Charge injection into organic semiconductors
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Chapter 3

Hole injection in a polymer light-emitting diode

3.1 Introduction

Now we gained knowledge about the mechanism of the charge injection into a semiconducting polymer (chapter 2), it is interesting to find out how such an injection limited contact influences the electro-optical characteristics of a polymer light emitting diode.

In order to understand the role of an injection limited contact, the bulk properties of the semiconducting polymer must be known. For the OC$_{11}$C$_{10}$-PPV based PLED, the properties of both the electron and hole transport as well as the recombination are well known [19]. As a result, it is an ideal model system to investigate the limited hole injection into a PLED. Therefore, injection limited (IL) PLEDs based on OC$_{11}$C$_{10}$-PPV have experimentally been investigated, replacing the Ohmic ITO contact with a Ag anode (figure 3.1).

Since the field- and temperature dependence of the hole injection from the Ag contact into the OC$_{11}$C$_{10}$-PPV is known, (chapter 2 and Ref. [64]) the current and light output of this IL-PLED can be predicted by incorporating the hole injection into the PLED device model (paragraph 3.2). It is expected from these calculations that the current and light output of the device
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will be strongly reduced due to the hindered hole injection from the Ag contact. At low voltages the expected reduction of the current and light output due to the presence of the hole contact barrier is indeed observed. However, at higher bias (>7 V) the experimental light and current density exhibit a strong increase, which is attributed to an enhanced electric field at the injection-limited hole contact due to trapped electrons.

### 3.2 Incorporation of the hole injection into the device model

As a first attempt to incorporate charge injection into PLED device models the classical diffusion-limited thermionic emission model has been used [65,66]. However, we have now demonstrated (chapter 2 and Ref. [64]) that the classical thermionic emission is not the proper model for charge injection into OC$_{10}$-PPV, and we have to use the hopping based injection model instead (equation 1.25). By incorporating this hopping based injection model into the PLED device model also PLEDs with strongly hindered hole injection can be investigated.

The device model is outlined shortly below, see also Ref. [19]. For operating biases in PLEDs, the electric field is relatively high and the diffusion is negligible in the bulk of the material. Consequently, the device current is the sum of the electron and hole drift current:

$$ J = J_p + J_n = e\mu_p p E + e\mu_n n E $$

with $E$ the electric field, $p$ and $n$ respectively the hole and electron concentration and $\mu_p, \mu_n$ the hole and electron mobility. The electric field throughout the device is calculated by the Poisson equation:

$$ \varepsilon \frac{dE}{dx} = p - n - n_t $$

with $\varepsilon$ is the dielectric permeability of the semiconductor, and $n_t$ the concentration of trapped electrons. The limited hole injection is incorporated via the current-electric field relation (equation 1.25). For a given current the electric field at the hole contact is then known and serves as the starting field for equation 3.2. This procedure is similar to the one employed in an analytic model for single carrier transport in a PLED with an injection limited contact [21].

For the material under consideration, OC$_{10}$-PPV, the hole mobility parameters are listed in paragraph 1.3.1. The bulk limited electron current is a few orders of magnitude lower than the hole current [29, 30] and can be described by a lower electron mobility [30], or by a trap limited electron current, with the transport parameters of the hole mobility, together with an electron trap [29]. Combining the results of the electron- and hole transport a device model for PLEDs has been proposed in which the recombination of electrons and holes is of the Langevin-type, in which the rate-limiting step is the diffusion of electrons and holes toward each other [19]. The continuity equation then gives:

$$ \frac{1}{e} \frac{dJ_n}{dx} = -\frac{1}{e} \frac{dJ_p}{dx} = B p(x) n(x) $$

with $B$ the recombination constant, determined by Langevin recombination [19],

$$ B = \frac{e}{\varepsilon} (\mu_n + \mu_p). $$
3.3 Experimental

The light output of the device is proportional to the total number of recombinations, reduced by the non-radiative recombination as a result of the spin statistics and non-radiative recombination centers and further reduced by the losses in the device.

