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Initial transport of photogenerated charge carriers in π-conjugated polymers

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We have clarified the initial transport of photogenerated charge carriers in two π-conjugated polymers, namely regiorandom poly(3-hexylthiophene) and copolymer poly(9,9-dioctylfluorene-*co*-bis-*N*,*N*′-(4-butylphenyl)- bis-*N*,*N*′-phenyl-1,4-phenylenediamine), using integral mode time of flight. We show how to deconvolute the factors that contribute to the fast initial (pretrapping) transport and eliminate the normally important role of the photogeneration efficiency. We can then determine the dependence of the initial transport distance on applied electric field and temperature, $l_f(F,T)$. We analyze $l_f(F,T)$ using a model where only the charge carriers which thermalize down to an energy not less than kT from the Coulomb potential maximum in a given electric field, immediately after photoexcitation, participate in the drift. We obtain excellent agreement between our experimental results and the model, showing that the initial fast carriers move a distance $l_f \sim 20-100$ nm with high mobility before being trapped. The mobility-lifetime product $(\mu_0 \tau_f)$ of the fast carriers is of the order $(1-2)\times 10^{-11}$ cm^2/V s in these two π-conjugated polymers despite significant differences in their detailed chemical structure.

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I. INTRODUCTION

The nature of the photogeneration and initial transport of charge carriers in π-conjugated polymers is still debated extensively in the literature.[1,2] In π-conjugated polymers, the very first part of the time-of-flight (TOF) photocurrent transient decays down to a stationary drift-velocity value on picosecond time scales [see Fig. 1(a)].[3,4] To measure the initial current one has to use the somewhat complex Austin-switch strip-line technique,[3,4] or use very thin films in steady-state photoconductivity experiments.[5] However, using standard photoconductivity techniques, only the product of the quantum efficiency of the charge generation, η and the mobility and lifetime of the charge carriers can be measured, making the analysis somewhat difficult. In this paper we show how to measure the initial transport distance independent of the quantum efficiency for charge carrier generation using the integral mode TOF in the sandwich configuration.

II. THEORY

The typical shapes of differential ($RC < t_{tr}$) and integral ($RC > t_{tr}$) mode TOF photocurrent transients are shown in Fig. 1(a) (here R is the load resistance, C the capacitance of the sandwich-type sample, and t_{tr} the time for the charge carriers to drift through the interelectrode distance). The fast decay of the initial photocurrent (in the differential mode) or the very initial step of collected charge (in integral mode) is caused by the fast initial transport distance of charge carriers following photoexcitation, within the applied electric field. The fast initial transport distance (l_f) may be estimated using Hecht's expression. When the total photogenerated charge Q_0 drifts through the inter-electrode distance (d), i.e., the lifetime of charge carriers (τ) is much longer than t_{tr}; then[6]

$$\frac{Q_f}{Q_0} = \begin{cases} l_f/d & \text{in case of surface photogeneration} \\ 2l_f/d & \text{in case of bulk photogeneration,} \end{cases} \quad (1)$$

where Q_f is the amount of the collected charge that traveled the distance l_f. The goal of this paper is to estimate whether l_f is governed by the time for the charge carriers to travel the pretrapping distance into shallow states, or by the dimensions of the polymer. As a first approximation to the first case, l_f corresponds to the drift distance $l_f \cong l_{dr} = \mu_0 \tau_f F$ (where μ_0 is the fast mobility, τ_f the fast trapping time, and F the electric field). In this case l_f will show a linear electric field dependence. In the other case, when the extent of the

