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Light-induced EPR study of charge transfer in poly(3-hexylthiophene)/fullerene bulk heterojunction

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The first results of the light-induced EPR study of magnetic, relaxation, and dynamic parameters of charge carriers background photoinduced by optical photons (1.7–3.4 eV) in poly(3-hexylthiophene)/fullerene bulk heterojunctions are described. All magnetic resonance parameters for positively charged polaron and negatively charged fullerene ion-radical in radical pairs photoinduced in the composite were determined separately by the steady-state microwave saturation method. Paramagnetic susceptibility of charge carriers reflects their activation dynamics and exchange interaction. A decay of long-living radical pairs depends on the spatial distance between photoinduced charge carriers. The one-dimensional polaron diffusion along the polymer chain and fullerene rotation near the main molecular axis was shown to follow activation Elliot hopping model and to be governed by photon energy. The difference in activation energies of the charge carriers' dynamics and in their dependence on the exciting photon energy proves their noninteracting character in the polymer/fullerene composite. Main magnetic, relaxation and dynamics parameters of charge carriers are governed by the photon energy band due to inhomogeneity of distribution of polymer and fullerene domains in the composite.

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I. INTRODUCTION

During the past 2 decades, research has been increasing in the field of synthesis and characterization of molecules with extended π-electron delocalization considering as perspective materials for molecular electronics. Among elements of molecular electronics, organic plastic solar cells seem to be most suitable for polymer photovoltaics, which at present time stipulates their wide investigation.[1,2]

Plastic solar cells consist of fullerene molecules embedded into conjugated polymer matrices. They form the so-called "bulk heterojunction" and act as electron acceptor (electron transporter, n-type material) and electron donor (hole transporter, p-type material), respectively. A definitive advantage of a bulk heterojunction is that it can be made by simply mixing these materials in an organic solvent and casting with, e.g., well-known spin coating techniques. Soluble polythiophene, poly(3-alkylthiophene) (P3AT), and fullerene derivatives were proven[3,4] to be the most efficient components of plastic solar cells. Beyond photoinduced charge separation, positive carriers are transported to electrodes by polarons diffusing in the polymer phase and electrons by hopping between fullerene domains.

The irradiation of such bulk heterojunction by light with photon energy $h\nu_{\mathrm{ph}}$ higher than the π-π^* energy gap of the conjugated polymer E_g leads normally to the formation of ion-radical pairs, polarons $P^{+\bullet}$ (donor D) on polymer chains and fullerene anion-radicals $\mathrm{C}_{60}^{-\bullet}$ (acceptor A). Light first excites the donor, the excitation is delocalized on the donor-acceptor (D-A) complex before initiation of charge transfer, leading to an ion-radical pair, and finally charge separation can be stabilized possibly by carrier delocalization on the D^+ (or A^-) species by structural relaxation.[5] The donor and acceptor units are spatially close but are not covalently bonded. At each step, the D-A system can relax back to the ground state releasing energy to the "lattice" in the form of either as heat or by emitting light. This process revealed by time-resolved spectroscopy[6,7] occurs in the femtosecond time domain, whereas electron back transfer with charge annihilation is much slower possibly due to dynamics and relative slow structural relaxation. Understanding photoexcitation, recombination of charge carriers, and other electronic processes realized in conjugated polymers is of fundamental interest for both material characterization and molecular device fabrication.

Bulk heterojunction is characterized by efficient light-excited charge generation at the interface between polymer macromolecules and fullerenes with different electron affinities. The efficiency of solar cells with such bulk heterojunctions has overcome the 5% barrier, and current efficiency is within 5%–6%.[2] This parameter is governed by the polaron binding energy, a finite number of charge carriers, and their mobility in organic solar cells, which are lower as compared with crystalline semiconductors, and therefore by the structural and electronic properties of polymer matrix and fullerene derivative embedded. Charge recombination is considered to be predominantly a nongeminate process governing effectiveness of polymer/fullerene solar cells.[8,9] Normally, the delay of charge carriers consists of prompt and persistent contributions.[10,11] The excitation light intensity dependence of prompt process is of activation bimolecular type and implies mutual annihilation within the created radical

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pair.[12] The persistent contribution is independent of the excitation intensity and originates from deep traps due to disorder.[10] Bimolecular and quadrimolecular recombination was shown[13] to be dominant in the P3AT/fullerene composite, respectively, at lower and higher intensity of excited irradiation.

Except the intermolecular charge transport, quasi-one-dimensional (Q1D) charge transfer by polaron along polymer chains and a rotational motion of fullerene molecules are also realized in such polymer/fullerene system. Undoubtedly, all these molecular and electronic processes should be correlated. Understanding the basic physics underlying the electron relaxation and dynamic behavior of fullerene-modified organic polymers is essential for the optimization of devices based on these materials. However, they are not yet sufficiently understood in detail the processes carrying out in plastic solar cells and there is no generally applicable model available.

Photoinduced charge transfer in a polymer/fullerene composite can be registered by different methods, e.g., optical absorption, photoluminescence, and conductometry.[14] This process is accompanied by the formation of pairs $P^{+\bullet}-C_{60}^{-\bullet}$ of paramagnetic centers, each with spin $S=1/2$. This accounts for the widely used light-induced EPR (LEPR) as a direct method for the investigation of fullerene-modified P3AT (Refs. 13 and 15–17). LEPR measurements revealed the existence of two radicals with different line shapes, magnetic resonance parameters, and saturation behaviors. The main magnetic, relaxation, and dynamics properties of spin pairs photoinduced in fullerene-modified poly(3-dodecylthiophene) (P3DDT) were shown[18,19] to depend on the energy of excited photons. In principle, the spins photoinduced may coact with own charged microenvironment through exchange or dipole-dipole interactions. Such interactions are not too strong in plastic solar cells that allow mobile polarons on a conjugated polymer backbone and the fullerene anions to recess with the rate faster than 10^{-9} s. That is a reason why both charge carriers excited in the polymer/fullerene composite are characterized by considerable long lifetime and can be registered separately.

We showed[20,21] that among soluble fullerene derivatives with different side alkyl substitutes the [6,6]-phenyl-C_{61}-butanoic acid methyl ester (PCBM) should to be suitable electron acceptor in plastic solar cells. It was found[22] that mobility and stability of charge carriers increase considerably in bulk heterojunction formed by the poly(3-hexylthiophene) (P3HT) chains with PCBM molecules, as compared with other P3AT matrix. Much longer charge carrier lifetime achieved in the P3HT/PCBM composites should therefore lead to higher concentration of charge carriers and their reduced recombination rate. It was explained by better structural order in the presence of interface dipoles, creating a potential barrier for carrier recombination in the P3HT/PCBM composite. Specific nanomorphology of this system could result in screened Coulomb potential between the radical pairs photoexcited in its bulk heterojunction and facilitate their splitting into noninteracting charge carriers with a reduced probability of their further annihilation. This implies that much longer carrier lifetimes can be achieved at the same concentrations, which finally results in higher photocurrent and higher power conversion efficiency of the P3HT/PCBM solar cells. Such features predestined the use of P3HT as electron donor and PCBM as electron acceptor in the present study.

