IDENTIFICATIONS OF PHASE STRUCTURES AND TRANSITIONS OF A
BENZO[κ]FLUORANTHENE DERIVATIVE FOR POTENTIAL USE IN ORGANIC
FIELD EFFECT TRANSISTORS

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Vershima Tachia
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IDENTIFICATIONS OF PHASE STRUCTURES AND TRANSITIONS OF A
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Vershima Tachia
Dissertation

Approved: ______________________________
Advisor
Dr. Stephen Z. D. Cheng

Accepted: ______________________________
Department Chair
Dr. Coleen Pugh

Committee Member
Dr. Mesfin Tsige

Dean of the College
Dr. Stephen Z. D. Cheng

Committee Member
Dr. Gustavo Carri

Dean of the Graduate School
Dr. George R. Newkome

Committee Member
Dr. Toshikazu Miyoshi

Date

Committee Member
Dr. Xiong Gong
Organic semiconducting materials entice interest due to current and potential applications in electronic devices such as organic field effect transistors (OFETs). Air stable sulfur-hetero oligoarenes based on the benzo[k]fluoranthene unit have been developed for potential use in OFETs. Research has been conducted on a particular benzo[k]fluoranthene derivative with flexible alkyl side chains. Its chemical nomenclature is 2,5-dihexyl-7,14-dipentylacenaphtho [1',2':6,7] naphtho [1,2-b:4,3-b'] dithiophene, shorthanded as PJ-C₆H₁₃.

Experiments used to identify phase structures and transitions for PJ-C₆H₁₃ include thermal gravimetric analysis (TGA), polarized light microscopy (PLM), differential scanning calorimetry (DSC), one- and two-dimensional wide angle X-ray diffraction (1D WAXD and 2D WAXD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and Cerius² computer simulation. TGA demonstrates that the molecule is thermally stable, and PLM demonstrates that the elongated crystals exhibit negative birefringence. According to DSC and 1D WAXD data, this particular molecule undergoes three phase transitions, and they are all enantiotropic and crystal-crystal transitions. The SAED and 2D WAXD patterns have determined that the unit cell at room temperature is orthorhombic with dimensions of \( a = 0.52 \text{ nm} \), \( b = 2.29 \text{ nm} \), \( c = 3.45 \text{ nm} \), and \( \alpha = \beta = \gamma = 90^\circ \), and the unit cell structures for all three condensed phases are orthorhombic with little variation between the unit cell lengths. There are four
molecules per unit cell as determined by the density measurement, and the Cerius$^2$
computer simulation suggests that the space group is $P2_12_12_1$.

Other small molecules have been briefly characterized also. Field effect transistor
performance parameters are presented for other molecule derivatives with the same
sulfur-fused benzo[k]fluoranthene unit. Certain properties of a different sulfur-fused
heteroacene unit were provided as well.
ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

In comparison with inorganic semiconducting materials such as silicon, organic semiconductors can be easily processed with low cost and low temperature processing techniques, which enable large area electronics fabricated on a flexible substrate. Moreover, their optoelectronic properties can be tuned through chemical engineering. Therefore, organic field effect transistors (OFETs) have been extensively employed in organic-based electronic circuits. Thiophene-based molecules have demonstrated to be promising organic semiconductors for OFETs. Since thiophene derivatives can be chemically modified and exhibit good thermal stabilities, various thiophene-containing structures have been synthesized.

In previous contributions closely related to this current research, several \( \pi \)-extended, condensed, sulfur-rich benzothiophenes favoring \( \pi-\pi \) interaction were reported. Such oligoarenes can form bulk quantity individual microwires through self-assembly. The organic transistors based on these molecules with the mobility of 0.01 cm\(^2\) V\(^{-1}\) s\(^{-1}\) were successfully achieved, demonstrating a processing strategy for air stable \( \pi \)-extended condensed benzothiophenes with good performance. Theoretical calculations and experimental results suggest that the charge carrier transporting is usually maximized along the \( \pi-\pi \) stacking orientation. Another previous work applied fluoranthene and benzo[k]fluoranthene derivatives to serve as the basic skeleton to prepare a blue light
emitter for organic light emitting diodes (OLEDs). Such a \(\pi\)-extended planar core containing sulfur atoms was employed to facilitate molecular self-association driven by \(\pi\)-\(\pi\) stacking.

Based on these previous works, a family of sulfur-hetero oligoarenes based on fluoranthene and benzo[k]fluoranthene units with good stability in air was synthesized.\(^1\) These fused thiophene aromatic molecules were developed as new organic semiconductors to avoid sterically induced twist between proximal aromatic rings. Such large planar conjugated molecules with flexible side chains provided a variety of intra- and intermolecular interactions in these thiophene-based materials, such as van der Waals interactions, \(\pi\)-\(\pi\) stacking, and sulfur-sulfur interactions, to essentially achieve high charge carrier mobilities.\(^3,6,7\) In this particular research, a specific molecule shorthanded PJ-C\(_6\)H\(_{13}\) combined the benzo[k]fluoranthene unit and the peripheral sulfur atoms with flexible alkyl side chains, which has the potential to be beneficial to device performance in OFETs. The objectives of this research are to identify the condensed state phase structures and transitions of this molecule. Characteristics of other sulfur-fused heteroacene molecule derivatives are presented as well.

The background information related to this research is given in Chapter II. In this chapter, the physics and materials of organic semiconductors and OFETs are discussed, as well as synthetic methods.

The material synthesis, sample preparation, instruments, and experimental procedures of PJ-C\(_6\)H\(_{13}\) are described in Chapter III. The experiments used in this research include thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), polarized light microscopy (PLM), one- and two-dimensional wide angle X-ray
diffraction (1D WAXD and 2D WAXD), transmission electron diffraction (TEM), selected area electron diffraction (SAED), and Cerius	extsuperscript{2} computer simulation.

The molecule, 2,5-dihexyl-7,14-dipentylacenaphtho [1',2':6,7] naphtho [1,2-\textit{b}:4,3-\textit{b'}] dithiophene (PJ-C\textsubscript{6}H\textsubscript{13}), is discussed in Chapter IV. Its thermodynamic transition properties and structural changes were determined by DSC and 1D WAXD. The unit cell dimensions of its phase structures were determined by 2D WAXD, TEM, and SAED.

Other small molecules are discussed in Chapter V, including field effect transistor characterization of other benzo[k]fluoranthene derivatives and several characteristics of a different fused heteroacene unit derivative.

In the last chapter, Chapter VI, a brief summary of the research findings is described.
CHAPTER II
BACKGROUND

2.1 Motivation

Interest in organic field effect transistors (OFETs) stems from the low thermal energy required to fabricate these devices and their high degree of mechanical flexibility. Since no covalent bonds need to be broken or re-formed, organic semiconductor materials can be manipulated using modest thermal energy, and these materials can be engineered to self-assemble into favorable configurations for device performance. Printed and evaporated materials can form semiconducting channels on virtually any substrate, on other active devices, or on glass. Applications of OFETs include displays, sensors, imagers, and radio-frequency identification (RFID). 8

2.2 Early History

In 1982, Ebisawa, Kurokawa, and Nara at the Ibaraki Electrical Communication Laboratory fabricated metal-insulator-semiconductor (MIS) diodes, using polyacetylene as the semiconductor. 9 Although the device operated in depletion mode, the authors suggested that this type of device appears promising for thin film transistors. Another significant milestone was the development of the first organic field effect transistor (OFET) in 1986 by Tsumura, Koezuka, and Ando of the Mitsubishi Electric Corporation. 10 This first OFET utilized polythiophene as a semiconductor and established a large modulation of its source-drain current by applied gate biases.
Other milestones further gained interest in organic semiconductors. Tang in 1986 highlighted that the two-layer (heterojunction) organic photovoltaic cell differs from conventional single-layer cells in that the interface between two thin organic layers is crucial in determining its photovoltaic properties. In particular, the interface region is primarily responsible for the photogeneration of charges. This generation efficiency is only weakly dependent on the bias field, and therefore advancing over the limitation of single-layer cells and providing the two-layer cell with a significantly higher fill factor.

Tang and Van Slyke in 1987 highlighted a double-layer, thin-film organic light emitting diode with electroluminescent (EL) characteristics. In contrast to single layer organic EL cells, the double layer EL diode provides one layer capable of only monopolar transport.

2.3 Energy Levels

On an isolated molecule, there are energy levels known as molecular orbitals that are discrete. They are the product of the combination of atomic orbitals that comprise the molecule. Some of the molecular orbitals will be filled with electrons when the molecule is in the ground state, and the higher levels will be empty. The two most interesting molecular orbitals are the frontier states: the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), as shown in Figure 2.1. Work function for n-type devices (injecting electrons) line up with the LUMO, and p-type contacts (injecting holes) line up with the HOMO. The Fermi energy \( (E_F) \) is often defined as the “highest” energy that the electrons assume at zero degrees Kelvin.
Vacuum level

Higher MOs
LUMO
E_F
HOMO
Lower MOs

| Empty states | Work function | HOMO-LUMO Gap | Filled states |

Figure 2.1 Energy levels and filled/empty states for an organic semiconductor in the absence of thermal excitation or doping.\(^8\)

2.4 Charge and Energy Carriers in Conjugated Polymer Chains

The structure of polyacetylene, shown in Figure 2.2, has two states that are energetically degenerate, i.e. the same energy level. It is possible for these two states to coexist on the same chain with a boundary between them. At the phase wall between these two states, a charge might be carried on the polymer chain, as illustrated in Figure 2.3.\(^8\)

![Two resonance forms of polyacetylene.](image)

Figure 2.2 Two resonance forms of polyacetylene.\(^8\)

![Single positively charged polaron on polyacetylene.](image)

Figure 2.3 Single positively charged polaron on polyacetylene.\(^8\)

This combination of two resonance forms is known as a polaron. A charge can sustain itself on the unsatisfied bond indicated by the (+) sign in Figure 2.3, and this charge can be moved along the molecule by an electric field. This phenomenon is
responsible for the generation charge states in organic semiconductors. A similar situation can be generated by a dopant that might oxidize or reduce one of the bonds along the chain, creating a free electron or hole. Polarons can also become combined in more complicated structures with greater charge or carriers such as excitons where positively and negatively charged polarons attract each other and form an electrically neutral energy carrier. \(^8\) A number of charge and energy carriers can be found in polymer and small molecule organic semiconductors, with a few summarized in Table 2.1.\(^{14}\)

<table>
<thead>
<tr>
<th>Carrier</th>
<th>Components</th>
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<tr>
<td>Negative bipolaron</td>
<td>- -</td>
</tr>
<tr>
<td>Negative polaron</td>
<td>-</td>
</tr>
<tr>
<td>Exciton</td>
<td>+ -</td>
</tr>
<tr>
<td>Positive polaron</td>
<td>+</td>
</tr>
<tr>
<td>Positive bipolaron</td>
<td>+ +</td>
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2.5 OFET Structure and Operation

This section discusses the basic parameters and equations used to model OFETs and the schematic structure and device operation of OFETs.

