

INTRA-MOLECULAR PROPERTIES OF DMeOPP_V STUDIED BY QUANTUM MOLECULAR DYNAMICS

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Abstract

Introducing methoxy electron donor groups into a poly(para-phenylene vinylene) (PPV) chain will lead to the appearance of unique electronic properties at the molecular scale which should affect the overall properties of light-emitting diodes based on these polymers.

Self-consistent quantum molecular dynamics calculations have been used to provide information on intra-molecular properties of poly(2,5-dimethoxy-para-phenylene vinylene) (DMeOPP_V), which are relevant for the modelling and characterization of polymer light-emitting diodes at nanometric length scale. We focus our attention in those properties that have been somewhat neglected in previous literature: the charge distribution associated with positive and negative charge carriers and their intra-molecular mobility when an electric field is applied.

Keywords: Quantum molecular dynamics modelling, intra-molecular charge mobility, DMeOPP_V.

1. Introduction

The performance of thin-film light-emitting diodes (LEDs) based on poly(*p*-phenylene-vinylene) (PPV) has experienced impressive improvements in recent years [1]. So far, much of the scientific effort has been directed to obtaining PPV derivatives and copolymers to be used in colour tunable light-emitting diodes. The efficiency of these polymer light-emitting diodes depends on molecular properties and chain arrangement. While there have been several

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studies on the effect of derivatization on the electronic structure of PPV [2], few systematic studies have been done on understanding changes in the intra-molecular properties when varying the applied electric field [3]. This lack is surprising since changes in the applied electric field can result in substantial changes in charge mobility of both PPV and its derivatives, which should affect the overall device efficiency.

In this paper we calculate the charge-induced defects resulting from injected electrons and holes into a poly(2,5-dimethoxy-*para*-phenylene-vinylene) (DMeOPPV) isolated chain with 16 monomer units and present results from dynamic simulations of charge transport in this polymer molecule as a function of the electric field strength along the polymer chain. We also present results from its static properties, such as the ionization potential and the electron affinity, in an attempt to understand the importance of these properties for the injection of both electrons and holes from the appropriated electrodes or from other molecules in the polymer layer of light-emitting diodes based on this material. Both results have implications for the performance of such devices and they should be considered in their model at mesoscopic scale [4].

2. Theoretical method

For conjugated polymers which are flexible and have strong electron-lattice interaction, methods combining molecular dynamics with self-consistent quantum mechanical methods need to be used. We have chosen to use the CNDO (Complete Neglect of Differential Overlap) method to perform the electronic structure calculations because it can handle polymer molecules of reasonable size, such as that considered in this paper, and it has been tested and validated in previous calculations with polyacetylene (PA) [5, 6], polydiacetylene (PDA) [5, 7], polythiophene (PT) [5], poly(*p*-phenylene-vinylene) (PPV) [8-10] and cyano-substituted PPV (CN-PPV) [3]. After the electronic structure calculations have been

performed, atomic forces are calculated as the negative derivatives of the total self-consistent energy and atomic trajectories are obtained by solving Newton's equation of motion. Details concerning the computational implementation of the approach described above in the CHEMOS code is given in references [5, 11].

3. Results and discussion

3.1. Static properties

In the course of calculating intra-molecular properties of DMeOPPV, we will concentrate on the properties of a planar and finite chain of DMeOPPV with 16 repeat units. Its optimised molecular structure, shown in figure 1, has a chain length of 0.665 nm per monomer unit. The injection of electrons and holes in this conjugated polymer chain leads to charge-induced defects (charge dressed with lattice distortion) in the polymer backbone of a polaron type, similar to those predicted for PPV [8, 9], which are accompanied by a change in its electronic structure.

The amount of charge stored on both methoxy electron-donor groups and PPV backbone is shown in Table 1 and the distribution of the injected charge per element is given in Table 2. Negative injected charge is mainly localised on PPV backbone due to electron-donor capabilities of methoxy groups. In contrast with CN-PPV [3], single injected charge (either negative or positive) is mainly localized on carbon atoms of DMeOPPV whereas double injected charges are mainly localized on the hydrogen atoms.

The changes in the charges localized on the methoxy atoms due to positive and negative charge injection is shown in figure 2. These results show five main features. First, there is charge stored in the atoms of all elements of the methoxy group. Second, the charge is mainly stored in the oxygen and the hydrogen atoms. Third, the charge stored in the oxygen atoms of the methoxy groups is localized on the same position as the charge stored in both carbon and hydrogen atoms of the PPV backbone (figure 3). The spreading of charge for the oxygen

atoms (approximately four monomer units) is similar to the width of the charge-induced distortion in the PPV backbone. Fourth, carbon atoms of the methoxy groups do not show charge alternation as the carbon atoms of the PPV backbone (figure 3). Fifth, the charge stored in both carbon and hydrogen atoms of methoxy groups is localized on the edges of the charge-induced defects in the PPV backbone.

