STUDIES OF ELECTRONIC TRANSPORT IN NOVEL SMECTIC AND
DISCOTIC LIQUID CRYSTALLINE ORGANIC SEMICONDUCTORS

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CHAPTER 1

INTRODUCTION

1.1 SINGLE CRYSTAL OR CRYSTALLINE SOLID

An ideal crystalline solid or a single crystal is defined as an atomic arrangement that has translational symmetry in all the three-dimensions. An object has translational symmetry if it looks the same after a particular translation. These materials, ideally, have a high degree of order throughout their entire volume. The structure of a crystalline solid is determined by studying the structure of its unit cell and then by stacking these cells. In general, a crystalline solid has defects, which are defined as deviations from the perfect crystalline lattice.

If a material consists of multiple grains of high degree of order over many atomic or molecular dimensions separated from one another by grain boundaries, it is called polycrystalline material. These ordered regions may vary in size and orientation with respect to one another.

Materials with an ordered structure extending only a few atomic or molecular lengths are amorphous or non-crystalline solids.

Two-dimensional representations of single crystal, polycrystalline, and amorphous materials are shown in Figure 1-1 [1].
1.2 ENERGY BANDS IN CRYSTALLINE SOLIDS

An isolated atom possesses a discrete set of electron energy levels or atomic orbitals. When several atoms are brought together to form a molecule, each energy level of the electron splits into a number of sub-energy levels. This number is proportional to the number of atoms. For a large number of atoms in a solid, the number of orbitals of electrons becomes so large that the difference in energy between two adjacent energy levels turns out to be very small. Consequently, the set of discrete energy levels is considered as a band of energy. The bands occupied by valence electrons are called valence bands and the upper bands with energies higher than valence bands are called conduction bands.

The forbidden gap between the valence band and the conduction band is called the band gap, which does not contain any energy level, no matter how many atoms are
aggregated. The band structure is the basis for differentiating between the three electrical material categories: metals, semiconductors and insulators as shown in Figure 1-2 [2].

![Figure 1-2: Typical energy bands of different materials (reproduced from [2]).](image)

In metals, the uppermost energy band is partly filled or the uppermost filled band and the next unoccupied band overlap in energy allowing the electrons in the uppermost band to find neighboring vacant states to move into, and thus behave as free particles. Thus a metallic material is conductive at any temperature [3].

In insulators, the valence band is completely filled and the conduction band is empty. The width of the band gap is so large that the electrons cannot jump from the valence band to the conduction band even at high temperature. Therefore, the insulator is always non-conductive. For example, at room temperature (300 K), the thermal energy ($k_B T$) is 0.025 eV, which is much smaller than its band gap width of a diamond, which is...
6 eV (see section 1.2.1). Hence, the diamond behaves as an extremely good insulator at room temperature.

In semiconductors, the width of the band gap is smaller than that in the insulator. The band gap for a semiconductor is in the order of 1 eV, e.g., 0.78 eV for germanium and 1.2 eV for silicon at 0 K. The energy needed for transition of the valence electron into a free state is between 0.1 to 3 eV in the majority of semiconductors and about 6 to 8 eV in insulators at room temperature [4].

At absolute zero, the semiconductor behaves as an insulator because the valence band becomes completely filled and the conduction band becomes empty. As examples, I will discuss the band structures of carbon atoms in the diamond (a crystalline form of carbon) and silicon atoms in the silicon crystal in the next section.

For a pure semiconductor and an insulator, the Fermi level lies near the middle of the forbidden energy gap, whereas for a metal, the Fermi level lies within the conduction band [3]. The electrical resistivity of a pure metal may be as low as $10^{-10}$ ohm-cm and that of an insulator may be as high as $10^{22}$ ohm-cm [7].

1.2.1 The energy band structure of the carbon atoms in diamond

In an isolated carbon atom, there are two electrons in the two discrete energy levels of the n=1 shell and four electrons in the eight discrete energy levels of the n=2 shell as shown in Figure 1-3 [2]. The remaining four energy levels in the n=2 shell are empty. When the interatomic distance is decreased, the discrete energy levels broaden out into bands, and eventually the bands corresponding to the sub shells 2s and 2p of the n=2
overlap. For further decrease in interatomic distance, splitting occurs between the upper four states and the lower four states which creates a band gap \( (E_g = 6 \text{ eV}) \) at the equilibrium spacing. At room temperature \((300 \text{ K})\), the thermal energy \((k_B T)\) is 0.025 eV, which is much smaller than \(E_g\) (6 eV). Hence, the diamond behaves as an extremely good insulator at room temperature.

Figure 1-3: The energy band structure of the carbon atoms in diamond. The dark circles represent filled state and the hollow circles represent the empty states (reproduced from [2]).

1.2.2 The energy band structure of the silicon atoms in its crystal form

In Figure 1-4, the x-axis represents the nearest neighbor spacing ‘\(a\)’ of the silicon atoms, which decreases from \(\infty\) for isolated atoms to inter-atomic equilibrium distance \(a_o\) (= 0.235 nm) for a silicon crystal. The y-axis represents the potential energy \(V(x)\) seen by a test electron.
Figure 1-4: The development of one-electron energy bands in silicon solid from the discrete energy levels in the isolated atom (reproduced from [5]).

Figure 1-4 [5] (a) shows the discrete energy levels in an isolated silicon atom with the valence levels -6.53 eV of 3p² and -13.57 eV of 3s². Figure 1-4 (b) shows shifting and broadening of energy levels of the isolated silicon atoms into bands of energy levels when (neutral) silicon atoms are moved close to each other to form a crystal. Figure 1-4(c) shows the periodic potential energy, V(x) seen by the test electron due to the Coulomb electrostatic force of the periodic arrangement of Si⁺⁺⁺ cores and the other valence electrons. The periodicity of this potential energy is a₀ inside the silicon bulk. It
rises towards the vacuum level, 0 eV, as the electron moves away from the Si surface into vacuum.

This figure also shows that as ‘α’ is decreased, the 3s and 3p valence electron energy levels are split and broadened into conduction and valence bands separated by the energy gap, $E_g$, e.g., 1.2 eV for silicon.

The upper and lower edges of the conduction band are marked as $E_c'$ and $E_c$, respectively. Similarly, the upper and lower edges of the valence bands are, marked $E_v$ and $E_v'$, respectively.

1.2.3 Band gap formation in crystalline solid

A band gap formation can be explained by the band theory, which is based on the one-electron approximation and the translational symmetry of the crystal [6]. The band theory in semiconductors is explained by two models [7]: the nearly free electron model and the tight binding model. The first model is particularly good for a high energy electron marked by 1 in the conduction band in Figure 1-4 and the second model is good for the low energy electron marked by 2 in the valence band. Here, I discuss only the nearly free electron model in detail.

1.2.3.1 Nearly free electron model

In an ideal crystal, i.e., free of defects and impurities for infinite dimension, the effective periodic potential $V(r)$ is translationally symmetric defined by $V(\vec{r}) = V(\vec{r} + \vec{T})$, where $\vec{T} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$. Here, $n_1$, $n_2$, and $n_3$ are integers and $\vec{a}_1$, $\vec{a}_2$, and $\vec{a}_3$ are
three non-coplanar primitive lattice translational vectors. A single electron in the solid is assumed to move in an effective crystal potential $V(\mathbf{r})$. In the first approximation, the crystal is considered as a perfect crystal with the molecules fixed at lattice points. Phonons and the departure from a perfect lattice are treated as small perturbations. I will discuss phonons in detail in the next section.

The general solution of the Schrödinger equation,

$$\frac{-\hbar^2 \nabla^2}{2m} \psi_{ka} + V(\mathbf{r})\psi_{ka} = E_\alpha(\mathbf{k})\psi_{ka}$$

(1.1)

with a periodic potential $V(\mathbf{r})$ is given by a Bloch function,

$$\psi_{ka}(\mathbf{r}) = u_{ka}(\mathbf{r}) \exp(i\mathbf{k}.\mathbf{r})$$

(1.2)

where $u_{ka}(\mathbf{r})$ is a periodic amplitude modulation function with periodicity of the crystal lattice vector; $u_{ka}(\mathbf{r}) = u_{ka}(\mathbf{r} + \mathbf{T})$ and $\exp(i\mathbf{k}.\mathbf{r})$ is a plane traveling wave. The symbols ‘m’ and ‘$\mathbf{k}$’ represent the free electron mass and the wave vector of the electron (or hole), and $\alpha$ denotes the band index, which allows the existence of more than one independent state with the same crystal momentum, $\mathbf{k}$. The condition for using the Bloch function is that the charge carrier must interact weakly with the lattice.

If the periodic potential $V(\mathbf{r})$ is very small or approaching zero, then one will get a plane wave solution, $\exp(i\mathbf{k}.\mathbf{r})$ with constant $u_{ka}(\mathbf{r})$. The Eigen value $E_\alpha(\mathbf{k})$ gives the band energy. At constant potential, the energy-momentum relationship of the plane wave is given by $E(k) = \frac{\hbar^2 k^2}{2m}$. However, the potential in the crystal is periodic instead of
constant due to the presence of atoms or atomic cores situated at lattice points, which are arranged in translationally symmetric form. It causes the continuous parabolic \( E - \vec{k} \) diagram of a free electron to break up into bands of allowed energy. The two adjacent allowed energy bands are separated by a band gap, where no traveling wave solutions exist. In one-dimension, equations (1.1) and (1.2) become, respectively,

\[
-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)
\]  

(1.3)

and

\[
\psi(x) = \exp(ikx)u(x)
\]  

(1.4)

Since, the potential energy \( V(x) \) and \( u(x) \) are periodic functions; they can be expanded into Fourier series as

\[
V(x) = \sum_v V_v \exp(iK_v x) \quad \text{and} \quad u(x) = \sum_n U_n \exp(iK_n x)
\]

Here \( V_v \) and \( U_n \) are the expansion coefficients with \( v = 0, \pm 1, \pm 2 \ldots \) and \( n = 0, \pm 1, \pm 2 \ldots \)

\( K_v \) and \( K_n \) are known as the translation vector of the reciprocal lattice in the \( \vec{k} \)-space and expressed by

\[
K_{m1} = 2\pi m \frac{a_2 \times a_3}{a_1.(a_2 \times a_3)} \quad K_{m2} = 2\pi m \frac{a_3 \times a_1}{a_1.(a_2 \times a_3)} \quad K_{m3} = 2\pi m \frac{a_1 \times a_2}{a_1.(a_2 \times a_3)}
\]

where \( a_1, a_2, \) and \( a_3 \) are the primitive vectors of the crystal lattice.

For simplicity, a cubic lattice of lattice constant \( a \) is considered here so that

\( K_v = 2\pi \frac{v}{a} \) and \( K_n = 2\pi \frac{n}{a} \) with ‘\( a \’ \) as the crystal lattice [5].
Figure 1-5: Energy vs. wavevector for an electron in a monatomic linear lattice of lattice constant, $a$. The energy gap $E_g$ shown is associated with the first Bragg reflection at $k = \pm \pi/a$ [7].

At $k = \pm \pi/a$, the wavefunctions are standing waves because at this particular value of $k$, the wavefunctions are made up of equal parts of wave traveling to the right or to the left. There are two standing waves $\psi(\pm)$ and $\psi(-)$, which are as follows.

$$\psi_-(x) = \psi(-) = 2iU_0 \sin\left(\frac{\pi x}{a}\right)$$ \hspace{1cm} (1.5)

$$\psi_+(x) = \psi(+) = 2U_0 \cos\left(\frac{\pi x}{a}\right)$$ \hspace{1cm} (1.6)

The detailed derivation of these two wave functions from equations (1.3) and (1.4), is found in appendix section 1.9.1.
The wave functions $\psi(+) \ (\psi(-))$ piles up electronic charges on the cores of the positive ions (in the region between the ions), thereby lowering (raising) the potential energy in comparison with the average potential energy seen by a traveling wave [7].

The probability density $\rho$ of a particle is proportional to $\psi^*\psi$. For a pure traveling wave,

$$\rho \propto \exp(-ikx) \exp(ikx) = 1$$

This is unity giving constant charge density throughout the space. But it does not remain constant for the standing waves. For the standing wave $\psi(+)\ in (1.6)$,

$$\rho(+) = |\psi(+)|^2 \alpha \cos^2 \left( \frac{\pi x}{a} \right)$$

This function piles up electrons on the positive ions centered at $x = 0, a, 2a...$ in Figure 1-6 where the potential energy is the lowest. For the other standing wave $\psi(-)$, the probability density is

$$\rho(-) = |\psi(-)|^2 \alpha \sin^2 \left( \frac{\pi x}{a} \right)$$
which concentrates electrons away from the ion cores. In Figure 1-6, the electron concentrations are shown for the standing waves $\psi(\pm)$, and $\psi(-)$, and for a traveling wave.

Two standing wavefunctions $\psi(\pm)$ and $\psi(-)$ given by equations (1.5) and (1.6) give two possible energies, $E_+$ and $E_-$ at $k = \pi/a$.

When one calculates the average values of the potential energy over these three charge distributions, the potential energy ($E_\pm$) of $\rho(\pm)$ is found to be lower than that of the traveling wave, whereas the potential energy ($E_-$) of $\rho(-)$ is found to be higher than the traveling wave. Therefore, the width of the energy gap, $E_g$, is formed if the energies of $\rho(-)$ and $\rho(\pm)$ differ by $E_g$.

Thus, the standing waves $\psi(\pm)$ and $\psi(-)$ pile up electrons at different regions, and therefore, possess different values of the potential energy. This is the origin of the energy gap.

1.2.3.2 The tight binding model

The approximation that starts with a linear combination of atomic orbitals (LCAO) is known as the tight binding model. When two separated neutral atoms are brought together to form a crystal, their charge distributions overlap and the Coulomb interaction between two atomic cores splits each energy level of the electrons into two separated energy levels.

For $N$ atoms, $N$ energy levels are formed for each energy level of the isolated atom and thereby spreading them into bands. It means each state of given quantum
numbers \((p, d, \text{etc.})\) of the free atom in the crystal is spread into a band of energies. The width of the band is proportional to the strength of the overlap interaction between neighboring atoms.

Consider two hydrogen atoms with wavefunctions \(\psi_A\) and \(\psi_B\), each with an electron in the 1s ground state. As the atoms are brought together, their wavefunctions overlap to form two possible LCAO, i.e., \(\psi_A \pm \psi_B\). Each combination (\(\psi_A + \psi_B\) or \(\psi_A - \psi_B\)) shares an electron with two protons. In \(\psi_A + \psi_B\), the electron spends most of the time in the region midway between the two protons experiencing the attractive potential of both protons at once and resulting in increase its binding energy. In \(\psi_A - \psi_B\), the situation is just a reverse of \(\psi_A + \psi_B\) case because the probability density of finding the electrons in midway between the nuclei vanishes resulting in no extra binding energy. Because of the presence of the extra binding energy in the former case, the electron in the hydrogen molecules gets two energy levels separated by the energy gap.

1.3 AMORPHOUS SEMICONDUCTOR (NON-CRYSTALLINE SOLID)

In covalently bonded materials, one type of defect concerns the atomic coordination, which occurs due to either over- or under-coordination with respect to the normal coordination [8]. When an additional covalent bond is formed between an already fully coordinated atom and another atom by utilizing a non-bonding lone pair electron, over-coordinated defects are formed. The over-coordinated defects are called floating bonds. Under-coordinated defects occur when one or more covalent electrons on an atom
cannot form covalent bonds with the neighboring atoms. Such non-bonding orbitals are simply regarded as dangling bonds.

In amorphous Si, there are also many weak and strained bonds of lengths between 2.5 and 3 Å, which are usually longer than a fully coordinated Si-Si bond of length 2.5 Å. The presence of strained and weak bonds gives tail states. The band tail states lie above the valence and below the conduction band edges.

In both crystalline and amorphous semiconductors, the electronic configuration of individual atoms is the same but the atomic configuration is different due to the lack of long range order in the amorphous semiconductor. However, an amorphous semiconductor has some fully coordinated atomic networking of short range order. Therefore, it has also delocalized states of the crystalline semiconductor with both the valence and conduction bands formed by the covalent bonding of atoms. The delocalized states in amorphous semiconductors are commonly known as extended states. The transport of charge carriers in the conduction and valence extended states of amorphous semiconductors are basically the same as that of charge carriers in the conduction and valence bands of crystalline semiconductor.

The edges separating the conduction and valence extended states with tail states are called the electron and hole mobility edges, respectively. Unlike crystalline semiconductors, the energy gap in amorphous semiconductors is not well defined due to the presence of tail states and dangling bond states.
1.3.1 Molecular orbitals

According to theories of atomic structure, the exact location of an electron in an atom cannot be determined. However, there is a probability of finding an electron at a given distance and direction from the nucleus. This probability is determined by the wave function for the electron, which is called an atomic orbital [9].

When two atomic orbitals of two atoms overlap with each other to form a bond, the atomic orbitals lose their identity and a pair of new orbitals is formed. The new orbitals are called molecular orbitals [10]. The two atomic orbitals give two molecular orbitals.

Bonding Molecular Orbital: One molecular orbital is derived by adding two in-phase atomic orbitals in the overlapping region. It is called a bonding molecular orbital and has a lower energy than the starting atomic orbitals. Electrons that occupy this molecular orbital provide electron density in the region between the nuclei and reinforce bonding between two nuclei. Thus, the probability of finding the electrons occupying this molecular orbital in that region is very high.

Antibonding Molecular Orbital: The other molecular orbital is derived by adding two out of phase atomic orbitals in the overlapping region, i.e., the wavefunctions of these orbitals combine out of phase, cancelling their amplitudes with each other and giving rise to a node. It is called an antibonding molecular orbital and has a higher energy than that of the original atomic orbitals.

The formation of molecular orbitals involves both s and p-orbitals and occurs in two different ways, called σ-bonds and π-bonds [11]. These two types of bonds can be
distinguished by the nature of their overlapping and their location with respect to the internuclear axis (a line which connects the nuclei of two bonded atoms) [12].

**σ-bond:** In σ-bond, the orbitals always overlap along the internuclear axis. Therefore, the bond is centered directly between the two nuclei and the electron densities will be high along the internuclear axis. The σ-bonds formed by s-orbitals are shorter, stronger and more stable than any other σ-bonds formed by two p-orbitals, or s-orbital and p-orbital. The antibonding molecular orbital corresponding to the σ-bond is denoted by the σ*-bond.

![Figure 1-7: The overlap of two s-orbitals to form σ-bond or σ*-bond.](image1)

Figure 1-7: The overlap of two s-orbitals to form σ-bond or σ*-bond.

![Figure 1-8: The overlap of s-orbital and p-orbital to form σ-bond or σ*-bond.](image2)

Figure 1-8: The overlap of s-orbital and p-orbital to form σ-bond or σ*-bond.

![Figure 1-9: The overlap of two p-orbitals to form σ-bond or σ*-bond.](image3)

Figure 1-9: The overlap of two p-orbitals to form σ-bond or σ*-bond.
Figure 1-10: An energy diagram for the bonding and antibonding combinations that are created upon formation of the hydrogen molecule from two hydrogen atoms (reproduced from [16]).

**π-bond:** In π-bond, two lobes of a p-orbital of one atom overlap in parallel with two lobes of a p-orbital of another atom forming two electron clouds above and below the internuclear axis. Only one of the orbitals’ nodal planes passes through both of the involved nuclei. The atomic orbitals of electrons in π-bond do not overlap in the region directly between atoms so that they do not interfere with the electrons in the σ-bond. The strength of the π-bond is proportional to the amount of overlap of two orbitals. The π-bonds are usually weaker than the σ-bonds.

Figure 1-11: The sideways overlap of two p-orbitals to form a π-bond and a π*-bond.
A single covalent bond between two atoms is always a $\sigma$-bond. A double bond involves one $\sigma$-bond and one $\pi$-bond. A triple bond involves another $\pi$-bond with its two electron clouds centered behind and in front of the two nuclei. The combination of $\pi$-bond and $\sigma$-bond is stronger than either bond by itself. Electrons in $\pi$-bonds are more diffused in space than those in the $\sigma$-bonds. The antibonding molecular orbital corresponding to the $\pi$-bond is denoted by the $\pi^*$-bond.

### 1.3.2 Hybrid orbitals

Hybrid orbitals are formed from the linear combination of a set of molecular orbitals. The different types of hybridized orbitals are categorized by the set of mixing orbitals. Only three types will be discussed here; (1) sp$^3$-hybrid orbitals (2) sp$^2$-hybrid orbitals and (3) sp-hybrid orbitals.

#### 1.3.2.1 sp$^3$-hybrid orbitals

The hybridization of one 2s and three mutually orthogonal 2p-orbitals ($p_x$, $p_y$, and $p_z$) creates a set of four equivalent degenerated sp$^3$-hybrid orbitals, which assumes a tetrahedral shape to attend the lowest possible energy state. For example, in methane, four sp$^3$-hybridized orbitals of the carbon atom separately form $\sigma$-bonds with s-orbital hydrogen atoms as shown in Figure 1-12. Mathematically the four hybridized orbitals ($\psi_1$, $\psi_2$, $\psi_3$, and $\psi_4$) are expressed as

\[
\psi_1 = s + p_x + p_y + p_z, \quad \psi_3 = s - p_x + p_y - p_z,
\]
\[
\psi_2 = s + p_x - p_y - p_z, \quad \psi_4 = s - p_x - p_y + p_z.
\]
where the coefficients have been so chosen that the lobes of these sp\(^3\)-hybrid orbitals point directly towards the apices of a regular tetrahedron as shown in Figure 1-12 (c).

![Figure 1-12: sp\(^3\)-hybrid orbitals in methane.](image)

(a) The s and p-orbitals of the carbon atom and their sp\(^3\)-hybrid orbitals. (b) Molecular structure of methane. (c) The four sp\(^3\)-hybrid orbitals pointing towards the apices of a regular tetrahedron (reproduced from [13]).

### 1.3.2.2 sp\(^2\)-hybrid orbitals

The sp\(^2\)-hybrid orbital is obtained by mixing one 2s and the two 2p-orbitals (p\(_x\) and p\(_y\)). This creates a set of three equivalent orbitals directed 120° apart from each other. The third unhybridized p-orbital (p\(_z\)) remains unchanged, perpendicular to the plane of sp\(^2\)-hybridized orbitals. The mathematical expression for sp\(^2\)-orbitals are expressed as
where the normalization of hybrid orbitals requires that \( c_1^2 + c_2^2 + c_3^2 = 1 \) and \( c_4^2 + c_5^2 = 1 \) [13]. For example, in the ethylene molecule (C\(_2\)H\(_4\)), one sp\(^2\)-hybrid orbital of one carbon atom overlaps with one sp\(^2\)-hybrid orbital of another carbon atom to form a \( \sigma \)-bond. The remaining pair of sp\(^2\)-hybrid orbitals from each carbon atom overlaps with s-orbital of hydrogen atoms to form \( \sigma \)-bonds. The sp\(^2\)-orbitals generate highly localized electron density between any two carbon and hydrogen atoms in the nodal plane coinciding with the plane of the molecule.

Figure 1-13: sp\(^2\)-hybrid orbitals in ethylene.

(a) The s and p-orbitals of a carbon atom and their sp\(^2\)-hybrid orbitals. (b) The sp\(^2\)-hybrid orbitals. The third unhybridized p\(_z\)-orbital, which would be perpendicular to the plane of the paper, is not shown in the figure. (c) \( \sigma \) and \( \pi \)-bonds in an ethylene molecule formed by sp\(^2\)-hybridization and p-orbital.
The unhybridized p-orbitals overlap to form the $\pi$–bond as shown in Figure 1-13(c) and establish a delocalized electron density above and below the plane of the carbon atoms when another $\pi$–bonds and/or lone pairs or empty p-orbitals are available.

In many organic semiconductors, the overlapping of the unhybridized p-orbitals and the $\text{sp}^2$-hybridized orbitals in molecules form alternate single and double carbon-carbon bonds. Benzene, naphthalene, anthracene, tetracene and pentacene molecules are examples of such compounds.

![Energy diagram of molecular orbitals for carbon-carbon bonds in ethylene](image)

Figure 1-14: An energy diagram of the molecular orbitals for the carbon-carbon bonds in ethylene.

It has four C-H $\sigma$-bonds and one C-C $\sigma$-bond generated by the combination of three $\text{sp}^2$-hybrid orbitals on each carbon atom, and one C-C $\pi$-bond generated by combination p-orbital on each carbon atom. Similarly, according to the molecular orbital theory, there also have to be four C-H anti sigma ($\sigma^*$) bonds, one C-C $\sigma^*$-bond and one C-C anti pi ($\pi^*$) bond [14].
1.3.2.3 sp-hybrid orbitals

The sp-hybrid orbital is obtained by mixing one 2s orbital and one of three 2p-orbitals, which result two linear sp equivalent orbitals directed 180° apart from each other, and two remaining unchanged p-orbitals. The two remaining unhybridized orbitals are responsible for the π-bond formation. For example, in acetylene (C\textsubscript{2}H\textsubscript{2}), the overlapping between one sp–hybrid orbital from each carbon atom forms a σ-bond and similarly, the overlapping between unhybridized p-orbitals form two π-bonds. The remaining one sp-hybrid orbital forms another σ-bond with s-orbital of hydrogen atom.

![Diagram of sp-hybrid orbital in acetylene](image)

Figure 1-15: sp-hybrid orbital in acetylene.

(a) The s and p-orbitals of the carbon atom and their sp-hybrid orbitals. (b) The figure shows sp-hybrid orbitals and two unhybridized p\textsubscript{x}-orbital and p\textsubscript{y}-orbital. (c) The figure shows the chemical bonding in acetylene (ethyne) (C\textsubscript{2}H\textsubscript{2}) molecule which consists of sp–sp overlap between the two carbon atoms forming a σ-bond and two π-bonds formed by p–p overlap.
1.3.3 Benzene molecule

The understanding of $\pi$-electrons system and the structure of the benzene molecule is very closely related to the physics of charge carrier conduction in organic semiconductors, e.g., organic semiconductors like naphthalene, anthracene, tetracene, pentacene consist of two, three, four and five fused benzene rings, respectively.

(a) Free electron model for benzene. The energy level of the molecular orbitals for benzene showing that the bonding orbitals are completely filled by the six available $\pi$ electrons [16, 15]. (b) $\sigma$ and $\pi$-bonds in the benzene molecule. The rings above and below the plane show the delocalized $\pi$-electrons [14].

According to the Hückel’s rule, a molecule is aromatic when it has a planar, uninterrupted, and cyclic $\pi$-electron system that contains $4n+2$ $\pi$-electrons, where $n = 0, 1, 2, 3, 4$ and so on [16]. Hückel found that the resulting molecular orbitals (MOs) in aromatic molecules have relative ordered energy values as shown in Figure 1-16, where the MOs of the lowest energy are the bonding orbitals and the MOs of the highest energy
are the antibonding orbitals. In the molecule, if the antibonding orbitals are empty and the bonding orbitals are filled completely by an odd number of pairs, i.e., $2(2n+1)$ or $2, 6, 10, 14$ and so on, $\pi$-electrons, such molecule become more stable than other unsaturated compounds that contain carbon-carbon double bonds or triple bonds such as in alkenes or alkynes.

Benzene has six carbon atoms, which give three $\pi$-bonding orbitals and three $\pi$-antibonding orbitals. Its six $\pi$-electrons will fill all three $\pi$-bonding orbitals completely leaving all three $\pi$-antibonding orbitals vacant. Therefore, the benzene molecule is more stable than other unsaturated molecules.

Another reason for the stability of the benzene molecule is the delocalized $\pi$-electron system as shown in Figure 1-16 (b). It can be interpreted in terms of binding energy. The $\pi$-electrons in the molecule experience two types of energies; (i) the Coulomb energy and (ii) the resonance energy. The Coulomb energy is the binding energy of an electron in a 2p-orbital and is constant for all carbon atoms. The resonance energy is the binding energy of an electron in the field of two or more nuclei. This energy will be zero if the electron is localized a single nucleus and non-zero if the electron is delocalized around the multiple nuclei [17]. Since the $\pi$-electrons are delocalized in benzene molecules, the binding energy of a $\pi$-electron is more than that in a fixed alternating single and double bonding system making the benzene molecule more stable than the system.
1.4 CHARGE TRANSPORT MECHANISM

The charge carrier transport properties in materials depend on the packing of the chains, molecular ordering, the density of impurities and structural defects [18]. The transport mechanism in the material can be described mainly as the result of either a band transport or a hopping transport.

1.4.1 Band transport theory

The charge carrier transport in a molecular single crystal with substantial mobility, such as pentacene, at low temperature can be treated by the band transport mechanism [19]. In the band transport mechanism, there are weak interactions between delocalized charge carriers and the lattice phonons. This means the carriers are occasionally scattered by phonons so that the mean free paths are much longer than the lattice constant [20,21]. The requirement for this mechanism at room temperature is a bare bandwidth or an effective bandwidth of at least 0.1 eV [22], where the positive (or negative) charge carriers are fully delocalized.

When the temperature is increased, the scattering of charge carriers by lattice phonons increases resulting in a decrease in the mean free path and hence a decrease in the charge carrier mobilities. At an elevated temperature when the mean free path for the charge carrier becomes less than the lattice constant, the charge carrier is expected to be localized and its transport is operated by polaron hopping mechanism [23], which is discussed in the section 1.4.2.
The charge carrier mobility, which is defined by the drift velocity per unit electric field, in a single crystal without defects can be very high and it decreases with increasing lattice imperfection [6]. The motion of a charge carrier in a crystal under the action of an external electric field is analyzed by assuming the charge carrier as a free particle with a mass different from its original free electron mass. The new mass is called the effective mass denoted by \( m^* \). It is defined in terms of the wave number \( k \) (\( k = 2\pi/\lambda, \lambda \) is the de Broglie Wavelength) as

\[
m^* = \hbar^2 \left( \frac{d^2 k}{d\epsilon^2} \right)
\]

The behavior of such a quasi-particle is explained by energy band theory and the Bloch wave function.

