Optical and ESR studies on poly(3-alkylthiophene)/fullerene composites for solar cells

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Abstract

Optical measurements (absorption coefficients, photoluminescence) and light-induced electron spin resonance (LESR) technique were used to study photoinduced charge generation and charge transfer in conjugated polymer / fullerene composites. The quenching of fluorescence by C_{60} gives a first indication of an effective charge transfer from P3DDT to C_{60}. At 77 K two kinds of LESR signals were identified, one of polaron ($P^{+\cdot}$) on the polymer chain and one of radical anion ($C_{60}^{-\cdot}$) of fullerene. The relaxation rates of generated paramagnetic centres were estimated by microwave power saturation studies. Moreover for the first centre ($P^{+\cdot}$) two contributions to the LESR signal were observed: a permanent one and a photoinduced one. The light intensity dependence of the photoinduced $P^{+\cdot}$ and $C_{60}^{-\cdot}$ ESR signals is of bimolecular type ($I^{0.5}$). Solar cells based on P3DDT/ C_{60} and P3DDT/ PCBM are prepared and characterised.

Keywords: solar cells, polythiophene, conjugated polymers; fullerene, light-induced electron spin resonance (LESR)

1. Introduction

Conjugated polymers like poly(3-alkylthiophenes) are a subject of great research interest due to their wide range of applications in polymer electronic devices such as light-emitting diodes (LEDs), field effect transistors (FETs), lasers and organic solar cells [1]. The discovery of ultrafast charge transfer in p-conducting polymer/fullerene composites by Sariciftci and Heeger in 1992 [2] brought an crucial milestone in the field of polymer solar cells.

LESR is a promising method to investigate charge transport mechanisms in conducting polymers and polymer-acceptor composites, which play a central role in the photophysics of polymer solar cells [3]. In this paper poly(3-dodecylthiophene) (P3DDT)/C_{60}-fullerene composites are investigated.

2. Experimental

C_{60}-fullerene (98%) and regioregular poly(3-dodecylthiophene) (P3DDT) were purchased from Aldrich, PEDOT:PSS (poly(3,4-ethylenedioxythiophene)) doped with poly(styrenesulfonate) is a commercial product of Bayer AG. PCBM ([6,6]-phenyl-C_{61}-butanoic acid methyl ester) comes from the laboratory of J.C. Hummelen at the University of Groningen.

The absorption coefficients were obtained from the analysis of ellipsometric spectra, measured with a Woollam VSAE® variable angle spectroscopic ellipsometer with rotating analyser.

P3DDT   [6,6]-PCBM
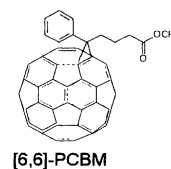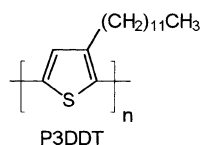
The photoluminescence spectra were measured by exciting the samples with the 459 nm line of Ar^+ laser at 80 K. For ESR experiments films of following composites were studied: P3DDT/C_{60} 2:1 and 3:1 wt. ratio. The EPR experiments were carried out using a BRUKER X-band spectrometer ELEXSYS E500 at 77K. Photolysis was performed with ILA 120-1 Ar^+ laser operating at $\lambda = 488$ nm. For the solar cells a layer from PEDOT:PSS (~100 nm) followed by the photoactive layer of P3DDT/C_{60} (2:3 wt.

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ratio) or P3DDT/[6,6]-PCBM (1:2 wt. ratio) were spincoated (80-100 nm) onto an ITO polyester foil.

Intermediate drying steps after each layer were inserted. The cells were completed by an aluminium top electrode deposited by vacuum evaporation. A source monitor unit (SMU) HP 4142 was used to record the I/V curves by illuminating with 14 mW/cm² white-light of a xenon lamp.

3. Results and Discussion

The absorption coefficients of pure P3DDT compared with that of a blend of P3DDT/C_{60} (1:1 wt. ratio) are presented in Fig.1b. The optical absorption is a simple superposition of the optical absorption spectra of the two components. That means there is no ground state doping by C_{60}.

