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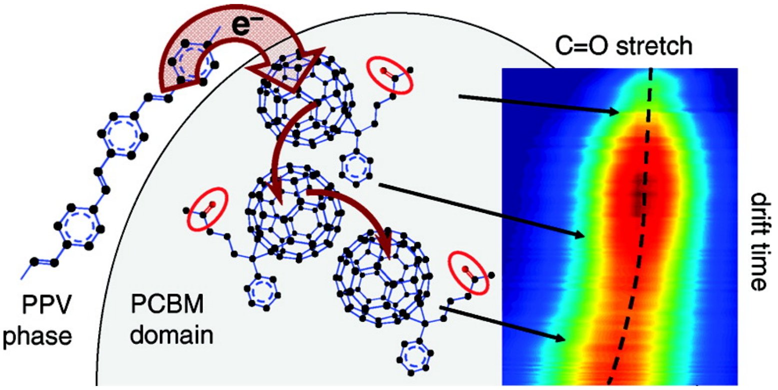

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Watching Electrons Move in Real Time: Ultrafast Infrared Spectroscopy of a Polymer Blend Photovoltaic Material

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Abstract: The dynamics of photoinduced charge separation and the motion of the resulting electrons are examined in an organic photovoltaic material with a combination of ultrafast two-dimensional infrared (2D IR) and visible pump−infrared probe (Vis-IR) spectroscopy. The carbonyl (C═O) stretch of the butyric acid methyl ester group of a functionalized fullerene, PCBM, is probed as a local vibrational reporter of the dynamics in a blend of the fullerene with a conjugated polymer, CN-MEH-PPV. Charge transfer occurs preferentially at the interfaces between the roughly spherical domains of fullerene molecules and the polymer. Comparison of the Vis-IR and 2D IR spectra reveals that the fullerene molecules at the interfaces of the domains possess higher frequency carbonyl vibrational modes, while molecules in the centers of the domains have lower frequency modes relative to the center of the transition. The correlation between the frequency of a carbonyl mode and the spatial position of its host fullerene molecule provides a means to observe the motion of electrons within individual domains through the spectral evolution of the carbonyl bleach. From the spectral evolution, we find that the average radial velocity of electrons is 1−2 m/s, which suggests an intrinsic mobility that is at least one order of magnitude greater than the mobility in the polymer blend. The results indicate that organic solar cells with higher mobility and thus efficiency may be realized by controlling the morphology of the polymer and fullerene materials.

I. Introduction

Organic solar cells promise solar energy at dramatically lower cost per watt of generated electrical power compared with traditional inorganic technologies such as silicon solar cells.[1−4] Significant advancements in the efficiency of organic solar cells have been achieved through the development of the bulk heterojunction[5−7] and the hybrid planar-mixed heterojunction concepts.[4,8,9] Both approaches attempt to maximize the surface area contact between electron donating and electron accepting materials while optimizing the charge carrier mobility in the photovoltaic (PV) active layer. Despite significant progress, the efficiencies of organic solar cells remain low, in large part because charge carriers in the PV active layers have low mobility,[10] which causes the cells to have high series resistance. Device developers compensate for the high series resistance by making the active layers very thin, but this practice limits the efficiency of solar cells by reducing the optical absorption probability so that not all of the incident photons can be used to generate photocurrent.[10]

The mobility of charge carriers in organic solar cells is low because the organic semiconductors on which the cells are based are molecular in nature.[11] That molecular nature causes the semiconductors to be excitonic materials.[12] Therefore, room temperature thermal energy is not sufficient to separate the photoexcitations into free electrons and holes. Rather, pairs of positive and negative charge carriers, called polaron pairs,[13] must encounter interfaces between electron donating and accepting materials to be efficiently separated. Therefore, organic solar cells must possess a high interfacial density.[3−5] Once separated, charge carriers migrate to the electrodes of a solar cell to generate photocurrent. Because organic semiconductors are molecular in nature, charge transport occurs primarily through a hopping mechanism,[14] which depends strongly on the degree of molecular order.[15] To navigate the tenuous balance of competing needs for high molecular order and for high interfacial density, it is necessary to know the origin of the low

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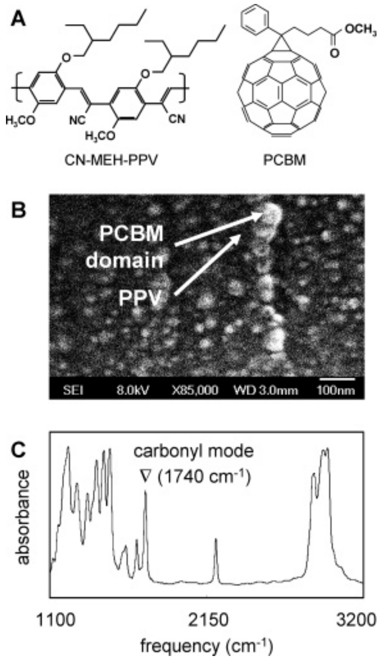

Figure 1. (A) Structures of CN-MEH-PPV and PCBM. (B) SEM image of the morphology of the polymer blend. (C) Linear infrared absorption spectrum of the polymer blend.

mobility—does the high density of interfaces cause disorder at the molecular level which reduces the intrinsic mobility of the materials? Or, do interfacial boundaries in the charge migration pathways primarily inhibit the transport of charge carriers as they migrate to the electrodes?

We used a combination of two-dimensional infrared (2D IR) and visible pump−infrared probe (Vis-IR) spectroscopy to examine an organic PV material at the molecular level as a means to identify the principal reason for the low carrier mobility in organic solar cells. A polymer blend was examined that was composed of the conjugated polymer, CN-MEH-PPV, and the electron accepting functionalized fullerene, PCBM (Figure 1A). The SEM micrograph in Figure 1B depicts a cross section of the polymer blend. The morphology is dominated by roughly spherical domains of the fullerene molecules that are surrounded by the polymer.[6,7,16] The carbonyl (C═O) stretch of the fullerene molecules, which appears at a frequency of 1740 cm^{-1}, was examined as the reporting group to measure the structure and dynamics of the system. The linear infrared absorption spectrum of the sample is represented in Figure 1C. The frequency of the carbonyl group has been found to be sensitive to the local molecular electric field acting on the C═O bond in a variety of chemical environments.[17−19]

The sensitivity of the carbonyl group to its supramolecular environment enables us to compare structural and reactivity information from the 2D IR and Vis-IR methods. We find a correlation between the frequency of the carbonyl groups and the radial position of their host fullerene molecules and use the correlation to estimate the average radial velocity of electrons as they move from the interfaces toward the centers of the roughly spherical fullerene domains. The radial velocity of 1−2 m/s suggests that the intrinsic mobility of electrons in individual fullerene domains is at least one order of magnitude higher than their mobility in the composite polymer blend material. This finding further suggests that the efficiency of organic solar cells may be markedly increased if the phase-separation of the electron donor and acceptor materials can be controlled to eliminate interfacial boundaries along the charge migration paths.

