exp[-C\hat{\sigma}^2] \exp \left[ \frac{1}{2}(\hat{\sigma}^2 - \hat{\sigma})(2na^3)\delta \right], \quad \hat{\sigma} = \frac{\sigma}{kT}, \]  

(1.9a)

\[ \delta = \frac{2\ln(\hat{\sigma}^2 - \hat{\sigma}) - \ln(\ln(4))}{\hat{\sigma}^2}, \]  

(1.9b)

\[ f(T, E) = \exp \left\{ \frac{0.44(\hat{\sigma}^3/2 - 2.2)}{\sqrt{1 + 0.8 \left( \frac{eaE}{\sigma} \right)^2}} \right\}, \]  

(1.9c)

where \( C = 0.42 \), \( a \) is the intersite distance which is related to the transport site density as \( a = N^{-1/3} \), and \( \mu_0 \) is the mobility at the limit of zero field, zero carrier density and infinite temperature. This model, in the limit of zero density is equivalent to Equation 1.5 developed by Bässler. Field dependence can be approximated by an empirical Poole-Frenkel model, \( \mu \propto \exp(\gamma \sqrt{E}) \) as well. Because of the inclusion of both density- and field effects, the EGDM model is well suited to describe the charge transport in polymer SCL diodes. Therefore, we have used this model for mobility to simulate the measured experimental transport data in this dissertation.

### 1.6 Charge Trapping in Organic Semiconductors

Figure 1.7(a) schematically shows both electron and hole transport and their radiative and non-radiative recombination in a PLED. As demonstrated in Figure 1.7(b), the hole transport is trap-free space-charge limited but the electron transport is reduced by at least 3 orders of magnitude due to the presence of trapping states below the LUMO. As a result, the electron current shows a few distinctive features that can be observed in Figure 1.7(b). First, it exhibits a strong voltage dependence, resulting in a very steep slope of the \( J - V \) curve on a log-log scale (about 6 that is much higher than 2, the slope for trap-free SCLC). Second, the downward \( J - V \) sweep does not follow the upward sweep but is much lower. This hysteresis shows that some electrons stay trapped inside the device and disturb the internal field, making the down-scan to be much lower than the up-scan. Trapping effects not only enhance the current dependence on applied field but also its thickness dependence. Furthermore, its temperature dependence decreases when it is compared to the hole transport.

The dependence of \( J - V \) slope in log-log scale were investigated for a wide range of conjugated polymers.\(^{[20,21]}\) It was demonstrated that the \( \log J - \log V \) slope for the electron current is dependent on the energy position of the LUMO level. Figure 1.8 shows this relation for the polymers investigated; here only the data for MEH-PPV are added.
1.6. Charge Trapping in Organic Semiconductors

Figure 1.7: (a). This figure schematically shows that hole transport is trap free, but electron transport is strongly limited by the presence of trapping levels in the forbidden band gap (red circles below the LUMO). With the existence of trap states two type of recombinations are possible: Langevin radiative recombination between free holes and electrons and Shockley-Read-Hall (SRH) trap-assisted recombination between trapped electrons and free holes, (b) typical experimental $J-V$ results for hole, electron and PLED currents (all can be compared with standard SCLC current)

to the published graph. This figure shows that for polymers with lower LUMO level, the slope of log$J$—log$V$ is decreasing, and when the LUMO reaches $-3.8$ eV or lower the slope becomes equal to 2, which is the signature of trap-free SCLC. Based on this finding, a common energy level for trapping of electrons for all studied polymers was found below the vacuum level inside the forbidden band gap, which has a typical energy depth of $\sim -3.6$ eV, and density of $3 - 5 \times 10^{23}$ m$^{-3}$. Having a specific energy level for electron trapping indicates that it may have an extrinsic origin like impurities (such as water and oxygen). It was reported by Nicolai et al. that a possible candidate for trapping are (H$_2$O)$_2$—O$_2$ complexes, which can be introduced during material synthesis procedure.[20] This means that, most probably, traps are not coming from structural defects like kinks in the polymer.

