

Probing Charge Transfer and Hot Carrier Dynamics in Organic Solar Cells with Terahertz Spectroscopy

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ABSTRACT

Time-resolved terahertz spectroscopy (TRTS) was used to explore charge generation, transfer, and the role of hot carriers in organic solar cell materials. Two model molecular photovoltaic systems were investigated: with zinc phthalocyanine (ZnPc) or alpha-sexathiophene (α -6T) as the electron donors and buckminsterfullerene (C_{60}) as the electron acceptor. TRTS provides charge carrier conductivity dynamics comprised of changes in both population and mobility. By using time-resolved optical spectroscopy in conjunction with TRTS, these two contributions can be disentangled. The sub-picosecond photo-induced conductivity decay dynamics of C_{60} were revealed to be caused by auto-ionization: the intrinsic process by which charge is generated in molecular solids. In donor-acceptor blends, the long-lived photo-induced conductivity is used for weight fraction optimization of the constituents. In nanoscale multi-layer films, the photo-induced conductivity identifies optimal layer thicknesses. In films of ZnPc/ C_{60} , electron transfer from ZnPc yields hot charges that localize and become less mobile as they thermalize. Excitation of high-lying Franck Condon states in C_{60} followed by hole-transfer to ZnPc similarly produces hot charge carriers that self-localize; charge transfer clearly precedes carrier cooling. This picture is contrasted to charge transfer in α -6T/ C_{60} , where hole transfer takes place from a thermalized state and produces equilibrium carriers that do not show characteristic signs of cooling and self-localization. These results illustrate the value of terahertz spectroscopic methods for probing charge transfer reactions.

Keywords: terahertz spectroscopy, carrier dynamics, organic solar cells

1. INTRODUCTION

The performance of organic solar cells has significantly improved in recent years, with power conversion efficiencies exceeding 10%. [1, 2] In order to achieve these and further gains, much attention has been given to understanding the influence of the sample morphology [3-5] and of charge transfer states [6] on photocurrent generation and loss mechanisms. It is clear that both play important roles in the rapid charge generation that would otherwise seem at odds with the excitonic nature of organic semiconductors. However, a debate has emerged as to whether efficient charge separation occurs via hot charge transfer excitons or energy-gradient driven molecular hopping. While many ultrafast spectroscopic measurements show increasing evidence for the important role of hot charge transfer excitons, [7] device-like charge collections measurements show no significant gains from hot excitations. [8] Central to this debate is the question of whether large donor-acceptor energy level offsets are needed to generate efficient photocurrent. The answer to this question has consequences for efforts aimed at increasing the open circuit voltage of organic photovoltaic cells. [9]

The excitonic nature of organic semiconductors stems from their low dielectric constants and strong electron-phonon interactions. The former leads to unscreened Coulombic attraction between electrons and holes, and the latter leads to structural relaxation of the excited state into a lower energy configuration. In order to separate charges, energetically downhill charge transfer reactions are engineered into organic solar cells. Typically charge transfer occurs at a donor-acceptor heterojunction where the energy-level offset overcomes the exciton binding energy and favorable reorganization energies inhibit back transfer. The state that initially forms upon charge transfer is a charge transfer exciton (CTE), comprised of a hole in the donor and an electron in the acceptor that are held by mutual attraction at the donor-acceptor interface. Within Onsager theory, the interaction between electrons and holes is governed by a Coulombic potential that is inversely proportional to dielectric constant and electron-hole separation. Delocalization

increases the electron-hole separation and weakens the mutual attraction, increasing the probability that the CTE dissociates into separate charges. So-called “hot” CTE states with excess energy are more delocalized, which is thought to be a key factor in driving charge separation.[7, 10] Entropy considerations may also play a role, through the increase in multiplicity of charge-separated states available to delocalized CTEs.[11] Due to the required reorganization energy, Marcus theory suggests that an optimum excess energy may exist, above which CTEs dissociate with lower probabilities.[12] Hot CTEs may be important only if the rate of charge separation is higher than the rate of thermalization. If instead, the CTE cools prior to energy transfer, other factors may influence efficient charge separation from relaxed CTEs.[8] Local morphology may play an important role in increasing delocalization, independent of CTE energy.[13] High charge carrier mobility may also help CTE dissociation by similarly contributing to increased delocalization and inhibiting geminate recombination. Finally, internal electric fields may reduce the barrier to charge separation in the downfield direction, thus increasing the charge separation probability. It is not yet clear to what degree each of these factors contributes to charge separation.

