Effect of spin traps on charge transport in low-bandgap copolymer: fullerene composites

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A B S T R A C T

Light-Induced EPR study of magnetic, relaxation and dynamic parameters of spin charge carriers background photoinduced in bulk heterojunctions of composites formed by poly[2,7-(9,9-dioctylfluorene)-*alt*-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PFO-DBT) and poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) with methanofullerene [6,6]-phenyl-C_{61}-butyric acid methyl ester is described. A part of polarons is captured by deep spin traps whose number and energy depth are governed by the structure, morphology of a copolymer matrix and also by the photon energy. Both the composites exhibit photo-response within photon energy/wavelength 1.32–3.14 eV/940-395 nm region which is wider than that of other polymer composites. Magnetic, relaxation and dynamics parameters of spin charge carriers were shown to be governed by their exchange interaction and photon energy. Specific morphology of the composites causes selectivity of these parameters to the photon energy. It was shown that the anisotropy of spin mobility through bulk heterojunctions reflects the system dimensionality and is governed by the photon properties. The replacement of the PFO-DBT backbone by the PCDTBT matrix leads increases the ordering of a copolymer, decreases the number of spin traps and changes a mechanism of charge recombination. The decay of free charge carriers was interpreted in terms of the trapping-detrapping spin diffusion in bulk heterojunctions.

1. Introduction

Conjugated polymers with extended π-electron systems in their main chain attract much interest due to their perspective use as flexible active matrix for new electronic devices including photovoltaic [1]. Basically, photoactive layers of organic solar cells consist of two materials as donor and acceptor subsystems. Soluble derivatives of polythiophene, poly(3-alkylthiophenes) (P3AT), and fullerene, [6,6]-phenyl-C_{x1}-butyric acid methyl ester ($PC_{x1}BM$, $x = 6,7$), are traditionally used for such purposes as electron donor and acceptor, respectively [1]. Once composites of such materials are illuminated, spinless excitons are first formed in their bulk heterojunctions (BHJ). These quasi-particles can geminate ultrafast dissociate forming Coulomb bound electron-hole pairs (charge-transfer states) of electrons on the acceptor moiety and holes on the donor moiety. Then electrons and holes can leave the donor:acceptor interface relaxing into more favorable energy levels [2]. With increasing distance from the material interface, the Coulomb attraction becomes less, and finally, the electrons and holes become independent of each other, forming quasi-pairs or charge-separated states. Finally, charge separation leads to the formation of unbound (free) positively charged

polarons on polymer chains and negatively charged radical on fullerene globes. After this stage, charge carrier recombination can occur. The separation and recombination of free charge carriers can be considered as concurring opposite directed processes. Recombination of opposite charge carriers can either be geminate, between electrons and holes originating from the same photo-generated exciton, or non-geminate, between separated charge carriers. The geminate recombination of polaron-fullerene pairs is monomolecular and, therefore, a first order process. The non-geminate, bimolecular recombination of separated polaron-fullerene quasi-pairs following Langevin theory of a second order.

The main parameter of photovoltaic devices is efficiency of power conversion which is mainly governed by the structure of polymer:fullerene BHJ. Among polymer semiconductors, low-bandgap copolymer poly[N-9′-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT, see Fig. 1 for its molecular structure) appeared to be one of the most functional matrix for use in organic electronics and photonics [3]. The use of fullerene-modified PCDTBT allowed reaching power conversion efficiency more than 8% for solar cells that exceeds considerably than that obtained for P3AT-based

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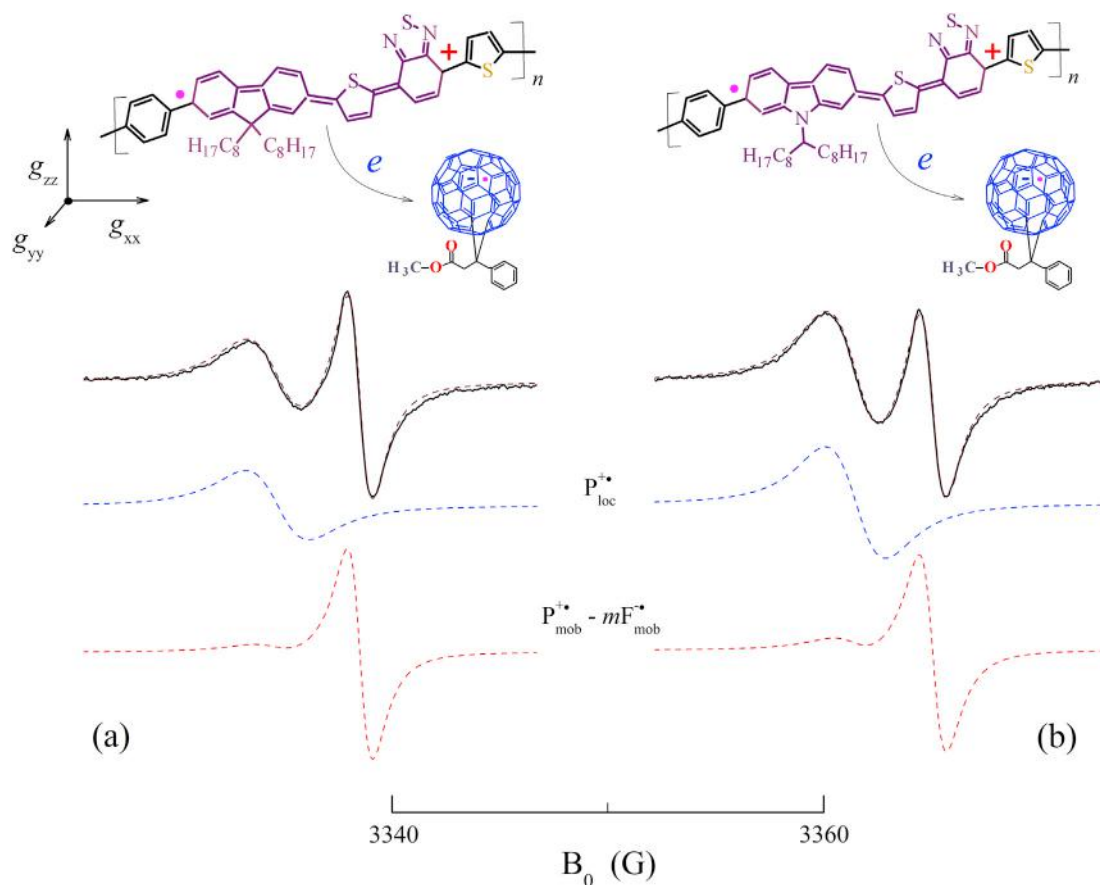 *E-mail address:* kivirus@gmail.com (V.I. Krinichnyi).