In band theory, the mobility of the charge carrier is calculated by using Einstein’s equations (see equations (1.38) and (1.39) of the appendix section 1.9.2). It is given by

\[
\mu = \frac{eD}{k_BT}
\]

where the diffusion constant \( D = \langle \tau_R \nu^2 \rangle \) [24], and

\[
\mu = \frac{e}{k_BT} \langle \tau_R \nu^2 \rangle
\]

where \( \tau_R \) is a relaxation time, \( \nu \) is the velocity of charge carrier, and the symbol \( \langle \ \rangle \) indicates the thermal averaging [25]. The mobility, \( \mu \), is related to the drift velocity of charge carriers by \( \nu = \mu E \).
For the wide bandwidth case, where the energy bandwidth \( W > k_B T \) and the electric field is zero, the kinetic energy of the charge carrier is given by

\[
\frac{1}{2} m' \nu^2 = \frac{1}{2} k_B T
\]

\[
\nu^2 = \frac{k_B T}{m'}
\]

(1.11)

A large value of the effective mass corresponds to a low mobility. From equations (1.10) and (1.11), the mobility of the normal (wide band) semiconductors can be written as

\[
\mu = \frac{e\tau_R}{m'}
\]

(1.12)

For the narrow bandwidth, where \( W < k_B T \), all \( k \) states in the band are thermally occupied instead of just the minimum energy states of the band.

1.4.2 Hopping transport theory

The hopping transport theory generally applies in the presence of a significant static disorder, dynamic fluctuations, and/or impurities [26]. In this section, the polaron hopping conduction will be discussed.

POLARON: When excess charge carriers interact with the lattice of a solid, a distortion in the atomic network around the charge carriers in the solid occurs. Thus, the charge carriers are trapped by the potential well of the resultant lattice polarization and the energy of the system of charge carriers and displaced atoms is lowered. The
combined effect of lattice distortion and lowering of energy is such that the charge carriers move slower than free particles and the distortion also moves along with it as particles dressed with vibronic polarization clouds. The charge carrier surrounded by a distorted lattice is called a polaron. There are two types of polaron: large and small defined by the conditions $d > a$ and $d \sim a$ respectively. Here, $a$ is a lattice constant and $d$ is a electron-phonon correlation length, which represents the polaron size [27].

Figure 1-17: Polaron-The displacements vary slowly with position and one may imagine an electron wave packet spread over many lattice distances moving with its accompanying distortion through the crystal [28].

A free electron, a polaron, and a self-trapped electron refer to the same particle but traveling in different types of crystalline media. It is like a ball (electron) rolling from a concrete surface that reaches a sandy beach (becomes a polaron) and then falls into mud and stops (becomes self-trapped electron). In this sense, zero coupling between electron and phonon means a very rigid crystalline structure, weak coupling means less rigidity and strong coupling means a soft-crystalline structure. Generally, the strength of the charge carrier-phonon interaction is considered linearly proportional to the atomic displacement coordinates. In crystalline solids, atomic displacements due to vibrations can be expanded in terms of a phonon wave vector.
A hopping theory for the transport of a charge carrier interacting with molecular vibrations was introduced by Holstein polaron model. In this model, Hamiltonian for single-electron problem in one dimensional momentum space is given by [29].

\[
\hat{H} = -2t \sum_k \cos(k) c_k^\dagger c_k + \omega_0 \sum_k b_q^\dagger b_q - \frac{g}{\sqrt{N}} \sum_{k,q} c_{k+q}^\dagger c_k \left( b_{-q}^\dagger + b_q \right)
\]  

(1.13)

where \( N \) is the number of lattice sites (\( N \rightarrow \infty \)). \( c_k^\dagger \) and \( b_q^\dagger \) are the creation operator for the electron and phonon, respectively. The electron is described in the tight-binding nearest-neighbor approximation. \( t \) is the electron hopping energy, \( g \) is the electron-phonon coupling energy. Here \( \omega_0 \), the phonon energy, is taken as the unit of energy. Besides \( t/\omega_0 \) and \( g/\omega_0 \), the two other parameters used are the binding energy of the polaron \( \epsilon_p = g^2/\omega_0 \) and the dimensionless parameter \( \lambda = \epsilon_p/t \). Unlike \( g \), \( \epsilon_p \) and \( \lambda \) are adiabatic parameters in the sense that they do not depend of the mass of the nucleus.

In this model, the coupling was taken to be linear in the phonon coordinates [21,30] and the behavior of the one dimensional polaron is described by distinguishing between adiabatic and nonadiabatic contributions. The polaron dynamics are adiabatic when the electron follows the motion of the lattice deformation almost instantaneously and nonadiabatic when the electron is temporarily detached from the deformation. The adiabatic regime is represented by a large value of the ratio \( t/\omega_0 \) (i.e. fast electron vs. slow lattice) whereas the nonadiabatic regime is represented by a small value of the ratio \( t/\omega_0 \) (i.e. slow electron vs. fast lattice). The Holstein model contains the essential physics governing the polaron formation in the presence of a coupling between electrons and...
phonons. A strong coupling is distinguished from a weak coupling by the size of the electron-phonon spatial correlation, which is reduced to a single lattice site in the strong coupling limit so that one obtains heavy, strongly pinned small polaron states. The
Holstein polaron exhibits fundamentally different behaviors from weak coupling to strong coupling, from adiabatic to nonadiabatic, and from large to small polarons.

The relationship between various aspects of polaron states can be specified by five regimes in phase diagram as shown in Figure 1-18: the weak-coupling regime, the regime of large adiabatic polarons, the regime of small adiabatic polarons, the transitory regime of small pinned polarons for which the adiabatic and nonadiabatic contributions are inextricably mixed in the polaron dispersion properties, and the regime of small nonadiabatic polarons.

In Figure 1-18, the blue regime under the solid curve, \( g^2 \sim 1 + 2 \sqrt{t} \) is the weak coupling regime of large nonadiabatic polaron. In this regime, the electron is weakly dressed by the phonon cloud and the polaron binding energy (\( \Delta_{pol} \)) is smaller than phonon energy (\( \hbar \omega_0 \)). In this regime, \( d \) is independent of \( g \) and the both local and translational dynamics of the polaron are nonadiabatic. The local dynamic means the local interaction between the electron and the phonon. The translational dynamic means the joint motion of the electron and the phonon field along the lattice.

The non-adiabatic to adiabatic crossover in the local dynamics is represented by the solid curve (\( g^2 \sim 1 + 2 \sqrt{t} \)).

The green regime between the solid curve and the straight line formed by circles (\( g \sim 1 + \sqrt{t} \)) is the regime of large adiabatic polarons. In this regime, the polarons behave as free particles with large effective mass and the lattice is treated classically as continuum approximation because the linear dimensions of the polaron are large enough
compared to a lattice spacing so that the lattice deformation due to the polaron movement is not noticeably changed by the lattice discreteness.

The straight line \((g \sim 1+\sqrt{t})\) drawn by the large circles represent polaron self-trapping because it is the crossover regime between localized polarons (above the circles) and delocalized polarons (below the circles). The medium circles \((1 \leq t \leq 20)\) in the line correspond to the white area, in which the polaron hopping involves a mixture of adiabatic and nonadiabatic processes. The smallest circles in the line corresponding to \(t \leq 1\) and \(g \sim 1\) is the crossover between the weak-coupling regime and the regime of small nonadiabatic polarons. The thick dashed curve close to this line denotes the crossover between large polarons and small polarons.

The yellow regime between the straight line formed by circles \((g \sim 1+\sqrt{t})\) and the dotted curve \((t\sim g)\) is the regime of small adiabatic polarons. In this regime, the translational dynamic is adiabatic because the electron and the lattice deformation hop together to the neighboring site.

The red regime, the left side of the dot-dashed line \((t \sim 1)\), is small nonadiabatic polaron regime. In this regime, the translational dynamic is nonadiabatic because the electron is too slow to follow the lattice deformation such that the electron hops to the neighboring site by detaching itself from the lattice deformation field [29].

In hopping theory, the charge carrier mobilities are usually calculated by the hopping rate \((\nu)\) between two molecules at a distance ‘\(a\)’ apart. The diffusion constant \(D\) in the hopping theory is expressed as [31]

\[
D = a^2\nu
\]
From equations (1.14) and (1.37), one gets Einstein’s relation

\[ \mu = \frac{e\alpha^2 v}{k_B T} \]  

(1.15)

1.5 ORGANIC SEMICONDUCTORS

An organic semiconductor (OS) is considered one of the most useful candidates in the fabrication of electronic devices such as organic field effect transistors (OFETs), photovoltaic cells and organic light-emitting diodes (OLEDs) [32]. They were first utilized in the industrial fabrication of organic photoconductive coatings for xerographic photoreceptors (OPCs) [33]. They are used commercially in small displays.

Organic semiconductors are aggregations of molecules, which are held together often by a weak forces. Therefore, they are fundamentally different from a conventional inorganic semiconductor, in which the atoms are held by covalent bonds. However, the atoms within the molecule of an organic semiconductor are held together by covalent bonds like \( \sigma \)-bonds and \( \pi \)-bonds. The binding force between two molecules in an organic semiconductor is relatively weak, which makes the resulting electronic bandwidths narrow. The bandwidth for such case is expected to be about 0.01 to 0.1 eV [22], which is the order of thermal energies, phonon energies and polaron binding energies. In inorganic semiconductors, the electronic bandwidths are broad and larger than the other energies mentioned above. The electron-phonon coupling is weak in the inorganic semiconductor, whereas it is strong in the organic semiconductor. The mean free path for the charge
carrier in an inorganic semiconductor may be several times the lattice constant whereas it is of the order of the lattice constant in an organic semiconductor. The charge carrier mobility in the inorganic semiconductor is often higher than that in the organic semiconductor.

In a single crystal, a close coupling of the $\pi$-systems of the molecules can produce remarkable transport properties, including band transport up to room temperature [19]. The charge transport mechanism in polycrystalline and amorphous layers show hopping transport [34, 33, 35].

Some examples of organic semiconductors are the derivatives of benzene, phenylene, triphenylene, naphthalene and thiophene [36]. These materials show a special potential for the generation and the transport of charge carriers that can be used in electronics and optoelectronic devices.

1.5.1 From single crystal to liquid crystal as an organic semiconductor

Single crystals of organic semiconductors may possess high mobilities. However, there are practical limitations in using the single crystals due to the difficulty in the growth and the processing of defect free bulk single crystals and their incorporation into device structures. In an actual crystal, different types of defects are always present, e.g., intrinsic point defects (vacancies, interstitials), extended defects (dislocations, stacking faults, lattice distortions, grain boundaries) and chemical impurities (substitutional atoms or interstitial atoms or molecules).
For device applications such as photoreceptors for xerographic copiers and organic electroluminescent devices, organic semiconductors are required to have large area uniformity for the charge carrier transport. It is very difficult to achieve such uniformity in the single crystals. This type of uniformity can be achieved only by films of polycrystalline, amorphous, or liquid crystalline semiconductors.

These amorphous semiconductors have become increasingly important because of their significance in many diverse applications including inexpensive solar cells, thin film transistors, image scanners, electrophotography, optical recording, gas sensors, and switching and memory elements.

However, transport of charge carriers in both organic and inorganic materials suffers greatly during the process of conversion from single crystal to amorphous solid. In the case of silicon, its charge carrier mobility decreases from > 1000 cm$^2$/Vs to ~ 1 cm$^2$/Vs in its amorphous form. An example of an organic material is pentacene. According to Akinori Saeki et al. [37], the photoinduced carrier mobility of pentacene thin films prepared by thermal vapor deposition was found to be around 0.7 cm$^2$/Vs whereas its charge carrier mobility in a highly purified single crystal form was to be found 35 cm$^2$/Vs. This is a huge deterioration in the charge carrier mobility in pentacene when its form is changed from the single crystal to the deposited amorphous material. This is the problem encountered using amorphous or non crystalline organic semiconductors.
To overcome this problem, liquid crystal materials were developed as alternative organic semiconductors with both a liquid-like structural flexibility and a crystal-like molecular arrangement that favors the large area uniformity.

1.6 LIQUID CRYSTALS

A liquid crystal (LC) is substance that has properties in between liquid and crystal. The difference between crystals and liquids is that the crystals have long-range order of the molecular positions as well as their orientations in three dimensions whereas in the liquids they do not [38].

Liquid crystals are two types: thermotropic and lyotropic on the basis of their phase transition process. Thermotropic LCs exhibit phase transitions as the function of temperature only, whereas the lyotropic LCs exhibit phase transitions as the function of both the temperature and its concentration in a solvent. However, the lyotropic LC is not included in this dissertation.

Liquid crystals can be also divided into two types on the basis of the mesogen’s structure. The LC of rod-like mesogen is called calamitic LC and the LC of disk-like mesogen is called discotic LC.

1.6.1 Calamitic liquid crystals

Calamitic liquid crystals are formed by the rod-like molecules with their orientation along a direction of their longer axis. A typical structure of a calamitic LCs is schematically shown below.
Where x and x' are side groups, A and B are aromatic rings and, L is a linking group. The length and flexibility of the side group affects the type of LC phases and the phase transitions. Some common side groups are alkyl groups ($C_nH_{2n+1}$) and alkoxy groups ($C_nH_{2n+1}O$). Most LC mesogens contain two or more aromatic rings, those aromatic rings can be benzene, phenyl, pyridine, thiophene, etc. or combinations of these. The linking group makes an important contribution to the phase transition and physical properties such as the birefringence. The liquid crystal molecules are generally 2 - 4 nm in length and 0.4 - 0.6 nm in width. Phenyl naphthalene and 2-phenyl benzothiazole derivatives are examples of the calamitic LCs, which are promising electronic materials in practical applications [39].

Calamitic liquid crystals are divided into different mesophases on the basis of translational and orientational order of molecules, i.e., nematic phases and smectic (Sm) mesophases. The nematic mesophase is characterized by molecules, which tend to orient along a particular direction with long range orientational order but without any particular positional order. The preferred direction is characterized by an average direction of all molecules, which is called the director.
The smectic mesophases (Sm) can be subdivided into a number of different types. Some of them are SmA, SmB (hexatic), SmB (crystal), SmC, SmE, SmF, SmG, SmH, SmI, SmJ, SmK, etc.

In SmA, the molecules are located within the liquid-like layers with the director perpendicular on average to the plane of the layer. Therefore, the layer thickness, ‘d’, is roughly the same as the molecular length ‘l’. In SmC, the molecules in the layers are parallel and tilted in arrangement with respect to the normal of the layers by a tilt angle θ. Hence the layer thickness of SmC is \( d = l \cos θ \). In both smectic phases, the molecules have no particular positional order within the layer. There is a liquid-like motion of the rods in each layer and no correlation of the molecular positions from one layer to the next. The layers can easily slide.

In SmB (hexatic), SmF, and SmI, there is also one-dimensional order, which forms the layer structure as SmA and SmC phases do. Additionally, there is also two-dimensional translational order within the layers and two-dimensional bond symmetry. The molecules of this class of liquid crystals are arranged into a hexatic lattice. In SmB (hexatic), the molecules within the layers are aligned perpendicularly to the layers, but the molecules of SmF and SmI phases within layers are tilted with respect to the layer normal by a tilt angle. The azimuthal angle of the tilt direction or the projection onto the smectic layers of SmF and SmI phases are different. In the former case, the projections of molecules onto the layer point to the edge of the hexatic, while in the latter case, to the apex.
In SmB (crystal), SmG, SmJ, SmE, SmH, and SmK phases of the liquid crystals, the molecules are highly ordered and the smectic layers are strongly correlated. The correlation length ranges from tens to hundreds of layers. The way of stacking of successive layers may be either AAA……, ABABABAB………, or ABCABCABC….. These six smectic liquid crystals are actually very similar to real crystals, but they do exhibit a significant disorder in both translational and orientational order.

In SmB (crystal), the molecules are perpendicular to layers and are arranged in a hexatic lattice within layers. This symmetry is the same as that of the SmB (hexatic) phase. In both SmB phases, their molecules within smectic layers rotate more freely around their long axes or rotate in groups simultaneously. However, in SmB (crystal), the molecular ordering are higher and the correlation of smectic layers are stronger than SmB (hexatic).

The molecules within the SmG and SmI phases are tilted with respect to the layers while the molecules of SmB (crystal) phase are aligned more or less perpendicular to the layers. The crystallography classifications of these three liquid crystal phases are the same as the SmB (hexatic), SmF and SmI phases. The structural relation of the SmG and SmJ phases with the SmL phase is similar to that of the SmF and SmI phases with the SmB (hexatic).

The molecules of the SmE phase within the smectic layers tend to be perpendicular to the smectic layers, but they are unable to rotate freely with respect to the long molecular axis. The SmH and SmK phases differ from the SmE phase only in their tilted molecules within the layers. The molecules of the SmH phase are tilted to the edge of the
hexatic while in SmK phase to the apex. The details of all these smectic mesophases with figures are given in the section 3.7.

1.6.2 Discotic liquid crystals

Discotic liquid crystals (DLCs) are formed by planar disc like molecules orientated in a direction of their shorter axis. In such molecules, there is a significant difference between the magnitude of its height (i.e., length) and its width (i.e., the diameter) as shown in Figure 1-20 [40]. They usually consist of rigid, flat $\pi$-electron conjugated molecular cores attached with four or more flexible aliphatic side chains. The core unit is mostly aromatic and its geometry is often symmetric with an appropriate number of side chains to make the molecule symmetric.

Figure 1-20: (a) Triphenylene based DLC- 1-nitro-2,3,6,7,10,11 hexakis(pentyloxy)triphenylene (NO$_2$-HAT5) (b) Truxene based DLC – Hexaalkoxytruxene.
Some examples of DLCs are symmetrically substituted benzene, triphenylene, truxene, etc. linked via ester or ether bonds to normal alkyl chains [41]. Esters are derived from carboxylic acids, which contains the -COOH group. The hydrogen in this group is replaced by a hydrocarbon group to form an ester. The hydrocarbon groups could be an alkyl group like methyl or ethyl, or one containing a benzene ring like phenyl. Ether is a class of organic compounds which contain an oxygen atom connected to two (substituted) alkyl or aryl groups of general formula R–O–R'. The alkyls form homologous series with the general formula C_nH_{2n+1}, and the aryl refers to any functional group or substituent derived from a simple aromatic ring, e.g., phenyl (C_6H_5), which is derived from benzene. A truxene is the organic compound, which consists of a core of four benzene rings. The three radial rings are symmetrically attached to the central ring as shown in Figure 1-20 (b).

DLCs are subdivided into different mesophases, e.g., nematic phase (N_D), hexagonal discotic phase (Col_h), ordered hexagonal columnar phase (Col_{ho}), disordered hexagonal columnar phase (Col_{hd}), ordered rectangular columnar phase (Col_{ro}), disordered rectangular columnar phase (Col_{rd}), tilted columnar phase (Col_t), etc.

1.6.2.1 Nematic discotic phases

The nematic discotic phase has an orientationally ordered arrangement of the discs, i.e., the normals of the molecular discs tend to align along the director but the mass centers of molecules do not have any positional order as shown in Figure 1-21.
1.6.2.2 Columnar discotic phases

The discotic columnar phases are formed by stacking DLC molecules with one on top of the other in columns. The columns are arranged in a two-dimensional lattice of either hexatic or rectangular arrays. The axis of the column may be parallel or tilted with respect to the normal of the disc. Within the columns, the spacings of the molecules are either constant or random. The intercolumnar space is occupied by highly disordered liquid like, insulating aliphatic side chains. The distance between two discs within the columns is typically about 3 - 4 Å, whereas the intercolumnar distance, depending on the size and length of the side chains, is more than 18 Å [42].

In this phase, in general, there is no lateral correlation between the molecules with neighboring columns. The columns can freely slide relative to each other and the molecules can randomly reorient about the columnar axes [41].

1.6.3 Liquid crystals as organic semiconductors

LC materials, exhibiting orientational and two-dimensional (2D) positional order, represent an intermediate class of materials between single crystals and amorphous disordered materials. A liquid like structure in both discotic and smectic LCs is responsible for the dynamic nature of structural defects that play the role of trapping
sites, which are different from the static nature of charge traps in polymers and organic crystals. The charge carrier mobility in liquid crystal is affected by trapping and detrapping processes. The LCs have self-healing property as defects in the layer structure can be repaired by a simple heating and cooling process or by its own fluctuating nature of intrastack separation. For example, due to the self healing effects in the mesophase of discotic LCs, barriers have limited effectiveness in blocking conduction along the stack as any defect molecule will not remain in any one stack for a long time [43,44]. Such self-healing character of positional disorder (the trapping sites) significantly increases charge mobility in LCs in comparison with polymers.

Other advantages of liquid crystalline materials as semiconductors are their excellent mobilities in their mesophases (especially high ordered smectic phases, see section no. 1.6.5), well ordered molecular alignment that can be controlled by an external electric or magnetic fields reducing the grain boundary defects that trap the charge carriers, and good contact to the surface of metals which is essential for device applications [45]. The fluid nature of the liquid crystals greatly helps in the realization of large-area uniformity when the cell technology in liquid-crystal display devices is applied. The liquid crystalline semiconductors represent an interesting category of organic semiconductors because of their spontaneous alignment behavior and good solubility into organic solvents [34].

The following chronology is found in the history of liquid crystalline semiconductors [46]. In 1960s, Kusabayashi and Labes studied photoconductivities of rod-like liquid crystals. In 1977, the first discotic liquid crystal was found by
Chandrasekhar. In 1982, Simon and his co-workers pointed out that discotic liquid crystals could be used as one-dimensional conductors. In the 1980’s, people attempted to synthesize chemically doped discotic liquid crystals to obtain highly conductive [46], charge transfer (CT) complexes. However, these CT complexes decomposed on heating. In the 1990’s people pursued measuring high conductivities of non-doped materials, i.e., chemically pure discotic liquid crystals [46].

Triphenylene (Figure 1-22) based LCs are interesting materials for technical applications in the field of electrophotography and as transport materials in light-emitting diodes [47].

![Triphenylene based discotic liquid crystal](image)

**Figure 1-22: Triphenylene based discotic liquid crystal.**

### 1.6.4 Discotic liquid crystals as organic semiconductors

In section 1.6.2, I discussed about the discotic liquid crystals and its columnar mesophase. In this section I will discuss about the charge transport behavior in its columnar phase. The transport of the charge carrier perpendicular to the columns is more
complex than that parallel to the columns because the charge has to cross insulating hydrocarbon regions of the width of at least 15 Å to move from one column to another column. A simple estimate, using an exponential wave-function overlap, gives a jump rate perpendicular to the columns ($W_\perp$) of order $10^{-6}$ and that parallel to the columns ($W_\parallel$) with the typical value of $10^{12}$ given in the article [53]. This implies that there is an immense difference between the conductivity along the direction parallel and perpendicular to the column axis due to the insulating effect of the alkyl or alkoxy side chains. Therefore the charge transport is found to be highly anisotropic. The ratio of the charge transport along the direction parallel to the column axis to that perpendicular to the axis is very high with ratio greater than 1000:1 [53,48]. Such a type of molecular arrangement enables one-dimensional transport of charge and energy migration within the columns [49].

This transport behavior and the previously mentioned advantages of LCs make the discotic systems useful materials for technical applications such as photocopying, electrophotography, nonlinear optics, molecular electronics, photoconducting systems, light emitting diodes, photovoltaic solar cells, optical data storage devices, hybrid computer chips for molecular electronics, etc. [49,50].

As reported by Adam et al. [35], the mobilities of typical discotic LCs were found to be order of $10^{-3}$ cm$^2$/Vs in the discotic mesophase of hexapentyloxytriphenylene and $10^{-1}$ cm$^2$/Vs in the helical plastic phase of the hexahexylthiotriphenylene [51]. The latter is considered to be one of the highest charge mobilities for a triphenylene based photoconducting system [52].
The charge transport mechanism in the discotic LCs mesophase seems to be an incoherent hopping process as found in the experiment of frequency dependence of the conductivity parallel to the columnar stacks [47,53]. The discotic molecules self-assemble into columns having a significant overlap of delocalized π-electrons on adjacent molecules, thereby providing quasi-one-dimensional channels for facile charge transport.

Transport in the columnar phase of the discotic LCs, hexapentyloxytriphenylene, has been investigated by the time-of-flight technique over a range of temperatures and electric fields by V. Duzhko et al. [54]. These results were interpreted in the framework of correlated polaron motion as described by the nonadiabatic low-temperature limit of Holstein’s polaron theory developed for a one dimensional diatomic chain.

It has been found that the charge mobilities can be increased by increasing the ordering of the columnar mesophases. Therefore, the research on triphenylene based liquid crystals has attempted to introduce chemical modifications designed to increase the columnar ordering in terms of the average length of ordered stacking arrays along the column [52,55].

1.6.5 Calamitic liquid crystals as organic semiconductors

Calamitic LCs, especially smectic mesophases, have been shown to be a promising alternative to crystalline organic semiconductors. In fact, there are many types of smectic mesophases, e.g.,A,B,C,E,F,G,H,I,J,K,… etc. (see the section 1.9.3). The degree of molecular ordering in each smectic mesophase is different. It has been found that the higher the order the higher the charge carrier mobility [56]. For example, in the
smectic series SmA, SmB and SmE of 2-phenylnaphthalene derivatives, in which the molecular director is normal to the smectic layers, the ambipolar carrier mobility, $1 \times 10^{-2}$ cm$^2$/Vs, of the ordered SmE phase with orthorhombic symmetry was higher than the value of $1.6 \times 10^{-3}$ cm$^2$/Vs found in the less-ordered SmB phase with hexagonal symmetry. Similarly, the charge carrier mobility in the SmB phase was higher than that ($2.5 \times 10^{-4}$ cm$^2$/Vs) found in the SmA phase, in which there is no molecular ordering within the smectic layer. Analogous to the above series, in the SmC, SmF and SmG phases of terthiophene derivatives, in which the molecular director tilts with respect to the layer, the charge carrier mobilities were found to be $5 \times 10^{-4}$ cm$^2$/Vs, $4 \times 10^{-3}$ cm$^2$/Vs and $2 \times 10^{-2}$ cm$^2$/Vs, respectively [56].

Certain molecular structures are associated with enhanced mobility. Studies of calamitic liquid crystals show that the introduction of a sulfur atom in a molecule plays a significant role in a close molecular packing and enhances the intermolecular overlap of the molecular orbitals. Thiophene is a ring, which contains a sulfur atom and produces better hopping conduction of charged carriers [58]. The charge carrier mobilities of higher ordered smectic phases of thiophene oligomers such as quinquethiophene and sexithiophene derivatives were found from $10^{-2}$ to $10^{-1}$ cm$^2$/Vs [57, 34]. Similarly from the other reports, an asymmetrically substituted quaterthiophene (3-QTP-yne-4) including an acetylene group also exhibits a high mobility up to 0.1 cm$^2$/Vs in a highly ordered smectic mesophase [33,58]. We will discuss thiophene containing LCs below.
Another useful building block is pyridine, which is associated with the higher ordered smectic phases around room temperature [33]. We will discuss some pyridine containing LCs in a later chapter.

The objective of my research is to study the charge carrier transport in the calamitic LCs containing benzene, pyridine and thiophene rings and the discotic LCs containing triphenylene.
1.7 EXPERIMENTAL METHODS TO MEASURE THE MOBILITY

There are a number of experimental methods that are used to measure the mobility of the charge carrier in the materials. These methods are based either on electric transport or magnetic interaction. The brief description of all these methods is provided in the article by N. Karl [59].

The electric transport methods are (a) the time-of-flight (TOF) method, (b) the xerographic discharge method, (c) the equilibrium charge carrier extraction method, (d) drift current methods under limited range conditions, (e) the space-charge-limited-current (SCLC) method, (f) the conductivity/concentration (σ/n) method [60,61], (g) the field effect transistor (FET) method and (h) the surface acousto-electric traveling wave (SAW) method. The magnetic interaction methods are (a) Hall effect, (b) magneto-resistance and (c) cyclotron resonance. In my experiment, I have used the time of flight method.

1.8 BRIEF OF EACH CHAPTER

The detail of experimental methodology that I used during the experiments for the study of the charge carrier transport in chapters three, four and five will be explained in chapter two. The same experimental set up has also been used for chapter six. However, the experiment here required an additional set up namely the design and construction of an instrument that measures the charge carrier transport study in a freely suspended film of a sample.

In my dissertation, I have included the results of only those five samples for which I have a complete set of data for the study of the charge carrier transport. Four of
them were calamitic liquid crystals and one of them is a discotic liquid crystal. The first sample is 1,4-di-(5-n-tridecythien-2-yl)-benzene discussed in chapter three. The second sample is NO₂-HAT5 [1-nitro-2, 3, 6, 7, 10, 11-hexakis (pentyloxy) triphenylene] discussed in chapter four. The third sample, 5,5’-di-(alkyl-pyridin-yl)-2,2’ bithiophenes, are discussed in chapter five. They are C10 [5,5’-i-(5-n-decyl-pyridin-2-yl)-2,2’-bithiophenes] and C9 [ 5,5’-d i-(5-n-nonyl-pyridin-2-yl)-2,2’-bithiophenes ]. The fourth sample is 8PNPO12 (2-(4’-octylphenyl)-6-dodecyloxynaphthalene) discussed in chapter six.

