Influence of Solute Concentration on Meniscus-Guided Coating of Highly Crystalline Organic Thin Films

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Meniscus-guided coating methods are a successful approach to precipitate highly crystalline organic thin films at the tip of a receding meniscus. Their optimization nevertheless requires better understanding of the underlying fluid- and thermodynamics. Here, the systematic investigation of the impact of solute concentration is reported on the morphology and electrical characteristics of highly crystalline films of two benchmark organic semiconductors: C₈-BTBT and TIPS-Pentacene. Building on the previous model that predicts the ideal coating speed by balancing substrate motion with solvent evaporation, the approach combines a complete fluid dynamics simulation, including solute transport and precipitation, with a broad set of experimental results. The fluid dynamics modeling confirms that precipitation is strongly enhanced at the tip of the meniscus, regardless of the solute concentration in the bulk of solution. This relative independence explains why the film morphology is little affected by the solute concentration. On the other hand, a rise in concentration results in thicker films. This is rationalized by the mass balance during precipitation. Furthermore, a rise in concentration generally results in films with better electrical characteristics, while the presence of the solute has limited impact on the optimal coating speed that remains close to the ideal balanced speed.

resulting in a shallow meniscus front at the edge of the receding solution drop. Enhanced solvent evaporation at the edge of this meniscus leads to supersaturation of the solution and precipitation of the organic solute onto the advancing crystalline thin film.

Optimization of these coating techniques is complex, owing to the many fluid- and thermodynamic phenomena concurrently leading to solute precipitation and film growth.^[9,13,19,23] Besides, these techniques are governed by a multitude of process parameters such as coating speed v , substrate temperature T , solvent choice, etc., and only few guidelines are available that help process optimization. A fundamental distinction between two processing regimes has been previously established that is ultimately set by the balance between solvent evaporation and coating speed: the evaporative regime at “slow” coating speeds and the Landau–Levich regime at “fast” coating speeds.^[24,25] In the evaporative regime, the coating speed is chosen close to the

equilibrium meniscus receding speed governed by solvent evaporation. In previous works on this regime, we defined guidelines to select the optimum coating speed^[19] and substrate surface treatment^[22] as a function of solvent, organic semiconductor, and substrate temperature. Pursuing further this clarification effort, here, we address the impact of solute concentration c_s on the formation of highly crystalline organic thin films by meniscus-guided coating techniques in the evaporative regime.

In our previous work on coating speed, we proposed a predictive model for the optimal coating speed v_{ps} measured from the equilibrium meniscus recession speed in pure solvents only.^[19] This model assumed evaporative regime and a minimal impact of the solute on the meniscus receding speed. Here, we elaborate on the effect of solute concentration on the optimum zone-casting speed and measure the solute concentration dependent optimal coating speed v_{sc} for two temperatures, two solvents, and two organic semiconductors. We use both modeling and experimental work to verify that all processing conditions close to v_{ps} belong to the evaporative regime and that the solute dissolved in the drop and precipitating at the meniscus front only has a marginal impact on the optimal coating speed. In other words, the optimal speed with solute v_{sc} remains close to the optimal speed with pure solvent only v_{ps} . Nevertheless,

1. Introduction

Organic thin film transistors (OTFTs) are promising candidates for next-generation flexible electronics.^[1–4] Recent advances have demonstrated devices with charge carrier mobilities beyond $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, based on highly crystalline organic thin films.^[5–10] These films are typically processed on inert substrates using meniscus-guided coating techniques such as solution shearing,^[10–13] dip coating,^[14–16] zone casting,^[17–19] and others.^[9,20,21] These solution coating techniques drag a droplet of solution laterally across a highly lyophilic surface,^[22]

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increasing the solute concentration c_s results in increased film thickness and improved electrical performance.

This paper is organized as follows: First, we present fluid dynamics simulations of the zone-casting process to clarify solvent evaporation in the atmosphere as well as solution flow and solute transport inside the solution drop. Next, we show experimental results that reveal the impact of the solute concentration on thin film morphology and thickness. Finally, we discuss the influence of solute concentration on the electrical characteristics of the thin films of organic semiconductors. The main learnings are summarized in the conclusion section.

2. Results and Discussion

Our experimental study covers two substrate temperatures, two solvents, and two small molecular organic semiconductors, thereby defining four sets of processing conditions: 1) C₈-BTBT in heptane at room temperature, 2) C₈-BTBT in heptane at $T = 50^\circ\text{C}$, 3) C₈-BTBT in hexane at room temperature, and 4) TIPS-Pentacene in heptane at room temperature (also see Table 1). For each set, we tested four inlet solute concentrations ranging from $c_{s,\text{in}} = 0.1\text{--}0.4\text{ wt\%}$. And, for each concentration, we tested at least four different coating speeds v varying over at least one order of magnitude. Each v was chosen as a multiple of the pure solvent meniscus receding speed v_{ps} predicted by the model in ref. [19]. In total, 80 different process conditions were tested, which covers a wide processing range and helps the generalization of our results to the broad spectrum of meniscus-guided coating techniques. In the simulation study, we especially focused on set (2) at $v = v_{\text{ps}}$, but also explored the cases of hexane and T variations.