Fig. 1. LEPR spectra of charge carriers background photoinduced at $h\nu_{ph}/\lambda_{ph} = 2.38/520$ eV/nm and 77 K in BHJ formed by macromolecules of PFO-DBT (*a*) and PCDTBT (*b*) with globes of $PC_{61}BM$. Dashed lines show theoretical Lorentzian sum spectra and their contributions caused by localized polarons $P_{loc}^{+\bullet}$ and highly mobilized radical quasi-pairs, $P_{mob}^{+\bullet} \leftrightarrow mF_{mob}^{-\bullet}$ numerically calculated using $g_{iso}^{P} = 2.00231$, $\Delta B_{pp}^{P} = 2.25$ G, $\Delta B_{pp}^{mF} = 1.17$ G, a concentration ratio $[mF_{mob}^{-\bullet}]:[P_{loc}^{+\bullet}] = 0.42$ (*a*) and $g_{iso}^{P} = 2.00209$, $\Delta B_{pp}^{P} = 2.17$ G, $\Delta B_{pp}^{mF} = 1.31$ G, $[mF_{mob}^{-\bullet}]:[P_{loc}^{+\bullet}] = 0.36$ (*b*). The charge transfer from polymer chain to methanofullerene globe accompanied by the formation on the polymer chain of polaron with an elementary positive charge and spin $S = \frac{1}{2}$ is shown schematically.

systems. Such outstanding results were explained [4] mainly by ultrafast charge separation in the PCDTBT:PC$_{71}$BM composite before localization of the primary excitation to form a bound exciton in contrast with, e.g., P3AT-based BHJ, where photoinduced charge separation happens after diffusion of the polymer exciton to a fullerene interface. The other important property is the morphology of a polymer:fullerene composite. This characteristic of fullerene-modified PCDTBT was demonstrated [5] to be laterally oriented with "column-like" bilayer ordered copolymer matrix with methanofullerene embedded between its chains. The dimensionality of low-bandgap copolymer backbone with such morphology should be higher than that of P3AT matrices. Gutzler, at al. showed [6] that higher π-overlapping in 2D thiophene-based polymers hinders their torsional twisting and, therefore, lowers their bandgap. This accelerates polaron hopping through well-ordered bilayer surfaces to the anode and electron motion to the cathode inside methanofullerene pools located between bilayers of the matrix.

In main polymer:fullerene systems there occur non-geminate charge recombination which consists of prompt bimolecular and persistent contributions [7]. The prompt process is of activation bimolecular type mutual spin annihilation within the initially created radical quasi-pairs, whereas the persistent contribution originates from deep spin traps reversibly formed in polymer matrix due to its disorder. Such process in low-bandgap system is usually analyzed within the framework of a model based on concomitant geminate recombination of charge-transfer states and non-geminate recombination of free charge carriers. It was shown [8], that the small number of initial excitons fast nanosecond recombine,

e.g., in the PCDTBT:PC$_{61}$BM and thus do not contribute to the photo-current through its BHJ, whereas the main part of excitons creates free charge carriers on an ultrafast time scale that contribute to the photo-current and then non-geminate recombine.

It is evident that the efficiency of energy conversion by a polymer:-fullerene BHJ is governed mainly by the number and dynamics of separated spin charge carriers whose number must exceed the number of recombined free charge carriers. Various methods may register only an effective concentration of free paramagnetic centers (PCs) as different number of forward fast initiating and reversed slow recombining opposite charge carriers upon continuous illumination of respective polymer:fullerene BHJ. Because the main charge carriers possess a spin, their formation, dynamics and recombination were expected and proved to be spin-assisted [2]. This was the reason why the Light-Induced Electron Paramagnetic Resonance (LEPR) becomes as one of the most powerful method for the study of spin-assisted processes carrying out in organic polymer:fullerene systems [2,9]. Indeed, the evidence for a successful charge transfer is based on the fact that excitons initiated by light photons have zero spin and, therefore, cannot be detected by the method. If the exciton is split in a polymer:fullerene interface, polarons and fullerene anion radicals both with half integer spin are created in BHJ that originates an EPR signal. The amount of light induced quasi-pairs of charge carriers can be simply determined by the "light on-light off" method using comparison of EPR spectra before and after illumination. Although, charge transfer states exist for about 100 ps [10] they cannot be directly observed by the method. By consequence, detectable EPR

signals correspond to species persisting on longer time-scales, e.g., both type of charge carriers in the charge-separated state. Generally, these PCs are characterized by close weakly anisotropic g-factors, so they demonstrate at commonly used X-band (3-cm, 9.7 GHz) waveband EPR partly overlapping doublet of lines attributed to both charge carriers. LEPR study of various polymer:fullerene composites at this waveband showed [11] that upon illumination some polarons are fixed in trap sites which number and depth are governed by a structure of BHJ and an energy of initiating photons. Exchange- and multi-trap assisted recombination of free charge carriers are governed by their dynamics as well as by structure and morphology of their microenvironment. It should be noted that the higher spectral resolution and, therefore, more detailed information about such systems can be obtained at millimeter W- (3-mm, 95 GHz) and D- (2-mm, 130 GHz) wavebands EPR [10,12,13]. Although the mechanism and dynamics of charge generation and recombination in various polymer:fullerene BHJ have been intensively studied by many research groups, but their details are still debated. In particular the role of reversible photoinduction of spin traps on spin-assisted interaction, relaxation and dynamics in polymer:fullerene BHJ, an important step for the understanding of device functionality, is also still under active discussion. Besides, the nature of the excited states, the coupling mechanism and the relaxation pathways following photoexcitation are yet to be clarified.