Here we examine charge transfer in two model molecular donor-acceptor systems comprised of either zinc phthalocyanine (ZnPc) or α -sexithiophene (α -6T) as an electron donor and Buckminsterfullerene (C_{60}) as the electron acceptor. High efficiency organic photovoltaic cells have been achieved using thiophenes and phthalocyanines.[14] The energy level offsets in each donor-acceptor system allow for the important role of excess driving energy to be explored. We apply both transient absorption and time-resolved terahertz spectroscopy to monitor the photogenerated excited state species as well as the photo-induced conductivity. Together, this provides insight into the evolution of the populations of excitons and charge separated species as well as the transient charge carrier mobility. By varying the excitation photon energy, we can compare the results of creating either hot or cool charge transfer excitons in order to determine the role of excess energy on charge separation.

2. METHODOLOGY

ZnPc, α -6T, and C_{60} were purified by vacuum train sublimation prior to use. Organic thin films (~300nm thick) were deposited onto quartz substrates by thermal evaporation under vacuum (10^{-7} Torr). Composite films were prepared by co-sublimation while those consisting of nanometer-thick layers were prepared by alternating layer deposition of the constituents. Layer thicknesses varying from 1 nm to 10 nm were determined using a quartz crystal microbalance. The optical absorption spectrum was measured with a spectrophotometer, while measurements at optical density < 0.1 were conducted using a custom spectrometer with an integrating sphere.

Transient absorption (TA) measurements were based on a 1kHz Ti:Sapphire amplifier with a fundamental wavelength of 775 nm whose output was split to generate excitation and probe pulses. The frequency-doubled output was used for photo-excitation, while the excited state spectra were measured using a white light continuum probe generated in a sapphire plate. The white-light probe was sent through a scanning monochromator, which allows for the excited state spectrum to be recorded as well as for specific probe wavelengths, e.g. corresponding to the ground state bleach (GSB) or excited state absorption (ESA), to be selected. The dynamics of these excited-state populations were recorded by varying the delay, i.e. optical path length, between the excitation and probe pulses using a mechanical delay stage.

Time-resolved terahertz spectroscopy (TRTS)[15] was based on a 1kHz Ti:Sapphire amplifier with a fundamental wavelength of 800 nm and a 60 fs pulse width whose output was split to generate excitation and probe pulses. Optical excitation pulses were generated either by frequency-doubling the output to 400 nm or by pumping a near-infrared optical parametric amplifier that was subsequently frequency-doubled to 615 nm. Terahertz (THz) probe pulses were generated by optical rectification in a 2 mm thick [110] ZnTe crystal and coherently detected by free-space electro-optic sampling in a second ZnTe crystal. Coherent detection of the THz probe pulse electric field allows for simultaneous determination of the refractive index and absorption, or equivalently the complex conductivity.

Photo-induced conductivity dynamics were recorded by monitoring the change in the peak THz waveform electric field amplitude as a function of time after photo-excitation. This is done by first fixing the delay, i.e. optical path length, between the pulse that generates the THz waveform and the pulse that samples its electric field amplitude, then scanning the delay between the excitation pulse and the THz pulse. It can be shown that the change in the peak THz electric field is proportional to the changes in the real conductivity, while photo-induced phase shifts more easily measured at the zero-crossing of the THz electric field are dominated by changes in the imaginary conductivity.[16] The complex frequency-dependent conductivity was extracted from scans measuring the change in the transmitted THz pulse at a

given delay after photo-excitation using the thin film approximation.[17] All measurements were performed in a dry-air purged box to minimize THz absorption by atmospheric water vapor.

