



Hole injection from an ITO|PEDT anode into the hole transporting layer of an OLED probed by bias induced absorption

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Abstract

Poly(3,4-ethylenedioxythiophene) and poly(styrenesulfonic acid) (PEDT:PSS) is commonly used as buffer layer between indium tin oxide anode and the emitting layer in organic light emitting diodes. To understand the beneficial effect of PEDT:PSS to the device performance, the interface between the buffer layer and a hole transport layer (HTL), i.e. 1,3,5-tris-(*N,N*-bis(4,5-methoxy-phenyl)aminophenyl)benzene (TDAPB), has been investigated by spectroscopical means. The number of radical cations in the HTL has been monitored quantitatively by bias induced absorption measurements as a function of voltage. The results are discussed in terms of (a) chemical interaction between TDAPB and PEDT:PSS and (b) charge accumulation at the interface of TDAPB/tris(8-hydroxyquinolinato)aluminium (Alq₃). The in situ formation of TDAPB⁺ after deposition is believed to be the reason for ohmic contacts at the interface, improving hole injection into the HTL.

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1. Introduction

Owing to its high conductivity and its transparency within the relevant spectral range combined with low cost fabrication, indium tin oxide (ITO) deposited on top of a glass substrate is the preferred anode for hole injection into light emit-

ting diodes. However, the long term stability of the electrode remains to be a problem. It is known that under action of a high electric field there is some chemical degradation occurring and reactive products such as indium cations can migrate into the bulk of the dielectric [1,2]. Surface roughness of commercial ITO enhances this effect [3].

In order to eliminate these shortcomings one can insert a transparent buffer layer between ITO and the hole transporting layer (HTL). To reduce the electric field at the ITO-interface the material has to be conductive and, concomitantly, must

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have the ability to inject holes into the diode structure. The ultimate goal is that the buffer is able to form an ohmic anode, i.e. supply a space charge limited current (SCLC) of holes. This imposes a restriction regarding the energy barrier at the pertinent interface [4]. The layer should also be fabricated at ease via spin coating and one has to guarantee that the solvents used in the course of cell fabrication are mutually incompatible.

A layer which has profitably been used is a dispersion of poly(3,4-ethylenedioxythiophene) (PEDT) and poly(styrenesulfonic acid) (PSS), and has been commercialised by Starck under the trade mark of Baytron® P [5]. The specific resistance of the composite used here (AI 4083) is about 500 Ωcm . This comparable low resistance with respect to the subsequent deposited organic layers ensures the electric field to be negligible within this buffer layer. The PEDT:PSS layer forms therefore the anode in this device set-up.

The purpose of this work is to discuss (i) the mechanism by which hole injection from PEDT:PSS into the HTL occurs and (ii) why it can form an ohmic electrode. The experimental technique employed is the absorption due to radical cations of the hole transporting material as a function of the applied bias.

2. Experimental

The system investigated here is a multi layer organic light emitting diodes (OLED) consisting of an ITO|PEDT:PSS-Anode, 1,3,5-tris-(*N,N*-bis(4,5-methoxy-phenyl)aminophenyl)benzene (TDAPB) as a hole transporting material, tris(8-hydroxyquinolinato)aluminium (Alq_3) as both electron transporting (ETL) and emitting layer, and a Mg:Ag (10:1) cathode. *I*–*L*–*V*-characteristics and lifetime data of this device set up have been reported before [6].

