ROLE OF INTERFACIAL, STATIC AND DYNAMIC DISORDER ON HIGH PERFORMANCE ORGANIC FIELD-EFFECT TRANSISTORS

A Dissertation in
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by
Jwala M. Adhikari

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The dissertation of Jwala M. Adhikari was reviewed and approved* by the following:

Enrique D. Gomez
Associate Professor of Chemical Engineering
Dissertation Advisor
Chair of Committee

Michael A. Hickner
Associate Professor of Materials Science and Engineering, Chemical Engineering

Michael J. Janik
Associate Professor of Chemical Engineering

Qing Wang
Professor of Materials Science and Engineering

Phillip E. Savage
Professor of Chemical Engineering
Head of the Department of Chemical Engineering

*Signatures are on file in the Graduate School
ABSTRACT

The internet and electronic devices have become integral to our everyday life. As the world is beginning to march towards the Internet of Things, surging interest has been focused on low-cost functional electronics. However, the industry of electronics is inundated with traditional inorganic semiconductors. Silicon and germanium based inorganic semiconductors are rigid and fragile, requiring expensive processing. On the other hand, organic semiconductors based electronic devices, namely field effect transistors (FETs) and light-emitting diodes (LEDs), offer a feasible alternative to their inorganic counterparts. Not only are organic semiconductors soft and flexible, but they also possess advantages such as solution processability and chemical modifications. Despite the lucrative advantages, the performance of organic semiconductor-based devices is significantly lower. For instance, the highest hole mobility in one of the best performing organic FETs is two orders of magnitude lower than in inorganic transistors. Moreover, the behavior of organic semiconductors is very complex and is readily susceptible to their surroundings. Due to such complex nature of organic semiconductors, an unambiguous road map to high-performing organic FETs (OFETs) is still missing.

The focus of this dissertation is on elucidating and tuning different factors that govern the performance of OFETs. An OFET is a complex structure comprised of three metal electrodes, an active layer (semiconducting layer) and a gate insulator (dielectric layer). One of the key parameters that determine the performance of OFETs is charge carrier mobility. The charge mobility of an OFET is affected by various factors—mainly
the chemical structure of an active layer material, the morphology of an active layer and the interactions at the semiconductor-dielectric interface.

To understand the role of chemical structure on the performance of organic semiconductor, octyl side-chains are added to [1]benzothieno[3,2-b]benzothiophene (BTBT) core. BTBT is a liquid crystalline material with poor solubility and weak semiconducting properties. The addition of alkyl side-chains is expected to increase the solubility of the core. However, the average FET hole mobility in the single crystalline BTBT with two octyl side-chains (C₈BTBT) (μ = 6.0±1.0 cm²/V·s) is three orders of magnitude higher than in the single crystalline BTBT core itself. The use of a single crystalline layer rules out any morphological effect on the performances. Moreover, the intrinsic charge transport parameters of single crystals predicted using Density Functional Theory (DFT) calculations remain essentially the same. Since both morphology and crystal structure seem to have virtually no effect on the measured charge mobilities of BTBT derivatives, what else could have affected the charge mobilities? It is hypothesized that inter-molecular dynamics may be an unaccounted factor. To probe the collective inter-molecular motions—also known as phonon—inelastic neutron scattering (INS) is performed. The results from INS show that lattice vibrations are significant in the BTBT core. In contrast, the vibration modes are completely diminished in C₈BTBT, suggesting that the addition of octyl side-chains suppresses lattice vibrations in the BTBT core. The alkyl side-chain assisted reduced electron-phonon coupling may have led to the enhanced hole mobility in C₈BTBT.

In addition, the morphology of C₈BTBT thin films is also optimized to improve an average hole mobility in FETs. It has been found that by melting and quenching spun-
cast C₈BTBT films, the average hole mobility of FETs is improved by a factor of five. Grazing incidence wide angle X-ray scattering (GIWAS) results show that the melting and quenching enhanced crystal texturing and led to stronger orientation order in the C₈BTBT films. The melting and quenching process is believed to be vital in obviating the processing history and in controlling the thermodynamic driving force for crystallization.

The effect of a gate insulator on the performance of FETs is also investigated using a novel, photopatternable, high-k fluoropolymer, poly(vinylidene fluoride-bromotrifluoroethylene) P(VDF-BTFE), where the BTFE moieties enable cross-linking through thermal- or photo-curing of dielectric materials with relative permittivities between 8 and 11. Organic single crystal field effect transistors based on rubrene active layers and crosslinked P(VDF-BTFE) gate dielectrics have shown hole mobilities as high as 12 cm²V⁻¹s⁻¹, three times higher than the average hole mobilities for devices comprising PVDF-based fluoropolymers or SiO₂ as the dielectric layer. FETs comprising cross-linked P(VDF-BTFE) dielectric layers show the smallest interfacial trap density among all other fluorinated PVDF-based polymers, leading us to believe that cross-linking P(VDF-BTFE) films reduces energetic disorder at the dielectric-semiconductor interface. Fourier transform infrared spectroscopy results suggest that crosslinking enhances the population of trans conformations with respect to the neat polymer, demonstrating that cross-linking minimizes interfacial charge traps and hence enhances hole mobility by tuning chain conformations.
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Chapter 1

Introduction

1.1 Life, electronics and the internet of everything

“The only thing that is constant is change.” A famous Greek philosopher, Heraclitus of Ephesus, wrote some 2000 years ago.\textsuperscript{1,2} Things evolve, and so has the way we use our electronics. Computers, which were generally large, costly systems in large corporations, universities and government agencies about 50 years ago, are now at the fingertips of nearly 40% of the world’s population in the form of smartphones.\textsuperscript{3-5} The number is destined to rise. Research has shown that by 2020, the number will take a gigantic leap to 70% (Figure 1-1).\textsuperscript{5}

It is inevitable that the world is marching towards a new technological revolution—the Internet of Things. The internet and electronic devices have become integral part of our everyday life. The way people generate, store and share information has made a paradigm shift in just a decade. People are becoming cord cutters for more mobile and easily accessible wireless and cloud technologies such as smartphones, tablets and Dropbox\textsuperscript{TM}, for instance. Periodical edited news medium is slowly turning into a routine of the past since the dawn of Facebook\textsuperscript{TM} and Twitter\textsuperscript{TM}. More and more things that surround us in our home or office are becoming connected to the internet in some form. A report by Gartner\textsuperscript{®} speculates that by 2020 the number of intermittently internet-
connected devices will surpass 200 billion. This expanding frontier of the internet is driving an information explosion. Bridging the internet and electronics creates a broad spectrum of possibilities which are yet to be explored.

![Figure 1-1: Smartphone subscriptions per region from 2014-2020 reported by Ericsson™. Source: The image is taken from a report published by Ericsson™ on their website.](image)

Even today, electronic industry is dominated by traditional inorganic semiconductors such as silicon and germanium. Despite their high charge carrier mobilities (> 1000 cm²V⁻¹s⁻¹), inorganic semiconductors, which are composed of very strong covalently bonded atoms, are rigid and relatively fragile. In addition, the traditional semiconductors require a high temperature (> 600 °C) vacuum deposition steps and expensive lithography processes in a meticulously maintained ultra clean lab that increases their manufacturing costs. These factors limit inorganic semiconductor based field-effect transistors (FETs) to applications requiring high switching speed. Applications that require large area coverage, structural flexibility, low temperature
processing, and especially low cost, have not yet been fulfilled. Such applications include electronic paper displays, sensing devices and electronic identification tags, to name a few. Portions of the health industry that involve sensing devices and artificial organs are some of the biggest beneficiaries.\textsuperscript{11} Although hydrogenated amorphous silicon (a-Si:H) has been commonly used in large area applications, high temperature processing (\( > 350 \degree \text{C} \)) limits its deposition on inexpensive plastic or paper substrates.\textsuperscript{8} Consequently, a plethora of niche applications of electronic devices is yet to be exploited (Figure 1-2).

Organic semiconductors, which are comprised of molecules held by weak van der Waals forces, open a door widely to new prospects of electronic devices. Organic materials are soft, light weight and low temperature processible (Figure 1-3). Since the discovery of a conducting plastic in 1977, and the initial demonstration of field-effect conduction in organic small molecules and conjugated polymers, the number of research
groups exploring the field of organic electronics has exploded, especially in last several decades (Figure 1-4). The reasons for this surge of interest are numerous. Organic semiconductor based field effect transistors (OFETs) have already surpassed the performance benchmark of amorphous silicon (a-Si) thin film transistors (TFTS) with field effect mobilities of 1 cm²V⁻¹s⁻¹ and ON/OFF current ratios of 10⁸. Currently, the record charge mobility (µ) value for solution processed thin single crystalline film OFET is 31 cm²V⁻¹s⁻¹.

Even though the relatively low mobility of OFETs cannot outweigh the performance of inorganic single crystal based TFTs, a suitably modified organic semiconductor can be the superior candidate for room temperature processing by a combination of low-cost solution processing and roll-to-roll printing. Such advantages make them ideally suited for the realization of low-end, large-area electronics on flexible substrates. In addition, the luxury of addition and deletion of useful functional groups
in organic materials through design and synthesis routes adds structural freedom in material design process.

1.2 Charge transport in organic semiconductors

Organic materials—small molecules and polymers—are composed of hydrocarbon molecules with a backbone of carbon atoms. Unlike its silicon (Si) and germanium (Ge) neighbor elements in the periodic table, carbon possesses a unique feature of being able to exist under three different configurations: sp, sp² and sp³. Organic materials that comprise sp² hybridized carbons become conjugated organic materials. A conjugated molecule consists of alternating single and double carbon bond which give rise to a series of overlapping π orbitals. The resulting π orbitals allow the delocalization of π electrons that extend all over the conjugated molecule. These delocalized π electrons

Figure 1-4: Evolution of charge mobility of organic semiconductors over years.⁸,¹⁵
Commonly exploited high performing organic semiconductors are listed in Table 1.

Table 1-1: Chemical structure of commonly used organic semiconductors

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,7-Dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8BTBT)</td>
<td><img src="image1" alt="Chemical structure image" /></td>
</tr>
<tr>
<td>Rubrene</td>
<td><img src="image2" alt="Chemical structure image" /></td>
</tr>
<tr>
<td>6,13-Bis(triisopropylsilylethynyl)pentacene</td>
<td><img src="image3" alt="Chemical structure image" /></td>
</tr>
<tr>
<td>Dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene</td>
<td><img src="image4" alt="Chemical structure image" /></td>
</tr>
<tr>
<td>Poly(3-hexylthiophene) (P3HT)</td>
<td><img src="image5" alt="Chemical structure image" /></td>
</tr>
</tbody>
</table>
A widely accepted mechanism of charge transport in organic semiconductors is a hopping transport process, even though highly purified crystals of some organic molecules have demonstrated that the charge mobility enhances similarly to inorganic semiconductors when lowering temperature.\textsuperscript{19,20} Unlike in inorganic solids, since the intermolecular forces between molecules in organic semiconductors are weak van der Waals interactions, the charge carrier path between two molecules is phonon (lattice vibration mode) assisted and therefore, thermally activated.\textsuperscript{19,21} Therefore, charge carriers in organic semiconductor follow a hopping transport process. A charge hopping model is basically an electron or hole transfer reaction in which an electron or hole is transferred from one molecule to another. The charges localize on a molecule for a time long enough such that it induces the nuclei to relax to their optimal geometry, resulting in a lattice deformation around the molecule and forming a polaron.\textsuperscript{21} In other words, polaron hopping is a self-exchange electron transfer reaction where a charge hops from an ionized site to an adjacent neutral site, and is responsible for the macroscopically observed carrier mobility of organic semiconductors.\textsuperscript{22} The hopping rate can be described as

\[
k_{\text{hopping}} = \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi k_B T^3}} t^2 \exp \left( -\frac{\lambda}{4k_B T} \right),
\]

where \( T \) is the temperature, \( \lambda \) is the reorganization energy, \( t \) is the transfer integral, and \( h \) and \( k_B \) are the Planck and Boltzmann constants. As illustrated in \textbf{Equation 1-1}, two key intrinsic parameters govern the rate of charge hopping at microscopic level: transfer integral \( (t) \) and reorganization energy \( (\lambda) \).

The transfer integral is a result of an energetic splitting of a given electronic level of an isolated chain when interacting with another isolated chain. In organic
semiconductors, the energy level splitting is related to the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) level. The higher the HOMO bandwidth, the higher the hole mobility (Figure 1-5). The transfer integrals represent the strength of the interaction and, hence, the ease of transfer of a charge between two interacting chains. Intuitively, the separation between two interacting molecules should diminish the magnitude of their electronic coupling. In fact, it has been observed that the transfer integral decays exponentially when the interchain distance is increased. Figure 1-6 illustrates the relationship between the electronic splitting of the HOMO LUMO levels in a cofacial dimer of two tetracene molecules as a function of the intermolecular separation.

Figure 1-5: Schematic representation of the bonding-antibonding interactions between energy levels of a pair of ethylene molecules. Large clusters of interactions among stacked molecules forms the valence and conduction bands.
Reorganization energy, on the other hand, reflects the strength of electron-phonon mode, which needs to be minimized for efficient charge hopping. It is the sum of geometrical relaxation energies of a molecule and its neighbor on the movement of the charge carriers. The key parameter to quantify the charge hopping process or charge transport is the charge carrier mobility. In the absence of an external potential, charge carriers move randomly, such that the net movement of charge carriers is zero.

Figure 1-6: The amplitudes of electronic splitting behavior of the HOMO and LUMO levels in a cofacial dimer made of a pair of tetracene molecules decays exponentially with the increasing intermolecular distance. Reprinted with permission from American Chemical Society publications (2016).
In the presence of an external field, however, charge carriers within organic solids gain acceleration. The charge carriers drift their average position, due to collisions and scattering events as they travel, resulting in an average drift velocity.\textsuperscript{19} The mobility of charge carriers (\(\mu\)) can then be defined as the ratio between the carrier drift velocity (\(v\)) and the magnitude of the applied electric field (\(E\)):

\[
\mu = \left(\frac{v}{E}\right)
\]  

(1 - 2)

The resulting unit of the charge mobility is cm\(^2/V\cdot s\), which qualitatively represents how fast a charge carrier will move in a medium if an electric field is applied. Charge mobility can be determined experimentally in several ways. Time of flight (TOF), space-charge limited current (SCLC) measurements using diode configuration, and a carrier extraction method by linearly increasing voltage (CELIV) are popular techniques, to name few.\textsuperscript{19,25} Unfortunately, theories relating to most of these techniques are still in nascent phase and not universally accepted yet.

1.3 Principle of organic field effect transistors

A commonly used technique to study the carrier mobility of semiconducting thin films involves field-effect transistors (FETs). The field-effect concept that dates back to 1930, is a phenomenon in which the conductivity of a semiconductor changes due to the application of an electric field normal to its surface.\textsuperscript{26} Field-effect transistors comprising organic semiconductors are called organic field-effect transistors (OFETs). An OFET, which typically operates as a capacitor, is composed of three basic elements:
(i) a semiconductor film or active layer, (ii) an insulating layer or dielectric layer, (iii) three electrodes consisting of source, drain, and gate. As shown schematically in Figure 1-7, a semiconductor film connects two of the metal electrodes, namely the source (S) and the drain (D), and the third electrode or the gate is separated from the semiconductor film by the gate insulator (dielectric) layer. The distance between the source and the drain is called the channel length (L), and the transverse dimension of the FET is the channel width (W). There are three common configurations of OFETs, designated by the way the three electrodes are arranged: top-gate with bottom-contacts, bottom-gate with top-contacts, and top-gate with top-contacts.

