

MODELLING CHARGE TRANSPORT PROPERTIES OF CYANO-SUBSTITUTED PPV

Helena M. G. Correia, Marta M. D. Ramos*

Departamento de Física, Universidade do Minho, Largo do Paço,
4700-320 Braga, Portugal

Abstract

In recent years poly (*p*-phenylenevinylene) (PPV) and its derivatives have attracted much interest due to their applications in light-emitting diodes (LEDs). One of the issues that determine device performance is the transport of charge carriers along the polymer strands. For that reason, we investigate the influence of cyano substitution on geometry and electronic behaviour of PPV chains using self-consistent quantum molecular dynamics simulations.

Our results suggest that substitution by cyano groups induce distortion in the PPV chains and a charge rearrangement among the polymer atoms. Specifically addressed is the issue concerning estimates of charge (electron and hole) mobility by computer experiments. Significant differences

* Corresponding Author: Tel:+351 253 604330; Fax:+351 253 678 981; E-mail:marta@fisica.uminho.pt

have been found both in the strength of the electric field needed to move positive and negative charge carriers along the polymer chain as well as in charge mobility.

Keywords: Molecular modelling, charge transport, CN-PPV.

1. Introduction

A large number of conjugated polymers have been used as charge transporting or emissive layer in light-emitting diodes (LEDs) [1]. Research has been particularly focused on poly (para-phenylenevinylene) (PPV) and its derivatives because of their high efficiencies.

Electroluminescence generated via injection of electrons (or holes) from a scanning tunnelling microscope (STM) into the lowest (highest) unoccupied (occupied) molecular orbital level on the polymer molecule has been used to obtain information about the electronic properties of the polymer film at molecular scale [2]. Understanding the processes which contributes to the variation of electroluminescence efficiency at nanometric length scale will be important in improving polymer LEDs.

Although charge transport in PPV and its derivatives is currently of great interest since it affects device efficiency, there is little understanding at molecular scale. Continuum macroscopic models widely used to predict charge transport in polymer based devices are no longer valid at this length scale. Quantum molecular dynamics methods are ideally suited to study charge transport in these polymers which present strong electron-lattice coupling [3,4].

The aim of this paper is to predict the effects of the cyano substitution on individual PPV molecules and assess the consequences for charge transport along these polymer molecules. We report here the self-consistent calculation of the static properties for a cyano-substituted PPV molecule with 16 repeat units in its neutral and charge states, as well as charge mobility along the polymer molecule. The effect of substitution site is also discussed.

2. Theoretical method

The calculations presented here are based on the CHEMOS code [5] that combines self-consistent quantum chemistry at CNDO (Complete Neglect of Differential Overlap) level, using a linear combination of atomic orbitals and a cluster model framework, with molecular dynamics. The CNDO method is embodied into molecular dynamics with forces calculated self-consistently at each time step without numerical differentiation.

3. Results and discussion

3.1. Static properties

The effect of cyano substitution on the ground state geometry of PPV molecules is found by examining planar molecules of poly (2-cyano-para-phenylenevinylene) (2-CN-PPV) and poly (7-cyano-para-phenylenevinylene) (7-CN-PPV) with 16 monomer units.

The cyano substitution on the PPV backbone induces distortion in the molecule along the molecular plane (see Fig. 1). The distortion is larger when the cyano groups are located on the phenylene rings rather than on the vinylene moieties due to the greater electron-accepting capabilities of the cyano groups located on the phenylene ring.

The injection of charges (electrons or holes) to both PPV and cyano-substituted PPV molecules leads to change in their electronic structure. The calculated ionisation potential (energy to remove an electron) and electron affinity (energy gain on adding an electron) are summarised in Table 1 together with other theoretical results.

Our results suggest that mono-cyano substitution of PPV lead to an asymmetric increase of ionisation potential and electron affinity with respect to PPV. As a consequence the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of cyano-substituted PPV is reduced. These results are in agreement with a simple

chemical analysis based on electron accepting character of cyano substituents. The CNDO method seems to predict the same trends as the VEH method [6]. The energies involved in adding or removing a second electron from a mono-charged 2-CN-PPV molecule are different than the corresponding energies for 7-CN-PPV and greater than those for PPV. With respect to PPV, substitution on phenylenes leads to an increase of 0.51 eV for removing the second electron and 0.96 eV for adding the second electron, while substitution on the vinylenes leads to an enhancement of 0.47 eV and 1.25 eV, respectively.

