# Orientation of Semiconducting Polymers via Swift Printing and Drawing Techniques for High Performance Organic Electronic Devices

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Recent developments in the field of organic electronics are being triggered by various approaches aiming towards enhancing the charge transport in thin-films of processable organic semiconductors such as novel molecular design, synthesis and increasing their crystallinity and molecular orientation adopting various thin film fabrication techniques. However, intriguing challenges associated with serious health and environment hazards due to inevitable use of halogenated solvents are needed to be addressed amicably before the practical realization of organic electronic devices. In order to address this issue, thin film fabrication techniques like floating-film transfer and friction transfer have been utilized to demonstrate environment friendly and sustainable fabrication of large area thin-films possessing adequate uniformity without comprising the facile charge transport. Organic field effect transistors were fabricated using different regions of the large-area thin films ($\gtrsim$10 cm$^2$) and by optimizing casting conditions, uniformity in the field effect mobility ($\mu$) was demonstrated. Besides this, as compared to most commonly used spin coating, one order of magnitude enhancement in the $\mu$ was successfully achieved utilizing oriented thin films fabricated by our methods.

## 1.  Introduction

Cost effective and simple thin film processing techniques have made the organic semiconductors a promising contender for electronic device applications. The past decade has witnessed significant scientific efforts to improve the charge transport characteristics of the organic semiconductors by tuning their chemical structure or by varying the film fabrication techniques in order to enhance the macromolecular ordering. Since conjugated polymers (CPs) offer better solution rheology and compatibility with solvent-free drawing techniques may be more suitable for large area thin film fabrication. Due to quasi-one-dimensional nature of CPs, their backbone orientation and self-assembly have been extensively explored to improve the optoelectronic characteristics of the devices [1]. Although good solubility of CPs in common halogenated solvents are being frequently implemented for the research and development at the laboratory scale, the serious health and environment hazards cannot be avoided at large scale roll-to-roll fabrication needed for the commercialization of the organic electronic devices. Apart from this, controlling device to device variation, at large scale is also essential. Therefore, to overcome these challenges, efficient solution processing or solvent free techniques need to be explored [1–3]. Herein, two techniques such as floating-film transfer method (FTM) and friction transfer (FT), which has been widely implemented and improvised by our group is being reported.
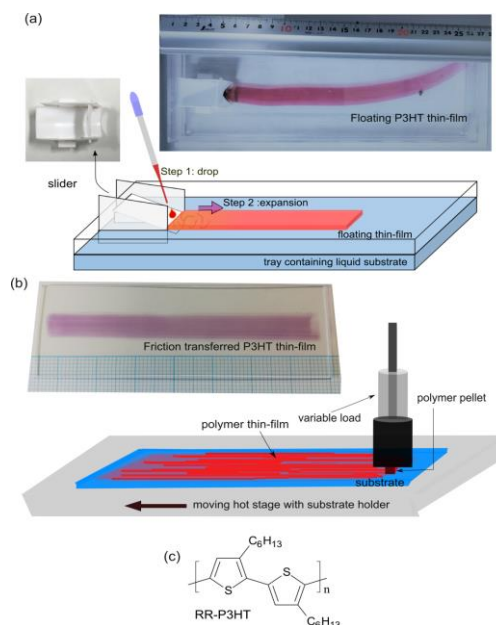


Fig. 1. Schematic representation for the mechanism of thin film fabrication by FTM and (b) friction transfer techniques, the representative thin films fabricated by them are shown in the insets. The custom made slider is shown in the left insets (a). (c) Molecular structure of regioregular-P3HT.

