

## Light-induced EPR study of charge transfer in P3HT/*bis*-PCBM bulk heterojunctions

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Radical pairs, polarons and fullerene anion radicals photoinduced by photons with energy of 1.98 – 2.73 eV in bulk heterojunctions formed by poly(3-hexylthiophene) (P3HT) with *bis*(1-[3-(methoxycarbonyl)propyl]-1-phenyl)-[6.6]C<sub>62</sub> (*bis*-PCBM) fullerene derivative have been studied by direct light-induced EPR (LEPR) method in a wide temperature range. A part of photoinduced polarons are pinned in trap sites which number and depth are governed by an ordering of the polymer/fullerene system and energy of initiating photons. It was shown that dynamics and recombination of mobile polarons and counter fullerene anion radicals are governed by their exchange- and multi-trap assisted diffusion. Relaxation and dynamics parameters of both the charge carriers were determined separately by the steady-state saturation method. These parameters are governed by structure and conformation of the carriers' microenvironment as well as by the energy of irradiating photons. Longitudinal diffusion of polarons was shown to depend on lattice phonons of crystalline domains embedded into an amorphous polymer matrix. The energy barrier required for polaron interchain hopping is higher than that its intrachain diffusion. Pseudorotation of fullerene derivatives in a polymer matrix was shown to follow the activation Pike model. © 2011 Author(s). This article is distributed under a Creative Commons Attribution Non-Commercial Share Alike 3.0 Unported License. [doi:10.1063/1.3599411]

### I. INTRODUCTION

In bulk heterojunction solar cells,<sup>1,2</sup> in which power conversion efficiency have already attained about 6%,<sup>3</sup> light photons generate singlet excitons, which are strongly bound due to weak screening in polymer semiconductor.<sup>4</sup> Such solar cells consist of an interpenetrating adsorbing network of fullerene globes embedded into polymer matrix. Soluble derivatives of polythiophene, poly(3-alkylthiophene) (P3AT), and fullerene, 1-[3-(methoxycarbonyl)propyl]-1-phenyl-[6.6]C<sub>61</sub> (PCBM methanofullerene,  $mC_{61}^{-\bullet}$ ), are frequently used as electron donor and acceptor, respectively.<sup>5</sup> A relative position of the HOMO–LUMO levels and the choice of electrode materials which might show suitable work functions are basic requirements to make an optimal solar cell. If the HOMO of the donor (HOMO<sub>D</sub>) lies higher than that of the acceptor (HOMO<sub>A</sub>) and additionally LUMO<sub>D</sub> > LUMO<sub>A</sub>, D→A charge transfer becomes energetically favorable for the electron. This provokes the turnover exciton to the (D-A)<sup>\*</sup> complex which collapses into the D<sup>+•</sup>-A<sup>-•</sup> radical pair due to structural relaxation.<sup>6</sup> To dissociate the exciton must be generated in close vicinity to the donor/acceptor interface, because its diffusion length is typically 5–7 nm.<sup>7</sup> Since a hole possesses high mobility along a polymer backbone, the radicals are scattered in this radical pair, so then two noninteracting spins, D<sup>+•</sup> and A<sup>-•</sup>, are stabilized in bulk heterojunction. A long spatial distance lowers the probability of their collision and recombination that provides longer lifetime. This explains why the forward process occurs in the femtosecond time domain,<sup>8</sup> whereas back electron transfer with charge annihilation occurs in much longer timescale. At each step, the D–A system can relax back

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to the ground state releasing energy to the lattice either as heat or emitted light. To maximize light converting properties, a donor should maintain a low HOMO energy level and a narrow band gap. An optimal energy difference  $LUMO_D - LUMO_A$  should be 0.3 – 0.5 eV.<sup>9</sup> However, this value minimally reached for bulk heterojunctions formed by PCBM and poly(3-hexylthiophene) (P3HT) is much higher, namely, 1.1 eV. This results in so relatively low efficiency of such solar cells.

There are some ways to reduce the above mentioned energy offset. One of them is to reduce the  $LUMO_D$  level, however, it can increase efficiency up to 6.5 % only.<sup>10</sup> A higher limit (8.4%) was predicted<sup>10</sup> to be more beneficial for a single-layer solar cell when the  $LUMO_A$  offset is reduced to 0.5 eV. Recently, Lenes *et al.*<sup>11</sup> have suggested to use another fullerene derivative as electron acceptor, namely, *bis*(1-[3-(methoxycarbonyl)propyl]-1-phenyl)-[6.6]C<sub>62</sub> (*bis*-PCBM methanofullerene, *bmC*<sub>62</sub><sup>\*</sup>) in which the fullerene cage is functionalized by two methanobridged PBM side groups, with a higher (by ~0.1 eV)  $LUMO_A$  than that of PCBM. Indeed, the replacement of PCBM by *bis*-PCBM in plastic solar cells was shown by optical microscopy<sup>12</sup> to improve their electronic properties. However, it was shown<sup>13</sup> that photoluminescence dynamics becomes slower at such replacement due to the reorganization of bulk heterojunction. Besides, quantum efficiency can be reduced due to possible formation of triplets from intersystem crossing of the excitons or by intersystem crossing of the charge separated states followed by charge recombination.<sup>14</sup>

Magnetic, relaxation and dynamics properties of polarons P<sup>+</sup>• (holes) stabilized in different organic polymer semiconductors were studied by direct conventional<sup>15,16</sup> and high-frequency/high-field<sup>17,18</sup> electron paramagnetic resonance (EPR) spectroscopy. In organic solar cells, fullerene anion radicals also possess spin  $S = \frac{1}{2}$  and pseudorotate between polymer chains. As the excitons dissociate into ion radicals, mobile polarons flee from the fullerene anions along a conjugated polymer backbone faster than 10<sup>-9</sup> s. That is a reason why spins in radical pairs can be considered as non-interacting; they are long-lived and demonstrate separate LEPR spectra. This accounts for a wide use of the light-induced EPR (LEPR) as direct method for investigation of fullerene-modified conjugated polymers.<sup>1,19</sup> LEPR measurements revealed the photoinducing under light irradiation of organic polymer/fullerene composite of polarons and fullerene anion radicals with different line shapes, magnetic resonance parameters and saturation properties. They are stabilized in different phases of a disordered polymer/fullerene bulk heterojunctions. The system inhomogeneity leads to the arising of traps in polymer matrix occupied by some carriers, so that changes their magnetic resonance parameters and complicates effective LEPR spectrum. So, by using such direct method it appears to be possible to control the texture and other structural and electronic properties of photovoltaic devices for the further increase in their efficiency. However, up today such LEPR studies are carried out mainly at helium temperatures when dynamic processes in organic photovoltaics appear to be frozen. Recently, we showed<sup>20,21</sup> that a LEPR spectra of charge carriers photoinduced in P3AT/PCBM bulk heterojunctions indeed contains contributions of mobile and pinned charge carriers with different spectrum shapes. Magnetic, relaxation and dynamics parameters of these radicals were demonstrated to be governed by the energy of initiated photons  $h\nu_{ph}$ .<sup>19-22</sup>

Herein, we present results of the LEPR study of main properties of charge carriers photoinduced in the P3HT/*bis*-PCBM bulk heterojunctions. We demonstrate the increase of dimensionality of this composition under the replacement of PCBM by *bis*-PCBM. Such substitution increases the planarity of a polymer matrix, decreases the number of traps, and, therefore, accelerates charge transfer through bulk heterojunctions.

