



## Effects of single-walled carbon nanotubes on the optical and photo-conductive properties of their composite films with regio-regular poly(3-hexylthiophene)



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### H I G H L I G H T S

- Optical properties of single-walled carbon nanotubes/P3HT films are investigated.
- The insertion of SWNTs leads to an improvement of structural organization.
- Composite films shows photoluminescence quenching at low SWNTs concentration.
- Existence of a fast photo-induced electron transfer between SWNTs and P3HT.
- These two effects are of crucial importance for applications in photovoltaic cells.

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### A B S T R A C T

The effect of a small admixture of single-walled carbon nanotubes (SWNTs) HiPCO (high pressure carbon monoxide) (from 0.5 to 2 wt%) on the supramolecular structure in regio-regular poly(3-hexylthiophene) (RR-P3HT) thin films is studied and their optical and photoconductivity properties are investigated. It is demonstrated that the presence of such small amounts of nanotubes improves the structural organization in the films as evidenced by X-ray diffraction (XRD) studies. This is confirmed by UV–visible optical absorption investigations which clearly show a better conjugation of P3HT in the presence of nanotubes. In Raman spectra of composites, changes in intensities and frequencies of the radial breathing modes are observed upon addition of nanotubes. This can be rationalized by a modification of the resonance conditions caused by a selective dispersion and wrapping of SWNTs via  $\pi$ -interaction ( $\pi$ -stacking). As a consequence of these interactions, a dramatic photoluminescence (PL) quenching is observed which becomes more and more pronounced with increasing the nanotube content. This implies a fast photo-induced electron transfer favoured by a large area of the SWNTs/P3HT interface and strong interactions between these two components. An increase in the composite photocurrent by at least one-order of magnitude, as compared to the case of pure P3HT film, is the most pronounced effect of this electron transfer. These two effects are of crucial importance for the application of the investigated composites in bulk hetero-junction photovoltaic cells (BHJPCs) and organic photo-detectors (OPDs).

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## 1. Introduction

In the field of nanotechnology, organic nano-composite materials are nowadays of significant importance both in terms of fundamental and practical issues. They are generally composed of a polymeric host matrix in which are dispersed nano-particles. The interest of such composites is to benefit from both properties of the

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polymeric matrix and those of the dispersed nanophase which exhibits specific features originating from its nanoscale size. These polymeric nanocomposites are intensively used as active materials in organic optoelectronic devices due to a low-cost processing, a mechanical flexibility, a light weight and its colour-tunability [1,2]. The most investigated polymeric nano-composites are those using nano-particles of SiO<sub>2</sub>, TiO<sub>2</sub>, single-walled or multi-walled carbon nanotubes (SWNTs, MWNTs), fullerenes etc... associated with conjugated polymers such as poly(*p*-phenylene vinylene) (PPV), polythiophene (PTH) and their derivatives [3–6].

However, the critical step in the elaboration of nano-composite films is the nanotube dispersion and their stabilization in an appropriate solvent without degradation of their remarkable electronic properties [7,8]. Indeed, SWNTs have a natural tendency to form bundles [9] and therefore, an adequate dispersant for pristine nanotubes is yet to be found [10–12], even if several approaches have been used to overcome their aggregation when introduced in polymer matrices. In this context, in order to preserve the intrinsic electronic properties of SWNTs, we have chosen in this work a non-covalent functionalization approach by using P3HT as the polymeric host matrix. This choice is justified because this polymer has a high solubility, a low band gap and a good thermal stability. Furthermore, free charge carriers are highly mobile and exhibit almost the best mobility within known conjugated polymers due to the existence of well-ordered phases with favours  $\pi$ -stacking [13,14]. This feature is advantageous for potential applications in OPVs (organic photovoltaics) and OFETs (organic field-effect transistors). Moreover, P3HT is a highly photosensitive material with sufficient absorption of visible light then allowing its successful utilization as an optical absorber in OPVs or OPDs (organic photodetectors). Chloroform has been used for the dissolution of the polymer and the dispersion of SWNTs providing appropriate conditions for P3HT to form a self-organized ordered structure. Despite considerable efforts devoted to the study of these nano-composites, their performances are still generally below expectations. Several reports agree that SWNTs in large amounts form bundles of both semi-conducting and metallic nanotubes (sc-SWNTs and m-SWNTs) species as due to intertube van der Waals interactions [9]. In fact, it has been shown in several systems that small amounts of SWNTs incorporated into the polymer matrix can improve significantly the electrical, optoelectronic and mechanical properties such composites. Several groups [15–20] have attempted to replace the fullerene derivatives with CNTs as an electron acceptor and carrier in bulk heterojunction devices or/and OPV cells, etc... For example, devices have been built using P3HT-functionalized MWNTs [21], poly-(3,4-ethylenedioxythiophene):poly(styrenesulfonate) PEDOT-PSS-SWNTs [22] or functionalized SWNTs associated with a series of polymer/fullerene photovoltaic structures [23,24]. The authors interpret the improvement of the cell efficiency by the extension of the exciton dissociation volume, the change of the transport properties in the nanotube network as well an improved dispersion of nanotubes and an increase of the SWNT/polymer interface. Stilianakis et al. report an increased conductivity and photoconductivity in bulk heterojunctions based on SWNTs/PEDOT:PSS [22] and Nunzi and his group an improved current density in devices P3HT-PCBM composites [25].

