

COMPUTATIONAL STUDY OF THE PRESENCE OF DEFECTS IN SEMICONDUCTING POLYMERS ON EXCITON FORMATION

Helena M. G. Correia¹, Hélder M. C. Barbosa¹, Marta M. D. Ramos^{1*}

¹Departamento de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

ABSTRACT

Although semiconducting polymers are very attractive to be used in optoelectronic devices due to their molecular structure, they are not pristine semiconductors. After deposition it is possible to find out several structural and chemical defects, with different origins, that strongly influence exciton dynamics since they create deep energetic sites, where excitons can migrate leading to their quenching or reducing exciton diffusion length. By using a self-consistent quantum molecular dynamics method we performed a computational study to understand the influence of well-known polymer defects on excitons dynamics. Our results show that these defects influences mainly intramolecular exciton localization and exciton energy.

Keywords: Quantum modelling, Singlet exciton, Triplet exciton, Exciton formation energy, Semiconductor polymer.

1. INTRODUCTION

During the past decade a great progress has been made in the understanding of optical properties of conjugated polymers [1]. Among these polymers, poly(p-phenylene vinylene) (PPV) has attracted a great deal of attention as an active material for photovoltaic cells, photo-detectors, electrically pumped lasers and light-emitting diodes (LEDs) [2]. For all these optical devices the efficiency depends on the exciton formation and exciton migration processes, among other factors.

The literature concerning the spectroscopic and photophysical behaviour of conjugated polymer systems clearly indicates that exciton formation processes in these materials are mainly intra-chain processes. Experimental results suggest that the optical properties of conjugated polymers are directly influenced by the presence of structural and chemical defects on the polymer network [3]. Therefore, the effect of these defects on the formation of both singlet and triplet intra-molecular excitons can be described on the basis of quantum mechanical calculations performed on isolated conjugated polymer segments of different size.

Since conjugated polymer systems, such as PPV, have strong electron-lattice interactions [4], there are doubts about the validity of the usual rigid lattice assumption on the conventional exciton formation theories to be applied to such systems [5], and so for understanding the effects of the presence of defects in polymer strands on exciton formation and their energies at molecular scale.

In this work we concentrate on the effect of structural and chemical defects on the formation of the lowest singlet and triplet excited states of isolated PPV strands, namely their effects on charge distribution, structural relaxation induced by exciton formation and exciton formation energy.

2. COMPUTATIONAL METHODS AND MODEL

Conjugated polymers are quite different from inorganic materials, since they are flexible and have strong electron-lattice interactions. Thus, exciton formation is expected to induce lattice distortions at molecular level which should affect the intra-molecular excitation processes.

Since the electronic and lattice motions influence each other, they must be treated self-consistently. To address these basic issues the theoretical approach we adopt combines a self-consistent quantum chemistry method with a molecular dynamics method [6]. After selecting a starting geometry for the polymer molecule, the electronic structure calculations

* marta@fisica.uminho.pt; phone +351253604330; fax +351 253 678 981

were performed using an approximate self-consistent-field molecular orbital method called CNDO (Complete Neglect of Differential Overlap) [7], which is a semi-empirical application of Hartree-Fock theory, until self-consistency in energy is achieved. Once the electronic problem has been solved, the gradients of the total self-consistent energy, evaluated at each atomic position, yield the atomic force and a molecular dynamical method is used to move the atoms during 1fs according to newtonian equations of motion. Both electronic structure calculations and atomic relaxation are repeated in parallel until a minimum energy is achieved for the polymer molecule.

The above approach has been used to study the behaviour of neutral PPV molecules with and without defects and lengths ranging from 3 to 11 monomers units, in their ground state and the lowest singlet and triplet states, and to obtain their intra-molecular properties, namely the fully relaxed molecular geometry, the electronic structure, the wave function and the Mulliken atomic charges (the net charge at each atom).

