

The effect of thermal annealing on dopant site choice in conjugated polymers



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ARTICLE INFO

Article history:

Received 15 October 2015

Received in revised form

15 January 2016

Accepted 20 February 2016

Available online 14 March 2016

Keywords:

Organic electronics

Molecular doping

Molecular diffusion

Thermal stability

ABSTRACT

Solution-processed organic electronic devices often consist of layers of polar and non-polar polymers. In addition, either of these layers could be doped with small molecular dopants. It is extremely important for device stability to understand the diffusion behavior of these molecular dopants under the thermal stress and whether the dopants have preference for the polar or the non-polar polymer layers. In this work, a widely used molecular dopant 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) was chosen to investigate dopant site preference upon thermal annealing between the polar thiophene poly(thiophene-3-[2-(2-methoxy-ethoxy)ethoxy]-2,5-diyl) (S-P3MEET) and non-polar thiophene poly(3-hexylthiophene) (P3HT). F4TCNQ is able to p-type dope both P3HT and S-P3MEET. Further doping studies of S-P3MEET using near edge X-ray absorption fine structure spectroscopy, conductivity measurements and atomic force microscopy show that the F4TCNQ additive competes for doping sites with the covalently attached dopants on the S-P3MEET. Calorimetry measurements reveal that the F4TCNQ interacts strongly with the side-chains of the S-P3MEET, increasing the melting temperature of the side-chains by 30 °C with 5 wt% dopant loading. Next, the thermal stability of doping in the polar/non-polar (S-P3MEET/P3HT) bilayer architectures was investigated. Steady-state absorbance and fluorescence results show that F4TCNQ binds much more strongly in S-P3MEET than P3HT and very little F4TCNQ is found in the P3HT layer after annealing. In combination with reflectometry measurements, we show that F4TCNQ remains in the SP3MEET layer with annealing to 210 °C even though the sublimation temperature for neat F4TCNQ is about 80 °C. In contrast, F4TCNQ slowly diffuses out of P3HT at room temperature. We attribute this difference in binding the F4TCNQ anion to the ability of the ethyl-oxy side-chains of the S-P3MEET to orient around the charged dopant molecule and thereby to stabilize its position. This study suggests that polar side-chains could be engineered to increase the thermal stability of molecular dopant position.

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1. Introduction

Organic electronic materials and devices have recently been extensively studied because they show the potential to replace inorganic components for some applications, including organic photovoltaics (OPVs) and organic light emitting diodes (OLEDs) [1–3]. Organic electronic devices often consist of multiple thin (5–100 nm) layers, each of which has a specific electronic and/or optical function. It is tempting to assume that the device will

operate as if each layer is discrete, pure, and has sharp interfaces. In practice, however, it is difficult to control the composition and morphology of these layered materials because of chemical reactions at layer interfaces and diffusion of mobile species through the interface [4,5]. Since the thermal stability of the layers and interfaces are essential in determining the quality and stability of the devices, the characterization of organic layer properties in connection with thermal stress is imperative in understanding the mechanisms involved in device degradation [6,7].

Many solution-processed organic electronic devices incorporate a polar (hydrophilic) layer and a non-polar (hydrophobic) layer because the use of orthogonal solvents allows layer stacking (Fig. 1). In fact, the most widely used material in solution-processed

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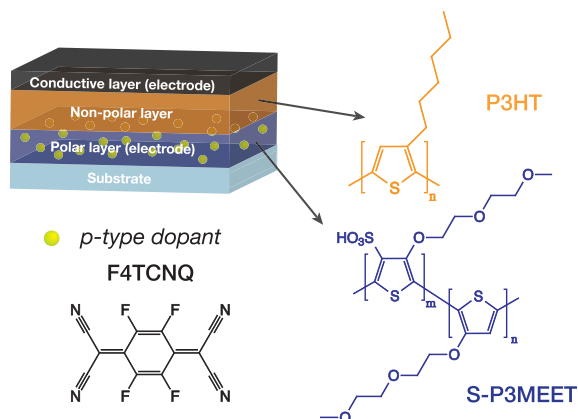


Fig. 1. Schematic diagram of a typical solution-processed device structure (upper left) and molecular structures of P3HT (upper right), S-P3MEET (bottom right) and F4TCNQ (bottom left).

organic electronic devices is the transparent conductive polymer poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) because of this layering ability [8–11]. However, even covalently bound ionic dopants have been shown to cause inadvertent doping of adjacent layers. Excess polymeric dopant (PSS) has a tendency to phase segregate into a surface layer on top of the PEDOT:PSS mixture, and after heat treatment mix with and dope the adjacent non-polar semiconducting polymer layer [12–15]. A similar effect has also been observed in mixtures of another polymeric dopant, perfluorinated ionomer (PFI), with poly(thiophene-3-[2-(2-methoxy-ethoxy)ethoxy]-2,5-diyl) (S-P3MEET). It was shown that PFI tends to phase separate out of the polymer due to its low miscibility in conjugated polymers, forming a PFI-rich skin between S-P3MEET and poly(3-hexylthiophene) (P3HT) layers. In this case, the location of the dopant remains stable under considerable thermal stress, which implies that reduced mixing can hinder undesired doping [16]. This relationship between ionic dopant miscibility and contact doping across a polar/non-polar interface was recently quantified for a variety of self-doped polymers [17].

