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Barrierless Free Carrier Formation in an Organic Photovoltaic Material Measured with Ultrafast Vibrational Spectroscopy

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Free carrier formation, the escape of electrons and holes from Coulombically bound radical pairs at donor/acceptor interfaces, is an essential step in the cascade of photochemical reactions in organic photovoltaic (OPV) materials.[1] Electrons and holes are believed to be Coulombically bound to donor/acceptor interfaces by a few tenths of an electronvolt (eV).[2] The efficiency of free carrier formation can strongly influence the charge collection characteristics of organic solar cells. Two mechanisms have been proposed for this process. One proposal suggests that excess vibrational energy remaining in bound radical pairs following electron transfer provides the energy needed to overcome the electron−hole Coulombic attraction.[3,4] Another proposal suggests that electric fields at donor/acceptor interfaces arising from interface dipoles[5−7] decrease this Coulombic attraction.[8] We term these mechanisms phonon-assisted and electric-field-assisted free carrier formation, respectively.

To gain insight into the relative importance of these mechanisms, we performed temperature dependent visible pump-infrared probe (vis−IR) spectroscopic studies of the dynamics of free carrier formation in a 1:1 (by mass) blend of the conjugated polymer, CN-MEH-PPV, with the electron-accepting functionalized fullerene, PCBM (Figure 1a). As we will show, the temperature dependence of the rate of escape of electrons from the interfaces reveals that charge separation is effectively barrierless. The energy needed to overcome the Coulombic attraction of electrons and holes arises from the photochemical reaction rather than from the thermal bath, resulting in a temperature independent rate of escape of electrons from the interfaces on ultrafast time scales in this polymer blend.

We previously demonstrated that the vibrational frequency of the carbonyl (C=O) stretch of PCBM is sensitive to the location of the molecules relative to the interfaces formed between PCBM clusters and CN-MEH-PPV.[9] The carbonyl frequency, which is higher at the interfaces, is influenced by a vibrational Stark shift[10] in conjunction with a solvatochromic shift[11] arising from interactions with the polymer phase. We estimate that the solvatochromic shift is much larger than the Stark shift.[8] The observed trend in carbonyl frequency and radial position within the roughly spherical domains of PCBM[9] is illustrated in Figure 1b.

The instrumentation used in this study has been described in detail.[9] Briefly, an ultrafast Ti:sapphire laser system is used to produce short (100 fs) infrared pulses tuned to the carbonyl absorption of PCBM at 1740 cm^{-1}. Short visible pulses are also produced by the laser system and are tuned to 550 nm to predominantly excite the polymer with minimal direct excitation of PCBM. For the experiments described here, a cryostat was introduced to control the temperature of the polymer blend and to maintain a vacuum around the sample during all experiments.

Transient vis-IR spectra of a 1:1 CN-MEH-PPV:PCBM polymer blend centered on the carbonyl stretch of PCBM are displayed in Figure 2a that were measured at 300 K. The reduced neutral
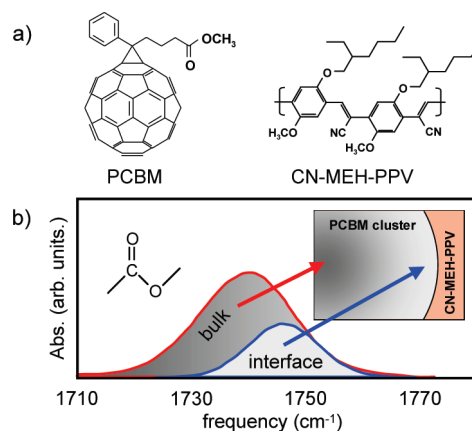
Figure 1. (a) Structures of PCBM and CN-MEH-PPV. (b) Schematic illustration of the carbonyl absorption spectrum with assignments to the corresponding interfacial and bulk regions of the PCBM clusters.
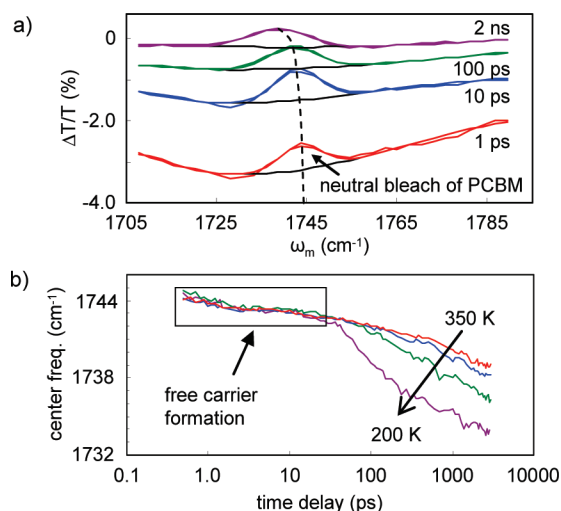
Figure 2. (a) vis−IR spectra of the CN-MEH-PPV:PCBM polymer blend following optical excitation at 550 nm measured at 300 K. (b) Plot of the carbonyl bleach center frequency versus the corresponding time delay measured at 350, 300, 250, and 200 K.

