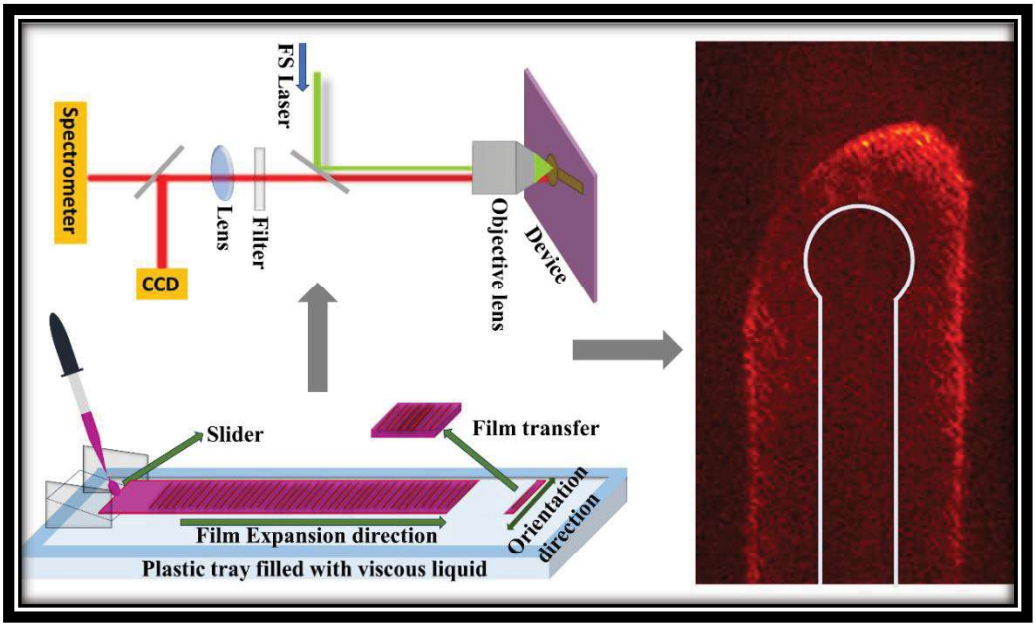
Chapter 3

Exploring Anisotropic Charge Transport in Highly Oriented P4T2F-HD Thin Films via Second Harmonic Generation (SHG) Analysis



In this chapter, we fabricated P4T2F-HD thin film at liquid -air interface using UFTM. Further molecular orientation and the anisotropy in the thin films was confirmed through anisotropic carrier transport studies using TRM-SHG imaging. The real-time visualization of charge movement allowed for precise characterization of carrier mobility along different axes, highlighting the relationship between molecular arrangement and electronic performance.

3.1.Introduction:

In the dynamic field of organic electronics, conducting polymers have garnered significant attention as cornerstone materials, distinguished by their exceptional mechanical flexibility, ease of processing in solution, and adjustable electrical properties[73-77]. These distinctive characteristics have facilitated their widespread application across a diverse array of electronic devices, including organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), field-effect transistors (FETs), and sensors[78-81]. The burgeoning fascination with these materials is largely fuelled by their potential to redefine the landscape of electronic devices, promising lightweight, flexible, and economically viable alternatives to conventional inorganic semiconductor[82, 83]. The orientation of polymer chains within films is a crucial factor that significantly influences the performance and effectiveness of devices made from conducting polymers[84, 85]. The anisotropy, or directional arrangement, of these chains significantly influences the electronic properties of the materials, which, in turn, directly affects device functionality[85-87]. The orientation of polymer chains not only impacts charge transport mechanisms but also affects optical properties and mechanical durability, which are essential for the overall performance of electronic devices[77, 88].

Researchers have developed various methodologies to induce and examine the orientation of polymer chains within films to control this anisotropy. Techniques ranging from mechanical stretching, dip coating, and off-centered spin-coat to applying electric or magnetic fields during film formation have been explored to achieve the desired alignment of polymer chains[43, 89, 90]. Among these methods, the Unidirectional floating film transfer (UFTM) technique stands out for its ability to produce highly oriented thin films[51]. Such strategies are instrumental in elucidating the structure-property relationships in conducting polymers, paving the way for material customization for

specific applications[91]. Anisotropy in charge carrier transport is a key determinant of the electronic properties and, consequently, the performance of devices based on conducting polymers[40]. The way material properties vary with direction affects how efficiently charge carriers move through the polymer matrix. Specifically, when polymer chains are aligned, it can lead to anisotropic charge transport, where the movement of charge carriers like electrons and holes differs based on their direction[92]. This phenomenon is crucial for optimizing electronic devices as it can significantly enhance device performance by enabling more efficient charge transport in the preferred direction[93]. Thus, understanding and manipulating the anisotropy of conducting polymers is a foundational objective for advancing the capabilities of organic electronic devices. Addressing the challenges of characterizing anisotropic properties at the microscale requires sophisticated analytical techniques to detail structural and electronic variations within thin films. Second-harmonic generation (SHG) analysis serves as an effective method for this purpose. SHG, a nonlinear optical process in which two photons merge to create a new photon with double the energy and half the wavelength of the original photons, is particularly responsive to the symmetry and structural alignment of materials[69, 94].

