

Recombination of photogenerated and injected charge carriers in π -conjugated polymer/fullerene blends

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Abstract

In regioregular poly(3-hexylthiophene) /1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene (RR P3HT/PCBM) bulk heterojunction structures the recombination features of photogenerated and of double injection charge carriers are compared. The investigations have been made using time-of-flight (TOF), charge extraction by linearly increasing voltage (CELIV), and double injection transient methods. In both cases when electric field is absent (photogeneration case) and in various electric fields (double injection case) the bimolecular recombination coefficient (β) has been estimated $10^3 \div 10^4$ times lower than Langevin's one (β_L). The weak dependence of β on electric field was obtained and activation energy of β lower than of β_L one was estimated.

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1. Introduction

Recently, due to probable low-cost and technological simplicity, the interest in polymer solar cells grows up [1]. Compared to crystalline semiconductors organic semiconductors have much lower charge carrier mobility due to hopping transport, causing Langevin-type bimolecular recombination of charge carriers [2]. This effect can reduce the efficiency of solar cells fabricated from these materials. However, in bulk-heterojunction solar cells photogenerated charge carriers will be transported along different pathways in the bi-continuous network leading to a reduced probability for recombination [3].

In this paper the bimolecular recombination in bulk heterojunction π -conjugated polymer/fullerene blends: RR P3HT/PCBM is investigated. Generally, the charge carrier recombination is measured from the photocurrent transients after excitation by short pulse of light. However, in organic materials the transients of current are caused by relaxation with time of both photogenerated charge carrier density and mobility. This report is

focused on brief review and comparison of various bimolecular recombination investigation methods: a) extraction of photogenerated charge by linearly increasing voltage (photo-CELIV) method, using of which the dependencies of photoexcited charge carrier density and mobility on time ($n(t)$ and $\mu(t)$, respectively) can be measured [4]; b) integral time-of-flight (TOF) technique, which can be used for estimation of a ratio of bimolecular recombination coefficients β/β_L (here $\beta_L = e(\mu_n + \mu_p)/\epsilon\epsilon_0$ is coefficient of Langevin recombination) [3]; c) double injection (DI) current, analysis of which's transients at different electric field can give possibility to measure dependence of β/β_L ratio on electric field [5,6]. From experimentally measured dependencies of β/β_L ratio on electric field and temperature the nature of bimolecular recombination reduction is discussed.

2. Experiment

The sandwich type structure consisting of on ITO-coated transparent electrode, PEDOT layer, active layer ($1 \div 2 \mu\text{m}$ thick) prepared by spin coating of 1:1 weight ratio mixture of PCBM and RR-P3HT and Al evaporated on top of structure. The sample was illuminated through ITO by 532 or 1164 nm laser pulse.

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For measurement of $n(t)$ and $\mu(t)$ the photo-CELIV method was used: charge carriers were excited by short light pulse and within the given delay duration (t_{del}) the linearly increasing voltage pulse (increase rate $A=dU/dt$) of backward direction was applied onto sample electrodes. The pulse of current transient consisting of inter-electrode capacity current ($j(0)=\epsilon\epsilon_0 A/d$; d is thickness of layer) and conductivity current of extracted charge carriers (Δj) was analyzed (see Fig. 1a) [7]. From the duration when extraction current reaches maximum (at t_{max}) the charge carrier mobility can be estimated according to expressions:

$$\mu = \begin{cases} \frac{2d^2}{3At_{\text{max}}^2} & \text{when } \tau_\sigma \gg t_{\text{tr}} \\ \frac{d^2 \tau_\sigma}{At_{\text{max}}^2} & \text{when } \tau_\sigma \ll t_{\text{tr}} \end{cases} \quad (1)$$

