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The role of spin exchange in charge transfer in low-bandgap polymer: Fullerene bulk heterojunctions

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Formation, relaxation and dynamics of polarons and methanofullerene anion radicals photoinitiated in poly[N-9′′-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)]:-[6,6]-phenyl-C_{61}-butyric acid methyl ester (PCDTBT:$PC_{61}BM$) bulk heterojunctions were studied mainly by light-induced EPR (LEPR) spectroscopy in wide photon energy and temperature ranges. Some polarons are pinned by spin traps whose number and depth are governed by the composite morphology and photon energy. The proximity of the photon energy and the polymer bandgap reduces the number of such traps, inhibits recombination of mobile charge carriers, and facilitates their mobility in polymer network. Spin relaxation and charge carrier dynamics were studied by the steady-state saturation method at wide range of temperature and photon energy. These processes were shown to be governed by spin exchange as well as by the photon energy. Charge transfer in the composite is governed by the polaron scattering on the lattice phonons of crystalline domains embedded into amorphous polymer matrix and its activation hopping between polymer layers. The energy barrier required for polaron interchain hopping exceeds that of its intrachain diffusion. Anisotropy of polaron dynamics in the PCDTBT:PC61BM composite is less than that of poly(3-alkylthiophenes)-based systems that evidences for better ordering of the former. Lorentzian shape of LEPR lines of both charge carriers, lower concentration of spin traps as well as behaviours of the main magnetic resonance parameters were explained by layer ordered morphology of polymer matrix. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4890995]

I. INTRODUCTION

The utilization of semiconducting organic conjugated polymers as active components of novel photovoltaic devices offers significant potential advantages over convenient materials in terms of ease of processing, formation of large surface areas, and lower costs. For example, bulk heterojunctions (BHJ) formed by regioregular poly(3-hexylthiophene) (P3HT),[1] and other polythiophene derivatives[2] with fullerene derivatives have been extensively studied over the last decade, resulting in solar cells with a power conversion efficiency between 3.0% and 5.0%. Although BHJ formed by the P3HT macromolecules with [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$, see Fig. 1 for the molecular structure) methanofullerene has previously been shown to produce light conversion efficiencies of about 5%, new systems of materials are needed to improve this parameter for further practical applications. Higher power-conversion efficiency of such BHJ can be reached, e.g., by using of *bis*-$PC_{61}BM$ instead of $PC_{61}BM$.[3] Another way to improve this important parameter is seen in decreasing of the bandgap of the active polymer matrix. Indeed, the bandgap of P3HT matrix lies near 1.9 eV which limits absorbance of light photons with higher energy. So, to harvest more solar photons, thereby increasing the power conversion efficiency, one should use polymers with lower bandgap in such device. Understanding the charge separation and charge transport in such materials at a molecular level is crucial for improving the efficiency of the solar cells. In optimized polymer:fullerene BHJ, the ultrafast photoinduced charge separation is a quantitative process that occurs in about 100 fs.[4] Poly[N-9”-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT, see also Fig. 1 for its molecular structure) with bandgap less than 1.9 eV[5,6] have been discovered[7] to be one of the most efficient low-bandgap semiconducting polymers for use in organic thin film transistors and solar cells.[8] The light conversion efficient of the PCDTBT:$PC_{71}BM$ composite layer has recently reached[9] 7.2% due to a relatively low highest occupied molecular orbital (HOMO) level of active matrix and an internal quantum efficiency approaching 100%.[10] Such outstanding results were explained[4] mainly by ultrafast charge separation in the PCDTBT:$PC_{71}BM$ composite before localization of the primary excitation to form a bound exciton in contrast with, e.g., P3HT-based one, where photoinduced charge separation happens after diffusion of the polymer exciton to a fullerene interface. The other important property, the morphology of the PCDTBT:$PC_{71}BM$ BHJ has demonstrated[9, 11] to be laterally oriented with “column-like” bilayer ordered polymer matrix with methanofullerene embedded between its chains that improves the carrier mobility, in particular electron mobility.[12] The dimensionality of the PCDTBT backbone with such morphology should be higher than that of P3AT matrices. Gutzler *et al.* showed[13] that higher π-overlapping in 2D thiophene-based polymers

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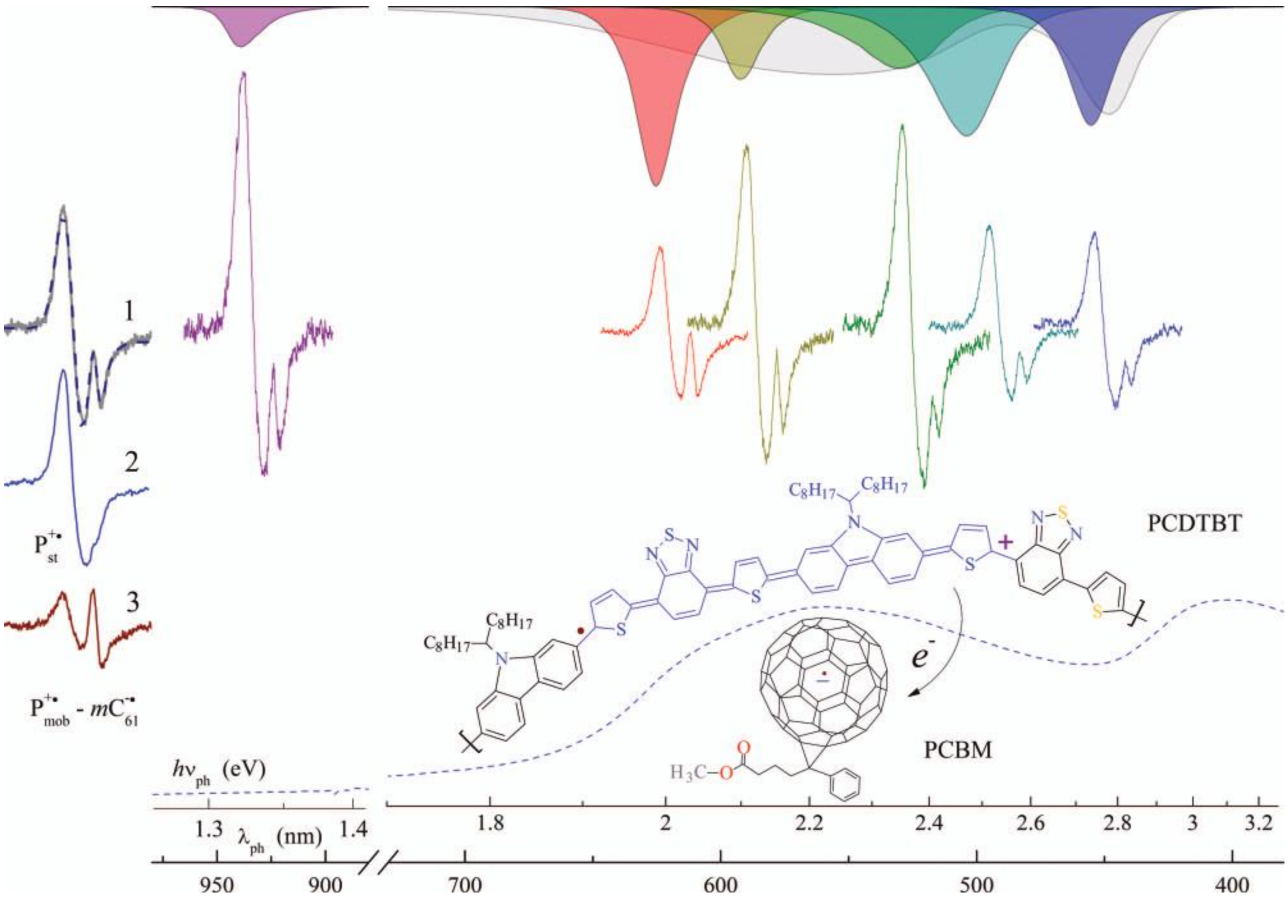

