



# Investigation of p-dopant diffusion in polymer films and bulk heterojunctions: Stable spatially-confined doping for all-solution processed solar cells



An Dai<sup>a</sup>, Alan Wan<sup>b</sup>, Charles Magee<sup>b</sup>, Yadong Zhang<sup>c</sup>, Stephen Barlow<sup>c</sup>, Seth R. Marder<sup>c</sup>, Antoine Kahn<sup>a,\*</sup>

<sup>a</sup> Department of Electrical Engineering, Princeton University, Princeton, NJ 08544, USA

<sup>b</sup> Evans Analytical Group<sup>®</sup> (EAG), East Windsor, NJ 08520, USA

<sup>c</sup> Center for Organic Photonics and Electronics and School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA

## ARTICLE INFO

### Article history:

Received 28 January 2015

Received in revised form 7 April 2015

Accepted 23 April 2015

Available online 23 April 2015

### Keywords:

Lamination

Polymer

Doping

Molybdenum complex

Diffusion

## ABSTRACT

The spatial stability of the soluble p-dopant molybdenum tris[1-(methoxycarbonyl)-2-(trifluoromethyl)ethane-1,2-dithiolene] in polymer and polymer blend films is investigated via secondary ion mass spectrometry and current–voltage measurements. Bi-layer and tri-layer model structures, P3HT/doped P3HT and P3HT:ICBA/doped P3HT/P3HT:ICBA respectively, are fabricated using soft-contact transfer lamination to study the diffusion of the dopant. While the dopant is very mobile in pure P3HT, it is far more stable at the interface with the P3HT:ICBA bulk heterojunction. Our findings suggest a promising route to achieve spatially-confined doping with long-term stability, leading to hole-collection/injection contacts for all-solution processed polymer devices.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Electrical doping of organic semiconductors has attracted considerable attention since the early use of alkali metals [1] and alkali metal carboxylates [2] as n-dopants in organic light-emitting diodes in the late 1990s. In the past two decades, progress has been made in understanding fundamental doping mechanisms [3–6], optimizing device performance [7–12], and developing efficient molecular n- and p-dopants [13–17]. A variety of vacuum-processible p-dopants, including tetrafluorotetracyano-quinodimethane (F<sub>4</sub>-TCNQ) [3–5,7,10], molybdenum trioxide (MoO<sub>3</sub>) [14], and molybdenum tris-[1,2-bis(trifluoromethyl)ethane-1,2-dithiolene] (Mo(tfd)<sub>3</sub>) [15], and n-dopants, including decamethylcobaltocene (CoCp<sup>2</sup>) [13], bis(terpyridine)ruthenium (Ru(terpy)<sub>2</sub>) [12,18] and air-stable dimers of metallocenes and other organometallic sandwich compounds [6,11,16], have been investigated and used in organic devices. Recently, powerful solution-processible molecular n- and p-dopants have also been developed [9,17], expanding the scope of molecular doping to polymers and solution-deposited small molecules.

The present work focuses on the issue of molecular dopant diffusion in polymer films, specifically in structures in which dopants are initially confined in a narrow region of the device. Spatial confinement of dopants is used to enhance carrier injection at an interface without doping the rest of the structure, or to create a built-in potential, for example in a p-i-n device. In our work, dopants are introduced via soft-contact transfer lamination (SCTL) of a separately prepared ultra-thin doped polymer layer [9]. Enhancement of carrier injection by several orders of magnitude has been demonstrated as a result of this procedure, and is attributable to the doping-induced lowering of the electrode-polymer hole-injection barrier. However, such a structure comprises by design a large dopant concentration gradient across the laminated interface, and the possibility of dopant diffusion from the laminated layer into the organic device needs to be considered. Neutral or ionized dopants can act as exciton quenchers in light-emitting and harvesting devices [19–21], and charge carriers contributed by dopants can degrade the on/off current ratio of an organic transistor when present in excessive concentration in the channel [11]. The stability of dopants with respect to diffusion in the host matrix is, therefore, critical to the efficiency, stability and lifetime of the device.

Extensive diffusion of dopants such as lithium (Li) or molybdenum tri-oxide (MoO<sub>3</sub>) has been observed in various small-molecule

\* Corresponding author.