In order to study the distortion induced by exciton formation in PPV molecules with and without defects we define a dimerisation parameter, which represents the degree of dimerisation along the conjugated molecule, by:

$$d_n = \left| (b_{n,n+1} - b_{n-1,n}) \right| \quad (1)$$

Where $b_{n,n+1}$ is the bond length between carbon atoms n and $n + 1$.

In the calculations reported here, we use the CNDO parameters selected by Pople and Beveridge [7]. Besides, we treat spin polarisation by recourse to the unrestricted Hartree-Fock (UHF) method [7, 8], where the self-consistent-field (SCF) wave function is written as a single Slater determinant in which alpha and beta spin electrons are assigned to two independent sets of spatial orbitals. Moreover, each molecular orbital is expressed as a linear combination of atomic orbitals (LCAO) and a minimal basis set is used. The unrestricted Hartree-Fock wave function is not an eigenfunction of the total spin operator \hat{S}^2 . Thus, the UHF wave function of singlet (or triplet) exciton does not describe a pure singlet (or triplet) state, but has a mixture of other multiplicities [7, 8].

In the theoretical approach followed here, the lowest singlet and triplet excited states are obtained by promoting a single electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) from the ground state isolated PPV molecule with and without defects. Our approach goes beyond standard quantum chemistry analyses since it recognizes that exciton formation can induce lattice distortion and charge rearrangement among the polymer atoms, and it allows them to be included systematically and self-consistently in the electronic structure calculation of both singlet and triplet excitons.

3. RESULTS AND DISCUSSION

The ground state relaxed geometries and Mulliken atomic charge distribution of uncharged PPV strands with and without defects were found by examining molecules with the number of repeated units from 3 to 11, starting off straight planar molecules. Five different defective strands were considered in this work [9]. Figure 1 shows the relaxed geometries obtained for a PPV strand of seven repeated units long with and without defects and the position of the structural and chemical defects for the defective strands.

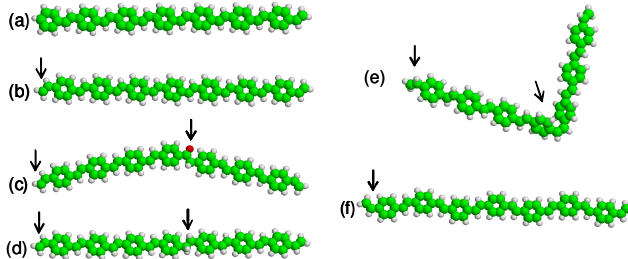


Figure 1. The ground state geometry of uncharged PPV strands with 7 repeated units long and with the following defects: (a) defect-free; (b) a vinyl termination end on the left-hand side; (c) a vinyl termination end on the left-hand side and the formation of a non-aromatic carbonyl group; (d) a vinyl termination end on the left-hand side and the saturation of a vinyl group with hydrogen; (e) a vinyl termination end on the left-hand side and a

configurational defect consisting of a change in the relative orientations of the phenyl groups; (f) a vinyl termination end on the left-hand side and a conformational defect consisting of an interruption in the 1D translational symmetry. The arrows indicate the position of the defects, which were chosen considering their importance reported in [9].

In order to study the effect of singlet and triplet exciton formation on the geometry of isolated PPV strands with and without defects depicted in Figure 1, we calculated the change in the dimerisation pattern, given by equation (1), of both singlet and triplet excitons relative to the ground-state chain. The results obtained for a PPV strand of 7 monomer units with and without defects are shown in Figure 2. For a defect-free PPV strand, the exciton formation induces distortion in the central region of the polymer backbone, as a result of changes in adjacent carbon-carbon bond lengths of the same region where distortion occurs. Although the distortion width induced by singlet and triplet exciton formation is similar for most of defective strands, their localization and amplitude is slightly different. Changing the termination end of the defect-free PPV strand does not seem to change the distortion induced by singlet and triplet exciton formation, compared to defect-free PPV strand. However, the formation of singlet and triplet excitons in PPV strands with the other structural and chemical defects, shown in Figure 1, leads to changes on the distortion localization, as well as changes on distortion width, amplitude and shape for the chemical defect associated with the presence of a non-aromatic carbonyl group.