FIG. 1. LEPR spectra of charge carriers background photoinduced at 77 K in BHJ formed by macromolecules of PCDTBT with globes of $PC_{61}BM$ as function of the photon energy $h\nu_{ph}$ (linewidth λ_{ph}) normalized to the intensity of light sources. From left to right are shown the spectra obtained at irradiation of the samples by white light and by the light with photon energy $h\nu_{ph}$ = 1.32, 1.98, 2.10, 2.34, 2.46, and 2.73 eV. At the left are shown theoretical sum spectra (*1*, dashed lines) and their Lorentzian contributions caused by stabilized polarons $P^{+\bullet}_{st}$ (*2*) and highly mobilezed radical quasi-pairs, $P^{+\bullet}_{mob} \leftrightarrow mF^{-\bullet}_{mob}$ (*3*) numerically calculated using $\Delta B^{P}_{pp} = 1.37$ G, $\Delta B^{mF}_{pp} = 1.13$ G and a concentration ratio $[P^{+\bullet}_{st}]:[P^{+\bullet}_{mob} \leftrightarrow mF^{-\bullet}_{mob}] = 1:14$. Above dashed lines show irradiation spectra of the light sources normalized to their intensity and below dashed line shows IR-Vis absorption spectrum of the PCDTBT:$PC_{61}BM$ composite. The charge transfer from PCDTBT to the methanofullerene accompanied by the formation on the polymer chain of polaron with an elementary positive charge and spin $S = \frac{1}{2}$ is shown schematically. The positions of LEPR spectra of polarons, $P^{+\bullet}_{mob}$, and methanofullerene anion radicals, $mF^{-\bullet}_{mob}$, are shown as well.

hinders their torsional twisting and, therefore, lowers their bandgap. This allows holes to hop through such well-ordered bilayer PCDTBT surfaces to the anode and electrons to move to the cathode inside methanofullerene pools located between these bilayers. This is evidence that charge dynamics is another important parameter affecting device light conversion efficiency. Higher charge carrier mobility of the polymer increases the diffusion length of electrons and photoinitiated holes and decreases the probability of their recombination in the active layer.

Both the charge carriers photoinitiated in polymer:fullerene BHJ, polarons, and methanofullerene anion radicals possess electron spin $S = \frac{1}{2}$. Pulsed, electrically[14] or absorption detected magnetic resonance[15] can be used for the study of spin-assisted processes. However, Light-Induced Electron Paramagnetic Resonance (LEPR) is one of the most powerful direct methods for the study of such multispin systems.[16–18] It allows to obtain main parameters of spin pairs taking part in charge transfer and recombination in HBJ. More widely such a method has been used for the study of composites of $PC_{61}BM$ embedded into polymer matrix which demonstrate LEPR spectra of two overlapping but distinct lines of appropriate methanofullerene anion radicals and polarons with effective (isotropic) g-factors lying near 1.9996 and 2.0025, respectively. On the other hand, photoinitiated $PC_{71}BM$ demonstrates LEPR spectrum at $g_{iso} = 2.0040$.[19] This complicates respective LEPR spectra of appropriate polymer:fullerene composite and, therefore, limits the method even at high electron precession frequencies.[18,20] Although an expanding study of PCDTBT-based systems is widely being carrying out, till now no literature data exist on their spin properties governing charge transfer mechanism.

Earlier we have shown by LEPR method that charge photoinduction, separation, dynamics, and recombination in different polymer:fullerene systems are governed not only by structure properties of their ingredients and BHJ nanotreatment by various irradiations[17] but also by the energy of initiated photons.[21–23] Such a method can unambiguously be also used for the study of processes carrying out with spin charge carriers in the novel PCDTBT-based composites, especially because Tong *et al.* pointed out[24] that the carrier generation efficiency in such systems should be an order of magnitude larger but essentially independent of the energy of the exciting photons. Recently, Niklas *et al.*[18] have determined the main values of anisotropic *g*-factors and some other parameters of fullerene-modified PCDTBT including the distance (∼4–6 nm) of spin delocalization along its chain. The understanding of the basic physics underlying the electron relaxation and dynamic behavior of fullerene-modified PCDTBT is essential for the optimization of devices based on these materials, however, there is till now no information of such investigations.

Hereby we report a detailed LEPR study of magnetic, relaxation and dynamic parameters of polarons and methanofullerene anion-radicals photoinduced in the PCDTBT:PC_{61}BM BHJ by photons with different energy in a wide temperature region. Non-interacting feature of these charge carriers in radical pairs and, therefore, their different interaction with own microenvironment were shown to allow determining separately their relaxation and dynamic parameters and analyzing in details all spin-assisted processes in the PCDTBT:PC_{61}BM composite. It was confirmed additionally that LEPR investigation of the main magnetic resonance properties of such novel systems represents a helpful and powerful tool to evaluate potential materials for plastic photonics applications. Finally, we discuss possible mechanisms of charge transfer in layer ordered BHJ.

II. EXPERIMENTAL

In the study we used poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) with the backbone chains separation, $b = 1.89$ nm, and the length of linear backbone segment, $c = 2.09$ nm,[9] distributed by the St-Jean Photochemicals Inc. (SJPC), Canada and 99.5% [6,6]-phenyl-C_{61}-butyric acid methyl ester (PC_{61}BM) methanofullerene distributed by Solenne BV, The Netherlands. Chemical structures of these ingredients are shown schematically in Fig. 1.

PCDTBT:PC_{61}BM composite was prepared as following. First 0.002 M solution of PCDTBT in chlorobenzene/dichlorobenzene (3:1 volume ratio) mixture was prepared. This solution was treated by ultrasonic cleaner bath DADI DA-968 (50 W) for 5 min with following warming at $T = 333$ K within 5 min. Methanofullerene was added into so treated solution amounting PCDTBT:PC_{61}BM ratio to be 1:4 after which the resulting solution was additionally maintained at $T = 333$ K within 20 h to PC_{61}BM complete dissolution. The prepared solution was casted serially into both sites of ceramic plate and dried until polymer/fullerene composite was formed as double-sided film, both with the size of ∼4 × 8 mm^2 and thickness of ∼0.1 mm.

The sample was permanently irradiated by the Luxeon III achromatic (white, color temperature of 5500 K, 4200 lx) and nearly monochromatic light with the photon energy $h\nu_{ph}$ (wavelength λ_{ph}, illuminance I_l) of 1.32 eV (940 nm, 1600 lx), 1.98 eV (625 nm, 7040 lx), 2.10 eV (590 nm, 2830 lx), 2.34 eV (530 nm, 2410 lx), 2.46 eV (505 nm, 5010 lx), and 2.73 eV (455 nm, 4620 lx) LED light sources directly in the microwave (MW) cavity through quartz light guide. Integral illuminance I_l of these sources was estimated using a broadband IMO-2N output power light irradiation bolometer in combination with a digital luxmeter LX1010BS for the further normalization of spin susceptibility. In order to decompose overlapping signals for estimation more precisely their parameters, the “light on-light off” method with subsequent annealing was applied. The optical irradiation spectra of these light sources and absorption spectra of the PCDTBT:PC_{61}BM composite shown in Fig. 1 were obtained using a Shimadzu UV-VIS-NIR scanning UV-3101PC spectrophotometer. The composite demonstrates optical spectrum with the $h\nu_{ph}$ extremes at ∼2.21 eV (560 nm) and 3.10 eV (400 nm) lying near those characteristic of PCDTBT:PC_{61}BM (see Fig. 1).[25] Two other peaks situated at 4.70 eV (264 nm) and 3.76 eV (330 nm) attributed to methanofullerene are not shown.

