Ultrafast Terahertz Spectroscopy for Measuring Carrier Dynamics in Nanoscale Photovoltaic Materials

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ABSTRACT

Femtosecond pump-probe methods are useful tools for investigating transient electronic and vibrational states of conducting materials and molecular photochemistry. Ultraviolet and visible excitation pulses (<150 fs, <20 μJ, 400-800 nm) with time-delayed broadband terahertz (~500 GHz to 3 THz) probing pulses (Time-Resolved Terahertz Spectroscopy; TRTS) are used to measure linear spectroscopic transmission changes resulting from exciton and free carrier population in organic semiconducting thin films. Picosecond timescale exciton geminate recombination and longer-time free-carrier conduction in semiconductor polymers and nanolayered donor-acceptor films are discussed. Systems investigated with terahertz probe pulses include thiophene-based polymers (P3HT, PBTTT) studied as drop and spin-cast films on transparent quartz substrates. The relative conductivity of these films increases with increasing P3HT polymer molecular weight, structural regularity, and the fused rings in PBTTT further increases conduction. Recent studies of composite and nanolayered films (by vapor deposition) containing alternating Zn-phthalocyanine (ZnPc) and buckminsterfullerene (C_{60}) also yield high conduction that scales linearly with the number of interfaces and total film thickness. We find evidence for a short-lived charge transfer state of C_{60} that decays within several picoseconds of excitation. In contrast, both composite and multilayered films exhibit long-lived THz dynamics that depends on the composition and structure of the films. The optimum composition for charge transfer within composite films is observed for a ~1:1 blend of ZnPc with C_{60} and a 4:1 blend of P3HT with Phenyl C_{61} Butyric Acid Methyl Ester (PCBM) while an increase in charge photo-generation with decreasing layer thickness (2 nm) exhibits the strongest THz signal. These findings parallel results for FET polymer transistor devices pointing to the advantage of optically measuring material properties before device test.

Keywords: Organic photovoltaic, Buckminsterfullerene, PCBM, P3HT, PBTTT, Phthalocyanine, THz Spectroscopy

I. INTRODUCTION

Organic semiconductors are a class of materials with the propensity for a variety of applications, including photovoltaics and solar cells. The performance of solid-state organic solar cells has improved dramatically in the last few years, with certified power conversion efficiencies under simulated solar illumination exceeding 5%.[1,2,3,4] The structure of an organic solar cell is governed by the excitonic nature of these materials, and the photocurrent in an organic solar cell is generated by a photoinduced charge transfer between a donor and an acceptor molecule. A difference between the electron donor and acceptor electron affinity or ionization potential (or both) drives the charge transfer reaction.

The earliest organic solar cells with reasonable power conversion efficiencies were multi-layer structures fabricated by Tang.[5] Charge separation occurs at the interface between two materials, generally referred to as an organic heterojunction, and charge transport occurs through the respective layers. The primary limitation of such a structure is that only absorption near the heterojunction contributes to the photocurrent. A primary alternative design uses a blend of the electron donor and acceptor, the so-called bulk heterojunction, in which the entire film is photoactive. Such structures have virtually 100% charge separation efficiency. However, charge transport can be problematic with short-range recombination and conduction pathway dead-ends limiting device efficiency. Balancing the competing demands of efficient charge separation and transport is the primary challenge facing the field of organic photovoltaics. Figure 1 illustrates the two archetypical structures used for organic-based photovoltaic solar cell devices.