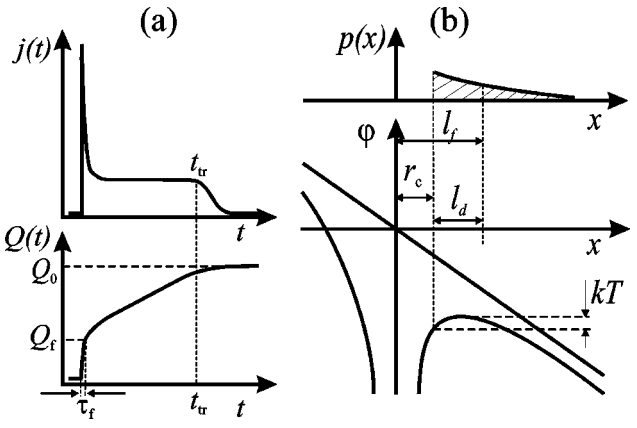

FIG. 1. (a) Schematic photocurrent transients in differential mode (upper panel) and integral mode (lower panel). The transient time (t_{tr}) of the charge carriers as well as the trapping time (τ_f) of the fast carriers is indicated in the figure. (b) Schematic view of the potential well and the probability $p(x)$ for the photogenerated charges that escaped geminate recombination (i.e., thermalized outside r_c) to move a distance x in an applied electric field along the x axis. The average pretrapping distance l_d due to drift and diffusion is shown.

polymer segment over which intrachain transport can readily occur (in the direction of the electric field) determines Q_f, l_f is equal to that distance and is *independent* of the field. Thus the electric field dependence of l_f allows us to determine whether the initial drift distance is limited by distance (chain length, crystalline region, etc.) or (trapping) time. We will proceed by studying the first case more accurately, and we will do this by taking into account the initial separation (r_c) of charge carriers immediately after photoexcitation as well as their diffusion length (l_{diff}) and drift distance (l_{dr}) before they are trapped into shallow traps.

The almost temperature independent quantum efficiency for charge generation obtained in organic semiconductors has recently been explained by Arkhipov *et al.*[7] The excess photon energy locally forms a vibrational heat bath with an effective temperature T_{eff}, which allows charge carriers to escape from the potential well formed by Coulomb and external electric fields. However, at high temperatures T_{eff} is approximately equal to T, and thus, for simplicity, we will use the Onsager model. According to Onsager's theory[8] at high electric fields only those charge carriers that, immediately after photogeneration, thermalize down to an energy no more than kT below the Coulomb potential maximum in the direction of electric field participate in the drift, i.e., the charge carriers that thermalize within a distance longer than $r_c(F)$ [see Fig. 1(b)]. Therefore, for the estimation of $r_c(F)$ at high electric fields ($F>10^4$ V/cm) it is sufficient to use the one-dimensional description; however, in the theory for calculation of the quantum efficiency of charge generation the three dimensional model is necessary. Thus, in the direction of the electric field the distance $r_c(F)$ is estimated from the equality

$$\frac{e^2}{4\pi\varepsilon\varepsilon_0 r_c}+eFr_c=kT+2\sqrt{\frac{e^3F}{4\pi\varepsilon\varepsilon_0}}. \tag{2}$$

Here the first term on the left hand side is the Coulomb potential of the geminate pair, the second term is the potential of the extrinsic electric field, and the second term on the right hand side corresponds to the maximum value of the total potential in the direction of electric field [see Fig. 1(b)].

To account for the drift and diffusion of the charge carriers that have thermalized outside $r_c(F)$ we proceed by noting that for typical values of $\mu_0\tau_f\sim(1-2)\times10^{-11}$ cm^2/V (see below) the diffusion distance component $l_{diff}=\sqrt{kT\mu_0\tau_f/e}\sim5$–$7$ nm is shorter than the Coulomb radius $r_c(0)=e^2/4\pi\varepsilon\varepsilon_0kT\sim19$ nm (for $\varepsilon=3$), and that the charge carriers that diffuse against the electric field will therefore recombine geminately. Thus, the one-dimensional case is sufficient for evaluation of the initial transport distance. We further note that at high electric fields l_f is mainly caused by the drift distance component $l_{dr}=\mu_0\tau_fF$. A more accurate calculation of the diffusion and drift distance at high electric field may be obtained by solving the continuity equation[9] from where the probability for the charge carriers to move distance x is $p\propto\exp(-x/l_d)$, and we can write

$$l_d=\frac{2kT}{eF}\frac{1}{\sqrt{4\dfrac{kT}{eF^2\mu_0\tau_f}+1}-1}=\frac{l_{dr}}{2}+\sqrt{\frac{l_{dr}^2}{4}+l_{diff}^2}. \tag{3}$$

Hence, from the initial part of the photocurrent transient, we can estimate the initial transport distance as $l_f=r_c(F)+l_d$. In Fig. 3 the calculated $l_f(F)$ at different $\mu_0\tau_f$ is shown. The decrease of $l_f(F)$ with electric field is caused by a decrease of $r_c(F)$, while an increase of $l_f(F)$ is caused by the increase of $l_{dr}(F)$.

