Charge Recombination in P3HT/PC₇₀BM Composite Studied by Light-Induced EPR

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ABSTRACT: A composite of conductive polythiophene P3HT and soluble fullerene derivative $PC_{70}BM$ (the material widely used as the active layer in organic photovoltaics devices) was studied by light-induced EPR (LEPR). In contrast to P3HT/PC₆₀BM composite, LEPR signal in P3HT/PC₇₀BM can be detected in a wide temperature range up to room temperature. This signal was attributed to charge carriers P3HT⁺ and PC₇₀BM⁻. The dependence of the intensity of LEPR signal on light intensity and the decay of LEPR signal upon switching light off are interpreted in frame of trap-limited bimolecular recombination model with finite rate of back electron transfer in [P3HT⁺ PC₇₀BM⁻] encounter complex at polymer–fullerene interface. The apparent recombination order was found to be close to p = 3.5 for the temperature range from 100 K to room temperature. For temperatures above 150 K Arrhenius behavior of effective recombination rate constant was obtained with the activation energy $E_a = 0.16 \pm 0.01$ eV, which is larger than analogous values for P3HT/PC₆₀BM reported previously. This difference is attributed to the change of polymer/fullerene interface induced by the replacement of PC₆₀BM by PC₇₀BM.



INTRODUCTION

Composites of conductive polymers and fullerene derivatives attract attention of many researchers as a promising material for active layer of organic solar cells.^{1–5} During recent years organic solar cells exhibited a significant progress and reached power conversion efficiency (PCE) values about 10.7%.^{6–8} Despite this progress in organic photovoltaics (OPV), the mechanisms of free charge formation and recombination processes determining PCE in OPV devices still are not completely understood. According to the concept of bulk heterojunction, the active layer of solar cell is a composite containing donor and acceptor domains,^{9,10} and the free charge formation mechanism is described by the following steps:^{2,11–22}

- 1. After light absorption excitons are formed. They can reach donor-acceptor interface in the course of diffusion through the domains in composite.
- 2. At the donor-acceptor interface, the exciton can dissociate into a charge-transfer state where the hole and the electron are spatially separated but still bound by Coulomb attraction.
- 3. Charge-transfer states either recombine²³ or overcome binding energy and dissociate into free charge carriers.

Charge separation efficiency in organic solar cells is known to be about $90\%^{24,25}$ and can not be improved significantly. Therefore, other processes limiting PCE,²⁶ such as nongeminate (bulk) recombination of free charges in active layer,²³ incomplete absorption of the solar irradiation⁶ and loss of solar cell voltage caused by mismatch of work function of electrode materials²⁷ are important for improving OPV device performance.

Since the free charge recombination is one of the main processes limiting PCE, numerous works are devoted to its mechanism determination. Most of the recombination studies of OPV materials were done on composites containing fullerene C₆₀ or its derivatives, usually [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₀BM) (Figure 1), as electron acceptor and conductive polymers as electron donor.²⁸ Free charge recombination in such composites was studied by various methods: transient absorption spectroscopy,^{29-33'} electron paramagnetic resonance (EPR),^{34,35} photogenerated charge carrier extraction by linearly increasing voltage, double injection current transient technique and time-of-flight measurements.^{36,37} It is known that recombination in this system can not be described by Langevin bimolecular recombination model.³⁸ Measurements of the recombination rate in polymer/ fullerene composites result in much lower value than predicted by Langevin theory.³⁹ Many different mechanisms were proposed to explain this recombination process. Among them are quadrimolecular recombination,^{34,35} trap-limited bimolecular recombination,^{29–33,40,41} trimolecular recombination,³⁶ twodimensional Langevin recombination,³⁷ and slow back electron transfer caused by finite reaction radius.⁴² While an exact recombination mechanism is still under discussion, a trap-

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Figure 1. Molecular structures of P3HT, PC₆₀BM, and PC₇₀BM.

limited bimolecular recombination model is most commonly assumed at present. The quadrimolecular recombination model was recently discarded by its authors and replaced by traplimited bimolecular recombination model.⁴³

Much less attention is drawn to charge recombination in composites with acceptor component other than $PC_{60}BM$. Therefore, the question arises: whether the features of recombination mechanism are specific only to composites containing C_{60} or its derivatives? For example, to our knowledge, no studies devoted to free charge recombination in analogous composites where $PC_{60}BM$ is replaced by other popular fullerene derivative [6,6]-phenyl- C_{71} -butyric acid methyl ester ($PC_{70}BM$; Figure 1) have been reported up to date. At the same time it is known that $PC_{70}BM$ -based composites exhibit better performance as an active layer in solar cells.

