P H Y S I C A L   R E V I E W   L E T T E R S

Below-Gap Excitation of π-Conjugated Polymer-Fullerene Blends: Implications for Bulk Organic Heterojunction Solar Cells

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We used a variety of optoelectronic techniques such as broadband fs transient and cw photomodulation spectroscopies, electroabsorption, and short-circuit photocurrent in bulk heterojunctions organic solar cells for studying the photophysics in π-conjugated polymer-fullerene blends with *below-gap excitation*. In contrast to the traditional view, we found that below-gap excitation, which is incapable of generating intrachain excitons, nevertheless efficiently generates polarons on the polymer chains and fullerene molecules. The polaron action spectrum extends deep inside the gap as a result of a charge-transfer complex state formed between the polymer chain and fullerene molecule. With appropriate design engineering the long-lived polarons might be harvested in solar cell devices.

The most efficient organic solar cells to date are based on bulk heterojunctions (BHT) of π-conjugated polymer-fullerene blends, with up to ~5.5% certified power conversion efficiency [1]. Traditionally, the mechanism of charge separation in polymers that are lightly doped with C_{60} has been considered to be a single-step electron transfer from the photoexcited polymer chain onto the fullerene acceptor molecule [2]. Additionally, it has been proposed that an interfacial dipole formation at the donor-acceptor interface assists charge separation in more heavily doped polymer (blend) films [3]. Recently, however a range of reports have indicated that the photoinduced charge separation process in the blend involves one or more intermediate steps. One such step may be the photogeneration of a Coulomb bound polaron pair occupying a charge-transfer complex (CTC) state formed between the polymer and the fullerene [4]. Evidence for such an intermediate state consists of: (i) reports of long wavelength (near-IR) photoluminescence from films, and near-IR electroluminescence from organic light emitting diodes based on polymer-fullerene blends [4]; and (ii) weak absorption tail below the polymer gap [4–6]. However, more direct evidence is needed for revisiting the photoinduced charge-transfer mechanism in the blends; and this may be crucial for improving the power conversion efficiency of all-organic solar cells.

In this work we study the photophysics with below-gap (BG) excitation of films and solar cells based on blends of a substituted poly-phenylene-vinylene (PPV) derivative: 2-methoxy-5 − (2′-ethylhexyloxy) (MEH-PPV) [Fig. 1(a) inset] and C_{60}; using a variety of transient and steady state optoelectronic techniques, which provide more direct evidence for the existence of a CTC state deep inside the energy gap. The techniques used here include fs transient and cw photomodulation (PM) spectroscopies, electroabsorption (EA), and short-circuit photocurrent (PC) in BHT organic solar cells. Using below-gap excitation with photon energy, $\hbar\omega$ at 1.55 eV we found that localized polarons

are *instantaneously* photogenerated on the polymer chains and C_{60} molecules, without involving intrachain excitons as the first step for the charge separation. Moreover, the polarons action spectrum extends down to $\hbar\omega \sim 1.3$ eV. Additionally, EA spectroscopy reveals the existence of a prominent below-gap band at $\hbar\omega \sim 1.55$ eV, which we identify as due to the lowest lying CTC state formed between the polymer and C_{60}. Being localized, the long-lived polarons with below-gap excitation do not contribute substantially to the solar cell PC having traditional structure. However, they might be more efficiently harvested with a more properly designed solar cell.

The MEH-PPV and C_{60} powders were bought from ADS (Canada). The 1:1 (in weight) MEH-PPV–C_{60} blends were prepared from solution of 2 mg/ml each of both polymer and C_{60} in toluene that was thoroughly dissolved by an ultrasonic mixer for ~4 h, and subsequently drop cast on KBr substrates. For cw PM measurements with below-gap excitation we prepared an intentionally thick film with optical density >4 throughout the visible spectral range. For the BHT organic solar cells we used a standard fabrication method [7], where the active MEH-PPV–C_{60} blend was sandwiched in between a hole- (PEDOT-PSS) and electron- (LiF) transport layers, caped by a transparent ITO and Al electrode, respectively. The *I-V* response and short-circuit PC (I_{sc}) action spectrum were measured under illumination from a xenon lamp, of which intensity was normalized by the device optical absorbance.