II. Experimental Section

An ultrafast Ti:sapphire laser is used to pump two optical parametric amplifiers (OPAs) in order to carry out three distinct experiments. One OPA is used to generate mid-IR pulses at 5.8 μm with 6 μJ pulse energy and 100 fs duration for the 2D IR and polarization resolved IR pump−probe experiments and as the probe for the Vis-IR experiment. A second OPA generates pump pulses for the Vis-IR experiment at 550 nm with $\sim$ 1 μJ pulse energy and 100 fs duration at the sample. The 2D IR experiments are performed with the two pulse self-heterodyned pump − probe approach.[20,21] The IR pulses from the first OPA are split into two pulses with a 30:1 intensity ratio. The less intense probe pulse is focused at the sample with a 200 μm diameter spot size. The more intense pump pulse passes through a Fabry−Perot interferometer to create a continuously adjustable pump spectrum with a full width at half-maximum of $\sim$5 cm^{-1} that is stabilized to within $\pm$1 cm^{-1}. The spot size at the sample is 250 μm. Polarization resolved IR pump−probe studies are carried out by passing the probe beam through a polarizer that is held by a computer controlled optical rotator (Newport Corp.) that toggles between parallel and perpendicular polarizations relative to the pump beam. The time delay for the Vis-IR experiment is adjusted with a computer controlled 0.6 m linear translation stage. All experiments utilize a 64-element mercury cadmium telluride dual array detector (Infrared Systems/Infrared Associates) to capture 32 probe frequencies simultaneously through a spectrograph (JY Horiba) while facilitating single shot normalization.

The polymer blend sample is mounted on a two-dimensional computer-controlled translation stage to allow for automated raster scanning during the experiment which ensures that a fresh spot on the sample is examined for each data point collected. For 2D IR and polarization resolved IR pump−probe experiments, a reflective sample geometry is used in which the organic PV material is coated on the surface of a silver mirror.[20] The mirror reflects the IR beams so that they do not encounter window materials in their overlap region. This procedure virtually eliminates any nonresonant signal and allows us to analyze the polarization resolved pump−probe data near the time origin of the experiment. We utilize a transmissive sample geometry for the Vis-IR experiments. Charge transfer in the polymer blend creates a high density of electrons that significantly changes the refractive index. This change modulates the reflectivity of the sample, which in turn affects the signal level in the reflective geometry. The transmissive geometry is dramatically less sensitive to this effect and allows us to measure purely absorptive contributions to the spectra. The entire beam path and sample area in the experiment are encompassed by a nitrogen-purged enclosure to remove ambient H_2O and most of the CO_2. All experiments are conducted at room temperature.

The polymer blend is prepared by combining the fullerene (PCBM, American Dye Source) and the polymer (CN-MEH-PPV, H.W. Sands) in chlorobenzene (1.2% and 1.1% by mass, respectively). The solution containing both polymer and fullerene species is drop cast onto a silver mirror or a CaF_2 window and is spun at 80 RPM to ensure that the film dries uniformly. The mass ratio of CN-MEH-PPV to PCBM in

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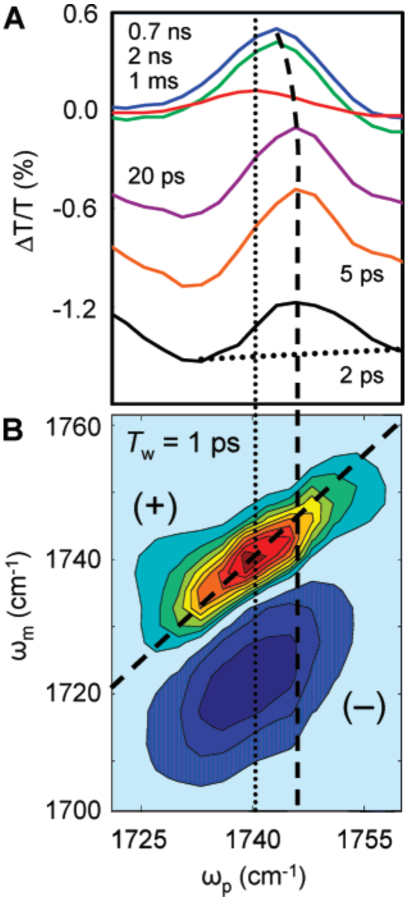

Figure 2. (A) Vis-IR spectra of the 0←1 transition of PCBM molecules that accept electrons following optical excitation at 400 nm. (B) 2D IR spectrum of the 0←1 transition of all PCBM molecules in the polymer blend.

the film is 1:1.1 which we refer to as a 1:1 mixture throughout the text. The film thickness is 3 μm for all experiments that are presented below. The morphology of the film is uniform throughout its thickness and is characterized by 50−100 nm domains of PCBM that are surrounded by the polymer (see Figure 1B).

III. Results

2D IR spectroscopy provides information about the distribution of environments that exist in the fullerene domains of the polymer blend. We use the self-heterodyned pump−probe approach to measure 2D IR spectra[20,21] in which two IR pulses, whose relative time delay can be adjusted, are focused into the material. One of the pulses, the pump pulse, has a spectrum of ~5 cm^{-1} and is used to mark a subset of fullerene molecules by populating the vibrational excited-state of their carbonyl modes. A second pulse measures the corresponding changes in transmission at the ground to first excited state (0←1) and first to second excited state (1←2) vibrational transitions of the molecules that were excited. The 2D IR spectrum (Figure 2B) is created by combining many probe spectra that are recorded with different pump pulse frequencies into a single two-dimensional surface. The horizontal axis, ω_p, represents the center frequency of the pump pulse. The vertical axis, ω_m, displays the probe frequency at which a change in transmission of the sample is measured for a given ω_p frequency. The contours in the spectrum correspond to 10% intervals of the maximum positive signal. The shapes of the 0←1 and 1←2 vibrational features are elongated along the diagonal (slanted dashed line, Figure 2B) because the distribution of environments in the material creates a spatially varying molecular electric field which inhomogeneously broadens the carbonyl mode.[17−19] In protein environments, the frequency of the carbonyl stretch of the polypeptide backbone, known as the amide I band, is sensitive to the structure of its local environment.[22−26] The carbonyl mode of PCBM molecules in the polymer blend exhibits a similar sensitivity.

Vis-IR spectroscopy provides information about the environments in the fullerene domains that are involved in charge transfer and the subsequent evolution of the electrons in the domains. An ultrafast 400 nm optical pump pulse is used to excite an electronic transition of the polymer. The excited-state in the polymer results in a broad absorption in the mid-infrared region[27,28] that is detected with an infrared probe pulse whose time delay can be varied relative to the optical pump pulse. The broad absorption gives rise to the time dependent offset in the Vis-IR spectra (Figure 2A). Excited states in polymer chains that are near fullerene domains can transfer electrons to the fullerene molecules.[29−32] The charge-transfer process decreases the absorption and increases the transmission of the probe pulse at the 0←1 transition of the carbonyl mode of neutral ground state fullerene molecules. The increased transmission at the 0←1 transition, termed a bleach here and throughout the text, appears superimposed on the broad absorption offset of the polymer and is highlighted by the horizontal dotted line (2 ps spectrum, Figure 2A).

Because we primarily excite the polymer but probe the carbonyl mode of PCBM, the center frequency and shape of the bleach in the Vis-IR spectra provides information about the neutral ground state fullerene molecules that accept electrons from the polymer. Comparison of the center frequencies of the 0←1 transition in the 2D IR spectrum (Figure 2B) and the bleach in the Vis-IR spectra (Figure 2A) indicates that not all fullerene molecules in the polymer blend participate in charge transfer. The active set of molecules resides in particular environments that cause their carbonyl modes to have higher frequencies compared with the center of the equilibrium transition. The dotted and dashed vertical lines (Figure 2) highlight the 6 cm^{-1} difference in the center frequencies of the active set of molecules versus the equilibrium distribution. The 1-ms transient spectrum presented in Figure 2A displays a long-lived bleach of the carbonyl mode with a center frequency that matches the equilibrium absorption spectrum of the sample. We are able to use the bleach in the 1 ms transient spectrum as an internal frequency standard to verify the 6 cm^{-1} difference between the bleach in the Vis-IR spectra and the 0←1 transition in the 2D

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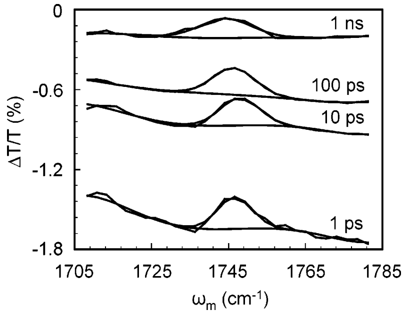

Figure 3. Vis-IR spectra following optical excitation of the polymer blend at 550 nm. Overlaid on the data are best fit spectra used to extract the C=O stretch bleach. See text for details.

