

# Effect of spin localization on charge transport in low-bandgap bilayered ordered nanocomposites



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## ABSTRACT

Direct Light-Induced Electron Paramagnetic Resonance was used for comparative study of magnetic, relaxation and dynamic parameters of spin charge carriers, polarons and methanofullerene anion radicals, photoinduced in bulk heterojunctions of composites formed by low-bandgap copolymers, 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<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM). A fraction of polarons is captured by deep spin traps reversibly initiated in the copolymer backbone due to its disordering. The number and energy depth of the traps are governed by the structure of copolymer matrix and photon energy. Both composites exhibit photo-response within photon energy/wavelength 1.32–3.14 eV/940–395 nm regions which is wider than those of other polymer composites. The magnetic, relaxation and dynamics parameters of the spin charge carriers were shown to be governed by the exchange interaction of their spins and photon energy. The specific morphology of the composites provokes extreme selectivity of these parameters to photon energy. The anisotropy of polaron mobility through bulk heterojunctions was shown to reflect the system dimensionality and is dependent on the photon energy. Compared to PFO-DBT, the structure of the PCDTBT composite is more organised, resulting in a decrease in the number of spin traps and a change in the order of the charge recombination process. The decay of free charge carriers is interpreted in terms of the trapping-detrapping spin diffusion in bulk heterojunctions.

## 1. Introduction

Conjugated polymers with extended  $\pi$ -electron systems in their main chain attract much interest due to their perspective use as flexible active matrix for new electronic devices including photovoltaic elements [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<sub>x1</sub>-butyric acid methyl ester (PC<sub>x1</sub>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 respective

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 molecules. After this stage, charge carrier recombination can occur. The separation and recombination of free charge carriers can be considered as concurring opposite directed processes. The geminate recombination of polaron-fullerene pairs is monomolecular and, therefore, a first order process. The non-geminate, bimolecular recombination of separated polaron-fullerene pairs following Langevin theory of a second order.

The main parameter of photovoltaic devices is efficiency of power conversion which is mainly governed by a structure of polymer:fullerene BHJ. Among polymer semiconductors, poly[N-9'-heptadecanyl-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 creating, e.g., field effect transistors with the charge carrier mobility of 17 cm<sup>2</sup>/Vs [4] and solar cells with the power conversion efficiency near 10% [5] that exceeds those obtained for P3AT-based systems. Such

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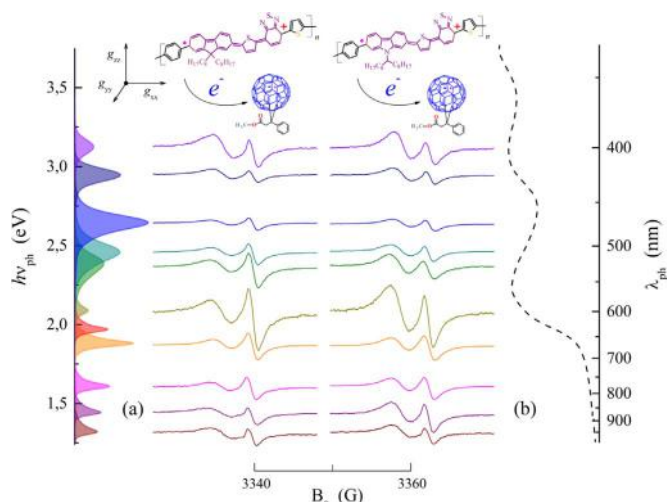


Fig. 1. Some X-band (9.7 GHz/340 mT) LEPR spectra of charge carriers background photoinduced by photons with different energy  $h\nu_{ph}$  at 77 K in bulk heterojunctions formed by PFO-DBT (a) and PCDTBT (b) copolymers with molecules of PC<sub>61</sub>BM normalized to the luminous emittance of the light sources  $I_l$ . Left filled lines represent irradiation spectra of respective light sources. Right dashed line shows exemplary UV-Vis-IR absorption spectrum of the PCDTBT:PC<sub>61</sub>BM composite [28]. The copolymers and methanofullerene are shown schematically as well.

outstanding results can be explained [6] mainly by ultrafast charge separation in the PCDTBT:PC<sub>71</sub>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 [7,8] to be laterally oriented with “column-like” bilayer ordered copolymer matrix with methanofullerene embedded between its chains. The dimension of low-bandgap copolymer backbone with such morphology should be higher than that of P3AT matrices. Gutzler et al. showed [9] that the higher  $\pi$ -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. Besides, these copolymers contain electron donor and acceptor groups, carbazole (in case of the PCDTBT) and benzothiadiazole, respectively, which originate their other important feature, ambipolarity. One can expect the photogeneration in such ambipolar copolymers and their nanocomposites, as in their metalorganic analogs [10], of intralayer excitons within one layer and interlayer excitons whom polarons and free electrons are initiated in respective groups of adjacent layers. The recombination of charge carriers formed from these excitons should occur with different order, rate and be accompanied by the emission of photons with different energy. The lifetime of the intralayer excitons and respective spin pairs is relatively short, however, the high density and mobility of these quasi-particles can be decisive in creation of more effective organic light-emitting diodes and lasers. This parameter of less mobile interlayer excitons is much larger, therefore the spin charge carriers formed in respective neighboring groups of copolymers can be used as logical '0' and '1' in organic memory cells.

