Blade Coating Aligned, High-Performance, Semiconducting-Polymer Transistors

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Recent demonstration of mobilities in excess of 10 cm²V⁻¹s⁻¹ have energized research in solution deposition of polymers for thin film transistor applications. Due to the lamella motif of most soluble, semiconducting polymers, the local mobility is intrinsically anisotropic. Therefore, fabrication of aligned films is of interest for optimization of device performance. Many techniques have been developed to control film alignment, including solution deposition via directed flows and deposition on topologically structured substrates. We report device and detailed structural analysis (ultraviolet-visible absorption, IR absorption, near-edge X-ray absorption (NEXAFS), grazing incidence X-ray diffraction, and atomic force microscopy) results from blade coating two high performing semiconducting polymers on unpatterned and nanostructured substrates. Blade coating exhibits two distinct operational regimes: the Landau-Levich or horizontal dip coating regime and the evaporative regime. We find that in the evaporative deposition regime, aligned films are produced on unpatterned substrates with the polymer chain director perpendicular to the coating direction. Both NEXAFS and device measurements indicate the coating induced orientation is nucleated at the air interface. Nanostructured substrates produce anisotropic bottom contact devices with the polymer chain at the buried interface oriented along the direction of the substrate grooves, independent of coating regime and coating direction. Real time studies of film drying establish that alignment occurs at extremely high volume-fraction conditions, suggesting mediation via a lyotropic phase. In all cases, the final films appear to exhibit high degrees of crystalline order. The independent control of alignment at the air and substrate interfaces via coating conditions and substrate treatment, respectively, enable detailed assessment of structure-function relationships that suggest the improved performance of the nanostructure aligned films arise from alignment of the less ordered material in the crystallite interphase regions.

INTRODUCTION

Ubiquitous computing is poised to revolutionize diverse aspects of commerce, from industry 4.0,¹ through the internet of things,² to point-of-care health management.^{3,4} The potential disruption is predicated on the marriage of autonomous management protocols with large numbers of smart, distributed sensors. The realization of this marriage requires inexpensive, form factor agnostic, large area electronics supporting the necessary sensors and displays. Printed electronics has received significant interest as a means to manufacture the relevant large area infrastructure.^{5,6} Polymer organic semiconductors (OSCs) are the base for promising inks as they are compatible with diverse deposition technologies and can be processed at low temperatures compatible with flexible and/or disposable substrates^{7,8}. The intrinsic molecular anisotropy of semiconducting polymers (ribbons of conjugated transport paths) and the nature of their self-assembly imply that the charge transport in polymer OSCs (and most OSCs in general) is anisotropic. This opens the opportunity for device optimization via the production of macroscopically aligned films. There are a diversity of means to inducing anisotropy in OSC films that have recently been reviewed^{9,10} including deposition on patterned substrates,^{11,12} control of the coating processes itself, ^{13–18} and post processing, such as buffing techniques¹⁹ and applied strain.²⁰ Care must be taken in assessing deposition schemes as they relate to improved thin film transistor (TFT) performance. While highly anisotropic device characteristics can be obtained, the highest mobility of the aligned device can be *lower* than the analogous isotropic device due to the alignment of deleterious defects.²¹

We report full structural and device characterization of two high performing semiconducting polymers, PCDTPT (poly[4-(4,4- dihexadecyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)- alt -[1,2,5] thiadiazolo[3,4-c]pyridine])²² and CDTBTZ (poly[2,6-(4,4-bis-alkyl-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)])²³ (see schematic 1) deposited by blade-coating on both unstructured and nanostructured substrates. It has recently been demonstrated that light texturing ("nanogrooving") of the substrate by unidirectional abrasion with nanodiamond ultra lapping film results in polymer films with net alignment and highly anisotropic TFT characteristics when deposited by slow, controlled, "tunnel drying."^{12,24} We perform structural analysis by both bulk sensitive [ultravioletvisible (UV-vis) absorption, IR absorption, grazing incidence X-ray diffraction, (GIXD)] and surface sensitive [near-edge X-ray absorption fine-structure (NEXAFS), atomic force microscopy (AFM)] techniques. Under certain coating conditions, film alignment develops on unpatterned substrates with the chain axis aligned perpendicular to the coating direction. For all coating conditions, alignment develops on nanogrooved substrates with the chain axis aligned along the nanogroove director. Bottomgate bottom-contact (BGBC) devices on nanogrooved substrates exhibit significant improvement in the mobility for transport along the chain axis direction. Real time measurements during film drying indicate the mechanism of chain alignment involves passage through a lyotropic phase. This appears to result in highly crystalline films for all process conditions. The ability to form both synergistic (coating alignment and substrate alignment collinear) and frustrated (coating alignment and substrate alignment perpendicular) films allows detailed structural studies. The origin of the improved mobility is suggested to arise from alignment in the less-ordered crystallite interphase regions.

METHODS

PCDTPT and CDTBTZ were provided by 1-material.²⁵ The vendor specified mass average relative molecular mass, Mw (polystyrene standard) and dispersity index, *D*, was Mw=72 kg mol⁻¹ and *D*=2.5 for

PCDTPT and Mw=(30 to 60) kg mol⁻¹ and D=(2.0 to 3.0) for CDTBTZ. Anhydrous chloroform (CF) and odichlorobenzene (oDCB) were purchased from Sigma Aldrich. All materials were used as received. Coating solutions were 4 mg/mL in 1:3 by volume oDCB:CF solvent. Solutions were stored in polytetrafluoroethylene based mininert vials to limit evaporative loss of CF. Coating was performed with a custom, low angle blade coater described previously.²⁶ The substrate temperature was 30 °C and the blade height 200 µm. All films were subjected to a 20 min 200 °C anneal after deposition.

Substrates for UV-vis measurements were glass slides, for NEXAFS, AFM and X-ray diffraction, Si wafer fragments with a native oxide layer. All substrates were cleaned by sequential ultrasonic treatment in CF and isopropyl alcohol (10 min) followed by 10 min UV-ozone (UVO) treatment. Nanogrooved substrates were prepared by unidirectional lapping (≈15 cm length) on 100 nm diamond lapping film (3M 631X) with 5 or 10 passes. Nanogrooved substrates were cleaned after structuring. All substrates were made hydrophobic by a hexamethyldisilazane (HMDS Sigma Aldrich) vapor treatment: 10 min at 2.4 Pa (18 mTorr) at 120 °C.

Substrates for BGBC TFT devices were patterned by photolithography. Either Au or Pt contacts \approx 40 nm thick were deposited on a Ti adhesion layer (\approx 5 nm) on \approx (200 or 300) nm (determined by ellipsometry) SiO₂ dielectrics grown on an n++ Si wafer. Device substrates were nanogrooved after contact deposition. To avoid delamination of contacts, device substrates were not ultrasonically cleaned, only solvent rinsed prior to UVO treatment and subsequent HMDS treatment. The contact pattern was of combinatorial design, containing 1 mm wide channels of varying length (10 to 100) μ m and channel orientation (parallel and perpendicular to the coating direction (**S1**).

The DC electrical characteristics of discrete TFTs were measured at room temperature in a nitrogen purged probe station using a semiconductor parameter analyzer. The gate contact was made to the wafer backside. Isolation was achieved by mechanically scribing the active layer around the device under test. The effective field-effect mobility in the saturation regime was calculated from the following relationship:

$$\mu = \frac{2}{C_i} \frac{L}{W} \frac{\partial I_D^{1/2}}{\partial V_{GS}} \tag{1}$$

where μ is mobility, C_i is the capacitance per unit area for the silicon dioxide gate dielectric (assuming a relative dielectric constant of 3.9), and W and L are the transistor channel width and length, respectively. An averaged value for $\partial I_D^{1/2} / \partial V_{GS}$ was determined from the slope of the line fitted to the last 20 V (from -40 V to -60 V at V_{SD}=-60 V) of the transfer curves (plot of $\sqrt{I_D}$ vs. V_{GS}).