E-mail address: [kahn@princeton.edu](mailto:kahn@princeton.edu) (A. Kahn).

films [22,23], and attributed in part to their small size. The larger molecular p-dopant  $F_4$ -TCNQ was found to diffuse in zinc phthalocyanine (ZnPc) [5] or 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP) [24], two partially crystalline materials, but to be spatially stable in N,N'-di-[(1-naphthyl)-N,N'-diphenyl]-1,1'-biphenyl)-4,4'-diamine ( $\alpha$ -NPD) [25], a typically amorphous material. Mo(tfd)<sub>3</sub> was also found to be stable in  $\alpha$ -NPD [15]. Both the size of the dopant and the structure of the organic semiconductor are therefore presumably important in terms of dopant spatial stability.

Studies of the distribution and stability of dopants in polymer films have been very sparse to date. We recently reported on the solution-based p-doping of P3HT with a new soluble dopant, molybdenum tris[1-(methoxycarbonyl)-2-(trifluoromethyl)-ethane-1,2-dithiolene] (Mo(tfd-CO<sub>2</sub>Me)<sub>3</sub>) [9]. Using soft-contact lamination of ultra-thin (30 nm) p-doped P3HT layers, we demonstrated significant enhancement of hole injection into undoped P3HT, as well as efficient hole collection from solution-processed bulk-heterojunction solar cells composed of P3HT and either 6,6-phenyl-C61-butyric acid methyl ester (PCBM) or P3HT:indene-C<sub>60</sub> bis-adduct (ICBA). The present paper extends this work with an investigation of the diffusion of (Mo(tfd-CO<sub>2</sub>Me)<sub>3</sub>) into pure P3HT and into the P3HT:ICBA blend active layer. Dopant diffusion is characterized via secondary ion mass spectrometry (SIMS) and current density–voltage ( $J$ – $V$ ) measurements. Whereas the dopant is found to diffuse extensively in pure P3HT, it is found to be far more stable at the interface with the bulk-heterojunction blend.

## 2. Experimental procedures

The p-dopant Mo(tfd-CO<sub>2</sub>Me)<sub>3</sub> was synthesized as reported elsewhere [9]. P3HT and ICBA were obtained from Merck Chemicals Ltd. and Sigma Aldrich, respectively, and used as received. P3HT was dissolved in chlorobenzene (10–30 mg mL<sup>-1</sup>) and stirred at 45 °C for 4 h. Mo(tfd-CO<sub>2</sub>Me)<sub>3</sub> was also dissolved in chlorobenzene (2–4 mg mL<sup>-1</sup>). The dopant concentration of 3.8 wt% used in this work was achieved by mixing appropriate amounts of the two solutions, followed by 10 h stirring at 45 °C. In the remainder of the paper, the doping concentration is given in wt%, with the understanding that 1 wt% of Mo(tfd-CO<sub>2</sub>Me)<sub>3</sub> in P3HT corresponds to one dopant molecule per ~450 P3HT monomers.

SIMS measurements were performed by the Evans Analytical Group (EAG). Samples were prepared in the Princeton laboratory, then transferred to EAG for SIMS measurements conducted after about a week. Samples were analyzed using Oxygen primary ion on a PHI 6600 model quadrupole analyzer SIMS instrument; conditions were optimized to give the best detection limit for measuring

Mo positive atomic ions. Samples used for SIMS analysis were deposited on Si substrates pre-cleaned by sequential sonication steps in acetone and isopropanol (15 min each). The samples had the following structures: (a) Si/3.8 wt% doped P3HT (70 nm), (b) Si/3.8 wt% doped P3HT(70 nm)/P3HT (80 nm) and (c) Si/P3HT:ICBA (150 nm)/3.8 wt% doped P3HT (30 nm)/P3HT:ICBA (150 nm) (Fig. 1). These multilayers were fabricated via soft-contact transfer lamination (SCTL) of the separately prepared undoped and doped layers. The details of the lamination procedure were introduced elsewhere [9]. Doped P3HT films in direct contact with the Si substrate were spin-coated in N<sub>2</sub> from an appropriately mixed host-dopant co-solution (ca. 10–20 mg mL<sup>-1</sup> in chlorobenzene) at 1500 rpm for 40 s, followed by annealing at 110 °C for 10 min, giving ca. 30–100 nm thick films. Films prepared for SCTL were originally spin-coated on a UV-ozone treated Si surface with no subsequent annealing, then transferred to a PDMS stamp [9]. For bulk heterojunction (BHJ) films, P3HT and ICBA were mixed in 1,2-dichlorobenzene with a 1:1 weight ratio (40 mg mL<sup>-1</sup>). BHJ films (150 nm) were formed by spin-coating at 1500 rpm for 60 s. The active layer was then solvent-annealed overnight, and then annealed on a hot plate at 160 °C for 10 min in N<sub>2</sub>, while the polymer layer (doped, undoped P3HT or bulk-heterojunction P3HT:ICBA blend) to be transferred via lamination was initially spun in N<sub>2</sub> onto a UV-ozone exposed silicon substrate, with no subsequent annealing. The films were then taken out of the N<sub>2</sub> environment for the SCTL lamination procedure. No post-fabrication annealing was performed on sample (c), while sample (b) were either not annealed or annealed at 100 °C for 10 min in N<sub>2</sub>.

