Computational Study of the Influence of Polymer/Polymer Interface Formation on Bilayer-LED Functioning

Hélder M. C. Barbosa[1, 2, a], Marta M. D. Ramos[1,2, b] and Helena M. G. Correia[2,c]

[1]Department of Physics, University of Minho

[2]Centre of Physics, University of Minho

Campus de Gualtar, 4710-057 Braga, Portugal

[a]helder@fisica.uminho.pt, [b]marta@fisica.uminho.pt, [c]hcorreia@fisica.uminho.pt

Abstract. The actual interest on polymer light emitting diodes (PLEDs) is based on the fact that they are easy to process, which reduces the cost of fabrication and thus opening a new branch in the electronic market – the low-cost electronics. However, these devices present a limited efficiency compared to their inorganic counterparts mainly due to the unbalanced charge injection, which reduces the fluorescence emission. One of the first strategies to improve PLEDs efficiency was using a bilayer structure composed by two polymers to improve charge injection and transport, and at the same time tunne charge recombination zone to reduce the effect of the electrodes on exciton quenching. Although this is a very ingenious device architecture some of these bilayer devices showed a lower efficiency than it was expected. The reason for that is attributed to the dissolution of the first polymer layer by the solvent used for the deposition of the second polymer layer, which do not allow to create a define polymer/polymer interface. Although cross-linking the first polymer layer can solve this problem, there is not a clear understanding why the presence of a graded interface between both polymer layers can lead to a change on PLED efficiency.
In order to clarify the effect of a graded polymer/polymer interface as compared to a sharp one on the functioning of a PLED, we performed computer experiments using a mesoscopic model of a bilayer PLED developed by us that considers the morphology of both polymers at nanoscale and their properties at molecular scale. The results present in this work show clearly a significant change on the charge recombination profile within the polymer device depending on the type of interface formed between the two polymers, which can be a plausible explanation for the loss of efficiency in the bilayer 7-CN-PPV/PPV LED.

Introduction

One of the reasons for choosing semiconducting polymers instead of their inorganic counterparts is mainly their easy processability, allied with the possibility to tune their molecular properties by chemical manipulation and produce very thin films on flexible subtracts [1]. In general, polymer light emitting diodes (PLEDs) are made by depositing the semiconducting polymer between two electrodes using the spin-coating technique. However, PLEDs that use a single polymer layer as the active component exhibit several problems related to charge injection, transport and recombination [2]. To minimize these problems which affects device performance a bilayer structure made of poly(p-phenylene vinylene) (PPV) and a cyano-PPV was proposed [3]. The use of these two semiconducting polymers reduce the zero-field barrier height at polymer/electrode interface, which improves unipolar charge injection with the applied bias and, at the same time each polymer layer improves a single carrier transport towards the bulk, forming a hole/electron transport layer (HTL/ETL). Since the molecular properties of both semiconducting polymers are different (i.e.

ionization potential, electron affinity and intramolecular charge mobility), an energy barrier is created at polymer/polymer interface that leads to charge transport blocking, improves charge recombination and thus exciton formation [1, 3]. Since the band-edge offset of the two polymers at the interface is smaller than the singlet exciton binding energy, the exciton is stable at the interface, favouring its radiative decay [4]. As a result there is an increase on charge injection, and an increase of charge recombination [5] far from the electrodes which reduces the effect of the electrodes on exciton quenching [6, 7] .

Nevertheless, the fabrication of such bilayer structures have severe limitations since the majority of the polymers used in these structures share the same solvent and the deposition of the upper polymer layer tends to dissolve the underlying polymer one, leading to a mixing of both polymer layers at polymer/polymer interface [2, 8], that has found application in photovoltaic devices [9, 10]. Although, it is possible to circumvent this effect by cross-linking the underline polymer [8, 11]. However, there is a not clear understanding why the presence of a graded polymer/polymer interface influences the functioning of a PLED as compared with the one that has a well define interface. To clarify this issue we performed dynamic Monte Carlo simulations of a bilayer PLED functioning with and without a graded distribution of the two polymers at polymer/polymer interface.

