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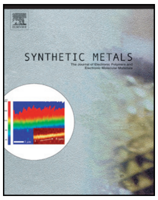

Influence of morphology of low-band-gap PCDTBT:$PC_{71}BM$ composite on photoinduced charge transfer: LEPR spectroscopy study

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Light-induced electron paramagnetic resonance (LEPR) study the steady-state of spin charge carriers initiated by Vis-NIR irradiation with the energy (wavelength) of 1.32–2.73 eV (940–455 nm) in organic composite of a low-band-gap poly(*N*-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)) (PCDTBT) with a [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) within a wide temperature range is reported. LEPR spectra of the PCDTBT:$PC_{71}BM$ composite were deconvoluted and the main resonance parameters of polarons and anion radicals of methanofullerene were determined. The reversible formation of spin traps in polymer backbone, whose number, distribution and depth governed by the photon energy, has being shown. A part of photoinduced charge carriers is pinned by such traps resulting in formation of domains with different band gaps and photon sensitivity. Relaxation and dynamics parameters of all the charge carriers determined separately by the steady-state saturation method were shown to depend extremely on the energy of exciting photons. Polaron diffusion along polymer chains was analyzed in terms of spin interaction with the lattice phonons of crystalline domains embedded into amorphous polymer matrix. Activation of polaron hopping over the energetic barrier is characteristic for the charge transfer between polymer chains. Small-angle librations of methanofullerene cages in the polymer matrix were shown to follow the Markus model. Our results suggest that C_{70}-counter-ions embedded into the PCDTBT backbone strengthen an overlapping of molecular orbitals and provoke a layered morphology of appropriate composite. This regularizes the polymer matrix, hinders the formation of spin traps and accelerates spin dynamics that in turn facilitates charge transport through bulk heterojunctions. It was shown that the spin-assisted photon-electron conversion is realized in the composite within the visible and near-infrared range of the sun spectrum with comparable efficiency.

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1. Introduction

The discovery of the photovoltaic effect in organic composite of an electron-donating conjugated polymer and an electron-accepting fullerene and its intensive study clearly demonstrated the formation of excitons upon light illumination. The exitons can be transformed into donor-acceptor complexes collapsing into radical pairs, namely positively charged polarons delocalized along polymer chains and negatively charged fullerene anion radicals embedded into polymer matrix [1]. This confirmed a disruption of strongly bound neutral excitons into spin-charge-carrying quasi-pairs on a picosecond time scale due to photoinduced electron hopping from the conjugated polymer to the fullerene cage. This effect can be used for the realization of low-cost printable, portable and flexible renewable energy sources [2]. Previous research has mainly focused on bulk heterojunctions (BHJ) formed by conjugated polymers and fullerene derivatives. One key characteristic for such compounds is the nanophase separation between polymer and fullerene subsystems, which leads to a large interface for charge dissociation, and bicontinuous pathways for charge transport. The soluble poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) mainly used for such purposes as electron donor and acceptor, respectively, allowed to reach power conversion efficiency of 4–5% [3]. So small efficiency is explained by relatively large band gap of P3HT (~1.9 eV) limiting the fraction of the solar spectrum and the relatively small energy difference between the highest occupied molecular orbital (HOMO) of P3HT and the lowest unoccupied molecular orbital (LUMO) of $PC_{61}BM$. In order to improve the light power conversion efficiency, these energies defined by the polymer band gap and HOMO should be decreased.

