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Carrier Transport Enhancement in Conjugated Polymers through Interfacial Self-Assembly of Solution-State Aggregates

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ABSTRACT:

We demonstrate that local and long range orders of poly(3-hexylthiophene) (P3HT) semicrystalline films can be synergistically improved by combining chemical functionalization of the substrate with solution-state disentanglement and pre-aggregation of P3HT in a theta solvent, leading to a very significant enhancement of the field effect carrier mobility. The pre-aggregation and surface functionalization effects combine to enhance the carrier mobility nearly 100-fold as compared with standard film preparation by spin-coating, and nearly 10-fold increase over the benefits of pre-aggregation alone. *In situ* quartz crystal microbalance with dissipation (QCM-D) experiments reveal enhanced deposition of pre-aggregates on surfaces modified with an alkyl-terminated self-assembled monolayer (SAM) in comparison to un-aggregated polymer chains. Additional investigations reveal the combined pre-aggregation and surface functionalization significantly enhances local order of the conjugated polymer through planarization and extension of the conjugated backbone of the polymer which clearly translate to significant improvements of

carrier transport at the semiconductor-dielectric interface in organic thin film transistors. This study points to opportunities in combining complementary routes, such as well-known pre-aggregation with substrate chemical functionalization, to enhance the polymer self-assembly and improve its interfacial order with benefits for transport properties.

Keywords: conjugated polymers; charge transport; organic thin film transistor; aggregation; surface functionalization

1. INTRODUCTION

Conjugated polymers have attracted a great deal of attention in recent years because of their ever-improving electronic, optoelectronic and photovoltaic properties.¹⁻⁴ The semi-flexible poly(3-hexylthiophene) (P3HT) is the archetypal semi-crystalline conjugated polymer used in organic electronics and photovoltaics and has been investigated extensively to develop an understanding of structure-property-performance relations.⁵⁻¹⁰ A number of recent studies have demonstrated that molecular ordering along the polymer backbone and between chains is far more important to carrier transport in high molecular weight (Mw) polymer films than domain boundaries.¹¹⁻¹⁶ However, high Mw semi-flexible polymers are thought to be difficult to push into a highly molecularly ordered state due to entanglements and interactions which can inhibit molecular diffusion and challenge conformational transitions.^{11,13,17} Polymer crystallization improves the molecular stacking order and planarization of the backbone in the solid state, hence there have been a number of reports linking crystalline order to carrier transport.^{7,18,19} Along this line, several strategies have been pursued to control molecular self-assembly and thin film microstructure, including by decreasing chain entanglements in the solution state,^{12,13,17} tuning solution-processing conditions,²⁰⁻²⁴ surface functionalization with a self-assembled monolayer (SAM)²⁵⁻²⁷ and applying post-deposition thermal/solvent vapour annealing.²⁸⁻³⁰

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3 It has been shown that chain entanglements in high Mw polymers mediate pre-aggregation in theta
4 solvents prior to solution-casting.^{12,13} Chain entanglements inhibit chain conformational changes in
5 conditions where the solution approaches its solubility limit. Hence, disentanglement results in facile
6 pre-aggregation of a large number of nuclei with uniform size distribution, leading – among other
7 things – to a reduction of the specific viscosity of the solution and to easier diffusivity of
8 pre-aggregates and chains.^{12,31} During solution drying, disentangled chains and pre-aggregates
9 therefore more easily assemble into structures exhibiting enhanced backbone planarity, lamellar
10 thickness and extended π - π^* conjugation.³²

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21 Molecular self-assembly during solution-casting can be influenced by surface functionalization
22 with a SAM, an effect widely recognized in solution-processed small-molecule organic
23 semiconductors.³³⁻³⁶ In case of polymers, the effects have been attributed to minimizing polar
24 moieties^{37,38} and inducing molecular orientation and interfacial order at the dielectric surface.³⁹⁻⁴²
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29 We therefore take the view that the enhanced mobility of species in a disentangled polymer solution
30 can be synergistically coupled with appropriate chemical modifications of the substrate to enhance
31 self-assembly and formation of high quality semicrystalline conjugated polymers.