IR spectrum. In fact, the bleach spectrum at 1 ms matches the linear IR spectrum in both center frequency and line shape which indicates that the anionic ground state of PCBM does not absorb in the spectral window examined here.

Although excitation of the polymer blend at 400 nm conveniently provides an internal frequency standard, the absorption of PCBM at this wavelength compared to the polymer absorption is not well suited to studying directional charge transfer from the polymer to PCBM. Out of a total optical density of $\sim$4, the PCBM component contributes an optical density of $\sim$1 at 400 nm. This relatively large absorption results in approximately 33% of the pump photons being absorbed by PCBM. The fraction of photons absorbed by PCBM can be reduced to about 10% by utilizing an excitation wavelength of 550 nm. The 550 nm wavelength falls in a local minimum between two forbidden optical transitions of the fullerene[33] and overlaps the rising edge of the polymer absorption. Transient vibrational spectra following 550 nm excitation are displayed at several time delays in Figure 3. The transient spectra are similar to the spectra collected with a 400-nm excitation wavelength with the exception that the long-lived bleach is not observed in the 1 ms spectrum. It is possible that the long-lived bleach in the 400-nm data results from having excited the fullerene directly or from wavelength dependence of the charge recombination dynamics or another photochemical process. We are currently measuring the time scale for back electron transfer following excitation at 355 and 532 nm in the polymer blend (using the second and third harmonics of a YAG laser) to determine whether a wavelength dependence exists. In the subsequent discussion, we analyze the 550 nm excitation wavelength data because of the smaller contribution of PCBM molecules that are directly excited by the pump pulse. The spectra are presented on a wider frequency scale compared with Figure 2 to emphasize that the bleach can be easily separated from the absorption offset.

The contribution of PCBM to the sample absorption at 400 and 550 nm was determined by matching the absorption spectrum of a film of pure PCBM to the long wavelength tail of the sample spectrum where the polymer has negligible absorption. Out of a total optical density of 2.8 at 550 nm, the PCBM component of the blend contributes about 0.3 to the absorbance. We calculated the fraction of photons that were absorbed by PCBM as the pump beam propagated through the polymer blend by numerically dividing the 3-μm thick film into one thousand 3-nm thick layers. The optical density of each layer is low enough that the photon flux can be considered to be constant throughout each layer. The transmission of each layer was calculated, and the fraction of photons absorbed by each component was computed according to their respective optical densities in the 3-nm thick layer. By summing the contributions from all 1000 layers, the fraction of photons absorbed by the PCBM component could be estimated to be about 10%.

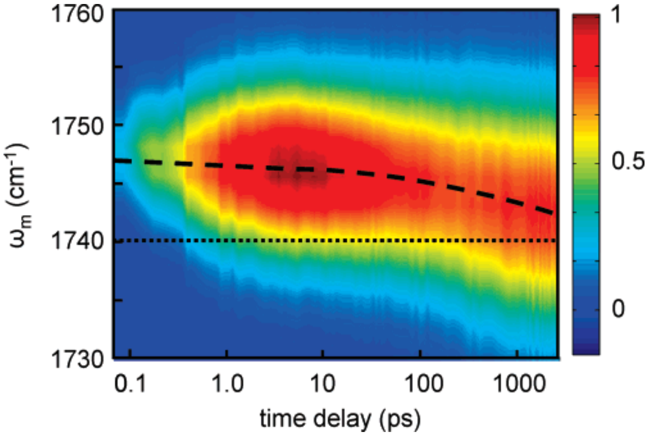

Figure 4. Two-dimensional surface plot of the carbonyl bleach spectrum versus the corresponding time delay.

The bleach spectra were extracted from the Vis-IR data collected with the 550 nm excitation wavelength using a least-squares fitting procedure. The absorption offset was modeled with a third-order polynomial, and the bleach was characterized with a Gaussian line shape. Unique Gaussian and polynomial functions were generated for each time delay that is recorded in the data starting from 50 fs. Before this time delay, the bleach features in the spectra are too small to obtain an accurate fit. The sum of the Gaussian and polynomial functions are overlaid on the Vis-IR spectra for comparison in Figure 3. The polynomials with the Gaussian functions omitted are visible as the lines under the bleach features in each spectrum. The comparison demonstrates that the fitting procedure provides a high-fidelity description of both the absorption offset and the bleach spectrum. We will refer to the best fit Gaussian function of a particular Vis-IR spectrum as the carbonyl bleach of neutral ground state PCBM molecules in the subsequent discussion. Figure 4 displays the carbonyl bleach spectra at each time delay recorded in the experiment plotted versus their corresponding time delay as a two-dimensional surface plot. The dashed curve in Figure 4 is a guide for the eye that highlights the shift of the bleach toward the equilibrium spectrum whose center is indicated by the horizontal dotted line.

To gain information about the subset of PCBM molecules that absorbs at frequencies higher than the center of the transition, we examined the frequency shift of the carbonyl group of PCBM as a function of the polymer content. Linear IR absorption spectra of four films are represented in Figure 5. The spectra were collected at room temperature and have been normalized for comparison. The spectrum of a film of pure PCBM (labeled PCBM) appears with a peak at 1735 cm^{-1}. The addition of a small amount of polymer to the film corresponding to 3% relative to the mass of PCBM shifts the carbonyl absorption to 1738 cm^{-1} (see spectrum labeled 0.03:1). The spectrum corresponding to the film with a mass ratio of 1:1 for CN-MEH-PPV to PCBM exhibits a carbonyl peak at 1740 cm^{-1}

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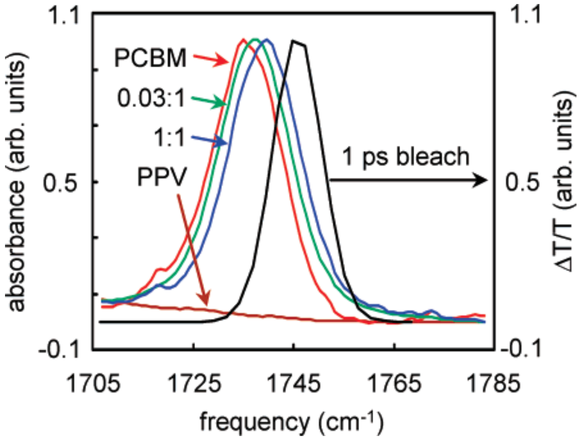

Figure 5. Comparison of linear IR spectra of polymer blend films with various polymer and PCBM content in the region of the carbonyl stretch. Spectrum labels: **PCBM**, spectrum of pure PCBM film with no polymer content; **0.03:1** and **1:1**, spectra of films with indicated mass ratios of CN-MEH-PPV to PCBM; **PPV**, spectrum of pure CN-MEH-PPV film with no PCBM content. The spectrum of the 1-ps bleach from the Vis-IR data has been plotted for comparison.

