Enhancing Carrier Mobilities in Organic Thin-Film Transistors Through Morphological Changes at the Semiconductor/Dielectric Interface Using Supercritical Carbon Dioxide Processing

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Supporting Information

ABSTRACT: Charge-carrier mobilities in poly(3-hexylthiophene) (P3HT) organic thin-film transistors (OTFTs) increase 5-fold when OTFTs composed of P3HT films on trichloro (1H, 1H, 2H, 2H-perfluorooctyl) silane (FTS) monolayers supported on SiO2 dielectric substrates (P3HT/FTS/SiO2/Si) are subjected to supercritical carbon dioxide (scCO2) processing. In contrast, carrier mobilities in P3HT/octadecyltrichlorosilane (OTS)/SiO2 OTFTs processed using scCO2 are comparable to mobilities measured in as-cast P3HT/OTS/SiO2/Si devices. Topographical images of the free and buried interfaces of P3HT films reveal that scCO2 selectively alters the P3HT morphology near the buried P3HT/FTS-SiO2 interface; identical processing has negligible effects at the P3HT/OTS-SiO2 interface. A combination of spectroscopic ellipsometry and grazing-incidence X-ray diffraction experiments indicate insignificant change in the orientation distribution of the intermolecular π−π stacking direction of P3HT/FTS with scCO2 processing. The improved mobilities are instead correlated with enhanced in-plane orientation of the conjugated chain backbone of P3HT after scCO2 annealing. These findings suggest a strong dependence of polymer processing on the nature of polymer/substrate interface and the important role of backbone orientation toward dictating charge transport of OTFTs.

KEYWORDS: conjugated polymer, scCO2 processing, ellipsometry, backbone orientation, self-assembled monolayers, organic thin film transistor, structure-transport relationship

1. INTRODUCTION

Conjugated polymers continue to be of interest for diverse applications ranging from xerography, light-emitting diodes, flexible electronics, and solar-energy conversion because of their mechanical flexibility, solution processability and the fact that molecular design strategies can be readily exploited to tailor their optical and electronic properties. Charge-carrier mobility, which influences device performance in organic light-emitting diodes (OLEDs), field-effect transistors (OFETs) and organic photovoltaics (OPVs), is sensitive to the thin-film morphology of conjugated polymers. A thorough understanding of the relationship between charge carrier mobility and thin-film morphology is critical for the field of organic electronics, as this information would be invaluable for improving device performance.

Poly(3-hexylthiophene) (P3HT) is one of the most commonly used conjugated polymers in organic electronics. The morphology of P3HT films is composed of crystallites, whose orientation and size vary relative to each other, and amorphous regions. The crystallites are composed of P3HT chains stacked in both the π−π and alkyl side-chain stacking directions, forming the so-called lamella structure. Charge transport in P3HT is highly anisotropic, as it is dictated by local chain conformation. Charge transport is most efficient along the polymer chain backbone, that is, along the (001) direction (intrachain transport), provided the backbone is free of distortions and defects. Interchain hopping in the π-stacking direction (010) is slower, and carrier hopping in the (100) direction along the alkyl side chains is the slowest. In OTFT devices, in which carriers move laterally, it is generally accepted that the best transport properties are achieved when the polymer chains are preferentially oriented in an edge-on orientation with a high degree of in-plane π-stacking as opposed to a face-on orientation. The highest carrier mobilities for devices comprised of P3HT are reported under these conditions, as well as for devices comprising many other high performance...
The work of adhesion, or interfacial tension, between the polymer and the substrate should influence the chain mobility at the charge transport interface and could result in different sensitivity of the polymer film toward processing. One approach to control the strength of the interactions between the polymer chains and substrate is by treating the dielectric surface with different self-assembled monolayers (SAMs). In this manuscript, we report a strategy to control and investigate the influence of the backbone orientation on the in-plane carrier mobility of P3HT devices using postdeposition supercritical carbon dioxide (scCO₂) processing on P3HT thin films atop two different SAM-treated silicon dioxide substrates: octadecyltrichlorosilane (OTS) and trichloro-(1H,1H,2H,2H-perfluorooctyl)silane (FTS). Compared to other processing methods, such as thermal annealing, solvent casting, solvent annealing or sequential solvent casting, scCO₂ processing has the advantages of being environmentally-friendly, abundant and nonflammable. Additionally, the solvent quality of scCO₂ can be finely tuned by changing temperature (35–70 °C) and pressure (7–20 MPa).

