Electronic Properties of Organic Photovoltaic rr-P3HT/C_{60} Ordered Blend

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The need for clean and renewable energy sources has recently promoted research on organic photovoltaic cells (OPCs) to reduce the cost of solar energy by exploiting the large-scale and low-cost fabrication techniques associated with polymers. Photon absorption, occurring in an electron donor material, creates excitons which are dissociated into free charge carriers when encountering an interface with an electron acceptor material. Bulk heterojunctions of donor and acceptor are used to reduce exciton recombination in the donor and to achieve power conversion efficiencies up to 5% [1,2]. However, the efficiency of OPCs has to reach 10% before they can be competitive in the solar cell market which is currently dominated by polycrystalline silicon [3]. One possible way to achieve such target is through the engineering of the donor-acceptor structure, which requires a better fundamental understanding of the physical processes taking place in these organic systems.

A computational study on a promising donor-acceptor system is performed to investigate the influence of structural order within the blend on the resulting electronic properties. The donor is regioregular head-to-tail poly(3-hexylthiophene-2,5-diyl) (rrP3HT), which self-assemble into microcrystalline domains [4] of high charge carrier mobility [5], while the acceptor is buckminsterfullerene (C_{60}), allowing an ultrafast charge transfer between the donor and the acceptor [1]. First principles DFT computations were performed with SIESTA [6] within the local density approximation (LDA) using periodic boundary conditions, norm-conserving Troullier-Martins pseudopotentials and linear combination of numerical atomic orbitals basis sets. The molecular geometries were optimized using the DFT calculated forces and stresses in a quasi-Newton method following the Broyden-Fletcher-Goldfarb-Shanno (BFGS) procedure to update the Hessian matrix. The optimization was stopped when the maximum force in the system was less than 10^{-2} eV/Å and the total energy variation between two iterations was less than 5×10^{-4} eV.

Bulk donor-acceptor heterojunctions were studied by diluting a rrP3HT crystal network by C_{60}s. The geometric and electronic properties of the rrP3HT crystal used as reference were obtained in previous work [7]. Multiple configurations with various positions and orientations of the C_{60}s (Fig. 1(A)) were optimized as a function of distance between the C_{60}s and the rrP3HT chains (Fig. 1(B)). The first configuration, where the C_{60} pentagonal face is between two hexylthiophene monomers, is slightly more stable than the second and third configurations. The inclusion of C_{60}s in the rrP3HT crystal also reduces the HOMO bandwidth in the π-stacking and backbone direction compared to the rrP3HT crystal by respectively annihilating the interchain π-π coupling, and by lifting the degeneracies at the Brillouin zone edge. The LUMO of the heterojunction is formed of one of the C_{60} triply degenerated states and exhibits very small dispersion. The HOMO wavefunction is similar to the HOMO of the rrP3HT crystal, while the LUMO is strongly localized on the C_{60} (Fig. 1(C)).

The influence of the distance between the C_{60}s and the rrP3HT chains in the π-stacking direction on the band structure was also studied (Fig. 1(D)). An increased pressure, reducing this distance,

causes a small decrease of the HOMO bandwidth in both the π-stacking and backbone directions, while it causes a small increase of the LUMO bandwidth in these two directions. Furthermore, the increased pressure stabilizes in energy the HOMO and destabilizes the LUMO, resulting in a marked augmentation of the bandgap. Finally, the number of rrP3HT chains between C_{60}s in the π-stacking direction was varied. Adding rrP3HT chains in the heterojunction pushes the LUMO band down and reduces the bandgap.

The results discussed above were obtained in the ground state picture. The next step in our study is to use time-dependent DFT to compute the excited states of these systems. These excited states should include an electronic bridging state overlapping the rrP3HT and the C_{60} [8]. Nevertheless, the results presented here clearly reveal that the positions of the band levels can be modulated by pressure or by the dilution degree of C_{60}s in the rrP3HT crystal network. This important observation will lead to the engineering of the band alignment of future OPCs to optimize their power conversion efficiencies.

References:

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Figures:

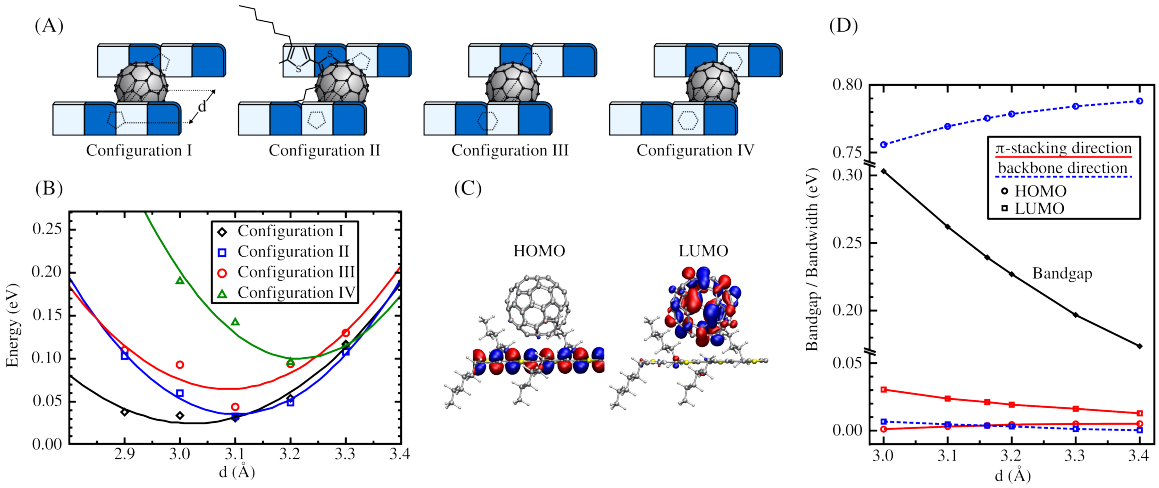

FIG. 1 – (A) Considered configurations of donor-acceptor bulk heterojunctions. (B) Total energy of the configurations as a function of distance between the C_{60}s and the rrP3HT chains. (C) HOMO and LUMO wavefunctions. (D) Variation of the band structure properties as a function of distance between the C_{60}s and the rrP3HT chains.