We report the first LEPR study of magnetic, relaxation, and dynamic parameters of polarons and fullerene anion-radicals photoinduced in the P3HT/PCBM bulk heterojunction by photons with energy of $h\nu_{ph}=1.7-3.4$ eV (here $h=\hbar/2\pi$ is the Plank constant and ν_{ph} is the photon frequency) in a wide temperature region. We demonstrate noninteracting feature of polaron and fullerene charge carriers and therefore their different interaction with their own microenvironment. This allowed us to determine separately the relaxation and dynamic parameters of these charge carriers and to analyze their dynamics in the P3HT/PCBM composite. Main magnetic, relaxation, and dynamics parameters of these paramagnetic centers were shown to be governed by the photon energy band due to different domains inhomogeneously distributed in the composite.

II. EXPERIMENTAL

In the study were used PCBM and regioregular P3HT distributed by the Solenne BV®, Netherlands, and Rieke Metals®, USA, respectively. Their approximately 1 wt % concentration solution in chlorbenzene at a 1:1 weight ratio was placed into ceramic plane and dried some times (two to three) until the P3HT/PCBM composite was formed as film with the size of approximately 4×8 mm^2 and thickness of approximately 0.1 mm. At the second stage of the study, this sample was annealed for 1 h at 400 K in inert atmosphere.

EPR 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 LEPR spectra of the P3HT/PCBM system and its components were registered at 90–340 K in dry nitrogen atmosphere using a BRT SKB IOH temperature controller and at 77 K in quartz Dewar filled by liquid nitrogen. The LEPR spectra were measured at permanent illumination of the P3HT/PCBM composite directly in a microwave cavity of the EPR spectrometer by the DM-4T white light source with a KGM 12-100-5 halogen lamp. The absorption spectra were obtained at ac modulation amplitude of 5–15 mG. The illumination spectrum was changed by appropriate glass filter sets. The shape of this spectrum changes within the light spectral range used (Fig. 1). This complicated the analysis of the interdependence of photon and charge carriers properties. However, they could be analyzed qualitatively. The signal-to-noise ratio of the LEPR spectra was improved by an averaging of several (typical four to six) acquisitions.

Both spin-lattice T_1 and spin-spin T_2 relaxation times were determined using the well-known steady-state microwave saturation method.[23] For these purposes, the magnetic term B_1 of microwave field in the cavity center determined from the analysis of the narrowing of the diphenylpicrylhydrazyl (DPPH) single microcrystal EPR single line was increased from 1.5 mG up to 0.48 G. DPPH standard with $g=2.0036$ was also used for estimation of g-factors. Total

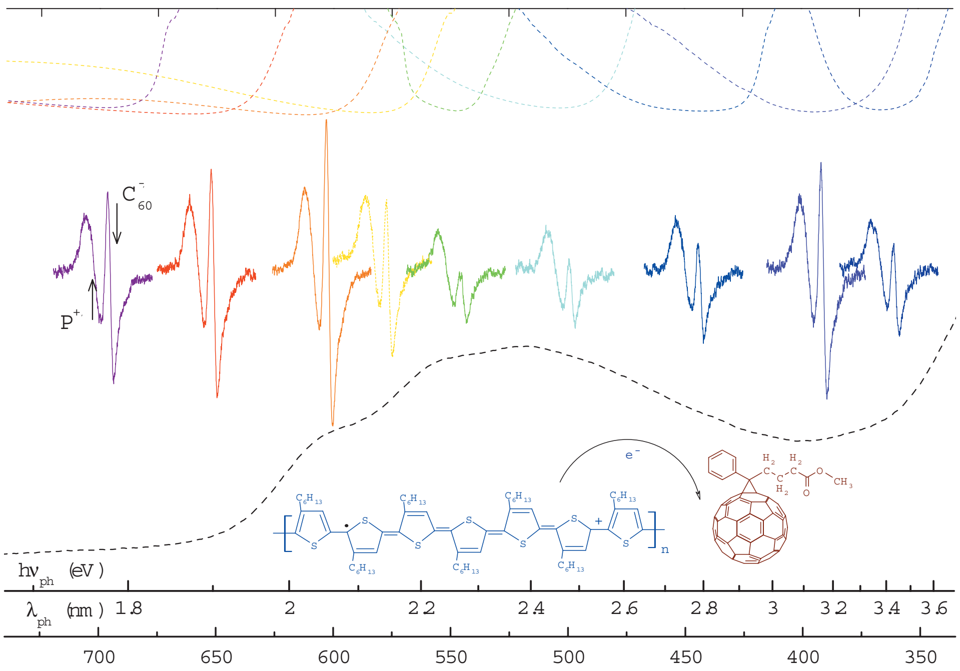

FIG. 1. LEPR spectra of radical pairs $P^{+\bullet}-C_{60}^{-\bullet}$ background photoinduced at 77 K in bulk heterojunctions of the PCBM with chains of the P3HT by light with different photon energy $h\nu_{ph}$ (linewidth λ_{ph}) and bands at identical experimental conditions far from microwave saturation. Appropriate irradiation spectra of the light source and absorption spectrum of the initial P3HT/PCBM composite are shown respectively by the upper and lower dashed lines. The positions of polaron $P^{+\bullet}$ and fullerene anion-radical $C_{60}^{-\bullet}$ are shown. The structures of the P3HT with a mobile polaron and PCBM are shown as well.

paramagnetic susceptibility of the radical pairs photoinduced in the bulk heterojunction was determined from their double integrated individual LEPR spectra far from their saturation conditions. The optical irradiation spectra of the light source and absorption spectrum of the P3HT/PCBM composite were obtained using the Shimadzu® UV-vis scanning UV-3101PC spectrophotometer. The inaccuracy of the determination of the peak-to-peak linewidth ΔB_{pp} and the value of g-factor is consequently $\pm 2\times 10^{-2}$ G and $\pm 2\times 10^{-4}$. Processing and simulations of the EPR spectra were done with the Bruker® WINEPR SIMFONIA program.

III. RESULTS AND DISCUSSIONS

A. Magnetic resonance parameters

1. Line shape and g-factor

Detached P3HT и PCBM are characterized by the absence of both “dark” and photoinduced LEPR signals in the whole temperature range. As these components form the P3HT/PCBM composite and it is irradiated by visible light directly in a cavity of the EPR spectrometer, two overlapping LEPR lines appear at $T\leq 200$ K (Fig. 1). The mobile polarons excited on a conjugated polymer backbone are moving away from the fullerene anions faster than 10^{-9} s. That is a reason why the spins in radical pairs can be considered as noninteracting; they possess long lifetimes and demonstrate separate LEPR spectra. Indeed, the integrated LEPR signal of the P3HT/PCBM composite demonstrates at 77 K two overlapping but clearly registered peaks.

