Charge injection into organic semiconductors
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Chapter 4

Electron-enhanced hole injection in blue polyfluorene based polymer LEDs

4.1 Introduction

From the studies on the Ag/OC\textsubscript{10}C\textsubscript{10}-PPV model system (chapter 3) the following conclusions for PLEDs with a strongly hindered hole injection can be drawn: First, a hole injection barrier of typically 1 eV will reduce the hole injection with 3-5 orders of magnitude. Secondly, at high fields the presence of electrons might strongly enhance the hole injection and resulting device efficiency.

In this chapter we want to treat the charge injection into a blue PLED. A widely studied class of polymers for blue PLEDs are the polyfluorenes [69], a well known example is poly(9,9-dioctylfluorene) (PFO) [17]. The mismatch between the work-function of common electrodes like Indium Tin Oxide (ITO) (4.8 eV) and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) (5.2 eV) and the HOMO of PFO (5.8 eV [17], 6.1 eV [18]) typically ranges from 0.7-1.1 eV. Therefore, it is expected that the hole current for PFO based PLEDs is injection limited (IL) due to the presence of an interface barrier between the positive electrode and the highest occupied molecular orbital (HOMO) of PFO. As a result the energy band diagram of a PEDOT:PSS/PFO/Ca device strongly resembles the diagram of a Ag/OC\textsubscript{10}C\textsubscript{10}-PPV/Ca based PLED (compare inset of figure 4.2 with figure 3.1), with a large injection barrier for holes and an Ohmic contact for electrons.

Studies on the efficiency of the charge injection from PEDOT:PSS into PFO indeed indicate a large reduction ($10^{-3}$) of the hole current [17]. As a result, it is expected that the IL hole contact will strongly reduce the performance of a PEDOT:PSS/PFO-based PLED. Furthermore, also in PFO accumulation of electrons at the hole contact has been observed from electroabsorption measurements [70], identical to the interface electron trap in the OC\textsubscript{10}C\textsubscript{10}-PPV IL-PLED. It has further been demonstrated that the electro-optical characteristics of such a PEDOT:PSS/PFO-
based PLED are strongly enhanced upon the first voltage cycle, resulting even in an Ohmic contact of PEDOT:PSS on PFO [71]. Furthermore, it has been shown that with an electron blocking top contact the hole injection is not enhanced, indicating that electrons play a role in the increase of the hole injection.

Due to the large bandgap of blue emitting polymers it is very difficult to make an Ohmic hole contact using metals or indium tin oxide (ITO). Therefore, understanding of the mechanism responsible for the enhanced hole injection is important for the design of efficient blue emitting PLEDS. In this chapter we focus on the role of the electrons in the switching during the first voltage cycle. It is demonstrated that the low current in the PEDOT:PSS/PFO/Ca PLED (PEDOT PLED) device preceding the switching effect is electron dominated. This electron dominated current can be manipulated by the reactive end groups on the PFO chain. It is shown that by replacing this end groups with monomer units via end-capping, the electron current can be strongly enhanced. This enhanced electron current is accompanied by a reduction of the voltage required for the switch-on of the device. The dependence of the switching voltage on sample thickness confirms that the effect is governed by the concentration of electrons at the hole injection contact. From impedance spectroscopy measurements it is found that after switching typically $10^{17}$ electrons $m^{-2}$ have been accumulated at the anode interface. Enhancing the electron injection by replacing Al (Ref. [71]) with Ca also leads, as expected, to a strong decrease of the switching voltage. Another important observation is that the enhanced hole injection is specific for the PEDOT:PSS/PFO interface, and does not occur for ITO and Ag bottom contacts. This, together with the observed sharpness of the transition, points to a mechanism in which the trapped electrons give rise to a strong dipole across a thin insulating injection barrier present at the PEDOT:PSS interface. At the moment that the dipole is sufficiently large, holes from the PEDOT:PSS will directly tunnel into the transport states of the PFO, giving rise to a sharp increase of the hole current.

