

Electron and Hole Contributions to the Terahertz Photoconductivity of a Conjugated Polymer:Fullerene Blend Identified

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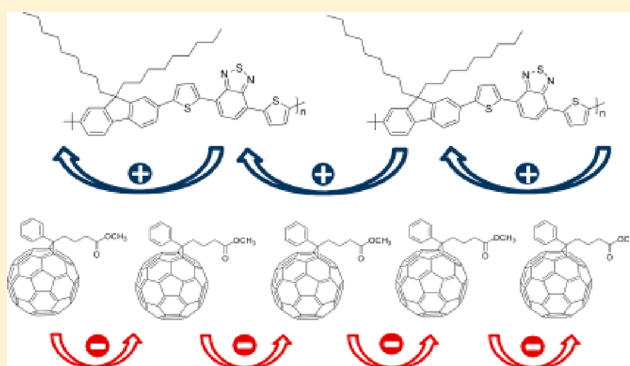
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ABSTRACT: Time-resolved terahertz spectroscopy was employed for the investigation of charge-transport dynamics in benzothiadiazolo-dithiophene polyfluorene ([2,7-(9,9-dioctylfluorene)-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]) (APFO-3) polymers with various chain lengths and in its monomer form, all blended with an electron acceptor ([6,6]-phenyl-C61-butyric acid methyl ester, PCBM). Upon photoexcitation, charged polaron pairs are created, negative charges are transferred to fullerenes, while positive polarons remain on polymers/monomers. Vastly different hole mobility in polymer and monomer blends allows us to distinguish the hole and electron contributions to the carrier mobility.



SECTION: Energy Conversion and Storage; Energy and Charge Transport

The search for inexpensive and easily manufacturable solar cell materials has attracted extensive research on conjugated organic semiconductors.¹ To understand and optimize the efficiency of the most promising polymer/fullerene bulk heterojunction systems,² comprehensive study focusing on the charge transport on the earliest time scale is required. Several recent papers on these systems reported the dynamics of charge carriers in the picosecond time regime.^{3–8} In the generally accepted picture, electrons are almost immediately transferred to the fullerene balls, leaving free holes on the polymer chains.⁹ However, it is quite difficult to characterize charge transport on picosecond time scales. One of the few available techniques is time-resolved terahertz (THz) spectroscopy (TRTS); on the other hand, the spectra of THz photoconductivity are still far from being fully understood.^{10,11} In particular, the effective masses of electrons and holes are undefined in organic semiconductors, which prevents the estimation of the mobilities of distinct charge carriers. As a result, there has been no clear experimental evidence to confirm whether the THz photoconductivity is really dominated by holes, electrons, or both.

In this work, we show that for a polymer/fullerene blend positive polarons on the polymer are the major contributors to the THz photoconductivity with electrons in the fullerene phase responsible for a minor part. For this purpose, we measured and compared the THz spectra of the polymer blends with increasing molecular weights and its monomer blend counterpart. The use of different chain lengths should give rise

to largely different hole conductivities as holes moving along longer chains should be much more mobile.^{8,12}

The primary result of TRTS measurements is the photoconductivity spectrum $\Delta\sigma$ normalized by the excited charge density $e_0 n_{\text{exc}}$ which generally corresponds to the sum of products of the quantum yields ξ of excitations and their mobility spectra μ

$$\frac{\Delta\sigma}{e_0 n_{\text{exc}}} = \xi_e \mu_e(f) + \xi_h \mu_h(f)$$

The subscripts e and h stand here for electrons and holes, respectively. The essential steps required to establish the sole contribution of the electron and hole mobilities from the THz photoconductivity spectra thus include (1) determination of the photon to charge conversion efficiencies ξ_e and ξ_h and their evolution on the same time scale where THz response was measured and (2) finding a system where only one of the mobilities can be intentionally varied.