In the present work light-induced continuous wave EPR (LEPR) was used to study recombination in a composite of $PC_{70}BM$ and conductive polymer poly(3-hexylthiophene) (P3HT; Figure 1). This method allows to determine the apparent recombination order by observing the LEPR signal intensity dependence on excitation light intensity and by measuring LEPR signal decay after light is turned off.^{34,35} We found that LEPR signal in P3HT/PC₇₀BM can be observed in a wide temperature range up to room temperature, in sharp contrast to LEPR signal in P3HT/PC₆₀BM, which disappears upon temperature increase approximately at 200 K. Thus, the goal of this work was to describe the features of recombination in P3HT/PC₇₀BM and to trace the differences of charge recombination rate in P3HT/PC₇₀BM and in P3HT/PC₆₀BM.

EXPERIMENTAL SECTION

Regioregular P3HT and $PC_{70}BM$ (purity 99.995% and 99%, respectively, purchased from Sigma-Aldrich) were dissolved in toluene (weight ratio 1:1) and mixed with ultrasonic mixer QSonica Microson XL2000. Several freeze-pump-thaw cycles were performed, than solvent was evaporated and sample tube (o.d. Five mm) was pumped. Sample was annealed at 10^{-2} Torr, 150 °C for about 10 min. All measurements were performed on X-band EPR spectrometer Bruker ELEXSYS E 580. ER4118X-MD-5W1 dielectric cavity and Oxford ESR 900 cryostat were used. Temperature was set using Oxford ITC 503 temperature controller and additionally measured by ER4131VT device. For each temperature the microwave

power was chosen low enough to avoid CW EPR signal saturation. Modulation frequency was 100 kHz, modulation amplitude was 1G. To measure light EPR signal the sample was irradiated by halogen lamp. The emission spectrum of this lamp was close to AM1.5, although it did not match AM1.5 perfectly. In order to obtain LEPR signal light minus dark EPR spectrum was calculated. EPR signal intensity was determined as the double integral of the EPR line using the automatic baseline correction procedure. For calculation of the number of spins in the sample a CuCl₂·2H₂O crystal with known weight and number of the electron spins was used as the standard. The total number of light-induced spins in the P3HT/PC70BM sample was calculated from double integral of LEPR spectrum. These spins were assigned to electrons and holes in equal amount, due to symmetric nature of charge generation and recombination in this system. The concentration of the electrons (holes) was calculated by dividing the number of the electrons (holes) in the sample by the sample volume 0.5 $\rm mm^3$ estimated from the weight of $\rm P3HT/PC_{70}BM$ in the sample. The intensity of light reaching the sample was varied in the $0.1-250 \text{ mW/cm}^2$ range, resulting in steady-state free charge concentration $10^{16}-10^{17}$ cm⁻³. To ensure precise g value determination necessary for spectrum modeling the nLi-F standard⁴⁴ was attached to the sample tube. To obtain EPR signal decay magnetic field was fixed in the maximum of lightinduced CW EPR signal and the light was turned off during the measurement. The decay of this signal is associated with charge recombination kinetics.

RESULTS AND DISCUSSION

EPR Spectra Modeling. Light and dark EPR spectra were measured in a wide temperature range extending from 80 K up to room temperature (Figure 2). Most probably, the dark signal



Figure 2. Light, dark, and light-induced CW EPR spectra of P3HT/ $\rm PC_{70}BM$ composite at 100 K and at room temperature.

is caused by residual oxygen in the sample that acts as an electron acceptor.⁴⁵ In order to ensure that the observed LEPR signal indeed originates from $P3HT^+$ and $PC_{70}BM^-$ radicals for the whole temperature range from 80 K to room temperature the modeling of LEPR spectra was done.

