

Supporting Information

Understanding Interfacial Alignment in Solution Coated Conjugated Polymer Thin Films

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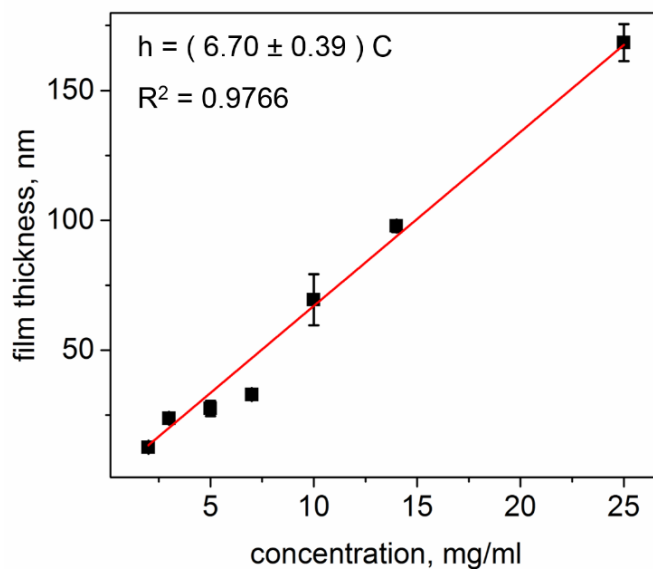


Figure S1. Film thickness as a function of solution concentration. The evaporation rate of the solvent can be calculated from the evaporation regime model by Le Berre *et. al.* in meniscus guided coating derived from mass balance.¹ The equation is $Q_{evap} = \frac{h\rho Lv}{C}$, where h is the thickness of the film, ρ is the density of the solute, L is the width of the meniscus, v is the speed of the moving blade or substrate and C is the solution concentration. In this equation, Q_{evap} is the evaporation rate in volume per time. The density of the solute (DPP2T-TT) is 1.15 g/cm^3 , the blade velocity is 0.5 mm/s , and the width of the meniscus is 1 cm . The slope from Figure S1 is $\frac{h}{C} = 6.7 \frac{\text{nm}}{\text{mg/cm}^3}$. Therefore, the averaged evaporation rate across all concentration is $Q_{evap} = 0.0385 \frac{\text{mm}^3}{\text{s}}$.

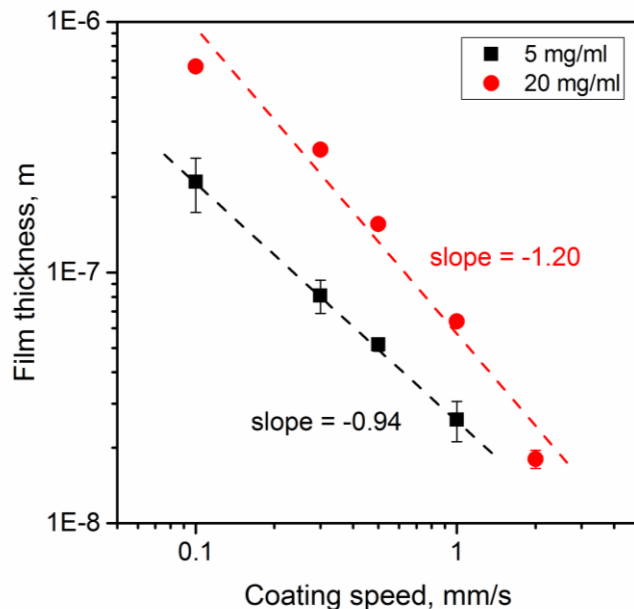


Figure S2. Film thickness and coating speed relation for DPP2T-TT coated from chloroform. Mass balance in the evaporation regime by Le Berre et al.¹ indicates the relationship between film thickness and coating speed satisfy equation $h = \frac{Q_{evap}\rho L}{c} v^{-1}$. From a double logarithm plot of film thickness versus coating speed, the exponent for coating speed equals to the slope and the value of the evaporation rate is embedded in the intercept. Because of the good agreement between the slopes ($\alpha_5 = -0.94$ and $\alpha_{20} = -1.20$) in the figure with the mass balance equation ($\alpha = -1$), we can confidently state that the experiments presented in the manuscript falls in the evaporation regime.