Device Model and Simulation Method

PLEDs with a bilayer structure are made by the deposition of the polymer thin film by spin-coating. As a result of this deposition technique, the morphology of the polymer film at nanoscale is a mixture of long polymer chains, similar to a "spaghetti structure", that are lied on planes parallel to the electrodes surface. Each chain is composed by straight rigid conjugated segments linked by kinks and twists that lead to the disruption of the conjugation [12]. Thus the polymer bulk can be seen as an ensemble of stiff-chain segments whose long molecular axis is parallel to the electrodes surface [13].

In order to mimic this nanostructure we placed randomly between two planar electrodes, separated by 100 nm from each other (model axis), rigid rods that represent the stiff-chain segments, with their long axis parallel to the electrodes surface. During the polymer network building we impose a minimum distance (0.650 nm) between two segments and between those and the electrodes, as well as a mean value (7 monomers) for a Gaussian distribution of segment lengths, taken from previous theoretical and experimental results reported elsewhere [13, 14]. Using this strategy we built two bilayer polymer networks with the architecture cathode/ poly(7-cyano-para-phenylenevinylene)(7-CN-PPV)/poly(para-phenylenevinylene) (PPV)/anode, where 7-CN-PPV/PPV works like a ETL/HTL. The first bilayer polymer network has a sharp interface located at 50 nm from the electrodes, whereas the second one is made of graded layer of both polymers spread throughout the device. It is possible to achieve the second layer architecture of mixed polymers with a gradient distribution of both polymers [9, 10], when for instance, it is not given enough time to occur a complete phase separation of both polymers, evaporating the solvent by increasing significantly the temperature which froze the mix of the two polymers [2, 15].

To study the electric behaviour of these devices, we use a nanoscale model based on a dynamic Monte Carlo method that considers time evolution of the hopping processes of charge injection/collection from/by the electrodes and intermolecular charge transport (i.e. charge transport between polymer segments). The hopping frequency of each one of them between sites i and j is given by:

$$w_{ij} = w_0 \times f(\theta) \times g(r_{ij}) \times h(\Delta E_{ij}) \tag{1}$$

w_0 represents the *attempt-to-escape* frequency of a charge in the absence of other factors that mediated the hopping process, namely the influence of the direction of the local electric field (which is the sum of the applied electric field, the field due to charge distribution within the polymer network and the field due to electrode polarization) ($f(\theta)$), the influence of the hopping distance ($g(r_{ij})$) and the influence of the energy barrier height that a charge has to overcome to hop between two sites ($h(\Delta E_{ij})$). This last term takes into account the applied bias voltage and the difference between the ionization potential/electron affinity of the involved polymer segments on hole/electron hopping, or the electrode work function and ionization potential/electron affinity for hole/electron injection.

For a certain charge, the probability of occurrence each process is given by:

$$p_{ij} = \frac{w_{ij}}{\sum w_i} \tag{2}$$

Where $\sum w_i$ represents the sum of all charge hopping frequencies to the neighbour sites. The final position that a charge can occupy after a hopping process takes place is the one that exhibits the highest probability. Our model also includes the processes of intramolecular charge transport, that occurs if the local electric field is higher than the field needed to move the injected charge along the polymer segment, and intramolecular charge recombination, that occurs if two charges of opposite sign meet on the same segment and the local electric field is not strong enough to maintain the charges on opposite sites of the segment. A detailed description of model and all the processes consider can be found in ref. [14, 16, 17] and the molecular properties used in this work as input parameters were taken from ref. [12]. The time evolution is followed by adding time steps, which the time interval corresponds to the smallest time of occurrence of all processes. This strategy is based on the First Reaction Method [18].