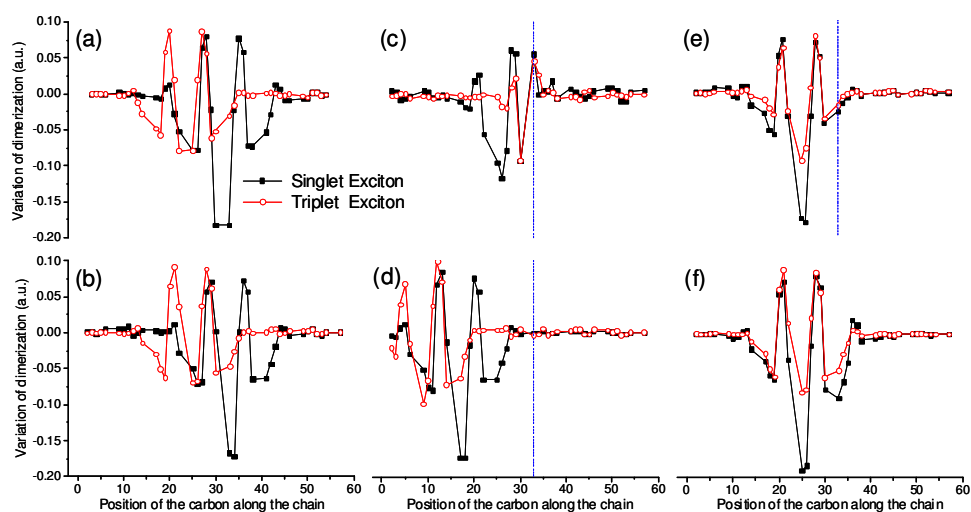


Figure 2. Change in the difference between adjacent carbon-carbon bond lengths along the backbone caused by the formation of a singlet and triplet exciton in the PPV strands depicted in Figure 1. The marks indicate the data points that were calculated explicitly, whilst the curves are simply a guide to the eye. The vertical broken lines indicate the position of the defect.

The distortion induced by singlet and triplet exciton formation in PPV strands with and without defects is accompanied by a charge rearrangement among the carbon atoms of the polymer backbone at the distortion site (see Figure 3). We notice that the structural and chemical defects do not change the nature of the distributed charge associated with singlet and triplet exciton formation, i.e. for triplet excitons there is a charge alternation on adjacent carbon atoms, whereas the formation of singlet exciton leads to dipole charge storage of on carbon atoms.

