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Molecular Alignment and Morphology Control Techniques for Liquid Crystal Organic Semiconductors

Eric Carlson
University of Colorado at Boulder, carlsone73@gmail.com

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MOLECULAR ALIGNMENT AND MORPHOLOGY CONTROL TECHNIQUES FOR LIQUID CRYSTAL ORGANIC SEMICONDUCTORS

By

Eric D. Carlson

B.A., St. Olaf College, 2013

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This thesis entitled:
Molecular Alignment and Morphology Control Techniques for Liquid Crystal Organic Semiconductors
written by Eric D. Carlson
has been approved for the Department of Chemistry

__________________________
(David M Walba)

__________________________
(Sean Eric Shaheen)

Date____________________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline
ABSTRACT

Since the dawn of the digital age that began with the discovery of semiconductors in 1947, digital electronics have changed the way humanity operates. As technology continues to mature, the need for new, multifunctional, and affordable electronics grows stronger. Organic semiconductors (OSCs) fill this need as low cost, highly-flexible, easily-processible, and biocompatible materials for a new wave of flexible, wearable, and biosensing electronics. One major barrier to commercialization of organic electronics, however, is the relatively poor electrical performance of current versions of these devices. Because device performance primarily depends on the electronic structure of the material it is important to develop and understand techniques to improve the molecular order and alignment, and thus, electronic structure in OSC materials. In this work we explore the use of soft lithography and solvent processing of thin films to control the molecular alignment and morphology in two liquid crystal (LC) OSC systems.

First, we use the soft lithography techniques of capillary force molding and template-assisted self-assembly with an elastomeric polydimethylsiloxane (PDMS) microchannel mold to align the exotic helical nanofilament (HNF) LC phase. We find that the use of PDMS preferentially aligns the highly crystalline HNF “nanowires”, and after removal of the mold, leaves exposed well-aligned, freestanding microchannels of HNFs. We also studied the relationship between thin film morphology and solvent composition in spin coated thin films of the monoalkyl-[1]benzothieno[3,2-b][1]benzothiophene (BTBT) LC OSC derivatives Th-BTBT-C8 and Th-
BTBT-C10. In thin films of both Th-BTBT-C8 and Th-BTBT-C10 spin coated from chlorobenzene (CB), terraced mounds are observed, to the best of our knowledge, for the first time in an OSC material. We also find that mixing CB and chloroform (CF) at a ratio of 20% to 80% produces the highest quality thin films of Th-BTBT-C10. Thin films made from the same solvent mixtures are shown to have improved charge transport over CB, CF and other solvent mixture ratios in organic field-effect transistors (OFETs). The use of solvent mixture engineering to improve electronic properties of OSC thin films extends to another monoalkyl-BTBT derivative, Ph-BTBT-C8, where the 20% CB to 80% CF solvent mixture produces films with superior charge transport over films made from either CB or CF solutions alone. This trend is not observed in two other dialkyl-BTBT derivatives. Overall, we find that the novel use of PDMS microchannels to align HNFs, and solvent engineering to improve thin film morphology and electrical properties of LC OSCs, can be used to help move the field of organic electronics towards commercialization.
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<tr>
<td>4Q</td>
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<tr>
<td>6P</td>
<td>p-Sexiphenyl</td>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<td>Helical Nanofilament Phase</td>
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<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
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| ITIC    | 2,2’-[[6,6,12,12-Tetrakis(4-hexylphenyl)-6,12-dihydrodithieno[2,3-d:2’,3’- 
|         | d’]-s-indaceno[1,2-b:5,6-b’]dithiophene-2,8-diyl]bis[methylidyne(3-oxo- 
|         | 1H-indene-2,1(3H)-diylidene)]bis[propanedinitrile] |
| LC      | Liquid Crystal |
| LCD     | Liquid Crystal Display |
| LED     | Light-emitting diode |
| LUMO    | Lowest unoccupied molecular orbital |
| ML      | Monolayer |
| MOSFET  | Metal-oxide semiconductor field-effect transistor |
| N       | Nematic Phase |
| OFET    | Organic field-effect transistor |
| OLED    | Organic light-emitting diode |
| OPV     | Organic photovoltaic |
| OSC     | Organic semiconductor |
| P3HT    | Poly(3-hexylthiophene-2,5-diyl) |
PBDTTT-C-T Poly[[4,8-bis[5-(2-ethylhexyl)-2-thienyl]benzo[1,2-b:4,5-b']
dithiophene-2,6-diyl][2-(2-ethyl-1-oxohexyl)thieno[3,4-b]thiophenediy]]
PCBM Phenyl-C61-butyric acid methyl ester
PDMS Polydimethylsiloxane
PEDOT:PSS Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PFBT Pentafluorobenzylthiol
POM Polarized Optical Microscopy
PPV Poly(p-phenylene vinylene)
PTCDA Perylene-3,4,9,10-tetracarboxylic dianhydride
PVD Physical Vapor Deposition
SAM Self-assembled Monolayer
SAXS Small Angle X-Ray Scattering
SEM Scanning Electron Microscopy
SmA Smectic A Phase
SmC Smectic C Phase
SmE Smectic E Phase
SPA Semiconductor Parameter Analyzer
TASA Template Assisted Self-Assembly
TIPS-pentacene 6,13-Bis(triisopropylsilylethynyl)pentacene
THF Tetrahydrofuran
TPD N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine
XRD X-Ray Diffraction
1 INTRODUCTION TO LIQUID CRYSTAL SEMIDOCONDUCTORS

1.1 History and Motivation

Since the digital revolution that began in 1947 with the fabrication of the first point contact germanium transistor by John Bardeen and Walter Brattain at Bell Labs, semiconductors and transistors—digital switches—have been an integral part of modern life. Transistors can be found in everything from the transistor radio and televisions to computers and cell phones. The ubiquity of semiconductors is even more expansive yet; they are used as the light absorbing materials in photovoltaics\(^1\)–\(^4\) (solar cells) and the light emitting materials in light-emitting diodes (LEDs)\(^5\)\(^,\)\(^6\).

Elemental silicon is the most commonly used semiconductor in everyday applications and can be found in many electronics and photovoltaic devices. Other semiconductors such as gallium nitride, cadmium selenide, or indium phosphide that are composed of elements from two different groups on the periodic table are commonly used in many applications such as LEDs\(^12\), photovoltaics\(^10\), and quantum dots\(^7\)\(^,\)\(^8\). Other classes of semiconductors such as metal oxides and perovskites can be used in sensors\(^9\) and photovoltaics\(^10\) respectively. More recently, though, extensive research has been done on the use of organic semiconductors (OSCs) in electronic devices\(^11\)–\(^15\).

OSCs, organic materials that exhibit semiconducting properties, have an advantage over inorganic semiconductors in flexible\(^16\)\(^,\)\(^17\), wearable\(^18\), and biosensing\(^19\) applications because they are light, relatively inexpensive, easy to process, mechanically flexible, and biologically inert. OSCs have been used in organic field-effect transistors (OFETs)\(^20\), organic photovoltaics (OPV)\(^21\)\(^,\)\(^22\), and organic light-emitting diodes (OLEDs)\(^23\). However, the performance, scalability, and reproducibility of these OSC-based electronic devices falls well short of their inorganic
counterparts, leaving many of these potential applications unrealized. One major reason for this is due to the disorder apparent in organic materials. This problem has attracted significant attention in recent years and attempts to form well-ordered or even single crystal OSCs have been numerous\textsuperscript{24–26}.

Further, efforts to better understand the molecular morphology and charge transport in these organic materials have further improved electronic device performance and reproducibility\textsuperscript{12,27–29}. Together, these studies have resulted in large advances in organic electronics and photovoltaics leading to the beginning stages of commercialization\textsuperscript{30}. Though, as the commercialization of organic electronics advances, it is ever-important to devise simple processes to control the molecular alignment and morphology of OSCs and understand the underlying physical mechanisms that govern them.

1.2 Organic Semiconductors

1.2.1 Chemical Structure of Common Organic Semiconductors

OSC\textsuperscript{s} consist \(\pi\)-conjugated hydrocarbons and are generally classified as small molecules or polymers. These conjugated regions are small, can be two-dimensional or three-dimensional, and are generally aromatic. Other atoms such as sulfur, nitrogen, oxygen, and fluorine are frequently incorporated into the molecular structure as heteroatoms or electrophilic aromatic substituents. In polymers, conjugation extends along the polymer backbone, and in small molecules, conjugation extends over most of the molecule. OSC\textsuperscript{s} are commonly synthesized with aliphatic side chains that branch off from the conjugated region of the molecule or polymer to increase solubility in organic solvent.
There are many OSC motifs, but we will highlight a few here outlined by Figure 1.1. Two-dimensional poly/oligothiophene OSCs such as P3HT (Figure 1.1a) and 4T (Figure 1.1b) and conjugated polymers, including PVV (Figure 1.1n), can have a linear structure, while other two-
dimensional OSCs such as 1,4,5,8-tetraazaphenanthrene (Figure 1.1h) and PTCDA (Figure 1.1d) are disk-like and TPD (Figure 1.1o) is more flexible. Three-dimensional OSCs can be spherical as in PCBM (Figure 1.1i) or branched as in PBDTTT-C-T (Figure 1.1e) and ITIC (Figure 1.1l). Further, heteroacenes such as tetracene (Figure 1.1c) take advantage of a linear fused ring system that increases the crystallinity and conjugation. Synthetic efforts have been pursued to produce novel thiophenes fused ring systems such as that present in BTBT (Figure 1.1j) and DNTT (Figure 1.1g)\textsuperscript{31}. Aliphatic side chains have also been added to pentacene and BTBT to produce highly soluble TIPS-pentacene (Figure 1.1f) and C8-BTBT-C8 (Figure 1.1k). Organometallic complexes such as Alq3 (Figure 1.1m) are commonly used in OLEDs.

1.2.2 Electronic Structure of Organic Semiconductors

The electronic structure of OSCs is fundamentally different from inorganic semiconductors where the crystal lattice is made up covalent bonds. In OSCs, molecular crystal lattices are held together by weakly interacting Van der Waals forces, leading to a lack of delocalization of electrons. This drastically impacts the electronic structure and thus charge transport in OSCs.

In conjugated molecules, sp\textsuperscript{2} hybridized orbitals strongly overlap to form \( \sigma \) and \( \sigma^* \) bonding and antibonding molecular orbitals. The remaining \( p_z \) orbitals weakly overlap, forming \( \pi \) and \( \pi^* \) bonding and antibonding molecular orbitals. This weak overlap results in smaller energy splitting for the latter, resulting in the formation of the molecule’s highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), also called the frontier orbitals. The band gap (\( E_g \)) of the material can be estimated as the difference in energy between the HOMO and
LUMO of the molecule. In OSCs, the band gap is very large and can be as high as 3-4 eV\textsuperscript{29,32}. The molecular orbital diagram formation of the frontier orbitals in ethene shown in Figure 1.2\textsuperscript{32}.

![Molecular orbital diagram](image)

**Fig. 1.2.** a) The molecular orbital diagram for the carbon-carbon bond in ethene and resulting frontier orbitals. b) A visualization of the sp\textsuperscript{2} and p\textsubscript{z} orbital overlap in ethene.

Because the dielectric constant in organic materials is relatively low, the binding energy of electron hole pairs is large and free carriers do not exist in high concentrations in OSCs at room temperature, making OSCs intrinsically insulating. Thus, a charge must be added to the molecular network for conduction to occur. In devices such as OLEDs and OFETs this is achieved through
the injection of a charge through a metal electrode at the molecular interface and by the absorption of electromagnetic radiation and splitting of excitonic pairs in OPVs.

Further, in molecular solids, crystal lattices are held together with weakly interacting Van der Waals bonds, and the orbital overlap in adjacent molecules is relatively low and delocalization of electrons is minimal. This results in very narrow valence and conduction bands ($<< 0.5$ eV) compared to the wide valence and conduction bands observed in inorganic semiconductors ($\sim 3$ eV)$^{29}$. In well-ordered crystals, orbital overlap is greater forming wider bands that approach 0.5 eV$^{33}$ and increase delocalization over the crystal structure. Band-like transport is possible in these systems as is observed in naphthalene, pentacene, rubrene, and C8-BTBT-C8$^{12,34}$. This has been confirmed through the observation of the effective electron mass approaching the free electron mass$^{35}$. However, in amorphous crystals and polymers, a large degree of disorder is present, which reduces delocalization, and a thermally activated hopping mechanism of charge transport dominates.

1.2.3 Charge Transport in Organic Semiconductors

The mechanism for charge transport in OSCs is highly depended on the degree of crystallinity and order within the material. Band-like transport is expected to dominate when the electronic coupling is high as is the case in well-ordered crystalline OSCs$^{36,37}$ and as described previously has be observed in single crystal OSCs$^{12}$. Band transport in low carrier density materials can be described using the Drude model$^{38}$. In the Drude model, is assumed that delocalized carriers are free to move under the influence of an electric field. When electronic coupling is weak and the localization of charges occurs, as is the case in disordered OSCs, a thermally activated hopping transport mechanism dominates.
Thermally activated hopping transport is generally described through the formation of the “small” polaron as first described by Holstein. As a charge moves from its localized position on one molecule to another, the molecule accepting the charge must change its conformation to shield the charge it is accepting, thus coupling the charge with a lattice vibration (phonon). This coupling forms a polaron. The rate of charge transfer between two sites can described using an electron transfer (ET) model. The rate, \( k_{if} \), where \( i \) and \( f \) are initial and final states can be described using the Arrhenius equation at the classical high temperature limit, and Marcus Theory can describe the rate

\[
\log_{10} k_{if} = \log_{10} \left( \frac{4\pi |V_{if}|^2}{h \sqrt{4\pi \lambda kT}} \right) - \left( \frac{(\Delta G^\circ - \lambda)^2}{4\lambda kT} \right). \tag{1.1}
\]

In Equation 1.1, \( V_{if} = \langle \psi_i | V | \psi_f \rangle \) is the overlap integral which is found from the electronic coupling matrix of two adjacent molecules, and \( \lambda \) is the reorganization energy induced by the charge transfer. Further, \( \Delta G^\circ \) is the difference in the Gibbs free energy between the two sites during the charge transfer. This equation is limited to the case where there is weak electronic coupling and electron-phonon coupling dominates. When electronic coupling dominates, the hopping mechanism can be thought of as a self-exchange and \( \Delta G^\circ = 0 \). In this case, the charge transfer rate is only dependent on the electronic coupling between adjacent sites and the reorganization energy. Thus, the charge transport rate is highly dependent on these two terms. If electronic coupling is maximized, and/or the reorganization energy is minimized, charge transport can approach band-like transport where the delocalization is across the entire system.

1.2.4 Charge Carriers in Semiconductors and Mobility

Semiconductors are considered p-type when the majority charge carrier is a hole and considered n-type when the majority charge carrier is an electron. When holes and electrons are
both charge carriers in a semiconductor, it is considered ambipolar. Inorganic semiconductors like silicon intrinsically have relatively high densities of both holes and electrons and is naturally ambipolar. In OSCs the characterization of charge transport is more complicated and depends on which frontier orbital (HOMO or LUMO) transport occurs\textsuperscript{40,41}. Doping a semiconductor with an electron donor or acceptor can increase the density of electrons or holes and increases its n-type or p-type character. It is possible to dope in both inorganic and organic semiconductors.

Macroscopically the rate of charge transport can be described by and is directly related to the charge carrier mobility $\mu$. Charge carrier mobility can be described using Equation 1.2

$$\mu = \frac{v}{E}. \quad (1.2)$$

In this equation, $v$ is the drift velocity of the charge and $E$ is the magnitude of the electric field applied to the material. In short, charge carrier mobility describes the velocity in which a charge moves through a semiconductor (or metal) given an electric field. Equation 1.2 can be used to describe the movement of both negative and positive (electron and hole) charges, and hole mobility, electron mobility, or both associated may be directly or indirectly measured in an electronic device. Mobility, however, is not truly constant and depends on many factors including temperature\textsuperscript{35}, electric field\textsuperscript{42}, and carrier concentration\textsuperscript{43}.

1.3 Liquid Crystals

1.3.1 Liquid Crystal Semiconductors

Liquid Crystals (LCs) exhibit one or multiple phases, called mesophases, that have some properties of both solids and liquids and are commonly referred to as ordered fluids. There are many different LC mesophases, and they can be thermotropic (temperature dependent) or lyotropic
(concentration dependent). Since the discovery of LC behavior in cholesteryl benzoate by Friedrich Reinzitzer in 1888\textsuperscript{44}, LCs have been widely studied for their unique electro-optic\textsuperscript{45} properties, most notably in liquid crystal displays (LCDs)\textsuperscript{46}. Further, thermochromic properties have been used in thermometers\textsuperscript{47} and photochromic properties have been exploited in photonic applications such as holography\textsuperscript{48}.

More recently, however, interest has grown in using LCs as semiconductors in OFETs\textsuperscript{49–52}. LCs are organic small molecules that are structurally made up of a rigid aromatic ‘core’ and flexible alkyl ‘tails’. These two structural components give rise to liquid crystallinity and can be utilized in solution processed thin film OSC applications. Further, LC phases can be aligned using electric\textsuperscript{53} and magnetic\textsuperscript{54} fields, alignment layers\textsuperscript{55,56}, and lithography\textsuperscript{57,58}, resulting in bulk molecular alignment. Theoretically, the order present in aligned LC phases can be retained in room temperature crystal phases obtained by cooling below the melting point\textsuperscript{59}. Initially, discotic LC materials were utilized as OSCs due to their high level of order within each column of columnar phases\textsuperscript{60}. More recently, calamitic LCs have been utilized in as OSCs in OFETs\textsuperscript{49,51}. There is also evidence that annealing LC materials at a temperature just below the crystal to LC phase transition adds enough thermal energy to improve thin film morphology and increase electronic coupling through the formation of bilayers\textsuperscript{51,52}. There is further potential yet to utilizing highly ordered BCLC phases in OSC applications\textsuperscript{61}. In this section LC phase behavior of both calamitic LCs and BCLCs will be discussed.
1.3.2 Liquid Crystal Structure

In LCs, interactions between aromatic cores promote some long-range positional order while the flexible alkyl tails promote fluidity in most LC phases. There are two major structural motifs of small molecule LC OSCs—calamitic and discotic phases. Only calamitic LCs will be discussed in this work—there are excellent reviews that cover discotic LC OSCs in depth\textsuperscript{62}. The third structural motif, bent-core LCs, has the potential to be used in OSC applications as well. Calamitic LCs (Figure 1.3a) are ‘rod-like’ molecules that have a linear aromatic core and alkyl tails that branch from one or both ends of the molecular long axes. Discotic LCs (Figure 1.3b) are

![Diagram of calamitic and discotic LC structures](image)

**Fig. 1.3.** Examples of a) calamitic (rod-like) and b) bent-core (banana) liquid crystal structures and schematics drawings.
‘disk-like’ molecules that are made up of a disk-shaped aromatic core and alkyl tails that branch off radially from the center. Further, bent-core LCs (BCLCs) are ‘banana’ or ‘chevron’ shaped molecules that have either a rigid aromatic core and tails that branch off of each bent wing (Figure 1.3a) or a flexible spacer with aromatic wings (Figure 1.3b). Long range positional order is present in each motif, but each exhibit distinct mesophases and bulk material properties.

1.3.3 Liquid Crystal Phases

In LCs, thermotropic mesophases can exist within a large temperature range, from at well below room temperature and up to temperatures greater than 200 °C. A given phase can have a broad temperature range of greater than 50 °C or a narrow range less than 1 °C and can be monotropic (only kinetically stable for some period of time but thermodynamically unstable) or enantiotropic (thermodynamically stable). On cooling from an isotropic liquid, a LC material will exhibit successively more ordered mesophases until a mesophase to crystal or glass transition occurs, demonstrating a delicate interplay between enthalpy and entropy is important in LC phase formation. At a given temperature, thermal motion must be low enough to allow for the existence of a lower entropy state, which is enabled by enhanced enthalpy of formation of a phase. A phase transition can be thought of as a change in free energy as a function of other thermodynamic variables. In a general sense, there are two types of transitions that are observed between phases—first and second order. A first order transition involves latent heat and is discontinuous between the first derivative of free energy and a thermodynamic variable. First order transitions are commonly observed in transitions between gasses, liquids, solids, and liquid crystals. A second order transition is continuous between the first derivative of free energy and a thermodynamic variable and is commonly observed in LC materials where the transition between two phases is
If we want to describe a system based on its Gibbs Free Energy, we can use the famous description using Equation 1.1

\[ \Delta G = \Delta H - T \Delta S \]  

(1.3)

where \( \Delta G \) is the change in Gibbs Free Energy, \( \Delta H \) is the change in enthalpy, \( T \) is temperature in kelvin, and \( \Delta S \) is the change in entropy. Each phase has a well-defined \( \Delta H \) and \( \Delta S \) that are both temperature dependent.

If we \( \Delta G \) with respect to temperature, \( -\Delta S \) is the slope, and we can better understand how the entropy of the system in will dictate the observed phase at a given temperature. To minimize Gibbs Free Energy, at low temperature, the phase with the lowest entropy is observed (generally a solid phase). As the temperature is increased, the entropy of the phase increases, which decreases Gibbs Free Energy. Eventually the curve will intersect with another curve that describes another phase for the particular material. A phase transition occurs at these intersection points to continue to minimize the Gibbs Free Energy. In LC systems the entropy is dictated by a careful balance between the interaction of cores and tails of the molecules in the condensed phase. The addition of alkyl tails adds degrees of freedom, and thus entropy of the system, leading to the observation of more disordered phases. The tail length relative to the core-to-core interactions then plays an integral role in LC phase formation. A brief description of phase behavior is outlined here; an excellent detailed description of LC phases can be outlined in Dierking’s monograph “Textures of Liquid Crystals”\textsuperscript{63}.

1.3.4 Calamitic Liquid Crystal Phases

In calamitic LCs, on cooling from isotropic, the nematic phase is very commonly observed. On further cooling one or more smectic phases are often observed. An illustration of this can be
The nematic phase (N) is the least ordered LC phase and is characterized by local orientational order where the average molecular long axis, also referred to as the molecular director $\mathbf{n}$ spontaneously orients in the same general direction. In smectic phases an added level of order is present as the molecules nanophase segregate into layers. In smectic layers, aromatic cores pack together within the “middle” of the layers, and aliphatic tails pack at the layer interface. Many various smectic phases have been observed in calamitic mesogens with the most common being the smectic A (SmA), Smectic C (SmC), and smectic E (SmE) phases.

The SmA phase is simplest smectic phase where each molecule has rotational freedom, out of layer fluctuations are present, and only short range orientational and positional order exists. The SmC phase introduces tilted layers where the long molecular axis is tilted at some angle with
respect to the layer planes in the phase. In the SmE phase, out of layer fluctuations and molecular rotations are suppressed, and herringbone stacking is observed within the layer. The SmE phase has also been described as a soft crystal phase due to its high level of both orientational and positional order, and high sheer modulus relative to the more fluid N and SmA/SmC phases. An example of a common phase progression in a calamitic mesogen would be isotropic to N to SmA to SmE to crystal. Such a material is considered optimal for use in OSC applications due to the fact that N phase can be relatively easily aligned macroscopically and the subsequently higher order phases can propagate this high level of long-range order in the crystal phase. Thus, LC OSC materials that contain a highly ordered smectic phase such as the SmE phase are preferred.

1.3.5 Bent-Core Liquid Crystal Phases

BCLC phase behavior is much more complex than in calamitic or discotic LCs due to the added bend to the molecular shape. In general, BCLCs have two directors that describe the molecular orientation—the polar director $\bar{p}$ and the molecular director $\bar{n}$. The polar director points in the direction of the bend in the molecule while the molecular director points along the “bow” of the molecule, normal to the “bend direction”. Eight ‘banana’ phases specific to BCLCs have been discovered to date, these being termed B1-B8. However, BCLCs have also been shown to form other phases including nematic, smectic, and polar smectic phases. For the sake of discussion, only phases relevant to this work will be discussed.

One of the most widely studied BCLC phase is the B2 phase. This phase is historically significant, exhibiting the first fluid conglomerates (spontaneous separation of macroscopic chiral domains in a fluid of achiral molecules) is characterized by the formation of tilted smectic layers similar to the SmC phase in calamitic LCs where the molecular director is tilted at some angle with
respect to the layers. However, due to the polar director present in BCLCs, polar switching behavior is observed. This polarity and bend can produce a chiral fluid phase, even though the molecules composing the phase are achiral in the isotropic phase. There are four possible polar structures formed in the B2 phase shown in Figure 1.5. These four structures are formed when the polar director either points in the same (ferroelectric) or opposite (antiferroelectric) direction in adjacent layers, and when the molecular tilt is either the same (synclinic) or alternates (anticlinic) between layers. In the cases where the polar director and tilt direction is the same—ferroelectric/synclinic and antiferroelectric/anticlinic—the phase is chiral, implying the phase is of single handedness. Further, the B3 phase is a phase is commonly seen at temperatures below the B2 phase and above the B4 phase. The B3 phase exhibits X-ray scattering indicative of a highly ordered smectic phase and is not well understood at this time. It is suggested, however, that the molecules are tilted at some angle to the layers and there is a high degree of order within each molecular layer.

![Fig. 1.5. Schematic of possible structures of the B2 phase. Each form is named for the smectic C phase. The first subscript is either ‘A’ or ‘S’ for anticlinic or synclinic. The ‘P’ indicates that the phase is polar, and the second subscripts ‘F’ or ‘A’ indicate ferroelectric or antiferroelectric.](image)

Fig. 1.5. Schematic of possible structures of the B2 phase. Each form is named for the smectic C phase. The first subscript is either ‘A’ or ‘S’ for anticlinic or synclinic. The ’P’ indicates that the phase is polar, and the second subscripts ’F’ or ’A’ indicate ferroelectric or antiferroelectric.
The B4 or dark conglomerate (DC) phases of LCs are phases that form polar smectic layers and are characterized by long range saddle-splay curvature. This curvature arises due to a torsional strain between molecular half-layers that are stretched orthogonally to one another. This strain is relieved by a twisting of the layers where one half-layer expands and the other contracts. In bulk, these structures are said to have negative Gaussian curvature. Depending on the overall structure of the phase, it can be classified as a sponge phase\textsuperscript{68} or the Helical Nanofilament (HNF) phase\textsuperscript{61}. The sponge phase is characterized by the plumber’s nightmare structure shown in Figure 1.6, right). The HNF phase (Figure 1.6, left), which presents as an organic nanocrystalline material based upon solid-state NMR data\textsuperscript{69}, is distinguished by the formation of long twisted filaments that are limited in height and width but will grow until impeded by another domain or boundary. The filaments in HNFs are homochiral, and single-handed domains of filaments grow from a single nucleation site\textsuperscript{70}. Upon cooling of the HNF phase, a glass transition is commonly seen, and a “frozen” HNF phase is observed. The HNF phase has been widely studied because of its interesting

\textbf{Fig. 1.6.} Drawings of the Helical Nanofilament (left) and Sponge (right) phases of bent-core liquid crystals. They are characterized by saddle splay deformations of polar smectic layers\textsuperscript{62}. Image was adapted with permission.
and exotic structure. From an OSC perspective, the HNFs are interesting because they contain well-ordered and periodic extended conjugation along the length of the filament that can potentially be utilized as a ‘nanowire’ to efficiently transport charge in organic electronics.