When possible, we present our results using unitless normalized parameters. v , the coating speed, as well as u , the fluid velocity in the solution, are both normalized by v_{ps} : $v^* = v/v_{\text{ps}}$, $u^* = u/v_{\text{ps}}$. The molecular solute concentration in solution c_s is normalized by the saturated concentration $c_{s,\text{lim}}$ that marks the solubility limit: $c_s^* = c_s/c_{s,\text{lim}}$. Finally, the solvent vapor concentration in air c_v is normalized by the equilibrium solvent vapor concentration: $c_v^* = c_v/c_{v,\text{eq}}$ where $c_{v,\text{eq}} = p_v/RT$ and p_v is the solvent vapor pressure at T and R is the ideal gas constant. The values of several normalizing parameters are given in Table 1 for the four different sets of process conditions. The use of normalized parameters permits the direct comparison of results obtained with different process conditions (see Figure S2 in the Supporting Information).

2.1. Fluid Dynamics Simulations

Modeling the zone-casting process provides insights that are useful for result interpretation.^[9,13] We used finite element analysis and several sets of physical models to set up a comprehensive and realistic simulation of our setup, as detailed in the Experimental Section. As shown in Figure 1a for heptane at $T = 50^\circ\text{C}$ (process condition set (2) in Table 1), after geometry optimization, the solution drop formed between the casting head and the substrate presents two menisci with concave shape. Both menisci have, by design, a low contact angle of $\theta = 5^\circ$ with the lyophilic substrate, that is a prerequisite to successful meniscus-guided coating.^[22] The short front meniscus, where the crystalline film precipitates, is pinned on the bottom left corner of the casting head. On the other hand, the long back meniscus is not pinned: Its free edge, forming a 90° contact angle to the casting head can be translated along the substrate to absorb variations in solution supply without affecting much the deposition process. Experimentally, when forming the solution drop, we monitor the motion of the back meniscus to an intermediate position between the solution inlet and the back edge of the casting head. Following Young–Laplace equation, the concave meniscus shape is caused by the lower hydrostatic pressure inside the drop compared to the surrounding air. As the surface tension of heptane is low, the radius of curvature of the menisci is also low, which explains the extension of the front meniscus far beyond the corner of the casting head.

Figure 1a,b shows both the normalized solvent vapor concentration in air c_v^* as well the normalized solvent speed inside the drop u^* . Along the edges of the menisci, $c_v^* = 1$ is set by the equilibrium solvent vapor pressure and it gradually decreases as solvent vapor diffuses away. Figure 1d details the diffusive flux of solvent vapor Φ_v along the edge of the front meniscus for different T . The exponential progression of Φ_v with T in Figure 1d reflects the Arrhenius temperature activation of the solvent vapor pressure p_v . At the tip of the meniscus, Φ_v is enhanced by a factor 50 as compared to its value in the middle of the meniscus. This enhancement, in line with previous literature results,^[13,25,26] is again explained by the much lower geometrical confinement of the tip of the meniscus which provides stronger concentration gradients that drive solvent vapor diffusion. The solution flow inside the drop is principally governed by the solvent consumption at both menisci, in approximately equal amounts, and by the substrate motion at speed v under the casting head that entrains the solution from the back to the front meniscus. Figure 1a,b is computed for $v^* = 1$ where $v = v_{\text{ps}}$ ($=90\text{ }\mu\text{m s}^{-1}$ for heptane at $T = 50^\circ\text{C}$) and the meniscus recedes

Table 1. Parameters and output results for four sets of process conditions tested experimentally. v_{ps} is the pure solvent coating speed calculated from the model in ref. [19]. $\dot{V}_{\text{in}}$ is the experimental solution volume flow rate needed to keep the meniscus volume constant during the coating process. $c_{s,\text{lim}}$ is the solubility limit of that process condition. p_v is the solvent vapor pressure at the process temperature. $\dot{m}_{v,\text{fm}}$ is the mass flow rate of liquid solvent lost by evaporation at the front meniscus. For generality, the flow rates $\dot{V}_{\text{in}}$ and $\dot{m}_{v,\text{fm}}$ are corrected by the width of the casting head (4 cm).

