ABSTRACT

We present photoconductivity of high-performance functionalized pentacene and anthradithiophene thin films on time scales from picoseconds to many seconds after photoexcitation. The polycrystalline thin films were deposited from solution on glass substrates with patterned interdigitated aluminum electrodes. In studies of fast transient photoconductivity, the samples were excited with laser pulses of ~100 fs duration at a wavelength of 400 nm, and the photocurrent due to transport of photoexcited charge carriers was monitored using 50 GHz digital sampling oscilloscope. The photoconductivity at longer (milliseconds through seconds) time scales was investigated using continuous wave (cw) illumination and a source-delay-measure unit. Both experiments were performed under conditions of varied electric field strength, fluence and temperature. In all samples, we observed fast charge carrier photogeneration (<30 ps, limited by time resolution of our setup) followed by decay of the photocurrent over the period of ~5-50 ns, depending on the material, due to charge trapping and recombination, linear dependence of the peak photoconductivity on the fluence and super-linear dependence of the peak photocurrent on the applied electric field.

INTRODUCTION

Organic semiconductors are of interest due to their potential applications in molecular electronics and photonics [1]. In order to develop organic semiconductor devices, it is important to understand the mechanisms of (photo)conductivity in organic materials. However, using thin-film device structures and traditional dc methods (such as field-effect transistor and space-charge-limited current geometries) to characterize intrinsic electronic properties of materials is complicated, in part due to the influence of defects on the overall electronic response of the device. In contrast, monitoring of the charge carrier dynamics on short time scales after excitation allows for probing charge transport properties prior to trapping at defects. Therefore, it makes it possible to study both intrinsic charge transport and the process of charge trapping. Extension to longer time scales allows for exploring the charge detrapping processes and equilibrium charge transport mechanisms, relevant for devices operating in the dc regime such as thin-film transistors.

In this paper, we report on the time-resolved transient photoconductivity of high-performance functionalized pentacene and anthradithiophene derivatives, measured using a high-bandwidth digital sampling oscilloscope. In all materials studied, charge carriers are photogenerated on the time scale of tens of picoseconds (ps), limited by the time resolution of our setup. Differences in charge carrier dynamics at nanosecond time scales are observed in pentacene and anthradithiophene derivatives. Photoconductivity obtained upon illumination of the samples with either pulsed or continuous wave light increases as the temperature decreases.

MATERIALS

The materials we have investigated are pentacene derivatives functionalized with triisoproplysilylethynil side-groups (Pc-TIPS, Fig.1(a)) [2, 3] and fluorinated anthradithiophene derivatives, also functionalized with TIPS groups (ADT-TIPS-F, Fig.1(b)) [4]. Both materials exhibit "brick-wall"-type crystal packing that favors two-dimensional charge carrier transport [2,3]. Thin polycrystalline films of these materials were prepared by drop-casting from toluene solution onto glass substrates, on which aluminum interdigitated electrode pairs had been

deposited by photolithography. Spacing between the fingers of the interdigitation is 25 μm. Two types of interdigitated sample geometry were investigated, with the fingers width of 25 μm or 50 μm.

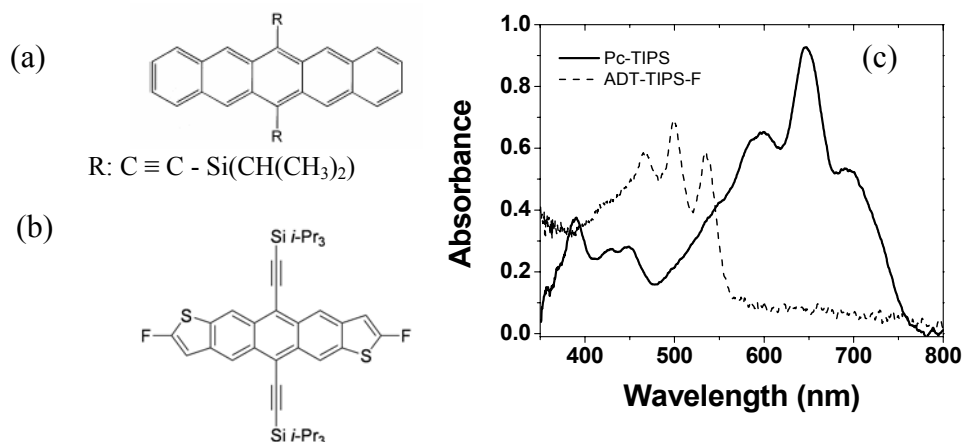Typical absorption spectra of the Pc-TIPS and ADT-TIPS-F films are shown in Fig.1(c).

