Mesoscopic modelling of bipolar charge evolution in CN-PPV LEDs

Marta M.D. Ramos[a,*], Helena M.G. Correia[a], R. Mendes Ribeiro[a], A.M. Stoneham[b]

[a] *Departamento de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal*
[b] *Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK*

Abstract

Since various changes are possible in the molecular structure of the repeat unit, substituted poly(para-phenylenevinylene) (PPV) has been used as active component in light-emitting diodes (LEDs) to obtain light emission in a wide range of colours.

A major aspect determining device performance is the competition between current flow, trapping and recombination within the polymer layer. By suitable Monte Carlo calculations, we have performed computer experiments in which bipolar charge carriers are injected at constant rate in polymer networks made of cyano-substituted PPV chains with variable length and orientation. The intra-molecular electronic properties used in these simulations were calculated by a quantum molecular dynamics method. In order to assess the influence of cyano-substitution on the properties of single-layer PPV LEDs, we have focused our attention on bipolar charge evolution in time. Specifically addressed are the differences in electric field strength needed for intra-molecular charge mobility of electrons and holes and their consequences at mesoscopic scale.
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1. Introduction

Burroughes et al. [1] were the first to report in 1990 the use of thin poly(para-phenylene-vinylene) (PPV) films for producing single-layer polymer light-emitting diodes (PLEDs). These PLEDs produce yellow light. However, the polymer PPV can be modified by chemical substitution to produce other PLEDs of different colours. The wavelength of the emitted light depends on the energy gap of the PPV derivatives. The biggest challenge yet is to find how PPV derivatives, such as those obtained when we introduce cyano electron-accepting groups into the PPV chain [2], affect the performance of PLEDs based on those materials, as compared to that of PPV.

In the current technology being pursued, PLEDs formed by spin coating have a polymer layer of chain molecules, with different number of repeat units in length, lying on a flat substrate in an irregular network. Therefore, PLEDs are quite different from inorganic semiconductor light-emitting diodes and should not be modelled assuming the polymer layer as a continuous medium.

Since the intra-molecular and intermolecular bipolar charge transport in the polymer layer influence each other, they both must be included in a numerical model of PLEDs. To address the above issues, we developed a mesoscopic model of single-layer PLEDs [3,4] to simulate the bipolar charge transport, trapping and recombination in networks made of polymer chains with variable length, orientation and molecular properties. In the work presented here, we used this mesoscopic model to study the influence of cyano-substitution at different substitution sites on the performance of a single-layer PLED based on CN-PPV with chain arrangement parallel to the electrode surface.

2. Device model and simulation method

We simulated bipolar charge transport through three-dimensional networks of straight chains of poly(2-cyano-

* Corresponding author. Tel.: +351 253 604330; fax: +351 253 678981.
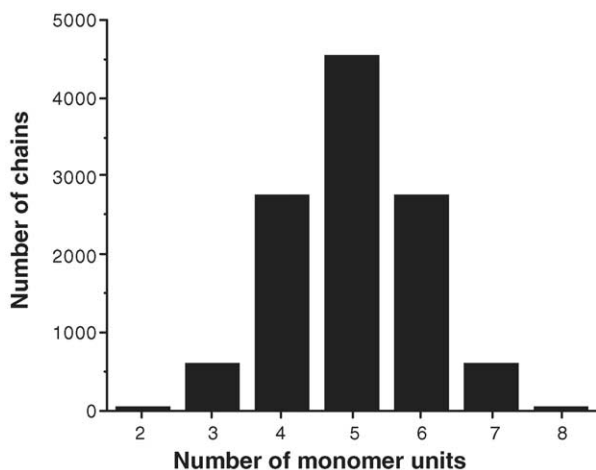*E-mail address:* marta@fisica.uminho.pt (M.M.D. Ramos).