The energy needed to remove an electron or add a hole to a neutral molecule (ionization potential, IP) and the energy gained on adding an electron or removing a hole from the same molecule (electron affinity, EA) were calculated from the following equations:

$$EA = \frac{E(N+1) - E(N)}{(N+1) - N}$$

(1)

$$IP = \frac{E(N-1) - E(N)}{(N-1) - N}$$

(2)

where $E(N)$ is the ground-state energy of a relaxed neutral DMeOPPV molecule with N electrons.

At the CNDO level of theory, the ionization potential of a DMeOPPV chain with 16 monomer units is calculated to decrease by 3.01 eV and the electron affinity to increase by 0.89 eV, when comparing to the PPV values for a chain of the same length [12]. These results are not in agreement with Brédas's calculations, using the Valence Effective Hamiltonian (VEH) method [2], which predict that methoxy substitution decreases both the ionization potential and the electron affinity with respect to PPV. However, the asymmetric change of ionization potential and electron affinity predicted by CNDO for DMeOPPV leads to a decrease in its bandgap, when comparing to the PPV value, which is in qualitative agreement with both experimental and VEH data [2].

The ionization potential and the electron affinity of a DMeOPPV molecule with 16 repeat units were calculated from equations (1) and (2) by examining the neutral as well as monopositive and mononegative ion ground-states. Since their binding energies are strongly dependent on the CNDO parameters and basis set used, the absolute value of the calculated ionization potential and the electron affinity for PPV [12] and DMeOPPV may not be correct. However, we expect the predicted trends for the changes in ionization potential and electron affinity of DMeOPPV relative to PPV to be reliable. From our results, it is clear that changes in both ionization potential and electron affinity should affect electron-injection and hole-injection processes in DMeOPPV chains, especially in those bound to the electrodes, which should have serious implications on the efficiency of light emitting diodes based on this PPV derivative.

3.2. Dynamic properties

In order to assess the influence of the external applied electric field on intra-molecular mobility of charge induced-defects in DMeOPPV, we have focused our attention on a DMeOPPV chain with 16 repeat units because it is sufficiently large to allow the monitorization of polaron-like transport along the chain.

The field-dependent charge (either electrons or holes) mobility along the DMeOPPV chain was obtained by calculating the injected charge velocity per unit applied electric field. The results obtained are shown in figure 4. The distortion velocity was also calculated as a function of the applied field. For small electric fields lower than a certain value, no charge mobility was predicted for both electrons and holes. When the applied field is just above this threshold value, the lattice distortion follows the injected electrons, and the polaron-like carriers move along the DMeOPPV chain with low mobility (approximately $0.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for a chain with one negative charged polaron and $0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for a chain with two isolated negative charged polarons). These results are in good agreement with the $0.42 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for

the mobility of the positive charge carriers along the fully conjugated MEH-PPV chain determined from pulsed radiolysis experiments [13]. For high electric fields, the lattice distortion responds slowly to the negative charge motion and a high mobility regime is reached because the charge carrier is now a free-electron. For positive injected charges only the high mobility regime is predicted as a result of free-hole transport along the DMeOPPV chain. Moreover, the dimethoxy substitution in PPV molecule increases the difference between the electric field thresholds needed to move positive and negative single carriers along the polymer molecule relative to PPV [12, 14]. Since the above results can affect bipolar charge transport in light-emitting diodes which use a copolymer of PPV and DMeOPPV as active layer [15], one should consider the effect of intra-molecular charge transport for the interpretation and understanding of the observed device characteristics.

4. Conclusions

In this work the authors have studied the static and dynamic intra-molecular properties of poly(2,5-dimethoxy-*para*-phenylene-vinylene) (DMeOPPV) concerning the injection of electrons and holes in this conjugated polymer chains and their mobility along the chain. Our results suggest that both electron and hole injection lead to charge-induced defects in the polymer backbone similar to those predicted for PPV and charge rearrangement amongst carbon and hydrogen atoms of the methoxy groups far from the defect site. The ionization potential is predicted to increase whereas the electron affinity decreases with respect to the PPV values for a chain of the same length. The asymmetric change in both ionization potential and electron affinity of individual chains should contribute to the bandgap decrease of DMeOPPV measured experimentally. Intra-molecular charge mobility in DMeOPPV is quite different from PPV due to the electron donor capabilities of the methoxy groups. Based on our results, we suggest free hole transport for applied electric fields above the threshold whereas

both free electron and negative polaron-like transport can be realized in these polymer chains by tuning the strength of the applied field.