Magnetic resonance experiments were performed using an X-band (3-cm, 9.7 GHz) PS-100X spectrometer with 100 kHz field *ac* modulation for phase-lock detection. The “dark” (EPR) and light-induced (LEPR) spectra of the sample and its ingredients were obtained in the 90–340 K temperature range in dry nitrogen atmosphere using a BRT SKB IOH temperature controller and at $T = 77$ K in a quartz Dewar filled with liquid nitrogen. To improve the signal-to-noise ratio of the LEPR spectra, the averaging several (typical 4–6) acquisitions were averaged. The total paramagnetic susceptibility of both charge carriers stabilized in the samples was determined using double integration of their lines deconvoluted from effective LEPR spectra and that of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) nitroxide radical obtained far from their MW saturation 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 1.0 G, respectively. Diphenylpicrylhydrazyl (DPPH) single microcrystal standard with $g = 2.0036$ was also used for the estimation of the *g*-factor of both charge carriers. The *g*-factor, absorption intensity, peak-to-peak line width ΔB_{pp}, and energetic parameters of charge carriers were determined with $\pm 1 \times 10^{-4}$, ±1.2%, $\pm 1 \times 10^{-2}$ G, and ±5% accuracy, respectively. Spin-lattice T_1 and spin-spin T_2 relaxation times were measured by steady-state saturation method.[26] All experimental spectra were simulated numerically for deconvolution with the programs SimFonia V.1.25 (Bruker BioSpin, Rheinstetten), using second order perturbation theory and delivered virtually identical parameters as well as OriginLab V.7.5 (OriginLab Co., Northampton).

III. RESULTS AND DISCUSSIONS

A. Spectral composition, shape, and *g*-factor

In contrast with other initial conjugated polymers, e.g., P3HT and poly(3-dodecylthiophene) (P3DDT), PCDTBT is characterized by “dark” EPR spectrum typical for localized PC which changed slightly under its irradiation by visible light over the entire range of temperatures studied. Neither the “dark” nor the photoinitiated spectra demonstrates PC_{61}BM.

Figure 1 shows LEPR spectra of charge carriers stabilized and reversibly photoinitiated in the PCDTBT:PC_{61}BM sample under its irradiation in a MW cavity of the EPR spectrometer by light with photon energy of 1.32−2.73 eV in comparison with its IR-Vis optical spectrum. In the latter, the low energy, broad and featureless absorption band with a peak at $h\nu_{\mathrm{ph}} = 2.23$ eV ($\lambda_{\mathrm{ph}} = 560$ nm) corresponds to the intramolecular charge transfer transition, whereas meanwhile the pronounced absorption lines in the higher energy region $h\nu_{\mathrm{ph}} = 3.09$, 3.72, and 4.70 eV ($\lambda_{\mathrm{ph}} = 400$, 333, and 264 nm) (the two latter lines are not shown) are attributed to the fullerene units. This leads to an increase in the intensity of the initial EPR spectrum and the appearance of the second line at higher magnetic fields (see Fig. 1). Following previous studies, these low- and high-field signals can be unequivocally assigned to radical pairs of the positively charged polaron $\mathrm{P}_{\mathrm{mob}}^{+\bullet}$ diffusing along the polymer and negatively charged methanofullerene anion radical $m\mathrm{F}_{\mathrm{mob}}^{-\bullet}$ reorientating in polymer matrix. There are some unusual effects which should be emphasized. The main of them is that the LEPR signal of the sample appears under its irradiation even in the near infrared region, $h\nu_{\mathrm{ph}} = 1.32$ eV ($\lambda_{\mathrm{ph}} = 940$ nm), where the absorption band is nearly nulled (Fig. 1). The intensity of this signal is comparable to that obtained at higher photon frequencies. This fact can be originated, e.g., by a nonlinear optical effect in the bulk of the PCDTBT:PC$_{61}$BM composite converting the photon frequency/energy into the higher value. In order to verify such a supposition, we attempted to observe the appearance of an optical second harmonic under PCDTBT:PC$_{61}$BM illumination, however, without a positive result. So, it can be assumed that the formation of spin pairs indeed occurs in the sample BHJ under their excitation by infrared quanta. Besides, the comparison of an intensity of all LEPR and optical spectra presented in Fig. 1 shows that the intensity of the former does definitely not correlates neither with the number of optical quanta reaching the sample surface nor with those absorbed by the sample. This does not confirm the conclusion made by Tong *et al.*[24] that the efficiency of carrier generation in the PCDTBT:fullerene BHJ should be essentially independent of the excitation wavelength. Various hypotheses can be supposed for explanation of these effects. One of them could be the interaction of charge carriers with MW field. Indeed, only for those relatively isolated excitons is there a reasonably high probability that a metastable PC will result from the optical production of an electron-hole pair by means of the trapping of one carrier and the hopping away of the other.[27] Thus, the separation and, therefore, life time of radical quasi-pairs $\mathrm{P}_{\mathrm{mob}}^{+\bullet} \leftrightarrow m\mathrm{F}_{\mathrm{mob}}^{-\bullet}$ initiated by light will generally increase with electron spin precession frequency ω_{e}. One, therefore, can take into account a combination of different processes affecting electronic transport through PCDTBT:PC$_{61}$BM BHJ.

In order to analyze in details all magnetic resonance parameters as a function of different effects, sum LEPR spectra should be deconvoluted by using numerical simulation as it was made in the case of other polymer/fullerene systems.[19,20,22,23] Such algorithm in combination with the "light on-light off" method allowed us to determine separately all main magnetic resonance parameters of both charge carriers stabilized and photoinitiated in the PCDTBT:PC$_{61}$BM BHJ at wide regions of the temperature and photon energy. The best fit was achieved supposing stabilization in a polymer backbone of polarons $\mathrm{P}_{\mathrm{st}}^{+\bullet}$, characterized by the anisotropic Lorentzian spectrum *2* in the left of Fig. 1 with the following main values of Lande **g**-tensor, $g_{\mathrm{xx}} = 2.003_{05}$, $g_{\mathrm{yy}} = 2.002_{62}$, $g_{\mathrm{zz}} = 2.000_{95}$. The anisotropic nature of the $\mathrm{P}_{\mathrm{st}}^{+\bullet}$ spectrum is *prima facie* evidence for its perceptible spin-orbit interaction with the nucleus of nitrogen and sulfur heteroatoms in the polymer network as well as slow mobility. The molecule can take any orientation relative to the *z*-axis, i.e., the polymer backbone direction as is derived from the presence of both the g_{xx} and g_{yy} components in the spectra for all orientations of the film BHJ. Thus, the *g*-factor anisotropy is a result of inhomogeneous distribution of additional fields along the *x* and *y* directions within the plane of the polymer σ-skeleton rather than along its perpendicular *z* direction. The number of such polarons somewhat increases at irradiation of the PCDTBT:PC$_{61}$BM composite. Besides, in the system appear highly mobile radical pairs $\mathrm{P}_{\mathrm{mob}}^{+\bullet} \leftrightarrow m\mathrm{F}_{\mathrm{mob}}^{-\bullet}$ with appropriate effective (isotropic) *g*-factors, $g_{\mathrm{iso}}^{\mathrm{P}} = 2.002_{20}$ typical for PC in organic systems and $g_{\mathrm{iso}}^{m\mathrm{F}} = 2.000_{55}$ whom respective contribution *3* is also shown in the left of Fig. 1. The latter value lies close to that obtained for other fullerene anion radicals;[18,20,28] however, it slightly exceeds that obtained for PC$_{61}$BM embedded into P3HT and P3DDT matrices.[17,22,29] The absence of a Gaussian contribution in LEPR spectra of these charge carriers argues, as in case of the P3HT/*bis*-PC$_{61}$BM composite, in favor of a smaller number of spin traps, as well as their faster dynamics in the sample under study. So, analogously to other polymer:PC$_{61}$BM systems,[30] each LEPR spectrum presented in Fig. 1 consists of line *2* of polarons $\mathrm{P}_{\mathrm{st}}^{+\bullet}$ stabilized in the polymer matrix and double spectrum *3* of highly mobilized radical quasi-pairs $\mathrm{P}_{\mathrm{mob}}^{+\bullet} \leftrightarrow m\mathrm{F}_{\mathrm{mob}}^{-\bullet}$. However, two main differences of the composite under study from the known systems should be emphasized. Hyperfine polaron interaction with neighboring hydrogen and heteroatoms should broaden its spectrum and cause its Gaussian shape. Such a line shape is also characteristic of spins captured by energetically deep traps. This leads to the appearance of appropriate Gaussian contributions in LEPR spectra of P3HT:PC$_{61}$BM and analogous composites. Both charge carriers stabilized and photoinitiated in the PCDTBT:PC$_{61}$BM composite, however, are characterized by Lorentzian line shapes. This fact was not registered in a previous LEPR study of various polymer/fullerene composites and should likely indicate lower number of spin traps and higher spin dynamics in the system under study.