The fluorescence emission spectra in Figure 1a show a significant quenching (down to 0.8%) of APFO-3mono's fluorescence quantum yield upon the addition of PCBM. A similarly efficient quenching (down to 0.4%) was observed upon the addition of PCBM into APFO-3poly.¹⁶ This efficient

Received: July 23, 2012

Accepted: August 17, 2012

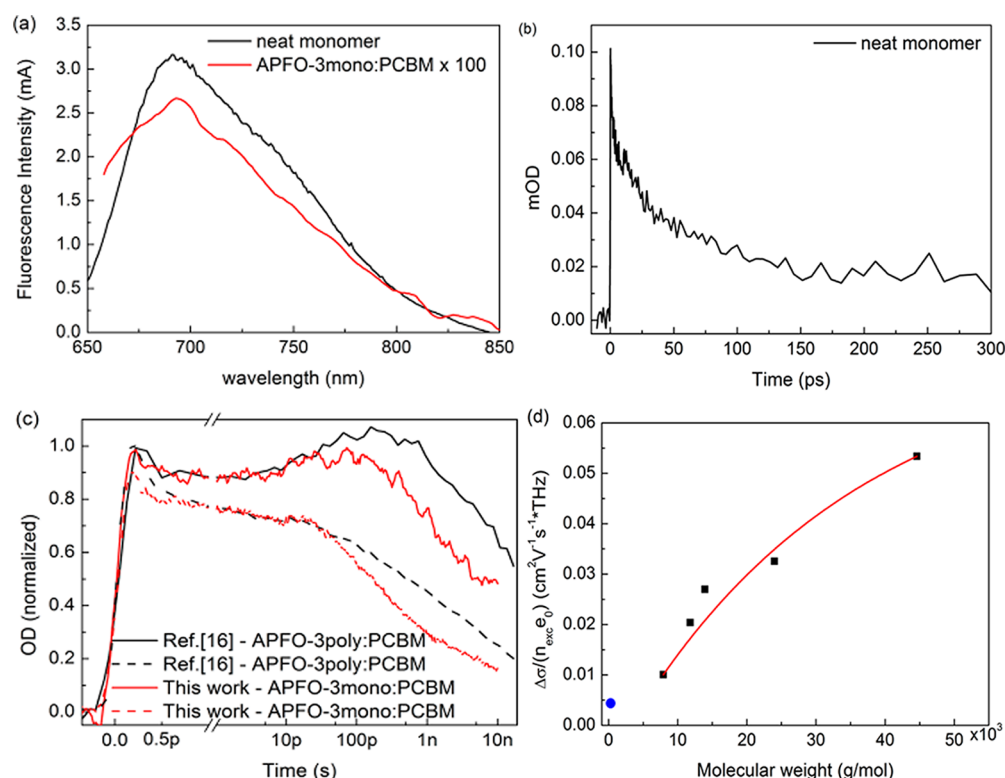


Figure 1. (a) Fluorescence spectra of neat APFO-3mono (black line) and APFO-3mono:PCBM blend (red line). (b) TA kinetics of neat APFO-3 monomer. (c) TA kinetics (normalized) of APFO-3mono:PCBM (red trace) and APFO-3poly:PCBM ($M_w = 11\,800$ g/mol) (black trace) at low (2×10^{13} ph/cm² per pulse, solid line) and high (8×10^{14} ph/cm² per pulse, dashed line) excitation densities, respectively. (d) Normalized transient conductivity (averaged between 0.4 and 1.1 THz) of polymers with different molecular weights, measured 1.5 ps after photoexcitation (8×10^{14} ph/cm² per pulse). Blue circle is the mobility of the monomer. The curve only guides the eye. All measurements were done with 580 nm excitations. Probing in panels b and c was done at 900 nm.