Set #	Semiconductor	Solvent	T [$^\circ\text{C}$]	v_{ps} [$\mu\text{m s}^{-1}$]	$\dot{V}_{\text{in}}$ [$\mu\text{L min}^{-1}\text{ cm}^{-1}$]	$c_{s,\text{lim}}$ [wt%]	p_v [kPa]	$\dot{m}_{v,\text{fm}}$ [$\mu\text{g ms}^{-1}$]
1)	C ₈ -BTBT	Heptane	20	25	3 ± 1	0.5	4.7	528
2)	C ₈ -BTBT	Heptane	50	90	11 ± 2	0.6	18.8	2274
3)	C ₈ -BTBT	Hexane	20	65	9 ± 2	0.6	16.1	1942
4)	TIPS-P5	Heptane	20	25	3 ± 1	1.0	4.7	528

Figure 1. Simulation of zone-casting process with realistic geometry and process conditions (heptane, $T = 50\text{ °C}$, $\nu = \nu_{ps} = 90\text{ }\mu\text{m s}^{-1}$). The drop geometry is stabilized by a multiphase laminar flow model with moving boundary. a,b) Surface plots of solvent vapor concentration c_v^* and liquid solvent velocity u^* . Red arrows are diffusive flux of solvent vapor, and black arrows are liquid solvent velocity. The flux of evaporating solvent on the menisci is matched by a flux of liquid solvent inside the drop. c) Surface plots of solute concentration c_s^* in the front meniscus region for different inlet concentrations $c_{s,in}$. c_s^* is always close to 1 ($c_s = c_{s,lim}$) at the tip of the meniscus, indicating precipitation due to the enhanced solvent evaporation. d) Evaporating flux Φ_v of solvent along the front meniscus edge (green arrow in (b)) for different T . At the tip of the meniscus, evaporation is enhanced by a factor 50 compared to the center of the meniscus, thanks to less geometrical confinement. e) Solute concentration c_s^* along the bottom edge of the drop, close to the front meniscus (black arrow in (c)) for different $c_{s,in}$. c_s^* rises to saturation when approaching the tip of the meniscus at $x = 0$. f) Evolution of the solute flux Φ_s with $c_{s,in}$ along the bottom edge of the drop, at different distances x from the tip of the meniscus. When approaching the tip, the solute supply tends to saturate with increasing $c_{s,in}$.

by evaporation as fast as the substrate moves underneath. Due to the entrainment, the solution speed u^* reaches a maximum unity value at the substrate boundary, which transports a consequent amount of solution toward the front meniscus. As not all solvent can evaporate on the front meniscus, a small counter flow is created at the top of the drop, resulting in the formation of a vortex cell that is well visible in the white streamlines of Figure 1a,b.

Figure 1c shows maps of solute concentration c_s^* for different values of the inlet solute concentration $c_{s,in}$. In the bulk of the solution drop, far from the menisci, the solution concentration is principally determined by the inlet solution concentration: $c_s \sim c_{s,in}$. But as the solution moves toward the menisci, c_s rises above $c_{s,in}$ due to solvent evaporation along the menisci edges. Solute motion within the drop is caused both by the convective transport with solvent flow and by the diffusive transport away from the concentrated menisci edges (see Figure S3 in the Supporting Information). Diffusive fluxes, however, are lower in magnitude than convective fluxes, approximately by a factor 20. In consequence, the large flow at the bottom of the drop convectively carries much solute toward the tip of the front meniscus. As solvent evaporation is especially strong in this position, c_s easily reaches saturation even for the lowest inlet solution concentration $c_{s,in}$. This observation is also shown in Figure 1e that plots c_s^* along the bottom edge of the solution drop, at its interface with the substrate, starting from the tip of the front meniscus in $x = 0$. In all cases, even for very low $c_{s,in}$, c_s saturates when approaching the tip of the meniscus. Hence, the enhancement of evaporation at the tip of the meniscus is essential to the success of meniscus-guided coating techniques as it guarantees solution saturation at the place of film formation, independently from the bulk concentration inside the solution drop. Besides, we also monitor in Figure 1f the total flux of solute Φ_s upon approaching the tip of the meniscus along the same bottom edge. Far from the tip, at $x = 1.5$ mm, Φ_s rises linearly with $c_{s,in}$ as the solute flux results from the local product of the solution velocity u and the solute concentration c_s . When moving toward the tip of the meniscus, u stays constant but c_s rises as shown in Figure 1d. As a consequence, Φ_s also increases upon lowering x . This trend, however, saturates with $c_{s,in}$ as the rise in c_s is ultimately limited by the solubility limit. As seen later, this saturation with $c_{s,in}$ of solute transport toward the tip of the meniscus is reflected in the experimental results.

