Light-induced EPR study of spin-assisted charge transport in PFOT:PC$_{61}$BM composite

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A B S T R A C T

Magnetic resonance, relaxation and dynamic parameters of polaron spins and methanfullerene radical anions, initiated by the infrared-visible-ultraviolet photons in bulk heterojunctions of the composite formed by narrow-band poly[(9,9-dioctylfluorenyl-2.7-diyl)-co-(bithiophene)] (PFOT, F8T2) copolymer and [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM) globules were investigated by the direct Light-Induced Electron Paramagnetic Resonance (LEPR) spectroscopy. It was shown that some of the polarons are captured by spin traps formed in the copolymer matrix due to its disordering. The number, spatial distribution and energy depth of such traps depend on the structure and morphology of composite. It is shown that the main parameters of both charge carriers are determined by the exchange interaction of the spin ensembles, as well as the energy of the photons. The formation of spin traps in the copolymer matrix and the exchange interaction between different spin packets cause the extreme sensitivity of the composite's magnetic resonance and electronic parameters to the number and energy of the initiating photons. The predominant photoinitiation of localized polarons in the copolymer matrix was demonstrated. This process is substantially accelerated when the composite is illuminated by photons with the energy lying near 1.8 and 2.7 eV. The recombination of both charge carriers can be described in terms of a bimolecular process of the second order. It was found that the contributions of polarons and methanofullerene radical anions to the effective paramagnetic susceptibility increase substantially near the photon energy of 2.6 and 2.1 eV due to the exchange interaction of these charge carriers. It is shown that the mobility of polarons varies monotonically throughout all the photon energy range, whereas the librational spin dynamics of the methanofullerene globules is substantially accelerated near the photon energy of 2.0 and 2.7 eV.

1. Introduction

Organic π-conjugated polymers attract great interest due to their perspective utilization as flexible functional matrix for electronic, spintronics and photovoltaic molecular devices [1,2]. Photovoltaic cells converting solar energy into electricity mainly consist of two subsystems: the polymer donor moiety able to supply an electron under external irradiation and the nearest fullerene one accepting this electron. Irradiation of a polymer:fullerene bulk heterojunction (BHJ) by photons of visible light band leads to formation of excitons or electron-hole pairs (charge-transfer states) bound by the electrostatic Coulombic force. Such spinless and electrically neutral quasiparticles tend to dissociate, and such a process is governed by their charge-transfer state. Spin-dependent conversion of the singlet exciton into a triplet one before its dissociation into the charge-transfer state was shown, e.g., in the study of BHJ formed by poly(3-hexylthiophene-2,5-diyl) alias P3HT with [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM) [3]. Exciton

dissociation is accompanied by formation of positively charged polarons in polymer matrix and free electrons on fullerene counter-anions. These charge carriers can leave BHJ relaxing into more favorable energy levels [1]. Photoinitiation and recombination of charge carriers carry out as oppositely directed processes with different rate constants. The difference between their constants determines an effective number of free charge carriers reaching the electrodes, and, consequently, the efficiency of energy conversion.

The structure and morphology of polymer:fullerene composites play an important role determining its efficiency of power conversion. Indeed, the use of narrow-bandgap BHJ formed by poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] alias PCDTBT copolymer and [6,6]-phenyl-C$_{71}$-butyric acid methyl ester alias PC$_{71}$BM instead of P3HT traditionally used earlier as best electron donor in organic solar cells [2] allowed to increase this parameter more than twice [4,5]. It was shown [6,7] that the morphology of the PCDTBT:PC$_{71}$BM BHJ is laterally oriented with "column-

like" bilayer ordered copolymer matrix with methanofullerene embedded between its chains. The higher power efficiency of the PCDTBT:PC$_{71}$BM composite was explained [8] by ultrafast charge separation before localization of an excitation to form in its BHJ a bound exciton in contrast with P3AT-based composites, in which photoinduced charge separation follows after diffusion of the polymer exciton to a fullerene interface. Higher π-overlapping in so ordered two-dimensional polymer backbone hinders its torsional twisting and, therefore, decreases the energy of its bandgap [9]. This accelerates charge hopping along and between copolymer bilayers and, thus, increases the device efficiency. Milichko et al. showed [10], that irradiation of bilayer ordered inorganic composite originates the photoinitiation of two type excitons in its bulk, namely intralayer excitons inside each layer and also interlayer excitons, whose electrons and holes are formed on neighboring layers. Photoinitiation of such excitons one may expect also in narrow-bandgap copolymer composites.

Because the PCDTBT and other analogous copolymers are characterized by ambipolarity, that is consist of the donor and acceptor groups (e.g., carbazole and benzothiadiazole, respectively, in the PCDTBT copolymer), the intralayer excitons can dissociate into pairs of spin hole and anion radical in these groups, respectively. So, the morphology of the composite should predetermine the state of exciton which additionally influences electronic properties of these systems. The lifetime of the intralayer excitations and the resultant spin pairs is shorter than that of the less mobile interlayer excitons. Besides, the spins of charge carriers formed in result of dissociation of interlayer excitons can be described as quantum entangled [11]. This allows one to obtain correlations of electronic parameters of a composite with the main parameters of resulting spin charge carriers which can be used in spintronics and quantum computing.

Charge recombination process is governed by different factors. First of them is the order and mechanism of this process which depend on the structure and morphology of a polymer:fullerene composite [12]. The simplest, monomolecular can be geminate between polaron and free electron in initial quasi-pairs and follows the first order. When the bounded charge carriers overcome the Coulombic force, they tend to be separated on considerable distance and become non-interacting. This is why they can recombine with opposite charged carriers of other polaron-electron quasi-pairs in frames of non-geminate process of second order.

So, understanding the details of charge separation, transport and recombination in such materials at a molecular level is crucial for improving the electronic properties and efficiency of appropriated elements of molecular electronics. However, the correlation between the quantum efficiency, dynamics of charge carriers and energy of photons within the BHJ absorption spectrum yet to be established.