An aqueous solution of Baytron® P(AI 4083) (Starck GmbH, Leverkusen) was spin coated at a speed of 1800 cycles per minute on top of an ITO coated glass (Baltracon 255) which had been cleaned in various solvents. The solution contained 1.6 wt.% PEDT:PSS. The residual water was removed at 120 °C. The next layer consists of the

hole transporting material TDAPB, spin coated from an 1.5 wt.% solution in tetrahydrofurane (THF) to an effective thickness of 100 nm. Because water and THF are mutually incompatible the PEDT:PSS film is resistant against etching via THF. Due to anticipated swelling at the interface, we estimate the reduced thickness of the HTL to be 90 nm in our calculations. Afterwards a 60 nm thick layer of Alq_3 was vapour deposited forming both electron transporting (ETL) and light emitting layer. A Mg:Ag (10:1) cathode, formed by co-evaporating magnesium and silver at a rate of 2.0 and 0.2 nm/s, respectively, completed the device which was subsequently encapsulated. The energy scheme of the device is shown in Fig. 1.

A rectangular periodic voltage of a frequency of 330 Hz and an amplitude of -1 V was applied to the OLED (function generator Toellner TOE7720) and the modulated change of light absorption within a wavelength regime 600–950 nm where the TDAPB⁺ cation absorbs was monitored employing an 100 W halogen lamp and a monochromator (Oriel 7240). The light reflected from the metal cathode was detected by a Si-photodiode (Lambda Physik, UDT pin 10). A phase-sensitive amplifier (Stanford Research SR 830) recorded the in-phase component ΔI of the recorded probing light I_0 . It yields the relative change of the absorption $\Delta I/I_0$

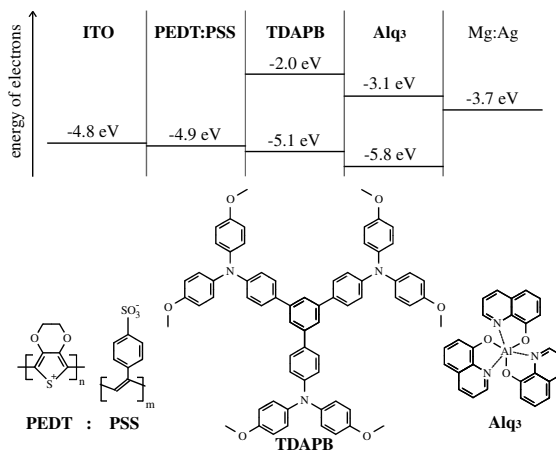


Fig. 1. Energy level scheme of the OLED and molecular structure of the used materials. The LUMO levels are taken from the optical absorption thus ignoring the exciton binding energy and vacuum level shifts.

due to TDAPB⁺, i.e. the differential absorption spectrum. Furthermore, the amplitude of the voltage was varied yielding a bias dependent set of differential absorption spectra. The latter could be analysed in terms of a voltage dependent amplitude of the absorption peak. The absorption spectrum of the radical cation in solution was obtained as described in [7].

3. Results and discussion

Fig. 2 shows the differential absorption spectrum induced by applying a periodic voltage U to the OLED. It agrees with the absorption spectrum of the radical cation, TDAPB⁺, measured in solution [8]. In the vicinity of $U = 0$ the amplitude of the absorption peak varies linearly with voltage (Fig. 3). The dc-current in this regime is negligible compared to the displacement current. The OLED acts electrically as a plate capacitor with two dielectrics, the HTL and the ETL. By variation of the applied bias U a change in the plate charge following coulombs law: $U = E \cdot d = (\sigma/\epsilon_{\text{rel}}) \cdot d$ is induced. In case of $U = 0$ the change of plate charge density σ due to a change of applied bias can be calculated directly. Therefore, based upon the absorption cross-section of TDAPB⁺ the number of the positive charges inside the dielectric can be determined quantitatively. At reverse bias

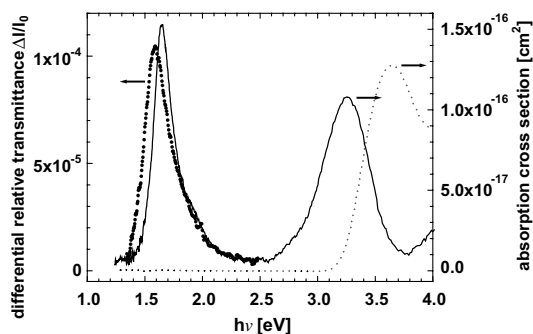


Fig. 2. Comparison of the TDAPB absorption spectrum in solution (dotted line), the absorption spectrum of the radical cation TDAPB⁺ (full line, peak at 1.65 eV) and the bleaching spectrum of the OLED under negative bias of -5 V (dots, peak at 1.59 eV). The peak shift of 60 meV is independent of the applied bias, explained in terms of solvation effect.

