Mesoscopic Modelling of Polymer-Based Optoelectronic Devices

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Summary:

Substantial progress has been made in fabricating optoelectronic devices using polymers as an active material. In polymer light emitting diodes (PLEDs), a balanced injection of electrons and holes from the electrodes is fundamental to increase their performance. Using a mesoscopic model based on a generalized Monte-Carlo method, we studied the influence of changing zero-field barrier heights at both electrode/polymer interfaces in the performance of a PLED with an active layer of poly(*para*-phenylenevinylene) (PPV). Our results show that by controlling the electrodes work functions it is possible to tune the region inside the device where charge recombination preferentially takes place.

Introduction

The use of conjugated polymers as an active material in light emitting diodes (PLEDs) is one of the conquests of the organic electronics. To achieve a good performance, a balanced charge carrier injection (i.e. equal number of electrons and holes injected) for a high light-output and efficiency is required[1], and for this purpose many injecting materials has been employed[2] . In the absence of surface states that may pin the Fermi level in the electrode/polymer interface or the presence of impurities that may lead to a depletion zone, the dark injection (external current due to the applied bias) that flows from the electrodes to the organic material is controlled by the potential barriers height that exist between them. The barriers that control hole and electron injection, in the absence of an applied electric field (zero-field barrier height), are given by $\Delta_h = I - \Phi_{anode}$ and $\Delta_e = \Phi_{cathode} - A$[3], where I and A are the ionization potential and electron affinity of the polymer chains, Φ is the work function of the electrode used, Δ_h and Δ_e are the zero-field barrier heights for hole and electron injection. Changing the work function of the electrodes will lead to different values of the zero-field barrier heights and as a consequence the injection current can either be injection limited (i.e. the barrier height controls the number of charges injected) or space charge limited (i.e. the electrode supplies more charge carriers than the sample can support). To control the potential barriers at the electrode/polymer interfaces and to achieve a more balanced

charge injection, several research groups have developed new processing conditions for the electrodes, like the use of oxygen plasma for ITO processing, or using combinations of other materials with the conventional electrodes, like the use of a LiF thin layer between the cathode and the polymer. In this paper we use a mesoscopic model based on a generalized Monte Carlo method to gain insight of the influence of the changes made in the electrodes work function, and thus the zero-field barrier heights, on the performance of a PLED. Our results show a direct relation between the potential barrier heights and the position inside the device where charges of opposite sign tend to recombine.

Device Model and Simulation Method

It is known that a PLED consists of a sandwich structure where the conjugated polymer film is deposited onto an ITO anode and covered by a top metallic cathode[4]. The deposition of the polymer layer, usually made by a spin-coating process, leads to the orientation of polymer chains mainly parallel to the electrodes. The chains are made of conjugated segments with lengths less than 10 monomer units[5, 6], separated by kinks and twists, and each segment behaves like a straight chain. By considering this, we constructed a polymer network where the polymer chains of poly(*para*-phenylenevinylene) (PPV) are made of stiff-chain segments with different lengths and their axis are parallel to both electrodes. In our polymer layer,

with 100 nm thickness, the number of monomers in each chain segment obeys a Gaussian distribution of lenghts with an average segment length of 5 monomers. Then we simulated charge injection and transport through this polymer structure using an improved version of our mesoscopic model described elsewhere[7]. In the current version of the model we have explicitly modelled the electrodes, where charge injection now depends on the characteristics of the potential barrier at electrode/polymer interfaces. In our model, the zero-field barrier height at the electrode/polymer interface is dictated by the difference between the work function of the anode (or cathode) used and the average ionization potential (or electron affinity), of the polymer chains for holes injection (or electrons injection). Since the molecular properties of conjugated segments depends on their length and we have a Gaussian distribution of segment lengths in the polymer layer, it seems reasonable to use the average value of the ionization potentials and electron affinities to calculate the zero-field barrier heights. Although these values indicate how easy electron and hole injection can occur, the actual charge injection from the electrode will depend on the applied electric field, the properties of the conducting polymer, the space charge distribution in the polymer network and the electrode polarization due to the presence of injected charges in the polymer layer. All these aspects have to be considered in the calculation of the potential barrier height before a charge is injected. The effect of the electrodes does not affect only the process of