Since energies are strongly dependent on CNDO parameters and basis set used, the absolute value of the calculated ionisation potential and electron affinities may not be corrected. However we expect the predicted trends to be reliable.

The changes in the atomic charges of 2-CN-PPV atoms due to positive and negative charge injection are given in Fig. 2. The resulting charge distributions show four main features. First, there is charge stored on the atoms of all elements. Second, despite the presence of a conjugated system, the charge is localised in the same small region of the molecule for all elements. Third, the injection of two electrons (or holes) gives two well-separated distributions of charge. Fourth, only carbon atoms show charge alternation. For 7-CN-PPV similar charge distribution patterns were found. In this case, the amplitudes and shapes are different for positive and negative charged molecules. The amount of charge stored on carbon, hydrogen and nitrogen atoms of cyano-substituted PPV molecules is shown in Table 2.

In contrast with PPV [3], only positive charges are mainly localised on carbon atoms of both cyano-substituted PPV molecules.

As in PPV, the injection of charge into cyano-substituted molecules leads to geometric relaxation that changes the difference between adjacent carbon-carbon bond lengths of the polymer backbone at charge localisation sites. These charge-induced defects resemble those obtained for PPV [7,8].

3.2. *Dynamic properties*

In order to study the effect of cyano substitution on charge transport of PPV molecules, we calculate the velocity of the injected charge density along the cyano-substituted PPV molecules as a function of the applied electric field. The charge mobility (defined as charge velocity per unit applied field) in cyano-substituted PPV molecules is shown in Fig. 3 in comparison with charge mobility in PPV reported elsewhere [9,10]. In parallel, we have also estimated the mobility of the dimerization features corresponding to the injected charges.

From these results it is clear that the field dependence of the charge mobility with three main regimes is only observed for electrons in 2-CN-PPV and both electrons and holes in PPV and 7-CN-PPV. First, when the field is lower than the threshold the injected charge does not move. Second, for an electric field just above the threshold, both charge and distortion patterns move slowly along the molecule. Third, for an applied field higher than a certain value the charge is already found at the chain end on the first molecular dynamics time step whereas the distortion pattern remains on its initial position in absence of that applied field. This leads to the high-mobility regime. In 2-CN-PPV the mobility of holes changes directly from no mobility to the high-mobility regime.

The electric field for high-mobility of holes in 2-CN-PPV is much lower than the corresponding field for PPV. Besides, electron mobility just occurs for higher field. This may suggest a marked imbalance in the mobility of electrons and holes in 2-CN-PPV: holes should dominate the transport. In contrast, electron high-mobility occurs for lower electric field than hole mobility in 7-CN-PPV. These results have major implications for bipolar charge transport in cyano-substituted PPV layers at mesoscopic level.

4. Conclusions

The mono-cyano substitution of PPV chains leads to an asymmetric increase of ionisation potential and electron affinity, but it does not seem to affect the position of the charge-induced defects in the absence of an applied electric field. When an electric field greater than the threshold is applied the injected charges moves along the cyano-substituted molecules. The value of charge mobility depends on the strength of the electric field as well as on charge sign and substitution position. Therefore, either electrons or holes can dominate the intramolecular charge transport in cyano-substituted PPV. These results should have a serious influence on migration of charge within the nanometric cyano-substituted PPV layers and they should be incorporated in the modelling of charge transport at this length scale. Quantum molecular dynamics calculations, such as those reported here, are a useful tool for understanding the mobility of charge within a single polymer molecule as well as for providing data for the mesoscopic modeling, which is currently impossible to obtain experimentally.

Acknowledgement

FCT and POCTI supported this work under project POCTI/CTM/41574/2001.

References

- [1] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlung and W. R. Salaneck, *Nature* 397 (1999) 121.
- [2] D. G. Lidzey, S. F. Alvarado, P. f. Seidler, A. Bleyer, D. D. C. Bradley, *Appl. Phys. Lett.*, 71 (1997) 2008.
- [3] A. M. Almeida, M. M. D. Ramos, R. M. Ribeiro, *Macromol. Symp.*, 181 (2002) 479.