For the broadband transient PM spectroscopy we used the fs two-color pump-probe correlation technique with *two laser systems* based on Ti:sapphire oscillator [8]: a low power (energy/pulse ~0.1 nJ), high repetition rate (~80 MHz) laser for the mid-IR spectral range; and a high power (energy/pulse ~10 μJ), low repetition rate (~1 kHz) laser for the near-IR to visible spectral range. The pump $\hbar\omega$ for both laser systems was either below-gap excitation at 1.55 eV, or above-gap (AG) excitation using frequency doubling at 3.1 eV. For the low intensity mea-
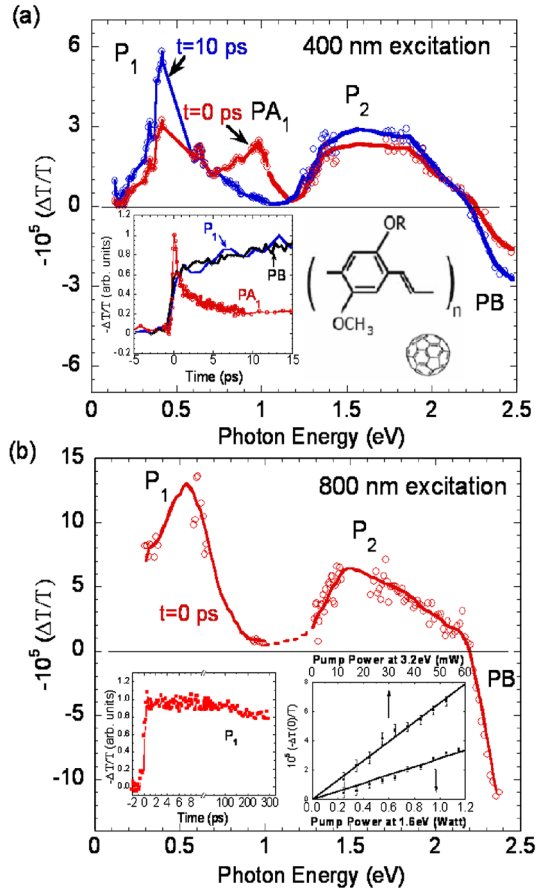
FIG. 1 (color online). The transient PM spectrum of MEH-PPV–C_{60} (1:1) blend film with *above gap* (a) at $t = 0$ (red) and 10 ps (blue), and *below-gap* (b) excitation at $t = 0$. The polaron PA bands P_1 and P_2, exciton PA_1, and PB band are assigned. The insets in (a) show the ultrafast dynamics of the various bands up to 15 ps, and the polymer and fullerene backbone structures, respectively. The insets in (b) shows the P_1 band dynamics up to 300 ps (left) and its excitation intensity dependence with above-gap and below-gap $\hbar\omega$ (right).

surements we used an optical parametric oscillator (Opal, Spectra Physics) as a probe beam with $\hbar\omega$ from 0.2 to 1.05 eV [8]. The probe beam for the high intensity measurements was white light supercontinuum with $\hbar\omega$ from 1.15 to 2.7 eV. The transient PM signal, $\Delta T/T(t)$ is the fractional change in transmission, T, which is negative for photoinduced absorption (PA), and positive for photobleaching (PB).

The pump beam for the broad-band cw PM spectra was an Ar^+ at 2.5 eV (AG) or Ti:sapphire at 1.55 eV (BG) excitation that was modulated at various frequencies, f; and an incandescent tungsten/halogen lamp for the probe [9]. The PM signal was measured using either a phase sensitive lock-in technique with a monochromator, and various combinations of grating, filters, and solid state photodetectors for $0.3 < \hbar\omega$ (probe) <2.7 eV; or averaging ~6000 scans of pump "on" and "off" using a FTIR spectrometer for $0.05 < \hbar\omega$ (probe) <0.4 eV [9]. For the PA action spectrum of polarons we used a xenon incandes-

cent lamp of which beam was dispersed through a second monochromator, and normalized for obtaining the incident photon for the photoinduced absorption of polarons. The EA spectrum was obtained by measuring the electric field induced ΔT using a lock-in amplifier set at $2f$ due to field modulation at f; where the film was deposited on a specially designed structure that contained interlocked electrodes [10].

