

***Coupled Structural and Dynamical Responses in
Organic Semiconductors
Probed by Time and Frequency-Resolved
Spectroscopy***

by

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*Dedicated to my
Grandfather*

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Abstract

Photovoltaics has emerged as a promising technology in the global transition toward renewable energy. Organic conjugated polymers such as poly(3-hexylthiophene) (P3HT) offer a promising alternative to silicon-based materials by combining tunable optoelectronic properties with low-cost solution processing and mechanical flexibility. Although the efficiency of P3HT-based photovoltaic devices has improved significantly over the past decade, their performance remains limited and is not yet comparable to that of silicon-based technologies. Understanding the fundamentals behind the efficiency limitations requires a detailed investigation of the photophysical processes that govern carrier generation and their transport in photovoltaic systems. In this Ph.D. thesis, light-matter interactions are utilized to investigate how P3HT and a commonly used flexible substrate, poly(ethylene terephthalate) (PET), respond to external perturbations such as electric fields, mechanical stretching, and processing temperature. Experiments are performed in both time and frequency domains to study the interplay between molecular structure, charge dynamics, and mechanical deformation.

In the first part of the thesis, results obtained from time-resolved studies are presented. Femtosecond transient absorption pump-probe spectroscopy is used to examine the influence of electric field and mechanical stretching on the dynamics of photoexcited charge pairs in P3HT. By probing the photoexcited species at approximately 638 nm, a clear influence of both perturbations on charge-pair dynamics is observed. In the electric-field-dependent study, by employing a below band-gap excitation in a P3HT film on glass and a P3HT-based diode, we have observed that polaron pairs (PPs) in P3HT can be generated not only by hot-exciton dissociation but also by photons below the optical band-gap. The transient response probed at 638 nm exhibit a fast component associated with PPs and a slower component attributed to delocalized polaron pairs (DP_2s). By applying an external electric field, we have observed that bimolecular annihilation of DP_2s competes with recombination processes. Subsequently, the impact of uniaxial stretching on neat P3HT films was investigated. A bi-exponential kinetic response persists with the contribution of PPs and DP_2s . Mechanical stretching of up to 7% reveals a population redistribution between PPs and DP_2s , which can be explained based on polymer chain

alignment. Once the level of applied stretching exceeds the 7% , the transient response shows a complex response which can be explained based on the effective transfer of strain and formation of microcracks.

The second part of the thesis employs Raman spectroscopy and ultraviolet-visible (UV-Vis) absorption spectroscopy to study the impact of mechanical stretching on these polymer systems. UV-Vis measurements show that P3HT thin films and Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS)/P3HT bilayers retain an essentially constant optical band-gap up to 7% tensile strain, regardless of annealing conditions or stack configuration. At 10 % strain the band-gap widens by 4-5 meV, marking a threshold where mechanical accommodation yields to electronic perturbation. Raman spectroscopy probing the ring-skeleton modes at 1445 cm^{-1} (C=C) and 1377 cm^{-1} (C-C) in P3HT thin films spin-coated on a PET substrate reveals that these modes are sensitive to applied mechanical stretching. By analyzing the evolution of the Full Width at Half Maximum (FWHM) and the Raman band positions of these two vibrational modes, it becomes possible to separate temperature-induced morphological changes, which influence polymer rigidity, from mechanically induced chain alignment effects. The combined analysis of these spectral parameters therefore provides a sensitive probe of the structural response of P3HT, enabling a deeper understanding of its behavior in flexible electronic applications. Since PET is a common flexible substrate for P3HT-based flexible photovoltaic devices, its mechanical and optical properties were also characterized. UV-Vis absorbance measurements on amorphous PET films stretched up to 30% revealed significant increases in absorption across the visible and UV regions. Raman spectra showed that strains above 5 % cause irreversible shifts in Raman band and broadened FWHM, implying partial molecular reorganization and the emergence of structural order. These observations underscore that PET's optical transparency and molecular structure are strain-dependent and must be considered when designing flexible devices.

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List of Publications

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2. Ayush K. Ranga, Mahya Ghorab, Patrice Donfack, Debkumar Rana, Mojtaba Joodaki, Veit Wagner, Arnulf Materny
Time-Resolved Analysis of Polaron-Pair Dynamics in Flexible P3HT Films (manuscript ready to be submitted).
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4. Mahya Ghorab, Ayush K. Ranga, Arnulf Materny, Veit Wagner, Mojtaba Joodaki
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2. Sahar Khandan, Anupam Sarkar, Arun Pal, Bassem S. Bassil, Friedrich Matteo Lüderitz, Marziyeh Kianihaftlang, Matthias S. Ullrich, Levente Kiss, Ayush K. Ranga, Arnulf Materny, and Ulrich Kortz. Peroxo-Containing Heteropolyanions $[XW_3O_7(O_2)_2O]^{6-}$ ($X = HPO_4^{2-}$, $HAsO_4^{2-}$, $CH_3AsO_3^{2-}$): Synthesis, Structure, and Solution Properties (ready for submission).

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1. European conference on non-linear spectroscopy (ECONOS-2025, Paris): Talk delivered on Direct route of ultrafast charge-pair generation upon below-band-gap excitation in P3HT: effect of external electric field.
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List of Acronyms

BBO: Beta-Barium Borate
CPA: Chirped Pulse Amplification
DFG: Difference Frequency Generation
DP: Delocalized Polaron
DP₂: Delocalized Polaron Pair Species
FWHM: Full Width at Half Maximum
GVD: Group Velocity Dispersion
IR: Infrared
OPA: Optical Parametric Amplifier
OPG: Optical Parametric Generation
PET: Poly(ethylene terephthalate)
PEDOT:PSS: Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate
PP: Polaron Pair
P3HT: Poly(3-hexylthiophene-2,5-diyl)
rr-P3HT: Regioregular Poly(3-hexylthiophene-2,5-diyl)
SHG: Second Harmonic Generation
SFG: Sum Frequency Generation
TA: Transient Absorption
UV-Vis: Ultraviolet–Visible Spectroscopy

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Chapter 1

Introduction

To minimize the redundancy and repetition in the thesis, this section presents a concise overview of the fundamentals of organic semiconductors and the experimental techniques used in this Ph.D. thesis. Detailed introductions tailored to each study are provided in the respective chapters.

1.1 Organic semiconductors and their application in photovoltaic devices

Recent progress in organic semiconductors has highlighted their potential as low-cost, lightweight, and mechanically flexible materials for optoelectronic applications, particularly in organic photovoltaic devices [2–4]. In comparison to state-of-the-art silicon-based technologies, organic semiconductor devices offer attractive advantages arising from solution processability and compatibility with large-area fabrication [5, 6]. Upon optical excitation, semiconducting materials generate electron-hole pairs, commonly referred to as excitons[7–10]. In inorganic semiconductors, thermal energy at room temperature is often sufficient to separate these charge carriers, allowing them to contribute directly to photocurrent generation. In contrast, organic semiconductors have low dielectric constant, resulting in strongly bound excitons that are localized over a small number of molecules. The dissociation of these bound electron-hole pairs into mobile charge carriers is therefore a nontrivial process and constitutes a central limitation to device efficiency[10–12]. Consequently, the performance of organic photovoltaic devices is governed not only by light absorption but also by the sequence of microscopic processes connecting exciton formation to free carrier generation.

Poly(3-hexylthiophene) (P3HT) is one of the most extensively studied conjugated polymers in the field of organic semiconductors and has served for more than two decades as a

benchmark material for both fundamental and device-oriented investigations[5, 8, 13]. The material’s popularity arises from its strong visible-light absorption, relatively high hole mobility, and good solution processability, all of which facilitate reproducible large-area devices [14, 15]. The semicrystalline nature of P3HT, characterized by ordered lamellar domains that coexist with amorphous regions, allows its optoelectronic properties to be systematically tuned through processing parameters such as solvent choice, thermal annealing, and mechanical deformation [16–18]. In addition, the well-resolved vibronic structure in its optical absorption spectra and the pronounced sensitivity of its Raman-active vibrational modes to backbone conformation and π -electron delocalization make P3HT particularly well suited for spectroscopic investigations [19–21]. As a result, P3HT has become a model system for exploring the relationships between molecular structure, excited-state dynamics, and charge-transport behavior in organic optoelectronic devices.

Laser-based spectroscopic techniques play a central role in studying the elementary processes that govern the response of P3HT and related materials. Time-resolved spectroscopy provides direct access to charge-carrier dynamics following photoexcitation, enabling the identification of excitonic, charge-transfer, and polaronic species and their evolution on ultrashort (fs) time scales [10, 11]. Complementary structural insight is obtained from Raman spectroscopy, which probes vibrational modes associated with specific molecular motions and is highly sensitive to backbone planarity, intermolecular interactions, and mechanical deformation [22–24]. Steady-state UV-Vis absorption spectroscopy further contributes by probing electronic transitions, thereby providing indirect information on conjugation length and molecular ordering. Variations in absorption line shape and vibronic structure are commonly used to assess changes in morphology induced by processing conditions, thermal treatment, or external perturbations [19, 25, 26]. The combined use of these techniques establishes a comprehensive framework linking molecular structure, excited-state dynamics, and macroscopic device performance, which forms the basis of the investigations presented in this thesis.

1.2 Laser spectroscopy for organic semiconductors

The development of time-resolved laser spectroscopy represented a major milestone in experimental science by enabling the direct observation of transient processes on ultrafast time scales. Advances in picosecond and femtosecond laser technology made it possible to monitor the evolution of excited states immediately following photoexcitation, fundamentally transforming the study of non-equilibrium phenomena in molecular and condensed-matter systems. These developments led to the establishment of femtochemistry, where chemical reactions and energy relaxation pathways could be followed in real time, providing unprecedented insight into coupled electronic and nuclear dynamics [27].

The application of time-resolved spectroscopy to organic semiconductors proved particularly impactful due to the intrinsically dynamic and heterogeneous nature of photoexcited states in these materials [10, 19, 28]. Strongly bound excitons, localized electronic states, and a manifold of intermediate species such as charge-transfer states and polarons give rise to complex relaxation pathways that cannot be captured by steady-state measurements alone. Ultrafast pump-probe spectroscopy has enabled direct identification of these species and their interconversion mechanisms, revealing that charge generation in organic semiconductors often proceeds through multiple competing channels rather than a single-step dissociation process [6, 12, 29]. Such insights have been instrumental in clarifying efficiency-limiting processes in organic solar cells and guiding the design of materials and device architectures that favor long-lived charge-separated states.

Within the scope of this thesis, femtosecond transient absorption pump-probe spectroscopy is employed to investigate the excited-state dynamics of P3HT-based systems under varying experimental conditions. The studies presented in Chapters 4 and 5 focus on the influence of external electric fields and mechanical deformation on the dynamics of photoinduced charge carriers. These investigations provide insight into how external perturbations modify population pathways and lifetimes of bound and delocalized charge species in device-relevant configurations.

In parallel with time-resolved techniques, Raman spectroscopy offers a complementary probe of the structural degrees of freedom that govern electronic behavior in organic semiconductors. Raman-active vibrational modes in conjugated polymers are strongly coupled to the π -electron system and are therefore sensitive to backbone conformation, chain planarity, and intermolecular interactions [19, 30]. Changes in Raman band position, FWHM, and relative intensity have been widely employed to assess molecular order, doping effects, and mechanical deformation. Importantly, Raman spectroscopy enables non-destructive characterization of multilayer device stacks, providing insight into interfacial coupling and strain transfer under realistic device conditions [24, 31].

Steady-state optical absorption spectroscopy in the ultraviolet and visible spectral ranges has likewise served as a foundational tool in organic semiconductor research. UV-Vis spectroscopy provides direct access to electronic transitions, optical band gaps, and vibronic structure, allowing the influence of molecular conjugation, aggregation, and solid-state packing to be systematically assessed [19, 25, 29]. In conjugated polymers such as P3HT, variations in absorption line shape and vibronic intensity ratios are commonly used as indicators of molecular order and effective conjugation length, thereby establishing direct links between processing conditions and optoelectronic functionality.

Raman spectroscopy and UV-Vis absorption spectroscopy are employed in chapters 7, 8 and 9 to investigate the impact of mechanical deformation on P3HT- and PET-based systems relevant to flexible optoelectronic applications. Chapter 7 and chapter 8 fo-

cuses on strain-induced modifications in the optical and structural properties of PET substrates and P3HT thin films, while chapter 9 examines the strain and temperature dependence of key Raman-active vibrational modes in P3HT. Together, these studies highlight how mechanical and thermal perturbations influence both structural organization and spectroscopic response in flexible device architectures.

The combined use of time-resolved spectroscopy, Raman spectroscopy, and UV-Vis absorption spectroscopy thus enables a multiscale understanding of organic semiconductors, linking ultrafast excited-state dynamics to molecular structure and macroscopic device behavior. This integrated spectroscopic framework has transformed organic semiconductor research from a largely phenomenological field into one guided by quantitative mechanistic insight. The investigations presented in this thesis build upon this framework to explore the coupled structural and dynamical responses of polymer-based semiconductor systems under conditions relevant to device operation and flexible optoelectronic applications.

Time-Domain Studies

In the first part of the thesis, results obtained from time-domain spectroscopy are presented. For the experiments, time-resolved femtosecond transient absorption spectroscopy was performed on different samples with applied external perturbations. Subsequent chapters 4 and 5 present the results obtained from two different studies.

Chapter 2

Time-Resolved Spectroscopy

2.1 Overview

This chapter provides an overview of nonlinear spectroscopy and the fundamental concepts underlying nonlinear optical interactions. When materials are exposed to sufficiently intense electromagnetic fields, their response deviates from a linear to non-linear response. Such nonlinear processes include sum-frequency generation, difference-frequency generation, and higher harmonic generation. The basic theoretical framework governing these effects is introduced to establish the foundation for their spectroscopic relevance and applications.

2.2 Basics Of Nonlinear Spectroscopy

When electromagnetic radiation interacts with matter, the oscillating electric field perturbs the equilibrium charge distribution within atoms or molecules. The electron cloud is displaced relative to the positively charged nucleus, giving rise to an induced dipole moment. The collective response of these induced dipoles determines how the material interacts with the incident field and governs its optical properties.

On a macroscopic scale, this response is described by the polarization of the medium, defined as the dipole moment per unit volume. In the presence of weak electromagnetic fields, the displacement of the electron cloud remains small compared to interatomic distances. Under these conditions, the restoring force acting on the displaced charges can be approximated as proportional to the displacement, and the system can be modeled as a harmonic oscillator. This linear approximation leads to a polarization that is directly proportional to the applied electric field and forms the basis of linear optical interactions.

$$\mathbf{P} = \epsilon_0 \chi^{(1)} \mathbf{E} \quad (2.1)$$

where ε_0 is the permittivity of free space and $\chi^{(1)}$ is the linear electric susceptibility. In the case of ultrafast spectroscopy, due to the involvement of very high peak power; a harmonic oscillator cannot be used to approximate the system. To take into account anharmonicity created by high laser powers, an anharmonic oscillator approximation can be used. This can be done by Taylor series expansion of polarization: The polarization created can be written as:

$$P = \varepsilon_0 (\chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \dots) \quad (2.2)$$

Here $\chi^{(2)}$ and $\chi^{(3)}$ are the second- and third-order nonlinear susceptibilities, respectively. In the case of nonlinear optics, the response of the material is a very important factor to be taken into account, which is reflected especially by second and third-order susceptibilities. The correlation of polarization induced in the system and the incident electric field can be given by solving the Maxwell equations:

$$\nabla^2 E = \varepsilon_0 \mu_0 \frac{\partial^2 E}{\partial t^2} + \mu_0 \frac{\partial^2 P}{\partial t^2} \quad (2.3)$$

Where μ_0 is the magnetic permeability. This equation can be further solved in terms of speed of light and refractive index of material as:

$$\nabla^2 E = \frac{\eta^2}{c^2} \frac{\partial^2 E}{\partial t^2} + \frac{1}{\varepsilon_0} \frac{\partial^2 P}{\partial t^2} \quad (2.4)$$

Where η is the refractive index of the medium. The solution of polarization can be given by:

$$P(r, t) = P e^{(ik \cdot r - i\omega t)} \quad (2.5)$$

Where k is the wave vector associated with the incident field, and ω is the angular frequency. It is clear from the solution of the Maxwell equation that Polarization P is dependent on wave-vector k and angular frequency of the incident field ω . In the case of non-linear optics, the wave vector and angular frequency can be written as a summation of different components. This follows a very crucial component in ultrafast spectroscopy, which is the conservation of momentum and energy, which, for certain processes, results in phase-matching conditions for the involved laser pulses and the resulting signal.

2.3 Different nonlinear processes

In this section, several nonlinear optical processes that are relevant to the experiments presented in this thesis are briefly introduced. These processes form the basis for frequency conversion techniques that enable access to different spectral regions. In our laboratory,

for example, nonlinear interactions are employed in conjunction with two optical parametric amplifiers to generate tunable radiation at selected frequencies required for the experimental investigations.

A basic understanding of different nonlinear phenomena can be developed by considering an incident electromagnetic wave as a plane wave with angular frequency ω oscillating in time, which can be written as

$$E(t) = E_0 \cos(\omega t) \quad (2.6)$$

Then, the induced polarization due to this field can be written as

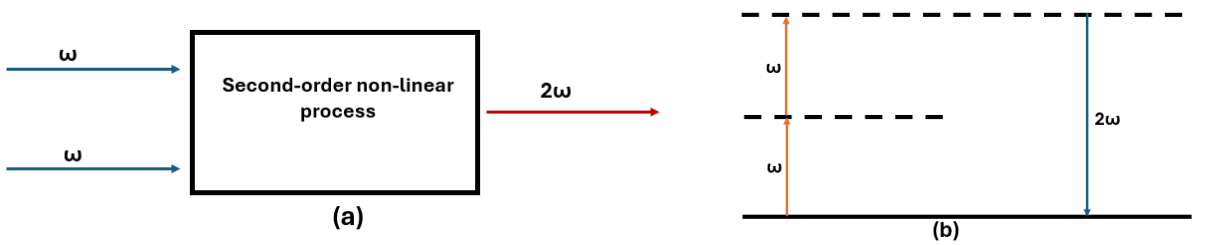
$$P = \varepsilon_0 (\chi^{(1)} E_1 \cos(\omega t) + \chi^{(2)} E_1^2 \cos^2(\omega t) + \chi^{(3)} E_1^3 \cos^3(\omega t) + \dots). \quad (2.7)$$

Using the trigonometric identities $\cos^2 x = \frac{1}{2}(1 + \cos 2x)$ and $\cos^3 x = \frac{1}{4}(3 \cos x + \cos 3x)$, this expression can be rewritten as

$$P = \varepsilon_0 \left(\chi^{(1)} E_1 \cos(\omega t) + \frac{\chi^{(2)}}{2} E_1^2 [1 + \cos(2\omega t)] + \frac{\chi^{(3)}}{4} E_1^3 [3 \cos(\omega t) + \cos(3\omega t)] + \dots \right). \quad (2.8)$$

From this expression, it becomes evident that nonlinear interactions give rise to electromagnetic fields whose frequencies correspond to combinations of the incident frequencies. These newly generated components are not arbitrary; their formation is governed by fundamental conservation laws, namely the conservation of energy and momentum (often expressed as phase-matching or wave-vector conservation conditions). Only when these conditions are satisfied can efficient frequency conversion occur.

The contribution oscillating at twice the fundamental frequency corresponds to second harmonic generation (SHG), while the component at three times the fundamental frequency represents third harmonic generation (THG). Higher-order nonlinearities similarly lead to the generation of additional harmonic and mixed-frequency components. Figure 2.1 shows the schematics and energy level diagram for the second harmonic generation.



(a) Schematic of second harmonic generation.

(b) Energy-level representation of SHG.

Figure 2.1: Illustration of second harmonic generation (SHG): (a) frequency mixing in a nonlinear medium and (b) corresponding energy-level diagram.

2.3.1 Sum frequency and difference frequency generation

The origin of sum-frequency generation (SFG; see Figure 2.2) and difference-frequency generation (DFG; see Figure 2.3) can be understood by considering two plane waves with angular frequencies ω_1 and ω_2 , given by

$$E = E_1 \cos \omega_1 t + E_2 \cos \omega_2 t \dots \dots \dots (2.9)$$

Plugging in this term to calculate only the second-order term will give:

$$P^{(2)} = \varepsilon_0 \chi^{(2)} (E_1 \cos \omega_1 t + E_2 \cos \omega_2 t)^2 (2.10)$$

Rewriting this equation yields the terms of sum frequency, difference frequency, and second harmonic generation:

$$P^{(2)} = E_1^2 + E_2^2 + E_1^2 \cos(2\omega_1 t) + E_2^2 \cos(2\omega_2 t) + \frac{E_1 E_2}{2} \cos(\omega_1 + \omega_2)t + \frac{E_1 E_2}{2} \cos(\omega_1 - \omega_2)t (2.11)$$

The term in Eq. 2.11 not depending on the frequency give rise to DC components not playing a role in our case. The schematics of sum frequency generation and difference frequency generation are given in Figure 2.2 and Figure 2.3, respectively.

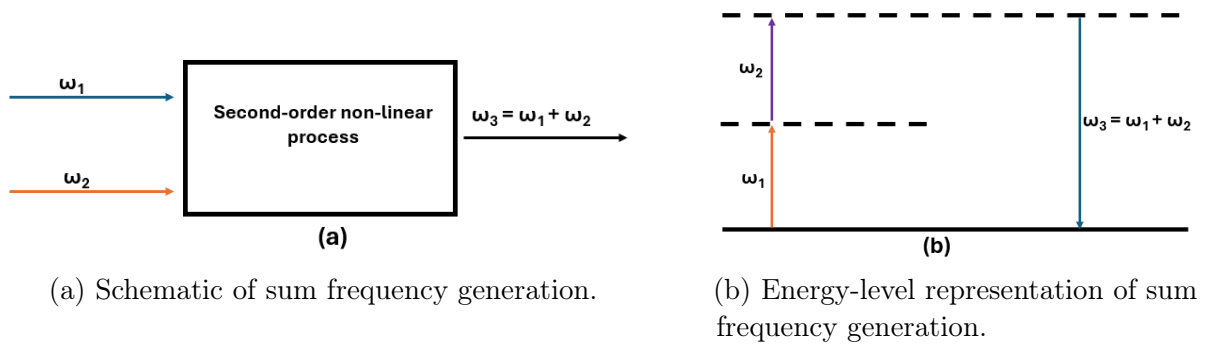


Figure 2.2: Illustration of sum frequency generation (SFG): (a) frequency mixing in a nonlinear medium and (b) corresponding energy-level diagram.

2.3.2 Optical Parametric generation

Optical parametric amplification (OPA) is employed in our laboratory to generate tunable laser wavelengths required for the experiments described in this thesis. Two such devices (TOPAS systems) are used, enabling the generation of two independently tunable ultrafast pulses. OPA can be regarded as the inverse process of sum-frequency generation. Instead of combining two input frequencies to produce radiation at a higher frequency, a single

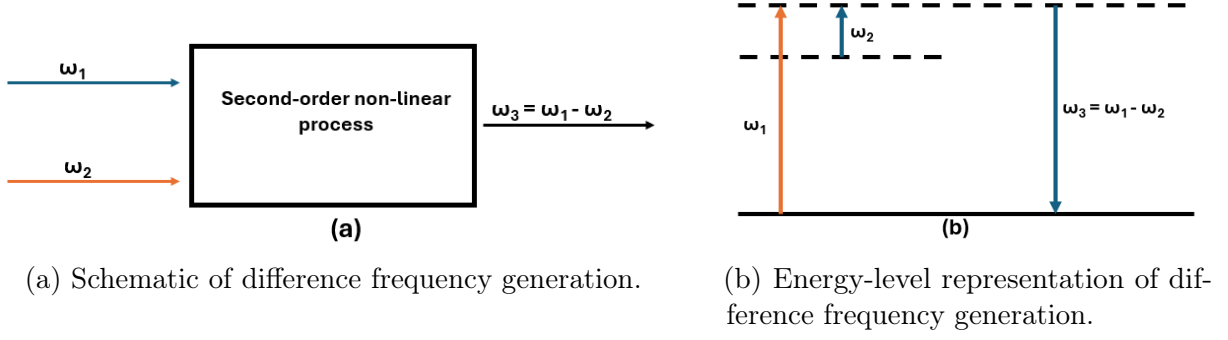


Figure 2.3: Illustration of second harmonic generation (SHG): (a) frequency mixing in a nonlinear medium and (b) corresponding energy-level diagram.

high-frequency pump photon is converted into two lower-frequency photons through a nonlinear interaction.

In this process, the incident laser beam, referred to as the pump, has the angular frequency ω_p (in our case, the output of a Chirped pulse amplification (CPA) femtosecond laser centered at approximately 800 nm). Within a suitable nonlinear crystal, the pump photon is converted into two photons known as the signal and idler, with angular frequencies ω_s and ω_i , respectively. Energy conservation requires that

$$\omega_p = \omega_s + \omega_i, \quad (2.12)$$

while momentum conservation, often referred to as the phase-matching condition, imposes the additional constraint

$$\mathbf{k}_p = \mathbf{k}_s + \mathbf{k}_i, \quad (2.13)$$

where $\mathbf{k}_p$, $\mathbf{k}_s$, and $\mathbf{k}_i$ denote the corresponding wave vectors of the pump, signal, and idler beams. Efficient parametric amplification occurs only when both energy and momentum conservation conditions are simultaneously satisfied.

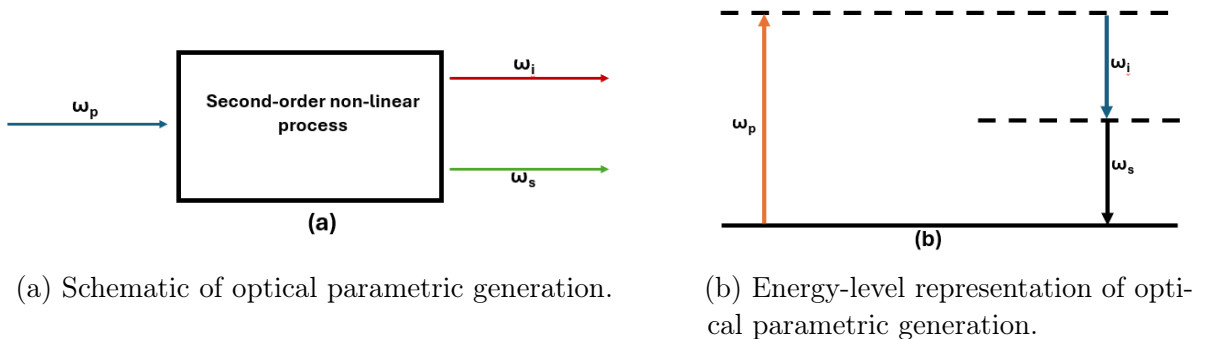


Figure 2.4: Illustration of second harmonic generation (SHG): (a) frequency mixing in a nonlinear medium and (b) corresponding energy-level diagram.

The schematic representation and corresponding energy-level diagram of the optical

parametric generation process are shown in Figure 2.4. While the sum of the signal and idler frequencies is constrained by energy conservation to equal the pump frequency, their relative distribution is determined by the phase-matching condition. In practice, this can be adjusted by varying the phase-matching angle, for example through rotation of the nonlinear crystal in which the second-order interaction takes place.

2.4 Pump Probe Spectroscopy

In this thesis, pump-probe spectroscopy is employed to investigate the dynamics of charge carriers on ultrashort time scales. The temporal resolution of the experiment is determined by the cross-correlation of the pump and probe pulses and, in our setup, lies in the range of approximately 100-150 fs. In this technique, an initial pump pulse (ω_{pu}) excites the system, and the subsequent evolution of the excited states is monitored by a time-delayed probe pulse (ω_{pr}). The photoinduced species that emerge from this excitation exhibit characteristic transient absorption features. In a transient absorption experiment, the delayed probe pulse measures changes in transmission as a function of pump-probe delay time. More specifically, the pump pulse excites the system from the ground state S_0 to an excited state S_1 . The probe pulse can subsequently promote the system to a higher-lying state, for example from S_1 to S_2 (see Figure 2.5). Variations in the probe transmission reflect changes in the population of S_1 and provide information about the temporal evolution of the excited species, such as excitons, polarons and, polaron pairs.

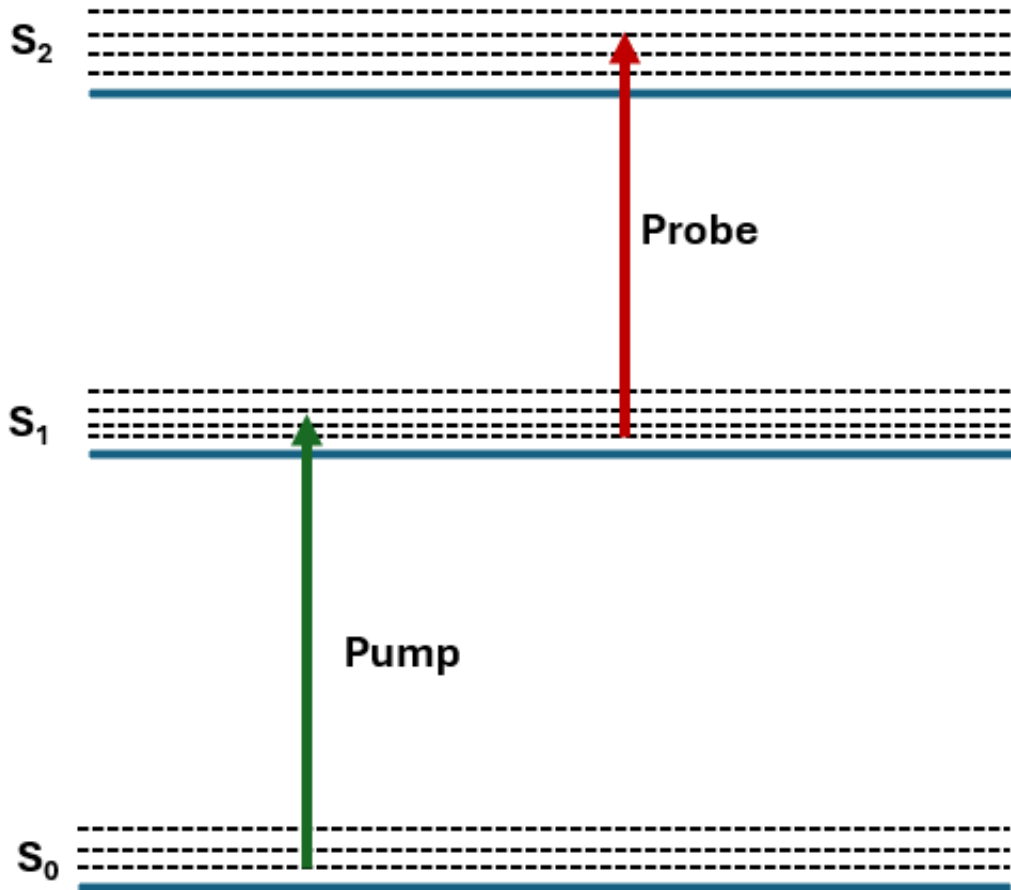


Figure 2.5: Schematic of pump-probe spectroscopy.

2.4.1 Optical Kerr-effect

For temporal calibration of our laser beams, we employ pump-probe spectroscopy to study the non-linear response in Carbon-disulphide(CS_2). An optical Kerr-effect experiment is performed using visible pump and probe pulses. In a typical Kerr-effect experiment, an intense pump pulse propagating through a nonlinear medium (CS_2 in our case) induces a transient change in the refractive index that is proportional to the instantaneous pump intensity. This effect originates from the third-order nonlinear susceptibility of the medium and leads to a pump-induced birefringence.

The strong electric field of the pump pulse transiently aligns the CS_2 molecules along its polarization direction, thereby modifying the optical properties of the medium. To determine the exact temporal overlap of pump and probe pulses, the probe beam is polarized at 45° with respect to the pump polarization and analyzed after passing through the Kerr medium using a crossed polarizer. When pump and probe pulses overlap spatially and temporally, the induced birefringence causes a rotation of the probe polarization, resulting in a measurable change in its transmitted intensity. By recording the transient

change in probe transmission as a function of pump-probe delay (see Figure 2.6, the point of maximum Kerr signal defines the temporal overlap of the two pulses. This reference point is identified as time zero for all subsequent pump-probe measurements.

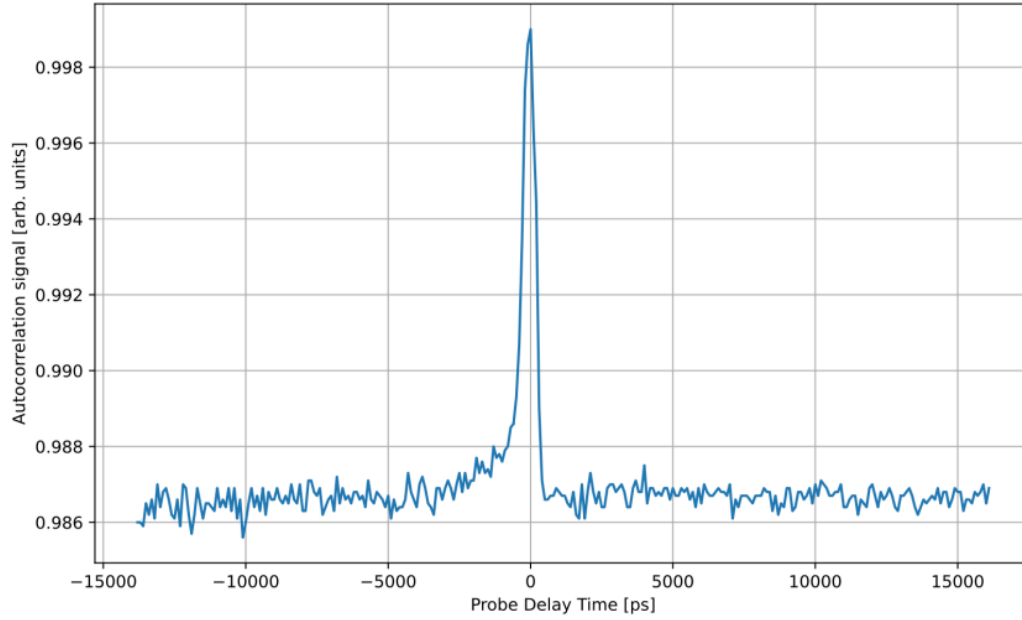


Figure 2.6: Optical Kerr-effect signal used to determine the temporal overlap of pump and probe pulses (time zero).

Chapter 3

Experimental Details

In this chapter, a detailed description of our time-resolved femtosecond transient absorption spectroscopy is presented. Since, the entire setup is composed of many special techniques and parts, a detailed description of each part is discussed.

3.1 Femtosecond Laser - CPA 2010:

In our setup, femtosecond laser pulses are generated by a CPA-2010, Clark-MXR Inc. Laser system. The femtosecond pulses are generated in a fiber laser with low power and then amplified in a colliding-pulse amplifier (CPA), which here is based on Ti:Sapphire system pumped by a Nd:YAG laser. The output wavelength is centered at 775 nm. The laser comprises two subsections

Bottom level	Top level
Diode laser	Regenerative Ti: Sapphire amplifier
SERF fiber oscillator	ORC-1000 frequency-doubled Nd:YAG pump laser
Pulse stretcher	Pulse compressor

In more detail, the SERF fiber laser operates as an active fiber ring laser and is pumped by a solid-state diode laser with a wavelength of 980 nm. It employs an additive pulse mode-locking technique. The SERF fiber laser emits light at a wavelength of 1550 nm, which is then doubled in frequency using a lithium niobate ($LiNbO_3$). This results in femtosecond (fs) pulses with a wavelength of 775 nm and a temporal width of approximately 100 fs. These pulses are used as seed pulses with a repetition rate of 40 MHz. Upon passing through a pulse stretcher, the pulses are stretched to a duration of around 200 ps. The stretched seed pulses are then amplified by a Ti:Sapphire regenerative amplifier, which is pumped by a frequency-doubled Nd:YAG laser (ORC-1000, Clark-MXR) operating

at a repetition rate of 1 kHz. The stretched pulses are coupled into and out of the regenerative amplifier using a Pockels cell. Inside the regenerative amplifier, the stretched pulses undergo multiple round trips through the active medium to achieve maximum amplification. The amplified pulses are subsequently directed to a pulse compressor, where they are compressed to approximately 150 fs using a holographic transmission grating-based compressor setup. The final output pulses have an energy of 1 mJ per pulse and a repetition rate of 1 kHz.

3.2 Optical Parametric Amplifiers - TOPAS

In our experimental setup, two optical parametric amplifiers (OPAs, TOPAS systems from Light Conversion) are used to generate tunable wavelengths for our pump-probe measurements. The output of the CPA laser (775 nm) is used to pump two TOPAS sources. The primary pump is divided into two beams using a 50:50 beam splitter, each directed to an independent OPA.

The wavelength conversion within the TOPAS is based on optical parametric generation in combination with frequency doubling and nonlinear frequency mixing processes discussed earlier in chapter 2. Inside TOPAS, the incoming pump beam is first divided using a 10:90 beam splitter. The 10% intensity is further split into two equal parts using a 50:50 beam splitter. One part of the 10% beam is used to generate a broadband white-light continuum in a Barium borate (BBO) crystal. This white light acts as a seed for the amplification process. The seed is subsequently amplified in multiple passes through nonlinear crystals. After initial amplification stages, the signal is spectrally dispersed using a diffraction grating. A computer-controlled system rotates the grating to select the desired wavelength component for further amplification. The selected seed pulse is temporally and spatially overlapped with additional portions of the pump beam and undergoes further amplification stages. The 90% of the pump beam is utilized in the final amplification pass, resulting in strong output beams at three frequencies: the signal (ω_{signal}), the idler (ω_{idler}), and the residual pump (ω_{pump}). The signal and idler wavelengths are tunable via the software-controlled grating system and enable access to a broad spectral range extending from the ultraviolet to the infrared. The generated frequencies obey the energy conservation condition

$$\omega_p = \omega_{\text{signal}} + \omega_{\text{idler}}. \quad (3.1)$$

3.3 Pulse Compression

During wavelength generation and amplification inside the TOPAS systems, the laser pulses propagate through many dispersive optical material, including nonlinear crystals,

lenses and beam splitters. As a consequence of normal group-velocity dispersion (GVD) in these materials, the broadband femtosecond pulses acquire a positive chirp, meaning that higher-wavelength components propagate faster than lower-wavelength components. This temporal separation of spectral components leads to pulse broadening and a reduction in peak intensity. To compensate for the accumulated positive dispersion, the output of each TOPAS is passed through a standard two-prism compressor arrangement. By appropriately adjusting the prism separation and insertion depth, negative group-delay dispersion is introduced, counteracting the material dispersion acquired along the beam path. This compression stage restores the pulses to a duration close to their Fourier-transform limit, resulting in femtosecond pulses with a temporal width of approximately 80-90 fs. These compressed pulses from compressors are then utilized as pump and probe pulses for our experiments.

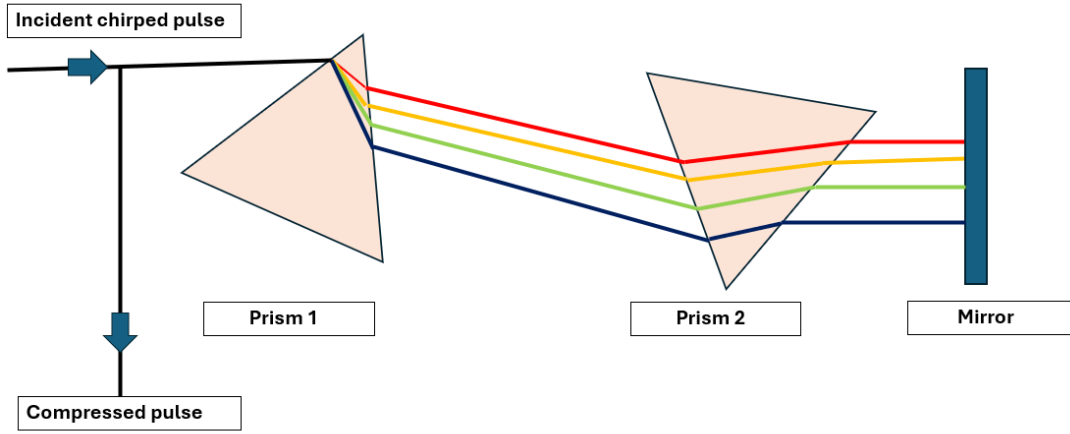


Figure 3.1: Prism compression setup used in our time-resolved setup for pulse compression.

3.4 Pulse Characterization

In order to characterize the pulse for temporal quality, an autocorrelator is used in our experimental setup. To measure the temporal width of chirp-compensated pump and probe beams, an autocorrelation is performed using an autocorrelator device. A Michelson interferometer type arrangement is used to split the beam into two equal parts using 50:50 beam splitter. These components traveled parallel to one another and are focused by a lens into a nonlinear beta-barium borate (BBO) crystal. Within the crystal, the two pulses interact to generate a sum-frequency (SF) signal. Owing to the phase-matching conditions, the SF signal produced by the temporal overlap of both pulses (i.e., the autocorrelation signal) is spatially separated from the second-harmonic signals generated by the individual pulses.

The resulting SF signal is measured as a function of the temporal delay between the two

pulses. A pinhole and an appropriate spectral filter are used to isolate only the ultraviolet SF component before detection with a photodiode. If the temporal intensity profile of the initial pulse is given by $I(t)$, the SF signal corresponds to the intensity autocorrelation function

$$I_{\text{SF}}(\tau) = \int_{-\infty}^{\infty} I(t) I(t - \tau) dt. \quad (3.2)$$

For pulses with a hyperbolic secant squared temporal profile with τ_p as pulse duration,

$$I(t) = I_0 \text{sech}^2\left(\frac{t}{\tau_p}\right), \quad (3.3)$$

the full width at half maximum (FWHM) of the intensity autocorrelation trace, Δt_{AC} , is related to the pulse duration (intensity FWHM), Δt_p , by the deconvolution factor

$$\Delta t_p = \frac{\Delta t_{\text{AC}}}{1.54}. \quad (3.4)$$

Thus, the actual pulse duration is obtained by dividing the measured autocorrelation width by 1.54 when assuming a sech^2 pulse shape.

3.5 Delay-Stage

Figure 3.2 shows a scheme of pump-probe setup including the time-delay stage used in our setup. In this setup, a very precise timing control of pump and probe pulses is achieved by employing retro-reflector mirrors. The mirrors are mounted on a movable delay stage which can be controlled using a computer. This arrangement in our experimental setup can provide a maximum temporal delay of 500 ps with a temporal resolution well-below the pulse duration.

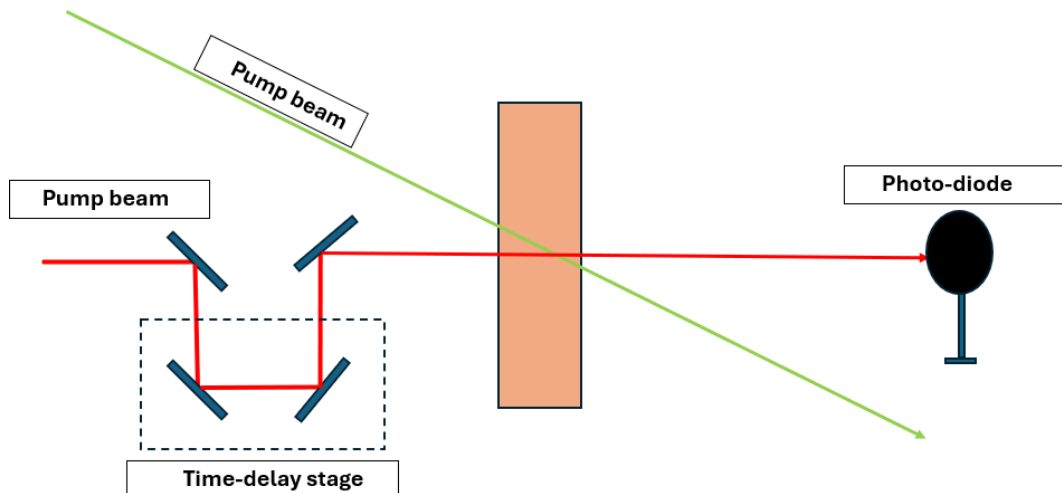


Figure 3.2: Schematic of pump-probe setup.

3.6 Detector

To monitor the change in probe transmission, the transmitted probe beam is detected using a photodiode. A photodiode is a semiconductor device that converts incident optical power into an electrical current using photoelectric effect. When photons with sufficient energy are absorbed in the depletion region of the diode, electron-hole pairs are generated. Under reverse bias, these charge carriers are rapidly separated by the internal electric field, producing a photocurrent proportional to the incident light intensity.

In the pump-probe experiment, the pump pulse excites the sample, and the time-delayed probe pulse investigates the evolving excited-state population. Any pump-induced change in absorption or transmission of the probe beam results in a corresponding change in the photocurrent generated by the photodiode. By recording this photocurrent as a function of pump-probe delay time, the transient dynamics of the excited species can be determined.

3.7 Boxcar Integrator

For the final signal detection, a boxcar integrator was employed. The output from photodiode is fed to the boxcar amplifier. Boxcar amplifier integrates and amplifies the detector output within a defined temporal window called gate, while suppressing signal components occurring outside this interval. In this way, the instrument performs gated amplification combined with temporal averaging, which significantly improves the signal-to-noise ratio. The reduction of noise arises from three main mechanisms: (i) The integration of the detector signal within the selected gate averages the signal over the defined time interval, thereby statistically reducing random noise contributions within

the gate. (ii) Temporal gating allows the isolation of the short-lived signal generated by excitation with femtosecond pulses from noise occurring outside the relevant time window. In transient absorption measurements, the useful signal is confined to the duration of the probe pulse. In our setup, the gate width was 1.5 ns. (iii) Signal averaging over multiple laser shots introduces an effective low-pass filtering behavior, reducing high-frequency noise components and further enhancing measurement stability.

3.8 Time-Resolved Femtosecond Transient Absorption Spectroscopy Setup

Fig. 4.7 represents our femtosecond time-resolved transient absorption spectroscopy measurement setup. By combining all the techniques and setups discussed in earlier sections, we use a Ti:sapphire regenerative amplifier (CPA 2010, Clark-MXR) operating at 1 kHz, with a central wavelength of 775 nm to generate pulses with energies of 1 mJ, and a pulse duration of 150 fs. This source pumps two optical parametric amplifiers (TOPAS, Light Conversion) to provide tunable visible pump and probe pulses. For the time-resolved experiments, we have used visible pump and probe pulses. More details regarding the choice of pump and probe wavelength are also discussed in the respective chapters. These pulses were compressed to sub-120 fs duration via prism compressors and aligned collinearly with parallel polarizations. Two delay stages were used to create a delay between pump and probe beams by reflecting the beams from a retro-reflector mirror mounted on adjustable linear stages. The two delay stages used in the experiments can provide a maximum delay of 100 ps between the two pulses. The parallel pump and probe beams from the delay stages were focused on the sample using a 20 cm focal-length lens. A change in probe transmission was detected using a photodiode, and the signal was integrated and amplified with a boxcar amplifier.