We carried out comparative LEPR study of spin and electronic properties of the structurally close PFO-DBT:PC$_{61}$BM and PCDTBT:PC$_{61}$BM composites upon their irradiation by wide-range energy of the light photons. The use of direct methodical approaches allowed us to determine correlation of structural, morphological properties of these systems with spin relaxation, dynamics of spin charge carriers and also with the spin traps reversible initiated in both low-bandgap copolymer BHJ. It was shown for the first time that the minor structural variation of a copolymer matrix changes sufficiently electronic properties of respective nanocomposite. Besides varying the light illumination band, it becomes possible to achieve a sensitivity of charge transfer to the photon energy.

2. Materials and methods

In experiments as electron donor subsystem were used Sigma-Aldrich® poly[2,7-(9,9-dioctylfluorene)-alt-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PFO-DBT), poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) and [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM) methanofullerene distributed by Solenne BV, The Netherlands as electron accepter subsystem. Chemical structures of these ingredients are shown schematically in Fig. 1.

Both the polymer:fullerene composites were prepared simultaneously as following. First 1.4 mg of PFO-TBT (or PCDTBT) and 5.6 mg of PC$_{61}$BM were solved in 1 ml of dichlorobenzene. Both the solutions were treated by ultrasonic in cleaner DADI DA-968 (50 W) for 5 min with following warming at $T = 333$ K within 5 min. Then 5.6 mg of PC$_{61}$BM was added to the so-treated solutions amounting optimal polymer:fullerene ratio to be 1:4 [14]. The resulting solutions were additionally maintained at $T = 333$ K for 20 h until complete PC$_{61}$BM dissolution, casted thrice by 10 μl into both sites of an individual ceramic plate and dried in air until the samples were formed as double-sided films. The films totally contained ca. 0.1 mg of PFO-DBT (or PCDTBT) and ca. 0.4 mg of PC$_{61}$BM and were ca. 4×8 mm^2 in size and ca. 0.1 mm in thickness.

The samples were permanently irradiated by monochromatic light sources based on Luxeon® 5 Watt light emitting diodes with photon energy/wavelength, $h\nu_{ph}/\lambda_{ph}$, of 1.32–3.14/940-395 eV/nm directly in the microwave (MW) cavity through short quartz light guide. The I_l value of these sources was estimated using a broadband IMO-2N output power light irradiation bolometer in combination with a digital luxmeter LX-1010BS and was used for the further normalization of spin concentration photoinitiated in the samples.

EPR measurements were made using an X-band (3-cm, 9.7 GHz) PS-

100X spectrometer with maximal MW power of 150 mW (that is equivalent to the magnetic term B_1 of MW irradiation in the cavity center of 0.51 G) and 100 kHz field ac modulation for phase-lock detection. The LEPR spectra of the polymer:fullerene composites were registered at 77 K in quartz Dewar filled with liquid nitrogen. The signal-to-noise ratio of the LEPR spectra was improved by averaging several (typical 4–6) acquisitions. The measurements of effective magnetic susceptibility of the "dark" (domestic) PCs and those photoinduced in a polymer:fullerene BHJ were performed using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) stable nitroxide radical. The contributions of different PCs were determined precisely by using the "light on-light off" method accompanied with the computer simulation and deconvolution of effective LEPR spectra [11,13,15]. Processing and simulations of the EPR spectra were done with the EPRWin, EasySpin and OriginLab softwares. Absorption LEPR spectra were doubly integrated far from MW saturation conditions when the magnetic term B_1 of MW field and amplitude B_m of ac modulation in the cavity center did not exceed 0.05 and 1 G, respectively. Diphenylpicrylhydrazyl (DPPH) single microcrystal standard with $g = 2.0036$ was used for the estimation of the g-factor of all spin charge carriers. The determination accuracies of the EPR line intensity I, g-factor and peak-to-peak linewidth ΔB_{pp} were determined to be 5%, $\pm 2 \times 10^{-4}$ and $\pm 2 \times 10^{-2}$ G, respectively. Both the spin-lattice T_1 and spin-spin T_2 relaxation times were determined using the steady-state MW saturation method [16].

