

Light-Induced EPR Spectroscopy of Charge Transfer in Low-Band-Gap PCDTBT:PC₇₁BM Bulk Heterojunctions

Victor I. Krinichnyi and Evgenija I. Yudanova

Abstract—The light-induced electron paramagnetic resonance (LEPR) study of spin charge carrier steady-state initiated by IR–Vis photons in an organic composite of a low-band-gap poly(N-9'-heptadecanyl-2, 7-carbazole-alt-5, 5-(4', 7'-di-2-thienyl-2', 1', 3'-benzothiadiazole)) with a [6, 6]-phenyl-C₇₁-butyric acid methyl ester is reported. LEPR spectra of the composite were deconvoluted, and the main resonance parameters of polarons and anion radicals of methanofullerene were determined. The reversible formation in polymer backbone of spin traps, whose number, distribution, and depth is governed by the photon energy, has been shown. Part of the photoinduced charge carriers is pinned by such traps, resulting in the formation in the composite of polymer and fullerene domains with different band gaps and photon sensitivity. Relaxation and dynamics parameters of spin charge carriers were shown to depend on the energy of exciting photons. The mechanisms of polaron diffusion along and between polymer chains, as well as librations of methanofullerene cages in a polymer matrix, were proposed. Our results suggest that the use of C₇₀-counterions as an electron acceptor in the composite provokes its layered morphology. This hinders the formation of spin traps, increases the path length for charge carriers, and, therefore, accelerates their spin-assisted relaxation and dynamics through bulk heterojunctions within the visible and infrared regions of the sun spectrum with comparable effectiveness.

Index Terms—Magnetic susceptibility, millimeter wave measurements, organic photovoltaics (PV), paramagnetic resonance, polaron, polymer- and small-molecule-based organic PV, relaxation.

I. INTRODUCTION

THE discovery of the photovoltaic (PV) effect in an organic composite of an electron-donating conjugated polymer and an electron-accepting fullerene and its intensive study clearly demonstrated the formation upon light illumination of excitons which can be transformed into donor–acceptor complexes collapsing into radical pairs, positively charged polarons delocalized along polymer chains, and negatively charged fullerene anion radicals embedded into polymer matrix [1]. This evidenced a breaking down of strongly bound neutral excitons on a picosecond time scale into spin-charge-carrying quasi-pairs due to photoinduced electron hopping from the conjugated polymer to the fullerene cage. This effect can be used

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The authors are with the Institute of Problems of Chemical Physics, Chernogolovka 142432, Russia (e-mail: kivi@cat.icp.ac.ru; yudan@icp.ac.ru).

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for the realization of low-cost printable, portable, and flexible renewable energy sources [2]. Previous research has mainly focused on bulk heterojunctions (BHJ) formed by conjugated polymers and fullerene derivatives. One key characteristic for such compounds is the nanophase separation between polymer and fullerene subsystems, which leads to a large interface for charge dissociation, and bicontinuous pathways for charge transport. The soluble poly(3-hexylthiophene) alias P3HT and [6,6]-phenyl-C₆₁-butyric acid methyl ester alias PC₆₁BM mainly used for such purposes as electron donor and acceptor, respectively, allowed reaching a power conversion efficiency of 4–5% [3]. The efficiency becomes so small because of the relatively large band gap of P3HT (~1.9 eV) limiting the fraction of the solar spectrum and the relatively small energy difference between the highest occupied molecular orbital (HOMO) of P3HT and the lowest unoccupied molecular orbital (LUMO) of PC₆₁BM. In order to improve the light power conversion efficiency, these energies defined by the polymer band gap and HOMO should be decreased.

Recently, several low-band-gap copolymers based on poly(2,7-carbazole) derivatives were developed to absorb the wider solar spectrum with deeper HOMO [4], [5]. These polymers are characterized by the internal charge transfer from an electron-rich unit to an electron-deficient moiety within each repeating unit. Tuning of their light-absorption ability and energy levels foredoomed extensive development and study. Among them, poly[[9-(1-octylonyl)-9H-carbazole-2, 7-diyl]-2, 5-thiophenediyl-2, 1, 3-benzothiadiazole-4, 7-diyl-2, 5-thiophenediyl] alias PCDTBT (shown schematically in Fig. 1) with a band gap near 1.88 eV [6] was discovered [7] to be one of the most efficient matrices for organic plastic field-effect transistors and solar cells [8]–[11]. The light conversion efficiency of the PCDTBT:PC₇₁BM composite layer was recently reached 6–7% [12], [13] because of a relatively deep HOMO of active matrix and maximal internal quantum efficiency approaching. The higher light absorbance is due to the lower spherical symmetry of the fullerene in PC₇₁BM cage, as compared with PC₆₁BM globe in appropriate PCDTBT:PC_{x1}BM BHJ [14]. However, it should be noted that the extended spectral range of absorption may be overbalanced by recombination losses or, alternatively, by wasteful triplet formation [15]. Higher efficiency was reached due mainly to ultrafast charge separation in the PCDTBT:PC₇₁BM composite before localization of the primary excitation to form a bound exciton in contrast with conventional polymer:fullerene systems [16]. Besides, morphology of the PCDTBT:PC₇₁BM BHJ becomes laterally oriented with a