## II. EXPERIMENTAL

In the study we used *bis*-PCBM methanofullerene obtained from Solenne BV and regioregular P3HT obtained from Rieke Metals. Chemical structures of these components are shown schematically in Fig. 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 polymer/fullerene composites were formed as films with the size of ca. 4 x 8 mm<sup>2</sup> and thickness of ca. 0.1 mm. To determine maximal concentration of polarons which can be stabilized in polymer matrices, initial P3HT/*bis*-PCBM composite was treated by dry iodine vapor as described earlier.<sup>21</sup>

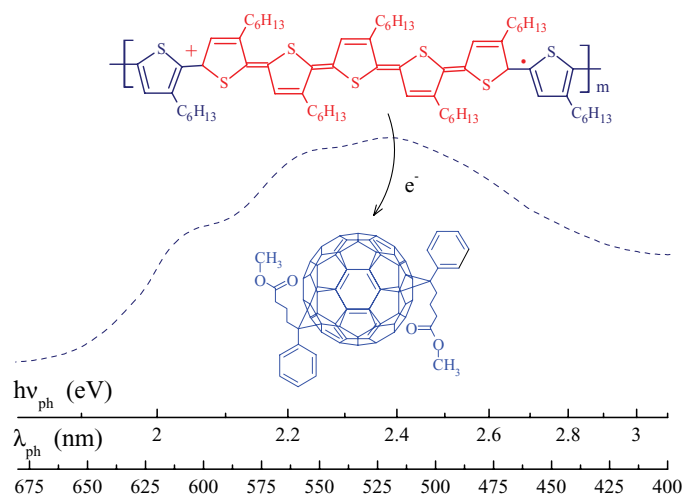


FIG. 1. Schematic representation of the extraction of an elemental charge transfer from the regioregular P3HT chain (above) to the *bis*-PCBM globe (below) following by the formation of mobile polaron on the former. UV-Vis absorption spectrum of the P3HT/*bis*-PCBM composite are shown by dashed line as function of the photon energy  $h\nu_{ph}$  (linewidth  $\lambda_{ph}$ ).

The optical absorption spectrum of the composite was obtained using a Shimadzu UV-VIS-NIR scanning UV-3101PC spectrophotometer is also shown in Fig. 1. It demonstrates the extrema at ca. 2.03 eV (612 nm), 2.20 eV (563 nm), and 2.39 eV (519 nm), characteristic of regioregular P3HT<sup>23</sup> and two peaks at 4.54 eV (273 nm) and 3.68 eV (337 nm) (outside of the Figure) attributed to methanofullerene.

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 MW cavity was permanently irradiated by Luxeon III LXHL-LW3C (5500 K, 80 lm), LXHL-LD3C (625 nm, 1.98 eV, 100 lm), LXHL-LL3C (590 nm, 2.10 eV, 80 lm), LXHL-LM3C (530 nm, 2.34 eV, 80 lm), LXHL-LE3C (505 nm, 2.46 eV, 80 lm), and LXHL-LR3C (455 nm, 2.73 eV, 450 mW) with a spectral half bandwidth of ca. 0.1 eV (except LXHL-LW3C) LED light sources. Their firm supplied irradiation spectra are shown in Fig. 2. Effective integral irradiation doses of these sources were estimated using an IMO-2N output power light irradiation bolometer to be rationed as 1.20:1.19:0.47:0.99:1.00:1.86, respectively. These ratios were used for the further normalization of spin susceptibility. “Dark” and photoinduced EPR spectra of the polymer/fullerene system and its ingredients were obtained at 77 K in quartz Dewar filled with liquid nitrogen and at 90 - 340 K in dry nitrogen atmosphere 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 mK/K at 20K) and stability (0.5 K) placed near the sample. Gaseous nitrogen flow with the stability of 0.1% makes it possible to vary 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. Diphenylpicrylhydrazyl (DPPH) single microcrystal standard with  $g_{iso} = 2.00360$  was used for estimation of *g*-factor of both charge carriers. To improve the signal-to-noise ratio of the LEPR spectra the averaging several (typical 4 - 6) acquisitions was made. The measurements of effective magnetic susceptibility of the “dark” (domestic) paramagnetic centers (PC) and PC photoinduced in polymer/fullerene bulk heterojunctions were performed using a 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) nitroxide radical. Absorption LEPR spectra were doubly integrated far from MW saturation conditions when magnetic term  $B_1$  of MW field and amplitude  $B_m$  of *ac* modulation in the cavity center did not exceed 5  $\mu$ T and 0.1 mT, respectively. All relaxation parameters of both type charge carriers were determined separately using the steady-state saturation method.<sup>24</sup> 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.

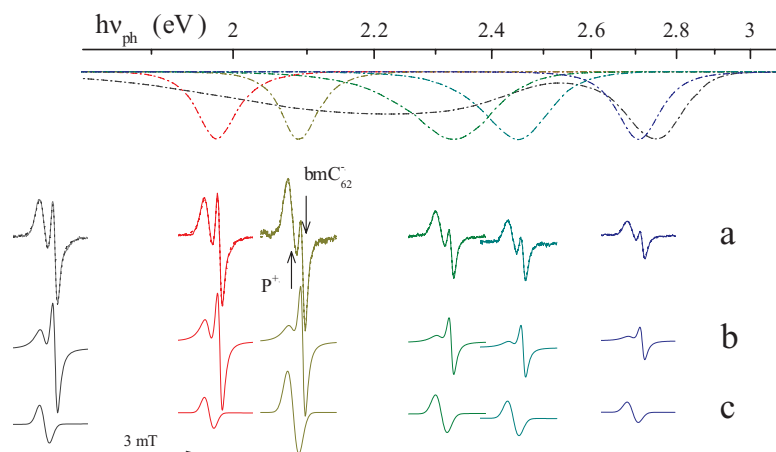


FIG. 2. *a* – X-band (9.7 GHz/340 mT) LEPR spectra of charge carriers background photoinduced at 77 K in bulk heterojunctions formed by macromolecules of regioregular P3HT with globes of *bis*-PCBM by (from left to right) white light and by the light with photon energy  $h\nu_{ph}$  (linewidth  $\lambda_{ph}$ ) of 1.98 eV (625 nm), 2.10 eV (590 nm), 2.33 eV (530 nm), 2.46 eV (505 nm), and 2.72 eV (455 nm). The intensities of the spectra are normalized to the output power of light sources (see experimental part). Sum spectra (*a*, dashed lines) as well as their Lorentzian contributions caused by mobile radical quasi-pairs,  $P_{mob}^{+\bullet} \leftrightarrow bmF_{mob}^{-\bullet}$  (*b*), and Gaussian ones originated by localized polarons,  $P_{loc}^{+\bullet}$  (*c*), theoretically calculated using respective magnetic resonance parameters and concentration ratios are also shown. The positions of LEPR spectra of polarons,  $P^{+\bullet}$ , and methanofullerene anion radicals,  $bmC_{62}^{-\bullet}$ , are shown as well. Top dash-dotted lines represent irradiation spectra of the light sources.