This study focuses on a thin film of P4T2F-HD that is highly oriented and prepared via the UFTM. This technique accurately fabricates the thin film at the air-liquid interface, employing a mixture of ethylene glycol and glycerol in a 3:1 ratio as the sub-phase liquid medium. The oriented film was then incorporated into OFETs to explore the influence of anisotropy on the charge transport characteristics inherent to P4T2F-HD-based films. Through the SHG measurements, we meticulously analyzed the anisotropy of carrier transport within these films. SHG analysis allowed us to visualize and accurately quantify the anisotropic carrier transport phenomena directly. By integrating the advanced film fabrication techniques of UFTM with insightful SHG measurements, this work seeks to

enhance the understanding of the impact of polymer chain orientation on the electronic properties of conducting polymers. Besides, it explores charge transport mechanisms in oriented films and advance the fabrication of more efficient, high-performance organic electronic devices, thereby enhancing the fields of materials science and organic electronics.

3.2. Materials and Methods:

The polymer P4T2F-HD was Purchased from Ossilla Co with an average molecular weight of (M_w ~ 44 KDa). Furthermore, essential reagents such as ethylene glycol, glycerol, methanol, IPA and chloroform were purchased from Sigma Aldrich, while a 300 nm-thick silicon dioxide (SiO_2)-coated Si wafer, was sourced from Global Nanotech Ltd.

3.2.1. Thin Film and OFET Fabrication:

The P4T2F-HD ink was prepared using anhydrous chloroform for a 15 mg/ml concentration. It was heated to 50°C and stirred for one hour to ensure a homogeneous solution. The process included ultrasonication for 10 minutes in a Yamato Branson ultrasonic bath, an essential step intended to encourage the formation of aggregates in the solution. For the fabrication of UFTM thin films, a precise volume of 10 µl of the conjugated polymer (CP) solution was gently positioned next to a specifically designed slider on the liquid sub-phase. This setup allowed for controlled expansion of the film in one direction, as illustrated in ***Figure 3.1.*** This technique allowed for the distinct alignment of the polymer chains based on the hydrophobicity levels of their side chains, with CPs having more hydrophobic side chains aligning edge-on and those with less hydrophobic side chains aligning face-on upon deposition on a hydrophilic liquid substrate, specifically ethylene glycol at 40 °C. Once formed at the polymer-air interface, the thin films were moved to their designated substrates and cleaned with methanol to eliminate any residual sub-phase liquid from the fabrication process. Following the cleaning, the films underwent

annealing for 10 minutes at 120 °C in a nitrogen-filled atmosphere inside a glove box, followed by a gradual cooling period of 30 minutes. These carefully prepared thin films underwent further characterization. OFETs were fabricated on a highly p-doped Si substrate, which had a thickness of 300 nm. The device fabrication began with a thorough cleaning regimen, initially using Hellmanex solution, followed by a series of washes in hot, double-distilled water. Subsequent steps included ultrasonication in acetone and IPA, each for ten-minute intervals, and a drying step involving annealing at 120 °C for half an hour. A plasma cleaning stage was incorporated to enhance the substrate's cleanliness, and for improved hydrophobicity, the substrate was immersed in an ODTS/toluene solution for two hours.

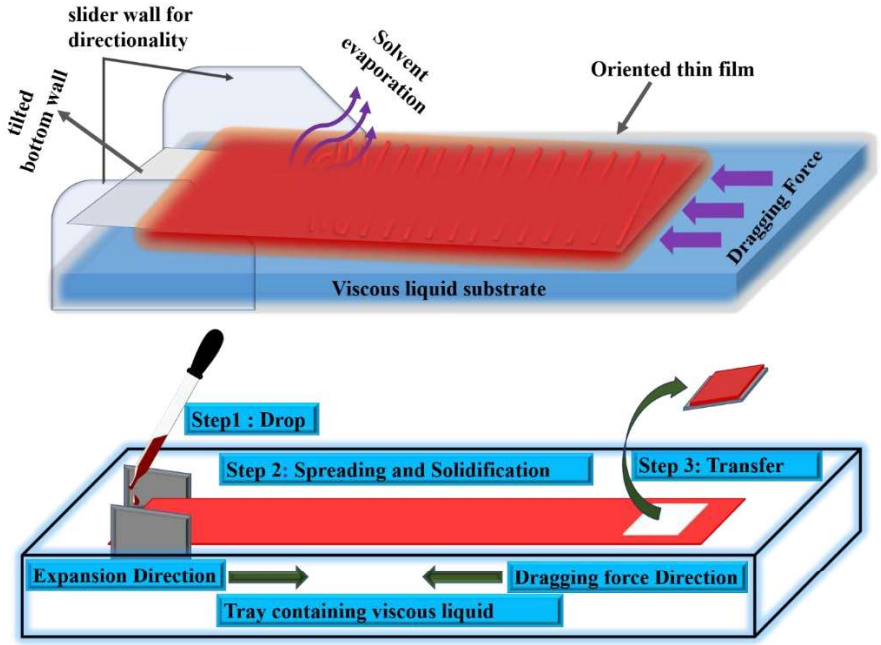


Figure 3. 1 *Represents the schematic of the Unidirectional floating film Transfer Method (UFTM).*

