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# Bias-dependent current efficiency in polymer light-emitting diodes

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## Abstract

The current efficiency (CE) of single-layer poly-p-phenylene vinylene-based light-emitting diodes (PLEDs) at low voltages is poor and strongly bias dependent, which has been attributed to the quenching of excitons at the metallic cathode. In the absence of exciton quenching the CE is expected to be voltage independent. We have verified this hypothesis by investigating the electro-optical properties of double-layer PLEDs, where an additional polymeric electron transport layer (ETL) is inserted between the light-emitting layer and the cathode. It is confirmed that for ETLs with thicknesses of 40 nm or larger, where exciton quenching is strongly weakened, the conversion efficiency is indeed voltage independent. Reducing the ETL to 20 nm leads to a pronounced improvement of both quantum and power efficiencies of the PLED at low voltages.

## 1. Introduction

The opto-electronic properties of polymer light-emitting diodes (PLEDs) are currently attracting much interest, due to the specific properties of these materials [1, 2]; PLEDs are easy to manufacture, cheap, lightweight, flexible, have pure colours and wide viewing angles. An important property of PLEDs is the current efficiency (CE), representing their ability to convert current into light. In PLEDs based on the conjugated polymer poly(phenylene vinylene) (PPV) or its derivatives, it has been observed that the current efficiency is strongly reduced at low voltages. This effect has been explained by non-radiative energy transfer of excitons to the metallic cathode. The electron conduction in the PPV derivatives has been found to be smaller than the hole conduction, which was attributed to the presence of traps [3] or lower electron mobility [4]. For PLEDs, in which both electrons and holes are injected, the different conduction of electrons and holes is directly responsible for the distribution of the light output in the polymer layer. Model calculations on single-layer PLEDs demonstrated that at low voltages most of the excitons are formed close to the cathode, due to the reduced electron transport in PPVs [3]. Since excitons are efficiently quenched by metal contacts [5], such an exciton distribution is expected to result in a low CE at low voltages. For higher voltages, the exciton concentration is

more uniformly distributed throughout the PLED device, and exciton quenching is expected to become less important. The increase of CE with voltage could be modelled by assuming a quenching region of typically 10 nm for single-layer dialkoxy-PPV LEDs [3]. From photoluminescent experiments, a typical width of the quenching region of 20 nm has been obtained for cyano derivatives of PPV [5]. Since this is in reasonable agreement with the 10 nm estimation from the PLED device model it seems to justify the dominance of exciton quenching at the cathode on the bias dependence of the current efficiency.

In recent studies [6–8], it has been demonstrated that the injection of holes in PLEDs is strongly influenced by the presence of electrons. The presence of traps or an extraction barrier at the anode causes accumulation of electrons close to the hole injecting contact. As a result the local electric field at the anode is strongly enhanced, leading to an improved hole injection. Furthermore, these trapped charges are also responsible for screening of the electric field in the PLED [9]. The opposite process, enhancement of the electron injection due to the presence of holes at the cathode, will also lead to bias-dependent efficiency; at low bias the amount of injected holes is relatively small, and the electron injection will be poor, leading to a low current efficiency. With increasing bias the hole concentration increases, thereby increasing the field at the cathode and switching on the electron injection, leading to an increase of the efficiency.

In order to discriminate between the role of exciton quenching and a field enhanced electron injection efficiency, we incorporate an electron transport layer (ETL) between the metallic cathode and the light-emitting polymer. Such a layer, as also applied in small molecule devices [10], prevents the transport of excitons towards the metal and additionally confines the holes within the device. For this the ETL should have a large bandgap in order to prohibit the transport of excitons from the recombination layer into the ETL, as well as to block hole injection into the ETL layer. The model calculations on single-layer PLEDs with an Ohmic electron contact predicted that the absence of exciton quenching will result in a voltage independent CE, being directly at its maximum value after turn-on. Thus, in a double-layer device a voltage independent CE is expected when exciton quenching is sufficiently blocked. On the other hand, the holes that are blocked at the interface between the light-emitting polymer and the ETL will gradually increase the electric field at the cathode with increasing bias voltage. As a result, also in a double-layer device the conversion efficiency will still exhibit a strong enhancement with increasing bias voltage when it is governed by a field enhanced electron injection.