In each chapter, I have tried to fit our experimental results with existing models. Some of our results could be explained very well by the available models and some are not.

1.9 APPENDIX

1.9.1 Appendix A: Derivation of standing wave function

Since, the potential energy \( V(x) \) is periodic in space, it can be expanded into Fourier series as

\[
V(x) = \sum_{\nu} V_{\nu} \exp(iK_{\nu}x)
\]  

(1.16)

where \( V_{\nu} \) are the expansion coefficients with \( \nu = 0, \pm 1, \pm 2, \ldots \) and \( K_{\nu} = 2 \pi \nu / \lambda \). Since the influence of the periodic potential, \( V(x) \), is very small at nearly free electrons model, only the \( V_0 \), \( V_{+1} \) and \( V_{-1} \) are the important coefficients in equation (1.16). Therefore,
If the origin of the coordinate is chosen, such that $V(x)$ is an even function, $V(x)$ is equal to $V(-x)$, i.e., $V_{-1} = V_{+1}$. Also, $V(x)$ must be a real function of position. On the bases of these assumptions, $V(x)$ in equation (1.17) can be approximated as

$$V(x) = V_0 + V_1 \exp(iK_1x) + V_{-1} \exp(iK_{-1}x)$$

(1.17)

where $K_1 = \frac{2\pi}{\lambda}$ with a wavelength ‘$\lambda$’.

Since the function $u(x)$ is also a periodic function, it can be also expanded into a Fourier series as

$$u(x) = \sum_n U_n \exp(iK_nx)$$

(1.19)

where $U_n$ are the expansion coefficients with $n = 0, \pm 1, \pm 2, \ldots$ and $K_n = 2\pi n/\lambda$. $K_n$ is known as the translation vector of the reciprocal lattice in the k-space. From equations (1.4) and (1.19), we can get

$$\psi(x) = \sum_n U_n \exp[i(k + K_n)x]$$

(1.20)

For the same reason given above for $V(x)$, we would expect only the lowest three terms of the Fourier expansion of $u(x)$ to be important. Then,

$$\psi(x) = [U_0 + U_1 \exp(iK_1x) + U_{-1} \exp(iK_{-1}x)]\exp(ikx)$$

(1.21)

Let us find the solutions where $U_0$ and $U_{-1}$ dominate, then we have

$$\psi(x) = [U_0 + U_{-1}\exp(iK_{-1}x)]\exp(ikx)$$

(1.22)
Substituting the values of $V(x)$ and $\psi(x)$ from (1.18) and (1.22), respectively into (1.3) and then integrating (1.3) over $x = 0$ to $x = a$ after multiplying both sides by $\exp(-i k x)$, we get

$$U_{-1} V_1 = \left[ \frac{\hbar^2 k^2}{2m} - E + V_0 \right] U_0$$  \hspace{1cm} (1.23)

or,

$$\frac{U_{-1}}{U_0} = \left[ \frac{\hbar^2 k^2}{2m} - E + V_0 \right] V^{-1}$$  \hspace{1cm} (1.24)

Similarly, multiplying (1.3) by $\exp[-i(k+K_\perp) x]$ and integrating over $x = 0$ to $x = a$ we get,

$$U_0 V_{-1} = \left[ \frac{\hbar^2 (k+K_\perp)^2}{2m} - E + V_0 \right] U_{-1}$$  \hspace{1cm} (1.25)

and

$$\frac{U_{-1}}{U_0} = V_{-1} \left[ \frac{\hbar^2 (k+K_\perp)^2}{2m} - E + V_0 \right]^{-1}$$  \hspace{1cm} (1.26)

A nontrivial solution of $U_0$ and $U_{-1}$ requires that the ratio $U_{-1}/U_0$ from equations (1.24) and (1.26) should be equal, i.e.,

$$\frac{U_{-1}}{U_0} = \left[ \frac{\hbar^2 k^2}{2m} - E + V_0 \right] V^{-1} = V_{-1} \left[ \frac{\hbar^2 (k+K_\perp)^2}{2m} - E + V_0 \right]^{-1}$$  \hspace{1cm} (1.27)

or,

$$\left[ \frac{\hbar^2 k^2}{2m} - E + V_0 \right] \left[ \frac{\hbar^2 (k+K_\perp)^2}{2m} - E + V_0 \right] = V V_{-1}$$  \hspace{1cm} (1.28)
We can see from equation (1.28) that at some values of \( k \), the two square bracketed terms are equal. This equality occurs when \( k^2 = (k + K_{-1})^2 \), or \( k = \pm (k + K_{-1}) \), or \( k = -(k + K_{-1}) \) or \( k = -\frac{K_{-1}}{2} \) or \( K_{-1} = -2k \), which gives

\[
\left[ \left( \frac{\hbar^2 k^2}{2m} \right) - E + V_0 \right]^2 = VV_{-1}
\]

(1.29)

Physically, this is the condition of Bragg Reflection. At this condition, the wavelength of the electron wave (\( \lambda = 2\pi/k \)) is equal to twice the lattice spacing, 2\( a \), or the electron wave is phase-shifted by \( ka = \pi \) or 180° after traveling through a distance equal to one lattice spacing, \( a \). At this wavelength, the electron can have two possible allowed energies separated by an energy gap. This is demonstrated by substituting \( k = -\pi/a \) or \( k = \pi/a \) into (1.28) which gives

\[
\left[ E - V_0 - \frac{\hbar^2}{2m} \left( \frac{\pi}{a} \right)^2 \right]^2 = |V_1|^2
\]

or,

\[
E_{\pm} - V_0 = \frac{\hbar^2}{2m} \left( \frac{\pi}{a} \right)^2 \pm |V_1|^2
\]

(1.30)

Thus, at \( k = \pi/a \), we have two possible allowed energies. They are separated by an energy gap of size, \( E_G = E_+ - E_\pm = 2 |V_1| \).
Two wavefunctions can be seen at the energy gap, \( k=\pi/a \), because of the presence of two possible energies, \( E^+ \) and \( E^- \). The condition that the two bracketed terms in (1.28) are both equal to \( |V_1| \) or \(-|V_{-1}| \) giving \( E_G = 2|V_1| \), Eq. (1.27) implies that either \( U_0 = +U_{-1} \) or \( U_0 = -U_{-1} \). Using \( U_0 = \pm U_{-1} \) and \( k=\pi/a \), equation (1.22) becomes

\[
\psi_\pm(x) = U_0 \left[ 1 \pm \exp\left( \frac{-i2\pi x}{a} \right) \exp\left( \frac{i\pi x}{a} \right) \right]
\]

Giving,

\[
\psi_-(x) = \psi(-) = 2iU_0 \sin\left( \frac{\pi x}{a} \right)
\]

\[
\psi_+(x) = \psi(+) = 2U_0 \cos\left( \frac{\pi x}{a} \right)
\]

**1.9.2 Appendix B: Einstein’s equations**

The current densities \( J_c \) and \( J_h \) for electrons and holes in the solids are given by

\[
\vec{J}_h = \left\{ \mu_h p(x) \vec{E} - D_h \vec{\nabla} p(x) \right\} e,
\]

and

\[
\vec{J}_c = \left\{ -\mu_c n(x) \vec{E} - D_c \vec{\nabla} n(x) \right\} (-e),
\]

respectively. In the equations, the terms with subscripts “c” and “h” are associated with the electron and the hole, respectively, \( \mu \) represents the charge carrier mobility, and \( D \) represent the diffusion coefficient. The first and second terms in the right side of the equation represent a drift current and a diffusion current, respectively. The number of
electrons and holes per unit volume in the conduction and valence bands are \( n(x) \) and \( p(x) \), respectively [62].

Let \( V = -|E| x \) represents an electrostatic potential corresponding to a uniform electric field \( \vec{E} \), and \( \mu_{cp} \) is the chemical potential. \( E_c \) and \( E_v \) are the energies of the conduction and valence bands, respectively. \( N_c \) and \( N_v \) are the effective densities of available states in the conduction and valence bands. Then, \( n(x) \) and \( p(x) \) are given by

\[
n(x) \approx N_c \exp \left( \frac{-E_c + eV(x) + \mu_{cp}}{k_B T} \right)
\]

and

\[
p(x) \approx N_v \exp \left( \frac{E_v - eV(x) - \mu_{cp}}{k_B T} \right),
\]

respectively. Here, \( k_B \) is the Boltzmann constant. In equilibrium, \( \vec{J} \) and \( \vec{J}_h \) vanish, then from (1.34) and (1.37),

\[
\mu_h = \frac{eD_h}{k_B T}
\]

Similarly, from (1.35) and (1.36),

\[
\mu_c = \frac{eD_c}{k_B T}
\]

These Equations (1.38) and (1.39) are called Einstein’s equations for the charge carrier mobilities.
1.9.3 Appendix C: Table of the smectic liquid crystal types

![Diagram of smectic liquid crystal types]

Figure 1-23: Side view and top view of the molecular ordering in the smectic phases of liquid crystals. Triangles or arrows represent tilt directions of molecules [63].
1.10 REFERENCES


[34] M. Funahashi and J. Hanna “High Carrier Mobility up to 0.1 cm²/Vs at Ambient Temperatures in Thiophene-Based Smectic Liquid Crystals”, Adv. Mater., Vol. 17, 5, 594 (2005).


CHAPTER 2

EXPERIMENTAL PROCEDURE

2.1 INTRODUCTION

In the experiments, the charge carrier mobility of the material was measured using the time of flight (TOF) technique. In this technique, the material is sandwiched between two electrodes. One of the electrodes must be semitransparent in order to illuminate the experimental material using a light pulse obtained from a laser. The wavelength of the light must be within the range absorbed by the material. Laser irradiation on the material leads to the creation of electron-hole pairs. The electric charges generated in the bulk of the material due to irradiation may give space charges [7], which can be controlled by adjusting the light intensity to avoid the space charge effect. Also, the penetration depth of incident laser light in the experimental material must be much less than the thickness of the sample. Usually, it must be much less than 1 μm, so that the charge carriers are formed only in the thin layer of the material near the front illuminated electrode [1]. In our experiment, the sample thickness was varied from the 10 μm of the commercially available cell (see Figure 2-9) to 25 μm for the lab made cell (see Figure 2-11).
Depending on the polarity of an applied electric field, the electrons or holes drift across the sample generating a displacement current. This current is amplified by using an amplifier and recorded by a digital oscilloscope.

![Schematic diagram of the experiment using the time of flight technique.](image)

Figure 2-1: Schematic diagram of the experiment using the time of flight technique.

With the positive polarity of the applied voltage (V) at the illuminated electrode (see Figure 2-1), the electrons move towards the illuminated electrode and neutralize the positive ions at the surface. This leaves a sheet of holes which travel across the sample with a drift velocity ($v$) towards the opposite electrode inducing a displacement current, $I(t)$, in the external circuit [2].
The transit time, \( \tau \), is defined as the time taken by the sheet of holes to reach the opposite electrode from the point of its creation. For the experiment, \( \tau \) must be much longer than the duration of the light pulse, which was 10 ns in our experiments. \( \tau \) must also be longer than the time constant RC of the external circuit [1].

The drift mobility \( \mu \) of the charge carriers is defined as the ratio of the drift velocity “\( \nu \)” to the electric field “\( E \)”. The charge carriers can be either positive ions or negative ions or electrons or holes

\[
\mu = \frac{\nu}{E} = \frac{d/\tau}{V/d} = \frac{d^2}{V\tau}
\]

where \( d \) is the thickness of the sample, \( \nu = \frac{d}{\tau} \) and \( E = \frac{V}{d} \) This is the main formula for the experiment. Once \( d \), \( V \) and \( \tau \) are known, \( \mu \) can be calculated.
2.2 EXPERIMENTAL SET UP

Figure 2-2: Basic set up of optical components.

Figure 2-3: (a) Basic set up of the electronic components with a side view of the cell and (b) A top view of the cell.


The basic setup of the optical components and the electronic components for the TOF technique are shown in Figure 2-2 and Figure 2-3. The laser consists of the Nd:YAG laser (part 2 in Figure 2-2) made of 1% Neodymium doped Yttrium Aluminum Garnet
(Y₃Al₅O₁₂) synthetic crystal. It emits light with a fundamental wavelength of 1064 nm. The source can be also used to generate the other harmonic wavelengths of 532 nm, 355 nm and 266 nm by using interchangeable optional harmonic generators as shown in Figure 2-5.

Figure 2-4: Continuum Electro Optics Inc. (Model: SL II-10) laser source [3].

Figure 2-5: Optical layout of Nd:YAG laser.

(1) Rear mirror (2) Pockels cell (3) λ/4 Plate (4) Dielectric polarizer (5) Oscillator rod (6) Gaussian output coupler (7) Optional harmonic generators (8) Graphite resonator structure (9) Dichroic separation (10) 1064 nm Dichroic mirrors (11) Beam block [4].
The light from the main optical box is passed through the SSP (Surelite Separation Package, part 3 in Figure 2-2) box. The SSP box contains a pair of dichroic mirrors, also called separators, (part 4 in Figure 2-2) to provide pure harmonic light.

There are three sets of paired dichroic mirrors; one set to separate the second harmonic light of 532 nm, one for the third harmonic light of 355 nm and one for the fourth harmonic light of 266 nm. Only one pair is used at a time in experimenting on a particular sample depending upon the desired wavelength. The light is passed through the quartz slide as shown in part 7 of Figure 2-2, which reflects some part of the incident light towards the fast trigger detector of the digital oscilloscope as shown in part 8 in Figure 2-2.

The transmitted light from the quartz slide is bent twice at an angle of 90° by two mirrors (parts 9 and 10 in Figure 2-2) and then passed through the Raman Shifter (part 12 in Figure 2-2).

The Raman Shifter works on the principle of the Raman effect (Raman scattering). According to this principle, when monochromatic radiation is passed through gas, there is a probability of interaction between the incident photons and the gas molecules. This will scatter the photons inelastically, causing the loss (Stokes scattering) or gain (anti-Stokes scattering) of energy, and shifting the frequency of the scattered photons. Hence, the transmitted light from the Raman Shifter, is composed of different wavelengths called Raman spectra, which is then dispersed by a prism (see 13 of Figure 2-2). In the resultant series of Raman spectra, one wavelength, which is absorbed by the
experimental material maximally, is deflected towards the material and the unwanted spectra are directed into a beam dump. The details of the Raman Shifter and the available wavelengths for our experiment are given in the appendix section 2.6.1.

In the experiment, the Raman shifted photons of the wavelength 319 nm were used to generate the charge carriers in the material 1-nitro-2,3,6,7,10,11-hexakis-pentyloxy-triphenylene (NO$_2$-HAT5), 2-dodecyloxy-6-(4-octylphenyl)-naphthalene (8PNPO12) and 1,4-di-(5-n-tridecylthien-2-yl)-benzene and the wavelength 435 nm was used in the material 5,5’-di-(alkyl-pyridin-yl)-2,2’-bithiophenes.

Figure 2-6: INSTEC- HCS302 microscope hot and cold stage.
The light from the prism is reflected by the mirrors (parts 14 and 16 in Figure 2-2) toward the experimental material (part 20 in Figure 2-2) kept inside the hot stage (part 18 in Figure 2-2) manufactured by INSTEC: Model HCS302 [5] as shown in Figure 2-6. The temperature is controlled by a PID temperature controller (Lake Shore 331).

This hot stage also gives optical access to the experimental material so that the domain structure of the sample can be viewed easily on a video screen with the help of a polarized light illuminating the sample, a polarizing microscope and a camera (parts 17, 20, and 21, respectively in Figure 2-2). The interior of the hot stage is large enough to accommodate the experimental cells (see section 2.4).

Most of the instruments in our experiment were interfaced with the computer via IEEE-488 for real time data acquisition. The Yorick language was used as computer programming code to communicate with the instruments. A part of the Yorick programming language that was used frequently for scanning and analyzing the traces in the digital oscilloscope is given in the section 2.6.2 - appendix II.

A pair of connecting wires, also called a voltage wire (22 in Figure 2-3) and a signal wire (23 in Figure 2-3), were connected to the terminals of a voltage source (31 in Figure 2-3), which creates the electric field across the sample, and the input terminal of a transimpedance (current to voltage converter) amplifier, respectively. The manufacturer of the amplifier is Electro Optical Components, Inc (29 in Figure 2-3) Model: HCA-200M-20K-C. It is a high speed current to voltage amplifier with a bandwidth of dc-200 MHz and a transimpedance (Gain) 2 x 10^4 V/A.
The amplifier output is connected to a digital oscilloscope (Lecroy Wave Runner LT364L 500MHz 1GS/S DSO). In the experiment, an SRS (Stanford Research Systems) Model DS345 30MHz Synthesized Function Generator (Low Voltage Power Supply) with the combination of a voltage gain amplifier (part 33 in Figure 2-3) and SRS PS325/2500V-25w are used as the voltage sources.

If a high signal is produced across the sample because of electrical breakdown in the cell, it may damage the current amplifier. To protect the current amplifier, a pair of diodes (28 in the Figure 2-3) was connected between the input of the amplifier and the ground.

2.3 TRACES IN TIME OF FLIGHT (TOF) EXPERIMENTS

The ideal and the real traces (current vs. time) in the TOF experiment are shown in Figure 2-7 [1]. The idealized trace illustrates a sheet of charge carriers moving with a constant velocity until the charges are absorbed at the electrode at a transit time ($\tau$). At $\tau$, the charge carriers leave the sample and no longer contribute to the current. However the shape of the real trace is different from the ideal trace as shown in Figure 2-7.

The real trace consists of the current spike immediately after the short light pulse, the plateau, the shoulder or transition region and the dispersive tail. The current spike at $t=0$ is produced by the rapid drift of charge carriers through the thin layer of the sample because of trapping of the charges and movement of the charge carriers towards the light illuminated electrode.
Figure 2-7: (a) Idealized and real current traces (b) a typical trace in which a clear transit time can be located in the linear scale of the graph.

These charge carriers are holes and electrons generated from the incident light. The shoulder or the transition region is the demarcation point between the plateau and the
dispersive tail. In the time axis, this point, which is the inflection point in a current trace, is called $\tau$, a time of flight. This is the time taken by the initial sheet of carriers to reach the opposite electrode from the point of its generation. The slow drop-off or the tail following the transit time is due to the dispersion of the carrier packet as it drifts through the sample [6].

The deviation of the real trace shape from its ideal one might have many causes, [1]. Some of them are (a) the RC response time, (b) the loss of carriers due to deep trapping, (c) the variation in drift mobility of the sheet of charge carrier as a function of its position “x” due to sample inhomogeneity, (d) the local electric-field variation due to trapped space charge and (e) the spreading of the sheet of charge carriers to a magnitude comparable to thickness of the sample.

The reason (a) is usually responsible for the practical limitations of the transient experiment as given by the condition $RC << \tau << \tau_D$, where $\tau_D$ is a deep trapping lifetime, $R$ is the resistance of the external circuit and $C$ is the capacitance of the sample as shown in Figure 2-1. A current induced across $R$ due to the drifting carriers across the sample in the presence of the applied potential will fall rapidly as the carriers arrive at the counter electrode at the transit time ($\tau$). So the response time $RC$ of the circuit must be always less than $\tau$. For example, the capacitance of our experimental cell was generally in the order of $10^{10}$ F and the resistance in the circuit was 50 $\Omega$. It makes the response time of the experiment $5 \times 10^{-9}$ s. Usually, the transit times for all samples that I used for the
experiment were not less than $10^{-6}$ sec which is very high compared to the instrument response time.

![Figure 2-8](image)

Figure 2-8: (c) A typical dispersive trace in linear scale in which it is difficult to locate the transit time and (d) the same dispersive trace in logarithmic scale.

Sometime if the trace is too dispersive, it is very difficult to locate the transit time. In such traces, logarithm scales are used in both axes to find the transit time.

There are some limitations in this experiment. The dielectric breakdown at high field limits the application of high voltage. The disturbance due to noise limits the experiment in a low field when little charge is generated. The phase transition temperatures of the material limit the experimental temperature range. The internal field may also be disturbed by the injected charge. A contact between the sample and the electrode may
cause electrochemical reactions resulting in contamination and reduction of the quality of the sample. It is also difficult to change the alignment of molecules in-situ because the sample is sandwiched between two electrodes. It cannot degas in-situ, i.e., the gas trapped between electrodes at the time of filling the cell cannot be removed. When the top electrode is made negative, a rapidly decaying current is observed due to the electrons being absorbed by residual oxygen trapped within the electrodes [7] making it difficult to measure the electron mobility. It is because of the higher electronegativity of the oxygen atom, which is 3.44 (just below the Fluorine atom with the highest electronegativity of 3.98 in the periodic table). Just for reference, the electronegativity of a carbon atom and a hydrogen atom are 2.55 and 2.20, respectively [8].

2.4 EXPERIMENTAL CELL PREPARATION

In the experiment, I used two types of cells. The first one was a ready made commercial ITO (Indium Tin Oxide) cell of thickness 10 µm (manufactured by E.H.C. Cl., Ltd). This cell was ready to fill with sample by capillary action. A small amount of the sample was put at the one side of the cell and heated to its isotropic phase (melting point) using the hot stage. Once the isotropic phase is reached, the melted sample enters the cell itself by capillary action.
The second type of cell was made manually in the lab with two commercially available (manufactured by E.H.C. Cl., Ltd) ITO coated glass plates (each of size 22 mm x 25 mm). The ITO coated regions at the center with dimensions 11 mm x 11 mm were electrodes. Each plate has an ITO coated line at the side, which joined with the central ITO electrode. These lines were used to connect the signal and voltage wires.

The bottom electrode plate was first placed on the hot stage at the room temperature with its ITO coated region facing up. Glass microspheres of size 20.2 (± 1.4 μm) were spread over the four corners of the bottom plate without disturbing the ITO coated region. The top electrode plate was gently put over the glass microspheres by facing the ITO region towards the bottom plate.
Figure 2-10: ITO coated single glass plate which was substrate or electrode for the cell.

The top plate was slightly shifted (about 1.5 mm) towards the left to expose ITO lines for wire connections.

As described above for the commercial cell, a small amount of the experimental material was put on the one side of the bottom plate without disturbing the top plate and heated to the isotropic phase using the hot stage. Since the material enters the cell by capillary action, it is very important to know the temperature of the isotropic phase (i.e. conventional liquid phase) of the experimental material.

The isotropic phases of the experimental materials were determined by DSC (Differential Scanning Calorimetry). For NO₂-HAT5, 8PNPO12, 1,4-di-(5-n-tridecylthien-2-yl)-benzene and 5,5’-di-(alkyl-pyridin-yl)-2,2’-bithiophenes used in the
experiment, the melting temperatures were 141 °C (Figure 4-2), 123 °C (Figure 6-18), 137 °C (Figure 3-2), and 188 °C and 187 °C (Figure 5-3 and Figure 5-4), respectively.

Once the cell was filled, it was cooled down slowly to room temperature. The whole process had to be carried out without disturbing the position of the top and the bottom plates. Then the cell was put in the holding mount which consists of two metal plates. The lower metal plate was bigger than the cell while the upper one was smaller than the cell as shown in Figure 2-11.

Figure 2-11: (a) The top view of the holding mount and (b) The transverse view of the holding mount.
The upper metal plate had a hole at the center and four springs attached at the corners. The hole was used to pass the laser light. The purpose of using the spring was to hold the cell tightly between the lower and the upper metal plates when the two metal plates were screwed together.

Before the holding mount was developed, epoxy was first tried to hold the electrodes together. However, the epoxy contaminated the sample. Therefore, the holding mount described was used to minimize the contamination of the sample.

During the experiment it was also very important that all of the equipment like ITO plates, the tweezers, the holding mount, the hot stage, the spatula, etc., be cleaned before their use to minimize contamination. Cleaning was done by washing with acetone and ethanol and by blowing nitrogen gas.

The cell was heated again to its isotropic phase above the clearing temperature and cooled down slowly to the experimental temperature. Depending upon the nature of the material, the cooling rate would be different for different materials to get larger domains and hence a good signal. For example, the cooling rate for NO₂-HAT5 explained in the chapter five was 0.01°C/sec. The process of repeated heating and cooling also helped to make the thickness of the cell uniform due to the pressure of the spring.

The cell was now a capacitor with tentative effective area around 9.5 mm x 11 mm. However the effective area was different for different cells, as was the thickness. The thickness of the capacitor was determined by comparing the capacitance of the cell with the capacitance of a commercially available 10 µm cell filled with the same
material. The capacitance of the cell was measured by a Quadtech 1920 Precision LCR meter [9]. The formula for the thickness calculation is given below.

\[ d = \frac{C_0 A}{C A_0} d_o \]

where, \( C_0 \) = Capacitance of the commercial cell filled with the material; \( A_0 \) = Effective area of the electrodes of the commercial cell; \( A \) = Effective area of the electrodes for the experimental cell; \( C \) = Capacitance of the experimental cell; \( d_o \) = The distance between two electrodes for the commercial cell (10 µm for this case).

2.5 DETERMINATION OF THE ABSORBING WAVELENGTH OF A SAMPLE

The maximum absorbing wavelength of the experimental material was determined by using an HP - Agilent 8453 Diode Array Spectrophotometer. It is a UV-visible spectroscopy based on a photo diode array detector [10] consisting of a light source from 190 to 1100 nm, a slit of 1-nm width and, a diode detector array. Once the light has been passed through the material of interest, the entrance slit and the dispersion device, it reaches a detector. In the computer, we see the absorbance versus wavelength plot, which is the absorbed intensity of light passing through the solution of the material after subtracting the absorbed intensity of the light through the pure solvent.
Figure 2-12: UV-absorption spectra for NO₂-HAT5 which clearly shows the absorption at 319 nm.

The solution of the experimental sample made with the suitable solvent like CH₂Cl₂ of the photometric grade was placed in standard quartz cuvettes of 1.0 cm path-length. The solution must be diluted so that the maximum absorbance would be within 0.2 to 0.9 in units of the optical density as shown in Figure 2-12 for the material 1,4-di-(5-n-tridecylthien-2-yl)-benzene. In this figure, it is clear that the wavelength of the light which is absorbed maximally by the material is around 345 nm and that the maximum absorbance is 0.17. But this wavelength was not available from the Raman Shifter as shown in the table 2-1. The nearest available wavelength in the table was 319 nm. However, the absorbed amount of the incident light at 319 nm wavelength was sufficient to create charge in a thin layer of the sample.
2.6 APPENDIX

2.6.1 Appendix A: The Raman Shifter and the available wavelengths [11,12]

The Raman Shifter works on the principle of the Raman Effect. According to this principle, when a monochromatic radiation is passed through gas, there is a probability of interaction of the incident photons with the gas molecules and then a scattering of the photons. This will result in either loss (Stokes scattering) or gain (anti-Stokes scattering) of energy, shifting the frequency of the scattered photons down or up. Such a phenomenon of an inelastic scattering is called Raman Effect or Raman Scattering. Hence the light, after exiting from the Raman Shifter, is composed of different wavelengths.

If \( f_i \) and \( f_s \) are the frequencies of the incident photon and the scattered photon, the Raman Shift is given by

\[
\Delta f = f_i - f_s
\]

The shift depends on the nature of scattering medium. If \( f_i > f_s \), the output radiation consist of Stokes lines. If \( f_i < f_s \), the output radiation consist of anti-Stokes lines. Stokes lines are frequently much more intense than the anti-Stokes lines because there is a high probability of transferring energy from the photons to the molecules.

A conventional Raman Shifter consists of a gas tube or gas cell of about 50 cm in length as shown in the part 12 of Figure 2-2, which contains high-pressure gas up to 30 atm. The gas may be hydrogen, methane, deuterium and a few other gases. I have used
hydrogen gas in the cell which is also called Raman medium. Raman shifting techniques employ vibrational modes in gas molecules to shift the wave number $\tilde{\nu}_H$, which is 4155 cm$^{-1}$ [12] for the hydrogen molecule. The input radiation of the frequency ($f_i = c/\lambda_i$) is focused into the center of the cell, where stimulated Raman oscillation and wave mixing generate a number of Stokes and anti-Stokes shifted frequencies as output radiation. The wave mixing occurs by using the output of radiation from one process as the input for the

![Figure 2-13](image)

Figure 2-13: (a) The first Stokes scattering and (b) The second Stokes scattering.

![Figure 2-14](image)

Figure 2-14: (c) The first anti-Stokes scattering and (d) The second anti-Stokes scattering.
next, ultimately shifting visible wavelength into the ultraviolet or infrared range as shown in Figure 2-13 and Figure 2-14. The output radiation from the cell is collimated by the lens (as shown in the part 11 of Figure 2-2), which is then dispersed by a prism into different wavelengths (as shown in the part 13 of Figure 2-2). The unwanted radiation is directed into a beam dump, while the desired wavelengths illuminate the experiment.

$\lambda_i$ is the wavelength of the input radiation from the laser source. For our experiment with Nd:YAG laser, the subscript $i = 2, 3, \text{and } 4$ represent $2^{\text{nd}}, 3^{\text{rd}}, \text{and } 4^{\text{th}}$ harmonic wavelengths which are $\lambda_2=532 \text{ nm}, \lambda_3=355 \text{ nm}, \text{and } \lambda_4=266 \text{ nm}$, respectively.

The energy of the input radiation ($E_i$) is given by

$$E_i = hf_i = \frac{ch}{\lambda_i}$$

where $c = 3 \times 10^8 \text{ m/s}$ and $h = 6.626 \times 10^{-34} \text{ Js}$, then

$$E_2 = \frac{ch}{\lambda_2} = 3.7 \times 10^{-19} \text{ J}$$
$$E_3 = \frac{ch}{\lambda_3} = 5.6 \times 10^{-19} \text{ J}$$
$$E_4 = \frac{ch}{\lambda_4} = 7.5 \times 10^{-19} \text{ J}$$

Now, the wave number, the frequency, the wave length and the energy of the vibrational mode of a hydrogen molecule are $\bar{\nu}_H, f_H, \lambda_H$, and $E_H$, respectively.