### 4.2 Experimental

Four types of devices have been investigated, all consisting of a spin-coated layer of the polymer PFO sandwiched between two electrodes. Two of these device types are designed to be bipolar: an ITO/PFO/Ca PLED (ITO PLED) and an ITO/PEDOT:PSS/PFO/Ca PLED (PEDOT PLED). Furthermore, for the investigation of the hole injection ITO/PEDOT:PSS/PFO/Au hole-only devices have been constructed, with an electron-blocking Au top contact. In order to discriminate whether the current in the ITO PLED and the PEDOT PLED is dominated by the (reduced) hole or the electron current also devices have been constructed where the ITO bottom contact has been covered by Ag (ITO/Ag/PFO/Ca). Ag has a work-function of only 4.3 eV [16], as compared to the 5.8-6.0 eV of the HOMO of PFO. Therefore, such a device is expected to be completely dominated by the electron-current that is injected from the Ca top contact (electron-only device). For these four types of devices DC current density - voltage (J-V)-, impedance-, and transient electroluminescence measurements have been performed.
4.2.1 Polymer synthesis

The poly(9,9-dioctylfluorene) (PFO) has been synthesized via Suzuki coupling [72]. The polymerization has been performed in an inert atmosphere. Monomers are 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)-9,9-dioctylfluorene and 2,7-dibromo-9,9-dioctylfluorene. In figure 4.1 the reaction scheme is shown for three different syntheses of PFO. This three types of PFO have different electrical characteristics as will be explained in paragraph 4.3, and are named PFO(1), PFO(2) and PFO(3) (see figure). When in this chapter is referred to PFO, without further indication, PFO(3) is meant.

![Reaction scheme for PFO synthesis](image)

Figure 4.1: The basic synthesis of 9,9-dioctyl-PF according to Suzuki [72], resulting in PFO(1), together with end-capping with the 9,9-dioctyl-fluorene monomer (PFO(2)) and the benzene monomer (PFO(3)).

PFO(1) and PFO(2) have been synthesized in one single batch. After finishing the polymerization, to a part of the solution 4,4,5,5-tetramethyl-1,3,2-dioxaborolyl-9,9-dioctylfluorene (end-capping reagent) and some fresh catalyst have been added to obtain the end-capping of PFO(2). For the synthesis of PFO(3), after finishing the polymerization, 4,4,5,5-tetramethyl-1,3,2-dioxaborolylbenzene (end-capping reagent) and some fresh catalyst were added. The polymers are carefully purified to remove catalyst residues. Then, the polymers were dried and isolated. Finally, GPC measurements have been performed to determine the molecular weight. For polymers PFO(1) and PFO(2) a molecular weight $M_W = 34300$ g/mol has been found, and for PFO(3) the molecular weight amounts to $M_W = 27500$ g/mol (according to polystyrene standards). NMR spectra have been taken and are identical.

4.3 Results

4.3.1 Electro-optical characteristics of a PEDOT:PSS/PFO/Ca LED

Figure 4.2a shows a current-density voltage ($J - V$) measurement for a "fresh"PEDOT PLED (i.e. electrically addressed for the first time). It is observed that this figure strongly resembles the electrical characteristics as shown by Poplavskyy et al. [71]. A remarkable difference is the very low switching voltage $V_{\text{switch}}$, due to the thin film and the Ohmic Ca contact.
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Figure 4.2: Current density-voltage ($J - V$) characteristics of an ITO/PEDOT:PSS/PFO/Ca/Al PLED (PEDOT PLED) at room temperature (a), together with light output (b). The squares show the first electrical addressing and solid lines correspond to the second cycle. Thickness of the active layer is $d = 85$ nm. The inset shows the energy diagram for such a PEDOT PLED. The numbers 1, 2, and 3 mark the different regimes in the plot.

