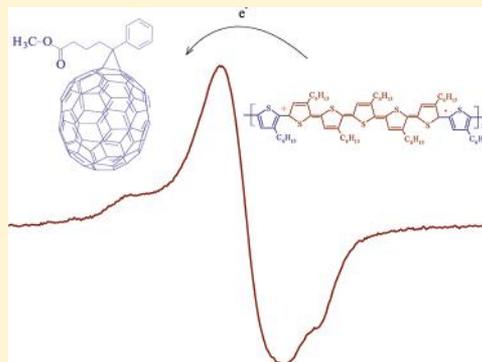


Light-Induced EPR Study of Charge Transfer in P3HT/PC₇₁BM Bulk Heterojunctions

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ABSTRACT: Radical pairs, polarons, and fullerene anion radicals photo-induced by photons with energy of 1.98–2.73 eV in bulk heterojunctions formed by regioregular poly(3-hexylthiophene) (P3HT) with (6,6)-phenyl-C₇₁-butyric acid ester (PC₇₁BM) methanofullerene have been studied by the direct light-induced EPR (LEPR) method at a wide temperature region. LEPR spectra of the P3HT/PC₇₁BM composite were deconvoluted, and the main magnetic resonance parameters of these charge carriers have been determined. A part of photoinduced polarons is pinned by large-depth traps in the polymer matrix. It was shown that magnetic resonance, relaxation, and dynamics parameters of photoinduced charge carriers depend extremely on the energy of initiated photons. Relaxation and dynamics parameters of both the charge carriers were determined separately by the steady-state saturation method. Longitudinal diffusion of polarons was analyzed in terms of spin interaction with the lattice phonons of crystalline domains embedded into an amorphous polymer matrix. The interchain spin hopping is determined by the number and depth of the traps photoinitiated in the polymer matrix. Pseudorotation of methanofullerene molecules in a polymer matrix was shown to follow the activation Pike model. The replacement in the composite of PC₆₁BM acceptors by PC₇₁BM ones accelerates electron relaxation, hinders the formation of spin traps, and favors more ordered (crystalline) structure of bulk heterojunction that facilitates charge transfer in the P3HT/PC₇₁BM composite.



INTRODUCTION

Among photovoltaic systems,¹ polymer bulk heterojunction (BHJ) solar cells based on composites of an electron-donating conjugated polymer and an electron-accepting fullerene offer promise for the realization of a perspective flexible renewable energy source.² Over the past decade, research has focused mainly on BHJ formed by regioregular poly(3-hexylthiophene) (P3HT) with (6,6)-phenyl-C₆₁-butyric acid ester (PC₆₁BM) methanofullerene.³ Although BHJ solar cell performance has steadily improved, with power conversion efficiencies approaching 8%,⁴ further improvements in efficiency are required for large-scale commercialization. The irradiation of such BHJ by visible light with photon energy $h\nu_{\text{ph}}$ higher than the π - π^* energy gap of the conjugated polymer E_g leads to the formation

of singlet excitons on the polymer chain (D, donor), $D \xrightarrow{h\nu_{\text{ph}}} D^*$, which are strongly bound due to weak screening in the polymer semiconductor.⁵ Such an exciton can cover the neighboring fullerene globe (A, acceptor), forming a more extended exciton, $D^* + A \rightarrow (D-A)^*$, in the polymer bulk.⁶ During the next stage, the charge transfer $(D-A)^* \rightarrow (D^{\delta+}-A^{\delta-})^*$ is initiated, and these excitons are reorganized into the donor-acceptor complexes which then collapse into radical pairs, $(D^{\delta+}-A^{\delta-})^* \rightarrow (D^{\bullet+}-A^{\bullet-})$, due to structural relaxation. Polaron hole $D^{\bullet+}$ possesses high mobility along the polymer chain, so such formed radical pairs are finally separated into two independent spin charge carriers, $(D^{\bullet+}-A^{\bullet-}) \rightarrow D^{\bullet+}-A^{\bullet-}$.

Both photoinduced charge carriers possess spin $S = 1/2$, so their main magnetic, relaxation, and dynamics properties at

wide ranges of temperature and energy of initiated irradiation can be determined by using direct light-induced electron paramagnetic resonance (LEPR) spectroscopy. Such a method allows one to control the texture and other structural and electronic properties of photovoltaic devices for the further improvement of their conversion efficiency.^{7,8} However, the P3HT/PC₆₁BM composite possesses a low absorption coefficient in the visible spectral region and, as a consequence, a relatively small contribution to the photocurrent. Besides, until today partial LEPR studies were carried out mainly at helium temperatures when dynamic processes in organic photovoltaics are frozen. Finally, we have shown^{9,10} that the BHJ inhomogeneity leads to the arising in the polymer matrix of traps occupied by some free charge carriers, which changes their magnetic resonance parameters and complicates the effective LEPR spectrum. The number and depth of such traps are governed by the photon energy.