1.4 Theory of Thin Film Nucleation and Growth

Charge transport and charge carrier mobility are highly dependent on the electronic coupling between adjacent molecules. One way to control the electronic overlap is through the optimization of the OSC morphology through processing, and thus, the techniques used to fabricate thin films play a crucial role in device performance. The formation of thin films in vacuum depositions is well understood and has been studied at length. Here, we will briefly discuss thin film nucleation and growth in this section. Further, we will outline the concept of terrace formation in the presence of an edge-step barrier.

1.4.1 Thin Film Nucleation

Thin film formation has been widely studied in inorganic materials and more recently in organic materials. In both cases, it is believed that the mechanism for thin film growth is similar, and thus, much of the theoretical framework is similar\textsuperscript{71,72}. Atoms or molecules in the gas or vapor phase flow towards a surface at some flux $F$. When an isotropic atom or molecule condenses from the vapor phase or solvent onto the surface, it is adsorbed and is sometimes called an adatom or ad-molecule. After adsorption, the adatom or ad-molecule may diffuse across the surface at some rate $\nu_{D}$, sometimes called the hop rate, which is dependent on the diffusion barrier, $E_{D}$. This relationship is given by the Arrhenius Law in Equation 1.4

$$\nu_{D} = \nu_{0} e^{-E_{D}/k_{B}T}.$$  

(1.4)
Here, $\nu_0$ is the adatom vibrational frequency, $k_B$ is the Boltzmann constant and $T$ is the temperature of the substrate. The adatom, after adsorption may also desorb from the surface that is also governed by an energy barrier, $E_A$. In the case that a thin film nucleates and grows, $E_D \ll E_A$.

![Diagram](image)

**Fig. 1.7.** The various processes of adatoms or ad-molecules on surfaces during deposition. In organic thin film formation, the molecule condenses on the surface at a flux, $F$. Then once the ad-molecule is absorbed onto the surface, it diffuses across the surface with a small barrier, $E_D$ that governs the rate of hopping on the surface. When two or more ad-molecules collide and stick together, their binding energy can be described as $E_{j,i}$. An ad-molecule can desorb from the surface if it overcomes a barrier $E_A$.

Nucleation in thin films occurs when diffusing adatom or at-molecule monomers collide on the surface and stick together with binding energy $E_{j,i}$. This diffusion and nucleation process can be described by diffusion-limited aggregation and is characterized by fractal growth patterns.$^{73}$ At some point, as more adatoms or ad-molecules stick to the nucleus, a critical nucleus with a critical radius is reached, and the nucleus becomes stable. A picture of the absorption, diffusion, and nucleation process can be seen in Figure 1.7. In many cases the size of a critical nucleus is small and in organic systems has been estimated to be one molecule.$^{74}$
1.4.2 Thin Film Growth Mechanism

After the density of critical nuclei is sufficient, any further addition of adatoms to the surface will result in two-dimensional island growth because the adatom mean free path is shorter than the distance between nuclei. As deposition continues, these two-dimensional islands will eventually grow together to form a thin film. It has been determined that the surface kinetics are depended on the ratio of the deposition rate or flux and the rate of diffusion on the surface where \( R = \frac{v_D}{F} \). Nucleation density \( N \) and average island size \( A(\theta) \) can then be found from Equation 1.572

\[
N = CR^{i(i+2)} \approx \frac{\theta}{A(\theta)}
\]  

(1.5)

where \( i \) is the number of monomers in a critical nucleus and \( \theta \) is the coverage measured in molecular layers (ML). This also implies that parameters such as deposition rate, substrate temperature, surface energy of the substrate, and solvent (in solution processed films) will determine the growth kinetics.

---

**Fig. 1.8.** The three thin film growth mechanisms dependent on surface energy—
a) islands (Volts-Amperes), b) layer-by-layer (Frank-Van der Merwe), and c) layer-by-layer to island (Stranski-Krastanov).
Thin film growth will occur with different mechanisms as outlined in Figure 1.8. First, layer-by-layer growth (Frank-van der Merwe) may be observed. In this case a second ML will not form until the previous ML has completely covered the substrate. Also, island formation and growth may be observed (Volmer-Weber), and is characterized by terraces of single atom or molecule thickness is preferred and subsequent layers are formed before complete coverage of the previous layer. There is also an intermediate mechanism that occurs (Stranski-Krastanov). In this case, layer-by-layer growth is first observed followed by island formation in subsequent layers.

In organic films, the reality is somewhat different. Because the interactions between organic molecules is limited to van der Waals interactions and the molecular shape is generally anisotropic, the initial growth mode is dependent on anisotropic interactions with the surface and adjacent molecules. This ensures that the growth mode of organic thin films is significantly more complicated and harder to predict. Generally speaking, though, the growth mode of a particular film can be observed experimentally.

1.4.3 The Step-Edge Barrier

In thicker films, a distributed growth model can be applied. In this case, during deposition, an adatom or ad-molecule lands on the \( nth \) layer and can diffuse within the layer to incorporate itself into the \( n + 1 \) layer or can diffuse down to the \( n - 1 \) layer and incorporate itself into the \( nth \) layer. The frequency in which an adatom or ad-molecule diffuses from the \( nth \) layer to the \( n - 1 \) layer is determined by an energy barrier \( E_{ES} \) called the step-edge or Ehrlich Schwoebel barrier, and the rate of interlayer diffusion can be described generally by Equation 1.6

\[
\nu_{ES} = \nu_0 e^{\frac{-E_{ES}}{k_B T}}.
\]  
(1.6)
This equation is similar to that of the hopping rate in surface diffusion described by Equation 1.3 and $\nu_D$ is the frequency in which an adatom or ad-molecule diffuses to the edge of a terrace.

Another way to think of the step-edge barrier is as the difference between the energy barrier of interlayer and intralayer diffusion given by $E_{ES} = E_S - E_D$, where $E_S$ is the energy barrier at a terrace edge and is depicted in Figure 1.9. Many attempts have been made to calculate the step-edge barrier in both inorganic and organic thin films$^{74,78-81}$. The presence of a large edge-step barrier promotes terrace-like structures and the minimization of interlayer mass transport$^{82}$, where in layer-by-layer growth, molecules tend to diffuse to the $n-1$ layer before the nucleation of the $nth$ layer.

**Fig. 1.9.** A description of the step-edge barrier. a) As an adatom or ad-molecule diffuses along the nth layer of a film, it will either diffuse and join the n+1 terrace or diffuse across the step-edge barrier and join the n-1 layer. b) A representation of the barriers associated with diffusion and the step-edge.
1.5 Organic Field-Effect Transistors

OFETs are organic electronic components that have the potential to be utilized in logic circuits in flexible electronics. They are also commonly used to characterize individual semiconductor materials by measuring the field-effect mobility of both n-type and p-type semiconductors. While there are other techniques to characterize OSCs including time of flight (TOF) and carrier extraction by linearly increasing voltage (CELIV)\(^83\), OFETs commonly used to characterize OSCs because of their application in electronics. We will review basic OFET device materials, structure, operation, device engineering, and parameter extraction.

1.5.1 Device Materials and Geometry

OFETs are fabricated through a lithographic process by stacking multiple layers of components on a substrate including a gate electrode that produces an electric field, a dielectric insulating layer, a semiconductor layer, and drain and source electrodes that apply bias to the conduction channel in the device. A wide range of materials can be in the fabrication of a device and are chosen based on the desired properties of a particular device.

Traditionally, substrates are rigid materials like silicon or a glass microscope slide but can also be a flexible polymer or even human skin\(^84–86\). Gate electrodes can be any conductive material such as gold, silver, or aluminum. In many devices used to characterize semiconductor properties, a highly doped Si substrate is used. Dielectric materials must be insulating materials, and SiO\(_2\) or insulating polymers are frequently chosen. The choice of insulator can be important as its interface with the semiconducting material can have a large impact on device performance\(^87\). The semiconducting layer, called the active layer, is generally chosen as the material that is to be tested. This can be pure molecular or polymer semiconductors\(^15,21\), blends of polymers\(^88\), blends of
polymers and small molecules\textsuperscript{89}, or doped materials\textsuperscript{90–92} depending on desired morphological or electrical properties in the device. The drain and source electrodes in most OFETs are made of metals such as gold or silver, and are chosen based on the ability of the metal to inject charge into the semiconducting layer. Conductive polymer electrodes like PEDOT:PSS can be used to make flexible devices\textsuperscript{93}. The selection of appropriate drain and source electrodes will be discussed in 1.5.2.

There are four general geometries used in the fabrication of OFET devices: 1) bottom-gate, bottom-contact, 2) bottom-gate, top-contact, 3) top-gate, bottom-contact, and 4) top-gate, top-contact (Figure 1.4). These geometries describe the order in which the layers are stacked within a device. There are two necessary conditions that a device of any geometry must meet. First, the active layer cannot come into contact with the gate electrode and must be separated by the insulating dielectric layer. Second, the drain and source electrodes must not contact the gate electrode and must be separated by the dielectric layer, active layer or both. All four geometries follow these conditions.

**Fig. 1.10.** Depiction of the four basic OFET geometries: a) bottom-gate top-contact, b) bottom-gate bottom-contact, c) top-gate top-contact, and d) top-gate bottom-contact.
The bottom-gate, bottom-contact geometry is fabricated by depositing a gate electrode followed by a dielectric layer, source and drain electrodes, and the active layer. The bottom-gate top contact geometry moves the electrodes from between the dielectric and active layer to the top of the active layer. The top-gate geometries move the gate from the bottom of the device to the top. In a top-gate bottom-contact device, drain and source electrodes are deposited onto a substrate followed by the active layer, dielectric layer, and the gate electrode. In the top-contact device, the drain and source electrodes sit between the active layer and the dielectric layer. Each device is equivalent in theory and have the same operating principles. Though, there is evidence that device geometry impacts various device parameters including charge carrier mobility\textsuperscript{94}.

1.5.2 Electrode Work Function and Charge Injection

One important factor in OFET design is that of the energy level matching of the source and drain electrodes with the HOMO or LUMO of the organic semiconductor. For the purposes of this discussion, we will assume that the electrodes make ohmic contact, that is the metal-semiconductor interface is a low resistance junction. While non-ohmic contact is common in OFETs, it is beyond the scope of our discussion here.

In the case of a p-type (n-type) OSC the HOMO (LUMO) energy level must closely match the work function of the electrode ($\Phi_{el}$). If an electrode with a work function that closely matches that of the HOMO energy level of the p-type OSC being used, the tunneling distance is small, resulting in a better functioning OFET device. Likewise, in n-type semiconductors, the work function must align with the LUMO energy level for electron injection. As depicted in Figure 1.11, if the metal electrode’s work function is much greater than the molecule’s HOMO (LUMO) a barrier of distance $\Delta_h$ ($\Delta_e$) restricts hole (electron) injection. This results in the necessary choice of
an electrode that will closely match the required orbital of the OSC in the device. Gold and silver are commonly used for p-type OSCs because of their work functions sit very low compared to vacuum at about -5.1 eV and -4.7 eV respectively. Aluminum is commonly used for n-type OSCs because its work function sits relatively close to vacuum at about -4.0 eV.

In many p-type devices, $\Delta_h$ is still too large to overcome when using simple bare gold or silver electrodes. One way to reduce $\Delta_h$ beyond its intrinsic value is to modify $\Phi_{el}$ through the application of SAMs on the electrode surface and in many cases is a necessary step in device fabrication. Thiolate SAMs can be formed by placing your, the sulfur will adsorb to the gold surface. A dipole moment in the direction of the gold surface is created between the gold and the thiolate SAM. It has been shown that the dipole grows in magnitude with an increasing alkane chain length. This is due to the increasing dipole moment of the SAM and results in a raising of the effective work function ($\Phi_{eff}$) with respect to vacuum level. If the thiolate SAM contains

---

Fig. 1.11. Depiction of charge injection with a positive forward bias with a) well-aligned HOMO/LUMO and work function energies and low injection barriers ($\Delta_h$ and $\Delta_e$), and b) poorly aligned HOMO/LUMO and work function energies and large injection barriers. Image adapted from Sean Shaheen.

---

In many p-type devices, $\Delta_h$ is still too large to overcome when using simple bare gold or silver electrodes. One way to reduce $\Delta_h$ beyond its intrinsic value is to modify $\Phi_{el}$ through the application of SAMs on the electrode surface and in many cases is a necessary step in device fabrication. Thiolate SAMs can be formed by placing your, the sulfur will adsorb to the gold surface. A dipole moment in the direction of the gold surface is created between the gold and the thiolate SAM. It has been shown that the dipole grows in magnitude with an increasing alkane chain length. This is due to the increasing dipole moment of the SAM and results in a raising of the effective work function ($\Phi_{eff}$) with respect to vacuum level. If the thiolate SAM contains
electronegative functional groups such as fluorine opposite of the sulfur, the dipole moment can be reverse and point away from the gold surface, lowering $\Phi_{\text{eff}}$ with respect to vacuum level$^{98}$. In many OSCs, the HOMO level sits just below the work function of gold and SAMs with dipoles and a fluorinated thiol SAM is used to improve the charge injection into the device including pentafluorobenzyl thiol (PFBT)$^{99}$.

1.5.3 Organic Field-Effect Transistor Mobility Values for Common Organic Semiconductors

Here we present a list of field-effect mobility values for some common OSC materials that were presented in Figure 1.1.

<table>
<thead>
<tr>
<th>Organic Semiconductor</th>
<th>Type</th>
<th>Mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8-BTBT-C8</td>
<td>p</td>
<td>34</td>
</tr>
<tr>
<td>Tetracene</td>
<td>p</td>
<td>2.4</td>
</tr>
<tr>
<td>TIPS-pentacene</td>
<td>p</td>
<td>4.6</td>
</tr>
<tr>
<td>P3HT</td>
<td>p</td>
<td>0.12</td>
</tr>
<tr>
<td>DNTT</td>
<td>p</td>
<td>8.3</td>
</tr>
<tr>
<td>PCBM</td>
<td>n</td>
<td>0.2</td>
</tr>
<tr>
<td>ITIC</td>
<td>n</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Table 1.1. Summary of field-effect mobilities for some common OSCs
2 EXPERIMENTAL

2.1 Introduction

In this dissertation multiple techniques are used to fabricate and analyze OSC morphologies and OFET device characteristics. In this section we will first review the theory and practical operation of relevant analysis techniques. This will be followed by an overview of some of the experimental techniques that were used in this work. A complete version of the experimental materials and methods can be found in Appendix I.

2.2 Analysis Techniques

2.2.1 Polarized Optical Microscopy

The most common tool to study and characterize LC materials is polarized optical microscopy (POM). POM uses plane polarized light from a polarizing microscope to study molecular packing and macroscopic molecular orientation in materials. In LCs this can help determine both the phase and some optical properties of the material through the observation of the POM textures that are observed. Generally, LCs are viewed by filling cells that consist of two confining plates made of glass separated by about 4 µm thick spacers. Phases can be observed with and without uniform alignment layers. This section will briefly outline the operating principle of the POM and describe textures of relevant LC phases. A more comprehensive review of LC phases and POM textures can be found in Dierking’s book63.
The polarizing microscope is a microscope that consists of a light source that is filtered through a sheet polarizer that illuminates a sample on a hot stage that can precisely control the sample’s temperature with plane polarized light. The light interacts with the birefringent sample and then passes through a magnifying objective. The light then passes through a second sheet polarizer called the analyzer that is rotated 90° to the polarizer. The light is then collected by a either an eyepiece or a camera to observe both resulting texture and birefringence. An annotated photograph of a polarizing microscope can be seen in Figure 2.1.

**Fig. 2.1.** Photograph of a polarized light microscope used to observe and characterize liquid crystal textures in the Walba Laboratory annotated with labels.
LC phases, as is the case in crystalline but not isotropic phases, are optically anisotropic. In other words, the index of refraction is dependent on the direction of light propagation. These optically anisotropic phases are birefringent and can be uniaxial or biaxial. The N and SmA phases are uniaxial and have only two optic axes. In uniaxial phases, the measure of birefringence can be determined by the difference between the index of refraction parallel and perpendicular to the optic axis and can be described by the Equation 2.1

$$\Delta n = n_{\parallel} - n_{\perp}.$$  \hspace{1cm} (2.1)

In this equation, $\Delta n$ is the birefringence, $n_{\parallel}$ is the index of refraction parallel to the optic axis, and $n_{\perp}$ is the index of refraction perpendicular to the optic axis. In biaxial phases, a third index of refraction is added due to the loss of the symmetry in the phase and can be seen in tilted smectic phases. In both uniaxial and biaxial phases, birefringence can be thought of as the projection of the optic axis onto the plane of the sample.

As the light passes through the polarizer, it is split into two components, the ordinary and extraordinary rays, $n_o$ and $n_e$ respectively. They are perpendicular to one another and propagate through the sample at different velocities, leading to a phase difference. Both the indices of refraction $n_o$ and $n_e$ are related to $n_{\parallel}$ and $n_{\perp}$, and thus, the ordinary and extraordinary light interacts with the molecular long and short axes respectively and is rotated. The observed light can be described by the Equation 2.2

$$I = I_o \sin^2 2\varphi \sin^2 \frac{\pi}{\lambda} (n_e - n_o) d.$$  \hspace{1cm} (2.2)

In this equation, the first term describes the light after passing through the sample where $I_o$ is the light intensity after it crosses through the polarizer and $\varphi$ is the azimuthal angle that describes the angle between the analyzer and the projection of the optic axis in the sample. The second term in Equation 2.2 describes the color observed in the POM where $\lambda$ is the vacuum wavelength and $d$ is
the sample thickness. The first term of Equation 2.2 implies that the intensity of light is directly related to the orientation of the molecule where the light intensity is at a maximum when the projection of the optic axis is 45° to the polarizer or analyzer. Further, if the optic axis is perpendicular to the direction of light propagation, the intensity is zero, and the sample will appear dark.

Some examples of POM textures can be seen in Figure 2.2 and are from a comprehensive overview of LC textures by Dierking. A schlierin texture (Figure 2.2a) can be seen in the nematic phase where the orientation of the local molecular director can be seen through light intensity. In the smectic phases such as SmA (Figure 2.2b), SmC (Figure 2.2c), and SmE (Figure 2.2d), fan textures are observed. The SmC phase, if grown in below the SmA phase, a broken texture can be

![Fig. 2.2](image-url)

**Fig. 2.2.** Polarized optical microscopy textures of some common liquid crystal phases in planar aligned liquid crystal cells. A schlierin texture is a characteristic of the a) nematic phase. The characteristic fan texture of smectic phases is observed in the b) SmA, c) SmC, and d) SmE phases. A broken fan texture can be seen in the SmC phase after cooling from the SmA phase, while striations perpendicular to the fan direction are a characteristic of the SmE texture. A focal conic texture is observed in the e) B2 phase, and a blue focal conic texture with very low birefringence is characteristic of the f) B4 phase. Images reproduced with permission.
observed. The texture is not significantly different between the two phases, but due to the tilt of the SmC phase relative to the SmA phase, on cooling into the SmC phase, the layers contract forming this broken texture. In the SmE phase, striations can be seen perpendicular to the fan direction that arise from the orthogonal directions within the interlayer herringbone packing of the phase. The B2 phase (Figure 2.2e) has a characteristic focal conic texture where the layers arrange themselves perpendicular to the cell around a Dupin cycle. The B4 phase (Figure 2.2f) is characterized by a blue focal conic texture with very low birefringence.

2.2.2 X-Ray Diffraction

X-ray diffraction (XRD) is a tool that utilizes X-ray electromagnetic radiation to elucidate information about the atomic or molecular structure of materials. It is a crucial tool in the characterization of LC phases but is also used in the characterization of molecular alignment and molecular morphology in OSC thin films. In XRD, X-rays are bombarded at a sample where they are diffracted at areas of high electron density scattering the light. The light is collected with a detector and information about the material’s structure can be determined.

XRD follows Bragg’s Law where the photons with a similar wavelength to the atomic spacings, interact with the electron density in the material. Bragg’s Law is described by Equation 2.3

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

In Equation 2.3, \( d \) is the interlayer distance, \( \theta \) is the angle between the incoming or outgoing beam and the sample plane, \( n \) is a positive integer, and \( \lambda \) is the wavelength of the incident X-ray beam. Figure 2.3 depicts a schematic of Bragg’s Law where is satisfied. In this case, if atomic or molecular planes are spaced at some uniform distance \( d \) from one another, the path length is an
integer multiple of the wavelength and constructive interference is observed where the strength of a diffraction peak is directly correlated to the long range correlation in the material. The scattered X-rays can be collected with a detector and information about various crystallographic planes in the material can be determined.

In XRD, the angle of diffraction is inversely proportional to the crystallographic feature. Thus, by plotting the diffraction spatially in a Å⁻¹ by Å⁻¹ plot the molecular correlation length or layer spacing can be determined in unaligned LC samples at small angles. In highly ordered LC phases where interlayer ordering is present, this same two-dimensional plot gives information about the interlayer correlation lengths at wide angles. The Bragg diffraction can be either sharp or diffuse depending on the long range positional order of a LC phase. For example, because of the lack of long range positional order in the nematic phase, diffuse scattering is expected, but in a highly ordered smectic phase like the SmE, diffraction peaks are sharp. Because diffraction is

![Diagram of Bragg Diffraction](image)

**Fig. 2.3.** A schematic of Bragg Diffraction when the Bragg’s Law is satisfied. The distance the incident beam travels is proportional to the distance between crystallographic planes in the material through the relationship of \( d \sin \theta \), where the sum of incident beam and diffracted beam is \( 2d \sin \theta \). Constructive interference is observed when this relationship is equal to an integer multiple of the incident beam wavelength.

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orthogonal to the molecular plane, XRD can also give information about the molecular orientation. In unaligned samples, diffraction is expected at all angles. Diffraction at one angle or a small range of angles indicates that the molecules are uniformly aligned perpendicular to that angle.

2.2.3 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a scanning probe microscope used to characterize the surface of a material and is commonly used in the characterization of thin films. An AFM measures the force between a probe tip and the surface as it scans a small area of the sample, gathering information about the surface including mechanical, electrical, magnetic, and optical properties. However, in the analysis of thin films, AFM is most commonly used to gather information about the height and morphology of a sample’s surface.

An AFM setup generally consists of a probe, probe holder, and laser. The probe is the piece that interacts with the sample and has a nanometer sharp tip that extends off of the end of a long cantilever, which is then attached to a larger chip. The probe, which is generally made of silicon (Si) or silicon nitride (Si₃N₄) for most applications, is generally inserted into a probe holder that is inserted into the larger microscope housing. As the probe scans across the sample, its motion is monitored by a laser that is reflected off of the end of the cantilever. As the probe moves side to side and up and down, the laser’s motion is detected and recorded by a position sensitive photodetector. This signal is then converted into an image using software. There are two main scanning modes that AFMs will use to collect images—constant force contact mode and tapping mode.

Constant force mode is generally used to image hard surfaces, and the probe is in contact with the sample surface and moves along the surface as it scans. The amount of force that the
cantilever is pushing the surface with is measured. Tapping mode is useful in the imaging of soft materials such as organic molecules and polymers because it does not damage the surface due the lower torsional forces present compared to contact mode. In tapping mode, a shaker piezo is used to control the frequency at which the probe oscillates at the surface, normally set near the resonant frequency of the probe and is determined by the stiffness of the probe itself. As the shaker piezo oscillates the probe near the surface, it can be modeled as a harmonic oscillator which can be described with Hooke’s Law in Equation 2.4

\[ F = -k x. \]  
(2.4)

In this equation, \( F \) is the force exerted on the probe tip by the surface, \( k \) is the spring constant measured in N m\(^{-1}\), and \( x \) is the displacement of the probe tip called the tip deflection in AFM. As the probe tip is brought closer to the sample, the amplitude of the oscillation is damped by the interaction with the surface of a sample A schematic of an AFM setup can be seen in Figure 2.4a, and an image of the Asylum Research MFP-3D AFM setup used in this work can be seen in Figure 2.4b.

In practice, a setpoint for the oscillation amplitude of the probe tip on the surface is chosen by the user, and the tip is brought close to the surface such that the oscillations are dampened to match the setpoint. As the tip scans across the surface, further change in the amplitude of the oscillation is affected by the profile of the surface. Changes in oscillation amplitude and probe tip height measured by the photodetector is controlled through a feedback loop such that the instrument keeps height of the probe tip and amplitude of the oscillations remain constant. This
process gives both height and amplitude data describing the sample’s surface. Examples of the resulting colorized AFM images can be seen in Figure 2.4c.

2.2.4 Organic Field-Effect Transistor Mobility Measurements

OFETs are characterized on a probe station under nitrogen or vacuum using a semiconductor parameter analyzer (SPA) consisting of multiple source meter units to measure
device characteristics. The measurement requires three points—one for each of the source and drain electrodes and one to gate the device via the gate electrode. This section will describe the general operating principles of OFETs. The characterization of important device parameters will be discussed in 2.2.6.

OFETs, as in other field-effect transistors, function as an electrical switch that is modulated by an electric field. Thus, without the application of an electric field to the gate electrode, current through the device is effectively zero, and the device is switched off. When a bias is applied to the gate electrode (\(V_G\)) above a threshold voltage (\(V_{th}\)) an electric field is formed and charge will build up on opposite sides of the dielectric layer similar to that of a parallel plate capacitor with the two acting terminals being the gate electrode and the semiconductor layer. This charge migration creates a conductive channel between the source and drain electrodes in the semiconducting layer. As the gate bias increases in magnitude, the charge carrier density increases in the conduction channel, allowing more charge carriers to move between the source and drain electrodes (Figure 2.5).