Here $\tau_\sigma = \epsilon\epsilon_0/\sigma$ is dielectric relaxation time, σ is bulk conductivity of sample. By changing t_{del} the dependence of $\mu(t)$ was measured (Fig. 1b). Simultaneously, from an area difference of extraction current transients with and without photoexcitation, the density of photoexcited charge carriers, at a given t_{del} , was estimated (see Fig. 1a). The $n(t)$ was measured by changing delay duration (Fig. 1b). The possible influence of intrinsic potential of solar cell to amount of extracted charge was eliminated using compensating offset voltage (U_{of} in Fig. 1a). Assuming that bimolecular recombination prevails the β can be estimated by fitting $\mu(t)$ and $n(t)$ experimental results to expression:

$$n(t) = \left(\frac{1}{n(0)} + \beta t \right)^{-1}. \quad (3)$$

Another one method, which allowed estimate the β/β_L ratio, was based on measurement of extracted charge (Q) dependence on intensity (L) of exciting light pulse using integral TOF method [3]. In case if recombination is absent $Q \sim L$. When the monomolecular recombination prevails $Q(L) \sim \ln L$. In case of bimolecular recombination the dependence of extracted charge on L saturates at maximal extracted charge Q_s . Thus

$$\frac{\beta}{\beta_L} = \frac{CU_0}{Q_s} \cdot \frac{t_{\text{tr}}}{t_e}. \quad (4)$$

Here t_{tr} is drift time of small charge; $t_e = t_{1/2}(L_s) - t_{1/2}(L \rightarrow 0)$ is extraction time estimated as difference of current transient half-widths $t_{1/2}(L_s)$ when amount of extracted charge saturates at L_s and $t_{1/2}(L \rightarrow 0)$ at low intensity of light pulse.

The third method is based on analysis of double injection current transients when rectangular voltage pulse of forward direction is applied onto sample electrodes [5]. An injection current is

$$j = 2\sqrt{\frac{\epsilon\epsilon_0\mu_n\mu_p(\mu_n + \mu_p)}{\beta}} \frac{U^2}{d^3} = 2\epsilon\epsilon_0\sqrt{\frac{\beta_L}{\beta}} \mu_n\mu_p \frac{U^2}{d^3},$$

when $\tau_\sigma \gg t_a$; (5)

$$j = \frac{8}{9} e \sqrt{\frac{(\mu_p + \mu_n)\mu_p\mu_n(n_0 - p_0)}{\beta}} \cdot \frac{U^{3/2}}{d^2} = \frac{8}{9} \cdot \frac{U}{d} \epsilon\epsilon_0 \sqrt{\frac{\beta_L}{\beta}} \cdot \frac{1}{\tau_\sigma t_a},$$

when $\tau_\sigma \ll t_a$. (6)