The figure shows the LEPR spectra of radical pairs formed by positively charged polarons $P^{+\bullet}$ with isotropic (effective) $g_{iso}=2.0017$ and negatively charged anion-radicals $C_{60}^{-\bullet}$ with effective $g_{iso}=1.9996$ background photoinduced at 77 K in bulk heterojunctions P3HT/PCBM as function of the photon energy $h\nu_{ph}$ (linewidth λ_{ph}). An absorption spectrum of the composite is presented in the same figure. Subsequent LEPR measurement cycles of heating up to room temperature, cooling down to $T\leq 200$ K, illumination with light, switching light off, and heating up again yield identical results. It is seen that the intensity and shape of the sum LEPR spectrum do not follow definitely an effective photon number absorbed by the composite. This fact indicates that the resulting LEPR spectrum is governed not only by the number of the photons absorbed but also by their energy.

Generally, the deviation Δg of the g-factor of polarons in such conjugated π-electron systems from the free-electron g-factor, $g_e=2.002\,32$, is due to noncompensated orbital momentum, which induces an additional magnetic field during the consequence of $\sigma\to\pi\to\sigma^*$ excitations. In this case this parameter should depend on the spin-orbit coupling λ and the energy differences between the σ and π levels, $\Delta E_{\sigma\pi}$, and between the π and σ^* levels, $\Delta E_{\pi\sigma^*}$,

$$\Delta g = -\frac{\lambda}{3}(\Delta E_{\sigma\pi}^{-1} - \Delta E_{\pi\sigma^*}^{-1}). \tag{1}$$

The orbital moment due to a direct π-π^* excitation is negligible and shows up on the neighboring C atoms only. On the other hand, the g-factor anisotropy is induced by additional fields along x and y directions within the plane of σ skeleton and not along the perpendicular z direction. Indeed, our high-field/frequency EPR study of the structurally close poly(3-octylthiophene) (P3OT) showed[24,25] that the interaction of an unpaired electron delocalized on polaron with sulfur heteroatoms involving into the polymer backbone leads to axial anisotropy of its g-factor, $g_{xx}=2.004\,09$, $g_{yy}=2.003\,32$, and $g_{zz}=2.002\,35$. The effective g_{iso} of anion-radicals $C_{60}^{-\bullet}$ is typical of fullerene anion-radicals.[26] De Ceuster *et al.* showed[27] that the spin density in the $C_{60}^{-\bullet}$ anion-radical embedded into organic polymer matrix is characterized by rhombic symmetry and, therefore, anisotropic g-factor, $g_{xx}=2.000\,31$, $g_{yy}=2.000\,11$, and $g_{zz}=1.998\,21$. As in case of the initial C_{60} molecule,[28] the deviation of g-factor of the PCBM anion-radical from g_e is due to the fact that their orbital angular moment is not completely quenched. Due to the dynamical

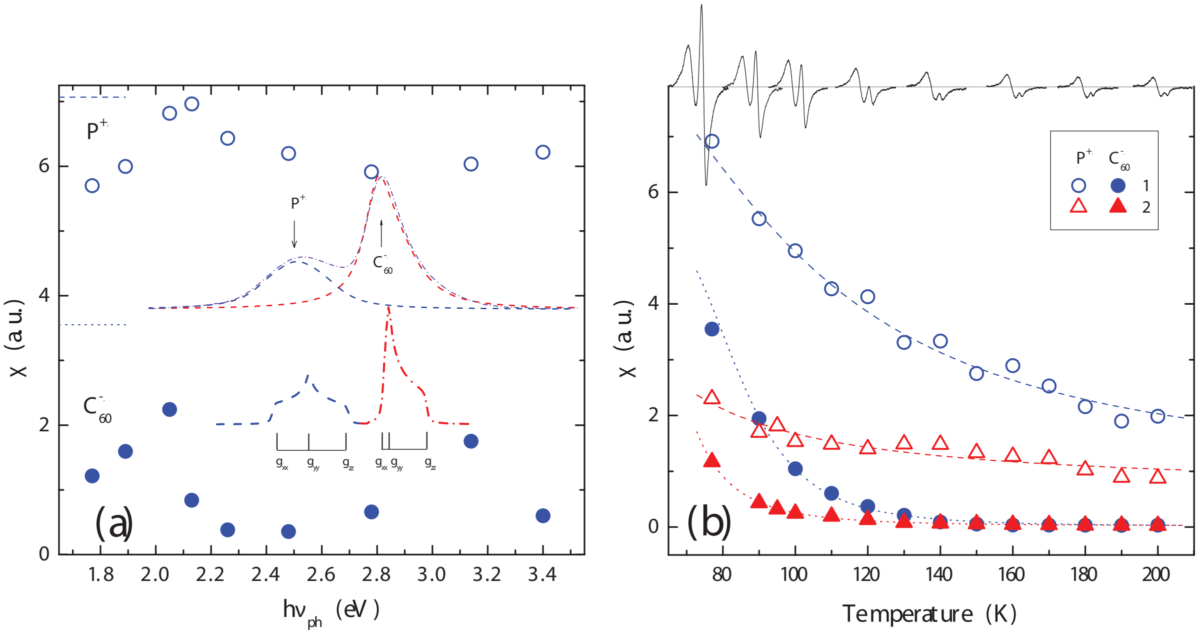

FIG. 2. (a) Paramagnetic susceptibility χ of the polarons $P^{+\bullet}$ (open points) and fullerene anion-radicals $C_{60}^{-\bullet}$ (filled points) photoinduced at 77 K in the initial P3HT/PCBM composite as function of the photon energy $h\nu_{\mathrm{ph}}$. The parameters determined at steady-state irradiation by white light are shown by the dashed and dotted line sections, respectively. In the inset are shown integral contributions of both charge carriers characterizing the abovementioned anisotropic g_{ii}-factors with a sum LEPR spectrum. (b) Temperature dependence of the χ parameter determined for the $P^{+\bullet}$ (open points) and $C_{60}^{-\bullet}$ (filled points) charge carriers photoinduced by white light in the initial (1) and annealed (at 400 K for 1 h) (2) P3HT/PCBM composites. The dependences calculated from Eq. (5) with ΔE_{ij} presented in Table I are shown by dashed lines. In the top are shown LEPR spectra of radical pairs steady-state photoinduced in the P3HT/PCBM composite at respective temperatures.

Jahn–Teller effect accompanying structural molecular deformation, the isotropic nature of the icosahedral C_{60} molecule is distorted after the formation of the $C_{60}^{-\bullet}$ anion-radical, resulting in an axial or even lower symmetry.[29] This is also realized in the case of fullerene derivative radicals,[27] which the high symmetry is lowered by the bond to the phenyl side chain prior to electron trapping. An asymmetrical distribution of spin density in both the polaron and fullerene anion-radical leads also to a tonsorial character of their linewidth.[24,25,27] This should be taken into account in precise calculation of an effective LEPR spectrum of the P3AT matrix with embedded PCBM.