The final steps involved rinsing with toluene and a second annealing phase at 80 °C to finalize the hydrophobic surface modification. The carefully prepared thin film was lifted onto the substrate using the UFTM. Following the transfer, annealing step at 120 °C for 30 minutes was conducted to ensure the film's optimal characteristics. A gold layer with 100

nm thickness was thermally evaporated to finalize the device fabrication to create the electrodes. A nickel shadow mask was utilized to accurately define the source-drain channels, which are 50 µm in length and 2.8 mm. For anisotropy by SHG round shaped electrodes were fabricated as shown in ***Figure 3.6 (b)***.

3.3.Results and Discussion:

3.3.1. Structural Characterization:

The out-of-plane X-ray diffraction (XRD) characterization of P4T2F-HD thin films has been conducted to elucidate their molecular orientation. As illustrated in ***Figure 3.2(b)***, the XRD pattern reveals pronounced diffraction peaks, notably at the (100) and (200) planes, indicating a high degree of crystalline order and uniform stacking of the polymer chains parallel to the film surface. The sharpness and intensity of the (100) peak suggest a strong edge-on orientation, which is associated with efficient charge transport pathways[66]. The schematic in ***Figure 3.2(a)*** depicts the experimental setup for the out-of-plane XRD analysis, highlighting the alignment of the source, the oriented P4T2F-HD polymer film, and the detector. These findings confirm the successful fabrication of highly ordered P4T2F-HD films with a well-defined molecular orientation that is anticipated to contribute to superior electronic performance in organic electronics applications.

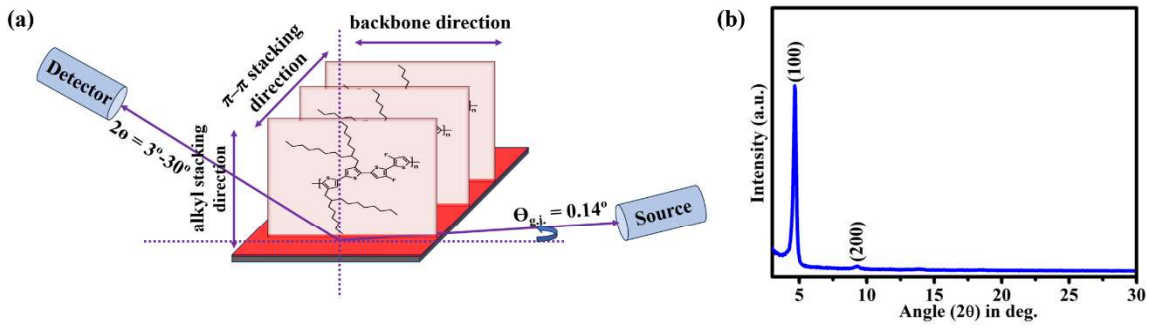


Figure 3. 2 (a) *Schematic representation for the out-of-plane instrument,* ***(b)*** *out-of-plane XRD pattern of P4T2F-Thin film.*

3.3.2. Optical Characterization:

The thin film of P4T2F-HD, fabricated using the UFTM, was subjected to optical characterization using polarized UV-visible spectroscopy. The absorption Band of P4T2F-HD are between 480-630nm, as depicted in ***Figure 3.3 (a)***. The molecular orientation of the P4T2F-HD film was evaluated using the optical dichroic ratio (DR), a metric derived by examining the UV spectrum under polarized light across various angles. The dichroic ratio typically measures the orientation within the films, DR = A∥/A⊥, where A∥ and A⊥ denote the peak absorbances at λmax parallel and perpendicular to the main chain, respectively. [95]. The figure reveals an enhanced orientation from 0 to 90 degrees of polarization. The UV-visible absorption spectra showcased significant anisotropic behavior in the P4T2F-HD films, with a marked peak at λ_{max}, representative of the polymer's main absorption band, displaying distinct intensity fluctuations as the polarization angle shifted from 0° to 360° as shown in ***Figure 3.3(b)***. Such variance signals the extent of molecular Orientation within the film. The DR, deduced from the polarization-dependent absorption, offered a quantifiable anisotropy index, indicating superior alignment along specific axes.