- [4] A. M. Almeida, M. M. D. Ramos, H. G. Correia, *Comp. Mater. Sci.* 27 (2003) 128.
- [5] D. S. Wallace, A. M. Stoneham, W. Hayes, A. J. Fisher, A. H. Harker, *J. Phys. Condens. Matter* 3 (1991) 3879.
- [6] J. L. Brédas, *Adv Mater.*, 7 (1995) 263.
- [7] A. M. Almeida, M. M. D. Ramos, *Synth. Met.*, 122 (2001) 165.
- [8] M. M. D. Ramos, A. M. Almeida, *Vacuum*, 64 (2002) 99.
- [9] A. M. Stoneham, M. M. D. Ramos, A. M. Almeida, H. G. Correia, R. M. Ribeiro, H. Ness, A. J. Fisher, *J. Phys. Condens. Matter* 14 (2002) 9877.
- [10] A. M. Almeida, M. M. D. Ramos, H. G. Correia, *Comput. Mater. Sci.*, 27 (2003) 128.

Table 1: Ionisation potential (IP) and electron affinity (EA) of PPV, 2-CN-PPV and 7-CN-PPV

Polymer	Calculated		VEH [6]	
	IP (eV)	EA (eV)	IP (eV)	EA (eV)
PPV	8.63	0.41	5.05	2.73
2-CN-PPV	8.94	0.92	5.15	2.91
7-CN-PPV	8.88	1.00		

Table 2: Charge stored in carbon, hydrogen and nitrogen atoms of cyano-substituted PPV.

Polymer	Molecular charge	Charge (%)		
		Carbon atoms	Hydrogen atoms	Nitrogen atoms
2-CN-PPV	-1	28	51	21
	+1	50	37	13
	-2	40	43	17
	+2	63	27	10
7-CN-PPV	-1	52	31	17
	+1	65	30	5
	-2	39	33	28
	+2	55	34	11

List of figure captions:

Figure 1. Top view of the optimised molecular structure of PPV (a), 2-CN-PPV (b) and 7-CN-PPV (c) fragments with 16 repeat units and their monomers, calculated by self-consistent quantum chemistry molecular dynamics.

Figure 2. Changes in atomic charges for carbon, hydrogen and nitrogen atoms of 2-CN-PPV fragment caused the injection of electrons ($Q = -1$ and $Q = -2$) and holes ($Q = +1$ and $Q = +2$). The marks indicate the data points that were calculated explicitly, whilst the curves are simply a guide to the eye.

Figure 3. Calculated intra-molecular mobility as a function of electric field for PPV (top), 2-CN-PPV (bottom left) and 7-CN-PPV (bottom right) showing results for electrons (filled marks) and holes (empty marks). In all cases the molecules were 16 repeat units long.