Similar TOF $j(t)$ transients (fast decay to a flat quasistationary part) may also be obtained in other cases. We note that in π-conjugated polymers the polarization of initially created (in picosecond time scale) excitons will average out during times longer than the exciton lifetime, and therefore will be absent in $Q(t)$ on nanosecond time scales.

In the case of surface-generated charge carriers, the diffusion of carriers in a direction opposed to the electric field is possible. In low electric fields ($F<kT\alpha/e$), and when the surface recombination rate is infinite, the current will drop to[10]

$$\frac{j}{j(0)}=\frac{1}{1+\dfrac{kT\alpha}{eF}}, \tag{4}$$

during the diffusion time ($\tau=1/D\alpha^2$). Here α is the absorption coefficient. This may be checked by changing the wavelength of the exciting laser light if $\alpha(\lambda)$ is known.

The initial photocurrent spike may also appear when the amount of photogenerated charges approaches the space charge mode, and is caused by the instantaneous screening of the electric field in the photogeneration depth (α^{-1}). In this case,[11]

$$\frac{Q_f}{CU}=\frac{1+\ln\dfrac{Q_0}{CU}}{\alpha d}. \tag{5}$$

Here U the applied voltage on the sample electrodes. To elucidate space charge effects one can measure the Q_f/CU dependence on the light intensity.

III. EXPERIMENT

The measurements were made in the small charge mode ($Q_0\ll CU$) of integral TOF [see Fig. 1(a)], i.e. $RC\gg t_{tr}$. The integral TOF allows us to directly measure the initial transport distance (l_f) *separated* from the quantum efficiency for charge carrier generation according to Eq. 1.

Sandwich type samples were used, where the π-conjugated polymers, namely regiorandom poly(3-hexylthiophene) (RRa-PHT) and a copolymer poly[9,9-dioctylfluorene-*co*-bis-*N*,*N*′-(4-butylphenyl)-bis-*N*,*N*′-phenyl-1,4-phenylenediamine] (PFB), were deposited on top of ITO coated glass substrates and contacted with a semitransparent Al electrode evaporated on top. The RRa-

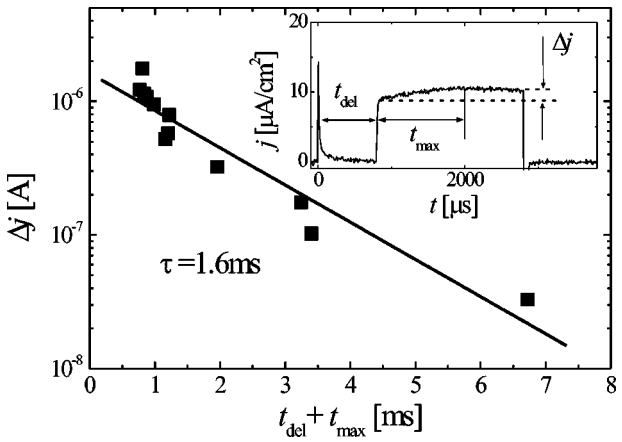

FIG. 2. The lifetime $\tau \sim 1.6$ms, of the long-lived photogenerated charge carriers, Δj in RRa-PHT as measured using the modified CELIV method (Ref. 12). In the inset the experimental curve for the measurement is shown. The laser pulse is applied at $t=0$, and after a delay time t_{del} the photogenerated charge carriers are extracted.