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Recently, several low-band-gap co-polymers based on poly(2,7-carbazole) derivatives were developed to absorb the wider solar spectrum with deeper HOMO [4]. These polymers are characterized by the internal charge transfer from an electron-rich unit to an electron-deficient moiety within each repeating unit. Tuning of their light-absorption ability and energy levels foredoomed extensive development and study. Among them, poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT) (see Fig. 1 for its molecular structure) with band gap near 1.88 eV [5] were discovered [6] to be one of the most efficient matrix for organic plastic field-effect transistors and solar cells [7]. Due to a relatively deep HOMO of active matrix and maximal internal quantum efficiency the light conversion efficiency of the PCDTBT:PC$_{71}$BM composite layer reached 6–7% recently [8]. The higher light absorbance is due to the lower spherical symmetry of the fullerene in PC$_{71}$BM cage as compared to PC$_{61}$BM globe in appropriate PCDTBT:PC$_{x1}$BM BHJ [9]. One, however, should note that the extended spectral range of absorption may be overbalanced by recombination losses, or alternatively, by wasteful triplet formation [10]. Higher efficiency was achieved mainly due to ultrafast charge separation in the PCDTBT:PC$_{71}$BM composite before localization of the primary excitation to form a bound exciton in contrast with conventional polymer:fullerene systems [11]. Besides, morphology of the PCDTBT:PC$_{71}$BM BHJ becomes laterally oriented with “column-like” bilayer ordered polymer backbone [12] that improves the intralayer carrier mobility. Higher π-overlaping in such two-dimensional polymer backbone hinders its torsional twisting and, therefore, decreases the energy of its band gap [13]. This also accelerates charge hopping along and between PCDTBT bilayers. This evidences that charge dynamics is another important parameter affecting device light conversion efficiency. An understanding of the charge separation, transport and recombination in such materials at a molecular level is crucial for the improving of the electronic properties and efficiency of appropriate molecular electronics. However, the link between the quantum efficiency, dynamics of charge carriers and energy of photons within the BHJ absorption spectrum is yet to be established.