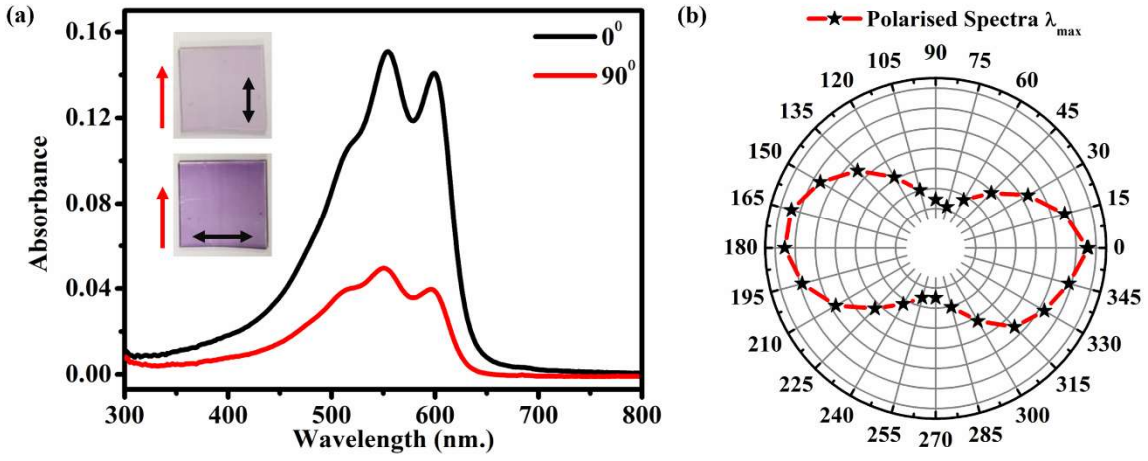


Figure 3. 3 (a) *Represents the Polarized spectra of P4T2F-HD, the inset image represents the thin film fabricated by UFTM in which the red arrow shows the direction of flow, and the black arrow presents the polarizer position.* ***(b)*** *represents the polarized absorbance from 0° - 360°*

3.3.3. Surface Characterization:

Figure 3.4 (a) and ***3.4(b)*** presents an atomic force microscopy (AFM) image that confirms the surface roughness and the orientation within a polymer thin film sample. The average roughness measured from the AFM analysis is approximately 1.5 nm, indicating a relatively smooth surface at the nanoscale. This high-resolution topographical mapping provides critical insights into the nanoscale features of the polymer, which are essential for understanding its anisotropic characteristics of the polymer orientation and crucial for predicating the material's behavior under different orientations.

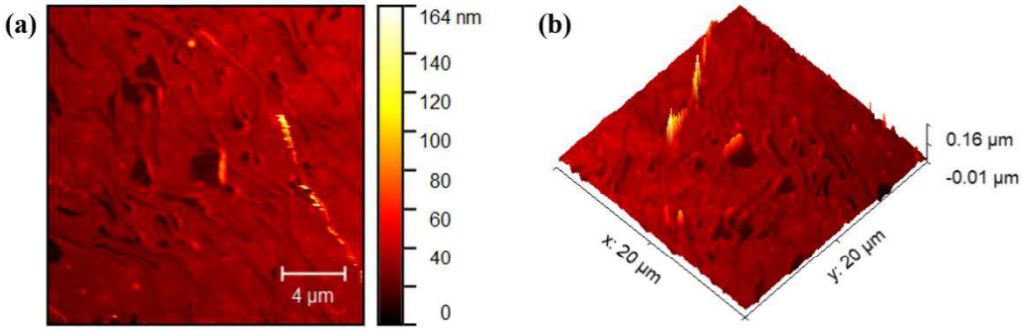


Figure 3. 4 (a) *Represents the AFM image of P4T2F-HD* ***(b)*** *3D AFM image of P4T2F-HD*

3.3.4. Electrical Characterization:

This work particularly concentrated on analyzing the impact of anisotropy on the electrical properties of thin films. The emphasis was on understanding the orientation and alignment of molecules within these films and how such structural characteristics affect their electrical properties. Our study examines the phenomena through bottom-gate, top-contact (BGTC) OFETs, where the direction of film spreading is aligned both parallel and perpendicular to the source-to-drain electric field in the channel, as illustrated in ***Figure 3.5 (c)***. The electrical properties of the FETs were measured under ambient conditions, at room temperature, with a relative humidity of 50%, in a darkened environment, utilizing a Keithley 2612 source meter for the analysis. For the determination of the saturated field-

effect mobility (μ_{sat}) and the threshold voltage of the device, we used a method based on fitting a linear equation to the $I_{DS}^{1/2}$ - V_G curve, following the procedure detailed in ***equation 3.1*** provided.

$$I_{DS} = \frac{W\mu_{sat}C_{ox}}{2L}(V_G - V_{TH})^2 \qquad (3.1)$$

In the specified equation, I_{DS} symbolizes the saturated drain current, C_{ox} is indicative of the dielectric's areal capacitance, which here was10 nF/cm^2. V_{TH} is the abbreviation for the threshold voltage. Furthermore, L and W are the channel's length and width, measured at 50 μm and 2.8 mm, respectively. The term μ_{sat} represents the field-effect mobility in the saturation regime. V_{DS} and V_G, on the other hand, denote the voltage differences between the drain and source and between the gate and source, respectively.