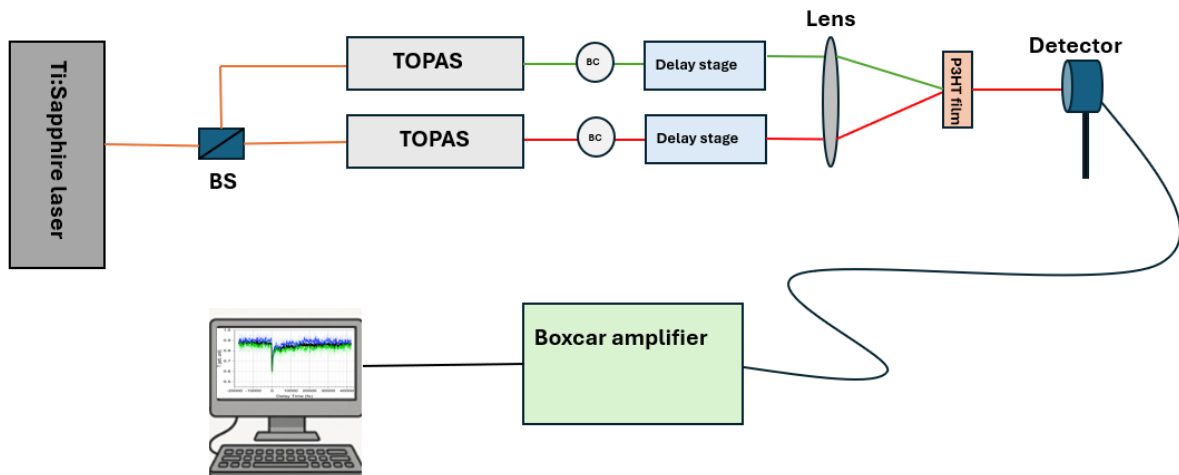


Figure 3.3: Time-resolved femtosecond pump-probe spectroscopy setup.

3.9 Sample Preparation

During the Ph.D. thesis, multiple optimization processes have been followed to fabricate thin films and photovoltaic devices based on P3HT. We have used the spin coating method to fabricate even layers of desired thickness ranges. By changing the spin speed and solution concentration, the desired thickness of approx. 200 nm is achieved.

For stretching based projects, all thin films were coated on a PET substrate. Once the initial processing of PET substrate was achieved, all samples were spin coated inside a clean room, and post processing such as annealing and stretching were carried out in accordance to the specific projects. Further detailed descriptions are provided in subsequent chapters.

In addition to the thin films used in different projects, optimization of the sample preparation for photovoltaic devices is also carried out inside the clean room. Two different types of substrate are used to fabricate P3HT based photovoltaic devices in a diode configuration. The detailed description of the fabrication process and the final efficiency achieved is presented in the next section.

3.9.1 P3HT only Diode on Glass Substrate

Figure 3.4 shows the P3HT only diode type device fabricated on rigid glass substrate.

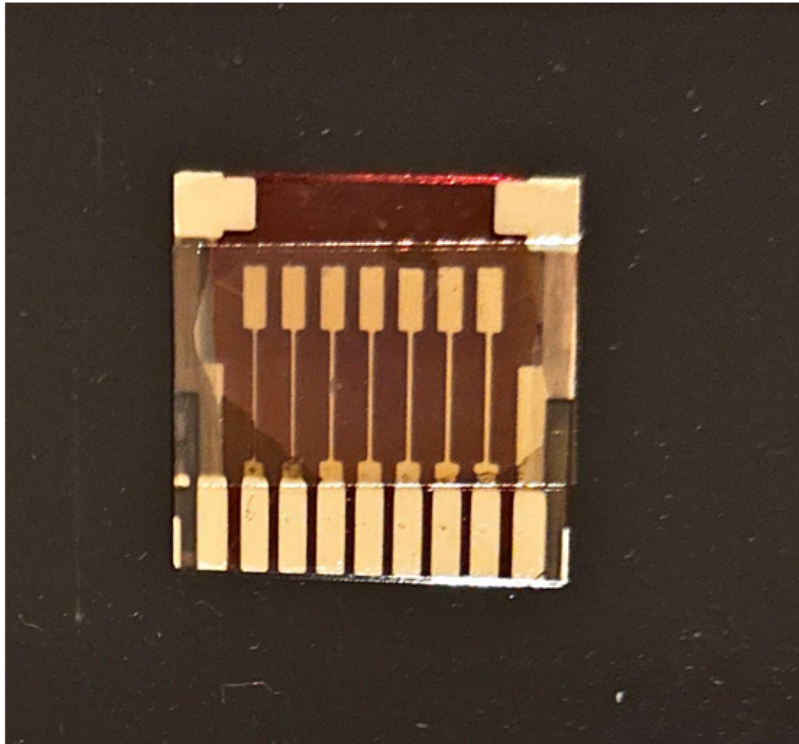


Figure 3.4: A P3HT only diode prepared on rigid glass substrate

The P3HT based devices were fabricated using solution processing inside a cleanroom environment in order to minimize particulate and organic contamination. The fabrication sequence consisted of substrate patterning, deposition of active semiconducting layers by spin coating, intermediate thermal annealing steps, and final top-electrode deposition by sputtering. Particular care was taken at each stage to ensure reproducibility and uniform film formation.

Substrate preparation

Indium tin oxide (ITO)-coated glass substrates were used as the bottom electrode. To prevent electrical short-circuits between the bottom and top contacts, the ITO layer was patterned prior to device fabrication. The substrates were first cleaned sequentially with acetone and isopropanol to remove surface residues. Subsequently, half of the ITO-coated surface was protected using a Kapton tape, while the exposed region was chemically etched in a heated $\text{H}_2\text{O}:\text{HCl}:\text{HNO}_3$ solution (5:4:1 volume ratio) at 60°C for 6 minutes.

After etching, the substrates were thoroughly rinsed with deionized water, dried using a nitrogen gun, and the protective tape was removed. To further eliminate organic contaminants and improve surface wettability, patterned substrates were treated with a UV-ozone cleaner for 10 minutes immediately before layer deposition.

Layer deposition

For the electron transport layer, zinc oxide (ZnO) was employed. The ZnO precursor solution was prepared by dissolving zinc acetate dihydrate in a solvent mixture of 2-methoxyethanol and ethanolamine, followed by stirring overnight to ensure complete dissolution and homogeneity. The solution was spin-coated onto the patterned ITO substrates at 5000 rpm for 30 s and subsequently annealed at 180°C for 30 minutes to form a compact and uniform ZnO layer.

The active layer consisting of poly(3-hexylthiophene) (P3HT) was dissolved in chlorobenzene at a concentration of 30 mg/mL and stirred overnight to obtain a homogeneous solution. The solution was spin-coated on top of the ZnO layer at 3000 rpm for 35 s. Post-deposition thermal annealing was carried out in two steps, first at 75°C and subsequently at 100°C, to improve film morphology, enhance polymer ordering, and promote better interfacial contact with the underlying layer.

Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) was used as the hole transport layer. A PEDOT:PSS solution (Clevios HTL Solar) containing 2 wt% Zonyl FS-300 as a wetting additive was prepared and spin-coated at 5000 rpm for 60 s onto the P3HT layer. The deposited film was annealed at 75°C for 10 minutes to remove residual solvent and stabilize the layer.

Top electrode

Silver (Ag) top contacts were deposited by sputtering through a shadow mask that defined seven identical devices on each substrate. Each device had an active area of 0.089 cm^2 . Following electrode deposition, the completed devices were transferred to and stored inside a glove box under controlled atmosphere and reduced light exposure before electrical characterization.

3.9.2 P3HT only Diode on PET Substrate

Figure 3.5 shows the P3HT only diode type device fabricated on flexible PET substrate. For the fabrication of the flexible devices, polyethylene terephthalate (PET) was used as the supporting substrate. To ensure mechanical stability during spin-coating and subsequent deposition of the top electrodes, the PET foil was temporarily fixed onto a glass slide using adhesive tape. This arrangement provided a rigid backing during processing while preserving the flexibility of the substrate. After completion of the device stack, the PET-supported diode was carefully detached from the glass, yielding a fully flexible device.

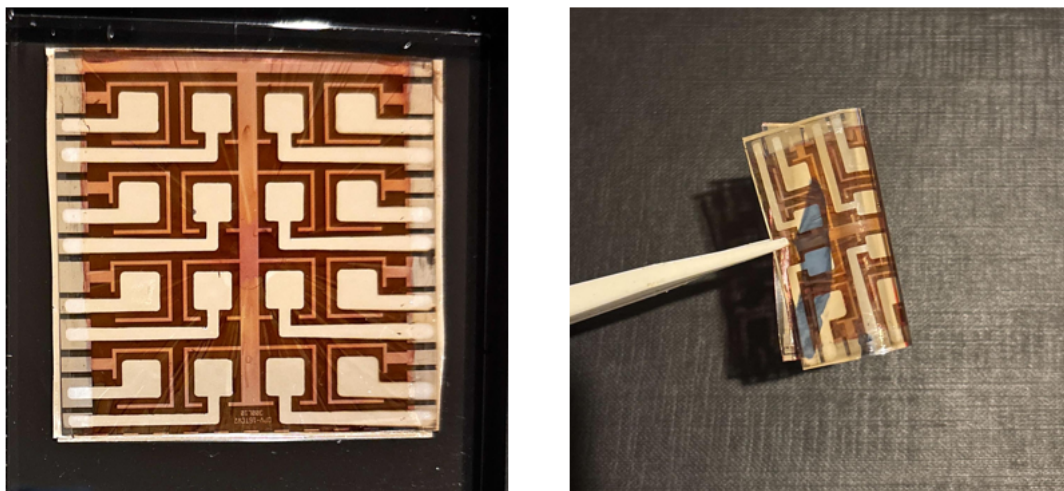


Figure 3.5: A P3HT only diode prepared on flexible PET substrate

The PET substrate additionally offers high optical transparency, allowing efficient transmission of incident light into the photoactive layer. In this architecture, a printed silver mesh electrode was integrated onto the flexible PET foil to act as the bottom contact. To improve lateral charge transport and ensure homogeneous current collection across the active area, a highly conductive layer of PEDOT:PSS was deposited on top of the silver mesh, thereby completing the bottom electrode structure for the PET-based solar cells.

Other steps involving deposition of HTL, P3HT and ETL are similar to the steps followed for device on glass + ITO substrate. The top electrode of silver was deposited using

sputter coating and the shadow mask used for the device on PET has 16 devices with active area of 0.025 cm^2 each.

3.10 Current - Voltage Characterization using Solar Simulator

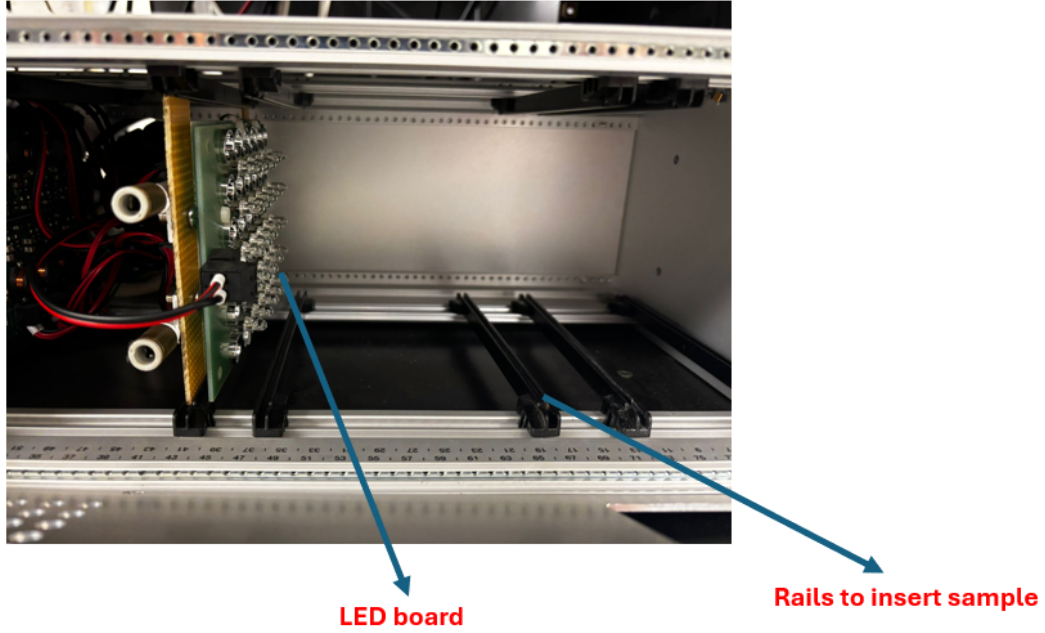


Figure 3.6: Solar simulator used for current-voltage measurements.

Figure 3.6 shows the setup used to measure the current-voltage characteristics of the fabricated diodes. To perform the measurements, a solar simulator was employed to reproduce the conditions of the sunlight during the measurements. The setup was calibrated to provide standard AM1.5 (Air Mass 1.5) spectral conditions with an intensity of 1000 W m^{-2} .

Figure 3.7 shows the circuit board used to apply the sweeping voltage to the metal contacts. Figure 3.7 (a) represents the circuit used to measure the diode on glass substrate and Figure 3.7 (b) represents the circuit used to measure the diode on PET substrate.

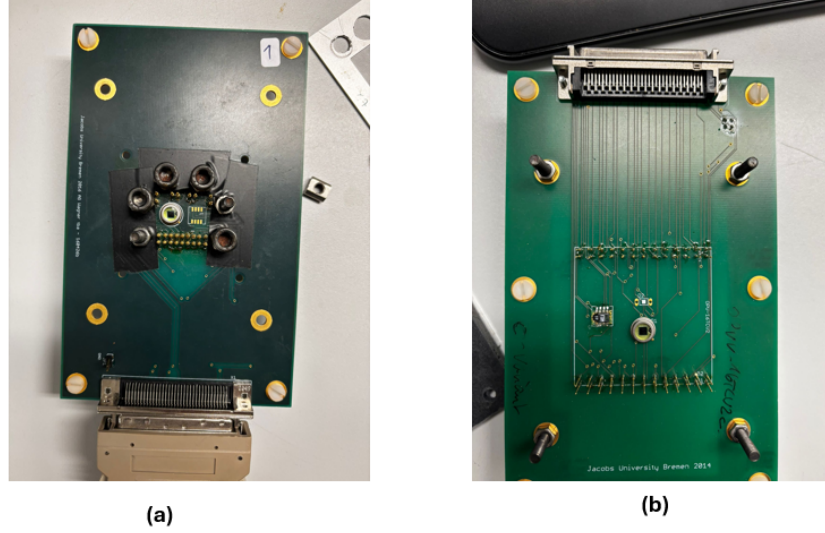


Figure 3.7: Controllers used to read the I-V characteristics for (a) device with 7 diodes on glass substrate (b) device with 16 diodes on PET substrate.

3.11 I-V Characteristics for Device on Glass Substrate

The photovoltaic performance of a solar cell is determined from its current-voltage (I-V) characteristics recorded under calibrated illumination:

$$P_{\text{in}} = 1000 \text{ W m}^{-2}. \quad (3.5)$$

The I-V curve provides direct access to the fundamental device parameters such as the short-circuit current density (J_{SC}), the open-circuit voltage (V_{OC}), the fill factor (FF), and the power conversion efficiency (η).

The short-circuit current density is defined as the current density at zero applied voltage,

$$J_{\text{SC}} = J(V = 0), \quad (3.6)$$

which corresponds to the maximum photocurrent generated when the device terminals are shorted.

The open-circuit voltage is defined as the voltage at which the net current vanishes,

$$J(V_{\text{OC}}) = 0. \quad (3.7)$$

The electrical output power density at any operating voltage V is given by

$$P(V) = J(V) V. \quad (3.8)$$

The maximum power point (MPP) is obtained at (V_m, J_m) such that

$$P_{\max} = J_m V_m. \quad (3.9)$$

The fill factor (FF), which quantifies the squareness of the I-V curve, is defined as

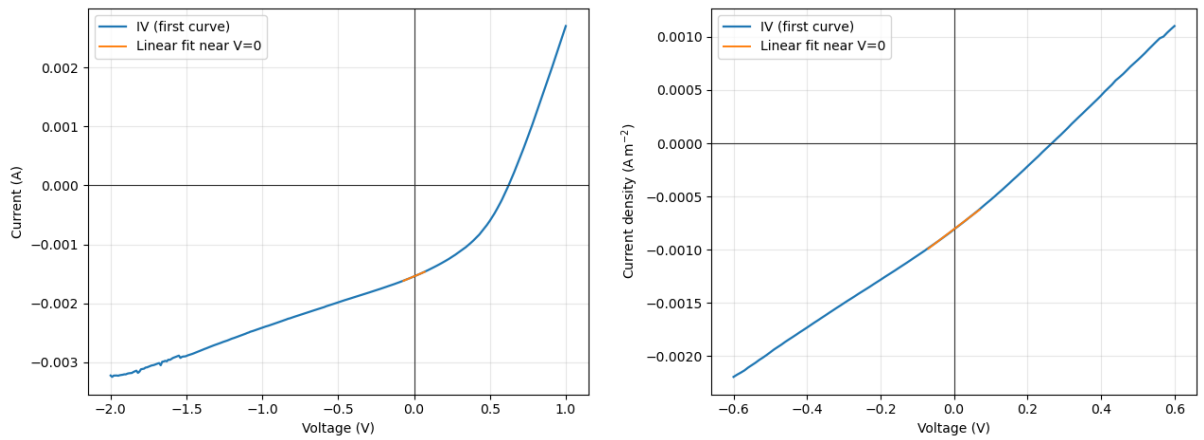
$$\text{FF} = \frac{J_m V_m}{J_{\text{SC}} V_{\text{OC}}}. \quad (3.10)$$

Finally, the power conversion efficiency (η) is defined as the ratio of the maximum electrical output power to the incident optical power:

$$\eta = \frac{P_{\max}}{P_{\text{in}}} = \frac{J_{\text{SC}} V_{\text{OC}} \text{FF}}{P_{\text{in}}}. \quad (3.11)$$

The efficiency therefore, depends simultaneously on current generation, voltage output, and resistive/recombination losses encapsulated in the fill factor. Together, these parameters provide a comprehensive description of the photovoltaic performance and enable direct comparison between different device architectures and processing conditions.

The device was mounted onto a dedicated sample-holder circuit board as shown in figure. 3.7, where contact pins established individual electrical connections to each device as well as to the bottom electrode. The circuit board was interfaced with the respective measurement instruments for current-voltage characterization. Figure 3.8 shows the normalized current-voltage curve measured with the solar simulator.



(a) P3HT diode on rigid glass substrate.

(b) P3HT diode on flexible PET substrate.

Figure 3.8: Current-voltage (I-V) characteristics of P3HT-only diodes fabricated on (a) glass and (b) PET substrates under AM1.5 illumination.

Parameters extracted from the I-V curves are listed below in table 3.1

Table 3.1: Photovoltaic parameters of P3HT only diode fabricated on glass and PET substrates under AM1.5 illumination.

Parameter	Glass Substrate	PET Substrate
V_{OC} (V)	1.423	0.308
J_{SC} (mA cm^{-2})	17.337	32.287
V_m (V)	0.390	0.130
J_m (mA cm^{-2})	10.542	17.625
P_{max} (mW cm^{-2})	4.112	2.291
Fill Factor (%)	16.67	23.04
Power Conversion Efficiency (%)	4.11	2.29

The photovoltaic parameters extracted from devices fabricated on glass and PET substrates reveal a clear performance difference. The device prepared on rigid glass exhibits a higher power conversion efficiency (4.11%) compared to the flexible PET-based device (2.29%), indicating that the glass-supported architecture is presently better optimized in terms of voltage output and overall power generation. Such performance discrepancies between rigid and flexible substrates are widely reported in the literature and are often attributed to differences in electrode quality, series resistance, interfacial contact properties, and morphological variations of the active layer.

To address these limitations in flexible devices, various external perturbations, particularly mechanical stretching have been explored as strategies to tailor microstructure and potentially enhance charge transport. In this thesis, a systematic spectroscopic investigation of different layers has been performed to develop a fundamental understanding of how structural modifications, especially chain alignment and microstructural rearrangements, influence the optoelectronic response.

Rather than focusing solely on device-level optimization, a bottom-up approach was adopted. Individual layers and their combinations were studied under controlled mechanical deformation in order to correlate microscopic structural changes with macroscopic electronic performance. This approach provides insight into how strain-induced chain alignment and defect formation contribute to efficiency variations observed between rigid and flexible device architectures.

Chapter 4

Direct Route of Ultrafast Charge-Pair Generation Upon Below-Band-Gap Excitation in P3HT: Effect of External Electric Field

Overview

This chapter provides the fundamental basis for understanding the response of photoexcited species in P3HT under external perturbations. Unlike the subsequent chapters, which investigate mechanical stretching and temperature effects, this study focuses on the influence of an applied electric field on polaron-pair (PP) dynamics [11]. The results offer important insight into the generation, recombination, and field-dependent behavior of PPs, thereby establishing a reference framework for comparing different types of perturbations in later chapters.

The content of this chapter are published in Physical Chemistry Chemical Physics: Debkumar Rana, Ayush K. Ranga, Arnulf Materny - (PCCP), DOI: 10.1039/D4CP04342A (Paper) Phys. Chem. Chem. Phys., 2025, 27, 4475-4486 :

Abstract

The generation and decay mechanism of polaron pairs (PPs) are relevant for a better understanding of photophysical processes in organic semiconductors such as Poly 3-hexylthiophene-2,5-diyl (P3HT). A widely suggested model assumes that ultrafast PP generation occurs mainly from hot-exciton dissociation within < 100 fs. In our experiments presented here, we have performed a wavelength-dependent transient pump-probe study

to investigate the generation mechanism of the PP states. Interestingly, we have found that a below-band-gap excitation can generate the PP states efficiently even with a very low absorption strength at the pump-laser wavelength. This process has been found in neat P3HT thin film as well as in a P3HT-only diode configuration. In addition, besides the fast PP dynamics, we have also observed longer-lived species, which can tentatively be assigned to delocalized PP states. To gain more information, we have studied the PP dynamics under the influence of a static external field in reverse and forward bias for different excitation fluences. From this, we conclude that the bimolecular annihilation process of delocalized PPs states competes with a recombination process. The external electric field speeds up the rate of the recombination process when the annihilation process is saturated at high fluences.

4.1 Introduction

Grasping the mechanisms of charge photogeneration is crucial for the optimized design of new materials aimed at enhancing the power-conversion efficiency of organic thin-film solar cells [32, 33]. In an organic solar cell, the generation of charge happens in mainly three steps: the formation of bound electron-hole pairs in the form of excitons, the migration of excitons to the interface between electron donor and acceptor materials, and the dissociation of excitons into an interfacial charge-transfer state [34, 35], with the hole and electron sitting on the neighboring donor and acceptor molecules. It is well-known that a significant amount of the electron-hole pairs can escape from their Coulombic interaction to produce the charges as photocurrent. However, the mechanism of the efficient charge photogeneration remains unclarified. Different charge-photogeneration mechanisms have been proposed, such as “hot-excitons” [36–39] or “cold-excitons” [40–44] mechanisms, charge delocalization [45, 46], high local charge mobility [47], and so forth, some of which lead to contradictory results.

Transient absorption (TA) spectroscopy on a femtosecond time scale is a unique tool to investigate the charge species such as excitons and polarons. Poly(3-hexylthiophene-2,5-diyl) (P3HT) is widely explored as a promising donor material especially for solar-cell technology. P3HT has commonly been used as a donor material in the photovoltaic blends with phenyl-C61-butyric-acid methyl ester (PCBM) [48–54]. The ultrafast generation of photoexcited species in pure P3HT is well known. Excitons, polaron pairs (PPs), and polarons are observed after photoexcitation in P3HT based on their different photoinduced absorption (PA) bands [55–57]. Here, the generation and decay mechanisms of the PPs is of great interest. It is well-established that upon the above-band-gap excitation, the hot-exciton dissociation process generates the PPs states within less-than 100 fs [55, 57]. However, also different scenarios are commonly invoked, like the rapid formation of PPs by exciton dissociation [58] or the PP formation from delocalized coherent excitations [59].

Recent theoretical work [60, 61] suggests that strong coherent coupling between electronic and vibrational degrees of freedom, that is, vibronic coupling, may generate the PPs very efficiently, similar to seminal models for polaron motion in solids [62]. Antonietta et al. [63] reported the origin of PPs from vibronic coupling of P3HT using two-dimensional spectroscopy with sub-20 fs pulses.

The different mechanisms of generating the PPs have been discussed in our earlier work [64, 65]. In our present work, we focus on the generation and the decay mechanisms of PPs after a below-band-gap excitation. The process of generation of PPs is still unclear when the system is excited with energies below the bandgap. Earlier, it has been reported that the absorption tail extending into the infrared may be due to the (1.35 eV / 919 nm) triplet state previously seen in the electroluminescence spectra of polythiophenes [66, 67]. Although, the direct excitation of triplet states is spin forbidden, the presence of the heavy sulfur atom could provide the necessary spin-orbit coupling weakly allowing this transition. These triplet states might also be responsible for the generation of PPs. For P3HT:PCBM, Parkinson et al. [68] have reported that the observation of a low-energy feature in absorption and photoluminescence measurements can lead to the suggestion that low-energy photons may create weakly bound PPs formed between the highest occupied molecular orbital HOMO of the polymer and the lowest unoccupied molecular orbital LUMO of PCBM. Matheson et al. [69] and Simon et al. [70] have investigated the charge-pair generation in P3HT:PCBM after below-band-gap excitation. Based on these two studies they concluded that interfacial dipoles at the donor/acceptor interface can cause the generation of charge pair states. The generation of PPs after below-band-gap excitation is of great scientific interest as the generation mechanism is very complex. To further investigate this process, we have performed experiments to study the dynamics of PPs arising from a low-energy excitation under varying conditions like different excitation fluences and external electric fields.

An organic solar cell device requires different layers of electrical contacts; the organic semiconducting material is sandwiched between an electron-transport and a hole-transport layer. Due to the potential difference of these asymmetric layers, the device behaves like a diode and exhibits an internal electric field. This internal field has an influence on the PP dynamics as we have demonstrated previously [64, 65]. Recent studies of the effect of an applied external electric field in P3HT have focused on the exciton and/or charge carrier dynamics using time-resolved photoluminescence spectroscopy [71, 72]. In order to obtain more information about the generation and decay mechanisms of the PPs generated after low-energy excitation, we further explore the role of external electric fields. In the first part of this manuscript, we discuss the generation and decay mechanism of PPs in a neat P3HT thin film. Later, the focus is going to be on the role of internal and external electric fields applied to a P3HT-only diode. Additionally, we have varied the excitation (pump) fluence to investigate the role of annihilation processes and to exclude the role of

multi-photon excitations.

4.2 Experimental Methods

4.2.1 Device fabrication

P3HT ($M_w = 34\text{--}41$ k, average regioregularity = 89–94 %, poly-dispersity index PDI = 1.5) was purchased from Rieke Metal and dissolved in chlorobenzene. The complete details of the device fabrication have been discussed in our earlier work [64]. The solution of P3HT in chlorobenzene is used to prepare the thin film and the device. As substrate for the P3HT thin film a glass plate was used. We have fabricated the P3HT device under ambient conditions. The solar cell stack for this device i.e. electron and hole-transport layers, glass substrate coated with ITO and the P3HT layer were prepared step by step. The measured thickness of the deposited P3HT layer is 200 nm. As mentioned above, the device fabricated in the solar-cell configuration behaves like a diode due to the asymmetric contacts deposited on the two sides of the P3HT layer, which also result in an internal electric field of 0.8 V. More information on the sample and its properties can be found in the supplementary information. The UV-Vis absorption spectrum is shown in figure. S1, the structure of the device in figure. S2 and the curve resulting from an I-V characterization in figure. S3. In the I-V curve, a small amount of current is present in our device also in the dark, which means that P3HT generates charges even in the absence of light. These charges may originate from the distortion of the P3HT side chain itself or the interface between ZnO and P3HT. After the sample preparation, in order to minimize oxygen doping, the fabricated layer-stack sample is immediately stored overnight in a glove box under N_2 atmosphere where it is air-bubble-free encapsulated with a top layer consisting of epoxy resin and a glass sheet followed by 3 min curing in an UVA cube. The same process has been followed before and after each optical and electrical measurement. Still, a very low amount of oxygen doping might remain, but we did not find any significant change in our UV-Vis absorption spectra or in the I-V characteristics. To see the effect of oxygen doping, one can intentionally dope the P3HT, as for example Herrmann et al. [73] have demonstrated. They dipped regioregular P3HT films in a $FeCl_3$ solution to increase the level of oxidation-induced P3HT cations and observed changes of the optical absorption due to oxidation, which we do not observe.

4.2.2 Femtosecond transient absorption spectroscopy

Section 3.8 shows a detailed description of our femtosecond transient absorption spectroscopy setup. For this study, the beam cross-sections used for the calculation of the fluences are 1256 and 1017 μm^2 , respectively. Both pump and probe beams were com-

pressed to less than 120 fs using a set of prism compressors and then made parallel and kept with parallel polarizations for the measurements. We have not used a reference beam to observe the stability of the laser beam fluctuation for each time delay since the fluctuation of our laser intensities is very small; it would have been bigger in a white-light experiment. The main beam of the Ti:Sapphire laser of wavelength at 775 nm is monitored constantly and its power fluctuation is less than 1%. The optical parametric amplifiers used to generate the pump and probe wavelengths emit intensities with slightly more fluctuations (approx. 5-10%) due to the involvement of non-linear processes. However, these fluctuations could be minimized by averaging accumulating 1000 pulses per second and recording 30 loops. Therefore, the errors due to beam fluctuations were reduced considerably.

4.3 Results and Discussion

4.3.1 Polaron-Pair Dynamics in Neat P3HT Thin Film

At first, we considered the PP dynamics in a neat P3HT thin film. In the following, we present the results obtained for different pump and probe wavelengths and for varying pump-laser intensities.

Wavelength-dependent pump-probe measurement

We have measured the transient pump-probe dynamics of a neat P3HT thin film on a glass substrate by first varying pump and probe wavelengths. Figure 4.1 shows the normalized dynamics patterns observed. To exclude any ground-state contributions, the excited-state absorption is modeled by calculating the relative differential probe pulse transmission ($\Delta T/T$) using the following equation:

$$\frac{\Delta T}{T} = \frac{T_{\text{pump-on}} - T_{\text{pump-off}}}{T_{\text{pump-off}}} \quad (4.1)$$

where $T_{\text{pump-on}}$ and $T_{\text{pump-off}}$ represent the transmitted probe-pulse intensities with and without an initial pump-pulse interaction, respectively. Initially, we selected a pump and probe wavelength of 488 nm, where P3HT exhibits strong absorption due to the 0-2 transition. Figure 4.1 (A) shows the ground-state bleach (GSB) signal of P3HT, which is expected as we are using the same probe wavelength to track the recovery of the ground state. Similarly, Fig. 1 (B) presents the GSB signal with both the pump and probe at 612 nm, where P3HT absorbs due to H-aggregates (also related to the 0-0 transition). The ground-state recovery is faster in both cases but the contribution of the long-lived component is different from what we have observed for 488 nm.

As mentioned earlier [64], P3HT shows a photoinduced (transient) absorption at 638 nm

due to the PP species. Therefore, we measured the pump-probe dynamics of PPs by probing at 638 nm, using varying pump wavelengths. We started with excitations at 488 and 612 nm. As shown in panels (C) and (D) of Fig. 1, a sharp decrease in the transmission of the 638 nm probe pulse is observed. This is attributed to photoinduced absorption from the instantaneously photo-generated PPs. The signal intensity quickly recovers (indicated by reduced transmission) at positive time delays as most of the absorbing PPs decay. The observed photoinduced absorption decay dynamics consist of a fast and a very slow component. The latter component remains flat within our measurement window, since it is limited to a few hundred picoseconds due to the delay stages used in our experimental setup.

Next, we fixed the probe wavelength at 638 nm and adjusted the pump wavelength

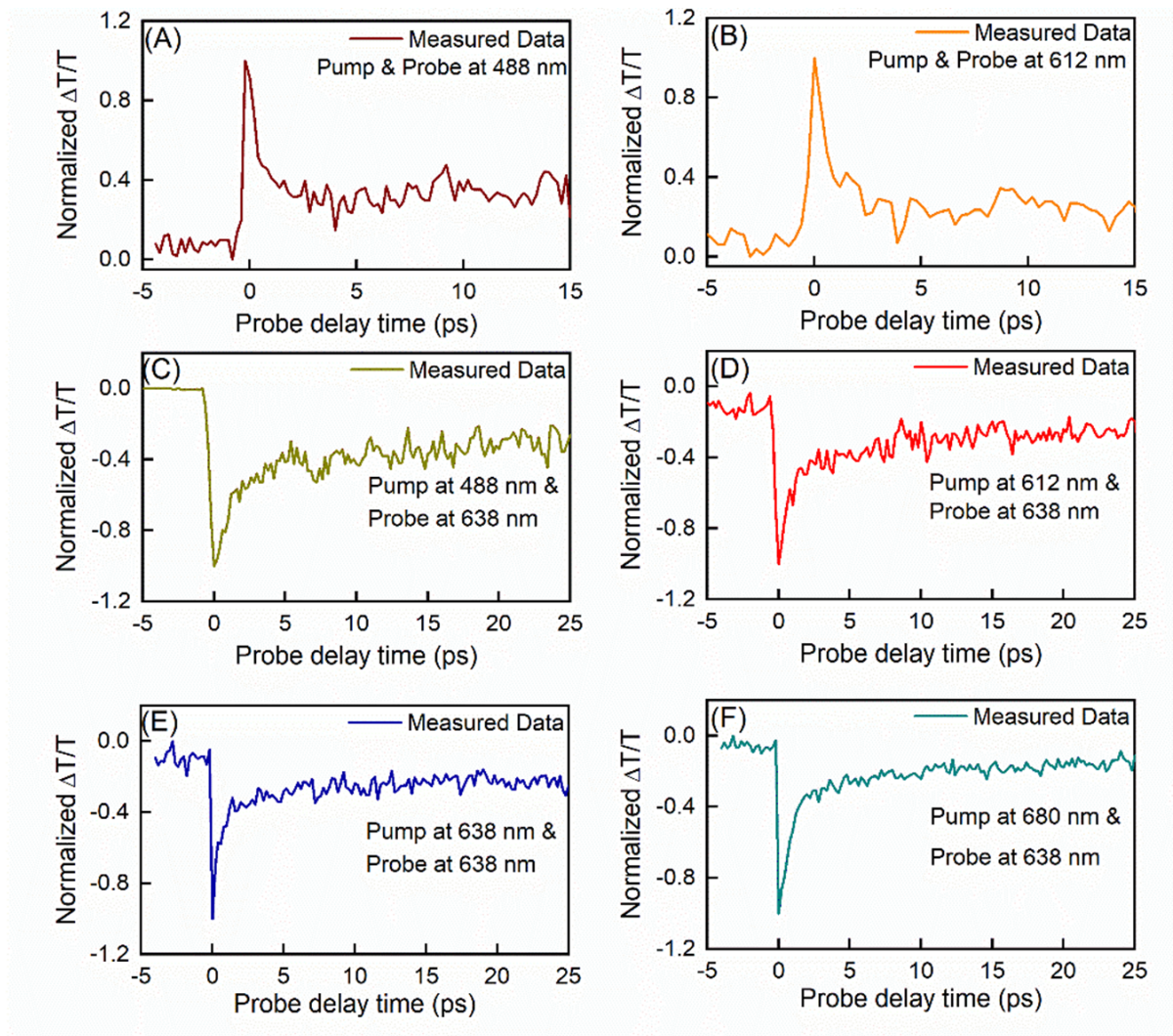


Figure 4.1: Differential transient transmission dynamics ($\Delta T/T$) obtained from the neat P3HT thin film at 12 J/cm^2 fluence, where both pump and probe wavelengths were varied.

to 638 nm as well. Like for the 488 nm / 488 nm and 612 nm / 612 nm experiments discussed above, we expected a decay of the absorption, suggesting ground state bleach

(GSB) dynamics. However, we observed a very strong TA signal, which can be assigned to the PPs (see panel (E) of Fig. 1). Finally, we moved the pump wavelength to 680 nm, where the P3HT absorption is quite low (see Fig. S1 in the supplementary information). After excitation, a strong TA signal (see panel (F) of Fig. 1) was observed like for the 638 nm excitation. The probe wavelength is still in resonance with the PP absorption. Obviously, there is an efficient generation of PPs even when the pump laser wavelength is chosen such that the photon energies are less than the bandgap energy of P3HT. This was already observed by other groups [68], but has not yet been well understood. Therefore, we have carried out further investigations in this case.

Intensity-dependent pump-probe measurement

We continued our investigation to obtain more information about the origin of the PP signal when both the pump and probe wavelengths are set to 638 nm. By varying the excitation (pump) fluence from 4 to 36 $\mu\text{J cm}^{-2}$, we recorded the TA signal of the neat P3HT thin film, as shown in Fig. 4.2.

The experiments have been carried out starting at very low excitation intensity (4 J/cm^2) where possible to avoid damage. In the case of the P3HT diode, the signal is very weak at this low pump fluence, as shown in Fig. 4.5(A). The parallel configuration provided more signal compared to the magic angle configuration. We also had more pump scatter in our transient signal. Considering the signal-to-noise ratio, we decided to continue the measurements in the parallel configuration. In general, the polarization between pump and probe pulses is usually set at magic angle (MA, 54.7°), to ensure isotropic signals. The kinetics measured at 638 nm could be different when measuring at the magic angle (different absolute numbers of t_1 and t_2). However, we were mainly interested in the origin and general behavior of the PP signal after excitation below band gap. Very recently, we also have performed polarization-dependent measurements of the anisotropy of the transient absorption signal, which still must be evaluated carefully and are not included in this work now.

It is very important to mention that we do not observe any thermal or heating effect causing a sample damage with below-band-gap excitation. In all our experiments we have carefully checked whether some permanent damage might occur, which would certainly falsify our results. We therefore have started with a rather small fluence of only 4 $\mu\text{J cm}^{-2}$. For all fluences applied for our experiments, we have firstly observed no “loop-to-loop” changes of the transients, and a repetition of the experiments also did not result in a loss of reproducibility. With our experiments, we are also on the “safe side” since the below-band-gap excitation sees a very low absorbance.

The inset shows the intensity of the TA signal at 0 ps, as a function of the pump intensity. We observed a linear increase in signal intensity with increasing excitation fluence. We

applied a linear fit ($y = a + b \cdot x$) to the $\Delta T/T$ signal, which is in an excellent agreement with our data. This linear dependence on the pump intensity excludes the possibility of a contribution from non-linear processes like a two-photon absorption, which could result in a PP generation from excited electronic states.

The dynamics shown in Fig. 4.2 are similar to those observed for PPs arising from

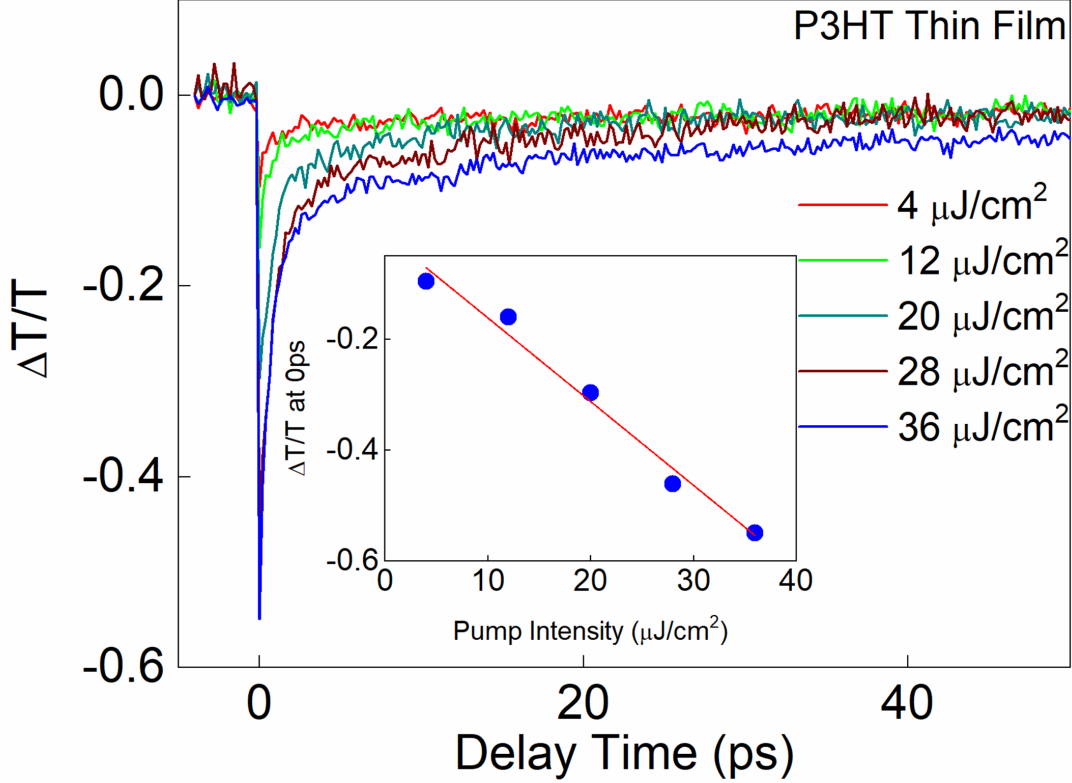


Figure 4.2: Differential transient transmission dynamics ($\Delta T/T$) obtained from the neat P3HT thin film at different excitation fluence, where pump and probe both were at 638 nm.

above-band-gap excitation of hot excitons. The steep decrease in 638 nm probe pulse transmission is due to photo-induced absorption by instantaneously photo-generated PPs, most of which rapidly decay at positive time delay. The observed overall dynamics are rather well approximated by assuming two decay processes and is found to be well described by a bi-exponential decay fitting function. The transient response was fitted using $\frac{\Delta T}{T} = Y_0 + A_1 \exp\left(-\frac{t}{t_1}\right) + A_2 \exp\left(-\frac{t}{t_2}\right)$. The fitting parameters Y_0 (offset), A_1 , A_2 (amplitudes), and t_1 , t_2 (time constants) are given in Table 4.1. The decay parameters in Table 4.1 represent an average value from three TA curves with each curve recorded as an average of 30 loops (statistical errors are given in each case). The observed behavior is reproduced in different experiments on different spots on the thin film. The fitting results of the decay kinetics are shown in Fig. S5.

Table 4.1: Exponential fitting parameters of the photo-induced TA at 638 nm describing the ultrafast PP decay dynamics in neat P3HT film after 638 nm excitation at different pump fluences.

Excitation Fluence ($\mu\text{J}/\text{cm}^2$)	t_1 (fs)	t_2 (ps)	A_1 (%)	A_2 (%)	Y_0 (%)
4	613 ± 110	19.99 ± 3.6	60.51 ± 0.01	17.77 ± 0.05	21.72 ± 0.01
12	653 ± 90	15.49 ± 2.9	60.41 ± 0.01	21.69 ± 0.01	17.90 ± 0.01
20	740 ± 120	10.56 ± 1.1	59.85 ± 0.02	26.59 ± 0.01	13.56 ± 0.01
28	793 ± 140	14.95 ± 1.2	60.45 ± 0.01	28.85 ± 0.01	10.70 ± 0.01
36	656 ± 92	14.36 ± 0.7	61.46 ± 0.01	28.87 ± 0.01	9.67 ± 0.01

In our previous study [64], using TA experiments with a pump wavelength of 520 nm and probe wavelength of 638 nm, we observed that the PPs dynamics could be well described by a single exponential decay function with an offset, and the dynamics were independent of excitation intensity. However, in the present study, our analysis indicates that a mono-exponential function is insufficient to fit the decay kinetics – a second time constant is required.

The first time constant t_1 represents the PPs dynamics, which remain independent of excitation fluence and are comparable to those observed with 520 nm excitation. We have presented in Fig. S4. In contrast, the second time constant t_2 is slower and shows a dependence on excitation intensity. As the excitation fluence increases, the decay rate associated with t_2 accelerates within $20 \mu\text{J cm}^{-2}$. At very high fluences (28 and $36 \mu\text{J cm}^{-2}$), t_2 starts to increase again and eventually saturates. The amplitude A_1 of the PP signal corresponding to the t_1 dynamics is bigger than A_2 measuring the contribution of the t_2 dynamics. A_1 remains unchanged when the excitation fluence is varied from 4 to $36 \mu\text{J cm}^{-2}$, however A_2 increases; at the same time the constant background Y_0 is decreasing.

The second time constant t_2 is rather slow compared to t_1 , which we assign to the PP lifetime based on the observations made for above-band-gap excitation. It is difficult to unambiguously determine which species are contributing to these dynamics. It has been reported earlier that excimers, delocalized polarons (DP2), oxidized cations etc. all contribute to the TA at 638 nm [74, 75]. However, since the other species except for the DP2 are long lived (> 100 ps), t_2 can be likely assigned to the dynamics of DP2. The offset, Y_0 , can be attributed to trap states. As mentioned above, t_2 is intensity dependent. Therefore, we propose a bimolecular annihilation process to explain the decay dynamics observed in the fluence range of 4-20 $\mu\text{J cm}^{-2}$. The bimolecular annihilation process is intensity dependent as two excitons interact with each other and transfer their energy. The probability for this interaction is proportional to the square of the exciton density. This quadratic dependence arises because the probability of two excitons meeting is related to the number of excitons present. We have used this concept here in case of the delocalized

PPs. The decay kinetics can be modelled as described in equation (2),

$$\frac{dn_x}{dt} = -\frac{n_x}{\tau} - \gamma n_x^2 \quad (4.2)$$

where n_x is the excitation density, τ is the dissociation lifetime and γ is the annihilation rate constant [76–78]. The solution of the above equation can be written as

$$n(t) = \frac{n_x(0) \exp\left(-\frac{t}{\tau}\right)}{1 + \gamma\tau n_x(0) \left(1 - \exp\left(-\frac{t}{\tau}\right)\right)} \quad (4.3)$$

We used this equation to fit all the kinetics shown in Fig. 2. The fitting parameters are listed in Table 4.2 and the fittings are shown in Fig. S6

Table 2: Fitting parameters of the photo-induced TA at 638 nm describing the ultrafast PPs decay dynamics in neat P3HT film, after 638 nm initial excitation with different fluences. The kinetic model of the bimolecular annihilation process fits the dynamics

Table 4.2: Fitting parameters of the photo-induced TA at 638 nm describing the ultrafast PPs decay dynamics in neat P3HT film, after 638 nm initial excitation with different fluences.