Fig. 1. The distribution of chain lengths (measured in monomer units) in the polymer networks of the type discussed in the text.

para-phenylenevinylene) (2-CN-PPV) [2], poly(7-cyano-para-phenylenevinylene) (7-CN-PPV) [2] and poly(8-cyano-para-phenylenevinylene) (8-CN-PPV) [5] with the distribution of chain lengths given in Fig. 1. These simulations are compared with the ones obtained for PPV with the same polymer networks as CN-PPV. The chemical structures of all the molecules are shown in Fig. 2. Five different polymer networks with the long chain axes parallel to the electrode surface were investigated for each material. These polymer networks have thickness of 100 nm, a surface-area bound to the electrodes of $400\,nm^2$ and density $0.3\,g\,cm^{-3}$. This density is similar to the one we obtained for chain arrangements with totally random orientation [3,4]. The construction of the polymer films is based on a random process, which prohibits the occupation of the same space by more than one chain and any cross-linking between different chains. The polymer network was built by placing individual straight chains of various lengths at random in the gap between the electrodes, with their long molecular axis parallel to the electrode surface but not parallel to each other and their molecular plane having
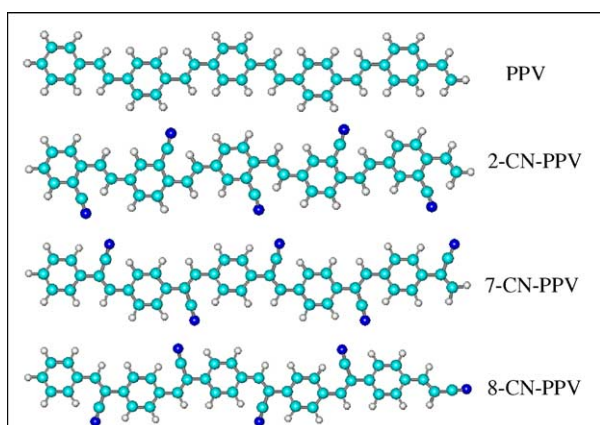

Fig. 2. Schematic diagram of the molecular structures of the polymers used.

any orientation relative to the electrode surface. The results we describe here are for polymer cells with periodic boundary conditions along the directions parallel to the electrode surface.

When an external electric field ranging from 1 to 3 MV/cm is applied between the electrodes, one electron and one hole are injected into the polymer film via cathode and anode, respectively, through randomly chosen chains bound to those electrodes. An electron–hole pair is injected simultaneously at each computer iteration, which corresponds to one inter-chain jump.

The charge percolation through the polymer network was simulated by considering the hopping of both electrons and holes between charge transporting states of neighbouring molecules. The charges are under the influence of the local electric field, which is the sum of the external applied electric field, the field generated by the other charges within the polymer layer and the field due to electrode polarization. The hopping rate has the form given in references [3,6] and it is dependent on the strength and direction of the local electric field, on the inter-chain distance, on the Coulomb blockade, as well as on the energy barrier between the transport states of neighbouring molecules that has to be overcome by the charge carriers. The probability of hopping processes falls with the angle between the directions of the local electric field and the jump path, the hopping distance and the height of the energetic barrier, which has to be crossed by the charge carriers. The height of such a barrier is assumed to be the sum of two contributions. One arises from the difference in the electron affinity (for hole transport) or ionization potential (for electron transport) of two polymer chains involved in the hopping process. The other is due to the potential difference along the jump path. Because of Coulomb blockade, no two carriers of the same sign are allowed on a polymer chain. Each charge jumps into one of the neighbouring chains, chosen randomly, provided that the hopping rate is greater than 10^{-5} and that the hopping probability is greater than 90%. Otherwise it stays there and contributes to the space charge. Given that the intra-molecular charge motion is much faster than the inter-molecular one [7], the injected charge can recombine with an opposite charge that is present on that chain, or it can move instantaneously to the chain-end favoured by the local electric field if its component along the chain axis is greater than the electric field needed for intra-molecular charge mobility; otherwise it moves towards the centre of the chain which is energetically more favourable [2]. As noted already, recombination occurs during the course of the simulation whenever two oppositely charged carriers meet on the same chain, since the electric field needed for exciton decay into an isolated polaron pair of different signs is higher than the local electric field involved in the simulations which tends to separate the pair. In the present work we do not allow inter-chain recombination.

