A Facile Approach to Improve Interchain Packing Order and Charge Mobilities by Self-Assembly of Conjugated Polymers on Water

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The past decades have witnessed the significant progresses in the development of organic and polymeric semiconductors with high charge mobilities.[1–4] Various conjugated molecules and polymers have been investigated intensively.[5–11] These studies reveal that intermolecular/interchain packing and thin film crystallinity play a vital role in determining the charge transporting properties.[12,13] The most distinct advantage for polymeric semiconductors (conjugated polymers) is the solution processability. However, thin films of conjugated polymers are conventionally processed with spin-coated technique and exhibit low crystallinities even after post-treatments such as thermal annealing.[14] Such thin films usually contain crystalline and amorphous domains.[15] A few polymers such as poly(4,4,9,9-tetradecyl-4,9-dihydro-s,2,7-indaceno[1,2-b:5,6-b’]dithiophene-benzothiadiazole) (IDTBT)[16] and Poly[N-(9’-heptadecanyl)2,7-carbazole-alt-5,5-(4’′,7’′-di-2-thienyl-2′′,1′′,3′′-benzothiadiazole)] (PCDTBT)[15] with low crystallinity were reported to exhibit relatively high charge mobilities, which is attributed to the low energetic disorder of the polymeric backbones.[15] However, more studies also manifest that thin films of conjugated polymers with more ordered structures show better charge transporting performances.[7,8,17] Several approaches have been devised to improve the crystallinities of conjugated polymer chains and thus boost the charge mobilities by using zone casting,[17] solution shearing,[18] nanogrooved substrates,[19] and capillary forces.[3] Some of us have recently reported an efficient approach to improve the interchain packing order and thus enhance charge mobilities for conjugated D

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(donor)–A (acceptor) polymers by incorporation of tiny amounts of ionic additive in the thin films. It needs to point out that additional instruments or procedures are required for all these approaches.

Herein, we report a facile and effective approach to improve interchain packing order, thin film crystallinities and charge mobilities for conjugated polymers by solvent evaporation induced self-assembly of conjugated polymers on water, which is referred as to AOW. This AOW approach can be easily operated by dropping the conjugated polymer solution onto the water surface, and the resulting thin films can be transferred to solid substrates easily. The resulting thin films of conjugated polymers show ordered structures and improved thin film crystallinities, in comparison with those prepared with spin-coating, drop-casting, and Langmuir–Schaefer methods. Notably, thin film charge mobilities of conjugated polymers through AOW approach are boosted remarkably by comparing with the respective spin-coated, drop-casted, and Langmuir–Schaefer thin films. Moreover, this new approach can be utilized to easily fabricate the array of field-effect transistors (FETs) with high charge mobilities in an economic way.

The AOW method is illustrated in Figure 1. A solution of the polymer with low concentration (0.1 mg mL\(^{-1}\)) was dropped onto the water, followed by transferring the assembly film to the substrate after evaporation of solvents (for details, see the Experimental Section). Thin films prepared with this facile approach were used for structural characterization and fabrication of FETs. We have employed this AOW approach to prepare thin films of six typical conjugated semiconducting polymers (see Figures 2 and 3) in order to improve their thin film crystallinities and charge mobilities.

First, we demonstrated the easiness and effectiveness of AOW approach with PDPP4T (Figure 2). 50 µL of PDPP4T solution was dropped on water surface at room temperature (25 °C). After about 3.0 min, thin film was formed (see Video S1 in Supporting Information) and easily transferred to solid substrates including glass, SiO\(_2\)/Si, and OTS (octadecyltrichlorosilane)-modified SiO\(_2\)/Si for characterizations. The thin film obtained with this AOW approach was characterized with polarized optical microscopy (POM) and atomic force microscopy (AFM). As shown in Figure 2b, bright stripes from POM images were observed initially for the AOW thin film of PDPP4T under crosspole conditions. By rotating the sample for 45°, parts of stripes became dark, but scattering bright spots were still observable. Bright stripes were detected again by further rotating the sample for 45° as shown in Figure 2b. Such variation of POM images implies that the stripes within the AOW thin film of PDPP4T are composed of crystalline domains, but they are not completely aligned. Based on the AFM image, the AOW thin film of PDPP4T contains regularly arranged stripes and grooves (Figure 2c). The average width and height of each stripe are around 5 µm and 50 nm, respectively, while the average height of each groove is about 5 nm. Such hierarchically organized structure hints the ordered arrangement of polymer chains within thin film of PDPP4T through the self-assembly on water. In comparison, such well-arranged stripes were not detected from the AFM image (Figure 2c) for the corresponding spin-coated thin film of PDPP4T.