In FTM, by placing one drop (~10 – 15 $\mu$L) of CP solution on an orthogonal liquid substrate a solid floating film is obtained, which can be easily stamped on the desired substrate without causing chemical or mechanical damage to the underlying layers [4,5]. Recently, facile fabrication of large area ribbon-shaped CP thin-film was also demonstrated by controlling the film expansion direction through a custom made slider, as shown in Fig. 1 [6]. Utilizing friction transfer (FT) technique, considerable macromolecular orientation anisotropy and its impact on charge transport characteristics of the CP thin-films have been demonstrated [1]. Recently we have reported almost one order magnitude enhancement in the field effect mobility ($\mu$) of friction transferred CP thin film by tuning the surface energy of the dielectric interface [3]. In this work, both of the techniques like FTM and FT were utilized to demonstrate the eco-friendly and economical ways for large area fabrication of thin films using most widely used CP Poly(3-hexylthiophene) (P3HT) and the uniformity in their charge transport were also analyzed by fabricating organic field effect transistors (OFETs) with different parts of the large thin-films. The uniformity in $\mu$ for large area thin-films cast through both techniques validates their feasibility towards large scale application. For the FTM based thin-films one order enhancement in $\mu$ was also obtained compared to conventional spin-coated thin films.

## 2. Experimental Section

Regioregular (RR) P3HT, super-dehydrated chloroform, octadecyltrichlorosilane (OTS) and 1-octadecene were purchased from Sigma-Aldrich. Ethylene glycol and the cleaning solvents were supplied by Wako Chemicals, Japan. OFETs were fabricated on highly p-doped Si substrates with 100 nm thermally grown $SiO_2$ at top. Substrates were cleaned by sonicating them in acetone, chloroform, and isopropanol for 10 min each followed by annealing at 150°C for 1 h under ambient conditions. For OFETs with FTM or spin-coated P3HT thin-films, self-assembled monolayer (SAM) was grown on the $SiO_2$ surfaces by treating them with OTS following our previous work [7]. Ribbon shaped P3HT films were fabricated by FTM by placing a drop of P3HT solution (2% w/w) in super-dehydrated chloroform at the slider/ethylene glycol interface in order to promote unidirectional spreading of the thin floating films, as shown in Fig. 1(a). Temperature of the liquid substrate was kept ~ 30 °C. The FTM thin-films were stamped on SAM treated Si/SiO$_2$ substrates and annealed at 100 °C for 15 min under Argon atmosphere to evaporate residual solvents. For friction transfer, the P3HT pellets were prepared according to the previous report [8] and they were drawn against the bare substrate under optimized conditions such as stage temperature of 80 °C, stage speed of 50

mm/min, and squeezing load of 15 kgf/cm$^2$. For reference, the P3HT solution (0.5% w/w in super-dehydrated chloroform) was spun on SAM treated Si/SiO$_2$ substrates at 1500 rpm for 30 s and the samples were also annealed under identical conditions of FTM. Fabrication of the OFETs were completed by patterning thermally evaporated Gold (under ~ $10^{-6}$ Torr) as source and drain electrodes using Nickle shadow masks with channel length and width of 20 $\mu$m and 2 mm respectively. The output and transfer characteristics of the OFETs were measured with a Keithley 2612 two-channel source-measure unit. Field effect mobilities were calculated from the saturation regions of the transfer curves as discussed in detail in our earlier publication [9].

## 3. Results and Discussion

Reproducibility and uniformity of the thin film characteristics of devices are highly desired for their large area implemenation. Keeping this mind, large area thin-films were fabricated through two techniques like FTM and FT, and corresponding charge transport uniformity was demonstrated by fabricating OFETs with different regions of the thin-films. Large area thin-film of RR-P3HT fabricated by FTM, is shown in Fig. 2 (a). When a drop of CP solution is placed at the interface of slider and liquid substrate, it starts to expand opposite to the inclined surface of slider and the reverse compressive force is imparted at the interface by viscous liquid substrate. Further, the simultaneous evaporation of the volatile solvent results in to the macromolecular ordering in the floating solid thin-films [6,9]. It is well reported that in the FTM thin-films, the macromolecular orientation in the thin film occurs perpendicular to the film expansion direction [7,10]. Likewise, the macromolecular orientation along the
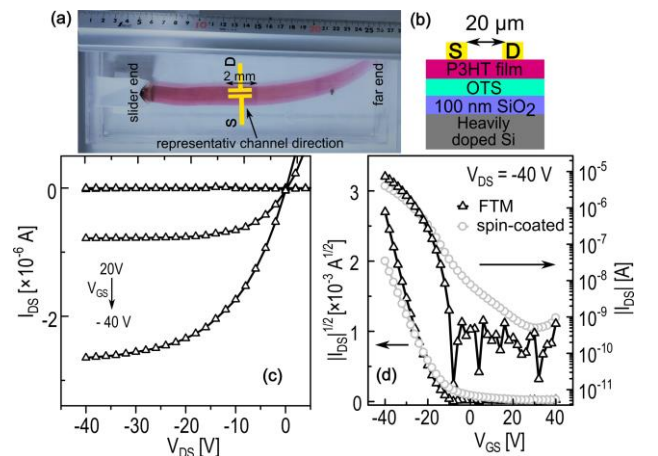


