ELUCIDATING PROCESSING-STRUCTURE-FUNCTION RELATIONSHIPS IN SOLUTION-PROCESSED, ORGANIC-SEMICONDUCTOR THIN FILMS FOR TRANSISTOR APPLICATIONS

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Abstract

Solution-processed, organic-semiconductor thin films comprising spherulites are structurally complex. Low-angle grain boundaries exist within spherulites to accommodate a large distribution of molecular orientations about the radial axis. Interspherulite boundaries (ISBs) also exist where two spherulites impinge. To determine how these structural heterogeneities affect charge transport, we first developed a fundamental understanding of the structural development of solution-processable triethyilsilylethynyl anthradithiophene (TES ADT) organic-semiconductor thin films. We then developed methods to control the structure of TES ADT thin films in order to elucidate structure-function relationships in organic thin-film transistors (OTFTs).

To control the nucleation density in TES ADT thin films, fractional amounts of small-molecule additives were used to seed TES ADT crystallization. By increasing the concentration of small-molecule additives in TES ADT thin films, the average spherulite diameter was varied from 3 mm to 30 µm. After nucleation, spherulites propagate radially outwards at a constant rate until neighboring spherulites impinge. The growth rate of TES ADT spherulites can vary by a factor of three depending on the surface energy of the underlying substrate. By selectively patterning the underlying substrate to have regions of different surface energies, we imposed differential growth rates of TES ADT to guide crystallization along pre-specified, nonlinear patterns. This method of guided crystallization was used to engineer ISBs having low and high angles of molecular orientation mismatch.
The ability to specify the nucleation density and control the direction of crystallization in TES ADT thin films were then employed to decouple how the structure of spherulites affects charge transport in the active layers of OTFTs. By testing arrays of transistors within a single spherulite, intraspherulite charge transport was found to be independent of the general molecular orientation, but dominated by low-angle intraspherulite grain boundaries. By measuring charge transport across single engineered ISBs, high-angle ISBs were found to act as significant barriers to charge transport. Small-molecule additives were also incorporated into the active layers of TES ADT OTFTs to vary the number of ISBs in the active channel. OTFT device performance degraded with increasing number of ISBs in the active channel, since charge transport is dominated by high-angle ISBs.
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Chapter 1: Introduction

Organic electronics, that is, electronic devices employing carbon-based materials as the charge transport medium, is a rapidly expanding field of research promising novel technologies, such as electronic papers and flexible displays. Solution-processed organic semiconductors, in particular, will enable inexpensive processing techniques capable of large-area coverage to be used in the fabrication of such devices. These compounds can be dissolved in organic solvents and subsequently deposited as electrically-active films via methods, such as spin coating, drop casting, or inkjet printing. These processes can take place on arbitrary substrates, such as flexible, transparent plastics, at ambient pressure and temperature. Significant research efforts in this field have thus focused on improving charge transport through solution-processed, organic-semiconductor thin films.

The most commonly device platform to measure charge transport through organic-semiconductor thin films is the organic thin-film transistor (OTFT), which modulates current flow in electronic circuits. Since the first solution-processed OTFTs were reported in 1988, device mobilities have steadily improved from $10^{-5}$ cm$^2$/V-s$^{[1]}$ to more than 1 cm$^2$/V-s$^{[2-4]}$. Despite success, achieving such high device performance routinely and robustly is still largely an Edisonian, trial-and-error approach. While it is commonly accepted that the structure in the active layers of devices can influence OTFT performance, we still lack a fundamental understanding of processing-structure-function relationships that allow the prediction of device properties based on the chemical structures of organic semiconductors. A major challenge in obtaining such knowledge
lies in the inherent structural complexities of organic semiconductor thin films. Starting with one compound that is of fundamental interest to the community as a solution-processed organic semiconductor, this thesis examines methods to engineer the structure of electrically-active thin films in order to explore correlations between the structure of the active layers of OTFTs to overall device performance. In doing so, we shed light on important structural development that can influence charge transport; such research will greatly aid in guiding the future development of solution-processed organic semiconductors for high-performance OTFTs.

The difficulty in studying structure-function relationships in solution-processed, organic-semiconductor thin films lies in their structural complexity. With the advantage of rapid deposition of solution-processed, organic-semiconductor thin films comes the disadvantage that these films comprise structures that are kinetically trapped in states far from thermodynamic equilibrium after solvent-vapor annealing. Solution-processed, organic-semiconductor thin films thus adopt a wide variety of morphologies, ranging from being completely amorphous to being polycrystalline. Because charge transport through organic-semiconductor thin films relies on π-orbital overlap between adjacent molecules, the crystallinity and orientation of molecules in these films are critical. Understanding how to control crystallization and subsequently using this knowledge to explore structure-function relationships in the active layers of OTFTs will thus contribute greatly towards commercializing solution-processed, organic semiconductor-based devices.

In order to control crystallization in organic-semiconductor thin films, it is first necessary to have a comprehensive understanding of the crystallization process. In this
thesis, we focus on the nucleation and growth of spherulites. Spherulites are radially-symmetric, crystalline superstructures, ubiquitous in both natural and synthetic materials\textsuperscript{[5]}, that are frequently observed in solution-processed, organic-semiconductor thin films\textsuperscript{[6-8]}. Spherulites nucleate from a single point, and they grow radially outwards in a space-filling manner. In order to grow symmetrically outwards, spherulites necessarily incorporate a distribution of orientations about the radial axis; this is achieved by secondary nucleation of grains at the spherulitic growth front. As such, spherulites are complex superstructures comprising many smaller grains all generally oriented in the radial direction from the spherulite center. Both intraspherulite boundaries between grains within spherulites and interspherulite boundaries (ISBs) between adjacent spherulites thus exist, both of which can impact charge transport. Because they appear in many organic-semiconductor systems\textsuperscript{[6-8]}, understanding how charge is transported across these different boundaries is critical to the field of organic electronics.

In this thesis, we seek to develop a fundamental understanding of nucleation and growth in order to control the structure of solution-processed, organic-semiconductor thin films. In doing so, we can decouple and untangle the complexities of the active layers of devices in order to systematically study how the structure can influence device performance in solution-processed OTFTs. For these studies, we have chosen to focus on triethyilsilylethynyl anthradithiophene (TES ADT), a solution-processable, small-molecule organic semiconductor first synthesized by the Anthony group in 2004\textsuperscript{[9]}. TES ADT is an ideal system to study the nucleation and growth of spherulites because we can spin coat TES ADT to form a largely amorphous film and then induce crystallization via spherulitic growth by exposing the film to 1,2-dichloroethane (DCE) vapor\textsuperscript{[10]}. To gain a
deeper understanding of spherulitic growth, we examine how factors, such as DCE solvent-vapor concentration, the presence of additives in the film, and the surface energy of the underlying substrate, affect the nucleation and rate of spherulitic growth in Chapter 4.

Having established a basic understanding of spherulitic growth in TES ADT thin films, we proceed to develop methods to control the nucleation density and crystallization direction of TES ADT spherulites. Chapter 5 details the use of small-molecule additives to seed the nucleation of TES ADT spherulites. Specifically, we examine how the physical properties of additives, such as their tendency to crystallize, solubility in the casting solvent, and miscibility with TES ADT, impact their effectiveness in seeding TES ADT crystallization. In doing so, we suggest specific physical properties of the additives to achieve desired nucleation densities in two-component, organic-semiconductor thin films.

In addition to gaining control over the nucleation density in TES ADT thin films, we also develop a method to guide the propagation direction of the crystallization front in Chapter 6. Specifically, we have found that the growth rate of TES ADT spherulites depends strongly on the surface energy of the underlying substrate. By patterning the underlying substrate to have regions of different surface energies, we can thus promote fast crystallization of TES ADT along arbitrary, non-linear paths while suppressing crystallization in all other directions. Using this method, we are able to engineer the formation of ISBs at pre-specified angles of molecular orientation mismatch between adjacent spherulites. This ability will in turn allow us to study charge transport as a function of the angle of molecular orientation mismatch at ISBs. Such control over the
direction of crystallization in organic-semiconductor thin films has the potential to lead to novel technologies requiring the spatial patterning of material properties within thin films.

Using these methods to control the nucleation density and the direction of crystallization, in Chapter 7 we explore structure-function relationships in TES ADT OTFTs. Having established that the structure of TES ADT thin films is complex, with structural heterogeneities existing on multiple length scales, we begin by exploring charge transport within a single spherulite. Because TES ADT spherulites can easily span 3 mm, we can fabricate arrays of OTFTs on a single spherulite. By measuring the device performance of OTFTs at different locations within a spherulite, we examine how the presence of low-angle intraspherulite grain boundaries affects charge transport in the absence of ISBs. By engineering ISBs with pre-specified angles of molecular orientation mismatch, we then study charge transport across single ISBs with prescribed angles of molecular orientation mismatch. Finally, combining these two results, we study charge transport in TES ADT OTFTs comprising multiple spherulites – and thus multiple ISBs – by correlating OTFT device mobility to the number of ISBs in the active channel. Collectively, we present a comprehensive study on charge transport through polycrystalline thin films comprising spherulites.

Finally, in Chapter 8, we conclude with a summary of the work presented in this thesis, as well as suggestions for future experiments. These experiments include probing the electronic properties of two-component, organic-semiconductor systems and controlling not only the density of nucleation, but also the location of nucleation in solution-processed organic-semiconductor thin films. Currently, nucleation in TES ADT
thin films is spatially random, occurring on dust particles and defects. The ability to pre-specify the location at which nucleation begins will in turn allow us to pre-specify the location of crystallization. In exploring these areas, we hope future projects will move solution-processed, organic-semiconductor thin films one step closer towards commercialization.
References


Chapter 2: Background

Organic semiconductors are currently being intensively researched as active layers for electronics to enable novel technologies, such as electronic papers and flexible displays. Electronic devices traditionally use inorganic semiconductors as active layers. These inorganic counterparts often comprise highly ordered, covalently-bonded crystals. When excess holes or electrons are inserted into the crystal lattice via elemental doping, these charges can move freely through the network of covalently-bonded atoms in an applied electric field to generate current flow. Organic semiconductors, on the other hand, exhibit weaker Van der Waals-type interactions between molecules, with charge transport that occurs via hopping enabled by π-orbital overlap between adjacent aligned molecules. Because the mechanism of charge transport in organic semiconductors is fundamentally different from that of inorganic semiconductors, the mobility of charges in these systems is orders of magnitude smaller than their inorganic counterparts. Nevertheless, the ease of processing organic semiconductors and their chemical versatility in terms of ease of synthesis and subsequent functionalization have made them prime candidates for electronic devices. Devices using organic-semiconductor thin films as active layers can also be fabricated through cost-efficient processing techniques making them inexpensive alternatives to inorganic-based devices in low-current applications. A huge effort is thus currently focused on enhancing the electronic properties of organic-semiconductor thin films by seeking methods to control their morphology to enhance charge transport and developing low-cost fabrication methods for organic semiconductor-based devices.
Charge transport in organic semiconductors occurs via hopping through a $\pi$-orbital overlap network of the conjugated cores of these compounds. Due to their extensive conjugation, these compounds are often insoluble in organic solvents; organic small-molecule semiconductors have thus historically been deposited onto substrates by thermal evaporation under reduced-pressure conditions. While this method of deposition leads to well-controlled growth of high-quality films, it is an energy- and capital-intensive process, often with stringent processing conditions, such as the necessity of high vacuum and elevated temperatures, during deposition. In an effort to move to large-area processing of active layers in organic electronics at ambient temperatures and pressures, researchers began to explore solution-based processing methodologies using compounds that can be dissolved in common organic solvents and subsequently deposited via methods, such as spin coating or drop casting\textsuperscript{[1]}. The first solution-processed organic semiconductors were based on polymers, such as poly(3-alkyl thiophene)\textsuperscript{[2]}. These semiconducting polymers afford the use of rapid deposition techniques at room temperature and ambient pressure. Upon solvent evaporation, however, they often exist in semicrystalline or amorphous states. In these systems, poor alignment of the polymer chains disrupts the $\pi$-orbital overlap network, negatively impacting charge transport through these films. As will be discussed in greater detail in Section 2.2.2, charge transport through solution-processed semiconducting polymer thin films has thus been historically lower compared to that through thermally-evaporated organic small-molecule thin films.

Compared to polymers, small molecules, given their size relative to high-molecular weight polymers, tend to crystallize more readily. More recently, researchers have thus
begun to explore solution-processable organic small-molecules. Early work explored the use of soluble pentacene precursors that could be subsequently converted back to electrically-active pentacene after film deposition via thermal annealing\textsuperscript{[3, 4]}. Mobilities before and after thermal annealing of the active layer were measured to be \(2 \times 10^{-3} \text{ cm}^2/\text{V-s}\) and \(0.2 \text{ cm}^2/\text{V-s}\), respectively\textsuperscript{[3]}. The field of solution-processable organic small molecules began gaining widespread attention with the pioneering work of John Anthony’s group at the University of Kentucky, wherein small-molecule organic semiconductors are functionalized with bulky side groups that not only impart solubility to the molecule, but also promote co-facial packing\textsuperscript{[5]}. By functionalizing pentacene with triisopropylsilyl ethynyl side groups, researchers were able to impart solubility to the pentacene derivative in organic solvents while maintaining its electrical activity\textsuperscript{[6]}. Mobilities as high as \(1 \text{ cm}^2/\text{V-s}\) have been achieved with transistors comprising such small-molecule organic semiconductors deposited from solution\textsuperscript{[7]}. Since the introduction of such molecules in 2001, hundreds of studies have been published on the synthesis and characterization of solution-processable, organic-semiconductor small molecules with bulky side groups\textsuperscript{[6, 8]}.

This thesis focuses on the structure and charge transport properties of films comprising a solution-processable, organic-semiconductor small molecule, triethylsilyl ethynyl anthradithiophene (TES ADT), first synthesized by the Anthony group in 2004\textsuperscript{[9]}. Specifically, we studied processing-structure-function relationships in organic thin-film transistors (OTFTs) comprising TES ADT as active layers. Such relationships will enable us to determine device characteristics \textit{a priori} and enable careful design of next-generation organic semiconductors and processing conditions. In this
chapter, we provide descriptions of OTFTs and how they operate; solution-processable organic semiconductors; and current understanding of structure-function relationships between the morphology of organic-semiconductor thin films and OTFT performance. We also discuss the tools that were used to characterize the morphology in these films, namely, grazing-incidence x-ray diffraction (GIXD) and conductive atomic force microscopy (c-AFM). Finally, we end the chapter with a brief overview of TES ADT. In particular, we will establish our motivations for choosing TES ADT for this study.

2.1 Operation and testing of OTFTs

The primary platform used for comparing the electronic properties of organic semiconductors in electronic applications is the OTFT. Transistors, one of the basic building blocks of electronic circuits, act as switches to modulate current flow. OTFTs comprise four main components: source and drain electrodes, an organic-semiconductor active layer (ca. 10 - 200 nm), a dielectric layer, and a gate electrode. The evaluation of the electronic properties of organic semiconductors using OTFT platforms necessarily depends on the device architecture, as well as the intrinsic properties of the active layers. Figure 2.1 shows two configurations of OTFTs used in this thesis. Both configurations utilize the bottom-gate architecture, with doped-Si acting as the gate electrode and electrically-insulating SiO₂ as the dielectric layer. Figure 2.1a shows a bottom-gate, top-contact configuration, in which the organic-semiconductor active layer is deposited directly on top of the gate dielectric; gold source and drain electrodes are then evaporated on top of the active layer. In a bottom-gate, bottom-contact configuration, on the other hand, the gold electrodes are evaporated onto the SiO₂ dielectric layer prior to deposition.
of the organic-semiconductor active layer (refer to Figure 2.1b). Top-contact configurations have been demonstrated to improve charge injection from the electrode to the organic-semiconductor active layer\textsuperscript{[10]}. In this configuration, the active layer is deposited on the flat dielectric surface prior to electrode deposition. In contrast, in the bottom-contact configuration, the active layer is deposited on a surface with topographical features, comprising the source and drain electrodes. The presence of these features can cause defects to form at the active layer/electrode interface, resulting in a decrease in OTFT performance\textsuperscript{[11]}. For fragile organic-semiconductor active layers, however, the bottom-contact configuration is preferable to avoid damage to the active layer during the subsequent energetic electrode deposition process. In TES ADT thin films, for example, metal deposition via electron-beam evaporation has been shown to damage the underlying active layer\textsuperscript{[12]}. A less energetic deposition process of thermal evaporation is thus employed to make electrical contact to TES ADT instead\textsuperscript{[13]}.

In the absence of an external electric field, organic semiconductors are electrically insulating. When a voltage is applied across the source and drain electrodes, current thus cannot flow through the active layer. To enable current flow through the active layer, a voltage needs to be applied across the source and gate electrodes also. Although the dielectric layer prevents current flow between the two electrodes, the applied source-gate voltage creates an electric field, which capacitively influences the distribution of charges in the active layer. Specifically, when a positive gate bias is applied, electrons accumulate at the active layer-dielectric interface. Likewise, when a negative gate bias is applied, holes accumulate at the active layer-dielectric interface. This accumulation of charges creates a channel through which electrons or holes can now flow, respectively. The
magnitude of the current flow between the source and drain electrodes thus depends on both the voltage drop across the source and drain electrodes, $V_{SD}$ (i.e., the driving force), and the gate bias, $V_G$ (i.e., the size of the channel for current flow).

To compare the electrical behavior of OTFTs, we typically collect both the output and transfer characteristics. To collect the output characteristics, the source-drain current, $I_{SD}$, is measured as a function of $V_{SD}$ at increasing $V_G$. Figure 2.2 shows representative output characteristics of an OTFT in which its $V_{SD}$ is varied from 0 to -50 V, and the gate bias is increased from +10 to -50 V in steps of -10 V. From the output characteristics, we observe that at a positive gate bias of +10 V, the OTFT is in its “off” state, with negligible current flow between the source and drain electrodes. At increasingly negative values of $V_G$, the device turns on. Accordingly, the current levels increase as $V_G$ increases. There are two regimes in the output characteristics, a linear regime, in which $I_{SD}$ depends linearly on $V_{SD}$; and a saturation regime, in which $I_{SD}$ is independent of $V_{SD}$. In the saturation regime, increasing $V_{SD}$ does not result in higher current levels.

OTFTs are generally characterized by three main parameters: the mobility, $\mu$; the threshold voltage, $V_T$; and the on/off ratio. The mobility represents how quickly charges move through the active layer under an applied electric field; the threshold voltage represents the $V_G$ at which the device turns on; and the on/off ratio is the ratio of the current level when the device is turned on to the current level when the device is turned off. It is possible to calculate the transistor mobility from the transfer characteristics in both the linear and saturation regimes. Because transistor mobilities are most frequently calculated from the transfer characteristics in the saturation regime in the literature\textsuperscript{[14]}, we also use the transfer characteristics in the saturation regime to calculate device
mobilities in this thesis. From the device characteristics in the saturation regime, it is possible to calculate the device mobility, $\mu$, using the following equation:\textsuperscript{[15]}:

$$I_{SD} = C_i \frac{W}{2L} \mu (V_G - V_T)^2$$  \hspace{1cm} (2.1)

where $I_{SD}$ is the source-drain current, $C_i$ is the capacitance of the dielectric layer (10 nF/cm$^2$ in the case of 300-nm thermally-grown silicon oxide), $W$ and $L$ are the channel width and length, respectively (refer to Figure 2.3), $V_G$ is the gate voltage and $V_T$ is the threshold voltage. Rearranging Equation 2.1 to solve for $\mu$, we can write:

$$\mu^{1/2} = \left( \frac{2L}{C_i W} \right)^{1/2} \left( \frac{V_G}{V_G - V_T} \right) \frac{I_{SD}^{1/2}}{V_G}$$  \hspace{1cm} (2.2)

The values of $\mu$ and $V_T$ can thus also be easily calculated from the transfer characteristics of the OTFT, where $I_{SD}$ is measured as a function of $V_G$ in the saturation regime at constant $V_{SD}$. Figure 2.4 shows a representative transfer curve of an OTFT. Using Equation 2.2, we can calculate $\mu$ from the slope of $I_{SD}^{1/2}$ and $V_G$ of the transfer characteristics. Furthermore, $V_T$ can be calculated from the curve at $I_{SD}^{1/2} = 0$, as shown in Figure 2.4. The on/off ratio can be calculated by dividing the current in the saturation regime by the current when $V_{SD} = 0$.

In the case of solution-processed OTFTs, device mobilities typically range from $10^{-4}$ cm$^2$/V-s to as high as 1 cm$^2$/V-s\textsuperscript{[16, 17]}, surpassing the mobility of amorphous silicon transistors, at approximately 0.1 cm$^2$/V-s\textsuperscript{[15]}. $V_T$’s are typically between 0 to 20 V, while on/off ratios can range from $10^2$ - $10^6$\textsuperscript{[13, 16, 18]}. Because OTFT mobilities depend strongly on the morphology in the active layers, significant research efforts have focused on developing processing-structure-function relationships in these devices. In the next section of this chapter, we will discuss inherent molecular properties of organic
semiconductors comprising the active layers, as well as morphological factors that can affect device mobilities of solution-processed organic thin-film transistors.

2.2 Solution-processed small-molecule organic semiconductors

Over the past two decades, solution-processed organic semiconductors have been gaining widespread attention in the research community as promising candidates for the active layers for organic electronic devices due to their ease of processing and chemical versatility. Among the first solution-processed OTFTs reported in the literature were those based on polymers, such as derivatives of polythiophene and soluble polyacetylene precursors, with device mobilities on the order of $10^{-4}$ to $10^{-5}$ cm$^2$/V-s. OTFT mobilities of polymeric OTFTs have since improved to as high as 0.1 cm$^2$/V-s in the case of poly(3-hexylthiophene), P3HT, transistors. Further, with the development of chemistries to incorporate alkyl chains to polymers, their solubility in common solvents has also increased substantially.

A significant challenge still facing polymer-based active layers is the polydispersity in molecular weight and regioregularity among batches and from batch to batch. These factors can significantly impact the overall film crystallinity, and thus, device performance. In P3HT-based OTFTs, for example, improving the regioregularity of P3HT from 86% to 96% leads to an increase in the total crystallinity of the film from 12 to 21%, and accordingly to an improvement in OTFT mobility from $6.4 \times 10^{-4}$ cm$^2$/V-s to $1.1 \times 10^{-3}$ cm$^2$/V-s. This example also highlights an important point that polymer thin films are semicrystalline at best, with both crystalline and amorphous regions present due to poor motility of the long polymer chains to reorganize and crystallize during film
formation or processing. The synthesis of soluble small-molecule organic semiconductors has thus been intensively researched in recent years to address these issues. Solution-processable small-molecule organic semiconductors retain the compatibility with facile processing techniques, such as spin coating and drop casting, that are attractive for processing polymer thin films, while eliminating variations within batches and from one batch to another. Small-molecule organic-semiconductor thin films can also generally reach a higher degree of crystallinity compared to polymeric materials due to the higher motility of small molecules to rearrange during film formation and processing compared to long polymer chains\textsuperscript{[11]}. Under appropriate processing conditions, OTFTs comprising solution-processed small-molecule organic semiconductor thin films as the active layers can readily achieve device mobilities between 0.1 and 4 cm\textsuperscript{2}/V-s\textsuperscript{[18, 27-29]}. Increasing the solubility of small-molecule organic semiconductors in organic solvents can be achieved through the attachment of alkyl chains to the conjugated core\textsuperscript{[30-32]}, the same method employed to improve the solubility of conjugated polymers. Figures 2.5a and b show the chemical structures of two examples of small-molecule organic semiconductors, namely an alkylated hexabenzocoronene derivative\textsuperscript{[30]} and dihexyl-α-pentathiophene\textsuperscript{[33]} in which the parent organic semiconductor compound has been functionalized with alkyl chains to improve their solubility in organic solvents. More recently, the Anthony group has demonstrated the ability to synthesize novel acene derivatives with bulky silyl-based substituents attached to the conjugated core. The chemical structure of one such example, 6,13-bis(triisopropylsilylethynyl) pentacene, TIPS pen\textsuperscript{[5]}, is displayed in Figure 2.5c. These derivatives are also highly soluble in organic solvents. By systematically tuning the size of the substituent, researchers have
further been able to tune the packing motif of these small-molecule organic semiconductors in the solid state\[^8\]. When the size of the substituent is approximately half the length of the acene core, molecules tend to stack in a brickwork manner\[^8\]. Unsubstituted pentacene, for example, crystallizes in a herringbone manner (refer to Figure 2.6a), while TIPS pen – comprising a pentacene core with bulky substituents approximately half the length of pentacene attached – crystallizes in a brickwork manner because the bulky silyl groups disrupt edge-to-face interactions between adjacent molecules\[^6\] (refer to Figure 2.6b). The presence of bulky side groups also promotes co-facial packing of molecules. With the introduction of bulky substituents, the intermolecular spacings of for unsubstituted pentacene and TIPS pen is 3.47 Å\[^5\], compared to 6.27 Å for unsubstituted pentacene\[^34\]. Through increasing the size of the silyl group beyond half the length of the acene core, Anthony and coworkers have also synthesized pentacene derivatives that crystallize in a slip-stack manner\[^6\] (refer to Figure 2.6c). OTFTs comprising derivatives that crystallize in a slip-stack manner to consistently exhibit lower mobilities compared to those comprising solution-processed acenes that crystallize in a brickwork manner. This observation suggests that charge transport through organic-semiconductor thin films is strongly influenced by the packing motif in the active layer\[^6\]. Calculating the transfer integrals of interacting molecules, which describes the ease of charge transfer between adjacent molecules, Brédas and coworkers found that the intermolecular spacing should be below approximately 4 Å for efficient charge hopping to occur in sexithienyl systems\[^35\]. They also found that the lateral displacement of molecules with respect to one another can significantly impact the charge transfer rate between molecules. For pentacene derivatives, for example,
molecules that pack in a herringbone structure exhibit larger lateral displacement than those that pack in a brickwork structure\[^5\]. Accordingly, single crystals comprising molecules that pack in a herringbone structure display resistances of \(8 \times 10^9\ \Omega\)-cm compared to only \(2.5 \times 10^6\ \Omega\)-cm for single crystals comprising molecules that pack in a brickwork structure\[^5, 8\]. More recently, Bao and coworkers used a solution-shearing technique to introduce lattice strain to TIPS pen crystals, resulting in a decrease in the \(\pi-\pi\) stacking distance from 3.33 Å to 3.08 Å\[^29\]. OTFT mobility accordingly increased from 0.8 cm\(^2\)/V-s for OTFTs comprising unstrained TIPS pen crystals in the active layer to 4.6 cm\(^2\)/V-s for OTFTs comprising strained TIPS pen crystals in the active layer. The ability to tune both the packing motif and the intermolecular spacing between molecules in crystals is thus critical for designing high-performing organic electronic devices.

Imparting solubility to an organic semiconductor via altering its chemical structure thus necessarily affects its packing motif and crystal structure, and in turn its optical and electronic properties, such as photoabsorptivity and conductivity, respectively. Case in point are functionalized phenylenethiophene oligomers. Although the solubility of phenylene-thiophene oligomers increases when the size of the solubilizing side group is increased, the presence of a larger side group impedes charge transport between neighboring molecules, thereby decreasing overall device mobility in OTFTs comprising these oligomers as active layers\[^36\].

Beyond the chemical structure and crystal packing of solution-processable organic semiconductors, the degree of crystallinity and average crystal size in the active layer also affects OTFT performance. Solution-processed organic-semiconductor thin films exist in a kinetically-trapped state far from thermodynamic equilibrium due to the
rapidity of structural development during film processing. The degree of crystallinity and crystal size in these films, which determines the extent of π-orbital overlap between molecules and its relative orientation with respect to the ideal charge transport direction in OTFTs, can significantly impact charge transport. In the following section, we discuss methods for depositing solution-processed organic-semiconductor films and how such conditions impact crystallization and thus device performance in OTFTs comprising these films as active layers.

2.2.1 Deposition of solution-processable organic semiconductors

Imparting solubility to small-molecule organic semiconductors allows one to take advantage of simple processing methods to form organic-semiconductor thin films for electronic applications. The simplest method of depositing solution-processed organic semiconductors onto substrates is drop casting. In this technique, the organic semiconductor is first dissolved in a good solvent, such as chloroform, toluene, or chlorobenzene. Drops of the organic-semiconductor solution are placed on a substrate. The solvent is then allowed to evaporate, resulting in a rough film whose overall crystallinity is largely determined by the rate of solvent evaporation. To improve the uniformity of drop-cast films, doctor blading, in which a blade is dragged across the organic-semiconductor solution on the substrate surface before solvent evaporation, can be employed. Another method of producing uniform thin films is spin coating, in which the substrate is spun after deposition of the solution, usually at a rate of 500 - 5000 revolutions per minute (rpm). Rapid solvent evaporation during the spinning of the substrates results in films with uniform thickness.
While the aforementioned methods are extensively employed in the research community to fabricate OTFTs, these techniques indiscriminately deposit the organic semiconductor over the entire substrate surface, so patterning the organic semiconductor requires additional pre- or post-deposition steps\textsuperscript{37-43}. To selectively deposit organic semiconductor onto regions of the substrate, processes, such as inkjet printing and screen printing, have been employed instead. In inkjet printing, the organic-semiconductor solution is dispelled from a micrometer-scale nozzle onto the substrate through the use of a printer\textsuperscript{44}. This technique allows for precise deposition of organic semiconductor features on the scale of 100 µm. In addition, several organic-semiconductor solutions can be printed sequentially onto a single substrate. In screen printing, a solution containing the organic semiconductor is transferred onto a substrate through a screen mask which contains the desired pattern\textsuperscript{45,46}. The pattern is limited to a resolution of ~75 µm\textsuperscript{47}. In both of these methods, solution viscosity and solvent evaporation rate are critical in maintaining film integrity and in determining the final morphology of the film\textsuperscript{48,49}.

Solvent choice and deposition methods are two critical factors that can determine the degree of crystallinity and crystal size in small-molecule organic-semiconductor thin films, which in turn have been shown to strongly influence the device performance of OTFTs comprising these films as active layers. In general, deposition methods that allow more time for solvent to evaporate, such as drop casting, lead to improved crystallinity\textsuperscript{16}, compared to methods, such as spin coating. Furthermore, solvents with high-boiling points evaporate more slowly during deposition, allowing more time for crystallization of the organic semiconductor to occur compared to when low-boiling point solvents are employed. We have previously demonstrated, for example, that the
morphology of drop-cast TIPS pen films depends strongly on the boiling point of the solvent from which the film is deposited\textsuperscript{[27]}. Films deposited from high-boiling point solvents, such as toluene and chlorobenzene, displayed a higher degree of crystallinity compared to films deposited from low-boiling point solvents, such as chloroform and tetrahydrofuran, because the higher-boiling point solvents evaporate more slowly, thus allowing more time for crystallization of TIPS pen to occur during film formation. Accordingly, TIPS pen OTFTs comprising active layers deposited from chlorobenzene display mobilities of $0.10 \pm 0.05 \text{ cm}^2/\text{V-s}$, compared to only $0.018 \pm 0.005 \text{ cm}^2/\text{V-s}$ for OTFTs comprising active layers deposited from chloroform\textsuperscript{[27]}.

In addition to altering the processing conditions to influence crystallization in these films, significant research efforts have focused on tuning the morphology of solution-processed organic semiconductor thin films via post-deposition processing techniques, such thermal\textsuperscript{[50-52]} and solvent-vapor annealing\textsuperscript{[10, 18, 53-56]}. In the following section, we will highlight several of these methods and examine how they can be used to provide fine control over the final morphology of organic-semiconductor thin films.

2.2.2 Structure-function relationships in OTFTs

Organic-semiconductor thin films deposited from solution adopt a wide range of morphologies depending on the relative speeds of crystallization and solvent evaporation. The crystallization of solution-processed organic-semiconductor thin films occurs rapidly and depends on processing parameters, such as solvent choice, concentration, deposition method, and substrate surface properties\textsuperscript{[57]}. In organic-semiconductor thin films, the degree of crystallinity and molecular orientation of organic semiconductors are important
considerations in fabricating high-performing OTFTs. Increasing the degree of crystallinity in the active layers of OTFTs has been shown to improve mobilities in many different organic semiconductor systems\textsuperscript{[18, 50-52, 58-68]}. Thermal annealing of OTFTs is a commonly employed method to improve device performance by increasing the degree of crystallinity in the active layer\textsuperscript{[50-52]}. Dodabalapur and coworkers, for example, observed an order of magnitude increase in the hole mobility from 0.06 cm\(^2\)/V-s to 0.2 cm\(^2\)/V-s after post-deposition thermal annealing of a solution-deposited diketopyrrolopyrrole-benzothiadiazole-based copolymer at 200\(^\circ\)C to increase the crystallinity of the film\textsuperscript{[52]}.