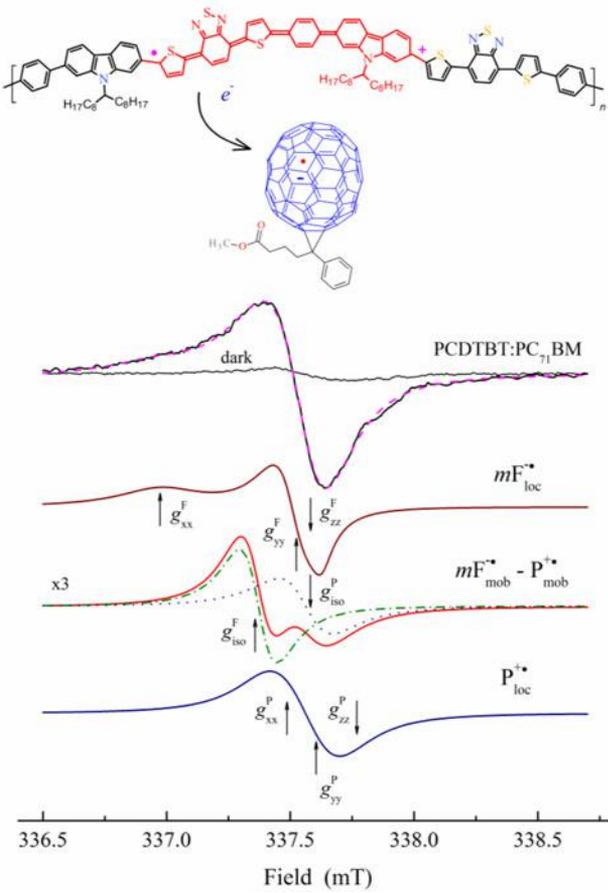


Fig. 1. Dark and background irradiated by white light with the color temperature $T_c = 5500$ K at $T = 77$ K 3-cm waveband LEPR spectra of the PCDTBT:PC₇₁ BM composite (1), attributed to localized methanofullerene anion radicals $mF_{loc}^{\bullet\bullet}$ and polarons $P_{loc}^{\bullet\bullet}$, as well as mobile radical quasi-pairs $P_{mob}^{\bullet\bullet} - mF_{mob}^{\bullet\bullet}$. The main values of their g -tensors g_{ii} and isotropic g -factors g_{iso} are shown as well. The spectrum calculated using $g_{iso}^P = 2.0024$ and $g_{iso}^{mF} = 2.0036$ determined from the fitting for $P_{mob}^{\bullet\bullet}$ and $mF_{mob}^{\bullet\bullet}$, respectively, fixed shifts $g_{iso}^P - g_{xx} = -7.3 \times 10^{-4}$, $g_{iso}^P - g_{yy} = 7.0 \times 10^{-5}$, $g_{iso}^P - g_{zz} = 6.7 \times 10^{-4}$, $g_{iso}^{mF} - g_{xx} = -2.37 \times 10^{-3}$, $g_{iso}^{mF} - g_{yy} = 8.3 \times 10^{-4}$, $g_{iso}^{mF} - g_{zz} = 1.53 \times 10^{-3}$, determined at D-band EPR for $P_{loc}^{\bullet\bullet}$ and $mF_{loc}^{\bullet\bullet}$, respectively, immobilized in the PCDTBT:PC₇₁ BM BHJ (see the text), and concentration ratio for these charge carriers $[P_{loc}^{\bullet\bullet}]:[P_{mob}^{\bullet\bullet}]:[mF_{loc}^{\bullet\bullet}]:[mF_{mob}^{\bullet\bullet}] = 1.00:1.39:2.37:1.39$ is shown by dashed line. Spectral terms calculated for $P_{mob}^{\bullet\bullet}$ and $mF_{mob}^{\bullet\bullet}$ are shown by dotted and dash-dotted lines, respectively. At the top, the formation of polaron and methanofullerene charge carriers accompanying by the transfer of an electron from the PCDTBT chain to the PC₇₁ BM cage is also shown schematically. It should be noted that a polaron is normally delocalized on nearly three PCDTBT units [26].

“column-like” bilayer ordered polymer backbone [17], [18] that improves the intralayer carrier mobility. Higher π -overlapping in such a 2-D polymer backbone hinders its torsional twisting and, therefore, decreases the energy of its band gap [19]. This also accelerates charge hopping along and between PCDTBT bilayers. This is evidenced that charge dynamics also affects the efficiency of device light conversion. Understanding the charge separation, transport, and recombination in such materials at a molecular level is crucial for improving the electronic properties and efficiency of appropriated elements of molecular

electronics. However, the link between the quantum efficiency, dynamics of charge carriers, and energy of photons within the BHJ absorption spectrum has yet to be established.

Opposite charge carriers are characterized by spin $S = 1/2$; therefore, their magnetic, relaxation, and dynamic properties can be undoubtedly studied in detail by inter alia light-induced electron paramagnetic resonance (LEPR) spectroscopy [2], [20]–[22]. The method appeared to be a very efficient tool for studying electronic transfers within BHJ on the molecular scale because it allows *in situ* detection of the paramagnetic species resulting from such transfers. LEPR measurements, especially at millimeter wavebands [23]–[26], revealed the existence of polarons and fullerene counterions with different line shapes, EPR parameters, and saturation properties. The method allowed detecting electron relaxation in combination with the microwave (MW) power saturation method and lifetime [27], as well as recombination processes [28], [29] of spin charge carriers in various polymer:fullerene systems. Niklas *et al.* [26] determined by using the D-band (130 GHz) LEPR method the main values of g -tensors, $g_{xx} = 2.0032$, $g_{yy} = 2.0024$, $g_{zz} = 2.0018$ for polarons and $g_{xx} = 2.0060$, $g_{yy} = 2.0028$, $g_{zz} = 2.0021$ for methanofullerene anion radicals photoinduced in the PCDTBT:PC₇₁BM composite at $T = 50$ K. Main properties of charge carriers in molecular electronic materials were proved to be spin-dependent [30]. This means that their spin origin can play a key role in the controlling and handling of electronic properties of photovoltaic devices by the EPR spectroscopy. Composition, relaxation, and dynamics of charge carriers photoinduced in organic semiconductors are governed by spin-dependent exciton-charge interactions and consistent with the model of spin-assisted recombination of polaron pairs [31]. Therefore, the study of photoinitiated electronic processes in polymer:fullerene systems under spin resonance could help us in creation of novel organic photovoltaic and spintronic devices. However, the dynamics and interaction of different spin ensembles affecting conversion efficiency of such and other polymer:fullerene BHJs are under debate, and there are no simple picture cleaning spin-resonance-assisted processes in organic photoexcited systems.

It was shown that a part of polarons formed after exciton initiation under irradiation of polymer backbone is pinned by spin traps whose number and depth are governed by the composite morphology and photon energy [32], [33]. Spin relaxation and charge carrier dynamics were shown to be governed by spin exchange and by the photon energy [32]–[35]. Formation, relaxation, and dynamics of these charge carriers in the PCDTBT:PC₆₁BM BHJ were studied in wide photon energy and temperature ranges [36]. The essential LEPR response of this composite appeared to be registered upon its irradiation even by IR photons with the energy (wavelength) of 1.32 eV (940 nm), where the optical absorption band is reset. This means that the spin concentration in the sample does not definitely correlate with the number of optical quanta reached and absorbed by the sample. This does not confirm the conclusion made by Tong *et al.* [37] that the efficiency of carrier initiation in the fullerene-modified PCDTBT should be essentially independent of the excitation photon energy within the sun spectrum.

Here, we use direct LEPR spectroscopy combined with the MW steady-state saturation method to study the magnetic, relaxation, and electronic properties of charge-separated states of the PCDTBT:PC₇₁BM BHJ upon wider range IR–Vis illumination. It is demonstrated that the use of the PC₇₁BM counterions instead of the PC₆₁BM ones in an appropriate composite leads to an arrangement of polymer matrix that increases its planarity, decreases the number of spin traps, and, therefore, accelerates spin dynamics in BHJ. The composite with PCDTBT matrix was confirmed to converse photons into spin charge carriers not only under visible light but at infrared irradiation with comparable effectiveness as well.

II. MATERIALS AND METHODS

A. Materials

In the study, poly[N-9'-heptadecanyl-2, 7-carbazole-alt-5, 5-(4',7'-di-2-thienyl-2', 1', 3'-benzothiadiazole)] (PCDTBT) distributed by the St-Jean Photochemicals Inc. and 99.5% [6, 6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) obtained from Solenne BV without further purification were used. The insert of Fig. 1 shows schematically chemical structures of these ingredients. First, 0.7 mg of PCDTBT was diluted in 0.5 ml of chlorobenzene:di-chlorobenzene (3:1) mixture. This solution was treated in ultrasonic bath LT-05C (60 W) for 5 min with following heating at $T = 333$ K within 5 min. Fullerene derivative was added to the so-treated solution amounting PCDTBT:PC₇₁BM ratio to be 1:4, after which the resulting solution was additionally maintained at $T = 333$ K within 20 h for PC₇₁BM complete dissolution. The prepared solution was serially casted into both sites of ceramic plate and dried until polymer:fullerene composite was formed as double-sided film, both with the size of ca. $8 \times 4 \times 0.1$ mm³.

