

# Imaging of morphological changes and phase segregation in doped polymeric semiconductors



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## ABSTRACT

The electrical conductivity and morphological characteristics of two conjugated polymers, P3HT and PCPDTBT, p-doped with the strong electron acceptor tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) are studied as a function of dopant concentration. By combining scanning and transmission electron microscopy, SEM and TEM, with electrical characterization, we observe a correlation between the saturation in electrical conductivity and the formation of dopant rich clusters. We demonstrate that SEM is a useful technique to observe imaging contrast for locating doped regions in thin polymer films, while in parallel monitoring the surface morphology. The results are relevant for the understanding of structure property relationships in doped conjugated polymers.

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## 1. Introduction

A prerequisite for the success of organic electronics in the current information-technology and renewable energy markets is performance and reliability. Recent scientific efforts toward this milestone focus on the use of dopant molecules to improve the electrical transport characteristics of light emitting diodes and solar cells [1–4]. Doping has been also demonstrated to be critical for tuning the carrier injection properties at metal-semiconductor interfaces, potentially leading to full control over device parameters [5–7]. Spatially controlled positioning of dopants can be used to tune injection [6,8], improve carrier drift/diffusion in transport layers [9–11] and also charge separation at heterojunctions [12].

In organic devices based on small molecules, control of dopant positioning can be achieved by sequential evaporation of individual materials to form layered stacks [1]. In contrast, the controlled positioning of dopants in solution processable organic semiconductors, such as conjugated polymers, remains a

challenge. Particularly for low mobility solution deposited materials, there is substantial interest in tuning electronic processes by doping [13,14]. The physical origin of doping, i.e., the interactions between the organic semiconductor and dopant molecule, has recently seen renewed interest [15–17]. Systematic studies of carrier transport properties as a function of the dopant/semiconductor weight ratio often demonstrate saturation in the key parameters (mobility and conductivity) above a certain threshold [13,18]. However, there are few detailed investigations on the correlation between morphology and the efficacy of doping [19,20].

While the influence of dopants on the electrical parameters of organic semiconductors has been addressed, one crucial question that has been poorly addressed is the morphology of the doped semiconductors, i.e., the distribution of dopants in the film but more critically, the role of (charged) dopant molecules in changing the organic semiconductor morphology. This latter aspect is expected to be highly relevant considering the widely reported and discussed effects of meso-morphology on the optical and electrical characteristics of organic semiconductors [21–23]. In this respect, experiments performed by Ha and Kahn on imaging single dopants by STM [15] are extremely valuable, but limited to very thin films exhibiting the high crystallinity required for this technique. Very recently, Donhauser et al. [24] have reported the imaging of inorganic dopant clusters in vacuum sublimed small molecule

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films by transmission electron microscopy, suggesting the utility of electron microscopy to study doped organic semiconductor films. It is apparent that experimental strategies are required which allow for the visualization of dopant distributions and resulting mesoscopic morphology of doped polymeric films.

Here, we present a study on the morphology of two widely-studied conjugated polymers: poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl]] (PCPDTBT) and poly(3-hexylthiophene) (P3HT) doped at different concentrations with the organic molecule 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ). The polymeric materials are known to be model systems for solar cells and field effect transistors, respectively. Our material choice was also motivated by the idea of comparing polymers with intrinsically different electronic structures; PCPDTBT is a prototype donor-acceptor copolymer with an intrachain charge transfer character [25,26], while P3HT is a prototypical conjugated homopolymer based on thiophene repeat units. Since both PCPDTBT and P3HT are well-known hole transporting materials we p-doped them with the strong electron acceptor F4-TCNQ. To the best of our knowledge we are not aware of studies on the morphology of doped conjugated copolymers such as PCPDTBT. We show that low voltage (<1 kV) scanning electron microscopy (SEM) can in parallel monitor the film surface morphology and the dopant distribution with nanometer spatial resolution in the film plane. We comment on the origin of this useful contrast by comparing the surface morphological information from SEM with results from atomic force microscopy (AFM). In addition, we cross correlate the doping induced contrast in SEM with photoluminescence (PL) confocal imaging which is sensitive to doping because of localized PL quenching. We report on morphology changes in the polymer films and clustering of dopants at two different critical concentrations for the two polymers. Interestingly, the critical concentrations are directly correlated to the saturation in conductivity of the films investigated by electrical measurements. The results highlight SEM as a tool to investigate the morphology of doped polymeric semiconductors and suggest a correlation between morphology and saturation in conductivity for doped conjugated polymers.