2.5.1 Basic Parameters of OFETs

Fundamentally, transistors are resistors where the charge carrier density is a function of a third terminal. This resistor model is the basis for all simple models of transistor behavior. By convention, currents are positive when flowing into the device. Positive values of \(I_S\), \(I_D\), and \(I_G\) are the currents flowing into the source, drain, and gate, respectively. Voltages are traditionally referenced to the source, so \(V_{DS}\) and \(V_{GS}\) are the drain and gate voltages. \(L\) is the channel length (in the direction of current travel) and \(W\)
is the device width (the dimension in the plane of current flow perpendicular to the
length). $C_{OX}$ is the specific gate dielectric capacitance in F cm$^{-2}$. Table 2.2 summarizes
these parameters.$^8$

Table 2.2 Traditional Si transistor parameters and conventional units for OFET
modeling.$^8$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Meaning</th>
<th>Units</th>
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<tr>
<td>$I_S$</td>
<td>Source current</td>
<td>A</td>
</tr>
<tr>
<td>$I_G$</td>
<td>Gate current</td>
<td>A</td>
</tr>
<tr>
<td>$I_D$</td>
<td>Drain current</td>
<td>A</td>
</tr>
<tr>
<td>$V_{GS}$</td>
<td>Gate voltage</td>
<td>V</td>
</tr>
<tr>
<td>$V_{DS}$</td>
<td>Drain voltage</td>
<td>V</td>
</tr>
<tr>
<td>$W$</td>
<td>Width</td>
<td>µm</td>
</tr>
<tr>
<td>$L$</td>
<td>Length</td>
<td>µm</td>
</tr>
<tr>
<td>$C_{OX}$</td>
<td>Gate capacitance</td>
<td>F cm$^{-2}$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Mobility</td>
<td>cm$^2$ V$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$V_T$</td>
<td>Threshold voltage</td>
<td>V</td>
</tr>
<tr>
<td>$Q$</td>
<td>Sheet charge density</td>
<td>C cm$^{-2}$</td>
</tr>
</tbody>
</table>

2.5.2 OFET Structure

Figure 2.4 shows a model structure of an OFET. In an OFET, the charge carriers
tavel in the channel parallel to the surface of the gate dielectric. The source and drain
electrodes provide access to the channel and are engineered to inject charge under bias
The channel is the gap between the source and drain whose conductance is switched, adjusting the conductance of the whole device. The gate is separated from the channel by the gate dielectric, forming a capacitor to the channel charge sheet. The gate dielectric allows the creation of a field across the semiconductor and the resultant accumulation and depletion of carriers.  

2.5.3 OFET Operation

Figure 2.5 shows a typical p-type OFET device operation (It has the same labels and legend as Figure 2.4), and Figure 2.6 is a schematic diagram of current vs. voltage with noted regions of operation.  

The contacts of OFETs are engineered to have good electrical access to the channel. When the channel is depleted through the gate there are fewer mobile charges and less current flows. When the channel is accumulated, there are more charges and more conductivity.
The threshold voltage \( V_T \) is the gate voltage at which a perceptible current begins to flow in the device. In Figure 2.5a, under biases where \( V_{GS} < V_T \), the device is in cutoff. There is no current in an OFET because of no available mobile carriers (as shown in Figure 2.6):\(^8\)

\[ I_D = 0A \]

As shown in Figure 2.5b, at small \( V_{DS} \) and larger \( V_{GS} \) where \( V_{GS} > V_T \) and \( V_{GS} - V_{DS} > V_T \), the transistor is said to be in the linear region. For small values of \( V_{DS} \), the device is a resistor whose resistance is determined by the gate voltage. For larger values of \( V_{DS} \), the device is a current source whose magnitude is determined by the gate voltage.

The resistivity is determined by the mobility and geometrical factors \( \left( \mu \frac{W}{L} \right) \), and the charge carrier density is determined by the capacitance and the applied voltage beyond the threshold \( (C_{OX} * (V_{GS} - V_T)) \). The linear region gives a current of (as shown in Figure 2.6):\(^8\)

\[ I_D = \frac{W}{L} \mu C_{OX} \left( V_{GS} - V_T - \frac{V_{DS}}{2} \right)V_{DS} \]

Figure 2.5  p-type OFET operation.\(^8\)
As $V_{DS}$ is increased further, when $V_{GS} - V_{DS} < V_T$, the channel current increases until the field from the drain cancels the gate field and applies less than the threshold field ($V_{GS} - V_{DS} < V_T$). At that point, $I_D$ slows its rate of increase because of the onset of pinch-off, and the device appears to saturate, as shown in Figure 2.5c. The current at the saturation point can be determined by substituting $V_{DS} = V_{GS} - V_T$ in the linear region equation and simplifying (as shown in Figure 2.6):

$$I_D = \frac{1}{2} \frac{W}{L} \mu_{OX} (V_{GS} - V_T)^2$$

![Figure 2.6](image)

**Figure 2.6** Current flow vs. voltage in an OFET.

2.5.3.1 Mobility

Mobility is the relationship between the carrier speed in a material and the applied electric field. Mobility is defined as:

$$\mu = \frac{Velocity}{E}$$
The current that flows is the amount of charge contained in a volume swept at the speed of the charge carrier movement. For a sheet charge density $Q$ and a width $W$, the amount of charge contained in a solid swept out in this manner yields a current of:

$$ I = \frac{\text{Charge}}{\text{Unit time}} $$

$$ I = QW\mu E $$

And therefore the mobility is defined by:

$$ \mu = \frac{I}{QWE} $$

This model assumes a linear relationship between carrier velocity and electric field, which is generally true at low electric fields. In OFETs, the relationship is non-linear at larger electric fields and also dependent on the charge carrier concentration.$^8$

It is possible to measure the mobility of carriers directly in the linear region of operation.$^{15}$ The total current in the transistor deep in the linear region can be treated like a resistor:

$$ \mu = \frac{\text{Velocity}}{E} $$

$$ Q = \frac{C_{\text{Channel}}(V_{GS} - V_T)}{WL} $$

$$ \mu = \frac{I_D}{WQV_{DS}} $$

$$ \mu = \frac{I_D}{W C_{\text{Channel}}(V_{GS} - V_T)V_{DS}} $$

$$ \mu = \frac{I_D L^2}{C_{\text{Channel}}(V_{GS} - V_T)V_{DS}} $$
This method has the advantage of being based only on the fundamental definition of mobility, and it is only effective in the linear region where the charge carrier density is approximately constant across the channel, i.e. where $V_{DS}$ is small (0.1V or less).

2.5.3.2 Threshold Voltage

The measurement of threshold voltage is somewhat complicated by the relatively gradual turn-on of the device. In OFETs, there is no single definition that is universally accepted. The term threshold voltage is generally used in the OFET community to specify the gate voltage at which current begins to flow at the onset of accumulation.\(^8\)

A simple method for determining the threshold voltage is to extrapolate the linear part of a $\sqrt{I_D} - V_{GS}$ curve to the intercept on the $V_{GS}$ axis, as shown in Figure 2.7. This figure indicates the voltage at which there is some increase in current, and the device transitions from cut-off to a region of operation in which the device is conducting current. This method is convenient, simple to implement, and provides a definition of threshold which is understandable from a current flow perspective (i.e. when current starts to flow, $V_{GS}$ has exceeded $V_T$).\(^8\)

![Figure 2.7](image)

Figure 2.7 The extrapolation of $V_T$ from the $\sqrt{I_D} - V_{GS}$ transfer characteristic. The inset shows the section of the $I_D$-$V_{GS}$ output characteristic where the transfer curves are taken.\(^8\)
There are several limitations to the extrapolation approach, as illustrated in Figure 2.8. First, the turn-on in the subthreshold region of operation is not as abrupt; significant current can flow before the device enters the extrapolated higher conductance region in the transfer curve (Region A). Second, regions may not be linear in comparison to the model; these scenarios lead to some ambiguity in the threshold voltage determination (Region B). Third, the extrapolated zero point has no universally agreed upon physical significance; it is the extrapolation of the expression for \( \sqrt{I_D} \) into a region in which the model does not apply.\(^8\)

![Figure 2.8 Limitations of determining the threshold voltage through linear extrapolation. In region A, there is significant current flow below the nominal \( V_T \). Region B shows a non-linear current increase in the “linear” region of device operation.\(^8\)]](image)

2.6 Organic Semiconductor Materials for OFETs

Organic semiconductor materials are generally polymers or small molecules made from a small foundational group of conjugated monomer units. It is almost impossible to catalog all OFET materials; however, most materials in common use can be placed into one of a few classes. Figure 2.9 shows the most common polymers for organic
semiconductors in general, and Figure 2.10 shows common semiconducting materials for OFETs specifically.

![Diagram of semiconductor materials](image)

**Figure 2.9** Most common semiconducting polymers.

![Diagram of organic semiconductor materials](image)

**Figure 2.10** Organic semiconductor materials for OFETs.
2.6.1 p-Type Polymer Semiconductors

This section discusses the early research and subsequent advances of p-type polymer semiconductor materials for OFETs.

2.6.1.1 Regioregular Polythiophenes

Initial work in polythiophenes as transistor materials was started in 1986 and used insoluble, electropolymerized polythiophenes that were electrochemically de-doped to produce a material which could be accumulated and depleted. A polythiophene derivative was developed by Jen et al. which added alkyl side chains to the thiophene monomer and made the polymer soluble without disturbing conjugation in the backbone. Assadi et al. applied this more practical material to make transistors, which were spun-casted and showed essentially a better performance than the electrochemically polymerized material. These accomplishments ignited excitement about the possibility of printable semiconductor systems that could be made with the same economies of scale as printed paper media.