### III. RESULTS AND DISCUSSIONS

#### A. Spectral composition and *g*-factor

Detached regioregular P3HT and *bis*-PCBM shown in Fig. 1 are characterized by the absence of both “dark” and photoinduced LEPR signals over the entire range of temperatures studied. Their composite irradiated by visible light directly in a cavity of the EPR spectrometer, two overlapping LEPR lines appear reversibly at  $T \leq 200$  K (Fig. 2). Low- and high-field lines were attributed to positively charged polarons  $P^{+\bullet}$  with isotropic (effective)  $g_{iso}^P$  and negatively charged methanofullerene with effective  $g_{iso}^F$  background photoinduced in the P3HT/*bis*-PCBM bulk heterojunctions. The effective values  $g_{iso}^P = 2.0023$  and  $g_{iso}^F = 2.0007$  are close to those obtained for charge carriers photoinduced in other polymer/fullerene composites,<sup>19,25</sup> however, exceed those,  $g_{iso}^P = 2.0017$  and  $g_{iso}^F = 1.9996$ , obtained for P3HT/PCBM.<sup>21</sup> Note, that the  $g_{iso}^P$  value of the latter measured more accurately at W-band (94 GHz) EPR is equal to 2.00187.<sup>26</sup> These parameters were appeared to become weakly temperature dependent than those of the P3HT/PCBM composite.<sup>21</sup> As in case of other polymer/fullerene systems,<sup>20,21</sup> LEPR spectra of the P3HT/*bis*-PCBM bulk heterojunctions consists of two Lorentzian contributions of mobile polarons and *bis*-methanofullerene anion radicals in quasi-pairs  $P_{mob}^{+\bullet} \leftrightarrow bmF_{mob}^{-\bullet}$  as well as a Gaussian contribution of localized polarons,  $P_{loc}^{+\bullet}$ , pinned in polymer traps (see Fig. 2). It should be to note that, as compared with the P3HT/PCBM system, there is absent contribution of pinned fullerene radicals,  $bmF_{loc}^{+\bullet}$ . This implies that the number of deep traps able to capture a radical anion in the P3HT/*bis*-PCBM composite is sufficiently lower than that in the P3HT/PCBM one due to the better ordinary of the former. The best fit of the LEPR spectra of the samples was achieved using a convolution of Gaussian and Lorentzian line shapes, which means that electron excitation leads to inhomogeneous and homogeneous line broadening, respectively, due to unresolved hyperfine interaction of unpaired spin with neighboring protons and also to its different mobility.

Effective *g*-factor of polarons is strongly governed by the structure and conformation of a conjugated  $\pi$ -electron system. Our high-frequency (140 GHz) EPR study of structurally close poly(3-octylthiophene) showed<sup>27</sup> that an unpaired electron delocalized on polaron and extended

over  $L$  lattice units weakly interacts with sulfur heteroatoms involved in the polymer backbone. This provokes rhombic symmetry of spin density and, therefore, anisotropic  $g$ -factor and linewidth. Since the backbone of the polymer can be expected to lie preferably parallel to the film substrate,<sup>28</sup> the lowest principal  $g$ -value is associated with the polymer backbone. The macromolecule can take any orientation relative to the  $z$ -axis, i.e. the polymer backbone direction as it derives from the presence of both the  $g_{xx}$  and  $g_{yy}$  components in the spectra for all orientations of the film. 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  $\sigma$ -skeleton rather than along its perpendicular  $z$  direction. This was confirmed later at millimeter waveband LEPR study of the P3HT/PCBM composite. Thus, it was shown that the spin of polarons photoinduced in the P3HT chains is also characterized by rhombic symmetry originating anisotropic  $g$ -factor with  $g_{xx} = 2.0028$ ,  $g_{yy} = 2.0019$ ,  $g_{zz} = 2.0009$  at W-band (94 GHz) EPR<sup>26</sup> and  $g_{xx} = 2.00380$ ,  $g_{yy} = 2.00230$ ,  $g_{zz} = 2.00110$  at D-band (130 GHz) EPR.<sup>29</sup> Spin distribution in the  $mC_{61}^{\bullet}$  anion radical embedded into P3HT matrix is also characterized by rhombic symmetry that leads to respective anisotropy of its  $g$ -factor with  $g_{xx} = 2.00058$ ,  $g_{yy} = 2.00045$ ,  $g_{zz} = 1.99845$ .<sup>29</sup>

P3HT HOMO energy level depends on the overlap of adjacent thiophene MOs and, therefore, is expected to shift with ring angle<sup>30</sup> similarly to the valence band involved in the  $\pi$ - $\pi^*$  transition. The band gap, LUMO – HOMO, should depend on torsion angle  $\theta$  between the planes of the neighboring thiophene rings,<sup>31</sup> being near  $30^\circ$  in regioregular P3HT.<sup>32</sup> A decrease in  $g_{iso}^p$  occurs at electron excitation from the unoccupied shell to the antibonding orbit,  $\pi \rightarrow \sigma^*$ .<sup>33</sup> Comparing the data obtained for P3HT/PCBM<sup>21</sup> with those presented above, one may conclude that the energy of antibonding orbits decreases as *bis*-PCBM is embedded into the P3HT matrix instead of PCBM. This increases  $g_{iso}^p$  of the P3HT/*bis*-PCBM composite and decreases the slope of its temperature dependency characteristic of more ordered system. Indeed, the changes in total energy with the torsion angle  $\theta$  appear as effective steric potential energy. The angular dependence of this energy is anharmonic, with larger angles becoming more probable with the temperature increase. In this case the decrease of molecular regioregularity or a greater distortion of the thiophene rings out of coplanarity reduces charge mobility along the polymer chains.<sup>34</sup> This is usually attributed to a decrease in the effective conjugation lengths of the chain segments. The intrachain transfer integral  $t_{1D}$  is primarily governed by the degree of overlap between the  $p_z$  atomic orbitals of the carbon atoms forming polymer units and, therefore, should evolve a square-cosine function of the torsion angle  $\theta$ .<sup>35</sup> This allows one to evaluate the decrease in the  $\theta$  value by  $\sim 10^\circ$  at the replacement of the PCBM by *bis*-PCBM in the P3HT/methanofullerene system. This fact and the weaker temperature dependence of  $g$ -factors of both charge carriers in the P3HT/*bis*-PCBM composite indicate the growing in planarity and ordering of polymer matrix occurring at such replacement.

## B. Paramagnetic susceptibility

The limiting number of polarons  $n_p$  and fullerene anion radicals  $n_f$  simultaneously formed per each polymer unit in the P3HT/*bis*-PCBM bulk heterojunctions can be determined, as in the case of analogous systems,<sup>21</sup> by  $I_2$ -doping of the sample. Limiting paramagnetic susceptibility  $\chi$  of iodine-treated composite was determined at 310 and 77 K to be  $8.7 \times 10^{-6}$  and  $9.9 \times 10^{-5}$  emu/mole, respectively. The analysis showed that the cooling of the sample leads to the appearance of anisotropic Gaussian term in its sum EPR spectra attributed to strongly frozen polarons. The ratio of a number of mobile to frozen polarons at 77 K is appeared to be near 7:1. Mobile polarons initiated in the sample by the  $I_2$ -doping demonstrate at 310 K single Lorentzian EPR spectra with peak-to-peak linewidth  $\Delta B_{pp}$  of 0.56 mT, which are broader than that (0.4 mT)<sup>21</sup> obtained for polarons stabilized in the P3HT/PCBM matrix and other conjugated polymers.<sup>18</sup> Such broadening of the EPR line becomes most likely due to stronger dipole-dipole interaction between charged polarons. The contribution to linewidth due to such interaction can be estimated as  $\Delta B_{dd} = \mu_B R_0^{-3} = 4/3 \pi \mu_B n_p$ , where  $\mu_B$  is Bohr magneton,  $R_0$  is distance between polarons proportional to their concentration  $n_p$  on the polymer chain. At 77 K, the  $\Delta B_{pp}$  values of mobile and trapped polarons are equal to 0.18 and 0.19 mT and characterized by Lorentzian and Gaussian distribution of spin packets, respectively. Assuming intrinsic linewidth of polarons  $\Delta B_{pp}^0 = 0.15$  mT in regioregular P3HT,<sup>36</sup> one can obtain

