Enhancement of Charge Transfer in Thermally-expanded and Strain-stabilized TIPS-pentacene Thin Films

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Enhancement of Charge Transfer in Thermally-expanded and Strain-stabilized TIPS-pentacene Thin Films

A Dissertation Presented

by

Yang Li

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of

The University of Vermont

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**Abstract**

Two of the most critical experimentally accessible properties of small-molecule organic semiconductor materials are the charge carrier mobility, which probes charge transport, and the optical absorption spectrum which probes the energy levels of excited states. The impact of molecular packing on the optical and charge transport properties are often treated separately. However, these effects are actually linked at a fundamental level, and it is of interest to understand the interrelationship between them, as well as how they respond to strain and thermal expansion. In this dissertation, we highlight the fundamental relationship between these two phenomena in 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene).

We present an extensive study of the optical and electronic properties of TIPS-pentacene films utilizing *in situ* X-ray diffraction, optical spectroscopy and *ab initio* density functional theory. The influence of molecular packing on the properties are reported for thin films deposited in the temperature range from 25°C to 140°C, and for films that are strain-stabilized at their as-deposited lattice spacings after cooling to room temperature. Anisotropic thermal expansion causes relative displacement of neighboring molecules while maintaining a nearly constant stacking distance. This leads to a large blueshift in the absorption spectrum as the temperature increases. The blueshift largely reverses a redshift at room temperature compared to the solution absorption spectrum. A reduction in the ratio of the first two vibronic peaks relative to the solution spectrum is also observed. This combination of electronic and vibronic effects is a signature of charge transfer excitonic coupling with a positive coupling constant $J_{CT}$, which depends sensitively on the alignment of the nodes of the frontier molecular orbitals with those on neighboring molecules. These effects are also correlated with the sign and magnitude of electron and hole charge transfer integrals $t_e$ and $t_h$ that provide additional evidence for charge transfer mediated coupling at room temperature, as well as insight into the origin of an experimentally observed enhancement of the field-effect transistor mobility in strain-stabilized thin films. The results suggest approaches to improve carrier mobility in strained thin films and for optical monitoring of electronic changes.

The effect of average intermolecular distance on emission properties of TIPS-pentacene solutions and polystyrene/TIPS-pentacene blend films were studied by varying the TIPS-pentacene concentration and the mass ratio of the host polymer to TIPS-pentacene. In the blend films, it is found that the excited TIPS-pentacene molecules give strong emission when the mean intermolecular spacing is larger than 6 nm but prefer to decay via a non-radiative way when mean intermolecular separation is reduced to 3 nm.
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Chapter 1

Introduction

1.1 General Introduction

1.1.1 Application of Organic Semiconductors

Electronic devices play an important role in our society ranging from basic home appliances to modern technological devices. Most electronic devices in our daily life are based on inorganic semiconducting materials such as silicon, germanium, and gallium arsenide [20,21]. However, the mechanical and chemical properties of inorganic semiconductors have restricted the types of devices that can be built. For example, inorganic materials generally require high processing temperatures and vacuum based processes, making the inorganic electronics difficult to be fabricated on thermally sensitive substrates or in large area. Meanwhile, inorganic materials possess limited mechanical flexibility, precluding the construction of bendable electronic devices.

Carbon-based organic semiconductor materials has the potential to overcome some of the shortcomings associated with inorganic semiconductor materials. The organic
semiconductor materials are soft and mechanically flexible, allowing for construction of electronic devices with good sustainability in complex stress environments like bending, stretching, and twisting [1,22,23]. Organic semiconductor materials can be processed in large area using cost-effective methods such as roll-to-roll processing and inkjet printing at room temperature, which obviates the need for costly vapor deposition that inorganic counterparts require [24–26]. Beyond their unique mechanical properties and economic benefits, organic semiconductors also have other advantages like light weight, compatibility with arbitrary substrates and great chemical tunability. The electronic properties of organic materials can be controlled through conventional wet chemistry, allowing for tuning materials properties depending on the target application. Generally, organic semiconductors are classified into two groups based on their weight: polymers and small molecules. Some of the most common organic semiconductors are shown in Fig. 1.1.

Figure 1.1: Chemical structure of representative small-molecule and polymer semiconductors.
Up to 40 years ago, the organic electronic and optical phenomena were considered to be a domain of pure research. Organic semiconductors started to attract industrial interest in mid-1980s, with the first demonstration of a low voltage and efficient thin film light emitting diode by Tang [27]. Soon after that, successful fabrications of organic field effect transistors (OFETs) from conjugated polymers and oligomers were reported [28,29]. These early studies opened the door to the possibility of using organic thin films as a foundation for high performance electronic devices. Currently a worldwide effort involving universities, national Laboratories, major electronics firms and smaller companies are actively working in this area. Up to now, organic light emitting device already has commercial products and the charge transport mobility of OFETs has reached $10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ which is higher than the amorphous Si [6,30,31]. Fig. 1.2 shows several applications of flexible organic electronic devices.

1.1.2 \textbf{π-bonds in Organic Semiconductors}

The nature of bonding in organic semiconductors is fundamentally different from inorganic semiconductor. Crystalline inorganic semiconductors are strongly covalently bonded throughout the material, whereas organic semiconductors are typically \(\pi\) bonded molecules and the bonding in these structures interact mainly through weak van der Waals forces. The \(\pi\)-electron system is formed by overlap of \(p_z\) orbitals that caused by \(sp^2\) hybridization of carbon atoms in the molecules. The electron configuration of a free carbon atom in its ground state is \(1s^22s^22p^2\). The carbon atom can bond to four atoms by an excitation (or promotion) of an electron from the doubly occupied \(2s\) orbital to the empty \(2p\) orbital, producing four singly occupied orbitals (one \(2s\) orbital and three \(2p\) orbitals). From molecular physics, three degenerate or-
bitals are constructed out of the 2s orbital and two of the three 2p orbitals (usually denoted \( p_x \) and \( p_y \)). These three \( sp^2 \) hybridised orbitals are coplanar and oriented at 120 degrees relative to one another. Chemical bonds formed by them are called \( \sigma \) bonds. The \( \sigma \) bonds are localized between the bonding carbon atoms. The third 2p orbital, denoted as \( p_z \), remains unhybridised and is directed perpendicular to the plane of the \( sp^2 \) orbitals, and thus to the plane of the carbon atoms. The \( p_z \) orbitals of neighboring atoms overlap, which leads to a \( \pi \) bond formation and to a delocalized density of electrons above and below the plane of the molecule.

When each adjacent atom in a row of have a $p_z$ orbital with the same orientation, the $p_z$ orbitals will combine to make $\pi$ orbitals that extend over all those atoms. The atoms in such a set have a conjugated $\pi$ system. For example, the overall electron distribution in an anthracene molecule is shown in Fig. 1.3. The $\pi$ bonds form two different states: the highest occupied molecular orbital (HOMO) that corresponds to a bonding conformation and the lowest unoccupied molecular orbital (LUMO) that corresponds to an anti-bonding conformation. The HOMO and LUMO orbitals of a single anthracene molecule are also given in Fig. 1.3.

![Figure 1.3: Above: the overall distribution of the $\pi$ electrons in the electronic ground state of the anthracene molecule, $C_{14}H_{10}$. Centre: the distribution of the $\pi$ electron in the HOMO. Below: the distribution of the $\pi$ electron in the LUMO. Image is reproduced with permission from reference [4]. Copyright (2005) WILEY-VCH.](image)

The difference in energy between HOMO and LUMO determines the wavelength of light that the molecule can mainly absorb. Since the contribution of the $\pi$ electrons to bonding of the molecule is weak, most molecular crystals possess electronic excitation energies in the range of near-ultraviolet range (200 to 400 nm) or in the visible range.
(400 to 750 nm), making UV-Visible absorption spectroscopy a convenient technique to probe the energy gap of molecular crystals.

### 1.1.3 Solution Coating Methods

Solution processing of electronic devices based on small organic molecules or conjugated polymers have attracted significant attention over the last several decades as it is promising to reduce processing costs compared to conventional vacuum based processes. A wide range of solution-based methods have been employed for the deposition of organic semiconductor thin films including spin coating [32], drop casting [33], spray coating [34], inkjet printing [6, 35], slot-die coating [36, 37], zone casting [36, 38, 39], hollow pen writing [7, 40], dip coating [41] and blade coating [42] etc. The hollow pen writing, zone casting, slot-die coating, dip coating and blade coating can be classified as meniscus guided coating methods. The term “meniscus-guided” refers to the fact that a meniscus forms when the solution comes in contact with the substrate, in effect guiding and controlling film crystallization at the substrate-solvent-air contact line while the substrate moves.

Spin coating is one of the most important techniques in depositing uniform organic thin films onto flat surfaces. The typical spin coating operation involves application of a small amount of coating material that dissolved in liquid to the center of the substrate. The substrate is then rotated at high speed in order to spread the liquid towards the edge of the substrate by centrifugal force, leaving a thin film on the surface. After any remaining solvent has evaporated, a thin film with a thickness ranging from a few nanometers to a few microns can be obtained. The spin coating process is shown in Fig. 1.4(a). Spin coating is widely used in industry due to its
ability to quickly and easily produce very uniform films. Meanwhile the thickness and morphology of the final film obtained at a given concentration and spin speed are highly reproducible.

Inkjet printing is a material-conserving deposition technique that relies on the formation of individual droplets that are ejected from a nozzle. The coating material that dissolved or dispersed in a solvent is used as ink. The formation of the droplet through the nozzle can be achieved either thermally or piezoelectrically. Then ejected drop falls under action of gravity and air resistance until it impinges on the substrate. Finally the droplet spreads under momentum acquired in the motion and dries to form a solid thin film. The film quality made by this technique heavily depends on the ink’s physical properties like the viscosity and surface tension [43]. Fig. 1.4(b) presents an example of depositing single crystal C8-BTBT film by inkjet printing.

Figure 1.4: The schematic of (a) spin coating. Reproduced with permission from reference [5]. Copyright (2017) American Chemical Society. (b) inkjet printing. Reproduced with permission from reference [6]. Copyright (2011) Springer Nature. and (c) hollow pen writing. Reproduced from reference [7] with the permission of AIP Publishing.
Compared to spin coating and inkjet printing, meniscus guided coating techniques have unique advantages including compatible to roll-to-roll processing, can produce films with extremely high uniformity, and key factors (such as grain structure and film thickness) can be easily controlled \[7,40,42,44,45\]. As an example, the schematic of hollow pen writing technique is shown in Fig. 1.4(c). The solution is filled into a glass capillary by capillary action. The solvent evaporates from the meniscus zone and the solute is deposited on the moving substrate. To make high-quality films using this process, parameters (such as withdrawal speed) must be optimized \[7,44\]. Atmospheric factors (such as substrate temperature, airflow, cleanliness of substrate, etc) and liquid properties (surface tension, viscosity, etc) also play important roles in determining the final film quality.

1.1.4 Molecular Packing of Small Molecules

An organic crystal can be considered as being made up of identical molecules stacked regularly and closely by intermolecular interactions such as hydrogen bonds, charge transfer or van der Waals forces. The molecular arrangement, namely the packing motif, plays a very important role in the organic electronic device performance. As summarized in the Fig.1.5, there are four main possible packing motifs in organic solid states \[8\], named (A) herringbone packing motif without $\pi - \pi$ overlap between adjacent molecules (e.g., pentacene \[46\], C8-BTBT \[47\]); (B) herringbone packing with $\pi - \pi$ overlap between adjacent molecules (e.g., rubrene \[48\]); (C) one dimensional (1D) $\pi - \pi$ stacking (e.g. PTCDI-C8 \[49\], TES-pentacene \[33\]); (D) two dimensional $\pi - \pi$ stacking (e.g. TIPS-pentacene \[50\], PDIF-CN2 \[51\]).
Large $\pi - \pi$ overlap can produce a more efficient route for transporting charge carriers from one molecule to its neighbour molecule. Many high performance OFETs reported were using semiconductors which adopted the $\pi - \pi$ stacking motif as active layers, such as rubrene (a high performance p-type organic semiconductor [48]) and PDIF-CN2 (a high performance n-type organic semiconductor [51]). However, many organic semiconductors with herringbone packing mode also exhibited high charge carrier mobility in experiments such as pentacene and C8-BTBT. Recent theoretical study has shown that these high mobility herring bone packing compounds are less sensitive to molecular vibrations which contribute to a high charge transport mobility [52], as we will discussed in Section 1.3.

In each packing motif, it can be seen that the molecular arrangements are different along different orientations. As a result, structure anisotropy is unavoidable. Such structural anisotropy leads to anisotropic properties from optical absorption [53], exciton diffusion [54] to charge transport [40].
1.2 **Basics of Organic Field Effect Transistors (OFETs)**

1.2.1 **Working Principle of OFETs**

An OFET (its cross-section is shown in Fig. 1.6(a)) consists of a conductor called gate (made of metal or a highly doped semiconductor) and a dielectric layer of thickness $d$ (resulting in capacitance density $C_i = \epsilon_r \epsilon_0 / d$, with $\epsilon_r$ the relative dielectric constant and $\epsilon_0$ the vacuum permittivity) and an organic semiconductor layer. Source and drain electrodes are attached directly to the semiconductor layer with a channel width $W$ and a channel length $L$.

The basic operation of the OFETs relies on the charge density modulation in the semiconductor layer by applying a gate voltage. Fig. 1.6(b-d) illustrates the basic operating regimes of an OFET and associated I-V characteristics. For N type semiconductor, positive $V_g$ needs to be applied to induce electrons at the interface whereas for P type semiconductor negative $V_g$ needs to be applied to induce holes. The induced charge density ($Q$) is proportional to $V_g$ and the capacitance $C_i$ of the dielectric layer:

$$Q = C_i V_g$$ (1.1)

However, a part of the induced charges will not contribute to the current as deep traps have to be filled first. The applied gate voltage $V_g$ has to be higher than a critical threshold voltage $V_{th}$ in order to make additionally induced charges mobile.
Thus the effective gate voltage that contributing to the current in the OFET is given by \( V_g - V_{th} \). The effective charge density can be expressed by:

\[
Q_{eff} = C_i (V_g - V_{th}) \tag{1.2}
\]

The charges are injected and collected by the source and drain electrodes, respectively. If \( V_g \) is smaller than \( V_{th} \), there is lack of mobile charge carriers when source-drain bias \( V_d \) is applied thus the drain-source current \( I_d \) in the organic semiconductor is very low and the device is in its “off” state. If \( V_g \) is greater the \( V_{th} \), a high charge density is created next to the dielectric interface and current can flow through a very thin region that it is called the “channel” between the source and drain when \( V_d \) is applied. A linear gradient of charge density from the source to the drain forms when \( V_d \) is much smaller than \( V_g - V_{th} \), resulting in the \( I_d \) is directly proportional to \( V_d \), as shown in Fig. 1.6(b)). This region is typically called the linear regime. As the \( V_d \) increases to \( V_g - V_{th} \), The transition to saturation region occurs because the channel gets “pinched off” at the drain end (Fig. 1.6(c)). Further increasing \( V_d \) continues to affect the channel because the pinch-off point slightly moves closer to the source and the saturation-region drain current \( I_{d, sat} \) will stays approximately the same (Fig. 1.6(d)).

### 1.2.2 I-V Characteristics

Gradual channel approximation is used to calculate the I-V characteristics of OFETs. It is assumed that the electric field component along the channel dominates compared to the electric filed component the perpendicular to the channel. Thus voltage is
considered to be gradually changing along the channel from source to drain.

\[ Q(x) = C_i V_{eff} = C_i [(V_g - V_{th} - V(x)] \]  

(1.3)
In linear region, i.e. \((V_g - V_{th}) >> V_d\), the current density from source to drain can be put with Ohm’s law as:

\[
\frac{I_d}{W} = Q(x)\mu \frac{dV}{dx}
\]  

(1.4)

where \(W\) is the channel width and \(\mu\) is carrier mobility. Separation of the variables leads to:

\[
\int_0^L \frac{I_d}{W} dx = \int_{V_d}^{V_d} Q(x)\mu dV
\]

(1.5)

Assuming that the mobility and threshold voltage are independent of the gate voltage, the gradual channel expression for the drain current is derived:

\[
I_d = \frac{W}{L} C_i\mu [(V_g - V_{th})V_d - \frac{V_d^2}{2}]
\]

(1.6)

in the linear region, \((V_g - V_{th}) >> V_d\), it is appropriate to drop the \(V_d^2/2\) term:

\[
I_{d,linear} = \frac{W}{L} C_i\mu [(V_g - V_{th})V_d]
\]

(1.7)

with above equation, the mobility of linear region can be determined from the slope of a \(V_g\) sweep at fixed \(V_d\).

\[
\mu_{lin} = \frac{L}{WC_i V_d} \frac{\partial I_d}{\partial V_g}
\]

(1.8)

In the saturated regime, when \((V_g - V_{th}) \leq V_d\), the channel is pinched off at the drain electrode and the current is assumed not to increase any further with increasing
$V_d$. Substitution of $V_d$ with $(V_g - V_{th})$ in equation 1.6 yields the current-voltage equations in the saturated region:

$$I_{d,saturated} = \frac{W}{2L} C_i \mu (V_g - V_{th})^2$$

(1.9)

Because of the quadratic dependency on $V_g$, the saturated mobility can now be derived from a linear fit to $\sqrt{I_d}$ versus $V_g$:

$$\mu_{sat} = \frac{2L}{WC_i} \frac{\partial \sqrt{I_d}}{\partial V_g}$$

(1.10)

The x-axis intercept of this fit is commonly taken for the saturated threshold voltage. Note that in thin film transistors the channel lengths should be at least ten times greater than the dielectric thickness in order to ensure ideal I-V characteristics. A space charge limiting current effect can occur at small channel length which prevents saturation in the output characteristics [55].

---

**Figure 1.7**: I-V characteristics of an n-channel OFTE: (a) output characteristics indicating the linear and saturation regions; (b) transfer characteristics in the linear region; (c) transfer characteristics in the saturation region. The image is reproduced with permission from reference [9]. Copyright (2007) American Chemical Society.
1.2.3 OFETs Architectures

As shown in Fig. 4.1, OFETs have four basic structures including bottom-gate/top-contact, bottom-gate/bottom-contact, top-gate/bottom-contact and top-gate/top-contact. Depending on the positions of the source/drain electrodes and the channel, they are either staggered or coplanar geometry. In a staggered configuration, the source/drain contacts and the insulator layer are on the opposite part of the channel (Fig. 4.1(a) and Fig. 4.1(c)). Charges have to travel through semiconductor layer before they reach the channel. Whereas in a coplanar configuration, the source/drain contacts and the insulator layer are on the same part of the channel thus charges can be directly injected into the channel (Fig. 4.1(b) and Fig. 4.1(d)). Thin film transistors using the same semiconductor material as active layer can display quite dissimilar device characteristics in different structures [56].

The most commonly used device geometry of OFETs is the bottom-gate/top-contact type. This is partly because silicon wafer is a commercially available high-quality substrate with thermally grown SiO$_2$ oxide that can act as gate dielectric [44, 57, 58]. Organic dielectrics have also been used in OFETs since they can be solution-processed at room temperature and can be easily applied in top-gate transistors where the organic dielectric are typically spin coated on top of the semiconductor layer by using solvents that are orthogonal to the semiconductor [32, 59]. Due to their high optical transparency, organic dielectrics are especially suitable for some applications like photo-responsive OFETs [60].
1.2.4 CONTACT RESISTANCE

Conventional metal-oxide-silicon transistor have Ohmic contacts as the charges are injected from a metal contact to heavily doped silicon. However, for organic thin film transistors, the contact is generally Schottky contact because a potential energy barrier forms at the electrode-semiconductor junction. OFETs usually have an $R_c$ value in a range of $10^2$-$10^6 \, \Omega \cdot \text{cm}$ as compared to that of metal-oxide-silicon transistors where $R_c$ is less than 0.1 $\Omega \cdot \text{cm}$ [61–63]. Therefore, the device performance of organic transistors can be significantly improved by a small enhancement of injection.

As a primary method, reducing contact resistance can be achieved by changing the work function of the contact electrodes by modification of metals using self-assembled monolayers (SAMs) or thermally evaporating a metal oxide layer between the metal electrode and semiconductor film [64]. As an example, Fig. 1.9 shows that inserting
a thermally evaporated a high work function MoO$_x$ layer between Au electrode and C8-BTBT semiconductor contributes to a reduced contact resistance and enhanced current [11].

![Diagram of OFET structure](image)

Figure 1.9: Using an insertion layer to improve OFET injection: (a) Schematic representation, (b) transfer characteristics. Reproduced from reference [11], with the permission of AIP Publishing.

The most common two-terminal methods to evaluate the contact resistance in OFETs is the transfer line method (TLM). As shown in Fig. 1.9, the total resistance ($R_{\text{total}}$) of the transistor is the sum of contact resistance ($R_c$) and channel resistance ($R_{ch}$). According to Equation 1.7, in the linear region ($(V_g - V_{th}) \gg V_d$), the $R_{ch}$ is:

$$R_{ch} = \frac{L}{WC_i\mu(V_g - V_{th})} \quad (1.11)$$

As shown in Equation 1.11, the $R_{ch}$ is correlated linearly with the channel length. The $R_c$ can be considered to be independent from channel length, then total resistance
$R_{\text{total}}$ can be expressed by:

$$R_{\text{total}} = R_c + \frac{L}{WC_i\mu(V_g - V_{th})} \quad (1.12)$$

In this equation, we make the channel width $W$ for a constant, then $R_{\text{total}}$ can be treated as a function of channel length $L$ of the OFETs. In order to apply the TLM, multiple transistors with different channel lengths need to be characterized. With a linear fit to the total resistance versus channel length, contact and channel resistance can be derived from the $y$-axis intersect and slope respectively. The method is illustrated schematically in Fig. 1.10. Contact resistances are typically multiplied by the channel width to normalize them, which is a common representation to help the general comparability of devices with different channel widths. Therefore units for contact resistance is $\Omega \cdot \text{cm}$.

Figure 1.10: Contact resistance evaluation by TLM. (A) Schematic image of the OFET channel and micrograph of the fabricated OFETs for TLM measurement. (B) TLM plots for the OFETs at various gate voltages. $R_{\text{total}}W$ values are extracted from the two-terminal device characteristics. (C) A magnified view at the intercept in (B). Reproduced from reference [12] with permission.
1.3 **Charge Transport Mechanisms**

Charge carrier mobility is commonly used to rate organic semiconducting materials for their suitability in applications such as OFETs or photovoltaics. In this part we will review three charge transport models and discuss what currently limits charge carrier mobility in crystals of organic semiconductors.

### 1.3.1 Hopping Model

Charge carrier mobilities in good organic semiconductors are in the range of 1-10 \( \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) [30,31,48,65,66]. Although it is higher than the mobility of amorphous Si, it is still orders of magnitude lower than in crystalline Si or graphene. The reason for such low mobilities is usually explained by the localization of charge carriers caused by small polaron formation [67,68]. In organic semiconductors, lattice vibrations (phonon) leads to the localization of charge carriers thus charge carriers transport via incoherent hopping.

The electronic hopping rate \( (W) \) between two adjacent molecules is given by the Marcus-Hush equation [69]:

\[
W = \frac{t^2}{\hbar} \left( \frac{\pi}{\lambda k_B T} \right)^{1/2} \exp \left( -\frac{\lambda}{4k_B T} \right)
\]

where \( t \) is the charge transfer integral between neighboring molecules in the organic crystal, \( \lambda \) is the reorganization energy, \( T \) is the temperature, and \( k_B \) is the Boltzmann constant. The charge transfer integral is defined as the splitting the frontier molecular orbital between adjacent molecules (the detail will be given in Section 2.4.
in Chapter 2). The reorganization energy describes the energy loss when a charge carrier passes through a molecule.

Assuming that the quantum coherence is lost after each hopping, the hopping mobility takes following form [70]:

$$\mu(T) = \mu_0 t^2 \left( \frac{\pi}{4\lambda(k_B T)^3} \right)^{1/2} \exp \left( -\frac{\lambda}{4k_B T} \right)$$ (1.14)

In the hopping transport, the charge carrier mobility is typically thermally activated, i.e., charge carrier mobility increases as the temperature increases.

### 1.3.2 Band Model

Several organic semiconductors (TIPS-Pentacene, TMTES-Pentacene, Cn-BTBT, Cn-DNTT and rubrene) are reported to have a field effect mobility that found increasing as decreasing temperature over a broad temperature range [30–32, 71, 72]. This temperature dependence of mobility behavior challenges the hopping theory and it is consistent with a band model where the charge carriers are considered to travel as highly delocalized plan waves with a mean free path that is much larger than the nearest neighbor distance. In the band model, the charge carrier mobility is limited by collisions of charge carriers with crystal defects and phonons (lattice vibrations).

The mobility in this limit can be written as [73]:

$$\mu = \frac{et_s}{m^*}$$ (1.15)

where $t_s$ is the average time between collisions, $e$ is the electron charge and $m^*$
is the effective mass of charge carrier which is inversely proportional to the charge transfer integral. Since the frequency of scattering events increases with increasing temperature, resulting in the mobility increases with decreasing temperature.

1.3.3 Transient Localization Model

Charge transfer in organic semiconductor crystals is determined by two parameters: the charge transfer integral and the reorganization energy. The charge transfer integral tends to promote charge delocalization whereas the reorganization energy tends to localize the charge carrier on a single molecule. In organic semiconductors, charge transfer integral is often on the same order of magnitude as reorganization energy, which makes both band and hopping mechanisms discussed above inapplicable for quantitative purposes [73–75].

As we have discussed above, the charge transport in organic semiconductor has previously been assumed to be through hopping of localized carriers since the semiclassical mean-free-path of carriers is found to be less than the intermolecular distance. However, recent experimental results exhibit band-like mobility characterized by increasing mobility as the temperature decreases, which seems to imply that charge carriers are delocalized [32,72]. This ambiguous localized/delocalized behavior has spurred the adoption of a new paradigm, where dynamic disorder caused by molecular thermal vibrations is sufficient to break the translational symmetry of the electronic Hamiltonian, producing transient localization of the charge carriers while maintaining coherence over a characteristic length scale $L$ on the order of the molecular spacing [70,73,74,76].

Based on the transient localization model, the analytical formula for the charge
mobility [52]:

\[ \mu = \frac{e}{k_B T} \frac{L(\tau)^2}{2\tau} \]  

(1.16)

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( e \) is the electric charge, \( \tau \) is the fluctuation time given by the inverse of typical intermolecular oscillation frequency, and \( L(\tau) \) is the transient localization length that depends on charge transfer integral and its sensitivity to thermal vibration.

There are large molecular motions in crystalline organic semiconductors at room temperature due to their weak van der Waals intermolecular interactions. Based on the transient localization model, the mobility of OFETs is intrinsically limited by this large dynamic disorder. It suggests ways to increase \( L \) by (i) reducing the sensitivity of the charge transfer integral to thermal vibrations, and (ii) designing materials that have reduced dynamic disorder [70,73].