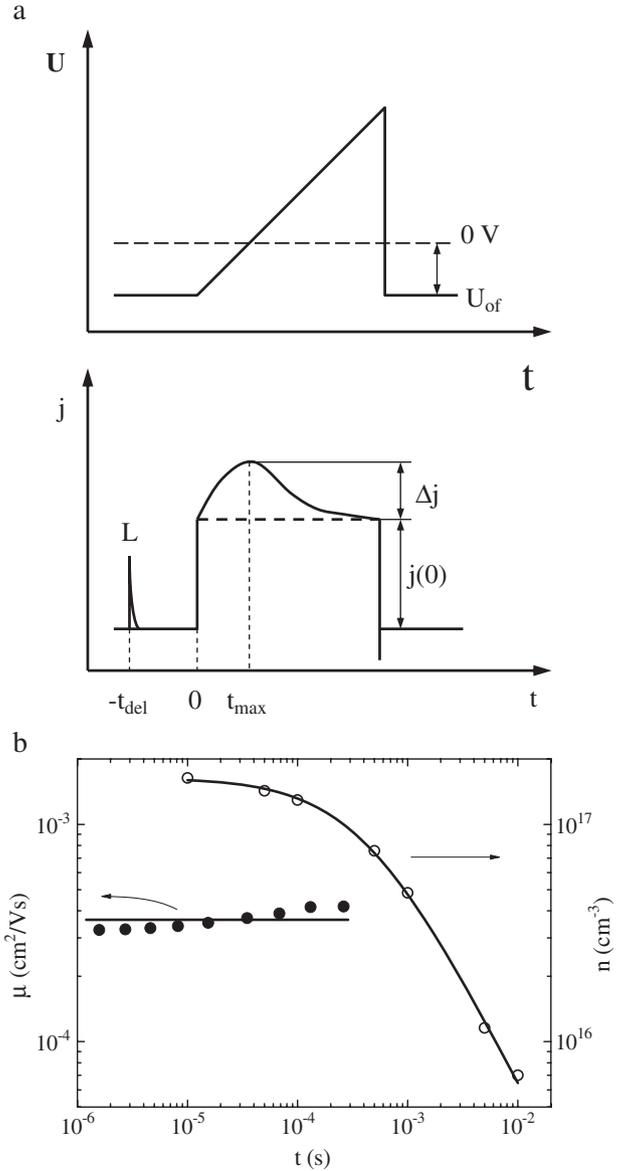


Fig. 1. a) Schematic illustration of the photo-CELIV method. U is the applied voltage onto the sample electrodes; j is the corresponding current transient. The dashed line corresponds to extraction current transient in dark; the full line corresponds to extraction current transient upon a short pulse of light. b) Dependencies of charge carrier mobility μ and density n on delay time between light and voltage pulses.

Here t_a is drift time of charge carriers with ambipolar mobility (μ_a). The t_a is estimated as duration when dj/dt of DI current transient reaches maximum. In Fig. 3b positions of t_a at different voltage are marked by dashes [6].

3. Results and discussion

In Fig. 1b there are shown $n(t)$ and $\mu(t)$ dependencies estimated using photo-CELIV technique. From $\mu(t)$ dependence the $\beta(t)$ relaxation was estimated and compared with numerically modelled $n(t)$ dependence in case of Langevin recombination. Such a case was also demonstrated in PCBM/MDMO-PPV blend [8]. In investigated (RR P3HT/PCBM)

solar cell mobility of faster carriers was independent of time and was approximately equal to $3 \cdot 10^{-4} \text{ cm}^2/\text{Vs}$, which is close to value estimated in [9]. Thus, the $\beta_L \approx 1.6 \cdot 10^{-10} \text{ cm}^3\text{s}^{-1}$ was calculated, and from fitting results according to Eq. (3) $\beta = 1.5 \cdot 10^{-14} \text{ cm}^3\text{s}^{-1}$ has been estimated.

Using CELIV technique [7] at room temperature was measured the blend's bulk conductivity, which gave that $\tau_\sigma \approx 2 \text{ }\mu\text{s}$, i.e. τ_σ was shorter than charge carrier transit time in case of both at intrinsic voltage (U_i) and at used experimental voltages onto sample electrodes. Thus, in investigated blend the density of equilibrium charge carriers $n \gg \epsilon\epsilon_0 U_i/d$, which, in turn, caused that the screening depth was shorter than thickness of layer and the electric field was concentrated at electrode. Even using offset voltage, which must compensate U_i , cannot prevent the redistribution of electric field in inter-electrode space. This caused non-homogeneous redistribution of photogenerated charge carriers in the bulk of sample and their partial extraction by intrinsic electric field. These factors can influence the accuracy of estimated values of bimolecular recombination coefficient.