The electrical characteristics in figure 4.2a can be divided in three regimes: In regime 1, a strongly reduced current is observed. In this regime, the hole current is negligible and the current is carried by electrons. From the absence of light output in regime 1 it is also observed that the current is unipolar. Then, at a voltage $V_{\text{switch}}$ of typically $3-4$ V, a sudden transition is observed and the current is increased by several orders of magnitude (regime 2). Together with the transition of the current from low to high, also the light output of the device has switched on (figure 4.2b). The switching is shifted to higher voltages if the voltage is swept too fast ($\lesssim 0.1 \text{s}/0.1 \text{V}$). Therefore, the voltage has been swept with a delay time of $0.3 \text{s}/0.1 \text{V}$. For longer delay times no further reduction of the switching voltage is observed. When the voltage is further increased and subsequently decreased towards zero the current stays in this on-state (regime 3). For subsequent voltage cycles the current follows the high regime (solid lines in figures 4.2a,b). For the receding $J - V$ curve a small dip is observed. This has been observed before by Riess et al. [73] in NPB/Alq3 systems and is explained by release of charge from deep traps.

For applications it is relevant to know whether the observed switching effect is permanent, for example due to a chemical reaction at the interface. Then the PFO based PLED has to be programmed only once before it is being used. However, as shown in figure 4.3, the on-state of the device is not permanent. On a long time scale, the PEDOT PLED tends to return to its original off-state. Sixteen days after the initial switching of the device to its on-state, the device follows the low current of regime 1 for low voltages, and switches at $V_{\text{switch}} \sim 4.5$ V. From figure 4.3 it can be estimated that full recovery of the off-state takes $\sim 1$ month ($\sim 10^6 \text{s}$) at RT.
Figure 4.3: \( J - V \) characteristics as a function of time at room temperature. Thickness \( d = 100 \) nm. The very first \( J - V \) curve (fresh) is shown, together with the \( J - V \) curve after 16 days. After the fresh \( J - V \) scan a subsequent \( J - V \) scan has been made to ensure the on-state is obtained (not shown).

4.3.2 Regime 1: electron dominated \( J - V \) characteristics

For the understanding of the switching effect first the origin of the low current in regime 1 is investigated. It is demonstrated that the low current in regime 1 is also observed for an ITO PLED and an ITO/Ag/PFO/Ca (electron only) device, as shown in figure 4.4.

Since at low voltages the current density for the PLEDs with a PEDOT, ITO or Ag anode are equivalent it is concluded that the electron current is dominant in these devices. A contribution from the hole current would give a large difference in current between these devices, as the hole injection barrier amounts to 0.7 eV for PEDOT, 1 eV for ITO and 2 eV for Ag, respectively. Furthermore, it is observed that the hole current does not switch on in the devices with an ITO or Ag bottom contact.

It is observed that for a PEDOT:PSS/PFO/Au device, where the electron injection is blocked, the injection-limited hole current from PEDOT:PSS is 2-3 orders of magnitude smaller than the electron current. Furthermore, it is demonstrated that the IL hole current is 5-6 orders of magnitude below the on-state current of the PEDOT PLED. This indicates the presence of a large injection barrier of PEDOT:PSS on PFO. This measurement also demonstrates that the switch effect is not present for a PEDOT PLED with an electron blocking Au contact, in agreement with observations in literature [71]. This means that electrons are required in order to switch the hole current in the PEDOT PLED on.

Knowing that the current in regime 1 is electron dominated enables us to further investigate the role of electrons in the switching effect. Apart from modifying the electron current by a
change of the cathode (Au vs. Ca) it is found that the electron current can also be modified by a specific step in the synthesis of PFO. The presence of reactive end groups, required for the polymerization, strongly influences the magnitude of the electron current. In figure 4.1 the reaction scheme is shown for three different syntheses of PFO. PFO(1) still contains both the reactive end groups whereas in PFO(2) and PFO(3) one of the reactive end groups has been replaced by mono-functionalized fluorene or benzene. Adding end capping reagent during the polymerization will reduce the molecular weight and give rise to variations in polymer length for different end-capping [74]. Therefore, the end-capping is performed after the polymerization has been finished. From GPC it is found that the molecular weight for the three polymers PFO(1-3) is typically 30,000 g/mol. It has already been found that end-capping has a strong influence on the electroluminescence of PF2/6, a similar polyfluorene [74]. This has been attributed to aggregates in the original non-end-capped polymer. Here we show that the end-capping has a major influence on the electron transport. In figure 4.5a the electrical characteristics of PEDOT PLEDs made with each of these syntheses of PFO is shown. The devices have all been made within one process-run to exclude processing variations. It is directly observed that the current in regime 1 is strongly dependent on the followed scheme. For PFO(1), where the reactive end groups are still present, the electron current is very low. For PFO(2), where the Br end group has been replaced by a fluorene monomer, and PFO(3), that has been end-capped with a phenyl group, the electron current is much higher. For the three PFO types, also electroluminescence...
4.3 Results

