Invited paper

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Hot-carriers in organic photovoltaics

Abstract: Photogenerated charge carriers in organic photovoltaics (OPVs) suffer relaxation and recombination losses. However, extracting these carriers at higher energy ('Hot-carriers') has been found to be effective to overcome such loss pathways and improve efficiency of OPVs. Excess energy and long delocalization length promotes hot-carrier escape from Coulombic attraction and dissociation into free charges. Here, I have reviewed the ways to generate hot-carriers and their extraction in organic backbones. In-depth understanding of their energetics and dynamics will help designing hot-carrier photovoltaics.

Keywords: Charge-transfer; delocalization; Diamond Jubilee Issue; exciton; hot-carriers; organic photovoltaics; relaxation; ultrafast.

Introduction

The incumbent energy crunch due to limited fossil fuel resources has led scientists to develop photovoltaic technologies (solar cell) that generate electricity utilizing sunlight as renewable energy sources. The active layer of a solar cell absorbs a photon and converts it into free charge carriers at the terminal electrode. Over the past three decades, photovoltaics utilizing organic semiconductors gained particular importance as these are light weight, flexible and chemically tunable. These can be conjugated polymer or small molecule based semiconductors. Absorption of light by the organic active layer leads to generation of a Coulombically bound electron-hole pair known as an exciton. The real challenge is to dissociate this primary exciton and generate free charges. The energy cost required to split the exciton into free charges is an order of magnitude larger than thermal energy at room temperature. One way to circumvent this issue is by dissociating the strongly-bound exciton in the presence of a suitable acceptor (typically fullerene derivatives) where it forms a weakly bound charge-transfer (CT) exciton and becomes comparatively easier to split (as shown in Fig. 1). The separated charges are then collected at their corresponding electrodes in order to provide electricity. The efficiency of a solar cell is defined as short-circuit current (I_{sc}) multiplied with open-circuit voltage (V_{oc}). I_{sc} of a device is determined by the number of free carriers extracted per photon absorbed while V_{oc} is determined by the energy of the extracted carriers. Despite all the advancements in the field, OPV suffers low power conversion efficiency (PCE)- the maximum single-junction cell efficiency achieved to date is 17 % [1]. Competitive processes like charge carrier relaxation (shown by downward curly arrow in Fig. 1) and recombination (shown by downward dash line) inhibit free carrier generation. Most OPVs typically demonstrate energy losses in the range of 0.7–1 eV (nearly 50 % of the total energy absorbed) [2]. In order to minimize energy loss and improve carrier density, it is imperative to understand the loss mechanisms and molecular parameters that govern it.

With the advent of new ultrafast techniques, it becomes easier to track the excited state processes with femtosecond (1 fs = 10^{-15} s = 10^{-3} picosecond [ps]) time-resolution. Carrier relaxation processes in organic

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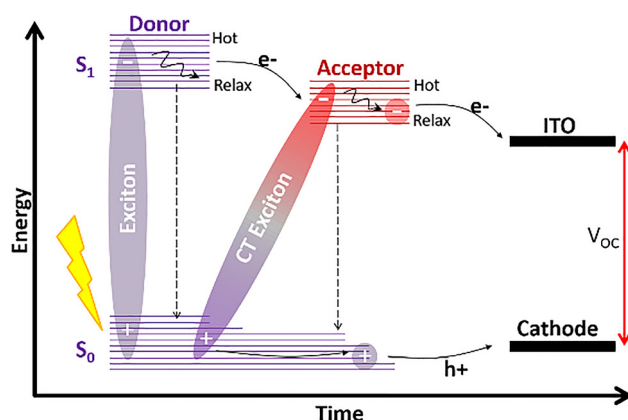e-mail: palas.1989@gmail.com. https://orcid.org/0000-0003-1262-6249

Fig. 1: Free-energy state diagram of the photophysical processes in an organic photovoltaics (OPVs). The photogenerated exciton in the donor backbone travels to the donor:acceptor interface and forms charge transfer exciton which then dissociates into separated charges and collected at the electrodes (indium tin oxide [ITO] as anode and Al/Ag as cathode). This process is accompanied by energy relaxation (curly arrow) and carrier recombination (dash arrow).