$\bar{\nu}_H = 4155 \text{ cm}^{-1}, \quad f_H = c \bar{\nu}_H = 1.25 \times 10^{14} \text{ s}^{-1}, \quad \lambda_H = \frac{1}{\bar{\nu}_H} = 2406.7 \text{ nm}$ and

$E_H = ch \bar{\nu}_H = 8.26 \times 10^{-20} \text{ J}$. The output radiation from the gas cell are given by

$$E_{i,n} = E_i - n E_H$$
where \( n = 1, 2, 3 \ldots \) represent the number of Stokes lines and \( n = -1, -2, -3 \ldots \) represent the number of Anti-Stokes lines. The wavelength \( \lambda_{i,n} \) of output radiation is given by

\[
\lambda_{i,n} = \frac{c \text{h}}{E_i - nE_H} = \frac{c}{f_i - nf_H}
\]

Table 2-1: The output radiation for the 2\(^{\text{nd}}\), 3\(^{\text{rd}}\) and 4\(^{\text{th}}\) harmonic are composed of the following wavelengths of the light.

<table>
<thead>
<tr>
<th></th>
<th>( \lambda_{4,n} = 266 \text{ nm} )</th>
<th>( \lambda_{3,n} = 355 \text{ nm} )</th>
<th>( \lambda_{2,n} = 532 \text{ nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>398</td>
<td>636</td>
<td>1579</td>
</tr>
<tr>
<td>2</td>
<td>342</td>
<td>503</td>
<td>954</td>
</tr>
<tr>
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<td>299</td>
<td>416</td>
<td>683</td>
</tr>
<tr>
<td>4</td>
<td>240</td>
<td>309</td>
<td>436</td>
</tr>
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<tr>
<td></td>
<td></td>
<td>184</td>
<td>282</td>
</tr>
<tr>
<td></td>
<td></td>
<td>171</td>
<td>253</td>
</tr>
</tbody>
</table>
2.6.2 Appendix B: Yorick codes for scanning the traces in the digital oscilloscope

“tscan.i” and analyzing the traces “tofanalyze.i”

#include “tscan.i”
#include "ycode/ls331.i"
#include "ycode/ps325.i"
#include "ycode/lecroy.i"
#include "ycode/laser.i"
#include "ycode/gui.i"
#include "ycode/keithley_mult.i"
#include "ycode/kodak.i"
#include "pnm.i"
#include "mod_vars.i"
#include "ds345.i"
#include "math_stuff.i"
#include "lecroy.i"
#include "nice.i"
#include "poly.i"
#include "filter.i"
#include "band_filt.i"

func save_one(fn,chan=, lv=, use_ds345=, tek=
{ fn=get_new_filename(fn);
  if (!tek) {d=read_wave(chan=chan);
    par=get_params(d);
    dat=get_data(par,d);
  } else {
    read_tek_waveform(par,dat,chan=chan);
    t=get_temp();
    v=readhv(use_ds345);
    v_hp=hp_multimeter_value();
    date=get_date_string();
    f=createb(fn);
    scope_average(nn,par,dat,ac=ac);
    f=createb(fn);
    t=get_temp();
    date=get_date_string();
    if (ac!=[]) {is_ac=1;
      v=ac; }
    is_ac=0;
  }
  include “tofanalyze.i”
  include "ycode/math_stuff.i"
  include "ycode/lecroy.i"
  include "ycode/nice.i"
  include "ycode/poly.i"
  include "pnm.i"
  include "filter.i"
  include "ycode/band_filt.i"
  colors=[-3,-5,-6,-7,-8,-9,-10];
  v=readhv(use_ds345);
  { ibclr, hp_multimeter_id;
    hp_mult=hp_multimeter_value();
    v=double(v);
    save,f,date,par,dat,t,v,is_ac, hp_mult;
    close,f;
  }
}
func plot_one(fn,color=,fr=,scale=, zero=, offset=,lgx=,lgy=,skip=,notch_par=) {

    /* DOCUMENT
    plot_one(fn,color=,fr=,scale=,zero=,offset=,lgx=,lgy=,skip=,notch_par=)
    fr is bessel filter frequency zero,skip are ti2mes - subtract avg of t>skip, t<zero
    offset is additive offset
    scale is multiplicative scale after offset, zero
    lgy, lgy are base enotch_par is 2x1 array, freq.
    and width in Hz
    */
    if (scale==[]) scale=1.;
    f=openb(fn);
    tma=time_array(f.par);
    y=f.dat;
    write, format="Temperature = %f\n",f.t;
    write, format="Voltage = %f\n",f.v;
    write, format="# Averages = %d\n",(f.par).sweeps_per_acq;
    write, format="File %s\n",fn;
    skip=(skip==[])?-1e30:skip;
    y1=y;
    if (notch_par!=[]) {
        y1=notch(tma,y1,notch_par(1),notch_par(2));
    } else {
        if (fr!=[]) {
            y1=filter_bessel(tma,y1,fr);
        }
        if (zero!=[]) {
            ll=where((tma>skip)*(tma<zero));
            y1=avg(y1(ll));
        }
        if (offset!=[]) y1=offset;
        y1*=scale;
        if (lgx!=[]) {
            l=where(tma>0);
            tma=log10(tma(l));
            y1=y1(l);
        }
        if (lgy!=[]) {
            ll=where(y1<=0);
            lp=where(y1>0);
            y1=log10(abs(y1));
            if (is_array(ll)) {
                plotl,tma(ll),y1(ll),color=color,type="dash";
            } else {
                plotl,tma,y1,color=color;
            }
        } else { plotl,tma,y1,color=color; }
    }
}
2.7 REFERENCES


CHAPTER 3

A TEST OF POLARON BAND THEORY: A HIGHLY ORDERED, HIGH MOBILITY ORGANIC SEMICONDUCTOR GROWN FROM A MESOPHASE OF TTB [1,4-DI-(5-N-TRIDECYLTHIEN-2-YL)-BENZENE]

3.1 INTRODUCTION

The basic introduction of organic semiconductors and liquid crystals was given in sections 1.5 and 1.6, respectively. In the latter section, I have also discussed why liquid crystals are promising as organic semiconductors to replace the polymer and single crystal organic semiconductors. Discotic and calamitic liquid crystals as organic semiconductors also have been discussed in the sections 1.6.4 and 1.6.5, respectively. In this chapter, I will discuss the charge transport of the calamitic liquid crystal containing a thiophene-benzene-thiophene core with alkyl tails.

Generally, there are two types of conduction in non-metallic solids. The first type of conduction is associated with delocalized motion and described by a band model as described in the section 1.4.1. In this conduction, the charge carriers are delocalized and move as plane waves in a broad carrier band with a relatively large mean free path. For
example, the hole motion in germanium, where the valance bandwidth is $\approx 3$ eV, the scattering time $\tau = \mu m/e \approx 10^{-3}$ s and the mean free path (at $T = 300$ K) is $\approx 1000$ Å, which is much larger than a typical lattice constant, 2.45 Å. However, the band width in germanium depends on the temperature and $\tau$ depends on phonons and the temperature. In a real crystal, lattice vibrations (phonons) scatter the charge carriers and reduce the charge carrier mobility ($\mu$). Therefore, the increase in temperature, which increases the phonon population, will decrease the mobility. In such a case, the charge carrier mobility ($\mu$) value is dependent on the temperature as $\mu \sim T^n$ with $n > 1$.

The second type of conduction is associated with the localized carrier motion and described by a hopping model as described in the section 1.4.2. The carriers are localized due to irregular lattices, site defects or potential wells caused by the lattice polarization due to a charge carrier. In this conduction, the charge carrier moves by hopping from one site to the other and the lattice vibration plays a big role in moving the carrier as well. Therefore, the hopping conduction is an activated process, in which the charge carrier mobility increases with increasing temperature. In this case, $\mu < 1$ cm$^2$/Vs and is dependent on the temperature as $\mu \sim \exp (-\Delta/k_B T)$, where $\Delta$ is an activation energy.

The main difference between the band model and the hopping model is that the former model gives importance to the collective character of conduction states and the later gives the importance to the molecular character of conduction states.

Some molecular crystals like anthracene, in which $\mu \approx 1$ cm$^2$/Vs [1], possess the characteristics of both models due to the weak intermolecular interaction. This is shown
by the existence of two different temperature regions, where the mobility is dependent differently on temperatures.

The behavior of the charge carrier mobility of organic semiconductors as a function of temperature and electric field, $\mu(T,E)$, may change qualitatively based on, for example, the polarizability of the host lattice, the phonon spectrum, the band gap and the electronic bandwidth of the valence (for hole transport) or conduction (electron) band. Many refinements of the basic ideas of T. Holstein [2] have been developed, dealing with both non-adiabatic [3] (hopping conduction with temperature dependent activation) and adiabatic [4] (tunneling-dominated or band-like) transport. I report here studies of a material that exhibits polaron band behavior.

### 3.2 MOLECULAR STRUCTURE OF THE EXPERIMENTAL MATERIAL

In this chapter, I present the electronic properties of the crystal smectic phases of the liquid crystal 1,4-di-(5-n-tridecylthien-2-yl)-benzene (TBT) [5] synthesized by Y Getmanenko (appendix B). The material has a central core unit of a thiophene-benzene-thiophene with the structure as shown in Figure 3-1. Both ends of core unit are attached with alkyl tails C$_{13}$H$_{27}$.

![Figure 3-1](image)

**Figure 3-1**: (a) 1,4-di-(5-n-tridecylthien-2-yl)-benzene and (b) Molecular structure of thiophene.
I have already introduced the benzene molecule in the section 1.3.3. Therefore, here, I introduce only the thiophene molecule.

Thiophenes have been extensively investigated for their promising optoelectronic properties. Their applications have been found in field effect transistors. It is an aromatic heterocyclic compound (C₄H₄S) with a five-membered ring. The presence of highly polarizable sulfur atoms [6] increases the transfer integral between thiophene molecules due to a large van der Waal’s radius and plays an important role in the charge carrier transport phenomenon and in close molecular packing of the thiophene molecules. The implication is that the introduction of the sulfur atom in the molecule helps to upgrade the hopping conduction of all charged carriers [7].

The presence of coplanarity or torsional distortion about the bonds between rings also determines the extent of intramolecular π-electron delocalization. In general a coplanar arrangement leads to a denser packing and more π-electron delocalization, which are both favorable conditions for the optimization of optoelectronic properties in these thiophenes. The high degree of molecular and crystalline ordering has been reported in the well-defined oligothiophenes [8].

An oligothiophene is the chain of a finite number of thiophene molecules, e.g. quarterthiophene. The mobility in quarterthiophene-based liquid-crystalline semiconductors was found 0.1 cm²/Vs in highly ordered smectic phases around room temperature [9]. The same value of the mobility was also reported in a material which contains the same thiophene-benzene-thiophene core as ours [7]. The charge carrier mobility in dialkyl-substituted oligothiophene derivatives, which exhibits mesophase
above room temperature, was also found to be high [10,11,12]. Since the materials in this experiment contain two thiophene molecules, we expect high charge carrier mobility in this material.

The oligothiophenes give a high degree of molecular and crystalline ordering [8]. They have been used as one of the important organic semiconductors with potential applications in electronics devices, e.g., thin film transistors, photovoltaic solar cells, light-emitting diodes, light modulators, photochromic switches and laser microcavities.

M. Funahashi et al. [13] reported that dialkylterthiphene derivatives (thiophene based liquid crystals), which possessed self-organization of molecular alignment, exhibited a very fast electron and hole transport in smectic mesophases. Both mobilities were independent of electric field and temperature. In this material, they found the electron and hole mobilities are $5 \times 10^{-4}$ cm$^2$/Vs in SmC phase. With the upgrade of molecular alignment from SmC to SmF and from SmF to SmG, the values rise up to $2 \times 10^{-3}$ cm$^2$/Vs and $1 \times 10^{-2}$ cm$^2$/Vs, respectively. Funahashi, M. et al [9] also has reported charge carrier mobilities up to 0.1 cm$^2$/Vs for an asymmetrically substituted quaterthiophene, which is in highly ordered smectic phases at room temperature.

3.3 EXPERIMENT

The experimental setup for the time of flight technique method to measure the hole mobility was explained in the section 2.2. In this experiment, the cell was prepared manually in the lab and its thickness was measured by using Quadtech 1920 Precision
LCR meter, as described in the section 2.4. Laser pulse intensities were kept low to avoid space-charge effects (manifesting as TOF traces that rise during the charge transit period).

3.3.1 Filling up the cell and the domain formation

The cell in the holding mount was heated on the hot stage at a temperature of 140 °C, which is slightly higher than the clearing temperature (SmF – Isotropic phase transition) of the material as shown by DSC thermogram in Figure 3-2. The material was kept at the side of the cell and was heated to its isotropic phase until it melted. The melted material entered the cell by the capillary action. Then, it was slowly cooled down at the rate of about .01 °C/sec into the liquid crystalline phase.

Differential scanning calorimetry (Figure 3-2), powder x-ray diffraction (Figure 3-10) and polarized light microscopy indicate the phase sequence Cr\(_1\) - 76.6 °C - SmH 91.7 °C - SmG °C - 122.4 °C - SmF 134.0 °C - I (on cooling) [14]. The structure of different smectic phases are explained in the appendix section 3.7.1 and the sketch of the smectic liquid crystals is shown in the section 1.9.3.
Figure 3-2: Differential Scanning Calorimetry (DSC) thermogram of TBT. After the polarized optical microscopy analysis and the powder x-ray diffraction, the mesophases are confirmed as SmH, SmG and SmF.

3.3.2 Determination of the absorbing wavelength of the experimental material

The detailed process for the determination of the wavelength of the light absorbed by the material by using HP 8453 UV-Visible Spectro-Photometer has been explained in section 2.5. The sample solution was made with CH$_2$Cl$_2$. The absorbed amount of the incident light at 320 nm wavelength was sufficient to create the holes in the sample.
Figure 3-3: UV-absorption spectra for the TBT material at two different concentrations. They clearly show the absorption of light at 319 nm.

3.4 OBSERVATION

3.4.1 The field independence of the mobility at constant temperature

The electric field dependence of the mobility at different temperatures for the material is as shown in Figure 3-5. Starting from the higher temperature, the measurements were taken in the temperature range from 139 °C to 79 °C with a step of 10 °C. The material was first heated to its clearing temperature then cooled down slowly at a rate of 0.01 °C per second. Below 74 °C, the signal is completely dispersive, i.e., the transit time was hard to locate at temperatures above 139 °C, there was no signal detected. The
99 observations were taken in both low field regime and high field regime. The electric field range was from $2.9 \times 10^3$ V/cm to $8.9 \times 10^3$ V/cm with a step variation of 750 V/cm for the low electric field regime. The electric field range was from $6.5 \times 10^3$ V/cm to $4.0 \times 10^4$ V/cm with a step variation of 2200 V/cm for the higher field regime. The step was made bigger at high electric field to save the cell from damaging due to the laser light at high voltage. From the observation, it was found that the charge carrier mobility is almost constant with the electric field as it can be seen in Figure 3-4, where the time of flight is decreasing proportionally with increasing electric field as we can see from lower graph to upper graph.

![Figure 3-4: The TOF traces for the hole mobility with the electric field variation at 129 °C.](image)
While experimenting at the higher electric field, the presence of any saturated drift velocity with the electric field was also checked. This phenomenon is called “relaxation by optical phonon emission” or the hot-carrier effect. In this phenomenon, it is assumed that the charge carrier is accelerated by the applied field, increasing its momentum and thereby gaining energy. Once the energy becomes high enough, it generates optical phonons. This process is repeated continuously. The continuation of this process gives a drift velocity which is independent of the field [15]. If this is the case, the
mobility should decrease with increasing electric field. But this characteristic was not observed in this experimental material, i.e., there is no significant decrease in the mobility with the higher field. To conclude, there was no indication of the hot carrier effect.

The possibility of negative carrier transport was also checked, but no signal was observed. That is, TOF traces for the electron mobility were too dispersive to allow for the measurement.
3.4.2 The temperature dependence of the hole mobility at constant electric field

![Graph showing TOF traces at different temperatures.](image)

Figure 3-6: TOF traces at different temperature at the same electric field $E = 5400 \text{ V/cm}$.

$T_1 > 134 ^\circ \text{C} > T_{\text{SmF}} > 122.4 ^\circ \text{C} > T_{\text{SmG}} > 91.7 ^\circ \text{C} > T_{\text{SmH}} > 76.6 ^\circ \text{C} > T_{\text{Cr1}}$
The time of flight traces at different temperatures at constant electric field $E = 5400$ V/cm and the temperature dependence of the hole mobility taken by cooling the material from its isotropic phase are shown in Figure 3-6 and Figure 3-7 respectively. The temperature range over which the data could be collected was limited due to the trapping of the charge carriers at low temperature regime and the melting of the material at high temperature regime.

Figure 3-7: The temperature dependence of the hole mobility at 5400 V/cm. Only the changes at the isotropic to SmF transition is clearly visible, as the mobility suddenly jumps when $T$ decreases.
Figure 3-8: The temperature dependence of the hole mobility at 5400 V/cm on a semilog scale.

Figure 3-9: The temperature dependence of the mobility in the form of power law ($\mu \sim T^n$).
At a constant electric field, the mobility increases with decreasing temperature. The electric field was maintained at \( E = 5.4 \times 10^5 \) V/m. As the temperature decreases, there is a sudden increase in the mobility at the transition from isotropic to SmF mesosphere.

### 3.4.3 Powder x-ray diffraction

![Figure 3-10: Powder diffraction results for (left to right) the SmF, SmG, and Cr phases.](image)

Note both the high degree of order in the mesophase and the similarity of the structures of the smectic phases and the crystal.

Powder x-ray studies were performed by Prof. Satyan Kumar and his coworkers at the Advanced Photon Source at Argonne National Laboratory using 0.765335 Å photons with the sample contained in a Lindeman capillary. Figure 3-10 shows the powder diffraction data in the SmF, SmG and Cr phases.
3.4.4 Polarized-light photomicrographs of the liquid crystal phases

The polarized optical microscopy analysis clearly showed the formation of the SmF phase directly from the isotropic liquid. This is a rare transition and only a few mesogens [16, 17, 18, 19] to our best knowledge were reported to exhibit Iso-SmF transition since the discovery by Walton and Goodby [20] in 1984. Several natural textures of the SmF phase were observed including the mosaic and fan-like textures. An unusual texture that resembled lava or stacked disks was also observed. The distinctive texture of the SmF phase with a sphere divided into 6 segments [20] was observed on uncovered film, but this texture was transient in time and very difficult to get a good photograph of.

All data taken on cooling from the isotropic phase (transition temperatures may differ slightly from those found using the DSC instrument).
Figure 3-11: SmF phase at 135.1 °C and 126.1 °C.
Figure 3-12: SmG phase at 93 °C and 83.3 °C.
Figure 3-13: SmG phase at 77.4°C.

Figure 3-14: Crystal phase at 47.8°C.
3.5 RESULTS AND DISCUSSIONS

The isotropic to the ordered SmF phase transition has a major effect on the mobility with $\mu$ increasing a factor of 3.4 as the sample enters the mesophase. As $T$ falls, the mobility sharply yet smoothly increases, to a maximum $> 0.1$ cm$^2$/Vs at the lowest temperature measured. Such large mobilities generally arise from two factors: firstly, favorable single-molecule physics (hinted at in the large isotropic values of $\mu$) and secondly, a high degree of long-range ordering. In Figure 3-10, we show powder diffraction data in the SmF phase, which imply very large positional order correlation lengths, both orthogonal (112.2 nm) and parallel (10.85 nm) to the smectic planes. For comparison, the maximum correlations lengths measured in magnetically-aligned free-standing films in the SmF phase of the liquid crystal TB10A [21] in either direction are less than 20 nm (albeit only slightly below the SmI to SmF transition temperature). Correlations have also been measured across the SmF to SmG transition (i.e., similar to TTB) in the liquid crystal HBHA by Kumar [22], who found in-plane lengths of $\sim 20$ nm in the SmF phase, increasing to $\sim 150$ nm in the SmG phase. TTB, therefore, appears to be very ordered indeed in the high temperature SmF phase.

Interestingly, there are structural transitions at $T_{SmF} \rightarrow T_{SmG} \approx 395$ K and $T_{SmG} \rightarrow T_{SmH} \approx 365$ K, with little (if any) signature in the mobility. The SmF phase is characterized by hexagonally-ordered tilted layers, typically with little inter-layer positions (though the layers do not readily rotate relative to one another) [23]. The SmG phase, on the other hand, is a 3-dimensional pseudo-hexagonal crystal phase where the
(tilted) molecules are relatively free to rotate about their long axis. Since \( \mu \) does not suddenly change at the F-G transition, we conclude that the relative ordering of the layers is not as important in hole transport as the ordering within layers. The SmH phase is a monoclinic crystal where molecules can only rotate by 180° (i.e., they may flip) about their long axis. It therefore differs from the SmG phase in symmetry (four nearest neighbors rather than six) and in the rotational freedom of the mesogens. However, as at the F-G transition, there is no obvious change in mobility at the transition. (There may, however be a slight change in the slope of the data at this transition, though the limited temperature range makes it difficult to judge - see Figure 3-8) Interestingly, X-ray studies of SmF-SmG-SmH transitions [24] in terephthalbis-(4n)-alkylanilines find that the layer spacing changes very little at both the SmF-SmG, and SmG-SmH transitions. (Note that, at the time this reference was written, the G phase was referred to as the H phase, and vice-versa). The molecular tilt angle is also essentially constant through the SmF-SmG phase change. In other words, the actual structural changes that occur at these phase boundaries are minor. If these facts remain true for our material, they offer a natural explanation of both the lack of jumps in mobility at phase boundaries, and of the seemingly uniform behavior of \( \mu(T) \) over the entire temperature range. In light of this information, and given the smoothness of the mobility as a function of \( T \), we choose to describe the entire crystal smectic temperature range using a single theoretical approach, keeping in mind that there may be quantitative changes in behavior unique to each phase.
Our data in the crystal smectic phases may be well described by either a power-law form \( \mu \sim T^{-n} \) as shown in Figure 3-9 or by an exponential, \( \mu \sim \exp(-\alpha T) \), as shown in the Figure 3-8.

Theories of polaron hopping [4, 25] predict that at high temperatures

\[
\mu(T) = \frac{1}{T^{3/2}} \exp(-E_{\text{pol}} / 2kT)
\]

(1.40)

where \( E_{\text{pol}} \) is the small-polaron binding energy. At very high \( T \), \( kT >> E_{\text{pol}} \) (i.e., hot enough to dissociate polarons), this gives \( \mu \sim T^{-1.5} \). It is very unlikely that our data are in this regime, since typical polaron binding energies [25] are several tens of meV, or several times \( kT \). Indeed, we have computed \( E_{\text{pol}} \) for a molecule corresponding to the thiophene-benzene-thiophene core of our liquid crystal (with no tails). We followed the procedure of ref. [25] using unrestricted density functional theory, the B3LYP hybrid functional, and the 6-311g** basis set to compute \( E_{\text{pol}} \). We found \( E_{\text{pol}} = 192 \text{ meV} \), far greater than thermal energies which is \( kT_{\text{expt}} \sim 30 \text{meV} \) for our experiment.

In our data, the value of \( n \) for the power law was found as 10.5, far greater than the 1.5 predicted theoretically [4,25] or the \( n \sim 2 - 4 \) found in other organics [26] (we note that the SmF, SmG, and SmH phases, if analyzed separately, all independently demand very large slopes). We therefore conclude that polaron hopping theories are inapplicable to our results. We also found an evidence to prove that the model of hopping conduction in the presence of disorder is inapplicable to our results too. It is described in the next paragraph.
Figure 3-15: The mobility derived from log-log plots of highly dispersive traces at fixed field (squares) are essentially the same as those from far less dispersive transients (circles, at various electric fields). Inset: Example more and less dispersive TOF transients at 90 °C.

As carriers traverse a sample in a time-of-flight (TOF) experiment, they interact with impurities and other types of disorder within the sample. It has long been known that traps and other defects can affect the measured TOF, and therefore the mobility [27,28]. Generally, one defines the TOF as the average carrier arrival time at the far electrode. If we operationally define the TOF as the inflection point in a current trace, as explained the section 2, the experimentally measured mobility may be too high (i.e., it represents the arrival of the leading edge of the dispersed charge cloud rather than the average arrival time). We do indeed observe dispersive transients in some (but not all) runs, especially at
lower temperatures. Interestingly, however, there does not appear to be any significant
difference between mobilities measured using extremely dispersive transients (where log-
log plots are needed to see the inflection point) and those extracted from far less
dispersive data that clearly show plateaus on linear graphs. This is shown in Figure 3-15,
where we plot the data of Figure 3-7 with a set of mobilities extracted from wide variety
of far less dispersive data sets at many voltages- the agreement is excellent throughout (as
we will show in detail, below, \( \mu \) is independent of field). This is not what is expected in
detailed models of hopping conduction in the presence of disorder [27], and is evidence
that a different mechanism is operative here.

A general result of polaron band theories, such as that described by Silbey and
Munn [4], and presented in the early theory of Holstein [2], is that there is a narrow
crossover temperature regime (characteristic temperature \( T_a \)) between non-adiabatic and
adiabatic conduction, with the latter taking over at lower \( T \). The crossover temperature is
critical in describing our results: above \( T_a \), \( \mu(T) \) has positive slope while below \( T_a \), the
mobility typically has negative slope and can exhibit qualitatively exponential behavior.

Let \( B \) be the bare polaron bandwidth and \( \tilde{B} \) be the effective polaron bandwidth or
the renormalized (Huang-Rhys) bandwidth [29], which decreases sharply with increasing
temperature. \( \tilde{B} \) exhibits a strong temperature dependence due to electron-phonon
interaction. In the approximation that the charge carrier couples to only one phonon
branch of an energy \( \hbar \omega \) with the dimensionless electron-phonon coupling constant \( g \), the
effective bandwidth as a function of temperature is given by the equation [29,30].
\[
\tilde{B} = B \exp \left\{ -\frac{g^2}{\tanh \left( \frac{\beta \hbar \omega}{2} \right)} \right\} 
\]

(3.1)

Four parameters that control both \( T_a \) and the shape of \( \mu(T) \) are the electron bandwidth, \( B \), the characteristic optical phonon frequency, \( \omega \), the phonon bandwidth, \( \Delta \) and the dimensionless electron-phonon coupling, \( g \). The predicted mobility, both above and below \( T_a \), is given by R. Silbey and R. Munn [4].

\[
\mu(T) = \mu_H + \mu_T \\
\mu_H = \frac{\beta ea^2}{\pi^2 h [I_0(y) - 1]} \frac{\tilde{B}^2 + \Gamma^2}{\sqrt{\tilde{B}^2 + 2\Gamma^2}} \\
\mu_T = \frac{\beta ea^2}{4h} \pi^\frac{3}{2} [I_0(y) - 1] \frac{\tilde{B}^2}{\sqrt{2\tilde{B}^2 + \Gamma^2}} \exp \left\{ -\frac{1}{4} \frac{\beta^2 \tilde{B}^4}{2\tilde{B}^2 + \Gamma^2} \right\} 
\]

(3.3)

Where \( y = 4g^2 \sqrt{n(n+1)} \) with \( \mu_H \) and \( \mu_T \) the hopping and tunneling contributions to mobility, \( \beta = 1/ k_B T \), \( k_B \) is the Boltzman’s constant and \( a \) is the intermolecular distance. \( \Gamma \) is a modified phonon bandwidth, given by R. Silbey and R. Munn [4], which is expressed by \( \Gamma = \Delta \sqrt{y} \) at temperature high enough to make \( y > 1 \) and \( \Gamma = \Delta \) for \( y \leq 1 \). \( n \) is the phonon distribution function, \( n = 1/\exp(\beta \hbar \omega) - 1/ \). The hyperbolic Bessel function \( I_0(y) \) is a sharply increasing function of its argument and therefore of \( T \) (\( y \sim n \) and \( n \) increases with \( T \)).

We have used the x-ray derived value of \( a = 4.2 \text{ nm} \) (i.e., we assume transport is dominated by motion orthogonal to the smectic layering). It is noted that these
expressions provide a prediction for the mobility in absolute units. Given the small region of temperature (even though we consider both the SmG and SmH phases collectively in our analysis), it is impossible to constrain all of the four parameters. However, we found that, in order to move the low-T quasi-exponential region of \( \mu \) to the high experimental temperature range and to account for the measured values of mobility, the model requires large coupling \( g \geq 1 \) and small raw electronic bandwidth \( B \ll \hbar \omega \). (The data do not constrain \( B \) except that they require \( B/\hbar \omega \ll 1 \). In this regime, we must then have either large phonon bandwidth \( \Delta > \hbar \omega \) and/or high center frequency, \( \omega \). This is logical - the value of the crossover temperature \( T_a \) is set partly by the phonon energies the system supports, i.e., either by \( \omega \) itself or by the high energy tail of the Gaussian distribution whose width is set by \( \Delta \).

