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Phys. Rev. B **91**, 075436 — Published 26 February 2015

DOI: [10.1103/PhysRevB.91.075436](https://doi.org/10.1103/PhysRevB.91.075436)

Charge Transfer from Delocalized Excited States in a Bulk Heterojunction Material

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Abstract

Charge generation in an organic photovoltaic blend was investigated using transient absorption spectroscopy. In films of pure electron donating material, sub-picosecond spectral oscillations were observed and assigned to torsional modes associated with excited state relaxation and localization. These modes are systematically suppressed in the presence of fullerene, indicating that a significant fraction of charge transfer occurs prior to excited state localization.

Introduction

The elementary charge transfer process that drives photocurrent in organic bulk heterojunction (BHJ) solar cells is the subject of a large ongoing research effort motivated, in part, by the promise of inexpensive renewable energy. Electron and hole transfer processes occur at the heterojunction interface between two organic materials of different electron affinity and

ionization potentials,¹⁻³ eventually resulting in mobile charge carriers and solar cell photocurrent. The Coulomb attraction between charge carriers across the heterojunction interface gives rise to a manifold of states referred to as charge transfer (CT) excitons. These states have been detected with absorption,⁴ photoconductivity,⁵ photoluminescence,⁶ electroluminescence,⁷ two-photon photoemission,⁸ transient absorption,⁹ time resolved photoluminescence,¹⁰ and are the subject of an extensive review.¹¹ Simplistic predictions about the binding energy of the charge transfer state based on the macroscopic dielectric constant suggest that CT excitons are tightly bound, and cannot contribute meaningfully to photocurrent production. However, solar cells have internal quantum efficiencies approaching unity,¹² and do not display any drop in efficiency, even when the CT exciton states are excited directly.^{13, 14}

A mechanistic understanding of the charge generation process has been pursued for several years in order to explain these apparent discrepancies. Current opinion can be roughly divided between researchers who emphasize the role of energetic and morphological inhomogeneities¹⁵⁻²¹ and those emphasizing kinetic processes.²²⁻³⁴ Guo and Inganas provide a concise review of many the leading viewpoints.³⁵ Three questions are important in evaluating a proposed mechanism for charge generation. One, “Can the mechanism occur; does it have evidence that supports it?” Next, “Is the mechanism important for the current class of high performing BHJ’s?” Finally, “Could the mechanism be used to develop better materials and devices for widespread application?” It is important to have all three criteria in mind when evaluating charge generation mechanisms because it seems increasingly likely that more than one satisfies the first criterion.

Our viewpoint is that transient excited state delocalization does occur and can exert a beneficial influence on the charge generation yield of organic solar cells.³¹ Moreover, we assert

that this process also satisfies the third criterion of importance; the initial delocalization is robust enough to use in the design of solar cells that are both efficient and relatively insensitive to film processing.³⁶ High efficiency and insensitivity to processing are some of the requirements of widespread technological application. Finally and perhaps most importantly, ultrafast excited state processes in organic semiconducting materials are incompletely understood, most notably the relationship between excitons and charge carriers as well as the processes that contribute to their localization.³⁷

It is known that an oriented polydiacetylene chain can support a delocalized excited state that extends in excess of microns.³⁸ However, disorder in polymeric and molecular films results in localized excited states on long timescales. On ultrafast timescales, we have argued that even in disordered films, the excited state is highly delocalized on the basis of fundamental uncertainty and the diffraction limit that specifies natural length-scales of the electromagnetic field.³⁶ In the case of laser radiation, macroscopic field coherence lengths ensure the correctness of the conclusion if not the applicability of the whole argument.³⁹⁻⁴³ However, this analysis runs counter to descriptions of incoherent light which emphasize arbitrarily small coherence lengths and could, in theory, create an arbitrarily localized photoexcitation.⁴⁴ In simple terms, the question hinges on the effective volume of a photon, a question relevant to the refractive index of gasses.⁴⁵ If transient excited state delocalization is to be important for solar cell function, it is important that the mechanism be consistent with incoherent light excitation, and not rely on coherence properties of the electromagnetic field, which strictly speaking applies only to laser illumination.