quenching suggests direct electron transfer from excited polymer/monomer to PCBM without any significant energy transfer between monomer molecules or between polymer segments.^{16,17} This interpretation is further supported by the fact that no time-resolved fluorescence (with streak camera detection and time resolution of ~ 3 ps) could be observed for both blends, whereas significant fluorescence was measured for neat monomer and polymer films. Figure 1b shows the excited-state decay of the neat monomer. Similar to the decay of the polymer,¹⁶ it is nonexponential with a $1/e$ lifetime of ~ 50 ps. From these excited-state lifetimes of APFO-3 monomer and polymer together with the relative fluorescence yields given above, a fluorescence quenching time (and thus charge generation) of ~ 200 – 400 fs is estimated for both monomer and polymer blends. This implies that the initial quantum yield of charges (ξ_e, ξ_h) exceeds 99%.

Following the analysis described in detail in ref 16, the transient absorption (TA) kinetics in Figure 1c provides information about carrier density time dependence. For both blends at low excitation intensity there is an initial ultrafast decay (~ 200 fs) reflecting the generation of charges, followed by a weak rise, interpreted as separation of charges and finally decay on the hundreds of picoseconds and nanosecond time scale reflecting geminate charge recombination. At higher carrier densities, this slow decay becomes faster due to nongeminate recombination. At very high excitation densities (e.g., 8×10^{14} photons/cm² per pulse in Figure 1c), an even faster, few-picoseconds decay of the TA kinetics also becomes apparent, which has previously been attributed to a charge-pair

quenching process.¹⁶ (We will discuss this further below.) From Figure 1c, we can see that the TA kinetics of both polymer and monomer blends are very similar at all excitation densities. The monomer blend kinetics exhibits a somewhat faster decay in the several-hundred picosecond time range. This difference in dynamics of slow geminate and nongeminate recombination involving relatively large distances of transport is not surprising and in no way influences the conclusions of this work regarding the nature of majority carriers in polymer and monomer blends. These results, together with the fluorescence quenching discussed above, show three important things: (1) the yield and the temporal characteristics of charge generation in monomer and polymer blends are very similar; (2) the decay of carrier concentration at low densities occurs on the time scale of many hundreds of picoseconds and slower for both monomer and polymer blends; (3) at high excitation intensities, there is an initial few-picoseconds decay due to charge-pair quenching, the same in polymer and monomer blends. This implies that any differences in THz response of APFO-3 monomer and polymer blends discussed below can be related to differences in their carrier mobilities only.

Photogenerated charges may move more easily in the longer segments of a polymer chain than in, or between, short monomer units. Whereas the impact of polymer chain length was investigated in the past,^{8,12} there are so far no calculations available for the photoconductivity of monomer:PCBM blends. Here we have performed a detailed atomistic simulation of hole mobility in APFO-3 monomer and polymer materials. The simulation approach is based on an extension of the recently

introduced multiscale methodology for the simulation of charge-carrier transport in disordered organic materials.²⁴ In brief, the atomic structure of the material is obtained from a classical molecular dynamics simulation and is used as input for the quantum mechanical calculation of energies and wave functions of electronic states.²⁵ The probabilities for phonon-assisted hole hopping from one state to another are obtained next using equation 3 from ref 26. This formula is an excellent approximation to the formula that one obtains by taking into account the interaction of holes with all phonon modes (equation 1 from ref 26). Hole mobility at THz frequencies, in the limit of low-carrier density, is then calculated using Kubo's linear response formula. In the calculations, we assume that the charges are in thermal equilibrium with the lattice. In the experiments, we have strictly speaking nonequilibrium carriers; on the other hand, because we are interested in the spectra measured for several-picosecond time delays, we believe that the carriers are already thermalized and that a possible excess energy is negligible compared with thermal energy. In the simulation, we obtained that the mobility of holes in the APFO-3 polymer material at 1 THz and at room temperature is $\mu_h = (0.73 - 0.62i) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, whereas in the material consisting of APFO-3 monomers it is equal to $\mu_h = (0.00052 - 0.0017i) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. These results clearly show that the hole mobility in the APFO-3 polymer material is several orders of magnitude larger than in the APFO-3 monomer material (unpublished results). It is known that the primary photoproducts in APFO-3poly:PCBM are charge polaron pairs where the positive polaron is located to the polymer while the negative ones are residing on PCBM.^{6,7,16–20} The measured photoconductivity spectra in Figure 2 thus, in principle, contain contributions both from holes in APFO-3 and from electrons in PCBM. There are three possible scenarios for the origin of conductivity spectra in the polymer and monomer blends. (1) The response is dominated by electrons both in monomer and polymer blends. (2) Holes dominate the response in both blends. (3) The response is dominated by electrons for monomer blend and by holes for polymer blend. We can rule out case 1 because it would yield identical photoconductivity spectrum for both monomer and polymer blends, contrary to the results of our measurements. With regard to the simulation results where the mobilities differ by several orders of magnitude between polymer and monomer, the possibility 2 is also unlikely. As a consequence, the feasible scenario is case 3; in the polymer blend the photoconductivity is dominated by holes moving on APFO-3 chains, whereas electrons in PCBM dominated the photoconductivity in the monomer blend.