1.4 Optical Excitation in Organic Semiconductors

For organic electronics involving the absorption of light, an understanding of how molecular interactions affecting excited states helps to provide guidance on improving the device’s performance and developing new materials. For example, the significance of the absorbance characteristics can be easily appreciated for organic solar cells as the absorption spectrum dictates the frequencies of radiation that can be absorbed that later be converted to electrical energy.

The optical excitation energy of molecular crystals is very sensitive to the sur-
rounding environment. In case of isolated molecules, all excitations have to occur within one single molecule. While in solids interactions between several molecules take place. Thus isolated molecules (or molecules in dilute solution) can exhibit entirely different absorbance characteristics than the bulk material (i.e. the aggregate, film, or crystal). In the following we will discuss three basic effects that cause absorbance excitation energy shift including (i) the solvatochromic effect, [77–79] (ii) Coulombic coupling [13,80] and (iii) Frenkel/CT exciton mixing [81,82].

1.4.1 Solvent Effect

The solvatochromic effect refers to a dependence of excitation energy with the solvent polarity. It reflects the ability of neighboring molecules to stabilize the polar ground state and polar excited state via dipole-dipole, quadrupole-quadrupole, and dipole-quadrupole interactions [83]. If polarities of the ground and excited state of a chromophore are different, a change in the environmental polarity leads to differential stabilization of both states, thus a change in the energy gap between these electronic levels will be observed. Generally speaking, dye molecules with a large change in their permanent dipole moment upon excitation exhibit a strong solvatochromism. Negative solvatochromism corresponds to a blue shift with increasing solvent polarity and positive solvatochromism corresponds to a red shift with increasing solvent polarity. Examples of positive and negative solvatochromic dyes can be easily found in literature [84]. It is worth to note that the solvent effect can also occur in a nonpolar solvent where the solvent molecules do not have a permanent dipole moment but their electron clouds can be polarized by charge density of the solute molecule via inductive and dispersive solute-solvent interactions [85].
1.4.2 **Coulombic Coupling Effect**

Over the past few decades, many efforts have been made to understand how molecular packing determines the optical properties of organic semiconductors [80, 81, 86, 87]. The simplest model was proposed over five decades ago by Michael Kasha [80]. In this model, the excitons in organic molecular crystals are treated as strongly localized Frenkel excitons and the exciton coupling is mainly Coulombic coupling.

![Diagram](image.png)

*Figure 1.11: (a) Transition dipole geometry for evaluating the Coulombic coupling under the point dipole approximation. Exciton energy bands of Kasha (b) J-aggregates and (c) H-aggregates. (d) Ideal absorption spectra for J- and H-aggregates. The image is reproduced with permission from reference [13]. Copyright (2017) American Chemical Society.*
The Coulombic coupling $J_{\text{Coul}}$ comes from the dipole interactions between the transition dipoles. It can be estimated by a point-dipole approximation [13, 80]:

$$J_{\text{Coul}} \approx \frac{\mu^2(1 - 3\cos^2 \theta)}{4\pi \varepsilon R^3} \tag{1.17}$$

where $\mu$ is the transition dipole moment, $R$ is the intermolecular distance, $\theta$ is the angle between $\mu$ and $R$ and $\varepsilon$ is the optical dielectric constant of the medium.

Kasha model predicts when dipole moments align “face-to-face” ($54.7^\circ < \theta < 90^\circ$), it will cause spectral blue-shift as $J_{\text{Coul}} > 0$ (H-aggregates). When the dipoles align “head-to-tail” ($\theta < 54.7^\circ$), it will lead to a spectral redshift (J-aggregates). It should be noted that the point dipole approximation is a crude way to estimate the Coulombic coupling between the transition dipoles. However, more sophisticated treatments of the Coulombic coupling using quantum-chemical calculations give a qualitatively similar picture in literature [88].

1.4.3 FRENKEL/CT EXCITON COUPLING EFFECT

Excitons in organic semiconductors can be tightly bound to a single molecule (Frenkel type) or they can be composed of charges separated by one or a few molecular spacings (charge transfer type). In many previous studies, an energy shift in the optical absorption spectra of certain organic semiconductors is found to be highly sensitive to small changes of the molecular packing [89, 90]. This effect, termed “crystallochromy”, occurs when the energy difference between the Frenkel exciton and charge transfer (CT) excited states is small, so that neutral molecular excitations and charge transfer excitations mix via electron and hole transfer [13, 81, 91, 92]. The interference between
these states produces a short-range coupling that results in a significant shift in the absorption bands relative to the (highly localized) Frenkel exciton [13,92–95]. The sensitivity to the crystal packing arises since these effects depend on the overlap of the nodal patterns of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of neighboring molecules, which is sensitive to sub-angstrom relative motion. The excitation energy shift caused by CT/Frenkel exciton mixing can be characterized by the magnitude of the hole and electron charge transfer integrals $t_h$ and $t_e$.

A simple dimer model can be used to illustrate how the Frenkel/CT mixing affects the excitation energy. A dimer has two molecules A and B and its Frenkel exciton states can be expressed by $|A^*B\rangle$ and $|AB^*\rangle$ where star sign means the molecule is excited. Similarly the two charge transfer states can be expressed by $|A^+B^-\rangle$ and $|A^-B^+\rangle$ where plus sign indicates a hole is on the molecule and minus sign indicates an electron is on the molecule. The Frenkel and CT excitons are coupled via the electron/hole dissociation integrals ($D_e/D_h$) which correspond the process that the electron/hole of an excited molecule transfers to the LUMO/HOMO of its unexcited neighbor molecule. The electron and hole dissociation integrals can be estimated by electron and hole transfer integrals ($t_e$ and $t_h$) [82]:

$$\langle A^*B|H|A^+B^-\rangle = \langle AB^*|H|A^-B^+\rangle = D_e \approx t_e$$  \hspace{1cm} (1.18)

$$\langle A^*B|H|A^-B^+\rangle = \langle AB^*|H|A^+B^-\rangle = D_h \approx t_h$$ \hspace{1cm} (1.19)

The Frenkel exciton can be expressed by a linear combination of the two Frenkel
states:

\[ |F_{\pm} \rangle = \frac{|A^* B\rangle \pm |AB^*\rangle}{\sqrt{2}} \quad (1.20) \]

Similarly the CT exciton can be expressed by:

\[ |CT_{\pm} \rangle = \frac{|A^+ B^-\rangle \pm |A^- B^+\rangle}{\sqrt{2}} \quad (1.21) \]

The Frenkel excitons only couple to CT excitons with same symmetry, i.e. \( |F_+ \rangle \) couples with \( |CT_+ \rangle \) and \( |F_- \rangle \) couples with \( |CT_- \rangle \). Since the antisymmetric Frenkel exciton has zero dipole moment, we only need to consider the coupling between the symmetric ones \([81, 82]\), i.e., \( |F_+ \rangle \) and \( |CT_+ \rangle \). The coupling is:

\[ \langle F_+ | H | CT_+ \rangle = t_e + t_h \quad (1.22) \]

The energy of Frenkel exciton is:

\[ \langle F_+ | H | F_+ \rangle = E_F \quad (1.23) \]

The energy of CT exciton is:

\[ \langle CT_+ | H | CT_+ \rangle = E_{CT} \quad (1.24) \]

where \( E_F \) is the excitation energy of creating Frenkel exciton on a molecule in the film (it includes the solvent effect and Coulombic coupling effect on the excitation energy of the monomer in the solution), \( E_{CT} \) is the energy to create CT exciton.

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The Hamiltonian of the two symmetric states is

\[ H = \begin{bmatrix} E_F & t_e + t_h \\ t_e + t_h & E_{CT} \end{bmatrix} \]

By diagonalizing this two by two matrix, we can solve for the eigenvalues for the two states after coupling:

\[ E_\pm = \frac{E_{CT} + E_F}{2} \pm \sqrt{\left( \frac{E_{CT} - E_F}{2} \right)^2 + (t_e + t_h)^2} \quad (1.25) \]

Since the energy of CT state is usually higher than the energy of Frenkel exciton state, the \( E_{CT} \) will be repelled upward and \( E_F \) with be repelled downward with an amount governed by \( |t_h + t_e| \) [82]. Similar results can also be obtained for one dimensional model [13,94]. As only the Frenkel-like energy level contains the bulk of the oscillator strength, the Frenkel/CT mix will cause redshift of the excitation energy as long as the CT state is higher than Frenkel exciton state.

1.5 Outline of this Dissertation

The structure of this thesis is as follows: the first chapter presents the basic concepts of organic semiconductors and gives a detailed description on the working principle of organic thin film transistors. This chapter also aims to review some basic charge transport mechanisms and structure dependence of optical transition gap in organic semiconductors. The second chapter gives a detailed description on the semiconductor material TIPS-pentacene that has been extensively studied in this dissertation and experimental techniques employed to deposit and characterize the TIPS-pentacene thin
films. The third chapter presents the results of thermal expansion caused structure evolution in TIPS-pentacene thin films and the stabilization mechanism of the high temperature structure to room temperature. In forth chapter, the field effect mobility of TIPS-pentacene room temperature phase and strain-stabilized high temperature phase are characterized by fabricating TIPS-pentacene based field effect thin film transistors. We follow recommended best practices in the literature to get the reliable mobility values including reporting the linear mobility as the mobility of record, and ruling out gate voltage-dependent of the estimated mobility. In fifth chapter, we have established a reliable structure-property relationships for TIPS-pentacene thin films based on our results on TIPS-pentacene molecular orientation, transition dipoles direction, the field effect mobility characterization and charge transfer integral calculation. Finally, in the sixth chapter, the photoluminescence properties of TIPS-pentacene solutions and polystyrene/TIPS-pentacene blend films are presented.
Chapter 2

Materials and Methods

This chapter covers all general information related to the materials and characterization methods used in this dissertation. In Section 2.1, an overview on TIPS-pentacene is given including its phase transition, molecular packing, charge transport and singlet fission properties. Section 2.2 describes the thin film deposition technique that we used to control the thickness and grain structure of TIPS-pentacene thin films based on the previous work in our group [17,18]. The details on the TIPS-pentacene based thin film transistor fabrication are also included in this section. Section 2.3 introduces the techniques used to characterize the crystallinity, macroscopic morphology and molecular packing of TIPS-pentacene thin films. In Section 2.4, the details on the charge transfer integral calculation are given.

2.1 Overview of TIPS-pentacene

TIPS-pentacene (≥ 99%) crystals are purchased from Millipore Sigma and directly used in our experiments without further purification. TIPS-pentacene is a well-known
high performance small molecule organic semiconductor and it is widely used in OFETs with a mobility in the range of 0.4-1.2 cm²V⁻¹s⁻¹ that have been achieved in the literature [32,65,96]. It has excellent solubility in a range of common organic solvents making it easy to process into devices. TIPS-pentacene adopted a 2D-brickwall packing, as shown in Fig. 2.1(c). The face-to-face packing of TIPS pentacene in crystalline form is optimal for orbital overlap, leading to a relatively high but directionally anisotropic carrier mobility [7,40]. The bulk TIPS-pentacene crystal has two solid-solid phase transitions. One is at 124°C and the other one is at 185°C (Fig. 2.1(d)). We refer to the phase obtained at room temperature as Form I and the phase obtained above 124°C but below 185°C as Form II. The stable phase above 185°C is named Form III. These three phases are all reported to belong to triclinic space group [14,97].

The transfer integral in TIPS-pentacene Form I undergoes large fluctuations because of molecular thermal motions [15,98], as shown in Fig. 2.1(e). This effect, known as dynamic disorder, causes the charge carriers to be strongly localized onto individual molecules which is detrimental to the charge transport [15,98]. The theoretical estimated mobility of TIPS-pentacene Form I is around 0.9 cm²V⁻¹s⁻¹ based on the transient localization model, which is much lower compared to other organic semiconductors with smaller dynamic disorder like rubrene and pentacene [52].

Except for its widely application in OFETs, TIPS-pentacene has also been successfully implemented in solar cells since it is a well-known singlet fission material. Singlet fission a spin-conserving process that produces two triplet excited states from one photoexcited singlet state if their energies satisfy the relation \( E(S_1) \geq 2 \times E(T_1) \). The singlet fission organic solar cells can, in theory, achieve 45% power conversion
efficiency breaking the original 33% Shockley-Queisser limit for single-junction solar cell [99]. Walker and coworkers demonstrated nearly a triplet yield of 200% occurred in TIPS-pentacene concentrated solution using chloroform as solvent and the scheme for the singlet fission process is shown in Fig. 2.2. [16]. Yang et al. reported solution processed singlet fission solar cells made by combining PbS/PbSe nanocrystals with TIPS-pentacene with an internal quantum efficiency up to 160 ± 40% was observed [100].

Figure 2.1: Overview of TIPS-pentacene (a-c): structure, space group and molecular packing of TIPS-pentacene materials. (d) differential scanning calorimetry (DSC) curve of TIPS-pentacene crystal. The image is adapted with permission from reference [14]. Copyright (2014) American Chemical Society. (e) thermal vibration caused thermal diffuse scattering in the electron diffraction patterns of TIPS-pentacene and the effect of thermal vibration on the charge transfer integrals. The image is adapted with permission from reference [15]. Copyright (2013) Springer Nature.
2.2 Sample Preparation

2.2.1 Thin Film Deposition

A hollow pen writing method was developed in 2008 by our group to solution cast TIPS-pentacene thin films [40]. The hollow rectangular glass capillary with size of 0.5 × 5.0 mm² I.D. (Wale apparatus Co. 4905-100) is utilized to hold TIPS-pentacene solutions by capillary forces. The narrow cross section of the glass capillary enables it draw in solution spontaneously by capillary action, making filling and cleaning it straightforward. The glass capillary is bent to form an L shape so that the capillary can hold enough solution in the horizontal part to coat at least a 20 mm long film. The film deposition setup is depicted in Fig. 2.3. A substrate is mounted on a computer-controlled linear translation stage (Newport, M-VP-25XA). Before de-
position, the filled capillary is lowered to allow the micro droplet on the end of the capillary to contact with the substrate. Once a stable meniscus forms between the capillary and the substrate, the TIPS-pentacene thin film deposition can be done by withdrawing the substrate at a controlled rate, typically 0.01-25 mm/s. Our writing stage is equipped with a thermoelectric module (Merck Technologies) for deposition temperature control over the range from 10°C to 140°C. A polarized optical microscopy (Olympus BXFM) is equipped, enabling us to take optical videos in real time to study the deposition process.

Figure 2.3: Schematic of thin film deposition setup. The image is reproduced from reference [17] with permission.

Hollow pen writing method can produce thin films with different morphology and grain size by varying the deposition speed. As shown in Fig. 2.4, three different growth regimes can be identified when TIPS-pentacene thin films are deposited at room temperature with varied deposition speed. If deposition speeds below a critical
speed (< 1 mm/s), in the convective regime, the liquid solution transforms into a solid form at a well defined contact line. Oriented crystal films with centimeter long grain size can be easily produced because the crystallization is seeded by the previously formed crystalline film as it emerges from the meniscus [40]. At higher speeds (> 4 mm/s), the drying line is moving faster than the solvent is evaporating. A liquid layer is pulled out first then crystallization occurs via spontaneous nucleation and growth from a supersaturated solution, often leading to a “fan-like” grain morphology. This regime is known as the Landau-Levich-Derjaguin (LLD) regime. In the intermediate regime (1 - 4 mm/s), spherulitic-type grains can be obtained with crystallization front oriented along the writing direction [18].

![THREE GROWTH REGIMES](image)

*Figure 2.4: Polarized optical images of TIPS pentacene thin films deposited by hollow capillary writer at three different growth regimes. The image is reproduced from reference [18] with permission.*

Fig. 2.5 shows results when the deposition speed is close to the intermediate regime where the dynamic meniscus is beginning to stretch into a continuous wet film. Three regions of the film are observed during the deposition process: (i) the
meniscus showing color fringes due to the rapidly varying thickness of the solution is at the left side of each image, (ii) a narrow featureless region is visible near the middle, and (iii) the solid film with crystalline grain structure. The middle region, which we refer to as the supersaturated region is completely dark in 90° cross-polarized microscopy and does not exhibit any color fringes, indicating that it is a very thin isotropic layer. The width of this region increases from 22 µm at a writing speed of 0.2 mm/s to 59 µm at 0.4 mm/s, to 198 µm at 1 mm/s as shown in Fig. 2.5 (a-c).

Figure 2.5: Optical microscopy images at different writing speeds: (a) 0.2 mm/s, (b) 0.4 mm/s, (c) 1 mm/s, (d) 0.4 mm/s at higher magnification. Films were prepared at 25°C on silicon wafers with 300 nm silicon dioxide layer. The solution concentration was 8.7 mg/ml. From left to right, three regions can be seen during thin film deposition: meniscus, supersaturated region and solid film. The scale bars are 200 µm for (a)-(c), and 50 µm for (d).

The film thickness can also be well controlled by varying the deposition speed. At low deposition speed (in the convective region), the evaporation rate is faster than
the “movement” of the contact line. Therefore as soon as the solution is fed into the front part of the meniscus, the solvent is evaporated. More solution is fed into the contact line by capillary flow and again the solvent is evaporated. This is capillary feeding. Thus in this region, the lower the deposition speed is, the thicker the film will be. Based on our previous study, the film thickness varies as a power law with the writing speed where the exponent is -1 [17, 18].

![Figure 2.6: TIPS Pentacene film thickness as a function of deposition speed for three different concentrations: 5 wt\%, 3 wt\% and 1 wt\%. The solid lines are from the theoretical prediction given by theory. Image is reproduced from reference [18] with permission.](image)

At high deposition speed (in the LLD regime), the solution is pulled out first due to the viscous force and dry afterwards. The solid film thickness is determined by the liquid layer thickness and solution concentration. It is found that the thin liquid film thickness in LLD region increases with increasing writing speed with an exponent of 2/3 [17, 18]. The intermediate region between the convective region and the LLD region can be accurately modeled by a combination of the models above [17, 18, 101].
Overall a V-shaped dependence of thickness on withdrawal speed can be obtained, as shown in Fig. 2.6.

### 2.2.2 Transistor Fabrication

Bottom-gate/top-contact, top-gate/bottom-contact and bottom-gate/bottom-contact structured transistors are fabricated to characterize the field effect mobility of TIPS-pentacene thin films. Fig. 2.7 shows schematic representations of these three different organic thin film transistor architectures. The glass substrates (fused silica corning 7980 of UV grade) and silicon wafer substrates (Ossila Ltd organization) that used for substrates were pre-diced to a standard size of 15 mm × 20 mm. The glass substrate is polished both sides with a roughness smaller than 0.7 nm. The silicon wafer substrate has a 330 nm thick SiO₂ layer to act as dielectric layer.

![Figure 2.7: TIPS-pentacene based thin film transistors with different geometries.](image)

Since our hollow rectangular capillary has a size of 0.5 mm × 5.0 mm I.D., it can only be utilized to write narrow films with a width around 5 mm. For transistor arrays, a custom-designed slot writer with a slot size of 0.5 mm × 20 mm was used to deposit TIPS-pentacene films to make the film fully cover the substrate. The metal electrodes were deposited through a shadow mask on the samples in an ultra-high...
vacuum system with a base pressure of around $4 \times 10^{-6}$ Torr. The transistor channel was aligned with the film deposition direction. Many other experimental details like substrate cleaning and surface treatment will be given in the experimental part in Chapter 4.

2.3 Sample Characterization

2.3.1 Morphology and Grain Structure Characterization

Optical microscopy in bright field mode and polarized light mode are two most common techniques applied in the examination of organic thin film’s morphology and grain structure [102, 103]. Bright-field microscopy is the simplest of all the optical microscopy illumination techniques. It illuminates the entire sample with direct light and observes it with transmitted or reflected light. This type of microscopy features a bright background and sample contrast comes from absorbance of light in the sample. Polarized reflected light microscopy is a technique that is suitable for examining different crystalline domains in optical anisotropic materials. In the polarized mode, the illuminating beam encounters a polarizer before the light waves are directed into the objective. Then the linearly polarized light waves are focused onto the specimen surface and reflected back into the objective. After leaving the objective aperture as a parallel bundle of wavefronts, the light is then projected onto a second polarizer oriented at $90^\circ$ with respect to the polarizer. The second polarizer only lets light of a defined direction pass. Hence, this polarizer analyzes the direction of the light
reflected from the thin film and is called analyzer.

Anisotropic thin films have fast and slow optical axes. Depending on the crystal orientation, more or less light will pass the analyzer. One can distinguish different crystal orientations based on the brightness of the reflected light from different regions. The maximum crystal brightness is obtained when the slow axis is rotated at 45° or 135° [102]. No rotation of the slow axis results in minimum crystal brightness. If the film is of single crystalline nature, the whole image changes from bright to dark when rotating the sample by 45°. If it is polycrystalline, there will be grains with different brightnesses next to each other, which are also changing brightness when rotating the sample. Completely amorphous films do not change brightness during rotation.

2.3.2 Structural Characterization

Single-crystal X-ray Diffraction

Single-crystal X-ray diffraction is a non-destructive analytical technique which provides detailed structural information for crystalline solids, including unit cell parameters, crystal system, space group, atom locations, bond types, band length and bond angles. Samples for single-crystal X-ray diffraction should be sufficiently large (ideal crystals averaging 150-250 µm in size), pure in composition and unfractured. X-ray diffraction is based on constructive interference of monochromatic X-rays and the crystal that is mounted on a goniometer. Peaks of diffracted intensity are observed on a CCD detector when conditions satisfy Bragg’s Law (Fig. 2.8): \( n\lambda = 2d\sin\theta \), where \( n \) is an integer, \( d \) is the spacing between the adjacent crystal planes, \( \theta \) is the diffraction angle, and \( \lambda \) is the wavelength of incident X-ray. To solve for the full structure of the crystal, diffractometer automatically orients the crystal and the detector
thus all possible diffraction directions of the lattice can be attained.

The single crystal X-ray diffraction data of TIPS-pentacene Form I crystal was collected with a Bruker Apex II CCD single-crystal diffractometer at 23°C. Plate shaped single grain TIPS-pentacene were purchased from Millipore Sigma and directly used. After data collection, APEX II software package was used to automatically search for diffraction peaks and identify and refine the parameters of the unit cell.

**Figure 2.8: Diagram of Bragg’s law.**

**Grazing Incidence X-ray Scattering**

X-ray diffraction from thin films with a thickness below 30 nm often suffers from low signal intensity and poor signal to background ratio. The most common technique to analyze these thin films is to use grazing incidence X-ray scattering. This measurement is performed at very low incident angles (0.1 to 3°) so it can increases the path length of the X-ray beam through the film which helps to increase the scattering intensity from the film while reduces the diffracted intensity from the substrate.

At early times, grazing incidence X-ray scattering measurement usually takes many hours to obtain one useful scattering profile for a sample. With the rapid revolution in instrumentation at synchrotron, the working efficiency of grazing incidence X-ray scattering is significantly increased [104,105]. Now the necessary data
acquisition time can be decreased to less than 1 ms, which opens the route to in situ and in operando studies. Among the grazing-incidence techniques, grazing incidence small angle X-ray scattering (GISAXS) and grazing incidence wide angle X-ray scattering (GIWAXS) are developed first. As shown in Fig. 2.9, a sample is placed in the path of a X-ray beam with an incident angle about 0.14°. The resulting scattering pattern is recorded by a 2D detector. Typical sample-to-detector distance for GISAXS is in the range of 130-500 cm, and for GIWAXS it is about 10-50 cm, making GIWAXS suitable to probe molecular length-scales and GISAXS suitable to probe larger structure.

![Figure 2.9: A sketch of the scattering geometry used in GISAXS and GIWAXS. The image is reproduced from reference [19] with permission.](image)

Fig. 2.9 illustrates this scattering geometry for GISAXS and GIWAXS. The incident angle is denoted $\alpha_i$, exit angle is denoted $\alpha_f$ and in-plane angle is denoted $\psi$. With the wavelength $\lambda$, the wave vector transfer $q$ is given by [19]:

$$q = \frac{2\pi}{\lambda}.$$
\[ q = k_f - k_i = \frac{2\pi}{\lambda} \begin{pmatrix} \cos(\alpha_f)\cos(\psi) - \cos(\alpha_i) \\ \cos(\alpha_f)\sin(\psi) \\ \sin(\alpha_i) + \sin(\alpha_f) \end{pmatrix} \] (2.1)

Our in situ microbeam grazing incidence wide-angle X-ray scattering (µGIWAXS) experiments were carried out in Cornell High Energy Synchrotron Source (CHESS) at beamline D1 [106]. X-rays with an energy of 10.74 keV (=1.15 Å) were focused to a beam size of 20 µm × 20 µm using a single-bounce X-ray capillary. The incidence angle was 0.14° and the scattering patterns were recorded using a Pilatus 200K area detector with a pixel size of 172 µm. Si/SiO\(_2\) wafers were used as substrates for all X-ray experiments.

### 2.3.3 Electrical Characterization

The electrical measurements were carried out on a probe stage (Cascade M150) with Keithley 2636 dual source meter units. The saturated and linear field effect mobilities were measured at saturation and linear regime respectively by transfer characteristic measurement. In this dissertation, to ensure accurate mobility extraction, we plot the mobility \(\mu_{\text{sat}}\) and \(\mu_{\text{lin}}\) versus the gate voltage \(V_g\). In this way, mobility overestimations are easily visible. Other characteristics that can be extracted from the transfer curves are the on-off ratio, which is the ratio between the maximum \(I_d\) measured in the on and in the off region (typically in the range of \(10^4\) to \(10^7\) in this dissertation) and the hysteresis, which is defined by the maximum voltage difference between the forward and backward current sweep. For bottom-gate/bottom-contact transistors, contact resistances are extracted from the linear regions in the output curves of transistors.
with variable channel lengths by transmission line method (TLM). Readers are referred to the Section 1.2 in Chapter 1 to gain detailed information on the working principle of organic thin film transistor.

2.4 Charge Transfer Integral Calculation

Energy Splitting in Dimer

The charge transport properties of organic semiconductors strongly depend on the extent of charge transfer integral. The issue of determining accurate charge transfer integral values has long received significant attention in many research areas including materials science, biology, chemistry, and physics. The most simple approach is referred to as the “energy splitting in dimer” (ESID) method [107–109]. The electronic coupling between the highest occupied molecular orbitals ($t_{\text{HOMO}}$) is half the energetic splitting of the HOMO and HOMO - 1 in a dimer system. Similarly, the electronic coupling between the lowest unoccupied molecular orbitals ($t_{\text{LUMO}}$) is half the energetic splitting of LUMO and LUMO + 1 orbital in the dimer.

Take electron transport as an example, the pairs of frontier orbitals are governed by simple Hamiltonians [92]:

$$H = \begin{bmatrix} E_{\text{LUMO}} & t_{\text{LUMO}} \\ t_{\text{LUMO}} & E_{\text{LUMO}} \end{bmatrix}$$

with eigenstates defined by symmetric or antisymmetric superpositions of the molecular orbitals,
\[ \psi_{LUMO}^\pm = \frac{1}{\sqrt{2}} \left( \frac{1}{\pm 1} \right) \] (2.2)

and eigenvalues,

\[ E_{LUMO}^\pm = E_{LUMO} \pm t_{LUMO}. \] (2.3)

The sign of the \( t_{LUMO} \) is obtained from the inspection of the frontier orbitals in the dimer.