2. Paramagnetic susceptibility

According to the main principle of charge separation and long-live stabilization, the number of polaronic charge carriers must be equal to that of the fullerene anion-radicals. In other words, the shape of the appropriate LEPR spectrum must be independent of the number and energy of absorbed photons. However, it is rather far from this conception for the P3HT/PCBM studied as in the case of the structural close P3DDT/PCBM composite.[18,19,30] It is seen from Fig. 2(a) that the ratio χ_P/χ_{C60} of spin concentrations of the $P^{+\bullet}$ and $C_{60}^{-\bullet}$ radicals increases significantly from approximately two for white light up to 17 for middle frequency band used. There are different factors leading to such discrepancy, e.g., a different ordering of the composites or/and a possible collapse of polaron pairs into spinless bipolarons. In this case, however, the above spin concentration ratio should be less than unit. It was shown[18,19,31] that a variation in irradiation photon energy $h\nu_{\mathrm{ph}}$ can also change P3AT/PCBM LEPR spectra. Indeed, Fig. 2(a) demonstrates that the increase in the $h\nu_{\mathrm{ph}}$ value leads to the change in relative concentrations of polarons $P^{+\bullet}$ and fullerene anion-radicals $C_{60}^{-\bullet}$ photoinduced in the P3HT/PCBM composite with extrema at $h\nu_{\mathrm{ph}} \approx 2.0$ and 3.1 eV. This means that the spinless charge carriers formed at irradiation of this composite by photons with $h\nu_{\mathrm{ph}} \approx 2.1-2.5$ eV should prevail over polarons.

The nature and dynamics of charge carriers in radical pairs can also contribute to their effective LEPR spectrum. Figure 2(b) shows the temperature dependence of paramagnetic susceptibility χ of charge carriers steady-state photoinduced in the initial and annealed P3HT/PCBM composites. One can notice that the fullerene ion-radicals excited in the initial sample demonstrate stronger $\chi(T)$ temperature dependence than polarons, especially at the low-temperature region. At the annealing of the composite, both the charge carriers become slightly temperature dependent and their spin concentration ratio χ_P/χ_{C60} decreases significantly. Such effect can be interpreted as following.

Let a positively charged polaron diffuse along a polymer chain from one initial site i to other available site j close to a position occupied by a negatively charged fullerene molecule. Charge hops more easily between fullerenes than from polaron and fullerene, and an effective charge recombination is still limited by the transport of polaron toward fullerene molecule. Charge recombination is mainly stipulates by sequential processes, namely, positive charge transfer by polaron hopping along a polymer chain and its transfer from polymer chain to a site occupied by a fullerene anion. Polaronic dynamics in undoped and slightly doped conjugated polymers is highly anisotropic.[25,32] Therefore, the probability of a charge transfer along a polymer chain exceeds considerably that of its transfer between polymer macromolecules.

The positive charge can tunnel from polaron toward fullerene and recombine with its negative charge during the time,[33]

$$\tau(R_{ij}^{|}) = \tau_{\mathrm{pn}}^{0} \exp\left(\frac{2R_{ij}^{|}}{a_0}\right), \tag{2}$$

where τ_{pn}^{0} is the attempt to jump time for positive charge tunneling from polymer chain to fullerene, $R_{ij}^{|}$ is spatial separation of sites i and j, and a_0 is the effective localization (Bohr) radius. Charge can also be transferred by the polaron thermally assisted multistep tunneling through energy barrier $\Delta E_{ij}=E_j-E_i$ with the time[33]

$$\tau(R_{ij},E_a) = \tau_{\mathrm{pp}}^{0} \exp\left(\frac{2R_{ij}}{a_0}\right)\exp\left(\frac{\Delta E_{ij}}{k_B T}\right), \tag{3}$$

The decay of polaron charge carriers in regioregular P3AT consists of temperature independent fast and exponentially temperature dependent slow contributions.[11] In addition to the abovementioned tunneling and activation processes, there should be one more contribution of polarons to effective spin susceptibility. Positive charge on polaron can recombine not obviously with a first negative charge on fullerene but with other one. Thus, the probability of annihilation of charges can differ from the unit. Besides, the polaron is characterized by Q1D mobility. Such fundamental properties of this specific charge carrier require considering also the contribution to its paramagnetic susceptibility due to exchange interaction of both types of paramagnetic centers. Positively charged polaron Q1D hopping from site i to site j with frequency ω_{hop} may collide with the fullerene radical anion located near the polymer matrix. While polaron is mobile, the fullerene molecule can be considered as a translative fixed but rotating near its own main molecular axis. In this case the spin flip-flop probability p during a collision should depend on the amplitude of exchange and ω_{hop} value as[34]

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

where $\alpha=(3/2)2\pi J/\hbar\omega_{\mathrm{hop}}$ and J is the constant of exchange interaction of spins in a radical pair. Therefore, weak and strong exchange limits can be realized. In the case of weak or strong exchange, the increase in ω_{hop} may result in the decrease or increase in exchange frequency, respectively. If the ratio $J/\hbar$ exceeds the frequency of collision of both types of spins, the condition of strong interaction is realized in the system, leading to a direct relation of spin-spin interaction and polaron diffusion frequencies, so then $\lim(p)=0.5$, which is independent of J and ω_{hop}. In the opposite case, $p \propto J^2/\omega_{\mathrm{hop}}^{-2}$. It is evident that the longer both the above tunneling times or/and the lesser the probability p become, the smaller the number of ion-radical pairs to have the possibility to recombine, and therefore higher spin susceptibility should be registered. A combination of the above equations takes therefore the general form of this main parameter for polarons in polymer/fullerene composite as

TABLE I. The ΔE_{ij}, E_a, E_{ph}, and E_b values (all in eV) determined from Eqs. (5), (6), (13), and (14), respectively, for radical pairs photoinduced by white light in the initial and annealed (at 400 K for 1 h) P3HT/PCBM composites.

	Initial		Annealed	
Radical parameter	$P^{+\bullet}$	$C_{60}^{-\bullet}$	$P^{+\bullet}$	$C_{60}^{-\bullet}$
ΔE_{ij}	0.012	0.042	0.008	0.045
E_a	0.015		0.017	
E_{ph}	0.034		0.021	
E_b		0.032		0.007

$$\chi_P = \chi_{\mathrm{pn}} + \chi_P^0 \frac{\hbar}{J}\left(\alpha + \frac{1}{\alpha}\right). \tag{5}$$

Assuming the above introduced activation character for polaron multistep hopping with the frequency $\omega_{\mathrm{hop}} = \omega_{\mathrm{hop}}^{0} \exp(-\Delta E_{ij}/k_B T)$ and the absence of interaction between fullerene anion-radicals, one can determine ΔE_{ij} (see Table I) and J parameters from individual temperature dependences of paramagnetic susceptibility.

It is seen from Fig. 2(b) that the experimental data are fitted well by Eq. (5) with the ΔE_{ij} values summarized in Table I. ΔE_{ij} obtained for polarons photoinduced by white light in the initial P3HT/PCBM composite slightly decreases after its heat treatment, whereas this value determined for fullerene anion-radicals changes remarkably smaller (see Table I). One can conclude that polaronic dynamics in the annealed P3HT/PCBM composite is activated at comparatively smaller ΔE_{ij} than in the initial one. This occurs due probably to the more structural inhomogeneity of the initial P3HT matrix. The J constant was analyzed to change slightly within 0.2–0.35 eV. This value sufficiently exceeds an appropriate constant of spin collision of nitroxide radicals with paramagnetic ions in liquids, $J \leq 0.01$ eV,[35] but lie near $J \approx 0.36$ eV, which we obtained for the interaction of polarons with the oxygen molecules in polyaniline highly doped by p-toluenesulfonic acid.[36,37] Comparing the above presented data with those obtained in the LEPR study of the P3DDT/PCBM composite,[18,19,30] one can also conclude the higher stability of charge carriers photoinduced in the P3HT/PCBM system under study, especially by the high-energy photon region. This can evidence better homogeneity of this composite.