The main values of the **g**-tensor of the stabilized polarons can be determined from equation,[31–33]

$$\begin{vmatrix} g_{xx} & & \\ & g_{yy} & \\ & & g_{zz} \end{vmatrix} = \begin{vmatrix} 2\left(1+\dfrac{\lambda\rho(0)}{\Delta E_{n\pi*}}\right) & & \\ & 2\left(1+\dfrac{\lambda\rho(0)}{\Delta E_{\sigma\pi*}}\right) & \\ & & 2 \end{vmatrix}, \qquad (1)$$

where λ is the spin-orbit coupling constant, $\rho(0)$ is the spin density in a heteroatom location, $\Delta E_{\mathrm{n}\pi*}$ and $\Delta E_{\sigma\pi*}$ are the energies that an unpaired electron acquires in its $n \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ transitions, respectively. As in the case of other π-conjugated systems,[18,20,34–36] the principal *x*-axis of these carriers was chosen to be parallel to the longest macromolecular *c*-axis, the *y*-axis to be lie in the thiophene plane, and the *z*-axis to be directed along the p_{z} combined orbital

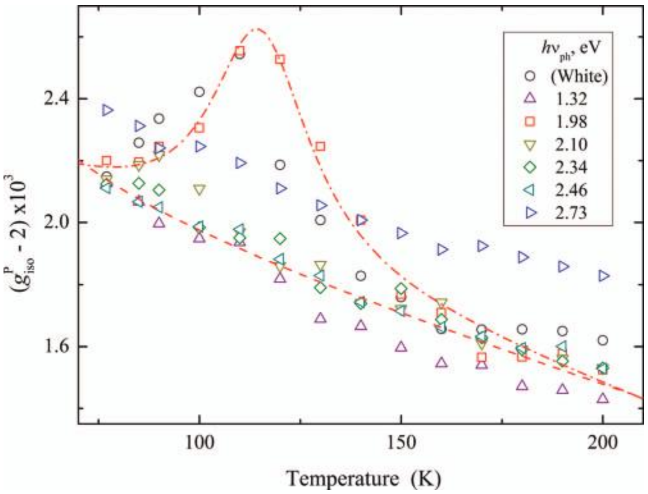

FIG. 2. The value of $g_{\rm iso}^{\rm P}$ for polarons photoinduced in the PCDTBT:PC$_{61}$BM BHJ as a function of temperature and photon energy $h\nu_{\rm ph}$. Dashed line shows the dependence calculated from Eq. (2) with $E_{\rm l}$ = 0.008 eV. The dashed-dotted line is drawn arbitrarily only for illustration to guide the eye.

perpendicular to *x*- and *y*-axes. Methanofullerene anion radicals photoinduced in the system under study demonstrate nearly temperature independent $g_{\rm iso}^{m\rm F}$, as in case of other analogous composites.[22,23] On the other hand, this parameter of mobile polarons, $g_{\rm iso}^{\rm P}$, was varied as a function of temperature and photon energy $h\nu_{\rm ph}$ (see Fig. 2). It is seen from the Figure that the warming of the sample leads to the decrease in $g_{\rm iso}^{\rm P}$ due to increase in the transition energies at the excitation of an electron from the unoccupied shell to the antibonding orbit $\pi\rightarrow\sigma^*$.[32] Peculiar extreme $g_{\rm iso}^{\rm P}(T)$ dependences obtained for polarons photoinitiated by wideband white and monochromic light with photon energy $h\nu_{\rm ph} = 1.98$ eV can, probably, be explained by competitive impact of the above electron exciting transitions. Monotonic temperature dependences presented in Fig. 2 can be explained *inter alia* by joint harmonic librations of polymer units and chains together with localized polarons which change the backbone dimensionality[13] and modulate the charge transfer integrals.[37] This should change the effective *g*-factor as

$$g_{\rm iso}^{\rm P} = g_0 + \frac{A}{\hbar\omega_{\rm l}}\coth\left(\frac{\hbar\omega_{\rm l}}{2k_{\rm B}T}\right), \qquad (2)$$

where g_0 and A are constants, $\hbar = h/2\pi$ is the Planck constant, $\omega_{\rm l} = \omega_0\exp(-E_{\rm l}/k_{\rm B}T)$ is librational frequency, $E_{\rm l}$ is the energy required for the activation of such a motion, and $k_{\rm B}$ is the Boltzmann constant. Figure 2 shows that the $g_{\rm iso}^{\rm P}(T)$ dependences experimentally obtained can be fitted by Eq. (2) with $E_{\rm l}$ summarized in Table I. One can note weak temperature and photon frequency dependency of this value except for irradiation of the composite by phonons with $h\nu_{\rm ph}$ = 1.98 eV (which exist also in white light) lying near the polymer bandgap (1.88 eV).[6] This effect can possibly be explained by the change of effective dimensionality of the polymer matrix[13] and is additional evidence for the better ordering of PCDTBT:PC$_{61}$BM BHJ in comparison with analogous composites with, e.g., P3HT and P3DDT matrices.[22,23] Temperature sensitivity of the polaron *g*-factor decreases at $T \geq 200$ K. Besides, the concentration of both types of charge carriers decreases dramatically at these temperatures that limits significantly the precision of determination of their main magnetic resonance parameters. Such effect can be attributed to fluctuations in local symmetry of the octyl side groups relative to the main polymer axis. These groups begin to move at the glass transition of the polymer matrix near 200 K,[38] their local relaxation contributes to the topological disorder in the polymer structure and leads to the increase in energy barriers for charge transport. The temperature dependence of *g*-factors is argued to be due to a coupling of the holes to local vibrations of the chains or/and side octyl groups along a backbone of the polymer matrix. This means that photoinitiated spins act as a nanoscopic probe of molecular and polaron dynamics in the composite under study. More detailed information can be obtained at higher registration (spin precession) frequencies EPR increasing spectral resolution.

So, the absence in the LEPR spectra of Gaussian signals of localized charge carriers can evidence for high

TABLE I. The illuminance of light sources $I_{\rm l}$ (in lx), energy $E_{\rm l}$ determined from Eq. (2), ΔE_{ij} from Eq. (3), ΔE_{ij} from Eq. (5), $E_{\rm a}$ from Eq. (6), $E_{\rm ph}$ from Eq. (9), $E_{\rm b}$ from Eq. (10), and $E_{\rm r}$ from Eq. (11) (all in eV) for the PCDTBT:PC$_{61}$BM composite illuminated by different photons at temperature range of 77–200 K.