**Generalized Electronic Coupling**

The ESID approach does not account for spatial overlap and therefore the electronic couplings estimated in this way could substantially deviate from the actual values [110]. Löwdins symmetric transformation is applied to generate an orthonormal basis set [111]. In the symmetrically orthonormalized basis, the electronic coupling between the HOMOs (\( t_{HOMO} \)) are finally expressed as

\[ t_{HOMO} = \frac{J_{AB} - \frac{1}{2}(H_{AA} + H_{BB})S_{AB}}{1 - S_{AB}^2} \] (2.4)

where \( J_{AB} = \langle \varphi_{HOMO}^A | h_{ks} | \varphi_{HOMO}^B \rangle \), \( S_{AB} = \langle \varphi_{HOMO}^A | \varphi_{HOMO}^B \rangle \), \( H_{AA} = \langle \varphi_{HOMO}^A | h_{ks} | \varphi_{HOMO}^A \rangle \), \( H_{BB} = \langle \varphi_{HOMO}^B | h_{ks} | \varphi_{HOMO}^B \rangle \).

The \( h_{ks} \) is the the one electron operator (Kohn-Sham Hamiltonian). The electronic coupling between the LUMOs (\( t_{LUMO} \)) can be calculated by same method by changing the HOMO into LUMO in above equation. The electron charge transfer integral is obtained by \( t_e = t_{LUMO} \) and the hole charge transfer integral is obtained by \( t_h = -t_{HOMO} \) [112].

The \( t_{HOMO} \) and \( t_{LUMO} \) of TIPS-pentacene dimers in this dissertation were calculated using the ADF (Amsterdam density functional) package [113]. The PW91 [114]
exchange-correlation function and the TZP basis set were used in the calculation for both Dimer I ([100] direction) and dimer II ([110] direction). The signs of electronic couplings ($t_{HOMO}$ and $t_{LUMO}$) were determined by the translational symmetry of the molecular orbitals of the dimer.
Chapter 3

TIPS-Pentacene Phase Transition and Form II Strain-stabilization

3.1 Introduction

Previous work in our group [101] has shown that strained small molecule organic semiconductor thin films can be obtained by solution deposition at elevated temperatures (60°C and 90°C for TIPS-pentacene). The strain is introduced after the deposition when the sample temperature is changed, as a result of the very large thermal expansion coefficient of the solid film relative to typical substrate materials such as silicon and glass. [101] Highly strained films are obtained after cooling unless the strain is relieved by cracking or buckling. In addition, TIPS-pentacene undergoes a bulk phase transition at 124°C [97] and it has been reported that it is possible to stabilize thin films in the high temperature phase, known as Form II, to ambient conditions. [115] Here, we report that in situ optical spectroscopy is highly sensitive to changes in molecular packing and to thermal expansion effects over narrow temperature ranges.
We utilize this effect during thermal cycling in combination with X-ray diffraction measurements to verify that Form II TIPS-pentacene films deposited at 135°C can be stabilized to room temperature if the film thickness is below the critical thickness for cracking. We have also performed similar experiments on room temperature phase (Form I) TIPS-pentacene thin films written at 25°C. No phase transition occurs even when the sample is heated to 135°C, which provides an additional confirmation of the strain-stabilization model since no reduction of the transition temperature is observed.

This chapter is organized as follows: the experimental details for all samples used in this chapter are summarized in the experimental section (Section 3.2). The real time optical microscopy, *in situ* X-ray and real time optical spectroscopy results on TIPS-pentacene phase transition are given in Section 3.3.1. The stabilization mechanism of Form II to room temperature is discussed in Section 3.3.2.

### 3.2 Experiments

All TIPS-pentacene thin films in Chapter 3 were prepared by the pen writing method. Details on this deposition method are given in Section 2.2 in Chapter 2. Film thickness were characterized either by an atomic force microscopy (AFM) or by a Dektak XT stylus profilometer. The experimental conditions for all samples are summarized in Table 3.1 and they are individually described below.

**Real Time Optical Microscopy Study**

TIPS-pentacene (≥ 99%) crystals were purchased from Millipore Sigma and directly used in our experiments. Single-crystal sample was placed in a temperature controlled
microscope stage (Linkam THMS600) under an optical microscope (Olympus BXFM) to observe the shape change during heating and cooling cycles. The sample was heated from 30°C to 210°C with a heating rate of 2°C/min. After staying at 210°C for 1 min, the sample was cooled back to 30°C with the same rate. Time-lapse images were taken for all real time experiments under bright field mode with a frame rate of 4 frames per minute. Image analysis was performed with softwares Free Studio, illustrator, and Image J.

![Figure 3.1: (a) Schematic of the optical reflectance and microscope system. A mirror with an aperture is inserted into the light path to select a small area of interest, as indicated by the dark spot in (b). (b) The optical image of sample 3C1. (c) A typical reflection spectrum of sample 3C1.](image)

**Strain-free X-ray Scattering vs. Deposition Temperature**

TIPS-pentacene thin films were prepared in the temperature range from 25°C to 134°C using toluene or mesitylene as solvent. In the grazing incidence X-ray scattering experiments, heavily doped n-type (100) silicon wafers with a 300 nm thermally grown
Table 3.1: Deposition conditions of TIPS-pentacene thin films discussed in Chapter 3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Figure</th>
<th>Temp. (°C)</th>
<th>Conc. (mg/ml)</th>
<th>Speed (mm/s)</th>
<th>Substrate</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3A1-3A11</td>
<td>3.5, 3.6</td>
<td>25-134</td>
<td>1.5</td>
<td>0.05</td>
<td>Si/SiO₂</td>
<td>70-580</td>
</tr>
<tr>
<td>3B1-3B11</td>
<td>3.5, 3.6, 3.7</td>
<td>25-134</td>
<td>1.5</td>
<td>25</td>
<td>Si/SiO₂</td>
<td>∼100</td>
</tr>
<tr>
<td>3C1-3C12</td>
<td>3.8</td>
<td>25-135</td>
<td>1.5</td>
<td>0.05</td>
<td>glass</td>
<td>60-550</td>
</tr>
<tr>
<td>3D1</td>
<td>3.9</td>
<td>25</td>
<td>10</td>
<td>0.02</td>
<td>glass</td>
<td>230</td>
</tr>
<tr>
<td>3E1-3E7</td>
<td>3.9</td>
<td>125</td>
<td>2.1</td>
<td>0.02-0.4</td>
<td>glass</td>
<td>44-740</td>
</tr>
<tr>
<td>3F1-3F6</td>
<td>3.10</td>
<td>125</td>
<td>2.1</td>
<td>0.02-0.4</td>
<td>Si/SiO₂</td>
<td>44-740</td>
</tr>
<tr>
<td>3G1</td>
<td>3.11</td>
<td>25</td>
<td>8</td>
<td>4</td>
<td>glass</td>
<td>32</td>
</tr>
<tr>
<td>3G2</td>
<td>3.11</td>
<td>135</td>
<td>20</td>
<td>8</td>
<td>glass</td>
<td>26</td>
</tr>
<tr>
<td>3G3</td>
<td>3.11</td>
<td>135</td>
<td>22</td>
<td>4</td>
<td>Si/SiO₂</td>
<td>30</td>
</tr>
</tbody>
</table>

Silicon oxide layer were used as substrates to minimize the scattering noise from the substrate. Toluene was only used as solvent at room temperature deposition. Since mesitylene has higher boiling temperature, it was used as solvent when the deposition temperature was greater than 25°C. We both made aligned films (samples 3A1-3A11) and polycrystalline films (samples 3B1-3B11) at different deposition temperatures. In situ microbeam grazing incidence wide-angle X-ray scattering (μGIWAXS) was carried out at the temperature those samples were made in Cornell High Energy Synchrotron Source (CHESS) at beamline D1 with the beam direction perpendicular to the film writing deposition. A series X-ray scan was done on each sample by moving the sample in writing direction with a step of 0.1 mm and 30-60 frames was collected for each sample. X-ray results of the aligned films were used to study the molecular orientation and X-ray results of polycrystalline films were used to study the unit cell parameters evolution versus deposition temperature.

**Strain-free Optical Spectra vs. Deposition Temperature**

Samples 3C1-3C12 were made on glass substrates in the temperature range from 25°C to 135°C. Optical spectra of freshly made crystalline films recorded at their deposition
temperatures in order to determine the intrinsic unstrained optical absorption peak position at each temperature. The system includes an integrated UV-Vis spectrometer (Angstrom Sun Technologies Inc.) to acquire reflectance spectra over a selected small area, as shown in Fig. 3.1. The optical spectra measurement was done in reflection mode thus the absorption features appear as downward peaks. Spectra were converted to absolute reflection percentage by comparison with a silicon mirror with a well-known reflectivity. A silicon mirror was placed behind the glass substrates, which serves to improve the signal and absorption contrast, as well as reducing peak shifts due to index of refraction dispersion.

**Cracking of Films During Cooling vs. Film Thickness**

TIPS-pentacene films with different thicknesses have been made at 125°C on glass slide (samples 3E1-3E7). The samples cooled to room temperature while acquiring *in situ* optical spectra. Samples were mounted on a thermoelectric module for temperature control. Another batch of samples (samples 3F1-3F6) have been made under the same condition except that the silicon with a 300 nm thermally grown silicon oxide layer was used as substrates for polarized microscopy experiments since the grain structure contrast is enhanced due to an optical interference effect produced by the oxide layer.

A thick Form I sample (sample 3D1) was made at 25°C on glass substrate and heated to 125°C while acquiring *in situ* optical spectra. An optical microscope with ultra-long working distance objective lenses is used to observe the thin film buckling or cracking behavior during annealing or cooling for all these samples.

**Metastable Polymorph Fabrication and Stabilization**

Thin TIPS-pentacene Form I film (sample 3G1) and Form II film (sample 3G2) have
been made on glass with a thickness around 30 nm. The thermal stability has been studied by *in situ* optical spectra. A thin Form II film (sample 3G3) made on Si/SiO$_2$ wafer at 135°C and *in situ* µGIWAXS was carried out at its deposition temperature and when it was cooled to room temperature.

### 3.3 RESULTS AND DISCUSSION

#### 3.3.1 TIPS-PENTACENE PHASE TRANSITION

**Optical Microscopy Study**

One single-crystal sample was subject to heating and cooling rate of 2°C/min in the temperature range between 30°C and 210°C. The plot of percent change of the edge is shown in Fig. 3.2. A surprising large thermal expansion effect is observed in the thermal cycle. The edge length exhibits up to a 22% expansion as the temperature increases from 30°C to 210°C. A sudden change in length is observed near 186°C, consistent with the solid-state Form II to Form III transition occurring at 185°C identified by bulk DSC [14]. Edge length change in the full heating and cooling cycle shows a distinct 11°C hysteresis, indicating the Form II to Form III transition is a first-order phase transition. This result is consistent with bulk DSC which showing the Form II to Form III transition has a hysteresis about 15°C [14]. The optical images of the TIPS-pentacene single crystal during the thermal cycle are shown in Fig. 3.3. One can see that there are phase boundaries occurrence during heating and cooling at 186°C and 175°C respectively, indicating that the Form II to Form III phase transition occur via nucleation and growth process which future confirms that
the Form II to Form III transition is a first-order phase transition.

![Figure 3.2](image)

Figure 3.2: Plot of percent change of the edge of a typical TIPS-pentacene single crystal in a thermal cycle. The data is plotted as 1°C per step when the temperature is near the phase transition temperature with the rest plotted as 5°C per step. The edge is indicated by the double-headed arrow in Fig. 3.3.

Unlike the Form II to Form III transition, the Form I to Form II transition is more gradual and continuous. We noticed that the thermal expansion coefficient is almost tripled in the temperature range of from 120 to 130°C compared to the thermal expansion coefficient when the temperature is below 120°C. But there is no nucleation and growth process occur during the heating and cooling cycle. A small hysteresis about 1 or 2°C can be barely seen in Fig. 3.2.
Figure 3.3: Optical images of a TIPS-pentacene single crystal during a thermal cycle. The edge length (indicated by the double-headed arrow) change versus temperature is plotted in Fig. 3.2. The images were taken under a bright field.

It is noticed that there is color change in the single crystal when the phase transition happens so we plot the color intensity change vs. temperature and the result is given in Fig. 3.4. Two spikes at 186°C and 175°C can be seen in the plot, corresponding to the Form II to Form III phase transitions. Clearly there is a 11°C hysteresis for the Form II to Form III phase transition, which is consistent with what we saw in the shape change in Fig. 3.2. For the Form I to Form II transition, the color change is less dramatic compared to the Form II to Form III transition, but a hysteresis about 2.5°C can still be seen. This is consistent with the bulk DSC result, which showing the Form I to Form II transition has a hysteresis about 3°C [14,97].
To study the Form I to Form II transition in detail, we carried out *in situ* X-ray and real time optical spectroscopy study on TIPS-pentacene thin films.

**Figure 3.4:** The color intensity is plotted vs. temperature. The red box in the inset image shows the region we used to calculate the color intensity.

**X-ray Study**

*In situ* µGIWAXS was carried out to study the thermal driven structure evolution of aligned films and polycrystalline films made in the temperature range from 25 °C to 134 °C. The aligned films (samples 3A1-3A11) were made at a slow speed 0.05 mm/s whereas the polycrystalline film (samples 3B1-3B11) were made at a high speed 25 mm/s. Typical grain morphologies of aligned films and polycrystalline films made at 25°C and 134°C are given in Fig. 3.5(a-d). The thickness information is shown in
Fig. 3.5(e). Since the polarized optical images were taken at room temperature after the sample was cooled down, the thick film (580 nm) made at 134° cracked [116] after cooling, as can be seen in Fig. 3.5(c).

Figure 3.5: Polarized optical images (a-d) and film thicknesses (e) of TIPS-pentacene films deposited at 0.05 mm/s and 25 mm/s from a 1.5 mg/ml solution at different temperatures. (a) and (b): Polarized optical images of films deposited at 0.05 mm/s (sample 3A1) and 25 mm/s (sample 3B1) respectively at 25°C. The white arrow is the writing direction; (c) and (d): Polarized optical images of samples made at 135°C with a writing speed of 0.05 mm/s (sample 3A11) and 25 mm/s respectively (sample 3B11). The optical images were taken after the samples were cooled to room temperature. (e): blue and red squares give the film thickness versus deposition temperature when the writing speed was kept at 0.05 mm/s (samples 3A1-3A11) and 25 mm/s (samples 3B1-3B11).

Our previous studies [7, 40, 101] have shown that the film morphology prepared by the hollow pen writing method is highly dependent on the writing speed. At low writing speed (0.05 mm/s) the crystallization of TIPS-pentacene is an evaporation-induced process occurring at the contact line. Oriented and nearly single crystalline films were produced because the crystallization was seeded by the solid film emerging from the meniscus. During deposition, grain boundary forms and runs close to parallel to the writing direction, as can be seen in Fig.3.5(a) and Fig.3.5(c). This growth region is the convective regime in which the film thickness is proportional to the sol-
vent vapor pressure [7,101], resulting in the film thickness increased dramatically for the aligned film as increasing the deposition temperature. At high writing speed (25 mm/s), the growth region is known as the Laudau-Levich-Derjaguin (LLD) regime. A liquid layer will be pulled out first and dry afterwards resulting in polycrystalline film with fan shaped grains (Fig.3.5(b) and Fig.3.5(d)). In LLD region, the film thickness depends on writing speed rather than solvent vapor pressure [7,101], thus the film thickness almost unchanged as increasing deposition temperature.

Figure 3.6: The $Q_{xy}$ shifts for aligned TIPS-pentacene films (samples 3A1-3A11) deposited at 0.05mm/s and polycrystalline films (samples 3B1-3B11) deposited at 25 mm/s.

*In situ* X-ray data were collected at the deposition temperature so it gives the equilibrium structure at the deposition temperature. The X-ray beam direction was perpendicular to the writing direction of our films. For aligned films, only (10L) and
(20L) are observed, indicating that the X-ray beam is incident at a small angle to the (100) crystalline plane. For the polycrystalline films, more peaks can be seen as the grains are randomly oriented. The $Q_{xy}$ values of (11L), (10L) and (01L) for these polycrystalline films are given in Fig. 3.6. We saw a gradual and continuous peak position shift as increasing the deposition temperature. Although the samples made at 0.05 mm/s and 25 mm/s have huge difference in film morphology and film thickness, the (01L) and (11L) have similar peak position and same evolution trend, indicating the unit cell parameters are mainly determined by deposition temperature and confinement effect did not play an important role here. The structure evolution we observed here is due to the large thermal expansion coefficient of TIPS-pentacene. The thermal expansion is due to the presence of anharmonicity in the potential energy surface. This effect can be more pronounced in weakly-bonded molecular crystals [117]. Chen et al. [97] reported bulk TIPS-pentacene has a phase transition at 124 °C and speculated that the phase transition involves the rearrangement of the two bulky side groups. Since the structure is mainly sensitively to the packing of molecular core so there is no sudden change in structure around 124°C in our X-ray data. In the real time optical microscopy study of TIPS-pentacene single crystal, we see the thermal expansion effect is more pronounced in the temperature range of from 120 to 130°C (Fig. 3.2), which is not observed our X-ray study. This might due to the crystalline grain size of TIPS-pentacene thin films is much smaller compared to the single crystals which broaden the transition.

For the polycrystalline films, there are enough diffraction peaks to solve for the unit cell parameters which are shown in Fig. 3.7. The unit cell parameter were calculated from the (11L), (10L) and (01L) peak positions (their $Q_{xy}$ and $Q_z$ values)
The obtained TIPS-pentacene unit cell parameters for the Form I thin film (sample 3B1) are \( a = 7.78 \, \text{Å}, \ b = 7.75 \, \text{Å}, \ c = 16.7 \, \text{Å}, \ \alpha = 89.4^{\circ}, \ \beta = 77.9^{\circ}, \ \gamma = 81.1^{\circ}. \)

The obtained TIPS-pentacene unit cell parameters for the Form II thin film (sample 3B11) are \( a = 8.69 \, \text{Å}, \ b = 7.66 \, \text{Å}, \ c = 16.8 \, \text{Å}, \ \alpha = 87.8^{\circ}, \ \beta = 78.9^{\circ}, \ \gamma = 71.0^{\circ}. \)

From Form I to Form II, the main change is the increase of \( a \)-axis and decrease of \( \gamma \) angle. The change of unit cell \( a \)-axis and the product of \( b \sin \gamma \) versus deposition temperature for samples 3B1-3B11 are shown in Fig. 3.7(c).

As increasing the deposition temperature from 25°C to 134°C, the \( a \)-axis expands by about 12% whereas the \( b \sin \gamma \) shrinks by more than 5%. The 12% expansion along the \( a \)-axis from Form I to Form II agrees with what we have seen in the edge length change of the single crystal in Fig. 3.2, indicating the long edge of the single crystal
is along the [100] direction. We noticed the (102) reflection splits into two from Form I to Form II. This is because the \( Q_z \) of (\( \bar{1}01 \)) and (102) for Form I are 0.56 and 0.59 respectively, which makes it difficult to distinguish these reflections in Form I. Whereas for Form II, the \( Q_z \) of (\( \bar{1}01 \)) and (102) change to 0.53 and 0.61 respectively, so that they are clearly separated. X-ray data exhibits TIPS-pentacene has large anisotropic thermal expansion from from 25° to 134°.

**Reflectrometry Study**

As we have discussed above, the strain is introduced upon changing the temperature of solid films due to thermal expansion or by a phase transformation. We anticipate that strain can cause noticeable peak shifts in absorption spectra. Therefore, we have carried out a study of the optical spectra of freshly made crystalline films recorded at their deposition temperatures in order determine the intrinsic unstrained optical absorption peak position at each temperature. We also utilize relatively thick films (>100 nm) in order to minimize the potential influence of surface or interface confinement effects on the molecular packing. These results provide a reference for additional measurements on strained layers as a function of film thickness, which we report below. Fig. 3.8(a) shows examples of spectra covering the entire range of the low temperature phase (Form I) from room temperature up to and beyond the bulk transition to Form II at 124°C. We plot the spectra as a function of photon energy instead of wavelength in order to more easily see the excitation energy shift direction. Since we plot these spectra as reflection percentage, absorption features appear as downward peaks.

Since the reflection feature we labeled A1 is the strongest among the three lowest energy features, this peak height was chosen to study the structural evolution, as
shown in Fig. 3.8 (b). The most pronounced features of this plot are the blue shift of the reflection features as the temperature is increased and the excellent sensitivity of the method to deposition temperature changes as small as 10 °C.

The results are in good agreement with X-ray diffraction results for bulk powder samples if we interpret the temperature dependence as being related to thermal expansion effects. Since the optical excitation energy is determined by the exciton coupling energy, the optical absorption features are mainly sensitive to the packing of the molecular cores. It is not surprising that there is no sudden jump at the transition temperature, which one would normally expect for a first order phase transition. TIPS-pentacene is a molecular crystal that exhibits a reversible phase transition at
122-124°C. Phase transitions in solids have been classified in several ways. The traditional classifications of phase transitions are first-order and second-order (continuous) transitions. According to the thermodynamic classification, first-order transitions involve a discontinuous change in the first derivatives of the free energy (e.g., volume, entropy) at a definite transition temperature. In second-order transitions there is a change of slope, but no discontinuity in the temperature dependence of the volume or entropy. As far as mechanisms are concerned, first-order transitions are generally believed to occur by nucleation of one phase within the other, followed by its growth. The lack of first-order transition behavior in the packing of the core molecules is a key result, since it helps to explain why we can sweep the temperature of samples through the phase transition without re-nucleating the grain structure, which we do not observe (See the following sections).

3.3.2 TIPS-pentacene Form II Stabilization

Cracking of Films during Cooling vs. Film Thickness

In previous work, strained lattices were obtained by depositing TIPS-pentacene thin films at elevated temperatures (60 °C and 90 °C). When thin films are constrained to a substrate with a much smaller coefficient of thermal expansion, elastic energy builds up during cooling of the sample, and it relaxes as free edges are created through cracking. Since the elastic energy is proportional to the film thickness, thinner films can accommodate a higher strain before failing. In principle, films that are not entirely continuous can release strain without cracking. However, we find that in practice cracks generally appear with a final spacing of a few microns, so that pinholes and even stripe-like morphologies have a minimal effect on the cracking behavior.
We have prepared films with different thicknesses at 125 °C (samples 3E1-3E7) and then cooled them to 25 °C while acquiring in situ optical spectra during the cooling process. *In situ* optical spectroscopy results for the cooling process are shown in Fig. 3.9, and Table 3.2 summarizes the writing conditions, film thicknesses, and the cracking temperatures.

![Figure 3.9](image)

**Figure 3.9:** (a) Comparison of heating and cooling for thicker films. The left sequence shows the deformation and cracking of a thick film made at 125 °C during cooling (740 nm, sample 3E1), and the sequence on the right shows buckling and cracking of a thick film made at 25 °C during heating (sample 3D1). The scale bars are 50 µm. (b) *In situ* optical reflectance spectroscopy A1 peak positions for each sample as a function of temperature. Blue circles: film made at 125 °C and then cooled to 25 °C. Red circles: film made at 25 °C and then heated up to 135 °C. Black squares: absorption peak positions of unstrained films reproduced from Fig. 3.8. (c) Thickness dependence of real-time optical reflection peak shifts in the cooling process. Samples with different thickness were made at 125 °C on glass slides (samples 3E1-3E7) and then cooled down to 25 °C. The film thicknesses, writing speeds, and cracking temperatures are shown in Table 3.2. The black square symbols with error bars show the peak position for strain-free films prepared at different temperatures reproduced from Fig. 3.8. The colored square markers and arrows indicate the temperatures that cracks start to appear.

We can see in Fig. 3.9(a) that the 740 nm thick film cracks almost immediately during cooling. Our strain model predicts that when the thickness is large, the strain
energy quickly exceeds the cracking threshold, thus causing the reflectance peaks to shift towards their strain-relaxed positions. Consequently, the optical data for this sample nearly tracks the behavior of the unstrained films, as we observed in Fig. 3.9(b).

We can distinguish between a nucleation driven phase transformation and strain relaxation by the sequence of cracking. In the first case, the cracks propagate outward from a nucleation point, as we have recently observed during crystallization of C8-BTBT from solution [57]. In the second case, cracks appear with widely distributed positions and then increase in density, i.e. there is no obvious center of nucleation. As we can see in Fig. 3.9(a), the cracking appears progressively and the grain structure is unchanged, suggesting that the cracking is due to strain. Fig. 3.9(a) also shows results for a thick film prepared at 25°C (sample 3D1) and then subsequently heated to 125°C. During heating the films buckle due to compression rather than cracking from tension. Buckling also leads to cracking and also relaxes strain so that we do not observe a large hysteresis between the heating and cooling curves in Fig. 3.9(b).

The absorption peak positions versus temperature during cooling for several additional samples listed in Table 3.2 are shown in Fig. 3.9(c). The peak positions are all nearly the same at the starting temperature in spite the large range of thicknesses because they are initially unstrained. A strong correlation between cracking of the film and the observed shifting of the absorption peaks can be seen. This behavior is consistent with the strain model, which predicts that thinner films can accommodate a higher strain, and thus the cracking temperature is depressed further and further as the film thickness is reduced. Moreover, the optical peak positions relax towards the unstrained positions as the temperature is lowered once the temperature is de-
Table 3.2: Cracking temperatures versus film thickness for films written at 125°C on glass slides.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Writing speed (mm/s)</th>
<th>Thickness (nm)</th>
<th>$T_{cr}$ (°C)</th>
<th>$\Delta T_{cr}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3E1</td>
<td>0.02</td>
<td>740</td>
<td>123</td>
<td>2</td>
</tr>
<tr>
<td>3E2</td>
<td>0.05</td>
<td>320</td>
<td>110</td>
<td>15</td>
</tr>
<tr>
<td>3E3</td>
<td>0.08</td>
<td>177</td>
<td>89</td>
<td>36</td>
</tr>
<tr>
<td>3E4</td>
<td>0.1</td>
<td>148</td>
<td>69</td>
<td>56</td>
</tr>
<tr>
<td>3E5</td>
<td>0.2</td>
<td>105</td>
<td>57</td>
<td>68</td>
</tr>
<tr>
<td>3E6</td>
<td>0.3</td>
<td>70</td>
<td>44</td>
<td>81</td>
</tr>
<tr>
<td>3E7</td>
<td>0.4</td>
<td>44</td>
<td>–</td>
<td>100$^{a}$</td>
</tr>
</tbody>
</table>

$^{a}$ This film did not crack.

cracked below the cracking temperature. However, they shift gradually rather than abruptly and the peak width does not broaden appreciably. This suggest that the film distributes strain relaxation over a region roughly comparable to the crack spacing.