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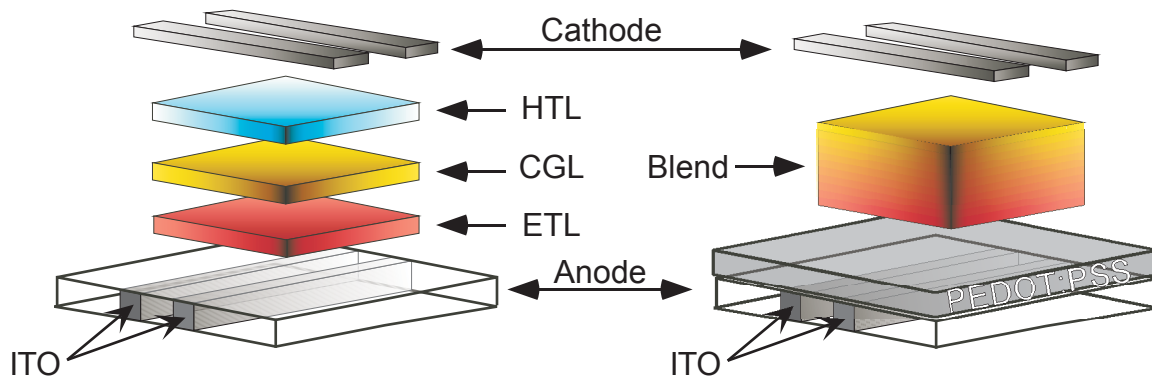
Figure 1. Schematics of multi-layer (left) and bulk heterojunction (right) organic solar cells. HTL = hole transport layer. CGL = charge generation layer. ETL = electron transport layer. The anode in a multi-layer cell is most commonly a conductive oxide such as indium tin oxide (ITO). Blended heterojunction films studied here are comprised of a conducting polymer, such as poly(3- hexathiophene) mixed with electron trapping Phenyl C_{61} Butyric Acid Methyl Ester (P3HT:PCBM).

Molecular semiconductors possess superior purity and charge mobility with respect to polymer semiconductors, yet the efficiency of polymer-based cells has outpaced their molecular counterparts. Solution processing and subsequent annealing of polymer/fullerene blends leads to a phase-segregated morphology resulting in high internal quantum efficiency and balanced charge transport.[2] In contrast, co-deposition of molecular semiconductors results in an evenly blended morphology with poorer charge transport. One approach, with the promise to combine efficient charge photo-generation in bulk heterojunction (polymer) cells with the efficient charge transport of the layered (molecular) cells, has been to sandwich composite layers between charge transport layers. This design could enhance charge photo-generation without sacrificing the higher mobility of individual neat layers. A comparison study of the intrinsic properties of blended films and charge generation layers is therefore warranted and given here. We also investigated multi-layer structures, both as models for organic solar cells as well as possible charge generation layers.

In a TRTS experiment, the differential THz transmission signal arises from an absorptive pump pulse induced change in the THz probe pulse peak transmission amplitude recorded as a function of the relative time delay between the THz probe and pump pulses. When pump pulses excite the films (at time $t = 0$), carriers are generated and evolve in time. The differential transmission signal contains information about the ultrafast carrier dynamics during their generation, evolution and subsequent recombination. Carrier population at the time of generation cannot be directly estimated from the measured response, but relative photon-to-carrier efficiency comparisons of the films under investigation can be performed. At any given time delay the measured differential THz transmission is proportional to the product of the effective mobility and carrier density, which is proportional to the carrier generation efficiency. The carrier dynamics measured by TRTS for films reviewed here are complex, exhibiting lifetime components with decay times ranging from 10^{-12} to 10^{-9} sec. Relative strengths of the individual decay components and their lifetimes are sensitive to the film structure and composition. The investigation of early-time film dynamics offers unique opportunities to improve the photoconductive characteristics of the active materials by better understanding the carrier evolution properties.

II. EXPERIMENTAL

P3HT and PBTTT polymers were purchased from the Sigma-Aldrich Co. and EMD Chemicals Inc. and used as received without further purification.[6] The molecular weight range of P3HT (17.5 kD to 150 kD) is assumed to be a high molecular weight range and the cast film morphologies from these samples was expected to be similar. Spin or drop cast samples were prepared on THz-transparent quartz slides (GM-7525, GM Associates Inc.[6]) from saturated solutions (unless otherwise specified) of P3HT or PBTTT dispersed in chloroform, xylenes, or toluene. Optical density (OD) measurements and UV-Visible ellipsometry indicated the spin cast films were ca. 50 nm to 100 nm thick while the drop cast films were >10 μm thick. An amorphous quartz substrate was chosen because oriented z-cut quartz generates weak

UV pump pulse-induced THz interference signals of similar magnitude to the measured film transient response. All THz measurements were carried out from freshly prepared materials stored in the dark.