B. Methods

- 1) *Light sources:* The sample was permanently irradiated by the solid-state polychromic LXHL-LW3C (white, color temperature $T_c = 5500$ K, 5800 lx) and monochromic YT-5WIR850-H (1.32 eV/940 nm, 860 lx), HH-5WP2TR8502112-M-P (1.46 eV/850 nm, 1160 lx), HH-5WP2TR7702112-M-P (1.61 eV/770 nm, 1280 lx), HH-5WP2XR2112-T-P (1.91 eV/650 nm, 1180 lx), LXHL-LD3C (1.98 eV/625 nm, 5150 lx), LXHL-LL3C (2.10 eV/590 nm, 2500 lx), LXHL-LM3C (2.34 eV/530 nm, 3130 lx), LXHL-LE3C (2.46 eV/505 nm, 6200 lx), HH-5WP2AG2112-T-P (2.53 eV/490 nm, 6000 lx), LXHL-LR3C (2.73 eV/455 nm, 6150 lx) LED light sources with a spectral half bandwidth of ca. 15 nm/0.1 eV directly in the MW cavity through quartz light guide. Integral illuminance (I , lx) 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 concentration. In order to decompose overlapping signals for estimation more precisely their parameters, the “light on-light off” method with subsequent annealing was applied.

- 2) *EPR measurements:* All spectra were obtained using an X-band (3-cm, 9.7 GHz) PS-100X spectrometer with maximal MW power of 150 mW and 100-kHz field *ac* modulation for phase-lock detection. The former allowed reaching magnetic term B_1 of MW field up to 0.48 mT. “Dark” and photoinduced EPR spectra of the composite were obtained at 77 K in quartz Dewar filled with liquid nitrogen and at 90–340 K in dry nitrogen flow using a BRT SKB IOH temperature controller. In the latter case, the temperature is controlled by calibrated Cu/Cu:Fe thermocouple with high sensitivity (15 μ V/K at 20 K) and stability (0.5 K) situated around the sample. Gaseous nitrogen flow with the stability of 0.1% makes it possible to vary temperature in the EPR cavity center with the error of 0.3 K. All the spectra were recorded under the same gain, modulation, accumulation times, accumulation number, and MW power. The signal-to-noise ratio of the LEPR spectra was improved by signal averaging at several (typically four to six) acquisitions. The number of all paramagnetic centers stabilized and photoinitiated in the composite was determined using comparable double integration of their contributions accurately deconvoluted from effective LEPR spectra and that of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) nitroxide radical registered far from their MW saturation when the value of B_1 and amplitude of *ac* modulation B_m in the cavity center did not exceed 0.005 and 0.1 mT, respectively. Operating conditions were chosen to avoid significant power saturation and modulation broadening, whereas electron relaxation parameters of both type charge carriers were determined separately using the steady-state saturation method [38] at $B_1 \leq 0.048$ mT. Processing and simulations of the EPR spectra were performed with the Bruker SimFonia and OriginLab softwares. The error of determination of the spectral amplitude, width, and position does not exceed $\pm 3.8\%$, ± 1.2 , and $\pm 0.11\%$.

III. RESULTS AND DISCUSSION

A. Spin Composition and Electron Paramagnetic Resonance Parameters

Fig. 1 exhibits EPR spectra of the PCDTBT:PC₇₁BM composite obtained without and with its background irradiation by polychromic (white, 5500 K) light at $T = 77$ K directly in the cavity of EPR spectrometer. Normally, shadowed polymer:fullerene samples demonstrate weak-single EPR spectra attributed to intrinsic paramagnetic defects (see, e.g., [23], [26], and [39]). The dark EPR spectrum of the composite under study presented in Fig. 1 was analyzed to be also due to its interaction with few IR photons inside the spectrometer (see below). LEPR spectra consist of lines contributed from paramagnetic centers with different concentration, mobility, and EPR parameters.

PCDTBT contains some *S* and *N* heteroatoms with perceptible nuclear magnetic moment, therefore characterizing by different hyperfine constant. Weak spin–orbit interaction of an unpaired electron delocalized on a polaron with such heteroatoms was shown by the high-field EPR spectroscopy [40], [41] to provoke

rhombic symmetry of spin density and, therefore, anisotropic g -factor and linewidth. Since the backbone of a conjugated polymer is preferably parallel to the film substrate [3], the lowest principal g -value, i.e., g_{zz} , is normally associated with the polymer backbone. This parameter is governed by the structure and morphology of polymer matrix, hyperfine interaction of a polaron spin with a heteroatom nuclear, etc. EPR parameters of a fullerene anion radical are also weakly anisotropic. However, in contrast with a polaron, unpaired electron is localized rather on its C_{x0} -cage and weakly interacts with side groups [25]. If these spins move in condensed media, these parameters are averaged shifting to an effective (isotropic) g -factor, $g_{iso} = (g_{xx} + g_{yy} + g_{zz})/3$. The linewidth of these charge carriers is also averaged.

In order to obtain and analyze these parameters, one should deconvolute such spectra using the “light on–light off” procedure [25], [26], [33]. Each light photon initiates *a priori* a pair of opposite mobile charge carriers with averaged magnetic parameters. The part of these carriers is captured by spin traps; therefore, anisotropy of their LEPR spectra becomes more obvious. Using under these assumptions the main values of g -tensors determined for charge carriers initiated in the PCDTBT:PC₇₁BM at 130-GHz waveband EPR by laser photons with the energy/wavelength of 2.33 eV/532 nm [26], one can obtain separately their magnetic resonance, relaxation, and dynamics parameters. Therefore, sum experimental LEPR spectra of the system under study as in the case of other PC₇₁BM-based polymer composites [25], [26], [33] were assigned to mobile radical quasi-pairs of the positively charged polarons $P_{mob}^{+\bullet}$ moving along polymer chains and methanofullerene anion radicals $mF_{mob}^{-\bullet}$ pseudorotating near own main molecular axis within polymer matrix, as well as respective paramagnetic centers $P_{mob}^{+\bullet}$ and $mF_{loc}^{-\bullet}$ captured by spin traps reversibly photoinduced in this matrix. Spectral contributions of these spins are also presented in Fig. 1. All terms of the sum spectra were analyzed to be characterized by Lorentzian line shape. As in the case of the P3HT:PC₆₁BM [32], [42] and PCDTBT:PC₆₁BM [36] composites, this argues in favor of a smaller number of spin traps and faster spin dynamics in the sample under study.