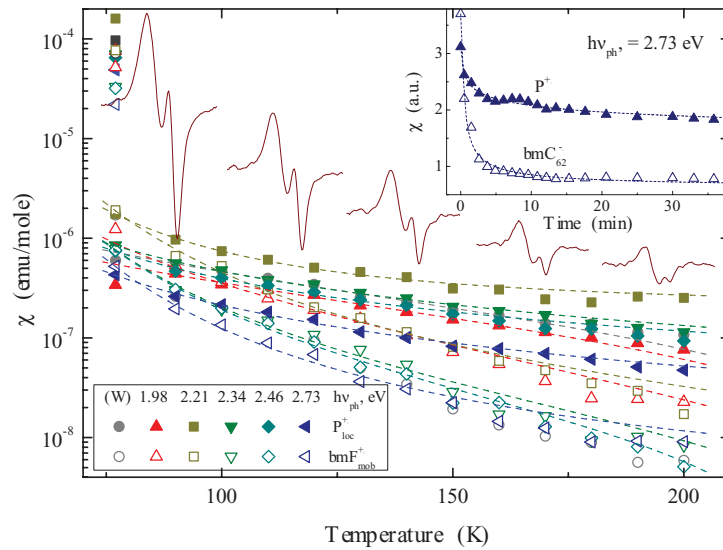


FIG. 3. Temperature dependence of paramagnetic susceptibility of the  $P_{loc}^{+\bullet}$  and  $bmF_{mob}^{\bullet}$  charge carriers photoinduced in bulk heterojunctions P3HT/*bis*-PCBM by photons with different energy  $h\nu_{ph}$ . Respective limiting values evaluated for these carriers at 77 K by using  $I_2$ -doping of the composite are shown as well. Dashed lines show some dependences calculated from Eq.(3) with  $\Delta E_{ij}$  summarized in Table I. LEPR spectra of these heterojunctions registered at respective temperatures are shown at the top. In the insert are shown the decay of spin susceptibilities of pinned polarons  $P_{loc}^{+\bullet}$  (filled points) and pseudorotating methanofullerene anion radicals  $bmF_{mob}^{\bullet}$  (open points) photoinduced in the bulk heterojunction of P3HT/*bis*-PCBM system by photons with  $h\nu_{ph} = 2.73$  eV at 77 K. Dashed lines show the dependences calculated from Eq.(4) with  $E_0$  summarized in Table I. The error does not exceed the square points.

$R_0 \approx 1.3$  nm from the line broadening due to dipole-dipole interaction in P3HT/*bis*-PCBM. The maximum density of polaron transport states was estimated,<sup>37</sup> e.g., for regioregular P3HT to be near  $10^{21}$   $\text{cm}^{-3}$  assuming that one polaron occupies approximately five monomer units. Intrinsic concentration of doping-initiated polarons counting only upon polymer fraction in the P3HT/*bis*-PCBM composite was determined at 77 K to be  $2.2 \times 10^{19}$   $\text{cm}^{-3}$ . This value lies near  $2 \times 10^{19}$   $\text{cm}^{-3}$  obtained for concentration of acceptors in ZnO-treated P3HT.<sup>38</sup> Effective concentration calculated for both polymer and fullerene phases in the composite under study is  $2.1 \times 10^{18}$   $\text{cm}^{-3}$ . This allows one to evaluate an effective number of both types of charge carriers per each polymer unit initiated in the polymer/fullerene composites by light irradiation (see Fig. 3) and  $I_2$ -initiated polarons,  $n_p = 3.8 \times 10^{-3}$  emu/mole. The  $n_p$  values obtained are considerably lower than that,  $n_p \approx 0.05$ , estimated for polarons excited in doped polyaniline.<sup>39</sup>

The fitting of LEPR spectra of the P3HT/*bis*-PCBM composite allowed us to obtain separately all terms of its effective paramagnetic susceptibility  $\chi$  as contributions of mobile and localized polarons  $\chi_P$  and methanofullerene anion radicals  $\chi_F$ . Figure 3 illustrates the changes in LEPR spectra of the P3HT/*bis*-PCBM composite with its heating and temperature dependences of all contributions into sum  $\chi$ . Since concentration of main charge carriers decreases dramatically at  $T > 200$  K, the precision of determination of their spin susceptibility falls significantly.

Fast initiation and consequent slow recombination of spin charge carriers in polymer/fullerene bulk heterojunctions at background illumination allow one to register spin susceptibility as a differential result of these processes. The probability of the latter is mainly governed by polaron multistage diffusion along a polymer chain through an energetic barrier and further electron tunneling from a fullerene anion to a polymer chain.<sup>40</sup> Motion of polarons is assumed to be described by the a multiple trapping in sites with respective energy  $E_t$ .<sup>41,42</sup> Since crystalline subsystems in a composite are characterized by different band gaps, their  $E_t$  energies are also different and distributed exponentially. If energy of a trapped polaron exceeds  $E_t$ , it is occasionally thermally detrapped to the free state. A positive charge of polaron is not required to be recombined with negative charge on first fullerene. Diffusing along polymer backbone with positive elemental charge it may collide with the

TABLE I. Energies  $\Delta E_{ij}$  in Eq.(3), and  $E_0$  in Eq.(4) determined for charge carriers in the P3HT/*bis*-PCBM composite irradiated by polychromatic white and monochromatic light with different photon energy  $h\nu_{ph}$  (all in eV).

Parameter	White	$h\nu_{ph}$				
		1.98	2.10	2.34	2.46	2.73
$\Delta E_{ij}^a$	0.0027	0.0014	0.0288	0.0140	0.0162	0.0177
$\Delta E_{ij}^b$	0.0171	0.0239	0.0404	0.0350	0.0375	0.0413
$E_0^a$	0.0309	0.0409	0.0272	0.0184	0.0144	0.0107
$E_0^b$	0.0080	0.0202	0.0136	0.0198	0.0222	0.0227

<sup>a</sup>determined for  $P_{loc}^{+\bullet}$ .