Electron spins in organic semiconductors provide a remarkable way to handle the main parameters of organic devices directly changing the spin state. Because the main charge carriers possess a spin, their formation, dynamics and recombination were expected and proved to be spin-assisted [1]. It is evident that the efficiency of energy conversion by a polymer:fullerene composite is governed mainly by the number and dynamics of separated spin charge carriers whose number should exceed the number of recombined charge carriers. As a rule, various indirect methods may only register an effective concentration of paramagnetic centers formed in result of forward fast initiation and reversed slow recombination of opposite charge carriers upon continuous irradiation of polymer:fullerene BHJ. The only direct Light-Induced Electron Paramagnetic Resonance (LEPR) spectroscopy becomes as one of the most powerful method for the study of all spin-assisted processes carrying out in polymer:fullerene systems [1,13]. It may to detect directly the state of the initial exciton, its possible conversion and dissociation into spin charge carriers [3] following by all the stages of their formation, motion and recombination. The number of light photons induced quasi-pairs of charge carriers can be determined by the "light on-light off" method using comparison of EPR spectra before and after

light illumination. Both the spin charge carriers possess close weakly anisotropic g-factors, so they demonstrate at frequently used X-band (3-cm, 9.7 GHz) EPR partly overlapping doublet of their contributions. At this waveband EPR were studied in details spin-dependent initiation, relaxation, dynamics and recombination of spin charge carriers in various polymer:fullerene composites [14] including those based on the narrow-bandgap PCDTBT and poly[2,7-(9,9-dioctylfluorene)-alt-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PFO-DBT) copolymers [15,16]. It was shown that upon illumination of copolymer:fullerene composites some part of charge carriers are fixed in trap sites formed in copolymer backbone due to its disordering. The number, distribution and depth of spin traps are governed by a structure and morphology of bulk heterojunction. Exchange- and trap-assisted recombination of charge carriers are governed by spin dynamics, and also by structure and morphology of spin microenvironment. Such process in the analogous PFO-DBT:PC$_{61}$BM and PCDTBT:PC$_{61}$BM composites was shown to follow second and first order, respectively.

We report here the results of detailed LEPR study of initiation, relaxation and dynamics of charge carriers photoinitiated in the nanocomposite formed by narrow-bandgap poly[[(9,9-dioctylfluorenyl-2.7-diyl)-co-(bithiophene)] (PFOT, F8T2) copolymer and PC$_{61}$BM at wide range of photon energy. The use of direct method allowed us to reveal the spin-assistance of magnetic, relaxation and dynamics parameters of spin charge carriers photoinitiated in this system, to identify the mechanism of their recombination in its BHJ and also to reveal a selectivity of these parameters to the photon energy.

2. Experimental details

In the work, poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(bithiophene)] (PFOT, F8T2), distributed by American Dye Source, Inc., USA, with energies of the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) of $E_{HOMO} = 5.50$ eV and $E_{LUMO} = 3.10$ eV, respectively, and an optical bandgap of $2\Delta = 2.40$ eV [17] was used as the electron donor phase. [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM) methanofullerene distributed by Solenne BV, The Netherlands, with $E_{HOMO} = 6.18$ eV, $E_{LUMO} = 3.70$ eV [18] was used as the electron acceptor phase. Chemical structures of these ingredients are schematically shown in Fig. 1.

The PFOT:PC$_{61}$BM sample was prepared as following. First 1.8 mg of PFOT was solved in 1.1 ml of dichlorobenzene, treated inside the ultrasonic cleaner DADI DA-968 (50 W) for 10 min, heated for 30 min at $T = 333$ K and then once more ultrasound treated for 10 min until to reach a clear yellow solution. Then 3.7 mg of PC$_{61}$BM was added into 0.5 ml of the so-treated solution followed by heating for 2.5 h at $T = 333$ K and then held at room temperature for 20 h. Concentrations of the PFOT and PC$_{61}$BM were determined to be 3×10^{-3} M and 2×10^{-3} M, respectively. Finally, 55 μl of the resulting solution was casted by 5 μl drops into both sites of thin ceramic plate and dried in air consistently until the sample was formed as double-sided films of near 4×8 mm^2 in size and near 0.1 mm in thickness. In order to avoid a contact of the sample with the water and air, all manipulations were performed in dry inert atmosphere.