The stability of dopants in P3HT was also investigated through electrical measurements on two types of structures: (Device A) ITO/PEDOT:PSS 4083 (40 nm)/3.8 wt% doped P3HT (80 nm)/P3HT (90 nm)/Ag and (Device B) ITO/PEDOT:PSS 4083 (40 nm)/P3HT (90 nm)/3.8 wt% doped P3HT (80 nm)/Ag (Fig. 4(b)). The ITO substrates were sequentially sonicated in Alconox<sup>R</sup>, acetone, and isopropanol (15 min each), and UV-ozone treated for 30 min. PEDOT:PSS was spin-coated at 5000 rpm for 40 s to create a 40 nm film, and annealed at 150 °C for 5 min in N<sub>2</sub>. Arrays of 1 mm<sup>2</sup> top Ag contacts were evaporated in a vacuum chamber through a shadow mask. To test for dopant stability at the interface with a bulk heterojunction, inverted solar cells were made with the following structure: ITO/PEIE (polyethylenimine ethoxylated)/P3HT:ICBA (200 nm)/3.8 wt% P3HT (30 nm)/Ag, with ITO/PEIE for electron collection at the bottom and doped P3HT laminated on the top for hole collection. The fabrication procedure was reported elsewhere [9]. Ag contacts were deposited through a shadow mask in a vacuum thermal evaporator (EvoVac, Angstrom Engineering Inc.) at a base pressure of  $7 \times 10^{-7}$  Torr; the effective area of the

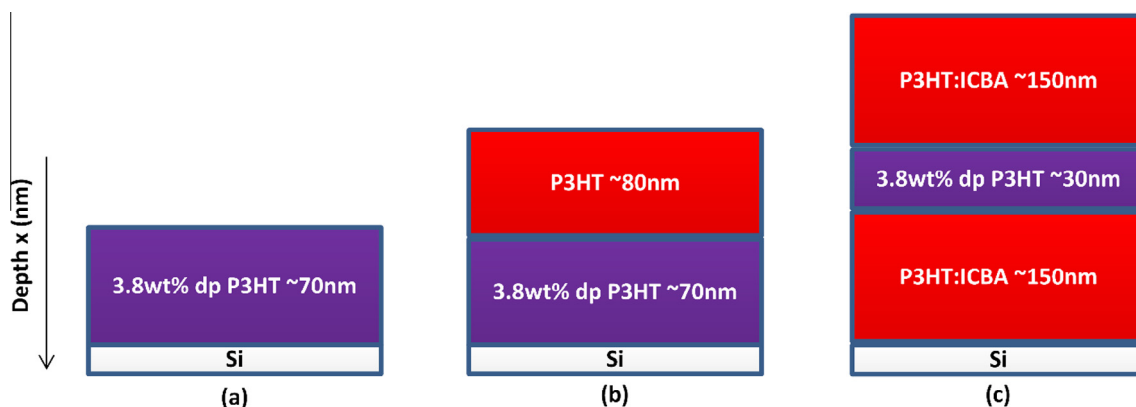


Fig. 1. Sample structures for SIMS analysis.

Download English Version:

<https://daneshyari.com/en/article/7701553>

Download Persian Version:

<https://daneshyari.com/article/7701553>

[Daneshyari.com](https://daneshyari.com)