Excitation fluence ($\mu\text{J}/\text{cm}^2$)	$n_x(0)$ (cm^{-3})	γ (cm^3/s)	τ (ps)
4	5.06×10^{16}	$(1.08 \pm 0.21) \times 10^{-6}$	3.91 ± 0.86
12	2.65×10^{17}	$(7.20 \pm 0.11) \times 10^{-7}$	6.01 ± 0.99
20	9.65×10^{17}	$(2.70 \pm 0.11) \times 10^{-7}$	11.77 ± 1.20
28	2.02×10^{18}	$(1.80 \pm 0.11) \times 10^{-7}$	16.08 ± 1.80
36	2.95×10^{18}	$(1.80 \pm 0.11) \times 10^{-7}$	17.13 ± 1.50

observed at 638 nm very well. We can estimate the excitation density, which is increasing with pump fluence. After 20 the annihilation process appears to be saturated. In the saturation regime, the dissociation process is slower. We have plotted the annihilation rate constant with the change of excitation fluence in Fig. S7.

As result from our P3HT thin film studies, we conclude that the generation of PPs in neat P3HT thin films occurs immediately after the pump excitation even with energies below the band-gap energy. The efficient production of PPs may arise from one of the following: (i) electronic states between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of P3HT, (ii) a vibronic coupling state or (iii) trap states within P3HT. In the neat P3HT thin film, we observe two distinct dynamics corresponding to two different species: the PP and the DP_2 . While the PP dynamics are independent of excitation intensity, the DP_2 dynamics show intensity dependence pointing to a bimolecular annihilation process. This was supported by applying a bimolecular annihilation kinetic model, which helped us in understanding the annihilation and dissociation behaviour. Due to the increase in the annihilation rate constant with increasing pump intensity, the DP_2 dynamics get faster until a saturation

is reached. At the same time, some of the trap states seem to be released to DP_2 states, which slows down the dynamics.

4.3.2 Polaron-Pair Dynamics in P3HT Diode

After having investigated the dynamics in neat P3HT films, it is also of great interest to study the PP dynamics in a typical device. For this, we have prepared a P3HT device in a diode-like configuration. The P3HT layer is sandwiched between an electron (ZnO + ITO) and a hole transport layer (PEDOT:PSS + Ag), which also allow to apply an external electric field. Due to the potential difference of the asymmetric contacts, we have a built-in-potential in the diode resulting in a reverse bias of 0.8 V. In our experiment, we have applied an external electric field in reverse and forward bias. In forward bias, the external electric field can compensate the built-in-potential in the diode. First, we present the results from intensity-dependent pump-probe experiments on the P3HT diode without any external electrical field. Then, we show the outcome of our field-dependent studies.

4.3.3 Intensity-dependent pump-probe measurement

Figure 4.3 shows the PP dynamics of the P3HT diode probed at 638 nm after excitation with 638 nm pump wavelength where the pump fluence is varied from 4 to 36 $\mu\text{J cm}^{-2}$. In the inset, a plot of the TA signal at 0 ps as a function of the pump intensity is shown. Like for the neat thin film case, we again found a linear behavior, which excludes the possibility of two photon processes. At a first glance, the decay traces are like those observed for the neat P3HT thin film. However, as mentioned above, the diode has a built-in potential due to the different contacts, which should influence the dynamics. Like for the case of the neat P3HT film, we fit the overall decay dynamics in the P3HT device by applying exponential functions. A close analysis reveals that the PP dynamics in this case are well described by a bi-exponential decay model using a fitting function of the form of $\frac{\Delta T}{T} = Y_0 + A_1 \exp\left(-\frac{t}{t_1}\right) + A_2 \exp\left(-\frac{t}{t_2}\right)$, where again Y_0 is the offset, A_1 and A_2 are the amplitudes, and t_1 and t_2 are the decay times characterizing the two exponential decay components. The decay parameters are extracted from the fitting as shown in Table 4.3.

Table 4.3 shows that the first time constant t_1 , which represents the PP dynamics, seems to remain unchanged (within the error range) for different excitation fluences. However, the second time constant t_2 exhibits a clear fluence dependence; the decay rate gets faster with increasing pump intensity. Between 4 and 20 $\mu\text{J cm}^{-2}$, the t_2 dynamics are slower compared to those observed in the thin film. Interestingly, when the excitation fluence exceeds 20 $\mu\text{J cm}^{-2}$, the t_2 dynamics become faster than those in the thin film. The differences are due to the internal electric field. Furthermore, at higher fluences, ranging

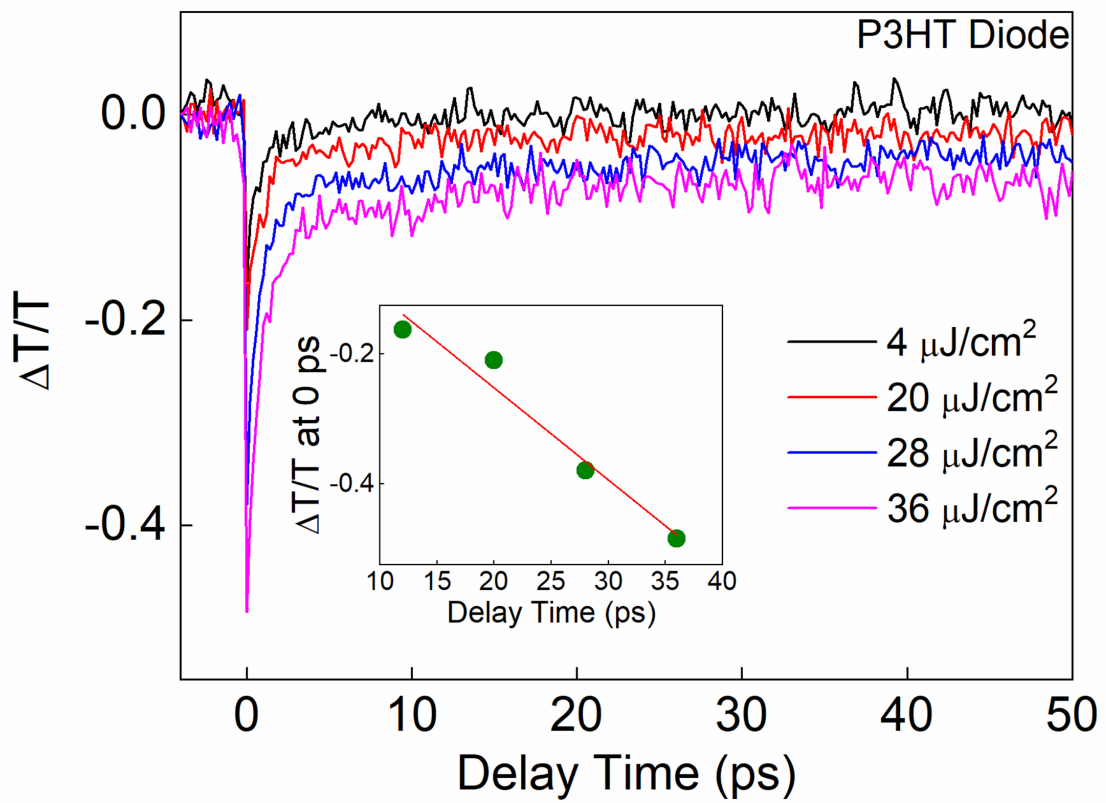


Figure 4.3: Differential transient transmission dynamics ($\Delta T/T$) obtained from the neat P3HT diode at different excitation fluences, where pump and probe were both at 638 nm.

from 28 to 36 $\mu\text{J cm}^{-2}$, t_2 approaches a constant value. This saturation behavior has also been observed for the thin P3HT film.

Table 4.3: Exponential fitting parameters of the TA dynamics probed at 638 nm describing the ultrafast PP decay dynamics in a neat P3HT diode (built-in-potential is present), after 638 nm initial pump excitation with different fluences.

Excitation Fluence ($\mu\text{J cm}^{-2}$)	t_1 (fs)	t_2 (ps)	A_1 (%)	A_2 (%)	Y_0 (%)
4	890 ± 171	34.27 ± 1.1	50.14 ± 0.01	29.85 ± 0.05	20.01 ± 0.01
20	751 ± 38	27.14 ± 3.1	77.14 ± 0.01	15.54 ± 0.05	07.32 ± 0.01
28	612 ± 67	09.91 ± 1.1	69.14 ± 0.03	20.85 ± 0.02	10.01 ± 0.01
36	833 ± 73	11.67 ± 0.9	68.21 ± 0.01	18.76 ± 0.05	13.03 ± 0.01

While there are similarities between the film and diode decay dynamics, the deviation seems to be field-induced. In the following two sections, the decay dynamics under the influence of external electric fields are studied.

External-field-dependent pump-probe measurement: forward bias

In the above-mentioned diode experiment, for a 0 V external voltage, a non-zero internal field due to the built-in potential of -0.8 V remains active inside P3HT device. To investigate the possibility of elimination of this field induced effect, we have operated the P3HT device with an external voltage of 0.8 V in forward bias compensating the built-in potential. Figure 4.4 shows the transient-absorption dynamics of the PPs observed under these conditions. Fitting the transients yields similar time constants for t_1 and t_2 for the different excitation fluences as in the neat-film case; the fitting results are summarized in Table 4.4. Despite the internal field compensation, the addition of various layers in the device of course influences the dynamics. However, a comparable behavior to the neat P3HT thin film is observed. Moreover, it is evident that the internal field changes the dynamics, which we already have reported earlier [64, 65].

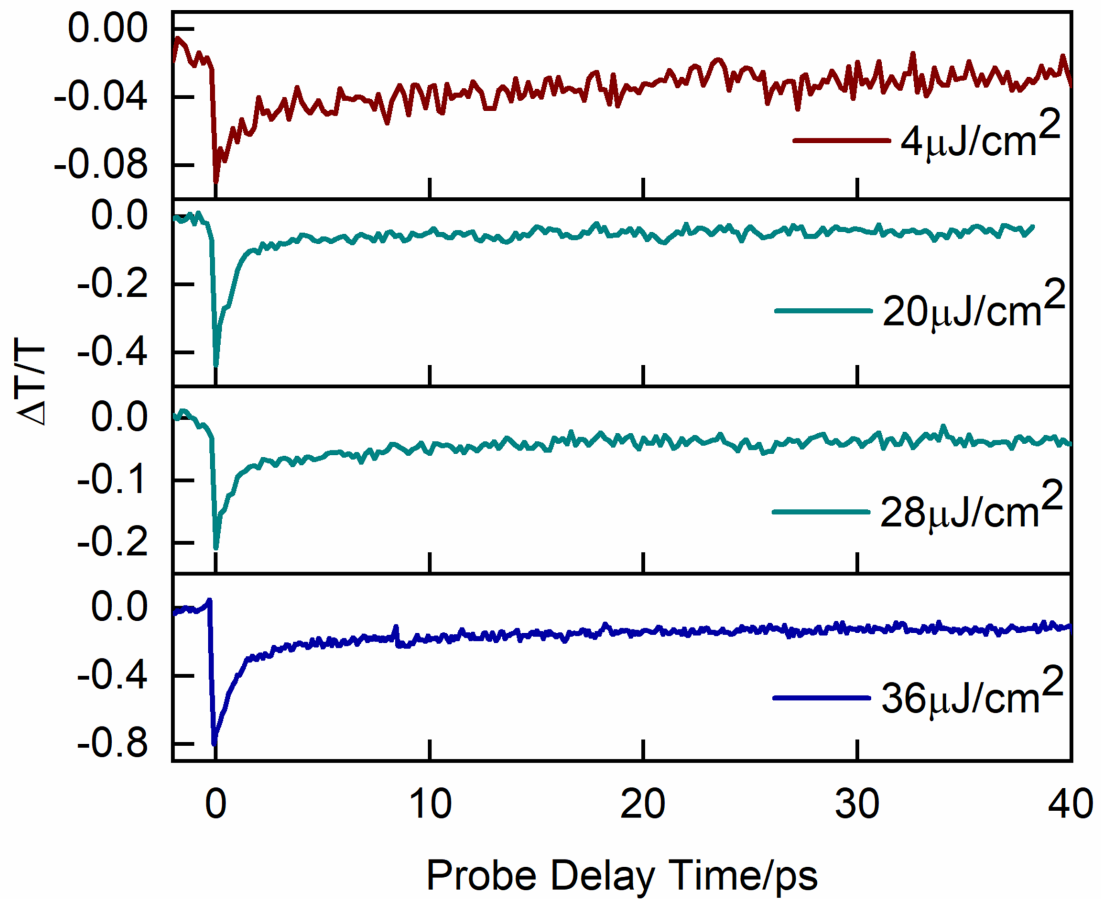


Figure 4.4: Differential transient transmission dynamics ($\Delta T/T$) obtained from the neat P3HT diode with an external applied field in forward bias of 0.8 V compensating the internal field for different excitation fluences. Pump and probe wavelengths are both at 638 nm.

Table 4.4: Exponential fitting parameters of the photo-induced TA at 638 nm. The ultrafast PP decay dynamics in a P3HT-only diode were measured with compensated internal field after 638 nm initial pump excitation with different fluences.

Excitation Fluence ($\mu\text{J cm}^{-2}$)	t_1 (fs)	t_2 (ps)	A_1 (%)	A_2 (%)	Y_0 (%)
4	807 $\pm$ 140	18.02 $\pm$ 3.5	39.91 $\pm$ 0.01	32.85 $\pm$ 0.01	27.24 $\pm$ 0.01
20	749 $\pm$ 45	10.37 $\pm$ 2.8	76.16 $\pm$ 0.01	12.56 $\pm$ 0.02	11.28 $\pm$ 0.01
28	659 $\pm$ 140	14.30 $\pm$ 1.2	71.20 $\pm$ 0.01	18.56 $\pm$ 0.01	10.24 $\pm$ 0.01
36	903 $\pm$ 32	13.68 $\pm$ 0.6	65.20 $\pm$ 0.01	18.29 $\pm$ 0.01	16.51 $\pm$ 0.01

External-field-dependent pump-probe measurement: reverse bias

In the experiments presented in the last section, an external field was used to compensate the internal field. In this section, an external field in reverse bias is added to increase the internal field. Figure 4.5 shows the TA dynamics observed from the P3HT diode after pump pulse excitation with different fluences and with different electric fields in reverse bias externally applied. In the insets of Fig. 5 (A-D) we plot the $\Delta T/T$ signal at 0 ps as a function of the applied electric field.

A field-induced quenching depending on the applied reverse bias is evident from the data presented. This is the first and clear evidence of an immediate field-induced dissociation, which occurs immediately after excitation with increasing efficiency for increasing electric field strength. An ultrafast field-induced dissociation of the primary pre-assembled states competes with the direct formation of the PPs and explains the PP absorption reduction at 0 ps. To support this assumption, we have carefully collected the data and repeated the experiments to ensure reproducibility. The field-dependent data are taken on different spots of the P3HT diode and averaged over 30 loops for each measurement. The collected information is an average from multiple scans. While the dynamics are reproducible, due to the inhomogeneity of the material, the absolute absorption values are varying, which might have to do also with reflection losses at the additional layers.

We first highlight the overall field-induced changes in the P3HT PP decay patterns before we discuss a possible physical interpretation later. As mentioned above, during the excitation-fluence-dependent study we found that there are two different regimes (below and above 20). This was already observed for the field-free case of the neat P3HT film. However, the t_2 dynamics behave differently for the diode. Therefore, below we present the data analysis in two different subsections.

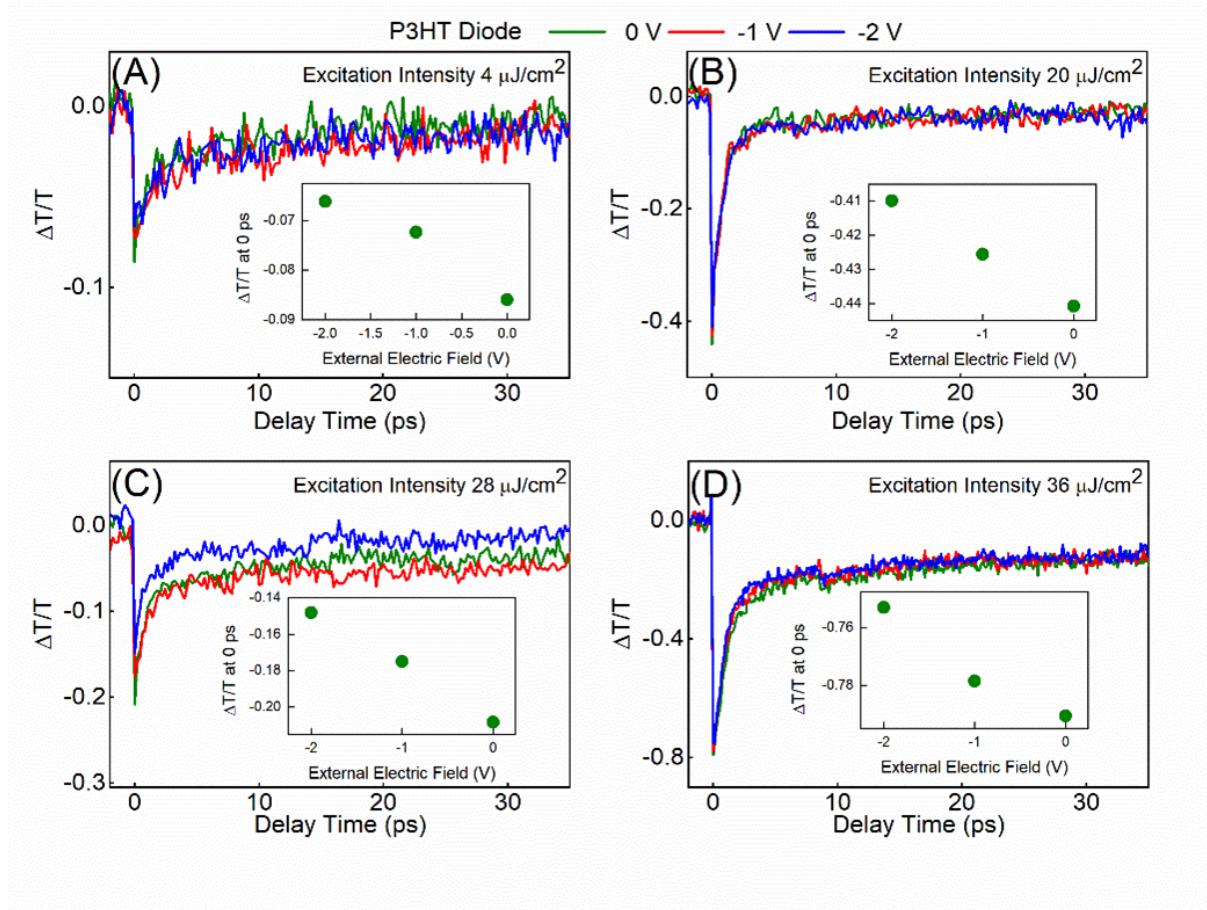


Figure 4.5: Differential transient transmission dynamics ($\Delta T/T$) obtained from the neat P3HT diode for an applied external applied field in reverse bias with 0, -1, and -2 V (built-in potential must be added) at different excitation fluences. Pump and probe wavelengths are both at 638 nm, and excitation intensities of (A)4, (B)20, (C) 28, and (D)36 $\mu\text{J}/\text{cm}^2$ are used here.

At lower excitation intensity. The fitting parameters of the PP and DP2 dynamics at 638 nm for electric field strengths of both 4 and 20 are shown in Table 4.5.

Table 4.5: Exponential fitting parameters of the photo-induced TA at 638 nm describing the ultrafast PP decay dynamics in a P3HT-only diode after 638 nm excitation with pump fluences (PF) of 4 and 20 $\mu\text{J}/\text{cm}^2$ under different external applied electric fields (EEF).

EEF (V)	Net Field (V)	t_1 (fs)	t_2 (ps)	A_1 (%)	A_2 (%)	Y_0 (%)
PF = 4 $\mu\text{J}/\text{cm}^2$						
0	-0.8	890 ± 171	34.27 ± 1.1	50.14 ± 0.01	29.85 ± 0.05	20.01 ± 0.01
-1.0	-1.8	891 ± 130	15.24 ± 1.8	42.97 ± 0.01	29.72 ± 0.01	27.31 ± 0.01
-2.0	-2.8	864 ± 119	13.14 ± 2.1	46.90 ± 0.02	26.65 ± 0.01	26.45 ± 0.01
PF = 20 $\mu\text{J}/\text{cm}^2$						
0	-0.8	751 ± 38	27.15 ± 3.1	77.14 ± 0.01	15.54 ± 0.05	7.32 ± 0.01
-1.0	-1.8	692 ± 42	9.27 ± 2.9	75.40 ± 0.01	13.22 ± 0.01	11.38 ± 0.01
-2.0	-2.8	769 ± 57	7.34 ± 0.7	74.37 ± 0.03	13.31 ± 0.02	12.32 ± 0.01

Without external field (0 V) we only have the built-in-potential and the net electric field is -0.8 V. Similarly, the external electric fields -1 and -2 V represent net electric fields of -1.8 and -2.8 V, respectively. In our earlier study[33], with above-band-gap excitation of hot excitons, we have concluded that the field-induced PP dissociation makes the PP decay faster. Here, in our present study, when the PPs are generated due to below-band-gap excitation, we did not observe any influence of the external electric field on t_1 , i.e. the PP dynamics. Although there is a mild field induced quenching happening at 0 ps due to the loss of initial population, the PP dynamics remain constant. On the other hand, when we consider the effect of the external electric field on the dynamics of DP2, we have observed that the value of t_2 is rather big (slow dynamics) at 0 V, which can be explained by the static polarization effect. Then, with the increment of the external electric field strength in reverse bias the value of t_2 becomes smaller (faster dynamics). While the change from 0 to -1 V is drastic, it is almost negligible for the step from -1 to -2 V. This observation is true for both the excitation fluences, 4 and 20 . The fitted curves for both the excitation fluences are provided in Figs. S8 and S9.

At higher excitation intensity. At higher excitation intensities of 28 and 36 $\mu\text{J}/\text{cm}^2$, where the bimolecular process has reached saturation, the fitting parameters for the PP and DP2 dynamics at 638 nm under varying external electric field strengths (in reverse bias) are shown in Table 4.6.

We have observed that the PP dynamics, represented by t_1 , remains unchanged despite the increase of the external electric field strength. This behavior is consistent with

Table 4.6: Exponential fitting parameters of the photo-induced TA at 638 nm describing the ultrafast PP decay dynamics in a P3HT-only diode after 638 nm excitation with pump fluences (PF) of 28 and 36 $\mu\text{J}/\text{cm}^2$ under different external applied electric fields (EEF).

EEF (V)	Net Field (V)	t_1 (fs)	t_2 (ps)	A_1 (%)	A_2 (%)	Y_0 (%)
PF = 28 $\mu\text{J}/\text{cm}^2$						
0	-0.8	612 ± 67	9.91 ± 1.1	69.14 ± 0.03	20.85 ± 0.02	10.01 ± 0.01
-1.0	-1.8	726 ± 87	16.62 ± 1.9	71.91 ± 0.01	18.87 ± 0.01	9.22 ± 0.01
-2.0	-2.8	612 ± 67	21.47 ± 1.1	68.79 ± 0.03	21.10 ± 0.02	10.11 ± 0.01
PF = 36 $\mu\text{J}/\text{cm}^2$						
0	-0.8	833 ± 73	11.67 ± 0.9	68.21 ± 0.01	18.76 ± 0.05	13.03 ± 0.01
-1.0	-1.8	981 ± 28	15.37 ± 0.6	66.74 ± 0.01	19.05 ± 0.01	14.21 ± 0.01
-2.0	-2.8	912 ± 26	18.29 ± 0.7	67.34 ± 0.02	19.54 ± 0.01	13.12 ± 0.01

the observations made at lower excitation fluences or under forward bias conditions. However, the dynamics the DP2 are of particular interest. The fitted curves for both these intensities are provided in Figs. S10 and S11. In our observation, we noticed that, as the external electric field strength increases in reverse bias, slower dynamics (increased t_2 time constant) are observed at both 28 and 36 $\mu\text{J}/\text{cm}^2$. While the bi-exponential fitting provides a general view of the processes occurring on these different time scales, the possible mechanisms induced by the external electric field still must be discussed.

4.4 Discussion of Results Obtained for P3HT-Only Diode

As demonstrated above, the applied external electric field results in two different behaviors for the two regimes of excitation fluences. This raises the question: can the internal and external electric fields influence the bimolecular process? An electric-field effect on the annihilation rate constant has been discussed for polyfluorene by Gadermaier et al. [79] for a fixed pump fluence. To investigate this further in P3HT with a broad range of excitation fluence, we have applied equation (2b) to model the complete data set, which includes various excitation fluences and electric field strengths, to gain deeper insights. We have chosen three representative external electric voltages, -0.8, -1.8, and -2.8 V. Considering the thickness of the P3HT (200 nm), the effective fields are in the MV/cm. The external electric fields cover a wide range from 4 to 14 MV/cm. This should sufficiently demonstrate the influence of the fields on the dynamics. Using the annihilation model, we have extracted the dissociation time constants and annihilation rate constants for these different scenarios. Tables S1

and S2 list the time constants with their errors. At higher excitation fluences, the annihilation rate constant (Fig. 6 (B)) decreases as the external field increases, indicating a slower annihilation process. However, the dissociation time constant (Fig. 6 (D)) continues to increase, suggesting that dissociation is still happening more rapidly, even under stronger external fields. This contrasting behavior highlights the complex effect of the external field on the annihilation and dissociation processes at different fluences.

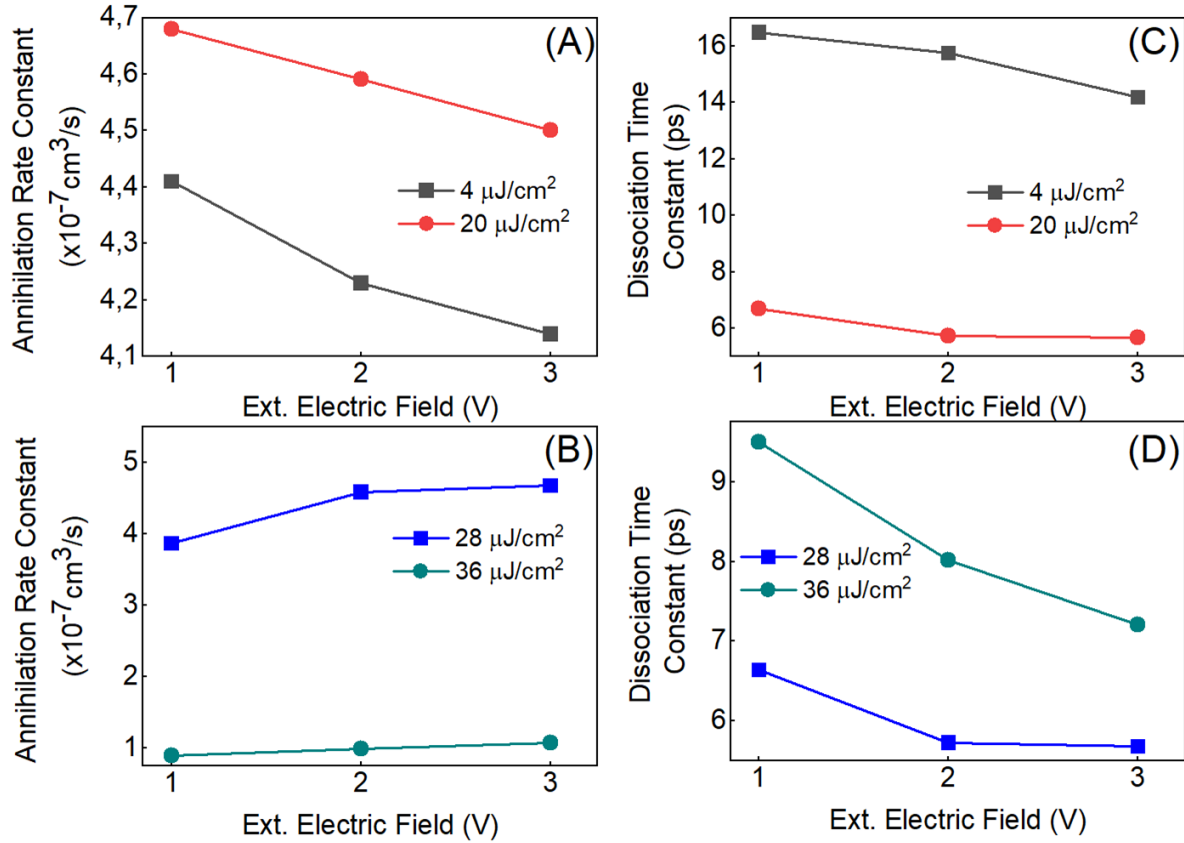


Figure 4.6: (A) and (B) represent the annihilation rate constants and (C) and (D) the dissociation time constants obtained for the P3HT-only diode for different external applied fields in reverse bias with 0, -1, and -2 V (built-in-potential has to be added) at different excitation fluences. Error bars are shown for each point (compare Tables S1 and S2).

When comparing the annihilation process in panel (A), we observed that the annihilation rate constant gets slower with the increase in the excitation fluence (smaller value of annihilation rate constant (γ) means that the annihilation is faster). However, at $4 \mu\text{J cm}^{-2}$, the dissociation time constant in panel (C) is significantly higher than at other fluences. Additionally, the transmittance in the P3HT diode at $4 \mu\text{J cm}^{-2}$ is quite low, which results in comparatively noisy data and affects the reliability of the measurements. The annihilation model works properly only when the time constant can be fixed in a particular range (shown in Fig. S12). Therefore, the unusually high dissociation

time constant derived from the $4 \mu\text{J cm}^{-2}$ dataset is challenging to explain. Excluding the $4 \mu\text{J cm}^{-2}$ data, the dissociation process becomes slower as the excitation fluence increases, which can be attributed to the more rapid annihilation process occurring at higher fluences. When comparing the annihilation process in panel (B), we have found that the annihilation gets faster with the increase in the excitation fluence. This results in making the dissociation process slower, which is shown in panel (D) with the increase in the excitation fluence from 28 to $36 \mu\text{J cm}^{-2}$. The DP2 dissociation induced by the external electric field is still visible at higher excitation intensities.

4.5 Conclusion

We have performed transient absorption (TA) spectroscopy on a neat P3HT thin film and a P3HT-only diode to investigate the origin of the polaron pair (PP) state following a below-band-gap excitation. While previous studies have focused on PP generation from hot excitonic states after above-band-gap excitation, our observations demonstrate that PPs can be very efficiently generated also upon a below-band-gap excitation. We have confirmed that there are no nonlinear multi-photon processes involved as the TA signal exhibits a linear dependence on pump fluence.

When P3HT is excited with a 638 nm pump pulse (below-band-gap excitation), both PPs and delocalized polaron states (DP2) are generated. The PP dynamics are independent of the pump excitation intensity, while the DP2 dynamics changes with excitation intensity. We found that DP2 are involved in bimolecular processes, with the annihilation rate constant is increasing as the pump fluence rises, reaching saturation at very high fluences. To explore the effect of electric fields, we have applied varying external fields to the P3HT-only diode. Increasing the internal reverse bias by a variable external field in reverse bias and also compensating it by applying an external field in forward bias resulted in interesting changes of the dynamics. Our aim was to better understand how the electric fields impact the PP and DP2 dynamics, given their inevitable presence in real semiconductor devices. We observed that at lower excitation fluences, the external electric field accelerates the DP2 decay, while at higher intensities, it slows down the process. These findings are crucial for optimizing device performance, as we show that on-band and below-band-gap excitation can help prevent device damage. Since the annihilation process observed serves as a loss channel for charge generation, controlling the balance between excitation fluence and external electric fields offers a way to regulate the charge generation process and enhance device efficiency. These results are of relevance for device applications because they open up a new direction to optimize the charge transport phenomena in organic semiconductor by controlling the excitation of charge pair species.

The different processes are summarized in Scheme 1.

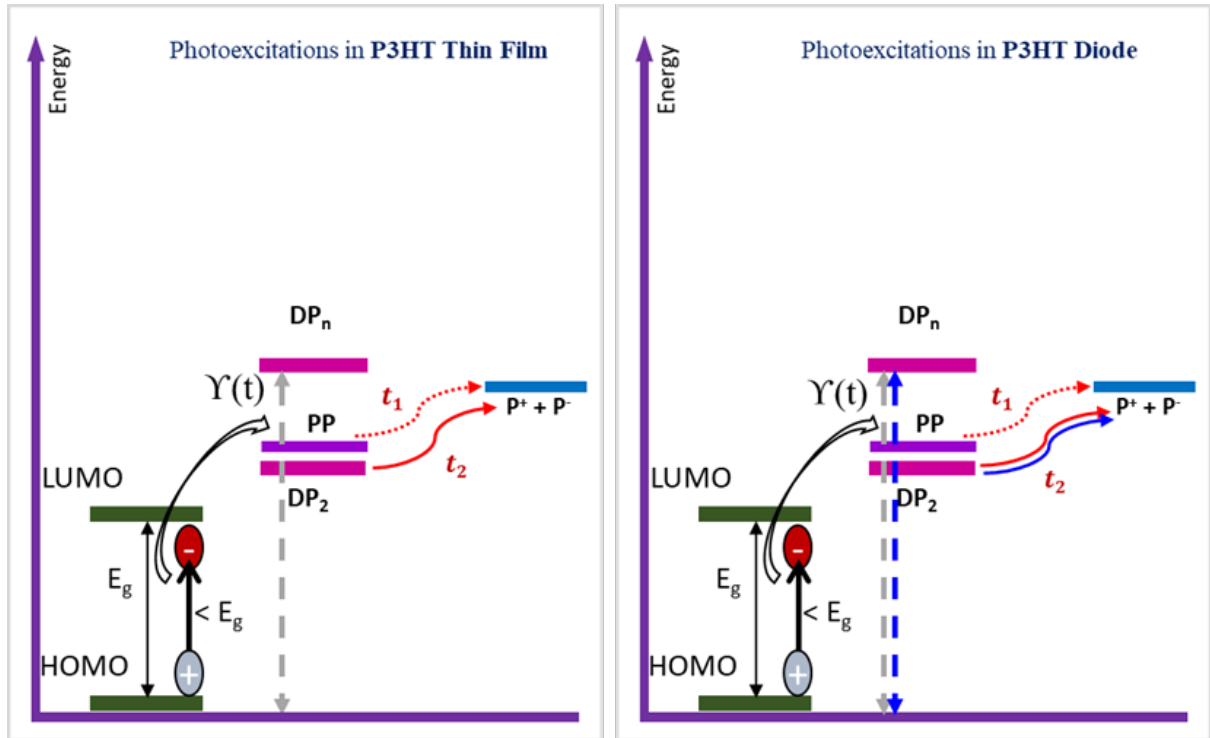


Figure 4.7: Schematic presentation of generation and decay mechanisms of PPs in P3HT upon below-band-gap excitation for (left) the P3HT thin film and (right) the P3HT-only diode. E_g is the band gap energy, PP represents polaron pairs, DP_2 and DP_n represent the delocalized polarons, P^+ and P^- represent the polarons, (t) is the annihilation rate constant, and t_1 and t_2 represent the dissociation rates of PPs and DP_2 , respectively. Blue lines indicate the electric field dependency.

Scheme 1 presents the generation and decay mechanism of polaron-pairs after photoexcitation in the P3HT thin film and diode. Based on our study, the polaron pair is generated directly for below band gap (E_g) excitation, which applies to both thin film and diode. We have not only seen the polaron-pair, but also the delocalized polarons after direct photoexcitation. In our earlier work [64, 65], we found that the polaron pairs and delocalized polarons decay to localized polarons (presented by the full and dotted red lines and time constants t_1 and t_2 in the scheme, respectively). The energy levels of the polaron pair, delocalized polaron and localized polaron are included according to the results from our previous studies [64, 65]. In the diode, we must consider the additional electric field, which is influencing the dissociation and bimolecular annihilation processes. We have indicated the field dependent processes adding blue lines in our scheme.

In summary, we would like to list the important points in the following:

- Our study has shed light onto an interesting charge generation-process. We have focused on PPs, which have been little investigated in the past. Up to now, nearly exclusively dynamics induced by above-band-gap excitation have been studied. In our work, we demonstrated that below-band-gap excitation cannot only also result in PPs, but that this process is even more efficient than that considered up to now. This is interesting since it allows to create devices, which make use of a considerably wider light spectrum for charge generation.
- Below-band-gap excitation seeing only little absorbance at the same time results in less heat generation compared to the excitation at maximum absorption. Thermal stability is very important for organic semiconductors, which makes it even more attractive to also utilize the generation pathways below band gap.
- The addition of external electric fields and the variation of excitation fluence result in some additional information about the involved processes. Further experiments will however be required to better understand what states and what processes contribute.
- Upon below-band-gap excitation, we have seen two decay dynamics in both the P3HT thin film and the P3HT-only diode.
If we compensate the built-in-potential (-0.8 V) by applying a forward bias to the diode, the observed dynamics in both samples are behaving equally.
- In reverse bias, the diode shows a clearly different behavior compared to the film for the delay times covered by our experiments. Varying the excitation

intensity results in different contributing processes; one can distinguish between the low-excitation-fluence and the high-excitation-fluence case. For lower excitation fluences, we see a decrease of t_2 assigned to the DP2 dynamics with increasing fluence, which is due to the bimolecular annihilation process becoming more efficient. At the same time, the PP dissociation is getting slower. For high excitation fluences, the annihilation reaches saturation. Depending on the excitation-fluence range, an applied electric field can speed up the dissociation and annihilation processes. This is an interesting result since electric fields might be useful for enhancing the efficiency of light-induced charge generation processes in practical applications.

Supplementary Information

S1. UV-Vis Absorption of P3HT

The UV-Vis absorption of neat P3HT thin film is shown in Fig. S1. The regioregular P3HT thin film shows a broad absorption from 365 nm to 680 nm with three distinct features at 507, 553 and 598 nm. The spin-cast thin film shows the characteristic transitions related to inter-chain exciton delocalization and a significant coupling to vibrations. The ratio of the amplitudes of the A_{0-0} (598 nm) and the A_{0-1} (553 nm) peaks is characteristic for partially ordered H-aggregate-like chains coexisting with non-aggregated chain sequences. The absorption strength on the higher wavelength side after 620 nm is extremely low, but not zero.

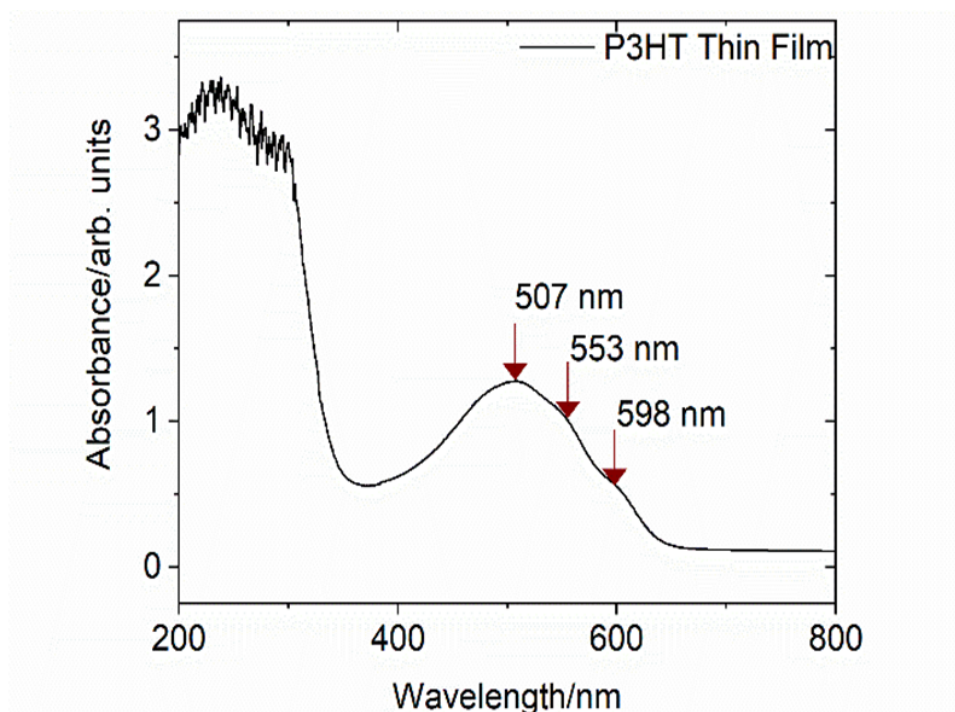


Figure S1: UV-Vis absorption spectrum of neat P3HT thin film.

S2. IV Characteristics of P3HT-Only Diode

The arrangement of the P3HT-only diode shown in Fig. S2 allows for the application of an external electric field. The asymmetry of the layers results in an internal field of -0.8 V.

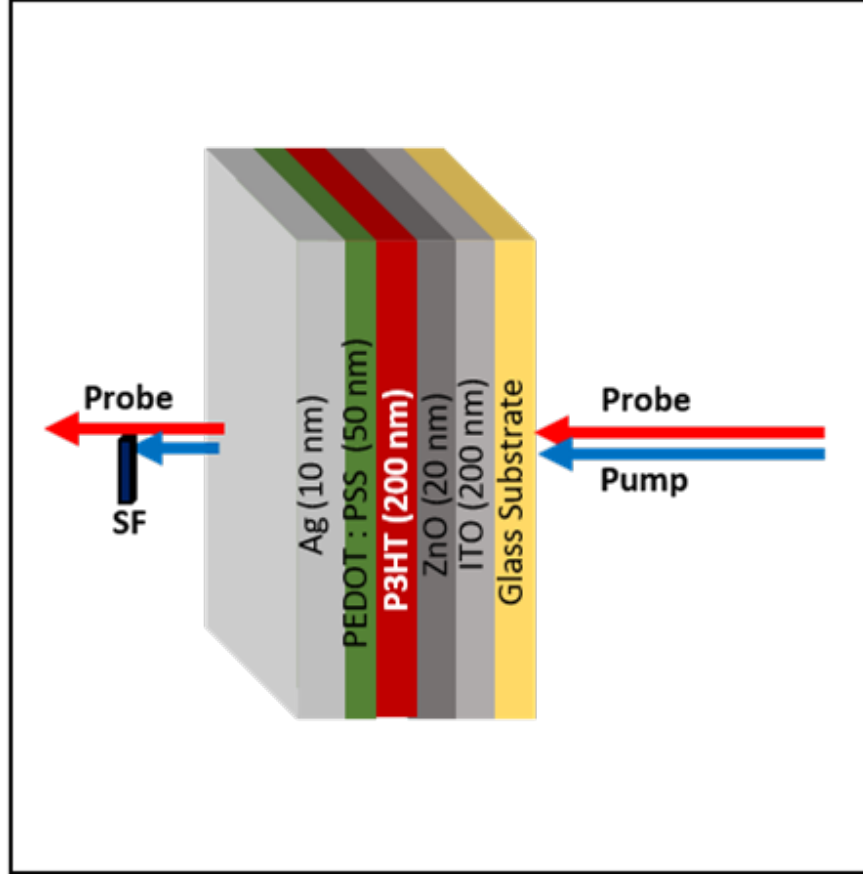


Figure S2: Schematic representation of the P3HT-only diode structure.

Figure S3 shows the current-voltage (I-V) characteristics of the P3HT device measured in the dark and when light is shining on it. An illumination with an air mass 1.5 sun spectrum, which is equivalent to a power density of 100 mW cm^{-2} was used for the measurement under light.

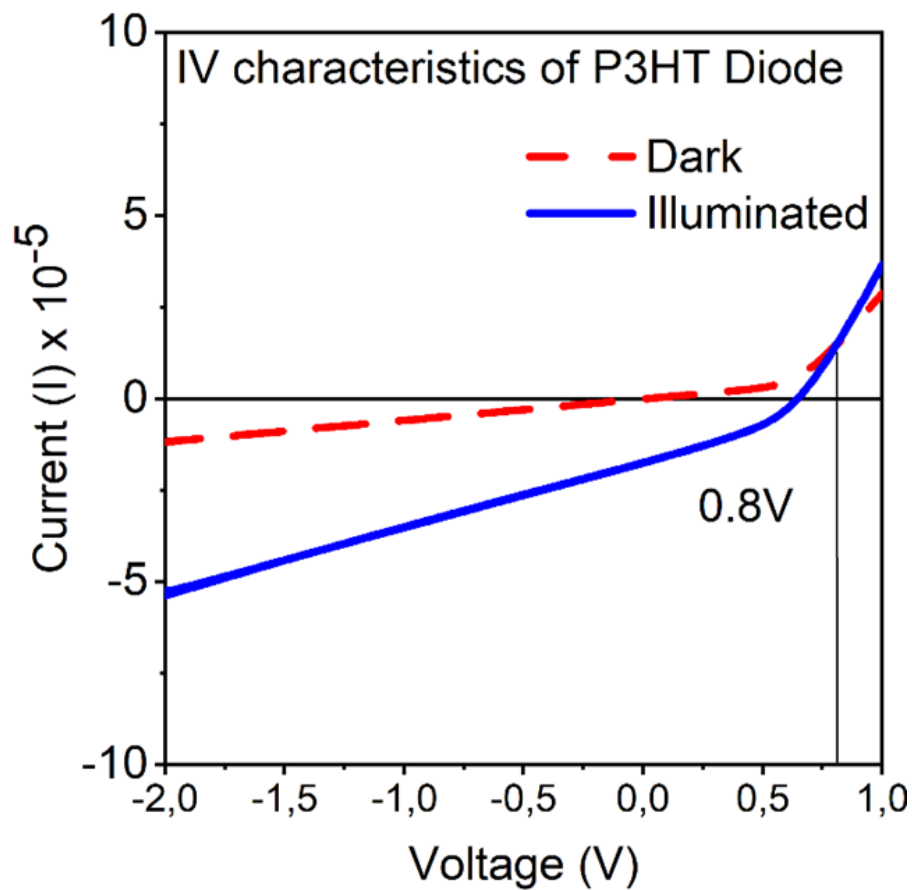


Figure S3: Current-voltage (I-V) characteristics of the P3HT device measured in the dark and under illumination (AM 1.5, 100 mW cm⁻²).