Figure 1. Molecular structures of (a) Pc-TIPS and (b) ADT-TIPS-F. (c) Absorption spectra of typical polycrystalline Pc-TIPS and ADT-TIPS-F films.

EXPERIMENTAL SETUPS

Electronic properties of the samples were explored using three different approaches. In particular, current in the absence of illumination, photocurrent under steady-state, continuous-wave (cw) laser illumination, and transient photocurrent in response to pulsed laser illumination were measured.

Current flowing through a sample in the absence of illumination (referred to as a "dark current") was measured using the Keithley 237 source-measure unit.

The experimental setup for measurements of the cw and transient photoresponse is depicted in Figs. 2(a) and (b), respectively. For measurements of the cw photoresponse (Fig.2(a)), the interdigitated sample area (1 x 1 mm, inset of Fig.2(a)) was illuminated with 532-nm cw NdYVO$_4$ laser at the intensity of ~30-300 mW/cm^2. The voltage was applied to the sample using Keithley 237 source-measure unit. The beam was chopped at 510Hz, and the photoresponse was measured using a Stanford Research Systems SRS830 lock-in amplifier.

In the case of the transient photoresponse, 800-nm pulses of approximately 100 fs duration, from a Ti:Sapphire amplified laser system (1 kHz, 1 mJ/pulse), are frequency-doubled in a BBO crystal to yield 400-nm pulses incident upon the sample. The range of incident pulse fluence was ~0.01 – 0.1 mJ/cm^2. The voltage was applied, and the transient photocurrent due to charge carriers generated in the sample by the laser pulse and moving under applied electric field resulted in a transient voltage signal across the load resistor. This signal was amplified by a Centellax 30dB 50GHz-bandwidth inverting amplifier and registered by a Tektronix CSA8200 digital sampling oscilloscope (DSO) equipped with the 50 GHz-bandwidth sampling head (80E01). The front end of the CSA8200 sampling module is protected from voltage transients by a Picosecond Pulse Labs Model 5509 DC block.
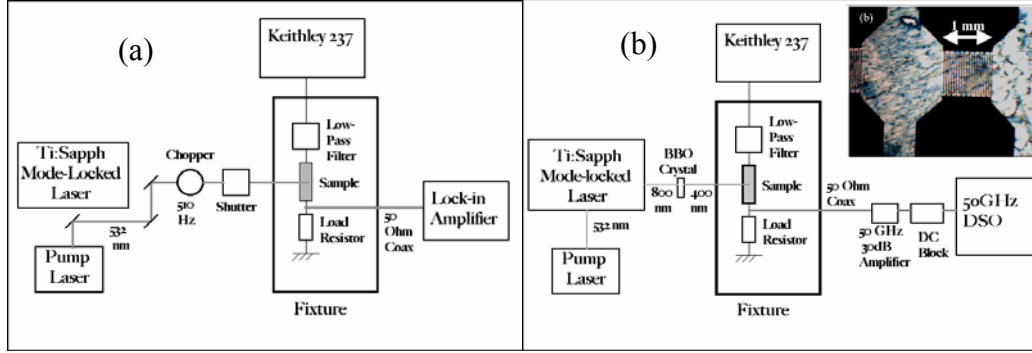
Figure 2. Experimental setups for measurement of (a) cw and (b) transient photoconductivity. Inset shows Pc-TIPS thin film on interdigitated-electrode substrate.