Neglecting the mobility of holes in the monomer blend (with regard to the multiscale calculations), we get an electron mobility $\mu_e \approx 0.003 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ from Figure 2b. This value is consistent with the transient Stark spectroscopy measurement of PCBM, which provided an electron mobility $\mu_e = 0.0048 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at zero electric field.²² Contribution of electrons to photoconductivity was also observed at microwave frequencies in the P3HT:PCBM blend at much longer times (nanoseconds) after photoexcitation.²³ We also found experimentally that direct above-gap excitation (400 nm) of PCBM produces a transient conductivity with comparable magnitude and with a very short lifetime (~ 0.5 ps). Under our experimental conditions (excitation wavelength of 580 nm), only a minority of photons is absorbed by PCBM in the blends. This means that the photoconductivity due to direct PCBM photoexcitation is negligible compared with the observed response.

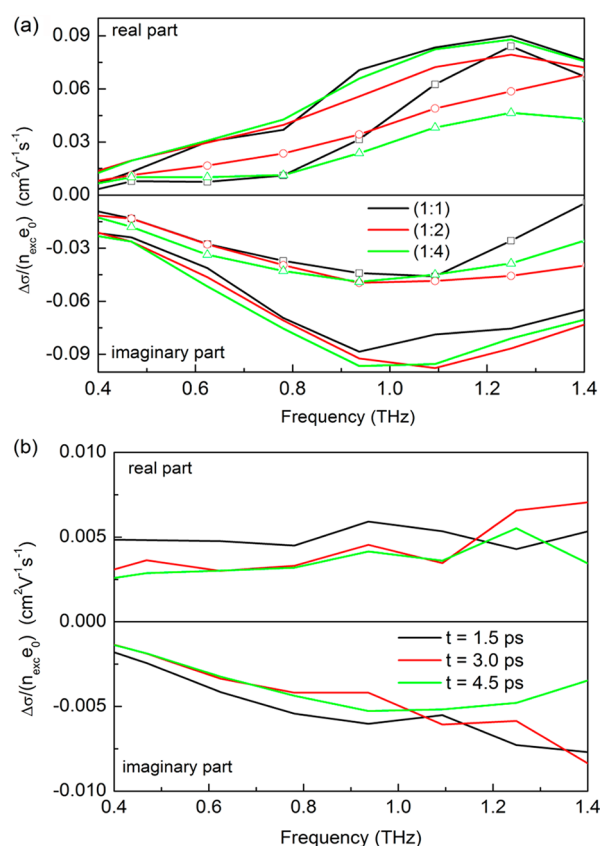


Figure 2. Normalized transient conductivity spectra of (a) APFO-3poly:PCBM ($M_w = 11\,800 \text{ g/mol}$) blends with various acceptor concentrations (lines and lines with symbol measured at 0.5 and 1.5 ps pump-probe delay, respectively) and (b) APFO-3mono:PCBM at three representative pump-probe delays.