The devices made using these two techniques were essentially amorphous. Electropolymerized polythiophene has no strong organizing force for crystallinity, and the large groups used to solubilize polythiophene sterically interfere with chain-to-chain packing. Chen et al. made a significant breakthrough in 1995 with the development of regiocontrolled polythiophene using a specialized zinc catalyst. As illustrated in Figure 2.11, this regioregular alkyl substituted polythiophene exhibited significantly improved behavior such as electroconductivity due to superior packing while retaining the processing advantages of solubility.
Figure 2.11 The four possible conformational triads of alkyl substituted polythiophene, where R is the alkyl functionalizing group. The HT-HT conformation has been found to stack the best.

2.6.1.2 Polythiophene-based Liquid Crystalline Materials

The organizational capabilities of soluble polythiophenes can be further enhanced by creating structures that retain a high degree of regioregularity but have a reduced activation energy for conformational readjustment and crystallization. One approach to achieving this goal was through reduction of the steric hindrance caused by the solubilizing side groups of the polymer material. A family of polythiophenes (poly(3,3‴-dialkyl-quaterthiophene)s, PQT) was developed by Ong et al. in which a 4-unit thiophene repeating unit is used and only two units are substituted, as shown in Figure 2.12a. Due to its greater orientational freedom and decreased crowding between chains,
this material was liquid crystalline and can be thermally processed into highly crystalline thin films by controlled heating and quenching of the crystalline state. The reduced substitution also leads to greater oxidative stability.

Further optimization can be achieved by engineering the monomer units to increase the π-π coupling between adjacent units. In Figure 2.12b, for example, a copolymer of thienothiophene and thiophene repeat units has been shown to stiffen the polymer backbone. This stiffening increases the crystallinity of the device beyond that achievable with regioregular P3HT or PQT-family materials.

Figure 2.12  Two advanced polythiophene derivatives with liquid crystal properties (a) PQT\textsuperscript{19} (b) poly(2,5-bis(3-alkylthiophen-2-yl) thieno[3,2-b]thiophene).\textsuperscript{20}
2.6.2 p-Type Small Molecule Semiconductors

This section discusses the basic structures and their subsequent derivatives of p-type small molecule semiconductor materials that have been relevant in research and application for OFETs.

2.6.2.1 Acenes

Fused ring structures form a large variety of organic semiconductor materials. Many of these fused ring assemblies are planar and rigid, which leads to good stacking properties. Acenes, which can have better π-π overlap between neighboring molecules, improves transport and overall OFET performance. The acenes are a series of fused benzene rings and are shown in Figure 2.13. Acenes and their derivatives are key candidates for organic semiconductors. Tetracene and pentacene are particularly interesting small molecules for OFETs. Both strongly organize to form polycrystalline films with good transport properties on insulating substrates and can also form large single crystals under appropriate conditions.\(^{21}\)
2.6.2.1.1 Pentacene

Pentacene is the most popular organic semiconductor for OFET fabrication and is a benchmark of organic semiconductors with high mobility ($\mu = 1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).\textsuperscript{22} Its efficient charge transport is mainly attributed to the extended $\pi$-system with strong intermolecular overlaps as well as the proper energy level of the highest occupied molecular orbital (HOMO: -5.1 eV) for efficient hole injection (e.g. Au: -5.1 eV) and transport.\textsuperscript{21}

Despite its popularity, pentacene is not ideal. Pentacene has poor solubility in common organic solvents and can only be deposited using vacuum processes. Pentacene is relatively easily oxidized, especially at the 6,13 positions, which disrupts transport and crystallization in devices. Also, pentacene can condense into two crystal phases that are
closely related, but not perfectly matched. This situation often leads to polymorphic crystal growth, which can lead to mismatched grains and decreased OFET performance.\textsuperscript{8}

Pentacene derivatives have been developed to add functionality to the basic pentacene unit. As shown in Figure 2.14, Afzali et al.\textsuperscript{23} developed a family of soluble pentacene precursors exhibiting a transistor mobility up to 0.89 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} with an on/off ratio over 10\textsuperscript{7}. These materials can be converted into well packed pentacene films on exposure to heat.

![Figure 2.14 Soluble pentacene precursor.\textsuperscript{23}](image)

2.6.2.1.2 Tetracene

Tetracene attracted attention because of its better solubility and stability than pentacene. Goldmann et al.\textsuperscript{24} investigated the single crystals of tetracene and found its mobility to be as high as 1.3 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}. Moon et al.\textsuperscript{25} synthesized a series of soluble halogenated tetracene derivatives, and they found that the mono-halo tetracene derivatives (Figure 2.15a and Figure 2.15b) were arranged in a pattern with alternating pairs of edge-to-face and face-to-face molecular packing, while the dihalo derivative (Figure 2.15c) demonstrated strong π-stacking overlaps in a face-to-face molecular
packing. Tetracene derivative for Figure 2.15c exhibited mobility of 1.6 cm² V⁻¹ s⁻¹; however, mobility is only 10⁻³ cm² V⁻¹ s⁻¹ for Figure 2.15a and Figure 2.15b, suggesting a correlation between solid-state structure and charge carrier mobility.

Figure 2.15  Tetracene derivatives²⁴,²⁵

As shown in Figure 2.16, Sundar et al.²⁶ investigated the transport properties of rubrene crystals (a tetracene derivative), and they found anisotropic mobility with 15.4 cm² V⁻¹ s⁻¹ along the b axis and 4.4 cm² V⁻¹ s⁻¹ along the a axis. These results suggest that field effect experiments at organic crystal surfaces should consider mobility anisotropy and highlight the importance of controlling the orientation of the organic crystal relative to the OFET channel.

Figure 2.16  Rubrene,²⁶ a tetracene derivative
2.6.2.1.3 Anthracene

Anthracene has also received much interest in OFETs. The maximum field effect mobility was observed to be only 0.02 cm$^2$ V$^{-1}$ s$^{-1}$ in unsubstituted anthracene single crystals.$^{27}$ Wang et al.$^{28}$ synthesized anthracene derivatives (BPEA, Figure 2.17a and BNEA, Figure 2.17b) through incorporation of carbon-carbon triple bonds into the side chains. The introduction of carbon-carbon triple bonds decreased the steric repulsion between the plane of substitutions (benzene ring) and the plane of the core (anthracene) and lead to long-range $\pi$-$\pi$ intermolecular interactions. Indeed, higher mobilities were observed for Figure 2.17a (0.73 cm$^2$ V$^{-1}$ s$^{-1}$) and Figure 2.17b (0.52 cm$^2$ V$^{-1}$ s$^{-1}$).

Figure 2.17  Antracene derivatives$^{28}$ a) BPEA, b) BNEA
2.6.2.2 Heteroacenes

In this section, the heteroacenes discussed here are acenes infused with thiophenes that create the rigid core composite.

2.6.2.2.1 Pentathienoacene

Pentathienoacene (PTA, Figure 2.18) was applied in OFETs by Xiao et al.\textsuperscript{29} PTA has a similar molecular shape to pentacene, but with five thiophene rings substituting the benzene rings. In comparison with pentacene, PTA contains essentially less hydrogen atoms in the molecular periphery and therefore interact together efficiently through intermolecular S-S contacts in the solid state, so that a slipped $\pi$-stacking model with a short distance of 3.52 Å was demonstrated. Such planar and extended $\pi$-conjugation molecules gave a lower HOMO energy level of -5.3 eV and a larger band gap of 3.29 eV than those of pentacene (HOMO: -5.1 eV, band gap: 1.8 eV), indicating improved air stability of PTA. However, the synthesis of PTA is difficult and complicated, and its mobility of 0.045 cm$^2$ V$^{-1}$ s$^{-1}$ is at least one degree of magnitude lower than that of pentacene.

![Pentathienoacene (PTA)](image)

Figure 2.18 Pentathienoacene (PTA)\textsuperscript{29}
2.6.2.2.2 Heteroacenes with One Thiophene Ring

Tang et al.\textsuperscript{30} presented two asymmetric linear pentacene and tetracene derivatives containing fused thiophene units. Figure 2.19b had a slightly lower HOMO energy level of -5.17 eV and higher band gap of 1.96 eV than those of pentacene, showing higher stability. Figure 2.19b also exhibited a thin film mobility of 0.47 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} (under the same conditions pentacene was 0.5 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}). For Figure 2.19a, thin film mobility was only 0.15 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} probably due to its large grain boundaries in films.

![Figure 2.19 Heteroacenes with one thiophene ring.\textsuperscript{30}]

2.6.2.2.3 C\textsubscript{n}-BTBT

As shown in Figure 2.20, Ebata et al.\textsuperscript{31} developed a series of 2,7-dialkyl substituted BTBT molecules C\textsubscript{n}-BTBT for solution-processable OFETs. They introduced two solubilizing alkyl groups in the molecular long axis direction of the core to facilitate lateral intermolecular interaction.

![Figure 2.20 BTBT Derivatives (C\textsubscript{n}-BTBT)\textsuperscript{31}]

\textsuperscript{25}
Table 2.3 summarizes the OFET characteristics of the devices evaluated under ambient conditions without any precautions to eliminate air and moisture.\textsuperscript{32} For $n = 5-9$, the molecules showed increased solubility in CHCl$_3$ as increasing the alkyl chain length. However, after $n > 10$, the molecules showed decreased solubility in CHCl$_3$, and the solubility further decreased with increasing length of solubilizing chains. This result may be due to the increased van der Waals interactions between alkyl chains and the decreased solubility of the longer alkyl chains in CHCl$_3$. Solution-processed OFET devices based on these BTBT derivatives all showed hole mobility over 0.1 cm$^2$ V$^{-1}$ s$^{-1}$. For $n = 5-10$, the hole mobilities of the derivatives with even-numbered chains outperformed those derivatives with odd-numbered chains, but the trend was reversed for $n = 10-14$. High field-effect mobility up to 2.75 cm$^2$ V$^{-1}$ s$^{-1}$ was observed for C$_{13}$-BTBT. The hole mobilities in these materials were affected not only by the odd-even effect but also by the length effect of the flexible chains. Both effects influence the molecular packing and charge transport.
Table 2.3  OFET Characteristics of Cₙ-BTBT

<table>
<thead>
<tr>
<th>n</th>
<th>Solubility in CHCl₃ (g L⁻¹)</th>
<th>μₜₕ,ₘₜₐₓ (cm² V⁻¹ s⁻¹)</th>
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</tr>
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</tr>
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<td>14</td>
<td>2.3</td>
<td>0.72</td>
</tr>
</tbody>
</table>

2.6.3 n-Type Organic Semiconductors

The n-type organic semiconductors are important for p-n diodes, bipolar transistors, and complementary circuits. However, to date, n-type organic semiconductors with high mobility are relatively rare and significantly lagging behind p-type semiconductors. One reason is the low stability of most n-type organic semiconductors in air. Moreover, the normally used electrodes (such as Au, Ag, etc.) with high work function are favorable for the injection of holes instead of electrons. The electrodes with low work function (such as Ca, Al, Mg, etc.) are easily oxidized and unstable in ambient conditions. Therefore, the search of n-type semiconductors with high performance and environmental stability is currently a challenge.²¹

2.6.3.1 Electronegative Substituents

One effective approach for n-type organic semiconductors is to convert known p-type materials into n-type by modifying with strong electronegative substituents to lower the lowest unoccupied molecular orbital (LUMO) energy levels of materials for electron
injection and transport. Amongst the electronegative substituents (-F, -CN, -Cl, -NO$_2$, etc.), fluorine (-F) is the most electronegative and relatively small, and it is widely used as the effective electron-withdrawing group. Representative examples are hexadecafluoro copper pthalocyanine (F$_{16}$CuPc, Figure 2.21) and perfluorinated pentacene (Figure 2.22), in which all hydrogen atoms are replaced with F. The mobility of F$_{16}$CuPc was found to be around 0.02 cm$^2$ V$^{-1}$ s$^{-1}$, and the mobility of perfluorinated pentacene was 0.024 cm$^2$ V$^{-1}$ s$^{-1}$.