3. Results and discussion

3.1. LEPR spectra composition and magnetic resonance parameters

Fig. 1 shows exemplary X-band spectra LEPR obtained at $T = 77$ K under irradiation of the PFO-DBT:PC$_{61}$BM and PCDTBT:PC$_{61}$BM composites by photons with $h\nu_{ph} = 2.38$ eV. As in the case of analogous polymer:fullerene composites [11], these spectra were attributed to polarons photoinitiated on copolymer chains and PC$_{61}$BM methanofullerene anion radicals situated between them. Analyzing the intensity of the LEPR one can note that they does not definitely correlates neither with the number of optical quanta reaching the sample surface nor with those absorbed by the sample. Indeed, the intensity of the EPR signal was shown not to change significantly in the IR region, where the absorption band is nearly nulled [17]. Furthermore, both the samples absorb more effective quanta with the energy $h\nu_{ph} \approx 2.1$ eV lying near their optical bandgap ($2\Delta = 1.87$ eV [14]) and vice versa absorb minimum quanta with $h\nu_{ph} \approx 2.7$ eV. This does not confirm the conclusion made by Tong et al. [18] that the efficiency of the carrier initiation, e.g., in the PCDTBT:fullerene composite should be essentially independent of the excitation wavelength. Various hypotheses can be supposed for explanation of this discrepancy. One of them could be the interaction of spin charge carriers with a MW field. If the initial excitons can be considered as relatively isolated quasi-particles there should be a reasonably high probability that a metastable PCs may result from the optical production of an electron-hole pairs by means of the trapping of their one carrier and the hopping away of the other [19]. This means that the time of separation and life of photoinitiated radical quasi-pairs polaron-electron should generally increase with the electron spin precession frequency ω_e. However, different processes affecting electronic transport through BHJ should be carried out in such systems. In order to determine main magnetic resonance parameters of radical quasi-pairs and to analyze their change with experimental conditions, sum LEPR spectra of the samples were deconvoluted as it was made in the case of other polymer:fullerene systems [11,13,15]. Such algorithm in combination with the "light on-light off" method allowed us to obtain separately all magnetic resonance parameters of all PCs stabilized and photoinitiated in both the PFO-DBT:PC$_{61}$BM and PCDTBT:PC$_{61}$BM composites at wide region of photon energy at $T = 77$ K. Fig. 1 depicts also the contributions due to polarons pinned in polymer spin traps P$_{loc}^{+\bullet}$ and mobile quasi-pairs

$P^{+\bullet}_{mob} \leftrightarrow mF^{-\bullet}_{mob}$. The best fit of experimental LEPR spectra of the samples showed the absence in them of contribution of pinned methanofullerene radicals normally registered in other polymer:fullerene composites [11]. This implies the lower number of deep traps able to capture radical anions and the faster dynamics of the latters due to more ordered copolymer composites under study.

Effective/isotropic splitting Landé g-factor was measured for methanofullerene anion radicals to be $g^{mF}_{iso} = 1.999_{89}$ and was appeared to depend weakly on the structure of polymer matrix and photon energy. It was shown at D-band EPR [15] that these PCs photoinitiated in the same composite are characterized by weakly anisotropic **g**-tensor with the main values $g_{xx} = 2.0006$, $g_{yy} = 2.0005$, $g_{zz} = 1.9985$, so then $g^{mF}_{iso} = \frac{1}{3}\Sigma g_{ii} = 1.9999$ which is close to that obtained above. The spin of polarons interacts with own environment that also leads to a weak anisotropy of their g-factor. Polarons formed as product of exciton dissociation in, e.g., PCDTBT:PC$_{61}$BM composite are characterized by **g**-tensor with $g_{xx} = 2.0032$, $g_{yy} = 2.0024$, $g_{zz} = 2.0018$, and $g^{P}_{iso} = 2.0025$ [15]. In contrast with the above negative charge carriers, g-factor of polarons reveals higher dependence on the structure of polymer matrix (see Fig. 1). The same values obtained for the samples under study are in good agreement with g^{P}_{iso} determined for analogous composites at wide wavebands EPR [11]. The orientation of the principal axes of the polaron **g**-tensor is given in Fig. 1. The g_{xx} value lies in the plane of the polymer π-system and perpendicular to the main axis of the monomer units is more sensitive to the interatomic distances and to the heteroatom involving in the polymer backbone. The g_{yy} value is less sensitive to the properties of polaron environment and g_{zz} is most insensitive among all terms of **g**-tensor.

Generally, an effective g-factor of PCs can be written as [20]

$$g_{iso} = \frac{g_e}{3}\left[1 + \lambda\rho(0)\left(\frac{1}{\Delta E_{n\pi*}} + \frac{1}{\Delta E_{\sigma\pi*}}\right)\right], \qquad (1)$$

where $g_e = 2.002319$ is the Landé splitting factor for free electron, λ is the constant of spin-orbit spin coupling with a heteroatom, $\rho(0)$ is the spin density on a heteroatom, $\Delta E_{n\pi*}$ and $\Delta E_{\sigma\pi*}$ are the energy of spin $n\rightarrow\pi*$ and $\sigma\rightarrow\pi*$ transitions, respectively [20,21]. Fig. 2 shows how g^{P}_{iso} parameter of the samples changes upon their illumination by photons with different energy. It is seen from the Figure that effective g-factor of polarons in both composites demonstrates extreme dependence on the
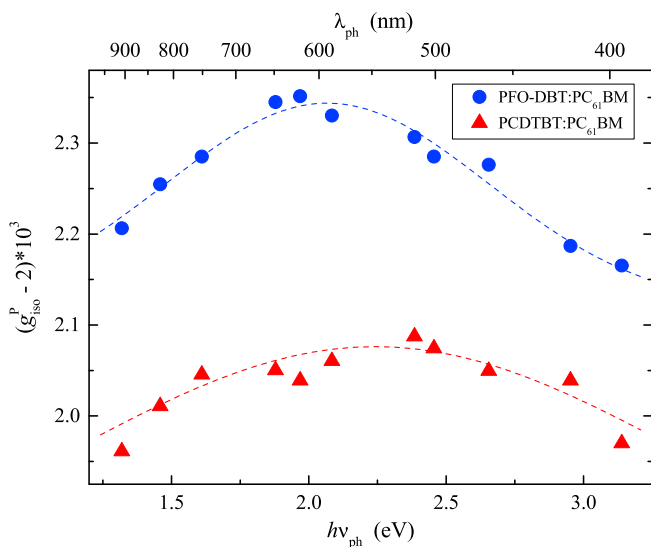