By variation of the scCO₂ solvent quality and treatment duration, P3HT films with different backbone orientation angles were achieved. The orientation angles were extracted from spectroscopic ellipsometry data using a theoretical model developed by Spano. Atomic force microscopy (AFM) images of the free and buried interfaces of P3HT films indicate that scCO₂ preferentially changes the polymer structure at the buried interfaces. The highest carrier mobilities were measured in devices comprised of films with the highest in-plane alignments, or smallest θ. As grazing-incidence X-ray diffraction measurements indicate minimal morphological changes in the depths of the films, our results suggest that the enhancement in carrier mobility originates from changes in backbone orientation at the dielectric interface.

2. EXPERIMENTS

2.1. Sample Preparation. All substrates were cleaned by ultrasonication in Alconox detergent solution, DI water, acetone, and boiling isopropanol for 5 min each; the substrates were subsequently exposed to UV–ozone cleaning for 20 min. The substrates were then transferred to a nitrogen glovebox, where self-assembled monolayers (SAM) of either octadecyltrichlorosilane (OTS) (Gelest Inc.) or trichloro-(1H,1H,2H,2H-perfluorooctyl)silane (FTS) were prepared. OTS was deposited by immersing the substrates in a mixture of OTS and hexadecane (1:250 by volume) for 14 h while stirring. FTS was deposited by placing the substrates inside a close vessel together with ca. 200 μL FTS and heating up to 150 °C for 2 h. Unlike OTS deposition, FTS deposition was carried out in the vapor phase. The chemical structures of OTS and FTS are shown in Figure S1.

Solutions of 4 mg/mL P3HT (Rieke Metal, 95% regioregularity, M₅ = 50,000 g mol⁻¹) were prepared by dissolving the polymer in chloroform and shaken overnight before filtering. The filtered solutions were then spun onto the OTS- or FTS-treated substrates at spin-speeds of 1000 rpm for 2 min. To deposit P3HT on FTS, the solution was allowed to sit on FTS for 20–30 s before spin-casting due to the low surface energy of FTS. The thicknesses of the as-cast P3HT films ranged from 30 to 35 nm, as measured by ellipsometry. All samples were stored in the glovebox until the devices were made and measurements were performed; exposure to the outside environment was minimized during transfer to a separate glovebox for OTFT measurements. All chemicals used in this study were purchased from Sigma-Aldrich unless otherwise noted.
2.2. Supercritical Carbon Dioxide (scCO2) Processing of Polymers. The solvent quality of supercritical CO2 can be easily tuned by varying temperature and pressure. In this study, two scCO2 processing conditions were chosen, as identified on the CO2 phase diagram in Figure S1. The first processing condition is at $T = 35^\circ$C and $P = 15$ MPa, which results in a high-density CO2 (0.8 g/mL). The second processing condition, which results in a low-density CO2 (0.45 g/mL), is at $T = 50^\circ$C and $P = 10.5$ MPa. The polymer films were first loaded into a stainless steel cell for scCO2 annealing. Prior to annealing, the cell was twice purged with CO2 (Cryogenic gases, purity 99.98%) to minimize the amount of air inside the cell. The entire cell was then immersed in a water bath, which had been preheated to the desired temperature using a heating circulator (Julabo Inc.). CO2 was then introduced into the cell using a manual pressure generator (High-Pressure Equipment Co.), with the pressure being monitored with a strain gauge pressure transducer (Sensotec). After annealing, the cell was immersed in an ice bath for slow depressurization, at a rate of approximately 1.5 MPa/min.

