BAND-ALIGNMENT ENGINEERING OF ORGANIC PHOTOVOLTAIC MATERIALS

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Organic solar cells have attracted a great deal of interest for their foreseen possibility of producing low-cost energy from light. Devices with power conversion efficiency near 5% have been reported in the literature [1]. Although the actual market for solar cell is dominated by polycrystalline silicon based devices, the use of highly efficient organic materials will become significant once the 10% power conversion efficiency mark is reached. One of the approaches to reach the 10% power conversion efficiency is to increase the charge carrier mobility. Indeed, the structural organization in organic materials for field effect transistors has been demonstrated to play a significant role in carrier mobility [2-4]. However, more efforts are needed to understand such structural effects in donor-acceptor blends used in high performance organic photovoltaic devices.

The present paper is a computational study on the structural and electronic properties of regioregular head-to-tail poly(3-hexylthiophene-2,5-diyl) (rrP3HT). We have also investigated a promising donor-acceptor blend composed of buckminsterfullerene (C_{60}) for acceptor and rrP3HT for donor. The rrP3HT polymer has been chosen for its tendency to self-assemble into microcrystalline domains, for its good mobility (up to 0.1 cm^2/Vs [2]) and processability. First principles DFT calculations were performed using the SIESTA software package [5] within local density approximation (LDA) and periodic boundary conditions. Norm-conserving Troullier-Martins pseudopotentials were used with a linear combination of numerical atomic orbitals basis set. Molecular geometries were fully optimized following a Broyden algorithm on the DFT calculated forces and stresses. The different parameters defining the pseudopotentials and basis set were validated by comparing the optimized molecular geometry and known calculated band structure of isolated polythiophene (PT) chains [6-7].

The structural and electronic properties of rrP3HT crystal were thoroughly investigated in order to be used as reference for the donor-acceptor blend. Multiple configurations of rrP3HT crystal were considered to find the most stable configuration (Fig. 1) which compares favorably to the structure observed experimentally [8-10]. Analysis of the wavefunctions symmetry was used to unfold the band structure and to determine the bandwidths. An increasing dispersion of the HOMO and LUMO bands and a reduction of the band gap energy are observed when a pressure in the π-stacking direction is applied to the system (Fig. 1).

Bulk donor-acceptor heterojunctions were studied by introducing C_{60} into the rrP3HT network. The insertion of C_{60} reduces the bandwidth of the polymer states in the π-stacking and the backbone directions. The nature of the HOMO in the blend is similar to the HOMO in the rrP3HT crystal but with some electron delocalization over the C_{60}s, while the LUMO is strongly localized on the C_{60} (Fig. 2). The results obtained clearly indicate that the structural order between the two phases in the donor-acceptor bulk heterojunction strongly influences the resulting electronic properties. These results for the donor-acceptor blend, along with those for the rrP3HT network,

suggest that their electronic properties can be tuned by engineering the material structure properties. Indeed, the displacement of the band levels with structural organization calculated for these materials can be used to optimize the band alignment in the organic photovoltaic device.

References:

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Figures:

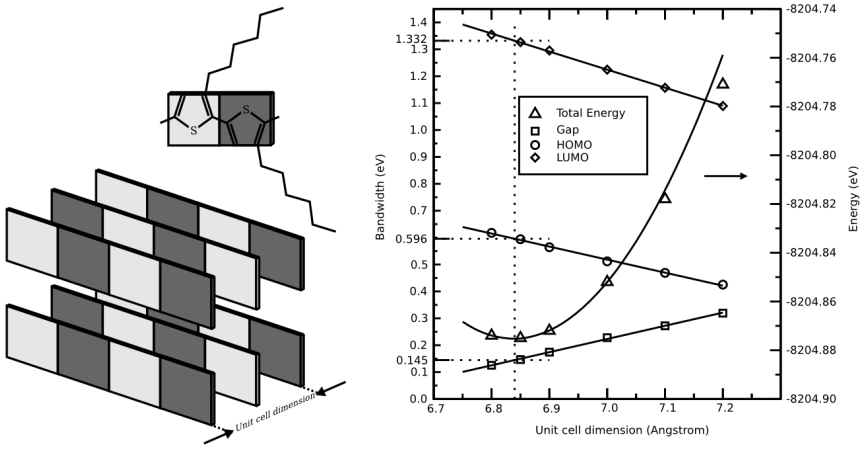

FIG. 1 – Left : Schematic optimal configuration of rrP3HT crystal. Right : Graph of the influence of the unit cell dimension on different electronic properties of the rrP3HT crystal.

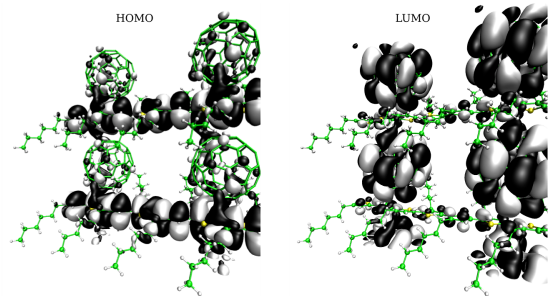

FIG. 2 – HOMO (left) and LUMO (right) wavefunctions of a rrP3HT/C_{60} bulk heterojunction.