Another popular method to improve the crystallinity in thin films is solvent-vapor annealing\textsuperscript{[10, 18, 53-56]}. As will be discussed in the last section of this chapter and in Chapter 4, our group has previously demonstrated that exposure of TES ADT thin films to solvent vapor can significantly improve the degree of crystallinity by allowing molecular rearrangement to occur, thereby dramatically improving device performance of OTFTs comprising solvent-vapor annealed TES ADT films as active layers\textsuperscript{[10, 18, 54]}.

Not only is the degree of crystallinity important in determining device performance, crystal orientation can also significantly impact charge transport through the active layer. Organic semiconductors commonly adopt a preferential orientation with respect to the substrate normal due to interactions with the underlying substrate\textsuperscript{[69-71]}, with negligible in-plane orientation. Based on studies of charge transport in organic-semiconductor single crystals\textsuperscript{[72, 73]}, it is widely accepted that OTFT mobility is highest when the \(\pi\)-stacking direction is aligned with the direction of charge transport across the channel. Several techniques have thus been developed to induce preferential orientation of molecules in organic-semiconductor thin films such that the \(\pi\)-stacking direction is
parallel to the charge transport direction, including the use of rubbed[60, 68, 74, 75] or photoaligned substrates[62], the use of temperature gradients to induce directional crystallization[69], or gravitational flow to align molecules[28]. Using these methods to induce preferential in-plane molecular orientation in organic-semiconductor thin films, researchers have demonstrated improved device mobility. Sele and coworkers, for example, reported a more than two-fold difference in the mobility of TIPS pen OTFTs by altering the macroscopic alignment of TIPS pen molecules with respect to the channel[28], suggesting that the in-plane molecular orientation of crystals can significantly impact OTFT mobility.

Finally, the overall size of crystals in organic-semiconductor active layers can also significantly impact overall device performance. Polycrystalline thin films comprising grains necessitates the presence of grain boundaries that can act as barriers to charge transport from one grain to another due to misorientation of molecules and the presence of trap sites at the boundaries. Several studies on OTFTs with thermally-evaporated active layers have shown that device performance is positively correlated to the average crystal size (or negatively correlated with the grain boundary density) in the active layer[76-78]. Surface potential measurements also indicate the existence of an energy barrier at grain boundaries in organic-semiconductor thin films[79-81]. The impact of such boundaries in the active layers of OTFTs will be discussed in greater detail in Chapter 7, where we present a systematic study of the dependence of OTFT mobility on spherulite size in solution-processed TES ADT thin films, as well as quantification of the resistance of spherulite boundaries in these films.
The structural heterogeneities in the active layers within OTFTs exist at different length scales. Figure 2.7 illustrates how such structural heterogeneities that exist in the active layers of organic electronic devices are intertwined on several length scales\cite{57}. On the molecular length scale, the alignment of molecules and their packing can influence the degree of $\pi$-orbital overlap between adjacent molecules. At the nanometer to micron length scale, grains can vary in both size and orientation. In semicrystalline polymer thin films, interconnectivity also becomes important as polymer chains can bridge adjacent crystallites\cite{82}. Furthermore, if two components are blended to form in a single film, phase separation can exist on the hundreds of nanometers to submillimeter length scale.

As previously discussed, structural heterogeneities at these different length scales can strongly influence charge transport through the active layers of OTFTs. Decoupling the individual contributions of the structural heterogeneities, however, has proven exceedingly difficult because they are often intertwined. In order to establish structure-function relationships between the morphology in the active layers and device performance of OTFTs, it is necessary to examine the hierarchical structuring of organic-semiconductor thin films that traverses all these length scales. In doing so, we will be able to understand how the morphologies at each length scale combine to affect overall device performance.

To establish structure-function relationships between OTFT device performance and the degree of crystallinity, crystal orientation and crystal size in the active layers of devices, it is necessary to have access to tools that allow the characterization of active layer morphologies. In the next section, we will discuss in detail two techniques, grazing-
incidence x-ray diffraction and conductive atomic force microscopy, that were employed extensively in this thesis to study the structure of TES ADT thin films.

2.3 Characterization tools for studying the morphology of organic thin films

To study the morphology of organic-semiconductor thin films, researchers have drawn on a wide variety of techniques, such as optical microscopy\cite{18,70}, tunneling electron microscopy\cite{83}, and scanning electron microscopy\cite{84}, to visualize the surfaces and cross-sections of organic-semiconductor thin films; near-edge x-ray absorption fine structure spectroscopy (NEXAFS) to probe the ensemble-average orientation of molecules and the composition at the surfaces of these films\cite{84,85}. When optical contrast exists between crystalline and amorphous domains, such as in the case of TES ADT, optical microscopy can be a powerful tool in observing structural rearrangement on the micron to millimeter length scale. In this thesis, we use optical microscopy extensively to visualize the growth of TES ADT spherulites during solvent-vapor annealing. Furthermore, because these films are only tens to hundreds of nanometers thick, surface sensitive measurements, such as grazing-incidence x-ray diffraction and atomic force microscopy, have been especially useful in quantitatively characterizing the morphology of organic-semiconductor thin films on the molecular to micron length scale. In the following sections, we will briefly describe these two techniques, which are used extensively in the later chapters of this thesis.
2.3.1 Grazing-incidence x-ray diffraction

Diffraction techniques rely on the constructive interference of incident x-rays when they interact elastically with periodically-spaced features, such as the lattice planes within crystals. Figure 2.8 illustrates constructive interference of incident x-rays after interactions with periodically-spaced lattice planes of a crystal. The conditions necessary for constructive interference to occur are described by Bragg’s Law:

\[ \lambda = 2d \sin \theta \]  

(2.3)

where \( \lambda \) is the wavelength of the incident x-ray, \( d \) is the characteristic spacing between planes, and \( 2\theta \) is the scattering angle. Depending on the source, the wavelengths of x-rays for diffraction experiments typically range from 1 – 3 Å, on the order of the spacing between molecular planes in organic crystals.

Traditional diffraction techniques conducted in transmission mode for examining the crystalline properties of materials, in which the incident beam passes directly through the sample, are incompatible with studying the active layers of organic electronic devices since these thin films are deposited on substrates that are not transparent to x-rays. Further, they often degrade quickly under direct, high-intensity beams used during transmission experiments. Instead, we have turned to grazing-incidence x-ray diffraction (GIXD), a surface-sensitive technique used to characterize the crystal structure, orientation, and degree of crystallinity in thin films on the order of 100-nm thick. In this method, the incident x-ray beam interacts with the film at a grazing angle. Figure 2.9 shows the geometry of GIXD experiments. The incident x-ray angle is chosen to be above the critical angle of the organic film but below the critical angle of the underlying substrate[86]. In this geometry, the x-ray beam penetrates the entire organic layer but is
reflected off the underlying substrate. The respective critical angles can be determined via reflectivity measurements, in which the intensity of the reflected beam (at an angle of 2θ) is measured as a function of the incident x-ray angle, θ. Figure 2.10 shows an example of a reflectivity trace taken on a 100-nm thick TES ADT thin film spun cast onto a SiO₂ substrate. The critical angles of the organic film and SiO₂ substrate at 0.13° and 0.19° are labeled, respectively. At higher θ values, we observe interference fringes that arise from the phase difference of x-rays that are reflected off the surface of the organic layer and those that are reflected off of the underlying substrate. From the spacing of the fringes, we can calculate the film thickness. For maximum intensity in GIXD experiments, the incident angle should be set just below the critical angle of the substrate[86].

The observed diffraction patterns in GIXD experiments are in reciprocal space, quantified by a scattering vector, q. To convert q in reciprocal space to the corresponding characteristic spacing, d, we can use the following relation:

\[ q = \frac{2\pi}{d} \]  

(2.4)

From the diffraction pattern in reciprocal space, we can gain information not only about the crystal structure, but also the crystal orientation and relative degree of crystallinity. Figure 2.11 shows a representative diffraction pattern of a drop-cast chlorinated 5,11-bis(triethylsilylethynyl) anthradithiophene, Cl-TES ADT, thin film on a SiO₂ substrate. Based on the location of the reflections, one can gain information on the crystal structure, primarily by comparing their locations to those predicted by x-ray single-crystal crystallography. In the case of Cl-TES ADT thin films, we found the crystals to adopt a polymorph different from that of the single-crystal structure, but closely matching that of
a high-temperature polymorph of another TES ADT derivative, fluorinated 5,11-
bis(triethylsilylethynyl) anthradithiophene F-TES ADT\textsuperscript{[87]}. Furthermore, the azimuthally-
integrated scattered intensity of the reflections is directly correlated to the degree of
crystallinity in the film. If a reference of known absolute crystallinity is available, it is
possible to use the intensity of the reflections to quantify the absolute crystallinity of the
samples. Finally, the uniformity of the diffracted intensity along a particular q provides
information about crystal orientation. When the pattern displays rings having uniform
azimuthal intensity, the sample is isotropic and there is no preferential crystal orientation.
Oftentimes, the organic semiconductor adopts a preferential out-of-plane orientation due
to interactions with the underlying surface\textsuperscript{[88]}. A diffraction pattern of such a film, in this
case solvent-vapor annealed TES ADT, is shown in Figure 2.12. Here, instead of
azimuthally-uniform intensity along the reflections, we see diffraction spots. The
locations of the spots are determined by the lattice dimensions of the crystal structure, as
well as the orientation of the crystals with respect to the substrate surface. In solvent-
 vapor annealed TES ADT thin films, the molecules are all oriented with their \(\pi\)-planes
perpendicular to the substrate normal. Intensity anisotropy in the out-of-plane direction
thus provides orientation information about the crystals in the organic-semiconductor thin
films.

To quantitatively measure the degree of orientational disorder in a system, one can
also collect \(\phi\)-scans. In these scans, the intensity of a reflection in the diffraction pattern
of a sample is measured as the sample is rotated in the path of the incident x-ray beam.
The full-width at half-the-maximum intensity (FWHM) of \(\phi\)-scans is a measure of degree
of spread in molecular orientations about the rotation axis. A \(\phi\)-scan on the (600)
reflection of single-crystal rubrene, for example, has a FWHM of 0.02°, indicating very little orientational disorder within the crystal\textsuperscript{[89]}, while A ϕ-scan on the (100) reflection of a directionally-crystallized P3HT thin film is three orders of magnitude higher, at a value of 10\textsuperscript{0}[69].

Importantly, GIXD patterns can only provide relative degrees of crystallinity among films comprising the same organic semiconductor. For statements on the absolute crystallinity of a film, it is necessary to predict the expected intensity of a given reflection based on the geometry and electron density of the unit cell of the single crystal, or to reference against a standard with a known degree of crystallinity. Still, GIXD is a powerful tool in studying the relative crystallinities in organic-semiconductor thin films. We thus employ this technique frequently in subsequent chapters to study the crystallinity and crystal orientation of organic-semiconductor thin films in order to establish how their structure-function relationships.

2.3.2  Conductive atomic force microscopy

In the field of organic electronics, characterization tools capable of simultaneously collecting information on both material and electronic properties on the microscopic length scale are increasing in popularity. These techniques allow direct correlations to be drawn between the morphology of films and their electronic properties, such as photoconductivity\textsuperscript{[90]} and surface potential\textsuperscript{[84, 91]}. Conductive atomic force microscopy (c-AFM), for example, is a variation of the commonly used atomic force microscopy (AFM). As its name suggests, c-AFM can measure the local conductivity of a film with <0.1 µm spatial resolution while simultaneously mapping the surface topography of the
film. In conventional AFM experiments, a laser beam is reflected off of a tip (refer to Figure 2.13) as it is dragged (contact mode) or tapped (tapping mode) along the surface of the organic-semiconductor thin film. The movement of the reflected laser beam on a photodiode as the tip moves across the surface can be translated into the relative local height of the film surface. By scanning the tip along a surface over small areas, usually ranging from 0.5 to 30 µm², it is possible to generate a 3-D map of the surface topography.

C-AFM operates in the same manner as AFM, but also collects electrical current laterally across or perpendicularly through the film during measurements. Figure 2.14a shows a diagram of the experimental setup for collecting lateral current measurements, in which an electrode is evaporated on top of the organic thin film. The tip serves as the second electrode. Figure 2.14b shows a diagram of the experimental setup for collecting vertical current measurements, in which the organic semiconductor layer is deposited on top of an electrode. Since the AFM tip acts as the counter electrode, it must be coated with a conductive metal, such as chromium, prior to measurements. During measurements, a voltage is applied across the conductive pad and tip and the current across or through the film is recorded. The height profile is simultaneously recorded, allowing one to directly map the current flow to the surface topography of the film. C-AFM measurements have been used to measure the resistance of grain boundaries in thermally-evaporated organic-semiconductor thin films⁹² and of organic single crystals⁹², as well as map current flow in phase-separated, two-component organic-semiconductor blends⁹³. In this thesis, we use both AFM and c-AFM to study solution-processed organic-semiconductor thin films. In Chapter 7 specifically, we will
demonstrate the use of c-AFM in visualizing the barrier to charge transport that exists at high-angle interspherulite boundaries.

2.4 Triethylsilylethynyl anthradithiophene (TES ADT)

In the final section of this chapter, we focus on TES ADT, the solution-processable organic semiconductor we chose to study in this dissertation research. TES ADT, first synthesized by the Anthony group in 2004\textsuperscript{[9]}, has an electrically-active anthradithiophene core with bulky silyl substituents attached to impart solubility to the molecule. Figure 2.15 displays the chemical structure of TES ADT. TES ADT stacks in a brickwork manner when crystallized\textsuperscript{[17]}, with significant \(\pi\)-orbital overlap between adjacent molecules to allow for charges to hop between molecules; OTFTs comprising crystalline TES ADT as the active layers have reported mobilities as high as 1 cm\(^2\)/V-s\textsuperscript{[17]}. Due to its promising electrical characteristics and high solubility in common organic solvents, dozens of manuscripts have been published exploring the material and the electronic properties of thin films comprising TES ADT and its derivatives in the past seven years\textsuperscript{[10, 18, 54, 87, 91, 94, 95]}.

We have chosen to study TES ADT in this work largely due to its unique thin film properties. When first deposited onto substrates via spin coating, TES ADT thin films display only limited ordering (refer to Chapter 4). Subsequent post-deposition processing thus allows us to control the crystallization of TES ADT. In other organic-semiconductor systems, crystallization often occurs during film formation and is thus exceedingly difficult to control\textsuperscript{[22, 27, 95]}. In 2007, our group reported that the crystallinity of spun-cast TES ADT thin films could be dramatically improved via solvent-vapor annealing\textsuperscript{[18]}.
When as-spun films are exposed to solvent vapors, spherulitic growth is induced, with TES ADT spherulites adopting a triclinic crystal structure similar to that found in TES ADT single crystals\textsuperscript{17,70}. Figures 2.16 and 2.17 display the optical micrographs and UV-visible absorption spectra of TES ADT thin films, respectively, before and after solvent-vapor annealing. As can be seen from these figures, significant structural rearrangement occurs as a result of exposure to solvent vapors, resulting in a change in the optical properties of the film. The decrease in absorbance at $\lambda = 305$ nm when TES ADT is crystallized, as seen in Figure 2.17, is likely due to anisotropy in light absorption along different crystallographic directions of the TES ADT molecule. When crystallized, TES ADT adopts a single out-of-plane orientation, with its anthradithiophene core perpendicular to the substrate normal\textsuperscript{70}. We also observe a slight red-shift of the absorption spectra in solvent-vapor annealed TES ADT thin films, consistent with an increase in $\pi$-orbital overlap between molecules\textsuperscript{96}. The crystallization of TES ADT thin films leads to an enhancement in device mobility from $0.002 \text{ cm}^2/\text{V-s}$ in OTFTs comprising as-spun films as the active layer to $0.1 \text{ cm}^2/\text{V-s}$ in OTFTs comprising solvent-vapor annealed films as the active layer\textsuperscript{18}.

Compared to other organic semiconductors, with which crystallization often occurs during film deposition, the driving force for TES ADT to crystallize is weak, allowing us to deposit TES ADT films exhibiting only limited ordering\textsuperscript{10}. We can subsequently controllably crystallize TES ADT through solvent-vapor annealing; we have thus effectively decoupled film formation from crystallization in TES ADT. From differential scanning calorimetry (DSC) measurements of TES ADT powder, we have observed that TES ADT displays a solid-state phase transition at $130 \, ^\circ\text{C}$ and melts at $150 \, ^\circ\text{C}$. Figure
2.18 displays a DSC thermogram of TES ADT. The melting point of TES ADT is significantly lower compared to other small-molecule organic semiconductors, such as tetracene, which melts at 340 °C\[^97\]. Furthermore, the enthalpies of the order-order and melt transitions in TES ADT are approximately 23 and 24 J/g\[^10\], respectively, more than an order of magnitude smaller than the melt enthalpy of tetracene, at 695.6 J/g\[^97\]. The low melting temperature and small melt enthalpy of TES ADT suggest that its tendency to crystallize is weak, allowing us to deposit films with limited ordering upon solvent evaporation after spin coating and subsequently induce crystallization via solvent-vapor annealing. The ability to controllably induce crystallization in TES ADT thin films, as well as observe the structural changes via optical microscopy, is central to this thesis, allowing us examine the kinetics of crystallization (Chapters 4 and 5), and to direct crystallization within a film (Chapter 6), which we have in turn used to establish structure-function relationships in solution-processed TES ADT OTFTs (Chapter 7).

2.5 Conclusions

Solution-processed small-molecule organic semiconductors are appealing candidates as active layers of OTFTs due to their chemical versatility, ease of processing, and ability to achieve high degrees of crystallinity. For the advancement of solution-processed OTFTs in commercial applications, it is essential to establish processing-structure-function relationships of these materials in order to understand how the chemical structure of organic semiconductors can affect crystallization behavior during device fabrication, which in turn will impact overall device performance. Such information will enable the rational design of next-generation organic semiconductors for device
applications with specific optical and electronic requirements. Here, we have provided a background that will serve as a basis for discussion in future chapters and motivated the experiments presented in this thesis to study processing-structure-function relationships in solution-processed TES ADT OTFTs.
**Figure 2.1.** Schematic illustration of OTFTs in a) a bottom-gate, top-contact configuration and b) a bottom-gate, bottom-contact configuration.

**Figure 2.2.** Representative output characteristics for an OTFT that exhibits hole transport characteristics. The gate voltage is increased from +10 to -50 V in steps of -10 V as the source-drain voltage is swept from 0 to -50 V.
Figure 2.3. Top view of top-contact OTFT with the channel length and width between the source and drain electrodes labeled.

Figure 2.4. Representative transfer characteristics curve of an OTFT. The source-drain voltage was maintained at -50 V during measurements. The mobility, $\mu$, is calculated from the slope of the curve. The threshold voltage, $V_T$, of the device is also labeled.
Figure 2.5. Chemical structures of common solution-processable, small-molecule organic semiconductors, including a) alkylated hexabenzocoronene$^{[30]}$, b) dihexyl-α-pentathiophene$^{[33]}$, and c) 6,13-bis(triisopropylsilylethynyl) pentacene, TIPS pen$^{[5]}$.

Figure 2.6. Schematic illustration of the different types of packing motifs, including a) herringbone, b) brickwork and c) slipstack. Black lines represent the conjugated planes of the molecules.
Figure 2.7. An illustration of the three different length scales at which structural heterogeneities within the active layers of organic electronic devices exist. [Reproduced from S.S. Lee and Y.-L. Loo. *Annu. Rev. Chem. Biomol. Eng.* (2010), 1, 59]
Figure 2.8. An illustration of constructive interference of x-rays when they interact with planes at periodic spacings. $\theta$ represents the x-ray incident angle and $d$ represents the characteristic spacing between planes. [Adapted from W. Callister. Material Science and Engineering: An Introduction, 7th edition. (2006), John Wiley and Sons]

Figure 2.9. Geometry of grazing-incidence x-ray diffraction experiments.
Figure 2.10. Reflectivity trace of a 100-nm thick TES ADT film spun cast on a SiO$_2$ substrate. Then angle at which x-rays begin interacting with the sample, the critical angles of the TES ADT organic thin film and the SiO$_2$ substrate are labeled, as well as the interference fringes, the spacings of which indicate the film thickness.
Figure 2.11. An example of a 2-D diffraction pattern of a drop-cast Cl-TES ADT thin film with no preferential orientation of crystals.
Figure 2.12. An example of a 2-D diffraction pattern of a spun-cast, crystalline TES ADT thin film in which the crystals are preferentially oriented in the out-of-plane direction.
**Figure 2.13.** Scanning electron microscopy image of an AFM tip. [Reproduced from www.schaefer-tec.com]

**Figure 2.14.** Schematic illustrations of c-AFM experiments measuring a) lateral conductivity of the organic-semiconductor thin film parallel to the substrate surface and b) vertical conductivity through the organic-semiconductor thin film.
Figure 2.15. Chemical structure of TES ADT.

Figure 2.16. Optical micrographs of the same region of a TES ADT thin film a) before and b) after solvent-vapor annealing.
Figure 2.17. Comparison of absorbance spectra of an as-spun TES ADT thin film and the same film after solvent-vapor annealing.

Figure 2.18. Differential scanning calorimetry (DSC) thermogram of TES ADT powder on heating at 10°C/min.
References


Chapter 3 : Experimental Methods

In this chapter, we provide details on sample preparation and characterization techniques, as well as device fabrication and testing. In Section 3.1, we discuss TES ADT deposition and processing. In Section 3.2, we provide experimental details for techniques used to characterize these films and the underlying substrates, including grazing-incidence x-ray diffraction and atomic force microscopy. In Section 3.3, we discuss OTFT fabrication and device testing, as well as resistivity measurements using a four-probe setup. All experimental steps were performed in air.

3.1 TES ADT thin film fabrication

3.1.1 Substrate preparation

300 nm SiO$_2$/doped-Si wafers purchased from Process Specialties were used as substrates for TES ADT thin films in this thesis. The wafers were rinsed sequentially with acetone, isopropyl alcohol, and deionized water and then dried with house nitrogen prior to further surface modification, spin coating of TES ADT, or deposition of gold electrodes for bottom-contact organic thin-film transistors (OTFTs). Unless otherwise specified, TES ADT thin films were spun cast directly onto the pre-cleaned wafers.

To measure the dependence of TES ADT spherulitic growth rate on the surface energy of the underlying substrate (refer to Chapter 4), surface modifications were made to the 300 nm SiO$_2$/doped-Si wafers prior TES ADT deposition. Ultraviolet ozone (UVO)-treated SiO$_2$/doped-Si substrates were prepared by exposing pre-cleaned SiO$_2$/doped-Si wafers to UVO (Jelight UVO Cleaner, Model No. 42) for 10 minutes.
Hexylmethyldisilazane (HMDS; Fluka International)-treated substrates were prepared by spin coating HMDS at 3000 rpm for 30 s on pre-cleaned SiO$_2$/doped-Si wafers. Gold patterns and electrodes were prepared by evaporating 2 nm Ti followed by 35-nm thick Au by electron-beam deposition on pre-cleaned SiO$_2$/doped-Si wafers. UVO-treated Au surfaces were prepared by exposing pre-patterned Au substrates to UVO for 10 min prior to TES ADT deposition. Dimethylbenzenethiol (DMBT), pentafluorobenzenethiol (PFBT), and butanethiol (BT)-treated Au surfaces were prepared by soaking pre-patterned Au substrates in 7.5 mM ethanol solutions for 20 min immediately after removal of the substrates from the evaporation chamber. The substrates were then sonicated in ethanol for 2 min to remove any physisorbed compounds and dried with nitrogen prior to TES ADT deposition.

For directed crystallization experiments (Chapter 6), 35 nm Au pads were evaporated onto SiO$_2$/doped-Si substrates through shadow masks via electron-beam deposition. The substrates were then immersed in a 7.5 mM solution of PFBT in ethanol for 20 min immediately after removal of the substrates from the evaporation chamber. The substrates were then sonicated in ethanol for 2 min to remove any physisorbed compounds and dried with nitrogen prior to TES ADT deposition. After sonication, PFBT remained only on the Au regions of the substrates given preferential Au-thiol interactions$^{[1]}$.

3.1.2 TES ADT deposition

TES ADT was synthesized by Dr. Marsha Loth and Dr. Balaji Purushothaman, members of John Anthony’s group at the University of Kentucky, according to previously published procedures$^{[2]}$. To form thin films, TES ADT was first dissolved in
toluene at a concentration of 2 wt%. TES ADT photobleaches easily; in order to avoid degradation due to light exposure, solutions were made in 4 ml amber vials. Since TES ADT is susceptible to degradation over a period of tens of minutes in solution, and this degradation has led to a significant increase in nucleation density in TES ADT thin films upon solvent-vapor annealing, only 100 – 200 µl aliquots of TES ADT solution were thus made at a time (sufficient for spin coating 1 substrate), and the solutions were allowed to sit for only 4 – 5 min prior to spin coating. Fresh solutions were made for each subsequent spin coating. The solutions (unfiltered) were spun cast onto the substrates at 1000 rpm for 60 s, resulting in a final film thickness of 100 nm. After spin coating, the substrates were immediately transferred to a hot plate and annealed at 90 °C for 2 min in order to remove any residual toluene.

For experiments on two-component organic-semiconductor thin films comprising TES ADT and another small-molecule organic semiconductor (refer to Chapter 5), the second organic semiconductor was added to TES ADT/toluene solution in concentrations ranging from 0.1 – 10 mol% relative to TES ADT prior to spin coating, with both compounds fully dissolved in toluene. The organic semiconductors used as additives were fluorinated bis(triethylsilyl)ethynyl anthradithiophene, F-TES ADT\textsuperscript{[3]}; chlorinated bis(triethylsilyl)ethynyl anthradithiophene, Cl-TES ADT; brominated bis(triethylsilyl)ethynyl anthradithiophene, Br-TES ADT; iodinated bis(triethylsilyl)ethynyl anthradithiophene, I-TES ADT; 2,8-diethyl-5,11-bis(triethylsilyl)ethynyl anthradithiophene, ethyl-TES ADT\textsuperscript{[4]}; triisopropylsilyl)ethynyl pentacene, TIPS pen\textsuperscript{[5]}; triisobutylsilyl)ethynyl pentacene, TIBS pen\textsuperscript{[6]}; triethylsilyl)ethynyl tetracene-derivatized fullerene, TES Tet Fu\textsuperscript{[7]}; and phenyl-C\textsubscript{61}-butyric acid methyl ester,
PCBM. The chemical structures of the TES ADT derivatives, TIBS pen, TES Tet Fu, and PCBM are shown in Figure 3.1. For the chemical structure of TIPS pen, refer to Figure 2.5c. Solutions comprising small concentrations, usually between 1 - 2 wt%, of the additives in toluene were first prepared separately in an amber vial. An appropriate volume of the solution comprising the additive of interest was then added to the 2 wt% TES ADT solution to reach the desired molar ratio of additive to TES ADT. These solutions were allowed to sit for 3 – 4 min before they were spun cast at 1000 rpm for 60 s onto pre-cleaned SiO2/doped-Si substrates.

Films comprising 50/50 mol% blends of TES ADT and the desired additive were also made. For these films, powders of TES ADT and the desired additive were weighed into the same vial at the appropriate molar ratios. Toluene was then added until a concentration of 2 wt % total concentration (TES ADT + additive) was achieved. The solutions were allowed to sit for 3 – 4 minutes prior to spin coating at 1000 rpm for 60 s onto pre-cleaned SiO2/doped-Si substrates.

To probe molecule-substrate interactions between TES ADT and substrates having different surface energies (refer to Chapter 4), TES ADT was spun cast from a 0.1 mg/ml solution in chloroform onto UVO-treated SiO2, bare SiO2, and HMDS-treated SiO2 substrates. At these low concentrations, we observed submonolayer coverage of TES ADT, allowing us to examine its wetting characteristics on the various substrates. These substrates were chosen because of their low roughness (rms = 0.2 nm) compared to the surface roughness of Au and SAM-treated Au substrates (rms = 4 nm). Chloroform was chosen as a solvent because it evaporates quickly compared to toluene during spin coating. While solutions spun cast from toluene completely dewet the substrates at these
low concentrations, solutions spun cast from chloroform result in the formation of islands of TES ADT on these substrates. As will be discussed in Chapter 5, we have observed that 100-nm thick TES ADT films spun cast from chloroform display no visible differences in their crystallization behavior during solvent-vapor annealing compared to films spun cast from toluene; we thus expect chloroform to be an acceptable substitute for toluene in examining molecule-substrate interactions.

3.1.3 Solvent-vapor annealing to induce crystallization

A previous graduate student in our group, Dr. Kimberly Dickey, discovered that exposure of TES ADT thin films to solvent vapor, such as 1,2-dichloroethane (DCE) and toluene, induced spherulitic growth in the films\[8\]. We used this method extensively in this thesis, exposing TES ADT thin films to DCE solvent vapor for a period of 20 s – 10 minutes, usually until the film is fully crystalline as noted by the impingement of neighboring spherulites. DCE was chosen as the solvent because TES ADT tends to dewet from the substrate when exposed to toluene vapors due to its high solubility in toluene compared to DCE\[8\]. The time of solvent-vapor annealing depends on the nucleation density of spherulites in the film, which in turn is determined by the concentration of additive incorporated into TES ADT solution prior to spin coating (refer to Chapter 5).

Due to the toxicity of DCE, all solvent-vapor annealing took place in a chemical fume hood. Figure 3.2 shows an illustration of the method used to expose the samples to DCE vapor. First, 4 ml of DCE is placed in the bottom of a glass petri dish (6 cm in diameter). The sample is then taped upside-down onto the petri dish cover. The cover is then placed
on top of the petri dish to expose the sample to DCE solvent vapor. Exposure times were limited to 20 s increments – beyond this period of time, DCE solvent-vapor concentration can build to a point where it induces dewetting of TES ADT from the underlying substrate. Figure 3.3 shows a comparison of a film exposed to DCE solvent vapor in increments of 20s for a total time of 5 minutes to one that was exposed continuously to DCE solvent for a period of minutes. In the film that was exposed continuously to DCE solvent vapor, microscopic dewetting of TES ADT from the underlying substrate can be observed.

Although capable of inducing spherulitic growth in TES ADT thin films, the setup depicted in in Figure 3.2 has two major drawbacks: the concentration of DCE solvent vapor cannot be regulated, and we cannot observe the sample during exposure to DCE solvent vapor. For in situ observation of the spherulitic growth process at a constant DCE solvent vapor, we thus built a solvent-vapor annealing chamber with a glass viewport so that samples could be observed with an optical microscope during exposure to DCE solvent vapor (refer to Figure 3.4). Figure 3.5 schematizes the entire solvent-vapor annealing setup. House nitrogen is first flowed through a pressure regulator, which maintained the pressure at 5 psi for all experiments. Under normal operation, valves 1, 2, and 6 remain closed. With valves 3 and 4 open, the nitrogen stream can be then bubbled through the DCE reservoir and through flow meter 1, which maintains the overall flow rate at 5 m³/hr. The stream, now with DCE solvent vapor, is directed via valve 5 to either vent to the chemical fume hood or to the sample chamber before venting into the fume hood. After loading the sample into the sample chamber, the flow is first directed to the chemical fume hood. After focusing the sample under the microscope, we can switch so
the streams flowing through the sample chamber while quickly starting the recording of optical micrographs of the film at 5 s intervals. During in situ observation of spherulitic growth, a steady flow of nitrogen with DCE solvent vapor is maintained at 5 m$^3$/hr through the sample chamber, but this volumetric flow rate can be increased to as high as 30 m$^3$/hr.

To estimate the concentration of solvent vapor in the nitrogen stream, we measured the change in the volume of DCE in the reservoir over time. Assuming that the evaporation of DCE is constant with time, we divided the total amount of DCE evaporated by the total time elapsed and by the nitrogen flow rate to obtain an estimate of the instantaneous concentration of DCE in nitrogen. We found that under normal operation, the nitrogen stream contains 0.019 vol% DCE vapor. In order to determine the dependence of TES ADT spherulitic growth on the DCE vapor concentration in the nitrogen stream, we introduced a second stream of pure nitrogen to dilute the stream passing through the DCE reservoir. This stream can be introduced by opening valve 1. The extent of dilution is determined by the flow rate set by flow meter 2. A 1:1 vol/vol dilution of the nitrogen stream with DCE vapor can be achieved, for example, by setting the flow rate through flow meter 1 equal to that through flow meter 2. Unless specified, valve 1 remained closed during in situ experiments, so that the samples were exposed to a constant DCE concentration of 0.019 vol% in nitrogen during solvent-vapor annealing.

Finally, valves 2 and 6 are used to test for leaks in our setup. Because the optical microscope is operated outside the chemical fume hood, it is imperative to test for leaks in the system after loading each sample to ensure that all DCE vapor is properly vented. After loading the sample into the sample chamber, valve 2 can be opened, and valves 3,
4, and 6 remain closed. If the system is free of leaks, the flow rates through flow meters 1 and 2 should decrease to 0 m$^3$/hr.