Figure 4.5: (a) $J - V$ characteristics of the three polymers, with thicknesses $d = 90$ nm for PFO(1), $d = 105$ nm for PFO(2) and $d = 85$ nm for PFO(3). (b) EL spectra for the three polymers, normalized to their integrated intensity.

(EL) spectra have been recorded. It is observed that for higher current densities the contribution of blue light becomes higher, as has been observed in literature [74]. For a fair comparison, the EL spectra are recorded at a constant current density ($\sim 10^3$ A/m$^2$). From the EL-spectra (figure 4.5b) it is observed that PFO(1) is dominated by green emission (maximum 520 nm), while the end-capped PFO(2) shows both a blue (430 nm, 450 nm) and a green component (530 nm). PFO(3) has no green emission peaks, but three blue/blue-green peaks (420 nm, 450 nm, 500 nm). It is also observed that the EL-spectra do not change for subsequent electrical conditioning.

4.3.3 Regime 2: switch-on

From figure 4.5a it is observed that the switching voltage $V_{\text{switch}}$ lowers when the electron current is higher. A possible origin is a modification of the PEDOT:PSS/PFO interface by the electron current [75]. A higher electron current implies a faster modification and switching takes places at lower voltages. At the other hand, a larger electron current can be caused by an increase of free carriers in the device. An increase of free carriers is most likely the result of a reduction of the number of bulk traps in the device. More free electrons will result in a stronger accumulation of electrons at the hole injecting contact. This will also give rise to switching at lower voltages. In order to discriminate whether it is the electron current itself or the electron concentration at the anode that dominates the switching effect the effect of sample thickness on switching voltage has been studied. Using PFO (3) the switching voltage as a function of thickness is plotted in figure 4.6. It is observed that the switching voltage scales with the square of the thickness (solid line). For space charge limited charge transport, the concentration of electrons at the anode (distance L from the cathode) scales with thickness as $n(L) \propto V/L^2$ [68]. Consequently, the observed quadratic scaling with $L$ demonstrates that all devices switch when
the electron concentration at the anode reaches a certain value. This implies that the switching is governed by the amount of (trapped) electrons at the anode.

\[ V_{\text{switch}} - V_{\text{bi}} (V) \]

**Figure 4.6:** Thickness dependence of the switching voltage \( V_{\text{switch}} \), compensated for the built in voltage. The solid line corresponds to quadratic behaviour (slope 2).

A very useful technique for analyzing charge concentrations at interfaces is impedance spectroscopy (IS) [76]. With this technique, the real and imaginary part of the impedance is measured as a function of frequency. From the impedance scan the different charge layers can be separated by treating them as equivalent \( RC \)-circuits. In figure 4.7 the real and imaginary part of the impedance are plotted in a Nyquist-diagram (\( f = 20 \text{ Hz} - 1 \text{ MHz} \)). It shows IS for a fresh PEDOT PLED, where figure 4.7a is at \( V = 3 \text{ V} \), characteristic for \( V \leq 3 \text{ V} \), and figure 4.7b is for \( V = 3.2 \text{ V} \). For \( V < 3 \text{ V} \), one large semicircle is observed, corresponding to one charge layer with a large differential resistance. Modeling this device as a parallel \( RC \)-circuit (inset figure 4.7a) gives a (differential) capacitance \( C_1 = 2.3 \text{ nF} \), which is in agreement with the geometrical capacitance using \( \varepsilon_r = 2.1 \). At a slightly higher voltage, \( V = 3.2 \text{ V} \), the device starts to switch on, as has been observed from the photodiode current during the IS. As shown in figure 4.7b at \( V = 3.2 \text{ V} \) a clear double semicircle is observed. Modeling the device as a double \( RC \)-circuit (inset of figure 4.7b), capacitance values of \( C_1 = 2.1 \text{ nF} \) and \( C_2 = 70 \text{ nF} \) have been obtained for \( V = 3.2 \text{ V} \).

