Dynamic processes of charge-transfer excitons at the donor-acceptor interface of organic thin-film solar cells

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   Sunlight is a versatile power generation source that generates charge and power generation energy by causing electronic excitation of devices, photocatalysis, and solar heating, and solar cells are devices that convert solar energy, a renewable resource, into electrical energy. It has been reported that non-fullerene organic thin-film solar cells using π-conjugated non-fullerene as acceptor molecules are effective in increasing the short circuit current due to the high absorption efficiency of visible light in the D/A layer.[1,2] Therefore, the key point should be the dynamic process of "exciton" generated at the interface of D/A stacked structures and the photoelectric conversion mechanism, and it is important to clarify the formation and dissociation of exciton and the diffusion process of generated carriers.[3] Two hypotheses have been formulated for the process by which photoinduced excitons generate free carriers (electrons and holes). One is the "*cool process*" in which excitons generated on the D side relax to the charge-transfer state at the D/A interface and thermally unbind the charge-transfer state to generate a charge-separated state, i.e., free electron carriers, and the other is the "*hot process*" in which excitons do not relax to the charge-transfer state at the D/A interface but generate free The other is a process called "hot process" in which excitons generate free electron carriers without relaxing to a charge transfer state at the D/A interface. The applicant found that in highly efficient organic solar cells, the Frenkel-type exciton generated on the D side becomes a charge-transfer (Wannier-type) exciton at the interface, and its size (electron-hole distance) is correlated with conversion efficiency.[4-6]

   The charge-transfer exciton at the initial stage of formation is a weakly bound electron-hole polaron pair, and the process of their dissociation into free electron polarons and hole polarons without relaxing to the charge-transfer state is predicted to correspond to the "hot process". Therefore, the choice between the Cool process and the Hot process is thought to be due to the electro-kinetic interactions in the exciton state at the interface. In order to systematically elucidate the mechanism of charge generation, we
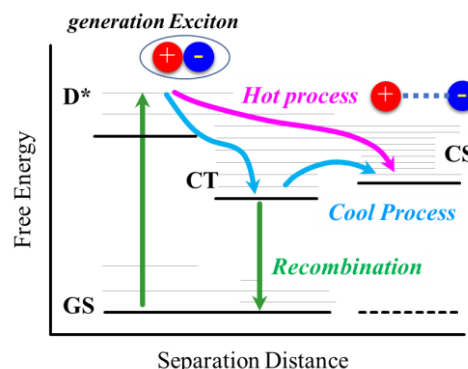

Figure 1 Energetics of relevant states at D/A interfaces.

performed DFT calculations of organic thin-film solar cells with a polymer donor molecule PTB7 and non-fullerene acceptor molecules BTAx (x = 1, 3), which exhibit high external quantum efficiency in bulk heterostructure with appropriate acceptor molecules. calculations to study the charge dissociation process of excitons (Figure 1).[7]
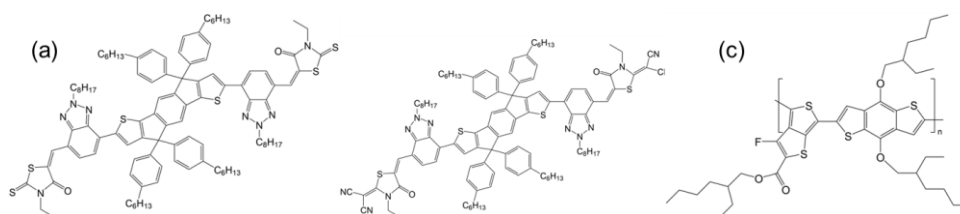

Figure 2 Chemical formula of acceptor and donor molecules (a) BTA1 (b)BTA3 and (c) PTB7

In this study, we use time-dependent density functional theory calculations to obtain the electronic excitations of D/A molecular complexes, analyze the electronic structure of charge-transfer excitons at the D/A interface, and determine the electron-hole distance. In addition, coupling calculations of electron transfer/excitation energy transfer, structural optimization of charge-transfer exciton states, and analysis of vibronic interactions will be used to analyze the possibility of electron-hole polaron pair formation, as well as the mechanism of free electron and hole polaron formation.

From the analysis of the electronic total coupling of the D/A complex, we predicted that the weaker the Coulomb coupling, the longer the charge transfer distance (exciton diffusion length) and the larger the exciton size, and the easier the state of charge separation (dissociation).[8] From the viewpoint that the relaxation of the initially generated charge-transfer exciton to the charge-transfer state and the relaxation of the charge-transfer state to the electronic ground state, i.e., the recombination process, are governed by the vibronic interactions in these states, the vibronic interactions in the photoabsorption and photoemission processes, i.e., the exciton-phonon We focus on the correlation with the Huang-Rhys factor, which indicates the strength of the exciton-phonon coupling, and non-adiabatic relaxation. 【ref. This body consists of 585 words.】

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