In a strictly 1D chain model, a single charge carrier added onto the polymer chain forms a spin $\frac{1}{2}$ polaron, with two allowed optical transitions, P_1 and P_2 below the optical gap [9]. In addition, because of the relatively strong electron-phonon coupling in π-conjugated polymers, the polaron excitation renormalizes the frequencies of the Raman-active amplitude modes. The small polaronic mass causes these IR-active vibrations (IRAV) to possess large oscillator strengths [9]. Once the electron-hole interaction is added to the model Hamiltonian, then the excited states become excitonic in nature with alternating odd (B_u) and even (A_g) parity symmetry [11]. Within this model the lowest lying singlet π-exciton in PPV-like chains is the $1B_u$, which is strongly coupled to an A_g state, namely, the mA_g. This produces a strong optical transition, PA_1 in the mid-IR that characterizes the intrachain exciton [8,10]. The characteristic PA bands P_1 and P_2 and IRAV's for polarons; and PA_1 for excitons facilitate the study of these two different transient photoexcitations in the PM spectrum of π-conjugated polymers [8–10].

Figures 1(a) and 1(b) show the transient PM spectra of a 1:1 MEH-PPV–C_{60} blend with AG (400 nm) and BG (800 nm) excitation, respectively. The $t = 0$ PM spectrum with above-gap excitation (a) contains three PA bands peaked at about 0.4 eV (P_1), 1.5 eV (P_2), and 1.0 eV (PA_1), which are, respectively, due to intrachain polarons and excitons; and an accompanying PB band above 2.2 eV. The left inset to Fig. 1(a) shows that P_1 polaron and PB (at 2.5 eV) both increase with time simultaneously with PA_1 exciton decay [12], so that at $t \sim 10$ ps only the polaron PA bands P_1 and P_2 remain in the PM spectrum; this in contrast to pristine MEH-PPV [8]. The transient PM spectrum shows that with above-gap excitation the intrachain excitons separate into polarons via an electron transfer reaction from the polymer chain (donor) onto the C_{60} molecule (acceptor); and/or vice versa, with holes transferred from C_{60} onto the polymer [12]. This is a somewhat modified traditional photoinduced charge-transfer mechanism postulated to occur in the blend [12].

Figure 1(b) shows, however that with below-gap excitation, which is not capable of generating intrachain excitons on the polymer (PA_1 is not formed in the PM spectrum at $t = 0$), and the PA excitation intensity dependence remains linear [Fig. 1(b) right inset], polarons are still photogenerated with estimated quantum efficiency (QE) of ~100%. This can be inferred from the two polaron bands P_1 and P_2 in the PM spectrum that are generated instantaneously [Fig. 1(b) left inset], and the PA strength relative to the

absorbed photon density. This indicates that the 1.55 eV pump is a direct transition into a state that is formed at energies *below* the polymer and fullerene optical gaps, which is capable of creating separated charges on the polymer and fullerene without the need of an intermediate step, such as intrachain exciton. This mechanism can be readily explained if the state involved is a CTC lying inside the gap, below the donor and acceptor lowest lying singlet and triplet excitons [4].