The output characteristics of the perpendicular and parallel aligned film are shown in ***Figures 3.5 (a) & 3.5 (b)***, respectively, and transfer characteristics are shown in ***Figure 3.5(d)***. The average field-effect mobility in the saturation regime, calculated for directions parallel ($\mu_{SAT}^{\parallel}$)and perpendicular ($\mu_{SAT}^{\perp}$) to the film spreading direction, was estimated at 6×10^{-2} cm^2/V.s and 4.01×10^{-3} cm^2/V.s, respectively. The alignment of polymer chains plays a crucial role in the performance and mobility of OFETs. Proper alignment of these chains facilitates efficient charge carrier transport along the backbone of the polymer, enhancing the mobility of the OFET. This is because the molecular orbitals of the polymer chains overlap better when the chains are well-aligned, allowing for easier movement of charge carriers. When fabricating OFETs, the orientation of the thin film relative to the direction of film expansion significantly influences the device's charge carrier mobility. Devices fabricated with their active layer oriented parallel to the film expansion direction tend to exhibit higher mobility. This occurs as the polymer chains achieve greater uniformity in alignment perpendicular to the direction of film expansion, which facilitates efficient

charge transport along the polymer backbone. This alignment minimizes the scattering of charge carriers, thus improving mobility. To verify the orientation of the thin film and the alignment of the polymer chains, TRM-SHG measurements were performed. This technique provides detailed understanding of how molecular alignment effects OFET performance, contributing to the development of high-mobility organic electronic devices.

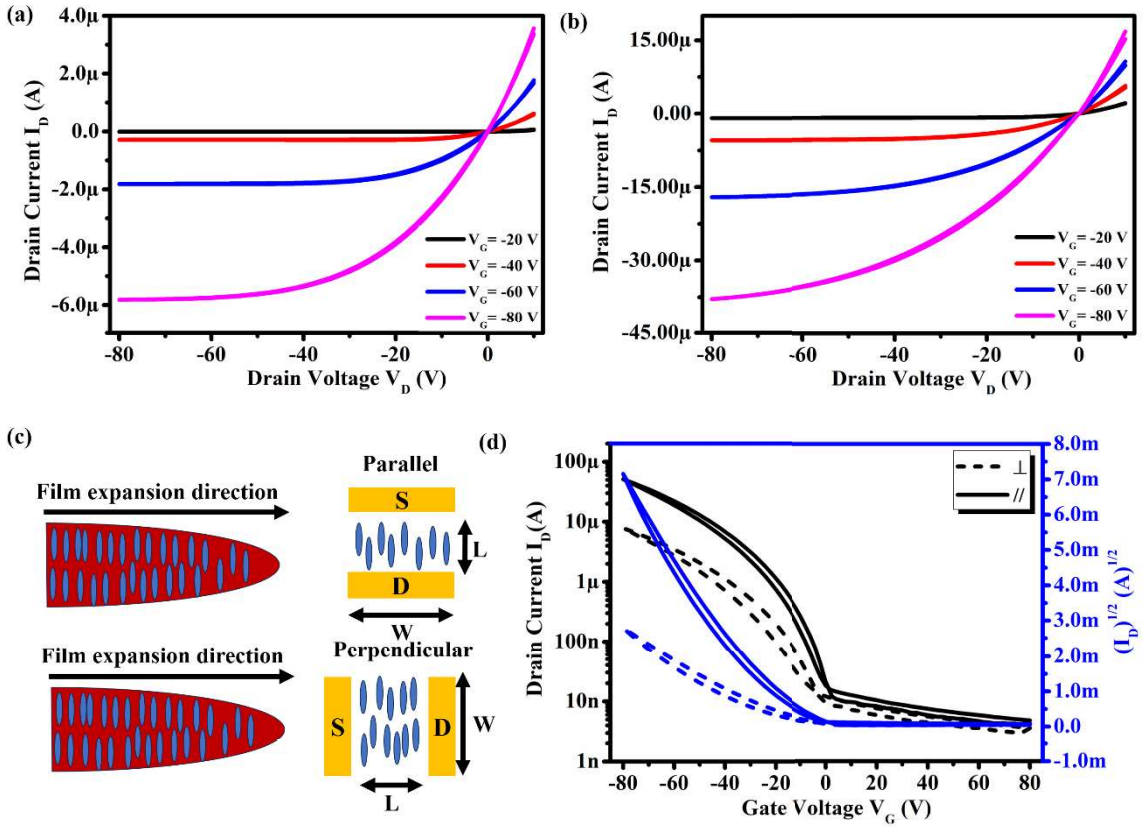


Figure 3. 5 ***(a)*** *Represents the Output characteristics of perpendicular aligned film* ***(b)*** *the Output characteristics of parallel aligned film* ***(c)*** *represents the schematic of film expansion with channel alignment where L, and W represents channel length and width* ***(d)*** *represents the thin transfer characteristics of parallel and perpendicular aligned film.*