UV-vis spectra were acquired with a fiber-coupled diode-array-based spectrometer with a Glan-Taylor polarizer and a combined deuterium:quartz-tungsten-halogen source. Real-time, normal-incidence, UV-vis measurements employed a two-channel, master slave spectrometer (Ocean Optics SD2000) for acquisition of the two polarized transmission spectra and an independent single channel spectrometer (Ocean Optics HR2000+) for near normal incidence reflection measurements. IR absorption spectra were acquired for films on double side polished Si substrate with a commercial instrument and a custom p-polarized, Brewster-angle transmission accessory based on a wire grid polarizer.²⁷

GIXD measurements were performed at both the Advanced Light Source²⁸ beam line 7-3-3 and beamline 11-3 at the Stanford Synchrotron Research Laboratory.²³ At line 7-3-3 the beam energy was 10 keV and a 2D-image detector (Dectris Pilatus 1M) was located at a distance of ca. 280 mm from the sample center. The measurements were performed in ambient air.²⁹ The x-ray beam was attenuated to minimize sample damage. The detector was calibrated with a silver behenate standard. At SSRL the beam energy was 12 keV and a 2D-image detector (MARS2800) was located at a distance of ca. 400 mm from the sample center. The detector was calibrated with a LaB₆ standard. The measurements were performed in a He ambient to limit scatter. GIXD data was reduced with the Nika software package.³⁰

NEXAFS was done at both the National Institute of Standards and Technology (NIST) beamline U7A of the National Synchrotron Light Source and the soft X-ray beamline at the Australian Synchrotron. At U7A NEXAFS carbon K-edge collection was performed in partial electron yield (PEY) mode with a grid bias of -50 V. Spectra were normalized with respect to carbon concentration by their intensity at 330 eV. At the Australian Synchrotron, PEY data was acquired with a retarding voltage of 210 V and normalized at 320 $eV.^{31}$ For azimuthal scans (at normal incidence) 7 angles were recorded (-20, 0, 20, 45, 70, 90, 110) ° while for polar scans (along the azimuthal direction of maximum intensity) 5 angles were recorded (90, 70, 55, 40, 20) °. NEXAFS of the buried polymer interface was performed on films delaminated with the assistance of a parylene support, as described previously.³² Analysis was performed with the help of the QANT tool³³ implement in Igor Pro. Further details of the NEXAFS data processing can be found elsewhere.³⁴

RESULTS AND DISCUSSION

The results are presented in three primary sections. The first section is a discussion of the coating and alignment phenomenology, focusing on optical, NEXAFS characterization and TFT performance. The second section explores the mechanism of alignment, based on in-situ optical measurements. The third section explores the structural origin of the improved TFT performance.

Observation of Alignment. As has been discussed by various authors^{35,36} blade coating from low viscosity solutions can be described as occurring in two regimes. At high blade velocities, one is in the horizontal dip-coating, or Landau-Levich (L-L) regime.^{37,38} The wet film thickness, *h*, increases with increasing velocity, v as $h = kv^n$ where k is a constant and $n\approx 2/3$. At low velocities, in the evaporative regime, where mass-transport due to convection at the moving contact line (and Marangoni effects, etc.) influences the behavior, the film thickness increases with decreasing velocity as $h = kv^{-n}$. Fundamental studies suggest n in the range 1 to 2.^{35,39} Thickness vs coating speed studies are a simple means to establish the two coating regimes.



Scheme 1. Polymers used in current study. Also shown is a schematic of the blade coater employed and the definition of relative orientations: a) probe electric field, E, parallel (para) to the coating direction, coating direction para to the channel, nanogrooves along the channel. b) E perpendicular (perp) to the coating direction, coating direction perp to the channel, nanogrooves across the channel.

PCDTPT On Unpatterned Substrates. Shown in Figure 1a are representative UV-vis transmission spectra with normal-incident linearly polarized light of a PCDTPT film coated at low velocity (0.2 mm/s) on an unpatterned glass substrate. Clear anisotropy can be observed in the spectra, with the highest absorbance with the incident electric field perpendicular to the coating direction.

Shown in Figure 1b is a summary of the UV-vis characteristics vs. the blade speed. The average absorbance near λ_{max} of 890 nm should be a valid proxy for film thickness in the absence of significant changes in out-plane alignment. One can clearly see the film deposition behavior change from the evaporative regime at low velocities ($t \sim v^{-0.55\pm.04}$) to the Landau-Levich regime at high velocities (t increasing as $v^{+0.75\pm.15}$). We choose to summarize the in-plane anisotropy with the normalized parameter

$$R_{UV-vis} \equiv \frac{Abs_{\perp} - Abs_{\parallel}}{Abs_{\perp} + Abs_{\parallel}}$$

where \perp corresponds to the incident electric field vector perpendicular to the coating direction and || corresponds to the incident electric field vector parallel to the coating direction as detailed in schematic 1. A rich evolution in the anisotropy is observed. As the dominant transition dipole is along

the chain axis, one finds the chains align perpendicular to the coating direction at low speeds, align parallel to the coating direction in the transition between evaporative and Landau-Levich regimes, and become randomized at high blade velocities. Based on Figure 1 we focus all further characterization on two coating conditions: 0.2 mm/s, well in the evaporative regime, and 20 mm/s, in the Landau-Levich regime. Typical film thicknesses, based on spectroscopic ellipsometry, of the two coating conditions are \approx 150 nm for 0.2 mm/s and \approx 30 nm for 20 mm/s.



Figure 1 a) Typical UV-vis absorbance spectra of a blade coated PCDTPT film. b) Coating speed dependence of derived quantities: UV-vis anisotropy R and average absorbance at 890 nm. Error bars are the range of duplicate measurements.

Shown in Figure 2 are typical I-V output and transfer characteristics for a BCBG device coated at 0.2 mm/s where significant alignment was observed in the UV-vis. The devices show very little hysteresis and a small 'bird-beak' (slow turn on) at low V_{DS} suggestive of contact resistance. Typical average saturation mobility extracted from the high V_{GS} range (-60 to -40) V is 0.7 cm²V⁻¹s⁻¹. In contrast to the UV-vis anisotropy (R_{UV-vis} =0.23±.09, see Figure 1), the mobility exhibits no significant anisotropy. The normalized mobility anisotropy (defined analogous to Eq. 1 where \perp corresponds to the coating direction para to the channel director as in Schematic 1) is R_{μ} = 0.00 ± 0.02 (error bar the standard deviation of 6 device pairs).



Figure 2. Top: I-V output curve for a PCDTPT device, coated at 0.2 mm/s, with 50 μ m channel length and 300 nm gate oxide thickness. V_{GS} -10V label omitted for clarity. Bottom: transfer curve at V_{DS}=-60V and derived $\sqrt{I_{SD}}$. Also shown is the region (open squares) fit (red line) to extract the saturation mobility.

We have performed surface sensitive NEXAFS studies to characterize the alignment of the films at the top (air interface) and at the bottom (dielectric interface) after delamination with a parylene support.³² Shown in Figure 3 are spectra taken from the top surface of a film coated at 0.2 mm/s at the C 1s edge at normal incidence, as a function of the azimuthal angle ϕ of the linearly polarized X-ray beam. The congested structure from (284 to 286.5) eV are transitions into the π^* manifold of the conjugated backbone.⁴⁰ All transitions in this region are expected to have a transition dipole, TD, perpendicular to the plane of the polymer backbone. There is evidence for a high degree of in-plane orientation. The NEXAFS signal exhibits a maximum at 90°, when the X-ray *E*-field is along the blading direction, implying the polymer chain axis is perpendicular to the coating direction, consistent with the UV-vis. However, the normalized NEXAFS anisotropy *R*_{NEXAFS}=0.89, is significantly larger than observed for UV-vis (≈0.2). Also shown in Figure 3 are NEXAFS results for the bottom of the film, exposed via delamination. Unlike the top surface, there is very little evidence for in-plane orientation at the buried interface.