![Figure 2.21 Hexadecafluoro copper pthalocyanine (F$_{16}$CuPc)](image)

![Figure 2.22 Perfluorinated pentacene](image)
2.6.3.2 Perylene Derivatives (PDIs)

Perylene derivatives (PDIs, Figure 2.23) are promising candidates as the electron deficient \( \pi \)-system cores for the design of n-channel OFET materials, because their large electron affinities facilitate electron accumulation. Also, it is easy to introduce various substituents at the imide N atoms or \( \pi \)-system cores for tuning of the molecular self-assembly abilities. In Figure 2.23a, Malenfant et al.\(^{35}\) reported that thin films exhibited electron mobility up to 0.6 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \), and Chesterfield et al.\(^{36}\) further increased it to 1.7 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) by fine controlling the deposition conditions. In Figure 2.23b, Gundlach et al.\(^{37}\) used tridecyl substitute derivatives as a semiconducting layer for OFETs, achieving an electron mobility of 0.58 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \). By annealing at 140\(^\circ\)C after the device fabrication, the mobility could be further improved up to 2.1 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \).\(^{38}\)

![Figure 2.23 Perylene derivatives (PDIs)\(^{35-38}\)](image)

2.6.3.3 Fullerene (C\(_{60}\))

C\(_{60}\) is an important n-type organic semiconductor (Figure 2.24). C\(_{60}\) exhibits a relatively low lying LUMO energy level that is triply degenerate and therefore behaves as an electron acceptor that is able to accept up to six electrons in solution.\(^{39}\) Since its field effect mobility was first reported in 1995,\(^{40}\) the performance of C\(_{60}\)-based OFETs has
experienced advances with electron mobilities from 0.08 cm$^2$ V$^{-1}$ s$^{-1}$ to 6 cm$^2$ V$^{-1}$ s$^{-1}$. However, a major disadvantage of fullerene is its rapid performance degradation upon exposure to air. Fullerene has produced numerous derivatives.

![Fullerene (C$_{60}$)](image)

**Figure 2.24** Fullerene (C$_{60}$)$^{39-41}$

2.6.4 Material Requirements for High Performance

The remarkable advances of organic semiconductors are greatly improving the organic electronic industry. However, there are still some fundamental needs to better understand organic semiconductors, such as the origin of high mobility and the development of new strategies for further controlling synthesis and enhancement of OFETs performance. Molecular structures, molecular packing, as well as optimal electronic structures, play key roles in OFETs. It should be also noted that organic semiconductors are struggling for (i) improved mobility for organic circuits and organic chips; (ii) not only high mobility, but also high air stability and solution processability; (iii) extending their family with more n-type and ambipolar candidates.$^{21}$
2.7 Synthetic Methods of Semiconducting Polymers

The need for new multifunctional materials able to combine properties such as self-organization and semiconduction has induced material scientists to explore new strategies for the preparation of molecules exhibiting a certain complexity. Different chemical functions have to be incorporated in the same molecule to achieve multifunctionality, and this requires a strong and precise planning of the molecules.\textsuperscript{43} High specific functions require a hierarchical organization of matter starting from the basic molecule to the final arrangement of an object at the nano-microscale dimension.\textsuperscript{44}

Conducting polymers offered the promise of achieving a new generation of polymers: materials which exhibit the electrical and optical properties of metals and semiconductors and which retain the attractive mechanical properties and processing advantages of polymers.\textsuperscript{45}

The field has evolved from the early work on polyacetylene (the First Generation material, Figure 2.25) to a proper focus on soluble and processible polymers and copolymers. Poly(paraphenylenevinylene), polythiophenes, and polyfluorenes were made soluble and processible by the addition of alkyl or alkoxy side chains. The soluble PPVs, PATs, and PFOs are perhaps the most important examples of the Second Generation of semiconducting polymers (Figure 2.25).\textsuperscript{46}
Molecular structures of some of the more important First and Second Generation semiconducting polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacetylene (PA)</td>
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</tr>
<tr>
<td>Polyparaphenylene (PPP)</td>
<td><img src="image" alt="Polyparaphenylene" /></td>
</tr>
<tr>
<td>Polyparaphenylene vinylene (PPV)</td>
<td><img src="image" alt="Polyparaphenylene vinylene" /></td>
</tr>
<tr>
<td>Polythiophene (PT)</td>
<td><img src="image" alt="Polythiophene" /></td>
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<tr>
<td>Polypyrrole (PPy)</td>
<td><img src="image" alt="Polypyrrole" /></td>
</tr>
<tr>
<td>Polyethylene dioxythiophene (PEDOT)</td>
<td><img src="image" alt="Polyethylene dioxythiophene" /></td>
</tr>
<tr>
<td>Poly(2,5 dialkoxyl) paraparylene vinylene (e.g. MEH-PPV)</td>
<td><img src="image" alt="Poly(2,5 dialkoxyl) paraparylene vinylene" /></td>
</tr>
<tr>
<td>Poly(3-alkyl) thiophene (P3AT) (R-methyl, butyl, etc.)</td>
<td><img src="image" alt="Poly(3-alkyl) thiophene" /></td>
</tr>
<tr>
<td>Polyfluorene (PFO)</td>
<td><img src="image" alt="Polyfluorene" /></td>
</tr>
<tr>
<td>Polyaniline (PANI)</td>
<td><img src="image" alt="Polyaniline" /></td>
</tr>
</tbody>
</table>

Figure 2.25 Molecular structures of some of the more important First and Second Generation semiconducting polymers.

2.7.1 Polyacetylene (PA)

Shirakawa's route to polyacetylene is an extension of the work first described by Natta et al (Figure 2.26). The initiator concentration used is significantly higher than that used in Natta’s solution phase work.

![Shirakawa's route to polyacetylene](image)

Figure 2.26 Shirakawa's route to polyacetylene.

The main advantage of Luttinger’s method over that developed by Shirakawa is that it allows the polymerization reaction to be carried out even in the presence of water and oxygen (Figure 2.27).
Kumada-Corriu coupling is a reaction between an alkyl or aryl Grignard reagent and an aryl or vinyl halocarbon catalyzed by nickel or palladium (Figure 2.28).\textsuperscript{48}

The Durham route involves ring opening metathesis polymerization (ROMP) that yields precursor polyacetylene with well defined chain-ends, molecular weights and polydispersities (Figure 2.29). The precursor polyacetylene can be thermally converted to the equivalent polyacetylene structures by elimination of hexafluoroxylene.\textsuperscript{49}
Durham’s two-stage route to polyacetylene may be obtained in high yield in a single step (Figure 2.30). Durham’s modified route overcomes the inconvenience of handling the reactant at low temperature.

2.7.2 Polyparaphenylenevinylene (PPV)

In its fully converted form PPV is totally insoluble and unprocessable, and as a result it is most commonly prepared via the soluble precursor polymer route developed
by Wessling. Polymerization of the bis-sulfonium salt yields the soluble precursor polymer that can then processed into a thin film, before thermal elimination to yield PPV. In the Wessling route, the base-catalyzed polymerization occurs in aqueous solution (Figure 2.31).\textsuperscript{51}

![Figure 2.31 Wessling precursor route to PPV.\textsuperscript{51}](image)

The Wessling precursor route is a well known method. However, the Wessling precursor is only soluble in water based solvent mixtures. Furthermore it is rather unstable and difficult to characterize. The new class of precursor polymers was used on PPVs (Figure 2.32). These polymers are soluble in a wide variety of organic solvents depending on the sulphoxy side chain.\textsuperscript{52}

![Figure 2.32 PPV synthesized from the precursor polymer.\textsuperscript{52}](image)
A method allows PPV to be obtained at low temperature from the bromide sulfonium salt polyelectrolyte (Figure 2.33).\(^5\)

\[
\begin{align*}
1a & \quad \text{\(285^\circ C/6\)h} \\
1b & \quad \text{\(100^\circ C/6\)h}
\end{align*}
\]

Figure 2.33 Synthesis of PPV from different precursor polymers at low temperatures.\(^5\)

The Gilch reaction is attractive from the industrial point of view, but suffers from the fact that its mechanism is not yet fully understood. This lack of mechanistic knowledge is mainly because the reaction proceeds very fast even at low temperatures. A more detailed mechanistic picture is proposed (Figure 2.34).\(^5\)

\[
\begin{align*}
1 & \quad \text{Activation of starting material} \\
2 & \quad \text{Dimension} \\
3 & \quad + n 2
\end{align*}
\]

Figure 2.34 Gilch polymerization leading to PPVs.\(^5\)
The Horner-Wittig reaction (Figure 2.35) allows the polymer to have an n character, i.e. the polymer better supports negative charges, but there are impurities of the catalyst remaining in the polymer.\textsuperscript{55}

Figure 2.35  Horner-Wittig reaction to preparation of PPV.\textsuperscript{55}

The withdrawing effect of -CN groups influences the electric properties so that this polymer, when used as active layer in a LED, gives the same external efficiency both with calcium and aluminum as cathode (Figure 2.36). This is the result of the modification of both the band gap and the electronic affinity.\textsuperscript{56}

Figure 2.36  CN-PPV Synthesis.\textsuperscript{56}

2.7.3 Polyalkylthiophenes (PAT)

A common approach to the synthesis the thiophene group involves the participation of 1,4-dicarbonyl compounds. In the thiophene case, the 1,4-dicarbonyl compound is reacted with a source of sulfur, usually from phosphorus sulfides such as
Lawesson’s reagent or bis-(trimethylsilyl)sulfide. 3,5-dihydro-1,2-dioxines can readily converted into 1,4-dicarbonyl compounds by treatment with an amine base via a Kornblum–de la Mare rearrangement (Figure 2.37).57

![Figure 2.37 Paal-Knorr synthesis of thiophene and pyrrole monomer.](image)

A synthetic method to synthesize regioregular, head-to-tail coupled poly(3-alkylthiophenes) using magnesium-halogen exchange (Grignard metathesis) called the GRIM method. The GRIM (Grignard metathesis) method is an important synthetic method that can easily provide regioregular, head-to-tail PATs (Figure 2.38).58

![Figure 2.38 Synthesis of PATs by the Grignard Metathesis (GRIM) Method.](image)
The unexpected regiocontrol displayed in the Grignard metathesis step makes this reaction very promising. This method produces regioregular poly(3-alkylthiophenes) very quickly, economically (avoiding expensive MgBr₂ and ZnCl₂ reagents), and in high yields (Figure 2.39).⁵⁹

![Synthesis of coupled, regioregular poly(3-dodecylthiophene).]  

