Study of the 2D self-assembly of conjugated systems

Keg Peisi

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STUDY OF THE 2D SELF-ASSEMBLY OF CONJUGATED SYSTEMS

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School of Materials Science and Engineering

A thesis submitted to the Nanyang Technological University
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Abbreviations

PQT-12	poly(3,3'''-didodecylquaterthiophene)
GPC	gel permeation chromatography
MALDI-MS	matrix-assisted laser desorption ionization-mass spectrometry
STM	scanning tunneling microscopy
AFM	atomic force microscopy
MFM	magnetic force microscopy
SNOM	scanning near-field optical microscopy
EFM	electrostatic force microscopy
UHV-STM	ultra high vacuum scanning tunneling microscopy
HOPG	highly oriented pyrolytic graphite
FCC	face-centered-cubic
OTFTs	organic thin film transistors
P3ATs	poly(3-alkylthiophene-2,5-diyl)s
XRD	x-ray diffraction
FETs	field-effect transistors
P3HT	poly(3-hexylthiophene)
TEM	transmission electron microscopy
CPK	Corey-Pauling-Koltun
DFT	Density functional theory
UV-Vis	Ultraviolet-Visible

DSC	Differential Scanning Calorimetry
TGA	Thermogravimetric Analysis
PL	Photoluminescence
CV	Cyclic Voltammetry
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
FFT	Fast Fourier Transform

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Summary

The study of conjugated molecular systems has been a popular research area in electronic device applications for decades. Much research has been devoted to the synthesis and fabrication of these molecular systems into miniature devices. However, research on the electronic properties and performance of these materials is often not investigated in detail. Moreover, the addition of soluble pendant groups on the conjugated backbones of these systems, for better solubility, tends to disrupt the conjugation of the systems because of induced steric hindrances. The aim of this project is to study the effects of molecular architecture on molecular packing and conjugation of the molecular systems.

In this project, the self-assembly of conjugated molecular systems was studied in ambient conditions by using the scanning tunneling microscopy technique at the liquid/solid interface on atomically flat substrates. This technique images the electron density of adsorbed species on conducting surfaces, from which the molecular packing order of the molecular adsorbed species can be determined.

Conjugated polymers, the poly (3,3'''-didodecylquaterthiophene)s - PQT-12 that was synthesized earlier as a thin film transistor material and poly(3-hexylthiophene)s – P3HT was studied. STM images showed neat lamellar rows of polythiophenes chains on both highly oriented pyrolytic graphite (HOPG) and Au(111) substrates. Alkyl chain interdigitation between lamellar rows of the PQT-12 monolayer was observed but not for the P3HT monolayer.

Conjugated oligomeric molecules which were designed and synthesized to eliminate polydispersity issues and inconsistent polymerization rates were observed to self-assemble with domains larger than the polymers. Oligothienothiophenes with varying side group positions and terminal group functionalities were observed to possess similar packing order on HOPG substrates with well-interdigitated alkyl chains. However on Au(111), molecules with bulkier terminal groups tend to pack closely with no interdigitated chains. Similarly, anthracene-based oligomers with varying lengths of terminal alkyl chains were also observed to pack closely on Au(111), but with interdigitated chains on HOPG.

This work demonstrates the importance of alkyl substituent chains and the influence of the substrate on the self-assembly of molecules. Long alkyl chains allow molecules to pack with well-interdigitated network in neat lamellar structures, giving flat-lying molecules. In addition, due to the commensurability between the alkyl chains and HOPG substrate, these chains tend to lie stretch-out and parallel to the surface.

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In this chapter, the background and motivation for the study are presented. The use of the Scanning Tunneling Microscopy as the primary source of investigation is explained and the objectives of this research project are described.

1.1 Background and Motivation

In the recent decades, there has been a substantial growth of interest in the research of nanomaterials for applications in electronic, biological, cosmetic and medicinal fields.^[1-3] Today, because of the miniaturization of electronic components, electronic devices such as computer systems and mobile phones are now multi-functional and can operate at high efficiencies. Through manipulation and assembly of molecules, scientists can now fabricate devices at the molecular-scale, and there is even the possibility of single molecule devices.^[4, 5] However, because of the resolution limitations of the characterization instruments, it is difficult to physically observe the molecular assemblies. In 1981, the development of the Scanning Tunneling Microscope by Binnig, Rohrer and Gerber allowed the visualization of objects at the nanometer scale level through the principle of electron tunneling.^[6-9] Using this technique, the self-assembly of molecules onto surfaces and electron transport could be inferred. This led to a better understanding of the study of electronic devices in the nanoscale, hence more research in the development of miniature electron devices in the nanoscale.

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In recent years, conjugated molecular systems have shown great potential as semiconducting or conducting materials for use in the field of molecular electronics.^[10-14] These conjugated molecular systems could also be easily modified by various synthetic methods to obtain suitable functionalities to provide a flexible source for researchers to design appropriate molecular architectures for their applications.^[15, 16] However, the electronic properties and performance of these conjugated systems depend very much on their molecular packing as well as the morphology of thin films. The importance of molecular ordering in the films can be observed in the classical example of poly(3-alkylthiophene)s, where head-to-tail coupled polymers are known to give better device performance than regio-random polymers.^[11, 17] Thus, the conductivity of these conjugated systems appears to be highly dependent on their structural conformations.

In addition, these conjugated systems are generally insoluble in common solvents, hence, attachment of soluble pendant groups on the conjugated backbone of these systems are investigated. These soluble pendant groups are typically straight alkyl chains, which promote van der Waals interactions between the solvent molecules. However, by improving the solubility of the conjugated system, the alkyl chains tend to affect its structural conformation, resulting in a disruption to the effective conjugation of the systems. This problem motivated recent focus on research in enhancing the co-planarity of the conjugated systems to promote conjugation.

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In another problem, due to the exceptional small size of these systems, typical surface thin film characterization techniques such as scanning electron microscopy (SEM), atomic force microscopy (AFM) and x-ray diffraction (XRD) either lack the resolution to enable one to visualize the molecular assembly successfully or provides only an average characteristic of the film. However, with the development of the scanning tunneling microscopy, the observation of molecular self-assembly of these conjugated systems became possible; thus prompting an increase in research on the two-dimensional molecular behaviour of these systems.

1.2 Research Objective

The study of conjugated molecular systems for molecular electronics is typically concentrated on its syntheses, bulk properties and its device performance.^[11, 18-25] From the chemists' perspective, many studies are devoted to the synthesis of new novel conducting materials with better solubility, packing arrangements and electron donating/accepting properties.^[15] On the other hand, engineers are more concerned with the device performance of these materials when fabricated as thin film devices. However, the electronic properties and performance of these materials typically depend very much on the molecular packing of the molecules. Furthermore, it was also found that the conductance of thin film devices typically resides only on the first one or two monolayers.^[26] Hence, it is necessary to understand the organization of the molecules in the resultant monolayer. The assembly of molecules on adsorption tends to affect the overall performance of the film device, particularly if the molecule has

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tendencies to twist as a result of the steric hindrances of attached bulky groups in the molecular structure. Hence, it is crucial to understand the assembly pattern of these molecules at the molecular level, an area generally neglected in current research. In this research we are interested particularly in the self-assembly of conjugated systems when adsorbed on surfaces in a two-dimensional manner. In other words, we are interested in understanding how the molecular design affects the organization of these molecules, and how these organizations or the lack thereof affect the properties of the film and devices. In this thesis, the study of the self-assembly of two different types of conjugated systems: - the thiophene and acene-based systems is conducted. These systems are synthesized with different alkyl chain lengths attached to the main conjugated core to improve its solubility. However, improving the solubility of the system can sometimes lead to further problems, such as a disruption in the conjugation of the system and issues in molecular packing. In this work, we explore the optimum architecture for the organization of these systems on adsorption on two different highly ordered substrates, the HOPG and Au(111) surfaces. These substrates are typically chosen due to their atomically flat surfaces and conductivity.

The adsorption and organization of these molecules onto surfaces are typically dependent on the molecular interactions between the molecules and the molecules-substrate. Hence, it is in our aim to investigate the influence of molecular architecture on the self-assembly properties of these conjugated systems on surfaces. The use of the Scanning Tunneling Microscope will be the primary tool used to investigate the self assembly monolayers. In addition to that, other characterization techniques are

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also employed to study the influence of molecular architecture on assembly properties and their device application functionality.

The objectives in this research are summarized as follows:

- To establish the importance of molecular architecture on the self-assembly of molecules.
- To investigate the interactions (molecule-molecule and molecule-substrate) involved in the molecular packing in the 2D self-assembly.
- To establish and understand the relationship between molecular self-assembly and its device performance.

1.3 Organization of thesis

This thesis is divided into 9 chapters.

Chapter 1 outlines the background and motivation behind this thesis, and discusses the objectives and purpose of the work.

Chapter 2 provides a brief literature review, introducing the concept of conjugated systems and self-assembly. A short description of the conjugated molecular systems that would be studied in this work is also presented.

Chapter 3 is dedicated to the experimental procedures and requirements for the research. A detailed description of the scanning tunneling microscopy technique is presented. The importance of substrates and solvent choices which are critical to

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obtaining good results are also highlighted. Brief synthetic routes of the studied molecular systems are also included.

Chapter 4 - 6 describes the results and discussion of this thesis. A more detailed literature review on the specific conjugated molecular systems is presented at the beginning of each of the chapters to provide a deeper understanding of the various research work that have been carried out on the systems.

Chapter 7 summarizes and concludes the work carried out in this thesis. Recommendations for future work to be carried out are also presented.

Chapter 8 lists the references that were mentioned in this thesis.

Chapter 9 provides a list of publications and conferences where part of the work in this thesis is published and presented.

2 Literature Review

The concept of conjugation in molecular systems is introduced in this chapter using a few common polymeric examples and their applications in molecular electronics applications. Self-assembly interactions between the molecules and substrates are also described here, which are one of the major investigations in this thesis.

2.1 Conjugated Systems

Since the accidental discovery of polyacetylene by Shirakawa and co-workers in the 1970s^[27], there has been overwhelming interest in research on conducting or semiconducting polymers. Studies carried out on these materials revealed a “ π -conjugated network”, typically consisting of alternating single and double bonds in their structure. Carbon atoms are typically sp^2 hybridized in a threefold coordinated state forming σ bonds in a conjugated polymer molecule. This leaves the remaining p_z orbitals to overlap to form π bonds, delocalized to form a continuous π electron system over the backbone of the molecule. As these π bonds are weaker, the orbitals appear at higher energies. Furthermore, energy required to excite electrons from bonding π orbitals to antibonding π orbitals is low, hence only a small energy gap exists between the unoccupied and occupied orbitals of the molecules. This energy gap for conjugated polymers usually lies in the range of 1-3 eV, comparable to

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semiconductors.^[28] Hence, these materials were viewed as potential materials for electronic devices.

However, the limitations in the earlier synthesized polyacetylene, such as poor chemical stability and processability, resulted in there being little use for the material. Hence, studies were carried out to alter the chemical structures of these materials to allow for better solubility and stability for wider processing methods. Other conjugated polymers were also synthesized thereafter. **Figure 2.1** illustrates some typical conjugated polymers that have been studied by various research groups.^{[27, 29,}

30]

Figure 2.1 Chemical formulae of common conjugated polymers.

To promote better processability of these conjugated polymers, long flexible aliphatic chains are typically attached to the conjugated backbone. This often results in improved solubility of the molecules in organic solvents, however jeopardizing its

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conjugation and packing order. Thus, much research was carried out to develop new conjugated polymer systems that are chemically stable and electrically conductive, yet processable in typical conditions.

2.1.1 Molecular Electronics Applications

Much research effort in recent years has been focused on replacing inorganic silicon technology with active organic materials for electronics applications. Organic materials have the potential to reduce production costs, increase performance and enhance flexibility through a reduction in processing temperatures and component size.^[31, 32] The possibility of producing thin conductive films and use of single molecules to fabricate devices soon become a goal to many researchers.^[4, 5, 33] Polymeric organic films that are conducting either in their doped or undoped states have been intensively studied by various research groups.^[22, 26, 34, 35] These conducting polymers were proposed as replacements for expensive inorganic counterparts as they are cheaper to produce and can be easily modified to suit the required applications.

Materials based on organic conjugated systems have been shown to possess promising qualities for electronic applications such as light emitting diodes, sensors, organic field effect transistors and solar cells.^[10, 12-14, 20]

However, the use of organic materials in such electronic devices depends very much on the molecular packing and orientation of the materials in the thin film. It has been

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found that closely packed molecules often have better charge carrier mobilities due to the greater π overlap from the smaller intermolecular distance.^[36, 37] The molecular design of these systems plays a crucial role in the molecular packing and orientation of the molecules. Thus, to enhance the π overlapping of the systems through closer packing of the molecules, molecular engineering of the organic materials has to be carried out.^[15, 16] Conjugated polymers and oligomers synthesized with specific functional groups promoted intermolecular interactions such as van der Waals forces, π - π stacking and hydrogen bonding to give closer packing and enhanced flexibility. This, however tends to jeopardize the effective conjugation of the molecular system. The addition of functional groups can sometimes lead to steric hindrances intramolecularly, resulting in twists and bends in the formerly planar backbone of the molecular system, thus breaking the conjugation.^[34]

On adsorption, conjugated systems typically undergo self-assembly to form well-ordered layers. This adsorption process, however could lead to significant change in the configuration of the system, affecting the overall conjugation of the film.^[38] Hence it is necessary to understand the interactions involved in the self-assembly of molecules.

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2.1.2 Polythiophenes

The investigation of the two-dimensional self-assembly of polythiophenes would be discussed in further detail in Chapter 4 of this thesis. Polythiophenes consist of electron-rich thiophene rings polymerized together to form a chain of conjugated network, as illustrated in **Figure 2.2**. These polythiophenes have been intensively studied for thin film applications as they have high tendency to undergo self-assembly onto surfaces giving well-ordered layers with co-planar backbone that is beneficial to electron-hole transport.^[39]

Figure 2.2 Illustration of chemical structure of polythiophenes.

In this project, two types of polythiophenes will be investigated using the STM technique at the liquid/solid interface. These polythiophenes are, poly(3,3''-didodecylquaterthiophene) (PQT-12) and poly(3-hexylthiophene) (P3HT). Both polythiophenes have been studied intensively for their applications as organic thin film semiconductors and solar cells.^[11, 17-20, 23] However, only little data has been reported about their molecular self-assembly.

In Chapter 4, a more detailed review on work previously carried out on the alkyl-substituted polythiophenes will be described, after which a result and discussion will be presented.

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2.1.3 Oligothienothiophenes

Though much research was focused on the use of polymers as semiconducting material in electronic devices, many researchers soon found that problems such as the low degree of polymerization and the polydispersity of polymers tend to impede their functions.^[28, 40] Therefore, oligomers were synthesized to resolve these problems. These conjugated oligomers served as structural models to their parent polymers in the study of their crystal structures.^[41, 42] Furthermore, their molecular weights can be easily controlled through the synthesis, since polymerization is no longer needed. It is also easier to obtain molecules with high purity, which enhances molecular packing. In Chapter 5, we present the results and discussion of the self-assembly of a group of oligothienothiophenes. These oligothienothiophenes were synthesized in view of their applications as OTFTs and solar cells, inspired by the polythienothiophenes that McCulloch and co-workers reported earlier.^[43] A more detailed review will be presented on the oligothiophene research prior to the results and discussion to provide a better understanding in the research of the oligomers.

2.1.4 Anthracene Systems

Anthracene belongs to a group of linear polycyclic aromatic hydrocarbon which recently has also attracted much interest for electronic devices applications.^[44] These hydrocarbons are composed of laterally fused aromatic rings. Examples of typical small polycyclic aromatic hydrocarbons are naphthalenes, anthracenes, tetracenes,

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pentacenes and big molecules such as triphenylenes and coronenes. To expand the conjugation, oligomers of these polycyclic aromatic hydrocarbons are synthesized, with alkyl groups attached to the main backbone to enhance solubility. In Chapter 6, an introduction to a few anthracene based oligomers that were investigated for OTFT applications will be presented. The results and discussion of the self-assembly of this novel group of anthracene-based oligomers that are joined by ethynylene bonds will be presented afterward.

2.2 Self-Assembly Interactions

The molecular self-assembly of molecules on surfaces giving organized monolayers is typically driven by a variety of factors. This includes interactions between the molecules themselves, termed “molecule-molecule interactions”, and between the molecules and substrates, which is termed as “molecule-substrate interactions”. As such, it is crucial to understand these interactions in order to design the required ordered structures for specific applications.

2.2.1 Molecule-molecule interactions

Molecules tend to interact with other molecules through a variety of ways. These intermolecular interactions, though weak, are essential in the self assembly of these systems on adsorption. Non-covalent interactions such as hydrogen bonding, hydrophilic/hydrophobic forces, electrostatic attractions, π - π interactions and van der

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Waals forces play an important part in the assembly of these molecules. Oligo-p-phenylene vinylenes and dioxaborines functionalized with hydrogen bonding groups were demonstrated to form assembled structures that were very much dependent by the hydrogen bonding between molecules on adsorption.^[45, 46] Yang and co-workers also demonstrated that octadecylnitrobenzene assembled on graphite surface due to π - π interactions which resulted in conformational buckling of the alkyl chains.^[47]

2.2.2 Molecule-substrate interactions

Molecules can attach to substrate surfaces in two different ways, through physisorption or chemisorption. Both of these ways are dependent on the conditions of the substrates and the functional groups attached on the molecule main chain, which influence the adsorption manner of the molecules.

2.2.2.1 Physisorption

Physisorption refers to the adsorption of molecules onto surfaces without the presence of any chemical bonding between the 2 interacting systems. This is typically driven by the van der Waals forces of interaction between the molecules and surface, which are weak attraction forces compared to the covalently bonded intramolecular bonds. Only a small enthalpy change is required to adsorb or desorb the molecules from the surface. The typical enthalpy change of physisorption lies between 10 kJmol^{-1} to 40

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kJ mol^{-1} .^[48] As a molecule approaches a surface, it experiences both attractive and repulsive forces, as demonstrated by the Lennard-Jones potential curve in **Figure 2.3**.

Figure 2.3 Lennard-Jones potential curve displaying the combination of both the attractive and repulsive forces a system experiences.

Attractive forces at the long range bring the molecules close to the surface. However in close proximity, due to the overlap of electron orbitals, repulsive forces occur. As these forces are relatively smaller and insufficient to break or distort the chemical bonding in the molecule, physisorption of molecules onto surfaces are typically reversible and non-destructive. Examples of classic physisorption studies carried out under the STM include long chained *n*-alkanes and liquid crystal molecules on HOPG surfaces.^[49-51] These molecules self-assembled on graphite surfaces giving neat well-packed monolayers.

Long chain n-alkanes on HOPG surface

On adsorption on the freshly cleaved highly oriented pyrolytic graphite (HOPG) surface, long chain *n*-alkane molecules such as hexatriacontane ($n\text{-C}_{36}\text{H}_{74}$) and

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pentacontane ($n\text{-C}_{50}\text{H}_{102}$) assemble into neat lamellar structures, as observed at the liquid/solid interface STM imaging. These long chains organized with their alkyl chains extended and stretched out, parallel to the plane axis of the HOPG surface. **Figure 2.4** illustrates constant current STM images of $n\text{-C}_{36}\text{H}_{74}$ chains self-assembled on HOPG surface that was performed as part of the work in this thesis. These physisorbed chains can be desorbed from the surface upon high voltage pulsing, restoring the original pristine state of HOPG substrate surface.

Figure 2.4 Corey-Pauling-Koltun (CPK) molecular models superimposed on constant current STM image of $n\text{-C}_{36}\text{H}_{74}$ monolayer on HOPG. (10 nm x 10nm, $I_t = 42$ pA, $V_t = -159$ mV)

2.2.2.2 Chemisorption

Chemisorption refers to the adsorption of molecules onto the surfaces via chemical bonding to the surface molecules. Compared to the enthalpy for physisorption, binding energies for chemisorption are higher. An estimated binding energy of ~ 40 kcal mol⁻¹ has been reported for the gold-sulfur (Au-S) bond when an alkanethiol

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chemisorbed onto the gold surface.^[52] Adsorbing molecules in this case also prefer binding sites on surface that maximizes their coordination number with the substrates, to form tight, closed-pack structures.

Alkanethiols on Au(111)

On adsorption onto reconstructed Au(111) surface, alkanethiols tends to spontaneously form well-ordered monolayers. Constant current STM imaging at the liquid/solid interface revealed “holes” or pits on the monolayer, formed from the chemisorption of the alkanethiols.^[53, 54] These “holes” are caused by the chemical erosion of the Au surface as alkanethiols molecules attach itself to the surface by chemical bonding.^[53, 55-57] **Figure 2.5** shows chemisorbed monolayers of dodecanethiol on Au(111) surface, exhibiting the “holes”, which were consistent with the height on an Au atom.

Figure 2.5 (a) Constant current STM image of dodecanethiol monolayer on Au(111) exhibiting “holes”. (100 nm x 100 nm, $I_t = 100$ pA, $V_t = 300$ mV) (b) Line profile across these features showing the depth of the “holes”.

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These eroded gold atoms dissolve in the solvent solution, and on re-adsorption, attach themselves to existing substrates steps. **Figure 2.6** illustrates the changes of the Au(111) surface as time changes. Edges of the steps were observed to be more jagged, and “holes” developed into wider features as more of the alkanethiol molecules attach itself on the surface. These experiments were performed, along with the physisorption of *n*-alkanes on HOPG to determine the efficiency and stability of the STM equipment.