Figure 2d shows the 2D grazing-incidence wide-angle X-ray scattering (GIWAXS) pattern for thin film of PDPP4T prepared with the AOW method and that with spin-coated method for comparison. Thin film of PDPP4T assembled on water shows scattering signals at \(q_y\) direction (out-of-plane) up to fourth order at \(q_y = 0.32, 0.63, 0.95, \text{ and } 1.26 \text{ Å}^{-1}\), due to the lamellar stacking of alkyl chains with a \(d\)-spacing of 19.4 Å. An additional weak and broad signal appears at \(q_y = 1.69 \text{ Å}^{-1}\), which is attributed to the interchain \(\pi\)–\(\pi\) stacking with a distance of 3.7 Å. At \(q_y\) direction (in-plane) a strong scattering signal emerges at \(q_y = 1.66 \text{ Å}^{-1}\), corresponding to a \(\pi\)–\(\pi\) stacking distance of 3.8 Å, which is shorter than that of (3.9 Å) for the spin-coated thin film of PDPP4T. Additionally, a sharp scattering signal at \(q_y = 0.31 \text{ Å}^{-1}\) appears for the AOW thin film at \(q_y\) direction, which is not observable for the spin-coated thin film of PDPP4T. Moreover, the scattering signals of the thin film assembled on water become sharper. For instance, as shown in Table S1 in the Supporting Information, the full width at half maximum for the signal at \(q_y = 0.32 \text{ Å}^{-1}\) of (100) is 0.037 Å\(^{-1}\) for the thin film assembled on water, which is smaller than that of the respective scattering signal (0.060 Å\(^{-1}\)) for the spin-coated thin film. On the basis of these GIWAXS data, it can be concluded that polymer chains of PDPP4T are more orderly packed and thin film crystallinity is significantly improved by using the AOW method.

Encouraged by this discovery, we extended this facile approach to other...
semiconducting polymers including conjugated D–A polymers such as poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl)thieno[3,2-b]thiophene)] (PDPPTT), poly[N,N’-(2-octyldecanoyl)-isoindigo-alt-thieno[3,2-b]thiophene] (PIIDTT), IDTBT, and poly[4,8-bis(5-(2-ethylhexyl)thieno-2-yl)benzo-[1,2-b:4,5-b’][dithiophene-2,6-diyl]-alt-(2-(2-ethylhexanoyl)-thieno[3,4-b][thiophen-4,6-diyl])] (PBDTTT-C-T) as well as poly[3-hexylthiophene-2,5-diyl] (P3HT) (Figure 3). Figures S1–S3 in the Supporting Information show AFM and GIWAXS patterns for thin films of PDPPTT, PIIDTT, and P3HT, which were fabricated with AOW method. As detailed in the Supporting Information, polymer chains of PDPPTT, PIIDTT, and P3HT are packed to form more ordered structures on substrates by using the AOW method. In comparison with the respective spin-coated thin films, thin films of PDPPTT, PIIDTT, and P3HT prepared with the AOW method display improved crystallinity based on the GIWAXS data (Figures S1–S3 and Table S1, Supporting Information); Sharper scattering signals up to fourth and even fifth order (owing to the lamellar stacking of alkyl chains) and noticeable signals owing to the interchain π–π stacking were observed for these thin films with AOW method. For instance, both (300) and (400) scattering signals at $q_z$ direction of the AOW thin film of PDPPTT become less dispersive than the respective ones of the spin-coated thin film of PDPPTT on the basis of 2D GIWAXS patterns shown in Figure S1c in the Supporting Information. For PIIDTT, the (500) signal at $q_z$ direction due to the lamellar stacking of alkyl chains was observed for the AOW thin film, whereas it was not detected for the spin-coated one. Moreover, polymer chains of PDPPTT, PIIDTT, and P3HT are predominantly arranged in the edge-on mode on the substrate with the AOW method. In comparison, both face-on and edge-on packing modes coexist within the spin-coated thin films of PDPPTT and PIIDTT, and polymeric chains of P3HT are packed dominantly with the face-on mode for the spin-coated thin film.

