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Performance of a polymer light-emitting diode with enhanced charge carrier mobility

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Abstract

The device characteristics of a polymer light-emitting diode (PLED) based on a poly(*p*-phenylene vinylene) (PPV) derivative with an enhanced charge carrier mobility have been investigated. Improvement of the mobility, which has been obtained by a decrease of the energetic disorder in the polymer, is expected to increase the power efficiency of a PLED. However, it is demonstrated that an increased mobility leads to a decrease as well as to a slower rise of the quantum efficiency with voltage. This performance reduction is explained in terms of an increased quenching of the electroluminescence (EL) at the cathode. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polymer light-emitting diode; Charge carrier mobility; Quantum efficiency

1. Introduction

Understanding of the device operation of a polymer light-emitting diode (PLED) is essential for the improvement of present devices. It is evident that the transport properties of injected electrons and holes are a key process with regard to the device performance of a PLED. After the discovery of electroluminescence (EL) in poly(*p*-phenylene vinylene) (PPV) [1] investigations on charge transport have been focused on this class of materials. Recent experiments [2] have demonstrated that the charge transport in dialkoxy PPV-based PLEDs is space-charge limited, implying that current flow is governed by the charge-carrier mobility. The hole mobility μ_p exhibits a dependence on electric field E according to $\ln \mu_p \propto \sqrt{E}$ [3], as has also been observed from time-of-flight experiments in many molecularly doped polymers and amorphous glasses [4]. It has been proposed that the microscopic origin of the observed mobility arises from hopping between sites that are subject to both positional and energetic disorder [5]. For light generation injected charge carriers have to move through the polymer layer over a certain distance before they can recombine. The recombination process of the oppositely charged carriers in PPV has been shown to be of the Langevin type [6]. As a result the rate-limiting step in the bimolecular recombination process is the diffusion of electrons and holes towards each other in their mutual Coulomb field. Thus, in a PLED both charge transport and charge recombination are governed by the charge carrier mobility. Consequently, the quantum efficiency of a PLED, which represents light-output/current, is expected to be independent on the mobility and temperature. However, a decreasing mobility will lead to an increase of the voltage V required to maintain a certain amount of light-output L (or corresponding current density J), giving rise to a decrease of the power efficiency L/VJ. Thus, for an optimal device performance of a PLED, the charge carrier mobility is a crucial parameter. In a recent study, the hole mobility of various PPV-derivatives with different side-chains has been investigated [7]. It appeared that polymers with a high degree of regularity can significantly increase the mobility, due to a reduction of the energetic disorder and likely the better ordering in the solid state. In Fig. 1, the chemical structure of our standard dialkoxy OC_1C_{10} PPV is shown together with a $OC_{10}C_{10}$ PPV. The presence of the two bulky $OC_{10}H_{21}$ side-chains in the $OC_{10}C_{10}$ gives rise to an increase of the hole mobility of one order of magnitude [7]. By comparing the observed mobilities with a (correlated) Gaussian disorder model [5,8], a width of the Gaussian density of states of 112 and 93 meV has been obtained for the OC_1C_{10} and $OC_{10}C_{10}$, respectively. In the present study, the device performance of a $OC_{10}C_{10}$-based PLED

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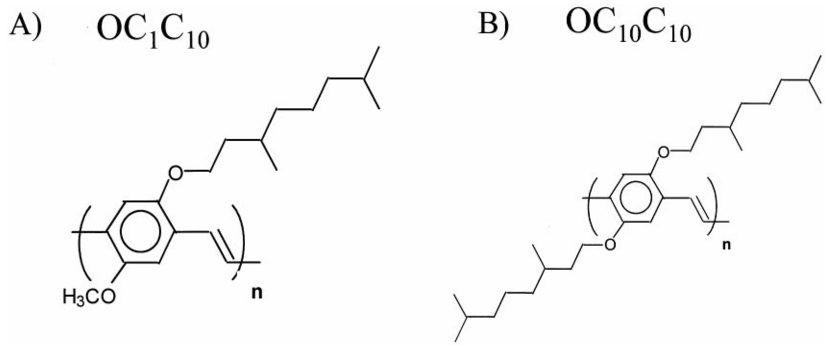

Fig. 1. Chemical structure of the two polymers studied: (A) OC_1C_{10}-PPV and (B) $OC_{10}C_{10}$-PPV.

with an enhanced mobility is compared with the performance of our standard OC_1C_{10} devices. Surprisingly, the expected increase of the power efficiency is not observed. This unexpected behaviour is explained from the fact that a reduction of energetic disorder not only enhances the charge carrier mobility but also the quenching of the EL at the cathode. Model calculations show that a mobilily increase from 3×10^{-11} to 2×10^{-10} m^2/V s is accompanied by an enhancement of the quenching region in the PLED from 8 to 20 nm.