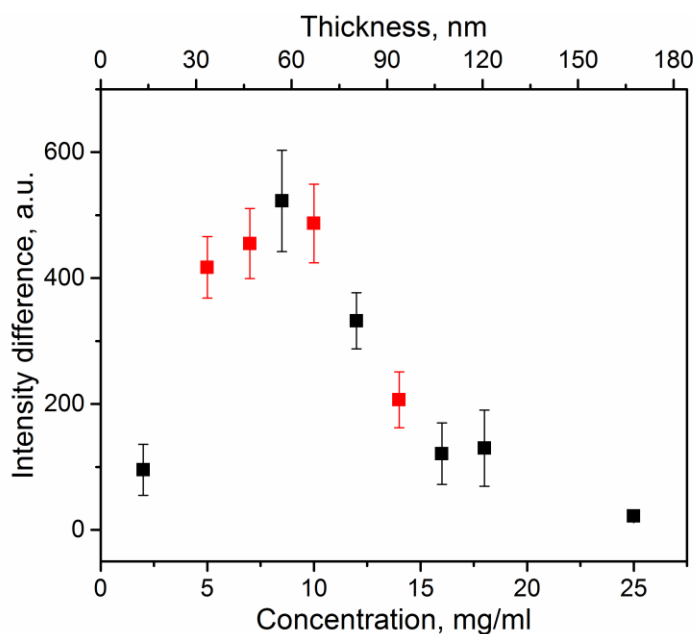


Figure S3. Birefringence of solution coated films as a function of film thickness/solution concentration. The birefringence is calculated as the average intensity difference between the optical images of films with coating direction oriented 0° and 45° with respect to the axis of the polarizer. The data points in red correspond to images presented in Figure 1 with film thickness of 28 nm, 33 nm, 69 nm and 98 nm respectively. Error bars were from intensity obtained from multiple data points on one image.

SANS measurements:

SANS profiles for DPPTT dissolved in chloroform can be seen in Figure S4 & Table S1. The polymers are fit with a cylinder model form factor as described in the following equation:²

$$I(q) = \frac{scale}{V} \int_0^{\pi/2} \left(2(\Delta\rho)V \frac{\sin(qL \cos \alpha / 2)}{(qL \cos \alpha / 2)} \frac{J_1(qr \sin \alpha)}{(qr \sin \alpha)} \right)^2 \sin \alpha d\alpha + bkg \quad (\text{Eqn. S1})$$

where V is the volume of the cylinder, r is the radius of the cylinder, L is the length of the cylinder, $\Delta\rho$ is the scattering length density contrast between the solvent and cylinder and bkg is the scattering background. All fits show good agreement with the model at $q > 0.02 \text{ \AA}^{-1}$. The radius of the cylinder (*e.g.*, polymer backbone) was found to be concentration independent at 1.7 nm. However, an inverse relationship is observed between concentration and the length of isolated cylinders obtained from fitting. This behavior is consistent with increased interchain interactions for polymer solutions above c^* (*i.e.*, critical overlap concentration).³ Figure S7 also shows that at low- q the cylinder model deviates from the scattering. As the polymer concentration increases the point of deviation, indicated by an arrow in the figure, shifts to higher- q (*i.e.*, shorter length scales). This increase in low- q scattering is also consistent with interchain interactions and the shift to higher- q indicates interactions are happening at smaller length scales.

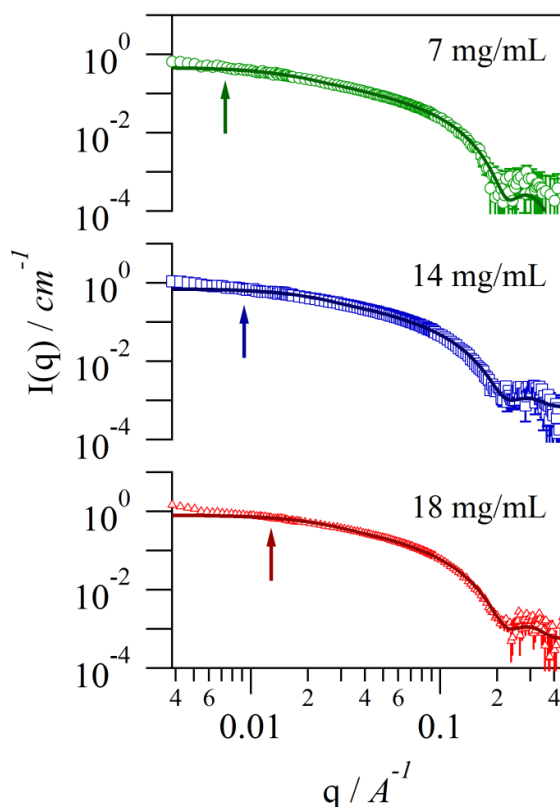


Figure S4. SANS profiles for DPPTT dissolved in chloroform at different concentrations. Solid lines correspond to cylinder model fits. Arrows highlight deviation from the model at low- q .