![Schematic of the electrical function of p-type OFET device. As the gate electrode (gray) is negatively biased, holes build up at the OSC (red) and dielectric (green) interface creating a conduction layer. A bias applied between the source and drain electrodes (gold) holes move through the conduction layer from the source to the drain where current can be measured.](image)

**Fig. 2.5.** Schematic of the electrical function of \(p\)-type OFET device. As the gate electrode (gray) is negatively biased, holes build up at the OSC (red) and dielectric (green) interface creating a conduction layer. A bias applied between the source and drain electrodes (gold) holes move through the conduction layer from the source to the drain where current can be measured.
The selection of the sign of the bias on the gate electrode is important depending on the type of charge carriers intrinsic in a material. In the case of a p-type (n-type) semiconductor, a negative (positive) bias must be applied to the gate electrode in order to place holes (electrons) along the interface between the dielectric and semiconducting layers, leaving a positive (negative) conduction channel between the source and drain electrodes for hole (electron) conduction. Conduction in the semiconducting layer is observed when the application of a bias across the conducting channel from source to drain electrodes occurs. This is achieved by applying a bias to one of the electrodes and grounding the other. Out of convention, for organic semiconductors the source electrode is grounded and a bias is applied to the drain electrode. If the semiconductor is p-

![Fig. 2.6. A typical output characteristic for a p-type OFET. Drain current is plotted as a function of drain voltage at discrete gate voltages. At low drain voltages, the drain current increases linearly the pinch-off point is reached and the device becomes saturated with charge and the drain current is independent of drain voltage. The black arrows indicate the scan direction.](image-url)
type a negative bias is applied to the drain electrode. Holes from the source electrode are then injected into the HOMO of the organic semiconductor. If the bias is small, conduction will be insignificant, but as the bias increases, the HOMO and LUMO bands bend toward and away from the negatively biased electrode respectively. This band bending creates a pathway for the holes to travel from the source electrode towards the negatively biased drain electrode, moving ‘uphill’ in potential resulting in a lower energy state.

At low source-drain voltages, the OFET behaves as a resistor, and thus at a given $V_G$ as the drain-source voltage ($V_D$) is increased, the drain current ($I_D$) increases linearly, and the device is said to be in the linear regime. As the drain-source bias is increased further, the field that has been created by the applied bias at the gate electrode will begin to cancel near the drain electrode. This reduces the charge density near the drain electrode, leading to a slower increase of current with increased drain-source bias. When $V_{SD}=V_G-V_{th}$, the effective electric field will be reduced to zero in the region near the drain electrode. This is called the ‘pinch off’ point. Past this point, the current is independent of the source-drain voltage, and the device is said to be in the saturated regime\textsuperscript{12,20}. This behavior can be illustrated as in Figure 2.6 with an IV curve called an output characteristic where the $V_{SD}$ applied to the source electrode is plotted on the x-axis and the drain current measured at the drain electrode is plotted on the y-axis at various gate biases. An output curve is characterized first by a linearly increasing drain current as the source-drain bias increases. Once the ‘pinch off’ point is reached and the device enters the saturation regime, the curve flattens, and as the drain-source bias increases, the drain current remains constant.

The transfer characteristic (Figure 2.7) is observed when the bias applied to $V_G$ is plotted on the x-axis and $I_D$ measured is plotted on the y-axis at a particular source-drain voltage. This demonstrates the switch-like behavior of OFETs. Below the threshold voltage, the current between
the drain and source electrodes will be zero. Above the threshold voltage, \( I_D \) increases linearly when in the linear regime and quadratically when in the saturation regime.

![Graph](image)

**Fig. 2.7.** A typical transfer characteristic for a p-type OFET in the saturated regime. Drain current is plotted as a function of gate voltage at discrete drain-source voltages. The red curve is the log plot of drain-source current and the blue curve is the square root of the drain current. The black arrows indicate the scan direction.

2.2.5 Semiconductor Parameter Extraction

Practical function of an OFET for parameter extraction will follow a model similar to that of a metal-oxide semiconductor field-effect transistor (MOSFET). While, the mechanism is fundamentally different in OSCs, the macroscopic model for MOSFETs serves as a useful tool to describe OFET function. As mentioned in 2.2.5, when the gate bias is less than the threshold voltage of a device \( (V_G < V_{th}) \) the device will be turned off and no current is measured between the drain and source electrodes. When the gate voltage is increased above \( V_{th} \), the device is turned on.
With the application of a small bias \((V_D < V_G-V_{th})\) at the drain electrode, the current increases linearly, and thus a linear model is used to extract the mobility parameter as in Equation 2.5

\[
I_D = \mu C \frac{W}{L} (V_G - V_{th}) V_D. \tag{2.5}
\]

In this equation, \(\mu\) is the mobility, \(C\) is the capacitance per unit area of the dielectric layer, \(W\) is the width of the channel, and \(L\) is the length of the channel. Using the same assumptions as the linear model, the quadratic model can also be used. The quadratic model takes the variation of charge density in the conduction layer of the OSC into account. This model is rarely used in parameter extraction and is described by Equation 2.6

\[
I_D = \mu C \frac{W}{L} [(V_G - V_{th}) V_D - \frac{V_D^2}{2}]. \tag{2.6}
\]

As the drain bias is increased and after the ‘pinch off’ point is reached \((V_{SD} < V_G - V_T)\), the device can be modeled using the saturation model described by Equation 2.7

\[
I_D = \mu C \frac{W}{L} \frac{(V_G - V_{th})^2}{2}. \tag{2.7}
\]

The complete derivation of these equations can be found using various treatments in multiple books and reviews\(^{1,4,11}\).

The principle parameter that determines device performance is its charge carrier mobility \((\mu)\). To extract the mobility value, the most common approach is to extract charge carrier mobility from the transfer curves of a device while in both the linear and saturation regime. In practice, one can plot gate voltage minus the threshold voltage versus the drain current \((V_G \text{ vs. } I_D)\) in the linear regime or the square root of the drain current \((V_G \text{ vs. } \sqrt{I_D})\) in the saturated regime. Both plots should theoretically be linear giving a slope of \(\mu C \frac{W}{L} V_D\) and \(\sqrt{\mu C \frac{W}{2L}}\) respectively. The slope of these lines as taken from a linear regression are used to calculate the charge carrier mobility. An example of this plot for the saturated regime can be seen on the left side of Figure 2.8.
The charge density varies considerably between the source and drain electrode. With this, the mobility in the channel is highly variable since it is dependent on the number of charge carriers available. Thus, the value extracted for mobility is a mean value. Together, the extraction of mobility in both the linear and saturated regions using their respective models can help determine whether a material may be an effective semiconductor. It is important to understand that the charge carrier mobility parameter may be a characteristic of the OFET device and may not be a property of the material. That is to say that semiconductor performance in OFETs is device specific.

There are two other device parameters that are used to characterize the performance of a device, threshold voltage and on-off ratio. The threshold voltage is integral in the performance of a device in that it describes the voltage that must be applied to the gate electrode to turn the device on. A low threshold voltage is desired and required for commercial devices. Threshold voltage is commonly determined by extrapolating to $I_D=0$V from the linear slope of the square root of the

**Fig. 2.8.** The charge carrier mobility can be extracted from a saturated regime transfer curve (left). The gate voltage is plotted versus the square root of the drain current and a linear regression is performed. The slope of the regression is then used to find the charge carrier mobility. The threshold voltage can be extrapolated from the x-intercept of the linear regression (right).
The on-off ratio can be described as the ratio of the drain current when the device is in the on state to the drain current when the device is in the off state. More specifically, it can be described by Equation 2.8 as

\[
\frac{I_{\text{on}}}{I_{\text{off}}} = \frac{\mu C^2 \nu_D^2}{\sigma q N_a d^2},
\]

where \( \sigma \) is the conductivity, \( C \) is the capacitance per unit area of the dielectric, \( q \) is the charge of the hole or electron, \( N_a \) is the doping density, and \( d \) is the thickness of the semiconductor layer. In practice the on-off ratio can be estimated by taking the saturated drain current and dividing by the drain current when \( V_G < V_{\text{th}} \).

A recent commentary in Nature Materials describes a method to determine the reliability of the model used to calculate charge carrier mobility both the linear and saturated regimes using the reliability factors, \( r_{\text{lin}} \) and \( r_{\text{sat}} \). The calculation of both \( r_{\text{lin}} \) and \( r_{\text{sat}} \) can be described by Equations 2.9 and 2.10 respectively.

\[
\begin{align*}
    r_{\text{lin}} &= \left( \frac{|I_D|_{\text{max}} - |I_D^0|}{|V_G|_{\text{max}}} \right) / \left( \frac{\partial |I_D|}{\partial V_G} \right)_{\text{claimed}} \quad (2.9) \\
    r_{\text{sat}} &= \left( \frac{|I_D|_{\text{max}} - |I_D^0|}{|V_G|_{\text{max}}} \right) / \left( \frac{\partial |I_D|}{\partial V_G} \right)_{\text{claimed}} \quad (2.10)
\end{align*}
\]

Where \( |I_D|_{\text{max}} \) is the maximum drain current measured in either the linear or saturated regime, \( |I_D^0| \) is the drain current measured when \( V_G = 0 \) V, \( |V_G|_{\text{max}} \) is the maximum gate voltage, and the derivative terms are the slope of the line used to calculate the charge carrier mobility in experimental data. These equations indicate that in a perfect OFET, with a \( V_{\text{th}} = 0 \) V and a perfectly linear \( I-V \) curve, \( r = 1 \). An \( r \) value not equal to 1 indicates that there is a nonideality in the model used to calculate the charge carrier mobility. While the reliability factor is important in understanding how well data fits the MOSFET equations, it also has its drawbacks. Specifically,
the reliability factor will not equal 1 for any device that does not have a $V_{th} = 0$ V. This is ideal in device engineering but is not always possible to achieve this in reality, especially in devices using novel materials. This value will be calculated and discussed for the devices tested in this work.

2.3 Experimental Techniques

2.3.1 Soft Lithography

Soft lithography is a lithography technique that uses elastomer molds, masks, and stamps rather than light or electron-beams as in traditional lithography to form microstructures on surfaces\textsuperscript{101,102}. Generally, a pattern for printing is created and built up on silicon substrates using traditional lithography techniques. This is called the master copy or master. Then an elastomer monomer and curing agent are poured over the mold, degassed, and cured to form a negative of the master. This process is referred to as replica molding. The most commonly used elastomer is polydimethylsiloxane (PDMS) because it is easy to work with and is inexpensive. The PDMS mold can then be used to form or house micropatterns and is commonly used in microelectronic and microfluidic devices. One of the advantages of soft lithography is that the mold can be reused multiple times to print many devices. Most commonly in microelectronics and organic electronics, PDMS molds are used to print patterned OSCs to form arrays of electronic devices\textsuperscript{103}, to aid in engineering of nanoscale devices\textsuperscript{104}, or to increase the order of OSC crystalline structures\textsuperscript{105}. To do this, multiple techniques can be implemented including microcontact printing, microtransfer molding, and capillary micromolding.

In microcontact printing, a PDMS stamp formed by replica molding is soaked in a liquid prepolymer or isotropic liquid as a type of ‘ink’. The coated mold is then stamped onto a substrate.
In this method, only the raised surfaces come into contact with the substrate surface, printing ‘ink’ in specifically patterned areas. In microtransfer printing, a PDMS mold is inverted and filled with either liquid prepolymer. Excess material is removed and the stamp is then placed polymer side down on a substrate and cured. The mold is then removed to expose the micropatterned structures. In capillary molding, a micropatterned PDMS mold with openings on at least two ends is placed on a substrate to form a seal. Then the mold is filled with a liquid polymer or isotropic liquid using capillary force and cured or cooled to room temperature. The mold is then removed exposing the micropatterned structures. The most common micropattern used in capillary molding is a network of microchannels and is the general technique used in this dissertation.

2.3.2 Solution Processing in Organic Thin Films

Charge transport and charge carrier mobility are highly dependent on the electronic coupling between adjacent molecules. One way to control the electronic overlap is through the optimization of OSC morphology through processing, and thus, the techniques used to fabricate OFETs play a crucial role in device performance. Another advantage of OSCs is the ability to use solution processing to form thin film active layers in devices. Polymer dielectric materials can be solution processed as well. There are many solution processing techniques that have been implemented to grow uniform thin films of organic molecules and polymers and each have their advantages and disadvantages.

Meniscus guided coating is the term used for a group of coating processes including dip coating, zone casting, blade coating, and solution shearing. In these processes, an OSC containing solution is mechanically pulled across a substrate to induce ordered crystalline growth in thin films as the solution dries. Molecular or polymer alignment in the film is achieved through physical
pulling of the solution across the substrate. The most commonly used meniscus guided coating method is blade coating (Figure 2.9, left) and has been used to form highly ordered films of small molecule films\(^{25,26}\). In blade coating, both the temperature of the substrate and the blade speed can be controlled, and it has been shown that the blade speed can influence the orientation of polymer semiconductors\(^{107}\).

![Blade Coating](image1) ![Inkjet Printing](image2) ![Spin Coating](image3)

**Fig. 2.9.** Schematic describing common thin film processing techniques of organic semiconductors.

Printing techniques such as inkjet printing (Figure 2.9, center) or spray coating are the most technologically advanced coating techniques and require precise equipment. Film printing uses various mechanisms to “print” precise patterns of OSCs. Generally, a solvent is loaded into a printing head via injection or capillary force and ejected using a piezoelectric or aerosolization. These techniques can be used to pattern more complex arrays of devices and can produce highly crystalline films with greater performance, but the instruments used in printing can be costly.

Spin coating is one of the most common forms of solution processing and is the primary thin film processing technique used in this work. In this process, a solution consisting of an organic material is deposited onto a substrate, and the substrate is accelerated radially to a constant speed to dry the solvent, leaving a thin film of organic material behind (Figure 2.9, right). This process
is fast and easy resulting in fast film formation. This fast film formation leads to small grain sizes, high density of defects in the film, and a high variability of film quality between batches. Controlling parameters such as spin speed, ramp rate, and spin time all can be controlled to improves and perfect thin film morphology. Off-center spin coating has been implemented to further control the direction of film nucleation, and has been utilized to fabricate high performing OFETs\textsuperscript{108}. 
3 THE ALIGNMENT OF HELICAL NANOFILAMENTS IN FREESTANDING MICROCHANNELS

3.1 Introduction to NOBOW and the Helical Nanofilament Phase

The HNF phase is comprised of self-assembled, nanophase-segregated, and highly ordered chiral helical filaments from achiral molecules\textsuperscript{61}. Due to the high degree of crystallinity observed in the aromatic layers in HNFs, they can be described as supramolecular “nanowires” and are of great interest in this work because of their potential use as extremely well-ordered OSCs. To this point, several mesogens have been shown to form HNFs including the benzylideneaniline\textsuperscript{109} and flexible spacer\textsuperscript{110} moieties. Other HNF moieties have not been completely explored, and it may be possible to synthesize bent-core materials that have favorable semiconducting properties.

The HNF phase is described by well-defined and tilted polar smectic layers with hexagonal interlayer order. This combination of molecular tilt and polar order introduces chirality. The phase is further defined by aromatic and aliphatic sublayers. The aromatic sublayer has been observed to be highly crystalline and can be further divided into two orthogonal half-layers, which induce torsional strain (Figure 3.1, center). This strain is expressed through local saddle-splay deformations by an expansion and contraction of the top and bottom halves of each layer respectively (Figure 3.1, right). The strain is relieved by the spontaneous growth of helical filaments with negative gaussian curvature. The curvature in the filaments is non-uniform and decreases as the filaments grow wider, and thus, are limited in height and width (~30nm), corresponding to a limited number (~8) of smectic layers. The length of each filament is
theoretically unlimited and will grow unconstrained until confined by a boundary such as another domain.  

In NOBOW (P-9-OIMB) (Figure 3.1, left), a widely studied HNF forming material, on cooling from isotropic, the B2 phase is formed (Figure 3.2a). It is comprised of a mixture of SmC$_S$P$_A$ and SmC$_A$P$_A$ ordering and is generally characterized by focal conic or broken fan texture in POM. On further cooling, the highly-ordered, smectic-like B3 phase (Figure 3.2b) with tilted hexagonal interlayer order grows in. Less is known about the B3 phase, but it generally grows in between the B2 and B4 phases. The planar texture is similar to that of the B2, though a small change in birefringence can be observed in some regions. In NOBOW, the B3 phase is metastable and upon further cooling, HNFs grow in slowly. Under POM, the brightly colored, and highly birefringent B3 phase, slowly darkens until the characteristic low birefringence of HNFs is

Fig. 3.1. Schematic drawing of NOBOW as a BCLC where $\mathbf{n}$ is the molecular director, and $\mathbf{b}$ is the bow direction where $\mathbf{P}$ is along $\mathbf{b}$ (left). During HNF formation, within each layer, $\mathbf{n}$ is tilted at ~45° and two aromatic sublayers are orthogonal to one another causing torsional strain (middle). This leads to the formation of a saddle splay deformation. A $\frac{1}{4}$ pitch of the filament can be seen (right). Adapted with permission.
observed (Figure 3.2c). Under increased illumination, a blue colored broken smectic texture can be seen (Figure 3.2d). Because of the unique and difficult to study structure of the HNF, SEM, AFM and transmission electron microscopy (TEM) (Figure 3.2e) have been used to observe the structure of HNFs\textsuperscript{61,70,111}. This reveals bundles of long filaments that have coherent twist.

Previous studies have attempted to control the nucleation, growth, and orientation of HNFs by using surface energy\textsuperscript{113}, micro-confinement\textsuperscript{114,115}, nanoconfinement\textsuperscript{116}, and shearing\textsuperscript{111}. Together, these experiments have shown great control over the growth direction and overall orientation of HNFs, however, to this point, a single robust method has not been used to print well-aligned HNFs for use in organic electronic devices. In this chapter, we will discuss how LC phases

![Fig. 3.2. POM images of NOBOW on glass (a-d), and a TEM micrograph of HNFs (e). On cooling from isotropic melt, the B2 phase (a) can be seen with a smectic texture. Further cooling into the B3 phase (b) shows no overall change in texture but a small change in birefringence is seen. On transition to the HNF phase (c), birefringence is dramatically decreased and almost no texture can be observed. On increased illumination of the HNF phase (d), a bluish, broken smectic texture is observed. To view the structure of HNFs, TEM can be used (e). A schematic of an HNF is used to show the HNF orientation in the TEM image, represented by $Z$.](image-url)
align in bulk under different surface conditions in LC cells and explore this phenomenon with NOBOW in PDMS cells. We will then show how the soft lithography technique of capillary molding with PDMS microchannels can be used print bulk-aligned HNFs in freestanding microchannels.

3.2 Understanding Liquid Crystal Alignment in Surface Modified Cells

One advantageous property of LCs is that they can be aligned in LC cells using alignment layers. When the LC material fills the cell, coated surfaces can induce bulk alignment of the LC phase. The two general ways in which a calamitic (and bent-core) LC phase can orient itself in a cell are planar (and uniform planar) alignment (Figure 3.3, left) and homeotropic alignment (Figure 3.3, right). Planar alignment, with orientation of the molecular director, \( n \), parallel to the confining substrates, and homeotropic alignment, with orientation of the director perpendicular to the confining substrates, can be achieved for nematogenic calamitic LCs with relative ease. In most systems, however, planar alignment is significantly easier to achieve, even on cleaned glass substrates. In POM, planar alignment commonly gives bright colors and interesting textures that are crucial to phase identification because the optic axis is perpendicular to the viewing axis.

Fig. 3.3. Examples of planar (left) and homeotropic alignment (right). In homeotropic alignment, the molecular director is perpendicular to the confining plates, and in planar alignment the molecular director is parallel to the confining plates.
Homeotropic alignment, on the other hand, is significantly harder to achieve and results in optically isotropic or low birefringence schlierin textures as the optic axis is parallel to the viewing axis.

Control over molecular orientation and morphology in calamitic LCs has been widely studied. Alignment of calamitic LCs is critically important in a large majority of applications, including information displays and other electro-optic devices. Many techniques have been employed to align both nematic and smectic phases. For example, parallel alignment has been achieved by photo-alignment, and alignment on mechanically rubbing polymer coated glass substrates, on glass substrate surfaces treated by oblique evaporation of $\text{SiO}_x$, and by application of electric fields. Homeotropic alignment, while significantly more rare, has been achieved by using substrates coated with a surfactant such as lecithin or stearic acid.

Alignment of bent-core LCs (BCLCs) is much more challenging. Here, we look at NOBOW in LC cells with PDMS alignment layers that appear to induce homeotropic alignment and influence the nucleation of HNFs as observed through the formation of spherulites, which are nearly spherical and densely branched crystalline structures that are commonly observed in polymers (and other materials) on slow cooling from isotropic melt and have been previously observed in HNFs of NOBOW in mixtures with 8CB.

3.3 Homeotropic Alignment of NOBOW in Polydimethylsiloxane Cells

Polydimethylsiloxane (PDMS) thin films have been used to create hydrophobic surfaces in many applications. Here, we demonstrate that PDMS thin films provide a general approach for homeotropic alignment of NOBOW, likely due to a strong attractive interaction between the PDMS-coated surface and the NOBOW’s hydrophobic aliphatic tails. Every mesogenic phase
observed showed homeotropic alignment in these cells in POM. This alignment phenomenon also appears to have an effect on the observed morphology of the HNF phase as they nucleate as spherulites. To better understand the interaction between NOBOW and PDMS both contact angle measurements and differential scanning calorimetry experiments were conducted. Further examples of other BCLCs that exhibit homeotropic alignment in PDMS coated cells can be found in Appendix II.

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**Fig. 3.4.** POM textures of NOBOW in PDMS coated cells. On cooling from isotropic, the B2 phase (a) grows in with a dark schlieren texture. Further, cooling into the B3 phase (b) exhibits a colorful marble texture. HNFs (c) with very low birefringence nucleate in spherulites from the B3 and cannot be observed under low illumination. Increasing the illumination (d) shows the Maltese cross texture characteristic in spherulite growth. The spherulites grow until they meet another domain with a parabolic interface.
A LC cell prepared with glass plates each coated with a PDMS thin film was filled with the classic benzylideneaniline dimer mesogen, NOBOW, above its clearing point, and observed under POM. The samples were heated to 180 °C then cooled at a rate of 5 °C min⁻¹. Above 172 °C, NOBOW is an isotropic liquid. On cooling, the B2 phase grows in with low birefringence. A schlieren texture (Figure 3.4a) indicative of homeotropic molecular alignment on the PDMS surface is observed. On further cooling, the B3 phase grows in with a more highly birefringent colorful marble texture, as shown in Figure 3.4b. The birefringence observed in the B3 phase is higher than that seen in the B2 phase may be explained by the hexagonal intra-layer ordering present in the B3 phase. The lack of clear domain boundaries in the texture may be due to a slightly non-uniform cell thickness arising from defects on the PDMS surface.

Fig. 3.5. An example of homochiral domains in HNF spherulites in PDMS cells under POM. When uncrossing the analyzer 3° left and right near spherulite boundaries chirality is observed as the polarized light is rotated in opposite directions.

With slow cooling, the HNF phase (Figure 3.4c) slowly nucleated out of the B3 phase well below the B3 to HNF transition temperature normally observed on glass (~145 °C). The phase nucleates as large spherulites. Each spherulite grows out radially until it meets another and can be up to multiple millimeters in diameter. The growth is slow and uniform with circular boundaries that become parabolic at domain interfaces. The birefringence of the HNFs in the PDMS coated
cells is very low, which is consistent with previously reported birefringence values of |Δn| < ~0.001\(^7\). Increasing the illumination (Figure 3.4d) reveals a clear Maltese cross texture indicating that the filaments aligned 45° to the crossed polarizers exhibits a measurable birefringence due to the local anisotropy of filaments where the average optic axis points out radially from the nucleation center. When uncrossing the polarizers even a small amount, left- and right-handed domains of HNFs can be observed as in figure 3.5. This indicates that each spherulite nucleates as a homochiral domain as has been previously reported in spherulites of HNFs\(^{111}\).

To better understand the relative surface energies of glass and PDMS that may attribute to the change in bulk phase alignment from planar to homeotropic, contact angle measurements were taken. Neat NOBOW was placed on clean PDMS and glass substrates and heated to 210ºC to ensure that NOBOW was in the isotropic phase. While the contact angle in each case was difficult to determine exactly, the contact angle between NOBOW and the two surfaces were estimated. The contact angle of NOBOW on the two surfaces can be seen in Figure 3.6. The contact angle between NOBOW and glass is ~25° whereas the contact angle between NOBOW and the PDMS surface is ~50°. This indicates that there is a substantial difference in the surface energy of PDMS and glass, resulting in different interactions at the NOBOW-surface interface in each material.

![Fig. 3.6. Contact angle measurements of PDMS (50°) and glass (25°) with isotropic NOBOW at 210ºC. The substantial difference between apparent contact angles made between the substrates and the NOBOW indicate that the PDMS has a lower relative surface energy compared to the surface energy of glass.](image)
The glass surface exhibits a relatively higher surface energy giving a more “molecule-philic” interaction where the surface more strongly interacts with NOBOW’s aromatic cores, leading to planar alignment. The PDMS surface exhibits a lower surface energy that results in a more “molecule-phobic” interaction that leads to a stronger interaction between NOBOW’s aliphatic tails and the surface, leading to homeotropic alignment. The PDMS alignment layer affects the surface interactions and molecular alignment in the cell. The PDMS surface is methylated, comparing well with the hydrophobic surface of a surfactant layer commonly used to induce homeotropic alignment. The methylated surface has a low surface energy and is easily wetted by alkyl groups. PDMS is slightly porous and will further allow for the slight intercalation of aliphatic groups. This environment is optimal for the homeotropic alignment of LC materials due to their long aliphatic tails. The tails are able to strongly interact with the surface and intercalate with the PDMS, inducing strong homeotropic alignment.

A clear depression of the B3 to HNF phase transition temperature was observed in the PDMS cells under POM. To quantify any difference in phase transition temperatures between PDMS and glass, a differential scanning calorimetry experiment (DSC) was conducted. DSC is an experiment that uses a reference sample to quantify phase transitions in materials. Both PDMS and glass cells filled with NOBOW were placed in the DSC. The samples were first heated and then cooled at 5 °C min⁻¹. The phase transition temperatures were recorded by observation of the enthalpy associated with each transition (Figure 3.7). The transition temperatures were then associated with the phase transitions observed under POM in order to characterize each phase transition.

In the glass cell, on heating, a phase transition from the HNF phase to the B2 phase was observed at 154.8 °C and the transition from the B2 to isotropic phase was observed at 174.6 °C.
On cooling, the isotropic to B2 phase transition was observed at 172.2 °C, the B2 to B3 phase transition at 145.5 °C, and the B3 to HNF phase transition at 141.6 °C. This phase behavior in the glass cell is consistent with reported phase transition temperatures for NOBOW\textsuperscript{70}. In the PDMS cell on heating, the HNF to B2 and B2 to isotropic phase transitions occur at 155.7 °C and 176.0 °C respectively. On cooling, the isotropic to B2 phase transition was observed at 172.4 °C and the B2 to B3 phase transition was observed at 145.4 °C. The B3 to HNF phase transition occurred at 136.6 °C.