## 2. Experiment

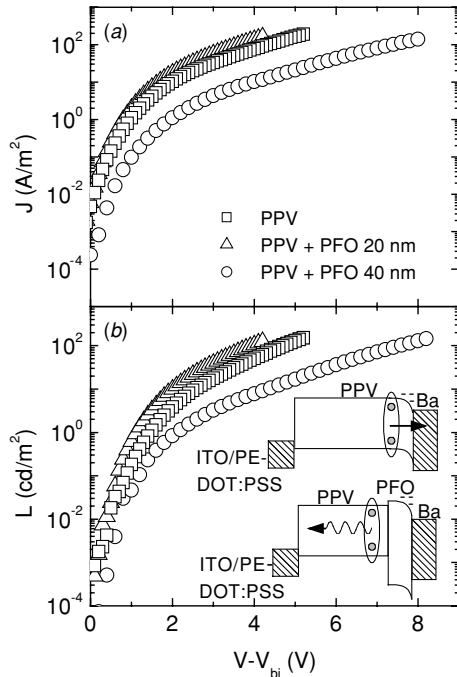
For PLEDs, the preparation of multilayers from solution is more problematic as compared to the evaporated small molecule LEDs, because the bottom layer can be dissolved during the application of a subsequent layer. In an earlier study by Greenham *et al*, it has been shown that the use of a polymeric heterojunction can indeed strongly improve the efficiency [1]. In these devices a bottom layer of a precursor PPV is used, which is insoluble after conversion. Due to a band offset in both the LUMO and HOMO levels both the electrons and the holes are blocked at the heterojunction interface. The build-up of space charge at the heterojunction enables tunnelling of one (or both) of the charge carriers to the opposite layer, and recombination takes place close to the heterojunction interface, leading to improved conversion efficiencies. A disadvantage of this approach is that the tunnelling process requires a highly charged heterojunction, leading to an increase of the driving voltage. In the present study, we use heterostructures consisting of a newly developed PPV derivative with tunable solubility [12] as light-emitting layer and poly(9,9-dioctylfluorene) (PFO) as ETL. In this heterostructure the LUMO of the ETL aligns with the LUMO of the light-emitting layer, whereas an energy barrier between the HOMO levels prevents holes to enter the ETL. Consequently, the electron transport from the ETL into the recombination layer is not hindered. We have found that the addition of the PFO transport layer strongly improves the conversion efficiency of the PPV-based PLED at low voltages, and for layer thicknesses >40 nm the CE is bias independent, in correspondence with the absence of exciton quenching. This observation proves that the reduction of the CE at low bias indeed originates from the quenching of excitons at the cathode, as has been suggested before [3].

In this study we have made double-layer structures with a spincoated bottom layer of a PPV derivative, followed by a

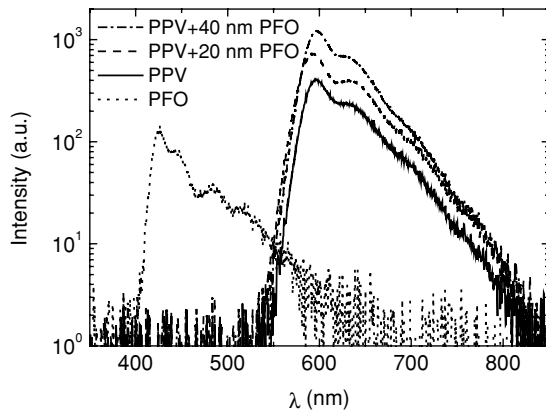
spincoated top layer of PFO. The bottom PPV-based layer is a random copolymer of poly[2,5-bis(2'-ethylhexyloxy)-1,4-phenylenevinylene] (BEH-PPV) and poly[2,5-bis(2'-methylbutyloxy)-1,4-phenylenevinylene] (BMB-PPV). By changing the ratio of the highly soluble BEH-PPV and the insoluble BMB-PPV the solubility of the copolymer can be tuned, without changing its charge transport properties [12]. In a 1:3 BEH-co-BMB-PPV ratio the film can be spin cast from chloroform and is insoluble in toluene, which permits spincoating of the PFO layer on top. The double layer has been fabricated on bottom contacts of indium tin oxide (ITO) as well as on ITO covered with poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS). The PPV copolymer bottom layer has a thickness of 180 nm in the single-layer device, whereas in the double-layer device a thickness of 160 nm is used. The thickness of the top PFO layer varied between 20 and 100 nm. As a top contact, barium (Ba) capped with a thick aluminium (Al) layer has been used. Current density–voltage measurements have been taken, and simultaneously the light output is measured with a photodiode. The light intensity  $L$  is calibrated with a Minolta L110 Luminance meter.