The normalized transient THz conductivity of APFO-3poly:PCBM is at least six times higher than that of the APFO-3mono:PCBM (Figures 1d and 2). Within experimental error, these spectra are independent of the blending ratio, thus supporting our assignment of the response as coming from holes on the polymer rather than from electrons. Because the same very high yield and high rate of charge generation were previously reported for a wide range of APFO-3poly:PCBM ratios,¹⁷ such results demonstrate that the hole mobilities are independent of the blend ratio. We also measured a spectrally averaged normalized transient THz conductivity of blends made of APFO-3poly with different chain lengths (Figure 1d). A strong dependence of the mobility with the polymer chain length was observed, which can only be understood if the dominating THz response in the polymer blends originates from hole mobility. We note that a higher mobility may be achieved as a result of both longer chains as well as better molecular ordering. In fact, our calculations show that higher mobility is obtained for the monomer with side chains compared with that without side chains, which has stronger energetic disorder (unpublished results).

Figure 3 shows the temporal evolution of the THz photoconductivity of APFO-3poly:PCBM (both 1:1 and 1:4 blends), APFO-3mono:PCBM, and of a few other blends. The kinetics are almost identical for all of the systems. The rapid onset shows that charge carriers are formed within the instrumental time resolution (~ 100 fs). Subsequently, the photoconductivity decays to 20% after 7 ps and continuously

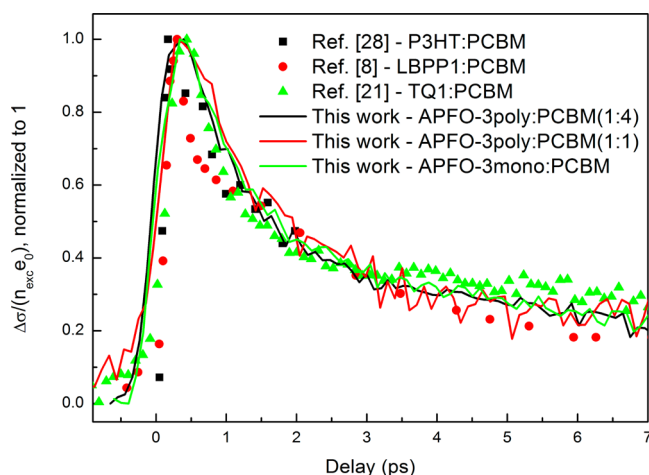


Figure 3. Evolution of (normalized to 1) transient conductivity of APFO-3poly:PCBM ($M_w = 11\,800$ g/mol, 1:1 and 1:4), APFO-3mono:PCBM, and previously reported blends. Data points from refs 8 and 28 were adapted with permission. Copyright 2009 and 2011 American Physical Society.

decreases for at least several hundreds of picoseconds. In the past, this fast decay was explained as charge carrier cooling,^{4,7} self-localization, and formation of excitons.²⁸ The excitation densities used in all of this THz work are in the range of 10^{14} to 10^{15} photons/cm² per pulse (this corresponds to 1.4×10^{15} to 1.4×10^{16} photons/cm³ per pulse in 1:4 APFO-3poly:PCBM blend, ref 29), necessitated by the requirements for a sufficiently high signal-to-noise in the measurements. Recently, we showed for APFO-3poly:PCBM and another polymer blend TQ1:PCBM (TQ1 = poly[2,3-bis-(3-octyloxyphenyl)-quinoxaline-5,8-diyl-*alt*-thiophene-2,5-diyl], also included in Figure 3) that the universally observed few-picosecond decay of THz conductivity for these two polymer:fullerene blends is due to the nonlinear charge-pair quenching. When the excitation density in the THz measurements was lowered by a factor of ~ 100 (to $\sim 10^{13}$ photons/cm² per pulse), the fast decay disappears and the THz decay is now on the several hundreds of picoseconds time scale.²¹