![Graph](image)

**Fig. 3.7.** DSC curves of NOBOW in a glass cell (left) and a PDMS coated cell (right).

On heating, the B3 phase is not observed in either cell as is expected; it is a monotropic phase only seen on cooling. Also, the phase transition temperatures on heating were only minimally affected by the change in surface. On cooling, the isotropic to B2 and B2 to B3 phase transitions were largely unchanged between the two cells. In the glass cell on cooling, however, the B2 to B3 and B3 to HNF phase transitions are overlap. This indicates that the B3 phase is short-
lived before HNFs nucleate. In the PDMS cells, the B3 to HNF phase transition temperature was suppressed significantly compared to the glass cells. This indicates that the phase may be stabilized in the PDMS cells, leading to further undercooling of the B3 phase.

The energy associated with the B3 to HNF transition in both glass and PDMS can be estimated from the DSC to quantify the added energy barrier due to the PDMS surface stabilization. The heat associated with the B3 to HNF transition in the glass cells is 0.48 kcal mol$^{-1}$ and the transition in the PDMS cell is 4.96 kcal mol$^{-1}$. This indicates that the interaction between NOBOW’s tails and the PDMS surface increases the enthalpy of transition between the B3 and HNF phase by about 4.5 kcal mol$^{-1}$ by stabilizing the B3 phase. In this case, as cooling continues, the difference in free energy between the two phases increases. Eventually, the a large difference in free energy between the two phases is greater than the stabilization induced by the PDMS surface and acts as a driving force in HNF nucleation. The transition temperature, however, has been significantly undercooled. Undercooling ($\Delta T = T_m - T_c$), in nucleation theory, is defined as the difference in the phase transition temperature on heating and cooling. In the glass cell $\Delta T = 13.2 ^\circ C$ and 18.9 $^\circ C$ in the PDMS cell—a difference of 5.7 $^\circ C$. A large degree of undercooling, along with a viscous fluid, is requisite in and acts as driving force in rapid crystallization of spherulites$^{128}$. This explains the observation of spherulite nucleation in PDMS cells but not in glass cells—the undercooling in glass cells is not sufficient to induce spherulite nucleation whereas it is sufficient in PDMS cells.

The requirement that the homeotropic alignment of the B3 phase is broken during the formation of saddle-splay deformations might explain the higher degree of undercooling and subsequent nucleation of spherulites of HNFs observed in the PDMS cells. On transition from the B2 to the B3 phase, the surface interaction is unchanged in the both the PDMS and glass cells, thus
similar transition temperatures are observed. However, in the PDMS cell, the transition to the HNF phase from the B3 disrupts the surface interaction as the homeotropic aligned smectic layers splay. The destabilization of the smectic layers as saddle-splay deformations form during HNF nucleation may be able to be visualized in homeotropic cells. Under POM, a single “wave-like” ripple can be observed radiating out in all directions through the B3 phase at the B3 to HNF phase transition temperature as seen in Figure 3.9. Following the ripple, dark circular spots—HNF spherulites—begin to radiate from the same spot that the ripple originated. As the spherulites continue to grow, they follow the ripple movement, and the ripple radiates outward until runs into an adjacent spherulite domain. It is speculated that these ripples must be a type of nucleation front that can be seen under POM as the smectic layers undergo deformations due to the inter-layer mismatch during the HNF phase transition.

![Fig. 3.8. The observation of ‘wave-like’ ripples on cooling from the B3 phase just before HNF spherulite nucleation. The white arrows point to the ripples observed under POM.](image)

In PDMS coated cells, the B3 phase has been stabilized and is homeotropically aligned to the confining plates, and thus, during the B3 to HNF phase transition smectic layer deformations can be observed. As the layer orientation changes from homeotropic to curved through this ripple effect, an increase in birefringence is observed. This nucleation front, to the best of our knowledge,
has not been seen before in glass cells of NOBOW (planar aligned) under POM. In glass cells, the B3 temperature range is small and no conformational changes can be seen in the form of a nucleation front as the HNF phase grows in as a dark broken smectic texture as previously seen in Figure 3.2c. The smectic layer deformations in planar aligned glass cells must cause a decrease in birefringence as the layers splay in and out of plane. Without a directional and uniform filament nucleation, the macroscopic change in birefringence is not observed as the HNF phase grows in from the B3.

We observed bulk homeotropic alignment in both the B2 and B3 LC phases of NOBOW in PDMS coated cells under POM. This compares to planar alignment that is normally observed in glass cells. Further, HNFs nucleate as spherulites in the PDMS cells. To better understand the interaction between NOBOW and the PDMS surface that leads to homeotropic alignment and spherulite nucleation, contact angle and DSC experiments were performed. It appears that the relatively low surface energy of PDMS promotes aliphatic tail interaction, promoting homeotropic alignment of the B2 and B3 phases of NOBOW. Further, this interaction stabilizes the flat smectic layers. On nucleation of the HNF phase, the deformation and eventual twist in the layers disrupts this interaction, leading to a depression in the nucleation temperature, increasing the observed undercooling at the B3 to HNF transition. This undercooling effect is integral to the formation of spherulites. Further, we speculate that the nucleation front where the smectic layers are distorted just before HNF nucleation can be observed in the PDMS cells through a “wave-like” ripple.

3.4 Template-Assisted Self-Assembly of Liquid Crystal Materials

PDMS stamps from soft lithography are commonly used to micropattern organic thin films through multiple processes and capillary molding using microchannels has been used to pattern...
and align smectic LC OSCs in OFETs\textsuperscript{58} using a technique called template-assisted self-assembly (TASA)\textsuperscript{133}. In the use of TASA to micropattern LC OSCs, the PDMS microchannels were filled with LC material at isotropic temperatures and cooling (on a gradient) through ordered smectic phases into the room temperature crystal phase can induce bulk alignment in the crystalline films. It is thought that the topographical confinement of the microchannels are at least, in part, responsible for the alignment of the mesophase and crystal phase. Other studies have further examined LC defects\textsuperscript{134,135} and alignment\textsuperscript{136} in PDMS microchannels.

Fig. 3.9. Schematic drawing of the TASA Method using PDMS microchannels and optical microscope images of PDMS molds. First the mold is placed on a substrate (left). The mold is then filled with isotropic liquid and cooled to room temperature (center). The mold is then removed, exposing freestanding microchannels (right) (a). The PDMS molds made from a silicon microchannel master consist of centimeter long microchannels (left). The microchannels extend to the edge of the mold to fill with isotropic fluids using capillary force (center). The cross-sectional dimension of the microchannel reveals uniform size with few defects (right).

In this work, freestanding microchannels of NOBOW were fabricated according to the procedure in Appendix I to direct the self-assembly and induce bulk orientational growth of HNFs through the TASA method (Figure 3.10a) using PDMS molds (Figure 3.10b). were observed with
POM, XRD, and SEM to determine HNF alignment. The microchannel aspect ratio was then studied as a means to understand the confinement effect in the PDMS microchannel molds. Finally, a brief description and model of nucleation and alignment in the microchannels will be discussed.

3.5 Topographical Confinement of Helical Nanofilaments in Microchannel Molds

PDMS microchannel molds with a cross-sectional dimension of 5 µm in width and 10 µm in height were filled with NOBOW at ~180 ºC and cooled to room temperature. The PDMS mold was then removed, exposing freestanding microchannels. Under POM, when the channel direction is parallel to the cross polarizers, birefringence is almost completely extinguished (Figure 3.11a). A low intensity blue color can be seen in the microchannels due to light scattering that is often seen in the HNF phase, suggesting that HNF formation occurred within the channels on cooling. Upon rotation of the stage 45º from the crossed polarizers, maximum birefringence in all microchannels in the field of view is observed, suggesting uniform molecular orientation is present in the channels (Figure 3.11b). The birefringence in the microchannels was estimated to be \( \Delta n \approx 0.05 \), significantly higher than what is observed in unaligned HNFs and similar to what has been reported in aligned systems\(^{115}\). Material fills the channels without fractures or defects over spans of hundreds of micrometers. Unfilled regions of microchannels can be attributed to defects in the mold that were produced on fabrication (Figure 3.11c, d). Due to a clear distinction between microchannels as seen through stripes of relatively high and zero birefringence, no material is present between the isolated microchannels.

When uncrossing the cross polarizers a few degrees in either direction optical rotation of light is observed (Figure 3.11e). Large chiral domains are observed within the channels. Domains appear to span the entire width of channel and along the length of the channel until reaching an
adjacent domain. The chirality is not preserved among domains in adjacent channels suggesting a lack of communication between microchannels, and that the nucleation of HNFs in a particular channel is independent of the surrounding microchannels. The lack of a single chiral domain in each microchannel indicates that there are multiple nucleation sites present. This could be due to small temperature gradients on the heating stage surface. For the same reason, using thermal gradients did not significantly impact the number of nucleation sites in microchannels.

![Fig. 3.10. POM images of freestanding microchannels of NOBOW HNFs.](image)

To directly view the freestanding microchannels, AFM was performed. A sample of freestanding microchannels with cross-sectional dimension of 5 µm in width and 10 µm in height.
on a clean glass microscope slide was placed into an isolated AFM chamber and imaged using tapping mode. The oblique streaks seen on the edges of the channel are due to the tip slipping along the side of the channel during the scan. The surface of the microchannels can be seen clearly.

![AFM images of aligned HNFs in freestanding microchannels](image)

**Fig. 3.11.** AFM images of aligned HNFs in freestanding microchannels. The rope-like texture indicates the formation of HNFs with coherent twist (a, b). The stripe orientation indicates that the HNFs are aligned along the length of the microchannel (a). A height profile of the surface was taken to measure the HNF helix half-pitch (b). The profile reveals that the half-pitch is ~120 nm.
A rope-like texture commonly seen in AFM of HNFs is observed (Figure 3.12a). The bulk formation of close packed HNFs gives the rope-like texture as the filaments grow parallel to one another with a well-defined pitch length and a macroscopically coherent and homochiral twist. This pattern is also helpful in determining the orientation of the filaments. Because the rope-like texture is evidence of coherent twist in the helices of multiple filaments, the filament orientation, \( Z \), is perpendicular to the stripes (Figure 3.12a, b). The stripes in the rope-like texture, in large part, run perpendicular to the channel, indicating that the HNFs are well oriented along the channel direction. A height profile was taken along the HNF orientation to determine the helix half-pitch length along the black line in Figure 3.12b. The height profile shows periodic a periodic surface modulation as is expected from the helix pitch. The peaks are uniformly spaced at ~120 nm corresponding to the helix half-pitch, which is consistent with previously reported values in NOBOW HNFs\textsuperscript{61,115}.

Transmission small angle X-Ray scattering (SAXS) experiments were conducted on the microchannels with cross-sectional dimensions of 5\( \mu \text{m} \) in width and 10 \( \mu \text{m} \) in height. The sample substrate used was very thin glass that is only 50 \( \mu \text{m} \) thick to increase the signal to noise ratio, because the beam is dampened as it passes through amorphous glass. The microchannel covered substrate was placed perpendicular to the X-ray beam with the microchannels running vertically in the x-direction. An 8.05 KeV X-ray beam was then diffracted off the sample and collected by a detector 1.577 m away from the sample (Figure 3.13a).

The 2D plot of the diffraction shows diffuse scattering in a ring observed with high intensity perpendicular to the channel direction at \( q = 0.13 \ \text{Å}^{-1} \), which corresponds to a layer spacing of about 4.8 nm (Figure 3.13b). This matches well with the layer spacing previously reported in NOBOW HNFs\textsuperscript{61}. The maximum scattering intensity can be observed at about 90\(^{\circ}\) to
the channel direction and can be attributed to the bulk layer orientation in the microchannels. Based on Bragg’s law, diffraction is observed perpendicular direction to the layer and parallel to the layer normal. Due to the twist in HNFs, all other layer orientations will not be detected. This indicates that in large part, the layer normal is perpendicular to the channel direction. Further, in HNFs, the layer normal is perpendicular to the long axis of the filament and are oriented along the length of the microchannel.

![Diagram showing SAXS setup and data](image)

**Fig. 3.12.** SAXS data from the freestanding microchannels. The X-ray beam was directed through a sample of vertically oriented microchannels (a). The diffraction pattern at $q = 0.13 \text{ Å}^{-1}$ indicates that the scattering is the most intense perpendicular to the channel direction corresponding to the orientation of the layers in the HNFs and general bulk alignment of HNFs along the microchannels (b). An azimuthal trace was taken of the normalized intensity at $q = 0.13 \text{ Å}^{-1}$ to reveal that ~85% of the filaments are aligned within 30° of the microchannel direction (c). The red line in (c) represents the normalized intensity in an unaligned sample.
To view a distribution of layer orientations in the microchannels, an azimuthal trace of the normalized intensity at q = 0.13Å⁻¹ and noise reduction was performed. Two strong peaks are observed centered around ~90° and ~270° (Figure 3.13c). A fairly large shoulder can be seen at ~95° and ~275°, most likely due to a proportion of channels that were disturbed during the mold lift-off process. The proportion of HNFs aligned along the microchannel direction appears to be quite high, which coincides with the large change in birefringence seen upon rotation of the microchannels 45° under POM and the aligned HNFs seen in AFM. By taking an integral of the normalized intensity over the range of diffraction angles, we were able to determine that ~85% of the filaments are aligned within 30° of the microchannel direction. Assuming that there is no preferred direction along the microchannel, one would expect that ~33% of the filaments to be oriented within 30° of the microchannels, compared to the ~85% observed. This indicates that most of the bulk filaments are oriented along the length of the microchannel rather than in random orientations as is normally seen in bulk HNF systems. The 30° threshold was chosen to represent a HNF’s ability to span the entire length of a 5 µm long organic transistor channel in a 5µm microchannel. In this case, a filament that nucleates at the center of the 5 µm wide microchannel can grow ~5 µm before it is terminated by a physical boundary—the PDMS mold.

To determine if this result is statistically significant, we compared the degree of alignment in bulk to randomly oriented HNFs. To do this, the sum of the normalized intensity of the azimuthal trace was calculated and averaged over 360°. The average normalized intensity over all angles was calculated to be ~0.20, giving an estimate for the expected intensity in an unaligned sample. This value is represented by a red line in Figure 3.13c. While azimuthal trace is visually distinct from a randomly oriented sample, we attempted to determine if the observed alignment in the microchannel is statistically significant. A two-sample t-test assuming unequal variances was
conducted using the data that corresponds to diffraction from filaments oriented along the length of the microchannels—30° from perpendicular to the microchannel direction. With a p-value < 0.0001, the null hypothesis was rejected and we can confidently conclude that the diffraction pattern that gives intense peaks at 90° and 270° cannot be due to randomly oriented HNFs.

3.6 The Effect of Microchannel Aspect Ratio on HNF Alignment

Bulk alignment is unambiguous in microchannel cross-sectional dimensions of 5 µm in width and 10 µm in height. To further probe the effect that topographical confinement and aspect ratio, \( \eta \), defined as the height to width ratio \( (\eta = h/w) \) of the microchannel cross-sectional dimensions has on the alignment of HNFs, microchannels with multiple aspect ratios were observed. Microchannels with cross-sectional width by height dimensions of 5 µm by 10 µm \( (\eta = 2) \), 5 µm by 5 µm \( (\eta = 1) \), 5 by 3 µm \( (\eta = 0.6) \), 5 µm by 1 µm \( (\eta = 0.2) \), 10 µm by 5 µm \( (\eta = 0.5) \), 10 µm by 3 µm \( (\eta = 0.3) \), and 10 µm by 1 µm \( (\eta = 0.1) \) were placed on glass substrates and filled with isotropic NOBOW. The molds were cooled to room temperature and remove to reveal microchannels and observed under POM.

The relative birefringence in each sample observed and was used to qualitatively determine the level of alignment in each microchannel. The apparent birefringence with the microchannels rotated 45° from the cross polarizers differs drastically between the samples. It appears that the microchannels with larger aspect ratios exhibit a larger birefringence (Figure 3.14a). On examination of the microchannels with lower apparent birefringence, individual microchannels have extremely low birefringence (Figure 3.14b). This suggests that the aspect ratio is critical in the bulk alignment of HNFs in the microchannels. With high exposure, regions of high birefringence, mostly near the edge of the microchannels and a blueish broken smectic texture
characteristic of HNFs on glass is seen in the center of the microchannels. This suggests that most of the HNFs nucleated without spherulite growth while there is a small portion of HNFs near the PDMS surface that nucleated from spherulites and are aligned parallel to the channel direction.

![Image](image.png)

**Fig. 3.13.** POM images of microchannels with varying aspect ratios. Higher relative birefringence is observed in microchannels with an aspect ratio of $\eta \approx 0.6$ (a). Microchannels with a small aspect ratio of $\eta \approx 0.3$ has extremely low birefringence at the same exposure (b). In an overexposed image, brighter regions are observed near the channel edges and broken smectic texture is observed in the channel center (c). Red arrows represent the microchannel direction.

To quantify the HNF alignment in microchannels with different aspect ratios, light transmission measurements were taken. The transmission of light observed with the microchannels parallel with the crossed polarizers and 45° to the crossed polarizers was measured by taking grayscale images with a DSLR camera. The total light intensity in each image was summed and normalized by dividing by the channel height as the transmission of light is thickness dependent. The ratio of the transmission between the images with the microchannels aligned parallel and 45° to the crossed polarizers was determined and plotted versus aspect ratio (Figure 3.15).

Microchannels with a $\eta < 0.6$ show almost no difference in transmission between the two orientations. At a $\eta \geq 0.6$, a significant and measurable difference in the ratio of transmission is observed between the two microchannel orientations. The difference in transmission between the microchannels with larger aspect ratio only continues to increase slightly as the aspect ratio
increases, indicating that the degree of HNF alignment does not significantly increase as the microchannel aspect ratio increases. Rather, the alignment effect of HNFs in the microchannels is mostly binary. The point at which the HNFs align in bulk parallel to the microchannel direction can be described as a critical aspect ratio. The plot in Figure 3.15 displays a jump in transmission between the microchannels with an aspect ratio of $\eta \approx 0.5$ and $\eta \approx 0.6$, giving a critical aspect ratio equal to $\eta \approx 0.55$.

![Figure 3.14](image)

**Fig. 3.14.** Plot of the normalized transmission ratio measured between the microchannels of HNFs when aligned parallel and perpendicular to the crossed polarizers. A larger ratio indicates better HNF alignment parallel to the microchannel direction. A critical aspect ratio of $\eta \approx 0.55$ is observed.

Confirming that bulk alignment is not observed in microchannels with aspect ratios below $\eta \approx 0.55$, AFM was performed to view the HNFs in microchannels with cross-sectional dimensions of 3 $\mu$m in width and 10 $\mu$m in height ($\eta = 0.3$). Images were taken of the channel surfaces reveal a rope-like texture indicative the coherent growth of HNFs (Figure 3.16). On the
microchannel surface, the HNFs appear to have nucleated in multiple domains and indicating that uniform nucleation and long-range alignment is not present in these microchannels. The small domains random filament orientation is consistent with what is expected on a glass surface, suggesting that the PDMS mold is not responsible for nucleation as is the case in microchannels with larger aspect ratios.

To further test the requirement of strong PDMS-tail interaction in the alignment of HNFs in microchannels, the hydrophobic surface of PDMS was modified by treating the molds with O₂ plasma. This process should make the PDMS surfaces highly polar through the formation of -OH groups. Both 5 µm by 3 µm (η = 0.6) and 10 µm by 3µm (η = 0.3) microchannels were used. Under POM, both sets of microchannels showed broken smectic textures with very low

Fig. 3.15. An AFM image of the surface of a microchannel with cross-sectional dimensions of 3 µm in width and 10 µm in height (η = 0.3). The white double arrow indicated the channel direction. Multiple HNF domains with random grow orientations are observed, indicating that bulk HNF alignment is not present in these microchannels.
birefringence (Figure 3.17). Changing the surface conditions from hydrophobic to hydrophilic has reduced the PDMS-LC tail interactions, reducing the degree of undercooling and subsequent spherulite nucleation. This is further evidence of the importance of the PDMS surface energy in the system.

![Fig. 3.16. POM images of HNF filed microchannels treated with O₂ plasma. Any bulk orientational control has been suppressed in microchannels with an aspect ratio of η = 0.6 (a) and η = 0.3 (b). The exposure in both images has been increased slightly to observe the HNF on glass texture.](image)

3.7 Observation of HNF Nucleation in Polydimethylsiloxane Microchannels

The nucleation of HNFs in the PDMS microchannels was observed under POM. A PDMS mold with cross-sectional dimensions of 5 μm in width and 10 μm in height was placed on a clean piece of glass and filled with isotropic NOBOW and cooled room temperature at 5 °C min⁻¹ and the phase transitions were observed with the channels rotated 45° to the crossed polarizers to ensure maximum birefringence. On cooling from isotropic, the B2 phase grows in with a solid green texture at 172 °C. The phase appears to grow in at specific sites and grow along the length of the microchannel (Figure 3.18a). On further cooling to 145 °C, the B3 phase grows in rapidly from
one end of a channel to another to form a solid light pink and yellow texture (Figure 3.18a). The birefringence in each channel is the same but differs from microchannel to microchannel and might be due to the variable amount that each channel is filled leading to different apparent cell thicknesses. In both cases, large domains appear to be uniformly oriented in the microchannels.

![Fig. 3.17. POM images of HNF nucleation in microchannels on cooling. The B2 grows in as a solid green texture followed by a light pink texture of the B3 (a). The nucleation of HNF spherulites is observed just after the deformation of the B3 phase (a). On closer observation of the B3 pane in a), HNF nucleation sites are observed as slight defects in the microchannels that do not completely disappear in the HNF phase (b). On observation of the second HNF pane, directional growth of HNFs is observed (c). The HNFs grow along the channels towards the B3 deformations.](image-url)
Like in the PDMS cells, the B3 phase is stabilized in the microchannels and undercools before nucleation of HNFs.

Around 137 °C, the solid texture begins to break in each channel and defect-like textures appear similar to the ripple seen just before HNF formation in the PDMS cells in 3.3. Just as these sites appear, solid blue domains grow in opposite directions along the microchannels. The blue domains will grow until they meet another blue domain growing in the opposite direction. On closer observation of the B3 phase just before HNF nucleation, defects appear at the HNF nucleation sites that do not complete disappear in the HNF phase and may be a result of spherulite nucleation (Figure 3.18b). The nucleation front of the HNFs is observed growing towards B3 defects along the microchannels (Figure 3.18c). The nucleation and growth of the HNF phase is reminiscent of the spherulites that grow in PDMS cells, though, in this case, the growth direction is primarily along the microchannels. This suggests that the PDMS is at least, in part, responsible for how HNFs nucleate and grow in the microchannels.

To better understand the influence that the interaction between the B3 phase and the PDMS walls has on HNF alignment during nucleation in the microchannels, we attempt to suppress the B3 phase and observe the isotropic to HNF phase transition previously observed in NOBOW when mixed at low concentrations with 8CB\textsuperscript{111}. 8CB is a calamitic mesogen that exhibits both the nematic and SmA phases (Figure 3.19, inset) and has a melting point well below the B3 to HNF transition in NOBOW, ensuring all of the material surrounding HNF nucleation is isotropic. In this experiment, NOBOW and 8CB mixtures with varying concentrations were made and filled into PDMS molds on clean glass substrates with cross-sectional dimensions of 5 µm in width and 10 µm in height. The samples were observed under crossed polarizers on cooling at a rate of 5 °C min\textsuperscript{-1}. 
In mixtures with high concentrations of NOBOW (>10 wt%), the phase transitions are similar to neat NOBOW in microchannels (Figure 3.19). The HNF phase transition temperature is depressed to temperatures similar to what is expected in PDMS cells and microchannels and grows in below the B2 and B3 phases. As the concentration of 8CB increases, the temperature range of the B2 and B3 decreases (Figure 3.20a). The B3 appears to be suppressed in 8CB concentrations above 50 wt%, but this is most likely due to the depression of the isotropic to B2 transition below the B2 to B3 phase transition. In 90 wt% 8CB, the B2 phase is suppressed completely and the isotropic to HNF transition is observed (Figure 3.20b). The HNF phase still appears to be well aligned as the maximum birefringence is observed at 45º from the crossed polarizers. The birefringence appears to decrease as the concentration of 8CB increases (though not measured), most likely due to fewer HNFs in each microchannel.

![Graph showing phase transitions](image)

**Fig. 3.18.** A plot of the phase transition temperatures as recorded from POM for NOBOW and 8CB mixtures. As the concentration of 8CB increases, the B2 and B3 phases are suppressed and in 90 wt% 8CB, NOBOW undergoes an isotropic to HNF phase transition. The chemical structure and phase transitions of 8CB can be seen as an inset on the plot.
The isotropic to HNF transition was not observed until 90 wt% 8CB was present in the mixture. In glass cells, this was observed at significantly lower (~25 wt%) 8CB concentration. This can be explained by the strong interaction between NOBOW’s aliphatic tails and the PDMS surface that appears to stabilize the B2 phase along with the B3 phase as previously observed. In glass cells, the latent heat and thus nucleation barrier of the HNF phase decreases as the concentration of 8CB increases. This is in direct competition with the increased nucleation barrier due to the stabilization of the higher temperature phases on the PDMS surface. The decreased nucleation barrier due to the mixture with isotropic 8CB is not enough to overcome the energy barrier imposed by the phase stabilization until the 8CB concentration is ~90%. HNFs that nucleate out of the isotropic phase appear to be well aligned as is the case in every mixture. This is significant as it indicates that the nucleation itself is responsible for alignment of the HNFs in the microchannels and the orientation of the B2 and B3 plays a significantly smaller role in this 8CB mixture. Even still, the isotropic to HNF transition is still observed and HNFs appear to be well aligned in the microchannels. This indicates that the observed planar alignment in the B2 and
B3 phases are not necessary for HNFs to align parallel to microchannel direction in the microchannels, and the criterion of alignment is related to the nucleation of spherulites itself.

**Fig. 3.19.** POM images of HNF nucleation out of 8CB solutions in the microchannels. The HNF phase grows out of the B3 phase in at lower 8CB concentrations (a). In 90 wt% concentrations of 8CB the isotropic to HNF phase is observed (b). The HNFs appear to be well-aligned when nucleating out of the isotropic 8CB.