3. Linewidth

Effective (isotropic) peak-to-peak linewidths $\Delta B_{\mathrm{pp}}^{(0)}$ obtained for the $P^{+\bullet}$ and $C_{60}^{-\bullet}$ radicals in the absence of their microwave saturation, when $B_1 \to 0$, are presented in Fig. 3 as a function of photon energy and temperature. It is seen from the Fig. 3(a) that this parameter determined for both charge carriers changes nonmonotonically with $h\nu_{\mathrm{ph}}$, demonstrating the extrema near 2.0 and 3.1 eV. The first extreme lies near the band-gap energy of $E_g^{\mathrm{opt}}=1.92$ eV of the polymer matrix,[38] whereas the second one can probably be attributed to inhomogeneous distribution of domains with different ordering (and hence band-gap energies) in the polymer/fullerene bulk heterojunction.

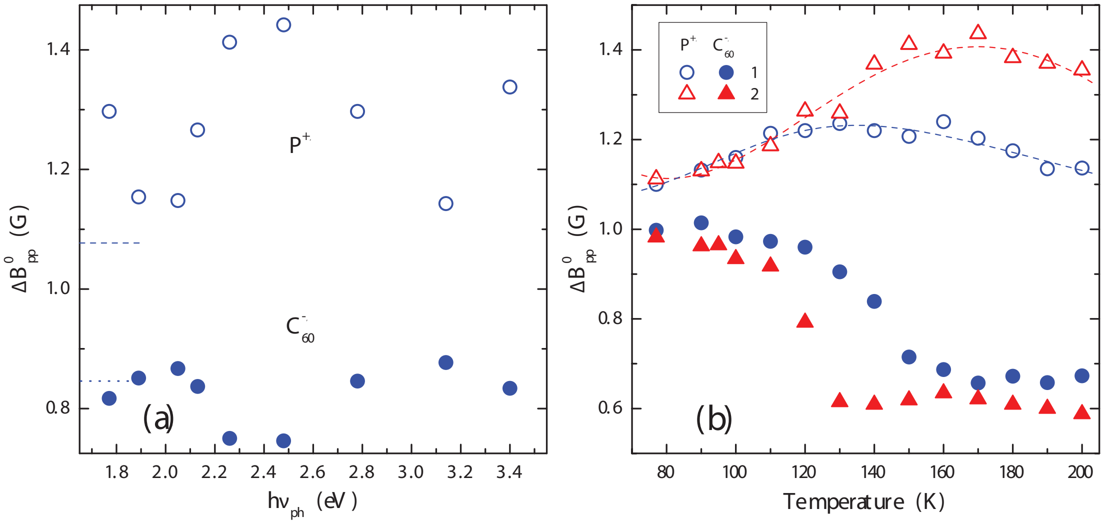

FIG. 3. (a) A lower limit of the peak-to-peak linewidth $\Delta B_{pp}^{(0)}$ of the polarons $P^{+\bullet}$ (open points) and fullerene anion-radicals $C_{60}^{-\bullet}$ (filled points) steady-state photoinduced at 77 K in the P3HT/PCBM composite as a function of the photon energy $h\nu_{ph}$. The parameters determined at steady-state irradiation by white light are shown by the dashed and dotted line sections, respectively. (b) Temperature dependence of the linewidth determined for the $P^{+\bullet}$ (open points) and $C_{60}^{-\bullet}$ (filled points) charge carriers photoinduced by white light in the initial (1) and annealed (at 400 K for 1 h) (2) P3HT/PCBM composites. Dashed lines show the dependences calculated from Eq. (6) with E_a presented in Table I.

The polarons photoinduced in both the initial and annealed P3HT/PCBM composites demonstrate extremal temperature dependence of linewidth. Extrapolation to room temperature gives $\Delta B_{pp}^{(0)}=0.9$ G that lies near that obtained for polarons stabilized in P3HT/PCBM[20,21] and photoinduced in P3DDT/PCBM[18,19,30] matrixes. However, this value is considerably less then that determined for undoped polythiophene[39] that is evidence of weaker spin interaction with the P3AT lattice. Assuming exchange and activation interaction of a fullerene anion-radical quasifixed between polymer chains with polaron hopping along the chain with the rate ω_{hop}, the dependences presented in Fig. 3(b) can probably also be described in terms of the abovementioned Houze–Nechtschein approach.[34] According to this theory, the collision of localized and mobile spins should additionally broaden the absorption line by the value

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

where p is probability described by Eq. (4), $\omega_{hop} = \omega_{hop}^0 \exp(-E_a/k_BT)$, E_a is the activation energy, and C is the number of paramagnetic centers per each polymer unit.

The dependences calculated from Eq. (6) with E_a presented in Table I are also shown in Fig. 3(b). The analysis of the data presented allows a conclusion can be made, namely, that the energy required for activation of polaron diffusion in the P3HT/PCBM composite changes only slightly at its heat treatment.

It is seen that main magnetic resonance parameters of charge carriers are governed by the energy of exciting photons within irradiation band. This can be realized either at the formation of spin pairs with different properties in homogeneous composite fragments or at the excitation of identical charge carriers in heterogeneous domains of the system under study. Different spin pairs can be photoinduced as a result of photon-initiated appearance of traps with different depths in the polymer matrix. However, the difference in the parameters of paramagnetic centers revealed seems to be rather in result of their interaction with own microenvironment in domains inhomogeneously distributed in the polymer/fullerene composite. Different orderings of these domains can be a reason for their different band-gaps and hence their sensitivity to photons with defined but different energy. This can give rise to a variation in an interaction of paramagnetic centers with a lattice and other spins.

B. Recombination of charge carriers

In solar cells, both charges diffusing to the opposite electrodes must reach them prior to recombination. If these chargers after their transfer are still bound by the Coulomb potential, which is typical for such compounds with low-mobile charge carriers as P3AT/PCBM, they cannot escape from each other's attraction and will finally recombine. When the distance of a carrier dissipation is longer than the Coulomb radius, the excitons photoinduced in bulk heterojunction can be split into positive and negative charge carriers. To fulfill this condition the Coulomb field must be shielded or charge carrier hopping distance must exceed the Coulomb radius. In this case charges are transferred to the electrodes either by the diffusion of appropriate carriers or by the drift induced by electric field. In order to excite a radical pair by each photon, charge carrier transit time t_{tr} should be shorter considerably than the lifetime of a radical pair τ, i.e., $t_{tr} \ll \tau$. The former value is determined by charge carrier mobility μ, sample thickness d, and the electric field E inside the film, $t_{tr}=d/\mu E$. If photocurrent is governed by the carrier drift in the applied electric field, the drift distance $l_{dr}=\mu\tau E$. If photocurrent is governed by carrier diffusion, the diffusion distance $l_{diff}=(D\tau)^{1/2}=(\mu\tau k_B T/e)^{1/2}$, where D is the diffusion coefficient and e is elemental electron charge. Thus, the $\mu\tau$ product governs the average distance passed by the charge carrier before recombination and therefore is an