Light power conversion efficiency of plastic solar cells can partly be improved by the replacement of the PC₆₁BM methanofullerene by the bis-PC₆₁BM one.¹⁰ Photoluminescence and atomic force microscopy studies showed¹¹ wider and stronger absorption of PC₇₁BM than the analogous C₆₀ derivative. Since optical absorption is closely related to crystallinity of polymer/fullerene composites, it was inferred that, e.g., the P3HT/PC₇₁BM composite is more crystalline

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than the P3HT/PC₆₁BM one and, therefore, demonstrates higher (~33%) current density and power conversion efficiency. This increases the applicability of C₇₀-based composites in various photovoltaic devices, while the understanding of the elementary processes of exciton initiation, charge separation, stabilization, and recombination should be a prerequisite for improving the efficiency of such photovoltaic systems. Indeed, the formation of C₇₀ radical anions initiates a subgap photoinduced absorption band at 0.92 eV,¹² hidden in the spectra of polymer/PC₇₁BM composites, which allows for more exact studies of charge-separated states in such systems. On the other hand, a comparative multifrequency EPR study of the P3HT/PC₆₁BM and P3HT/PC₇₁BM composites has demonstrated¹³ a significant difference in deconvoluted LEPR spectra of both charge carriers. Indeed, the effective, isotropic, *g*-factors of the methanofullerene anion radicals photoinduced in these composites were obtained to be 1.99983 and 2.00360, respectively. These values differ from the appropriate value $g_{\text{iso}} = 2.00237$ obtained for polarons photoinduced in the former composite by $\Delta g_{\text{iso}} = -2.54 \times 10^{-3}$ and $\Delta g_{\text{iso}} = 1.23 \times 10^{-3}$, respectively. This evidences the decrease in absolute spectral resolution as PC₆₁BM is replaced by PC₇₁BM counterion in a respective composite which makes the direct identification of the respective LEPR spectrum rather speculative. Besides, there is little known about the composition, relaxation, and dynamics of spin charge carriers photoinduced in C₇₀ containing composites.

Here, we report the comprehensive LEPR study of the main magnetic, relaxation, and dynamics properties of charge carriers photoinduced in HBJ of the P3HT/PC₇₁BM composite made with the conventional X-band (9.5 GHz) EPR technique at wide regions of temperature and photon energy. It was shown that light irradiation initiates the formation in BHJ of free charge carriers and traps which parameters are governed by the structure of both BHJ components. The data obtained were compared with those recently reported for BHJ formed by P3HT with other methanofullerenes. It was shown that the replacement of the C₆₀ globe by the C₇₀ one accelerates electron relaxation, hinders the formation of spin traps, and favors a more ordered (crystalline) P3HT/PC₇₁BM composite that facilitates charge transfer through its BHJ.

EXPERIMENTAL SECTION

In the study, we used PC₇₁BM methanofullerene (99% fullerene purity) obtained from Solenne BV and regioregular P3HT (50 000 MW, 90–94% regioregularity) distributed by Rieke Metals, which are schematically shown in Figure 1. Their ca. 1 wt. % concentration solution in chlorobenzene at a 1:1 wt. ratio was casted serially into a ceramic plane and dried until the appropriate composite was formed as films with the size of ca. 4 × 8 mm² and thickness of ca. 0.1 mm. The sample was annealed at 403 K in a dry argon atmosphere for 10 min.

EPR measurements were performed using an X-band (3-cm, 9.7 GHz) PS-100X spectrometer with maximal microwave (MW) power of 150 mW and 100 kHz field *ac* modulation for phase-lock detection. The sample placed in the center of the MW cavity was permanently irradiated by Luxeon III LXHL-LW3C (5500 K), LXHL-LD3C (625 nm, 1.98 eV), LXHL-LL3C (590 nm, 2.10 eV), LXHL-LM3C (530 nm, 2.34 eV), LXHL-LE3C (505 nm, 2.46 eV), and LXHL-LR3C (455 nm, 2.73 eV) solid-state light sources whose illumination power was calibrated using an IMO-2N output power light irradiation bolometer. “Dark” and photoinduced EPR spectra of the

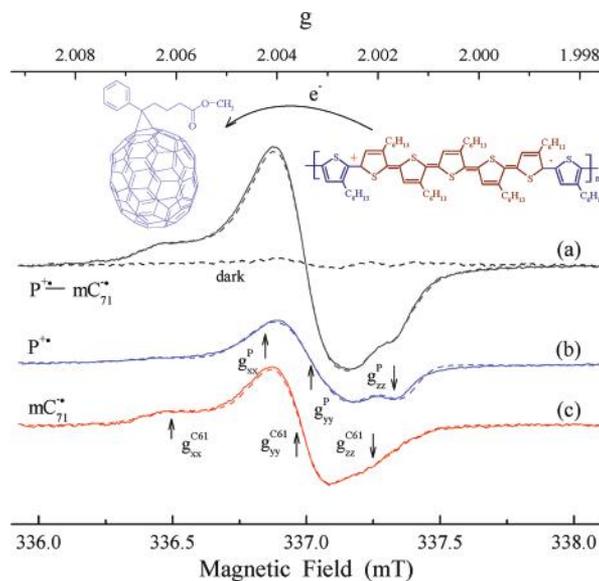


Figure 1. LEPR spectra of radical pairs $P^{+\bullet}-mC_{71}^{\bullet}$ (a) as well as their contributions due to polarons $P^{+\bullet}$ (b) and methanofullerene anion radicals mC_{71}^{\bullet} (c) background photoinduced in P3HT/PC₇₁BM bulk heterojunctions by photons with $h\nu_{\text{ph}} = 2.10$ eV at 77 K (a). Dashed lines show the spectra calculated using the terms of their *g*-tensor obtained (see the text). Photoinitiation of a polaron on a polymer chain accompanied by electron transfer to a methanofullerene globe is schematically shown. The positions of photoinduced radicals and terms of their *g*-tensors are shown as well.