Normally, photoinitiation of such charge carriers occurs in the femtosecond time scale, whereas electron back transfer with charge annihilation is much slower due to relatively fast dynamics and slow structural relaxation in such a system [43], [44]. This is why an effective number of spin charge carriers should inversely depend on the probability of their recombination. Such a process is determined by spin multistage activation diffusion along a polymer chain and tunneling from a chain to a fullerene anion [45]. The decay of mobile charge carriers photoinitiated in a polymer:fullerene system consists of temperature-independent fast and exponentially temperature-dependent slow contributions [32], [35], [46]. These processes are, respectively, ascribed to bimolecular recombination of mobile and less-mobile charge carriers trapped in deeper states [47]. As in the case of PCDTBT:PC₆₁BM BHJ [36], the illumination of the composite under study, however, leads to drastic decrease in spin concentration in its BHJ. This is the evidence

for fewer spin traps in this matrix that can also improve the electronic properties of this system.

B. Spin Concentration

Effective concentration of all spins photoinduced in the PCDTBT:PC₇₁BM BHJ under permanent illumination by white light was determined to be $N = 3.3 \times 10^{19}$ spin/g at $T = 77$ K. This value is less than that by a factor of ~ 3 determined for PCDTBT:PC₆₁BM composite at analogous experimental conditions. This fact may indicate, e.g., the formation of a smaller number of trapped charge carriers and their faster recombination in the system under study. Because spin concentration is a function of spin traps [47], the number of charge carriers depends on the energy of initiating photons $h\nu_{ph}$, as it is shown in Fig. 2(a). This can be explained by the reversible formation of spin traps in polymer matrix upon its light illumination. The number, depth, and distribution of such traps were shown [33], [36] to depend on the structure of polymer matrix and energy of the light photons. It is seen from Fig. 2(a) that the number of localized methanofullerene anion radicals obtained at $h\nu_{ph}/\lambda_{ph} \approx 2.25$ eV/550 nm is slightly more than that determined for white light. Such an effect may be due to simultaneous formation of spin traps with different distribution and depth. In this case, a series of spin location and dislocation can be realized; therefore, one can detect only effective number of localized spins not obviously equal to that registered under monochromatic illumination. A more significant change of spin concentration with a frequency occurs for mobile quasi-pairs $P_{mob}^{+\bullet} - mF_{mob}^{-\bullet}$. Rather extreme dependence of spin number on the photon energy is registered for photon of visible light band at $h\nu_{ph}/\lambda_{ph} \approx 2.7$ eV/460 nm lying around characteristic extremes registered in both the optical and photon-to-current efficiency spectra of morphologically optimized PCDTBT:PC₇₁BM films [37], [48].

Two main features should be noticed from an analysis of the data presented. One of them is the initiation of spin charge carriers not only by photons of visible light photons (whose right subbands are restricted by horizontal dashed segments) but also by near-IR ones (left sub-band) analogously to that as it was detected in the case of the PCDTBT:PC₆₁BM system [36]. Thus, one can conclude that the weak spectrum obtained in the absence of light irradiation and shown in Fig. 1 might be attributed to the same paramagnetic centers originated due to interior IR irradiation of different scheme warmed elements of EPR spectrometer. Besides, the number of photons absorbed by the polymer:fullerene system does not correlate with an effective number of spins initiated by these photons.

Once the temperature of the composite rises, the number of spin charge carriers decreases, as it shown in Fig. 2(b). Such spin decay can be explained in terms of its recombination with opposite charge carrier during polaron quasi-1-D (Q1D) motion. When such carrier diffuses in polymer backbone between initial i and final j sites, it spends the energy ΔE_{ij} . This follows by its recombination with opposite charge on fullerene globe. Therefore, the decay of both spin charge carriers should follow

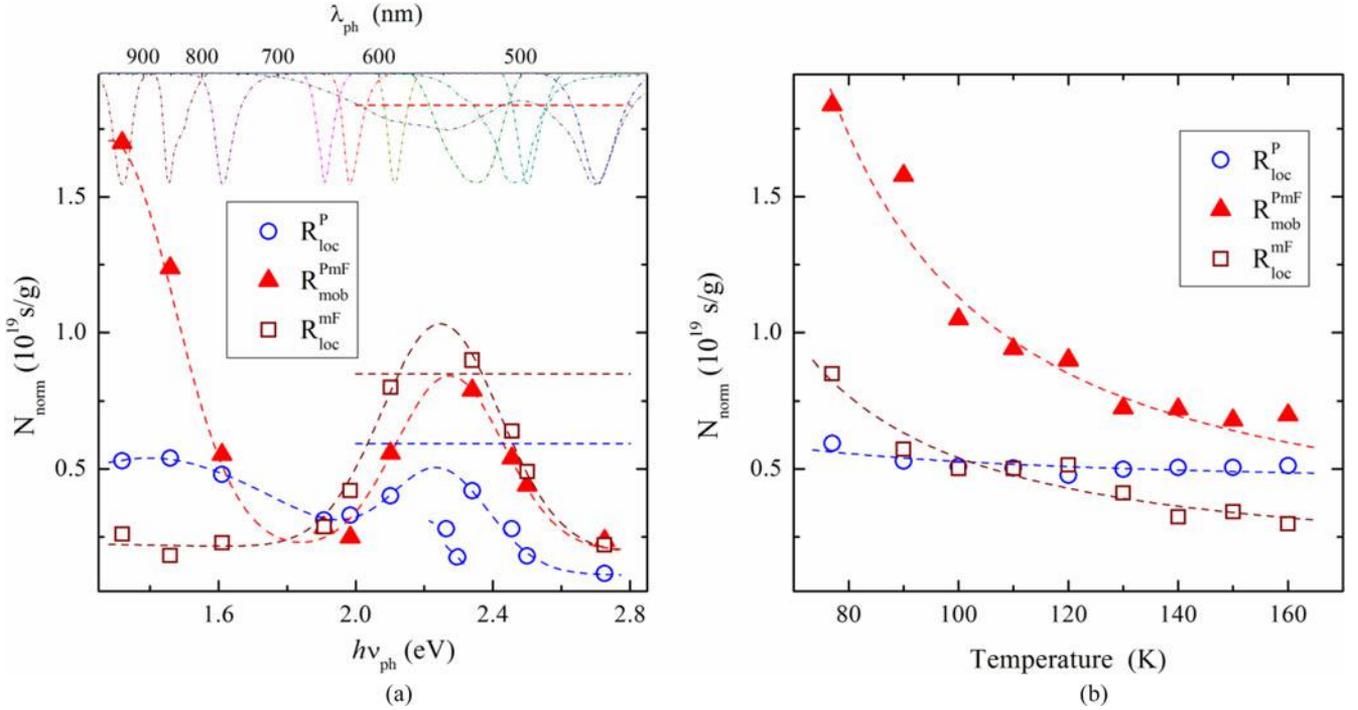


Fig. 2. (a) Concentration of immobilized charge carriers $\text{P}_{\text{loc}}^{+\bullet}$, $\text{mF}_{\text{loc}}^{-\bullet}$ and mobile quasi-pairs $\text{P}_{\text{mob}}^{+\bullet} - \text{mF}_{\text{mob}}^{-\bullet}$ photoinduced in the PCDTBT:PC₇₁ BM composite at $T = 77$ K as a function of photon energy $h\nu_{\text{ph}}$ (wavelength λ_{ph}) normalized to illuminance I of light sources. Respective values determined for these centers initiated in the system by white light are shown by the bottom, middle, and top horizontal dashed lines, respectively. These sectors are limited by the emission band of a white light source. Top dashed-dotted lines show the spectra of polychromatic white and monochromatic light sources. Dashed lines connecting the experimental points are painted arbitrarily only for illustration to guide the eye. (b) Temperature dependence of concentration of these charge carriers photoinduced in the composite by photons of white light with $T_c = 5500$ K. Up-to-down dashed lines show the dependences calculated from (1) with $\Delta E_{ij} = 0.015$, 0.002, and 0.012 eV, respectively.