We also investigated conjugated polymers PBDTTT-C-T and IDTBT with the AOW approach. As shown in Figures S4 and S5 in the Supporting Information, thin films of PBDTTT-C-T and IDTBT show only broad and weak scattering signals and thus they are almost amorphous, being similar to the respective spin-coated thin films. Therefore, this AOW approach cannot improve thin film crystallinitities for PBDTTT-C-T and IDTBT.
whose spin-coated thin films are also amorphous. This may be due to their low crystallinity natures as reported before.\cite{15,16} These results demonstrate that this AOW approach is effective for conjugated polymers which exhibit tendency to form crystalline thin films, while this approach is not applicable for these conjugated polymers which are less inclined to assemble into ordered structures.

The formation of ordered structures through AOW method is attributed to “stick-and-slip”\cite{20} motion induced by solvent evaporation at contact line of solution droplet. As an example, the self-assembly process of PDPP4T on water was investigated with optical microscopy. As shown in Figure 4a and the Video S1 in Supporting Information, in which the pink and green areas represent water and polymer solute, respectively, the evaporation of solvents led to the repeated “stick-and-slip” motion of contact line. As a result, green stripes owing to the pinning of polymer assemblies were gradually formed. The formation of such green stripes is likely caused by coffee-ring effect as schematically illustrated in Figure 4b. Moreover, the hydrophobic nature of these polymers forces the polymer chains to pack densely with edge-on mode in order to minimize the contact of polymer chains with water. This agrees well with the observation that polymer chains of PDPP4T, PDPPTT, and PIDTT adopt predominant edge-on mode on the basis of 2D GIWAXS data.

The solvent evaporation process affects the formation of ordered structures for conjugated polymers with AOW method. Among the solvents which can dissolve PDPP4T, chloroform is the best solvent for the formation of ordered AOW thin film. For example, thin film with stripe-like structures was not formed on the basis of the AFM image (see Figure S6, Supporting Information) when the polymer solution was prepared with chlorobenzene which owns lower volatility than chloroform. We also prepared AOW thin films of PDPP4T at

![Figure 4](image-url)

**Figure 4.** a) Microscopic observation of PDPP4T during the formation process of stripes on water surface. The pink areas represent water surfaces, while the dark-green areas represent polymer (PDPP4T) solution droplets, and pale green annular stripes of polymer assemblies are formed on pink region. b) Schematic illustration of coffee ring effect induced assembly of polymer on water. c) Hole mobilities of thin films of investigated polymers prepared with AOW and spin-coated approaches. All data were based on statistics of at least 50 BGBC FET devices with $W = 1400 \mu m$, $L = 50 \mu m$. The mobilities of PDPP4T, PDPPTT, and PIDTT were extracted at low $V_C$ region. d) Hole mobility distribution for $8 \times 12$ FETs array fabricated with AOW method.
0 and 31 °C (besides 25 °C) by using chloroform as the solvent. In both cases thin films with regularly arranged stripes were obtained as shown in Figure S7 in the Supporting Information in which AFM images of these two thin films are displayed. This indicates the effect of temperature on the formation of AOW thin films with ordered structures is weak in the temperature range of 0–31 °C because of the relatively high volatility of chloroform.