## 3. Results and discussion

In the inset of figure 1, the schematic band diagram of the double-layer PLED is given. The LUMO of the PPV copolymer and PFO amount to 2.9 eV [13] and 2.6 eV [14], respectively. On the other hand, the HOMO of the PPV copolymer and PFO amount to 5.3 eV [13] and 5.8–6.0 eV [14, 15] respectively, resulting in a 0.5–0.7 eV hole injection barrier that blocks the hole injection from the PPV into the PFO. Furthermore, the  $\sim 0.8$  eV difference in bandgap also leads to an electron injection barrier of 0.1–0.3 eV and prohibits the transport of excitons from the PPV layer into the PFO layer. In figure 1(a), the current density as a function of voltage ( $J$ – $V$ ) is shown for a single-layer LED of the PPV copolymer (PPV), as well as double-layer LEDs where PFO layers of 20 and 40 nm are added to the PPV layer. The applied voltage is corrected for the built-in voltage  $V_{bi}$  of the devices, which typically amounts to  $V_{bi} = 1.8$  V. It is observed that the single-layer LED and the LED with 20 nm ETL, both with a total thickness of 180 nm, have similar characteristics. Due the low electron mobility of PFO [7] even an ETL of only 20 nm is expected to increase the operating voltage of the device. The absence of this additional voltage drop in the ETL can be explained by the accumulation of electrons due to the presence of an Ohmic Ba/Al contact. This Ohmic contact is formed due to the low work function of Ba (2.6 eV) combined with the fact that reactive metals such as Ca and Ba dope the polymer by donating electrons to the  $\pi$ -system [2]. Calculations with a drift-diffusion device model reveal that this accumulation region (as sketched in the inset of figure 1(b)) typically extends over  $\sim 20$  nm from the contact in the device. As a result for the device with an ETL of only 20 nm no significant additional voltage drop is present. For the 40 nm ETL device, however, the top layer is thicker than the accumulation length. The resulting extra voltage drop across the ETL consequently shifts the  $J$ – $V$  characteristics to higher voltages. In figure 2, the EL spectra of the single-layer

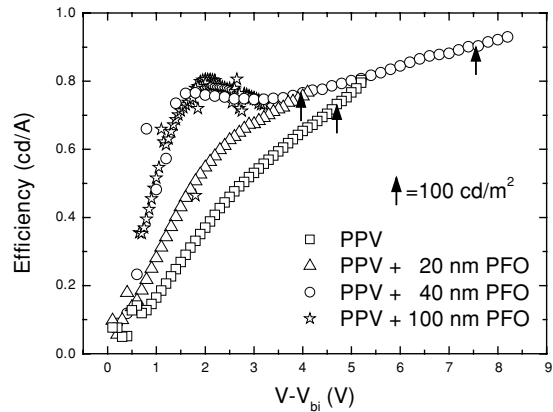


**Figure 1.** (a) Current density  $J$  as a function of internal voltage  $V-V_{bi}$  (bias corrected for built-in voltage) for a single-layer PLED and two double-layer PLEDs. The single-layer PLED (squares) has a PPV thickness of  $d_{PPV} = 180$  nm, whereas the double-layer PLEDs have a bottom PPV layer with a thickness of  $d_{PPV} = 160$  nm and different top layer thicknesses of  $d_{PFO} = 20$  nm (triangles) and  $d_{PFO} = 40$  nm (circles). (b) The light output for the same devices. The inset shows a schematic representation of the exciton quenching for a single-layer (PPV) and the blocking of the quenching for a PPV/PFO double-layer device. Also shown is the band bending at the cathode due to accumulation. Built-in voltage:  $V_{bi} = 1.8$  V.