<sup>b</sup>determined for  $bmF_{mob}^{-\bullet}$ .

nearest fullerene radical anion located between polymer chains and then to recombine with a charge on a subsequent counter-anion. Assuming that polaron motion is not disturbed by the presence of fullerene molecules, we can conclude that the collision duration is governed by polaron diffusion. As it walks randomly along the chain, it passes a given fullerene molecule with frequency  $\nu_c \approx \omega_{hop}/L^2$ . The polaron that diffuses between initial  $i$  and final  $j$  sites spatially separated by distance  $R_{ij}$  spends the energy equal to the difference of their depths,  $\Delta E_{ij}$ . Thus, the Miller—Abrahams energy-dependent factor should appear in the equation for paramagnetic susceptibility<sup>41</sup>

$$\chi = \chi_0 \exp\left(-\frac{2R_{ij}}{r}\right) \exp\left(\frac{\Delta E_{ij}}{k_B T}\right), \quad (1)$$

where  $r$  is effective localization (Bohr) radius of a charge carrier. A positive charge of polaron is not required to be recombined with negative charge on first fullerene, it can to recombine with a charge on a subsequent counter-ion. The fullerene molecules can be considered as fast relaxing impurities, and the spin flip-flop probability  $p$  during such a collision should depend on the exchange amplitude and the frequency of polaron diffusion  $\omega_{hop}$  as<sup>39,43</sup>

$$p = \frac{1}{2} \cdot \frac{\alpha^2}{1 + \alpha^2}, \quad (2)$$

where  $\alpha = (3/2) 2\pi J/\hbar\omega_{hop}$  and  $J$  is a constant of exchange interaction of spins in a interim radical pair. It is evident that the longer time of charge tunneling or/and the lower probability  $p$ , the smaller a number of photoinduced charge carriers able to recombine and, therefore, the higher a spin susceptibility should be registered. Generally, weak and strong exchange limits can be realized in such spin system. In the case of weak or strong exchange, the increase of  $\omega_{hop}$  may result in the decrease or the increase in exchange frequency, respectively. A combination of Eqs.(1) and (2) affords a general form of this main parameter for polarons in polymer/fullerene composite:

$$\chi = \chi_0 \frac{2(1 + \alpha^2)}{\alpha^2} \exp\left(-\frac{2R_{ij}}{r}\right) \exp\left(\frac{\Delta E_{ij}}{k_B T}\right). \quad (3)$$

Assuming the absence of a dipole-dipole interaction between fullerene anion radicals, one can evaluate energy  $\Delta E_{ij}$  for all charge carriers from temperature dependences of their paramagnetic susceptibility (see Table I). As it is seen from Fig. 3, the net electronic processes in the composites can be described in terms of spin exchange with  $\Delta E_{ij}$  presented in Table I.

It is evident that the energy required for polaron trapping in the polymer matrix is lower than that obtained for other charge carriers.  $\Delta E_{ij}$  evaluated from  $\chi(T)$  for mobile radicals increases considerably indicating higher energy required for their trapping in the system. This value becomes larger for methanofullerene if it is pinned by a polymer matrix of the P3HT/PCBM composite.<sup>21</sup> The data obtained evidence one more that all spin-assisted processes are governed mainly by the structure of radical anion as well as by the nature and dynamics of charge carriers photoinduced in bulk heterojunction. It is seen that the  $\chi$  value of both charge carriers becomes distinctly higher at characteristic energy  $h\nu_{ph} \approx 2.1$  eV lying near the band gap of P3AT.<sup>44</sup> Such a dependence of spin concentration on photon energy can be explained either by the formation of spin pairs with different

properties in homogeneous (higher ordered) composite fragments or by the excitation of identical charge carriers in heterogeneous domains (lower ordered) of the system under study. Different spin pairs can be photoinduced as a result of the photon-assisted appearance of traps with different energy depths in a polymer matrix. However, the revealed difference in the parameters of radicals seems to be a result of their interaction with their microenvironment in domains inhomogeneously distributed in polymer/fullerene composite. Different ordering of these domains can be a reason for variation in their band gap energy leading, hence, to their sensitivity to photons with definite but different energies. This can give rise to the change in the interaction of charge carriers with a lattice and other spins. Effective spin susceptibility of the sample under study somewhat exceeds that obtained for P3HT/PCBM.<sup>21</sup> This effect and the absence of trapped anion radicals in the former allowed to conclude additionally more ordered bulk heterojunctions in the P3HT/*bis*-PCBM composite which interfere in the formation of traps.

If one includes Coulomb interactions, this should affect the activation energy for either defrosting or thermally assisted tunnelling by an amount  $U_c = e^2/4\pi\epsilon\epsilon_0r$ , where  $e$  is elemental charge,  $\epsilon$  is a dielectric constant, and  $r$  is charge pair separation. Assuming  $\epsilon = 3.4$  for P3HT,<sup>45</sup> minimum separation of charge carriers is equal to the radius of  $\pi$  electrons on the C atoms  $a$  which two times longer than the Bohr radius, i.e. 0.106 nm,  $r$  equal to interchain separation, 0.38 nm,<sup>23</sup> one obtains the decrease in  $U_c$  from  $\sim 0.4$  eV down to 0.02 eV during dissociation of an initial radical pair. Therefore, both the photoinduced polaron and the anion radical should indeed be considered as noninteracting that prolongs their life.

When initiating background illumination is switched off, photoinitiation of charge carriers in bulk heterojunction stops and the concentration of spin charge carriers excited starts to decrease as shown in the insert of Fig. 3. Live time of charge carriers seems to be much longer than  $t \sim 0.1 \mu s$  obtained by optical absorption spectroscopy for relevant recombination times of mobile photoexcitations in organic solar cells.<sup>2,46</sup> So, the data presented are mainly pertinent to carriers trapped in polymer matrix. Charge recombination, generally, is described as a thermally activated bimolecular recombination<sup>47</sup> which consists of temperature-independent fast and exponentially temperature-dependent slow steps.<sup>37</sup> At the latter step, polaronic charge carrier can either be retrapped by vacant trap sites or recombine with electron on fullerene radical anion. Trapping and retrapping of a polaron reduces its energy that results in its localization into deeper trap and in the increase in number of localized polarons with time. So, the decay curves presented can be interpreted in terms of bulk recombination between holes and electrons during their repeated trapping into and detrapping from trap sites with different depths in energetically disordered semiconductor.<sup>42</sup> Analysing LEPR spectra, it becomes possible to separate the decay of mobile and pinned spin charge carriers excited in the composite. The traps in such a system should be characterized by different energy depths and energy distribution  $E_0$ . Polarons fast translative diffuse along a polymer backbone, and fullerene anion radicals can be considered to be immobilized between polymer chains. This approach predicts the following law for decay of charge carriers:<sup>42</sup>

$$\frac{n(t)}{n_0} = \frac{\pi\alpha\delta(1+\alpha)\nu_d}{\sin(\pi\alpha)} t^{-\alpha}, \quad (4)$$

where  $n_0$  is the initial number of polarons at  $t = 0$ ,  $\delta$  is the gamma function,  $\alpha = k_B T/E_0$ ,  $\nu_d$  is the attempt jump frequency for polaron detrapping.

The dependences calculated with  $E_0$  presented in Table I for charge carriers photoinduced in the bulk heterojunctions studied are also presented in Fig. 3. It is shown that Eq.(4) fits well the experimental data presented in the Figure. Therefore, the decay of long-lived charge carriers originated from initial spin pairs photoinduced in the polymer/fullerene composite can successfully be described in terms of the above model in which the low-temperature recombination rate is strongly governed by temperature and the width of energy distribution of trap sites.