It was reported that such "stick-and-slip" motion of contact line led to the assembly of nonconjugated polymers into ordered structures on solid substrate (not on water surface). Notably, the solvent-evaporation induced self-assembly with AOW approach occurs on water surface, being different from previous reports in which the assembly of organic and polymeric semiconductors into ordered structures was conducted on solid substrates in confined geometries. The assembly of a few small conjugated molecules on water to form crystalline thin films with high charge mobilities has been recently reported. In fact, we employed spin-coated and drop-cast methods to prepare thin films of PDPP4T on plasma treated SiO2/Si substrate which shows lower contact angle (35.7°) and thus higher surface energy than OTS-modified SiO2/Si substrate with a contact angle of 83.8° (Figure S8a, Supporting Information). Figure S8b in the Supporting Information displays the AFM images of these thin films. Clearly, these thin films exhibit no stripe-like structures. This result manifests that self-assembly of conjugated polymers on water surface is important to form semiconducting thin films with ordered structures by using AOW method.

The AOW thin film of PDPP4T was also transferred onto plasma treated SiO2/Si substrate which shows higher surface energy than OTS-modified SiO2/Si substrate. As shown in Figure S8 in the Supporting Information, stripe-like structure was retained and was not obviously influenced by the surface energy feature of substrates. Moreover, the possibility of further assembly of polymer chains on the substrate owing to water evaporation can be ruled out because morphologies of thin films of PDPP4T were almost the same although they were prepared in different humidities ranging from 28% to 90% relative humidity (RH).

Based on the fact that thin films of PDPP4T, PDPPPTT, PIIDTT, and P3HT prepared with the AOW approach show improved crystallinities as discussed above, these thin films are expected to exhibit high charge mobilities. Thin film charge mobilities were extracted on the basis of the semiconducting performances of the respective bottom gate/bottom contact (BGBC) FETs. As an example, Figure S11a,A in the Supporting Information shows the transfer and output curves of the FETs with thin films of PDPP4T through AOW approach and spin-coated method, respectively. Obviously, the on-state current (I on) ≈7.68 × 10−4 A at VGSS = −40 V, VDS = −100 V for the FET with the AOW thin film is much higher than that (≈1.14 × 10−4 A) for the spin-coated thin film. We note that the transfer characteristics are not ideal, which is probably due to contact issues in BGBC FET devices. In fact, such nonideal transfer characteristics was observed for FETs with conjugated D–A polymers. The hole charge mobilities were extracted by fitting the respective plots of IDSS/VG versus VG at both low VG and high VG regions as shown in Figure S11 in the Supporting Information. As listed in Table 1, the average (μf) and maxima saturated mobilities (μmax) are 8.15 and 11.66 cm2 V−1 s−1 at low VG region, respectively, for the as-prepared AOW thin film of PDPP4T. In comparison, the respective μf and μmax are just 0.8 and 1.05 cm2 V−1 s−1 for the spin-coated thin film of PDPP4T without thermal treatment. The average charge mobilities by fitting at high VG region are 2.01 and 0.22 cm2 V−1 s−1 for the AOW and the spin-coated thin films of PDPP4T, respectively (see μf in Table 1). Moreover, the AOW thin film of PDPP4T also exhibits higher linear mobility (2.01 cm2 V−1 s−1) than the spin-coated thin film (0.27 cm2 V−1 s−1) as listed in Table 1. These data clearly indicate that thin film charge mobility can be dramatically boosted for PDPP4T by employing the AOW method without additional post-treatments such as thermal annealing (Figure 4c). We also compared the FET mobilities of PDPP4T thin films fabricated by using AOW and spin-coated methods after thermal annealing. As shown in Table S2 in the Supporting Information, the average mobility (by fitting at low VG region) of the AOW thin film of PDPP4T was boosted to 9.97 cm2 V−1 s−1 after thermal annealing at 120 °C. Under the same annealing condition, the average mobility of the spin-coated thin film of PDPP4T was enhanced only to 2.66 cm2 V−1 s−1. Additionally, it was noted that the on–off current ratio (Ion/Ioff), threshold voltage (Vth) for the AOW thin film of PDPP4T are comparable to those of the spin-coated thin film (see Table 1).