As mentioned above, electron trapping negatively affects the performance of PLEDs; the unbalanced transport (asymmetric hole and electron transport, shown in Figure 1.7(b)) gives rise to a reduced spatial overlap between the electrons and holes and it enhances Shockley-Read-Hall (SRH) trap-assisted recombination, which is non-radiative and therefore a loss process. Therefore, it is important to understand the physics of trap-limited transport. In 1956, Lampert already evaluated the effect of a discrete trap level on the device current.[22] He demonstrated that the current density is similar to the trap-free SCLC but drops by a factor of $\vartheta$

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \vartheta \frac{V^2}{L^3},$$ (1.10a)
Figure 1.8: The slope of the trap-limited log/−logVis shown versus LUMO level for different polymers; it is adapted from ref. [20]; only MEH-PPV was added to it.

\[ \theta = \frac{N}{N_t} \exp\left(-\frac{E_{tc}}{kT}\right), \]  

(1.10b)

where \( N \) and \( N_t \) are the densities of transport and trap states, respectively, and \( E_{tc} \) is the energetic trap depth with respect to the valence- (hole trap) or conduction (electron trap) band. This formalism shows that the current is lowered by traps until all trap states are filled by carriers. Immediately after filling of the traps (called the trap-filled limit) a sharp increase of the current occurs, and the current rises from trap-limited to a trap-free SCLC. This trap-filled limit has been observed in inorganic semiconductors, but was not reported for conjugated polymers. The reason is that polymers have a distribution of localized trap states instead of discrete trap level. In case of electron traps, these traps are distributed in energy below the conduction band, as schematically shown in Figure 1.7(a). Then the trap-limited current will have a different dependence on voltage than the one of Equation 1.10 for a discrete trap. The most used energy distributions are either exponential or Gaussian, which we briefly review here. In 1962, Mark and Helfrich studied the case of an exponential distribution of trapping states in solids and formulated the corresponding trap-limited transport. In their calculations, the density of traps is assumed to have an exponential relation as below

\[ D_{\text{exp},t} = \frac{N_t}{k T_t} \exp\left(\frac{|E - (E_c - E_{tc})|}{k T_t}\right), \]  

(1.11)

where \( T_t \) is the characteristic temperature of the traps and \( E_{tc} \) is the energy of traps measured from the top of the valance- (hole traps) or conduction (electron traps) band.
(E_c). With this distribution, solving the Poisson equation results for the trap-limited current in

\[ J_{\text{TLC}} = N_c q \mu_n \left( \frac{\varepsilon_0 \varepsilon_r}{q N_t \exp(E_{tc}/kT_t)} \right)^r \left[ \left( \frac{2r + 1}{r + 1} \right)^{r+1} \left( \frac{r}{r + 1} \right)^r \right] \frac{V^{r+1}}{L^{2r+1}}, \tag{1.12} \]

where \( q \) is the elementary charge, \( \mu_n \) the free electron mobility, and \( r = T_t/T \). According to Equation 1.12, the value of \( r \) can be directly derived from the slope of \( \log J - \log V \). Since charge transport in conjugated polymers is described with hopping through a Gaussian density of states (DOS) as discussed in the section of the mobility, it would be rational to also assume a Gaussian distribution for traps.\[^{[23]}\]

For electrons a Gaussianly distributed trap states are defined as

\[ D_{\text{Gauss},t} = \frac{N_t}{\sqrt{2\pi} \sigma_t} \exp \left( -\frac{E - (E_c - E_{tc})}{2 \sigma_t^2} \right), \tag{1.13} \]

where \( \sigma_t \) is defined as the width of Gaussianly distributed traps, \( E_{tc} \) is the trap depth defined as the energy difference between the center of the trap distribution and the conduction band or, in case of a disordered semiconductor the center of the Gaussian LUMO as shown in the Figure 1.7(a) \( (E_c - E_{tc}) \) defines the trap energy). Hwang and Kao, assuming a Gaussian trap distribution, found that the trap-limited current is given a similar equation as Equation 1.12, but where \( r \) is now dependent on the Gaussian distribution width, \( \sigma_t \),

\[ r = \left( 1 + 2\pi \left( \frac{\sigma_t}{4kT} \right)^2 \right)^{1/2}. \tag{1.14} \]