Figure 2.6 (a) Constant current STM imaging of the dodecanethiol on Au(111) illustrating the chemical erosion of the step edges. (270 nm x 270 nm, $I_t = 100$ pA, $V_t = 300$ mV) (b) STM image after 1 hour at the same location. (270 nm x 270 nm, $I_t = 100$ pA, $V_t = 300$ mV)

In order to probe into the packing and orientation behaviour of these organic materials, characterization techniques that allow molecular level resolution are typically required. Early reports by Dodabalapur and co-workers have indicated that conductance in organic film devices reside only in the first one or two monolayers^[26], hence it is necessary to choose characterization techniques that can look into such

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nano-scale dimensions. In this project, the STM will be used extensively to investigate the molecular packing arrangements of the conjugated systems studied. The STM allows the visualization of self-assembled molecules through imaging the electron density of states by the quantum tunneling effect of electrons. Thus, the packing arrangements of the investigated conjugated systems can be easily revealed using this technique.

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This chapter describes the experimental technique and procedures used in this thesis. The primary instrument used in this work, Scanning Tunneling Microscopy is discussed in great detail with reference to its working principle and function. Atomically flat substrates that are crucial to the investigation would also be introduced, with the molecular systems that are to be studied in this thesis.

3.1 Introduction to the Scanning Probe Microscopies

In 1981, G. Binnig, H. Rohrer and coworkers^[6] at the IBM Zurich Research Laboratory developed a powerful technique – the scanning tunneling microscope (STM) to study surfaces at the atomic level. They were awarded the Nobel prize for Physics in 1986 for this invention. STM is a promising technique based on the quantum tunneling effect that is useful for investigating the arrangement of atoms and molecules on conducting surfaces. This invention was later followed by the development of a family of scanning probe microscopy techniques, which are summarized as follows:

- Scanning Tunneling Microscopy (STM)^[6-8]

A metallic conductive tip is positioned very close to the sample surface. Due to this proximity, the wave functions of the electronic orbitals overlapped and the electrons can tunnel through the tip to the substrate and vice versa.

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- Atomic Force Microscopy (AFM)^[58]

To solve the problems of imaging samples with low electrical conductivity or insulators, Binnig and co-workers invented the AFM in 1986. The AFM probes the sample surface with a sharp tip which is located at a free end of a cantilever. In typical AFM instruments, deflections of the cantilever are determined by laser reflections from a position- sensitive photodetector which is capable of measuring displacements as small as 10 Å. This displacement is due to the interaction between the sample and the tip that results in a force causing the cantilever to bend. Other detection methods include the use of optical interferometry^[59], and piezoresistive sensors.^[60-62]

- Magnetic Force Microscopy (MFM)^[63]

MFM can be used to obtain the spatial distribution of magnetism on the sample surface by measuring the magnetic interaction between sample and ferromagnetic thin film coated tip.

- Scanning Near-Field Optical Microscopy (SNOM)^[64]

The SNOM is a scanning optical microscopy technique that uses a passing laser light source through an optical fiber. The optical fiber tip is placed very close to the sample surface, closer than the wavelength of light. The tip-surface distance is measured through the force interaction between them.

- Electrostatic Force Microscopy (EFM)^[65]

This technique studies the spatial variation of surface charges by cantilever deflection similar to that of the AFM. The cantilever hovers above the sample surface and a voltage is applied between the sample and tip. Due to static

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charges, the cantilever deflects. Thus the charge carrier density can be determined.

These microscopes operate on these common principles:

1. A probe is being brought near the sample surface.
2. Probe-sample interaction brings about small changes in the distance between them.
3. A piezoelectric element connected to the probe allows for small changes in these distances to be precisely measured in the angströms scale.
4. A feedback control system mechanism of the microscope controls the distance between the probe and the sample.

3.2 Scanning Tunneling Microscopy

The ability of the STM technique to probe into the nano-scale dimensions of surfaces has inspired many researchers to prefer this technique to other characterization methods. Through the control of the tunneling current between the tip and the sample surface, one can obtain topographical information of the surface. As the current tunnels through the small gap between the tip and sample surface, the local density of states (LDOS) of the sample can also be measured.^[66, 67]

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3.2.1 Working Principle of the STM

A bias voltage is applied between a sharp metallic tip and the conducting sample to be imaged. When the tip and sample distance is within a close separation of only a few atomic diameters, electrons can “jump” from the tip to the surface or vice versa, and this “jumping” is known as the tunneling effect.

Figure 3.1 Illustration of tunneling effect between tip and sample. Pink arrow indicates the direction of current, dependent of the voltage applied at tip.

Figure 3.1 shows an illustration of the tunneling effect between the tip of the STM and the sample surface. A tunneling current is generated when the wave functions of the tip and sample overlapped and thus this technique is known as scanning tunneling microscopy. **Figure 3.2** shows a schematic representation of an STM with an enlarged detail of the tip and sample surface. The tunneling probability of electrons has an exponential dependence on the separation distance between the tip and the sample; hence, a small change in distance results in a big change in the current.

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Figure 3.2 Schematic representation of a STM.

A simple expression for this tunneling current behavior is:

$$I_t = Ve^{-cd} \quad (1)$$

where V is the bias applied between the tip and sample separated by a distance d ; I_t is the tunneling current and c being a constant.^[66, 67]

The distance between the tip and the sample surface can be controlled by adjusting the bias voltage applied. In a typical STM experiment, the tunneling current is often kept at a fixed value, such that the distance between the tip and the sample surface is kept constant, hence the term constant current imaging.

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3.2.2 Applications of the STM

Metal and semiconducting surfaces

The first samples to be imaged under the STM were metal surfaces. The reconstruction of Au(110) surfaces were first imaged Binnig and co-workers.^[9] Subsequently, other metal structures such as Pt(100), Pd(100), Au(100), Au(111) and Ag(111) were also imaged under UHV or ambient environments.^[66, 68-70]

The observation of the Si(111) – (7x7) surface structure under the STM was one of the greatest success of the STM. The structure was first atomically resolved^[71] under ultrahigh vacuum (UHV) conditions, consistent with the superlattice model proposed by Takayanagi and co-worker^[72]. The other semiconducting surface that was commonly imaged under the STM include the GaAs(110)^[73] surface due to its potential applications in various fields and its ease to cleave in the (110) directions.^[67]

Organic adsorbates

The adsorption of organic molecules on substrate surfaces has been studied extensively using the STM.^[45, 74-78] Conducting molecules with aromatic rings were initially deposited onto conducting surfaces and imaged under ultra high vacuum scanning tunneling microscopy (UHV-STM) to reveal its molecular properties and molecule-substrate interactions. Successive studies of organic adsorbates were also

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carried out under the ambient STM technique, at the liquid/solid interface which allows the in-situ examination of molecules assembly at the surface. This allows the understanding of the topography and electronic structure of the organic adsorbates on surface at the molecular level.

Biological applications

Since organic molecules on surfaces were successfully studied using STM, it should be feasible to investigate biomolecules, such as DNA and protein structures, on surfaces. However, problems arise from the need of conducting substrates and the mobility of the biomolecules proved to be a hindrance. Furthermore, the imaging of DNA strands on a common STM substrate, such as HOPG, was highly difficult due to the inbuilt “DNA-like” defect of the cleaved surface^[79] The strand-like features appeared to exhibit periodicity and meander across the HOPG steps, which could be easily mistaken to be DNA molecules depositing on HOPG surfaces.

3.3 STM at the liquid/solid interface

All STM investigations carried out in this project were performed at the liquid/solid interface.^[45, 75, 78, 80-83] The liquid/solid interface technique allows images to be captured in-situ, providing time-dependent studies for the self-assembly mechanism. Also, it acts as a “UHV-like” environment while scanning as it provides a “shield” from the contaminants in the surrounding atmosphere and prevents the molecules from

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coming into contact with any possible static charges due to high percentage of humidity in the surrounding air. **Figure 3.3** shows a schematic representation of the liquid/solid interface configuration for the STM work discussed in this thesis.

Figure 3.3 Schematic representation of the liquid/solid interface.

3.3.1 Deposition method

Sample molecules or polymers were first dissolved in a solvent solution prior to deposition. For samples which were not as soluble, the mixture solutions were sonicated at about 45 °C for 15 min or until a homogeneous mixture is obtained. A drop of this solution was then deposited on a clean substrate before the STM imaging was carried out. Images were recorded after a few minutes when the thermal drift is stabilized and when the images were consistent.

3.3.2 Solvent Choice

For the liquid/solid interface STM method, the choice of solvent used was selected with the following considerations:

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- low volatility, to allow measurements for several hours with the tip still immersed in the solution,
- non-polar solvent, to reduce possible interactions between the solvent and the polymers/ molecules studied,
- chemically inert to the polymers or molecules to be investigated, and
- stable to the surrounding environment.

In this project *n*-tetradecane was used as the solvent for all investigations. *N*-tetradecane (99+%) solution is obtained from Sigma-Aldrich and is widely used as a medium for STM investigations due to its chemical inertness and low volatility. Furthermore, the simple alkane molecule is non-toxic and non-polar, and would not affect in any inter-molecular interactions. Other choices for solvent that are typically used for investigations at the solid/liquid interface included 1-phenyloctane and 1,2,4 trichlorobenzene.

3.3.3 Apparatus

STM investigations at the liquid/solid interface in this project were carried out using the PicoLE system from Agilent Technologies (formerly Molecular Imaging). The piezo scanner used in this system allows investigations to be carried out to a 10 μm scan length to nm scale. Pt/Ir (90:10) wire from Goodfellow drawn to 0.25 mm thick was used as an imaging tip. Tips were mechanically cut prior to use to produce atomically sharp and clean tip surface just before experiments.

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3.4 Substrates Preparation

The quality of the substrates used for the STM investigations plays a critical role in the self-assembly studies. It is necessary to obtain atomically flat and clean surfaces for successful imaging. Hence substrates that can qualify such requirements are limited to only few choices. Surface roughness of these substrates have to be of smaller magnitudes in terms of its dimensions to allow obvious recognition between the features of the substrate and molecules. Furthermore, experiments were carried out in ambient conditions, therefore the chemical inertness of the substrates is necessary. In addition, the substrates must be electrically conducting to allow currents to tunnel through. Thus, it is essential to look into the choice and preparation of these substrates prior to deposition experiments. Commonly studied substrates for the self-assembly investigations in the molecular scale include highly ordered pyrolytic graphite (HOPG), gold (111), and molybdenum sulfide.

In this work, we used highly ordered pyrolytic graphite (HOPG) and reconstructed gold substrates for our investigations due to their atomically flat surfaces and conductivity.

3.4.1 Highly ordered pyrolytic graphite (HOPG)

Graphite is thermodynamically the most stable allotrope of carbon, where each graphite layer consists of a regular hexagonal network of carbon rings. Within each

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layer, the carbon atoms are strongly bonded together by covalent σ bonds in a planar form. These σ bonds are made up of sp^2 orbitals and the remaining $2p_z$ orbitals overlap with each other to form a delocalized π -system of electrons, thus making graphite a good electrical conductor. The carbon atoms within a graphite layer are organized in a hexagonal network and have a C-C distance of 1.42 Å and an in-plane lattice constant of 2.46 Å as illustrated in **Figure 3.4(a)**. The graphite layer planes are stacked 3.35 Å apart and are held together by van der Waals forces in a stacking sequence of ABAB..., where every other layer is shifted by 1.42 Å in the horizontal axis relative to each other. As such, within each surface unit cell, 2 non-equivalent carbon atom sites occur. One carbon atom (α carbon atom) has a neighboring carbon atom directly below in the second layer, whereas the other carbon atom (β carbon atom) is located above a hollow site in the second layer, as demonstrated in **Figure 3.4(b)**.

Figure 3.4 Structure of graphite. (a) Interlayer stacking of graphite plane. (b) Top-view illustration of graphite sheets.

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In our STM experiments, commercially available highly ordered pyrolytic graphite (HOPG) from Goodfellow was used as the conducting substrate due to its ease in preparation. Atomically smooth and clean HOPG surfaces were obtained by cleaving the substrate using the adhesive tape. This atomically flat surface is also chemically inert, hence a very ideal surface to study the physisorption of various molecules. Furthermore, HOPG substrates are also typically used for STM calibration for high resolution imaging. Hence, it was crucial to obtain sufficiently well-defined and correctly calibrated high resolution STM images of HOPG surfaces prior to any investigations of the adsorption of molecules. **Figure 3.5** shows a high resolution image of a freshly cleaved HOPG surface in the *n*-tetradecane/HOPG interface.

Figure 3.5 High resolution image of HOPG obtained in the *n*-tetradecane/HOPG interface. (a) 4 nm x 4 nm STM image. ($I_t = 88$ pA, $V_t = -116$ mV) (b) 2 nm x 2 nm STM image ($I_t = 88$ pA, $V_t = -116$ mV), showing hexagonal lattice arrangement with a lattice constant of about 2.46 Å.

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3.4.2 Reconstructed gold (111) surface

Clean metal surfaces typically undergo surface reconstruction, where the surface atoms assume a different structure compared to the bulk structure to reduce its surface energy. The Au(111) surface is usually used in STM measurements as it is the only face-centered-cubic (fcc) metal that exhibits a reconstructed closed-packed (111) surface on annealing. The reconstruction results in a $(23 \times \sqrt{3})$ surface, where there is a compression of about 4.4% in the $[1\bar{1}0]$ directions, resulting in 23 surface atoms on the top layer occupying 22 bulk atom positions in the second layer as illustrated in **Figure 3.6**.^[84]

Figure 3.6 Structure of reconstructed Au(111) surface. (a) Unit cell of gold atoms with no reconstruction. (b) Schematic view of reconstructed Au(111) surface from top view. Illustration adapted from Darling and co-workers.^[84]

This superstructure is often referred to as the herringbone reconstruction of Au(111) surface, and can be observed under high resolution STM imaging of freshly annealed surfaces. **Figure 3.7** shows a high resolution image of a reconstructed Au(111) surface exhibiting the herringbone feature.

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In our work, Au(111) substrates from Molecular Imaging purchased through SPI Supplies were flame annealed at about 500-600 K just before the experiments using a butane gas burner until an orange glow was observed on the mica sheet edges. These Au(111) substrates were epitaxially grown onto green mica in high vacuum, giving a 150 nm thick Au(111) surface which has flat terraces. Freshly annealed samples are organic contaminant free and display the unique herringbone reconstructed feature.

Figure 3.7 (a) Constant current STM image of an annealed Au(111) surface. (500 nm x 500 nm, $I_t = 90$ pA, $V_t = -215$ mV) (b) High resolution image of reconstructed Au(111) surface obtained in the *n*-tetradecane/Au(111) interface. (80 nm x 80 nm, $I_t = 90$ pA, $V_t = -215$ mV).

Atomically flat terraces of less than 300 nm could be obtained from these substrates but was not possible to obtain when the author evaporated gold on silicon substrates due to the uneven nature of the silicon dioxide layer.

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3.5 Molecules for imaging

Pure hexatriacontane molecules ($C_{36}H_{74}$) and 1-dodecanethiol ($C_{12}H_{24}SH$) were obtained from Sigma-Aldrich and were used to demonstrate classic physisorption and chemisorption studies in this system. Regioregularly pure poly(3-hexylthiophene) polymer was also obtained from Sigma-Aldrich. All materials were used without further purification.

Next, the molecules that were investigated in the course of this thesis work will be discussed further in the subsequent chapters.

3.5.1 Polythiophenes

One of the conjugated systems that is studied in this work is polyquaterthiophene-12 (PQT). This polymer was provided with courtesy from Ong and co-workers in Xerox, Canada. The polymer was synthesized using $FeCl_3$ -mediated oxidative coupling polymerization.^[18] The molecular weight and distribution were determined by gel permeation chromatography (GPC) using polystyrene standards ($M_w = 22900 \text{ g mol}^{-1}$, $M_n = 17300 \text{ g mol}^{-1}$ and $M_w/M_n = 1.32$ respectively). Absolute molecular weight was determined using matrix-assisted laser desorption ionization-mass spectrometry (MALDI-MS) and was found to be $5323\text{--}6647 \text{ g mol}^{-1}$.^[85] In this work, the organization of this polymer was studied using STM after deposition onto both HOPG and reconstructed Au(111) substrates. To investigate the effects of the alkyl chains

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substitution on adsorption, these STM images were compared with the images of P3HT on similar substrates.

3.5.2 Oligothiophenethiophenes

In Chapter 5, oligomer derivatives of oligothiophenes were synthesized and the characterization of these oligomers will be discussed in more details. The thienothiophene molecules were synthesized through Stille coupling and Suzuki coupling.^[86] **Figures 3.8** and **3.9** briefly outline the syntheses procedures for obtaining the 4 molecules. Molecules **1a** and **1b** were synthesized by utilizing a one-pot Stille coupling^[87] between 2,5-dibromothiopheno[3,2-b]thiophene (**4**) and the corresponding freshly prepared tri-*n*-butylstannyl derivatives of tributyl(4-dodecyl-5-phenyl-thiophen-2-yl)stannane (**3a**) for **1a**, and tributyl(4-dodecyl-5-naphthalen-2-yl-thiophen-2-yl)stannane (**3b**) for **1b**, in the presence of catalytic $\text{PdCl}_2(\text{PPh}_3)_2$ in refluxing THF (**Figure 3.8**).

Figure 3.8 Synthesis of **1a** and **1b** oligomers.

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Molecules **2a** and **2b** were synthesized by the Suzuki coupling of 2,5-bis(5-bromo-3-dodecylthiophen-2-yl)thieno[3,2-b]thiophene (**6**) and the appropriate aryl-boronic acid (**7**) [phenylboronic acid for **2a** or naphthalen-2-ylboronic acid for **2b**] using $\text{Pd}(\text{PPh}_3)_4$ under reflux in THF in good yield (Figure 3.9).

Figure 3.9 Synthesis of **2a** and **2b** oligomers.

All these molecules are soluble in organic solvents such as CHCl_3 , toluene and THF, and can be easily purified by column chromatography and recrystallization. The structures of the molecules **1a**, **1b**, **2a** and **2b** were characterized by ^1H , ^{13}C NMR, elemental analysis and matrix-assisted laser desorption ionization–time of flight (MALDI-TOF) mass spectrometry. Results obtained were consistent with the predicted chemical structures. In Chapter 5, the discussion on the characterization data obtained from the 2D self-assembly of this set of molecules, on two different substrates using the STM will be presented. Also, a brief discussion of the bulk material properties will be presented as a comparison to the thin film properties investigated.

3 Experimental Section

3.5.3 Anthracene molecules

Anthracene molecules described in detail in **Chapter 6**, were synthesized by a collaborator in the University of Bari, Italy.^[88] Synthesis outline is illustrated in **Figure 3.10** for the anthracene molecules (**B3A**, **O3A**, **D3A** and **E3A**), details on methods can be found in the earlier publication^[88] and thesis of Dell'Aquila.^[89]

Figure 3.10 Synthesis of **B3A**, **O3A**, **D3A** and **E3A** molecules.

((i) for molecule **B3A**: 1) *n*-BuLi, Et₂O, -78 °C – 0 °C, 1h; 2) *n*-BuBr, overnight,
(ii) for molecule **O3A**, **D3A** and **E3A**: 1) PhLi, Et₂O, RT, 3h; 2) RBr, overnight.)

Similar to the polythiophenes and oligothienothiophenes, the 2D self-assembly of this set of molecules was also carried out using the STM on HOPG and Au(111) substrates. The thin film properties were also compared to the bulk material properties. Bulk material properties results were obtained courtesy of our collaborator.

4 Polythiophenes

In the beginning of this chapter, a brief review on polythiophenes as semiconducting materials is presented. After which the experimental data is presented and detailed discussion is carried out and reported. Two different polythiophenes, the polyquarterthiophenes and the polyhexylthiophenes are studied in this chapter.

4.1 Introduction

Among commonly studied conjugated polymers, polythiophenes appeared to be one of the most highly investigated. However, as with polyacetylene, unsubstituted pure polythiophenes have excellent conductive properties but very poor solubility due to the strong π - π interactions between the thiophene rings. Hence, extensive work on synthesizing polythiophenes that are both solution processable and conducting was carried out. Different alkyl substituents on the thiophene backbone was synthesized and investigated.^[90-93] Elsenbaumer and coworkers reported a series of poly(3-alkylthiophenes), which were environmentally stable and soluble.^[90, 92, 94] These materials were easily processable and have excellent thermal and environmental stability, and are soluble in organic solvents. These characteristics allow polythiophenes materials to perform very well in organic thin film transistors (OTFTs), photovoltaic devices and sensors.^[10, 13, 14, 20] High field effect mobilities (~ 0.1 - $0.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and good stabilities in solution processed organic semiconductors have been reported.^[11, 17, 19, 20, 36, 43] Furthermore, alkyl substituted polythiophenes

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chains can also aid in the packing and organization of the polymer through alkyl chain interdigitation via van der Waals interactions.^[77, 95]

In addition to that, regioregularity also plays an important role in the packing of these polythiophenes, which in turn affects the electronic properties. Alkyl chains can be incorporated into the polymer chains either in the head-to-head (HH) or head-to-tail (HT) configuration as illustrated in **Figure 4.1**.