Fig. 2. The value of g^{P}_{iso} for polarons photoinduced in the PFO-DBT:PC$_{61}$BM and PCDTBT:PC$_{61}$BM bulk heterojunctions as a function of photon energy $h\nu_{ph}$ at $T = 77$ K. The above and below dashed lines show dependences calculated from Eq. (2) with $g_0 = 2.00212$, $k_1 = 1.09 \times 10^{-7}$, $E_c = 2.07$ eV, $\sigma = 1.17$ eV and $g_0 = 2.00178$, $k_1 = 5.48 \times 10^{-7}$, $E_c = 2.24$ eV, $\sigma = 1.95$ eV, respectively.

photon energy $h\nu_{ph}$. They can be fitted, e.g., by Gaussian function

$$g_{iso} = g_0 + \sqrt{\frac{2k_1}{\pi\sigma^2}}\exp\left(-\frac{2(E - E_c)^2}{\sigma^2}\right), \qquad (2)$$

where g_0 and g_1 are constants, E_c is the characteristic energy, and σ is deviation of the energy. Figure shows that the experimental data obtained for the PFO-DBT:PC$_{61}$BM and PCDTBT:PC$_{61}$BM composites are fitted well by Eq. (2) with $E_c = 2.07$ eV, $\sigma = 1.17$ eV and $E_c = 2.24$ eV, $\sigma = 1.95$ eV, respectively. One can conclude that the irradiation of the composites leads to reversible formation in their polymer backbone of spin traps that changes (also reversibly) polymer morphology and, therefore, the energy of spin excitation on respective level. This originates a dependence of their effective g-factor on the photon frequency with characteristic distribution, position and deviation.

3.2. Spin susceptibility

Another important parameter reflecting an efficiency of the photon-exciton-charge conversion in polymer:fullerene BHJ is effective number of resulting spin charge carriers. It was noted above that the absorption of a photon by polymer network leads to the formation of exciton and subsequent electron transfer from polymer chain to fullerene globe. Starting from this moment two processes start in the polymer:fullerene system, namely the motion of charge carriers through BHJ followed by their recombination. Besides, spin traps reversible forming under illumination of polymer matrix should be also taken into account. They are characterized by spatial distribution, energy depth and, therefore, specific sensitivity to different photons [11]. In result of the energy conversion, only part of the spin carriers reaches electrodes. It is quite obvious that the efficiency of such process depends on the number of free charge carriers. It was shown [11] that the initiation and recombination of charge carriers are spin-assisted processes which can be described in terms of the exchange interaction of the polarons hopping along the solitary polymer chains with spins captured in spin traps. These processes can, therefore, be characterized by the ratio of the number of mobile charge carriers to that captured by spin traps. In this case polarons are described as quasi-particles randomly walking along the chains with the frequency ω_{hop}. Assuming that their motion is not disturbed by the presence of methanofullerene molecules and both the carriers possess spin $S = \frac{1}{2}$, we can conclude that the probability of their collision is governed by the polaron hopping [22,23],

$$p_{ss} = \frac{1}{2}\cdot\frac{\alpha^2}{1 + \alpha^2}, \qquad (3)$$

where $\alpha = 3J_{ex}L^2/2\hbar\omega_{hop}$, J_{ex} is the constant of exchange interaction of spins in a radical quasi-pairs, L is a factor of spin delocalization over a polaron equal approximately to three units in PCDTBT [15], and $\hbar = h/2\pi$ is the Plank constant. If the ratio $J_{ex}/\hbar$ exceeds the frequency of collision of both types of spins, the condition of strong interaction is realized in the system. This leads to the direct relation of spin-spin interaction rate and polaron diffusion frequency, so then $\lim(p) = 1/2$. In the opposite case $\lim(p) \propto J^2_{ex}\omega^{-2}_{hop}$. This means that the acceleration of polaron mobility should lead to the decrease/increase in the exchange frequency at weak/strong spin exchange limit and, therefore, to a respective dependence for spin-spin interaction.

Fig. 3 depicts the dependence of the relative concentration of charge carriers in the composites under study on the energy of initiating photons $h\nu_{ph}$. One can note two main features of the data presented. The first of them is the higher relative concentration in both the systems of localized carriers in comparison with that of mobile methanofullerene anion radicals. Another feature is the non-linear dependence of the number of both charge carriers on the photon energy. As it is shown in Fig. 3, the concentration of the $P^{+\bullet}_{loc}$ and $mF^{-\bullet}_{mob}$ charge carriers is characterized by
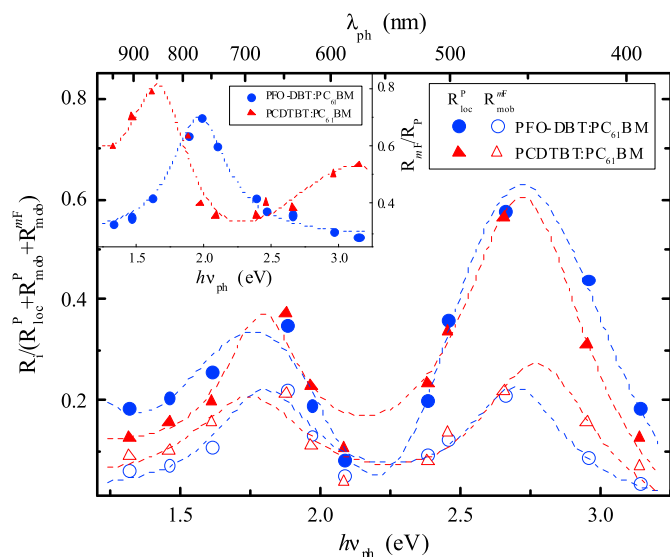
Fig. 3. Relative concentrations, $[P^{+\bullet}_{loc}]/[P^{+\bullet}_{loc} + P^{+\bullet}_{mob} + mF^{-\bullet}_{mob}]$, $[mF^{-\bullet}_{mob}]/[P^{+\bullet}_{loc} + P^{+\bullet}_{mob} + mF^{-\bullet}_{mob}]$, and their ratio $[mF^{-\bullet}_{mob}]/[P^{+\bullet}_{loc}]$ (insert) determined for polaron $P^{+\bullet}$ and methanofullerene anion radical $mF^{+\bullet}$ charge carriers photoinitiated in the PFO-DBT:PC$_{61}$BM and PCDTBT:PC$_{61}$BM bulk heterojunctions at $T = 77$ K as a function of photon energy $h\nu_{ph}$. The values obtained were normalized to the luminous emittance of the light sources I_l. The dashed lines are drawn arbitrarily only for illustration to guide the eye.

