

Circular Flow Alignment of Polymeric Semiconductor Thin Films on Air-Liquid Interfaces

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Abstract

Orientational control of polymeric semiconductors (PSs) is a fundamental technology for understanding and improving the carrier transport properties. Although PS thin films have been fabricated through facile solution processes, complex convection flows during solvent evaporation often limit the controllability of orientation in terms of scalability and reproducibility. To address these problems, we developed a circular flow alignment method for PS thin films. On the circularly flowing glycerol inside a container, PS solutions were dropped to obtain thin films at the air-liquid interface. The resulting thin films showed alignment of the main chains along the flow direction, where the effects of convection flows during solvent evaporation were suppressed. Anisotropic

characteristics were observed in the thin-film structure evaluated by X-ray diffraction measurements, optical absorption, and carrier transport properties, which support the uniaxial alignment of the PS main chains. In field-effect transistors, a mobility of $0.13 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was observed under atmospheric conditions, which was four times higher than that of spin-coated thin films. Considering that macroscopic liquid flows are easily controlled, the proposed flow alignment may serve as a scalable and facile method for fabricating highly aligned PS thin films for various applications.

Introduction

Polymeric semiconductors (PSs) feature flexibility, solution processability, and tunable electronic properties by molecular design, which has led to their applications including field-effect transistors (FETs),^{1,2} diodes,^{3,4} and thermoelectric generators.^{5,6} Alignment of PSs is a key technology for understanding and improving their electronic properties.^{2,7,8} In addition to uniaxial alignment of the polymer main chains, it is important to achieve edge-on or face-on orientations depending on the target application. In FETs and applications using lateral carrier transport, the edge-on orientation is advantageous. Although methods such as high-temperature rubbing,⁷ solution shearing,⁹ and bar coating^{10,11} have yielded highly aligned polymer chains, the control of edge-on and face-on orientations is not always compatible. In addition, when a solution process is employed to fabricate aligned polymer films, multiple conditions need to be optimized under effects such as interactions between the substrate and polymer solution and convection flows in heated and drying solutions,¹² which may limit reproducibility and scalability.

Recently, aligned PS thin films with edge-on orientation have been fabricated using air-liquid interfaces.^{13–18} The fabricated thin films were transferred to the target substrates for use in devices. The air-liquid interface without attachment to solid substrates seems to allow the self-assembly of PSs into ordered structures by casting polymer solutions on liquid surfaces. By choosing the appropriate liquid subphase, the Langmuir-Blodgett method on

a heated liquid surface was demonstrated to utilize the compression force as the driving force for uniaxial alignment of PSs, which resulted in high mobility and conductivity after doping.^{13,19,20} Despite these advantages, it has been still difficult to control the alignment direction in a large area uniformly owing to the complex fluid flow dynamics that are affected by factors such as solution evaporation and the interaction between the polymer solution and the liquid substrate. Therefore, the precise control of convection effects during solvent evaporation is crucial in solution processes conducted on both liquid and solid substrates.

As a versatile alignment method, flow-induced alignment has been commonly employed for the highly ordered orientation of carbon nanotubes,²¹ PEDOT:PSS,²² liquid crystal polymers^{23,24} and hydrogels.²⁵ For instance, in the 3D printing of liquid crystal polymers, shear and extensional forces effectively induce uniaxial alignment along the flow direction, resulting in unprecedented stiffness and toughness of the material.^{23,24} However, such uniaxial flow alignment methods have been limited to the fabrication of fibrous structures and not thin films with two-dimensional sheet structures, which is critically important for the carrier transport properties.

Herein, we developed a novel method to utilize microscopically controlled liquid flow for uniaxial alignment of PSs at the air-liquid interface (Fig. 1a). The PS solutions were cast on a viscous liquid, glycerol, which flowed continuously in a container. Thanks to this controlled liquid flow, PSs main chains were aligned along the flow direction, which was confirmed by X-ray diffraction and polarized optical spectroscopy. Improved carrier transport properties along the alignment direction were evaluated using FETs. Our study highlights a simple method to suppress the effects of convection flow during the solution process, which has often limited the controllability of various solution processes. Scaling up our method may be feasible by flow path design, which highlights the advantage of using flowing liquid substrates in solution processes.