The analysis of the experimental data allows one to conclude the crucial role of the photon energy on the formation and energy properties of the traps in a bulk heterojunction of disordered systems. The width of energy distribution of the traps in the P3HT/*bis*-PCBM system decreases with growing  $h\nu_{ph}$ . On the other hand, mobile charge carriers are characterized by extremal  $E_0(h\nu_{ph})$



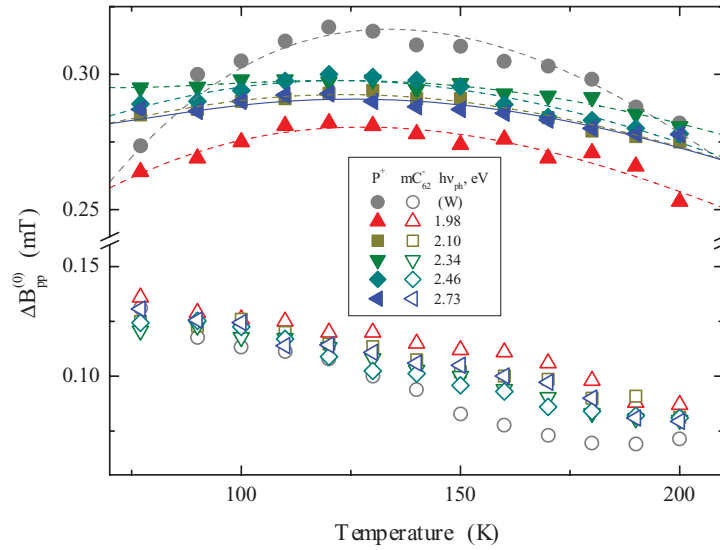


FIG. 4. Linewidth of charge carriers photoinduced in the P3HT/*bis*-PCBM composite as a function of temperature and photon energy  $h\nu_{ph}$ . Dashed lines show the dependences calculated from Eq.(8) with  $E_i$  presented in Table II. The symbol (0) in  $\Delta B_{pp}^{(0)}$  implies that the LEPR spectra were measured far from MW saturation, when  $B_1 \rightarrow 0$ . The error does not exceed the square points.

dependences with a minimum at  $\sim 2.1$  eV (Table I). This indicates that the local structure and ordering govern the depth of spin traps and their distribution in this composite.

### C. Linewidth

Effective EPR linewidth of both charge carriers photoinduced in the P3HT/*bis*-PCBM composite is presented in Fig. 4 as a function of temperature and photon energy. It is seen that this value obtained for polarons is characterized by  $\cap$ -like temperature dependence with the extreme lying near 130 K, whereas linewidth of the methanofullerene anion radicals demonstrates more monotonic temperature dependence and decreases with the system heating. This value is mainly determined by transverse (spin-spin) relaxation time  $T_2$ . However, there are several relaxation processes in a polymer/fullerene system which cause the shortening of  $T_2$  and hence the broadening of the LEPR line. One of them is spin longitudinal (spin-lattice) relaxation on the lattice phonons with time  $T_1$ , which shortens the lifetime of a spin state and therefore broadens the line. If we represent all other possible relaxation processes by time  $T_2^l$ , we can write for effective peak-to-peak width  $\Delta B_{pp}$  of a Lorentzian line<sup>48</sup>

$$\Delta B_{pp} = \frac{2}{\sqrt{3}\gamma_e} \cdot \frac{1}{T_2} = \frac{2}{\sqrt{3}\gamma_e} \cdot \left( \frac{1}{T_2^l} + \frac{1}{2T_1} \right). \quad (5)$$

Paramagnetic centers of both spin reservoirs can dipole-dipole interact. Besides, sulphur and hydrogen atoms in a polymer/fullerene composite possess a nuclear magnetic moment initiating the hyperfine interaction between the electrons and the nuclei. (<sup>13</sup>C has a natural abundance of only 1.1% in the composite studied, so seems to contribute weakly to both linewidths). Polaron translational and fullerene pseudorotational diffusion in a polymer/fullerene composite should also be taken into account. While polaron possesses high mobility, the fullerene molecule can be considered as a translative fixed one, but pseudorotating near its own main molecular axis. In this case a polaron should interact with its unpaired electron with the collision probability  $p$  expressed by Eq.(4), so then its absorption line should additionally be broadened by the value<sup>39</sup>

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

TABLE II. Energies  $E_t$  in Eq.(8),  $E_{ph}$  in Eq.(11),  $\sigma_0$  and  $E_t$  in Eq.(12), and  $E_b$  in Eq.(13) characteristic of mobile charge carriers photoinduced in the P3HT/*bis*-PCBM composite by polychromatic white and monochromatic light with different photon energy  $h\nu_{ph}$  (all in eV).

Parameter	$h\nu_{ph}$					
	white	1.98	2.10	2.34	2.46	2.73
$E_t^a$	0.0453	0.0479	0.0495	0.0468	0.0509	0.0503
$E_{ph}$	0.0615	0.0765	0.0751	0.0909	0.0875	0.0650
$\sigma_0$	0.0193	0.0167	0.0219	0.0174	0.0160	0.0206
$E_t^b$	0.1228	0.1283	0.1294	0.1275	0.1189	0.1250
$E^b$	0.0627	0.0770	0.0423	0.0786	0.0565	0.0588

<sup>a</sup>obtained from  $\Delta B_{pp}(T)$  dependences,

<sup>b</sup>obtained from  $D_{3D}(T)$  dependences.

where  $n_f$  is a number of methanofullerene radicals per polymer unit. The rate of charge hopping between two adjacent identical thiophene rings can be estimated to a good approximation using a semiclassical Marcus theory adopted for conjugated polymers<sup>34,35</sup>

$$\omega_{hop} = \frac{4\pi^2}{\hbar} \frac{t_{1D}^2}{\sqrt{4\pi E_r k_B T}} \exp\left(-\frac{E_r}{4k_B T}\right), \quad (7)$$

where  $t_{1D}$  is electronic coupling between initial and final states (intrachain transfer integral) and  $E_r$  is both the inner- and outer-sphere reorganization energy of charge carriers due to their interaction with the lattice phonons. The  $t_{1D}$  value was obtained for regioregular P3HT to be equal to 1.18 eV and to decrease slightly with temperature, whereas its distribution broadens a line due to thermal motion of the rings.<sup>49</sup> This is similar to charge transfer in organic crystals modulated by disorder caused by thermal molecular motion.<sup>50</sup> Note that the  $n_f$  parameter is temperature dependent that should be included into finalized equation. Combination of Eqs.(6) and (7) yields

$$\delta(\Delta\omega) = \frac{\pi t_{1D}^2 n_f(T)}{\hbar \sqrt{\frac{E_r k_B T}{\pi}}} \cdot \frac{\exp\left(-\frac{E_r}{4k_B T}\right)}{1 + \left[\frac{3J}{2t_{1D}^2} \sqrt{\frac{E_r k_B T}{\pi}} \exp\left(\frac{E_r}{4k_B T}\right)\right]^{-2}}. \quad (8)$$

The dependences calculated from Eq.(8) with  $E_t$  summarized in Table II and<sup>49</sup>  $t_{1D} = 1.18$  eV are presented in Fig. 4. The fitting is evidence of the applicability of these approaches for interpretation of electronic processes realized in the composite studied. The energy  $E_t$  obtained lies near that evaluated for regioregular P3HT from ac conductometric (0.080 eV)<sup>51</sup> and <sup>13</sup>C NMR (0.067 – 0.085 eV at  $T < 250$  K)<sup>52</sup> data. Figure 4 shows that linewidth of the methanofullerene anion radicals decreases with the system heating. Besides, this value decreases at the replace of the PCBM acceptor by *bis*-PCBM in polymer/fullerene composite.<sup>21</sup> The latter fact additionally indicates more ordered structure of the P3HT/*bis*-PCBM composite as compared with P3HT/PCBM one.