Table S1. Parameters extracted from the fitting of SANS profiles (Figure 1) with a cylinder model (Equation 1).

Concentration (mg/mL)	Cylinder Radius (nm)	Cylinder Length (nm)	Interchain Interaction Length Scale (nm)
7	1.7	28	84
14	1.7	22	69
18	1.7	19	49

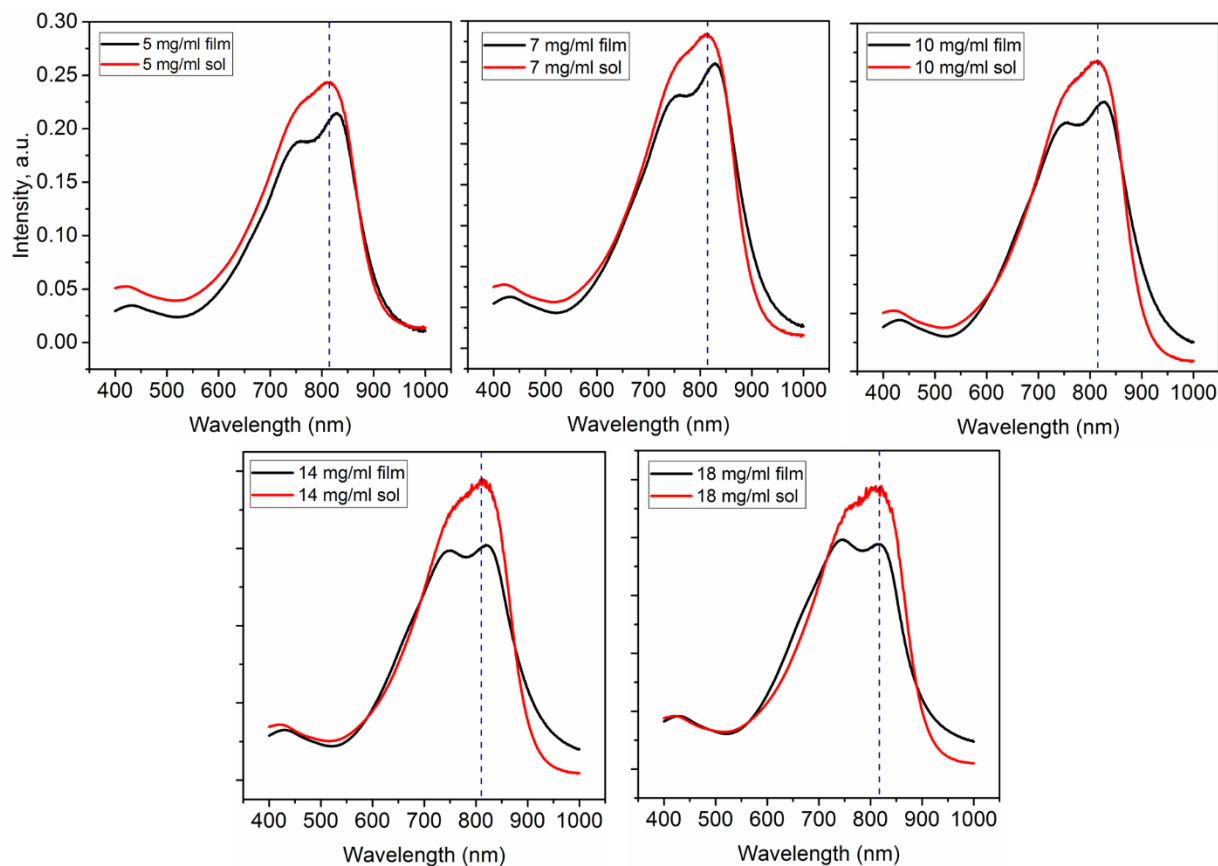


Figure S5. Solution state and corresponding solid state UV-vis spectra for DPP2T-TT at various concentrations. Consistent position and shape of the solution state spectra at all concentrations indicate similar polymer conformation and aggregation state. Blue shift of the solid state spectra indicates increasing aggregation with increasing concentration in thin films.