Results and Discussion

Fig. 1 shows the average monomer distribution of PPV and 7-CN-PPV inside the bilayer networks throughout the model axis for sharp and graded interfaces. In order to have a sharp interface (Fig. 1 (a)) we impose a restriction on PPV and 7-CN-PPV polymer strand distribution, being the interface located at 50 nm from both electrodes surface. For the graded bilayer interface (Fig. 1 (b)) the distribution of PPV and 7-CN-PPV polymer strands have a gradient from the cathode (0 nm)/anode (100 nm) to the opposite electrode. We choose this two types of polymer strand distributions since they are the two extreme cases that what can happen in a real polymer bilayer network.
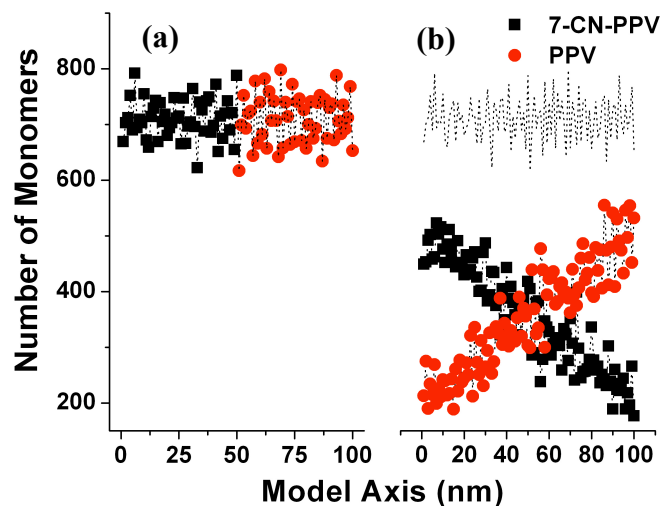
Figure 1 – Monomer distribution of PPV (circles) and 7-CN-PPV (squares) throughout the bilayer polymer network with a sharp (a) and graded (b) interface between both polymers. The lines are just a guide to the eye.