Figure 4.1 Possible alkyl chain substitution in the polythiophenes structure

Head-to-head couplings typically cause the thiophene rings to twist due to steric hindrances, hence resulting in the loss of conjugation. On the other hand, head-to-tail couplings generally give planar conformations, resulting in highly conjugated polymers. In a regiorandom poly(3-alkylthiophene), both HH and HT configurations can be present in the same polymer chain, while in a regioregular poly(3-alkylthiophene), only one type of configuration is repeated throughout the chain. Regioregularity promotes the self-assembly of the polymer chain into highly ordered domains, where the substituted alkyl chains interdigitate due to van der Waals interaction, giving rise to higher molecular ordering, as shown in **Figure 4.2**.

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Figure 4.2 Scheme showing the interchain digitation between P3AT chains.

Being solution processable, regioregular poly(3-alkylthiophene-2,5-diyl)s (P3ATs) is an excellent model material for furthering our fundamental understanding of how the molecular design of these classes of organic semiconductors can affect the molecular level assembly and how this might be related to their excellent device characteristics. At the thin film level, due to their highly regular chain structure, these regioregular P3ATs films chains self-organize into two-dimensional sheets of lamellar structures, with interchain stacking revealed by x-ray diffraction (XRD) studies, as illustrated in **Figure 4.3.**^[11]

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Figure 4.3 Illustration of two-dimensional sheets of polymer chains with interchain stacking between the alkyl chains.

Scanning tunneling microscopy (STM) studies which were carried out on these alkylthiophenes also demonstrated well-organized lamella rows of polymer chains over large domains.^[77, 95-97] However, these images failed to reveal the interdigitated network of the alkyl chains that resulted in the lamella rows. Thus, more focus would be given to the observation of the interdigitated network of the alkyl chains in the 2D self-assembly. Field-effect transistors (FETs) made of regioregular poly(3-hexylthiophene) (P3HT) have been reported to demonstrate field-effect mobilities as high as $0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.^[11, 20] The reason behind such high mobility is very likely to be the organization of the chains.

4.2 Polyquaterthiophenes

Figure 4.4 Chemical structure of PQT-12.

Polyquaterthiophenes are very similar to the simple polythiophenes except the repeat unit consists of four thiophene rings. A dodecyl chains substituted polyquaterthiophene has been previously reported as a solution processable, regioregular polythiophene that exhibits excellent performance as an organic thin film transistor material under ambient conditions.^[18, 19, 23] Poly(3,3''-didodecylquaterthiophene) (PQT-12) possesses 2 dodecyl chains per monomeric unit as illustrated by the chemical structure in **Figure 4.4**. The dodecyl chains allow the molecules to be solution processable and also enable the molecules to achieve a high degree of molecular self-organization.

In addition, the long PQT backbone also allows for extended π -conjugation and oxidative stability, thus making it a suitable semiconductor material. Wu and co-workers demonstrated that a high degree of structural order in PQT-12 thin film can be readily accomplished through liquid-crystalline phase transition on proper surfaces to give rise to efficient charge transport.^[23] OTFTs made from PQT-12 thin films exhibited excellent FET performance with a mobility of $0.18 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and current on/off ratios of 10^7 . It has also been concluded that PQT-12 readily self-organizes

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into highly ordered lamellar π - π stacking structures in solid state through intermolecular side-chain interdigitation.^[18]

Although the morphology ordering of these PQT-12 semiconductor thin films has been investigated extensively using atomic force microscopy (AFM), x-ray diffraction (XRD)^[18, 19], and transmission electron microscopy (TEM)^[23, 85], little work has been done to understand the molecular scale organization of the polymer chains in the monolayer regime. XRD studies only allow the interpretation of polymer chain packing up to the resolution of several monolayers^[18, 19, 23] but fail to give molecular packing information at the molecule-substrate interface. However, it was also found that the conductance of cast semiconductor films resides only on the first one or two monolayers^[26], hence it is necessary to understand the organization of molecules in the monolayer.

In this work, the self-assembly of PQT-12 molecules in two-dimensional adsorbed layers at the liquid/solid interface was studied. Sub-molecular resolutions of the polymer chain packing were achieved through ambient STM technique, allowing for the first time, the visualization of alkyl chain interdigitation in a polymer monolayer on a highly oriented pyrolytic graphite (HOPG) and Au(111) substrate surface. Earlier studies of the self assembly of oligothiophenes on HOPG have been well-established and published. Alkylated oligothiophenes have been reported to adsorb in a “flat –lying” manner, with their alkyl chain spread out and extended, parallel to the surface.^[76, 83, 98] However, in the alkylated polythiophenes only lamellar rows with

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apparent chain foldings could be observed without the direct visualization of the alkyl chains.^[77, 97] It is hoped that the molecular packing and conformation of PQT-12 observed can help us to understand how the molecular design of polymers and oligomers can affect the self-organization of long chain and large molecules, and in turn understand the organic thin film device behaviour.

4.2.1 Understanding the Self-Assembly behaviour of PQT-12

To understand the effects of molecular architecture on the organization of PQT polymer, the polymer was deposited onto two surfaces – HOPG and Au.

4.2.1.1 STM studies of PQT-12 on HOPG surfaces

The STM image in **Figure 4.5(a)** shows a typical region where a stable, physisorbed monolayer of PQT-12 molecules formed spontaneously on the HOPG surface.

Figure 4.5 (a) Constant current STM image of PQT-12 at the *n*-tetradecane/HOPG interface. (150 nm x 150 nm, $I_t = 79$ pA, $V_t = -492$ mV) White line arrows indicate the three main crystallographic axes on HOPG. (b) Histogram of chain length distribution of PQT-12.

Different domains of the self-organized polymer chains in lamellar structures which are well-distributed across the surface can be observed. In each of these domains, the lamellae appear to orientate according to the three crystallographic axes of the

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underlying HOPG substrate. As the polymer structure has an electron-rich system concentrated at the thiophene ring on the main chain backbone, it tends to appear brighter due to the higher tunneling currents. These self-assembled domains have dimensions in the range of 100 x 50 nm, and they are mostly made up of short, linear segments. Interestingly, this image shows that these domains consist of not only linear segments, but also U-shaped PQT-12 segments. This observation provides a clue on the organization of the chains, which would be described in greater detail later in the chapter.

A histogram of oligomeric PQT-12 chain length can be obtained from the STM images and is shown in **Figure 4.5(b)**. To minimize all possible errors, only the easily identifiable individual chains in the images were measured. From the histogram, it can be observed that the PQT-12 chain lengths fall between 5 and 26 nm, with the average length at 14.5 nm. MALDI mass spectral analysis carried out earlier showed that the PQT-12 sample had a molecular weight of about 5300-6800 g mol⁻¹.^[23] Calculated based on the repeating length of PQT-12 monomer (15.5 Å)^[18], the molecular weight corresponds to about 12.4 – 15.5 nm of the molecular chain length. Hence the value determined from the STM measurements was in agreement with the MALDI mass spectral analysis results that were reported for this polymer mentioned in earlier work.^[23]

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Figure 4.6 Illustration of CPK models of PQT-12 chains adsorbed on the graphite sheet with alkyl chains following the crystallographic axes of the substrate.

Single-crystal XRD studies on quaterthiophene monomer molecules conducted by Pan and co-workers indicated pendant dodecyl chains extended out, perpendicular to its main backbone.^[99] Because of the commensurability of the alkyl chains to the HOPG surface, it was assumed that the dodecyl chains were lying parallel to the main crystallographic axes of the HOPG substrate. A schematic diagram of the organization of PQT-12 with reference to the HOPG substrate is illustrated in the model in **Figure 4.6**. This is generally the case for alkyl substituted conjugated systems, hence implying that the alkyl chains play a significant role in the organization of the polymer on the HOPG substrate.^[99-103]

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When the self-assembled domains are imaged at a higher resolution as shown in **Figure 4.7**, the apparent chain packing order of the polymers can be observed, where the lamellae features are measured to be 2.2 nm apart. These lamellae features appeared to have a zigzag formation, with an obvious dodecyl chain interdigitation between neighbouring polymer chains. Dodecyl chains are oriented perpendicular to the main backbone of the PQT-12 and appear on the STM images as a line of 6 spots, which corresponded to half the number of methylene groups in the alkyl side chains. The reason for this may be because the other six methylene groups were lying on the HOPG substrate. This phenomenon is typically observed for alkanes on HOPG surface because of the commensurability between the alkane chains and graphite sheet, resulting in only half the amount of $-\text{CH}_2$ groups appearing in the STM images.^[101, 104] The main driving force for the observed packing is the van der Waals interactions between the interdigitating alkyl chains.

An interesting feature to note is the presence of co-adsorbed molecules in the cavities formed between the dodecyl chains. As seen in **Figure 4.7(b)**, it is evident that these chains are isolated and not connected to any PQT-12 main chain. These chains are about 1.5-1.6 nm in length, corresponding to the dimensions of the solvent molecule-*n*-tetradecane. Hence we can conclude that these “extra” molecules observed are indeed co-adsorbed molecules and are not related to the PQT molecules.

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Figure 4.7 (a) Constant current high resolution STM images of PQT-12 chains at the *n*-tetradecane/HOPG interface. (6.5 nm x 6.5 nm, $I_t = 70$ pA, $V_t = -524$ mV). (b) High resolution three-dimensional view of an STM image with co-adsorbed solvent molecules. (6.4 nm x 6.4 nm, $I_t = 86$ pA, $V_t = 301$ mV).

Figure 4.8 (a) High resolution STM image of PQT-12 on HOPG. (9 nm x 9 nm, $I_t = 86$ pA, $V_t = 301$ mV). (b) Proposed packing of the PQT-12 chains based on the STM imaging.

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Based on the high resolution STM images that we have obtained for PQT, we proposed a possible packing model for these molecules (**Figure 4.8(b)**). As can be seen, the backbone will have a slight twist in order to maintain the thiophene bond angles and accommodate the observed zigzag structures (**Figure 4.7(a)**).

The brighter contrast in certain parts of the thiophene chains can also be attributed to this proposed twisting and the zigzag orientation of the PQT-12 chains. This zigzag orientation of the PQT-12 chains gives rise to cavities between two neighbouring chains. These cavities have lengths of about 2.3 nm and widths of about 0.9 nm across, thus allow for a single *n*-tetradecane molecule to be adsorbed. This co-adsorbed *n*-tetradecane molecule is clearly visible in **Figures 4.7** and **4.8** and in other high resolution STM images of similar samples.

Interesting U-shaped and closed ring segments were also observed in addition to the typical lamellar chains of the PQT-12 self-assembled layer, as shown in **Figure 4.9(a)** and **4.9(b)**. Lengths of all U-shaped and closed rings were measured to be around 20 nm and the bends typically adopt a 90° angle. The bending of chains was assumed to be caused by an all *syn*-conformation and the rotational disorder of *syn*- and *anti*-conformation of the thiophene units.

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Figure 4.9 Constant current STM images of PQT-12 chains. (a) U-shaped segments with neighbouring linear chains. (13 nm x 19 nm, $I_t = 70$ pA, $V_t = -524$ mV). (b) Closed ring segments with adjacent linear chains. (13 nm x 19 nm, $I_t = 70$ pA, $V_t = -524$ mV). (c) Proposed model structure of the bending of chain segment resulting in the U-shaped and closed ring segments of the PQT-12 layer on the HOPG surface.

The proposed molecular packing of the polymeric chain resulting in U-shaped and closed ring segments are shown in **Figure 4.9(c)**. Thiophene units could have assumed *syn*-conformations through the bent segment, thus disrupting the linearity of the segment. Bent segments also seemed to have a slightly blurred appearance in the STM image compared to the linear sections. This could be attributed to either the movement of the dodecyl chains on the backbone or their out-of-plane orientation with respect to the main chains. Thus, the dodecyl chains were not visible on the

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outside of the bent sections as compared to those that were well-interdigitated with neighbouring linear chains.

Figure 4.10 Schematic illustration of the packing of PQT-12 chains on silicon substrate surface. (OTS8 pretreatment layer not drawn here)

Due to the ability of interdigitation to organize the PQT molecules as shown in a two dimensional organization, we can understand why, in the case of surface treated SiO_2 , we can make use of the alkyl chains on the surface to organize the subsequent PQT. On octyltrichlorosilane (OTS8) pretreated SiO_2 surface, the polymer chains were aligned “edge-on” due to the influence of the silane layers as reported by Ong and co-workers.^[18, 19] Long range intermolecular side-chain interdigitations leading to the formation of lamellar π - π stacking of the PQT-12 chains were assumed through AFM and XRD studies.^[19, 23, 85, 99] **Figure 4.10** gives a simple illustration of how the chains are packed on the SiO_2 surface. However, through the STM investigations, we observed “flat-lying” PQT-12 chains on the HOPG surface instead. This could be attributed to the preferential epitaxial alignment of dodecyl chains onto the HOPG

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surface, which is energetically more stable as compared to the “edge-on” adsorption of PQT-12 with dodecyl chains perpendicular to the substrate surface.^[50] Azumi and co-workers had reported the close relation of single-crystal XRD studies and STM investigations on β -substituted oligothiophenes.^[103] These molecules were observed to possess the same molecular order on a two-dimensionally organized monolayer on the HOPG surface as one layer of its three-dimensional crystal. Single-crystal XRD studies carried out on monomeric PQT-12 units also appeared to adopt a similar structural packing order as that observed in our STM imaging results.^[99, 103]

On comparing the STM imaging results of the self-assembly of PQT-12 on a HOPG surface with previous AFM studies, as reported in Beng and co-workers, it can be observed that although the PQT-12 chains assemble in a “flat-lying” orientation in STM imaging and “edge-on” orientation as proposed from AFM investigations, both arrangements appear to adopt similar alkyl chain interdigitated structures.^[19, 23] Both the monolayer observed in STM imaging and the vertical layer of the lamellar π - π stacking proposed from AFM imaging seemed comparable.

It was earlier shown that rod-like structures were observed throughout the surface of SiO₂ where the widths of the rods were about 10-15 nm. In our STM investigations, the average chain length was also observed to fall within this range. Hence, we can infer that our investigations of the assembly of PQT-12 on a HOPG surface are comparable to the AFM studies on SiO₂ in one of the dimensions.

4.2.1.2 STM studies of PQT-12 on Au(111) surfaces

For comparison, we also studied a case where the molecules interaction with substrate is weaker. In this section, we will look at the organization of PQT-12 on Au(111) surface. PQT-12 assumes a slightly more disordered monolayer on an Au surface compared to HOPG. More bent segments of the molecules were observed, as shown in Figure 4.11.

Figure 4.11 (a) Constant current STM image of PQT-12 chains at the *n*-tetradecane/Au(111) interface. (38 nm x 38 nm, $I_t = 80$ pA, $V_t = 610$ mV). (b) High resolution STM images showing alkyl chain interdigitation. (12 nm x 12 nm, $I_t = 80$ pA, $V_t = 653$ mV).

However, it is important to note that alkyl chain interdigitation of adjacent chains is still highly visible, and certain domains of the monolayer appeared to have parallel lamellar regions, similar to those observed in the monolayer on HOPG substrates. Distances between lamellae were also determined to be 2.2-2.3 nm, similar to that on

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HOPG substrates. This implies that the packing on the substrates is still very much dependent on the interdigitation of the dodecyl chains on the PQT-12 backbone.

From the STM studies conducted on the two different substrates, it can be deduced that alkyl chains on the polymer backbone play a more important role in the packing of the polymers than the effect of the substrates on the adsorption. However, as compared to Au(111) substrate, the commensurability between the alkyl chains and the HOPG substrate surface led to larger domains of well-packed polymers. In addition, domains with well-packed polymers observed on the Au(111) substrate were lesser as compared to those on HOPG substrate. The observation of solvent tetradecane molecules co-adsorbing into the monolayers on Au(111) was not as obvious in the monolayers on HOPG. As the monolayers on Au(111) were not as stable as those on HOPG, it was difficult to produce high resolution images, thus the co-adsorption of tetradecane molecules into the monolayers was not as clearly imaged as those on HOPG substrate.

Despite efforts from various research groups to study the interactions between polythiophenes and Au(111), the results are still controversial and contradictory.^[105-108] Earlier studies showed no significant chemical interactions between the Au atoms and thiophene molecules through XPS studies for both thiophene molecules and P3HT on Au, compared to other substrates such as vanadium, chromium and copper.^[105, 106] However, Noh and co-workers later showed evidence of possible chemical interactions between the thiophene molecules and on Au(111) surface through XPS

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studies of peak shifts.^[107, 108] Furthermore, STM images showed “pit” holes on the Au(111) surface, indicating that chemical interactions between the molecules and Au(111) are present. Hence, it is still not possible to conclude the presence of chemical interactions between the polythiophenes and Au(111) surface.

As the STM images of PQT-12 on Au(111) in **Figure 6.11** did not show any “pit”-holes due to chemical interactions with the sulphur from the thiophene units, we can assume that interactions between the PQT-12 and Au(111) surface were purely physical. Physical interactions such as van der Waals forces are present rather than covalent Au-S bonds.

4.3 Poly(3-hexylthiophenes)

Figure 4.12 Chemical structure of P3HT.

To help with the understanding of how molecular design affects thiophene molecules, another polymer, the poly(3-hexylthiophene) (P3HT), was investigated using the same methods. Regioregular P3HT is made up of a polythiophene conjugated backbone substituted with hexyl chains at the 3-position. As P3HT has shorter alkyl chain substituents and longer average polymer chain lengths, it would be interesting to determine how the organization of this polymer differs from the PQT-12 discussed previously. P3HT has demonstrated excellent semiconducting properties with field-effect mobilities as high as $0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.^[11, 17, 20] Sirringhaus and co-workers reported that P3HT films self-assembled into lamellar structures with two-dimensional conjugated sheets formed through interchain stacking.^[11] Earlier studies on the self-assembly of P3HT on HOPG surfaces revealed well-ordered domains of aligned polymer chains and were oriented according to the three crystallographic axes of the HOPG substrate.^[77, 95-97] However, a sub-molecular resolution of these monolayers was not achieved previously. Furthermore, polarized infrared spectroscopy and grazing angle XRD performed on the P3HT films by Kline and co-workers indicated results contradictory to the typical understanding of the alkyl chain interdigitation in P3HT.^[34] Hexyl chains on the polymer backbone were discovered to be highly

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disordered and not in an all-trans conformation.^[109] The group then compared P3HT, PQT-12 and pBTTTs (polythienothiophenes) and concluded that the hexyl chains were not interdigitating as they were earlier proposed to be so, and that the side-chain attachment density affects order and device performances of polythiophenes. Both PQT-12 and pBTTTs were revealed to assemble with alkyl chain interdigitation between polymer chains.

In this study, STM investigations were carried out to look into the organization of the monolayers of P3HT on HOPG and Au(111) substrates in order to determine if the length of alkyl chains and side-chain attachment density play important roles in the packing of the polymer chains.

4.3.1 Self-Assembly studies of P3HT

Similar to the studies on PQT-12, the polymer was deposited on two surfaces – HOPG and Au, in order to understand the molecular architecture on the organization of P3HT polymer.

4.3.1.1 STM studies of P3HT on HOPG surfaces

Figure 4.13 (a) Constant current STM image of P3HT chains at the *n*-tetradecane/HOPG interface. (140 nm x 140 nm, $I_t = 95$ pA, $V_t = -500$ mV). (b) STM image showing closed rings and curved segments of the P3HT chains. (25 nm x 25 nm, $I_t = 80$ pA, $V_t = 500$ mV).

Similar to the monolayer of PQT-12 on HOPG surface, P3HT also forms a stable physisorbed monolayer spontaneously. The self assembled layer is as shown in **Figure 4.13(a)**. The domains of the lamellar chains also seem to orientate according to the three crystallographic axes of the underlying HOPG substrate, as illustrated in the model shown in **Figure 4.14**. They are indicated by the three arrows. However,

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the packing of the P3HT molecules in the monolayer appears to be denser compared to the organization seen for PQT. At a higher resolution (**Figure 4.13(b)**), closed ring and U-shaped segments of the polymer chains were observed, similar to those of PQT-12. These findings were consistent with those earlier reported by Grevin and co-workers for “dry” samples.^[95-97]

Figure 4.14. Illustration of CPK models of P3HT chains adsorbed on the graphite sheet with alkyl chains following the crystallographic axes of the substrate. White arrows indicate the three crystallographic axes of HOPG surface.

Through their studies, the authors proposed that these P3HT chains self-assemble into the HOPG surface forming lamellar chain structures via the alkyl chain interdigitation of the hexyl substituted side chains. Nonetheless, no evidence of the alkyl chain interdigitation has been observed.

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Figure 4.15 shows a sub-molecular STM image of the P3HT monolayer at the *n*-tetradecane/HOPG interface. It can be observed, though faintly, that the darker zones between the bright lamellar chains were partially filled with alkyl chains. These chains are the hexyl substituted chains on the P3HT. Inter-lamellar distances from the images were determined to be ~ 1.4 nm, results which are consistent with those published.^[95-97]

Figure 4.15 Constant current high resolution STM image of P3HT chains at the *n*-tetradecane/HOPG interface. (8.6nm x 8.6 nm, $I_t = 100$ pA, $V_t = 500$ mV).