3. RESULTS

First we examine the excited state behavior of neat C_{60} films, Figure 1a. Photo-excitation at 400 nm (3.1 eV) leads to an instrument limited rise in photo-induced conductivity measured via TRTS. This is followed by an ultrafast exponential decay (500 fs) to a slowly decaying residual conductivity. These dynamics were absent from both C_{60} in solution and C_{60} isolated in a polystyrene matrix,[18] implying that they do not originate from intramolecular excited states. On the other hand, photo-excitation of C_{60} at 615 nm (2 eV) yields no observable photo-induced conductivity. This indicates that there is a threshold energy necessary to produce charge separated species in C_{60} . Early studies of C_{60} reported a 2.3 eV threshold for transient photocurrent,[19] suggesting the existence of intermolecular charge transfer states. Excited state dynamics in C_{60} probed at 550 nm (2.25 eV) via TA, which was previously assigned to charge transfer excitons (CTE),[20] show a multiexponential decay with an initial fast component that matches the photo-induced conductivity decay. Therefore, we conclude that this photo-induced conductivity decay is dominated by recombination and not changes in mobility.

We assign the C_{60} dynamics to autoionization,[21] which is the intrinsic method of charge carrier generation in organic solids. Here, excitation to a higher-lying Franck-Condon state allows for charge transfer to a neighboring molecule of the same type. The created geminate pair can then either recombine or escape the Coulomb potential via a thermally-activated process to form charge carriers, Figure 1b. In terms of Onsager theory, the excess energy of this hot CTE increases the electron-hole separation and thus the probability of charge separation. The fast photo-induced conductivity and CTE population decays are consistent with hot CTE relaxation times.[11, 22, 23] Here, many electrons do not escape the Coulomb potential and the hot CTE undergoes a form of self-trapping as it cools. The resulting bound CTE has insufficient polarizability to significantly absorb at THz frequencies.[17, 24] From our measurements, we infer that the 0.3 eV excess energy above the absorption edge that is given to an exciton upon 615 nm excitation is insufficient for autoionization.

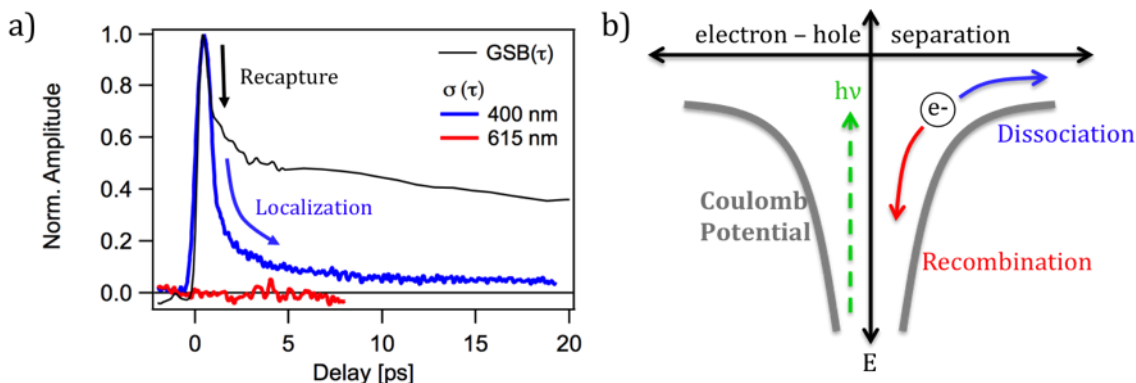


Figure 1. (a) Ground state bleach probed at 550 nm (black) and TRTS conductivity dynamics in C_{60} resulting from 400 nm (blue) and 615 nm (red) excitation. (b) Schematic of the autoionization process where higher excitation energies lead to greater delocalization and a higher probability of exciton dissociation.