The final film morphologies of a series of samples deposited at 125 °C (samples 3F1-3F6) and then cooled to room temperature are shown in Fig. 3.10. We note that the results closely reproduce the film thicknesses and grain morphologies of the films deposited on glass described above, but the thermally oxidized Si substrates used for this set of samples produce higher quality optical images owing to the reflection from the substrate itself, as opposed to glass which reflects very little light. The images reveal that the density and size of the cracks changes as the film thickness is reduced. The crack directions are mostly perpendicular to the writing direction (the stripe direction, close to the $a$-axis of TIPS-pentacene), consistent with the fact that the films tend to contract along the $a$-axis by a large amount during the cooling due to the large thermal expansion coefficient along that direction. For the thicker films (266 and 164 nm), numerous straight features are observed that do not appear to be cracks. Rather, we speculate that they are deformation-induced twins since they exhibit polarization contrast that is rotated with respect to the orientation of the
surrounding grains. As the film thickness is reduced (134 and 95 nm) the straight features are gradually replaced by more jagged, open cracks. This pattern persists at 64 nm, except in a few thinner spots. Finally, when the film thickness is 38 nm, cracks are entirely absent.

Figure 3.10: Polarized optical microscopy images of films prepared at 125 °C and then cooled to room temperature (samples 3F1-3F6). The writing speeds in (a-f) are 0.05, 0.08, 0.1, 0.2, 0.3 and 0.4 mm/s respectively and the corresponding film thicknesses are 266, 164, 134, 95, 64 and 38 nm. The writing direction is along the long axis of the grains in each case. The film deposition conditions are identical to those given in Table 3.2, except that they were deposited onto Si/SiO₂ substrates instead of glass slides in order to improve the optical contrast to grain structure and defects.

These results strongly support the strain model since the data shows that the films are strained, and that deformation and cracking are a result of strain exceeding a critical limit. One could also invoke possible interface energetic effects or confinement effects to qualitatively explain some of the phenomena. However, strain is a volume effect, and as such it is expected to strongly dominate over interface effects for layers more than 1 to 2 unit cells in thickness.

Metastable Polymorph Fabrication and Stabilization
In this section we report thermal stability results for Form I and Form II films during thermal cycling between 25 °C and 135 °C. The goal of this study is to observe whether the optical peaks can shift when lateral relaxation of the film is constrained by the substrate and no cracking or buckling occurs. This situation can be modeled by adding a strain term to the free-energy equations that govern the phase transition, which favor the unstrained phase under a given set of conditions. In the present case, since we predetermine the strain by controlling the deposition temperature, we are able to engineer one or the other phase to be the unstrained phase.

Very thin films (about 30 nm thick) are obtained that have an isotropic in-plane structure composed of spherulitic grains. This type of grain structure is effectively a two-dimensional powder structure, which greatly simplifies grazing incidence wide-angle X-ray scattering (GIWAXS) measurements since reflections from grains with many different in-plane orientations can be obtained in a single exposure. The films also have the advantage of being highly continuous.

*In situ* optical reflection results are shown in Fig. 3.11 for samples 3G1 and 3G2. No cracks appear in either film after thermal cycling. For the Form II sample, there is only a very small shift in the peak position during the cooling and heating cycle, indicating that Form II can be stabilized to 25 °C if no cracks occur to relieve the strain. The Form I films are stable at room temperature indefinitely, and during annealing up to 135 °C. A small reversible peak shift is observed when the sample is heated from 25°C to 135°C. Temperature cycles with longer annealing times at 135 °C (not shown) have not revealed any additional peak shift—that is, the peak position does not progressively shift with time. It is conceivable that a small amount of reversible buckling occurs during heating. Alternately, there could be a reversible
rotation of the molecules within the unit cell, even though the overall lattice constants are constrained by the substrate.

Figure 3.11: (a) In situ reflection spectroscopy data for constrained TIPS-pentacene thin films during cooling and heating cycles. The upper data set is for a Form II film with a thickness of about 26 nm, and the lower data set is for a 32 nm Form I film. These two films are listed as 3G2 and 3G1 respectively in Table 3.1. (b,c) In situ µGIWAXS of a Form II TIPS-pentacene thin film made at 135 °C. This sample is referred to as 3G3 in Table 3.1. (b) X-ray scattering pattern at the deposition temperature of 135 °C. (c) X-ray scattering pattern of the same film after cooling to 25 °C.

The stability of Form I up to and beyond the bulk transition temperature at 124 °C is a key results since it is inconsistent with certain models for polymorph stabilization that postulate interface energetics or confinement effects as a mechanism for the stabilization. These models predict that the transition temperature between Form II and Form I should be suppressed further and further as the film thickness is reduced.
and interface energetics become dominant, and that Form II can be stabilized at room temperature for a thin enough film. As a consequence, Form I thin films should spontaneously transform to Form II well below the bulk transformation temperature, potentially even (eventually) at room temperature for very thin films. In contrast, as we have already mentioned above, we do not observe such an effect in Fig. 3.11. In addition, we have shown that there is no large nucleation barrier for the Form I to Form II transition, since it would cause a large hysteresis in the heating part of the temperature cycle, which we do not observe in Fig. 3.9. Thus, our results clearly confirm that strain is the only plausible mechanism behind polymorph stabilization of TIPS-pentacene thin films, in agreement with previous work.

In order to verify that the optical spectroscopy results correlate to structure, we have also performed X-ray diffraction experiments on TIPS-pentacene thin films. Fig. 3.11(b-c) show in situ grazing incidence X-ray scattering results for a Form II thin film (sample 3G3). The film was deposited at 135 °C and then cooled to 25 °C. The film is composed of comet-shaped spherulitic grains, and that no cracks appeared as the film was cooled to 25 °C (verified by AFM). Comparing Fig. 3.11(b) and Fig. 3.11(c), we see that the (10L), (01L), (11L), and (20L) reflections do not shift significantly in the in-plane (Q||) direction. This indicates that the crystalline lattice is constrained to the substrate. However, some of the reflections shift along the Qz direction, which indicates that there is a vertical contraction or reorganization within the crystalline unit cell as the sample is cooled. These results are completely consistent with the optical spectroscopy results shown in Fig. 3.11, which suggest that there is almost no change in the molecular packing within each crystalline layer as the Form II sample is cooled to 25 °C.
A Form I sample was fabricated at 25°C (Sample 3G1) for comparison. Most interestingly, we see that the in-plane lattice constants for the Form II sample (sample 3G2) hardly change on cooling to 25 °C, indicating that the film is constrained to the substrate. This confirms the conclusion of our optical study that the crystalline lattice is constrained to the substrate under conditions where no cracking occurs. We also note that it has previously been found that the $a$-axis of aligned TIPS-pentacene thin films prepared by the pen writer method is parallel to the deposition direction. The large positive thermal expansion along the $a$-axis in an aligned film means that cracks tend to occur perpendicular to the writing direction when samples are cooled from high temperature to room temperature. As we have already noted, this observation explains the predominant direction of the cracks in aligned thin films, such as those shown in Fig.3.10.

### 3.4 Conclusions

Strain-free TIPS-pentacene films exhibit a temperature-dependent blue shift of optical absorption peaks due to a continuous thermally driven change of the crystalline packing. As crystalline films are cooled to ambient temperature they become strained although cracking of thicker films is observed, which allows the strain to partially relax. Below a critical thickness, cracking is not observed and grazing incidence X-ray diffraction measurements confirm that the thinnest films are constrained to the lattice constants corresponding to the temperature at which they were deposited. Both Form I and Form II can be strain-stabilized when the film thickness is about 30 nm. Strain dominates over other potential effects such as confinement since strain energy...
is proportional to the volume of the film that is, because it is a bulk effect rather than an interface effect. This provides the key to producing metastable polymorphs since very thin films can be highly strained without exceeding a critical value of the strain energy where cracks are produced.

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Chapter 4

TIPS-pentacene Form I and Form II Mobility Characterization

4.1 Introduction

In Chapter 3, we have showed that TIPS-pentacene Form II can be strain-stabilized to room temperature. In Appendix A, we discussed how to get aligned Form II film be eliminating a dewetting behavior. Being able to make aligned TIPS-pentacene films place us in a good position towards making organic transistors that possess a field effect mobility close to the intrinsic mobility of the material since the limitation from grain boundaries on charge transport is avoided. In this chapter, we will characterize the mobility of TIPS-pentacene room temperature Form I and strain-stabilized Form II by fabricating OFETs with different geometries. The structure of this chapter is as follows: In Section 4.2, the experimental details on the substrate cleaning procedure and transistor fabrication are given. The electrical properties of TIPS-pentacene based organic transistors were characterized in staggered geometries.
including bottom-gate/top-contact type (Section 4.3.1) and top-gate/bottom-contact type (Section 4.3.2). In Section 4.3.3, we made coplanar TIPS-pentacene transistors using bottom-gate/bottom-contact geometry. In all three geometries, both TIPS-pentacene Form I and strain-stabilized Form II films were used as active layers to characterize their hole transport mobility.

4.2 Experiments

The experimental conditions for all samples are summarized in Table 4.1. The glass and silicon wafer substrates that used for making transistors were pre-diced to a standard substrate size of 15 mm \( \times \) 20 mm. TIPS-pentacene thin films (samples 4A1-4A4) were prepared by the hollow capillary pen-writer method. Our hollow rectangular capillary has a size of 0.5 mm \( \times \) 5.0 mm I.D. thus it can only be utilized to write narrow films with a width around 5 mm. A custom-designed slot writer with a size of 0.5 mm \( \times \) 20 mm was used to replace the glass capillary to deposit TIPS-pentacene films for the rest samples in Table 4.1 so the film can fully cover the substrate. Film thickness was measured for each sample by a Dektak XT stylus profilometer. Before mobility characterization, a scratch was made around each transistor to reduce leakage current. The experimental details for transistor fabrication are described below.

**Bottom-Gate/Top-Contact Transistors**

Silicon wafers with a 330 nm thermally grown silicon oxide layer were purchased from Ossila company and used as substrates. The substrates were cleaned by four different procedures to study the effect of surface treatment on the electronic perfor-
1) Ultrasonic cleaning: the substrate was sonicated in deionized water, acetone, and isopropanol for 10 min (sample 4A1). 2) Ultrasonic cleaning plus UV-Ozone treatment: the wafer was ultrasonically cleaned in deionized water, acetone and isopropanol for 10 min then UV-Ozone treated for 20 min to remove any organic materials that absorbed onto the substrate (sample 4A2). 3) Ultrasonic cleaning plus phenyltriethoxysilane (PTES) treatment. The wafer was first ultrasonically cleaned and then the PTES treatment was accomplished by immersing the cleaned wafer into a toluene solution of 3 wt% PTES and heated to 110 °C for 15 h [101, 116]. After the treatment, the substrate was rinsed in toluene, acetone and isopropanol for 1 min each (sample 4A3). 4) Ultrasonic cleaning plus Piranna acid clean plus PTES treatment: the wafer was ultrasonically cleaned first and then it was cleaned in a 7:3 (v/v) mixture of concentrated sulfuric acid and 30% hydrogen peroxide (piranha solution) for 20 min. After removal from the acid bath, the substrate was thoroughly washed in deionized water and then air dried. After Piranna acid cleaning, the PTES treatment was accomplished as described above and then rinsed in toluene, acetone and isopropanol for 1 min each (sample 4A4). All wafers were used to deposit TIPS-pentacene films right after their cleaning to minimize contamination from the air. After the semiconductor films had been deposited, 30-40 nm gold contacts were evaporated using a shadow mask to form arrays of source and drain electrodes with a channel length of 30 μm and a channel width of 1000 μm. The schematic of TIPS-pentacene based bottom-gate/top-contact transistor is shown in Fig. 4.1(a). For each sample, 10 transistor measurements were performed.

To study the effect of phase transition on charge transport properties, TIPS-pentacene Form I film (deposited at 25°C, sample 4A5) and TIPS-pentacene Form II
Table 4.1: Deposition conditions of TIPS-pentacene thin films used for mobility characterization in Chapter 4.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Geometry</th>
<th>Temp. (°C)</th>
<th>Conc. (mg/ml)</th>
<th>Speed (mm/s)</th>
<th>Cleaning</th>
<th>Thickness</th>
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<tbody>
<tr>
<td>4A1</td>
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<td>25</td>
<td>9</td>
<td>0.1</td>
<td>ultrasonic</td>
<td>30 nm</td>
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<tr>
<td>4A2</td>
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<td>9</td>
<td>0.1</td>
<td>UV-ozone</td>
<td>30 nm</td>
</tr>
<tr>
<td>4A3</td>
<td>bgtc</td>
<td>25</td>
<td>9</td>
<td>0.1</td>
<td>PTES</td>
<td>30 nm</td>
</tr>
<tr>
<td>4A4</td>
<td>bgtc</td>
<td>25</td>
<td>9</td>
<td>0.1</td>
<td>Piranha/PTES</td>
<td>30 nm</td>
</tr>
<tr>
<td>4A5</td>
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<td>25 nm</td>
</tr>
<tr>
<td>4A6</td>
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<td>25 nm</td>
</tr>
<tr>
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<td>tgbc</td>
<td>25</td>
<td>20</td>
<td>0.05</td>
<td>PTES</td>
<td>25 nm</td>
</tr>
<tr>
<td>4B2</td>
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<td>0.6</td>
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<td>30 nm</td>
</tr>
<tr>
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<td>bgbc</td>
<td>25</td>
<td>20</td>
<td>0.05</td>
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<td>25 nm</td>
</tr>
<tr>
<td>4C2</td>
<td>bgbc</td>
<td>130</td>
<td>10</td>
<td>0.6</td>
<td>PTES</td>
<td>30 nm</td>
</tr>
</tbody>
</table>

film (deposited at 130°C, sample 4A6) were used as active layers in bottom-gate/top-contact organic field-effect transistors. The concentration and writing speed for sample 4A5 were 20 mg/ml and 0.05 mm/s respectively since these conditions produce optimized grain structure using our micro-slot writer. Since sample 4A6 was deposited at 130°C, the Form film had to be relatively thin to avoid cracking when it was cooled to room temperature. Form II film (sample 4A6) was prepared from a blend of 1,2-dichlorobenzene (DCB) and mesitylene with a volume ratio of 4:1 at 0.8 mm/s, resulting in a 25 nm thick film. After the semiconductor films were deposited, gold contacts were evaporated using a shadow mask to form arrays of source and drain electrodes with a channel length of 30 µm and a channel width of 1000 µm. For each sample, 15-18 transistor measurements were performed.

**Top-Gate/Bottom-Contact Transistors**

Glass slides (fused silica corning 7980 of UV grade) with a size of 15 mm × 20
mm were polished both sides with a roughness smaller than 0.7 nm and used as substrates. The glass slides were first ultrasonic cleaned in deionized water, acetone, isopropanol for 10 min and then the PTES treated. After PTES treatment, the glass slides were rinsed in toluene, acetone and isopropanol for 1 min each. Then gold contacts (30 nm) were evaporated using a shadow mask to form arrays of source and drain electrodes with a channel lengths of 30 µm and a channel width of 1000 µm. The pentafluorobenzene thiol (PFBT) treatment was done to increase the work function of gold. These contacts were treated for 20 min using 30 mM solution of PFBT in isopropanol followed by a 2 min rinse in pure isopropanol and a 15 min annealing at 60 °C.

Samples 4B1 and 4B2 were deposited in air. The deposition speed, concentration and TIPS-pentacene film thickness information can be found in Table 4.1. CYTOP 809A (AGC Chemicals Co.) was employed as the dielectric layer for sample 4B1 and CYTOP 809M (AGC Chemicals Co.) was used as the dielectric layer for sample 4B2. The volume ratio of CYTOP to its solvent (CT-SOLV180) was 2:1. The CYTOP layer was spin coated onto TIPS-pentacene layer with a speed of 1000 rpm then annealed at 100 °C for 20 min. Finally a 100 nm thick aluminum layer was thermally evaporated using a shadow mask in a bell jar to serve as the gate electrode.

For sample 4B3 and 4B4, both the TIPS-pentacene film and CYTOP layer fabrication were carried out in Nitrogen environment. The TIPS-pentacene Form I film (sample 4B3) was deposited from pure toluene solution and Form II film (sample 4B4) was prepared from a blend of DCB and mesitylene with a volume ratio of 4:1. The TIPS-pentacene film was annealed at 100°C for 10 min then a CYTOP layer was prepared also by the micro-slot writer from a 809M CYTOP solution using CT-
SOLV100E as solvent. The volume ratio of 809M CYTOP to the solvent was 1:1.5 and the deposition speed was 4 mm/s. The sample was annealed at 100 °C for 20 min and it gave a 1100 nm thick CYTOP layer. Finally a 100 nm thick aluminum layer was thermally evaporated using a shadow mask in a bell jar to serve as the gate electrode. The schematic of TIPS-pentacene based bottom-gate/top-contact transistor is shown in Fig. 4.1(b). For each sample, 14-15 transistors were characterized.

Figure 4.1: Schematic TIPS-pentacene based transistors using (a) bottom-gate/top-contact geometry, (b) top-gate/bottom-contact geometry and (c) bottom-gate/bottom-contact geometry.

Bottom-Gate/Bottom-Contact Transistors

The heavily doped n-type (100) Si wafer with a 330 nm thermal oxide layer was used in a bottom gate geometry as the gate contact and dielectric layer. The wafers were first ultrasonically cleaned and then PTES treated. Gold contacts were evaporated using a shadow mask to form arrays of source and drain electrodes with variable channel length. The channel lengths were 30 μm, 40μm 50μm, 60μm and 80μm. The channel width was fixed at 1000 μm. These contacts were then treated for 20 min using 30 mM solution of PFBT in isopropanol followed by a 2 min rinse in pure isopropanol and a 15 min annealing at 60 °C. The deposition condition for TIPS-pentacene Form I film (sample 4C1) and Form II film (sample 4C2) were given in
Table 4.1. The schematic of TIPS-pentacene based bottom-gate/top-contact transis-
tor is shown in Fig. 4.1. For each sample, 18-19 transistors were characterized.

4.3 RESULTS AND DISCUSSION

4.3.1 BOTTOM-GATE/TOP-CONTACT TRANSISTORS

Effect of Cleaning Procedure on the Device Performance

The biggest advantage of using bottom-gate/top-contact geometry is that we can use the commercially available high-quality wafer as substrate. A typical TIPS-pentacene Form I based bottom-gate/top-contact transistor is shown in Fig. 4.2. The channel length \( L \) is 30 \( \mu \)m and channel width \( W \) is 1000 \( \mu \)m. The large W/L ratio is used here to eliminate the current fringe effect which could cause mobility overestimation [118].

![Figure 4.2: (a) Top view of a typical TIPS-pentacene bottom-gate/top-contact thin film transistor made in our lab. The TIPS-pentacene film was deposited at 0.1 mm/s at 25° C by hollow pen writing method. This transistor has a channel width of 1000 \( \mu \)m and a channel length of 30 \( \mu \)m. (b) same transistor at higher magnification. The optical images were taken under bright field.](image-url)
A typical TIPS-pentacene Form I film used for mobility characterization is shown in Fig. 4.3. Large grains with millimeter size can be obtained along the writing direction at slow writing speed [7,101,116]. The average grain size perpendicular to the writing direction is around 200µm. Previous study in our group shows that the grain boundary is well defined twin boundary and it is along the [100] crystallographic axis [7]. Assuming the bulk crystal structure [50], the angle between the molecular long axis and [100] is 28° [7]. So, by using polarized microscopy, the reflected light intensity is expected to become extinct upon rotating the sample by ±28° relative to the writing direction, which can be clearly seen in Fig. 4.3.

Figure 4.3: (a,b) Polarized optical images of a typical TIPS-pentacene Form I film that we made for mobility characterization (samples 4A1-4A4 have almost identical grain structure). (a) Thin film rotate by 28° clockwise to show one type of grain when its reflection is extinct. (b) Thin film rotated by 28° counter-clockwise to show the twin grains when in extinction. (c) and (d): optical images of the film at higher magnification.
Figure 4.4: Typical transfer curves for TIPS-pentacene based bottom-gate/top-contact transistors using different surface cleaning or treatment methods. (a) the wafer substrate was cleaned by ultrasonic cleaning (4A1); (b) the surface was cleaned by UV-Ozone treatment (4A2); (c) The surface was PTES treated after ultrasonic cleaning (4A3); (d) the surface was cleaned in Piranha acid and then PTES treated (4A4).

For field effect thin film transistors, the dielectric organic semiconductor interface is crucial since the charge carriers are within a few nanometers of this interface. Unfortunately, SiO$_2$ is notorious for charge carrier trapping, possibly due to bulk defects and surface hydroxyl groups [119,120]. If the wafer substrate was only cleaning by ultrasonic in organic solvents, the average saturation mobility of Form I based transistors is 0.36 cm$^2$V$^{-1}$s$^{-1}$, as shown in Fig. 4.4(a). Although UV-Ozone treatment can effectively remove the organic contamination on the wafer surface, it did not
help much on passivate the surface traps. In fact, UV-Ozone treatment tend to create more surface traps as the mobility is decreased to 0.23 cm²V⁻¹s⁻¹ and the hysteresis becomes larger, as can be seen in Fig. 4.4(b). In literature, self-assembled monolayers that can chemically grafted onto silicon wafers are widely used to tune the threshold voltages in solution-deposited organic thin film transistors [121–124]. In our case, we attempt to passivate the surface traps of SiO₂ by turning the surface hydroxyl groups into phenyl groups, thus a non polar PTES SAM was used to modify SiO₂ surface. The transistor used PTES treated wafer exhibits a slight threshold voltage shift compared to untreated ones, but the mobility value is increased from 0.36 cm²V⁻¹s⁻¹ to 0.6 cm²V⁻¹s⁻¹ and hysteresis in the transfer curve is negligible, showing in Fig. 4.4(c). These results indicate PTES treatment after ultrasonic cleaning can effectively passivate the traps on the SiO₂ surface. We also tried to use Piranha acid to clean the substrate before PTES treatment, but we find that this step does not contribute to a further improvement on the mobility.

**Mobility Enhancement in Form II Phase**

To study the charge transport property of Form II, we deposited thin TIPS-pentacene film (sample 4A6) at 130°C and stabilized the high temperature phase to room temperature by strain effect [101,116]. The film deposited at high substrate temperature become strained during cooling due to the mismatch between the thermal expansion coefficients of the TIPS-pentacene film and the wafer substrate. Since strain energy is proportional to film thickness, thicker films crack during cooling and release strain; this allows the lattice constants to relax to nearly strain-free values during cooling to room temperature. On the other hand, thinner films can accommodate a higher strain. Thus, the cracking temperature is depressed further and further.
as the film thickness is reduced. By making the Form II film thin enough, no cracks occur and the high temperature unit cell constants can be fully strain-stabilized to ambient temperature [116].

![Figure 4.5: (a-b) Polarized optical images of the TIPS-pentacene Form I film with gold source and drain deposited on top of it (sample 4A5). (c-d) Polarized optical images of the TIPS-pentacene Form II film with gold source and drain deposited on top of it (sample 4A6).](image)

The hole mobility of TIPS-pentacene Form I (sample 4A5) and strain stabilized Form II (sample 4A6) were measured at room temperature by making bottom-gate/top-contact thin film transistors using either TIPS-pentacene Form I or strain stabilized Form II film as active layer. The film morphologies are shown in Fig. 4.5. Crystalline grains are observed to be much longer along the writing direction than the transistor channel length (30 µm).

The output curves, transfer curves and $V_g$ dependence of the mobility are given
in Fig. 4.6. The gate voltage dependence of the mobility (Fig. 4.6 (c)) does not have a pronounced mobility overestimation peak due to non-linear charge injection, which is an experimental artifact frequently found in the literature [125]. For bottom-gate/top-contact transistors, the average mobility of TIPS-pentacene made at 25°C is 0.6 (± 0.1) cm²V⁻¹s⁻¹, the average threshold voltage is -3 V and on/off ratio is above 10⁵. The average mobility of TIPS-pentacene made at 130°C is 2.1 (± 0.4) cm²V⁻¹s⁻¹, threshold voltage is -23 V and on/off ratio is above 10⁵. Therefore the mobility is increased by about a factor of three using a strained film as the active layer.

![Figure 4.6: (a) Typical saturation transfer curve for the Form I film based bottom-gate/top-contact transistors made at 25°C (sample 4A5); (b) typical saturation transfer curve for the Form II film based bottom-gate/top-contact transistors. The film was made at 130°C and then stabilized to 25°C (sample 4A6). (c) gate dependent saturation mobilities for the sample 4A5 and sample 4A6; (d-e) typical output curves for the sample 4A5 and sample 4A6.](image)

In bottom-gate/top-contact transistors, an S shaped turn on effect results from
non-linear contact resistance [64,125] can be clearly seen in the output curves, as can be seen in Fig. 4.6(d-e), indicating that big contact resistance exist between the TIPS-pentacene layer and gold electrode. Contact resistance results from the fact that a fraction of the applied voltage is necessary to transfer the charges from the electrode surface to the semiconductor layer. The big contact resistance is caused by the energetic mismatch between the electrode work function and the transport level of the organic semiconductor which hampers the injection process. Gold film is used as the contact metal due to its relatively high work function (4.8 eV) compared to other metals [126,127], but it is still lower than the highest occupied molecular orbital (HOMO) level of TIPS-pentacene which is reported to be 5.3 eV [128]. Thus the Schottky barrier between the Au and TIPS-pentacene layer results in the diotic behavior of the output curve in the linear regime.

4.3.2 Top-Gate/Bottom-Contact Transistors

In the bottom-gate/top-contact geometry structured transistors, the mobility of TIPS-pentacene transistor could be limited by the contact resistance and the surface traps on PTES treated SiO$_2$. To eliminate these effects, we made top-gate/bottom-contact TIPS-pentacene transistors where gold electrodes were modified with PFBT self-assembled monolayer and SiO$_2$ dielectric was replaced by a CYTOP polymer dielectric layer.

Two types of CYTOP were employed as the dielectric layer: type 809A with an end group of -COOH and type 809M with an end group of -CONH$_2$ where R stands for alkyl. We first made both TIPS-pentacene Form I film and CYTOP film in air and the transistor data is summarized in Table 4.2. We find that using
809A CYTOP (sample 4B1) as dielectric layer the Form I mobility is found to be only 0.08 cm$^2$V$^{-1}$s$^{-1}$ with large positive threshold voltage + 30 V and a low on/off ratio (below 1000). The mobility is improved to 0.3 cm$^2$V$^{-1}$s$^{-1}$ and the on/off ratio is increased to 10$^4$ if we use 809M CYTOP (sample 4B2) instead of 809A CYTOP. The fact that the 809M CYTOP gives better results than 809A CYTOP could result from the polarization of their end groups. The 809A’s end functional group is -COOH which has hydrogen bonding in it. Due to the large electronegativity between H atom and O atom, OH bond is strongly polarized thus a great number of hole carriers will be trapped by the polarized OH groups in the channel. On the other hand, the 809M’s end functional group is -CONH Si(OR)$_n$ where R stands for alkyl. The electronegativity between C and O or C and H are small so the charge trapping effect caused by the end group is small.