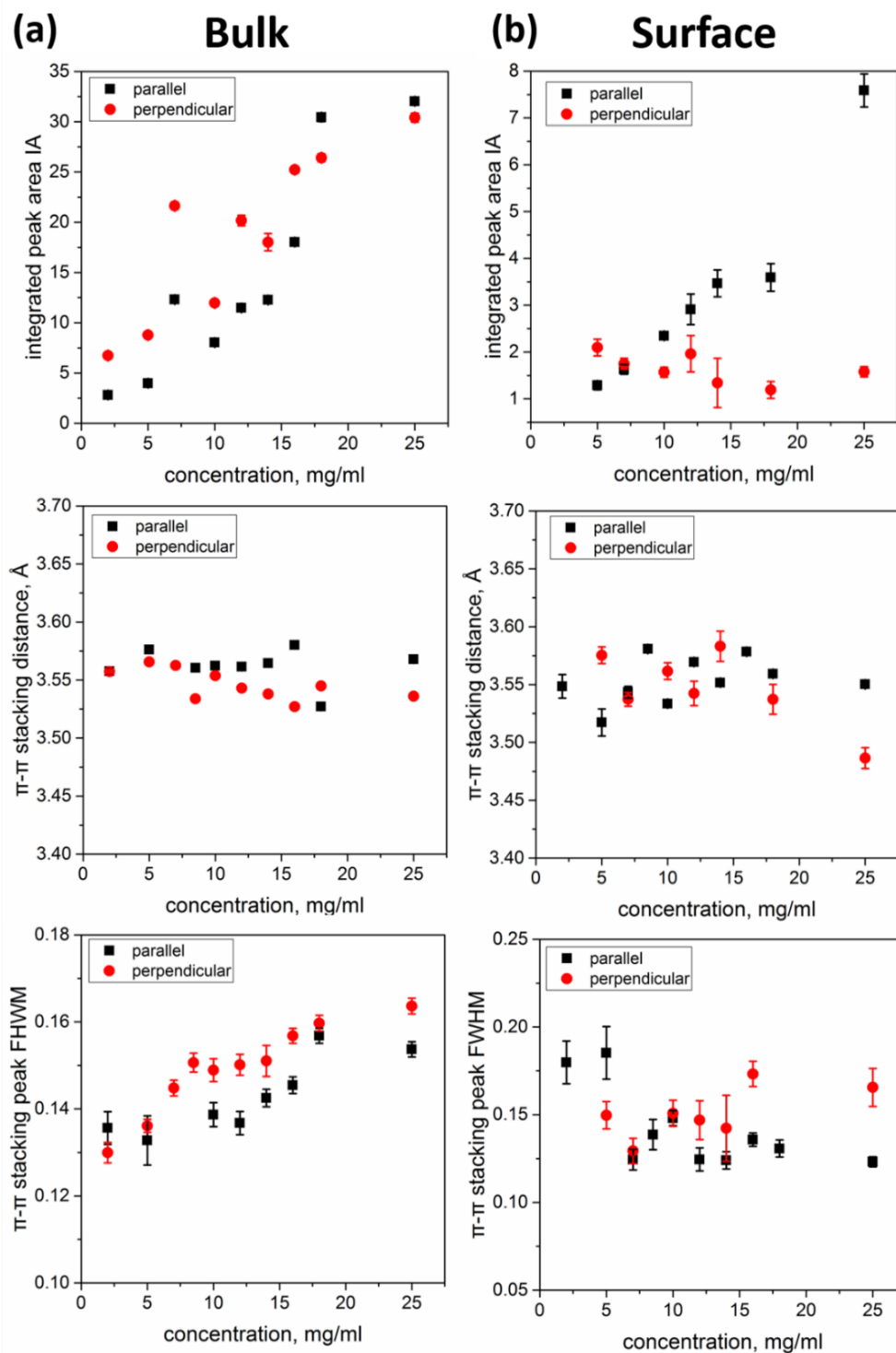


Figure S6. GIWAXS analysis performed on the edge-on π - π stacking peak from parallel and perpendicular measurements for the (a) bulk film and (b) air-film interface.