Figure 3. a) NEXAFS results for top surface of a PCDTPT film coated at 0.2 mm/s as a function of azimuthal angle ϕ at normal incidence. 0° corresponds to the in-plane *E*-field perpendicular to the blading direction. b) summary of the azimuthal dependence of the NEXAFS signal for the π^* manifold for both the top (open) and bottom (closed) of the film. Lines are fits to the form A+ B $\cos(\phi-\phi_0)^2$.

The NEXAFS, UV-vis and TFT data are simply reconciled by the hypothesis that films at 0.2 mm/s have a vertical gradient in in-plane order, with the highest alignment at the air interface and essentially no anisotropy at the buried, gate-dielectric interface. Under these conditions, the bulk average anisotropy (UV-vis) will be weaker than the NEXAFS at the top, and the TFT anisotropy (negligible) will correspond to the NEXAFS bottom alignment.

PCDTPT On Patterned Substrates. Experiments were repeated on nanopatterned (grooved) substrates. Atomic force microscopy (AFM) studies of substrates (S2) unidirectionally abraded with 100 nm nanodiamond lapping film indicate shallow features (≲5 nm depth) compared to the gate dielectric thickness (≥200 nm) that are dilute (≈1 groove per 50 nm) consistent with earlier reports.^{12,24} Due to the intrinsic orientation resulting from blade-coating, one needs to define four possible sample conditions (see Scheme 1). The nanogroove orientation can be along the TFT channel or across the TFT channel and the coating direction either parallel to the TFT channel or perpendicular to the TFT channel. Shown in Figure 4 is the summary of the extracted saturation regime mobility for all 4 conditions, for deposition in both the slow, evaporative regime (0.2 mm/s) and the fast, L-L regime (20 mm/s). UV-vis measurements (S3) indicate that the transition from evaporative to L-L regimes does not vary significantly with the relative alignment of the coating direction with the nanogroove direction. Also shown in Figure 4 is the summary of the results on unpatterned substrates for ease of comparison. As with the unpatterned substrates, there is no significant correlation between the blade-coating direction and the extracted mobility. However, as reported with tunnel drying^{12,24,41} there is a significant correlation between the orientation of the nanogrooves and the saturation regime mobility, R_{μ} =0.91±0.01 with *R* defined as $\frac{\mu_{along} - \mu_{across}}{\mu_{along} + \mu_{across}}$ (error bar the standard deviation of the mean of measurements on 6 device pairs). Note that there is a dramatic increase in the mobility when the nanogrooves are in the along direction relative to the unpatterned substrate: the average improvement is 5x for the 4 conditions (fast, slow, perp, para). This significantly exceeds the 2x expected for a simple orientation effect relative to an isotropic case (vide infra), implying that the nanogrooving influences both the local structure and the alignment. While the mobility strongly correlates to the nanogroove orientation, there is only a weak dependence, at best, on the relationship between mobility and blade speed, similar to the unpatterned case. The \approx 20 ratio of along versus across mobility reflects both the 5x increase in mobility vs. unpatterned for the along case and a 4x decrease in mobility for the across case.



Figure 4. Summary of saturation mobility extracted from (80 and 100) μm channel length devices fabricated by blade coated deposition of PCDTPT as a function of both substrate patterning and blade coating orientation. Schematic 1 defines the patterning notation: along, across, and coating notation: perp and para. Error bars are range of measurements for (80 and 100) μm long channels. Representative output curves for the 12 conditions are presented in S4.

The high mobilities observed in the nanogrooved along case can challenge contact injection and give rise to non-ideal device characteristics. Shown in Figure 5 are the transfer and output characteristics of the best device (saturation mobility $5.6 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, channel length $100 \,\mu\text{m}$). While exhibiting slight hysteresis, the output curves show little evidence of contact effects. Shown as an inset to Figure 5 is the channel length dependence of the saturation mobility. The decrease in saturation mobility with decreasing channel length (increasing current density) is suggestive of contact resistance limitation for the shorter channel devices. The transfer curve exhibits a voltage threshold greater than the voltage turn on in the output curve, indicating a nonideal device. Shown in supplemental are fits of the output characteristics to both the simple gradual channel approximation(S5a) and the unified model of Marinov, et al.⁴² (S5a) that suggest a weak V_{GS} dependence of the mobility.

In studies of tunnel dried devices, saturation mobilities in excess of 20 cm²V⁻¹s⁻¹ have been reported, based on the low gate voltage region of the saturation transfer curve.^{24,41} This remarkable transconductance was associated with significant device hysteresis and possible channel charging.⁴³ The interpretation of transconductance for nonideal devices is complex, as discussed by multiple

authors.^{44,45} In this work (that differs from the tunnel dying studies in both deposition technique and in channel treatment) very little hysteresis and no gate-bias stress were observed.



Figure 5. Top: I-V output curve for a PCDTPT device, coated at 0.2 mm/s on a nanogrooved substrate in the across, perp configuration with 100 μ m channel length and 200 nm gate oxide thickness. Bottom: transfer curve and $\sqrt{I_{SD}}$. Also shown is the region used for linear fit to saturation mobility. Inset: saturation mobility vs channel length.

NEXAFS measurements were recorded on the 6 conditions summarized in Figure 4 (fast and slow deposition, coating direction para and perp, nanogrooves along and across) for both the top and bottom (revealed by parylene delamination) of the films. Figure 6 summarizes the anisotropy at normal incidence R_{NEXAFS} and the corresponding bottom gate mobility anisotropy R_{μ} for films coated at both (0.2 and 20) mm/s. The top of all films coated in the slow, evaporative regime exhibit high in-plane alignment, independent of the bottom, nanogroove orientation. The top of the films coated in the L-L-regime exhibit little anisotropy, consistent with Figure 1. In both coating regimes, the bottom is isotropic in the absence of nanogrooves and highly anisotropic on structured substrates. In all cases, the mobility anisotropy has the same sign as the bottom NEXAFS anisotropy, independent of top film order. Also note that, in general, the mobility in the across condition, relative to the unpatterned case, may arise from factors beyond the intrinsic anisotropy of the film mobility. Specifically, some decrease in mobility may be due to the typical decrease seen for rough dielectrics.⁴⁶



Figure 6. Comparison of anisotropy factors: *R* for the top and bottom interfaces of PCDTPT films, as determined by NEXAFS, and TFT saturation mobility. Top row, films coated at 0.2 mm/s, in the evaporative regime, bottom row, films coated at 20 mm/s in the Landau-Levich regime. Error bars on NEXAFS are 1 σ derived from fits to ϕ dependence, on μ are range from duplicate measurements.

The nanogroove induced alignment of the blade coated films clearly has significant impact on the bottom gate TFT performance, making the devices extremely anisotropic and producing significant (>5x) improvement in the maximum mobility relative to the isotropic devices. We have attempted top gate measurements to assess the influence of the blading induced alignment on mobility. Details are provided in the supplemental (S6). In general, the devices were non-ideal and poorly reproducible. Top gate (bottom contact) devices exhibit moderate mobility anisotropies (R \approx 0.4), less than observed for NEXAFS (R of 0.5 to 0.8). Importantly, the extracted saturation mobilities were significantly lower ($\leq 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-2}$) than observed for bottom contact devices, suggesting a nonideality in the device fabrication. High, anisotropic mobilities have been obtained in top gate devices for other polymer systems deposited by wire bar¹⁶ and flexible blade⁴⁷ techniques.