injection. When a charge is injected and stays near the electrode/polymer interface, its movement can be conditioned by the polarization of that electrode. The electric field created by the image charges can be strong enough so that charge stays trapped near the electrode or even returns to it. For the charges that percolates through the polymer network, their movement can be either along the conjugated segment of the polymer chain (intra-molecular mobility), or by a process of hopping (inter-molecular mobility) between different conjugated segments. In both cases, charge mobility will depend on the local electric field (the sum of the applied electric field, the field due to space charge distribution and the field due to electrodes polarization), on its sign and the morphology of the polymer network. Recombination is achieved when two charges of different signs in the same polymer segment have higher probability to meet each other than to be separated by the local electric field along the molecular axis. Since our objective in this work is to understand how the changes in the electrodes work function, and thus the zero-field barrier height, affect the balance and the number of electrons and holes injection, and thus the PLED performance, we paid attention to the processes of charge injection and recombination, and the way that space charge distribution affects the internal electric field. For that we applied an electric field of 3 MV/cm and we have changed in the same way the zero-field barrier height at both electrode/polymer interfaces.

Results and Discussion

When the zero-field barrier height at both electrode/polymer interfaces, Δ, varies from 0 to 1 eV, the number of injected charges into the polymer network remains roughly constant for $\Delta \leq 0.4$ eV and decreases as the barrier height increases for $\Delta > 0.4$ eV, reaching the value of zero when $\Delta = 1$ eV, as shown in Fig. 1. The reason for the behaviour found for $\Delta \leq 0.4$ eV lies on the fact that since the applied electric field is strong enough, the charge injection in this case is independent of the potential barriers height and the number of injected charges depends only on charge mobility through the polymer network. Fig. 2a shows that, for a zero-field barrier height equal to 0.1 eV, electrons tends to accumulate preferentially near the cathode (0 nm), whereas holes accumulate preferentially near the anode (100 nm) and there is a gradient in hole and electron distribution through the polymer network. This space charge distribution is similar for all the zero-field barrier heights smaller or equal to 0.4 eV. When the zero-field barrier height is greater than 0.4 eV, the gradient in electron and hole distribution tends to vanish and a decrease in the number of charges stored within the polymer layer occurs (see Fig. 2b). The way that charges distribute along the polymer network will influence the internal electric field. Fig. 3 shows the internal electric field when the zero-field barrier heights are 0.1 eV and 0.7 eV. Despite the applied electric field is 3 MV/cm, the electric field near the electrodes is almost zero for a potential barrier of 0.1 eV, being close to 2 MV/cm when

the potential barrier is 0.7 eV. When $\Delta \leq 0.4$ eV, the accumulation of electrons near the cathode and holes near the anode affect significantly the internal electric field near the electrodes, and the space charge gradient that is established allows that the internal electric field reaches a maximum value in the middle of the polymer network (50 nm). When the zero-field barrier heights are higher than 0.4 eV, the profile of the internal electric field tends to be more flat. In this case, the internal electric field decreases in the middle of the network and increases near the electrodes as the zero-field barrier heights increases. Ours simulations shows that there are similar profiles of the recombination efficiency along the polymer network when potential barriers at the electrode/polymer interfaces are lower or equal to 0.4 eV. An exemple of these profiles can be seen in Fig. 4 for $\Delta=0.1$ eV, which shows negligible recombination close to the electrodes and a maximum recombination events occurring in the middle of the polymer layer. This position for the maximum recombination efficiency is explained by the fact that electrons and holes have similar probability of being injected and they percolate through the polymer layer with similar mobilities, therefore the probability they meet on the same chain and recombine increases as we move away from the electrodes. For $\Delta>0.4$ eV, the concentration of injected charges in the polymer layer decreases and for a charge meet another charge of opposite sign it needs to move a larger distance. Since the number of charges of opposite sign stored in the network

is smaller, the probability of a charge to reach the opposite electrode/polymer interface without recombination is higher and increases as the zero-field barrier height increase. When that charge is close to the collecting electrode, a competition between charge collection by the electrode and charge hopping between neighbouring chains will occur. The charges that are not collected by the electrode can easily recombine with an injected charge of opposite sign, which will increase the number of recombination events near the electrode as we can see in Fig. 4. Since the efficiency of PLEDs depends on the number of recombination events that takes place far from the electrodes[8], our results suggest that the PLEDs based on PPV with $\Delta \leq 0.4$ eV should have higher efficiency.