Employing Ni-catalyzed polymerization, highly regioregular PATs were obtainable. The synthetic procedure followed is outlined for a series of PATs containing an oxygen atom in the side chain (Figure 2.40). The degree of regioregularity has been found to be in the range of 96%–100%.⁶⁰
This PAT reaction is based on a Pd(OAc)$_2$ Heck-like coupling of iodo-alkylthiophenes, in the presence of potassium carbonate as base and tetraalkylammonium salts. The macromolecules thus obtained are regioregular functionalized oligomers bearing an iodide at the chain end (Figure 2.41).}

PAT synthesis based on the coupling of 2,5-bis(chloromercurio)-3-alkylthiophenes and the alternating copolymerization with carbon monoxide to produce poly(3-alkylthienyl ketone)s (PATKs), a new class of polythiophene copolymers. These
syntheses represent the first use of organomercurials for making soluble, well-characterized polyarylenes and polyarylene ketones (Figure 2.42).  

![Chemical Reaction Diagram]

Figure 2.42 Synthesis of poly(3-alkythienyl ketone)s (PATKs).

This polymerization is based on the method of Kobayashi. 3-(Butylthio)thiophene was prepared in high yield (96%). The polymerization method based on Kobayashi’s procedure affords a regioregular HT poly[3-(butylthio) thiophene] soluble in all the common organic solvents (Figure 2.43). This synthetic route enables a soluble and characterizable polymer to be obtained.

41
The transition-metal-catalyzed C-C coupling technique was developed by Yamamoto et al. for the synthesis of poly(p-phenylene) and polymethylene. In this synthesis, transition metal acetylacetonates (metal 2,4-pentanedionates) were used as catalysts instead of metal halides and complexes because of better solubility in THF, thus avoiding polymer contamination that might be caused by the insoluble catalysts (Figure 2.44). The yield of poly(2,5-thienylene) strongly depends on the reaction temperature and the type of catalyst used. Low reaction temperature generally leads to poor yield of thiophene polymer. Nickel acetylacetonate is by far the most effective catalyst. The catalytic activity of the transition metal acetylacetonate shows the following trend $\text{Ni(AcAc)}_2 > \text{Fe(AcAc)}_3 > \text{Co(AcAc)}_2$.\(^{64}\)
The synthesis of a regioregular head-to-tail poly[3-(alkylthio)thiophene] in which the sulfur atom of the substituent is directly connected to the 3-position of the thiophene ring, and followed by a long alkyl chain. The regiocontrolled synthesis of polythiophenes provides a novel route to the highly electroconductive and regioregular HT poly(3-functionalized thiophenes) with a heteroatom S direct connection to the 3-position of the thiophene ring in the polymer units (Figure 2.45).
2.7.4 Polyfluorene (PFO)

Polyfluorenes are an important class of electroactive and photoactive materials. The exceptional chemical and physical versatility of these polymers provides an opportunity to expand their utility into areas involving electrical and optical properties. Figure 2.46 shows some synthetic methods of PFO.

Figure 2.46 Schematics of the polymerization of fluorenes from (a) Yamamoto, (b) Suzuki, or (c) Stille coupling reactions.
Route I provides an effective method to introduce the two same substituents into the C9 position of fluorene. Mullen has employed synthetic route I to introduce two bulky triphenylamine groups into the C9 position of fluorine (Figure 2.47). Chou has also exploited synthetic route I to achieve coupling of “Frechet-type” dendrons and POSS to fluorene. Route II mainly involves an addition reaction of the Grignard reagent to fluorenone and a Friedel-Crafts reaction of tertiary alcohol. Wong has achieved a series of efficient large-gap blue-light emitters and hole-transporting materials with highly morphological stability via route II (Figure 2.47).67

\[
\text{Route I} \quad \begin{array}{c}
\text{Fluorenone} + \text{Ar}_1 \\
\rightarrow \\
\text{Fluorene}
\end{array}
\]

\[
\text{Route II} \quad \begin{array}{c}
\text{Fluorenone} + \text{Ar}_1\text{-MgBr} \\
\rightarrow \\
\text{Fluorene}
\end{array}
\]

Figure 2.47 Two synthetic routes for the preparation of 9,9-diarylfluorene.67

Suzuki couplings between 2,7-dibromofluorene derivatives and fluorene derivatives bearing diboronic moieties allowed the preparation of many polymers, including the novel acidic conjugated polymers (Figure 2.48). The luminescent and electrical (through base-doping) properties of these conjugated polymers could be very useful for the development of light-emitting devices.68
The incorporation of pyridinyl unit into polymer backbone increases the electron affinity of the polymers, which not only makes the copolymers to be n-dopable and capable of better electron transportation, but also makes the polymers more resistant to oxidation (Figure 2.49).
Polyindenofluorenes with aryl substituents on the methine bridges have been prepared in high yields by a short, efficient synthetic route (Figure 2.50). These polymers, unlike previous indenofluorene-based polymers, show stable blue PL and EL emission. The improved stability is attributed to the greater resistance of the polymers to oxidation.

Figure 2.49  Synthesis of novel blue light-emitting alternating copolymers of 9,9-dioctylfluorene or 9,9-dihexylfluorene with various dibromopyridines through the Suzuki coupling reaction.\textsuperscript{69}
A new POSS (polyhedral oligomeric silsesquioxane)-substituted polyfluorene was synthesized from the nickel-catalyzed Yamamoto coupling reaction (Figure 2.51). The incorporation of the POSS group inhibited interchain interaction and fluorenone formation, which leads to reduce undesired green emission (>500 nm) of poly(dialkylfluorene)s and to improve the thermal stability of PFPOSSs.\textsuperscript{71}

\textsuperscript{*} i) (a) Ni(COD)\textsubscript{2}, COD, DMF, 2,2'-dipyridyl, toluene, 80 °C, 3 days; (b) 9-bromoanthracene, 80 °C, 24 h.
A novel starlike polyfluorene derivative, PFO-SQ, was synthesized by the Ni-catalyzed reaction of octa(2-(4-bromophenyl)ethyl)octasilsesquioxane (OBPE-SQ) and polydioctylfluoroene (PFO) (Figure 2.52). Incorporation of the silsesquioxane core into polyfluorene could significantly reduce aggregation as well as enhance the thermal stability.\textsuperscript{72}

Figure 2.52  Synthesis of PFO and PFO-SQ.\textsuperscript{72}
3.1 Material Synthesis

The molecular sample being experimented has the chemical nomenclature of 2,5-dihexyl-7,14-dipentylacenaphtho [1',2':6,7] naphtho [1,2-b:4,3-b'] dithiophene, shorthanded to PJ-C\textsubscript{6}H\textsubscript{13}. It was synthesized by the Pei Research Group of Peking University and used as received. The “PJ” portion of the name refers to Dr. Jian Pei since his laboratory synthesized this molecule, and the “C\textsubscript{6}H\textsubscript{13}” portion of the name refers to the atomic composition of the alkyl chains. Figure 3.1 shows the fluoranthene and benzo[k]fluoranthene units, Figure 3.2 illustrates the synthetic approach to the designed sulfur-hetero benzo[k]fluoranthene unit, and Figure 3.3 presents the final molecular structure that is being characterized.

Figure 3.1 Fluoranthene and benzo[k]fluoranthene units.
Figure 3.2 Synthesis of the sulfur-hetero benzo[k]fluoranthene molecule.¹

Figure 3.3 2,5-dihexyl-7,14-dipentylacenaphtho [1',2':6,7] naphtho [1,2-b:4,3-b'] dithiophene
3.2 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) was carried out using a TGA Q500 V20.7 Build 32. Approximately 1.272 mg of the molecule was used for the TGA experiment, and the sample was heated from 30°C to 600°C at a heating rate of 10°C/min under a nitrogen atmosphere. The temperatures at 2% and 5% weight loss of the molecule were obtained and used to estimate the thermal and thermo-oxidative stability of the samples, respectively. The temperature at the 2% weight loss of the sample serves as the upper limit for other experiments, such as differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXD).

3.3 Polarized Light Microscopy (PLM)

Optical properties were studied with a polarized light microscope (PLM, Olympus BH-2) coupled with a Mettler hot stage (FP-90). The sample used for PLM was prepared by melting it between a cover glass and a glass slide and then annealing at a certain temperature. PLM with a phase contrast lens confirmed single crystal formations before transmission electron microscopy (TEM) measurements. With the hot stage and a polarizer, PLM determined the existence of birefringence. The first order (full wave) retardation plate was utilized with the PLM to determine the optical sign of the birefringent crystals.

3.4 Differential Scanning Calorimetry (DSC)

The thermal properties of the phase transitions were characterized with a Perkin-Elmer PYRIS Diamond DSC with an Intracooler 2P apparatus. For the DSC experiment, 2.860 mg of sample was used, and the sample and reference pan weights were identical to each other (26.173 mg) to the precision of ±0.001 mg. The instrument was warmed up at
least one hour before the first run. The temperature and heat flow scales were calibrated at different heating and cooling rates (1-40°C/min) using standard materials. The baseline was subtracted from each run. The samples were heated above their melting points to eliminate thermal history. The cooling experiments were always carried out before the heating experiments, and the cooling and heating rates were identical (±2.5°C/min, ±5°C/min, ±10°C/min, ±20°C/min, ±40°C/min). The transition temperatures were determined by measuring onset and peak temperatures from both the cooling and heating experiments. The temperature range of the scans was between -50°C to 220°C, which was much lower than the 2% weight loss temperature of the molecule.