2.2. Effect of Solute Concentration on Film Morphology

We performed a systematic morphology study of thin films of C₈-BTBT zone-cast from heptane solutions at a substrate temperature $T = 50$ °C with increasing solute concentrations $c_{s,in}$ and coating speeds v^* , corresponding to the set of process condition (2) in Table 1. **Figure 2** shows the evolution of film morphology, assessed by polarized light microscopy (PLM) and atomic force microscopy (AFM). All PLM images were acquired with the same light exposure, hence thinner films result in a decreasing image brightness. The PLM images of all films reveal long range crystallinity along the casting direction, but higher resolution AFM images show that many voids are

present within single crystalline domains. We have previously shown that the presence of these defects is inherent to the film formation process.^[8]

At the slowest coating speed $v^* = 0.5$ (left column), the film thickness increases with increasing $c_{s,in}$. This is shown by the brightness increase in PLM images and an increasing average film thickness h measured by AFM, from $h = 34$ nm at $c_{s,in} = 0.1$ wt% to 46 nm at 0.3 wt%. AFM imaging at $c_{s,in} = 0.4$ wt% was not possible due to the high film roughness. Indeed, as shown in the low resolution PLM images, the films roughen up with the increase in $c_{s,in}$, due to the formation of large aggregates that appear as coffee ring lines orthogonal to the direction of coating. Between these aggregates, AFM shows a relatively stable morphology, independent of $c_{s,in}$, at the microscopic scale. At the highest $c_{s,in} = 0.4$ wt%, this trend results in a very rough film with complete coverage of solute aggregates over the full sample.

At higher coating speeds, aggregates are no longer visible in the PLM images. On the other hand, a thickness increase with $c_{s,in}$ is still observed. For the coating speed of $v^* = 1$ (middle column), that is when the substrate is translated as fast as a meniscus of pure solvent evaporatively recedes, the average film thickness increases from $h = 16$ nm at $c_s = 0.1$ wt% to 25 nm at 0.4 wt%. Apart from this thickness difference, all films show similar morphologies, independent of $c_{s,in}$. Upon increasing the coating speed further to $v^* = 2$ (right column), we again observe an increase in average film thickness from $h = 9$ nm at $c_{s,in} = 0.1$ wt% to 13 nm at 0.4 wt%. At this elevated v^* , the increase in $c_{s,in}$ also results in a change in morphology at the microscopic scale. At a concentration of 0.4 wt%, we obtain a well-connected film with some voids and ribbons (Figure 2x). Upon reducing $c_{s,in}$, the films become more porous with more pronounced voids and ribbons. As shown in Figure 2f at $c_{s,in} = 0.1$ wt%, the film is mainly composed of thin ribbons with several branches and dead-ends.

As indicated in the Experimental Section, the experimental solution resupply rate at the inlet $\dot{V}_{in}$ is set by solvent evaporation dynamics, which, in first order, are independent from v^* and $c_{s,in}$. In other words, for a given set of process conditions, the experimental $\dot{V}_{in}$ is constant (see Table 1). Therefore, coating at speeds substantially lower than the ideal $v^* = 1$ results in an oversupply of solute as the substrate is not translated fast enough to absorb all supplementary solute material. In consequence, this triggers a global rise in solute concentration c_s and we speculate that this results in localized supersaturation and homogeneous nucleation and growth of crystallites within the solution. These crystallites sediment on the substrate, forming the large aggregates that perturb film formation. Aggregate formation worsens with higher $c_{s,in}$ (see Figure 2s). Similarly, coating at speeds substantially higher than $v^* = 1$ may result in an undersupply of solute, as the solution supply at a constant rate does not deliver enough solute to ensure full film coverage. Lack of film coverage worsens with lower $c_{s,in}$ (see Figure 2f). When coating at $v^* = 1$, a satisfactory balance between solute supply and film formation is found for all tested $c_{s,in}$. In this case, the film morphology is remarkably independent of $c_{s,in}$. We assign this independence to the solution saturation at the tip of the front meniscus, regardless of the bulk solute concentration, as observed in the simulation results in Figure 1c,f.

Figure 2. Morphology at different inlet solute concentration $c_{s,in}$ and coating speeds v^* for the zone-casting of C_8 -BTBT in heptane at a substrate temperature of $T = 50^\circ\text{C}$, corresponding to a pure solvent meniscus receding speed of $v_{ps} = 90\ \mu\text{m s}^{-1}$. For each condition, the thin film is imaged by PLM (left) and AFM (right). Casting at $v^* = 1$ delivers good film morphologies for all $c_{s,in}$. Slower v^* ($=0.5$) leads to precipitation of aggregates on the film, especially for high $c_{s,in}$. Faster v^* ($=2$) leads to more voids and dead ends in the film, especially for low $c_{s,in}$. The black arrows in (a) and (b) show the coating direction.

In summary, increased inlet solute concentration $c_{s,in}$ always results in increased average film thickness h . At slow coating speeds $v^* < 1$, solute oversupply also results in macroscopic aggregate formation that perturb film growth. At medium speed $v^* \approx 1$, the thin film morphology remains broadly independent from $c_{s,in}$. We assign this to the fact that the solution always reaches saturation at the tip of the front meniscus independently from the bulk solute concentration. At elevated speeds $v^* > 1$, solute undersupply results in less-connected films at the microscopic level. Lower concentrations are therefore preferred at low coating speeds, while higher concentrations are more favorable for higher coating speeds. Similar morphological observations were made for the three other sets of process conditions: 1) C_8 -BTBT in heptane at room temperature, 3) C_8 -BTBT in hexane at room temperature, and 4) TIPS-Pentacene in heptane at room temperature.