Zinc phthalocyanine was purchased from Aldrich and C_{60} was purchased from SES.[6] Both materials were purified twice via vacuum train sublimation prior to use. The organic layers were deposited onto a quartz substrate by vacuum thermal evaporation under a background pressure of $<1.3 \times 10^{-4}$ Pa ($<10^{-6}$ Torr) at a rate of ~0.5-1 Å/s. Composite samples were prepared by simultaneous evaporation of ZnPc and C_{60} whereas multi-layer structures were prepared by alternately opening and closing shutters in front of the furnaces. The blend films were deposited by varying mass ratios of ZnPc and C_{60}; neat films of ZnPc and C_{60} were also prepared. Multilayered film structure is formed by vapor deposition of alternating layers of ZnPc or C_{60}. The alternating layer thickness ranged from 2 nm to 40 nm in multilayer films and the sample thickness was estimated by measuring the evaporation rates before and after depositing the organic layers. Rates were found to be relatively constant throughout a deposition, varying no more than 10%. Optical absorption spectra were measured with an HP 8423 UV/Visible spectrophotometer and not corrected for interference.

Details of the kHz repetition-rate Ti:Sapphire laser amplifier-based TRTS apparatus were reported elsewhere.[7] Thin films were typically excited with 400 nm [3 eV, fluence of $(5.7 \pm 0.2) \times 10^{14}$ photons/cm^2], 60 fs pulses and interrogated with optically gated and synchronized time-delayed ultrafast THz probe pulses (ca. 0.5 ps FWHM with center frequency at ~1 THz). The TRTS instrument has ca. 0.5 ps time resolution based on response measurements of a double-side polished silicon wafer. Therefore, the peak amplitude of the differential transmission near $t = 0$ ps may not be directly proportional to the instantaneous photoconductivity, but reflects an integrated value detected by the system. The strongest observed pump-induced modulation in the THz field is less than 3% of the peak transmitted THz field amplitude if all the light is absorbed. Time-resolved data was obtained by averaging 20-60 time-delay sweeps. The TRTS spectrometer was contained inside a plastic housing purged with water and CO_2-free air to minimize water vapor interference effects. All samples were preconditioned inside the dry spectrometer or held under vacuum in a cryostat for 1 hour before measurements were conducted. We did not observe photo-oxidation or photo-bleaching of the films over the course of the experiments. Time zero and the instrumental risetime were measured using the double-side polished silicon wafer as a reference sample and is $t = 0$ is defined as the half-rise of the observed modulation.

III. RESULTS AND DISCUSSION

III(a) Optical Absorption Spectra

As examples, Figure 2 shows the UV-visible absorption spectra of C_{60}, ZnPc, composite film of C_{60} and ZnPc (50% by weight) and a ZnPc/C_{60} super-lattice with 10 nm thick layers. The absorbance varies from 78% to 94% at the excitation wavelength. Total film thicknesses ranged from 160 nm to 250 nm. As the extinction coefficients of C_{60} and ZnPc are quite low at the excitation wavelength, variations in excitation density are relatively moderate throughout the films. The composite and superlattice films exhibit characteristic absorption features of pure ZnPc and C_{60}. For spectra of blended structures, there was narrowing observed at a raio as low as 2 weight % C_{60} in ZnPc with the fully reduced splitting observed with films containing 75 weight % ZnPc or less. The second feature worth noting is the absorption peak at 450 nm arising from C_{60}. This peak is not observed from C_{60} in solution and therefore arises from interactions amongst neighboring fullerenes. This feature is not seen in the composite films with more than 20 weight % ZnPc, but is observed in all superlattice films. Hence, the multilayered structure shows increased crystallinity, even when the layer thickness is only equivalent to several C_{60} molecules. This feature is evidence for phase segregation during the deposition of ultrathin layers, a desirable property for use in a bulk heterojunction cell. P3HT (or PBTTT) with PCBM exhibit similar UV-visible absorption features.[7]
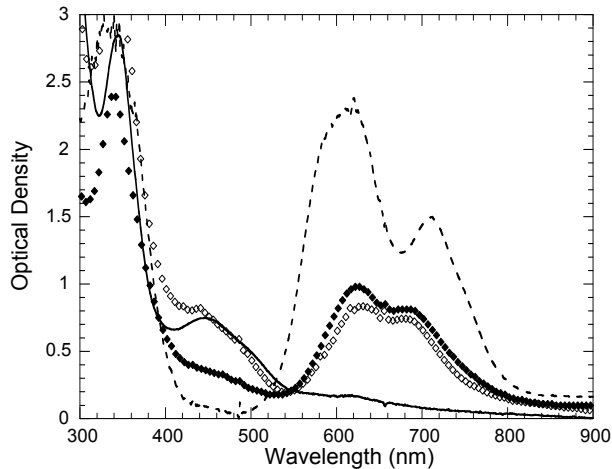
Figure 2. Absorption spectra of neat ZnPc (dashed line), neat C_{60} (solid line), a composite film containing 50% each C_{60} and ZnPc by weight (filled symbols), and a ZnPc/C_{60} superlattice with 10 nm thick layers (open symbols).
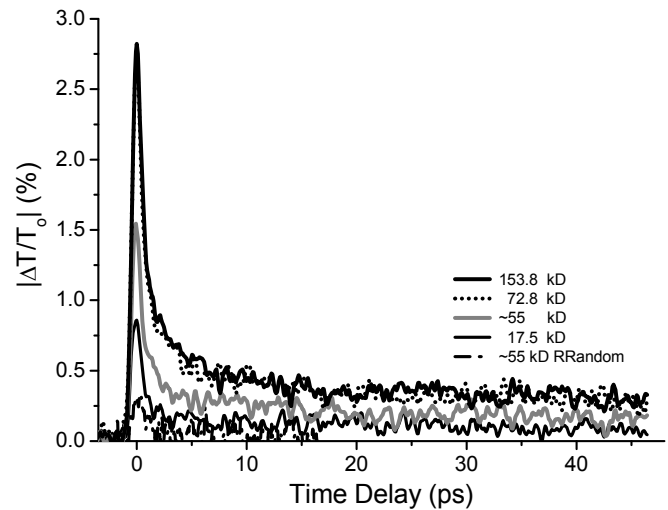
Figure 3. UV (400 nm) pump induced modulation of the transmitted peak THz field of P3HT films varying with molecular weight and regio-randomness measured as a function of pump-probe delay time.