At high excitation density the APFO-3mono:PCBM and APFO-3poly:PCBM blends have very similar TA decays (Figure 1c), exhibiting the few-picosecond charge-pair quenching process. Therefore, this comparison between TA and THz dynamics of APFO-3poly and APFO-3mono blends not only shows that charge-generation yield and recombination at low intensity are very similar but also shows that the charge-pair quenching process at high intensity is very similar in both materials. The fact that this process proceeds with identical kinetics (within experimental error) in both APFO-3 polymer and monomer blends is consequently the reason to the almost identical picosecond time scale decay of the THz conductivity for both blends. The onset of charge-pair annihilation was estimated to be at carrier densities $\sim 10^{14}$ to 10^{15} photons/cm³ per pulse for both APFO-3 polymer and monomer blends. We note that this value can be used as a crude estimate of the carrier density, but a more reliable value requires knowledge of the absorption coefficient of a material at the excitation wavelength (not easily obtained from literature) and film thickness and also requires a reasonable homogeneous distribution of carriers over the film thickness, that is, requiring an optically thin film. The films used here are optically thick to ensure good light absorption and consequently sufficiently

strong THz signals. These complications should be considered when using photon densities as a measure of carrier density.

In summary, we have shown that polarons with both polarities contribute to the THz conductivity spectra of APFO-3:PCBM blends. Whereas the THz photoconductivity of the polymeric blends is dominated by positive polarons in agreement with previous claims, the photoconductivity of the monomeric blend is almost entirely due to negative polarons. The THz photoconductivity was found to increase with increasing polymer molecular weight, as a result of increased chain length and increased molecular ordering. Because of the high excitation densities employed in typical time-resolved THz experiments, charge-pair quenching occurs, which explains the same picosecond THz conductivity decay dynamics observed in the polymer and monomer blends. The identification of conjugated polymer:PCBM THz photoconductivity as mainly a hole-related property, combined with the clarification of the intrinsic time scale of carrier mobility decay, is a finding that we believe will be important for future design of novel materials.

EXPERIMENTAL METHODS

The polymers [2,7-(9,9-dioctylfluorene)-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]^{13,14} (APFO-3poly) with weight average molecular weights of 7 900, 11 800, 13 900, 24 000, and 44 600 g/mol and its monomer derivative phenyl-end-capped (4,7-bis(5-phenylthiophen-2-yl)benzo[c][1,2,5]-thiadiazole) (APFO-3mono) ($M_w = 453$ g/mol) form were blended with commercially available [6,6]phenyl-C₆₁-butyric acid methyl ester (PCBM) (Sigma Aldrich) at 1:4 weight ratio. We also prepared 1:1 and 1:2 weight ratios for APFO-3 with molecular weight 11 800 g/mol. Purification and preparation conditions of the thin films for fluorescence and TA measurements were adopted from ref 6. For terahertz measurements, a rather thick film is needed for better signal-to-noise ratio. In this case, the solution was dropcast on a quartz glass and dried in an open environment.

The THz photoconductivity was measured in a setup described in ref 21. Details of the analysis relating the measured transient transmittance to the THz photoconductivity of the samples are described in detail, for example, in refs 11 and 15.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The Swedish Energy Agency (STEM), the Swedish Research Council, the Knut&Alice Wallenberg foundation and the European Research Council (Advanced Investigator Grant to VS, 226136-VISCHEM) are acknowledged. Financial support by the Academy of Sciences of the Czech Republic (project M100101218) is also acknowledged. N.V. is supported by European Community FP7 Marie Curie Career Integration Grant (ELECTROMAT), Serbian Ministry of Science (ON171017), and FP7 projects PRACE-IIP, PRACE-2IP, HP-SEE, and EGI-InSPIRE. Stefan Hellström is acknowledged for the synthesis of polymer samples. S.F. is supported by EC FP7 ONE-P project.

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