In polymer:fullerene systems non-geminate charge recombination consists of prompt bimolecular and persistent contributions [11,12]. The prompt process is a bimolecular mutual spin annihilation within the initially created radical pairs [13], whereas the persistent contribution originates from deep spin traps reversibly formed in polymer matrix due to its disorder [11]. 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 [14], that the small number of initial excitons recombine in nanosecond timeframes, e.g., in the PCDTBT:PC<sub>61</sub>BM and thus do not contribute to the photocurrent through its BHJ, whereas the most excitons creates free charge carriers on an ultrafast time scale that contribute to the photocurrent and then non-geminately 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. Because these charge carriers possess a spin, their formation, dynamics and recombination were expected and proved to be spin-assisted [2]. Most methods, however, can provide information only on effective concentration of free carriers photo-initiated upon illumination of polymer:fullerene BHJ. This was the reason why Light-Induced Electron Paramagnetic Resonance (LEPR) becomes as one of the most powerful method for the study of all spin-assisted processes carrying out in organic polymer:fullerene systems [2,15–18]. 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 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 [19] 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. Polarons and methanofullerene anion radicals PC<sub>61</sub>BM in are characterized by weakly anisotropic  $g$ -factors with effective  $g_{iso} = 2.00213$  and  $1.99987$ , respectively [20], so they demonstrate at commonly used X-band (3-cm, 9.7 GHz) waveband EPR partly overlapping doublet of lines registered at lower and higher magnetic fields, respectively. Such LEPR spectrum is typical also for other polymer composites with such the electron acceptor [18]. LEPR study of various polymer:fullerene composites at this waveband showed [18] that upon illumination a part of both spin charge carriers are fixed in trap sites whose number and depth are governed by a structure of the BHJ and an energy of the 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 micro-environment. 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 [19,21,22]. Although the mechanism and dynamics of charge generation and recombination in various polymer:fullerene BHJ have been intensively studied by many research groups, 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<sub>61</sub>BM and PCDTBT:PC<sub>61</sub>BM composites upon their irradiation by photons with a range of energies. 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 the 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. Experimental

The 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) with energies of the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) of  $E_{\text{HOMO}} = 5.40$  eV and  $E_{\text{LUMO}} = 3.53$  eV, respectively, and an optical bandgap of  $2\Delta = 1.87$  eV [23], and also poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) with  $E_{\text{HOMO}} = 5.45$  eV,  $E_{\text{LUMO}} = 3.58$  eV, and  $2\Delta = 1.87$  eV [24,25]. [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) methanofullerene distributed by Solenne BV, The Netherlands, with  $E_{\text{HOMO}} = 6.18$  eV,  $E_{\text{LUMO}} = 3.70$  eV [26] was used as the electron acceptor subsystem. Chemical structures of these ingredients are shown schematically in Fig. 1.

Both the copolymer:fullerene composites were prepared simultaneously with optimal ingredient weight ratio 1:4 [24]. First 1.4 mg of PFO-TBT (or PCDTBT) and 5.6 mg of PC<sub>61</sub>BM were dissolved in 1 ml of dichlorobenzene. Both the solutions underwent ultrasonic treatment (DADI DA-968, 50 W) for 5 min with following warming at  $T = 333$  K within 5 min. The solutions were then maintained at  $T = 333$  K for 20 h until complete PC<sub>61</sub>BM dissolution, casted thrice by 10  $\mu\text{l}$  into both sides of an individual ceramic plate with subsequent drying in the air until the samples formed double-sided films. The films totally contained ca. 0.1 mg of PFO-DBT (or PCDTBT) and ca. 0.4 mg of PC<sub>61</sub>BM and were ca.  $4 \times 8$  mm<sup>2</sup> in size and ca. 0.1 mm in thickness.

The samples were permanently irradiated by Luxeon® 5 W achromatic, white, LED light sources with correlated color temperature  $T_c$  and luminous emittance  $I_l$  of 15000 K and 3020 lx, 5500 K and 4000 lx, 3300 K and 2480 lx as well as by 5 W nearly monochromatic LED light sources with the photon energy  $h\nu_{\text{ph}}$  (wavelength  $\lambda_{\text{ph}}$ , 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) 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. The  $I_l$  values were 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 copolymer: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” (intrinsic) paramagnetic centers (PCs) and those photoinduced in a copolymer: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 [18,20,22]. 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 line intensity  $I$ ,  $g$ -factor and peak-to-peak linewidth  $\Delta B_{\text{pp}}$  were determined to be 5%,  $\pm 2 \times 10^{-4}$  and  $\pm 2 \times 10^{-2}$  G, respectively. Both spin-lattice  $T_1$  and spin-spin  $T_2$  relaxation times were determined using the steady-state MW

saturation method [27].