Next we examine the $ZnPc:C_{60}$ donor:acceptor system. In both the blends and nanoscale multilayered films, bi-exponential photo-induced conductivity dynamics are observed. No photoinduced conductivity response is observed in neat $ZnPc$, which recent measurements suggest may require a higher degree of crystallinity than achieved through sublimation in order to provide significant delocalization and support long-range charge separation.[25] The rapid initial decay of the photo-induced conductivity is absent from the excited state dynamics of the multilayered films probed at 550 nm, which corresponds to transitions of the $ZnPc$ cations, Figure 2a. The observed linear fluence dependence indicates that the fluences used here are not sufficiently high as to produce polaron pair annihilation, which can lead to rapid recombination.[26] The lack of correlation between the excited state and conductivity dynamics indicates that the

later is dominated by changes in mobility following charge transfer.[27] Here, the transferred charge carriers possess excess energy and greater mobility, which decreases as the carriers cool and become more localized. This is consistent with recent measurements showing that carriers are generated within 100 fs in polymer:fullerene blends and localize within 1 ps as they thermalize.[28] The excited state and photoinduced conductivity dynamics are correlated for delays > 20 ps, where recombination dominates the changes in conductivity.[21]

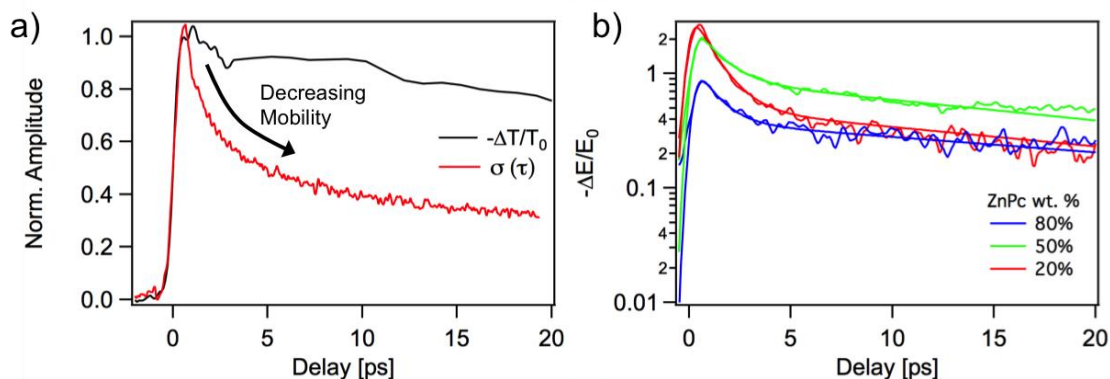


Figure 2. (a) ZnPc cation dynamics (black) measured via TA at 550 nm and conductivity dynamics (red) measured via TRTS in the ZnPc:C₆₀ donor:acceptor system. (b) TRTS conductivity dynamics in ZnPc:C₆₀ co-sublimed films as a function of the percent weight of ZnPc.

The long-lived component of the photoinduced conductivity, which is proportional to the charge carrier concentration, exhibits a clear dependence on the blend composition for ZnPc:C₆₀, Figure 2b. The optimum weight fraction is found to be 50% donor and 50% acceptor.[18] This may be related to the need for both a sufficiently crystallized donor[29] and large acceptor domain sizes[13] in order to achieve efficient charge separation.