The sample was permanently irradiated inside the microwave (MW) cavity via short quartz light guide by Luxeon® 5 W achromatic, white, LED lighr sources with correlated color temperature T_c of 15,000 K, 5500 K and 3300 K as well as by nearly monochromatic 5 W LED light sources with the photon energy $h\nu_{ph}$/wavelength λ_{ph}/luminous emittance I_l of 1.32 eV/940 nm/750 lx, 1.46 eV/850 nm/870 lx, 1.61 eV/770 nm/1160 lx, 1.88 eV/660 nm/1950 lx, 1.97 eV/630 nm/1110 lx, 2.10 eV/590 nm/450 lx, 2.34 eV/530 nm/960 lx, 2.48 eV/500 nm/1500 lx, 2.64 eV/470 nm/2450 lx, 2.95 eV/420 nm/1520 lx, and 3.14 eV/395 nm/630 lx. The I_l value of these sources estimated using a broadband IMO-2 N output power light irradiation bolometer in combination with a digital luxmeter LX-1010BS was used for the further normalization of spin concentration photoinitiated in the sample.
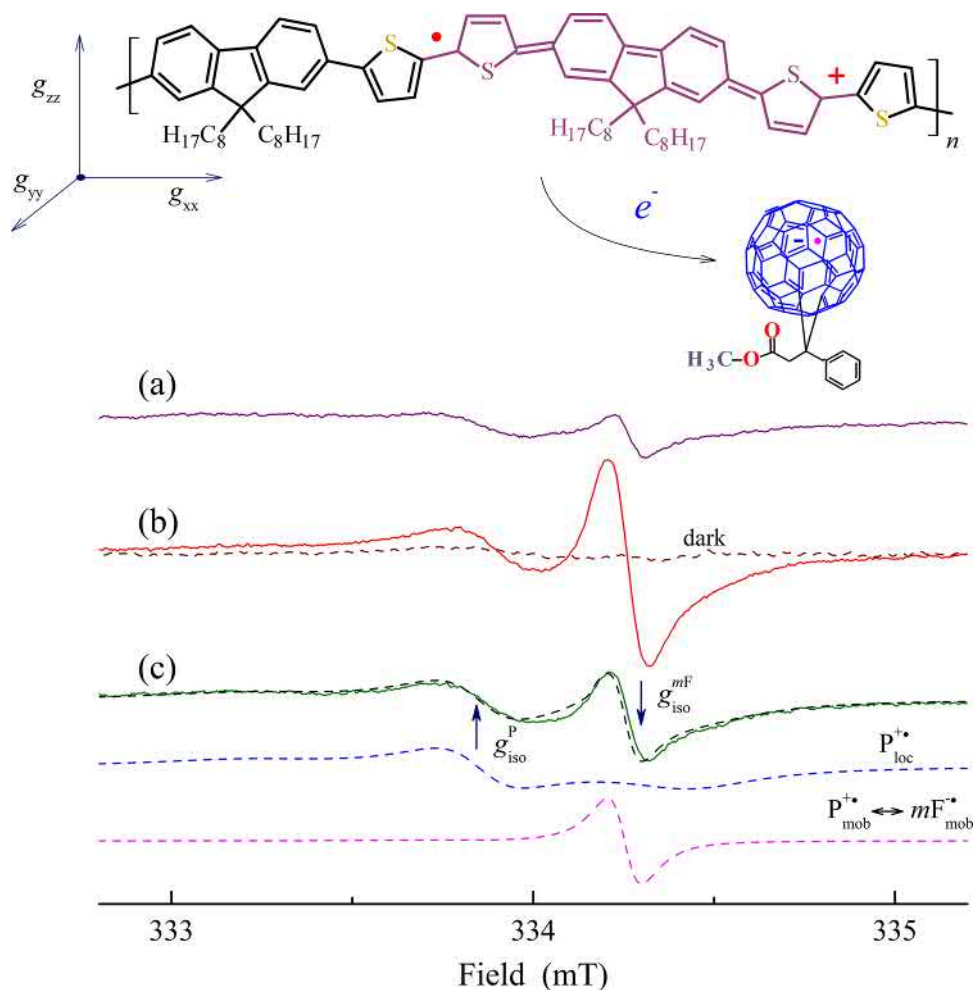
Fig. 1. The LEPR spectra of charge carriers steady-state photoinduced by photons with energies of $h\nu_{ph} = 1.46$ (*a*), 1.88 (*b*) and 2.38 eV (*c*) at 77 K in bulk heterojunctions formed by PFOT macromolecules with $PC_{61}BM$ spheres normalized to the luminosity value I_l of light sources. The exemplary EPR signal registered before the illumination of the sample is shown by dashed line in (*b*). The top to bottom dashed lines in (*c*) show the total spectrum and their contributions due to localized polarons $P_{loc}^{+\bullet}$ and mobilized radical pairs $P_{mob}^{+\bullet} \leftrightarrow mF_{mob}^{-\bullet}$ numerically calculated using $\Delta B_{pp}^{P} = 0.291\,m\,T$, $\Delta B_{pp}^{mF} = 0.094\,m\,T$ and concentration ratio $[mF_{mob}^{-\bullet}]:[P_{loc}^{+\bullet}] = 1.0:9.9$. The transfer of an elementary charge from a copolymer chain to a methanofullerene molecule accompanied by the formation of a polaron with a positive charge and spin $S = ½$ is shown schematically.

EPR measurements were made using an X-band (3-cm, 9.7 GHz) PS-100X spectrometer with maximal MW power of 150 mW (with the value of magnetic term $B_1 = 51$ µT) in a center of the cavity) and 100 kHz field *ac* modulation for phase-lock detection. All LEPR spectra of the composite were registered at 77 K in quartz Dewar containing liquid nitrogen far from MW saturation conditions, when the values B_1 and amplitude of *ac* modulation B_m in the cavity center did not exceed 5 µT and 0.1 m T, respectively. The signal-to-noise ratio of the LEPR spectra was increased by averaging several acquisitions. The measurement of sum paramagnetic susceptibility with and without illumination of the sample BHJ was realized using 2,2,6,6-tetramethylpiperidine-1-oxyl stable nitroxide radical. Processing and simulations of the EPR spectra were made using the EPRWin, EasySpin and OriginLab software. Concentration of both the localized and mobile charge carriers was determined precisely by using the "light on-light off" method, deconvolution of effective LEPR spectra [14,19,20] and subsequent double integration of their respective contributions. Diphenylpicrylhydrazyl (DPPH) single microcrystal standard with $g = 2.0036$ was used for the estimation of *g*-factors of all spin charge carriers. The accuracies of determination of the line intensity I, *g*-factor and peak-to-peak linewidth ΔB_{pp} were estimated to be 5%, $\pm 2 \times 10^{-4}$ and ± 2 µT, respectively. Both spin-lattice T_1 and spin-spin T_2 relaxation times were determined using the steady-state MW saturation method [21].