composite were obtained at 77 K in quartz Dewar filled with liquid nitrogen and at the 90–340 K region in a dry nitrogen atmosphere using a BRT SKB IOH temperature controller. In the latter case, the temperature is controlled by a calibrated Cu/Cu:Fe thermocouple with high sensitivity (15 mV/K at 20 K) and stability (0.5 K) situated near the sample. Gaseous nitrogen flow with the stability of 0.1% makes it possible to vary the temperature in the EPR cavity center with the stability of 0.3 K. The signal-to-noise ratio of the LEPR spectra was improved by signal averaging at several (typical 4–6) acquisitions. The diphenylpicrylhydrazyl (DPPH) single microcrystal standard with $g_{\text{iso}} = 2.00360$ was used for estimation of the *g*-factor of both paramagnetic centers. Absorption LEPR spectra were doubly integrated far from MW saturation conditions when the magnetic term B_1 of the MW field and amplitude B_m of *ac* modulation in the cavity center did not exceed 5 μ T and 0.1 mT, respectively. All relaxation parameters of both types of charge carriers were determined separately using the steady-state saturation method.¹⁴ The error of determination of activation energies was near 5%. Processing and simulations of the EPR spectra were performed with the Bruker WinEPR SimFonia and OriginLab Origin programs.

RESULTS AND DISCUSSION

Prior to illumination, only a weak “dark” EPR signal was observed in all temperature ranges (see Figure 1a). It was attributed to the edge- and/or cross-localized paramagnetic centers. Under background illumination at temperatures below 160 K, two lines appear in the LEPR spectrum of the composite (Figure 1a), attributed to polarons diffusing in the polymer backbone and methanofullerene anion radicals pseudorotating (or hopping between their own low-temperature and high-temperature phases) between polymer chains. Since the

concentration of main charge carriers decreases dramatically at $T > 160$ K, the precision of determination of their spin susceptibility falls significantly. If one switches off the illumination, the intensity of the sum LEPR signal decreases sharply; its part remains persistent (Figure 1b) and can be eliminated only by warming the sample. This means that some parallel processes can be realized in the background irradiate polymer/fullerene composite, namely, direct formation of pairs of mobile spin charge carriers and a pinning of a part of them by polymer traps and reverse recombination of polarons and methanofullerene anion radicals.^{9,10,15} The analysis has shown that the direct processes occur considerably faster as PC₆₁BM molecules are replaced by PC₇₁BM ones in the composite. Besides, the only polaronic carriers are captured by spin traps in the P3HT/PC₇₁BM composite analogously to that as it happens in the P3HT/bis-PC₆₁BM one.¹⁰

Earlier, we showed from a comparative 2 mm (140 GHz) and 3 cm (10 GHz) waveband EPR study¹⁶ that an unpaired electron delocalized on a polaron in poly(3-alkylthiophenes) weakly interacts with sulfur heteroatoms involved in the polymer backbone. This provokes rhombic symmetry of spin density and, therefore, anisotropic g -factor and line width. Since the backbone of the polymer lies preferably parallel to the film substrate,¹⁷ the lowest principal g -value, g_{zz} is associated with the polymer backbone. The macromolecule can take any orientation relative to the z -axis, i.e., the polymer backbone direction as is derived from the presence of both the g_{xx} and g_{yy} components in the spectra for all BHJ orientations in the sample. Thus, the g -factor anisotropy is a result of inhomogeneous distribution of additional fields along the x and y directions within the plane of the polymer σ -skeleton rather than along its perpendicular z direction. The analogous conclusion was made later during 3 mm (94 GHz)¹⁸ and 2 mm (130 GHz)¹³ waveband EPR study of polarons photoinduced in the P3HT matrix allowed to determine the main terms of their g -tensor, $g_{xx} = 2.0028$, $g_{yy} = 2.0019$, $g_{zz} = 2.0009$ and $g_{xx} = 2.0038$, $g_{yy} = 2.0023$, $g_{zz} = 2.0011$, respectively. The main values of the g -tensor were determined for the polarons P^{•+} photoinduced and captured by traps in the P3HT/PC₇₁BM composite matrix under study to be $g_{xx} = 2.004$, $g_{yy} = 2.002$, and $g_{zz} = 2.001$ ($g_{\text{iso}} = 2.002$) at 77 K. The contribution of the methanofullerene charge carriers $mF_{71}^{\bullet-}$ can then be obtained by the deconvolution of the sum LEPR spectrum of both charge carriers into two individual spectra under the assumption that optical photons initiate an equal number of positively and negatively charged carriers. If this is so, the $mF_{71}^{\bullet-}$ spectrum (Figure 1c) may simply be obtained by the extraction of the P^{•+} spectrum (Figure 1b) from the initial LEPR one shown in Figure 1a. Such a deconvolution procedure allowed us to determine $g_{xx} = 2.006$, $g_{yy} = 2.003$, $g_{zz} = 2.002$ ($g_{\text{iso}} = 2.004$) for $mF_{71}^{\bullet-}$ anion radicals photoinduced in the P3HT/PC₇₁BM composite under study. It is evident from the figure that the spectra of both charge carriers are fitted well by those calculated with the above obtained g -tensor terms. These values lie near those determined at higher spectral resolution.^{13,18} If the effective g -factor of different $F_{61}^{\bullet-}$ anion radicals is normally less than the g -factor of the free electron,^{9,10,13,19} ($g_e = 2.00232$), the g_{iso} value of the $mF_{71}^{\bullet-}$ anion radical exceeds g_e .^{13,20} This is in agreement with the study of respective anion radicals in crystalline ($g_{\text{iso}} = 2.0047$)^{21,22} and dissolved^{22,23} C₇₀. Such an effect has been supposed²⁴ to appear due to different Jahn–Teller dynamics of C₆₀ and C₇₀ molecules, which might contribute to different signs of the g -value shifts. According to

