

Magnetic resonance studies on conjugated polymer fullerene mixtures

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Abstract

In this paper photoluminescence (PLDMR) and photocurrent detected magnetic resonance (PCDMR) studies on pure and fullerene doped conjugated polymer films and photodiodes are reported. A strong dependence of the PLDMR and PCDMR signals on the fullerene concentration is observed.

Keywords: Magnetic resonance, conjugated polymer, fullerene, ODMR

Introduction

Photoinduced electron transfer in solid-state composites of conjugated polymers and fullerenes has attracted considerable scientific and technological attention [1]. The possibility of utilising this effect for photovoltaic energy conversion is especially interesting [1]. The photoinduced forward electron transfer from the polymer to the fullerene occurs within 100 fs and the charge-separated state is very long lived [1]. By doping the conjugated polymer matrix with a few weight (wt) % of fullerene a strong quenching of the photoluminescence and an increase of the photoconductivity of nearly two orders of magnitude has been observed [1]. Light-induced electron spin resonance (LESR) studies have been reported revealing the appearance of two LESR signals [1,2]. These signals are attributed to the radical anion of the fullerene molecule and the positive polaron on the conjugated chain. For composites of MDMO-PPV/PCBM (1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C₆₀) two g-values of $g=1.9995$ for PCBM radical anion and $g=2.0025$ for PPV radical cation have been reported [2]. Magnetic resonance techniques e.g. photoluminescence detected magnetic resonance (PLDMR) and photocurrent detected magnetic resonance (PCDMR) have been used to investigate thin film conjugated polymer devices [3,4]. In this contribution the influence of doping a conjugated polymer with fullerene molecules on the PLDMR and PCDMR spectra will be discussed.

Experimental

All films are prepared from toluene solutions containing the same concentration of MDMO-PPV (~0.3 wt %) and have a thickness of ~100 nm. For PLDMR films were prepared by doctor blading technique. The preparation of the thin film devices was done as follows: PEDOT:PSS (poly(ethylene dioxythiophene doped with polystyrene sulphonic acid) and the photo-active material were deposited by spin cast technique on a cleaned ITO covered substrate. Aluminum was evaporated as second electrode. The PCDMR experiments were carried out using devices with an active area of 4 mm². The samples were contacted with thin copper wires and sealed in a NMR-tube in Ar-atmosphere. The samples were placed in a rectangular TE₁₀₂ cavity with two windows for optical access inside the magnet of a commercial X-band ESR-Spectrometer (Bruker EMX). The microwave power (up to 200.7 mW) was modulated with a p-i-n modulator. The gun diode frequency was locked to an additional cylindrical cavity. Samples were excited either by an Ar⁺-Laser or a xenon lamp spectrally dispersed by a single grid monochromator. A lock-in amplifier was used to detect the synchronous changes of the photocurrent on the square-wave modulated microwave power while gradually sweeping the magnetic field. Due to the rather slow response of the electrical signal on the modulation of the microwave irradiation, PCDMR experiments were carried out at low modulation frequencies (<300 Hz). The

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PCDMR experiments were carried out at room temperature. For the PLDMR experiments the same arrangement as illustrated above were used. The samples were excited by an Ar⁺-Laser. A lens was used to create an image of the sample on the active area of a silicon diode. The current of the detection diode was fed into a lock-in amplifier to detect the synchronous changes of the photoluminescence. The measurements were carried out at 8 K.

Results

Figure 1 shows the amplitudes of the PCDMR-spectra and the relative changes of the short circuit photocurrent as a function of the fullerene concentration present in the films. The amplitude of the resonant signal first increases with increasing fullerene concentration and then decreases and vanishes at high PCBM concentrations. The relative changes $\delta I_{SC}/I_{SC}$ gradually decreases because the short circuit photocurrent increases rapidly with increasing fullerene concentration. Figure 2 shows the amplitudes of the PLDMR spectra and the relative changes of the photoluminescence as a function of the fullerene concentration. The amplitude of the resonant signal increases with increasing fullerene concentration up to 3%. The relative changes $\delta PL/PL$ increases even more rapidly because the photoluminescence decreases with increasing fullerene concentration. The PLDMR results presented here are in qualitative agreement with experiments presented in [5].

Discussion

The experimental results shown above can be discussed in the framework of polaron pairs [6-8]. In conjugated

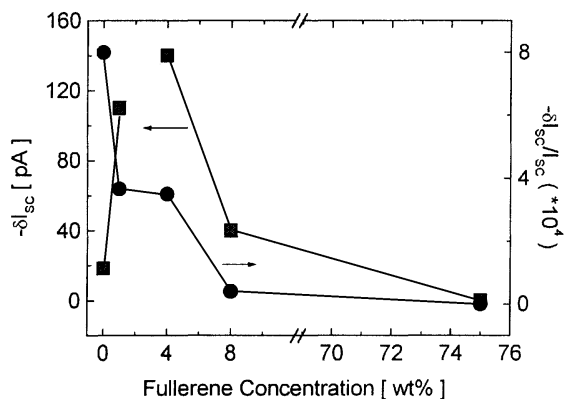


Fig. 1. Relative (squares) and absolute (circles) resonant changes of the short circuit photocurrent as a function of the fullerene conc., T=300 K

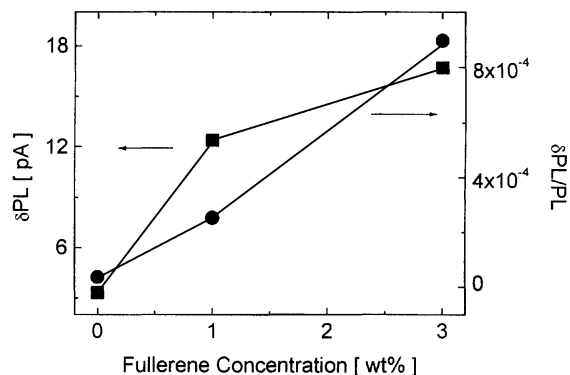


Fig. 2. Relative (squares) and absolute (circles) resonant changes of the photoluminescence as a function of the fullerene concentration, T=8 K.

polymers absorbed photons create singlet excited states on the polymer chain. A fraction of these excited states dissociate and spin-correlated radical pairs (polaron pairs) are formed. These pairs are initially formed in a state having mainly singlet character. An applied magnetic field, different hyperfine couplings and magnetic resonance conditions can alter the spin state of the pair. Different spin states have different recombination/dissociation probabilities. The observed magnetic resonance signal is proportional to the number of pairs present in the film. Adding small amounts of fullerenes, the generation of polymer-cation/PCBM-anion pairs is enhanced due to direct charge transfer. It has been demonstrated that these pairs also influence the magnetic resonance spectrum [8]. At small fullerene concentrations the signals increase. At higher concentrations the electron transferred to the fullerene can undergo another transfer step to a nearby fullerene and the pair is dissociated. Therefore, at higher fullerene concentrations the pair formation is quenched.

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