2.3. Carrier Mobility Measurements. OTFTs were fabricated in top-contact, bottom-gate configurations on highly doped Si substrates with a 300 nm thermally grown SiO2 layer (Encompass Inc.). Source and drain gold electrodes (Kurt J. Lesker, 99.999%) were vacuum-deposited on top of the polymer film to form transistors with a channel length and width of 50 and 500 μm, respectively. All OTFT measurements were performed in an oxygen-free and moisture-free N2-filled glovebox using the Agilent 4156C Parameter Analyzer. The mobility $\mu$ was extracted from the current measured at the drain ($I_{DS}$) by fitting the transfer curve in the saturation regime ($V_D = -80$ V) using the following equation:

$$I_{DS} = \frac{WC}{2L} \cdot \mu \cdot (V_D - V_T)^2$$

(1)

In this equation, $W$ and $L$ are the channel width and length, $C_i = 10$ nF/cm² is the capacitance per unit area for a 300 nm thick SiO2 layer, and $V_D$ and $V_T$ are the gate and threshold voltages, respectively.

2.4. Ellipsometry. Variable-angle spectroscopic ellipsometry (VASE) measurements were performed using the M-2000 Ellipsometer (J. A. Woollam Co.). The experiments were carried out on polymer films deposited using identical conditions onto two different Si substrates; one substrate with a thin layer of native oxide and the other with a layer of thermally grown SiO$_2$ that is 500 nm thick (Encompass Inc.). The measurements were performed in reflection mode at 55°, 60°, 65°, 70°, and 75°. The data were then fit simultaneously using the CompleteEASE software, provided by J. A. Woollam Co., in order to determine the thickness and optical constants of P3HT. To identify the best fit for P3HT optical constants, we “built” a model such that the sample’s structure was Si/SiO$_2$/SAM/P3HT. Before spin-coating the polymer layer, the SAM-modified substrates were measured to correctly determine the optical constants of both SAMs. The optical constants of P3HT in the Si/SiO$_2$/SAM/P3HT configuration were then determined by fitting two samples simultaneously, using the optical constants for the SAMs found in the previous step. The optical constants of the Si, native oxide and thermally grown SiO$_2$ were taken from CompleteEASE software’s library database. The multisample analysis was necessary to increase the uniqueness of the fits due to the strong correlations between the fitting parameters.

2.5. Grazing-Incidence X-ray Diffraction (GIXD). GIXD experiments were performed on the G1 line (9.95 ± 0.1 keV) at the Cornell High Energy Synchrotron Source. The beam was 0.05 mm tall and 1 mm wide. The X-ray beam was aligned such that it was above the critical angle of the polymer film, yet below the critical angle of the substrate. The scattered intensity was collected using a two-dimensional CCD detector, positioned 111.5 mm from the center of the sample. A background image collected from a 500 nm SiO$_2$ substrate has been subtracted from each image.

2.6. Atomic Force Microscopy (AFM). Surface topographies of the top and buried interfaces of P3HT films were measured using an Asylum Research MFP-3D stand-alone AFM in tapping mode with a CT300–25 Aspire probe (spring constant 40 N/m and radius of curvature of 8 nm). The buried interfaces were obtained by delaminating P3HT films from the SAM-treated SiO$_2$ substrates using a featureless poly(dimethylsiloxane) (PDMS) (Dow Corning Sylgard 184) layer. Details of the delamination technique are reported elsewhere.