For top-gate/bottom-contact transistors made in air (sample 4B2), the averaged saturation mobility for the TIPS-pentacene Form I film (0.3 cm$^2$V$^{-1}$s$^{-1}$) is only half of the mobility value that we typically get for the bottom-gate/top-contact geometry transistors (sample 4A5). This is probably due to the fact that TIPS-pentacene can be photooxidized with the presence of oxygen. In the bottom-gate/top-contact geometry, TIPS-pentacene molecules grown on the SiO$_2$ surface during deposition are protect by the solution and after deposition oxygen has to diffuse into the interface to photooxide the molecules at the active layer. Thus the fresh made bottom-gate/top-contact transistor usually exhibits good electronic performance if we measure their electronic performance right after they have been made. On the other hand, in the top-gate/bottom-contact geometry, the active is the top layer of the TIPS-pentacene film. If we deposit TIPS-pentacene film in the air, molecules in the top layer are
Table 4.2: Electric performance of TIPS-pentacene Form I based top-gate/bottom-contact transistors made in air (samples 4B1 and 4B2).

<table>
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<tr>
<th>Active layer</th>
<th>dielectric layer</th>
<th>saturated mobility (cm²V⁻¹s⁻¹)</th>
<th>(V_{th}) (V)</th>
<th>on/off ratio</th>
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</thead>
<tbody>
<tr>
<td>Form I (sam. 4B1)</td>
<td>809A CYTOP</td>
<td>0.08 (±0.02)</td>
<td>+30 (±5)</td>
<td>∼10⁴</td>
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<tr>
<td>Form I (sam. 4B2)</td>
<td>809M CYTOP</td>
<td>0.3 (±0.05)</td>
<td>+15 (±3)</td>
<td>∼10⁴</td>
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</tbody>
</table>

exposed to air thus they can be easily photooxidized. Photooxidation of pentacene and its derivatives has been reported by several groups [129–131]. The impurities at the active layer are detrimental to the charge transport, resulting in a low charge transport mobility in the top-gate/bottom-contact structured transistor.

To avoid photoxidization, we deposited TIPS-pentacene films and CYTOP layers in nitrogen environment. The hole mobility of TIPS-pentacene Form I (sample 4B3) and strain stabilized Form II (sample 4B4) have been measured at room temperature using either TIPS-pentacene Form I or strain stabilized Form II films as active layers. The output curves of a Form I based transistor and Form II based transistor are shown in Fig. 4.7(a) and Fig. 4.7(b). The Form I film and strain-stabilized Form II morphology are shown in Fig. 4.7(c) and Fig. 4.7(d). Crystalline grains are observed to be much longer along the writing direction than the transistor channel length (30 µm). Fig. 4.7(a, b) shows that the drain current \(I_d\) increases linearly as increasing the drain voltage \(V_d\) in the linear region \((V_d \ll V_g)\), indicating the contact resistance between the Form I or Form II film and PFBT treated gold pattern is small. This is because PFBT-modified gold electrodes have their work function increased close to the HOMO level of TIPS-pentacene [127,128]. The Form II based transistors have higher \(I_d\) under the same gate voltage compared to Form I based transistor, indicating the Form II film has higher hole mobility.
Figure 4.7: (a) Output curve of a typical top-gate/bottom-contact TIPS-pentacene based transistor using the Form I film as active layer (sample 4B3). The inset is exploded view of top gate bottom contact transistor using a TIPS-pentacene film as the active layer and CYTOP film as dielectric layer; (b) Output curve of a typical top-gate/bottom-contact TIPS-pentacene based transistor using the Form II film as active layer (sample 4B4); (c) polarized optical image of the Form I based transistor that goes with (a); (d) polarized optical image of the Form II based transistor that goes with (b).

The field effect hole mobilities are calculated from transfer curves in both saturation and linear region and the results are summarized in Fig. 4.8. Typical saturation transfer curves for TIPS-pentacene Form I and Form II films are shown in Fig. 4.8(a) and Fig. 4.8(b). The saturation mobility for the Form I transistor is $1.0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and the saturation mobility for TIPS-pentacene Form II is $3.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The gate voltage dependence of the saturation mobility (Fig. 4.8(c)) does not have a
pronounced mobility-overestimation peak due to non-linear charge injection, which is an experimental artifact frequently found in the literature [125]. The linear transfer curves for the same transistors are given in Fig. 4.8(d) and the gate voltage dependence of the linear mobility is shown in Fig. 4.8(e). For the Form I based transistor, its linear mobility is $0.9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ which is almost equal to its saturation mobility. The linear mobility for the Form II based transistor is about $2.9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ which is also close to its saturation mobility.

The average linear mobility of TIPS-pentacene Form I is $0.8 \pm 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. It is close to its average saturation mobility which is $0.9 \pm 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The average
threshold voltage is \(-2(\pm 3)\) V and on/off ratio is about \(10^4\). For stain-stabilized Form II, the average linear and saturation mobility are \(2.6 (\pm 0.3) \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\) and \(2.9 (\pm 0.5) \text{ cm}^2\text{V}^{-1}\text{s}^{-1}\) respectively. The average threshold voltage is \(-3 (\pm 3)\) V and on/off ratio is also about \(10^4\). Therefore the mobility is increased by about a factor of three using a strained film as the active layer.

The top-gate/bottom-contact transistors have slightly higher mobility compared to bottom-gate/top-contact transistors. This is probably because the CYTOP layer has fewer surface traps compared to PTES treated SiO\(_2\). The trap density in the active layer depends on the dielectric constant \((\varepsilon)\) of the dielectric materials [132]. In a field effect transistor, the dielectric layer will be polarized after applying a gate voltage. The polarized dielectric layer exerts an attractive force on the charge carriers which increases the tendency toward carrier self-trapping. As the attractive force is larger for larger \(\varepsilon\), this qualitatively explains why the mobility is increased if we reduce \(\varepsilon\) from 3.9 for SiO\(_2\) to 2.0 for CYTOP.

**4.3.3 Bottom-Gate/Bottom-Contact Transistors**

In last section, we have shown that top-gate/bottom-contact TIPS-pentacene based transistors exhibit excellent electronic performance. However, this structure presents serious problems for fabricating technologically important devices due to the potential damage to the active layer during the subsequent process steps including the dielectric layer deposition, the gate electrode patterning and wiring. Instead, a bottom-gate/bottom contact structure is strongly favored for its simplicity. To make bottom-gate/bottom-contact TIPS-pentacene based transistor, gold was deposited onto PTES treated Si/SiO\(_2\) substrate first. The channel length was varied
from 30 \( \mu \text{m} \) to 80 \( \mu \text{m} \) in order to characterize the contact resistance by transmission line method. After gold deposition, PFBT treatment was carried out to tune the work function of the gold electrode followed by TIPS-pentacene film deposition.

**Effect of Annealing on the Device Performance**

The polarized images of a typical TIPS-pentacene Form I film based bottom-gate/bottom-contact structure transistor are shown in Fig. 4.9 (sample 4C1). The TIPS-pentacene Form I film contains large grains and the grain structure maintained as they cross the PFBT treated gold, contributing a fully continuous and smooth TIPS-pentacene film in the channel. The averaged saturation mobility data for the fresh made sample is shown in Fig. 4.10. As one can seen, the averaged saturation mobility for Form I is about 0.25 cm\(^2\)V\(^{-1}\)s\(^{-1}\) and it is independence of the channel length. The influence of annealing treatment on the OFET performance has been investigated. Compared to the fresh made sample, the field-effect mobility of OFET annealed at 100\(^\circ\)C for 30 minutes is slightly increased by about 10\%. Prolong the annealing treatment time from 30 minutes to 90 minutes has no further contribution to the mobility increase.

![Figure 4.9: (a) Polarized optical image of a TIPS-pentacene Form I based bottom-gate/bottom-contact transistor (sample 4C1); (b) same transistor at a higher magnification.](image)
Typical transfer and output curves of a fresh made bottom-gate/bottom-contact TIPS-pentacene Form I based transistor are given in Fig. 4.11(a) and Fig. 4.11(b) respectively. Some hysteresis in the transfer curve can be seen in the fresh made transistor. After annealing for 30 min at 100°C, the $I_d$ current is slightly increased in the output curve and the hysteresis in the transfer curve becomes negligible. The threshold voltage in the transfer curve shifts from +8 V to zero. The device performance improvement after annealing is probably due to increased crystallinity and molecular ordering of the semiconductor thin film.

Figure 4.10: Effect of annealing time on the hole mobility of the bottom-gate/bottom-contact structured transistor (sample 4C1). (a) hole mobility of the as-prepared sample and after it was annealed at 100°C for 30 minutes. (b) mobility comparison after the sample was annealed at 100°C for 30 minutes and annealed at 100°C for 90 minutes.

In the bottom-gate/bottom-contact structured transistor, the averaged saturation mobility for Form I film is 0.28 cm²V⁻¹s⁻¹, which is much lower than top-gate/bottom-contact structured transistors, in which Form I film exhibits an averaged saturation mobility about 0.9 cm²V⁻¹s⁻¹. The lower mobility in the bottom-gate/bottom-contact transistor should not be caused by structural defects (grain
boundaries) since the TIPS-pentacene film used here has almost identical grain structure compared to the one we used in top-gate/bottom-contact structured transistors.

Figure 4.11: (a-b) Output and transfer curves for the fresh made bottom-gate/bottom-contact transistor (sample 4C1); (c-d) the output and transfer curve for the same transistor after annealing at 100°C for 30 min.

One of the most important parameters affecting charge transport characteristics is the transistor geometry [133]. The device geometry of OFETs can be divided into two basic categories, coplanar and staggered configurations. In a coplanar configuration, the source drain contacts and the insulator layer are on the same part of the channel. Whereas in a staggered configuration the source drain contacts and the insulator layer are on the opposite part of the channel. It is generally believed that coplanar configuration devices have higher contact resistance ($R_C$) which limits the injection of carriers into the channel and lower the field effect mobility [133]. As the bottom-gate/bottom-contact geometry belongs to coplanar configuration while the
Table 4.3: Effect of thermal annealing on the contact resistance ($R_C \cdot W$) of the sample 4C1.

<table>
<thead>
<tr>
<th></th>
<th>$V_g = -20$ V</th>
<th>$V_g = -40$ V</th>
<th>$V_g = -60$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh sample</td>
<td>3.0 $k\Omega \cdot cm$</td>
<td>1.6 $k\Omega \cdot cm$</td>
<td>1.2 $k\Omega \cdot cm$</td>
</tr>
<tr>
<td>Annealed for 10 min</td>
<td>8.2 $k\Omega \cdot cm$</td>
<td>2.1 $k\Omega \cdot cm$</td>
<td>1.3 $k\Omega \cdot cm$</td>
</tr>
<tr>
<td>Annealed for 30 min</td>
<td>17.4 $k\Omega \cdot cm$</td>
<td>3.4 $k\Omega \cdot cm$</td>
<td>1.8 $k\Omega \cdot cm$</td>
</tr>
<tr>
<td>Annealed for 90 min</td>
<td>41.0 $k\Omega \cdot cm$</td>
<td>11.0 $k\Omega \cdot cm$</td>
<td>8.0 $k\Omega \cdot cm$</td>
</tr>
</tbody>
</table>

Top-gate/bottom-contact geometry belongs to staggered configuration, we assume that the lower mobility in bottom-gate/bottom-contact TIPS-pentacene based transistor is due to large contact resistance. To check this assumption, we estimated the contact resistance using the transmission line method (TLM).

Contact resistance measurement was carried out from $I_d-V_d$ characteristics in the linear region in the output curve. The slope of linear fitting $I_d-V_d$ gives the reverse of the total resistance of the transistor ($1/R_{total}$). The total resistance $R_{total}$ of OFETs can be expressed by the following equation (the derivation of this equation can be seen in the Section 1.2 in the Chapter 1.):

$$R_{total} = R_C + \frac{L}{WC_i\mu(V_g - V_{th})} \quad (4.1)$$

In above equation, the channel width $W$ for a constant, which is 1000 $\mu$m. The $R_{total}$ can be treated as a function of channel length $L$ of the OFETs. So $R_C$ can be calculated from the intercept of axis of $R_{total}$, by varying channel lengths. Contact and total resistances are multiplied by the channel width since this is a common representation to help the general comparability of devices with different channel widths in the literature. The $R_{total} \cdot W$ for various channel length at different annealing time were plotted in Fig. 4.12 and the $R_{contact} \cdot W$ values which obtained from the
intercept of the linear fitting of $R_{total} \cdot W$ are listed in Table 4.3.

As one can see in the Fig. 4.12, the $R_C \cdot W$ (the $y$-axis intercept) only accounts for a small portion of the $R_{total} \cdot W$, i.e., the total resistance of the transistor is dominated by the channel resistance. Even after the contact resistance has increased by 10 times by annealing the transistors for 90 min (shown in Table 4.3), the total resistance is still dominated by the channel resistance (Fig. 4.12 (d)) and the field effect mobility is almost unchanged (Fig. 4.10 (b)).

In Fig. 4.12, the total resistance decreases with increasing gate voltage, likely due to the increase in carrier density in the channel and near the contacts, which has an
effect similar to contact doping [134]. We can also see the $R_C \cdot W$ decreases with increasing gate voltage in Table 4.3. This is because $R_{total} \cdot W$ is a function of the gate voltage, $R_C \cdot W$ inherits a gate voltage dependence, even if injection in itself is not gate voltage dependent [61].

Based on the discussion, the low mobility of TIPS-pentacene Form I in bottom-gate/bottom-contact geometry transistor should not be caused by contact resistance. The low mobility is probably due to the drawbacks associated with the coplanar structure itself. For example, it is reported that in the coplanar structured transistor, the current is mainly injected from the side edge the source electrode. The contact area is so small that it injects a high current density directly into the accumulation layer. In the staggered structure, the contact area is much larger, and the injection current density is significantly lower by more than 2-3 orders of magnitude. Therefore, the charge injection in the coplanar structure is more susceptible to any preexisting or stress-generated trap or defect in the semiconductor [56]. Furthermore, in the coplanar structure it is expected that there are additional defects associated with the semiconducting films covers the abrupt edge profile of the side wall where the charge injection takes place [56].

**Mobility Enhancement in Form II Phase**

In above section, we characterized the field effect mobility of Form I film in bottom-gate/bottom-contact structured transistor. To characterize the mobility of Form II phase in this structure, a Form II film was made at 130° on PTES treated wafer with PFBT treated gold patterns and then strain-stabilized to room temperature (sample 4C2). The channel length is also varied from 30 µm to 80 µm to evaluate the contact resistance using transmission line method. Its polarized optical images are shown
in Fig.4.13. There are no cracks can be seen in the film which means the Form II structure is fully strain-stabilized to room temperature. The film has large grain size along the writing direction to eliminate the limitation of grain boundaries on mobility.

![Figure 4.13: (a) Polarized optical image for a typical bottom-gate/bottom-contact structured transistor using a strain-stabilized TIPS-pentacene Form II film as active layer (sample 4C2). (b) same transistor at higher magnification](image)

The field effect hole mobilities are calculated from transfer curves in both saturation and linear region and the results are summarized in Fig. 4.14(a) for samples 4C1 and 4C2. Typical saturation transfer curves for TIPS-pentacene Form I and Form II films are shown in Fig. 4.14(c) and Fig. 4.14(d). The averaged saturation mobility ($\mu_{sat}$) for the Form I transistor is $0.28 \pm 0.02$ cm$^2$V$^{-1}$s$^{-1}$ and the averaged saturation mobility for TIPS-pentacene Form II is $0.65 \pm 0.06$ cm$^2$V$^{-1}$s$^{-1}$. The mobility does not show channel length dependence, indicating the contact resistance is still small compared to the channel resistance. The linear transfer curves for the same transistors are given in Fig. 4.14(c). For the Form I based transistor, its linear mobility ($\mu_{lin}$) is $0.22 \pm 0.02$ cm$^2$V$^{-1}$s$^{-1}$. The linear mobility ($\mu_{lin}$) for the Form II based transistor is about $0.6 \pm 0.05$ cm$^2$V$^{-1}$s$^{-1}$. Both are close to their saturation mobility ($\mu_{sat}$). Overall, the strain-stabilized Form II has a mobility that around 2.5 times higher than the Form I based transistor in the bottom-gate/bottom-contact
Figure 4.14: (a) Mobility of Form I film (sample 4C1) and strain-stabilized Form II film (sample 4C2) in bottom-gate/bottom-contact geometry structured transistor; (b) linear transfer curve for Form I and Form II based transistors with a channel length of 30 µm; (c and d) typical saturation transfer curve for Form I and Form II based transistors with a channel length of 30µm.

Besides the mobility values, we also calculated the threshold voltage ($V_{th}$), sub-threshold swing (ss swing [135]) and on/off ratio from the saturation transfer curves for sample 4C1 and 4C2. The ss swing is defined by:

$$S = \frac{dV_g}{d\log I_d}$$  \hspace{1cm} (4.2)

The ss swing is a measure of how rapidly the device switches from the off state to the on state. A ss swing that in the range of 0.5-1 dec/V is usually reported for high
Table 4.4: Electric performance of TIPS-pentacene Form I and Form II thin films (sample 4C1 and sample 4C2) in bottom-gate/bottom-contact structured transistor.

<table>
<thead>
<tr>
<th>phase</th>
<th>$\mu_{sat}$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>$\mu_{lin}$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>$V_{th}$ (V)</th>
<th>ss swing (dec/V)</th>
<th>on/off ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Form I</td>
<td>0.65 (±0.06)</td>
<td>0.60 (±0.05)</td>
<td>+1 (±2)</td>
<td>1.1 (±0.3)</td>
<td>$10^7$</td>
</tr>
<tr>
<td>Form II</td>
<td>0.26 (±0.02)</td>
<td>0.22 (±0.02)</td>
<td>-3 (±2)</td>
<td>1.0 (±0.1)</td>
<td>$10^6$</td>
</tr>
</tbody>
</table>

performance OFETs [65,135]. All the calculated parameters are summarized in Table 4.4. We can see that except for the low mobility, the bottom-gate/bottom-contact structured transistors exhibit excellent device performance including a threshold voltage that close to zero, a ss swing that is around 1 dec/V and an on/off ratio that above $10^6$. A threshold voltage that close to zero enable the transistors to turn on at small gate voltages. The high on/off ratio is due to the low leakage current of Form I and Form II based transistors which is around $10^{-10}$.

4.4 Conclusions

We characterized the TIPS-pentacene Form I and strain-stabilized Form II mobility by making bottom-gate/top-contact, top-gate/bottom-contact and bottom-gate/bottom-contact structured transistors. Our results indicate that the strain-stabilized Form II has a field effect mobility that about 3 times higher than Form I in spite of the transistor geometry we used. After optimizing the gate dielectric, contact resistance and transistor geometry, ideal I-V characteristics can be obtained by using top-gate/bottom-contact structured transistor.

A large spread of mobility values have been reported in the literature for TIPS-pentacene. For example, surprisingly high mobility has been reported for both TIPS-
pentacene Form I and Form II. The “record” highest average mobility reported for TIPS-pentacene Form I is 6.9 cm$^2$V$^{-1}$s$^{-1}$, while for Form II it is 8.1 cm$^2$V$^{-1}$s$^{-1}$ [115, 136]. However, reproducible values from different groups [32, 65, 96] suggest that the TIPS-pentacene Form I has a field effect mobility that is actually somewhat lower, in the range of 0.4-1.2 cm$^2$V$^{-1}$s$^{-1}$, which is consistent with the transient localization model [52]. It has been cautioned that overestimation of mobility could result from voltage-dependent contact resistance effects [63, 125]. In contrast, our results follow recommended best practices in the literature, such as reporting the linear mobility as the mobility of record, and ruling out gate-voltage dependence of the estimated mobility [137]. In top-gate/bottom-contact structured transistors, the average linear mobility for TIPS-pentacene Form I is 0.8 (± 0.1) cm$^2$V$^{-1}$s$^{-1}$ and for strain-stabilized TIPS-pentacene Form II is 2.6 (± 0.3) cm$^2$V$^{-1}$s$^{-1}$. 
Chapter 5

Structure-property Relationships in TIPS-pentacene Thin Films

5.1 Introduction

Two of the most critical experimentally accessible properties of small-molecule organic semiconductor materials are the charge carrier mobility and the optical absorption spectrum. A deep understanding of how the structure affects these properties is a key challenge [90, 138]. It is vital to understand the fundamental mechanisms of carrier transport in order to design new materials that will lead to high performance organic thin film transistors with faster operation and lower power consumption [57, 110, 139]. In the case of optical absorption, an understanding of how molecular interactions affecting excited states helps to provide guidance on improving the photovoltaic device’s performance as the absorption spectrum dictates the frequencies of radiation that can be absorbed that later be converted to electrical energy. In literature, the impact of molecular packing on the optical and charge transport properties are often treated...
Table 5.1: Deposition conditions of TIPS-pentacene thin films used in Chapter 5.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temp. (°C)</th>
<th>Conc. (mg/ml)</th>
<th>Speed (mm/s)</th>
<th>Substrate</th>
<th>Solvent</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5A</td>
<td>90</td>
<td>1.5</td>
<td>0.05</td>
<td>Si/SiO₂</td>
<td>Mesitylene</td>
<td>210</td>
</tr>
<tr>
<td>5B</td>
<td>25</td>
<td>44</td>
<td>0.08</td>
<td>glass</td>
<td>Toluene</td>
<td>620</td>
</tr>
<tr>
<td>5C</td>
<td>25</td>
<td>25</td>
<td>0.02</td>
<td>glass</td>
<td>Toluene</td>
<td>650</td>
</tr>
</tbody>
</table>

separately. In this chapter, we highlight the fundamental relationship between these two phenomena in TIPS-pentacene.

The structure of this chapter is as follows: In Section 5.2, we summarize the experimental details for all samples and calculation details on charge transfer integral calculation and structure optimization. In Section 5.3.1, we address the basic structural and electronic properties of TIPS-pentacene thin films. These include the crystallographic orientation of twin grains [7,140] and the directions of transition dipoles relative to the molecular axis [33,141]. Although there is existing literature on these effects, we examine them in detail in order to clarify the correct structure-property relationships. In Section 5.3.2, we show that the large thermal expansion of TIPS-pentacene modulates the charge transfer integrals and their sensitively to dynamic disorder, which explains the enhancement of the hole transport in strain-stabilized thin films as we have seen in Chapter 4. In Section 5.3.3, we show that the optical excitation energies can also be tuned by thermal expansion effects and we investigate how this is also related to the change of the theoretically-determined charge transfer integrals.
5.2 Experiments

The experimental conditions of three TIPS-pentacene thin films used in this chapter are summarized in Table 5.1. Film thickness was measured by a Dektak XT stylus profilometer. The experimental conditions for each sample are individually described below.

Sample 5A was deposited at 90°C with a low writing speed of 0.05 mm/s in order to obtain highly oriented grains. In situ microbeam grazing incidence wide-angle X-ray scattering (µGIWAXS) was carried out at the Cornell High Energy Synchrotron Source (CHESS), beamline D1. The X-ray incidence direction in each case was perpendicular to the film’s writing direction. This data was used to study the molecular orientation of the grains. Polarized optical microscopy was performed using a Zeiss microscope (Axioskop 40) after the sample was cooled to room temperature.

Sample 5B was deposited on a ultrasonically cleaned and UV-Ozone treated microscope glass slide to collect polarized absorption spectra. The film was deposited at a relatively low writing speed (0.08 mm/s) from a 44 mg/ml toluene solution to get large oriented grain size (> 100 µm). The film was relatively thick (620 nm) so that it would have strong absorbance. A schematic setup of the single-grain polarization spectroscopy is shown in Fig. 5.1(a). Briefly, the setup is as follows: a thin film on a glass substrate is placed in a temperature controlled microscope stage (Linkam THMS600) which is mounted on a rotation stage, and a fixed polarizer is placed between the light source and the sample. An optical microscope (Olympus BXFM) with an integrated UV-Vis spectrometer (Angstrom Sun Technologies Inc.) is used to acquire absorption spectra within a single grain (Fig. 5.1(b-c)). Polarized absorption
spectra were collected at each angle over the range -30° and 60° with respect to the grain boundary in order to map out the polarization dependence of the absorption along both the short and long axes of the TIPS-pentacene core.

Figure 5.1: (a) Schematic of the set up for polarized transmission spectrum collection. A polarizer is placed under a rotational sample stage and the polarization is put along the writing direction. A mirror with an aperture is inserted into the light path to select a small area of interest. (b) The polarized optical image of a sample deposited at 0.08 mm/s at 25°C on glass substrate (sample 5B). The large grain size enables us to put the transmission data collection spot in a single grain since the data collection spot is about 50 µm in diameter under 20 times magnification lens. The white arrow indicates the writing direction of the film. The angle was set to be 0° when the polarization was along the writing direction. (c) Typical polarized absorption spectra. Red: the sample was rotate by -30° to the writing direction. Green: the sample was placed at 0°. Blue: the sample was rotated by 60°.

To study the influence of the thermal expansion on the optical properties, sample 5C was deposited on a glass slide at 0.02 mm/s in order to obtain large grain size. The temperature dependence of single-grain polarized spectra were collected using the setup in Fig. 5.1. The sample was 650 nm thick. Such large thickness films can
expand and contract freely without being significantly influenced by the substrate during annealing up to 140°C and subsequent cooling. The heating and cooling rate was 2°C/min for these temperature scans, and temperature steps of 10°C were carried out. The temperature was maintained at each step for about 10 mins and polarized absorption spectra were collected at -30° and 60° with respect to the grain boundary.

The intermolecular electronic couplings between the highest occupied and lowest unoccupied molecular orbitals \((t_h \text{ and } t_e)\) of TIPS-pentacene dimers are calculated using the ADF (Amsterdam density functional) package [113]. The details are given in the Section 2.4 in Chapter 2.

![Figure 5.2](image)

*Figure 5.2: Form I full structure is obtained by single crystal X-ray scattering (left) and the Form II full structure is obtained by a combination of thin film X-ray scattering and computational structure optimization (right).*

In order to study how the molecular packing evolves from Form I to Form II, we solved the full structures of these two phases. As shown in Fig. 5.2, X-ray diffraction data were collected at 23°C for a TIPS-pentacene single crystal using a Bruker Apex II CCD single-crystal diffractometer. This data was used to obtain the
full structure of the room temperature Form I phase. The unit cell parameters of
the TIPS-pentacene high temperature phase were obtained at 134°C from the \textit{in situ}
µGIWAXS on a thin film sample (same sample used in Chapter 3, named 3A11).
We did not obtain the full structure from the X-ray data in this case since it was
not possible to measure enough reflections from the thin film to obtain a reliable
structure. Instead a geometry optimization with the lattice constants constrained to
the experimentally measured values was performed using the BAND program with
PBE functional and D3 dispersion correction with Becke-Johnson damping PBE-
D3(BJ). The TZP basis set was used in the geometry optimization.