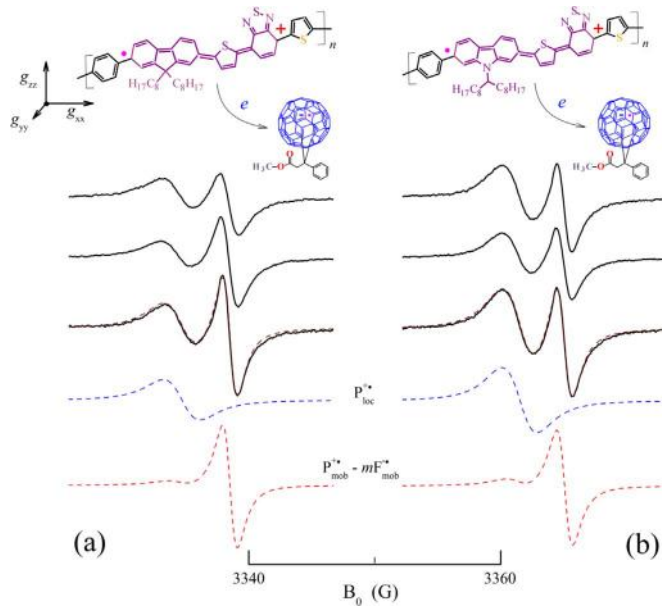
## 3. Results and discussion

### 3.1. LEPR spectra composition and magnetic resonance parameters

Fig. 1 shows X-band spectra LEPR obtained at  $T = 77$  K under irradiation of the PFO-DBT:PC<sub>61</sub>BM and PCDTBT:PC<sub>61</sub>BM composites by photons with different energy  $h\nu_{\text{ph}}$ . As in the case of analogous copolymer:fullerene composites [18], these spectra were attributed to polarons photoinitiated on copolymer chains and PC<sub>61</sub>BM methanofullerene anion radicals situated between them registered at low and high magnetic field, respectively. Emittance spectra of the light sources are shown at the left. Exemplary optical spectrum obtained for the latter sample [28] is also shown at the right by dashed line. Comparing the intensity of the LEPR and optical spectra presented one can note that the former does not correlate with the number of optical quanta reaching the sample surface and with those absorbed by the sample. Indeed, the intensity of the EPR signal does not change significantly in the IR region, where the absorption band is nearly nulled (Fig. 1). Furthermore, both the samples absorb more effective quanta with the energy  $h\nu_{\text{ph}} \approx 2.1$  eV lying near their optical bandgap  $2\Delta$  and vice versa absorb minimum quanta with  $h\nu_{\text{ph}} \approx 2.7$  eV. This does not support the conclusion made by Tong, et al. [29] 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 proposed for explanation of this discrepancy. One of them can be the effect of the spin traps' density and distribution over copolymer bulk on the HOMO and LUMO energy positions of the polymer matrix. Another factor can 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 [30]. This means that the time of separation and life of photo-initiated polaron-electron radical pairs should generally increase with the electron spin precession frequency  $\omega_e$ . However, different processes affecting electronic transport through BHJ should be carried out in such systems.

In order to determine main magnetic resonance parameters of all radicals and to analyze their change with experimental conditions, sum LEPR spectra of the samples were deconvoluted by using numerical simulation as it was made in the case of other polymer:fullerene systems [18,20,22]. 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<sub>61</sub>BM and PCDTBT:PC<sub>61</sub>BM composites at wide region of photon energy at  $T = 77$  K. Fig. 2 depicts exemplary LEPR spectra of the samples irradiated by white light with correlated color temperature  $T_c = 5500$  K as well as their contributions due to polarons pinned in copolymer spin traps  $P_{\text{loc}}^{+}$  and mobile pairs  $P_{\text{mob}}^{+} \leftrightarrow mF_{\text{mob}}^{-}$ . The best fit of experimental LEPR spectra of both the samples showed the low concentration of pinned methanofullerene radicals normally registered in other polymer:fullerene composites [18]. Such effect was also registered, e.g., at the replacement of the PC<sub>61</sub>BM electron acceptors by bis-PC<sub>61</sub>BM ones in respective composite with regioregular poly(3-hexylthiophene) (P3HT) [17]. This fact was explained by the better ordering of P3HT:bis-PC<sub>61</sub>BM BHJ. The number of localized fullerene charge carriers was shown [31] to be sufficiently large in the PCDTBT:PC<sub>71</sub>BM BHJ. The lower concentration of such spins in the samples under study can be explained, e.g. by their easier quasi-rotation in own bulkier interlayer pockets. So, the low number of deep traps able to capture radical anions in both the PFO-DBT:PC<sub>61</sub>BM and PCDTBT:PC<sub>61</sub>BM BHJ should be explained by higher amplitude of quasi-rotation of methanofullerene anion radicals in these composites.

Effective/isotropic splitting Landé  $g$ -factor was measured for



**Fig. 2.** LEPR spectra of charge carriers background photoinduced by achromatic, white light source with various correlated color temperature  $T_c$  at 77 K in BHJ formed by macromolecules of PFO-DBT (a) and PCDTBT (b) with molecules of PC<sub>61</sub>BM normalized to the luminous emittance of the light sources  $I_l$ . Dashed lines show theoretical Lorentzian sum spectra fitting the lower experimental spectra measured at  $T_c = 3300$  K and their contributions caused by localized polarons  $P_{loc}^{+}$  and highly mobilized radical pairs,  $P_{mob}^{+} \leftrightarrow mF_{mob}^{-}$ , numerically calculated using  $g_{iso}^P = 2.00228$ ,  $\Delta B_{pp}^P = 2.28$  G,  $\Delta B_{pp}^{mF} = 1.25$  G, a concentration ratio  $[mF_{mob}^{-}]/[P_{loc}^{+}] = 0.555$  (a) and  $g_{iso}^P = 2.00205$ ,  $\Delta B_{pp}^P = 2.08$  G,  $\Delta B_{pp}^{mF} = 1.29$  G,  $[mF_{mob}^{-}]/[P_{loc}^{+}] = 0.715$  (b). The charge transfer from copolymer chain to methanofullerene molecule accompanied by the formation on the copolymer chain of polaron with an elementary positive charge and spin  $S = 1/2$  is shown schematically.