The following control experiments by using drop-casting and Langmuir–Schaefer methods further demonstrate the advantage of AOW approach. We dropped the solution of PDPP4T with a concentration of 0.1 mg mL−1 onto the OTS/SiO2/Si substrate, and the resulting thin film after drying shows poor charge-transporting performance with the maxima and average mobilities of 0.24 and 0.15 cm2 V−1 s−1, which were measured under the same conditions as for the thin film of PDPP4T fabricated with AOW approach. This agrees well with the observation that the drop-casting thin film shows no stripe-like structure (see the AFM image in Figure S9a, Supporting Information). In fact, this thin film contains random aggregates of different sizes. This is also confirmed by the GIXWS result (Figure S9b, Supporting Information), which showed low crystallinity compared to that by using AOW method. Thus, the evaporation-driven self-assembly of polymer chains on water is vital for the formation of ordered structure with high crystallinity for PDPP4T. Alternatively, thin films of PDPP4T were also prepared with Langmuir–Schaefer technique at air–water interface at different surface pressures according to the surface pressure (σ) versus mean monomeric area isotherm (Figure S10a, Supporting Information). The resulting thin films show poor morphology and low crystallinity based on their AFM images and GIXWS results (see Figure S10b,c, Supporting Information) with low charge mobilities. For instance, the average hole mobility for the thin film prepared at 40 mN m−1 was measured to 0.003/0.0049 cm2 V−1 s−1, being much lower than that of the AOW thin film.

Such mobility enhancement also holds true for PDPPTT, PIIDTT, and P3HT by using the AOW approach (see Figure 4c and Figure S11, Supporting Information, and Table 1). The transfer and output curves of FETs with both AOW and spin-coated thin films of PDPPTT, PIIDTT, and P3HT are
shown in Figure S11 in the Supporting Information. For PDPPTT, the average and maxima saturated mobilities are incremented from 1.79 and 2.41 cm² V⁻¹ s⁻¹ for the spin-coated thin film to 5.40 and 5.73 cm² V⁻¹ s⁻¹ (extracted at low V_G region), respectively, with the AOW approach. The linear charge mobility (μ_Lin) also increases from 0.31 cm² V⁻¹ s⁻¹ to 1.03 cm² V⁻¹ s⁻¹ by employing the AOW approach (see Table 1). Both saturated and linear mobilities are enhanced by approximately three times for PDPPTT by using the AOW approach. Similarly, charge mobilities can reach 7.09 and 1.50×10⁻² cm² V⁻¹ s⁻¹, being approximately seven and ten times of the respective spin-coated thin films, for PIIDTT and P3HT by using the AOW approach, whereas the on/off current ratio (I_on/I_off), threshold voltage (V_TH) are not affected (see Table 1).

As reported early, the transfer characteristics of FETs with thin films of PDPP4T and PIIDTT is nonideal (see Figures S11, Supporting Information). Their charge mobilities were extracted by fitting the respective plots of I_D vs. V_G at both low V_G and high V_G regions. As listed in Table 1, the average charge mobilities (extracted at high V_G region) of AOW thin films of PDPPTT and PIIDTT are higher than those of the respective spin-coated thin films.

For IDTBT, both the saturated (1.02 cm² V⁻¹ s⁻¹) and linear (0.54 cm² V⁻¹ s⁻¹) charge mobilities for the AOW thin film are comparable to those of the spin-coated thin film, while charge mobilities for PBDTTT-C-T are reduced by employing the AOW approach. This is indeed in agreement with the fact that thin film crystallinity is not improved for IDTBT and PBDTTT-C-T by using AOW approach as discussed above.

This facile AOW approach can be utilized to easily fabricate the array of FETs in an economic way. As an example, 50 μL (0.1 mg mL⁻¹) of PDPP4T was dropped onto the water surface and the resulting thin film was transferred onto the OTS-modified Si/SiO₂ substrate on which the 8×12 array of source/drain Au electrodes were deposited. As a result, the 8×12 array of BGC FETs was fabricated. Figure 4d shows the distribution of hole mobilities of the 96 FETs. The average mobility is 6.78 cm² V⁻¹ s⁻¹ (extracted at low V_G region) and 81% of the devices exhibit mobilities higher than 3.0 cm² V⁻¹ s⁻¹. It is noted that =20 μL of the polymer solution (5.0 mg mL⁻¹) is needed usually to fabricate 8×12 array of FETs with the spin-coated technique. Therefore, this AOW approach is not only simple and facile but also economic for the fabrication of arrays of FETs, which are potentially useful for organic circuits.