5.3 RESULTS AND DISCUSSION

5.3.1 MOLECULAR PACKING GEOMETRY AND TRANSITION DIPOLE DIRECTIONS

In this section, we determine the crystalline orientation of aligned TIPS-pentacene
films and the directions of transition dipoles relative to the molecular axes. This
information is crucial for understanding the structure-property relationships.

\textbf{Molecular Packing Geometry}

\textit{In situ} X-ray scattering data for sample 5A is shown in Fig. 5.3(a) which was
collected at the deposition temperature. The X-ray beam direction is perpendicular
to the writing direction of our film and only (10L) and (20L) are observed, indicating
that the X-ray beam is incident at a small angle to the (100) crystalline plane. A
polarized optical image of the sample is shown in Fig. 5.3(b). The image was taken
after the sample was cooled to room temperature. Cracks that had formed during cooling are visible in the image. This sample was intentionally fabricated with a relatively large film thickness (210 nm) in order to induce cracking during the cooling process, so that we can determine the orientation of the dominant cracks. In all of our aligned TIPS-pentacene thin films, the grain boundaries of the film are parallel to the writing direction.

Figure 5.3: (a) A typical X-ray scattering image for an aligned TIPS-pentacene film deposited at 90 °C (sample 5A in Table 5.1). In situ X-ray scattering was carried out at the deposition temperature and the X-ray beam was perpendicular to the writing direction. (b) A polarized optical image of the sample taken after it was cooled to room temperature. V-shaped cracks are formed and the angle between the cracks and twin boundary is about 40°. (c) and (d) A model of twin grains formed in TIPS-pentacene thin films. The twin boundary is along a-axis which also corresponds to the pen-writing direction.
Table 5.2: Lattice constants of single TIPS-pentacene crystal at 23°C and thin films deposited at 25°C (Sample 3A1) and at 134°C (Sample 3A11).

<table>
<thead>
<tr>
<th>Phase (Temp. °C)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (deg.)</th>
<th>β (deg.)</th>
<th>γ (deg.)</th>
<th>bsinγ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk (23)</td>
<td>7.7325</td>
<td>7.7656</td>
<td>16.9395</td>
<td>88.544</td>
<td>77.922</td>
<td>82.264</td>
<td>7.6949</td>
</tr>
<tr>
<td>Thin film I (25)</td>
<td>7.78</td>
<td>7.75</td>
<td>16.70</td>
<td>89.4</td>
<td>77.9</td>
<td>81.1</td>
<td>7.66</td>
</tr>
<tr>
<td>Thin film II (134)</td>
<td>8.69</td>
<td>7.66</td>
<td>16.83</td>
<td>87.8</td>
<td>78.9</td>
<td>71.0</td>
<td>7.24</td>
</tr>
<tr>
<td>% Difference*</td>
<td>+11.7</td>
<td>-0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-5.5</td>
</tr>
</tbody>
</table>

* Difference between thin films made and measured at 134°C, and 25°C.

Table 5.3: The d-spacing difference between Form I thin Film and Form II thin Film.

<table>
<thead>
<tr>
<th>Phase (Temp. °C)</th>
<th>d_{100}</th>
<th>d_{010}</th>
<th>d_{110}</th>
<th>d_{1-10}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin film I (25)</td>
<td>7.51</td>
<td>7.65</td>
<td>5.84</td>
<td>4.99</td>
</tr>
<tr>
<td>Thin film II (134°C)</td>
<td>8.07</td>
<td>7.24</td>
<td>6.55</td>
<td>4.69</td>
</tr>
<tr>
<td>Difference</td>
<td>7.5%</td>
<td>-5.4%</td>
<td>12.2%</td>
<td>-6.0%</td>
</tr>
</tbody>
</table>

From 25°C to 134°C, the unit cell a-axis is expanded by more than 10% and the product bsinγ is reduced by more than 5%, as shown in Table 5.2. The crystallographic d-spacings for Form I and Form II structures were calculated from their unit cell parameters and the calculated d-spacings are shown in Table 5.3. As we can see, the (110) d spacing has the biggest change which indicating cracks tend to occur along (110) plane when cooling a thick high-temperature made sample to room temperature.

The molecular orientation within the grains is illustrated in Fig. 5.3(c-d) based on a model that we have proposed in previous work [7]. In this model, the grain boundaries are twins oriented along the a-axis of the unit cell. The molecular orientation within one grain can be obtained by rotating the crystal in neighboring twin by an angle of 180° about an axis perpendicular to the boundary. In Fig. 5.3(c-d), the angle between the a-axis and the long axis of the molecule is 28°(calculated using the structure file of the room temperature phase). This is consistent with Fig. 5.3(a)
that the twin boundary is along the [100] direction. This conclusion is also supported by evidence from several other groups [58,62].

The cracking pattern is another important clue to help determine the molecular orientation. The cracks are V-shaped and the angle between the cracks and grain boundary in Fig. 5.3(b) is found to be 40°, which is very close the orientation of (110) planes (see Fig. 5.3(c)). A similar orientation of cracks has previously been observed [33,140]. We find that the (110) d-spacing undergoes the largest change during cooling (Table 5.3), so the cracks tend to occur along these planes. For very thick films (not shown) cracks often occur along other directions in addition to the (110) oriented cracks [97,116,140].

\[ \text{Figure 5.4: (a): Typical single grain polarized absorption spectra when the sample is rotated from -90° to 60° respect to the twin boundary with a step of 10°. From the low energy to the high energy side, we labeled the absorption peaks as 1, 2, 3, 4, 5 and 6. (b) Schematic of TIPS-pentacene molecule structure plotted using the structure file for the room temperature phase, top view. At 0°, the twin boundary is along the polarized direction. The red arrow indicates the direction of transition dipole of peak 1. Note that its direction is in the plane of the molecule and it has a small component in the plane of the film due to the tilt of the molecule along its long axis; (c) Angle dependence of absorbance of peak 1. This sample is sample 5B in Table 5.1.} \]

**Direction of Transition Dipoles**

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We can also correlate the packing geometry with its polarization-dependent optical absorbance. Here we use single-crystalline-grain polarized absorption spectra to determine the transition dipole directions. The data collection spot is put within a single grain as shown in Fig. 5.1(b). When the polarization direction is along the twin boundary we define the angle to be $\theta = 0^\circ$. The sample is rotated in steps of $10^\circ$ to collect the polarized absorption spectra. Thirty-six polarized absorption spectra were collected in total, and ten of them are plotted in Fig. 5.4(a). The peaks are labeled as 1, 2, 3, 4, 5 and 6 starting from the long wavelength side [141]. In order to get the absorbance values of all six peaks, the data is fitted with a Lorentz oscillator model [142]. The absorbance data is fitted by the equation [143]:

$$A(\theta) = -\log_{10}(10^{-A_{\text{min}} \sin^2(\theta - \theta_0)} + 10^{-A_{\text{max}} \cos^2(\theta - \theta_0)})$$  \hspace{1cm} (5.1)

The fitting parameters $A_{\text{max}}$, $A_{\text{min}}$ and $\theta_0$ are given in Table 5.4 for all six peaks. An example of the fitted data for peak 1 is shown in Fig. 5.4(c) and the complete series is shown in Fig. 5.5. The angle $\theta_0$ is the angle that gives the maximum absorbance. We find that peak 1 becomes strongest when the rotation angle is $60^\circ$, whereas peaks 3 and 5 become strongest when the rotation angle is $-30^\circ$. As we discussed in the last section, the angle between the long axis of the molecule and the crystallographic $a$-axis is $-28^\circ$ and the angle between short axis of molecule and $a$-axis is $62^\circ$. These results indicate that the transition dipole for peak 1, which corresponds to the singlet $S_0 - S_1$ transition, is along the molecular short axis.
Table 5.4: Fitting parameters for the polarized absorption spectra of sample 5B.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Peak 1</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
<th>Peak 5</th>
<th>Peak 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position (eV)</td>
<td>Short</td>
<td>1.77</td>
<td>1.90/1.92</td>
<td>2.07/2.11</td>
<td>2.30</td>
<td>2.76</td>
</tr>
<tr>
<td>Width (eV)</td>
<td>0.118</td>
<td>0.08</td>
<td>0.269</td>
<td>0.313</td>
<td>0.143</td>
<td>0.233</td>
</tr>
<tr>
<td>(A_{min})</td>
<td>0.02</td>
<td>0.42</td>
<td>0.14</td>
<td>0.06</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>(A_{max})</td>
<td>0.55</td>
<td>0.49</td>
<td>1.09</td>
<td>0.59</td>
<td>1.12</td>
<td>1.08</td>
</tr>
<tr>
<td>(\theta_0(\degree))</td>
<td>58.6</td>
<td>59.0</td>
<td>326.2</td>
<td>331.8</td>
<td>328.3</td>
<td>328.8</td>
</tr>
</tbody>
</table>

Figure 5.5: (a-f) Polar plots of absorbance as a function of polarization angle from peak 1 to peak 6. The dashed lines are the fitting curves and the fitting results are given in Table 5.4. The fitted peak positions were given. A peak shift have been observed for peak 2 and 3 as the polarization is changed from along the short axis of the molecule to the long axis of the molecule. This sample is sample 5B in Table 5.1.

The observation that the transition dipole of peak 1 is along the short axis of the molecule can be justified from selection rules based on the symmetry of the molecular orbitals. Unsubstituted pentacene has \(D_{2h}\) symmetry and its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states.
belong to the $B_{1g}$ and $B_{2u}$ group representations respectively, as shown in Fig. 5.6. The selection rules determine that the HOMO to LUMO transition is only allowed along the short-axis for the molecule. The TIPS-pentacene molecule belongs to the lower symmetry $C_i$ point group due to the fact that it has two side groups. The side groups and the lower symmetry of the crystalline environment break the selection rule for pentacene, but this is a small perturbation that results in weak optical activity for polarization along other directions [46, 144].

In Fig. 5.5, we can see that the transition dipole of peak 1 is the only one that is along the short axis of the molecule and that the transition dipoles of peak 3-6 are along the long axis of the molecule. These peaks are enhanced relative to peak 1 since the long axis of the molecule is parallel to the plane of the thin film, while transition
dipoles along the short axis have only a small component in the plane of the film. Peak 2 doesn’t show much polarization dependence as we discuss below [141].

**Origin of the Aggregation-induced Spectral Shift**

Polarized absorption spectra along the short axis and along the long axis of molecules within a single grain are shown in Fig. 5.7. Three peaks can be observed in Fig. 5.7(a) which are labeled as peak 1, 2(S), 3(S). In Fig. 5.7(b), five peaks can be observed and are labeled as Peak 2(L), 3(L), 4, 5, 6. The absorption spectrum of a TIPS pentacene solution (0.9 mg/ml in toluene) is plotted as a dash line in Fig. 5.7. It has five absorption peaks at 643 nm, 593 nm, 550 nm, 438 nm and 415 nm. The first three peaks are the Frank-Condon series of the first excited singlet state ($S_0 - S_1$ excitation).

Returning to the description of the thin film spectra, the transition dipole of peak 1 is the only one that is found to be along the short axis of the molecule. Fig. 5.7(a) also shows that it has a large redshift relative to the solution state. Peaks 2(S) and 2(L) are very close in position and have similar absorbance magnitudes. We note that the polar plot of peak 2 shown in Fig. 5.5 is a mixture of these two, so it doesn’t exhibit much polarization dependence. Peak 3 is also a mixture of Peak 3(S) and Peak 3(L). However, since peak 3(S) has a much smaller absorbance compared to 3(L), the polar plot of peak 3 still exhibit fairly strong polarization dependence. Peaks 5 and 6 of the solid film have absorption peaks around 440 nm, very close to two corresponding peaks in solution, indicating that they probably have the same origin. Absorbance in the short-axis polarized spectrum is significantly reduced relative to the long axis spectrum. For example, the Peak 1/ Peak 5 intensity ratio is weak in the solid-film spectrum relative to the solution spectrum. This is because the tilt
angle of TIPS-pentacene molecules in the thin film is about $10^\circ$, thus the transition dipole along the short axis of the molecule only has a small component ($\sin 10^\circ$) in the plane of the thin film, causing the peak intensity to be attenuated to only $0.03 (\sin^2 10^\circ)$ of its full value.

Our experimental results are in substantial agreement with a first-principles many-body perturbation study of quasiparticle excitations based on the GW approximation by Sharifzadeh et al. [141]. They show that peak 1 (originating from state $S_1$ in their notation) couples strongly to light polarized along the molecule’s short axis and the rest of the peaks come from a combination of multiple excited states. They consider peak 2 to be caused by three nearly-degenerate states ($S_2, S_3$, and $S_4$), which result from the long-range order and $\pi$ orbital overlap in the organic crystal. Optical transitions to $S_2$ and $S_3$ have the same polarization dependence as $S_1$, while $S_4$ is exactly out of phase (this is consistent with the weak angular dependence for peak 2 in Fig. 5.5). Based on their calculations, peaks 3 and 4 in our notation come from a mixture of numerous states. This can explain why the widths of both peaks 3 and 4 are larger than the widths of peaks 1 and 2 (Table 5.4). For peaks 3 and 4 in our data, the net transition dipole moment is mainly aligned with the molecular backbone, so they both exhibit strong angular dependence and reach maximum absorbance when light is polarized along the long axis of the molecule. This detail doesn’t agree with Sharifzadeh’s calculation, which predicts that peaks 3 and 4 should be maximized when light is polarized along the short axis of the molecule [141]. Peaks 5 and 6 also have large $A_{max}/A_{min}$ ratios, which suggests that the transitions contributing to these two peaks are also mainly allowed along the long axis of the molecule, which is in agreement with Sharifzadeh’s results. [141].
In contrast to the good agreement with ab-initio calculations discussed above, we note that the prediction of the optical peak shift in solid films based on simple Coulomb coupling does not explain our experimental results for the lowest energy transition (peak 1). According to Kasha et al. [80], the Coulomb coupling \( J_{\text{Coul}} \) comes from the dipole interactions between the transition dipoles which can be estimated by a point-dipole approximation:

\[
J_{\text{Coul}} \approx \frac{\mu^2(1 - 3\cos^2\theta)}{4\pi\varepsilon R^3}
\]  

(5.2)

where \( \mu \) is the transition dipole moment, \( R \) is the intermolecular distance, \( \theta \) is the angle between \( \mu \) and \( R \) and \( \varepsilon \) is the optical dielectric constant of the medium. We note that more accurate treatments of the Coulomb coupling based on atomic transition charge densities give a qualitatively similar picture [88]. In the TIPS-pentacene
crystal, the transition dipoles along the short axis of the molecular backbone are “side-by-side” oriented (θ is about 80° for both dimer I and dimer II). Thus, peak 1 is expected to be blueshifted since $J_{\text{Coul}}$ is positive, i.e. our results show that Coulomb coupling predicts the wrong direction for the shift of peak 1 in Fig. 5.7(a).

It has been pointed out by Spano and co-workers that the intensity ratio of the lowest energy absorption peak to its first vibronic replica (0-0/0-1) is a more reliable signature of the sign and magnitude of the excitonic coupling than the peak shift since other phenomena may dominate the peak shift. Taking the $1(s)/2(s)$ ratio in Fig. 5.7 of ≈1.25 as the 0-0/0-1 ratio we see that it is significantly diminished compared to the corresponding ratio in the solution spectrum (≈2.2). A reduced ratio indicates H-type coupling ($J > 0$) in agreement with our expectation from the packing geometry. However, the magnitude of the redshift is quite large (54 nm, or in energy units 146 meV), while as we noted above there should be a blueshift for pure H-type Coulomb coupling. This contradiction can be resolved since H-type behavior in combination with a large solution to crystal redshift is a characteristic of mixing between Frenkel and charge transfer (CT) excitons in the absence of strong Coulomb coupling. [13] Although this situation may seem unnatural, such behavior has been found to be a fairly accurate description for several acenes, including tetracene and pentacene. [145] In this case, the strength of the coupling is characterized by the charge transfer coupling $J_{\text{CT}}$, with $J_{\text{CT}} > 0$ for H-type and $|J_{\text{CT}}| \gg |J_{\text{Coul}}|$.

In Section 5.3.3 we discuss how charge transfer plays a dominant role in determining the spectral shift of peak. First, in Section 5.3.2 we discuss enhancement in the hole transport.
Table 5.5: Electric performance of top-gate/bottom-contact structured TIPS-pentacene based transistors (data is reproduced from Chapter 4).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\mu_{sat}$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>$\mu_{lin}$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>$V_{th}$ (V)</th>
<th>on/off ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>4B3 (Form I)</td>
<td>0.9 ($\pm$ 0.1)</td>
<td>0.8 ($\pm$ 0.1)</td>
<td>-2 ($\pm$ 3)</td>
<td>$10^4$</td>
</tr>
<tr>
<td>4B4 (Form II)</td>
<td>2.9 ($\pm$ 0.5)</td>
<td>2.6 ($\pm$ 0.3)</td>
<td>-3 ($\pm$ 3)</td>
<td>$10^4$</td>
</tr>
</tbody>
</table>

5.3.2 Tuning the Charge Carrier Transport

In Chapter 4, we characterized TIPS-pentacene Form I and strain-stabilized Form film’s charge transport properties by using different transistor structures. Ideal I-V characteristics can be obtained by using top-gate/bottom-contact structured transistor. The device performance results of Form I and strain-stabilized Form II based transistors are listed in Table 5.5. Note that the mobilities we characterized are along the writing direction ([100] direction). From Form I to strain-stabilized Form II, the increase is about a factor of three for both linear and saturation mobility.

TIPS-pentacene has two distinct dimers with a relatively large molecular orbital overlap. Dimer I is along the [100] direction and dimer II is along the [\bar{1}10] direction. A schematic of dimer I and dimer II for TIPS-pentacene Form I and Form II are shown in Fig. 5.8(a). The charge transfer integrals in a dimer depend on the nodal structure of highest occupied and lowest unoccupied molecular orbitals and the relative displacement of neighboring molecules. Varying the temperature causes neighboring molecules to move relative to each other, leading to a large modulation of charge transport properties. We consider a dimer made of two TIPS-pentacene molecules and study the variation of the charge transfer integral when one molecule “slides” with respect to the other on parallel planes with a constant separation of 3.4 Å, which is a good approximation of the structure change at various temperatures.
from experimental results. The direction along the long axis of the molecule is defined as the $x$-axis and the direction along the short axis is defined as the $y$-axis. The map of $t_h$ and $t_e$ are shown in Fig. 5.8(c) and (d) where $t_h$ and $t_e$ are the hole and electron transfer integrals respectively.

The sign and magnitude of $t_h$ and $t_e$ are found to be highly sensitive to the relative positions of the molecules in the dimer [146]. The calculated $t_h$ and $t_e$ for the room temperature phase Form I and high temperature phase Form II are given in Table 5.6. In references, the transfer integrals in TIPS-pentacene [146,147] are usually calculated using a low temperature structure obtained at -100°C [50]. This low temperature phase has its $a$ lattice constant equal to 7.5650 Å. This parameter is different than our room temperature bulk Form I structure, which has $a = 7.7325$ Å. The $\Delta x$ and $\Delta y$ for the dimer I of the -100°C structure are 6.70 Å and 0.89 Å respectively which are slightly smaller than our Form I phase whose $\Delta x$ and $\Delta y$ are 6.86 Å and 1.03 Å respectively. Even though this low temperature structure is similar to our room temperature phase, it still leads to noticeably different charge transfer integrals. For example, the calculated $t_h$ for dimer I using our room temperature Form I phase is 2.6 meV but it is -23.5 meV for low temperature structure.

The unit cell of Form II is obtained by X-ray diffraction and the molecular packing geometry is obtained by DFT energy minimization with constrained lattice constants. From Form I to Form II, the $\Delta x$ and $\Delta y$ displacements increased for dimer I. For dimer II, the $\Delta x$ decreased while the $\Delta y$ increased. We noticed that for our geometry optimized Form II, the $\pi-\pi$ stacking distances for both dimers are still around 3.4-3.5 Å. This is different from X-ray diffraction results in the literature, which suggest that Form II dimer I has a much smaller $\pi-\pi$ stacking distance (3.23 Å) compared to the
\( \pi - \pi \) stacking distance of Form II dimer II (3.65 Å) [14]. We note that the results in the literature were based on a small number of X-ray reflections (30), which leads to larger uncertainties in the structural parameters compared to typical single-crystal X-ray results.

The large hole mobility of Form II strain stabilized thin films can be attributed to the increased hole charge transfer integral along dimer I and the reduced sensitivity of the charge transfer integral to dynamic disorder. It was reported that TIPS-pentacene has large thermal dynamic disorder due to molecular vibrations along the long axis.

**Figure 5.8**: (a): Schematic of dimer I and II for Form I; (b) Schematic of dimer I and II for Form II; (c) the map of hole charge transfer integral \( t_h \); (d) the map of electron transfer integral \( t_e \). Magenta circles are the dimer I and II positions for the Form I and green circles are the positions for the Form II.
Table 5.6: Calculated hole and electron transfer integrals.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Dimer</th>
<th>Δx (Å)</th>
<th>Δy (Å)</th>
<th>π − π (Å)</th>
<th>th (meV)</th>
<th>te (meV)</th>
<th>th + te (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>DI</td>
<td>6.86</td>
<td>1.03</td>
<td>3.41</td>
<td>2.6</td>
<td>-121.2</td>
<td>-118.6</td>
</tr>
<tr>
<td>134</td>
<td>DI</td>
<td>7.87</td>
<td>1.49</td>
<td>3.36</td>
<td>33.4</td>
<td>-0.3</td>
<td>33.1</td>
</tr>
<tr>
<td>23</td>
<td>DII</td>
<td>9.47</td>
<td>1.65</td>
<td>3.39</td>
<td>4.0</td>
<td>56.8</td>
<td>60.8</td>
</tr>
<tr>
<td>134</td>
<td>DII</td>
<td>8.68</td>
<td>1.77</td>
<td>3.52</td>
<td>5.7</td>
<td>56.4</td>
<td>62.1</td>
</tr>
</tbody>
</table>

of the molecule [15, 98]. The dynamic disorder localizes the charge carriers and is detrimental to charge transport. Based on the transient localization model, reducing the sensitivity of the charge transfer integral to the dynamic disorder or suppressing the dynamic disorder are more effective ways to improve the charge mobility than by just increasing the absolute value of charge transfer integral [52]. In Fig. 5.8(c), we can see that the \( t_h \) of Form I is highly sensitive to the molecular vibration along the long axis of the molecule since the gradient of the hole mobility along the \( x \)-direction at the magenta dot in Fig. 5.8(c) is relatively large. On the other hand, the \( t_h \) of Form II is less sensitive to thermal motion since it sits near a saddle point (green dot). Thus the increased mobility along Form II dimer I can be partially attributed to the reduced sensitivity of charge transport to dynamic lattice disorder.

To carry this discussion further, we can estimate the transient localization length of hole carriers from our experimentally measured hole mobility and compare the difference between TIPS-pentacene Form I and Form II. Based on the transient localization model, the analytical formula for the charge mobility is given by [52]:

\[
\mu = \frac{e}{k_B T} \frac{L(\tau)^2}{2\tau}
\]  

(5.3)

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( e \) is the electric charge, \( \tau \) is the fluctuation time given by the inverse of typical intermolecular oscillation fre-
quency, and \( L(\tau) \) is the transient localization length that depends on charge transfer integral and its sensitivity to thermal vibration. The fluctuation time \( \tau \) is given to be 0.15 ps for TIPS-pentacene [52]. Utilizing our experimentally measured average saturation mobility of Form I which is 0.85 cm\(^2\)V\(^{-1}\)s\(^{-1}\) one can estimate the corresponding transient localization length for Form I. The results is \( L = 8.1 \, \text{Å} \), which is only slightly larger than the lattice constant of Form I whose \( a = 7.78 \, \text{Å} \). Similarly the transient localization length for Form II is estimated as 15.0 Å for its average saturation mobility of 2.9 cm\(^2\)V\(^{-1}\)s\(^{-1}\). The suppressed transient localization length is thus attributed to both a small charge transfer integral and large sensitivity to dynamic disorder as illustrated in Fig. 5.8(c) and reported in several theoretical studies [52,148].

5.3.3 Tuning the Optical Excitation Energies

Impact of structural changes on the optical absorbance

Results of a study of the temperature dependence of absorption are shown in Fig. 5.9. The polarized absorption spectra along both the long and short axes were collected by heating a thick TIPS-pentacene film (Sample 5C). The absorption peak shift caused by the reversible temperature-dependent structure evolution is gradual and continuous. Due to the large thickness (650 nm), the film has cracks that allow it to keep adjusting to it’s equilibrium lattice constants as the temperature changes. We observe that peak 1 in Fig. 5.9(a) exhibits a total blueshift of about 25 nm between 30\(^\circ\)C and 140\(^\circ\)C (from 695 nm to 670 nm).
The large sensitivity of the peak positions to temperature is consistent with the modulation of charge transfer effects as the structure changes due to thermal expansion. We note that a theoretical study of the electron-hole correlation function for the first four excited states in crystalline TIPS-pentacene has been carried out by Sharifzadeh et al. [141] In that study, the electron-hole correlation for the low energy excitation corresponding to peak 1 is found to be mainly along the direction that corresponds to dimer I. This result helps to tie together our experimental observations, since we found in Section 6.3.2 that there is a large change in $\Delta x$ and $\Delta y$ in dimer I as the temperature is changed and these shifts produce a large modulation of the charge transfer integrals $t_e$ and $t_h$ for dimer I. In the next subsection, we discuss a semiquantitative one-dimensional (1D) model, which gives insight on how the excitation energies depend on the charge transfer integrals.
Charge transfer effect on the lowest optical excitation energy

In this section we discuss the structure sensitivity of the lowest energy optical excitation energy (peak 1). In the solid state, there are several factors that can affect the optical excitation energy including: (i) Coulombic coupling [13,80] and (ii) Frenkel/CT exciton mixing. As we have discussed above, Coulombic coupling does not explain the shift from solution to solid film. We find that it also fails the explain the temperature dependence since from Form I to Form II the Coulombic coupling is expected to be weakened as the molecular centers move further apart. This should cause peak 1 to redshift, which is inconsistent with our experimental results for the temperature dependence shown in Fig. 5.9(a).