3.3.5. TRM-SHG Measurements:

To elucidate the directional charge transport in thin films, I employed a cutting-edge technique known as TRM-SHG, which is adept at mapping the vectorial pathways of carrier movement within films of organic semiconductors[69-71]. Conventional methods like I–V curve tracing and Time-of-Flight (TOF) measurements provide valuable data on mobility

anisotropy; however, they lack the angular resolution needed to pinpoint the exact directions of highest and lowest carrier mobility due to their inherent limited angular resolution[96, 97]. TRM-SHG overcomes this limitation by offering a comprehensive view of carrier mobility, enabling precise identification of directions with both superior and

both superior and inferior mobility, along with their magnitude, directly from the captured images[72]. Furthermore, TRM-SHG provides an in-depth analysis of the transport phenomenon, offering direct evaluation of the inherent anisotropy of mobility and the corresponding activation energies[30]. The investigation of carrier distribution in thin film devices was conducted using the electric field-induced SHG (EFISHG) technique. When a static electric field E (0) is applied, and the material is concurrently irradiated with a powerful laser beam, a second-order nonlinear polarization response is induced[33]. This response is described by the following ***equation 3.2***.

$$P_{(2\omega)} = \epsilon 0 \chi^{(2)} E(\omega) E(\omega) + \epsilon_0 \chi^{(3)} E(0) E(\omega) E(\omega) \qquad (3.2)$$

In this equation, the first term relates to the standard SHG effect, which is negligible in materials that possess inversion symmetry because all tensor components disappear under such symmetric conditions. The second term arises from the influence of the static electric field $E(0)$, which is the main contribution to the SHG signal in centrosymmetric materials when an electric field is applied. This interaction is the cornerstone of the EFISHG effect, where the static electric field $E(0)$ consists of both an imposed external field (E_{ext}) and an intrinsic space-charge field (E_{sc}) [34]. Observing the EFISHG signal allows for a detailed mapping of electric and carrier distribution, shedding light on the spatial properties of carrier dynamics. The enhancement of this technique into a time-resolved measurements opens the way for live tracking of transient carrier distribution phenomena. TRM-SHG, this sophisticated instrument, provides a live depiction of carrier activity by manipulating the delay interval[71]. The delay period refers to the time difference between the

application of a voltage pulse upon the device and the irradiation of the laser pulse. Employing this methodology gives a comprehensive view of the carrier activities within the device, merging both spatial distribution and temporal evolution to deliver a complete picture of the internal processes governing carrier dynamics.

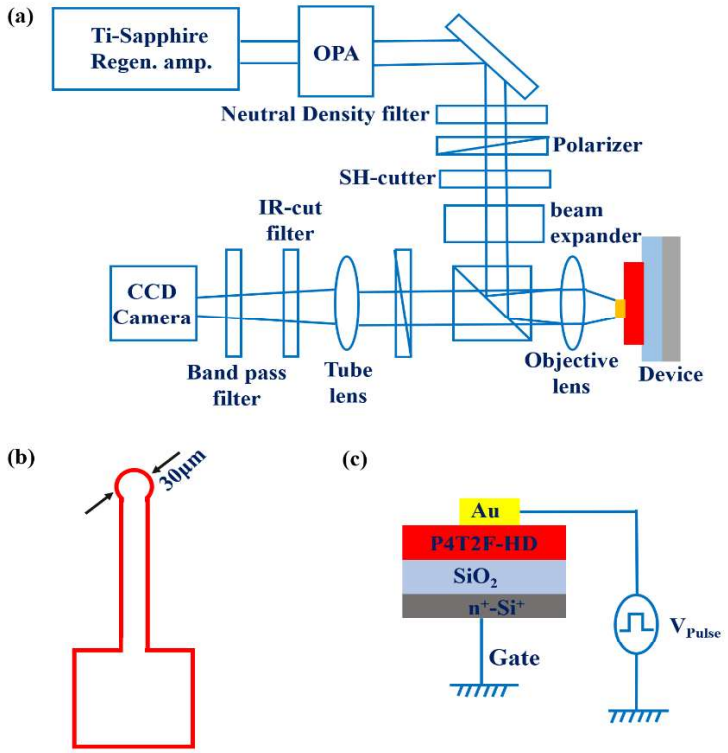


Figure 3. 6 ***(a)*** *Setup of the optical apparatus for Time-Resolved Microscopic Second Harmonic Generation (TRM-SHG) exploration.* ***(b)*** *Schematic of the circular electrode configuration,* ***(c)*** *Structure of the examined specimen.*