Fig. 2. Digital image of the ribbon-shaped FTM fabricated thin film of P3HT (a) and representative OFET-channel direction with respect to the orientation. OFETs device architecture (b), representative output (c) and transfer (d) characteristics of the OFETs with the thin-films.

width of P3HT-ribbon was confirmed by polarized electronic absorption spectroscopy and thickness uniformity was also verified by our newly proposed 2D-positional mapping technique [11]. Thanks to the integration of the polarizer, XYZ stage controller and photonic mult-channel analyzer, which led to swift and simulateneous mapping of orientation and film uniformity. The middle part of the large area ribbon-shaped thin film (from 5 cm to 12 cm with respect to the slider end) of P3HT having very high degree of uniformity in the film thickness and molecular orientation was selected for the OFET fabrication.

The OFETs were fabricated by keeping the channel along the width of P3HT-ribbon, the device architecture and corresponding charge transport characteristics are shown in the Fig. 2 (b - d). Output and transfer characteristics represent clear p-type characteristics. From the perusal of Figure 2 (d), it is clear that the OFETs fabricated with FTM film possessed clear transition from off to on region and higher on/off ratio as compared to its spin-coated counterpart as evidenced from the electronic parameters summarized in the Table I. The higher $\mu$ in case of FTM films can be attributed to improved crystallinity agreeing well with the previous report [4]. It is worth to mention here that for the OFETs fabricated with the extremely far end of the P3HT-ribbon, the maximum $\mu$ of $\sim$ 0.03 cm$^2$V$^{-1}$s$^{-1}$ was obtained from the saturation regions of the transfer characteristics. Nonetheless, for the remaining portion (except 2 - 3 cm of far end film) almost uniform $\mu \sim$ 0.012 cm$^2$V$^{-1}$s$^{-1}$ was obtained. During the film expansion, the far region of the film had maximum freedom for expansion followed by the enhanced viscous drag by the bottom liquid substrate. Therefore, the higher $\mu$ observed for the far end region of the P3HT- film can be attributed to relatively higher macromolecular ordering in that region and a similar trend was also witnessed for different CPs in our earlier publications [6,11].

In order to demonstrate uniformity in charge transport of the FT processed thin-films, OFETs were also fabricated with different portions of the large area FT-P3HT thin-films fabricated on the same substrates as shown in Fig. 3(a). For the FT thin films the orientation of CP backbones is reported to be along the drawing direction and in this work also it was verified not only by the polarized electronic absorption spectroscopy but also the in-plane and out-of-plane X-ray diffractometry [1,3]. Therefore, the channels of OFETs were kept along the drawing direction. Since on OTS treated SiO$_2$, it was difficult to draw P3HT thin-film, therefore, bare SiO$_2$ substrates were utilized for OFET fabrication while the representative transport characteristics and the device structure are shown in Figure 3 (b, c). The output and transfer characteristics of the corresponding OFETs