S3. Transient at 520 nm Excitation

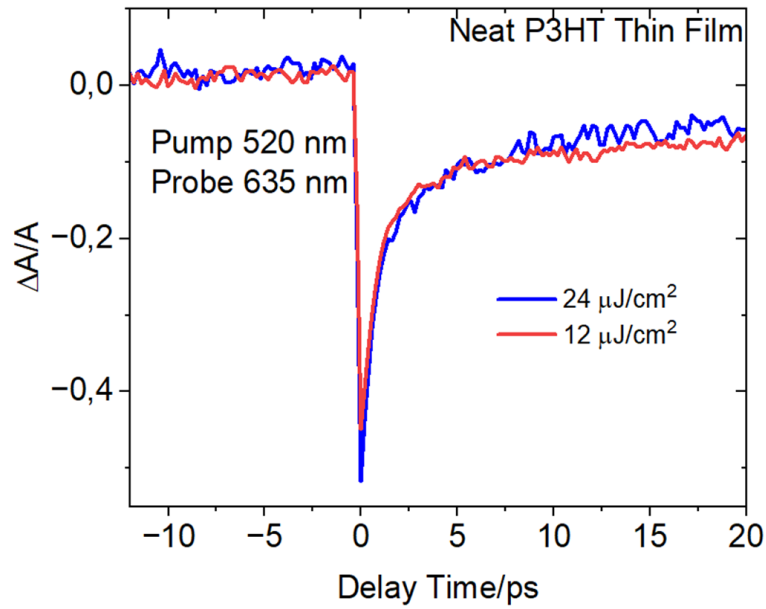


Figure S4: Differential transient transmission dynamics ($\Delta T/T$) obtained from the neat P3HT thin film probing the polaron pair dynamics at 635 nm after 520 nm excitation with two different fluences.

S4. Fitting Results

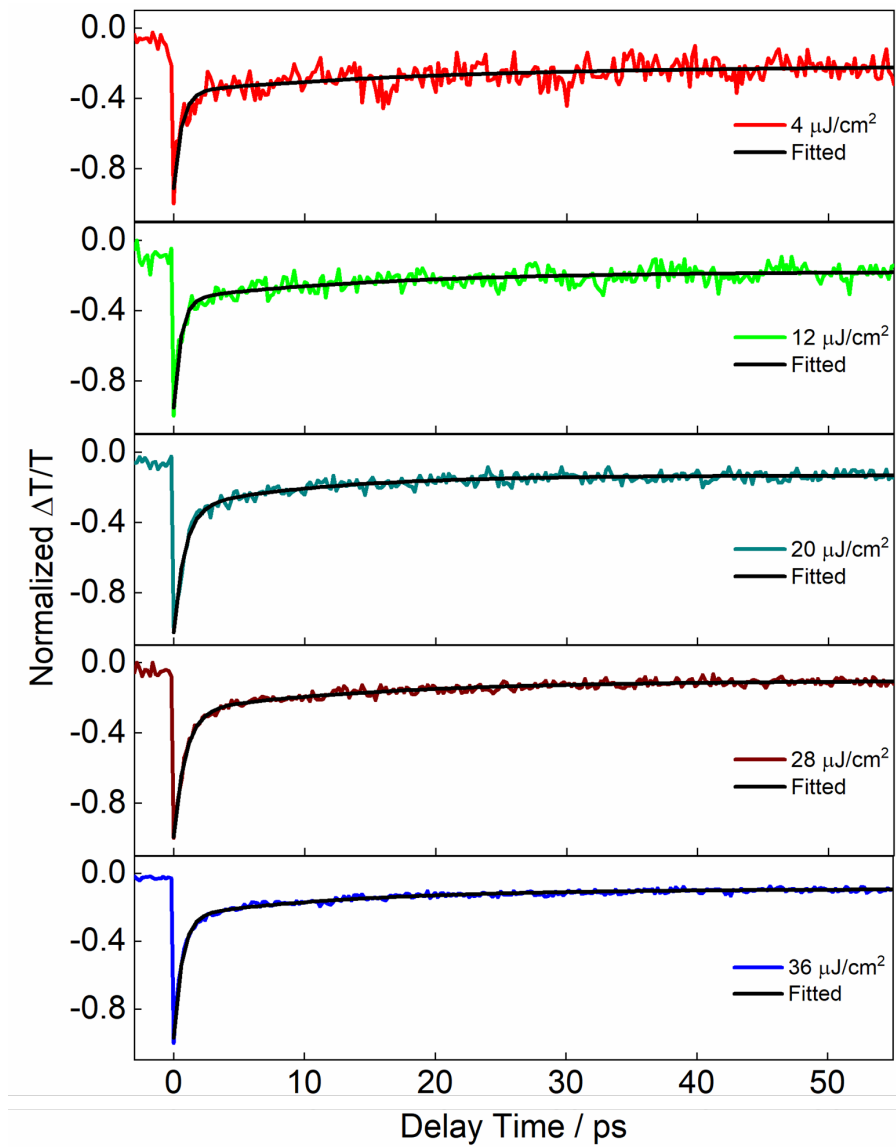


Figure S5: Fitting results using the exponential model for the differential transient transmission dynamics ($\Delta T/T$) obtained from the neat P3HT thin film at different excitation fluences, where pump and probe both were at 638 nm

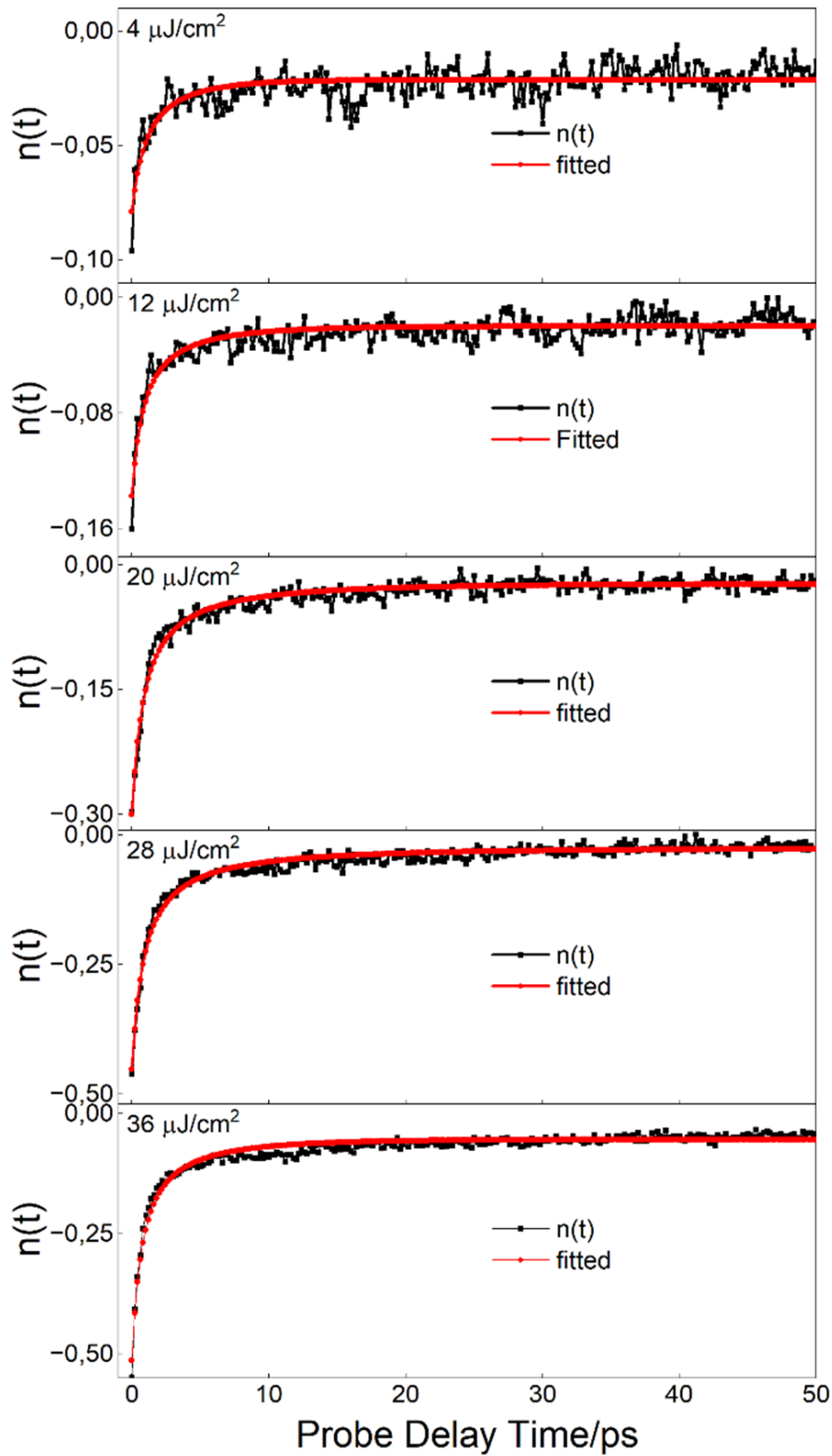


Figure S6: Fitting results using the annihilation model for the differential transient transmission dynamics ($\Delta T/T$) obtained from the neat P3HT thin film at different excitation fluences, where pump and probe both were at 638 nm.

S5. Annihilation Rate

We have plotted the annihilation rate with the change of excitation fluence in Fig. S4. At higher excitation fluences, the annihilation rate is constant.

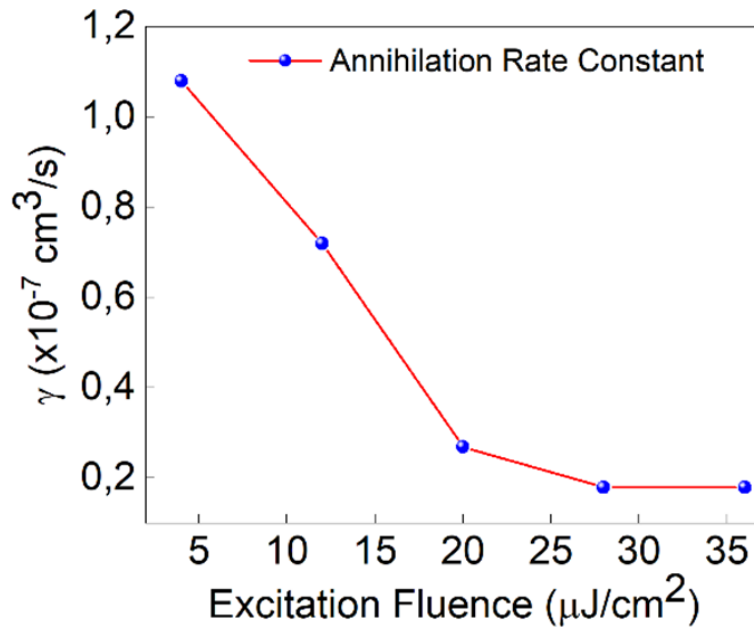


Figure S7: Annihilation rate constant of delocalized polarons in neat P3HT thin film.

S6. Fitting of Observed Dynamics

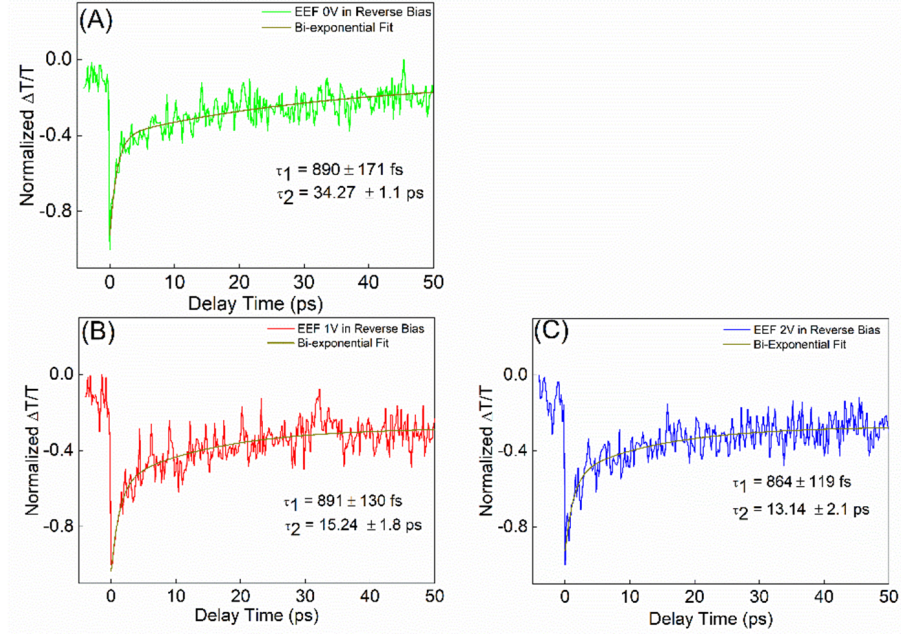


Figure S8: Fitting results using the exponential model for the differential transient transmission dynamics ($\Delta T/T$) obtained from the P3HT device where the external electric field is varied. For the experiment, a pump excitation fluence of $4 J/cm^2$ was chosen.

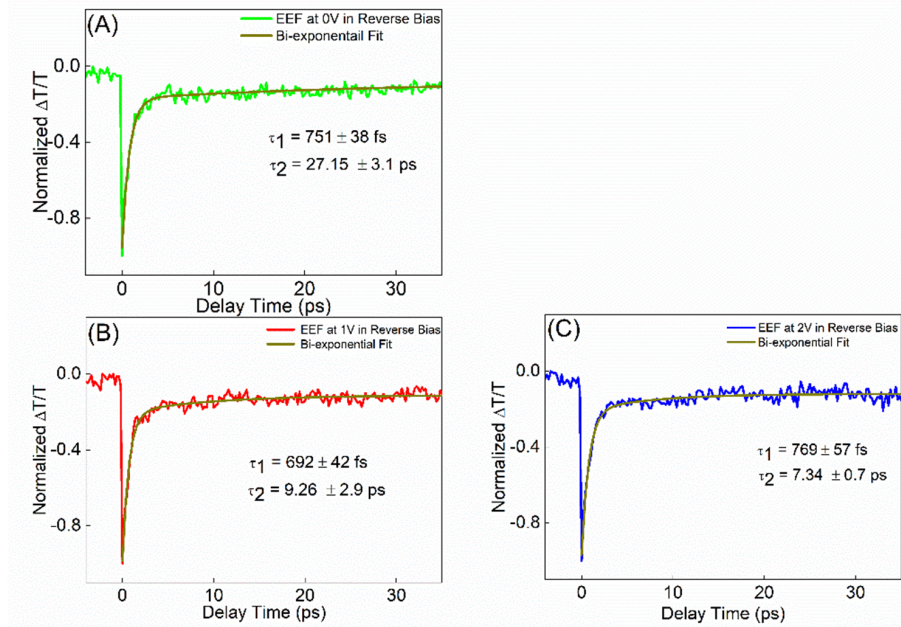


Figure S9: Fitting results using the exponential model for the differential transient transmission dynamics ($\Delta T/T$) obtained from the P3HT device where the external electric field is varied. For the experiment, a pump excitation fluence of $20 J/cm^2$ was chosen.

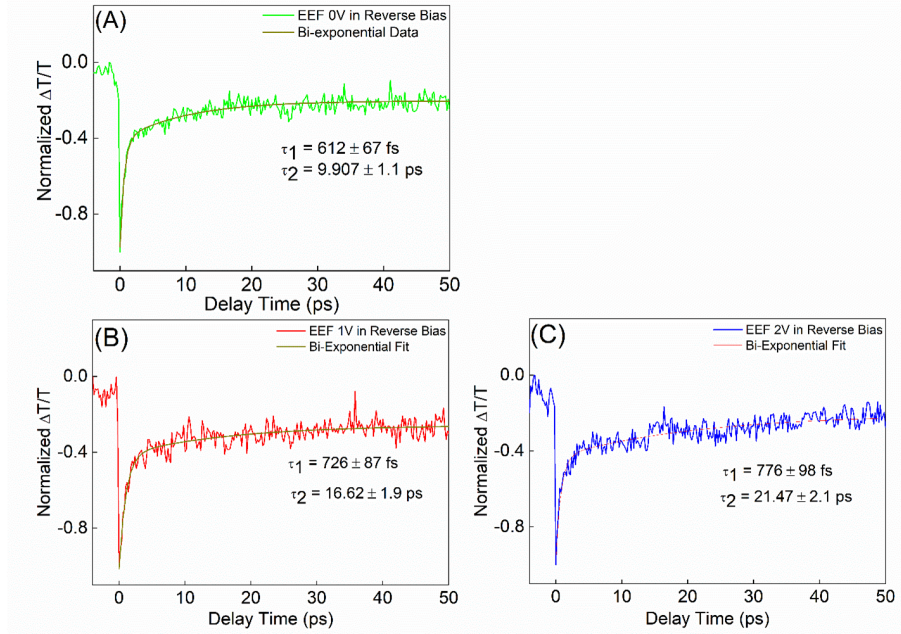


Figure S10: Fitting results using the exponential model for the differential transient transmission dynamics ($\Delta T/T$) obtained from the P3HT device where the external electric field is varied. For the experiment, a pump excitation fluence of $28 J/cm^2$ was chosen.

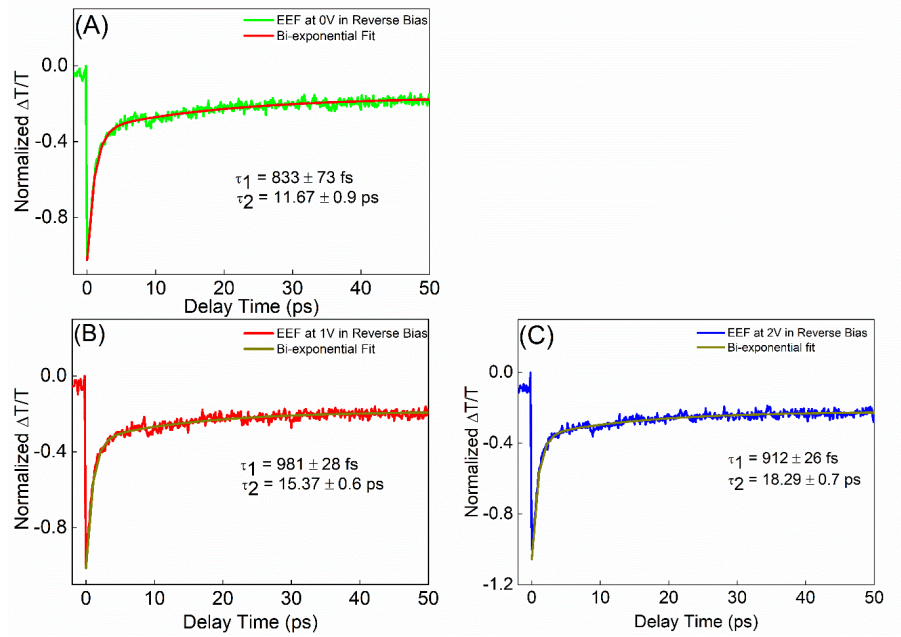


Figure S11: Fitting results using the exponential model for the differential transient transmission dynamics ($\Delta T/T$) obtained from the P3HT device where the external electric field is varied. For the experiment, a pump excitation fluence of $36 J/cm^2$ was chosen.

Fitting of observed dynamics using annihilation model

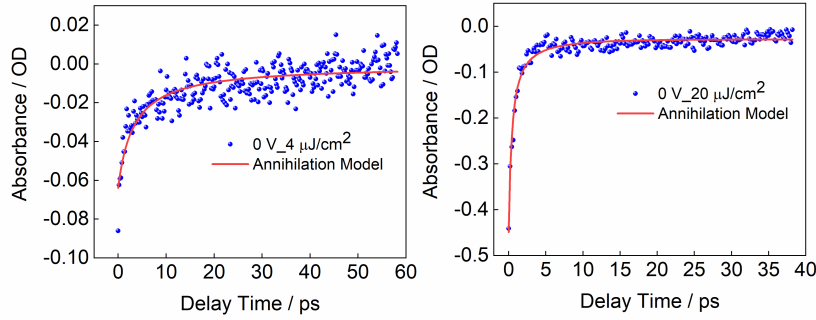


Figure S12: Fitting results using the annihilation model for the differential transient transmission dynamics ($\Delta T/T$) obtained from the P3HT device where the external electric field is 0 V and hence only the built-in potential is present. For the experiment, a pump excitation fluence of 4 and 20 J/cm^2 was chosen.

Fitting parameters obtained using annihilation model

Table S1: The annihilation rate constants obtained for the neat P3HT diode for an external applied field in reverse bias with 0, -1, and -2 V (built-in-potential must be added) at different excitation fluences (compare plots in Fig. 6 (A) and (B)).

	4 $\mu J/cm^2$	20 $\mu J/cm^2$	28 $\mu J/cm^2$	36 $\mu J/cm^2$
0 V	$(4.41 \pm 0.015) \times 10^{-7}$	$(4.68 \pm 0.013) \times 10^{-7}$	$(3.87 \pm 0.011) \times 10^{-7}$	$(9.00 \pm 0.015) \times 10^{-8}$
-1 V	$(4.23 \pm 0.03) \times 10^{-7}$	$(4.59 \pm 0.015) \times 10^{-7}$	$(4.59 \pm 0.021) \times 10^{-7}$	$(9.00 \pm 0.013) \times 10^{-8}$
-2 V	$(4.14 \pm 0.02) \times 10^{-7}$	$(4.50 \pm 0.017) \times 10^{-7}$	$(4.68 \pm 0.016) \times 10^{-7}$	$(1.08 \pm 0.014) \times 10^{-8}$

Table S2: The dissociation time constants obtained for the neat P3HT diode for an external applied field in reverse bias with 0, -1, and -2 V (built-in potential must be added) at different excitation fluences (compare plots in Fig. 6 (C) and (D)).

	4 $\mu J/cm^2$	20 $\mu J/cm^2$	28 $\mu J/cm^2$	36 $\mu J/cm^2$
0 V	16.47 ± 0.11	6.68 ± 0.02	6.64 ± 0.02	9.51 ± 0.02
-1 V	15.74 ± 0.09	5.74 ± 0.01	5.73 ± 0.01	8.02 ± 0.02
-2 V	14.17 ± 0.06	5.68 ± 0.02	5.68 ± 0.01	7.21 ± 0.02

Chapter 5

Time-Resolved Analysis of Polaron-Pair Dynamics in Flexible P3HT Films

Overview

In this chapter, we have investigated the influence of mechanical stretching on the ultrafast charge-carrier dynamics in P3HT, investigated using femtosecond pump-probe spectroscopy. By applying controlled uniaxial strain to the polymer films, this study examines how structural deformation affects the transient response of photoexcited species, particularly polaron pairs. The work aims to establish a direct link between mechanically induced structural modifications and changes in excited-state dynamics in a flexible organic semiconductor. Through systematic time-resolved measurements under strain, this chapter provides insight into the dynamical consequences of mechanical perturbation. The manuscript describing this study has been prepared and will be submitted for publication shortly.

Details of the manuscript:

Time-Resolved Analysis of Polaron-Pair Dynamics in Flexible P3HT Films:
Ayush k. Ranga, Mahya Ghorab, Patrice Donfack, DebKumar Rana, Veit Wagner, Mojtaba Joodaki, Arnulf Materny.

Abstract

The application of tensile stretching to semiconducting conjugated polymers is widely implemented to enhance the chain alignment of the polymer backbone, which might result in improved electrical performance. Poly(3-hexylthiophene) (P3HT) is a benchmark conjugated polymer in which photoexcitation generates a manifold of species whose dynamics range from ultrafast (~ 100 fs) to much slower (sub-microsecond) time scales.

In this work, we examine how uniaxial stretching affects the dynamics of charge-pair species in neat P3HT films fabricated on a polyethylene terephthalate (PET) substrate. Femtosecond time-resolved pump-probe measurements with varying tensile strain on P3HT films excited at 520 nm and probed at 638 nm were analysed using a bi-exponential decay model with an ultrafast component assigned to the dynamics of polaron pairs (PPs) and a slower component attributed to the dynamics of delocalized polaron pairs (DP_{2s}). The strain response of both species was studied by applying up to 15% nominal strain to the films. This analysis revealed that mechanical stretching impacts the dynamics of PPs in a moderate strain regime ($< 7\%$) by redistributing the population of slower decaying DP_{2s} to faster decaying PPs, while at higher values of applied strain, the overall dynamics shows a complex behavior that cannot be explained based on nominal strain alone, but by an interplay between secondary and unpredictable strain-induced effects such as effective strain transfer and reduced absorption. Photophysical investigation under mechanical stretching can offer fundamental insight into strain-induced changes in the dynamics of photo-generated species. These findings, showing an internal population redistribution from slower to faster decaying photogenerated species in P3HT, may well prove relevant for the optimization of flexible optoelectronic devices.

5.1 Introduction

Conjugated polymers combine mechanical compliance with delocalized electronic states, making them promising materials for flexible organic photovoltaics [2], field-effect transistors [3], and sensors [4]. Poly(3-hexylthiophene) (P3HT) serves as a benchmark donor-type semiconductor owing to its easy processability [5] and well-resolved photophysical pathways [6]. Upon photoexcitation, a hierarchy of species is generated in P3HT, and investigating their dynamics under externally applied perturbations is essential for advancing charge-generation and transport efficiencies [7–9]. The initially created hot excitons relax on a sub-100 fs time scale and promptly generate free carriers in the form of polarons, as well as bound electron-hole pairs, commonly referred to as polaron pairs (PPs) [12, 13, 80]. Once formed, PPs can follow multiple relaxation pathways, as they may recombine geminately and contribute as a loss channel in real devices [81], dissociate into free polarons that enhance device efficiency, or evolve into more delocalized polaronic states often termed DP_1 and DP_{2s} [29]. In addition to this, singlet excitons can undergo intersystem crossing to form triplet excitons, which are spin-forbidden to decay radiatively and therefore decay on much longer sub-microsecond time scales [82]. The relative populations and lifetimes of these species are sensitive to polymer packing, film morphology, and external perturbations such as electric fields, chemical doping, and chain alignment [16, 83].

Building on this framework, the present study focuses on the ultrafast dynamics of PPs in neat P3HT films. PPs are coupled to the polymer via Coulombic interactions [84], and

changes in polymer chain packing or alignment can therefore influence their formation, dissociation, and recombination pathways [85]. Unlike excitons, PPs are acutely sensitive to interchain coupling and torsional freedom because the surrounding lattice governs their binding energy and relaxation pathways [86]. This sensitivity makes polaron pairs an excellent probe for developing a fundamental understanding of how microstructural modifications, such as chain alignment, lamellar spacing, or the formation of localized trap states, affect the earliest steps of charge generation in conjugated polymers.

Mechanical stretching is proven to be an effective method for tuning the microstructure of conjugated polymer films used in flexible electronics [19, 87, 88]. At low strain levels, uniaxial stretching can induce partial backbone alignment and modify the formation and dissociation pathways of charge carriers [17, 89]. However, as strain increases, micro-cracks and structural defects can disrupt conjugation, reduce interchain coherence, and introduce additional trap states that complicate the interpretation of transient dynamics [17, 90–92]. Previous spectroscopic studies have reported improved performances in flexible devices and films by depositing polymers onto pre-stretched substrates such as PDMS [19, 93] and stretching non-annealed semiconducting films [94]. In these approaches, the applied strain is either accommodated by the compliant substrate or redistributed through microstructural rearrangement in the polymer, allowing larger macroscopic strains accommodation [17]. Although these approaches demonstrate pronounced changes in charge transport and photophysics, they do not fully represent realistic device-processing conditions. In P3HT-based systems, thermal annealing remains integral to promoting crystalline domain growth and optimizing electronic coupling [95–97], and stamping a pre-stretched film on another substrate does not align well with large-scale device fabrication. Apart from this, a growing number of theoretical studies have also explored how mechanical stretching modifies the electronic properties of conjugated polymers [91, 98]. More recently, a theoretical and experimental work combining density-functional theory with Raman spectroscopy to study the strain and electric fields effect on molecular vibrations and electronic structure has shown that the mismatch between the theoretical predictions and experimental results is due to the more complex nature of the conjugated polymer and the nature of strain transfer to the films [30]. Theoretical treatments generally assume idealised chain geometries, uniform strain, and negligible substrate interactions. Many parameters, including chain length, non-effective transfer of strain, and introduction of stiffness due to annealing, must be adjusted to match experimental conditions, making direct comparison at least challenging, if not unfeasible. In this work, we therefore investigate mechanically induced changes in ultrafast PP dynamics in P3HT films that are processed under device-relevant conditions. By applying strain only after film fabrication is complete, our measurements directly probe how post-processing mechanical deformation influences the fate of generated PPs.

We have performed time-resolved femtosecond transient absorption spectroscopy using

520 nm pump and 638 nm probe beams. Previous studies have shown that the probe wavelength at 638 nm is in resonance with the absorption of polaron-pairs (PPs) in P3HT, which typically dominates the transient response at this wavelength [11, 28]. While additional charge-related species may also exhibit weak absorption near this spectral region [28], their relative population is generally small, and they do not contribute appreciably to the transient signal under standard experimental conditions [9]. Consequently, pump-probe measurements on neat P3HT films deposited on rigid glass substrates often report dynamics that can be described by a single exponential component, particularly when higher excitation powers are employed [9, 83]. In contrast, the use of a flexible PET substrate imposes limits on the excitation fluence in our experiments due to its lower thermal tolerance, necessitating operation at reduced pump powers. Under these low-power conditions, contributions from multiple excited-state populations become experimentally resolvable, resulting in photoinduced absorption dynamics at 638 nm that are more accurately captured by a bi-exponential fitting model. The extracted parameters from the bi-exponential fitting model were then analysed with the applied nominal strain in P3HT films. The results will be discussed in this paper.

5.2 Fabrication of Thin Film on PET Substrate

Figure 5.1 shows the as-prepared flexible rr-P3HT thin film on PET. Regioregular poly 3-hexylthiophene (rr-P3HT) (average molecular weight $M_w = 20\text{--}45$ kDa from Sigma-Aldrich) was used to prepare the thin films. The film processing technique is similar to that of our earlier works [26]. Flexible polyethylene terephthalate (PET) substrate films of thickness $57.3\text{ }\mu\text{m}$ were cut into $5 \times 5\text{ cm}^2$ squares and stuck to glass via an epoxy tape. The films were then cleaned with a 3:2 propanol/acetone solution, dried under nitrogen, and subjected to 5 min of UV-ozone treatment to remove any organic contamination. A 33 mg mL^{-1} solution of P3HT in anhydrous chlorobenzene was stirred overnight at $50\text{ }^\circ\text{C}$ to ensure complete dissolution. Immediately before coating, the PET substrates were heated to $75\text{ }^\circ\text{C}$ for 10 min to improve the adhesion between the solution and the substrates. Films were spin-coated by dispensing $400\text{ }\mu\text{L}$ of the polymer solution on the PET substrate and spinning at 1500 rpm for 30 s, yielding $\approx 150\text{--}200\text{ nm}$ film thickness. After deposition, the films were annealed at $75\text{ }^\circ\text{C}$ for 5 min and then placed in a glove-box overnight before using them for further experiments.

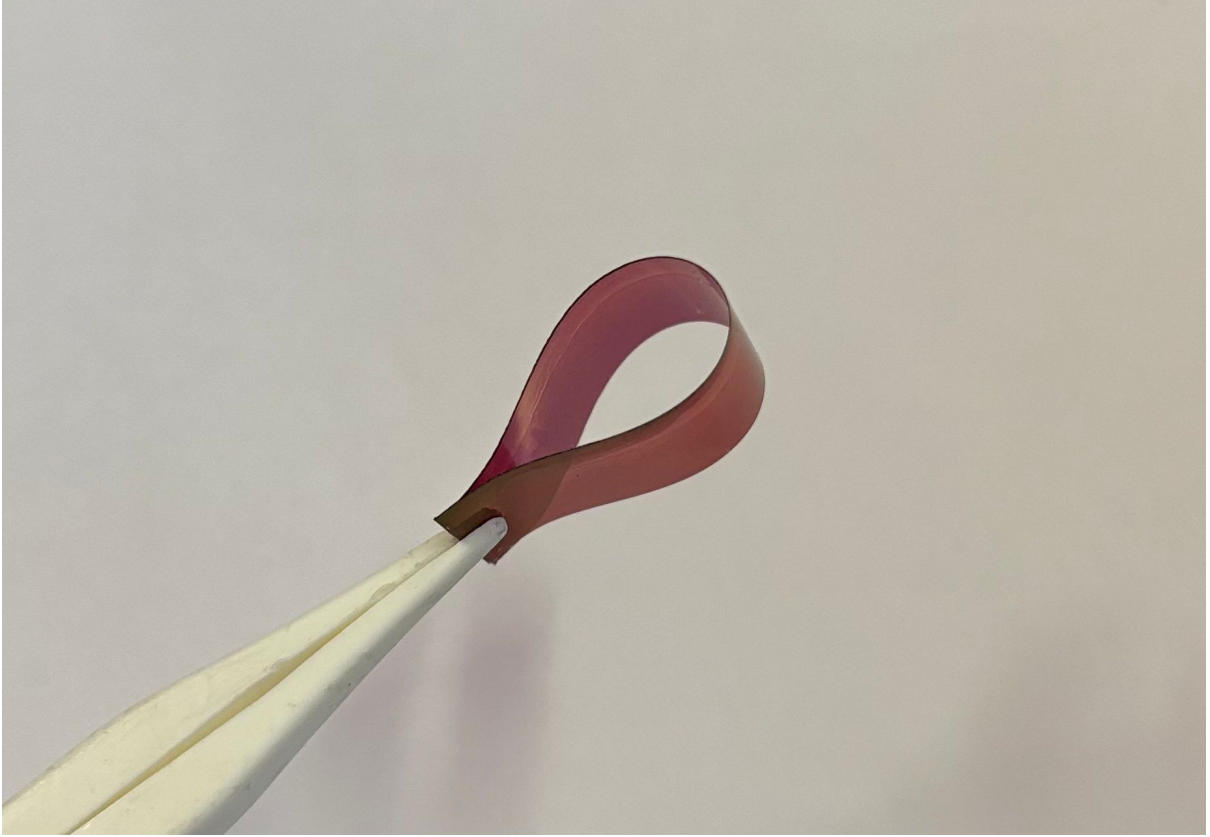


Figure 5.1: P3HT film spin-coated on PET substrate.

5.3 Stretching

After thermal treatment, films were removed from the glass underneath, and all the films were cut into rectangular strips measuring 15×33 mm to preserve the aspect ratio and ensure uniform strain distribution. For tensile testing, a 25 mm gauge section of each specimen was stretched, with 4 mm at each end retained in the grips of the stretching device. Uniaxial tension was applied using a custom mechanical stretcher equipped with a precision linear actuator. The actuator's calibration yielded a displacement increment of $6.25 \mu\text{m}$ per microstep, enabling consistent and precise strain increments. The maximum applied strain was limited to 15 %, as higher strains produced significant deformation in the PET support that would dominate the spectroscopic response. Nominal strains of 3, 5, 7, 10 and 15 % were investigated; the nominal strain ε was defined as $\varepsilon = \Delta L / L_0$, where ΔL is the change in gauge length and L_0 is the original gauge length. All stretching and subsequent pump-probe measurements were performed at room temperature to avoid thermal softening or morphology changes.

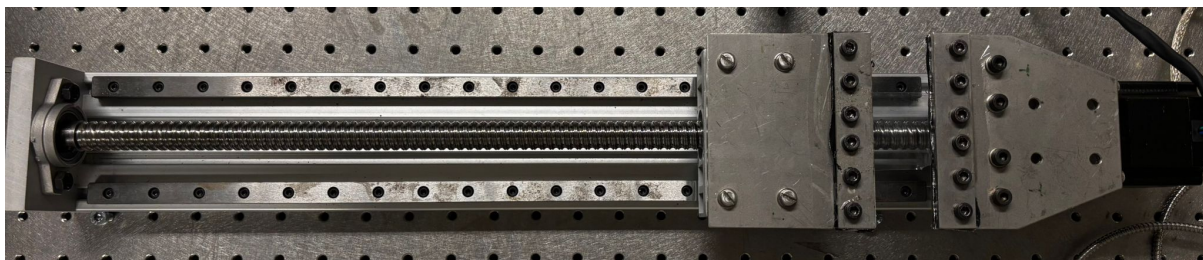


Figure 5.2: Stretcher device used for applying mechanical strain to P3HT films.

5.4 Time-Resolved Measurements

As discussed earlier in section 3.8, for this study, we have used 520 nm pump and 638 nm probe pulses. The parallel pump and probe beams from the delay stages were focused on the sample using a 20 cm focal-length lens. The polarization of both pump and probe pulses was kept parallel to the stretching direction of the film. A change in probe transmission was detected using a photodiode. More details regarding the setup can be found in the description of the experimental section.

5.5 Results and Discussion

Fig. 5.3 shows representative transient absorption spectra of the unstretched and stretched P3HT films measured at 30 μ W pump excitation and plotted as the normalized change in probe transmission $\Delta T/T$ as function of probe delay time. The transient absorption response of pristine unstretched P3HT films serves as a reference for all subsequent strain-dependent measurements. Pump-probe measurements were performed at three different points to take the inhomogeneity in spin-coated films into account, with 10 averaging loops recorded at each position, for a total of three different points. Spin coating is known to produce films with small thickness variations, surface roughness, and local morphological disorder, even under carefully controlled fabrication conditions [99, 100]. Such inhomogeneities can lead to position-dependent variations in optical density, which in turn introduce a degree of statistical variability in ultrafast pump-probe measurements. This effect is expected to become more pronounced as mechanical deformation introduces additional structural disorder and defects into the film. In addition, measurements performed at higher excitation powers revealed a progressive decrease in the absolute probe absorption at $t = 0$ ps with each subsequent loop, where $t = 0$ ps corresponds to the time at which the pump and probe beams overlap both spatially and temporally. Examining this effect is essential for a proper interpretation of the resulting transient kinetic data.

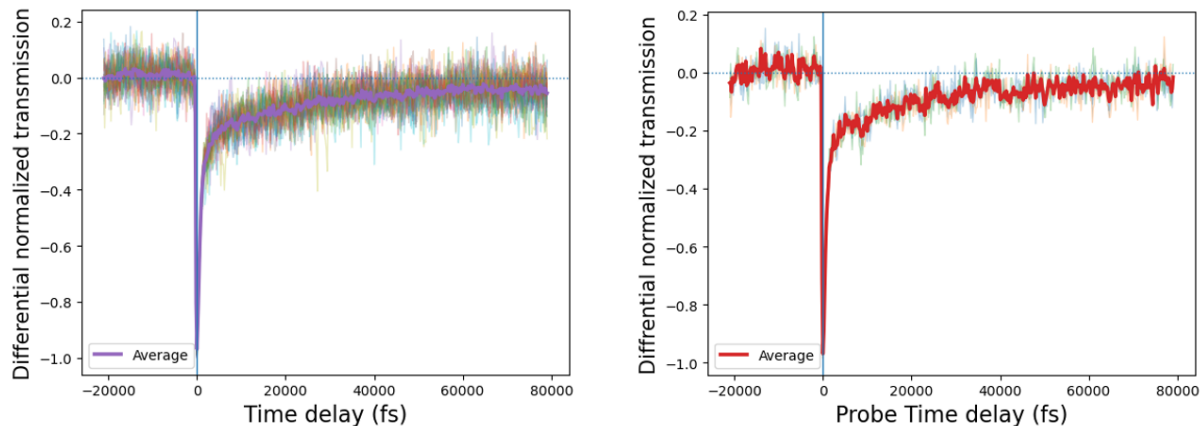


Figure 5.3: Transient absorption spectrum of unstretched P3HT film (left) and 3% stretched P3HT film (right).

5.5.1 Power optimization

A careful assessment of the excitation density is essential in pump-probe experiments, since high power may induce non-linear decay processes, most notably bimolecular exciton annihilation [101, 102]. To prevent sample damage and other effects due to high power, we have performed a power-dependent pump-probe experiment on unstretched P3HT film by varying the pump power from 15 to 60 μW as shown in Fig. 5.4. By keeping the probe fluence constant, we monitored the absorbance at $t = 0$ ps. There we have observed a linear dependency of the absorption upto 40 μW pump power; for higher powers the absorption started to change nonlinearly. We therefore selected 30 μW as the optimal pump power for all of our pump-probe measurements, which yielded a good signal-to-noise ratio and prevented unwanted nonlinear effects and sample damage. This behavior is similar to the intensity dependence reported by Rana *et al.*, who observed a linear increase in the transient $t = 0$ ps at 638 nm with excitation fluence in neat P3HT [11]. By optimizing the power for the measurement we ensure that exciton-exciton annihilation and other non-linear effects could be neglected at the used pump powers, such that strain-induced changes in the dynamics can be followed.

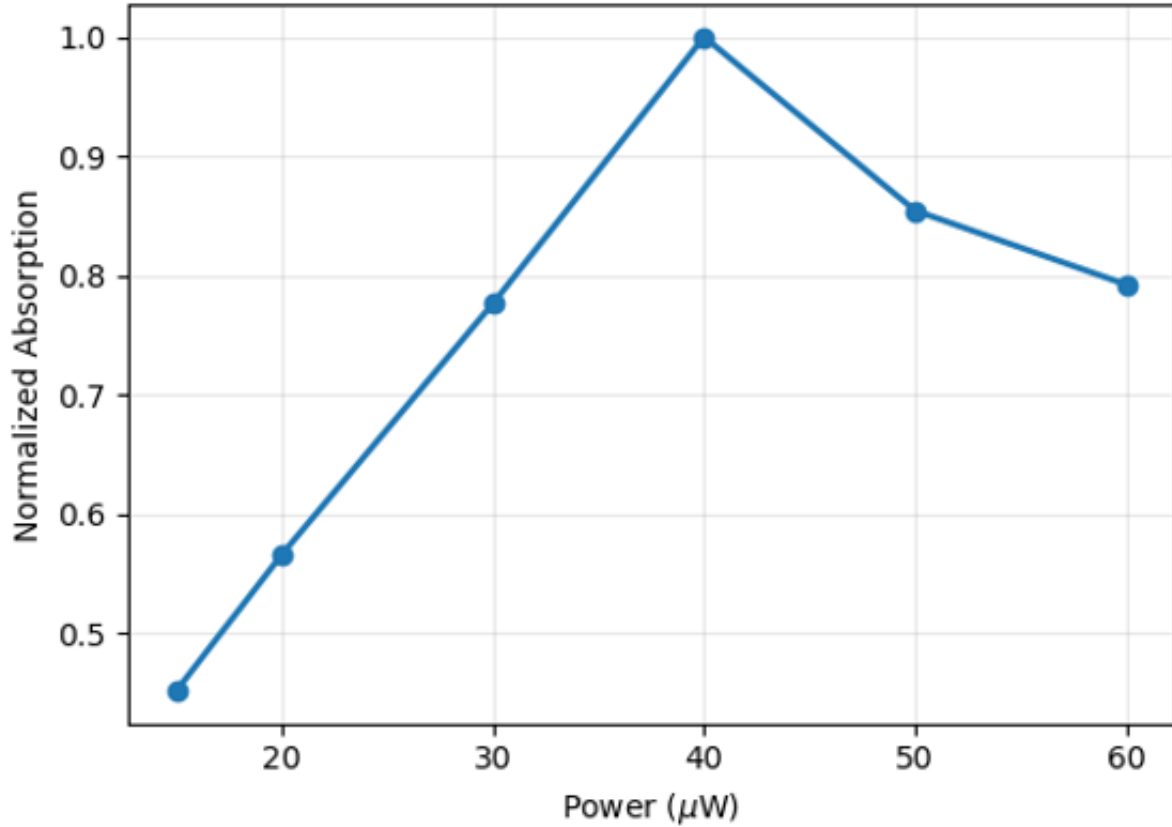


Figure 5.4: Change in absorption of probe at $t = 0$ ps with changing pump power.

5.5.2 Decay kinetics

The positive time delay dynamics in the transients shown in Fig. 3 were systematically analyzed using a bi-exponential decay function given by the model equation (1),

$$\frac{\Delta T}{T}(t) = Y_0 + A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right), \quad (5.1)$$

where A_1 and A_2 represent the amplitudes of the fast and slow decay components with corresponding time constants τ_1 and τ_2 , respectively. These components correspond to different decaying species. The offset term Y_0 accounts for species that do not decay within the experimentally accessible time window. This fitting framework allows us to perform a quantitative analysis of the contributing photoexcited species in terms of populations (A_1, A_2, Y_0) and lifetimes (τ_1, τ_2) as a function of applied mechanical strain from 3 to 15% to gain molecular-level insights into strain-induced changes. Table 1 shows all the fitting parameters for all samples (0%: unstretched and 3-15% stretched). The obtained values are reproducible within the error limits given in the table 5.1

Strain (%)	A_1 (%)	A_2 (%)	τ_1 (fs)	τ_2 (ps)	y_0 (%)
0	73.9 ± 0.2	21.0 ± 0.2	819.5 ± 10.0	20.2 ± 0.4	3.6 ± 0.1
3	76.2 ± 0.3	19.9 ± 0.3	816.3 ± 14.2	19.0 ± 0.6	3.8 ± 0.1
5	77.7 ± 0.2	17.6 ± 0.2	901.9 ± 12.8	21.6 ± 0.7	4.5 ± 0.1
7	77.7 ± 0.2	16.5 ± 0.1	865.1 ± 9.4	21.1 ± 0.5	5.7 ± 0.1
10	76.6 ± 0.3	19.0 ± 0.2	893.3 ± 15.0	25.5 ± 0.9	3.3 ± 0.1
15	78.2 ± 0.2	17.2 ± 0.2	1051.8 ± 15.0	36.6 ± 1.9	4.5 ± 0.3

Table 5.1: Strain dependence of bi-exponential fitting parameters extracted from normalized transient absorption dynamics of P3HT films on PET.

5.5.3 Photoinduced absorption onset vs. stretching

Figure 5.5 shows the absolute change in probe absorption at $t = 0$ ps as a function of uniaxial strain. Up to $\varepsilon \approx 7\%$, the $t = 0$ ps signal remains in a narrow band (0.32–0.35), indicating that neither the optical density of the film nor the initial population of photoexcited species changes appreciably with modest stretching. Beyond $\sim 7\%$, however, the time-zero signal decreases to ~ 0.28 at 10% and 0.27 at 15% strain. Since the pump and probe powers are fixed, this loss of absorption can not stem from saturation due to filling of the excited state; rather, it implies a reduction in the effective optical path length of the film. Such behaviour is consistent with the onset of micro-cracks and thickness reduction in the P3HT layer [2, 87]. The relatively large error bar on the transient response for the 15% applied strain is also conclusive evidence of defect-dominated measurement at 15% stretching, which results in statistically noisier measurements compared to other stretching percentages. Under uniaxial stretching, polymer films experience a contraction in thickness in the direction perpendicular to the applied strain. Once the applied strain surpasses the elastic regime, the formation and broadening of micro-cracks can reduce the effective cross-section and impact the local optical density [103].