2.3. Influence of Coating Speed and Solute Concentration on Film Thickness

In the previous section, we observed a variation of average film thickness h with both inlet solute concentration $c_{s,in}$ and coating

speed v^* . A detailed study of this variation shines light on the dynamics of solute precipitation. In the evaporative regime, the solute mass balance between the thin organic film and the solute in the front meniscus region is given by^[24,25]

$$h v \rho_s = \frac{\bar{c}_{s,fm} \dot{m}_{v,fm}}{\rho_v} = \dot{m}_{s,fm} \quad (1)$$

with ρ_s , the density of the solid organic film, ρ_v is the density of the liquid solvent, $\bar{c}_{s,fm}$, the average solute concentration at the edge of the front meniscus, where precipitation occurs, $\dot{m}_{v,fm}$, the width-corrected mass flow rate of liquid solvent that evaporates from the front meniscus, and $\dot{m}_{s,fm}$, the mass flow rate of solute that precipitates at the front meniscus (both in $\text{kg m}^{-1}\text{s}^{-1}$). In this expression, $\dot{m}_{v,fm}$ can be evaluated from the simulations (see Table 1). On the other hand, since supersaturation heavily varies along the edge of the front meniscus and the exact localization and mechanism of precipitation are unresolved, $\bar{c}_{s,fm}$ is a priori unknown.

Figure 3 shows double logarithmic plots of h versus v^* for the four sets of process conditions and four values of $c_{s,in}$. In all cases, h is proportional to $v^{*\alpha}$ with $\alpha \approx -0.9$ obtained as the slope of a linear fit to the $\log(h)$ versus $\log(v^*)$ data. This

Figure 3. Average film thickness h as a function of normalized coating speed v^* and inlet solute concentration $c_{s,in}$ for different experimental conditions. Straight lines are experimental fits to the data points according to $h \propto v^{\alpha}$. For each subfigure, one value of α is extracted by fitting together the data from different $c_{s,in}$. All curves show slopes close to the theoretical value of $\alpha = -1$, indicating that the coating is done in the evaporative regime.

is close to the $\alpha = -1$ theoretically predicted by Equation (1) and thereby confirms that zone-casting at a speed in the range of the pure solvent meniscus receding speed v_{ps} operates in the evaporative regime, in good agreement with previous experimental results ($\alpha \approx -1.1$).^[24] In contrast, operation in the Landau–Levich regime would deliver positive values for α . The slope α is also independent from the solute concentration $c_{s,in}$, which was theoretically predicted earlier.^[25] As stressed in the morphology study, this independence is caused by the solution saturation at the tip of the meniscus quite independently from bulk solute concentration.

As noted in the morphology section, the average film thickness h increases with solute concentration for all four sets of process conditions. This is illustrated in Figure 4a that shows h for films processed at $v^* = 1$ and uses reduced concentration $c_{s,in}^*$ in abscissa to better compare the different process

conditions (raw data is in Figure S4, Supporting Information). The zone-casting of TIPS-Pentacene in process (4) delivers much thicker films than the corresponding C₈-BTBT process (1) with the same coating speed, temperature and solvent. In all cases, h tends to saturate as $c_{s,in}$ rises toward the solubility limit.

A second interesting output parameter is the solute precipitation rate $\dot{m}_{s,fm}$. Following Equation (1), $\dot{m}_{s,fm}$ can be obtained from the slope of a linear fit to plots of h versus v^{-1} (see Figure S5 in the Supporting Information). Applying this analysis to all data in Figure 3 delivers the evolution of $\dot{m}_{s,fm}$ with $c_{s,in}^*$ in Figure 4b for all four sets of process conditions. As expected, solvents with faster evaporation dynamics as well as higher substrate temperatures lead to an increased precipitation rate. Moreover, as TIPS-Pentacene yields thicker films, its precipitation rate is higher than for the equivalent C₈-BTBT process (1). From these precipitation rates, one can in principle calculate

Figure 4. a) Film thickness h , b) precipitation rate $\dot{m}_{s,fm}$, and c) normalized precipitation rate $\dot{m}_{s,fm}^*$ (normalized according to solvent mass flow rate along the meniscus) as a function of solute inlet concentration $c_{s,in}^*$. Higher concentrations lead to thicker films, while the film thickness seems to saturate when reaching the solubility limit. Different solvents, temperatures, and small molecules lead to different film heights due to different growth characteristics.

the resupply rate that is necessary to achieve a steady state operation, provided that solute losses in the process remain limited (see Note S2 in the Supporting Information for considerations on the global mass balance over the casting head).