semiconductor occur in the timescale between 100 fs–10 ps. One of the ways proposed to circumvent such loss-processes is by extracting charge carriers with high-energy (hot-carriers) that are easy to dissociate due to lower binding energy and high carrier mobility. Generating such hot-carriers can improve the V_{oc} as the charges are extracted at high energy. In addition, I_{sc} also increases with long-range charge delocalization due to reduced binding energy and hence easier to dissociate the hot-excitons. Therefore, hot-carrier–based solar cells can reach potential efficiency close to the thermodynamical limit in ideal conditions.

It has been shown that charge separation in efficient OPVs is facilitated by hot-CT state delocalization [3]. Rapid, long range charge separation in photovoltaic active layer has been explained in different ways. Collini and Scholes [4] observed highly efficient exciton migration in tens of femtoseconds may be due to coherent energy transfer along conjugated polymer chains. Some recent studies proposed the role of coherent vibronic coupling between the initially delocalized photogenerated exciton and the CT state in driving ultrafast exciton dissociation [5, 6]. Several reports highlighted the importance of excess energy in hot-excitons as driving force for exciton migration, dissociation, and charge separation [7]. Computational studies have shown that high density of state (DOS) and long-range electron-hole separation play a crucial role for improved efficiency [8, 9]. However, which one plays key role for efficient charge generation between higher-lying delocalized electronic states and excess vibrational energy concept is still debated.

In excited states, carrier generation competes with cooling of hot-CT. Relaxation of hot CT states within 1 ps has been observed using time-resolved two-photon photoemission (2PPE) [10]. This is why delocalization of hot-charges is important to reduce the binding energy and then extract charges immediately before carrier relaxation. The quest for obtaining efficient hot-carriers and their extraction in OPVs demands critical understanding of energetics and timescales of the underlying photophysical processes. Here, I have reviewed different approaches proposed to improve hot-carrier generation and it's extraction in OPVs. Some of these are listed below.

Absorption of high-energy light

Grancini and colleagues observed that absorption of sufficiently high excitation-photon energy compared with the optical bandgap of the semiconducting material can lead to the generation of hot-CT exciton in <50 fs in a polymer (PCDTBT)/fullerene system [11]. Then these hot-carriers can dissociate into lattice-bound charges (polarons) on even faster timescales and improve free-carrier generation in solar cells. Similarly, Dimitrov et al. reported that an increase of photon energy by 0.2 eV above the bandgap could double both quantum yields of free charges as well as efficiency of polymer/fullerene blend [7]. Fig. 2a shows the pump-push-photocurrent dynamics for three different pump excitations at different pump-push delays. Maximum value of push-pulse induced photocurrent (δJ/J) signal indicates larger number of bound-CT states present after initial pump absorption (here it is 900 nm) that can be re-excited by push-pulses to generate free charges. On the other

hand, minimum value of δJ/J for 680 nm excitation indicates lowest number of bound-CT states present which leads to weak photocurrent generation in presence of push-pulses. This is depicted in Fig. 2b where excitation by high-energy photon (red arrow) leads to generation of hot-CT states that can easily go to charge separated state while low-energy photon generates relaxed-CT state. It has been explained in terms of excess energy of hot-CT state to overcome the deep Coulomb attraction. However, how the excess photon-energy behaves towards different materials and morphologies is not clear yet.

LUMO energy offset between donor and acceptor

Energy offset of the lowest unoccupied molecular orbital (LUMO) levels at donor-acceptor interface is driving force for charge transfer state formation in OPVs. In case of fullerene-based acceptors, this offset of ~300 meV allows the electron to be injected from donor polymer to the fullerene acceptor efficiently. However, this high offset lowers the energy of the intermolecular charge transfer state and causes loss of V_{oc} relative to the optical energy gap. Fullerene-based acceptors typically provide V_{oc} of 0.5 V causing nearly 50 % loss of total photon-energy absorbed. The emergence of non-fullerene based acceptors has drastically changed the field. The maximum V_{oc} achieved using these acceptors till date is beyond 1.2 V [12]. Recently, much attention has been given to minimize the energetic offset between either the ionization energies or the electron affinities of the donor and acceptor orbitals which increases the energy of the interfacial CT states (hot-CT state), hybridizes the CT states and local-exciton, and increases V_{oc} of the system [13]. Although it is not clear how smaller offsets may affect the carrier separation and its timescale.