3. Results and discussions

3.1. LEPR spectra composition and magnetic resonance parameters

Fig. 1 shows exemplary LEPR spectra of the PFOT:$PC_{61}BM$ composite obtained under its irradiation by photons with different energy $h\nu_{ph}$ at $T = 77$ K. As in the case of other polymer:fullerene composites [14], the spectra were attributed to polarons diffusing along and between copolymer chains and $PC_{61}BM$ methanofullerene radical anions moving between them (see Fig. 1), both formed as product of excitons dissociation. In order to determine the contributions and magnetic resonance parameters of these charge carriers, experimental LEPR spectra of the illuminated and darkness sample were deconvoluted by using computer simulation, as in the case of other polymer:fullerene composites [14,19,20]. This allowed obtaining separately the main magnetic resonant parameters of spin packets photoinitiated in the composite by the light photons with different energies $h\nu_{ph}$. Fig. 1 depicts also the theoretically calculated sum LEPR spectrum and its contributions due to the polarons $P_{loc}^{+\bullet}$ captured by spin traps and mobile quasi-pairs $P_{mob}^{+\bullet} \leftrightarrow mF_{mob}^{-\bullet}$. The best fit of experimental LEPR spectra evidences the absence in them of contribution of pinned methanofullerene radicals which are usually registered in some other polymer:fullerene composites [14]. This implies the lower number of energetically deep

traps able to capture radical anions and the faster dynamics of the latters due to more ordered copolymer composite under study.

An isotropic splitting Landé *g*-factor was determined for methanofullerene radical anions to be $g_{iso}^{mF} = 1.999_{89}$ and was appeared to depend weakly on the photon energy $h\nu_{ph}$. This value lies near $g_{iso}^{mF} = 1.9994_8$ [19] and 1.999_{87} [20] obtained for such radical at millimeter waveband EPR. The same parameter of polarons reflects a stronger dependence on their microenvironment in polymer matrix. The orientation of the main axes of their **g**-tensor is shown in Fig. 1. The g_{xx} value lies in the plane of the polymer π-system and is directed perpendicular to the principal copolymer axis. It is governed by the energy $\Delta E_{n\pi^*}$ required for the $n \rightarrow \pi^*$ spin excitation, spin interaction with a heteroatom with the constant λ and its density on a heteroatom $\rho(0)$, $g_{xx} \propto \lambda\rho(0)/\Delta E_{n\pi^*}$, which causes its higher sensitivity to the interatomic distances and also spin-orbit interaction with heteroatoms involving in the polymer backbone [22]. The term g_{yy} depends on the spin $\sigma \rightarrow \pi^*$ transition, it is proportional to the fraction $\lambda\rho(0)/\Delta E_{\sigma\pi^*}$ and, therefore, has lower sensitivity to the properties of polaron microenvironment. Among all terms of **g**-tensor, g_{zz} is least affected by the properties of copolymer backbone. A part of the immobilized polarons can be realized with copolymer illumination, which increases the number of mobile spins and their interaction with other spin ensembles. This leads to a change in the spin density and a corresponding energy splitting. The best fitting yields for polarons excited in the PFOT:PC$_{61}$BM composite $g_{xx} = 2.006_{04}$, $g_{yy} = 2.002_{17}$, $g_{zz} = 1.998_{66}$, and $g_{iso}^P = 2.002_{29}$. The latter value lies near $g_{iso}^P = 2.002_{47} - 2.003_{30}$ determined for polarons formed in some other photovoltaic systems [14,20] including narrow-bandgap copolymer composites [15,16]. The same parameter determined for polarons photoinitiated in the sample under study by white light sources with different color temperatures are summarized in Table 1.

Fig. 2 exhibits the g_{iso}^P value of polarons formed in the PFOT:PC$_{61}$BM BHJ upon their illumination by photons with different energy $h\nu_{ph}$. It is seen from the Figure that this parameter demonstrates extreme dependence on the photon frequency. They may be characterized, e.g., by the Gaussian distribution,

$$g_{iso} = g_0 + \sqrt{\frac{2k_1}{\pi\sigma^2}} \exp\left(-\frac{2(E - E_c)^2}{\sigma^2}\right), \tag{1}$$

where g_0 and k_1 are constants, E_c is the characteristic energy, and σ is

Table 1

The isotropic *g*-factor of polarons g_{iso}^P, the peak-to-peak width of the polarons ΔB_{pp}^P and methanofullerene radical anions ΔB_{pp}^{mF}, the ratio of the concentration of mobile methanofullerene radical anions to the concentration of localized polarons $[mF^{\bullet-}]/[P_{loc}^{\bullet+}]$, the spin-lattice and spin-spin relaxation times of polarons, T_1^P and T_2^P, respectively, the polaron diffusion coefficients along, D_{1D}^P, and between, D_{3D}^P, copolymer chains, as well as librational diffusion of methanofullerene molecules near their main molecular axis D_{lb}^{mF}, determined under illumination of the PFOT:PC$_{61}$BM BHJ with achromatic, white light with the different correlated color temperature T_c at $T = 77$ K.

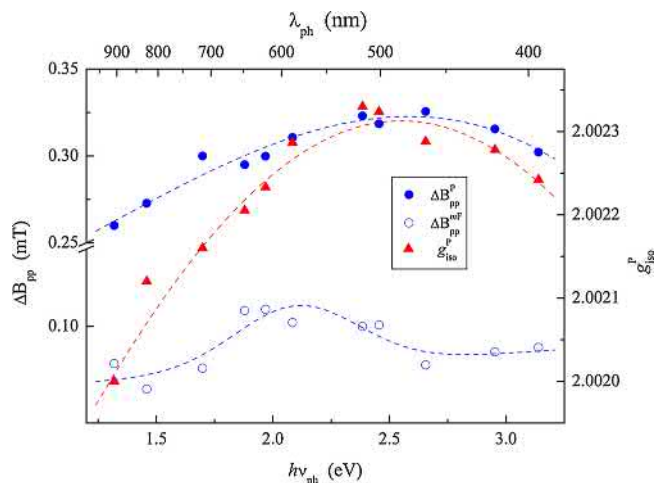| T_c, K Parameter	15000	5500	3300
g_{iso}^P	2.002_{22}	2.002_{27}	2.002_{34}
ΔB_{pp}^P, mT	0.289	0.297	0.317
ΔB_{pp}^{mF}, mT	0.103	0.107	0.105
n_{mob}^{mF}/n_{loc}	0.113	0.097	0.077
T_1^P, s	1.37×10^{-6}	8.46×10^{-7}	1.23×10^{-6}
T_2^P, s	2.27×10^{-8}	2.21×10^{-8}	2.07×10^{-8}
T_1^{mF}, s	1.04×10^{-6}	6.33×10^{-7}	1.03×10^{-6}
T_2^{mF}, s	6.35×10^{-8}	6.13×10^{-8}	6.26×10^{-8}
D_{1D}^P, rad/s	6.20×10^{11}	2.93×10^{11}	4.99×10^{11}
D_{3D}^P, rad/s	2.68×10^6	6.75×10^6	2.77×10^6
D_{lb}^{mF}, rad/s	7.24×10^{10}	1.03×10^{11}	1.23×10^{11}