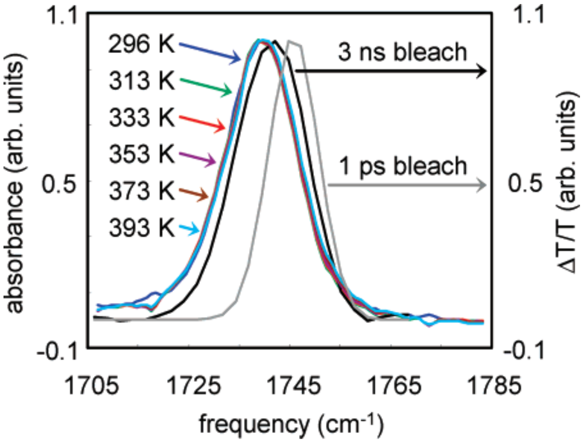

Figure 6. Comparison of linear IR spectra of films of the 1:1 polymer blend of CN-MEH-PPV and PCBM in the region of the carbonyl stretch collected at the indicated temperatures. The 1-ps and 3-ns bleach spectra from the Vis-IR data have been included for comparison.

(labeled 1:1). Films of this composition were examined with the 2D IR and Vis-IR methods that are described above. A spectrum of a film of pure CN-MEH-PPV (labeled PPV) is included to demonstrate that the spectral shift to higher frequency with increasing polymer content does not result from spectral contributions from the polymer itself. Rather, the spectral shift results from the influence of the polymer on the absorption spectrum of PCBM. The spectrum of the carbonyl bleach at 1-ps time delay that was obtained from the Vis-IR data using the fitting procedure described above is included for comparison. The comparison shows that the component of the carbonyl bleach spectrum that arises from the addition of polymer to the PCBM film is also the component that is preferentially involved in charge transfer.

We explored the possibility that the time dependent spectral shift of the carbonyl group of PCBM toward the equilibrium frequency (see Figure 4) might result from heating effects caused by deposition of energy in the polymer blend by the excitation pulse. Figure 6 displays linear IR spectra of the carbonyl stretch of PCBM in the 1:1 polymer blend with CN-MEH-PPV that were collected at 296, 313, 333, 353, 373, and 393 K. The 1-ps and 3-ns carbonyl bleach spectra that were obtained from the Vis-IR data are also included for comparison. The linear IR spectra were collected by first heating the polymer blend to the maximum temperature sampled to allow any morphological changes to occur that might result from annealing the blend at elevated temperature. Linear IR spectra were then recorded at 20 K intervals until the sample cooled to room temperature. The comparison indicates that the spectra undergo less than 0.5 cm^{-1} shift and negligible change in width across the 97 K temperature change. In fact, the precaution of allowing the film to anneal prior to collecting the temperature-dependent spectra was unnecessary because the carbonyl peak frequency measured at room temperature before and after the heating cycle differed by much less than 1 cm^{-1}. The small variations in the spectra that appear at 1718 cm^{-1} and 1773 cm^{-1} result from variations in the ambient water content in the air during the experiment.

The examination of inhomogeneously broadened line shapes with ultrafast 2D IR spectroscopy can provide information about the underlying vibrational dynamics that is not available from linear IR spectroscopy.[34−43] Figure 7A displays 2D IR spectra collected at 1 and 10 ps time delays between the infrared pump and probe pulses.[20] The 1 ps spectrum is reproduced from Figure 2B for comparison to the spectrum at the longer delay time. The spectra have been normalized to their maximum positive signal, and the contours represent 10% intervals. By inspection, it is apparent that the line shapes do not undergo significant change within 10 ps, which suggests that spectral diffusion[44] occurs very slowly. Although the line shapes are largely unchanged over the time period recorded in the spectra, the amplitude of the signal decays by a factor of ∼100 due to vibrational relaxation.[20] The corresponding decrease in the signal-to-noise ratio is exhibited by small distortions in the $0 \leftarrow 1$ and $1 \leftarrow 2$ peak shapes in the 10 ps spectrum.

To examine the time dependence of the line shapes more quantitatively, one-dimensional (1D) horizontal slices were extracted from the center of the carbonyl transition in the 2D IR spectra at an ω_m frequency of 1740 cm^{-1}. The 1D slices extracted from the 1 and 10 ps 2D IR spectra are plotted versus the ω_p frequency axis in Figure 7B. The locations within the 2D IR spectra from which the slices were extracted are indicated by the horizontal dotted lines in Figure 7A. The slices have been normalized, and the linear IR absorption spectrum of the sample has been included to facilitate comparison. The 1D slices contain a limited number of frequency points because the pump frequency was varied in 3 cm^{-1} steps across the ω_p frequency axis.

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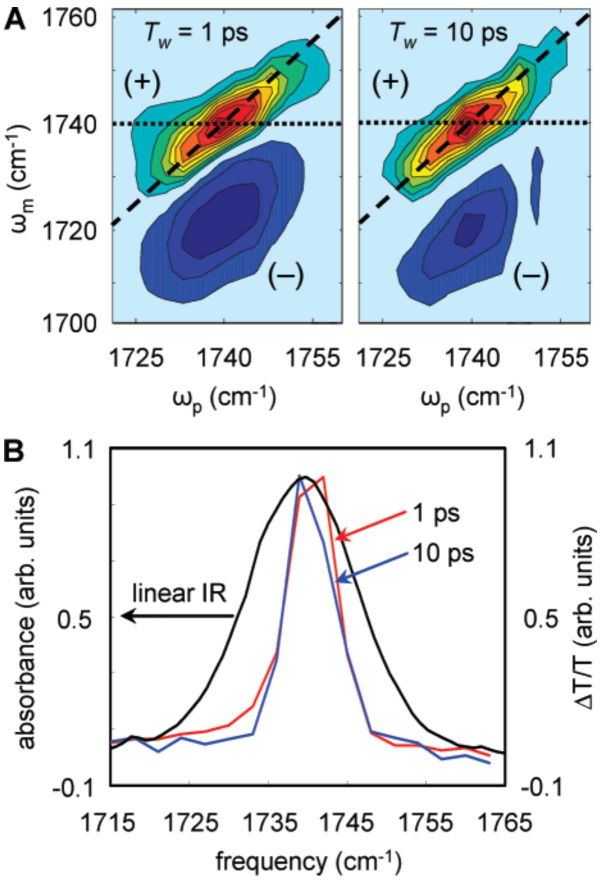

Figure 7. (A) 2D IR spectra of the carbonyl stretch of PCBM measured at 1 and 10 ps time delays. (B) one-dimensional slices taken from 1- and 10-ps 2D IR spectra along the ω_p frequency axis at an ω_m frequency of 1740 cm^{-1}. The linear IR spectrum of the sample is included for comparison. The spectra demonstrate that spectral diffusion does not occur on the 10 ps time scale.