![Figure 1-7: Schematic of a bottom-gate-top contact OFET configuration](image)

The gate voltage induces a conducting channel of charges, and the drain-source voltage ($V_{DS}$) drives these charges from source to drain along the conducting channel. In a p-type OFET, when a negative voltage is applied to the gate ($V_{GS}$), a conducting channel of holes is induced at the dielectric-semiconductor. For positive $V_{GS}$, the current ($I_{DS}$) is almost negligible and the device is in the “OFF” mode. For the negative $V_{GS}$, the current...
starts rising and the device enters the “ON” mode. The gate voltage for which the device turns on is called the threshold voltage \( V_{Th} \). At a low negative drain-source voltage, the current between the source and the drain \( I_{DS} \) increases linearly following Ohm’s law. This is called the linear regime. In this regime, drain-source current is a function of the channel dimensions \( W, L \), the capacitance of the gate insulator \( C \), \( V_{GS} \), and \( V_{Th} \). The charge carrier mobility \( \mu \) in the linear regime is represented in Equation 1-3.\(^7\)

\[
I_{ds} = \left( \frac{W}{L} \right) \mu C (V_{GS} - V_{Th}) V_{DS}
\]

When \( V_{DS} \) rivals \( V_{GS} \), i.e. \( V_{DS} > V_{GS} - V_{Th} \), the voltage drop at the drain contact falls to zero, and the conducting channel will be pinched off. This corresponds to the saturation regime, where the current becomes independent of the drain voltage. At this point, the transistor basically saturates and follows the Equation 1-4.\(^7\)

\[
I_{ds} = \left( \frac{W}{2L} \right) \mu C (V_{GS} - V_T)^2
\]

**Figure 1-8** represents electrical characteristics of a typical C8BTBT thin film OFET. Despite minimal hysteresis in transfer characteristics (**Figure 1-8a**), which is not uncommon in organic semiconductors, the device shows near zero threshold voltage \( V_{Th} \) and over \( 10^6 \) ON/OFF current ratio. While the intersection of \( I_{DS}^{0.5} \) with the x-axis represents the \( V_{Th} \), the ratio of the maximum ON-current and the OFF-current gives the device ON/OFF ratio. Any charge traps at the dielectric interface or leakage through the dielectric layer significantly affect these parameters of an OFET. Output characteristics of the device are shown in **Figure 1-8b**. The linearly rising \( I_{DS} \) as a function of \( V_{DS} \) at lower \( V_{DS} \) for different \( V_{GS} \) is a signature of the linear regime. The linear region indicates that the device has minimal effect due to contact resistance at the electrode-
semiconductor interface. Eventually, the source-drain current becomes independent of the source-drain voltage and the devices enter the saturation regime. Due the prevalence of gate voltage dependent hole mobility in organic semiconductors, it is imperative that differential hole mobility should be calculated as a function of gate voltage for the accurate extraction of the average hole mobility in the saturation regime, as shown in Figure 1-8c,

Figure 1-8: a) Transfer characteristics; b) Output characteristics and c) Differential hole mobility of C₈BTBT thin film OFET.
1.4 References


Chapter 2

Objectives and Approaches

2.1 Charge mobility in organic field effect transistors (OFETs)

As discussed briefly in the previous chapter, one of the key parameters that determine the performance of an OFET is charge mobility. The higher the mobility, the faster the device is. A typical OFET is a product of five different entities: source and drain electrodes, semiconducting active layer, gate insulator and gate electrode. In order to behave optimally, an OFET should be an optimized combination of materials that go into it. The choice of active layer material, active layer morphology, manufacturing procedures, post-manufacturing treatment and ambient conditions can significantly alter the electrical properties of any device. In spite of a plethora of scientific publications in the field of OFETs in the last several decades, a clear road map to achieve an ideal OFET that can rival inorganic Si-based transistors still remains a mystery to scientists.1-4

The main reason is that a wealth of fundamental scientific questions regarding the details of charge transport behavior in organic semiconductors is still unanswered. While engineers and material scientists tend to focus on the engineering aspects of fabrication
process and the process optimization, the majority of physicists and chemists focus on the theoretical understanding, design and synthesis of efficient materials. Through collaboration among scientists and engineers across various fields, research efforts can be focused on elucidating the fundamental architecture of organic semiconductors and gate insulators at the molecular scale, and how they translate into the electrical characteristics of macroscopic devices. As such, efficient OFETs are the outcome of interplay among organic semiconductors (active layer), their morphology and the interactions of active layer with gate dielectric interface (Figure 2-1). Consequently, in order to achieve high performance OFETs, a right organic semiconductor with an enhanced thin film morphology that interacts productively with the gate dielectric surface is warranted.

Figure 2-1: Schematic showing key factors that govern the performance of OFETs
2.2 Chemical structure of an active layer material

Changing the chemical structure of organic semiconductors has been shown to affect the electronic performances of the materials. This is one of the most common methods used to design high performance organic semiconductor devices.\textsuperscript{5-7} Theoretical prediction of the high-performance novel organic semiconductor materials is hindered by the large number of factors influencing charge carrier mobility in OFETs, including synthetic methods, device geometry, contacts, device interfaces, thin-film growth, and the molecular packing in the solid.\textsuperscript{8} Therefore, a challenge one faces is the choice of the right molecule for synthesis.

1-benzothieno[3,2-b][1]-benzothiopene (BTBT) is a promising core structure that has been widely exploited in recent years (\textbf{Figure 2-2}).\textsuperscript{9-11} BTBT is barely soluble in most common organic solvents such as toluene or chlorobenzene. However, Takimiya, et al. have solution processed the core as an active layer in OFETs after adding solubilizing alkyl groups.\textsuperscript{12} The group has also demonstrated that addition of alkyl groups of different chain length leads to varying hole mobility among the soluble BTBT derivatives.\textsuperscript{12,13} The highest reported C\textsubscript{n}BTBT has octyl groups on each of its ends and has a hole mobility of 31 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}.\textsuperscript{9} From the electronics point of view, long alkyl chains create bulky insulating layers between the semiconducting pi-pi stacks along the polycrystalline thin film, which limits the vertical transport and dilutes the number of pi-pi systems very close to the channel interface. The shorter alkyl chain, on the other hand, improves the charge carrier mobilities. The shorter alkyl chain, however, also exhibits problems with the homogenous film formation for BTBTs due to their high tendency to crystallize.\textsuperscript{14,15}
In addition, scientists have predicted that alkyl groups provide an anchoring effect by bringing BTBT cores closer, maximizing the intermolecular coupling.\textsuperscript{13,15}

Despite many speculations, the exact relationship between the chemical structure and electronic properties is clearly understood yet. It is believed that besides the key intrinsic parameters, namely transfer integral and reorganization energy, the lattice vibration mode also affects the macroscopic properties of an OFET. We hypothesize that addition of alkyl groups suppresses those lattice vibration in the BTBT core, thereby enhancing hole mobility.

![Chemical Structure of a) BTBT core b) dioctyl BTBT (C\textsubscript{8}BTBT)](image.png)

Figure 2-2: Chemical Structure of a) BTBT core b) dioctyl BTBT (C\textsubscript{8}BTBT)

\subsection*{2.3 Active layer morphology}

A disorder and impurity free active layer is also one of the prerequisites to achieve excellence in OFETs. Such morphological quality of an active layer, however, is hard to achieve because the factors such as solid state phases, film growth modes, grain sizes and grain boundaries have a significant impact. Moreover, various processing conditions such as solvent nature, surface treatments, and processing modes affect active layer morphology significantly.\textsuperscript{16} As a result, OFETs with poor active layer morphology may not be the appropriate vehicles for achieving high performing devices.\textsuperscript{17}
Controlled crystallization is one of the highly exploited techniques in the field of OFETs to enhance the thin film ordering of organic semiconducting small molecules. In such molecules, charge transport is governed by the coupling between adjacent molecules in the unit lattice and connectivity between grains in crystalline materials. As a consequence, the crystallization of small molecule semiconductors in the active layer of organic thin film transistors (OTFTs) can significantly affect charge mobilities of devices. In some cases, promoting crystallization simply provides percolating pathways for low-resistance charge conduction, while in others the types of grain boundaries are perturbed to maximize charge hopping between grains.

Several processing methods have been proposed to control the morphology of the active layer in small molecule OTFTs. Single crystals of C8BTBT have been demonstrated with inkjet printing of two solvents, one a good solvent for C8-BTBT carrying the molecule and a second poor solvent to induce crystallization. Using a blade patterned with an array of micropillars, 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) crystals have been aligned to demonstrate a two order of magnitude increase in charge mobility in the direction of alignment when compared to active layers with isotropic films. Depositing or annealing organic semiconductors at temperatures above the melting temperature but below the liquid crystal to isotropic transition leads to enhanced order in the active layer and improved device performance. These studies demonstrate promising processing approaches aimed at controlling the crystallization of organic semiconductors.
Understanding the behavior of active layer at the gate-dielectric interface is also equally important to achieve excellent OFETs. Morphology as well as the semiconducting behavior of an active layer has been shown to be strongly affected by the type of gate insulators used (Figure 2-4). Gate insulators provide a platform for the morphological evolution of organic semiconductors during processing such that their surface energy and intermolecular interactions at the interface with the active layer play a

Figure 2-3: a) An optical image micro-pillar patterned TIPS-pentacene single-crystalline domains (blue) on a SiO2 substrate (purple) treated with octadecyltrichlorosilane (OTS). The logo on the side represents the size of a dime. b) Schematic of solution shearing with patterned micro-pillars. The arrow points towards the shearing direction.

2.4 Gate insulator interface

Understanding the behavior of active layer at the gate-dielectric interface is also equally important to achieve excellent OFETs. Morphology as well as the semiconducting behavior of an active layer has been shown to be strongly affected by the type of gate insulators used (Figure 2-4). Gate insulators provide a platform for the morphological evolution of organic semiconductors during processing such that their surface energy and intermolecular interactions at the interface with the active layer play a
critical role. Therefore, controlling and optimizing the semiconductor-dielectric interface are essential for substantial improvements in OFET performances.

Figure 2-4: A) Schematic showing introduction of disorder at the active interface by polar groups of gate insulator. B) Dependence of field effect mobility on various gate dielectric used. It is shown that with the increase in $k$, the field effect mobility decreases. Shown on the top left is the molecular structure of the organic semiconductor.\(^1\)

Both inorganic and organic gate insulators are commonly used in OFETs. Due to the high density charge traps, such as Si-OH, and or/ H$_2$O, limited charge transport performance and lowered device performances have been observed OFETs comprising SiO$_2$ as a gate insulator. Moreover, SiO$_2$ is limited by relatively small dielectric constant ($k = 3.9$) and expensive high temperature processing.
On the contrary, organic/polymer gate dielectrics are a promising alternative to oxides. Tuning the chemistry of various polymers, for example with the inclusion of polar groups, may lead to solution-processable and flexible materials with high dielectric constants and consequently high capacitance. The polar groups associated with high-\(k\) polymers, however, can contribute to energetic disorder at the dielectric-semiconductor interface, thereby inducing a sub band-gap density of states that can act as charge traps. Thus, development of novel high-\(k\) gate insulators with suppressed energetic disorder is warranted in the course of achieving high mobility devices.

2.5 Approaches

2.5.1 Rapid fabrication of organic single crystals

Since the properties of an OFET strongly depend on the fabrication conditions and the active layer morphology, polycrystalline semiconducting thin films may not be the appropriate vehicles for illuminating basic transport mechanisms in organic materials. Devices based on single-crystals are popular alternative to elucidate fundamental behavior of OFETs. O. Jurchescu et al. have reported that the mobility (\(\mu=6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\)) of single crystal OFETs of soluble anthradithiopene (diF-TES ADT) is roughly ten times higher than that of thin film OFETs. Z. Bao’s group increased the hole mobility of TIPS-pentacene by two orders of magnitude by altering a polycrystalline film into a single crystalline layer. The use of single crystal of organic materials minimizes imperfections and impurities by providing near-perfect order over its entirety. The lack
of grain boundaries and defects enhances performance of single crystal OFETs compared to polycrystalline OFETs. Furthermore, single crystals are very convenient tool to study novel gate dielectrics and to deconvolute their effect in OFETs.

Despite the lucrative benefits of single crystals, growing and handling organic crystals is a daunting task. Using a solvent method may take weeks to grow the crystals, and the crystallization is not generally reproducible. A variety of unknown factors deteriorates, and even kills the process. Moreover, organic single crystals are very prone to rapid degradation in the presence of air, moisture and light. They are very delicate and need special tools for handling, which should be used meticulously. Therefore, it is crucial that a rapid crystal growing technique, which could be controlled and reproduced, should be utilized.

Anti-solvent crystallization (ASC) is a very common technique in pharmaceutical industries for rapid solution based crystallization. The highest reported mobility for solution processed OFETs is also based on the anti-solvent crystallization (ASC) method. The method is quick, finishing within several hours unlike other commonly used solution based crystallization methods that could last for weeks. In ASC, a saturated solution is turned into a supersaturated solution by adding a large amount (by volume) of anti-solvent. The anti-solvent is a solvent that is soluble with the original solvent but not the solutes. As a result, solutes which are insoluble in the added anti solvent crystallize out of the system as single crystals.

1mg/ml of toluene solution of desired organic small molecules is prepared in a clean vial and is left to stir for half an hour. In a clean beaker, the solution is mixed with methanol in the volume ratio of 1:7. The beaker is covered with clean aluminum foil and
left inside fume hood to crystallize. The process would typically complete within 3-5 hours. **Figure 2-5** shows single crystals of different organic small molecules grown using the technique. Crystals of different sizes were grown ranging from 50 µm to 800 µm in length.

The anti-solvent method is also used to grow BTBT derivatives single crystals. 0.4 mg/ml solution of a BTBT derivative and dichloromethane was mixed with hexane in 1:3 ratio by volume. After stirring the resulting solution for about ten minutes, it was transferred to a clean glass vial using a 0.2 µm pore-sized filter. Nice thin platelets of crystals as big as 500 microns were formed after 24 hours. For crystallography, crystals are left in the solution vial to maintain their integrity. On the other hand, for device preparation, the crystals are placed in vacuum oven for 24 hours to get rid of any trapped solvents. Trapped solvents tend to introduce defects in organic crystals.
Solution techniques may not always be convenient for all types of materials. Solution methods not only the method tends to introduce defects in crystals, but they may also not be productive for some materials, like rubrene, for instance. Rubrene is highly sensitive to oxygen and light. As a consequence, physical vapor transport (PVT)—a commonly used non solution technique to grow organic crystals—is also used.\textsuperscript{49,50} The PVT method involves the sublimation of organic materials in the hot zone of a horizontal furnace tube in an inert environment maintained by the constant flow of a nobel gas. The vapor phase is then allowed to travel with the nobel gas towards the colder regions along the tube where it crystallizes. If impurities are present in the starting material, crystallization zones are distinct among various materials because of the differences in
their crystallization temperature and density. Therefore, the PVT method can also be used for purification of organic semiconductors.

About 50 mg of Rubrene (99.99%, Sigma) is placed at the sublimation zone of a 400 mm long and 18mm wide quartz tube (Figure 2-6). The sublimation zone is about 100 mm for the tube inlet. The tube is sealed with Teflon™ caps on both sides of the tube, only leaving inlets and outlets for ultra-pure Argon gas. The flow rate of the gas is controlled through a flowmeter and is maintained at 50 ml/s. Higher flowrate can lead to rather rapid crystallization of rubrene vapor, thereby compromising the crystal quality. Slower flow rate gives enough time for rubrene vapors to nucleate and crystallize slowly, leading to better crystal quality. Half an hour should be allowed to purge the tube with Argon before starting the procedure after loading the starting material. The temperature at the sublimation is maintained at 310 °C using the heating tape around the tube. Temperature gradient is very crucial for the vapor molecules to cool down as they move along the tube. It is maintained by using two heating tapes at two different temperatures: 310 °C and 280 °C. The process usually takes several hours to one day to complete. At the end of the process, the furnace should be left at least half an hour to cool down with the gas flowing on before opening. The vapor molecules crystallize in the crystallization zone, usually within the 20 cm from the sublimation zone. The sizes of the single crystal range from 200 µm to 1 cm in length. The typical thickness of the single crystal is 1 µm. Distinct crystallization zones may also be observed further down the tube (Figure 2-7). The crystallized material, which is usually impurities, should not come in contact with the crystallized rubrene single crystals. Rubrene single crystals are meticulously hand-
picked under polarized microscope using the crystallographic tools from MiTegen™. An example of PVT grown rubrene single crystal is shown in **Figure 2-8**.

![Figure 2-6: Digital photograph showing the PVT set up of Gomez Lab. A, B, C, D, E are flowmeter, Teflon™ cap, heating tape coiled over a quartz tube (furnace), thermocouple reader, temperature controller, inlet and outlet of Argon gas respectively.](image)

![Figure 2-7: 400mm long quartz tube after a run. Sublimation zone, crystallization zone and impurities zone are distinct. Rubrene is the source material.](image)
2.5.2 Fabrication of organic field effect transistors

Field effect transistors (FETs) are made both for single crystals as well as thin films of organic small molecules (Figure 2-9). Single crystal OFETs are prepared using the bottom-gate (gate electrode is on the bottom) top contact (metal electrode pads on the top of the active layer) configuration. In this method, a heavily doped silicon wafer with a 300 nm thick thermally oxidized SiO₂ layer on the top is cleaned with isopropanol followed by acetone in an ultrasonication bath for 5 minutes each. The wafer is then treated with UV ozone for 20 min to pacify any organic impurities on the substrate. Surface treatment is performed with silazane—usually hexamethyldisilazane (HMDS) is preferred—to pacify any charge trapping hydroxyl groups. Organic single crystals are picked with crystallographic tools under polarized optical microscope. The crystals are then transferred to the clean wafer where they are electrostatically attached to the substrate. Thinner crystals are usually preferred for better attachment on the substrate, which leads to better device performance. Using water based graphite paste, graphite electrodes are painted on the longitudinal ends of the laminated crystals. The electrodes

Figure 2-8: a) Closure view of PVT grown rubrene single crystals. b) Optical image of a PVT grown rubrene single crystal.
would be used as the source and drain. The devices are left in a vacuum oven overnight to remove any trapped water in the devices. For crystals with small dimensions whose length is less than 200 µm, a bottom gate bottom contact configuration is used, where single crystals sit on the top of a lithographically patterned 100 nm thick gold pads of a 300 nm thick thermally oxidized SiO$_2$ surface.

Figure 2-9: a) Bottom-gate, top-contact rubrene single crystal (yellow) FET on a SiO$_2$ surface (grey) with graphite paste on the longitudinal ends as source and drain (black). b) Bottom-gate, bottom-contact lithographically patterned OFETs with active layer spun-cast on the top. Each pair of yellow gold pads represents an OFET.

Thin film OFETs are prepared on a bottom-gate, bottom-contact thin films transistors configuration. Approximately 100 nm thick gold electrodes are patterned using conventional lithography on a clean 300 nm thick thermally grown silicon dioxide wafer comprising highly doped silicon on the bottom as a gate electrode (C = 10.6 nF cm$^{-2}$, Process Specialties, Inc.). Hexamethyldisilazane (HMDS) (99 %, Sigma-Aldrich) is spun-cast at 4000 rpm on the patterned substrates to functionalize the surface.$^{51,52}$ The HMDS treated substrates are annealed for 90 seconds at 90 °C. Solutions of organic small molecules were made at a 10 mg/mL concentration in anhydrous toluene. The solutions were stirred at ambient temperature inside a glovebox overnight before spin casting.
Films are cast on patterned SiO\textsubscript{2} substrates by spin-coating the solutions at 700 rpm-2500 rpm, resulting in approximately 45 nm-100 nm thick active layers. The spun-cast films are usually baked for 3-5 minutes at 80 °C-100 °C depending on the material and the solvents used.