Fig. 2. Distance between the positive and negative peaks of the LEPR spectra of polarons and methanofullerene radical anions (filled and unfilled circles, respectively), as well as the *g*-factor of polarons (filled triangles), photoinitiated in the PFOT:PC$_{61}$BM BHJ at $T = 77$ K as a function of photon energy $h\nu_{ph}$. The upper and lower dashed lines are drawn arbitrarily solely for illustrative purposes. The mean dashed line shows the dependence calculated from Eq. (1) with $E_c = 2.54$ eV and $\sigma = 1.72$ eV.

deviation of the energy. Fig. 2 shows that the data obtained for the sample experimentally under study follow well Eq. (1) with $E_c = 2.54$ eV, $\sigma = 1.72$ eV. These values exceed those obtained for the structural close PFO-DBT:PC$_{61}$BM and PCDTBT:PC$_{61}$BM nanocomposites [15,16] possible due to their more ordered morphology. One can conclude that the structural disordering of the composite causes the formation in its BHJ of spin traps with different numbers, energy depth, and spatial distribution. This affects the interaction of mobile and trapped spin carriers, depending on the energy of the initiating photons. In this case the light photons can be considered as quantum probe of position, distribution, and deviation of such traps in the sample under study.

3.2. LEPR linewidth

Peak-to-peak linewidths of polarons ΔB_{pp}^P and methanofullerene radical anions ΔB_{pp}^{mF} photoinitiated in the PFOT:PC$_{61}$BM composite at $T = 77$ K depend on the photon energy $h\nu_{ph}$ as it is shown in Fig. 2. Linewidths determined for the sample irradiated by white light sources with different color temperatures are also presented in Table 1.

Generally, the LEPR spectral components of spins can be broadened in result of the frequency dependent *g*-strain resulting from the inhomogeneous distribution of *g*-factor in disordered system and frequency independent field-strain due to unresolved hyperfine couplings [23]. The latter process was shown [24] to predominate in structurally close copolymers, which should be taken into account when analyzing the total broadening of the spectra. Additional spectral broadening may occur due to the exchange interaction of different spin packets [25].

It was shown [14] that the main processes passing in fullerenemodified polymer systems are spin-assisted and can be described in terms of exchange interaction of polarons hopping along polymer chains with spins captured by high-energetic traps. The probability of collision of such centers with spin $S = \frac{1}{2}$ is governed by the size and hopping rate of mobile carriers [25,26],

$$p_{ss} = \frac{1}{2} \cdot \frac{\alpha^2}{1 + \alpha^2}, \tag{2}$$

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 quasiparticle, $\hbar = h/2\pi$ is the Plank constant, and ω_{hop} is the

frequency of intrachain spin hopping. If the ratio $J_{ex}/\hbar$ exceeds the frequency of spin collision, the condition of strong interaction is realized in the system. In opposite case, when $J_{ex}/\hbar < \omega_{hop}$, this interaction becomes weak. This should lead to the extreme dependence of the above p value between these limits in organic solids and, therefore, originate the extremeness of spin-assisted processes in various multi-spin polymer semiconductors [14,27,28].

Fig. 2 confirms the influence of the photon energy on exchange interaction of spin charge carriers photoinitiated in the sample under study. This effect can also be interpreted in frames of the above approach of exchange interaction of mobile polarons with charge carriers captured in polymer backbone. In this case the collision of interacting spins should broaden their absorption EPR line by the value [25,26]

$$\delta(\Delta\omega) = p_{ss}\,\omega_{hop}n_i, \qquad (3)$$

where n_i is the number of guest spins per polymer unit. At weak (strong) spin exchange limit the acceleration of polaron mobility should result in decrease (increase) of the exchange frequency and, therefore, the signal linewidth. Such effect seems to be realized also in result of exchange interaction of polarons and methanofullerene radical anions formed in the PFOT:PC_{61}BM BHJ whose linewidths reach maxima at $h\nu_{ph} \approx 2.6$ and 2.1 eV, respectively. This indicates stronger exchange interaction of polarons, in comparison with fullerene anion radical.

3.3. Spin susceptibility

Once an exciton is formed in the polymer:fullerene composite, it can either dissociate with monomolecular rate constant k_d, or recombine with back electron transfer rate constant k_r. In this case paramagnetic resonance can be registered only when k_d exceeds k_r. The latter constant depends on the number and energetic depth of spin traps formed in disordered polymer matrix. This means that only a part of spin charge carriers reaches electrodes. This is equal to the ratio of a number of mobile charge carriers to that captured by spin traps. Because some immobilized polarons can be realized by the light photons and both the charge carriers possess a spin, dynamics processes also become spin-assisted and sensitive to the photon energy [14]. In this case an effective charge transfer through copolymer BHJ can be interpreted in framework of exchange interaction of the polarons hopping along the solitary polymer chains with spins captured in spin traps with the above probability p.