3.3 Experimental

In order to clarify the effect of a contact barrier on the electro-optical characteristics of an IL-PLED, four different device types have been investigated, all consisting of a spin-coated layer of the polymer OC$_1$C$_{10}$-PPV sandwiched between two electrodes. As a reference, an ITO/OC$_1$C$_{10}$-PPV/Ca PLED with two Ohmic contacts is made. Then, the injection-limited ITO/Ag/OC$_1$C$_{10}$-PPV/Ca PLED (IL-PLED) has been constructed, where the ITO bottom contact has been covered by Ag (figure 3.1). For the investigation of reduced hole injection from the Ag electrode ITO/Ag/PPV/Ag devices have used, with an electron-blocking Ag top contact. This devices have been described in paragraph 2.3. In order to discriminate whether the current in the IL-PLED is dominated by the (reduced) hole or the electron current also Ytterbium/PPV/Ca electron-only devices have been investigated.

3.4 Enhanced hole injection in the presence of electrons

Figure 3.2a shows the current-density voltage ($J-V$) plot for the ITO/Ag/PPV/Ca IL-PLED together with the electron-only Yb/PPV/Ca and the ITO/Ag/PPV/Ag device. It is demonstrated that the hole current injected from a Ag contact is about one order of magnitude smaller than the bulk-limited electron current. As a result the current of the IL-PLED is expected to be identical to the electron current, which is verified by the calculations using the PLED device model including hopping-based injection (solid line). Experimentally, it is observed (figure 3.2a) that for low bias the current density-voltage ($J-V$) characteristics of the ITO/Ag/PPV/Ca IL-PLED are indeed identical with the electron-only characteristics. However, at an applied bias of typically $V = 7 \text{ V}$ the current starts to depart from the expected electron current. Since the space-charge limited electron current shown in figure 3.2a is the maximum current an electron-only device can contain, the increase of the IL-PLED must arise from an increased hole injection. This is confirmed by the observed light output of the IL-PLED, shown in figure 3.2b. The light output is proportional to the product of electron and hole density [19]. thus the reduced hole injection decreases the light output of the IL-PLED compared with a bulk-limited PLED. It is observed from figure 3.2b that at low voltages the light output of the IL-PLED is indeed decreased by several orders of magnitude as compared to the ITO/PPV/Ca device. The difference between the calculated and measured light output is caused by the detection limit of the light sensor. The rapid increase of the light output above 7 V, compared with the calculated light output, also points towards a large enhancement of the hole injection from the Ag contact into the polymer.

3.4.1 Electron traps at hole contact

A possible explanation for the enhanced hole injection at high voltages is an interfacial layer at the Ag anode with electron traps (see inset figure 3.3). At sufficient voltages these traps become
Figure 3.2: (a) $J - V$ at room temperature for a Ag/PPV/Ca IL-PLED. For comparison, an ITO/Ag/PPV/Ag IL hole-only device and an Yb/PPV/Ca electron-only device are also shown, all with film thickness $L = 240$ nm. The solid line represents the numerically calculated $J - V$ characteristics of the IL-PLED for a hole injection barrier $\phi_b = 0.95$ eV. (b) Light output of the ITO/PPV/Ca (PLED) and Ag/PPV/Ca (IL-PLED) device at room temperature. The solid lines represent the calculated light output without interface traps. The difference with the experimental light output of the IL-PLED at low bias is due to the detection limit of the photodiode.

filled and the trapped electrons will increase the electric field at the Ag/PPV interface, leading to an enhanced hole injection. It should be noted that such electron-traps remain unfilled in an ITO/Ag/PPV/Ag hole-only device and therefore do not play a role in the investigation of the injection-limited hole current [64]. We have incorporated electron traps in an interfacial layer extending a few nm from the contact. The effect of these traps are described by a single parameter that represents the ratio of free electrons $n$ and trapped electrons $n_t$:

$$\theta = \frac{n}{n + n_t}. \tag{3.5}$$

In figure 3.3 the $J - V$ characteristic of the ITO/Ag/PPV/Ca IL-PLED is shown, together with the calculated current from the device model where next to hopping-based injection also interface traps have been included. The only unknown parameter in the device model is the trap parameter $\theta$ (equation 3.5). It is demonstrated (figure 3.3a) that the strong increase of the experimental current at high voltages is consistently described by introducing an interfacial layer of electron traps. Also the light output calculated with this small interfacial trap region is in good agreement with the experimentally obtained characteristics (figure 3.3b).