Transient excited state delocalization is well known feature of photosynthetic light harvesting proteins,⁴⁶⁻⁵⁰ and was also recently observed in molecular dimers.⁵¹ Excited state

delocalization in these contexts relies on coherences between excited states of the system. The photoexcited state exists in a quantum mechanical superposition of individual excited states until the phase relationship between them is lost, resulting in localization to a single state. The most common explanation for these coherences that can last up to a picosecond, relies on relatively strong intermolecular interactions and a subtle coupling to vibrational modes that encourage the rephrasing of the coherent state.⁵⁰

In organic and polymeric films, time resolved photoluminescence measurements provide evidence for excited state delocalization; the Stoke's shift takes hundreds of fs to occur^{33, 37} and the time evolution of the lineshape can be used to describe the localization process.⁵² Coherent spectroscopy has been used to investigate the excited state localization process in polymers for nearly a decade.^{28, 53-56} In particular, torsional vibrations of poly(3-hexylthiophene) (P3HT) were found to be chiefly responsible for a loss of coherence between excited states in two-color three photon echo peak shift measurements.⁵⁶ More recently, it was found that vibrational coherences in the excited state are transmitted to the products of the ultrafast charge transfer reaction in organic solar cells. Both the electron in the fullerene²⁷ and the hole generated in the electron donating polymer²⁸ experience coherent vibrations following charge transfer. The latter work also demonstrates that the excited state is at least as large as the photogenerated hole. The transmission of vibrational coherences, and their importance in the charge generation reaction were theoretically predicted by Bittner and co-workers.^{57, 58}

On the basis of transient absorption measurements we proposed that excited state delocalization influences the charge generation process in BHJ materials.^{31, 36, 59} In these measurements, a large fraction of ultrafast charge generation is observed compared to that occurring after the well characterized process of exciton diffusion.^{60, 61} Exciton diffusion length-

scales have been studied through steady-state photoluminescence measurements on bilayer films,⁶² but agreement between different types of measurements has not been entirely satisfactory. However, these studies seem to suggest that any short lived excited state transport dynamics must exhibit nearly identical length-scale dependencies as incoherently diffusing excitons. One would then expect for samples with reasonably similar length-scales to find a fixed ratio between ultrafast charge generation and the one that occurs following exciton diffusion, independent of the exact morphology. In line with this expectation, a variety of optimized BHJ materials exhibited an uncanny similarity in their charge generation dynamics.³⁶ Moreover, in order to rule out the effect of sample morphology in ultrafast charge generation process,⁶³ we performed experiments on a solution processed bilayer sample using photopolymerized C₆₀ as the electron acceptor (thus preventing intermixing between layers). In this configuration, most of the charges were still generated on short timescales, demonstrating the presence of excited state delocalization.⁵⁹ The key signature of the ultrafast mechanism is an abrupt slowing of charge generation after 100-200 fs. It is therefore important that the mechanism that supports exciton delocalization ceases after these timescales. Delocalization occurring via coherences between excited states neatly explains these observations and fits into the known photophysical behavior of organic semiconductors.

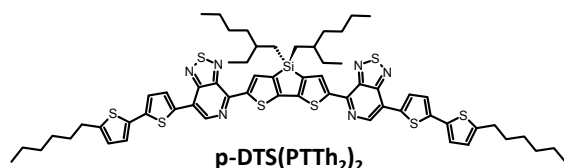
For transient excited state delocalization to play a role in the function of an organic solar cell it is important that the charge transfer timescale be competitive with localization timescales. For systems with charge transfer timescales greater than 100-200 fs, one would not expect short-lived excited state delocalization to play a role in the charge generation process. This provides insight into the importance of fast charge transfer reactions in fullerene-polymer cells and articulates an important design principle to increase solar cell efficiencies in systems comprising

non-fullerene acceptors. That excited state delocalization can lead to efficient charge separation seems intuitively obvious; at short timescales any exciton binding energy would be very small. Finally, we note that excited state delocalization is likely sufficient but not always necessary for efficient charge generation. Some charges are generated following excited state localization and diffusion; these charges must also separate in solar cells with near unit quantum efficiency.¹²

Here we study the charge generation process in an organic BHJ material using transient absorption. We find subpicosecond oscillations in the spectra that we assign to torsional vibrations of the electron donating material. A previous study has linked this mode to a loss of excited state coherence,⁵⁶ and we use this mode as an indicator of excited state localization. These modes are systematically suppressed in the presence of fullerene, indicating that a significant fraction of charge transfer occurs prior to excited state localization.

