Structure-property insights from heterojunction interfacial excitons

Márcio T. do N. Varella

Institute of Physics, University of São Paulo, São Paulo, SP, Brazil

mvarella@if.usp.br

The formation of interfacial charge-transfer (CT) excitons is believed to mediate the charge separation in organic solar cells. The experimental data suggest that different exciton dissociation mechanisms would be relevant, involving both high-energy (hot) and low-energy (cold) CT states. We explored a prototypical organic heretojunction comprising fullerene acceptors and dual-band donor polymers composed of thiophene (T), benzothiadiazole (BT), and benzotriazole (BTz) subunits. We considered several interface models varying the size, relative positions and orientations of the donor and acceptor domains (see Figure 1).

The electronic excitation spectra were obtained with the time-dependent long-range-corrected density-functional tight-binding (LC-TD-DFTB) method [1], and the excited states were analyzed with the fragment-based one-electron transition density matrix [2]. The CT excitons were then characterized according to their size, localization, intensity, and energy distribution.

The complexes with edge-on orientation were found to have denser spectra of low-energy CT states compared to the complexes with face-on orientation. The edge-on orientation would thus favor dissociation following relaxation to cold CT excitons, while the dissociation of hot excitons would be favored by the face-on orientation. The size and degree of charge transfer of the low-lying CT states also tend to be larger in the interface models with edge-on orientation. Finally, we found that larger excitons are produced by the delocalization of the electrons perpendicularly to the donor:acceptor interface. The results reported in this talk were published in a recent paper [3].

Index Terms: organic photovoltaics, excitons, density-functional tight-binding

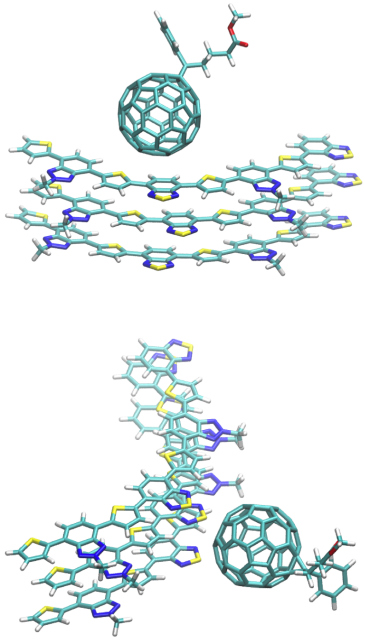

Figure 1: *Models for donor:acceptor interfaces with face-on (top) and edge-on (bottom) orientation. The acceptor is composed of stacked oligomers of T, BT and BTz subunits, while the acceptor is a fullerene (PCBM) unit. The sulfur atoms are indicated in yellow, oxygen in red, nitrogen in deep blue, carbon in light blue, and hydrogen in white.*

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