the classical Stone theory of g -factors,²⁵ negative deviation of the g -factor from g_e is due to spin–orbit coupling with empty p - or d -orbitals, while spin–orbit coupling with occupied orbitals leads to positive g -factor deviation. The latter case is typical for most organic radicals. Thus, a difference in g -values of $mF_{61}^{\bullet-}$ and $mF_{71}^{\bullet-}$ anion radicals indicates the different electronic structure of their molecular orbitals. Nevertheless, there is no united theory explaining spin properties of these fullerene radicals yet.

The deconvolution of the initial LEPR spectrum allowed us to obtain separately all magnetic resonance parameters of both charge carriers. As in the case of analogous polymer/fullerene systems,^{8–10} effective paramagnetic susceptibility χ of the P3HT/PC₇₁BM composite was analyzed as a contribution of polarons χ_p and methanofullerene anion radicals χ_f . The limiting number of polarons n_p and methanofullerene anion radicals n_f simultaneously formed per each polymer unit in the P3HT/PC₇₁BM bulk heterojunctions was determined at 77 K and $h\nu_{\text{ph}} = 2.10$ eV to be 9.7×10^{-5} and 7.7×10^{-5} , respectively. The former parameters obtained are considerably lower than $n_p \approx 0.05$, estimated for polarons excited in doped polyaniline.²⁶

To analyze the effect of the energy of initiated photons on magnetic resonance parameters, paramagnetic susceptibility and line width of both the charge carriers photoinduced in the P3HT/PC₇₁BM composite by light sources with different photon energy $h\nu_{\text{ph}}$ (see Table 1) were measured. It is seen

Table 1. Effective Paramagnetic Susceptibility χ and Linewidth $\Delta B_{\text{pp}}^{(0)}$ of the Polaron and Methanofullerene Charge Carriers Photoinduced in the P3HT/PC₇₁BM Composite by Polychromatic White and Monochromatic Light with Different Photon Energy $h\nu_{\text{ph}}$ at 77 K^a

parameter	white	$h\nu_{\text{ph}}$, eV				
		1.98	2.10	2.34	2.46	2.73
$\chi,^b$ au	1.01	0.84	1.91	0.78	0.75	0.41
$\chi,^c$ au	0.56	0.36	1.00	0.35	0.38	0.22
$\Delta B_{\text{pp}}^{(0),b}$ mT	0.236	0.238	0.244	0.233	0.234	0.234
$\Delta B_{\text{pp}}^{(0),c}$ mT	0.145	0.138	0.156	0.151	0.153	0.149

^aThe upper (0) symbol in $\Delta B_{\text{pp}}^{(0)}$ is introduced to mean that this parameter is measured far from the spectrum microwave saturation.

^bDetermined for polarons. ^cDetermined for methanofullerene anion radicals.

from the table that the χ value of both charge carriers becomes distinctly higher at characteristic $h\nu_{\text{ph}} \approx 2.10$ eV, which lies near the band gap of P3AT.²⁷ Such a dependence of spin concentration on photon energy can be explained by the excitation of charge carriers in polymer and methanofullerene domains heterogeneously distributed in the system under study. Different ordering of these domains can be a reason for variation in their band gap energy, leading, hence, to their sensitivity to photons with different energies. This can give rise to the change in the interaction of charge carriers with a lattice and other spins. Indeed, $\Delta B_{\text{pp}}^{(0)}$ values obtained for both the charge carriers also demonstrate an extreme at the same $h\nu_{\text{ph}}$. It predestined the dominance of the further temperature study of the composite at this $h\nu_{\text{ph}}$.

Earlier we showed^{10,15} that the light illumination of a polymer/fullerene composite excites in its BHJ radical pairs and forms energetic traps where a part of the spin charge carriers are stabilized. As the background illumination is switched off,

mobile charge carriers recombine fast, and the pinned spins are collapsed for a longer time. It was noted above that these reverse processes proceed in the composite under study considerably faster than in the P3HT/PC₆₁BM BHJ. Such a difference can be explained by the smaller number and depth of spin traps photoinduced in more ordered domains distributed in the former. The number of so-formed long-living charge carriers is governed by various properties of structure and conformation properties of donor and acceptor. Figure 2