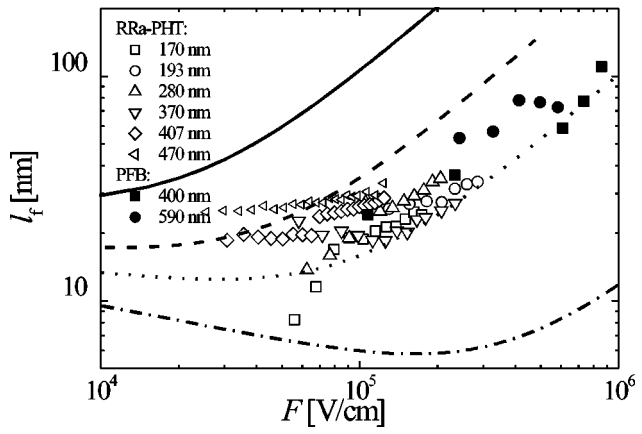

FIG. 3. The calculated initial transport (pre-trapping) distance l_f of the charge carriers as a function of electric field for different $\mu_0\tau_f$-products; $\mu_0\tau_f = 10^{-10}$ cm^2/V (solid line), $\mu_0\tau_f = 3\times10^{-11}$ cm^2/V (dashed line), $\mu_0\tau_f = 10^{-11}$ cm^2/V (dotted line), and $\mu_0\tau_f = 10^{-12}$ cm^2/V (dash-dotted line). The experimental data points for several film thicknesses of thin RRa-PHT (open symbols) and PFB (filled symbols) films are shown.

PHT was purchased from Sigma Aldrich and used without further treatment. The PFB was provided by the Dow Chemical Company. The samples were made as thin films with thickness in the range 193–590 nm. We have corrected the effective drift distance of the charge carriers for the effectively thinner film caused by the finite absorption depth. The charge carriers were photoexcited by light pulses of 7-ns duration from a 337 nm wavelength N_2 laser, or by pulses of either 18-ps or 6-ns duration of the third (355 nm) or fourth (275 nm) harmonic wavelength of a YAG:Nd (YAG is yttrium aluminum garnet) laser.

The very important fact that we need to collect all the photogenerated charges has been carefully checked using a modified extraction current transient technique,[12] i.e., extraction of the photogenerated charge carriers (photo-CELIV) after a delay time between the laser pulse and applied voltage, see Fig. 2, inset. The measured lifetime of the charge carriers in RRa-PHT is $\tau = 1.6$ ms, i.e., well in excess of the transient time in submicrometer thick films. For the nondispersive PFB the extraction of all charges is obtained even in several-μm-thick films.[13]

IV. RESULTS AND DISCUSSION

In Fig. 3 the calculated values of l_f when $T = 300$ K and $\varepsilon = 3$ for different $\mu_0\tau_f$ are shown together with the experimentally measured l_f for several film thicknesses of both RRa-PHT and PFB. When electric field is lower than $\sim 10^4$ V/cm, l_f is determined by the Coulomb radius and the diffusion distance. In a higher electric field the decreasing of l_f is caused by the decrease of r_c (with increasing quantum efficiency for charge generation in parallel). A further increase of electric field leads to an increase of l_f, due to the drift of the charge carriers before trapping to the drift states. The similarity of experimentally measured l_f to the calculated $l(F)$ dependence allows us to evaluate $\mu_0\tau_f \simeq (1-2)\times10^{-11}$ cm^2/V in the measured polymers. From the Austin switch experiments in P3HT (Ref. 3) and poly(p-phenylene vinylene) (Ref. 4) a value of $\tau_f \approx 100$ps was measured. With this value the initial fast charge carrier mobility would be $\mu_0 \cong 0.1$–0.2 cm^2/V s.

Both in the Onsager theory[8] and in the theory developed by Arkhipov *et al.*[7] for the initial escape of geminate recombination, the thermalization distance l_t strongly depends on the photon-energy of the exciting light. From our experimentally measured values of quantum efficiency (in the range of 0.01–1 %), l_t was estimated in the range 1–3 nm.[14] We experimentally estimated that l_f is independent of the photon energy [see Fig. 4(a)] and that its value is much larger than l_t; thus l_f is mainly caused by the pretrapping drift and diffusion distance l_d. The deviation from the theoretical curve at low fields is caused by increasing difficulties in collecting all the charges in this particular sample.