**Table 1**

Isotropic  $g$ -factor of polarons  $g_{iso}^P$ , peak-to-peak linewidth of polarons  $\Delta B_{pp}^P$  and methanofullerene anion radicals  $\Delta B_{pp}^{mF}$ , concentration ratio of mobile methanofullerene anion radicals to that of localized polarons  $[mF_{mob}^{-}]/[P_{loc}^{+}]$ , spin-lattice and spin-spin relaxation times of polarons,  $T_1^P$  and  $T_2^P$ , respectively, coefficients of polaron diffusion along,  $D_{1D}^P$ , and between,  $D_{3D}^P$ , copolymer chains, and methanofullerene pseudo-rotation near the main molecular axis  $D_{rot}^{mF}$ , determined at illumination of the PFO-DBT:PC<sub>61</sub>BM and PCDTBT:PC<sub>61</sub>BM BHJ by achromatic, white light with different correlated color temperature  $T_c$  at  $T = 77$  K.

Parameter	PFO-DBT:PC <sub>61</sub> BM			PCDTBT:PC <sub>61</sub> BM		
	15000	5500	3300	15000	5500	3300
$g_{iso}^P$	2.002 <sub>26</sub>	2.002 <sub>37</sub>	2.002 <sub>28</sub>	2.002 <sub>07</sub>	2.002 <sub>09</sub>	2.002 <sub>05</sub>
$\Delta B_{pp}^P$ , G	2.17	2.18	2.28	1.10	2.05	2.08
$\Delta B_{pp}^{mF}$ , G	1.24	1.32	1.25	1.25	1.40	1.29
$[mF_{mob}^{-}]/[P_{loc}^{+}]$	0.731	0.924	0.555	0.469	1.010	0.715
$T_1^P$ , s	$1.32 \times 10^{-6}$	$2.45 \times 10^{-6}$	$1.46 \times 10^{-6}$	$2.08 \times 10^{-6}$	$7.53 \times 10^{-7}$	$2.04 \times 10^{-6}$
$T_2^P$ , s	$3.02 \times 10^{-8}$	$3.01 \times 10^{-8}$	$2.88 \times 10^{-8}$	$3.12 \times 10^{-8}$	$3.19 \times 10^{-8}$	$3.15 \times 10^{-8}$
$T_1^{mF}$ , s	$5.92 \times 10^{-7}$	$7.41 \times 10^{-7}$	$5.23 \times 10^{-7}$	$1.11 \times 10^{-6}$	$4.37 \times 10^{-7}$	$4.35 \times 10^{-7}$
$T_2^{mF}$ , s	$5.29 \times 10^{-8}$	$4.99 \times 10^{-8}$	$5.27 \times 10^{-6}$	$5.25 \times 10^{-8}$	$4.68 \times 10^{-8}$	$5.08 \times 10^{-8}$
$D_{1D}^P$ , rad/s	$1.20 \times 10^{12}$	$4.69 \times 10^{12}$	$1.37 \times 10^{12}$	$2.74 \times 10^{12}$	$4.51 \times 10^{11}$	$2.84 \times 10^{12}$
$D_{3D}^P$ , rad/s	$5.18 \times 10^6$	$1.47 \times 10^6$	$3.79 \times 10^6$	$2.21 \times 10^6$	$1.83 \times 10^7$	$2.32 \times 10^6$
$D_{rot}^{mF}$ , rad/s	$2.96 \times 10^{10}$	$1.63 \times 10^{10}$	$4.59 \times 10^{10}$	$1.94 \times 10^{10}$	$2.68 \times 10^{10}$	$4.94 \times 10^{10}$

methanofullerene anion radicals to be  $g_{iso}^{mF} = 1.99989$  and appeared to depend weakly on the structure of polymer matrix and photon energy. These PCs photoinitiated interact with own microenvironment and, therefore, are characterized by weakly anisotropic  $g$ -tensor [19–22]. The main values of the polarons in the same composite are  $g_{xx} = 2.0006$ ,  $g_{yy} = 2.0005$ ,  $g_{zz} = 1.9985$  [20], so then  $g_{iso}^{mF} = 1/3 \sum g_{ii} = 1.9999$  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. Such charge carriers formed as product of exciton dissociation in, e.g., PCDTBT:PC<sub>61</sub>BM composite are characterized by  $g$ -tensor with  $g_{xx} = 2.0032$ ,  $g_{yy} = 2.0024$ ,  $g_{zz} = 2.0018$ , and  $g_{iso}^P = 2.0025$  [20]. In contrast with the above negative charge carriers,  $g$ -factor of polarons reveals higher dependence on the structure of copolymer matrix (see Fig. 1, 2 and Table 1). The same values obtained for the samples under study are in good agreement with  $g_{iso}^P$  determined for analogous composites at wide wavebands EPR [18]. The orientation of the principal axes of the polaron  $g$ -tensor is given in Fig. 1 and Fig. 2. The  $g_{xx}$  value lies in the plane of the polymer  $\pi$ -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 copolymer 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.