These results should have influence on both injection and transport of bipolar charge in light emitting diodes with dimethoxy-substituted PPV layers as active components. Quantum molecular dynamics calculations, such as those reported here, are a useful tool for understanding the nature of charge carriers in these organic devices as well as for providing data for the mesoscopic modelling of DMeOPPv light emitting diodes, which is currently almost impossible to obtain experimentally.

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Table 1: Charge stored in methoxy groups and PPV backbone as a result of electron and hole injection into a dimethoxy-substituted PPV (DMeOPPV) chain with 16 repeat units.

Molecular charge	Charge (%)	
	Methoxy groups	PPV backbone
-1	29	71
+1	78	22
-2	19	81
+2	74	26

Table 2: Charge stored in carbon, hydrogen and nitrogen atoms of dimethoxy-substituted PPV (DMeOPPV) chain with 16 repeat units as a result of electron and hole injection.

Polymer chain	Molecular charge	Charge (%)		
		Carbon atoms	Hydrogen atoms	Oxygen atoms
DMeOPPV	-1	52	31	17
	+1	65	30	5
	-2	44	50	6
	+2	8	75	17

List of figure captions:

Figure 1. Top view of the optimised molecular structure of DMeOPPV chain with 16 repeat units, calculated by self-consistent quantum chemistry molecular dynamics at CNDO level.

Figure 2. Changes in atomic charges for carbon, hydrogen and oxygen atoms of the methoxy groups caused by the injection of electrons ($Q = -1$ and $Q = -2$) and holes ($Q = +1$ and $Q = +2$) DMeOPPV chain with 16 repeat units. The marks indicate the data points that were calculated explicitly, whilst the curves are simply a guide to the eye.

Figure 3. Changes in atomic charges for carbon and hydrogen atoms of the PPV backbone caused by the injection of electrons ($Q = -1$ and $Q = -2$) and holes ($Q = +1$ and $Q = +2$) in DMeOPPV chain with 16 repeat units. The marks indicate the data points that were calculated explicitly, whilst the curves are simply a guide to the eye.

Figure 4. Calculated intra-molecular mobility as a function of the applied electric field along the molecular axis for a DMeOPPV chain with 16 repeat units showing results for both negative (filled marks) and positive (empty marks) charge carriers.

