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Regular Article

Molecular Insight into Energy Loss in Organic Solar Cells

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Abstract: With the rapid development of A-D-A non-fullerene acceptors, organic solar cells (OSCs) have made significant progress. However, compared to inorganic and perovskite solar cells, the energy loss in OSCs remains relatively large. In this Perspective, we summarize our recent computational advances in elucidating the mechanisms of energy loss in OSCs at the molecular level. We highlight strategies to minimize voltage loss during charge generation, suppress triplet-channel recombination, and reduce non-radiative voltage loss by modulating both molecular and aggregation structures.

Key words: organic solar cells, voltage loss, triplet recombination, aggregation, multiscale simulations.

Introduction

Organic solar cells (OSCs) hold great promise for applications in building-integrated photovoltaics and wearable electronics, due to their unique advantages of light weight, flexibility, semi-transparency, and suitability for large-area solution processing.[1] The active layer of OSCs typically consists of electron-donor and electron-acceptor semiconducting materials, which are blended to form nanoscale phase-separated morphologies. Because of the low dielectric constants of organic semiconductors, absorption of sunlight forms Frenkel excitons. To produce photocurrent, these excitons need to diffuse to the donor/acceptor (D/A) interface and split into free charge carriers (FC). Subsequently, the free holes and electrons migrate along the donor and acceptor materials toward and are collected by the anode and cathode, respectively. Meanwhile, charge recombination, which occurs during generation and migration, should be suppressed. From the perspective of excited states, dissociation of the photogenerated singlet excitons (S_1) into FC is mediated by singlet charge-transfer (CT) states, while non-geminate recombination of FC leads to the formation of both singlet and triplet CT excitons ($^{S}CT_1$ and $^{T}CT_1$) in 1:3 ratio following the spin statistics (**Figure 1**) [2,3]. The $^{S}CT_1$ states can decay into the ground state (S_0) via radiative and non-radiative pathways. The recombination of the $^{T}CT_1$ states occurs through the low-lying triplet excitons (T_1, usually on the narrow-bandgap materials), which constitutes a major terminal loss channel of photocurrent.

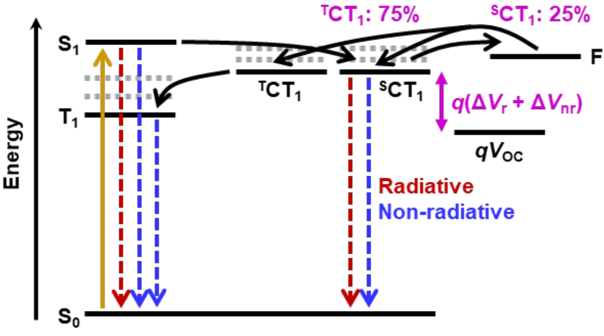

Figure 1. Excited-state Jablonski diagram for describing the charge generation and energy loss processes in organic solar cells.

The open-circuit voltage (V_{OC}) in OSCs is determined by the energy of the lowest CT states (E_{CT}), as well as recombination processes [4]. The requirement for exciton dissociation (ED) driving forces (ΔE_{CT}, i.e., the energy difference between S_1 and $^{S}CT_1$ states) thus leads to an extra voltage loss. According to the detailed balance theory (first proposed by Shockley and Queisser), the voltage loss due to radiative recombination (ΔV_{r}) is inevitable (0.25-0.3 V) for any type of solar cells, while the voltage loss due to non-radiative recombination (ΔV_{nr}) is intrinsically linked to the device's electroluminescence external quantum efficiency (EQE_{EL}):

$$\Delta V_{\mathrm{nr}} = (-k_B T/q) * ln(EQE_{\mathrm{EL}})$$

where k_{B} is the Boltzmann constant, T is temperature, and q is the elementary charge [5,6]. An ideal $EQE_{\mathrm{EL}} = 1$ results in $\Delta V_{\mathrm{nr}} = 0$, whereas a reduction in EQE_{EL} by one order of magnitude increases the ΔV_{nr} by 0.058 V at room temperature. The EQE_{EL} can be expressed as:

$$EQE_{\mathrm{EL}} = \gamma \Phi_{\mathrm{PL}} \chi \eta_{\mathrm{out}}$$

where γ is the charge balance factor (often engineered to be 1), Φ_{PL} is the photoluminescence quantum yield, χ is the fraction of recombination events that decay radiatively, and η_{out} is the photon out-coupling efficiency (typically about 0.3). For OSCs, Φ_{PL} is related to the rates of radiative (k_{r}) and non-radiative (k_{nr}) recombination of the $^{\mathrm{S}}\mathrm{CT}_1$ state ($\Phi_{\mathrm{PL}} = k_{\mathrm{r}}/(k_{\mathrm{r}} + k_{\mathrm{nr}})$, with $k_{\mathrm{nr}} >> k_{\mathrm{r}}$ in most cases), and the decay of T_1 to S_0 limits χ to below 25%. Therefore, to simultaneously reduce both photocurrent and voltage losses, it is essential to suppress non-radiative recombination of the $^{\mathrm{S}}\mathrm{CT}_1$ state and the triplet recombination channel.

In the early stage of OSC development, fullerene derivatives (e.g., $\mathrm{PC}_{71}\mathrm{BM}$), renowned for their excellent electron-accepting and electron-transporting properties, were the primary choice for acceptor materials [7]. Due to the weak visible and near-infrared absorption of fullerenes, fullerene-based OSCs commonly use narrow- or medium-bandgap small molecules or polymers as donors (e.g., PffBT4T-2OD, also known as PCE11) [8]. However, fullerene-based OSCs require a large ED driving force (ΔE_{CT} >0.3 eV) and suffer from severe non-radiative voltage losses (ΔV_{nr} >0.3 V), limiting their power conversion efficiencies (PCEs) to 11-12%. The emergence of narrow-bandgap A-D-A-type small-molecule acceptors (e.g., IT-4F and Y6) has changed the landscape [9,10]. Non-fullerene OSCs can achieve high-yield charge generation with a near-zero ΔE_{CT} and have a smaller ΔV_{nr} of ~0.2 V [11,12]. When combined with Y6 derivatives and wide-bandgap D-A copolymer donors (PM6 and D18), the highest PCEs of non-fullerene OSCs have surpassed the 20% milestone [13-16]. Nevertheless, compared with those of inorganic and perovskite counterparts, the ΔV_{nr} of the state-of-the-art OSCs is still larger (e.g., only 0.027 V in high-quality GaAs devices) [17]. Moreover, the highest short-circuit current density (J_{SC}) and fill factor of OSCs just reach 85-90% of the Shockley-Queisser limit. Hence, to further enhance the organic photovoltaic performance, it is imperative to deeply understand the molecular origins of energy loss and develop effective strategies to mitigate it.

Multiscale theoretical simulations, which combine quantum chemistry (QC) calculations and molecular dynamics (MD) simulations, can provide insights into the mechanisms of charge generation, charge transport, and energy loss in OSCs at the molecular level [12,18-20]. In this Perspective, we focus on reviewing our recent computational efforts on energy loss, highlighting how to minimize voltage loss during charge generation, suppress the triplet recombination channel, and decrease non-radiative voltage loss. Prior to that, a computational protocol will be briefly introduced.

Computational protocol

The electronic structure and dynamics of excited states in OSCs rely on not only molecular structures but also aggregation structures. We adopt QC calculations to construct model intermolecular geometries and MD simulations to produce mesoscopic molecular packing morphology.[18] Note that, the solvent evaporation and thermal annealing processes can be reliably imitated by quasi-equilibrium MD. Then, excited-state electronic structure properties and intermolecular electronic couplings can be obtained by QC calculations. The electronic structure calculations are mainly conducted by (time-dependent) density functional theory, with tuned long-range corrected hybrid functionals to achieve reasonable accuracy.