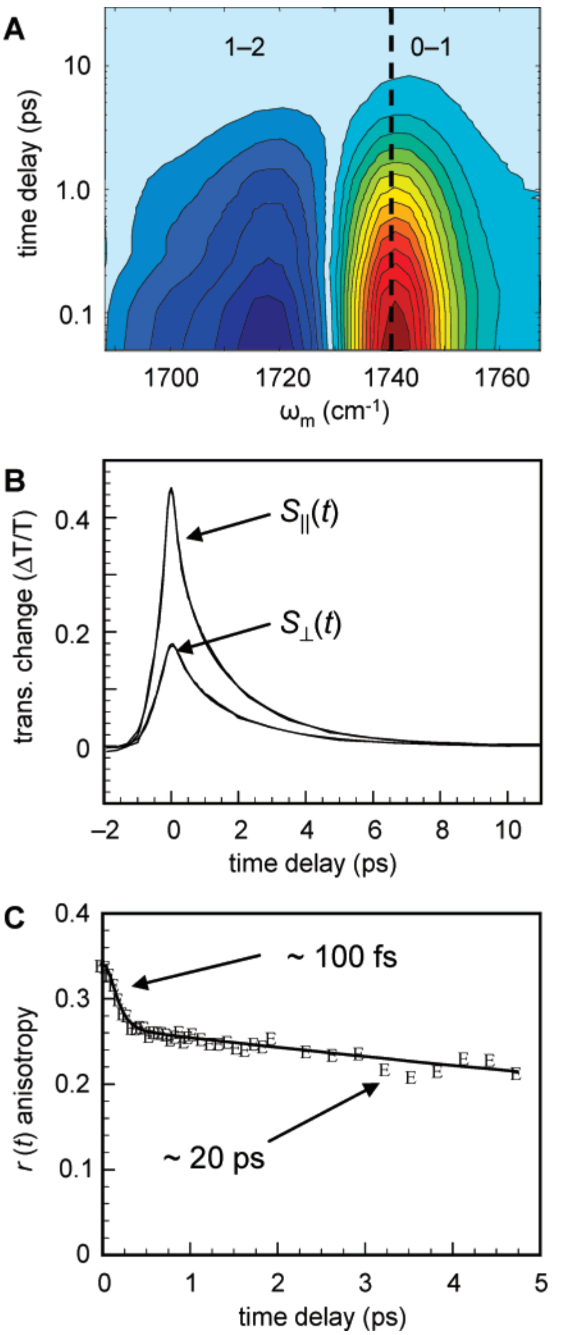

Figure 8. (A) Dispersed IR pump−probe spectra plotted versus time delay. (B) Kinetics traces at 1740 cm^{-1} measured with parallel and perpendicular polarizations of the pump and probe pulses. (C) Anisotropy decay measured at 1740 cm^{-1} indicating facile orientational motion of the carbonyl bond. Fast orientational motion occurs on the 10-ps time scale, but this motion does not cause spectral diffusion.

Orientational relaxation dynamics in condensed phase systems can provide information about local environments.[45−47] If the local environments surrounding carbonyl groups of PCBM molecules cause the vibrational transition of the molecules to be inhomogeneously broadened, then the orientational motion will be associated with spectral diffusion. The absence of spectral diffusion in the carbonyl stretch on the 10-ps time scale suggests that orientational relaxation of the carbonyl group may not occur on this time scale. We examined the time dependent anisotropy of the carbonyl group of PCBM in the 1:1 polymer blend using polarization resolved IR pump−probe spectroscopy to determine whether orientational motion occurs on the 10 ps time scale. The experiments differ from the 2D IR experiments in that the full infrared spectrum is utilized in the pump pulse with a corresponding pulse duration of 120 fs. Pump−probe spectra that were collected with parallel pump and probe polarizations are displayed as changes in transmission in Figure 8A. The horizontal axis, ω_m, represents the probe frequency, and the vertical axis is the time delay plotted on a logarithmic scale at which a probe spectrum was recorded. The contours represent 7% intervals of the maximum positive signal. The data show the $0 \leftarrow 1$ transition on the right side of the panel around 1740 cm^{-1} and the $1 \leftarrow 2$ transition on the left side around 1720 cm^{-1}.

Kinetics traces which report the time evolution of the pump−probe signal at 1740 cm^{-1} are depicted in Figure 8B for parallel, $S_{||}(t)$, and also for perpendicular, $S_{\perp}(t)$, polarizations of the pump and probe pulses. The anisotropy decay of the carbonyl mode, $r(t)$, was calculated from the traces using $r(t) = (S_{||}(t) - S_{\perp}(t))/(S_{||}(t) + 2S_{\perp}(t))$. The anisotropy decay trace that is obtained from the data in Figure 8B is represented in Figure 8C. The decay of the anisotropy indicates that the carbonyl bond undergoes significant orientational motion on the 5-ps time

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scale,[20] yet this motion does not result in spectral diffusion (cross reference Figure 7).

IV. Discussion

A. Spectral Assignments and Correlation to Morphology. In this section, the assignment of transient vibrational features observed in the Vis-IR spectra is discussed and correlated with the underlying morphology of the material. Excitation of the polymer blend at 550 nm results in ultrafast electron transfer from the polymer to PCBM. The formation of the PCBM anion reduces the population of neutral ground state PCBM molecules, which results in a bleach of the carbonyl mode at 1746 cm^{-1} (see Figure 3). The maximum area of the bleach spectrum that occurs at 5 ps indicates that 0.3% of the PCBM molecules in the sample either accept an electron or are excited by the pump pulse at this time delay. Direct optical excitation of PCBM appears with a pulse limited rise. Electron transfer from polymer segments to PCBM occurs on multiple time scales ranging from 45 fs[30] to 1 ps.[48] The area of the bleach spectrum at 150 fs (the end of the pulse overlap region) is about 25% of the area at 5 ps. The bleach area at 150 fs includes both contributions from ultrafast electron transfer and direct excitation of PCBM. At present, we are unable to separate these contributions on the basis of their time dependence because the processes occur too quickly to be resolved in our experiment. However, we are able to separate the contributions on the basis of their corresponding bleach spectra. The center frequency of the bleach that appears at 150 fs is essentially the same as at 5 ps (see Figure 4). We have directly excited a film of pure PCBM and found that the resulting bleach is not shifted 6 cm^{-1} to higher frequency relative to the center of the carbonyl transition of the film. The observation that the bleach center in Figure 4 is shifted to higher frequency by 6 cm^{-1} from the earliest time that it can be observed indicates that the bleach has the same origin at 150 fs and at 5 ps, namely electron transfer—not direct excitation of PCBM. Consequently, we interpret the bleach of the carbonyl mode in the Vis-IR data following 550 nm excitation as occurring exclusively from electron transfer from CN-MEH-PPV to PCBM.

Figure 5 displays the results of a linear IR investigation of the nature of PCBM molecules whose carbonyl modes appear above 1740 cm^{-1}. The carbonyl absorption of a film of pure PCBM is centered at 1735 cm^{-1} (spectrum labeled PCBM). With increasing polymer content, the carbonyl group exhibits a progressive shift of 5 cm^{-1} to higher frequency. The polymer itself contributes only a broad tail in this spectral region. Simple addition of the broad tail to the pure PCBM carbonyl peak cannot explain the direction of the observed shift with increasing polymer content because the summation of the spectra would result in a peak that is shifted slightly to lower frequency relative to the spectrum of pure PCBM. The shift of the carbonyl mode to higher frequency results from the interaction of the polymer with the PCBM molecules. Therefore, the higher frequency side of the transition is assigned to PCBM molecules that reside near polymer domains in the film. The side of the transition below 1740 cm^{-1} is assigned to PCBM molecules that have little interaction with the polymer and by extension are far from the polymer layers. This interpretation is consistent with the carbonyl bleach in the 1-ps Vis-IR spectrum which is reproduced in Figure 5 for comparison. PCBM molecules must reside near polymer segments in order to accept electrons because electron transfer is highly distance dependent.[14,15,49] The bleach spectrum that primarily results from electron transfer overlaps the side of the carbonyl transition that appears when the polymer is blended into the PCBM film.

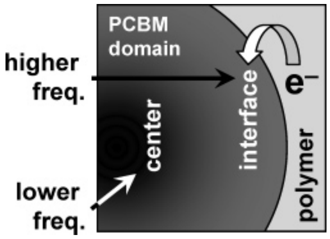

Figure 9. Schematic of the interface of a PCBM domain where charge transfer occurs.