3.5 One- and Two-Dimensional Wide Angle X-ray Diffraction (1D WAXD and 2D WAXD)

One-dimensional wide angle X-ray diffraction (1D WAXD) diffraction patterns were obtained with a MultiFlex 40kW/30mA X-ray (Cu Kα radiation) generator coupled to a diffractometer. The wavelength of the radiation was 0.154 nm. The beam size for the MultiFlex 40kW was controlled by a divergence slit of 1°, a scattering slit of 1°, and a receiving slit of 0.3 mm. A hot stage was equipped to the diffractometer to study phase structure transitions as a function of temperature. The temperature range was conducted under vacuum between 35°C and 215°C at 5°C increments, first cooling and then heating. The samples were scanned across a 2θ range of 2.5° to 35° at a 2°/min scanning rate at every 5°C temperature increment, and each new temperature had a waiting time of 5 minutes before the angular scan to allow molecular arrangement stabilization. The peak positions were calibrated using silicon powder in the high angle region (>15°) and silver
behenate in the low angle region (<15°). Background scattering was subtracted from the sample patterns. The 2D WAXD experiments were performed by Dr. Hao-Jan Sun at The University of Pennsylvania. The samples were annealed and then scanned at each set temperature in this order: -56°C, -60°C, 50°C, 150°C, 190°C, 200°C, 210°C. Background scattering was subtracted from the sample patterns, and the resulting raw data was used for further analysis.

Before the 1D WAXD experiment, the PJ-C₆H₁₃ molecule was melted and mounted on an aluminum substrate at 215°C for 15 minutes, and then it was quenched in liquid nitrogen for 15 minutes. The sample for 2D WAXD analysis was melted and thermally annealed overnight at 185°C under an inert atmosphere before being sent to Dr. Hao-Jan Sun at The University of Pennsylvania. The crystal unit cells were determined by constructing reciprocal lattices.

3.6 Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED)

TEM experiments were carried out with a Philips Tecnai 12 using an accelerating voltage of 120 kV. Thin films were prepared by solution-casting a dilute 0.2 w/v % sample/dichloromethane solution on carbon coated cover glass or mica surface for TEM. For the benzoic acid samples, an additional thin layer of benzoic acid powder was applied on a carbon coated mica slide, and then the slide was rinsed with methanol. The thin films were heated above the melting point and then cooled down to a certain temperature to crystallize. After crystallization, the samples were removed from the cover glass or mica surface, floated on the surface of water, and collected on copper grids.
SAED patterns of samples were obtained using a TEM tilting stage (± 50°) to determine the crystal structure parameters. The camera length was set usually at 2.1 m, and most calibrations of the SAED d-spacings were carried out using evaporated thallium chloride (TlCl) standard, which has the largest spacing diffraction of 0.384 nm. For the benzoic acid samples, calibration of the SAED d-spacings was carried out using evaporated aluminum standard, which has the largest spacing diffraction of 0.234 nm.

3.7 Cerius² Computer Simulation

Computer refinement was conducted to find the solutions with the least error between the calculated values and the experimental results of the WAXD and SAED data. Crystallographic simulation was performed using Cerius² (Version 4.6) simulation software from Accelrys. The lowest energy conformation of a single small molecule was chosen as the starting conformation. Basic unit cell parameters determined by crystallographic experimental data from 2D WAXD and SAED experiments and the density measurement were used in order to build the crystal unit cell and determine the space group. The positions of atoms in this unit cell were judged by comparing their calculated diffraction patterns with those of experiments.
CHAPTER IV
IDENTIFICATIONS OF PHASE STRUCTURES AND TRANSITIONS OF A
BENZO[K]FLUORANTHENE DERIVATIVE

4.1 Thermodynamic Transition Properties and Structural Changes

The thermal gravimetric analysis (TGA) showed that the benzo[k]fluoranthene derivative PJ-C₆H₁₃ was thermally stable due to a 98% weight maintenance above 300°C. As shown in Figure 4.1, 98% weight retention occurred at 317°C, and 95% weight retention occurred at 335°C. Based on personal discussion, maximum temperature for DSC is (T₉₅₋₅₀°C), which for this molecule is at 285°C.

![TGA of PJ-C₆H₁₃](image)

Figure 4.1  TGA of PJ-C₆H₁₃
PLM helped determine the existence of crystallization, the existence of birefringence, and the optical sign of the birefringence. In Figure 4.2a, under unpolarized light shows that the molecular sample PJ-C₆H₁₃ exhibits some degree of crystallization. In Figure 4.2b, the polarizer determined that the PJ-C₆H₁₃ crystals exhibit birefringence. When the crystal was aligned 45° to the direction of the polarizer, the birefringence was maximized. At a position parallel to the polarizer, the birefringence of the crystal became minimal. This observation implies that the optical axis is indeed along the direction of π-π stacking, which dominates the 1D growth of the crystal. The colors in Figure 4.2c represent interference that is generated by the additive effects of the crystals and the first order retardation plate. The optical sign of birefringence for PJ-C₆H₁₃ crystals is negative because the crystals are green-blue in the southeast-northwest direction and yellow in the northeast-southwest direction.

Figure 4.2 PLM of PJ-C₆H₁₃ under (a) unpolarized light, (b) polarized light, (c) retardation plate
The DSC thermal diagrams of PJ-C₆H₁₃ at different cooling and subsequent heating rates (2.5-40°C/min) are shown in Figure 4.3 and Figure 4.4, respectively. DSC results showed a total of three phase transitions. The third phase transition at the lowest temperature range during some of the higher cooling and heating rates (-20°C/min, ±40°C/min) was not detected because of the experimental limit of the DSC instrument. The two phase transitions in the higher temperature ranges were the main focus in analyzing the DSC data, because the third phase transition at the lowest temperature range of -20°C to -40°C is hypothesized to be mostly alkyl chain fluctuations. The two higher temperature phase transitions were observed during the cooling rates and corresponding heating rates, which indicates that these thermal transitions are enantiotropic. The melting endotherm is over 30°C higher than the exotherm during cooling, commonly indicating a crystallization process.

![DSC Cooling](image)

Figure 4.3  DSC cooling of PJ-C₆H₁₃
The different cooling and heating rates were used to study the rate dependence of the thermal transition temperatures. For the 2.5°C/min cooling rate, the transition peak temperatures were -35.5°C, 157.8°C and 179.3°C, and the heats of transition were -17.8 kJ/mol, -9.9 kJ/mol, and -66.5 kJ/mol, respectively. For the 2.5°C/min heating rate, the transition peak temperatures were -25.2°C, 192.0°C and 206.2°C, and the heats of transition were 19.4 kJ/mol, 16.6 kJ/mol, and 68.3 kJ/mol, respectively. For increasing cooling rates, the peak transition temperatures consistently decrease, and the overall change in enthalpy eventually decreases, although it is inconsistent at times. For increasing heating rates, the peak transition temperatures consistently increase, and the overall change in enthalpy consistently decreases.

Although DSC experiments are sensitive to heat absorption and release events, this technique cannot provide direct information about structural changes and molecular interactions. Therefore, 1D WAXD experiments at different temperatures are utilized to identify the corresponding structural changes.
1D WAXD experiments were conducted to determine the structural transformations in the molecule. Figure 4.5 and Figure 4.6 show selected 1D WAXD patterns of the PJ-C₆H₁₃ molecule. PJ-C₆H₁₃ was measured at a cooling rate and subsequent heating rate between 35°C and 215°C at intervals of 5°C at a 2θ angle scanning rate of 2°C/min per fixed temperature. These figures show that within this particular temperature region, there are two phase transitions. During cooling, the phase transitions occur between 190°C-195°C and between 165°C-170°C. During heating, the phase transitions occur between 200°C-205°C and between 210°C-215°C. The two condensed phases of PJ-C₆H₁₃ exhibit sharp diffraction peaks at both high and low 2θ angles. This observation is direct evidence that the two phases are crystalline phases.

![1D WAXD Cooling](image)

Figure 4.5 1D WAXD cooling of PJ-C₆H₁₃
Figure 4.6 1D WAXD heating of PJ-C₆H₁₃

Figure 4.7 and Figure 4.8 compare the cooling and heating results, respectively, between 1D WAXD and DSC. These figures show that the DSC and 1D WAXD transition temperature ranges are consistent between each other; in addition, the two different phases are both crystalline.

Figure 4.7 1D WAXD and DSC cooling comparison of PJ-C₆H₁₃
4.2 Identifications of Crystal Structures

As shown by the DSC results earlier, the PJ-C₆H₁₃ molecule has three condensed phases: low temperature phase, intermediate temperature phase, and high temperature phase. Figure 4.9 shows TEM bright field image of a PJ-C₆H₁₃ crystal at room temperature, which is in its intermediate temperature phase. The long axis is designated as the \(a\)-axis, and the short axis is designated as the \(b\)-axis. All of the SAED patterns were taken in the intermediate temperature phase of the crystals.
Figure 4.9 TEM bright field image of a PJ-C$_6$H$_{13}$ crystal.