III(b) Time-Resolved Terahertz Spectroscopy of neat and blended films of P3HT and PCBM [7]

Figure 3 shows the time-dependent pump-induced decrease of the THz transmission for four different molecular weight P3HT polymer films. The differential transmission amplitude clearly increases with increasing molecular weight of the P3HT polymers. All TRTS molecular weight (MW) dependence measurements were carried out on thick (> 10 μm and OD > 3 at 400 nm) drop cast samples made from saturated (~10 mg/ml) P3HT/Xylene solutions. The estimated optical penetration depth (1/α) at 400 nm is ~220 nm. Films with OD > 3 at the pump wavelength ensures absorption of all the pump light by the polymer film. Excluding the structurally regio-random 55 kD sample (dash-dot line), the lowest molecular weight (17.5 kD) P3HT film (thin-solid line) showed the lowest differential change in the THz transmission. Both 153.8 kD (solid line) and 72.8 kD (dotted line) P3HT films generated very similar differential THz transmission changes with the highest MW P3HT sample (153.8 kD) yielding a ~5 % increase in signal over the 72.8 kD sample. In all cases, and as has been observed both in P3HT and MEH-PPV film systems,[8] the time-dependent THz response shows initial complex ultrafast decay components followed by a very slow (~ns timescale) component. The relative changes in signal intensity are in good agreement with corresponding device mobility measurements.

The room temperature carrier absorption decay dynamics observed in our experiments (Figure 3) are similar to ones reported elsewhere.[8,9] The decay in photoconductivity of all examined P3HT films exhibits multi-exponential relaxation behavior. The ultrafast component is most likely the result of a very fast electron-hole geminate recombination process. The time resolution is limited by the rise-time response of our instrument (~1 ps baseline to peak) as measured from the silicon time zero single-sided reflection transient. Intermediate decay contributions most likely originate from local carrier recombination processes that are expected to be most sensitive to the amorphous material structure. The longest, nearly flat decay constant estimated to be ~1 ns, is expected to be carrier diffusion limited. These results suggest that the photogenerated carriers may live longer than several ns in these polymer films.

One of the most striking observed results was the comparison between the transient response of regio-random and regio-regular 55 kD P3HT films. The results shown in Fig. 3 (dash-dotted versus gray lines, respectively) demonstrate the importance of local structural regularity and how it potentially affects and enhances carrier mobility. The measured peak transmission signal change is almost an order of magnitude smaller for the regio-random sample than for the regio-regular P3HT film and decays to nearly zero signal (to within the experimental noise) on a very short timescale (within a

few ps). The difference between the two films becomes increasingly large with time suggesting that many orders of magnitude difference in conductivity (or mobility) exists for long timescale measurements, as is found in device measurements.