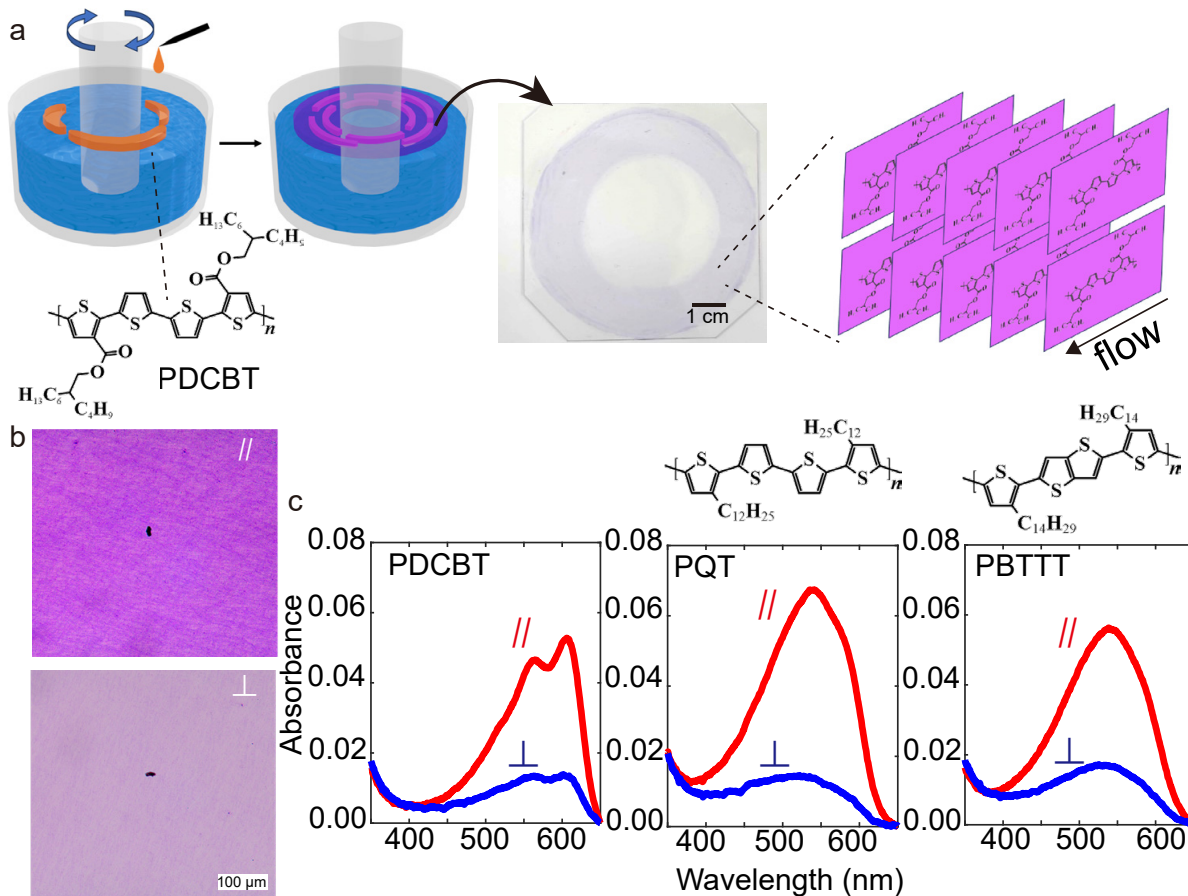


Figure 1: Circular flow alignment of PS thin films. (a) Illustrations of circular flow alignment method together with the chemical and thin-film structures of PDCBT and a photo of fabricated thin film. (b) Microscope images of fabricated ultrathin PDCBT film taken with the incident polarized light parallel (||) or perpendicular (⊥). (c) Polarized UV-vis spectra of PDCBT, PQT, and PBTTT thin films fabricated using our method. The incident light polarization was parallel or perpendicular to the flow direction.

Results and discussion

Film Preparations by the Circular Flow Alignment Method

As a candidate material showing high carrier mobility and air stability, the polymer semiconductor poly[(4,4'-bis(2-butyloctoxycarbonyl)-[2,2'-bithiophene]-5,5'-diyl)-alt-(2,2'-bithiophene-5,5'-diyl)] (PDCBT) was employed in this study. Compared with the well-studied poly(2,5-bis(3-tetradecylthiophene-2-yl)thieno[3,2-b]thiophene) (PBTTT),^{16,26} PDCBT exhibits a shorter π -stacking distance and a deeper highest occupied molecular orbital (HOMO) energy level.^{27,28}

The deep HOMO energy is attributed to the electron-withdrawing carboxylate substitutes in PDCBT, which are advantageous for improving the air stability of FETs^{29,30} and the performance of solar cells.^{27–29}