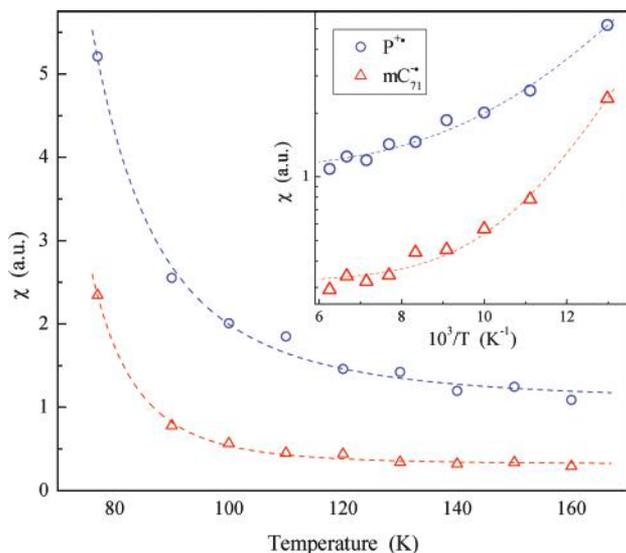


Figure 2. Linear and Arrhenius (inset) temperature dependences of spin susceptibility χ determined for the polarons $P^{\bullet\bullet}$ (circles) and methanofullerene anion radicals $mC_{71}^{\bullet\bullet}$ (triangles) photoinduced in the P3HT/PC₇₁BM composite at the photon energy $h\nu_{ph} = 2.10$ eV and 77 K. By the above and below dashed lines are shown the dependences calculated from eq 1 with ΔE_{ij} equal to 0.042 and 0.064 eV, respectively. The error margins are of the order of the symbol size.

illustrates the change in these values with the sample heating. These dependences were interpreted as a combination result of multistage trap-assisted polaron diffusion²⁸ along a polymer chain through an energetic barrier ΔE_{ij} accompanied by its exchange with the spin of methanofullerene pseudorotating near the polymer chain.²⁹ These processes should originate the following temperature dependence of paramagnetic susceptibility

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

where $\alpha = (3/2)2\pi J/\hbar\omega_d$ and J is a constant of exchange interaction of spins in an interim radical pair; k_B is the Bohr constant; $\hbar = h/2\pi$ is the Plank constant; and ω_d is the rate of polaron diffusion. Assuming the absence of a dipole–dipole interaction between fullerene anion radicals, one can evaluate energy ΔE_{ij} for polarons and methanofullerene anion radicals to be 0.042 and 0.064 eV, respectively. It is evident that the energy required for polaron trapping in the polymer matrix is lower than that obtained for another charge carrier. Besides, these parameters exceed those obtained for C₆₀-treated P3HT.^{9,10} This can, probably, be explained by the more aspheric globe of the PC₇₁BM anion-radical. As seen from Figure 2, the net electronic processes in the composites can indeed be described in terms of the above-mentioned approaches.

The effective EPR line width $\Delta B_{pp}^{(0)}$ of both charge carriers photoinduced in the P3HT/PC₇₁BM composite is presented in Figure 3 as a function of temperature. It is seen that this

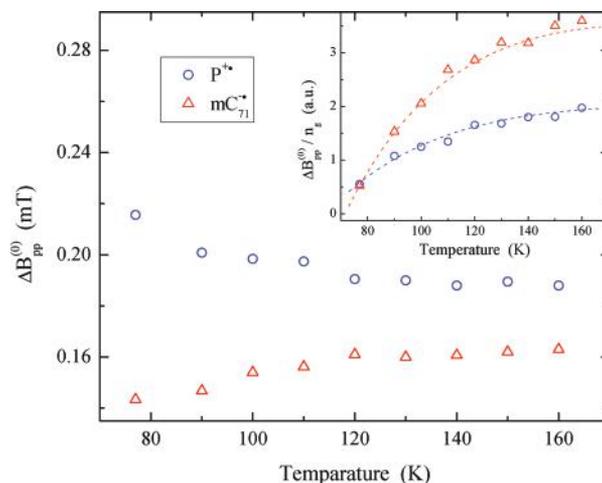


Figure 3. Temperature dependence of the initial and normalized to the n_g value peak-to-peak line width $\Delta B_{pp}^{(0)}$ determined for the central component of the polaron $P^{\bullet\bullet}$ (circles) and methanofullerene anion radicals $mC_{71}^{\bullet\bullet}$ (triangles) photoinduced in the P3HT/PC₇₁BM composite by photons with $h\nu_{ph} = 2.10$ eV. The upper (0) symbol in $\Delta B_{pp}^{(0)}$ means that this parameter is measured far from the spectrum microwave saturation. The dependences calculated from eq 2 with the $E_r = 0.0032$ and 0.0034 are shown by the above and below dashed lines. The error margins are of the order of the symbol size.

parameter obtained for polarons decreases with the system heating, whereas the line width of anion radicals demonstrates opposite temperature dependence. As in the case of other polymer/fullerene composites,^{9,10} the dependences presented can be interpreted in terms of exchange interaction of polarons diffusing along the polymer chain with the methanofullerene molecules moving near their own main molecular axis. The line width in result of such interaction should change with the temperature as¹⁰

$$\Delta B_{pp}^{(0)} = \frac{\pi t_{1D}^2 n_g(T)}{\hbar \sqrt{\frac{E_r k_B T}{\pi}}} \cdot \frac{\exp\left(-\frac{E_r}{4k_B T}\right)}{1 + \left[\frac{3J}{2t_{1D}^2} \sqrt{\frac{E_r k_B T}{\pi}} \exp\left(\frac{E_r}{4k_B T}\right) \right]^2} \quad (2)$$

where t_{1D} is the electronic coupling between the initial and final states (intrachain transfer integral) equal to 1.18 eV for P3HT;³⁰ n_g is a number of guest radicals per polymer unit; and E_r is both the inner- and outer-sphere reorganization energy of charge carriers due to their interaction with the lattice phonons.