Current-voltage characteristics are measured using a Keithley 2636A Sourcemeter inside an N\textsubscript{2} glovebox in the Gomez lab. FET characterization is described in great detail in Chapter 1 under Principle of OFETs.

2.5.3 **Morphological characterization of organic thin films and single crystals**

Crystals or solid films of conjugated organic small molecules are held together weakly by van der Waals force. The degree of crystalline order or the density of defects varies to a large extent in organic solids. The typical microstructure of an organic crystalline film is destined to have some level of molecular defects, impurities, disorders, grain boundaries, and amorphous regions. The details of microstructures are crucial because long range order in organic films determines the interactions among neighboring molecules. The interactions among neighbors strongly affect the intermolecular overlap and, hence, the electronic structure of the film. Moreover, the connectivity among crystalline domains provides the percolating pathways for efficient charge intermolecular hopping. All of these nanoscale and microscopic properties of conjugated solids strongly affect macroscopic electronic performance of OFETs.
**Atomic force microscopy**

Atomic force microscopy (AFM) provides the high resolution topographical features of organic films. AFM generally involves profiling only the top few nanometer layers of a film using sharp tips, usually with apex diameter in 2-10 nm range. Roughness, step heights of molecular arrangement and grain boundaries are the examples of main information one can extract from organic semiconducting films surface using AFM.$^{53,54}$

In atomic force microscope technique, a sharp tip located at the free end of a cantilever is brought into close proximity of a sample and scanned over the surface (Figure 2-10). The tip and the cantilever are usually a single unit made of silicon, with common dimensions of 2-10 nm for the diameter of the tip, and 100 μm for the length of the cantilever. In any basic operation of AFM, as the sharp tip approaches the sample surface, the tip-sample interaction becomes increasingly repulsive and causes a deflection in the cantilever, which is controlled by a piezoelectric actuator. The deflected motion of the cantilever is detected by a laser beam, which is deflected from the back side of the cantilever to a photodetector. The photodetector translates signals received through the raised and lowered features on the sample surface into an accurate topographic map of the surface features.
Figure 2-11 represents the AFM images of a rubrene single crystal, and pristine and cross-linked thin films of poly(vinylidene difluoride) (PVDF)-based fluoropolymer with their surface roughness. Rubrene single crystals exhibit molecular terracing. The step height of the molecular terracing is 1.4 nm (Figure 2-11b), which suggests that it is an orthorhombic single crystal with the surface normal in the [100] direction. The surface roughness (Root mean square) of the PVDF-based polymer thin films is in the range of 25-26 nm. A Bruker Icon AFM at the Penn State MCL facility is used to study organic materials in the peak force tapping mode.

AFM images are insufficient to reveal the buried morphological structure of organic films. Crystalline domains and ordering of molecules in a film may be visible from the top, but the degree of crystallinity, orientation and other quantitative information about the ordering of the film cannot be extracted from the surface topographic profiling. Such information about the organic films are usually revealed by X-ray diffraction.
Figure 2-11: a) AFM image showing the molecular terracing on a rubrene crystal surface. b) Surface height as a function of scanned position on the crystal surface. The step heights are roughly about 1.4 nm corresponding to orthorhombic crystal structure. c) Topographical maps of crosslinked and pristine P(VDF-BTFE) thin film. RMS for both surface is in the range of 25-26 nm.
X-ray Scattering

Grazing incidence X-ray diffraction (GIXD) is a commonly used technique to probe the crystallographic details of crystalline materials and the microstructure of thin films. Also known as grazing incidence X-ray scattering (GIXS), the technique is usually performed in a lab. However, with obvious benefits of very intense X-ray sources, such as synchrotron radiation facilities located at national laboratories around the U.S.A, GIXS is becoming increasingly more popular.\textsuperscript{53,54}

X-ray diffraction is a nondestructive characterization technique that can be used to probe the entire bulk of an organic film to reveal its crystallinity, crystal size and orientation. The technique is particularly important for organic films because the films are weak X-ray scatters. Moreover, wave length of X-ray ranges from 10 nm to 0.01 nm, which is in the same scale of covalent bonds and atomic radii. In GIXD, usually, incident angle is kept below critical angle (typically $\sim 0.2^\circ$ for 8 keV X-rays and an organic film) so that X-rays travel only along the sample surface an evanescent plane wave. Tuning the angle of incidence of X-rays is a common method to control the intensity and noise from both highly crystalline and disordered samples.\textsuperscript{53,54}

The fundamental operation of X-ray diffraction involves Bragg’s law. As an incident X-ray beam strikes an organic film at specific incident angles and wavelengths, total reflection occurs and some of the X-rays are diffracted by the film. When the outgoing waves have the same phase, constructive interference occurs following the Bragg’s law. In Figure 2-12, the angle of reflection from two planes of atoms in a solid can be written as
where $d$ is the distance between the two planes and $\theta$ is the angle of incidence. As such the path difference between the two waves undergoing interference is $2d\sin\theta$. If the wavelength of the incident wave is $\lambda$, Bragg’s law can be written as:

$$n\lambda = 2ds\sin\theta,$$

where $n$ is a positive integer. Therefore, the angle of diffraction can be related to the crystallographic planes of the film through the Bragg’s law. The direction of the diffracted beam can be utilized to study the orientation of the planes.

Figure 2-12: Schematic showing two X-ray beams with identical wavelength and phase diffracted from atomic planes. If diffracted with constructive interference, they follow the Bragg’s law.
The magnitude and direction of the scattering vector \( (q) \) can also be extracted using the diffraction data. For an elastic scattering, the magnitude of the scattering vector \( (q) \) is:

\[
q = \frac{4\pi}{\lambda} \sin \theta
\]

Combining the scattering vector and the Bragg’s law equation gives an alternative representation of Bragg’s law:

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

Diffracted peaks can be read in different ways in the X-ray detector (Figure 2-13). Films with random crystal orientation produce a ring of diffraction on the detector. However, for the films with both preferred out-of-plane and in-plane orientations, the detector will read spots for each narrowly oriented crystallographic plane and arcs for a broader orientation distribution. While, analyzing the scan along the \( q_z \) direction provides the information about plane spacing, studying the rocking curve along the azimuthal angles gives the distribution of plane orientation.\(^{53,54}\)
Figure 2-13: Diagram showing the diffraction patterns based on the different microstructures. a) a ring of diffraction is observed for randomly oriented films b) an arc for a film with broad orientation distribution c) highly ordered film gives a spot. d) $q_z$ scan direction for measuring plane spacing and orientation distribution.\(^{53}\)

**Figure 2-14** represents representative X-ray scattering images of small molecule (C8BTBT) films as a function of different processing conditions. The X-ray scattering at Advanced Light Source (Berkeley National Lab) is used to study the crystallinity and orientation of C8BTBT films. For the melted and quenched C8BTBT film, sharper diffraction patterns are observed which signifies the highly oriented film (**Figure 2-14** c).
Figure 2-14: GIWAXS (Grazing Incidence Wide Angle X-ray Scattering) data taken at an incident angle of 0.175 degrees for thin films of C8-BTBT. (a) Not annealed, (b) annealed at 80 °C, and (c) melted at 109 °C and quenched to 80 °C. C8-BTBT films after melting and quenching exhibit sharper diffraction peaks, as shown in the insets.
**Polarized optical microscopy**

Crystals of most organic semiconductors are birefringent. By inspecting a film under an optical microscope in the polarized light, long range order of the film can be detected. A highly oriented single crystalline layer under crossed polarized light, for instance, can be observed as an illuminating uniform bright light and the medium surrounding the crystal would turn dark (Figure 2-15 a). Crossed-polarized light can help in distinguishing highly oriented parts of a polycrystalline film from the less oriented ones (Figure 2-15 b). The technique is also a crucial step in the quick selection process of good quality single crystals for OFET fabrication.

Figure 2-15: Cross-polarized images of a) rubrene single crystal b) highly ordered C8BTBT film. Brighter parts on both of the images represent highly ordered microstructures.
2.6 Dissertation overview

This dissertation consists of seven chapters. In the Chapter 3, a novel way of enhancing the hole mobility of rubrene single crystal OFETs is demonstrated. By using a cross-linked high-k PVDF-based fluoropolymer, poly(vinylidene fluoride-bromotrifluoroethylene) P(VDF-BTFE) as a gate insulator, the charge mobility of rubrene single crystal (OFETs) is enhanced by about three orders of magnitude as opposed to OFETs comprising the same uncross-linked fluoropolymer as a gate insulator. Fourier transform infrared spectroscopy (FTIR) analysis suggests that cross-linking is linked to a distinct morphological evolution of the gate dielectric film. It is found that population of TTTG (T = trans, G = gauche) conformation is dominant in the cross-linked P(VDF-BTFE) unlike in the pristine co-polymer. It is believed that the large number of trans population in the cross-linked films leads to minimal chain twisting and chain mobility in the films, resulting in the reduced dipolar interactions at the semiconductor-dielectric interface. Consequently, the energetic disorders at the interface of OFETs comprising the cross-linked fluoropolymer as a gate insulator are minimized, and hole mobilities are enhanced.

Chapter 4 presents a processing method to control the crystallization of the thin films of organic small molecule, 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C₈BTBT). By melting films prior to annealing at a specific quench temperature, a local order enhancement in the polycrystalline films has been shown. The technique has yielded films with higher degrees of orientational order and, therefore enhanced charge mobilities in OFETs by a factor of five than in OFETs comprising as-cast films. The
results are reproduced from Reference 55 with permission from The Royal Society of Chemistry.

In chapter 5, the role of the chemical structure of organic semiconductor on the performance of OFETs is elucidated. The role of alkyl side chain group in a conjugated small molecule is studied. By measuring the single crystal hole mobility of [1]benzothieno[3,2-b]benzothiophene (BTBT) core, 2-octyl[1] benzothieno[3,2-b]benzothiophene (mC₈BTBT), and 2,7-dioctyl-[1]benzothieno[3,2-b]benzothiophene (C₈BTBT), it is found that the single crystal FET hole mobility in C₈BTBT (μ = 8.1 cm²V⁻¹s⁻¹) is three orders of magnitude higher than in BTBT, even though the intrinsic charge transport parameters of the BTBT derivatives remain virtually unchanged. The lattice vibrations of BTBT, mC₈BTBT and C₈BTBT are probed with inelastic neutron scattering (INS). INS results suggest that the addition of alkyl side chains suppresses the intermolecular lattice vibrations, and its interference with the free charge carriers, thereby enhancing the charge carrier mobility.

Chapter 6 represents the initial proof of concept towards understanding the charge transport behavior of organic semiconductors in the vertical direction. Unlike in conventional OFETs, charge carrier in diodes, for instance, travel in the vertical direction. However, the basic fundamental study of charge transport behavior until today is mainly driven by the research relating the horizontal charge transport process. The details of the charge transport behavior in organic semiconductors are still the fluid stage. It is believed that studying the movement of charge carriers from different direction may help in solidifying the concept of charge hopping process. For instance, studying both horizontal and vertical charge transport phenomena of regioregular poly(3-hexylthiophene) (P3HT)
as a function of its molecular weight (MW), the discrepancy in the measured FET as well as space charge limited (SCLC) mobility can be understood. It is hypothesized that the enhanced FET hole mobility in P3HT films with higher MW is the result of stronger molecular alignment of the P3HT films at the dielectric interface.

Chapter 7 concludes the dissertation with the summary of the presented work, and the recommendations for future work.
2.7 References


Giri, G., Park, S., Vosgueritchian, M., Shulaker, M. M. & Bao, Z. High-Mobility, Aligned Crystalline Domains of TIPS-Pentacene with Metastable Polymorphs


Chapter 3

Cross-linking Novel High-k Fluoropolymer Gate Insulator to Enhance Charge Mobilities in Rubrene Single Crystal Field Effect Transistors

Here, a photopatternable high-k fluoropolymer, poly(vinylidene fluoride-bromotrifluoroethylene) P(VDF-BTFE), with a dielectric constant (k) between 8 and 11 is demonstrated. Using rubrene single crystals as the active layer, charge mobilities exceeding 10 cm²V⁻¹s⁻¹ are achieved in thin film transistors with P(VDF-BTFE) gate dielectrics. Furthermore, the bromotrifluoroethylene moiety enables photo-crosslinking and stabilization of gate insulator films while also significantly enhancing the population of trans torsional conformations of the chains. We hypothesize that crosslinking reduces energetic disorder at the dielectric-semiconductor interface by controlling the chain conformations of P(VDF-BTFE), thereby leading to approximately a three-fold enhancement in the charge mobility of rubrene OFETs.

3.1 Introduction

Organic field effect transistors (OFETs) continue to attract wide-spread interest because of their potential to enable low-cost flexible electronic devices.[1] High-
performance OFETs require a gate insulator capable of high capacitance and minimal current leakage to the gate electrode.\[2\] Oxides, such as silicon dioxide or aluminum oxide, are commonly used as gate dielectrics because of their high electrical breakdown strength, even though they often lead to problems associated with charge trapping at the dielectric-semiconductor interface.\[3\] Furthermore, many inorganic dielectrics such as silicon oxide can be difficult to deposit from solution for transistor applications and challenging to integrate with flexible electronics.\[4\]

Polymer dielectrics are a promising alternative to oxides.\[5, 6\] Tuning the chemistry of various polymers, for example with the inclusion of polar groups, may lead to solution-processable and flexible materials with high dielectric constants and consequently high capacitance. High-k polymers such as poly(vinyl alcohol) (PVA, k = 10) and cyanoethylpallulan, (CYPEL, k =12) have demonstrated mobilities of 0.04 cm\(^2\)V\(^{-1}\)s\(^{-1}\) when the active layer is poly(3-butylthiophene).\[7\] PVA, however, is hydrophilic and likely absorbs water, limiting the stability of devices.\[8\] OFETs using CYPEL not only exhibit strong hysteresis and but also have a low on/off ratio (~ 10).\[9\] Furthermore, the polar groups associated with high-k polymers can contribute to energetic disorder at the dielectric-semiconductor interface, thereby inducing a sub band-gap density of states that can act as charge traps.\[10\] Thus, development of novel gate insulators is warranted.

Fluoropolymers are a class of materials that possess exceptional stability due to the strong constituent carbon-fluorine bonds and high dielectric constants due to the polarizability of fluorine-containing groups. Two of the most commonly used fluoropolymeric dielectrics are poly(vinylidine difluoride) (PVDF) and Poly 1,1,2,4,4,5,5,6,7,7 - decafluor - 3 oxa - 1,6 -heptadiene (Cyclic Transparent Optical
Polymer, CYTOP™. PVDF and its copolymers/terpolymers are used for many purposes, including as ferroelectric gate insulators in ferroelectric FETs (FeFETs) for nonvolatile organic memory. Charge mobilities in devices composed of fluorinated dielectrics approach 6 cm²V⁻¹s⁻¹, when, for example, the active layer is a single crystal of rubrene. A limitation of fluorinated materials, however, is that post-synthesis functionalization to tune the materials properties can be challenging. For example, cross-linking of fluorinated materials to stabilize dielectric layers is challenging.

Here we describe a photopatternable, high-k fluoropolymer, poly(vinylidene fluoride-bromotrifluoroethylene) P(VDF-BTFE), where the BTFE moieties enable cross-linking through thermal- or photo-curing of dielectric materials with relative permittivities between 8 and 11. The combination of P(VDF-BTFE) gate dielectrics and rubrene single crystal active layers leads to charge mobilities exceeding 10 cm²V⁻¹s⁻¹ in thin film transistors, which is over an order of magnitude higher than that of rubrene single crystal FETs comprising poly(vinylidene fluoride–tetrafluoroethylene) P(VDF-TeFE) as gate dielectrics. PVDF or its copolymers/terpolymers gated OFETs with commonly exploited organic semiconductors such as pentacene and P3HT have charge mobilities under 0.5 cm²V⁻¹s⁻¹. The highest reported rubrene single crystal OFETs with fluorinated gate dielectrics is 6 cm²V⁻¹s⁻¹. Furthermore, we find that not only does cross-linking impart stability to the P(VDF-BTFE) films, it also enhances charge mobilities within transistors by a factor of three with respect to devices based on uncross-linked P(VDF-BTFE). Cross-linking enhances the relative population of trans conformations along the backbone of P(VDF-BTFE), leading us to hypothesize that
cross-linking reduces dipole disorder at the dielectric-semiconductor interface and thereby enhances charge mobilities in transistors.

3.2 Results

PVDF is a ferroelectric polymer with strong intermolecular interactions that lead to crystalline order. As such, perturbations to the polymer backbone can alter the structure and properties of PVDF-based materials.\cite{16} Here we co-polymerize BTFE with PVDF (Figure 3-1a), where the C-Br bond is susceptible to free radical attack and opens the possibility for cross-linking of the backbone.\cite{17} Furthermore, although PVDF is ferroelectric with energy storage densities of 2.6 Jcm$^{-3}$ in capacitors, Figure 3-1b shows that the measured polarization of P(VDF-BTFE) has no apparent hysteresis up to electric fields of 200 MVm$^{-1}$.\cite{18} Thus, P(VDF-BTFE) has the potential to respond quickly to applied fields when used as a gate insulator in field-effect transistors.