Experimental

Films of pure p-DTS(PTTh₂)₂ (see Fig. 1) were cast from chlorobenzene solution at a concentration of 40 mg/ml. When blended with PC₇₁BM, it forms an



5,5'-bis{(4-(7-hexylthiophen-2-yl)thiophen-2-yl)-[1,2,5]thiadiazolo [3,4-c]pyridine-3,3'-di-2-ethylhexylsilylene-2,2'-bithiophene

Figure 1. Chemical structure and name of electron donating material used.

efficient BHJ material.^{64, 65} BHJ films of p-DTS(PTTh₂)₂ and PC₇₁BM were formed from dichlorobenzene solution with an additive (1,8 diiodooctane) at a concentration of 0.25% (v/v); solute concentrations were 40 mg/ml. Films were formed inside an inert atmosphere glove box by spin casting at 1700 RPM onto sapphire discs before annealing at 70 °C. Solar cells were fabricated and tested as described previously⁶⁵ The basic photophysical properties of p-DTS(PTTh₂)₂ including its charge generation dynamics were the subject of previous studies.^{31, 66}

Transient absorption experiments were conducted with a 1 kHz amplified Ti:sapphire oscillator that outputs at a wavelength of 790 nm with a temporal pulse width of 100 fs. The pump had a pulse energy of $80 - 120 \mu\text{J}/\text{cm}^2$; the dynamics presented here did not display power dependence. Time resolution was achieved with a delay line in the pump path that was carefully aligned to avoid beam walk-off. The probe pulse was focused into a 1 mm thick sapphire disk to generate the white light used to measure visible and near-IR spectra. The probe pulse was split before reaching the sample to provide a reference path to aid in the correction of intensity fluctuations. In addition, synchronous chopping of the probe enabled the subtraction of an accurate dark count reading, which tends to drift over time. All spectra were manually corrected for the temporal chirp present in the white light continuum. The polarization angle between pump and probe beams was 54 ± 1 degrees. Lastly, spectra were collected with a silicon CCD camera that was calibrated using a series of narrow band pass filters.

Fluorescence measurements were collected on a PTI fluorometer with an excitation wavelength of 400 nm. Relative photoluminescence intensity was estimated by the collected intensity at 820 nm for each of the four samples, which were of the same thickness, illuminated with the same intensity, and held at the same position relative to the detector and source.

Results

Fig. 2 shows the results of a transient absorption experiment on films of pure p-DTS(PTTh₂)₂ when excited with 395 nm light. The value of the transient absorption is presented with a color scale, with blue features indicating a decrease in the absorption and green and brown features indicating an increase. Oscillations in the spectra are clearly observable in Fig. 2(a) with a period of ~500 ps. This observation corresponds very well with the known properties of compression waves (sound propagation) in thin films^{67, 68} and with a highly similar molecule, d-DTS(PTTh₂)₂ in particular.⁶⁹ Fig. 2(b) displays spectral oscillations at shorter timescales ($t < 2$ ps). Because these modes are in the THz regime, they are not due to long wavelength compression waves, but rather to either intramolecular torsional modes and/or short wavelength intermolecular vibrations.

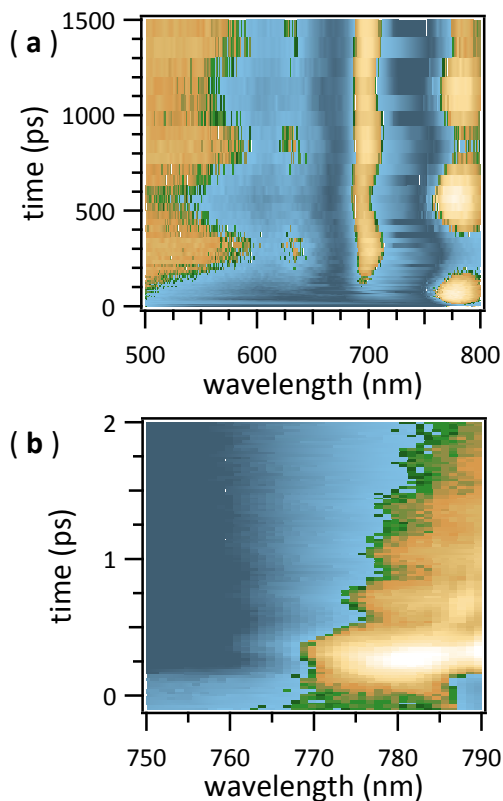
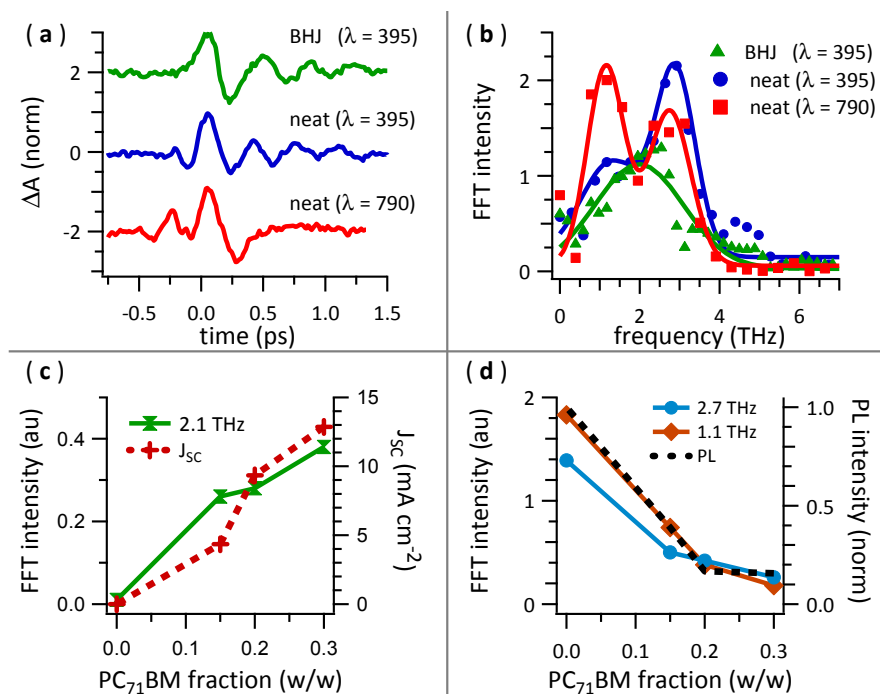