The circular flow alignment method was employed to fabricate the oriented PDCBT ultrathin films. Fig. 1a shows a schematic illustration of the method in which the polymer main chains are highly aligned along the viscous liquid flow at room temperature. First, a glass cylinder was submerged in a circular container filled with glycerol and then rotated at a speed of 20 rpm. The cylinder was fixed onto a Tornado N(Next) PSTC-103 to precisely control rotational speed. At the cylinder periphery, the rotation speed corresponds to *ca.* 40 mm/s, which is likely sufficient to drive polymer chain alignment, considering that a shear rate of less than 1 mm/s was previously reported to uniaxially align polymer chains during solution shearing.⁹ The inside of the container was covered with a PTFE coating to minimize the friction between glycerol and the container surface. A single droplet (*ca.* 30 μ L) of the PDCBT solution in a mixture of chloroform and 1-chloronaphthalene was dropped onto the glycerol surface flowing along the bottle rotation. To prevent film formation before spreading the solution on the glycerol surface, 1-chloronaphthalene with high boiling point was added to decrease the evaporation rate of the solvent. The cylinder was rotated until the solvent evaporated within 5 min. The resulting film was formed around the cylinder showing a ring shape. Nonuniform films were also observed between the ring-shaped film and the wall of the container, which were not employed in the following experiments. When the target substrate plane was in horizontal contact with the fabricated films, similar to the Langmuir-Schaefer method,³¹ the films were easily transferred to the target substrates.

Fig. 1b shows the polarized optical microscopy (POM) images of the fabricated PDCBT film. The incident polarized light was shed from the bottom of the substrate and the transmitted light was observed using a microscope. The color of the PDCBT film became darker when the light polarization was parallel to the flow direction during the film formation process than when they were perpendicular to each other. This result indicates the

macroscopic anisotropy of the fabricated PDCBT films. Optical anisotropy was also confirmed by polarized UV-vis absorption spectroscopy. To demonstrate the applicability of our method to various PSs, we employed three types of PSs, namely PDCBT, PBTTT and poly(3,3''-didodecyl[2,2':5',2'':5'',2'''-quaterthiophene]-5,5'''-diyl) (PQT). As shown in Fig. 1c, the higher absorbance was observed when the flow direction and light polarization were parallel to each other, which confirms alignment of main chains to this direction for the employed PSs. The dichroic ratios were calculated to be 3.5, 5.1, 3.7 for PDCBT, PQT, and PBTTT, respectively, based on the area of absorption peaks with the incident polarized light parallel and perpendicular to the flow direction. In the UV-vis spectra of the PDCBT thin film, two peaks were observed at approximately 560 nm and 600 nm, which indicate π - π interactions in the thin films.²⁹ Details of the thin-film structures are discussed based on X-ray diffraction in the following section. The observed successful alignments of PSs should be ascribed to the continuous flow of glycerol in our system. Here, the system with circular flow provides a facile way to make the PSs in contact with the flowing subphase during the slow solvent evaporation process.

Structural Analysis

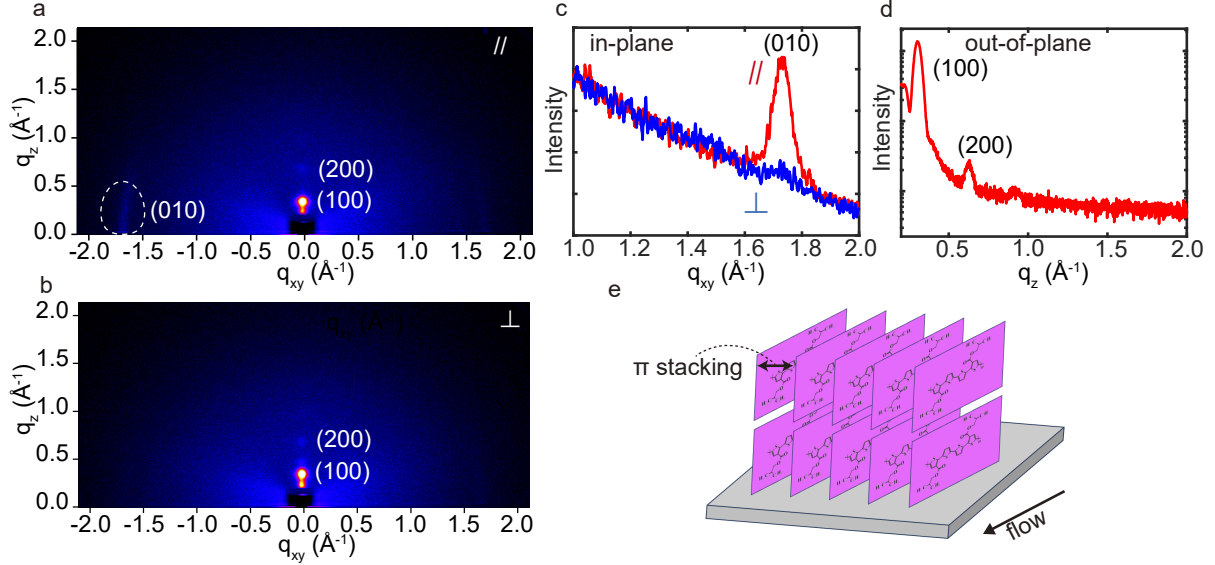


Figure 2: GIWAXS images of the aligned PDCBT film. GIWAXS images with the incident X-ray (a) parallel and (b) perpendicular to the flow direction. One-dimensional profiled converted from the images in the (c) in-plane direction. (d) An out-of-plane diffraction using the theta/two theta method. (e) Schematics of the uniaxially aligned PDCBT with edge-on orientation.