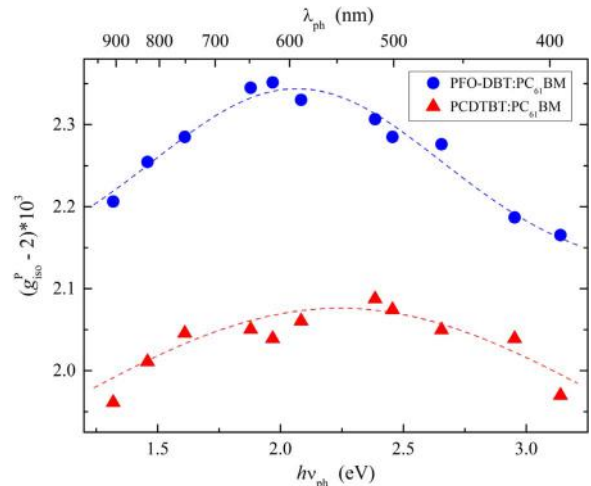
Generally, an effective  $g$ -factor of PCs can be written as [32]

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

where  $g_e = 2.002319$  is the Landé splitting factor for free electron,  $\lambda$  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 [32,33]. Fig. 3 shows how  $g_{iso}^P$  parameter of the samples changes upon their illumination by photons with different energy. These parameters obtained for polarons photoinitiated in the composites under study by achromatic, white light with different correlated color temperature  $T_c$  are also summarized in Table 1. It is seen from the Figure that effective  $g$ -factor of polarons in both composites demonstrates extreme dependence on the photon energy  $h\nu_{ph}$ . They can be fitted, e.g., by Gaussian function

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

where  $g_0$  and  $k_1$  are constants,  $E_c$  is the characteristic energy, and  $\sigma$  is deviation of the energy. Figure shows that the experimental data



**Fig. 3.** The value of  $g_{iso}^P$  for polarons photoinduced in the PFO-DBT:PC<sub>61</sub>BM and PCDTBT:PC<sub>61</sub>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  $g_0 = 2.00212$ ,  $k_1 = 1.09 \times 10^{-7}$ ,  $E_c = 2.067$  eV,  $\sigma = 1.174$  eV and  $g_0 = 2.00178$ ,  $k_1 = 5.48 \times 10^{-7}$ ,  $E_c = 2.244$  eV,  $\sigma = 1.945$  eV, respectively.

obtained for the PFO-DBT:PC<sub>61</sub>BM and PCDTBT:PC<sub>61</sub>BM composites are fitted well by Eq. (2) with  $E_c = 2.067$  eV,  $\sigma = 1.174$  eV and  $E_c = 2.244$  eV,  $\sigma = 1.945$  eV, respectively. One can conclude that the irradiation of the composites leads to the reversible formation of spin traps in their copolymer backbone. This changes (also reversibly) the properties of microenvironment of captured spins and, therefore, the energy of their resonant excitation on respective levels. The formation of such traps results in 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 molecule. Starting from this moment two processes begin in the polymer:fullerene system, namely the motion of charge carriers through BHJ followed by their recombination. In addition, spin traps reversibly 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 [18]. As a 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 [18] 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  $\omega_{\text{hop}}$ . Assuming that their motion is not disturbed by the presence of methanofullerene molecules and both the carriers possess spin  $S = 1/2$ , we can conclude that the probability of their collision is governed by the polaron hopping [34,35],

$$P_{\text{ss}} = \frac{1}{2} \frac{\alpha^2}{1 + \alpha^2}, \quad (3)$$

where  $\alpha = 3J_{\text{ex}}L^2/2\hbar\omega_{\text{hop}}$ ,  $J_{\text{ex}}$  is the constant of exchange interaction of spins in the initial radical pairs,  $L$  is a factor of spin delocalization over a polaron equal approximately to three units in PCDTBT [20], and  $\hbar = h/2\pi$  is the Planck constant. If the ratio  $J_{\text{ex}}/\hbar$  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  $\lim(p) \propto J_{\text{ex}}^2\omega_{\text{hop}}^{-2}$ . 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. 4 depicts the dependence of the relative concentration of charge carriers in the composites under study on the energy of initiating photons  $h\nu_{\text{ph}}$ . One can note two main features of the data presented. The first is the higher relative concentration of localized carriers in both systems 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. 4, the concentration of the  $P_{\text{loc}}^{+\cdot}$  and  $mF_{\text{mob}}^{-\cdot}$  charge carriers is characterized by dependence with explicit extremes lying near 1.8 and 2.8 eV. The analogous dependences were also obtained for both charge carriers photoinitiated in the PCDTBT:PC<sub>71</sub>BM [31], however, with extremes shifted to the lower photon energies. Such a peculiarity can probably be as a result of specific morphology, band structure of the samples with inhomogeneously distributed spin traps as well as different energy levels occupied by spin charge carriers in their bandgap. Therefore, the higher concentration ratio  $[mF_{\text{mob}}^{-\cdot}]/[P_{\text{loc}}^{+\cdot}]$  (or/and  $[P_{\text{mob}}^{+\cdot}]/[P_{\text{loc}}^{+\cdot}]$ ), the