The ability to crosslink P(VDF-BTFE) through free radical chemistries enables stabilization of polymer films and photopatterning. We added dicumyl peroxide (DCP) and triallyl isocyanurate (TAIC) crosslinkers to P(VDF-BTFE) and exposed the film to ultraviolet light for several hours. Figure 3-1c represents frequency dependent dielectric properties of the crosslinked and uncrosslinked copolymers. The dielectric constant of the copolymer decreases from 11.4 to 8.4 with crosslinking. This decrease of the dielectric constant with crosslinking is not surprising, as we expect crosslinking to reduce the molecular motion of chains and inhibit dipole responses to applied electric fields. At frequencies below 100 Hz, the loss tangent is lower for the crosslinked copolymer.
Furthermore, the dielectric breakdown field is increased with crosslinking, from 3.3 MVcm\(^{-1}\) for the pristine copolymer to 5.3 MVcm\(^{-1}\) after crosslinking.

Figure 3-1: Properties of P(VDF-BTFE). a) Chemical Structure of poly(vinylidene fluoride-bromotrifluoroethylene) P(VDF-BTFE). The C-Br bond is susceptible to free radical attack. (b) Polarization of crosslinked P(VDF-BTFE) as a function of electric field. The linear curve with negligible hysteresis indicates non-ferroelectric behavior. (c)
Dielectric constant and loss tangent as a function of frequency for P(VDF-BTFE) and crosslinked P(VDF-BTFE). After crosslinking, the dielectric constant and loss tangent decrease. d) Photo-patterned crosslinked P(VDF-BTFE). The bright area is the exposed Si and the dark area is P(VDF-BTFE) crosslinked using UV light.

**Figure 3-1d** shows examples of photopatterning P(VDF-BTFE), where the crosslinking is controlled through shadow masks and the un-crosslinked polymer is removed through solvent exposure. Although the results shown in **Figure 3-1d** suggest low line edge roughness, we leave characterization of the pattern-transfer efficacy for future work. Nevertheless, Figure 1 shows that crosslinked P(VDF-BTFE) is a promising material for photopatterned high-k gate dielectrics.

We fabricated bottom-gate top-contact field-effect transistors to test P(VDF-BTFE) as a gate insulator. P(VDF-BTFE) copolymer films are hot pressed at temperatures ranging from 100 °C to 200 °C to achieve thicknesses of 6-7 µm on a highly doped clean silicon substrate. The resulting capacitance for the gate insulator films range from 1.0 nFcm⁻² to 1.5 nFcm⁻², with typical current leakage to the gate below 7 x 10⁻¹⁰ A at VGS = -50 V. To minimize the role of morphology of the active layer on transistor properties, we used pre-grown rubrene single crystals as the active layer. Single crystals were grown using horizontal physical vapor transport.[¹⁹] After approximately eight hours of crystal growth, thin red-colored plate-like (thickness 0.2 – 1 µm) rubrene crystals ranging from several hundred micrometers to millimeters in length and width are obtained.

Only well-faceted two-dimensional single crystals that exhibit uniform contrast and smoothness under polarized microscope are chosen for devices (**Figure 3-2a**). The out-of-plane X-ray diffraction data with narrow (001) peaks (**Figure 3-2b**) and Atomic
Force Microscopy (AFM) images with molecular terracing of 1.4 nm (Figure 3-2c) suggest orthorhombic crystals with the surface normal in the [100] direction.\textsuperscript{[20]} The rubrene single crystals are carefully laminated onto the gate/dielectric substrates. Aqueous graphite paste is utilized to deposit source and drain electrodes.\textsuperscript{[6, 21]}

![Figure 3-2: Characterization of rubrene single crystals. (a) Cross-polarized optical micrographs of a representative rubrene crystal. (b) Out-of-plane X-ray diffraction intensities as a function of scattering vector $q$ of a rubrene crystal. The presence of only the (00l) family of reflections is consistent with the scattering from a single crystal. (c) AFM image showing molecular terracing on a crystal surface. Inset shows the step heights.](image)

We compare the electrical characteristics of transistors based on rubrene active layers and eight different dielectrics: poly(vinylidene fluoride) (PVDF), pristine P(VDF-BTFE), crosslinked P(VDF-BTFE), poly(vinylidene fluoride-tetrafluoroethylene)
P(VDF-trFE), poly(vinylidene fluoride-hexafluoropropylene) P(VDF-HFP), poly(vinylidene fluoride-chlorotrifluoroethylene) P(VDF-CTFE), benzocyclobutene (BCB), and silicon dioxide. **Figure 3-3a** shows the transfer characteristics of a representative transistor that has crosslinked P(VDF-BTFE) as the gate insulator. At a source-drain voltage of -50 V, the transfer curves exhibit small hysteresis, near zero threshold voltage and an on/off ratio of about $10^5$. The output characteristics for rubrene transistors are shown in **Figure 3-3b**. The OFET curves behave linearly at lower source drain voltages and approach saturation at higher voltages (above -30 V), suggesting minimal contact problems. We compute the mobility as a function of gate voltage, as shown in **Figure 3-3c**. The field-effect mobilities within rubrene single crystal OFETs composed of crosslinked P(VDF-BTFE) are on average 9.6±1.7 cm$^2$V$^{-1}$s$^{-1}$ and as high as 12 cm$^2$V$^{-1}$s$^{-1}$. In contrast, the average hole mobility for devices comprising uncrosslinked P(VDF-BTFE), P(VDF-trFE), PVDF or SiO$_2$ is about 4 cm$^2$V$^{-1}$s$^{-1}$ (**Table 3-1**, detailed device characteristics are included in Figure S1 of the Supporting Information). The mobilities of devices incorporating crosslinked P(VDF-BTFE) as the gate dielectric are remarkably high, and comparable to devices incorporating BCB as the gate dielectric, although BCB has a much lower dielectric constant ($k = 2.7$).
Figure 3-3: Electrical characteristics of a representative device with a rubrene single crystal as the active layer and with crosslinked P(VDF-BTFE) as the gate insulator. (a) Transfer characteristics (source-drain voltage: -50 V) including the gate leakage current and (b) output characteristics. (c) Mobility as a function of gate voltage for a rubrene transistor on P(VDF-BTFE). We take the mobility of this device to be 11.7 cm²V⁻¹s⁻¹ by averaging the mobility from $V_g = -36$ V to $V_g = -50$ V. The capacitance of the 7.2 µm thick crosslinked P(VDF-BTFE) dielectric layer is 1.0 nFcm⁻².
In addition to high mobilities, devices incorporating P(VDF-BTFE) as the gate insulator show low sub-threshold slopes ($S$), near 1.4 V/decade. We can account for the overall capacitance of the dielectric layer by calculating the normalized subthreshold slope, $S_i = SC_i$. The calculated normalized slope is 1.5 VnF/decade cm$^2$, which is lower than a-Si:H FETs and pentacene thin-film transistors for which $S_i$ values are 10 VnF/decade cm$^2$ and 15-80 VnF/decade cm$^2$, respectively.$^{[22]}$ Transistors based on rubrene single crystals and CYTOP gate dielectric layers exhibit hole mobilities of 5.7 cm$^2$V$^{-1}$s$^{-1}$ and $S_i$ of 1.6 VnF/decade cm$^2$.$^{[12, 13]}$ Because the sub-threshold slope characterizes the field-effect onset, it is often assumed it reflects the quality of insulator/semiconductor interfaces.$^{[23]}$ Thus, the high mobilities and low sub-threshold
slopes observed in crosslinked P(VDF-BTFE) transistors suggests that the improved performance over devices incorporating other polymer dielectrics is a result of the dielectric/active layer interface.

We hypothesize that crosslinking P(VDF-BTFE) leads to a reduction of traps at the dielectric/semiconductor interface. We calculated the maximum number of interface traps present from subthreshold slopes, assuming the densities of deep bulk traps and interface traps are independent of energy\cite{24}. As shown in Figure 3-4, rubrene devices comprising crosslinked P(VDF-BTFE) dielectric layers show the smallest interfacial trap density among all other fluorinated PVDF-based polymers. Given that the chemistries of the fluorinated polymers studied here are similar, it remains a question of how P(VDF-BTFE) dielectrics reduces trap densities.

Figure 3-4: Hole mobility versus maximum interfacial trap density for rubrene single crystal TFT devices using various dielectrics. As the interfacial trap density increases, the charge mobility decreases. The highest mobilities are achieved with crosslinked polymers as the gate dielectric, crosslinked P(VDF-BTFE) or BCB.
3.3 Discussions

One possibility is that by reducing energetic disorder at the dielectric-semiconductor interface we have decreased the interfacial trap density and enhanced charge mobilities.\textsuperscript{[10, 25]} To elucidate the role of crosslinking in P(VDF-BTFE), we examined the populations of P(VDF-BTFE) chain conformations through Fourier transform infrared spectroscopy (FTIR). By integrating the FTIR peaks (Figure 3-5) that correspond to the $\gamma$, $\alpha$, and $\beta$ phases we examine the relative populations of TTTG, TG, and all-trans (T: trans, G: gauche) conformations.

![Figure 3-5: Chain conformations from FTIR of various fluorinated polymers. a) FTIR spectra for four different polymers, pristine P(VDF-BTFE) (pristine), crosslinked P(VDF-BTFE) (X-linked), P(VDF-TrFE), P(PVDF-HFP), P(VDF-CTFE) and PVDF.](image)

Extracting chain conformation populations from FTIR data of pristine and crosslinked P(VDF-BTFE), as well as PVDF, P(VDF-CTFE), P(VDF-HFP) and P(PVDF-trFE), shows TTTG conformations mostly dominate. Nevertheless, TG and all-
trans conformations are lower in the crosslinked sample than in the pristine P(VDF-BTFE) (Figure 3-6a). While dominant yet equally proportionate all-trans and TTTG conformations are prevalent in P(PVDF-trFE), on the other hand, in P(VDF) and P(VDF-CTFE), the population of TTTG conformation is the lowest. We hypothesize that the higher uniformity in chains conformations in crosslinked P(VDF-BTFE) leads to lower heterogeneity within the local environment and therefore less energetic disorder.

Furthermore, the enhancement of TTTG chain conformations in the gate insulator layer indicates a larger population of trans conformations and a reduction of chain twisting. Thus, we expect a reduction in the energetic disorder induced by misoriented dipoles. In contrast, the larger population of TG conformations in pristine P(VDF-BTFE), P(VDF-CTFE) and PVDF implies chain torsions and leads to larger interfacial trap densities (Figure 3-4).

We compare the percentage of TTTG conformations in the various polymer dielectrics to the charge mobility of respective devices in Figure 3-6b. A clear linear trend is apparent. Because the TTTG conformation corresponds to a phase in polymers based on PVDF, we hypothesize that this phase presents a minimal trap density at the semiconductor interface while retaining a high $k$. 
In summary, we have shown that crosslinked P(VDF-BTFE) is a promising material for photopatterned and stable gate dielectrics. Crosslinking enhances the population of trans conformations respect to the neat polymer, demonstrating that crosslinking can affect chain conformations. Organic single crystal field effect transistors based on rubrene active layers and crosslinked P(VDF-BTFE) gate dielectrics have

Figure 3-6: Populations of chain conformations from FTIR peaks at 505 cm\(^{-1}\), 614 cm\(^{-1}\), and 1280 cm\(^{-1}\) associated with the \(\gamma\), \(\alpha\), and \(\beta\) phases, respectively. Each of the phases is dominated by specific chain conformations: TTTG for \(\gamma\), TG for \(\alpha\), and all-trans for \(\beta\) (T-trans, G-gauche). TTTG is the dominant confirmation in crosslinked P(VDF-BTFE). TG conformations are dominant in P(VDF). c) Average hole mobility plotted as a function of TTTG population on six different PVDF-based dielectric films suggests that TTTG chain conformation favors OFET device performance.
shown hole mobilities as high as 12 cm²V⁻¹s⁻¹, three times higher than the average hole mobilities for devices comprising PVDF-based fluoropolymers or SiO₂ as the dielectric layer. We hypothesize that the enhanced hole mobility is due to a reduction of dipole disorder and consequently energetic disorder at the dielectric-semiconductor interface.

3.4 Experimental Section

Crystal Growth
Rubrene (sublimed grade) was purchased from Sigma-Aldrich, and was used as received. Single crystals of rubrene were grown from the source material using horizontal physical vapor transport. Thin plate-like (thickness 0.2 – 1 µm) rubrene crystals ranging from several micrometers to millimeters in length and width were obtained. The process took approximately 12 hours. Only single crystals that exhibit uniform contrast and smoothness under polarized microscope were chosen for device fabrication.

Polymer film preparation
Films of P(VDF-BTFE) were prepared by hot pressing polymer powders.⁷⁻¹⁷, ⁲⁶ Three grams of 9 mol. % BTFE P(VDF-BTFE) copolymer was freezer milled with 3/3 wt. % each of dicumyl peroxide (DCP) and triallyl isocyanurate (TAIC) in liquid nitrogen. By placing the powder mixture in the center of a four inch heavily doped p-type silicon wafer, the wafer was sandwiched between two stainless steel plates and two sheets of Teflon to prevent polymer from adhering to the plates. The sample was then placed in the hot press. To melt all components before applying pressure, the temperature was increased to 100 °C. Once the temperature was reached, pressure was increased by 500
psi every five minutes up to 6000 psi as the temperature was increased to 200 °C. The sample was allowed to sit for six hours where the crosslinking occurred. A thin film of crosslinked P(VDF-BTFE) was obtained. The film thickness varied from approximately six to seven microns.

Similarly, P(VDF) (thickness ~ 3.5 µm) and (PVDF-trFE) (thickness ~ 14 µm) samples were prepared by placing powder polymers on a silicon wafer and heating in a hot press to 200 °C. Pressure was increased by 500 psi every 5 minutes up to 5000 psi. The samples were then left at the temperature and the pressure for 5 hours. BCB films were prepared by filtering as received liquid BCB (The Dow Chemical Company) and spinning on Si wafer at 4000 rpm. The resulting films (thickness ~ 12 µm) were cured at 250 °C in inert environment for an hour.

Device fabrication

Bottom-gate, top-contact FETs were fabricated by laminating high quality rubrene single crystals on various dielectric films. Graphite electrodes (aqueous colloidal graphite, Ted Pella Inc.) were painted on two ends of the longer axes of crystals. The devices were left in vacuum overnight to get rid of any trapped water.

Characterization

Hole mobilities of devices (µ) were calculated in the saturated regime of FETs from the source-drain current (I_DS) vs. gate voltage (V_GS) equation:

\[ I_{DS} = \left( \frac{W}{2L} \right) \mu C_i (V_{GS} - V_T)^2 \]  \hspace{1cm} (1)

where \( C_i \) is the specific capacitance of the insulator (about 1.0 nFcm\(^{-2}\) for 7 µm thick P(VDF-BTFE), \( W \) is the channel width, \( L \) is the channel length and \( V_T \) is the threshold
voltage. Current-voltage characteristics were measured using a Keithley 2636A Sourcemeter inside an N₂ glovebox. AFM Bruker Icon is used to study rubrene single crystal surface in a peak force tapping mode. X-ray scattering data is collected using PANalytical XPert Pro MPD theta-theta Diffractometer. FTIR spectra are obtained on a Bruker V70 FTIR using an attenuated total reflectance (ATR) mode with a Harrick MVP-Pro Star equipped with a diamond prism. For the dielectric measurements the polymers were sputter coated with gold using a Denton Vacuum Desk IV sputter coater under an argon atmosphere at 50 mtorr with the instrument setting of 47% power for 125 seconds. The estimated electrode thickness was 30 nm. Polarization measurements are performed using a modified Sawyer-Tower circuit with a Trek model 30/20 ±30 kV high voltage amplifier system in Galden HT insulating fluid using a triangular unipolar bias at 10 Hz. Room temperature complex dielectric constant as a function of frequency were analysed using an Agilent E4980A LCR meter at a 2 V bias.
3.5 Supporting Information

Characteristics of devices with different gate insulators

Figure 3-S1 shows transfer characteristics and output characteristics of rubrene single crystal OFETs comprising various dielectric films. Device fabrication and electrical measurements were performed in a similar manner as devices comprising crosslinked P(VDF-BTFE) (see methods section). The threshold voltage \( V_{th} \) was close to zero and the on/off ratio is high for all devices, near \( 10^5 \). Evidence of contact resistance and hysteresis are minimal in most devices.
Figure 3-S1: Transfer characteristics (a, d, g, j, m, p, s), output characteristics (b, e, h, k, n, q, t), and mobility vs gate voltage (c, f, i, l, o, r, u) of rubrene single crystal OFETS comprising various gate dielectric layers.
Optical images of rubrene single crystal OFETs

**Figure 3-S2** represents optical images of typical OFETs with different gate dielectric surfaces. To annul the effect of irregularities in the shapes and sizes of rubrene single crystals, imaginary quadrilaterals are drawn to estimate the L/W ratios. Water based graphite paste are painted on the longitudinal ends of the crystals. The paste acts as metal electrodes (source/drain). It is discussed in more details in the Methods and Materials section.

