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Dynamics of charge carriers photoinduced in poly(3-dodecylthiophene)/fullerene composite

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Abstract

Radical pairs, polarons and fullerene anion-radicals, photoinduced by laser with photon energies of 1.88, 2.22 and 2.75 eV in the poly(3-dodecylthiophene)/[6,6]-phenyl-C_{61}-butanoic acid methyl ester (P3DDT/PCBM) bulk heterojunction, were studied over a wide temperature range. The number of these centers was found to decrease with the increase in laser photon energy. Both the spin–lattice and spin–spin relaxation times of fullerene anion-radicals and the spin–spin relaxation time of polarons change monotonically with temperature, whereas the interaction of polarons with the lattice is characterized by extreme temperature dependence. The one-dimensional polaron diffusion along the polymer chain and the rotation of fullerene near it own main axis was shown to follow the activation Elliot hopping model and to be governed by the photon energy. The deviation in activation energies for polaron and anion-radical motion and the difference in their dependence on the laser photon energy prove the non-interacting character of these charge carriers photoinduced in the P3DDT/PCBM bulk heterojunction.

Keywords: LEPR; Polythiophene and derivatives; Fullerene; Polaron; Relaxation

1. Introduction

Conjugated polymers and their composites with fullerenes are interesting materials for various molecular electronic applications, e.g., light-emitting diodes [1] and thin film field effect transistors on flexible substrates [2]. Among the most widely studied photovoltaic devices are thin plastic solar cells [3–5].

The soluble fullerene derivative [6,6]-phenyl-C_{61}-butanoic acid methyl ester (PCBM), when embedded into poly(3-alkylthiophenes) (P3AT) or other conjugated polymer, performs as strong electron acceptor whose lowest unoccupied molecular orbital lies below the excitonic state. It was found that irradiation of the “bulk heterojunction” formed by fullerene with a polymer matrix initiates electron transfer from a polymer chain to a fullerene molecule. This process was revealed by time-resolved spectroscopy to occur in the femtosecond time domain [6–9], whereas the electron back-transfer is much slower [10]. Plastic solar cells with power conversion efficiency up to 5% have been demonstrated [11,12]. Photoinduced electron migration through a heterojunction results in the effective formation of a metastable charge-separated state. Light first excites the donor (D), the excitation is delocalized on the donor–acceptor (D–A) complex before initiation of charge transfer, leading to an ion radical pair and finally charge separation can be stabilized, possibly by carrier delocalization on the D^+ (or A^-) species by structural relaxation [13].

The efficiency of plastic solar cells appears to be due to the combined effects of ultrafast electron transfer from photoexcited polymer to fullerene [14], the large interfacial area for charge separation due to intimate blending of the materials [15] and efficient carrier transport across a thin film. Charge recombination is considered to be a predominantly non-geminate process governing effectiveness of polymer/fullerene solar cells [9,16–20]. That is why photoinduction of charge carrier pairs and their recombination

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are the most interesting points. However, they are not yet sufficiently understood in detail and there is no generally applicable model available.

The charge is transferred in initial conjugated polymers by non-linear excitations, polarons $P^{+\cdot}$ characterized by spin $S = 1/2$ and high mobility along a conjugated polymer backbone [21]. Their magnetic, relaxation and dynamic properties have been studied by conventional [22,23] and high-frequency [24–26] electron paramagnetic resonance (EPR) methods. Photoinduced charge transfer is also accompanied by the formation of anion-radicals $C_{61}^{-\cdot}$ with spin $S = 1/2$. This accounts for the widespread use of light-induced EPR (LEPR) for investigation of fullerene-modified P3AT [27–32] and other conjugated polymers [33,34]. LEPR measurements revealed the existence of two radicals with different line shapes, magnetic-resonance parameters and saturation properties. Photoinduced radical pairs can annihilate through bimolecular recombination [35] with the activation energy of 0.1 eV [27].

In addition to intermolecular charge transport, charge transfer by polarons along (Q1D) and between (Q3D) polymer chains and the rotational motion of fullerene molecules are also realized in these polymer/fullerene systems. These molecular and electronic processes should undoubtedly be correlated in P3AT/PCBM systems. However, such correlations have not yet been studied.