2. Experimental

The devices under investigation consist of three layers on top of a glass substrate. As a bottom contact, the anode, a patterned indium-tin-oxide (ITO) is used which is optically transparent. On top of the ITO the fully conjugated PPV-derivatives OC_1C_{10} or $OC_{10}C_{10}$ are spin coated as the active layer. As a top contact, a low work function metal electrode (Ca), the cathode, is evaporated. The thickness of the active layers used in this study amounts to 200 nm, as measured by a Dektak 3030 surface profiler. The device fabrication as well as *J–V* and *L–V* measurements are performed in nitrogen atmosphere. The experimental *J–V* characteristics of the OC_1C_{10} and $OC_{10}C_{10}$-basd PLEDs are shown in Fig. 2.

The *J–V* characteristics are modelled using a device model for PLEDs which has recently been reported [9]. In this model, the hole mobility is represented by $\mu_p(E) = \mu_0 \exp(\gamma/\sqrt{E})$. Furthermore, the electron transport is limited by traps and the Langevin recombination constant is given by $B = q/\varepsilon(\mu_p + \mu_n)$, with ε, the dielectric constant and μ_n, the electron mobility. Applying this model to the room temperature *J–V* characteristics of Fig. 2 (solid lines), a zero-field mobility $\mu_0 = 3 \times 10^{-11}$ m^2/V s and a $\gamma = 4.5 \times 10^{-4}$ $(m/V)^{1/2}$ has been obtained for OC_1C_{10}. For the $OC_{10}C_{10}$ derivative with enhanced mobility, a $\mu_0 = 2 \times 10^{-10}$ m^2/V s and a $\gamma = 4.0 \times 10^{-4}$ $(m/V)^{1/2}$ has been obtained, in agreement with the results following from hole-only devices [7]. Thus, from the *J–V* characteristics, it appears that there is nearly a factor of 10 difference in the mobility of the two PPV-derivatives.

In order to quantitatively estimate the effect of an enhanced charge carrier mobility on the performance of a PLED, the device characteristics of our standard OC_1C_{10} LEDs with a thickness of 200 nm are considered. In Fig. 3, the light-output *L* is shown as a function of applied voltage *V*. From Fig. 3, it appears that for this OC_1C_{10} LED the voltage required to obtain 100 cd/m^2, which is typical for applications, amounts to 4.5 V. As stated above, due to Langevin recombination, the quantum efficiency is expected to be independent on the mobility. As a result, a mobility increase of a factor of 10, which by definition gives rise to a similar increase of the current, will also enhance the light-output by a factor of 10. An increased light-output by a factor of 10 is also plotted in Fig. 3 (solid line). It appears that the voltage required for 100 cd/m^2 drops from 4.5 to 3.0 V as a result of such a mobility increase. Thus, it is expected that the enhanced mobility of the $OC_{10}C_{10}$ derivative will give rise to a gain in the power efficiency of typically a factor 1.5.

As a next step the quantum efficiency QE (=*L*/*J*) of the standard OC_1C_{10} LED is considered, as shown in Fig. 4.

The maximum of the external QE amounts to 1.6%. The rise of QE with *V* is a consequence of the unbalanced charge transport in PPV. From model calculations [9,10], it has been obtained that the light-output in a PLED is mainly confined

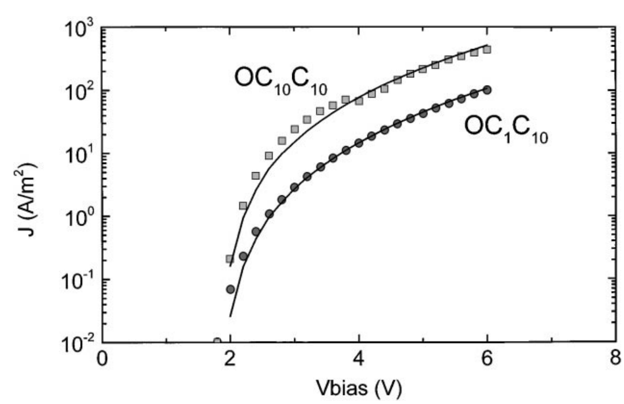

Fig. 2. Room temperature current density vs. voltage (*J–V*) characteristics for the OC_1C_{10}-PPV and $OC_{10}C_{10}$-PPV based LEDs with a layer thickness of 200 nm. The zero-field mobility μ_0 for the OC_1C_{10}-PPV and $OC_{10}C_{10}$-PPV amount to 3×10^{-11} m^2/V s and 2×10^{-10} m^2/V, respectively.

