



Theoretical investigation on the electronic and charge transport characteristics of push–pull molecules for organic photovoltaic cells



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ABSTRACT

We theoretically investigated the electronic and charge transport characteristics of ditolylaminothienyl–benzothiadiazole–dicyanovinylene (DTDCTB), ditolylaminophenyl–benzothiadiazole–dicyanovinylene (DTDCPB) and ditolylaminothienyl–pyrimidine–dicyanovinylene (DTDCTP) push–pull molecules consisting of donor–acceptor–acceptor (D–A–A) configurations for a donor photoactive layer having low energy gaps in organic photovoltaic cells (OPVCs). They commonly have a strong electron-withdrawing moiety and hence conspicuously deep-lying highest occupied molecular orbital (HOMO) levels, leading to high open circuit voltages (V_{OC}) in OPVCs. In addition, they commonly have low hole reorganization energy due to the fully delocalized wave function of the HOMO on over the entire molecule, and high electron reorganization energy due to their contracted wave functions of the lowest unoccupied molecular orbital (LUMO) on a D moiety. However, their theoretically calculated hole and electron mobility (μ_h and μ_e) based on Marcus theory in the molecular crystalline is dissimilar: DTDCTB showed the higher μ_h than μ_e , DTDCPB showed the similar μ_h and μ_e and DTDCTP showed the higher μ_e than μ_h , which can explain the tendency of their short circuit current (J_{SC}) in OPVCs. This originates from significantly different electronic coupling, although they have similar π – π coplanar molecular packing in appearance.

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1. Introduction

In the last two decades, the power conversion efficiency (PCE) of organic photovoltaic cells (OPVCs) has increased remarkably and approached near 10%, and they are now regarded as a commercial product. OPVCs are operated by the sequence of (1) photon absorption and exciton generation in an organic photoactive layer, (2) exciton diffusion and dissociation at the donor/acceptor interface, (3) charge transfer toward the electrodes and photocurrent collections [1]. To maximize the PCE of OPVCs, all conditions in this sequence for photocurrent generation must be optimized. In this regard, various methods to optimize OPVCs have been introduced, such as inserting an appropriate hole/electron collecting layer, controlling the morphology of organic photoactive layers for high

mobility, and adopting tandem structures for broad absorption of incident light [2–4].

One of the strategies to increase the PCE is the synthesis of new organic photoactive molecules having low energy gaps that can absorb a broad range of incident light [5,6]. Recently, Wong's group reported highly efficient donor materials for OPVCs which consist of donor–acceptor–acceptor (D–A–A) configurations [7–9]. These molecules are comprised of electron donating ditolylaminothienyl–electron withdrawing benzothiadiazole–electron accepting dicyanovinylene moieties (DTDCTB), electron donating ditolylaminophenyl–electron withdrawing benzothiadiazole–electron accepting dicyanovinylene moieties (DTDCPB) and electron donating ditolylaminothienyl–electron withdrawing pyrimidine–electron accepting dicyanovinylene moieties (DTDCTP), respectively. OPVCs with these molecules show considerably large short circuit current densities (J_{SC}) that originate from their wide-ranged photon absorption. In addition, their open circuit voltages (V_{OC}) can be easily modified by introducing the electron-withdrawing moiety leading to the deep HOMO level. That is, the key parameters of OPVCs can be easily controlled

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with the proper combination of donor and acceptor moieties. In spite of these interesting and highly desirable schemes, a fundamental understanding of the electronic and charge transport characteristics of these molecules has been lacking. Such understanding is indispensable in order to design adequate molecules for OPVCs.

In this respect, we theoretically investigated the electronic and charge transport characteristics of DTDCTB, DTDCPB and DTDCTP molecules with density functional theory (DFT) calculations in this study. Conventionally, these kinds of molecules are called “push–pull” molecules since the electron-donating moiety pushes the electron and the electron-accepting moiety pulls it within the molecule. These molecules would be expected as having strong intramolecular electron transfer characteristics between D–A moieties which can contribute to high mobility (μ) [5,10]. However, the hole/electron transport in organic solids is not only determined by the intramolecular properties. For example, tris-(8-hydroxyquinoline) aluminum (Alq₃), which is a conventional electron transport layer in organic light-emitting devices, shows one order of magnitude higher electron mobility (μ_e) than hole mobility (μ_h), and this asymmetric μ has been understood by calculating intermolecular electronic coupling and transfer integrals (V) [11–13]. Although Alq₃ has a lower hole reorganization energy (λ_h) than electron reorganization energy (λ_e), a conspicuously higher electron transfer integral (V_e) than hole transfer integral (V_h) result in higher μ_e of Alq₃. Therefore, V should be considered along with the reorganization energy (λ) to evaluate the μ of organic semiconducting materials reliably. In this study, we evaluated the theoretical μ of DTDCTB, DTDCPB and DTDCTP by considering both λ and V , which could predict the experimental μ in many cases [14,15]. We also discuss the origin of different λ and V for each molecule and the correlation between theoretically calculated electronic/charge transport characteristics and experimental OPVC device parameters. This study would give a helpful guide to optimization of organic photoactive layers in OPVCs.