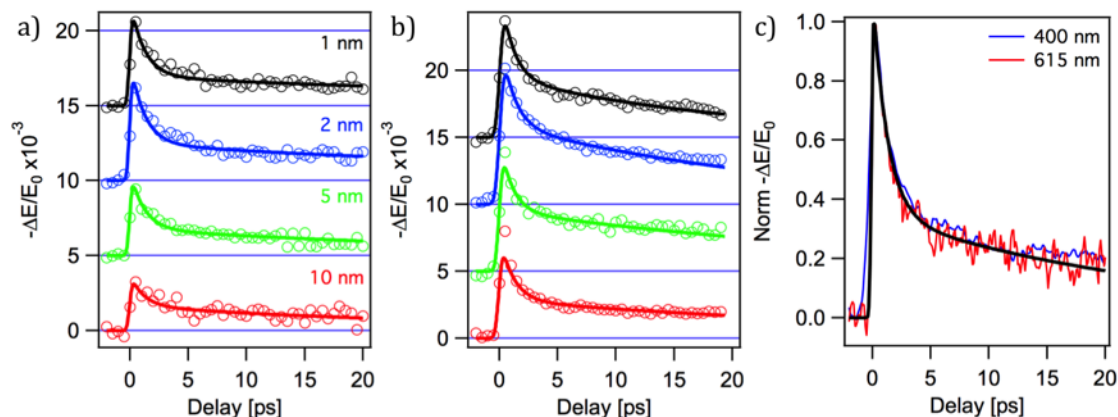


Figure 3. TRTS conductivity dynamics in ZnPc:C₆₀ multilayered films shown as a function of layer thickness for (a) 615 nm excitation and (b) 400 nm excitation. (c) Comparison between the TRTS conductivity dynamics resulting from 400 nm (blue) and 615 nm (red) excitation in ZnPc:C₆₀ blends. Solid lines are fits to the data.[27]

The photo-induced conductivity depends on the layer thickness for the nanoscale multilayered films. This is most easily observed for 615 nm excitation, which is primarily absorbed by the ZnPc, Figure 3a. Here, the peak photoinduced conductivity increases as the layer thickness decreases, however the conductivity decay rate is independent of thickness.

This is also true when exciting the ZnPc:C₆₀ multilayered films with 400 nm light, Figure 3b, however there we see an additional short-lived peak. This peak matches the C₆₀ autoionization dynamics and becomes more pronounced for thicker layers, indicating it comes from regions of bulk C₆₀.

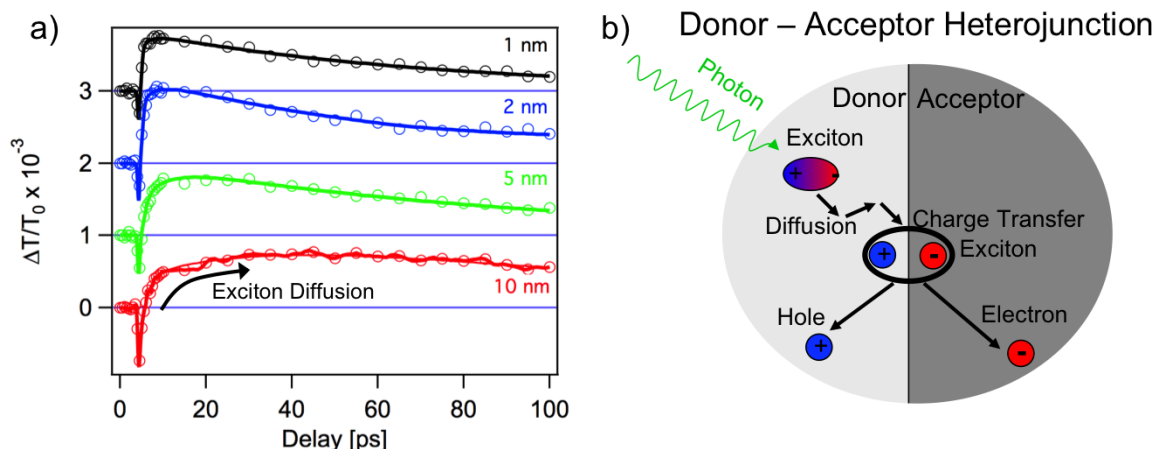


Figure 4. (a) ZnPc Ground state bleach dynamics in ZnPc:C₆₀ multilayered films probed at 675 nm after 387.5 nm excitation as a function of layer thickness. Solid lines are Monte Carlo simulations of exciton diffusion in C₆₀. (b) Schematic showing the processes of absorption, exciton creation, diffusion, CTE formation that precede charge separation in a donor-acceptor heterojunction.