The model, however, is limited to \( \Delta/\hbar \omega < 1 \) (so that the phonon distribution can be modeled as a Gaussian [4]). Letting the phonon bandwidth take on a maximal value, say \( \Delta/\hbar \omega = 0.5 \), we found that the data may be fit albeit with \( \hbar \omega k_B \approx 440 \text{ K} \). Typical acenes and simple aromatics like perylene have experimentally measured phonon bands centered around 200 K or less (an oft-used approximate value is 100 cm\(^{-1}\) \(\approx 150 \text{ K} \)). It is hard to understand why a relatively “floppy” molecule like ours would have a much stiffer lattice than these materials. Indeed, the small electronic bandwidth would suggest that the molecular cores are relatively weakly interacting, which at least naively would lead to a softer lattice. We therefore conclude that the present model is quantitatively incorrect. Given the simplifications inherent in the theory (greatly simplified phonon band structure, including the limitations on \( \Delta \), the assumed isotropy of the phonon
spectrum, etc.), this is not too surprising. We note that more complete theories including non-local electron-phonon interactions [31, 32] are unlikely to resolve our difficulties since they seem to reduce the slope at low T, while our data demand moving the regime of quasi-exponential growth to higher temperature. Given the large mobilities in this material, along with the presumed softness of the highly-ordered smectic “lattice”, perhaps a more promising direction is supplied by theories of intermediate bandwidth organic semiconductors, such as those explored by Kenkre and Coworkers [33].

The electric field dependence of the mobility is a powerful probe of the microscopics. In the case of hopping conduction [3], $\mu(E)$ can be super-exponential. On the contrary, we find the $E$ is irrelevant. In Figure 3-5, we show the hole mobility over a wide range of field and temperatures in each phase. In every case, $\mu$ is essentially independent of field, i.e., ohmic. This is consistent with a band model. We note that we do not observe any sign of a drop in mobility at large fields that would indicate hot-carrier effects.

There are a number of other highly ordered smectics that have been studied as semiconductors [13, 34, 35, 36, 37], some (though by no means all) with mobilities in the 0.1 cm$^2$/Vs range. To our knowledge, however, this is the first smectic H material so studied, and the first very high mobility smectic with polaron band-like transport. It is interesting and potentially of practical utility that the highly crystalline H phase of 1,4-di-(5-n-tridecylthien-2-yl)-benzene supports high-quality hole transport in our 20 µm cells, since, in our experience, “true” crystal phases grown from smectics usually have too much structural disorder (and therefore trapping) to even show measurable TOF
transients. One possible explanation is that the highest temperature crystal smectic, SmG, inherits the impressive long-range order of the mesophase, both orthogonal and parallel to the smectic planes, which in turn templates the H phase. Very similar behavior, in which oligothiophenes with SmF phases templated a polycrystal supporting high mobility conduction, has previously been reported, though with quite different temperature dependences than our results [13,38]. Unfortunately, no correlation lengths were reported for comparison with our material. This would be a worthwhile direction for further work.

The powder diffraction results shown in Figure 3-10 suggest that the SmF state templates the structure of the SmG (and eventually the SmH) highly crystalline smectic phases, which presumably forms in larger, better ordered grains due to the order of the higher temperature smectic. This presents a very interesting technological advantage of these crystal smectics: thin samples of a high-mobility essentially crystalline organic may be grown with large-grained structure by using a less-ordered smectic phase as a template. Indeed, by using standard methods to align the liquid crystal phase (appropriately rubbed polyimide alignment layers, magnetic and electric fields, etc.), it may be possible to stabilize a fully crystalline thin film via the mesophase. The implications for device (for example, thin film transistor) development, where a high-mobility film must be produced, preferably at low temperatures, are obvious. Another interesting possibility is to use the mesophase to anneal away damage in the semiconductor and then to re-crystallize the ordered film in-situ.

This system is not the first liquid crystal with a thiophene-benzene-thiophene core found to have a high mobility. In 2005 Oikawa et al. [7] measured $\mu(T)$ in the C$_8$ analog
of our material and found similar mobilities, though the increase with decreasing T was less pronounced. Whether this is due to an intrinsic difference in the materials or to cell thickness (they used 15.9 µm), alignment, or cooling rate is unknown. The authors of [7] found the phase assignment I 145 °C Sm1 87 °C Sm2 71 °C Sm3 47 °C Cr, i.e., three unidentified smectic phases followed by a crystal phase on cooling. This is similar to our results. Interestingly, Oikawa et al. found large (∼ 0.1 cm²/V s) mobilities in the lower mesophases, and much higher values of µ in the highest temperature smectic Sm1 phase than we find in our SmF regime. Obviously, further mobility and structural studies (including phase assignment) of this series are warranted.

Duzhko et al. [26] found evidence for polaron band transport in a very different mesogen, the hexapentyloxytriphenylene (HAT5), a discotic material with a mobility at least three orders of magnitude smaller than that of the present material’s SmH phase. Apparently, charge transport via renormalized polaronic bands is a fairly generic occurrence in organics of widely differing morphology. Our material, 1,4-di-(5-n-tridecylthien-2-yl)-benzene, appears to be a prototype narrow polaron band semiconductor, which presents opportunities for refining the relevant theories. The principal theoretical question is, why is “the low temperature regime” accessed for T greater than the likely phonon frequencies? We also find that the high mobility essentially crystalline phases may be reliably formed in thin films by using the high temperature liquid crystalline state as a template, opening interesting technological vistas.
3.6 CONCLUSIONS

1. At constant electric field, the hole mobility increases with decreasing temperature. In the isotropic (I) phase, the mobility is $6 \times 10^{-3} \text{ cm}^2/\text{Vs}$ and changes very slowly with the temperature. As the temperature decreases, there is a sudden increase in the mobility when transition occurs from the I-phase to the first mesophase (SmF). Since there is the sizable jump in mobility (a factor of 3.4) at the transition from the disordered I-phase to the ordered SmF phase, the ordering of the molecules has much effect on the mobility.

2. Since the mobility does not suddenly change at the smF-smG transition, the relative ordering of the layers is not as important in hole transport as the ordering within layers.

3. The exact alignment of adjacent molecular cores is not critical for transport because the mobility does not suddenly change at the SmG-SmH transition. The main difference of SmH from SmG is symmetry (four nearest neighbors in SmH rather than six in SmG) and in the rotational freedom of the mesogens.

4. In the low temperature mesophases, a rapid increase of mobility occurs as the temperature decreases.

5. The maximum mobility received was greater than $0.1 \text{ cm}^2/\text{Vs}$ at the lowest temperature measured in low temperature mesophase. This material is of real interest for, e.g., thin-film transistor fabrication due to high mobility at low T mesophase.
6. The powder diffraction results suggest that the highly ordered high temperature smectic-F phase templates the formation of very ordered smectic phases SmG and SmH. Therefore, thin samples of a high-mobility essentially crystalline organic may be grown with large-grained structure, which may have implications for device development. In our experience, “true” crystal phases grown from smectics usually have too much structural disorder for TOF measurement.

7. The hole mobility is independent of electric field over a wide range of field at all measured values of temperatures.

8. No hot-carrier effect was found.

9. The polaron hopping theories are inapplicable to our results.

10. To our knowledge, this material is the first SmH mesophase so studied, which gives very high mobility with polaron band-like transport.

11. We report here studies of a material that exhibits polaron band behavior. However, while qualitatively consistent with transport via polaron bands, we find that it is quantitatively difficult to explain the data with physically realistic parameters. In particular, the data demand either quite large typical optical phonon frequencies and/or phonon bandwidths.

12. Existing models are not enough to interpret our results because these theories interpret our material as molecules, which are much stiffer than that of fully aromatic materials like acenes. A complete modified theory is required for example – theories including non-local phonon interactions, theories of intermediate bandwidth organic semiconductors.
3.7 APPENDIX

3.7.1 Appendix A: Side view (top figure) and top view (bottom figure) of the molecular ordering in different smectic phases.

**Smectic A** – In SmA, the molecules are located within the liquid like layers with its director perpendicular on average to the plane of the layer. The lateral distribution of the molecules within each layer is random, and the molecules within the layers are able to rotate freely about their long axes. So the layer thickness ‘d’ is roughly the same as the molecular length ‘l’.

**Smectic C** – In SmC, the molecules in the layers are parallel and tilted in arrangement with respect to the normal of the layers by a tilt angle ‘θ’. Hence the layer thickness in
SmC phase is \( d = l \cos \theta \). As in SmA, in SmC phase too, the molecules have no particular positional order within the layer. There is a liquid-like motion of the rods in each layer and no correlation of the molecular positions from one layer to the next. In each layer, the mass centers of the molecules are randomly distributed as in isotropic liquids. The layers can easily slide.

**Smectic B** – In SmB (hexatic), there is also one-dimensional order, which forms the layer structure as in SmA and SmC phases and in addition, there is also the two dimensional translational order within the layers and two dimension bond symmetry. The molecules are arranged into a hexatic lattice in layers with the molecular centers positioned hexagonally closed packed array.

**Smectic E** – This phase has higher order of the molecules within the layers. The order went beyond that within single layers, i.e., this phase exhibits a stronger correlation
between smectic layers, the range of correlation length goes from tens to hundreds of layers. The molecules of the SmE phase within the smectic layers tend to be perpendicular to the smectic layers, but they are unable to rotate freely with respect to the long molecular axis.

**Smectic F** – This phase is similar to SmB but the molecules are packed in layers with their long axes tilted with respect to the layer planes. The azimuthal of the tilt direction or the projection onto the smectic layers of SmF point to the edge of the hexatic. If it points to the apex, it is called SmI, not shown in figure.

**Smectic G** – The phase is similar to SmF but there is a stronger correlation between smectic layers as in SmE.

**Smectic H** – Its structure is equivalent to that of SmE phase, except that the molecules have their long axes tilted with respect to the normal to the layer planes. The molecules
of the SmH phase are tilted to the edge of the hexatic. If the molecules are tilted to the apex of the hexatic, it is called SmK, not shown in figure.

3.7.2 Appendix B: Details of the synthesis of the thiophene-benzene-thiophene mesogen (This was done by Y Getmanenko).

The mesogen 1,4-di-(5-n-tridecylthiophen-2-yl)-benzene was prepared in 66% yield by the Stille coupling of 1,4-dibromobenzene with 2-n-tributylstannyl-5-n-tridecylthiophene (2) which was synthesized in 88.3% yield from 2-n-tridecylthiophene (described earlier [39]) by the reaction with n-BuLi followed by the trapping of the lithiated species with tri-n-butyltin chloride. The material (3) was extensively purified by Kugelrohr distillation (two times) and recrystallization from distilled 1-PrOH (three times) prior to mobility measurements.

![Chemical Structure](image)

**Experimental**

Solvents: THF was distilled from sodium benzophenone ketyl, n-BuLi (2.5M in hexanes), anhydrous DMF and tributyltin chloride were used as received. The catalyst tetrakis(triphenylphosphine)palladium(0) was prepared from PdCl₂ by reduction with hydrazine hydrate in DMSO [40].

**2-(Tri-n-butylstannyl)-5-n-tridecylthiophene (2)**
An oven-dried three-necked flask equipped with magnetic stir-bar, bubbler and nitrogen inlet was charged with 2-\textit{n}-tridecylthiophene (1) (0.04 mol, 10.66 g) and anhydrous THF (40 ml). The solution was cooled in acetone/CO\textsubscript{2} bath) and \textit{n}-BuLi (2.5M in hexanes, 0.04 mol, 16 ml) was added dropwise to the suspension of (1) (the precipitation occurred on cooling below –65 °C). The reaction mixture was warmed up slowly (over 1 hour) to ~10 °C and tri-\textit{n}-butyltin chloride (96% purity, 0.044 mol, 14.92 g) was added via syringe. During addition of Bu\textsubscript{3}SnCl the light red reaction mixture became darker in color, but after several minutes of stirring it became cloudy and color disappeared. The mixture was refluxed for 22 hours (precipitation was observed), cooled to room temperature, quenched with several ml of water, transferred to a round-bottom flask, and the solvent was removed by rotary evaporation. Water (20 ml) was added to the residue and organic matter was extracted with hexanes (50 ml, then 6×25 ml). The combined organic phases were washed with brine, and then dried over MgSO\textsubscript{4}. The crude material was Kugelrohr distilled, and the product was collected at 205 °C/0.12 mm Hg as yellowish oil (19.64 g, 88.3% yield). $^1$H NMR (CDCl\textsubscript{3}, 400 MHz): δ 0.90-0.98 (m, 12H), 1.09-1.15 (m, 6H), 1.27-1.42 (m, 22H), 1.55-1.63 (m, 6H), 1.65-1.76 (m, 2H), 2.83-2.91 (t, $J = 6.08$ Hz, 2H), 6.92-6.96 (d, $J = 1.83$ Hz, 1H), 7.00-7.05 (d, $J = 2.91$ Hz, 1H); $^{13}$C NMR (CDCl\textsubscript{3}, 100 MHz): δ 10.73, 13.69, 14.15, 22.72, 27.30, 28.99, 29.31, 29.42, 29.60, 29.69, 29.97, 31.84, 31.95, 125.26 (CH), 133.73 (quaternary C), 135.20 (CH), 151.66 (quaternary C) (several $^{13}$C signals for alkyl groups overlapped and the number of the resonances is smaller than expected).
1,4-Di-(5-\textit{n}-tridecylthiophen-2-\textit{y}l)-benzene (3)

An oven-dried two-necked flask, equipped with septum, thermometer, nitrogen inlet and magnetic stirbar, was charged with 1,4-dibromobenzene (2 mmol, 0.47 g), 2-tri-\textit{n}-butylstannyl-5-\textit{n}-tridecylthiophene (2) (2.2 eq., 4.4 mmol, 2.44 g), Pd(\text{PPh}_3)_4 (1 mol\% based on 1,4-dibromobenzene, 0.02 mmol, 0.023 g) and 10 ml of anhydrous DMF. The reaction mixture was heated with a heat-gun (145-150 °C) and it became dark in 2-3 minutes. The reaction mixture was cooled to room temperature, treated with 20 ml of ice-water, the precipitate was separated by vacuum filtration, washed with 50 ml of hexanes, and the crude material was isolated as light yellowish-greenish solid (0.87 g, 71.9\% crude yield). The crude material was dissolved in CH$_2$Cl$_2$ under heating, and the solution was filtered through Al$_2$O$_3$ column (20 g, neutral, boiling CH$_2$Cl$_2$ as eluant first, then hot CHCl$_3$). First several fractions (colorless with white precipitate) were combined, treated with 10 ml of 1-PrOH and the resulting solution was concentrated. The title compound was isolated as white shiny solid (0.54 g). The yellowish fractions (CHCl$_3$ as eluant) were combined, treated with 10 ml of 1-PrOH, concentrated, cooled, and the yellowish solid (slightly contaminated product) was isolated (0.26 g, total yield 0.80 g, 92\% recovery, 66\% yield). The material (3) was Kugelrohr distilled twice (230-240 °C/0.12 mm Hg) and recrystallized three times from distilled 1-PrOH prior the mobility measurements. FT-IR (cm$^{-1}$): 3069, 3034, 2954, 2918, 2849, 1592, 1559, 1493, 1468, 1393, 1294, 1137, 1020, 955, 875, 840, 810, 794, 723. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 0.85-0.92 (t, $J = 6.85$ Hz, 6H), 1.22-1.32 (m, 40H), 1.66-1.74 (m, 4H), 2.78-2.85 (t, $J = 7.66$ Hz, 4H), 6.73-76 (d, $J = 3.56$ Hz, 2H), 7.11-7.14 (d, $J = 3.57$ Hz, 2H), 7.51-7.56 (s,
\(^{13}\text{C}\) NMR (CDCl\(_3\), 100 MHz): 14.14, 22.72, 29.13, 29.39, 29.58, 29.68, 30.31, 31.68, 31.95, 122.54 (CH), 125.08 (CH), 125.73 (CH), 133.38 (quaternary C), 141.27 (quaternary C), 145.79 (quaternary C) (several \(^{13}\text{C}\) signal for alkyl group overlapped and the number of the resonances is smaller than expected). Analysis calculated for \(\text{C}_{40}\text{H}_{62}\text{S}_2\): C, 79.14; H, 10.29; S, 10.56. Found: C, 78.87; H, 10.75; S, 10.79.

3.8 REFERENCES


[5] This compound was synthesized at Prof. Robert Twieg’s laboratory at Chemistry Department of Kent State University.


The smectic-F phase is relatively unusual, with 363 entries in the Liquid Crystal 2003 database. A very useful review of the various smectics may be found in Gray and Goodby, “Smectic Liquid Crystals - Textures and Structures”, page 153 (2004).


[22] S. Kumar, J. Physique 44, 123 (1983), note, however, that the technique used for the extraction of correlation lengths was approximate.


4.1 INTRODUCTION

An introductory discussion of discotic liquid crystals (DLCs) was given in section 1.6.2. DLCs as organic semiconductors were also introduced in section 1.6.4, where the anisotropic mobility behavior in the discotic columnar phase was discussed. This type of behavior can be exploited to make one dimensional molecular wires, which are important for molecular device applications. On the other hand, the photoconducting materials should also be stable and preserve their properties in a wide temperature range for their use in device applications. These facts are motivations for this experiment.

The study of the charge transport properties in the discotic mesogen of NO$_2$-HAT5 (1-nitro-2,3,6,7,10,11-hexakis (pentyloxy) triphenylene), a triphenylene based liquid crystal, is presented in this chapter.

4.1.1 Mechanism of charge conduction in the columnar DLC

In DLCs, the overlap of $\pi$-orbitals forms energetically closely spaced but spatially delocalized electronic energy levels. The highest occupied energy levels constitute the valence band (VB) and the lowest unoccupied levels constitute the conduction band.
The width of the band gap $E_g$ between the VB and CB, determines the intrinsic electronic properties of the material. Additionally, the molecular structure and their relative positions within the stacks also determine the charge transport properties [1].

Results on the frequency dependent conductivity showed that the conduction along the columns of columnar DLCs can be explained with a single charge carrier transport process in which the carrier hops between localized states [2]. For example, in columnar DLCs based on triphenylene derivatives, the charge carrier transport can be described by a one dimensional hopping system within a narrow Gaussian distribution [3,4]. However, the narrow distribution makes it difficult to observe the electric field and temperature dependence of charge carrier mobilities within the short range of temperature and electric field available for the experiment [5].

4.1.2 Enhancement of the temperature and the field dependences of the mobility by molecular dipoles

A molecular dipole can be introduced into the molecules of the semiconductor to enlarge the width of the Gaussian distribution. This may increase the range of the temperature and the field dependencies of the charge carrier mobility in the material [6]. This can be illustrated in terms of the fluctuation of electrostatic potentials, which are generated by a random distribution of permanent dipoles. The total width of DOS (Density of States) is determined by a dipolar component due to the host molecule and the dopant molecule, and a van der Waals component [6]. Since the potential energy of
an extra charge ‘q’ in a potential V is qV, the random addition of dipoles increases the fluctuations of hopping site energies that the charge carriers experience [6].

In this study, the nonpolar discotic liquid crystal 2,3,6,7,10,11 hexapentyloxytriphenylene (HAT5) is contrasted with the dipolar NO$_2$-HAT5 by introducing a NO$_2$ moiety to enlarge the Gaussian distribution so that one can study the transport property of discotic mesophases over a wide range of temperature and electric field.
4.1.3 Molecular structure of NO$_2$-HAT5

The molecular structure of 1-nitro-2,3,6,7,10,11-hexapentyloxy triphenylene (NO$_2$- HAT5) is as shown in Figure 4-1.

![Molecular structure of NO$_2$-HAT5](image)

Figure 4-1: Molecular structure of NO$_2$-HAT5.
4.2 EXPERIMENT

The experimental setup was explained in detail in the section 2.2. In this experiment, the cell was prepared manually in the lab and the thickness of the cell was measured as described in section 2.4.

Figure 4-2: DSC diagram of NO₂-HAT5 for the temperature range from -40 °C to 155 °C.

The change in slope at -21.7 °C is nothing to do with the sample. The slope is also observed in the DSC of other materials too, e.g. Indium metal. In the diagram, I and D represent the isotropic and the discotic phases.
The empty cell in the holding mount was heated on the hot stage at a temperature slightly higher than the transition temperature (the melting point 136.1 °C) between the liquid crystal and the isotropic phase determined by DSC diagram as shown in Figure 4-2.

The material NO₂-HAT5 was put at the side of the cell and heated to its isotropic phase. The cell was filled with the material using capillary action. Then, it was slowly cooled down to its columnar phase by cooling at the rate 0.6 °C/min. The advantage of the slow cooling was to enable large domains and homeotropic alignment of molecules with a columnar axis normal to the electrode surface. A domain size of around 200 µm was determined using polarizing optical microscopy (Figure 4-3). The cell thickness is determined by the diameter of glass microsphere spacers placed between two electrodes. In my experiment, the diameter of microspheres was around 20 µm, hence the thickness of the cell was also around 20 µm.
The absorption spectrum of NO$_2$-HAT5 sample was determined using the HP 8453 UV-Visible Spectro-Photometer as described in the section 2.5. The solution of the sample was made with CH$_2$Cl$_2$. The UV-absorption spectra for NO$_2$-HAT5 at two different concentrations are shown in Figure 4-4. The figure shows that the maximum absorption occurs at around 280 nm, which is also strongly absorbed by the glass electrode of the cell. In our lab, the shortest available spectrum from Raman Shifter that is not absorbed by the glass was 320 nm, which also lies within the range of the absorption region as shown in Figure 4-4. In the experiment, this wavelength was sufficient to generate charge carriers on the material.

The temperature of the sample was controlled by using a Lake Shore 331 temperature controller and the electric field across the sample was applied using the high
voltage power supply (Stanford Research Systems - Inc Model PS325/2500 V-25 W) as described in the section 2.2.

Figure 4-4: UV-absorption spectra for NO$_2$-HAT5 at two different concentrations, which clearly show strong absorption of light at 320 nm.
In the time of flight experiment, large intensities light may produce space charge effects and make it difficult to locate the transient time on the trace. Therefore, a polarizer was used in the experiment to control the intensity of the light. Figure 4-5 shows typical traces at $T = 40 \, ^\circ\text{C}$ and $V=100 \, \text{V}$ with different intensities of the light. All traces give the same TOF.

Figure 4-5: TOF traces of hole transport at typical $T= 40 \, ^\circ\text{C}$ and $V = 100 \, \text{V}$. All three traces give the same TOF.
4.3 OBSERVATION

I studied the charge carrier transport by varying the electric field at constant temperature and varying the temperature at constant electric field. In both cases, I found that the mobility increases with increasing either parameters.

I also performed a partial experiment in the low temperature region from -10 °C to -60°C.

4.3.1 The electric field dependence of the hole mobility at constant temperature

Figure 4-6: TOF traces of hole transport in different electric fields at 120 °C.
The time of flight traces of hole transport in different electric fields at 120 °C and 20 °C are shown in Figure 4-6 and Figure 4-7 respectively.

Figure 4-7: TOF traces of hole transport in different electric fields at 20 °C.

An electric field dependence of the charge carrier mobility (μ vs. E) at different temperatures for the temperature ranges 20 °C to 120 °C and -10°C to -60°C are shown in Figure 4-8 and Figure 4-9, respectively. The range of the electric fields for a particular temperature was limited by electrical breakdown at high field and a noise problem at low
field. Some data at low electric fields were not included in the figures due to dispersive traces.

Figure 4-8: Field dependence of the mobility in NO$_2$-HAT5 from 20 °C to 120 °C in $\mu$ vs. E representation.
Figure 4-9: Field dependence of the mobility in NO$_2$-HAT5 at the temperatures from -10°C to -60 °C in $\mu$ vs. E representation.
4.3.2 The temperature dependence of the mobility at constant electric field

![TOF traces in different temperatures](image)

Figure 4-10: TOF traces in different temperatures (35 °C to 125 °C) at $1.67 \times 10^5$ V/cm.

The inset diagram represents the same traces of the temperature $T_1$, $T_2$, and $T_3$ in large time scale so that the transient time can be located clearly.
The time of flight traces of hole transport in different temperatures at the electric field $1.67 \times 10^5$ V/cm is as shown in Figure 4-10. The temperature dependence of the charge carrier mobility ($\ln \mu$ vs. $T$) at electric fields of $1.7 \times 10^5$ V/cm and $1.4 \times 10^5$ V/cm is shown in Figure 4-11. As will be described later, Anick M. van de Craats et al. [7] has reported such a temperature dependence of the mobility in DLCs [3].

Figure 4-11: The temperature ($T$) dependence of the hole mobility ($\ln \mu$) in NO$_2$-HAT5 with increasing $T$ at $1.7 \times 10^5$ V/cm and with decreasing $T$ at $1.4 \times 10^5$ V/cm.
4.4 RESULTS AND DISCUSSIONS

In columnar phases of DLCs, the stacked aromatic nuclei provide a conduction pathway along the columns whereas the surrounding sheath of alkyl chains suppresses the column to column conduction [5]. I found that that our results can be explained by the empirical expression, Eq. (4.3) proposed by I. Bleyl et al. [3] using a Monte Carlo simulation [5] for one dimensional conduction.

Before we go to this expression, it would be good to start from the basic theory.

4.4.1 Basic theory

Anick M. van de Craats et al. [7] has described an effect of the positional disorder of aromatic disks along the columnar stacks of central aromatic units in one dimensional charge carrier transport in a DLC. Here the positional disorder means a nonparallel arrangement of the discs as shown in Figure 4-12 (a) and a longitudinal as well as a lateral displacement of discs within the stacks as shown in Figure 4-12 (b)

Figure 4-12: The positional disorder due to (a) the nonparallel alignment of the discs and (b) the lateral and longitudinal displacement.
(a) The out of well transport

(b) Over the barrier transport

(c) Miller-Abrahams transport mechanism

(d) The polaronic transport mode

Figure 4-13: Schematic representation of the energy landscapes used in the different models of charge carrier transport [7].
The interaction between the disordered discs and the adjacent discs produce one dimensional energetic disorder (\(\sigma\)) [8]. Energy disorder is characterized by the potential energy profiles with traps of random energy depths (\(E^t_k\)) and/or barriers with random energy heights (\(E^b_k\)). The superscripts \(t\) and \(b\) represent trap and barrier respectively and the subscript \(k\) represents a position of a trap or the localization of the charge between two barriers. A charge carrier is temporarily localized either in one of these traps or between adjacent random barriers. The charge then hops either between two traps, Figure 4-13 (a), or over the barrier between adjacent sites, Figure 4-13 (b), via thermal activation [7]. This results in incoherent charge transport along the direction of the columnar stacks by consecutive hopping transitions from one localization site to another. The transition rate is given by

\[
W_{\pm 1} = v_0 \exp \left( -\frac{\Delta}{k_B T} \right)
\]

where \(k\) is a site index and \(k \pm 1\) are its adjacent site indices, \(\Delta = E^t_k \text{ or } E^b_k\), \(v_0\) is the attempt frequency, \(k_B\) is the Boltzmann constant, and \(T\) is the temperature. Contrary to the thermally activated transition, the charge may also penetrate the barrier by tunneling assisted hopping, which is described by the Miller-Abrahams model given by Eq. (4.2) (see Figure 4-13 (c)). The rate of tunneling transitions through a random barrier depends on the site energies [7].

In addition, if a charge carrier induces a lattice distortion around itself, the resulting polaron must pass between sites (see Figure 4-13 (d)). For polarons with a
binding energy, \( \lambda_p \) and site energy \( E_k^p \), the transition rate in disordered materials \([7]\) is given by

\[
W_{k\pm1} = \nu_0 \exp \left[ -\frac{\left(E_{k \pm 1}^p - E_k^p + 2\lambda_p\right)^2}{8k_BT\lambda_p} \right]
\]

We have described the four types of possible charge carrier transport in one-dimensional columnar DLCs. In the first type, a charge hops out of traps. In the second type, a charge hops over barriers. In the third type, a charge hops by tunneling. In the fourth type, a charge in the form of a polaron hops from one site to other.

We want to describe charge transport in a columnar discotic mesophase by a one-dimensional hopping model using the simplest approach making only three necessary assumptions for the hopping process. They are also justified by the experimental observations \([3]\).

(a) The incoherent charge transport by consecutive transitions from one localization site to another with jump like motion occurs along the direction parallel to the axis of the columnar stacks.

