

The interplay of electronic structure, molecular orientation and charge transport in organic semiconductors: Poly(thiophene) and poly(bithiophene)



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ABSTRACT

Ultrathin films of poly(thiophene) (PT) and poly(bithiophene) (PBT) were prepared by electrochemical route using ionic liquid (BFEE) as medium and electrolyte. Distinct morphologies and electrical properties were observed in these materials. To evaluate its response in photovoltaics, these films were used as active layer in bilayer geometry solar cells with the electron acceptor molecule C₆₀. The best performance was observed for PT films. In order to probe the differences in molecular dynamics and structural order, ultrafast electron dynamics in the low-femtosecond regime was evaluated by resonant Auger spectroscopy using the core–hole clock method at the sulfur K absorption edge. Electron delocalization times for the different polymeric films were derived as a function of the excitation energy. Photoabsorption measurements were conducted and molecular orientation derived. These results corroborated with the morphology found for these films and thus the performance of PT and PBT in the devices, and with the proposed conduction mechanism.

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1. Introduction

The research concerning conjugated polymers for photovoltaic devices has been focused on the power conversion efficiency, the issues of stability, operational lifetime, and processing [1–6]. Also, it should be emphasized that the combination of high efficiency, long lifetime, and large area processing has not been achieved for the same material currently. To meet this challenge of unification, the

delicate interplay between many parameters such as processing, morphology, carrier transport, photochemistry, and molecular dynamics at the active layer and interfaces needs to be controlled [4,7–11].

Poly(thiophene) (PT) is one of the most studied conducting polymer and shows good stability to oxygen and moisture in both the dedoped and doped forms but it is necessary high potentials for the polymerization of the thiophene monomer, over the oxidation potential of the poly(thiophene), that may cause an irreversible oxidation of the polymer chains [12–16]. Lower oxidation potential has been found for bithiophene in comparison with thiophene [17,18]. The study performed also suggests that poly(bithiophene) (PBT) has the highest average conjugation length of the polymer chains. PBT is generally

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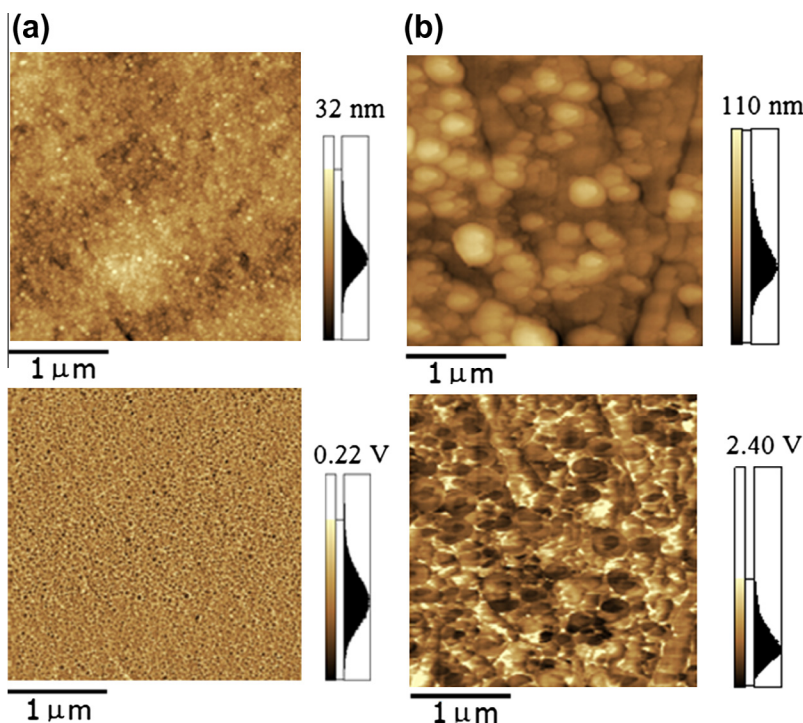


Fig. 1. Height (top) and phase (bottom) AFM images of (a) PT and (b) PBT prepared in BFEE.

synthesized by electrochemical oxidation of bithiophene monomer in organic media and tends to present higher amount of regular α , α' - linking of the monomeric units while PT films present a disordered cross-linked polymer structure. However, the reduced solubility of bithiophene monomer, when compared with the thiophene monomer, in different mediums may reflect negatively in the morphology of the thin film [18,19].

Studies of interfacial electronic structure and ultrafast charge transfer (CT) are relevant topics for understanding the transport properties of conjugated polymer and improve their performance in photovoltaic device applications [20,21]. Pulse laser pump–probe spectroscopy is the most used techniques for CT dynamic studies [22–25]. In this case the dynamic of optically excited state as a function of delay time after excitation are investigated. This technique is restricted by the extension of the laser pulse, allowing studying only processes occurring in the time scale above hundred femtoseconds (10^{-15} s). Besides laser-based pump–probe methods the so-called core–hole clock (CHC) approach using resonant Auger spectroscopy emerge as an alternative, with some advantages [26,27]. The short core hole lifetimes used as internal clock in this methodology allow access to dynamic processes in very low time scale (in the range of femtoseconds down to hundred attoseconds (10^{-18} s)) and also to probe the atomic specificity of core levels.

In this work we investigate the impact of using thiophene or bithiophene monomer in electrochemical synthesis of thiophene based polymer using ionic liquid Boron Trifluoride Diethyl Etherate (BFEE). We studied the morphology, electronic structure, optical and electrical

behavior in solar cells. Molecular orientation and charge transfer dynamics using the core–hole clock methodology were also investigated in order to add information about the polymeric films regarding their use in photovoltaic devices.

2. Experimental

A layer of PT or PBT was electrochemically deposited, using a potentiostat AUTOLAB 3530 with GPES system, onto ITO/glass substrates by using three electrodes cell (WE:ITO; CE:Pt plate 1 cm^2 and RE:Ag, \varnothing 2 mm) applying +1.5 V and +0.6 V, to obtain PT and PBT respectively, in a potentiostatic mode from a Boron Trifluoride Diethyl

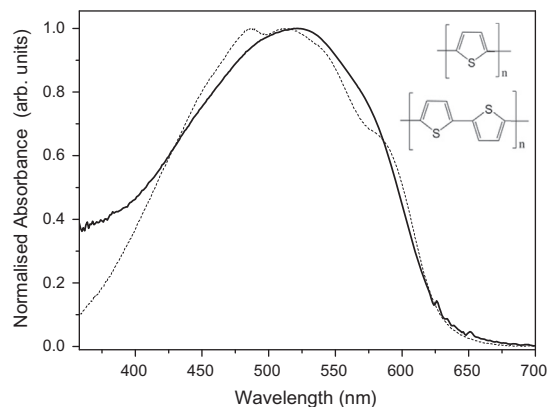


Fig. 2. Absorbance spectra of PT (solid line) and PBT (dotted line) films. Inset: the structure of thiophene and bithiophene monomers.

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