![Optical images of rubrene single crystal OFETs](image)

Figure 3-S2: Rubrene single crystal OFETs (a) on a P(VDF-BTFE) gate dielectric film (b) on a SiO2 gate dielectric. Imaginary red quadrilaterals are drawn to estimate the

Atomic force microscopy (AFM) images of gate dielectric surfaces

Surface topography of different gate dielectrics was analyzed using an AFM Bruker Icon and are represented in **Figure 3-S3**. The root mean square (RMS) for four different types of fluorinated co-polymer films is in the range of 23-27 nm, indictaing similar surface roughnesses among these films. Spun-cast ad cured BCB films have a significantly lower RMS than the rest of the polymer films, with a value of 0.4 nm.
Figure 3-S3: AFM images of different gate dielectric surfaces
3.6 References


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Kalb, W. L., Mathis, T., Haas, S., Stassen, a. F. & Batlogg, B. Organic small molecule field-effect transistors with Cytop™ gate dielectric: Eliminating gate


Chapter 4

Controlling Crystallization to Improve Charge Mobilities in Transistors Based on 2,7-Dioctyl[1]benzothieno[3,2-b][1]benzo thiophene

4.1 Abstract

Long-range order at multiple length scales in small molecule semiconductors is critical to achieve effective electrical charge transport. As a consequence, processing strategies are often important for the fabrication of high-performance devices, such as thin-film transistors. We demonstrate that melting followed by quenching at a fixed temperature can obviate prior processing, control the crystallization process, and lead to enhanced charge mobilities in thin-film transistors based on 2,7-dioctyl[1]benzothieno[3,2-b][1]benzo thiophene active layers. Melting followed by quenching to 80 °C yields films with higher degrees of orientational order, and therefore charge mobilities in devices that are higher by a factor of five over films annealed at the same temperature directly after film casting. (Reproduced from Ref. 34 with permission from the Royal Society of Chemistry)

4.2 Introduction

Charge transport in small molecule organic semiconductors is governed by the coupling between adjacent molecules in the unit lattice and connectivity between grains in crystalline materials\(^1\text{-}^7\). As a consequence, the crystallization of small molecule
semiconductors in the active layer of organic thin film transistors (OTFTs) can significantly affect charge mobilities of devices. In some cases, promoting crystallization simply provides percolating pathways for low-resistance charge conduction, while in others the types of grain boundaries are perturbed to maximize charge hopping between grains\textsuperscript{8-11}.

Several processing methods have been proposed to control the morphology of the active layer in small molecule OTFTs\textsuperscript{12-21}. Single crystals of 2,7-dioctyl[1]benzothieno[3,2-\textit{b}][1]benzothiophene (C8-BTBT) have been demonstrated with inkjet printing of two solvents, one a good solvent for C8-BTBT carrying the molecule and a second poor solvent to induce crystallization\textsuperscript{13}. Using a blade patterned with an array of micropillars, 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) crystals have been aligned to demonstrate a two order of magnitude increase in charge mobility in the direction of alignment when compared to active layers with isotropic films\textsuperscript{12, 18, 22}. Depositing or annealing organic semiconductors at temperatures above the melting temperature but below the liquid crystal to isotropic transition leads to enhanced order in the active layer and improved device performance\textsuperscript{23, 24}. These studies demonstrate promising processing approaches aimed at controlling the crystallization of organic semiconductors.

Here we demonstrate that melting films prior to annealing at a specific quench temperature can control the crystallization in C8-BTBT films. Melt and quench experiments demonstrate a local order enhancement in polycrystalline films. Such films also exhibit higher charge mobilities over the films annealed below the melting
temperature. By erasing the processing history prior to annealing, this approach leads to systematic control of crystallization through control of the quench temperature.

4.3 Results

Bottom-gate, bottom-contact thin film transistors with C8-BTBT films spun cast as active layers were fabricated to extract charge mobilities as previously described. Briefly, approximately 100 nm thick gold electrodes were printed using conventional lithography on a clean 300 nm thick thermally grown silicon dioxide wafer comprising highly doped silicon on the bottom as a gate electrode (C = 10.6 nF cm$^{-2}$, Process Specialties, Inc.). We spun-cast hexamethyldisilazane (HMDS) (99 %, Sigma-Aldrich) at 4000 rpm on patterned substrates to functionalize the surface.$^{25,26}$

As received C8-BTBT (Lumtec) was purified through recrystallization from toluene.$^{27}$ Concentrated 75 mg/ml C8-BTBT solutions were made in anhydrous toluene (99.99 %, Sigma-Aldrich) at 50 °C. Solutions were further heated to 60 °C to ensure complete dissolution. The solutions were cooled to ca. 5 °C for approximately five hours to induce crystallization. C8-BTBT crystals were recovered through filtering, and the final product is white, instead of a slight yellow prior to purification. Purified C8-BTBT was then put under vacuum at room temperature for 24 hours to minimize residual solvent. The yield for recrystallization is approximately 25%. Solutions of purified C8-BTBT were made at a 10 mg/mL concentration in anhydrous toluene. The solutions were stirred at ambient temperature inside a glovebox for 1 hour before spin casting. Films
were cast on patterned SiO₂ substrates by spin-coating C8-BTBT solutions at 700 rpm, resulting in approximately 45 nm thick active layers.

Differential scanning calorimetry (DSC) data shows a melting temperature of 109 °C for C8-BTBT (Figure S1 of the Supplementary Information). A second peak is visible in the DSC data near 124 °C that could indicate melting of a small population of more stable crystals or a liquid crystal to isotropic transition. Nevertheless, we first melt the active layer in C8-BTBT devices on a hot plate at 109 °C for one minute. Although it is possible that the sample is not fully melted, higher temperatures lead to rapid dewetting (Figure 4-S2). The melted samples were then rapidly quenched to different temperatures by transferring to an adjacent hot plate at the desired quench temperature. Solution processing and quenching take place inside a nitrogen-purged glove box. Melting, or at least partial melting, of C8-BTBT films will minimize effects of prior processing. Moreover, we hypothesize that quenching C8-BTBT films at different temperatures enables us to control crystallization kinetics, thereby controlling the degree of order in the film²⁸,²⁹.

The electrical properties of C8-BTBT OTFTs were measured inside a nitrogen glovebox using a Keithley 2636A Sourcemeter. Figure 1 shows electrical characteristics of a typical device quenched at 80 °C and annealed at that temperature for 3 min. Transfer characteristics at a source-drain voltage of -60 V (Figure 4-1a) of the device show minimal hysteresis, on/off current ratios above 10⁶, and threshold voltages near zero. Even though some contact resistance issues are evident in output characteristics (Figure 4-1b), the device appears to reach saturation at high source-drain voltages. The mobilities extracted in the saturation regime as a function of gate voltage are shown in Figure 4-1c.
Mobilities increase as the gate voltage becomes more negative and the device turns on, then mobilities saturate and begin to decrease. The decrease at high negative gate voltages is likely indicative of the device falling out of saturation as the magnitude of the gate voltage exceeds the magnitude of the source-drain voltage plus the threshold voltage. Thus, we take the hole mobility for devices as the average of mobilities between $V_G$ of -20 V and -50 V. In Figure 1c, the mobility we extract is 2.5 cm$^2$V$^{-1}$s$^{-1}$.

![Graphs](image1.png)

Figure 4-1 a) Transfer characteristics, b) output characteristics, and (c) hole mobility for a C8-BTBT device that was annealed at 109 oC for one minute and subsequently quenched to 80 oC for 3 min.
Figure 4-2 shows the hole mobilities extracted from devices where the active layer was melted and then quenched at various temperatures for 3 min. Approximately 15 devices were tested for each condition. Mobilities are highest for devices where C8-BTBT films were melted at 109 °C and recrystallized at 80 °C. Lowering the quench temperature by 5 °C decreases charge mobilities by almost a factor of two. Increasing the quench temperature by 10 °C also decreases charge mobilities for C8-BTBT devices by a factor of two.

As a control, we also annealed C8-BTBT devices at 80 °C for three minutes directly after solvent casting. Devices annealed at 80 °C after casting exhibit charge mobilities of 0.40 ± 0.10 cm²V⁻¹s⁻¹, while devices with as-cast C8-BTBT active layers exhibit charge mobilities of 0.20 ± 0.01 cm²V⁻¹s⁻¹. The on/off ratio for all devices is near 10⁶, while the threshold voltage decreases from about 5 V for as-cast and annealed devices to -3 V for
quenched devices (Figure S3 of the Supplementary Information). Annealing after melting the C8-BTBT active layer leads to higher device charge mobilities than annealing directly after casting.

We hypothesize that enhanced charge mobilities in quenched C8-BTBT films are due to different C8-BTBT thin film morphologies. We examined the microstructure of C8-BTBT films after various processing conditions using grazing-incidence wide angle X-ray scattering (GIWAXS) at Beamline 7.3.3 of the Advanced Light Source (X-ray energy of 10 keV). The diffraction data for all samples shown in Figure 4-3 suggest that C8-BTBT crystallites are strongly oriented with the crystallographic c axis along the substrate normal. The similarities in the film texturing and location of diffraction peaks suggest the same polymorph is observed in all samples. Nevertheless, C8-BTBT films quenched at 80 °C shows sharper diffraction features compared to both as-cast and C8-BTBT films annealed at 80 °C after casting, potentially indicating stronger long-range order.

The crystallite orientations of C8-BTBT films were quantified through pole figures obtained from rocking curves around the (300) reflection using a Rigaku DMAX-Rapid II Microdiffractometer. We chose the (300) peak because of the low reflectivity background near $q_z = 0.7 \, \text{Å}^{-1}$. Table 4-S1 of the Supplementary Information shows that melting and quenching films at 80 °C leads to slightly larger coherence lengths (~15 nm) than for as cast films (~14 nm) or after annealing films at 80 °C (~13 nm), as obtained from the full-width at half maximum intensity of the (300) reflection.
Figure 4-3: GIWAXS data taken at an incident angle of 0.175 degrees for thin films of C8-BTBT. (a) Not annealed, (b) annealed at 80 °C, and (c) melted at 109 °C and
quenched to 80 °C. C8-BTBT films after melting and quenching exhibit sharper diffraction peaks, as shown in the insets.

Intensities at the (300) reflection as a function of azimuthal angle are shown in Figure 4-4. As-cast films and films annealed at 80 °C for three minutes have similar crystallite orientations. Films of C8-BTBT that were melted and quenched at 80 °C have narrower crystallite orientation distributions compared to as-cast samples and samples annealed at 80 °C without melting. As shown in Figure 4-S4 and Figure 4-S5, atomic Force Microscopy images reveal well-defined molecular steps and polarized optical microscopy images show stronger liquid crystalline order for samples that were melted and quenched, supporting our conclusion that order is enhanced through this protocol.

![Normalized intensity vs azimuthal angle](image)

**Figure 4-4:** Rocking scan intensities as a function of azimuthal angle for C8-BTBT films. Intensities are normalized to the maximum intensity for each sample. Narrower distributions of crystallite orientations are apparent in C8-BTBT films that were melted and quenched to 80 °C when compared to as-cast films and films annealed at 80 °C.

We hypothesize that the sharper GIWAXS peaks shown in Figure 4-3 for C8-BTBT films quenched at 80 °C are indicative of stronger crystallite texturing, which is apparent in the narrower crystallite distribution shown in Figure 4-4. We also hypothesize that a
narrower distribution of crystallite orientations leads to higher charge mobilities in thin film transistors\textsuperscript{33}. **Figure 4-5** compares the full width at half maximum (FWHM) in $\omega$ of the active layer with thin film transistor mobilities. A trend is apparent, where broader orientation distributions in the active layer lead to lower device mobilities. An exception is found for films quenched at 95 °C, where the device mobilities are low for the apparent narrow distribution of crystallite orientations. We speculate that quenching at this high temperature may compromise film continuity, as suggested by optical micrographs shown in **Figure 4-S2** and **Figure 4-S4**. Overall, melting films prior to annealing leads to more oriented crystallites and consequently, higher charge mobilities in devices.

![Graph showing the relationship between FWHM and mobility](image)

**Figure 4-5**: Device mobilities versus orientational order from rocking scans in terms of the FWHM in degrees of azimuthal angle $\omega$. Samples are labelled with either the quenching temperature, with As cast for un-annealed samples, or with Annealed at 80 °C for samples annealed directly after spin casting.
4.4 Discussions

We speculate that melting and quenching increases the orientational order by controlling the crystallization process. Furthermore, the DSC data shown in Figure 4-S1 suggests a liquid crystalline phase exists above the crystal melting temperature. Thus, it is possible that annealing for 1 min at the melting temperature may induce liquid crystalline order in the active layer, which has been shown to enhance organic thin film transistor mobilities. Nevertheless, the dependence of the film structure and device mobilities on the quench temperature suggests that control of the crystallization process in the active layer is crucial for device performance and afforded by melting prior to thermal annealing.

In summary, we can enhance crystal texturing by melting and quenching C8-BTBT films. The stronger orientational order in the active layer of thin film transistors leads to an increase in hole mobilities by a factor of five. A distinct advantage of melting films prior to annealing is obviating the effects of processing history prior to thermal annealing. Varying the quench temperature should affect crystallization kinetics by controlling the thermodynamic driving force for crystallization, thus providing a systematic approach to control the structure in the active layer of organic thin film transistors.
4.5 Supporting Information

*Differential scanning calorimetry (DSC) result of C8-BTBT*

Differential scanning calorimetry results of C8-BTBT are shown in Figure S1. The crystallization temperature ($T_C$) and melting temperature ($T_m$) for C8-BTBT are 98 °C and 109 °C, respectively. Another peak at approximately 124 °C is also apparent, which is likely due to a liquid crystal to isotropic transition.

Figure 4-S1: Differential scanning calorimetry results for C8-BTBT. (a) Two peaks are apparent in heating scans, a melting temperature ($T_m$) at 109 °C and a liquid crystal to isotropic transition at 124 °C. (b) Same as (a) with a narrower temperature range.
**Polarized optical micrographs (POM) as a function of temperature**

Using a polarized optical microscope equipped with a heating stage, bright field and cross-polarized images of C8-BTBT films were taken at various temperatures. Figure S2 shows evidence of birefringence at 109 °C, suggesting a liquid crystalline phase. As the temperature increases beyond 109 °C, birefringence decreases and dewetting becomes apparent.

![Figure 4-S2: Optical micrographs of C8-BTBT films as a function of temperature. Bright field (top) and cross-polarized (bottom) optical microscopy images as a function of temperature. From left to right: 25 °C, 80 °C, 109 °C, 115 °C, 125 °C, and 135 °C respectively. Scale bar is 100 µm.](image)

**Device characteristics for C8-BTBT thin film transistors**

Transfer and output characteristics of transistor devices processed with different conditions are shown in Figure S3. The on/off ratio is high for all devices, near 10^6, but contact resistance and hysteresis are evident. The threshold voltage moves to negative voltages for devices that were melted at 109 °C prior to annealing.
As cast

\[ V_{th} (V) = 6 | \frac{I_{on}}{I_{off}} = 1.4 \times 10^6 \]

Annealed at 80 °C

\[ V_{th} (V) = 5 | \frac{I_{on}}{I_{off}} = 3.8 \times 10^6 \]

Quenched at 75 °C

\[ V_{th} (V) = -3 | \frac{I_{on}}{I_{off}} = 6.2 \times 10^6 \]

Quenched at 80 °C

\[ V_{th} (V) = -3 | \frac{I_{on}}{I_{off}} = 1.1 \times 10^7 \]
Using the X-ray rocking scan data, the full width at half maximum (FWHM) in scattering vector $q$ of the (300) reflection in Scherrer’s equation (with a shape factor of 1) yields the coherence lengths of C8-BTBT films under various processing conditions.
shown in Table 4-S1. We can also quantify the breadth of the distribution of crystallite orientations by taking the FWHM in azimuthal angle of pole figures obtained from rocking scans around the (300) reflection using a Rigaku DMAX-Rapid II Microdiffractometer. The coherence lengths and FWHM in of the active layer are compared to the thin film transistor mobilities in Table S1. Films that were melted and quenched at 80 °C show a slightly larger coherence length and smaller FWHM in than films processed at other conditions.

Table 4-S1: FWHM of rocking scan intensities and charge mobilities of thin film transistors for various processing conditions

<table>
<thead>
<tr>
<th>Processing condition</th>
<th>Coherence length (nm)</th>
<th>FWHM (degrees in )</th>
<th>Mobility (cm²V⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-cast</td>
<td>14.1</td>
<td>5.5</td>
<td>0.20 ± 0.01</td>
</tr>
<tr>
<td>Annealed at 80 °C</td>
<td>12.7</td>
<td>5.4</td>
<td>0.40 ± 0.10</td>
</tr>
<tr>
<td>Quenched at 75 °C</td>
<td>13.5</td>
<td>4.5</td>
<td>1.3 ± 0.3</td>
</tr>
<tr>
<td>Quenched at 80 °C</td>
<td>14.8</td>
<td>4.3</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td>Quenched at 85 °C</td>
<td>13.9</td>
<td>4.1</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>Quenched at 90 °C</td>
<td>13.7</td>
<td>4.8</td>
<td>0.93 ± 0.10</td>
</tr>
<tr>
<td>Quenched at 95 °C</td>
<td>12.9</td>
<td>4.0</td>
<td>0.41 ± 0.10</td>
</tr>
</tbody>
</table>

Optical microscopy and AFM images of C8-BTBT thin films

Figure 4-S4 shows optical microscopy (OM) and atomic force microscopy (AFM) images of C8-BTBT films after various processing conditions. The OM micrographs appear to show more holes in the channel regions after quenching at high temperatures (90 and 95 °C).
Figure 4-S4: Optical microscopy (left) and AFM images (right) for C8-BTBT films after various processing conditions. Scale bar is 50 μm in the optical micrographs.
Figure 4-S5: Bright light (left) and polarized optical microscopy (right) images of C8-BTBT film after various processing conditions. Scaler bar is 100 μm.
All films show the evidence of molecular terracing in AFM images, although the molecular terracing in quenched films is more apparent. The step height is 2.9 nm, which corresponds to the interlayer distance in the crystallographic $c$-axis. Polarized optical microscopy (POM) images in Figure 4-S5 show some features for quenched films that suggest the presence of domains aligned over large distances, and that are consistent with a liquid crystalline structure.
4.6 References

Chapter 5

Suppressed Lattice Fluctuations Improves the Hole Mobility of [1]benzothieno[3,2-b]benzo thiophene (BTBT) Core

In Chapter 5, [1]benzothieno[3,2-b]benzothiophene (BTBT) core, 2-octyl[1]benzothieno[3,2-b]benzothiophene (mC8BTBT), and 2,7-dioctyl-[1]benzothieno[3,2-b]benzothiophene (C8BTBT) are synthesized, and their FET hole mobilities are studied. It is found that the single crystal FET mobility in C8BTBT (μ = 8.1 cm²V⁻¹s⁻¹) is three orders of magnitude higher than in BTBT, even though the intrinsic charge transport parameters of BTBT derivatives remain virtually unchanged. The lattice vibrations of BTBT, mC8BTBT and C8BTBT are also measured with inelastic neutron scattering. The neutron scattering results suggest that the addition of alkyl side chains suppresses the intermolecular lattice vibrations and their interference with free charge carriers, thereby enhancing the hole mobility of C8BTBT.