The fixture in which the sample is placed was optimized for minimal parasitic impedances which may distort the transient signal. All signal paths were made as close to zero-length as possible to minimized stray inductances; special placement of fixture elements with respect to one another minimized stray capacitances.

All experiments were repeated as a function of temperature, voltage and, in the case of the photoresponse, incident beam intensity. Temperature variation of samples has been achieved using Peltier thermoelectric devices, which provided a temperature range of ~285-335 K.

RESULTS AND DISCUSSION

Dark current and cw photoconductivity

In all samples, dark current (I_d) exhibited nearly linear dependence on the applied voltage (solid squares in Fig.3, $I_d \sim V^a$, a = 0.9 ± 0.1), which suggests close to Ohmic behavior at the metal-organic interface.

At 532-nm cw illumination with light intensity of ~100 mW/cm^2, the observed photocurrent was at least an order of magnitude higher than the dark current in both Pc-TIPS and ADT-TIPS-F samples (empty circles in Fig.3). The photocurrent increased linearly with the incident light intensity. The voltage dependence of the photocurrent (I_{ph}) was super-linear (e.g. $I_{ph} \sim V^b$, b = 1.25 ± 0.03 in the case of Pc-TIPS in Fig.3), which suggests slightly electric field-dependent charge photogeneration efficiency, charge carrier mobility or both. Temperature dependence of cw illumination-induced photocurrent is shown in Fig. 4. Interestingly, in both materials the signal decreases as the temperature increases, in contrast to the behavior expected from charge carriers photogenerated via exciton dissociation [3]. A power-law fit to the data ($I_{ph} \sim T^{-\alpha}$) yields a power-law exponent of α = 2.1 ± 0.3, which is consistent with that observed in charge carrier mobility measurements in ultra-pure pentacene [5], rubrene [6] and tetracene single crystals [7] in a similar temperature range.
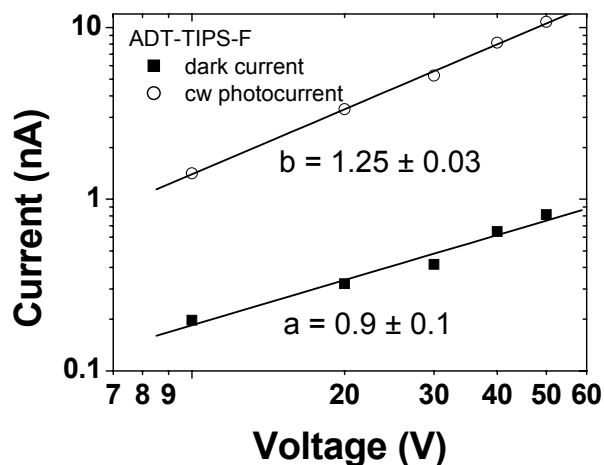
Figure 3. Dependence of the dark current (I_d, solid squares) and cw photocurrent (I_{ph}, empty circles) on the applied voltage (V) observed in ADT-TIPS-F film. Lines correspond to power-law fits ($I_d \sim V^a$ and $I_{ph} \sim V^b$), with the power-law exponents a and b indicated on the graph.
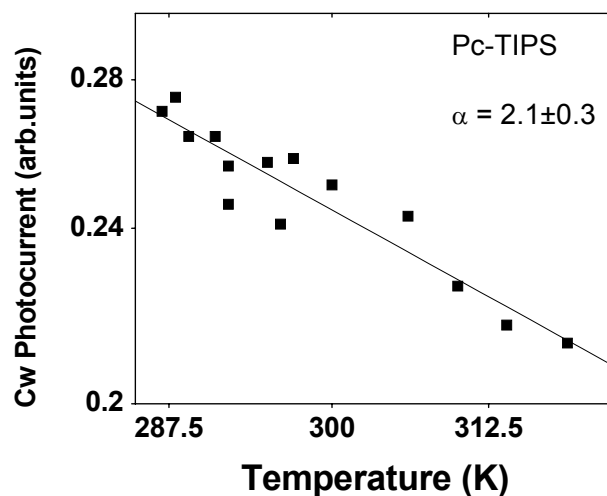

Figure 4. Temperature (T) dependence of cw photoresponse (I_{ph}) of Pc-TIPS thin film (solid squares). A power-law fit ($I_{ph} \sim T^{-\alpha}$) to the data yields the exponent of $\alpha = 2.1 \pm 0.3$.