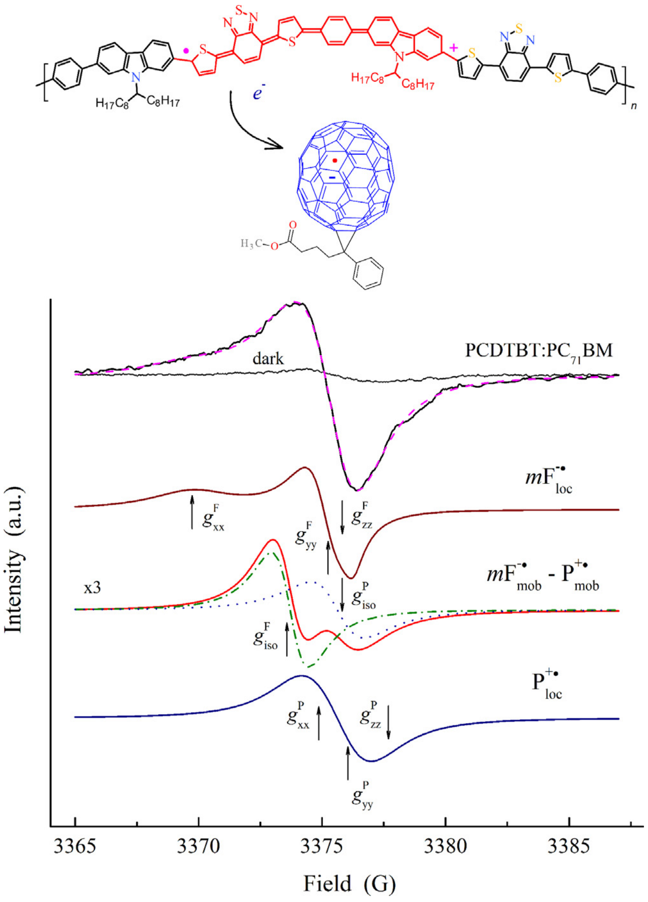

Fig. 1. Dark and background irradiated by white light with the color temperature $T_c = 5500$ K at $T = 77$ K 3-cm waveband LEPR spectra of the PCDTBT:PC$_{71}$BM composite (1), attributed to localized methanofullerene anion radicals $mF^{\bullet-}_{loc}$ and polarons $P^{\bullet+}_{loc}$ as well as mobile radical quasi-pairs $P^{\bullet+}_{mob}$–$mF^{\bullet-}_{mob}$. The main values of their **g**-tensors, g_{ii}, and isotropic g-factors, g_{iso}, are shown as well. The spectrum calculated using $g^{P}_{iso} = 2.0024$ and $g^{mF}_{iso} = 2.0036$ determined from the fitting for $P^{\bullet+}_{mob}$ and $mF^{\bullet-}_{mob}$, respectively, fixed shifts $g^{P}_{iso} - g_{xx} = -7.3 \times 10^{-4}$, $g^{P}_{iso} - g_{yy} = 7.0 \times 10^{-5}$, $g^{P}_{iso} - g_{zz} = 6.7 \times 10^{-4}$, $g^{mF}_{iso} - g_{xx} = -2.37 \times 10^{-3}$, $g^{mF}_{iso} - g_{yy} = 8.3 \times 10^{-4}$, $g^{mF}_{iso} - g_{zz} = 1.53 \times 10^{-3}$, determined at D-band EPR for $P^{\bullet+}_{loc}$ and $mF^{\bullet-}_{loc}$, respectively, immobilized in the PCDTBT:PC$_{71}$BM BHJ (see the text), and concentration ratio for these charge carriers $[P^{\bullet+}_{loc}]:[P^{\bullet+}_{mob}]:[mF^{\bullet-}_{loc}]:[mF^{\bullet-}_{mob}] = 1.00:1.39:2.37:1.39$ is shown by dashed line. Spectral terms calculated for $P^{\bullet+}_{mob}$ and $mF^{\bullet-}_{mob}$ are shown by dotted and dash-dotted lines, respectively. At the top, the formation of polaron and methanofullerene charge carriers accompanying by the transfer of an electron from PCDTBT chain to PC$_{71}$BM cage is also shown schematically. It should be noted that a polaron is normally delocalized on nearly three PCDTBT units.

Opposite charge carriers are characterized by spin $S = 1/2$, so their magnetic, relaxation and dynamic properties can be undoubtedly studied in details by inter alia light-induced electron paramagnetic resonance (LEPR) spectroscopy [2,14,15]. The method appeared to be a very efficient tool for the investigation of electronic transfers within BHJ on the molecular scale because it allows in situ detection of the paramagnetic species resulting from such transfers. LEPR measurements, especially at millimeter wavebands [16–18], revealed the existence of polarons and fullerene counter-ions with different line shapes, EPR parameters and saturation properties. The method in combination with the microwave (MW) power saturation method allowed detecting electron relaxation, lifetime [19] and recombination [20] of spin charge carriers in various polymer:fullerene systems. Niklas et al. determined [18] the main values of **g**-tensors, $g_{xx} = 2.0032$, $g_{yy} = 2.0024$, $g_{zz} = 2.0018$ for polarons and $g_{xx} = 2.0060$, $g_{yy} = 2.0028$, $g_{zz} = 2.0021$ by D-band (130 GHz) LEPR method for methanofullerene anion radicals photoinduced in the PCDTBT:PC$_{71}$BM composite at $T = 50$ K. A recombination of charge carriers was proved to be spin-dependent [21]. This means that their spin origin can play a key role in the controlling and handling of electronic properties of photovoltaic devices by the EPR spectroscopy. Composition, relaxation and dynamics of charge carriers photoinduced in organic semiconductors are governed by spin-dependent exciton-charge interactions and consistent with the model of spin-assisted recombination of polaron pairs [22]. So, the study of photoinitiated electronic processes in polymer:fullerene systems under spin resonance could to help us in creation of novel organic photovoltaic and spintronic devices. However, the dynamics and interaction of different spin ensembles affecting conversion efficiency of such and other polymer:fullerene BHJ are under debate and there not simple picture cleaning spin resonance-assisted processes in organic photoexcited systems.

It was shown by us that a part of polarons formed after exciton formation in result of irradiation of polymer backbone is pinned by spin traps whose the number and depth are governed by the composite morphology and photon energy [23,24]. Spin relaxation and charge carrier dynamics were shown to be governed by spin exchange and by the photon energy [23–26]. Formation, relaxation and dynamics of these charge carriers in the PCDTBT:PC$_{61}$BM BHJ were studied in wide photon energy and temperature ranges [27]. Essential LEPR response of this composite appeared to be registered upon its irradiation even by IR photons with the

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