(b) The charge transporting energy levels (the highest occupied molecular orbital levels in the case of hole transport) are characterized by a Gaussian energy distribution of width, \( \sigma \) and mean energy, \( \varepsilon \). The origin of \( \sigma \) could be fluctuations in the polarization energy (an interaction of a charge carrier with dipoles) as well as dipolar interactions in the case of asymmetric molecules or impurity molecules at a low density \([9]\).
(c) The charge carriers are assumed to hop along and against the field direction only between adjacent transport sites. The hopping rate $v_{ij}$ between site $i$ and the adjacent site $j$ is assumed to follow the Miller-Abrahams type expression [10] given by

$$
\rho(\varepsilon) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left( -\frac{\varepsilon^2}{2\sigma^2} \right)
$$

(4.1)

where $\varepsilon_i$ and $\varepsilon_j$ are the energies at the sites $i$ and $j$. $v_0$ is the attempt-to-jump frequency, $\Delta R_{ij} = |R_i - R_j|$ and $\gamma a = \Gamma$ is the average wave function overlap factor with $a$ being the intersite hopping distance and $\gamma$ the spatial decay constant of the wave function. The overlap integral of the wave functions of adjacent sites is normally unknown; therefore one can only assume that $\Gamma$ is characterized by a normal distribution with a variance, $\Sigma$, which includes variations in the intersite distance as well as variations in $\gamma$. $\Gamma_{ij} = \Gamma_i + \Gamma_j = 2\gamma_i a = \text{the wave function overlap parameter among two sites } i \text{ and } j$. $\Gamma_i$ and $\Gamma_j$ are randomly and independently following a Gaussian distribution with standard deviation $\delta \Gamma$. The standard deviation of $\Gamma_{ij} = \Sigma = \sqrt{2} \delta \Gamma$. In the presence of the electric field $E$, the site energies $\varepsilon_i$ and $\varepsilon_j$ also include the electrostatic terms so that $|\varepsilon_i - \varepsilon_j| = eEa$ [3].

$$
v_{ij} = v_0 \exp(-2\gamma a \frac{\Delta R_{ij}}{a}) \exp\left( -\frac{(\varepsilon_j - \varepsilon_i) / kT}{kT} \right) \quad \varepsilon_j > \varepsilon_i
$$

$$
v_{ij} = v_0 \exp(-2\gamma a \frac{\Delta R_{ij}}{a}) \quad \varepsilon_j < \varepsilon_i
$$

(4.2)
4.4.2 Mathematical expressions for one dimensional charge carrier mobility

Assuming the above three conditions, I. Bleyl et al. [3] proposed the following charge carrier mobility for one dimensional hopping. This empirical expression was derived by using a Monte Carlo simulation [5]:

\[
\mu(\hat{\sigma}, \Sigma, E) = \mu_0 \exp\left(-0.9\sigma^2\right) \exp\left(C\left((\hat{\sigma} - \Sigma)E^{1/2}\right)\right), \quad \Sigma \geq 1.5
\]  

(4.3)

where \( E \) = the electric field, \( k \) = Boltzmann constant, \( T \) = the absolute temperature, \( \mu \) = the charge carrier mobility, \( \mu_0 = \mu_0(T \rightarrow \infty, E = 0) \) = the value of the mobility as \( 1/T \rightarrow 0 \) at zero electric field, and \( \hat{\sigma} = \sigma/kT \) with \( \sigma \) = the parameter that measures the width of the Gaussian energy disorder. The constant \( C \) is proportional to \( a^{1/2} \) [3, 11, 12].

4.4.2.1 Determination of parameters from \( \mu \) vs. \( E \) at constant \( T \)

From Eq. (4.3),

\[
\ln \mu = \ln \mu_0 - 0.9\sigma^2 + C((\hat{\sigma} - \Sigma)E^{1/2})
\]  

(4.4)

At \( E = 0 \), \( \mu = \mu(E=0) = \mu_{zf} \) = the zero field mobility.

\[
\ln \mu_{zf} = \ln \mu_0 - (0.9\sigma^2)
\]

\[
\ln \mu_{zf} = \ln \mu_0 - \left(\frac{0.9\sigma}{k}\right)^2 \frac{1}{T^2}
\]  

(4.5)

from equations (4.4) and (4.5),

\[
\ln \mu = \ln \mu_{zf} + C(\hat{\sigma} - \Sigma)E^{1/2}
\]

(4.6)

where,
\[
A = C(\hat{\sigma} - \Sigma) \\
A = -C\Sigma + \left(\frac{C\sigma}{k}\right) \frac{1}{T}
\]  

(4.7)

For each value of temperature, \( \ln \mu_f \) and A can be determined from the intercept and slope of the graph of \( \ln \mu \) vs \( E^{\frac{1}{2}} \) respectively as shown in Eq.(4.6).

From Eq.(4.5) and the graph of \( \ln \mu_f \) vs. \( T^{-2} \), \( \mu_0 \) and \( \sigma \) can be determined by the intercept and slope of the graph. Similarly from equation (4.7), \( \Sigma \) and C can be determined from the intercept and slope of the graph of the graph A vs. \( T^{-1} \), respectively.

In summary, the following steps will explain how we extract the material parameters from our data using Eq. (4.3).

1. For each temperature T, a graph is plotted of \( \ln \mu \) vs \( E^{\frac{1}{2}} \), which is predicted to be a straight line (see Eq.(4.6)).

2. From this graph, an intercept and a slope are determined for each T. The intercept gives \( \ln \mu_f \) and the slope gives A (see Eq.(4.6)).

3. A graph of \( \ln \mu_f \) vs. \( 1/T^2 \), which is also predicted to be a straight line is plotted (see Eq.(4.5)). The intercept and slope of this line give \( \ln \mu_o \), i.e. \( \mu_o \) and \( (0.9 \sigma/k)^2 \), i.e. \( \sigma \) respectively.

4. A graph is plotted of A vs. \( 1/T \), which is a straight line, see Eq (4.7). The intercept and slope of this line give \( C\Sigma \) and \( (C\sigma/k) \) respectively.

5. Using the value of \( \sigma \) from the step 3 and \( (C\sigma/k) \) from the step 4, C is determined. Then \( \Sigma \) is determined from \( C\Sigma \).
4.4.2.2 Determination of parameters from $\mu$ vs. $T$ at constant $E$

If $E$ is constant, we may rewrite equation (4.3) as

$$\mu = \mu_0 \exp \left( -\left( \frac{0.9\sigma}{k} \right)^2 \frac{1}{T^2} \right) \exp \left( \left( \frac{C\sigma E^{\frac{1}{2}}}{k} \right) \frac{1}{T} \right) \exp \left( -C \sum E^{\frac{1}{2}} \right)$$

which may be written,

$$\mu = \alpha \exp \left( \frac{\beta}{T} \right) \exp \left( -\frac{\gamma}{T^2} \right)$$

(4.8)

where,

$$\alpha = \ln \mu_0 \exp \left( -C \sum \sqrt{E} \right),$$

$$\beta = \left( \frac{C\sigma \sqrt{E}}{k} \right), \quad \text{then} \quad C = \frac{\beta k}{\sigma \sqrt{E}}$$

(4.9)

$$\gamma = \left( \frac{0.9\sigma}{k} \right)^2, \quad \text{then} \quad \sigma = \frac{k}{0.9 \sqrt{\gamma}}$$

We may fit Eq.(4.8) to the data using standard non-linear fitting routines, from which $C$ and $\sigma$ can be found independently whereas $\mu$ depends on the selection of $\Sigma$’s value. Hence, we have two options to retrieve the parameter’s value, either by analyzing data of electric field dependence of mobility at constant temperature or the data of temperature dependence of mobility at constant electric field.
4.4.3 Results and parameter values ($\mu_o$, $\sigma$, $\nu_{\text{eff}}$, $C$ and $\Sigma$)

4.4.3.1 High temperature results: Calculation of parameters from the data of $\mu$ vs. $E$ at constant $T$ (from $T = 20$ °C to 120 °C)

Figure 4-14: Field dependence of the mobility in NO$_2$-HAT5 from 20 °C to 120 °C in $\ln\mu$ vs. $E^{1/2}$ representation.
Figure 4-15: Temperature dependence of $\ln \mu_{zf}$ for NO$_2$-HAT5 at different temperatures. For each temperature, $\ln \mu_{zf}$ is the intercept of the line $\ln \mu$ vs. $\sqrt{E}$ for that temperature in Figure 4-14.

As seen in Figure 4-15, there is a little decrease in the slope after the temperature range between 80 °C and 90 °C. It might be due to some transition phase, where the charge carrier mobility may be determined by the phenomena such as a temperature-dependent order parameter, which should have a strong influence on the energy and spatial disorder in the material making it difficult to analyze the data for higher temperatures [3]. Therefore, the sample was checked by DSC (Figure 4-2) and optical polarizing microscopy (Figure 4-15) to observe if there was any phase transition present.
in this temperature region. However, it was confirmed from both methods that there were no transition evident.

Figure 4-16: Textures of NO$_2$-HAT5 at different temperatures (a) 80 °C, (b) 85 °C, (c) 90 °C, and (d) 95 °C. No significant change was observed in these pictures.
Figure 4-15 is the plot of $T^2$ versus $\ln \mu_{zf}$, which is the intercept of the plot of $\ln \mu$ vs. $\sqrt{E}$ (see in Figure 4-14 and Eq.(4.6)). As given by Eq.(4.5), the intercept and the slope of the plot $T^2$ versus $\ln \mu_{zf}$ give $\ln \mu_o$ and $-\left(\frac{0.9\sigma}{k}\right)^2$.

I found $\ln \mu_o = -2.766$, i.e., $\mu_o = \exp(-2.766)$

$$\mu_o = 0.063 \text{ cm}^2/\text{Vs}$$

Similarly, $-\left(\frac{0.9\sigma}{k}\right)^2 = -9.41 \times 10^5$ and $k = \text{Boltzmann constant} = 8.62 \times 10^{-5} \text{ eV / K}$ giving

$$\sigma = 93 \text{ meV} \quad (4.10)$$

The jump frequency ($v_{\text{eff}}$) can be calculated from $\mu_o$ as [3]

$$\mu_o = K a^2 v_{\text{eff}}$$

where $K$ = a proportionality constant = 16.4 V$^{-1}$, $a$ = a hopping constant = 3.6 Å [13].

Using the values of $\mu_o$ and $a$, I have calculated $v_{\text{eff}}$ as

$$v_{\text{eff}} = 3.0 \times 10^{12} \text{ s}^{-1}$$

which lies within the hopping frequency range $10^{12} \text{ s}^{-1} \leq v_{\text{energy}} \leq 3 \times 10^{13} \text{ s}^{-1}$ calculated by Ingo Bleyl et al. [3] for the triphenylene mesophase.
Figure 4-17: Temperature dependence of A (the slope of the plot lnμ vs. √E, see Figure 4-8 and Eq.(4.6)).

Figure 4-17 is the plot of the inverse temperature vs. A, which is the slope of the plot lnμ vs. √E (Figure 4-15) as given by Eq.(4.6). The intercept and the slope of this plot give -CΣ and Cσ/k, respectively as given by Eq. (4.7). From this plot, I found

-CΣ = -0.0145 and Cσ/k = 6.018

Substituting the value of σ from Eq.(4.10),

C = .0053 (cm / V)^{1/2}

Similarly, substituting the value of C to the intercept (-CΣ ),

Σ = 2.6
4.4.3.2 Low temperature results: Calculation of parameters from the results of $\mu$ vs. $E$ at constant $T$ (from $T = -10^\circ$C to $-60^\circ$C)

Figure 4-18: Field dependence of the mobility in NO$_2$-HAT5 at different temperatures from -10$^\circ$C to -60$^\circ$C in $\ln\mu$ vs. $\sqrt{E}$ representation.
Figure 4-19: Temperature ($T^2$) dependence of the mobility at zero field ($\mu_{zf}$) for NO$_2$-HAT5 for the temperatures from -10 $^\circ$C to -60 $^\circ$C.

Figure 4-19 is the plot of $T^2$ versus $\ln \mu_{zf}$ for the temperature from -10 $^\circ$C to -60 $^\circ$C.

The intercept of the plot gives

$$\ln \mu_0 = -1.7$$

giving

$$\mu_0 = 0.18 \text{ cm}^2/\text{Vs}$$

Similarly, the slope of the plot gives

$$-\left(\frac{0.9\sigma}{k}\right)^2 = -1.03 \times 10^6$$

implying that,

$$\sigma = 97 \text{ meV} \quad \text{(4.11)}$$
Substituting the value of $\mu_o$ in $\mu_o = K a^2 \nu_{\text{eff}}$ and taking $K$ (a proportionality constant) = 16.4 V$^{-1}$, and $a$ = a hopping constant = 3.6 Å, gives

$$\nu_{\text{eff}} = 8.5 \times 10^{12} \text{ s}^{-1}$$

Figure 4-20: Temperature dependence of $A$, which is the slope of $\ln \mu$ vs $\sqrt{E}$.

Figure 4-20 is the plot of the inverse temperature versus $A$ for the temperature -10 °C to -60 °C. The intercept and slope of this plot give $-C\Sigma = -0.0141$ and $C\sigma/k = 5.52$, respectively.

Substituting the value of $\sigma$ from Eq. (4.11),

$$C = .0049 \text{ (cm / V)}^{1/2}$$

Similarly substituting the value of $C$ to the intercept,

$$\Sigma = 2.9$$
Hanna [5] found $\mu_o$ and $\sigma$ to be 0.86 cm$^2$/Vs and 102 meV respectively for the similar material NO$_2$-HAT6, which is only differed by a slight changed in the aliphatic chain length as compare to our material but he has not mentioned the values of $\Sigma$ and $C$. However, we roughly estimated $\Sigma$ and $C$ from the plot of $\ln \mu$ vs. $E^{1/2}$ for 40 °C and 70 °C presented in the article. We found $C = 0.00695$ and $\Sigma = 3.15$. Table 4-1 compares the values of different parameters of our material for the temperature range 20 °C to 120 °C and -10 °C to -60 °C and of Hanna’s material.

Table 4-1:

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>Our Result on NO$_2$-HAT5</th>
<th>Our Result on NO$_2$-HAT5</th>
<th>Hanna’s Result on NO$_2$-HAT6</th>
</tr>
</thead>
<tbody>
<tr>
<td>-60 to -10</td>
<td>0.18 ± 0.14</td>
<td>0.06 ± 0.01</td>
<td>0.86</td>
</tr>
<tr>
<td>20 to 120</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-20 to 60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_o$ (cm$^2$/Vs)</td>
<td>0.18 ± 0.14</td>
<td>0.06 ± 0.01</td>
<td>0.86</td>
</tr>
<tr>
<td>$\sigma$ (meV)</td>
<td>97 ± 2</td>
<td>93 ± 1</td>
<td>102</td>
</tr>
<tr>
<td>$C (\sqrt{ \frac{cm}{V}})$</td>
<td>0.0049 ± 0.00027</td>
<td>0.0056 ± 0.00011</td>
<td>0.0069</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>2.9 ± 0.29</td>
<td>2.6 ± 0.073</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Table 4-1 compares the values of parameters $\mu_o$, $\sigma$, $\Sigma$, and $C$ and their uncertainties $\delta \mu_o$, $\delta \sigma$, $\delta \Sigma$, and $\delta C$ at low and high temperatures of NO$_2$-HAT5 with that of NO$_2$-HAT6. Please see the appendix 4.6 for the detail of the calculation.

The table shows that both disorder parameters ($\sigma$ and $\Sigma$) and $C$ at low temperatures are similar with that at high temperatures.
Similarly, for Hanna’s material, both disorder parameters and C are slightly higher than that of our material. It might be due to the temperature range taken in Hanna’s analysis, where the results of higher temperatures region (> 60 °C) [5] have been skipped because the relation between lnμ and T² was not linear in this region. It has not been explained in the article why those data did not fit in the linear plot although the temperature range of the discotic phase in the material falls between -20 °C to 137 °C.

We found a factor of three difference in the value of μ₀ between the low and high temperature ranges for our material. Hanna found μ₀ many times greater than ours. The main reason for this is that the determination of μ₀ is very sensitive to the slope of the fitting line in the plot of lnμzf vs. E¹/².

4.4.3.3 Calculation of parameters from the results of μ vs. T at constant E (E =1.7 x 10⁵ V/cm and E =1.4 x 10⁵ V/cm)

Our results of the temperature dependence of the mobility also follow the empirical expression, Eq.(4.3) [3]. I fitted our results found by varying the temperature from 20 °C to 130 °C for two typical electric fields, E₁ =1.67 x 10⁵ V/cm and E₂ =1.42 x 10⁵ V/cm in Eq.(4.3) (see Figure 4-21).
Figure 4-21: The non-linear plot of temperature dependence of the hole mobility in NO$_2$-HAT5 at the electric fields $1.67 \times 10^5$ V/cm and $1.42 \times 10^5$ V/cm.

At $E_1$, $\alpha = 2.301 \times 10^{-9}$ cm$^2$/Vs, $\sigma = 142$ meV, $C= 0.016$ (cm/V)$^{1/2}$. If we assume $\Sigma = 2.6$ from section 4.4.3.1, then $\mu_o = 0.011$ cm$^2$/Vs. The correlation matrix of the parameters is

$$
\begin{bmatrix}
1.00 & 0.99 & 0.99 \\
0.99 & 1.00 & 0.99 \\
0.99 & 0.99 & 1.00
\end{bmatrix}
$$

The standard deviation for $\alpha$, $\sigma$ and $C$ are respectively are $1.28 \times 10^{-9}$ cm$^2$/Vs, 0.0024 meV and 0.0004 (cm/V)$^{1/2}$.

At $E_2$, $\alpha = 2.011 \times 10^{-9}$ cm$^2$/Vs, $\sigma = 143$ meV, $C= 0.015$ (cm/V)$^{1/2}$, if we assume $\Sigma = 2.6$, then $\mu_o = 0.014$ cm$^2$/Vs. The correlation matrix of the parameters is
The standard deviation for \( \alpha \), \( \sigma \) and \( C \) are respectively 1.52 \( \times 10^{-9} \) \( \text{cm}^2/\text{Vs} \), 0.0032 meV, and 0.0005 (cm/V)^{1/2}.

At both electric fields, all elements of the correlation matrices are close to unity. This means that the parameter’s values determined in these fits are very highly correlated.

4.4.3.4 Summary of the analysis

Table 4-2:

<table>
<thead>
<tr>
<th>plot</th>
<th>( \sigma ) (meV)</th>
<th>( \mu_o ) (cm(^2)/Vs)</th>
<th>( \nu_{\text{eff}} ) (s(^{-1}))</th>
<th>( C ) (cm/(V)^{1/2})</th>
<th>( \Sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T = 20 , ^\circ\text{C to 120 , ^\circ\text{C}} )</td>
<td>( \ln \mu ) vs. ( E^{1/2} )</td>
<td>93</td>
<td>0.06</td>
<td>2.8 ( \times 10^{12} )</td>
<td>0.0056</td>
</tr>
<tr>
<td>( T = -10 , ^\circ\text{C to -60 , ^\circ\text{C}} )</td>
<td>( \ln \mu ) vs. ( E^{1/2} )</td>
<td>97</td>
<td>0.18</td>
<td>8.4 ( \times 10^{12} )</td>
<td>0.0049</td>
</tr>
<tr>
<td>( E = 1.42 \times 10^5 , \text{V/cm} )</td>
<td>( \ln \mu ) vs. ( T^{-1} )</td>
<td>142</td>
<td>0.011</td>
<td>5.2 ( \times 10^{11} )</td>
<td>0.016</td>
</tr>
<tr>
<td>( E = 1.67 \times 10^5 , \text{V/cm} )</td>
<td>( \ln \mu ) vs. ( T^{-1} )</td>
<td>143</td>
<td>0.014</td>
<td>6.6 ( \times 10^{11} )</td>
<td>0.015</td>
</tr>
</tbody>
</table>

* \( \Sigma \) was taken from the electric field dependence mobility at high temperature range.

Table 4-2 shows the comparison of results from the two different analyses (1) \( \ln \mu \) vs. \( E^{1/2} \) and (2) \( \ln \mu \) vs. \( T^{-1} \). The value of \( \sigma \) and \( C \) are respectively 47% and 200% higher in the latter analysis than in the former analysis. Although the data in the latter case are fitted very well with the empirical relation, the values of the parameters from the plot \( \ln \mu \) vs. \( T^{-1} \) are suspect due to the following reasons.
(a) $\mu_0$ and $\Sigma$ cannot be calculated independently i.e., $\Sigma$ must be put in by hand.

(b) The correlation matrices of the parameters show that the parameters are very highly correlated.

Therefore, we conclude that the values of parameters from the latter analysis are not very meaningful.

### 4.4.4 Comparison between HAT5 and NO$_2$-HAT5

Our results can be compared with the results for the related material HAT5. The difference between HAT5 and NO$_2$-HAT5 is an NO$_2$ group, which converts a non-polar molecule HAT5 to a dipolar molecule NO$_2$-HAT5. As discussed earlier, the hole mobility in NO$_2$-HAT5 increases with increasing temperature and electric field. The results can be interpreted as a somewhat disorder dominated hopping conduction that comes from the strong dipole of the nitro group.

D. Adam et al. found that the hole mobility is independent of electric field and temperature in HAT5 [14]. As presented in his article, for the electric field range from $1 \times 10^4$ V/cm to $2.5 \times 10^5$ V/cm at 75 $^\circ$C, he found the hole mobility of HAT5 as $1 \times 10^{-3}$ cm$^2$/Vs.

However, V. Duzhko et al. [15] found that the hole mobility of HAT5 decreases with the temperature by a power law, $T^{-n}$, in the high electric field regime with $n$ depending on the strength of electric field. However, the mobility is independent of the electric field in the low electric field regime below $1 \times 10^5$ V/cm. At the temperature 85 $^\circ$C, he found the hole mobility in HAT5 to be $6.5 \times 10^{-4}$ cm$^2$/Vs at electric fields below
1 \times 10^5 \text{ V/cm}. V. Duzhko has interpreted these results in a framework of correlated polaron motion as described by the non-adiabatic low-temperature limit of Holstein’s polaron theory developed for a one-dimensional diatomic chain.

Both HAT5 and NO$_2$-HAT5 possess rotational and the positional disorders in their columnar phase. However, the presence of the strong dipole due to the nitro group increases further the energy disorder of the localized state in NO$_2$-HAT5. Hence, the hole mobility in NO$_2$-HAT5 becomes less than that in HAT5 and is described by disorder dominated hopping conduction as compared to HAT5. For example, at an electric field of 8.2 \times 10^4 \text{ V/cm}, we found the hole mobility of NO$_2$-HAT5 to be 5.7 \times 10^{-5} \text{ cm}^2/\text{Vs}, 7.7 \times 10^{-5} \text{ cm}^2/\text{Vs} and 9.6 \times 10^{-5} \text{ cm}^2/\text{Vs} at temperatures of 70 °C, 80 °C and 90 °C respectively. These hole mobilities are less than that of HAT5 at the same electric field and temperature range as measured by D. Adam[14] and V. Duzhko [15].

![Figure 4-22: DSC diagram of HAT5.](image-url)
NO$_2$-HATn have hexagonal columnar phases, which are stable over a greater temperature range than those of HATn [16]. On cooling, the temperature range for the discotic mesophase of the NO$_2$-HAT5 is from 133.4°C (Col$_h$ – I) to at least -40 °C confirmed by our DSC diagram (see Figure 4-2). Below -40 °C, the phase is unknown because of the temperature limitation of the DSC instrument. On cooling, the temperature range for the discotic mesophase of HAT5 is from 120 °C (Col$_h$ – I) to 43.3 °C (see Figure 4-22). The increase of clearing temperature (Col$_h$ – I) from 122 °C for HAT5 to 141 °C for NO$_2$-HAT5 might be due to an enhanced ring–ring interaction in the column, which may be due to the persistence of dimers with anti-aligned dipoles in the nitro compound. So the greater temperature range of NO$_2$-HAT5 mesophase may be the result of strong dipole–dipole interactions, making the effective mesogen a super-disk of two NO$_2$-HAT5 molecules.

4.5 CONCLUSIONS

1) Hole transport has been measured using the time-of-flight technique on the discotic hexagonal columnar phase containing a strongly dipolar nitro substituent in NO$_2$-HAT5.

2) Unlike some discotic columnar systems, for which the charge carrier mobility is weakly dependent on the temperature and the electric field, NO$_2$-HAT5 shows a strong temperature and field dependent hole mobility.
3) Our results for the temperature dependent mobility follow the empirical expression proposed by Ingo Bleyl et al. and established from fits to Monte Carlo simulations for one-dimensional hopping conduction [3].

4) The relation between the electric field dependence and the hole mobility follow the Poole-Frenkle relation [14].

5) The calculated energy disorder parameter ($\sigma = 93\text{meV}$) for our material is almost equal to that ($\sigma=102\text{meV}$) of the similar material NO$_2$-HAT6 [5]. These values may be compared to that ($\sigma = 48\text{meV}$) of the non-nitrated HAT4 dimer H4TD10 obtained by an equivalent treatment [3].

6) The calculated energy disorder parameter, $\sigma$, is comparable to that of dipole-substituted amorphous molecular solids [6]. This suggests that the charge transport is disorder dominated hopping conduction.

7) The disorder in NO$_2$-HAT5 is enhanced by the strong dipole of the nitro group as compared to HAT5.

8) Since NO$_2$-HAT5 can exist in a discotic columnar phase for a wide range of temperatures, such photo-conducting materials may be very useful for applications in electronic devices. However, the mobility in this material at low temperature is relatively low.

9) Our results did not fit the empirical expression proposed by H. Bässler for three dimensional hopping [11] with any set of parameters. This implies that the hopping conduction in the material is not three dimensional.
4.6 APPENDIX: CALCULATION OF UNCERTAINTIES (δµo, δσ, δΣ, AND δC ) OF THE PARAMETERS

\[ \sigma = \sigma / kT \]

From Eq. (4.4)

\[ \ln \mu = \ln \mu_0 - (0.9\hat{\sigma})^2 + C(\hat{\sigma} - \Sigma)E^{1/2} \]

\[ \ln \mu = \ln \mu_\alpha + AE^{1/2} \]

where, \( \ln \mu_\alpha = \ln \mu_0 - (0.9\hat{\sigma})^2 \)

\[ \ln \mu_\alpha = \ln \mu_0 - \left( \frac{0.9\sigma}{k} \right)^2 \frac{1}{T^2} \]

\[ \ln \mu_\alpha = A_0 + A_1 \frac{1}{T^2} \]

where,

\[ A_0 = \ln \mu_0 \quad (4.12) \]

\[ A_1 = -\left( \frac{0.9\sigma}{k} \right)^2 \quad (4.13) \]

Where, \( A = C(\hat{\sigma} - \Sigma) \)

From Eq. (4.6) \( A = -C\Sigma + \left( \frac{C\sigma}{k} \right) \frac{1}{T} \)

\[ A = B_0 + B_1 \frac{1}{T} \]

where,

\[ B_0 = -C \Sigma \quad (4.14) \]

\[ B_1 = C\sigma/k \quad (4.15) \]

High Temp (20 °C to 120 °C)

Table:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_0 )</td>
<td>(-2.76615)</td>
<td>(0.16638)</td>
</tr>
<tr>
<td>( A_1 )</td>
<td>(-941414.67)</td>
<td>(18751.55)</td>
</tr>
</tbody>
</table>

A=B_0+B_1/T (Figure 4-17)

Low Temp (-10 °C to - 60 °C)

Table:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_0 )</td>
<td>(-1.69811)</td>
<td>(0.76158)</td>
</tr>
<tr>
<td>( A_1 )</td>
<td>(-1.02763e6)</td>
<td>(0.03655548)</td>
</tr>
</tbody>
</table>

A=B_0+B_1/T (Figure 4-20)
Summary of intercepts, slopes and their errors derived from linear fitting at high and low temperatures.

<table>
<thead>
<tr>
<th></th>
<th>(A_o)</th>
<th>(\delta A_o)</th>
<th>(A_1)</th>
<th>(\delta A_1)</th>
<th>(B_o)</th>
<th>(\delta B_o)</th>
<th>(B_1)</th>
<th>(\delta B_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hi T</td>
<td>-2.77</td>
<td>0.166</td>
<td>9.41e5</td>
<td>1.88e4</td>
<td>0.01449</td>
<td>0.000297</td>
<td>6.02</td>
<td>0.10</td>
</tr>
<tr>
<td>Lo T</td>
<td>-1.70</td>
<td>0.762</td>
<td>1.03e6</td>
<td>4.20e4</td>
<td>0.01405</td>
<td>0.00119</td>
<td>5.51</td>
<td>0.28</td>
</tr>
</tbody>
</table>

From Eq. (4.12)

\[
\mu_o = \exp(A_o) \quad \delta \mu_o = \frac{\partial \mu}{\partial A_o} \delta A_o
\]

\[
\delta \mu_o = \exp(A_o) \times \delta A_o
\]

From Eq. (4.13)

\[
A_1 = \left( \frac{0.9 \sigma}{k} \right)^2 \quad \sigma = \frac{k}{0.9 \sqrt{A_i}} \quad \delta \sigma = \frac{\partial \sigma}{\partial A_i} \delta A_i
\]

\[
\delta \sigma = \frac{k}{0.9} \frac{1}{2 \sqrt{A_i}} \delta A_i
\]

From Eq. (4.15)

\[
B_i = \frac{C \sigma}{k} = C \frac{k \sqrt{A_i}}{k 0.9} = C \frac{\sqrt{A_i}}{0.9} \quad \therefore C = \frac{0.9 B_i}{\sqrt{A_i}} \quad \delta C = \sqrt{\left( \frac{\partial C}{\partial B_i} \delta B_i \right)^2 + \left( \frac{\partial C}{\partial A_i} \delta A_i \right)^2}
\]
\[ \delta C = \sqrt{\left(\frac{0.9}{\sqrt{A_i}} \delta B_o\right)^2 + \left(-\frac{0.9B_o}{2(A_i)^{3/2}} \delta A_i\right)^2} \]

From Eq. (4.15)

\[ B_o = -C \Sigma \quad \Sigma = -\frac{B_o}{C} \quad \therefore \Sigma = -\frac{B_o\sqrt{A_i}}{0.9B_i} \]

\[ \delta \Sigma = \sqrt{\left(\frac{\delta \Sigma}{\delta B_o} \delta B_o\right)^2 + \left(\frac{\delta \Sigma}{\delta B_1} \delta B_1\right)^2 + \left(\frac{\delta \Sigma}{\delta A_i} \delta A_i\right)^2} \]

\[ \delta \Sigma = \sqrt{\left(\frac{\sqrt{A_i}}{0.9B_i} \delta B_o\right)^2 + \left(\frac{B_o\sqrt{A_i}}{0.9 \times (B_i)^{3/2}} \delta B_1\right)^2 + \left(\frac{B_o}{0.9B_i \sqrt{A_i}} \delta A_i\right)^2} \]

Summary of parameters’ values and their uncertainties for high and low temperatures

<table>
<thead>
<tr>
<th></th>
<th>(\mu_o)</th>
<th>(\delta\mu_o)</th>
<th>(\sigma)</th>
<th>(\delta\sigma)</th>
<th>C</th>
<th>(\delta C)</th>
<th>(\Sigma)</th>
<th>(\delta\Sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hi T</td>
<td>0.063</td>
<td>0.01</td>
<td>0.093</td>
<td>0.00093</td>
<td>0.0056</td>
<td>0.00011</td>
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<td>0.073</td>
</tr>
<tr>
<td>Lo T</td>
<td>0.183</td>
<td>0.14</td>
<td>0.097</td>
<td>0.00198</td>
<td>0.0049</td>
<td>0.00027</td>
<td>2.89</td>
<td>0.29</td>
</tr>
</tbody>
</table>
4.7 REFERENCES


CHAPTER 5

THE STUDY OF CHARGE CARRIER TRANSPORT IN THE CALAMITIC LIQUID CRYSTALS 5, 5'-DI-(ALKYL-PYRIDIN-YL)-2,2’ BITHIOPHENES

5.1 INTRODUCTION

In this section, we will study the electronic transport property of a calamitic liquid crystal containing a core unit of two pairs of pyridine and thiophene molecules.