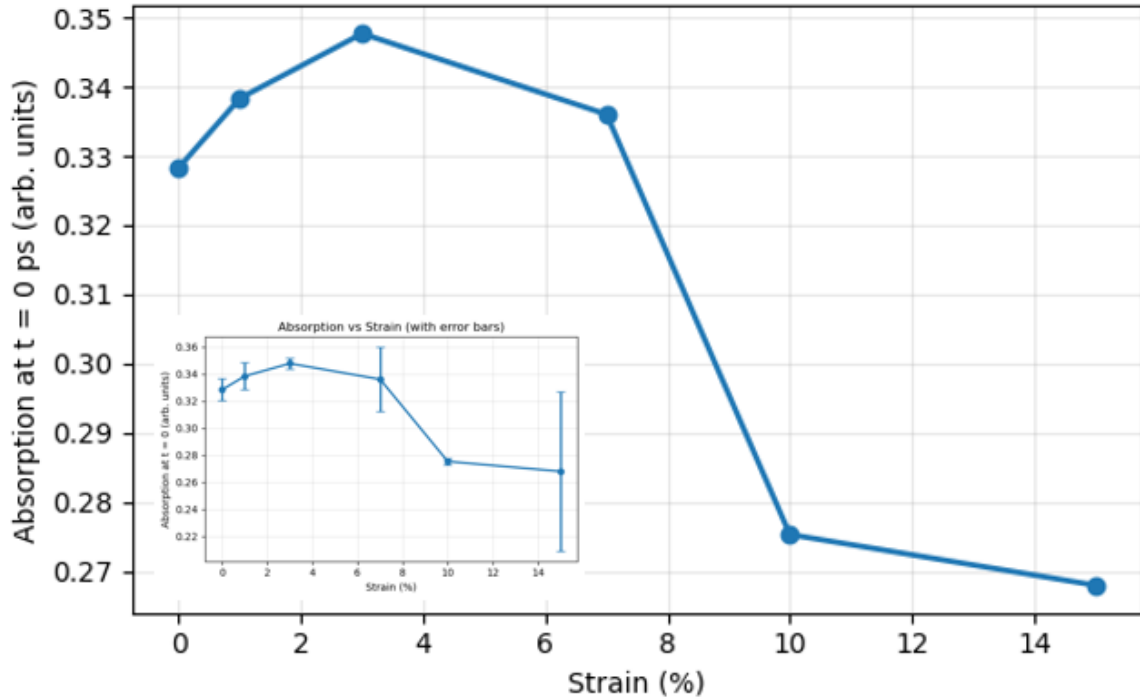


Figure 5.5: Change in absorption of probe at $t = 0$ ps with applied stretching.

Mechano-optoelectronic studies of conjugated-polymer thin films support this interpretation. In P3HT:PCBM and related systems, tensile strain has been shown to reduce the short-circuit current, external quantum efficiency, and optical absorption because the active layer thins and micro-cracks open under stretching [17]. The authors attribute these reductions to the thinning of the film thickness and morphological changes induced by strain, which lower the overlap of conjugated chains and the amount of photoactive material. Our observation of a nearly constant time-zero absorption up to 7% strain followed by a decrease at higher strain therefore predicts that P3HT films can accommodate small deformations (up to approx. 7%) without significant change in optical density, but once the elastic limit is reached cracks form, the film fastly thins and defects start to reduce the effective absorption cross section of both pump and probe beams, leading to a measurable decline in photoinduced absorbance and an increasing inhomogeneity reflected in the PP dynamics.

5.5.4 Amplitudes A_1 and A_2

Although statistical considerations can minimize the local effect in small values of applied strain, with larger stretching, the observations become more complex. Some of the interpretations of the data obtained for higher applied strain values are thus not trivial. The superposition of several induced effects might even only allow for the presentation of qualitative changes. All transient signals presented in this work correspond to normalized

transmission, obtained by subtracting the pump-off signal and normalizing to the probe intensity, thereby eliminating contributions from ground-state absorption and long-term drift.

The transient response probed at 638 nm in P3HT films is in resonance with PPs and, the typical time constant for their decay is around 0.8 ps, which is consistent with the time constants observed in our experiments [9, 11, 83]. After careful literature survey and experimental observations, the faster decaying species with amplitude A_1 is assigned to the population of polaron pairs (PPs). As shown in Fig. 5.6, the amplitude A_1 increases from the unstretched film up to $\sim 5\%$ strain and then saturates till $\sim 7\%$ before decreasing at higher stretching values (compare Figure 6a). The linear increase in the population of A_1 till 5-7% reflects overall improvement in chain alignment in the thin films that favours the generation of PPs. The sudden drop at 10% strain correlates with the onset of micro-crack formation that reduces the effective strain transmitted to the polymer film. The measured A_1 at 10% matches the value of A_1 expected around 3%, suggesting that the actual strain experienced by the film is lower than the applied value. The slight increase in population of A_1 at 15% strain, indicates that with micro-cracks, the three-point average per transient is insufficient to catch the overall picture due to an even higher point-to-point variation in recorded transients.

In addition to PP, several other species also show photoinduced absorption at this probe

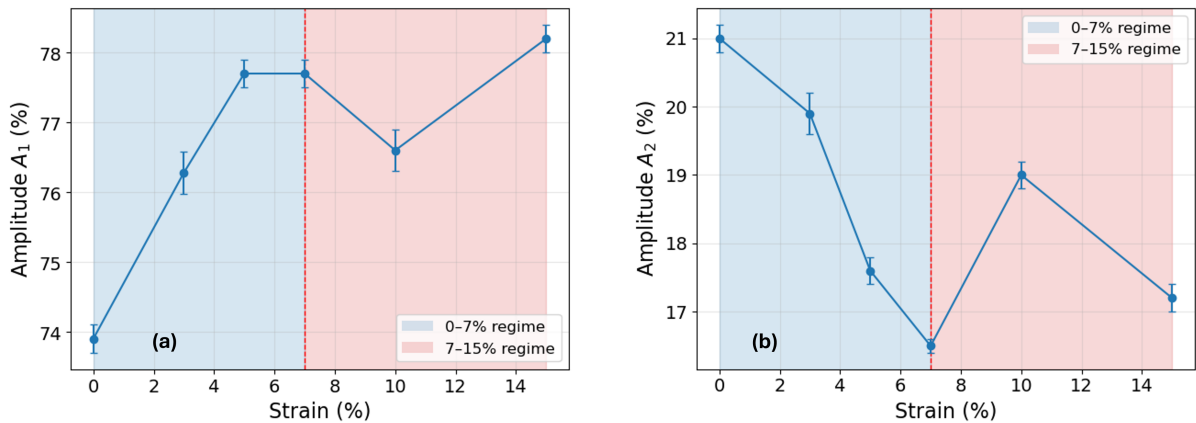


Figure 5.6: Change in (a) amplitude A_1 of PPs and (b) A_2 of DP_2s with applied stretching.

wavelength, including excimers, oxidized cations, and DP_2s [11, 29]. Previously, a study by R. Österbacka et al. have demonstrated that due to delocalization of polarons in the ordered phase of rr-P3HT, a photoinduced absorption is observed around a similar wavelength and attributed to delocalized polarons (DP_2s) [29]. Consistent with this, we have also assigned the photoinduced absorption at 650 nm to DP_2s in our previous work [11]. In this work, the slower-decay amplitude A_2 , assigned to DP_2s , exhibits the opposite trend compared to A_1 as it decreases with strain up to $\sim 7\%$ and then shows a shallow

maximum at 10 %, followed by a decline at 15 % (see Figure 6b). Comparing A_1 and A_2 , clear evidence of population transfer between these two states can be assumed. The initial decrease of A_2 suggests that improved order favours PP formation over the delocalised channel. Micro-cracks at higher strain (see 10% data) likely disrupt extended conjugation paths and introduce local disorder, which can trap polarons. At even higher strain (see 15 % result), continued crack development will fragment the percolation network further, suppressing long-range delocalisation and further reducing A_2 .

Constant offset Y_0

The constant offset Y_0 is attributed to the population of species, which does not decay on the time delay offered by our delay stages in the experimental setup. In literature, Y_0 is often attributed to trapped polaron species, which can outlive the typical exciton lifetime [9, 82]. Consistent with the previous literature, we have attributed Y_0 to the population of trapped polaron-pairs. As shown in Fig. 5.7, the offset Y_0 increases up to about 7 % strain and then drops sharply at higher strains, reaching a minimum at 10 % before partially recovering at 15 %. The initial rise of Y_0 may result from strain-induced alignment creating deeper trap sites or stabilizing charge pairs. The microcrack formation starting at 10% strain first partially removes trap states formed before by chain alignment. Then, at even higher strain values (15%) the disordered system begins to offer new trap sites resulting in an increase of trapped PPs. More importantly, the behaviour of Y_0 is proportional to the population redistribution between A_1 and A_2 such that the population A_2 is being redistributed between the two channels $A_2 = A_1 + Y_0$. Initially, up to 5% applied strain, this redistribution is dominated by an increase in the population of A_1 , at higher values of strain (between 5 and 7%) , this redistribution is dominated by an increase in Y_0 . The redistribution of A_2 at higher strain is in line with the formation of microcracks, which first removes some of the trap states formed by chain alignment before the trap sites resulting from the cracks start to dominate.

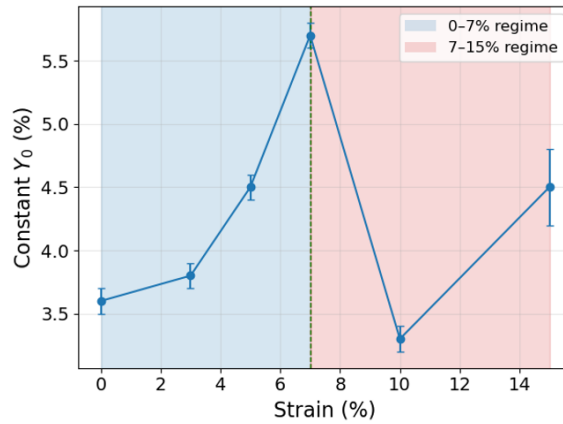


Figure 5.7: Change in amplitude Y_0 assigned to longer living species with applied stretching.

5.5.5 Time constants τ_1 and τ_2

As shown in Fig. 5.8, the fast time constant τ_1 remains within a narrow window of 0.8–0.9 ps from 0 to 10 % strain and then increases to ~ 1.05 ps at 15 %. Given the instrumental response of ~ 150 fs, the modest variation observed in τ_1 lies close to the experimental resolution, indicating that the intrinsic decay pathway associated with this component is largely preserved at low and moderate strain. Literature reports suggest that PP lifetimes are relatively insensitive to external perturbations such as pump fluence or static electric fields when excited with below band gap energies [11], reflecting the intrinsic timescale of hot-exciton dissociation and polaron-pair recombination. Within this framework, the gradual increase of τ_1 at modest strain is most consistently attributed to an internal redistribution of population between PPs and DP_2s related channels, rather than a fundamental slowing of PP recombination. At higher strain values, however, the more pronounced increase in τ_1 likely reflects the onset of strain-induced morphological disruption, such as microcrack formation, which alters the local dielectric environment and carrier mobility and thereby perturbs the effective decay pathways captured by the transient fitting model.

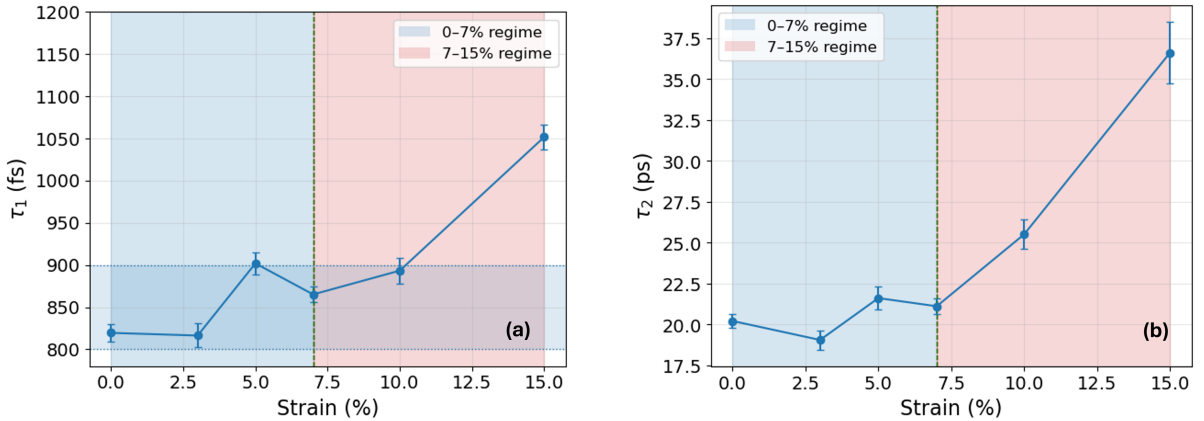


Figure 5.8: Change in (a) time constant τ_1 of PPs and (b) τ_2 DP_2s with applied stretching.

The slower time constant τ_2 exhibits a gradual increase with strain, followed by a steeper rise at higher strain levels. In field-dependent transient absorption studies, this component has been associated with DP_2s states, whose lifetime depends on carrier annihilation and trapping dynamics [11]. In the present measurements, the use of optimized excitation power ensures that fluence-dependent effects are minimized, indicating that the observed evolution of τ_2 arises predominantly from mechanical deformation. At low strain, the moderate increase in τ_2 is consistent with an internal population redistribution from longer-lived states related to DP_2s , potentially facilitated by subtle changes in molecular

packing or interchain coupling. At higher strain, the rapid growth of τ_2 is more plausibly attributed to strain-induced microcracks and increased morphological heterogeneity, which compromise the validity of a simple bi-exponential description in the statistical framework of 3-point measurement. In conclusion, the time constants τ_1 and τ_2 can be interpreted as a mathematical consequence of the population redistribution rather than actual slowing down of the decay channels. This observation points to the optimization of overall charge-carrier dynamics by a transfer of the population of slower decaying species to fast decaying species in a modest strain range, which in turn also supports the slowing down of decay pathways.

5.6 Conclusion

In conclusion, the results demonstrate that mechanical stretching systematically influences the relative populations of polaron pairs (PPs), delocalised polarons (DP_2s), and long-lived trapped carriers (Y_0) in P3HT thin films. At modest tensile strain up to approximately 7%, a redistribution of photoexcited species is observed, characterised by an increased PPs population accompanied by a reduction in the DP_2s contribution. This regime reflects an intrinsic strain response of the polymer film, where molecular reorganisation occurs without introducing significant structural damage. Beyond this threshold, at higher applied strains, the system enters a qualitatively different mechanical regime. The formation of microcracks introduces pronounced inhomogeneity, leading to a non-trivial modification of the transient dynamics. Notably, the extracted amplitudes A_1 and A_2 at 10 and 15% strain closely resemble those obtained at around 3 and 7% strain, despite the substantially larger nominal strain applied. This behaviour indicates that the effective strain experienced by the intact polymer domains no longer scales with the externally applied deformation. Instead, strain relaxation through microcrack formation limits further uniform molecular rearrangement. The concurrent reduction in the time-zero transient absorption signal at 10 and 15% strain provides additional support for this interpretation, consistent with a loss of effective optical density due to cracking and thickness reduction. Taken together, these findings show that small tensile strains, comparable to those arising from thermal expansion mismatches or mechanical compliance in flexible and foldable optoelectronic devices, can be well tolerated and can even induce subtle improvements in photophysical performance. In this moderate-strain regime, the internal redistribution of photoexcited species favours PP over DP_2 formation, attributed to trap-assisted localization of polaron pairs, a balance that is likely beneficial for device operation. In contrast, at higher strain levels, the increasing contribution of DP_2s and the onset of structural damage lead to unpredictable photophysical responses and signal the onset of mechanical degradation. These results underline the importance of distinguishing between modest strain, tolerable

strain, and excessive deformation when evaluating the mechanical limits and functional stability of flexible organic semiconductor devices.

Frequency-Domain Studies

In the first part of the thesis, results obtained from frequency-domain spectroscopy are presented. For the experiments, Raman spectroscopy and Ultraviolet-Visible (Uv-Vis) absorption spectroscopy was performed on different samples with applied external perturbations. Subsequent chapters 7,8 and 9 present the results obtained from two different studies.

Chapter 6

Frequency-Resolved Spectroscopy

In this section, a detailed description of Raman spectroscopy and UV-Vis spectroscopy is given. We have employed these techniques to probe the impact of mechanical stretching on structural properties of our samples. The Raman spectroscopy experiments are performed in-situ while the test samples are in a stretched state whereas due to experimental limitations, all the UV-Vis experiments are performed ex-situ.

6.1 Raman Spectroscopy

Raman spectroscopy is a powerful spectroscopic technique based on the inelastic scattering of light. When the electromagnetic radiation of incident light interacts with a material, most photons are elastically scattered without a change in energy. This process, known as Rayleigh scattering, corresponds to the dominant scattering contribution. However, a very small fraction (1 in a million) of the scattered photons, however undergo energy exchange with the molecular system, resulting in a frequency shift relative to the incident radiation. This phenomena is first observed by Indian scientist C.V. Raman and called as Raman scattering.

Raman scattering arises from the interaction of the incident electric field with the molecular polarizability. During this interaction, the molecule is transiently driven into a virtual energy state. The scattered photon may then emerge with either lower or higher energy depending on whether energy is transferred to or from the molecular vibrational modes. The observed frequency shifts correspond to transitions between quantized vibrational energy levels of the molecule and therefore provide direct information about its vibrational structure.

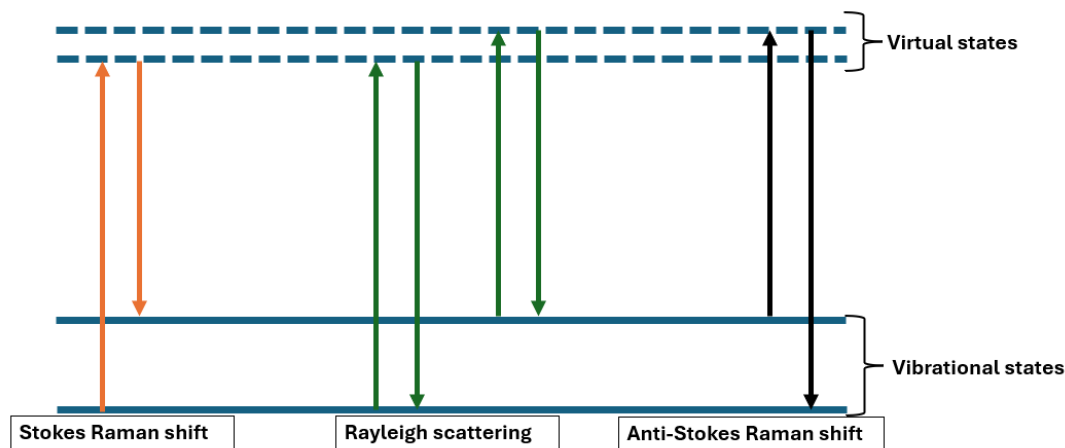


Figure 6.1: Schematic of pump-probe setup.

Depending on the nature of energy transfer, Raman scattering is classified into two types:

Stokes Raman scattering: The scattered photon has lower energy (longer wavelength) than the incident photon. In this case, the molecule absorbs energy and is promoted from the vibrational ground state to a higher vibrational state. In general, majority of the Raman signal consists of Stokes signal.

Anti-Stokes Raman scattering: The scattered photon has higher energy (shorter wavelength) than the incident photon. Here, the molecule loses vibrational energy and transitions from an excited vibrational state to a lower one. The anti-Stokes signal is in general very weak and needs special spectroscopic techniques to be studied, namely Coherent Anti-Stokes Raman scattering.

The measurable quantity in Raman spectroscopy is the energy difference between the incident and scattered photons, commonly expressed as the Raman shift (typically in cm^{-1}). This shift is independent of the excitation wavelength and is characteristic of the molecular vibrational modes of the material under investigation.

6.1.1 Classical theory of Raman spectroscopy

A scattering of light can be interpreted as redirection of light when it goes through inhomogeneity. Molecules are made up of positively charged nuclei embedded in negatively charged electron clouds. When an EM wave is incident on a molecule, electron clouds and nuclei respond by moving in opposite directions in accordance with Coulomb's law. As an EM wave interacts with a molecule, the electron orbits are perturbed periodically with the same frequency as the incident EM wave. This perturbation results in the periodic separation of charge within the molecule. This separation of charge is known as induced dipole moment and this oscillating induced dipole moment is manifested as the source of EM radiation and thereby results in the scattering of light.

For small magnitudes of electric field, the induced dipole moment can be given by:

$$\mu = \alpha E \quad (6.1)$$

where α is called polarizability and is a property of matter. As the electric field is oscillating with a sufficiently large frequency, the electron clouds of small inertia will be able to follow these oscillations and get distorted. The extent of this distortion is what we call polarizability. This ability to perturb the molecule depends on the location of each atom and thus α is a function of the position of the atom. We can write the incident oscillating field as:

$$E = E_0 \cos(2\pi\nu_0 t) \quad (6.2)$$

where ν_0 is the frequency of the incoming field. We can write the induced dipole moment as $\mu_{ind} = \alpha E_0 \cos(2\pi\nu_0 t)$. Now, the physical displacement of atoms about the equilibrium position due to such a field can be written as

$$dQ = Q_0 \cos(2\pi\nu_m t) \quad (6.3)$$

The polarizability can be expanded around the equilibrium position as

$$\alpha = \alpha_0 + \left(\frac{d\alpha}{dq} \right) dq, \quad (6.4)$$

where α_0 is the polarizability at the equilibrium position. Substituting the vibrational displacement

$$dq = Q_0 \cos(2\pi\nu_m t), \quad (6.5)$$

we obtain

$$\alpha = \alpha_0 + \left(\frac{d\alpha}{dq} \right) Q_0 \cos(2\pi\nu_m t). \quad (6.6)$$

Using $E = E_0 \cos(2\pi\nu_0 t)$, the induced dipole moment becomes

$$\mu_{ind} = \alpha_0 E_0 \cos(2\pi\nu_0 t) + \frac{1}{2} \left(\frac{d\alpha}{dq} \right) Q_0 E_0 [\cos(2\pi(\nu_0 - \nu_m)t) + \cos(2\pi(\nu_0 + \nu_m)t)]. \quad (6.7)$$

The above equation is a direct implication of the fact that the induced dipole moments are created at three different frequencies. These frequencies correspond to ν_0 for Rayleigh scattering and the other two $(\nu_0 - \nu_m)$ and $(\nu_0 + \nu_m)$ correspond to Stokes and anti-Stokes Raman scattering, respectively.

From the above equation, it is noteworthy that for Raman scattering the most important condition will be the change of polarizability. This change can be accompanied by a rotational or vibrational displacement of atoms corresponding to a particular rotational

or vibrational mode resulting in a change in polarizability.

6.1.2 Raman setup

In this thesis, all Raman measurements were performed on table top Raman setup from Horiba Jobin-Yvon T64000 spectrometer. An Argon ion gas laser is used to excite the samples at 514.4 nm. A 50X objective was used to collect the scattered light. The scattered light is then filtered for any Rayleigh background signal using a notch filter. After filtering the signal, only inelastically scattered photons are detected using a charge-coupled device (CCD) detector. The detector scatters the photons into different components using a 1200 lines/mm diffraction grating. The output from the CCD is then measured as a Raman spectra using a computer.

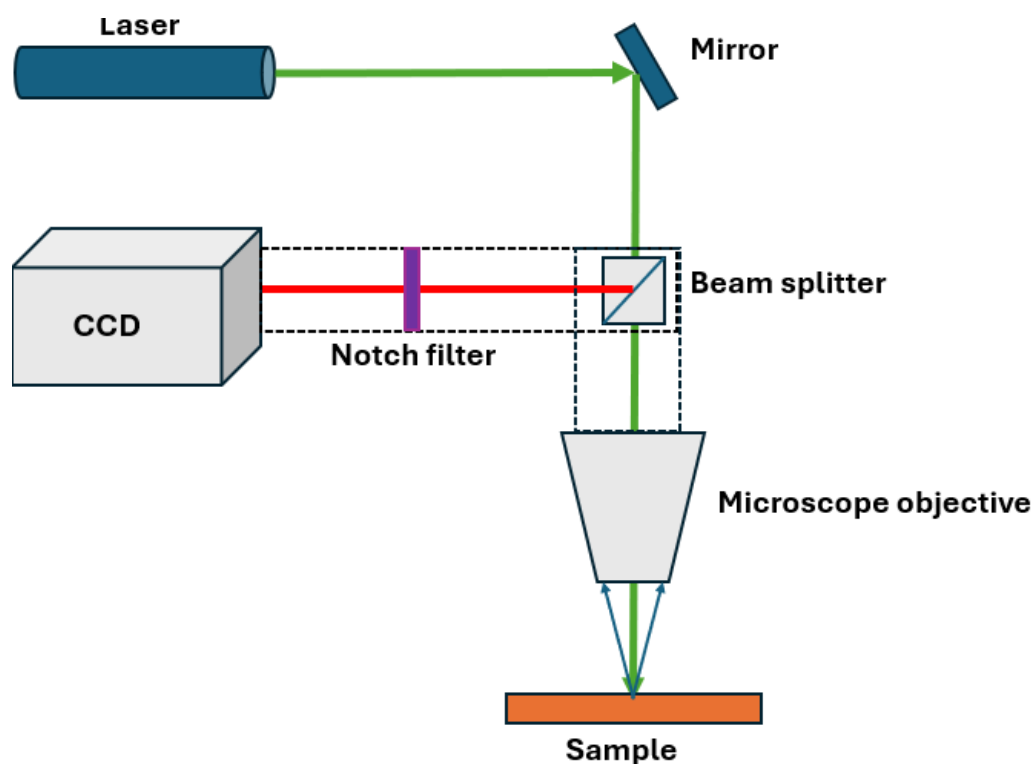


Figure 6.2: Schematic of Raman setup.

6.2 UV-Vis Spectroscopy

UV-Vis spectroscopy is commonly used to study the interaction of a material with ultraviolet and visible radiation. A broadband light source illuminates the sample, and the transmitted light is spectrally dispersed using a monochromator grating and detected by a photodetector. The recorded spectrum provides information about electronic transitions and excitonic features of the material. The absorbance is related to the attenuation of the transmitted intensity given by the Beer-Lambert law,

$$A = \varepsilon c d, \quad (6.8)$$

where A is the absorbance, c is the concentration, d is the optical path length, and ε is the molar extinction coefficient measured in $\text{L mol}^{-1} \text{cm}^{-1}$. For solid samples, the measured signal depends on the intrinsic absorption coefficient as well as sample thickness and surface reflection. In general, the absorbance can be expressed in terms of transmittance T as

$$A = -\log_{10}(T), \quad (6.9)$$

with T defined as the ratio of transmitted to incident intensity. In the present study, UV-Vis spectroscopy is primarily used to characterize the optical absorption features of the investigated materials.

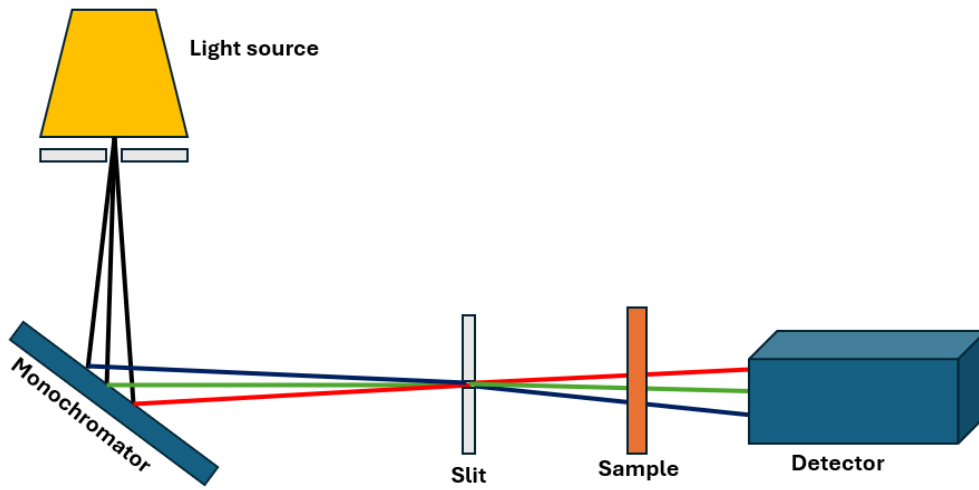


Figure 6.3: Schematic of UV-Vis spectrometer.

Chapter 7

Strain-Induced Optical and Molecular Transformations in PET Films for Organic Electronic Applications

Overview

This chapter examines the impact of mechanical stretching on polyethylene terephthalate (PET), a substrate widely used in flexible optoelectronic and photovoltaic devices. Since PET serves as the mechanical support in many flexible architectures, understanding its structural and optical response under strain is essential for reliable device design [25]. The study combines Raman spectroscopy and UV–Vis absorption spectroscopy to investigate strain-induced modifications in the molecular structure and optical properties of PET films. The results of this work have been published as:

M. Ghorab, Ayush .K. Ranga, P. Donfack, A. Materny, V. Wagner, and M. Joodaki - “Strain-Induced Optical and Molecular Transformations in Poly(Ethylene Terephthalate) Films for Organic Electronic Applications”. *Advanced Photonics Research* (2025), p. 2500081. doi:10.1002/adpr.202500081.

7.1 Abstract

Poly(ethylene terephthalate) (PET) films are widely used in flexible electronics and optoelectronics, where mechanical durability and optical performance under strain are essential for device reliability. This study investigates the effects of cold-drawing amorphous PET under ambient conditions on its optical and molecular characteristics, using ultraviolet–visible (UV–Vis) and Raman spectroscopy. It examines how varying strain levels, from 0% (unstretched) to 30%, affect transparency, vibrational modes, and molecular

reorganization. UV–Vis absorbance measurements, performed ex-situ after strain release, reveal persistent changes in light transmission, including up to 100% increased absorption in the UVA and visible regions, particularly following large deformations. Raman spectra show that strains above 5% cause irreversible shifts in vibrational lines and increased full width at half maximum (FWHM). These spectral changes suggest partial molecular reorientation and emerging structural order, consistent with prior reports on cold-drawn amorphous PET. The phonon mode coupled with C–O stretching [O–CH₂] shows the strongest response to mechanical stress. This work provides insight into strain-induced optical and structural changes in PET, informing strategies to improve the performance of PET-based devices in strain-sensitive applications such as organic solar cells (OSCs), organic light-emitting diodes (OLEDs), and flexible sensors.

7.2 Introduction

Flexible and stretchable materials are central to advancements in technologies such as organic solar cells (OSCs), organic light-emitting diodes (OLEDs), and strain sensors, where mechanical durability and optical stability under strain are critical for reliable device performance[18, 104, 105]. Among these, poly(ethylene terephthalate) (PET) remains a widely adopted substrate due to its excellent optical transmission, mechanical robustness, and ease of processing [106, 107]. Although widely utilized, PET’s structural and optical response to cold drawing under ambient conditions remains insufficiently understood. This knowledge is essential for the rational design of PET-based devices, where mechanical deformations often occur during use [108–110].

In OSCs and flexible electronics, PET typically serves as the first interface that interacts with light before reaching functional layers. Consequently, its optical properties, particularly within the visible spectrum, are vital for maximizing light transmission[111, 112]. Mechanical strain, such as stretching or compression, can induce reorientation of molecular chains and alter crystallinity, thereby affecting light scattering, absorption, and refractive index. Understanding these effects is key for evaluating material degradation and ensuring optical fidelity during dynamic operation [113, 114].

Several foundational studies have aimed to connect vibrational spectroscopy with mechanical stress and polymer orientation in PET. Bower and Lewis developed a rigorous theoretical and experimental framework that linked Raman shift anisotropy with polarization direction and stress orientation in both isotropic and uniaxially oriented PET. Their model provided predictive relationships for how Raman bands shift and vary in intensity under different stress geometries, offering tools to interpret molecular deformation in strained polymers [115]. Webster and Bower later built upon this framework by demonstrating a linear relationship between hydrostatic pressure and the Raman shift of the 1616 cm^{−1} mode, reinforcing how external mechanical fields affect

chain packing and intermolecular interactions [116]. These works provide theoretical and experimental context for interpreting the Raman spectral changes observed in this study, particularly in relation to chain orientation under uniaxial strain at ambient conditions. Other investigations—such as those by Bin *et al.* and Laskarakis *et al.*—focused on PET’s response to biaxial strain at elevated temperatures, where polymer chains possess enough mobility to undergo reorganization and crystallization. Their studies revealed how strain modifies mechanical stiffness, birefringence, and electronic transitions, contributing to a broader understanding of anisotropic behavior during processing[109, 117–119]. Similarly, González-Córdova *et al.* [120] used angular-dependent Raman spectroscopy to characterize stress-induced anisotropy in uniaxially strained PET, while Zhou *et al.*[121] applied Mueller matrix ellipsometry to monitor optical axis evolution under load.

However, most prior studies have concentrated on deformation above the glass transition temperature ($T_g \sim 80\text{--}90^\circ\text{C}$), where thermal energy facilitates molecular rearrangements and crystallization [109, 117]. In contrast, the present work focuses on uniaxial strain at room temperature, a regime in which molecular mobility is significantly reduced. Under these conditions, crystallization is suppressed, and the role of amorphous regions becomes more pronounced, leading to vibrational and optical behaviors distinct from those observed in thermally activated processes. These effects are particularly relevant in flexible electronics, where device deformation occurs under ambient, non-annealed conditions.

To systematically explore these behaviors, this study investigates a broad strain range (1–30%) and analyzes 13 Raman-active modes across time to track structural evolution. Detailed attention is paid to frequency shifts, FWHM changes, and intensity variations—all essential for interpreting deformation mechanisms and optical consequences under practical conditions.

Among the most closely aligned prior works is that of Keum *et al.*, who investigated the structural evolution in PET fibers using synchrotron X-ray diffraction and infrared (IR) spectroscopy. As part of their broader study on crystallization pathways, they identified the presence of a smectic-C-type transient mesophase in cold-drawn PET, marked by tilted chain arrangements and a two-stage crystallization process [122]. Although their focus extended beyond room-temperature deformation, the initial structural features observed under cold-drawing conditions offer a useful framework for interpreting early-stage molecular ordering. These insights are particularly relevant to the current study’s focus on vibrational and optical responses in amorphous PET subjected to uniaxial strain at ambient temperature.

Accordingly, this study addresses a critical gap in current understanding by characterizing the structural and optical responses of amorphous PET subjected to cold drawing under ambient conditions. The results provide relevant insights important for the development and reliability of PET-based components in flexible optoelectronic applications, where

mechanical strain is inherent and post-deformation thermal annealing is often impractical.

7.3 Experimental Methods and Setup

This work has utilized ultraviolet–visible (UV–Vis) absorption and Raman spectroscopy to examine the optical and vibrational responses of PET films under mechanical strain. Figure 7.1 illustrates the custom-built stretcher device designed to apply precise, controlled tensile strain to PET samples. Measurements were performed both in-situ and ex-situ, depending on the experimental technique. The device is controlled by an Arduino board, which regulates the application of strain. PET films were securely clamped at both ends of the stretcher and incrementally strained at levels of 1%, 2%, 3%, 4%, 5%, 10%, 15%, 20%, 25%, and 30%.

UV-Vis absorption spectroscopy offers a straightforward, fast, and cost-effective method to assess the absorbance and transmittance of materials in the ultraviolet and visible wavelength ranges. This technique is particularly valuable for quantifying changes in transparency resulting from mechanical strain [14, 123]. For PET films subjected to mechanical strain, UV–Vis absorption spectroscopy offers a rapid and quantitative means of evaluating changes in transparency across defined wavelength regions. In this study, UV–Vis measurements were conducted ex-situ after strain release to monitor strain-induced alterations in film transparency — a goal for which ex-situ analysis is both sufficient and appropriate. While in-situ UV–Vis could capture transient or reversible optical changes during active loading, the present focus is on the residual, persistent changes relevant to the material’s functional performance after deformation. Nonetheless, UV–Vis spectroscopy primarily reflects bulk optical behavior and offers limited insight into the molecular mechanisms underlying these changes, which are instead probed through in-situ Raman spectroscopy conducted during strain application.

In contrast, Raman spectroscopy provides a deeper understanding of structural dynamics by probing molecular vibrations directly linked to the material’s molecular architecture. Raman spectroscopy enables in-situ measurements as a non-destructive technique, allowing real-time observation of structural variations under strain [124, 125]. By correlating Raman data with UV-Vis findings, it becomes possible to detect these transparency changes and elucidate their causes by identifying the specific molecular mechanisms responsible. This dual-modality assessment leverages the complementary strengths of UV–Vis and Raman spectroscopy to explore PET’s optical and structural evolution under mechanical strain.

UV-Vis absorbance measurements were performed on the PET film after each strain exposure. A more detailed description of the UV-Vis setup is discussed in section 6.2. The PET roll used in this study was sourced industrially, originally manufactured as a

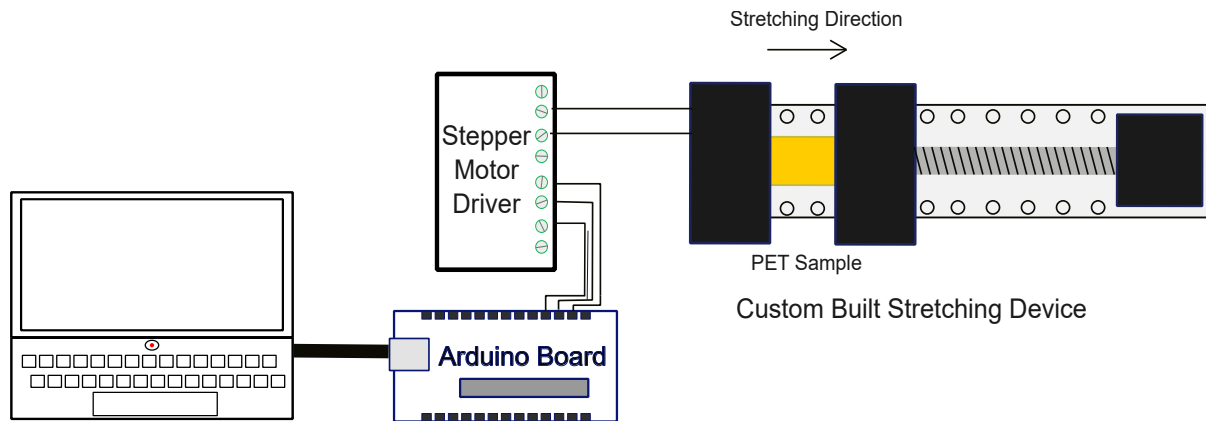


Figure 7.1: Custom-built stretching device; the stretcher is controlled by an Arduino board, via a motor controller.

transparent substrate for organic solar cell (OSC) applications, with a density of $16.8 \times 10^5 \text{ g/m}^3$. Owing to its intended use in optoelectronic devices, the material exhibits an amorphous morphology optimized for maximal optical clarity. The films were cut into standardized dimensions of $15 \text{ mm} \times 33 \text{ mm}$ to fit the UV-Vis device sample holder size and ensure uniformity throughout the experiments. Each strain level was maintained for 30 minutes for structural relaxation and accurate spectral measurements. A new, unstretched film was used for each strain value to ensure consistent and independent measurements. The strain was calculated as the percentage elongation relative to the original film length ($\epsilon = \frac{\Delta L}{L}$).

Although in-situ UV-Vis absorption spectroscopy under applied strain would provide real-time insights into optical responses, it was not feasible in the present study due to instrumental constraints. Specifically, the mechanical stretcher could not be integrated within the UV-Vis spectrometer chamber. As an alternative, we employed an ex-situ approach, acquiring absorption spectra immediately after the application and release of mechanical strain.

While this method does not capture transient or fully reversible phenomena, it offers valuable insight into persistent optical modifications, residual stress, and strain-induced changes that remain after mechanical relaxation. These observations are particularly relevant for evaluating the stability and optical reliability of polymer substrates under mechanical deformation in flexible optoelectronic devices. UV-Vis absorption measurements were performed using a PerkinElmer Lambda 12 spectrophotometer, with PET films positioned directly in the optical beam path to enable accurate characterization of strain-induced spectral changes. All measurements were conducted using unpolarized light, thereby capturing the intrinsic, orientation-averaged absorption behavior of the samples. Spectra were recorded over the 200–1000 nm wavelength range, and baseline correction was applied using air as a reference. As the first step, before applying strain, four spectra were recorded for each sample by rotating the film to capture variations across

its surface. The PET piece was rotated by 180° on each side, resulting in two measurement areas: two lines of 11 mm in length and 0.5 mm in width, located on the left and right sides of the sample center. The sample was then mounted on the custom-built stretcher, subjected to a specified strain level for 30 minutes, and released. Following strain release, the same rotational approach was used to record another set of four spectra. The spectra were averaged to account for variations across the film and provide a more representative understanding of how strain affects its optical transparency. Changes in absorbance were analyzed to assess strain's impact on the films' optical properties. Figure 7.2 presents the cross-section of the PET samples before and after strain exposure. Applying strain values greater than 20% induces distortions in the structure, making thickness measurements with an optical microscope difficult due to the appearance of shadows. The thickness of the sample was measured at different positions and an average thickness was calculated from these values (see Fig.2). It reduced from an average value of $57.271\ \mu\text{m}$ to $44.342\ \mu\text{m}$ responding to strain.

A detailed description of Raman spectroscopy setup used for the experiments is discussed in section 6.1.2. For the calibration of Raman spectrometer wave numbers, the aromatic toluene breathing mode at $1003.7\ \text{cm}^{-1}$ was used. The laser was set to have an excitation polarization parallel to the strain axis. Measurements were taken directly on the strained PET films at regular intervals of 5 minutes during the 30-minute strain application. The Raman spectra data were analyzed to extract line positions, full width at half maximum (FWHM), and intensity variations for key vibration modes.

7.4 Optical and Molecular Responses of PET Under Strain

The interplay between mechanical strain and PET's optical properties is the key focus of this study to gain insights into how structural changes at the molecular level translate to observable optical behavior. These implications are particularly significant for applications that balance mechanical flexibility and optical device performance, such as OSCs, flexible electronics, and strain sensors [126].

The results are presented in two parts: First, UV-Vis absorption spectroscopy explores how strain affects the optical transparency of PET films, focusing on changes in absorbance across different strain levels. However, while UV-Vis reveals the transparency alterations, it does not provide insight into the underlying molecular mechanisms. To address this, in-situ Raman spectroscopy is employed to uncover the changes observed from vibration modes most sensitive to mechanical deformation, linking molecular reorganization to observed optical variations. These results are discussed in the second part.

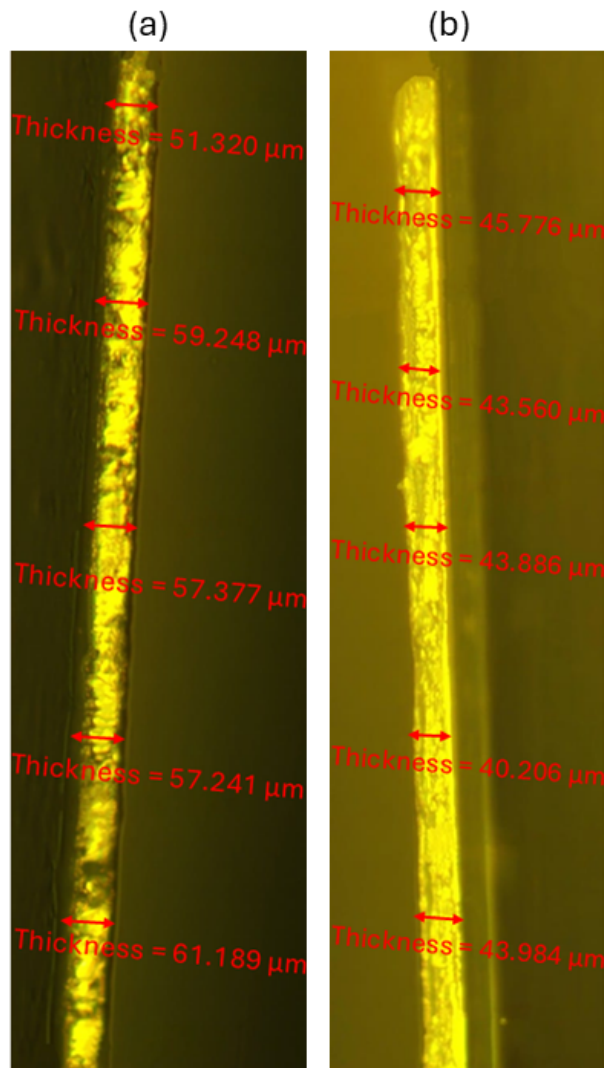


Figure 7.2: The PET sample's thickness was measured at different positions. (a) without stretching and (b) after 20% stretching; the thickness deduction resulting from the strain exposure is observed. The images were captured using a Carl Zeiss Axiotech 100HD light microscope equipped with an Axiocam 105 color camera.

7.4.1 Strain-Induced Optical Variations

Panel (a) of Fig. 7.3 shows the UV-Vis absorbance characteristics of an unstretched PET sample at room temperature. Given the transparency of PET in the visible region (400-700 nm), only minimal absorbance is observed. Panel (b) of Fig. 7.3 presents the absorbance spectra of all thin-film PET samples subjected to varying strain levels after stress release. It reflects PET's typical behavior and intrinsic properties, where the absorption is stronger near the UV region and decreases for higher wavelengths, moving toward the visible spectrum. However, as the strain percentage increases from 1 to 30%, there is a general increase in the absorbance for the UV-Vis spectrum. Increasing strain would lead to higher absorbance values for the PET films, which is particularly noticeable in the mid-range wavelengths (around 400-500 nm). This effect would interrupt the light transmission to the active layer, potentially decreasing the OSC's efficiency. Figure 7.4 illustrates the

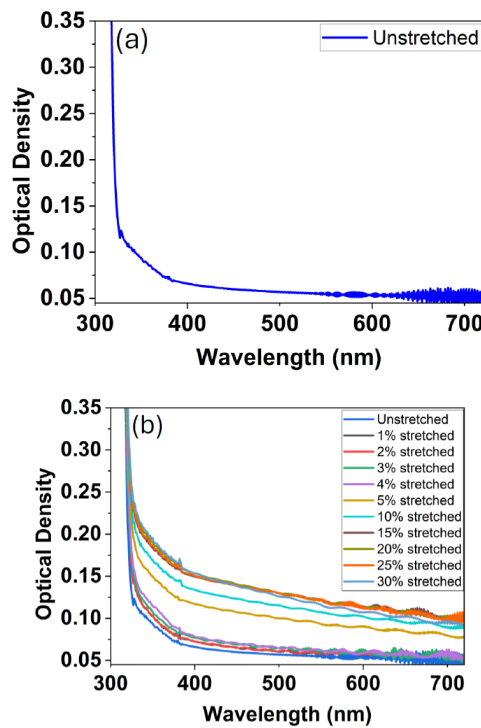


Figure 7.3: UV-Vis absorbance plots of PET samples: (a) unstretched PET and (b) strained PET.

absorbance variation in the UV-Vis spectrum. To produce this graph, the wavelength range between 320 and 700 nm was divided into smaller segments, each corresponding to a specific color band of the visible spectrum. The absorbance values within these ranges were summed and normalized to the unstretched values (0%) to represent each color region's overall contribution. These regions were categorized as follows: dark violet

range 320–400 nm, purple range 400–450 nm, blue range from 450–495 nm, green range from 495–570 nm, yellow range from 570–590 nm, orange range from 590–620 nm, and red range from 620–700 nm. The bars in the graph are color-coded to align with the visible spectrum, visually linking the wavelength ranges to their respective colors. This approach allowed for a clear comparison of the absorbance response of PET thin films under varying applied strains, emphasizing differences in absorbance across the spectral regions. As the strain level increases from 0% (unstretched) to 30%, there is a notable increase in absorbance values, especially for purple and blue wavelengths.