The temperature dependence of the initial transport distance was also measured and shown in Fig. 4(b) together with the calculated temperature dependence using Eqs. (2) and (3). The temperature dependence is in good agreement with the model using temperature independent $\mu_0\tau_f = 2\times10^{-11}$ cm^2/V for RRa-PHT. Note the temperature independent l_f (within the experimental errors). The similarity of the initial fast drift of these otherwise very different polymers suggests that the initial drift in π-conjugated polymers might have more general features.

We note that these results are also in excellent agreement with other results on the fast mobility in π-conjugated polymers in the literature. By analyzing the temperature dependent mobility within the Gaussian disorder model proposed by Bässler the infinite temperature mobility at zero-field has the values in the range 0.01–1 cm^2/V s,[15] and in particular in PFO (the homopolymer of the fluorene part of PFB) it has been estimated to be 0.4 cm^2/V s.[13] Moses *et al.* measured a pretrapping drift distance of $\sim$90 nm at an electric field of $F = 1.33\times10^5$ V/cm in poly[5-(2′-ethyl hexyloxy)-2-methoxy-1,4-phenylenevinylene] (MEH-PPV), using cw photoconductivity,[5] where a fast carrier sweep out was ob-

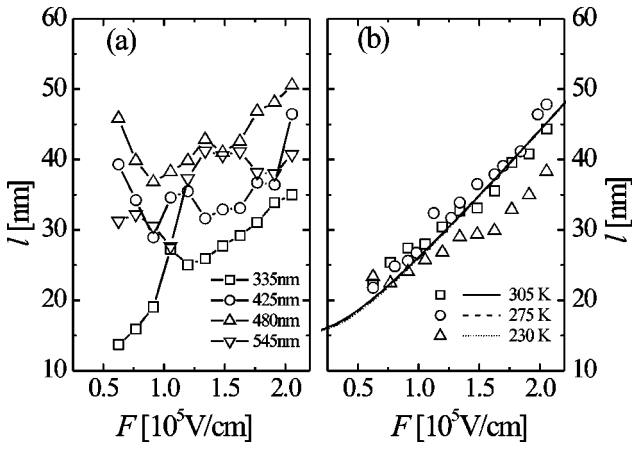

FIG. 4. In (a) the photon energy dependence of $l(F)$ is shown in RRa-PHT, in (b) the temperature dependence of the initial transport distance measured at 305 K (squares), 275 K (circles), and 230 K (up triangles) for RRa-PHT. The calculated temperature dependences using $\varepsilon=3$ and temperature independent $\mu_0\tau_f=2\times10^{-11}$ cm^2/V with $T=305$ K (full line), $T=275$ K (dashed line), and $T=230$ K (dotted line).

served in very thin films. Grozema *et al.* estimated the isolated chain mobilities using time-resolved microwave conductivity techniques in a large set of polymers, including MEH-PPV, P3HT, and polyfluorenes, in excellent agreement with our findings.[16] In recent ultrafast pump-probe experiments in the presence of a modulated electric field, the fast mobility could be deduced by fitting the recombination dynamics, and it was observed that after 1 ps, the fast mobility is approx 1 cm^2/V s, and decays in about 50 ps to an almost constant value of $\sim10^{-2}$ cm^2/V s.[17]

In conclusion, we have presented a way to separate the charge carrier generation efficiency from the initial drift of photogenerated charge carriers using integral TOF. We have used this method to estimate the initial (pretrapping) transport distance in two very different π-conjugated polymers, namely, RRa-PHT and PFB, and obtained a similar value: $\mu_0\tau_f\simeq(1-2)\times10^{-11}$ cm^2/V. The similarity in $l_f(F,T)$ for the two polymers is striking, suggesting that the initial transport is more general in π-conjugated systems, independent of the detailed differences in chemical structure.

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