### 3.8 Model of HNF Alignment in PDMS Microchannels

To complete the picture of HNF alignment parallel to the PDMS microchannel direction we attempt to create a model of alignment consistent with the observations of HNF nucleation in topographically confined in microchannels. These observations indicate that aspect ratio and spherulite nucleation are important in this model.
To understand how the aspect ratio determines HNF alignment in PDMS microchannels we will first discuss general LC alignment in PDMS microchannels. When microchannels are rotated 45° to the crossed polarizers, low transmission caused by an optically isotropic orientation is due to “bulk” alignment of the molecules perpendicular with respect to the viewing direction. Large transmission values correspond to planar alignment with respect to the viewing direction. With NOBOW, as with other LC materials that have aliphatic tails, will always prefer homeotropic alignment at a PDMS surface (and planar to the glass surface). In PDMS microchannels, with two competing orthogonal surfaces belonging to the microchannel walls and surface, there is a competition observed in the bulk orientation. Close to each wall, the molecules will prefer homeotropic alignment, but the bulk will appear either planar or homeotropic to the viewing angle depending on the bulk molecular orientation. This orientation is determined by the relative strength of the interactions at each surface, which depends on the ratio of surface area of the walls to the surface. In low aspect ratio microchannels, bulk homeotropic alignment is observed (Figure 3.21a, right), and in high aspect ratio microchannels, bulk planar alignment is observed (figure 3.21a, left). There is then a critical aspect ratio in which the bulk orientation changes from bulk homeotropic to bulk planar alignment. At that point, the light transmission through the phase under POM increases linearly as the aspect ratio increase.

Alignment of HNFs is not as simple. As previously observed in 8CB mixtures, spherulite nucleation in the absence of bulk orientation of the B2 and B3 phases is not a condition of aligned HNFs but spherulite nucleation itself is a necessary condition for aligned HNFs. In 8CB mixtures, spherulite nucleation is a result of decreasing the latent heat of the isotropic to HNF phase transition. In neat NOBOW, however, spherulite nucleation is a result of the undercooling caused by strong PDMS-LC tail interactions. Specifically, as seen in the transmission measurements, this
Interaction is strongest in microchannels with a large aspect ratio. In microchannels with large aspect ratios, the bulk alignment of the B3 phase is consistent along the PDMS walls and the glass surface, with the PDMS interactions dominating (Figure 3.21a, left image). In these microchannels a large degree of undercooling and spherulite nucleation is observed. In small aspect ratio microchannels, the bulk alignment of the B3 phase is determined by the surface of the PDMS microchannel and the glass surface. This competition leads to weaker PDMS-tail interactions and defects within the smectic layers of the B3 phase (Figure 3.21a, right image). In this case, the surface interactions with the PDMS are not strong enough to cause significant undercooling and spherulite nucleation is not observed. Rather a low birefringence broken smectic texture is observed consistent with HNF nucleation on glass surfaces. The condition of spherulite nucleation in HNF alignment means that the surface interaction is either strong enough to produce alignment in the microchannels or it is not; partial long range alignment can never be achieved, leading to a binary alignment system.

For spherulite nucleation either out of neat NOBOW or 8CB, HNFs grow along the length of the channel and the HNFs align in bulk. For nucleation of a single spherulite, the nucleus radiates out in all directions. However, due to the confinement effect of the microchannel, the nucleus preferentially grows along the length of the microchannel and bulk alignment of the phase is generally observed (Figure 3.21b). This phenomenon can be explained by the larger gain in free energy as filaments grow longer. Longer filaments result in a lower surface area to volume ratio as they grow over the same volume when compared to shorter filaments. Because the filament radius is fixed, it is thus favorable to have fewer individual filaments and thus fewer filament ends. In the two extreme conditions, filaments that grow perpendicular the microchannel direction have a slightly higher surface area to volume ratio over filaments that grow parallel to the microchannel.
direction over the span over the size of a few hundred micrometer domain as is seen in spherulites. This difference is the driving force that orients filaments parallel to the microchannel direction.

**Fig. 3.20.** A simple schematic of alignment and Spherulite nucleation in the microchannels. The general alignment in microchannels with large and small aspect ratios (a). In the B2 and phase the layers are tilted but still give the same observed behavior as in uniaxial materials as seen in the POM images. When spherulite nucleation occurs in the microchannels, the preferred growth direction is mostly parallel to the length of the microchannels (b).
3.9 Conclusion

It is clear that the strong surface anchoring of the aliphatic tails in NOBOW, increases the energy barrier of HNF nucleation in PDMS cells, resulting in undercooling and HNF spherulites. Also, bulk alignment of HNFs parallel to the microchannel direction is observed in PDMS microchannels on glass when the microchannel aspect ratio is greater than $\eta \approx 0.55$. This is a result of the bulk planar alignment of the B3 phase in microchannels with small aspect ratios. Bulk planar alignment of the B3 phase ensures that the aliphatic tails of NOBOW strongly interact with the PDMS, causing large undercooling of the B3 to HNF phase transition and HNF spherulite growth. In 90 wt% 8CB mixtures an isotropic to HNF transition is observed, and the strong interaction in the B3 phase is removed. However, the 8CB mixtures still induces spherulite nucleation, and HNF alignment is still observed, indicating that spherulite nucleation is critical to bulk HNF alignment. As the spherulites nucleate and travel grow parallel to the length of the microchannels to reduce their surface area to volume ratio, inducing bulk alignment of HNFs parallel to the microchannel direction.

These experiments have just begun to explore HNF alignment in PDMS cells and microchannels. More can be done to change microchannel surface conditions to induce other bulk alignment orientations of HNFs and further the understanding of the alignment mechanism in the microchannels. Most importantly, however, the TASA technique can be used to micropattern well-aligned HNFs in organic electronic devices. Future work must be done to characterize the charge transport properties of aligned HNFs. Due to the surface properties of PDMS this technique can be expanded to other LC materials and mesophases. Some preliminary observations of other BCLCs in the PDMS microchannels can be found in Appendix II.

4.1  Introduction

The formation of OSC thin films is an integral part in the fabrication of many organic electronic devices. Because charge transport and ultimately device performance are related to the order present in the thin film, it is important to understand how to produce films with a high degree of molecular order expressed as coherent packing of molecular orbitals over multiple micrometers. It is also important to understand the parameters that influence a molecular order in the thin film to inform new procedures to improve charge transport and ultimately the device characteristics.

The study of thin film processing of small organic molecules is extensive and has been explored through both solution and vacuum deposition. In vacuum deposition, thin film growth closely mimics theory that was outlined in 1.4. Surface wetting conditions must be carefully considered to control surface structure\textsuperscript{137}. Though in proper conditions, terrace structures are commonly produced with a significant and measurable step-edge barrier as is observed in para-seixphenyl (6P)\textsuperscript{74}. A similar terrace structure has been widely observed in pentacene thin films\textsuperscript{72,138,139}. Work has also been done to understand diffusion limited aggregation (DLA) and resulting fractal mound-growth of the pentacene ad-molecule on the substrate surface\textsuperscript{140}. These terrace structures represent a growth mode intermediate to layer-by-layer formation that is ideal in two-dimensional charge transport. In solution-processed thin films, much of the recent work has been done to improve the molecular morphology of thin films through novel processing techniques\textsuperscript{141}. The primary techniques currently used to induce well-order crystals with favorable molecular morphology use some form of directional coating that orients crystal domains on
nucleation. Further improvements to molecular order have been achieved through both solvent vapor annealing\textsuperscript{142} and thermal annealing\textsuperscript{143}. To this point, to the best of our knowledge, solvent mixtures have not studied to control molecular morphology in thin films, but in theory solvent mixtures can provide control over solvent properties, and thus, the thin film morphology. In this work, we study the effect that individual solvents have on the thin film structure of the novel BTBT derivative, Th-BTBT-C8. Further, studies were done to observe the effects of processing conditions and solvent mixtures have on thin film morphology of another BTBT derivative, Th-BTBT-C10.

4.2 Chemical Structure and Morphology Control in BTBT Derivatives to Improve Charge Transport Properties

Many BTBT derivatives have been previously synthesized and characterized for their electrical properties\textsuperscript{49,51,108,144–146}. Currently, the BTBT motif is one of the most promising for the development of commercial organic electronics for its availability in solution processing and excellent charge transport properties\textsuperscript{108}. Chemically, BTBT, as previously shown through C8-BTBT-C8 in Figure 1.1 and in Figure 4.1a, is a fused conjugated ring system of two thiophenes sandwiched between two benzene rings. Generally, to increase the solubility of this system, one or two carbon chains are added to the 2 and/or 7 carbon positions on the ring system. In the case that BTBT has only one carbon chain, another un-fused conjugated ring may be added to the other position.

The structure of single tailed BTBT derivatives generally have LC properties that result in the existence of highly ordered LC phases such as the SmE phase. In thin film processing of these materials, attempts have been made to exploit these LC properties. It was first shown that spin
coating in the SmA LC phase of C10-BTBT-C10 improved the charge carrier mobility in OFETs by 6 times compared to room temperature. Further, in Ph-BTBT-C10, where one C10 carbon chain is replaced with a phenyl ring promotes the more highly ordered SmE phase, after spin coating in the LC phase, thermal annealing just below the crystal to SmE phase transition causes the formation of a bilayer, improving the charge carrier mobility in OFETs by 7 times. Ultimately, the clear advantage of using LC materials as OSCs is their ability to align LC phases.

Fig. 4.1. The structural motif of the BTBT fused ring system (a). In this work we will look at thin films of Th-BTBT-C10 (b). On cooling, the bâtonnet texture of the SmA is observed below the isotropic phase (c). On further cooling, the SmE phase grows in (c). Upon further cooling, the texture does not change, but a peak in the DSC shows that a glass transition is observed at 73 ºC (not shown).
and using that alignment to induce alignment in the room temperature crystal phase. This was shown using a methoxy-phenyl substituted BTBT material—MeO-Ph-BTBT-C8. This BTBT derivative exhibits the N phase at high temperature and was aligned using a rubbed polyimide alignment layer. Alignment achieved in the nematic phase was retained in the crystal phase, improving directional charge transport in OFETs. Though, this approach may not be universal. It is important to optimize solution processing of BTBT derivatives.

Using the single-tailed BTBT motif, Dayan Wei synthesized Th-BTBT-C8 and Th-BTBT-C10, BTBT derivatives that have either a C8 or C10 alkyl tail and a single bonded thiophene ring branched at the 2 and 7 positions of the fused BTBT ring system (Figure 4.1b). Both Th-BTBT-C8 and Th-BTBT-C10 have been shown to exhibit both the SmA and SmE LC phases. On heating, the SmE phase grows in at 91 °C, the SmA phase grows in at 224 °C, and the isotropic grows in at 242 °C in Th-BTBT-C8. And on cooling, the SmA phase grows in at 241 °C and the SmE grows in at 222 °C. With further cooling, under POM, no clear crystallization event occurs and rather a glass transition is observed at 50 °C. In Th-BTBT-C10, on heating, the SmE phase grows in at 112 °C, the SmA phase grows in at 219 °C, and the isotropic grows in at 236 °C. On cooling, the SmA phase grows in at 236 °C (Figure 4.1c, left) and the SmE grows in at 218 °C (Figure 4.1c, right). Similar to Th-BTBT-C8, a glass transition is observed at 73 °C. In both cases, the glass transition is ideal as the high degree of order present in the SmE phase can potentially be transferred to the crystal phase in melt processing. Only the POM textures are observed in Th-BTBT-C10 as they are virtually identical to Th-BTBT-C8.
4.3 Th-BTBT-C8 Thin Film Solvent Study

To study how solvent effects the morphology of Th-BTBT-C8 in solution processed thin films, thin films of Th-BTBT-C8 were spin coated at 3000 rpm for 30 s on clean glass substrates using 1 mg mL⁻¹, 2 mg mL⁻¹, and 4 mg mL⁻¹ solutions of Th-BTBT-C8 in chloroform (CF), tetrahydrofuran (THF), chlorobenzene (CB), and toluene in a nitrogen filled glovebox. The films were then removed from the glove box and measured under POM.

Fig. 4.2. POM images of Th-BTBT-C10 thin films spin coated out of CF (a, b, c), THF (d, e, f), and CB (g, h, i) at different concentrations.
The POM images show varying domain size across both concentrations and solvents. The 1 mg mL\(^{-1}\) solutions (Figure 4.2a, d, g) give small domains. In both the CF (Figure 4.2a) and THF (Figure 4.2b) the films are either exceedingly thin or domains are isolated. The CB film (Figure 4.2g) appears to have larger connected domains. In the 4 mg mL\(^{-1}\) films (Figure 4.2c, f, i), small crystallites on the film surface appear, most likely due to an overconcentration of the solution. No film is observed in the areas around the crystallites in both the CF (Figure 4.2c) and THF films (Figure 4.1f), further indicating that the formation of these crystallites negatively impacts uniform thin film formation. On the other hand, the crystallites in the CB film (Figure 4.2i), appear to grow on top of other surface features. In the 2 mg mL\(^{-1}\) thin films (Figure 4.1b, e, h), it appears that overall, the domains are larger than in the less concentrated solutions, but do not produce significant large crystallites on the substrate surface. The domains in the thin film out of the CB solution (Figure 4.2h) appear to span up to \(\sim 25\ \mu m\) in diameter. This is very promising for use in organic electronics.

To better understand the surface morphology in each of the thin films, AFM was performed using tapping mode. Observation of the three films gives drastically different morphologies and root mean squared (RMS) roughness measurements. As seen in Figure 4.3a, the film from the CF solution is very rough with an RMS roughness of 12.6 nm and lacks any well-defined surface structures. The surface has large peaks and deep valleys. The thin film produced from the THF solution (Figure 4.3b) was only slightly smoother with an RMS roughness of 10.6 nm, though a clear layer structure is observed. Each step on the surface appears to be multiple molecular layers in height. The thin film produced from the CB solution (Figure 4.3c) has an RMS roughness of 2.0 nm and clear island mounds of terraces have formed with multiple large steps. On some of the steps, fractal-like structures are observed suggesting that the layer formation is a diffusion limited
aggregation (DLA) process. Small spots that appear to be quite tall appear in many of the AFM scans of thin films that were formed out of CB during spin coating and have been previously reported in vacuum deposited films of another BTBT derivative\textsuperscript{147}. They could be clusters of molecules that did not nucleate in the film. To the best of our knowledge, this is the first time clear, pyramid-like island terrace structures, similar to what is observed out of vacuum deposition, have been observed in an organic thin film formed through solution processing\textsuperscript{74,140}.

To gain insight into the layer structure and molecular orientation in each of the films, height profiles were taken. In the film made from CF, no clear steps are measured and observed features are more than 15 nm in height (Figure 4.4a). In comparison, the THF films show clear steps that vary in height, but most appear to be between 5 nm and 20 nm that correspond to multiples of the molecular length, which for Th-BTBT, was calculated to be $\sim$2.5 nm. This indicates that the molecules are generally oriented perpendicular to the substrate surface in these films. Specifically, a step that is 13 nm in height is shown in Figure 4.4b. In the films from CB, terrace step heights are $\sim$2.5 nm (Figure 4.4c) indicating that each step is a single molecular layer. From the profile trace, the texture of smaller spots on each step appear to be $\sim$0.5 – 0.8 nm in height. These values

\textbf{Fig. 4.3.} Thin film morphology of Th-BTBT-C8 as observed by tapping mode AFM from chloroform (a), tetrahydrofuran (b), and chlorobenzene (c).
match closely with the interlayer spacing observed in the WAXS diffraction pattern of Th-BTBT-C8 where the a-axis is ~0.6 nm and b-axis is ~0.8 nm. These might be clusters of Th-BTBT-C8 that are tilted on their side. The terraces observed on spin coating out of CB moves in the right step to producing continuous films through layer by layer growth. The stepped terraces indicate that a step-edge barrier is present in these films.

\[ \text{~13 nm} \]

\[ \text{~2.5 nm} \]

\[ \text{~2.5 nm} \]

![Fig. 4.4. AFM images and height profiles of the three thin films of Th-BTBT-C8. Undefined step heights are observed in the films from CF (a). In the films from THF, layers are large and not uniform in height, though generally multiples of the molecular height (~2.5 nm) (b). Terrace steps observed in films from CB are all ~2.5 nm, indicating that each step is one molecule thick (c).} \]
The effect of solvent on Th-BTBT-C8 thin film morphology was further explored by spin coating out of 2 mg mL\(^{-1}\) solutions toluene and dimethylformamide (DMF) at 3000 rpm for 30 s. Both solutions have high boiling points, similar to CB, though while toluene is aromatic, DMF is not. The thin films were observed under tapping mode AFM to reveal the surface morphology. The films made from the DMF solution (Figure 4.5a) appear to be extremely smooth with an RMS roughness of 1.8 nm. There also appear to be geometric steps about 30 m \(\mu\)m to 40 \(\mu\)m in diameter,

![AFM images showing the surface morphology of Th-BTBT-C8 thin films made by spin coating out of DMF (a, b) and toluene (c, d). Thin films made from toluene are smooth and lack any real defining surface features; clumps of molecules appear to stick to the film surface. In thin films made from toluene, terraced mounds are observed similar to what is seen in films made from CB.](image_url)

**Fig. 4.5.** AFM images showing the surface morphology of Th-BTBT-C8 thin films made by spin coating out of DMF (a, b) and toluene (c, d). Thin films made from toluene are smooth and lack any real defining surface features; clumps of molecules appear to stick to the film surface. In thin films made from toluene, terraced mounds are observed similar to what is seen in films made from CB.
the height profile trace of the surface indicates that these steps are ~2.6 nm corresponding to Th-BTBT-C8 steps. On closer observation of this film, small clumps of material appear to cover the surface. The height of the clumps was measured to be ~5 nm and may be a small cluster of Th-BTBT-C8 molecules (Figure 4.5b). The thin film made from the toluene solution at large scale appears to form a network of terrace mounds on a large scale (Figure 4.5c). The RMS surface roughness of this film is 4.9 nm, indicating that the surface morphology is rougher than the film made from toluene. The image in Figure 4.5d is a zoomed in scan of the region outlined in white in Figure 4.5c. The surface of the film clearly shows well-formed terrace structures with multiple steps. The terraced mounds are nonuniform and appear to grow starting at different film thicknesses, further indicating that new layers begin forming locally before a previous layer completely forms. Among the lowest level of layers, a fractal growth pattern is observed, indicating that DLA is the growth mechanism in the layers. On the top of some of the terraces there are branched crystallites. This has been observed in systems of 6P terraced mounds and has been attributed to the crystal morphology seen in the growth of planar oriented molecules.

The unique and interesting terraced mounds observed in the CB and toluene thin films prompted further study. An AFM image of a 50 µm² area of a Th-BTBT-C8 thin film made from a CB solution reveals that terraces readily form over the entire surface (Figure 4.a). Compared to the controlled growth of terraced mounds observed in vacuum deposited films, the mounds grown out of CB during spin coating are not uniform in height and diameter. In the images, each step is represented by a different shade. Some mounds appear to be 4 to 5 steps above the lowest observed layer of the film, while some small islands are observed that are only one step above the lowest layer of the film. This indicates the nucleation is not uniform across the entire film and the terrace structure and height is location dependent. This most likely arises from small gradients in solution.
concentration and temperature on the substrate surface during nucleation. The trace represented by a red line from the inset of Figure 4.6a in Figure 4.6b shows a terrace with three large steps that are ~2.5 nm in height, corresponding to roughly perpendicular Th-BTBT-C8 molecules in each terrace step. At the very top of the terrace structure there is a small step that appears as a peak that is ~0.8 nm, most likely corresponding to Th-BTBT-C8 molecules tilted on their side.

![Image](image.png)

**Fig. 4.6.** The AFM images of the island mounds of terraces shows that these structures are formed over large areas of the film with a non-uniform height, shape, and height (a). As seen in the inset of (a), on closer observation, many of the mounds may form at defect sites such as screw dislocations. A trace of the terraced mounds shows uniform layers with a height of ~2.5 nm (c). The small spike at the top of the terrace is ~0.8 nm and corresponds to the Th-BTBT-C8 molecules laying on their side. In the lower right of the inset in (a) a pair of terraces is observed, indicating that a screw dislocation may be present due to dislocation-assisted growth.

As discussed previously in 1.4.3, mound shaped terraces form due to the instability caused in the presence an edge-step (Ehrlich-Schwoebel) barrier (ESB). In the presence of an ESB, the inability of ad-molecules to diffuse to a lower layer creates an effective bias in upward diffusion.
Newly deposited molecules will be prevented from diffusing to a lower step resulting in the formation of mound shaped terraces. In controlled slow vacuum deposition of inorganic and organic materials, terraces are formed with uniform height, width, and concentration\textsuperscript{148}. In the case of solution processed mounds of Th-BTBT-C8, the deposition time scale is on the order of a few seconds rather than over minutes or hours. This significantly shorter time scale results in less uniform growth. In thin films of Th-BTBT-C8, it appears that the mounds grow starting on different layers, and the terrace height and width are variable. Further, as is the case in Figure 4.7a, many terraces grow in a spiral pattern or as is the case in the white box in Figure 4.6b, in pairs, which may be indicative of a screw dislocations commonly seen as films thicken under a dislocation-assisted growth mode\textsuperscript{72}. Now we will explore how concentration and temperature of the Th-BTBT-C8 solutions effects the formation of mound shaped terraces in an attempt to understand the driving force of mound formation in thin films of Th-BTBT-C8.

In an attempt to view the nucleation of the film and layer-by-layer growth of the Th-BTBT mounds out of CB, thin films were produced by spin coating dilute 1 mg mL\textsuperscript{-1}, 0.5 mg mL\textsuperscript{-1}, and 0.25 mg mL\textsuperscript{-1} solutions of Th-BTBT-C8 at 3000 rpm for 30s on clean glass substrates. The films were then observed under tapping mode AFM to reveal the surface morphology. In the thin films made from the 1 mg mL\textsuperscript{-1} and the 0.5 mg mL\textsuperscript{-1} solutions, the terrace mounds are still observed (Figure 4.7a, b). In the thin film made from the 0.25 mg mL\textsuperscript{-1} solution, a single layer that covers most of the substrate is observed (Figure 4.7c). It appears that at least in this region, the concentration has been diluted enough to suppress the formation of terrace mounds on the surface. The bright marks in the dark regions represent the glass surface as the bright specs seen in this area are similar to what is observed on bare glass, and this is the first monolayer on the glass surface. The edges of the layer show fractal patterns, which is further evidence of DLA. The fractal
The observation of Th-BTBT-C8 thin films in diluted concentrations of 1 mg mL\(^{-1}\) (a), 0.5 mg mL\(^{-1}\) (b), and 0.25 mg mL\(^{-1}\) (c) under tapping mode AFM. The thin film made from the 0.25 mg mL\(^{-1}\) solution shows a single layer with fractal-like layer edges, which is evidence of DLA. A height profile (white line in c) shows that the layer is \(~1.7\) nm thick due to a \(47^\circ\) tilt of the Th-BTBT-C8 molecules in the layer (d). A fractal analysis of the DLA growth in (c) gives a fractal dimension of 1.86 using a box count method over the white box outlined in (c).

Fractal dimension was determined to be \(D = 1.86\) using fractal dimension analysis using a box count, which matches closely with what is expected on coarsening of fractal geometry towards a fully covered surface \((D = 2)\) in DLA on a surface\(^{140}\). A trace of one of the spaces in the layer reveals \(~1.7\) nm step (Figure 4.6d). This indicates that the Th-BTBT-C8 molecules are not perfectly perpendicular to the surface and are tilted at \(~47^\circ\) to the surface normal. This is due to the interaction between the aromatic core and the polar glass surface. The tilted orientation near the substrate surface is likely only observed in the first few monolayers and has been observed...
previously\textsuperscript{74,139}. The observation of layers oriented closer to 90° to the surface in thicker films suggests that as subsequent layers grow, the orientation changes from tilted to perpendicular.

![AFM images of Th-BTBT-C8 thin films formed at different temperatures.](image)

**Fig. 4.8.** AFM images of Th-BTBT-C8 thin films formed at 25 °C (a), 60 °C (b), 90 °C (b), and 130 °C (d). The RMS roughness appears to slightly decrease in the thin films processed at elevated temperature compared to the thin film at room temperature (e). The change in RMS roughness may not be significant, indicating that temperature does not greatly impact thin film morphology in the solution processed CB films.

In thin film growth of Th-BTBT-C8, it is expected that the rate of diffusion on the surface, will determine how thin films begin to grow. The diffusion rate can be controlled by increasing the temperature of the substrate. At high temperatures, the surface diffusion is fast and ad-molecules move across the surface quickly to form fewer, large domains. As the film continues to grow, according to Monte Carlo simulations, the mounds will have a larger diameter with fewer steps\textsuperscript{149}, even if the ESB is the same at all temperatures. One would expect the extra thermal energy present in the system at higher temperatures to increase the rate of diffusion downward to lower
steps. To better understand the role of surface diffusion on thin film morphology the temperature of the solvent and substrate is varied. The choice to also heat the solution was to ensure that the entire system was at nearly the same temperature during the deposition process.

Th-BTBT-C8 thin films were made by spin coating 2 mg mL\(^{-1}\) CB solutions at 3000 rpm for 30 s at four different temperatures—25 °C, 60 °C, 90 °C, and 130 °C. The thin films morphology was analyzed under AFM. Figure 4.8 shows AFM images the thin film morphology at each temperature. There is no significant morphological change in in the thin films between different temperatures. In each film, terrace mounds are observed. The number and size of the mounds do not appear to drastically change at higher temperatures as expected. Taking RMS roughness values (Figure 4.8e) indicate that the roughness of the room temperature thin film is about twice that of the 60 °C and 90 °C temperature films (~8.5 nm to ~4.5 nm), but increasing the temperature beyond that does not appear to have a great effect on the overall morphology of the terraced mounds. In fact, that RMS roughness appears to increase to ~5.6 nm at 130 °C. This might be because at this temperature Th-BTBT-C8 exists in the SmE LC phase, which may slightly increase the disorder of the film on mound formation. This would indicate that in this system during the formation of terraced mounds, there may be no benefit to spin coating in a highly ordered LC phase to increase order in the thin film. The overall trend in the RMS roughness is most likely insignificant, indicating that temperature does not greatly impact the formation of the mound structures in Th-BTBT-C8 thin films.

To understand the evolution of the terraced mound structures that form in thin films of Th-BTBT-C8 out of CB and the disorganized crystallites that form in thin films of Th-BTBT-C8 out CF, the two solvents were mixed at definite volume fractions. Because CB and CF are miscible, the properties of the solvent mixture should change with the change in concentration of each of
the individual solvents. Thin films of Th-BTBT-C10, another Th-BTBT-Cn derivative, were made by spin coating out of the mixed solutions. The thin films were analyzed under AFM and grazing incidence wide angle x-ray scattering (GIWAXS) to study the morphological and structural properties of the thin films.