Conclusions

Our mesoscopic device model, in which the polymer morphology and properties of the molecules and electrodes are explicitly included, has proven to be a successful tool to study the influence of the barrier height on charge, internal electric field and recombination distribution of a single-layer PLED based on PPV, with similar zero-field barrier height at both electrode/polymer interfaces. This work has shown that although the barrier height has no effect on balance the charge injection, it crucially affects the distribution of charge, internal electric field and recombination efficiency throughout the polymer layer, which has implications for the efficiency of

PLEDs. It was also found that, for an applied electric field of 3 MV/cm, the PLEDs with zero-field barrier height lower or equal to 0.4 eV have the highest recombination efficiency in the centre of the polymer film and the lowest non-luminescent recombination efficiency near the electrodes. On the basis of these theoretical results, we conclude that achieving balanced charge injection with low zero-field barrier height at both electrode/polymer interfaces might be a viable strategy to optimize the performance of PLEDs.

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Figure Captions

Fig. 1 – The total number of injected charges (electrons and holes) into the polymer network as a function of the zero-field barrier height at both polymer/electrode interfaces. The line is just a guide to the eye.

Fig. 2 – Number of electrons and holes stored along the model axis (defined as the axis perpendicular to the electrodes surface) when the zero-field barrier height at both electrode/polymer interfaces is: (a) 0.1 eV and (b) 0.7 eV.

Fig. 3 – The internal electric field along the model axis perpendicular to the electrode surfaces for a zero-field barrier height at both electrode/polymer interfaces is equal to 0.1 eV (squares) and 0.7 eV (circles). The dot line at 3 MV/cm corresponds to the applied electric field. The lines are just a guide to the eyes.

Fig. 4 – Recombination efficiency (proportion of injected electron-hole pairs which recombine) along the model axis (defined as the axis perpendicular to the electrode surfaces) for a zero-field barrier height at both electrode/polymer interfaces of 0.1 eV (squares) and 0.7 eV (circles). The lines are just a guide to the eyes.

Text for Table of Contents

We studied the effect of changing barrier height at electrode/polymer interfaces on the functioning of polymer LED based on PPV, using a mesoscopic model. We found that similar barriers with low height favours charge recombination in the centre of the polymer layer, and improves device performance.

Fig. 1

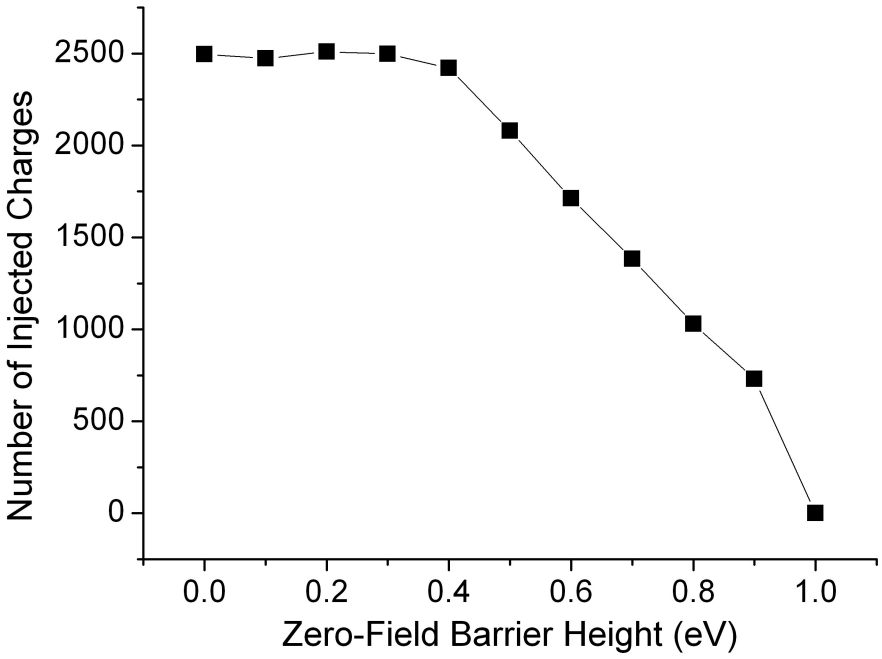

Number of Injected Charges
2500
2000
1500
1000
500
0
0.0
0.2
0.4
0.6
0.8
1.0
Zero-Field Barrier Height (eV)