the Miller–Abrahams energy-dependent equation [49]:

$$N(\Delta E_{ij}) = N_0 \exp\left(\frac{\Delta E_{ij}}{k_B T}\right) \quad (1)$$

where N_0 is an initial number of spins, k_B is the Boltzmann constant. It is seen from Fig. 2(b) that the dependences calculated from (1) with $\Delta E_{ij} = 0.002$, 0.012, and 0.015 eV fit well with the experimental data obtained for the $\text{P}_{\text{loc}}^{+\bullet}$, $\text{mF}_{\text{loc}}^{-\bullet}$ and $\text{P}_{\text{mob}}^{+\bullet} - \text{mF}_{\text{mob}}^{-\bullet}$ charge carriers, respectively. Pandey *et al.* have shown [50] that the charge is transferred through PCDTBT:PC₇₁ BM BHJ mainly by holes. This fact may explain the higher value of ΔE_{ij} obtained for opposite charge carriers.

C. Light-Induced Electron Paramagnetic Resonance Linewidth

Generally, linewidth of paramagnetic centers in solids is governed by their hyperfine interaction with neighboring nuclei. Interaction between electronic spins should also accelerate their relaxation and, therefore, broaden EPR spectra. An additional line broadening can be due to spin translational or/and reorientational dynamics. Immobilization of paramagnetic centers by spin traps should also broaden their effective EPR line. The linewidths of both charge carriers photoinduced in the PCDTBT:PC₇₁ BM BHJ by photons of different energy at $T = 77$ K are summarized in Table I. The analysis of the data presented allows concluding the notable monotonic line

broadening with increasing photon energy. This evidences that the number and depth of such traps are governed by the energy of initiating phonons.

A polaron $\text{P}_{\text{mob}}^{+\bullet}$ hopping along the polymer chain with the rate ν_{hop} can interact with unpaired electrons of methanofullerene anion radicals, quasi-rotating or captured by the spin traps, considering as more fixed centers as compared with diffusing polarons. This process should additionally broaden individual line by the value [51]

$$\delta(\Delta\omega) = \frac{\alpha^2 \nu_{\text{hop}} n_i}{2(1 + \alpha^2)} \quad (2)$$

where $\alpha = (3/2)2\pi J/h\nu_{\text{hop}}$, J is the constant of exchange interaction of spins in a radical pair, h is the Plank constant, $\nu_{\text{hop}} = \nu_{\text{hop}}^{(0)} \exp(-E_a/k_B T)$, prefactor $\nu_{\text{hop}}^{(0)}$ is the hopping attempt frequency, E_a is the activation of polaron motion along polymer chain, and n_i is a number of radicals per polymer unit. Weak and strong exchange limits can be realized in such a multi-spin system. In the case of weak or strong exchange, the increase of ν_{hop} may result in the decrease or the increase in exchange frequency, respectively.

Isotropic widths of both contributions into an effective LEPR spectrum of the PCDTBT:PC₇₁ BM composite are shown in Fig. 3 as a function of temperature. The concentration of respective spins per polymer unit n_i is also governed by the temperature. Therefore, in order to analyze real spin exchange on

TABLE I
PEAK-TO-PEAK LINEWIDTH $\Delta B_{pp}^{(0)}$, SPIN-LATTICE T_1 , SPIN-SPIN T_2 RELAXATION TIMES, AND ANISOTROPY OF SPIN DYNAMICS, $A = D_{1D}/D_{3D}$, DETERMINED FOR CHARGE CARRIERS INITIATED IN THE PCDTBT:PC₇₁ BM BHJ BY PHOTONS WITH DIFFERENT ENERGY $h\nu_{ph}/\lambda_{ph}$ AT $T = 77$ K

Parameter	White	$h\nu_{ph}/\lambda_{ph}$, eV/nm									
		1.32 / 940	1.46 / 850	1.61 / 770	1.91 / 650	1.98 / 625	2.10 / 590	2.34 / 530	2.46 / 505	2.53 / 490	2.73 / 455
$\Delta B_{pp}^{(0), a)}$ mT	0.174	0.221	0.149	0.166	0.182	0.203	0.233	0.213	0.197	0.196	0.252
$\Delta B_{pp}^{(0), b)}$ mT	0.147	0.183	0.168	0.189	0.171	0.162	0.172	0.229	0.251	0.242	0.231
$T_1^P, c)$ 10^{-6} s	2.30	2.91	1.93	1.71	1.52	1.51	1.33	1.03	1.16	1.28	2.21
$T_1^{mF}, d)$ 10^{-6} s	0.67	0.51	0.79	1.03	2.05	2.15	1.66	0.69	0.71	0.93	1.02
$T_1^{mF}, e)$ 10^{-6} s	0.04	1.29	1.03	0.83	0.83	0.58	0.27	0.31	0.31	0.25	0.16
$T_2^P, a)$ 10^{-8} s	3.78	2.44	2.63	2.68	2.89	2.85	2.94	3.09	3.34	3.35	2.74
$T_2^{mF}, b)$ 10^{-8} s	5.72	3.59	3.91	4.02	4.10	4.11	3.86	2.86	2.61	2.72	2.84
$A, 10^5$	49	66	34	21	7.6	6.3	2.1	0.78	0.82	1.9	47

Notes: ^{a)}determined for polarons $P^{+\bullet}$, ^{b)}determined for methanofullerene anion radicals $mF_{loc}^{-\bullet}$, ^{c)}determined for immobilized polarons $P_{loc}^{+\bullet}$, ^{d)}determined for immobilized methanofullerene anion radicals $mF_{loc}^{-\bullet}$, ^{e)}determined for mobile methanofullerene anion radicals $mF_{mob}^{-\bullet}$.