Upon normalizing the precipitation rate $\dot{m}_{s,fm}$ with the mass flow rate of solvent evaporating along the front meniscus $\dot{m}_{v,fm}$ obtained from simulations in Table 1, we obtain a normalized precipitation rate $\dot{m}_{s,fm}^*$ plotted for the four set of process conditions in Figure 4c. In this fully normalized plot, the curves obtained for process conditions (1), (2), and (3) with C₈-BTBT all superimpose, showing that these systems have the same behavior despite their temperature and solvent differences. On the other hand, the process system (4) with TIPS-Pentacene is again an outlier, with twice as large values of $\dot{m}_{s,fm}^*$. The reason behind the enhanced precipitation dynamics in TIPS-Pentacene remains unclear but hints toward fundamentally different precipitation mechanisms.

Finally, the three deposition markers h , $\dot{m}_{s,fm}$, and $\dot{m}_{s,fm}^*$ analyzed in Figure 4 saturate as $c_{s,in}$ rises toward the solubility limit. We assign this to the saturation in solute supply when approaching the tip of the front meniscus. Indeed, the simulations in Figure 1e show that solute flux Φ_s saturates with $c_{s,in}$ when approaching the tip of the front meniscus.

2.4. Effect of Concentration on Film Electrical Performance

In this last section, we study the effect of solute concentration on the electrical properties of the zone-cast films. To this end, we fabricated bottom-gate top-contact TFTs by casting the thin film of organic semiconductor on common gate silicon substrates with a 130 nm thermal oxide as gate dielectric. Shadow-mask evaporated F₆TCNNQ and Au served as source and drain electrodes with good electrical characteristics.^[27,28] Figure 5 shows typical electrical characteristics of devices based on thin

films of C₈-BTBT and TIPS-Pentacene. Each process condition can lead to well-behaved transfer curves in the saturation regime, with on-off ratios $>10^6$, small subthreshold slopes, small onset voltages, and a clear plateau in the mobility over a large gate voltage range. The effective mobility in saturation is extracted using the conventional gradual channel approximation model. We use this method with caution as nonlinearity in device characteristics have been shown to cause serious mobility overestimation.^[27–29] It can be seen in Figure 5b,d that the mobility saturates with gate voltage both for C₈-BTBT and TIPS-Pentacene. The plateau in the on-region is used to extract the saturation mobility. The highest aggregate charge carrier mobilities are in the range 4–5 and 0.5 cm² V^{−1} s^{−1} for TFTs based on zone-cast films of C₈-BTBT and TIPS-Pentacene, respectively.

For each of the four sets of conditions, we plot in Figure 6a the average aggregate charge carrier mobility as a function of the normalized coating speed v^* . In all cases, the mobility shows a local maximum, pointing to the existence of an optimal coating speed v_{sc} in the presence of solute that may be different from the optimal speed in pure solvent v_{ps} . By fitting a Gaussian through each set of data, v_{sc} is extracted as the position of the center of the Gaussian peak. As a result, the normalized optimal coating speed $v_{sc}^* = v_{sc}/v_{ps}$ is reported in Figure 6b as a function of normalized inlet solute concentration $c_{s,in}^*$. For C₈-BTBT, v_{sc} remains in the vicinity of the predicted pure solvent speed v_{ps} and very slightly increases with $c_{s,in}^*$, showing that optimal coating at higher solute concentration requires slightly faster coating speeds. But deviations of the optimal coating speed v_{sc} from the pure solvent meniscus receding speed v_{ps} remain limited, showing that pure solvent dynamics are a sufficient predictor for v_{sc} . In the case of TIPS-Pentacene, v_{sc} is consistently the double of v_{ps} over the whole solute concentration range. This is reminiscent of the doubled precipitation dynamics of TIPS-Pentacene as compared to C₈-BTBT

Figure 5. Typical electrical characteristics of zone-cast samples with a,b) C₈-BTBT and c,d) TIPS-Pentacene as the organic semiconductor. Transfer and mobility curves of bottom-gate, top-contact type OTFT in the saturation regime with the drain voltage at -40 V. Channel dimensions are $190\text{ }\mu\text{m}/2035\text{ }\mu\text{m}$; SiO₂ dielectric thickness is 130 nm . Leakage currents stay below 10^{-9} A for all the measured devices independently of the gate voltage. Zone casting of the organic semiconductor is done in heptane at room temperature with a concentration of $0.3\text{ wt\%}$. The coating speeds correspond to the optimal speed v_{sc} required to reach the highest electrical performance (12.5 and $50\text{ }\mu\text{m s}^{-1}$ for C₈-BTBT and TIPS-Pentacene, respectively). Red dotted lines in the mobility plots correspond to the reported mobility values, extracted from the plateau of the mobility curve.

emphasized in Figure 4c. Considering the faster precipitation of this molecule, a matching increase in coating speed v is necessary to form films with the best electrical characteristics. This suggests that beyond pure solvent dynamics, the choice of solute may also impact the optimal coating speed if it has fast precipitation dynamics.