Figure 2(a) shows that the cw PA spectrum of polarons photogenerated with below-gap and above-gap $\hbar\omega$ are indistinguishable from each other; both spectra contain the signature of separated polarons, namely, IRAVs, as well as two PA bands P_1 and P_2. We thus conclude that a mechanism exists in the blend through which below-gap excitation is able to generate separated charges on the polymer chains; in agreement with the transient spectrum in Fig. 1(b). However the polarons generated with below-gap excitation are much longer lived [Fig. 2(a) inset], since the P_1 band frequency dependent steeply increases at low f down to ~10 Hz for below-gap excitation, whereas the P_1 increase at low f saturates at ~100 Hz for above-gap polarons. In fact by fitting the frequency dependencies
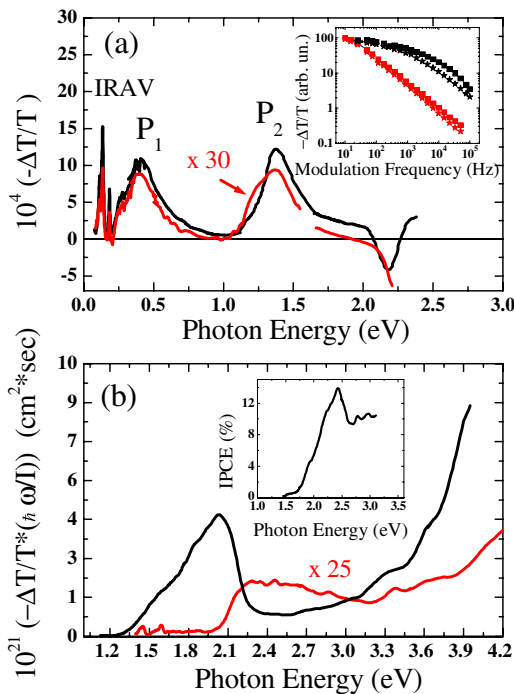

FIG. 2 (color online). (a) The cw PM spectrum of MEH-PPV–C_{60} (1:1) blend film at 80 K, obtained with above gap (black) and below-gap (red, ×30) excitation. The polaron PA bands P_1, P_2 and IRAV's are assigned. The inset shows the polaron P_1 band modulation frequency response measured with above-gap (black) and below-gap (red) excitation at two intensities that differ by a factor 5. (b) The P_1 action spectra/impinging photon of the MEH-PPV–C_{60} blend (black) and pristine MEH-PPV films (red, ×25). The inset shows the action spectrum of the short-circuit current in a solar cell based on the MEH-PPV–C_{60} blend.

we found that the polaron lifetime with below-gap excitation is about *two-orders of magnitude longer* than that of polarons with above-gap excitation, whereas their excitation intensity dependence saturates at moderately high intensity. This dynamics cannot be explained simply by bimolecular recombination kinetics [13], where the polaron density with below-gap excitation is much smaller (see the decay kinetics in Fig. 2(a) for various excitation intensities). We thus conclude that polarons with below-gap excitation are more localized, having much slower recombination kinetics.

Figure 2(b) shows the polaron P_1 action spectrum in pristine MEH-PPV and MEH-PPV–C_{60} blend. From the action spectra we conclude that polarons in the *pristine* polymer are photogenerated *exclusively* with above-gap excitation, having a clear onset at the polymer optical gap (~2.1 eV). In contrast, polarons in the blend can be photogenerated with below-gap excitation with high QE down to ~1.3 eV. The *apparent* band in the action spectrum for $\hbar\omega < 2$ eV is caused by the immense increase in the polaron lifetime with below-gap excitation; and thus for calculating the effective of polarons below-gap polarons, the action spectrum shown in Fig. 2(b) should be reduced by the ratio of below-gap and above-gap polaron lifetime (a factor of ~120). Nevertheless the below-gap absorption also steeply decreases at low $\hbar\omega$ [Fig. 3(a) inset], so that these two effects somewhat compensate each other, giving a *substantial* polaron QE for below-gap excitation in the blend.

The inset in Fig. 2(b) shows the PC action spectrum in a MEH-PPV–C_{60} (1:1) solar cell device. Although the PC spectrum has a below-gap tail down to ~1.5 eV [5,6], the PC signal is substantially lower with below-gap than with above-gap excitation; in sharp contrast with the P_1 action spectrum shown in Fig. 2(b). This is compelling evidence that below-gap excitation results in polarons that are less capable to substantially contribute to the device photovoltaic response, because they are less mobile compared to polarons generated with above-gap excitation. However the below-gap photogenerated polarons might be still harvested in solar cells with more proper design engineering. In the present solar cell design the localized below-gap polarons are detrimental, because they serve as traps and recombination centers for the more mobile photocarriers generated in the device with above-gap excitation.