Timescale for carrier extraction

The photogenerated electron-hole pair has to overcome Coulomb attraction in order to generate free charges. But it undergoes several relaxation pathways to minimize its energy and shorter electron-hole distance. Time-resolved two-photon photoemission (2PPE) spectroscopy has been used to track the formation of this hot-CT exciton in 100 fs followed by its relaxation in 1 ps timescale in a zinc-phthalocyanine (ZnPc)/fullerene (C_{60}) donor-acceptor model [10, 14]. Fig. 3a shows the 2PPE spectra at different pump-probe delays [14]. The photogenerated singlet state (S_1 with peak centered at 1.6 eV) on ZnPc undergoes charge transfer at the ZnPc/C60 interface to generate hot-CT exciton (CT_h peak centered at 1.36 eV) in 100 fs. This high energy CT exciton decreases its energy with time and forms low-energy relaxed CT excitons (CT_1 and CT_2 with peaks centered at <1 eV) in 2 ps. The delocalization length of CT states during this evolution changes from 4 nm (in hot-CT_h) to 1–3 nm (in relaxed CT_1 and CT_2) as depicted in Fig. 3b. This relaxation of CT exciton results into a loss of energy
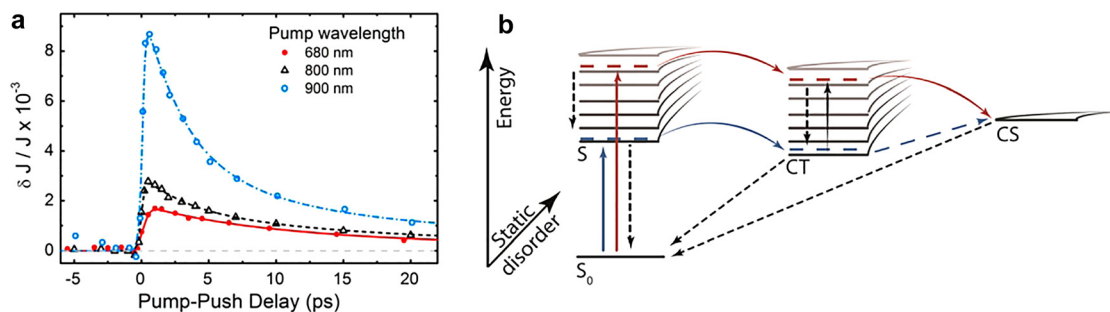

Fig. 2: a) Pump-push-photocurrent experiment at different excitation pump wavelengths showing the change in photocurrent (δJ/J) as a function of pump-push delays. b) Energy level diagram depicting absorption of light with high energy (red arrows) and low energy (blue arrows) which are then followed by charge transfer and charge separation processes. Reprinted with permission from Ref. [7]. Copyright 2012 American Chemical Society.

of 300 meV. Large binding energy of the relaxed CT state makes it difficult to dissociate into free charges and recombination will be likely the consequence. Therefore immediate charge separation (in <1 ps timescale) before the hot-CT state relaxes would be necessary to avoid trapping of charges in deep Coulomb wells. Charge separation assisting processes like long-range delocalization, free energy gradient at the interface or making the instantaneous exciton more polarizable have to occur before the carrier cooling and thermalisation timescale of 1 ps. Thus timescale for carrier extraction becomes extremely important in OPVs. Device architectures that help immediate extraction of charges from hot-CT exciton can potentially exceed the cooling limit. In addition, molecular parameters that can improve lifetime of hot-CT states should be investigated so that there is sufficient time to extract these hot-carriers.