To first ensure the thin film morphology of Th-BTBT-C10 is similar to that of Th-BTBT-C8, thin films of Th-BTBT-C10 were made by spin coating 2 mg mL\(^{-1}\) solutions of CB and CF at 3000 rpm for 30 s on clean glass substrates. On observation under tapping mode AFM, it was confirmed that the surface morphology between the Th-BTBT-C10 and Th-BTBT-C8 is the same in both thin films. Seen in Figure 4.9a, the surface morphology of the CF film, large peaks and deep valleys define the surface. It appears that each domain is made up of mostly small crystallites. The surface morphology of the CB film (Figure 4.9b), the same terrace structure is observed. The terrace steps correspond to ~2.7 nm, equivalent to the molecular length of Th-BTBT-C10. This shows that these surface structures are consistent between Th-BTBT-Cn derivatives but also allows us to use either in future studies.

![Fig. 4.9. AFM images of the surface morphology of spin coated thin films of Th-BTBT-C10 out CF (a) and CB (b).](image)
4.4 Determining the Edge-Step Barrier in Th-BTBT-C10 Terraced Mounds from Chlorobenzene

With the formation of fairly uniform terraced mounds similar to what is observed in vacuum deposition of organic molecules, the ESB can be calculated. Using an analysis that was used on the small molecule OSC 6P,\textsuperscript{74,150} we calculate the ESB of Th-BTBT-C10 in spin coated thin films made from chlorobenzene solution. First, the nucleation density of the mound shaped terrace is dependent on the flux of incoming particles and the rate of diffusion on the surface which can be described by Equation 4.1. The nucleation density, \( N \), can be described by equation 4.1

\[
N \sim \frac{1}{\lambda^2} \sim \left( \frac{e}{i^*} \right)^{i*/D(i^*+2)}
\]

In Equation 4.1, \( \lambda \) is the average mound separation determined by the average mound radius, \( i^* \) is the nucleation density and \( D = 2 \) for a two-dimensional diffusion process. We will assume for our rough calculation that \( i^* = 1 \), though in reality that may not be the case. The edge-step hopping rate described by Equation 1.6 can determined by the top terrace diameter with the relationship in Equation 4.2

\[
l \propto \left( \frac{\nu}{F} \right)^{1/5}
\]

where \( l \) is the top terrace diameter. Equation 4.2 assumes that \( l \) is the largest diameter that a terrace will grow before a next layer will nucleate as a step. With experimental data for the mound density, the top step diameter, and the deposition rate of 8.4 nm/s, the additional barrier due to the ESB, \( \Delta E_{ES} \), is determined by combining Equations 4.1 and 4.2. After analyzing 219 terraced mounds over 11 images, we determined the mound separation to be 6.1 \( \pm \) 0.3 \( \mu \)m (assuming an average mound diameter of 5.6 \( \mu \)m and 500 nm between mounds and space filling packing) and the top step diameter to 1.11 \( \pm \) 0.06 \( \mu \)m, we calculate the additional ESB for the Th-BTBT-C10 terraced mounds to be 0.48 \( \pm \) 0.06 eV. The value of the ESB is slightly smaller than what has been
estimated for 6P from vacuum deposition on a mica substrate. The smaller calculated ESB is most likely due to the fact that the molecular length of Th-BTBT-C10 is ~0.3 nm less than 6P. Overall, this barrier is significant and plays a large role in the observation of terraced mounds in thin films of Th-BTBT-C10 made from chlorobenzene solution.

4.5 Solvent Mixture Studies of Th-BTBT-C10

Observation of the morphology of the thin films made from the other chlorobenzene and chloroform solvent mixtures under tapping mode AFM, reveals similar terraced mounds. The ratio

![Figure 4.10](image)

**Fig. 4.10.** The morphological evolution of Th-BTBT-C10 thin films in chlorobenzene and chloroform solvent mixtures (a) 100:0, (b) 80:20, (c) 60:40, (d) 40:60, (e) 20:80, and (f) 0:100. The inset in (f) shows disordered domains between the large oval structures in the thin film made from the 0:100 solution.
of area covered in tall terraces to short terraces appears to decrease between the thin film made from the 100:0 (Figure 4.10a), 80:20 (Figure 4.10b), and 60:40 solutions (Figure 4.10c). Though, the overall morphology appears to be fairly similar, it should be noted that terrace diameter does increase slightly as the chloroform concentration increases. In the thin film made from the 40:60 solution (Figure 4.10d), this changes drastically—terraced mounds have many more steps. The terraced mounds appear to have very tall prolate spheroid formations in some areas that are 20-30 nm in height. The thin film made from the 20:80 solution (Figure 4.10e) appears to have a significant shift in morphology. Only a few steps are observed on the underlaying surface, indicating that, at least to some extent interlayer mass transport was present during deposition, resulting in layer-by-layer growth. On the surface of the smooth film, prolate spheroid formations structures are also present. The structures are up to 100 nm tall and their height profiles reveal a general terraced mound shape, but single layers cannot be resolved. The prolate spheroid formations persist in the thin film made from the 0:100 solution, seen in Figure 4.10f. The prolate spheroid formations appear to be 150 nm in height. In between these peaks, small domains without any apparent layer structure is observed. This is confirmed in the inset of Figure 4.10.

We also characterized the internal molecular orientation of these specific morphologies using grazing incidence wide angle X-Ray Scattering (GIWAXS). In all of the thin films, two dimensional diffraction patterns show scattering only in the y-direction, indicating that the molecules are roughly perpendicular to the substrate (Figure 4.11a-f). The diffraction at wide angle due to interlayer ordering is much stronger in the thin film made from the 0:100 solution compared to the thin film made from the 0:100 solution. This suggests that a thin film made using chlorobenzene does not possess significant long range interlayer ordering and is substantially more amorphous within the molecular layers. Interlayer order is observed in the thin film made from the
20:80 solution mixture, but the scattering intensity is weak. The intensity of the wide angle scattering decreases as the chlorobenzene concentration increases.

With the goal of developing a model to describe the differences in observed morphology in the thin films, we calculate the average deposition rate during spin coating, given by the ratio of the thin film height to the spin coating dry time. The dry time for each solvent was measured optically. The thickness of a thin fluid layer can be estimated by its color due to the constructive interference of light reflecting off of the top and bottom surfaces of the layer. By timing how long it takes for an opaque SiO₂ on Si substrate covered in solution to change from green (color due to thin layer of solvent) to pinkish-blue (color of dry substrate) on spin coating can give an estimate

**Fig. 4.11.** GIWAXS diffraction patterns of Th-BTBT-C10. GIWAXS diffraction patterns of thin films of Th-BTBT-C10 spin coated from (a) 100:0, (b) 80:20, (c) 60:40, (d) 40:60, (e) 20:80, and (f) 0:100 solvent mixture. In all of the thin films, a layer structure is observed with scattering perpendicular to the substrate surface. In the 0:100 and to a lesser extent in the 20:80 thin film, diffraction at wide angles is observed, indicating that long range interlayer order exists.

With the goal of developing a model to describe the differences in observed morphology in the thin films, we calculate the average deposition rate during spin coating, given by the ratio of the thin film height to the spin coating dry time. The dry time for each solvent was measured optically. The thickness of a thin fluid layer can be estimated by its color due to the constructive interference of light reflecting off of the top and bottom surfaces of the layer. By timing how long it takes for an opaque SiO₂ on Si substrate covered in solution to change from green (color due to thin layer of solvent) to pinkish-blue (color of dry substrate) on spin coating can give an estimate
of the time it takes for a thin film to be deposited on a glass surface. From the average dry time calculated for each solvent mixture, it is determined that as the concentration of chloroform increases, the dry time decreases exponentially, as is seen in the plot in Figure 4.12a. This is expected as the boiling point is a good indicator of solvent volatility, and the boiling point of chloroform is 61 °C and the boiling point of chlorobenzene is 132 °C.

To determine the amount of material deposited in each thin film, the height of each film made from each of the solvent mixtures was measured. The film height was determined by scoring each film with a razor blade. The depth of each score was measured by tapping mode AFM. A plot of the concentration dependent height can be seen in Figure 4.12b. The height increases roughly linearly as the CB concentration decreases. The height of a thin film should increase with roughly a square root dependence on the solvent volatility. If we assume that the solvent volatility increases

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**Fig. 4.12.** The dry time and thin film thickness from each solution was determined. (a) The dry time the thin film on spin coating. (b) The film height as measured by AFM. (c) The calculation of average deposition rate during the spin coating process follows an exponential model shown with the dashed black line.
linearly as the chloroform to chlorobenzene ratio increases, we would expect to see a square root increase in the film height. This is not the case, confirming that the bulk solvent volatility, and thus, dry time does not change linearly as we change the concentration of the two solvents.

Given the film height and the effective deposition time, we can estimate the average deposition rate of the Th-BTBT-C10 molecules onto the surface during spin coating of each solvent mixture. A plot of the mixture dependent deposition rate of Th-BTBT-C10 onto the surface can be seen in Figure 4.12c. The increase in the flux as the 100:0 concentration decreases fits to an exponential model. This is due the trend observed in the dry time. Further, the average deposition rate is 8.4 nm/s in the 100:0 solution and 82.5 nm/s in the 0:100 solution. The Th-BTBT-C10 deposition rate is 10x higher in the chloroform solution. The difference in morphology for the thin films made from these two solvents is significant and consistent with these findings. Slower deposition should allow for larger domains to form, whereas in faster deposition, smaller domains will dominate the morphology.

Using deposition rate data, a simple model can be used to understand the variability in surface morphology. The morphology appears to be dependent on deposition rate, where extremely high deposition rates result in rough films with small domains. To understand this observation, we can compare the deposition rate versus a molecule’s residence time on a particular island. The residence time can be described using Equation 4.3, which can be thought of as the time a molecule spends on a particular terrace step,

\[ \tau = \left( \frac{aL^2}{\nu} \right) + \left( \frac{bL}{\nu'} \right). \]  

In equation 4.3, \( L \) is the particular island’s circumference, \( a \) and \( b \) are geometry dependent constants \( \nu \) and \( \nu' \) are the diffusion and step-edge hopping rates respectively. In this equation, the first term describes the residence time on a particular step due to diffusion and the second term...
describes the additional residence time due to an ESB. If we assume that the ESB does not change significantly between solvent systems and rather just the dynamics of the diffusion process, the only competing process to the formation of large, uniform domains is the deposition rate. The deposition rate directly determines the arrival rate of molecules to the surface which can be described using Equation 4.4,

\[ \Delta t = \frac{1}{FA}. \]  

(4.4)

Here, \( \Delta t \) is the time between arrival of the molecules, \( F \) is the deposition rate per unit area, and \( A \) is the area of the step. In vacuum deposition, \( \tau \) is significantly smaller than \( \Delta t \), however, in solution deposition, \( \Delta t \) is decreased significantly as the deposition time is drastically decreased.

We this model to both ends of the observed morphology sequence in Figure 4.10. In the thin film spin coated from chlorobenzene (Figure 4.10a), \( \tau \) is smaller than \( \Delta t \), explaining the well-defined terrace mound morphology. In the thin film spin coated from chloroform (Figure 4.10f), \( \tau \) must approach \( \Delta t \), explaining the large prolate spheroid formations. In this case, the molecules do not have time to diffuse on the surface to create large, terraced domains. Rather, each molecule nucleated in the thin film near where it was deposited and was subsequently fixed in place by molecules being deposited on top of it.

This effect can be quantified. Using the deposition rate in the two extreme cases, in the thin films formed from chlorobenzene and chloroform, average arrival times are determined to be \( \sim 0.12 \) s and \( \sim 0.01 \) s, respectively. While the Th-BTBT-C10 diffusion rate has not been determined, the residence time from Equation 4.3 will be dominated in both cases by the ESB. Using the calculated ESB of 0.48 eV and an average terrace step size of 1.11 \( \mu \)m, determined from the average top terrace width in the thin films made from the 100:0 solution, the residence time \( \tau \sim 0.006 \) s. This confirms that the arrival time of Th-BTBT-C10 is on the order of the residence time in the thin
films made from chloroform, whereas the average arrival time in the thin films made from chlorobenzene solutions is 10x the residence time. The order of magnitude difference in these two time scales can account for significant difference in morphology.

It is important to note that the arrival time calculated for thin films made from chlorobenzene is still $\sim10^3$ times greater than controlled vacuum deposition. This relatively fast deposition rate, coupled with fluctuations in both solvent concentration and substrate surface temperature, and surface defects result in the large degree of heterogeneity observed in the thin film morphology of spin coated Th-BTBT-C10 thin films. Overall, this simple model is successful in explaining differences in the morphologies observed between thin films spin coated from chloroform and chlorobenzene. However, due to the lack of a linear relationship between solvent concentration and deposition rate, this model fails to fully capture the minute differences in morphologies produced from solvent mixtures.

In addition to the model previously discussed for the simple case of pure chloroform and chlorobenzene solutions, we need to consider the relative diffusion rate on the surface during the formation of the first terrace step and the instantaneous deposition rate during spin coating to describe the morphologies produced from solvent mixtures. The increased size of terrace mounds observed in Figure 4.10b-c over Figure 4.10a suggests that the diffusion rate increases as the concentration of chloroform increases. The increased diffusion rate of molecules on the surface can be explained by solvent-surface interactions. The aromatic core in chlorobenzene will orient itself more closely to planar to the polar glass surface as has been previously observed on silica surfaces in simulations.\textsuperscript{151} Chloroform, on the other hand, does not interact with the glass surface as strongly, confirmed through the determination of the relative heats of adsorption of
chlorobenzene and chloroform on glass.\textsuperscript{152} Because the deposition rate is fairly constant and relatively slow, the increased diffusion rate results in larger terrace mounds.

In Figure 4.10d, the formation of large terrace steps is still observed; however, prolate spheroid formations are also observed on the top of terraces. This could be due to an increase in the deposition rate during the spin coating process, where at some point, the arrival time approaches the residence time on the terrace step. This effect is even more pronounced in Figure 3e where, because of the high concentration of chloroform, the diffusion rate is very high, but the time before the arrival time approaches the residence time is significantly decreased. This results in the formation of large terrace steps followed by large prolate spheroid formations. Overall, to better fit this behavior, further work needs to be done to more carefully quantify the instantaneous deposition rate during spin coating.

4.6 Trends in the Solvent Dependent Morphology of Th-BTBT-C8 and Th-BTBT-C10

Producing highly uniform thin films of OSCs for organic electronics applications is extremely important to improve device performance. Ideally, highly crystalline, smooth films produced by layer-by-layer growth are preferred. Frequently, however, terraced mounds form as layer-by-layer growth is presented with a sufficiently large ESB. We have attempted to understand how processing conditions effect the Th-BTBT-Cn thin film morphology and driving force the formation of terraced mounds. We then attempted to control the morphology of these mounds by making CB:CF solvent mixtures.

The formation of the terraced shaped mounds does not appear to be impacted by temperature, and while dilute solutions of Th-BTBT-C8 in CB appear to elucidate the thin film evolution, concentration of Th-BTBT-C8 in CB does not impact the overall mound structures that
are observed on the surface of the thin films. It is clear that the choice of solvent is important in controlling the thin film morphology, but that is not in itself noteworthy. The evolution of disorganized film growth in CF to terraced mounds in CB appears to stem from the relative volatility of each of the solvents and resulting deposition rate. In both CF and CB, the molecules prefer to stand up on deposition, which should, in theory, be preferable in the formation of terraced mounds, but the high deposition rate during spin coating from CF disallows diffusion and thus, smaller domains without clear terraces produces a rough surface. Even though the diffusion rate is expected to be higher in CF compared to CB, as evidenced by larger terraces and ultimately more uniform films in the 40:60 and 20:80 mixtures respectively, the arrival time of new material is too high in CF solutions to allow for large scale diffusion of the molecules on the surface.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling Point</th>
<th>Film Morphology</th>
<th>RMS Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF</td>
<td>61 ºC</td>
<td>Small, Rough</td>
<td>12.6</td>
</tr>
<tr>
<td>THF</td>
<td>66 ºC</td>
<td>Large Steps</td>
<td>10.6</td>
</tr>
<tr>
<td>Toluene</td>
<td>110 ºC</td>
<td>Terraced Mounds</td>
<td>4.9</td>
</tr>
<tr>
<td>CB</td>
<td>132 ºC</td>
<td>Terraced Mounds</td>
<td>2.0</td>
</tr>
<tr>
<td>DMF</td>
<td>153 ºC</td>
<td>Smooth, Steps</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 4.1. Summary of Th-BTBT-C8 thin film morphology by spin coating from different solvents

This evolution of thin film morphology can be observed further when looking at the other solvents studied. The Th-BTBT-C8 thin films produced from THF (B.P. = 66 ºC) show multiple steps that are multiple molecular lengths in height and the surface is also rough similar to the films produced out of CF. Again, the deposition rate in this low boiling point solvent is exceedingly high, resulting in a less than ideal thin film morphology. The formation of terraced mounds in thin films made from toluene (B.P. = 110 ºC) and eventual smooth thin films made from DMF (B.P = 153 ºC) follow this same trend. Table 4.1 summarizes the solvent-morphology relationship in Th-
BTBT-Cn films. This can also be seen in blade coated thin films of Th-BTBT-C8 in 1,2-dichlorobenzene (DCB) and 1,2,4-trichlorobenzene (TCB) in Appendix II.

4.7 Conclusion

This work has elucidated how Th-BTBT-Cn thin film morphology is impacted by solvent choice. Both CB and toluene gave terraced mound morphology indicative of an ESB. In terraced mounds of Th-BTBT-C8 made from a CB solution, the difference in the ESB was calculated to be 1.25 eV. To the best of our knowledge, this is the first time that clear, distinct terraced mounds have been seen out of spin coating from solvent in an organic thin film. The mixing of CB and CF gives more insight into the observed film morphologies and how they may arise. In mixing of CB and CF, further resulted in optimizing thin film morphology to form what appear to be uniform thin films made from roughly layer-by-layer growth. Future work needs to be done to better understand the evolution of the film growth out of solvent through in situ time resolved measurements. Also, this study can be expanded to other solvent systems and mixtures to gain a better understanding of the large variety of thin film morphologies observed. To understand if similar trends hold with other materials, similar solvent studies must be done.

5.1 BTBT Derivatives in Organic Field-Effect Transistors

OFETs are the most common device to characterize charge transport properties in OSC materials, and many BTBT derivatives have been characterized in these devices. As has been previously stated, the alkyl substituted BTBT derivatives are some of the most promising solution process OSC materials today. After a series of diakyl-BTBT derivatives were synthesized in 2007 and characterized in solution processed OFETs with charge carrier mobility values above 1 cm² V⁻¹ s⁻¹, many have attempted to improve upon the structure and device fabrication techniques to increase measured OFET mobilities. In 2014, C8-BTBT-C8 was used in OFETs with measured mobility values up to 34 cm² V⁻¹ s⁻¹. While, high mobility values are important for the eventual commercialization of organic electronics, it is also important to ensure that devices can be fabricated using simple solution processing techniques with few steps and materials.

We explored the thin film morphology of various Th-BTBT-C8 and Th-BTBT-C10 thin films in Chapter 4. We found that solvent choice is important in the formation of highly ordered thin films. This is especially true in Th-BTBT-C10 thin films produced from CB and CF mixtures. Terraced mounds dominate the morphology of thin films produced from CB solutions and small unorganized domains dominate the morphology of films produced from CF. The mixture of the two solvents produces more uniform thin films. In this chapter we will look at the charge transport properties of the thin films made from CB:CF solvent mixtures in OFETs. We then expand this study by characterizing OFETs fabricated with other BTBT derivatives synthesized by Dayan Wei in the Walba Laboratory.
5.2 Effect of Solvent Engineering on Charge Transport in Organic Field-Effect Transistors

To study the charge transport properties of Th-BTBT-C10, the charge carrier mobility in OFETs. Bottom gate, bottom contact OFETs (Figure 5.1a) were fabricated by thermally evaporating 5 nm of Cr and 45 nm of Au on SiO$_2$/Si$^{++}$ substrates through a shadow mask. The device channels varied in size with all combinations of $L = 200 \, \mu m$, $150 \, \mu m$, and $100 \, \mu m$ and $W = 1000 \, \mu m$, $2000 \, \mu m$, and $5000 \, \mu m$. The substrates were placed in a PFBT in isopropanol solution overnight to reduce the energy level mismatch. 2 mg mL$^{-1}$ solutions of Th-BTBT-C10 in the six solvent mixtures from Chapter 4 were spin coated at 3000 rpm for 30 s onto the OFET substrates. An image of OFET substrate after spin coating can be seen in Figure 5.1b. The OFETs were then characterized using a SPA. We investigated the Th-BTBT-C10 OFETs by extracting values for the hole carrier mobility in the linear and saturated regimes using Equation 2.5 and Equation 2.7 respectively. The threshold voltage and on/off ratios were also determined.

Both output and transfer characteristics were observed for each of the processing conditions. Sample curves for the 20:80 solvent mixture are displayed in Figure 5.2. In each of the conditions, the output curves increase linearly before saturating at higher gate voltages as expected.

![Fig. 5.1. A schematic of the bottom gate, bottom contact Th-BTBT-C10 OFET devices (a), and a picture of Th-BTBT-C10 OFETs on a SiO$_2$/Si$^{++}$ substrate (b).](image-url)
The transfer curves show a delayed turn on gate voltage, indicating that a significant threshold is present. This is greatly reduced from devices that do not use the PFBT SAM where devices were observed to have a $V_{Th} > -80$ V, though further work needs to be done to eliminate the observed threshold voltages. In the saturated regime, the square roots of the transfer characteristic plots appear to generally follow a linear trend.

![Image](image.png)

**Fig. 5.2.** Output (a) and transfer (b) characteristics for Th-BTBT-C10 OFETs made from the 20:80 solvent mixture. This device presented a saturated mobility of 0.325 cm$^2$ V$^{-1}$ s$^{-1}$.

In the devices spin coated out of CB, the average charge carrier mobility in the linear regime was determined to be $0.036 \pm 0.002$ cm$^2$ V$^{-1}$ s$^{-1}$ and $0.067 \pm 0.003$ cm$^2$ V$^{-1}$ s$^{-1}$ in the saturated regime. Similarly, the devices spin coated out of CF were determined to have a linear regime mobility of $0.036 \pm 0.002$ cm$^2$ V$^{-1}$ s$^{-1}$ and a saturated regime mobility of $0.081 \pm 0.010$ cm$^2$ V$^{-1}$ s$^{-1}$. In the OFETs made from the mixture of CB and CF, the charge mobility in both the linear and saturated regimes is higher than that in either solvent individually. The general trend is that...
the charge carrier mobility increases as the CF concentration increases until the 20:80 solvent mixture where the average linear regime charge carrier mobility was determined to be 0.166 ± 0.006 cm² V⁻¹ s⁻¹ and the average saturated regime charge carrier mobility was determined to be 0.323 ± 0.017 cm² V⁻¹ s⁻¹. The maximum observed saturated regime mobility was determined to be 0.446 cm² V⁻¹ s⁻¹. The 20:80 solvent mixture results in a ~4x increase in saturated mobility over either the CF or CB solutions (Figure 5.3a). To our knowledge, this is the first time that solvent mixtures have been employed in spin coating to improve the charge transport properties of a material in OFETs. A summary of the measured charge carrier mobility values, threshold voltages, and on/off ratios can be seen in Table 4.1.

![Graphs showing mobility and threshold voltage variations](image)

**Fig. 5.3.** The effect that thermal annealing has on the saturated mobility (a) and threshold voltage (b) on devices made from different solvent mixtures.

The average threshold voltages for these OFETs are all between -12.5 ± 1.0 V (devices made from CB solution) and -25.1 ± 0.6 V (40:60 solution). The threshold voltage appears to increase in devices as the CF concentration increases up to 40% of the solvent mixture then decreases again as the CF concentration continues to increase. However, the average threshold
voltage measured in the devices made from the CF solution is $-21.1 \pm 2.9$ V and larger than what is measured in the CB devices. The on/off ratio in these devices was determined by taking the maximum current at $V_G = -60$ V and dividing that by the average drain current when in the ‘off’ state when $V_G < V_{Th}$ (10 V to -5 V for most devices) taken in a separate measurement. The on/off ratio is channel dimension dependent as expected. In channels with small L and large W, the maximum drain current is higher than in channels with large L and small W. The observed on/off ratio in devices made from CF solutions is $> ~3 \times 10^5$ and $> ~4 \times 10^5$ in devices made from CB. In the devices made from 20:80 solvent mixtures the on/off ratio was increased to $> ~2 \times 10^6$. Maximum On/Off ratios were determined from channels with $W = 5000 \ \mu m$.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Linear Mobility (cm² V⁻¹ s⁻¹)</th>
<th>Saturated Mobility (cm² V⁻¹ s⁻¹)</th>
<th>Threshold Voltage (V)</th>
<th>Max On/Off</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td>0.0362 ± 0.002</td>
<td>0.0676 ± 0.003</td>
<td>-12.5 ± 1.0</td>
<td>3 x 10⁵</td>
</tr>
<tr>
<td>TA CB</td>
<td>0.0217 ± 0.011</td>
<td>0.0468 ± 0.024</td>
<td>-24.2 ± 6.0</td>
<td>4 x 10⁴</td>
</tr>
<tr>
<td>80:20</td>
<td>0.0162 ± 0.003</td>
<td>0.0276 ± 0.002</td>
<td>-19.2 ± 0.7</td>
<td>2 x 10⁵</td>
</tr>
<tr>
<td>TA 80:20</td>
<td>0.0013 ± 0.003</td>
<td>0.0034 ± 0.001</td>
<td>-22.3 ± 0.7</td>
<td>9 x 10³</td>
</tr>
<tr>
<td>60:40</td>
<td>0.1109 ± 0.014</td>
<td>0.1841 ± 0.020</td>
<td>-25.1 ± 0.6</td>
<td>1 x 10⁶</td>
</tr>
<tr>
<td>TA 60:40</td>
<td>0.0307 ± 0.007</td>
<td>0.0699 ± 0.014</td>
<td>-23.9 ± 0.8</td>
<td>5 x 10⁵</td>
</tr>
<tr>
<td>40:60</td>
<td>0.0731 ± 0.004</td>
<td>0.1487 ± 0.007</td>
<td>-21.5 ± 1.4</td>
<td>5 x 10⁵</td>
</tr>
<tr>
<td>TA 40:60</td>
<td>0.0375 ± 0.008</td>
<td>0.1055 ± 0.023</td>
<td>-20.5 ± 1.5</td>
<td>1 x 10⁵</td>
</tr>
<tr>
<td>20:80</td>
<td>0.1658 ± 0.006</td>
<td>0.3233 ± 0.017</td>
<td>-17.6 ± 0.6</td>
<td>2 x 10⁶</td>
</tr>
<tr>
<td>TA 20:80</td>
<td>0.1556 ± 0.011</td>
<td>0.3483 ± 0.023</td>
<td>-16.1 ± 0.8</td>
<td>2 x 10⁶</td>
</tr>
<tr>
<td>CF</td>
<td>0.0358 ± 0.002</td>
<td>0.0805 ± 0.010</td>
<td>-21.1 ± 2.9</td>
<td>3 x 10⁵</td>
</tr>
<tr>
<td>TA CF</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table 5.1.** Summary of Th-BTBT-C10 OFET statistics before and after thermal annealing (TA).