3. RESULTS AND DISCUSSION

The in-plane hole mobilities of devices comprised of P3HT films spun on top of OTS and FTS are shown in Figure 2a as a function of high-density scCO2 annealing time. The transfer curves of all devices are available in the Figure S2. A clear difference between samples spun on top of OTS and FTS is observed. While the device mobilities of films cast atop OTS appear to be unaffected by scCO2 processing, mobilities for devices comprised of films cast on FTS increase with processing time, saturating after approximately 1 h. In addition to the increase in mobility for devices on FTS substrates, we observe a gradual shift of the threshold voltage toward positive values with increasing treatment time, as seen in Figure 2b. The shift in threshold voltage typically indicates a change in the interfacial dipoles or charge carriers/traps density at the dielectric/polymer interfaces. While the exact origin of the threshold voltage shift in our work is unclear, this observation suggests that scCO2 interacts and alters the structure of P3HT or FTS at the polymer/dielectric interface.

To definitively probe whether the improved mobilities originate from changes in the structure of P3HT or FTS or both, two sets of control experiments were performed. In the first set of experiments, we anneal the P3HT/FTS films in high-density scCO2 for 5 h. Afterward, we delaminate and transfer the annealed P3HT film onto OTS-treated Si/SiO$_2$ substrates. We also delaminate as-cast P3HT/FTS and transfer these films onto OTS-treated Si/SiO$_2$ substrates. Details of the transfer
However, because the $eV$ are normally used to calculate backbone orientation.

Upon annealing with high-density scCO$_2$ for 5 h, we observe enhanced absorption in the in-plane direction and reduced absorption in the out-of-plane direction, indicating that the polymer chains are more preferentially oriented parallel to the substrate after scCO$_2$ annealing. The polymer backbone orientation with respect to the substrate can be quantified using the dichroic ratio, $R$, defined by the ratio between the out-of-plane and in-plane oscillation strength at the position corresponding to the $\pi-\pi^*$ transition dipole moment.\textsuperscript{43,53} With respect to P3HT, the dichroic ratios at either $\pi$ or $\pi^*$ are normally used to calculate backbone orientation. However, because the 0–0 oscillation strength in P3HT is affected by intermolecular interactions,\textsuperscript{43} quantification with

$$A_{\text{aggregate}} \propto \sum_{m=0}^{\infty} \left( \frac{S_m}{m!} \right) \times \left( 1 - \frac{W e^{-S}}{2E_p} \sum_{n \neq m} \frac{S^n}{n!(n-m)} \right)^2 \times e^\left(\frac{E-E_0-WS e^{-S}}{2E_p}\right)/(2\pi^2)$$

In this equation, $A$ is the absorption of the aggregates as a function of photon energy, $E$; $S$ is the Huang--Rhys factor, representing the overlap between vibrational states and assumed to be 1; $m$ corresponds to different energy levels and $E_p = 0.179$ eV is the energy of C=C symmetric stretch mode. Here, the three fitting parameters are the exciton bandwidth, $W$, the transition energy, $E_0$, and the energetic disorder, $\sigma$ (or the Gaussian width of the absorption peaks). The fits for the aggregate region of each component using eq 1 are illustrated in Figure 3b–e. As seen in Figure 3b–e, the Spano model successfully reproduces the aggregate features in both the in-plane and out-of-plane absorption spectra before and after annealing. Moreover, because the amorphous spectra can be obtained from the absorption spectra, it is also possible to compute the average backbone orientation in the amorphous regions using a similar approach. We integrate the amorphous spectra in order to calculate the total oscillation strength of the transition in the amorphous region. The average backbone orientation angle $\theta$ within the aggregate and the amorphous regions were computed using the same approach previously reported.\textsuperscript{47,53}
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R\textsubscript{aggregate} = \frac{A\textsubscript{out-of-plane}}{A\textsubscript{in-plane}} = \frac{2\left(\sin^2 \theta\right)}{\left(\cos^2 \theta\right)} \quad (3a)

R\textsubscript{amorphous} = \frac{A\textsubscript{out-of-plane}}{A\textsubscript{in-plane}} = \frac{2\left(\sin^2 \theta\right)}{\left(\cos^2 \theta\right)} \quad (3b)

Here, and A\textsubscript{aggregate} and A\textsubscript{amorphous} are the areas of the aggregate and amorphous spectra, and \theta\textsubscript{aggregate} and \theta\textsubscript{amorphous} are ensemble-average backbone orientation angles in the aggregate and amorphous regions, respectively. Using the aforementioned approach, we calculate the backbone orientation angles of P3HT on top of FTS and OTS after processing with scCO\textsubscript{2}. Figure 4 shows the time evolution of both \theta\textsubscript{aggregate} and \theta\textsubscript{amorphous}.