Figure 4.10 and Figure 4.11 are SAED patterns from crystals on the same copper grid. Figure 4.10 shows an untilted SAED pattern with the labeled orientations of $a^*$-axis and $b^*$-axis, and the $c^*$-axis is perpendicular to the $a^*$-$b^*$ plane. The angle $\gamma^* = 90^\circ$, and since by definition $\theta = 180^\circ - \theta^* = 90^\circ$. Figure 4.11 shows SAED tilting patterns along the $a^*$-axis of the angles $\pm 10^\circ$, $\pm 20^\circ$, $\pm 30^\circ$, and $\pm 45^\circ$; the positive angles are along the top row, and the corresponding negative angles are along the bottom row. When tilting along the $a^*$-axis, the positive tilt patterns are mirror images with their corresponding negative tilt patterns ($10^\circ$ tilt is mirror image of $-10^\circ$ tilt, etc.) in both $d$-spacing and intensity. Therefore, angle $\alpha^*$ between the $b^*$-axis and the $c^*$-axis equals $90^\circ$, and by definition, $\alpha = 90^\circ$. With angles $\gamma = \alpha = 90^\circ$, the unit cell is either a monoclinic or orthorhombic lattice, because $a^* \neq b^*$, and $\beta^*$ is unknown.
Figure 4.10 Untilted SAED pattern along the $a^\ast$-axis

Figure 4.11 SAED along the $a^\ast$-axis at (a) 10° tilt, (b) 20° tilt, (c) 30° tilt, (d) 45° tilt, (e) -10° tilt, (f) -20° tilt, (g) -30° tilt, and (h) -45° tilt

Figure 4.12a shows an untilted SAED pattern with the labeled orientations of $a^\ast$-axis and $b^\ast$-axis, and Figure 4.12b shows the SAED pattern of the same sample tilted to -10° along the $b^\ast$-axis. Tilting along the $b^\ast$-axis in order to ultimately determine $c$ and $\beta$ has proven to be difficult; numerous measurements have resulted in large
inconsistencies of the diffraction patterns and *d-spacing*. Some of these inconsistencies include tilting angles of different copper grids prepared from the same solution and tilting angles of different crystals within the same copper grid. Fortunately, another reliable method was used to determine *c* and the *β* angle, which was the addition of benzoic acid to the solution.\(^{75,81,82}\)

Figure 4.12 SAED along the \(b^*\)-axis at (a) 0° (no tilt) and (b) -10° tilt

Figure 4.13 shows a SAED pattern that added benzoic acid to the PJ-C\(_6\)H\(_{13}\) solution with the labeled orientations of *a* and *c*-axis, and the \(b^*\)-axis is perpendicular to the \(a^*-c^*\) plane. Benzoic acid causes epitaxial orientation of the PJ-C\(_6\)H\(_{13}\) crystals,\(^{75,81}\) so the crystal plane is oriented perpendicular to the copper grid. The *a* axis in Figure 4.13 has the same *d-spacing* as the earlier SAED patterns, so the other orthogonal axis is *c*-axis. The corresponding angle \(β^* = 90^\circ\), so angle \(β = 90^\circ\). Since it has been shown that all three angles are orthogonal \((α = β = γ = 90^\circ)\), the unit cell is determined to be orthorhombic. Further observation that \(β = 90^\circ\) is shown with 2D WAXD data.
In collaboration with 1D WAXD and SAED, the 2D WAXD patterns in Figure 4.14 were determined to have the $a^*$-axis lying along the meridian and the $b^*$-axis and $c^*$-axis lying along the equator. There are no apparent arcs off-center of the meridian and equator, so it was determined that the corresponding axes are orthogonal and the corresponding angles $\beta = \gamma = 90^\circ$. TEM tilting demonstrates that $\gamma = 90^\circ$ and $\alpha = 90^\circ$, benzoic acid demonstrates that $\beta = 90^\circ$, and 2D WAXD demonstrates that $\beta = 90^\circ$ and $\gamma = 90^\circ$. In conclusion, these multiple experiments give confirmation that all three orthogonal angles are $90^\circ$, and therefore the unit cell is orthorhombic. The reciprocal lattice lengths $a^*$, $b^*$, and $c^*$ and corresponding unit cell lengths $a$, $b$, and $c$ were then determined using the combination and collaboration of 1D WAXD, 2D WAXD, and SAED patterns.

In order to precisely identify the different phase structures of PJ-C$_6$H$_{13}$, the molecule was melted and thermally annealed overnight at 185°C under an inert atmosphere before being sent to Dr. Hao-Jan Sun at The University of Pennsylvania for 2D WAXD analysis. Figure 4.14 shows 2D WAXD patterns of PJ-C$_6$H$_{13}$ at -60°C, 50°C, and 210°C, respectively. The crystal structures were determined by analyzing the
diffraction arcs in the diffraction pattern. The unit cell of the lowest temperature phase in Figure 4.14a was determined to be orthorhombic with dimensions of $a = 0.51$ nm, $b = 2.21$ nm, $c = 3.44$ nm, and $\alpha = \beta = \gamma = 90^\circ$. There are four molecules in each unit cell, and the calculated crystallographic density is $1.140 \text{ g/cm}^3$. The experimental and calculated diffraction angles ($2\theta$) and $d$-spacing values of the lowest temperature phase are listed in Table 4.1.

Figure 4.14 2D WAXD of PJ-C$_6$H$_{13}$ at (a) -60°C, (b) 50°C, and (c) 210°C
Table 4.1 Crystallographic Parameters of the Low Temperature Phase in PJ-C₆H₁₃

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</table>

ᵃ Experimental values observed in Fig. 42a. ᵇ Calculated based on the orthorhombic cell of \(a = 0.51\) nm, \(b = 2.21\) nm, \(c = 3.44\) nm, and \(\alpha = \beta = \gamma = 90^\circ\).

Figure 4.14b shows the 2D WAXD diffraction pattern of the intermediate temperature crystalline phase. The experimentally observed and calculated \(d\)-spacings and diffraction angles (2θ) of the intermediate temperature phase are listed in Table 4.2. The unit cell of the intermediate temperature phase is identified as orthorhombic with dimensions of \(a = 0.52\) nm, \(b = 2.29\) nm, \(c = 3.45\) nm, and \(\alpha = \beta = \gamma = 90^\circ\). The calculated crystallographic density is 1.086 g/cm³ with four molecules in each unit cell. The experimentally measured density of this phase is 1.085 g/cm³. The structure of the intermediate temperature crystalline phase was confirmed by 1D WAXD diffraction peaks and by SAED patterns from single crystals at room temperature. Also, previous DSC and 1D WAXD studies confirm that at room temperature PJ-C₆H₁₃ is in the intermediate temperature crystalline phase.
Table 4.2 Crystallographic Parameters of the Intermediate Temperature Phase in PJ-C₆H₁₃

<table>
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<tr>
<th>(hkl) plane</th>
<th>2θ (degree)</th>
<th>d-spacing (nm)</th>
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<td>23.3</td>
</tr>
</tbody>
</table>

ᵃ Experimental values observed in Fig. 42b. ᵇ Calculated based on the orthorhombic cell of \(a = 0.52\) nm, \(b = 2.29\) nm, \(c = 3.45\) nm, and \(\alpha = \beta = \gamma = 90°\).

The untilted SAED patterns of the intermediate temperature phase single crystal samples at room temperature are shown in Figure 4.10 and Figure 4.12a. Because \(\gamma^* = \gamma = 90°\), these two untilted SAED patterns are from the [001] zone. After measuring numerous SAED patterns, it has been concluded that both the \(a^*-axis\) and the \(b^*-axis\) experience secondary scattering with respect to odd-numbered diffraction spots; the even-numbered diffraction spots always appear, while secondary scattering occasionally prevents extinction of odd-numbered diffraction spots. The benzoic acid SAED pattern in Figure 4.13b has been determined that the diffraction spots along the \(c^*-axis\) are even-numbered in collaboration with 1D WAXD and 2D WAXD data analysis; the odd-numbered diffraction spots are extinct. Perpendicular to the \(a^*-axis\), the first layer (1k0)
has a \textit{d-spacing} of 0.52 \text{nm}. Along the \textit{b*}-axis, even-numbered diffraction spots are consistent with a \textit{d-spacing} of 1.15 \text{nm} for (020). Along the \textit{c*}-axis, diffraction spots have a \textit{d-spacing} of 1.73 \text{nm} for (002). Therefore, the unit cell dimension lengths ($a = 0.52 \text{ nm}$, $b = 2.30 \text{ nm}$, $c = 3.46 \text{ nm}$) of the SAED patterns agree well with the 1D WAXD diffraction peaks and the 2D WAXD analysis of Figure 4.14b and Table 4.2.

The -10° tilted SAED pattern of Figure 4.12b was determined to be from the [101] zone. The [101] zone can be obtained by tilting the sample about 9° around the $b*$-axis, as calculated from the 2D WAXD unit cell dimensions of the intermediate temperature phase. Also, along the first diffraction layer (1k1) perpendicular to the $a*$-axis, the \textit{d-spacings} and intensities of the diffraction spots are different than from Figure 4.12a, suggesting a different diffraction zone. The even-numbered diffraction spots along the $b*$-axis can be assigned with a \textit{d-spacing} of 1.12 \text{nm} for (021), which is similar with the (021) diffraction calculated from the 2D WAXD analysis of Figure 4.14b and Table 4.2. The \textit{d-spacing} of the first layer diffraction spot (101) on the $a*$-axis is 0.50 \text{nm}, which is also similar with the (101) diffraction calculated from the 2D WAXD analysis. Therefore, the diffraction pattern of Figure 4.12b can be identified as the [101] zone. By analyzing untitled and tilted SAED patterns and 2D WAXD data, the crystallographic parameters of the intermediate temperature phase in PJ-C$_6$H$_{13}$ are confirmed.

Figure 4.14c shows the 2D WAXD diffraction pattern from the high temperature crystalline phase of PJ-C$_6$H$_{13}$. The structure of this phase was determined to be orthorhombic with dimensions of $a = 0.53 \text{ nm}$, $b = 2.31 \text{ nm}$, $c = 3.60 \text{ nm}$, and $\alpha = \beta = \gamma = 90°$. The crystallographic density was calculated to be 1.048 g/cm$^3$ with four molecules
in each unit cell. The experimental and calculated diffraction angles ($2\theta$) and $d$-spacing values are listed in Table 4.3.

Table 4.3  Crystallographic Parameters of the High Temperature Phase in PJ-C$_6$H$_{13}$

<table>
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<th>(hkl) plane</th>
<th>$2\theta$ (degree)</th>
<th>$d$-spacing (nm)</th>
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<td>calc$^b$</td>
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<tr>
<td>060</td>
<td>23.4</td>
<td>23.1</td>
</tr>
</tbody>
</table>

$^a$ Experimental values observed in Fig. 42c. $^b$ Calculated based on the orthorhombic cell of $a = 0.53$ nm, $b = 2.31$ nm, $c = 3.60$ nm, and $\alpha = \beta = \gamma = 90^\circ$.