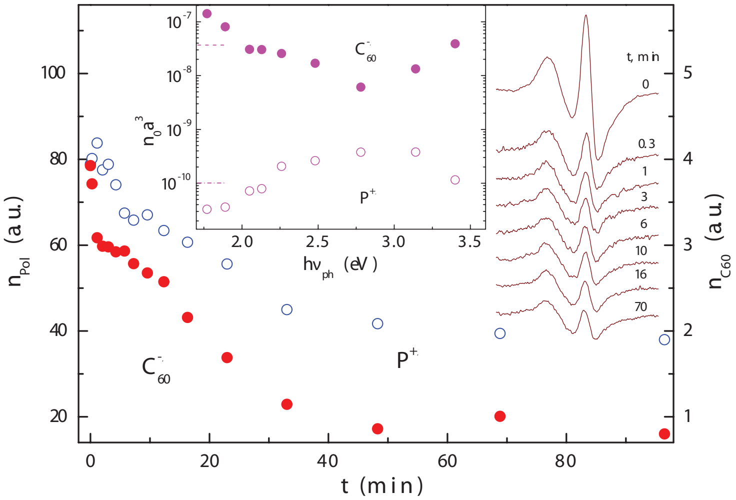

FIG. 4. Time dependence of the concentration of polarons $P^{+\bullet}$ (open points) and anion-radicals $C_{60}^{-\bullet}$ (filled points) photoinduced in the P3HT/PCBM composite after the light irradiation (550 nm) blackout. In the right inset are shown LEPR spectra of the composite registered at different times t after the light blackout, whereas the central inset demonstrates the change in the n_0a^3 term in Eq. (10) of these charge carriers photoinduced in the composite with the photon energy $h\nu_{ph}$.

important parameter determining whether the efficiency of solar cells is limited by charge transport and recombination.

If one switches off excited light irradiation of the P3HT/PCBM composite, the concentration of spin pairs excited in its bulk heterojunction starts to decrease and the LEPR line shape changes as it is shown in Fig. 4. There can be different progress for a radical pairs after the irradiation interruption, namely, their instantaneous collapse or splitting into noninteracting charge carriers due to polaron diffusion away. The rate of a further recombination of charge carriers with effective localization radius a separated by a distance R can be written as[40]

$$\nu(R) = \nu_0 \exp\left(-\frac{2R}{a}\right), \tag{7}$$

where ν_0 is an attempt to recombine frequency. Undoubtedly, both charge carriers have different localization radii. The localization radius of a negative charged carrier should be of the order of the radius of the PCBM globule. The distance R should depend, e.g., on the length of a side alkyl chain substituent in the P3AT/fullerene composite.[41] Polaron stabilized in P3AT is normally distributed over five monomer units.[11,42] The nearest-neighbor distance $R(t)$ of spin pair with the typical radiative lifetime τ_0 changes with time t as

$$R(t) = \frac{a}{2}\ln\left(\frac{t}{\tau_0}\right). \tag{8}$$

Assuming that photoexcitation is turned off at some initial time $t_0=0$ at a charge carrier concentration n_0 and taking into account a time period of geminate recombination t_1-t_0, one can write for concentration of charge carriers,

$$n(R) = \frac{n_1}{1+\dfrac{4\pi}{3}n_1(R^3-R_1^3)}, \tag{9}$$

where R is specified by Eq. (8), $R_1=R(t_1)$ describes the distance between the nearest-neighbor charge carriers at time t_1 after which solely nongeminate recombination is assumed, and n_1 is the charge carrier concentration at time t_1. It follows from Eq. (9) that the time dependence of the residual carrier concentration does not follow a simple exponential decay but shows a more logarithmic time behavior. After very long times, i.e., at large R and $t>t_1$, one obtains $n(R)=[(4\pi/3)R^3]^{-1}$, which is independent of initial carrier density n_1 and also n_0. As it follows from the above $\nu(R)$ equation, the photoexcited charge carriers have comparable long lifetimes, which are solely ascribed to the large distances between the remaining trapped charge carriers. The excited carrier concentration n_1 follows directly from LEPR measurements, whereas a and $\tau_0=\nu_0^{-1}$ values can be guessed in a physically reasonable range. Finally, the concentration of spin pairs should follow the relation[40]

$$\frac{n(t)}{n_0} = \frac{\dfrac{n_1}{n_0}}{1+\left(\dfrac{n_1}{n_0}\right)\dfrac{\pi}{6}n_0a^3\left[\ln^3\left(\dfrac{t}{\tau_0}\right)-\ln^3\left(\dfrac{t_1}{\tau_0}\right)\right]}. \tag{10}$$

The analysis showed that depending on the photon energy band the spin concentration initially photoexcited at $t=0$ is governed by some factors. The n_0a^3 terms in Eq. (10) determined for both photoexcited charge carriers are also shown in the inset of Fig. 4 as function of the photon energy $h\nu_{ph}$. As the figure indicates, these values change symbatically with $h\nu_{ph}$. It was shown that Eq. (10) fits well the experimental data presented in Fig. 4. The analogous effects were registered also for other P3AT/PCBM systems. Therefore, a decay of long-living spin pairs photoinduced in P3HT/PCBM and similar composites can successfully be described in the framework of the above model in which the low-temperature recombination rate is particularly strongly dependent on the spatial distance between photoinduced charge carriers. The long lifetimes are solely ascribed to the long spatial distances that build up among the remaining photoinduced charge carriers, which did not recombine at a shorter time.

C. Electron relaxation and dynamics of charge carriers

The increase in steady-state microwave power leads to the broadening of the LEPR spectrum accompanied by nonlinear increase in its amplitude. As in the case of other conjugated polymers,[32,43] this occurs as a result of microwave