To understand the influence of the presence of sharp and graded bilayer interfaces on the functioning of PLEDs, we performed computer simulations using our model and applying a bias ranging from 3.5 V to 7.5 V, that correspond to typical bias voltage values of functioning of these devices. Fig. 2 shows the results obtained for the electric behaviour of both bilayer polymer LEDs. When the applied bias increases, an increase of the current density (J) for both bilayers is predicted (Fig. 2 (a)), which is reflected on the recombination rate (R) (Fig. 2(b)). However this increase is more pronounced for the graded interface at low bias than for the sharp one. The reason for this different behaviour is due to the difference on the energetic disorder inside the polymer network. The energetic disorder has its origin on the polymer chemistry and the polymer segment length distribution. For the case of the graded interface, the energetic disorder is higher due to the effect of the mixture of PPV and 7-CN-PPV polymer segments, which leads to a higher charge injection, charge recombination rate and charge density (ρ) as compared with the sharp interface (Fig. 2 (c)). With the increase of the applied bias the effect of the different energetic disorder just tends to limit the amount of charge stored on both bilayers, being the J and R similar.
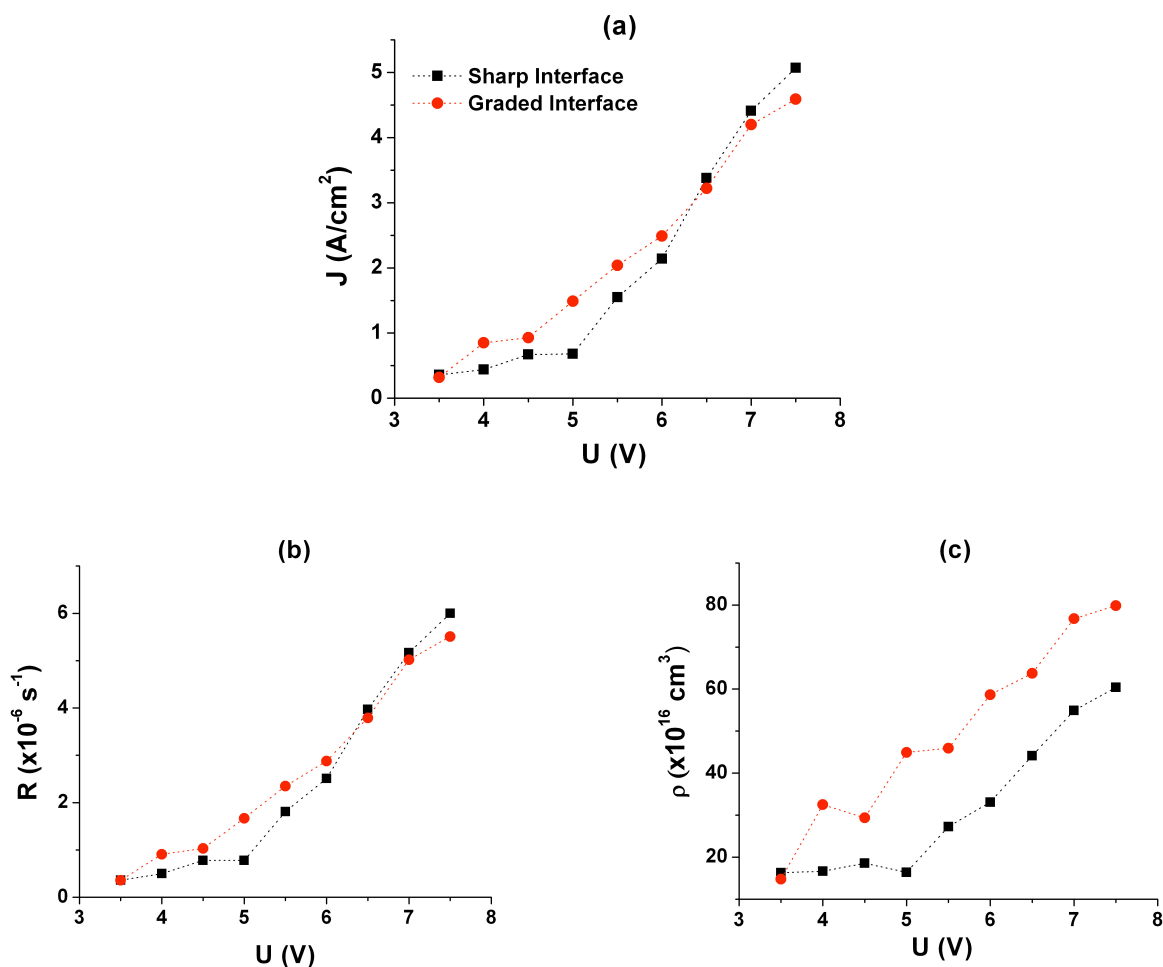

Figure 2 – Current density (a), recombination rate (b) and charge density (c) for the sharp (squares) and graded (circles) bilayer interfaces and for an applied bias ranging from 3.5 V to 7.5 V. The lines are just a guide to the eyes.

At first sight it seems that a PLED with a graded bilayer interface is more efficient that a sharp one at low bias. However, if we look at ρ distribution (holes and electrons) throughout the model axis