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In this study, we demonstrate the powerful benefits of combining polymer aggregation in a theta
solution with chain disentanglement and surface chemical functionalization at the solution-solid
interface to induce important and meaningful changes in the local order and backbone planarization
of a semiflexible conjugated polymer. The combined effects yield significant impact on carrier
transport in the conjugated polymer film in the context of organic thin film transistors (OTFTs). *In*
situ quartz crystal microbalance with dissipation (QCM-D) experiments reveal important differences
in the rate and mechanism of self-assembly of the polymer for pristine and well-aggregated
formulations on untreated and chemically modified surfaces. The resulting films were subsequently
characterized in terms of microstructure and morphology using a combination of x-ray diffraction,
grazing incidence wide angle X-ray scattering (GIWAXS), and transmission electron microscopy

(TEM). Ultraviolet-visible (UV-Vis) absorption spectroscopy was combined with quantitative analysis using the Spano model fit approach to estimate the photophysical aggregation and backbone planarity.^{43,44} Our investigation clearly demonstrates that aggregating high quality polymer domains in a theta solvent and letting the solution dry on an alkyl-terminated SAM influences its deposition behaviour to the point that local and long range orders are affected and the carrier mobility of the polymer semiconductor is greatly affected. These results point to existence of synergistic routes to enhancing the transport properties of conjugated polymers in the context of OTFT applications and beyond.

2. EXPERIMENTAL METHODOLOGY

Materials: Regioregular P3HT (Mw = 67 kDa; regioregularity RR = 98.5%; Sigma-Aldrich Co.) and toluene (99.8% anhydrous; Sigma-Aldrich Co.) were used without further purification.

Pre-treatment: P3HT was dissolved in 1 mL of toluene (0.5 wt.%) at elevated temperature 60 °C for 10 min and then kept stirring in dark environment over two days at room temperature. A small glass vial of the P3HT solution was placed in an ultrasonic bath at room temperature for 0, 2, 4, 6 and 8 min at a power level of (30 W/L) to alter the solution state aggregation.

Surface-treatment: 46 μ l/mL octyltrichlorosilane (OTS) solution in toluene was cast onto a UV/ozone cleaned Si/SiO₂ wafer to cover the entire surface and was allowed to partially assemble for 30 min; the substrate was then washed with toluene and rinsed with DI water. For TEM characterization, 30 nm PEDOT-PSS layer was cast on Si/SiO₂ wafer and dried at 110 °C for 10 min, followed by planting OTS monolayer.

Post-treatment: Annealing has been carried out at temperatures from 130 °C for 5 min in N₂- filled glove-box, followed by a slow cooling down to room temperature.

Device Fabrication and Characterization: As ultrasonicated for various time period 0.5 wt% solutions of organic semiconductor P3HT in toluene were spin-coated (SPIN 150) onto OTS treated

substrates at a rate of 1000 rpm for 30 sec. Gold source -drain electrodes were evaporated through a shadow mask with a channel width (W) of 500 μm and length (L) of 30 μm . All electrical measurements were performed with a Keithely 4200 Semiconductor Characterization System in ambient air.

Characterizations: The thickness of spin-coated films was measured by M-2000 variable angle spectroscopic ellipsometer (J. A. Woollam, Inc). The different incidence angle 55° , 65° and 75° were mounted for accurate fitting. Its spectra spanned over ca. 200 nm wavelengths to ca. 1800 nm. The thin-films showed ca. 30 nm. Analysis of the ellipsometric data was performed using complete EASETM and WVASE32 software (J.A. Woollam Co., Inc.).

Rheology measurements were carried out on an Anton Paar MCR-301 rheometer at a constant shear rate of (100 s^{-1}).

Quartz Crystal Microbalance and Dissipation (QCM-D): QCM-D measurements were obtained in Flow Module accessory of the E4 instrument with a flow speed of 50 $\mu\text{L}/\text{min}$ at room temperature (Q-sense). A QCM-D (Q-sense) and Quartz sensor crystals (Q-sense) coated with/without OTS were used to characterize the effect of the substrate modification on the P3HT precursors adsorption behaviour. The results were interpreted with a Kelvin-Voigt viscoelastic model to obtain the deposited thickness. The thickness of the seed layer, with the density of polymer $1.3\text{ g}/\text{mm}^3$, was calculated by Voigt model from the 3rd, 5th, 7th and 9th overtones of frequency and dissipation. Changes in dissipation and frequency of the fifth overtone are represented in the main text.

