Modeling Polymer/Fullerene Heterojunctions: A Case Study for the Interfaces PTPD3T/ PCBM and PBTI3T/PCBM

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INTRODUCTION

Due to increased energy demand, one of the great current global problems is to promote the generation of energy to supply the industrial sector, the higher energy consumer. Each year it needs more and more energy to increase production and maintain the current supplies. However, in the current social conjuncture, humankind faces a dilemma: how to continue development, minimizing damage to the environment? This fact takes greater proportions when you consider that the traditional sources of energy resources, such as minerals, organic compounds and water resources are limited and exhaustible. In this sense, science seeks the development and improvement of alternative means of power generation, we can emphasize mainly the use of solar energy based on photovoltaic effect - conversion of sunlight into electrical energy - which is characterized by being a clean and sustainable energy source[1].

In recent decades, studies related to the construction of organic solar cells (OSCs) have gained prominence, because they combine very important features for the productive sector: the low environmental impact and the potential of cost-effectiveness that can lead to the development and overcoming model inorganic cells. The photon absorption mechanism in organic compounds leads to the formation of the exciton, a bonded pair of electron-hole that is electrically neutral, due to the strong electron-lattice interaction. Due to this reason, the optical absorption in organic materials does not lead directly to free electrons and holes carries to generate electric current, first the exciton must be dissociated, which is why the charge transport mechanism in heterojunction donor-acceptor polymer (D-A) [2]. Studies to investigate the exciton dissociation modes are crucial to describe the principles of operation of OSCs.

In this work, using an ideal organic system of isolated molecules (model dimer), computational methods of molecular dynamics and DFT were applied on it, being possible to characterize the molecular structures, energy band gaps, and charge separation states. Furthermore, understanding the excitonic character by analyzing the electric dipole properties is crucial to establish new ways to study the exciton dissociation[3-6]. Such characteristics can serve as a guidance for further studies aimed at increasing the energy conversion efficiency of the photovoltaic effect applied on OSCs.

METHODS

Model dimers of increasing complexity have been considered. However, the starting point of the computational simulation methods presents an ideal configuration of a D-A interface compounded by PTPD3T and PBTI3T molecules and a tailed C_{60} and C_{70} (PCBM) to investigate the energy variations in a less degree of details. The polymers were submitted to validation tests of the force-field. Molecular dynamics calculations were performed on Materials Studio.

In a second moment, using Gaussian, the induced molecular dipole momentum was evaluated in isolated systems of the polymers appraise the levels of theory by quantum-chemical calculations using DFT method (B3LYP functional). The same procedure was applied on the tailed C_{60} and C_{70}.

RESULTS AND DISCUSSION

Experimental results show that the π-stacking phenomenon occurs in regions formed by similar structures to those studied polymers[7]. First, two isolated polymer systems (PTPD3T and PBTI3T) were built. Figure 1 provides a view them in two thin films. The structures were submitted to geometry optimization procedures (parameters).

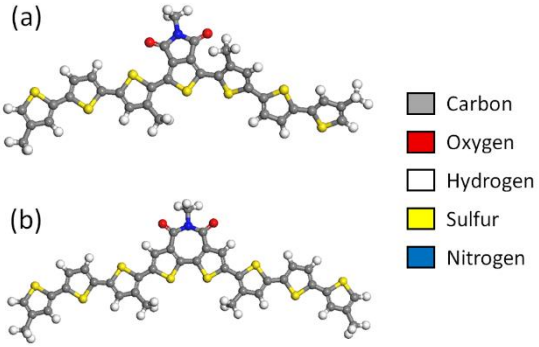

Figure 1 – Polymers PTPD3T (a) and PTBI3T (b).

For purposes of force field and model validation, a micro-region of PTBD3T polymer was constructed. It is formed by two sheets of the polymer which were submitted to molecular dynamics for a time of 30ns using the Universal force-field. From the results of molecular dynamics, the two layers remain connected by a long-range interaction between them. This fact is relevant, because it validates the use of the system and the force-field, showing that the π-stacking phenomenon also occurs process simulation. Figure 2 refers to the last snapshot of the molecular dynamics method and model validation.

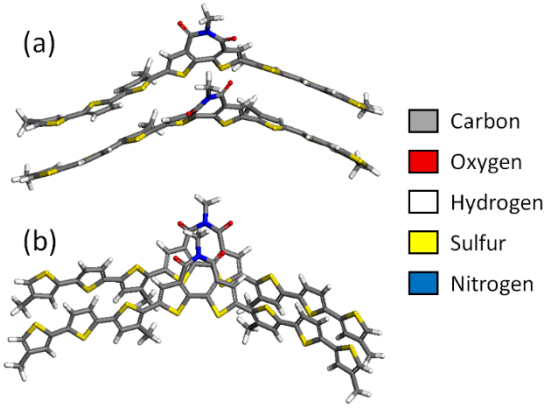

Figure 2 – Different views of the micro-regions Pentacenes after the molecular dynamics process.

After this validation, two other structures were also constructed, PC60BM and PC70BM, which can be seen in Figure 3. They also were submitted to geometry optimization processes. In the four raised structures, computer calculations and simulations were performed in the DFT (using B3LYP functional) that allowed obtaining the dipole moments of each unit, which are shown in Table 1.

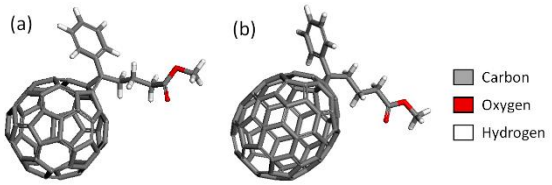

Figure 3 – PC60BM (a) and PC70BM (b) structures.

Structure	Dipole Moment		
	μ_x	μ_y	μ_z
PTPD3T	-0.5987251	1.1092229	-0.2560705
PTBI3T	-0.0072081	2.5723123	0.187208
PC60BM	1.3026876	0.2402921	-0.0795589
PC70BM	1.1435207	1.3755452	1.0676037

Table 1 – Dipole Moments for the structures after DFT calculations.

CONCLUSIONS

For a first study, the computational procedures and methods used showed results consistent with empirical observations. Knowing the molecular behaviors separately contribute to a future analysis of a D-A system, when polymers are interacting with PCBM.

For future works, the PCBM molecules can be set to float on a parallel plane to the surface of polymers. Variations in the magnitude and direction of the induced dipole moment can be evaluated. To characterize the electronic structure of the molecules at the interfaces performing quantum–chemical calculations on small- and medium-size system. Also, it is possible to evaluate some properties to analyze the interface dipole, the Millikan net charge and the levels of energy of the molecular orbitals.

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