Spectra were simulated using Easy Spin 4.5.0 program packet.⁴⁶ Resonant magnetic field for each radical (P3HT⁺ and PC₇₀BM⁻) in solid state was determined by the following equation:

$$B_{\rm res}(\theta, \phi) = \frac{\hbar \omega / \beta_e}{g_{XX} \sin^2 \theta \cos^2 \phi + g_{YY} \sin^2 \theta \sin^2 \phi + g_{ZZ} \cos^2 \theta}$$
(1)

where ω is the operating frequency of EPR spectrometer, β_e is Bohr magneton, θ and φ are polar and azimuthal angles, respectively, for direction of the external magnetic field *B* in the frame of *g*-tensor principal axes. Line shape in polycrystalline material was calculated by averaging over all possible angles:

$$F(B) = \frac{1}{4\pi} \iint f(B - B_{\rm res}(\theta, \phi)) \sin \theta d\theta d\phi$$
(2)

Here the individual line shape f(B) was assumed to be a Gaussian function

$$f(B) = \left(\frac{2}{\pi}\right)^{1/2} \frac{1}{\Delta B} \exp\left[-2\left(\frac{B}{\Delta B}\right)^2\right]$$
(3)

with the anisotropic line width determined as

$$\Delta B(\theta, \phi) = (\Delta B_x^2 \sin^2 \theta \cos^2 \phi + \Delta B_y^2 \sin^2 \theta \sin^2 \phi + \Delta B_z^2 \cos^2 \theta)^{1/2}$$
(4)

The spectrum was calculated as a sum of equal contributions of two radicals $P3HT^+$ and $PC_{70}BM^-$, each having anisotropic *g* tensor and line width (Figure 3a). Magnetic interactions



Figure 3. (a) $P3HT^+$ and $PC_{70}BM^-$ contributions to simulated LEPR spectra for 80K, (b)-(d) LEPR spectra modeling for different temperatures.

between radicals were assumed to be negligible. The previously reported principal g-values for $P3HT^{+47-49}$ and $PC_{70}BM^{-48,49}$ were determined by high-field CW EPR spectroscopy. In current work the initial g-values were taken from literature data, these values were varied slightly during fitting. Several examples of the fitted spectra are shown in Figure 3b–d. Quite good agreement between experimental and simulated LEPR spectra is typically reached.

At 80 K the following parameters were used for modeling: $g_{\text{P3HT}} = (2.0028; 2.0024; 2.0070), \Delta B_{\text{P3HT}} = (2.48; 1.848; 4.72)$ MHz, $g_{PC70BM} = (2.0051; 2.0090; 2.0021)$, $\Delta B_{PC70BM} = (3.10;$ 2.16; 1.31) MHz. Generally, line width and principal g-tensor components were weakly temperature dependent both for P3HT⁺ and PC₇₀BM⁻ radicals, except those, which are listed in Table 1. The decrease of line width for P3HT⁺ with temperature growing is probably caused by P3HT phase transition at about 200 K, which leads to partial averaging of hyperfine interaction with protons of P3HT due to increased side chain mobility.⁵⁰ The increase of ΔB_x with a corresponding decrease of g_x for PC₇₀BM⁻ with temperature growing can be explained by partial averaging of its g-tensor by libration motions, similarly to the case of nitroxide radicals in disordered media.^{51,52} Similar effect also was observed in LESR experiments on triplet state of fullerene C₇₀ in molecular glasses.⁵³ In that case the broadening of the outermost spectral features with decrease of the overall width of the EPR spectrum was caused by partial averaging of zero-field splitting tensor due to increased orientational mobility of C70 at elevated temperatures. It is also possible that g-tensor of PC70BM⁻ is partly averaged at higher temperatures as a result of fast hopping of the electron between PC70BM molecules.