The trap-limited current given by Equation 1.12 provides insight in how to understand and interpret trap-limited transport. It clearly shows how the current depends on the density of transport and trapping sites. We will show that this is a key point to minimize trapping effects by dilution of both trap and transport sites, which will be discussed in chapter 6 of this dissertation. It also should be noted that in order to derive Equation 1.12 many simplifications were made; it was assumed that the diffusion current is negligible, that the mobility is a constant and that the density of trapped charges is much higher than the free carrier density (that means most of injected carriers are trapped, \( n_t \gg n \)). Therefore, for a more accurate description of trap-limited transport, taking into account diffusion as well as a density- and field dependent mobility numerical device simulations are required.

### 1.7 Numerical Calculations

The drift-diffusion model calculates the device current assuming a one-dimensional continuum system for a semiconductor that is sandwiched between two electrodes. In this formalism, all physical quantities are a function of the distance from the electrodes. This
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model solves three coupled equations to derive the current in a bipolar system like a PLED. The drift-diffusion equations for one-dimension are given by

\[ J_n = \mu_n(T, E, n) \left( qn(x)E(x) + kT \frac{dn(x)}{dx} \right), \]  
\[ J_p = \mu_n(T, E, p) \left( qp(x)E(x) - kT \frac{dp(x)}{dx} \right), \]
\[ J_{tot} = J_n + J_p, \]

where \( n(x) \) and \( p(x) \) are the density of free carriers and \( E(x) \) is the electric field as a function of distance from cathode or anode. To calculate the electric field inside the device, the Poisson equation has to be solved with taking into account the presence of free (holes and electrons) and trapped (electrons) carriers as well;

\[ \frac{dE(x)}{dx} = \frac{q}{\varepsilon_0 \varepsilon_r} \left[ p(x) - n(x) - n_t(x) \right], \]
\[ V = \int_0^L E(x)dx. \]

To guarantee particle conservation, also the continuity equation should be taken into account. In steady state condition, where the carrier concentration is not a function of time, the continuity equations reduce to;

\[ \frac{1}{q} \frac{\partial J_n(x)}{\partial x} = - \frac{1}{q} \frac{\partial J_p(x)}{\partial x} = R(x), \]

where \( R(x) \) is the recombination rate that will be discussed in the next section.

1.8 Evaluation of Efficiency in PLEDs

The efficiency of a PLED is defined as the ratio of generated photons to the number of injected electrons and holes that form excitons (known as internal quantum efficiency, IQE). In ideal case, this efficiency ratio is 1 or the device is 100% efficient. To find out how to optimize the efficiency in a PLED, it is necessary to understand radiative recombination and loss effects. Radiative recombination is a Langevin type recombination, where the limiting step is the diffusion of electrons and hole towards each other due to Coulombic attraction. This recombination occurs in materials that have a very short mean free path for transport (that is expected for energetic disordered materials) in comparison to the critical Coulombic capture length, \( r_c \), which is defined as the distance where the Coulombic energy between an electron-hole pair is higher than the thermal energy \( kT \),

\[ \frac{q^2}{4\pi \varepsilon_0 \varepsilon_r r_c} \geq kT, \]
1.8. Evaluation of Efficiency in PLEDs

From this relation, for polymers ($\varepsilon_r = 3$) at room temperature $r_c$ typically amounts to 19 nm, which this is clearly much higher than a typical hopping distance that is normally about 1-2 nm. It has been demonstrated that in conjugated polymers radiative recombination is indeed of the Langevin type.\[24\] The Langevin recombination rate is proportional to the product of hole and electron density with a prefactor that is proportional to the sum of the carrier mobilities

$$R_L = \frac{q}{\varepsilon_0 \varepsilon_r} [\mu_n(T, E, n) + \mu_p(T, E, p)] (np - n_i^2) = B_L(np - n_i^2). \quad (1.19)$$