5.1 Introduction

Organic small molecules have continued demonstrating themselves as promising semiconducting materials for the next generation organic electronics. For instance, rubrene, (2,7-dioctyl-[1]benzothieno[3,2-b]benzothiophene) C8BTBT and TIPS-pentacene have shown charge mobilities exceeding 10cm²V⁻¹s⁻¹.1-4 Despite having charge mobility comparable with that of amorphous silicon, organic solids are comprised of weakly packed structure through weak Van der Waals intermolecular interactions, which led to a hopping process for the movement of charge carriers.5 The weak molecular architecture
of organic molecules is a limiting step for the efficient charge transport with the organic solids. Consequently, the electronic properties of organic small molecules including charge transport are governed by weakly packed lattice structure.

To tune the charge transport in organic semiconductors, scientists have been trying various processing techniques, studying different fundamental aspects theoretically and experimentally, and engineering numerous device configurations.\textsuperscript{1,6-11} Changing the chemical structure of organic semiconductors, and studying the structure-property relationship are one of the most common methods used to design high-performance novel organic semiconductors.\textsuperscript{12-14} However, understanding the properties of novel organic materials is hindered by a large number of factors influencing charge carrier mobility in organic field effect transistors (OFETs), including synthetic methods, device geometry, contacts, device interfaces, thin-film growth, and molecular packing in organic solids.\textsuperscript{11} Therefore, a challenge one faces is the choice to pick a right molecule for OFETs.

The molecular architecture of organic small molecules is very sensitive to chemical functional groups and positions the groups are added to. Properly designed side-chains can bring conjugated core closer and decrease energy gaps, while misplaced side-groups can destroy the overlap of electronic orbitals and deteriorate charge hopping process.\textsuperscript{11,12,15,16} The deformation of lattice and the displacement in lattice parameters are common in the weakly held architecture of organic solids, resulting in collective lattice dynamics—also known as phonon. In crystalline structure, lattice dynamics could play an important role in electron-phonon coupling and affect the charge transport.\textsuperscript{17-21}

\textsuperscript{1}benzothieno[3,2-b][1]-benzothiopene (BTBT) is a promising core structure that has been widely exploited in recent years.\textsuperscript{1,22,23} BTBT is poorly soluble in most common
organic solvents such as toluene or chlorobenzene. However, Takimiya, et al. have solution processed the core as an active layer in OFETs after adding solubilizing alkyl groups.\textsuperscript{24} The group has also demonstrated that addition of alkyl groups of different chain length leads to varying hole mobility among the soluble BTBT derivatives.\textsuperscript{15,24} The highest reported C\textsubscript{8}BTBT has octyl groups on each of its ends, and has a hole mobility of 31 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}.\textsuperscript{22} The question remains why the addition of mere solubilizing alkyl groups disrupts the electronic properties of BTBT core.

From the electronic point of view, long alkyl chains create bulky insulating layers between the semiconducting pi-pi stacks along the polycrystalline thin film, which limits the vertical transport and dilutes the number of pi-pi systems very close to the channel interface. The shorter alkyl chain, on the other hand, improves the charge carrier mobilities. The shorter alkyl chain, however, exhibits problems in the homogenous film formation for BTBTs due to their high tendency to crystallize.\textsuperscript{25,26} Furthermore, scientists have also theorized that alkyl groups provide an anchoring effect by bringing BTBT cores closer, maximizing the intermolecular coupling.\textsuperscript{15,26} Despite many speculations, a convincing relationship between the alkyl side chains and electronic properties has not been well-established yet.

It is believed that on the top of key intrinsic parameters, namely transfer integral and reorganization energy, lattice fluctuations within a crystal lattice also affect the macroscopic properties of OFETs. By adding single and double octyl groups to BTBT core, single crystal FET hole mobilities of the BTBT derivatives are studied both computationally and experimentally. It is found that the single crystal FET mobility in C\textsubscript{8}BTBT (\(\mu \sim 8\) cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}) is three orders of magnitude higher than in BTBT single
crystal, even though the intrinsic charge transport parameters remain virtually unchanged. The lattice vibration of BTBT, mC8BTBT and C8BTBT is also measured with inelastic neutron scattering (INS). INS results suggest that the addition of alkyl side chains suppresses the intermolecular lattice vibration and its interference with free charge carriers. We hypothesize that addition of alkyl groups suppresses those lattice vibration in the BTBT core, thereby enhancing hole mobility.

5.2 Results

Systematic addition of alkyl side chains to a conjugated core can help in elucidating the effect of alkyl groups on the electronic properties of the conjugated core. By adding octyl chain to a [1]benzothieno[3,2-b]benzothiophene (BTBT) core in two different ways: single arm and double arm, charge transport properties of BTBT core has been studied. BTBT core with single arm and double arms of octyl group are called 2-octyl[1]benzothieno[3,2-b]benzothiophene (mC8BTBT), and 2,7-dioctyl-[1]benzothieno[3,2-b]benzothiophene (C8BTBT) respectively (Figure 5-1).
BTBT, mC₈BTBT and C₈BTBT are synthesized following the protocol described in Synthesis section under Methods and Materials. Before using the synthesized yellowish amorphous powder of the BTBT derivatives as active layers in bottom gate bottom contact thin film transistors (TFTs), the BTBT derivatives are further solution crystallized in toluene and recovered as whitish shiny crystalline product. It has been found that unpurified yellowish powder of C₈BTBT leads to deterioration of TFT properties and over three orders of magnitude drop in hole mobility. It is imperative that white crystalline product BTBT derivatives should only be used study the charge transport properties.

TFTs of BTBT derivatives are prepared on cleaned lithographically gold-patterned silicon dioxide (SiO₂) substrates. In order to remove any charge trapping impurities, the substrates are cleaned with acetone followed by isopropyl alcohol (IPA) and treated under UV-Ozone. Hexamethyldisiloxane (HMDS) is also spin-casted to further reduce any charge trapping groups. Bottom gate bottom contact TFTs prepared by
spin-casting 0.4 wt. % each BTBT derivatives and toluene solution on the HMDs treated substrate show very distinct characteristics. In fact, hole mobility of BTBT core increased by an order of magnitude with the addition of an octyl group and by two orders of magnitude with the addition of two octyl groups. Average thin film hole mobilities of BTBT derivatives are plotted in Figure 5-2, which for BTBT core, mC₈BTBT and C₈BTBT are 0.03 ± 0.01 cm²V⁻¹s⁻¹, 0.27 ± 0.03 cm²V⁻¹s⁻¹ and 3.21 ± 0.49 cm²V⁻¹s⁻¹. Device characteristics are shown in Figure 5-S1-S3.

The alkyl side-chains are not conductive. The only purpose of adding such greasy groups is to increase the solubility of the BTBT core. Yet, a trend of decreased charge mobility when alkyl side-chains are added is observed. From current state of understanding, the origin of the enhancement in charge mobility by adding alkyl side-chains is still not well-understood.

![Figure 5-2: Log plot of thin film mobility of BTBT core and its derivatives with single and double arm](image)

The alkyl side-chains are not conductive. The only purpose of adding the greasy groups is to increase the solubility of BTBT core. Yet, a trend of decreased charge
mobility when alkyl side-chains are added is observed. From current state of understanding, the origin of the enhancement in charge mobility by adding alkyl side-chains is still not well-understood.

A very obvious factor that affects electronic performance organic TFTs is thin film morphology. X-ray scattering and atomic force microscopies (AFM) are used to characterize thin film properties such as crystallinity and molecular terracing. All three BTBT derivatives demonstrate highly crystalline films with well-defined grain boundaries domains (Figure 5-S6, 5-S8). Even though features of grain boundaries may be distinct among films, the results are still inconclusive mainly because the chemistry of BTBT derivatives is different.

The difference in the chemistry of BTBT derivatives warrants that intrinsic charge transport properties of BTBT derivatives be probed, which requires numerical calculation of charge transport parameters as well as electrical measurement of single crystal FETs. Not only will that circumvent the effect of thin film morphology, if any, but also will provide true charge transport parameters.

Intrinsic charge transport in organic conjugated molecules are governed by two key parameters: 1) transfer integral that reflects the magnitude of electronic coupling between two oligomers and 2) reorganization energy which describes geometric relaxation of the oligomers and its surroundings on the movement of the charge carriers. Density functional theory (DFT) calculations are performed to evaluate the key charge transport parameters of BTBT derivatives using the Gaussian 09 software package for a system consisting of four molecules. Figure 5-3 shows single crystal structure of the BTBT derivatives with three possible intermolecular charge hopping
directions for the system. Detailed single crystal structures along with the corresponding powder X-ray diffraction (Figure 5-S7) are shown in the Supplementary Section. X-ray diffraction results suggest that the respective crystal structure of the BTBT derivatives remain unchanged in thin films, powder and single crystals.

Reorganization energies, transfer integrals and hopping rates are calculated which are shown in Table 5-1. It is apparent that reorganization energy increases slightly from 0.23 eV to 0.25 eV between BTBT core and C₈BTBT. Moreover, transfer integrals remain virtually indifferent. As opposed to three orders of magnitude change in hole mobility with just an addition of greasy octyl groups, the calculated hopping rates from the intrinsic charge transport parameters among BTBT derivatives are not significantly different.
The results suggest that the orders of magnitude difference in hole mobility among BTBT derivatives may not be answered until the numerical predictions of intrinsic charge transport is complemented with experimental results. As such, we also prepared and measured device properties of single crystal OFETs. Single crystals FETs having no active layer grain boundary effect is one of the best possible ways to measure intrinsic charge transport properties of organic semiconductors experimentally.

The single crystals of BTBT derivatives are prepared on clean HMDS treated SiO$_2$ using anti-solvent crystallization. Bright uniform contrast of well-defined geometry in the cross-polarized images and sharp molecular step-heights in the AFM images suggest the single crystalline domain of BTBT derivatives (Figure 5-4, 5-5). The molecular step-heights of the BTBT derivatives correspond to lattice constant $c$ of monoclinic, triclinic and monoclinic crystal structures respectively. Water-based graphite

<table>
<thead>
<tr>
<th>Materials</th>
<th>Reorganization Energy (eV)</th>
<th>Hopping directions</th>
<th>Transfer integral (eV)</th>
<th>Hopping rate ($s^{-1}$)</th>
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</thead>
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<tr>
<td>BTBT</td>
<td>0.226</td>
<td>a</td>
<td>0.0133</td>
<td>6.98 $10^{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b</td>
<td>0.0297</td>
<td>3.54 $10^{12}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c</td>
<td>0.0267</td>
<td>2.79 $10^{12}$</td>
</tr>
<tr>
<td>mC$_8$BTBT</td>
<td>0.238</td>
<td>a</td>
<td>0.0165</td>
<td>9.22 $10^{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b</td>
<td>0.0476</td>
<td>7.72 $10^{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c</td>
<td>0.0245</td>
<td>2.04 $10^{11}$</td>
</tr>
<tr>
<td>C$_8$BTBT</td>
<td>0.249</td>
<td>a</td>
<td>0.0146</td>
<td>6.30 $10^{11}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b</td>
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<td></td>
<td></td>
<td>c</td>
<td>0.0256</td>
<td>1.95 $10^{11}$</td>
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</table>
paste is used on the longitudinal ends of single crystals as source and drain. A representative SCFET is shown in Figure 5-6.

Figure 5-4: Optical micrographs of single crystals of BTBT derivatives grown using anti-solvent method
Figure 5-5: AFM images of the single crystals of BTBT derivatives. The step-height corresponds to the lattice constant c of their respective single crystal structure.
Figure 5-7 shows the log plot of average hole mobility of thin film FETs and single crystal FETs. While the average hole mobility of BTBT core remains practically the same about $0.02 \pm 0.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, single crystal hole mobility of C$_8$BTBT doubles compared to that of thin film hole mobility. The average hole mobility of C$_8$BTBT SCFETs is $6.0 \pm 1.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, the highest being $8.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. On the contrary, average hole mobility of single crystal mC$_8$BTBT FETs, which is $2.9 \pm 1.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, escalated by almost an order of magnitude than that of thin film hole mobility. The highest measured single crystal hole mobility of mC$_8$BTBT is $4.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. It is to our best knowledge that this is the first time single crystal as well as thin film hole mobility of mC$_8$BTBT is ever reported. The increment in the single crystal hole mobility of the BTBT derivatives is believed to be the result of absence of disorders due to grain boundaries in the active layer.
Device properties including log plot of differential hole mobility of the highest performing BTBT single crystal and C₈BTBT single crystal FET are compared in Figure 5-8. For the devices shown, we take the hole mobility of BTBT and C₈BTBT SCFETs to be 0.03 cm²V⁻¹s⁻¹ and 8.1 cm²V⁻¹s⁻¹ respectively. This is a significant enhancement in the hole mobility just by an addition of greasy alkyl chains which are only supposed to increase the solubility of a BTBT core. Similarly, on-off current ratio (I_{on/off}) also increases by three orders of magnitude (I_{on/off} BTBT ~ 10⁴, I_{on/off} C₈BTBT ~ 10⁷). Threshold voltage (V_{th}) for both device are close to zero. Despite having significant differences in the electrical properties, both representative organic devices shown in Figure 5-8 show excellent transfer characteristics as well output characteristics with minimal effect of contacts in their performance. Hole mobility of the highest performing mC₈BTBT SCFET is is 4.5 cm²V⁻¹s⁻¹. Electrical properties of the mC₈BTBT device are presented in the Figure 5-S4.

Figure 5-7: Log plot of thin film mobility versus single crystal hole mobility of BTBT core and its derivatives with single and double arm
It is evident from Figure 5-7 and Figure 5-8 that indeed the addition of alkyl groups not only alters the solubility of BTBT core, but also its charge transport properties. Question remains, however, how it affects the electronic properties because
DFT calculation results (Table 5-1) show that the intrinsic parameters that are believed to mainly govern the charge transport in such conjugated molecules are not significantly altered unlike the hole mobility. Takimiya et. al. believe that addition of alkyl groups increases intermolecular interaction among BTBT core layers\(^{32}\). However, a concrete experimental evidence of alkyl side-chain role in the charge transport properties of BTBT core is still unavailable.

It has been known in inorganic semiconductor that the lattice dynamics is another factor that governs the charge transport. Using similar analogy, we hypothesize that when side chains are added the lattice dynamics, commonly known as phonon, are damped. The suppressed phonon modes will decrease electron-phonon interactions, thereby leading to better charge transport as seen in C\(_8\)BTBT. This is supported by our inelastic neutrons scattering experiment where we observed that both coherent inelastic scattering intensity are decreased when octyl side chains are added to BTBT core.

The lattice vibrations of BTBT, mC\(_8\)BTBT, and C\(_8\)BTBT are examined with inelastic neutron scattering using the Cold Neutron Chopper Spectrometer (CNCS) at Spallation Neutron Source in Oak Ridge National Lab, TN.\(^{33}\) When a neutron beam interacts with nuclei of a sample, neutrons can lose or gain energy by exciting or terminating phonons. The change of energy corresponding to the quantized energy of phonon is measured by the time of flight chopper spectrometer. Since protonated samples suffer from strong incoherent scattering due to the large incoherent scattering cross section of hydrogen atoms, we also synthesized mC\(_8\)BTBT-d\(_{15}\) and C\(_8\)BTBT-d\(_{30}\) with partially deuterated side-chains. Deuterated samples highlight the collective dynamics of the conjugated core and increase the signal to noise ratio,
We measure the scattering function $S(Q, \omega)$ from 2K to 360K at 13 different temperatures and we use three incident energies ($E_0=1.9\text{meV}$, $6.3\text{meV}$, and $26\text{meV}$) to cover dynamics from 100s of femtosecond to ps. $\omega$ and $Q$ represents energy change and momentum transfer respectively. The scattering intensity of the BTBT derivatives at 300 K with incident energy of $26\text{meV}$ is shown in Figure 5-9. All the scattering signals collected falls into the kinematic region where neutron energy and momentum conservation is observed. The central red line with the highest intensity represents elastic neutron scattering, and the darker spots on the line come from Bragg powder diffraction of the crystalline structure. The scattering beyond the elastic line is a result of thermal motion of the molecules. Higher inelastic scattering energy indicates faster motion. In these organic crystals, the motion observed include: intramolecular vibration and intermolecular vibration. The latter occupies a lower energy level. Here, we will mainly discuss the effect of intermolecular vibration on charge transport because the energy range we use covers the energy level of such vibrations.
Figure 5-9a represents three inelastic scattering intensities around the energy of 4meV, 18meV, and 22meV for BTBT molecule. The DFT calculation of a single stabilized BTBT molecule predicts that the lowest intra-molecular vibration energy of the BTBT core is above 6meV (Figure 5-S10), thereby suggesting that the 4meV excitation originates from collective intermolecular vibrations. When alkyl side chains are introduced to BTBT cores, the low energy inelastic scattering line merged with the elastic
scattering line as shown in Figure 5-9 b and c. The decrease in excitation energy level suggests a slower BTBT core lattice dynamics in alkylated derivatives. The scattering intensity \( S(Q, \omega) \) as a function of energy can be directly seen in Figure 5-10.