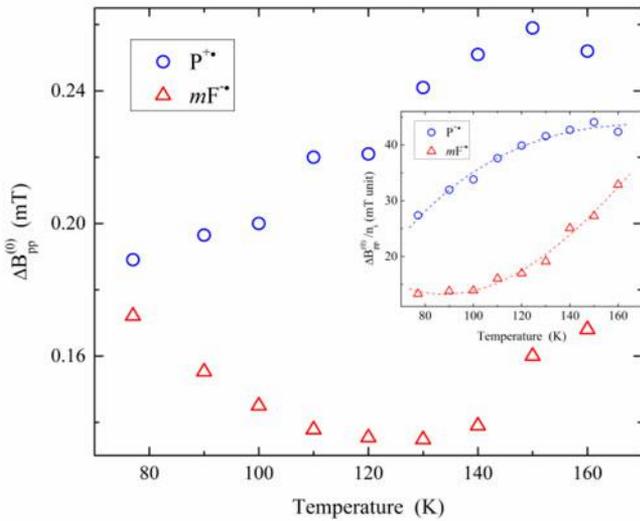


Fig. 3. Temperature dependence of the effective peak-to-peak linewidth $\Delta B_{pp}^{(0)}$ determined for the polarons $P^{+\bullet}$ (circles) and methanofullerene anion radicals $mF_{71}^{-\bullet}$ (triangles) photoinduced in the PCDTBT:PC₇₁ BM composite by photons of white light with $T_c = 5500$ K. The upper (0) symbol in $\Delta B_{pp}^{(0)}$ means that this parameter is measured far from the spectrum MW saturation. The same values divided by the number of appropriate charge carriers per a polymer unit $\Delta B_{pp}^{(0)}/n$ are shown as function of temperature. The dependences calculated from (2) with $\nu_{hop}^{(0)} = 2.9 \times 10^7$ s⁻¹, $E_a = 0.008$ eV and $\nu_{hop}^{(0)} = 3.3 \times 10^7$ s⁻¹, $E_a = 0.009$ eV are shown by the top and bottom dashed lines. The error margins do not exceed the symbol size.

linewidth, one should consider the $\Delta B_{pp}^{(0)}/n_i$ ratio. Taking into account such a relation, the dependences calculated from (2) with $E_a = 0.008$ and 0.009 eV are also shown in the insert of Fig. 3. This evidences the applicability of the approach proposed above for spin interactions realized in the composite under study. It is seen from the figure that the linewidth of polarons and methanofullerene anion radicals differently depends on the temperature. As in the case of the PCDTBT:PC₆₁ BM BHJ [36], it can be due to the different nature and the mechanism of motion of spin charge carriers in domains inhomogeneously distributed in the composite under study. Such inhomogeneity is more

characteristic for methanofullerene cages than for the polaronic phase, possibly due to more ordered layer morphology of the composite matrix [52]. This possibility causes a difference in activation energies obtained for both charge carriers. An opposite temperature dependence of their linewidths can be explained by different interaction with nearest environment analogously to that as it is realized in other BHJ [22], [53]. The energies E_a necessary to activate the motion of polaronic and methanofullerene charge carriers in the PCDTBT:PC₇₁ BM BHJ were appeared to be considerably smaller than those (0.028 and 0.013 eV, respectively) obtained for the PCDTBT:PC₆₁ BM composite at the same experimental conditions [36]. This is additional evidence of a more ordered structure of the composite under study.

D. Spin Relaxation and Dynamics

With the increase of magnetic term B_1 of MW field, the intensity of LEPR spectra of polarons and methanofullerene anion radicals stabilized and photoinitiated in the PCDTBT:PC₇₁ BM BHJ first linearly increases, plateaus starting from some B_1 value, and then decreases due to manifestation of an MW saturation effect [38]. Because the saturation behavior of the LEPR of polymer:fullerenes BHJ indicates a different relaxation mechanism of both charge carriers [54], this allows us to determine separately the spin-lattice T_1 and spin-spin T_2 relaxation times of these paramagnetic centers at wide regions of the temperature and photon energy $h\nu_{ph}$. Relaxation times obtained for charge carriers photoinduced in the system under study at different $h\nu_{ph}$ and $T = 77$ K are summarized in Table I.

On analyzing of the data obtained, one can conclude that the spin-lattice relaxation of charge carriers $P_{loc}^{+\bullet}$ and $mF_{mob}^{-\bullet}$ accelerates rather monotonically with the increase of $h\nu_{ph}$. The interaction of immobilized polaron with own environments, however, decreases at $h\nu_{ph} = 2.73$ eV. The same relaxation parameter of $mF_{loc}^{-\bullet}$ increases remarkably only at $h\nu_{ph} \approx 1.9$ – 2.1 eV, changing weakly at the lower and higher photon energy. All the centers demonstrate weak $T_2(h\nu_{ph})$ dependence within all the energy region used (see Table I). The temperature also slightly affects spin-spin relaxation of all spin packets (not presented). The T_1 value of immobilized polarons changes weakly within the temperature range 77–160 K. On the other hand, opposite charge