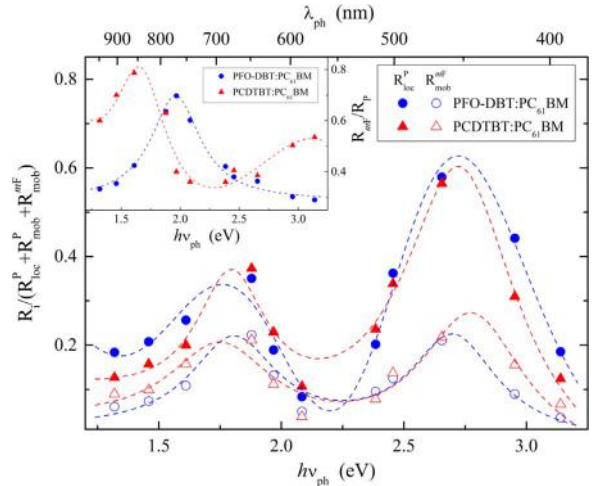


Fig. 4. Relative concentrations,  $[P_{\text{loc}}^{+\cdot}]/[P_{\text{loc}}^{+\cdot} + P_{\text{mob}}^{+\cdot} + mF_{\text{mob}}^{-\cdot}]$ ,  $[mF_{\text{mob}}^{-\cdot}]/[P_{\text{loc}}^{+\cdot} + P_{\text{mob}}^{+\cdot} + mF_{\text{mob}}^{-\cdot}]$ , and their ratio  $[mF_{\text{mob}}^{-\cdot}]/[P_{\text{loc}}^{+\cdot}]$  (insert) determined for polaron  $P^{+\cdot}$  and methanofullerene anion radical  $mF^{-\cdot}$  charge carriers photoinitiated in the PFO-DBT:PC<sub>61</sub>BM and PCDTBT:PC<sub>61</sub>BM bulk heterojunctions at  $T = 77$  K as a function of photon energy  $h\nu_{\text{ph}}$ . 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.

better electronic properties should be expected for respective photovoltaic system. In the insert of Fig. 4 are shown such a ratio as function of the photon energy  $h\nu_{\text{ph}}$  obtained for composites under study. The same parameters obtained upon the samples irradiation by white light are summarized in Table 1. It is seen that these ratios determined for the PFO-DBT:PC<sub>61</sub>BM and PCDTBT:PC<sub>61</sub>BM composites change significantly with  $h\nu_{\text{ph}}$  with characteristic values lying near 2.0 and 1.7 eV, respectively. The results obtained show that the replacement of the PFO-DBT matrix by the PCDTBT backbone 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 decrease. This is depicted in Fig. 5 where the decay of

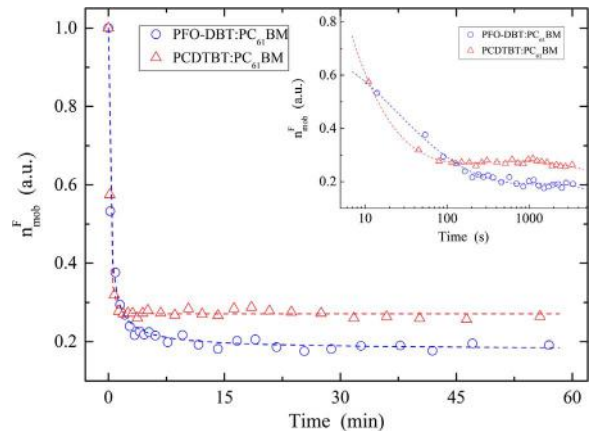


Fig. 5. The decay of the methanofullerene charge carriers photoinitiated in the PFO-DBT:PC<sub>61</sub>BM and PCDTBT:PC<sub>61</sub>BM bulk heterojunctions by white light with correlation color temperature  $T_c = 5500$  K at  $T = 77$  K. Dashed lines show the dependences calculated from Eq. (4) well fitting experimental data with  $k_r = 3.46 \times 10^{-6} \text{ s}^{-1}$ ,  $m = 2.245$  and  $k_r = 1.27 \times 10^{-2} \text{ s}^{-1}$ ,  $m = 1.232$ , respectively. In the insert are shown the same experimental data fitted by Eq. (5) with  $E_0 = 0.0102$  and  $0.0046$  eV, respectively.

spin charge carriers in both the PFO-DBT:PC<sub>61</sub>BM and PCDTBT:PC<sub>61</sub>BM systems is shown. The structure and morphology of the samples should govern the mechanism and order of spin recombination. The simplest, monomolecular process can be geminate between electrons and polarons originated from photoinitiated excitons 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 molecule. 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. 5 demonstrates also the experimental decay curves obtained at  $T = 77$  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 [36]:

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

where  $n_0$  is the initial number of polarons at the initial time ( $t = 0$ ) of recombination process,  $m$  is the recombination order. Fitting of the decay curves measured for the PCDTBT:PC<sub>61</sub>BM system can be described by Eq. (4) with  $k_r = 1.27 \times 10^{-2} \text{ s}^{-1}$  and  $m = 1.232$  (see Fig. 5). 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<sub>61</sub>BM yields  $k_r = 3.46 \times 10^{-6} \text{ s}^{-1}$  and  $m = 2.245$ . The value  $m$  obtained for this sample lies near  $m = 2.0$  obtained for Langevin recombination in other polymer:fullerene composites [37,38]. Therefore, one can conclude that in contrast to the PCDTBT:PC<sub>61</sub>BM, charge recombination in the PFO-DBT:PC<sub>61</sub>BM BHJ is second order process rather than first order. This can be due to the lower number of spin traps formed under illumination of such more ordered matrix. The same process in less ordered PFO-DBT:PC<sub>61</sub>BM matrix with higher number of spin traps follows a second order.

Analyzing LEPR spectra, it becomes possible to separate the decay of mobile and pinned spin charge carriers excited in 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 [39] 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 [39]:

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

where  $\delta$  is the gamma function,  $\alpha = k_B T/E_0$ ,  $v_d$  is the attempt jump frequency for polaron detrapping,  $E_0$  is distribution of the trap energy Fig. 5 shows that experimental data obtained for the PFO-DBT:PC<sub>61</sub>BM and PCDTBT:PC<sub>61</sub>BM composites at  $T = 77$  K can be described in terms of this approach implying  $E_0 = 0.010_2$  and  $0.004_6$  eV, respectively. It is evident that the replacement of the PFO-DBT matrix by the PCDTBT backbone 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 copolymer: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.

