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Multiscale description of molecular packing and electronic processes in small-molecule organic solar cells

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ABSTRACT

This paper summarizes our recent works on theoretical modelling of molecular packing and electronic processes in small-molecule organic solar cells. Firstly, we used quantum-chemical calculations to illustrate exciton-dissociation and charge-recombination processes at the DTDCTB/C₆₀ interface and particularly emphasize the major role of hot charge-transfer states in the exciton-dissociation processes. Then, we systematically analyzed the influence of DTDCTB surfaces with different features on the vacuum vapor deposition growth and packing morphologies of C₆₀ via atomistic molecular dynamics simulations, and found that the formation of crystalline fullerene is the result of an integrated impact of stability, landscape, and molecular orientation of the substrate surfaces. Also, we investigated the impact of different film-processing conditions, such as solvent evaporation rates and thermal annealing, on molecular packing configurations in a neat small-molecule donor material, DPP(TBFu)₂, and discussed the correlation between charge mobility and molecular packing via atomistic simulations in combination with electronic-structure calculations and kinetic Monte Carlo simulations.

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1. Introduction

Owing to the peculiarities of low cost, light weight, mechanical flexibility, large-area capability, and ease of fabrication, organic photovoltaics (OPVs) have attracted much attention over the past two decades [1–7]. Recent efforts have pushed the power conversion efficiencies (PCEs) exceeding 10% for both polymer-based [8,9] and small molecule-based [10–14] organic solar cells (OSCs) employing a single photoactive layer. Nevertheless, it still does not reach commercial viability. In general, the active layer consists of two distinct components of electron-rich donor (D) and electron-deficient acceptor (A) materials with a bilayer or bulk heterojunction architecture. In order to achieve an efficient OPV operation, a series of successive electronic processes must be optimized within the active layer, including (1) exciton formation by sunlight absorption in D and/or A materials, (2) exciton diffusion to the D/A interface before decaying to the ground state,

(3) exciton dissociation (ED) into charge-transfer (CT) states at the D/A interface, where hole and electron are still weakly electrostatically bounded, (4) hole and electron separation into free charge carriers and migration along D and A toward the anode and cathode, respectively, and (5) finally hole and electron collection at the respective electrode [2,15,16]. In the meanwhile time, the undesirable (geminate, bimolecular, trap-assisted, etc.) charge recombination (CR) processes must be prevented, thus requiring a fine balancing act.

Critical to these key processes are the molecular packing configurations in the active layer, especially the D/A intermolecular arrangements at the interface [15–22]. Recent quantum-chemical studies on model constructed and molecular dynamics (MD) simulated D/A complexes pointed out that, the competition between ED and geminate CR is closely relevant to the interfacial packing [17,23,24]. Except the exquisite interface engineering, the impact of hot CT states in the ED process has also been emerged [23,25–27]. Some recent experiments revealed that hot CT excitons could dissociate into free charge carriers within several hundreds of femtoseconds before decaying into the lowest CT (CT₀) state [25–27]. These will be the focus of Section 2 where we take the example of DTDCTB/C₆₀ complexes to clarify the ED and CR mechanisms [23]. The OSCs based on DTDCTB/fullerene heterojunctions have

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been widely investigated and achieved a relatively high PCE of exceeding 8% [28–39]. Importantly, our calculations pointed to that hot CT states dominate the ED process in the DTDCTB/C₆₀ complexes, which is favorable to obtain ultrafast charge separation.

Although modulation of the active layer morphologies for efficient generation of free carriers has been successfully achieved by several different preparation procedures [1,19,20,40–43], it still remains very difficult to experimentally probe the molecular self-assembly processes and packing structures [44], especially the myriad morphologies available in the active layer. This will severely hinder obtaining reliable structure–property relationships and further improving the device performance. It is the reason why atomistic MD simulations are increasingly used as a powerful tool to obtain further understanding of the buried bulk and interfacial morphologies [24,45–51], which will be the focus of Section 3. In this part, we summarize the modeling schemes of vapor-deposition and solution-processing processes and our two recent works. First, the impact of different DTDCTB surfaces on fullerene packing and interfacial morphologies are analyzed [24]. Second, the effect of solvent evaporation rate and thermal annealing on the molecular packing morphology and charge transport is unraveled for a diketopyrrolopyrrole (DPP)-based small-molecule donor material [51], DPP(TBFu)₂ [52–55], which displays excellent hole mobility.