### 3.4.2 A close look at the origin of the enhanced hole injection

To give more insight in the process of enhanced hole injection, the potential landscape near the Ag hole injecting contact is plotted in figure 3.4 for both the case of no interface traps and the case of interface traps. This plot is obtained by integrating the electric field that has been
3.4 Enhanced hole injection in the presence of electrons

Figure 3.3: (a) $J - V$ at room temperature for a Ag/PPV/Ca IL-PLED. film thickness $L = 240$ nm. The solid line represents the numerically calculated $J - V$ characteristics of the IL-PLED for a hole injection barrier $\phi_b = 0.95$ eV in the presence of electron traps close to the Ag electrode, with a free-to-trapped carrier ratio $\theta = 7 \times 10^{-5}$. (b) Light output of the ITO/PPV/Ca (PLED) and Ag/PPV/Ca (IL-PLED) device at room temperature. The solid lines represent the calculated light output without interface traps, the dashed line shows the light output of the IL-PLED with traps at the Ag contact.

calculated by the device model, and taking into account the potential energy lowering due to the image force effect. This image force induced potential lowering is also taken into account in the hopping based injection model (equation 1.25) that is used in the device model as the boundary condition for hole injection. It is observed from figure 3.4 that the presence of Ag-PPV interface traps strongly enhance the band-bending near the contact. As a result, jumps into tail states require less energy. Apart from that, the escape from the site to which the carrier is injected is also a strong function from the electric field (equation 1.27). The hole injection is therefore enhanced by several orders of magnitude, compared with the hole injection from a contact with no electron traps. For high enough field at the interface the hole injection current will dominate the device current, in accordance with the observations from figure 3.2. It should be noted that our results are modelled by an enhanced electric field near the hole injecting interface, which enhances the hole injection. This is physically different from a process that might on first hand seems identical: enhanced tunneling of holes across a small interfacial insulating layer [67]. The difference is explained in figure 3.5. In figure 3.5a the situation is schematically depicted for electron traps close to the hole injecting interface, as we have used in our calculation to explain the enhanced hole injection in the OC$_1$C$_{10}$-PPV based IL-PLED. In figure 3.5b, the situation of a small insulating layer at the anode is explained. This model has been used to explain the enhanced performance of double-carrier devices of a polyfluorene derivative [67]. The anode blocks the electron extraction from the device, which results in an electron accumulation close to the contact. This results in a dipole across the insulating layer at the anode, and this enhances the hole injection. On first hand, only the way the electron accumulation is functionalized (traps in figure 3.5a vs blocking at a tunnel barrier in figure 3.5b) seems to differ. However,
Figure 3.4: Electrostatic potential near the hole injecting electrode at an applied bias of 15V. The dotted lines indicate the potential due to the electric field only, whereas the solid lines illustrate the potential landscape when image force is included (equation 1.10). The arrows indicate the jump to a nearest neighbour distance in the polymer, which is the most probable first hop the injected carriers will make.

Figure 3.5: Schematic representation of two different mechanisms of enhanced hole injection: (a) The presence of interface traps near the hole injecting contact, as used in our work to explain the observed increase in the IL-PLED current at large biases. (b) Presence of an interfacial tunneling layer that blocks electrons from extraction, and thereby creates a dipole that enhances hole injection, as is used in Ref. [67].
the main difference is the enhanced electric field vs the effect of an electric dipole across an insulating layer. In the latter case, the holes tunnel through a small insulating layer into equienergetic states in the conjugated polymer, a process that more resembles Fowler-Nordheim behaviour [56]. It is explained in paragraph 3.4.4 why the electron tunneling model is not used.

3.4.3 Temperature dependence of the enhanced hole injection

In figure 3.6 the temperature dependence (T-dependence) of the \( J - V \) characteristics of the ITO/Ag/PPV/Ca IL-PLED is shown, together with the calculated current from the device model, including interface traps. It is observed that the T-dependence of the enhanced current can be consistently explained by the inclusion of a small region of interface traps. The ratio \( \theta \) found from the \( J - V \) characteristics is plotted in figure 3.7 as function of temperature. For a single-level shallow trap in a band-like semiconductor, the T-dependence of the ratio \( \theta \) is given by [68]

\[
\theta = \frac{n}{n + n_t} = \frac{N_C}{N_t} \exp \left( -\frac{E_C - E_t}{kT} \right),
\]

where \( N_C \) is the effective density of states of the band, \( N_t \) the number of trap sites, and \( E_C - E_t \) the trap depth. However, for strongly disordered semiconductors the transport sites have a Gaussian distribution of energies (DOS) [12], characterized by an energy width \( \sigma \). From mobility measurements on OC\(_3\)C\(_{10}\)-PPV a typical energy width of \( \sigma = 0.11 - 0.12 \) eV has been obtained [44]. In such a disordered system the ratio \( \theta \) between free and trapped carriers