Additional measurements on composite films containing P3HT and PBCM were conducted and the results shown in Figure 4. A 4:1 weight ratio yielded the largest change in THz signal suggesting this film has the best nanoscale
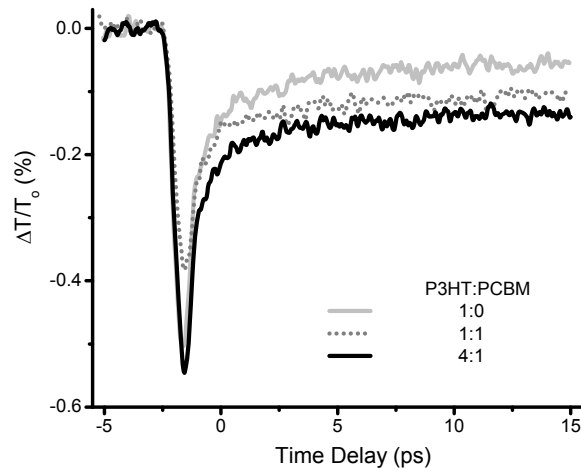

Figure 4. Effect of adding C_{60} (PCBM) electron traps to cast films of P3HT with varying weight percent ratios. A composite film with 25 weight % PCBM improves relative film conductivity by about a factor of two.

morphology for increased conductivity. These simple relative THz signal measurements demonstrate the strength of using THz methods to directly distinguish between highly conductive versus near-insulator behavior of polymeric materials.

III(c) Time-Resolved Terahertz Spectroscopy of neat films of PBTTT and P3HT[10]

Figure 5 compares the pump-induced differential THz transmission response of as-cast (AC) and above liquid-crystal
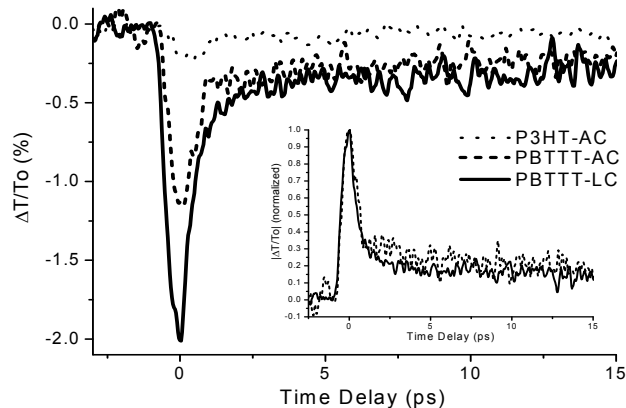

Figure 5. Time-resolved differential transmission decays of as-cast (AC), liquid crystalline temperature annealed (LC) PBTTT and as-cast P3HT films on quartz substrates. Data are corrected for optical density variations. The inset compares the peak normalized $|\Delta T/T_0|$ signal decays for PBTTT-AC and PBTTT-LC.

temperature annealed (LC) PBTTT films (heated to 450K for 5 min) to a similarly as-cast P3HT film. The THz differential transmission ($\Delta T/T_0$) shows the fractional decrease in THz peak field transmission through the sample when the sample is excited at 400 nm compared to that of an unexcited film as a function of pump-probe delay time. The inset shows the peak-normalized $|\Delta T/T_0|$ decay dynamics comparison for three different films. The recovery of $\Delta T/T_0$ (or decay in $|\Delta T/T_0|$) with time corresponds to the disappearance of free carriers mainly by recombination processes. The samples investigated here were spin-cast in the same set-up and manner as casting thin-film transistors, thus enabling close comparison of THz and device measurements. The PBTTT films thicknesses were less than 30 nm with optical densities OD < 0.05, and the P3HT film thickness was less than 50 nm with OD ~0.1 at 400 nm. The UV spectra of the films are very similar, and their absorption maximums are 560 nm for P3HT, 545 nm for PBTTT-AC and 559 nm for PBTTT-LC. The THz differential transmission data are corrected for sample optical density variations at 400 nm since higher OD results in more generated carriers and proportionally stronger signal levels.