Thermal annealing has been employed countless times to improve the device characteristics of many polymer⁵³,¹⁴⁷ and small molecule⁵⁰,¹⁴³ OSC thin films by adding thermal
energy to relax kinetically trapped molecular orientations, thus improving overall film morphology. Here, thermal annealing of the devices for 5 min in Th-BTBT-C10’s SmE phase at 85 °C appears to decrease the charge carrier mobility in devices made from all solvent mixtures besides the 20:80 solvent mixture where the average saturated mobility increases slightly to 0.348 ± 0.023 cm² V⁻¹ s⁻¹ with the highest observed mobility of 0.484 ± cm² V⁻¹ s⁻¹. Further, thermal annealing increased the average threshold voltage in the devices made from the two highest concentration CB solutions but was lowered slightly in the devices made from the other three solvent mixtures. Overall, the threshold voltage decreases slightly as the CF solution concentration increases in the thermally annealed devices. The devices made from the CF solution did not work after the thermal annealing process. This trend can be observed in Figure 5.2b.

To better understand how the thermal annealing process effected the thin film morphology, the spin coated thin films of Th-BTBT-C10 were analyzed under tapping mode AFM after thermally annealing at 85 °C for 5 min. In the thin film made from the CF solution, the films do not appear to drastically change their surface morphology on thermal annealing and are very rough (Figure 5.3f). Large fractal patterns at lower step levels can be seen in the thin film made from the CB, indicating that the added heat during thermal annealing induces some rapid diffusion from higher terrace steps to lower regions (Figure 5.3a). In the 80:20 (Figure 5.3b) and 60:40 (Figure 5.3c) solvent mixtures, the lower steps seem to have coalesced but smaller regions of fractal patterns still remain. However, the thin films made from the 40:60 (Figure 5.3d) solvent mixture start to show small round domains that appear to fill in between the mounds. The thin films made from the 20:80 (Figure 5.3e) solution mixtures appear to have changed somewhat more drastically. The tall terraces have decreased in size and only a few steps are visible from the surface. In the thin film made from the 20:80 solution shows an even more uniform surface than its pre-annealed...
morphology. Small circular domains grow in rows between large flat domains of steps that are ~2.5 nm tall. Further, the tall terraced shaped crystallites observed on the surface have decreased in height from ~200 nm in the pre-annealed films to ~50 nm in the annealed films. This suggests that during the annealing process, the added thermal energy allows for molecules to diffuse down from the top of these tall terraces to the bulk of the film.

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**Fig. 5.4.** Tapping mode AFM images of the Th-BTBT-C10 thin films after thermal annealing for 5 min at 85 °C.
The improved thin film morphology in the film made from the 20:80 solution may explain the small increase in the charge carrier mobility observed after thermal annealing. However, the decrease in the other devices does not appear to follow any specific trend as molecules appear to diffuse to lower terrace steps in thin films made from all solvent mixtures except CF, though, to different extents. The reason for the decrease in the charge carrier mobility in these films could have to do with a change in molecular ordering at the SiO$_2$ surface and is not observable under AFM. To probe the differences observed in morphology between the pre-annealed and post-annealed films, top contact devices could be fabricated and characterized. While thermal annealing of the thin films does not appear to improve the device characteristics, the clear trend in charge carrier mobility does appear to generally be explained by the improvement in film quality in the 20:80 solvent mixture over the lower CF concentration solvent mixtures, CB, and CF. In thin films made from CB solutions, large separated terraced mound structure coupled with the ~10 total monolayers produced out of CB solutions may result in the low charge transport observed. The thin films made from CF appear to produce rough films with small domains that will inherently limit charge transport at boundaries. However, the high crystallinity observed in the thin films thin films made from CF results in the slightly higher average charge carrier mobility over the more amorphous, layered films made from CB.

Finally, the reliability factor was determined for each device and a summary is provided in Table 5.2. In general, the reliability factor is calculated to determine how well the model used to calculate the charge carrier mobility value fits the data with $r = 1$ being a perfect fit. Most of the devices have a reliability factor of $\sim 0.3 – 0.7$. Two general trends are observed. First, the average model used to calculate the saturated mobility does not fit the data as well as the model used to calculate the linear mobility across all solution mixtures. And second, the model used to calculate
the saturated mobility before and after thermal annealing follows a similar trend to that of charge

carrier mobility where the model fit is worsens in devices made from all solvent conditions except
in the 20:80 solvent mixture, which slightly improves (Figure 5.3a). Overall, however, no clear
and statistically significant trend is observed in the model fits before and after thermal annealing
for all solution mixtures.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Linear $r$</th>
<th>Saturated $r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td>0.67 ± 0.01</td>
<td>0.55 ± 0.02</td>
</tr>
<tr>
<td>TA CB</td>
<td>0.51 ± 0.01</td>
<td>0.31 ± 0.08</td>
</tr>
<tr>
<td>80:20</td>
<td>0.59 ± 0.01</td>
<td>0.43 ± 0.02</td>
</tr>
<tr>
<td>TA 80:20</td>
<td>0.58 ± 0.02</td>
<td>0.35 ± 0.01</td>
</tr>
<tr>
<td>60:40</td>
<td>0.43 ± 0.01</td>
<td>0.31 ± 0.01</td>
</tr>
<tr>
<td>TA 60:40</td>
<td>0.46 ± 0.01</td>
<td>0.32 ± 0.01</td>
</tr>
<tr>
<td>40:60</td>
<td>0.46 ± 0.01</td>
<td>0.34 ± 0.01</td>
</tr>
<tr>
<td>TA 40:60</td>
<td>0.48 ± 0.01</td>
<td>0.29 ± 0.02</td>
</tr>
<tr>
<td>20:80</td>
<td>0.53 ± 0.02</td>
<td>0.44 ± 0.01</td>
</tr>
<tr>
<td>TA 20:80</td>
<td>0.56 ± 0.02</td>
<td>0.45 ± 0.01</td>
</tr>
<tr>
<td>CF</td>
<td>0.53 ± 0.02</td>
<td>0.41 ± 0.02</td>
</tr>
</tbody>
</table>

Table 5.2. Summary of Th-BTBT-C10 OFET reliability factors before and after thermal annealing (TA).

Further, it is important to note that the reliability factor assumes that the threshold voltage
is 0 V, and the predicts a worse fit as the threshold voltage increases if all else is equal. This is
observed in both the linear and saturated regime in the pre-annealed devices where the reliability
factor increases linearly with as the threshold voltage decreases (Figure 5.3b), suggesting that the
high threshold voltages observed in the devices are the major contributing factor in the moderately
low observed reliability factors. This same trend is not observed in the post-annealed devices, and
thus indicates that the reliability factor is dependent on other non-idealities in the device itself.
This is further evidence that the thermal annealing process impacts a combination of both the bulk electronic structure, as well as, the contact with the source and drain electrodes.

Fig. 5.5. The reliability factor was calculated for each device to compare the calculated mobility to an ideal OFET curve with $V_{Th} = 0V$. The trend observed in the saturated regime reliability factor in devices before and after thermal annealing follows a similar trend to that of the calculated saturate mobilities (a). The reliability factor in pre-thermal annealed devices increases as threshold voltage decreases, suggesting that this is a major factor in the relatively low calculated reliability factors (b).
5.3 Liquid Crystal Phase Characterization of Three BTBT Derivatives

Three other BTBT derivatives were used to confirm how the use of solvent mixture systems impacts charge transport in a variety of structures. Each of these materials were synthesized by Dayan Wei in the Walba Lab. First, we look at two dialkyl substituted BTBT derivatives—the classic soluble BTBT derivative\textsuperscript{153}, C8-BTBT-C8 and C7O-BTBT-C8 that substitutes one of the C8 carbon groups with a septoxy- group. To then compare the result from Th-BTBT-C10 with another monoalkyl substituted BTBT derivative—Ph-BTBT-C8. The chemical structures of each of these materials can be seen in Figure 5.6.

\textbf{Fig. 5.6.} POM images and phase transition temperatures taken from DSC scans for C8-BTBT-C8 (a), Ph-BTBT-C8 (b), and C7O-BTBT-C8 (c). Data was collected by Dayan Wei.
Each of these materials display LC phases thermally above the crystal phase at room temperature. While C8-BTBT-C8 has been previously synthesized and characterized, to the best of our knowledge Ph-BTBT-C8 and C70-BTBT-C8 are novel materials and were characterized by Dayan Wei and will be summarized here. Both POM and phase transition temperatures taken from DSC data can be seen in Figure 5.6. Each of the materials exhibits smectic phases as is the case in many alkyl-substituted BTBT derivatives. C8-BTBT-C8 (Figure 5.6a) exhibits only the SmA phase on heating, between 110 °C and 126 °C, and on cooling between 125 °C and 99 °C. C70-BTBT-C8 (Figure 5.6c) exhibits the more ordered SmG LC phase, which can be thought of as a tilted SmE phase. On heating of C70-BTBT-C8, a crystal to SmG transition at 101 °C, SmG to SmA transition at 108 °C, and a SmA to isotropic transition at 149 °C is observed. On cooling, an isotropic to SmA transition at 147 °C, SmA to SmC transition at 121 °C, SmC to SmG transition at 105 °C, and a SmG to crystal transition at 83 °C are all observed. The SmC phase appears to be monotropic. In the monoalkyl-substituted BTBT derivative, Ph-BTBT-C8 (Figure 5.6b), the SmE phase is observed. On heating a crystal to SmE transition at 151 °C, SmE to SmA transition at 216 °C, and SmA to isotropic transition at 230 °C is observed. On cooling an isotropic to SmA transition at 229 °C, a SmA to SmE transition at 214 °C both are observed. However, on further cooling, a glass transition is observed at 66 °C.

5.4 Characterization of BTBT Derivative Organic Field-Effect Transistors

To characterize these materials we fabricated bottom gate, bottom contact OFETs. First, 5 nm of Cr and 45 nm of Au were thermally evaporated onto clean SiO2/Si++ substrates. The substrates were then placed in a 5 mM solution of PFBT in isopropanol overnight. 2 mg mL⁻¹
solutions of each of the three materials were made in each of CB, 20:80, and CF and spin coated at 3000 rpm for 30 s onto the substrates. Device characteristics were analyzed on a SPA.

Bother output and transfer characteristics were collected for each processing condition. Example characteristics from the devices made from Ph-BTBT-C8 spin coated from the 20:80 solvent mixture can be seen in Figure 5.7. The output characteristics for all of the devices appear to show OFET behavior and current increases linearly at low source-drain voltages before saturation is observed at higher source-drain voltages (Figure 5.7a). Just as with the Th-BTBT-C10 devices, the transfer characteristics in the saturated regime show a delayed turn on voltage indicating that there is a significant threshold voltage. The observed threshold voltage is extremely variable between processing conditions even in the same material. In the saturated regime transfer characteristics, the square root of the drain current appears to be linear with respect to increasing drain-source voltage (Figure 5.7b).

After analyzing data from over 200 devices, it appears that in both C8-BTBT-C8 and C7O-BTBT-C8, the films made from CB solutions give the highest calculated charge carrier mobilities. In C8-BTBT-C8 the calculated charge carrier mobility is 0.661 ± 0.161 cm² V⁻¹ s⁻¹ in the linear regime and 0.945 ± 0.247 cm² V⁻¹ s⁻¹ in the saturated regime. In C7O-BTBT-C8, the calculated charge carrier mobility is significantly lower than in C8-BTBT-C8 and is 0.016 ± 0.002 cm² V⁻¹ s⁻¹ in the linear regime and 0.0324 ± 0.003 cm² V⁻¹ s⁻¹ in the saturated regime. There is not a clear trend between the other two solvent combinations for the dialkyl-BTBT derivatives but the average mobility values calculated were significantly lower than in CB. In Ph-BTBT-C8, however, the 20:80 solvent mixture gives the highest charge carrier mobility and was determined to be 0.102 ± 0.011 cm² V⁻¹ s⁻¹ in the linear regime and 0.139 ± 0.014 cm² V⁻¹ s⁻¹ in the saturated regime. Further, the devices made with CB have a higher calculated mobility than CF, but the mobility values are
lower than in the devices made from the 20:80 solvent mixture. A summary of the trends in mobility observed between chosen solvent mixtures can be seen in Table 5.3.

As mentioned previously, the threshold voltage appears to be material dependent as is expected. Also, in each of the three materials tested, devices made from CF exhibit a higher threshold voltage than either the CB or 20:80 solvent mixture. This trend can be seen in Table 5.3 and displays the importance of solvent choice on not only the charge transport properties of the thin film and charge carrier mobility, but also threshold voltage. Because there is not a clear trend between the threshold voltage between devices made from CB and 20:80, the desired solvent might need to weigh both desired threshold voltage and charge carrier mobility. We acknowledge that the measured threshold voltages are significantly higher than desired in OFET devices. The high threshold voltage in many devices makes them impractical in commercial applications, and more work can be done to minimize threshold voltage in these devices in future work. On/off ratios were

![Fig. 5.7. Output (a) and transfer (b) characteristics of the OFETs made from the 20:80 solvent mixture solution for Ph-BTBT-C8 derivative.](image-url)
also calculated for all devices from all materials and solvent combinations. The maximum On/Off ratios were determined from channels with $W = 5000 \, \mu m$.

<table>
<thead>
<tr>
<th>Material / Solution</th>
<th>Linear Mobility (cm² V⁻¹ s⁻¹)</th>
<th>Saturated Mobility (cm² V⁻¹ s⁻¹)</th>
<th>Threshold Voltage (V)</th>
<th>Max On/Off</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7O / CF</td>
<td>0.025 ± 0.007</td>
<td>0.022 ± 0.003</td>
<td>-23.6 ± 0.4</td>
<td>1 x 10⁵</td>
</tr>
<tr>
<td>C7O / 20:80</td>
<td>0.014 ± 0.006</td>
<td>0.016 ± 0.002</td>
<td>-21.2 ± 1.2</td>
<td>9 x 10⁴</td>
</tr>
<tr>
<td>C7O / CB</td>
<td>0.016 ± 0.002</td>
<td>0.032 ± 0.002</td>
<td>-20.8 ± 0.8</td>
<td>9 x 10⁴</td>
</tr>
<tr>
<td>C8 / CF</td>
<td>0.054 ± 0.007</td>
<td>0.107 ± 0.012</td>
<td>-31.7 ± 0.4</td>
<td>4 x 10⁴</td>
</tr>
<tr>
<td>C8 / 20:80</td>
<td>0.156 ± 0.029</td>
<td>0.173 ± 0.03</td>
<td>-13.7 ± 1.0</td>
<td>1 x 10⁶</td>
</tr>
<tr>
<td>C8 / CB</td>
<td>0.661 ± 0.161</td>
<td>0.945 ± 0.247</td>
<td>-28.7 ± 1.5</td>
<td>3 x 10⁷</td>
</tr>
<tr>
<td>Ph / CF</td>
<td>0.005 ± 0.001</td>
<td>0.013 ± 0.001</td>
<td>-26.5 ± 1.0</td>
<td>8 x 10⁴</td>
</tr>
<tr>
<td>Ph / 20:80</td>
<td>0.102 ± 0.011</td>
<td>0.139 ± 0.015</td>
<td>-13.4 ± 0.7</td>
<td>7 x 10⁵</td>
</tr>
<tr>
<td>Ph / CB</td>
<td>0.031 ± 0.004</td>
<td>0.055 ± 0.006</td>
<td>-16.2 ± 0.4</td>
<td>5 x 10⁵</td>
</tr>
</tbody>
</table>

Table 5.3. Summary table of BTBT derivative OFET statistics made from different solutions.

The reliability factor for each device was also determined and averaged and are summarized in Table 5.4. Overall, the model used to calculate the charge carrier mobility in these devices appears to fit the data worse. The $r$ values for both the linear regime and the saturated regime span $\sim 0.2 – 0.6$. The reason for this, just as in the Th-BTBT-C10 OFETs is most likely due to the very large threshold voltages observed in many of the devices. For practical applications of these materials in organic electronics, work must be done to reduce the threshold voltage. It is even important to reduce the threshold voltage in all devices to determine more representative and consistent mobility values in these bottom gate, bottom contact devices.

The trend seen in mobility between solvents further elucidates a trend first observed in Th-BTBT-C10 as the increase in saturated charge carrier mobility in devices made with the 20:80 solvent mixture of Ph-BTBT-C8 was $\sim 2.5x$ that of devices made from CB and over 10x that of devices made from CF. This trend, however, was not seen in either of the dialkyl-BTBT
derivatives—C8-BTBT-C8 or C7O-BTBT-C8. On the other hand, each did show generally that CB is a significantly better solvent in the fabrication of dialkyl-BTBT OFETs over CF. This is most likely due to the relative solvent dry time in both solvents, though more work needs to be done to better understand this relationship. In the monoalkyl-BTBT derivatives, Ph-BTBT-C8 and Th-BTBT-C10, where the 20:80 solvent mixture produced the best quality OFETs, suggests that in both cases, the thin film morphology is greatly improved by the mixture of solvents.

<table>
<thead>
<tr>
<th>Material / Solvent</th>
<th>Linear r</th>
<th>Saturated r</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7O / CF</td>
<td>0.41 ± 0.02</td>
<td>0.36 ± 0.01</td>
</tr>
<tr>
<td>C7O / 20:80</td>
<td>0.57 ± 0.02</td>
<td>0.41 ± 0.02</td>
</tr>
<tr>
<td>C7O / CB</td>
<td>0.49 ± 0.01</td>
<td>0.43 ± 0.01</td>
</tr>
<tr>
<td>C8 / CF</td>
<td>0.34 ± 0.02</td>
<td>0.18 ± 0.01</td>
</tr>
<tr>
<td>C8 / 20:80</td>
<td>0.43 ± 0.02</td>
<td>0.57 ± 0.02</td>
</tr>
<tr>
<td>C8 / CB</td>
<td>0.36 ± 0.03</td>
<td>0.25 ± 0.03</td>
</tr>
<tr>
<td>Ph / CF</td>
<td>0.43 ± 0.02</td>
<td>0.31 ± 0.02</td>
</tr>
<tr>
<td>Ph / 20:80</td>
<td>0.63 ± 0.01</td>
<td>0.63 ± 0.02</td>
</tr>
<tr>
<td>Ph / CB</td>
<td>0.59 ± 0.01</td>
<td>0.54 ± 0.01</td>
</tr>
</tbody>
</table>

Table 5.4. Summary of the reliability factor (r) in the BTBT derivative OFETs from different solutions.

A comparison of the optical textures of both Th-BTBT-C10 and Ph-BTBT-C8 on SiO2/Si++ substrates in films made from the 20:80 solvent mixtures and CB can further explain the observed difference in measured charge carrier mobility. Figure 5.8 shows the drastic change in morphology between the films made from each solvent. In the films made from 20:80 solvent mixtures show large visible domains that are 50-100 µm in diameter, whereas in the films made from CB show a uniform, film with no defining features. These large domains that come close to spanning the entire length of these channels may explain the large increase in charge transport properties in these devices. More work needs to be done, however, to fully characterize the thin films of Ph-BTBT-C8 made from CB:CF solvent mixtures.
Finally, we attempted to fabricate bottom gate, bottom contact OFETs with each of the BTBT derivatives by spin coating in their respective LC phases out of CB. Theoretically, during the spin coating process, as the film coalesces and the solvent dries, the high temperature promotes a well ordered layer structure with few cracks and pinholes as observed previously in C10-BTBT-C10. To do this, 2 mg mL\(^{-1}\) CB solutions of each material, OFET substrate, and pipet tip were heated above each material’s respective glass/crystal transition temperature observed on cooling. Then devices were fabricated by removing the substrate from the hot plate and spin coating as quickly as possible. This fabrication technique led to devices that did not work in most materials, but the Th-BTBT-C10 and C8-BTBT-C8 devices did work. Preliminary results were taken from these devices. The C8-BTBT-C8 devices showed a significant drop in charge carrier mobility.

**Fig. 5.8.** Optical images of OFET channels with a W = 5000 µm and L = 100 µm. A significant difference can be seen between the morphology between the thin films made from the 20:80 solvent mixture and CB in both Ph-BTBT-C8 (a, b) and Th-BTBT-C10 (c, d). In the films made from the 20:80 solvent mixture, large domains that span up to 100 µm in diameter are observed.
compared to devices fabricated at room temperature. The saturated regime mobility was determined to be $0.127 \pm 0.017 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ compared to $0.945 \pm 0.247 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ reported in 5.3. In the case of the Th-BTBT-C10 devices, the saturated regime mobility was determined to be $0.086 \pm 0.247 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a slight increase in mobility over what is reported at room temperature in 5.2 ($0.068 \pm 0.003 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). To this point, this data is inconclusive. More work needs to be done to determine if spin coating at LC temperatures is ubiquitous in improving the thin film morphology and electrical properties in OFETs over spin coating at room temperature in dialkyl-BTBT and monoalkyl-BTBT derivatives.

5.5 The Use of Solvent Engineering to Improve Charge Transport in Dialkyl-BTBT Derivatives

We characterized OFETs fabricated by spin coating two monoalkyl-BTBT and two dialkyl-BTBT derivatives out of various solvent systems. The various solvent systems produced thin films from spin coating with a range of charge transport properties. First, a series of solvent mixtures of CB and CF were used with Th-BTBT-C10, resulting in a clear trend that shows improved device characteristics in the solvent mixtures, with the 20:80 mixture giving devices with saturated charge carrier mobilities up to $0.403 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. To the best of our knowledge, this is the first time that the use of solvent mixtures have been used to improve the charge transport properties in spin coated organic thin films. On thermal annealing of the 20:80 film only, an increase in saturated charge carrier mobility was observed up to $0.476 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This effect was not seen in other mixtures, and more work needs to be done to completely understand this as AFM shows improved domain size and quality of the thin films after thermal annealing.

To better understand the trend observed in Th-BTBT-C10, another monoalkyl-BTBT derivative, Ph-BTBT-C8, and two dialkyl-BTBT derivatives, C8-BTBT-C8 and C7O-BTBT-C8
were studied in OFETs. Three solvent systems—CB, 20:80, and CF—were used to spin coat each material. In both dialkyl-BTBT derivatives, the films made from CB have the best charge transport properties. In Ph-BTBT-C8, the film made from 20:80 solvent mixtures have the best charge transport properties, which follows the same trend observed in Th-BTBT-C10. Further, the two films appear optically similar with large domains. This indicates that this technique of solvent mixing can help to improve the mobility in monoalkyl-BTBT derivatives through improvement of thin film morphology and increased domain sizes.

Much more work can be done to study other solvent mixtures with new solvents. This process can be optimized on a material by material basis. It would be worthwhile to further explore how the LC ordering can improve charge transport in Th-BTBT-Cn materials. This can be compared to existing results from Ph-BTBT-C10 and C10-BTBT-C10\textsuperscript{49}. Processing at LC temperatures should, in theory, improve the charge carrier mobility in at least the monoalkyl-BTBT derivatives. This processing technique can also be explored in solvent mixtures to further improve device performance. Still, using solvent mixtures to improve charge transport properties in OSCs looks to be a promising future avenue in solution processing.
6 SUMMARY AND CONCLUSIONS: MOLECULAR ALIGNMENT AND MORPHOLOGY CONTROL TECHNIQUES FOR LIQUID CRYSTAL ORGANIC SEMICONDUCTORS

In this work we investigated both liquid crystal alignment techniques and thin film processing conditions to control molecular alignment and morphology through both a soft lithography printing technique and the more traditional solution processing spin coating technique.

The use of PDMS microchannel molds proves to be a successful technique to produce consistent molecular orientation and alignment in HNFs of NOBOW parallel to the microchannel direction. Studies that look at the molecular anchoring of NOBOW on PDMS in LC cells show that the molecule align homeotropic to the PDMS surface in the B2 and B3 phases. This alignment also introduces strong tail-PDMS interactions, resulting in a somewhat large energy barrier during transition to the HNF phase. This causes overcooling and subsequent spherulite nucleation. When confined in large aspect ratio microchannels, the nucleation is the same as in LC cells, but the nucleation is physically confined to the microchannels causing bulk HNF alignment. More needs to be done to understand the ordering in in the microchannels by doing more to change the PDMS microchannel environment. However, as the goal of this work is to align HNFs for organic electronics applications, future work must include fabrication and characterization of freestanding HNF microchannels in OFETs.

A study into the solvent dependent morphology in spin coated thin films of Th-BTBT-C8 and Th-BTBT-C10 resulted in the observation of terraced mounds that are frequently observed in vacuum deposition of OSCs but not from solution. Further studies that probed deposition time, temperature, and solution composition help elucidate why terraced mounds form out of solvent in CB and toluene but not CF, THF, or DMF. Terraced mounds appear to form when the deposition
rate and diffusion rate of the molecules on the surface are slow. Likewise, a more disordered film with small domains is observed when the residence time is comparable to the arrival time during deposition even if the diffusion rate is high. Mixtures of CB and CF show the progression between terraced mounds and disordered films. A solvent mixture of 20:80 appears to give smooth morphology, most likely due to fast diffusion rate and a slow enough deposition time to allow for the diffusion to form uniform thin films. More work needs to be done to characterize the internal and chemical structure of these thin films, as well, as the evolution of the thin film formation on deposition in real time using spectroscopic techniques. Work can also be done to explore the thin film morphology in other solvents and solvent mixtures, as well as with other OSC materials. Further work can be done to observe the morphology of thin films processed at LC temperatures.