Figure 3 presents also the dependences calculated from eq 2 with $E_r = 0.034$ and 0.032 eV for polarons and for methanofullerene anion radicals, respectively, normalized to the respective $n_g(T)$ function. These values appeared to be smaller than E_r evaluated for charge carriers initiated in regioregular P3HT³¹ and also in its composites with PC₆₁BM and bis-PC₆₁BM methanofullerenes.¹⁰ This fact additionally indicates more ordered structure with shallower traps in the P3HT/PC₇₁BM system under study as compared with C₆₀-based polymer/methanofullerene composites.

As the magnetic term B_1 of microwave irradiation increases, individual absorption lines of both the charge carriers are broadened, and their intensity I changes nonlinearly as seen in

Figure 4. This happens due to the steady-state saturation of the whole spin reservoirs allowing one to determine separately the

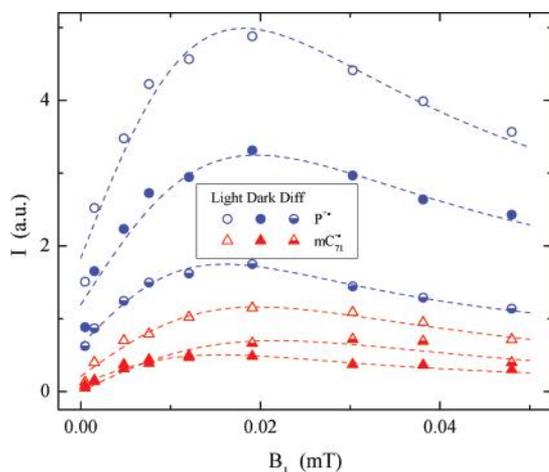


Figure 4. Intensity I of the polaron $P^{+\bullet}$ (circles) and methanofullerene anion radicals $mC_{71}^{\bullet-}$ (triangles) central component LEPR spectra obtained under irradiation at $h\nu_{\text{ph}} = 2.10$ eV (open points) after irradiation switch off (filled points) and as a resulting irradiation effect (semifilled points) at 90 K as a function of the B_1 term of the MW field. Top-to-down dashed lines show dependences calculated from eq 3 with $T_1 = 6.76 \times 10^{-7}$ and $T_2 = 7.24 \times 10^{-8}$ s, $T_1 = 5.73 \times 10^{-7}$ and $T_2 = 7.32 \times 10^{-8}$ s, $T_1 = 8.71 \times 10^{-7}$ and $T_2 = 7.24 \times 10^{-8}$ s, $T_1 = 4.15 \times 10^{-7}$ and $T_2 = 1.01 \times 10^{-7}$ s, $T_1 = 3.33 \times 10^{-7}$ and $T_2 = 1.01 \times 10^{-7}$ s, and $T_1 = 7.27 \times 10^{-7}$ and $T_2 = 9.16 \times 10^{-8}$ s, respectively. The error margins are of the order of the symbol size.

effective spin–lattice T_1 and spin–spin T_2 relaxation times from relations¹⁴

$$I = I_0^{(0)} B_1 (1 + \gamma_e^2 B_1^2 T_1 T_2)^{-3/2} \quad (3)$$

$$\Delta B_{\text{pp}} = \Delta B_{\text{pp}}^{(0)} \sqrt{1 + \gamma_e^2 B_1^2 T_1 T_2} \quad (4)$$

where γ_e is the gyromagnetic ratio for the free electron. The upper (0) symbols in $I_0^{(0)}$ and $\Delta B_{\text{pp}}^{(0)}$ mean that these parameters are measured far from the spectrum microwave saturation. The functions calculated from eq 3 with appropriated relaxation times are also shown in Figure 4.

Effective relaxation parameters of the polaronic and methanofullerene radicals using such a methodology are presented in Figure 5. It is seen from the figure that electron relaxation of polarons changes monotonically with the temperature. At the same time, an interaction of the methanofullerene anion radicals with the lattice phonons gives rise to extreme temperature dependence with characteristic $T_c \approx 110$ K. It should be noted that no such effect was registered earlier in the study of regioregular C_{60} -modified P3HT.¹⁰ T_c lies near $T = 100$ – 110 K, at which an electron relaxation of the photoexcited triplet state of fullerene C_{70} molecules embedded into organic (terphenyl and decalin) glasses accelerates sharply due to the interaction of thermally activated $^3C_{70}$ uniaxial dynamics with fast collective molecular librations in the matrices.³² Under the light illumination, the spin–lattice relaxation time of these charge carriers decreases (see Figure 5). The replacement of the $PC_{61}BM$ methanofullerene by the $PC_{71}BM$ one shortens its T_1 value at $T \leq T_c$ due to stronger interaction of the latter with the polymer lattice. This