Transmission electron microscopy (TEM): TEM experiments were carried out on a FEI Tecnai 12 operated at 120 kV accelerating voltage. Samples for TEM were prepared by floating thin-film on a 300 mesh copper grid. The surface analysis for the samples was carried out by AFM “Agilent 5400 SPM”.

Grazing incidence wide angle X-ray scattering (GIWAXS): GIWAXS measurement was carried out on D-line, Cornell High Energy Synchrotron Source (CHESS) at Cornell University. A 0.5×0.1

mm beam size with a wavelength of 1.1688 Å and wide band pass (1.47%) was generated from double-bounce multilayer monochromator. The incidence angle was 0.15° with respect to the substrate plane, as established by performing x-ray reflectivity using an ion chamber. A 50 x 50 mm charged coupling device (CCD) area detector (Medoptics) with pixel size of 46.9 μm was placed at a distance of 101.21 mm from the sample stage. A 1.5 mm-wide tantalum rod was used to block the intense scattering at low angles of incidence.

Grazing incidence X-ray diffraction (XRD): XRD measurement was carried out in a scanning interval of 2θ between 3 and 20. We employed an incident angle ($R = 0.2$) slightly above the critical angle ($R_c = 0.18$).

3. RESULTS AND DISCUSSION

3.1 Polymer entanglement and pre-aggregation in solution

High Mw P3HT dissolved in a theta solvent, such as toluene at room temperature, is known to aggregate.^{17,45} However, chain entanglements due to the length of the polymer chains inhibit molecular diffusivity and coil-to-rod phase transformation, leading to poor nucleation/micro-crystallization in solution. Low energy ultrasonication has been shown to reduce chain entanglements and promote the formation of ordered aggregates in theta solvents, which can be confirmed by measuring the optical properties of the polymer solution.^{12,13} The UV-Vis absorption spectra of P3HT in toluene at room temperature (**Figure 1a**) show a clear absorption peak at ca. 605 nm, associated to inter-chain interactions.⁴⁶ Ultrasonication induces a significant increase in photophysical aggregation and effectively results in an increased local order in terms of intermolecular and intramolecular interactions. We also observe a slight decrease of the specific viscosity of the solution from 0.52 to 0.40 after treating the solution (**Figure 1b**), confirming a reduction of the chain entanglements in solution. These results, combined with prior analysis by dynamic light scattering,^{13,47} paint the pictures of the pristine and disentangled solutions illustrated in

Figures 1c, whereby the ultrasonicated polymer solution is more akin to a suspension of monodisperse P3HT aggregates with few dissolved chains effectively reducing the number of entanglements in solution.

Figure 1. (a) Normalized UV-Vis absorption of P3HT solution showing chain disentanglements influencing pre-aggregation. (b) Specific viscosity of P3HT solution confirming low chain entanglements after solution treatment. (c) Schematic model showing solution state of polymer before and after chain disentanglements.

3.2 OTFT device performance

Organic thin film transistors in the bottom-gate top-contact (BGTC) architecture were fabricated on n-doped Si substrates (gate) with SiO₂ as gate dielectric and evaporated gold source and drain (Figure 2a). The P3HT layer was spin-cast from a 0.5 wt.% toluene solution treated with ultrasonication.¹³ In Figure 2b, we plot the saturation hole mobility with respect to ultrasonication

time for the as-cast (square) and thermal annealed (dot) films on untreated SiO₂ gate dielectric (See **Table S1** for details). The data reveal a ~20-fold increase of mobility between the as-cast (0 min) and ultrasonicated (6 & 8 min) cases. Thermal annealing further increases the carrier mobility of samples treated for 6 min or less, with the peak mobility observed at an optimal ultrasonication time of 4 min with a mobility of 0.015 cm²V⁻¹s⁻¹. It is important to note that the combination of ultrasonication and thermal annealing yields faster carrier transport than what can be achieved by annealing alone. Surface modification of the gate dielectric with an octadecyltrichlorosilane (OTS) SAM followed by annealing further improves carrier transport by nearly an order of magnitude. In the case of pristine solution the mobility increases to 0.035 cm²V⁻¹s⁻¹ on OTS/SiO₂, while ultrasonicated solutions yield a remarkable mobility as high as 0.156 cm²V⁻¹s⁻¹. This performance is two orders of magnitude superior to P3HT films prepared from pristine solutions on untreated SiO₂ without thermal annealing. Note that the impact of thermal annealing is more negligible when comparing surface modification and ultrasonication, which indicates potentially significantly hints that self-assembly behaviour of pre-aggregates on surface functionalized substrate influences P3HT order and charge mobility. The decreases in V_{th} and increases in on/off ratio are summarized in **Table S1** and **Figure S1**. As mobility increases, on/off ratio also increases while V_{th} decreases.