### 3.2 Sample characterization

#### 3.2.1 Optical microscopy

To characterize the average spherulite size in TES ADT thin films and to observe spherulitic growth during solvent-vapor annealing, we used a Nikon Eclipse ME 600L Metallurgical Microscope equipped with a CCD camera. Typical magnifications ranged from 15.6x to 625x. The microscope was operated in reflection mode, with the reflected light passing through a polarizer before it is collected by the camera. Images were collected using a Nikon DXM 1200 camera. For kinetic studies of TES ADT spherulitic growth during exposure to solvent vapor, the camera was set to collect images in 5 s increments. For samples that crystallized within 10 - 20 s of their initial to exposure to DCE solvent vapor, a high-speed Sony XCD-710CR camera was instead used to take images every 0.5 s. Image analysis to calculate the fractional area crystallized was carried out using ImageJ software (version 1.45).

#### 3.2.2 Grazing-incidence x-ray diffraction (GIXD) experiments

To study the crystal structure and molecular orientation within TES ADT thin films, we employed GIXD. The majority of GIXD experiments were performed at the Cornell High Energy Synchrotron Source (CHESS) on beamline G-2$^{[9]}$ with x-rays at 8.64 ± 0.01 keV ($\lambda = 0.1435$ nm). Figure 3.6 shows the scattering geometry of the beamline. The wavelength was selected using a Be single-crystal monochromator, labeled in Figure 3.6.
Before interacting with the sample, motorized slits, labeled S1 and S2, were used to define a 0.2 x 3 (V x H) mm$^2$ beam, with a typical flux of 2x10$^{10}$ photons/s. The x-ray incident angle was set to 0.16°, which was determined to be above the critical angle of the organic layer and below the critical angle of the underlying SiO$_2$/doped-Si substrate (refer to Figure 2.9). Diffracted x-rays were collected using a 640-element 1D diode-array, of which each element incorporates its own pulse counting electronics capable of count rates of ~10$^5$ photons/s. A set of 0.1° Soller slits was used on the detector arm to provide an in-plane resolution of 0.16°. 2-D diffraction patterns were collected by scanning the detector along the q$_{xy}$ direction. To collect a φ-scan on a given reflection (refer to Section 2.3.1), the intensity of a reflection was measured as the sample was rotated about the substrate normal in the path of the incident x-ray beam. Matlab was used for data analysis (refer to Appendix 1 for the Matlab codes for plotting 2-D images and for extracting 1-D line cuts along q$_{xy}$, and the intensities as a function of azimuthal angle, ω).

Several grazing-incidence x-ray diffraction (GIXD) experiments were also performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 7-2$^{[10]}$. Experiments were conducted at ambient conditions with an x-ray energy of 8.0 keV (λ = 0.155 nm) and an incident angle of 0.17°. The diffracted beam was collimated with 1 milliradian Soller slits (corresponding to a resolution of ~ 0.05°) and detected with a Vortex point detector. For each sample, several scans thus had to be collected at different q$_{xy}$’s in order to map the locations of reflections in 2-D reciprocal space. For background information on the theory behind GIXD, refer to Chapter 2. For all experiments conducted at both CHESS and SSRL, TES ADT film thicknesses were maintained at 100 nm. Furthermore, the intensities of the scattered x-rays were normalized by the incoming
x-ray intensities and collection time so that relative intensities among samples can be compared quantitatively. The scattered x-ray signal is collimated before being collected at the detector to largely eliminate background scattering, so no background corrections were performed.

3.2.3 Atomic force microscopy imaging

Atomic force microscopy (AFM) images were collected using a Veeco Dimension NanoMan AFM to study the topography of the organic-semiconductor thin films. The AFM was operated in tapping mode using stiff Veeco AFM tips with spring constants between 20 – 80 N/m (model RTESP). For conductive-AFM experiments, the AFM was operated in contact mode using flexible Veeco AFM tips with spring constants between 1 – 5 N/m. A lower spring constant is necessary to operate in contact mode in order to avoid film damage as the tip drags along the film surface. The tips were coated with a conductive chromium layer in order to collect current (model SCM-PIT). Prior to measurements, top-contact gold electrodes were evaporated on top of the organic-semiconductor thin film; simultaneous scanning and recording of the currents provided qualitative measurement of the lateral conductivity. To create a current map of the film, +2 V bias was applied across the electrode and the tip while the tip scanned along the surface of the film. Current flow from the electrode to the tip was simultaneously collected with height information of the film surface. For background information on the theory behind AFM and conductive-AFM, refer to Section 2.3.2.
3.2.4 Contact-angle measurements

To determine the surface energy of substrates, contact-angle measurements were performed using a Ramé-Hart goniometer. The static contact angles of both water and glycerol were recorded once on three separate substrates for each different surface treatment. The average and standard deviation values provided the surface energies of these surfaces via the Owens and Wendt model[11]:

\[
1 + \cos \theta = 2\sqrt{\gamma_s^d \left( \frac{\gamma_l^d}{\gamma_{lv}} \right)} + 2\sqrt{\gamma_s^h \left( \frac{\gamma_l^h}{\gamma_{lv}} \right)}
\] (3.1)

where \( \theta \) is the contact angle; \( \gamma_s^d \) and \( \gamma_l^d \) represent the dispersive force contributions to the free energy of the solid and liquid phase; \( \gamma_s^h \) and \( \gamma_l^h \) represent the hydrogen bonding force contributions to the free energy of the solid and liquid phase; and \( \gamma_{lv} \) is the surface free energy of the liquid. The values of \( \gamma_{lv} \), \( \gamma_l^h \), and \( \gamma_l^d \) for water were assumed to be 72.8 ergs/cm\(^2\), 51.0 ergs/cm\(^2\) and 21.8 ergs/cm\(^2\), respectively[11]. The values of \( \gamma_{lv} \), \( \gamma_l^h \), and \( \gamma_l^d \) for glycerol were taken to be 63.4 ergs/cm\(^2\), 26.4 ergs/cm\(^2\), and 37.0 ergs/cm\(^2\), respectively, per literature[12]. We solved a system of two equations[13] using the values for glycerol and water, respectively, to obtain \( \gamma_s^d \) and \( \gamma_s^h \). The surface energy of the film was then calculated as the sum of \( \gamma_s^d \) and \( \gamma_s^h \).[11]

3.2.5 Differential scanning calorimetry experiments

Differential scanning calorimetry (DSC) thermograms were collected using a Perkin-Elmer Pyris 1 DSC from which we measured the melting temperatures and melting enthalpies of organic semiconductors. In DSC experiments, the differential heat needed to increase the temperature of a pan containing a compound at a constant heat ramp
compared that for an empty reference pan. When the compound undergoes an endothermic phase transition, such as a melt transition, a peak is observed in the differential heat signal. The area under the peak corresponds to the melt enthalpy of the material. For these experiments, aluminum pans were used to hold the samples. For baseline scans, empty aluminum pans were placed in both the reference and sample holders. The temperature was increased at a rate of 10 °C/min between pre-specified start and end temperatures (between 30 °C and 300 °C, for example). For sample scans, 2 – 4 mg of the organic semiconductor in powder form was placed in aluminum pans and placed in the sample holder, while an empty pan was placed in the reference holder. The baseline scan was subtracted from the sample scan to account for differences between the left and right holders.

3.3 OTFT fabrication and testing

To fabricate bottom-gate, bottom-contact OTFTs, 2-nm thick Ti followed by 50-nm thick Au pads were deposited via electron-beam evaporation directly onto pre-cleaned SiO$_2$/doped-Si substrates prior to TES ADT film deposition through shadow masks, as electrodes. For bottom-contact devices, the channel length and width were held constant at 600 µm and 4000 µm, respectively. For bottom-gate, top-contact OTFTs, gold pads were instead deposited on top of the deposited and solvent-vapor annealed TES ADT films. Previously, we found that depositing top-contact electrodes via electron-beam evaporation can damage the underlying TES ADT, leading to an increase in contact resistance\cite{14}. Instead, we deposited top-contact gold electrodes via thermal evaporation to minimize damage to the active layer. Source and drain electrodes were defined using
transmission electron microscopy (TEM) sample grids, with channel lengths and widths of 50 µm and 204 µm, respectively. After the deposition of TES ADT and the definition of source and drain electrodes, we used a buffered hydrofluoric acid etch or we mechanically scratched through the oxide to expose the doped-Si gate for contact. OTFTs were tested using an Agilent 4145B Semiconductor Parameter Analyzer. To collect output characteristics, the source-drain voltage was swept from 0 to -50 V as the gate voltage was increased from +30 to -50 V in increments of -10 V. To collect transfer characteristics, the gate voltage was swept from +30 to -50 V, while the source-drain voltage was maintained at -50 V. For diagrams of bottom-gate, top- and bottom-contact OTFTs and procedures on how to calculate device mobilities, refer to Section 2.1.

Four-probe measurements were conducted on TES ADT thin films, on which four contacts equally spaced 50 µm apart were deposited, using an Agilent 4145B Semiconductor Parameter Analyzer. The widths of the electrodes were 204 µm, as defined by the TEM grids. Figure 3.6 shows the experimental setup for these measurements, in which the resistance through TES ADT films is calculated by measuring the potential drop between the inner electrodes as a result of current flow across the outer two electrodes in order to eliminate contact resistance. The resistances were calculated using the simple $V = IR$ relationship.

### 3.4 Conclusions

In this chapter, we provided details concerning sample preparation, characterization, and device testing for the experiments in this thesis. In Chapter 4, we will provide an in-depth study of spherulitic growth in TES ADT thin films during exposure to DCE solvent.
vapor. In Chapter 5, we will discuss in detail the impact of the presence of organic-semiconductor additives in TES ADT thin films on the spherulite density, as well as its nucleation and crystallization process. We will then present a method for guiding crystallization in TES ADT thin films in Chapter 6. Using this method, we engineer interspherulite boundaries having both low- and high-angles of molecular orientation mismatch. Finally, in Chapter 7, we will use the processing methods developed in Chapters 5 and 6 to carry out a comprehensive study of charge transport in TES ADT OTFTs. Specifically, we will study charge transport within single spherulites and across engineered low- and high-angle single interspherulite boundaries, as well as the overall impact of the number of interspherulite boundaries in the active channel on device mobility.
Figure 3.1. Chemical structures of a) TES ADT derivatives with fluorine, chlorine, bromine, iodine and ethyl substituents, b) TIBS pen, c) TES Tet Fu, and d) PCBM.

Figure 3.2. Setup for exposing TES ADT thin films to DCE solvent vapor in a glass petri dish.
Figure 3.3. a) A TES ADT thin film that had been exposed to DCE solvent vapor in 20 s increments for a total of 5 min using the setup shown in Figure 3.2. The film comprises spherulites approximately 3 mm in diameter. b) A TES ADT thin film that had been exposed to DCE solvent vapor continuously for a period of 5 min. In this film, spherulitic growth was accompanied by dewetting of the film from the underlying substrate.
Figure 3.4. Photograph of the solvent-vapor annealing sample chamber with a glass viewport for *in situ* observation of TES ADT spherulitic growth.

Figure 3.5. Schematic of solvent-vapor annealing setup.
Figure 3.6. Scattering geometry of beamline G-2 at CHESS. The Be Laue crystal is used to select the energy of the incident x-ray beam. S1 and S2 are slits to define size of the incoming x-ray beam. The sample is placed on the diffractometer, which has motion in z, \( \phi \), and \( \Psi \) directions. The diffracted x-rays pass through a Soller collimator to reduce noise from scattering before the signal is collected in a linear gas detector. [Reproduced from Smilgies, D-M., et al. J. Synchrotron Rad. (2005), 12, 807]
Figure 3.7. Schematic of four-probe measurement setup.
References


Chapter 4: Spherulitic growth in TES ADT thin films

Crystallization of in single-component, organic-semiconductor thin films often occurs through nucleation and growth, either concurrent with solvent evaporation during film formation, or during post-deposition treatments. The extent of nucleation largely determines the final size of crystalline domains, while the extent of growth determines the final degree of crystallinity. Both the size of crystalline domains and the degree of crystallinity can significantly impact charge transport, as discussed in detail in Section 2.2.2. A fundamental understanding of nucleation and growth is thus critical in gaining control over structural development in these systems. By developing methods to control the film structure, we can systematically tune the film structure in order to study structure-function relationships in OTFTs. In TES ADT thin films, crystallization occurs through the nucleation and growth of spherulites. In order to grow symmetrically outwards, spherulites incorporate a large distribution of molecular orientations about the radial axis, which is achieved by secondary nucleation of grains at the spherulitic growth front. As such, spherulites are complex superstructures comprising many smaller grains all generally oriented in the radial direction from the initial nucleation point. In this chapter, we explore the factors that affect the growth of TES ADT spherulites. In doing so, we lay the groundwork for future chapters in which we detail methods of controlling nucleation and guiding crystallization in TES ADT thin films.

Spherulitic growth is a common mode of crystallization in a wide variety of systems, including naturally-occurring minerals and organic small molecules\textsuperscript{[1]}. Perhaps most commonly, spherulites are readily observed in many types of semi-crystalline polymers\textsuperscript{[2]}. These polymers crystallize by chain folding, forming lamellar stacks that
emanate radially outwards from a single nucleation point\textsuperscript{[3]}. As a polymer spherulite grows, amorphous regions are incorporated into the structure to maintain its space-filling growth habit.\textsuperscript{[2, 3]} This type of spherulitic growth is also seen in many small-molecule systems\textsuperscript{[4-6]}, in which their thermodynamic-equilibrium structures often comprise faceted crystals. Through modeling, Douglas and coworkers found that such small-molecule systems can form spherulites, particularly when these compounds are highly viscous\textsuperscript{[7]}. In these systems, the rotational motion of molecules is significantly limited compared to their translational motion (so molecules can translate large distances before they are able to rotate from their initial orientations)\textsuperscript{[8]}. Because the rotational motion of molecules in these systems is restricted, they in turn nucleate secondary grains that are off-axis at the growth front of spherulites. The wide distribution of molecular orientations within spherulites is evident in their complex birefringent patterns under polarized light\textsuperscript{[2, 9]}, and can also be measured by techniques, such as selected-area x-ray diffraction\textsuperscript{[10]}. 

In TES ADT thin films, we observe spherulitic growth when the films are exposed to DCE solvent vapor. Because DCE is a good solvent for TES ADT, DCE solvent vapor can plasticize TES ADT, allowing local rearrangement to occur. This environment promotes the nucleation and growth of TES ADT spherulites; these spherulites can easily reach diameters larger than 3 mm on clean substrates\textsuperscript{[11]}. Understanding the factors that affect spherulitic growth and the structure of spherulites is critical for this thesis. In subsequent chapters, we will present systematic studies on controlling the average number density of spherulites by selectively adding nucleating agents (Chapter 5). We show in Chapter 6 that we can disrupt the radial symmetry of spherulites to guide crystallization around bends and corners based on growth rate differences induced by
differential underlying surface energies. We then use these methods to elucidate structure-function relationships between the structure in the active layer and OTFT device performance. Specifically, we study both intra- and interspherulite charge transport in TES ADT thin films in Chapter 7. Herein, we provide an in-depth characterization of spherulitic growth in TES ADT thin films by elucidating the structure in TES ADT thin films before and after solvent-vapor annealing, and exploring its kinetics of crystallization.

4.1 Structure of as-spun TES ADT thin films

To understand spherulitic growth in TES ADT thin films, we first studied the film structure before and after solvent-vapor annealing via optical microscopy and grazing-incidence x-ray diffraction (GIXD). Figure 4.1 displays optical micrographs of a TES ADT thin film before and after solvent-vapor annealing. Compared to the optical micrograph of a solvent-vapor annealed TES ADT thin film, such as that shown in Figure 4.1b, the as-spun TES ADT thin film in Figure 4.1a appears featureless. This observation led us to initially believe that as-spun TES ADT thin films are amorphous\textsuperscript{[11, 12]}. From GIXD experiments, however, we found that limited ordering does in fact exist in as-spun TES ADT thin films\textsuperscript{[13]}. Figure 4.2 shows a 2-D diffraction pattern collected on an as-spun TES ADT thin film. This diffraction pattern does not match that predicted by the triclinic crystal structure of TES ADT single crystals\textsuperscript{[14]}, indicating that as-spun TES ADT adopts a previously undocumented polymorph. The intensities of the reflections are

1 – 2 orders of magnitude smaller than what we observe in the GIXD patterns of solvent-vapor annealed TES ADT thin films. We thus believe that as-spun TES ADT thin films are largely amorphous, although precise quantification of the extent of crystallinity is difficult. Without single-crystal data on this polymorph, we do not know the expected intensities of the reflections as a function of the total crystallinity.

Although we cannot precisely calculate the total degree of crystallinity from the diffraction pattern, we can estimate the crystal structure of this polymorph. The presence of periodic diffraction spots in the q_z direction, as opposed to azimuthally-uniform reflections, reveals that TES ADT is uniquely oriented in the out-of-plane direction. By analyzing the diffraction pattern, we were able to identify the best-fit lattice parameters (lengths a, b, and c, and angles α, β, and γ) for the unit cell of the as-spun polymorph. A key observation that aided in the determination of the crystal structure was that all of the reflections in the out-of-plane direction (along q_z) are evenly spaced at intervals of 0.065 Å⁻¹, corresponding to a d-spacing of 97.1 Å. We arbitrarily assigned this dimension to the c-axis of the unit cell. The periodic spacing in the out-of-plane direction also indicates that the crystal structure is monoclinic, with angles α and β equal to 90°. With only three degrees of freedom (a, b, and γ), we proceeded to use least-squares regression to determine the best-fit parameters that would best describe our experimental data. Table 4.1 lists the best-fit lattice dimensions of the monoclinic crystal structure observed in as-spun TES ADT films. In Figure 4.3a, the locations of the reflections predicted by the best-fit lattice parameters are overlayed on top of the observed diffraction pattern as white open circles. Figure 4.3b shows a 1-D comparison of the experimental data summed over all q_z’s (equivalent to a powder x-ray diffraction trace); the predicted
reflections based on the best-fit lattice parameters, with Miller indices labeled, are also provided for comparison. As can be seen from Figure 4.3, there is close agreement between the predicted and actual locations of the reflections. The predicted unit cell is large, comprising approximately 50 TES ADT molecules, suggesting that as-spun TES ADT forms a superlattice. We cannot, however, completely rule out the presence of twin boundaries which can also result in an overestimation of lattice dimensions\(^1\)

\[\text{4.2 Structure of TES ADT spherulites}\]

When as-spun TES ADT is exposed to DCE solvent vapor, crystallization occurs through the growth of spherulites. The optical micrograph of a solvent-vapor annealed TES ADT thin film displayed in Figure 4.1b shows that spherulite coverage is complete across the entire film, suggesting that the film is fully crystalline. To determine the crystal structure of TES ADT spherulites, we collected 2-D GIXD diffraction patterns on solvent-vapor annealed TES ADT thin films. Figure 4.4 displays a diffraction pattern for one such film. As in the case of the diffraction pattern of as-spun TES ADT films, the diffraction pattern of solvent-vapor annealed TES ADT thin films comprises diffraction spots, indicating a unique out-of-plane orientation. The diffraction pattern closely matches that predicted by the crystal structure determined by single-crystal crystallography with TES ADT preferentially oriented with its c-axis aligned in the out-of-plane direction. Small adjustments in the lattice dimensions using least-square regression were, however, necessary to match exactly the observed diffraction pattern (refer to Table 4.1). These differences are likely due to the fact that the single-crystal data was obtained at 100 K to reduce scattering\(^1\), while GIXD patterns on TES ADT thin
films were obtained at room temperature. The reflections in Figure 4.4 are labeled with their Miller indices. Importantly, there are no reflections of the monoclinic crystal structure in the diffraction pattern of solvent-vapor annealed TES ADT thin films, indicating that this polymorph is completely converted into the triclinic polymorph during solvent-vapor annealing. Furthermore, the intensities of these reflections are 1-2 orders of magnitude larger than those observed in the diffraction patterns of as-spun TES ADT. Optical micrographs of solvent-vapor annealed TES ADT thin films do not show any amorphous regions. Assuming that these films are completely crystalline and the scattering cross-sections between the two polymorphs are comparable, we estimate the crystallinity of the monoclinic polymorph to be at least 1–2 orders of magnitude lower than that of the solvent-vapor annealed sample based on the differences in the intensities of reflections in the respective GIXD patterns. For direct comparison of the relative intensities, Figure 4.5 displays the GIXD patterns of an as-spun TES ADT thin film and that of a solvent-vapor annealed TES ADT thin film in which the intensities are plotted on a linear scale (in all other GIXD patterns, the intensities are plotted on a log scale for clarity). Because the monoclinic crystal structure has not been observed under any other processing conditions of TES ADT thin films, we believe that the monoclinic polymorph formed during spin coating is metastable, while the triclinic polymorph is the thermodynamically-stable phase of TES ADT crystals.

As previously mentioned, spherulites are comprised of many smaller grains all generally oriented along the radial axis. In TES ADT spherulites, these grains adopt a triclinic crystal structure. Furthermore, we have found that the grains are oriented such that the π-stacking direction is generally parallel to the radial direction from the
spherulite center – we will provide a more in-depth discussion of how we determined this information in Chapter 6. As such, spherulitic systems comprise structural heterogeneities traversing multiple length scales. Within spherulites, the presence of small grains necessitates the formation of intraspherulite low-angle grain boundaries on the submicron to micron length scale. On the micron to millimeter length scale, interspherulite boundaries (ISBs) also exist. Both low-angle intraspherulite grain boundaries and ISBs can impact charge transport, as will be discussed in Chapter 7. To facilitate discussion of the structural heterogeneities in TES ADT thin films, here we provide an illustration of the structure of TES ADT spherulites, Figure 4.6a displays a diagram of a polycrystalline TES ADT thin film in which three spherulites impinge; the centers of each are highlighted by red circles. The π-planes of TES ADT molecules are represented by short gray lines; these are generally oriented with respect to their respective spherulite centers. Between the smaller grains that comprise spherulites exist intraspherulite grain boundaries, as illustrated by the dashed black lines. At intraspherulite grain boundaries, the molecules in adjacent spherulites are generally aligned in the same direction. As illustrated in Figure 4.6a, these grain boundaries are low-angle in nature, since all grains are generally oriented with the radial director of the spherulite. At ISBs between two spherulites, on the other hand, the angle of molecular orientation mismatch between molecules, illustrated in Figure 4.6b, can vary. Figure 4.6a displays both low-angle (blue line) and high-angle (red line) ISBs. The angle of molecular orientation mismatch across these boundaries depends on where the nucleation centers are located with respect to one another. Along a single ISB, it is also possible to have both low- and high-angle regions of molecular orientation mismatch due to the large distribution of orientations.
incorporated within spherulites. Figure 4.7 displays an optical micrograph of a solvent-vapor annealed TES ADT thin film with the ISBs highlighted. The blue portions of the ISBs represent regions in which the angle of molecular orientation mismatch is low, while the red portions of the ISBs represent regions in which the angle of molecular orientation mismatch is high. Thin films comprising spherulites are thus complex in their structure, comprising low-angle, intraspherulite grain boundaries and both low- and high-angle ISBs. These boundaries can significantly impact charge transport through the films. To decouple their individual contributions, we have developed a method to engineer individual low- and high-angle ISBs, and explore in depth the impact of both intraspherulite grain boundaries and ISBs on charge transport through TES ADT thin films in Chapter 7.

4.3 Controlling the size of TES ADT spherulites

In exploring the structure of TES ADT thin films, it is also important to consider the diameter of spherulites that form during solvent-vapor annealing. As shown in Figure 4.6, ISBs are formed when spherulites impinge upon one another during solvent-vapor annealing. The density of these ISBs, which we will demonstrate to significantly impact charge transport in Chapter 7, is determined by the size of the spherulites given a pre-specified OTFT channel length. By measuring the average spherulite diameter and approximating spherulites as circles, we can estimate the average number density of spherulites, \(<S>\), using the following equation:

---

\[ <S> = \frac{1}{\pi \frac{L^2}{4}} \]  

(4.1)

where \( L \) is the average spherulite diameter. Following the standard substrate cleaning procedure outlined in Chapter 3, we readily obtain spherulites larger than 3 mm in diameter, corresponding to \( <S> \) of 0.2 spherulites/mm\(^2\). This nucleation density is dictated by the number of dust particles and defects on the substrate surface\(^{[11, 12]}\). Recently, we discovered that through the addition of fractional amounts of a small-molecule additive, fluorinated 5,11-bis(triethysilylethynyl) anthradithiophene (F-TES ADT; for its chemical structure, refer to Figure 3.1a), to TES ADT thin films in concentrations between 0 – 7 mol% relative to TES ADT, we can increase the nucleation density substantially, thereby decreasing the average spherulite diameter from 3 mm to as small as 30 \( \mu \)m, corresponding to an \( <S> \) of \( 2 \times 10^3 \) spherulites/mm\(^2\). Figure 4.8 displays optical micrographs of TES ADT thin films with varying amounts of F-TES ADT after solvent-vapor annealing. From these images, it is clear that \( <S> \) increases with increasing F-TES ADT concentration, indicating that F-TES ADT can act as nuclei for TES ADT crystallization. Figure 4.9 quantitatively displays the dependence of \( <S> \) on F-TES ADT concentration in TES ADT thin films. Below a concentration of approximately 0.5 mol%, F-TES ADT does not aid in nucleating TES ADT crystallization, and \( <S> \) remains constant at 0.2 spherulites/mm\(^2\). At F-TES ADT concentrations between 0.5 and 3 mol%, \( <S> \) increases exponentially with F-TES ADT concentration, from 0.2 spherulites/mm\(^2\) to \( 2 \times 10^3 \) spherulites/mm\(^2\). In this range of concentrations, F-TES ADT acts as nuclei for TES ADT crystallization. Finally, above an F-TES ADT concentration of 3 mol%, \( <S> \) becomes independent of the F-TES ADT concentration, indicating that incorporating
additional amounts of F-TES ADT does not increase the number of active nuclei. By replacing F-TES ADT with other additives, in Chapter 5, we explore the physical properties of additives that affect the dependence of $<S>$ on additive concentration. Furthermore, the ability to vary $<S>$ over 4 orders of magnitude has allowed us to study how the ISB density in the active layers of OTFTs impacts device mobility. We will report the results of such experiments in Chapter 7.

4.4 Crystallization kinetics in TES ADT thin films

Thus far, we have discussed the structure of TES ADT thin films before and after solvent-vapor annealing. In this section, we explore the kinetics of spherulitic growth. Using the solvent-vapor annealing setup detailed in Chapter 3, we are able to observe the \textit{in situ} growth of TES ADT spherulites during exposure to a constant concentration of DCE solvent vapor of 0.019 vol%. Figure 4.10 shows time-lapsed optical micrographs of spherulitic growth in TES ADT thin films deposited on pre-cleaned SiO$_2$/doped-Si during exposure to DCE solvent vapor. Through analysis of these images, we can track the crystallization process and identify how factors, such as the presence of additives or the surface energy of the underlying substrate, influence TES ADT crystallization. In Section 4.4.1, we examine the spherulitic growth process in neat TES ADT thin films. In Section 4.4.2, we explore the same process for TES ADT thin films with fractional amounts of F-TES ADT. Finally, in Section 4.4.3, we study how the surface energy of the underlying substrate can influence the growth rate of TES ADT spherulites.
4.4.1 Crystallization kinetics in neat TES ADT thin films

To explore the kinetics of TES ADT crystallization, we begin by studying the crystallization process in TES ADT thin films deposited on pre-cleaned SiO$_2$/doped-Si. Using images shown in Figure 4.10, we can measure the growth rate of spherulites during solvent-vapor annealing. Figure 4.11 displays a representative plot of the TES ADT spherulite radius as a function of solvent-vapor annealing time in the presence of 0.019 vol% of DCE in nitrogen. The non-zero x-intercept is due to lag time between the start of data collection and the start of DCE solvent-vapor exposure, as well as the lag time necessary to reach the critical DCE solvent-vapor concentration in the sample chamber. As can be seen from the figure, the radial growth rate of spherulites is constant with time. From the slope of the curve, we calculated the spherulitic growth rate to be 24 ± 3 µm/s. This growth rate can be reduced by decreasing the DCE concentration in nitrogen during solvent-vapor annealing. Figure 4.12 shows the dependence of spherulitic growth rate on the concentration of DCE solvent vapor in the inlet stream. As expected, the growth rate decreases as the DCE vol% decreases. We also note that the dependence of growth rate on DCE vol% does not pass through the origin, indicating that a minimum steady-state concentration of DCE solvent vapor in the inlet stream is needed before spherulitic growth can occur. We hypothesize that below a concentration of 0.005 mol%, the amount of DCE solvent vapor is insufficient to plasticize the TES ADT thin film to allow for molecules to rearrange and crystallize within the time frame of our experiments. For all other kinetic experiments presented in this thesis, the DCE solvent-vapor concentration was kept constant at 0.019 vol%.
In addition to calculating the spherulitic growth rate, we can also measure the fractional area crystallized as a function of time. Figure 4.13 shows the fractional area crystallized of a TES ADT thin film with solvent-vapor annealing. The curves show a sigmoidal dependence, reminiscent of polymer crystallization during which an initial induction period associated with nucleation is followed by subsequent growth until neighboring spherulites impinge\cite{17,18}. The kinetics of crystallization in such systems has been well captured by the Avrami equation\cite{19-21}, which describes the change in the fractional area crystallized, $X(t)$, as a function of time:

$$\ln[1-X(t)]=-kt^n$$ (4.2)

where $k$ is the rate constant for crystallization, and $n$ is the Avrami exponent. The Avrami exponent, $n$, indicates the dimensionality of the system as well as the type of nucleation\cite{22}. To understand the significance of $n$, we examined the equations that lead up to the Avrami equation. The Avrami equation assumes that nucleation events are spatially random, crystallization occurs symmetrically outwards from the nucleation point, crystallization is arrested when adjacent spherulites impinge upon one another, and the crystallization rate is independent of time. These assumptions are consistent with our observations of TES ADT spherulitic growth, where nucleation is spatially random in films, spherulites grow radially outwards from the spherulite center, and the crystallization rate is constant with time (refer to Figure 4.11). Furthermore, because the diameter of TES ADT spherulites is $3 – 5$ orders of magnitude larger than the thickness of the films, we assume TES ADT spherulitic growth to be two-dimensional. Taking into account these assumptions, we write the following expression for $X(t)$:
where $N_{\text{tot}}(t)$ is the total number of nucleation events per unit time and per fractional area uncrystallized at time, $t$, and $v$ is the velocity of spherulitic growth. In other words, each nucleation event per fractional area uncrystallized per unit time, $N_{\text{tot}}(t)$, results in the growth of a single spherulite, that grows radially outwards at a rate of $v$. In any given unit of time, the change in the fractional area crystallized for a single spherulite can thus be expressed as $\pi v^2(t-t_1)^2$. $N_{\text{tot}}(t)$ can be further modeled as a sum of two types of nucleation processes, one in which nucleation occurs instantaneous at the beginning of the crystallization process and growth proceeds without additional nucleation events, and one in which the appearance of new nuclei is distributed over the course of crystallization:

$$N_{\text{tot}}(t)=N_0 \delta(t)+\alpha t^\gamma$$

(4.4)

where $N_0$ represents the number of pre-formed nuclei which can nucleate crystallization at the beginning of the crystallization process, $\delta(t)$ represents a delta function indicating that nucleation occurs at a single instant in time, $\alpha$ represents the rate of appearance of distributed nuclei, and $\gamma$ is the time dependence of the distributed nucleation process.

When $\gamma = -1$, the second term disappears with increasing time, so nucleation events are concentrated at the beginning of the crystallization process. When $\gamma = 0$, the time dependence of the second term disappears, so the nucleation rate is constant throughout the crystallization process. $\gamma > 0$ refers to a situation where the rate of appearance of active nuclei increases with time. Combining Equations 4.3 and 4.4 and integrating, we can write:

$$\ln(1-X(t))=-\pi v^2[N_0 t^2+c_1 \alpha t^{\gamma+1}]$$

(4.5)
where $c_i$ is a constant. Comparing Equation 4.5 to the functional form of the Avrami equation shown in Equation 4.2, we observe that $\gamma = -1$ corresponds to $n = 2$, and $\gamma = 0$ corresponds to $n = 3$. Thus, for two-dimensional systems, $n = 2$ indicates that all nucleation events occur instantaneously at the onset of crystallization, while $n = 3$ corresponds to a case where nucleation events per fractional area uncrystallized are evenly distributed throughout the crystallization process. By fitting the dependence of $X(t)$ on the solvent-vapor annealing time for TES ADT thin films, we found that the Avrami equation captures the sigmoidal curve shape of our data well with $n = 2$, indicating that nucleation occurs at the beginning of the solvent-vapor annealing process\cite{22}. Examination of the optical micrographs in Figure 4.10 indeed confirms that nucleation occurs at the onset of solvent-vapor annealing.