Recombination Order Determination. To analyze lightinduced processes in the P3HT/PC70BM composite we used generally accepted kinetic model, which can be briefly summarized as following. Diffusion of excitons to donor/ acceptor interface and their splitting occurs at picoseconds domain, which is far beyond the resolution of our EPR method. For this reason steady-state concentration of excitons is close to zero and it is not treated explicitly. Electrons and holes are generated at the donor/acceptor interface and then quickly moved to their respective phases. We use simplifying assumption that dissociation of charge-transfer states is fast, so their concentration is also close to zero. The recombination of the electrons and holes occurs at the donor/acceptor interface and, strictly speaking, can not be described by the bulk reaction rate constant. However, the characteristic time of the charge carrier diffusion over the distance of 100 nm is about 200 ns,⁵⁴ and it is even smaller for the characteristic size of donor and acceptor domains in the P3HT/PCBM composite (in order of 15 nm).⁵⁵ Since this time scale is much shorter than the characteristic time of nongeminate recombination in P3HT/PCBM composites, electrons and holes travel many times between the boundaries of their respective domains before recombination, and nearly uniform concentration of the charges is established in the composite. For this reason, the

Table 1. Temperature Dependence of Line Width and Principal g-Tensor Components of P3HT⁺ and PC₇₀BM⁻ Radicals

temp, K	80	100	125	150	175	200	250	300
ΔB_z for P3HT ⁺ , MHz	4, 72	4, 76	3, 79	3, 70	2, 08	1, 98	1, 56	1, 95
ΔB_x for PC ₇₀ BM ⁻ , MHz	3, 10	3, 43	6, 03	7, 24	8, 13	8, 95	9, 27	8, 42
g_x for PC ₇₀ BM ⁻	2.0051	2.0051	2.0042	2.0039	2.0037	2.0040	2.0041	2.0040

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effective bulk recombination rate constant can be introduced. The process of nongeminate recombination in donor/acceptor composites implies that electron and hole meet each other at donor/acceptor interface. This process should be distinguished from surface recombination that occurs in operating solar cells and implies simultaneous capturing of electron and hole by the surface of the electrode.⁵⁶ Since there are no electrodes in our blend samples, surface recombination is not relevant for the present study.

In the frame of this approach charge generation and recombination can be formally described as bulk processes by the following rate equation, similar to the equation proposed earlier:^{34,35}

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \Phi I - k_0 N^p \tag{5}$$

where *N* is bulk concentration of holes and electrons in their respective phases (equal concentration for P3HT⁺ and PC₇₀BM⁻ is assumed because charge generation and recombination are symmetric, and total volumes of donor and acceptor phases are approximately equal in our samples), Φ is charge separation efficiency, *I* is the number of photons absorbed per unit volume during one second, k_0 is the effective recombination rate, and *p* is the apparent recombination order. *I* and *N* are proportional to light intensity I_{light} and light-induced EPR signal intensity I_{EPR} , respectively. Thus, in steady-state conditions (dN/dt = 0) the recombination order can be determined from I_{EPR} dependence on I_{light} :

$$I_{\rm EPR} \propto I_{\rm light}^{1/p}$$
 (6)

It should be noted that our simple model does not consider explicitly the transport properties of charge carriers, which may be largely different for electrons and holes. Instead, they are effectively taken into account by the parameters k_0 and p.

Figure 4 shows the experimental I_{EPR} dependence on I_{light} at different temperatures. The apparent recombination order was determined by fitting experimental results with eq 6. Obtained p values are 3.33, 3.85, 3.70, and 3.45 for the temperature values 100, 200, 250, and 300 K, respectively; thus, the recombination is evidently more complex than Langevin bimolecular process.



Figure 4. Representative dependences of LEPR signal intensity on light intensity for P3HT/PC₇₀BM composite at different temperatures (symbols). Power law approximation of these dependences for apparent recombination order p determination (lines).

Another way to determine the apparent recombination order is to use transient response of the LEPR intensity upon light illumination turning off. Signal decay associated with free charge recombination was measured at the point of maximum LEPR signal. It can be fitted using the solution of rate equation:

1...