5.2 MOLECULAR STRUCTURE AND ITS PHASE TRANSITIONS

5.2.1 Pyridine and thiophene

Pyridine is an aromatic heterocyclic compound with the formula C₅H₅N in a six-membered ring. It is a simple organic compound structurally related to benzene, in which one CH group in the six-membered ring is replaced by a nitrogen atom.

Figure 5-1: Molecular structure of pyridine [1].
The details about the thiophene molecules and oligothiophenes, and the important role of the sulfur atom in the charge carrier transport were discussed in the section 3.2. Since the materials in this experiment contain two thiophene molecules, we expect high charge carrier mobility in this material.

Liquid crystals containing pyridine show complex mesomorphic behavior. Higher ordered mesophases like SmG and SmH are often observed in some pyridine containing liquid crystal near room temperature [2].

There are some processing advantages of mesomorphic behavior in materials, such as liquid crystals containing terthiophene, as observed by Breemen et al. [3]. From such materials, we can make aligned, defect-free and highly ordered monodomains with a large orbital overlap of neighboring molecules, which can give high mobility. Upon cooling from their isotropic phase, their gradual increase in order and slow transitions between phases leads to such monodomains. They have reported that they were able to form monodomains up to the size 150 mm in diameter. They have also reported one order increase in the charge carrier mobility of the monodomain material as compared to that of multidomain material.

These facts make the pyridine and thiophene based liquid crystals attractive candidates for the study of their charge carrier mobility and their applications in the electronic devices.

Since our material contains both thiophene and pyridine molecules, it is interesting to study its charge transport properties.
5.2.2 Molecular structure of the experimental materials

The materials used in our experiment are C9 \(5,5'$-di-(5$-n$)-nonyl$-pyridin-2$-yl$)-2,2'$-bithiophenes\) and C10 \(5,5'$-di-(5$-n$)-decyl$-pyridin-2$-yl$)-2,2'$-bithiophenes\) [4]. The molecular structure of these materials is shown in Figure 5-2. For detail synthesis procedures of C10 and C9, please see appendices 5.7.1 and 5.7.2 respectively.

Both ends of the core unit in C9 and C10 are attached with aliphatic chains, \(C_9H_{19}\) for C9 and \(C_{10}H_{21}\) for C10, respectively.

![Molecular structure of C10 (R= C\textsubscript{10}H\textsubscript{21}) and C9 (R= C\textsubscript{9}H\textsubscript{19}).](image)

5.2.3 Phase transition temperatures of C9 and C10 [2]

![DSC thermogram of C9.](image)
Transition temperatures (in cooling) measured by Optical Microscopy:

for C9 are K [4.2] Sm1 [59.7] SmG/K1 [185.1] SmC [187.1] N [188.3] Isotropic
and for C10 are K [48.5] Sm1 [96.1] SmG/K1 [179.0] SmC [186.7] Isotropic.

Transition temperatures by DSC analysis:

for C9 31.3, 63.9, 187.9 (Heating) and 4.2, 59.7, 185.7, 186.4, 187.9 (Cooling)
for C10 52.3, 107.7, 182.4, 187.9 (Heating) and 47.2, 98.2, 179.4, 185.7 (Cooling)

5.3 EXPERIMENT

Carrier mobility is measured with the time of flight (TOF) method as described in chapter 2. In this experiment, I used a laser light of wavelength 435 nm. The laser light with this wavelength has high intensity and hence generates a huge amount of charge. This creates an additional electric field resulting in a fast sweep of the charge carriers. Consequently, it reduces the time of flight and hence increases the mobility. Therefore, this experiment is limited by the space charge effect. For a given temperature and
voltage, I used a polarizer to control the intensity of the light so that TOF was almost constant with the change of the intensity.

Commercially available 10 micron cells [5] were capillary filled with liquid crystal at its isotropic phase as explained in chapter 2. The TOF measurement for the varying electric field was taken at a temperature of 351 K for C9. For C10, it was taken at temperature 341 K. At the lower temperature, a lower voltage gave dispersive traces, which made it difficult to locate the transient time for the TOF in the trace. At the higher temperature, a higher voltage produced space charge. In this case, the current went up with the time before the transient time was reached making it difficult to locate the transient time on the trace.
5.4 OBSERVATION

5.4.1 C10 [5, 5'-di-(5-n-decyl-pyridin-2-yl)-2,2'-bithiophenes]

Figure 5-5: The hole mobility vs. temperature for C10 at $3 \times 10^4$ V/cm at Sm1-SmG phase.

Figure 5-6: The electron mobility vs. temperature for C10 at $3 \times 10^4$ V/cm Sm1-SmG phase.
I observed the hole and electron mobilities for C10 by varying the temperature at the constant electric field of $3 \times 10^4$ V/cm. The charge carrier mobilities for the holes and electrons are almost independent or a very weakly dependent on the temperature for this material as shown in Figure 5-5 (for the hole mobility) and in Figure 5-6 (for the electron mobility). This can also be remarked in the traces where the TOFs are almost identical for all temperatures at the electric field of $3 \times 10^4$ V/cm as shown in Figure 5-7.

![Figure 5-7: The TOF traces of hole transport in C10 at $3\times10^4$ V/cm with temperature variation from 321 K to 371 K at Sm1-SmG phases.](image)

I also observed the charge carrier mobilities for both the holes and electrons by varying the electric field at constant temperatures of 341 K. I found that the charge carrier mobilities are strongly dependent on the electric field as shown in Figure 5-8 for the hole mobility and Figure 5-9 for the electron mobility. The mobilities decreased with
increasing the electric field for the both type of charge carriers. However, it does not vanish at higher fields but instead reaches saturation.

Figure 5-8: The hole mobility vs. electric field for C10 at 341 K at Sm1 phase.

Figure 5-9: The electron mobility vs. electric field for C10 at 341 K at Sm1 phase.
Figure 5-10: The TOF traces of hole transport in C10 at 341 K (SmG phase) with the electric field variation.

Figure 5-11: The TOF traces of electron transport in C10 at 341 K (Sm1 phase) with the electric field variation.
5.4.2 C9 [5,5’-di-(5-n-nonyl-pyridin-2-yl)-2,2’-bithiophenes]

I also observed the hole and electron mobilities for C9 material (see Appendix 5.7.2 for its synthesis procedure) by varying the electric field at the constant temperature of 351 K. Like C10, the charge carrier mobilities are strongly dependent on the electric field as shown in Figure 5-13 for the hole mobility and Figure 5-14 for the electron mobility. I observed that there is a decrease in mobility with increase in the electric field for both types of charge carriers. However, they also do not vanish by increasing the field but reach the saturation at higher fields similar to the C10 material.

Figure 5-12: The TOF traces of hole transport in C9 at 351 K (SmG phase) with the electric field variation.
Figure 5-13: The hole mobility vs. electric field for C9 at 351 K (SmG phase).

Figure 5-14: The electron mobility vs. electric field for C9 at 351 K (SmG phase).
I also observed the behavior of the electron mobility by varying the temperature as shown in Figure 5-15. Like C10, the charge carrier mobilities are almost independent or have a very weak dependence on the temperature for this material too. This can be noted in the traces where TOFs for all temperatures at the electric field $5 \times 10^4$ V/cm are the same as shown in Figure 5-16. Because of the dispersive traces at the lower temperature with the lower voltage and the space charge effects at the higher temperature with the higher voltage, the data for this compound were very limited.

Figure 5-15: The electron mobility vs. temperature for C9 at $5 \times 10^4$ V/cm at SmG phase.
Figure 5-16: The TOF traces for C9 at $5 \times 10^4$ V/cm with temperature variation at SmG phase.
5.5 RESULTS AND DISCUSSIONS

In general, it is difficult to measure the electron mobility in organic materials due to the high electron affinity of oxygen. But, here, both electron and hole mobilities of C9 and C10 were measured. Our observations showed that both types of charge carrier mobilities were strongly electric field dependent in both C10 and C9. The mobility decreased continuously with increasing the electric field up to $6 \times 10^4$ V/cm after which it became almost independent of the electric field.

The hole and electron mobilities are not affected significantly by the change in temperature for the both of C10 and C9 over our temperature range. This argues against transport due to ions.

5.5.1 Observations on heating and cooling processes

I performed the TOF experiment in C10 by varying the temperature at constant electric field for both heating and cooling processes. The experiments were also performed for slow and fast rate of processes. The better charge carrier mobility is expected in the slow cooling process because it reduces the energetic and spatial disorder producing better molecular alignment. However, no significant differences have been observed in all these processes.
5.5.2 Observation of the materials synthesized by two different mechanisms

I carried out the TOF experiment on C10 materials synthesized by different methods (see Appendix 5.7.1). No significant changes were noticed in the hole and electron mobilities of all these materials. We conclude that the charge carrier mobilities of C10 were independent of synthesis methods.

5.5.3 Higher mobility of C9 than C10

The hole and electron mobilities of C9 were almost two times greater than that of C10 for the same electric fields.

5.5.4 The introduction of nitrogen atoms in the aromatic core does not help to increase the mobility

Pyridine moieties often induce very ordered smectic phases and therefore, one might expect large mobilities. However, the mobilities of bis-alkylpyridinyl-2,2'-bithiophenes (C10 and C9) were measured of the order of $10^{-4}$ cm$^2$/Vs, which was an order of magnitude smaller than the mobility $10^{-3}$ cm$^2$/Vs of bis-alkylphenyl-2,2'-bithiophenes [6]. Hence, more theoretical work needs to be done for better understanding of the roles of pyridine in determining structure and mobility.

5.5.5 The electric field dependence of the mobility

Qualitatively, a similar type of electric field dependent mobilities have been observed in TAPC doped BPPC at 329 K [7] and poly(3-hexylthiophene) at 310 K [8].
However, the mobilities of BPPC and poly(3-hexylthiophene) depend on the temperature as well.

There are at least three theories of hopping conduction that might be applicable to these materials. Central to all of the theories is the basic picture of the hopping rate between two sites being proportional to the product of a transfer integral (J) depending on the overlap of, e.g., HOMO orbitals for hole transport, and a Boltzmann-like factor involving $\Delta \varepsilon$, the difference in site energies.

Firstly, the model of Emin [9], based on the pioneering work of Holstein [10], considers carriers in an ordered system. Here the field dependence can arise due to the carrier’s need to absorb/emit phonons as they jump from a site and relax from their field-accelerated states to a new site. A larger field thus leads to a greater number of carrier-phonon vertices and therefore strongly decreased mobility. Indeed, in many cases, $\mu \sim \exp[-E^2] \to 0$ as $E \to \infty$.

Other theories include the effects of various sorts of disorder on the hopping. Energetic (diagonal) disorder, characterized by a width, $\sigma$, arises when there is dispersion in the energy of hopping sites. Positional (off diagonal) disorder, represented by $\Sigma$, arises either when sites are not equidistant or the molecular orientations (e.g., the relative orientation of the molecules’ $\pi$-orbitals) on the sites are different. One such theory assumes spatially uncorrelated Gaussian-distributed disorder [11] while the other invokes spatially correlated disorder arising from the comparatively long-range fields of random dipoles. We will find it sufficient to discuss the former, in the context of which we describe the experimental consequences of different combinations of $\sigma$ and $\Sigma$ [11].
Consider first the case of small $\sigma$ and $\Sigma$. In this case the integral $J$ is constant and each site offers almost the same energy to the carrier. Therefore, the hopping rate is field independent and the mobility $\mu \sim R/E \sim 1/E \to 0$ for large $E$.

In the case of $\sigma \neq 0, \Sigma = 0$, i.e., pure diagonal disorder, the application of an electric field tilts the free-energy surface, reducing the activation energy required to hop. With increasing $E$, the inter-site jump rate increases and so does $\mu$. Both of these cases do not agree with the data.

A more interesting situation manifests when $\Sigma \neq 0$. Here, there exist sites that act as traps ("dead ends") where there is insufficient overlap ($J \sim 0$) to easily pass to another site. When $E$ is small this is not a problem-the charge can simply hop "backwards" to a previous site. However, as $E$ increases a backwards hop involves a Boltzmann factor $\exp[-eEa/kT]$ ($a$ is the hopping distance) and the mobility therefore falls with $E$. If the energetic disorder is also substantial, the simulations of Bässler [11] find that the aforementioned reduction in the activation energy overcomes the effects of "dead-ends" at sufficiently large fields and the mobility rises, i.e., $\mu$ is non-monotonic (or at least almost flat for large fields). As seen in Figure 5-8 and Figure 5-9, our measured mobility as a function of field reaches a "plateau" at around $E \sim 10^5$ V/cm, consistent with the beginning of a reversal in sign of $d\mu/dE$.

Some caveats are in order. Firstly, the TOF current transients were quite dispersive, though they generally retained clear changes in slope that we identified with TOF. As has been discussed in ref. [12], Scott et. al., this definition of the TOF in dispersive media can be highly deceptive, with the "real" TOF being substantially larger
than one obtained using our procedure. To this end, we have tried the semi-
phenomenological approach of ref. [12]. Unfortunately, our data do not appear to
conform to the functional form proposed in this reference. A better approach would be
the Monte – Carlo modeling of ref. [11]. We note, however, that we believe that the
qualitative features discussed here (decreasing μ with E, a plateau at high E, and little T
dependence) will probably remain regardless of the definition of the TOF.

Secondly, the application of Bässler’s model raises a number of difficult
questions.

(i) The theory predicts temperature dependence. We find an essentially
temperature-independent mobility. While T-independent transport has been observed
before, i.e., in hexaalkyloxytriphenylenes, it appears to be due to dynamic disorder [10],
which is unlikely (though not impossible) in the present highly ordered systems.

(ii) We note that the theory of ref. [11] indicates that, for the development of a
plateau-like feature in μ(E), the normalized disorder parameter $\sigma' = \sigma/k_B T$ must be $\sim 1.5$
or greater. For our data at $T=70$ °C , this implies $\sigma/k_B \sim 511.5$ K which, in turn, implies
that the mobility should be an increasing function of T in the experimental regime, $\mu \sim
\exp[-1\times10^5/T^2]$. This is not observed.

(iii) Furthermore, the theory depends on substantial energetic and positional
disorder. It is not clear how such disorder might arise in our samples.

These issues require further study, the former via accessing larger regimes of T
and E, and the latter by structural studies of the rather puzzling $S_2$ phase found in C9 and
C10 at these temperatures.
5.6 CONCLUSIONS

1. We studied the mobilities of both types of charge carriers i.e. electrons and holes in the smectic liquid crystals C9 \([5,5'\text{-di-}(5-n\text{-nonyl-pyridin-2-yl})-2,2'\text{-bithiophenes}]\) and C10 \([5,5'\text{-di-}(5-n\text{-decyl-pyridin-2-yl})-2,2'\text{-bithiophenes}]\).

2. Compound to the equivalent phenyl compounds, Pyridines, though known to assist in the formation of high-order smectic phases, appear to lower mobility.

3. Both electron and hole mobilities were strongly electric field dependent in both materials. The mobility decreased continuously with increasing electric field up to a certain value, after which the mobility becomes constant.

4. Both types of charge carrier mobilities are independent or very weakly dependent on the temperature.

5. We tentatively describe our data using Bässler’s Theory of disordered hopping conduction.

6. The mobility of C9 was greater than C10.

7. The mechanism of synthesis of C10 material did not make any difference in the result of the charge carrier mobility.

8. The experiment performed in heating and cooling process did not change any result in the measurement of the charge carrier mobility.
5.7 APPENDIX

5.7.1 Synthesis of C10 (This was done by Y. Getmanenko)

5.7.1.1 First Method

1-Bromodecane (8 equiv., 12 mmol, 2.66 g) was added dropwise to a suspension of Mg turnings (14.4 mmol, 0.34 g, activated by heating with a crystal of iodine) in anhydrous Et₂O (20 ml). The solution turned cloudy after several minutes of stirring. The reaction mixture was refluxed for an hour and cooled to room temperature. This freshly prepared Grignard reagent was added to the suspension of aryl dibromide (1.5 mmol, 0.72 g) and NiCl₂(dppe) (20 mol%, 0.3 mmol, 0.16 g) in 60 ml of anhydrous THF. The reaction was completed after refluxing for 3 hours and addition of ~7 equivalents of alkyl Grignard. The reaction mixture was cooled down to room temperature and vacuum filtered to remove insoluble matter. After evaporation of the solvent the solid was dissolved in 20 ml of CH₂Cl₂ and chromatographed (silica gel, CH₂Cl₂:hexanes=35:15). A shiny yellow powder (0.5 g, 55.6% yield) was isolated after evaporation of the solvent from combined fractions. The bright yellow-orange crystals (0.47 g) were dissolved in several ml of CHCl₃ with heating and the solution was applied to the top of the column (10 g of basic Al₂O₃). The column was eluted with 100 ml of CH₂Cl₂, the yellow solution was collected (an orange band stayed at the top of the column), and the solvent was removed under reduced pressure. The material was recrystallized from i-PrOH (0.39
g, 83% recovery). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 0.83-0.91 (t, J=6.68 Hz, 6H, 2CH$_3$), 1.21-1.40 (m, 28H), 1.56-1.64 (m, 4H), 2.57-2.62 (t, J=7.63 Hz, 4H), 7.20-7.24 (d, J=3.85 Hz, 2H), 7.41-7.45 Hz (d, J=3.87 Hz, 2H), 7.47-7.52 (dd, J=8.12 Hz, 2.16 Hz, 2H), 7.54-7.60 (d, J=8.18 Hz, 2H), 8.37-8.40 (d, J=1.59 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 14.27, 22.83, 29.26, 29.47, 29.58, 29.72, 29.74, 31.26, 32.04, 32.95, 118.34, 124.73, 124.84, 136.66, 136.70, 138.90, 143.99, 149.77, 150.04. Analysis calculated for C$_{38}$H$_{52}$N$_2$S$_2$: C, 75.95; H, 8.72; N, 4.66; S, 10.67. Found: C, 75.61; H, 8.46; N, 4.59; S, 10.72.

5.7.1.2 Second Method

2,2’-Bithiophene (0.0044 mol, 0.73 g) was placed into an oven-dried three-necked flask and dissolved in 22 ml of anhydrous THF. The resulting solution was cooled down to $\sim$60 °C (acetone/CO$_2$ bath) and n-BuLi (2.5M in hexanes, 0.0088 mol, 3.52 ml) was added dropwise (-60-40 °C internal temperature). Thick white precipitate formed after stirring for several minutes, the cooling bath was removed and the mixture was allowed to warm up to 0 °C over an hour. The reaction mixture was cooled down $\sim$30 °C, and a solution of ZnCl$_2$ (0.01056 mol, 1.40 g) in 10 ml of anhydrous THF was added to a thick suspension (30-0 °C internal temperature). The mixture was stirred for ah hour, and the cloudy solution was added to a yellow solution of 2-iodo-5-n-decyl and Pd(PPh$_3$)$_4$ in 10 ml of anhydrous THF. The reaction mixture became bright yellow and cloudy. After stirring for several hours the bright yellow mixture with yellow precipitate was transferred into a round bottom flask and the solvents were removed by rotary
evaporation. The residue was treated with 50 ml water, and the yellow solid was separated by vacuum filtration. The crude material (2.92 g, a bit wet) was dissolved in 100 ml of CH₂Cl₂, gravity filtered while hot, concentrated down to ~50 ml, and the bright yellow solution was filtered through Al₂O₃ (basic, 60 g). The solvent was removed from combined fractions, and the residue was recrystallized from 2-PrOH (450 ml). Purified product was isolated as yellow solid in 61.3% yield (1.60 g).

This material was purified for mobility measurements by column chromatography using Biotage column and distilled CH₂Cl₂ (1.47 g, 94.8% recovery). The traces of impurities (MS (APCI): 765.0) were partially removed by this step. The solvent was removed from combined fractions; the solid was dissolved in distilled toluene (75 ml), the bright yellow solution was refluxed with 60 ml of charcoal for several hours, gravity filtered while hot, concentrated by boiling off the solvent, and cooled. The yellow solid was dissolved in CH₂Cl₂ (heating) and chromatographed (160 g of basic Al₂O₃, CH₂Cl₂:hexanes=1:1 as eluant). The material was further purified by recrystallization from distilled CH₂Cl₂. Slow cooling produced large bright yellow crystals suitable for single crystal X-ray diffraction. MS (APCI): 601.0 (calculated FW 600.3572).

5.7.1.3 Third Method

5,5’-Dibromo-2,2’-bithiophene (1.82 mmol, 0.59 g) and 2-tri-n-butylstannyl-5-n-decylpyridine (2.2 equiv., 4 mmol, 2.03 g) were mixed in an oven-dried three-necked flask equipped with magnetic stirbar, nitrogen inlet, bubbler and thermometer.
Anhydrous DMF (10 ml) and Pd(PPh₃)₄ (1 mol%, 0.02 mmol, 0.023 g) were added under nitrogen atmosphere, the bright yellow suspension was heated for 2 hours (135 ºC internal temperature). The cooled mixture with orange precipitate was transferred into a beaker with 75 ml of ice water and orange gummy solid formed. The cloudy yellowish aqueous solution was decanted off and this orange gummy solid was refluxed with 400 ml of EtOH, gravity filtered to remove insoluble orange solid, and the bright yellow solution was concentrated down to 75 ml. The yellow-orange solid formed on cooling was separated by vacuum filtration (0.29 g). This solid was further purified for a mobility measurements by a series of several chromatographic columns and recrystallizations (silica gel, CH₂Cl₂ as eluant (1st column), crystallization (1-PrOH), column chromatography (20 g of basic Al₂O₃, CH₂Cl₂:hexanes=1:1 as eluant (2nd column), and Biotage column (distilled CH₂Cl₂ as eluant), recrystallization (distilled 1-PrOH).

5.7.2 Synthesis of C9 [5,5’-di-(5-nonyl-pyridin-2-yl)-2,2’-bithiophenes]

1-Bromononane (8 equiv., 12 mmol, 2.49 g) was added dropwise to a suspension of Mg turnings (14.4 mmol, 0.35 g, activated by heating with a crystal of iodine) in anhydrous THF (15 ml). The solution turned cloudy after several minutes of stirring. The reaction mixture was refluxed until most of magnesium dissolved. This freshly prepared Grignard reagent was added in portions to the suspension of aryl dibromide (1.5 mmol, 0.72 g) and NiCl₂(dppe) (20 mol%, 0.3 mmol, 0.16 g) in 60 ml of anhydrous THF. The reaction was completed after refluxing for 8 hours and addition of 5 equivalents of alkyl Grignard. The reaction mixture was cooled down to room temperature and vacuum filtered to
remove insoluble matter. After evaporation of the solvent under reduced pressure the residue was treated with water, and the yellow-green solid was vacuum filtered and dried. Crude material (0.72 g, 83.5% crude yield) was chromatographed (silica gel, CH₂Cl₂:hexanes=1:1, then CH₂Cl₂). The yellow powder was isolated in 30% yield (0.25 g). Purified material (0.21 g) was dissolved in 10 ml of CHCl₃ (heating), yellow solution was applied to the top of the column (basic Al₂O₃, 15 g), and eluted with CHCl₃ (~70 ml). The yellow solid obtained after evaporation of solvent from combined fractions was recrystallized from ~30-40 ml of 1-PrOH (0.15 g, 70% recovery). ¹H NMR (CDCl₃, 300 MHz): δ 0.80-0.91 (t, J=6.71 Hz, 6H, 2CH₃), 1.20-1.40 (m, 24H), 1.57-1.63 (m, 4H), 2.55-2.65 (t, J=7.62 Hz, 4H), 7.21-7.24 (d, J=3.87 Hz, 2H), 7.42-7.45 Hz (d, J=3.88 Hz, 2H), 7.46-7.53 (dd, J=8.18 Hz, 2.14 Hz, 2H), 7.54-7.60 (d, J=8.12 Hz, 2H), 8.37-8.41 (d, J=1.54 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz): δ 14.28, 22.83, 29.27, 29.46, 29.59, 29.68, 31.27, 32.03, 32.96, 118.37, 124.79, 124.87, 136.71, 136.78, 138.91, 143.93, 149.74, 150.01. Analysis calculated for C₃₆H₄₈N₂S₂: C, 75.47; H, 8.44; N, 4.89; S, 11.19. Found: C, 75.46; H, 8.49; N, 4.84; S, 11.11.

5.8 REFERENCES


[4] These materials were prepared by Dr. Y. Getmanenko and Prof. R Twieg at Chemistry Department, KSU.


CHAPTER 6

DESIGN AND CONSTRUCTION OF A DEVICE TO MEASURE THE

MOBILITY IN THE FREELY SUSPENDED FILM

6.1 INTRODUCTION

A standard conventional method to study the transport properties of liquid crystals is to measure the time-of-flight (TOF) of charge carriers in a sample sandwiched between two electrodes. This technique has advantages as well as disadvantages. The advantages are that preparation is easy and their alignment layers may be used for a variety of different applications. A disadvantage is that there is a direct contact between the sample and the electrode. This causes a high probability of material contamination and electrochemical reaction, reducing the quality of the sample. It is also difficult to change the alignment of molecules in-situ due to the surface contact between the electrodes and the material that bounds the alignment. The sample cannot degas in-situ, i.e., the gas trapped between electrodes at the time of filling the cell cannot be removed.

Therefore to minimize these disadvantages, I have developed a technique with C. Pokhrel to measure TOF in a free standing liquid crystalline film. This technique has the following advantages over samples contained in conventional cells; (a) the
external fields may couple easily to the molecular order, (b) there is no electrode contact with the sample, (c) the high voltage can be applied in vacuum when required, and (d) the electron mobility can be studied easily for a very wide range of the thicknesses (in principle, 100 nm to 200 µm).

6.2 DESIGN AND CONSTRUCTION OF THE EXPERIMENTAL SET UP

In this experiment, the carrier mobility in the free standing liquid crystalline film was measured by the time of flight (TOF) method. The experimental set up for the TOF technique was discussed in detail in chapter 2. In this experiment, the set up has two key differences; the first difference was the use of the freely suspended film untouched by any electrode and the second difference was that the entire experiment was carried out inside the vacuum system.

6.2.1 Making of a freely suspended film

In the current experiment, I have used the surface wiping technique to make a freely suspended film. In this technique, I encountered some technical difficulties during selection of different factors for film making. One of them was the selection of the material that forms the film. The second was the selection of the type of substrate and the third was the structure of the hole by which the film is suspended.

In the first attempt, I took a piece of Kapton as a substrate and made a cylindrical shaped hole in it. I selected Kapton of thickness 0.6 mm for the substrate because it was thin and moderately flexible, i.e., not hard and not soft. With a thinner
substrate we could maximize the electric field using the same available high voltage source. The advantage of the softer substrate was that it was easier to make a hole and drill smoothly in a straight cylindrical shape. However the commercially available Kapton posed a major problem. The problem was that the Kapton came as a laminate sheet glued together. So when it was cut to make a hole, the glue portion between the sheets fell out and touched the experimental material. It resulted in contamination causing no TOF signal to be generated from the freely suspended film in the experiment. To resolve this problem, I replaced Kapton by a piece of glass slide of thickness 0.9 mm as shown in Figure 6-1. I also tried a Quartz piece, which was thinner than glass. But it was difficult to cut the hole in desired shape in the quartz piece as it (hardness factor = 7) is harder than the glass (hardness factor = 5.5).

Figure 6-1: Straight cylindrical hole in the glass substrate.

I faced four problems with the straight cylindrical hole substrate. The first problem was that we could not make the film from all types of materials. I tried several materials such as hexapentyloxytriphenylene (HAT5), 1-nitro-2,3,6,7,10,11-
hexakis-pentyloxy-triphenylene (NO₂-HAT5), biphenyl, and 2-dodecyloxy-6-(4-octylphenyl)-naphthalene (8PNPO12).

At the isotropic phase, HAT5 and NO₂-HAT5 behaved similar to a water-like thin liquid while 8PNPO12 was similar to a soapy water type liquid. Therefore HAT5 and NO₂-HAT5 did not form the film whereas 8PNPO12 did. However 8PNPO12 also required much care in wiping over the surface of the substrate to make its film.

The second problem was, although I succeeded in making the 8PNPO12 film at its isotropic phase and preserved its continuity when it was cooled slowly to the temperature of its SmB phase, the film broke when it was further cooled down below this temperature.

The third problem was, since 8PNPO12 is a dipolar molecule, the applied voltage also produced a non-zero net force on the film. Since the film was too thin, it was pulled towards one of the electrodes when a higher field was applied and broke at a voltage well below the voltage required to sweep the generated charge carriers across the film.