As the alkyl substituents chains on P3HT are much shorter than the dodecyl chains on PQT-12, packing of the polymer chains does not allow the co-adsorption of *n*-tetradecane chains. Moreover, since each thiophene unit on the polymer backbone is substituted by a hexyl chain, the 2D packing of the polymer chains does not leave any “cavity” like those of PQT-12. Furthermore, since the most geometrically stable configuration of the thiophene units is the anti-conformation with the hexyl chains in opposite directions, the polymer chains do not twist on adsorption onto the substrates

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like the PQT-12 chains. Hence, it is extremely difficult to obtain a well-resolved high resolution image. This could be due to short length of the hexyl chains, or slight mobility of the chains. As such, these results seemed to agree with the findings of Kline and co-workers where the results indicated the hexyl chains to be liquid-like and disordered.^[34]

4.3.1.2 STM studies of P3HT on Au(111) surfaces

Figure 4.16 (a) Constant current STM image of P3HT chains at the *n*-tetradecane/Au(111) interface. (120 nm x 120 nm, $I_t = 75$ pA, $V_t = -200$ mV). (b) STM images showing closed rings and curved segments of the P3HT chains. (50 nm x 50 nm, $I_t = 80$ pA, $V_t = 200$ mV).

On the Au(111) surface, the P3HT monolayer appeared to have lesser order compared to P3HT on HOPG and the chains are no longer packed in neat and closely spaced lamellar rows over large domains, as seen in **Figure 4.16(a)**. Compared to the assembly on HOPG surface, more of the closed ring or curved segments of the polymer structures can be seen, as illustrated in **Figure 4.16(b)**. At a higher

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resolution, it is observed that the polymer chains were not as consistently spaced as compared to those lamellar chains on the HOPG surface (Figure 4.13). Polymer chains were also not aligned as parallel and straight but as curved and disordered.

Figure 4.17 (a) Constant current STM image of P3HT chains at the *n*-tetradecane/Au(111) interface. (15 nm x 15 nm, $I_t = 85$ pA, $V_t = -600$ mV). (b) Constant current STM image of P3HT chains at the *n*-tetradecane/HOPG interface. (15 nm x 15 nm, $I_t = 95$ pA, $V_t = 400$ mV).

On a HOPG surface, commensurability between the alkyl chains and the substrate surface results in the orientation of the lamellar chains to follow the crystallographic axes.^[101] However, on the Au(111) substrate, this is not true. The polymer chains no longer assemble in any preferential direction. In addition, distances between the P3HT chains on the Au(111) substrate are no longer consistent throughout like those on the HOPG substrate. The hexyl chains of the P3HT were not extended and stretched out like those on the HOPG surface. This indicated that the hexyl chains of the adjacent P3HT polymer chains were not interdigitating like those on HOPG substrate. This probably arises due to the incommensurability of the hexyl chains and

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the Au(111) substrate. Therefore the chains were not able to lie flat on the Au(111) surface like those on HOPG. The self-assembly of the polymer chains is thus only guided by interactions between the polymer backbone and the Au(111) substrate. Therefore, the monolayer on Au(111) appeared less ordered and without parallel lamellae structures.

4.4 Conclusion

An insight to the understanding of the interaction forces that control the self assembly of the polythiophenes can be obtained by comparing the STM investigations of the 2 polythiophenes, PQT-12 and P3HT. Both polythiophenes possess alkyl substituted chains on the backbone to promote processability and organization. On the two substrates investigated, obvious dodecyl chains interdigitation was observed for the monolayers of PQT-12; whereas for P3HT, the hexyl chain interdigitation was hardly visible on the HOPG surface and absent on the Au(111) surface.

As dodecyl chains on PQT-12 were twice as long as the hexyl chains on P3HT, van der Waals interaction between adjacent polymer chains is stronger for PQT-12. Furthermore, the dodecyl chains substituted thiophene rings were spaced apart by two unsubstituted thiophene rings. Hence less repulsion could occur; whereas for P3HT, all thiophene units were substituted with hexyl chains, giving rise to slight steric repulsions, and making it difficult for the alkyl chains on the P3HT backbone to interdigitate well with that from adjacent polymer chains. As a result, interdigitation

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can be observed on both HOPG and Au(111) substrates for PQT-12 chains. However for P3HT, the monolayer on Au(111) was disordered and spacing between the polymeric chains varied. The hexyl chains were not long enough to have van der Waals interactions with each other to overcome the influence of the Au(111) interaction with the polymer backbone.

Despite these differences, both polythiophenes have shown to be excellent OTFT materials with mobility of about $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ^[19, 110], where for typical applications, mobility is required to be $\geq 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the polymeric material to be used.^[111] However, the proposed packing of PQT-12 monolayers derived from STM studies seemed to contradict the device results obtained. As conjugation across polymer chains typically exists only if the polymer structure is co-planar for charge transfer, the proposed packing as shown in **Figures 4.7, 4.8 and 4.9** indicated twists in the polymer backbone, with certain regions of the chains being more brightly enhanced. Conjugation in this case would definitely be disrupted, and OTFT results in this case would not have been significant.

From our work, we can see that due to the nature of the commensurability between the dodecyl chains and the HOPG substrates, the PQT-12 chains existed in a twisted conformation in its 2D layer packing. As the monolayer is adsorbed flatly on the HOPG surface with the dodecyl chains stretched out parallel to the surface, the polymer chains would probably twist to allow the best stable conformation on adsorption. However, for PQT-12 chains that were spin-coated on OTS8 treated SiO_2

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surfaces fabricated devices, the dodecyl chains were interacting with the OTS8 chains due to van der Waals interactions. Thus the PQT-12 chains lie perpendicular to the SiO_2 surface.^[23] As such, they do not twist like those that were observed on STM investigations. Conjugation in this case is thus effective, yielding good charge transfer characteristics.

5 Oligothienothiophenes

Similar to the previous chapter, a brief review on oligothiophenes and the advantages of using oligomers is introduced in the initial part of the chapter. Subsequently, the experimental data on the characterization of a set of oligothienothiophenes is carried out along with the discussions of the results.

5.1 Introduction

Due to the difficulty in controlling polymerization rates, polymers in general have more inconsistent chain lengths and structural defects than oligomers. This generally leads to amorphous films. Therefore short chain oligomers may be a better candidate for studying the correlation between structural ordering and the properties of these materials. Oligothiophenes tend to organize into more ordered monolayers compared to polythiophenes at the liquid-solid interface observed under the STM. Hence, using oligothiophene molecules, it was easier to study the effects of structure on the packing compared to long polymeric chains which have the tendency to curl and bend at certain lengths.^[76, 77, 82, 83, 95, 96, 98, 103] These conjugated oligomers which possess high degrees of molecular and crystalline order are also often used as reference models to their parent polymers.^[36] The discovery of excellent charge properties of α -sexithiophenes(α -6T) in 1988 by Garnier and co-workers led researchers from all over the world to be interested in the oligothiophene family.^[112, 113] FETs with charge carrier mobilities of $0.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for α -octithiophene(α -8T) and $2.5 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

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for α -6T have been achieved when the substrates were heated during deposition in order for the molecules to achieve better ordering.^[36, 114]

However, unsubstituted oligothiophenes like those mentioned earlier, are typically insoluble in common solvents due to the lack of a “solvation shell”. Hence the deposition of these materials can only be restricted to vacuum techniques. To solve this problem, flexible alkyl chains are introduced at the β -positions of the thiophene rings, similar to that of the alkylation of polythiophenes to give P3ATs. In general, alkylated oligothiophenes have been observed to adsorb in a “flat-lying” manner on graphite surfaces, with their alkyl substituent chains spread out and extended, parallel to the substrate surface.^[76, 82, 83, 98, 103, 115-117] Through atomistic molecular dynamics simulation, Gus’kova and co-workers found that the adsorption of thiophene molecules onto substrate surfaces will result in the backbone of these molecules adopting planar conformations, despite torsion potentials that favor distorted conformations.^[118] Hence, it can be implied that the aliphatic long side chains tend to induce planarity in the system on adsorption.

Consistent with these theoretical simulations and predictions, Azumi and co-workers also observed in experimental scanning tunneling microscopy (STM) studies that in contrast to the neat lamellar organization of long chains alkylated oligothiophenes, short chain substituted oligothiophenes tend to adsorb in a rather “herringbone-like” monolayer organization.^[103] Thus this implied that the monolayer organization of

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these conjugated oligothiophenes system is very much dependent on the alkyl chain substitution on the backbone.

In this project, the assembly of a series of oligothiophene derivatives was investigated. These derivatives possess a fused pair of thiophene rings, referred to as a thieno[3,2-b]thiophene segment and are terminally capped with phenyl or naphthyl groups. McCulloch and co-workers had earlier reported charge carrier mobilities of $0.2 - 0.6 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and on/off ratios of 10^7 for their polythienothiophenes when fabricated into OTFT devices.^[43] First principles energy minimization using density functional theory (DFT) for the polymer also indicated that conjugated planes of polymer are substantially tilted within their crystalline polymer. This was also confirmed experimentally by a combination of polarized photon spectroscopy methods.^[119] **Figure 5.1** shows the chemical structure of the polymer possessing a monomeric unit of thieno[3,2-b]thiophene segment surrounded by two alkylated thiophene units. This semiconducting polymer combined both good processing properties such as solubility with good electrical properties such as mobility. Hence it will serve as a successful semiconductor material for the fabrication of OTFTs.

Figure 5.1 Chemical structure of polythienothiophene (poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene)) studied.

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These results hence motivated us to synthesize a series of oligothienothiophene derivatives for their potential use as OTFTs and photovoltaic material.

5.2 Oligothienothiophene derivatives

In this work, we present the results on the self-assembly studies of a group of alkyl-substituted oligothienothiophene derivatives on both highly oriented pyrolytic graphite (HOPG) and reconstructed Au(111) surfaces. These thieno[3,2-*b*]thiophenes have alkyl substituents at different positions and also different end-cap terminal groups. These variations allow us to determine the effects of the molecular design on its self assembly. As these molecules are structurally similar to a liquid crystalline polymer reported by McCulloch and co-workers^[43] as illustrated in **Figure 5.1**, it is anticipated that these molecules could provide similar favorable field effect mobilities and would also form ordered self-assembled structures on adsorption.^[120]

Figure 5.2 Chemical structures of oligothienothiophene derivative molecules investigated. (R = $C_{12}H_{25}$)

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The group of molecules investigated in this work are phenyl terminated 2,5-bis(4-dodecyl-5-phenylthiophen-2-yl)thieno[3,2-*b*]thiophene (**1a**) and 2,5-bis(3-dodecyl-5-phenylthiophen-2-yl)thieno[3,2-*b*]thiophene (**2a**), and the naphthyl terminated 2,5-bis(4-dodecyl-5-(naphthalen-2-yl)thiophen-2-yl)thieno[3,2-*b*]thiophene (**1b**) and 2,5-bis(3-dodecyl-5-(naphthalen-2-yl)thiophen-2-yl)thieno[3,2-*b*]thiophene (**2b**). The chemical structures of these molecules are shown in **Figure 5.2**. Thienothiophenes groups **1** and **2** differ by their alkyl chain substituted positions, whereas group **a** and **b** molecules differ by termination group - **a** is terminated by phenyl groups and **b** is terminated by naphthyl termination groups. It was hypothesized that the difference in the alkyl substituted positions would induce torsion within the molecule, resulting in a disruption in the π -conjugation and thus producing poor field effect properties. Thus, we used STM to study the effects of these variations in alkyl positions on the organization of these molecules, which are deposited on highly oriented pyrolytic graphite (HOPG) and Au(111) substrates at the liquid/solid interface, using *n*-tetradecane as the liquid medium.

In addition to the study of the thin film properties of these molecules through the use of the STM, the bulk properties of these materials were also briefly investigated. The photophysics of these molecules were studied using the UV-vis spectrometry, photoluminescence and cyclic voltammetry. Thermal properties of these molecules were also investigated through the use of the DSC and TGA. Finally, wide angle x-ray diffraction was also used to look into the extruded rods of these molecules. It is hoped that through the study of both the thin film and bulk properties, a more

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comprehensive understanding of the physical and chemical properties of the molecules can be acquired.

5.3 Self-Assembly Studies of Oligothienothiophenes

The packing of all the molecules on two different substrates, the HOPG and Au(111) surfaces, are investigated by using STM. This allows comparison of the effect molecule-substrate interactions on the organization of these molecules on similar surfaces.

5.3.1 STM studies of phenyl-capped 1a and 2a molecules on HOPG surfaces

STM investigations of the self-assembly of the molecules at the *n*-tetradecane/HOPG interface revealed stable physisorbed monolayers which formed spontaneously. This can be seen in **Figure 5.3**. Similar to typical images of self-assembled conjugated molecular systems, the brighter parts on the image correspond to the π -conjugated backbone of the molecule due to the higher tunneling currents. Molecules appeared to organize well into long parallel lamellae, spreading across large domains, which extend to more than 200 nm. High resolution imaging revealed that the molecules were organized largely by the influence of alkyl chain interdigitation, as observed in **Figure 5.3(b)** and **5.3(d)**.

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Figure 5.3 (a) Constant current STM image of **1a** at the *n*-tetradecane/HOPG interface (40 nm x 40 nm, $I_t = 75$ pA, $V_t = -200$ mV). (b) High resolution STM of **1a** (15 nm x 15 nm, $I_t = 79$ pA, $V_t = -258$ mV). (c) Proposed CPK model packing of **1a**, white rectangles representing unit cells. (d) Constant current STM image of **2a** at the *n*-tetradecane/HOPG interface (40 nm x 40 nm, $I_t = 75$ pA, $V_t = 120$ mV). (e) High resolution STM of **2a** (15 nm x 15 nm, $I_t = 80$ pA, $V_t = 100$ mV). (f) Proposed CPK model packing of **2a**, white rectangles representing unit cells.

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Molecules are guided to assemble mainly by the commensurability between the alkyl chains and the HOPG surface. These chains form adjacent lamellar rows interdigitating due to van der Waals interactions. The darker region between lamellar rows are occupied by well-aligned chains. Both molecules appear to adopt a similar packing order, as observed in the STM images. Although the molecules possess different alkyl substitution position, it was interesting to note that both self-assembled on HOPG having similar unit cell dimensions. The anticipated steric hindrance from the close proximity of the dodecyl chains on the conjugated core was not apparent in these monolayers and did not affect the self-assembly of **2a** in the 2D monolayer.

Unit cell dimensions determined from the STM images for **1a** are $a = 1.4 \pm 0.1$ nm; $b = 2.5 \pm 0.1$ nm; $\alpha = 79 \pm 2^\circ$ and for **2a** are $a = 1.4 \pm 0.1$ nm; $b = 2.9 \pm 0.1$ nm; $\alpha = 81 \pm 2^\circ$. From the monolayer packing, it can also be inferred that the compounds lie seemingly flat and planar on the surfaces upon adsorption, and the alkyl chains are all stretched out and extended.

5.3.2 STM studies of phenyl-capped **1a** and **2a** molecules on Au(111) surfaces

Similar to the monolayers formed on HOPG surface, molecules **1a** and **2a** also self-assembled into neat lamellar rows on Au(111). However, the domains were much smaller as compared to the monolayers on HOPG surface. Domain sizes range between 20-35 nm as compared to the large extensive domains of over 200nm for monolayers on HOPG surface. Furthermore, the lamellar rows were also oriented in

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different directions and disordered regions around the domain boundaries were also observed. **Figure 5.4** shows low resolution images of the monolayers of **1a** and **2a** on the Au(111) surface, exhibiting different domains and multi-directional orientations of the lamellar rows.

Figure 5.4. Constant current STM images of molecules on *n*-tetradecane/Au(111) interface exhibiting different domains. (a) Monolayer of **1a** (100 nm x 100 nm, $I_t = 75$ pA, $V_t = -210$ mV). (b) Monolayer of **2a** (100 nm x 100 nm, $I_t = 75$ pA, $V_t = 126$ mV).

Figure 5.5 Constant current STM images of **1a** on *n*-tetradecane/Au(111) interface at different regions exhibiting chirality. (a) (15 nm x 15 nm, $I_t = 89$ pA, $V_t = -59$ mV) (b) (15 nm x 15 nm, $I_t = 89$ pA, $V_t = -59$ mV)

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Lamellar rows appeared to be rope-like in structure, with well-interdigitated dodecyl chains observed in between the rows. Looking at the higher resolution images, chiral domains of the lamellar rows can be observed. **Figure 5.5** shows 2 images obtained from the STM imaging of the monolayer of **1a** on Au(111).

Comparing **Figure 5.5(a)** and **5.5(b)**, we can observe the difference in the adsorption patterns of the molecules onto the substrate surface. Following the CPK packing models derived from both the STM images, we can see that the molecular arrangements are mirror images of each other.

“Chiral” refers to objects that are not superimposable onto their mirror images. Human hands are the easiest and most common example in our everyday life that illustrates the concept of chirality. The left hand is a non-superimposable mirror image of the right hand, and vice versa, as demonstrated in **Figure 5.6**.

Figure 5.6 Illustration representing chirality using the left hands and right hands. The mirror images are non-superimposable onto each other.

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Similar to the left hand and right hand, CPK packing models in **Figure 5.7** illustrate the monolayer organization in the chiral domains for molecule **1a**.

Figure 5.7 Proposed CPK model packings of **1a**, illustrating the non-superimposable packings.

Unit cell dimensions determined from the chiral domains of **Figure 5.5** are:

Figure 5.5(a) $a = 1.4 \pm 0.1$ nm; $b = 2.6 \pm 0.1$ nm; $\alpha = 95 \pm 2^\circ$ and

Figure 5.5(b) $a = 1.3 \pm 0.1$ nm; $b = 2.5 \pm 0.1$ nm; $\alpha = 90 \pm 2^\circ$

Both dimensions are very similar, with only 5° difference in their α angles. The dimensions of the unit cells were also comparable to the monolayer unit cell dimensions on the HOPG surface. The difference lies in the α angles. Both monolayers on HOPG and Au(111) showed well defined interdigitated dodecyl chains from the adjacent lamellar rows.

Chirality in chemistry plays an important role in the field of drug discovery. One important case in history involving the chirality of drugs is the medication for morning sickness in pregnant women – thalidomide. Due to insufficient knowledge in

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chiral compounds, the drug led to many children born with severe deformities. Furthermore, the recent development of heterogenic catalysis which uses chiral modifiers to synthesize compounds enantioselectively also enhances the importance of chirality.^[121] Hence, chirality has become an important area of concern, especially for drug discovery and development.

Though all four molecules studied are achiral, they tend to result in two-dimensional chiral surface structures on adsorption. The adsorbed molecules have non-superimposable mirror images due to motion confinement by the surface planes. This phenomenon is not unusual and has been studied by many researchers.^[45, 74, 122-124] The appearance of the chiral domains on the substrates is probably due to the presence of a symmetry axis in the molecules and the long alkyl chains.^[74] Both enantiomorphic domains occur in the same amount, hence the overall monolayer is racemic. However, for heterogenic catalysis applications, homochiral domains would be preferred over racemic mixtures, thus future work on yielding specific homochiral surface arrangements should still be considered.

Monolayer of **2a** on Au(111) showed well-interdigitated lamellar rows with chiral domains similar to those observed for **1a**. However, as demonstrated in Figure 5.8(a) in the pink outlined region, a small domain of honeycomb-like packing structures could also be seen alongside the lamellar domains. On a higher resolution in Figure 5.8(c), this region appeared to adopt a very complex superstructure. Unit cell dimensions determined from the lamellar domains are $a = 1.3 \pm 0.1$ nm; $b = 2.5 \pm 0.1$

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nm; $\alpha = 92 \pm 2^\circ$. The complex superstructure appeared in smaller proportions as compared to the lamellar arrangements in the entire monolayer. These superstructures could possibly arise from the stacking of the molecules or tilting of the molecular backbone. Due to the complexity of the arrangement, it was not possible to propose a model packing, although high resolution STM images were obtained for the structures (**Figure 5.8(c)**). These superstructures were not observed for the monolayer of **1a** on Au(111), but only for the monolayer **2a** molecules. This is probably due to the steric hindrance in the molecule arising from the close proximity of the dodecyl groups; hence the **2a** molecules adopted twisted structures on assembling onto the Au(111) surface. On the other hand, this was not observed on HOPG, as the **2a** molecules preferred a “flat-lying” conformation with the dodecyl chains stretched out parallel to the surface, because of the commensurability of the dodecyl chains and the HOPG surface.^[101]

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Figure 5.8 Constant current STM images of **2a** on *n*-tetradecane/Au(111) interface at different regions exhibiting chirality. (a) Different domains showing different packing of the molecules. (43 nm x 43 nm, $I_t = 90$ pA, $V_t = -75$ mV) (b) High resolution STM image of monolayer exhibiting the lamellar packing. (15 nm x 15 nm, $I_t = 86$ pA, $V_t = -180$ mV) (c) High resolution STM image of monolayer exhibiting the honeycomb-like packing. (15 nm x 15 nm, $I_t = 90$ pA, $V_t = -80$ mV)

5.3.3 STM studies of naphthyl-capped **1b** and **2b** molecules on HOPG surfaces

Naphthyl-capped molecules self-assemble neatly into stable physisorbed monolayers on HOPG surfaces similar to that of the phenyl-capped molecules, with alkyl chains from the adjacent rows interdigitating to form neat lamellar domains. Unit cell dimensions determined from the STM images for **1b** are $a = 1.6 \pm 0.1$ nm; $b = 3.0 \pm 0.1$ nm; $\alpha = 81 \pm 2^\circ$ and for **2b** are $a = 1.6 \pm 0.1$ nm; $b = 2.9 \pm 0.1$ nm; $\alpha = 79 \pm 2^\circ$.