Removing disorder morphology

An organic solar cell consists of interpenetrated nanodomains of donor and acceptor molecules. Long-range charge delocalization and rapid separation are the key for escaping the Coulomb trap. Such electronic delocalization can be intramolecular (favored by long conjugation length in a polymer backbone) as well as intermolecular (favored by crystalline morphology resultant from proper orientation of chromophores). This brings up the role of film morphology on hot carrier generation, its transport and dissociation. Disorder morphology acts as a trap site that causes loss of carrier density. Thus minimizing density of trap states can improve I_{sc} of the system [15]. In addition, disorder morphology reduces delocalization and mobility of carriers as the carriers relax within the density of states [16]. This can again lead to reduced V_{oc} of the device. Thus making the film more crystalline (defect free) can potentially improve hot-carrier generation.

Planarity of semiconductor backbone

Planarity of polymer backbone can affect the energetics of carriers generated. The instantaneously generated exciton can undergo local torsional relaxation in ultrafast timescales [17]. This results into a planar and energy minimized backbone in the excited state. Recently we have tracked excited state Raman signal of the exciton in a donor-acceptor based low-bandgap copolymer as shown in Fig. 4a [18]. The enhanced Raman activity of the 1228 cm^{-1} C-H bending mode along with ultrafast red-shifting of the C=C stretching mode (1422 cm^{-1}) of bridge thiophene indicate that the thiophene bridge (that connects donor and acceptor rings) can undergo planarization. This leads to stabilization of photogenerated exciton in $200-500$ fs to form hot-ICT state followed by its cooling to localized-ICT state (see Fig. 4b). This relaxation is one of the major loss mechanisms in polymer based solar cells. One way to circumvent such issue is by using a planar backbone that minimizes the relaxation loss and generates the exciton having more energy i.e. hot-exciton. Therefore, by choosing materials
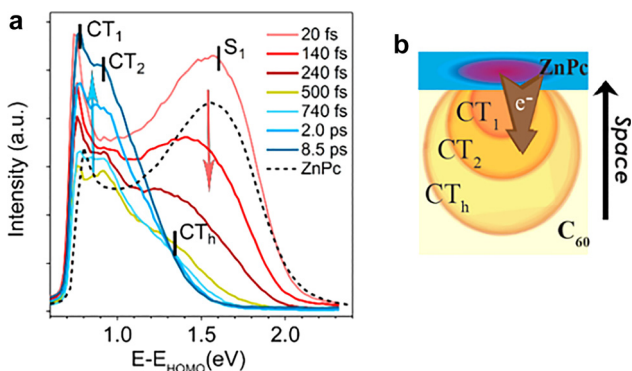

Fig. 3: a) The two-photon photoemission (2PPE) spectra of zinc-phthalocyanine (ZnPc)/fullerene system recorded at different time delays. Spectra evolve with time from S_1 to CT_h to CT_1 and CT_2. Black dash line is 2PPE spectrum for only ZnPc representing S_1 state which matches with the 20 fs spectrum for ZnPc/C$_{60}$ system. b) Schematic showing delocalization length decreases from CT_h to relaxed states CT_1 and CT_2. Reprinted with permission from Ref. [14]. Copyright 2017 American Chemical Society.
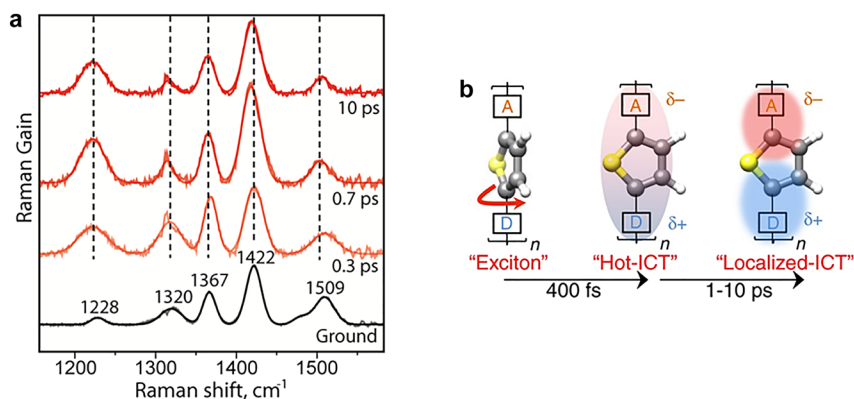
Fig. 4: a) Femtosecond stimulated Raman spectra of donor-bridge-acceptor based copolymer at different pump-probe time delays. 'Ground' represents ground state spectra. b) Schematic of the exciton relaxation via thiophene bridge planarization to generate hot delocalized intramolecular charge transfer state (ICT), and its subsequent cooling dynamics. Adapted from Ref. [18]. Copyright 2017 Springer Nature.