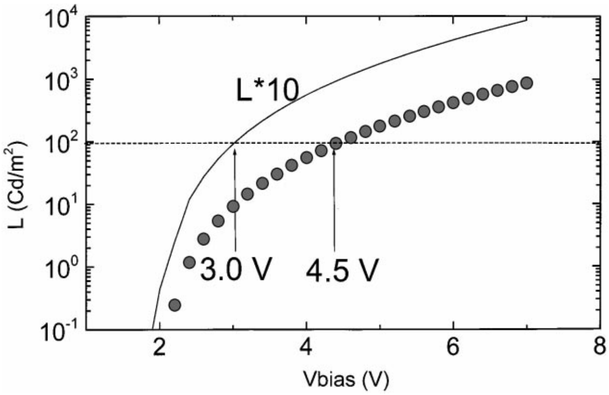

Fig. 3. Light-output vs. voltage characteristics of the OC_1C_{10} LED (symbol). A light-output of 100 cd/m^2 is obtained at 4.5 V. An increase of the light-output by a factor of 10 (solid line) would shift this voltage down towards 3.0 V.

in a region close to the cathode as a result of the reduced electron conduction. As a result, at low voltages, non-radiative recombination losses at the metallic cathode strongly reduce the efficiency of the device. At higher voltages, the difference between electron and hole transport becomes smaller [2,11] and the light is generated more homogeneously in the layer, which results in an increase of QE. In our device model, the quenching behaviour is approximated by neglecting the light-output in a region of width L_q adjacent to the cathode. As shown in Fig. 4 for the present OC_1C_{10} LED, agreement with experiment is obtained for $L_q = 8$ nm. The emission profile inside a PLED has been experimentally determined by Grüner et al. [12], who analysed the anisotropy in the EL of devices based on poly(*p*-phenylene) Langmuir Blodgett films. These experiments demonstrated an efficient quenching of the EL over a distance of about 20 nm in a region adjacent to the cathode. Furthermore, from photoluminescence (PL) experiments an effective quenching region of nearly 20 nm has been obtained for cyano derivatives of PPV [13]. It should be noted that in our model, the quenching region abruptly ends at a distance L_q, whereas experiments [12,13] show a more gradual increase of the light intensity with increasing distance from the cathode.

In order to demonstrate the effect of quenching, the calculated quantum efficiency for various L_q has been included in Fig. 4. An increase of L_q affects the quantum efficiency in two ways. First, the maximum QE decreases because a larger part of the PLED is not active in the light-generation process. Furthermore, the maximum QE is reached at higher voltages due to the fact the shift of the EL out of the quenching region requires larger voltages. The maximum QE is furthermore determined by the proportion between radiative and non-radiative recombination. The PL efficiency of the OC_1C_{10} and $OC_{10}C_{10}$ material amounts to 15 and 13%, respectively.

In Fig. 5, the experimental QE of the OC_1C_{10}- and $OC_{10}C_{10}$-based PLEDs are shown.

Due to the different PL efficiencies, it is expected that the QE of the $OC_{10}C_{10}$-based PLED is a factor of 13/15 lower than the observed QE of the OC_1C_{10}-based PLED, as indicated by the dashed line in Fig. 5. It appears that the maximum QE of the $OC_{10}C_{10}$-based PLED with enhanced mobility amounts to 1.1%. This is significantly lower than the 1.6% of the OC_1C_{10} PLED, as well as the expected 1.4% after correction for the PL efficiency (dashed line). Furthermore, the maximum QE is only reached at 7 V in contrast to the 5 V of the OC_1C_{10}. The only parameter in our device model which affects both the maximum QE as well as the rise of QE with V is the width of the quenching region L_q, as shown in Fig. 4. In Fig. 5, it is demonstrated that an increase of L_q from 8 to 20 nm leads to simultaneous agreement of both the rise of QE with V and the maximum attainable value of QE.

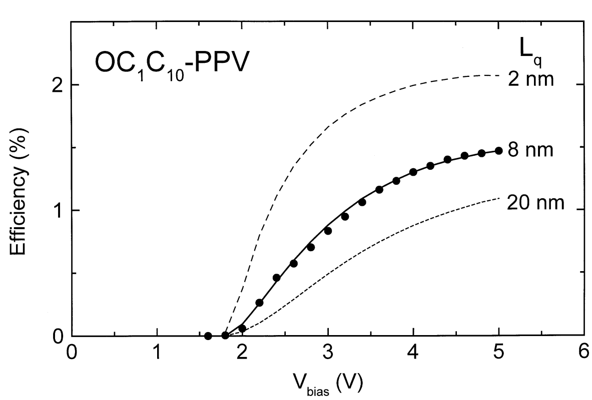

Fig. 4. Experimental quantum efficiency (symbol) as a function of voltage for the OC_1C_{10} LED. The maximum efficiency of the OC_1C_{10} LED amounts to 1.6% (photon/charge carrier). Also shown are model calculations (lines) for various lengths of the quenching region L_q at the cathode.