Minimizing voltage loss during charge generation

To maximize V_{OC} and J_{SC} concurrently, the ΔE_{CT} must be minimized without sacrificing charge generation efficiency. In OSCs with low driving forces, exciton dissociation proceeds mostly through the $^{\mathrm{S}}\mathrm{CT}_1$ state. This requires the electronic coupling between S_1 and $^{\mathrm{S}}\mathrm{CT}_1$ (V_{ED}) to be strong enough. Meanwhile, the non-radiative decay from $^{\mathrm{S}}\mathrm{CT}_1$ to S_0 should be suppressed. The k_{nr} of the $^{\mathrm{S}}\mathrm{CT}_1$ state can be estimated using the Marcus-Levich-Jortner tunneling formalism:

$$k_{\mathrm{nr}} = {V_{\mathrm{CR}}}^2 \sqrt{\frac{\pi}{\hbar^2 \lambda_{\mathrm{l}} k_{\mathrm{B}} T}} \times \sum_{\nu=0}^{\infty} \left\{ exp(-S_{\mathrm{eff}}) \frac{S_{\mathrm{eff}}^{\nu}}{\nu!} exp\left[-\frac{(-E_{\mathrm{CT}} + \lambda_{\mathrm{l}} + \nu\hbar\omega_{\mathrm{eff}})^2}{4\lambda_{\mathrm{l}} k_{\mathrm{B}} T} \right] \right\}$$

where V_{CR} denotes the electronic coupling between $^{\mathrm{S}}\mathrm{CT}_1$ and S_0, $\hbar$ is the reduced Planck constant, λ_{l} is the low-frequency reorganization energy (including both intramolecular and external contributions), ω_{eff} is the effective frequency corresponding to the intramolecular high-frequency vibration modes, and S_{eff} is the Huang-Rhys factor associated with the effective mode [21]. To reduce k_{nr}, it is necessary to increase E_{CT} and/or decrease the corresponding electronic coupling and reorganization energy. As the first-order approximation, the E_{CT} can be expressed as $E_{\mathrm{CT}} = (|E_{\mathrm{HOMO,D}}| - |(E_{\mathrm{LUMO,A}}|) + E_{\mathrm{Coul}}$, where $|E_{\mathrm{HOMO,D}}|$ is the energy of the highest occupied molecular orbital (HOMO) of the donor (or more strictly, the ionization potential of the donor), $|E_{\mathrm{LUMO,A}}|$ is the energy of the lowest unoccupied molecular orbital (LUMO) of the acceptor (or the electron affinity of the acceptor), and E_{Coul} represents the interfacial electron-hole Coulomb interaction energy. It is well-established that V_{ED}, V_{CR}, and E_{Coul} are all highly dependent on the D/A intermolecular relative orientations/positions [2,22].

To this end, we employed MD simulations to uncover the interfacial geometries in non-fullerene OSCs [23,24]. For example, in a representative all-small-molecule OSC of DRTB-T:IT-4F, IT-4F was found to be docked with the donor DRTB-T (also of the A-D-A-type) mainly via local π-π interaction between their electron-withdrawing end-groups (**Figure 2**a,b) [23]. This is due to the large steric hindrance of side chains on the backbone core, especially for IT-4F. Further QC calculations demonstrate that as IT-4F moves from the core to the terminal units of DRTB-T, both E_{Coul} (from approximately -0.3 to -0.2 eV) and V_{CR} (from around 22 to 8 meV) weaken significantly (Figure 2c). This is beneficial for suppressing $^{\mathrm{S}}\mathrm{CT}_1$ decay and facilitating charge separation (CS). Although V_{ED} also decreases because the HOMO of DRTB-T is more concentrated on the electron-donating units, it remains sufficiently large (~5 meV)