All three crystalline phases are orthorhombic, and the $a$-, $b$-, and $c$-axis dimensions of all these phases do not change significantly. The density of the low temperature phase is the greatest, suggesting that the alkyl chains are also ordered in that crystalline phase.$^{80}$
Figure 4.15 shows the computer model of PJ-C₆H₁₃ used in the Cerius² computer simulation. Computer calculations can provide confirmation of the unit cell structure and detailed atomic positions in the unit cell. These calculations can then generate a detailed molecular packing scheme. Based on the unit cell dimensions of \( a = 0.52 \) nm, \( b = 2.29 \) nm, \( c = 3.45 \) nm, and \( \alpha = \beta = \gamma = 90^\circ \) from the SAED and 2D WAXD results, the Cerius² computer simulation suggested that \( P2_12_12_1 \) was the space group of the intermediate temperature phase. The \( P2_12_12_1 \) space group was chosen because the odd-numbered diffraction spots are extinct for all \( a, b, \) and \( c \) lengths, and the density measurement matched the number of molecules per unit cell. To examine whether this simulated packing scheme fits to the real structure, the calculated diffraction patterns were generated and compared with the experimentally obtained diffraction patterns.⁷⁹,⁸³

![Computer model of PJ-C₆H₁₃](image)

Figure 4.15  Computer model of PJ-C₆H₁₃

After the simulated unit cell with the space group of \( P2_12_12_1 \) was constructed, the energy minimization was applied and the results were displayed. Figure 4.16 shows the
molecular packing scheme suggested by the computer calculations from the \( a-c \) plane (the [010] zone, Figure 4.16a), the \( a-b \) plane (the [001] zone, Figure 4.16b), and the \( b-c \) plane (the [100] zone, Figure 4.16c). The computer calculated SAED patterns of the [001] zone and [010] zone based on this scheme are shown in Figure 4.17a and Figure 4.17b, respectively. Both Figure 4.17a and Figure 4.17b are similar with the experimental observations (Figure 4.10 and Figure 4.13b, respectively).

Figure 4.16  Computer simulation molecular packing using space group \( P2_12_12_1 \) along the (a) \( a-c \) plane ([010] zone), (b) \( a-b \) plane ([001] zone), and (c) \( b-c \) plane ([100] zone).

Figure 4.17  Cerius\(^2\) computer simulation diffraction patterns of PJ-\( C_6H_{13} \) at the (a) [001] zone (b) [010] zone.
CHAPTER V
CHARACTERIZATIONS OF OTHER SMALL MOLECULES

5.1 Field Effect Transistor Characterization of Other Small Molecules with the Same Benzo[k]fluoranthene Unit

Organic field effect transistor devices using molecular derivatives of the same benzo[k]fluoranthene unit as PJ-C₆H₁₃ (Figure 5.1a-d) as the active layers were fabricated in a top-contact configuration to analyze the materials’ charge transport characteristics via evaluation of the current-voltage response. Both newly deposited films and thermal annealed films of these similar benzo[k]fluoranthene derivatives were employed as active layers in FET devices after gold metal was vacuum-deposited as an electrode. All OFET devices were tested under ambient condition several times, and their performance remained persistent over two weeks (stored in air), indicating the high stability of these transistors based on these benzo[k]fluoranthene derivatives as shown in Figure 5.1a-d.¹
Three performance parameters were extracted from the FET $I-V$ response curves: the charge carrier mobility ($\mu$), current on-off ratio ($I_{on}/I_{off}$), and threshold voltage ($V_{th}$). Performance data are summarized in Table 5.1, and output and transfer curves of annealing films of Figure 5.1a-d are depicted in Figure 5.2. The threshold voltages of the transistor device based on annealed films of the benzo[k]fluoranthene derivatives from Figure 5.1a-d are -5.9, -12.6, 8.5, and -37 V, respectively. The best performance was realized from Figure 5.1d. Hole mobility in annealed films of Figure 5.1d could reach as high as 0.083 cm$^2$ V$^{-1}$ s$^{-1}$, along with the current on/off ratio of $10^6$, without further
device optimization. These results indicate that these fluoranthene-based compounds are promising candidates for organic field-effect transistor active layer materials.¹

Figure 5.2 Electrical characterization of OFETs based on Figure 5.1a-d after thermal annealing. (a), (c), (e), (g): output curves of Figure 5.1a-d taken at different gate voltages, respectively. (b), (d), (f), (h): transfer curves of Figure 5.1a-d at constant $V_D = -60$ V, respectively.¹

---

of the largest crystalline grains among these four compounds annealing at 270°C. After thermal annealing, the smallest crystalline boundary was ca. 0.1 µm, which may be responsible for the enhancement in OFET performance. The longest crystal had the length of ca. 100 µm.}

The thin film transistor devices, prepared by the vacuum deposition of the materials onto bare OTS-treated SiO₂/Si substrate, without introducing materials such as hexaphenyl Si substrate, clearly shows the one-dimensional nanostructure can be achieved through simple experimental results, which would be used as the TFT (thin film transistor) active layer. We carefully compared the diffraction patterns of the films before and after thermal annealing to understand the change of the films' crystallinity of organic thin films in transistor devices. X-ray diffraction experiments have been carried out to acquire insight into the microstructure characterization of films before thermal annealing. After thermal annealing. The diffraction peak at 2θ of 10° degree obviously decreased and would enhance OFET performance parameters of OFETs based on these films.

Table 5.1  \textit{d-spacing} calculated from 2θ diffraction peaks of films of Figure 5.1a-d and performance parameters of OFETs based on these films:

<table>
<thead>
<tr>
<th></th>
<th>pristine film</th>
<th>annealed film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(D) (nm)</td>
<td>(\mu) (cm² V⁻¹ s⁻¹)</td>
</tr>
<tr>
<td>1.16</td>
<td>5.2 × 10⁻³</td>
<td>-1.4</td>
</tr>
<tr>
<td>N.D.⁴</td>
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<td>-9.8</td>
</tr>
<tr>
<td>1.60</td>
<td>1.7 × 10⁻⁴</td>
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<td>1.46</td>
<td>7.7 × 10⁻³</td>
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5.2 Characterization of a Sulfur-Fused Heteroacene Derivative

The end molecule in Figure 5.3, shorthanded as LWJ-62, was synthesized in two-step reaction sequences of Negishi cross-coupling followed by FeCl₃ oxidative cyclization. This molecule exhibited good thermal and oxidative stability, with the thermal decomposition temperature of 400°C under nitrogen atmosphere. The thin film transistors with carrier mobility of 0.01 cm² V⁻¹ s⁻¹ was easily realized from this molecule.
Figure 5.3 Synthesis of LWJ-62, an heteroacene derivative\textsuperscript{3}

The LWJ-62 performed as a p-channel transistor. Before annealing, the transistors exhibited low mobility, on the order of \(10^{-4}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\), with an on/off ratio of \(5 \times 10^{3}\). However, after annealing the thin film at 230\(^\circ\)C for 20 min, the device performance was significantly improved. Figure 5.4 shows the output and transfer characteristics of OFET devices after thermal annealing. The on/off ratio was as high as \(10^{5}\). The calculated hole mobility was 0.012 cm\(^2\) V\(^{-1}\) s\(^{-1}\) from the transfer curve, two orders of magnitude larger than that before annealing.\textsuperscript{3}
Figure 5.4  Electrical characterization of OFETs after thermal annealing: (a) plots of $I_D$ vs $V_D$ at various gate voltages; (b) plots of $I_D$ and $I_D^{1/2}$ vs $V_g$ at constant $V_D = -60 \, V$.

The DSC thermal diagrams of LWJ-62 at different cooling and subsequent heating rates (2.5-40°C/min) are shown in Figure 5.5 and Figure 5.6, respectively. DSC results showed a total of three phase transitions. The three temperature phase transitions were observed during the cooling rates and corresponding heating rates, which indicates that these thermal transitions are enantiotropic.\(^7\)
The different cooling and heating rates were used to study the rate dependence of the thermal transition temperatures. For the 2.5°C/min cooling rate, the transition peak temperatures were 18.2°C, 59.3°C and 158.1°C. For the 2.5°C/min heating rate, the transition peak temperatures were 41.3°C, 65.3°C and 165.7°C. For increasing cooling rates, the peak transition temperatures consistently decrease. For increasing heating rates, the peak transition temperatures gradually increase.
1D WAXD experiments were conducted to determine the phase transitions in the molecule. Figure 5.7 and Figure 5.8 show selected 1D WAXD patterns of the LWJ-62 molecule. LWJ-62 was measured at a cooling rate and subsequent heating rate between 30°C and 180°C at intervals of 5°C at a 2θ angle scanning rate of 2°C/min per fixed temperature. These figures show that within this particular temperature region, there are two phase transitions. During cooling, the phase transitions occur between 155°C-160°C and between 65°C-60°C. During heating, the phase transitions occur between 90°C-95°C and between 165°C-170°C.

Figure 5.7 1D WAXD cooling of LWJ-62
Figure 5.8 1D WAXD heating of LWJ-62

Figure 5.9 shows a TEM bright field image of a LWJ-62 crystal at room temperature. Figure 5.10 shows an untilted SAED pattern with the labeled orientations of $a^*\text{-axis}$ and $b^*\text{-axis}$, and the $c^*\text{-axis}$ is perpendicular to the $a^*-b^*$ plane. Assuming the unit cell is orthorhombic, preliminary calculations result in the angle $\gamma^* = \gamma = 90^\circ$, $a = 0.69$ nm, and $b = 1.88$ nm. The unit cell of this molecule is either monoclinic or orthorhombic.

Figure 5.9 TEM bright field image of LWJ-62
Figure 5.10  Untilted SAED pattern of LWJ-62
CHAPTER VI
SUMMARY

A particular sulfur-hetero benzo[k]fluoranthene derivative with flexible alkyl side chains was synthesized as potential use in OFETs. This molecule’s chemical nomenclature is 2,5-dihexyl-7,14-dipentylacenaphtho [1',2' : 6,7] naphtho [1,2-b:4,3-b'] dithiophene, shorthanded as PJ-C₆H₁₃. In summary, the structural properties of PJ-C₆H₁₃ were determined with experiments used to identify the phase structures and transitions.

PJ-C₆H₁₃ was shown to be thermally stable via TGA, and its crystals displayed negative birefringence via PLM. Based on phase transition properties by DSC and phase structure identification by 1D WAXD, there were three phase transitions that were all crystal-crystal and enantiotropic transitions, and the crystalline structures were similar between transitions. The unit cells of the three crystalline structures were all orthorhombic (α = β = γ = 90°) with minor variations in the unit cell lengths, as determined by SAED and 2D WAXD patterns. The unit cell at the intermediate temperature phase was orthorhombic with dimensions of a = 0.52 nm, b = 2.29 nm, and c = 3.45 nm. The density measurement determined that there were four molecules per unit cell, and the space group was $P2_12_12_1$ as suggested by the Cerius² computer simulation. Field effect transistor characterizations of similar benzo[k]fluoranthene derivatives to PJ-C₆H₁₃ and several findings of an air stable heteroacene derivative were also presented.
REFERENCES


82. Hsu, C. -H. University of Akron, Akron, OH. Personal communication, 2013.