CDTBTZ. We have performed analogous measurements on the similar, high performance polymer CDTBTZ (see scheme 1). Like PCDTPT, UV-vis studies indicate the two coating regimes: evaporative and Landau-Levich can be accessed over the blade speed range of (0.2 to 40) mm/s (**S7**). Like PCDTPT, the chain alignment in the evaporative regime is perpendicular to the coating direction. Unlike PCDTBT, the alignment does not flip with increasing speed, but only monotonically decreases. Mobility and NEXAFS results are summarized in Figures 7 and Fig. 8. In general the results are very similar to those of PCDTPT. Bottom contact devices with no nanogrooves exhibit no significant mobility anisotropy, even though the top of the films exhibit significant alignment. Nanogrooved bottom contact devices exhibit significant mobility anisotropy and a significant increase in the maximum mobility. In contrast to PCDTPT, the unfavourable mobility on nanogrooved substrates is not significantly lower than that for the ungrooved case.



Figure 7. Summary of saturation mobility extracted from (80 and 100) μ m channel length devices fabricated by blade-coated deposition of CDTBTZ as a function of both substrate patterning and blade coating orientation. Notation and error bars as in Figure 4.



Figure 8. Comparison of anisotropy factors: R for the top and bottom interfaces of CDTBTZ films, as determined by NEXAFS, and OTFT saturation mobility. Top row, films coated at 0.2 mm/s, in the evaporative regime, bottom row, films coated at 20 mm/s in the Landau-Levich regime. Error bars as in Figure 6.

Origin of Alignment. For the two systems studied, PCDTPT and CDTBTZ, we have clear evidence for alignment via two independent mechanisms: coating induced alignment, originating at the air interface

of the drying film, and nanogroove alignment originating at the structured substrate interface as indicated in Figure 9. For the films studied, both bottom gate TFT performance and interface sensitive NEXAFS indicate that the two alignment mechanisms do not significantly interact, implying a short vertical persistence length (vide infra). Alignment of liquid-crystalline molecules,^{48–50} single polymer systems,^{11,15} and block copolymer phase structures due to graphoepitaxy (substrate topology)^{51,52} is well studied. In the following, we will focus on the coating induced alignment.



Figure 9. Three cases of vertical orientation gradients observed in the evaporative coating regime. I: oriented top (chains perpendicular to coating direction) random bottom on un-grooved substrates. II: oriented top, perpendicularly oriented bottom on nanogrooved substrates ("along"). III: oriented top, co-oriented bottom on nanogrooved substrates ("across"). Diagram indicates edge on chain conformations, consistent with GIXD (vide infra).

Polymer chain alignment due to shear in concentrated melts (extrusion^{53,54}) and dilute solutions (extensional flow^{55,56}) is well established. However, in the present system, it is clear that the maximum alignment occurs at low coating speeds, in the evaporative regime, where coating induced shear is a minimum. It is also clear that the alignment mechanism is such that the chain axis is perpendicular to any shear field, incompatible with extensional flow. We have performed detailed in-situ optical measurements during film drying to provide additional insight into the coating mechanism. Using a glass substrate that has been metalized (AI) on one half, we simultaneously recorded near-normal incidence reflection spectra, to derive film thickness, and normal incidence transmission spectra. The transmitted light was split by a polarizer into two channels, parallel and perpendicular to the coating direction, to derive film anisotropy. Shown in Figure 10 are representative data for coating PCDTPT at 0.2 mm/s on an unpatterned substrate. Passage of the blade is clearly seen in the transition from an optically thick film (the solution bead under the glass blade) to the thin coated film that supports interference fringes. Blade passage is defined as +1 s. Coating in the evaporative regime, the strong gradient in film thickness through the meniscus (dropping from 200 μ m to \approx 1 μ m in about 2 s (\approx 0.4 mm) prohibited measurement of the meniscus profile. What is observed ≈50s after blade passage is the drying of the deposited oDCB enriched film. Because a mixed solvent (3:1 CF:oDCB) is employed, CF evaporation dominates in the meniscus, leaving an essentially pure oDCB film at a nominally initial concentration of 16 mg/mL after meniscus passage. Virtually identical results are obtained with CDTBTZ (see S8)



Figure 10 In-situ optical characterization of coating of PCDTPT at 0.2 mm/s on an unpatterned substrate. a) Absorbance₁₀ for *E*-field parallel to the coating direction. b) Absorbance₁₀ for *E*-field perpendicular to the coating direction. c) R_{UV-vis} d) Normal incidence reflection e) Integrated anisotropy (*R*) and film thickness, t f) typical reflection spectra at early times (2.25 s after blade passage) and when film is dry.

While the coating induced film anisotropy maximizes in the evaporative regime, from Figure 10e it is clear that the kinetic development of most of the anisotropy occurs long after the meniscus passes. In fact, the sharp increase in film anisotropy begins \approx 50 s after meniscus passage, when the film is only \approx 2x the final dry thickness, i.e., when the volume fraction of dry material is \geq 0.5. What is also clear in Figure 10 is that immediately after meniscus passage, there exists a small, *R*_{abs}≈0.05, anisotropy. This strongly suggests that the development of order in the evaporative coating regime is very similar to the development of order in blade coated poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (pBTTT).¹³ For pBTTT, "reverse coating" from a similar mixed solvent resulted in weakly anisotropic films. However, brief heating of the film into the melt state resulted (upon cooling) in highly anisotropic films (with the chain axis perpendicular to the coating direction). This was attributed to selective melting, leaving a surface rich with oriented seeds, combined with crystallization mediated by the thermotropic liquid-crystal phase of pBTTT. For PCDTPT, we propose that a surface, rich with oriented seeds created in the meniscus, templates a similar bulk ordering as the solution passes through a lyotropic liquid-crystal phase. A previous study of PCDTPT has suggested that it does not exhibit a lyotropic phase;⁵⁷ however, oDCB was not studied, and the solution concentrations were not in the relevant, 0.5 volume fraction range. In classic studies of polymers with rigid segments, the critical concentration for a lyotropic phase is determined mostly by the segment anisotropy and is relatively independent of both molecular weight and interaction parameter.⁵⁸ Critical volume fractions of ≈ 0.5 imply segment anisotropy (diameter/tube-length) of \approx 0.2. If we assume the diameter is the mean of the lamella (2.5 nm) and π - π (0.35 nm) distances of the crystal (vide infra), an anisotropy of 0.2 implies a tube-length of \approx 3 chain repeats.

While the maturation of the alignment appears to occur via a lyotropic phase, late in the film drying, the critical alignment "seed" develops in the meniscus. For the pBTTT system cited earlier, the observation of the polymer c-axis perpendicular to the coating direction was attributed to alignment of π -stacked "kabob" aggregates (aggregate long axis perpendicular to the c-axis) with the aggregate long axis parallel to the coating direction. For both PCDTPT^{12,41} and CDTBTZ,⁵⁹ literature (and supplemental AFM, **S9**) indicate that fibrillar aggregates are formed, but with the c-axis parallel to the long axis of the fibril ("shish"). This suggests the mechanism for order is that fibrils formed at the meniscus-air interface, during the rapid evaporation of the CF (possibly aided by both evaporative cooling and Marangoni mass transport) orient with their long axis perpendicular to the blading direction. It should be noted that in the solution coating of carbon nanotubes (CNTs), the tubes often adopt an orientation parallel to the meniscus front (perpendicular to the coating direction) presumably due to wetting interactions at the CNT, air, solution interface.^{60,61}

We have characterized the kinetics of the anisotropy development for the 12 conditions characterized above (PCDTBT and CDTBTZ; slow and fast deposition; unpatterned, grooved along and grooved across) with the results in the supplementary material (**S10**). In all cases, the development of the majority of the anisotropy occurs very late in the film drying process, well after the passage of the meniscus. Of particular note is the behaviour when coated in the evaporative regime on a grooved along substrate, resulting in perpendicular orientations at the air and buried interfaces, shown in Figure 11. At early times, the weak (0.05) anisotropy established in the meniscus is observed. Then there is a *decrease* in anisotropy, as the bottom of the film, templated by the grooves, begins to order, that is overtaken by the later maturation of the anisotropy of the top of the film, resulting in a weak net alignment, slightly favouring the alignment induced by the coating over that of the substrate. However, the substrate induced ordering occurs slightly *sooner* than that of the film surface, consistent with more effective

templating of order by the nanogrooves than the coating induced seed fibrils. The final degree of alignment at both interfaces will arise from a complex interplay between "seed" density/efficiency and vertical gradients in both solvent concentration and temperature due to evaporation.