Despite the large difference in impedance for \( V = 3 \text{ V} \) and \( V = 3.2 \text{ V} \), the values of the capacitance \( C_1 \) are quite close. This shows that \( C_1 \) is the bulk capacitance and that \( C_2 \), which is only observed clearly above 3 V, must definitely be related to the switch effect. In order to investigate the relation between this extra \( RC \)-circuit and the switch effect, a complete voltage sweep has been made. In figure 4.8, the differential capacitances \( C_1 \) and \( C_2 \) have been plotted. It is observed that \( C_1 \) does not depend on bias, as is expected for the geometrical capacitance. However, \( C_2 \), which is attributed to charging of the PEDOT:PSS/PFO interface, strongly de-
4.3 Results

Figure 4.7: Impedance spectroscopy (IS) of a PEDOT PLED with thickness \(d = 80\) nm at room temperature. Measurements are shown for an applied bias of (a) \(V = 3\) V and (b) \(V = 3.2\) V. The solid lines are fits from the equivalent circuits (insets).

-themed on the applied voltage and increases up to \(1\mu F\) at \(5\) V (figure 4.8). As a consequence, a lot of charge has been built-up during the voltage scan. Decreasing the voltage again, \(C_2\) sharply decreases below \(\sim 4\) V. The low capacity means that the charge built-up at the contact does not react on the modulation voltage. This implies that the charge that is accumulated at high voltage is trapped at the PEDOT:PSS/PFO interface.

The amount of charges at the PEDOT:PSS/PFO interface, \(N_i\), can be calculated by integrating the differential capacitance \(C_2\) as a function of voltage:

\[
N_i = \frac{1}{eA} \int_0^V C_2 dV. \tag{4.1}
\]

As the voltage over \(C_2\) does not equal the applied bias, it has been corrected by integrating the differential resistances of both circuits and finding the voltage drop over each circuit separately. The surface charge \(N_i\), calculated from equation 4.1 is plotted in figure 4.9.

Looking in more detail, figure 4.9 also contains three regimes: at small voltages on the advancing curve, charge is being built-up super-linearly. Then, at \(\sim 4\) V, saturation takes place (dQ/dV~constant, figure 4.8), and \(C_2\) behaves as a normal capacitor with a high capacity. For voltages < \(4\) V on the receding curve, excess charge remains at the interface. It is observed that the trapped surface charge concentration amounts to \(N_{it} = 1 \times 10^{17} \text{ m}^{-2}\). This is of the same order of magnitude as \(N_{it} = 2 \times 10^{16} \text{ m}^{-2}\) observed at a Ag/OC\textsubscript{10}PPV interface (see chapter 3 and Ref. [77]). This numbers show that a high interface density is required to enhance the hole injection.

4.3.4 Regime 3: on-state

In order to confirm whether the electro-optical characteristics of the PEDOT PLED in this regime are bulk limited [71] (implying Ohmic contacts), or still limited by the hole injection, we
Figure 4.8: Differential capacitances $C_1$ and $C_2$ as a function of applied bias. Capacitance $C_1$ is the bulk capacitance and the component $C_2$ corresponds to the charge layer at the interface between PEDOT:PSS and PFO.