Grazing incident wide-angle X-ray scattering (GIWAXS) was used to investigate the semi-crystalline structures of the PDCBT ultrathin films. The PDCBT ultrathin films were transferred to the substrate three times to increase the film thickness and scattering intensity (Fig. 2a, b). The scattering image obtained with a single ultrathin film is shown in Fig. S1. Based on the one-dimensional profiles (Fig. 2c, d), the fabricated thin films showed (h00) diffraction peaks in the out-of-plane direction and the (010) diffraction peak in the in-plane direction, which are characteristic of the edge-on orientation of this polymer (Fig. 2e). In the in-plane direction, the (010) diffraction peak corresponding to the π -stacking periodicity ($q = 1.73 \text{ \AA}^{-1}$) was observed when the incident X-ray and the flow direction during the circular flow alignment method was parallel, whereas no π -stacking peak was observed when the X-ray was perpendicular to the flow direction. The d -spacing in this direction had a short value of 3.63 \AA . From the width of the (010) diffraction peak, the

paracrystallinity $g = 7.6 \%$ was calculated based on the equation $g = \sqrt{\frac{1}{2\pi} \frac{\Delta q}{q}}$: Δq and q are the full width at half maximum (FWHM) and peak position of the obtained diffraction peak, respectively. The g value was as small as that of PBTTT ($g = 7.3 \%$),³² which is one of the most crystalline polymeric semiconducting materials.³³ In the out-of-plane direction, (h00) diffraction peaks were observed for both parallel and perpendicular incident X-rays to the flow direction with d -spacing of 20.1 Å. These results demonstrate the successful formation of edge-on-oriented, uniaxially aligned thin films with high π -stacking periodicity using our circular flow alignment method.

Microstructure of Ultrathin Films

The PDCBT film morphology was confirmed using atomic force microscopy (AFM, Fig. 3a-d). The spin-coated film possessed isotropically oriented small grains similar to those in a previous report^{29,30} (Fig. 3b). The PDCBT thin film prepared by the circular flow alignment method had a fibrous structure with narrow fibers aligned on the micrometer scale (Fig. 3a). The film thickness obtained using the circular flow alignment method was confirmed as *ca.* 8 nm (Fig. S2). The aligned PDCBT film exhibits a smoother surface morphology with a root mean square (RMS) roughness of 1.06 nm, represented within the black dashed line in Fig. 3c, compared to the spin-coated film (RMS = 2.01 nm). On the surface, steps of a few nanometers are observed in the magnified image (Fig. 3e), which is consistent with the calculated lamellar distance ($d_{100} = 20.1$ Å) from our X-ray diffraction analysis. These results suggest a highly ordered film structure with clear molecular steps.

OFET Characteristics

Improvements in the carrier transport properties by the circular flow alignment method were confirmed by FET measurements. The PDCBT thin films on the liquid surface were transferred onto a Si substrate with a 100 nm SiO₂ layer treated with a self-assembled monolayer (SAM). The SAM treatment plays an important role not only in improving FET properties

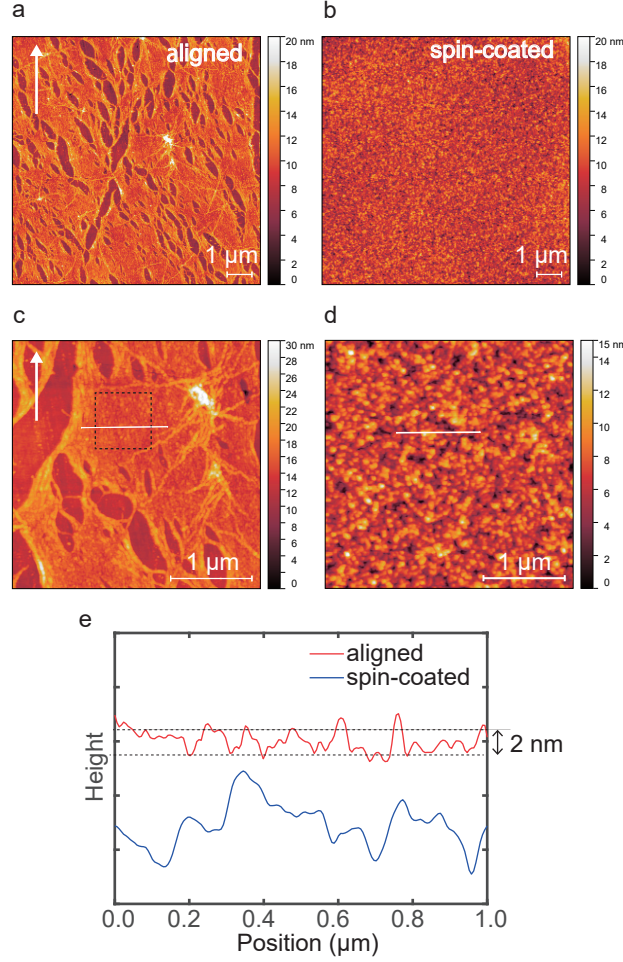


Figure 3: AFM images of PDCBT thin films. AFM images of the (a) aligned and (b) spin-coated PDCBT films. Magnified images of the (c) aligned and (d) spin-coated PDCBT films. (e) Height profiles of the aligned and spin-coated PDCBT thin films. The corresponding locations are shown as white lines in the figure c and d.