Fig. 3 depicts the change in concentrations of charge carriers in the PFOT:PC_{61}BM composite relative to sum spins with the photon energy $h\nu_{ph}$. One can to note that the concentration of localized polarons exceeds that of mobile fullerene radical anions. Besides, this parameter of both charge carriers obviously depends also on the photon energy. It is shown in Fig. 3 that the localized polarons $P_{loc}^{+\bullet}$ are characterized by concentration dependence with the extremes lying near 1.8 and 2.7 eV. Similar dependences were obtained for charge carriers photoinitiated in the structural close but more ambipolar PFO-DBT:PC_{61}BM and PCDTBT:PC_{61}BM composites, however, with the right extreme slightly shifted to the higher energy [15,16]. It should be noted that the PFOT:PC_{61}BM composite is typically characterized by optical absorption spectrum with a relatively wide ($h\nu_{ph} = 2.48$–2.75 eV) band attributed to copolymer matrix and some UV-peaks situated at $h\nu_{ph} \geq 3.76$ eV originated due to the PC_{61}BM [29]. The specific morphology of the sample under study causes the priority initiation in its matrix of localized polarons, whom number is appeared to be more sensitive to the energy of photons. On the other hand, the methanofullerene radical anions $mF_{mob}^{-\bullet}$ show the respective weaker extreme dependence with characteristic energy near 1.9 eV. The same dependence demonstrates concentration ratio of charge carriers n_{mob}^{mF}/n_{loc}^{P} (Fig. 3) (equal to the n_{mob}^{P}/n_{loc}^{P} one) that should reflect the efficiency of radiation energy conversion. Analogous extreme dependence was also observed in the study of PFO-DBT:PC_{61}BM and PCDTBT:PC_{61}BM BHJ [15,16]. Such effect can be explained, e.g., by the interaction of captured charge
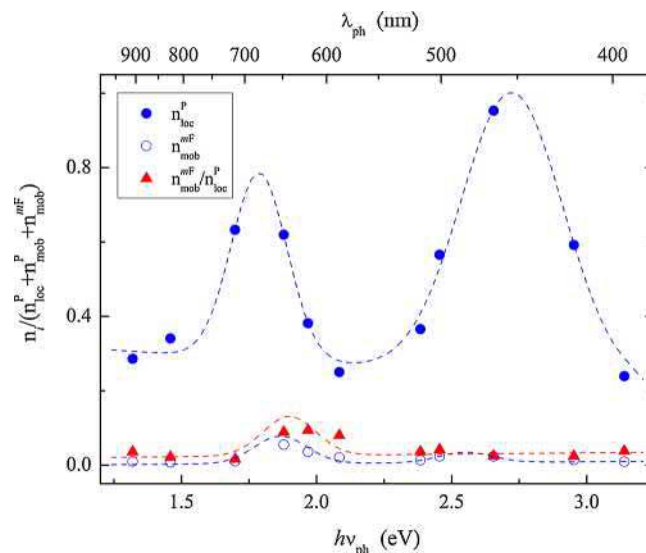

Fig. 3. Relative concentrations, $n_{loc}^{P}/(n_{loc}^{P} + n_{mob}^{P} + n_{mob}^{mF})$, $n_{mob}^{mF}/(n_{loc}^{P} + n_{mob}^{P} + n_{mob}^{mF})$, and the ratio n_{mob}^{mF}/n_{loc}^{P} of polarons and methanofullerene radical anions, photoinitiated in the PFOT:PC_{61}BM BHJ at $T = 77$ K, depending on the photon energy $h\nu_{ph}$. The values obtained are normalized to the luminosity of the light sources I_l. Dotted lines are drawn arbitrarily only for illustration to guide the eye.

carriers with the light photons releasing immobilized polarons from spin traps and, therefore, accelerating their recombination with oppositely charged charge carriers. This controls the exchange interaction of mobile and trapped charge carriers, so their magnetic resonance, relaxation and dynamics parameters become spin-assisted. The n_{mob}^{mF}/n_{loc}^{P} values obtained for the sample irradiation by different white light sources are also summarized in Table 1.

3.4. Spin recombination

Once the illumination of the sample is turned off, the spin charge carriers tend to recombine that leads to the decrease in their concentration. The fitting of sum LEPR spectra allows one to separate the decay of both spin charge carriers photoinitiated in polymer system. Fig. 4 depicts the decay of both charge carriers photoinitiated by white
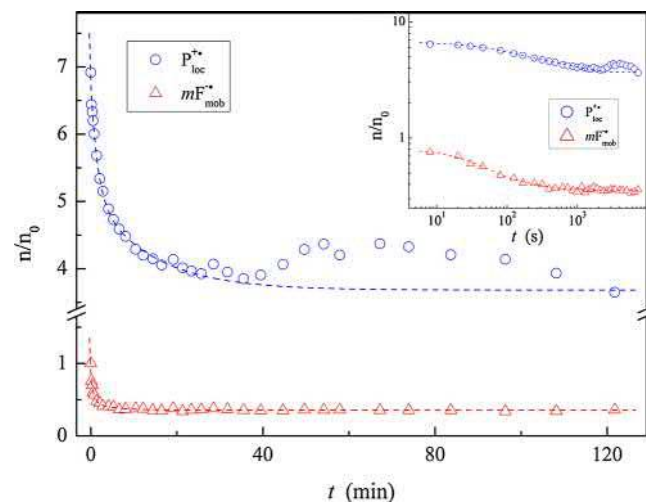

Fig. 4. Temporal decay of the concentrations of polarons and methanofullerene radical anions, photoinitiated in the PFOT:PC_{61}BM BHJ by a source of white light with correlating color temperature $T_c = 5500$ K at $T = 77$ K. The upper and lower dashed lines show the dependences calculated from Eq. (5) with $E_0 = 0.0486$ and 0.0139 eV, respectively.

light with color temperature $T_c = 5500\,K$ in the darkened PFOT:PC$_{61}$BM BHJ. The mechanism and order of such process should be governed by the structure and morphology of the sample. The simplest, is characterized by the geminate first order decay of electrons and polarons formed from photoinitiated excitons. If a positive charge of polaron does not recombine with an opposite charge of a first fullerene molecule, the charge decay process becomes bimolecular with the second order. In this case polaron diffusing along copolymer chains may collide with remote methoanofullerene anion radical located between copolymer layers. Assuming that polaron diffusion is not disturbed by the anion molecules, one can conclude that the collision duration is governed by polaron dynamics. The order of charge recombination process m can be evaluated analyzing the decay of spin concentration $n(t)$ after light switching off in frames of trap-limited recombination model [12]:

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

where n_0 is the initial number of spin charge carriers at the start of their recombination, when $t = 0$. The recombination orders were determined, e.g., for the PFO-DBT:PC$_{61}$BM and PCDTBT:PC$_{61}$BM BHJ to be 2.25 and 1.23 [15,16] indicating non-geminate and geminate decay in these systems, respectively. The k_r and m parameters were determined from Eq. (4) for both the P$_{loc}^{+\bullet}$ and mF$_{mob}^{-\bullet}$ charge carriers in the PFOT:PC$_{61}$BM composite under study to be 0.28 s^{-1}, 2.34 and 0.0014 s^{-1}, 2.23, respectively. This may indicate close morphology and ordering of the PFOT:PC$_{61}$BM and PFO-DBT:PC$_{61}$BM composites leading to non-geminate recombination process in their BHJ.

Spin traps formed in copolymer matrix due its disordering also play key role in recombination of spin charge carriers. Indeed, captured polaron can either be retrapped by vacant trap site or recombine with nearest opposite charge. Multistep trapping and retrapping of a polaron reduces its energy that results in its more probable localization into deep spin trap and, therefore, in the increase of concentration of such polarons with the time. The charge carriers can recombine during their repeated trapping into and detrapping from respective sites with energetically different depths distributed in disordered semiconductor. According to such approach, the decay of charge carriers photoinitiated in polymer system with energetically different spin traps has to follow the law [30]:

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

where $\kappa = k_B T / E_0$, E_0 is distribution of the trap energy, δ is the gamma function, and ν_d is the attempt jump frequency for polaron detrapping.

Fig. 4 shows that experimental data obtained at $T = 77\,K$ for localized polarons and mobile methanofullerene radical anions photoinitiated by white light in the PFOT:PC$_{61}$BM composite can be described in terms of the above approach implying $E_0 = 0.048_6$ and 0.013_9 eV, respectively, for the former at least at $t \le t_c \approx 40$ min. It is seen from the Figure that the decay of polarons deviated from the concept at $t \ge t_c$. Such discrepancy can be explained, e.g., by the capture of a part of mobile polarons by spin traps at $t \approx t_c$ that increases the effective number of localized polarons at the $40 \le t \le 120$ min time interval. Therefore, the decay of long-living charge carriers formed from dissociation of an initial excitons photoinduced in the PFOT:PC$_{61}$BM BHJ and subsequent spin pairs can successfully be described in terms of the above mentioned model in which the low-temperature recombination rate is strongly governed by the number and energy depth of trap sites differently distributed in copolymer backbone.

3.5. Spin relaxation and dynamics

When the magnetic term B_1 of MW irradiation reaches in the EPR resonator a certain critical value, EPR lines of all spin reservoirs begin
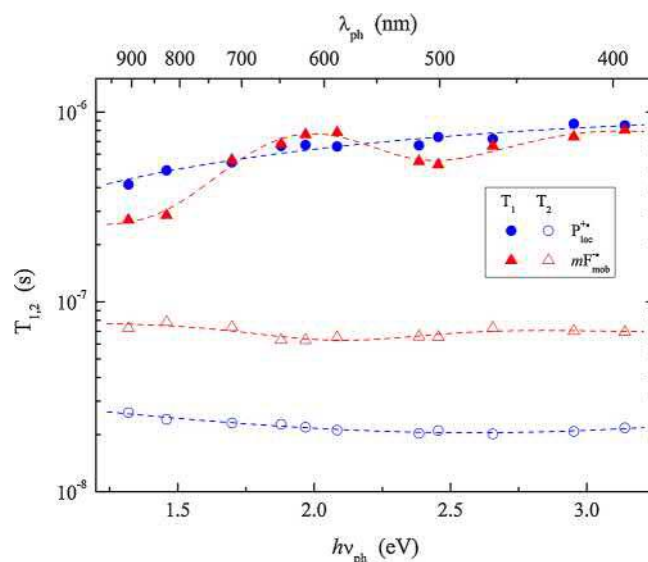
Fig. 5. Spin-lattice, T_1 (filled points), and spin-spin, T_2 (unfilled points), relaxation times of polarons P$^{+\bullet}$ and methanofullerene radical anions mF$^{+\bullet}$, photoinduced in the PFOT:PC$_{61}$BM composite by sources of monochromatic light with different photon energies $h\nu_{ph}$. Errors do not exceed the size of points. Dashed lines are drawn arbitrarily solely for illustrative purposes.

to broaden and to change non-linearly with B_1 due to their steady-state MW saturation. This allows one to determine separately the effective spin-lattice, T_1, and spin-spin, T_2, relaxation times for polarons and methanofullerene radical anions photoinitiated in the copolymer:fullerene BHJ [14]. These parameters determined for both charge carriers are presented in Fig. 5 as function of the photon energy $h\nu_{ph}$. Respective parameters obtained for the sample under study irradiation by white light sources with different color temperature T_c are summarized in Table 1.

Polarons captured by spin traps in a polymer network and diffusing along and between the polymer chains with respective diffusion coefficients D_{1D}^P and D_{3D}^P induce an additional magnetic field at the location of other spins that accelerates electron relaxation of all spin ensembles. Libration motion of methanofullerene molecules with coefficient D_{lb}^{mF} also induces an additional magnetic field and, therefore, additionally affects respective spin relaxation. Electron relaxation in organic solids is governed mainly by dipole-dipole interaction of the nearest spins. This allows writing the following equations connecting spin relaxation and dynamic parameters [31]:

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

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

where $\langle \omega^2 \rangle = 1/10 \, \gamma_e^4 \hbar^2 \, S(S+1)n\Sigma ij$ is the constant of spin dipole-dipole interaction in powder with the sum concentration $n = n_1 + n_2/\sqrt{2}$ of the localized (n_1) and mobile (n_2) spins per each copolymer unit and lattice sum Σij, $J(\omega_e) = (2D_{1D}\,\omega_e)^{-1/2}$ at $D_{1D} > > \omega_e > > D_{3D}^P$ or $J(0) = (2D_{1D}^\parallel D_{3D}^P)^{-1/2}$ at $D_{3D}^P > > \omega_e$ is a spectral density function for Q1D motion, $D_{1D}^\parallel = 4 \, D_{1D}^P / L^2$, ω_e is resonant angular frequency of the electron spin precession, and L is spin delocalization factor. The latter parameter means a number of polymer units along which the polaron spin is delocalized. $L = 3$ determined for PCDTBT [20] was use also for calculation of spin dynamics parameters in the PFOT:PC$_{61}$BM BHJ. Spin librations with correlation time τ_c is characterized by the following spectral density function $J(\omega_e) = 2\tau_c/(1 + \tau_c^2 \omega_e^2)$.