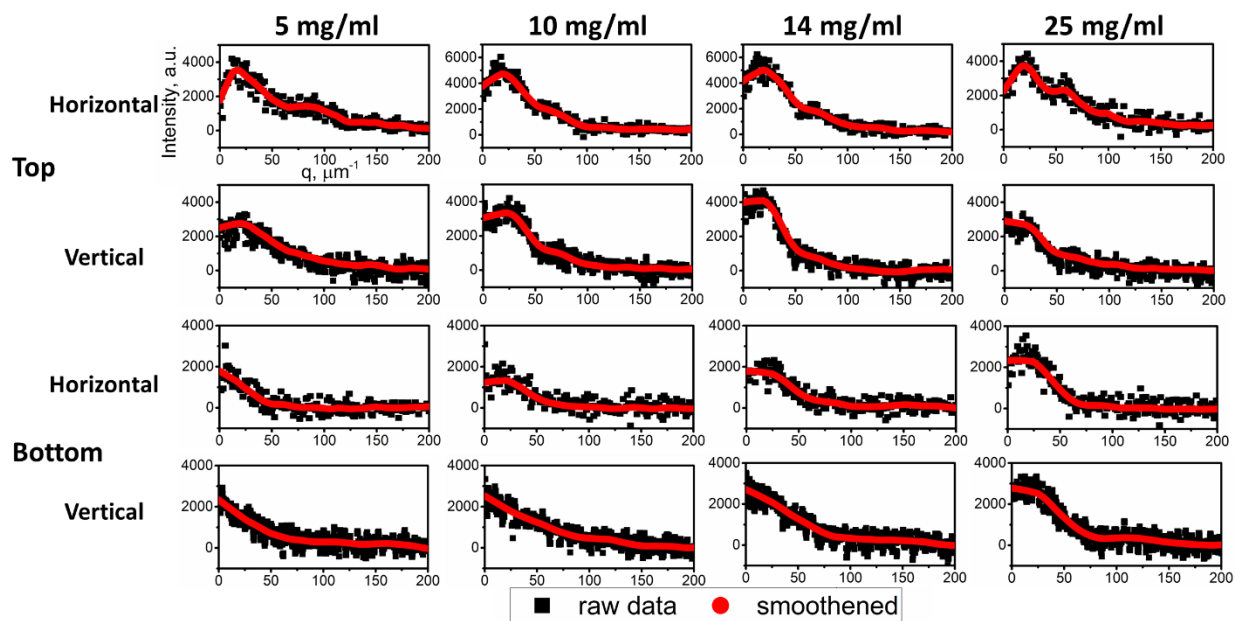


Figure S7. Raw and smoothed data from line-cuts along the horizontal (perpendicular to coating) and 5° offset with the vertical (parallel to coating) directions on the FFT images for top and bottom scans.

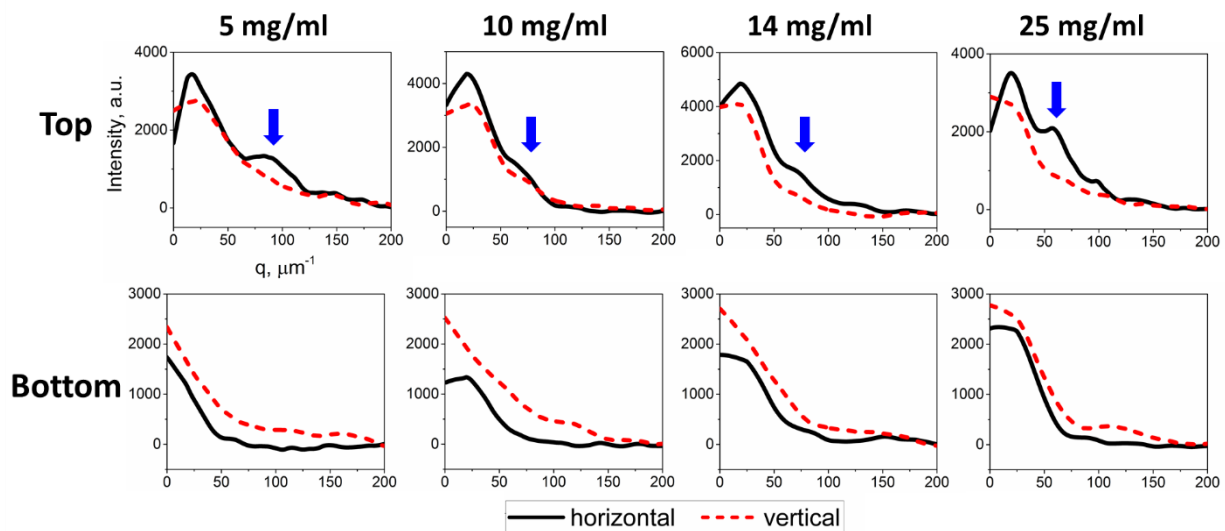


Figure S8: Overlay of the smoothed linecuts for top and bottom FFT images comparing horizontal vs. vertical intensity profiles. The 2nd order peaks in the top linecuts are indicated with the arrows.