Transient photoconductivity

The transient photoresponse, normalized at its peak value, obtained in Pc-TIPS and ADT-TIPS-F thin films upon excitation with 400-nm pulsed light is presented in Fig. 5(a). To the best of our knowledge, this is the first demonstration of fast photoresponse in thin films of these materials using direct measurements, and not the indirect non-contact techniques such as ultrafast optical pump – terahertz probe spectroscopy [3].Under the same experimental conditions, the photoresponse obtained in ADT-TIPS-F films was approximately a factor of 2 of that in Pc-TIPS films. While in Pc-TIPS films, the photocurrent decays completely on time scales of several nanoseconds, that in the ADT-TIPS-F films is much slower, on the order of at least 50 ns. This is consistent with fewer defects and stronger π-overlap in the ADT-TIPS-F film that promotes charge propagation over larger distances.

The rise-time of the transient photoresponse obtained in all samples was approximately 30 ps (inset of Fig. 5(a)), limited by time resolution of our sample fixture. This suggests fast charge carrier photogeneration, consistent with the results of optical pump-terahertz probe experiments in similar materials [3]. Work is currently underway to improve the sample fixture to the point where the time-resolution limitations of this setup are those solely of the DSO, which is capable of time resolution of ~7 ps. Nevertheless, the data in Fig.5(a) establishes an upper limit for carrier photogeneration-times under the influence of a constant applied electric field.

Similar to the case of the cw photocurrent, the amplitude of the transient photoresponse is a super-linear function of the applied electric field. Typical data obtained in Pc-TIPS film is shown in Fig. 5(b), which illustrates power-law dependence of the transient photocurrent amplitude (I_{ph}) on voltage (V), $I_{ph} \sim V^b$, with the power-law exponent b = 2.20 ± 0.04. This implies that transient photoconductivity exhibits an almost linear dependence on the electric field. However, the nature of this dependence (i.e. whether it is due to that of the photogeneration efficiency, charge carrier mobility or both) is currently unknown and requires further investigation. We note that no variation in decay dynamics with respect to voltage was observed.

The amplitude of the transient photoresponse varied linearly with the light fluence, which suggests negligible contribution to the photocurrent from nonlinear effects. Fig. 6(a) shows transients obtained at various fluences normalized by their peak values. In the range of fluences studied, no dependence of the decay dynamics on the fluence is observed. Therefore, there is no indication of either trap filling (which would lead to slower decay dynamics at higher fluences) or of bimolecular recombination (faster dynamics at higher fluences) under our experimental conditions in our samples.
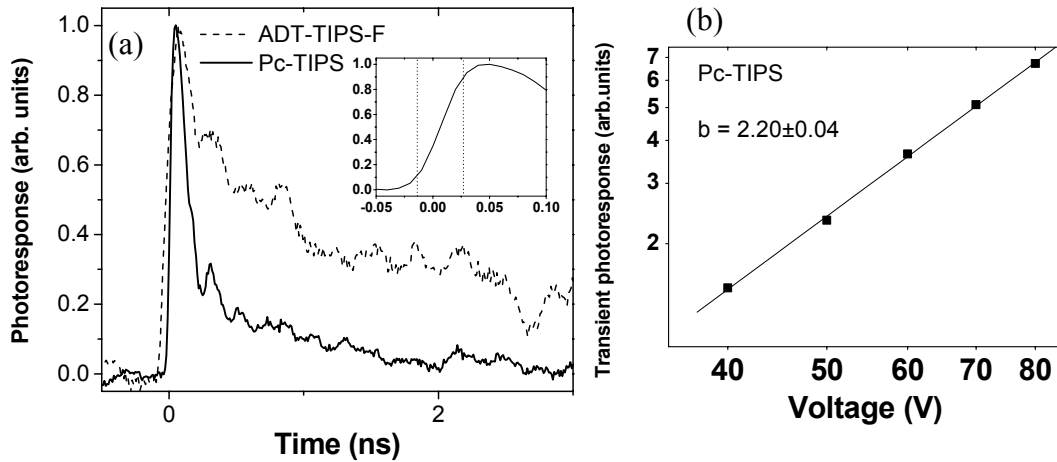