The fourth problem was hanging the top electrode to apply the electric field. Since the film stayed at the top surface of the hole, I could not sandwich the substrate between two electrodes. If I did so, the film touched the upper electrode and broke. So the top electrode had to be hung just above the experimental sample by keeping the spacer between the substrate and the top electrode. But if I used the hanging electrode, there would be a large gap between two electrodes, which required a higher voltage to get sufficient electric field to sweep the charges. However there were some
advantages of hanging the electrodes. By using the hanging electrodes, I could fit the experimental cell inside the chamber before making the thin film. That is, after fitting every components of the set up and heating the cell up to the isotropic temperature of the material, I could put the material on the surface of the substrate because the top surface would still be open. I could thus wipe it and place the upper electrode later. In this condition, I did not have to cool down the cell with the film to room temperature before fitting the setup. However this advantage was suppressed by the disadvantage of the large gap which requires high voltage.

This compelled us to think about another technique to make the film. In this technique, I made the hole “beveled shaped” on both sides.

![Figure 6-2: Thin film making set up – (1) Wiper (2) Glass slide and (3) Beveled hole.](image)

I took a piece of glass slide as a substrate. Its thickness was 0.93 mm. A circular hole of 2-3 mm diameter was made at the center of the glass piece. The hole was beveled from both sides using a special type of drill so that the diameter of the circular hole at the surface of the substrate was greater than that at the center of the thickness. It looked like a funnel shaped hole cut from both sides.
A small amount of the material, enough to make a film was heated on the surface of the substrate to the isotropic phase and wiped gently by a sharp edged blade over the hole. When the material was wiped, a layer of material was stretched over on the hole forming a film. The material on the beveled part of the hole also flowed slowly into the main hole circumference, helping the film to survive cooling to the room temperature. The film was strong enough to be fit into the electrode without breaking it at room temperature. This was one of the main advantages of the bevel shaped hole. This technique worked for all materials HAT5, NO₂-HAT5 and 8PNPO12 to make the film. However, after several attempts, finally I got the best signal in an 8PNPO12 film.

Figure 6-3: A glass substrate with a freely suspended film.
6.2.2 Construction of an experimental cell

The glass substrate with the freely suspended film was sandwiched between two transparent electrodes. I used the commercially available ITO plates as the electrodes. The film was untouched by the electrodes as shown in Figure 6-4. Pieces of Kapton tape were put between the electrodes and the substrate on both sides to drain out the air between the film and the electrodes during vacuum.

![Diagram](image)

Figure 6-4: The cross-section view of the substrate with the freely suspended film sandwiched between two transparent electrodes.

1) Substrate 2) Bevel 3) Freely suspended film 4) ITO as electrodes 5) ITO coated plate

The experimental cell design is as shown in Figure 6-5. In this figure, (1) is a piece of rectangular white Teflon which is the base of the experimental cell. (2) and (3) are two ITO coated transparent electrodes. (4) is a piece of glass slide used as a substrate to hold the film in the beveled hole (5) made at the center. This substrate is sandwiched between the two electrodes. (6) is the piece of thin Kapton which has been used as a clip to hold the electrodes and the substrate. (7) and (8) are the connecting junctions for the voltage wire and the signal wire, respectively. (9) is the
thermocouple which was fixed on the Teflon base to measure the temperature of the experimental cell. A photograph of the experimental cell is shown in Figure 6-6.

Figure 6-5: The schematic diagram of the experimental cell.

(1) Teflon base (2) Bottom electrode (3) Top electrode (4) Substrate a film holder (a piece of glass slide) (5) Liquid crystal film (6) Kapton clip (7) High voltage wire (8) Signal wire (9) Thermocouple (10) Connecting junctions to temperature controller.
The entire set up of experimental cell including the Teflon base was then freely mounted in the aluminum chamber holder as shown in Figure 6-7.
The whole assembly was then inserted inside the copper oven provided by Prof. S. Sprunt. The oven was fitted with two ribbon shaped heater strips as shown in Figure 6-8. When the heater is turned on, the sample gets radiantly heated. The temperature of the oven was controlled by a PID temperature controller with the help of the thermocouple fixed on the Teflon base.

The whole assembly was kept inside a vacuum chamber provided by Prof. S. Sprunt as shown in Figure 6-10. The objectives behind using the vacuum system were to avoid the electrical discharge through the air at high voltage, to avoid ionic transport in the air, and to degas the sample. The pressure inside the chamber was of the order of $10^{-6}$ torr.

Figure 6-8: The oven to heat the material fixed in the experimental cell.
Figure 6-9: The oven (Courtesy of Prof. S. Sprunt).

Figure 6-10: Schematic diagram of the vacuum chamber.
The experimental arrangement of the equipment, namely laser source, mirrors, prism, Raman shifter, temperature controller, and the amplifier, were exactly the same as described in the chapter 2. The only difference in this experimental set up is that I was using a very high voltage source and two more mirrors to bend the light vertically downward facing the upper window of the vacuum chamber which was in the horizontal position as shown in Figure 6-12. Since the thickness of the film is minimum at the center of its surface area, a lens was used to converge the light at the center. A vacuum pump was used to create vacuum inside the vacuum chamber.
During the vacuum process, the pressure was built up on the film due to an unequal vacuum creation above and below the film. There were two ways to run the vacuum system to take out the air from the vacuum chamber, i.e., before and after heating the cell. Both processes had advantage as well as disadvantage.
Figure 6-13: The experimental set up.

The top and bottom pictures respectively show the broad and closed views. (1) Laser, (2) Mirrors, (3) Raman shifter, (4) Prism, (5) Vacuum chamber
Figure 6-14: Inside view of the vacuum chamber from the glass window of the chamber.

If the vacuum system was run before heating the cell, the probability of breaking the film due to the built up of differential pressure was less. But it took a long time for the material to reach its experimental temperature because of the absence of air.

On the other hand, if I ran the vacuum system after heating the cell, the results were the reverse of the former process. There was a high probability of breaking the film but it took a very short time to heat the cell. So depending upon the nature of the film, I used both processes.
6.3 THEORY [1]

Figure 6-15: Schematic diagram of the freely suspended film.

(1) Laser light (319 nm), (2) ITO coated top electrode, (3) Film holder (glass slide), (4) ITO coated bottom electrode, (5) Liquid crystal film, (6) Current amplifier.

Let $L$ be the thickness of the sample and $l_1$ and $l_2$ the thicknesses of the gaps above and below the film, respectively. If $\sigma_1$ is the charge density on the top electrode, $\sigma_2$ on the bottom electrode and $\pm \sigma_0$ the density of charge pairs created by the laser, then, in a simple model in which trapping and diffusion of charges are ignored, the electric fields at various regions of the cell as shown in Figure 6-16 are given as
Here $\varepsilon$ and $\varepsilon_0$ are the electric permittivity of the material and the vacuum, respectively. $\varepsilon_r$ is the dielectric constant of the material.

If $x$ is the displacement of a positive charge sheet at time $t$ from the top surface of the material then we can write

$$ V = E_1 l_1 + E_2 x + E_3 (L-x) + E_4 l_2 $$

Figure 6-16: Schematic diagram of the charge distribution within a freely suspended film during the process of the hole flow toward the surface facing the electrode with negatively charged. 

$$ E_1 = \frac{\sigma_1}{\varepsilon_0} \quad E_2 = \frac{\sigma_1 - \sigma_0}{\varepsilon_r \varepsilon_0} \quad E_3 = \frac{\sigma_1}{\varepsilon_r \varepsilon_0} \quad E_4 = \frac{\sigma_1}{\varepsilon_0} $$
Since the total charge is conserved, replacing \( \sigma_1 \) by \( \sigma_2 \) in the equation (6.2), one get

\[
V = \frac{\sigma_2 l_1}{\varepsilon_o} + \frac{(\sigma_1 - \sigma_0)x}{\varepsilon_r\varepsilon_o} + \frac{\sigma_1 (L - x)}{\varepsilon_r\varepsilon_o} + \frac{\sigma_2 l_2}{\varepsilon_o}
\]

\[
V = \frac{\sigma_2 l_1}{\varepsilon_o} \left( l_1 + l_2 + \frac{L}{\varepsilon_r} \right) - \frac{\sigma_0 x}{\varepsilon_0 \varepsilon_r}
\]

(6.2)

where \( dx /dt \) is the drift velocity (\( v = \mu E \)) of the charge carrier and \( E \) is the effective electric field inside the sample. Here we have assumed \( \sigma_0 \ll \sigma_1 \).

\[
\sigma_2 = \frac{\varepsilon_0 V + \sigma_0 \left( \frac{x}{\varepsilon_r} \right)}{l_1 + l_2 + \frac{L}{\varepsilon_r}}
\]

\[
\frac{d\sigma_2}{dt} = \frac{\sigma_0 \left( \frac{dx}{dt} \right)}{\varepsilon_r (l_1 + l_2) + L}
\]

(6.3)

This equation gives the amount of current that is generated due to displacement of the charge sheet inside the sample, which is what was observed. Typical traces at various voltages in logarithmic scale and linear scale are shown in Figure 6-19 and Figure 6-20, respectively. Locating the transient time on each trace
as marked by an arrow, we could know the TOF for each voltage. Then we calculated mobility using the equation.

\[ \mu = \frac{L}{E \tau} \]  

(6.5)

If \( V \) is the applied voltage and \( \varepsilon_r \) the dielectric constant of the material, the effective electric field within the sample will be

\[ E = \frac{V}{(l_1 + l_2) \varepsilon_r + L} \]  

(6.6)

and the mobility [1]

\[ \mu = \frac{L[\varepsilon_r (l_1 + l_2) + L]}{\tau V} \]  

(6.7)
6.4 OBSERVATIONS AND RESULTS

Here I present the study of the hole mobility in the free standing film of the sample 8PNPO12. The molecular structure of the sample is as shown in Figure 6-17.

![Molecular structure of 8PNPO12](image)

Figure 6-17: Molecular structure of 8PNPO12.

It is a calamitic liquid crystal, i.e., 2-(4'-octylphenyl)-6-dodecyloxynaphthalene (8PNPO12) [2] with an SmB phase between 84.5 °C and 102 °C and an SmA phase between 102 °C and 123 °C. The mobility of 8PNPO12 at SmB is $1.6 \times 10^{-3}$ cm$^2$/Vs as measured by M. Funahashi et.al [4] using the conventional method.

![DSC thermogram of 8PNPO12](image)

Figure 6-18: DSC thermogram of the 8PNPO12.
Figure 6-19: TOF traces of the hole transport in 8PNPO12 at 2300 V and 4300 V in logarithmic scale.

Figure 6-20: TOF traces of the hole transport in 8PNPO12 at 2300 V, 3300 V and 4300 V in the linear scale.
Before 8PNPO12, I had also tried sample NO₂-HAT5. But 8PNPO12 was better than NO₂-HAT5 because the former has higher mobility than the latter one, i.e., the former requires a lower voltage to produce an observable signal than the latter one for the same thickness of the free standing film.

For example, 3000 V was sufficient for 8PNPO12 to see good signal whereas 9000 V was required for NO₂-HAT5. In our experiment, I was able to manage up to 5000 V without noise and electrical breakdown. Therefore, I selected 8PNPO12 for the study.

6.4.1 Thickness measurement

Two different methods were implemented to measure the thickness of the film. For the thick film, the method implemented was quite simple. The thickness was measured by using a high-resolution microscope. The sample at the room temperature was gently removed from the film holder and was visualized transversely under the microscope to measure the thickness.

For the thin film, I used a High-Resolution Fiber Optic spectrometer “HR4000CG-UV-NIR” from Ocean Optics Inc. to measure the thickness. This measurement technique is based on the principle of interference. In this experiment, a broadband light source is used. The light reflected from the upper and the lower surfaces of the film behave as two sources of light.
Here is a brief description of how the instrument works. To correct the instrument response variables, a reference spectrum is stored first. Then a collimated beam of light is incident on the film from the broadband light source with the help of an optical fiber. The light gets reflected from the upper and lower surfaces of the film. The reflected light is collected by another optical fiber and passed into the spectrometer. This resulting spectrum is displayed in the form of a graph of intensity versus wavelength. This spectrum is fitted with the standard expression of intensity given by

\[ I_\ell = \frac{4r_{10}^2 \sin^2 \beta}{1 - 2r_{10}^2 \cos 2\beta + r_{10}^4} \]  \hspace{1cm} (6.8)

The detailed derivation of above expression is given in appendix A. Here,

\[ r_{10} = \frac{\cos \theta_i - n_i \cos \theta_i}{\cos \theta_i + n_i \cos \theta_i} \quad \text{and} \quad \beta = \frac{2\pi}{\lambda} n_i d \cos \theta_i, \quad n_i = \text{the refractive index of the material.} \]

\[ \lambda = \text{the wavelength of the light,} \quad \theta_i \text{ and } \theta_t \text{ are the angle of incidence and the angle of the transmittance in the top surface of the film.} \quad d \text{ is the thickness of the film.} \]

In the expression, the given refractive index is always constant for the given material and the angle of the incidence is always constant for the given film. The angle can be measured geometrically. Therefore, in the expression, the thickness is the only parameter, which we can vary to fit the curve with the experimental spectrum. The thickness of the film is given by the value of the thickness in which the curve is fitted. Yorick computer code for measuring the thickness of the sample is given in appendix B.
The observations were taken at T=88°C in the SmB phase. The sample thickness was 130 μm. The thickness of the sample was measured using a high-resolution microscope as explained above. The geometry of our cell was L= 130 μm and l₁+l₂ = 0.81 mm and measured mobility was $4.2 \times 10^{-2} \text{ cm}^2/\text{Vs}$ in the SmB phase for $\varepsilon_r = 2.3$ [3] and V=4300 volts.

This value is much higher than the literature value of $1.6 \times 10^{-3} \text{ cm}^2/\text{Vs}$ [4]. This could be due to space charge effects [5], dispersion [6], or possibly a higher
mobility in the films. We note that we do not know the molecular orientation in our films, which may also affect the charge carrier mobility in the film.

It is also possible to have high mobility in the material suspended freely because it is free of contact from the electrodes and that might help in the better alignment of the molecules.

6.5 DISCUSSION

In this experiment, I measured the hole mobility on freely suspended liquid crystal film. Although great effort was needed to reproduce the result, I was able to repeat it many times. However, sometime it was very difficult to observe a clear change in the transient time on the trace with the changing electric field because I had only a small range of electric field due to the practical limitation of a large gap between the two electrodes. The available voltage range could produce only a small variation of the effective electric field across the material and hence the small change in the time of flight. The above fact can be explained more clearly in the following way.

In the experiment, the signal was dominated by the noise at lower voltages less than 2000 V making it hard to locate the time of flight whereas voltages higher than 5000 V could not be applied due to higher risk of electrical breakdown. However, sometimes, the signals at 2000 V were also noisy and the experimental cell could not be held at 5000 V for the time longer than one minute due to the high
probability of electrical breakdown. Therefore, the safe voltage range for the experimental cell was from 3000 V to 4000 V. Practically, the step of 1000 V was not sufficient to observe a clear change in the time of flight.

During the process of the experiment, I also found some substrates show conductive behavior when the electrodes directly touch its surface. For example, glass showed conductive behavior, while the quartz was absolutely non-conductive. However, I had put a piece of insulating Kapton tape between the substrate and the electrodes. I did the experiment for glass, quartz and Pyrex substrates using the insulator. There was no change in the results. Therefore, it was concluded that this type of conductive character of substrate did not affect our result.

I also did the experiment on the substrate without a hole and the substrate with an empty hole, i.e., without material, to check that the signal was really coming from the material. Both experiments gave no signals. Therefore, it confirmed that the signal was absolutely coming from the material.

In this experiment, I faced some technical problems. It took a lot of time and quite a lot of effort to solve these problems. Let’s discuss some of the important problems which are as follows.

1. Noise Problem
2. High Voltage Problem
3. Electrical Breakdown Problem
4. Substrate Contamination and Cleaning Problem
6.5.1 Noise problem

In a TOF experiment, the noise to signal ratio must always be small to make the trace more observable. But the magnitude of the signal itself was very small in this experiment. So, even the presence of a little noise created a significant problem in locating the transient time on the real trace.

I used different techniques to reduce the noise problems. One of them was the use of coaxial wires to connect all electronic components. The outer layer of the coaxial wire works as a Faraday’s Cage, which grounds the electromagnetic waves present as noise in the atmosphere and protects the central wire that carries the important signal. Some non-coaxial wires in the circuit were wrapped in aluminum foil to make a Faraday’s Cage. Since even a single non-coax piece induced the noise, I also wrapped any non-sealed conductor with foil.

We made every circuit wire as straight as possible because loops of wires are antennas.

I also found that a large or even a smaller aluminum electrode produced noise because it acted as an antenna. Hence, I used an ITO coated glass plate as the electrodes.

6.5.2 High voltage problem

This experiment requires high voltage to maintain the electric field needed to sweep the charge carriers from one side of the sample to its other side because of the...
large gap between the electrodes. In our experiment, I had used a piece of glass slide as a substrate. Its thickness could not be too thin or too thick. If it was very thin glass, it would be difficult to make the hole beveled on both sides. The beveled hole was very important to suspend the film freely without touching the surface of the electrodes. If the glass was very thick, it would require a very high voltage to maintain the electric field enough to drag the charges within the film. I used a glass slide of the thickness 0.93 mm which was very high as compared to the gap between two electrodes of the commercially available ITO cell where the gap usually varies from 5 µm to 25 µm.

One problem related to the high voltage sources was electrical breakdown due to the electrical discharge from high voltage wire to grounded objects like grounded wires, the wall of metallic chambers, etc. There was also a high risk of overheating the insulation of the high-voltage wire. Therefore, the wire carrying high voltage must be kept away from such objects and made up of a material of high melting point with good insulation. I used the wire labeled as “Dearborn Wire and Cable E31467 Style 3239” which could be used up to 30 KV DC and 150 °C.

The problem of sparking between electrodes was cured by making the soldered junction very smooth and flat. The small tip of the wire or soldering material at the junctions can cause sparking, because the electric charges are high at such pointed parts.

Beside these problems, intensive precautions for possible short circuits were taken both outside and inside the vacuum chamber.
6.5.3 Electrical breakdown problem

At high voltages, an electrical breakdown occurred even at voltages around 1500 V in the presence of air. Therefore, I filled the chamber with an inert gas such as nitrogen. It helped to only go up to voltages around 2000 V only, because it did not replace all air molecules trapped between the electrodes. This maximum voltage with nitrogen gas was not sufficient to perform the experiment.

That is why I used a turbo pump to create the vacuum inside the chamber. It can create a vacuum up to $10^{-7}$ torr which helped to apply 5000 V without electrical breakdown for a few minutes. However, the application of such a high voltage required intense care.

6.5.4 Substrate contamination and cleaning problem

Substrate cleaning to avoid material contamination also posed some problems during the experiment. A single substrate could not be used for multiple materials as it was very difficult to clean its beveled surfaces completely. Although the beveled part appeared very smooth to the naked eye, the random rough surface could be observed through the microscope. The experimental materials adhered to the rough surface areas could not be cleaned completely.

The single substrate could not be used multiple times for the same material because the quality of material deteriorates after heating and cooling many times.
6.6 CONCLUSIONS

The instrument discussed in this chapter can be used to couple an external field (an electrical field or a magnetic field) with the molecular ordering of the sample because the sample’s surface is free. Since there is no electrode contact with the sample, the probability of the electrochemical reaction reducing the quality of the sample is zero. A high voltage can be applied in vacuum when required. Since the experiment can be carried out in a vacuum, the probability of the oxidation of the material is very low and there is only minimal chance of the trapping of electrons by oxygen. Therefore the electron mobility can be studied easily. A very wide range of thicknesses can be studied (in principle, 100 nm – 200 μm).

The initial results are promising. Optical techniques to characterize the films are being implemented. It might be extended to discotic systems. A better high voltage system with extreme safety measures needs to be developed to improve the experiment. Better techniques to conserve freely suspended films can be developed. On the basis of the above experiment, a professional instrument with low noise problems and a high vacuum system can be designed to study the mobility of the charge carriers in a freely suspended film.
6.7 APPENDIX

6.7.1 Appendix A: Derivation of intensity

The phase difference ($\Delta \phi$) is defined as the phase angle by which one wave leads or lags the another. In vacuum, the phase difference is given by,

$$\Delta \phi = \frac{2\pi}{\lambda} \Delta x$$

where $\Delta x$ = the optical path difference and $\lambda$ = the wavelength of the light. If two beams travels $\Delta x_0$ and $\Delta x_1$ in two different media of refractive indices $n_o$ and $n_1$, before their recombination, the optical path difference between them is

$$\Delta x = n_1 \Delta x_1 - n_o \Delta x_0$$

If two light beams reflected from the film of thickness “d” and the refractive index “$n_1$”, the path between them can be calculated by using above expression as

$$\Delta x = 2n_1 d \cos \theta_i$$

$$\Delta \phi = \frac{2\pi}{\lambda} 2n_1 d \cos \theta_i$$

Let us assume a plane wave is incident upon the film of thickness “d” at an angle $\theta_i$. $A_o$ is the amplitude of the field associated with the incident plane wave in the medium of the refractive index $n_o$ and $A_1$ is the amplitude of the first reflected wave at an angle of the reflection $\theta_i$ ($= \theta_i$) on the top interface in the same medium. $A_2$ is the amplitude of the first transmitted wave in the medium of the refractive index $n$ at an angle of the transmission $\theta_t$ on the top interface. The transmitted wave both
reflects and transmits off the bottom interface. $A_3$ is the amplitude of internally reflected wave at an angle $\theta$, on the bottom interface.

Since the amplitude of the wave is decreased at each interface, the magnitude of the amplitude decreases successively after transmission or the reflection from the interface.

$$A_1 = r_{01}A_0$$
$$A_2 = t_{01}A_0$$
$$A_3 = r_{10}A_2 = r_{10}r_{01}A_0$$
$$A_4 = t_{10}A_3 = t_{10}r_{10}A_1 = t_{10}r_{01}t_{01}A_0$$
$$A_5 = r_{10}A_4 = r_{10}r_{10}r_{01}A_0 = r_{10}r_{01}t_{01}A_0$$

where $r_{01} =$ the ratio of the amplitude of the reflected wave to the amplitude of the incident wave from the interface between the ambient medium and the film. Here the reflected wave is at the ambient medium. $r_{10} =$ the ratio of the amplitude of the reflected wave to the amplitude of the incident wave from the interface between the thin film and the ambient medium. Here the reflected wave is at the thin film. $t_{01} =$ the ratio of the amplitude of the transmitted wave to the amplitude of the incident wave, $r_{12} =$ the coefficient of the internal reflection, $t_{10} =$ the coefficient of transmission from a dense medium to a rare medium.
We can show that $r_{01} = -r_{10}$ and $R + T = 1$

The reflectance $= R = r_{01}^2 = r_{10}^2$ is the intensity of the reflected wave. The transmittance $= T = t_{01}t_{10}$ is the intensity of the transmitted wave. The sum of all reflected terms is

\[ A_r = A_1 + A_4 + A_7 + A_{10} + \ldots \]

\[ A_r = r_{01}A_o + t_{01}t_{10}r_{10}A_o e^{-i2\beta} + t_{01}t_{10}r_{10}^2A_o e^{-i4\beta} + t_{01}t_{10}r_{10}^3A_o e^{-i6\beta} + \ldots \]

\[ A_r = [r_{01} + r_{10}t_{01}t_{10}(1 + r_{10}^2e^{-i2\beta} + r_{10}^4e^{-i4\beta} + \ldots) e^{-i2\beta}]A_o \]
Where \(2\beta = \Delta \phi\) is the phase change that the multiply-reflected wave inside the film experiences as it traverses the film once from one boundary to the other.

\[
\beta = \frac{2\pi}{\lambda} n d \cos \theta,
\]

\[
A_r = \left[ r_{01} + \frac{r_{01} r_{10} e^{-i2\beta}}{1 - r_{10}^2 e^{-i2\beta}} \right] A_o = \left[ -r_{10} + \frac{r_{10} r_{01} r_{10} e^{-i2\beta}}{1 - r_{10}^2 e^{-i2\beta}} \right] A_o = -r_{10} \left[ 1 - \frac{r_{10} T e^{-i2\beta}}{1 - r_{10}^2 e^{-i2\beta}} \right] A_o.
\]

Since \(r_{10}^2 + T = R + T = 1\). The total intensity of the reflected wave, \(I_r\), which is

\[
I_r = A_r A_r^* = r_{10}^2 \frac{(1 - e^{-i2\beta})(1 - e^{i2\beta})}{(1 - r_{12}^2 e^{-i2\beta})(1 - r_{12}^2 e^{i2\beta})} A_o^2 = r_{10}^2 \frac{2(1 - \cos 2\beta)}{1 - 2r_{12}^2 \cos 2\beta + r_{12}^4} A_o^2
\]

\[
I_r = \frac{4r_{10}^2 \sin^2 \beta}{1 - 2r_{10}^2 \cos 2\beta + r_{10}^4} A_o^2
\]

where \(r_{10}\) can be derived by using the application of Maxwell’s equations in the optics of plane waves as [7].

\[
r_{10} = \frac{\cos \theta - n_1 \cos \theta}{\cos \theta + n_1 \cos \theta}
\]
6.7.2 Appendix B: Yorick code to determine the thickness

```yorick
winkill,0;

window,style="boxed.gs",0,dpi=75;
func read_spec(fn) {
  f=open(fn,"r");
  do {
    s=rdline(f);
  } while (strpart(s,1:5)!=">>>>");
da=[];
a=b=0.;
doa={};
do {
  s=rdline(f);
  d=strpart(s,1:5)==">>>>";
  if (!d) {
    read,f,format="%f %f",a,b;
    grow,da,[[a,b]];
  }
} while (!d);
close,f;
return(da);
}
n=1.52;
theta1=27;
func calc(h) {
  theta=theta1*pi/180.;
  lam=span(300.,800.,10000);
  q=n*cos(asin(sin(theta)/n));
  c=cos(theta);
t=(c-q)/(c+q);
a=sin(2*pi*h/lam*q);
a1=cos(2*pi*h/lam*q);
A1=cos(2*2*pi*h/lam*q);
res=4*pi^2*a^2/(1.0+t^4-2*t^2*A1);
return(transpose([lam,res]));
}
spec_no_film="test.Master.Transmission";
func comp(fn,h) {
  v=read_spec(fn);
  v(2,)=avg(v(2,));
u=calc(h);
  l=where((v(1,)>300.0)*(v(1,)<800.0))
  aa=v(1,);
  bb=aa(1);
  cc=v(2,);
  dd=cc(1);
  window,0,style="boxed2.gs";
  plotl,bb,dd,type="solid";
x1=400;
x2=550;
  limits,x1,x2,-1.50
  plsys,2;
  plotl,u(1,),u(2,),color="blue",width=6;
  limits,x1,x2,-.04,.028;
}
```

6.8 REFERENCES


CHAPTER 7

CONCLUSION

Organic semiconductors (OSs) have major commercial potential with their possible use in electronic and optoelectronic devices. Major benefits of OSs over conventional semiconductors include mechanical flexibility, low temperature processing, very low cost, and ease of fabrication in large area electronic devices on plastic and paper substrates. Liquid crystals (LCs) are particularly interesting classes of OSs, both from the standpoints of fundamental physics and practical applications. In this dissertation, novel, interesting calamitic and discotic liquid crystalline organic semiconductors were discussed in terms of their electronic transport.

We explored a rod-like thiophene-benzene-thiophene-based smectic (1,4-di-(5-n-tridecylthien-2-yl)-benzene) system exhibiting polaron band behavior with very impressive hole transport. In this material, the so-called smectic-F phase templates the formation of even more ordered phases with very large mobilities. This means that one may create samples with large, essentially crystalline domains with little trapping at boundaries. The maximum mobility found in this material was greater than 0.1 cm²/Vs at the lowest temperature measured. Therefore, this material is very interesting for, e.g.,
thin-film transistor fabrication due to its high mobility near room temperature. A complete modified theory including non-local phonon interactions is needed for a better understanding of our results. Future experimental, including characterizing related mesogens and fabricating thin-film transistors would be very interesting.

We also measured electron and hole mobilities in a calamitic LC with a pyridine-thiophene-thiophene-pyridine core (5,5-di-(alkyl-pyridin-yl)-2,2’bithiophenes). The mobilities are strongly electric field and very weakly temperature dependent. Although pyridine-based LCs often exhibit very high order smectic phases and are therefore of interest as OSs, the mobilities of these materials were found to be quite low, even in high-order phases. A full explanation of this fact is not available. As a first step, we used Bässler's theory of hopping conduction in disordered systems. However, the results require further study for better understanding. In our laboratory, we have a set of such materials of same core unit but attached with different aliphatic chain length. Some of them are currently being studied, with very interesting preliminary results.

In another material, which is a triphenylene-based discotic LC (1-nitro-2,3,6,7,10,11-hexakis (pentyloxy) triphenylene), we found a strong temperature and field dependent hole mobility and the charge transport to be disorder dominated one-dimensional hopping conduction (a closely related theory to that of Bässler referred to above). Since the material can exist in a discotic columnar phase for a wide range of temperatures, it may be very useful for applications in electronic devices. However, the mobility in this material at low temperature is relatively low. The wide temperature range also makes it a promising “guinea pig” for future physics work.
We have also developed a technique to measure charge carrier mobility in freely suspended films of LCs in high vacuum, a technically demanding problem. As discussed in chapter six, this technique has potential advantages over experiments conducted in conventional cells. The initial results are promising. In the future, extension to other calamitic and discotic systems would be valuable. However, improvements in the apparatus (including better high voltage systems and film production and stabilization) are needed.