with planar backbone, the timescale as well as energetics of planarization will be modified and the absorbed energy can be utilized completely for carrier generation at higher V_{oc}. Indeed recent studies have found reduced voltage loss and increment in PCE by choosing planar backbone organic semiconductors [19, 20]. In-detail studies on correlating backbone planarity with carrier relaxation and photovoltaic performance will help to minimize loss channels in OPVs.

Re-excite the localized state into delocalized hot state

Photogenerated electron-hole pairs in the semiconductor backbone can undergo several relaxation pathways and become trapped into some localized state. However, this Coulomb trap has to be overcome in order to make free charges for efficient photocurrent generation. Bakulin and coworkers used IR pulses (2200 nm) that re-excite the relaxed localized charge transfer states (CT_0) to delocalized states (CT_n) in polymer:fullerene heterojunction (depicted in Fig. 5a) and observed improved photocurrent generation (as shown in Fig. 5b) [3]. This IR-pulse induced delocalized hot-carrier generation is the key for long-range charge separation and
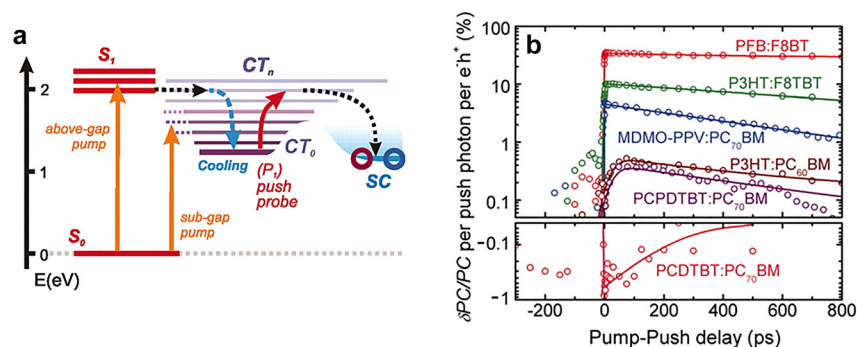

Fig. 5: a) Energy level diagram showing singlet, charge-transfer (localized CT_0 and delocalized CT_n) and separated-charge (SC) states. Solid arrows represent optical transitions (red arrow is the IR push pulse), and dashed arrows indicate energy/ charge-transfer processes. b) Pump-push-photocurrent experiments in a series of materials showing push pulse induced transient photo-current (PC) enhancement. From Ref. [3]. Reprinted with permission from AAAS.

results in improved photo-current generation. Based on the study on different materials as shown in Fig. 5b, they proposed that the extent to which this localized CT_0 state can be pushed to delocalized CT_n state depends on the material systems due to different degree of delocalization. But generally optical excitations can detrap these localized CT_0 states. This idea is also supported by recent work where a near-IR push pulse has been used to excite the relaxed exciton to its higher energy delocalized state and overcome the intrinsic coulomb attraction in polymer aggregates [21].