The Frenkel/CT exciton mixing can change the lowest optical excitation energy in high mobility materials since their frontier orbitals have significant orbital overlap. This effect provides the most plausible explanation for the temperature-dependent peak shift. A simple 1D model can be used to semiquantitatively illustrate how Frenkel/CT exciton mixing affects the excitation energy. The Frenkel and CT excitons are coupled via the electron and hole transfer integrals $t_e$ and $t_h$ [81,82]. Since the CT exciton energy is typically higher than the energy of the Frenkel exciton, $E_{CT}$ will be repelled upward and $E_F$ with be repelled downward by an amount governed by $|t_h + t_e|$ [13,94]. The energies of the coupled Frenkel state ($E_-$) and the CT exciton state ($E_+$) can be expressed as [13]:

$$E_{\pm} = \frac{E_{CT} + E_F}{2} \pm \sqrt{\left(\frac{E_{CT} - E_F}{2}\right)^2 + 2(t_e + t_h)^2}$$

(5.4)

As only the Frenkel-like energy level $E_-$ contains significant oscillator strength, Frenkel/CT mixing causes a redshift of the excitation energy. [13,82] Table 3 shows
that from Form I to Form II, \( t_h + t_e \) changes significantly from -118 meV to 33 meV for dimer I, but is almost unchanged for dimer II, as is plotted in Fig. 5.10(a). We assume that changes in \( \Delta x \) and \( \Delta y \) are linear as the temperature increases so we can calculate the temperature dependence of \( t_h + t_e \). The \( E_\perp \) is calculated using Eq. 5.4 with estimated \( E_{CT} = 2.10 \) eV and \( E_F = 1.87 \) eV and compared with our experimental data, as shown in Fig. 5.10(b). We see that the model significantly overshoots, particularly in the temperature range where \( t_e + t_h \) for dimer I is close to zero (\( E_\perp = E_F \) when \( t_e + t_h = 0 \)). Therefore, the data suggests that charge transfer along dimer II cannot be neglected. For simplicity, in the model shown in Fig. 5.10(b) we have also neglected polarization energy changes resulting from the temperature dependence of the molecular separation. However, the modulation of \( E_\perp \) through this mechanism is modest compared to that produced by the variation of \( |t_e + t_h| \).

Figure 5.10: (a) The change of \( t_h + t_e \) for TIPS-pentacene Dimer I and Dimer II as the structure changes from Form I to Form II. (b) the optical bandgap shift of peak 1 vs. thermally-driven structure evolution. The blue squares are the experimental data (sample 5C) and the black curve is based on the 1D Frenkel/CT exciton mixing model using \( t_h + t_e \) for dimer I only. (c) The temperature dependence of peak 3 (L) intensity on linear scale \( I/I_0 \).

A consequence of this model is that \( J_{CT} \) can be positive or negative depending on the signs of \( t_e t_h \) and \( E_{CT} - E_F \). In the limit \( |E_{CT} - E_F| \gg |t_e|, |t_h| \), it takes the simple
form \( J_{CT} = -2t_e t_h / (E_{CT} - E_F) \). [13, 82, 95, 149] Assuming \( E_{CT} > E_F \), the coupling is H-like when \( t_e t_h \) is negative, i.e. \( J_{CT} \) is positive. We can see in Table 5.6 that \( t_e \) and \( t_h \) have opposite signs for dimer I, which reinforces our experimental results that are consistent with \( J_{CT} > 0 \).

![Figure 5.11: Polarized spectra of sample 5C were collected during two heating-cooling cycles. (a): Peak 1 position vs. temperature; (b): Peak 3 position vs. temperature; (c) Peak 5 vs. temperature. The peak position of peak 1 were obtained when the sample was rotated by 60° (polarization direction is along the short axis of the molecule) and the peak position of 3 and 5 were obtained when the sample was rotated by -30° (polarization direction is along the long axis of the molecule). Due to its large thickness, cracks almost formed immediately during heating.](image)

The 1(s)/2(s) peak ratio changes significantly as a function of temperature in Fig. 5.9(a). Since the ratio is reduced as the temperature increases, the theory of Spano and co-workers predicts that the exciton bandwidth increases. [149] However, this intensity ratio change should be interpreted with caution since Sharifzadeh et al. find that peak 2(s) is unlikely to be solely the results of a vibronic progression. [141] Rather, there may be two other electronic excitations with the same polarization and at nearly the same wavelength. Thus, a bandwidth extracted from the 1(s)/2(s) ratio may be highly overestimated. We have argued in Section 5.3.1 that the reduced 0-0/0-
A ratio of $\approx 1.25$ is qualitatively consistent with H-type coupling. However, here we use an alternative method to obtain a quantitative estimate of the exciton bandwidth using the values of $E_{\text{CT}}$, $E_F$, $t_e$ and $t_h$ from our model and a generalized wavevector-dependent form of Eq. 5.4. [13,149] The result is that the exciton bandwidth is on the order of 10 meV for both Form I and Form II. We note that this approach suggests that the maximum dispersion switches from the direction of dimer I for Form I, to the direction of dimer II for Form II and that it becomes J-like ($J_{\text{CT}} < 0$).

**Temperature dependence of higher energy excitations**

In addition to the large peak shift of peak 1, Fig.5.10(c) shows a dramatic change is observed in the intensity $I$ of Peak 3(L) normalized to the incident light intensity $I_0$ as the temperature increases. The peak intensity ratio $I/I_0$ increases by a factor of 2.2, as shown in Fig.5.10(c) and the absorption maximum is blueshifted from 585 nm (2.120 eV) to 576 nm (2.153 eV) (see Fig. 5.11(b)). The results shown in Fig. 5.7 show that the Peak 3(L) does not occur for TIPS-pentacene monomers in solution, rather it is related to crystallization. Both its peak energy and peak intensity are determined by intermolecular interactions that are sensitive to thermal expansion effects. Peak 2(L) also exhibits significant temperature dependence, although it is not clear whether it is predominantly a change of intensity or wavelength.

## 5.4 Discussion

The $\pi-\pi$ stacking distance in molecular crystals is determined by attractive van der Waals binding in the dimer, balanced with electrostatics and exchange repulsion interactions. Since these forces are supersensitive to the molecular separation distance,
the $\pi$-$\pi$ stacking distance in $\pi$ conjugated materials tend to maintain at a constant value 3.4-3.5 Å, consistent with our experimental results. This places us in a position to discuss how the TIPS-pentacene crystals mechanically respond to changes in temperature or to mechanical strain.

In the literature, it is reported that compressive strain along the $\pi$-$\pi$ stacking distance reduces the molecular center-to-center distance thus enhance the charge transport [150]. However, our results indicates that $\pi$-$\pi$ stacking distance is nearly independent on the molecular center-to-center distance. It is likely that this same behavior can also take place when introducing strain on a crystal. For flat molecules packed in a brickwall stacking, molecules in a dimer should rotate under strain to keep a constant $\pi$-$\pi$ stacking distance as they are either stretched or compressed along a particular crystallographic direction. Thus, we predict that counterintuitively, tensile strain can increase charge mobility as long as relative the molecular positions move towards larger charge transfer integrals or towards reduced sensitivity to dynamic disorder (or both, as we observed in Fig. 5.8).

For Form I, the transient localization length is estimated to be only slightly larger than the molecular spacing in the dimer, indicating the field effect mobility is consistent with localized charge carriers. On the other hand for Form II the transient localization length is nearly doubled, thus the charge carriers could be mainly delocalized. These results predict that the Hall effect mobility for Form II will be close to its field effect mobility since the delocalized charge carriers can couple to the magnetic field through a Lorentz force equation. In contrast, for Form I, the Hall effect mobility has been found to be much smaller than its field effect mobility, which was attributed to charge carriers being too strongly localized to contribute to a Hall voltage [72].
In this chapter, our main achievement is that we have established reliable structure-property relationships for TIPS-pentacene thin films based on our results on TIPS-pentacene molecular orientation, transition dipoles direction and the field effect mobility characterization. Establishing clear structure-property relationships for TIPS-pentacene is challenging, and we have noticed that there are many disagreements and even contradictory results reported in the literature. Several of these issues include:

1) Multiple groups [140,151] have reported that the twin boundary of TIPS-pentacene twin grains is along [210] direction but our previous report [7] and others [58,62] have found that the boundary is along the [100] direction. It is not yet clear whether these differences are a result of different thin film deposition methods, or due to spurious results in the literature.

2) Experimental reports in the literature [33] find that the lowest energy absorption peak of TIPS-pentacene has its transition dipole along the long axis of the molecule, while a theoretical study [141] finds that the transition dipole of lowest energy absorption peak is along the short axis of the molecule. Our results clearly favor the latter finding.

5.5 Conclusions

In this chapter, we have clarified several questions related to the TIPS-pentacene molecular packing and transition dipole directions and we have described how the structure sensitivity of charge carrier mobility and low energy optical excitations are both essentially determined by the change of the magnitude of charge transfer integrals and their gradient with respect to molecular displacement in the crystal. The hole mobility of strain-stabilized Form II TIPS-pentacene is about three times higher.
than Form I due to the increased magnitude of the hole transfer integral and reduced sensitivity to dynamic disorder. This is a general approach to improve mobility by tuning the molecular positions in the solid towards positions where charge transfer integrals are large and insensitive to the molecular thermal vibrations. We anticipate that this approach can be applied to many other organic semiconductors to improve their charge carrier mobility since their structures can be tuned by a combination of thermal expansion and mechanical strain. We have also determined that the thermal expansion effect in TIPS-pentacene causes the molecules in the dimers to “slide” with respect to each other while maintaining an almost constant $\pi - \pi$ stacking distance. As a result, hole transfer is enhanced even though the molecular centers move further apart during thermal expansion, and the lowest energy absorption peak of TIPS-pentacene is blueshifted in Form II due to Frenkel/CT exciton mixing. The links between optical excitation and carrier transport via charge transfer integrals highlight the combination of structural, electronic and optical measurements with first principles theory as a powerful toolset to monitor and predict the properties of strain-engineered materials with improved carrier mobility or desirable optical properties.

Contents of this chapter is published in:

Chapter 6

Emission Quench in TIPS-pentacene Solutions and PS:TP Blend Films

6.1 Introduction

In the crystalline state, organic molecules pack densely and periodically, which facilitate attractive and noncovalent interactions between aromatic molecules (refer to as \( \pi-\pi \) stacking). The strong \( \pi-\pi \) interactions not only affect the charge transport and optical absorbance properties in organic thin films (as we have discussed in Chapter 5), but also contribute to some interesting phenomena like fluorescence quenching. For example, many organic semiconductors like TIPS-pentacene demonstrate strong emission in dilute solutions but very weak emission in crystalline films [152, 153].

Generally speaking, molecules that have face-to-face type packing in the solid films or aggregates can lead to emission quench [86, 154–156]. This phenomenon can be interpreted by a simple dimer model based on exciton theory [80]. In a dimer, the transition dipole interaction gives rise to two exciton states. When the transition
dipoles have face-to-face packing geometry, the out-of-phase dipole arrangement cor-
responds to a lower energy exciton state and in-phase dipole arrangement corresponds
to a higher energy exciton state. As the transition moment is given by the vector
sum of the individual transition dipole moments, only the absorption to the upper
exciton state is allowed. Subsequent rapid internal conversion from the upper ex-
citon state to the lower exciton state will quench the fluorescence from the upper
exciton state to the ground state. As radiative transitions from the lower exciton
state to the ground state are formally forbidden [80], the radiationless intersystem
crossing process is expected to lead to highly efficient triplet excitation in the dimer.
Other distinct mechanisms can also result in reduced emission like fission of a singlet
exciton to give two non-emissive triplets [157,158] and exciton quenching on defect
sites [159,160].

In this chapter, we will focus on study the emission properties of TIPS-pentacene
solutions and polystyrene(PS):TIPS-pentacene(TP): blend films. TIPS-pentacene is
well-known singlet fission material as the energy of its triplet states ($T_1$) is smaller
than half of the energy of its singlet states ($S_1$). TIPS-pentacene has already been
found to undergo exothermic singlet fission in concentrated solutions, nanoparticles
and crystalline films based on transient absorption spectroscopy studies [16,100,161,
162].

We have discovered a new way to get strong emission by blending it into polymer
thin films. In this chapter we describe an experiment to systematically increase
the concentration of TIPS-pentacene in both solutions and blend films to decrease
the average spacing between TIPS-pentacene molecules and studied its impact on
emission property.
6.2 Experiments

A series of TIPS-pentacene solutions (samples 6A1-6A10) were made to study the effect of concentration on emission property. The mean molecular spacing $R$ in a
solution is estimated by following equation:

\[ R = \left[ \frac{1}{N_A C} \right]^{1/3} \]  

(6.1)

where \( N_A \) is Avogadro’s number, and \( C \) is the molar concentration with a unit of mol/L. The change of mean intermolecular spacing \( (R) \) vs. concentration is given in Table 6.1. Toluene was used as solvent and the solutions were spontaneously fed into a round glass capillary with a diameter of 1 mm by capillary effect. The capillary was then placed on a Si wafer for photoluminescence (PL) spectra collection.

The experimental setup for PL spectra collection is shown in Fig. 6.1. A Zeiss microscope (Axioskop 40) equipped with a spectrometer was used to collect the PL images and PL spectra. A Zeiss filter Set 15 TRITC is placed in the light path which has three components: an excitation filter (BP 546/12), a dichroic beam splitter (FT 580) and an emission filter (LP 590). The excitation filter is used for selection of the excitation wavelength whose center wavelength is 546 nm with bandwidth of 12 nm from a light source. We used strong illuminating light so individual TIPS-pentacene molecule is more likely to collide with a photon and get excited. As the intensity of illuminating light is much higher than the emitted light from the sample, a filter has to be used to block out the illuminating light while letting the light with a wavelength larger than 590 nm pass through. This filter is referred to the emission filter in the Fig. 6.1(a). A mirror with an aperture is inserted into the light path above the filter to select a small area of interest. A typical PL microscope image of a dilute TIPS-pentacene solution (sample 6A4) is shown in Fig. 6.1(b) and its typical PL spectrum is shown in Fig. 6.1(c).

The experimental conditions of blend films made on Si substrates are summarized
Table 6.1: Mean molecular spacing $R$ in TIPS-pentacene solutions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc.(mol/L)</th>
<th>$R$ (nm)</th>
<th>Sample</th>
<th>Conc.(mol/L)</th>
<th>$R$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6A1</td>
<td>2*10^{-5}</td>
<td>44</td>
<td>6A6</td>
<td>1*10^{-3}</td>
<td>12</td>
</tr>
<tr>
<td>6A2</td>
<td>5*10^{-5}</td>
<td>32</td>
<td>6A7</td>
<td>2*10^{-3}</td>
<td>9.4</td>
</tr>
<tr>
<td>6A3</td>
<td>1*10^{-4}</td>
<td>26</td>
<td>6A8</td>
<td>5*10^{-3}</td>
<td>6.9</td>
</tr>
<tr>
<td>6A4</td>
<td>2.5*10^{-4}</td>
<td>19</td>
<td>6A9</td>
<td>1*10^{-2}</td>
<td>5.5</td>
</tr>
<tr>
<td>6A5</td>
<td>5*10^{-4}</td>
<td>15</td>
<td>6A10</td>
<td>4*10^{-2}</td>
<td>3.5</td>
</tr>
</tbody>
</table>

in Table 6.2. Pen writing method can be used to produce a PS:TP blend film (sample 6B1) with a thickness below 1 µm. As one can see in Fig. 6.2, the sample 6B1 with a PS:TP ratio of 100:1 gave strong red emission that can be seen by naked eye. As the signal is not strong enough to be detected using our setup (Fig. 6.1 (a)), drop casting was used to produce thicker PS:TP blend films. To study the effect of PS concentration on the film thickness and uniformity, two samples (sample 6B2 and sample 6B3) were drop cast from a blended solution in which PS to TP mass ratio was 100:1 but the PS concentration was increased from 30 mg/ml to 200 mg/ml.

To study the effect of PS:TP mass ratio on the emission property of blend films, a batch of samples (samples 6C1-6C8) were drop cast from PS:TP solutions in which the PS to TP weight ratio was varied from 500:1 to 5:1 while the PS concentration was fixed at 200 mg/ml. The deposition process is straightforward: a 0.05 ml PS:TP blend solution was dropped onto a UV-Ozone treated Si wafer and let it dry in the air. The mean intermolecular distance $R$ between TIPS-pentacene molecules in a PS:TP blend film is estimated by using following equation:

$$R = \left[\frac{M c}{N_A \rho_m}\right]^{1/3} \quad (6.2)$$

where $\rho_m$ is the mass density of the PS, which is 1.06 g/cm$^3$, $M$ is the molar mass of
the TIPS-pentacene, which is 639 g/mol, $N_A$ is Avogadro's number, and $c$ is the PS to TP mass ratio.

Figure 6.2: (a) and (b): molecular structure of TP and PS. (c) Bright red emission of a PS:TP blend film (sample 6B1) with a mass ratio of 100:1 is easily visible to naked eye. The film thickness is 500 nm. The film was deposited at room temperature with a speed of 25 mm/s by the pen writing method. Toluene was used as solvent. The PS and TP concentrations were 100 mg/ml and 1 mg/ml respectively.

The thickness dependent emission property of blend films was studied by making another batch of samples on glass slides (samples 6D1-6D4). The experimental conditions for this batch are summarized in Table 6.3. The PS concentration was 400 mg/ml and TIPS-pentacene concentration was 20 mg/ml, i.e., the PS:TP mass ratio was fixed at 20:1 for all four samples. During each spin coating process, a 0.1 ml blend solution was dropped onto an ultrasonically cleaned glass slide. The spin coating speed was varied from 0 rpm (i.e., drop coating) to 2000 rpm to make films with different thicknesses. The PL spectra of the blend films were collected using the same setup.
Table 6.2: Experimental conditions of PS:TP blend films deposited on Si wafers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate</th>
<th>Method</th>
<th>PS Conc. mg/ml</th>
<th>PS:TP</th>
<th>Mean spacing (R) nm</th>
<th>Thickness µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>6B1</td>
<td>Si</td>
<td>Pen writing</td>
<td>30</td>
<td>100:1</td>
<td>4.6</td>
<td>0.5</td>
</tr>
<tr>
<td>6B2</td>
<td>Si</td>
<td>Drop casting</td>
<td>30</td>
<td>100:1</td>
<td>4.6</td>
<td>1.0</td>
</tr>
<tr>
<td>6B3</td>
<td>Si</td>
<td>Drop casting</td>
<td>200</td>
<td>100:1</td>
<td>4.6</td>
<td>6.5</td>
</tr>
<tr>
<td>6C1</td>
<td>Si</td>
<td>Drop casting</td>
<td>200</td>
<td>500:1</td>
<td>7.9</td>
<td>6.0</td>
</tr>
<tr>
<td>6C2</td>
<td>Si</td>
<td>Drop casting</td>
<td>200</td>
<td>200:1</td>
<td>5.9</td>
<td>8.0</td>
</tr>
<tr>
<td>6C3</td>
<td>Si</td>
<td>Drop casting</td>
<td>200</td>
<td>100:1</td>
<td>4.6</td>
<td>6.3</td>
</tr>
<tr>
<td>6C4</td>
<td>Si</td>
<td>Drop casting</td>
<td>200</td>
<td>50:1</td>
<td>3.7</td>
<td>8.1</td>
</tr>
<tr>
<td>6C5</td>
<td>Si</td>
<td>Drop casting</td>
<td>200</td>
<td>20:1</td>
<td>2.7</td>
<td>9.0</td>
</tr>
<tr>
<td>6C6</td>
<td>Si</td>
<td>Drop casting</td>
<td>200</td>
<td>15:1</td>
<td>2.5</td>
<td>8.7</td>
</tr>
<tr>
<td>6C7</td>
<td>Si</td>
<td>Drop casting</td>
<td>200</td>
<td>10:1</td>
<td>phase separation</td>
<td>7.5</td>
</tr>
<tr>
<td>6C8</td>
<td>Si</td>
<td>Drop casting</td>
<td>200</td>
<td>5:1</td>
<td>phase separation</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Table 6.3: Experimental conditions of PS:TP blend films made on glass slides.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate</th>
<th>PS Conc. mg/ml</th>
<th>Method</th>
<th>Speed rpm</th>
<th>PS:TP</th>
<th>R nm</th>
<th>Thickness µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>6D1</td>
<td>glass</td>
<td>400</td>
<td>Drop casting</td>
<td>-</td>
<td>20:1</td>
<td>2.7</td>
<td>34</td>
</tr>
<tr>
<td>6D2</td>
<td>glass</td>
<td>400</td>
<td>Spin coating</td>
<td>100</td>
<td>20:1</td>
<td>2.7</td>
<td>13</td>
</tr>
<tr>
<td>6D3</td>
<td>glass</td>
<td>400</td>
<td>Spin coating</td>
<td>500</td>
<td>20:1</td>
<td>2.7</td>
<td>2.8</td>
</tr>
<tr>
<td>6D4</td>
<td>glass</td>
<td>400</td>
<td>Spin coating</td>
<td>2000</td>
<td>20:1</td>
<td>2.7</td>
<td>1.5</td>
</tr>
</tbody>
</table>

that shown in Fig. 6.1. The thicknesses of all blend films were measured by a Dektak XT stylus profilometer. The absorbance spectra of blend films made on glass sides (samples 6D1-6D4) were measured by a Cary 300 UV-visible spectrophotometer.

Time-resolved photoluminescence spectroscopy (TRPL) is an important technique as it provides both spectral and temporal evolution of the emission of a material after an excitation by a laser pulse. Time correlated single photon counting (TCSPC) mode is chosen to record the decay profiles of the fluorescence lifetime of PS:TP blend films.
6.3 RESULTS AND DISCUSSION

6.3.1 EMISSION QUENCH IN TIPS-PENTACENE SOLUTIONS

The effect of TIPS-pentacene concentration on the absorption and emission properties is shown in Fig. 6.3. Adsorption spectra and PL spectra were collected at room temperature for TIPS-pentacene solutions at a low concentration of $2.5 \times 10^{-4}$ mol/L (sample 6A4) and a higher concentration of $5 \times 10^{-3}$ mol/L (sample 6A8). As we have discussed in Chapter 5, the absorption spectra of TIPS-pentacene solutions show typical oligoacene vibronic structure with three peaks centered at 643 nm (0-0), 593 nm (0-1) and 550 nm (0-2). These three absorption peaks correspond to excitation energies at 1.93 eV, 2.09 eV and 2.25 eV respectively. The energy difference between 0-0 and 0-1 and energy difference between 0-1 and 0-2 are both 0.16 eV. This value agrees well with the C-C stretch mode (0.17 eV) along the short axis of TIPS-pentacene molecule [33, 163].

In the emission spectra, it is reasonable to label $E_1$ peak and $E_2$ peak as the vibrational series. This is based on the fact that the $E_1$ and $E_2$ peaks of a dilute TIPS-pentacene solution are centered at around 651 nm and 710 nm respectively. These two peaks have an energy separation of 0.16 eV, which in good agreement with the energy difference between the vibronic peaks in the absorption spectra, i.e. the PL spectrum exhibits a vibronic structure that complements the structure in the absorption spectrum.
Figure 6.3: Absorption (solid line) and photoluminescence (dashed line) spectra of TIPS-pentacene in toluene with a concentration of $2.5 \times 10^{-4}$ mol/L (sample 6A4, red) and $5 \times 10^{-3}$ mol/L (sample 6A8, blue). The emission spectra were taken by putting the solutions into round glass capillaries with a diameter of 1 mm. The absorption spectra were taken by putting the solutions into glass bottles with a diameter of 1 cm. The two emission spectra are on the same scale. The absorbance of the blue curve is divided by 20.

In TIPS-pentacene solutions the maximum absorption at 643 nm corresponds to the $S_0$-$S_1$ transition of TIPS-pentacene monomers. For organic molecules, when the excitation light is absorbed, it excites electrons to a higher-energy state. The electrons remain in the excited states for about $10^{-8}$ seconds for monomers and it is known as the fluorescence lifetime. The excited molecule loses a small amount of energy via vibrational relaxation before the energy emits and molecule returns to the ground state. Therefore the emission peak is generally redshifted compared to corresponding absorption peak. Based on above discussion, the fluorescence intensity of the transition at 653 nm ($E_1$ peak) can be assigned to $S_1$-$S_0$ transition and the 0.03 eV difference between absorption $A_{0-0}$ peak and emission $E_1$ peak is the so-called Stokes shift that primarily results from vibrational relaxation or dissipation.
and solvent reorganization.

Figure 6.4: PL spectra of TIPS-pentacene solutions (samples 6A1-6A10) as the concentration increased from $2 \times 10^{-5}$ mol/L to $4 \times 10^{-2}$ mol/L.

No absorption peak shift can be observed as the concentration changed from $2.5 \times 10^{-4}$ mol/L to $5 \times 10^{-3}$ mol/L. In fact, we collected absorption spectra for TIPS-pentacene solutions when the concentration was increased from $1 \times 10^{-6}$ mol/L to $4 \times 10^{-2}$ mol/L (data is not shown here) but no absorption peak shift was observed in this wide range. This result indicates that there is no formation of strongly coupled aggregates in the solution, even at a concentration ($4 \times 10^{-2}$ mol/L) that is near the saturation point of TIPS-pentacene in toluene ($9 \times 10^{-2}$ mol/L). On the contrary, the emission property of TIPS-pentacene solution is heavily concentration dependent. As shown in Fig. 6.3, the prevailing $E_1$ peak in PL spectra shows a trend of red shift and
an intensity decreasing relative the $E_2$ as the concentration when the concentration increases from $2.5 \times 10^{-4}$ mol/L to $5 \times 10^{-3}$ mol/L. These results are consistent with the results reported in literature [16,164]. The concentration dependence of $E_1$ peak position and $E_1/E_2$ intensity ratio in the PL spectra are caused by a self-absorption effect because the $E_1$ peak of the fluorescence spectrum significantly overlaps the $A_{0-0}$ peak in the absorption spectrum [165], as one can seen in Fig. 6.3.

![PL microscope images of TIPS-pentacene solutions (samples 6A1-6A10) when the concentration increased from $2 \times 10^{-5}$ mol/L to $4 \times 10^{-2}$ mol/L.](image)

Figure 6.5: PL microscope images of TIPS-pentacene solutions (samples 6A1-6A10) when the concentration increased from $2 \times 10^{-5}$ mol/L to $4 \times 10^{-2}$ mol/L.

The evolution of fluorescence emission intensity as a function of TIPS-pentacene concentration in toluene was performed by successive dilution of a $4 \times 10^{-2}$ solution with solvent. The PL spectra and PL microscope images were given in Fig. 6.4 and
Fig. 6.5 respectively. The $E_1$ and $E_2$ intensity change versus concentration are plotted in Fig. 6.6. When the concentration is below $1 \times 10^{-3}$ mol/L, the intensities of $E_1$ and $E_2$ increase as increasing TIPS-pentacene concentration. This arises from the fact that the number of emitting TIPS-pentacene monomers is proportional to the TIPS-pentacene concentration. The PL intensity of $E_2$ starts to decrease when the concentration is above $2 \times 10^{-3}$ mol/L, corresponds to a mean molecular spacing $R$ of 9.4 nm ($E_2$ intensity is used here as it is less sensitive to the self-absorption effect compared to $E_1$).