Similar to the phenyl capped molecules (**1a** and **2a**), these molecules organize into well-ordered domains extending to more than 200 nm. Molecules also appeared to lie seemingly flat and planar on the HOPG upon adsorption, with their alkyl chains stretched out and extended. Thus, a change of the terminal group from a phenyl to a naphthyl group did not affect the interactions between the molecule-to-molecule or the molecule-to-substrate. The bulkier naphthyl group did not result in any steric hindrance in the molecule to result in a twist in the molecule or to hinder the adsorption. Thus, in this case, the interactions between the alkyl chains and the HOPG surface played a more important role in the packing arrangement.

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Figure 5.9 (a) High resolution constant current STM image of **1b** at the *n*-tetradecane/HOPG interface (15 nm x 15 nm, $I_t = 80$ pA, $V_t = 320$ mV). (b) Proposed CPK model packing of **1b**, white rectangles representing unit cells. (c) High resolution constant current STM image of **2b** at the *n*-tetradecane/HOPG interface (15 nm x 15 nm, $I_t = 75$ pA, $V_t = -130$ mV). (d) Proposed CPK model packing of **2b**, white rectangles representing unit cells.

5.3.4 STM studies of naphthyl-capped **1b** and **2b** molecules on Au(111) surfaces

On the Au(111) surface, both molecules **1b** and **2b** formed dense and packed monolayers with neat lamellar rows in small domains. Domain boundaries were

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marked with small regions of disordered molecules, typical of the rest of the molecules on Au(111) surfaces as shown in **Figure 5.10**.

Figure 5.10 Constant current STM images of molecules on *n*-tetradecane/Au(111) interface exhibiting different domains. (a) Monolayer of **1b** (80 nm x 80 nm, $I_t = 65$ pA, $V_t = -215$ mV). (b) Monolayer of **2b** (80 nm x 80 nm, $I_t = 80$ pA, $V_t = 150$ mV).

On higher resolutions, molecules appeared to form closely packed lamellar rows with chiral domains, as separated by the white line in **Figure 5.11(a)**. These monolayers of **1b** and **2b** on Au(111) appeared to be very tightly packed and adopted a similar packing order, with unit cell dimensions as follows:

molecule 1b	$a = 0.8 \pm 0.1$ nm; $b = 2.7 \pm 0.1$ nm; $\alpha = 110 \pm 2^\circ$ and
molecule 2b	$a = 0.8 \pm 0.1$ nm; $b = 2.7 \pm 0.1$ nm; $\alpha = 85 \pm 2^\circ$.

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Figure 5.11 Constant current STM images of **1b** molecules on *n*-tetradecane/Au(111) interface in higher resolutions. (a) Monolayer of **1b** exhibiting chiral domains, separated by white line. (40 nm x 40 nm, $I_t = 90$ pA, $V_t = 100$ mV). (b) High resolution image **1b**, with no presence of alkyl side chains. (20 nm x 20 nm, $I_t = 90$ pA, $V_t = 200$ mV).

Looking at the higher resolution images, it is interesting to note that the dodecyl side chains were not visible. Monolayers appeared to be just simple unsubstituted conjugated molecules on Au(111). These images were similar to STM images of earlier investigations carried out by Kiel and co-workers, where α -sexithiophene films were sublimated on Au(111) surface in a UHV environment.^[125] In **Figure 5.12(a)** shows one of the submolecular images of the monolayer published, compared with the images obtained for the molecule **1b**. Both images look similar and comparable. Hence it was proposed that the dodecyl chains in these monolayers were not interdigitated and were probably folded below or above the molecules as in this case and thus were not visible in the images. As a result the molecules were packed closer as compared to the **1a** and **2a** molecules. In this case, the molecules were not guided to assembly in the monolayer by the alkyl chains like on HOPG. However, the

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molecules were packed according to the interactions between the conjugated core of the molecule and the substrate. Later as discussed in the next chapter, this was also exhibited in the studies for anthracene-based systems, where the molecules were closely packed, and with no visualization of the alkyl chains.

Figure 5.12 Sub-molecular resolutions of monolayer of (a) α -sexithiophene on Au(111) (10 nm x 10 nm, $I_t = 600$ pA, $V_t = -180$ mV) and (b) **1b** on Au(111) (10 nm x 10 nm, $I_t = 90$ pA, $V_t = 200$ mV).

Besides closely packed lamellar rows, molecules **2b** on Au(111) also exhibited honeycomb-like packing domains similar to those on **Figure 5.8(c)**. These complex structures were surrounded by lamellar domains and appeared to be in smaller concentrations in comparison.

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Figure 5.13 Constant current STM images of **2b** molecules on *n*-tetradecane/Au(111) interface in higher resolutions. (a) Monolayer of **2b** exhibiting different domains, separated by white and blue lines. (40 nm x 40 nm, $I_t = 80$ pA, $V_t = 250$ mV). (b) High resolution image **2b**, with no presence of alkyl side chains. (25 nm x 25 nm, $I_t = 80$ pA, $V_t = 150$ mV).

Unit cell dimensions of all the monolayers investigated on HOPG and Au(111) surfaces are summarized as follows in **Table 5.1**. On HOPG substrates, molecules appeared to pack in a similar order, with interdigitated dodecyl chains from adjacent rows. However, on the Au(111) substrates, naphthyl-capped molecules **1b** and **2b** appeared to assemble without the interdigitation of the dodecyl chains. Due to the “absence” of the alkyl chains, the molecules now pack closer in the lateral dimensions, thus the “*a*” dimensions in the unit cells of the monolayer on the Au(111) substrates appeared to be half of those on HOPG substrates. This is in contrast to the monolayer of **1a** and **2a** on Au(111), where the dodecyl chains were observed to be stretched out, giving a well-interdigitated network. In this case, for the monolayers of **1b** and **2b** on Au(111), π - π interactions between the bulkier naphthyl terminal groups were probably playing a more substantial role in the packing arrangements of the molecules. By

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packing in a tight “close-packed” arrangement, π - π interactions would be maximized as compared to the alkyl chain interdigitated arrangement.

Table 5.1 Unit cell dimensions of all the oligothienothiophenes investigated.

	<i>n</i> -tetradecane/HOPG			<i>n</i> -tetradecane/Au(111)		
	<i>a</i> (± 0.1 nm)	<i>b</i> (± 0.1 nm)	α ($\pm 2^\circ$)	<i>a</i> (± 0.1 nm)	<i>b</i> (± 0.1 nm)	α ($\pm 2^\circ$)
1a	1.4	2.5	79	1.4	2.5	93
2a	1.4	2.9	81	1.3	2.5	92
1b	1.6	3.0	81	0.8	2.7	110
2b	1.6	2.9	79	0.8	2.7	85

*dimensions are taken from average of the 2 chiral domains if chiral domains are present.

5.3.5 STM studies of defective regions

Occasionally, defective regions across the lamellae can be observed. These defective regions consist of missing rows of lamellae, measuring up to few hundreds of nanometers in length and can be found on all the monolayers on HOPG surfaces. When scanned at a higher resolution (refer to Figure 7.14c), it was found that these missing rows were essentially due to the co-adsorption of *n*-tetradecane solvent chains interacting with the dodecyl substituents on the molecule. Inter-lamellar distance across the missing row was determined to be 3 nm, more than twice the usual distance in a typical close packed region, as shown in **Figure 5.14(a)** for the molecule **1a**. CPK models superimposed on STM image in **Figure 5.14(d)** illustrates the co-adsorption of two solvent chains per two oligomers packed next to each other. Hence,

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to eliminate such co-adsorption of solvent chains, future work could involve the use of other solvents such as 1-phenyloctane or 1,2,4-trichlorobenzene.

Figure 5.14 Constant current STM images of 1a in the *n*-tetradecane/HOPG interface. (a) Distance across lamellae was measured to be around 3 nm across defective region, whereas the interlamellae distance of typical regions is less than half the distance (25 nm x 25 nm, $I_t = 75$ pA, $V_t = -100$ mV). (b) Higher resolution image of defective region with proposed CPK model superimposed (14 nm x 14 nm, $I_t = 75$ pA, $V_t = -100$ mV). (c) Sub-molecular resolution STM image across defective region of monolayer of 1a on HOPG substrate (7 nm x 7 nm, $I_t = 75$ pA, $V_t = -100$ mV). (d) Proposed CPK model packing of molecules in the region.

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5.4 Optical and Electrochemical Properties of Oligothienothiophenes

In order to gain more insight into the electronic structures and to determine the band gaps of the molecules, their optical and electrochemical properties were investigated. **Table 5.2** summarizes the results obtained from absorption spectroscopy, calorimetry and cyclic voltammetry of the molecules.

Table 5.2. Photophysics of the oligothienothiophenes.

	Adsorption λ_{max} (nm) ^a	Emission λ_{max} (nm) ^a	HOMO/LUMO (eV)	Band Gap (eV) ^b
1a	389	474	-5.25/-2.54	2.71
1b	409	480	-5.20/-2.61	2.66
2a	401	465	-5.28/-2.55	2.73
2b	407	478	-5.21/-2.54	2.67

^a λ_{max} values measured in THF solution.
^b values calculated from CV and UV-Vis absorption spectra band edge.

Adsorption and emission spectra of the oligothienothiophenes in dilute THF are shown in **Figure 5.15**. All molecules showed strong absorption wavelengths of 350-420 nm and emission wavelengths of 470-480 nm. Due to an increase in conjugation from the change of phenyl to naphthalene units as end-capping groups, the adsorption and emission wavelengths were red-shifted, as shown by the increase in the λ_{max} . HOMO-LUMO band gaps estimated from the end-adsorptions also decreased from the changing of the phenyl groups, verifying the improvement in conjugation. HOMO levels calculated from oxidation potentials obtained from cyclic voltammetry (CV) were lower than those typical of oligothiophenes, indicating the high stability of our

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molecules.^[21] Lower HOMO levels suppresses the vulnerability of the molecules to undergo oxidation, hence enhancing the stability.

Figure 5.15 UV-Vis and photoluminescence spectra of (a) 1a, 1b and (b) 2a, 2b.

In addition, HOMO levels of molecules also matched well with the work function of metallic gold (-5.1 eV); hence, efficient hole charge injection between the gold and semiconductor material is anticipated when fabricated as OTFT.^[126]

5.5 Thermal Properties of Oligothienothiophenes

The thermal properties of the molecules were determined by thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC). Results are summarized in Table 5.3.

Table 5.3. Thermal Properties of the oligothienothiophenes.

	T_m ($^{\circ}\text{C}$) ^a	T_d ($^{\circ}\text{C}$) ^b
1a	124	360
1b	114	395
2a	117	397
2b	118	400

^a T_m (melting temperature) values obtained from DSC measurements.

^b T_d (decomposition temperature) values from TGA measurements.

All oligothienothiophenes exhibited excellent thermal stabilities with decomposition temperatures near 400 $^{\circ}\text{C}$ for molecules **1b**, **2a** and **2b**, and 360 $^{\circ}\text{C}$ for molecule **1a**.

Figure 5.16 and 5.17 shows the DSC traces obtained for the molecules.

Figure 5.16 DSC scans for (a) **1a** and (b) **2a** at a rate of $10^{\circ}\text{Cmin}^{-1}$. Heating and cooling directions are indicated by the arrows.

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At the same cooling rate of $10\text{ }^{\circ}\text{Cmin}^{-1}$, it is interesting to note that only **2a** do not undergo any crystallization, while **1a** crystallizes at 75°C . As seen from its DSC trace in **Figure 5.16(b)**, molecule **2a** remained amorphous on cooling, and upon the 2nd heating cycle, two exothermic peaks appeared, assigned to the cold crystallizations. These differences probably arose from the influence of the side chain positions on the packing of the molecules in bulk, since **2a** experienced a slightly larger steric influence from the side chains. In addition, the melting temperature of **1a** (124°C) also appeared to be higher than that of **2a** (117°C), suggesting that there was a stronger interaction between the **1a** molecules due to better packing in the bulk.

Figure 5.17 DSC scans for (a) **1b** and (b) **2b** at a rate of $10\text{ }^{\circ}\text{Cmin}^{-1}$. Heating and cooling directions are indicated by the arrows.

Both the naphthyl terminated molecules **1b** and **2b**, exhibited a similar thermal history like those of **1a**. A change in the terminal group of molecule **1a** from a phenyl to a naphthyl group for **1b** decreased its melting temperature by $10\text{ }^{\circ}\text{C}$. This could be due to the increase in steric hindrance of the bulkier naphthyl group, hence giving a poorer packing of the molecules and, therefore, a lower melting temperature. However, this phenomenon did not hold for molecules **2a** and **2b**. Both molecules melted at similar

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temperatures (only 1 °C apart). The change to a bulkier terminal group did not affect the crystal packing of these molecules. Hence, in this case, the steric hindrance of the alkyl side chain for these molecules (**2a** and **2b**) had already played a strong part in the packing of the molecules, such that changing the terminal groups did not affect the packing further.

5.6 Optical Microscopy of Oligothienothiophenes 1a and 2a

To obtain further information on the supramolecular organization of the molecules, the phases were investigated using polarized optical microscopy (POM) with the help of Dr Pisula from the Max Planck Institute for Polymer Research. Molecules **1a** and **2a** showed well-ordered spherulites nucleated randomly over the whole sample during cooling from isotropic state, as shown in **Figure 5.18**. As observed from the POM images, molecules appeared to be in a semi-crystalline state when cooling at the rate of 25°C/min, on further heating over a second phase transition at 90°C, the spherulite sizes becomes smaller.

Figure 5.18 POM images of **2a** between cross-polarizers at 25°C crystallized (a) at a cooling rate of 25°C/min, (b) with an α -plate and (c) at 90°C.

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The spherulites revealed high anisotropy and long-range order was present. This was expressed by the Maltese cross, where isogyres followed the extinction of the analyzer/polarizer direction, indicating a radial alignment of the assemblies from the center. Using an α -plate and analyzing the red-blue distributions in the optical spherulite image, it was possible to determine that the spherulites were optically negative (**Figure 5.18(b)**). The refractive index parallel to the radial direction was smaller than that perpendicular to it. An identical optical behaviour of such optically negative spherulitic domains was also observed for small molecules organized in columnar systems.^[127-130] The analysis of the optical textures of **1a** and **2a** suggested that the oligothienothiophenes assemble in lamellar superstructures which in turn might be oriented macroscopically in the spherulite growth direction with an edge-on arrangement of the molecules. Domains of both molecules appeared to exceed several hundreds of micrometers, where the spherulite size and morphology is dependent on the cooling rate. Upon closer inspection of the spherulites of **2a**, a macroscopic periodicity along the radius was realized (**Figure 5.18**). The periodic contrast, due to birefringent effects, appeared as single fibrous structures, suggesting that there are helical twists of crystallites within the fibers. Extinction occurs in such banded spherulites when the optical axis of crystallites coincides with the polarization plane.^[131] In the case of **2a**, the macroscopic pitch was determined to be around 25 μm . However, after heating the film of **2a** over the second phase transition (observed in the DSC scan), the morphology changed to a more crystalline texture and the helical features disappeared, as shown in **Figure 5.18(c)**.

5.7 Supramolecular Organization of the Oligothienothiophenes by 2D-WAXS

The supramolecular orders of the molecules were investigated by using two-dimensional wide-angle x-ray scattering (2D-WAXS). The samples were prepared by filament extrusion^[132] below their melting point of 100 °C. **Figure 5.19** shows characteristic patterns for molecules **1a** and **2a** recorded at 30 °C, wherein no change of the solid state superstructure was observed with variations of temperature. The 2D patterns indicated highly ordered structures, where the distribution of the scattering intensities implies a perpendicular orientation of the molecules with their molecular planes to the fiber axis.

Figure 5.19 (a) 2D-WAXS pattern of **1a** at 30°C, (b) of **2a** at 30°C. (white dashed circle marks reflections related to the π -stacking and the red circle corresponds to the intra-lamella spacing)

The proposed supramolecular organization of molecules **2a** in the extruded filament is illustrated in **Figure 5.20**. The first wide angle meridional reflections related to a spacing of 0.48 nm are attributed to perpendicularly aligned molecules which are

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packed on top of each other due to π -stacking interaction forming a lamellar superstructure. The π -stacking distance of 0.34 nm is presented by additional off-meridional reflections which appear at an angle of 45° towards the meridional pattern plane. This angle is in agreement with the molecular tilting of **2a** towards the lamella axis (c axis) and to the herringbone single crystal structure of thieno[3,2-*b*]thiophene based molecules reported previously.^[133]

Figure 5.20 Schematic illustration of the supramolecular organization of **2a**. In the side view drawing, the red line corresponds to the intra-lamella spacing of 0.48 nm oriented along the alignment direction, whereas the blue line represents the π -stacking distance of 45° tilted oligomers. Parameters *a* and *b* are randomly distributed around *c* which coincides with the fiber axis.

Similar intra-lamella organization has also been determined for **1a**. The other axes of the unit cell, *a* and *b*, are randomly oriented around the fiber direction leading to reflections in the equatorial plane of the 2D pattern. For both cases, the orthorhombic unit cell was derived from the positions of the reflections. These packing parameters cannot be compared directly to the organization of thienothiophene-based polymers possessing the same dodecyl substituents. In this case, the *a* parameter was in

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agreement with the molecular length of the molecules, while b corresponded to the distance between the lamella. **Table 5.4** summarizes the lattice parameters determined from the 2D-WAX measurements.

Table 5.4 Parameters a and b for 2D-WAXS.

	a (nm)	b (nm)
1a	2.12	0.85
2a	2.23	0.92
1b	3.72	1.81
2b	4.20	1.74

These lamella structures were formed due to π -stacking interactions of the aromatic rods and the local phase separation between flexible alkyl side chains and the rigid rods. The higher the steric hindrance of the alkyl substituents, the more pronounced is the phase separation and hence a better macroscopic alignment in the extruded filament could be achieved. Apparently, in the case of **2a**, the side chains possess slightly larger steric hindrance due to their substitution position, hence softening the material and resulting in a better alignment during mechanical shearing in comparison to **1a**.

Figure 5.21 (a) 2D-WAXS pattern of **1b** at 30°C, (b) of **2b** at 30°C.

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Lattice parameters obtained through the 2D-WAXS data were different from the lattice parameters determined from the STM investigations. This is due to the effect of the mechanical shearing from the extrusion of the filament during the sample preparation. In addition, filament was also prepared in its pure melt phase, with no influence of solvent effect. However, the 2D-WAXS data complements the STM investigation as the former provides information of the π -stacking distance between the molecules, which the monolayer imaging STM is not capable in.

5.8 Electrical Characteristics of the Oligothienothiophenes

Preliminary transistor measurements were carried out on thin film transistors fabricated from the molecules - **1a** and **2a**. Typical FET electrical characteristics of the bottom-contact TFT and a top-contact TFT made from the spin-coated film from toluene in air is shown in **Figure 5.22**. All TFT devices were fabricated using heavily doped Si substrate with thermally grown SiO_2 as the dielectric gate.

Figure 5.22 Transfer characteristics of **1a** for (a) bottom-contact device and (b) top-contact device.

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Films of molecule **1a** were annealed in a vacuum oven at 70°C for an hour, followed by 100°C for 20 mins, and cooled under vacuum overnight to ensure that molecular ordering could take place. The bottom-contact device showed a charge carrier mobility of $5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an on/off ratio of 2×10^3 . Comparatively, the top-contact device performed better, with a higher mobility of $3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a higher on/off ratio of 4.5×10^4 . The better performance of the top-contact OTFT devices is typically attributed to small charge injection areas and poor ordering of the organic semiconductor on the electrodes in the bottom-contact geometry.^[134] Molecule **2a** on the other hand, failed to produce any positive transistor results. Device results of molecules **1b** and **2b** were still not available at the point when this report was written.

5.9 Conclusion

In summary, we have presented the characteristics of a series of newly synthesized oligothienothiophenes for organic semiconductor devices. These molecules differ in their substitution position of the alkyl chains and their end-capping terminal group. The presence of the long dodecyl chains helped improve the solubility of these molecules as well as their molecular ordering through van der Waals interaction, thus influencing their semiconducting properties positively. STM imaging of the molecules on HOPG and Au(111) substrates showed neat lamellar rows of well-organized films, with alkyl interdigitation of the dodecyl side chains in most of the cases. Thermal analyses also indicated excellent thermal and oxidation stability of the

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molecules. Furthermore, OTFT devices based on **1a** also exhibited excellent field-effect performances with high mobilities. However, devices fabricated based on **2a** failed to provide any positive transistor results. This could be due to the packing arrangement of the molecules in the thin film. Although on the HOPG substrate, both **1a** and **2a** molecules appeared to assemble with similar molecular packing, it is crucial to note that due to the commensurability effect of the alkyl chains and the HOPG surface^[101], both molecules were able to adopt neat lamellar structures with alkyl side chains stretched out interdigitating with adjacent rows. However, for the thin film devices, the molecules were deposited via spin coating on SiO₂ surfaces, which were not alkylated. Thus, it is believed that the **2a** molecules might not be able to pack as well as the **1a** molecules, since the dodecyl chains were positioned closer in the structure resulting in a certain degree of torsion in the molecule.

This investigation serves as a preliminary study towards creating new stable semiconducting oligomers for improved device performance applications. Further work on the material synthesis, device optimization and characterization are still on the way to further develop the materials.

6 Anthracene-Based Systems

In this chapter, a brief review on acene systems is carried out in the introduction. Consequently, experimental data from a set of four anthracene-based molecules will be presented and discussed in great detail.