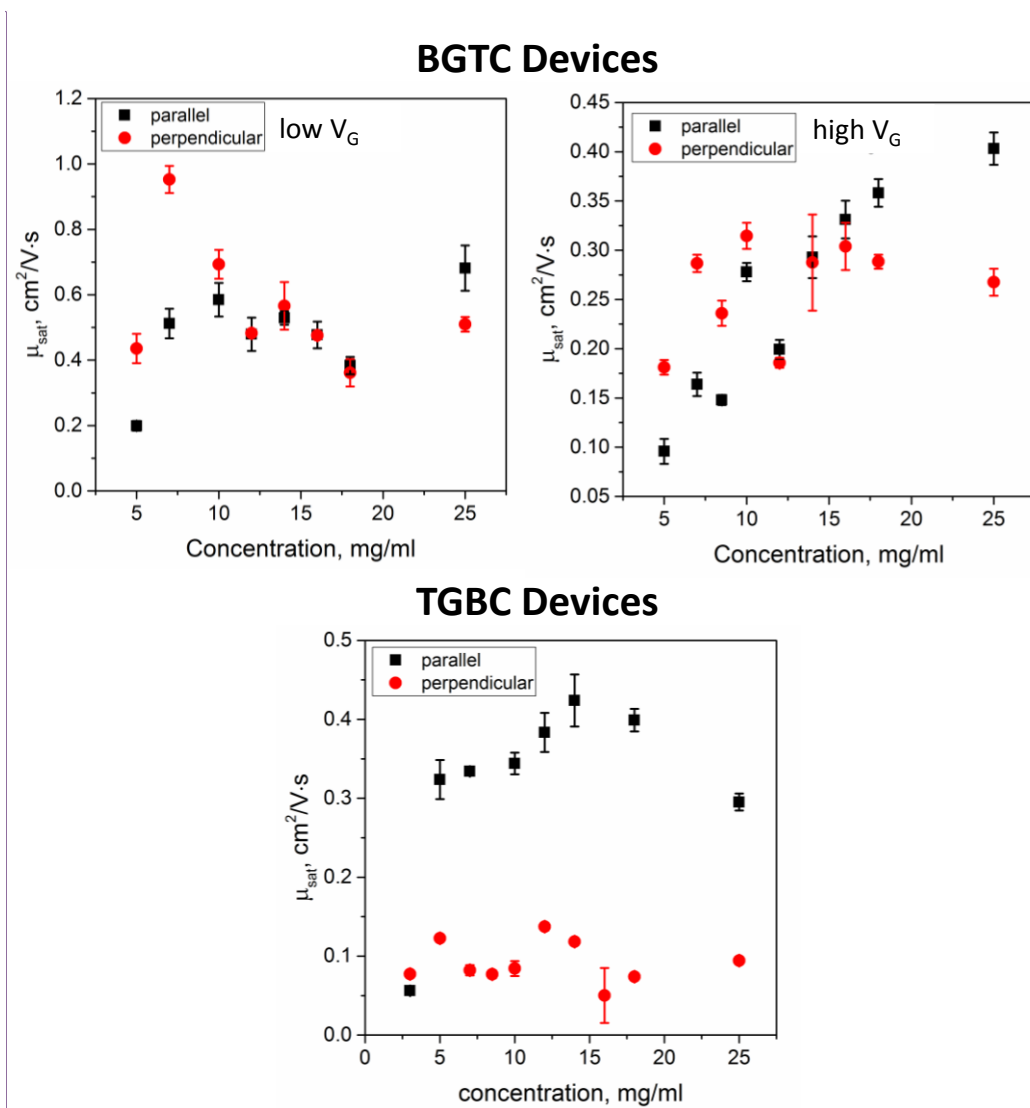


Figure S9. FET device measurements in the saturation regime in the parallel and perpendicular orientations for BGTC configuration (conductive channel at the bottom film-substrate interface) and TGBC configuration (conductive channel at the top air-film interface). For BGTC configuration, apparent mobilities were extracted at both low V_G (20 – 50 V) and high V_G (60 – 90 V).