As we have seen that the photoconductivity arises from ultrafast charge transfer between donor and acceptor, we can infer that it is dominated by the donor:acceptor interface. Excitation of a donor or acceptor molecule within a layer requires exciton migration to the interface prior to charge transfer. We can estimate the exciton diffusion time by monitoring the ZnPc ground-state bleach (GSB) via TA after excitation at 387.5 nm, Figure 4. At this wavelength, most of the light is absorbed by C₆₀. For the thickest layers, the GSB peak is delayed by 10s of picoseconds. Monte Carlo simulation of hopping between neighboring C₆₀ molecules in a face centered cubic lattice with 1.4 nm lattice spacing and unity probability of charge transfer at the ZnPc:C₆₀ interface yield a hopping rate of 2.5 THz for all layer thicknesses.[21] This corresponds to an exciton diffusion length of 10 nm, which is typical for an organic semiconductor. This estimate does not include long lived triplet states. We can therefore conclude that charge transfer from molecules excited within the bulk of these nanoscale layers does not contribute to the initial photoinduced conductivity transient. This explains the aforementioned dependence of photoinduced conductivity on layer thickness: as the layers become thinner we expect that a greater fraction of excited states to be created closer to the interface where they are able to contribute to charge separation.

Importantly, there appears to be little dependence of the conductivity dynamics on the excitation wavelength. While a direct comparison within the multilayered films is obscured by the C₆₀ autoionization peak, it is much more straightforward for the blended architecture. Here, it is clear that the decay dynamics are the same for 400 nm and 615 nm excitation, Figure 3c. When ZnPc is preferentially excited at 615 nm, electrons transfer into a high-lying excited state of C₆₀, resulting in a hot carrier. Similarly, when C₆₀ absorbs a 400 nm photon an electron directly excited into such a state, as discussed above for the case of autoionization. In the case of ZnPc:C₆₀, hole transfer into ZnPc occurs prior to electrons thermalizing in C₆₀, giving rise to the observed photoinduced conductivity dynamics. Clearly charge transfer can compete with hot CTE cooling.

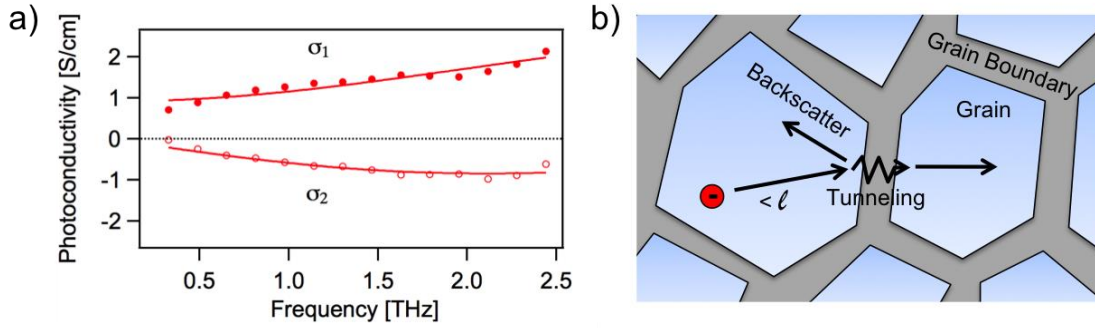


Figure 5. (a) Real (σ_1) and imaginary (σ_2) frequency-dependent conductivity in multilayered ZnPc:C₆₀ films with 5 nm layers. The solid lines are fits to the Drude-Smith model. (b) Schematic representation of charge carrier backscattering over distances less than the mean free path length (ℓ), which is described by the Drude-Smith model.

The complex frequency-dependent photoinduced conductivity in ZnPc:C₆₀ shows dispersive transport, Figure 5a, where the conductivity increases with frequency. Dispersive transport is characteristic of disordered systems. For Anderson disorder, random defects cause destructive interference among carrier scattering events, leading to localized transport. The effect of nanoscale disorder can be described by the Drude-Smith model,[30] which considers the probability of carrier backscattering from an electronic barrier reached within the charge carrier mean free path length, Figure 5b. Typical barriers include grain boundaries,[31] interfaces, nanoparticle surfaces,[32] or the potential associated with an impurity or defect. This model is typically used to describe the THz conductivity of polycrystalline organic semiconductors,[33] while single crystals show Drude-like transport.[34] Applying such a model to the extracted frequency-dependent conductivity results in a scattering time of 28 ± 2 fs and a backscatter parameter of -0.83 ± 0.01 where -1 represents complete backscatter. These values are comparable to those measured in polycrystalline polymeric systems,[33] and may be dominated by efficient transport in C₆₀ layers. No dependence on layer thickness was discernable with the uncertainty of these measurements.