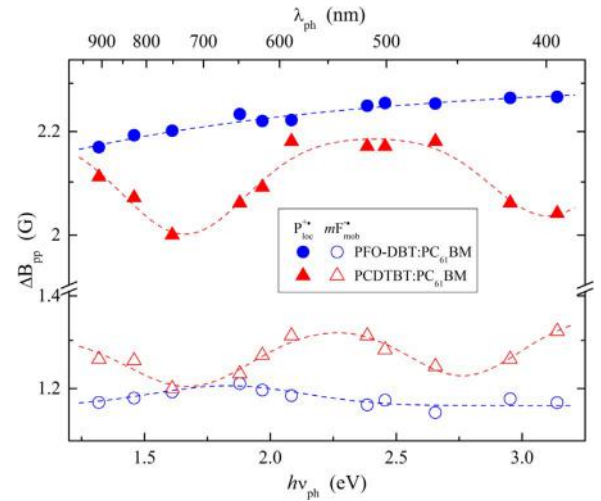


Fig. 6. The linewidth of polarons  $\Delta B_{pp}^P$  and methanofullerenes anion radicals  $\Delta B_{pp}^{mF}$  photoinitiated in the PFO-DBT:PC<sub>61</sub>BM and PCDTBT:PC<sub>61</sub>BM bulk heterojunctions at  $T = 77$  K as a function of photon energy  $h\nu_{ph}$ . The dashed lines are drawn arbitrarily only for illustration to guide the eye.

### 3.4. LEPR linewidth

Peak-to-peak linewidths of polarons  $\Delta B_{pp}^P$  and methanofullerenes anion radicals  $\Delta B_{pp}^{mF}$  photoinitiated in the PFO-DBT:PC<sub>61</sub>BM and PCDTBT:PC<sub>61</sub>BM BHJ at  $T = 77$  K are shown in Fig. 6 as a function of the photon energy  $h\nu_{ph}$ . These values determined at illuminations of the samples by achromatic white light are also summarized in Table 1. The change of such parameter can also be described in terms of the above mentioned exchange interaction of mobile polarons with spins captured in polymer backbone. The collision of these spins should broaden the absorption EPR line by the value [34,35]

$$\delta(\Delta\omega) = p_{ss}\omega_{hop}n_i, \quad (6)$$

where  $n_i$  is the number of guest spins per each polymer unit. According to this model, the acceleration of polaron mobility should result in decrease/increase of the exchange frequency at weak/strong spin exchange limit and, therefore, the signal linewidth and vice versa. Such situation is realized in various polymer semiconductors with several spin ensembles [18,40,41].

### 3.5. 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 [18]. These parameters determined for both spin charge carriers are presented in Fig. 7,a,b as function of the photon energy  $h\nu_{ph}$ . 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 molecule 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 [42]:

$$T_1^{-1}(\omega_e) = \langle\omega^2\rangle[2J(\omega_e) + 8J(2\omega_e)] \quad (7)$$