#### D. Spin relaxation and dynamics

The main relaxation parameters of polarons and fullerene anion radicals determined using steady-state saturation method<sup>24</sup> are presented in Fig. 5 as a function of temperature and photon energy. It is seen from the Figure that the interaction of most charge carriers with the lattice is characterized by monotonic temperature dependence. All relaxation parameters are governed by structural and conformation properties of the polymer/fullerene composite as well as by the energy of initiating phonons. Mobile polarons diffuse along and between polymer chains with respective translative diffusion coefficients  $D_{1D}$  and  $D_{3D}$ . Besides, methanofullerene molecules pseudorotate near own main axis with coefficient  $D_r$ . Such spin dynamics induce additional magnetic fields in the bulk heterojunction accelerating electron relaxation of both spin ensembles. As relaxation times of spins in conjugated polymers are defined mainly by their dipole-dipole interaction,<sup>18,53</sup> the following

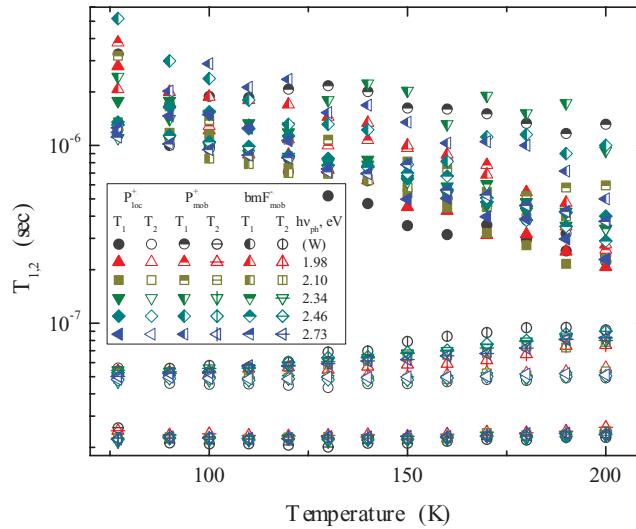


FIG. 5. Temperature dependence of spin-lattice  $T_1$  (filled and semi-filled points) and spin-spin  $T_2$  (open points) relaxation times of localized  $P_{loc}^{+\bullet}$  and mobile  $P_{mob}^{+\bullet}$  polarons as well as mobile methanofullerene anion radicals  $bmF_{mob}^{-\bullet}$  photoinduced in the P3HT/*bis*-PCBM composite by wide-band white light and by monochromatic light with different photon energy  $h\nu_{ph}$ . The error does not exceed the square points.

equations connecting their relaxation and dynamics parameters can be written:<sup>54</sup>

$$T_1^{-1}(\omega_e) = \langle \omega^2 \rangle [2J(\omega_e) + 8J(2\omega_e)], \quad (9)$$

$$T_2^{-1}(\omega_e) = \langle \omega^2 \rangle [3J(0) + 5J(\omega_e) + 2J(2\omega_e)], \quad (10)$$

where  $\langle \omega^2 \rangle = 1/10\gamma_e^4 \hbar^2 S(S+1)n\Sigma ij$  is a constant of a dipole-dipole interaction for powder with  $n$  spins per monomer unit and lattice sum  $\Sigma ij$ ,  $J(\omega_e) = (2D_{1D}^\dagger \omega_e)^{-1/2}$  at  $D_{1D}^\dagger \gg \omega_e \gg D_{3D}$  or  $J(0) = (2D_{1D}^\dagger D_{3D})^{-1/2}$  at  $D_{3D} \gg \omega_e$  is a spectral density function for Q1D motion,  $D_{1D}^\dagger = 4D_{1D}/L^2$ ,  $\omega_e$  is resonant angular frequency of electron spin precession, and  $L$  is the spatial extent of the polaron wavefunction equivalent approximately 4–5 monomer units for organic conjugated polymers, and, particularly, P3AT.<sup>37,55</sup> A similar spectral density function was earlier used in the study of spin dynamics in other conjugated polymers.<sup>15,18,56</sup> A spectral density function for rotational diffusion with correlation time  $\tau_c$  is  $J_{rot}(\omega_e) = 2\tau_c/(1+\tau_c^2\omega_e^2)$ .

Diffusion coefficients calculated from Eqs. (9) and (10) for both types of charge carriers photoinduced in the polymer/fullerene composite using the relaxation and susceptibility data obtained and the appropriate spectral density functions are presented in Fig. 6 as a function of the energy of initiating phonons and temperature. The Figure shows that the coefficient of polaron intrachain diffusion  $D_{1D}$  is governed sufficiently by the energy of initiated photons  $h\nu_{ph}$ . Comparison of the data presented with those obtained for P3HT/PCBM<sup>21</sup> evidences that the replacement of PCBM by *bis*-PCBM suppresses this effect. Besides, such a replacement increases anisotropy of polaron diffusion  $D_{1D}/D_{3D}$  in the P3HT matrix. This fact additionally justifies better planarity of the matrix with *bis*-PCBM molecules embedded. This is due to the fact that these more side-ramified methanofullerenes restrict the number of possible conformations able to be formed by two adjacent thiophene rings rotating about their shared C-C bond.

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

Intrachain polaron dynamics in the P3HT/*bis*-PCBM composite is characterized by strong temperature dependence (Fig. 6). Such a behavior can probably be associated with the scattering of polarons on the lattice phonons of crystalline domains immersed into an amorphous matrix. According to the model proposed for charge dynamics in crystalline domains of doped conjugated polymers, such scattering should affect polaron intrachain diffusion with an appropriate coefficient<sup>57</sup>

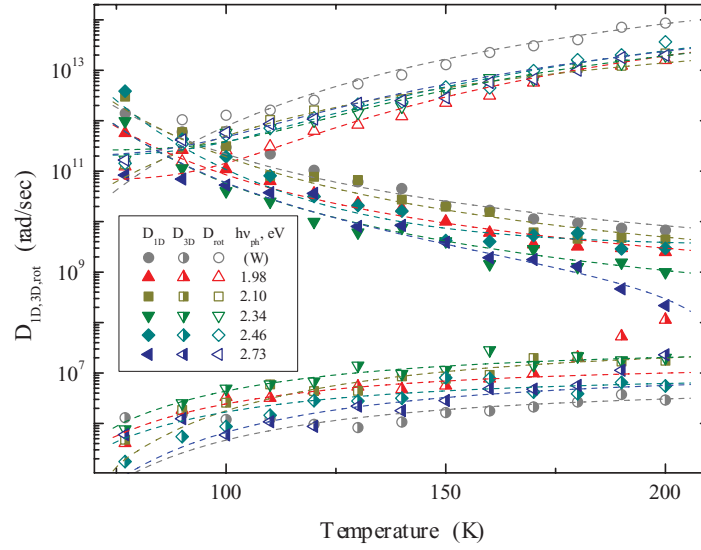


FIG. 6. Temperature dependence of intrachain ( $D_{1D}$ , filled points), interchain ( $D_{3D}$ , semi-filled points) and rotational diffusion ( $D_{rot}$ , open points) coefficients of mobile charge carriers  $P_{mob}^{+\bullet}$  and  $bmF_{mob}^{-\bullet}$  (left and right lines of the quasi-pairs (b) in Fig. 2, respectively) photoinduced in the P3HT/bis-PCBM composite by the polychromatic white and monochromatic light with different photon energy  $h\nu_{ph}$ . Dashed lines show the dependences calculated from Eqs.(11) to (13) with appropriate parameters presented in Table II. The error does not exceed the square points.

$$D_{1D} = \frac{\pi^2 M t_0^2 k_B^2 T^2}{h^3 \alpha_{eph}^2} \cdot \left[ \sinh\left(\frac{E_{ph}}{k_B T}\right) - 1 \right] = D_{1D}^{(0)} T^2 \cdot \left[ \sinh\left(\frac{E_{ph}}{k_B T}\right) - 1 \right] \quad (11)$$

where  $M$  is the mass of a polymer unit,  $t_0$  is the transfer integral equal for  $\pi$ -electron to  $\sim 2.5 - 3$  eV,  $\alpha_{eph}$  is a constant of electron-phonon interaction, and  $E_{ph}$  is phonon energy.