2. Theory and methodology

In general, the charge transport in solids occurs by two different mechanisms: band and hopping transport. In inorganic semiconductors, such as a Si, charge transport is governed by the energy band, due to strong covalent interactions. However, in many cases, the charge transport of organic semiconductors can be well described with the thermally activated hopping and diffusion model since they have weak intermolecular electronic coupling ($\lambda > V$). Hence, if the temperature is sufficiently high ($T = 300$ K in this study, which is a typical temperature for OPVC operation), we can deal with the charge transport process as a self-exchange interaction described by the semi-classical Marcus theory [16]. Then the charge hopping rate k is written by

$$k = \frac{4\pi^2}{h} V^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left[-\frac{\lambda}{4k_B T}\right] \quad (1)$$

where V is the transfer integral, λ is the reorganization energy, h is the Planck constant, T is the temperature in Kelvin, and k_B is the Boltzmann constant, respectively. As seen in Eq. (1), to maximize the charge hopping rate k , λ should be decreased while V should be increased.

λ means the geometrical relaxation energy when a molecule obtains or loses charges. Therefore, λ can be evaluated by the sum of energetic differences (1) between the neutral energy obtained with charged geometry [$E_0(Q^*)$] and the charged energy obtained with charged geometry [$E^*(Q^*)$] and (2) between the charged energy

obtained with the neutral geometry [$E^*(Q_0)$] and the neutral energy obtained with neutral geometry [$E_0(Q_0)$]. In other words,

$$\lambda = [E_0(Q^*) - E^*(Q^*)] + [E^*(Q_0) - E_0(Q_0)] \quad (2)$$

where the subscript 0 denotes the neutral state and the superscript * denotes the charged state, and E and Q denote the single point energy and molecular coordinates, respectively. In a strict sense, the total λ is composed of the internal λ (λ_{int}), which corresponds to intramolecular relaxation energy, and the external λ (λ_{ext}), which corresponds to the relaxation energy of the environmental medium. However, it is well known that λ_{ext} is much smaller than λ_{int} in many organic solid systems, and hence it can be assumed that λ_{ext} does not play an important role in the charge transport rate [17,18]. Therefore, we neglected λ_{ext} and only dealt with λ_{int} for simplicity in this study.

V means the electronic coupling between the initial and final orbital wave function during the charge hopping process, which can be written with bra-ket notation as

$$V = \left\langle \psi_i^{HOMO/LUMO} | F | \psi_f^{HOMO/LUMO} \right\rangle \quad (3)$$

where F is the Fock operator and Ψ_i and Ψ_f are the wave functions of the initial and final orbital, respectively. The superscripts indicate the frontier orbitals in which the charge hopping occurs, which are mostly at the HOMO level for holes and the LUMO level for electrons. In the past, the energy splitting in dimer (ESD) method was used to evaluate V simply. However, V from the ESD method is only reliable for highly symmetric intermolecular arrangements due to the electronic polarization [19]. Therefore, we calculated V with the direct coupling method, which directly calculates the electronic coupling between molecules in which the charge transfer occurs. We used the projection method, which is appropriate for any molecules, even those having 3-dimensional non-planar geometry [20,21]. The molecular pair for the V calculation was taken from the relative geometry of the nearest neighbors from X-ray crystallography analysis for the molecular crystal.

Following procedure to calculate the μ of organic semiconductor has shown quite reliable results for the decade [22–31]: from the charge hopping rate k_i [Eq. (1)] for the i th pathway (i th nearest neighbor), the diffusion coefficient D can be estimated with a space and time-averaged value as [32,33]

$$D = \frac{1}{2N} \lim_{t \rightarrow \infty} \frac{\langle l(t)^2 \rangle}{t} \approx \frac{1}{2N} \sum_i r_i^2 k_i P_i \quad (4)$$

where N is the dimensionality (=3), $l(t)$ is the distance between the charge's position at time t and its starting position at $t=0$, r_i is the molecular distance from the reference molecule to the nearest neighbor in the molecular crystalline, and P_i is the relative hopping probability for the i th pathway. The summation runs for all nearest neighbors. In short,

$$P_i = \frac{k_i}{\sum_j k_j} \quad (5)$$

In this case, D is the averaged diffusion coefficient for the anisotropic hopping process all over the nearest neighbor molecules (single-step approximation) [32,33]. This approximation often gives a good explanation in qualitative analysis for the experimental mobility with relatively cheap computational cost. Therefore, it could be a very efficient method to understand the electronic and charge transport characteristics of organic semiconducting materials at a glance.

We could obtain the μ based on the Einstein relation as

$$\mu = \frac{e}{k_B T} D \quad (6)$$

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