Next to radiative Langevin recombination, it was also shown that Shockley-Read-Hall (SRH) trap-assisted recombination occurs on conjugated polymers. Because SRH recombination is non-radiative it is a recombination process that limits the performance of the PLED.\[25–27\] This recombination occurs when a trapped electron ($\mu_n = 0$) captures a free hole. The competition between both processes determines the efficiency of a PLED. SRH recombination is given by

$$R_{SRH} = \frac{C_n C_p N_t (np - n_i^2)}{[C_n(n + n_l) + C_p(p + p_l)]} = B_{SRH}(np - n_i^2), \quad (1.20a)$$

$$n_l = n_i \exp\left(\frac{E_t - E_i}{kT}\right), \quad (1.20b)$$

$$p_l = n_i \exp\left(\frac{E_i - E_t}{kT}\right), \quad (1.20c)$$

with the capture coefficients for electrons and holes $C_n$ and $C_p$, respectively, given by\[25\]

$$C_n = \frac{q}{\varepsilon_0 \varepsilon_r} \mu_n(T, E, n), \quad C_p = \frac{q}{\varepsilon_0 \varepsilon_r} \mu_p(T, E, p), \quad (1.21)$$

According to these definitions, the recombination rate in continuity Equation (Equation 1.17) can be written as

$$R(x) = (B_L + B_{SRH}) \left(np - n_i^2\right). \quad (1.22)$$

However, SRH trap-assisted recombination is not the only loss process in a PLED. Electrode quenching is another process that limits PLEDs performance. This process occurs when excitons form directly next to a metallic electrode (within 10 nm). The exciton can then transfer their energy directly to the electrode due to long-range dipole-dipole interaction and decay non-radiatively. The more excitons are created close to the polymer-electrode interface, the stronger is this loss process. Furthermore, this non-radiative loss process will create a steep gradient in exciton concentration close to the electrodes and near the electrodes the population of excitons will decrease sharply. This concentration gradient will lead to a diffusion of excitons towards the polymer/electrode interface, thereby further enhance the quenching. To calculate the
Chapter 1. Introduction to Polymer Light-Emitting Diodes

exciton quenching, a one-dimensional diffusion equation is used for the exciton density distribution \( \epsilon(x, t) \)\(^{[28,29]} \)

\[
\frac{\partial \epsilon(x, t)}{\partial t} = D \frac{\partial^2 \epsilon(x, t)}{\partial x^2} - \frac{\epsilon(x, t)}{\tau_{\infty}} \left( 1 + \frac{x_0^3}{x^3} + \frac{x_0^3}{(L - x)^3} \right) + R_L(x). \tag{1.23}
\]

The first term on the right hand side, is the one-dimensional exciton diffusion. The second term represents exciton decay with a life-time of \( \tau_{\infty} \) being further enhanced by an inverse cube dependence on position with characteristic length, \( x_0 \), that represents the direct energy transfer to the electrode and \( L \) is the device thickness or the anode position. A characteristic length for \( x_0 \) was found to be about 4 nm.\(^{[29–31]} \) \( R_L(x) \) is the exciton generation term, which is governed by radiative Langevin recombination as discussed above.

The internal quantum efficiency (IQE) in PLEDs can be defined as ratio of radiative recombination to all radiative and loss effects, electrode quenching and SRH recombination

\[
\eta_{\text{IQE}} = \frac{\int_0^L R_L(x) \, dx}{\int_0^L [R_L(x) + R_{\text{SRH}}(x) + Q(x)] \, dx}, \tag{1.24}
\]

where \( Q(x) \) represent the number/density of excitons that decay in the electrode.

As next step, numerical simulations are performed to find out the relative strength of the radiative and non-radiative processes. Figure 1.9 shows the simulated results for the efficiency behavior of a typical MEH-PPV based PLED. It demonstrates that at low fields SRH recombination is the dominant recombination process. This means that upon injection of electrons into the polymer, first the electron traps will be filled that subsequently all recombine with free holes. With increasing voltage, more trap states will be filled and as a result the number of free electrons will strongly increase. The increase of free electron concentration will result in a strong enhancement of the radiative Langevin with applied voltage. The increased exciton formation will also lead to an enhanced quenching of excitons at the metallic cathode. But since the exciton population profile almost remains the same shape, the portion of the excitons that are quenched remains almost fixed at about 20%. The same simulation is done for the different device thicknesses at 100 \( \text{A/m}^2 \), which shows that in thin devices (with thicknesses lower than 50 nm) electrode quenching can be very strong, but for thicker devices trap-assisted recombination is the dominant loss effect.