Figure 5. (a) Transient photoresponse normalized at its peak value obtained in Pc-TIPS (solid line) and ADT-TIPS-F (dashed line) thin films. Inset illustrates an approximately 30 ps rise time, limited by the time resolution of our setup, indicative of fast charge carrier photogeneration. Differences in the decay dynamics observed in these films suggest differences in charge trapping properties. (b) Amplitude of the transient photoresponse (I_{ph}) as a function of applied voltage (V) obtained in Pc-TIPS film (solid squares). Line shows a power-law fit ($I_{ph} \sim V^b$) with the power-law exponent b indicated on the graph.
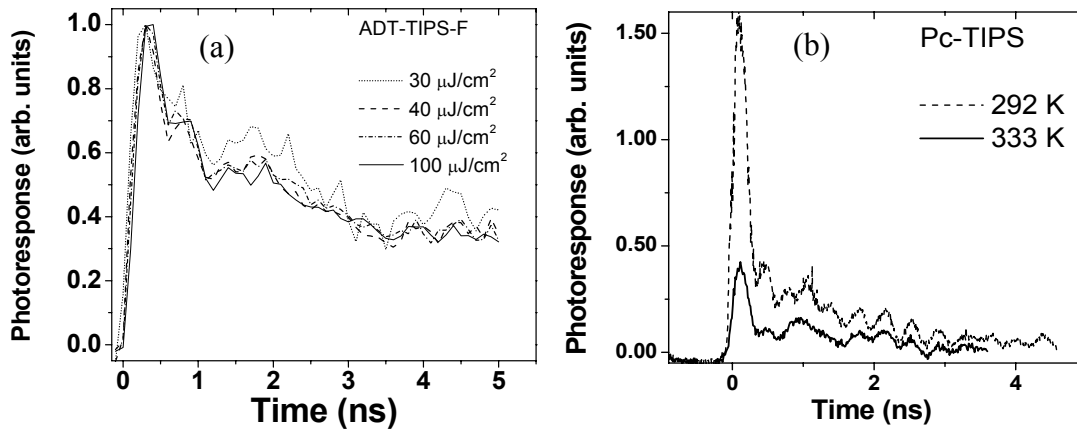
Figure 6. (a) Transient photoresponse normalized at its peak value obtained in ADT-TIPS-F film as a function of fluence. (b) Transient photoresponse obtained in Pc-TIPS film at two temperatures. As the temperature increases, the transient photoconductivity decreases.

In both Pc-TIPS and ADT-TIPS-F films, the amplitude of the transient photoresponse exhibits surprisingly strong temperature dependence: the signal dramatically decreases as the temperature increases (Fig. 6(b)). Although this result is consistent with the previous studies of ultrafast carrier dynamics in organic molecular crystals and thin films using non-contact ultrafast spectroscopy methods [3], the exact mechanism of this behavior is unknown and currently under investigation.

SUMMARY

We have demonstrated fast real-time photoresponse for functionalized pentacene and anthradithiophene derivatives. In all samples, we observed fast charge carrier photogeneration (<30 ps, limited by time resolution of our setup) followed by decay of the photocurrent over the period of several nanoseconds in the case pentacene and of many tens of nanoseconds in the case of anthradithiophene films. Linear dependence of the photoconductivity on the fluence and super-linear dependence of the photocurrent amplitude on the applied electric field are observed. Both cw and transient photoresponse in all samples increase with decreasing temperature.

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