



## ESR and LESR X-band study of morphology and charge carrier interaction in blended P3HT–SWCNT and P3HT–PCBM–SWCNT solid thin films

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### ARTICLE INFO

#### Article history:

Received 23 May 2011

Accepted 15 August 2011

Available online 19 September 2011

#### Keywords:

ESR

LESR

SWCNT

P3HT

### ABSTRACT

An electron spin resonance (ESR) X-band study of regio-regular poly(3-hexylthiophene) (RR-P3HT) and RR-P3HT/PCBM ([6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester) composites blended with a low concentration (~0.1–1%) of single wall carbon nanotubes (SWCNT) is presented. The substantial line-width broadening of polaron and PCBM anion radical ESR spectra was registered after SWCNT incorporation. The possibility of an electron spin exchange interaction between SWCNT conductive electrons and polymer polarons in the RR-P3HT:SWCNT blend without light illumination and between SWCNT conductive electrons and polymer polarons and PCBM anion radical electrons in the RR-P3HT:PCBM:SWCNT blend under light illumination is discussed. In addition, the unusually significant RR-P3HT film morphology (dominant crystalline phase orientation) is substantially altered, in particular a rotation of up to 90° of the P3HT crystalline phase relative to the film plane, due to SWCNT annexation in the polymer matrix, registered by the ESR spectra external magnetic field angular dependences.

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### 1. Introduction

Recently, studies of some possible applications of different carbon nanotube (CNT) types in the field of conjugated polymer/fullerene blend solar cells show that the incorporation of only around 1 wt% of CNTs in the active medium of bulk heterojunction solar cells (BHJSC) can have a slight positive influence on photovoltaic parameters [1–3]. The creation of functional SWCNT composites, SWCNT–ester [4] and fullerene–SWCNT [5] complexes, improves BHJSC photovoltaic parameters noticeably. However, it seems that the charge transport mechanism in BHJSC–SWCNT systems is not completely understood so far and needs further complex considerations. In this work we have studied the influence of two different types of SWCNTs incorporated in P3HT and P3HT:PCBM on the spin dynamics of polaron and PCBM anion radicals at 77 K and room temperature. The questions discussed here are related to the possibility of charge mobility increase in P3HT–SWCNT and P3HT–PCBM–SWCNT blends and their change in morphology due to SWCNT incorporation. Both of the above effects can significantly

influence the photovoltaic properties of BHJSC and were therefore one of the main goals of this work.

### 2. Experimental

SWCNT-I, synthesized by the HiPco process, were purchased from Carbon Nanotechnologies, Inc., and used as received, with an average diameter of 1.1 nm. RR P3HT (weight-averaged molecular weight,  $M_w \sim 50,000 \text{ g mol}^{-1}$  and regio-regularity, RR = 95%) and PCBM (99% pure) were purchased from Rieke Metals Inc. and Solenne B.V., respectively. We have synthesized SWCNT-II ourselves and prepared for the experiment by the arc discharge method [11] (only the purified SWCNTs-II was used for study). SWCNTs have been placed in vacuum for 2 h to remove surface oxygen contaminations. Both were dispersed in 1,4-dichlorobenzene. The P3HT was added to the solution of SWCNTs with the right ratio and sonicated in a middle-power bath for 1 h. The samples for ESR were drop cast from the blend solution on an ESR silent plastic sheet and encapsulated with commercial laminator.

The ESR spectra were recorded using the Bruker X-band spectrometer ELEXYS E500 operated at a frequency of 9.4 GHz and using a 150 W Xe-lamp for illumination in the case of LESR. An optical transmission resonator, ER 4104OR (Bruker BioSpin), provided a simple pathway for the light (~30 mW/cm<sup>2</sup>). All ESR

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