4.4.2 Crystallization kinetics in TES ADT thin films incorporating additives

In their seminal work on understanding spherulitic growth in polymer films, Keith and Padden found that while the presence of additives can increase the nucleation density, these additives can simultaneously suppress the growth rate of individual spherulites by accumulating at the spherulitic growth front\cite{23}. In this section, we examine how the incorporation of additives to increase $<S>$ in TES ADT thin films also affects the growth rate of TES ADT spherulites during solvent-vapor annealing. To test the influence of additives on the growth rate of TES ADT spherulites, we incorporated several small-molecule additives into TES ADT solutions in toluene prior to spin coating, including F-TES ADT, TIPS pen (refer to Figure 2.5c), and ethyl-TES ADT (refer Figure 3.1a). TIPS pen and ethyl-TES ADT will re-appear in Chapter 5 as additives to replace F-TES ADT
in seeding TES ADT spherulitic growth. Figure 4.14 displays the growth rate dependence of TES ADT spherulites on the additive concentration, ranging from 0 to 8 mol% relative to TES ADT, and solvent-vapor annealed at a DCE concentration of 0.019 vol%. As seen in the figure, we observe a gradual suppression of the spherulitic growth rate with increasing concentration of the additive for all three additives, from 23 µm/s when no additive is present to 5 µm/s with 8 mol% of the additive present. The dependence of the growth rate on the additive concentration is not a function of the type of additive, likely because the additives are similar in size. These results are in agreement with the polymer literature, indicating that the additives likely accumulate at the TES ADT spherulitic growth front, thereby decreasing its growth rate.

Since the presence of additives impacts the nucleation density of TES ADT, they will also necessarily affect the total time for TES ADT thin films to crystallize. Figure 4.15 displays the fractional area crystallized in TES ADT thin films in the presence of 0.5 to 2 mol% F-TES ADT as a function of solvent-vapor annealing time. For TES ADT thin films incorporating 0.5 mol% F-TES ADT, the time required for complete crystallization is approximately 175 s. In contrast, for TES ADT thin films incorporating 2 mol% F-TES ADT, the time for complete crystallization is only 7 s. Yet, because <S> is 4 orders of magnitude higher in TES ADT thin films with 2 mol% F-TES ADT compared to those with 0.5 mol% F-TES ADT, the total time to crystallize thin films of the same area is more than 20 times faster in specimens incorporating 2 mol% F-TES ADT. The process is thus dominated by the enhanced nucleation density as opposed to the suppression of the growth rate. By fitting these curves to the Avrami equation, we have found that the Avrami exponent, n, increases from 2 to 3 as F-TES ADT concentration increases. Figure
4.16 displays the dependence of \( n \) on F-TES ADT concentration in TES ADT thin films. The concentrations between which \( n \) transitions from 2 to 3 correspond to the region of exponential increase, shown in Figure 4.9. Based on Avrami kinetics, an increase from \( n = 2 \) to 3 in two-dimensional systems indicates a transition from an instantaneous nucleation process to a distributed one in which nucleation events occur at a constant rate throughout solvent-vapor annealing\[^{[22]}\]. Figure 4.17 displays time-lapse optical micrographs of crystallization in a TES ADT thin film incorporating 1 mol\% F-TES ADT. From these images, we can clearly observe the formation of new nuclei (highlighted by white circles) appearing throughout the crystallization process.

To quantify the number of new nuclei as a function of time, we counted the number of new spherulites in each frame taken every 5 s, such as those shown in Figure 4.17. The number of new spherulites, which corresponds to the number of new nucleation events, was then divided by the fractional area uncrystallized to calculate \( N_{\text{tot}}(t) \) and plotted as a function of solvent-vapor annealing time. Figure 4.18 shows \( N_{\text{tot}} \), normalized by the maximum \( N_{\text{tot}} \) for each sample, as a function of solvent-vapor annealing time for different F-TES ADT concentrations. Indeed, as the value of \( n \) transitions from 2 to 3 for increasing F-TES ADT concentrations, we observe a broadening of the distribution of the nucleation density per unit area uncrystallized, consistent with a change from instantaneous nucleation to distributed nucleation. That the nucleation process transitions from an instantaneous to a distributed one with increasing F-TES ADT concentration suggests that F-TES ADT nuclei are activated at different times during solvent-vapor annealing. The activation time is likely related to the size of the F-TES ADT nuclei, which in turn likely depends on the amount of time allowed for F-TES ADT molecules to
aggregate during film formation. If the rate of solvent evaporation during film formation could be decreased, it may be possible to increase the number of active F-TES ADT nuclei at a given concentration.

4.4.3 TES ADT growth rate dependence on the surface energy of the substrate

Finally, we turn our attention to how the underlying substrate can influence TES ADT spherulitic growth. In all the aforementioned kinetic experiments, TES ADT thin films were deposited onto pre-cleaned SiO$_2$/doped Si substrates. In light of previous literature reports indicating that the underlying substrate can influence crystallization kinetics in polymer thin films$^{[24-26]}$, here we examine how altering the surface energy of the underlying substrate can influence TES ADT crystallization. In Chapter 6, we will then extend our findings to guide TES ADT crystallization along arbitrary, non-linear paths.

To fabricate substrates with different surface energies, we used self-assembled monolayers (SAMs) and ultra-violet ozone (UVO) treatments on SiO$_2$ and Au surfaces (refer to Chapter 3 for detailed experimental methods). The surface energy of pre-cleaned SiO$_2$/doped-Si is 64.3 ± 0.7 ergs/cm$^2$. Au surfaces with a surface energy of 41 ± 1 ergs/cm$^2$ were prepared by evaporating 35-nm thick Au onto pre-cleaned SiO$_2$/doped-Si. To decrease the surface energy of Au to as low as 25 ± 1 ergs/cm$^2$, we adsorbed hydrophobic SAMs onto the Au surfaces through Au-thiol interactions. The SAMs employed were hexanethiol, pentafluorobenzenthiol (PFBT), and dimethylbenzenethiol, resulting in surface energies of 25 ± 1 ergs/cm$^2$, 27.3 ± 0.04 ergs/cm$^2$, and 34.1 ± 2

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ergs/cm$^2$, respectively. Hexamethyldisilazane (HMDS) was spun cast on pre-cleaned SiO$_2$/doped-Si substrates to achieve a surface energy of 32 ± 1 ergs/cm$^2$. To increase the surface energy of the underlying substrate to as high as 70.7 ± 0.3 and 73.5 ± 0.2 ergs/cm$^2$, UVO-treated pre-cleaned SiO$_2$/doped-Si and Au substrates were exposed to UVO treatment for 10 min, respectively. After SAM or UVO treatment, the substrates are chemically inert so we do not expect any chemical interactions between TES ADT and the underlying substrate to influence the overall growth rate. After modifying the substrates to have different surface energies, we proceeded to deposit TES ADT thin films on top of them and measure the growth rate of TES ADT spherulites during solvent-vapor annealing. Figure 4.19 displays the spherulite radius as a function of time for three representative samples: TES ADT deposited on pre-cleaned SiO$_2$/doped-Si, HMDS-treated SiO$_2$, and PFBT-treated Au. From the figure, we observe that the growth rate is fastest on pre-cleaned SiO$_2$/doped-Si and slowest on PFBT-treated Au. Figure 4.20 displays the growth rate dependence on the underlying substrate surface energy extracted from the slopes of the curves, such as those shown in Figure 4.19. The maximum growth rate of TES ADT spherulites is observed in films deposited on pre-cleaned SiO$_2$/doped-Si, at a rate of 24 ± 3 µm/s. Surprisingly, on substrates having both lower and higher surface energies compared to pre-cleaned SiO$_2$/doped-Si substrates, the growth rate of TES ADT spherulites is suppressed to approximately 9 ± 2 µm/s. This growth rate is almost three times lower than the growth rate of TES ADT spherulites on pre-cleaned SiO$_2$/doped-Si, indicating that the surface energy of the underlying substrate plays a significant role in influencing the crystallization of TES ADT during solvent-vapor annealing.
That the dependence of growth rate on the surface energy of the underlying substrate is non-monotonic indicates that two competing driving forces can suppress crystallization on both low- and high-surface energy substrates. To examine interactions between TES ADT and the underlying substrate, we collected atomic force microscopy (AFM) images of TES ADT thin films spun cast from dilute solutions onto the different substrates. When spun cast from low concentrations, there is incomplete coverage of TES ADT on the substrate, allowing us to probe molecule-substrate interactions. Figure 4.21 shows AFM images of TES ADT spun cast from dilute solutions onto hexamethyldisilazane-treated SiO$_2$/doped-Si, pre-cleaned SiO$_2$/doped-Si, and UVO-treated SiO$_2$/doped-Si. These substrates were chosen for their low roughness (rms = 0.2 nm), since the roughness of Au (rms = 4 nm) can obscure the identification of TES ADT monolayers. On pre-cleaned SiO$_2$/doped-Si and UVO-treated SiO$_2$/doped-Si substrates, TES ADT forms monolayer islands approximately 1 nm in height, while on HMDS-treated SiO$_2$, TES ADT dewets the substrate into 15-nm tall islands. Line profiles of the images can be seen in Figure 4.22. That TES ADT wets high-surface energy substrates is indicative of strong substrate-molecule interactions between TES ADT and the underlying substrate, likely similar to the favorable interactions reported between thin polymer films and their underlying substrates. Such attractive interactions are known to result in “reduced mobility layers” in which the polymer dynamics are severely hindered at this interface$^{[28]}$. On low-surface energy substrates, on the other hand, TES ADT aggregates into 15-nm tall islands in order to minimize unfavorable molecule-substrate interactions. Since strong molecule-substrate interactions suppress spherulitic growth on high-surface energy substrates, we expected the tendency of TES ADT molecules to self-aggregate on low-
surface energy substrates to result in an increase in the rate of spherulitic growth, when, in fact, we observe the opposite in Figure 4.20. This apparent contradiction suggests that another competing driving force is at play that dictates TES ADT growth rate on low-surface energy substrates.

To further probe how the surface energy of the underlying substrate can affect TES ADT crystallization, we collected high-resolution GIXD patterns of as-spun TES ADT films deposited on the various substrates. Figure 4.23 shows three such patterns collected on TES ADT thin films deposited on PFBT-treated Au, pre-cleaned SiO$_2$/doped-Si and UVO-treated Au. The intensities were normalized by the incoming intensities and collection time for accurate comparison. In all three patterns, we observe the reflections associated with the monoclinic polymorph of TES ADT. Surprisingly, we also observe reflections associated with the triclinic polymorph in as-spun TES ADT films deposited on low-surface energy PFBT-treated Au substrates. To compare the relative amounts of the triclinic and monoclinic polymorphs across the three samples, we compared intensities of three reflections associated with the triclinic polymorph and three reflections associated with monoclinic polymorph from the diffraction patterns of the samples, all normalized to the intensities of the corresponding reflections observed in the diffraction pattern of TES ADT spun cast on PFBT-treated Au. Figure 4.24 shows a comparison of normalized intensities of the (036), (0 3 12), and (317) reflections associated with the monoclinic polymorph and those of the (011), (101) and (Ī01) reflections associated with the triclinic polymorph observed in the diffraction patterns of as-spun TES ADT films on PFBT-treated Au, pre-cleaned SiO$_2$/doped-Si, and UVO-treated Au. While the relative intensities of the reflections associated with the monoclinic
structure are independent of the substrate surface energy, we see a dramatic drop in the relative intensities of reflections associated with the triclinic polymorph with increasing surface energy of the underlying substrate. This observation indicates that the volume of the film adopting the triclinic polymorph is largest in TES ADT thin films deposited on PFBT-treated Au and smallest in TES ADT thin films deposited on UVO-treated Au.

Our results suggest that low-surface energy substrates promote the formation of stable triclinic nanocrystals in as-spun TES ADT thin films. These nanocrystals, like additives, have a tendency to accumulate at the spherulitic growth front and suppress the growth rate of spherulites during solvent-vapor annealing. Surprisingly, these nanocrystals do not act as nuclei for TES ADT crystallization, as the nucleation density is constant at 0.2 spherulites/mm\(^2\) on all surfaces – further investigation is necessary to determine why these nanocrystals do not seed TES ADT crystallization. To quantitatively compare the nanocrystal density in as-spun TES ADT on different surfaces, we performed further analysis on the GIXD data. First, we used Scherrer’s equation\(^{[29]}\) to calculate the average size of triclinic nanocrystals in as-spun TES ADT films:

\[
L = \frac{\lambda}{\cos(\theta) * B}
\]  

(4.6)

Where \(L\) is the diameter of the nanocrystal, \(\lambda\) is the incident x-ray wavelength, and \(B\) is the full width of the peak at half the maximum intensity (FWHM) of the chosen reflection, expressed in radians. Figure 4.25 shows a horizontal line trace of across the (011) reflection at \(q_z = 0.5 \text{ A}^{-1}\) that appears in the diffraction pattern of an as-spun TES ADT film deposited on PFBT-treated Au. The FWMH was calculated by fitting the peak to a Gaussian distribution to be 0.18°. Using Equation 4.6, the nanocrystal size was calculated to be 49.1 nm. With knowledge of the average size of the triclinic
nanocrystals, we can then estimate the total concentration of nanocrystals in as-spun TES ADT thin films deposited on different surfaces. The intensity of any given reflection in an x-ray diffraction pattern is proportional to the concentration of crystals in the film. Furthermore, if we assume that solvent-vapor annealed TES ADT films are 100% crystalline, we can estimate the number of triclinic nanocrystals in as-spun TES ADT films deposited on different substrates by comparing the intensities of the same reflection in the diffraction patterns of the respective samples. Explicitly, we can write the following relationship:

$$I_{\text{SVA}} / \text{total volume sampled} = \frac{I_{\text{AS}}}{(# \text{ of nanocrystals})(\text{volume per nanocrystal})} \quad (4.7)$$

where $I_{\text{SVA}}$ is the intensity of the (011) reflection in the diffraction pattern of a solvent-vapor annealed TES ADT thin film and $I_{\text{AS}}$ is the intensity of the (011) reflection in the diffraction pattern of an as-spun TES ADT thin film. The total volume sampled by the incoming x-ray beam is the beam footprint (0.2 mm x 3 mm) multiplied by the depth of the film (100 nm), since the x-rays penetrate the entire depth of the film for these experiments. By assuming that the nanocrystals are spherical, we can write Equation 4.7 as:

$$\frac{I_{\text{SVA}}}{(0.2 \text{ mm})(3 \text{ mm})(100 \text{ nm})} = \frac{I_{\text{AS}}}{(# \text{ of nanocrystals}) \left[ \frac{4}{3} \pi \left(\frac{49.1 \text{ nm}}{2}\right)^3 \right]} \quad (4.8)$$

We found the maximum intensities of the (011) reflection to be 1200 and 45 counts for solvent-vapor annealed TES ADT and as-spun TES ADT on PFBT-treated Au, respectively. By substituting these values into Equation 4.8, we find the density of nanocrystals in as-spun TES ADT on PFBT-treated Au to be approximately 52 nanocrystals/µm². In as-spun TES ADT on pre-cleaned SiO₂/doped Si and UVO-treated
Au, the nanocrystal densities are 26 nanocrystals/µm$^2$ and 15 nanocrystals/µm$^2$, respectively.

Despite the fact that these nanocrystals adopt the same crystal structure as the fully crystallized spherulites, they are unlikely to be oriented with the same in-plane orientation as that at growth front of the spherulites. We believe differences in the in-plane orientation hinder the propagation of the spherulitic growth front since the nanocrystals are not easily incorporated into the growing spherulite, similar to having foreign additives in the film$^{[23]}$. To support this hypothesis, we compared the spherulitic growth rate dependence on the surface energy of the underlying substrate to the previously established dependence of spherulitic growth rate on the additive concentration in the film. Figure 4.26 shows a comparison of the growth rate dependence of TES ADT spherulites on the surface energy of the underlying substrate in the absence of additives (bottom x-axis) and the additive concentration for samples spun cast on pre-cleaned SiO$_2$/doped-Si substrates (top x-axis). As can be seen from the figure, close agreement exists between the two sets of data. The spherulitic growth rate on PFBT-treated Au of 9 µm/s, for example, is equivalent to the growth rate of TES ADT in the presence of 5 mol% of a small molecule additive for films deposited on pre-cleaned SiO$_2$/doped-Si. This observation suggests that like impurities, the triclinic nanocrystals can suppress spherulitic growth by accumulating at the growth front. Our findings from AFM and GIXD experiments thus point to the non-monotonic dependence of the spherulitic growth rate on substrate surface energy arising from a competition between strong molecule-substrate interactions on high-surface energy substrates and the formation of triclinic nanocrystals on low-surface energy substrates. Specifically, on
high-surface energy substrates, strong molecule-substrate interactions suppress the growth rate by decreasing the motion of TES ADT molecules to rearrange and crystallize during solvent-vapor annealing. On the other extreme, low-surface energy substrates promote the formation of stable triclinic nanocrystals in as-spun TES ADT thin films, which likely aggregate at the spherulitic growth front, thereby suppressing the overall growth rate. By patterning the underlying substrate to have regions of different surface energies, in Chapter 6 we will demonstrate the ability to guide crystallization along arbitrary paths in the plane of TES ADT thin films by exploiting the differential growth rates of TES ADT on these surfaces.

4.5 Conclusions

In this chapter we characterized the spherulitic growth of TES ADT. We found that a previously undocumented monoclinic crystal structure exists in as-spun TES ADT thin films, but completely converts to the stable triclinic polymorph during solvent-vapor annealing. TES ADT spherulites thus comprise only the triclinic polymorph. These spherulites are structurally complex, with heterogeneities, including low-angle intraspherulite grain boundaries and ISBs, existing across multiple length scales. We have also detailed how we can control the number density of spherulites in TES ADT thin films through the incorporation of fractional amounts of F-TES ADT that act as nuclei for spherulitic growth. Furthermore, we have examined the crystallization kinetics in TES ADT thin films during solvent-vapor annealing, specifically illustrating how the presence of additives and the surface energy of the underlying substrate can affect spherulitic growth. The results presented in this chapter provide the basis for later
chapters. In Chapter 5, for example, we explore how the physical parameters of small-molecule additives can impact their ability to seed TES ADT crystallization. In Chapter 6, we will detail how, through the manipulation of the substrate surface energy, we can control the direction of crystallization in TES ADT thin films. Due to the ubiquity of spherulitic growth in small-molecule organic-semiconductor thin films, a strong understanding of the growth process and structure of spherulites is important in order to establish structure-function relationships in OTFTs comprising these films as active layers.
Table 4.1. Comparison of lattice dimensions of the monoclinic crystal structure in as-spun TES ADT thin films, the triclinic crystal structure in solvent-vapor annealed thin films, and the crystal structure of TES ADT single crystals.

<table>
<thead>
<tr>
<th>Lattice parameter</th>
<th>Monoclinic polymorph</th>
<th>Triclinic polymorph</th>
<th>Single crystal$^{[30]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>18.5</td>
<td>6.9</td>
<td>6.7</td>
</tr>
<tr>
<td>b (Å)</td>
<td>21.8</td>
<td>7.4</td>
<td>7.2</td>
</tr>
<tr>
<td>c (Å)</td>
<td>97.1</td>
<td>16.7</td>
<td>16.7</td>
</tr>
<tr>
<td>α (°)</td>
<td>90.0</td>
<td>96.4</td>
<td>98.1</td>
</tr>
<tr>
<td>β (°)</td>
<td>90.0</td>
<td>92.0</td>
<td>94.5</td>
</tr>
<tr>
<td>γ (°)</td>
<td>89.5</td>
<td>105.6</td>
<td>103.9</td>
</tr>
</tbody>
</table>
Figure 4.1. Optical micrographs of TES ADT thin films a) before and b) after solvent-vapor annealing.

Figure 4.2. 2-D GIXD pattern of as-spun TES ADT.
Figure 4.3. a) 2-D GIXD pattern of as-spun TES ADT thin film with the calculated reflections overlayed as white open circles. b) Comparison of the experimental diffraction pattern summed over all $q_z$ values (red) and the expected reflections with Miller indices labeled.
Figure 4.4. 2-D diffraction pattern of a solvent-vapor annealed TES ADT thin film. The reflections, labeled with their Miller indices, match closely to those predicted by the triclinic crystal structure of single-crystalline TES ADT grown from solution and measured at 100 K\textsuperscript{[14]}. 
Figure 4.5. Comparison of GIXD patterns of an a) as-spun TES ADT thin film and b) solvent-vapor annealed TES ADT thin film, where the intensities of the reflections are plotted on a linear scale. Scale bars indicate the relative intensities of the reflections.
Figure 4.6. a) Illustration of TES ADT spherulites. Red circles indicate the nucleation points of three spherulites. Gray lines represent the π-planes of TES ADT molecules. Black dashed lines represent low-angle, intraspherulite grain boundaries. Blue solid lines represent low-angle ISBs. The red line represents a high-angle ISB. b) Illustration of how the angle of molecular orientation mismatch, \( \omega \), across an ISB is defined.
Figure 4.7. Optical micrograph of a solvent-vapor annealed TES ADT thin film with ISBs highlighted. Blue portions indicate regions where the angle of molecular orientation mismatch between adjacent spherulites is low (<15°), while red portions indicate regions where the angle of molecular orientation mismatch between adjacent spherulites is high (>15°).
**Figure 4.8.** Optical micrographs of TES ADT films with 0.8, 1.2, 1.8, and 2.5 mol% F-TES ADT (clockwise from the top left corner).

**Figure 4.9.** Dependence of $\langle S \rangle$ on the concentration of F-TES ADT in TES ADT thin films. The solid line is provided to guide the eye. Error bars represent the standard deviation of the diameter of 10 – 25 spherulites in each film.
Figure 4.10. Time-lapsed optical micrograph images of spherulitic growth in TES ADT thin films on pre-cleaned SiO$_2$/doped-Si during exposure to DCE solvent vapor. The elapsed times during exposure to DCE solvent vapor are labeled for clarity.
Figure 4.11. Representative plot of the spherulite radius as a function of exposure time to DCE solvent vapor. The spherulitic growth rate can be extracted from the slope of the curve. The non-zero x-intercept is due to lag time between the start of data collection and the start of DCE solvent-vapor exposure, as well as the lag time necessary to reach the critical DCE solvent-vapor concentration in the sample chamber.
Figure 4.12. Growth rate of TES ADT spherulites on pre-cleaned SiO$_2$/doped-Si substrates as a function of DCE solvent-vapor concentration in nitrogen. The error bars represent the standard deviation of three separate trials for each DCE concentration.

Figure 4.13. Fractional area crystallized of a TES ADT thin film as a function of solvent-vapor annealing time.
Figure 4.14. Growth rate dependence of TES ADT spherulites deposited on pre-cleaned SiO$_2$/doped-Si substrates as a function of additive concentration for three different additives.
Figure 4.15. Fractional area crystallized of TES ADT thin films with varying concentrations of F-TES ADT as a function solvent-vapor annealing time.

Figure 4.16. Dependence of the Avrami exponent, n, on the concentration of F-TES ADT in TES ADT thin films.
Figure 4.17. Time-lapse images in 10 s increments of nucleation and growth of TES ADT during exposure to DCE vapor. The films contain 1 mol% F-TES ADT. Newly formed spherulites are highlighted with white circles.

Figure 4.18. Normalized total nucleation events, $N_{\text{tot}}$, per area uncrystallized as a function of solvent-vapor annealing time (normalized to the total time needed for 100% crystallization) for the same data set shown in Figure 4.16. Curves have been shifted along the y-axis for clarity.
Figure 4.19. TES ADT spherulite radius as a function of solvent-vapor annealing time for TES ADT that is deposited on pre-cleaned SiO$_2$/doped-Si, HMDS-treated SiO$_2$, and PFBT-treated Au. The respective growth rates can be calculated from the slope of the curves. The non-zero x-intercept is due to lag time between the start of data collection and the start of DCE solvent-vapor exposure, as well as the lag time necessary to reach the critical DCE solvent-vapor concentration in the sample chamber.
**Figure 4.20.** Growth rate dependence of TES ADT spherulites on the surface energy of the underlying substrate. Error bars along the y-axis represent deviations in the growth rates of TES ADT spherulites on 3 to 5 films. Error bars along the x-axis represent deviations in the measured water and glycerol static angles used to calculate the surface energies. The solid line provides a guide to the eye.
Figure 4.21. AFM micrographs of TES ADT spun cast from dilute solutions in chloroform on a) HMDS-treated SiO$_2$/doped-Si, b) pre-cleaned SiO$_2$/doped-Si, and c) UVO-treated SiO$_2$/doped-Si substrates.

Figure 4.22. Line profiles of the AFM micrographs shown in Figure 4.22.
Figure 4.23. 2-D GIXD images of a) solvent-vapor annealed TES ADT thin film and of as-spun TES ADT thin films deposited on b) PFBT-treated Au, c) pre-cleaned SiO$_2$/doped-Si and d) UVO-treated Au. The (011), (101) and (101) reflections associated with the triclinic crystal structure of TES ADT, highlighted in dotted rectangles, appear with varying intensities in the patterns of the as-spun TES ADT thin films. The (036), (0 3 12), and (317) reflections associated with the monoclinic polymorph, highlighted by solid rectangles, appear with constant intensities in the patterns of the as-spun TES ADT thin films.
Figure 4.24. Comparison of peak intensities of reflections associated with the monoclinic and triclinic polymorphs in as-spun TES ADT films. The peak intensities are normalized to those from the diffraction pattern of as-spun TES ADT on PFBT-treated Au (27 ergs/cm²). The intensities of the reflections associated with the monoclinic crystal structure of TES ADT are constant across the three substrates, while the intensities of the reflections associated with the triclinic crystal structure of TES ADT dramatically decrease as the surface energy of the substrate increases.
Figure 4.25. A horizontal line trace at $q_z = 0.5 \text{ Å}^{-1}$ across the (011) reflection of the triclinic polymorph that appears in the diffraction pattern of as-spun TES ADT on PFBT-treated Au.
Figure 4.26. TES ADT spherulitic growth rate dependence on the surface energy of the underlying substrate (black symbols; bottom x-axis) compared to the growth rate dependence on the concentration of small-molecule impurities (blue symbols; top x-axis).
References


Chapter 5: Understanding heterogeneous nucleation in two-component, solution-processed, organic-semiconductor thin films

Blending two components to form thin films is a promising strategy to bring about unique or enhanced electronic properties in the active layers of organic electronic devices\(^\text{[1]}\). Bulk-heterojunction organic solar cells (OSCs), for example, utilize blends of two organic semiconductors with different energy levels in order to efficiently dissociate excitons for harvesting light\(^\text{[2]}\). Doping an organic-semiconductor host with fractional amounts of another organic semiconductor, or “guest”, has also been successfully employed to improve the mobility of organic thin-film transistors (OTFTs)\(^\text{[3, 4]}\), the conductivity of charge transport layers in organic light-emitting diodes (OLEDs)\(^\text{[5, 6]}\), and the luminescence of light-emitting layers in OLEDs\(^\text{[7-9]}\). In choosing organic-semiconductor pairs for such blends or guest-host systems, it is important to consider the respective electronic properties of the constituent components. Equally imperative is a comprehensive understanding of the morphological development of such systems\(^\text{[10]}\). In small quantities, the presence of a dopant, for example, can improve the crystallinity of the host material in the active layers of OTFTs, resulting in an improvement in device mobility\(^\text{[4, 11]}\). Aggregation of emissive dopants at high loading levels in guest-host OLEDs, on the other hand, can decrease the overall luminescence of the light-emitting layer\(^\text{[8, 9]}\). In light of the importance of the active layer morphology in determining overall device performance, it is critical that we understand how the physical parameters of one
compound in two-component, organic-semiconductor thin films influences the final film morphology. In this chapter, we thus focus on how the presence of additives affects the structural, rather than electronic properties, of TES ADT thin films.

During solvent-vapor annealing of TES ADT thin films, structural development occurs through nucleation and subsequent growth of spherulites. These processes play critical roles in determining the final film structure, with the nucleation density directly determining the average spherulite size. In Section 4.3, we demonstrated the ability to control the average number density of TES ADT spherulites, \(<S>\), over four orders of magnitude through the incorporation of fractional amounts of F-TES ADT. Interestingly, we observed that at concentrations below 0.5 mol\% F-TES ADT, there was no observable change in \(<S>\) from that observed in neat TES ADT thin films, at 0.2 spherulites/mm\(^2\). Between F-TES ADT concentrations of 0.5 and 2 mol\%, we observe an exponential increase in \(<S>\) with increasing F-TES ADT concentration. Finally, above a concentration of 2 mol\%, \(<S>\) becomes independent of the F-TES ADT concentration. Because of the importance of nucleation in determining the spherulite density of TES ADT thin films, we strive to understand what physical factors give rise to this dependence of \(<S>\) on additive concentration in this chapter. Such studies on two-component organic semiconductor systems in which one component is present in fractional amounts are highly relevant to doped-OTFTs\([4,12]\] and guest-host organic light-emitting diodes (OLEDs)\([13]\). By comparing the extent with which these additives can heterogeneously nucleate TES ADT during solvent-vapor annealing, we can determine the key attributes of the additives that influence their ability to act as nuclei.
TES ADT provides a unique opportunity to study heterogeneous nucleation in solution-processed organic-semiconductor thin films for several reasons. When spun cast onto substrates, TES ADT forms largely amorphous films, allowing us to controllably induce crystallization with subsequent solvent-vapor annealing\(^\text{[14]}\). During exposure to 1,2-dichloroethane (DCE) solvent vapors, TES ADT crystallizes through nucleation and growth of spherulites. Because each spherulite results from a single nucleus, tracking spherulite formation allows us to infer information about nucleation events. Furthermore, the diameters of TES ADT spherulites range from 30 µm – 3 mm, and as such are easily identifiable via optical microscopy. By measuring the average spherulite diameter, L, in TES ADT thin films after crystallization is complete, we can calculate the average number density of spherulites, \(<S>\), and thus the number of active nuclei, in the films (refer to Equation 4.1). Finally, under the processing conditions chosen for these studies, the time scale for spherulitic growth is on the order of seconds to minutes, which is convenient for \textit{in situ} observation of the crystallization process.

In Section 5.1, we examine the dependence of \(<S>\) on additive concentration for nine different small-molecule additives. We have selected the additives to be electrically-active and used concentrations ranging from 0 – 10 ml% relative to TES ADT so the findings of our study would be relevant to doped-OTFT and OLED systems\(^\text{[3-6]}\). By comparing the extent to which these additives can heterogeneously nucleate TES ADT during solvent-vapor annealing, we can determine the key attributes of the additives that influence their ability to act as nuclei. In Section 5.2, we explore the kinetics of TES ADT crystallization during solvent-vapor annealing by fitting the kinetics data to the well-known Avrami equation. We also examine the crystallization of TES ADT thin
films in the presence of additives without solvent-vapor annealing. Finally, in Section 5.3 we use grazing-incidence x-ray diffraction (GIXD) to probe how the presence of additives influences the crystal structure of TES ADT thin films.

5.1 The dependence of <S> on additive concentration

To compare the effectiveness of different small-molecule additives as nucleating agents in TES ADT thin films, we systematically varied the additive concentration incorporated in TES ADT thin films and compared <S> upon solvent-vapor annealing. In neat TES ADT thin films, heterogeneous nucleation occurs on dust particles and defects on the substrate surface[15]. Given our standard cleaning procedure (refer to Section 3.1.1), <S> is consistently 0.2 nuclei/mm$^2$. By incorporating additives, we can increase <S> to as high as 2000 nuclei/mm$^2$. Figure 5.1a and Figure 5.1b show the dependence of L, the average spherulite diameter, and <S>, the average number density of spherulites, on the additive concentration for a set of additives comprising chemical variants of TES ADT, respectively (refer to Figure 3.1a for chemical structures). These additives include F-TES ADT, chlorinated 5,11-bis(triethylsilylethynyl) anthradithiophene (Cl-TES ADT), brominated 5,11-bis(triethylsilylethynyl) anthradithiophene (Br-TES ADT), iodinated 5,11-bis(triethylsilylethynyl) anthradithiophene (I-TES ADT), and diethyl-5,11-bis(triethylsilylethynyl)anthradithiophene (ethyl-TES ADT). In Section 4.3, we found the dependence of <S> on F-TES ADT concentration to be sigmoidal in nature. The dependence of <S> on other additives also displays the same curve shape in Figure 5.1b, with three distinct concentration regimes. At concentrations below c*, the critical concentration at which additives begins to nucleate TES ADT, <S> remains constant at
approximately 0.2 spherulites/mm$^2$. Given that $<S>$ is constant and remains the same as that of neat TES ADT thin films, the incorporated additives must be ineffective at nucleating TES ADT and heterogeneous nucleation is still determined on dust particles or defects on the substrate surface. At intermediate additive concentrations, $S$ increases exponentially with a slope of $m$. The value of $m$ thus qualifies how effectively the additives can nucleate TES ADT. At high additive concentrations, $<S>$ plateaus at $<S_{\text{max}}>$ and becomes once again independent of additive concentration. In this region, increasing the additive concentration must not have resulted in the formation of more nuclei. To facilitate discussion, we have labeled $c^*$, $m$, and $<S_{\text{max}}>$ for clarity in Figure 1b.