A direct proof for the existence of a below-gap CTC in the blend is provided by the EA spectroscopy. Figures 3(a) and 3(b) summarize the respective EA spectra of pristine polymer and C_{60}, as well as their blend. In all cases we found that near the band-edge EA $\sim F^2$, where F is the field strength [10]. This has been explained as due a second order Stark shift of the lowest lying exciton state and its phonon replicas [14]. Indeed Fig. 3(a) shows a derivative-like feature with zero crossing at 2.2 eV ($\approx E(1B_u)$) for MEH-PPV [14], and 2.4 eV ($\approx$ charge-transfer state, CTS) for C_{60} [15]. Figure 3(b) shows that the EA spectrum in the blend for $\hbar\omega > 2$ eV is a superposition of the EA spectra
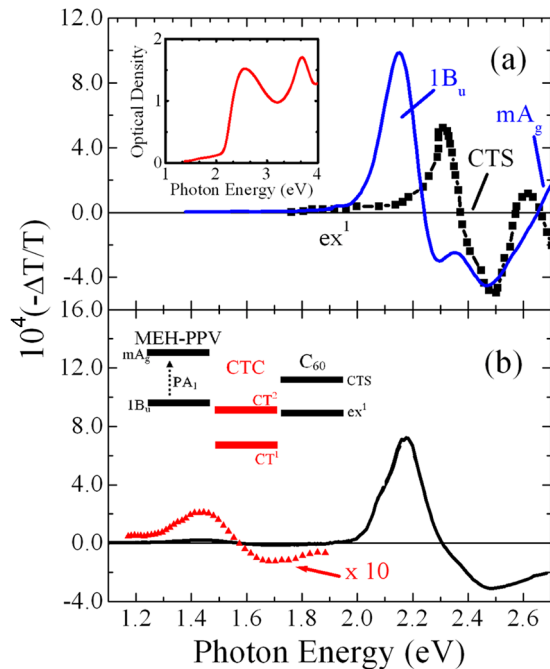
FIG. 3 (color online).   The EA spectra of pristine MEH-PPV (blue line) and C_{60} (black squares) (a); and MEH-PPV–C_{60} blend (b), where the below-gap spectrum is also shown multiplied by a factor of 10. The various bands $1B_u$, mA_g for the polymer [13], and CTS for the C_{60} [14] [for their definition see text and inset (b)] are assigned. The inset in (a) shows the absorption spectrum of the MEH-PPV–C_{60} blend; whereas the inset in (b) shows schematically the respective energies of the lowest lying excitons in the MEH-PPV and C_{60}, and those of the CTC formed between the polymer and fullerene.

of the constituents, which is somewhat broader due to excess disorder in the blend. However the EA spectrum of the blend also contains a prominent derivativelike feature in the near-IR region with zero-crossing at ~1.57 eV, similar in shape to the EA of the $1B_u$ state in the polymer [Fig. 3(a)]. We thus conclude that the near-IR feature is due to Stark shift of a CTC *excitonic state* that is formed in the blend below the optical gap of both constituents [16]. The below-gap absorption spectrum of the blend [Fig. 3(a) inset] indeed shows a long tail down to ~1.3 eV [4–6], that is too weak to produce a substantial contribution to the EA; unless the dipole moment of this below-gap state is very strong. Traditionally, a CTC state has strong dipole moment [15,16], and thus is a natural candidate to explain the below-gap state formed in the blend. This is schematically shown in Fig. 3(b) inset, where the CTC at ~1.57 eV in the blend lies below the lowest lying singlet excitons in MEH-PPV and C_{60}, respectively.

In summary we showed that polarons are photogenerated in (1:1) MEH-PPV–C_{60} blends with high QE with both above-gap and below-gap excitation. Using EA spectroscopy we identified a CTC state lying deep inside the gap that readily explains both the below-gap excitation and

near-IR photoluminescence in the blend. Using action spectra of polaron PA and PC in an organic solar cell we showed that the polaron generated with below-gap excitation are more localized compared with polarons with above-gap excitation, and thus do not substantially contribute to the PC in present devices. With more clever design of the solar cell, however, these below-gap polarons may also contribute to the PC, and consequently increase the power conversion efficiency. Similar results were also obtained in our laboratory with other polymer-fullerene blends, and we thus conclude that CTC in the blends are typical; blends that do not show CTC states are inferior for solar cell applications [4].

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