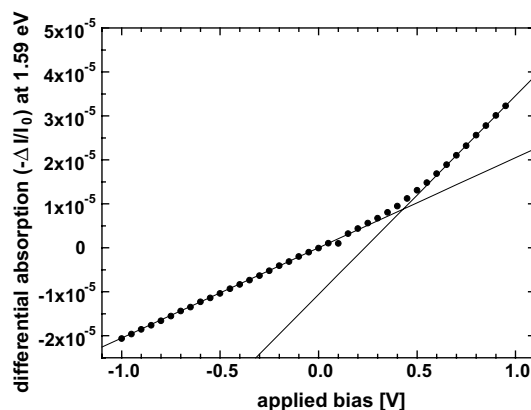


Fig. 3. Voltage dependent differential absorption and bleaching of the OLED at the maximum wavelength of TDAPB⁺-absorption. The intercept of the two linear fits at 0.43 V is attributed to the onset of hole injection into the HTL.

the calculated capacitance turns out to be that of an ideal plate capacitor formed by the TDAPB and Alq₃ layer using an average dielectric constant $\epsilon_{\text{rel}} = 4.5$. Upon increasing the reverse bias, $U < 0$, the number of negative charges inside the ITO|PEDT:PSS electrode increases, spectroscopically monitored via a decrease of the number of TDAPB⁺ cations. Since at reverse bias there can be no TDAPB⁺ cations inside the bulk, i.e. the decharging process TDAPB⁺ + e⁻ → TDAPB⁰ must occur at the PEDT:PSS|TDAPB interface only. Obviously, the reverse electric field must be generated by an effective negative layer of anions inside the electrode. Because the charging process of the plate capacitor can solely be described by the voltage dependent change of the number of TDAPB⁺ cations the number of anions must be stationary, i.e. independent of the applied voltage U . At $U = 0.43$ V, the anode becomes effectively neutral because the charge of excess anions at the surface of the PEDT:PSS layer is exactly compensated by the counter charge of the TDAPB⁺ cations. The differential absorption at $U < 0.43$ V is caused by the reduction of the hole transporting material, TDAPB⁺ + e⁻ → TDAPB⁰.

The above simple scheme is supported by chemical reasoning. Upon mixing PEDT:PSS the monomeric ethylenedioxythiophene (EDT) is polymerised oxidatively and charge neutrality is

established by the cationic PEDT⁺-segments. Upon adding a 1 wt.% of EDT per 6 wt.% of PSS one fraction of sulfonic acid groups forms a PEDT⁺:PSS⁻-salt and the remaining PSS stays neutral. When depositing a TDAPB layer on top of PEDT:PSS via spincoating, there will be a thin zone in which the PEDT⁺:PSS⁻-salt and TDAPB molecules coexist and the reaction PEDT⁺:PSS⁻ + TDAPB → PEDT:PSS⁻ + TDAPB⁺ occurs.

A similar mechanism where PSS is anticipated to p-dope poly[2-methoxy-5(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) at the interface, has been proposed to explain the improved hole injection due to PEDT:PSS into polymeric emitters [9].