By examining shifts in $m$, $c^*$, and $<S_{\text{max}}>$, we can compare the efficacies with which the different additives seed TES ADT spherulite growth and correlate these shifts to key attributes of the additives. From Figure 5.1b, we observe that $<S>$ has the same dependence on additive concentration when F-, Cl-, and Br-TES ADT are used as additives. For these curves, $m = 2.5$ decades of spherulites/mm$^2$ per mol% increase in additive concentration, $c^* = 0.5$ mol%, and $<S_{\text{max}}> = 2000$ nuclei/mm$^2$. This observation suggests that differences in the physical properties of these three compounds, such as solubility or crystal packing, are insufficient to affect their ability to nucleate TES ADT. When I-TES ADT and ethyl TES-ADT are used as additives, on the other hand, we observe large shifts in all three parameters. In the presence of I-TES ADT, $<S_{\text{max}}>$ shifts to 20 nuclei/mm$^2$ and $m$ decreases to 1 decade of spherulites/mm$^2$ per mol% increase in additive concentration. In the presence of ethyl-TES ADT, $<S_{\text{max}}>$ is also approximately 20 nuclei/mm$^2$, but $m$ decreases further to 0.4 decades of spherulites/mm$^2$ per mol%
increase in additive concentration, and c* increases to 2.7 mol%. To determine main factors that dictate nucleation in TES ADT thin films within this family of additives, we explored key differences in their physical properties.

5.1.1 Dependence of m on the additives’ ability to crystallize

One obvious correlation we observe is the systematic shallowing of m as the size of the substituent, R, increases from 114 pm with bromine to 140 pm with iodine to 262 pm with an ethyl substitution. Figure 5.2 displays the dependence of m on the size of the substituent. Below 114 pm, m is constant at 2.5 decades of spherulites/mm$^2$ per mol% increase in additive concentration. Above 114 pm, m decreases as the size of the substituent increases. The size of the substituents thus appears not to affect the additives’ nucleation efficacy until a critical threshold is crossed. Beyond this critical substituent size, the efficacy with which the compound can nucleate TES ADT decreases dramatically. Physically, a shallowing of m indicates that a higher concentration of I- or ethyl-TES ADT is required compared with F-, Cl-, and Br-TES ADT to affect $<S>$. To gain insight on how the size of the functionality of these additives influences m, we probed how these additives interact with TES ADT.

Because we incorporate only fractional amounts of the additives (< 10 mol%) into TES ADT thin films, it is exceedingly difficult to study how these additives behave in the presence of TES ADT. Figure 5.3 displays grazing-incidence x-ray diffraction (GIXD) images collected on solvent-vapor annealed TES ADT films with up to 6 mol% F-TES ADT, TIPS pen, and PCBM. These diffraction patterns exhibit reflections associated with TES ADT but do not reveal any reflections associated with the crystal structure of the
additives. To increase the contrast between TES ADT and the additives, we have chosen to study films cast from solutions comprising 50/50 mol% of TES ADT and the additives. In these blended films, TES ADT remains amorphous. In films comprising comparable quantities of the two components, constituent crystallization can be hindered by the presence of unlike species\textsuperscript{[16]}. In fact, we have observed that the presence of additives suppresses the crystallization rate of TES ADT\textsuperscript{[17]} by aggregating at the spherulitic growth front\textsuperscript{[18]}. By extrapolating the dependence of the spherulitic growth on additive concentration shown in Figure 4.15, we predict that the spherulitic growth rate is completely suppressed at an additive concentration of 10.4 mol%. It is thus not surprising that TES ADT remains amorphous in these 50/50 mol% blends. To estimate the relative abilities of the additives to crystallize in the presence of TES ADT, it is therefore important that the driving force for crystallization of the additives to be stronger than TES ADT. We can compare the relative driving force for crystallization by examining the melt enthalpies of the additives with that of TES ADT\textsuperscript{[19, 20]}. Figure 5.4 displays differential scanning calorimetry (DSC) thermograms of TES ADT, F-, Cl-, and ethyl-TES ADT. Br-TES ADT and I-TES ADT degrade before their melting point so we cannot report melt enthalpies for these compounds. When TES ADT is heated through its melting point of 153 °C, it exhibits a melt enthalpy of 20 J/g. The melt enthalpies of F- and Cl-TES ADT, on the other hand, are approximately 50 J/g. The melt enthalpy of ethyl-TES ADT is slightly larger than that of TES ADT, at a value of 34 J/g. Compared to quintessential organic semiconductors, such as tetracene, which exhibits a melt enthalpy of 695.6 J/g\textsuperscript{[21]}, the driving force for crystallization in TES ADT and the additives is an order of magnitude smaller. Still, because the additives have larger melt
enthalpies, and thus stronger tendencies to crystallize compared to TES ADT, we expect them to crystallize more readily in 50/50 mol% blends compared to TES ADT. Further evidence that TES ADT crystals are weaker compared to F- and Cl-TES ADT is the observation that TES ADT is largely amorphous as-spun and requires solvent-vapor annealing to induce crystallization\textsuperscript{[14]}, whereas both F-TES ADT\textsuperscript{[22]} and Cl-TES ADT crystallize readily upon solvent evaporation during spin coating.

We employed atomic force microscopy (AFM) to study the surface topography and GIXD to study the crystal structure and assess the relative crystallinities of these blends. Figure 5.5 displays AFM images and corresponding GIXD patterns of such films. The AFM height images shown in Figure 5.5a reveal the surface topography of the five TES ADT films comprising the different additives. For films containing 50 mol% F-, Cl-, and Br-TES ADT, we observe submicron- to micron-sized features; these are absent in the AFM height images of films comprising 50 mol% I-TES ADT and ethyl-TES ADT. To elucidate the structure of these features, we collected two-dimensional GIXD images on these same films. The GIXD images in Figure 5.5b were collected at an x-ray incident angle of 0.16° so incident x-rays can penetrate the entire depth of the 100 nm-thick film. For all GIXD experiments, the film thickness and acquisition time were held constant, and the diffraction patterns were normalized by the intensity of the incident x-ray beam to allow for comparison of relative intensities of the reflections, which provides an indication of the relative crystallinities, across the five samples. In the case of the film with 50 mol% F-TES ADT, we observe strong reflections, providing evidence that the features observed in the AFM micrograph are crystalline. The reflections in the GIXD pattern correspond to those predicted by the single-crystal structure of the high-
temperature polymorph of F-TES ADT\textsuperscript{[23]}, with the $\pi$-plane of F-TES ADT preferentially oriented out-of-plane. We do not observe the reflections associated with TES ADT, presumably because of its weak tendency to crystallize compared to F-TES ADT. For films comprising 50 mol\% Cl-TES ADT and Br-TES ADT, we also do not observe reflections associated with TES ADT, suggesting that the presence of these additives in high concentrations also suppresses TES ADT crystallization. Instead, the reflections match those seen in the diffraction pattern of the film comprising a blend of F-TES ADT and TES ADT, indicating that Cl-TES ADT and Br-TES ADT form polymorphs that are similar to that of F-TES ADT in the presence of TES ADT, and the anisotropic azimuthal intensity is consistent with the additives having their $\pi$-planes preferentially oriented perpendicular to the substrate. Furthermore, the intensities of the diffraction patterns of all three samples are comparable, suggesting that the additives crystallize to comparable extents. These results indicate that while the substituent size increases from 64 pm with fluorine, to 102 pm with chlorine, to 114 pm with bromine, these size differences are insufficient to affect the crystallization behavior of the additives in the presence of TES ADT. Consequently, the dependence of $<S>$ on additive concentration is the same when F-, Cl-, and Br-TES ADT are employed to seed the crystallization of TES ADT. For films comprising 50/50 mol\% blends of TES ADT and I-TES ADT, the reflections are also similar to those predicted by the high-temperature polymorph of F-TES ADT, but these reflections are azimuthally isotropic in their intensities. This observation indicates that crystallization of I-TES ADT occurs with no preferential orientation in the presence of TES ADT. Furthermore, the reflections are less intense than those of the diffraction patterns of blends comprising TES ADT with F-, Cl-, and Br-TES ADT. The weaker
intensities of the reflections suggest that the relative degree of crystallinity of films with I-TES ADT is lower than that in films with F-, Cl-, and Br-TES ADT. For films with 50 mol% ethyl-TES ADT, the GIXD pattern is featureless, consistent with the film being amorphous. Because the melt enthalpy of ethyl-TES ADT is comparable to that of TES ADT, we believe they disrupt each other’s native crystallization habit in 50/50 mol% blends.

Since the ability to seed TES ADT spherulitic growth hinges on the ability of the additives to form nuclei, we expect their tendency to crystallize in the presence of 50 mol% TES ADT to be directly related to their ability to aggregate into nuclei when present in smaller concentrations. In 50/50 mol% blends with TES ADT, I-TES ADT and ethyl-TES ADT crystallize to a lesser extent compared to F-, Cl-, and Br-TES ADT. At low concentrations, I-TES ADT and ethyl-TES ADT thus likely form correspondingly fewer nuclei. As such, higher concentrations of I- and ethyl-TES ADT are required to achieve the same $<S>$ compared to when F-, Cl-, and Br-TES ADT are used as additives. This trend is consistent with the progressive shallowing of the slope in Figure 5.1b, where the dependence of $<S>$ on additive concentration is strongest when F-, Cl-, and Br-TES ADT are used as additives; the dependence of $<S>$ on additive concentration becomes progressively weaker as we replace easily crystallizable F-, Cl-, and Br-TES ADT with I- and ethyl-TES ADT.

5.1.2 Dependence of $c^*$ on the additives’ solubility in toluene

The question still remains, however, as to what factors influence $c^*$ and $<S_{\text{max}}>$. Returning to Figure 5.1b, we observe that all the additives begin seeding TES ADT at $c^*$
= 0.5 mol%, except for ethyl-TES ADT. When ethyl-TES ADT is used as the additive, we do not observe significant changes in \( <S> \) until an additive concentration of 2.7 mol%. The most obvious difference in the molecular structures among the derivatives is that ethyl-TES ADT has an alkyl instead of a halogen substituent. We thus speculate that the shift in \( c^* \) is related to differences in the solubility of ethyl-TES ADT and the halogenated-TES ADT’s. It is well-known that adding alkyl chains to a molecule can significantly improve the solubility of the parent compound in organic solvents\[^{24}\]. Indeed, we estimate the solubility of ethyl-TES ADT in toluene, the solvent from which the films are cast, to be approximately 120 mM. In contrast, the solubilities of the F-, Cl-, Br-, and I-TES ADT in toluene are 43, 17, 9, and 6 mM, respectively. While we observe a systematic decrease in the solubility of these additives with increasing halogen size, these solubilities are all substantially lower than that of ethyl-TES ADT in toluene. Given this correlation, we attribute the shift in \( c^* \) in TES ADT films incorporating ethyl-TES ADT as the additive to its increased solubility compared to the halogenated-TES ADT derivatives in toluene. Since the additives must form aggregates whose sizes are above the critical nucleus size in order for nucleation to occur\[^{25}\], additives that are more soluble in the casting solvent are less likely to aggregate to form the critical nuclei required to initiate TES ADT crystallization. As such, additives that are more soluble will require a higher \( c^* \) to seed crystallization of TES ADT. Such solubility-dependent aggregation has been observed in poly(3-hexyl thiophene) (P3HT) - [6,6]-phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM) blends, in which fractional quantities of a poor solvent for P3HT are incorporated into the solution prior to deposition\[^{26, 27}\]. The poor solvent has a higher boiling point than the casting solvent; the presence of the poor solvent after the casting
solvent evaporates induces P3HT to aggregate. The opposite occurs in our case – since toluene is a good solvent for ethyl-TES ADT, residual toluene after spin coating retards ethyl-TES ADT aggregation into active nuclei having the critical dimensions to seed TES ADT crystallization.

To further verify the impact of the solubility of the additive in the casting solvent on its ability to nucleate TES ADT crystallization, we also explored a second set of additives whose core structures differ substantially from that of TES ADT. A fullerene derivative that is functionalized with triethylsilylethynyl tetracene (TES Tet Fu) exhibits a solubility of 5 mM in toluene (refer to Figure 3.1d); PCBM exhibits a solubility of 11 mM in toluene (refer to Figure 3.1c); TIPS pen\textsuperscript{28} exhibits a solubility of 69 mM in toluene (refer to Figure 2.5c); and triisobutylsilylethynyl pentacene (TIBS pen)\textsuperscript{29} exhibits a solubility of 90 mM in toluene (refer to Figure 3.1b). Figure 5.6 displays how $\langle S \rangle$ depends on the additive concentration for these four compounds. As expected, we observe a large shift in c* depending on the solubility of the additive. Figure 5.7 quantifies this relationship in which c* for all the 9 additives explored in this study is plotted against the solubility of the additives in toluene. We observe a strong and positive correlation between c* and the solubility of the additive. When TES Tet Fu and PCBM, with solubilities of 5 mM and 11 mM, respectively, are used as additives, the c*’s are 0.2 and 0.1 mol\%, respectively. In contrast, when TIPS pentacene and TIBS pentacene are used as additives, with solubilities of 69 and 90 mM, the c*’s are 2.0 and 2.5 mol\%, respectively.
5.1.3 Dependence of $S_{\text{max}}$ on the additives’ compatibility with TES ADT

Finally, we turn our attention to $<S_{\text{max}}>$, the maximum number density of spherulites achievable in TES ADT thin films. For all the additives explored, $<S>$ becomes independent of the additive concentration beyond a critical concentration, plateauing at $<S_{\text{max}}>$. This sigmoidal dependence wherein the nucleation density saturates at high additive loadings has also been observed in the crystallization of metal alloys$^{30, 31}$ and polymer films$^{32}$ incorporating nucleating agents. This phenomenon is attributed to the aggregation of additives into larger clusters, as opposed to more numerous, albeit smaller, clusters, at high loadings$^{31}$. Because the number of critical nuclei does not necessarily scale with concentration, a saturation of the nucleation density on the additive concentration results. In the case of TES ADT films, $<S_{\text{max}}>$ appears to be bimodal. More specifically, $<S_{\text{max}}>$ either adopts a value of $2 \pm 1 \times 10^3$ spherulites/mm$^2$ when F-, Cl-, and Br-TES ADT are used as the additives, or a value around $60 \pm 30$ spherulites/mm$^2$ when the other additives are employed. That the additives most similar to TES ADT in chemical structure, namely F-, Cl-, and Br-TES ADT, can form more nuclei at high concentrations compared to other additives indicates that $S_{\text{max}}$ is likely related to the chemical compatibility of the additive with TES ADT. When the additive is chemically similar to, and thus more soluble in, TES ADT, the driving force for the additive to phase separate locally is weak. On the other hand, for additives that are chemically dissimilar to TES ADT, the driving force for phase separation is stronger. This tendency to locally segregate effectively increases additive aggregation, as opposed to increasing the number of nuclei that are formed as the concentration is increased. This phenomenon is similar to that observed in bulk polyolefin systems, in which nucleating agents that are soluble in
the host polymer to ensure that the dopant is homogeneously to induce crystallization\textsuperscript{33,}\textsuperscript{34}. In this manner, the dopant forms smaller and more numerous nuclei, as opposed to aggregating into larger but less numerous nuclei, thereby increasing the overall nucleation density.

5.2 Kinetics of the nucleation and crystallization process

To gain a deeper understanding of the nucleation process, we also examined the kinetics of spherulitic growth in TES ADT thin films during exposure to DCE solvent vapor. As mentioned in Section 4.4, we assume the growth of TES ADT to be two-dimensional because the diameter of TES ADT spherulites is 2 – 4 orders of magnitude larger than the film thickness. For neat TES ADT thin films, we found the Avrami exponent, n, to be 2. For two-dimensional systems, an n of 2 indicates that the nucleation of spherulites occurs instantaneously during the initial exposure of the film to DCE solvent vapor, with no nucleation events occurring during later time points in the crystallization process. In TES ADT thin films with fractional amounts of F-TES ADT, on the other hand, we found that n increases from 2 to 3 with increasing F-TES ADT concentration, indicating that nucleation transitions from being instantaneous to being distributed (i.e., nucleation occurs throughout the crystallization process). To further examine how the other additives influence the kinetics of TES ADT crystallization, we performed the same analysis for TES ADT thin films incorporating varying concentrations of the nine additives. First, by counting the number of new nucleation events as a function of time, we qualitatively compared the nucleation mode with increasing additive concentrations for the nine different additives. Figure 5.8 shows the
normalized $N_{\text{tot}}$ values as a function of time for different additives as a function of concentration. As the additive concentration increases, we observe a broadening of the distribution of the nucleation density per unit area uncrystallized, consistent with a change from instantaneous nucleation to distributed nucleation. As the concentration of additive increases, the number of nuclei appearing at later times during crystallization also increases. These findings demonstrate that the presence of additives in TES ADT thin films causes a shift in nucleation mechanism from one that is instantaneous to one that is distributed.

To rigorously compare the nucleation mechanism in TES ADT thin films incorporating different additives at varying concentrations, we measured the fractional area crystallized as a function of time for films and fitted the data with the Avrami equation. Figure 5.9 displays $n$ as a function of additive concentration for the nine different additives used in this study. The dependence of $n$ on the additive concentration for the different additives follows the same trend observed in TES ADT thin films incorporating F-TES ADT – at low concentrations, $n = 2$; at intermediate concentrations, the value of $n$ increases from 2 to 3 with increasing additive concentrations; and at higher concentrations, $n$ stays constant at a value of 3. The concentration range at which $n$ transitions from 2 to 3 corresponds to the range of concentrations at which $<S>$ increases exponentially with additive concentration in Figure 5.1b. The onset of $n = 3$ corresponds to when $<S> = <S_{\text{max}}>$, in which the nucleation density saturates. That $n$ plateaus at 3 in this regime is expected, since larger values would correspond to a non-physical scenario in which the nucleation rate accelerates with crystallization. The fact that the incorporation of additives, irrespective of chemistry, increases $n$ from 2 to 3 in qualitatively the same
manner suggests that the fundamental mechanism of additive aggregation and subsequent nucleation of TES ADT spherulites is independent of the physical attributes of the additives. The extent with which these processes occur, however, is chemistry-specific and depends on the additives’ driving force to aggregate, their solubility in toluene, and their chemical compatibility with the host compound.

In the aforementioned experiments, the kinetics of crystallization were measured during exposure of the films to DCE solvent vapor. In neat TES ADT thin films, solvent-vapor annealing is necessary for TES ADT to rearrange and crystallize – in the absence of solvent vapors, the structure of as-spun TES ADT thin films remains unchanged in a period of 14 days. Interestingly, we discovered that TES ADT thin films incorporating additives can crystallize over a period of 48 hours without the need for solvent-vapor annealing. Figure 5.10 shows three diffraction patterns of as-spun TES ADT films with varying amounts of F-TES ADT collected 48 hours after the films were spun cast. The diffraction pattern of the neat TES ADT thin film displays reflections associated with the monoclinic polymorph. Weak reflections of the triclinic polymorph are also present, since these films were spun cast on SiO$_2$ surfaces (refer to Section 4.4.3). In contrast, the diffraction pattern of a TES ADT thin film with 3 mol% F-TES ADT collected 48 hours after spin coating displays reflections of both the monoclinic and triclinic polymorph at similar intensities, and that of a TES ADT thin film with 5 mol% FTES ADT displays reflections only associated with the triclinic polymorph. These results demonstrate that the presence of additives can sufficiently decrease the barrier to crystallization in TES ADT thin films such that crystallization can occur at room temperature and in the absence of solvent vapors. Such crystallization in the absence of solvent vapors has been
previously observed in TES ADT, although it is important to note that the films in that study did not intentionally incorporate additives\textsuperscript{[35]}. We believe that the discrepancy between the crystallization behaviors of pure TES ADT films in our experiments and those previously stem from differences in impurity content of the starting materials, since fractional amounts of impurities can lower the barrier to crystallization so solvent-vapor annealing is no longer required.

We have found the extent of crystallization of TES ADT in the absence of solvent vapors is dependent on the additive type and its concentration. For this study, we selected only six of the nine additives previously examined as nuclei for TES ADT crystallization, since CI-TES ADT and Br-TES ADT behave like F-TES ADT, TES Tet Fu behaves like PCBM, and TIBS pen behaves like TIPS pen in their efficacies in seeding TES ADT. Only the latter additives in each group were thus selected so we can study their relative abilities in decreasing the barrier to TES ADT crystallization in the absence of solvent vapors. To compare the relative abilities of these additives to decrease the barrier to TES ADT crystallization, we compared the relative intensities of the monoclinic and triclinic polymorphs in each of the films incorporating varying amounts of the six additives 48 hours after spin coating. Specifically, we measured the peak intensities of three characteristic reflections found in the monoclinic polymorph, the (0 3 1 2), (0 3 6), and (2 0 3) reflections, and three reflections found in the triclinic polymorph, the (0 1 1), (Ti 0 1), and (1 2 2) reflections, in the diffraction patterns of TES ADT films incorporating varying amounts of the 6 different additives. These reflections are labeled in Figure 5.10 for clarity. The intensities of the reflections were normalized by the intensities of the same reflections observed in the diffraction pattern of as-spun TES ADT films with no
additives to extract the relative growth or dissolution of the monoclinic and triclinic polymorphs, respectively. Figure 5.11 displays the normalized intensities of the three reflections associated with the triclinic polymorph (top row) and three reflections associated with the monoclinic polymorph (bottom row) for varying concentrations of the different additives. As can be seen in the graphs, with increasing F-TES ADT concentration, the intensities of the reflections associated with the triclinic polymorph increase over an order of magnitude compared to the intensities of the same reflections observed in the neat TES ADT thin film. This large increase in intensity correlates to the nucleation and growth of the triclinic polymorph of TES ADT. As the intensities of the reflections associated with the triclinic polymorph increase with increasing F-TES ADT concentration, the intensities of the reflections associated with the monoclinic polymorph of TES ADT correspondingly decrease by more than an order of magnitude. For other additives, the intensities of the reflections of both polymorphs are approximately the same as those observed in the neat TES ADT thin films and are only weakly dependent on the additive concentration. These results suggest that even in the absence of solvent vapors, F-TES ADT is unique in that it can substantially decrease the energy barrier to crystallization so that TES ADT spherulites can nucleate and grow without the need for solvent-vapor annealing, albeit over a much longer time scale. None of the other additives tested were able to seed TES ADT crystallization to the same extent, further supporting our findings that F-TES ADT is the most effective in seeding TES ADT spherulitic growth of the other additives tested. Given that Cl- and Br-TES ADT behave characteristically similar with F-TES ADT in seeding crystallization in TE ADT, we suspect that Cl- and Br-TES ADT can also substantially lower the barrier to
crystallization in TES ADT so that subsequent solvent-vapor annealing is not required. Returning to the work previously mentioned in which TES ADT crystallization was observed without solvent-vapor annealing and without the intentional incorporation of additives, we suspect that the samples contained compounds similar in structure to TES ADT, such as degradation products of TES ADT, such that the barrier to crystallization was sufficiently lowered.

5.3 Structural characterization of TES ADT in the presence of additives

Finally, we performed structural characterization on TES ADT thin films in the presence of additives to determine if the presence of additives disrupts its crystal packing. As shown in Figure 5.3, in 2-D x-ray diffraction patterns of solvent-vapor annealed TES ADT thin films incorporating 7 mol% of TES Tet Fu, F-TES ADT, and TIPS pen, we observe no evidence of reflections associated with the crystal structure of the additive. These images were taken at a resolution of 0.16° at the Cornell High Energy Synchrotron Source. To more closely examine the crystal structure of TES ADT thin films incorporating additives, we also collected high-resolution, 1-D x-ray diffraction data at beamline 7-2 at the Stanford Synchrotron Radiation Lightsource. Using a linear detector, this beamline has a resolution of 0.05°, allowing us to resolve peaks more precisely. Figure 5.12 displays 1-D line traces of GIXD diffraction patterns collected on TES ADT thin films incorporating between 0 – 2 mol% F-TES ADT. Line traces on a neat F-TES ADT thin film were also collected for comparison. In all, we collected line scans along the q_z direction at six different q_{xy} values for each sample. From Figure 5.12, we observe that the reflections associated with the diffraction pattern of TES ADT thin films
incorporating 0.7 – 2 mol% F-TES ADT match those associated the diffraction pattern of neat TES ADT, and not those of neat F-TES ADT. Figure 5.13 summarizes the locations of the reflections in a two-dimensional plot in q-space. These results demonstrate that the presence of F-TES ADT, at least at minute fractions of F-TES ADT, does not disrupt the lattice dimensions of TES ADT. Because the presence of F-TES ADT retards the growth rate of TES ADT spherulites (refer to Figure 4.14), we hypothesize that the majority of F-TES ADT accumulates at intra- and interspherulite boundaries. It is possible that some F-TES ADT molecules remain in the TES ADT phase, but do not disrupt the crystal packing of TES ADT. Given the weak intermolecular interactions between neighboring TES-ADT molecules (refer to Section 2.4), coupled with the fact that both the syn- and anti- isomers of TES ADT\[^{36}\] need to be accommodated within neat TES ADT crystals, it is possible that the inherent local disorder at the molecular level provides sufficient wiggle room to accommodate F-TES ADT without significantly affecting the crystal dimensions. That F-TES ADT and other additives do not disrupt the crystal structure of TES ADT will be important in Chapter 7, when we relate device mobility to \(<S>\) in TES ADT thin films. Because we can alter \(<S>\) through the incorporation of additives without affecting the crystal packing of TES ADT, we can thus isolate the impact of having interspherulite boundaries on charge transport.

### 5.4 Conclusions

In this chapter, we presented a systematic study of two-component, organic-semiconductor systems in which one component, the additive, is present in fractional (0.1 – 10 mol%) amounts. Specifically, we examined the key attributes that influence an
additive’s ability to act as nuclei for the crystallization of the second component. We have found that the ability of the additive to crystallize in the presence of the second component, the solubility of the additive in the casting solvent, and its compatibility with TES ADT all influence its effectiveness in seeding TES ADT crystallization. Identifying key attributes affecting the nucleation efficacy of small-molecule additives in solution-processed, organic-semiconductor thin films, has strong implications in the field of organic electronics. In systems incorporating dopants to improve device mobilities\textsuperscript{3,4}, as in the case of OTFTs, and conductivities\textsuperscript{5,6} and luminescence\textsuperscript{7-9} as in the case of OLEDs, there exists a competition between maximizing the dopant level to improve electronic and optical properties while minimizing disruption to the overall film morphology. As will be shown in detail in Chapter 7, grain boundaries in organic-semiconductor thin films, for example, have been demonstrated to act as barriers to charge transport in the active layers of OTFTs\textsuperscript{13-15}. By designing the dopants to have high solubilities in the casting solvent, one could minimize the nucleation density, and thus the density of grain boundaries, in the active layer while maximizing the dopant concentration. Likewise, in the active layers of OLEDs, large-scale aggregation of emissive dopants can lead to a decrease in overall light emission due to self-quenching of the dopant\textsuperscript{8,9}. In this chapter, we have found that the degree of local phase separation between the guest and host is related to the chemical compatibility of the two compounds. It is thus advantageous to design the dopant to be chemically similar to the host organic semiconductor in order to minimize phase separation. Such design parameters will aid future research in the prediction of the final film structures based on the chemical structures of the constituent compounds, particularly in complex systems such as two-component films.
Figure 5.1. Log-log plots of the dependence of the a) spherulite diameter, L and b) <S> on the concentration of five different TES ADT additives. Pertinent parameters, c* (minimum concentration needed to seed TES ADT spherulite growth), <S_{max}> (maximum number density of spherulites achievable), and m (slope), are defined in b. Error bars represent the standard deviations in the diameters of 10 – 25 spherulites used to calculate L and <S>.
Figure 5.2. Dependence of \( m \) on the atomic radius of the substituent attached to chemical variants of TES ADT. The dashed line indicates the critical threshold size of the substituent, beyond which increasing the substituent size dramatically reduces the efficacy of the additive in nucleating TES ADT. The chemical identities of the substituents are labeled for clarity.
Figure 5.3. 2-D GIXD patterns of solvent vapor-annealed TES ADT films incorporating 7 mol% of TES Tet Fu, F-TES ADT, and TIPS pen.
Figure 5.4. DSC thermograms of TES ADT and its derivatives. The scans are displaced along the y-axis for clarity.
Figure 5.5. a) AFM images and b) corresponding GIXD patterns for 50/50 mol% blends of TES ADT with the labeled TES ADT additives.

Figure 5.6. Dependence of $<S>$ on the additive concentration for five different additives.
Figure 5.7. The critical concentration, $c^*$, needed to begin seeding TES ADT spherulite growth as a function of the solubility of the additive in toluene. Error bars represent the deviation in solubilities measured for three samples. The solid line is provided to guide the eye.
Figure 5.8. Normalized nucleation events per unit area versus the normalized time for TES ADT films incorporating six different additives at various concentrations. For data in which F-TES ADT is the additive (also equivalent to Cl- and Br-TES ADT as additives), refer to Figure 4.18.
Figure 5.9. The Avrami exponent, n, as a function of the additive concentration for different additives.
Figure 5.10. GIXD images of three TES ADT films with 0, 3, and 5 mol% F-TES ADT. The films were spun cast 48 hours prior to collection of the diffraction patterns. The neat TES ADT film comprises the monoclinic polymorph, with weak reflections associated with the triclinic polymorph present. After 48 hours, the film with 5 mol% F-TES ADT has completely converted to the triclinic crystal structure seen in solvent-vapor annealed TES ADT films.
Figure 5.11. Peak intensities of 6 different reflections normalized by the peak intensities of the same reflections in an as-spun TES ADT film with no additive as a function of the additive concentration. The top row represents reflections associated with the triclinic crystal structure of TES ADT. The bottom row represents reflections associated with the monoclinic crystal structure of TES ADT.
Figure 5.12. GIXD line scans in the $q_z$ direction at constant $q_{xy}$ (specified in the top right corner of each graph) for a neat TES-ADT thin film, films with varying concentrations of FTES-ADT and for a neat FTES-ADT thin film. Line scans are arbitrarily scaled along the $y$-axis for clarity. Dashed lines highlight the center of peaks associated with the TES ADT crystal structure.
**Figure 5.13.** A composite graph detailing the diffraction of a neat TES-ADT film, that of a neat FTES-ADT film, as well as that of films comprising fractional quantities of FTES-ADT. The plot was constructed from one-dimensional line scans along the $q_z$ direction at specific $q_{xy}$ values shown in Figure 5.13.
References


Chapter 6: Guiding crystallization in TES ADT thin films

In addition to controlling the number density of spherulites in TES ADT thin films as demonstrated in the previous chapter, we also seek to guide the direction of crystallization in TES ADT thin films. Because spherulites grow isotropically outwards from a single nucleation point, it is necessary to disrupt this radially symmetric growth to control the direction of crystallization. In this chapter, we present a method to guide crystallization by inducing crystallization to propagate in prescribed directions while suppressing growth in other directions. In doing so, we can guide crystallization along arbitrary, nonlinear paths, allowing us to specify the molecular orientation of TES ADT molecules in the plane of the film with unprecedented spatial control.

The ability to control the orientation of molecules in thin films is of great significance in the field of materials engineering. Oriented films are desirable in a wide range of applications, such as organic light-emitting diodes with polarized electroluminescence\(^1\) and alignment layers for liquid crystal displays\(^2\). Oftentimes, the presence of the underlying substrate induces preferential out-of-plane orientation of molecules\(^3-5\). TES ADT\(^6\) and poly(3 hexyl-thiophene)\(^7\), a solution-processable semiconducting polymer, for example, both crystallize with their π-plane preferentially aligned perpendicular to substrate surfaces. While out-of-plane alignment of molecules can occur spontaneously upon deposition given strong molecule-substrate interactions, achieving in-plane alignment of molecules over large areas requires the application of external fields, such as

as shear forces\textsuperscript{8} and temperature gradients\textsuperscript{3}. Such techniques have been applied successfully to orient molecules unidirectionally in-plane, leading to an enhancement in material properties, such as tensile strength\textsuperscript{9} and electrical conductivity\textsuperscript{6, 8}. While uniaxial or even biaxial alignment of molecules in organic thin films has been demonstrated over large areas, the ability to prescribe the orientation of molecules in thin films along arbitrary patterns over large areas remains exceedingly difficult. In 1991, Wittmann and Smith demonstrated the ability to epitaxially template liquid crystals along helical poly(tetrafluoroethylene) patterns\textsuperscript{10}. Here, we instead exploit the differential crystallization rates of TES ADT on substrates having different surface energies to disrupt the radial symmetry of spherulitic growth. In doing so, we can control the crystallization direction in TES ADT thin films along pre-specified shapes and patterns, demonstrating unprecedented control over the in-plane orientation of molecules.

As spherulites grow radially outwards, they necessarily incorporate a large distribution of molecular orientations in order to maintain a circular, space-filling growth habit. In Chapter 4, we detailed the spherulitic growth of TES ADT and the factors that influence the spherulitic growth rate, such as the presence of impurities and the surface energy of the underlying substrate. In this chapter, we demonstrate a method to spatially pattern the in-plane molecular orientation in TES ADT thin films by taking advantage of differences in the spherulitic growth rate on substrates having different surface energies. By patterning the underlying substrate to have regions of different surface energies, we can promote growth along pre-specified paths, while suppressing growth elsewhere. In this manner, we effectively break the radial symmetry of spherulitic growth. Such surface patterning was previously demonstrated by Nealey and coworkers to guide the placement
of nanoscale, periodic phase-separated domains of block copolymers. Here, we extend this concept to control molecular ordering on the millimeter length scale.