![Figure 3.6: \( J - V \) of the IL-PLED at different temperatures. The solid lines represent the calculated device current including electron traps in an interfacial layer of a few nanometers near the Ag contact.](image-url)
Figure 3.7: Ratio $\theta$ of free and trapped electrons as a function of the temperature. The solid line represents the T-dependence for a Gaussian DOS with energy width $\sigma = 0.12$ eV and a trap depth $E_C - E_t = 0.6$ eV.

(equation 3.5) in case of a shallow trap is then given by

$$\theta = \frac{N_{sites}}{N_t} \exp \left( \frac{1}{2} \left( \frac{\sigma}{kT} \right)^2 - \frac{E_C - E_t}{kT} \right),$$

with $N_{sites}$ the number of transport sites. It is shown in figure 3.7 that the experimentally obtained $\theta$ is in agreement with equation 3.7 for a trap energy level $E_C - E_t = 0.6$ eV. Thus the observed rise as well as the T-dependence of the current of the IL-PLED can be simultaneously explained by the presence of electron traps near the Ag contact. The trap concentration $N_t$ in equation 3.7 has been found to be $N_t = 2 \times 10^{24}$ m$^{-3}$ for an interfacial layer extending $d = 10$ nm into the polymer. It should be noted that not the concentration of electron traps $N_t$ but the total number of electron traps per area, $N_{it} = N_t d = 2 \times 10^{16}$ m$^{-2}$, governs the $J-V$ characteristics. The increase of the electric field at the interface depends only weakly on the exact spatial distribution of the electron traps.

### 3.4.4 Barrier dependence of the enhanced hole injection

In order to investigate whether the enhanced hole injection at high fields occurs for electrodes other than Ag also IL-PLEDs with Indium (In) and Gallium (Ga) anodes have been investigated. From their work functions, energy barriers around 1 eV are expected for both In and Ga, although the injection properties could be more complicated due to possible chemical reactions at the interface [57]. Figure 3.8 demonstrates that also for In and Ga the current of the IL-PLED starts to deviate from the electron-only current (Yb) at high fields, pointing to an enhancement of the hole injection. However, the enhancement of the current for Ga and In shows a weaker dependence on the applied bias as compared to Ag. As the injection current is very sensitive to the
3.5 Conclusions

In conclusion, it has been demonstrated that at low voltages the characteristics of a PLED with a strongly hindered hole injection are governed by the transport properties of the electrons. The rise of the device current at high voltages, however, is caused by an enhancement of the hole injection. The field-, temperature- and barrier height dependence of the current of such an injection-limited PLED is consistently described by including an interfacial layer of electron traps at the hole contact.

**Figure 3.8:** IL-PLED device current at room temperature for different contact materials as a function of applied voltage. Thickness of the devices is $L = 240$ nm. The solid lines represent the numerically calculated $J - V$ characteristics for barrier heights $\phi_b$ of 0.95 and 1.1 eV respectively.

Injection energy barrier, the device current of the IL-PLED is also calculated for a barrier height of 1.1 eV, assuming the same concentration and depth of the interface traps. This calculated current density approaches the current of an IL-PLED with an In anode, as shown in figure 3.8. In the low bias regime (<7V) it is observed from figure 3.8 that the current of the IL-PLEDs with Ga, In and Ag fall on top of the electron-only (Yb) current. This behavior excludes an alternative explanation for the occurrence of enhanced hole injection in our devices, namely the presence of an electron-tunneling barrier at the anode [67], that is explained in paragraph 3.4.2. The fact that at low fields the current of the IL-PLED is anode independent would imply that exactly the same tunneling barrier would be formed on the noble metal Ag as on the reactive Yb, which is highly unlikely.

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