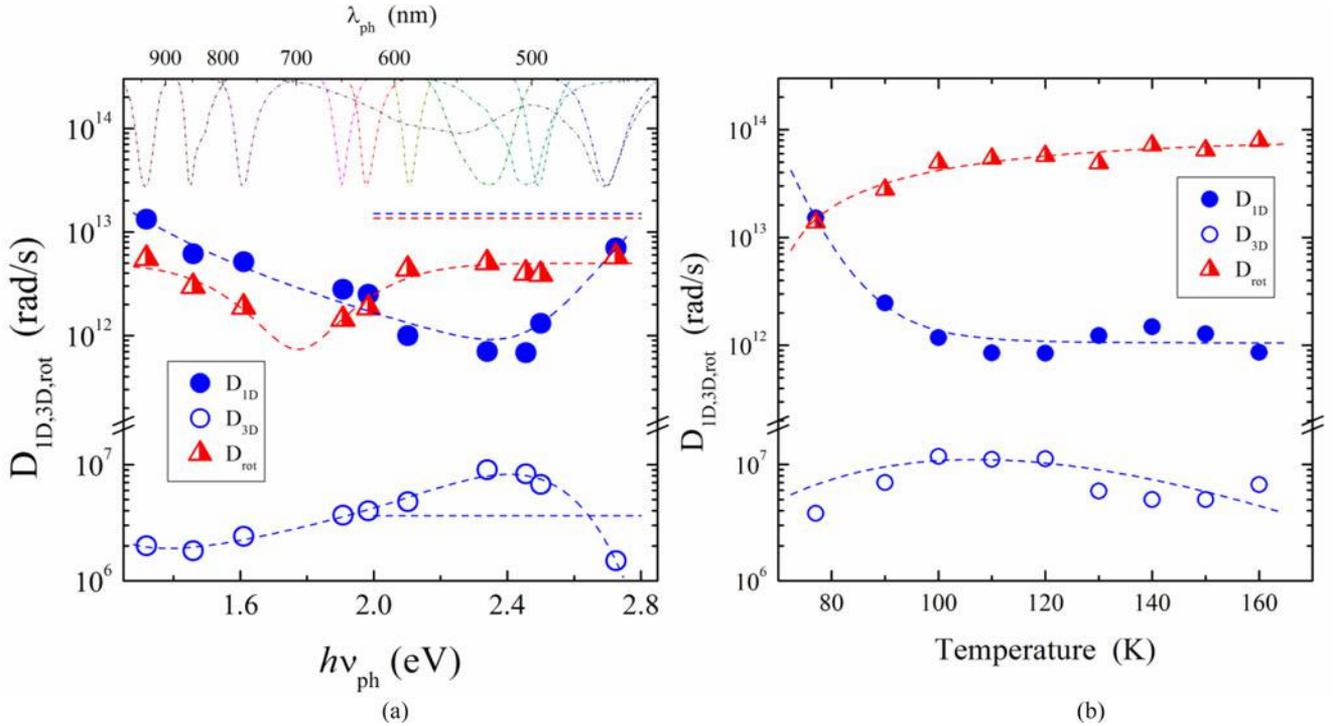


Fig. 4. (a) Coefficients of intrachain (D_{1D} , filled points) and interchain (D_{3D} , filled points) translative polaron $P_{mob}^{+\bullet}$ diffusion, as well as librative quasi-rotation (D_{rot} , semi-filled points), of the methanofullerene anion radicals $mF_{loc}^{-\bullet}$ determined for the PCDTBT:PC₇₁ BM composite at different photon energy/wavelength $h\nu_{ph}/\lambda_{ph}$ and $T = 77$ K. Respective values determined for these centers initiated in the system by polychromatic white light with $T_c = 5500$ K are shown by horizontal top, bottom, and middle dashed sectors, respectively. These sectors are limited by the emission band of a white light source. Top dashed-dotted lines show the spectra of polychromatic white and monochromatic light sources. Dashed lines connect experimental points only for illustration to guide the eye. (b) Temperature dependence of the above charge carriers parameters determined upon illumination of the PCDTBT:PC₇₁ BM composite by white light with $T_c = 5500$ K. Top-to-bottom dashed lines show the dependences calculated from (7) with $\omega_{rot}^{(0)} = 8.3 \times 10^{12} \text{ rad} \cdot \text{s}^{-1} \cdot \text{eV}$ and $E_t = 0.010 \text{ eV}$, (5) with $D_{1D}^{(0)} = 36.3 \text{ rad} \cdot \text{s}^{-1} \cdot \text{K}^{-1}$ and $E_{ph} = 0.124 \text{ eV}$, and (6) with $D_{3D}^{(0)} = 0.44 \text{ s}^{-1} \cdot \text{K}^{-2}$, $\omega_e = 6.1 \times 10^{10} \text{ rad} \cdot \text{s}^{-1}$, and $E_b = 0.072 \text{ eV}$.

carriers are characterized by much faster energy exchange with own environment, which accelerates their spin–lattice relaxation. The heating of the composite additionally steps up such exchange of $mF_{loc}^{-\bullet}$.

Spin relaxation is governed not only by the structure and morphology of the system but also by various spin-aided dynamics processes occurring in the PCDTBT:PC₇₁ BM BHJ, e.g., the polaron diffusion along Q1D and quasi-three-dimensional (Q3D) between polymer chains with coefficients D_{1D} and D_{3D} , respectively, and pseudo-rotating libration of methanofullerene anion radicals near own main molecular axis with coefficient D_{rot} . These processes lead to the appearance of an additional magnetic field in the whereabouts of electron and nuclear spins that accelerate electron relaxation of both charge carriers. Therefore, the following equations can be written for spin–lattice and spin–spin relaxation rates [55]:

$$T_1^{-1} = \langle \Delta\omega^2 \rangle [2J(\omega_e) + 8J(2\omega_e)] \quad (3)$$

$$T_2^{-1} = \langle \Delta\omega^2 \rangle [3J(0) + 5J(\omega_e) + 2J(2\omega_e)] \quad (4)$$

where $\langle \omega^2 \rangle = 1/10\gamma_e^4\hbar^2 S(S+1)n \sum_{ij} \Sigma_{ij}$ is a constant of a dipole–dipole interaction for a powder with the lattice sum Σ_{ij} , γ_e is the gyromagnetic ratio for electron, $\hbar = h/2\pi$, $n_i = n_{loc} + n_{mob}/\sqrt{2}$ is the probability of localized n_{loc} , and mobile n_{mob} spin situation on a lattice unit, $J(\omega_e) = (2D_{1D}^1\omega_e)^{-1/2}$

at $D_{1D}^1 \gg \omega_e \gg D_{3D}$ or $J(0) = (2D_{1D}^1 D_{3D})^{-1/2}$ at $D_{1D}^1 \gg \omega_e \gg D_{3D}$ is a spectral density function for Q1D motion, $D_{1D}^1 = 4D_{1D}/L^2$, ω_e is the resonant angular frequency of electron spin precession, and L is the spatial extent of the polaron wave function equivalent to approximately three units for PCDTBT [26]. The spectral density function for rotational librations with correlation time τ_c is $J(\omega_e) = 2\tau_c/(1 + \tau_c^2\omega_e^2)$.

Spin diffusion coefficients calculated from (3) and (4) for charge carriers photoinitiated in the PCDTBT:PC₇₁ BM BHJ using appropriate the spectral density functions, spin concentration, and relaxation data are presented in Fig. 4(a) as a function of the initiated photon energy $h\nu_{ph}$. The figure shows that the rates of polaron diffusion along and between polymer chains are governed by the energy of photons demonstrating extreme dependences with characteristic $h\nu_{ph} \approx 2.4 \text{ eV}$. Dynamics parameter of methanofullerene anion radicals also extremely depends on the photon energy with characteristic $h\nu_{ph} \approx 1.8 \text{ eV}$. This value lies near the band gap of the PCDTBT matrix, 1.88 eV [6]. It is seen from Table I that the anisotropy of polaron dynamics, $A = D_{1D}/D_{3D}$, in the PCDTBT:PC₇₁ BM composite decreases nearly exponentially with the increase of $h\nu_{ph}$ up to 2.5 eV without an extremum at 2.1 eV characteristic for PCDTBT:PC₆₁ BM BHJ [36]. This is evidence for more ordered BHJ under study at a wider intermediate $h\nu_{ph}$ region. An analogous strong

decrease in the anisotropy of polaron dynamics was registered in the study of charge transfer in MW-treated P3HT:PC₆₁BM composite [56]. This effect was explained by the ordering of polymer matrix and methanofullerene clusters under composite modification that facilitates spin mobility and decreases interaction of charge carriers in photoinduced radical quasi-pairs. The formation of appropriate crystallites in an amorphous polymer matrix extends a diffusion of charge carriers and increases an efficiency of light conversion.

Dynamics parameters of charge carriers photoinduced by wide-range white ($T_c = 5500$ K) light are presented in Fig. 4(b) as a function of the temperature. A more strong temperature-dependent characteristic for intrachain polaron dynamics can be described, as in the case of PC₆₁BM-modified PCDTBT [36], in terms of polaron scattering on the phonons of crystalline lattice domains embedded into an amorphous polymer matrix [57]. According to this model, such scattering should accelerate polaron intrachain diffusion by the value

$$D_{1D}(T) = D_{1D}^{(0)} T^2 \cdot \left[\sinh \left(\frac{E_{ph}}{k_B T} \right) - 1 \right] \quad (5)$$

where E_{ph} is the energy of lattice phonons. Indeed, it is seen from Fig. 4(b), where dependence calculated from (5) with $E_{ph} = 0.124$ eV is also presented, that this approach satisfactorily describes the experimental data obtained. The latter value lies near the energy of lattice phonons of various conjugated polymers (0.09–0.32 eV) [58] and plastic solar cells [22]; however, it is sufficiently less than that evaluated for polaron dynamics in the PCDTBT:PC₆₁BM BHJ [36].