Figure 1

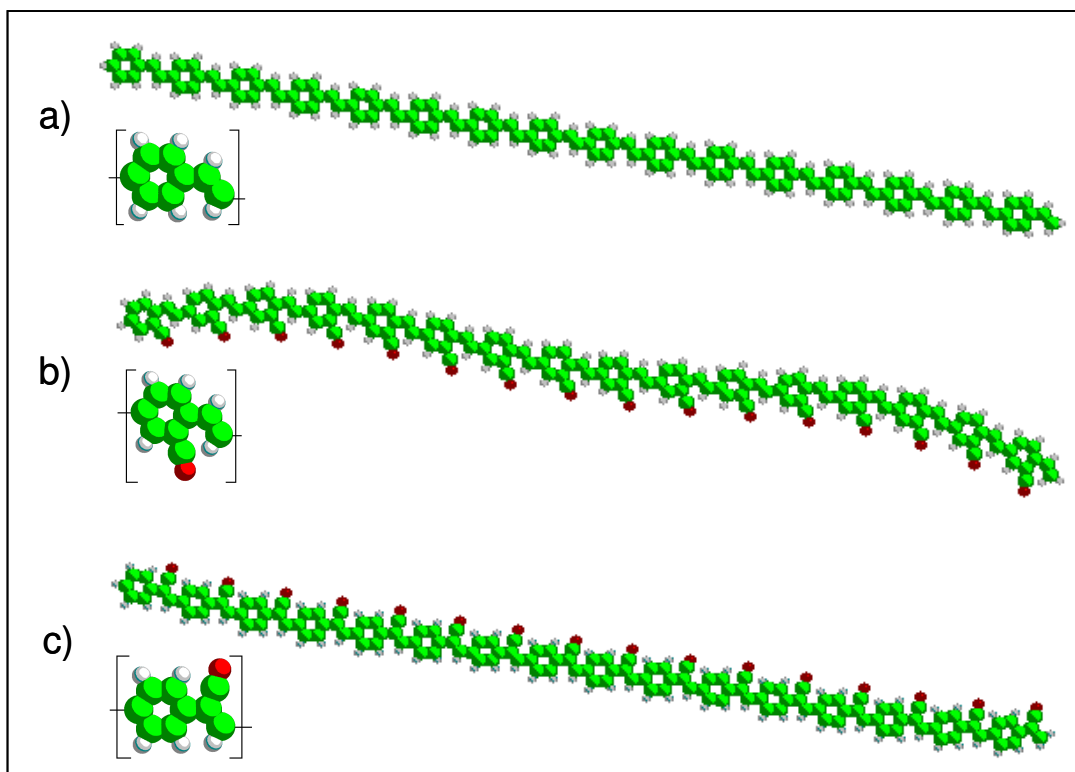


Figure 2

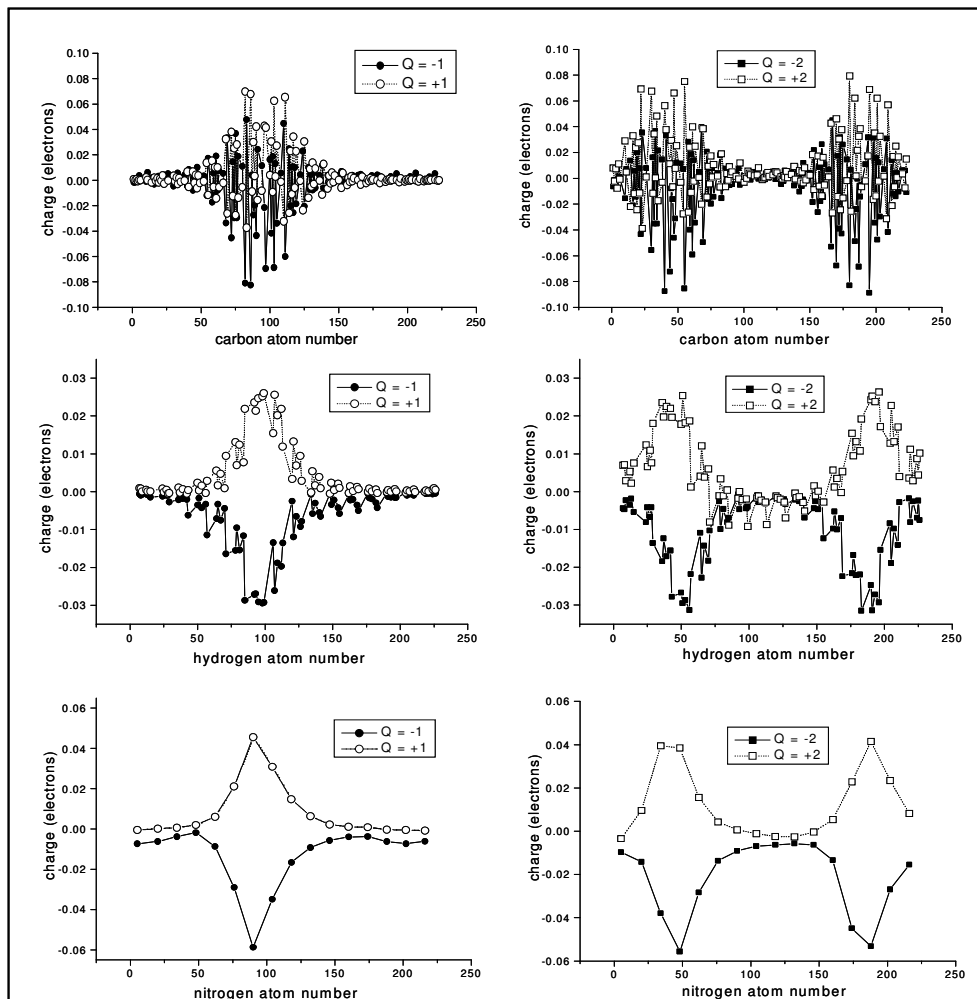


Figure 3