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -k_0 N^p \tag{7}$$

$$\frac{N}{N_0} = (1 + k_0 (p - 1) N_0^{p-1} t)^{-1/p-1}$$
(8)

where *t* is time after the light was turned off, *N* is charge concentration, which is proportional to EPR signal intensity $I_{\rm EPR}$ (concentrations of electrons and holes are assumed to be equal), N_0 is charge concentration at the moment when the light was turned off (t = 0), and k_0 is the effective recombination rate. While fitting experimental curve N(t), N_0 was fixed at the value measured at the moment of t = 0, and k and p were varied. Several curves with different initial light intensities are presented in Figure 5, ranging from $I_{\rm light} = 250$ mW/cm² in Figure 5a to $I_{\rm light} = 0.1$ mW/cm² in Figure 5d; for each case the best-fit curve is presented. The values of p obtained by fitting are close to 3.5, which is in good agreement with the recombination order values determined by the other methods described above.

Since powder P3HT/PC₇₀BM was used in the present study, no electric field is applied to the composite, in contrast to working solar cells. This is the main difference of our samples from the polymer–fullerene composites in real OPV devices. However, the influence of the applied electric field on the nongeminate recombination is moderate.⁵⁷

Previously, the tendency of the apparent recombination order decrease with temperature increase was reported for light-induced charge carriers in P3HT/PC₆₀BM composite.^{43,58} However, nearly temperature-independent apparent recombination order was obtained for bulk recombination in P3HT/PC₆₀BM composite in the range 150–300 K.⁵⁹ The temperature dependence of the *p* value for P3HT/PC₇₀BM composite will be discussed below.

Recombination Mechanism. From the obtained results it is clear that charge recombination in P3HT/PC₇₀BM composite can not be described by simple Langevin bimolecular recombination. This is not surprising, since significant deviation from the predictions of Langevin model was found in numerous studies of analogous P3HT/PC60BM composites. $^{29-39}$ Here, the model of trap-limited diffusion with recombination via encounter complex at donor-acceptor interface is suggested for interpreting the features of charge recombination in P3HT/PC70BM. Previously the model of trap-limited recombination was proposed for charge recombination in dye-sensitized solar cells (DSSC).⁶⁰ Later it was used for polymer-fullerene composites containing $PC_{60}BM$.^{29-33,40,41,43} The deviation from p = 2 was explained by the presence of exponential tail of localized states in the density of states (DoS) $g(E) \sim \exp(-E/E_0)$, where E is the energy of the state (electron or hole) and E_0 is a fixed parameter.41 The bimolecular recombination is slowed down because trapped charges can recombine only after thermally activated detrapping. Low excitation light intensity results in low charge concentration; therefore, the localized states are filled partially, but not completely. At high light intensities, all localized states are filled, and extra charge carriers occupy nonlocalized states. The presence of localized states leads to a



Figure 5. Transient response of the LEPR intensity upon the light illumination turning off at 105 K. The signal decay is associated with free charge recombination. The experimental LESR decay curves were fitted by the solution of rate eq 8, for different intensities of light illumination I_{light} .

bimolecular recombination rate dependence on charge carrier concentration. Thus, the rate equation can be rewritten in the following form:

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \Phi I - k(N)N^2 \tag{10}$$

If the power law dependence of bimolecular recombination rate constant $k(N) = k_0 N^{\beta}$ is assumed the observed recombination order *p* is equal to $\beta + 2$. It is known that β is strongly influenced by sample morphology: the higher the crystallinity of the sample, the lower the β value.⁶¹ Observed β values for room temperature vary between 3 for amorphous samples and 0.5 for crystalline ones.³²

The model of trap-limited bimolecular recombination with exponential DoS predicts temperature-dependent apparent reaction order $p = 1 + E_0/k_BT$, where k_B is Boltzmann constant and T is temperature. Temperature dependence of p was indeed observed in numerous studies of polymer/fullerene composites, mainly $P3HT/PC_{60}BM$.^{43,58,59} However, the dependence of p on the inverse temperature is weaker than linear. Notably, even at T = 2 K the apparent recombination order equals 6 for P3HT/PC₆₀BM composite, 62 while for room temperature it is close to 2.5. ⁵⁸ This may be caused by deviation of DoS from purely exponential form. It is established that for P3HT DoS is close to Gaussian form.⁶³ For this reason, although we suggest trap-limited bimolecular recombination for P3HT/PC₇₀BM composite, we do not assume linear dependence of the apparent reaction order on the inverse temperature. First we note that similarly to previous observations, this dependence is weak. Second, according to the predictions of the theory of trap-limited bimolecular recombination some tendency of *p* increase with temperature decrease can be traced. Deviation from this tendency at T = 100 K may be caused by increased role of tunneling recombination at low temperatures. For simplicity of further analysis we assume that apparent recombination order is independent of the temperature in the studied range 100-300 K and equals 3.5.