Surface functionalization-induced interfacial order was previously investigated by Salleo *et al.* through an *ex situ* study of thickness-dependent crystallinity and suggested the formation of a three-layer model.¹¹ Importantly it has been suggested that surface functionalization has an enhancing effect on interfacial order, with the effect limited to within approximately 10 nm of the modified interface,^{11,40} which means that the increased molecular order of polymer film at the interface with the OTS-treated substrate may arise from the increased interfacial order in very thin (less than ca. 10 nm) P3HT layer. Such benefits may arise from the interactions of the alkyl chains in the polymer with those of OTS,⁴⁰ and this calls for deeper investigation through *in situ* methods to reveal whether polymer adsorption is responsible for this.

Figure 2. (a) Schematic representation of P3HT transistors in the bottom-gate top-contact (BGTC) architecture. (b) Saturation hole mobilities with respect to ultrasonication time for the as-cast and thermal annealed films on untreated SiO₂ gate dielectric and OTS-treated SiO₂. The average mobility and error bar are calculated from a minimum of 4 devices.

3.3 P3HT thin film formation

The disentanglement and pre-aggregation of P3HT *via* ultrasonication and the functionalization of surface with OTS SAM are expected to influence how the polymer film forms at the solid-liquid interface.^{11,13} This can be challenging to investigate, as optical and X-ray scattering techniques previously developed to investigate film formation probe mainly the bulk and surface of the drying film, rather than its buried interface.⁴⁸⁻⁵⁵ We have recently shown that thin film deposition at the solid-liquid interface, solvent vapour annealing and ligand exchange in colloidal quantum dot solids can be monitored using a quartz crystal microbalance with dissipation (QCM-D) capability.⁵⁶⁻⁵⁸ QCM-D measures the change of frequency (Δf) and dissipation (ΔD) at the surface of the microbalance in relation to mass deposition or loss and changes in the viscoelastic properties of the

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4 adsorbed mass, respectively.⁵⁹⁻⁶¹ For the purpose of our study, we evaluate the rate and extent of
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6 P3HT deposition at the solid-solution interface on untreated and OTS-treated SiO₂-coated quartz
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8 sensor using pristine and ultrasonicated (4 min) solutions. The quartz crystal is stationary (not
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10 spinning) and the solution is cast in a closed flow cell so as to eliminate the effects of solution
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12 outflow and solvent evaporation. The P3HT solution (0.5 wt.%) in toluene is continuously flown
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14 over the SiO₂ or SiO₂/OTS-coated sensor, as shown in **Figure 3a**.
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Figure 3. (a) Schematic illustration of the QCM-D closed flow cell containing a SiO₂-coated quartz sensor. The P3HT solution is flown through the enclosed cell, preventing solvent evaporation. (b, c) Changes of frequency (Δf) and dissipation (ΔD), respectively, for the blank solvent as well as the pristine and ultrasonicated solutions as they flow over the untreated and OTS-treated SiO₂-coated quartz sensor. (d) The time-evolution of adsorbed thickness from pristine and ultrasonicated

solutions on SiO₂ and SiO₂/OTS surfaces, as calculated using the Voigt model. (e) ΔD vs. Δf trajectory plots for pristine and ultrasonicated solutions on untreated and OTS-treated SiO₂-coated quartz sensor showing significant differences in slope and growth mechanism.