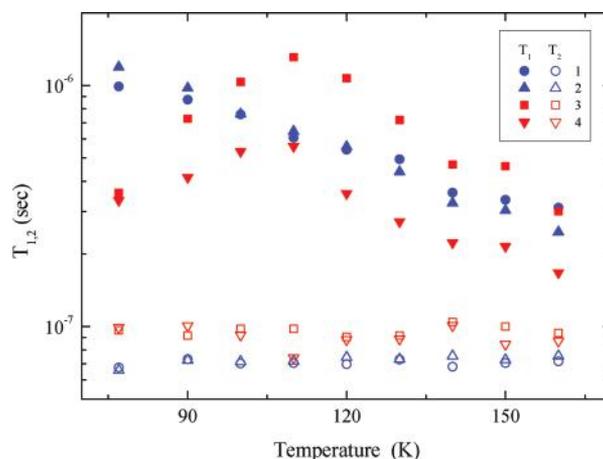


Figure 5. Temperature dependence of spin–lattice T_1 (filled points) and spin–spin T_2 (open points) relaxation times of the polarons $P^{+\bullet}$ (1,2) and methanofullerene anion radicals $mC_{71}^{\bullet-}$ (3,4) obtained without (1,3) and under (2,4) background light illumination of the P3HT/ $PC_{71}BM$ composite by photons with $h\nu_{\text{ph}} = 2.10$ eV. The error margins are of the order of the symbol size.

is in accordance with the solid-state ^{13}C NMR study of C_{60} and C_{70} .³³

Relaxation of both spin reservoirs is governed by molecular and spin dynamics in the composite under study. Polaron diffusion along and between polymer chains with coefficients D_{1D} and D_{3D} , respectively, and rotational hopping of the methanofullerene anion radical near its own main molecular axis with coefficient D_{rot} induce additional magnetic fields in the whereabouts of electron and nuclear spins which accelerate electron relaxation. As relaxation of spins in organic systems is defined mainly by their dipole–dipole interaction,^{34,35} these coefficients can be determined from the equations³⁶

$$T_1^{-1}(\omega_e) = \langle \omega^2 \rangle [2J(\omega_e) + 8J(2\omega_e)] \quad (5)$$

$$T_2^{-1}(\omega_e) = \langle \omega^2 \rangle [3J(0) + 5J(\omega_e) + 2J(2\omega_e)] \quad (6)$$

where $\langle \omega^2 \rangle = 1/10 \gamma_e^4 \hbar^2 S(S+1) n \sum ij$ is a constant of a dipole–dipole interaction for powder with n spins per monomer unit and lattice sum $\sum ij$; $J(\omega_e) = (2D_{1D}^2 \omega_e)^{-1/2}$ at $D_{1D}^2 \gg \omega_e \gg D_{3D}$ or $J(0) = (2D_{1D}^2 D_{3D}^2)^{-1/2}$ at $D_{3D}^2 \gg \omega_e$ is a spectral density function for Q1D motion, $D_{1D}^2 = 4D_{1D}/L^2$; ω_e is the resonant angular frequency of electron spin precession; and L is the spatial extent of the polaron wave function equivalent to 4–5 monomer units for organic conjugated polymers including P3AT.³⁷ A similar spectral density function was earlier used in the study of spin dynamics in other conjugated polymers.^{34,35,38} A spectral density function for rotational diffusion with correlation time τ_c is $J_{\text{rot}}(\omega_e) = 2\tau_c / (1 + \tau_c^2 \omega_e^2)$.

The dynamic parameters calculated from eqs 5 and 6 for both types of charge carriers photoinduced in the composite under study are presented in Figure 6 as a function of temperature. As in the case of other fullerene-modified P3HT BHJ,^{9,10} they demonstrate monotonic dependence on the temperature.

To account for the LEPR mobility data obtained, different theoretical models can be used.

Intrachain polaron dynamics in the P3HT/ $PC_{71}BM$ composite is characterized by strong temperature dependence (Figure 6). Such a behavior can be explained, e.g., by the scattering of polarons on the lattice phonons of crystalline

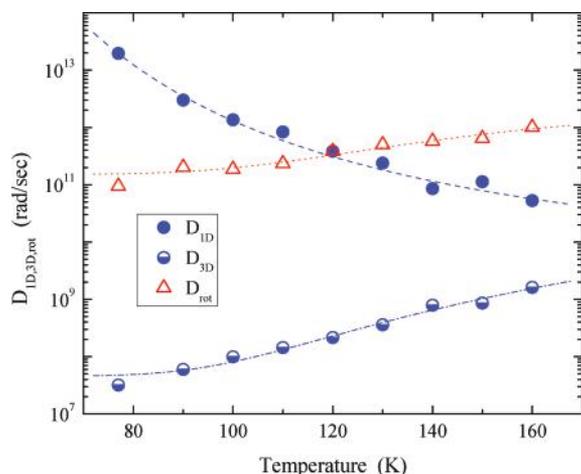


Figure 6. Temperature dependence of intrachain D_{1D} (filled points), interchain D_{3D} (semifilled points) coefficients of the polarons $P^{+\bullet}$, and rotational diffusion D_{rot} coefficient (open points) of the methanofullerene anion radicals mC_{71}^{\bullet} photoinduced in the P3HT/PC₇₁BM composite by photons with $h\nu_{ph} = 2.10$ eV. Dashed, dot-dashed, and dotted lines show the dependences calculated from eq 7 with $E_{ph} = 0.093_1$ eV, eq 8 with $E_t = 0.010_5$ eV, $T_{cr} = 130$ K, $\sigma_0 = 0.030_3$ eV, and eq 9 with $E_b = 0.061_1$ eV, $\alpha = 0.8$, respectively. The error margins are of the order of the symbol size.

