



Charge Transfer States in a polymer/fullerene photovoltaic interface: a Density Functional Theory study.

C. F.N. Marchiori⁽¹⁾, M. Koehler^{(1)*}

(1) Departamento de Física, Universidade Federal do Paraná, e-mail: koehler@fisica.ufpr.br

* Corresponding author.

- Abstract** – We study the electronic structure of the P3HT/fullerene supramolecule using density functional theory calculations. This simulations show that the mix of the polymer and fullerene wavefunctions give rise to a set of intragap charge transfer (CT) states at the polymer/fullerene interface. These overlap of wavefunctions produces a considerable charge transfer in the ground state. We find that an efficient exciton dissociation is possible because the CT states are energetically favorable intermediary levels for the electron transfer from the polymer to the fullerene and block the hole transfer, keeping the hole confined in the polymer chain next to the P3HT/fullerene system.

Organic photovoltaic devices based on a blend system consisting of a conjugated polymer acting as electron donor and fullerene molecules as acceptors have attracted the attention of the scientific community due to the efficient electron-hole pair dissociation at the heterojunction. At this interface the charge dissociation process takes place in the femtosecond time scale resulting in an efficient quenching of the polymer photoluminescence [1]. After dissociation, a geminated pair with the electron localized at the acceptor molecule and the hole localized at the polymer is formed. In spite of the low dielectric constant of organic materials, the probability of geminate pair separation into free charge carriers at the polymer/fullerene interface is close to 100% [2]. A sound explanation proposes the formation of an interfacial dipole at the donor/acceptor interface [2, 3] (pointing from the acceptor molecule to the donor molecule) which creates a potential well that confines the on-chain hole and a repulsive barrier that assist the pair separation. However, although there is experimental evidence that a dipole layer can be formed at polymer/acceptor interface, previous ab initio calculations found very little charge transfer from the poly-3-hexylthiophene (P3HT) to C60 in ground state. Some other aspects about the geminate pair separation remain poorly understood. Is not clear if the geminate pairs are bounded by a Coulomb potential or if there is a ground-state interaction where the polymer/fullerene wavefunctions overlap [4, 5] resulting in a set of intragap states at the interface known as charge-transfer states [6]. This states should make the photoinduced charge separation process to involve one or more intermediary steps for the electron transfer from the photoexcited polymer to the acceptor molecule. Furthermore, the excitation of the charge-transfer (CT) states using below-gap photon energies can instantaneously generate localized charge carriers in the polymer chain or in the fullerene molecule, without involving intrachain excitons. Recently a variety of optoelectronic techniques have provided strong experimental evidence of the presence of CT states in polymer/fullerene blends. The main features of the CT states and their relation with the dipole layer at polymer/fullerene interface remain little explored theoretically. In this work we study the electronic structure of the P3HT/C60 supramolecular system using Density Functional Theory (DFT) calculations in order to understand the energy levels alignment in this supramolecule providing useful insights to improve the efficiency of organic photovoltaic cells. We find that the overlap of the polymer and fullerene wavefunctions gives rise to a set of intragap CT states at the heterojunction interface. Due to this mix of wavefunctions, there is a considerable spontaneous charge transfer between the polymer and the C60 which creates a dipole across the polymer/C60 supramolecule. Finally we show that the CT states are favorable intermediary levels for electron transfer from the P3HT to the C60 but they simultaneously give rise to a barrier that confines the hole in the polymer chain next to the P3HT/C60 system. As a consequence, the spatial separation of the electrostatically bound electron-hole pair increases, enhancing the possibility of an efficient dissociation at the heterojunction upon the application of an external electric field.

References

- [1] M. Hallermann, S. Haneder, E. Da Como, *App. Phys. Lett.* 93 (2008) 053307.
- [2] V.I. Arkhipov, P. Heremans, and H. Bässler, *Appl. Phys. Lett.* 82 (2005) 4605.
- [3] M. Koehler, M.C. Santos, and M. G. E. da Luz, *J. App. Phys.* 99 (2006) 053702.
- [4] H. Vazquez, W. Gao, F. Flores, and A. Kahn, *Phys. Rev. B* 71 (2005) 041306(R).
- [5] H. Vazquez, F. Flores, and A. Kahn, *Org. Electron.* 8 (2007) 241.
- [6] M. Hallermann, S. Haneder, E. Da Como, *App. Phys. Lett.* 93 (2008) 053307.