Figure 11. Real-time evolution of the anisotropy parameter R_{abs} for PCDTPT coated at 0.2 mm/s on a substrate with nanogrooves parallel to the coating direction. Variation in both the distance to the measurement point and the final film thickness resulted in a later drying transition than in Figure 10.

The observed air interface alignment of the fibrillar axis is consistent with recent studies of blade-like coating by Patel *et al.* for PCDTPT in chlorobenzene solutions on unpatterned and nanogrooved substrates.⁴⁰ Due to constraints of the poor wetting of the solution on the hydrophobic substrate, they were unable to perform a detailed coating speed study to establish the evaporative and Landau-Levich regimes. However, when coating at 0.03 mm/s at room temperature that should be well in the evaporative limit, they found a high degree of alignment at the air interface, with the chain axis perpendicular to the coating direction, in accord with our mixed solvent results.

The observation of chain alignment perpendicular to the coating direction is in contrast to recent studies by Schott, et al.⁴⁷ and Shaw, et al.⁶² that have reported alignment in diketopyrole based polymers consistent with chain extension, not fibrillar alignment. Schott et al. used a novel, flexible blade coater, and Shaw et al. used a low angle coater very similar to that used in the current report. Both groups report high levels of anisotropy based on UV-vis, with the anisotropy maximizing at low blade speeds: $\approx 0.1 \text{ mm/s}$ for Schott et al. and 0.25 mm/s for Shaw et al. Both groups coated at elevated temperatures that would favour disaggregated polymers, and assure the adopted speeds were in the evaporative regime. Shaw et al. achieved UV-vis dichroic ratios of $\approx 7 (R_{UV-vis} \approx 0.75)$. However, bottom-gate transistors exhibited negligible transport anisotropy, suggesting that, as in this paper, anisotropy nucleated at the air interface. In contrast, Schott et al. report a mobility anisotropy of $\approx 14 (R_{UV-vis} \approx 0.875)$. This was attributed to a *reduction* in anisotropy at the air interface, relevant to the top gate transistors employed. The favourable mobility in the most oriented films: $\approx 5 \text{ cm}^2 \text{V}^-1\text{s}^{-1}$ was only $\approx 2\text{x}'$ s the mobility of isotropic films $\approx 2.4 \text{ cm}^2 \text{V}^-1\text{s}^{-1}$.

Influence of Alignment on Film Microstructure. Of particular note for the PCDTPT and CDTBTZ nanogrooved devices is the radical (>5x) improvement in aligned mobility over the unaligned system. Similar improvements have been reported for tunnel drying on nanogrooved substrates.¹² When

contrasted with the weaker ≈2x improvement observed by Shaw et al. (vide supra) and by O'Conner et al.²⁰ for strain oriented poly(3-hexylthiphene-2,5,diyl) (P3HT), one is lead to propose that the nanogrooves must, in addition to providing net alignment, serve to change the transport-critical microstructure of the channel region. The extreme vertical gradients in the in-plane order of the fashioned films (recall Figure 9) challenges the development of detailed structure-function relationships based on nominally bulk techniques (UV-vis, FTIR, GIXD). We will focus on two coating conditions: slow coating (0.2 mm/s) on a nanogrooved substrate with grooves perp to the coating direction, which results in homogeneous orientation between the top and bottom (Figure 9 III), and fast coating (20 mm/s) on unpatterned substrates which results in isotropic orientations on the top and bottom.

Shown in Figure 12 are GIXD images for CDTBTZ in the two (fast-UN and slow perp) coating cases and for PCDTPT in the oriented (slow-perp) case. For each film, data is recorded with $k_{//}$ (component of the incident X-ray momentum in the surface plane) either parallel or perpendicular to the coating direction. Complete GIXD results are shown in S12. In all cases, a high degree of edge-on local order is suggested by the appearance of 5 orders of the (00l) lamella diffraction along q_z , the distinct π - π diffraction (020) in the q_y plane, and multiple apparent cross-peaks. The fast-UN film is isotropic, as evidenced by the lack of anisotropy in the (020) feature in the q_y plane (see S13 for quantitative analysis), consistent with the minimum UV-vis, TFT and NEXAFS anisotropy. The significant azimuthal alignment of the slow-perp film is reflected in strong anisotropy of the in-plane (020). The alignment of the polymer c-axis *perpendicular* to the coating direction is confirmed by the strong (020) scattering with $k_{//}$ across the coating direction. Quantitative analysis of the in-plane order (S13) on the patterned

substrate suggests a bimodal distribution, with the angular full-width of the primary aligned component less than the 20° sampling resolution.



Figure 12 GIXD images for X-ray $k_{||}$ along (left) and across (right) the coating direction for top: CDTBTZ at 20 mm/s on an unpatterned substrate, middle CDTBTZ at 0.2 mm/s with grooves perp to coating direction and bottom, PCDTPT at 0.2 mm/s with grooves perp to coating direction. Schematic indicates direction of X-ray beam with respect to polymer stacking and coating direction.

The high degree of local order evident in Figure 12 suggests high absolute crystallinity (high volume fraction of crystalline regions); however, assessment of absolute crystallinity from diffraction is difficult. We have attempted to gauge the absolute crystallinity via comparison of the diffraction to that of pBTTT. pBTTT is considered nearly comprehensively crystalline⁶³ when processed through the thermotropic liquid crystalline (LC) phase.⁶⁴ Comparison of the normalized intensity of the pi-pi diffraction in the surface plane of both isotropic and aligned films of CDTBTZ-C16 and pBTTT-C16 (**S14**) indicates that, assuming similar structure factors, the two system exhibit quite comparable crystallinity. This indicates that both PCDTPT and CDTBTZ films are highly crystalline. This is notable in light of the

absence of reported melting endotherms in either polymer.^{22,23} The high crystallization is consistent with passage through a lyotropic phase (*vide supra*). Nearly comprehensive crystallinity is additionally supported by dark field TEM images (**S16**) that imply uniform crystal diffraction over \approx 91% of the film. A high degree of crystallinity is also supported by recent mechanical measurements of PCDTPT.⁶⁵ PCDTPT exhibits a very low cohesive fracture energy and crack onset strain, very similar to pBTTT and at significant odds with the ductile behavior of more semicrystalline polymers, such as P3HT.

A characteristic of the reference polymer pBTTT is interdigitation of the nominally all trans sidechains.⁶⁶ PCDTPT and CDTBTZ have similar sidechain density (but a distinctly different attachment configuration). We have performed detailed, polarized FTIR studies of both polymers (see **S15** and discussion). Based on the methylene asymmetric stretch frequency, we find that the side chains are in a disordered (liquid-like, collapsed) state. This, combined with the significantly larger lamella repeat distance: 2.6 nm compared to C16-pBTTT, 2.34 nm,⁶⁶ suggests that there is no interdigitation in the two polymers.

Returning to the GIXD there are no statistically relevant correlations between crystal structural parameters and processing, as detailed in Table 1. The slow coated films on nanogrooved substrates do have a slightly longer, (25 ± 6) %, (001) coherence length (error bar is standard deviation of the mean). This may, however, simply reflect the greater thickness of the films (see Figure 1). Note that, in all cases, the (001) coherence length is ≤ 20 nm, less than the film thickness. This is consistent with the observation of limited alignment persistence lengths and nominally independent orientation of the top and bottom interfaces (*vide supra*).