By comparison, molecular dopants are more traditionally used in small molecule evaporated devices. Since the dopant is a separate molecule, it can be co-evaporated with a hole or electron transport material and causes doping by forming charge transfer salts in-situ in specific layers [18,19]. This dopant type is used to tune the work function and/or induce selective n-type or p-type charge transport [20]. A disadvantage, however, is that these dopants are not covalently bound into position and thereby can diffuse into other layers within the device under thermal or electronic stress. The weaker van der Waals or Coulombic forces at play in these samples are not sufficient to bind the dopant into place [21,22]. Li et al. recently showed that 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) sublimates out of the N,N,N',N'-tetrakis(4-methoxy-phenyl)benzidine (MeO-TPD) mixed layer at $\sim 150^\circ\text{C}$ and diffuses at room temperature [23]. F4TCNQ has also been investigated as a p-type dopant for polymer samples using solution-processing with many of these studies focused on the non-polar polymer P3HT [24–26]. More recently, F4TCNQ was used to control the solubility of P3HT for patterning purposes and is likely therefore to be incorporated into solution-processed devices in the near future [27]. Unfortunately, little attention has been paid to the question of whether the molecular dopants have preference for the polar layer or for the non-polar layer, which is of high interest from the device stability perspective.

In this study, conjugated polymers, S-P3MEET and P3HT (Fig. 1),

will be used to fabricate the polar and non-polar layers, respectively. S-P3MEET and P3HT are chosen because 1) both materials have similar polythiophene backbones; 2) P3HT is the most widely used conjugated polymer while S-P3MEET has been shown as a promising alternative to PEDOT:PSS [28,16], and 3) S-P3MEET forms a thermally stable bilayer with P3HT, so we can study the transport of F4TCNQ without interference from mixing between the layers. The first part of this paper explores whether F4TCNQ is able to dope S-P3MEET. A comprehensive study on the electronic, morphological and thermal properties of the F4TCNQ doped S-P3MEET layer is performed. Next, a combination of absorbance/fluorescence spectroscopy and X-ray reflectometry techniques are used to investigate the location of F4TCNQ upon thermal annealing of bilayers of polar S-P3MEET and non-polar P3HT.

2. Materials and methods

2.1. Materials and sample preparation

The S-P3MEET formulation (Plexcore OC RG-1100) was provided by Plextronics, inc. F4TCNQ ($\geq 97\%$), Poly(3-hexylthiophene-2,5-diyl) and (P3HT) (Regioregular, $M_n = 54\text{--}75$ kDa) were purchased from Sigma-Aldrich. All chemicals were used as-received unless otherwise indicated.

For sample preparation, all substrates were cleaned using ultrasonic baths of acetone, 5% Mucosal solution, and deionized water, successively, followed by nitrogen drying. The substrates were then placed to a UV-ozone cleaner for 30 min before use. The F4TCNQ solution used to dope the S-P3MEET was prepared by dissolving F4TCNQ in a solvent mixture that consisted of 50% isopropyl alcohol, 40% 1,3-propanediol, and 10% deionized water by volume to a concentration of 1 mg/ml. Solutions of S-P3MEET and F4TCNQ were then mixed in appropriate ratios to achieve the desired doping levels. The films were then spin-coated on clean substrates from blend solutions, and placed on a hotplate at 110°C for 3 min to remove excess solvent.

2.2. Characterization

Steady-state absorbance and photoluminescence spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer and a Varian Eclipse photoluminescence spectrophotometer, respectively. The photoluminescence experiments were conducted using a 2.38 eV excitation beam to optically excite the P3HT. Spectroscopy measurements were performed on P3HT/F4TCNQ bilayer samples. For one of the P3HT/F4TCNQ bilayer samples, the P3HT was first spin-coated onto a glass substrate to form an 80 nm thick film. The sample was then placed in a MBraun thermal evaporator, which was pumped down to a pressure of 5×10^{-6} mbar before depositing 10 nm of F4TCNQ onto the P3HT film at a rate of ~ 0.2 Å/sec. Another P3HT/F4TCNQ bilayer was prepared by mechanically laminating the two individual layers together. This was accomplished by depositing the P3HT and F4TCNQ layers separately onto glass substrates and clamping the layers together with a force of approximately 0.3 N/cm². The two layers remained in contact for three weeks before the spectroscopy measurements were performed. For the S-P3MEET/P3HT bilayer sample, 60 nm P3HT layer was spin-coated on top of 60 nm undoped or doped S-P3MEET layer. The samples were measured before and after annealing. Last, the inverse P3HT/S-P3MEET bilayer sample was also prepared by spin-coating 60 nm S-P3MEET onto 60 nm F4TCNQ doped P3HT film.

Near edge X-ray absorption fine structure measurements were performed on beamline 6.3.1 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL). Thin films of

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