



Effects of iodine doping on small molecule organic semiconductors for high charge carrier mobility and photoconductivity



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ABSTRACT

Here we report the effects of iodine doping on small molecule organic semiconductors. Thin films of semiconducting p-DTS(FBTTh₂)₂ doped with 1–5 wt% iodine were fabricated and their photo-physical, crystallographic, morphological, and electrical properties were systematically analyzed. The doping significantly increased the energetic distance between the highest occupied molecular orbital (HOMO) and Fermi level of p-DTS(FBTTh₂)₂, typical for p-type doping. In addition, depletion mode transistor measurements showed an increase in the hole concentration with increasing dopant concentration. From grazing incidence X-ray diffraction (GIXD) analyses of iodine-doped p-DTS(FBTTh₂)₂ films, we observed significant changes in the crystal orientation at the optimal doping ratio of 1 wt%. Atomic force microscopy (AFM) analyses showed morphological changes with respect to dopant concentrations, which were in good agreement with the GIXD results. As a result, accumulation mode transistor measurements demonstrated an increase in the hole mobility by 54% at the optimized doping concentration compared to an undoped device. Furthermore, photoconductive device operation revealed that iodine-doping can induce dramatically enhanced photo-responsivity as high as 2.08 A/W. We demonstrate that iodine doping can be a simple and effective method for enhancing the performance of small molecule-based electronic devices, by optimizing the energy level configuration as well as enhancing intermolecular interactions.

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1. Introduction

Organic electronic devices have attracted a large amount of attention as they can be fabricated in large-areas by low-cost solution-based processes. Organic semiconductors, including polymeric semiconductors and small molecular semiconductors, have been used as the active layers of many electronic devices [1,2]. Especially, organic molecular semiconductors possess a unique merit such as a superior solubility and a monodispersity [3] which cannot be easily guaranteed by polymeric semiconductors inevitably with distribution of molecular weight, polydispersity and a low solubility. However, organic molecular semiconductors are still inferior to polymeric semiconductors in terms of the charge carrier mobility. Although some kinds of organic molecular semiconductors have shown extremely high charge carrier mobilities when fabricated as single crystals [4], in the polycrystalline thin

film state, they are not comparable with recently reported donor-acceptor copolymers with a rigid backbone structure [5].

To enhance the charge carrier mobility, especially under the gate-bias saturation regime generally used for organic field effect transistors (OFETs), increasing the charge carrier density of the semiconductor layer by chemical or electrochemical doping can be a facile and effective method [6–8]. Note that in the case of FET mode, the charge carrier density strongly affects the charge carrier mobility [9]. In the case of polymeric semiconductors, improved performances have been widely reported using electrochemical doping [8,10]. In most cases the doping resulted in charge transfer between the polymer and dopant molecules, which increased the charge carrier density. In a few cases, the crystallinity of the polymeric semiconductor was also affected by doping [10].

However, there have been very few reports on the effects of doping on enhancing the charge carrier mobility of small molecular semiconductors [11], especially for OFET applications. Typically, small molecules are much smaller than polymeric semiconductors and therefore, the morphology and structure of small molecules can be more dramatically affected by electrochemical doping. Here

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we report the effect of electrochemical doping on small molecular semiconductors. We have selected 7,7'-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl)bis(6-fluoro-4-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole) (p-DTS(FBTTh₂)₂) (as shown in Fig. 1a) as a host semiconductor [12,13] and iodine (I₂) as a p-type dopant. Ultraviolet photoelectron spectroscopy (UPS) analyses and depletion mode OFET measurements were undertaken to investigate the doping mechanism and the change of charge carrier density, respectively. Interestingly, two-dimensional (2D) grazing incidence X-ray diffraction (GIXD) data together with the morphologies observed by atomic-force microscopy (AFM) revealed that the edge-on orientation of p-DTS(FBTTh₂)₂ was greatly enhanced by electrochemical iodine doping. Finally, we fabricated top-contact/bottom-gate (TCBG) OFETs to analyse the charge transport behavior with p-DTS(FBTTh₂)₂/iodine blends, resulting in an increase in the hole mobility of 54% at the optimized doping concentration of 1 wt% compared to an undoped device.

2. Experimental

Materials: p-DTS(FBTTh₂)₂ and iodine were purchased from 1-Material and Sigma-Aldrich, respectively, and used as received.

Device fabrication: Top-contact OFETs were fabricated on a common gate of highly n-doped silicon with a 100-nm-thick thermally grown SiO₂ dielectric layer. The SiO₂ dielectric layer was modified with octyltrichlorosilane by dipping in a toluene solution. Solutions containing the p-DTS(FBTTh₂)₂/iodine mixtures were spin-coated at 1500 rpm using 0–5 wt% solutions to form active layers on FETs with a nominal thickness of 40 nm, as confirmed using a surface profilometer (Alpha Step 500, Tencor). All of the films were annealed at 80 °C for 10 min in a nitrogen-filled glove box. Gold source and drain electrodes (80 nm) were evaporated through a shadow mask. For photoconductive measurement, the same device was used. For all measurements, the channel widths and lengths were 1500 μm and 150 μm, respectively.