dependence with explicit extremes lying near 1.8 and 2.8 eV. Such a peculiarity can probably be as result of specific morphology and band structure of the samples with inhomogeneously distributed spin traps. It is quite clear that the higher concentration ratio $[mF^{-\bullet}_{mob}]/[P^{+\bullet}_{loc}]$ (or/and $[P^{+\bullet}_{mob}]/[P^{+\bullet}_{loc}]$), the better efficiency of energy conversion should be expected for respective system. In the insert of Fig. 3 are shown such a ratio as function of the photon energy $h\nu_{ph}$ obtained for composites under study. It is seen that these ratios determined for the PFO-DBT:PC$_{61}$BM and PCDTBT:PC$_{61}$BM composites change extremely with $h\nu_{ph}$ with characteristic values lying near 2.0 and 1.7 eV, respectively. The results obtained show that the replacement of PFO-DBT by PCDTBT leads to a significant change in the number and distribution of the spin traps in the composite backbone. This causes a change in electronic properties of the respective composite, including its efficiency of energy conversion.

3.3. Spin recombination

Once the initiating illumination of the samples is turned off, the photoinitiation of charge carriers stops and the concentration of spin charge carriers excited decrease. This is depicted in Fig. 4 where is shown the decay of spin charge carriers photoinitiated in both the PFO-DBT:PC$_{61}$BM and PCDTBT:PC$_{61}$BM systems at $h\nu_{ph}/\lambda_{ph} = 2.38/520$ eV/nm. The structure and morphology of the samples should govern the mechanism and order of spin recombination. The simplest, monomolecular process can be geminate between electron and polaron in quasi-pairs originating from a photoinitiated exciton and should be characterized by the first order. Generally, a positive charge of polaron is not required to be recombined with negative charge on a first fullerene globe. Such process becomes bimolecular and follows the second order. Polaron diffusing along polymer backbone may collide with the nearest fullerene radical anion located between polymer chains and then to recombine with a charge on a subsequent counter-anion. Assuming that polaron motion is not disturbed by the presence of fullerene molecules, we can conclude that the collision duration is governed by polaron dynamics. The order of charge recombination can be evaluated experimentally analyzing the decay of spin susceptibility after turn off the light. Fig. 4 demonstrates also the experimental decay curves obtained at

Fig. 4. The decay of the methanofullerene charge carriers photoinitiated in the PFO-DBT:PC$_{61}$BM and PCDTBT:PC$_{61}$BM bulk heterojunctions at $h\nu_{ph}/\lambda_{ph} = 2.38/520$ eV/nm and $T = 77$ K. Dashed lines show the dependences calculated from Eq. (4) well fitting experimental data with $k_r = 3.46 \times 10^{-6}$ s^{-1}, $m = 2.25$ and $k_r = 1.27 \times 10^{-2}$ s^{-1}, $m = 1.23$, respectively. In the insert are shown the same experimental data fitted by Eq. (5) with $E_0 = 0.011$ and 0.005 eV, respectively.

$T = 77$ K for mobile charge carriers with an initial concentrations n_0 after switching light off. These dependences can be described in frame of trap-limited recombination model [24]:

$$\frac{n(t)}{n_0} = \left(1 + k_r \cdot (m - 1) \cdot n_0^{m-1} \cdot t\right)^{\frac{1}{1-m}}, \tag{4}$$

where m is the recombination order. Fitting of the decay curves measured for the PCDTBT:PC$_{61}$BM system can be described by Eq. (4) with $k_r = 1.27 \times 10^{-2}$ s^{-1} and $m = 1.23$ (see Fig. 4). This means that the charge recombination is rather a monomolecular in this composite and, therefore, should follow the first order. On the other hand, the analogous fitting of the decay curve obtained for the PFO-DBT:PC$_{61}$BM yields $k_r = 3.46 \times 10^{-6}$ s^{-1} and $m = 2.25$. The value m obtained for this sample lies near $m = 2.0$ obtained for Langevin recombination in other polymer:fullerene composites [25]. Therefore, one can conclude that the geminate recombination of charge carriers in the PCDTBT:PC$_{61}$BM BHJ is rather monomolecular and therefore a first order process. This can be due to the lower number of spin traps formed under illumination of such more ordered matrix. This process in the PFO-DBT:PC$_{61}$BM sample follows a second order due to higher number of spin traps photoinitiated in its lower ordered matrix.