The input data required to the mesoscopic model are those concerning the length per monomer unit, the mini-
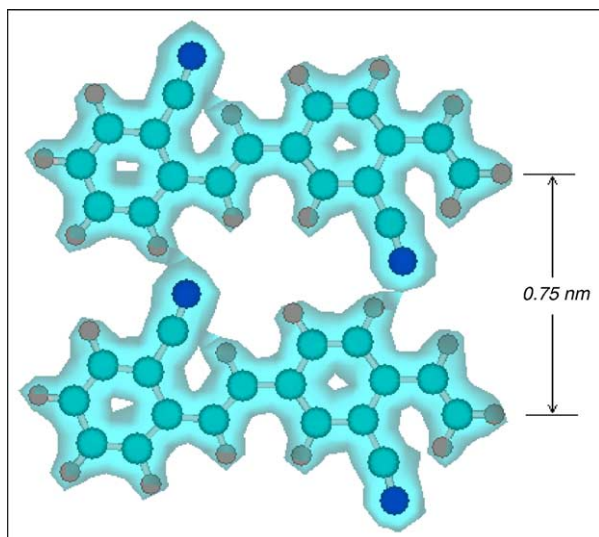
Fig. 3. Top view of the optimised molecular structure of two coplanar CN-PPV chains, showing the inter-chain equilibrium distance and the charge density isosurface.

mum inter-chain distance between two neighbouring CN-PPV molecules in the polymer network, the ionization potential and electron affinities of chains with different lengths and the electric field threshold for charge (electron or hole) mobility along the CN-PPV chains.

Since the planes of the molecular backbones in the network have a random orientation, we have considered the polymer chains as rigid rods when calculating the minimum inter-chain distance allowed. It is straightforward to generalise this approach to include the dependence of the minimum inter-chain distance on the relative orientation of the neighbour molecular backbone planes, but this is not done in the present calculations.

The choice of a minimum inter-chain distance of 0.75 nm for CN-PPV was based on the fact that in our self-consistent quantum molecular dynamics calculations, based on the CHEMOS code [8,9] this distance corresponds to the equilibrium distance between two CN-PPV chains with the configurations shown in Fig. 3. The minimum inter-chain distance of approximately 0.4 nm was predicted for cofacial configuration, but this is not the configuration in the present calculations. The variation of ionization potential and electron affinity of CN-PPV as a function of chain length (Fig. 4), the length of the CN-PPV monomer unit (0.639 nm) and the electric field threshold needed for intramolecular charge mobility to be considered (Table 1) were calculated using also the self-consistent quantum chemistry molecular dynamics method described in references [8,9]. Some of these results have already been reported elsewhere [2].

The ionization potential, the electron affinity and the electric field threshold for intramolecular polaron mobility in PPV were taken from reference [10]. The main features of these data are included in Fig. 4 and Table 1.
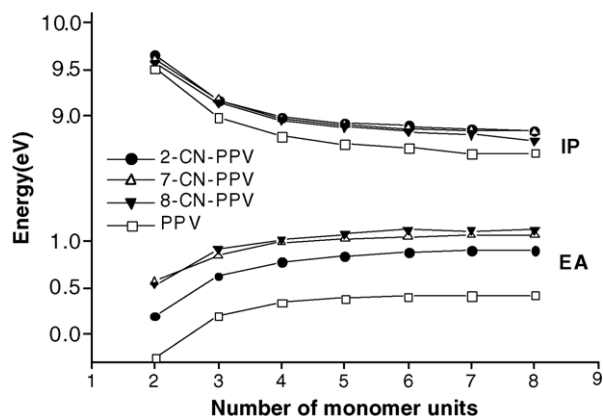

Fig. 4. Ionization potential (IP) and electron affinity (EA) as a function of chain length (measured in monomer units) for 2-CN-PPV, 7-CN-PPC, 8-CN-PPV and PPV [10].

Table 1
Electric field threshold for charge (electron and hole) mobility along the PPV [10], 2-CN-PPV, 7-CN-PPV and 8-CN-PPV chains with 16 repeat units.

| Polymer	Net charge	Electric field threshold (MV/cm)
PPV	+1	2.0 [10]
	−1	1.55 [10]
2-CN-PPV	+1	2.067
	−1	2.690
7-CN-PPV	+1	2.249
	−1	2.410
8-CN-PPV	+1	2.218
	−1	2.393

The geometry relaxation owing to the strong charge-lattice coupling was considered when we calculated the ionization potential and the electron affinity, using the energies for a fully relaxed chain in its neutral and charged states, as well as the charged polaron mobility along the chain. Therefore, the role of polaronic relaxation energies are taken in account in the mesoscopic simulations which include both intra- and inter-chain bipolar charge transport.