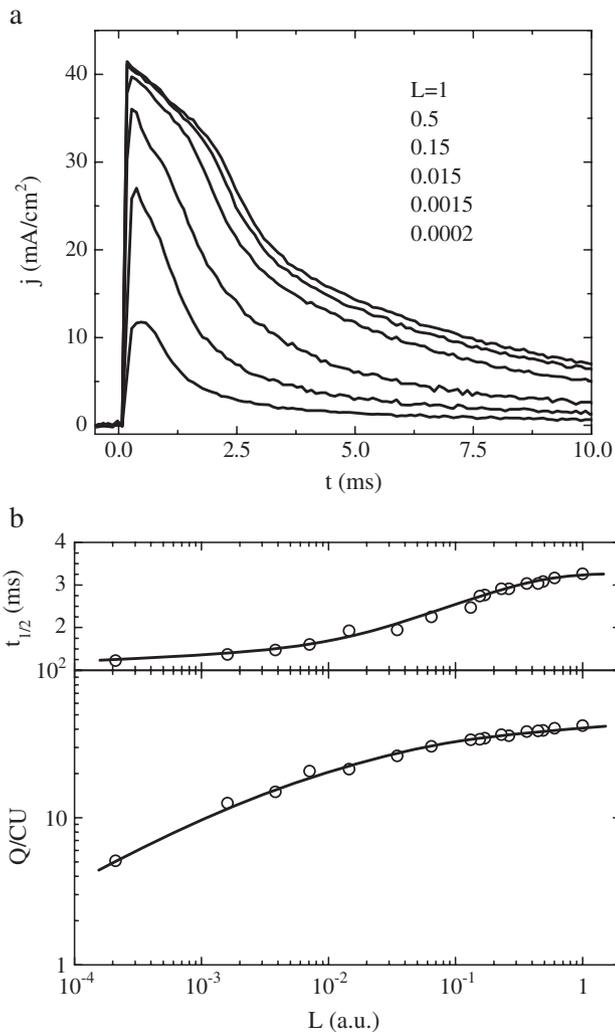


Fig. 2. a) Current transients of integral TOF at different intensity of light pulses ($U=4 \text{ V}$; L in arbitrary units). b) Extracted charge and half time of current transient as function on intensity of light pulses.

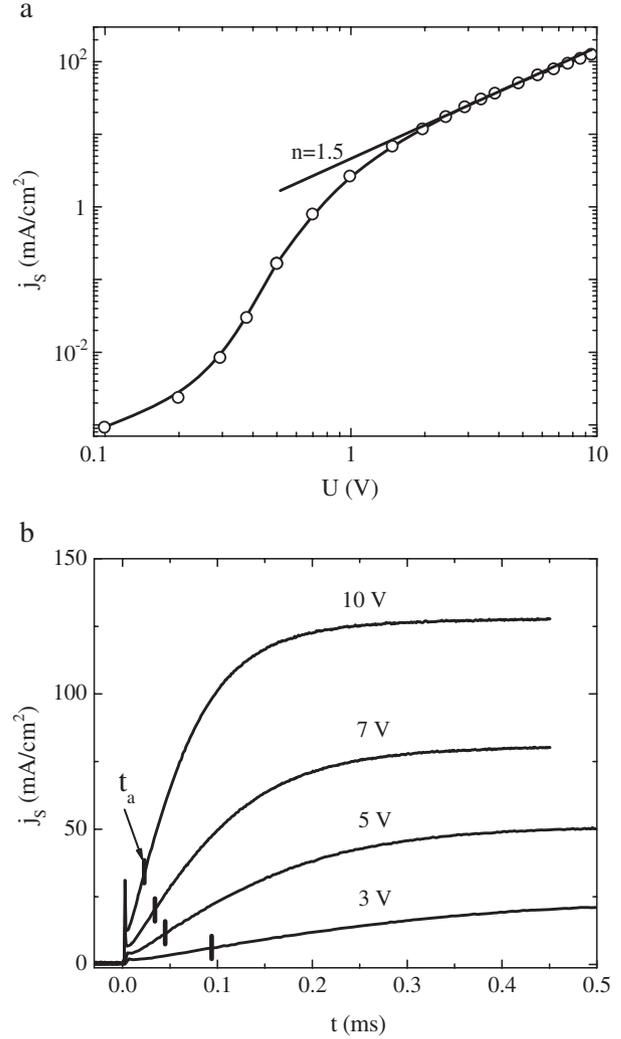


Fig. 3. a) I–V plot of double injection current ($d=2 \text{ }\mu\text{m}$). b) Double injection current transients at different voltages.