![Figure 6.6: (a) the $E_1$ and $E_2$ positions vs. concentration. (b) the peak ratio change vs. concentration. (c) $E_1$ intensity vs. concentration. (d) $E_2$ intensity vs. concentration. The spectra data is given in Fig. 6.4. The samples are 6A1-6A10 in Fig. 6.4.](image-url)
In literature, the emission quench of TIPS-pentacene solution is attributed to strongly coupled aggregates formation [164] so the radiative transitions from the exciton state to the ground state are formally forbidden [80] or the singlet fission process which provides a competing nonradiative pathway for the decay of singlet excitons [16]. As we observe neither an aggregation-induced absorption peak shift or an absorption peak ratio change in Fig. 6.3, we infer that strongly coupled aggregates are not formed in concentrated solutions. It is reported that TIPS-pentacene triplet states are produced in chloroform solutions when the mean intermolecular spacing $R$ is around 10 nm, and that a triplet yield of 200% can be achieved when $R$ is reduced to 3.5 nm [16]. These results are in good agreement with our observations in TIPS-pentacene solutions using toluene as solvent. It can be seen in Fig. 6.6 that $E_2$ starts to decrease when $R$ is 9.4 nm and the emission is almost fully quenched when $R$ is decreased to 3.5 nm. These observations indicate that TIPS-pentacene solutions exhibit almost identical concentration quenching effect independent of the solvent. The singlet fission has been proposed to be the main reason for the emission quench in concentrated TIPS-pentacene solutions, which is shown in Fig. 6.7.

![Proposed singlet fission process in concentrated TIPS-pentacene solutions. Red solid arrow is the allowed optical transition and dashed arrows are non-radiative decays. The $k_{nr}$ stands for the rate constant of the non-radiative process and $k_r$ stands for the radiative rate constant](image)

Figure 6.7: Proposed singlet fission process in concentrated TIPS-pentacene solutions. Red solid arrow is the allowed optical transition and dashed arrows are non-radiative decays. The $k_{nr}$ stands for the rate constant of the non-radiative process and $k_r$ stands for the radiative rate constant.
Spectroscopic studies have demonstrated that singlet fission forms proximal, spin-correlated triplet pair intermediates $^1(TT)$ on the hundreds of femtosecond time scale and the single fission process takes place via involvement of following sequence of intermediates [166–168]:

$$S_1 + S_0 \rightarrow^1 (TT) \leftrightharpoons ^1 (T...T) \leftrightharpoons T_1 + T_1$$

(6.3)

where the symbols $^1(TT)$ and $^1(T...T)$ are used to describe correlated triplet pair and separated triplet pair respectively. The separated triplet pairs is the product of the dissociation or spatial separation of the correlated triplet pairs.

As singlet fission process involves two molecules and the mean intermolecular spacing values ($R$) in our concentrated solutions ($\geq 3.5$ nm) are much larger than the unit cell length of TIPS-pentacene solid film (about 0.8 nm), the singlet fission process in solution occurs via diffusion [16]: the excited TIPS-pentacene molecules diffuse around to find a ground state molecule then decay by forming two triplet states. As triplets states are dark states, this singlet fission process causes the emission quench of concentrated TIPS-pentacene solution. As the singlet fission in solution is a diffusion limited process, its efficiency is expected to be enhanced as $R$ decreases, which explains continuous emission intensity decrease as the $R$ reduces from 9.4 nm to 3.5 nm (Fig. 6.6 (d)).

6.3.2 EMISSION QUENCH IN PS:TP BLEND FILMS

The emission quench in TIPS-pentacene solutions has been discussed in last section. In this part, we focus on study the emission property of polymer: TIPS-pentacene
blend films. It is a very interesting system because embedding singlet fission materials in a polymer matrix could be useful to integrate singlet fission into photovoltaic devices. We used polystyrene (PS) as host matrix since it has excellent solubility in toluene (maximum solubility is 600 mg/ml at 25°C).

![Figure 6.8](image)

*Figure 6.8: (a) PS:TP blend film drop casted from a toluene solution in which PS concentration is 30 mg/ml (sample 6B2). TIPS-pentacene concentration is 0.3 mg/ml so the mass ratio of PS:TP is 100:1). (b) PS:TP blend film drop casted from a toluene solution where the PS concentration is 200 mg/ml (sample 6B3). The TIPS-pentacene concentration is 2 mg/ml so the PS:TP mass ratio is 1:100. (c-d) Height profile of the films in (a) and (b).*

We used drop casting to produce thick PS:TP blend films to ensure we can collect a strong signal using our experimental setup (Fig. 6.1). The images of drop-cast films are shown in Fig. 6.8. If we use a PS solution with a low concentration such as 30 mg/ml (sample 6B2), we observe the droplet spreading until a maximum radius
is achieved. Subsequently, a stick-slip motion \cite{169} is observed at the contact line during the drying, leaving a non-uniform film (Fig. 6.8(a, c)). However, if the PS concentration is increased to 200 mg/ml (sample 6B3), the contact line is pinned during the drying process due to the high viscosity of the PS concentrated solution, leaving a uniform film, except that a thick rim forms at the edge due to the coffee stain effect \cite{169}, as shown in Fig. 6.8(b, d).

Figure 6.9: (a) Polarized optical image of PS:TP blend film with a ratio of 10:1 (sample 6C7). (b) Polarized optical image of PS:TP blend film with a ratio of 5:1 (sample 6C8).

A batch of samples with different concentrations of TIPS-pentacene in host PS polymer were prepared (samples 6C1-6C8). All film thicknesses are about 10 µm. The PS:TP mass ratio is varied from 500:1 to 5:1. We notice that the solid solubility of TIPS-pentacene in PS is about 1:15. As shown in Fig. 6.9, small TIPS-pentacene crystalline grains precipitate out when the PS:TP mass ratio is 10:1 (sample 6C7) and a continuous TIPS-pentacene film forms when the PS:TP mass ratio reaches 5:1 (sample 6C8). It is reported that small molecules with lower solubility, lower surface energy and lower molecular weight than polymer matrix are preferentially nucleate and growth at the air film interface, leading to a vertically phase-separated structure \cite{170,171}. Thus the TIPS-pentacene layer in Fig. 6.9 (b) is expected to
be on top of a PS layer rather than beneath it. The average molecular distance $R$ between TIPS-pentacene molecules is decreased from 7.9 nm to 2.5 nm as decreasing the PS:TP mass ratio from 500:1 to 15:1.

Figure 6.10: (a) PL spectra of PS:TP films drop casted from solutions with different PS:TP ratios (samples 6C1-6C7). The PS concentration is fixed at 200 mg/ml. The PS:TP mass ratio varied from 500:1 to 5:1. (b) the peak ratio vs PS:TP mass ratio. (c-d) the $E_1$ and $E_2$ intensity vs. PS:TP mass ratio.

The evolution of the fluorescence emission intensity as a function of PS:TP ratio is given in Fig. 6.10. The emission peaks centered around 653 nm ($E_1$) and 710 nm ($E_2$) have the same peak positions compared to TIPS-pentacene solution. The emission
intensity first increases when the PS:TP ratio decreases from 500:1 to 200:1 and then start to quench when the ratio is below 200:1 (corresponds to a $R$ smaller than 5.9 nm). The emission is almost completely quenched when the $R$ is 2.5 nm. This is similar to what we have observed in TIPS-pentacene solution. When the $R$ is decreased from 5.9 nm to 2.5 nm, it is still much larger than the length of TIPS-pentacene unit cell (≈0.8 nm). Considering TIPS-pentacene molecules are more difficult to diffuse in solid films than in solutions, if singlet fission is still responsible for the emission quenching, weakly coupled molecules that lack bulk structural order resembling the single-crystal arrangement might be forming in the blend films [162,172]. These weakly coupled aggregates are amorphous. The TIPS-pentacene molecules within the aggregates are disordered and have no strong intermolecular interaction, resulting in no obvious absorption peak shift compared to monomers [162,172].

The emission quench can be caused by other mechanisms like face-to-face-stacked dimer aggregates formation so the radiative transitions from the exciton state to the ground state are formally forbidden [80] or exciton quenching on the trapping sites [159,160]. However, no absorption peak shift or absorption peak ratio change have been observed in the blend films as we decreasing the PS:TP mass ratio, indicating it is unlikely that we have strongly coupled aggregates in the blend films. Emission quenching caused by trapping sites is only expected when the exciton diffusion length is similar or longer than the average distance between the quenching sites. One has to assume the number of quenching sites are dramatically increased as increasing the PS:TP mass ratio. However, it is reported that in polymer:TP nanoparticle blend films the singlet fission efficiency increases as decreasing the polymer:TP mass ratio [161]. Thus emission quench in the PS:TP blend films is more likely due to
singlet fission rather than trapping effects.

Figure 6.11: Absorption (solid line) and PL (dashed line) spectra of PS:TP blend films with different thickness (samples 6D1-6D4).

As decreasing PS:PS ratio from 500:1 to 5:1, the trends of $E_1$ and $E_2$ intensity change are very similar (Fig. 6.10(c-d)), which is not surprising as they are supposed to be 0-0 and 0-1 vibronic series. One can see that the $E_1$ and $E_2$ peak intensity ratio is reduced by a factor of three in Fig. 6.10(b) as the PS:TP mass ratio is decreased from 500:1 to 15:1. Similar to the solutions, this ratio change is also due to self-absorption effect caused by the overlap of absorption $A_{0-0}$ peak and emission $E_1$ peak. To verify this assumption, we made four samples (samples 6D1-6D4) on glass slides with fixed PS:TP ratio but varied thicknesses. Their absorbance and PL spectra were shown in Fig. 6.11. One can clearly see that as increasing the thickness from 1.5 $\mu$m to 34 $\mu$m, the $E_1$ and $E_2$ peak intensity ratio is reduced from 2.2 to 0.96. This is because as increasing the film thickness, the emitted phonons with energies around 653 nm are more likely to be absorbed by the ground state TIPS-pentancene molecule before it travel away from the sample compared to the emitted phonons with energies around
710 nm (E₂ peak has no overlap with absorption spectra). Thus the E₁/E₂ ratio is expected to decrease, which is consistent with the experimental results.

Effect of PS:TP ratio on the photoluminescence lifetimes of PS:TP blend films were studied by time-resolved PL experiments [173, 174]. The sample was excited by a laser pulse (wavelength 375 nm) then the PL intensity change vs. time was collected. The data are plotted in Fig. 6.12. The PL lifetimes for two emission peaks are almost identical, further supporting that E₁ and E₂ are vibronic series [175]. The PL lifetimes for both excitations are shortened as shortening the intermolecular distance, indicating the excited molecules decay more rapidly via a non-radiative pathway at low PS:TP ratio.

\[
\tau = (k_f + k_{nr})^{-1} \quad (6.4)
\]

Here \(k_{nr}\) stands for the rate constant of the non-radiative process and \(k_r\) stands for the radiative rate constant. The PL lifetime \(\tau\) is determined by the \(k_{nr}\) and \(k_r\):
The dependence of emission property on PS:TP ratio is summarized in Fig. 6.13. At a high PS:TP ratio, TIPS-pentacene molecules are far apart so we mainly have monomers in the blend films. The excited states mainly decay via radiation \(k_r\), which give strong emission. The \(k_{nf}\) can be ignored so the PL lifetime is mainly determined by \(k_r\). If the PS:TP mass ratio is as high as 200:1, the PL lifetime \(\tau\) is around 10.5 ns, which is very close to the PL lifetime of excited monomers in dilute solutions [16]. When the PS:TP ratio is reduced to 15:1, mainly weakly coupled TIPS-pentacene aggregates form in the blend films. The excited molecules in the aggregates prefer to decay via single fission or other non-radiative pathways, resulting in an efficient emission quench. Thus PL lifetime \(\tau\) is governed by \(k_{nf}\) at low PS:TP mass ratio and \(\tau\) is greatly shortened from 10.5 ns to 0.9 ns.

![Figure 6.13: (a) PL intensity vs. PS:TP ratio. The image is reproduced from Fig. 6.10(a). (b) PL lifetimes for PS:TP blend films obtained from time-resolved PL measurements. Data is obtained from Fig. 6.12.](image)

The quenching behavior as a function of TIPS-pentacene concentration in PS:TP
blend films is highly reminiscent of the solution results, which suggest that the reduced lifetime is related to the same mechanism. However, molecular diffusion is greatly inhibited in the solid state, which would prevent the continuous formation and dissociation of excimers that has been proposed as part of the singlet fission mechanism for TIPS-pentacene in solution [16]. On the other hand, singlet fission has been verified in weakly coupled TIPS-pentacene nanoparticles, which may prove to be more closely related to the PS:TP system [162,172]. Further studies of PS:TP and other polymer blends utilizing techniques such as transient absorption spectroscopy could be a highly fruitful avenue for further study.

6.4 Conclusions

In this chapter, we have studied the emission properties of TIPS-pentacene solutions and PS:TP blend films. The emission peaks centered around 653 nm ($E_1$) and 710 nm ($E_2$) are vibronic series and their concentration dependent peak ratio is caused by self-absorption effect. In PS:TP blend films, it is found that the excited TIPS-pentacene molecules give strong emission when the mean intermolecular spacing is larger than 6 nm but prefer to decay via a non-radiative pathway when mean intermolecular separation is reduced to 3 nm.
Chapter 7

Summary

In this dissertation, we have done an extensive study on the charge transport and optical properties of TIPS-pentacene. Our results indicate that the high temperature Form II phase of TIPS-pentacene can be strain-stabilized to room temperature. High quality thin film fabrication (large grain size, smooth, uniform thickness and no cracks) enables us to fabricate TIPS-pentacene based OFETs to extract reliable mobilities. The characterized saturation and linear mobilities of strain-stabilized Form II are found to be about three times higher than the Form I. The improved mobility is due to the molecular positions in Form II moved towards a position where hole transfer integral is larger and less sensitive to the molecular thermal vibrations compared to Form I phase. We anticipate that this approach can be applied to many other organic semiconductors to improve their charge carrier mobility since their structures can be tuned by a combination of thermal expansion and mechanical strain.

The influence of molecular packing on the optical properties are reported for thin films deposited in the temperature range from 25°C to 140°C. Anisotropic thermal expansion causes relative displacement of neighboring molecules while maintaining
a nearly constant stacking distance. This leads to a large blueshift in the absorption spectrum as the temperature increases. The blueshift is consistent with a Frenkel/charge transfer exciton coupling model, where the excitation energy depends sensitively on the alignment of the nodes of the frontier molecular orbitals with those on neighboring molecules. This effect is correlated with an enhancement of the field-effect transistor mobility in strain-stabilized thin films. The links between optical excitation and carrier transport via charge transfer integrals highlight the combination of structural, electronic and optical measurements with first principles theory as a powerful toolset to monitor and predict the properties of strain-engineered materials with improved carrier mobility or desirable optical properties.

We have achieved strong emission in PS:TP blend films when mean intermolecular separation is large than 5 nm. By reducing mean intermolecular separation from 5.9 nm to 2.5 nm, the excited TIPS-pentacene molecules are found to efficiently decay via a non-radiative pathway. The non-radiative pathway is considered to be singlet fission. Further studies of PS:TP and other polymer blends utilizing techniques such as transient absorption spectroscopy could be a highly fruitful avenue for further study.
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Appendix A

Contact Line Instability and Aligned TIPS-pentacene Film Deposition

In meniscus guided deposition methods, the crystallization happens at the solid-liquid-air three phase contact line, thus maintaining its stability is crucial to produce high quality thin films. However, a dewetting phenomena can be observed during pen-writing TIPS-pentacene films on ultrasonic cleaned wafers or glass slides. As shown in Fig. A.1, small “tears” burst out from the meniscus during film deposition, resulting in irregular crystalline dots formation rather than continuous films.

In literature, a similar “tears of wine” effect has been studied [176]. It is caused by the surface tension gradient, which can induce a flow from low surface tension region to high surface tension region (referred to as Marangoni flow) [176–178]. The Marangoni flow can be used as a supply of the solute molecules to crystallization front which help the growth of ordered structures [45,179]. But it can also trigger various intriguing phenomena like dewetting behavior and the fingering instability [178,180]. We speculate that the contact line instability we observed during TIPS-
Figure A.1: Optical microscopy images at different writing speeds (a) 0.1 mm/s; (b) 1.2 mm/s. The TIPS-pentacene concentration was 10 mg/ml and deposition temperature was 130 °C. Pure 1,2-dichlorobenzene (DCB) was used as solvent. The wafer substrates were sonicated in deionized water, acetone, and isopropanol for 10 min each before film deposition.

Pentacene film deposition is related to a concentration gradient caused Marangoni flow. Due to the strong evaporation, TIPS-pentacene is more concentrated near the contact line compared to the bulk meniscus. If concentrated TIPS-pentacene solutions have higher surface tension compared to dilute TIPS-pentacene solutions, the concentration gradient within the meniscus can result in a Marangoni flow which may cause a meniscus instability.

We used a binary solvent system to study how the concentration gradient affects the contact line stability. Toluene and DCB were chosen here because toluene has a vapor pressure (21 mmHg, 20°C) that is much higher than DCB (1 mmHg, 20°C). Thus a concentration gradient can be easily introduced by evaporation in the meniscus. The toluene to DCB volume ratio was 1 : 50 and the blend solvent was fed into our glass capillary. The capillary was lower to allow the micro droplet of the blend solvent at the end of the capillary to make contact with the ultrasonic cleaned wafer substrate. The development of contact line instability is shown in Fig. A.2. At $t =$
Figure A.2: Development of meniscus instability when a blend of toluene and DCB with a volume ratio of 1:50 in glass capillary contacted with an ultrasonic cleaned wafer at room temperature. (a) the blend solvent started to contact with the substrate; (b) undulations developed at the front line; (c) the undulations developed into bulges; (d) bulges developed into fingering.

0 s, the solution in the capillary started to contact with substrate. At t = 0.13 s, a thicker rim formed at the periphery of the meniscus and undulations was developed along the rim. At t = 0.2 s, the undulations grow into bulges and finally at t = 2.2 s the bulges developed into fingering instability.

The mechanism of contact line instability is proposed in Fig.A.3. Since the region that close to the contact line has a higher surface area to volume ratio than the bulk meniscus, it has much higher evaporation rate. The more volatile compound toluene evaporates more quickly than the less volatile compound DCB. Therefore DCB (37 mN/m), with a higher surface tension than toluene (28 mN/m), is left in higher concentration near the contact line than the bulk meniscus. The resulting gradient of surface tension, i.e., Marangoni flow, pulls liquid towards the contact line to form
a thick rim, as shown in Fig. A.3 (a). The rim can be treated as a liquid cylinder. It is unstable because it tends to break into droplets with the same volume but less surface area. This unstable rim is subjected to perturbations like thermal fluctuation or substrate surface heterogeneity. These perturbations could grow with time and develop into bulges and fingering instability (Fig. A.3 (b)).

![Diagram](image)

*Figure A.3: (a) the diagram shows that the concentration gradient caused Marangoni flow results in the rim formation at the meniscus front line. (b) The rim is unstable and develops into fingering instability.*

In Fig. A.4, we varied the DCB to toluene volume ratio from 1:100 to 1:10. As one can see, the rim stability heavily depends on the initial ratio of DCB to toluene. When the ratio is as low as 1:100, the collecting rim exhibits a tip-pattern where tips collects the solution. As increasing the DCB concentration, the liquid forms multiple thin streams and small droplets are ejecting out from the meniscus. These results indicate that the Marangoni flow rate depends on the DCB to toluene ratio. As increasing the DCB to toluene volume ratio from 1:100 to 1:10, larger concentration
gradient is developed near the contact line. It results in a stronger Marangoni flow that transfer the meniscus instability from a collecting mode to an ejecting mode. This behavior is similar to the dripping to jetting transition when one increasing the flow rate of water at a kitchen faucet [181,182].

As we have assumed, the dewetting behavior has two requisites: 1) rim formation caused by Marangoni effect; 2) rim instability caused by thermal fluctuation or substrate heterogeneity. Based on our experience, to eliminate the dewetting, one can either tune the liquid property to reduce Marangoni effect or improve the rim stability by reducing thermal fluctuation or improving substrate surface uniformity. The meniscus instability is probably due to the thermal fluctuations, and the amplitude is increased because of the solvent vapor gradient. There are also other possibilities could result in the dewetting behavior. For example, silicon surface can be treated
as a dirty surface as the Si-OH groups on the surface tend to absorb water or other organic contaminations via hydrogen bonding, resulting in nonuniform surface energy. A rim formed on this surface could be unstable as undulations can be developed. At a relatively low surface energy spot, liquid in the rim is repelled by the spot, forming a slight trough in the rim thickness [183]. The opposite occurs for a relatively high energy spot, for which the liquid is attracted to the spot, forming a region of slightly greater thickness in the rim.

Figure A.5: The stability of the meniscus when blend solvent (DCB : toluene = 1 : 50) in hollow glass capillary contacted with the (a) UV ozone treated wafer (b) ultrasonic cleaned wafer and (c) PTES treated wafer.

Figure A.6: (a-c): Contact angles of water droplets on UV-Ozone treated, ultrasonic cleaned and PTES treated wafer.

Here we applied UV-ozone treatment and phenyltriethoxysilane (PTES) treatment to the wafer (details can be seen in the experimental section of Chapter 4). PETS treatment enables a layer of PETS molecule chemically bonded to the wafer and UV-Ozone treatment can effectively remove any organic contamination absorbed on the wafer. Thus both methods can greatly improve the surface energy uniformity of
the substrate. After UV-Ozone and PTES treatment, the contact angle of the wafer changed from 55° to 16° and 78° respectively (data is shown in Fig. A.6). When we contacted the blend solvent (DCB: toluene = 1:50) in glass capillary with the wafer substrates, we can see that a collecting rim still formed at the contact line on both UV-Ozone treated (Fig. A.5(a)) and PTES treated wafer (Fig. A.5(c)), small fluctuation developed along rim which might result from thermal fluctuation. But overall the rim was stable rather than developing into fingerings (Fig. A.5 (b)).

Figure A.7: (a) Partially polarized optical image of a TIPS-pentacene film during deposition at 130° using pure DCB as solvent; (b) Cross polarized optical image of the film in (a) when it was cooled to 25°. (c) Partially polarized optical image of a TIPS-pentacene film during deposition at 130° using a blend of DCB and mesitylene as solvent. The rim formed at the contact is pointed by a white arrow; (d) Cross polarized optical image of the film in (c) when it was cooled to 25°. The deposition speed was 0.8 mm/s and concentration was 10 mg/ml. The wafers were PTES treated.

We showed that PTES or UV-Ozone treated wafer help to stabilize the contact line for the blend solvent. We used the same strategy to deposit aligned TIPS-pentacene thin films. As shown in Fig. A.7 (a), continuous and crack free films (20-30 nm thick)
can be obtained at 130°C on PTES treated wafers by using pure DCB or a blend of DCB and mesitylene as solvents.
Appendix B

Derive the Relationship between the Wave Vector Transfer and Unit Cell Parameters

A sketch of a triclinic unit cell is shown in Fig. B.1 with its $a$-axis set to be parallel to the $x$-axis of the Cartesian coordinate system. The vectors $\vec{a}$, $\vec{b}$, and $\vec{c}$ are the primitive vectors of the unit cell. In the Cartesian system, the primitive vectors $\vec{a}$
and $\vec{b}$ can be expressed as:

$$\vec{a} = (a, 0, 0) \quad (B.1)$$

$$\vec{b} = (b \cos \gamma, b \sin \gamma, 0) \quad (B.2)$$

Assume $\vec{c} = (x, y, z)$, the $x$, $y$ and $z$ values can be determined by following three equations:

$$\vec{a} \cdot \vec{c} = ac \cdot \cos \beta \quad (B.3)$$

$$\vec{b} \cdot \vec{c} = bc \cdot \cos \alpha \quad (B.4)$$

$$\vec{c} \cdot \vec{z} = d_{001} \quad (B.5)$$

where $\vec{z}$ is the unit vector along $z$-axis, $d_{001}$ is the spacing between (001) planes. The $x$, $y$ and $z$ values can be obtained by solving above three equations, thus the primitive vector $\vec{c}$ can be expressed as:

$$\vec{c} = \begin{pmatrix} 
  c \cdot \cos(\beta) \\
  c(\cos \alpha - \cos \beta \cos \gamma) / \sin \gamma \\
  d_{001}
\end{pmatrix} \quad (B.6)$$

For a triclinic unit cell, the $d_{001}$ can be calculated by:

$$d_{001} = \frac{c}{w \sin \gamma} \quad (B.7)$$
where

\[ w = \frac{1}{\sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2\cos \alpha \cos \beta \cos \gamma}} \]  

(B.8)

Based on Eq. B.6, Eq. B.7 and Eq. B.8, the \( \vec{c} \) can be expressed in a simpler form:

\[
\vec{c} = d_{001} \begin{pmatrix}
\cos \beta \cdot \sin \gamma \cdot w \\
(c \cos \alpha - \cos \beta \cdot \cos \gamma)w \\
1
\end{pmatrix}
\]  

(B.9)

In reciprocal space, the three reciprocal primitive vectors can be obtained through following formulae:

\[
\vec{a}_r = 2\pi \cdot \frac{b \times c}{V} \]  

(B.10)

\[
\vec{b}_r = 2\pi \cdot \frac{c \times a}{V} \]  

(B.11)

\[
\vec{c}_r = 2\pi \cdot \frac{a \times b}{V} \]  

(B.12)

where \( V \) is the volume of the unit cell. For a triclinic unit cell, we have:

\[ V = \frac{abc}{w} \]  

(B.13)

Plug Eq. B.2, Eq. B.9, Eq. B.13 into Eq. B10, the \( \vec{a}_r \) can be expressed by:
\[ \mathbf{a}_r = \frac{2\pi}{a} \begin{pmatrix} 1 & 0 \\ -\cot \gamma & 1/sin\gamma \\ (\cos\gamma\cos\alpha - \cos\beta) \cdot w/sin\gamma \end{pmatrix} \]  

(B.14)

Similarly, the \( \mathbf{b}_r \) and \( \mathbf{c}_r \) can be expressed by:

\[ \mathbf{b}_r = \frac{2\pi}{b} \begin{pmatrix} 0 & 0 \\ 1/sin\gamma & 0 \\ (\cos\gamma\cos\beta - \cos\alpha) \cdot w/sin\gamma \end{pmatrix} \]  

(B.15)

\[ \mathbf{c}_r = \begin{pmatrix} 0 \\ 0 \\ 2\pi/d_{001} \end{pmatrix} \]  

(B.16)

X-ray scattering from a lattice of molecules occurs only when the \( \mathbf{Q} \) satisfies following condition:

\[ \mathbf{Q} = h \cdot \mathbf{a}_r + k \cdot \mathbf{b}_r + l \cdot \mathbf{c}_r \]  

(B.17)

where \( h, k \) and \( l \) are miller indices of a plane and \( \mathbf{Q} \) is the wave vector transfer. Plug Eq. B.14, Eq. B.15 and Eq. B.16 into Eq. B.17, one can get the three component of \( \mathbf{Q} \):

\[ Q_x = 2\pi \frac{h}{a} \]  

(B.18)
\[ Q_y = 2\pi \left( -\frac{h \cdot \cot \gamma}{a} + \frac{k}{b \sin \gamma} \right) \] (B.19)

\[ Q_z = 2\pi \left( \frac{w \cdot h \left( \cos \gamma \cos \alpha - \cos \beta \right)}{a \sin \gamma} + \frac{w \cdot k \left( \cos \beta \cos \gamma - \cos \alpha \right)}{b \sin \gamma} + \frac{l}{d_{001}} \right) \] (B.20)