The calculation shown in Figure 1.9 demonstrates that the presence of electron traps strongly limits the PLED efficiency. To quantify the role of traps on device efficiency the efficiency is calculated as a function of electron trap density, as shown in Figure 1.10 for a PLED with a layer thickness of 60 nm. When the trap density is higher than \( 10^{24} \text{m}^{-3} \) the efficiency of this device is almost zero, due to dominance of trap-assisted recombination. With a reduction of the trap density, the efficiency rapidly increases and reaches to its
1.8. Evaluation of Efficiency in PLEDs

Figure 1.9: Simulation of relative contribution of loss effects that limit the PLED device efficiency, (a) for a 60 nm MEH-PPV diode versus applied voltage, (b) for MEH-PPV diode at 100A/m² versus device thickness; exciton diffusion length is assumed to be 6.7 nm.

maximum value at about $10^{22} m^{-3}$ trapping density. Further decrement of trapping density does not enhance the efficiency. Exciton quenching amounts to typically 20% when the trapping density is high, and decreases to 10% for balanced transport when the trap density is too low. Then a symmetric recombination profile will be formed throughout the emissive layer, where each electrode contributes to half (5%) of the total quenching losses.

The trapping density for conjugated polymers has been reported to be about $3 \times 10^{23} m^{-3}$. Here, it is found to be $2.1 \times 10^{23} m^{-3}$ for MEH-PPV and indicated by a red arrow in the Figure 1.10. Elimination of traps can have a huge effect on the device efficiency. The blue arrow in the figure demonstrate that a ten times reduction of traps in the polymer will increase the efficiency of a PLED more than 2 times. Since the trapping state density is about 0.1% of transporting sites, identification and elimination of traps is a big dilemma that is costly and time consuming. For extrinsic defects purification might be the way to reduce electron trapping effects. If the trap states originate from structural defects like kinks in the polymer chain purification of the polymer will not lead to any improvement. As an alternative solution, we present in this thesis that it is possible to simultaneously dilute trap states and transport sites.
1.9 Scope of the Dissertation

In this dissertation, we follow two main strategies to improve the efficiency of PLEDs. First, by making a multi-layer device, such that free carriers and excitons are separated from the electrodes, and therefore exciton quenching can be eliminated at the electrodes. The second method is elimination/dilution of trap states in the polymer that is expected to also improve PLED efficiency.

In Chapter 2 the operation of blue light-emitting diodes based on polyalkoxyspirobifluorene (PSF) with a varying amount of $N, N', N''$-tetraaryldiamino biphenyl (TAD) hole transport units (HTU) is investigated. Assuming that the electron transport is not affected by the incorporation of TAD units model calculations predict that a concentration of 5% HTU leads to an optimal efficiency for this blue-emitting polymer. However, experimentally an optimum performance is achieved for 10% TAD hole transport units. Analysis of the transport and recombination shows that PLEDs with 5%, 7.5% and 12.5% TAD units follow the predicted behavior. The enhanced performance of the polymer with 10% TAD originates from a decrease in the amount of electron traps, that is typically a factor of three lower than the universal value found in many polymers. This reduced amount of traps leads to a reduction of non-radiative recombination and exciton quenching at the cathode.

Chapter 3 addresses the quenching of excitons at the PEDOT:PSS anode in blue polyalkoxyspirobifluorene-arylamine polymer light-emitting diodes. Due to the combination of a higher electron mobility and the presence of electron traps, the recombination in this polymer zone shifts from the cathode to the anode with increasing voltage. The exciton quenching at the anode at higher voltages leads to an efficiency roll-off. The voltage dependence of the luminous efficiency is reproduced by a drift-diffusion model under the condition that quenching of excitons at the PEDOT:PSS anode and metallic
cathode are of equal strength. Experimentally, the efficiency roll-off at high voltages due to anode quenching is eliminated by the use of an electron-blocking layer between the anode and the light-emitting polymer.