The observed increase in visible light absorption is likely linked to strain-induced structural alterations at the molecular level. Previous studies on stretched PET suggest the formation of localized defects or energy states, which could account for increased visible absorption. However, detailed structural characterization (e.g., spectroscopy at cryogenic temperatures or defect-sensitive electron microscopy) is necessary to confirm the exact nature and presence of such localized states [109, 117]. Furthermore, strain-induced variations in local structural organization—such as partial molecular alignment or the formation of a mesophase—could enhance optical scattering and reduce transparency [122, 127, 128]. Direct verification through complementary structural characterization techniques (e.g., small-angle X-ray scattering, birefringence) is necessary for definitive conclusions regarding crystallinity or alignment changes. In addition, in-situ UV–Vis absorption spectroscopy, though not employed in the present study, could offer further insight into reversible optical responses during active deformation, particularly in the elastic regime. While our focus remains on persistent, post-deformation optical changes, future studies can benefit from integrating in-situ UV–Vis spectroscopy to better capture transient phenomena associated with strain application. Furthermore, there is a notable jump in absorbance

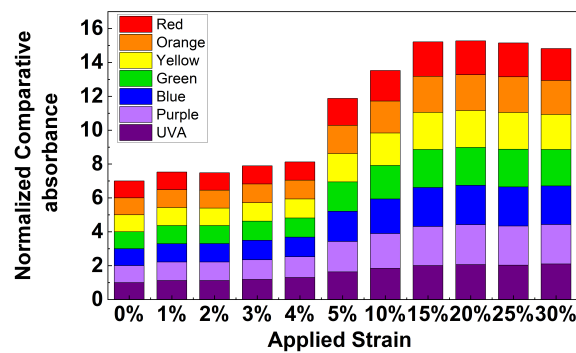


Figure 7.4: Normalized UV-Vis absorbance of PET films across different visible and UV spectral regions in response to varying residual applied strain. The bar graph highlights the absorbance contributions of specific wavelength ranges (dark violet, purple, blue, green, yellow, orange, and red; see also main text) at strain levels from 0 to 30%, showing a trend of increasing absorbance with higher strain.

values, particularly beyond 5% strain. This suggests the presence of a threshold beyond

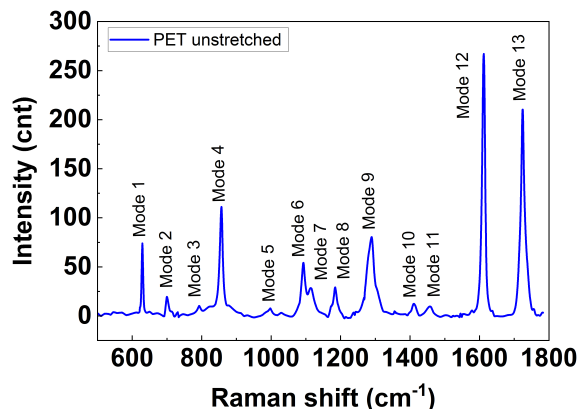


Figure 7.5: Raman spectrum of an unstretched PET film.

which structural changes in PET—such as mesophase development, increased chain alignment, or a higher density of local packing irregularities—result in significantly elevated light absorption and/or scattering. These effects likely reflect the onset of trans-rich conformational domains and optical anisotropy, phenomena commonly reported in cold-drawn PET systems [122, 128].

7.4.2 Strain-Induced Molecular Variations Probed by Raman Spectroscopy

In applications like OSCs where PET is used as a substrate, the observed changes in optical properties could affect the efficiency of light absorption and conversion, especially under mechanical stress. The transparency reduction in critical wavelengths is important for solar absorption since it reduces the overall performance of the solar cells. These data offer preliminary quantitative insights into how mechanical stress influences the optical response of PET, serving as a basis for future investigations and contributing to the understanding of material behavior in applications where mechanical and optical properties are coupled.

As mentioned above, in addition to the UV-Vis absorption measurements, we have conducted in-situ Raman spectroscopy on the stretched samples to gain deeper insights into structural alterations under applied strain. This analysis allows us to identify which molecular regions experience greater strain-induced changes and observe the PET molecule’s evolution over time while exposed to external strain. We discuss the results in the following section. The Raman spectroscopy data depicts changes in the orientation of polymer chains, crystallinity, or other structural aspects. Figure 7.5 shows a Raman spectrum of an unstretched piece of PET foil.

In this spectrum, 13 main modes are identified, listed in Table 7.1. The modes’ response to applied strain is analyzed by fitting Voigt profiles to the acquired spectra (see next

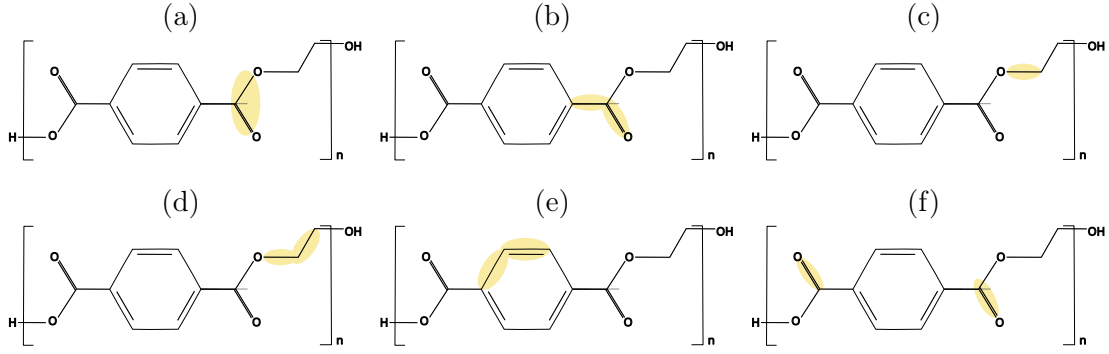


Figure 7.6: The schematics highlight the affected bonds for each mode, (a) corresponds to mode 1, (b) mode 3, (c) mode 5, (d) mode 6, (e) mode 12, and (f) mode 13.

Mode order	Vibration mode	Raman shift (cm^{-1})	Conformation
1	Scissors O-C-O [128]	~ 637	-
2	-	~ 705	-
3	C=O and ring ester C-C out-of-plane bending and ring torsion [129, 130]	~ 797	Gauche conformation [128]
4	Ester C(O)-O bending modes [129]	~ 858	-
5	C-O stretching [O-CH ₂] [130]	~ 997	Trans conformation
6	Ester C(O)-O, ethylene glycol C-C stretching [129, 131]	~ 1095	Trans conformation
7	Ring C-H in-plane bending, ester C(O)-O and ethylene glycol C-C stretching [131]	~ 1119	Gauche conformation
8	CH ₂ twisting mode [128]	~ 1186	-
9	C[O]-O stretching [129, 131]	~ 1292	-
10	C-H bending out of the plane of the benzene ring [129, 131]	~ 1417	-
11	CH ₂ vibration bending [129, 131]	~ 1464	-
12	C-C / C=C stretching modes [129]	~ 1613	-
13	Stretching vibration C=O [129]	~ 1725	Trans conformation

Table 7.1: Detected main modes in the Raman spectra of a PET sample

section). Figure 7.6 presents the demonstration of the corresponding bonds that contribute to the main Raman modes in the PET structure [120].

Raman Modes Wavenumber Variation in Response to Applied Strain

Spectra were initially recorded in the unstretched state, followed by strain measurements at 5-minute intervals for 30 minutes (transitional state T_1 to T_6). Additional spectra were captured immediately after applying the strain (T_0) as the first transition state during

strain application, and after releasing the sample from stress (labeled Relea. in heatmaps), resulting in a total of 9 recorded spectra per sample, including the unstretched state (labeled Unstrt. in heatmaps). All mode shifts and FWHM values were calculated by subtracting the corresponding unstretched values to assess the deviations. For intensity measurements, the data were normalized to the unstretched state for each sample to better understand the variations induced by stretching. The Raman modes of the molecules in the sample correspond to specific atomic movements within the molecular structure, such as stretching, bending, twisting, or rocking of molecular bonds (see Table 1). The line positions indicate the energy of the vibration mode, which gives information on the strength of the bonds and the changed interactions [132].

Figure 7.7 illustrates the variation of each line in response to strain across different transitional states. A uniform scale was applied across all heatmaps to ensure comparability. The results reveal that the behavior of the lines varies significantly; some exhibit only minor changes, while others undergo substantial variations when subjected to strain.

At low strain levels (1 to 4%), deviations in Raman mode positions are minimal and localized, affecting mainly specific modes such as 5 and 7 (see Table 7.2), corresponding to C-O stretching [$\text{O} - \text{CH}_2$] and C-C stretching of the ethylene glycol unit. These vibration modes show high susceptibility to minimal mechanical deformation. However, after releasing the strain, most modes return to their original positions, indicating elastic behavior with high reversibility. As the applied strain increases from 1% to 4%, modest spectral shifts become more pronounced, though they remain limited to a subset of vibrational modes. No evidence of substantial structural reorganization is detected, indicating that the material largely preserves its molecular integrity within this deformation range. This reversible behavior reflects the resilience and ability of the material to absorb minor mechanical stress without significant structural disruption. For the moderate strain range (5 to 10%), the Raman wavenumber shifts become more pronounced, as residual shifts persist after strain release. These shifts suggest the onset of molecular reconfiguration, which gradually transitions to more noticeable structural effects. By 5%, the deviations have stabilized across more modes, with cumulative structural effects becoming evident. The eighth mode, associated with CH_2 , shows particular sensitivity, marking the transition toward localized but more significant molecular changes. At 10% strain, the shifts become more widespread, impacting multiple modes such as C=O and ring ester C-C out-of-plane bending and ring torsion (mode 3), ethylene glycol C-C and C-O stretching (mode 6), CH_2 twisting (mode 8), and the ester O-C stretching (mode 9). Compared to lower strain levels, the range of spectral deviations narrows slightly but becomes more uniformly distributed across vibrational modes, suggesting a transition from localized to more widespread structural changes. Moreover, the ability of the material to recover baseline spectral positions upon strain release is progressively

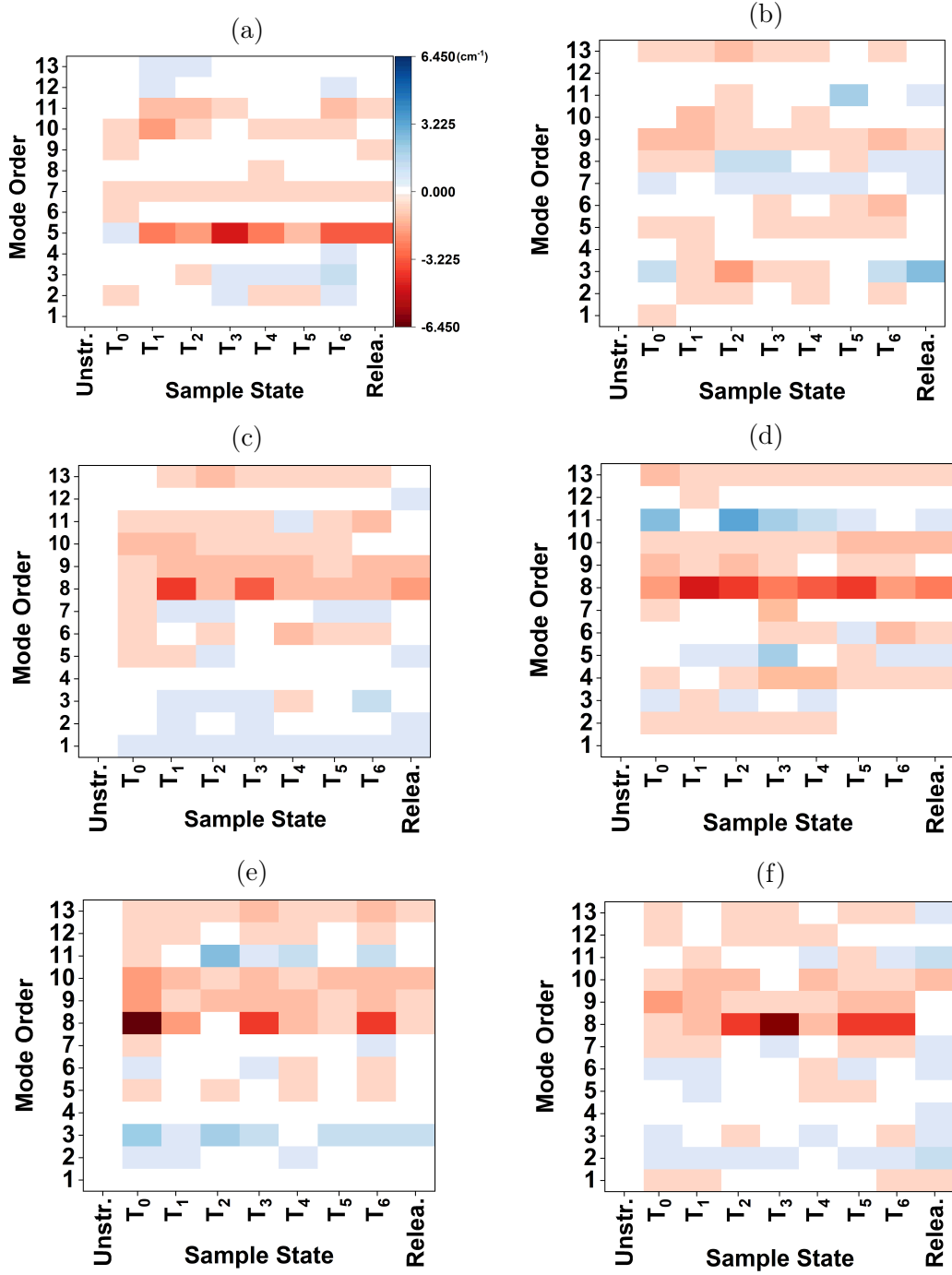


Figure 7.7: The graphs present the state evolution of relative Raman spectra mode positions for PET under (a) 1% (b) 5%, (c) 10%, (d) 15%, (e) 20%, and (f) 25% applied tensile strain. The heatmaps compare the mode positions at various transitional states (x-axis) from T_0 to T_6 during strain application and after strain release (Relea.) The color bar is unified across different heatmaps. For each sample state, the measured value of each mode is subtracted from the corresponding value in the unstretched state.

diminished. This molecular reorganization is accompanied by partial anisotropy, altering optical properties such as transparency (see UV-Vis response). Localized molecular alignment as well as the creation of defects would lead to light scattering and reduced transparency. Modes such as the ninth and eleventh (O-C stretching), which have shown minimal deviations at lower strains, now exhibit significant shifts, suggesting broader structural disruption. At higher strain levels (15–30%), Raman shifts become pronounced and persist even after strain release, particularly in vibrational modes 5 and 8, consistent with previous reports indicating sensitivity to stress-induced structural rearrangements in PET [115, 116]. Residual spectral deviations suggest permanent structural modifications; however, direct structural characterization (e.g., wide-angle X-ray diffraction (WAXD), electron microscopy) is required to unequivocally confirm the extent and nature of these transformations. At 30% strain, the material is exhibiting a complete transition from elastic to plastic behavior. Table 7.2 presents a comprehensive overview of the variation in the position of the modes in response to applied stress.

Strain Level	Key modes affected	Shift patterns	Reversibility after release	Conclusion
1%	5, 7	Large shifts, localized	High reversibility	Elastic behavior with minimal residual effects.
2%	5, 7, 10	Minor shifts, more modes affected	Partial reversibility	Increased sensitivity of modes; minimal residual effect.
3%	5, 7, 11	Moderate shifts, more spread across modes	Partial return to base-line	Further deviations, signs of increased sensitivity.
4%	5, 7, 10, 11	Noticeable shift increase with broader deviations	Limited return	Higher structural sensitivity with noticeable changes in mode behavior.
5%	3, 5, 8	Minor shifts, spread across most modes	Residual shifts remain	Signs of permanent changes, increased structural alterations.
10%	3, 6, 8, 9	Consistent shifts across multiple modes	Strong residual effects	Non-reversible response; extensive molecular changes start.
15%	8, 10, 11	Broader, strong deviations across many modes	Very limited return	High level of alteration with dominant irreversible effects.
20%	3, 8, 9, 10, 11	Large deviations, intense mode shifts	No recovery observed	Severe, likely permanent deformation across molecular structure.
25%	8, 9, 10	Consistent deviations across all modes	No recovery	Extensive reorganization, clear irreversible changes.
30%	All modes	Broad deviations, complete departure	No recovery	Permanent structural alteration, total loss of elasticity.

Table 7.2: Strain-level effects on Raman line wavenumber positions.

Raman modes FWHM Variation in Response to Applied Strain

The shapes of Raman lines are typically described by Voigt profiles, which are convolutions of Gaussian and Lorentz line shapes. This also considers inhomogeneous broadening mechanisms. In the case of a solid sample, the degree of FWHM broadening is often associated with structural disorder or heterogeneity in the material. As already reflected in the observed wavenumber shifts of the different vibrational modes, strain can introduce various local distortions, such as changes in the lengths or angles of the bonds within the polymer structure [132]. These local variations could shift the mode and broaden it, as the material under strain exhibits a range of slightly different vibration wavenumber due to the nonuniform stress distribution. Since strain often affects each molecular environment differently, the FWHM is sensitive to these subtle differences which can result

in larger variations compared to wavenumber mode shifts. FWHM captures the “spread” of stress-induced vibration states while wavenumber shifts reflect overall bond stiffening or softening and slight bond length adjustment, which leads to a shift in the vibration wavenumber. However, this effect is generally more uniform and subtle, reflecting an average change in bond lengths across the material rather than the localized variations contributing to broadening. Therefore, while the wavenumber shift shows a consistent structural adjustment under strain, it does not capture the localized disorder as effectively as FWHM, which is more sensitive to minor variations in molecular structure in response to strain [133]. These structural changes are of importance since they can strongly affect the electronic properties of the samples as has been demonstrated earlier [134]. Figure 7.8 shows the variation of FWHM response to different strain values. For a small amount of strain (1 to 4%) relatively strong broadening of FWHM is observed, which is primarily localized to the modes 3 and 5. Broadening stabilizes early around T_4 and show minimal recovery after release. For midrange strain values (5-10%) a noticeable broadening begins across most modes. At the 5% stretch, it has intensified across modes 3, 8, and 11. Persistent broadening after T_4 with partial recovery occurs after release. This stage can be considered as the initial step for the material to begin its transition from elastic to plastic deformation. Stress spreads across various modes, and strain-induced heterogeneity develops. For 10% stretch, FWHM values remain elevated with minimal but consistent residual effects, showing further structural sensitivity and permanent changes. At elevated strain (15–30%), Raman mode broadening becomes pronounced and irreversible, suggesting that irreversible deformation dominates, characterized by localized conformational distortions and extensive molecular reorganization. These distortions reflect a breakdown in uniform chain alignment, resulting in permanent structural misalignments that compromise the material’s elasticity and lead to long-term mechanical and optical changes. While the observed spectral broadening aligns with known indicators of molecular-level disruptions, complementary structural characterization would be necessary to definitively confirm widespread molecular reorganization[116, 120, 135]. Loss of elasticity and permanent structural changes are observable. Table 7.3 presents a comprehensive overview of the response to the FWHM variations in the observed mode.

Raman Modes Intensity Variation in Response to Applied Strain

The Raman mode intensity is related to the polarizability tensor, which describes how the electron cloud in a molecule deforms in response to incident light. Strain application would cause a change in the Raman intensity due to an alteration in the molecular symmetry of the molecule or crystalline parts of the polymer structure, which affects specific elements of this tensor. In our study, the laser excitation polarization is fixed and parallel to the strain axis, therefore, only a subset of the tensor elements is being probed.

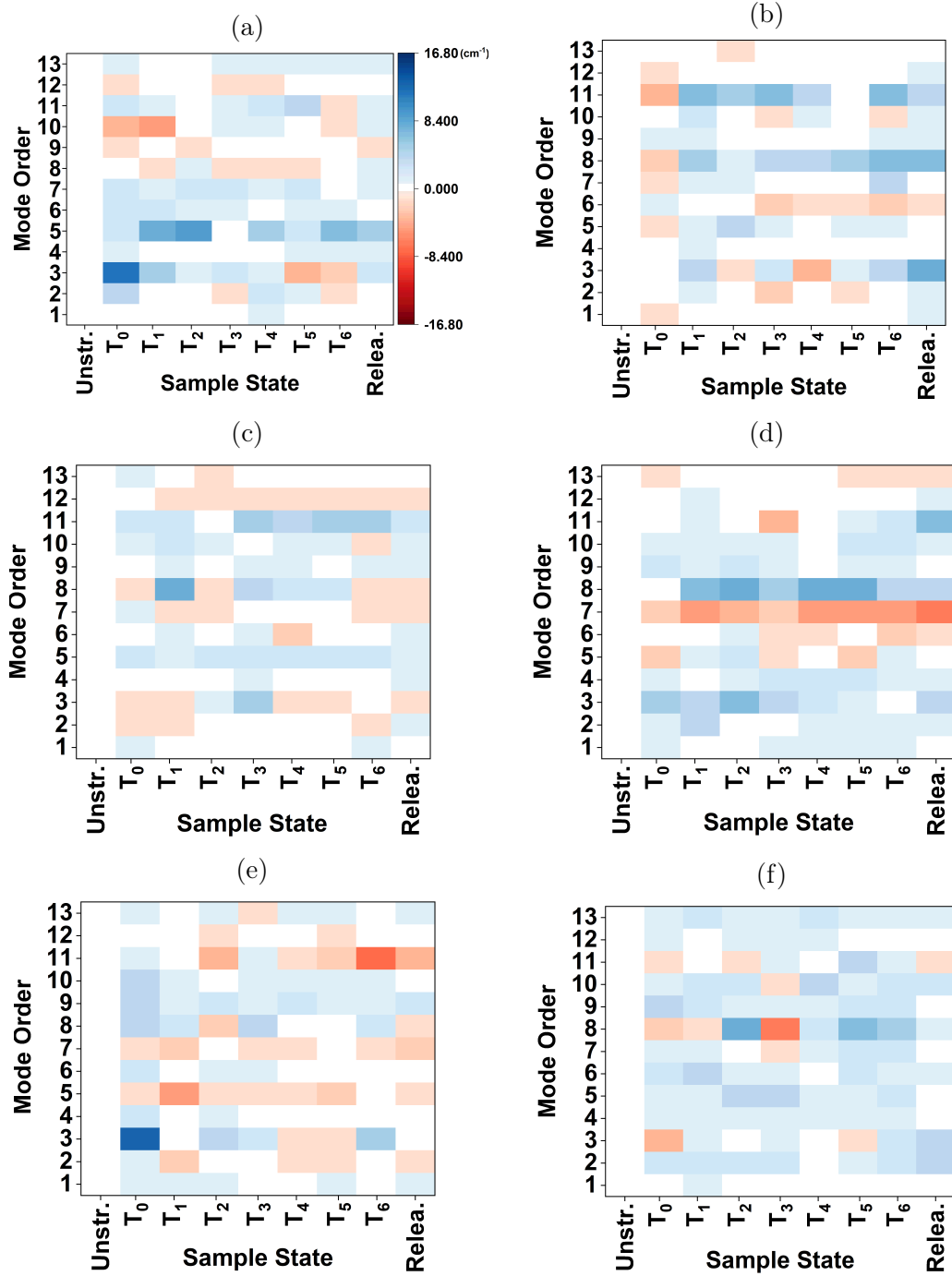


Figure 7.8: The graphs present the state evolution of relative Raman mode's FWHM variations for PET under (a) 1% (b) 5%, (c) 10%, (d) 15%, (e) 20%, and (f) 25% applied tensile strain. The heatmaps compare the mode's FWHM at various transional states (x-axis) from T_0 to T_6 during strain application and after strain release (Relea.) The color bar is unified across different heatmaps. For each sample state, the measured value of each mode is subtracted from the corresponding value in the unstretched state.

Strain Level	Key modes Affected	Shift Patterns	Reversibility After Release	Conclusion
1%	3, 5	large shifts, localized	High reversibility	Elastic behavior with minimal residual effects.
2%	3, 5, 7	moderate shifts and mainly localized	Partial reversibility	Early signs of structural sensitivity to strain.
3%	3, 5, 11	moderate shifts and mainly localized	Partial return to baseline	Increased molecular perturbations, sensitivity rising.
4%	3, 5, 7, 11	noticeable shifts	Limited return	Enhanced structural changes, limited elasticity.
5%	3, 8, 11	moderate shifts	Residual broadening remains	Onset of permanent structural alterations.
10%	3, 5, 8, 11	Broad, minimal deviations	Strong residual effects	Major irreversible alterations with dominant effects.
15%	3, 5, 7, 8	Broad, with strong deviations for certain peaks	Very limited return	Major irreversible alterations with dominant effects.
20%	Nearly all modes affected	small shifts across all modes	No recovery observed	Permanent deformation, structural reorganization.
25%	Nearly all modes affected	Severe, consistent deviations	No recovery	Extensive reorganization, clear irreversible changes.
30%	All modes	moderate shifts and broadening across all modes	No recovery	Permanent structural alteration, total loss of elasticity.

Table 7.3: Summary of strain-level effects and their impact on Raman mode FWHM broadening

Typically, with a fixed polarization parallel to the strain axis, the diagonal components of the polarizability tensor (e.g., α_{xx} , α_{yy} , α_{zz}), (depending on how the axes are defined) dominate the response. Off-diagonal terms (e.g., α_{xy}) require changes in polarization or more complex experimental setups to be observed [132].

By focusing on a fixed polarization, this study has isolated and examined the strain effects of the Raman-active modes directly along the strain axis. This provides a clear and reproducible dataset without adding the complexity of polarization rotation. Since we have already discussed wavenumber shifts and FWHM variations, adding intensity data completes the picture of the strain impacts on the Raman spectrum.

Figure 7.9 presents the intensity heatmaps for various levels of strain. Stretching by 1% causes slight intensity variations initially, but an intense increase when the sample is exposed for a longer time, particularly after the initial 25 minutes (T_5) and after the release. The fifths and eleventh modes exhibit noticeable intensity changes (increased intensity) relative to the unstretched state. At 3% strain, the intensity variations become more pronounced, and all the modes show strong intensity reduction from T_3 to T_6 . Despite the wavenumber and FWHM, mostly returning to their initial values after strain release, the intensity does not fully recover to its original level. For midrange strain values (5 to 10%), strain application results in a decrease in the intensity of modes. 5% strain

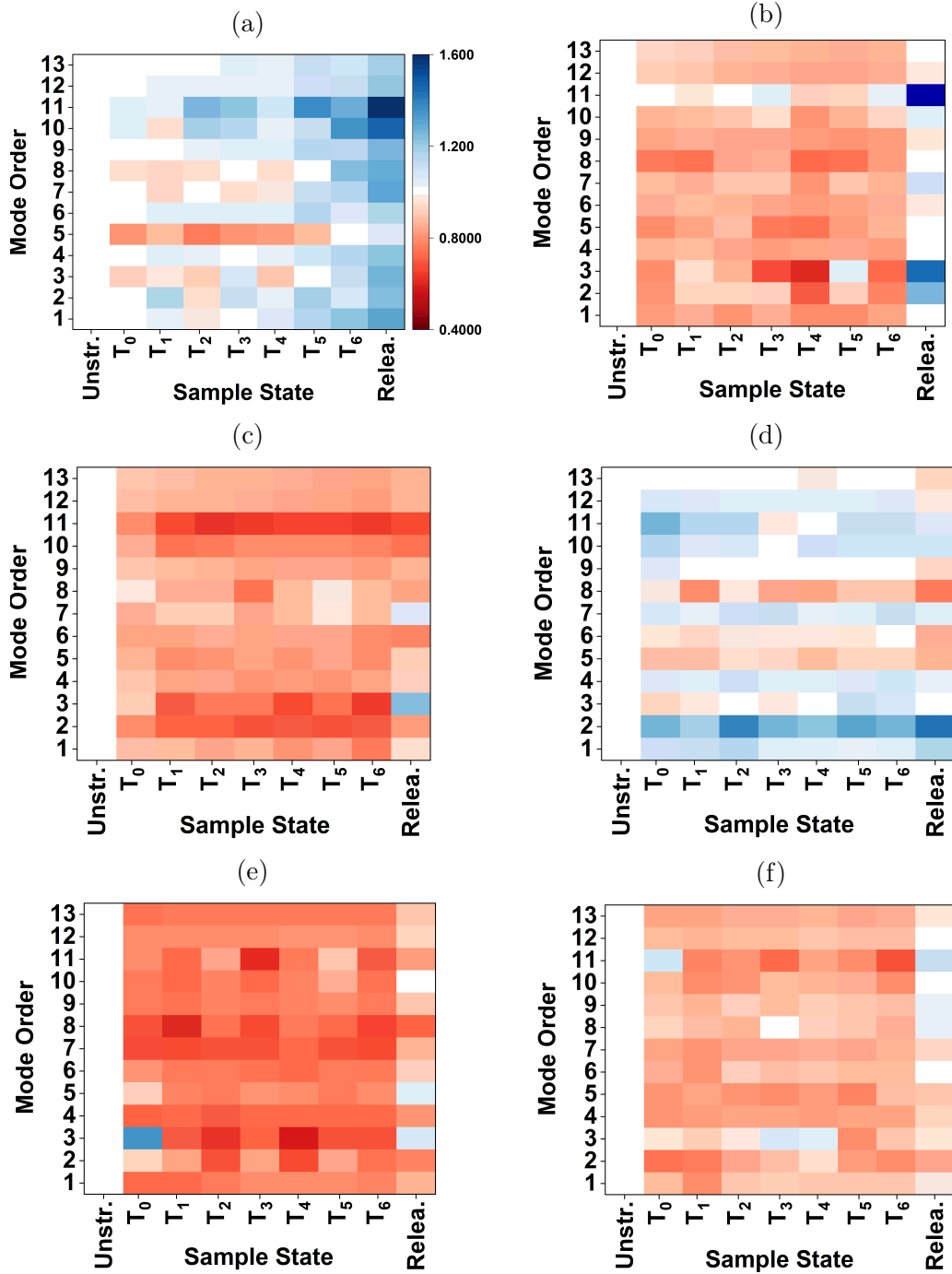


Figure 7.9: The graphs present the state evolution of normalized Raman line's intensity variations for PET under (a) 1% (b) 5%, (c) 10%, (d) 15%, (e) 20%, and (f) 25% applied tensile strain. The heatmaps compare the mode's intensity at various transitional states (x-axis) from T_0 to T_6 during strain application and after strain release (Relea.) The color bar is unified across different heatmaps. For each sample state, the measured value of each mode is normalized to the corresponding value in the unstretched state.

introduces more intensity fluctuations across multiple modes. Notably, modes 3, 5, and 8 begin to exhibit stronger intensity reduction. The elastic behavior of the material at low strains likely redistributes the Raman active modes, leading to slight polarization-related intensity shifts. Most changes are reversible upon strain release, while certain modes including 2, 3, and 7 experience an increase in the line intensity. Increasing the strain to 10% leads to a wide reduction in intensity, with modes 2, 3, and 11 showing a pronounced decrease. At 15% strain, the overall intensity distribution becomes irregular. While the intensity distinctly increases in the low-wavenumber modes including modes 2 and 3, modes like 5, 6, and 8 experience a reduction. Limited reversibility is observed upon release. At 20-30% strain, nearly all modes exhibit substantial intensity drop. At 30% strain, the intensity heatmap shows a reduction in intensity for most modes, except the 5, which experiences a strong increase in all states. This suggests selective loss of Raman activity in certain vibration modes while the polarizability of mode 5 is increasing. The near-total loss of reversibility in FWHM and wavenumber data is consistent with the irreversible nature of intensity alterations. Strain-induced molecular alignment creates directional optical properties, which may benefit certain polarization-sensitive applications but compromise isotropic transparency. Table 4 presents a comprehensive overview of the observed mode intensity variations response.

Strain Level	Key modes Affected	Intensity Patterns	Reversibility After Release	Conclusion
1%	5	Minimal intensity changes for low wavenumbers, localized to specific modes	minimum reversibility	Early signs of molecular alignment, strain-induced changes begin
2%	5, 11	Small increases in intensity for sensitive modes	minimum reversibility	-
3%	All modes	high-intensity decrease with broader spread	Partial return to baseline	Increased molecular perturbations affecting polarizability.
4%	5, 7, 11	Noticeable intensity fluctuations across modes	Limited return	Enhanced alignment along the strain axis; tensor alterations visible.
5%	All modes	Intensity changes stabilize	partial residual changes recovery	Onset of permanent molecular rearrangement; altered polarizability.
10%	All modes	Significant intensity deviations	moderate residual effects	Irreversible alignment and structural deformation dominate the response.
15%	2, 5, 8	Broad intensity changes, concentrated in sensitive modes	Very limited recovery	Major structural reorganization impacts polarizability tensor.
20%	All modes	Intense deviations with permanent changes across modes	No recovery	Severe deformation, permanent polarizability alterations evident.
25%	6th, 10th, 11th	Strong, consistent intensity deviations across spectrum	Very limited recovery	Irreversible structural reorganization and strong defect formation.
30%	All modes	Maximum intensity changes, broad and irreversible deviations	No recovery	Total loss of elasticity, complete reconfiguration of polarizability.

Table 7.4: Summary of strain-level effects and their impact on Raman mode intensity variation

Analysis of Gauche, Trans, and Amorphous Conformations Under Strain in PET

3.2.4.1. Modes Associated with Gauche and Trans Conformations The 1119 cm^{-1} band (mode 7), related to the gauche conformation of ethylene glycol (EG) units, exhibits alternating red and blue shifts, with the blue shift dominating for most strain values within the examined range. These shifts reflect the heterogeneous response of PET, where localized chain alignment restricts the rotational freedom of gauche conformers, consistent with the emergence of a mesophase. This phase represents a transitional structural regime between amorphous and crystalline states, distinguished by an increase in trans conformers and partial segmental alignment of polymer chains under strain. This intermediate state has been variously characterized in the literature, most notably as the TX (trans-rich

disordered) phase by Cole *et al.*[128], based on infrared (IR) spectral decomposition, and as a smectic-like mesophase by Keum *et al.*[122] through WAXD analysis of cold-drawn PET fibers. Despite differences in terminology, these studies converge on the recognition of a conformationally ordered yet non-crystalline molecular arrangement that emerges under mechanical deformation. This description more accurately captures the spectroscopic features and structural characteristics observed in our strained PET samples, without invoking assumptions of specific crystallographic symmetry. Furthermore, in the context of PET's response to strain, heterogeneity refers to the localized and non-uniform molecular behavior within the material. For mode 7, the observed redshifts are more pronounced at higher strain values, suggesting a slight disruption in intermolecular packing. The FWHM decrease of this mode at low strains is another indicator consistent with the partial alignment of molecular chains. The 998 cm^{-1} band (mode 5), associated with the trans C–C bond, predominantly exhibits redshifts across all strain levels. At low strains, a pronounced red shift indicates a weakening of intermolecular interactions and packing density. Furthermore, the broadening of FWHM in this mode reflects localized strain-induced distortions. The 1095 cm^{-1} band (mode 6), associated with C–O stretching in trans conformers, displays smaller but consistent redshifts across all strain levels. This mode represents structurally stable regions, with its FWHM and intensity varying minimally compared to other modes, suggesting that C–O bonds are more resistant to strain-induced disruptions. However, the slight broadening of FWHM remains consistent with the previously mentioned strain-induced distortions.

3.2.4.2. Modes Associated with Amorphous and PET Structural Integrity

The 1186 cm^{-1} band (mode 8), attributed to CH_2 twisting and associated with amorphous PET, exhibits distinct behavior under strain. At low strain levels (1–5%), its intensity fluctuates slightly, alternating between increases and decreases relative to the initial value, reflecting localized amorphous regions with a heterogeneous response. This behavior is consistent with the emergence of a trans-rich mesophase, where some amorphous regions persist while localized alignment initiates. At higher strain levels (> 5%), the intensity consistently decreases, indicating a progressive loss of amorphous character as chain orientation becomes more dominant. Additionally, the FWHM of mode 8 decreases across all strain levels, further reflecting the gradual transition from amorphous disorder to localized molecular alignment and more ordered states. Regarding the wavenumber shifts, alternating red and blue shifts are observed at low strains (1–5%), serving as another indicator of the heterogeneous response of amorphous regions. Beyond 5% strain, pronounced red shifts dominate, signaling significant packing disruptions and molecular bond elongation. The 1725 cm^{-1} band associated with the carbonyl (C=O) stretching mode is sensitive to the degree of crystallinity in PET, with higher frequencies and sharper peaks indicating a more crystalline structure. At low strain levels (1–5%), the band exhibits minor variations responding to strain. As the strain increases beyond 5%, a

redshift becomes more pronounced, indicating a significant weakening of the intermolecular interactions and an increased disruption of the density of the packing of chains. The reduction in the intensity of this band at higher strain levels aligns with growing disorder within the molecular structure, consistent with transitions observed in other vibrational modes.

7.5 Correlation of Raman and Absorption Spectroscopy Findings

The optical properties of PET under strain are intrinsically linked to its molecular structure, particularly the interplay between its amorphous and crystalline states, as well as strain-induced perturbations in molecular conformations and functional groups. In the amorphous state, PET consists of disordered polymer chains with a uniform refractive index, minimizing light scattering and maintaining high transparency. In contrast, the crystalline state introduces highly ordered and densely packed polymer chains, forming crystalline domains with refractive indices distinct from the surrounding amorphous regions. These boundaries scatter light, progressively reducing transparency as the degree of crystallinity increases. Strain exacerbates this effect by inducing structural transitions, creating defects, and perturbing chain packing, further enhancing light scattering and reducing transparency [135]. The integration of Raman and UV-Vis findings underscores the critical role of strain-induced molecular alignment and phase transitions in governing PET's optical behavior. The detailed behavior of key vibrational modes—the 998 cm^{-1} (mode 5), 1095 cm^{-1} (mode 6), 1119 cm^{-1} (mode 7), 1186 cm^{-1} (mode 8), and 1725 cm^{-1} (mode 13) bands—provides a molecular-level understanding of how strain influences structural evolution. At low strain levels (1–4%), PET maintains its transparency with negligible changes in optical properties. The Raman spectra suggest minimal molecular reorientation and negligible phase transitions, aligning with the absence of significant variations (up to 20%) in the UV-Vis absorption spectra, indicating preserved transparency and molecular integrity. As strain increases to intermediate levels (5–10%), PET's optical properties begin to show measurable changes. The Raman study offers a unique perspective on molecular-level order sensitivity in the response of PET to mechanical strain. This paves the way for future research to explore polarization-dependent measurements and the engineering of PET films with controlled molecular orientations, which introduce variations in the refractive index and result in light scattering and reduced transparency. UV-Vis spectra corroborate these findings, showing an increase in absorbance to up to 90% for the 10% applied strain in the visible spectrum, particularly in the blue and purple regions, due to structural transitions. At higher strain levels (15–30%), irreversible spectral features including substantial peak broadening and intensity reduction in critical vibrational modes

strongly suggest disruptions in molecular organization and partial structural disorder. Similar Raman signatures have been previously correlated with structural rearrangements in mechanically strained PET. However, explicit confirmation of the detailed structural transformations described here requires additional characterization, which we recommend for future investigations[115, 116]. UV–Vis absorption spectroscopy reveals an increase in absorbance exceeding 100% relative to the unstrained state, which is attributed to enhanced optical scattering and possible changes in molecular packing. This may reflect the development of mesophase ordering or conformational rearrangements that reduce the optical band gap, potentially due to increased local packing irregularities or strain-induced electronic inhomogeneities. The observed spectral changes suggest that residual stresses and associated structural heterogeneity induced by strain could contribute to the observed significant transparency loss and reduced optical clarity. This interpretation is supported by previous findings correlating stress-induced optical degradation with structural non-uniformities in PET [109, 117]. Additionally, optical anisotropy becomes pronounced, as strain-induced molecular alignment creates directionally dependent optical properties. Raman intensity variations further emphasize PET’s sensitivity to strain, with an average 30% reduction in Raman line intensity across all modes at 20% applied strain. As mentioned earlier, the Raman spectroscopy measurements were conducted while the PET samples were held under strain for 30 minutes at room temperature. Instead of a single transient state, multiple transient states were observed in the intermediate spectra, reflecting ongoing molecular adjustments. This behavior can be attributed to the inherent rigidity of PET at room temperature, which influences molecular mobility and limits immediate large-scale rearrangements. The observations suggest that PET’s molecular response under strain at room temperature primarily involves localized and gradual adjustments, rather than long-range relaxations occurring within a short time frame. This structural rigidity may also explain the dominance of heterogeneous responses in key Raman modes, as strain-induced changes in the amorphous and crystalline regions remain localized.

Beyond the spectroscopic interpretation, these findings also carry practical implications for applications where mechanical deformation influences optical or molecular behavior. Manufacturers can develop PET films with improved strain resistance, ensuring reliability in demanding environments by understanding the strain thresholds at which irreversible changes occur (e.g., above 10–15% strain). The pronounced intensity, FWHM, and wavenumber variations in Raman spectra under strain could be harnessed to create susceptible, polarization-dependent Raman sensors [136]. These sensors would be capable of precisely detecting localized stress or strain, making them ideal for applications in structural health monitoring or wearable electronics. By correlating strain-induced structural changes with optical degradation, the study offers a framework for predicting

the operational stability of PET-based devices, allowing for better material selection and design [137].

Moreover, the implications of this work can extend to other industries where PET is widely used, such as packaging and structural films. In mechanical engineering, PET's robustness under strain is crucial for applications like protective films and load-bearing components. The insights from this study can guide the development of PET materials with enhanced mechanical properties, such as higher tensile strength and improved elasticity. Understanding how strain impacts PET at a molecular level can aid in designing packaging materials that maintain transparency and durability under various stresses, contributing to sustainable and high-performance solutions. The study's focus on fixed polarization offers a unique perspective on the anisotropic response of PET to mechanical strain. This could pave the way for future research exploring developing Raman sensors optimized for different polarization configurations to enhance strain detection. As well as engineering PET films with controlled molecular orientations to achieve specific optical and mechanical characteristics for niche applications.

7.6 Conclusion

This study offers preliminary but scientifically grounded insights into the optical and structural responses of PET films subjected to mechanical strain under strictly ambient (room-temperature) conditions, without thermal annealing. By integrating UV–Vis absorption and Raman spectroscopy, the work elucidates the interplay between molecular conformation and optical behavior, capturing strain-induced effects that are distinct from those observed under elevated-temperature processing. At strain levels below 5%, PET maintains its optical transparency and molecular integrity, exhibiting only minor conformational adjustments and minimal chain alignment. These characteristics underscore its suitability for low-deformation applications such as optical coatings and flexible sensors. Beyond this threshold, more pronounced structural transitions occur, including increased chain orientation and the emergence of mesophase-like order, which contribute to optical anisotropy and enhanced light scattering, thereby reducing transparency. These observations are critical for informing strain thresholds in applications such as flexible displays and photovoltaic layers, where optical performance is tightly constrained. At higher strain levels (15–30%), the material undergoes irreversible structural reorganization, characterized by disrupted packing, conformational heterogeneity, and a breakdown of isotropic optical properties. These changes result in diminished transparency and elasticity but suggest promising utility for PET in strain-sensitive and polarization-dependent optical devices. In summary, this work contributes to the growing understanding of strain-induced molecular reordering in PET under non-thermal, realistic processing conditions, a regime

often underrepresented in the literature. While structural confirmation via advanced techniques lies beyond the present scope, the spectroscopic findings are consistent with prior studies reporting trans-rich conformational transitions and mesophase formation in similarly treated PET systems. Future work incorporating wide-angle X-ray diffraction, microscopy, birefringence analysis is encouraged to further validate and extend the insights established here.

Chapter 8

Assessing Band Gap Stability of Poly(3-hexylthiophene-2,5-diyl) (P3HT) Thin Films Under Uniaxial Tensile Strain for Flexible Electronic Applications

8.1 Overview

This chapter investigates the influence of mechanical stretching on the optical band gap of P3HT using UV–Vis absorption spectroscopy. As a key semiconducting component in flexible electronic devices, the stability of its electronic structure under mechanical deformation is of central importance for device performance and reliability. By systematically applying uniaxial strain to P3HT thin films, changes in the absorption edge and optical transitions are examined to assess strain-induced modifications of the band structure [26]. The content presented in this chapter is adapted, with the consent of all co-authors, from a manuscript that has been resubmitted to IEEE Access following the first round of peer review.

Details of the manuscript:

M. Ghorab, A. K. Ranga, A. Materny, V. Wagner, and M. Joodaki - “Assessing Bandgap Stability of Poly(3-hexylthiophene-2,5-diyl) (P3HT) Thin Films Under Uniaxial Tensile Strain for Flexible Electronic Applications.”

Abstract

Organic semiconductors intended for flexible electronic applications must retain stable optoelectronic properties under mechanical deformation. Since the optical band gap governs exciton generation and constrains photovoltaic voltage, its robustness under strain is a critical requirement for reliable device operation. In this work, we investigate strain-induced band gap variations in poly(3-hexylthiophene-2,5-diyl) (P3HT) thin-films deposited on flexible poly(ethylene terephthalate) (PET) substrates, studied both as single layers and in poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/P3HT stacks. The samples were subjected to controlled uniaxial tensile strains in the range of 1%-10%. The optical band gap was extracted from ultraviolet-visible (UV-Vis) absorption spectra using a standardized Tauc analysis, with statistical validation based on robust regression and equivalence testing. For all stacking configurations and annealing conditions, the band gap remains unchanged within experimental resolution up to 7% strain. At 10% strain, a small but consistent increase of approximately 4-5 meV is observed. This threshold-like response indicates a transition from mechanical strain accommodation dominated by morphological relaxation to a regime in which electronic perturbation becomes detectable. These results establish a quantitative strain window over which P3HT-based thin-films can be regarded as optically stable and provide practical guidance for mechanical modeling and the design of flexible organic optoelectronic devices.

8.2 Introduction

Over the past decade, a substantial body of research has emerged focusing on flexible and stretchable organic solar cells (OSCs). The primary goal of these studies, such as those by Wardani *et al.* [138], Dauzon *et al.* [139], and Wang *et al.* [140], has been to enhance device architectures for improved mechanical compliance, durability, and application versatility in wearable and bio-integrated electronics. While this body of work demonstrates significant progress, strain is generally framed as an external constraint to be mitigated, not as a dynamic variable intrinsically modulating the physical behavior of device materials [25, 141–145]. The influence of mechanical stress on the optoelectronic properties of functional layers, such as the active layer, remains only partially understood. The strain induced alterations include changes in optical absorption, molecular alignment, and charge transport pathways; ultimately modulating the device overall performance [146–149]. Yet such effects remain largely uncharacterized under realistic processing and application conditions, limiting both our predictive modeling capabilities and the rational design of truly strain-resilient photovoltaic systems.