but also in enabling uniform transfer of the PS films floating on a viscous hydrophilic liquid to the target substrate. After transferring the polymer film, the substrate was cleaned with water to remove the residual glycerol and annealed in a vacuum oven at 175 °C for 1 h. The Au electrodes were thermally deposited through a shadow mask to fabricate source and drain electrodes on the PDCBT thin film. This bottom-gate top-contact FET was then encapsulated by spin-coating a polymethylmethacrylate (PMMA) thin film. The final device structure is shown in Fig. 4a. Fig. 4b shows the output characteristics when the channel is parallel to the flow direction. Fig. 4c and 4d show the linear region with V_{DS} of -3 V

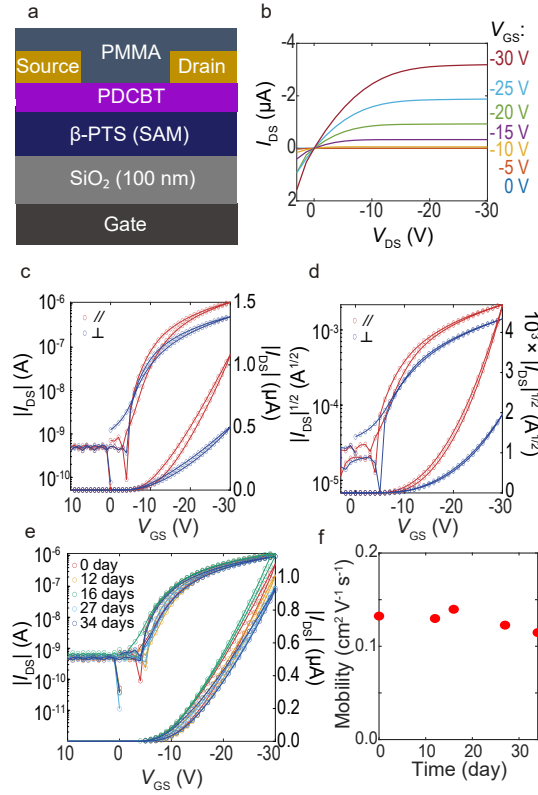


Figure 4: Characteristic of the fabricated PDCBT transistors. (a) An illustration of the device structure. (b) Output, (c) linear, and (d) saturation characteristics of the fabricated PDCBT transistors. Transistors with channels parallel and perpendicular to the flow direction are compared in the linear and saturation characteristics. (e) Linear characteristics and (f) mobilities measured for a device stored in ambient air. The times stored in air are denoted as legends. The channel was parallel to the flow direction for this transistor.

and the saturation region with V_{DS} of -30 V, respectively, which exhibit a typical p-type transistor operation. The hole mobility in the PDCBT-based FETs was higher in the direction parallel to the flow direction than in the perpendicular direction, which is reasonable considering the alignment of the main chains along the flow direction. The hole mobility in the linear region was calculated to be $0.13 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when the channel was parallel to the flow direction, which was higher than that of spin-coated PDCBT thin film transistors ($\mu = 0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) (Fig. S3). Our FET with the channel direction parallel to the flow direction was measured after storage under dark ambient conditions for up to 34 days. In

these measurements, only slight degradation was observed, which suggests good ambient stability of this device (Fig. 4e). The mobility was almost unchanged during the storage in air (Fig. 4f). Considering that semicrystalline polymers such as P3HT and PBTTT exhibit poor ambient stability,^{34,35} PDCBT with the deep HOMO level seems to be suitable for stable operation of devices in air. Above results demonstrate improvement in the mobility of the ambient stable polymer FET by our method.

Conclusions

We established the circular flow alignment method to fabricate highly aligned edge-on-oriented PS ultrathin films on air-liquid interfaces at room temperature. While the liquid flow has been mostly employed to fabricate one-dimensional fibrous structures, our method makes efficient use of liquid flow at the air-liquid interface to fabricate aligned thin films with two-dimensional packing structures. The molecular alignment direction was parallel to the liquid flow, as confirmed by polarized UV-Vis spectroscopy and GIWAXS measurements. The aligned PDCBT thin films exhibited improved mobility along the channel parallel to the flow direction compared to the spin-coated thin film. FET mobility of $0.13 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and operational stability under atmospheric conditions were observed for the aligned thin film. The proposed use of subphase flow will offer an easy way to control the molecular orientation during the solution process, which has been affected by convection flows during the solvent evaporation. In addition, scaling up our method may be feasible by flow path design, which will contribute to a wide range of applications of aligned PS thin films.