In the depicted experimental setup for TRM-SHG, presented in ***Figure 3.6 (a)***, the light source utilized was a femtosecond optical parametric amplifier (OPA, Opera Solo model by Coherent). This OPA was excited by a Titanium-Sapphire (Ti: Sapphire) regenerative amplifier system (Libra model, courtesy of Coherent), renowned for its high stability and precision, which are pivotal for this type of experiment. The laser system operated with an 80-femtosecond pulse duration and a 1 kHz repetition frequency. The OPA's fundamental output, using an objective lens, was accurately focused onto a circular electrode. The SHG signal produced by the sample was then carefully separated from the fundamental light and

any extraneous light through a filtering process. This step involved the deployment of infrared-cut and interference filters, indispensable for the SHG signal's isolation from background noise and optical disturbances. The refined SHG signal was subsequently captured and recorded with an advanced, cooled Charge-Coupled Device (CCD) camera (Newton model by Andor), selected for its exceptional sensitivity and minimal noise features, crucial for the detection of weak SH signals.

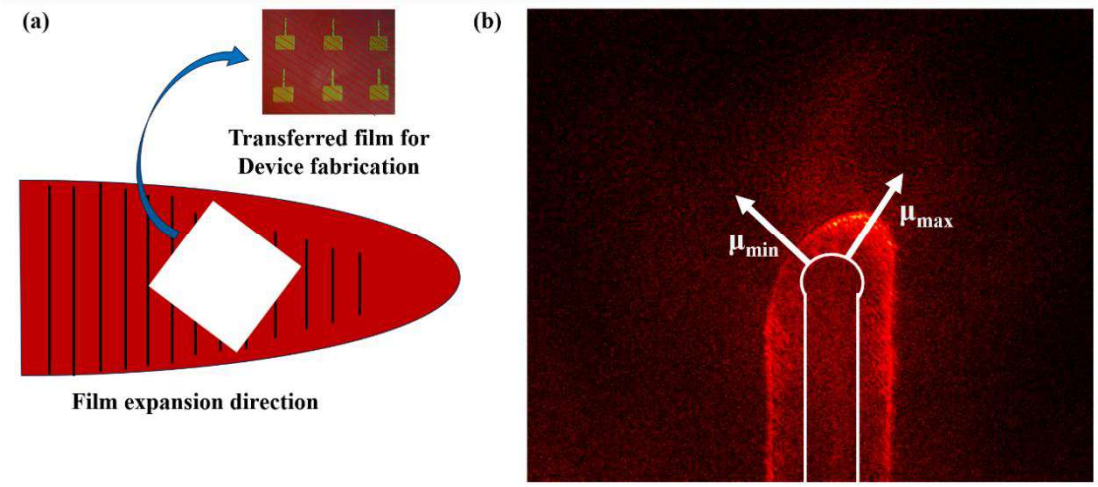


Figure 3. 7 (a) *Shows the stamped thin film from the orientation thin film, and lines on the thin films show the orientation polymer chains* ***(b)*** *time-resolved SHG image of the device*

In the exploration of TRM-SHG analysis, I chose a wavelength of 1120 nm for the incident light, capturing the SHG signal at 560 nm. ***Figure 3.8*** clearly displays the SHG images from the P4T2F-HD, with a prominent SHG signal concentrated around the central electrode, indicating its origination from the P4T2F-HD layer exclusively. A white marker outlines the edge of the electrode for visual clarity. For these images, a pulsed voltage of 120 V was applied to the circular electrode and the bottom electrode was connected to ground. The captured image reflects a specific instant, 100 nanoseconds after carrier injection, offering a snapshot of carrier distribution at that moment. Our analysis shows that the carriers disperse in various directions at differing speeds, as illustrated in ***Figure 3.7(b)***, with arrows marking the fastest and slowest carrier paths. This in-plane

inhomogeneity in carrier motion is related to the one-dimensional character of excitons in π-conjugated polymers, where the maximum absorption is in alignment with the polymer's primary chain or the film's orientation. It was observed that the carrier mobility is highest along the primary chain direction in the aligned P4T2F-HD film. This mobility is calculated using ***equation 4.3***, which describes the directional movement of carriers within the substance.

$$\mu = \frac{1x^2}{2Vt} \qquad \textbf{(4.3)}$$

Here, μ denotes carrier mobility, $\boldsymbol{x}$ indicates carrier front position, V is the applied voltage, and t is time. The mobility measured parallel to the polymer chain direction was 0.045 $cm^2/V.s$, and the perpendicular was 2.1×10^{-3} $cm^2/V.s$. Our experiment demonstrated carrier movement away from the edge of the top electrode upon application of voltage between the top and bottom gate electrode, akin to a scenario without a counter electrode, similar to a FET setup. Our hypothesis explains carrier movement as follows: Initially, when a pulse voltage is applied, carriers are injected from the top electrode and accumulate at the interface between the P4T2F-HD layer and the gate insulator. This accumulated charge creates a space charge field, acting as the propelling force for carrier movement. This phenomenon is also elucidated through an equivalent circuit model comprising a transmission line constructed from tiny resistors and capacitors arranged serially.