6.1 Introduction

Besides the typically studied polythiophenes and oligothiophenes, acene molecules such as anthracene, tetracene, and pentacene have also been shown to give promising results when used as organic semiconductor materials.^[135-137] Vacuum deposited films of acene molecules such as pentacene with mobilities of up to $3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and on/off ratios higher than 10^6 for have been reported.^[138, 139] However, pentacene exhibits poor stability and solubility. To resolve some of these issues, the functionalization of the pentacene molecule at the 6,13 positions has recently been carried out, resulting in hole mobilities as high as $0.17 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for solution processed thin films.^[140-142] Other acene-based molecules such as the large aromatic molecules coronenes, triphenylenes and rubrene which consist of several fused benzene rings have also attracted much interest from researchers in the field of molecular electronics. These materials adopt planar conformations with extensive π electron overlap systems and possess high degrees of molecular ordering. **Figure 6.1** shows some acene molecules commonly studied for electronic device applications. Another route towards the

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enhancement of acene stability is the use of smaller systems such as anthracene, that has in fact shown field-effect hole mobility of $0.02 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.^[143]

Figure 6.1 Chemical structures of typical acene molecules studied for electronic device applications.

Through time of flight techniques, hole mobilities in anthracene single crystals have been found to reach up to $3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at 300 K.^[144] In recent years, a number of research groups have been looking into anthracene derivatives for use in OTFT devices.^[136, 145, 146] To expand the π electron conjugation and to improve solubilities, oligomerization of anthracene molecules and substitution with functional groups was carried out. Most oligomers reported were extended through the 2,6 anthracene position, although the 9,10 position is the most synthetically accessible. This is because oligomerization at the 2,6 positions was predicted and found to give the best π -conjugation and highest planarity. This will lead to the molecules performing as excellent p-type organic semiconductors with high field-effect mobilities.^[136, 145, 146]

Figure 6.2 illustrates an anthracene oligomer, substituted at the 2,6 position, resulting in a three anthracene unit oligomer. Alkyl chains introduced at the 9,10 positions of

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the anthracene units produce oligo-2,6(9,10-bisalkynylanthrylene)s which exhibited hole mobilities of $\sim 3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[145]

Figure 6.2 Chemical structure of anthracene oligomer with a 2,6 substitution.

6.2 9,10-*ter*-anthrylene ethynylenes

Though the 9,10 positions were easily accessible for synthesis as mentioned earlier, oligomerization about the 9,10 positions resulted in dihedral angles up to 82° between neighboring units due to the strong steric hindrance resulting in a disruption in π -conjugation in the molecule, thus limiting its applications.^[147, 148] **Figure 6.3** shows a typical anthracene oligomer, substituted at the 9,10 position.

Figure 6.3 Chemical structure of anthracene oligomer with a 9,10 substitution.

However, oligomerization of the anthracenes through the 9,10 positions would be an effective alternative due to a possibility of higher charge delocalization across the oligomer laterally. Furthermore, the linking positions at 9,10 are the most reactive, hence synthesis of such oligomers could be carried out with much ease.

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The synthesis and OTFT performances of 9,10 substituted anthracene oligomers linked by ethynylene bonds has also been recently reported.^[88] These ethynylene bonds induce low rotational energy barriers, and are much more rigid than typical C-C bonds. Furthermore, ethynylene units were also known to be electron withdrawing, which would increase the ionization potential of the material and hence reduce the sensitivity of the material to air.^[149-151] **Figure 6.4** shows the molecular structure of the 9,10-*ter*-anthrylene ethynylene studied. In addition to the ethynylene bonds, alkyl chains were also added to the 10 positions of the terminal anthracenes, rendering the molecule soluble and reducing the reactivity of the core anthracene units.

Figure 6.4 Chemical structure of 9,10-*ter*-anthrylene ethynylene molecules.

The adsorption of alkylated molecules is typically mediated by intermolecular interactions between the molecule and the substrate through van der Waals interactions.^[152] The presence of alkyl chains and their lengths, as well as the presence of specific functional groups, often result in differences in the 2D molecular packing of the molecules as revealed by STM.^[76, 98, 103] Alkyl chain interdigitation is also essential in the ordering of 2D networks, as reported by many research groups.^[76, 77, 95, 98] Here, the relationship between the structural design of a series of 9,10-*ter*-anthrylene-ethynylene molecules and its self assembly are investigated by STM.

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Figure 6.5 Chemical structures of the four 9,10-ter-anthrylene ethynylene molecules with different side groups investigated in this work.

Alkyl chains of *n*-butyl, *n*-octyl, *n*-decyl and a branched chain 2-ethylhexyl were substituted to the main anthrylene ethynylene π -conjugated core and were investigated through a series of studies to determine the effect of the chemical structure on its properties. **Figure 6.5** shows the series of molecules investigated. The molecules were **B3A** (with *n*-butyl chains), **O3A** (with *n*-octyl chains), **E3A** (with branched 2-ethylhexyl chains) and **D3A** (with *n*-decyl). Synthetic routes of these molecules were mentioned earlier in the experimental section in **Section 3.5**.

6.3 Self Assembly studies of 9,10-ter-anthrylene ethynylenes molecules

All molecules were investigated by using STM to determine their two dimensional packing on two different substrates, the HOPG and Au(111) surfaces. This allows a comparison of the effects of molecule to-substrate interactions between the molecules and the surface on self-assembly. We will see that this difference in interaction can influence self-assembly and also the properties of the thin films eventually.

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6.3.1 STM studies of B3A, O3A, and D3A molecules on HOPG surfaces

Upon adsorption, **B3A**, **O3A** and **D3A** form highly ordered monolayers with large domains extending over tens to hundreds of nanometers covering the entire HOPG surface. Each domain consists of closed packed linear and parallel rows of molecules, except for **B3A** molecules. **Figure 6.6** shows high resolution STM images of the monolayers observed for the 3 molecules. Bright objects on the image corresponded to the three anthracene units in the molecule, where the brightness was due to the higher tunneling current from the more electron rich anthracene units compared to other parts of the image. Alkyl chains of adjacent rows of molecules were observed to interdigitate due to van der Waals interaction between the alkyl chains on **O3A** and **D3A** molecules. In addition, all three anthracene units of the molecule appeared to have similar brightness intensity on the images. Hence, it was assumed that the three units were lying flat and parallel to the HOPG surface, assuming a planar adsorption of the entire molecule. No twist angle or minimal dihedral angle was present between the anthracene units, and full conjugation between the anthracene units was possible.

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Figure 6.6 (a) Constant current STM image of B3A at the *n*-tetradecane/HOPG interface (15 nm x 15 nm, $I_t = 94$ pA, $V_t = 255$ mV). (b) Proposed molecular packing of B3A monolayer. (c) Constant current STM image of O3A at the *n*-tetradecane/HOPG interface (15 nm x 15 nm, $I_t = 86$ pA, $V_t = 400$ mV). (d) Proposed molecular packing of O3A monolayer. (e) Constant current STM

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image of **D3A** at the *n*-tetradecane/HOPG interface (15 nm x 15 nm, $I_t = 27$ pA, $V_t = 333$ mV). (f) Proposed molecular packing of **D3A** monolayer. Line boxes indicate unit cells.

In contrast to the lamellar packing of the longer chain molecules, **B3A** molecules seemed to assemble in a quasi-hexagonal packing order. The butyl chain of **B3A** appeared to be too short to allow efficient van der Waals interactions between neighboring molecules, and therefore did not form interdigitated lamellar rows on HOPG.

A similar observation has been reported by Azumi et al. where propyl substituted quaterthiophene did not assemble in neat lamellar rows in contrast to quaterthiophene substituted with hexyl or dodecyl chains.^[103] Fast fourier transform (FFT) carried out on the STM images of **B3A** and **D3A** molecules on HOPG substrates further revealed the packing orders of the two molecules. The FFT images in **Figure 6.7** confirm that **B3A** monolayer adopts a quasi-hexagonal packing as compared to the lamellar packing of the **D3A** monolayer.

In **Figure 6.6(a)**, end-capping alkyl chains were not resolved in the sub-molecular resolution image of **B3A** molecules self assembled at the *n*-tetradecane/HOPG interface. This could be attributed to the high mobility or the non-commensurability of the short alkyl chains to the graphite surface. The high mobility or the non-commensurability of the alky chain might have resulted in the molecules adopting a quasi-hexagonal organization.

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The STM studies revealed that the orientation and packing of the self assembled monolayers are similar for the longer chain substituted molecules, as shown in Figure 6.6(c) and 6.6(d). The only difference between the two dimensional assembly for the molecules was the distance between the adjacent lamellar rows, due to the presence of the alkyl chains. CPK packing models derived from the STM images of the molecular arrangement of the molecules are shown in Figure 6.6.

Figure 6.7 FFT carried out on (a) O3A monolayer on HOPG surface (inset: STM image of monolayer (50 nm x 50 nm, $I_t = 81$ pA, $V_t = -255$ mV)) and (b) D3A monolayer on HOPG surface (inset: STM image of monolayer (50 nm x 50 nm, $I_t = 25$ pA, $V_t = 350$ mV)).

6.3.2 STM studies of E3A molecules on HOPG surfaces

Branched alkyl chain terminated **E3A** was predicted to assemble with less order than the rest of the molecules due to difficulty for the neighbouring alkyl chains to interact through van der Waals forces. Larger steric hindrance for the branched chain groups induces lower flexibility of the system and hence a differential packing should be observed, as reported by Samori et al.^[78] However, STM images showed neat lamellar rows across large domains, although the monolayer took a few hours to form as compared to the straight chain terminated molecules on adsorption. **O3A** and **D3A** molecules formed a self-assembled, adsorbed monolayer spontaneously upon deposition of the solution droplet and imaging was done almost immediately after that. **Figure 6.8(a)** shows a high resolution STM image of the **E3A** monolayer absorbed on HOPG surface.

Figure 6.8 (a) Constant current STM image of **E3A** at the *n*-tetradecane/HOPG interface (15 nm x 15 nm, $I_t = 80$ pA, $V_t = 520$ mV). (b) Proposed molecular packing of monolayer. Line boxes indicate unit cells.

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As this molecule consists of branched alkyl chains as the substituting groups, the alkyl chains fail to lie flat on the HOPG surface because of their steric hindrance. Furthermore, the chains may be tilted out of the plane of the molecule, or their diffusivity is high with respect to the timescale of the STM scan, hence resulting in the unsuccessful visualization of the alkyl chains. Though the organization of the alkyl chains cannot be resolved in the high resolution studies, these molecules were still arranged in neat lamellar rows over a long range, similar to those of **O3A** (**Figure 6.6(c)**) and **D3A** (**Figure 6.6(e)**).

Although the branched chains appeared to be a hindrance to the assembly of the **E3A** molecules, they still play a role in the 2D packing, since lamellar rows are observed, as compared to quasi-hexagonal packing of **B3A**. In the case of **B3A**, due to the short chain length, there is insufficient interaction between the alkyl chains to provide a well-interdigitated row to give lamellar packing, thus only a quasi-hexagonal packing is observed. However for **E3A**, though bulky, the 2-ethylhexyl chains have certain degrees of interaction between adjacent rows of molecules, thus forming lamellar packing. However, it is still uncertain how the branched chains would orientate in order to maximize the van der Waals interaction between adjacent rows. A plausible CPK model for the self assembly of **E3A** molecule is shown in **Figure 6.8(b)**. The alkyl chains have been included in the CPK model though it is impossible to visualize them in the STM images.

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Table 6.1 Comparison of the unit-cell parameters of the two-dimensional adsorbates on both HOPG and Au(111) interfaces.

	<i>n</i> -tetradecane/HOPG				<i>n</i> -tetradecane/Au(111)			
	packing	<i>a</i> (±0.1nm)	<i>b</i> (±0.1nm)	<i>α</i> (±2°)	packing	<i>a</i> (±0.1nm)	<i>b</i> (±0.1nm)	<i>α</i> (±2°)
B3A	quasi-hcp	1.8	2.4	70	lamellar	1.2	2.5	80
O3A	lamellar	1.4	2.7	91	lamellar	1.2	2.5	84
D3A	lamellar	1.5	3.1	92	lamellar	1.2	2.5	81
E3A	lamellar	1.2	3.0	102	lamellar	1.2	2.6	80

Comparing the self assembled monolayer of the molecule, **B3A** (bearing *n*-butyl terminal alkyl chains), illustrated by the CPK model proposed in **Figure 6.6(b)**, the two dimensional organization of the molecules, **O3A** and **D3A**, appeared to pack closer in the vertical direction, as may be deduced by the shorter *a* distance (**Table 6.1**) in the unit cell parameters. A plausible explanation could be that the molecules are forced to pack closer from the alkyl chain interdigitation of molecules **O3A** and **D3A**. These molecules are guided to assemble on the substrate primarily by the commensurability of their long alkyl chains and the graphite surface. Due to the short butyl chain length of molecule **B3A**, the molecules prefer to assemble in a typical closed pack order, which has the lowest surface energy. However, for longer chain molecules **O3A**, **D3A** and **E3A**, alkyl chain interdigitaion due to van der Waals interactions was predominant and hence lamellar rows of molecules were observed. Thus, the molecular packing between these molecules appeared to be different and the butyl chains in molecule **B3A** could not be resolved in the STM images.

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With the help of Dr. Kapitanchuk from the Bogolyubov Institute For Theoretical Physics in Ukraine, geometrical optimization of the free standing anthrylene ethynylene molecules using DFT calculations were carried out. The calculations revealed that the molecules were most stable when the anthracene units were repelled 45° from each other. This is shown in the **Figure 6.9**. As the relative energy differences between the molecular models with different torsional angles were found to be fairly small (3kcal/mol), it is anticipated that these molecules may adopt a co-planar structure because of the strong interaction between the anthrylene ethynylene molecules and the substrate. This was verified by the STM images, where the brightness intensity was similar for all the anthracene units. Thus the 3 anthracene sub-units were probably lying flat on the HOPG surface, and not twisted as simulated, therefore, full conjugation could exist between the anthracene units when adsorbed on HOPG surface.

Figure 6.9 Difference of total energy of three anthracene backbone as function of the torsional of side anthracenes calculated by DFT.

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6.3.3 STM studies of B3A, O3A, E3A and D3A molecules on Au(111) surfaces

Contrary to what was observed on HOPG surfaces, all the molecules appeared to show the same packing monolayer on the reconstructed Au(111) surface, as shown in **Figure 6.10**. All the four molecules are assembled in parallel lamellar rows.

Figure 6.10 High resolution STM images at the *n*-tetradecane/Au(111) interface of (a) molecule B3A (15 nm x 15 nm, $I_t = 75$ pA, $V_t = 260$ mV), (b) O3A (15 nm x 15 nm, $I_t = 91$ pA, $V_t = 64$ mV), (c) E3A (15 nm x 15 nm, $I_t = 80$ pA, $V_t = 100$ mV) and (d) D3A (15 nm x 15 nm, $I_t = 90$ pA, $V_t = 200$ mV).

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The unit cell parameters, determined through the analysis of the STM images, were very similar (**Table 6.1**). Furthermore, for all the molecules, no terminal alkyl chains could be seen even by high resolution STM scan. Only the three electron rich anthracene units were visible, and they appeared to look like “bow-tie” structures. The molecules **O3A**, **D3A** and **E3A** appeared to be packed closer to each other in the lateral direction as compared to the assembly of these molecules on HOPG surfaces. In the latter case, the distances were essentially determined by the terminal alkyl chain lengths.

It is interesting to note that molecule **B3A** arranged differently on the two different substrates, although it was mentioned earlier that the butyl chains were too short to interdigitate into lamellar rows. On Au(111), **B3A** arranged in lamellar rows instead of the quasi-hexagonal organization observed on HOPG. Packing of the molecules appeared to be independent of the terminal alkyl chains. Hence, through the packings on HOPG, it can be deduced that although the butyl chains failed to interdigitate, they still played a part in the packing. To accommodate the short butyl chains, the molecules (**B3A**) were arranged slightly apart, thus keeping a quasi-hexagonal packing instead of packing in a lamellar row-like arrangement as on Au(111).

6.4 Conclusion from STM studies

The effects of alkyl chain length on the self assembly of the four 9,10-ter-anthrylene-ethynylenes at the *n*-tetradecane/substrate interface on both HOPG and Au(111) substrates has been systematically investigated using STM. Similar to other conjugated systems like that of the polythiophenes and oligothiophenes, lengths of substituted alkyl chains play a major role on the molecular packing of the molecules.^[76, 77, 103] This was demonstrated by the difference in the packing of **B3A** molecule, which possesses a shorter alkyl chain terminus group, compared to the rest of the molecules. Due to the commensurability of the HOPG surface and the alkyl chains, the molecules preferred a “flat-lying” configuration on the surface, with the long alkyl chains from adjacent molecules interacting through van der Waals forces, as observed for **O3A**, **D3A**, **E3A** molecules.

However, from the dimensions of the unit cells on the Au(111) surface, it can be concluded that all 4 molecules self-assemble with the same packing order. It appears that alkyl chains on the terminus end of the anthracene oligomers did not have any effect on the packing order of these oligomers. Despite having different chain lengths and branching, the molecules assemble in the same manner. From this observation, it can be deduced that the assembly is driven by the π electron rich anthracene units core rather than the alkyl terminal chains. Furthermore, the molecules appear to remain in their “twisted” configuration; hence are packed closer to each other in the lateral dimensions. It is also proposed that the alkyl chains are either folded below or above the anthracene units, thus not visible in the STM images.^[88]

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Future works arising from this study include the possibility of investigating ter-anthrylene ethynylenes possessing other functional groups. Functional groups such as the carboxylate or amino group on the alkyl chains could be synthesized and investigated under the STM to further study the influence of molecular architecture on the self-assembly properties and device performances of the molecules.

6.5 Optical and electrochemical properties of all the 9,10-*ter*-anthrylene ethynylenes

The band gaps of these anthracene molecules are important for its applications as the active material in organic thin film transistors devices and hence the photophysics of the molecules was investigated using UV-Vis and photoluminescence (PL) spectroscopy in dilute CHCl_3 or 1,2-dichlorobenzene (ODCB) solutions. Results are tabulated in **Table 6.2**.

Table 6.2 Photophysics for the 9,10-*ter*-anthrylene ethynylenes.

	Absorption (nm)			Emission (nm)		Band Gap (eV) ^c
	Solution ^a	Film ^b		Solution ^a	Film ^b	
B3A	505	549	597	569	711	2.19
O3A	505	535	600	570	699	2.19
D3A	504	535	603	568	677	2.19
E3A	505	548	593	569	706	2.19

(above data is referenced from Dell'Aquila's thesis^[89])

^aMaximum adsorption and emission wavelength in dilute CHCl_3 solutions.

^bFilms obtained by drop casting from saturated chloroform solutions.

^cEstimated from the onset of the UV-Vis adsorption spectra.

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A structureless adsorption band with a maximum of about 505 nm was observed for all the molecules. This can be attributed to the π - π^* transition of the conjugated backbone, as showed in the UV-vis and photoluminescence spectra of D3A of **Figure 6.11**. The HOMO/LUMO gap calculated from the onset of the adsorption spectra was 2.19 eV for all the molecules, which was almost similar to the band gap value of pentacene molecules in toluene solution, at 2.12 eV.^[153] In addition, our band gap values calculated were also better than those from the anthracene derivative films from Cui and co- workers which were extended through the 2,6 anthracene position (2.46 eV).^[145]

Figure 6.11 (a) Adsorption spectra of D3A in CHCl_3 and in solid state (drop casted). (b) Emission spectra of D3A in CHCl_3 and in solid state (drop casted) (above data is referenced from Dell'Aquila's thesis^[89])

The electrochemical behaviour of **D3A** was also studied in CH_2Cl_2 using Ag/Ag^+ as reference electrode (calibrated with respect to the Fc/Fc^+ couple). Cyclic voltammogram shows two quasi-reversible oxidation peaks at 1.05 V and 1.20 V and an irreversible oxidation peak at 1.49 V. Two irreversible reduction peaks at -1.26 V and -1.53 V were also observed. HOMO and LUMO energy levels, estimated from

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the onset of the first oxidation and reduction, are -5.23 eV and -3.15 eV respectively, giving an optical energy gap of 2.1 eV, which is in agreement with the optical gap found from the adsorption spectra in CHCl_3 (2.19 eV).

6.6 Thermal properties of all the 9,10-*ter*-anthrylene ethynylenes

The thermal properties of the molecules were determined by thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC). Results are summarized in Table 6.3.

Table 6.3 Thermal properties for the 9,10-*ter*-anthrylene ethynylenes.

	T_d ($^{\circ}\text{C}$) ^a	Other transition temperatures ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$) ^b
B3A	342.3	No thermal event before decomposition.	
O3A	360.0		260.7
D3A	375.9		247.1
E3A	364.1	212.8, 219.5, 228.3	233.5

(above data is referenced from Dell'Aquila's thesis^[89])

^aDecomposition temperature at 5% weight loss, as determined through TGA.

^bMelting point as determined through DSC.

Good thermal stability with high decomposition temperatures (at 5% weight loss) between 342.3 to 375.9 $^{\circ}\text{C}$ were revealed through TGA studies. As the terminal alkyl chains of the molecules increased in length (from **B3A** to **D3A**), the decomposition temperature increased simultaneously. This was due to a better packing of the molecules in bulk from the van der Waals interaction between the alkyl chains. As the alkyl chain became longer, the interaction between molecules becomes stronger,

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hence the high decomposition temperatures. For the molecules **O3A** and **D3A**, DSC scans revealed only single endothermic peaks attributed to the melting processes. The various thermal properties are tabulated in **Table 6.3**. However for the branched chain molecule **E3A**, four endothermic peaks were observed before decomposition at 233.5 °C. This is likely due to the branched chains of the molecule inducing liquid crystalline-like phases before melting. Short-chained molecules **B3A**, on the other hand, experienced no thermal events prior to decomposition. This implies that the packing of these short alkyl chain molecules was highly disordered and that it was not crystalline. This is not surprising as the butyl chains were probably too short to allow sufficient packing in the bulk. Furthermore, STM images of **B3A** on HOPG also showed little interaction of the butyl chains between molecules compared to the longer chain molecules (**O3A**, **D3A** and **E3A**). This shows that the **B3A** molecules are not as well-packed as the rest of the molecules, hence giving a non-crystalline structure and thus no thermal events prior to decomposition.

