Supporting Information

Structural Variability of the P3HT/PCBM Interface and Its Effects on the Electronic Structure and the Charge-Transfer Rates

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1. Details of the classical MD simulation

The simulated system consists of 160 PCBM molecules forming a side-on interface with a crystalline phase of type-I P3HT containing 24 chains, each consisting of 20 thiophene rings, arranged into four layers of six chains with side chains fully extended and non-interdigitated (as in the most stable polymorph of the polyalkylthiophenes).[1] The spacing between chains in the same layer (π-π stacking distance) was initially taken to be 3.82 Å and the spacing between P3HT layers was 16.2 Å. The initial configuration of the PCBM system was taken as a monoclinic crystal, with parameters a = 13.76 Å, b = 16.63 Å, c = 19.08 Å, and β = 105.3°, from the experimental (low-temperature) crystal structure.[2] For P3HT intra and intermolecular interactions were described using the recently published force field of Moreno *et al*[3]. PCBM was described using the force field used in a previous paper.[4] Initial systems of P3HT and PCBM were equilibrated separately by 1 ns of an NVT simulation at 100 K, followed by a 1 ns NPT runs at both 100 K and 300 K, respectively. The equilibrated PCBM system was taken and resized to obtain a cross-sectional area identical to that of the P3HT system. The PCBM molecules were aligned with the crystalline P3HT such that the PCBM sidechains lay parallel to the P3HT interface (Figure S1). The two systems were combined whilst leaving a gap of 3-4 Å between the P3HT and PCBM and the energy minimized followed by a 0.5 ns NVT run at 100 K. Following this an NPT run was performed at 100 K (0.5 ns). The systems were studied using constant NPT-MD simulations at 300 K and a pressure of 1 atm (temperature and pressure were controlled using a Nosé-Hoover thermostat and (anisotropic) barostat, with relaxation times of 0.2 and 1.0 ps, respectively). The equations of motion were integrated using a velocity-Verlet algorithm with a time-step of 1 fs. Simulations consisted of 5-10 ns of equilibration and 10 ns of data gathering. Long-range electrostatics were computed using a particle-particle particle-mesh (PPPM) sum. Non-bonded interactions were truncated with a cutoff of 12 Å. All simulations were performed using the LAMMPS simulation package.[5]

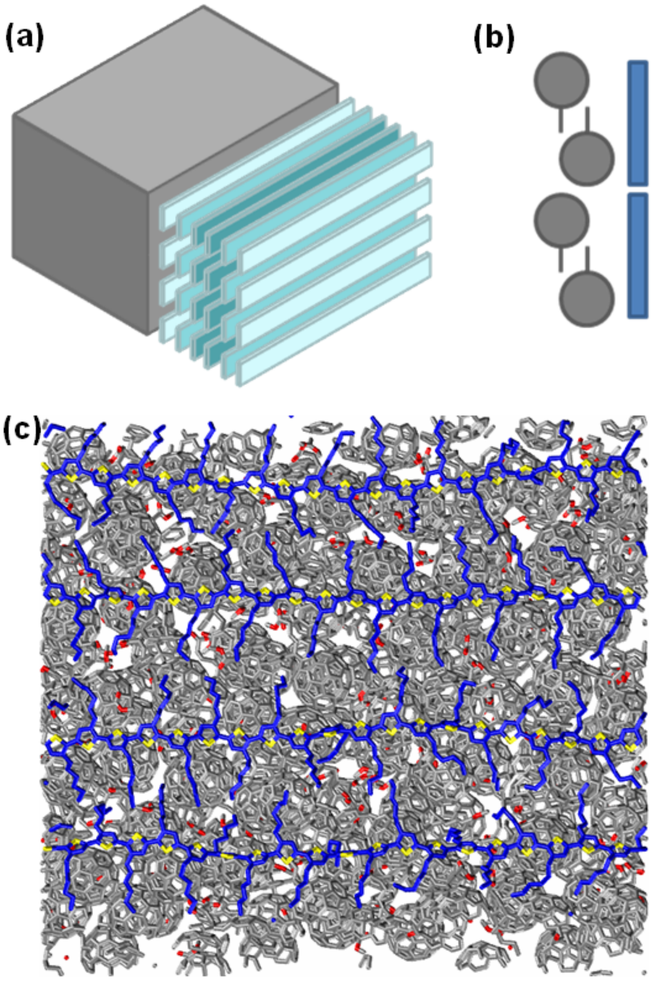

Figure S1 (a) Schematics of the simulated system containing a region of amorphous PCBM, denoted in grey, and a crystalline P3HT region, with the individual polymer chains denoted in blue. (b) Scheme of the parallel orientation of the PCBM sidechains orientation parallel to the interface. (c) Top view of the P3HT/PCBM interface where only the first P3HT layer is represented.

2. Geometries of Group 1 and Group 2 donor-acceptor pair

The 9 donor-acceptor pairs whose results are given in Figure 4 are illustrated in Figure S2 with the same numbering scheme used in the manuscript. These nine geometries are divided into two groups Group 1 (charge separated state) and Group 2 (charge-bridging states). Graphical inspection of the corresponding P3MT conformation (Figure S3) suggests that the geometries in Group 2 are more planar than those in Group 1. We computed the average (absolute value) of five dihedral angles between two neighboring thiophene rings quantitatively and found that this dihedral angles are larger than 26° for Group 1 (charge separated states) and smaller than 24° for Group 2 (charge-bridging states) (Figure 4d).