## 2. Materials and methods

### 2.1. Materials and electrical characterization

P3HT (regioregularity > 95%,  $M_w \sim 30,000$  g/mol) was purchased from Sigma-Aldrich and used as received. PCPDTBT ( $M_w \sim 20,000$  g/mol) was purchased from 1-Material and used as received. Chlorobenzene from Sigma-Aldrich (HPLC, spectroscopic grade, anhydrous) was used as solvent to prepare solutions which were stirred for 24 h at room temperature before deposition also at room temperature (20 °C). All concentration ratios are given in weight/weight% (w/w%). Samples for SEM/AFM were prepared with a home made doctor blade on silicon wafer with a thin layer of native oxide. Samples for photoluminescence mapping were prepared by coating on thin microscope slides from the same solutions used for the SEM/AFM samples. For conductivity experiments, the films were prepared inside a nitrogen filled glove-box on pre-structured indium-tin-oxide (ITO) coated glass substrates with an interdigitated channel: length of 75  $\mu\text{m}$ , width of 70  $\mu\text{m}$  and ITO thickness of 150 nm. The geometry constant was  $6.22 \text{ cm}^{-1}$ . Film thickness,  $100 \pm 10$  nm for all samples, was measured with a profilometer. The resistance was obtained from 4-probe measurements performed with a potentiostat/impedance module at  $V_{ac} = 20$  mV in the frequency range from 100 kHz–1 Hz in the dark and in a nitrogen atmosphere.

### 2.2. Electron microscopy

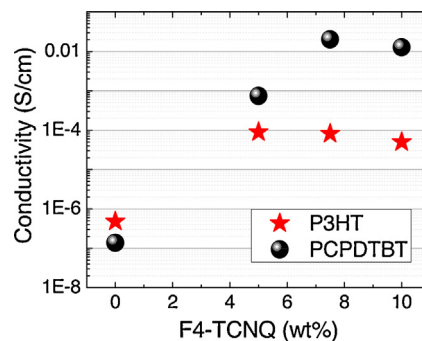
SEM Images were recorded with a Zeiss Ultra-Plus operating at 750 V accelerating voltage. Working distance was kept at 3.5 mm to ensure high collection efficiency of secondary electrons aided by the electrostatic lens and allowing efficient detection secondary electrons (SE2) simultaneously. Good electric contact with the sample stage was ensured for all samples to avoid any undesired charge build-up in the substrate. The microscope stage was not biased for any of the experiments. Transmission electron microscopy (TEM) images were obtained with a JEOL microscope operated at 100 kV. Image analysis was carried out using the software ImageJ. For the analysis, images taken at  $25,000\times$  magnification were used in all cases, with ca. 12 nm/pixel resolution. See Supporting information for further details.

### 2.3. Confocal laser scanning photoluminescence microscopy

Photoluminescence maps were taken with an Olympus IX81 FV5F-2 with an UPLANFL N 100 $\times$  objective. Excitation was performed with a 532 nm cw laser (Laser Quantum, Opus). Excitation power was 0.5 mW and was kept constant for all measurements. Samples were placed face down on the inverted microscope and photoluminescence was measured by a photomultiplier after passing through a bandpass filters centered on the PL bands of the respective polymers.

## 3. Results and discussion

Fig. 1 shows the electrical conductivity of PCPDTBT and P3HT thin films doped at different concentrations with F4-TCNQ. The conductivity of both samples exhibits saturation after the initial increase of more than two orders of magnitude in conductivity. Conductivity for samples with doping between 0 and 5% shows a monotonous increase without a maximum (not shown). Interestingly, saturation occurs at different F4-TCNQ concentrations for the two polymers. In P3HT it saturates at 5% doping and decrease at high levels (>7.5%), whereas in PCPDTBT saturation occurs at 7.5%. For P3HT, a similar trend in conductivity has been recently reported by Duong et al. [19], although our saturation value for conductivity,  $10^{-4}$  S/cm, and saturation F4-TCNQ concentration are smaller than what other authors have reported  $\sim 10\%$  [13]. We attribute this difference to the fact that the charge transport characteristics of P3HT depend dramatically on molecular weight [27]. In addition, our estimations of conductivity are performed with an impedance analysis that excludes displacement currents, injection resistance and ionic contributions which may result in



**Fig. 1.** Electrical conductivity of P3HT (red stars) and PCPDTBT (black dots) as a function of doping expressed as w/w% with respect to the polymer. Conductivity extracted from four probe experiments as detailed in Section 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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