The spin coated thin films of Th-BTBT-C10 made from CB:CF solvent mixtures were electrically characterized in OFETs. A trend in the measured charge carrier mobility of the films appears to coincide with the observed surface morphologies. The thin film made from 20:80 was determined to have the highest charge carrier mobility and overall best device characteristics. To expand this, two dialkyl-BTBT derivatives and one other monoalkyl-BTBT derivate were characterized in OFETs with various CB:CF mixtures. It appears that the monoalyl-BTBT derivative shows a similar trend as Th-BTBT-C10, suggesting that the use of solvent mixture engineering can be used to improve solution processed OFET performance in monoalkyl-substituted materials. More work could be done to fully characterize devices processed at temperatures where the material exhibits highly ordered LC phases. Further work needs to be done, however, to expand upon the trend seen in the solvent mixtures by changing solvent mixture composition and also material motif.
As the field of organic electronics become viable for commercialization, it is ever important to explore simple processing techniques that maximize molecular order and ultimately the electronic structure. The work presented in this dissertation, while just in its beginning stages, appears to do this in two ways. First, it uses a previously used technique in soft lithography to print well-aligned exotic nanowire structures. Second, it develops a new technique in solvent mixture engineering to improve not only thin film morphology, but also charge transport in OSC materials. Future work can improve upon and expand these techniques, leading to not only a better understanding of how to improve alignment and morphology in OSCs, but also to produce high performing organic electronic devices.
APPENDIX I: MATERIALS AND EXPERIMENTAL METHODS

7.1 Materials

All LC materials studied with the exception of 8CB were synthesized in the Walba Lab at the University of Colorado, Boulder. The phase properties and transition temperatures were found or confirmed by the Walba and Clark Labs at the University of Colorado, Boulder. A summary of the materials used and their phase transitions can be found in Table 7.1.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Phase Transitions on Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOBOW</td>
<td>Iso (172°C) B2 (145°C) B3 (138°C) HNF</td>
</tr>
<tr>
<td>8CB</td>
<td>Iso (41 °C) N (34 °C) SmA (22 °C) Cr</td>
</tr>
<tr>
<td>Th-BTBT-C8</td>
<td>Iso (241 °C) SmA (222 °C) SmE (50 °C) Glass</td>
</tr>
<tr>
<td>Th-BTBT-C10</td>
<td>Iso (235 °C) SmA (218 °C) SmE (73 °C) Glass</td>
</tr>
<tr>
<td>C8-BTBT-C8</td>
<td>Iso (125°C) SmA (99°C) Cr</td>
</tr>
<tr>
<td>7O-BTBT-C8</td>
<td>Iso (147 °C) SmA (121 °C) SmC (105 °C) SmG (83 °C) Cr</td>
</tr>
<tr>
<td>Ph-BTBT-C8</td>
<td>Iso (229 °C) SmA (214 °C) SmE (66 °C) Glass</td>
</tr>
<tr>
<td>W586</td>
<td>Iso (155 °C) SmA (136 °C) SmAPF (80 °C) Cr</td>
</tr>
<tr>
<td>W624</td>
<td>Iso (142 °C) B2 (138 °C) DC</td>
</tr>
<tr>
<td>W789</td>
<td>Iso (252 °C) N (245 °C) SmA (240 °C) SmAP (205 °C) HNF</td>
</tr>
<tr>
<td>W899</td>
<td>Iso (129 °C) HNF</td>
</tr>
</tbody>
</table>

Table 7.1. Summary of liquid crystal materials and phase transitions studied.

7.2 Polydimethylsiloxane Sample Preparation and Characterization

7.2.1 Polydimethylsiloxane Alignment Layer in Liquid Crystal Cells

Glass microscope slides were first cut into three sections that measured about 2.5cm by 2.5cm. The substrates were then sonicated in acetone and isopropyl alcohol for 10min each, and
dried using a stream of N₂. A 250 µL sample of a 10:1 mixture of PDMS to curing agent was spin coated onto the cleaned substrates for 30s at 6000 rpm and baked for 48 h at 80 °C. Substrates were made into LC cells by placing 3.14µm silica spacers and UV cured polymer “glue dots” on the PDMS coated sides of the substrates. The polymer was cured under 254 nm light for 30 min. The cells were filled by placing neat BCLC material on the edge of the cell and heated to isotropic. The isotropic material filled the cell using capillary force. When the cells were adequately filled, they were cooled to room temperature.

7.2.2 Polydimethylsiloxane Microchannel Mold Preparation

Silicon substrates were etched by collaborators of the Yoon group at KAIST to form 1cm long microchannels with profile dimensions of 10 µm by 5 µm, 5 µm by 10 µm, 3 µm by 10 µm, and 5 µm by 5 µm in height and width respectively. The substrates were then cleaned by sonication in acetone, isopropyl alcohol, and deionized water. The substrate surface was then treated by atmospheric plasma for 15 min. Following cleaning, the substrates and 200 µL of tridecafluoro-1,1,2,2-tetrahydrooctyltrichloro-silane (F-OTS) were place in a vacuum sealed desiccator for 2 hours to obtain the desired surface energy and then baked at 210 °C for 2 h. Samples were then taped to the bottom of a petri dish with double sided tape and a 10:1 mixture of polydimethylsiloxane (PDMS) and curing agent (SYLGARD 184, Dow Corning) were poured over the top and leveled. The samples were left to rest in ambient conditions to let air bubbles formed during mixing to dissipate. The petri dish was then baked at 80 °C for 2 h to allow the polymer mixture to cure. The PDMS molds were then cut out and removed from the substrate, exposing negatives of the etched microchannels.
7.2.3 Freestanding NOBOW Microchannel Sample Preparation

A PDMS mold was placed on top of a microscope cleaned with acetone. Neat NOBOW was placed at the open edge of the microchannels. The glass slide and mold were placed onto a hot stage and heated to 195 °C until the NOBOW melted and filled the microchannels using capillary force. The mold was then moved so that the edge was placed just over the edge of the hot stage and the sample was cooled to room temperature. During this process, a weight was placed on top of the mold to ensure contact of the mold to the glass substrate during cooling. Once cooled, the mold was carefully removed to expose the microchannels on the microscope slide.

7.2.4 NOBOW:8CB Mixture Sample Preparation

Five samples of NOBOW:8CB mixtures were made by mixing the following ratios of NOBOW and 8CB in a glass vial: 70% NOBOW to 30% 8CB, 50% NOBOW to 50% 8CB, 30% NOBOW to 70% 8CB, 20% NOBOW to 80% 8CB, and 10% NOBOW to 90% 8CB. The vial was then heated to 195 °C and stirred with a spatula. Before the sample could cool, it was centrifuged for 1 min at 3000 rpm. This process was repeated three times.

7.2.5 Miniature Cell Fabrication

Both glass and PDMS cells were made to fit into small aluminum DSC pans. For the glass cell, a glass cover slip cleaned in acetone was cut into small square pieces 3 mm by 3 mm. One piece was placed onto a hot plate and heated to ~195 °C and NOBOW was placed on top. After NOBOW melted, the second glass plate was placed on top, and the cell was removed from the hot plate. Likewise, the PDMS cell was made by curing a thin layer 10:1 PDMS to curing agent
mixture at 80 °C for 2 h in a plastic petri dish. Small 3 mm by 3 mm squares were cut from the cured PDMS layer. The PDMS cell was made similarly to the glass cell.

7.2.6 PDMS Cell and Microchannel Sample Characterization

Microchannel and PDMS LC cell textures were observed under crossed polarizers with a DSLR camera on a Nikon Optiphot 2 POL microscope equipped with an INSTEC temperature controlled hot stage. Images of the exposed microchannels were captured at room temperature, and images of the microchannels at higher temperatures were captured while the PDMS mold was still on the glass slide or while the PDMS microchannels were filled and rotated so that they were exposed to air. X-ray diffraction patterns of the microchannels were collected using a transmission small angle x-ray scattering technique where a sample on 50µm glass was exposed to an 8.05 keV x-ray beam over a 6 hour exposure time. AFM images of the microchannels were observed an Asylum Research MFP-3D atomic force microscope. Both HQ:NSC14/Al BS and HQ:CSC17/Al BS Mikromasch AFM tips were used to image sample surfaces in tapping mode. DSC curves were collected by placing miniature glass and PDMS cells into an aluminum testing pan. The pan was placed in a Mettler Toledo DSC 823 and heated to 185 °C and held for 5 min and cooled to 25 °C and held for 5 minutes twice—at a heating and cooling rate of 10 °C min⁻¹ and 5 °C min⁻¹.

7.3 Thin Film Sample Preparation and Characterization

7.3.1 Th-BTBT-C8 and Th-BTBT-C10 Thin Film Preparation

Glass microscope slides were diced into roughly 1cm by 1cm sections with a diamond scribe. The glass substrates were then cleaned in a 1% Hellmanex detergent in water solution and
deionized water followed by acetone and isopropyl alcohol. In between each step, the substrates were dried using compressed air. The cleaned substrates were then treated with O₂ plasma for about 5 minutes.

Multiple solutions of Th-BTBT-C8 and Th-BTBT-C10 were made with various concentrations and solvents. Multiple solutions of different concentrations of Th-BTBT-C8 and Th-BTBT-C10 in chloroform (CF), chlorobenzene (CB), and tetrahydrofuran (THF) were made. Further, Th-BTBT-C8 and Th-BTBT-C10 were dissolved in CB:CF mixtures to make 2mg/mL solutions that were 80%:20% CB:CF, 60%:40% CB:CF, 40%:60% CB:CF, and 20%:80% CB:CF. Th-BTBT-C10 was also dissolved in toluene and dimethylformamide (DMF) to make 2 mg mL⁻¹ solutions. Solutions were heated to 50 °C for 1 h to mix.

The solutions of Th-BTBT-C8 and Th-BTBT-C10 were spin coated onto the glass substrates inside of a glovebox with an N₂ atmosphere at room temperature. Spin coating speed and ramp time were varied, but spin time was held constant at 30 seconds. Samples were spin coated in a saturated solvent vapor atmosphere confined to the spin coating chamber.

7.3.2 Characterization of Th-BTBT-Cn Thin Films

Both Th-BTBT-C8 and Th-BTBT-C10 thin films were analyzed under crossed polarizers on a Nikon Optiphot 2 POL microscope equipped with an INSTEC temperature controlled hot stage. The exposure was increased to view the thin films and images were captured with a CCD camera. AFM images were taken using an Asylum Research MFP-3D atomic force microscope. Both HQ:NSC14/Al BS and HQ:CSC17/Al BS Mikromasch AFM tips were used to image sample surfaces in tapping mode. X-ray diffraction patterns of the thin films were collected using
GIWAXS where a sample on glass was exposed to an 8.05 keV x-ray beam over a 3 h exposure time at an oblique angle. The diffraction patterns were collected with a detector.

7.4 Organic Field-Effect Transistor Sample Preparation and Characterization

7.4.1 Bottom Contact Th-BTBT-C10 Thin Film Organic Field-Effect Transistor Fabrication

OFETs were fabricated using a bottom gate, bottom contact geometry. Silicon wafers (100 mm) with 300 nm of dry thermal oxide silicon dioxide grown on highly doped silicon (SiO$_2$/Si$^{++}$) from WaferPro were cut into roughly 2.5 cm by 2.5 cm squares with a diamond scribe and cleaned by sonication in acetone and isopropyl alcohol for 10 min each. The substrates were then treated with O$_2$ plasma for 5 min. The substrates were then placed in an Angstrom Engineering Aeres thermal evaporator and pumped down to 8 x 10$^{-8}$ Torr. Then, 5 nm of chromium as evaporated at a rate of 0.2 Å s$^{-1}$ followed by 45 nm of gold evaporated at a rate of 0.2 Å s$^{-1}$ for the first 4.5 nm and 0.5 Å s$^{-1}$ for the next 40.5 nm through a shadow mask to form OFET source and drain electrodes with lengths of 100 µm, 150µm, and 200 µm and widths of 1000 µm, 2000 µm, and 5000 µm. The substrates were then placed in a ~5 µM solution of PFBT in isopropyl alcohol and covered at room temperature for 18 h to form a thiol SAM on the gold electrodes. The substrates were then taken out of the PFBT solution and rinsed in isopropyl alcohol and sonicated in isopropanol for 20 min and dried with compressed air.

Solutions of 2mg mL$^{-1}$ Th-BTBT-C10 in 100% CB, 80%:20% CB:CF, 60%:40% CB:CF, 40%:60% CB:CF, 20%:80% CB:CF, and 100% CF were made and heated at 50 °C for 1 h. The solutions were spin coated on the PFBT treated substrates at 3000 rpm for 30 s with a ramp rate of 500 rpm s$^{-1}$ in a nitrogen atmosphere. The completed OFET devices were tested in a nitrogen
atmosphere with a Keithley 1500B Semiconductor Parameter Analyzer (SPA). Both transfer and output curves were collected for various individual devices and OFET parameters were extracted. In the case that the devices were thermally annealed, the Th-BTBT-C10 thin films were placed on a hot plate for 5 min at 85 °C in a glovebox in a N₂ atmosphere.

The number of devices characterized are as follows: 35 from CF solution, 18 from 20:80 mixture solution, 13 from 40:60 mixture solution, 16 from 60:40 mixture solution, 18 from 80:20 mixture solution, and 34 from CB. After thermally annealing, the number of devices characterized are as follows: 12 from 20:80 mixture solution, 7 from 40:60 mixture solution, 11 from 60:40 mixture solution, 11 from 80:20 mixture solution, 3 from CB.

7.4.2 Bottom Contact BTBT Derivative Organic Field-Effect Transistor Fabrication

OFETs were fabricated using a bottom gate, bottom contact geometry. Silicon wafers (100mm) with 300nm of dry thermal oxide silicon dioxide grown on highly doped silicon (SiOₓ/Si++) from WaferPro were cut into roughly 2.5 cm by 2.5 cm squares with a diamond scribe and cleaned by sonication in acetone and isopropyl alcohol for 10 min. The substrates were then treated with O₂ plasma for 5 min. The substrates were then placed in an Angstrom Engineering Aeres thermal evaporator and pumped down to 8 x 10⁻⁸ Torr. Then, 5 nm of chromium as evaporated at a rate of 0.2 Å s⁻¹ followed by 45 nm of gold evaporated at a rate of 0.2 Å s⁻¹ for the first 4.5 nm and 0.5 Å s⁻¹ for the next 40.5 nm through a shadow mask to form OFET source and drain electrodes with lengths of 100 µm, 150 µm, and 200 µm and widths of 1000 µm, 2000 µm, and 5000 µm. The substrates were then placed in a 5 µM solution of PFBT in isopropyl alcohol and covered at room temperature for 18 h to form a thiol SAM on the gold electrodes. The
substrates were then taken out of the PFBT solution and rinsed three times in isopropyl alcohol and then sonicated in isopropyl alcohol for 20 minutes and dried with compressed air.

Solutions of 2mg mL⁻¹ C8-BTBT-C8, C7O-BTBT-C8, and Ph-BTBT-C8 in 100% CB, 20%:80% CB:CF, and 100% CF were made and heated on a hotplate at 50 °C for 1 h. The solutions were spin coated on the PFBT treated substrates at 3000 rpm for 30 s with a ramp rate of 500 rpm s⁻¹ in a nitrogen atmosphere. To produce thin films by spin coating at the LC phase temperature, the C8-BTBT-C8 in CB solution and substrate were heated to 100 °C, the C7O-BTBT-C8 in CB solution was heated to 110 °C, and the Ph-BTBT-C8 in CB solution was heated to 90 °C. The Th-BTBT-C10 in CB solution and substrate were heated to 85 °C to compare with results from the previous section. For each sample, the heated substrate was then transferred to the spin coater, and the solution was pipetted onto the substrate with a heated pipet tip very quickly (> 5 s). The completed OFET devices were tested in a nitrogen atmosphere with a Keithley 1500B Semiconductor Parameter Analyzer (SPA). Both transfer and output curves were collected for various individual devices and OFET parameters were extracted.

The number of devices characterized were as follows: for C7O-BTBT-C8 –16 from 20:80 mixture solution, 16 from CB, and 15 from CF; for C8-BTBT-C8—16 from 20:80 mixture solution, 17 from CB, and 17 from CF; and for Ph-BTBT-C8—18 from 20:80 mixture, 21 from
CB, and 20 from CF. For the devices spin coated at LC temperatures from CB, 17 devices were characterized for C8-BTBT-C8 and 8 for Th-BTBT-C10.

Fig. 7.1. Photographs of instruments used thin film and OFET fabrication. a) Evaporation chamber, b) spin coater, c) glove box, d) semiconductor analyzer, e) probe station. An example of a bottom gate, bottom contact OFET (f).
8.1 Observation of Homeotropic Alignment of Bent-Core Liquid Crystals in Polydimethylsiloxane Cells

8.1.1 W586

A PDMS cell containing W586 (Figure 8.1a) was heated above its isotropic temperature and cooled. First, the SmA phase grew in with no observable birefringence as is expected in homeotropic aligned uniaxial phases, indicating that the sample possesses high quality homeotropic alignment (Figure 8.1b). On cooling into the biaxial SmAP$_F$ phase, a schlieren texture with low birefringence was observed (Figure 8.1c).

Fig. 8.1. POM images of homeotropic aligned W586. The uniaxial SmA phase shows an optically isotropic texture and no birefringence observed (a). The biaxial SmAP$_F$ phase exhibits a schlieren texture with low birefringence (b).
birefringence is observed (Figure 8.1c). This indicates that the homeotropic molecular orientation is retained from the SmA phase and the phase gains polar ordering and becomes weakly birefringent. The crystal phase grows in at 87 °C in spherulite domains (not shown). The spherulites grow again grow out radially in multi-millimeter domains.

8.1.2 W624

A PDMS cell containing W624 (Figure 8.2a) was heated above its isotropic temperature and cooled. The B2 phase (Figure 8.2b), which grows in from the isotropic phase on cooling, exhibits a schlieren texture in a clear departure from the striped bâtonnet texture seen in planar aligned cells of W624 (not shown). This suggests that the B2 phase is homeotropic in the PDMS cells. This is expected due to the similar structure and the shared B2 mesophase between NOBOW and W624, though the schlieren texture is significantly more birefringent. On cooling into the DC

![Chemical structure of W624](image)

**Fig. 8.2.** POM images of homeotropic aligned W624. The B2 phase shows a highly birefringent schlieren texture (a). The DC phase grows in as highly birefringent spherulites. That are up to 1 cm in diameter (b).
phase, large, centimeter diameter spherulite domains were formed (Figure 8.2c). The underlying morphology of spherulites of the DC phase is currently unknown. More work needs to be done to fully understand this morphology, though the oil on water texture may indicate homeotropic alignment of the DC phase as it has been seen in homeotropic aligned B3 in NOBOW.

8.1.3 W798

A PDMS cell was also filled with W798 and cooled from above its isotropic temperature. The short-lived N phase appeared as optically isotropic indicative of homeotropic alignment (Figure 8.3a). On further cooling, at the N to SmA phase transition front, a schlieren texture with low birefringence (Figure 8.3b, inset) appears for less than 5 s followed by a dark texture (Figure 8.3b). The transient schlieren texture indicates a clear phase transition with reorientation of the molecular director, n. The optically isotropic appearance of the SmA phase indicates that the alignment is homeotropic. This common phenomenon of a homeotropic alignment of the nematic phase inducing alignment in the smectic phase below was expected. Further cooling into the SmAP$_A$, seen in Figure 8.3c, resulted in a schlieren texture with high birefringence. The high birefringence can be explained by the small 60° bend angle present in W798 where n is parallel to the optic axis and to the layers. On cooling into the HNF phase, extremely large, broken spherulites grow in similar to what is seen in NOBOW.
8.2 Observation of Liquid Crystal Phases in Polydimethylsiloxane Microchannels

8.2.1 W586

A PDMS microchannel mold with cross-section dimensions of 5 µm in width and 10 µm in height was placed on a clean glass substrate and heated to 160 °C. The microchannels were filled...
with isotropic W586, a BCLC with a tricarbosilane terminated tail (Figure 8.4a), using capillary force. The microchannel cell was observed under POM on cooling. At 155 °C the SmA phase grows in as a gray/white monodomain texture (Figure 8.4b). This indicates that the molecules are parallel to the viewing direction, and thus, homeotropic to the walls. The low birefringence is most likely due to the fact that the polar director of the molecule is free to rotate. On continued cooling, a clear phase transition does not occur, rather the birefringence slowly increases until nucleation of a crystal phase at 80 °C. On slow cooling, rather than a quick, first order transition, a slow, second order transition is observed where the polar directors of the BC molecule slowly lock into the same bulk orientation in the ferroelectric state of the SmAP\textsubscript{F} phase (Figure 8.4c). Small amounts of material can be observed between at two one of the microchannels. This is most likely

![Image](image_url)

**Fig. 8.4.** POM images of W586 (a) in a PDMS microchannel mold. On cooling both the SmA (b) and the SmAP\textsubscript{F} (b) are observed. The increase in birefringence is gradual between the two phases and is due to the transition from a non-ferroelectric to ferroelectric state.
due to the fact that the PDMS mold is not being held down to the glass surface, and material was able to fill in between the microchannels. This effect, however, appears to be minimal. The observation of homeotropic alignment with respect to the PDMS walls in the microchannels is similar to what is observed with NOBOW in large aspect ratio microchannels. Interestingly, the tricarboxislane tail does not appear to reduce the degree of homeotropic alignment observed.

8.2.2 W624

Recently, Foley et. al. showed that the DC phase of BCLCs can be confined in nanopores to force the formation of HNFs. To test the bounds of the confinement needed to produce HNFs from DC phase forming molecules, we studied W624 (Figure 8.5a) in PDMS microchannels. A PDMS microchannel mold with cross-section dimensions of 5 µm in width and 10 µm in height was placed on a clean glass substrate and heated to 150 ºC. The microchannels were filled with isotropic W624 using capillary force. The sample was then cooled to room temperature and the mold removed. The room temperature DC phase was observed under POM and scanning electron microscopy.

Under POM, maximum birefringence is observed in the microchannels when they are rotated 45° to the crossed polarizers. However, interestingly, when rotated 45° to the left (Figure 8.5b) or the right, the birefringence appears to change by exhibiting either a white or brown color. For the most part, the color is consistent throughout an entire microchannel, but it does appear that in a small number of channels both birefringence colors exist. This suggests that the difference in birefringence might be due to different domains. When the microchannels are parallel with the crossed polarizers, the birefringence is almost completely extinguished (Figure 8.5d), suggesting that there is some kind of bulk orientation of the molecules in the DC phase. Strangely, when
slightly uncrossing the polarizers left or right, the same effect is observed as when the microchannels are rotated 45° to the crossed polarizers. The DC phase should be chiral and should display a difference in optical activity when observed under uncrossed polarizers, which is what

![Diagram of W624 molecule]

**Fig. 8.5.** The room temperature DC phase of W624 (a) in microchannels. Maximum birefringence is observed when the microchannels are rotated 45° to the cross polarizers (b, c). The birefringence of each domain depends on the rotation of direction. When the microchannels are parallel to the cross polarizers the birefringence is largely extinguished (d). When uncrossing the polarizers, some optical activity is observed matching the color observed on rotation.
we see here. We speculate that the different birefringence observed in the microchannel domains might oppositely handed.

The microchannels were coated with Pt and carbon and a liftoff process was completed. The mask was then observed under TEM by Michael Tuchband. In the microchannels, clear twisted layers are observed and fill the entire width of the microchannel (Figure 8.6a). The twist appears to be somewhat coherent and some anisotropy of the twist is observed parallel to the channel in some areas. However, it is not clear that HNFs have formed and in the bulk. On closer observation, layer edges are observed as is expected in TEM images of the DC phase but do not appear to be oriented in any particular direction. Overall, more work needs to be done to understand how the DC phase of W624 is affected by the PDMS microchannels and micro-confinement.

![Fig. 8.6. TEM images of the DC phase in microchannels. Twisted layers are observed in the microchannels with some potential anisotropy in the twist direction, but no clear HNFs are observed (a). On closer observation the edges of the twisted layers can be observed (b). No uniform layer orientation is observed either. The white scale bars are 500 nm.](image-url)
8.2.3 W899

From the work completed in Chapter 3, we know that the tail-PDMS interaction is responsible for the depressed HNF nucleation temperature in NOBOW. To test this hypothesis, a modified derivative of NOBOW, W899 (Figure 8.7a), was studied in the microchannels. W899 has the same LC core as NOBOW, but the tails are terminated with polar azide groups. A PDMS microchannel mold with cross-section dimensions of 5 µm in width and 10 µm in height was placed on a clean glass substrate and heated to 145 °C. The microchannels were filled with isotropic W899 using capillary force. On cooling, only the isotropic to HNF phase transition is observed, so

![Diagram of W899 molecule]

**Fig. 8.7.** POM images of the HNF phase of W899 (a) in PDMS microchannels. When the microchannels are rotated 45° to the crossed polarizers (b) or parallel to the crossed polarizers (b), low birefringence is observed. This indicates that the HNFs are not uniformly oriented in the microchannels, most likely due to the polar azide tails. The red arrows indicate the microchannel direction.
the microchannels were studied at room temperature. Low birefringence is observed when the microchannels are rotated at all angles to the crossed polarizers (Figure 8.7a, b). This indicates that the HNFs do not have any bulk uniform orientation and alignment in the microchannels. The polar tails do not interact strongly with the walls in the high aspect ratio microchannels, and no undercooling in the nucleation temperature is observed. Spherulite nucleation is not observed that would induce alignment does not occur. We are confident that the lack of higher temperature LC phases in W899 are not responsible for the lack of alignment because of the observation of aligned HNFs in the microchannels out of the isotropic phase in 8CB mixtures.

8.3 AFM Imaging of Thin Films

8.3.1 Thin Films of Th-BTBT-C8 Spin Coated from Dilute Methanol and Hexane Solutions

To better understand the effect of solvent, two more low boiling point solvents with different polarities were chosen: methanol and hexane. We attempted to make Th-BTBT-C8 thin films out of 2 mg mL\(^{-1}\) solutions of methanol and hexane, but Th-BTBT-C8 was not significantly soluble in either (0.1 mg mL\(^{-1}\) and 0.11 mg mL\(^{-1}\), respectively). Thin films were made by spin coating at 3000 rpm for 30 s on a clean glass substrate. The thin films were observed with tapping mode AFM. On observation of the substrate surface in both cases, there is evidence that very thin films were formed out of the dilute solutions. The thin film made from the methanol solution appears to have very small domains scattered across the surface (Figure 8.8a). On closer observation, these domains are about the size of the clusters of molecules observed on the terrace step surfaces in films from CB (Figure 8.8b). The height of these steps is ~5 nm. Other ridged ring patterns are observed with step heights of about 1 nm. This may be due to two layers of molecules.
that are laying on their side on the substrate surface, but the cause of this is unknown. The surface morphology of the thin film made from the hexane solution is drastically different. Small bâtonnet structures appear on the surface (Figure 8.8c). On closer observation, these bâtonnet are steps that are ~0.5 nm tall and correspond to the molecules laying on their side (Figure 8.8d). These film morphologies drastically differ from the thin films made from more concentrated solutions indicating that concentration plays a role in the bulk film morphology. More work needs to be done to make films from more concentrated solutions of Th-BTBT-C8 from similar solvents to understand how these solvents play a role in the thin film morphology of thicker films of Th-BTBT-C8.

**Fig. 8.8.** Tapping mode AFM images of Th-BTBT-C8 thin films made from spin coating out of low concentration methanol (a, b) and hexane solutions (c, d).
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