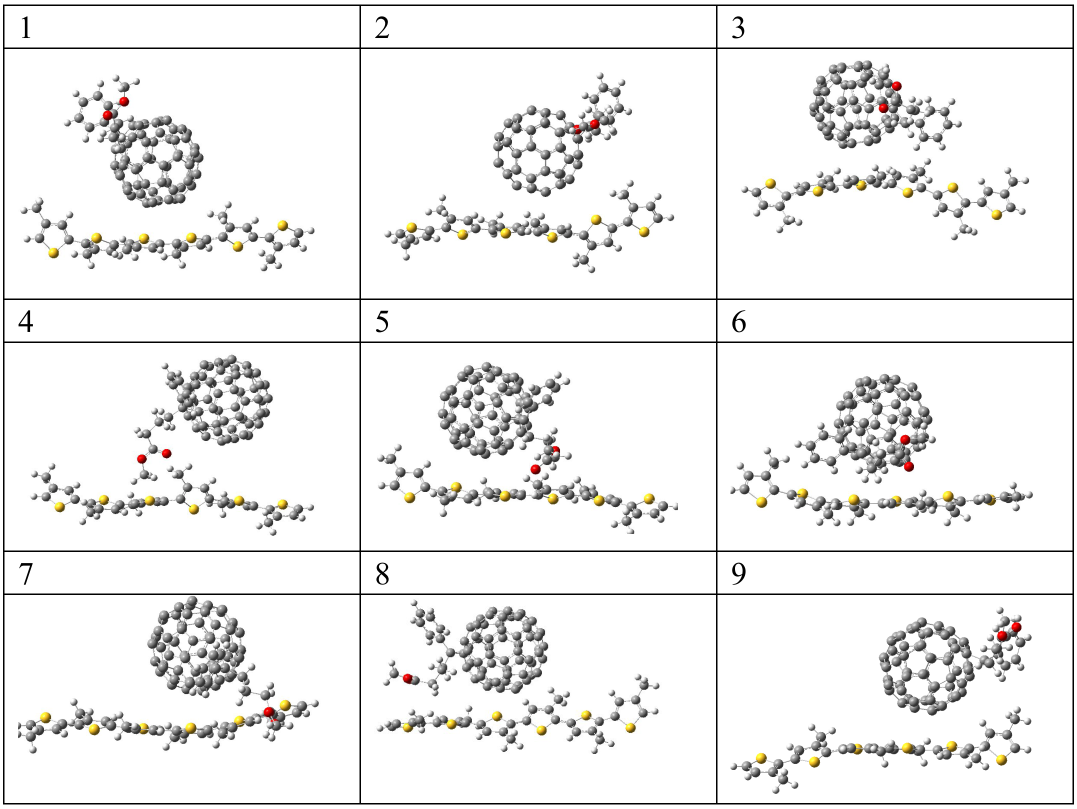

Figure S2. The optimized geometries of nine starting P3MT/PCBM geometries at 9.5 ns by DFT method, the order corresponds to the order in Figure 4.

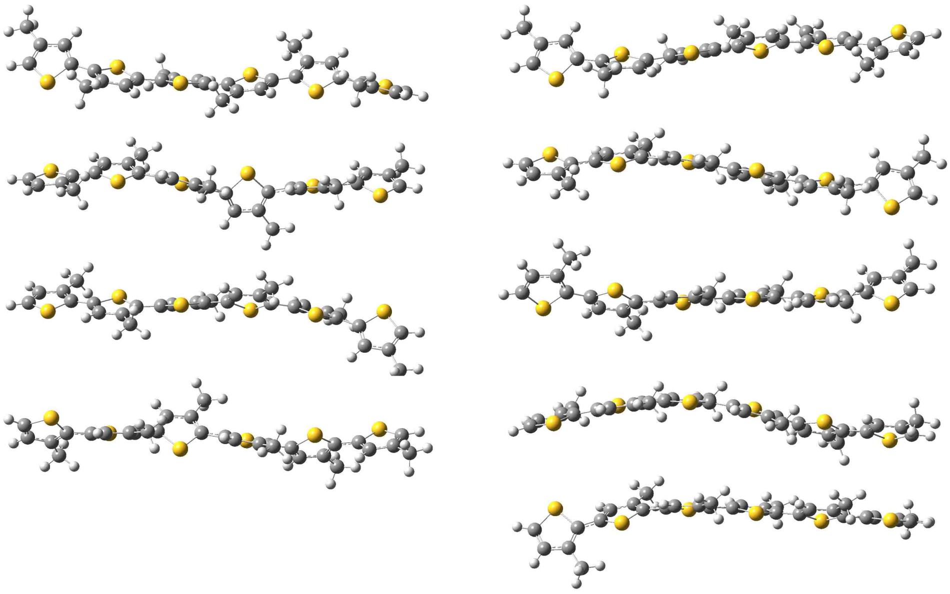

Figure S3. The ground state geometry of P3MT of Group 1 (left), leading to a charge separated state, and Group 2 (right), leading to a charge bridging state.

References:

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