Fig. 6 depicts how change the values of D_{1D}^P and D_{3D}^P determined for polaron intrachain and interchain hopping as well as the value of D_{lb}^{mF} determined for methanofullerene libration motion in the PFOT:PC$_{61}$BM composite calculated from Eqs. (6) and (7) with the photon energy $h\nu_{ph}$. The respective parameters of charge carriers photoinitiated in the
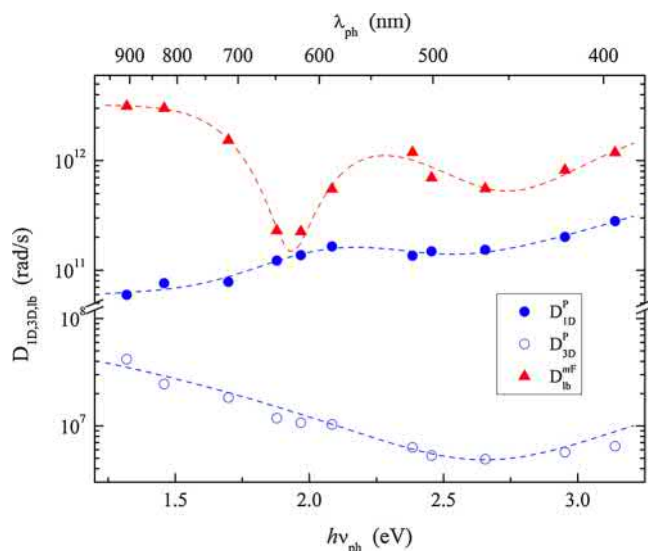
Fig. 6. Coefficients of translational diffusion of polarons $P^{+\cdot}$ along polymer chains, D_{1D} (filled circles), and between polymer chains, D_{3D} (unfilled circles), and librational diffusion of methanofullerene radical anions, D_{lb}, (filled triangles), photoinduced in the PFOT:PC_{61}BM composite by monochromatic light sources with different photon energy $h\nu_{ph}$. Errors do not exceed the size of points. Dashed lines are drawn arbitrarily solely for illustrative purposes.

composite under illumination by sources of white light with different correlated color temperature T_c are also summarized in Table 1. It can be seen from Fig. 6 that the values D_{1D}^P and D_{3D}^P weakly change with the photon energy. The anisotropy of spin dynamics D_{1D}^P/D_{3D}^P increases by 1.5 orders of magnitude with increasing photon energy in the range 1.32–3.14 eV. It should be noted that this value changes slightly in PFO-DBT:PC_{61}BM and increases by near an order of magnitude in PCDTBT:PC_{61}BM composites under such variation of $h\nu_{ph}$ [15,16]. On the other hands, methanofullerene globular molecules demonstrate extreme dependence of librational dynamics on the photon energy with characteristic points lying near 2.0 and 2.7 eV. These extremes are situated near to those obtained for PFO-DBT:PC_{61}BM composite [15,16]. Such effect can also be realized due to a change in the exchange interaction of different spin packets under irradiation of the PFOT:PC_{61}BM BHJ by initiating photons with certain energy.

Analysis of the data presented in Figs. 5 and 6 shows that the exchange interaction between spin charge carriers weakly affect their relaxation and dynamics parameters.

4. Conclusions

The results obtained clearly show that mobile positively charged polarons and negatively charged methanofullerene radical anions are expectable photoinitiated on neighboring layers of the PFOT:PC_{61}BM composite at near IR, visible and UV light bands. Some carriers transfers the charge, whereas a main part of polarons is captured by high-energetic spin traps with characteristic distribution, position and deviation formed in disordered copolymer backbone. This changes electronic properties of the composite, influencing its efficiency of energy conversion. The spatial distribution, depth and number of the traps are governed by the structure and morphology of the composite. Illumination of the composite realizes a part of immobilized polarons from such traps that changes exchange interaction of mobile and captured charge carriers and, therefore, causes spin-assisting of their magnetic resonance, relaxation and dynamics parameters. The formation of spin traps changes energetic level of spin excitation and originates bell-like dependence of the carriers' effective *g*-factor on the photon energy. The concentration of polarons captured in copolymer matrix shows extreme dependence on the photon energy with explicit

extremes around 1.8 and 2.7 eV, whereas such dependence of the methanofullerene radical anions demonstrates a weaker extreme dependence with characteristic energy lying near 1.9 eV. Non-geminate recombination process of spin charge carriers was interpreted in terms of multistep polaron trapping-detrapping in the copolymer matrix. Anisotropy of polaron dynamics increases monotonically with the growth of the photon energy. On the other hands, libration of methanofullerene molecules in this system demonstrates extreme dependence on the photon energy with the minima lying near 2.0 and 2.7 eV.

The sensitivity of the main parameters of charge carriers to the photon energy can be used for creation of elements of molecular electronics and spintronics with spin-light-assisted main characteristics. Both the polarons and methanofullerene radical anions act as intrachain and interlayer nanoscopic spin probes, respectively, which allows analyzing the structure and dynamics of their environment. The methodology described can be used also for the study of electronic properties of other organic multispin polymer systems.

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