also represent p-type characteristics and almost uniform $\mu \sim$ 0.0015 cm$^2$V$^{-1}$s$^{-1}$ was obtained for the different regions of the thin film, Fig. 3. It is worth to note here that FT thin films possessed comparatively rougher surface and of higher thickness as compared to the FTM thin-films. Although still exhaustive study is required to completely understand and quantify the role of contact resistance and access
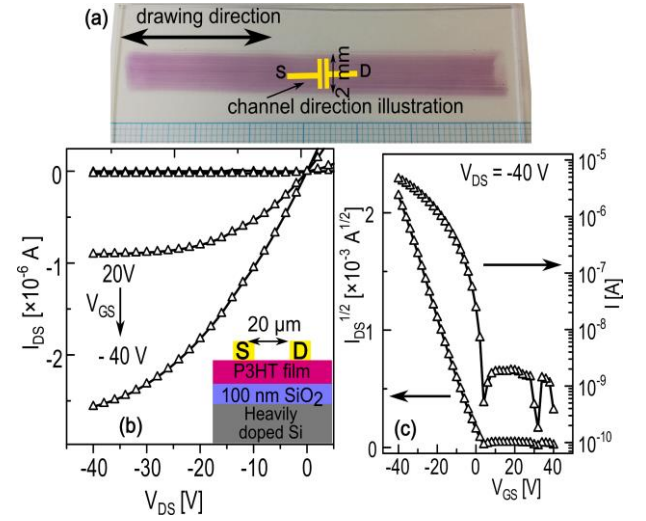


Fig. 3. (a) Digital image of the friction transferred P3HT thin-film and representative OFET-channel direction with respect to drawing direction, (b) representative output and (c) transfer characteristics of the OFETs with the thin-film. The OFETs architecture is shown in the Inset (b) with channel direction kept along the drawing direction.

resistance originated due to the non-uniform metal/CP interface and thicker active layer, the channel length were varied in order to overcome these effects [12–14]. It was observed that for higher channel length ($\gtrsim$100 $\mu$m), the $\mu$ improved and it became comparable to that obtained in the case of FTM film. Hence it indicated that by optimizing the OFET architecture, friction transferred CP thin-films can also be utilized for the large-area applications. We are also actively working in this direction and further research progress, optical anisotropy, thickness uniformity etc. for the FTM and friction transferred P3HT thin-films will be discussed in detail during the presentation.

Table I . The average field effect mobility ($\mu_{average}$) for the OFETs (with channel length and width of 20 $\mu$m and 2 mm respectively) fabricated with P3HT-thin films cast through various techniques.

| Casting technique | $\mu_{average}$ (cm$^2$V$^{-1}$s$^{-1}$) |
|---|---|
| Spin-coat | 0.0047 |
| FTM | 0.012 |
| Friction Transfer | 0.0015 |

It has been well documented that depending on the thin film processing, CPs adopt different configuration as face-on, edge-on and end-on and highly affect the device performance under consideration [1]. An edge-on molecular arrangement favours the planer charge charge transport and suitable for devices like OFETs while a face-on arrangement favours the vertical charge transport and suitable for the devices like diodes and solar cells. Spin-coated thin films of P3HT has been reported to widely adopt the face-on molecular arrangement while FTM generally provide edge-on oriented thin films. Using a number of CPs, we have clearly demonstrated that OFETs fabricated using FTM processed thin films always exhibited superior device performances as compared to their spin coated device counterparts [2,6,9]. At the same time, using both of the non-regiocontrolled (NR) as well as RR-P3HT, it has been shown that organic Schottky diodes fabricated using FTM thin films always gave inferior device performances especially in terms of rectification ratio of the devices as compared to that of their corresponding spin-coated device counterparts. This clearly validates that fact that molecular orientation plays a dominat role in controlling device performance for the nature of devices (vertical vs. planer) under consideration.

## 4. Conclusions

To address the existing challenges pertaining to the large area fabrication of organic electronic devicess, large area thin-films of P3HT as a representative CP, were fabricated using FTM as a sustainable technique with minimal solvent wastage and friction transfer as a solvent-free techniques. Further, uniformity in the thin films (area $\gtrsim 10$ cm$^2$) in terms of thickness and orientation along with electrical characteristics was successfully demonstrated utilizing polarized absorption spectroscopic technique and by fabricating OFETs, respectively. For the FTM and FT processed thin films of P3HT, one order of magnitude enhancement in $\mu$ was demonstrated compared to that of its most commonly using spin-coated thin films based device counterparts. Importance of nature of molecular orientation that is edge-on or face-on on controlling the planer and vertical charge transport was clarified by using thin films of P3HT fabricated by different methods and organic electronic devices like OFETs and Schottky diodes in to consideration. Now it can be concluded that for economically and environmentally sustainable fabrication of CP thin films at laboratory scale to large scale, both FTM and friction transfer are suitable techniques.

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