



Effect of spin localization on charge transport in low-bandgap bilayered ordered nanocomposites



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ABSTRACT

Direct Light-Induced Electron Paramagnetic Resonance was used for comparative study of magnetic, relaxation and dynamic parameters of spin charge carriers, polarons and methanofullerene anion radicals, photoinduced in bulk heterojunctions of composites formed by low-bandgap copolymers, poly[2,7-(9,9-dioctylfluorene)-*alt*-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PFO-DBT) and poly[N-9'-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) with methanofullerene [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM). A fraction of polarons is captured by deep spin traps reversibly initiated in the copolymer backbone due to its disordering. The number and energy depth of the traps are governed by the structure of copolymer matrix and photon energy. Both composites exhibit photo-response within photon energy/wavelength 1.32–3.14 eV/940–395 nm regions which is wider than those of other polymer composites. The magnetic, relaxation and dynamics parameters of the spin charge carriers were shown to be governed by the exchange interaction of their spins and photon energy. The specific morphology of the composites provokes extreme selectivity of these parameters to photon energy. The anisotropy of polaron mobility through bulk heterojunctions was shown to reflect the system dimensionality and is dependent on the photon energy. Compared to PFO-DBT, the structure of the PCDTBT composite is more organised, resulting in a decrease in the number of spin traps and a change in the order of the charge recombination process. The decay of free charge carriers is interpreted in terms of the trapping-detrapping spin diffusion in bulk heterojunctions.

1. Introduction

Conjugated polymers with extended π -electron systems in their main chain attract much interest due to their perspective use as flexible active matrix for new electronic devices including photovoltaic elements [1]. Basically, photoactive layers of organic solar cells consist of two materials as donor and acceptor subsystems. Soluble derivatives of polythiophene, poly(3-alkylthiophenes) (P3AT), and fullerene, [6,6]-phenyl-C_{x1}-butyric acid methyl ester (PC_{x1}BM, $x = 6,7$), are traditionally used for such purposes as electron donor and acceptor, respectively [1]. Once composites of such materials are illuminated, spinless excitons are first formed in their bulk heterojunctions (BHJ). These quasi-particles can geminate ultrafast dissociate forming Coulomb bound electron-hole pairs (charge-transfer states) of electrons on the acceptor moiety and holes on the donor moiety. Then electrons and holes can leave the donor:acceptor interface relaxing into more favorable energy levels [2]. With increasing distance from the material interface, the Coulomb attraction becomes less, and finally, the electrons and holes become independent of each other, forming respective

charge-separated states. Finally, charge separation leads to the formation of unbound (free) positively charged polarons on polymer chains and negatively charged radical on fullerene molecules. After this stage, charge carrier recombination can occur. The separation and recombination of free charge carriers can be considered as concurring opposite directed processes. The geminate recombination of polaron-fullerene pairs is monomolecular and, therefore, a first order process. The non-geminate, bimolecular recombination of separated polaron-fullerene pairs following Langevin theory of a second order.

The main parameter of photovoltaic devices is efficiency of power conversion which is mainly governed by a structure of polymer:fullerene BHJ. Among polymer semiconductors, poly[N-9'-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT, see Fig. 1 for its molecular structure) appeared to be one of the most functional matrix for use in organic electronics and photonics [3]. The use of fullerene-modified PCDTBT allowed creating, e.g., field effect transistors with the charge carrier mobility of 17 cm²/Vs [4] and solar cells with the power conversion efficiency near 10% [5] that exceeds those obtained for P3AT-based systems. Such

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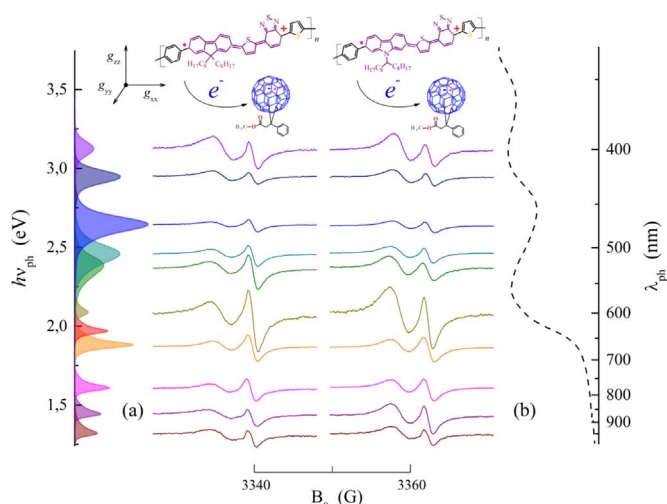


Fig. 1. Some X-band (9.7 GHz/340 mT) LEPR spectra of charge carriers background photoinduced by photons with different energy $h\nu_{ph}$ at 77 K in bulk heterojunctions formed by PFO-DBT (a) and PCDTBT (b) copolymers with molecules of PC₆₁BM normalized to the luminous emittance of the light sources I_l . Left filled lines represent irradiation spectra of respective light sources. Right dashed line shows exemplary UV-Vis-IR absorption spectrum of the PCDTBT:PC₆₁BM composite [28]. The copolymers and methanofullerene are shown schematically as well.