To properly address these knowledge gaps, it is important to briefly review prior investigations that have examined the impact of mechanical strain on the optoelectronic

and charge-transport properties of organic semiconductors. Early work by Sokolov *et al.* [150] focused on bending induced strain in organic field effect transistors (OFETs). The results revealed that charge carrier mobility is highly sensitive to the dielectric/semiconductor interface. These modifications were attributed to the dielectric surface energy, which perturbs orbital overlap and transport pathways at the interface. This study provided one of the first mechanistic explanations for strain sensitivity in device level geometries. However, it did not directly address optoelectronic properties such as band gap or absorption edge stability.

Subsequent studies expanded this scope to molecular semiconductors such as rubrene. Using scanning Kelvin probe microscopy and in-situ X-ray diffraction, Wu *et al.* [151] demonstrated that the work function (WF) of rubrene single crystals responds strongly to both tensile and compressive strain. Their findings, supported by density functional theory (DFT) calculations, indicated that the work function increases under tensile strain and decreases under compressive strain. In parallel, Kubo *et al.* [152] examined uniaxial tensile strain in organic semiconductors and observed anisotropic degradation of charge transport. They related this behavior to direction-dependent changes in intermolecular overlap and to enhanced dynamic disorder. These observations suggest that strain does not affect transport in a uniform manner but instead depends on both the axis of deformation and the packing orientation of the molecules. Together, these studies provided some of the first evidence demonstrating mechanical strain can alter essential electronic parameters in organic semiconductors. However, most of the mentioned investigations, were carried out on single crystals or highly ordered thin-films. Furthermore, while strain induced perturbations to molecular orbitals and charge transport have been demonstrated, their direct manifestation in macroscopic observables such as absorption edge shifts or photovoltaic performance metrics remain largely unexplored.

Building on these works, more efforts have shifted from small molecule crystals to polymeric semiconductors, where mechanical compliance and semicrystalline disorder create qualitatively different strain responses. Recent theoretical and ultrafast imaging studies have suggested that even modest strain can couple directly to the electronic structure of conjugated polymers, potentially altering band alignment or excitonic processes in well-characterized conjugated polymers such as poly(3-hexylthiophene) (P3HT) [141, 142]. Additional thin-film studies further underscore the sensitivity of conjugated polymers to structural perturbations. Bhargava and Singh showed that variations in thin-film formation and interfacial interactions can influence the electronic response of organic phototransistors, highlighting the role of morphology and local ordering [153]. Furthermore, Wang *et al.* demonstrated that modifications to the polymer backbone or linkage environment can systematically shift the optical band gap in band gap-engineered photocatalytic polymers [140]. These studies collectively reinforce the broader principle of the intrinsic sensitivity of the conjugated polymers' electronic

structure to structural changes. This effect is independent of the underlying mechanism, whether molecular packing, film formation, or chemical modification.

Despite these insights, the sensitivity of the optical band gap of conjugated-polymer thin-films to tensile strain under standard OSC fabrication conditions remains unresolved. Prior work has primarily relied on ultrafast probes, single-crystal semiconductors, or computationally idealized structures, which do not capture the morphological and structural complexity of practical thin-films. Consequently, existing studies offer limited guidance on how semicrystalline polymer films respond to mechanical deformation in device-relevant configurations. This uncertainty is significant since the optical band gap governs light absorption, exciton generation at the molecular scale, and ultimately dictates device level outputs such as open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF), and power conversion efficiency (PCE) [146–148, 154, 155].

In this study, we investigate whether mechanical strain in the range of 0-10% alters the optical band gap of P3HT thin-films deposited on flexible poly(ethylene terephthalate) (PET) substrates, both as single layer and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) /P3HT stacks. In practical applications such as foldable displays or wearable electronics, the tensile strain experienced by polymer substrates and electrode stacks is typically only a few percent. Values in the range of 1-5% are most commonly reported as the limit for reliable operation before mechanical degradation sets in [156].

The 1-7% window investigated in this study therefore encompasses and slightly exceeds realistic device conditions. By contrast, the 10% condition represents a deliberately severe deformation, included here to reveal the strain threshold at which measurable electronic changes begin to appear. To this end, we applied controlled tensile deformation using a custom-built stretcher and performed ultraviolet-visible (UV-Vis) absorption spectroscopy before and after stretching, extracting the band gap through a standardized Tauc analysis. This framework enables a quantitative assessment of band gap stability under macroscopic strain, allowing us to distinguish between a strain-invariant operating regime and the emergence of a threshold-like electronic response at higher deformation. As such, the present study provides a device-relevant benchmark for the optical robustness of P3HT-based thin-films under tensile strain.

8.3 Experimental Setup and Methods

8.3.1 Sample Preparation

Regioregular P3HT (rr-P3HT) with an average molecular weight of 20,000-45,000 g mol⁻¹ (Sigma-Aldrich) was used as the donor polymer. Flexible PET with a thickness of 57.3 μ m was sourced from a roll, manufactured for OSC applications, characterized by high optical clarity and an amorphous morphology [25]. For experimental use, PET sheets were cut

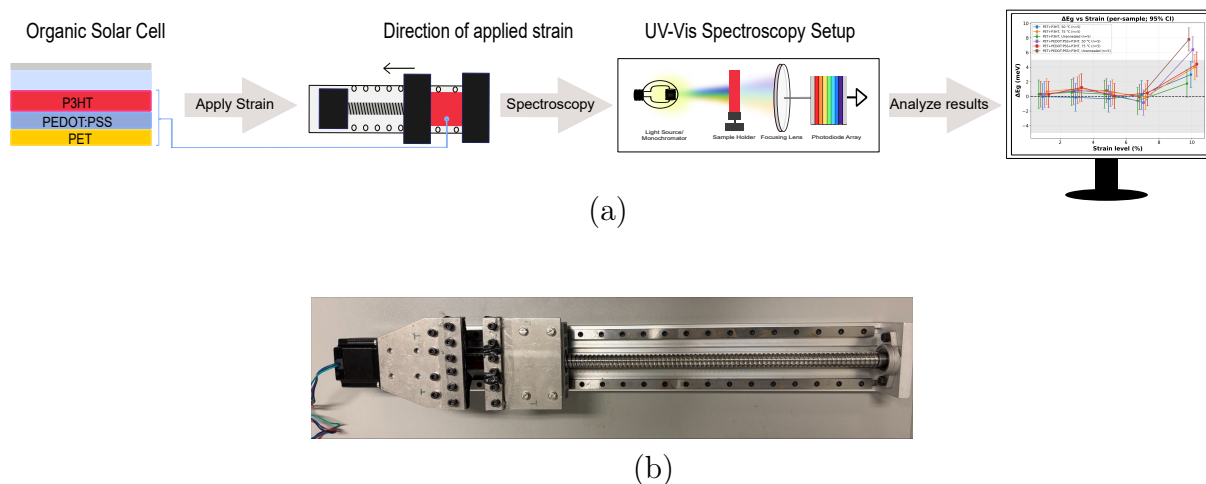


Figure 8.1: Two-panel overview of the measurement workflow and apparatus. **(a)** Schematic illustration of the experimental workflow. Samples were first characterized by UV–Vis spectroscopy in their unstretched state, then subjected to tensile strain for 30 minutes using a motorized stretcher, and subsequently transferred back to the spectrometer for a second UV–Vis measurement. **(b)** Photograph of the custom motorized stretcher used to apply strain. Note that the mechanical straining and optical measurements were performed sequentially (ex-situ).

into $5 \times 5 \text{ cm}^2$ pieces, cleaned sequentially with a 3:2 mixture of propanol and acetone, and dried with a nitrogen gun. Solution-processed films on PET often suffer from non-uniform thickness, poor wettability, and weak interfacial adhesion, especially over large substrate areas. To address these issues, the PET substrates were treated with UV–ozone for 5 minutes in a sealed chamber and pre-heated prior to deposition. These steps improved solution spreading, suppressed drying instabilities, and yielded reproducible film quality suitable for optical characterization.

A 33 mg mL^{-1} solution of P3HT in anhydrous chlorobenzene was prepared and stirred overnight at 50°C to ensure complete dissolution. The solution was maintained at elevated temperature to further facilitate uniform spreading during deposition. The PET substrates were pre-heated at 75°C for 10 minutes prior to deposition. Films were deposited by spin-coating $400 \text{ }\mu\text{L}$ of solution at 1500 rpm for 30 seconds. After deposition, the films were divided into three groups: (i) unannealed, (ii) annealed at 50°C for 5 minutes, and (iii) annealed at 75°C for 5 minutes.

In addition to the single-layer samples, bilayer structures incorporating a thin PEDOT:PSS hole-transport layer were fabricated. PEDOT:PSS primarily served as an adhesion-promoting interlayer to enhance mechanical coupling between PET and P3HT. The dispersion (98% PEDOT, 2% surfactant additive) was spin-coated at 5000 rpm for 60 seconds using $1000 \text{ }\mu\text{L}$ per sample, followed by annealing at 130°C for 30 minutes to remove residual solvent. The P3HT layer was then deposited under the same spin-coating

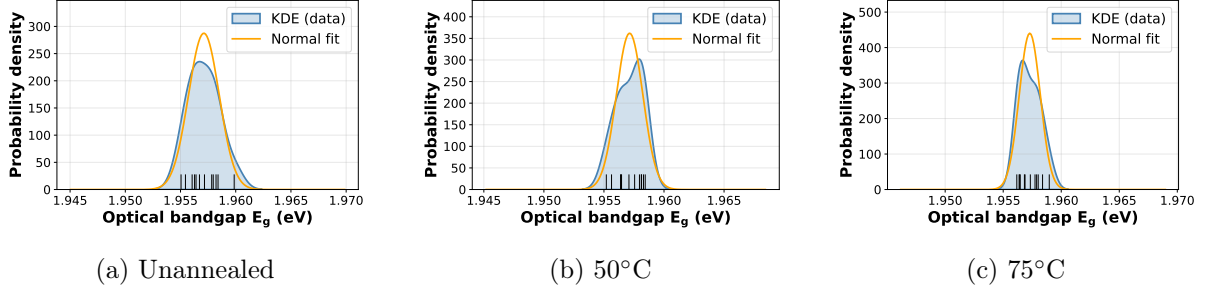


Figure 8.2: KDEs of the optical band gap E_g under three annealing conditions, with fitted normal distributions for reference. The KDEs use a Gaussian kernel (base function) and Scott’s bandwidth rule ($h = \sigma n^{-1/5}$, $n = 12$) [1]. Rug marks along the axis show the 12 measured E_g values for each condition.

conditions, yielding PET/PEDOT:PSS/P3HT stacks with improved mechanical stability.

8.3.2 Experimental Setup

After annealing, test specimens with dimensions of 15 mm $\times$ 33 mm were cut from the larger substrates. The effective gauge length between clamps was 25 mm, with 4 mm on each side reserved for clamping. Uniaxial tensile strain was applied using a custom-built mechanical stretcher based on a precision linear actuator. The strain was applied at a constant rate determined by the actuator rotation speed. With the stepper motor set to 30 revolutions min^{-1} and the SFU1605 ball screw providing a 5 mm pitch, the crosshead moved at 2.5 mm s^{-1} . For a 25 mm gauge length, this corresponds to a strain rate of 0.10 s^{-1} . The 1/4 micro stepping configuration provided a displacement resolution of 6.25 μm , equivalent to a strain increment of approximately 0.025%. All strain levels were reached through a single continuous ramp at this rate, held for 30 minutes, and then released before the optical measurements were repeated. The maximum strain applied in this study was limited to 10%. Beyond this point, PET substrates undergo pronounced mechanical distortion, which would dominate the spectral response and obscure any polymer specific effects [25]. In this study, strain values of 1%, 3%, 5%, 7% and 10% were applied. The strain (ε) was calculated as the ratio of the applied elongation ΔL to the initial gauge length L_0 ($\varepsilon = \Delta L/L_0$). All stretching and optical measurements were performed under ambient room temperature conditions, ensuring no softening or morphological changes associated with elevated temperatures.

UV-Vis absorption spectra were recorded using a PerkinElmer Lambda 12 operated in double-beam absorbance mode with unpolarized light. A single air auto-zero was performed at the beginning of each measurement session and retained for all subsequent scans. Spectra were collected from 200 to 1000 nm using a 1 nm spectral bandwidth and a 1 nm sampling interval, at a scan speed of 480 nm min^{-1} . To account for spatial variations across the films, each sample was measured at three vertical positions using a

stepped holder that displaced the substrate by 0, +2, and +4 mm. The three spectra were averaged to obtain a representative absorbance curve for each strain condition.

To ensure that the reported absorption spectra reflect only the active organic layers, the optical contribution of the PET substrate was explicitly accounted for. In a previous study, we characterized the strain response of bare PET under the same tensile conditions used here [25]. That dataset was used to subtract the PET baseline from all spectra collected in this work. As a result, the reported absorption and extracted band gaps correspond solely to P3HT or PEDOT:PSS/P3HT films, with any PET-related absorption or strain effects removed.

Strain application in this work followed a strain protocol as follows: each sample was first measured in its pristine state, then subjected to a fixed tensile strain for 30 minutes using the stretcher. After this period, the strain was released and the film was immediately transferred back to the spectrometer for re-measurement. Importantly, no relaxation time was allowed between strain release and optical characterization, ensuring that the spectra captured the post-deformation state of the film. To avoid artifacts from strain history, a fresh film was used for each strain level. Fig.8.1, depicts the schematic of this setup.

Mechanical strain in thin-film organic semiconductors can be investigated using several complementary experimental modalities, including in-situ measurements under applied load, cyclic or fatigue deformation, localized strain induced by bending radius or buckling, hydrostatic or pressure-based loading, and post-deformation analyses that probe persistent structural changes after unloading. Each approach emphasizes different aspects of the strain-property relationship and addresses distinct physical and device-relevant questions [151, 157, 158].

In this study, we focus on the post-deformation case. Here, “residual strain” refers to structural modifications in the organic layer that persist after the release of an applied tensile load, rather than a direct measurement of sample elongation before and after stretching. This approach probes morphological stability by capturing irreversible or long-lived changes that remain once mechanical stress is removed. Because the UV-Vis measurements are performed ex situ, this methodology does not resolve transient electronic responses during active deformation, nor does it fully separate instantaneous strain effects from structural changes accumulated during loading. From a device-reliability perspective, residual strain is particularly relevant, as long-term operation depends not only on transient behavior under load but also on whether the active layers recover or undergo permanent structural drift once strain is released, prior to subsequent use cycles. While in-situ spectroscopic measurements under applied strain are of clear fundamental interest, they fall outside the scope of the present work and will be addressed in future studies.

8.3.3 Tauc Analysis and Optical band gap Extraction

The electronic band gap in organic semiconductors can be characterized through multiple, complementary approaches. The fundamental gap, defined as the energy difference between the valence band maximum (VBM) and conduction band minimum (CBM), represents the intrinsic electronic structure of the material. This quantity can be accessed via first-principles band-structure calculations, or experimentally through the combination of photoelectron spectroscopy (PES) and inverse photoelectron spectroscopy (IPES), which directly probe the ionization and electron affinity levels, respectively [159]. In contrast, electrochemical techniques such as cyclic voltammetry (CV) produce the transport gap, corresponding to the energy required to generate free charge carriers, defined by the difference between the ionization potential (IP) and electron affinity (EA) [160].

In conjugated polymers, optical excitation typically generates bound excitons rather than free charges, due to the low dielectric screening and strong Coulomb interactions [161]. As a result, the optical gap, which dictates the absorption onset, is systematically smaller than the transport gap by the exciton binding energy. This optical transition plays a central role in defining the spectral window for photon harvesting and constrains the achievable V_{oc} in organic photovoltaics [162]. Optical properties of P3HT can be deduced in reflection geometry by ellipsometry or modulation spectroscopy [163], or more convenient in transmission by UV-Vis absorption. However, precise extraction of the optical gap from UV-Vis absorption spectra is often hindered by vibronic fine structure and inhomogeneous broadening arising from energetic disorder [164].

To determine the optical band gap, we employed the Tauc method [165, 166]. Although this method was originally formulated for interband transitions in inorganic semiconductors, it remains the standard approach for extracting a comparative optical gap in conjugated polymers, including P3HT. Since these materials exhibit bound excitons and vibronic structure, the Tauc-derived E_g represents an effective onset energy rather than a fundamental excitonic transition. Nevertheless, its widespread use in the OSC literature provides a consistent and reproducible framework for comparing band gap shifts across processing conditions and strain levels. This method relates the absorption coefficient α to photon energy $h\nu$ as:

$$(\alpha h\nu)^{\frac{1}{n}} = B(h\nu - E_g), \quad (8.1)$$

where α is the absorption coefficient, h is Planck's constant, ν is the photon frequency, E_g is the optical band gap, B is a proportionality constant, and n is the transition exponent that depends on the nature of the electronic transition ($n = \frac{1}{2}$ for direct allowed transitions and $n = 2$ for indirect allowed transitions) [167–172]. In this study, decadic absorbance A was used in place of the absorption coefficient α to eliminate the influence of film thickness variations on the band gap determination. Since $\alpha = (2.303/d)A$, where d is the film thickness. In this work, film thickness was verified by stylus profilometry on representative

samples prepared under identical processing conditions, yielding nominal thicknesses of approximately 200 nm for P3HT and 25 nm for PEDOT:PSS, consistent with prior reports under similar deposition conditions [173]. The film thickness was not measured individually for every specimen analyzed, which is acknowledged as an experimental limitation. However, since the optical band gap is extracted from the intercept of the Tauc construction, using the absorbance (A) directly in place of the absorption coefficient (α) merely rescales the vertical axis of the Tauc plot without affecting the x -intercept that defines E_g . As a result, residual sample-to-sample thickness variations, which is typically on the order of tens of nanometers for solution-processed films, do not influence the reported E_g values. This approach therefore provides a more robust and reproducible basis for comparative band gap analysis while decoupling the results from uncertainties associated with precise thickness determination.

For P3HT we adopted $n = 1/2$, which is considered for direct band gap semiconductors [162, 174]. For each specimen, three spectra were recorded, averaged, and smoothed with a Savitzky-Golay filter (polynomial degree 3). The absorbance spectrum was converted to photon energy using $h\nu$ [eV] = $1240/\lambda$ [nm], where λ is the wavelength, and the Tauc variables were defined as $x = h\nu$ and $y = (Ah\nu)^2$. To ensure a robust and reproducible determination of the optical band gap, the Tauc analysis was performed within a fixed energy interval from 1.90 to 2.026 eV. This interval was chosen to capture the lowest-energy linear rise associated with the absorption onset of P3HT, while excluding sub-gap tail states at lower energies and vibronically structured absorption at higher energies. Within this interval, multiple equally sized sub-windows were systematically evaluated.

Linear fits were performed using ordinary least squares (OLS) in centered form:

$$y = m(x - \bar{x}) + b_c, \quad (8.2)$$

where $\bar{x}$ is the mean energy in the window, m the slope, and b_c the centered intercept. The band gap was obtained from the x -intercept:

$$E_g = \bar{x} - \frac{b_c}{m}. \quad (8.3)$$

Uncertainty in E_g was estimated by error propagation (delta method) from the regression covariance matrix of m and b_c , using:

$$\frac{\partial E_g}{\partial m} = \frac{b_c}{m^2}, \quad \frac{\partial E_g}{\partial b_c} = -\frac{1}{m}. \quad (8.4)$$

This yielded standard errors (SEs) and 95% confidence intervals (CI) for each fit. Among all fixed-length windows within the chosen interval, the optimal fit was defined as the one with the smallest SE, provided that the coefficient of determination (R^2) exceeded 0.995

and the residuals showed no curvature. This window selection procedure was applied consistently across all samples and strain conditions, ensuring that the extracted band gap values are not biased by window selection or non-linear spectral regions. To account for instrument resolution, the 1 nm spectral resolution ($\approx 3\text{--}5$ meV at the P3HT onset) was adopted as the detection limit.

Twelve independent spectra were analyzed for each annealing condition (unannealed, 50 °C, 75 °C), reflecting the total number of experiments conducted per condition and stacking configuration. The extracted band gap values were then aggregated into condition-specific descriptor sets. For each set, the arithmetic mean band gap ($\overline{E}_g$) was reported as the central value, with the sample standard deviation (SD, σ) and variance (σ^2) quantifying variability arising from sample-to-sample fabrication differences. A 95% CI for the mean was calculated using the Student's t-distribution, $\overline{E}_g \pm t_{0.975, n-1} \cdot \sigma / \sqrt{n}$, to capture statistical uncertainty.

In parallel, R^2 values from individual linear fits were averaged to provide an overall metric of fit quality. Fig. 8.2 visualizes the distribution of E_g values across annealing conditions, kernel density estimates (KDEs) were plotted and overlaid with fitted normal distributions. These plots reveal narrowly distributed profiles that closely follow the fitted Gaussian functions, verifying the adequacy of a single-Gaussian description of the data. The use of twelve extracted E_g values per condition to construct both the KDE and the Gaussian fit reflects fabrication-induced variability follows a normal distribution. The small differences between KDE curves and the Gaussian fits can be attributed to the limited sample size ($n = 12$), rather than to systematic deviations from normality. A summary of the extracted parameters, including mean E_g , SD, CI, and average R^2 is provided in Table 8.1.

Table 8.1: Summary of optical band gap parameters for P3HT films. Values averaged over 12 spectra per condition.

Anneal Condition	Mean E_g	SD	95% CI	Mean R^2
Unannealed	1.9571	0.0013	1.9562 – 1.9579	0.997
50°C	1.9571	0.0011	1.9564 – 1.9578	0.997
75°C	1.9572	0.0009	1.9567 – 1.9578	0.997

The baseline values of E_g for unstrained P3HT films under different annealing conditions are summarized in Table 8.1. The mean values differ by less than 0.1 meV across conditions, indicating that the average optical gap remains essentially unchanged within experimental uncertainty. However, the width of the 95% CI narrows upon annealing, decreasing from 1.7 meV in the unannealed state to 1.1 meV at 75 °C. This reduction in variability reflects improved structural order and more uniform film morphology. At the relatively low annealing temperatures applied here, the dominant effect is thus a suppression of energetic

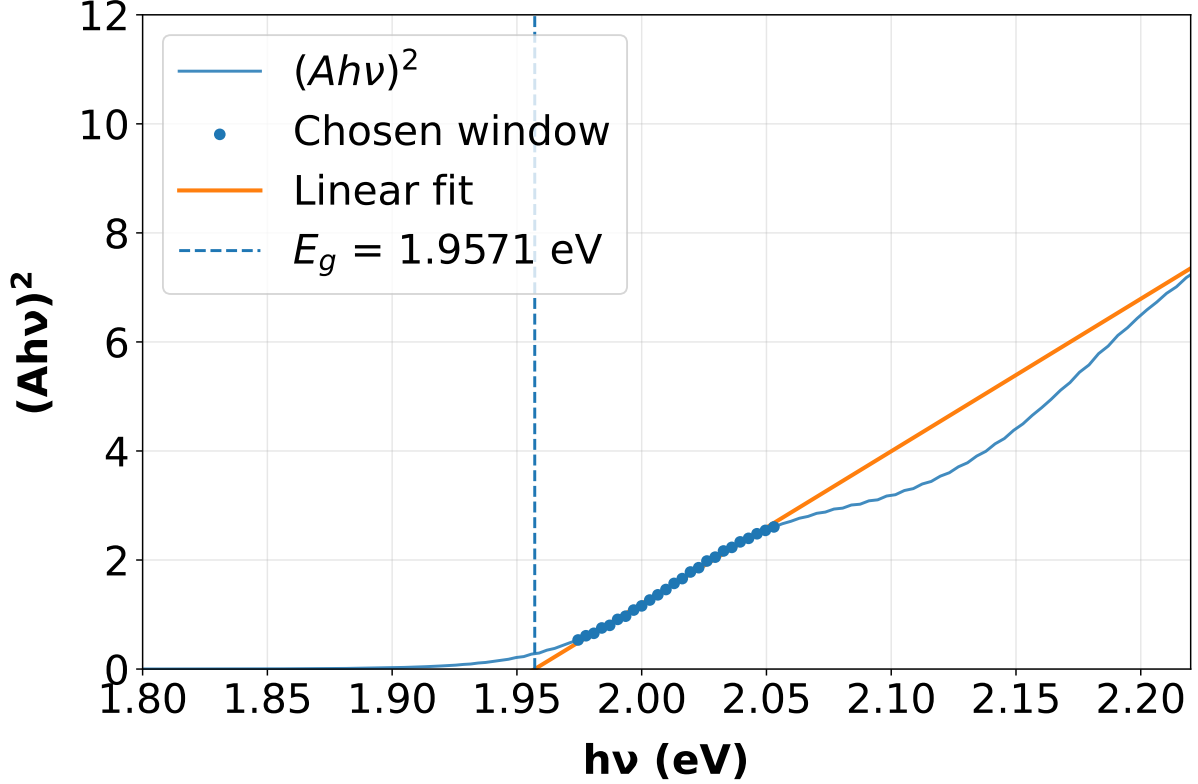


Figure 8.3: Representative Tauc plot illustrating the method used to extract the optical band gap E_g . The straight line corresponds to the optimal linear fit within the selected onset region, and the dashed vertical line marks the intercept used to determine E_g .

disorder rather than a pronounced shift in the mean band gap. These temperatures correspond to commonly employed fabrication protocols for P3HT-based organic solar cells on flexible substrates, where annealing is usually restricted to below ~ 80 °C. This observation is consistent with prior reports showing that thermal treatment enhances crystallinity in poly(3-alkylthiophenes) [173, 175, 176]. Fig. 8.3, depicts the Tauc method plot, which is used for the band gap extraction.

8.4 Results and Discussion

To access the effect of mechanical strain on the optical band gap, we calculated the per-sample difference

$$\Delta E_g = E_{g,\text{post}} - E_{g,\text{pre}},$$

where $E_{g,\text{pre}}$ and $E_{g,\text{post}}$ denote the band gaps measured before and after strain application, respectively. The uncertainties from the Tauc fits were carried through so that each ΔE_g value came with its own estimated error. The data were then grouped according to strain level, stacking configuration, and annealing temperature.

Table 8.2: Summary of statistical tests evaluating strain sensitivity of ΔE_g .

Contrast	Estimate	Confidence Interval	Test	Conclusion
Slope (0-7% strain)	-0.089 meV	90% CI [-0.173, -0.005]	TOST (margin ± 0.5 meV/%)	Effect statistically equivalent to zero; maximum shift ≤ 2 meV.
10% vs. pooled 1-7%	+4.27 meV	95% CI [2.38, 6.17]	Robust categorical regression (HC3)	Significant strain-induced permanent changes occur between 7 and 10%.

Across all conditions, the resulting shifts are generally small (on the order of a few meV). These values often fall within the experimental resolution limit of ± 5 meV, which is determined by the 1 nm spectrometer step size. Fig. 8.4 presents the aggregated results as ΔE_g versus strain, with 95% CIs. For strains up to 7%, the mean values fluctuate around zero and remain largely confined within the resolution band which would suggest the absence of a systematic effect. However, at 10% strain, all groups exhibit a reproducible increase in E_g of approximately -5 meV, which, while modest in magnitude, clearly exceeds the estimated statistical noise.

Considering that each strain level was measured on an independent specimen (i.e., one specimen per strain and per condition), the present dataset does not include between-specimen replication of ΔE_g at a fixed strain level (e.g., multiple independent measurements at 1% strain), which is acknowledged as an experimental limitation. The reported uncertainty therefore reflects the propagated Tauc-fit uncertainty and within-specimen spatial variability (three measurement positions). The strain dependence is assessed using pooled equivalence testing over the 1-7% strain range and robust regression contrasts comparing the 10% strain condition to the pooled 1-7% dataset.

These observations suggest a threshold-like response in the optical band gap, which is stable under moderate strain but increases noticeably upon entering the 10% regime. Two key questions arise from this behavior: (i) can the apparent minor variations below 7% be regarded as statistically negligible within experimental limits. (ii) how robust is the observed increase at 10% when we consider two matters: first, we must ensure that the pooled effect is not driven by a single experimental subgroup. In particular, no individual annealing or stacking condition should disproportionately influence the observed the 10% increase. Second, the regression model used to quantify this effect should remain valid

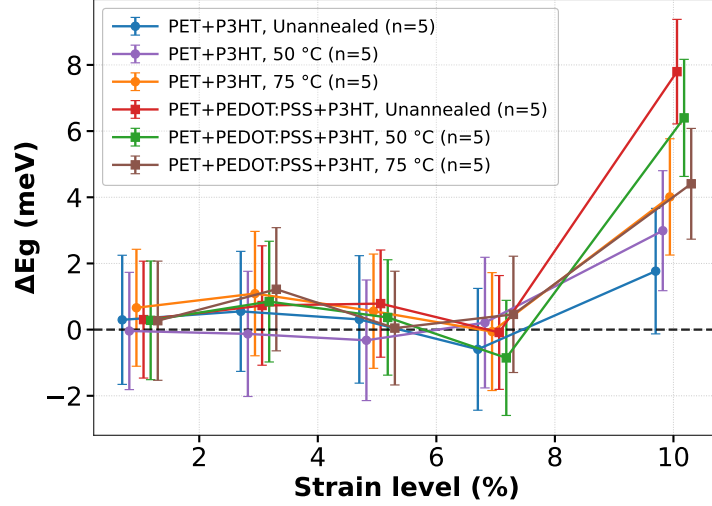


Figure 8.4: Mean band gap shift (ΔE_g) versus strain with 95% CIs across all stacks and annealing conditions.

even if the data deviate from ideal statistical assumptions, such as having constant error variance or normally distributed residuals.

8.4.1 Statistical Evaluation of Strain Sensitivity

To quantify the pattern of the observed strain behavior, we first fitted a pooled linear regression of ΔE_g versus strain using only the points at 1-7%. Here, “pooled” refers to combining all samples across annealing and stacking conditions into a single regression model, thereby yielding a global estimate of the slope while not explicitly modeling subgroup-specific effects. The estimated slope was -0.089 meV/% with a 90% CI of $[-0.173, -0.005]$ meV/%. We then applied a two one-sided test (TOST) for equivalence, using a pre-specified margin of ± 0.5 meV/%. This margin was chosen as a conservative tolerance for practically negligible trends in ΔE_g . The TOST yielded an extremely small p-value ($p < 10^{-14}$), providing strong evidence that the slope is statistically equivalent to zero. Thus, it can be concluded that the optical band gap remains effectively invariant below 7% strain.

To verify the robustness of the 10% shift, we re-expressed strain as a categorical factor and fitted a regression with heteroskedasticity-consistent (HC3) standard errors. This approach avoids relying on the usual regression assumption of normally distributed and homoscedastic errors, and it reduces the influence of unusual or outlying samples by widening their estimated uncertainty so they cannot dominate the overall result. The coefficient for the 10% condition was estimated at $+4.27$ meV (95% CI: $+2.38$ to $+6.17$ meV, $p = 9.4 \times 10^{-6}$). These values confirm the statistically decisive increase even under conservative assumptions. Table 8.2 summarizes these data.

Although each subgroup independently showed a positive 10% effect, to ensure that the pooled statistical contrast was not dominated by any single condition, we conducted leave-one-group-out sensitivity tests. Here, the overall 10% coefficient was re-estimated while systematically excluding one anneal/stack combination at a time. The resulting values ranged from 3.66 to 4.80 meV, and in all cases the 95% CIs remained strictly positive. This demonstrates that the band gap widening at 10% strain is a universal feature across annealing and stacking variations, not a subgroup-specific anomaly.

To examine whether the magnitude of the 10% effect depends on preparation or stack layers, we restricted the dataset to the 10% condition and fitted a categorical regression with annealing temperature and stack type as predictors. The results showed neither annealing temperature nor stacking configuration contributed significantly to the variance in ΔE_g (all $p > 0.2$, HC3 regression). Nevertheless, inspection of the group means suggests that stacks containing a PEDOT:PSS interlayer exhibit a slightly larger shift compared to bare PET/P3HT. This trend is consistent with more efficient and uniform strain transfer into the P3HT layer when the adhesive layer is present, which was indeed the intended purpose of introducing PEDOT:PSS.

Finally, to test whether the 10% increase merely reflects a continuation of the linear slope observed below 7%, we fitted a pooled model of the form

$$\Delta E_g \sim \text{strain} + \text{is10},$$

where is10 is a binary indicator for the 10% condition. This formulation separates the effect into a baseline linear trend and any additional changes specific to 10%. The deviation coefficient was estimated at +4.81 meV ($\text{SE} = 1.03$, $p = 3.1 \times 10^{-6}$). This confirms that the 10% regime exhibits a distinct upward departure from the pooled linear trend.

Together, these results demonstrate that the optical band gap of P3HT films remains stable up to 7% strain, but exhibits a robust and reproducible widening of approximately 4-5 meV at 10%. This effect is consistent across annealing and stacking variations and cannot be explained by extrapolation of the sub-threshold trend.

8.4.2 Physical Interpretation and Device-Level Implications

The negligible band gap shifts observed up to 7% strain suggest that the optoelectronic properties of P3HT films remain stable because strain is dissipated through intrinsic microstructural relaxation processes rather than electronic perturbation. Poly(3-hexylthiophene) is known to form semicrystalline films comprising ordered lamellae interspersed within amorphous matrices [175, 177]. These crystalline domains, stabilized by π - π stacking and lamellar alignment, have been shown to provide mechanical reinforcement and preserve charge transport properties under moderate strain. Strain in such films is accommodated through chain slippage or relaxation at phase boundaries [153, 178, 179]. In addition,

conformational reorganization within amorphous regions can occur, rather than direct deformation of the conjugated backbone. These mechanisms help maintain orbital overlap and prevent significant disruption of the electronic structure.

At higher strain levels (10%), the modest but statistically significant increase in optical band gap ($\Delta E_g \approx 4.5$ meV) likely reflects a structural perturbation beyond the deformation tolerance of these buffering mechanisms. High-magnitude tensile strain can induce torsional disorder, chain misalignment, or disruption of favorable stacking orientations [179]. These structural changes reduce the effective conjugation length and lead to a blue-shift of the absorption onset. This interpretation aligns qualitatively with the ultrafast microscopy results from Kim *et al.* [142], who observed that tensile perturbations suppress π -orbital overlap and transiently increase E_g on picosecond time scales. While their measurements capture local, rapidly applied strain, our ex-situ thin-film results represent the long-lived, residual outcome of deformation, revealing which microscopic effects persist once the film relaxes.

Importantly, the observed band gap modulation is largely independent of annealing condition or stack architecture. This suggests that the strain response is governed primarily by the semicrystalline network itself rather than interfacial coupling or surface chemistry. Moreover, since strain was applied and held for 30 minutes before the secondary UV–Vis measurement, the reported spectral shifts show the residual strain effects, reflecting post-deformation structural relaxation.

Bridging Molecular Simulations and Thin-Film Realities. While molecular-scale studies have elucidated fundamental strain–electronic coupling mechanisms, their results do not necessarily extrapolate to thin-film systems under real-world conditions. For instance, Menichetti *et al.* [141] used DFT to show that strain can shift the donor and acceptor levels at the P3HT/PCBM interface, modulating energy offsets relevant for exciton dissociation. Similarly, Kim *et al.* [142] used scanning ultrafast electron microscopy to capture transient strain-induced modulation of E_g in P3HT with sub-nanosecond temporal resolution. Both studies provide invaluable mechanistic insights at the molecular or nanoscale level.

The results presented here contextualize prior molecular- and nanoscale predictions of strain–electronic coupling. This is reflected in the macroscopic optical response of device-relevant organic semiconductor thin-films. While earlier studies demonstrated that localized tensile deformation can perturb electronic structure under idealized or highly confined conditions [141, 142], our measurements show that such effects do not translate into a measurable band gap response when strain is applied uniformly across a complete semicrystalline film.

This behavior is a direct consequence of the heterogeneous morphology of P3HT thin-films. Mechanical deformation is accommodated non-affinely through mesoscale relaxation pathways, including chain rearrangement in amorphous regions, reorganization of

crystalline–amorphous boundaries, and intergrain accommodation, rather than through uniform stretching of the π -conjugated backbone [178, 180]. These mechanisms dissipate applied stress while preserving intermolecular orbital overlap, effectively buffering the electronic structure against strain-induced perturbation.

As a result, the ensemble-averaged optical response remains stable even under residual tensile strains approaching 10%. This defines a deformation window within which P3HT thin-films can be regarded as electronically robust. This finding establishes a clear scale separation between microscopic strain sensitivity and macroscopic optical invariance. It also provides a physically grounded explanation for the apparent discrepancy between idealized predictions and device-relevant behavior.

Direct morphological imaging by AFM or SEM was not included, as ex-situ characterization of soft polymer films can be affected by strain relaxation during handling. The interpretation therefore draws on the well-established semicrystalline morphology of P3HT reported in the literature [153, 180, 181]. Importantly, the conclusions are derived from ensemble-averaged optical trends that are insensitive to local nanoscale heterogeneity. Future work will extend this framework through in-situ strain-dependent structural characterization to further elucidate morphology–property relationships under load.

8.5 Conclusion

Our results demonstrate that P3HT-based thin-films, both as single layers (PET/P3HT) and in PET/PEDOT:PSS/P3HT stacks, retain stable optical band gaps under tensile strain up to 7%, with no statistically significant change. This invariance holds across annealing conditions, indicating that the semicrystalline morphology of P3HT allows internal relaxation of strain without perturbing the electronic structure.

However, spectra recorded after applying 10% strain for 30 minutes revealed a consistent increase in E_g of approximately ~ 4 –5 meV. This would suggest a threshold above which torsional disorder or disrupted π – π stacking begins to alter the electronic structure. These findings bridge molecular predictions with thin-film realities, showing that thin-films do not exhibit continuous strain sensitivity as simulations might suggest, but rather a plateaued response up to a critical strain level.

For device simulation including finite element modeling (FEM) of flexible optoelectronics, this behavior allows simplification so that the optical band gap can be treated as a constant parameter up to 7% strain. This enables more accurate and efficient models focused on mechanical propagation and charge transport, rather than strain-modulated absorption. In general, our study provides a quantitative strain threshold for optical property stability in P3HT films, which supports their viability in long-term flexible device applications and informs design rules for strain-resilient organic photovoltaics.

Chapter 9

Temperature-strain interplay in P3HT: A Raman spectroscopic probe of chain alignment for flexible electronics

9.1 Overview

This chapter investigates how mechanical stretching and processing temperature jointly influence the structural behavior of regioregular P3HT thin films in flexible electronic configurations. By examining the interplay between strain-induced chain alignment and thermally induced ordering, the study addresses how mechanical and thermal conditions collectively govern molecular organization. Based on the content of this work, a final manuscript will be prepared soon. Details of the manuscript:

Ayush Kant Ranga, Mahya Ghorab, Veit Wagner, Mojtaba Joodaki, Arnulf Materny - Temperature-Strain Interplay in P3HT: A Raman Spectroscopic Probe of Chain alignment for Flexible Electronics.

Abstract

Strain-induced chain alignment has long been proposed as an effective method to enhance charge transport in organic semiconductors. Among these materials, poly(3-hexylthiophene) (P3HT) remains one of the most widely investigated conjugated polymers for applications ranging from flexible solar cells to field-effect transistors. However, when such materials are incorporated into flexible electronic architectures, mechanical deformation not only aligns polymer chains but can also introduce structural defects that deteriorate the performance of the device. Temperature is another equally critical parameter, as thermal annealing not only promotes the long-range ordering in polymers but can

also bring a certain level of rigidity to it. Despite the apparent relevance of both mechanical and thermal cues, their combined effect has not yet been systematically studied. Here, we investigate how uniaxial tensile strain interacts with controlled processing temperature in regioregular-P3HT (rr-P3HT) thin films deposited on Poly(ethylene terephthalate PET) substrates at 25°C (unannealed, i.e., room temperature drying), and annealed at 50 and 75 °C. These conditions represent manufacturing-relevant low-temperature processing conditions used in roll-to-roll fabrication of flexible organic electronics. We use Raman spectroscopy to monitor the vibrational fingerprint of rr-P3HT, focusing mainly on the ring-skeleton modes at approximately 1377 cm⁻¹ (C–C) and 1445 cm⁻¹ (C=C). These modes are sensitive to π -electron delocalization and thus report on the efficiency of charge-carrier transport. Later, we introduce a poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) interlayer between PET and P3HT to improve strain transfer between the underlying substrate and P3HT, which can enhance structural stability, thereby promoting more favourable chain alignment. Our results offer a coherent picture of how strain and temperature co-govern molecular ordering and highlight processing temperature as a key parameter that can either facilitate gentle alignment or lock the polymer into brittle, crack-prone microstructures.

9.2 Introduction

Conjugated-polymer semiconductors remain central to flexible electronics owing to their solution processability on lightweight plastic substrates [87, 88, 182]. They can tolerate mechanical deformation far better than inorganic semiconductors, enabling devices that can bend, stretch, and fold without significant loss of performance [87, 183, 184]. Poly(3-hexylthiophene) (P3HT) is among the most widely studied polymers and has become a benchmark system for exploring the interplay between structural order and charge transport for applications like solar cells and field-effect transistors [53, 185]. Recent studies have predicted that tensile deformation can orient the polymer backbone. This could potentially lead to strengthening the interchain interactions π - π and enhancing charge transport [88, 184, 186]. Optical measurements support this interpretation by revealing signatures of increased π stacking and greater polaron delocalization under strain [185]. However, most of this evidence arises from simulations or experimental conditions that deviate substantially from those used in large-area, manufacturing-relevant processing [187].

Experimentally, a major gap in the literature arises from the fact that most strain-dependent studies probe as-cast films or layers deposited on prestretched substrates [94]. Although these configurations can reveal P3HT’s intrinsic tendency to align under tension, they do not capture the role of the thermal history of devices [188]. Annealing promotes crystallization [189] and strengthens the interfacial adhesion [190], the increased

crystallinity have proven a direct impact on the stiffness of polymer blend films, which governs the crack-onset conditions in the polymer [191, 192]. Moreover, it modifies chain packing and increases film stiffness, shifting the response of stretching from smooth molecular alignment to the formation of microcracks [192, 193]. Consequently, the same nominal strain can result in entirely different molecular arrangements, depending on the thermal treatment. In other words, expected chain alignment upon stretching can also lead to the formation of microcracks.

Once microcracks form in these films, the mechanical environment becomes even more complex [30]. Crack formation redistributes local stress and reduces the actual strain experienced by the semicrystalline domains that carry excitons, polaron-pairs, delocalized excitons and polarons in such a system [30]. The other consequence of the formation of microcracks is slippage of metal contacts in the actual device and strain-induced defect formation in the substrate holding the semiconducting film [17]. The behavior of the supporting substrate adds another layer of complexity. Poly(ethylene terephthalate) (PET), which is widely used in flexible electronics, is not mechanically inert. Spectroscopic studies show that PET exhibits irreversible band shifts and linewidth changes once tensile deformation exceeds only a few percent [25]. Such substrate evolution alters frictional coupling and modulates strain transmission to the polymer semiconductor. In optoelectronic devices, the substrate, interfacial layers, and active layer form an integrated mechanical system, such that strain imposed on one component is transferred throughout the stack.

Raman spectroscopy offers a sensitive probe of how mechanical deformation alters the molecular order that governs charge transport in P3HT. Two vibrational modes are especially informative: the intra-ring C–C stretch near 1377 cm^{-1} and the symmetric C=C stretch near 1445 cm^{-1} [21]. The (1377 cm^{-1} mode is a signature of backbone planarity and torsional changes in the polymer chain, and the (1445 cm^{-1} mode is sensitive to changes in conjugation length of polymer and chain conformations [20]. Together, they provide a direct view of how the polymer structure reorganizes in response to applied strain. We quantified structural changes by fitting the Raman spectra and analyzing the changes in band position and full width at half maximum (FWHM) of the key bands. Earlier studies show that the 1377 cm^{-1} mode is insensitive to changes induced by better alignment in thin-films, for example, via thermal treatment and heterojunction formation with acceptor-type fullerene molecules. In contrast, the 1445 cm^{-1} mode can shift to lower wavenumbers as temperature-induced ordering in polymer chains increases [31].

In this study, P3HT films were spin-coated onto PET substrates and subsequently annealed at 25°C , i.e., kept at room temperature, 50°C , or 75°C before being stretched incrementally up to 10%. The non-annealed films exhibit a predominantly elastic response, reflected in a narrowing of the FWHM and only minor shifts in the Raman band position. In contrast, the annealed films show a markedly different behaviour: increasing the processing

temperature appears to rigidify the microstructure, effectively constraining chain mobility. This stiffening becomes most pronounced at 75°C, where the strain-induced broadening of the FWHM points to the development of microstructural defects under deformation. Introducing an intermediate PEDOT:PSS layer further modifies this response, enabling more efficient strain transfer and improved mechanical stability during stretching.

9.3 Sample Preparation and Experimental Method

9.3.1 Sample preparation

Figure 1 shows a flexible P3HT film coated on a PET substrate. The rr-P3HT with an average molecular weight between 20,000 and 45,000 g mol⁻¹ (Sigma-Aldrich) was used to fabricate the thin films. The underlying flexible substrate used was a PET film with a thickness of 57.3 µm. The substrate is optically transparent and predominantly amorphous. For all experiments, the PET sheets were cut into 5 × 5 cm² squares, cleaned with a 3:2 propanol/acetone mixture, and subsequently dried under a nitrogen stream. Surface wettability and adhesion were improved by a 5-minute UV–ozone treatment immediately before film deposition. A 33 mg mL⁻¹ solution of P3HT in anhydrous chlorobenzene was stirred overnight at 50°C to achieve complete dissolution. Before coating, the PET substrates were pre-heated at 75°C for 10 minutes. Films were then spin-coated using 400 µl of the P3HT solution at 1500 rpm for 30 seconds, resulting in 150-200 nm thickness. After deposition, the films were divided into three sets: (i) unannealed (room temperature drying at 25°C), (ii) annealed at 50°C for 5 minutes, and (iii) annealed at 75°C for 5 minutes.

In addition to single-layer samples, bilayers were fabricated by adding a thin hole-transport layer (HTL) of PEDOT:PSS. This layer was used primarily to enhance adhesion and for mechanical coupling between PET and P3HT for strain tests. A formulation comprising 98% PEDOT and 2% surfactant additives was spin-coated onto the PET substrates at 5000 rpm for 60 seconds using 1000 µl of dispersion per sample. The P3HT layer was then coated under the same spin-coating conditions as described above, resulting in PET/PEDOT:PSS/P3HT structures. Samples were placed in a glove box overnight before use in experiments.