In **Figures 3b** and **3c**, we plot the evolutions of Δf and ΔD for the blank solvent, as well as for the pristine and ultrasonicated solutions as they flow over the SiO₂ or SiO₂/OTS-coated sensor, respectively. The time-evolution of thickness (**Figure 3d**) of pristine and ultrasonicated solutions on SiO₂ and SiO₂/OTS surfaces was calculated using the Voigt model for viscoelastic materials,^{61,62} as detailed in supporting information and **Figure S2**. No mass uptake is detected when flowing the blank solvent. However, P3HT spontaneously deposits on the surface of the substrate, with a ~10 nm P3HT film forming at a rate of 1 nm/min on SiO₂ from an untreated solution, increasing nearly five-fold to 4.8 nm/min when an ultrasonicated solution is used on untreated substrate. The OTS-treatment further enhances the deposition rate to >7 nm/min, indicating that P3HT aggregates assemble easily at the interface and perhaps promote further deposition of P3HT from the solution on the pre-aggregates assembled at the solid-solution interface. A closer look at the evolutions of ΔD vs. Δf trajectory plots (**Figure 3e**) should reveal whether the P3HT deposition proceeds via the same mechanism or instead is influenced by pre-aggregation and/or functionalization of the substrate. In case of pristine P3HT solutions, mass uptake (decrease of Δf) on either surface is accompanied with a modest increase of dissipation, indicating formation of a relatively compact layer. By contrast, when the solution is pre-aggregated, the mass deposition is accompanied by a very steep increase of dissipation, indicating the growing film is viscoelastic. We interpret this as differences in solvation when the film is formed from P3HT chains or larger P3HT aggregates, which are more likely to form a mesoporous scaffold, which drags the solution as the quartz crystal oscillates in the transverse direction. The fact that the assembly of the pre-aggregated polymer at the solid-liquid interface is more dissipative is consistent with film formation proceeded by self-assembly of solvated

pre-aggregates of P3HT on the substrate surface, in contrast with the case of untreated solutions where interfacial assembly more likely proceeds via attachment of disordered polymer chains and subsequent aggregation at the solid-liquid interface through heterogeneous nucleation. In all cases, the OTS treatment enhances mass deposition with more pronounced viscoelastic behaviour, suggesting that the OTS-treated surface may have a preference for self-assembly of aggregates (both from the untreated and treated solutions) rather than solvated chains. We propose that this mechanism promotes the formation of a higher quality interface and better templates the solidification of the remaining polymer when the solution dries. The observation that ΔD vs Δf is generally linear for untreated solutions on either substrate but distinctly non-linear when the solution is pre-aggregated suggests changes occur in mass deposition mode over time in the latter case.⁶³ Indeed, the dissipation increases at a smaller rate for higher Δf , indicating that the solvated layer may gradually densify.

Of course, the above analysis was performed in an enclosed flow cell without the effects of solution outflow and solvent evaporation common to spin-coating. Nevertheless, we believe the experiment reveals important trends in the self-assembly behaviour, which are expected to be valid during solution-processing of thin films. The dramatically different self-assembly behaviour from pre-aggregated and pristine solutions indicates that spin-coating of pre-aggregated solutions should be first dominated by self-assembly of aggregates at the solution-solid interface. The presence of OTS treatment should also promote adhesion of the P3HT aggregates rather than solvated chains, thus promoting improved ordering at the semiconductor-dielectric interface.

3.4 Microstructure and morphology of P3HT films

The morphology and microstructure of spin-cast P3HT films were imaged using atomic force microscopy (AFM) and transmission electron microscopy (TEM), respectively, as shown in **Figure 4a**. The AFM micrographs of the top surface reveal the formation of micrometer-long fibrils in films

cast from pre-aggregated solutions, resulting in increasing surface roughness [root mean squared (RMS)] from 2.9 nm (4.4 nm) on SiO₂ (SiO₂/OTS) to 5.9 nm (6.4 nm). The surface morphology of the films cast on untreated and OTS-treated SiO₂ is otherwise indistinguishable. The TEM micrographs looking through the film reveal more extensive fibril formation on the OTS-treated substrate. The selected area electron diffraction (SAED) analysis of the samples also reveals stronger diffraction from the (020) diffraction peak corresponding to crystalline order along the π -stacking direction in the case of the film cast on OTS-treated SiO₂ (see **Figure S3** for details). These observations support the idea that the OTS-treatment promotes the self-assembly of pre-aggregates at the solid-liquid interface, which can subsequently grow into the extended fibrils. As spin coating is known to lose most of the solution through ejection and radial outflow,⁵¹ the strong interactions between the alkyl chains and the pre-aggregates and their tendency to more rapidly attach to the OTS-treated surface may contribute to increasing the concentration of aggregates near the solution-solid interface, while solvated P3HT is present in the middle and near the top of the solution. Hence, aggregates are less likely to be lost in the outflow, leading to a preferential outflow mechanism similar to recent reports in spin-cast polymer-molecule blend OTFTs.⁶⁴