Characterization: GIXD and UPS measurements were performed at the 3C and 4D beam lines at the Pohang Accelerator Laboratory (PAL), respectively. For GIXD measurements, the sample-to-detector distance was 210.83 mm and the incident wavelength

was 1.2413 Å. AFM images were collected using an XE-100 instrument from PISA. The electrical characteristics of the transistors were measured using a 4156A precision semiconductor parameter analyzer (Agilent Technologies). The current-voltage (J-V) measurements were conducted using Keithley 2400 Sourcemeater. For photocurrent measurements, a green laser diode with an intensity of 7.96 mW/cm² and wavelength of 532 nm was used.

3. Results and discussion

To confirm the extent of iodine-doping of the p-DTS(FBTTh₂)₂ films, UPS measurements were conducted and the results are summarized in Fig. 2a. It can be clearly seen that the onset energies shifted with increasing doping ratio. The onset energy indicates φ, the distance between the Fermi level and ionization energy [14]. Therefore, it can be shown that increased iodine doping significantly decreased φ, which is typical for a p-type doping mechanism. It seems that the iodine dopant acted an electron acceptor [15] in the p-DTS(FBTTh₂)₂ layer, i.e. electron transfer from p-DTS(FBTTh₂)₂ to iodine occurred. Fig. 2b shows the hole concentrations of p-DTS(FBTTh₂)₂ films with various dopant concentrations. The hole concentrations were obtained from depletion mode OFET measurements using the following equation [16]: $V_p = \frac{qNd^2}{2\epsilon\epsilon_0} \left(1 + 2\frac{C_s}{C_i}\right)$, where V_p is the pinch-off voltage, q is the elementary charge, N is the hole concentration, d is the film thickness, ε is the dielectric constant, ε₀ is the permittivity in a vacuum, C_s is the semiconductor capacitance, and C_i is the dielectric capacitance. In the depletion mode, OFETs consisting of p-DTS(FBTTh₂)₂ with various iodine doping ratios are under an increasing positive gate voltage and the holes are exorcised from the semiconductor/insulator interface. Hence, the drain current gradually decreases and finally reaches the pinch-off point when all channels are depleted [17]. As shown in Fig. 2b, the hole concentration increases gradually with increasing dopant concentration, which is in good agreement with the results of the UPS measurements. In OFETs, it is well known that the charge carrier density increases often result in charge carrier mobility increases [9]. Therefore, one can expect further enhancement of the charge carrier mobility by iodine-doping.

It is well known that the crystal orientation and/or degree of

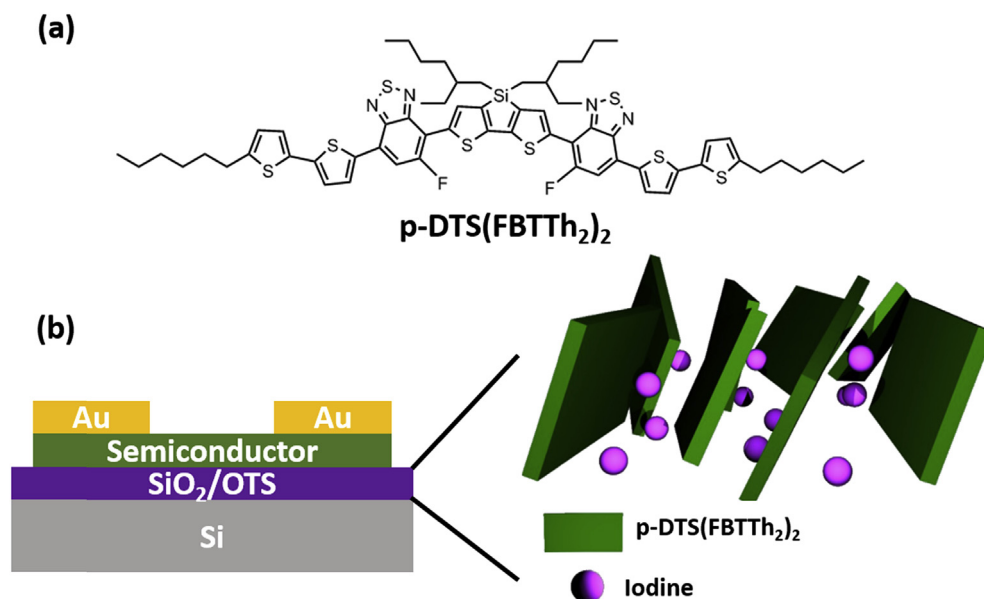


Fig. 1. (a) molecular structure of p-DTS(FBTTh₂)₂, (b) device structure of top-contact, bottom-gate OFETs and schematic of molecular arrangement in active layer.

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