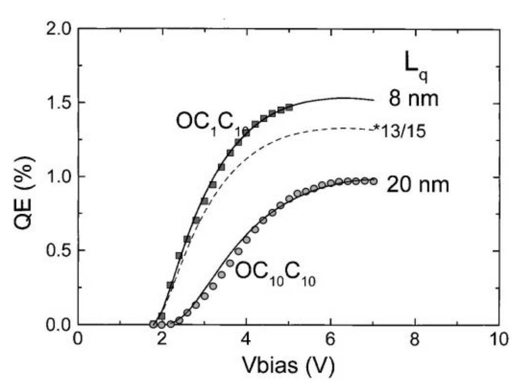

Fig. 5. External quantum efficiency as a function of applied voltage for the OC_1C_{10}-PPV and $OC_{10}C_{10}$-PPV based LEDs with a thickness of 200 nm from experiments (symbols) and model calculations (lines). For the $OC_{10}C_{10}$-PPV based LED, a maximum efficiency of 1.4% is expected after correction for the slightly lower photoluminescence efficiency (dashed line).The slower rise and lower quantum efficiency of the $OC_{10}C_{10}$ LED is accounted for by increasing the width of the quenching region L_q from 8 to 20 nm.

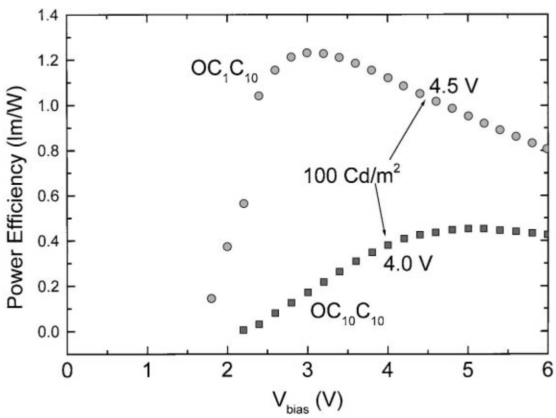

Fig. 6. Power efficiency as a function of applied voltage for the OC_1C_{10} $OC_{10}C_{10}$-based LEDs. Die to the reduced quantum efficiency, the voltage required for a light-output of 100 cd/m^2 only decreases from 4.5 to 4.0 V, in spite of the strong mobility increase.

The relation between charge carrier mobility and EL quenching is not straightforward. In the process of nonradiative energy transfer, various contributions play a role; bulk contributions, which reflect the interaction of an oscillating dipole with its image dipole, scattering by the metal surface, and exciton diffusion [14,15]. It should be noted that both charge transport and exciton diffusion are governed by the disordered Gaussian DOS. Enhancement of the mobility by a reduction of the energetic disorder will affect the hopping of charge carriers in the Gaussian DOS as well as the exciton diffusion, which is of the Förster type [16,17]. A deeper understanding of the relation between charge transport and EL-quenching will be a subject of further study.

The consequence of the increased quenching zone with regard to the power efficiency is demonstrated in Fig. 6.

The standard OC_1C_{10}-based PLED studied here reaches a maximum power efficiency of 1.3 lm/V around 3 V. At 100 cd/m^2, the power efficiency at 4.5 V amounts to 1.1 lm/W. In contrast, the maximum power efficiency of the $OC_{10}C_{10}$-based PLED only amounts to 0.5 lm/W. Furthermore, the 100 cd/m^2 light-output is not obtained at 3 V, as expected from Fig. 3, but only at 4 V due to tie reduced QE. Thus, in contrast to the expected gain of a factor 1.5 in the power efficiency of the PLED with the enhanced mobility, a *decrease* of a factor of 2 is obtained. This result indicates the a further enhancement of the power efficiency of a PLED requires a separation of the recombination zone and the cathode by means of an additional electron transport layer.

In conclusion, we have studied the role of the charge carrier mobility in the device performance of PLEDs of two PPV-derivatives. Reduction of the energetic disorder not only enhances the charge carrier mobility but also the width of the exciton quenching region adjacent to the cathode. The resulting decrease of the quantum efficiency reduces the power efficiency of the PLED at 100 cd/m^2 by a factor of 2.

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