In addition, FETs with AOW approach show relatively good operational stabilities. As shown in Figure 5la in the Supporting Information, the on and off currents of the FET with the assembly-on-water thin film of PDPP4T kept nearly constant by switching gate voltage between 0 and −30 V for over 700 cycles. We also did the double-sweep measurements for the transfer and output curves of FETs with AOW thin films of six polymers. As shown in Figure S13 in the Supporting Information, both transfer and output curves exhibit rather small hysteresis. The possible water residues in the AOW thin films, which may affect the device stability, can be easily removed by either blowing the thin films with dry N₂ or treating them under vacuum. Moreover, the semiconducting performance of

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### Table 1. Hole mobilities (saturated mobilities, maxima saturated mobilities, linear mobilities, and maxima linear mobilities), On currents, I_on/I_off ratios, threshold voltages, subthreshold slopes of BGBC FETs with thin films of PDPP4T, PDPPTT, PIIDTT, P3HT, PBDTTT-C-T, and IDTBT prepared with AOW, and spin-coated approaches.

| Polymer | Processing method | μ_Lin | μ_Lin | μ_Sat | μ_Sat | μ_Lin | μ_Lin | I_on | I_on | I_off | I_off | V_TH | Subthreshold Slopes |
|---------|-------------------|-------|-------|-------|-------|-------|-------|------|------|-------|-------|------|-------------------|
| PDPP4T  | Spin-coating      | 0.80  | 0.22  | 0.27  | 0.33  | 1.14  | 6    | 6–7  | 1    | 2.6–2.8 |
| AOW     | Spin-coating      | 8.15  | 2.01  | 2.01  | 2.71  | 7.68  | 6–7  | −1  | −1  | 1.1–1.3 |
| PDPPTT  | Spin-coating      | 1.79  | 0.18  | 0.31  | 0.45  | 1.05  | 6–7  | 6–7  | 6–7  | 2.3–2.4 |
| AOW     | Spin-coating      | 5.40  | 1.59  | 1.03  | 1.15  | 9.05  | 6–6  | 0   | 0   | 1.9–2.1 |
| PIIDTT  | Spin-coating      | 0.84  | 0.11  | 0.17  | 0.21  | 4.81  | 7–8  | 1    | 2.0–2.3 |
| AOW     | Spin-coating      | 6.28  | 2.30  | 1.52  | 1.97  | 1.03  | 7–8  | 0   | 1.1–1.2 |
| P3HT    | Spin-coating      | 7.3   | 2.9   | 3.2   | 1.58  | 10   | 3–4  | 0   | 8.1–9.1 |
| AOW     | Spin-coating      | 8.9   | 4.1   | 4.2   | 1.45  | 10   | 3–4  | 3   | 7.5–8.4 |
| IDTBT   | Spin-coating      | 1.16  | 0.60  | 0.64  | 2.07  | 10   | 6    | 0   | 1.1–1.3 |
| AOW     | Spin-coating      | 1.02  | 0.54  | 0.56  | 2.08  | 10   | 7–8  | 6–6  | 1.5–1.7 |
| PBDTTT-C-T | Spin-coating | 0.021 | 0.013 | 0.016 | 0.84  | 10   | 5   | 1   | 1.0–1.3 |
| AOW     | Spin-coating      | 0.012 | 0.008 | 0.0092 | 2.19 | 10   | 5   | 6   | 2.3–2.5 |

a)Saturated mobilities were extracted at low V_G region for polymer PDPP4T, PDPPTT, and PIIDTT. b)Saturated mobilities were extracted at high V_G region for polymer PDPP4T, PDPPTT, and PIIDTT, whose transfer characteristics are not ideal. When averaging charge mobility, data were based on statistics of at least 50 BGBC FET devices with W = 1400 μm and L = 50 μm.
FETs fabricated with this AOW approach is weakly affected by environmental humidity. As an example, the charge mobility for thin film of PDPPT4T prepared in air with 90% humidity is slightly reduced by comparing with that for the same AOW thin film prepared in air with 20% humidity as shown in Figure S12b in the Supporting Information. This may be attributed to the fact that AOW thin films show improved crystallinity, which (plus the hydrophobic nature of these polymers) can prevent the penetration of water molecules into the thin films.