\theta\textsubscript{amorphous} Under the influence of scCO\textsubscript{2} annealing, with the data at t = 0 corresponding to those extracted from the as-cast samples. We observe a higher orientation angle of polymer chains in the amorphous region compared with that in the aggregates, indicating that the average preferential orientation of the aggregates is more parallel to the substrate than that of the amorphous region. We note, however, that the orientation of the amorphous region is not completely random; a polymer chain oriented randomly within the film would have a value of \theta close to the isotropic angle \theta\textsubscript{isotropic} = 35.3°, corresponding to R = 1 and \theta = 1/3. The orientation angles for amorphous regions are within the range of 23°–25°, well below this isotropic angle, suggesting that even in the amorphous region, polymer chains still have a tendency to lie parallel to the substrates. This preferential orientation in the amorphous region could be due to confinement effects in thin film, in which the polymer chains are constrained by the air/polymer/polymer/substrate.\textsuperscript{50} Under the influence of scCO\textsubscript{2}, we see a similar decrease of \theta\textsubscript{amorphous} within 30 min in P3HT that had been deposited on both OTS and FTS cases. The fast response of the amorphous region is not surprising, because scCO\textsubscript{2} can penetrate and swell the amorphous regions more easily compared to their aggregate counterpart due to their lower density. The aggregate regions, on the other hand, respond slower and characteristically differently to scCO\textsubscript{2} annealing when P3HT is deposited on OTS and FTS. Figure 4 shows that when scCO\textsubscript{2} processing reduces \theta\textsubscript{aggregate} for films spun on FTS after 2 h, it has almost no effect on \theta\textsubscript{aggregate} for films spun on OTS.

To illustrate the importance of the polymer backbone orientation, Figure 5 shows the relationship between the device mobility and the polymer backbone orientation angle. We note that on a given substrate, the mobilities and orientation angles are identical after processing with either high- or low-density scCO\textsubscript{2}. We found that the hole mobilities increase with decreasing \theta\textsubscript{aggregate} or with the tendency of the aggregate domains to lie parallel to the substrates. We note that the significant changes in the in-plane transport characteristics are accompanied by only subtle changes in morphology probed by ellipsometry. A mere decrease of 3° in the average backbone orientation angle results in a 5-fold improvement in carrier mobility. In light of these observations, along with the observed threshold voltage shift shown Figure 2b, we hypothesize that the changes might occur strictly at the P3HT/SAM interface. In order to confirm our hypothesis, we further investigate the film morphology using GIXD and AFM.

To investigate any changes in the bulk morphology of the films, we employed GIXD measurements on the neat P3HT films and those treated with high-density scCO\textsubscript{2} fluid for 5 h. The two-dimensional GIXD patterns are shown in Figure 6a–d. Figure 6e and f shows line cuts of the two-dimensional GIXD patterns taken at q_{xy} = 0 and q_z = 0, respectively, representing one-dimensional X-ray traces in the out-of-plane and in-plane directions. The traces reveal the (100) and (010) reflections at 0.40 and 1.7 Å^{-1} respectively, consistent with a prior report on P3HT.\textsuperscript{12} For films deposited atop either OTS-treated or FTS-treated SiO\textsubscript{2}, the GIXD patterns show the (100) and (010) reflections along both the meridian and the equator. That the (100) and (010) reflections are present in both the in-plane and out-of-plane traces indicates that there are at least two populations of P3HT crystallites adopting either edge-on or face-on orientations, in good agreement with previous reports on P3HT films spun from volatile solvents.\textsuperscript{35} To further investigate the effect of scCO\textsubscript{2} processing on the structure of the P3HT films deposited atop OTS and FTS substrates, Figure 6g shows the intensity distribution of the (010) reflection as a function of the azimuthal angle. The azimuthal dependence of the (010) reflection is invariant across samples, indicating that the orientation of P3HT crystallites remain unchanged after postdeposition scCO\textsubscript{2} processing. These results suggest that bulk morphological changes cannot account