Consideration of the phase-separated morphology of the polymer blend that is depicted in Figure 1B strongly suggests that the frequency of the carbonyl mode of PCBM is correlated with the radial position of the molecules in the domains. This correlation is illustrated in Figure 9. Blends of PPV-based conjugated polymers and PCBM are known to phase separate into roughly spherical domains of PCBM that are surrounded by layers of the polymer.[6,7,16] Given the roughly spherical shape of the PCBM domains, we assert that PCBM molecules near the interfaces of the domains have carbonyl modes that appear around 1746 cm^{-1} because these molecules are closest to the polymer layers. The fact that the entire carbonyl transition shifts to higher frequency in the 1:1 polymer blend suggests that the presence of the polymer perturbs all of the PCBM molecules, even those at the centers of the domains. Therefore, we assert that PCBM molecules at the centers of the domains are perturbed by the polymer but to a lesser extent compared to molecules at the interfaces because of their increased separation from the polymer layers. Correspondingly, we assign the lower frequency portion of the carbonyl transition to PCBM molecules at the centers of the domains. These molecules are also not available to accept electrons because of their large separation from the polymer layers.

The dependence of the carbonyl frequency of PCBM on the proximity to the interfaces in the domains is an empirical observation that does not depend on the exact nature of the interaction that causes the frequency shift. However, the frequency shift can be understood by considering that the frequency is most likely coupled to its environment through the electric field that is generated by the surrounding molecules. A similar coupling mechanism has been found for a variety of vibrational modes including the amide I mode (C=O stretch) in proteins,[17−19] the C≡O ligand bound to myoglobin,[50−52] and the hydroxyl stretch in water.[34,53−55] PCBM molecules near

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interfaces experience electric fields with contributions from the polymer and other PCBM molecules, while molecules in the centers of the domains experience electric fields that originate exclusively from other PCBM molecules. Therefore, we ascribe the correlation of the carbonyl frequencies with the radial positions of their host PCBM molecules to the variation of the electric field in the domains that arises from mixing the materials in the spherical morphology of the polymer blend (see Figure 1B).

B. Time Dependence of the Carbonyl Bleach. Having assigned the higher frequency side of the carbonyl transition to molecules residing near the interfaces of PCBM domains and the lower frequency side to the centers of the domains, we are in a position to consider the origin of the spectral shift of the bleach to lower frequency with increasing time delay (cross reference Figure 4). The physical model pictured in Figure 9 would suggest that the time dependent shift of the bleach arises from the drift and/or diffusion of electrons from the interfaces to the centers of the domains. This model, appealing as it is, has numerous competing models which must be considered. We will explore alternate explanations in the following paragraphs before returning to this model.

Thermal Equilibration Model. Perhaps the most obvious alternate explanation for the time dependent spectral shift to lower frequency would be a temperature dependence of the carbonyl frequency. Relaxation within the excited-state vibrational manifolds of the polymer, electronic excited-state relaxation to form a hot ground electronic state, or charge recombination will deposit significant thermal energy into the polymer blend. This energy will be deposited initially in local environments creating islands of high-temperature that are separated by 3−4 nm (based on the laser spot size and photon flux). Thermal energy will then diffuse between these high-temperature islands to attain an equilibrated temperature within the laser spot in the sample. Assuming a speed of sound of 2000 m/s, thermal diffusion between high-temperature islands can take as little as 2 ps. Thermal diffusion will occur after the relaxation processes. Therefore, the spectral shift that is represented in Figure 4 might result from the superposition of several relaxation processes occurring on different timescales in the blend.

We have estimated a temperature change of 9 K within the laser spot in the sample in the limit that the high-temperature islands reach thermal equilibrium and no heat is dissipated into the surrounding material or substrate. This estimate is based on the specific heat and density of most polymers being ∼1 $Jg^{-1}K^{-1}$ and ∼1 gcm^{-3}, respectively.[56] The specific heat and density of crystalline C_{60} are 0.8 $Jg^{-1}K^{-1}$ and 1.6 gcm^{-3}, respectively.[57] For the purposes of this calculation, we assume that PCBM has the same specific heat and density as crystalline C_{60}. The specific heat and density of the 1:1 blend of CN-MEH-PPV and PCBM are taken as the weighted average of the properties of the two materials − that is 0.9 $Jg^{-1}K^{-1}$ and 1.3 gcm^{-3}, respectively. With a spot size of 250 μm (diameter containing 99% of the photons), a sample thickness of 3 μm, and a pulse energy of 1 μJ, the temperature change can be estimated. The temperature rise in the high-temperature islands before thermal diffusion will likely be much higher than 9 K.

To determine whether the formation and cooling of high-temperature islands might explain the spectral shift observed in Figure 4, we collected linear IR spectra of the 1:1 polymer blend at a variety of temperatures. Figure 6 represents linear IR spectra collected at 296, 313, 333, 353, 373, and 393 K. The 1-ps and 3-ns carbonyl bleach spectra that were obtained from the Vis-IR data are also included for comparison. The maximum temperature change examined in the linear IR spectra, 97 K, exceeds the equilibrated temperature change in the laser spot by an order of magnitude. This large change was examined to estimate the spectral shift that occurs as the high-temperature islands reach thermal equilibrium. Over a 97-K temperature rise, the carbonyl transition shifts to higher frequency by less than 0.5 cm^{-1} and exhibits negligible change in width. In contrast, we observe a 4 cm^{-1} shift in center frequency and a significant change in width from 11.5 cm^{-1} to 16.5 cm^{-1} full width at half-maximum (fwhm) between the 1-ps and 3-ns spectra, respectively. The comparison of the spectra represented in Figure 6 demonstrates that the weak temperature dependence of the carbonyl mode cannot explain the time dependent spectral shift observed in Figure 4. The lack of sensitivity of the carbonyl stretch to temperature likely results from the absence of hydrogen bonds in this system. Without strong coupling of the carbonyl group to a weakly bound moiety such as a hydrogen bond donor, even a 33% increase in the absolute temperature (97 K) apparently has little effect on the vibrational occupation or potential landscape of the carbonyl group.

Local Electron Redistribution Model. An alternate explanation for the time dependent spectral shift is that electrons preferentially transfer to PCBM molecules having carbonyl modes that absorb at 1746 cm^{-1} and subsequently diffuse or drift to neighboring molecules. If the molecules neighboring the transfer sites possess in the ensemble the equilibrium distribution of carbonyl frequencies, then the local redistribution of electrons can explain the shift of the bleach toward the equilibrium spectrum. The interfaces of the PCBM domains are very likely disordered because the blends were not annealed prior to the ultrafast infrared experiments. The disorder will create a distribution of environments surrounding the carbonyl groups. If the structures of the local environments are primarily responsible for determining the carbonyl frequencies, then the equilibrium distribution of frequencies will be randomly dispersed in the domains. Assuming that electrons initially transfer to higher frequency carbonyl sites, they would need to redistribute only within the local disordered interfacial regions in order to sample the equilibrium frequency distribution. However, if the carbonyl frequencies are not primarily determined by the structures of the local environments, then they must be determined by another influence that extends over length scales that are greater than the sizes of PCBM molecules plus their local environments. This latter case would suggest that electron redistribution over greater distances is necessary to explain the shift of the carbonyl bleach to the equilibrium spectrum.