outstanding results can be explained [6] mainly by ultrafast charge separation in the PCDTBT:PC₇₁BM composite before localization of the primary excitation to form a bound exciton in contrast with, e.g., P3AT-based BHJ, where photoinduced charge separation happens after diffusion of the polymer exciton to a fullerene interface. The other important property is the morphology of a polymer:fullerene composite. This characteristic of fullerene-modified PCDTBT was demonstrated [7,8] to be laterally oriented with “column-like” bilayer ordered copolymer matrix with methanofullerene embedded between its chains. The dimension of low-bandgap copolymer backbone with such morphology should be higher than that of P3AT matrices. Gutzler et al. showed [9] that the higher π -overlapping in 2D thiophene-based polymers hinders their torsional twisting and, therefore, lowers their bandgap. This accelerates polaron hopping through well-ordered bilayer surfaces to the anode and electron motion to the cathode inside methanofullerene pools located between bilayers of the matrix. Besides, these copolymers contain electron donor and acceptor groups, carbazole (in case of the PCDTBT) and benzothiadiazole, respectively, which originate their other important feature, ambipolarity. One can expect the photogeneration in such ambipolar copolymers and their nanocomposites, as in their metalorganic analogs [10], of intralayer excitons within one layer and interlayer excitons whom polarons and free electrons are initiated in respective groups of adjacent layers. The recombination of charge carriers formed from these excitons should occur with different order, rate and be accompanied by the emission of photons with different energy. The lifetime of the intralayer excitons and respective spin pairs is relatively short, however, the high density and mobility of these quasi-particles can be decisive in creation of more effective organic light-emitting diodes and lasers. This parameter of less mobile interlayer excitons is much larger, therefore the spin charge carriers formed in respective neighboring groups of copolymers can be used as logical '0' and '1' in organic memory cells.

In polymer:fullerene systems non-geminate charge recombination consists of prompt bimolecular and persistent contributions [11,12]. The prompt process is a bimolecular mutual spin annihilation within the initially created radical pairs [13], whereas the persistent contribution originates from deep spin traps reversibly formed in polymer matrix due to its disorder [11]. Such process in low-bandgap system is usually analyzed within the framework of a model based on concomitant geminate recombination of charge-transfer states and non-

geminate recombination of free charge carriers. It was shown [14], that the small number of initial excitons recombine in nanosecond timeframes, e.g., in the PCDTBT:PC₆₁BM and thus do not contribute to the photocurrent through its BHJ, whereas the most excitons creates free charge carriers on an ultrafast time scale that contribute to the photocurrent and then non-geminately recombine.

It is evident that the efficiency of energy conversion by a polymer:fullerene BHJ is governed mainly by the number and dynamics of separated spin charge carriers whose number must exceed the number of recombined free charge carriers. Because these charge carriers possess a spin, their formation, dynamics and recombination were expected and proved to be spin-assisted [2]. Most methods, however, can provide information only on effective concentration of free carriers photo-initiated upon illumination of polymer:fullerene BHJ. This was the reason why Light-Induced Electron Paramagnetic Resonance (LEPR) becomes as one of the most powerful method for the study of all spin-assisted processes carrying out in organic polymer:fullerene systems [2,15–18]. Indeed, the evidence for a successful charge transfer is based on the fact that excitons initiated by light photons have zero spin and, therefore, cannot be detected by the method. If the exciton is split in a polymer:fullerene interface, polarons and fullerene anion radicals both with half integer spin are created in BHJ that originates an EPR signal. The amount of light induced pairs of charge carriers can be simply determined by the “light on-light off” method using comparison of EPR spectra before and after illumination. Although, charge transfer states exist for about 100 ps [19] they cannot be directly observed by the method. By consequence, detectable EPR signals correspond to species persisting on longer time-scales, e.g., both type of charge carriers in the charge-separated state. Polarons and methanofullerene anion radicals PC₆₁BM in are characterized by weakly anisotropic g -factors with effective $g_{iso} = 2.00213$ and 1.99987 , respectively [20], so they demonstrate at commonly used X-band (3-cm, 9.7 GHz) waveband EPR partly overlapping doublet of lines registered at lower and higher magnetic fields, respectively. Such LEPR spectrum is typical also for other polymer composites with such the electron acceptor [18]. LEPR study of various polymer:fullerene composites at this waveband showed [18] that upon illumination a part of both spin charge carriers are fixed in trap sites whose number and depth are governed by a structure of the BHJ and an energy of the initiating photons. Exchange- and multi-trap assisted recombination of free charge carriers are governed by their dynamics as well as by structure and morphology of their micro-environment. It should be noted that the higher spectral resolution and, therefore, more detailed information about such systems can be obtained at millimeter W- (3-mm, 95 GHz) and D- (2-mm, 130 GHz) wavebands EPR [19,21,22]. Although the mechanism and dynamics of charge generation and recombination in various polymer:fullerene BHJ have been intensively studied by many research groups, their details are still debated. In particular the role of reversible photoinduction of spin traps on spin-assisted interaction, relaxation and dynamics in polymer:fullerene BHJ, an important step for the understanding of device functionality, is also still under active discussion. Besides, the nature of the excited states, the coupling mechanism and the relaxation pathways following photoexcitation are yet to be clarified.

We carried out comparative LEPR study of spin and electronic properties of the structurally close PFO-DBT:PC₆₁BM and PCDTBT:PC₆₁BM composites upon their irradiation by photons with a range of energies. The use of direct methodical approaches allowed us to determine correlation of structural, morphological properties of these systems with spin relaxation, dynamics of spin charge carriers and also with the spin traps reversible initiated in both low-bandgap copolymer BHJ. It was shown for the first time that the minor structural variation of a copolymer matrix changes sufficiently the electronic properties of respective nanocomposite. Besides varying the light illumination band, it becomes possible to achieve a sensitivity of charge transfer to the photon energy.

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