As seen in Figure 5, the THz differential transmission ($\Delta T/T_0$) is much larger for PBTTT-AC and PBTTT-LC films compared to that of P3HT-AC. The absolute value of $\Delta T/T_0$ for PBTTT-AC (dashed line) at 0 ps is approximately five-times greater than that of P3HT-AC (dotted line). When the PBTTT-AC film is heated above the 428K liquid-crystalline temperature, (PBTTT-LC, solid line), $|\Delta T/T_0|$ increased by roughly another factor of two and was an order of magnitude higher than that of the P3HT-AC film. Previous studies carried out in our group showed that annealing P3HT films cast from a low volatile solvent (e.g. xylenes) produce negligible changes in their differential THz transmission.[12]

III(d) Time Resolved Terahertz Spectroscopy of neat ZnPc and C_{60} films and blends of ZnPc and C_{60} [11]

Figure 6 shows the measured differential transmission data (uncorrected) of varying weight composite films of ZnPc and C_{60} as well as a film of neat C_{60}. No significant photo-induced THz signal was observed from a neat film of ZnPc. We observed complex decay dynamics for the photo-generated carriers that again depend on the composition of the films. In general, there is a very fast rise (increased THz absorption or reflection) upon excitation to a peak followed by a rapid decay within a few picoseconds and then a much slower decay. We first consider the short time rise and fall of the signal near t=0. The largest amplitude peak is observed for a neat C_{60} film, but this signal decays as a single exponential with a lifetime $\tau = 0.65 \pm 0.12$ ps. The instrumental risetime dynamics are independent of composition spanning 1.0 ± 0.1 ps from the onset of absorption to the peak. The short-time t>0 signal decays to the baseline within 10 ps and there is no evidence for significant photogeneration of long-lived carriers in neat C_{60}. The t~0 peak amplitude is proportional to the C_{60} content in the blended films suggesting that it originates from an intramolecular state and not from interactions between C_{60} and ZnPc. Explanations for the short-lived signal from C_{60} is ultrafast geminate recombination of excitons or THz absorption by a charge transfer (CT) state.[10] This state requires photoexcitation above 2.3 eV, consistent with our experimental conditions. One interesting question arises: Is the CT state a precursor to photocarrier generation or is it a short-lived state that decays and charge transfer occurs later? Whether or not this state is affected by the proximity of a ZnPc molecule can be elucidated through the dynamics of the THz signal.

The decay dynamics of the composite samples contain short-lived (ps) and more slowly (sub-ns) decaying components; these have been fit to the sum of multi-exponential decays but in every case, the decay dynamics can be adequately fit as the sum of two exponentials with a constant asymptotic background level. From the simpler fitting approach, the short time dynamics were found to be exponential but there is a residual deviation from the fit in the transition regime from the fast to slower decay. Bi-exponential time constants with amplitude fitting parameters for blends of C_{60} and ZnPc were obtained with R^2 fits >0.91. The slow decay can also be fit to an exponential, though the exact nature of this decay cannot be determined as the dynamics take place on a longer timescale than the pump-probe delay range (ca. 45 ps as shown). Residual signals were observed for time delays up to 500 ps. However, the decay dynamics must be related to diffusion mediated recombination and trapping of the generated charges. While we have no specific model for the early-time carrier decay dynamics, the long-lived carriers are of greatest technological interest since they are responsible for conduction and overall photo-conversion efficiency. As mentioned earlier, the relative THz signal level is proportional to the photoconductivity of the films and should be proportional to the efficiency of charge photogeneration. There is a clear dependence on the composition of the sample with the strongest signal at longer pump-probe delays (near t=50 ps) occurring for the sample with a 50/50 composition of C_{60} and ZnPc. It is worth noting the dependence of the fast decay lifetime on the ZnPc concentration. This increases from ca. 0.58 ps for neat C_{60} to (1.4 – 1.7) ps for samples containing >50% ZnPc suggesting that the optically excited C_{60} decay dynamics are affected by neighboring ZnPc molecules.
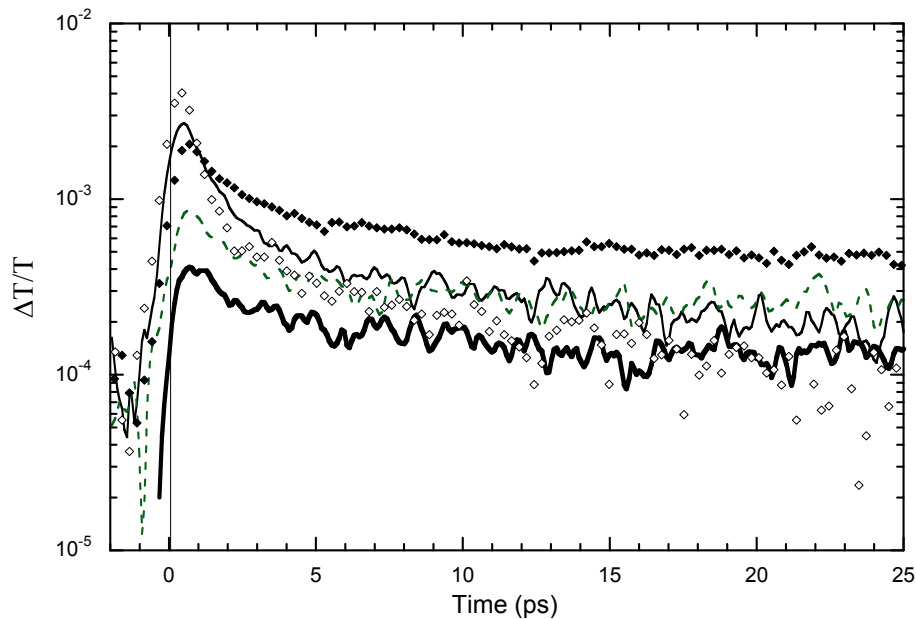
Figure 6. THz transients (not amplitude normalized) for mixed C_{60}:ZnPc (wt %) deposited films of neat C_{60} (open symbols), 75% C_{60} (dashed line), 50% C_{60} (filled symbols), 25% C_{60} (thin solid line), and 10% C_{60} (bold solid line).