6.1 Directing crystallization along linear paths

We first demonstrate directed crystallization of TES ADT along a straight path on a substrate with differential surface energies. To pattern regions having different surface energies on the underlying substrate, we evaporated 35-nm Au pads on top of pre-cleaned SiO$_2$/doped-Si substrates. The substrates were then immersed in an ethanol solution with pentafluorobenzenethiol (PFBT) (refer to Chapter 3 for experimental details). Through thiol-Au interactions, PFBT adsorbs selectively onto the Au pads, significantly decreasing the surface energy of Au, from 41 ± 1 ergs/cm$^2$ on bare Au to 27.3 ± 0.04 ergs/cm$^2$ on PFBT-treated Au. Because thiols do not react with SiO$_2$, the surface energy of SiO$_2$ remains constant at 64 ± 3 ergs/cm$^2$ before and after substrate immersion in PFBT solution. Thus, by appropriately evaporating Au patterns on the pre-cleaned SiO$_2$/doped-Si substrate and pre-treating these pads, we can induce a surface energy differential of 2 times on a single substrate. From Figure 4.21, we know that the growth rates of TES ADT on pre-cleaned SiO$_2$/doped-Si and PFBT-treated Au are 24 ± 3 µm/s and 9 ± 3 µm/s, respectively. After PFBT treatment of the Au pads, TES ADT is spun cast across the entire substrate. Figure 6.1 shows an illustration of the side view of one such film, demonstrating that TES ADT is uniformly deposited across both SiO$_2$ and PFBT-treated Au surfaces. Figure 6.2a shows time-lapsed optical micrographs of crystallization of a TES ADT thin film deposited on an untreated SiO$_2$ path defined by two 35-nm thick PFBT-treated Au strips. Given the difference in growth rates of TES
ADT on the two surfaces, crystallization of TES ADT occurs preferentially along the SiO$_2$ path. Specifically, only crystals whose fast growth axes are parallel to the path direction propagate quickly; crystals whose fast growth axes are oriented away from the path direction will propagate until they reach PFBT-treated Au, beyond which their growth rate is substantially suppressed. In this manner, crystallization occurs in registry with the underlying SiO$_2$ path. In contrast, Figure 6.2b shows time-lapsed optical micrographs of TES ADT crystallization when untreated Au – as opposed to PFBT-treated Au – strips are used. In this sample, TES ADT form spherulites, and these spherulites grow indiscriminately across the entire substrate since the growth rate of TES ADT on untreated Au is similar to that on pre-cleaned SiO$_2$/doped-Si substrates, at $20 \pm 1 \mu$m/s and $24 \pm 3 \mu$m/s, respectively.

In this technique of directed crystallization, the maximum pattern size over which we can direct TES ADT crystallization is limited by the nucleation density of TES ADT. In TES ADT thin films, regardless of the surface functionality of the underlying substrate, the nucleation density of TES ADT spherulites is approximately 0.2 nuclei/mm$^2$. This nucleation density is determined by the number of dust particles or defects on the substrate surface$^{[4]}$ and corresponds to average spherulite diameters of 3 mm. To determine the length scale over which crystallization can be guided, we need to consider the pattern dimensions in relation to the nucleation density and the relative crystallization rates. To facilitate discussion, Figure 6.3 illustrates a patterned substrate with SiO$_2$ paths surrounded by PFBT-treated Au. The path length, L, and width, W, as well as the pitch, P, between two paths are labeled. To observe directed crystallization, W must thus be less than 2 – 3 mm, or the average spherulite diameter. On the other hand, the minimum P
between adjacent paths is dictated by the difference in the crystallization rate on the two surfaces that define the patterns. While TES ADT crystallization largely occurs along SiO₂ paths, it does also proceed, albeit at a substantially slower rate, on PFBT-treated Au. To isolate crystallization between two adjacent paths, P must thus be at least equivalent to the characteristic length that is defined by the product of the ratio of the slow to the fast growth rates and the length of the pattern, L, as described by Equation 6.1 below:

\[ P \geq L \left( \frac{\text{slow growth rate}}{\text{fast growth rate}} \right) \]  

(6.1)

Using these guidelines, we can design the width and length of patterns, as well as the pitch between patterns, to appropriately direct TES ADT crystallization.

### 6.2 Structural characterization of directionally-crystallized TES ADT thin films

The ability to direct TES ADT crystallization along a straight SiO₂ path has allowed us to determine the molecular orientation at the growth front and to quantify the distribution of molecular orientations about the fast-growth axis of TES ADT spherulites. Identifying the crystallographic direction associated with the growth fronts of spherulites has traditionally only been accessible via high-energy techniques, such as micro-diffraction\[^{14}\], which selectively irradiate a small portion of a spherulite at a single time. Unfortunately, the fragility of TES ADT thin films\[^{15}\] precludes the use of direct, high-intensity beams for crystallographic studies. Instead, we conducted GIXD experiments on a directionally-crystallized TES ADT sample, such as that shown in Figure 6.4a. This sample was crystallized in the same manner as the film shown in Figure 6.2a. After solvent-vapor annealing, the gold pads and uncrystallized portions of TES ADT were
removed using acetone. Figure 6.4b shows the GIXD pattern obtained by placing the sample with its crystallization direction along the incident x-ray beam path during measurements. This method is reminiscent of fiber diffraction analysis, where polymer fibers are drawn or sheared to preferentially orient the chains in a single direction in order to determine the crystallographic structure of polymers\textsuperscript{16}. In the GIXD pattern of directionally-crystallized TES ADT, we only detect the (1\text{2}2) and (1\text{2}1) reflections in the GIXD pattern; the former reflection corresponds to the \(\pi\)-stack plane of TES ADT while the latter reflection corresponds to a plane that is tilted 11\(^{\circ}\) away from the \(\pi\)-stack plane. In contrast to the GIXD pattern of a polycrystalline TES ADT thin film in which all the reflections are present, such as that shown in Figure 4.4, no other reflections are observed. Our results thus indicate that the fast-growth direction during directed crystallization corresponds to the \(\pi\)-stacking direction of TES ADT. This observation is consistent with the fast growth direction corresponding to the \(\pi\)-stacking direction of other conjugated systems, such as alkylated-hexabenzocoronene\textsuperscript{17} and pyrene-based compounds\textsuperscript{18}. The ability to orient conjugated compounds along their \(\pi\)-stack direction is of particular importance to the field of organic electronics, where past research on organic single crystals has shown charge transport to be fastest along the \(\pi\)-stack direction\textsuperscript{19}.

By rotating the sample about the substrate normal during x-ray diffraction measurements, we can further quantify the distribution of molecular orientations about the growth direction by constructing \(\phi\)-scans. Figure 6.5 shows the intensity of the (1\text{2}2) reflection as a function of the sample rotation angle, \(\phi\). The maximum peak intensity occurs at 8 ± 5\(^{\circ}\) about the fast-growth axis, indicating that the mean direction of \(\pi\)-
stacking is slightly tilted from the fast-growth axis. The large standard deviation represents the error associated with aligning the TES ADT crystallization direction with the path of the incident x-ray beam. A similar φ-scan of another directionally-crystallized sample showed a tilt of $6 \pm 5^\circ$ of the $\pi$-stacking plane from the fast-growth direction, so we believe this tilt to be statistically significant. The full peak width at half the maximum intensity (FWHM) of the φ-scan is $20^\circ$, indicating a large spread in the molecular orientation with respect to the fast-growth direction. For clarity, the overlayed scheme in Figure 6.5 illustrates the degree of tilt of the $\pi$-stacking planes of TES ADT from the fast-growth direction for different φ values. As shown in the figure, TES ADT can be oriented as far as $20^\circ$ away from the mean $\pi$-stacking direction. This FWHM is three orders of magnitude larger than the FWHM of φ-scans carried out on rubrene single crystals, where the FWHM is $< 0.02^\circ$, indicating negligible orientation distribution$^{[20]}$. For comparison, the FWHM of φ-scans taken on directionally-crystallized poly(3-hexyl thiophene) films$^{[3]}$ and on block copolymer films in which the microdomains are preferentially aligned via zone casting$^{[21]}$ are $10^\circ$ and $30^\circ$, respectively. These samples, like TES ADT, incorporate a large distribution of orientations about the alignment axis. This large distribution of orientations about the mean of $\pi$-stacking direction in TES ADT thin films necessitates the formation of many low-angle intraspherulite grain boundaries. These low-angle grain boundaries in turn directly affect charge transport within spherulites, the details of which will be discussed in detail in Chapter 7. While the large FWHM in φ-scans of directionally-crystallized TES ADT thin films indicates the existence of a much larger degree of orientational disorder in these systems compared to that observed in single crystals, it is precisely this orientation distribution that has
allowed us to direct crystallization of TES ADT. By allowing the crystals that are preferentially oriented parallel to the path direction to propagate while suppressing other orientations, we can guide crystallization along paths on the millimeter length scale.

6.3 Directing crystallization along arbitrary paths

This method of directed crystallization in straight channels can be extended to guiding crystallization along arbitrary patterns. In Figure 6.6a, TES ADT is deposited uniformly across a substrate comprising a SiO$_2$ serpentine pattern surrounded by PFBT-treated Au. Upon exposure to DCE solvent vapor, TES ADT preferentially crystallizes along the serpentine pattern given the almost three-fold difference in growth rates on the two surfaces. The panels in Figures 6.6a - c show time-lapsed images of this directed crystallization process on substrates having different pre-specified patterns. That the growth fronts can successfully maneuver around sharp corners (Figures 6.6a and b) and along an annule (Figure 6.6c) relies on the fact that TES ADT crystallization samples a distribution of molecular orientations about the fast growth axis. Specifically, as the growth front reaches a corner, only the orientations that are parallel with the direction of the underlying SiO$_2$ path continue to propagate, while other orientations are suppressed as they encounter the PFBT-treated Au surfaces. For comparison, in Figure 6.6d, TES ADT is deposited uniformly across the same pre-patterned substrate as that shown in Figure 6.6a, but with untreated Au instead of PFBT-treated Au. Upon exposure to DCE solvent vapor, TES ADT spherulites grow indiscriminately across the entire substrate, with only slight distortions in the spherulite shape due to small differences in the growth rates of TES ADT on SiO$_2$ (24 ± 3 µm/s) and untreated Au (20 ± 1 µm/s). Specifically,
the spherulite grows slightly faster along directions comprising mostly SiO$_2$, resulting in an oblong spherulite.

6.4 Forming low- and high-angle interspherulite boundaries (ISBs)

In polycrystalline TES ADT thin films, interspherulite boundaries (ISBs) are formed when adjacent spherulites impinge. At ISBs, there exists a mismatch in the orientations of molecules across the boundaries. The angle of molecular orientation mismatch, or ISB angle, can range from $0^\circ$ – $90^\circ$, with angles less than $15^\circ$ characterized as “low-angle” ISBs$^{[22]}$. As shown in Figure 4.7, a single ISB can comprise regions characterized by a low angle of molecular orientation mismatch across the boundary and regions characterized by a high angle of molecular orientation mismatch across the boundary due to the large distribution of orientations incorporated within spherulites. Studying charge transport across ISBs as a function of ISB angle in polycrystalline TES ADT thin films is thus exceedingly difficult. Instead, we use our method of directing crystallization along pre-specified paths to engineer both exclusively low-angle and exclusively high-angle ISBs. Figure 6.7 displays time-lapsed optical micrographs of ISB formation in TES ADT thin films during exposure to solvent vapors. Figure 6.7a shows the crystallization of TES ADT in which nucleation occurred at two separate points along a straight SiO$_2$ path. When the crystallization fronts meet, a low-angle ISB is formed. Because a spread of orientations exists about the fast-growth axis at the propagation front, as determined in Section 6.2, the ISB angle is thus $0 \pm 20^\circ$. When crystallization is instead directed along a SiO$_2$ path with a $90^\circ$ corner, a high-angle ISB is formed, as shown in to Figure 6.7b. In
this case, the ISB angle is $90^\circ \pm 20^\circ$. It is important to note that because the nucleation of spherulites is spatially random throughout the films, the meeting of two growth fronts at the $90^\circ$ corner is a stochastic process. Usually, several samples must be made in order to form a single high-angle ISB. The relative orientations of TES ADT molecules along the paths are illustrated in the bottom images of Figure 6.7, with the black lines representing the $\pi$-plane of TES ADT. From the illustrations, it is apparent that the molecular orientation mismatch is negligible at the $0 \pm 20^\circ$ ISB, but large at the $90^\circ \pm 20^\circ$ ISB. We believe that this large mismatch in molecular orientations across high-angle ISBs results in high-angle ISBs being more electrically-resistive compared to low-angle ISBs. The impact of ISBs on charge transport is the subject of discussion in Chapter 7.

6.5 Conclusions

Because spherulitic growth is present in such a wide range of materials, this technique of directed crystallization can be applied to many areas of material science, including films for optical and electronic applications. In this chapter, we demonstrated that by patterning the underlying substrate to have regions of different surface energies, we can direct crystallization in TES ADT thin films along arbitrary, nonlinear patterns. This technique takes advantage of the nature of spherulitic growth, which samples a wide range of distributions about the fast growth axis. By promoting growth along directions that are parallel to the path direction and suppressing along other directions, we can guide crystallization around bends and corners. We also demonstrated the ability to form and isolate single ISBs, across which we will measure charge transport in Chapter 7. By unlocking the ability to exploit in two dimensions the unique material properties that
arise from aligned molecules, our technique of directed crystallization has the potential to lead to a myriad of new applications in the field of materials engineering, such as arbitrarily-shaped conductive pathways in polymer films and patterned coatings for polarized light applications.
Figure 6.1. A side profile of a TES ADT film deposited on pre-cleaned SiO$_2$/doped-Si substrate with PFBT-treated Au pads. Black slanted lines represent PFBT molecules adsorbed onto the Au surfaces through thiol-Au interactions.

Figure 6.2. a) Time-lapsed optical micrographs of TES ADT crystallization in a film deposited on a pre-cleaned SiO$_2$/doped-Si substrate with PFBT-treated Au strips. b) Time-lapsed optical micrographs of TES ADT spherulite growth in a film deposited on a pre-cleaned SiO$_2$/doped-Si substrate with untreated Au strips. The time point for each frame is labeled for clarity.
Figure 6.3. A schematic illustration of a patterned substrate with SiO$_2$ features (blue) spanning length, L, and width, W, spaced by pitch, P, surrounded by PFBT-treated Au (yellow).
Figure 6.4. a) Optical micrograph of directionally-crystallized TES ADT on a pre-cleaned SiO$_2$/doped-Si substrate. The PFBT-treated Au strips used to direct TES ADT crystallization were removed prior to GIXD experiments (the locations of which are indicated by red rectangles). b) Corresponding GIXD diffraction pattern of directionally-crystallized TES ADT with the crystallization direction aligned to the x-ray beam path. The (122) reflection corresponds to the $\pi$-stack direction of TES ADT. [Adapted from S.S. Lee, et al. Adv Mater. doi: 10.1002/adma.201104619 (accepted March 2012)]
Figure 6.5. φ-scan of the (122) reflection acquired while rotating the sample shown in Figure 6.4a about the substrate normal (inset shows the experimental geometry). The overlayed diagram illustrates the average degree of tilt away from the fast-growth direction for different φ values. Dashed lines represent the π-planes of TES ADT. [Adapted from S.S. Lee, et al. Adv Mater. doi: 10.1002/adma.201104619 (accepted March 2012)]
Figure 6.6. a-c) Time-lapsed optical micrographs of TES ADT crystallization on PFBT-treated Au/SiO$_2$ substrates preferentially progressing along the SiO$_2$ patterns. The arrows indicate the progression of crystallization fronts. d) Time-lapsed optical micrographs of TES ADT crystallization on untreated Au/SiO$_2$ substrates in which spherulites grow indiscriminately across both Au and SiO$_2$ surfaces. The time point for each frame is labeled for clarity. [Reproduced from S.S. Lee, et al. Adv Mater. doi: 10.1002/adma.201104619 (accepted March 2012)]
Figure 6.7. Time-lapsed images during crystallization of TES ADT films comprising a a) low-angle ISB and b) high-angle ISB. Bottom images illustrate the molecular orientation of TES ADT molecules within the channels, with the lines representing the conjugated $\pi$-plane. The black solid lines traversing the channel represent the ISBs. The time point for each frame is labeled for clarity.
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Chapter 7: Measuring intra- and interspherulite charge transport in TES ADT OTFTs

In organic-semiconductor systems, charge transport occurs through π-orbital overlap between adjacent molecules, with long-range propagation of the π-orbital network achieved through crystallization. Disruption of the π-orbital network due to the presence of structural heterogeneities results in a decrease in overall charge transport through organic-semiconductor thin films. As such, morphological parameters, such as the degree of crystallization and average crystal sizes, in the active layers of OTFTs are critical in determining overall device performance\[1\]. In previous chapters, we have focused on understanding how processing conditions affect the structure of solution-processed, TES ADT thin films and how we can in turn use this knowledge to systematically control the nucleation density of TES ADT and the crystallization direction the crystals that subsequently form. In this current chapter, we turn our attention to how structural heterogeneities in films comprising spherulites affect charge transport in TES ADT OTFTs.

To determine how structural disorder and heterogeneities, such as grain boundaries and variations in molecular orientation, impact charge transport through organic-semiconductor thin films, it is necessary to understand the inherent nature of charge transport in defect- and structural heterogeneity-free organic semiconductors. For this purpose, researchers have turned to the study of organic-semiconductor single crystals\[2-7\]. These systems, with near-perfect molecular ordering, are ideal for examining the intrinsic charge transport properties. For example, using a soft-contact lamination
technique to reversibly make electrical contact to a rubrene single crystal in a field-effect transistor (FET), Sundar and coworkers were able to rotate the single crystal and measure device mobilities as a function of the orientation of the rubrene crystal with respect to the charge transport direction of the device. Figure 7.1 displays a polar plot of the FET mobility as a function of the angle of rotation of the rubrene crystal with respect to the active channel. A maximum intrinsic mobility of 15.4 cm$^2$/V-s is observed when the rubrene crystal is rotated 180° or 360° from its initial orientation with respect to the active channel. These angles correspond to the b-axis of rubrene being aligned with the charge transport direction in the active channel. Figure 7.2 displays the molecular packing of a rubrene crystal, with its a and b axes labeled. From the figure, it is apparent that π-orbital overlap between adjacent molecules is maximized along the b axis. This experiment and others on organic-semiconductor single-crystals confirm that charge transport along different crystallographic directions of organic-semiconductor single crystals is anisotropic, with charge transport the fastest along the direction of maximum π-orbital overlap.

By aligning organic-semiconductor single crystals so that the direction of charge transport in FETs coincides with the direction of maximum π-orbital overlap in crystals, researchers have fabricated single-crystal FETs with mobilities surpassing 15 cm$^2$/V-s, whereas their thin-film counterparts typically exhibit mobilities on the order of 0.1 cm$^2$/V-s. Prohibitively long deposition times (24 – 48 hours is typical) and the requirement for highly-pure starting materials to grow organic-semiconductor single crystals, however, prevent these structurally near-perfect materials from being relevant for inexpensive organic electronic applications. Instead, the research community has
increasingly turned to organic-semiconductor thin films as promising candidates for the active layers of organic electronics. Because these active layers are rapidly deposited from the vapor or solution phase (over time frames on the order of seconds and minutes), they are polycrystalline in nature, incorporating a high degree of local variations in molecular ordering and orientation compared to their single-crystal counterparts. OTFTs with polycrystalline thin films as active layers thus generally achieve mobilities less than 1 cm²/V-s. These polycrystalline thin films are structurally complex. Boundaries that are formed between impinging grains, in particular, have been demonstrated to significantly impact charge transport as a mismatch in molecular orientation of disrupts the π-orbital network.

By systematically increasing the substrate temperature during thermal evaporation of sexithiophene, Horowitz and Hajlaoui varied the grain size in sexithiophene thin films from 60 to 330 nm. Using these films as active layers of OTFTs, for example, the device mobilities increase from 0.11 to 0.28 cm²/V-s with increasing grain size in the active layers. Because the average grain size is inversely proportional to the number of grain boundaries in the active layers, these results are consistent with the idea that grain boundaries can act as barriers to charge transport in OTFTs. Furthermore, by nucleating two sexithiophene grains from electrodes in close proximity with each other, the Frisbie group fabricated an OTFT comprising a single grain boundary in the active layer. Using conductive-AFM to measure charge transport across the grain boundary, they found the resistance within a single thermally-evaporated grain boundary to be an order of magnitude higher than the resistance of within sexithiophene grains. Studies on grain boundaries in solution-processed, organic-semiconductor thin films are comparatively
limited. Because crystallization in these thin films often occurs rapidly as the casting solvent evaporates during film formation, the isolation of single grain boundaries for charge transport studies has been prohibitively difficult. In one study, researchers successfully fabricated solution-processed F-TES ADT OTFTs with a single grain boundary in the active channel by inducing nucleation on chemically-modified electrodes\[^{16}\]. Using Kelvin probe microscopy, the researchers found evidence that is consistent with the presence of a charge transport barrier to exist at F-TES ADT grain boundaries. Such experiments demonstrate the significance of grain boundaries in determining the overall charge transport in organic-semiconductor thin films. Yet, quantitative elucidation of their contribution to device characteristics has been challenging.

In solution-processed, organic-semiconductor thin films comprising spherulites, grain boundaries exist at multiple length scales. Because of the radially-symmetric, space-filling nature of spherulitic growth, these crystalline superstructures incorporate a wide distribution of orientations about the radial axis. Spherulites thus comprise many smaller grains separated by low-angle grain boundaries on the submicron length scale, with the growth of these grains directed radially from its nucleation point. On the tens of microns to millimeter length scale, interspherulite boundaries (ISBs) between impinging spherulites also exist. The angle of molecular orientation mismatch at ISBs can range from 0 – 90°. Furthermore, because spherulites incorporate a large distribution of molecular orientations about the radial axis, the angle of molecular orientation mismatch can vary along a single ISB (refer to Figure 4.7). Understanding how these structural heterogeneities at different length scales individually contribute to overall charge
transport in OTFTs is critical in guiding the engineering of the structure of active layers to improve device performance.

The culmination of the work presented in this thesis lies in applying our collective knowledge of the nucleation, growth, and structural development of spherulites to elucidate how the structural complexities of TES ADT thin films influence the performance of OTFTs comprising them as active layers. Here, we decouple the impact of these structural heterogeneities at different length scales on charge transport through the active layers of OTFTs comprising spherulites. In Section 7.1, we present a systematic study of intraspherulite charge transport as a function of the molecular orientation in active channels of devices to examine how local variations in molecular orientation and the low-angle grain boundaries that consequently form within these spherulites impact OTFT characteristics. In Section 7.2, we measure the resistance across engineered ISBs having pre-specified angles of molecular orientation mismatch between adjacent spherulites. In Section 7.3, we combine our results to study the ensemble-average charge transport through OTFTs comprising polycrystalline TES ADT thin films in the active channels. Specifically, by controlling the number density of spherulites, we measure OTFT device performance as a function the number of ISBs in the active layers. We then compare the dependence of OTFT current in the linear regime on the number of ISBs in the active channels to that predicted with the resistance of single ISBs. Finally, in Section 7.4, we study how the presence of ISBs affects the air stability of TES ADT OTFTs.
7.1 Probing intraspherulite charge transport in TES ADT thin films

To decouple how structural heterogeneities affect charge transport on different length scales in films comprising spherulites, we first probed charge transport within single TES ADT spherulites. In Chapter 6, we found that the fast growth direction of TES ADT corresponds roughly to the \( \pi \)-stacking direction, with the \( \pi \)-planes of TES ADT tilted \( 8 \pm 5^\circ \) from the fast-growth axis. TES ADT thus \( \pi \)-stacks radially outwards to form radially-symmetric spherulites, corresponding also to the direction of maximum \( \pi \)-orbital overlap. Given this preferential \( \pi \)-stack orientation – as in the case of single crystal FETs – charge transport is expected to be fastest along the radial direction of TES ADT spherulites. Unlike organic-semiconductor single crystals, however, spherulites incorporate a distribution of molecular orientations about the radial axis. A single spherulite thus comprises many smaller grains that are separated by low-angle intraspherulite grain boundaries. In this section, we elucidate how the presence of a distribution of molecular orientations, and thus the presence of low-angle grain boundaries, impacts the anticipated charge transport anisotropy along the different crystallographic planes in organic-semiconductor single crystals within TES ADT spherulites.

To measure charge transport within TES ADT spherulites as a function of the general \( \pi \)-stacking direction in the active channel of OTFTs, we fabricated an array of OTFTs on a single spherulite. Central to this technique is the fact that TES ADT spherulites can grow larger than 3 mm in diameter, allowing us to fabricate dozens of devices on a single spherulite. Figures 7.3a and b display optical micrographs of the same TES ADT

spherulite before and after the deposition of 60-nm top contact Au electrodes. Our group has previously found that depositing top-contact electrodes via electron-beam deposition can damage the underlying TES ADT\cite{17}. We thus deposited the Au electrodes via thermal evaporation for these experiments. Thermal evaporation is less energetic than electron-beam deposition; in this manner, we are able to make electrical contact to TES ADT without inducing damage. The electrodes were defined using a transmission electron microscopy (TEM) sample grid; the channel length and width of individual devices are thus prescribed at 50 and 204 \(\mu\text{m}\), respectively. As shown in Figure 7.3b, we can define \(\theta\), the angle between the macroscopic radial axis of the spherulite and the vector defining the charge transport direction of the transistor for each device. As defined, \(\theta = 0^\circ\) or \(180^\circ\) corresponds to cases in which the mean \(\pi\)-stacking direction is generally aligned with the charge transport direction, whereas \(\theta = 90^\circ\) or \(270^\circ\) corresponds to cases in which the mean \(\pi\)-stacking direction is generally perpendicular to the charge transport direction.

Figure 7.4 displays illustrations of the channel regions of devices 13, 5, and 24 in Figure 7.3b, with black lines representing the \(\pi\)-planes of TES ADT and shaded domains representing different grains, each separated by a low-angle intraspherulite grain boundary. The angle of molecular orientation mismatch between these grains is low (defined as \(<15^\circ\)\cite{18}), due to the fact that they are all generally oriented along the radial axis of the spherulite. In the active channel of device 13 (top), TES ADT is generally oriented with its mean \(\pi\)-stacking direction parallel to the charge transport direction of the transistor (\(\theta = 178^\circ\)), whereas in the active channel of device 5 (middle), TES ADT is oriented with its mean \(\pi\)-stacking direction tilted approximately \(30^\circ\) away from the ideal
charge transport direction ($\theta = 128^\circ$). In the active channel of device 24 (bottom), the mean $\pi$-stacking direction is on average normal to the charge transport direction ($\theta = 276^\circ$).

Based on previous reports in which charge transport in organic-semiconductor single crystals is fastest along the $\pi$-stacking direction of organic semiconductors$^{[3, 4, 8, 19]}$, we hypothesized that the mobility of device 5 would be the highest and the mobility of device 24 to would be the lowest. Surprisingly, comparisons of the output and transfer curves of devices 13, 5, and 24, shown in Figures 7.5 and 7.6, respectively, indicate comparable OTFT device performance. From the transfer curves in the saturation regime, we estimated the mobilities for all three devices to be 0.38 cm$^2$/V-s, indicating that the general molecular orientation in the channels do not impact charge transport. Figure 7.7 displays a summary of the mobility, threshold voltage, $V_T$, and on/off ratio of 46 devices tested on two different TES ADT spherulites as function of $\theta$. As can be seen from these polar plots, we observe no correlation between $\theta$ and the device characteristics. The average mobility across all the devices is $0.37 \pm 0.03$ cm$^2$/V-s. The average $V_T$ and on/off ratio are $22 \pm 4$ V and $7 \pm 3 \times 10^3$, respectively. This $V_T$ is comparable to that we previously reported for TES ADT OTFTs with active channels comprising multiple spherulites$^{[20]}$. This abnormally high $V_T$ compared to OTFTs comprising other semiconductors$^{[12, 21]}$ stems from moisture adsorption at the organic semiconductor-dielectric interface$^{[22, 23]}$, as devices fabricated and tested in the glovebox (<0.1 ppm oxygen and water) consistently display $V_T$’s of $6 \pm 2$ V – this point will be further discussed in Section 7.4.
To understand why we observe isotropic charge transport within spherulites, it is necessary to examine differences in the structure of spherulites compared to organic-semiconductor single crystals. Organic-semiconductor single crystals display near-perfect molecular ordering. In contrast, the radially-symmetric, space-filling growth habit of spherulites necessitates the incorporation of a wide distribution of molecular orientations about the radial axis, leading to the formation of low-angle grain boundaries. To quantitatively compare the degree of orientational disorder in these systems, we can examine the full-width at half-the-maximum intensity (FWHM) of φ-scans collected using x-ray diffraction. In these scans, the intensity associated with a specific reflection in the diffraction pattern of a sample is measured as the sample is rotated in the path of the incident x-ray beam. φ-scans thus measure the degree of spread in molecular orientations about a given axis. A φ-scan on the (600) reflection of single-crystal rubrene, for example, has a FWHM of 0.02°, indicating very little orientational disorder within the crystal. To measure the degree of spread in molecular orientations about the fast-growth axis of TES ADT spherulites, we first directionally crystallized TES ADT along a straight SiO₂ path, as demonstrated in Section 6.2. We then rotated the sample about the substrate normal in the incident x-ray beam path while measuring the intensity of the (122) reflection, corresponding to the π-plane of TES ADT to collect a φ-scan. In doing so, we found the FWHM of the φ-scan to be 20°, indicating that the π-planes of TES ADT can be tilted as far as 20° away in either direction from the mean π-stacking direction (refer to Figure 6.5). This FWHM is three orders of magnitude larger than the FWHM observed in φ-scans of rubrene single crystals and twice as large as that observed in φ-scans of the (001) reflection of directionally-crystallized P3HT films, indicating
that TES ADT incorporates a large distribution of molecular orientations about the radial axis.

While a direct comparison to mobilities derived from OFETs comprising single crystals of TES ADT would have been ideal, our efforts to make single-crystal TES ADT OFETs were hindered by the inability to make efficient electrical contact to rough TES ADT single crystals using “flip chip”\cite{7} or other soft-contact lamination\cite{25} techniques. Attempts to form large single crystals directly on dielectric surfaces comprising bottom source and drain electrodes via drop casting or dip coating\cite{26,27} were also unsuccessful. Given that TES ADT crystallizes in the same brickwork-type packing motif as TIPS pen\cite{28,29}, and single crystals of TIPS pen display anisotropic photoconductivity along different crystallographic directions\cite{6}, it is not unreasonable to assume that charge transport anisotropy should also exist along different crystallographic directions of TES ADT. We can estimate to the first order how the spread in molecular orientation found in TES ADT spherulites affect charge transport anisotropy by assuming that TES ADT single crystals exhibit the same charge transport anisotropy as rubrene single crystals. Accounting for a ±20° spread in molecular orientation distribution, according to the data presented in Figure 7.1, we should thus still expect to see a two-fold charge transport anisotropy in our devices fabricated on single TES ADT spherulites\cite{3,4}. Our observation of isotropic charge transport within spherulites suggests that although the molecular orientation distribution in the active channels of OTFTs only comprises a subset of all possible orientations, the variations in molecular orientation about the radial axis causes any charge transport anisotropies that may exist along different crystallographic directions of TES ADT to be averaged out. Incorporation of a distribution of molecular
orientations about the radial axis necessitates the formation of many smaller grains
directed radially from the spherulite center, and thus, low-angle grain boundaries between
them. We are thus left to speculate that it is the presence of these low-angle grain
boundaries that are responsible for the smearing out of any charge transport anisotropy
we expected to see within single spherulites. Recently, Podzorov and coworkers
demonstrated that charge transport anisotropies along different crystallographic directions
of rubrene single crystals disappear at low temperatures. In this regime, charge transport
is limited by shallow traps that result from structural disorder in the crystal\cite{30}. In light of
this work, we further believe that shallow traps that exist at low-angle grain boundaries
introduced by the presence of a distribution of molecular orientations within spherulites,
can limit charge transport and smear out any charge transport anisotropies along different
molecular orientations. While it is commonly believed that charge transport is minimally
affected by the presence of low-angle grain boundaries,\cite{31} our results – consistent with
those of Podzorov and coworkers – thus suggest otherwise.

Our study of intraspherulite charge transport thus demonstrates that the existence of
low-angle grain boundaries within the channels of OTFTs are capable of averaging out
any charge transport anisotropies that may be present along different crystallographic
directions of TES ADT. We have measured the coefficient of variation (the standard
deviation normalized by the mean) of intraspherulite TES ADT OTFT mobility to be
0.08. For comparison, the average mobility of OTFTs comprising as-spun TES ADT was
measured to be $0.002 \pm 0.001 \text{ cm}^2/\text{V}\cdot\text{s}$\cite{20}, corresponding to a coefficient of variation of
0.50, and the average mobility of 73 TIPS pen OTFTs was measured to be $0.65 \pm 0.35
\text{ cm}^2/\text{V}\cdot\text{s}$\cite{12}, corresponding to a coefficient of variation of 0.54. Compared to other
solution-processed OTFTs, the highly-uniform charge transport in intraspherulite TES ADT OTFTs is advantageous for commercial applications requiring small variations in device performance over large areas.