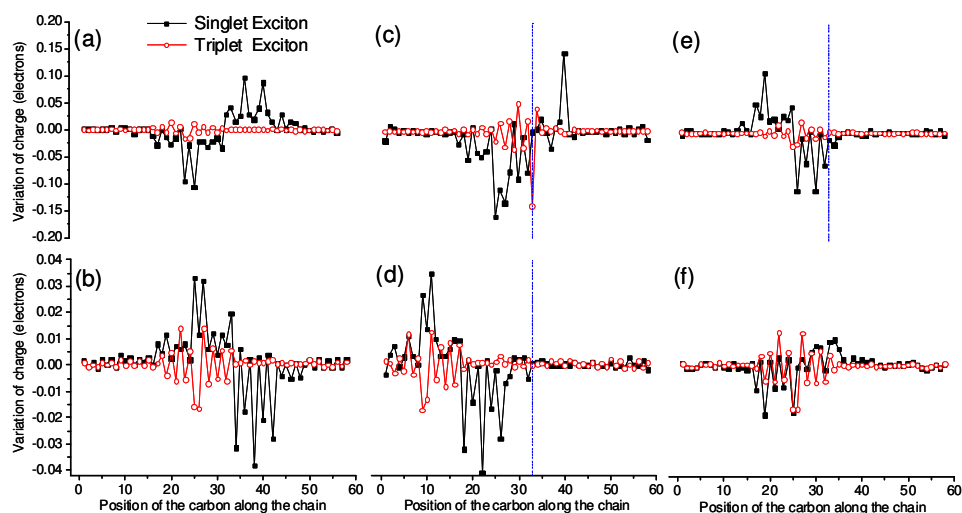


Figure 3. Changes in Mulliken charges for carbon atoms along the backbone of the PPV strands depicted in Figure 1 when a singlet and a triplet exciton is formed. The marks indicate the data points that were calculated explicitly, whilst the curves are simply a guide to the eye. The vertical broken lines indicate the position of the defect.

Since the difference in exciton energy between different strands of the polymer layer drives exciton migration within the polymer network, we must consider the effect of the structural and chemical defects on the singlet and triplet exciton energy formation of the PPV strands as a function of their length (measured in the number of monomer units). The singlet and triplet exciton energy formation (the energy needed to create a singlet and a triplet exciton from the neutral system on the ground-state) is calculated from the energy differences between the optimized geometry of neutral systems on their ground-state and lowest singlet and triplet excited state, respectively. Figure 4 shows the singlet and triplet exciton energy formation of PPV strands with different lengths and with the presence of the defects depicted in Figure 1.

Since the PPV strands, with and without defects, have positive singlet and triplet energy formation, a negative difference between the exciton formation energy of the defective PPV strand relative to the defect-free one signifies a potential trap for the exciton migration within the polymer network. Our results suggest that chemical defects linked with the presence of a vinyl termination end and a carbonyl group that are not part of the repeat unit that constitutes the backbone of the conjugated strand may act as traps for both singlet and triplet exciton migration regardless of the strand length, whereas the presence of a vinyl termination end and the saturation of the vinyl group with hydrogen is predicted to produce a shallow trap at longer strands only for singlet exciton migration. Among the defects considered in this work, the one containing a carbonyl group is predicted to be the deepest trap for exciton migration, the effect being more pronounced for triplet excitons. This result is in agreement with experimental ones that attribute to the presence of carbonyl group as a non-radiative relaxation channel for singlet excitons, and thereby quenching polymer luminescence [10, 11]. The presence of configurational defects does not seem to affect significantly both singlet and triplet exciton migration in PPV.

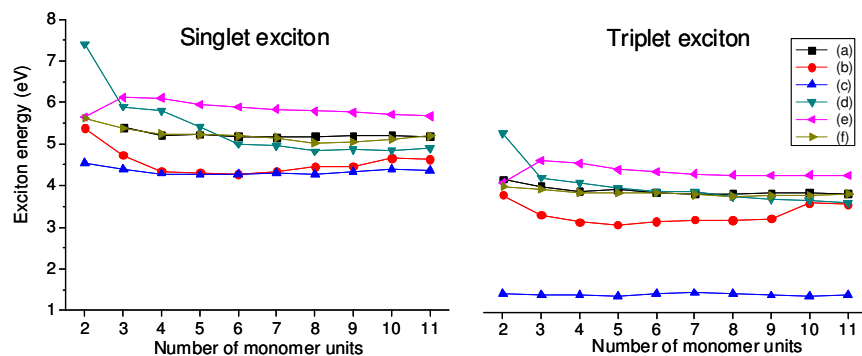


Figure 4. The energy of singlet and triplet excitons in PPV strands with variable length (measured in the number of repeat units) without (a) and with ((b) to (f)) defects shown in Figure 1. The lines through the calculated points are just a guide to the eye.

We should note that the calculated singlet and triplet exciton formation energies are strongly dependent on the CNDO parameters used and on the basis set of atomic orbitals used to construct the wave function; also, the CNDO approximations are too extreme to give a proper account of the spin polarisation contribution to the unpaired electron distribution in the molecule. Therefore, the absolute value of calculated singlet and triplet exciton formation energy may not be correct, but we expect the predicted trends for the effect of structural and chemical defects to be reliable since the errors on the calculated energies are systematic.