**Figure 2.** Electroluminescence spectra for four PLED devices: the single-layer PPV based (solid line), the PPV with a 20 nm PFO top layer (dashed line), the PPV with a 40 nm top layer (dash-dot line) and a bare PFO device (dotted). The EL spectra of all four devices are taken at a current density of typically  $100 \text{ A m}^{-2}$ .

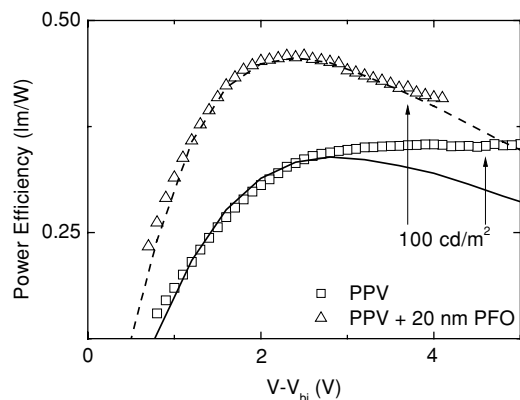
device (PPV) and the two double-layer devices with 20 and 40 nm PFO are depicted, together with the EL of a PFO single-layer reference device. It is demonstrated that all the light output of the double-layer devices, even down to intensities of 0.1% of the maximum, is emitted by the PPV copolymer layer. This shows that the 0.5–0.7 eV hole injection barrier



**Figure 3.** Efficiency ( $\text{cd A}^{-1}$ ) as a function of internal voltage. The arrows denote the  $100 \text{ cd m}^{-2}$  point (not shown for the device with 100 nm PFO).

adequately blocks the holes at the PPV/PFO interface. In an earlier study [7] we demonstrated that PEDOT:PSS, with a work function of 5.1 eV, does efficiently inject holes into the 5.8–6.0 HOMO of PFO. However, this efficient injection was specific for PEDOT:PSS and not for other anodes, and was found to originate from the built-up of electrons at the PEDOT:PSS interface. The fact that holes are not efficiently injected from the PPV copolymer into the PFO was verified by measuring selectively the hole transport across the PPV/PFO interface [16]. It was demonstrated that the HOMO offset between PPV and PFO reduced the hole transport by 4–5 orders of magnitude. This confirms our expectation that PFO is a good exciton and hole blocking layer.

Figure 1(b) shows the light intensity ( $L$ ) of the PPV single layer and PPV/PFO double-layer devices. A close inspection already indicates that addition of an ETL layer enhances the light output, compared with the current density. In figure 3 the conversion efficiency CE for the PPV copolymer single layer, as well as the double-layer PLEDs with a 20, 40 and 100 nm ETL of PFO are shown. The relatively low maximum efficiency of  $\sim 1 \text{ cd A}^{-1}$  results from the low photoluminescence (PL) efficiency of only 10% of this PPV copolymer with adjusted solubility. Light-emissive polymers used for commercial applications exhibit PL efficiencies of over 50%, but their solubility cannot be tuned yet, complicating their use in multilayer devices. First, it is observed that the single-layer PPV-based PLED shows the characteristic increase of the CE with applied bias. Furthermore, figure 3 shows that the CE of the 20 nm ETL is higher compared with the single-layer device, but still exhibits a gradual increase with voltage, indicative of residual exciton quenching. For the 40 nm and 100 nm ETL, the CE approaches a block function of voltage, as expected for a PLED with an Ohmic electron contact in the absence of exciton quenching [3]. At low voltages the CE sharply increases and then reaches a plateau followed by a slow rise. The sharp increase at low voltages arises from the fact that the electron transport in the PFO blocking layer is reduced by traps [7]. As a result at low voltages there is first a built-up of holes at the PPV/PFO interface, leading to an increase of the electric field in the PFO. This field pulls the electrons into the PPV leading to a sharp increase of the CE. The slow increase of the CE at higher