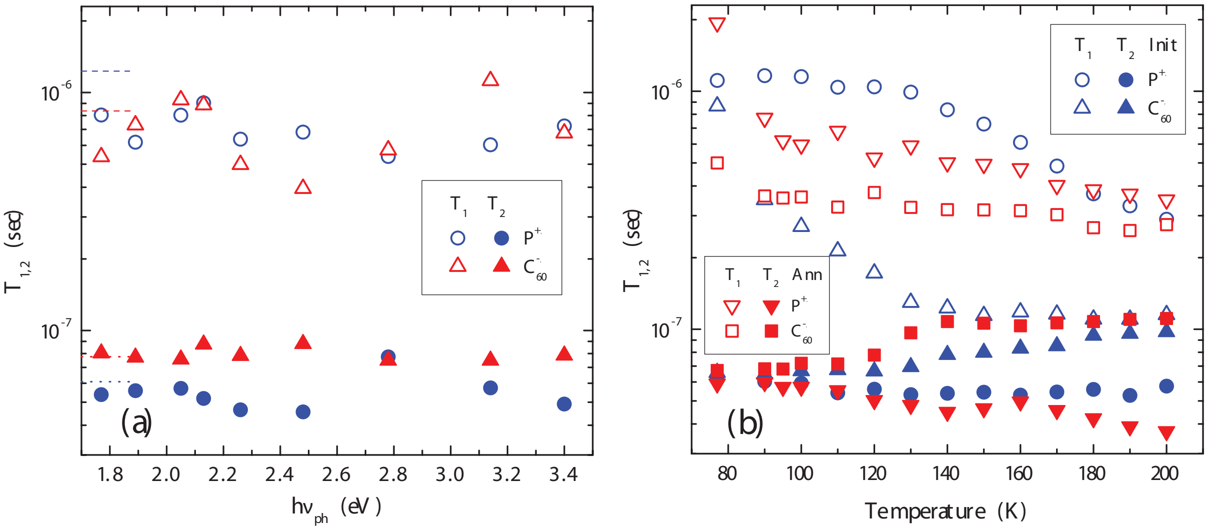

FIG. 5. (a) The spin-lattice T_1 (a) and spin-spin T_2 (b) relaxation times of the polarons $P^{+\bullet}$ (open points) and fullerene anion-radicals $C_{60}^{-\bullet}$ (filled points) steady-state photoinduced at 77 K in the P3HT/PCBM composite as function of the photon energy $h\nu_{ph}$. The parameters determined at steady-state irradiation by white light are shown by the dashed and dotted line sections, respectively. (b) Temperature dependence of the relaxation times determined for the $P^{+\bullet}$ (open points) and $C_{60}^{-\bullet}$ (filled points) charge carriers photoinduced by white light in the initial and annealed (at 400 K for 1 h) P3HT/PCBM composites.

steady-state saturation of spin packets excited in bulk heterojunctions. Since polarons and fullerene radical anions were proved to be independent of one another, such effect was used for a separate estimation of their spin-lattice T_1 and spin-spin T_2 relaxation times using a well-known procedure.[23]

The relaxation parameters of polarons and fullerene anion-radicals determined using such a method are presented in Fig. 5 as a function of the photon energy band and temperature. From the analysis of the data presented, one peculiarity can be noticed, namely, extremal $T_1(h\nu_{ph})$ dependence obtained for fullerene anion-radicals with characteristic values lying near 2.1 and 3.1 eV. Other parameters depend weaker on $h\nu_{ph}$. Electron relaxation of charge carriers photoinduced in the initial P3HT/PCBM composite changes monotonically with the temperature [Fig. 5(b)]. The annealing of the composite causes nonlinearity of the $T_2(T)$ function of both charge carriers near 140 K as well as the decrease in spin-lattice relaxation time of fullerene anion-radicals [Fig. 5(b)]. Such peculiarities argue that the mechanism and the rate of electron relaxation depend on structure and conformation of the initial and fullerene-modified polymer matrix. The data obtained show the effect of the photon energy on relaxation parameters of radical pairs photoinduced in polymer/fullerene composites. This can also be explained by the formation of charge carriers in differently ordered domains with respective band-gaps.

Various spin-aided dynamic processes occur in polymer/fullerene composites: Polaron diffusion along and between polymer chains with coefficient D_{1D} and D_{3D}, respectively, rotational diffusion of the fullerene radical anion about its own main molecular axis with coefficient D_{rot}, etc. These processes induce an additional magnetic field in the whereabouts of electron and nuclear spins, which, in turn, accelerate electron relaxation in both spin ensembles. As relaxation of the whole spin reservoir in organic conjugated polymer is defined mainly by a dipole-dipole interaction between electron spins,[32,44] these coefficients can be determined from equations[45]

$$T_1^{-1}(\omega) = \langle\omega^2\rangle[2J(\omega) + 8J(2\omega)], \tag{11}$$

$$T_2^{-1}(\omega) = \langle\omega^2\rangle[3J(0) + 5J(\omega) + 2J(2\omega)], \tag{12}$$

where $\langle\omega^2\rangle = 1/10\gamma_e^4\hbar^2 S(S+1)n\Sigma_{ij}$ is a constant of dipole-dipole interaction for powder, γ_e is a gyromagnetic ratio for electron, n is a number of polarons per each monomer, Σ_{ij} is a lattice sum for powderlike sample, $J(\omega) = (2D_{1D}^{|}\omega)^{-1/2}$ (at $D_{1D}^{|} \gg \omega \gg D_{3D}$), $J(0) = (2D_{1D}^{|}D_{3D})^{-1/2}$ (at $D_{3D} \gg \omega$) is a spectral density function for polaron longitudinal diffusion, $J(\omega) = \tau_c/(1+\tau_c^2\omega^2)$ is a spectral density function for fullerene rotation with correlation time τ_c and coefficient $D_{rot} = 1/6\tau_c$, respectively, at first (ω_e) and second $(2\omega_e)$ resonant angular frequencies of the electron spin precession, $D_{1D}^{|} = 4D_{1D}/L^2$, and L is a factor of spin delocalization over a polaron. If one suppose that the nearest spins are situated near the points of the P3HT cubic lattice with the side constant equal to the lattice constant b, the lattice sum can be simplified as $\Sigma_{ij} = 6.8d^{-6}$.[46]

The dynamic parameters calculated for both charge carriers photoexcited in the P3HT/PCBM composite from Eqs. (11) and (12) with $L=5$ for P3AT[11,42] and $b = 0.766$ nm for P3HT (Ref. 47) are presented in Fig. 6 as a function of photon energy band and temperature. The diffusion coefficients from the figure seem to depend on the photon energy band as well. Polaronic charge carriers demonstrate nonmonotonic dependence on the $h\nu_{ph}$ intrachain and interchain diffusion rates, with extrema lying near those obtained for other LEPR parameters. This fact proves additionally the existence of domains with different orderings and sensitivities to respective light photons in this composite.

Polarons photoinduced in the P3HT/PCBM bulk heterojunction demonstrate a sharper $D_{1D}(T)$ dependence than