Nevertheless, results of these investigations are expected to increase our knowledge of the effects of structural and chemical defects on intra-molecular exciton formation in PPV, as well as to provide information at molecular scale which is hard to obtain directly from the experiments and are very important to be included in the modelling of optoelectronic devices based on PPV at mesoscopic scale.

4. CONCLUSION

The excitation between the ground state and the lowest excited singlet and triplet states induces localized geometric relaxation and charge rearrangement among the carbon atoms within the distorted region for both defective and defect-free PPV strands. The charge rearrangements for the carbon atoms have opposite sign across the distortion region in the case of singlet exciton and a charge alternation within the distortion region is predicted for triplet exciton.

The presence of structural and chemical defects does not seem to change the nature of the formed intra-molecular excitons, but mainly the exciton induced-distortion localization on the polymer backbone and exciton energy formation. The defects associated with the change in the termination chain and the presence of a carbonyl bond are predicted to create energetic sites that work like trap for exciton diffusion in PPV, the effect being more pronounced for triplet exciton migration localized on oxygen-related defective strands.

Since the efficiency of PPV-based solar cells and light emitting diodes is mainly determined by singlet exciton formation, the effect of these defects on the decreasing number of migration events within the polymer layer can affect device efficiency differently for both applications.

KNOWLEDGEMEN

We are indebted to the Portuguese Foundation for Science and Technology (FCT) for financial support under the contract CONC-REEQ/443/EEI/2005. One of us (H.M.G.C.) is also indebted to FCT for financial support under the post-doctoral grant no. SFRH/BPD/64554/2009.

REFERENCES

- [1] Scheblykin, I. G., Yartsev, A., Pullerits, T. *et al.*, "Excited state and charge photogeneration dynamics in conjugated polymers," *Journal of Physical Chemistry B*, 111(23), 6303 (2007).
- [2] [Handbook of conducting polymers] Marcel Dekker, New York(1997).
- [3] Bäessler, H., [Primary photo excitations in conjugated polymers: Molecular exciton versus Band Model] World Scientific, Singapore(1997).
- [4] Ramos, M. M. D., and Almeida, A. M., "Charge-induced defects in poly-phenylene-vinylene (PPV)," *Vacuum*, 64(2), 99 (2001).
- [5] Beljonne, D., Cornil, J., Silbey, R. *et al.*, "Interchain interactions in conjugated materials: The exciton model versus the supermolecular approach," *Journal of Chemical Physics*, 112(10), 4749 (2000).
- [6] Wallace, D. S., Stoneham, A. M., Hayes, W. *et al.*, "Theory of Defects in Conducting Polymers .1. Theoretical Principles and Simple Applications," *Journal of Physics-Condensed Matter*, 3(22), 3879 (1991).
- [7] Pople, J. A., and Beveridge, D. L., [Approximate Molecular Orbital Theory] McGraw-Hill, New York(1970).
- [8] Murrell, J. N., and Harget, A. J., [Semi-empirical self-consistent-field molecular orbital theory of molecules] Wiley-Interscience., London(1972).
- [9] Pope, M., and Swenberg, C. E., [Electronic processes in inorganic crystals and polymers] Oxford University Press, (1999).
- [10] Hale, G. D., Jackson, J. B., Shmakova, O. E. *et al.*, "Enhancing the active lifetime of luminescent semiconducting polymers via doping with metal nanoshells," *Applied Physics Letters*, 78(11), 1502 (2001).
- [11] Lim, Y. T., Lee, T. W., Lee, H. C. *et al.*, "Impediment of photo-oxidation in PPV nanocomposites doped by metal-coated silica nanoparticles," *Synthetic Metals*, 128(2), 133 (2002).