Experimental

Materials: PDCBT with an estimated molecular weight of 30-80 kDa was purchased from Solaris (Lot: 22L400451) and used without any purification. The 0.3 wt% PDCBT solution was prepared in a mixture of chloroform and 1-chloronaphthalene at a weight ratio of 9:1. The

solution was maintained at 55°C on a hotplate and stirred overnight. As a reference, 0.3 wt% PDCBT solution dissolved in *o*-dichlorobenzene was prepared at 100 °C and spin-coated at a spinning speed at 2000 rpm. PBTTT-C14 and PQT-12 were purchased from Sigma-Aldrich and dissolved in *o*-dichlorobenzene and a mixture of chlorobenzene and 1-chloronaphthalene at a weight ratio of 9:1. Glycerol (Fujifilm Wako Pure Chemicals) was used as the liquid substrate. 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) for self-assembled monolayer (SAM) preparation was purchased from Tokyo chemical industry (TCI) and deposited onto a glass substrate for polarized light absorption spectroscopy. 2-(phenylethyl)trimethoxysilane(β -PTS) was also used as SAM for FET device measurement and was purchased from TCI. Poly(methyl methacrylate) (PMMA) with molecular weight of 300kDa was purchased from Polymer Source.

Film Characterization: Polarized UV-vis absorption spectra was obtained using a V-770 (JASCO) equipped with a GPH-506 polarizer. HMDS-treated glass substrates were used for optical spectroscopy. Polarized optical microscopy (POM) observations were performed using a BX-51 (Olympus). Grazing incident wide-angle X-ray scattering (GIWAXS) profiles were recorded on a SmartLab (Rigaku) with a MacroMax-007HF X-ray generator, employing Cu K α radiation ($\lambda = 0.15418$ nm).

FET Device Fabrication: Heavily doped Si with a 100 nm thermally grown SiO₂ layer was used as the substrate for FETs and the surface was treated with β -PTS. A PDCBT thin film was transferred to the substrate, washed with pure water, and annealed at 175°C in vacuum oven for 1h. After annealing, Au electrodes with 40 nm thickness were thermally deposited through a metal mask to fabricate source/drain electrodes. PMMA was dissolved in dehydrated butyl acetate at a concentration of 2 wt% and heated on a hot plate at 80°C with constant stirring at 300 rpm over night. The fabricated PDCBT film with Au electrodes was covered with PMMA encapsulation by spin-coating PMMA solution at 2000 rpm for 1 minute. The FET characteristics were all measured by 2634B system sourcemeter (Keithley) in air.

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Supporting Information Available

The Supporting Information is available free of charge at xxx. Information for GIWAXS, AFM, and FET characteristics of PDCBT thin films and a video of the fabrication process.

References

- (1) Xiao, M.; Ren, X.; Ji, K.; Chung, S.; Shi, X.; Han, J.; Yao, Z.; Tao, X.; Zelewski, S. J.; Nikolka, M.; others Achieving ideal transistor characteristics in conjugated polymer semiconductors. *Science Advances* **2023**, *9*, eadg8659.
- (2) Khim, D.; Luzio, A.; Bonacchini, G. E.; Pace, G.; Lee, M.-J.; Noh, Y.-Y.; Caironi, M. Uniaxial alignment of conjugated polymer films for high-performance organic field-effect transistors. *Advanced Materials* **2018**, *30*, 1705463.
- (3) Loganathan, K.; Scaccabarozzi, A. D.; Faber, H.; Ferrari, F.; Bizak, Z.; Yengel, E.; Naphade, D. R.; Gedda, M.; He, Q.; Solomeshch, O.; others 14 GHz Schottky Diodes Using ap-Doped Organic Polymer. *Advanced Materials* **2022**, *34*, 2108524.
- (4) Viola, F. A.; Brigante, B.; Colpani, P.; Dell ' Erba, G.; Mattoli, V.; Natali, D.; Caironi, M. A 13.56 MHz rectifier based on fully inkjet printed organic diodes. *Advanced Materials* **2020**, *32*, 2002329.