We have further investigated the microstructure and texture of the films by X-ray diffraction (XRD). The (100) out-of-plane lamellar diffraction intensity integrated from XRD measurements suggests increasing lamellar crystallinity and texture with ultrasonication time, both on SiO₂ and SiO₂/OTS substrates (**Figure 4b**). The enhancement of lamellar crystallinity appears to be measurably stronger on SiO₂/OTS, as highlighted by increasing integrated intensity of the diffraction peak. The crystalline correlation length of P3HT along the lamellar direction was calculated from the (100) peak width by the Debye-Scherrer method and is plotted in **Figure 4c**.⁶⁵ The correlation length decreases slightly from ca. 19 nm to ca. 17 nm with solution treatment time on both surfaces, indicative of the reduced crystallite size attributed to the effect of ultrasonication, as previously shown by dynamic light scattering.¹³ The full width at half maximum (FWHM) of the azimuthal

angular intensity distribution of the (100) Bragg sheet measured by GIWAXS is also plotted in **Figure 4d** (see **Figure S4** for more details). The FWHM is a measure of mosaicity and decreases monotonically on both surfaces with solution treatment, but does not seem to be affected by the surface treatment itself. This likely indicates that self-assembled pre-aggregates are preferentially oriented at the semiconductor-dielectric interface with their lamellar stacking plane parallel to the substrate plane.

3.5 Local order in P3HT films

We investigate how the combination of solution pre-aggregation and surface functionalization impact the local order in P3HT films. The photophysical aggregation of the conjugated monomer units, both in terms of inter-chain and intra-chain interactions, can be analysed by UV-Vis absorption (**Figure S5**). The absorption spectrum is composed of a lower energy contribution from photophysical aggregates and a higher energy contribution from more disordered chains. The spectra were modelled using the Spano model according to equation (1) below, which has been successfully implemented and described in detail elsewhere (**Figure 5a**):^{13,43,44,66-68}

$$A(E) \propto \sum_{m=0} \left(\frac{S^m}{m!} \right) \times \left(1 - \frac{W e^{-S}}{2E_p} \sum_{n \neq m} \frac{S^n}{n!n-(m)} \right)^2 \times \exp \left(\frac{(E - E_{0-0} - mE_p - 1/2 WS^m e^{-S})^2}{2\sigma^2} \right) \quad (1)$$

Here, A is the absorbance as a function of the photon energy (E), W is the free exciton bandwidth of the aggregates, S is the Huang-Rhys factor and fixed at 1.0 taken from a Franck-Condon fit, m and n are differing vibrational levels, E_{0-0} is the 0-0 transition energy, E_p is the intermolecular vibrational energy and taken as 0.18 eV, and σ is the Gaussian line width.

Figure 4. (a) Atomic force microscopy (AFM) and transmission electron microscopy (TEM) images showing crystalline morphologies for the entangled/disentangled films at both substrates. (b) The (100) Bragg peak intensity normalized to film thickness from XRD showing variation of lamellar stacking crystallinity for both films at OTS and SiO₂ substrates. (c) Correlation length of P3HT crystallites for both films at OTS and SiO₂ substrates. (d) The full width half maximum (FWHM) of the azimuthal-angle intensity of the $q_z = (100)$ peak from GIWAXS for both films at OTS and SiO₂ substrates.

Figure 5. (a) Absorption spectrum of P3HT thin-film subjected to the Spano analysis. (b) The fraction of film made up of aggregates. (c) The evolution of exciton bandwidth W of P3HT films. (d) Lamellar thickness of P3HT fibrils measured from plan-view TEM.