7.2 Probing interspherulite charge transport in TES ADT thin films

Having developed a comprehensive understanding of charge transport within spherulites, we next turned our attention to charge transport across single ISBs. Unlike the low-angle grain boundaries within spherulites, the angle of molecular orientation mismatch at ISBs can range from 0 – 90°. Furthermore, as shown in Figure 4.7, a single ISB can comprise regions of both low- and high-angle molecular orientation mismatch. To study the impact of the angle of molecular orientation mismatch across ISBs on charge transport, we thus engineered single, isolated low- and high-angle ISBs. Specifically, using the directed crystallization approach for forming single ISBs in TES ADT thin films detailed in Section 6.4, herein we study charge transport across pre-engineered single ISBs at two different angles of molecular orientation mismatch across the ISBs using conductive AFM in Section 7.4.1 and resistivity measurements in Section 7.4.2. In this technique, crystallization that is directed along a path exhibits a spread in molecular orientations that is limited to 20° with respect to the crystallization direction. As such, we can limit the spread of the angle of molecular orientation mismatch at engineered ISBs to ± 20°. In doing so, we can quantitatively compare charge transport across low-angle ISBs, with an angle of molecular orientation mismatch of 0 ± 20°, to that across high-angle ISBs, with an angle of molecular orientation mismatch of 90 ± 20° (refer to Figure 6.7).
7.2.1 Conductive-AFM studies on single ISBs

To probe charge transport across single ISBs as a function of the angle of molecular orientation mismatch, we employed conductive AFM. In this setup, a voltage is applied laterally across the sample while the AFM tip is scanned along the sample surface to collect two-dimensional current maps\textsuperscript{[32]}. Au electrodes were deposited via thermal evaporation on top of the TES ADT films to the left of the ISBs. A conductive AFM tip was used as the second electrode to collect current. Figure 7.8a shows optical micrographs of a sample with a low-angle ISB having an angle of molecular orientation mismatch of $0 \pm 20^\circ$ (top), and a sample with a high-angle ISB having an angle of molecular orientation mismatch of $90 \pm 20^\circ$ (bottom). Figure 7.8b shows contact-mode height images of the two films shown in Figure 7.8a near the ISBs. The dotted lines indicate the location of the ISBs. Current maps were simultaneously collected over the same regions at an applied sample bias of 2 V; these are shown in Figure 7.8c. For three low-angle ISBs tested, the average currents before and after the ISBs are $0.42 \pm 0.02$ and $0.38 \pm 0.01$ nA, respectively. Figure 7.9 contains the other current maps collected on other samples having low-angle ISBs. The current drop across low-angle ISBs is insignificant and indicates that when the angle of molecular orientation mismatch between adjacent spherulites is small, charge transport is not hampered across the ISB. On the other hand, we observe an order of magnitude drop in current levels across the high-angle ISBs in Figures 7.8 and 7.9, from $0.52 \pm 0.1$ and $0.06 \pm 0.01$ nA. These results demonstrate that the angle of molecular orientation mismatch can significantly impact the ability for charges to travel across the ISBs.
7.2.2 Four-probe measurements on single ISBs

To quantitatively measure the resistance of high-angle ISBs observed in conductive AFM experiments, we performed four-probe measurements to eliminate contact resistance. Using TEM grids as shadow masks, we evaporated an array of Au electrodes via thermal evaporation on top of TES ADT thin films with no ISBs and on those comprising single ISBs. For samples containing one ISB, the TEM grids were carefully aligned on the sample so that the ISB traversed the entire length between the two inner Au electrodes. Figure 7.10a shows optical micrographs of the four-probe geometry for films with no ISB (top), a low-angle ISB (middle), and a high-angle ISB (bottom). Four-probe measurements were then collected using the four electrodes highlighted by the colored boxes. Figure 7.10b shows the average current-voltage (I-V) characteristics for four devices of each configuration. The I-V characteristics are color coded to match the device configurations in Figure 7.10a. As can be seen from the figure, I-V characteristics of devices with no ISBs and low-angle ISBs are comparable, with resistances of 1.6 ± 0.1 MΩ and 1.8 ± 0.1 MΩ, respectively. These results suggest that low-angle ISBs do not pose a larger barrier to charge transport compared with the low-angle grain boundaries that are present within spherulites. In contrast, for devices with high-angle ISBs, the resistance of the channel is 2.7 ± 0.3 MΩ. In these samples, it thus appears that the angle of molecular orientation mismatch across the ISBs poses a more significant barrier to charge transport compared to low-angle intraspherulite grain boundaries.

From these experiments, we estimated the resistivity of a high-angle ISB to be ~22.4 MΩµm²/width of the ISB. For comparison, we also estimated the resistivity across grain
boundaries in thermally-evaporated sexithiophene thin films from experiments performed by Frisbie and coworkers using the values reported in their publication\textsuperscript{[15]}:

$$\rho = R_{GB} \frac{t(L_{GB})}{\text{width of GB}} = 25 \text{ G} \Omega \frac{(0.018 \mu\text{m})(1 \mu\text{m})}{\text{width of GB}} = 450 \text{ M} \Omega \mu\text{m}^2/\text{width of GB}$$  \hspace{1cm} (7.1)

where \( t \) is the film thickness and \( L_{GB} \) is the length of the grain boundary. Assuming that the width of the TES ADT ISB and sexithiophene grain boundary are the same, the resistivity of high-angle ISBs is an order of magnitude smaller than the resistivity of grain boundaries in thermally-evaporated sexithiophene thin films. While the different chemistries of sexithiophene and TES ADT may affect the resistivities of the boundaries, we assume these differences be a second-order effect given that the mobilities of sexithiophene\textsuperscript{[14]} and TES ADT\textsuperscript{[20, 33]} OTFTs are comparable. Having eliminated differences in chemical structures, we believe our results indicate that a fundamental differences between grain boundaries in thermally-evaporated thin films and ISBs in solution-processed thin films. In the case of grain boundaries in thermally-evaporated thin films, faceted growth of single-crystalline grains mandates that when two growing grains meet, the grain boundary exhibits a single angle of molecular orientation mismatch that is uniform along its entire length\textsuperscript{[34]}. In contrast, spherulites incorporate a large distribution of molecular orientations about the fast growth axis. As such, there can exist different gradual changes in the angle of molecular orientation mismatch along a single ISB (refer to Figure 4.7). Furthermore, the nature of how grain boundaries in thermally-evaporated thin films and ISBs in solution-processed thin films form may also affect the resistance across them. In the former case, molecules in the vapor phase nucleate on the substrate surface during deposition. Grains grow as molecules condense onto the substrate, filling in empty space on the substrate as they grow towards one another.
Figure 7.11a illustrates two grains growing towards each other during thermal evaporation. This process of deposition and grain growth leads to the formation of grain boundaries that may incorporate voids on the submicron length scale\textsuperscript{[35]}. Indeed, atomic force microscopy (AFM) images reveal that crevices exist at these grain boundaries, traversing almost the entire depth of the films\textsuperscript{[36]}. In solution-processed, organic-semiconductor thin films, on the other hand, all material comprising the final film is deposited at once as a uniform layer so there should be no microscopic voids or crevices within these films. Figure 7.11b illustrates crystallization in a solution-processed, organic-semiconductor thin film during solvent-vapor annealing. As crystallization occurs, molecules are trapped at the interface between two spherulites crystallizing towards each other. Despite not being oriented in the right direction, these molecules (colored in red in the figure) can still bridge neighboring spherulites to transport charge across boundaries. The connectivity between crystalline domains has recently been shown to be critical for charge transport through poly(3-hexyl thiophene) thin films\textsuperscript{[37]}. The presence of these connecting molecules between spherulites thus results in a smaller barrier to charge transport across ISBs compared to grain boundaries in thermally-evaporated thin films.

7.3 Device mobility dependence on the ISB density in the active layers of OTFTs\textsuperscript{2}

Having determined the individual contributions of low-angle intraspherulite grain boundaries, and low- and high-angle interspherulite boundaries on charge transport, in

this section, we combine these results to understand charge transport through polycrystalline TES ADT thin films comprising multiple spherulites and ISBs. Specifically, we fabricated a series of OTFTs with varying numbers of ISBs in the active layers. Following the procedure outlined in Section 4.3, we incorporated between 0 – 6 mol% F-TES ADT into TES ADT thin films to vary the spherulite size from 3000 µm, in the case of neat TES ADT, to 30 µm when more than 2 mol% F-TES ADT is present. Because F-TES ADT acts as nuclei for TES ADT crystallization, the average TES ADT spherulite size decreases as the concentration of F-TES ADT increases. The corresponding number of ISBs that charges must pass through to traverse the active channel of devices thus increase correspondingly with decreasing spherulite size and can be estimated by dividing the channel length of the device by the average spherulite size:

\[
\text{# of ISBs} = \frac{\text{channel length}}{\text{average spherulite size}}
\] (7.2)

By varying the average spherulite size, and thus the number of ISBs, in the active channels of TES ADT OTFTs, we can determine how the presence of multiple ISBs influences device performance.

To fabricate TES ADT OTFTs comprising active layers with varying numbers of ISBs, TES ADT solutions with increasing amounts of F-TES ADT were spun cast on top of 300 nm SiO$_2$/doped-Si substrates with pre-patterned Au electrodes. We chose the channel width and length of the OTFTs to be 600 µm and 4000 µm, respectively, to ensure that multiple spherulites were contained within the channel region for a wide range of spherulite sizes. Figure 7.12 shows optical micrographs of the channel regions of TES ADT OTFTs after solvent-vapor annealing; the active layers contain F-TES ADT with concentrations ranging from 0 – 2 mol%. As detailed in Section 4.3, the average
TES ADT spherulite size decays exponentially with increasing F-TES ADT concentration.

Interestingly, at high F-TES ADT concentrations (3 – 6 mol% relative to TES ADT), we found that TES ADT crystallizes spontaneously in the active channel region of the patterned substrates during spin coating. These films thus do not require to be exposed to post-deposition solvent-vapor annealing. This observation is in contrast to results shown in Section 4.3, where spontaneous crystallization upon spin coating was not observed in the range of F-TES ADT concentrations tested, from 0 – 7 mol% on unpatterned substrates. Figure 7.13 displays an optical micrograph of a TES ADT thin film with 4.7 mol% F-TES ADT that crystallized upon spin coating. From the image, it is clear that crystallization only occurred in the active channel of the device and not on the gold surfaces. This observation suggests that the edges of the Au electrodes induce nucleation of TES ADT spherulites during spin coating. Due to the difference in nucleation mechanism, the sizes of spherulites that crystallize upon spin coating are larger than that predicted by the spherulite size dependence on F-TES ADT concentration upon solvent-vapor annealing. At 4.7 mol% loading of F-TES ADT, for example, we would expect the average spherulite size to be approximately 30 µm based on data collected from solvent-vapor annealed films, when in fact the spherulites that form upon spin coating are approximately 90 µm. Figure 7.14 summarizes the dependence of TES ADT spherulite size, and correspondingly the number of ISBs, on F-TES ADT concentration, both for films exposed to DCE solvent vapor to induce crystallization and for films that crystallized upon spin coating.
After forming a series of TES ADT OTFTs with varying numbers of ISBs in the active layers, we proceeded to collect the output and transfer characteristics for each of the devices. Figure 7.15 shows output characteristics for four representative devices with increasing number of ISBs in the active layers. During device operation, the source-drain voltage was swept from 0 to -50 V in steps of 1 V at gate voltages increasing from +10 to -50 V in steps of 10 V. The current levels clearly decrease with increasing number of ISBs in the active layer, indicating that ISBs do in fact act as barriers for charge transport. For the OTFT with no ISBs in the active layer, the saturation current at $V_{SD} = -50$ V and $V_G = -50$ V is 31 µA. The performance of this device compares well to those of intraspherulitic devices presented earlier. For comparison, in the OTFT with 21 ISBs in the active layer, the saturation current at the same $V_{SD}$ and $V_G$ drops to 7 µA. Likewise, the transfer characteristics shown in Figure 7.16 also display a negative correlation between the source-drain current levels and the number of ISBs in the active layers. For these experiments, the source-drain voltage was maintained at -50 V, while the gate voltage was swept from +30 to -50 V in steps of 1 V.

From the transfer characteristics in the saturation regime, we calculated the device mobility for 20 OTFTs as a function of the number of ISBs in the active layers (refer to Equation 2.1). Figure 7.17 displays a graph of OTFT device mobility dependence on the number of ISBs in the active layers. The device mobility exponentially decays as the number of ISBs in the active layers increase. For OTFTs with no ISBs in the active layer, the mobility is 0.37 cm$^2$/V-s, matching the intraspherulite mobility measured in Section 7.1 for transistors fabricated within single spherulites. For OTFTs with 21 ISBs in the
active layers, the mobility decreases to 0.02 cm²/V-s. Table 7.1 lists all the mobilities, threshold voltages, and on/off ratios of the devices shown in Figure 7.17.

With the knowledge that charge transport is isotropic within spherulites (refer to Section 7.1), we can assume a single value for the spherulite mobility and fit the dependence of device mobility on the average spherulite size, L, in the active layers to a composite mobility model:\(^{38,39}\):

$$\frac{L + L_{ISB}}{\mu} = \frac{L}{\mu_S} + \frac{L_{ISB}}{\mu_{ISB}}$$  \hspace{1cm} (7.3)

where \(L_{ISB}\) is the width of the ISB, \(\mu\) is the measured mobility, \(\mu_S\) is the intraspherulite mobility and \(\mu_{ISB}\) is the mobility of an ISB. Equivalently, we can write the equation in terms of the number of ISBs in the active layer:

$$\frac{600/# \text{ of ISBs} + L_{ISB}}{\mu} = \frac{600/# \text{ of ISBs}}{\mu_S} + \frac{L_{ISB}}{\mu_{ISB}}$$  \hspace{1cm} (7.4)

where (600/# of ISBs) is equivalent to L. The model states that the observed mobility, \(\mu\), is a composite of \(\mu_S\) and \(\mu_{ISB}\), each scaled by the respective lengths of the spherulite and ISB. This model assumes a single ensemble-average value for \(\mu_{ISB}\), although we have previously demonstrated in Section 7.2 that \(\mu_{ISB}\) depends on the angle of mismatch between adjacent spherulites. Still, the composite mobility model describes the experimental data well; the fit to the data is shown in Figure 7.17. Assuming an \(L_{ISB}\) of 0.01 \(\mu\)m\(^{38}\), best fits to the model yielded \(\mu_{ISB} = 1.6 \times 10^{-5} \text{ cm}^2/\text{V-s}\), and \(\mu_S = 0.36 \text{ cm}^2/\text{V-s}\). The value of \(\mu_S\) is in close agreement with that measured for transistors fabricated on a single spherulite (refer to Section 7.1). Because we cannot directly measure the length of the ISB, we varied \(L_{ISB}\) by an order of magnitude in either direction, that is, from 0.1 \(\mu\)m to 0.001 \(\mu\)m, and refitted the model to our data in order to test the sensitivity of our fit.
Regardless of the value of $L_{\text{ISB}}$, $\mu_S$ remains constant at 0.36 cm$^2$/V-s. Instead, $\mu_{\text{ISB}}$ varies inversely with $L_{\text{ISB}}$, with values of 1.6x10$^{-4}$ and 1.6x10$^{-6}$ cm$^2$/V-s when $L_{\text{ISB}} = 0.1$ µm and 0.001 µm, respectively. Although $\mu_{\text{ISB}}$ varies widely with different values of $L_{\text{ISB}}$, in all cases, $\mu_{\text{ISB}}$ is at least three orders of magnitude smaller than $\mu_S$, supporting our results in Section 7.2 that ISBs can pose significant barriers to charge transport.

It is important to note that regardless of whether crystallization in the active layer is induced via exposure to solvent vapors or that it occurs spontaneously during spin coating, the dependence of device mobility on the number of ISBs in the active layer remains the same. That is, the device mobility is insensitive to the loading of F-TES ADT. Rather, it is the number of ISBs that dominates charge transport in these devices. This finding demonstrates that the addition of F-TES ADT does not degrade device performance. To achieve a spherulite size of 90 µm, for example, one could add 1.4 mol% (crystallized during solvent-vapor annealing) or 4.7 mol% of F-TES ADT (crystallized during spin coating). In both cases, the device mobility of OTFTs comprising these films as active layers is approximately 0.1 cm$^2$/V-s. These results are further supported by high-resolution GIXD experiments demonstrating that the presence of F-TES ADT does not disrupt the crystal structure of TES ADT (refer to Section 5.3).

Finally, we also compared I-V measurements of the OTFTs comprising varying numbers of ISBs in the active layers to the resistivity measured for high-angle ISBs in Section 7.2 in order to independently verify the consistency between the two measurements. Here, we extracted the current values from the linear regime at a source-drain voltage and gate voltage of -5 V and -10 V, respectively, from the same data set as that shown in Figure 7.17. To calculate the expected source-drain currents for TES ADT
OTFTs comprising active layers with varying numbers of ISBs based on the resistivity we measured for engineered high-angle ISBs, we assumed a simple resistors-in-series model in which the total resistance across the channel is equal to:

\[ R_{\text{total}} = R_{\text{contact}} + R_{\text{spherulite}} + (# \text{ of ISBs}) \cdot R_{\text{ISB}} \]  

(7.5)

where \( R_{\text{total}} \) is the total resistance in the active channel, \( R_{\text{contact}} \) is the contact resistance associated with injecting and extracting charges from the Au electrodes into and out of the active layer, \( R_{\text{spherulite}} \) is the resistance within a spherulite, and \( R_{\text{ISB}} \) is the resistance across a high-angle ISB. Using the device with no ISBs in the channel region, we estimated the sum of the contact resistance and spherulite resistance to be 1.5 M\( \Omega \). The source-drain current, \( I_{\text{SD}} \), was calculated using the relationship \( V = IR \):

\[ I_{\text{SD}} = \frac{V_{\text{SD}}}{R} = \frac{V_{\text{SD}}}{R_{\text{contact}} + R_{\text{spherulite}} + (# \text{ of ISBs}) \cdot \rho_{\text{ISB}} \cdot \frac{\text{width of ISB}}{(t_{\text{CTL}})(\text{channel length})}} \]  

(7.6)

where \( t_{\text{CTL}} \) is the thickness of the charge transport layer. The value of \( \rho_{\text{ISB}} \) was taken to be 22.4 M\( \Omega \text{µm}^2/\text{width of ISB} \), from our calculation across a high-angle ISB.

From Figure 4.7, we observe that the majority of the ISBs are characterized by a high angle of molecular orientation mismatch. For these calculations, we thus assumed that the ISBs are all high-angle in nature to estimate a lower bound of \( t_{\text{CTL}} \). By leaving \( t_{\text{CTL}} \) as a floating parameter during data fitting, we found that charge transport likely occurs in the first four monolayers of the film at the active layer/dielectric interface. These results are in close agreement with previous research on sexithiophene transistors\[^{40}\]. In those experiments, researchers found the field-induced conductance of transistors to be independent of film thickness beyond a thickness of 5 nm. These results indicate that charge transport occurs primarily in the first 1 – 2 monolayers of sexithiophene. Figure
7.18 shows the measured currents as a function of the number of ISBs compared to the expected currents, represented by the solid black line representing the fit when $t_{\text{CTL}}$ is set to 4 monolayers (or 6.7 nm). To assess the sensitivity of the fit to the value for $t_{\text{CTL}}$, we also plotted the dependence of the source-drain current on the number of ISBs by for $t_{\text{CTL}}$ values of 2 and 8 monolayers, or 1.7 and 13.3 nm, respectively. These results indicate that charge transport in polycrystalline TES ADT thin films is dominated by high-angle ISBs.

### 7.4 OTFT air stability dependence on ISB density in the active layer

Finally, we turn our attention to how the structure of ISBs in the active layers of TES ADT OTFTs impact the air stability of devices. In OTFTs with thermally-evaporated thin films as active layers, the presence of grain boundaries has been demonstrated to lead to a decrease in the air stability of OTFTs\(^{[22, 41-43]}\). Thermally-evaporated pentacene OTFTs, for example, degrade over a period of days and weeks when exposed to air; this degradation is manifested in a decrease in device mobility as well as a large shift in the threshold voltage\(^{[22, 41]}\). It is commonly accepted that water and oxygen can diffuse into the film at grain boundaries to react with pentacene near the pentacene/dielectric interface\(^{[42, 43]}\), where charge transport occurs during device operation\(^{[40]}\). This preferential adsorption of molecules at grain boundaries in thermally-evaporated thin films has been exploited for sensing applications\(^{[42-45]}\). Torsi and coworkers, for example, demonstrated that thermally-evaporated $\alpha,\omega$-dihexyl-$\alpha$-hexathiophene OTFTs can be used to detect the presence of alcohols, since the adsorption of alcohols through grain boundaries induces a decrease in the source-drain current\(^{[43]}\). In such a device, the
magnitude of the decrease was found to be positively correlated with the number of grain boundaries in the active layer, indicating that alcohols preferentially diffuse into the active layer via grain boundaries. These experiments demonstrate that not only do grain boundaries act as barriers to charge transport through organic-semiconductor thin films, the structural disorder that is present at grain boundaries can also affect the stability of the active layer when exposed to different environments and can act as routes for preferential diffusion of analytes into the active layer.

In this section, we examine how the presence of ISBs in the active layer of solution-processed TES ADT OTFTs affects the air stability of devices. Given the sensitivity of device performance to analyte adsorption through grain boundaries, such measurements allow us to indirectly compare differences in the nature of ISBs in solution-processed thin films to that of grain boundaries in thermally-evaporated thin films. Figure 7.19 displays an AFM micrograph of a thermally-evaporated pentacene thin film\(^{46}\). In the image, crevices between impinging pentacene grains are clearly visible. Because these crevices traverse almost the entire depth of the film\(^{36}\), they allow water and oxygen to penetrate to the film/dielectric interface where charge transport occurs during OTFT operation\(^{40}\). In solution-processed TES ADT thin films, on the other hand, crevices are not present at ISBs. As shown in AFM height images in Figure 7.8b, the surface topographies of TES ADT thin films are continuous across ISBs. By measuring device characteristics of TES ADT OTFTs over a period of 30 days as a function of the storage environment and number of ISBs in the active layers, we can examine if preferential diffusion of water and oxygen occur at ISBs in solution-processed TES ADT thin films, as in the case of grain boundaries in thermally-evaporated thin films.
For all the experiments reported up to this point in this thesis, processing and testing of TES ADT films had been carried out in air. Here, we instead deposited TES ADT films from anhydrous toluene solutions in a N$_2$ glove box (< 1 ppm H$_2$O, O$_2$). Solvent-vapor annealing in order to crystallize the films was also performed in the glove box. Two sets of bottom-contact OTFTs were fabricated, one in which there were no ISBs in the active channel and the other in which there were approximately 20 ISBs along the length of the active channel. This number of ISBs in the active channel was achieved by adding 2.5 mol% F-TES ADT to TES ADT solution prior to film deposition (refer to Section 4.3). Within each set, two devices were stored and tested in N$_2$ and two were stored and tested in air periodically over a period of 30 days. Figures 7.20a and b show the mobilities and $V_T$’s of the devices as a function of storage time in either N$_2$ or air. The average mobility of TES ADT OTFTs stored in air was measured to be 0.22 ± 0.03 for devices without ISBs in the active channel. This mobility is lower than that typically observed in TES ADT OTFTs previously presented in this chapter (refer to Figure 7.7a), and is likely due to differences in the environment during film processing. As expected, the average mobility of TES ADT OTFTs with 20 ISBS in the active channel is significantly lower, at a value of 0.05 ± 0.02 cm$^2$/V-s. These results are consistent with our finding that ISBs act as barriers to charge transport. For OTFTs stored in N$_2$, the average mobilities of TES ADT were measured to be 0.16 ± 0.01 and 0.011 ± 0.003 cm$^2$/V-s for devices without ISBs in the active channels and those with 20 ISBs in the active channels, respectively. For both sets of OTFTs with no ISBs and 20 ISBs in the active channel, the average mobilities of devices stored in N$_2$ are consistently lower than those stored in air. The lower mobilities of devices stored in N$_2$ likely stems from the fact
that these devices were not exposed to oxygen, as oxygen doping has been reported to increase the concentration of carriers in other organic semiconductor\cite{23, 47-49}. The conductivity of P3HT, for example, can increase from $10^{-8}$ S/cm to $10^{-5}$ S/cm upon exposure to air\cite{49}. That the mobilities of OTFTs stored in air, measured to be $0.22 \pm 0.03$ cm$^2$/V-s, do not recover fully to the values we typically observe in OTFTs fabricated in air may be indicative of incomplete oxygen doping. Table 7.2 lists the average mobilities and $V_T$’s for each set of conditions over a period of 30 days.

Figure 7.20b displays the dependence of $V_T$ on time for devices stored in air and $N_2$. For OTFTs stored in air, the average $V_T$ is $27 \pm 5$ V, independent of the number of ISBs in the active layer. This value is consistent with that observed in TES ADT OTFTs previously presented in this chapter and in the literature\cite{20}. In contrast, the average $V_T$ of OTFTs stored in $N_2$ is $6 \pm 2$ V, again independent of the number of ISBs in the active channel. This difference in $V_T$ likely stems from moisture adsorption at the active layer-dielectric interface. The fact that the $V_T$’s remain the same as a function of the number of ISBs in the active channel, however, is a strong indication that – unlike in the case of thermally evaporated pentacene – moisture diffusion does not occur preferentially through grain boundaries. Previous experiments reported a 10 V increase in $V_T$ of pentacene OTFTs upon exposure to moisture\cite{22}. That $V_T$ is independent of the number of ISBs in the active channel of TES ADT OTFTs is consistent with the absence of distinct topographical features, such as deep crevices that would allow for preferential diffusion of moisture into the active layer, at ISBs in TES ADT thin films. Rather, moisture diffusion must occur through TES ADT grains. This finding provides support that thermally-evaporated pentacene grain boundaries and solution-processed TES ADT ISBs
are inherently different. We speculate that preferential diffusion of oxygen and moisture does not occur at ISBs, but these molecules can diffuse directly into TES ADT spherulites. Diffusion of oxygen and moisture into pentacene single crystals has been observed to occur over a period of $1 - 2$ hours$^{[50]}$. In TES ADT OTFTs, on the other hand, the shift in $V_T$ from $6 \pm 2$ V in N$_2$ to $27 \pm 5$ V upon exposure to air is immediate. Figure 7.21 shows transfer curves of two devices, one with no ISBs and one with 21 ISBs in the active channel, tested first in N$_2$ and then tested again within minutes of exposure to air. These results suggest that water and oxygen can diffuse more readily through TES ADT crystals compared to pentacene crystals, although further experiments would be necessary to quantify the respective rates of diffusion. We also cannot exclude the possibility that oxygen and moisture preferentially diffuse to the active layer-dielectric interface at low-angle intraspherulite grain boundaries, although no distinct topographical features appear at these boundaries.

Interestingly, although we observe diffusion of both oxygen and moisture into the active layers of TES ADT OTFTs, both the device mobility and $V_T$ of TES ADT OTFTs stored in air are stable for at least a period of 30 days. Pentacene OTFTs, on the other hand, degrade over a period of days and weeks when stored in air$^{[22,41]}$. Our findings indicate that while the presence of moisture affects the absolute device characteristics of TES ADT OTFTs, it does not affect device stability over time; such air stability is critical for the commercialization of solution-processed organic electronic devices.
7.5 Conclusions

In this chapter, we have provided a comprehensive examination of charge transport through TES ADT thin films comprising spherulites. In Section 7.1, we found that within spherulites, OTFT device mobility is independent of the general molecular orientation in the active channels. This finding was initially surprising in light of studies on organic-semiconductor single crystals, in which charge transport is fastest along the direction of maximum \( \pi \)-orbital overlap\[^3, 4, 7, 8\]. Unlike organic-semiconductor single crystals, however, spherulites incorporate a large distribution of molecular orientations to accommodate their radially-symmetric, space filling growth habit. This distribution of molecular orientations in turn necessitates the formation of low-angle grain boundaries. It is the shallow traps that exist at these low-angle intraspherulite grain boundaries that dominate charge transport, effectively smearing out of any charge transport anisotropies along different crystallographic directions of TES ADT. Having established isotropic charge transport within spherulites, we next turned our attention to single ISBs formed by engineering crystallization fronts to impinge at prescribed angles of molecular orientation mismatch. Using our method of directed crystallization developed in Chapter 6 to engineer both low- and high-angle ISBs, in Section 7.2, we found that the resistances across low-angle ISBs having an angle of molecular orientation mismatch of \( 0 \pm 20^\circ \) to be comparable with that across low-angle intraspherulite boundaries. High-angle ISBs having an angle of molecular orientation mismatch of \( 90 \pm 20^\circ \), on the other hand, act as significant barriers to charge transport. Based on these findings, we examined TES ADT OTFTs whose active layers comprised multiple spherulites and ISBs in Section 7.3. By varying the number of ISBs in the active channels of devices, we found OTFT device
mobility to follow a composite mobility model, in which the observed mobility is a sum of the intraspherulite mobility and ISB mobility, each scaled by the lengths of spherulites and ISBs, respectively. The intraspherulite mobility predicted by the composite mobility model matches closely to that measured in OTFTs fabricated within single spherulites, at values of 0.36 and 0.37 cm²/V-s, respectively. To compare our results from Section 7.2 and 7.3, we used the resistance of high-angle ISBs measured in Section 7.2 to predict the source-drain current in OTFTs as a function of the number of ISBs in the active channels and compared these results to actual source-drain currents measured in OTFTs reported in Section 7.3. We found close agreement between the predicted and experimental data, indicating charge transport in polycrystalline TES ADT thin films is dominated by high-angle ISBs. Finally, in light of experiments on thermally-evaporated OTFTs indicating that moisture can diffuse to the active layer/dielectric interface at grain boundaries to degrade device performance, we studied the air stability of TES ADT OTFTs as a function of the number of ISBs in the active channels. We found V_T’s of OTFTs to be 27 ± 5 V in air, compared to 6 ± 2 V when tested in N₂. This difference is independent of the number of ISBs in the active channel, indicating that diffusion of oxygen and moisture into TES ADT active layers does not occur preferentially at ISBs. These results provide further evidence that the nature of ISBs in solution-processed thin films is different from that of grain boundaries in thermally-evaporated thin films. Furthermore, TES ADT devices are stable for a period of at least 30 days, indicating that TES ADT is less susceptible to degradation due to reactions with moisture compared to pentacene[22, 41]. Through the collective experiments presented in this chapter, we have successfully decoupled how structural heterogeneities in spherulite-forming TES ADT, and how they
affect charge transport at different length scales, contributing to our understanding of structure-function relationships in solution-processed OTFTs.
Table 7.1. OTFT device parameters as a function of the # of ISBs in the active channel.

Results are also graphically displayed in Figure 7.15.

<table>
<thead>
<tr>
<th># of ISBs</th>
<th>Mobility (cm$^2$/V-s)</th>
<th>$V_T$ (V)</th>
<th>On/off ratio</th>
<th>Crystallized upon spin coating?</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.35</td>
<td>5</td>
<td>7e3</td>
<td>No</td>
</tr>
<tr>
<td>0.4</td>
<td>0.32</td>
<td>8</td>
<td>7e3</td>
<td>No</td>
</tr>
<tr>
<td>0.5</td>
<td>0.25</td>
<td>10</td>
<td>5e3</td>
<td>No</td>
</tr>
<tr>
<td>0.9</td>
<td>0.17</td>
<td>10</td>
<td>3e3</td>
<td>No</td>
</tr>
<tr>
<td>1.0</td>
<td>0.19</td>
<td>7</td>
<td>4e3</td>
<td>No</td>
</tr>
<tr>
<td>1.2</td>
<td>0.15</td>
<td>17</td>
<td>3e3</td>
<td>No</td>
</tr>
<tr>
<td>1.2</td>
<td>0.18</td>
<td>14</td>
<td>6e3</td>
<td>No</td>
</tr>
<tr>
<td>1.9</td>
<td>0.23</td>
<td>11</td>
<td>3e3</td>
<td>No</td>
</tr>
<tr>
<td>2.8</td>
<td>0.22</td>
<td>7</td>
<td>5e3</td>
<td>No</td>
</tr>
<tr>
<td>4.5</td>
<td>0.13</td>
<td>15</td>
<td>2e3</td>
<td>Yes</td>
</tr>
<tr>
<td>4.6</td>
<td>0.10</td>
<td>8</td>
<td>3e3</td>
<td>No</td>
</tr>
<tr>
<td>6.7</td>
<td>0.09</td>
<td>11</td>
<td>2e3</td>
<td>No</td>
</tr>
<tr>
<td>7.1</td>
<td>0.13</td>
<td>10</td>
<td>5e3</td>
<td>No</td>
</tr>
<tr>
<td>8.1</td>
<td>0.11</td>
<td>10</td>
<td>4e3</td>
<td>Yes</td>
</tr>
<tr>
<td>9.4</td>
<td>0.10</td>
<td>16</td>
<td>3e3</td>
<td>Yes</td>
</tr>
<tr>
<td>11.8</td>
<td>0.04</td>
<td>7</td>
<td>2e3</td>
<td>No</td>
</tr>
<tr>
<td>20.7</td>
<td>0.07</td>
<td>14</td>
<td>8e2</td>
<td>No</td>
</tr>
<tr>
<td>24.0</td>
<td>0.02</td>
<td>17</td>
<td>9e2</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Table 7.2. Device mobilities and $V_T$’s as a function of # of ISBs in the active channel and storage environment. Results are also graphically displayed in Figure 7.18.