III(e) THz Response from Nanolayered films of ZnPc and C_{60} [9]

Studies of composite films determined that the optimum composition for a charge generation layer occurs for roughly equal weight percent blends of P3HT with PCMB or ZnPc and C_{60}. To better understand charge migration through the electron and hole transport layers, we studied multilayer structures consisting of alternately deposited layers of C_{60} and ZnPc. Figure 7 shows the experimental data for samples with layer thickness varying from 2 nm to 40 nm. The carrier generation and subsequent transport properties are complicated and highly dependent on the thickness of ZnPc and C_{60} layers. As with the composite films, the signal decays is multi-exponential with a fast component having a lifetime less than 2 ps and a slow decay component that occurs on a time scale longer than that of the experiment. The sample with 40 nm thick layers most closely resembles that of neat C_{60} with a weak, slowly decaying component originating from charge transfer at the organic heterojunctions. Amplitudes of the differential transmission at long pump-probe delay ($t >$ 10 ps) suggest that the relative efficiencies of these model active layers increases as the total number of layers increases. The intensity of the slowly decaying component also increases with decreasing layer thickness, as a greater fraction of the sample will be available for charge transfer. Exciton diffusion will be minimal during the short timescale of this experiment and thus photocarriers are generated only from excitations formed in proximity to the heterojunction.