Spin nature of charge carriers might be expected to have a large effect on *ac* mobility of polymer systems [59]. Therefore, as in the case of other conjugated polymers [60], [61] and polymer:fullerene composites [22], the interchain spin dynamics in the PCDTBT:PC₇₁BM BHJ can also be explained in the frames of the Pike [62] and Elliott [63] models based on the carrier hopping over the energy barrier E_b . Such an approach predicts the following diffusion coefficient for Q3D spin mobility:

$$D_{3D}(\omega_e T) = D_{3D}^{(0)} k_1 T^2 \omega_e^s \exp \left(- \frac{E_b}{k_B T} \right) \quad (6)$$

where k_1 is a constant, and $s = 1 - 6k_B T/E_b$ is the parameter reflecting polymer system dimensionality. As Fig. 4(b) evidences, this parameter indeed follows (6) with $E_b = 0.072$ eV at $\omega_e = 6.1 \times 10^{10} \text{ rad} \cdot \text{s}^{-1}$. It should be noted that the obtained E_b is nearly the same (0.079 eV) as necessary for polaron interchain diffusion in this matrix modified by PC₆₁BM [36].

Libration mobility of the PC₇₁BM cages can possibly be described in the framework of a semiclassical Marcus theory adopted for conjugated polymers [64], [65]. According to this approach, methanofullerene ion radicals should reorientate between polymer layers with the rate of

$$\omega_{rot} = \omega_{rot}^{(0)} \frac{1}{\sqrt{4E_r k_B T}} \exp \left(- \frac{E_r}{4k_B T} \right) \quad (7)$$

where E_r is both the inner- and outer-sphere reorganization energy of charge carriers due to their interaction with the

lattice phonons. Indeed, such dynamics of the PC₇₁BM cages is realized according to the Marcus theory with $E_r = 0.010$ eV [see Fig. 4(b)]. This parameter is considerably lower than that obtained for the PCDTBT:PC₆₁BM BHJ [36] due to a more ordered composite under study [52]; however, it lies near to that determined for activation of reorientation of PC₆₁BM anion radicals in poly(3-alkylthiophenes) [35], as well as C₆₀- and C₇₀-anions in polymethylmethacrylate and cyclohexane [66]. Fullerene reorientational hopping or rotation in pure C₆₀ requires much more activation energy (0.224 eV) [67]; therefore, the interaction of such charge carriers with own environment affecting their relaxation and dynamics should also be taken into account.

Therefore, one may conclude that spin charge carriers are initiated in the PCDTBT:PC₇₁BM BHJ within the visible and infrared regions of the sun spectrum with comparative quantum efficiency. This is not consistent with the data obtained by optical methods that pointed out a dramatic decrease in external quantum efficiency of this [13], [17], [48] and other [14], [48], [68] C₇₀-modified composites at near-IR sun spectrum. The use of PC₇₁BM counterion instead of PC₆₁BM one as an electron acceptor deepens overlapping of molecular orbitals in appropriate BHJ [26] that provokes lateral morphology of the composite [17]. This hinders the torsional twisting of polymer backbone and formation of spin traps in polymer matrix that increases the path length for charge carriers and, therefore, accelerates their relaxation and dynamics. This significantly extends the scope of respective elements with spin-assisted electronic properties.

IV. CONCLUSION

In summary, we have presented the first results of the comprehensive LEPR study of photoinitiation, relaxation, and dynamics in PCDTBT:PC₇₁BM composite of polarons diffusing along and between polymer chains and methanofullerene anion radicals librative moving between polymer lies. These processes are governed by the interaction of charge carriers with own microenvironment and other spin ensembles. The light photons also initiate spin traps in the polymer backbone, which capture part of these charge carriers. The number and depth of such traps are governed by the energy of photons. This originates the spin- and trap-assistance of all main magnetic resonance, recombination, relaxation, and dynamics processes carried out in the PCDTBT:PC₇₁BM composite. The use of C₇₀-cage instead of C₆₀-globe as an electron acceptor accelerates own pseudorotation electron relaxation in appropriate BHJ. This hinders the formation of spin traps and provokes the more ordered (crystalline) structure of the PCDTBT:PC₇₁BM composite with the layered morphology accelerating spin-assisted charge transport through BHJ. Such a composite converts energy of photons of visible light, as well as infrared irradiation into spin charge carriers that significantly extend the scope of energy conversion of such cells. The method can be efficiently used for the respective detailed study of analogous organic composites with low-band-gap matrices for the further creation of novel elements of organic electronics and spintronics.

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Victor I. Krinichnyi was born in Kazan, Russia, in 1953. He received the Diploma degree in radio-physics and electronics from the Kazan State University in 1975 and the Ph.D. and Sci.D. degrees in physics and mathematics from the Institute of Problems of Chemical Physics (RAS), Chernogolovka, Russia, in 1986 and 1993, respectively.

He then became an Engineer, a Principal Engineer, and a Young Scientific Researcher with the Institute of Chemical Physics, RAS (currently the Institute of Problems of Chemical Physics). He was an Engineer (1975–1979), a Principal Engineer (1979–1982), a Young Scientific Researcher (1982–1987), a Scientific Researcher (1987–1992), and a Senior Scientific Researcher (1992–1996) with the Institute of Problems of Chemical Physics RAS, where he has been a Leading Scientific Researcher since 1997. His research interests resulting from practical application of multifrequency EPR spectroscopy include the relaxation and dynamics of nonlinear charge carriers, solitons, and polarons, in conjugated polymers and their nanocomposites, mechanism of charge transport in molecular crystals, spin phenomena in condensed systems, as well as organic molecular electronics, photonics, and spintronics. He collaborated as an Invited Summer Researcher with the Center of Atomic Energy (1994), Grenoble, France; Merseburg University (1994); Jena University (1997); Stuttgart University (2001); and Ilmenau University (2010); Institute for Physical High Technology (2004), Jena; and the Polymer Research Institute (1998, 2000, 2002, 2003, 2004, 2005), Rudolstadt, Germany. He is the author of two monographs: *2-mm Wave Band EPR Spectroscopy of Condensed Systems* (Boca Raton, FL, USA: CRC, 1995) and *Multifrequency EPR Spectroscopy of Conjugated Polymers and Their Nanocomposites* (Boca Raton, FL, USA: CRC, 2016), five contributions in edited books, 11 reviews, and more than 100 articles.

Dr. Krinichnyi has been a Member of the International EPR (ESR) Society since 1992.



Evgenija I. Yudanova was born in Karaganda, Russia, in 1955. She received the Diploma of Engineer-Physicist from Moscow Physical-Technical Institute, Moscow Russia, in 1979 and the Ph.D. degree in chemical physics from the Institute of Chemical Physics (RAS) (now the Institute of Problems of Chemical Physics, RAS), Chernogolovka, Russia, in 1983.

Since 1983, she has been a Junior Researcher, Researcher and, since 1995, a Senior Researcher with the Institute of Problems of Chemical Physics,

RAS. She is the author of more than 53 articles. Her research interests include the processes of spin dynamic and magnetic interactions between different charge carriers in organic semiconductors, including photovoltaic polymer:fullerene composites, molecular complexes with partial charge transfer, metal-like conductivity, and phase transitions in organic conductors.