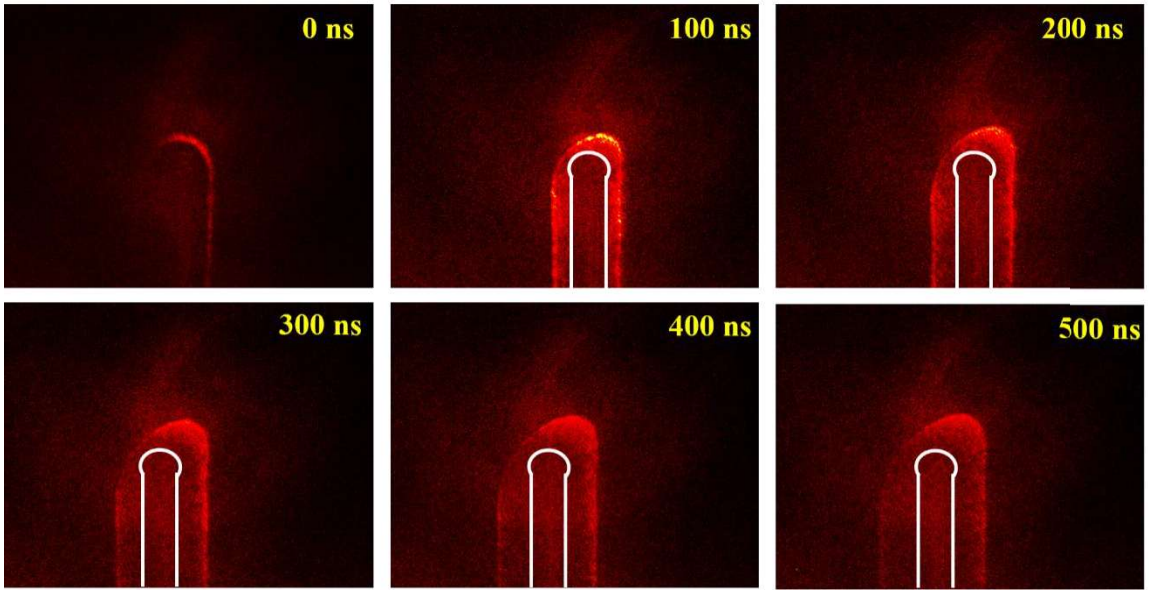


Figure 3. 8 *Represents the time-resolved SHG image of the device with different time intervals from 0 to 500ns.*

In this study, I investigated SHG by modulating the delay time between 0 ns and 500 ns in increments of 100 ns, as illustrated in ***Figure 3.8***. The analysis revealed that the initial phase of carrier displacement correlates with the square root of time, indicating a complex transport mechanism that extends beyond mere diffusion, influenced significantly by the spatial charge field as previously discussed. Furthermore, the spatial distribution of carriers emanating from the round-shaped electrode over time suggests a focus on carrier migration through the material rather than just their injection point. To ascertain the orientation of the deposited thin film, we positioned the film at a 45º angle relative to the flow direction, as shown in ***Figure 3.7(a)***. This orientation was confirmed using SHG imaging performed at various intervals, as shown in ***Figure 3.8***. Notably, there was a significant enhancement of charge carrier mobility along the direction of alignment, with decreased activity in directions perpendicular to the film's orientation. This behavior is likely due to the uniform alignment of polymer chains along the expansion direction of the film. Such an alignment enhances charge transport along the polymer backbone by reducing charge carrier

scattering, thereby significantly boosting carrier mobility within the thin film[98, 99]. This disparity underscores the anisotropic nature of charge transport in these materials, suggesting that even minor variations in the fabrication process or molecular alignment could significantly affect transport efficiency. These results clearly demonstrate the substantial impact of molecular orientation on the charge transport properties of P4T2F-HD thin films. The stark contrast in carrier velocities between the maximum and minimum directions emphasizes the crucial role of precise molecular alignment in enhancing the electrical performance of organic semiconductor devices. By carefully adjusting the orientation angle during the fabrication process, we can greatly improve directional charge transport, potentially leading to the development of more efficient and high-performing organic electronic devices.

3.4.Conclusion:

In conclusion, I investigated the anisotropic charge transport in highly oriented P4T2F-HD thin films, using both SHG analysis and conventional I-V characterization techniques, has provided substantial insights. This study indicates a distinct difference in mobility, which was 6×10^{-2} cm²/V.s along the direction parallel to the film orientation and 4.01×10^{-3} cm²/Vs in the perpendicular direction. SHG analysis further refined my understanding, revealing mobility values of about 0.045 cm²/Vs in the maximum direction and 2.1×10^{-3} cm²/Vs in the minimum direction. These results highlight the significant influence of molecular orientation on the electrical properties of the films, with a marked disparity in mobility and carrier velocity across different directions. This emphasizes the critical role of directional alignment in enhancing the performance of organic semiconductor devices.