The film photoluminescence spectra of P3DDT, P3DDT/C60 and P3DDT/PCBM are depicted in Fig.1a. The spectra of the blends show clearly a photoluminescence quenching effect caused by the presence of fullerenes. This is an indication of the charge transfer from P3DDT to fullerene as described by Sariciftci [1,2,4] for composites of p-conducting polymers and fullerene derivatives.
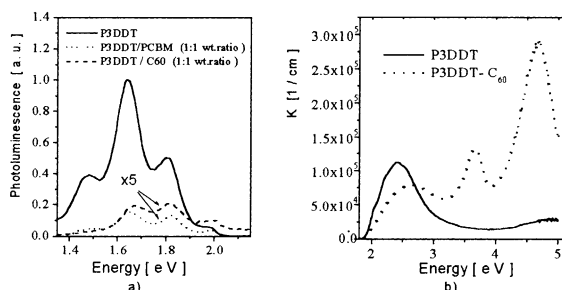

Fig.1. Photoluminescence of P3DDT, P3DDT/PCBM, P3DDT/C60 (a) and absorption coefficients (K) of P3DDT and P3DDT/C60 (b) in solid state

At 77 K two LESR signals were observed with light excitation at different light intensities. Typical ESR spectra with two relative concentrations of donor and acceptor are shown in fig.2a. The g-factor of the low field signal has a weak anisotropy with an average value of 2.0024. It can be attributed to positive polarons at the polymer chains ($P^{+\cdot}$) [5]. The g-factor of the high field component is about 2.000 which is typical for C_{60} –radical anion. It were also found dramatic differences in values of microwave power saturation for both radicals (for C_{60}^- radical it is more than 100 times higher). Spin-lattice and transverse relaxation times were determined by the saturation method. We obtained $T_1 \approx 8 \cdot 10^{-5}$ sec. for $P^{+\cdot}$. We then estimated that C_{60}^- spin-lattice relaxation time is at least 10 times shorter than T_1 of $P^{+\cdot}$. In general the light intensity dependence of the light-induced P^+ and C_{60}^- LESR signals is described by a function $S \propto I^{\alpha}$ where S is the double integrated ESR

signal intensity and α is a independent parameter. One example is shown in fig.2b.
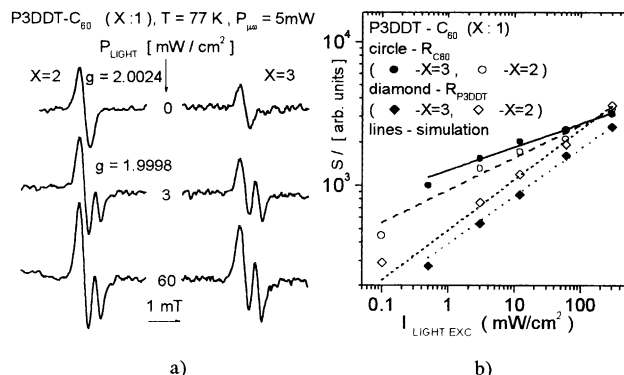

Fig.2a) LESR signal dependence on light intensity for two relative concentrations of P3DDT:C_{60} (X:1) , 2b) LESR signal intensity (S) dependence on light intensity (in log_{10} base) for two relative concentrations of P3DDT:C_{60} at 77 K.

Fig.3 shows the I/V characteristics of two solar cells based on P3DDT/C_{60} or PCBM in a logarithmic scale. Cell **I** has an open circuit potential $V_{oc} \sim 580$ mV, short circuit current $I_{sc} \sim 0.46$ mA/cm², fill factor FF~0.3 and overall energy conversion efficiency $\eta \sim 0.65$ %. Cell **II** gives V_{oc}~525 mV, I_{sc} ~1.2 mA/cm², FF~ 0.38 and $\eta \sim 1.7$ %.
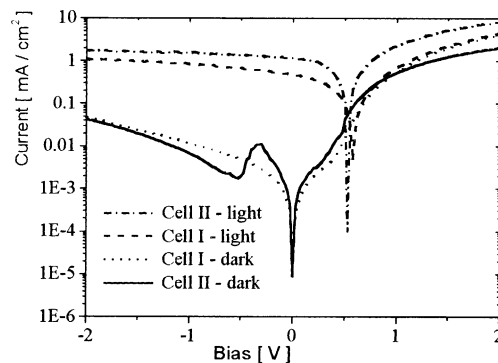

Fig.3 I/V characteristics of cell **I** (ITO/PEDOT/ P3DDT:C60 2:3 wt./Al) and of cell **II** (ITO/PEDOT/ P3DDT:PCBM 1:2 wt./Al)

Acknowledgement

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