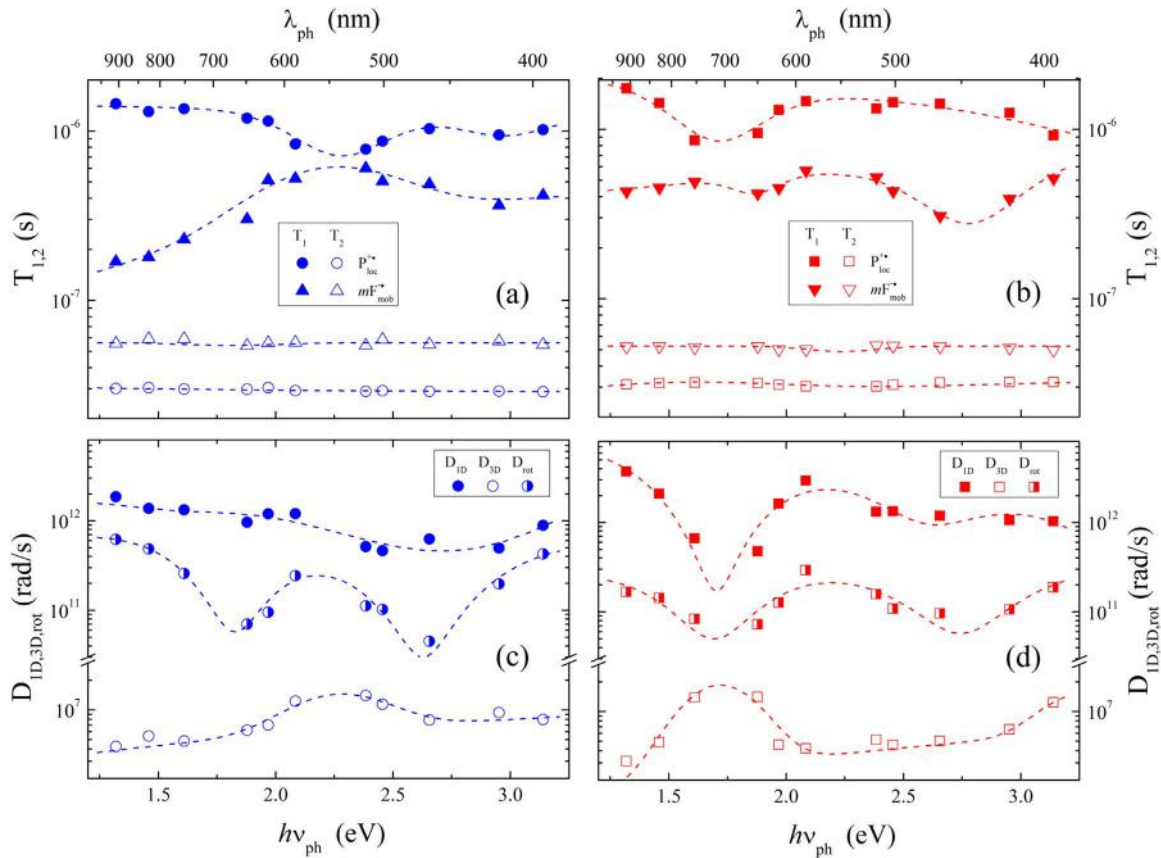


Fig. 7. Spin-lattice,  $T_1$  (filled points), and spin-spin,  $T_2$  (open points), relaxation times of polarons,  $P^{+}$ , and methanofullerene anion radicals,  $mF^{+}$ , (a,b) as well as translational intrachain,  $D_{1D}$  (filled points), hopping interchain,  $D_{3D}$  (open points), and pseudo-rotational,  $D_{rot}$  (semi-filled points), diffusion coefficients (c,d) of these charge carriers photoinduced in the PFO-DBT:PC<sub>61</sub>BM (a,c) and PCDTBT:PC<sub>61</sub>BM (b,d) 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.

$$T_2^{-1}(\omega_e) = \langle \omega^2 \rangle [3J(0) + 5J(\omega_e) + 2J(2\omega_e)] \quad (8)$$

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 the total concentration  $n = n_1 + n_2/\sqrt{2}$  of the trapped ( $n_1$ ) and mobile ( $n_2$ ) spins per each monomer unit and lattice sum  $\Sigma_{ij}, J(\omega_e) = (2D_{1D}^l \omega_e)^{-1/2}$  at  $D_{1D}^l \gg \omega_e \gg D_{3D}^p$  or  $J(0) = (2D_{1D}^l D_{3D}^p)^{-1/2}$  at  $D_{3D}^p \gg \omega_e$  is a spectral density function for Q1D motion,  $D_{1D}^l = 4D_{1D}^p/L^2$ ,  $\omega_e$  is resonant angular frequency of the electron spin precession. Spectral density function for rotational librations with correlation time  $\tau_c$  is  $J(\omega_e) = 2\tau_c/(1 + \tau_c^2 \omega_e^2)$ . The spin delocalization factor  $L$  was determined for PCDTBT to be equal three [20]. This value was used also for calculation spin dynamics parameters in the PFO-DBT:PC<sub>61</sub>BM BHJ.

Fig. 7,b,d 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. (7) and Eq. (8) as function of the photon energy  $h\nu_{ph}$ . The same parameters obtained for charge carriers photoinitiated in the composites under their illumination by achromatic, white light with different correlated color temperature  $T_c$  are also summarized in Table 1. It is seen from Fig. 7 that dynamics of polarons in the PFO-DBT:PC<sub>61</sub>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. When 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<sub>61</sub>BM composite. This makes spin dynamics easier and minimizes energy dispersion at charge transfer through BHJ of this system.

Comparative analysis of the data presented in Fig. 6 and Fig. 7 shows that the deceleration of diffusion of polarons photoinitiated, e.g., in the PCDTBT:PC<sub>61</sub>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 is valid also for methanofullerene anion radicals photoinitiated in the PFO-DBT:PC<sub>61</sub>BM composite.

#### 4. Conclusions

The results obtained show that mobile positively charged polarons and negatively charged methanofullerene anion radicals are initiated under illumination of BHJ in the PFO-DBT:PC<sub>61</sub>BM and PCDTBT:PC<sub>61</sub>BM composites. The main part of these carriers transfers the charge, whereas some quantity of polarons is captured by deep spin traps reversibly initiated in copolymer backbone. The spatial distribution, number, and energy depth of such traps depend on a structure and morphology of copolymer matrix as well as on the energy of initiating photons. The number, distribution and energy depth of spin traps change significantly when the PFO-DBT matrix in the composite is replaced by the PCDTBT backbone. 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<sub>61</sub>BM composite exceeds this parameter obtained for the PCDTBT:PC<sub>61</sub>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 appear as a result of specific morphology and band structure of the samples with spin traps inhomogeneously distributed in their bulk and may be used in optical sensors.

Recombination of spin charge carriers in the PCDTBT:PC<sub>61</sub>BM and PFO-DBT:PC<sub>61</sub>BM BHJ was interpreted to be respectively first and second order process due to the smaller number of spin traps photo-initiated in the former sample with a more ordered matrix. When the PFO-DBT macromolecules are replaced by of the PCDTBT chains in a composite, the energy distribution of such traps narrows. Therefore, the decay of long-lived charge carriers originated from spin pairs is governed by the type of an exciton initially photoinduced in copolymer matrix and can be interpreted in terms of spin trapping-detrapping stages in the copolymer:fullerene BHJ.

Dynamics of polarons photoinitiated in the PFO-DBT:PC<sub>61</sub>BM composite weakly depends on the photon energy, whereas pseudo-rotation of methanofullerene molecules in this system demonstrates extreme dependence on the photon energy with the minima near 1.8 and 2.8 eV. When the PFO-DBT matrix is replaced by the PCDTBT backbone, 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 copolymer 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<sub>61</sub>BM BHJ at such photon energy.

It was shown for the first time that the electronic properties of low-bandgap nanocomposites change significantly even at minor variation in the structure of their matrix. 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. Both the polarons and methanofullerene anion radicals play role of intrachain and interlayer spin probes, respectively, taking a possibility to analyze 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 composites.

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