(Fig. 3) we can see that their distribution depends on the bilayer interface profile. For the sharp interface, charges tend to be stored near it, being this effect higher with the increase of the applied bias, whereas for the graded interface the ρ distribution for holes and electrons throughout the polymer network have a gradient at high bias, following the PPV and 7-CN-PPV monomer distribution. This effect is due to the fact that the energetic disorder is localize at the sharp interface position creating an energy barrier for charge transport which leads to charge trapping, while for the graded interface the mixture of PPV and 7-CN-PPV segments destroys the well define energy barrier. Nevertheless, it is interesting to notice that with the increase of the applied bias, there is a larger increase of hole density on the ETL as compared with the electron density on the HTL. This is justified by the fact that the difference on the molecular properties of PPV and 7-CN-PPV leads to a higher energy barrier for electrons than for holes whose effect on charge blocking tends to be reduced with the applied bias.
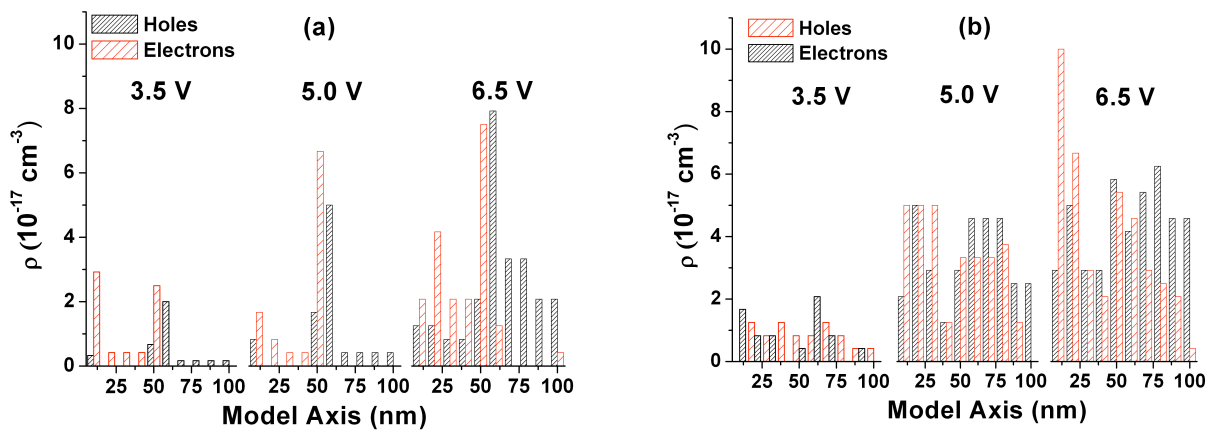

Figure 3 – Hole (dense bars) and electron (sparse bars) density distribution along the model axis for sharp (a) and graded (b) bilayer interfaces and applied bias of 3.5V, 5.0 V and 6.5 V.

The effect of the polymer/polymer interface formation is also reflected on the profile of charge recombination events. Fig. 5 shows the fraction of recombination events along the direction perpendicular to the electrodes surface for sharp and graded interfaces and different applied bias.
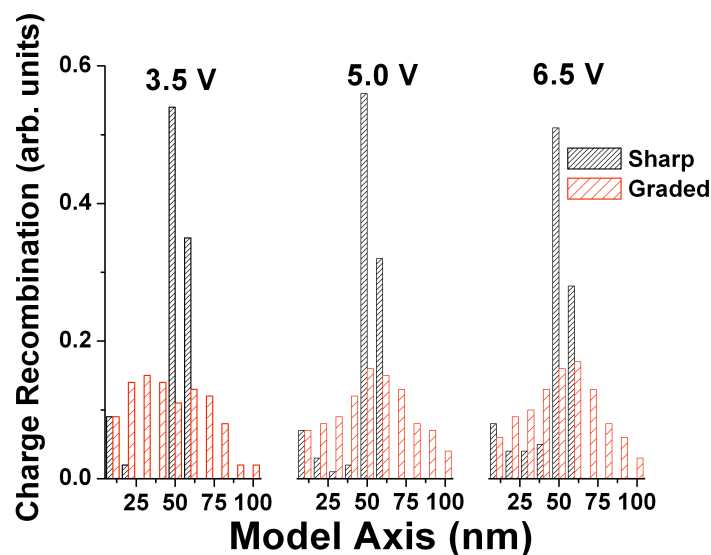

Figure 5 – Fraction of charges that undergo recombination for sharp (dense bars) and graded (sparse bars) bilayer interfaces throughout the model axis and for an applied bias of 3.5 V, 5.0 V, 6.5 V.

For the sharp interface the fraction of charge recombination events is significantly higher at the interface position as a result of the charge blocking effect. When the applied bias increases, the charge blocking effect decreases and the number of charge recombination events tends to increase mainly on the ETL and near the cathode. The number of charge recombination events near both electrodes are significantly higher for the graded interface as compared with the results obtained for the sharp interface, and charge recombination occurs throughout the polymer network. For this interface, the effect of electrodes on exciton quenching will be more pronounced than for the sharp interface, which will limit the exciton radiative decay and thus the PLED efficiency.