Fig. 2a demonstrates the current transients of integral TOF after sample electrode was illuminated by short pulse of light. From the saturation values of extracted charge and extraction

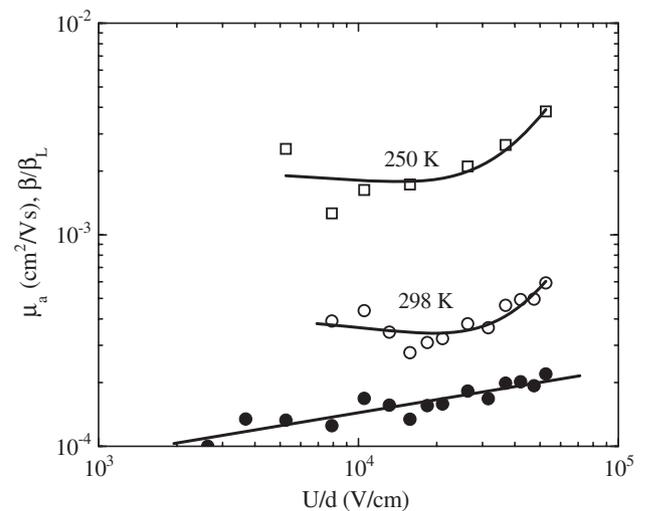


Fig. 4. β/β_L and ambipolar mobility μ_a dependencies on electric field.

time of $Q(L)$ and $t_e(L)$ dependencies (Fig. 2b), using Eq. (4), the β/β_L ratio was estimated. Since direct estimation of small charge drift time from TOF was not accurate, the t_{tr} was evaluated using mobility values from CELIV measurements in case of bulk excitation. In TOF experiment the electric field was screened during much shorter than t_e time, therefore, the $\beta/\beta_L=3.4\cdot 10^{-4}$ at $E=0$ was estimated.

From the in Fig. 3a shown I–V dependence of double injection current it is clearly seen that when $U < 1$ V the current through sample was limited by contact barrier. When $U > 1$ V the current density followed $j \sim U^{3/2}$ law, showing that plasma injection into semiconductor regime was investigated in case of bimolecular recombination. Experimentally observed delayed increase of current after voltage was applied (Fig. 3b), which is typical for double injection, confirmed that the I–V dependence corresponded to DI current too. From maximum of $dj(t)/dt$ the t_a was measured, and according to Eq. (6) the β/β_L ratio was estimated. Fig. 4 shows the β/β_L and the $\mu_a=d^2/Ut_a$ dependencies on electric field. There were obtained very low β/β_L value together with the increase of β/β_L ratio when temperature decreased (see Fig. 4), i.e., the much lower activation energy of β than one of β_L indicated possible influence of tunnelling to electron-hole recombination. However, at the same time a weak dependence of β/β_L ratio on electric field was obtained.

Finally, obtained experimental results confirmed that investigated bulk heterojunction structure is promising for solar cells. However, further investigations of recombination nature are necessary.

4. Conclusions

In bulk heterojunction RR P3HT/PCBM solar cell the TOF, CELIV and DI methods have been used for investigation of

charge carrier recombination. It was demonstrated that, due to high conductivity ($\tau_o < t_{tr}$) of blend, the electric field is concentrated at electrodes. This redistribution of electric field together with, typical for organic materials, immediate after photoexcitation relaxation with time of both the density and the mobility of photogenerated charge carriers impeded investigation of recombination. Experimentally it was estimated that the coefficient of bimolecular recombination is significantly ($10^3 \div 10^4$ times) lower than one of Langevin recombination. The low activation energy together with the weak dependence on electric field of bimolecular recombination coefficient confirmed that RR P3HT/PCBM bulk heterojunction is promising for solar cells.

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