6.7 Electronic structure calculations of all 4 molecules

With the help of Dr. Kapitanchuk, the electronic structure calculations of the molecules at the DFT/B3LYP/6-31G* level shown that all molecules had similar energies of frontier orbitals (about -4.7 eV for HOMO and -2.4 eV for LUMO), as illustrated in **Figure 6.12**.

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Figure 6.12 Frontier wave functions obtained for molecules in neutral ground state geometry. (a) HOMO and (b) LUMO.

Regardless of the alkyl substituents chain lengths, the shapes of the corresponding molecular wave functions are mainly defined by the three anthracene sub-units, but not dependent on the torsion between the units. HOMO and LUMO energy calculations for all the molecules are tabulated in **Table 6.4**. The calculated HOMO/LUMO gaps are also in reasonably close agreement with those determined via cyclic voltammetry (2.1 eV) and UV-vis spectra (2.19 eV).

Table 6.4 Calculated molecular energy levels (eV) are presented in the following:

Wave function	B3A	O3A	D3A	E3A
LUMO+3	− 0.321	− 0.311	− 0.311	− 0.329
LUMO+2	− 1.576	− 1.568	− 1.565	− 1.570
LUMO+1	− 1.837	− 1.825	− 1.821	− 1.833
LUMO	− 2.359	− 2.347	− 2.342	− 2.367
HOMO	− 4.697	− 4.686	− 4.686	− 4.697
HOMO−1	− 5.214	− 5.199	− 5.198	− 5.212
HOMO−2	− 5.579	− 5.563	− 5.563	− 5.580
HOMO−3	− 6.593	− 6.581	− 6.579	− 6.590
H/L gap	2.338	2.339	2.344	2.330

6.8 Electronic properties of all 4 molecules in OTFT devices

Preliminary transistor measurements were carried out on thin film transistors fabricated from the molecules **B3A**, **O3A**, **D3A** and **E3A**. Due to the short butyl chains on **B3A**, it is difficult to solubilise the molecules in chloroform for spin coating. Hence only drop casting was used to prepare **B3A** films for OTFT devices. Molecules **O3A**, **D3A** and **E3A** showed average mobilities in the range of 10^{-2} and 10^{-4} $\text{cm}^2/\text{V s}$ with good on/off ratios. OTFT devices fabricated with 10 nm **D3A** thin films on Si substrate by spin coating showed the best mobility results so far. An average mobility of $1.2 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and on/off ratios higher than 10^4 was reported, with the highest mobility obtained at $0.055 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.^[88]

Figure 6.13 FET characteristics (top contact device), deposition by spin coating **D3A** films. (a) output characteristics and (b) transfer characteristics at $V_{ds} = -30$ V.

Figure 6.13 shows the current-voltage characteristics for top contact devices with **D3A** film spin coated and annealed. The excellent performance of **D3A** thin films for OTFT devices can probably be attributed to its sufficiently long decyl side chains.

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These chains allowed interdigitation between adjacent rows, promoting packing of the molecules. Since the performance of such devices lies very much in the packing of molecules in the thin film^[11, 24, 36, 154, 155], it is believed that the **D3A** molecules are the most well-packed to enhance conjugation. Devices fabricated based on these **D3A** molecules often yield the best transistor device data as reported in the thesis of Dell'Aquila.^[89] This is probably due to the length of the terminal alkyl chain being the longest, allowing the most van der Waals interactions intermolecularly, and giving rise to better packing of the molecules in the film. With better packing, electron transport is optimized and therefore giving better results.

6.9 Conclusions

A series of four alkyl functionalized 9,10-*ter*-anthrylene ethynylene molecules has been presented in this chapter. The effects of terminal alkyl chain length (*n*-butyl, **B3A** *n*-octyl, **O3A** *n*-decyl, **D3A** 2-ethyl-hexyl, **E3A**) on the self-assembly of four 9,10-*ter*-anthrylene-ethynylenes has been investigated using the STM technique at the *n*-tetradecane/HOPG or at the *n*-tetradecane/Au(111) interfaces. The monolayers based on the molecule bearing the butyl alkyl chains (**B3A**) are strongly influenced by the substrate showing a quasi-hexagonal packing arrangement on HOPG and a lamellar packing on Au(111). Similar to other conjugated systems, both lengths of the substituted alkyl chains and the interactions between the molecules and the substrate have a strong influence on the molecular packing of the molecules. Due to the commensurability of the HOPG surface and the alkyl chains, the molecules preferred a

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“flat-lying” configuration of the surface, with their alkyl chains interacting with those of the adjacent molecules, as observed for molecule **O3A**, **D3A** and **E3A**. However, on the reconstructed Au(111) surface, the molecules remained in the “twisted” configuration that is hypothesized for the isolated molecule through DFT calculations, and a closer packing of the lamellae is observed in the lateral dimensions. On Au(111) the unit cell dimensions for all the molecules are very similar, irrespective of their differences in the terminal alkyl chain lengths. It is reasonable to think that the similar packing order is caused by the alkyl chains being folded below or above the *ter*-anthrylene-ethynylene cores, and this would also explain why they are not visualized in the STM images.

Thermal analyses of these materials revealed high thermal stability, while electrochemical studies indicated a HOMO level of -5.23 eV, which aligns with the work function of gold to assure good injection of charge carriers. A high field-effect mobility of $0.55 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was also realized with one of the molecules, currently the best obtained so far for anthracene-based molecule devices. Hence, we successfully investigated a series of 9,10-*ter*-anthrylene ethynylene oligomers for their self-assembling properties and their potential in OTFTs applications.

7 Overall Conclusions & Future Work

This thesis studied the self-assembly of conjugated molecular systems in terms of their intermolecular interactions, and the interactions between the molecules and substrates through the use of the scanning tunneling microscope at the solid/liquid interface. This STM technique allows the characterization of the two-dimensional self-assembly of molecules on conducting surfaces in ambient conditions, which is convenient and cost-effective. A summary of the important findings in this thesis is presented.

Polythiophenes

Regioregular polyquaterthiophenes (PQT-12) were observed to assemble in neat lamellar structures with well-interdigitated alkyl side chains on both HOPG and Au(111) substrates. Moreover, due to the presence of two unsubstituted thiophene rings in the monomeric unit of PQT-12, which resulted in a space between the interdigitated alkyl chains, co-adsorption of the *n*-tetradecane solvent chain was observed. On the other hand, no co-adsorption was observed when regioregular poly(3-hexylthiophene) chains were investigated under the same conditions. The reason for this difference is the sizes of the cavities available in each of the system for possible co-adsorption. Molecular arrangements obtained from the STM studies in this thesis were also coherent with one of the planes obtained from the 3D crystal packing of the polymer in bulk.

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Oligothienothiophenes

Newly synthesized oligothienothiophenes with different side chain positions and terminal groups were found to assemble in ordered lamellar structures that were analogous to typical alkyl substituted conjugated oligothiophenes^[76, 82, 83, 98, 103, 115-117] on HOPG substrates with well-interdigitated alkyl chains. These monolayers were assembled due to van der Waals interactions between the long intermolecular alkyl chains. The alkyl chains from neighbouring molecules interdigitate and they were visible in the STM images. On Au(111) however, a different molecular arrangement was observed. Molecules with the bulkier naphthyl terminating group were found to pack tightly with no visualizations of any alkyl chain interdigitation. Hence, the molecules were probably not assembling because of the intermolecular side chain interactions, but rather due to the stronger conjugated core backbone interaction with the Au(111) surface.

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Similar to the oligothienothiophene molecules, these oligomers also assemble with different molecular packing on different substrates. On HOPG, the molecules with longer alkyl chains arranged in neat lamellar rows with the adjacent terminal alkyl chains interdigitating with each other. Similar packing arrangement was obtained for the different anthracene molecules, with different unit cell dimensions due to the difference in alkyl chain lengths. Only the butyl chain terminated molecule was found

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to assemble in a quasi-hexagonal arrangement because of its short alkyl chain lengths. These chains were too short to allow van der Waals interaction to give an interdigitated network like those of the longer alkyl chains. On the contrary, on Au(111), all molecules self-assembled with the same unit cell dimensions, regardless of the difference in the terminal chain lengths. The molecules were packed closely to each other, with no visualization of the alkyl chains. This phenomenon is similar to the observation made earlier with the bulkier naphthyl group terminated oligothienothiophenes.

Conclusions

Through this work, we see the importance of the substitution of alkyl chains on the self-assembly of molecules. Long alkyl chains of dodecyl lengths allows long polymer chains of polyquaterthiophene to assemble in neat lamellar structures with an interdigitated network of alkyl chains. The same observation applies for the assembly of oligomeric molecules on HOPG surfaces. The influence of alkyl chains of the molecular packing of polymers and molecules have long been understood and investigated in terms of their bulk material property. However, at the monolayer interface, which is still a relatively new field, not much in-depth study has been completed. In this work, we compared the 2D self-assembly of the molecular systems to the bulk assembly and successfully proved that observations made under the STM imaging does coincide with one of the planes of the 3D crystal packing.

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On the other hand, the substrate also plays a very important part in molecular packing as demonstrated by the anthracene systems. Due to the commensurability between the alkyl chains and HOPG substrate, the molecules were observed to pack with alkyl chain interdigitation. However on Au(111), they were packed closely regardless of the alkyl chains. Hence, packing of the molecules in the bulk could probably follow the arrangements on Au(111), where the molecules were packed tightly.

Another observation learnt from this work is the effect of bulkier functional groups on the self-assembly. Although it has been reported that bulkier groups have higher tendency to disrupt the molecular assembly due to steric repulsions which resulted in disordered arrangements, this was not observed in our study. The molecules, on the other hand, were packed tightly as in the case of the naphthyl terminated oligothiophenes. This was probably due to the stronger π - π interactions between molecules as compared to the van der Waals interactions between the dodecyl chains.

Through this work, it can also be observed that the limitation of the STM in the study of thin film materials lies in its inability of studying the molecular self assembly of samples in its bulk form, as the study of the molecular interactions through the use of the STM essentially requires a monolayer arrangement of the molecules. Whereas, in thin film devices, films obtained generally consists of multi-layers and they are deposited using techniques such as spin-coating or evaporation. Thus in this study, only the two-dimensional interactions are taken into account, as we investigate only

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the monolayer arrangements. However, through our STM experiments of PQT-12, we realized that it is possible to relate the molecular arrangements of our STM measurements to one layer of the 3-dimensional crystal determined through single-crystal XRD studies.

Hence, the results obtained from the STM measurements, though lacking in the influence of the polymer-polymer interactions in the bulk were still comparable with single-crystal studies. Furthermore, the results obtained through STM measurements compared with other bulk thin film characterization data (single-crystal XRD, AFM) consistently showed a close relationship. Therefore, though the use of STM is limited to the study of the two-dimensional self assembly of thin films, it is however a useful technique in thin film characterization. In addition, it is the only characterization technique that allows researchers to “see” molecular self assembly.

Future Work

Although we have successfully established a close relationship between the alkyl substituent chains and the self-assembly packing order of the polythiophenes, we have yet to determine the optimal lengths that would be required for sufficient interactions between the chains to give well-interdigitated networks. Therefore, future recommendations for this work include the variation of substituent alkyl chain lengths on the polymers. Polythiophenes with butyl chains attachment giving poly(3-

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butylthiophene) could be investigated at the solid/liquid interface by STM to determine if the polythiophenes chains would self-assemble in lamellar rows similar to the hexyl chains substituted counterparts. Anthracene-based oligomers investigated in this work with short butyl chains were found to self-assemble differently from the molecules with the long chains, hence, it was anticipated that poly(3-butylthiophenes) might not pack in lamellar rows like the P3HT.

Thus systematic studies involving different substituent chain lengths of butyl, octyl, decyl, dodecyl, tetradecyl and hexadecyl could be carried out in the future in order to understand the chain length effects on the molecular packing of the polymer. Device results of these materials should also be obtained to allow a comparison between the device performance and the 2D molecular packing with the chain length variations.

In addition, a variation of the solvent used for the liquid/solid interface STM technique is also recommended for future investigations. Other solvent choices for the liquid/solid interface technique are 1-phenyloctane and 1,2,4-trichlorobenzene, which would probably eliminate the problem of co-adsorption, for example in the study of PQT-12 monolayer.

Possible future work recommendations include the use of molecules with active functional groups to investigate the interactions between molecules-to-molecules on adsorption. This could be carried out through the synthesis of molecules with functional groups such as substituting the alkyl chains of the conjugated molecules

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with carboxylic acid or amino end groups to promote hydrogen bonding. Supramolecular architectures can be formed through the molecular engineering of molecules with these reactive functional groups. A series of carboxylic acid functionalized oligothiophene molecules were synthesized by Xu and co-workers using the STM.^[156] Due to the hydrogen bonding between the molecules, various supramolecular architectures were observed. Thus, moving forward from this project, supramolecular architectures due to hydrogen bonding and van der Waals interactions between molecules can be studied via the technique of liquid/solid interface STM.

In addition, the odd and even effect of alkyl chains could also be investigated. In this project, work was focused on the chain length effects of the substituted alkyl chains, hence generally the even number of methylene groups is used in the experiments. Thus, moving on, anthrylene-ethynylene molecules with odd number of methylene groups could be investigated, to determine if the molecular organization could be different from those carried out in this work.

The use of the STM to investigate chemical reactions in the single molecule dimension could also be carried out. Hla and co-workers had earlier reported a real-time Ullman-type coupling reaction between iodobenzenes to yield biphenyl molecules, catalysed by the Cu(111) surface.^[157] Although the investigation of chemical reactions is limited by the speed of the STM in capturing the process, further developments in the technique might lead to more promising results in the near future.

8 References

- [1] C. N. R. Rao, A. K. Cheetham, *J. Mater. Chem.* **2001**, *11*, 2887.
- [2] J. L. West, N. J. Halas, *Annu. Rev. Biomed. Eng.* **2003**, *5*, 285.
- [3] J. Wu, W. Pisula, K. Mullen, *Chem. Rev.* **2007**, *107*, 718.
- [4] C. Joachim, J. K. Gimzewski, A. Aviram, *Nature* **2000**, *408*, 541.
- [5] A. Aviram, M. A. Ratner, *Chem. Phys. Lett.* **1974**, *29*, 277.
- [6] G. Binnig, H. Rohrer, C. Gerber, E. Weibel, *Appl. Phys. Lett.* **1982**, *40*, 178.
- [7] G. Binnig, H. Rohrer, C. Gerber, E. Weibel, *Surf. Sci.* **1982**, *126*, 236.
- [8] G. Binnig, H. Rohrer, C. Gerber, E. Weibel, *Phys. Rev. Lett.* **1983**, *50*, 120.
- [9] G. Binnig, H. Rohrer, C. Gerber, E. Weibel, *Surf. Sci.* **1983**, *131*, L379.
- [10] J. Roncali, *Chem. Rev.* **1992**, *92*, 711.
- [11] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, D. M. de Leeuw, *Nature* **1999**, *401*, 685.
- [12] C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913.
- [13] C. O. Too, G. G. Wallace, A. K. Burrell, G. E. Collis, D. L. Officer, E. W. Boge, S. G. Brodie, E. J. Evans, *Synth. Met.* **2001**, *123*, 53.
- [14] L. Torsi, A. Tafuri, N. Cioffi, M. C. Gallazzi, A. Sassella, L. Sabbatini, P. G. Zambonin, *Sens. Actuators, B* **2003**, *93*, 257.
- [15] J. Roncali, *Macromol. Rapid Commun.* **2007**, *28*, 1761.
- [16] P. Leclere, M. Surin, P. Brocorens, M. Cavallini, F. Biscarini, R. Lazzaroni, *Mater. Sci. Eng. R* **2007**, *55*, 1.
- [17] Z. Bao, A. Dodabalapur, A. J. Lovinger, *Appl. Phys. Lett.* **1996**, *69*, 4108.
- [18] B. S. Ong, Y. Wu, P. Liu, S. Gardner, *J. Am. Chem. Soc.* **2004**, *126*, 3378.
- [19] B. S. Ong, Y. Wu, P. Liu, S. Gardner, *Adv. Mater.* **2005**, *17*, 1141.
- [20] H. Sirringhaus, N. Tessler, R. H. Friend, *Science* **1998**, *280*, 1741.
- [21] Y. Wu, Y. Li, S. Gardner, B. S. Ong, *J. Am. Chem. Soc.* **2005**, *127*, 614.
- [22] Y. Wu, P. Liu, S. Gardner, B. S. Ong, *Chem. Mater.* **2005**, *17*, 221.
- [23] Y. Wu, P. Liu, B. S. Ong, T. Srikumar, N. Zhao, G. Botton, S. Zhu, *Appl. Phys. Lett.* **2005**, *86*, 142102.
- [24] H. E. Katz, Z. Bao, *J. Phys. Chem. B* **2000**, *104*, 671.
- [25] H. E. Katz, Z. Bao, S. L. Gilat, *Acc. Chem. Res.* **2001**, *34*, 359.
- [26] A. Dodabalapur, L. Torsi, H. E. Katz, *Science* **1995**, *268*, 270.
- [27] C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, A. G. MacDiarmid, *Phys. Rev. Lett.* **1977**, *39*, 1098.
- [28] R. Farchioni, G. Grosso, *Organic Electronic Materials: Conjugated Polymers and Low Molecular Weight Organic Solids*, Springer-Verlag, Berlin Heidelberg, **2001**.
- [29] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* **1990**, *347*, 539.
- [30] J. L. Bredas, R. Silbey, D. S. Boudreaux, R. R. Chance, *J. Am. Chem. Soc.* **1983**, *105*, 6555.

8 References

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- [31] C. D. Dimitrakopoulos, R. L. Malenfant, *Adv. Mater.* **2003**, *14*, 99.
- [32] J. A. Rogers, Z. Bao, H. E. Katz, A. Dodabalapur, *Thin-Film Transistors*, Marcel Dekker, New York, **2003**.
- [33] R. J. Hamers, *Nature* **2001**, *412*, 489.
- [34] R. J. Kline, D. M. DeLongchamp, D. A. Fischer, E. K. Lin, L. J., M. L. Chabinyc, M. F. Toney, M. Heeney, I. McCulloch, *Macromolecules* **2007**, *40*, 7960.
- [35] S. E. Shaheen, D. Vangeneugden, R. Kiebooms, D. Vanderzande, T. Fromherz, F. Padinger, C. J. Brabec, N. S. Sariciftci, *Synth. Met.* **2001**, *121*, 1583.
- [36] D. Fichou, *J. Mater. Chem.* **2000**, *10*, 571.
- [37] T. Minari, M. Seto, T. Nemoto, S. Isoda, K. Tsukagoshi, Y. Aoyagi, *Appl. Phys. Lett.* **2007**, *91*, 123501.
- [38] M. Surin, P. Leclere, S. De Feyter, M. M. S. Abdel-Mottaleb, F. C. De Schryver, O. Henze, W. J. Feast, R. Lazzaroni, *J. Phys. Chem. B* **2006**, *110*, 7898.
- [39] R. D. McCullough, *Adv. Mater.* **1998**, *10*, 93.
- [40] J. Roncali, *Acc. Chem. Res.* **2009**, *42*, 1719.
- [41] A. B. Koren, M. D. Curtis, J. W. Kampf, *Chem. Mater.* **2000**, *12*, 1519.
- [42] K. Mullen, M. Wegner, *Electronic Materials: the Oligomer Approach*, Wiley-VCH, New York, **1998**.
- [43] I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee, M. F. Toney, *Nature Materials* **2006**, *5*, 328.
- [44] M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891.
- [45] S. De Feyter, F. C. De Schryver, *J. Phys. Chem. B* **2005**, *109*, 4290.
- [46] D. Rohde, C.-J. Yan, L.-J. Wan, *Langmuir* **2006**, *22*, 4750.
- [47] Y. Yang, K. Deng, Q. Zeng, C. Wang, *Surf. Interface Anal.* **2006**, *38*.
- [48] H. Y. Erbil, *Surface Chemistry of Solid and Liquid Interfaces*, Blackwell Publishing, **2006**.
- [49] F. Charra, J. Cousty, *Phys. Rev. Lett.* **1998**, *80*, 1682.
- [50] R. Hentschke, B. L. Schurmann, J. P. Rabe, *J. Chem. Phys.* **1992**, *96*, 6213.
- [51] K. Perronet, F. Charra, *Surf. Sci.* **1998**, *551*, 213.
- [52] R. G. Nuzzo, L. H. Dubois, D. L. Allara, *J. Am. Chem. Soc.* **1990**, *112*, 558.
- [53] C. Schonenberger, J. A. M. Sondag-Huethorst, J. Jorritsma, L. G. J. Fokink, *Langmuir* **1994**, *10*, 611.
- [54] G. E. Poirier, M. J. Tarlov, *Langmuir* **1994**, *10*, 2853.
- [55] C. A. McDermott, M. T. McDermott, J.-B. Green, M. D. Porter, *J. Phys. Chem* **1995**, *99*, 13257.
- [56] K. Edinger, A. Golzhauser, K. Demota, C. Woll, M. Grunze, *Langmuir* **1993**, *9*, 4.
- [57] Y.-T. Kim, A. J. Bard, *Langmuir* **1992**, *8*, 1096.
- [58] G. Binnig, C. F. Quate, C. Gerber, *Phys. Rev. Lett.* **1986**, *56*, 930.
- [59] R. Erlandsson, G. M. McClelland, C. M. Mate, S. Chiang, *J. Vac. Sci. Technol. A* **1987**, *6*, 266.