Polymer	Coating	X-ray	Q _z (001)	ΔQz	Lz	Q _x (020)	ΔQx	Lx
	Condition	k	Å-1	Å-1	nm	Å⁻¹	Å-1	nm
CDT-BTZ	20 mm s ⁻¹	Perp	0.242	.045	14.	1.79	.11	5.7
	ungrooved	Para	0.240	.043	15.	1.79	.12	5.2
CDT-BTZ	0.2 mm s ⁻¹	Perp	0.243	.036	17.	1.79	.094	6.7
	grooved-perp	Para	0.244	.031	20.	1.78	.12	5.2
PCDTPT	20 mm s ⁻¹	Perp	0.244	.037	17.	1.77	.13	4.8
	ungrooved	Para	0.244	.034	18.	1.78	.14	4.5
PCDTPT	0.2 mm s ⁻¹	Perp	0.244	.027	23.	1.77	.12	5.2
	Grooved-perp	Para	0.246	.033	19.	1.77	.12	5.2

Table 1 Summary of GIXD characteristics. Q is momentum space position of the diffraction feature, ΔQ the full-width at half-maximum, L the coherence length from the Scherrer approximation.

The lack of any significant correlation between crystallinity or crystal domain structure and deposition conditions and thereby mobility is consistent with the hypothesis that, due to the presence of a lyotropic phase, all the films are highly crystalline, thus crystallinity cannot change significantly. However, GIXD characterizes the 'bulk' of the thin film, and the BGBC transistor performance is dominated by a thin (≈ 2 nm) layer at the gate interface.⁶⁷ Thus it is possible that the morphological origin of the improved performance is masked in the GIXD measurement. The partial electron yield NEXAFS measurements are surface sensitive and can provide insight into the buried interface as revealed by delamination. In addition to characterization of the azimuthal order (*vide supra*), angle of incidence NEXAFS measurements were performed, providing insight into the alignment of the normal of the conjugated backbone with respect to the surface normal. Shown in Figure 13 are typical results. For biaxial films, care must be taken in analysing the orientation distribution, as the polar and azimuthal distributions are convolved. As described by Weiss et al.,⁶⁸ and detailed in the supplemental, combining NEXAFS measurements in two configurations (such as Figure 3 and Figure 13) allows extraction of the usual uniaxial orientation factor: S=3nn-1=1/2(3<cos² θ >-1) and the biaxial orientation factor *P*=IImm=3/2(<sin² θ sin² φ >-<sin² θ cos² φ >) with θ the polar angle between the TD and the surface normal, ϕ the in-plane azimuthal angle, II, mm, nn are the orientation averages of the x, y, and z TD projection products. *S* varies from -1/2 for a perfect edge-on orientation and 1 for perfectly face-on. *P* varies from +/- 1.5. P is simply a rescaled R_{NEXAFS}. Derived *S* for the 24 conditions studied are summarized in Table 2. We also include the tilt angle of the TD from the normal, assuming <cos²> is represented by a delta-function. From *S*, we see that, consistent with the GIXD, the polymer chains are highly edge-on (TD near 90°). Unlike GIXD, NEXAFS reflects all material (crystalline and amorphous). The deviation of the TD from 90° can indicate a distribution in conjugated plane orientations, or suggest that the conjugated plane exhibits a distinct slip/tilt, as has been calculated for both P3HT⁶⁹ and pBTTT.⁷⁰ From Table 2, we see no significant variation in the S parameter for films coated on ungrooved substrates vs nanostructured substrates.



Figure 13. a) NEXAFS results for top surface of PCDTPT as a function of angle of incidence, θ . b) Summary of the polar angle dependence of the π^* manifold.

Table 2. Orientation	parameter S d	lerived from I	NEXAFS
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	No g			Groove along blade direction		Grooves perpendicular to blade direction	
		S [1]	θ	S	θ	S	θ
PCDTPT	Тор	38 ±.04	74°	29 ±.04	68°	41 ±.09	76°
0.2 mm/s	Bottom	$22 \pm .02$	64°	$24 \pm .02$	65°	$38 \pm .01$	74°
20 mm/s	Тор	$36 \pm .01$	72°	$21\pm.02$	64°	$25 \pm .02$	66°
	Bottom	$36 \pm .01$	72°	$26 \pm .03$	66°	$43 \pm .06$	77°
CDTBTZ [2]	Тор	$38\pm.09$	74°	$27 \pm .06$	67°	$30 \pm .12$	68°
0.2 mm/s 20 mm/s	Bottom	$34 \pm .05$	71°	$\textbf{28} \pm \textbf{.06}$	67°	$32 \pm .06$	69°
	Тор	$40 \pm .01$	75°	$40 \pm .01$	75°	$38 \pm .02$	74°
	Bottom	$29 \pm .01$	68°	$21 \pm .06$	64°	$27 \pm .09$	67°

1. Error bars are the standard uncertainty based on the nonlinear-least-squares fit, Except for CDTBTZ at 0.2 mm/s

2. Error bars are the range of measurements on independent films at the NSLS and Australian synchrotrons, indicating that film-to-film variation dominates the total uncertainty.

Implications on Transport and Conclusions. Structure-function relationships for polymer-based TFTs begin with acknowledgement that the microstructure (and transport) are heterogeneous. The most commonly adopted models identify regions of fast transport (crystalline regions,⁷¹ segments with low torsional disorder,⁷² etc.) separated by transport bottle necks (amorphous regions,⁷² interchain junctions,⁷³ etc.). In the simplest model for transport in anisotropic morphologies¹¹ one accounts only for alignment of the fast transport regions with a characteristic length L. Using the Einstein relationship between mobility and diffusion coefficient and assuming the transport bottle neck is unaffected by alignment, the result Is:

 $\frac{\mu_{||}}{\mu_{\perp}} = \frac{L^2 \langle \cos^2 \phi \rangle}{L^2 \langle \sin^2 \phi \rangle \langle \cos^2 \Theta \rangle}$

where ϕ is the in-plane azimuthal angle and Θ is the polar angle of the chain axis (fast transport direction). For a system with high polar order, $\langle \cos^2 \Theta \rangle \approx 1$ and $R_{\mu} \approx R_{UV-vis}$. It should be noted that in this theory, while the mobility anisotropy can diverge as $\mu_{\perp} \rightarrow 0$, the favourable mobility $\mu_{||} \propto \mu_0 \langle \cos^2 \phi \rangle$ will only increase a factor of 2 ($\langle \cos^2 \phi \rangle = 1$) over the isotropic case ($\langle \cos^2 \phi \rangle = 1/2$). It is in this context that the ≈ 5 times increase in μ for nanostructured substrates is remarkable.

All available structural metrics indicate no significant differences in morphology (crystal structure, degree of crystallinity, out-of-plane orientation) between the isotropic films (\approx 20 mm/s blade speed, unpatterned substrate) and comprehensively ordered (\approx 0.2 mm/s blade speed, nanogrooves along the transport direction, coating direction perp to the transport direction). This brings to the fore the severe challenge of developing structure-function relationships in organic semiconductors: the rate-limiting (critical) regions represent a dilute fraction of the material to which current characterization tools are often blind. We propose that the 5 times improvement lies not in a change of μ_0 , the mobility in the fast regions, but lies in the preceding assumption that the transport bottlenecks are unaffected by alignment. For semicrystalline polymer films, it is generally accepted that tie-chains between crystalline

regions dominate the transport in the amorphous regions.⁷³ It is thus likely that the improvement in total mobility comes from improved tie-chain transport, due to net alignment in the amorphous regions, as indicated in Scheme 2. Theoretical studies of transport in polythiophenes indicate significantly improved transport for nominally extended tie-chains.⁷⁴ This is consistent with earlier studies of anisotropic transport in strain aligned P3HT transistors.⁷⁵



Scheme 2. Proposed relationship between average order in crystalline regions and alignment of tiechains in amorphous regions.

By combining detailed device, structural, and in-situ measurements of the blade coating of PCDTPT and CDTBTZ we develop a comprehensive understanding of the film evolution and morphology. Coating driven alignment clearly develops at the air interface, likely via templating of a lyotropic phase by coating developed nuclei. The resultant vertical gradients in the alignment appear to be a common feature of aligned thin films. The lyotropic phase that facilitates alignment also appears to facilitate significant crystallinity, consistent with the high mobilities of the material sets. The local order, judged primarily by NEXAFS and GIXD, of both isotropic and aligned films is remarkably similar indicating that the significant improvement of device performance is related to changes in the crystal interphase regions.