Based on the Spano analysis, we have calculated the total fraction of photophysical aggregates, or aggregation fraction, as well as the exciton bandwidth, W , which is inversely related to the exciton conjugation length (also known as intra-chain exciton coupling) along the backbone. A decreasing exciton bandwidth is therefore indicative of improving backbone planarity.⁴⁴ The fraction of P3HT photophysical aggregates increases with ultrasonication time less than 6 min, but is systematically higher by ca. 1% on SiO₂/OTS as compared with bare SiO₂. The exciton bandwidth W is found to

decrease steadily with ultrasonication time, and is once again consistently lower on the SiO₂/OTS surface. These bulk measurements of the average local order over the entire film thickness indicate that surface functionalization and solution pre-treatments can improve the local order and backbone planarity within the polymer film. The lamellar thickness of P3HT fibrils is a key microstructural feature related to backbone extension/planarity and is measurable by TEM (**Figure S6**). In **Figure 5d** we show the increasing trend of lamellar thickness with ultrasonication time. The lamellar thickness increases more notably on the SiO₂/OTS substrate than on bare SiO₂, providing independent confirmation of the chain extension in the P3HT films yielding high carrier mobility. While the long range structural benefits of OTS functionalization of the substrate were found to be similar on bare and on OTS-treated surfaces, the local order and backbone planarity and extension are improved by the combination of these treatments. This observation further supports a growing body of work suggesting that local order may be more crucial to improving the operation of polymer-based OTFTs.^{13,17,66,69-72}

As mentioned above, the structural and optical analyses are bulk measurements, whereas transport measurements in the context of OTFTs is far more sensitive to the polymer order and conformation at the interface.¹¹ Since surface functionalization has an enhancing effect limited to within approximately 10 nm of the modified interface,^{11,40} we speculate that the measured improvements in local order averaged over the entire film depth may be even more pronounced at the interface, perhaps explaining the dramatic enhancement of carrier mobility by nearly two orders of magnitude.

4. CONCLUSIONS

P3HT-based OTFTs fabricated by spin-casting pristine and ultrasonicated solutions on bare and OTS-treated SiO₂ gate dielectric showed very significant enhancement of carrier mobility, by up to two orders of magnitude, pointing to important changes to the P3HT local and long range order at the

buried semiconductor-dielectric interface as well as in the bulk. The *in situ* QCM-D measurements revealed that P3HT solution in a theta solvent prefers to spontaneously adsorb at the solution-solid interface. When the P3HT solution was disentangled and pre-aggregated via ultrasonication, this promoted its rapid adsorption on the substrate, nearly 5 times faster than the pristine solution. The OTS surface treatment further promoted P3HT deposition at the solution-solid interface and appeared to promote the self-assembly of aggregates rather than solvated polymer chains.

The long range crystalline order (lamellar) and the local photophysical order in the P3HT films were evaluated by X-ray diffraction and optical absorption analyses, respectively. The analysis revealed enhanced lamellar crystallinity, texture and reduced mosaicity when the solution was pre-aggregated, but the structural benefits were found to be similar on bare and on OTS-treated surfaces. The local order, however, was distinctly better in terms of total fraction of photophysical aggregates as well as backbone conjugation length and planarity when the pre-aggregated solution was cast on the OTS-treated substrate.

The bulk measurements averaged the structural benefits over the entire film thickness. When taken with the dramatic improvements of carrier transport at the semiconductor-dielectric interface in OTFTs, they suggest important enhancements to interfacial ordering, which we attribute to the synergistic effects of polymer disentanglement/pre-aggregation on the one hand and enhanced interfacial adsorption and ordering on the OTS-terminated SiO₂ surface.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

Figure S1 and Table S1 summarize the electrical characteristics of representative OTFTs. Figure S2 shows the Voigt model used to analyze the QCM-D data. Additional experimental results, including electron diffraction, GIWAXS, UV-Vis absorption and TEM analyses are shown in Figures S3-S6.

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Notes

The authors declare no competing financial interest.

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TOC

We demonstrate that deposition of conjugated polymer aggregates can be vastly improved on surfaces modified with an alkyl-terminated self-assembled monolayer (SAM) in comparison to solvated polymer chain deposition on untreated surfaces. This leads to improved local order as well as planarization and extension of the conjugated backbone which significantly improves carrier transport in organic field effect transistors.

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130x82mm (150 x 150 DPI)