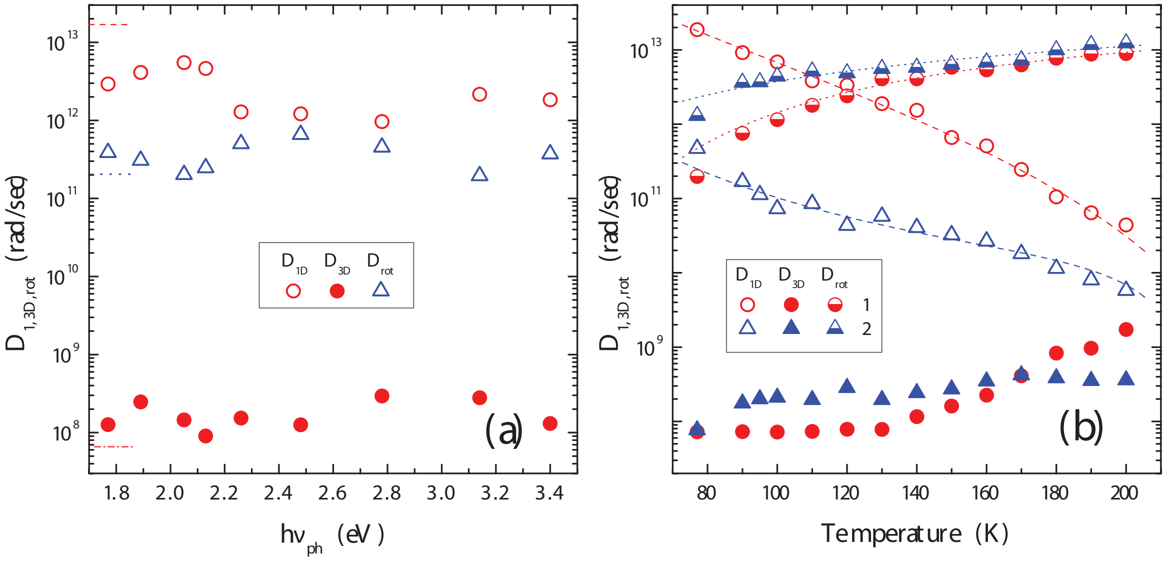

FIG. 6. (a) The coefficients of polarons $P^{+\bullet}$ hopping along (D_{1D}, open points) and between (D_{3D}, filled points) polymer chains and the coefficient of rotation of fullerene anion-radicals $C_{60}^{-\bullet}$ near the main axis (D_{rot}, semifilled points) steady-state photoinduced at 77 K in the P3HT/PCBM composite as function of the photon energy $h\nu_{ph}$. The parameters determined at steady-state irradiation by white light are shown by the dashed and dotted line sections, respectively. (b) Temperature dependence of the D_{1D}, D_{3D}, and D_{rot} parameters determined for the $P^{+\bullet}$ (open points) and $C_{60}^{-\bullet}$ (filled points) charge carriers photoinduced by white light in the initial (1) and annealed (at 400 K for 1 h) (2) P3HT/PCBM composites. The lines show the dependences calculated from Eqs. (13) and (14) with respective lattice phonon E_{ph} and activation barrier E_b energies; the latter is presented in Table I.

those photoinduced in the P3DDT/PCBM composite [Fig. 6(b)].[18,19,30] This can probably be explained, e.g., by a stronger interaction of these charge carriers with lattice phonons in the former matrix and described in terms of the Kivelson–Heeger model[48] of charge carrier scattering in the lattice of an ordered polymer matrix. According to this model, if polarons interact with the lattice optical phonons with energy E_{ph}, then the rate of their diffusion should depend on temperature as[48]

$$D_{1D}(T) = D_{1D}^{0} T^{2}\left[\sinh\left(\frac{E_{ph}}{k_B T}\right) - 1\right]. \tag{13}$$

Figure 6(b) shows that the experimental dependences $D_{1D}(T)$ obtained for both the initial and annealed P3HT/PCBM composites are well approximated by Eq. (13) with E_{ph} presented in Table I. The energies of lattice phonons obtained lie near that determined for P3OT (Ref. 25) and other conjugated polymers.[32,43,49] They also lie near the activation energy E_a of polaron mobility in P3HT (Ref. 50) but less then E_a determined for polaron diffusion in P3OT/PCBM composite[51] and poly(3-methylthiophene) (P3MT) matrix.[52]

The fullerene rotation diffusion can be explained in the frames of the Elliot model based on carrier hopping over energetic barrier E_b.[53] This model predicts the frequency and temperature dependent diffusion of a charge carrier with a coefficient

$$D_{rot}(\omega,T) = D_{rot}^{0} T^{2} \omega_e^{s} \exp\left(\frac{E_b}{k_B T}\right), \tag{14}$$

where the exponent $s = 1 - \alpha k_B T / E_b$ reflects system dimensionality and α is a constant. E_a and α values were obtained for, e.g., lightly doped P3MT to be respectively 1.1 eV and 6.[54]

The energy E_b required to activate fullerene rotational diffusion in the initial and annealed P3HT/PCBM composites is also presented in Table I. It is seen from Fig. 6(b) that the temperature dependences calculated from Eq. (14) with the E_b obtained approximate well the data experimentally obtained. The E_b determined for fullerene rotation in the P3HT matrix is considerably lower than that estimated for more crystalline solids.[55,56] However, it is close to that characteristic for the triphenylamine complex.[57]

Comparing the above data and the data obtained earlier for P3DDT/PCBM,[18,19,30] one can conclude that the rate of fullerene rotation in the P3AT/fullerene composite decreases by some orders of magnitude as the length of a side alkyl chain substituent increases, i.e., at the transfer from P3HT to P3DDT matrix. The thermal treatment reduces the anisotropy of polaron diffusion [Fig. 6(b)] and both the E_{ph} and E_b values in the P3HT/PCBM composite (see Table I). This is evidence of the increase in crystallinity of the treated system. Besides, at the temperature annealing of the composite with initially low-crystalline polymer matrix, the fullerene molecules embedded become more mobile and start to diffuse and form fullerene clusters. Due to such thermally initiated fullerene diffusion, the regions with low fullerene concentration appear in the polymer matrix where the polymer macromolecules can crystallize. As a result, polymer crystallites and fullerene clusters are formed upon annealing of the initial composite. Such treatment indeed improves additionally charge transport properties of the polymer/fullerene solar cells.

IV. CONCLUSION

Light excitation of the bulk heterojunction in the P3HT/PCBM composite leads to charge separation and transfer from a polymer chain to a fullerene molecule. This is accompanied by the excitation of two paramagnetic centers with rhombic symmetry and clearly resolved LEPR spectra, namely, the positively charged polaron $P^{+\bullet}$ on the polymer backbone and the negatively charged fullerene anion-radical $C_{60}^{-\bullet}$ located between polymer chains. Both radicals are spatially separated due to high mobility of a polaron charge carrier so that they become noninteracting and a probability of their recombination decreases. Weak interaction of paramagnetic centers in this radical pair stipulates a difference in their interaction with own microenvironment and therefore in their magnetic resonance and relaxation parameters. This leads to the saturation of a polaron at much lower microwave power as compared with fullerene anion-radical and allows therefore to determine separately all relaxation parameters for both charge carriers.

Photoinduced charge is transferred by polaron diffusing along a polymer chain near the position of a fullerene radical anion where they can recombine. The probability of the collapse of photoinduced radical pairs follows the activation law and is governed by the energy of initiating optical photons. The interaction of charge carriers with own microenvironment also depends on the photon energy band. Spin dynamics induces an additional magnetic field in the whereabouts of another spin that accelerates electron relaxation of both spin ensembles. This allowed all dynamic parameters of polarons and fullerene radical anions in the P3HT/PCBM composite to be calculated separately. Q1D longitudinal diffusion of polarons and rotational diffusion of fullerenes follow the activation mechanism and are governed by the photon energy. This can be a result of the formation of identical excitations in heterogeneous domains of the system. The temperature annealing of the composite enhances its dimensionality (crystallinity) due to the formation of polymer crystallites and fullerene clusters that improve main electronic properties of plastic solar cells. Therefore, the investigation of the properties of paramagnetic centers excited by various photons in the initial and treated polymer/fullerene systems may give a possibility to control their texture and other structural properties for the further increase in their efficient factor.

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