![Figure 5-10: a) Scattering function \( S(Q, \omega) \) of BTBT core and its derivatives as a function of energy change, \( \omega \) and momentum transfer, \( Q \) at 300K with incident neutron beam energy of 26 meV. b) Closer view of the plot a).](image)

The twin peaks located at 3.7meV of BTBT scattering shift to lower energy level. They become shoulders as side-chains are added and eventually merge with resolution. The intensity of the inelastic peaks also significantly decreases. In BTBT where inelastic peaks are prominent, compared to C\(_8\)BTBT where the inelastic peaks are under covered by incoherent quasi-elastic scattering indicating the lattice vibration slower. The evolution of inelastic scattering with time is also studied using Fourier-Transform
analysis. The time-dependent pair correlation function, $S(Q,t)$, which represents the correlation of atom positions at time $t$ relative to their positions at $t = 0$, is shown Figure 5-11. The results suggest that a strong vibration mode near one picosecond is present in BTBT core. On the contrary, the vibration mode diminishes significantly in mC$_8$BTBT, and practically vanishes in C$_8$BTBT.

![Figure 5-11: Time-dependent pair correlation function $S(Q, t)$ of BTBT core and its derivatives as a function of time, t and momentum transfer, Q at 0K to 330 K with incident neutron beam energy of 26 meV.](image-url)
5.3 Discussions

Troisi et. al. have shown that modes that modulate the intermolecular coupling in conjugated organic crystals are in the terahertz frequency range.\textsuperscript{20} For instance, in pentacene, the relaxation time of delocalized free charge carriers is on the time scale of 0.8 ps. It had also been shown that the modes that modulate charge transport in conjugated small molecules which requires charge delocalization among different molecular moieties most strongly reside in the ~ 1 THz range. Furthermore, they hypothesized that the low frequency in intermolecular modes is attributed to weak van der Waals force that helds organic small molecules.

Results from Figure 5-9, Figure 5-10 and Figure 5-11 suggest that lattice vibration is strongest in BTBT core and so is the phonon density. With the phonon mode close to 1 THz range as in pentacene, the strongest phonon-charge carrier interaction in BTBT core leads the lowest hole mobility. As the low frequency phonon mode withers with the addition of alkyl group hole mobility increases in the similar fashion. C8BTBT in which the phonon mode disappears completely, hole mobility is the highest.

Until now, it was unknown as to how the alkyl chain affects the charge transport in the BTBT core. We have measured the charge transport properties of single crystals of BTBT, mC8BTBT and C8BTBT both experimentally and computationally. Though intrinsic charge transport parameters predicted using DFT method remain virtually unchanged among the BTBT derivatives, single crystal FET hole mobility in BTBT is three orders of magnitude lower than in C8BTBT. Inelastic neutron scattering results suggest that low frequency phonon mode that interferes with free charge carriers is
suppressed with the addition of alkyl groups. We believe that lattice dynamics is also crucial factor that should be considered in material design process.

5.4 Methods

Synthesis

The two-step synthesis towards C8-BTBT was carried out using previous methods, starting from [1]benzothieno[3,2-b]benzothiophene (BTBT) as the starting material. From an unsubstituted BTBT core, Friedel-Crafts acylation was utilized to obtain the 2,7-diketone, which was subsequently reduced with hydrazine hydrate under Wolff-Kishner conditions, yielded the dialkyl C8-BTBT derivative. The material obtained from the WK reaction yielded an iridescent-slightly yellow, solid. Purification of this material via silica column chromatography, using hexanes as the eluent, removed all traces of the yellow impurity, resulting in an iridescent colorless solid.

Analytically pure material was obtained after recrystallization in toluene. Recrystallization occurred as standard procedure. The product solid was dissolved using hot toluene, then filtered (hot), and concentrated under vacuum. Once precipitation was observed in flask, solvent removal was stopped. The toluene product mixture was again heated to near boiling and excess toluene was slowly added until all solid was dissolved. The resulting solution was cooled to -20 °C overnight or until crystallization had ceased. The solid was collected via vacuum filtration and washed with cold toluene. Detailed synthesis and NMR results are included the manuscript being written.
**Crystal growth**

Anti-solvent method was used to grow BTBT derivatives single crystals. 0.4 mg/ml solution of a BTBT derivative and dichloromethane was mixed with less soluble hexane in 1:3 ratio by volume. After stirring the resulting solution for about ten minutes, it was transferred to a clean glass vial using a 0.2 microlitre filter. Nice thin platelets of crystals as big as 300 microns were formed after 24 hours. Single crystals for OFET fabrication were prepared on a cleaned HMDs treated substrate, which is explained in detail in the next section.

**Transistor fabrication**

Both thin film as well as single crystal OFETs was prepared using solution processed BTBT derivatives. Clean SiO2 as well as gold patterned substrates were first cleaned with acetone followed by isopropyl alcohol for ten minutes each in ultrasonicator. The solution-cleaned substrates were further treated under UV ozone lamp for another 20 minutes. Hexamethyl disilazane (HMDS) was spun-cast at 4000 rpm for a minute followed by 90 seconds of annealing. Thin film bottom gate bottom contact OFETs were prepared by spin-casting 0.4 mg/ml solution of a BTBT derivative and toluene on a lithographically gold patterned SiO2 substrate at 800 rpm for a minute. Bottom gate top contact single crystal OFETs were prepared by meticulously selecting good quality BTBT derivative single crystals grown on a silicon dioxide substrate using cross-polarized optical microscope. Water-based graphite was painted as source and drain.
Transistor characterization

Electrical characterization of OFETs was performed using a Keithley 2636A Sourcemeter inside an N\textsubscript{2} glovebox. Using measured source-drain current (IDS) and gate voltage (VGS), hole mobilities of devices (\(\mu\)) were calculated in the saturated regime of FETs from the source-drain current (IDS) vs. gate voltage (VGS) equation:

\[
I_{DS} = \left(\frac{W}{2L}\right) \mu C_i (V_{GS} - V_T)^2
\]

where \(C_i\) is the specific capacitance of the insulator (about 1.0 nFcm\(^{-2}\) for 7 \(\mu\)m thick P(VDF-BTFE), \(W\) is the channel width, \(L\) is the channel length and \(V_T\) is the threshold voltage.

DFT calculations

Numerical calculations were performed using the Gaussian09 software package for a system consisting of four BTBT derivatives molecules. The hybrid Hartree-Fock/DFT method B3LYP and a 6-311+G(d,p) basis set were employed to determine reorganization energies. Charge transfer integrals were obtained using a semi-empirical zindo(s) method.\(^{30,31}\)

Neutron Scattering

The deuterated BTBT derivative samples are grinded into powder and wrapped in Al foil. It is pressed down to the thickness of 0.2mm to achieve 10% scattering. The samples are examined with inelastic neutron scattering using the Cold Neutron Chopper Spectrometer (CNCS) at Spallation Neutron Source in Oak Ridge National Lab, TN. The inelastic scattering is measured using the time of flight chopper spectrometer.
5.5 Supplementary information

OFET characteristics of C₈BTBT

Figure 5-S1: a) Transfer characteristics; b) Output characteristics and c) Differential hole mobility of a C8BTBT thin film OFET.
OFET characteristics of mC8BTBT

Figure 5-S2: a) Transfer characteristics; b) Output characteristics and c) Differential hole mobility of an mC8BTBT thin film OFET.
OFET characteristics of BTBT

Figure 5-S3: a) Transfer characteristics; b) Output characteristics and c) Differential hole mobility of a BTBT thin film OFET.
OFET characteristics of mC₈BTBT single crystal OFET

Figure 5-S4: a) Transfer characteristics; b) Output characteristics and c) Differential hole mobility of a mC₈BTBT single crystal OFET.
Single crystal structure of BTBT derivatives

The single crystal structures and the lattice parameters of BTBT derivatives are shown in Figure 5-S5 and Table 5-S1. The single crystal structure of C₈BTBT is already published, and is obtained from Ref 15. The results obtained from AFM and X-ray scattering confirms that the single crystals of C₈BTBT used in OFETs are of monoclinic family.

![Figure 5-S5](image)

Figure 5-S5: Single crystal structure of BTBT derivatives. a) BTBT (monoclinic) b) mC₈BTBT (Triclinic) c) C₈BTBT (monoclinic)

<table>
<thead>
<tr>
<th></th>
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<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
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<td>mC₈BTBT</td>
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<tr>
<td>C₈BTBT</td>
<td>Monoclinic</td>
<td>5.927</td>
<td>7.88</td>
<td>29.18</td>
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</table>

Table 5-S1: Lattice parameters of a) BTBT b) mC₈BTBT c) C₈BTBT.
Atomic force microscopic images of the thin films of BTBT derivatives

Figure 5-S6: Atomic force microscopic images of the thin films of BTBT derivatives a) BTBt b) mC₈BTBT c) C₈BTBT.

Powder X-ray diffraction of BTBT derivatives

Figure 5-S7: Log plot of powder X-ray diffractions of BTBT derivatives showing prominent (001) peaks corresponding to their single crystal structures.
GIWAXS images of the thin films of BTBT derivatives

Figure 5-S8: GIWAXS images of the thin films of BTBT derivatives. a) BTBT b) mC₈BTBT c) C₈BTBT. The diffraction peaks in the z-direction signify (001) peaks corresponding to their single crystal structures, similarly to their powder X-ray diffractions.

Ultraviolet-visible (UV-Vis) spectroscopy of BTBT derivatives

The UV-Vis spectra of the solutions of BTBT derivatives have similar peaks at 330 nm. However, the UV-Vis spectra of the thin films of BTBT derivatives show that the peak near 345 nm is red shifted by about 10 nm in C₈BTBT.
Predicted IR spectra of a BTBT core using DFT calculation

Figure 5-S9: UV-Vis results of solutions and thin films of BTBT derivatives.

Figure 5-S10: Predicted IR spectra of an optimized BTBT core. The lowest energy of intra-molecular vibrations is above 6meV. Courtesy: Wenlin Zhang (Gomez/Milner Group)
5.6 References

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23 Illig, S. *et al.* Reducing dynamic disorder in small molecule organic semiconductors by suppressing large-amplitude thermal motions. (2016).


Chapter 6

Vertical charge transport in organic semiconductors

6.1 Introduction

Charge transport in organic semiconductors is heavily studied experimentally using organic field effect transistors (OFETs). In OFETs, when sufficient electric field is applied, charge carriers travel through a few nanometer wide ephemeral conduction layer created at the gate dielectric interface. As such, an OFET measures the mobility of organic semiconductors only in the horizontal direction along the plane of a semiconducting film (Figure 6-1). Consequently, the benefit of OFET measurements is mainly limited to the electronics involving transistors.¹

![Figure 6-1: Schematic showing charge transport direction in an OFET (left) configuration and a diode (right) configuration. S, D and G mean source, drain and gate respectively. White arrows show the direction of flow of charge carriers.](image)

The application of organic semiconductors is equally important in other applications such as organic light emitting diodes (OLEDs) and organic photovoltaics
(OPVs), where the charge carriers move perpendicular to the plane of semiconducting films (Figure 6-1).

It is imperative, therefore, that the charge transport behavior of conjugated molecules in the vertical direction should also be elucidated. The true nature of charge transport behavior in organic semiconductors can be well articulated by exploring charge carrier movements in both the vertical as well as the horizontal direction.

The movement of charge carriers in OFETs is also significantly affected by the morphological nature of gate insulator surface. In Chapter 3, we have shown that the polar functional groups of polymeric gate insulators can strongly interact with the conduction layer of organic semiconductors, thus introducing dipolar disorders. Dipolar interactions inhibit charge transport in organic semiconductors by introducing energetic disorder. In case of commonly used inorganic gate insulator, SiO$_2$, charge traps at gate insulator interface are widely considered an issue. Charge traps deteriorate the performance of OFETs, and, consequently, the charge mobility. As a consequence, the intrinsic charge transport behavior of organic semiconductors cannot be understood experimentally through the study of OFETs alone.

### 6.2 Objective

Recently, using molecular dynamics (MD) simulations, Zhang, et al. (Gomez/Milner Group) have demonstrated that semiflexible polymer chains align parallel to an impenetrable surface. The align layer is estimated to be about a persistence length, $L_p$ (Figure 6-2).
Figure 6-2: a) Cartoon showing parallel alignment of a semiflexible polymer to an impermeable substrate. b) Order parameter ($q$) profiles for chains with increasing chain length. The value of $q$ equals to -0.5 for the chains aligned perfectly parallel to the substrate and 0 for the isotropic orientations. For $N = 40$, the value of $q$ approaches -0.5, which signifies a parallel orientation. Reprinted with permission from American Chemical Society (2016).\textsuperscript{13}
Furthermore, the group has shown that the thickness of the ordered layer increases with the increasing chain length (Figure 6-2 b). Using diode set up, McGehee group has shown that the vertical mobility of regioregular (rr) poly(3-hexyl-thipohene) (P3HT) increases with the molecular weight. The increased vertical mobility has been attributed to the notion that higher molecular weight (MW) leads to more favorable morphological evolution of P3HT films. The same group has proposed similar theory for the increasing FET mobility of P3HT with the increasing MW. It is apparent from the Figure 6-3 the trend of mobility dependence on the increasing MW of P3HT is different depending on the direction of the measurement. Indeed, the increase in FET mobility is sharper than in diode mobility. The discrepancy has not been well understood yet.

Figure 6-3: Comparison of the hole mobility of rr-P3HT measure in the vertical direction (↑) and the horizontal direction (→) as a function of MW. The data is taken from papers by McGegee, et al. 14,15
We hypothesize that the FET hole mobility of regioregular rr-P3HT is enhanced due to the surface induced alignment at the gate insulator interface.

6.3 Methods and materials

One of the most convenient ways to deconvolute the effect of surface induced alignment in the charge transport properties of P3HT would be to study the charge transport in the vertical direction as well as the horizontal direction. A well-established FET method would be used to measure the mobility of rr-P3HT as a function of MW in horizontal direction. A conventional diode set up can be used to study charge transport behavior in vertical direction. The method of current extraction under linearly increasing voltages (CELIV) is another alternative.\textsuperscript{16,17}

Unfortunately, carrier mobility extraction from the direct current-voltage measurement in organic semiconductors is still in the nascent stage. In diode configuration, for instance, a widely exploited model for mobility extraction is the space-charge-limited current (SCLC) model (the Mott-Gurney square Law). The SCLC model follows the Equation 6-1,

\[
J = \frac{9}{8} \varepsilon \mu \frac{V^2}{L^3}
\]  \hspace{1cm} (6-1)

where \(J\) denotes the charge current density, \(\varepsilon\) the permittivity of the active layer, \(\mu\) the charge carrier mobility, \(V\) the voltage, \(L\) the active layer thickness.

A typical diode consists of a transparent glass substrate with an indium tin-oxide (ITO) layer, poly(3,4-ethylenedioxythiophene) :poly(4-styrenesulfonate) (PEDOT:PSS), rr-P3HT layer and aluminum layer respectively (Figure 6-4).
Here, ITO/PEDOT is the anode, and the aluminum is the cathode. PEDOT with an work function of 5.2 eV serves as a hole injection layer in to the highest occupied molecular orbitals (HOMO) of rr-P3HT. Aluminum, which owns a largely mismatched work function (4.2 eV) with the lowest unoccupied molecular orbitals (LUMO) (2.9 eV) of the active layer, prevents the injection of electrons into the device. Hence, a hole-only device is made.\textsuperscript{14} With the application of voltage, in the absence of traps, the charge carrier density scales quadratically and follows the Equation 6-1. Such characteristic SCLC behavior occurs when the number of injected charges reaches a maximum because their electrostatic potential prevents further injection of charges.\textsuperscript{4,18} In order to calculate hole mobility using SCLC model, it should be assumed that the hole mobility is field independent. In most of the films of conjugated molecules where disorders are inevitable, the SCLC model may not hold true, especially at higher electric field. Several other adjusted SCLC models could be found in literature.\textsuperscript{14,19}

I-V characteristics of an organic diode strongly depend on the thickness of an active layer. The research and development group of Samsung™ has demonstrated that
the hole mobility of N, N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine (NPD) increases with the increasing thickness of the active layer. By studying the I-V characteristics of NPD diodes comprised of various thickness ranging from 50 nm-1000nm, they have concluded that the hole mobility of NPD increases until the thickness is 300nm. Eventually, the hole mobility saturates and becomes insensitive to the thickness change (Figure 6-5a). The highest mobility calculated using the SCLC model approaches the intrinsic hole mobility extracted using the time of flight (TOF) measurement.