		$h\nu_{\rm ph}$, eV / λ (nm)					
Parameter	White	1.32/940	1.98 /625	2.10 /590	2.34 /530	2.46 /505	2.73/455
$I_{\rm l}$	4200	1600	7040	2830	2410	5020	4620
$E_{\rm l}$	0.006[a]	0.004	0.008[a]	0.003	0.002	0.004	0.004
ΔE_{ij},[b]	0.018	0.005	0.056	0.050	0.032	0.072	0.059
ΔE_{ij},[c]	0.048	0.051	0.068	0.060	0.076	0.065	0.058
$E_{\rm a}$,[b]	0.028	0.117	0.001	0.001	0.017	0.003	0.015
$E_{\rm a}$,[c]	0.013	0.013	0.014	0.019	0.020	0.018	0.018
$E_{\rm ph}$	0.121	0.098	0.049	0.074	0.080	0.043	0.120
$E_{\rm b}$	0.079	0.093	0.067	0.081	0.110	0.141	0.178
$E_{\rm r}$	0.218	0.085	0.102	0.046	0.081	0.074	0.216

[a] Determined for monotonic part.

[b] Determined for stabilized polarons.

[c] Determined for methanofullerene anion radicals.

ordering of PCDTBT layers and also for low number of energetically deep spin traps that facilitates charge transfer from the polymer chain to the methanofullerene cage. This is similar to cation radical *bis*(ethylenedithio)tetrathiafulvalene-based single crystals with alternating organic and inorganic layers. Such morphology leads to a Lorentzian line shape in EPR spectra of their charge carriers, characteristic of free electrons.[39]

B. Paramagnetic susceptibility

The paramagnetic susceptibility of both charge carriers contributing to the effective LEPR spectra in the 77–200 K range derived from these double-integrated spectra and normalized to the intensity of the light sources is shown in Fig. 3.

Both spins of each radical pairs photoinduced in close proximity should interact on the scale of a pair, either by exchange or by a dipolar mechanisms. These effects were not registered in the LEPR spectra of the polymer/fullerene composites because polarons diffuse along the conjugated polymer backbone away from the methanofullerene anion radicals faster than their possible exchange time, that is, $\tau_{ex} \le 10^{-9}$ s. This particularly leads to an unusually long lifetime of such charge carriers in polymer/fullerene BHJ. Photoinitiation of these charge carriers occurs in the femtosecond time scale,[40] whereas electron back transfer with charge annihilation is much slower possibly due to dynamics and relatively slow structural relaxation in such a system. This is a reason why its effective paramagnetic susceptibility should inversely depend on the probability of recombination of charge carriers. Such probability is determined by spin multistage activation diffusion along a polymer chain and tunneling from a chain to a fullerene anion.[41] Thus, the decay of mobile charge carriers photoinitiated in PCDTBT:PCBM BHJ should consists of temperature-independent fast and exponentially temperature-dependent slow contributions.[42] When a polaron diffuses between initial i and final j sites it spends the energy ΔE_{ij}, so paramagnetic susceptibility and, therefore, the decay of stabilized polarons $P_{st}^{+\bullet}$ should follow the equation with the Miller–Abrahams energy-dependent factor,[43]

$$\chi(\Delta E_{ij}) = \chi_0 \exp\left(\frac{\Delta E_{ij}}{k_B T}\right). \tag{3}$$

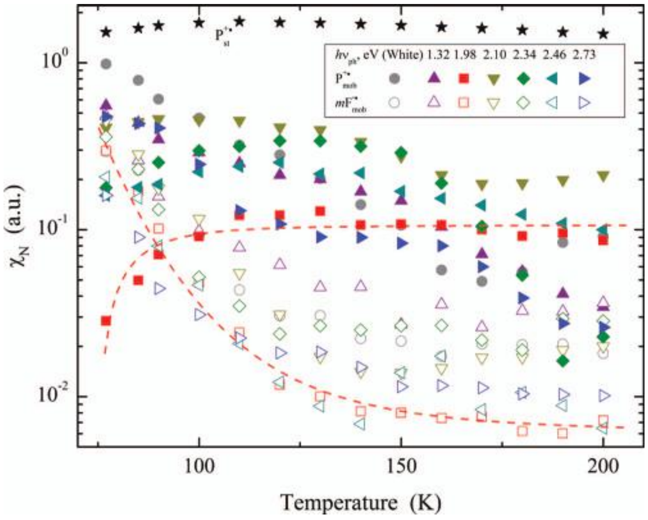

FIG. 3. Temperature dependence of paramagnetic susceptibility of polarons $P_{st}^{+\bullet}$ (filled points) and methanofullerene anion radicals $mF_{mob}^{-\bullet}$ (open points) stabilized (shown by stars) and photoinduced in BHJ formed by PCDTBT chains with the $PC_{61}BM$ methanofullerene by photons with different energy $h\nu_{ph}$. The susceptibility of photoinitiated charge carriers was normalized to illumination intensity I_1 of the light sources. Dashed lines show dependences calculated as an example for $h\nu_{ph} = 1.98$ eV from Eq. (3) with $\omega_0 = 5.0 \times 10^9$ rad/s and $\Delta E_{ji} = 0.056$ eV and Eq. (5) with $\omega_0 = 1.27 \times 10^{11}$ rad/s and $\Delta E_{ji} = 0.068$ eV.

In order to determine paramagnetic susceptibility of mobile radical pairs $P_{mob}^{+\bullet} \leftrightarrow mF_{mob}^{-\bullet}$, one should assume that a positive charge on a polaron is not required to be recombined with the first negative charge of the subsequent fullerene. Actually, a polaron hopping along the polymer chain beside the localization of the fullerene anion radical between polymer layers should interact with its unpaired electron. Therefore, the spin flip-flop probability p of a collision of these half-integer spins should depend on their exchange interaction and the polaron multistep hopping rate ω_{hop} as[44]

$$p = \frac{1}{2} \cdot \frac{\alpha^2}{1+\alpha^2}, \tag{4}$$

where $\alpha = (3/2)\ 2\pi J/\hbar\omega_{hop}$, $\hbar = h/2\pi$ is the Plank constant, J is the constant of exchange interaction of spins in a radical pair, and $\omega_{hop} = \omega_{hop}^{(0)}\exp(-E_a/k_B T)$. It is evident that the longer both of the above tunneling times or/and the lower the probability p, the smaller the number of opposite charge carriers capable to recombine and, therefore, the higher effective spin susceptibility should be detected. If PC of these spin reservoirs strongly or weakly exchange interact one with another, the increase of ω_{hop} may result in the increase or the decrease in their exchange frequency, respectively. A combination of Eqs. (3) and (4) yields

$$\chi(\Delta E_{ij}) = \chi_0 \frac{2\left(1+\alpha^2\right)}{\alpha^2} \exp\left(\frac{\Delta E_{ij}}{k_B T}\right). \tag{5}$$

Assuming the absence of a dipole-dipole interaction between methanofullerene anion radicals in pools, one can evaluate ΔE_{ij} from temperature dependences of paramagnetic susceptibility of all PC shown in Fig. 3. These values determined for both charge carriers are summarized in Table I. As it is seen from the figure, the spin-spin interaction processes in the composite can indeed be described by Eqs. (3) and (5).

It is evident that polaron diffusion in the PCDTBT matrix requires lower energy ΔE_{ij} as compared with mobile methanofullerene anion radicals.

The analysis of LEPR spectra presented in Fig. 1 allows concluding that their shape and intensity are governed not only by the number of the photons absorbed but also by their energy $h\nu_{ph}$. Figure 3 shows the changes in spin susceptibility of stabilized and mobile PC initiated in the composite by photons with different $h\nu_{ph}$. It is seen that the χ value of anion radicals is more temperature dependent when $h\nu_{ph} \approx 1.98$ and 2.73 eV. The former value lies near the bandgap energy obtained for PCDTBT (1.88 eV).[6] Such a dependence of spin concentration on photon energy can be explained either by the formation of spin pairs with different properties in the higher ordered phase of the PCDTBT composite or by the excitation of identical charge carriers in its lower ordered domains. The first case can be realized as a result of the photon-assisted appearance of spin traps with different depths in a polymer matrix. However, the shape of LEPR spectra analyzed above allowed us to conclude that such spin traps cannot be formed in the system under study, as it was pointed out in the study of some other polymer/fullerene composites.[22,23] The revealed difference in magnetic parameters of charge carriers seems rather to appeared due to their interaction with their microenvironment in domains inhomogeneously distributed in the composite. Such differently ordered domains can be characterized by different bandgaps that should to lead to their sensitivity to photon energy. This can give rise to the change in the interaction of PC with a lattice and other spins. Figure 3 shows that the illumination of the PCDTBT:PC$_{61}$BM composite by photons with $h\nu_{\mathrm{ph}} = 1.98$ eV at low temperatures induces minimum number of traps for polarons that leads to formation of a larger number of mobile spin pairs (see Fig. 3). Such photon frequency selectivity is governed by polymer structure, effective dimensionality and also by the properties of an acceptor involved in BHJ. Strong selectivity can be used, for example, in plastic sensoric photovoltaics, whereas the composites with low selectivity seem to be more suitable for higher efficient conversion of solar energy.