3. Results and discussion

In order to study the relationship between substitution position in CN-PPV and bipolar charge evolution in light-emitting diodes based on these materials, we calculated the fractions of injected charge that cross the polymer film to carry a current, recombine or contribute to the space-charge. We followed the charge evolution with time (measured in a computer timescale) from the initial state to the steady state. Only results corresponding to the steady state are presented in this section. Figs. 5–7 show the simulated current, recombination and trapping efficiency as a function of the external applied electric field for 2-CN-PPV, 7-CN-PPV, 8-CN-PPV, averaged over the five different polymer networks for each material and compared with the ones obtained for PPV. All the calculations were performed over the same electric field range as in the experiment with PPV and PPV derivative [11].
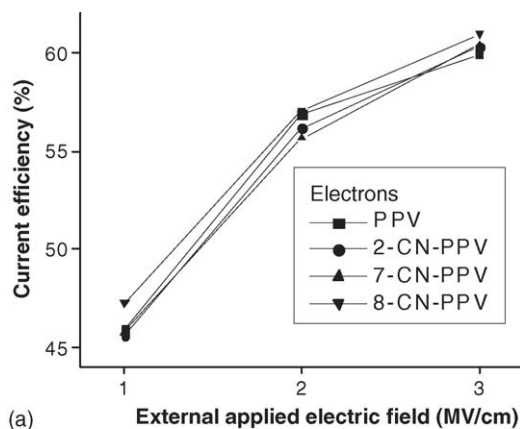
(a)
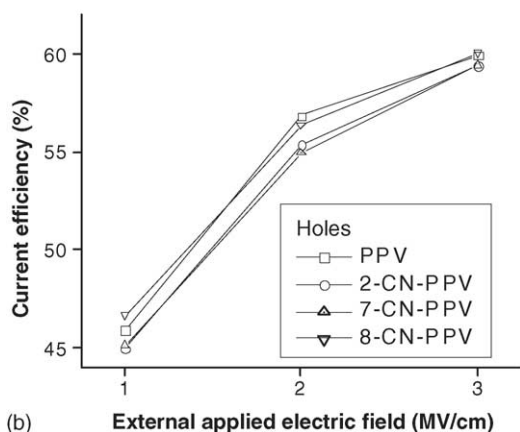
(b)

Fig. 5. Current efficiency (the proportion of charge carriers crossing the polymer film to reach the other electrode for (a) electrons and (b) holes. The lines are a guide to the eye.
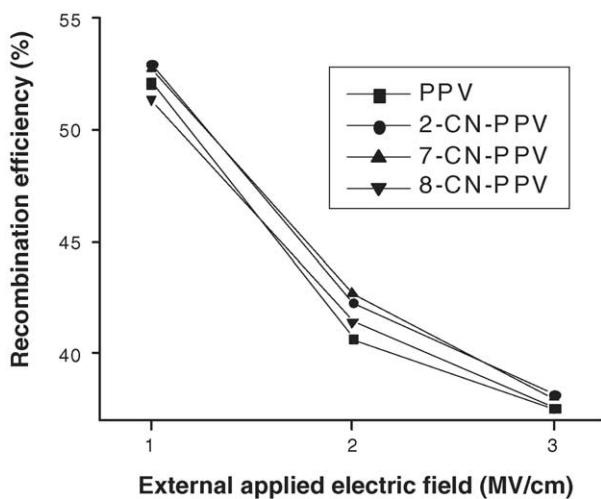