Figure 2. Transient absorption results on neat films of p-DTS(PTTh₂)₂. Measured signal rendered in color with negative signals in blue and positive signals in green and brown. Each panel represents the same data set, plotted on different time and wavelength scales.

A more precise examination of the frequency components involved in the spectral oscillations was obtained first by subtracting out the slowly varying background and normalizing the signal (Fig. 3(a)). A fast Fourier transform (FFT) was taken of the subtraction result and the FFT data was fit with Gaussian peaks (Fig. 3(b)). The pure film is characterized by two peaks, one centered at 2.7 THz and the other centered at 1.1 THz. The 2.7 THz mode can be assigned to an intermolecular torsional mode in accord with previous calculations.⁵⁷ We note specifically

that the 2.7 THz mode is too high in frequency to be the result of intermolecular vibrations. Estimates of the spring constant based on the molecular mass and the frequency of the vibration would require a value comparable with covalent stretching modes *e.g.* the C-H stretching mode. The 1.1 THz mode may be of a similar origin or it may be an intermolecular vibrational mode, which were recently shown to be important for exciton localization in zinc phthalocyanine.⁷⁰



Panel (a) Extracted oscillations from transient absorption data, normalized to their maximum intensity. (b) Fourier transform of extracted oscillations. (c) Amplitude of 2.1 THz peak and solar cell J_{SC} as a function of PC₇₁BM fraction. (d) Amplitude of 2.7 and 1.1 THz peaks, photoluminescence intensity as a function of PC₇₁BM fraction.

torsional relaxation processes in polyfluorene, which shows a greater wavelength dependence.⁷¹

Apparently, electron-phonon coupling to this mode is stronger in the lowest lying singlet excited state of p-DTS(PTTh₂)₂, possibly as a result of polarity between its electron donating and electron accepting moieties.

The phenomenon responsible for the excitation of the THz vibrational modes is a general feature of the relaxation processes in this system. Excitation at 790 nm is very near the optical gap of p-DTS(PTTh₂)₂ and we observe the same vibrational modes, albeit in a different ratio. This behavior contrasts with

Also found in Fig. 3(b) is the oscillation spectrum from an optimized BHJ material (30% PC₇₁BM) excited at 395 nm. This spectrum is characterized by a single peak centered at 2.1 THz. It was recently shown that vibrational coherences can result from the charge generation process^{27, 28} and the population of charge separated states has a direct effect on molecular torsions.⁷¹ The strong effect of charges on the frequency of torsional modes can be understood by noting that the contribution of quinoidal resonance forms will be affected by the charge state of the molecule; it will shift torsional mode frequencies. We note specifically that the changes in the observed THz vibrational modes are not due to morphology changes associated with adding PC₇₁BM. Neither the magnitude of the shift nor the change in the number of modes suggests a perturbative interaction resulting from subtle changes in sample morphology.