**Figure 4.** Power efficiency (PE) as a function of internal voltage. The symbols show the measured PE for a single-layer PPV (squares) and PPV+20 nm PFO (triangles). The lines are calculations of the PE for different quenching lengths:  $L_q = 30$  nm (solid),  $L_q = 15$  nm (dashed). Again, the arrows indicate the  $100 \text{ cd m}^{-2}$  point for the measured PEs.

voltages is most likely due to an optical effect. With increasing voltage the light-emission zone starts to shift away from the interface, which leads to an enhanced efficiency because of interference effects. We also observed that the CE for all the devices (no ETL, 20, 40 and 100 nm ETL) tend to collapse on one curve at biases larger than 5 V. Apparently, at sufficiently large bias also in the single-layer device exciton quenching becomes insignificant, since excitons are then generated more uniformly throughout the PPV layer. It should be noted that at high voltages the CE gradually decreases, for single-layer PPV-based PLEDs of 100 nm thickness this behaviour sets in for  $V-V_{bi}$  larger than 5 V. This reduced efficiency originates from field-assisted dissociation of the excitons as well as charge carrier induced scattering of excitons. For the present double-layer devices with thicknesses  $\sim 200$  nm these effects start to play a role for effective voltages larger than 10 V.

For applications, apart from the CE, the operating voltage of the PLED is also of great importance. This can be expressed in the power efficiency (PE). An increase of the operating voltage will lead to a reduction of the power efficiency  $PE = L/J \times V$ . In figure 4, the power efficiency PE is plotted for the single PPV layer and double-layer device with a 20 nm PFO layer. We demonstrate that the addition of an ETL layer of PFO leads to a significant increase of the PE at low voltages. It has already been suggested in the literature that the power efficiency will increase for smaller quenching length [17]. In figure 4, it is demonstrated that the addition of a small ETL layer is in accordance with an effective reduction of quenching length. The calculated lines have been performed with a device model [3], for different values of the quenching length in a single-layer device. It is demonstrated that the global features of the measured PE are reproduced by the calculation.

It is observed from figure 4 that the addition of a small ETL layer results in a higher PE at  $100 \text{ cd m}^{-2}$ , as indicated by the arrows. For the same total device thickness, the light output of  $100 \text{ cd m}^{-2}$  for the double-layer device (ETL = 20 nm) is reached at lower voltage and with a better efficiency. Therefore, the PE is improved. It should be noted that addition of a thin ETL layer allows for a thinner luminescent layer,

without losing the robustness of the device in terms of shorts. The device with 20 nm ETL has the same total thickness, as a consequence it has a comparable  $J-V$  characteristic and due to the reduced exciton quenching it has an enhanced light output. On the other hand, the device with 40 nm ETL, although the current efficiency is further improved (figure 3), has a lower PE at  $100 \text{ cd m}^{-2}$ , due to the higher operating voltage (7.6 V, figure 1(b)). This reduction of the PE is due to the relatively poor electron transport in PFO [7], as compared to the hole transport in PPV. Therefore, in order to prevent substantial voltage losses, the ETL top layer should not be too thick. The optimum performance therefore is the best compromise between reduction of the exciton quenching and enhancement of the operating voltage, and for PFO as an ETL the optimum is found for an ETL thickness of  $\sim 20$  nm.

## 4. Conclusions

In summary, we have investigated the origin of the bias dependence of the current efficiency (light output/current) in PLEDs. By the deposition of a thin ETL layer on the top of the emitting layer, quenching of excitons at the metallic cathode is abolished. It is expected that for Ohmic electrical contacts there is no bias dependence of the current efficiency for such a double-layer PLED. Hole enhanced electron injection efficiency, on the other hand, will lead to a bias-dependent CE in these double-layer devices. It is demonstrated that for top layers of PFO of 40 nm or more the CE is bias independent, proving that the reduced efficiency at low voltages in single-layer devices originates from strong exciton quenching. However, due to the relatively poor electron transport in PFO the power efficiency for a 40 nm ETL is strongly reduced. A 20 nm ETL of PFO is a better compromise for simultaneously improving the current and power efficiencies.

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