In all four sets of process conditions, variations in v and $c_{s,in}$ do not significantly impact the TFT onset and threshold voltages. On the other hand, increasing $c_{s,in}$ has a positive impact on TFT mobility, as can be seen in Figure 4c that reports the mobilities obtained from the height of the Gaussian fits. Note that these values represent an ideal value for the mobility, not a measured value. Hence, especially for the experiment of heptane at $50\text{ }^{\circ}\text{C}$, these values can be about 30% higher than the highest measured value. The increase of TFT mobility with $c_{s,in}$ may result from better, more connected thin film morphologies which is favorable to TFT characteristics,^[8] although morphological improvements remain limited when coating close to the optimal speed v_{sc} (see Figure 2). Increased $c_{s,in}$ also results in thicker films (see Figure 4a). This can negatively impact TFT performance through an increased access resistance, hence

higher contact resistance. But thicker films can also be more resistant to thermal damage during contact metallization and therefore yield lower contact resistance. All these effects participate with varying degrees to the monotonous increase of TFT mobility with inlet solute concentration in Figure 5c. This trend, however, could be different for other material systems and device topologies.

3. Summary

Meniscus-guided coating methods are ideally suited to form highly crystalline thin films of organic semiconductors by precipitation at the tip of a receding meniscus. The underlying fluid- and thermodynamical processes are however complex, which complicates the optimization of these methods. Here, we report on our systematic investigation of the relationship between inlet solute concentration and the morphology and electrical characteristics of highly crystalline films of C₈-BTBT and TIPS-Pentacene formed by zone-casting. We first present a realistic finite-element analysis of our setup that simulates the

Figure 6. Impact of the inlet solute concentration $c_{s,in}^*$ and coating speed v^* on the electrical performance of highly crystalline zone-cast films. a) The evolution of the average thin film transistor saturation mobility is given for the four sets of process conditions. Lines are Gaussian fits to the data points for each $c_{s,in}$. b) Optimal coating speed v_{sc}^* as a function of $c_{s,in}^*$ for the four sets of conditions. v_{sc}^* is determined from the positions of the centers of the Gaussian fits. Only TIPS-Pentacene shows a marked deviation of v_{sc}^* from the ideal pure solvent speed $v^* = 1$. c) Mobility at the optimal coating speed as a function of $c_{s,in}^*$ for the four sets of conditions. Mobility values are obtained from the height of the Gaussian fits. Higher solute concentrations lead to increased mobilities.

fluid dynamics in the deposition process. As output, we obtained models for the stable shape of the solution drop pinned between the substrate and the casting head; for the solute evaporation in the surrounding air; for the drop internal vortex flow entrained by the substrate motion and by the evaporation at the edges; and for the solute transport in the drop and its precipitation at the menisci edges. A main observation is the enhanced evaporation at the tip of the meniscus that leads to a strong localized solute saturation, irrespective of solute concentration in the bulk of the drop. This system is ideally suited for fast precipitation at the tip of the meniscus while being stabilized by the dampening of process variations in the bulk of the drop.

This relative independence of the precipitation from the bulk concentration is seen experimentally as the film morphology remains remarkably unaffected by variations of inlet concentration when processing at a coating speed that balances substrate motion with solvent evaporation rate. On the other hand, the experimental film thickness increases with solute concentration but quickly drops when the coating speed rises. A mass

balance analysis of this data confirms that our system operates in the evaporative regime where a rise in concentration results in enhanced precipitation rates. This enhancement saturates when the concentration evolves toward the solubility limit. This trend is independent from the choice of solvent or process temperature, but can be quite influenced by the nature of the solute, as TIPS-Pentacene precipitates at rates twice as large as for $\text{C}_8\text{-BTBT}$.

Finally, for the process conditions examined here, higher solute concentration generally delivers films with improved electrical characteristics. This is likely due to fewer defects in the film as well as less damage incurred during top-contact metallization. Besides, we extract the optimal coating speed as the coating speed that yields best electrical performance. In the case of $\text{C}_8\text{-BTBT}$, this optimal speed remains very close to the balanced speed defined for a pure solvent only. This confirms the limited impact of solute on solvent evaporation dynamics. For TIPS-Pentacene, the optimal speed is twice the balanced speed, which is a consequence of the enhanced precipitation rate of this material.

In conclusion, although the results leading to these findings were obtained on a zone-casting tool, we believe that they are generically applicable to the wide array of organic thin film coating techniques that rely on a meniscus dragged across a substrate. The enhanced solvent evaporation at the tip of the meniscus leads to localized solution supersaturation and film formation, quite independently of the dynamics governing the bulk of the solution drop captured between substrate and coating head.