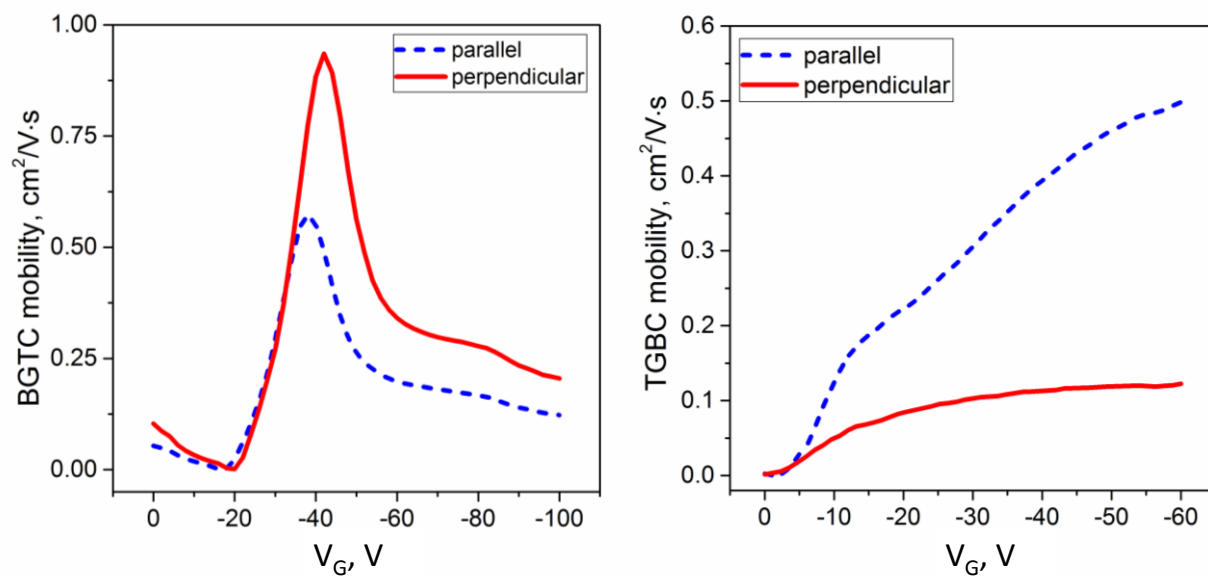


Figure S10. FET device mobility versus V_G for BGTC devices on films printed from 7 mg/ml solution and TGBC devices on films printed from 14 mg/ml solution.

Peclet number calculation:

The Peclet number is a dimensionless number comparing convective mass transport with diffusive mass transport. In our case we can compare the solvent evaporation rate with the solute diffusion rate to qualitatively understand which process is dominant. If the evaporation is dominant, the evaporation at the meniscus can induce a concentration gradient of the solute because the diffusion rate of solute is not fast enough to remove the solute from the high concentration regions. If the solute diffusion is dominant, the solute diffusion is able to remove solution from the meniscus front when the solvent is evaporating, creating an even distribution of concentration within the liquid. For this calculation, we assumed Pe to be constant across the meniscus, which may not reflect the actual distribution as both the evaporation rate and viscosity increases, while the liquid layer thickness decreases moving closer to the contact line. However, due to limited information, we cannot directly estimate Pe at the meniscus front. Accurate Peclet number calculation requires the knowledge of liquid layer thickness, evaporation rate and viscosity near the contact line, which could be simulated using coupled physics and finite element methods which will be pursued in subsequent studies.

The equation used for calculating Peclet number initially describes the geometry in a thin droplet⁴:

$$Pe = \frac{Eh_0}{D} \quad (\text{Eqn. S2})$$

where E is the evaporative flux of the solvent in volume per time per unit area, h_0 is the thickness of the droplet and D is the diffusion coefficient of the solute in the solvent. The evaporation rate of the solvent defined by Le Berre is shown in the caption of Figure S1 for evaporation rate calculation¹:

$$Q_{evap} = \frac{h\rho Lv}{C} \quad (\text{Eqn. S3})$$

where h is the thickness of the film, ρ is the density of the solute, L is the width of the meniscus, v is the speed of the moving blade or substrate and C is the concentration of solute in the solvent. In this equation, Q_{evap} is the evaporation rate in volume per time. Therefore,

$$Q_{evap} = ES \quad (\text{Eqn. S4})$$

where S is the area of the meniscus. If we define that l is the contour length of the meniscus, we have

$$Pe = \left[\frac{\rho v h_0}{lD} \right] \frac{h}{C} \quad (\text{Eqn. S5})$$

that the coefficients in the brackets are all constants, and the film thickness h and the solution concentration C are varying based on the experimental condition.

The blade velocity is 0.5 mm/s. The liquid thickness is 100 μm which the gap size between the substrate and the blade. The contour length of the meniscus is 117 μm based on the meniscus geometry. The density of DPP2T-TT is assumed to be in the range of 1-1.3 g/cm^3 , or around 1.15 g/cm^3 . The diffusion coefficient is $1 \times 10^{-6} \text{ cm}^2/\text{s}$ estimated with a rigid rod model developed by Tirado and coworkers.⁵ The dimension of the rod used for calculation is from SANS measurement

with 7 mg/ml DPP2T-TT in chloroform solution, resulting in 28 nm cylinder length and 1.7 nm diameter. Substituting the slope from Figure S1 $\frac{h}{c} = 6.7 \frac{\text{nm}}{\text{mg}/\text{cm}^3}$ we can obtain the average Peclet number for all concentrations as $Pe = 33$ ($Pe = 28.5\text{-}37.2$ using $1\text{-}1.3 \text{ g}/\text{cm}^3$ DPP2T-TT density).