domains embedded into the amorphous polymer matrix. According to such a model, polaron diffusion along a polymer chain with a diffusing coefficient D_{1D} should depend on the temperature as³⁹

$$D_{1D} = D_{1D}^{(0)} T^2 \left[\sinh\left(\frac{E_{ph}}{k_B T}\right) - 1 \right] \quad (7)$$

where E_{ph} is phonon energy.

Figure 6 evidences that the D_{1D} obtained for polarons follows well eq 7 with $E_{ph} = 0.093$ eV. The latter lies near the energy of lattice phonons, 0.09–0.32 eV, determined for other conjugated polymers^{35,40} and polymer/fullerene composites.^{8–10}

The interchain spin hopping dynamics can be analyzed, for example, in terms of the modified Hoesterey–Letson formalism of trap-controlled mobility.⁴¹ According to this model, the existence in a polymer matrix of the traps should lead to the following dependence for charge hopping between polymer chains

$$D_{3D} = D_{3D}^{(0)} \exp\left(\frac{E_t}{2k_B T_{cr}}\right) \exp\left[-\frac{E_t}{2k_B T} \left(\frac{\sigma_0}{k_B T}\right)^2\right] \quad (8)$$

where $T_{cr} = E_t/2k_B \ln(n_t)$ is critical temperature at which the transition from trap-controlled to trap-to-trap hopping transport regimes occurs; E_t and n_t are the depth and concentration of the traps, respectively; and σ_0 is the width of intrinsic energetic distributions of hopping states in the absence of traps.

Figure 6 shows also the temperature dependences calculated from eq 8 with $E_t = 0.010$ eV. The figure evidences that interchain polaron dynamics can indeed be controlled by traps formed in a polymer matrix under its irradiation. The E_t value obtained is considerably less than that characteristic of C₆₀-modified regioregular P3HT¹⁰ that additionally indicates a more ordered (crystalline) polymer matrix of the system under study.

To account for the methanofullerene mobility data, the modified Pike's model⁴² of single-phonon-assisted hopping of the charge carrier between localized states over potential barrier E_b can probably be used.⁴³ This model postulates the following frequency and temperature-dependent coefficient of rotating diffusion D_{rot} of globes as

$$D_{rot} = D_{rot}^{(0)} T^2 \omega_e^s \exp\left(-\frac{E_b}{k_B T}\right) \quad (9)$$

where the exponent $s = 1 - \alpha k_B T/E_b$ reflects system dimensionality and α is a constant.

The energy E_b necessary to activate methanofullerene angular diffusion in the P3HT/PC₇₁BM composite was obtained from the fitting of experimental data to be 0.061 eV. It is seen from Figure 6 that the model proposed explains well experimental data. The E_b value obtained exceeds that (0.02–0.03 eV) evaluated for low-temperature ³C₇₀ dynamics in different organic glassy matrices,^{32,44} 0.042 eV obtained for dynamics of the bis-PC₆₁BM anion radical embedded into the P3HT matrix;¹⁰ however, it is considerably less than that (0.220–0.283 eV) obtained for reorientation of C₇₀ molecules in the solid matrix.^{45,46} Assuming more anisotropic dynamics of C₇₀ molecules in solids than that of C₆₀ due to the more prolate spheroidal geometry of the former,^{33,46,47} a comparison of the pseudorotational dynamics of PC₆₁BM and PC₇₁BM methanofullerenes indicates that the latter reorients harder which can be attributed to different lattice ordering of respective composites.

CONCLUSIONS

In summary, we have presented the results of the comprehensive LEPR study of charge transfer through P3HT/PC₇₁BM BHJ. Under irradiation of the composite, two spin charge carriers are excited in its BHJ, polarons (holes) diffusing along polymer chains and methanofullerene anion radicals moving inside the polymer backbone. Simultaneously, energetic traps seized a part of polarons that are formed in the polymer matrix. The number of photoinduced radical pairs is governed by the multistage trap-assisted polaron activation diffusion along a polymer chain. All main magnetic resonance parameters of these charge carriers obtained from deconvolution of sum LEPR spectra were demonstrated to be governed by the energy of initiated photons. This fact indicates the existence in the composite of polymer and methanofullerene domains with different ordering and sensitivity to respective optical photons. Electron relaxation of spin pairs and intrachain polaron diffusion are also governed by the number and depth of spin traps light-initiated in the polymer matrix as well as by interaction with the lattice phonons. The replacement in the composite of PC₆₁BM acceptors by PC₇₁BM ones retards their pseudorotation, accelerates electron relaxation, and changes the electronic structure of their molecular orbitals. This hinders the formation of spin traps in the polymer matrix and favors more ordered (crystalline) structure that facilitates charge transfer through BHJ in the P3HT/PC₇₁BM composite.

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Notes

The authors declare no competing financial interest.

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