To make the connection between charge transfer and the changes in THz vibrational modes more clear, samples with different PC₇₁BM concentrations excited at 790 nm were studied. Subpicosecond oscillations were extracted from transient absorption dynamics in the same way as described above and the resulting FFT data was fit with three Gaussian peaks. The peak position and width were fixed in accord with the results of Fig. 3(b), the peak amplitudes were allowed to vary freely. The amplitude of the 2.1 THz mode is plotted with the short circuit current (J_{SC}) for the analogous solar cells. A clear correlation between the strength of this feature and the J_{SC} provides strong evidence that this mode is connected with the charge generation process. In addition, the amplitude of the 2.7 and 1.1 THz modes in the neat material are suppressed upon the addition of PC₇₁BM. This indicates that charge transfer processes quench these modes in the same way charge transfer quenches photoluminescence. In fact, Fig. 3(d) demonstrates this by a strong correlation between both types of quenching.

To summarize the experimental results, 2.7 and 1.1 THz oscillations are observed in the transient absorption spectrum of p-DTS(PTTh₂)₂. The 2.7 THz mode is excited regardless of pump wavelength, and we assign it to torsional vibrations of the molecule. Adding PC₇₁BM to the film systematically quenches the 2.7 and 1.1 THz modes of the neutral molecule and another mode at 2.1 THz appears in their stead. It is related to the charge generation process as demonstrated by its strong correlation with the short circuit current of the corresponding solar cell.

Discussion

In a series of papers published previously, we argued that excited state delocalization plays an important role in the operational mechanism of BHJ solar cells.^{31, 36, 59} The most recent work used a solution processed bilayer with photopolymerized C₆₀ as an electron accepting layer to completely eliminate any possibility of intermixing between donor and acceptor materials. Charge generation dynamics were weighted towards fast processes, establishing the important effect of transient excited state delocalization.

One potential point of contention in the aforementioned measurements was a complete reliance on charge generation dynamics as an indirect probe of the excited state delocalization. Addressing this question directly without making assumptions about the mechanism of delocalization proves to be an unresolved challenge. Although ultrafast time resolved photoluminescence lineshape measurements can address the size of a single excited state Eigenfunction,^{52, 72} the presence of coherences between excited states would result in wavefunctions with a significantly greater extent. This is a critical distinction as several observations of excited state coherences have been made.^{28, 53-56} Moreover, measurements that invoke charge carrier coherence²⁷⁻²⁹ are predicated on the existence of excited state coherence.

Another means of establishing indirect but complimentary evidence for charge transfer prior to excited state localization is to monitor spectral signatures of the localization process. If charge transfer occurs before localization, spectral signatures of localization will also be absent. As we have alluded to, delocalization can occur through a single Eigenfunction of the excited state Hamiltonian, or via coherences between states. Localization of the former is known to occur via interactions with carbon-carbon vibrational modes and were observed via transient absorption measurements with < 10 fs time resolution.⁷³ A loss of coherence between excited states is known to take place via torsional vibrations with a period of 3-4 THz.⁵⁶ We assign the 2.7 and 1.1 THz modes observed in neat films of p-DTS(PTTh₂)₂ as representative of a loss of excited state coherence. It follows that the quenching of these modes by adding PC₇₁BM to the film indicates charge transfer before a loss of excited state coherence. This behavior should be expected by comparing the timescales of charge transfer with the lifetime of the coherent excited state; the charge transfer timescale can be as short as 25 fs, which is less than reported lifetimes of the coherent excited state.²⁸

Summary

We presented the results of transient absorption measurements on blends of p-DTS(PTTh₂)₂ and PC₇₁BM that form an efficient organic photovoltaic material⁶⁵ and observed THz oscillations in the spectrum. Modes observed in neat films of p-DTS(PTTh₂)₂ at 2.7 and 1.1 THz were attributed to localization phenomena via a loss of excited state coherence.⁵⁶ These modes are systematically quenched upon the addition of PC₇₁BM, indicating that a significant amount of charge transfer occurs before a loss of excited state coherence. Whether or not coherent phenomena are strictly necessary in the charge separation process in modern BHJ materials is a topic of significant debate.³⁵ An important and interesting question, from our

perspective, is whether coherent phenomena can be used to create new designs for higher efficiency and more reliable photovoltaic materials.

Acknowledgements

This research was supported by the Institute for Collaborative Biotechnologies through grant W911NF-09-0001 from the U.S. Army Research Office. The content of the information does not necessarily reflect the position or the policy of the Government, and no official endorsement should be inferred. LGK thanks Yanming Sun for his help with sample preparation.

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