Figure 4.9: Surface charge density $N_i$ (equation 4.1) found from $C_2$ (figure 4.8) for a PEDOT PLED.
have measured the hole mobility with transient electroluminescence (TEL). In this technique [58] a voltage pulse of varying duration $\tau_{\text{pulse}}$ is applied, maintaining a constant repetition frequency. The delay time $\tau_d$ between the start of this pulse and the onset of the resulting electroluminescence is derived from the relation between photocurrent and pulse length $\tau_{\text{pulse}}$. This delay time $\tau_d$ is a direct measure of the transit time of the fastest carrier (holes) towards the recombination zone at the other electrode, from which the charge carrier mobility can directly be calculated:

$$\mu = \frac{L^2}{(V - V_{bi})\tau_d}$$ (4.2)

In OC$_1$C$_{10}$-PPV the observed mobility exhibited a dependence on sample thickness, which is an indication of dispersive transport [58]. From TOF experiments on PFO [17] it has been shown that the hole transport in PFO is non-dispersive. As a result the TEL technique will provide direct information on the charge carrier mobility. The results for two PEDOT PLEDs with different thicknesses are shown in figure 4.10.

Figure 4.10: The hole mobility as a function of electric field for two devices with thicknesses $d = 60$ nm and $d = 100$ nm, determined with transient electroluminescence (TEL). The solid line is a fit to equation 1.14.

It is observed that the mobility is indeed independent of the thickness, indicating non-dispersive hole transport. From the measurements in figure 4.10 a zero-field mobility $\mu_0 = 1.0 \times 10^{-9}$ m$^2$/Vs and a field prefactor $\alpha = 5.5 \times 10^{-5}$ (m/V)$^{1/2}$ have been found (equation 1.14). These values are in close agreement with a zero-field mobility $\mu_0 = 2.7 \times 10^{-9}$ m$^2$/Vs and a field prefactor $\alpha = 5.5 \times 10^{-5}$ (m/V)$^{1/2}$ from TOF experiments [17].

To see whether the hole contact after switching is Ohmic, we have calculated the hole current in a PLED from the hole mobility (figure 4.11). It is observed that the calculated hole current (dashed line) is slightly lower than the current of the PLED, which is identical to the behavior
Figure 4.11: $J - V$ characteristics of a PEDOT PLED ($d = 60$ nm, room temperature). The solid line corresponds to the calculated hole current for Ohmic contacts. The dashed line is the current density calculated from a PLED device model, including Langevin recombination. The PEDOT PLED has been corrected for a built-in voltage of $V_{bi} = 3.2$ V.

in PPV-based LEDs [19]. The electrons neutralize the holes and as a result a LED contains more holes than a hole-only device. Consequently, the current in an LED is slightly larger. In figure 4.11 also the bipolar current is calculated, assuming an exponential electron-trap distribution in the bulk with concentration $N_t = 2 \times 10^{24}$ m$^{-3}$, and Langevin recombination. The excellent agreement with the experimental PLED current demonstrates that the hole contact after switching is Ohmic. Furthermore, it should be noted that the voltage over the PEDOT PLED has been corrected by a large built-in voltage of $V_{bi}$ = 3.2 V. This large $V_{bi}$ is in agreement with the band gap of PFO [17], which is another indication that both the hole and electron contact are Ohmic, as the built-in voltage is determined by the difference in energy levels of both contacts.