4. Experimental Section

Sample Fabrication: Highly doped n^{++} silicon wafers covered with a 130 nm thick thermally grown silicon dioxide layer served as common gate substrates. These were cleaned sequentially in heated ultrasonic baths of detergent, deionized water, acetone, and isopropanol. After a UV/ozone treatment, the substrate surfaces were modified with phenethyl(trichloro)silane (PETS; from Sigma-Aldrich, 98%). C₈-BTBT (2,7-Dioctyl[1]benzothieno[3,2-*b*] [1]benzothiophene) was supplied by Sigma-Aldrich and purified prior to usage in a trizone purification oven; TIPS-Pentacene (6,13-Bis(triisopropylsilyl)ethynyl) was bought from Ossila and used as received. Solutions were prepared in anhydrous heptane (from Sigma-Aldrich, 99%) and anhydrous hexane (from Sigma-Aldrich, 95%) with varying concentrations. The solution coatings were performed using a home-built zone-casting setup as previously described.^[19] During the coating process, solution was continuously supplied by an automatic syringe pump in order to keep the meniscus shape constant. This refill rate was dependent of solvent choice and process temperature, but independent of substrate speed v and solute concentration c_s .

Thin Film Characterization: AFM studies were performed using a Bruker dimension edge scanning probe in tapping mode. Polarized microscopy images were obtained using an Olympus AX70 microscope in reflected light. TFTs were fabricated by evaporating 6 nm thick F₆TCNNQ and subsequently 50 nm thick gold through a shadow mask to form source and drain contacts. The transistor channel length and width was 190 and 2035 μm , respectively and the channel length was aligned with the casting direction. This value of the width was always used for the analysis, although the real channel width may be lower due to the presence of voids in the organic film.^[8] The samples were annealed after contact formation in a N₂-filled glove box at a temperature of 50 °C for 10 h to ensure good electrical characteristics.^[27–29] Electrical characterizations were done using an Agilent Agt1500 in dry air. Field-effect mobilities were evaluated in the saturation regime using the conventional transconductance analysis given by $\mu_{\text{eff,sat}} = (2L/W)(1/C_i)(\partial\sqrt{I_D}/\partial V_G)^2$, where C_i is the gate capacitance per unit area. Measurements were done with a gate bias V_G range from +10 to –40 V at a constant drain bias $V_D = -40$ V. A total of 80 TFTs were fabricated and averaged for each experimental condition (coating speed, substrate temperature, solvent, concentration—giving a total of 6400 devices in this study).

Fluid Dynamics Simulations: The COMSOL Multiphysics (Chemical Engineering module) finite element analysis software was used to self-consistently solve an incompressible laminar Navier–Stokes model including gravity for the fluid dynamics in the liquid drop and in surrounding air, a diffusion model for the transport of solvent vapor in air, and a convection–diffusion model for the transport of solute inside the solution. The simulations were limited to isothermal systems at atmospheric pressure. It was assumed that in the zone-casting process, solvent evaporation is limited by the rate of diffusion away from the meniscus edge. This assumption was reasonable considering the high vapor pressures of tested solvents and the compact system geometry that offered limited escape routes to diffusing solvent vapor.^[19] For the convection and diffusion models of solvent vapor in air and of molecular solute in solution, only highly diluted cases were considered.

Therefore, solutes were assumed to have neglectable impact on solution flow and fluid dynamics models were solved using pure solvents only. It was further assumed that the drop geometry was independent of substrate speed^[19] and that the resupply rate was only dependent upon evaporation dynamics, hence independent of solute concentration and substrate speed as verified during the experiments.

A realistic 2D model geometry was used with solvent-substrate contact angle $\theta = 5^\circ$, blade angle relative to the substrate = 10° , blade height above the substrate = 250 μm , and blade width = 5 mm. The geometry of the pure solvent drop pinned between casting head and substrate was first optimized using a moving mesh approach and then fixed for further fluid dynamics simulations (see Figure S1 in the Supporting Information). Next, the solvent vapor diffusion in air was computed by setting its partial pressure at vapor pressure along the meniscus edges and at zero far from the casting head (>10 cm). This simulation delivered the evaporative fluxes Φ , along the meniscus edges. Next, the pure solvent flow inside the drop was solved, with an output flux along the meniscus edges that matched the evaporative flux. A free flow condition was set at the inlet of the casting head to match the total evaporative solute flow rate. Finally, diffusive and convective transport of solute inside the solution was calculated by setting solute concentration $c_{s,\text{in}}$ at the inlet, and by allowing precipitation wherever the solution concentration c_s reaches the solubility limit $c_{s,\text{lim}}$. The precipitation model used a step function to distinguish under and supersaturation cases and a large reaction rate to ensure complete precipitation. No redissolution of precipitates was considered. This simple approach cannot capture subtle phenomena such as homogeneous nucleation in the solution or precipitation on a growing crystal front. Such phenomena are complex^[30–32] and are not entirely deciphered in today's state-of-the-art. The simple precipitation model succeeded in giving a global picture of solute transport and concentration in the meniscus region, which was sufficient to drive qualitative conclusions. Table S1 in the Supporting Information gives the main material parameters used throughout the simulations.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

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