<table>
<thead>
<tr>
<th># of ISBs</th>
<th>Storage in N₂ Mobility (cm²/V·s)</th>
<th>Storage in air Mobility (cm²/V·s)</th>
<th>Storage in N₂ $V_T$ (V)</th>
<th>Storage in air $V_T$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.011 ± 0.003</td>
<td>0.05 ± 0.02</td>
<td>7 ± 1</td>
<td>29 ± 3</td>
</tr>
<tr>
<td>0</td>
<td>0.16 ± 0.01</td>
<td>0.22 ± 0.03</td>
<td>6 ± 2</td>
<td>26 ± 2</td>
</tr>
</tbody>
</table>
**Figure 7.1.** Polar plot of the mobilities of rubrene single-crystal field-effect transistors as a function of the rotation angle of the rubrene crystal with respect to the active channel. [Reproduced from V.C. Sundar, et al. *Science* (2004), 303,1644]

**Figure 7.2.** Molecular packing within rubrene single crystals, with the a and b axes of the crystal labeled. [Reproduced from V.C. Sundar, et al. *Science* (2004), 303,1644]
**Figure 7.3.** a) Optical micrograph of a single TES ADT spherulite, with its nucleation point highlighted with a red circle. b) The same TES ADT spherulite after evaporation of top-contact Au electrodes, using a TEM grid as a shadow mask. Numbers indicate the channel region of each transistor tested. $\theta_1$ is the angle between the radial vector from the center of the spherulite, $(x_c, y_c)$ to transistor 1 $(x_1, y_1)$, and the vector corresponding to the charge transport direction. [Adapted from S.S. Lee, et al. *J. Am. Chem. Soc.* (accepted February 2012) doi: 10.1021/ja2116316]
Figure 7.4. Diagrams of the channel regions of devices 13, 5, and 24 (refer to Figure 7.3b), showing the different molecular orientations of TES ADT with respect to the channel length, L. Dashed lines represent the π-plane of TES ADT. The different shades of green represent individual intraspherulite grains separated by low-angle grain boundaries. [Adapted from S.S. Lee, et al. J. Am. Chem. Soc. (accepted February 2012) doi: 10.1021/ja2116316]
Figure 7.5. Representative output curves for devices 13, 5, and 24, labeled in Figure 7.3b. The gate voltage was increased from +10 V to -50 V in steps of 10 V. [Adapted from S.S. Lee, et al. *J. Am. Chem. Soc.* (accepted February 2012) doi: 10.1021/ja2116316]
Figure 7.6. Representative transfer curves for devices 13, 5, and 24 labeled in Figure 7.3b. The source-drain voltage was held at -50 V during these measurements. [Adapted from S.S. Lee, et al. J. Am. Chem. Soc. (accepted February 2012) doi: 10.1021/ja2116316]
Figure 7.7. Polar plots of a) device mobility, b) threshold voltage, $V_T$, and c) on/off ratio for 46 devices tested within two individual spherulites. [Adapted from S.S. Lee, et al. J. Am. Chem. Soc. (accepted February 2012) doi: 10.1021/ja2116316]
Figure 7.8. a) Optical micrographs of TES ADT films comprising a low-angle ISB having an angle of molecular orientation mismatch of $0 \pm 20^\circ$ (top) and a high-angle ISB having an angle of molecular orientation mismatch of $90 \pm 20^\circ$ (bottom), with top-contact gold electrodes evaporated on top of these films to the left of the ISBs. b) Corresponding AFM height images collected in contact mode across the ISBs (indicated by the white dashed lines). c) Corresponding current maps collected simultaneously with height images shown in b) at an applied bias of $+2$ V. The average current levels before and after the ISBs are labeled.
Figure 7.9. Additional current maps across (a, b) low-angle ISBs having angles of molecular orientation mismatch of $0 \pm 20^\circ$ (c, d) high-angle ISBs having angles of molecular orientation mismatch of $90 \pm 20^\circ$ in a total of four different samples. ISBs are highlighted with white dashed lines. The average current levels before and after the ISBs are labeled.
Figure 7.10. a) Optical micrographs of TES ADT films with arrays of gold pads evaporated on top. The gold pads were aligned on TES ADT films such that a single low-angle ISB (middle) and a single high-angle ISB (bottom) traverse the entire channel of the four-probe geometry in which the gold pads act as electrodes. The rectangles highlight the set of electrodes used in these measurements. The dashed lines indicate the position of the ISBs. b) I-V characteristics from four-probe measurements on the TES ADT films. The curves are color-coded to match the devices highlighted in a. Four samples were tested for each of the three types of devices. Error bars represent the spread of the I-V characteristics of the four samples.
**Figure 7.11.** Illustration of how a) GBs in thermally-evaporated thin films and b) ISBs in solution-processed thin films form. Arrows indicate the direction of fast growth. Black lines represent the π-planes of the organic semiconductor. Red lines in the bottom right image indicate molecules bridging the ISB.
Figure 7.12. Optical micrographs of the channel regions of TES ADT OTFTs with the following average spherulite sizes in the active layers (clockwise from top left corner): 2700 μm, 1570 μm, 310 μm, and 30 μm. [Adapted from S.S. Lee, et al. Adv. Mater. (2009), 21, 3605]

Figure 7.13. Optical micrograph of a TES ADT thin film with 4.7 mol% FTES ADT that spontaneously crystallized in the channel region upon spin coating.
Figure 7.14. a) Dependence of the average spherulite size in the active layer on the concentration of F-TES ADT plotted on a semi-log scale. b) Dependence of the number of ISBs in the active layer on the concentration of F-TES ADT plotted on a semi-log scale. Error bars represent the standard deviation of measurement of 10 to 25 grains in each film. [Adapted from S.S. Lee, et al. Adv. Mater. (2009), 21, 3605]
Figure 7.15. Representative output characteristics of TES ADT OTFTs with varying number of ISBs in the active layer. The gate voltage was increased from +10 V to -50 V in steps of 10 V. [Adapted from S.S. Lee, et al. Adv. Mater. (2009), 21, 3605]
Figure 7.16. Representative transfer curves for the same devices shown in Figure 7.15. $V_{SD}$ was held at -50 V. [Adapted from S.S. Lee, et al. Adv. Mater. (2009), 21, 3605]
Figure 7.17. Device mobility dependence on the number of ISBs in the active layers of TES ADT OTFTs plotted on a) a linear scale and b) a semi-log scale. Solid lines represent a fit to the data based on a composite mobility model. [Adapted from S.S. Lee, et al. *Adv. Mater.* (2009), 21, 3605]
Figure 7.18. Dependence of the current measured at $V_{SD} = -10 \, \text{V}$ and $V_G = -5 \, \text{V}$ for the same transistors shown in Figure 7.17 on the average number of ISBs in the active channels. Lines represent the calculated current using an ISB resistivity $22.4 \, \text{M}\Omega\mu\text{m}^2/\text{width of ISB}$ for three different CTL thicknesses to assess the sensitivity of the fit to this parameter.
pure pentacene deposition rates in the range of 0.5–3.5 Å/s. We used 97% temperature between 285 and 325 °C. Films were prepared between room evaporation system, keeping the temperature of the source hexadecane.

the substrate into a solution of OTS diluted with toluene or oxide and PECVD silicon oxide were formed by dip coating into account. The morphology of the material is correlated with the mobility of the organic thin film transistors in Sec. III.

behavior of the TFTs are discussed in Sec. IV D. The stability and the influence of bias stress on the mobility of the TFTs is compared for different dielectrics in Sec. IV C. The stability and the influence of bias stress on the mobility of the TFTs is discussed with a comparison of TFTs on thermal silicon nitride, which is a very promising dielectric material for large area organic electronics. The temperature dependent performance of polycrystalline pentacene TFTs the dielectric with existing display technology.

The pentacene films were deposited using a thermal evaporation system, with thickness of typically 100 nm. The roughness of the films can be treated by a self-assembled monolayer (SAM) and x-ray diffraction pattern in Fig. 3 contains a series of (00l) peaks, which correspond to a triclinic single crystal structure. The lattice spacing corresponds to a tilt of the molecules of 17.1° to the surface normal. The lattice spacing is similar to that of a polycrystalline sample, which consists of small crystallites with thickness of typically 100 nm. The roughness with TFT widths of 0.1–5 mm.


Figure 7.19. AFM height image of a thermally-evaporated pentacene thin film.
Figure 7.20. a) Mobility and b) $V_T$ of TES ADT OTFTs as a function of time and having active channels comprising no ISBs and an average of 20 ISBs along their channel lengths. For each type of active channel, two OTFTs were stored and tested in $N_2$, while the other two were stored and tested in air. Error bars represent the range spanned of the two values.
Figure 7.21. Transfer curves of TES ADT OTFTs with no ISBs and 20 ISBs in the active channels tested in a) N₂ environment and b) immediately after exposure to air.
References


Chapter 8: Conclusions and Future Work

Understanding how structural development takes place and how the final morphology of active layers in solution-processed organic electronic devices influences performance is critical for the advancement of organic electronics\textsuperscript{[1, 2]}]. In this thesis, we examined structure-function relationships of solution-processable triethysilylethynyl anthradithiophene (TES ADT)\textsuperscript{[3]} in the context of organic thin-film transistors (OTFTs). In TES ADT thin films, crystallization occurs through nucleation and growth of spherulites during exposure to 1,2-dichloroethane (DCE) solvent vapor\textsuperscript{[4]}. Through careful control over the nucleation density and the crystallization rate, we have been able to tune the average spherulite size in TES ADT thin films and also guide its crystallization along arbitrary, nonlinear patterns in the plane of the films. We then proceeded to study the charge transport properties of these active layers in OTFT device platforms, finding that the presence of low-angle intraspherulite boundaries leads to isotropic intraspherulite charge transport. Charge transport across interspherulite boundaries (ISBs) depends on angle of molecular orientation mismatch between adjacent spherulites, with charge transport across low-angle ISBs behaving the same as low-angle intraspherulite grain boundaries, and high-angle ISBs presenting a significant barrier to charge transport. In this final chapter, we provide a summary of these results, as well as recommendations for future experiments based on this work.
8.1 Summary

To gain a fundamental understanding of nucleation and crystallization in TES ADT thin films, we first performed in-depth characterization of TES ADT thin films before, during, and after solvent-vapor annealing. As spun on substrates, TES ADT thin films display only limited ordering, as evidenced by weak reflections in the GIXD pattern of as-spun TES ADT thin films. The locations of the reflections indicate the existence of a previously undocumented monoclinic polymorph of TES ADT that has thus far has only been observed in as-spun TES ADT thin films. Fractional amounts of the triclinic polymorph of TES ADT are also present. After exposure to DCE solvent vapor, we only observe the triclinic polymorph of TES ADT, with lattice parameters closely matching that of TES ADT single crystals grown from solution\cite{3}. This conversion occurs through nucleation and growth of spherulites. Unlike single crystals in which molecules are uniquely oriented on a lattice, spherulites incorporate a large distribution of molecular orientations about the radial axis to maintain their space-filling growth habit\cite{5}. Because spherulites frequently appear in solution-processed, organic-semiconductor thin films\cite{6-8}, it is thus critical to be able to control the formation of these structures and understand how their presence affects charge transport.

We first sought to control the average spherulite diameter in TES ADT thin films through the incorporation of small-molecule additives that act as nuclei to seed TES ADT crystallization. These additives, including derivatives of TES ADT, pentacene and fullerene, readily co-dissolve with TES ADT in toluene prior to spin coating. We found that all the additives act as nuclei for TES ADT crystallization to varying extents, with the number density of spherulites increasing with increasing additive concentration. By
increasing the additive concentrations from 0 to 10 mol% relative to TES ADT, we can vary the average spherulite diameter over two orders of magnitude, from approximately 3000 µm down to 30 µm, with the lower limit depending on the chemical structure of the additive\textsuperscript{[9]}. By systematically studying the nucleation behaviors of additives that are chemically and structurally different from TES ADT, we have been able to identify key physical parameters of organic semiconductors that govern structural development in two-component organic-semiconductor systems in which one component (i.e., the additive) is present in fractional amounts. The effectiveness of the additives in seeding TES ADT crystallization depends strongly on their physical properties, including their tendency to crystallize in the presence of TES ADT, their solubility in toluene, and their chemical compatibility with TES ADT. In doped-OTFT systems, for example, it is important to maximize loading of the dopant while maintain low nucleation densities. High doping levels allow one to achieve high conductivities, while low nucleation densities minimize grain boundaries that can impede charge transport. Our experiments suggest that the chemical structure of the dopant should be designed to be highly soluble in the casting solvent, as it should be chemically dissimilar from the host organic semiconductor in order to minimize the effectiveness of the dopant in acting as nuclei. In light of an ever-growing library of organic semiconductors available for solution-processable organic electronic applications, the ability to predict \textit{a priori} the final crystal size in two-component thin films based on the chemical structures of the constituent organic semiconductors is of great importance to guiding the rational design and selection the appropriate novel organic semiconductors.
Through *in situ* observation of spherulitic growth during solvent-vapor annealing, we also found that TES ADT crystallization obeys the Avrami equation\[10-12\], with spherulitic growth propagating two-dimensionally at a constant rate until neighboring spherulites impinge. In the absence of additives, the nucleation of spherulites is instantaneous, occurring during the initial exposure of TES ADT films to DCE solvent vapor. As additives are incorporated into TES ADT thin films at increasing concentrations, nucleation of spherulites transitions from an instantaneous to a distributed process, in which new nuclei form continually during exposure to solvent vapor. These results indicate that, at high loadings, the additives can either aggregate during solvent-vapor annealing to form nuclei, or that pre-formed aggregates exist and are activated at different times during exposure to DCE solvent vapor. Because the kinetics of structural rearrangement in solution-processed thin films can significantly impact the final film structure, establishing a fundamental understanding of nucleation and growth in these films is critical.

In addition to demonstrating control over the average spherulite diameter in TES ADT thin films, we can now also guide crystallization along non-linear patterns in the plane of films. Through the course of experimentation, we discovered that the growth rate of TES ADT spherulites depends on the surface energy of the underlying substrate. This dependence is non-monotonic, with both low-surface energy (25 ergs/cm\(^2\)) and high-surface energy (74 ergs/cm\(^2\)) substrates suppressing the growth rate of TES ADT by almost three-fold from its growth rate on pre-cleaned SiO\(_2\)/doped-Si, having an intermediate surface energy of 64 ergs/cm\(^2\). We have found strong molecule-substrate interactions to dominate crystallization on high-surface energy substrates, likely reducing
the ability of TES ADT molecules to rearrange and crystallize during solvent-vapor annealing. Low-surface energy substrates, on the other hand, promote the formation of stable TES ADT nanocrystals adopting the triclinic polymorph. We hypothesize that these nanocrystals can aggregate at the spherulitic growth front, suppressing the overall crystallization rate, much like impurities in polymer films\cite{13}. It is this competition between strong molecule-substrate interactions and the formation of stable nanocrystals that results in the nonmonotonic dependence of the growth rate of TES ADT spherulites on the surface energy of the underlying substrate.

By patterning the underlying substrate to have regions of different surface energies we have shown that we can introduce different crystallization rates on a single substrate. Using this approach, we can guide TES ADT crystallization along paths of arbitrary patterns and shapes. The surface energy of the path is chosen to promote fast TES ADT crystallization, while the surface energy of the regions surrounding the paths are chosen to suppress crystallization. This method takes advantage of the nature of spherulitic growth, which samples a large distribution of molecular orientations about the fast-growth axis. As crystallization progresses preferentially along a path, propagating grains whose fast-growth axes are parallel to the path direction will continue to grow, whereas grains whose fast-growth axes are oriented away form the path direction will only propagate until they reach the path boundary. At the path boundary where the surface energy changes drastically, the growth of these grains is suppressed. In this manner, we can direct TES ADT crystallization along non-linear patterns, demonstrating precise in-plane control of the crystallization direction over macroscopic length scales.
The ability to control nucleation and guide crystallization in TES ADT thin films has enabled us to elucidate structure-function relationships in OTFTs with active layers comprising spherulites. These crystalline superstructures are structurally complex, with structural heterogeneities spanning multiple length scales. On the submicron to micron length scale, low-angle intraspherulite grain boundaries exist within single spherulites. On the tens of microns to millimeter length scale, ISBs between impinging spherulites can also affect charge transport. By engineering the structure of the active layers, we have been able to decouple the impact of these structural heterogeneities at different length scales on charge transport.

To begin, we first studied intraspherulite charge transport in the absence of ISBs. In TES ADT spherulites, the molecules are generally oriented with the \( \pi \)-stack direction parallel to the radial axis from the center of the spherulite. Unlike single crystals in which the molecules are all uniquely oriented on a lattice, however, spherulites incorporate a large distribution of molecular orientations about the radial axis, and thus many low-angle intraspherulite grain boundaries, in order to maintain a space-filling growth habit. To probe how the presence of low-angle grain boundaries in the active channel of OTFTs affects device performance, we fabricated an array of source and drain electrodes on top of a single spherulite. Surprisingly, we found OTFT device mobility to be independent of whether or not the charge transport direction of the device was aligned with the radial direction of the spherulite. These results indicate that the presence of low-angle grain boundaries averages out any charge transport anisotropies that may exist along different crystallographic directions. We further hypothesize that shallow traps due to structural disorder\[^{14}\] exist at these low-angle grain boundaries and dominate charge transport,
smearing out any charge transport anisotropies that may exist along different crystallographic directions of TES ADT. Such isotropic charge transport may be ideal for commercial applications where variations in performance among devices need to be eliminated.

We next turned our attention to charge transport across single ISBs. By directing crystallization along patterns with straight paths and ones with 90° corners, we controllably engineered low- and high-angle ISBs and tested charge transport across them. By guiding two crystallization fronts towards each other along a straight path, we formed low-angle ISBs with an angle of molecular orientation mismatch of 0 ± 20°. By guiding the growth of two crystallization fronts towards each other along a path with a 90° corner, on the other hand, we formed high-angle ISBs, with an angle of molecular orientation mismatch of 90 ± 20°. Through conductive atomic force microscopy (c-AFM) experiments and resistance measurements using a four-probe geometry to eliminate contact resistance, we found that charge transport is hindered across high-angle ISBs, while charge transport across low-angle ISBs is equivalent to that across low-angle intraspherulite grain boundaries. These results indicate that the molecular orientation mismatch between adjacent spherulites at ISBs is important in determining the size of the barrier to charge transport at these boundaries.

To examine charge transport in TES ADT OTFTs comprising polycrystalline active layers in which multiple spherulites, and thus ISBs, exist, we fabricated a series of OTFTs with varying numbers of ISBs in the active channels. The number density of spherulites, and thus the number of ISBs, was varied by incorporating fractional amounts of a small-molecule additive to act as nuclei in the TES ADT active layers. We found that
OTFT device mobility decreases as the number of ISBs increases, supporting our finding that ISBs can present barriers to charge transport. The data is well-described by a composite mobility model\(^{[15,16]}\), in which the overall device mobility is assumed to be a composite of the intraspherulite mobility and the ISB mobility, each scaled by their respective lengths. By fitting our data to the model, we found the expected intraspherulite mobility to be 0.36 cm\(^2\)/V\(-s\), in close agreement to the actual intrapshurulite mobility we previously measured, at a value of 0.37 ± 0.03 cm\(^2\)/V\(-s\). Furthermore, the dependence of the OTFT source-drain current in the linear regime on the number of ISBs in the active channel was found to match closely with that predicted by assuming the ISBs to be resistors in series and assuming the resistance to be that measured across high-angle ISBs in four-probe measurements. These findings indicate that charge transport in polycrystalline TES ADT thin films is dominated by high-angle ISBs.

Finally, we tracked the air stability of TES ADT OTFTs stored in air and N\(_2\) as a function of the number of ISBs in the active channel. OTFT mobilities and threshold voltages were stable for at least 30 days, with the absolute device characteristics depending on the storage environment. OTFTs stored in N\(_2\) exhibited lower mobilities compared to devices stored in air, indicating that oxygen doping\(^{[17-20]}\) can improve the mobility in TES ADT OTFTs. As expected, the mobilities of TES ADT OTFTs with 21 ISBs were lower than the mobilities of OTFTs with no ISBs in the active channels, regardless of the storage environment. The threshold voltages of OTFTs also depended on the storage environment, with values of 27 ± 5 V and 6 ± 2 V for OTFTs stored in air and N\(_2\), respectively. The higher threshold voltage of OTFTs stored in air indicates that moisture can diffuse to the active layer/dielectric interface\(^{[21,22]}\). The threshold voltages
of TES ADT OTFTs, however, appear to be independent of the number of ISBs in the active channels. These results are in contrast to those for OTFTs with thermally-evaporated active layers, in which preferential diffusion of oxygen and moisture at grain boundaries causes significant degradation in device performance over a period of days and weeks\cite{23, 24}. Our findings indicate that diffusion of oxygen and moisture does not preferentially occur at ISBs in solution-processed TES ADT thin films. Instead, the threshold voltage invariance with ISB density strongly suggests that diffusion of moisture and oxygen to the active layer-dielectric interface occurs through TES ADT crystals. Furthermore, the diffusion of oxygen and moisture into TES ADT thin films does not degrade OTFT performance for a period of 30 days. These experiments suggest fundamental differences in the grain boundaries of thermally-evaporated thin films and ISBs in solution-processed thin films, in which the absence of voids and crevices do not allow preferential diffusion of moisture and oxygen at the ISBs.

### 8.2 Recommendations for future work

To build on the work presented in this thesis and move solution-processed organic semiconductor active layers for organic electronic devices towards commercialization, in the following sections, we recommend further experiments based on the findings reported herein.
8.2.1 Probing the electronic properties of two-component organic semiconductor systems

In Chapter 5, we extensively explored the structure of TES ADT thin films in the presence of small-molecule additives to understand how additive affects the nucleation and subsequent growth of TES ADT spherulites. In carrying out these experiments, we chose the additives to be electrically-active so that our research would be relevant to the active layers of actual devices. Moving forward, future studies should probe the electrical properties of these films to determine how the additives affect charge transport through TES ADT thin films. While we found that fractional amounts of F-TES ADT to not affect charge transport in TES ADT thin films\(^9\), it is possible that molecules with significantly different chemical structures and energy levels compared to TES ADT may influence charge transport. For example, when an electron-rich organic semiconductor, such as a fullerene derivative, is added to TES ADT, it would be of great interest to probe whether or not the electron mobility of TES ADT thin films is enhanced. We also recommend using the guidelines we established to select additives based on their solubility in the casting solvent, driving force to crystallize, and compatibility with the host organic semiconductor, to guide the choice of other material candidates beyond TES ADT. In guest-host organic light-emitting diodes (OLEDs), for example, we expect these guidelines to aid in designing guest molecules so as to increase their loading in the host, while maintaining large crystalline domains to facilitate fast charge transport.
8.2.2 Guiding crystallization on dielectric surfaces

In Chapter 6, we demonstrated the ability to guide TES ADT crystallization along nonlinear SiO$_2$/doped-Si paths using pentafluorobenzenethiol (PFBT)-treated Au to define the regions surrounding the paths on which crystallization is suppressed. Au was chosen to define the paths because it can be easily deposited via electron-beam evaporation in arbitrary patterns using shadow masks. The entire substrate can then be immersed in a solution containing PFBT, since thiols selectively bond to Au surfaces to form self-assembled monolayers (SAMs). In this manner, we can selectively alter the surface energy of the Au regions while leaving the surface energy of the SiO$_2$/doped-Si regions unchanged. To direct crystallization in the active channels of OTFTs, it will be necessary to replace the highly conductive gold layer with a dielectric. Removing the need for Au may be possible through directly patterning molecules that bond to SiO$_2$, such as those containing trichlorosilane groups, onto SiO$_2$/doped-Si$^{[25]}$. Patterning of such molecules on SiO$_2$ surfaces has been demonstrated through the use of polydimethylsiloxane (PDMS) stamps$^{[26,27]}$. In this method, a PDMS stamp is first coated with a solution containing the molecule. The stamp is then brought in contact with the SiO$_2$ surface to transfer the molecules from PDMS to SiO$_2$. Unfortunately, preliminary efforts to stamp trichlorosilane-based molecules directly onto SiO$_2$/doped-Si substrates have resulted in the deposition of rough multilayers, which inadvertently nucleated TES ADT. Bao and coworkers, for example, found the rms roughness of SiO$_2$ stamped with octadecyltrichlorosilane to be 15 nm, compared to an rms roughness of less than 0.5 nm for untreated SiO$_2$$^{[28]}$. In their work, the rough OTS-treated SiO$_2$ surfaces were also shown to induce preferential nucleation of organic-semiconductor crystals. With further
optimization of the molecule chemistry and deposition conditions, however, it may be
possible to deposit smooth layers of SAMs as pre-specified patterns on SiO$_2$/doped-Si.
Someya and coworkers, for example, have successfully deposited phosphonic acid-based
molecules as SAMs on plasma-grown aluminum oxide surfaces\cite{29}. Such ability will
make possible the fabrication of semiconducting pathways of different patterns and
shapes in organic-semiconductor active layers deposited directly on dielectric surfaces.

Also exciting is the possibility of guiding crystallization in other materials. Our
method takes advantage of spherulitic growth, a common mode of crystallization in
polymer and organic-semiconductor small-molecule thin films\cite{5}. By identifying substrate
surface treatments that can influence the growth rate of spherulites in different materials,
it would be possible to guide crystallization in the same manner as that seen in TES ADT.
One prerequisite to guiding crystallization is the ability to deposit the organic-
semiconductor thin film as a largely amorphous film so crystallization can be
subsequently induced in a controlled fashion through post-deposition processing
methods, such as thermal or solvent-vapor annealing. In this manner, molecule-substrate
interactions become important in dictating crystallization in the organic films. Identifying
molecule-substrate interactions that can influence crystallization rates in the organic thin
film, however, is compound-specific and must be individually optimized. Such substrate-
induced effects on crystallization kinetics have been observed in other systems\cite{30}, so we
believe this technique to be generally applicable to other organic compounds. The ability
to design free-form patterns \textit{a priori}, direct crystallization and induce preferential
orientation in the plane of organic thin films accordingly, promises the realization of
novel devices in which material properties, such as conductivity and luminescence, that are spatially patterned.

8.2.3 Spatial control over nucleation of TES ADT spherulites

In this thesis, we have demonstrated control over the nucleation density in TES ADT thin films. Once nucleation occurs, we can further guide the direction of crystallization. Still, the spatial patterning of nucleation events in TES ADT thin films has not been realized. In our system, the nucleation of spherulites is stochastic, with nucleation events spatially random throughout the film. By stamping islands of SAMs onto substrates prior to organic semiconductor deposition, researchers have demonstrated preferential nucleation of organic semiconductors to occur on the SAM-covered regions\[^{[28,31]}\]. In TES ADT thin films, we have observed the nucleation density to significantly increase on regions stamped with SAMs compared to unstamped regions on SiO\textsubscript{2}/doped-Si substrates. Through optimization of the stamp geometry and spacing such that the stamped regions are sufficiently small and far apart so each region induces a single nucleation event, it should be possible to pre-specify the location of nucleation, thus significantly increasing our control over the structuring of TES ADT thin films.

Solution-processed organic semiconductors promise to enable novel technologies based on flexible, large-area electronics. In this thesis, we sought to enhance our understanding of structural development in solution-processed, organic-semiconductor thin films and apply our knowledge to develop structure-function relationship for TES ADT OTFTs. With the recommended experiments set forth in Section 8.2, we believe that the work described here will further contribute towards efforts to gain precise control
over the structure of OTFT active layers, with the ultimate goal of improving device performance.
References


Appendix A: Matlab code to analyze GIXD data from beamline G-2 at CHESS

Here we reproduce the annotated Matlab code used to plot 2-D diffraction patterns collected on beamline G-2 at Cornell High Energy Synchrotron Source (CHESS). The code can be directly reproduced in Matlab in order to analyze data from G-2.

```
% This program plots the 2-D diffraction image collected on beamline G-2 at CHESS in q_z vs q_xy, and also q vs theta. To plot q vs theta, this program calls another function (ImToPolar; code written by Prakash Manandhar) to convert from rectangular to polar coordinates

E = 10.01;  % energy of xray beam in keV

%Data is stored from G-2 as an array file called "scandata". The image is stored as madata. The following commands extract the image matrix and the incident x-ray intensities that the image file can be normalized by
imd = scandata.madata;  %2-d diffraction image
i2d = scandata.spec.data(15,:);  %incoming x-ray intensities

%normalize image by intensity
av_i2 = mean(i2d);
for k=1:size(imd, 2)
    imd(:,k) =imd(:,k)/i2d(k) * av_i2;
end

%these lines extract the in-plane and out-of-plane theta values of the image
[s1,s2]=size(scandata.depth);
nu = scandata.spec.data(1,:);  %in-plane theta values
del = scandata.energy;  %out-of-plane theta values

%calculate qxy and qz
qz = 2*pi*E/12.4*sind(del);
qp = 4*pi*E/12.4*sind(nu/2);

%plot the image
imagesc(qp, qz, log(imd)); axis xy
xlabel('q_x_y (A^-1)'); ylabel ('q_z (A^-1)')
axis equal; axis tight
caxis([2 6])
```
colorbar
set(gcf, 'color', 'white');
set(gcf, 'InvertHardCopy', 'off');

%---convert to polar coordinates---

a = max(qp);  %to define range
b = 0.005;   %step size

[x,y]=meshgrid(-a:b:a);  %create a square grid symmetric about qxy,qz=0

c=size(x,2);
z1 = interp2(qp, qz, imd, x,y);

%convert to polar coordinates
z2 = ImToPolar(z1, 0, 1, c, c);
z2(isnan(z2)) = 0;

th=linspace(0, 360,c);
q = linspace(0,a,c);

%plot figure in polar coordinates
figure;
imagesc(th,q,log(z2));axis xy
axis([20 90 min(qp), max(qp)])
caxis([2 6])
set(gcf, 'color', 'white');
set(gcf, 'InvertHardCopy', 'off');
xlabel('omega')
ylabel('q')

%-----------------------------------------------

function [imP] = ImToPolar (imR, rMin, rMax, M, N)
% IMTOPOLAR converts rectangular image to polar form. The output image is
% an MxN image with M points along the r axis and N points along the theta
% axis. The origin of the image is assumed to be at the center of the given
% image. The image is assumed to be grayscale.
% Bilinear interpolation is used to interpolate between points not exactly
% in the image.

% rMin and rMax should be between 0 and 1 and rMin < rMax. r = 0 is the
% center of the image and r = 1 is half the width or height of the image.
%
% V0.1 7 Dec 2007 (Created), Prakash Manandhar pmanandhar@umassd.edu

[Mr Nr] = size(imR); % size of rectangular image
Om = (Mr+1)/2; % co-ordinates of the center of the image
On = (Nr+1)/2;
 sx = (Mr-1)/2; % scale factors
 sy = (Nr-1)/2;

imP = zeros(M, N);

delR = (rMax - rMin)/(M-1);
delT = 2*pi/N;

% loop in radius and
for ri = 1:M
    for ti = 1:N
        r = rMin + (ri - 1)*delR;
        t = (ti - 1)*delT;
        x = r*cos(t);
        y = r*sin(t);
        xR = x*sx + Om;
        yR = y*sy + On;
        imP (ri, ti) = interpolate (imR, xR, yR);
    end
end

function v = interpolate (imR, xR, yR)
    xf = floor(xR);
    xc = ceil(xR);
    yf = floor(yR);
    yc = ceil(yR);
    if xf == xc & yc == yf
        v = imR (xc, yc);
    elseif xf == xc
        v = imR (xf, yf) + (yR - yf)*(imR (xf, yc) - imR (xf, yf));
    elseif yf == yc
        v = imR (xf, yf) + (xR - xf)*(imR (xc, yf) - imR (xf, yf));
    else
        A = [ xf yf xf*yf 1
             xf yc xf*yc 1
             xc yf xc*yf 1
             xc yc xc*yc 1 ];
        r = [ imR(xf, yf)
              imR(xf, yc)
              imR(xc, yf)
              imR(xc, yc) ];
        a = A\double(r);
        w = [xR yR xR*yR 1];
        v = w*a;
    end
Appendix B: List of publications by S.S. Lee