The validity of this model can be tested by determining whether the carbonyl stretch frequency of PCBM is sensitive to the structure of the local environment. To test the model, the spectral diffusion of the carbonyl stretch can be compared with the corresponding orientational relaxation dynamics. As the

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carbonyl group undergoes orientational motion, the bond is forced to sample different regions of the local environment. If the local environment strongly influences the carbonyl frequency, then orientational motion of the bond will be associated with spectral diffusion of the carbonyl frequency. The anisotropy decay of the carbonyl stretch of neutral ground state PCBM is represented in Figure 8C. The fast decay component which decays on the 100-fs time scale was previously assigned to wobbling-in-a-cone orientational motion.[58,59] Following this motion, orientational diffusion of the molecules occurs on the ~20 ps time scale.[20] Fullerenes are known to undergo rapid orientational diffusion on the 10-ps time scale.[60−63] Our measurement reveals slightly slower dynamics because the pendant butyric acid methyl ester group may slow the rotational diffusion of the molecule.[20] The anisotropy decay demonstrates that significant reorientation of the PCBM molecules occurs on the 5 ps time scale.

The 2D IR spectra represented in Figure 7A display the 2-dimensional line shapes of the carbonyl stretch of neutral ground state PCBM at 1- and 10-ps time delays. The line shapes are elongated along the diagonal because the transition is inhomogeneously broadened. The degree of diagonal elongation appears to change very little between 1 and 10 ps. The time dependence of the line shape is displayed quantitatively in Figure 7B, where 1D horizontal slices that were extracted from the 2D IR spectra are presented. The locations in the 2D IR spectra where the slices were extracted are indicated by the horizontal dotted lines in Figure 7A. Horizontal slices[34,35] are presented because they enable us to examine the dynamic width of the $0 \leftarrow 1$ transition without significant interference from the $1 \leftarrow 2$ transition. The 1D slices from the 1- and 10-ps 2D IR spectra were fit with Gaussian functions yielding 6.9 and 7.0 cm^{-1} full widths at half-maximum, respectively. These widths are identical within experimental precision. By comparison, the linear IR absorption spectrum of the carbonyl stretch has a fwhm of 16.7 cm^{-1} indicating that extensive broadening of the 1D line shapes could be observed if spectral diffusion[44] occurred on the 10-ps time scale. The IR pump pulse frequency is determined by a piezo controlled actuator that results in a frequency precision of ±1 cm^{-1}. Slight variations in the pump pulse frequency during the experiment give rise to the 1 cm^{-1} difference in center frequency that appears in the 1D slices in Figure 7B. Although the center frequency of the pump pulse varies slightly in the experiment, the spectral width is constant to within much less than 1 cm^{-1}. We have verified the lack of spectral diffusion within 10 ps by collecting multiple sets of 2D IR spectra at several time delays between 1 and 10 ps. We consistently find that 1D slices extracted from the 2D line shapes do not broaden with increasing time delay. We should note that we have not measured the orientational motion or spectral diffusion of anionic ground state PCBM. The time scale for the fastest frequency shift in the carbonyl stretch (see Figure 4) compares with the orientational diffusion time of PCBM, suggesting that orientational diffusion of the anions might facilitate hopping of electrons between neighboring molecules. At present, we are unable to test this hypothesis directly.

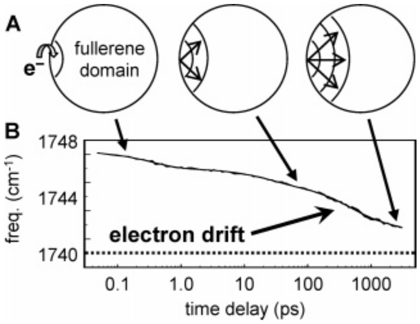

Figure 10. (A) Qualitative snapshots of the radial distributions of electrons as they move from the interfaces to the centers of PCBM domains. (B) Plot of the carbonyl bleach center frequency versus corresponding time delay. The arrows point to the approximate bleach center frequencies that correspond to the extent of movement.

The experimental results presented in Figures 7 and 8 indicate that PCBM molecules undergo rapid orientational motion, yet this motion does not result in spectral diffusion. This observation reveals that the structures of the local environments surrounding PCBM molecules are not the dominant influence determining the frequency of the carbonyl mode. Rather, structural variations that extend over length scales greater than the size of PCBM molecules plus their local environments appear to determine the frequency. We have observed that the carbonyl mode of PCBM shifts to higher frequency when the molecules interact with CN-MEH-PPV (cross reference Figure 5). We established in section IV.A that it is the proximity of PCBM molecules to the interfaces with the polymer that primarily determines the frequency of the carbonyl mode. Therefore, we conclude that the correlation of the carbonyl frequency of PCBM molecules with their radial position (see Figure 9) is necessary to explain the time-dependent shift of the carbonyl frequency that is represented in Figure 4. We wish to point out that the experimental results are consistent with structural disorder in the PCBM domains, but the disorder is not the dominant factor that determines the carbonyl frequency. Although it is very likely that local redistribution of electrons within the local environments occurs, this process is not the cause of the time dependent frequency shift of the carbonyl mode.

Radial Drift and/or Diffusion Model. The correlation between the vibrational frequency of the carbonyl stretch of PCBM and the radial position of the molecules in the PCBM domains indicates that the time dependent shift of the bleach frequency results from the drift and/or diffusion of electrons from the interfaces into the centers of the domains. The distribution of carbonyl frequencies that appear in the bleach at a given time delay is therefore related to the average radial distribution of electrons at that time. Figure 10B displays the center frequencies of the bleach spectra that are depicted in Figure 4 plotted relative to the corresponding time delay measured in the Vis-IR experiment. The time axis is represented on a logarithmic scale. Figure 10A illustrates the movement of electrons with three heuristic snapshots of the distribution of electrons within the domains as a function of increasing time delay. The arrows pointing from the snapshots to the curve in Figure 10B provide a qualitative association between the extent of electron motion and the corresponding carbonyl center

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frequency. As electrons move toward the centers of the domains, their average radial distribution changes, which causes the carbonyl bleach to approach the equilibrium spectrum which has a center at 1740 cm^{-1}.

Hole Diffusion Model. A final alternative explanation which is related to the radial drift and/or diffusion model must be considered. Might the time dependence of the bleach center frequency be explained by the diffusion of holes in the polymer rather then the motion of electrons in the PCBM domains? Since holes are created in the polymer phase by electron transfer and their charge influences the electric field experienced by the PCBM molecules, their motion can affect the bleach.

In consideration of this model, we first note that it is the bleach of neutral ground state PCBM molecules that appears in the Vis-IR spectra. Second, the influence of the holes on the neutral ground state PCBM molecules will be concentrated at the interfaces of the domains. The bleach that might result from the perturbation by the holes in the polymer would therefore appear on the higher frequency side of the transition. The penetration depth of the electric field caused by the holes into the PCBM domains will be greater for holes that are closer to the interfaces. A greater penetration depth will perturb PCBM molecules with lower frequency carbonyl modes. As the holes diffuse away from the interfaces into the polymer phase, the penetration depth of the electric field will decrease, resulting in a shift of the bleach to higher frequency. Since we observe a shift of the bleach to lower frequency, this process cannot explain the time dependence of the bleach frequency that is represented in Figure 4.

However, the diffusion of holes away from the interfaces might cause the bleach of the carbonyl mode to partially recover because the PCBM molecules that are perturbed by the holes will no longer be perturbed after the holes diffuse away. As we report in a separate publication,[48] the area of the bleach decreases by 12% from 5 to 100 ps. This recovery could result from back electron transfer or from the diffusion of holes away from the interfaces. We are currently searching for characteristic absorptions of the anion of PCBM and the cation of the polymer in order to identify which process is responsible for the partial recovery of the bleach. For now, we note that under certain circumstances, organic solar cells can achieve near unit photon to electron conversion efficiency[64] which suggests that ultrafast back electron transfer may not occur on ultrafast timescales in this system.