Therefore, according to experimental data, for our P3HT/ PC₇₀BM sample β value is close to 1.5. In stationary conditions, assuming $\beta = 1.5$, the effective recombination rate constant k_0 can be determined by the following equation

$$k_0 = \frac{\Phi I}{N^{3.5}} \tag{11}$$

From the Arrhenius plot of k_0 (Figure 6) it can be seen that charge recombination is temperature activated above the



Figure 6. Temperature dependence of the effective recombination rate k_0 for P3HT/PC₇₀BM. The red line shows fitting by Arrhenius equation. From the slope of this line the activation energy of bimolecular recombination $E_a = 0.16$ eV was determined.

transition temperature $T^* \approx 150$ K, with activation energy $E_a = 0.16 \pm 0.01$ eV. It is also seen that charge recombination rate becomes nearly temperature-independent at low temperatures. For calculations $\Phi = 1$ was assumed, since external quantum yield close to unity is usually observed for composited of P3HT with fullerenes.^{24,25}

It is well-known that concentration and temperature dependence of recombination rate in composites based on P3HT is complex. Recently it was shown that two contributions to recombination kinetics in P3HT/PC₆₀BM can be separated, which probably refer to trapped carriers and free carriers in P3HT.³² However, now our principal aim is to explain the difference in recombination kinetics in composites of P3HT with PC₆₀BM and PC₇₀BM. Recombination kinetics in the P3HT/PC₆₀BM composite was studied previously by LEPR,³⁵ and recombination activation energy in the range 0.05–0.09 eV

was observed, depending on mole fraction of $PC_{60}BM$. These values are significantly smaller than the activation energy for charge recombination in P3HT/PC₇₀BM composite $E_a = 0.16$ eV obtained in the present work. Although a slightly different recombination order was assumed for P3HT/PC₆₀BM (quadrimolecular recombination, p = 4),³⁵ it is quite close to p = 3.5 used in the present work. This small difference does not influence the derived activation energy substantially.

To explain this difference, the concept of encounter $complex^{64}$ can be used (Scheme 1). In frame of this kinetic

Scheme 1. Kinetic Scheme Describing the Mechanism of Charge Recombination in the Composite of Conductive Polymer (Donor, D) and Fullerene (Acceptor, A)

$$D^{+}+A^{-} \underbrace{\gamma_{D}}_{k_{d}} \{D^{+}A^{-}\} \xrightarrow{k_{r}} D^{+}A^{-}$$

scheme, the recombination of free charges in donor (P3HT) and acceptor (PC₆₀BM or PC₇₀BM) phase is a two-step process. First, the encounter complex [D⁺A⁻] at donor– acceptor interface is formed with bimolecular reaction rate constant $\gamma_{\rm D}$ determined by electron and hole mobilities which, in turn, are influenced by trap-limited diffusion and are governed by DoS. Since charge mobility is concentrationdependent in P3HT³² and probably also in fullerenes, $\gamma_{\rm D}$ depends on charge concentration and this is the origin of the deviation of the apparent reaction order from 2. The encounter complex can either dissociate with monomolecular rate constant $k_{\rm d}$, or recombine with back electron transfer rate constant $k_{\rm r}$. If $k_{\rm d} \gg k_{\rm r}$ the rate constant of the overall bimolecular recombination is