4.4 Discussion

The formation of an Ohmic hole contact on PFO has been attributed to trapped electrons that increase the electric field at the anode and consequently enhance the hole injection [71]. We have proposed this mechanism to explain the current enhancement in OC$_1$C$_{10}$-PPV based LEDs with a limited hole injection from a Ag contact (chapter 3 and Ref. [77]). However, there are a number of fundamental differences between the behavior of the Ag/PPV and PEDOT/PFO contacts. For OC$_1$C$_{10}$-PPV based PLEDs the enhanced current and light output are observed for different anodes, like Ga, In and Ag (paragraph 3.4.4). These different anodes have a very
different chemical interaction with the polymer and therefore the electron trap in an OC$_1$C$_{10}$-PPV based PLED is not related to the anode material, but is an intrinsic property of the polymer. On the other hand, for PFO the effect of an enhanced current is specifically observed for a PEDOT:PSS anode, and not for contacts like ITO or Ag. In this case, the electron trap at the interface must be the result of a specific interaction of the PFO and the PEDOT:PSS or related to a specific property of the PEDOT:PSS. Moreover, from the $J-V$ characteristics of a PEDOT PLED (figure 4.2) a very sharp transition is observed, whereas the increase in the $J-V$ characteristics of an OC$_1$C$_{10}$-PPV based PLED is more gradual and does not exhibit any hysteresis (figure 3.2). This is in contrast with the PEDOT/PFO PLED where the ’on-state’ is maintained with decreasing voltage. A further indication for the origin of the switching effect is the switching process is reversible on long time scale ($\sim 10^6$ s at RT, figure 4.3), which excludes chemical modifications of the interface as the origin of the switching behavior. The underlying principle must be physical, e.g. a deep trap. However, a deep trap alone is not sufficient to explain the effect; model calculations on an IL-PLED demonstrate that such a trap-level is gradually filled with increasing voltage and therefore gives rise to a gradual increase of the current, see figure 3.3. The sharp transition observed in the first $J-V$ scan (figure 4.2) points towards a different mechanism, like the presence of a thin tunnel barrier. Experiments with 3 eV electrons impinging a free PEDOT:PSS film show modification of the chemical compounds at the outermost region of the film, although reported for longer time scale (hours) [75]. Experimental evidence is found from X-ray experiments on a PEDOT:PSS layer that shows segregation of the PSS dopant towards the PEDOT:PSS surface forming a layer of PSSH at the interface of a few nm. It might be that this small layer forms a tunnel barrier and is therefore responsible for the sharp transition. In that case, the effect at the PEDOT:PSS/PFO interface is the charging of a small insulating layer through which holes must tunnel at a high field. The resulting dipole shifts the Fermi-level of PEDOT:PSS towards the HOMO of PFO and from a certain voltage the holes can directly tunnel into the transport states of the HOMO of PFO. The density of trapped electrons as determined from IS, $N_{tr} \sim 10^{17}$ m$^{-2}$, results in an electric field across the insulating layer of $E \sim 10^9$ V/m. An insulator thickness of only 1 nm therefore would result in a dipole of 1 V, equal to the difference in work-function of PEDOT:PSS and the HOMO of PFO. For poly(9,9-dioctylfluorene-co-benzothiadole), a polymer similar to PFO, Murata et al. [67] have modeled the device characteristics of a PLED with a PEDOT:PSS anode by including a tunnel barrier at the anode (see figure 3.5b). Their model calculations show that the generated electric field at a tunnel barrier indeed gives rise to a sharp increase of the hole injection. Finally, we have demonstrated that the electron transport in PFO can be manipulated via the synthesis route. The only difference between the polymers PFO(1), PFO(2), and PFO(3) is the last step, the replacement of one of the reactive end groups of the polymer by a fluorene or benzene monomer via end-capping. It is observed from figures 4.5a,b that the reduced electron transport is accompanied by an increase of the green 530 nm emission (PFO(1) and PFO(2)). The peak at 530 nm is attributed to emission from chromophores where the side chains have been replaced by a double-bonded Oxygen (fluorenone) [79]. Apparently, the fluorenone defects serve as efficient electron traps [79], as indicated by the reduced electron current of PFO(1-3). The presence of fluorenone defects might also explain the difference in switching voltage: It has already been mentioned in paragraph 4.3.3 that the switching voltage is controlled by the amount of electrons at the hole injecting contact. The amount of electrons at the hole injecting contact is in
turn determined by the number of bulk traps in the polymer. The lower switching voltage for PFO(2) and (3) with respect to PFO(1), is most likely due to a reduction of bulk traps in these PFO-batches.

4.5 Conclusions

In summary, it is found that the switching of a PFO based PLED is specific for a PEDOT:PSS hole contact. This can be due to specific properties of the PEDOT:PSS, or to a specific interaction of PEDOT:PSS with PFO, which does not occur for ITO or Ag. Furthermore, the device in the off-state is controlled by electron transport. This electron transport depends strongly on the way the polymer is end-capped. The bias at which a PEDOT PLED switches on is strongly dependent on the electron current (which is influenced by thickness of the active layer, cathode material and synthesis of the polymer), and it has been found that the electron concentration at the PEDOT:PSS/PFO contact controls the switching voltage of the device.