C. Electron Radial Velocity in PCBM Domains. From the time dependence of the bleach center frequency, we can measure the movement of electrons and estimate their average radial velocity in the PCBM domains. To quantify the time dependence, we fit the trace of the center frequency of the bleach versus the corresponding time delay in Figure 10B with a multiexponential function which is forced to reach the asymptotic limit of the equilibrium center frequency. We have pointed out that hole diffusion on the 5- to 100-ps time scale and possible orientational motion of the PCBM anions on the 20-ps time scale might interfere with the observed frequency shift dynamics. In recognition of these possible processes, we intentionally avoid interpreting the sub-100 ps component of the time dependent center frequency trace in terms of electron movement. The contribution of these processes to the frequency shift kinetics, if any, will be elucidated in a future publication. For now, we note that the longest component of the multiexponential fit through the data has a 10-ns time constant. In the interest of establishing a lower limit to the radial velocity of electrons, we interpret this longest time constant as a metric that indicates the movement of electrons toward the centers of the PCBM domains. The polymer blend contains 50−100 nm diameter fullerene domains as determined by SEM imaging (see Figure 1B) and is very similar in microstructure to materials that were recently reported by the Sariciftci group.[16] On the basis of a 60-nm average diameter, we estimate that electrons must traverse a radial distance of 15 nm for the bleach to converge to the equilibrium spectrum. Combining the estimated distance and time scale, we find the average radial velocity of electrons to be 15 nm/10 ns or 1−2 m/s.

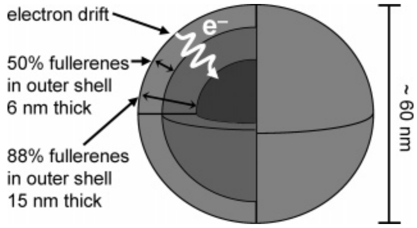

Figure 11. Schematic representation of a sectioned sphere showing shell thicknesses at which 50% and 88% of the volume of the sphere is encompassed.

The estimated 15 nm length scale is based on the volume distribution of a sphere. Figure 11 depicts a sectioned sphere showing that 88% of the volume of a 60 nm diameter sphere is contained in a 15 nm thick outer shell. Consequently, electrons that move 15 nm toward the center encounter on average 88% of the environments present in the PCBM domains. We assume that the bleach spectrum is not very sensitive to electrons diffusing into the remaining 12% of the volume. We should note that it is reasonable for the influence of the electric field on the carbonyl frequency to extend 10s of nanometers into the PCBM domains. In a recent molecular dynamics simulation of vibrational echo studies of carbonmonoxymyoglobin, the researchers found it necessary to calculate the electric field from the entire protein and the surrounding solvent in order to correlate the frequency fluctuations of the C≡O ligand measured in the experiment with the molecular dynamics simulation.[51] This fact indicates that vibrational probes are sensitive to molecular electric fields originating from species that are tens of nanometers away. We should also note that the spectral evolution of the carbonyl bleach does not result from interference from the anionic form of PCBM. The bleach spectrum converges to the linear absorption spectrum, which is only possible if the anion absorbs in a separate spectral window or is so broad that it cannot be distinguished from the absorption offset. The 1−2 m/s velocity serves as a lower limit because our experiments are sensitive only to the radial component of electron motion and because we have intentionally excluded the faster frequency shift dynamics from the calculation of the velocity.

Our measured radial velocity is at least one order of magnitude higher than the velocity of charge carriers in polymer blend solar cells that are composed of similar materials.[65,66] Recently, the mobility of charge carriers in a solar cell composed of MDMO−PPV and PCBM was measured to

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be ~4 × 10^{-4} cm^2/V-s. Photogenerated charges were extracted from the cell which had a 250-nm thick active layer in about 2.5 μs. From the thickness and time scale, we estimate that the average velocity, v, of charge carriers in the cell was ~0.1 m/s. If we treat charge carrier motion as resulting solely from drift, then the drift velocity of the carriers can be related to the mobility, μ, and the electric field, E, by $v = \mu E$. From the mobility and the drift velocity, we estimate the static electric field in the cell to be ~25 000 V/cm which corresponds to ~1 V potential difference across the active layer.[67]

We are in the process of estimating the electric field across the interfaces of the fullerene domains using vibrational Stark spectroscopy.[19,68] By characterizing the external electric field that is required to shift the carbonyl frequency of PCBM by 6 cm^{-1} (the frequency difference between the interfacial and center environments), we will experimentally determine the electric field in the domains. Assuming that the motion of the electrons results primarily from drift, we will be able to convert the velocity into a mobility. If, for the time being, we speculate that the electric fields in the fullerene domains are not quite as large as the field across the solar cell, then the mobility suggested by our experiments is comparable to the electron mobility measured in thin films of pure C_{60} and its soluble variants.[69,70] The pure fullerene materials do not contain interfaces between electron donating and accepting domains. We therefore speculate that the low mobility of organic solar cells fabricated from polymer blends of conjugated polymers and fullerenes principally results from the presence of interfacial boundaries in the charge migration paths, and not because of disorder at the molecular level that reduces the intrinsic rate of electron transport.

The dramatic difference in the measured velocity of electrons in individual PCBM domains compared to their velocity in organic solar cells calls into question the popular idea that PCBM domains in organic solar cells are close enough to transfer electrons from one domain to another without the electrons needing to tunnel through polymer layers. Recent investigations by Durrant and Nelson[71−73] indicate that charge recombination in organic solar cells can be understood by treating electrons as immobile and considering only the diffusion of holes which would suggest that electrons may be less mobile than previously believed. On the basis of our results, we speculate that the mobility of electrons may be significantly reduced by the presence of interfacial boundaries between the PCBM domains. These interfacial boundaries may be polymeric layers. We are in the process of using the covalent ring stretch mode around 1600 cm^{-1} as a vibrational probe of holes in the polymer in order to compare the velocities of electrons and holes in the same system to determine which carrier has higher mobility.

V. Concluding Remarks

The results of ultrafast two-dimensional infrared and visible pump-infrared probe spectroscopy were employed to study charge separation and the movement of the resulting electrons in a polymer blend PV material. Charge transfer is directly observed through the carbonyl (C═O) stretch of the functionalized fullerene, PCBM, that is blended with a conjugated polymer, CN-MEH-PPV. Analysis of the vibrational line shapes of the carbonyl spectra in the Vis-IR and 2D IR data in conjunction with other complementary experiments reveal that there is a correlation between the frequency of a carbonyl mode and the position of its host fullerene molecule. Only fullerene molecules at the interfaces of PCBM domains are involved in charge transfer. These molecules possess higher frequency carbonyl modes while PCBM molecules in the centers of domains have lower frequency modes.

The correlation between the frequency of a carbonyl mode and the radial position of its host fullerene molecule provides a means to observe the movement of electrons within individual domains through the spectral evolution of the carbonyl bleach. From the spectral evolution, we find that the radial velocity of electrons is 1−2 m/s, which suggests an intrinsic mobility that is at least an order of magnitude greater than the mobility in polymer blend PV materials. The study reveals that organic solar cells with dramatically higher mobility and thus efficiency might be developed if the geometries of the interpenetrating networks of electron donating and accepting materials can be controlled to eliminate interfacial boundaries along the charge migration pathways. We also demonstrate that the application of ultrafast infrared spectroscopy to study organic PV materials at the molecular level is useful to provide insight into the fundamental dynamics that determine the efficiency of organic solar cells.

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