C. Line width

Various static and dynamics factors can affect a line width of paramagnetic centers. One of them is the hyperfine interaction between the electrons and the nuclei of sulfur, nitrogen, and hydrogen atoms of the composite possessing appropriate nuclear magnetic moments. Polaron translational and fullerene reorientational diffusion in BHJ should also be taken into account. While a polaron possesses a high mobility, the fullerene molecule can be considered as a translatively fixed globe, however, reorientating near its own main molecular axis. In this case a polaron $\mathrm{P}^{+\bullet}_{\mathrm{mob}}$ hopping along the polymer chain with the rate ω_{hop} should interact with its unpaired electron $m\mathrm{F}^{-\bullet}_{\mathrm{mob}}$ with the collision probability p expressed by Eq. (4), so then its absorption line should additionally be broadened by the value,[44]

$$\delta(\Delta\omega) = p\omega_{\mathrm{hop}} n_i = \frac{1}{2}\omega_{\mathrm{hop}} n_i \left(\frac{\alpha^2}{1+\alpha^2}\right), \qquad (6)$$

where n_i is a number of radicals per polymer unit. The n_i parameter in Eq. (6) is temperature dependent that should be taken into account for the interpretation of line width of the experimentally obtained LEPR spectra.

Figure 4 shows the line widths of both charge carriers photoinitiated in the PCDTBT:PC$_{61}$BM composite and those normalized to the unit concentration n_i as function of temperature and photon energy $h\nu_{\mathrm{ph}}$. For this purpose the n_i values were obtained by using the "light on-light off" method. The dependences calculated from Eq. (6) and the exampled dependences fitting appropriate data obtained for $h\nu_{\mathrm{ph}} = 1.98$ eV are also presented in Fig. 4. The data presented are evidenced the applicability of the approach proposed above for interpretation of electronic processes realized in the composite under study. It is seen from the data that the line width of polarons and methanofullerene anion radicals differently depends not only on the temperature but also on the energy of the initiated photons. Besides, these charge carriers demonstrate different sign of own temperature dependence. It can be due to their different nature and dynamics mechanism in domains inhomogeneously distributed in the composite. Such inhomogeneity seems to be more characteristic for methanofullerene pools than for polaronic phase due possibly to more ordered, layer morphology of polymer matrix. Energy necessary for

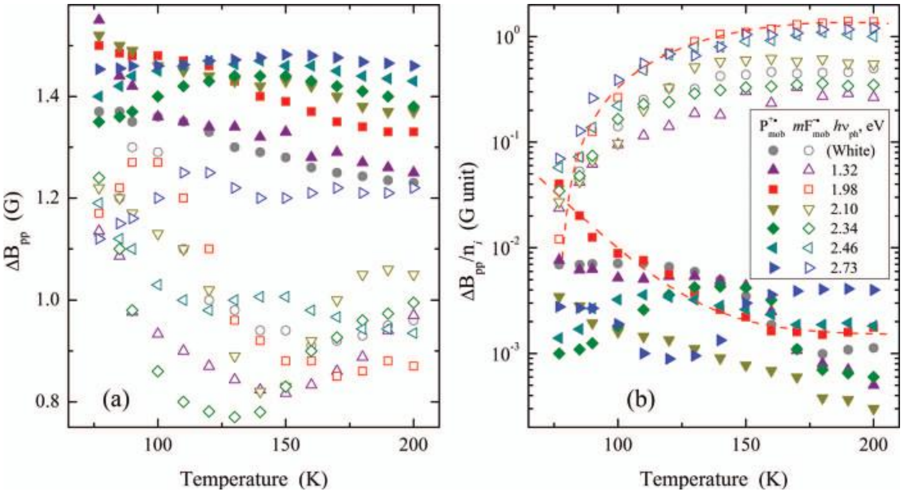

FIG. 4. Line width of stabilized and mobile charge carriers photoinduced in the PCDTBT:PC$_{61}$BM composite (a) and that normalized to their concentration per polymer unit n_i (b) as a function of temperature and photon energy $h\nu_{\mathrm{ph}}$. Above and below the dashed lines the dependences calculated as an example for $h\nu_{\mathrm{ph}} = 1.98$ eV from Eq. (6) with E_{a} equal to 0.014 and 0.001 eV, respectively. The symbol (0) in $\Delta B^{(0)}_{\mathrm{pp}}$ implies that the LEPR spectra were measured far from MW saturation, when $B_1 \rightarrow 0$.

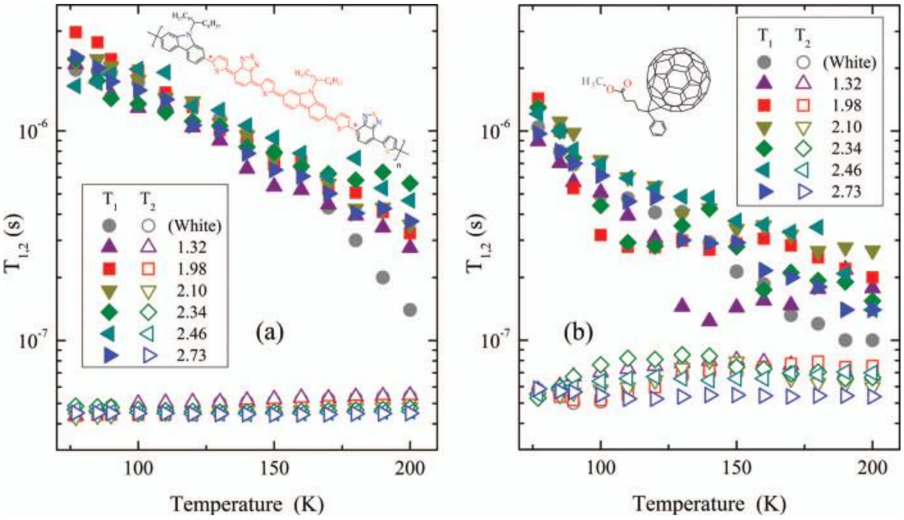

FIG. 5. Temperature dependence of spin-lattice, T_1 (filled points), and spin-spin, T_2 (open points), relaxation times of polarons (a) and methanofullerene ion radicals $m\mathrm{F}_{\mathrm{mob}}^{-\bullet}$ (b) photoinduced in the PCDTBT:PC$_{61}$BM composite by wide-band white and monochromatic light with different photon energy $h\nu_{\mathrm{ph}}$.

activation of both the charge carriers change slightly as $h\nu_{\mathrm{ph}}$ excesses the polymer bandgap. The photon-energy-correlation obtained for the main magnetic resonance parameters of the PCDTBT:PC$_{61}$BM BHJ, as in case of the P3DDT:PC$_{61}$BM composite,[45] can be used in creation of organic molecular devices with spin-assisted (spintronic) properties.