9.3.2 Experimental Method

Stretching method

Figure 2 shows the stretcher device used to apply the mechanical strain to the fabricated films. A custom-made mechanical stretcher device incorporating a precision linear actuator



Figure 9.1: A flexible P3HT film annealed at 75°C coated on a flexible PET substrate

was used to apply uniaxial tension. The actuator's calibration provided a displacement increment of 6.25 μm per microstep, enabling consistent and precise strain steps. The maximum strain applied was capped at 10% because strains beyond that level caused significant deformation of the PET substrate, which would dominate the spectral measurements and mask effects intrinsic to the polymer. Strain levels of 1, 3, 5, 7 and 10% were examined. The nominal strain (ε) was defined as the change in length (ΔL) divided by the original gauge length (L_0), i.e., $\varepsilon = \Delta L/L_0$. All stretching and Raman measurements were carried out at room temperature to avoid thermal softening or morphology changes that might occur at elevated temperatures.

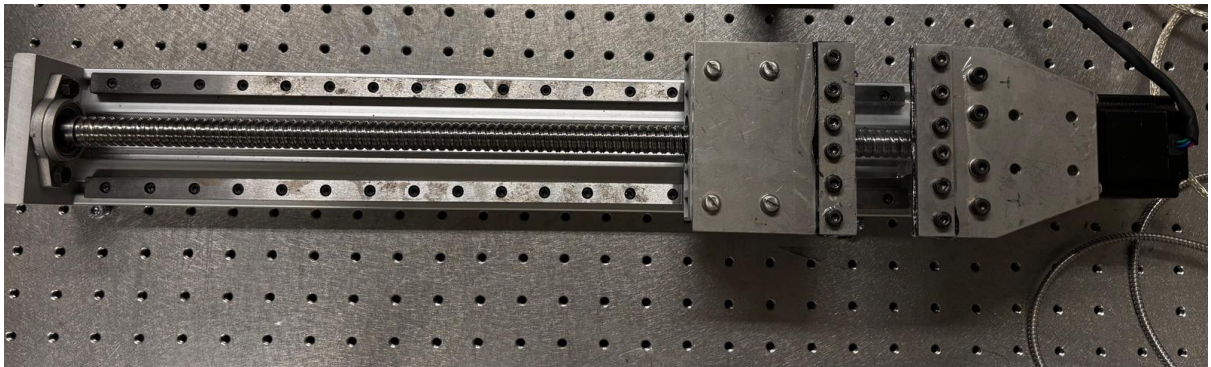


Figure 9.2: Custom-made stretcher device used to stretch the P3HT films

Raman spectroscopy

A detailed description of Raman spectroscopy setup used for all experiments is discussed in earlier section 6.1.2. Raman spectra were recorded directly on strained PET films every five minutes over a 30-minute stretching period. Post-processing included determination of peak positions, full widths at half maximum (FWHM), and intensity changes for key vibrational modes, which were processed using Jobin-Yvon’s NGS Labspec software. A reference spectrum taken from an unstretched sample was first used to assign the vibrational bands via the software’s peak-search function. Each identified band was then modelled using a Gaussian–Lorentzian line shape to extract its parameters. The primary focus was directed to two prominent bands that monitor π -electron delocalisation in P3HT-type polymers: the C–C skeletal stretching mode at 1377 cm^{-1} and the C=C stretching mode at 1445 cm^{-1} . Prior work has demonstrated that the positions and FWHMs of these bands change significantly upon polymer alignment, as a function of temperature and regioregularity [31].

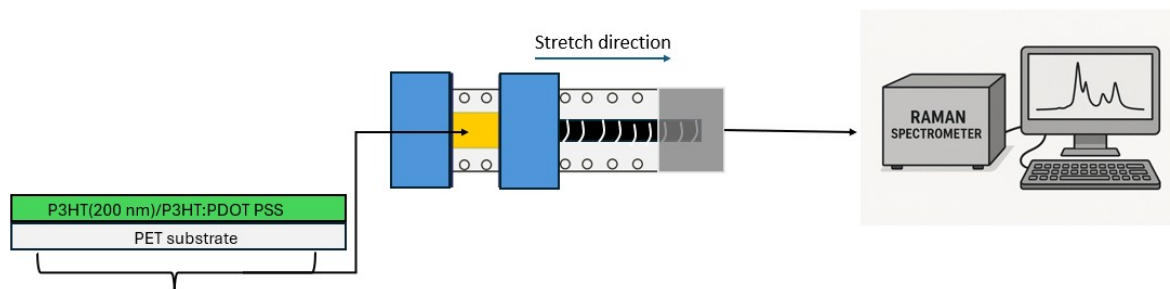


Figure 9.3: Schematic of experimental procedure used for experiments

9.4 Results and discussion

To understand the evolution of the FWHM of the 1377 cm^{-1} and 1445 cm^{-1} Raman bands responding to strain, we have plotted a time series of this evolution. T_0 represents the time when there is no delay between the applied strain and the spectral measurements. The *Rest* state represents the spectra measured after the strain was released. The total time before releasing the strain was 30 minutes. This method can therefore provide both transient and residual information about the response of these films. All plotted values represent the difference between the stretched and unstretched values of FWHM and band position of the same state. A Raman spectrum of a 75°C annealed P3HT film is shown in Figure 9.4. All spectra were measured at three different points for statistical purposes. All spectra were recorded for 10 seconds and averaged over four iterations. The laser power was optimized to 3 mW to eliminate any heat or bleaching-related effects on the sample. From the Raman spectra, we identified the dominant vibrational modes characteristic of

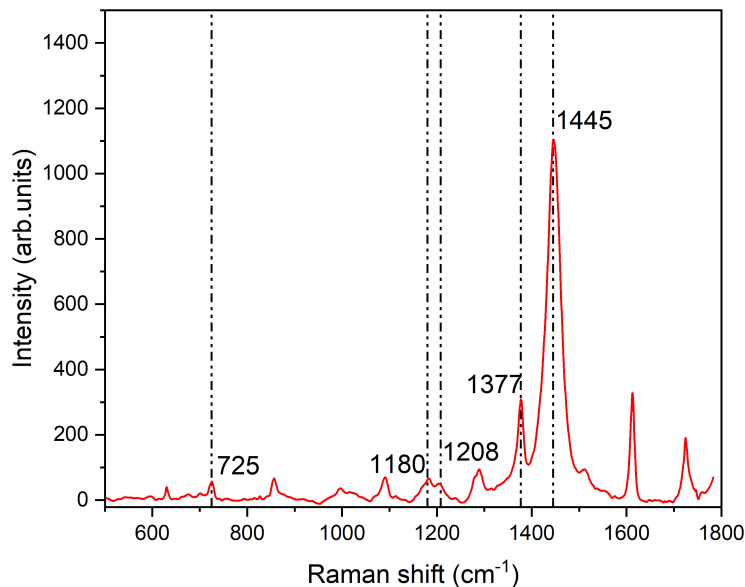


Figure 9.4: Raman spectrum of an unstretched P3HT-only film annealed at 75°C.

P3HT, which are summarized in Table 9.1. Additional bands originate from the underlying PET substrate; the strain response of these PET modes has been analyzed in detail in our previous work [25]. In the present study, we concentrate exclusively on the evolution of the two most structurally informative P3HT modes: the C–C stretch at 1377 cm^{-1} , and the C=C stretch at 1445 cm^{-1} . These bands provide the clearest insight into strain and temperature-induced changes in conjugation and backbone ordering.

S.No	Raman shift cm^{-1}	Assigned vibration
1	725	C-S-C deformation
2	1180	C-H bending mode
3	1208	Inter-ring C-C stretching
4	1377	Intra-ring C-C stretching
5	1445	Symmetric C=C stretching

Table 9.1: Raman bands for P3HT

9.4.1 Raman response of the 1377 cm^{-1} band under strain

The Raman band at $\sim 1377 \text{ cm}^{-1}$ in rr-P3HT is commonly assigned to an in-plane C–C skeletal stretching mode of the thiophene backbone, with a non-negligible contribution from motions involving the hexyl side chains [22, 23]. Fanchini and co-workers demonstrated that the corresponding feature near 1380 cm^{-1} is sensitive to nanoscale ordering and phase separation, with changes in intensity and linewidth reflecting variations in local

structural order [22]. More recently, Mosca et al. showed that the pair of backbone modes near 1377 and 1440 cm^{-1} act as sensitive fingerprints of π -electron delocalization, where increased effective conjugation length and backbone planarity lead to a redshift and spectral narrowing, while localization or enhanced torsional disorder produces blueshifts and linewidth broadening [24]. At the same time, infrared and Raman studies of P3HT degradation and composite formation indicate that vibrations in the 1377-1381 cm^{-1} region also carry significant CH_3 deformation character associated with side chains and defect-rich segments [23]. Taken together, these observations imply that the 1377 cm^{-1} band reports simultaneously on backbone conjugation and planarity, as well as on the conformational state of side chains and defect environments. Consequently, analysis of both the band position and full width at half maximum (FWHM) under mechanical strain provides a sensitive probe of how tensile load redistributes microscopic environments within the P3HT layer. In the following section, the strain response of the 1377 cm^{-1} band is analyzed for PET/P3HT and PET/PEDOT:PSS/P3HT stacks. For each stack, wavenumber shifts $\Delta\tilde{\nu}$ and FWHM changes ΔFWHM are evaluated relative to the corresponding unstretched reference spectrum, with negative or positive $\Delta\tilde{\nu}$ indicating red or blueshift and negative or positive ΔFWHM indicating spectral narrowing or broadening. Both the instantaneous response at T_0 and the post-unloading *Rest* state are considered to distinguish recoverable from retained strain-induced modifications.

Unannealed P3HT on PET. In Fig. 5 below, we have shown the evolution of the 1377 cm^{-1} band as a function of increasing strain at different temperatures. Panels (a) and (c) display the differences in apparent Raman band position. Panels (b) and (d) show the changes in FWHM as compared to the unstretched film. For unannealed PET/P3HT films, the 1377 cm^{-1} mode shows a very small wavenumber shift that is close to the detection limit under strain, but a consistent narrowing of the FWHM. This indicates that stretching does not significantly change the average backbone vibrational energy, but instead selectively highlights the subset of chains that are better aligned and more effectively coupled to the substrate. The intrinsically soft, heterogeneous morphology of unannealed P3HT allows tensile load to be accommodated mainly through reversible chain alignment and slight planarization, producing a narrower FWHM without major wavenumber shifts. After unloading (at *Rest*), very small residual changes in both peak position and linewidth persist, reflecting minor, irreversible microstructural adjustments accumulated during the 30-minute strain application. Overall, the unannealed films behave predominantly elastically with strain revealing a mechanically selected, better-aligned chain population and only subtle structural memory after unloading [22–24].

PET/P3HT annealed at 50°C. After mild thermal annealing at 50°C, the PET/P3HT films show a markedly different response from the unannealed samples. The 1377 cm^{-1}

band again exhibits only minimal, near-threshold wavenumber shifts, but its FWHM broadens at all strain levels, both at T_0 and $Rest$. This broadening reflects the more segmented, semi-crystalline microstructure produced by mild annealing, in which strain is distributed unevenly among crystalline lamellae, tie chains, and the constrained amorphous phase. As a result, tensile deformation produces a wider spread of local vibrational environments without significantly altering the average backbone planarity. The incomplete recovery of the Δ FWHM in the $Rest$ state indicates that some microstructural heterogeneity, likely small interfacial distortions or microcracks, persist after the 30-minute loading period. Overall, the 50°C films deform, resulting in heterogeneous FWHM in contrast to the clean chain-alignment behavior observed in the unannealed case, which is consistent with a stiffer morphology prone to cracks upon stretching [22, 192, 194].

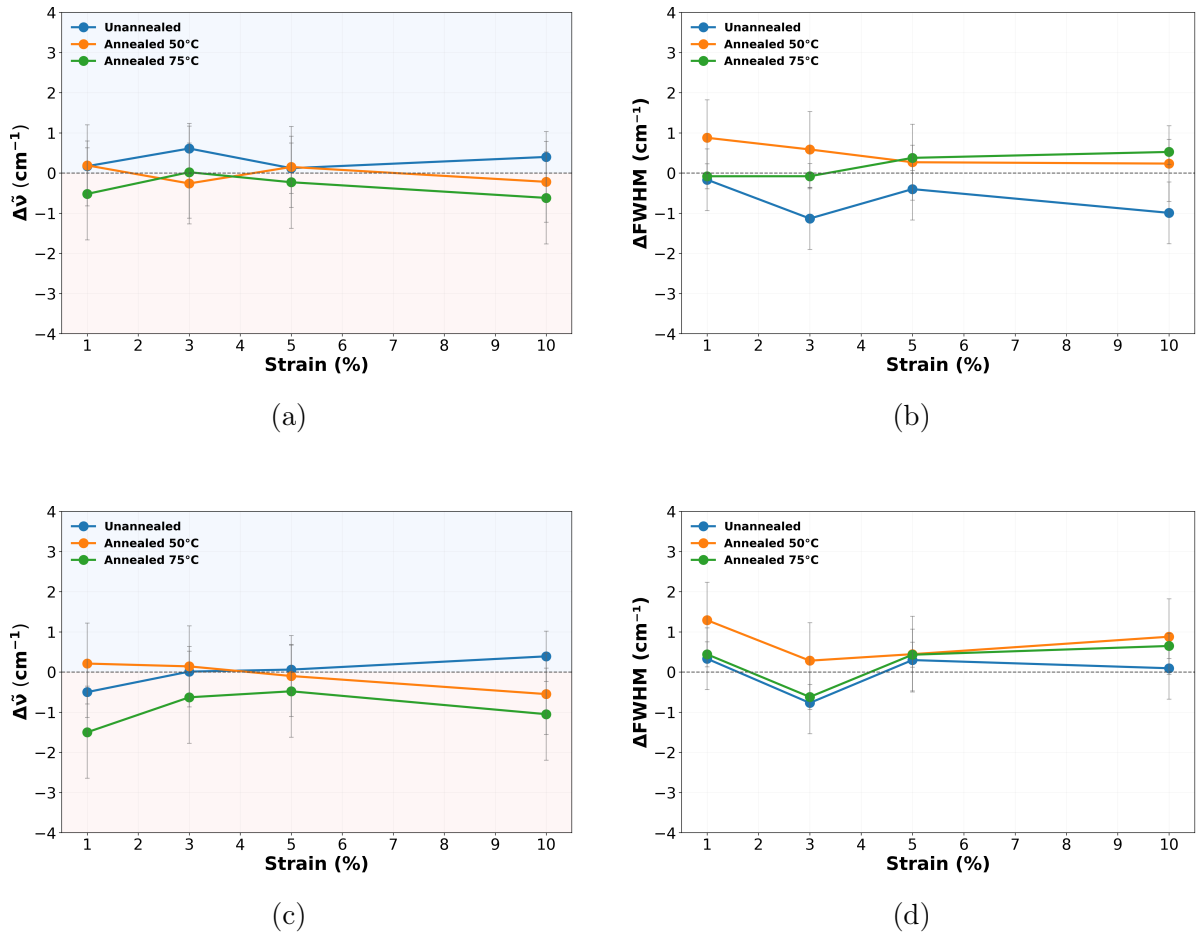


Figure 9.5: Strain dependence of the 1377 cm⁻¹ Raman band in PET/P3HT under different annealing conditions. (a) Band-position shift at the instantaneous T_0 state. (b) Corresponding FWHM variation at T_0 . (c) Band-position shift in the post-unloading $Rest$ state. (d) Corresponding FWHM variation in the $Rest$ state. Curves correspond to unannealed, 50°C-annealed, and 75°C-annealed films.

PET/P3HT annealed at 75°C. At 75°C annealing, where P3HT develops even higher ordered lamellar structure compared to other temperatures [195], the strain response

of the 1377 cm^{-1} band becomes more brittle than in the 50°C films. For small applied strain, the changes in FWHM are negligible, but as the applied strain approaches the 5% mark, the FWHM broadens even more than that of 50°C annealed film. Across all strain levels, the peak position at T_0 exhibits a small redshift that persists after unloading, indicating that deformation in these crystalline domains involves irreversible changes in the vibrational environment [193]. The accompanying linewidth evolution remains modest-narrowing at low strain and broadening at higher strain, consistent with an initial regime of coherent chain alignment followed by the emergence of heterogeneous microstructural distortions as applied strain increases. Overall, at 5% and above level of applied strain, the 75°C films exhibit a deformation pathway characteristic of a stiff, highly ordered morphology, in which load-bearing backbones are unable to relax elastically and instead develop irreversible strain-induced defects. More importantly, the observation at 75°C is more important compared to other annealing values, as it is representative of typical annealing temperatures involved in real device architecture, thus the observation here establish a safe deformation limit at around 5%.

9.4.2 Impact of PEDOT:PSS

In Fig. 6 below, we have shown the evolution of the 1377 cm^{-1} band as a function of increasing strain at different temperatures with an additional layer of PEDOT:PSS between PET and P3HT. Panels (a) and (c) display the differences in apparent Raman band position. Panels (b) and (d) show the changes in FWHM as compared to the unstretched film. Introducing a PEDOT:PSS interlayer between PET and P3HT modifies not only the mechanical stability but also the local electrostatic and chemical environment of the P3HT chains. PEDOT:PSS is much softer than PET and can both mediate and partially redistribute strain, while also improving adhesion and suppressing interfacial slippage between PET and P3HT [194, 196]. More importantly, the Raman band near 1377 cm^{-1} contains an overlapping contribution from the P3HT backbone and the PEDOT layer in the trilayer P3HT/PEDOT:PSS/PET configuration [197]. Consequently, this feature is most appropriately interpreted as a stack-level spectral marker rather than a mode uniquely associated with a single polymer component. Strain-induced variations in the band position and FWHM therefore, reflect the collective vibrational response of the multilayer system. The objective of this study was to assess how the presence of an adhesion interlayer (PEDOT:PSS), which is commonly used as a hole transport layer in organic photovoltaic architectures, influences the strain evolution of the Raman response [198, 199]. Because all strain-dependent changes are evaluated relative to the unstretched reference state of each stack, the PEDOT contribution does not alter the observed "trends" with respect to applied strain, but instead results in a systematic offset of the absolute spectral parameters. The measured changes may thus arise from

the intrinsic strain sensitivity of the constituent layers, the superposition of overlapping vibrational modes, and mechanical coupling at the interfaces, all of which are relevant to realistic device configurations.

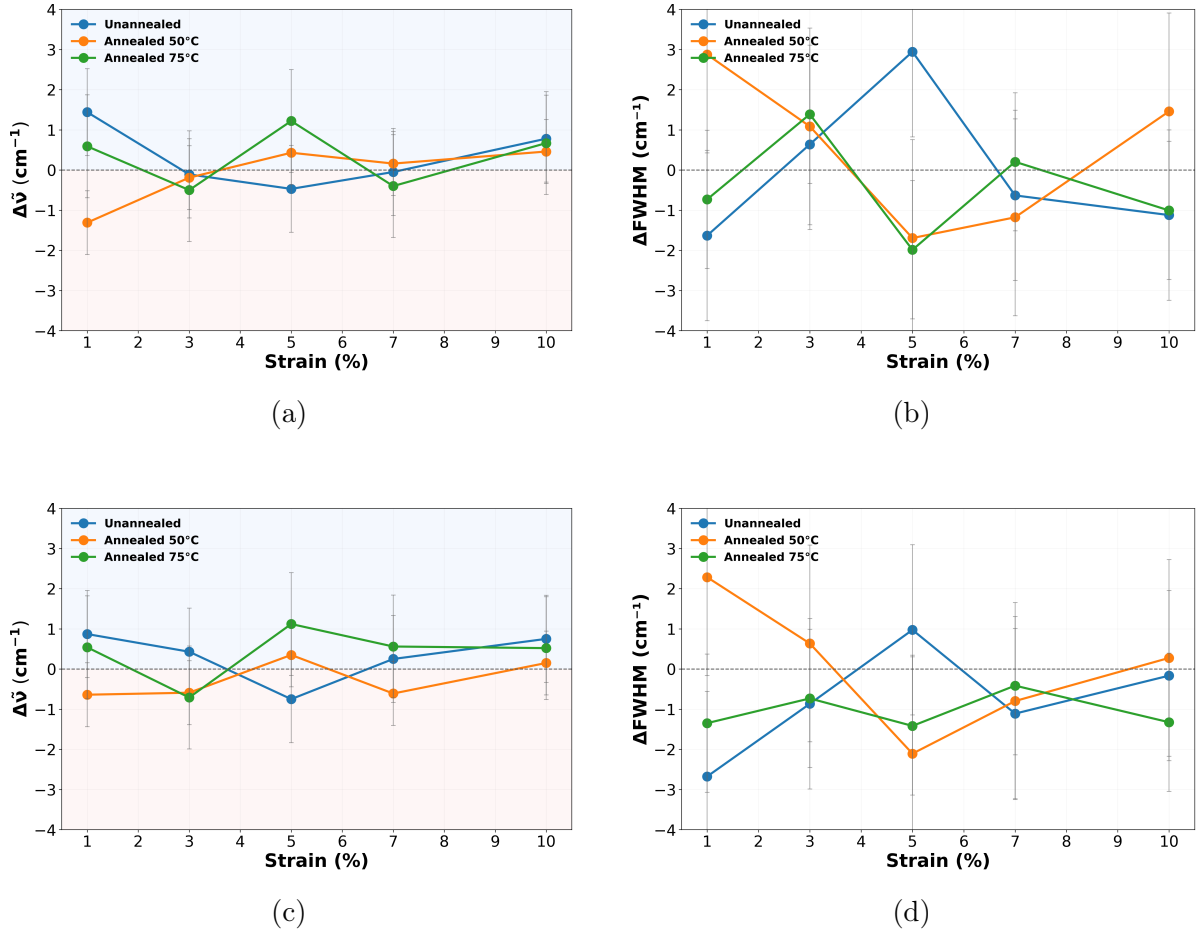


Figure 9.6: Strain dependence of the 1377 cm^{-1} Raman band in PET/PEDOT:PSS/P3HT under different annealing conditions. (a) Band-position shift at the instantaneous T_0 state. (b) Corresponding FWHM variation at T_0 . (c) Band-position shift in the post-unloading *Rest* state. (d) Corresponding FWHM variation in the *Rest* state. Curves correspond to unannealed, 50°C -annealed, and 75°C -annealed films.

Unannealed P3HT with PEDOT:PSS. In unannealed PET/PEDOT:PSS/P3HT stacks, introduction of PEDOT:PSS interlayer alters the early-stage response at 1% strain. The 1377 cm^{-1} band narrows strongly, indicating that PEDOT:PSS improves mechanical coupling and selectively engages a well-aligned subset of chains more effectively than in the PET/P3HT bilayer. At intermediate strain levels (3-5%), the band broadens and shifts slightly to lower frequency, reflecting a temporary increase in microstructural heterogeneity. At even higher strain (7-10%), the narrowing of FWHM suggests that the mechanically dominant chains regain control of the spectral response rather than giving way to irreversible damage. After unloading, only minor residual narrowing and small shifts remain, showing that the tri-layer accommodates strain largely elastically while

retaining a weak memory of chain selection.

Annealed P3HT with PEDOT:PSS (50°C). In the annealed PET/PEDOT:PSS/P3HT stacks, the strain-induced shifts of the 1377 cm^{-1} band remain small at all strain levels and are consistently weaker than in the corresponding PET/P3HT bilayers, reflecting the ability of PEDOT:PSS to redistribute the applied load. At 50°C, where P3HT is only moderately ordered, the response consists of dominant broadening initially but with additional strain, the FWHM becomes systematically narrower. The overall observed trend at 50°C is narrowing compared to 1%.

Annealed P3HT with PEDOT:PSS (75°C). Analyzing the stack, which is more relevant to a real organic semiconductor-based device, highly ordered 75°C films with PEDOT:PSS exert an even stronger stabilizing influence. The irreversible redshifts characteristic of the PET/P3HT bilayer are largely suppressed, and the FWHM remains only mildly affected, indicating that the interlayer prevents catastrophic lamellar distortion or defect accumulation at the interface. At the *Rest* state, the overall line width shows consistent narrowing as compared to all the stacks, which is due to increased homogeneity in Raman scattering arising from well-aligned subsets of polymer chains. Taken together, these results show that PEDOT:PSS functions as an effective mechanical buffer across the considered annealing conditions, smoothing strain gradients and preserving the structural integrity of P3HT. This is consistent with earlier investigations reporting stabilization due to the additional layer, with the most pronounced protective effect observed in the most crystalline films [17, 24].

9.4.3 Raman response of the 1445 cm^{-1} band under strain and annealing

The Raman band near 1445 cm^{-1} corresponds to the symmetric C=C stretching vibration of the P3HT backbone and is a highly sensitive spectroscopic probe of conjugation length, backbone torsion, and π - π stacking in conjugated polymers. Within this framework, wavenumber shifts $\Delta\tilde{\nu}$ of the 1445 cm^{-1} band primarily indicate changes in effective conjugation length and backbone planarity. Positive shifts (blueshifts) are associated with increased torsional disorder and reduced conjugation, whereas negative shifts (redshifts) may arise from backbone planarization, extended conjugation, or defect-induced softening of local force constants. Changes in FWHM reflect the distribution of local structural environments: narrowing corresponds to a more uniform subset of vibrational microenvironments, while broadening signifies heterogeneous strain fields, distributed disorder. These correlations are well established for P3HT and related conjugated polymers [31]. The analysis below follows the strain response framework established for the 1377 cm^{-1}

band. The 1445 cm^{-1} results are therefore not used to redefine deformation regimes, but rather to refine and contrast how strain accommodation differs between PET/P3HT and PET/PEDOT:PSS/P3HT stacks.

PET/P3HT unannealed. In Fig. 7 below, we have shown the evolution of the 1445 cm^{-1} band as a function of increasing strain at different temperatures. Panels (a) and (c) display the differences in apparent Raman band position. Panels (b) and (d) show the changes in FWHM as compared to the unstretched film. In unannealed PET/P3HT, stretching consistently produces a small blueshift, indicating that the dominant microscopic effect is increased torsional disorder and a shortening of conjugation segments along the P3HT chains. Notably, similar to the 1377 cm^{-1} band, the corresponding linewidth of 1445 cm^{-1} narrows at low and intermediate strains, showing that although the film becomes more disordered on average, the vibrational response is increasingly dominated by a subset of semi-ordered domains that efficiently transmit mechanical stress. This effect is characteristic of strain-assisted alignment in flexible photovoltaics and establishes safe deformation limits for P3HT of extended chain segments while the more amorphous portions remain mechanically inactive [200, 201]. Only at the highest strains (10%) does the linewidth broaden, signaling the onset of heterogeneous deformation. After strain release at *Rest*, the wavenumber is nearly fully recovered and the FWHM becomes narrower, reflecting the elasticity of these soft unannealed films [17].

PET/P3HT annealed at 50°C . The 50°C -annealed PET/P3HT films exhibit a more intricate balance between disordering and domain-specific deformation. Although the wavenumber response under load remains dominated by small blueshifts—indicating that the backbone continues to lose conjugation with tensile strain, the linewidth alternates between narrowing and broadening depending on the strain level. This behavior is typical of moderately semicrystalline P3HT, in which lamellar crystallites and amorphous regions share mechanical load in a nonuniform fashion. At some strains, only specific lamellar stacks or extended chain segments bear deformation, narrowing the linewidth; at others, a wider distribution of torsional configurations is activated, broadening the peak. The persistence of slight blueshifts after unloading at low-medium strains shows that a portion of the induced disorder is plastically retained, consistent with modest conformational rearrangements within semi-ordered domains.

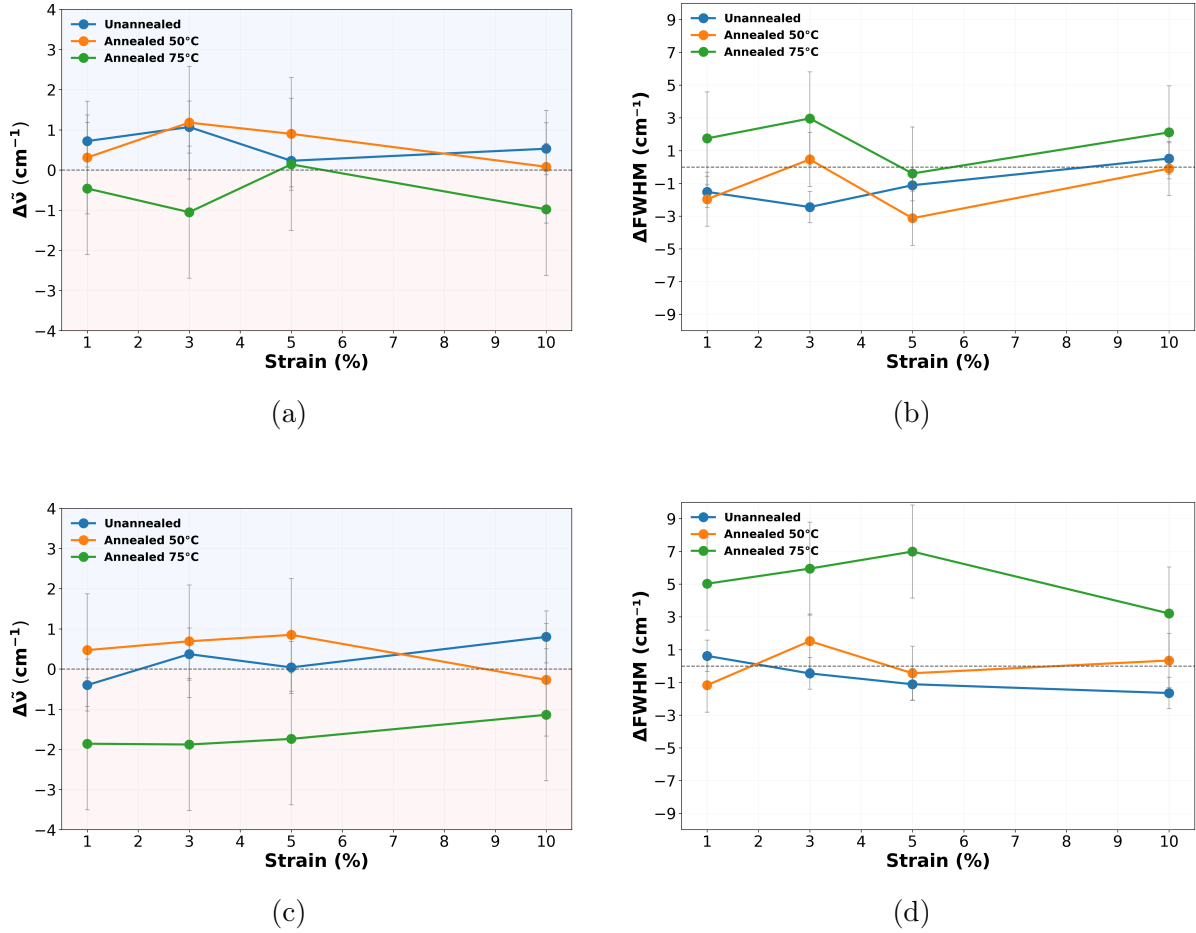


Figure 9.7: Strain dependence of the 1445 cm^{-1} Raman band in PET/P3HT under different annealing conditions. (a) Band-position shift at the instantaneous T_0 state. (b) Corresponding FWHM variation at T_0 . (c) Band-position shift in the post-unloading *Rest* state. (d) Corresponding FWHM variation in the *Rest* state. Curves correspond to unannealed, 50°C -annealed, and 75°C -annealed films.

PET/P3HT annealed at 75°C . A qualitatively different response was observed in the 75°C -annealed PET/P3HT films, where P3HT is substantially more crystalline and mechanically stiff [17]. Here, strain produces redshifts both during loading and after relaxation, accompanied by dramatic linewidth broadening (up to approximately $6\text{--}7\text{ cm}^{-1}$ at *Rest*). This combination is the spectroscopic hallmark of defect-dominated deformation rather than planarization. Highly ordered P3HT lamellae are brittle and prone to early crack onset, interlamellar slip, and strain localization [196, 202]. When such damage accumulates, bond-softening mechanisms and local mechanical decoupling lower the vibrational wavenumber (redshift), while the coexistence of intact, rotated, damaged, and fragmented chain segments produces a highly heterogeneous vibrational environment, manifested as substantial broadening. The irreversible nature of these shifts after unloading indicates that the microstructure of highly annealed (75°C) P3HT undergoes permanent, damage-mediated reorganization rather than reversible backbone

deformation.

9.4.4 Introduction of PEDOT:PSS

PEDOT:PSS unannealed In Fig. 8 below, we have shown the evolution of the 1445 cm^{-1} band as a function of increasing strain at different temperatures with an additional layer of PEDOT:PSS between PET and P3HT. Panels (a) and (c) display the differences in apparent Raman band position. Panels (b) and (d) show the changes in FWHM as compared to the unstretched film. Introducing a PEDOT:PSS interlayer alters these behaviors across all annealing conditions. In unannealed PET/PEDOT:PSS/P3HT, strain induces very minute blue and red shifts, and the linewidth fluctuations, though present, are consistently smaller and more controlled than in the corresponding bare PET/P3HT films. More importantly, apart from 1% strain, the changes in FWHM are also close to the detection limit, which shows that the overall impact of PEDOT:PSS manifests itself as a more stable Raman response.

Annealed P3HT with PEDOT:PSS (50°C). In the 50°C -annealed trilayers, the spectral evolution becomes more balanced: blueshifted and redshifted components coexist, linewidth changes alternate in sign, and the film evolves into a more stable load-bearing configuration at higher strains. Crucially, linewidth broadening is always far less extreme than in the bare PET/P3HT analog.

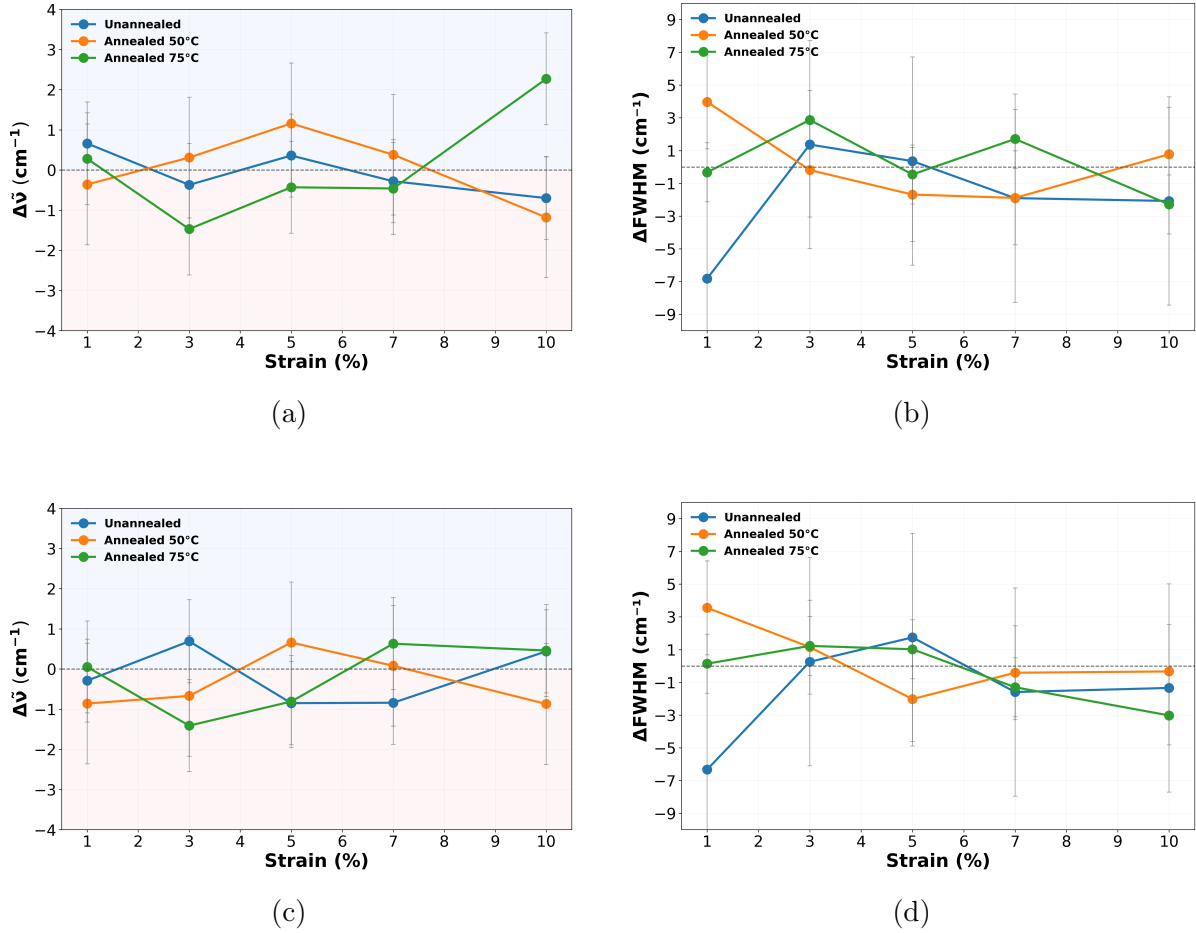


Figure 9.8: Strain dependence of the 1445 cm⁻¹ Raman band in PET/PEDOT:PSS/P3HT under different annealing conditions. (a) Band-position shift at the instantaneous T_0 state. (b) Corresponding FWHM variation at T_0 . (c) Band-position shift in the post-unloading *Rest* state. (d) Corresponding FWHM variation in the *Rest* state. Curves correspond to unannealed, 50°C-annealed, and 75°C-annealed films.

PEDOT:PSS at 75°C The most important and device-relevant stack shows the trends which are well in line with our argument of role of PEDOT:PSS as stabilizing layer. At 75°C-annealed PET/PEDOT:PSS/P3HT stacks, the presence of PEDOT:PSS suppresses the severe broadening and uniformly redshifted behavior observed in the brittle, highly crystalline P3HT films on bare PET. While some mid-strain broadening persists, reflecting partial lamellar rearrangement or defect formation, the overall vibrational signature lacks the catastrophic disordering seen in the absence of the interlayer. This demonstrates that PEDOT:PSS not only improves interfacial adhesion but also dissipates strain energy, allowing brittle P3HT domains to reorganize without undergoing widespread fracture.

9.5 Conclusion and Outlook

We have investigated how mechanical strain and thermal processing jointly govern the response of rr-P3HT thin films integrated on flexible PET substrates using Raman spectroscopy. By systematically tracking band-position shifts and FWHM under controlled stretching, we focused on the two dominant Raman-active modes at 1377 and 1445 cm^{-1} . The combined evolution of band position and linewidth is required to disentangle changes in average backbone configuration from variations in local microstructural heterogeneity. Thermal history emerges as a decisive parameter as the unannealed films deform primarily through reversible conformational adjustment whereas increasing annealing temperature progressively constrains structural mobility, promoting retention of strain-induced configurations and the onset of irreversible damage. In other words, the increased stiffness in annealed films have moved the focus of strain assisted chain alignment to microcracks or damage assisted heterogeneity. Finally, it is important to note a methodological and physical limitation inherent to the present analysis. Although a systematic and controlled experimental approach was employed to ensure that the Raman response provides direct insight into the underlying microscopic processes, the mechanical deformation of thin polymer films inevitably gives rise to microstructural damage that is spatially heterogeneous and, to some extent, stochastic in nature. Such physically relevant microdamage does not necessarily evolve monotonically with applied strain and can therefore manifest as nontrivial or apparently irregular trends in the extracted spectral parameters. This effect is further amplified by the intrinsically low scattering efficiency of Raman spectroscopy, which enhances the influence of local variations and signal fluctuations on the measured response. Consequently, the observed strain dependence should be interpreted in terms of dominant physical regimes and reproducible trends rather than as strictly continuous or deterministic trajectories.

The 1377 cm^{-1} mode provides insight into how tensile strain redistributes microscopic environments. In PET/P3HT, unannealed films exhibit negligible band-position shifts but pronounced FWHM narrowing, indicating selective engagement of mechanically coupled chain populations and largely elastic deformation. Mild annealing at 50 $^{\circ}\text{C}$ shifts the response toward systematic linewidth broadening with minimal wavenumber change, reflecting heterogeneous microstrain within a semi-crystalline morphology. At 75 $^{\circ}\text{C}$ annealing, small but persistent redshifts accompanied by enhanced linewidth broadening reveal a transition to brittle, defect-mediated deformation within highly ordered lamellar domains. Introducing a PEDOT:PSS interlayer modifies this behavior across all annealing conditions. In unannealed trilayers, PEDOT:PSS enhances mechanical coupling and suppresses localized stress concentrations, leading to smoother and more reversible linewidth variations. In annealed films, the interlayer suppresses large irreversible shifts and redistributes strain more uniformly, delaying microstructural damage. Overall,

PEDOT:PSS preserves strain sensitivity while shifting the balance toward recoverable deformation.

The 1445 cm^{-1} band, dominated by the symmetric C=C stretching vibration of the P3HT backbone, provides a more direct probe of backbone-level deformation. In PET/P3HT, unannealed films show strain-induced blueshifts accompanied by linewidth narrowing at low to intermediate strain, consistent with increased torsional disorder coexisting with selective engagement of load-bearing chains. At higher strain, linewidth broadening signals the onset of heterogeneous deformation. Moderate annealing at $50\text{ }^{\circ}\text{C}$ produces a mixed elastic-plastic response, with alternating narrowing and broadening reflecting nonuniform load sharing between crystalline and amorphous regions. In contrast, highly annealed films exhibit pronounced redshifts and strong linewidth broadening that persist after unloading, indicating irreversible, defect-dominated reorganization within brittle crystalline domains. The introduction of PEDOT:PSS again alters this response. In unannealed trilayers, strain-induced shifts and linewidth changes are modest and evolve smoothly, reflecting improved mechanical coupling and reduced strain localization. In annealed systems, PEDOT:PSS suppresses the severe broadening and uniformly redshifted behavior observed in PET/P3HT, even at high strain, demonstrating efficient dissipation of strain energy and stabilization of the P3HT microstructure.

Taken together, these results establish that mechanical stretching does not universally enhance order in conjugated polymer films. Instead, the strain response reflects a balance between processing-induced constraint and deformation-induced redistribution, governed jointly by thermal history and stack architecture. The PEDOT:PSS interlayer plays an active mechanical role by redistributing strain, suppressing defect accumulation, and stabilizing ordered domains, in addition to its established electronic function. Raman spectroscopy combined with controlled mechanical loading thus provides a direct probe into how backbone conformation, microstructural order, interfacial mechanics, and damage accumulation evolve under strain. The framework established here offers practical guidance for defining safe deformation regimes and for the rational design of mechanically robust organic semiconductor stacks for flexible and wearable optoelectronic applications.

Chapter 10

Conclusion and Outlook of Thesis

This Ph.D. thesis presents the research conducted at Constructor University in the field of time and frequency-resolved spectroscopy applied to organic semiconductors. The work was carried out under the scientific supervision of Prof. Dr. Arnulf Materny. At the same time, all sample preparation and device-related processing were performed in the laboratory of Prof. Dr. Veit Wagner at Constructor University. Within the broad class of conjugated polymers, poly(3-hexylthiophene) (P3HT) was selected as a model system to investigate the fundamental photophysical and structural mechanisms that govern the performance of organic photovoltaic materials. Complementary experimental approaches, including time-resolved femtosecond transient absorption spectroscopy, Raman spectroscopy, and UV–Vis absorption spectroscopy, were employed to develop both a fundamental and device-relevant understanding of photophysical processes and of mechanically induced structural modifications relevant to organic photovoltaic applications.

Chapter 4 discusses the generation and decay dynamics of polaron pairs (PPs) in neat P3HT thin films and diode structures. Through wavelength-dependent femtosecond pump–probe measurements, it was demonstrated that below-band-gap excitation can efficiently generate charge-pair states despite weak linear absorption at the excitation wavelength. These results challenge the commonly assumed exclusive hot-exciton dissociation pathway and instead indicate a direct excitation channel for PP formation. In addition to ultrafast decay components, longer-lived species were observed and assigned to more delocalized charge-pair states (DP_2). Field-dependent measurements under forward and reverse bias further revealed a competition between recombination and bimolecular annihilation processes, emphasizing the role of electric-field-assisted separation and interaction of charge carriers in P3HT-based devices.

Chapter 5 examined how mechanical strain influences ultrafast charge-carrier dynamics in neat P3HT films deposited on PET substrates. Femtosecond transient absorption mea-

surements revealed a redistribution of amplitudes and lifetimes within the bi-exponential decay components as a function of applied strain. Variations in the relative contributions of fast-decaying PPs and longer-lived DP_2 states indicate that mechanical deformation modifies intermolecular coupling, electronic delocalization, and recombination pathways. These findings establish a direct connection between macroscopic mechanical deformation and microscopic charge-transport dynamics.

Chapter 7 addresses the structural and vibrational response of PET substrates under mechanical stretching, investigated using Raman and UV–Vis spectroscopy. Systematic shifts in characteristic vibrational modes and changes in linewidths revealed strain-induced conformational rearrangements between *trans* and *gauche* configurations within the polymer backbone. The transition from largely reversible spectral shifts at low strain to irreversible modifications at higher deformation levels marks the onset of permanent structural reorganization. This analysis provides a necessary substrate reference framework, enabling a clear distinction between intrinsic P3HT responses and substrate-induced effects in flexible device configurations.

Chapter 8 focused on the strain-dependent optoelectronic response of P3HT films on flexible PET substrates. UV–Vis spectroscopy showed that the optical band gap remains largely invariant up to moderate uniaxial strain, indicating substantial electronic robustness under mechanical deformation. Beyond a critical strain threshold, subtle but systematic spectral changes emerged, suggesting modifications in interchain coupling and effective conjugation length. These results define quantitative strain limits within which the electronic structure of P3HT remains stable, offering practical guidelines for mechanically resilient flexible photovoltaic design.

In the final chapter 9, the combined effects of uniaxial strain and thermal annealing on the vibrational properties of regioregular P3HT films using Raman spectroscopy are investigated. Detailed analysis of the C–C and C=C stretching modes—including their peak positions and full width at half maximum—revealed a complex interplay between strain-induced chain alignment and thermally enhanced crystallinity. Films annealed at elevated temperatures exhibited increased structural rigidity and a more defect-dominated response under strain, whereas less ordered films showed comparatively reversible behavior. Importantly, the incorporation of a poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) interlayer significantly influenced the strain response, modifying both the magnitude and reversibility of Raman shifts. The presence of PEDOT:PSS altered strain transfer and interfacial coupling, highlighting the crucial role of device architecture in governing mechanical and vibrational stability. These observations collectively demonstrate that processing conditions and interfacial layers critically determine the mechanical tolerance and structural resilience of flexible organic semiconductor systems.

Taken together, the results of this thesis establish a coherent framework describing how excitation wavelength, electric fields, mechanical strain, thermal treatment, and interfacial engineering collectively govern the structural and dynamical behavior of P3HT and PET-based systems. By linking ultrafast charge dynamics with vibrational signatures and macroscopic mechanical effects, this work advances the understanding of structure–property relationships in organic semiconductors and provides experimentally grounded design principles for the development of robust, flexible photovoltaic devices.

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