The thickness of this intermixing zone at the interface PEDT:PSS|TDAPB has not been determined in detail. The range should however be at least in the order of interfaces between incompatible polymers, i.e. >2 nm [10], not taking into account additional swelling due to TDAPB deposition from THF-solution. Consequently the orientation of the dipoles formed by the charge pairs remains statistically random. Effectively no remarkable dipole layer is formed which might affect the built-in potential U_{BI} significantly. In the case of a negatively charged PEDT:PSS|TDAPB-interface, i.e. upon applying an external reverse bias, the concomitant reaction TDAPB⁺ + e⁻ → TDAPB⁰ leads to a surplus of the negative charge of the PSS⁻ and restores charge neutrality of some of the TDAPB molecules of the interface. Upon applying a lower negative bias this reaction is gradually reversed. Above a threshold voltage $U = 0.43$ V there is an additional increase of differential absorption $\Delta I/I_0$. Because only displacement currents contribute, this increase is due to an increase in capacitance of the plate capacitor. As a consequence the thickness of the dielectric d has to be reduced as further discussed below.

Note: If the external voltage is just $U = 0.43$ V, the anode is effectively neutral resulting in a field-free HTL. Even for $U > 0.43$ V charge balance is maintained because every positive charge formed at the anode due to TDAPB⁺ cationic radicals at the internal interface is responsible for subsequent hole transport across the HTL. The fact that charge neutrality at the PEDT:PSS|TDAPB inter-

face is always established, i.e. irrespective of the application of an external voltage $U > +0.43$ V, explains why this interface acts as an ohmic electrode. The electrode field at the PEDT: PSS|TDAPB interface vanishes and the reservoir of holes available for hole injection is solely determined by the transport capacity, i.e. by the space charge, inside the HTL. In Fig. 3 one notes an increase of the differential absorption at voltages $U > 0.43$ V by a factor of 2.2. As the concentration of TDAPB⁺ at the electrically neutral PEDT:PSS|TDAPB interface cannot be increased, this absorption is due to a thin sheet of TDAPB⁺ located at the internal TDAPB|Alq₃ interface. In physical terms, the HTL|ETL interface acts as a barrier for holes due to the difference in HOMO levels of 0.7 eV which are accumulated here. The number of holes is expected to be equal to the charge of a modified parallel plate capacitor with only the ETL acting as dielectric. With a thickness of 60 nm and with the dielectric constant of Alq₃ $\epsilon_R = 4.0$ the new capacitance is increased by a factor of 2.2. This fact is reflected in the change of the differential absorption at $U = 0.43$ V.

The SCLC-current inside the HTL and so the dc-current of the OLED stays negligible within the voltage range of $U = 0.43$ V to the EL-onset $U_{EL} = 2.0$ V, due to the field screening of the detected charge [8].

Although having shown the onset of hole injection being at $U = 0.43$ V, one has to emphasize that this voltage is not identical to the built-in potential U_{BI} . The latter is roughly estimated by the differences in work functions Φ_A of the electrode materials, ignoring vacuum level shifts [11]. In this OLED it is $U_{BI} \cdot e = \Phi_A(\text{PEDT:PSS}) - \Phi_A(\text{Mg:Ag}_{10:1}) = 4.9 - 3.7$ eV = 1.2 eV, with e meaning the charge of an electron. At this voltage the vacuum level is aligned and any potential shift $\Delta\Phi = \sigma \cdot d \cdot e \cdot (\epsilon_0 \epsilon_R)^{-1}$ due to internal charge per unit area σ is compensated by charge of opposite sign, with d being the distance between opposite charges and $(\epsilon_0 \epsilon_R)$ the dielectric constant of the material. As shown before, for $U > 0.43$ V there is an accumulation layer of holes at the ETL|HTL interface. At $U_{BI} = 1.2$ V the potential drop caused by this accumulated positive charge is just the voltage of the enhanced capacitor $1.2 - 0.43$ V \approx