absorption of PCBM resulting from the transfer of electrons from CN-MEH-PPV (termed a bleach peak) is superimposed on a broad absorption offset that arises from positive polarons in the polymer.[12] The bleach peak appears on the higher frequency side of the carbonyl linear absorption spectrum because molecules at the interfaces of the PCBM clusters primarily accept electrons from CN-MEH-PPV.[9] These molecules are the primary electron acceptors because electron transfer is highly distance dependent.[13] We have

independently verified that PCBM molecules at the interfaces possess higher frequency carbonyl bonds.[9]

A fitting procedure was developed to extract the shape of the bleach peak from the transient vibrational spectra.[9] From this fitting procedure, the time dependence of the carbonyl bleach center frequency can be quantified. Figure 2b displays the time dependence of the center frequency of the carbonyl bleach measured at 350, 300, 250, and 200 K versus time on a logarithmic scale. The correlation of the frequency of the carbonyl stretch with the radial position of the host PCBM molecules (Figure 1b) enables us to directly measure the motion of electrons as they diffuse from the interfaces (having the highest frequency carbonyl bonds) toward the centers of the PCBM clusters (having lower frequency carbonyl bonds). The motion of electrons away from the interfaces results in the time-dependent shift of the bleach to lower frequency that appears in Figure 2. The onset of this shift results from free carrier formation (see the region inscribed by the box in Figure 2b).[8] We demonstrated using two-dimensional IR spectroscopy that spectral diffusion does not occur in the carbonyl spectrum on the 1 ps and longer time scale in this polymer blend.[14] Thus, the data indicate that free carrier formation begins on the picosecond time scale, consistent with recent measurements by the Heeger group.[15] The shift of the carbonyl bleach toward lower frequency on longer time scales (>30 ps) indicates the continuation of electron motion in which electrons diffuse further into the PCBM clusters after free carrier formation has occurred. It should be noted that the frequency shift does not result from thermal redistribution in the film or from spectral interference from excited state or photoproduct species.[9] The carbonyl absorption of the PCBM negative polaron does not appear in this spectral window until the microsecond time scale due to vibrational dephasing by mobile electrons.[8]

The comparison of the time and temperature dependence of the bleach center frequency on the less than 30 ps time scale in Figure 2b indicates that the rate of free carrier formation does not change as a function of temperature within experimental precision. This result is inconsistent with a thermally activated process for which the rate at 200 K would be more than an order of magnitude smaller in comparison to the rate at 350 K (given an activation energy of 0.1 eV). The frequency shift dynamics indicate that free carrier formation occurs through a barrierless process. This result suggests that excess vibrational energy remaining in the bound radical pairs immediately following photoinduced electron transfer is responsible for enabling electrons to escape their Coulombic potentials. The presence of this excess vibrational energy does not depend on the temperature of the thermal bath, giving rise to temperature independent charge separation.

We assign the temperature dependent shift of the carbonyl bleach spectrum on the 30 ps and longer time scale to electron trapping in regions of the PCBM clusters with lower frequency carbonyl bonds. These lower frequency regions correspond to sites with greater molecular order (see Supporting Information). Electrons in these regions are expected to be more delocalized and thus have lower free energy, causing them to serve as shallow traps that are occupied preferentially at lower temperature. The correlation of the carbonyl frequency with radial position indicates that these ordered regions are not at the interfaces of the clusters. Since electrons primarily transfer to PCBM molecules at the interfaces, they must move away from the interfaces to enter these ordered regions. Thus, the onset of this trapping process indicates the upper limit to the time scale for separation of the geminate bound radical pairs.

The time scale of free carrier formation is surprisingly fast. We previously adopted an Arrhenius picture of free carrier formation to estimate an activation energy from the dynamics.[8] We proposed that the reduction in the effective barrier arose from the presence of interface dipoles at the CN-MEH-PPV:PCBM junctions. However, it is unclear whether interface dipoles form at these junctions because CN-MEH-PPV has a relatively high ionization potential and electron affinity.[16] Our temperature dependent measurements permit us to reinterpret the origin of the fast charge separation dynamics. In particular, the observation of barrierless charge separation is inconsistent with our previous report of a 0.1−0.15 eV barrier.[8] The temperature independent dynamics presented here suggest that the time scale for free carrier formation may be determined by the rate of vibrational energy redistribution in the bound radical pairs. We propose that vibrational energy originally in Franck−Condon active modes in the CN-MEH-PPV:PCBM electron transfer reaction redistributes into a distribution of vibrational modes including those involved in the transport of electrons between PCBM molecules on the few picosecond time scale.

In summary, we have directly measured the dynamics of free carrier formation in an organic photovoltaic polymer blend material consisting of CN-MEH-PPV and PCBM using ultrafast vibrational spectroscopy. Measurements of the dependence of the rate of this process on temperature reveal that free carrier formation occurs via a barrierless pathway in this polymer blend. The data reveal that energy needed to overcome the Coulombic attraction of bound radical pairs is derived from the photochemical reaction rather than from the thermal bath. It is hypothesized that the rate of free carrier formation is determined by the rate of vibrational energy redistribution. The phonon-assisted free carrier formation mechanism supported in this work is expected to be quite general in OPV materials.

Supporting Information Available: Temperature dependent data showing that electrons become trapped in low frequency carbonyl regions of PCBM at low temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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