Excitation of vibrational modes

Increasing experimental and theoretical evidences highlight dominant role of hot exciton dissociation on ultrafast time scales, likely assisted by coupled molecular vibrations [22, 23]. Bakulin et al. observed that excitation of certain vibrational modes of pentacene in the 1200–1500 cm^{-1} region using IR pulses leads to an enhanced photocurrent [24]. Fig. 6 contains a broad signal (at +30 ps) corresponding to enhanced photo-current. This can be explained because of intraband excitation that brings the associated charge carriers to higher-lying hot-state which is more delocalized and has higher mobility. On the other hand, the narrow-line response observed at certain IR frequencies corresponds to pentacene vibrational modes. Therefore vibrational excitation can lead to coupling between electronic and vibrational degrees of freedom that favors hot-carrier generation and enhancement of photocurrent. It is possible that excitation of few important modes in the polymer backbone like thiophene bridge torsional motion [18] could lead to direct hot-ICT formation and improve photocurrent generation. In future, vibration driven hot-carrier generation in various organic semiconductors will be an interesting field to explore.

Summary and perspective

Ultrafast relaxation and recombination losses in OPVs are unavoidable channels. But they could be minimized by generating hot-carriers efficiently. Here, I have described different ways to generate hot-states and how they impact into free carrier generation. It is quite evident that energetics and dynamics of hot-carriers are two crucial parameters that need to be optimized in order to control their nature. Hot-carriers in OPVs are limited by their short life-time (few hundreds of femtosecond) as they localize easily. We need to understand what molecular parameters can enhance their lifetime so that we get sufficient time to dissociate them. At the same time, long-range delocalization is required to dissociate and transport these carriers rapidly within their lifetime. Tuning proper orientation [25] of donor/acceptor materials could also be crucial to alter carrier delocalization lengths. New computational efforts could be useful to engineer such orientations. In the quest to
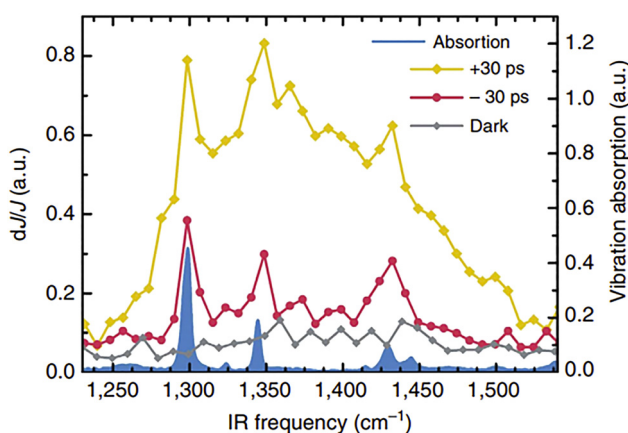

Fig. 6: Effect of frequency-resolved IR irradiation on the photoconductivity of the pentacene/C_{60} at different pump-push delay times, and a no-pump 'dark' measurement. Adapted from Ref. [24]. Copyright 2015 Springer Nature.

improve efficiency of solar cell, we will learn how to design the potential energy surface to dissociate the hot-carriers faster than energy relaxation or recombination processes, on timescale that can reach Quantum coherence limit. In addition, focus should be directed to minimize the relaxation losses. We should choose material that has low-reorganization energy due to planar and rigid backbone as well as suppressed torsional relaxation.

Unravelling multidimensional view of hot-carriers along time, energy and space will be challenging. Long-range charge separation is one of the important characteristics of the hot-carriers. However, it remains unclear what distance they can travel before relaxation and how delocalized electronic states can direct this transport. In detail understanding of the vibrational modes and coupling among these modes that aids hot-carrier delocalization or polarization will provide guidelines for chemically tuning the semiconducting materials. Time-resolved vibrational techniques like impulsive stimulated Raman and femtosecond stimulated Raman spectroscopy in conjunction with multidimensional electronic-vibrational spectroscopy could disentangle this puzzle. We should target materials with long-lived and delocalized charged wavefunctions. Critical understanding of these parameters and ways to improve these will enable us to develop future hot-carrier OPVs.

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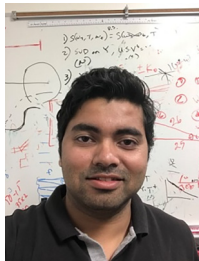
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