Analysing LEPR spectra, it becomes possible to separate the decay of mobile and pinned spin charge carriers excited in the polymer matrix. Localized polaronic charge carrier can either be retrapped by vacant trap site or recombine with opposite guest charge. Trapping and retrapping of a polaron reduces its energy that results in its localization into deeper trap and in the increase of number of localized polarons with the time. This process can be described in terms of the Tachiya's approach [26] of charges' recombination during their repeated trapping into and detrapping from trap sites with different depths in energetically disordered semiconductor. Such approach predicts the following law for decay of charge carriers photoinitiated in polymer system with spin traps characterized by different energy depth [26]:

$$\frac{n(t)}{n_0} = \frac{\pi \alpha \delta (1 + \alpha) \nu_d}{\sin(\pi \alpha)} t^{-\alpha}, \tag{5}$$

where n_0 is the initial number of polarons at the initial time ($t = 0$) of recombination process, δ is the gamma function, $\alpha = k_B T / E_0$, ν_d is the attempt jump frequency for polaron detrapping, E_0 is distribution of the trap energy Fig. 4 shows that experimental data obtained for the PFO-

DBT:PC$_{61}$BM and PCDTBT:PC$_{61}$BM composites at $T = 77$ K can be described in terms of this approach implying $E_0 = 0.011$ and 0.005 eV, respectively. It is evident that the replacement of the PFO-DBT matrix by the PCDTBT one leads to approximately twofold reduction of the energy E_0. Therefore, the decay of long-lived charge carriers originated from initial spin pairs photoinduced in the polymer:fullerene BHJ can successfully be described in terms of the above model in which the low-temperature recombination rate is strongly governed by the number and width of energy distribution of trap sites.

3.4. Spin relaxation and dynamics

As the magnetic term of MW irradiation B_1 reaches some characteristic value, the contributions of the absorption sum LEPR spectra begin to broaden and their amplitudes begin to change non-linearly with MW power due to the steady-state saturation of both spin reservoirs. This allows one to determine separately the effective spin-lattice, T_1, and spin-spin, T_2, relaxation times for all PCs stabilized and/or photoinitiated in a polymer:fullerene composite at different photon energy $h\nu_{ph}$ [11]. A part of polarons diffusing along and between the polymer chains with respective diffusion coefficients D_{1D}^P and D_{3D}^P induces an additional magnetic field in the whereabouts of another spins that, in turn, accelerates electron relaxation of whole spin ensemble. Pseudo-rotation of methanofullerene globe near own main molecular axis with coefficient D_{rot}^{mF} also induces an additional magnetic field and, therefore, affects spin relaxation of respective spin ensemble. As the relaxation times of these spins are governed mainly by their dipole-dipole interaction, the following equations can be written [27]:

$$T_1^{-1}(\omega_e) = \langle \omega^2 \rangle [2J(\omega_e) + 8J(2\omega_e)] \tag{6}$$

$$T_2^{-1}(\omega_e) = \langle \omega^2 \rangle [3J(0) + 5J(\omega_e) + 2J(2\omega_e)] \tag{7}$$

where $\langle \omega^2 \rangle = 1/10 \gamma_e^4 \hbar^2 S(S+1) n \Sigma ij$ is the constant of a dipole-dipole interaction for powder with n spin number per each monomer unit and lattice sum Σ_{ij}, $J(\omega_e) = (2D_{1D}^| \omega_e)^{-1/2}$ at $D_{1D}^| \gg \omega_e \gg D_{3D}^P$ or $J(0) = (2D_{1D}^{|D_{3D}^P})^{-1/2}$ at $D_{3D}^P \gg \omega_e$ is a spectral density function for Q1D motion of polarons and

$J(\omega_e) = \tau_c / (1 + \tau_c^2 \omega_e^2)$ is the spectral density function for fullerene rotational libration with correlation time τ_c, $D_{1D}^| = 4D_{1D}^P / L^2$, ω_e is resonant angular frequency of the electron spin precession. The spin delocalization factor L was determined for PCDTBT to be equal three [15]. This value was use also for calculation spin dynamics parameters in the PFO-DBT:PC$_{61}$BM BHJ.

Fig. 5 depicts the values of D_{1D}^P and D_{3D}^P determines for polaron dynamics as well as D_{rot}^{mF} of methanofullerene pseudo-rotation in both the samples calculated from Eq. (6) and Eq. (7) as function of the photon energy $h\nu_{ph}$. It is seen from Fig. 5 that dynamics of polarons in the PFO-DBT:PC$_{61}$BM composite weakly depends on the photon energy, whereas pseudo-rotation of methanofullerene is governed by the photon energy demonstrating extreme dependence with characteristic points lying near 1.8 and 2.8 eV. As the PFO-DBT matrix is replaced by the PCDTBT one, the above dynamics parameters start to depend stronger on the photon energy demonstrating respective dependences with extremes close to 1.8 eV. Such dissimilarity can be explained by different number and distribution of spin traps induced in these composites upon light illumination. Besides, at the some characteristic point the anisotropy of polaron dynamics D_{1D}^P / D_{3D}^P reaches a minimum that indicates the increase in dimensionality/ordering of the PCDTBT:PC$_{61}$BM composite. This makes spin dynamics easier and minimizes energy dispersion at charge transfer through BHJ of this system.

Comparative analysis of the data obtained showed that the deceleration of diffusion of polarons photoinitiated, e.g., in the PCDTBT:PC$_{61}$BM system narrows their LEPR spectrum. This can to reveal the existence of an exchange interaction between both charge carriers in the system. Such a conclusion should be valid also for methanofullerene anion radicals photoinitiated in the PFO-DBT:PC$_{61}$BM composite.