Fig. 6. Proportion of injected charge, which recombines within the polymer film for three different strengths of the external applied electric field. The lines are a guide to the eye.
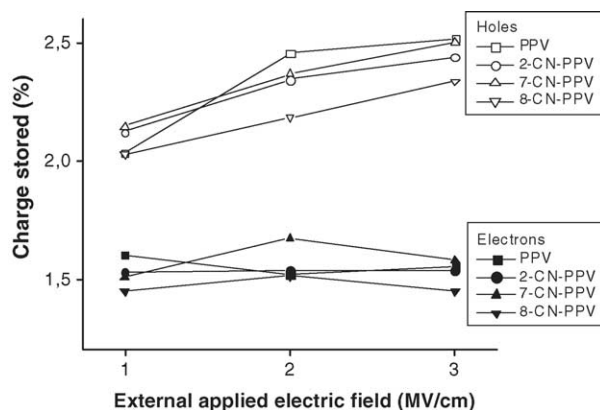

Fig. 7. Proportion of injected charge (electrons and holes) that is trapped or in transit within the polymer network in the steady state. The lines are a guide to the eye.

The most important features that we find for both PPV and CN-PPV is that recombination efficiency decreases as the applied electric field increases, but current and space charge show an opposite behaviour since injection efficiency is not considered to be affected by the space-charge in our model.

Although the electric field threshold for intra-molecular charge mobility of electrons and holes are different for both CN-PPV and PPV, no significant difference was predicted for their current efficiency for the same external applied electric field (see Fig. 5a and b). When the external applied electric field is lower than the field needed for both electron and hole mobility along the polymer chains (1 MV/cm), the recombination efficiencies of PPV and all CN-PPV are similar (Fig. 6). As the applied electric field is increased to 2 MV/cm, the recombination efficiency for CN-PPV becomes larger than for PPV. An increase the electric field strength increases the probability of charge hopping in the direction perpendicular to the electrodes, arising from the lowering of the potential barrier for these hopping processes, which leads to a change in the distribution of the remaining charges in the network. The field due to the space charge influences the charge mobility along the polymer chains and the hopping processes that occur parallel to the electrodes, which tends to separate electrons and holes paths through the network. This provides a decrease for recombination, the effect being stronger for PPV, which has the lowest electric field threshold for intra-chain mobility of polaronic charge carriers of both signs. The explicit Coulomb interaction between charges within the polymer network that was not simplified to an average space charge, affects the competition between charge flow perpendicular and parallel to the electrodes. This leads to recombination results for polymers with different electric field thresholds for bipolar charge mobility along the chains that are by no means intuitive. As the applied field is increased further, a new distribution of charges in transit in the network is obtained, which leads to both electrons and holes move to the chain end favoured by the local electric field either in PPV as in CN-PPV and recombination for
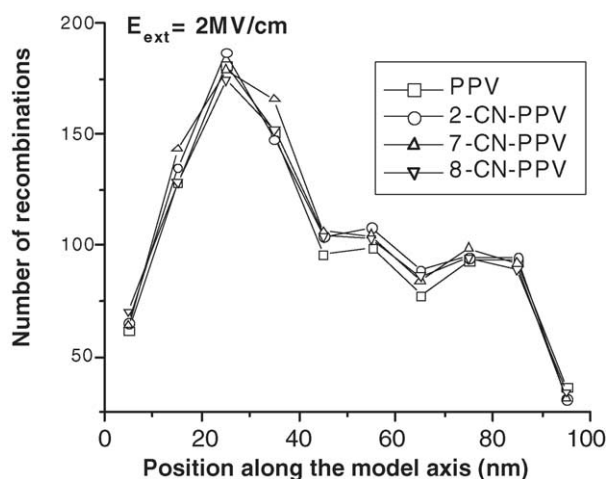
Fig. 8. Recombination distribution inside the polymer diode along the model axis perpendicular to the electrodes, for an external applied electric field of 2 MV/cm. The lines are a guide to the eye.