D. Spin relaxation and dynamics

As the magnetic term B_1 of microwave irradiation increases, the absorption lines of both photoinduced charge carriers start to broaden and their intensities change nonlinearly with B_1. This is due to fast passage of steady-state saturated polaron and methanofullerene anion radical spin reservoirs when their precession time becomes less than the effective relaxation time. Effective spin-lattice T_1 and spin-spin T_2 relaxation times of polarons and fullerene anion radicals determined using the steady-state saturation method[46] are presented in Fig. 5 as a function of temperature and photon energy. It is seen from Figure 5 that the interaction of most charge carriers with the polymer lattice is characterized by monotonic temperature dependence. However, the $m\mathrm{F}_{\mathrm{mob}}^{-\bullet}$ ion radicals, in contrast to polarons, demonstrate a sharper $T_1(T)$ function at low temperatures and more dispersed with the change in $h\nu_{\mathrm{ph}}$. This can possible be evidence of more ordered structure of the polymer matrix than that of methanofullerene pools.

Mobile polarons diffuse along and between PCDTBT chains with longitudinal and transverse diffusion coefficients $D_{1\mathrm{D}}$ and $D_{3\mathrm{D}}$, respectively. Besides, methanofullerene molecules reorientate around the own main molecular axis with coefficient D_{rot} in polymer matrix between its layers. Such spin dynamics induce additional magnetic fields in the BHJ accelerating electron relaxation of both spin ensembles. As relaxation times of spins in conjugated polymers are defined mainly by their dipole-dipole interaction,[34,47] the following general equations of magnetic resonance connecting their relaxation and dynamics parameters can be written:[31,48]

$$T_1^{-1}(\omega_{\mathrm{e}}) = \langle\omega^2\rangle[2J(\omega_{\mathrm{e}}) + 8J(2\omega_{\mathrm{e}})], \tag{7}$$

$$T_2^{-1}(\omega_{\mathrm{e}}) = \langle\omega^2\rangle[3J(0) + 5J(\omega_{\mathrm{e}}) + 2J(2\omega_{\mathrm{e}})], \tag{8}$$

where $\langle\omega^2\rangle = 1/10\gamma_{\mathrm{e}}^4\hbar^2 S(S+1)n\Sigma_{ij}$ is a constant of a dipole-dipole interaction for a powder with the lattice sum Σ_{ij}, $n = n_{\mathrm{loc}} + n_{\mathrm{mob}}/\sqrt{2}$ is the probability of localized, n_{loc}, and mobile, n_{mob}, spin situation on a lattice unit, $J(\omega_{\mathrm{e}}) = (2D_{1\mathrm{D}}^{|}\omega_{\mathrm{e}})^{-1/2}$ at $D_{1\mathrm{D}}^{|} \gg \omega_{\mathrm{e}} \gg D_{3\mathrm{D}}$ or $J(0) = (2D_{1\mathrm{D}}^{|}D_{3\mathrm{D}})^{-1/2}$ at $D_{3\mathrm{D}} \gg \omega_{\mathrm{e}}$ is a spectral density function for Q1D motion, $D_{1\mathrm{D}}^{|} = 4D_{1\mathrm{D}}/L^2$, ω_{e} is the resonant angular frequency of electron spin precession, and L is the spatial extent of the polaron wave function equivalent approximately 4–5 monomer units for organic conjugated polymers.[42,49] A similar spectral density function was earlier used in the study of spin dynamics in other conjugated polymers.[34,50] An appropriate spectral density function for rotational diffusion with correlation time τ_{c} is $J(\omega_{\mathrm{e}}) = 2\tau_{\mathrm{c}}/(1 + \tau_{\mathrm{c}}^2\omega_{\mathrm{e}}^2)$.

Spin diffusion coefficients calculated from Eqs. (7) and (8) for both types of charge carriers photoinduced in the PCDTBT:PC$_{61}$BM composite using appropriate relaxation and susceptibility data and the spectral density functions are presented in Fig. 6 as a function of both the temperature and initiated photon energy $h\nu_{\mathrm{ph}}$.

The figure shows that the values and frequency dispersion of all diffusion coefficients are characterized by weak dependence on the $h\nu_{\mathrm{ph}}$ value as in case of the P3HT/*bis*-PC$_{61}$BM composite which appeared to become more ordered than P3HT/PC$_{61}$BM and other known polymer/fullerene systems.[23]

The anisotropy of polaron dynamics, $A = D_{1\mathrm{D}}/D_{3\mathrm{D}}$, in the PCDTBT:PC$_{61}$BM composite is significantly lower than that obtained for analogous P3DDT:PC$_{61}$BM and P3HT:*bis*-PC$_{61}$BM BHJ,[22,51] that is typical for more ordered systems. This value determined at $T = 77$ K is charachterized by a U-like dependence on the photon energy $h\nu_{\mathrm{ph}}$ (see

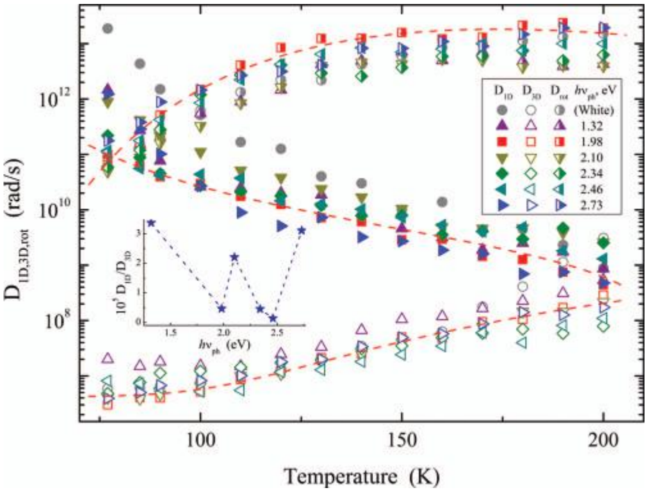

FIG. 6. Temperature dependence of intrachain (D_{1D}, filled points), interchain (D_{3D}, open points) and rotational diffusion (D_{rot}, semi-filled points) coefficients of mobile charge carriers $P^{+\bullet}_{mob}$ and $mF^{-\bullet}_{mob}$ photoinduced in the PCDTBT:PC$_{61}$BM composite by the polychromatic white and monochromatic light with different photon energy $h\nu_{ph}$ determined at their appropriate unit concentration n_i. Top-to-bottom dashed lines show the dependences calculated from Eq. (11) with $E_{ph} = 0.102$ eV, Eq. (9) with $E_b = 0.049$ eV, and Eq. (10) with $E_r = 0.067$ eV as well. The insert shows the anisotropy of polaron motion, $A = D_{1D}/D_{3D}$ as function of $h\nu_{ph}$. Dashed-dotted line shortly connects experimental points only for illustration to guide the eye.

inset of Fig. 6). This can probably be evidence of better ordering of the composite at intermediate $h\nu_{ph}$ and A values. One can only note an unusual feature of this dependence, namely the evident increase of an anisotropy of the polaron diffusion at $h\nu_{ph} = 2.10$ eV lying near the polymer bandgap. This effect can probably be explained by stronger interaction of the polymer matrix with such light photons. Indeed, the layer ordering of the polymer matrix allows longer polaron diffusion and formation of well-ordered PCBM pools located between these layers.[9,11] This can in principle lead to resonant electronic response on photon energy. If the latter becomes comparable with the polymer bandgap, the stronger polaron interaction with the lattice phonons can initiate the observed change in its g-factor and diffusion anisotropy. Earlier, we detected[52] an analogous decrease by two orders of magnetude in the anisotropy of polaron dynamics in the P3HT:PC$_{61}$BM composite as a result of its MW-treatment. This effect was explained by the increase of well-ordered polymer and methanofullerene clusters under such system modification that facilitates polaron diffusion, inhibits fullerene reorientation, and decreases interaction of charge carriers in photoinduced radical pairs. The formation of appropriate crystallites in an amorphous polymer matrix leads to the longer diffusion of charge carriers and higher light conversion efficiency. So, one can conclude better matrix planarity of the composite under study at illumination by such phonons that accelerares charge transport.