2. Excited-state charge-transfer processes at the donor/acceptor interface

2.1. Methodology

Electronic coupling between the local excited and charge-transfer states is one of the key parameters to evaluate the excited-state charge-transfer processes at the donor/acceptor interface. Several methods have been developed to compute electronic couplings, such as the fragment molecular orbital (FMO) method [56], energy level splitting (ELS) method [57], generalized Mulliken-Hush (GMH) model [58], and constrained density functional theory (CDFT) [59]. The electronic couplings provided by the FMO and ELS methods are originated from the interaction between frontier molecular orbitals based on the single-electron approximation. The GMH model can deal with many-electron states, but it is applicable only when the adiabatic states are constructed by two diabatic states. For the method based on CDFT, just the ground CT state can be considered. Recently, a diabatic-state approach was developed, which can calculate electronic couplings between any local and any CT states [17]. It is expressed as follows:

$$V_{ab} = \langle \Psi_a^{LE} | H | \Psi_b^{CT} \rangle \quad (1)$$

Here, Ψ_a^{LE} denotes the ground state or the excited state located on D or A, and Ψ_b^{CT} represents the CT state of the D-A complex, which are constructed as spin-adapted anti-symmetrized products of the isolated D and A wavefunctions,

$$\Psi_{ij}^{LE}(S, M) = \sum_{M_i M_j} C_{S_i M_i S_j M_j}^{SM} |\Psi_i^D(S_i, M_i) \Psi_j^A(S_j, M_j)| \quad (2)$$

$$\Psi_{km}^{CT}(S, M) = \sum_{M_k M_m} C_{S_k M_k S_m M_m}^{SM} |\Psi_k^{D^+}(S_k, M_k) \Psi_m^{A^-}(S_m, M_m)| \quad (3)$$

here, S and M are the total spin and spin projection of the D-A complex. $\Psi_i^{D/A}$ represents the i th excited state of the donor or acceptor with spin S_i and spin projection M_i , and $\Psi_k^{D^+/A^-}$ represents the positively-charged state of D or negatively-charged state of A. The Clebsch-Gordan coefficients ($C_{S_i M_i S_j M_j}^{SM}$) ensure that the linear combination of the products of the isolated wavefunctions is the

eigenfunction of the total spin. The isolated excited and charged states of D and A can be calculated by the intermediate neglect of differential overlap (INDO) Hamiltonian [60] coupled to a single configuration interaction (SCI) scheme. In our following work, the Mataga-Nishimoto potential was applied to describe the coulomb repulsion term [61,62].

Considering the degeneracies of the excited states of C₆₀ and the CT states, the effective electronic couplings (V_{eff}) are calculated as follows [17]:

$$V_{\text{eff}}^2 = \frac{1}{g_a} \sum_{ij} (\Psi_{ai} | H | \Psi_{bj})^2 \quad (4)$$

where g_a is the multiplicity of the initial diabatic state, and Ψ_{ai} and Ψ_{bj} are the initial and final degenerate diabatic states, respectively.

In the framework of semi-classical model of the Marcus electron-transfer theory [63], the ED and CR rates can be calculated by the following equation,

$$k_{ab} = V_{ab}^2 \sqrt{\frac{\pi}{\lambda k_B T \hbar^2}} \exp\left[-\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}\right] \quad (5)$$

Here, V_{ab} is the electronic coupling described above, λ the reorganization energy, ΔG the Gibbs free energy, k_B the Boltzmann constant, \hbar the reduced Planck constant, and T the temperature (set to 298.15 K in our study). It should be noted that compared with the Marcus theory, a much more complicated full quantum approach has been developed to calculate a more accurate rate through taking account of the nuclear tunneling effect [64–68].

Reorganization energy, λ consists of internal (λ_{int}) and external (λ_{ext}) contributions. λ_{int} for exciton dissociation can be evaluated as the total relaxation energies from their excited-state or ground-state geometries to ionic geometries, while for charge recombination it corresponds to the total relaxation energies from their ionic geometries to neutral geometries. In the case of flexible molecules, e.g. DTDCTB, the steric hindrance effect on λ_{int} can be very important in the solid state, and λ_{int} should be evaluated by a hybrid quantum mechanics/molecular mechanics (QM/MM) approach [69]. At present, it is still difficult to reliably estimate λ_{ext} , which is regarded as a variable and set to 0.06–0.20 eV in our study [70,71].

When the entropy contribution is ignored, Gibbs free energy, ΔG is equal to the energy difference between the initial and final diabatic states, and the energy of the diabatic state is calculated as the sum of the total energies of the isolated states of D and A and the Coulomb energy between D and A. For the local states, D and A are neutral and the Coulomb energies between D and A can be neglected. Therefore, the energies of local excited states are approximate to the excitation energies of the isolated D and A. However, the energies of the CT states must take into consideration the Coulomb interaction and can be estimated as [17]

$$E_{\text{CT}} = IP + EA + E_{\text{Coul}} \quad (6)$$

where IP and EA are the ionization potential of D and the electron affinity of A, respectively. E_{Coul} is the Coulomb energy between the cation of D and anion of A,

$$E_{\text{Coul}} = \sum_{d \in D^+, a \in A^-} \frac{q_d q_a}{4\pi \epsilon_0 \epsilon r_{da}} \quad (7)$$

Here, d and a represent the atoms in D and A, respectively. q_d and q_a denote their corresponding partial charges (they are calculated by an INDO Mulliken population analysis in our work) and r_{da} is the distance between atoms d and a . ϵ_0 and ϵ are dielectric constants of the vacuum and medium (set to 4 in our work), respectively.

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