Moreover, the key requirement of SCLC for mobility measurements is a good Ohmic contact between organic layer and metal electrodes. Scientists from South Korea have proposed an interfacial layer to enhance the Ohmic contact the metal-organic interface. They have demonstrated a perfect Ohmic contact for the ITO/NPD system using Rhenium oxide (ReO₃) as an interfacial layer between them (Figure 6-5b). To study the charge transport behavior of P3HT using diode, the two key factors need to be controlled.
Figure 6-5: a) Thickness dependent hole mobility of NPD extracted using SCLC method. Inset: thickness dependent hole mobility at 0.1 MV/cm. b) Logarithmic plot of current density vs electric field of hole-only devices with various high electron affinity (EA) materials as the interlayer or without an interlayer. The solid line represents calculated field-dependent SCLCs. Images reproduced with permissions from the American Institute of Physics and the Nature Publishing groups. 19,20
6.4 Initial results and discussions

As discussed in the previous section, to tune the key factors such as active layer thickness and ohmic contacts, NPD-based diodes are studied. Sublimed (>99.5 %, HPLC) grade NPD is purchased from Lumtec Corp and used without further purification. ITO-coated glass substrates (20 ohm/sq, Xin Yan Technology, Hong Kong) were cleaned using soap, followed by 10 min of sonication in acetone, then isopropanol. The substrates are treated finally with 15 min of ultraviolet light ozonation. PEDOT:PSS (Clevios P, Heraeus), is spun-cast on top of ITO at 4000 rpm for 2 min yielding a thickness of about 65 nm. The PEDOT:PSS/ITO substrates are baked for 10 min at 165 °C in air and then transferred to a nitrogen-filled glovebox. Three nanometer thick ReO$_3$ (Sigma) as well as Molybdenum oxide (MoO$_3$) layer (Acros) is also evaporated as interfacial layers on ITO substrates. NPD layer of various thickness ranging from 50 nm to 1000 nm are evaporated on the ITO substrates. Three nanometer thick ReO$_3$ (Sigma) and Molybdenum oxide (MoO$_3$) (Acros) are again evaporated onto the substrates with ReO$_3$ and MoO$_3$ layer before evaporating 100 nm thick Aluminum layer. A Keithley 2636A Sourcemeter is used to measure the current-voltage characteristics of the diodes.

As predicted, we observe substantial contrasts among the electrical characteristics of NPD diodes comprised of varying thickness of active layer and different interfacial layers. The results in Figure 6-6 suggest that current density of NPD-ReO$_3$-diodes with the increasing active layer thickness for the same electric field. For instance, current density of diode in 300 nm thick NPD is several orders of magnitude higher than in 50
nm thick NPD at 50 kV/cm. Similarly, the critical voltage drops significantly as the NPD thickness increases. Unlike typical diode behavior, the current density is not symmetric.

Figure 6-6: Current density of NPD-ReO3 diode with increasing thickness of the active layer as a function of applied electric field.

Diodes with identical active layer thickness are also tested to understand the effect of interfacial layer in the electrical performance. From the results in Figure 6-7, it is apparent that MoO3 and ReO3 are better interfacial layers for NPD diodes than clean or PEDOT because the effect of metal-organic contact is minimal in the former system. Another interesting observation is that, diode behavior of NPD-MoO3 system is more symmetric than NPD-ReO3 system (Figure 6-8). Similar to the results in (Figure 6-5) active layer thickness dependent diode behavior is also observed.
Figure 6-7: Current density of 300 nm thick NPD diode system with different interfacial layers as a function of applied electric field.

Figure 6-8: Current density with increasing thickness of the active layer as a function of applied electric field.
Figure 6-9: Comparison of current density as a function of applied electric field between NPD-ReO$_3$ system and NPD-MoO$_3$ system.
Moreover, the current density of diodes NPD-MoO$_3$ system is higher than NPD-ReO$_3$ system (Figure 6-9). It should be noted, however, that for the devices with 1000 nm thick NPD, the performance diminished. It is believed that the discontinuous layer of aluminum electrode over such thick active layer during the evaporation process caused the issue.

The effect of metal-organic contact is also analyzed for NPD-ReO$_3$ system and NPD-MoO$_3$ system (Figure 6-10). Unlike in the literature (Figure 6-5), current density of NPD-MoO$_3$ system shows more linear behavior at lower electric field than NPD-ReO$_3$ system implying that the effect of contact is minimized in the latter system. It also suggests that NPD-MoO$_3$ system shows perfect Ohmic contact complying with the requirement for the SCLC mobility measurements.

![Figure 6-10: Log-log plot of current density as a function of electric field.](image-url)
6.5 Conclusions

From the initial results of NPD-diode study, it has been found that NPD-MoO$_3$ system performs the best among all types of diodes investigated. Moreover, the performance of diodes with thicker active layer outweighs that with thinner active layer. To better understand the effect of the thickness of active layer, diodes with 700 nm and 1000 nm thick active should also be tested. It is warranted that the thicker layer of aluminum should be evaporated to avoid discontinuous electrode layer. Further investigations are needed before commencing the study of effect of molecular weight on a P3HT-diode system.
6.6 References


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14 Goh, C., Kline, R. J., McGehee, M. D., Kadnikova, E. N. & Fréchet, J. M. J. Molecular-weight-dependent mobilities in regioregular poly(3-hexyl-thiophene)


Chapter 7

Summary and Outlook

7.1 Summary

The internet of things is looming on the horizon. However, a plethora of opportunities that can arise from bridging the technological revolution with electronics has not been fully explored. Most of the electronics is still inundated with traditional inorganic Si-Ge-based architecture, which is tough, expensive and fragile. In contrast to conventional silicon or germanium, organic semiconductors offer a variety of possibilities to expand the reach of electronics. Not only are they soft, cheap and flexible, but they also open doors towards novel design, synthesis and engineering of organic materials. The immediate benefits of organic semiconductors are flexible displays, cheap sensors in some of the aspects of health-related field and affordable electronic tags. Devices comprising organic semiconductors include organic field effect transistors (OFETs), organic light emitting diodes (OLEDs) and organic photo voltaics (OPVs). Organic semiconductors have drawbacks as well. Unlike inorganic semiconductors, they are easily susceptible to disorder and degradation even in ambient conditions. In addition, extensive wide possibilities for material design have left chemists and material scientists puzzled to find just the right one. In addition, the performance of the highest performing organic semiconductors still cannot rival that of the highest
performing inorganic semiconductors. The right type of chemical structure, coupled with optimal processing condition and better understanding of device infrastructure, can lead material scientists and engineer one step closer to an ideal OFET.

One of the main objectives of this dissertation is to add stones towards the path of cheap functional electronics. As such, three different routes towards achieving high performance organic field effect transistors (OFETs) have been demonstrated. By proposing ways to reduce intrinsic disorder in small molecules, to optimize the morphology of active layers, and to minimize the dipolar interactions at the dielectric interface, a road map to achieving an ideal OFET has been presented.

7.1.1 Suppressed lattice fluctuations improve the hole mobility of [1]benzothieno[3,2-b]benzothiophene (BTBT) core

We have studied the role of alkyl side chains on the charge transport properties of the BTBT core. Theoretical calculations using density functional theory show that the intrinsic charge transport parameters remain essentially similar among the BTBT derivatives. However, FET hole mobilities of the BTBT derivatives show that dioctyl BTBT (C₈BTBT) has the highest mobility of all derivatives (Figure 7-1a). Inelastic neutron scattering (INS) results suggest that the addition of octyl side chains to the BTBT core suppresses its lattice vibrations (Figure 7-1b).³ The results suggest that the reduced electron-phonon coupling in C₈BTBT led to three orders of magnitude higher hole mobility.
We have demonstrated that the morphology of polycrystalline active layers plagued by grain boundaries and other thin film disorders can be tuned to achieve high mobility OFETs. By melting and quenching C8BTBT films, crystal texturing was enhanced. The stronger orientational order in the active layer of thin film transistors led to an increase in hole mobilities by a factor of five (Figure 7-2). A distinct advantage of melting films prior to annealing is obviating the effects of processing history prior to thermal annealing.

Figure 7-1: a) Log plot of thin film mobility versus single crystal hole mobility of BTBT core and its derivatives with single and double arm. b) Scattering function S(Q, ω) of BTBT core and its derivatives as a function of energy change, ω and momentum transfer, Q at 300K with incident neutron beam energy of 26 meV.

7.1.2 Improved long range order of C8BTBT film enhances its hole mobility

We have demonstrated that the morphology of polycrystalline active layers plagued by grain boundaries and other thin film disorders can be tuned to achieve high mobility OFETs. By melting and quenching C8BTBT films, crystal texturing was enhanced. The stronger orientational order in the active layer of thin film transistors led to an increase in hole mobilities by a factor of five (Figure 7-2). A distinct advantage of melting films prior to annealing is obviating the effects of processing history prior to thermal annealing.
7.1.3 Minimized energetic disorder at the gate dielectric interface leads to higher mobility

We have presented a photopatternable, high-k fluoropolymer, poly(vinylidene fluoride-bromotrifluoroethylene) P(VDF-BTFE), where the BTFE moieties enable cross-linking through thermal- or photo-curing of dielectric materials with relative permittivities between 8 and 11. We have shown that crosslinking enhances the population of trans conformations with respect to the neat polymer, demonstrating that crosslinking can affect chain conformations. Organic single crystal field effect transistors based on rubrene active layers and crosslinked P(VDF-BTFE) gate dielectrics have shown hole mobilities as high as 12 cm$^2$V$^{-1}$s$^{-1}$, three times higher than the average hole mobilities for devices comprising PVDF-based fluoropolymers or SiO$_2$ as the dielectric.
layer. The results suggest that the enhanced hole mobility is due to the reduced dipole fluctuations in the cross-linked P(VDF-BTFE) gate dielectrics, thereby minimizing the trap states at the dielectric-semiconductor interface (Figure 7-3).  

![Figure 7-3](image)

Figure 7-3: Hole mobility versus maximum interfacial trap density for rubrene single crystal TFT devices using various dielectrics. As the interfacial trap density increases, the charge mobility decreases. The highest mobilities are achieved with crosslinked polymers as the gate dielectric, crosslinked P(VDF-BTFE) or BCB.

### 7.2 Outlook and recommendations for future work

An OFET is a complex architecture comprised of different building blocks: electrodes, active layer and gate insulator. Unlike inorganic materials, predicting the behavior of organic materials is challenging. Despite the abundance of scientific publications in the field of organic semiconductors, researchers still lack a clear understanding of the charge transport behavior, and the key parameters that control the behavior. The community is showered with hundreds of scientific journals every week,
but it is still missing a concrete path towards high performance OFETs. Organic semiconductors need more work in their field in order to be fully commercialized in the electronics industry.

We have successfully demonstrated different ways to optimize the performance of OFETs. It is recommended that several research works be initiated following the work presented in the dissertation.

7.2.1 Vertical charge transport in organic semiconductors

Vertical charge transport in organic semiconductors is not a widely explored area. The Gomez group has demonstrated that horizontal charge transport in organic semiconductors can be affected by the interaction of the semiconductors at the dielectric interface and the resulting morphological evolution of the semiconductors.\(^4\) In chapter 3, it has been demonstrated that interfacial disorder at the dielectric interface alters the hole mobility of rubrene single crystals. Also, in chapter 6, it has been discussed that the interaction of a conjugated polymer with the impenetrable substrate initiates a molecular ordering at the interface, which increases with the increasing the molecular weight of the polymer.\(^5\)

Scientists have shown that the FET hole mobility of P3HT increases with increasing molecular weight (MW).\(^5,7\) However, a clear rationale for the trend is still unknown. We hypothesize that the hole mobility of regioregular rr-P3HT increases with increasing MW in P3HT due to the surface induced alignment at the gate insulator interface. Studying rr-P3HT charge transport behavior as a function of MW through
fabrication FETs and diodes should be beneficial in elucidating both vertical and horizontal charge transport behavior. It will further help deconvolute the effect of dielectric interface.

In addition to space charge limited current (SCLC) of hole mobility measurement, vertical charge transport can also be studied using the charge carrier extraction by linearly increasing voltage (CELIV) method and vertical OFETs. The schematic of a single crystal based vertical OFETs is outlined in (Figure 7-4). This technique would be crucial to obviate the gate insulator effect by measuring the current in the vertical direction, unlike conventional OFETs.

Figure 7-4: Schematic representing a vertical OFET. The drain electrode can made of water-based graphite paint on a laminated crystal surface. Image reproduced from the website of SPIE.12,13

7.2.2 Semiconductor-dielectric interface interactions

In chapter 3, it has been shown that cross-linking poly(vinylidene fluoride-bromotrifluoroethylene) P(VDF-BTFE) copolymer (9 mol% BTFE) leads to enhanced
TTTG conformation as opposed to the pristine polymer. The abundance of TTTG chain conformation helps to minimize dipolar disorder at the interface, thus enhancing the charge mobility of rubrene single crystal OFETs. Gandinski et al. (Wang Group, Penn State) have demonstrated that the chain conformation of P(VDF-BTFe) changes with the changing monomer content (Figure 7-5).\textsuperscript{14} The morphological evolution of the gate dielectric should have a profound effect on the performance of OFETs. Studying the behavior of OFETs comprising P(VDF-BTFe) copolymer with varying monomer content, should further help elucidate the chain conformation of the co-polymer.

![Figure 7-5: Conformation fractions of TTTG, TG, and all-trans (T-trans, G-gauche) chain conformations as a function of monomer composition. Reproduced with permission from The Royal Chemistry of Society.\textsuperscript{14}](image-url)
Defect free single crystals are rare. Despite the near-perfect order over entirety of a single crystal and absence of grain boundaries, performance differences have been reported for single crystal OFETs. Whereas the hole mobility (\( \mu \)) of thermally evaporated single crystal OFETs of diF-TES ADT is 6 cm\(^2\)V\(^-1\)s\(^-1\), the \( \mu \) of solution processed single crystal OFETs of diF-TES ADT is only 0.1 cm\(^2\)V\(^-1\)s\(^-1\). While rubrene single crystals grown from physical vapor transport exhibit hole mobilities near 4 cm\(^2\)V\(^-1\)s\(^-1\), the best performing rubrene single crystal grown from solution has a reported hole mobility of 1.6 cm\(^2\)V\(^-1\)s\(^-1\). The reason behind the disparity is not well understood. Since solution processed single crystals are preferred over thermally grown single crystals because the latter could be more expensive and more time consuming, it is essential to understand the diminished charge transport behavior of solution processed organic semiconductors. Moreover, the solution processing of single crystals will be useful in industrial applications, such as in an ink-jet printing. A possible reason could be the inevitability of disorder even in single crystals because they are comprised of weak van der Waals force.

Organic single crystal FETs from PVT grown rubrene crystals have an average hole mobility that is two orders of magnitude higher than that of solution processed rubrene single crystals. The average extracted hole mobility for the devices tested is 3.4 cm\(^2\)V\(^-1\)s\(^-1\) ± 0.2 cm\(^2\)V\(^-1\)s\(^-1\). The device with the best performance has a hole mobility of 3.7 cm\(^2\)V\(^-1\)s\(^-1\). On the other hand, rubrene single crystals obtained from the solution-based crystal growing technique could not perform as good as those grown from PVT. The average extracted hole mobility for the devices made from solution grown rubrene single
crystals is $0.011 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \pm 0.003 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. It is hypothesized that the disorder in the solution processed organic single crystals degrades their charge transport properties. In other words, solution processing introduces more disorder in single crystals than thermal evaporation.

Quantifying the degree of disorder in single crystals is a daunting task. Using X-ray beam lines at Stanford University, J. Rivnay, et al. have performed the quantitative analysis of lattice disorder and crystallite size in organic thin films.\textsuperscript{17} The same technique can be used to quantify the degree of disorder and interplanor spacing fluctuations in the organic single crystals. As shown in Figure 7-7, the increasing width of peaks with order signifies disorder dominant peaks (7-7a, 7-7b) and a roughly constant peak width means that the size effect is dominant (7-7a, 7-7c). The result suggests that disorder in poly(alkylthiophenothienothiophene) PBTTT is more prominent than in TIPS-pentacene. As the disorder of TIPS-pentacene and PBTTT are compared in the literature, disorder in crystals from different crystallization techniques can be analyzed to extract a relationship between the disorder and the electronic properties of organic single crystals.

Figure 7-6: Optical micrographs of rubrene single crystals grown using different solution based techniques.
Figure 7-7: (a) Peak width ($\Delta q$) as a function of order. b and c are the diffraction peaks of TIPS-pentacene and poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene), PBTTT.\textsuperscript{17}
7.3 References


Jwala M. Adhikari
305 Fernwood Ct · State College · PA 16803 · jwaladhr@gmail.com | +1-814-777-5104

EDUCATION

Ph. D. in Chemical Engineering, The Pennsylvania State University, University Park, PA  
Advisor: Prof. Enrique D. Gomez  
GPA: 3.72  
William H. Joyce Fellow  
May 2016

B.S. in Chemical Engineering, Brigham Young University, Provo, UT  
GPA: 3.71  
Awards & Distinctions: Dean’s List, Merit-based Full Tuition Scholarship, Rio Tinto Scholar, Vice-President- AIChE-BYU, Tau Beta Pi Engineering Honor Society  
Aug 2011

PUBLICATIONS

- “Crosslinking High-k Fluoropolymer Gate Dielectrics to Enhance Charge Mobilities in Rubrene Single Crystal Field Effect Transistors” Adhikari, J. M.; Gadinski, M.R.; Wang, Q.; Gomez, E.D., Manuscript Submitted, April 2016
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PRESENTATIONS

- “Organic field effect transistors: an avenue to a flexible iPad!” Adhikari, J.M. Invited Talk at Penn State Millenium Café, June 2014