The high value of the Peclet number indicates that, under the experimental conditions tested, evaporation of the solvent will be dominant and the DPP2T-TT solute can accumulate near the top interface of the meniscus. Therefore we hypothesize that crystalline DPP2T-TT fibers may form near the top interface first, inhibiting the crystallization in the bulk.

Diffusion coefficient calculation:

The translational diffusion coefficient for rod-shaped DPP2T-TT polymer was calculated using the model proposed by Tirado and coworkers.⁵ The translational diffusion coefficient for rod was defined for diffusion with two types of rod orientations: rod parallel to flow $D_t^{\parallel}$ and rod orthogonal to flow $D_t^{\perp}$. The equations are:

$$D_t^{\parallel} = \frac{k_B T}{2\pi\eta_0 L} \left(\ln p - 0.114 - \frac{0.15}{\ln 2p} - \frac{13.5}{(\ln 2p)^2} + \frac{37}{(\ln 2p)^3} - \frac{22}{(\ln 2p)^4} \right) \quad (\text{Eqn. S6})$$

$$D_t^{\perp} = \frac{k_B T}{4\pi\eta_0 L} \left(\ln p + 0.866 - \frac{0.15}{\ln 2p} - \frac{8.1}{(\ln 2p)^2} + \frac{18}{(\ln 2p)^3} - \frac{9}{(\ln 2p)^4} \right) \quad (\text{Eqn. S7})$$

where T is ambient temperature 300K, η_0 is the viscosity of chloroform $0.00053 \text{ Pa}\cdot\text{s}$, L is the rod length 28 nm, p is the aspect ratio L/d 16.5. The calculated values are $D_t^{\parallel} = 1 \times 10^{-6} \text{ cm}^2/\text{s}$ and $D_t^{\perp} = 7.4 \times 10^{-7} \text{ cm}^2/\text{s}$. To avoid over-estimation of the Peclet number, $D_t^{\parallel}$ was used in the calculation.

Vorticity discussion:

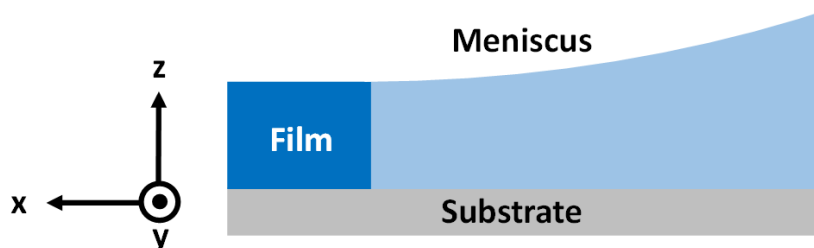


Figure S11. Geometry for meniscus guided coating near the contact line

For the meniscus guided coating geometry, relevant orientations can be defined in the Cartesian coordinate with x along the coating direction, y along the contact line (orthogonal to coating) and z orthogonal to the substrate plane. For vorticity, the vorticity tensor can be decoupled into the x, y, z directions.

$$\omega_x = \frac{\partial v_z}{\partial y} - \frac{\partial v_y}{\partial z} \quad (\text{Eqn. S8})$$

$$\omega_y = \frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x} \quad (\text{Eqn. S9})$$

$$\omega_z = \frac{\partial v_y}{\partial x} - \frac{\partial v_x}{\partial y} \quad (\text{Eqn. S10})$$

For the ω_x component, $v_y = 0$ due to 2D symmetry and v_z does not vary with y . Therefore $\omega_x = 0$. Similarly, for the ω_z component, $v_y = 0$ and v_x does not vary with y . Therefore $\omega_z = 0$. The only non-zero vorticity tensor is ω_y . The first term $\frac{\partial v_x}{\partial z}$ is the shear strain rate caused by the non-slip boundary condition. The shear strain rate is the highest at the liquid-substrate boundary and gradually decreases from substrate to meniscus because of the zero shear boundary condition at the free surface with $\frac{\partial v_x}{\partial z} = 0$. We assume that v_z is close to zero near the contact line due to lubrication approximation.⁶ In this case vorticity tensor ω_y is only influenced by the shear strain rate, with highest value near the substrate and lowest value at the free surface.

References

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