We have developed a facile and economic approach to assemble conjugated polymers into thin films with improved crystallinities. This is referred to as AOW approach. Six typical semiconducting polymers PDPPT4T, PDPPTT, PIIDTT, P3HT, IDTBT, and PBDDTT-C-T were investigated. On the basis of GIWAXS and AFM data, polymeric chains of PDPPT4T, PDPPTT, PIIDTT, and P3HT are assembled into more ordered structures with this AOW approach. Interestingly, polymer chains within thin films of these polymers adopt predominantly edge-on packing mode on substrates. The formation of more ordered structures is induced by the “stick-and-slip” motion of contact line after solvent evaporation and the hydrophobic nature of these polymers, which forces the polymer chains to pack densely with predominant edge-on mode in order to minimize the contact of polymer chains with water. Further studies show that this method is particularly effective for conjugated polymers which tend to form crystalline thin films. In comparison with those of spin-coated, drop-casted, and Langmuir-Schaefer thin films, charge mobilities for thin films of PDPPT4T, PDPPTT, PIIDTT, and P3HT are boosted significantly by using AOW approach. Moreover, the method is simple and effective to fabricate FET arrays with high average mobility of 6 cm² V⁻¹ s⁻¹. Therefore, this facile and economic approach for assembling semiconducting polymers into more ordered structures with high charge mobilities is potentially useful for the fabrication of organic circuits.

**Experimental Section**

*Fabrication of Polymer Thin Films by Using AOW Method:* All conjugated polymers were dissolved in chloroform with a concentration of 0.1 mg mL⁻¹. Specifically, the chloroform solutions of PDPPT4T, P3HT, PBDDTT-C-T, and IDTBT were prepared by stirring the solutions overnight at ambient condition, while those of PDPPTT and PIIDTT were formed by heating at 50 °C under nitrogen for 12 h. For film growth on water surface, 40 mL of deionized water was added into a vessel (diameter 60 mm, height 30 mm), and 50 μL of the polymer solution (0.1 mg mL⁻¹) was dropped onto the water surface with microsyringe. The growth of film was completed during several minutes after evaporation of solvents. Then, a substrate (glass, SiO₂/Si or OTS-modified SiO₂/Si with gold electrodes) was inserted at an angle into the water to transfer thin films on air-water interface to the substrate, and thin film was blown with dry nitrogen to remove residual water. The average thicknesses of stripes/grooves (area between stripes) of AOW thin films were 50 nm/5 nm for PDPPT4T, 22 nm/8 nm for PDPPTT, 40 nm/17 nm for PIIDTT, 65 nm/5 nm for P3HT, 29 nm/4 nm for IDTBT, and 33 nm/10 nm for PBDDTT-C-T. The characterizations of AOW thin films with POM, GIWAXS, and AFM, fabrication of FETs with AOW thin films, and the comparative experiments are included in the Supporting Information.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

charge mobility, conjugated polymers, packing order, self-assembly

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[29] It should be noted that the thin film mobilities fabricated by AOW method are higher than those of spin-coated ones, although the thin AOW films are not even in thickness. The good tolerance of thin film thickness by using AOW method is beneficial for future large-area device fabrications.

[30] Thin film of PDPP4T was also prepared on plasma treated SiO₂/Si substrate with drop-casting method. The thin film shows no stripe-like structure on the basis of the AFM image (see Figure S8b, Supporting Information). This thin film exhibits even poor semiconducting performance with average charge mobility of 0.0066 cm² V⁻¹ s⁻¹ because of the presence of –OH groups (as charge carrier traps) at the interface. Similarly, the spin-coated thin film of PDPP4T on plasma treated SiO₂/Si substrate also shows poor morphology and semiconducting performance with average charge mobility of 0.0073 cm² V⁻¹ s⁻¹.

[31] The average charge mobility extracted at high V_G region can reach 1.71 cm² V⁻¹ s⁻¹.