The understanding of the basic physics underlying the electron relaxation and dynamic behavior of fullerene-modified organic polymers is essential for the optimization of devices based on these materials. We report the LEPR study of magnetic, relaxation and dynamic parameters of polarons and fullerene anion-radicals photoinduced in a composite of PCBM embedded in poly(3-dodecylthiophene) (P3DDT) matrix, by a laser beam with photon energies of $h\nu_{ph} = 1.88$, 2.22 and 2.75 eV (here $h = \hbar/2\pi$ is the Planck constant and ν_{ph} is a photon frequency) over a wide temperature range. We demonstrate the non-interaction of paramagnetic centers (PCs) in radical pairs and, therefore, their different interactions with their own microenvironment. This allowed us to determine separately the relaxation and dynamic parameters of both type of PCs and to analyse the spin dynamic processes in the P3DDT/PCBM composite.

2. Experimental

This study used regioregular Aldrich® P3DDT [36] with lattice constants of $a = 2.583$ nm, $b = 0.775$ nm, $c = 0.777$ nm [37] and PCBM synthesized in the laboratory of Prof. J.C. Hummelen, University of Groningen [38]. Both components of the composite are shown schematically in Fig. 1. The chlorbenzene solution of P3DDT and PCBM, in 1:1 w/w ratio with a concentration of ~1 wt.%, was placed on a ceramic plate and dried, so that the P3DDT/PCBM composite was formed as a film ~4 × 8 mm^2 and ~0.1 mm thick.

EPR experiments were performed using a X-band (3 cm, 9.7 GHz) PS-100X spectrometer with 100 kHz field AC modulation for phase-lock detection. The "dark" (EPR) and light-induced (LEPR) spectra of the initial polymer and polymer/fullerene system were registered in the temperature range 90–340 K under a dry nitrogen atmosphere

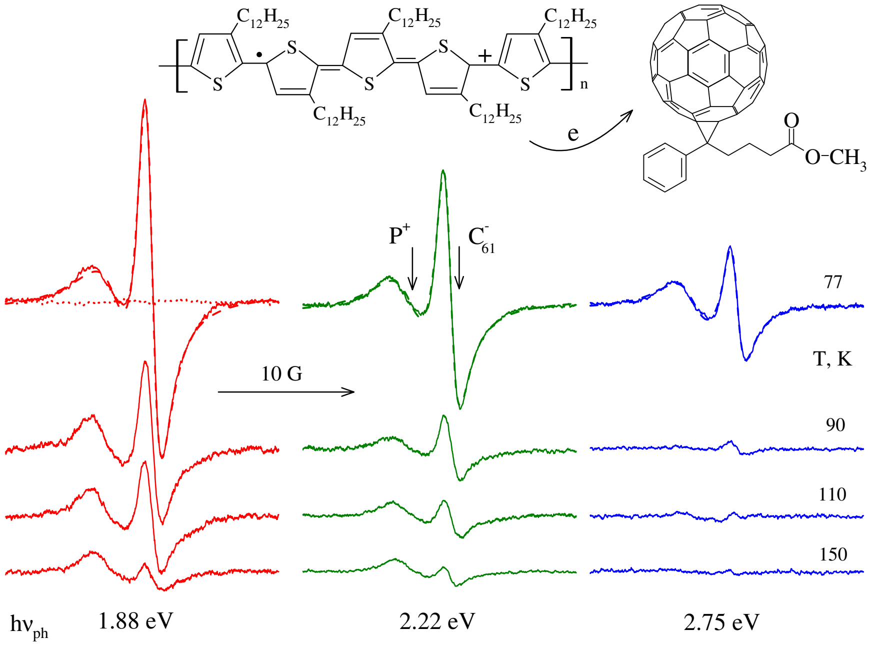

Fig. 1. X-band waveband LEPR spectra of the radical pairs photoinduced in the P3DDT/PCBM system by steady-state laser irradiation with different laser photon energies $h\nu_{ph}$ and registered at different temperatures. The dotted line shows the "dark" spectrum obtained before laser irradiation. Left-right dashed lines show sum LEPR spectra calculated using individual terms of g-tensors (see the text) and linewidth (see Table 1). At the top, both the P3DDT and PCBM components of the composite are also shown schematically.