- (5) Hamidi-Sakr, A.; Biniek, L.; Bantignies, J.-L.; Maurin, D.; Herrmann, L.; Leclerc, N.; L  v  que, P.; Vijayakumar, V.; Zimmermann, N.; Brinkmann, M. A Versatile Method to Fabricate Highly In-Plane Aligned Conducting Polymer Films with Anisotropic Charge Transport and Thermoelectric Properties: The Key Role of Alkyl Side Chain Layers on the Doping Mechanism. *Advanced Functional Materials* **2017**, *27*, 1700173.
- (6) Patel, S. N.; Glaudell, A. M.; Peterson, K. A.; Thomas, E. M.; O ’ Hara, K. A.; Lim, E.; Chabiny, M. L. Morphology controls the thermoelectric power factor of a doped semi-conducting polymer. *Science Advances* **2017**, *3*, e1700434.
- (7) Biniek, L.; Leclerc, N.; Heiser, T.; Bechara, R.; Brinkmann, M. Large Scale Alignment and Charge Transport Anisotropy of pBTTT Films Oriented by High Temperature Rubbing. *Macromolecules* **2013**, *46*, 4014–4023.
- (8) Biniek, L.; Pouget, S.; Djurado, D.; Gonthier, E.; Tremel, K.; Kayunkid, N.; Zaborova, E.; Crespo-Monteiro, N.; Boyron, O.; Leclerc, N.; others High-temperature rubbing: a versatile method to align π -conjugated polymers without alignment substrate. *Macromolecules* **2014**, *47*, 3871–3879.
- (9) Shaw, L.; Hayoz, P.; Diao, Y.; Reinspach, J. A.; To, J. W. F.; Toney, M. F.; Weitz, R. T.; Bao, Z. Direct Uniaxial Alignment of a Donor–Acceptor Semiconducting Polymer Using Single-Step Solution Shearing. *ACS Applied Materials & Interfaces* **2016**, *8*, 9285–9296, PMID: 26985638.
- (10) Bucella, S. G.; Luzio, A.; Gann, E.; Thomsen, L.; McNeill, C. R.; Pace, G.; Perinot, A.; Chen, Z.; Facchetti, A.; Caironi, M. Macroscopic and high-throughput printing of aligned nanostructured polymer semiconductors for MHz large-area electronics. *Nature Communications* **2015**, *6*, 8394.
- (11) Khim, D.; Han, H.; Baeg, K.-J.; Kim, J.; Kwak, S.-W.; Kim, D.-Y.; Noh, Y.-Y. Simple

- bar-coating process for large-area, high-performance organic field-effect transistors and ambipolar complementary integrated circuits. *Advanced Materials* **2013**, *25*, 4302–4308.
- (12) Gu, X.; Shaw, L.; Gu, K.; Toney, M. F.; Bao, Z. The meniscus-guided deposition of semiconducting polymers. *Nature Communications* **2018**, *9*, 534.
- (13) Ito, M.; Yamashita, Y.; Tsuneda, Y.; Mori, T.; Takeya, J.; Watanabe, S.; Ariga, K. 100 ° C-Langmuir-Blodgett Method for Fabricating Highly Oriented, Ultrathin Films of Polymeric Semiconductors. *ACS Applied Materials & Interfaces* **2020**, *12*, 56522–56529.
- (14) Morita, T.; Singh, V.; Nagamatsu, S.; Oku, S.; Takashima, W.; Kaneto, K. Enhancement of Transport Characteristics in Poly(3-hexylthiophene) Films Deposited with Floating Film Transfer Method. *Applied Physics Express* **2009**, *2*, 111502.
- (15) Pandey, M.; Pandey, S. S.; Nagamatsu, S.; Hayase, S.; Takashima, W. Solvent driven performance in thin floating-films of PBTTT for organic field effect transistor: Role of macroscopic orientation. *Organic Electronics* **2017**, *43*, 240–246.
- (16) Jana, S.; Pandey, R. K.; Prakash, R. Evolution of Edge-On Oriented Polymer Films Self-Assembled at the Air-Liquid Interface for High-Performance Electronic Device Applications. *ACS Applied Polymer Materials* **2022**, *4*, 4818–4828.
- (17) Pandey, M.; Sugita, Y.; Toyoda, J.; Katao, S.; Abe, R.; Cho, Y.; Benten, H.; Nakamura, M. Unidirectionally Aligned Donor-Acceptor Semiconducting Polymers in Floating Films for High-Performance Unipolar n-Channel Organic Transistors. *Advanced Electronic Materials* **2023**, *9*, 2201043.
- (18) Sharma, S.; Vats, A. K.; Tang, L.; Kaishan, F.; Toyoda, J.; Nagamatsu, S.; Ando, Y.; Tamagawa, M.; Tanaka, H.; Pandey, M.; Pandey, S. S. High field-effect mobility in oriented thin films of D-A type semiconducting polymers by engineering stable interfacial system. *Chemical Engineering Journal* **2023**, *469*, 143932.