There are two important results from these multilayer film studies. First, the $|\Delta T/T_0|$ signal from samples with 10 nm or thinner layers is comparable to that of the best composite bulk films. This is an indication that carrier mobility is highest in neat films. Most important is that the multilayer films retain their superior mobility even when the layer thickness corresponds to only a few molecular monolayers. Second, the decay of the THz signal is slower in the multilayer films than in composites. Figure 8 compares the THz absorption of different multi-layered samples to that of the 1:1 blend, normalized to the initial peak amplitude. These data indicate that photocarriers have separated into the distinct layered domains despite the possibility that interfacial disorder could disrupt mobility. Additional studies are underway to measure the relative THz response as a function of excitation wavelength, devising methods to perform electrical measurements on nanolayered photocells and alternative device structures with the anticipation of developing more efficient heterojunction molecular solar cells.
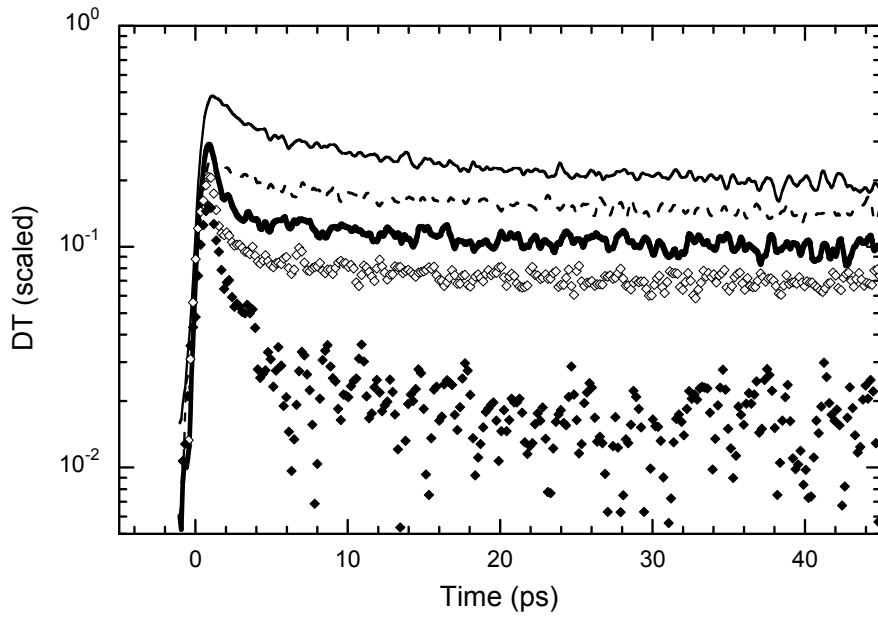
Figure 7. THz absorption transients for multilayer films of C_{60} and ZnPc with thicknesses of 2 nm (line), 5 nm (dashed line), 10 nm (bold line), 20 nm (open symbols) and 40 nm (filled symbols).
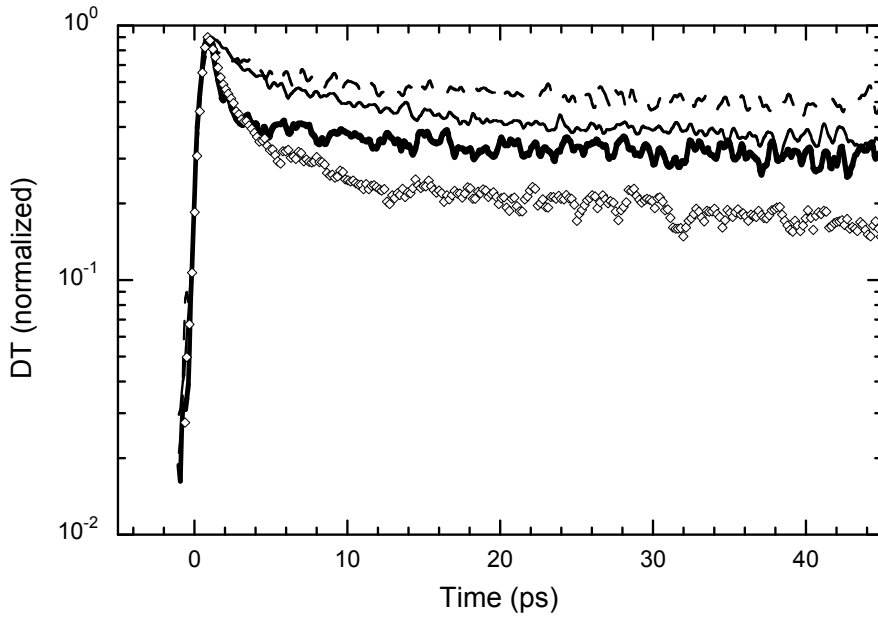

Figure 8. Normalized THz absorption transients for multi-layer films of C_{60} and ZnPc with thicknesses of 2 nm (line), 5 nm (dashed line), 10 nm (bold line), and a 1:1 ZnPc:C_{60} blend (open symbols).

IV. CONCLUSIONS

We studied the photo-excited carrier dynamics of model organic semiconductor films for photovoltaic thin-film and solar cell applications by time-resolved terahertz spectroscopy. The transient decay dynamics of neat P3HT and PBTTT films, composite films with PCBM and multi-layered films showed complex multi-component decay for all types of films. The optimum composition for a blended film was found to be a 1:1 ratio of $ZnPc:C_{60}$ while the largest signal was obtained for a 4:1 weight ratio of P3HT:PCBM. Photoexcitation at 400 nm of neat films of C_{60} and ZnPc did not result in the generation of long-lived carriers. For multi-layered $ZnPc:C60$ films, an increase in THz signal amplitude with decreasing layer thickness is observed with the thinnest layers (ca. 2-5 nm) giving the strongest signal and hence the highest conductivities. Furthermore, photocarrier population decay was slower (e.g., higher conductivity) in multilayered samples than in composite samples. These overall results suggest a different approach to increasing charge separation and maximizing free carrier generation occurs in layered organic photovoltaics based on sublimed molecular semiconductors.

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