Figure 6 evidences that the  $D_{1D}$  obtained for polaron from Eq.(9) follows well Eq.(11) with the phonon energy summarized in Table II. This value lies near the energy of lattice phonons, 0.09 – 0.32 eV determined for doped polyanilines<sup>58</sup> and 0.15 – 0.18 eV obtained for laser modified poly(*bis*-alkylthioacetylene).<sup>59</sup>  $E_{ph}$  evaluated for the P3HT/*bis*-PCBM composite appears to be sensitive to the energy of illuminated photons attaining maximum at  $h\nu_{ph} = 2.46$  eV.

The interchain spin hopping dynamics can be analyzed, for example, in terms of the Hoesterey-Letson formalism modified for amorphous low-dimensional systems.<sup>60</sup> According to this model, charge hopping between polymer chains should be controlled by the traps with concentration  $n_t$  and depth  $E_t$ . Taking into account the relation of the trap-controlled interchain mobility  $\mu_{3D}$  of a charge carrier on its diffusion coefficient  $D_{3D}$ ,  $\mu_{3D} = eD_{3D}d^2/k_B T$  and combining Eqs.(18) and (25) in Ref. 60 in the case of low trap concentration limit, we obtained for the latter

$$D_{3D} = \nu_0 \left(\frac{R_{ij}}{d}\right)^2 \exp\left(-\frac{2R_{ij}}{r}\right) \exp\left(\frac{E_t}{2k_B T_{cr}}\right) \exp\left[-\frac{E_t}{2k_B T} \left(\frac{\sigma_0}{k_B T}\right)^2\right], \quad (12)$$

where  $\nu_0$  is hopping attempt frequency,  $d$  is the lattice constant,  $T_{cr} = E_t/2k_B \ln(n_t)$  is critical temperature at which the transition from trap-controlled to trap-to-trap hopping transport regimes occurs, and  $\sigma_0$  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.(12) with  $T_{cr} = 127 - 140$  K as well as with  $\sigma_0$  and  $E_t$  summarized in Table II. The Figure evidences that interchain polaron dynamics can be described in the frames of the above mentioned theory. The analysis showed that the  $E_t$  values obtained for P3HT/PCBM prevail those characteristic of P3HT/*bis*-PCBM that is additional evidence of deeper traps formed in the former polymer matrix. This fact, probably, indicates the decrease in trap concentration due the increase in effective crystallinity of the polymer

matrix. The data presented show that the photon energy governs both the  $T_{ct}$  and  $E_t$  parameters simultaneously, which attain the maximal and the minimal values, respectively, at  $h\nu_{ph} \approx 2.5$  eV.

It is seen from Table II that  $E_t$  obtained from Eq.(8) exceeds that determined above from Eq.(12). Such discrepancy appeared due, probably, to more complex temperature dependence of the interchain spin diffusion coefficient. However, comparing the data presented one can note rather like extremal  $E_t(h\nu_{ph})$  dependences reaching minimum at  $h\nu_{ph} \approx 2.4$  eV.

It is well known<sup>61</sup> that the fullerene globes pseudorotate in solids hopping between the low-temperature and high-temperature phases with respective activation energy. To account for the fullerene pseudorotational mobility data, the Pike's model<sup>62</sup> of single-phonon-assisted hopping of charge carrier between localized states over potential barrier  $E_b$  can be used. This model postulates the dependence of the coefficient of rotating diffusion  $D_{rot}$  on frequency and temperature,

$$D_{rot} = D_{rot}^{(0)} T^2 \omega_e^s \exp\left(-\frac{E_b}{k_B T}\right), \quad (13)$$

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

The energies  $E_b$  necessary to activate methanofullerene pseudorotational diffusion in the polymer/fullerene composite under study are summarized in Table II. It is seen from Fig. 6 that the temperature dependences of dynamic parameters calculated from Eq.(13) with  $E_b$  determined well fit experimental data. These values depends on photon energy (see Table II) and lie near those obtained for molecular dynamics in, e.g., polycrystalline fullerene<sup>61</sup> and a triphenylamine fullerene complex.<sup>63</sup>

#### IV. SUMMARY

In summary, we have presented the first results of a detailed LEPR study of charge transfer through bulk heterojunctions formed in the P3HT/*bis*-PCBM composite. They evidence directly that the main magnetic resonance, relaxation and dynamic parameters of polarons and methanofullerene anion radicals are governed by the structure, conformation and ordering of bulk heterojunctions as well as by the energy of excited photons. This can be partly as a result of structural inhomogeneity of the polymer/fullerene composite, conditioning the photon-initiated appearance of traps with different depth and distribution. The data obtained allowed us to suggest the importance of the ring-torsion and ring-librative motions on the charge initiation, separation and diffusion in disordered organic systems. It was shown that a polaron diffusing along a polymer backbone exchanges with the spin of a counter methanofullerene radical anion in terms of the modified Marcus theory. Charge recombination was interpreted in terms of carrier multitrapping in energetically disordered semiconductor whose local structure and ordering govern the number, depth and distribution of charge traps. The interaction of most charge carriers with the lattice is characterized by monotonic temperature dependence. Electron relaxation of charge carriers was shown to be also governed by dynamics, structure and conformation of their microenvironment as well as by photon energy. Polaron scattering on phonons in the composite is determined by the energy of illuminated photons. Such selectivity to photon energy is governed by properties of donor and acceptor forming bulk heterojunction and can be used, for example, in plastic sensoric photovoltaics. The energetic barrier required for polaron interchain hopping predominantly prevails that of its intrachain diffusion in the composite. As predicted, the use in organic photovoltaics of *bis*-PCBM methanofullerene instead of PCBM indeed increases the planarity and ordering of active polymer matrix and minimizes the energy loss in charge transfer. Such replacement decreases the number of traps, facilitates local molecular vibrations and, therefore, accelerates charge transfer through a bulk heterojunction. On the other hand, the energy required for pseudorotation of methanofullerene globes in the composites somewhat increases at such acceptor replacement. This can be due to "freezing" of molecular pseudorotation in the P3HT/*bis*-PCBM composite with a higher degree of matrix conjugation. The charge-transfer state energy, geminate recombination and the overlap between donor and acceptor in a bulk heterojunction are important factors in triplet formation and should be taken into account when designing new organic photovoltaics.

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