CN-PPV becomes as efficient as for PPV again. We have also examined the spatial distribution of the recombination events (Fig. 8). For the structures considered here recombination occurs primarily far from both electrodes. These results suggest
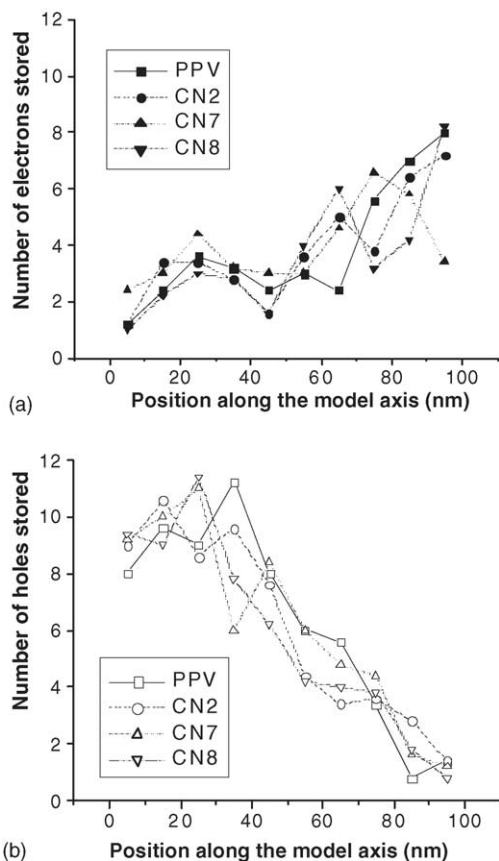

Fig. 9. Charge carrier distribution inside the polymer diode along the model axis perpendicular to the electrodes, for an external applied electric field of 3 MV/cm, corresponding to: (a) electrons and (b) holes. The lines are a guide to the eye.

that the higher recombination efficiency of CN-PPV relative to PPV is a result of an increase in the recombination events that take place far from the electrodes. This effect is more pronounced for both 2-CN-PPV and 7-CN-PPV.

Space-charge increases with the applied electric field, presumably because the charge mobility along the polymer chains leads to more 'dead end' paths. The charge distribution inside the polymer network in the steady state, for an external applied electric field of 3 MV/cm, is illustrated in Fig. 9. The number of electrons and holes stored in the network does not depend on the number of iterations needed for the steady state to be reached. There is more positive charge trapped or in transit within the polymer network than negative one, even for an external applied electric field of 3 MV/cm larger than the electric field threshold for intramolecular mobility of both electrons and holes in PPV and CN-PPV. This different charge accumulation for electrons and holes is mostly dictated by the differences in energetic barriers experienced by both charge carriers at inter-molecular hopping. The barrier heights for holes and electrons at the same inter-molecular hop depends on the difference between ionization potential (for electron transport) and electron affinity (for hole transport) as well as on the strength of the local electric field. An increase of holes and electrons far from the electrodes where they were injected is predicted as well.

4. Conclusions

Our mesoscopic simulation of bipolar charge evolution in CN-PPV has shown to be an aid to understanding the effect of side-substitution of PPV by cyano groups at several substitution positions on charge transport, recombination and trapping in light-emitting diodes with polymer chains with their long molecular axis parallel to the electrodes. For these polymer structures, the main effects predicted were an increase of recombination efficiency and a decrease in current efficiency relative to PPV for an applied electric field slightly lower than the electric field threshold for positive charge mobility along the CN-PPV chains. The small difference in the energy barriers for electron and hole inter-molecular mobilities perpendicular to the polymer chains caused the increased recombination to occur far from the electrodes. This work also shows negligible space charge when the polymer chains have their long molecular axis parallel to the electrodes. This result is largely independent of the applied electric field. Since the electric field threshold for intra-molecular charge mobility depends on the sign of the charge carrier involved and the strength of the local electric field affects the energy barrier for inter-molecular charge mobility, we expect greater electric field effects in terms of current transport and recombination efficiency for CN-PPV LEDs with polymer chains aligned perpendicular to the electrodes as well as for polymer networks with random oriented chains and significant differences relative to PPV-LEDs with the same polymer mesostructures. Naturally, the simulation results for charge

evolution in CN-PPV LEDs depend strongly on the polymer microstructure as well as on the rates of injection of electrons and holes from opposite electrodes into the polymer layer. Despite these limitations, device simulations, such as those reported here, gives an insight into cyano-substitution effects occurring in single layer PPV-LEDs with long chain axes parallel to the electrode surface and highlights the processes and properties that are critical for the functioning of this particular polymer mesostructure.

Acknowledgements

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