Fig.2

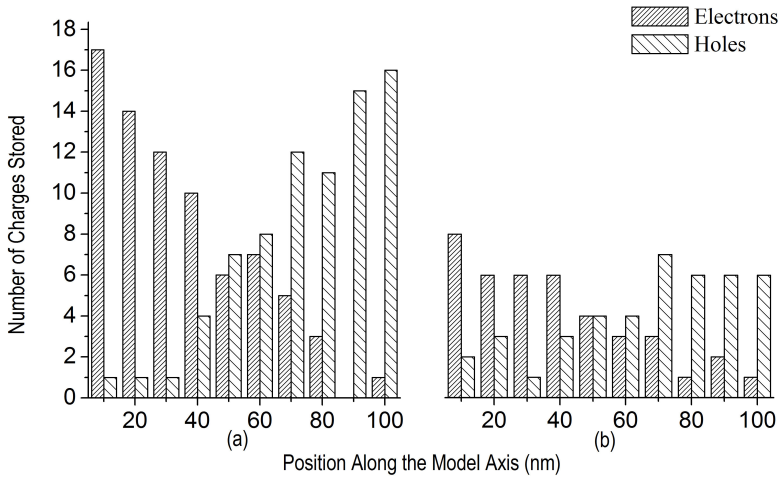

Electrons
Holes
Number of Charges Stored
0
2
4
6
8
10
12
14
16
18
20
40
60
80
100
(a)
(b)
Position Along the Model Axis (nm)

Fig. 3

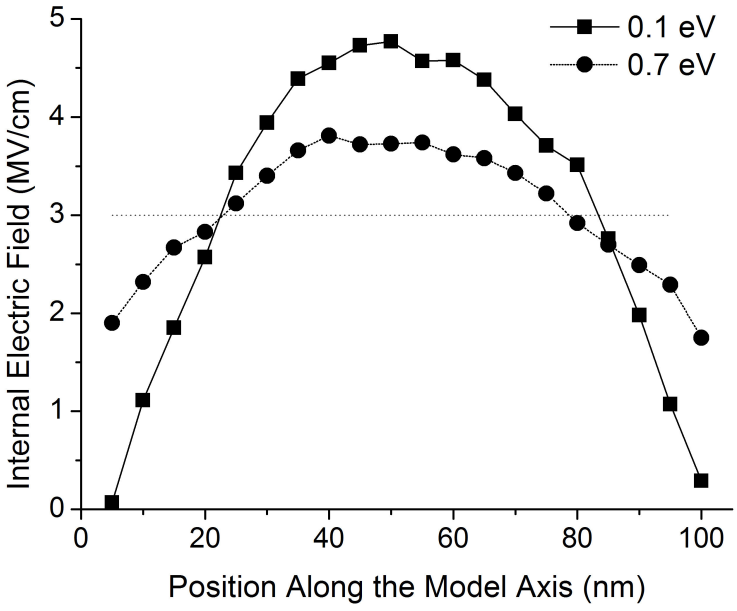
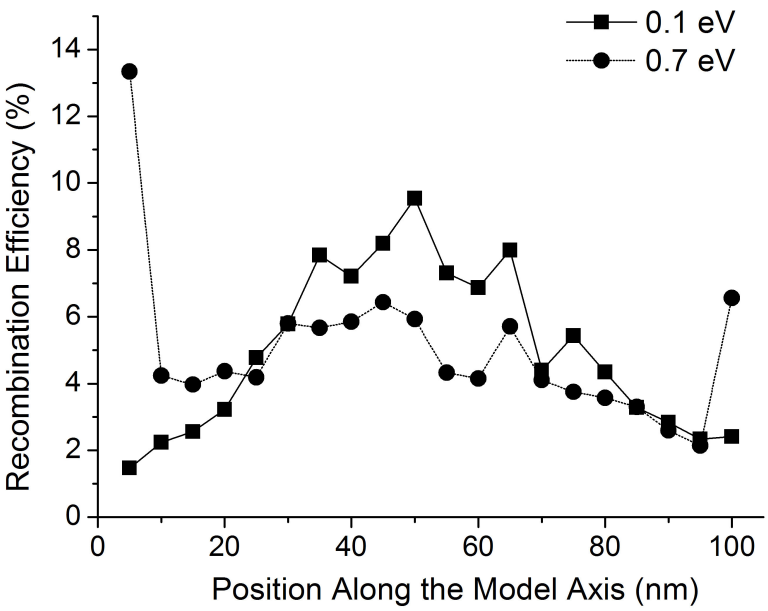

0.1 eV
0.7 eV
Internal Electric Field (MV/cm)
Position Along the Model Axis (nm)
0
1
2
3
4
5
0
20
40
60
80
100

Fig. 4


0.1 eV
0.7 eV
Recombination Efficiency (%)
Position Along the Model Axis (nm)
0
2
4
6
8
10
12
14
0
20
40
60
80
100