8 References

-
- [60] R. Jumpertz, A. v. d. Hart, O. Ohlsson, F. Saurenbach, J. Schelten, *Microelectron. Eng.* **1998**, 41/42, 441.
- [61] P. A. Rasmussen, J. Thaysen, S. Bouwstra, A. Boisen, *Sens. Actuators A* **2001**, 92, 96.
- [62] M. Tortonese, R. C. Barrett, C. F. Quate, *Appl. Phys. Lett.* **1993**, 62, 834.
- [63] Y. Martin, H. K. Wickramasinghe, *Appl. Phys. Lett.* **1987**, 50, 1455.
- [64] D. W. Phol, W. Denk, L. M., *Appl. Phys. Lett.* **1984**, 44, 651.
- [65] B. D. Terris, J. E. Stern, D. Rugar, H. J. Mamin, *Phys. Rev. Lett.* **1989**, 63, 2669.
- [66] R. Wiesendanger, H.-J. Guntherodt, *Scanning Tunneling Microscopy I and II*, Springer, Berlin, **1992**.
- [67] C. Bai, *Scanning Tunneling Microscopy and its Applications*, Springer - Verlag, Berlin, **2000**.
- [68] J. V. Barth, H. Brune, G. Ertl, *Phys. Rev. B* **1990**, 42, 9307.
- [69] U. Harten, A. M. Lahee, J. P. Toennies, C. Woll, *Phys. Rev. Lett.* **1985**, 54, 2619.
- [70] C. Woll, S. Chiang, R. J. Wilson, P. H. Lippel, *Phys. Rev. B* **1989**, 39, 7988.
- [71] U. Kohler, J. E. Demuth, R. J. Hamers, *J. Vac. Sci. Technol. A* **1989**, 7, 2860.
- [72] K. Takayanagi, Y. Tanishiro, *Phys. Rev. B* **1986**, 34, 1034.
- [73] R. M. Feenstra, J. A. Stroscio, J. Tersoff, A. P. Fein, *Phys. Rev. Lett.* **1987**, 58, 1192.
- [74] N. Katsonis, E. Lacaze, B. L. Feringa, *J. Mater. Chem.* **2008**, 18, 2065.
- [75] N. Katsonis, A. Marchenko, D. Fichou, *J. Am. Chem. Soc.* **2003**, 125, 13682.
- [76] E. Mena-Osteritz, *Advanced Materials* **2002**, 14, 609.
- [77] E. Mena-Osteritz, A. Meyer, B. M. W. Langeveld-Voss, R. A. J. Janssen, E. W. Meijer, P. Bauerle, *Angew. Chem. Int. Ed.* **2000**, 39, 2680.
- [78] P. Samori, A. Fechtenkotter, F. Jackel, T. Bohme, K. Mullen, J. P. Rabe, *J. Am. Chem. Soc.* **2001**, 123, 11462.
- [79] C. R. Clemmer, T. P. Beebe Jr, *Science* **1991**, 251, 640.
- [80] L. Piot, J. Wu, A. Marchenko, K. Mullen, D. Fichou, *J. Am. Chem. Soc.* **2005**, 127, 16245.
- [81] A. Popoff, D. Fichou, *Colloids Surf., B* **2008**, 63, 153.
- [82] R. Azumi, G. Gotz, P. Bauerle, *Synth. Met.* **1999**, 101, 569.
- [83] P. Bauerle, T. Fischer, B. Bidlingmeier, A. Stabel, J. P. Rabe, *Angew. Chem. Int. Ed.* **1995**, 34, 303.
- [84] S. B. Darling, A. W. Rosenbaum, Y. Wang, S. J. Sibener, *Langmuir* **2002**, 18, 7462.
- [85] N. Zhao, G. A. Botton, S. Zhu, A. Duft, B. S. Ong, Y. Wu, P. Liu, *Macromolecules* **2004**, 37, 8307.
- [86] M. O. Ahmed, C. Wang, P. Keg, W. Pisula, Y. M. Lam, B. S. Ong, S. C. Ng, Z. K. Chen, S. G. Mhaisalkar, *J. Mater. Chem.* **2009**, 19, 3449.
- [87] K. R. Radke, K. Ogawa, S. C. Rasmussen, *Org. Lett.* **2005**, 7, 5253.
- [88] A. Dell'Aquila, F. Marinelli, J. Tey, P. Keg, Y. M. Lam, O. L. Kapitanchuk, P. Mastroiilli, C. F. Nobile, P. Cosma, A. Marchenko, D. Fichou, S. G. Mhaisalkar, G. P. Suranna, L. Torsi, *J. Mater. Chem.* **2008**, 18, 786.
- [89] A. Dell'Aquila, Polytechnic of Bari (Bari, Italy), **2008**.

8 References

-
- [90] R. L. Elsenbaumer, K. Y. Jen, R. Oboodi, *Synth. Met.* **1986**, *15*, 169.
- [91] S. Hotta, S. D. D. V. Rughooputh, A. J. Heeger, F. Wudl, *Macromolecules* **1987**, *20*, 212.
- [92] K. Y. Jen, G. G. Miller, R. L. Elsenbaumer, *J. Chem. Soc., Chem. Commun.* **1986**, 1346.
- [93] M. Sato, S. Tanaka, K. Kaeriyama, *J. Chem. Soc., Chem. Commun.* **1986**, 873.
- [94] R. L. Elsenbaumer, K. Y. Jen, G. G. Miller, L. W. Shacklette, *Synth. Met.* **1987**, *18*, 277.
- [95] R. Payerne, M. Brun, P. Rannou, R. Baptist, B. Grevin, *Synth. Met.* **2004**, *146*, 311.
- [96] B. Grevin, P. Rannou, R. Payerne, A. Pron, J. P. Travers, *J. Chem. Phys.* **2003**, *118*, 7097.
- [97] B. Grevin, P. Rannou, R. Payerne, A. Pron, J. P. Travers, *Adv. Mater.* **2003**, *15*, 881.
- [98] A. Stabel, J. P. Rabe, *Synth. Met.* **1994**, *67*, 47.
- [99] H. Pan, P. Liu, Y. Li, B. S. Ong, S. Zhu, G. Xu, *Adv. Mater.* **2007**, *19*, 3240.
- [100] G. C. McGonigal, R. H. Bernhardt, D. J. Thomson, *Appl. Phys. Lett.* **1990**, *57*, 28.
- [101] J. P. Rabe, S. Buchholz, *Science* **1991**, *253*, 424.
- [102] G. Watel, F. Thibaudau, J. Cousty, *Surf. Sci. Lett.* **1993**, *281*, L297.
- [103] R. Azumi, G. Gotz, T. Debaerdemaeker, P. Bauerle, *Chem. Eur. J.* **2000**, *6*, 735.
- [104] D. M. Cyr, B. Venkataraman, G. W. Flynn, A. Black, G. M. Whitesides, *J. Phys. Chem* **1996**, *100*, 13747.
- [105] F. Elfeninat, C. Fredriksson, E. Sacher, A. Selmani, *J. Chem. Phys.* **1995**, *102*, 6153.
- [106] A. Lachkar, A. Selmani, E. Sacher, M. Leclerc, R. Mokhliss, *Synth. Met.* **1994**, *66*, 209.
- [107] J. Noh, K. Ito, T. Araki, M. Hara, *Surf. Sci.* **2003**, *532-535*, 1116.
- [108] J. Noh, K. Ito, K. Nakajima, J. Kim, H. Lee, M. Hara, *J. Phys. Chem* **2002**, *106*, 7139.
- [109] M. C. Gurau, D. M. DeLongchamp, B. M. Vogel, E. K. Lin, D. A. Fischer, S. Sambasivan, L. J. Richter, *Langmuir* **2007**, *23*, 834.
- [110] Z. Bao, A. Dodabalapur, A. J. Lovinger, *Appl. Phys. Lett.* **1996**, *69*, 4108.
- [111] B. S. Ong, Y. Wu, Y. Li, P. Liu, H. Pan, *Chem. Eur. J.* **2008**, *14*, 4766.
- [112] D. Fichou, G. Horowitz, Y. Nishikitani, F. Garnier, *Chemtronics* **1988**, *3*, 176.
- [113] G. Horowitz, D. Fichou, F. Garnier, *Solid State Comm.* **1989**, *70*, 385.
- [114] B. Servet, G. Horowitz, S. Ries, O. Lagorsse, P. Alnot, A. Yassar, F. Deloffre, P. Srivastava, R. Hajlaoui, P. Lang, F. Garnier, *Chem. Mater.* **1994**, *6*, 1809.
- [115] R. Stecher, B. Gompf, J. S. R. Munter, F. Effenberger, *Adv. Mater.* **1999**, *11*, 927.
- [116] M. M. S. Abdel-Mottaleb, G. Gotz, P. Kilickiran, P. Bauerle, E. Mena-Osteritz, *Langmuir* **2006**, *22*, 1443.
- [117] T. Kirschbaum, R. Azumi, E. Mena-Osteritz, P. Bauerle, *New J. Chem.* **1999**, 241.

8 References

-
- [118] O. A. Gus'kova, E. Mena-Osteritz, E. Schillinger, P. G. Khalatur, P. Bauerle, A. R. Khokhlov, *J. Phys. Chem. C* **2007**, *111*, 7165.
- [119] D. M. DeLongchamp, R. J. Kline, E. K. Lin, T. Fischer, L. J. Richter, L. A. Lucas, M. Heeney, I. McCulloch, J. E. Northrup, *Adv. Mater.* **2007**, *19*, 833.
- [120] D. M. DeLongchamp, R. J. Kline, E. K. Lin, T. Fischer, L. J. Richter, L. A. Lucas, M. Heeney, I. McCulloch, J. E. Northrup, *Adv. Mater.* **2007**, *19*, 833.
- [121] H. U. Blaser, *Tetrahedron Asymmetr.* **1991**, *2*, 843.
- [122] S. M. Barlow, R. Raval, *Surf. Sci. Rep.* **2003**, *50*, 201.
- [123] H. Fang, L. C. Giancarlo, G. W. Flynn, *J. Phys. Chem. B* **1998**, *102*, 7311.
- [124] G. P. Lopinski, D. J. Moffatt, D. D. M. Wayner, R. A. Wolkow, *Nature* **1998**, *392*, 909.
- [125] M. Kiel, K. Duncker, C. Hagendorf, W. Widdra, *Phys. Rev. B* **2007**, *75*, 195439.
- [126] Y. Sun, Y. Ma, Y. Liu, Y. Lin, Z. Wang, Y. Wang, C. Di, K. Xiao, X. Chen, W. Qiu, B. Zhang, G. Yu, W. Hu, D. Zhu, *Adv. Funct. Mater.* **2006**, *16*, 426.
- [127] W. Pisula, F. Dierschke, K. Mullen, *J. Mater. Chem.* **2006**, *16*, 4058.
- [128] W. Pisula, M. Kastler, D. Wasserfallen, T. Pakula, K. Mullen, *J. Am. Chem. Soc.* **2004**, *126*, 8074.
- [129] W. Pisula, Z. Tomovic, M. Wegner, R. Graf, M. J. Pouderoijen, E. W. Meijer, A. P. H. J. Schenning, *J. Mater. Chem.* **2008**, *18*, 2968.
- [130] H. Shen, K.-U. Jeong, H. Xiong, M. J. Graham, S. Leng, J. X. Zheng, H. Huang, M. Guo, F. W. Harris, S. Z. D. Cheng, *Soft Matter* **2006**, *2*, 232.
- [131] J. L. Hutter, J. Bechhoefer, *J. Crystal Growth*. **2000**, *217*, 332.
- [132] W. Pisula, Z. Tomovic, C. Simpson, M. Kastler, T. Pakula, K. Mullen, *Chem. Mater.* **2005**, *17*, 4296.
- [133] C. Videlot-Ackermann, J. Ackermann, H. Brisset, K. Kawamura, N. Yoshimoto, P. Raynal, A. El Kassmi, F. Fages, *J. Am. Chem. Soc.* **2005**, *127*, 16346.
- [134] H. Meng, J. Zheng, A. J. Lovinger, B. C. Wang, P. G. Van Patten, Z. Bao, *Chem. Mater.* **2003**, *15*, 1778.
- [135] F. Cicoira, C. Santato, F. Dinelli, M. Murgia, M. A. Loi, F. Biscarini, R. Zamboni, P. Heremans, M. Muccini, *Adv. Funct. Mater.* **2005**, *15*, 375.
- [136] K. Ito, T. Suzuki, Y. Sakamoto, D. Kubota, Y. Inoue, F. Sato, S. Tokito, *Angew. Chem. Int. Ed.* **2003**, *42*, 1159.
- [137] H. Kluak, D. J. Gundlach, J. A. Nichols, T. N. Jackson, *IEEE Trans. Electron Devices* **1999**, *46*, 1258.
- [138] D. W. Kelley, D. V. Muyres, P. F. Baude, T. P. Smith, T. D. Jones, *Mater. Res. Soc. Symp. Proc.* **2003**, *771*, L6.5.1.
- [139] H. Kluak, M. Halik, U. Zschieschang, G. Schmid, W. Radlik, W. Weber, *J. Appl. Phys.* **2002**, *92*, 5259.
- [140] J. E. Anthony, J. S. Brooks, D. L. Eaton, S. R. Parkin, *J. Am. Chem. Soc.* **2001**, *123*, 9482.
- [141] J. E. Anthony, D. L. Eaton, S. R. Parkin, *Org. Lett.* **2002**, *4*, 15.
- [142] C. D. Sheraw, T. Jackson, N., D. L. Eaton, J. E. Anthony, *Adv. Mater.* **2003**, *15*, 2009.

8 References

-
- [143] A. N. Aleshin, J. Y. Lee, S. W. Chu, J. S. Kim, J.-H. Park, *Appl. Phys. Lett.* **2004**, *84*, 5383.
 - [144] N. Karl, J. Marktanner, *Mol. Cryst. Liq. Cryst.* **2001**, *355*, 149.
 - [145] W. Cui, X. Zhang, X. Jiang, H. Tian, D. Yan, Y. Geng, X. Jing, F. Wang, *Org. Lett.* **2006**, *8*, 785.
 - [146] Y. Inoue, S. Tokito, K. Ito, T. Suzuki, *J. Appl. Phys.* **2004**, *95*, 5795.
 - [147] M. Baumgarten, U. Muller, A. Bohnen, K. Mullen, *Angew. Chem. Int. Ed.* **1992**, *31*, 448.
 - [148] U. Muller, M. Adam, K. Mullen, *Chem. Ber.* **1994**, *127*, 437.
 - [149] J. Cremer, P. Bauerle, M. M. Wienk, R. A. J. Janssen, *Chem. Mater.* **2006**, *18*, 5832.
 - [150] H. Hoppe, D. A. M. Egbe, D. Muhlbacherc, N. S. Sariciftci, *J. Mater. Chem.* **2004**, *14*, 3462.
 - [151] T. Yamamoto, W. Yamada, M. Takagi, K. Kizu, T. Maruyama, N. Ooba, S. Tomaru, T. Kurihara, T. Kaino, K. Kubota, *Macromolecules* **1994**, *27*, 6620.
 - [152] K. Tahara, C. A. Johnson II, T. Fujita, M. Sonoda, F. C. De Schryver, S. De Feyter, M. M. Haley, Y. Tobe, *Langmuir* **2007**, *23*, 10190.
 - [153] F. Garnier, *Phil. Trans.* **1997**, *355*, 815.
 - [154] A. R. Murphy, P. C. Chang, P. VanDyke, J. Liu, J. M. J. Frechet, V. Subramanian, D. M. DeLongchamp, S. Sambasivan, D. A. Fischer, E. K. Lin, *Chem. Mater.* **2005**, *17*, 6033.
 - [155] Y. D. Park, D. H. Kim, Y. Jang, J. H. Cho, M. Hwang, H. S. Lee, J. A. Lim, K. Cho, *Org. Electron.* **2006**, *7*, 514.
 - [156] L. P. Xu, J. R. Gong, L. J. Wan, T. G. Jiu, Y. L. Li, D. B. Zhu, K. Deng, *J. Phys. Chem. B* **2006**, *110*, 17043.
 - [157] S. W. Hla, L. Bartels, G. Meyer, K. H. Riedel, *Phys. Rev. Lett.* **2000**, *85*, 2777.

9 List of Publications and Conferences

Publications

1. Antonio Dell'Aquila, Francesco Marinelli, Junie Tey, Peisi Keg, Yeng-Ming Lam, Oleksiy L. Kapitanchuk, Piero Mastroilli, Cosimo F. Nobile, Pinalysa Cosma, Alexandr Marchenko, Denis Fichou, Subodh G. Mhaisalkar, Gian Paolo Suranna and Luisa Torsi , **"9,10-ter-anthrylene-ethynylene: a new molecular architecture for solution processed anthracene-based thin film transistors"**, *J. Mater. Chem.*, **2008**, 18, 786-791.
2. Keg Peisi, Anup Lohani, D. Fichou, Lam Yeng Ming, Wu Yiliang, Beng S. Ong, S.G. Mhaisalkar, **"Direct observation of alkyl chain interdigitation in conjugated polyquaterthiophene self-organized on graphite surfaces"**, *Macromol. Rapid Commun.*, **2008**, 29, 1197-1202.
3. Moawia O. Ahmed, Chunmei Wang, Peisi Keg, Wojciech Pisula, Yeng-Ming Lam, Beng S. Ong, Ng S. Choon, Z.-K. Chen and Subodh Mhaisalkar, **"Thieno[3,2-b]thiophene Oligomers and their Applications as p-Type Organic Semiconductors"**, *J. Mater. Chem.*, **2009**, 19, 3449-3456.
4. Peisi Keg, Antonio Dell'Aquila, Francesco Marinelli, Oleksiy L. Kapitanchuk, Denis Fichou, Piero Mastroilli, Giuseppe Romanazzi, Gian Paolo Suranna, Luisa Torsi, Yeng-Ming Lam, and Subodh G. Mhaisalkar, **"Solution processable ter-anthrylene-ethynylenes semiconductors: thin film transistor properties and STM study on HOPG and Au(111)"**, *J. Mater. Chem.*, **2010**, 20, 2448-2456.

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5. **“Effects of alkyl side chain positions and terminal group functionality on the self assembly of thieno[3,2-b]thiophene oligomers”**, (manuscript on preparation)

Conferences

Oral Presentations

1. P. Keg, A. Lohani, D. Fichou, Moawia O. Ahmed, Y. M. Lam, S. Mhaisalkar, **“STM Studies on the Molecular Ordering of Self-Assembled Conjugated Oligomers in the Liquid-Solid Interface”** *International Conference of Materials for Advanced Technologies (ICMAT), Singapore, 2007.*
2. A. Lohani, P. Keg, D. Fichou, Y. M. Lam, S. Mhaisalkar, **“STM Studies of polyquaterthiophene assembly on HOPG”**, *International Conference of Materials for Advanced Technologies (ICMAT), Singapore, 2007.*
3. F.Marinelli, A. Dell’Aquila, R.Grisora, P.Keg, Y. M. Lam, Y.Y. Zhang, P. Cosma, P.Mastrorilli, S. Mhaisalkar, S. Mochhala, C. F. Nobile, G.P. Suranna, L. Torsi, **“Novel Anthracene Oligomers Based OTFT Sensors for Toxic Gas Detection”**, *International Conference of Materials for Advanced Technologies (ICMAT), Singapore, 2007.*

Poster Presentations

1. Keg Peisi, Anup Lohani, Moawia Omer Ahmed, Wu Yiliang, Beng S. Ong, Lam Yeng Ming, D. Fichou, Subodh Mhaisalkar, **“Molecular Ordering studies of self-assembled conjugated polyquaterthiophene in the solid/liquid interface through STM investigations”** *European – Materials Research Society (EMRS) Spring Meeting, Strasbourg (France), 2007.*

9 List of Publications and Conferences

2. P.Keg, A. Dell'Aquila, F.Marinelli, Y. M. Lam, P. Mastrorilli, C. F. Nobile, P. Cosma, D. Fichou, G.P. Suranna, L. Torsi, S. Mhaisalkar **"Self-assembled molecular ordering of conjugated anthracene derivatives at the liquid/solid interface"** *European – Materials Research Society (EMRS) Spring Meeting, Strasbourg (France), 2008.*
3. P.Keg, Moawia O. Ahmed, Z. Chen, Beng S. Ong, Y. M. Lam, D. Fichou, S. Mhaisalkar **"Self-assembled molecular ordering of conjugated thiophene molecules at the liquid/solid interface"** *European – Materials Research Society (EMRS) Spring Meeting, Strasbourg (France), 2008.*
4. P.Keg, A. Lohani, D.Fichou, Y. M. Lam, Y. Wu, Beng S. Ong, S. Mhaisalkar **"Molecular ordering studies of conjugated polyquarterthiophene with the direct observation of alkyl chain interdigitation"** *European – Materials Research Society (EMRS) Spring Meeting, Strasbourg (France), 2008.*