ASSOCIATED CONTENT

Supporting Information

Additional figures and tables as described in the text. This material is available free of charge via the Internet at htt://pubs.acs.org

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Author Contributions

DW and MK contributed equally and performed coating optimization and device measurement. HWR

performed AFM, SE in situ measurements, RJK GIXD, DF, DD, EG, LT, CM NEXAFS. LR oversaw experimental design, analysis, and writing. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest

ACKNOWLEDGEMENTS

DW acknowledges a National Institute of Standards and Technology(NIST)/Montgomery College fellowship. MK acknowledges a NIST-Summer Undergraduate Research Fellowship (SURF). C.R.M. acknowledges support from the Australian research Council (DP130102616). We thank Oleg Kirillov for preparation of the BCBG substrates, and fabrication of the BGTG shadow masks. We thank Brendan O'Connor (NCSU) for the aligned pBTTT GIWAXS data. Portions of this research were carried out at the Stanford Synchrotron Radiation Laboratory (SSRL), a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences. We thank R.J. Kline for acquisition of GIWAXS data at SSRL. Additional parts of this research were undertaken at the Soft X-ray beamline of the Australian Synchrotron, part of the Australian Nuclear Science and Technology Organisation and beamline 7.3.3 at the Advanced Light Source, supported by the Director of the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. We also acknowledge use of the 7.3.3 sample-exchanging robot, which was supported by the Joint Center for Artificial Photosynthesis (JCAP) and DOE. Support at beam line 7.3.3 was provided by Eric Schaible and Polite Stewart.

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Supplemental Material for

Blade Coating Aligned, High-Performance, Semiconducting-Polymer Transistors

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S1. Image of combinatorial bottom gate OTFT electrode. Kinks in image are stitching errors in image acquisition software. Channel width for channel lengths (5 to 100) μ m is 1 mm.



S2. AFM images of a typical, 5-pass, nanostructured substrate: left (5 x 5) μ m image, right (1 x 1) μ m image. Also shown a typical line profile indicating shallow (\approx 1 nm) features.



S3. UV-vis anisotropy and average absorbance for PCDTPT films coated on unpatterned and nanogrooved substrates with coating direction along grooves (air and buried alignments crossed at low speeds), and coating across grooves (air and buried alignments parallel at low speeds).



S4. Output curves for 1mm wide, 100 μ m long channel, 300 nm gate oxide, BCBG, PCDTPT devices for the 12 conditions reported in Figure 4.



S5a. Top, fit of the output curve of Figure 5 (100 μ m channel length, 1 mm channel width, 200 nm gate oxide thickness, BCBG) to the simple gradual channel approximation:

$$\begin{split} I_{D} &= \frac{W \ \mu \ C}{L} \left((V_{GS} - V_{TH}) V_{DS} - \frac{V_{DS}^{2}}{2} \right), \qquad V_{DS} \ni |I_{D}| < |I_{sat}| \\ I_{D} &= I_{sat} = \frac{W \ \mu \ C}{2L} ((V_{GS} - V_{TH})^{2}), \ elsewhere. \end{split}$$

Best fit parameters are μ =(3.4±0.1) cm²V⁻¹s⁻¹, V_{TH}=-(4.9±0.8) V. The lower value of μ from the gradual channel fit, relative to the 5.6 cm²V⁻¹s⁻¹ from the fit to the transfer curve is reflective of the large apparent V_{TH} in the transfer data.



S5b. Top, fit of the output curves of Figure 5 (100 μ m channel length, 1 mm channel width, 200 nm gate oxide thickness, BCBG) to the unified TFT model of Marinov, et al.¹ that allows for a V_{GS} dependent mobility across the channel, of the form

$$\mu(x) = \frac{\mu_0}{4} \left\{ \frac{-[(V_{GS} - V_T) - V(x)]}{V_{aa}} \right\}^{\gamma}$$

Where we have set V_s=0.

Shown in the inset is V_{GS} dependent mobility. Shown in the lower panel is the *predicted* transfer characteristic from the fit to the 7 ($V_{GS} \in \{0, -10, -20, -30, -40, -50, -60\}V$) output curves. Note the simple power law does not fully capture the delayed turn on of the transfer curve. Proper attribution of the origin of the non-ideal transfer curve requires more detailed analysis.

Top Gate Devices were fabricated using a combinatorial shadow mask set that allowed transistors with two channel lengths (50 and 100) μ m and both orientations (across and along) to be tested with one film deposition. Evaporated bottom Au contacts were used with a 1100 nm thick (determined by ellipsometry) Cytop gate dielectric and Al gate.



S6a. Fabricated top gate device array. Channel lengths of both (50 and 100) μm are present.

Thinner gate dielectrics exhibited failure due to gate-contact shorts. However, the thick dielectric typically did not exhibit good saturation prior to dielectric breakdown. I-V curves, in general, were highly varied, exhibiting both significant threshold shifts and severe injection non-idealities. Shown in Fig S6b are the output curves obtained for the best-behaved device chip. The saturation mobility for the 12 displayed devices is reported in Table S1

Table S1 Bottom contact, Top gate mobilities. Uncertainties are one standard deviation of the mean.

	Perpendicular	Parallel	
Average μ/(cm ² V ⁻¹ s ⁻¹)	0.13+/-0.03	0.07+/-0.01	

The normalized mobility anisotropy R=-0.3+/-0.1. The high mobility devices are oriented such that the channel direction is perpendicular to the coating direction, such that the oriented chains are long the channel direction. Note that the magnitude of the mobility is significantly less than observed for bottom contact devices.



S6b. Output characteristics for the highlighted 12 adjacent top gate, bottom contact, PCDTPT 0.2 mm/s devices. The cytop dielectric thickness was 1100 nm; a dielectric constant of 2.05 was used in extraction of the saturation mobility.



S7. UV-vis anisotropy and average absorbance for CDTBTZ films coated on an unpatterned substrate. Uncertainties are range for two independent runs.



S8 in-situ optical characterization of coating of CDTBTZ at 0.2 mm/s on an ungrooved substrate. a) Aborbance₁₀ for E-field parallel to the coating direction. b) Aborbance₁₀ for E-field parallel to the coating direction. c) Absorbance based R d) Normal incidence reflection e) Integrated anisotropy (R) and film thickness. f) typical reflection spectra at early times and when film is dry.

PCDTPT, 0.2 mm/s nogroove, para, perp



S9 Summary in-situ UV-vis anisotropy results for all coating conditions of both polymers. Anisotropy results derived from average absorbance between (550 and 850) nm wavelength.

PCDTPT 0.2 mm/s no groove, para, perp











0.0

Height Sensor

0.0

PCDTPT 20 mm/s nogroove, para, perp



CDTBTZ 0.2 mm/s nogroove, para, perp

2.0 µm



S10 AFM studies of top surface of PCDTPT and CDTBTZ films coated under various conditions. For each series: top row topography, bottom row phase. Also shown are FFTs of the images. The narrow direction of the FFT corresponds to the long direction of the underlying fibral texture. Coating direction bottom to top in all cases



S11a Summary of NEXAFS polar scans for PCDTPT films. All data acquired at the Australian Synchrotron. The 4 character notation string is P (S|F) (N|A|P) (T|B) for PCDTPT (0.2 mm s⁻¹|20.mm s⁻¹) (nogrooves| grooves along channel|grooves perp to channel) (top|bottom). Thus, PSNT is PCDTPT, coated at 0.2 mm s⁻¹ on an unpatterned substrate, top surface.