$$k = \gamma_{\rm D} k_{\rm r} / k_{\rm d} \tag{12}$$

Although there is a large scattering of the reported electron mobilities μ for PC₆₀BM and PC₇₀BM, which are usually in the range 10⁻⁴ to 10⁻² cm² V⁻¹ s^{-1,65-69} typically the reported values are close for PC₆₀BM and PC₇₀BM. For example, $\mu = 2$ × 10⁻³ cm² V⁻¹ s⁻¹ for PC₆₀BM and $\mu = 10^{-3}$ cm² V⁻¹ s⁻¹ for PC₇₀BM were obtained.⁷⁰ Therefore, one can assume that electron mobilities in PC60BM and PC70BM are close, and, consequently, $\gamma_{\rm D}$ values for P3HT/PC_{60}BM and P3HT/ PC₇₀BM composites are also close. As it is evident from eq 12, the difference in bimolecular recombination rate in this case is determined by the difference in k_r/k_d ratio for the encounter complexes [P3HT⁺ PC₆₀BM⁻] and [P3HT⁺ PC₇₀BM⁻]. It is reasonable to suggest that dissociation of the encounter complex is activationless. This is supported by quantumchemical calculations of the fullerene/P3HT interface. Due to increased distortion of P3HT chains in contact with fullerene phase the energy of holes increases. This causes repelling of the holes from polymer/fullerene interface.⁷¹ Within the above assumption, the difference of the observed activation energy of bimolecular recombination in P3HT/PC60BM and P3HT/ $PC_{70}BM$ composites originates from the difference of k_r for the encounter complexes [P3HT⁺ PC₆₀BM⁻] and [P3HT⁺ PC₇₀BM⁻]. This difference can be caused by different geometries of the encounter complexes, because PC70BM molecule is larger than PC₆₀BM and hence larger distortion of P3HT chains is expected for P3HT/PC₇₀BM interface. Alternatively, the difference in back electron transfer rate can originate from the difference in electronic structure of PC₇₀BM

and $PC_{60}BM$. For testing these hypotheses a detailed quantum chemical calculation is needed, which was partly done for $[P3HT^+ PC_{60}BM^-]$ complex.⁷²

At temperatures below 150 K the dependence $k_0(T)$ is weak for P3HT/PC₇₀BM (see Figure 6). Similar temperature behavior of recombination rate was observed for numerous composites of polythiophenes with C₆₀ and PC₆₀BM,³⁵ which was explained by the contribution of another recombination channel, namely, tunneling of charge carriers. For the P3HT/ PC₆₀BM composite, tunneling recombination mechanism is observed at temperatures lower than 60 K.³⁵ For P3HT/ PC₇₀BM, the temperature of transition to tunneling regime is much higher, presumably because recombination activation energy for this composite is higher than for P3HT/PC₆₀BM.

Finally, the applicability of the developed model to real solar cells should be discussed. One of the assumptions of this model is equal concentration of electrons and holes, which seems to be its major limitation. For operating solar cell, this assumption does not always hold because of the large concentration gradient of charge carriers in the vicinity of the electrodes.^{73,74} However, numerical simulations predict nearly equal concentration of electrons and holes in the central part of the active layer of the device, that is, when the distance from cathode and anode is more than 10 nm.^{73,74} Therefore, our model can be applied to the "inner part" of the donor/acceptor layer of solar cell, which constitutes its major fraction. In view of large concentration gradient of charge carriers and their concentration-dependent transport properties, the recombination mechanism can be completely different in the vicinity of the electrodes.

LEPR signal in P3HT/PC70BM composite originating from charge carriers P3HT⁺ and PC₇₀BM⁻ was observed in a wide temperature range up to room temperature. Charge recombination in P3HT/PC70BM composite was described by traplimited bimolecular recombination model with finite rate of back electron transfer in [P3HT⁺ PC70BM⁻] encounter complex at polymer-fullerene interface. The power law recombination rate dependence on charge carrier concentration was obtained, with apparent reaction order close to 3.5 for the temperature range from 100 K to room temperature. At temperatures higher than 150 K the recombination activation energy $E_a = 0.16 \pm 0.01$ eV was determined. The difference between this value and the value previously reported for P3HT/PC₆₀BM composite is presumed to originate from the change in donor/acceptor interface caused by the replacement of PC₆₀BM by larger PC₇₀BM molecules.

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Notes

The authors declare no competing financial interest.

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