4. Conclusions

The results obtained show that spin mobile quasi-pairs, positively charged polarons and negatively charged methanofullerene anion radicals are initiated under illumination of BHJ in the PFO-DBT:PC$_{61}$BM and PCDTBT:PC$_{61}$BM composites. The main part of these carriers transfers the charge, whereas some quantity of polarons is captured by deep spin
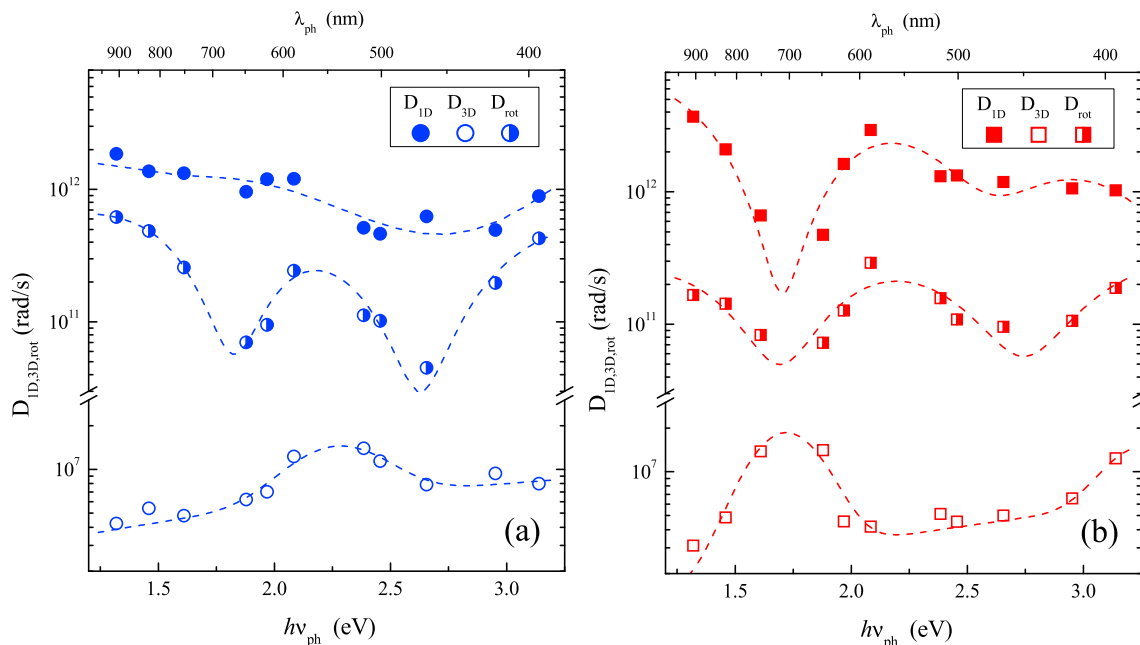

Fig. 5. Translational intrachain, D_{1D} (filled points), hopping interchain, D_{3D} (open points), and pseudo-rotational, D_{rot} (semi-filled points), diffusion coefficients determined from Eq. (6) and Eq. (7) for polarons, $P^{+\bullet}$, and methanofullerene anion radicals, $mF^{+\bullet}$, photoinduced in the PFO-DBT:PC$_{61}$BM (*a*) and PCDTBT:PC$_{61}$BM (*b*) composites by monochromatic light sources with different photon energy $h\nu_{ph}$. The error does not exceed the square points. The dashed lines are drawn arbitrarily only for illustration to guide the eye.

traps reversibly initiated in polymer backbone. The spatial distribution, number, and energy depth of such traps depend on a structure and morphology of polymer matrix as well as on the energy of initiating photons. The parameters of spin traps change significantly as the PFO-DBT matrix in the composite is replaced by the PCDTBT one. This causes a change in electronic properties of respective composite, including its efficiency of energy conversion.

Magnetic resonance, relaxation and dynamics parameters of mobile and fixed charge carriers are governed by their exchange interaction and, therefore, all the process carrying out in the copolymer composites become spin-assisted. Besides, these parameters were shown to be governed by the number and energy of initiating photons. Effective *g*-factor of polaron charge carriers stabilized in the PFO-DBT:$PC_{61}BM$ composite exceeds an appropriate parameter obtained for the PCDTBT:$PC_{61}BM$ system due mainly to the decrease in the energy of spin $\sigma \rightarrow \pi^*$ transition. This parameter is characterized by Gaussian distribution of over the photon energy and decreases at the replacement of the PFO-DBT macromolecules by the PCDTBT ones. Concentration of both charge carriers in the systems studied shows extreme dependence on the photon energy with explicit extremes around 1.8 and 2.8 eV. Such a peculiarity can appears as a result of specific morphology and band structure of the samples with spin traps inhomogeneously distributed in their bulk.

Recombination of spin charge carriers in the PCDTBT:$PC_{61}BM$ and PFO-DBT:$PC_{61}BM$ BHJ was interpreted to be respectively first and second order process due to the smaller number of spin traps photoinitiated in the former sample with a more ordered matrix. As of the PFO-DBT macromolecules are replaced by of the PCDTBT chains in a composite, the distribution of an energy of such traps narrows. Therefore, the decay of long-lived charge carriers originated from spin pairs initially photoinduced in the polymer:fullerene composites can be interpreted in terms of spin trapping-detrapping stages in BHJ.

Dynamics of polarons photoinitiated in the PFO-DBT:$PC_{61}BM$ composite weakly depends on the photon energy, whereas pseudo-rotation of methanofullerene globes in this system demonstrates extreme dependence on the photon energy with the minima near 1.8 and 2.8 eV. At the replacement of the PFO-DBT matrix by the PCDTBT one, these parameters become stronger dependent on the photon energy demonstrating extremes close to 1.8 eV. Such dissimilarity can be explained by different number and distribution of spin traps induced in these polymer matrices upon light illumination. The anisotropy of polaron mobility was shown to reach minimal value at 1.8 eV that indicates the higher dimensionality of the PCDTBT:$PC_{61}BM$ BHJ at such photon energy.

It was shown for the first time that electronic properties of low-bandgap nanocomposite change significantly even at minor variation of its matrix structure. The sensitivity of these properties to the energy of photons could be used for creation of perspective molecular electronic elements with spin-light-assisted magnetic and electronic characteristics. The methodology described can be used also for the study of electronic properties of other organic multispin polymer composites.

Acknowledgments

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