Figure 4. Evolution of the orientation angle \theta in the aggregate and amorphous regions under the influence of scCO\textsubscript{2} fluid. The films are prepared using high density CO\textsubscript{2} on top of FTS (a) and OTS (b). Data at t = 0 corresponding to as-cast samples.

Figure 5. In-plane hole mobilities as a function of orientation angle for all cases studied in this work.
for the observed increase in mobility for devices atop FTS-treated SiO2/Si with increased scCO2 annealing time.

As the increase in mobility with scCO2 processing does not stem from the bulk morphology, we performed atomic force microscopy (AFM) on both the polymer/air interface and the buried interface of P3HT films on OTS and FTS before and after scCO2 annealing. The AFM images in Figure 7 demonstrate that under all processing conditions and independent of dielectric surface treatment, the P3HT/air interface is featureless with no discernible differences. In sharp contrast, the buried interface of as-cast P3HT reveals distinct wrinkle structures with slightly larger features on FTS than on OTS. Upon annealing, these features are still present in films on OTS but vanish entirely for films on FTS. We note that the roughness of all surfaces here is less than 1 nm, suggesting that the observed wrinkles are not deformation or cracks induced by the delamination process.

Our AFM results unambiguously indicate that scCO2 annealing selectively alters the morphology of P3HT near the SAM/P3HT interface. The morphological changes in P3HT films on FTS are more significant than films on OTS, in good agreement with the ellipsometry measurements. A schematic of the film structure before and after scCO2 annealing is illustrated in Figure 8, in which most of the changes in morphology happen close to the buried interfaces.

The reasons for the larger morphological changes at the buried interface compared to the top interface could be understood from the following. When a film is cast onto a substrate, the chains at the polymer/substrate interface experience larger configurational entropy changes and thus

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**Figure 6.** (a–d) Grazing-incidence X-ray diffraction (GIXD) patterns of as-cast and scCO2 annealed samples spun on top of OTS and FTS. (e, f) Intensity traces of the 4 samples along the out-of-plane direction (qz) and in-plane direction (qxy). (g) Normalized angular distribution of (010) reflections.

**Figure 7.** 10 ×10 μm AFM images of P3HT’s top and buried interfaces, before and after scCO2 annealing. The scale bar is 2 μm.
higher state of stress than chains at the free surface. This hypothesis is corroborated by the observed wrinkle structure at the buried interface but rather smooth feature at the top surface. The presence of the scCO₂ solvent at the buried interface would lead to structural reorganization to relax the stresses. Hence it is unsurprising that the morphological structure would show larger changes at the polymer/substrate interface than the free surface, despite the fact that the scCO₂ concentration near the free surface might be higher than at the bottom interface. We note that for an unstable/metastable film, dewetting instabilities would generally be responsible for larger structural changes, typically evident at the free surface. The P3HT films examined here are however structurally stable.

On the other hand, the apparent difference in behavior of P3HT on top of OTS and FTS could stem from multiple reasons. First, because the interaction of any material with scCO₂ depends markedly on its chemical structure, we expect that using SAMs with different affinities toward scCO₂ would result in different interactions and hence different polymer morphologies. The specific interaction between scCO₂ and the dipoles of the C–F bond lead to an increased swelling and solubility of scCO₂ in fluorine-containing polymers, which is well-documented in the literature. Notably, due to their amphiphilicity in scCO₂, fluorine-containing copolymers have been widely used in dispersion polymerization using scCO₂ as reaction medium. We hypothesize that in the presence of scCO₂, FTS swells more than OTS, resulting in the P3HT/FTS interface being more scCO₂-rich than the P3HT/OTS interface and thus enhancing scCO₂–P3HT interactions at the buried interface as illustrated in Figure 8b and d. Second, fluorooalkyl compounds, such as FTS, are known to have lower surface energy than OTS because of the high electronegativity of fluorine. The lower surface energy of FTS would increase the segmental mobility of polymer chains near the substrate, making the polymer chains on FTS more prone to processing compared to those on OTS. As a result, a larger morphological change after scCO₂ annealing is observed in samples using FTS than samples using OTS.