Up to now, most of the groups obtained disappointing results with a very low conversion power efficiency of the PV cells, the causes of which being in part identified as: i) the incorporated m-SWNTs act as electron traps providing centres for the exciton recombination; ii) the inappropriate energy levels in SWNTs and P3HT, which provoke energy transfer instead of a charge separation; iii) the long length (up to several micrometers) of SWNTs, which are responsible for short-circuit in devices. As a consequence, each step in processes has to be precisely taken care to

enhance the exciton dissociation rate or suppress the recombination, and to increase carrier mobility in the composites.

In this paper, our aim is to better understand the photophysical properties of these nanocomposite films loaded with low SWNT concentrations (maximum 2% in mass) in order to minimize short-circuit effects. Notice by the way that our measurements have not been performed in the conditions of devices in use. XRD, UV-visible absorption, Raman scattering, Infra-red absorption and photoluminescence were used in order to obtain information on the dispersion state and the interaction between SWNTs and P3HT in thin films. We know that the photo-excitation of a conjugated polymer leads to the creation of excitons which undergo different decay processes, which can either be useful or detrimental for potential devices. For example, radiative recombination of excitons is desirable in LEDs but should be avoided in PV cells. Therefore, we have conducted a series of investigations in order to elucidate and understand the different mechanisms involved in exciton recombination in P3HT/SWNT nanocomposites and determine their properties in the objective of their use in organic devices.

## 2. Experimental details

### 2.1. Samples preparation

The regio-regular P3HT (RR-P3HT) used in this work (obtained from Rieke) has the following characteristics: average molecular weight  $M_w = 37.680 \text{ g mol}^{-1}$ , PDI = 1.48 (Polydispersity index) and regio-regularity HT (Head–Tail) >98.5% [26]. High purity SWNTs (residual iron catalyst 22%) were purchased from Carbon Nanotechnology, Inc., Texas, USA. They were prepared by the HiPCO method and typical diameters were in the range 0.8–1.2 nm and lengths between 0.1 and 1  $\mu\text{m}$ . Solutions of the polymer were prepared with chloroform (CHCl<sub>3</sub>), with a concentration of 1 mg ml<sup>-1</sup>. The obtained solution was then heated during 5 min in 50 °C to achieve a complete dissolution of the P3HT in the solvent. This dissolution is accompanied with a bathochromism phenomenon, the solution having a yellowish coloration after preparation, then changing from yellow to purple after one week at room temperature (RT), indicating the formation of P3HT fibrils as shown in Ref. [17]. Nano-composite films were prepared according to the following procedure. SWNTs were dispersed in the same solvent i.e. chloroform (although using chlorobenzene leads to similar results). An ultrasonic treatment was then applied to the SWNT dispersion using a generator working at 25 kHz, with a power of 60 W for 1 h at RT. Composite solutions were prepared by adding the P3HT solution directly to the SWNT dispersion solution in order to achieve SWNT concentrations of 0.5, 1 and 2% in mass, respectively. The obtained solution was then plunged again in an ultrasonic bath at RT, during a time of 15 min in order to ensure a better homogeneity of the solution and prevent any degradation of the components. Thin films of a typical thickness of 500 nm (measured by using a profilometer Brücker Dektak 8) were obtained by drop casting the solution on glass substrates and studied after a slow evaporation of the solvent at RT. In all optical experiments, we took a great care for using homogeneous samples in terms of film thickness. The transmission electron microscopy (TEM) images were obtained in bright field (BF) using a TECNAI G2/FEI microscope working at a voltage of 120 kV.

### 2.2. Characterization techniques

XRD patterns were obtained with a Siemens 5000 diffractometer (Cu K $\alpha$ , 40 kV, 30 mA) in a Bragg Brentano geometry. Raman spectra were recorded using a Nicolet Almega dispersive Raman spectrometer equipped with a visible Raman microscope and a

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