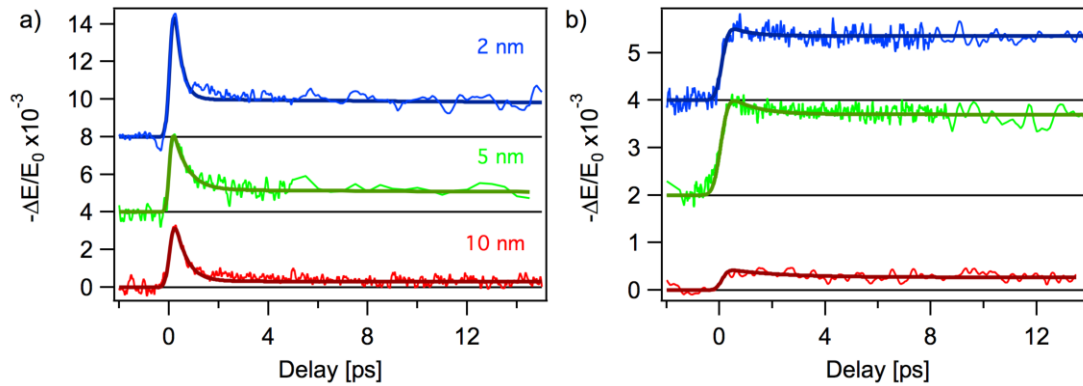


Figure 6. TRTS conductivity dynamics in α -6T:C₆₀ multilayer films as a function of layer thickness for (a) 400 nm and (b) 615 nm excitation. Solid lines are fits to the data.

Lastly, we examine the α -6T:C₆₀ donor:acceptor system. Photoexcitation with 400 nm light yields qualitatively similar results as those observed in ZnPc:C₆₀, Figure 6a. We observe a short-lived decay to a long-lived residual component. Here, 400 nm light preferentially excites α -6T, and electron transfer into a high-lying C₆₀ state results in a hot carrier.

However, photoexcitation at 615 nm yields very different results, Figure 6b. Here, only C₆₀ can absorb photons. As we have seen, this photon energy is insufficient for C₆₀ alone to generate charge-separated states. However, hole transfer to α -6T yields an equilibrium photoinduced conductivity that persists for > 100 ps. In this case, hole transfer occurs from a “cool” state.[27] This is consistent with emerging evidence that charge separation can occur efficiently even from the lowest ground-state accessible charge transfer states.[35] This demonstrates that charge transfer does not require hot CTEs and instead can occur from thermalized states without a large driving energy.

4. CONCLUSIONS

In summary, we have examined charge transfer in two model molecular systems using time-resolved terahertz spectroscopy and transient absorption spectroscopy. In the case of charge carriers, the former provides the product of the population and mobility, while the later provides only population information. We find, for photon energies above 2.3 eV, that autoionization in C₆₀ leads to charge generation. The signature of this process is a sub-picosecond recapture of charges that are unable to escape the electron-hole mutual (Coulombic) attraction. Addition of an electron donor material facilitates charge separation. In the case of ZnPc:C₆₀, the dissociation of charge transfer excitons yields hot charge carriers with excess mobility, which dissipates as charges cool to lower energy levels and localize due to molecular reorganization. This short-lived high mobility may facilitate charge separation in some systems and aid in reducing geminate recombination. This may contribute to reports of increased charge separation yields from hot charge-transfer excitons. In the case of α -6T:C₆₀, we see that charge transfer can occur from states with little excess energy. The observation of charge separation without a significant excess driving energy provides evidence that open circuit voltage losses could be minimized by the use of sufficiently crystalline materials.

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