In Chapter 4, we use MEH-PPV as a model polymer and we use PFO as hole-blocking layer (HBL) to eliminate quenching of excitons at the metallic cathode. We investigate a wide range of single-layer and bilayer PLEDs with different thicknesses consisting of a poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) emitting layer and a 20 nm poly(9,9’-dioctylfluorene) (PFO) HBL. The highest efficiency for both single-layer and bilayer devices is achieved when the total polymer layer thickness is \( \sim 90 \) nm. As a result, addition of an HBL to reduce cathode quenching is only effective when the luminescence enhancement due to microcavity effects in PLEDs is restored. The relative efficiency enhancement in bilayer devices as compared to single-layer devices varies from 283% for a 30 nm active layer to 20% for a 250 nm device.

One of the biggest challenges in the field of PLEDs is to increase their stability and lifetime. The main reason for the fast degradation of such devices is the use of highly-reactive metals, such as barium or calcium, as electrode material. In Chapter 5, we report the fabrication of an efficient PLED while using an air-stable partially oxidized aluminum (AlO_x) cathode. Usually, the relatively high work function of aluminum (\( -4.2 \) eV) imposes a large barrier for injecting electrons into the LUMO of the emissive polymer, which is frequently situated between \(-2.2\) and \(-3.0\) eV below the vacuum level. Here, we used F8BT as hole-blocking layer, which has a LUMO level of \(-3.3\) eV that is lower than that of MEH-PPV, \(-2.9\) eV. By partially oxidizing aluminum the work function can be decreased to \(-3.7 \pm 0.3\) eV. The combination of F8BT as hole blocking layer and oxidized Aluminum leads to voltage independent efficiencies that are even slightly higher as have been achieved for MEH-PPV diodes with reactive Ba/Al cathodes.

Chapter 6 deals with one of the most challenging topics in the field of polymer light-emitting diodes. As discussed, presence of electron traps reduces the light-output and most importantly the efficiency of the PLEDs. As shown in Equation 1.11 the current in a semiconductor containing traps is reduced by \( N/N_t \), with \( N \) the amount of transport sites, \( N_t \) the amount of traps and \( r \) a number that depends on the energy distribution of the traps. For \( r > 1 \) the possibility opens that trapping effects can be nearly eliminated when \( N \) and \( N_t \) are simultaneously reduced. Solution-processed conjugated polymers are an excellent model system to test this hypothesis, because they can be easily diluted by blending them with a large band gap semiconductor. We demonstrate that in conjugated polymer blends with 10% active semiconductor and 90% large band gap host the typical strong electron trapping can be effectively eliminated. As a result we were able to fabricate polymer light-emitting diodes with balanced electron and hole transport and reduced non-radiative trap-assisted recombination, leading to a doubling of their efficiency at nearly ten times lower material costs.

Since blue emitting polymers are very important in that sense they can be used as backbone for white light-emitting PLEDs, in Chapter 7 we tested the dilution method on one of the most used blue light-emitting polymers, PSF-TAD. As is common for many conjugated polymers used in light-emitting diodes (PLEDs) the charge transport in PSF-
TAD is dominated by holes. Although the free electron mobility is an order of magnitude higher than the hole mobility, the electron transport is strongly hindered by traps. By diluting PSF-TAD with the wide band gap polymer poly(9,9-di-n-octylfluorenyl-2,7-diyl) (PFO) the effect of electron trapping can be nearly eliminated. As a result, the transport in the PSF-TAD:PFO blend becomes electron dominated. Due to the higher electron mobility, polymer light-emitting diodes (PLEDs) made from these blends exhibit higher current and light-output as compared to hole-dominated PLEDs made from pristine PSF-TAD. The reduced amount of electron traps enhances their efficiency from 2 cd/A for the hole dominated PLED to 5.3 cd/A for the electron-dominated blend PLED.
References