Intrachain polaron dynamics in the composite is characterized by a strong temperature dependence, so the data presented in Fig. 6 can probably be described in terms of polaron scattering on the phonons of crystalline lattice domains embedded into an amorphous matrix.[53] According to this model, such scattering should result in polaron intrachain diffusion with an appropriate coefficient,

$$D_{1D} = \frac{\pi^2 M t_0^2 k_B^2 T^2}{h^3 \alpha_{eph}^2} \cdot \left[\sinh\left(\frac{E_{ph}}{k_B T}\right) - 1\right]$$

$$= D_{1D}^{(0)} T^2 \cdot \left[\sinh\left(\frac{E_{ph}}{k_B T}\right) - 1\right], \tag{9}$$

where M is the mass of a polymer unit, t_0 is the transfer integral equal for π-electron to ~2.5–3 eV, α_{eph} is a constant of electron-phonon interaction, and E_{ph} is phonon energy. This model was also used to interprete intrachain polaron diffusion in other conjugated polymers.[34,35,54]

All E_{ph} obtained for polaron diffusion in the PCDTBT:PC$_{61}$BM composite are summarized in the Table I. Fig. 6 evidences that the D_{1D} obtained for polarons initiated by photons with, e.g., $h\nu_{ph} = 1.98$ eV follows well Eq. (9) with $E_{ph} = 0.0493$ eV. This value lies near the energy of lattice phonons determined for various conjugated polymers (0.09–0.32 eV)[34] and plastic solar cells.

The interchain spin dynamics, as in case of analogous polymer/fullerene composites,[23] could be analyzed in terms of the Hoesterey-Letson concept[55] of the trap-controlled charge hoping between polymer layers. The analysis of the data obtained, however, have showed that such approach cannot be used for the interpretation of the $D_{3D}(T)$ dependences presented in Fig. 6. These values as well as methanofullerene reorientational diffusion coefficients $D_{rot}(T)$ can rather be explained in the frame of the Pike[56] and Elliott[57] models based on the carrier hopping over the energetic barrier E_b.[58] This can be due to a suggestion that the PC produced by the influence of light might be expected to have a large effect on the *ac* mobility of charge carriers.[27] Such approach predicts the frequency and temperature dependent diffusion coefficient of polaron charge carriers,

$$D_{3D}(\omega_e T) = D_{3D}^0 T^2 \omega_e^s \exp\left(\frac{E_b}{k_B T}\right), \tag{10}$$

where the exponent $s = 1 - 6k_B T/E_b$ reflects polymer system dimensionality. The respective energies E_b required to activate polaron transverse diffusion in the PCDTBT:PC$_{61}$BM composite are also summarized in the Table I.

Finally, reorientational mobility of the methanofullerene cages can possibly be described in the framework of a semiclassical Marcus theory adopted for conjugated polymers.[59] According to this approach, methanofullerene cages should reorientate between polymer layers with the rate of

$$\omega_{rot} = \frac{4\pi^2}{\hbar} \frac{t_r^2}{\sqrt{4\pi E_r k_B T}} \exp\left(-\frac{E_r}{4k_B T}\right)$$

$$= \omega_{rot}^{(0)} \frac{1}{\sqrt{4E_r k_B T}} \exp\left(-\frac{E_r}{4k_B T}\right), \tag{11}$$

where t_r is electronic coupling between initial and final states of the globe's motion and E_r is both the inner- and outer-sphere reorganization energy of charge carriers due to their interaction with the lattice phonons. Cheung *et al.* have obtained[60] weakly temperature dependent $t_r = 1.18$ eV for P3HT and have shown that its distribution broadens a line due to thermal motion of the rings like it happens in organic crystals.[61] This value was used for the calculation of dynamics parameters of methanofullerene in the sample under study. E_r values obtained and summarized in Table I exceed the energy required for activation of reorientation of C_{60} anions in polymethylmethacrylate (0.026 eV) and C_{70} globes in cyclohexane;[62] however, lye near those determined for a motion of fullerene derivatives in conjugated polymer matrices.[22,23] It should be noted that the E_r value obtained for methnofullerene photoinitiated by achromatic (white) and monochromic (with the photon energy of 1.98 and 2.73 eV) light becomes compatible to that (0.224 eV) required for activating fullerene reorientational hopping or rotation in pure C_{60}.[63] The data described consider the dynamics of solitary polarons and fullerene. Undoubtedly, the interaction of these charge carriers with the nearest spins, lattice phonons, etc., may also affect their relaxation and, therefore, should also be taken into account when interpreting the results.

IV. CONCLUSIONS

In conclusion, we investigated in detail the magnetic and electronic properties of spin charge carriers photoinitiated in the low-bandgap PCDTBT:PC_{61}BM BHJ. The results obtained evidence directly that the main magnetic resonance, relaxation, and dynamic parameters of polarons and methanofullerene anion radicals are governed by the structure, conformation, and ordering of the composite BHJ. These parameters were also shown to be governed by the energy of excited photons initiating polaron traps with different depth and distribution in the amorphous polymer phase. The data obtained by the LEPR and IR-Vis optical methods do not correlate especially, in infrared region. The illumination of the sample by photons with the energy lying near the polymer bandgap decreases the number of such traps at low temperatures. This decreases significantly the anisotropy of polaron dynamics due probably to collective interaction of charge carriers in layer-ordered two-dimensional PCDTBT matrix. Besides, this affects more noticeably the splitting of the polarons' σ, π, and σ^* levels, increases the number of mobile spin pairs, broadens the LEPR spectrum, slightly reduces spin interaction with the polymer network, and increases diffusion anisotropy in the polymer network.

The data obtained allowed us to suggest the importance of the layer ordering of the composite matrix. Such a morphology increases the planarity and crystallinity of the polymer matrix, suppresses the appearance of spin traps, facilitates local site molecular vibrations that accelerates charge transfer through BHJ and, therefore, increases the power conversion efficiency. It was shown that a polaron diffusing along a polymer chain exchange interacts with the spin of a counter methanofullerene anion radical. This result reveals that the latter spin acts as a nanoscopic probe of the polaron dynamics. This causes a variety of mechanisms of charge transport in the PCDTBT:PC_{61}BM BHJ.

Electron relaxation of methanofullerene anion radicals in this system was shown to be more dependent on the temperature and photon energy than that of polarons. Charge transfer is governed by polaron scattering on the lattice phonons of crystalline domains embedded into amorphous polymer matrix and its activation hopping between polymer layers. Methanofullerene cages reorientate between polymer layers according to the Marcus mechanism. These spin-assisted processes are governed mainly by the structure of ingredients of a composite as well as by the nature and dynamics of photoinduced charge carriers. The specific structure of the polymer matrix changes the energy levels of appropriate composite and shifts the competition between excited states in its BHJ.

Lowered concentration of spin traps, shape of LEPR spectra, and behaviours of the main magnetic resonance parameters revealed evidence rather for the layer ordered morphology of PCDTBT matrix. Therefore, as predicted, the use of this matrix instead of conventional P3AT polythiophene derivatives indeed increases the ordering of BHJ with PCBM and minimizes the energy loss in charge transfer in respective photovoltaic system. In order to determine an impact of the structure of a methanofullerene on the main electronic and spectroscopic properties of PCDTBT-based BHJ, the appropriate LEPR study of PCDTBT:PC_{71}BM should be made. Our results suggest an important role played by interchain coupling of different spin ensembles on a handling of charge transfer in BHJ. Initiation of spins by different photons allows making such handling more delicate that is a critical strategy in creating optimal systems with spin-assisted charge transfer. Since coherent spin dynamics in such organic BHJ is anisotropic, our strategy seems to make it possible obtaining complex correlations of anisotropic electron transport and spin dynamics for the further design of progressive molecular electronic and spintronic devices. Such experiments are in progress in our team.

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