S11b Summary of NEXAFS polar scans for CDTBTZ films. Data for 0.2 mm/s films acquired at NSLS. The 4 character notation string is C (S|F) (N|A|P) (T|B) for CDTBTZ (0.2 mm s⁻¹|20.mm s⁻¹) (nogrooves|grooves along channel|grooves perp to channel) (top|bottom). Thus, CSNT is CDTBTZ, coated at 0.2 mm s⁻¹ on an unpatterned substrate, top surface.

Following the development of Weiss² and neglecting 'pre-tilt' the film can be assumed to be of C_{2v} symmetry, the film frame is the lab frame and the Saupe matrix is

$$\vec{Q} = \begin{bmatrix} -\frac{S+P}{2} & 0 & 0\\ 0 & -\frac{S-P}{2} & 0\\ 0 & 0 & S \end{bmatrix}$$
 Eq. S1

In the film frame, the electric fields for the three canonical NEXAFS measurement configurations (k, X-ray wavevector: k// along coating direction, k// perpendicular to coating direction, k normally incident to the film) are

$$p_{along}: \begin{bmatrix} Sin[\theta] \\ 0 \\ Cos[\theta] \end{bmatrix} p_{perp}: \begin{bmatrix} 0 \\ Sin[\theta] \\ Cos[\theta] \end{bmatrix} p_{norm}: \begin{bmatrix} Sin[\emptyset] \\ Cos[\emptyset] \\ 0 \end{bmatrix} \quad \text{Eq. S2}$$

The intensity of a NEXAFS transition is given by

$$\frac{l}{l_{avg}} = 2p.Q.p + 1 \quad \text{Eq. S3}$$

Where I_{avg} is the intensity averaged over all possible electric field orientations. Inserting S1 and S2 into S3 we derive, for the three canonical configurations:

$$\frac{I_{along}}{I_{avg}} = \frac{1}{2}(2 - P + S + (P + 3S)Cos[2\theta])$$
$$\frac{I_{perp}}{I_{avg}} = \frac{1}{2}(2 + P + S - (P - 3S)Cos[2\theta])$$
$$\frac{I_{norm}}{I_{avg}} = 1 - S + P Cos[2\phi]$$

By performing a nonlinear-least-squares fit of any two combinations of the three configurations, one can derive S, P, and the scale factor I_{avg} accounting for the strength of the transition dipole and experimental details.



S12a GIXD for PCDTPT films. Notation is as in S11a: "P" PCDTPT, S|F (0.2 vs 20) mm/s, N|A|P (no groove, groove along coating direction, groove perpendicular to coating direction). Angles are the incident X-ray $k_{//}$ relative to the coating direction. Most data was recorded at SSRL at 0.12° angle of incidence, at a beam energy of 12.7 keV, and have been normalized for acquisition time and sample volume and are shown with the same maximum color value. The PSA film was anomalously thick and thus has a lower background with volume normalized. Data for the PFN and PFP samples was recorded at the ALS at 0.14° angle of incidence, at a beam energy of 10 keV, and have been normalized for acquisition time within the 0° and 90° pairs.



S12b GIXD recorded at an angle of incidence of 0.12° for CDTBTZ films. Notation is as in S11b: "C" CDTBTZ, S|F (0.2 vs 20) mm/s, N|A|P (no groove, groove along coating direction, groove perpendicular to coating direction). Angles are the incident X-ray $k_{//}$ relative to the coating direction. All images have been normalized for acquisition time and sample volume and are shown with the same maximum color value. Because of the difference in thickness of the 0.2 mm/s films (\approx 150 nm) vs the 20 mm/s films (\approx 30 nm) the signal to background degrades in the 20 mm/s images requiring a shift in the lower color value.



S13a Top: raw GIXD image for X-ray k// along coating direction for CDTBTZ coated at 0.2 mm/s on an ungrooved substrate (CSN, fig S11b). Bottom nonlinear least-squares fit to sector average from (0 to 20)°. Peak assignments, based on Ref [3], are in Table S2

Table S2.	GIXD	peak assignments for	CDTBTZ
	0.7.12		

Peak	Assignment	Location [Å ⁻¹]
0	(004)	1.15
2	alkyl halo	1.40
3	(006)	1.64
4	(020)	1.78



S13b Polar plots of the integrated intensity of the (020) feature in (0 to 20)° sector averages (see above) for CDTBTZ films coated at 0.2 mm/s on substrates with no grooved, grooves along the coating direction, and grooves perpendicular to the coating direction. Also shown are results for coating at 20 mm/s on an un grooved substrate. Intensities are corrected for integration time and probed volume (film thickness and sample length). 0° corresponds to the X-ray $k_{//}$ aligned with the coating direction. Also shown, as a guide to the eye, is a fit to a truncated Fourier series. For the grooved substrates, the coarse sampling (0, 20, 45, 70, 90)° does not fully capture the orientation distribution, although there is some evidence for a bimodal distribution. The synergistic sample (grooves perp to coating direction) clearly is the most aligned. Consistent with the UV-vis in Fig. S7, the 20 mm/s film is isotropic. Also shown is the sum over all in-plane angles for the 4 films. Although limited by the sampling, the sum suggests little variation in the π - π order across the various film preps, consistent with the assertion of comprehensive crystallinity.



S14 a. Comparison of raw GIXD images (correction for missing wedge not applied) of isotropic and aligned pBTTT-C16 and C16-CDTBTZ films. The data has been normalized for film thickness and count rate. The smaller π - π separation of CDTBTZ is apparent in the shift to higher q of the feature near 1.78 A⁻¹. The isotropic films are spun coat (pBTTT) and blade coated at 20 mm/s on unpatterned substrates (CDTBTZ). The aligned films were strain aligned (50% strain, pBTTT) and blade coated at 0.2 mm/s on a nanogrooved "across" (CDTBTZ). Note the comparable intensity and structure for the two polymers; five orders of (h00) scattering of the lamella repeat of the nominally edge-on crystallites are observed for both systems. The wider orientation distribution for the aligned CDTBTZ sample is due, in part to the greater film thickness 151 nm vs (20 to 35) nm for the other 3 samples.



S14 b. Comparison of sector averages from (0 to 30) degrees of the nominally in-the-surface-plane diffraction of isotropic and aligned pBTTT-C16 and C16-CDTBTZ films. The data has been normalized for film thickness and count rate. The smaller π - π separation of CDTBTZ is apparent in the shift to higher q of the feature near 1.78 A⁻¹. The isotropic films are spun coat (pBTTT) and blade coated at 20 mm/s on unpatterned substrates (CDTBTZ). The aligned films were strain aligned (50% strain, pBTTT) and blade coated at 0.2 mm/s on a nanogrooved "across" (CDTBTZ). Note the comparable intensity of the π - π intensity.



S15 Brewster angle S-pol IR transmission spectra with two orthogonal orientations of E-field to coating direction. Notation for in-plane component of the IR electric field (Ex) is perpendicular and parallel to the coating direction. Note anisotropy in the finger print region (1400-1600) cm⁻¹ of modes polarized along the chain axis.

Table S3 methylene asymmetric stretch frequencies for PCDTPT and CDTBTZ films, coated at 0.2 mm/s on various substrates. Also given are frequencies observed for highly ordered, isotropic pBTTT films, formed by annealing in the liquid crystal phase.

Film	No groove		Groove		Groove	
	perp		along		perp	
Ex	perp	parallel	perp	parallel	perp	parallel
PCDTPT d-	2924.6	2924.6	2924.6	2924.6	2924.7	2924.6
CDTBTZ d-	2924.6	2924.6	2922.6	2924.5	2924.2	2924.2
PBTTT-12	2920.0					
PBTTT-16	2919.4					



S16 Dark field TEM Images of CDTBTZ films coated at 0.2 mm/s on ungrooved, and grooved across (synergistic, type III of Figure 9, main text) substrates. Note that the π diffraction is along the coating direction in the bottom figure, consistent with comprehensive orientation of the chain axis perpendicular to both the grooves and coating direction. Also note the relative absence of minority orientation/unoriented material in both images, implying crystal diffraction over the majority (91.4%) of the field of view.

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