- (19) Yamashita, Y.; Hinkel, F.; Marszalek, T.; Zajackowski, W.; Pisula, W.; Baumgarten, M.; Matsui, H.; Müllen, K.; Takeya, J. Mobility Exceeding 10 cm²/(V·s) in Donor-Acceptor Polymer Transistors with Band-like Charge Transport. *Chemistry of Materials* **2016**, *28*, 420–424.
- (20) Ito, M.; Yamashita, Y.; Mori, T.; Ariga, K.; Takeya, J.; Watanabe, S. Band mobility exceeding 10 cm² V⁻¹ s⁻¹ assessed by field-effect and chemical double doping in semicrystalline polymeric semiconductors. *Applied Physics Letters* **2021**, *119*.
- (21) Zhang, S.; Koziol, K. K.; Kinloch, I. A.; Windle, A. H. Macroscopic fibers of well-aligned carbon nanotubes by wet spinning. *Small* **2008**, *4*, 1217–1222.
- (22) Jalili, R.; Razal, J. M.; Innis, P. C.; Wallace, G. G. One-step wet-spinning process of poly (3, 4-ethylenedioxythiophene): poly (styrenesulfonate) fibers and the origin of higher electrical conductivity. *Advanced Functional Materials* **2011**, *21*, 3363–3370.
- (23) Gantenbein, S.; Masania, K.; Woigk, W.; Sesseg, J. P.; Tervoort, T. A.; Studart, A. R. Three-dimensional printing of hierarchical liquid-crystal-polymer structures. *Nature* **2018**, *561*, 226–230.
- (24) Herbert, K. M.; Fowler, H. E.; McCracken, J. M.; Schlafmann, K. R.; Koch, J. A.; White, T. J. Synthesis and alignment of liquid crystalline elastomers. *Nature Reviews Materials* **2022**, *7*, 23–38.
- (25) Zhu, S.; Wang, S.; Huang, Y.; Tang, Q.; Fu, T.; Su, R.; Fan, C.; Xia, S.; Lee, P. S.; Lin, Y. Bioinspired structural hydrogels with highly ordered hierarchical orientations by flow-induced alignment of nanofibrils. *Nature Communications* **2024**, *15*, 118.
- (26) McCulloch, I.; Heeney, M.; Bailey, C.; Genevicius, K.; MacDonald, I.; Shkunov, M.; Sparrowe, D.; Tierney, S.; Wagner, R.; Zhang, W.; others Liquid-crystalline semiconducting polymers with high charge-carrier mobility. *Nature Materials* **2006**, *5*, 328–333.

- (27) Zhang, M.; Guo, X.; Ma, W.; Ade, H.; Hou, J. A Polythiophene Derivative with Superior Properties for Practical Application in Polymer Solar Cells. *Advanced Materials* **2014**, *26*, 5880–5885.
- (28) Wang, Q.; Li, M.; Zhang, X.; Qin, Y.; Wang, J.; Zhang, J.; Hou, J.; Janssen, R. A. J.; Geng, Y. Carboxylate-Substituted Polythiophenes for Efficient Fullerene-Free Polymer Solar Cells: The Effect of Chlorination on Their Properties. *Macromolecules* **2019**, *52*, 4464–4474.
- (29) Lee, Y. W.; Pak, K.; Park, S. Y.; An, N. G.; Lee, J.; Kim, J. Y.; Woo, H. Y. Regioisomeric Polythiophene Derivatives: Synthesis and Structure-Property Relationships for Organic Electronic Devices. *Macromolecular Research* **2020**, *28*, 772–781.
- (30) Wu, Y.-S.; Lin, Y.-C.; Hung, S.-Y.; Chen, C.-K.; Chiang, Y.-C.; Chueh, C.-C.; Chen, W.-C. Investigation of the Mobility-Stretchability Relationship of Ester-Substituted Polythiophene Derivatives. *Macromolecules* **2020**, *53*, 4968–4981.
- (31) Oliveira Jr, O. N.; Caseli, L.; Ariga, K. The past and the future of Langmuir and Langmuir–Blodgett films. *Chemical reviews* **2022**, *122*, 6459–6513.
- (32) Rivnay, J.; Noriega, R.; Kline, R. J.; Salleo, A.; Toney, M. F. Quantitative analysis of lattice disorder and crystallite size in organic semiconductor thin films. *Phys. Rev. B* **2011**, *84*, 045203.
- (33) Noriega, R.; Rivnay, J.; Vandewal, K.; Koch, F. P. V.; Stingelin, P.; Natalie adn Smith; Toney, M. F.; Salleo, A. A general relationship between disorder, aggregation and charge transport in conjugated polymers. *Nature Materials* **2013**, *12*, 1038–1044.
- (34) Ong, B. S.; Wu, Y.; Liu, P.; Gardner, S. High-Performance Semiconducting Polythiophenes for Organic Thin-Film Transistors. *Journal of the American Chemical Society* **2004**, *126*, 3378–3379, PMID: 15025437.

- (35) McCulloch, I. et al. Semiconducting Thienothiophene Copolymers: Design, Synthesis, Morphology, and Performance in Thin-Film Organic Transistors. *Advanced Materials* **2009**, *21*, 1091–1109.