We have shown that charge transport strongly correlates with the polymer backbone orientation angle in aggregate domains. In a semicrystalline film, the reduced conjugation lengths and increased band gaps of the amorphous regions are responsible for reduced carrier mobilities and thus confine transport within the aggregate regions. It is suggested that the carriers only move across the amorphous regions from aggregate to aggregate via single polymer chains known as tie-molecules. The orientation and molecular order within the aggregates therefore should influence charge transport. If the polymer chains within the aggregates have a low degree of in-plane alignment, a carrier would undergo interchain hopping in order to continue traveling laterally, resulting in lower mobilities. Carrier mobilities are significantly different for films cast on OTS and FTS, implicating the role of the backbone orientation.

Finally, we would like to point out that there exists other convincing evidence that this morphological factor is vital for carrier transport. The role of backbone orientation has been demonstrated by our previous work to be the main morphological factor affecting out-of-plane transport of the low band gap polymer poly[2,5-bis(2-ethylhexyl)-oxy] benzo-[1,2-b:4,5-b’]dithiophene-2,6-diy-alt-4-(2-ethylhexan-1-one)-thieno[3,4-b’]-thiophene-2,6-diy] (PBDTTT-C). Also, the degree of in-plane alignment of some high performing polymers used in OTFTs is shown to be exceptionally high, including poly[2,5-bis(3-tetracetylthiophen-2-yl)thieno[3,2-b’]-thiophene] (PBTTT) and some high mobility diketopyrrolopyrrole (DPP) copolymers, all exhibiting orientation angle \( \theta < 10^\circ \), in good agreement with our findings here.

4. CONCLUSION

In conclusion, we investigated the effect of scCO₂ processing on the structure and charge transport in P3HT films supported by two SAMs having different chemical structures and surface energies. The carrier mobilities increased 5-fold in the P3HT/FTS/SiO₂ OTFTs after processing in scCO₂, while the carrier mobility of P3HT/OTS/SiO₂ OTFTs remained unchanged. ScCO₂ has a strong affinity with the C–F bonds, providing enhanced mobility to the P3HT chains at the substrate. The changes in the topography at the buried interface are consistent with the predicted enhanced solubility of polymer chains in scCO₂ in that region. While no noticeable effects on the structure of P3HT/OTS films were observed, the in-plane alignment of the conjugated polymer backbone in the P3HT/FTS films improved as a result of scCO₂ processing. A close relationship between in-plane hole mobilities and backbone orientation in P3HT was measured; the highest mobilities were measured in devices comprised of films with the highest in-plane alignments, or smallest \( \theta \). Our data suggest that possessing polymer backbone orientation more parallel to the substrate is favorable for lateral charge transport. Our work suggests an effective way to control the morphology of conjugated polymers at the semiconductor/substrate interface. Further enhancement of carrier mobilities via this benign
processing method is also expected for other conjugated polymer systems, such as fluorine-containing polymers, which are known to have a strong affinity toward scCO\textsubscript{2} annealing.

### ASSOCIATED CONTENT

#### Supporting Information

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Phase diagram of CO\textsubscript{2} and the chemical structure of OTS and FTS, raw transfer characteristic curves of devices fabricated on top of FTS, OTS, annealing with high and low CO\textsubscript{2} density, and film transfer procedures and the transfer curve of the devices in the control experiments (PDF)

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#### Notes

The authors declare no competing financial interest.

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