Conclusions

In order to increase PLEDs efficiency to make them competitive with their inorganic counterparts, it is necessary to arrange new strategies and deeply understand these devices functioning. For the case of PLEDs with a bilayer architecture, our results show that the efficiency of PLEDs depends on the polymer/polymer interface formation. A sharp interface leads to the formation of an energy barrier that blocks charge transport, which increases the probability of charge recombination at interface position and confines exciton formation far from the electrodes. As a result, there is a decrease on exciton quenching by the electrodes. However, this effect tends to be less efficient with the increase of the applied bias, as it was suggested by our previous work [5]. Therefore our results suggest that the use of bilayers in PLEDs made of 7-CN-PPV/PPV are a good strategy for devices working at low bias if those devices have a sharp polymer/polymer interface. Although our model do not take into account all the physical process that are behind a PLED functioning, our results suggest that the spread of charge recombination events and exciton formation throughout the device increases the effect of electrodes on exciton quenching, which can lead to a decrease on the efficiency of a PLED with a graded interface.

References

[1] M.T. Bernius, M. Inbasekaran, J. O'Brien and W. Wu: Adv. Mater. 12/23 (2000) p. 1737
[2] E. Moons: J. Phys.-Condes. Matter 14/47 (2002) p. 12235
[3] N.C. Greenham, S.C. Moratti, D.D.C. Bradley, R.H. Friend and A.B. Holmes: 365/6447 (1993) p. 628
[4] R.H. Friend: Pure Appl. Chem. 73/3 (2001) p. 425
[5] H.M.C. Barbosa and M.M.D. Ramos: J. Mater. Sci.-Mater. El. 18 (2006) p. S25710.1007/s10854-007-9191-y.
[6] J.S. Kim, R.H. Friend, I. Grizzi and J.H. Burroughes: Appl. Phys. Lett. 87/2 (2005) p. 3023506 10.1063/1.1992658.
[7] H. Becker, S.E. Burns and R.H. Friend: Phys. Rev. B 56/4 (1997) p. 1893
[8] A. Charas, H. Alves, L. Alcacer and J. Morgado: Appl. Phys. Lett. 89/14 (2006) p. 143519 10.1063/1.2360243.
[9] C.J. Brabec, A. Cravino, D. Meissner, N.S. Sariciftci, M.T. Rispens, L. Sanchez, J.C. Hummelen and T. Fromherz, E-MRS 2001 Spring Meeting, Strasbourg, France, 2001, p. 368.
[10] L.C. Chen, D. Godovsky, O. Inganas, J.C. Hummelen, R.A.J. Janssens, M. Svensson and M.R. Andersson: Adv. Mater. 12/18 (2000) p. 1367
[11] G. Bernardo, A. Charas, L. Alcacer and J. Morgadoa: Appl. Phys. Lett. 91/6 (2007) p. 3063509 10.1063/1.2768636.

[12] A.M. Stoneham, M.M.D. Ramos, A.M. Almeida, H.M.G. Correia, R.M. Ribeiro, H. Ness and A.J. Fisher: J. Phys. Condens. Matter 14/42 (2002) p. 9877

[13] B.G. Sumpter, P. Kumar, A. Mehta, M.D. Barnes, W.A. Shelton and R.J. Harrison: J. Phys. Chem. B 109/16 (2005) p. 7671

[14] M.M.D. Ramos and H.M.G. Correia: J. Phys. Condens. Matter 18/16 (2006) p. S429

[15] M. Granstrom, K. Petritsch, A.C. Arias, A. Lux, M.R. Andersson and R.H. Friend: Nature 395/6699 (1998) p. 257

[16] H.M.C. Barbosa and M.M.D. Ramos: Plasma Process. Polym. 4 (2007) p. S104

[17] H.M.C. Barbosa and M.M.D. Ramos: Mat. Sci. Eng. B-Solid (2008) doi:10.1016/j.mseb.2008.09.031.

[18] J.J. Lukkien, J.P.L. Segers, P.A.J. Hilbers, R.J. Gelten and A.P.J. Jansen: Phys. Rev. E 58/2 (1998) p. 2598