0.8 V. The compensating voltage step of -0.8 V must be caused by negative charge, which has to be stored inside the residual dielectric, i.e. the Alq₃ layer. Assuming an isotropic distribution inside the bulk of this layer, the voltage independent trapped charge has a density of

$$\begin{aligned} n &= \Delta\Phi \cdot \epsilon_0 \epsilon_R / (1/2 \cdot d_{\text{ETL}}^2 \cdot e^2) \\ &\approx 0.8 \text{ eV} \cdot 4 \times 10^{-13} \text{ F cm}^{-1} / \\ &\quad (1/2 \cdot 3.6 \times 10^{-11} \text{ cm}^{-2} \cdot 1.6 \times 10^{-19} \text{ C} \cdot e) \\ &\approx 10^{17} \text{ cm}^{-3}. \end{aligned}$$

The resulting energy level diagram of the OLED is depicted in Fig. 4. Note that a charge density of 10^{17} cm^{-3} is built up by charges separated by 22 nm to each other. As the conjugation length is much smaller, these charges are localised and form an extremely inhomogeneous electric field. Having this in mind, the band bending shown in Fig. 4 is only an average in place. The negative charges are not repulsing mutually out of the layer, because they are trapped deeply. Not only does the existence of a permanent charge inside the Alq₃ layer explain the onset of hole injection at $U = 0.43 \text{ V} < U_{\text{BI}}$, it also predicts the onset of electron injection, i.e. the onset of EL should occur at $U_{\text{EL}} = U_{\text{BI}} + 0.8 \text{ V} = 2.0 \text{ V}$. This is confirmed by experiment, as the first light output detected with a photodiode is detected at 1.9 V [6].

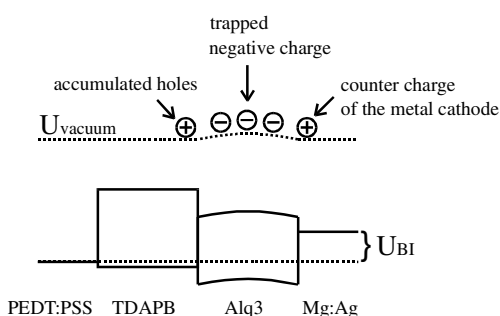


Fig. 4. Energy level diagram of the OLED under an applied voltage of $U = U_{\text{BI}} = 1.2 \text{ V}$. The permanent deeply trapped negative charge inside the Alq₃ layer induces positive counter charge at the Mg:Ag cathode. Only in the case of $U \geq U_{\text{EL}} = 2.0 \text{ V}$ the cathode is negatively charged. Note that the use of this model neglects the local character of the charges in organic amorphous materials and is only valid for an overall estimation of internal field distribution.

The reason for U_{EL} exceeding U_{BI} is the existence of a reverse biased cathodic part of the ETL due to the trapped negative space charge [12]. As sketched in Fig. 4, this negative charge is accompanied by a positive counter charge consisting of both TDAPB⁺-cations at the TDAPB|Alq₃ interface and a positively charged metal cathode. However, in order to inject electrons, the cathode has to be negatively charged. This is not the case until a voltage $U \geq U_{\text{EL}}$ is applied.

4. Conclusion

Bias induced absorption in the visible and near infrared is a powerful tool to identify, quantify and localise the positive charge in a multi layer OLED while tuning the applied voltage from reverse bias up to the onset of electroluminescence. While the existence of a positively charged accumulation layer between the HTL and the ETL is already well known, we have shown that (i) this charge consists of radical cations of the hole transporting material, (ii) the hole injection starts below the built-in voltage and (iii) the onset voltage of the electroluminescence is correlated with both, the built-in voltage and the onset voltage of hole injection by the existence of intrinsic negative charge inside the ETL.

At a bias at which hole injection takes place the anodic layers of ITO and PEDT:PSS, including their surfaces, are overall neutral, the PEDT:PSS|HTL interface consisting of an equal number of PSS⁻-anions and TDAPB⁺- and PEDT⁺-cations. At lower voltages where the HTL is reverse biased, the negative “anodic” charge is localised at the PEDT:PSS|HTL interface. This is due to a partial reduction of TDAPB⁺-cations to neutral TDAPB molecules resulting in a surplus of PSS⁻-anions.

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