Figure 1

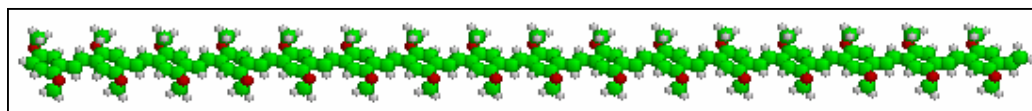


Figure 2

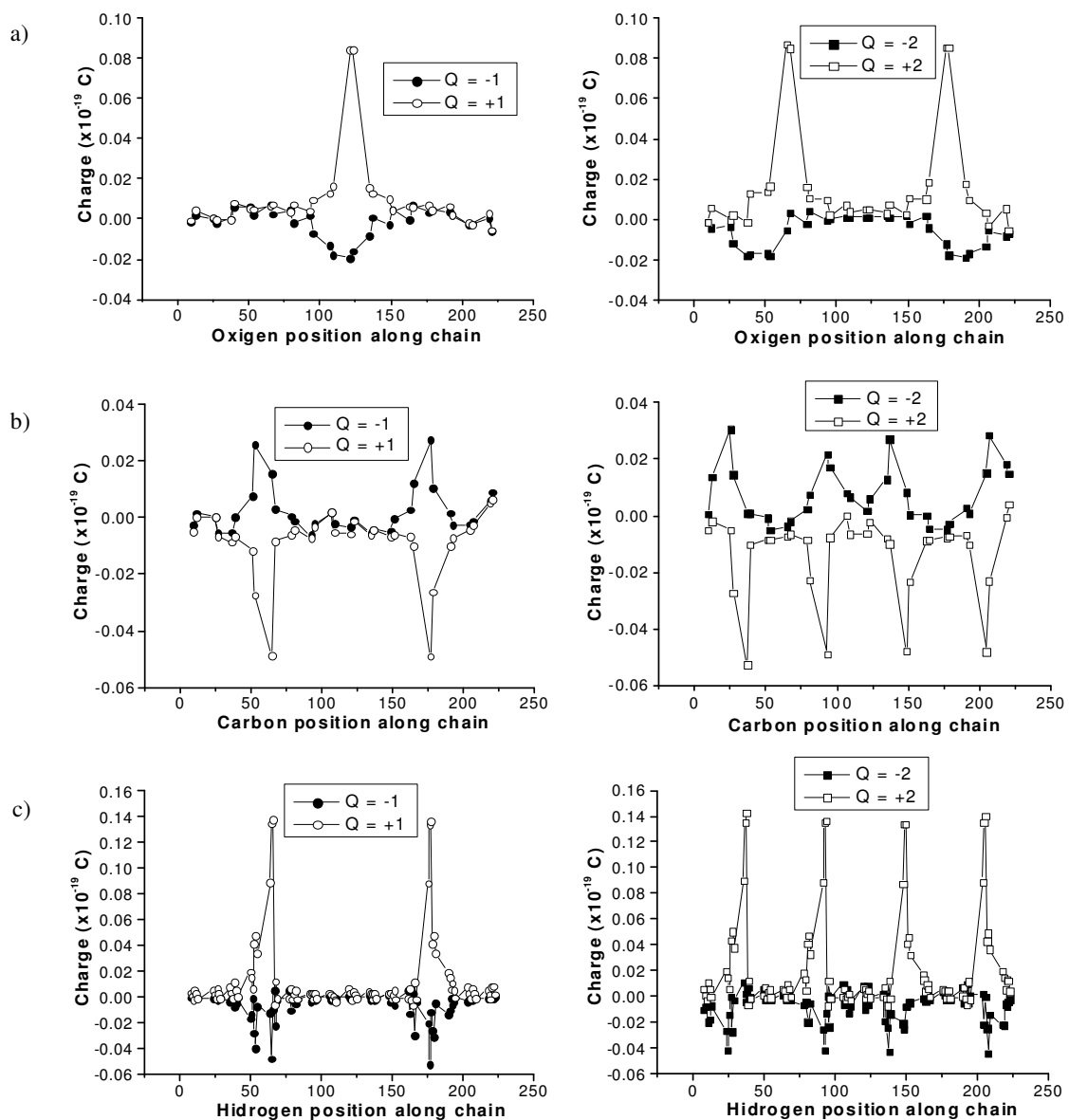


Figure 3

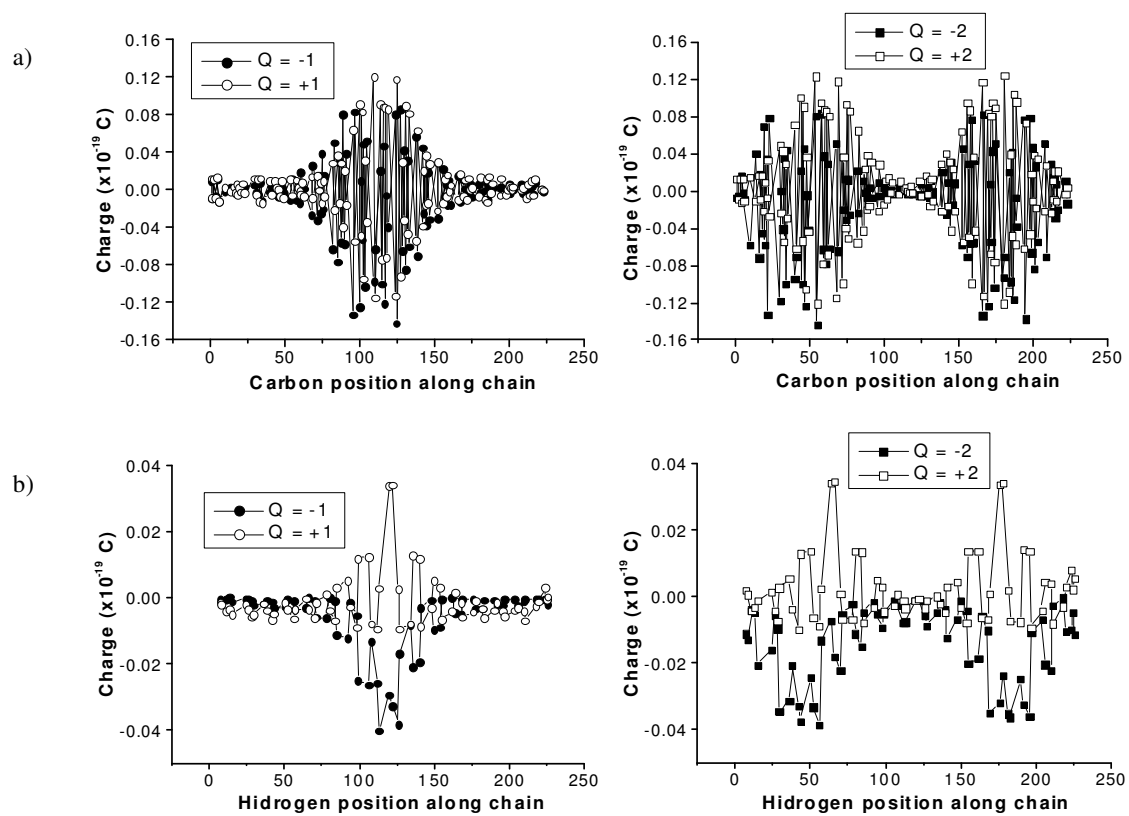


Figure 4

