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Wilson, Reid William

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Utilizing time-domain thermoreflectance (TDTR) and
Developing transient thermoreflectance (TTR) to investigate
Doping-induced changes in the thermal transport of
Chemically-doped semiconducting polymer systems

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy in Chemistry

by

Reid William Wilson

2026

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2026

ABSTRACT OF THE DISSERTATION

Utilizing time-domain thermoreflectance (TDTR) and
Developing transient thermoreflectance (TTR) to investigate
Doping-induced changes in the thermal transport of
Chemically-doped semiconducting polymer systems

by

Reid William Wilson

Doctor of Philosophy in Chemistry

University of California, Los Angeles, 2026

Professor Benjamin J. Schwartz, Chair

Chemically-doped conjugated polymers are a class of emerging semiconducting materials with unique and advantageous properties distinct from inorganic semiconductors, including solution processability, mechanical flexibility, highly tunable electronic behavior, and intrinsically low thermal conductivity. These properties make them promising candidates for thermoelectric applications, where temperature gradients are converted into electrical energy or vice versa. Such devices are relevant for applications ranging from industrial waste heat recovery to wearable electronics powered by body heat.

Research on chemically-doped conjugated polymers has historically focused on maximizing the thermoelectric power factor, which depends on the electrical conductivity and the Seebeck coefficient. However, full quantification of thermoelectric performance also requires

knowledge of the thermal conductivity to calculate the thermoelectric figure of merit, a measure of the degree of energetic conversion efficiency. Despite the importance of the figure of merit, the thermal conductivity of chemically-doped conjugated polymers remains poorly characterized. Most calculations of the figure of merit incorporate either thermal conductivity values that are representative of the undoped polymer or values from measurements embedded with a multitude of poor assumptions.

This lack of thermal conductivity measurements largely arises from experimental challenges. Conjugated polymers exhibit very low thermal conductivities (below $1 \text{ W m}^{-1} \text{ K}^{-2}$), resulting in weak measurement signals. Additionally, these materials are typically studied as thin films (tens to hundreds of nanometers thick), requiring careful modeling of adjacent layers that often have much higher thermal conductivities and thus dominate the thermal response. Many measurement techniques operate in high-frequency regimes, probing thermal diffusivity rather than conductivity directly, which necessitates the accurate knowledge of volumetric heat capacity to extract the thermal conductivity. Because volumetric heat capacity is rarely measured in doped polymer systems due to separate measurement challenges, researchers often unphysically assume it remains unchanged from the undoped polymer. Furthermore, doped conjugated polymers may be both heat-sensitive and chemically reactive when exposed to certain environmental conditions and materials, respectively, during various measurement techniques.

This thesis addresses these challenges by focusing on fully understanding the nature of changes in conjugated polymer thermal conductivity upon doping. The focus is on doped poly(3-hexylthiophene-2,5-diyl) (P3HT), a widely studied *p*-type conjugated polymer. The approach combines experimentally-measured volumetric heat capacities with thermoreflectance techniques that probe thermal diffusivity or effusivity. Structural analysis using X-ray diffraction is used to interpret changes in thermal transport, while electrical conductivity and Seebeck measurements enable a full evaluation of thermoelectric performance.

Chapter 2 of this thesis specifically examines how volumetric heat capacity, thermal conductivity, and the thermoelectric figure of merit vary as a function of different amounts of doping with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ). Conventional time-domain thermoreflectance (TDTR) is employed to measure cross-plane thermal conductivity. The results show that both the volumetric heat capacity and thermal conductivity vary non-monotonically with doping, contradicting the common assumption that these properties remain unchanged from the undoped state. These variations are linked to doping-induced changes in crystallinity, morphology, and the incorporation of dopant molecules at higher concentrations.

Chapter 3 of this thesis introduces a new technique, femtosecond transient thermoreflectance (fs-TTR), which uses a low-repetition-rate, high-pulse-energy amplified ultrafast laser, as well a newly-derived thermal model to interpret fs-TTR data. The new method has improved measurement accuracy compared to conventional TDTR of the cross-plane thermal conductivity, particularly for low-thermal-conductivity polymeric thin-films. For example, the lack of pulse accumulation-induced heat built-up from the low repetition rate allows control over the thermal penetration depth, preventing substrate effects from influencing the thermoreflectance signal. The easy achievability of large pump-probe spot-size ratios allows the measurement to achieve rigorous one-dimensional axial heat transport in materials with thermal anisotropy. The ability to spectrally probe the thermoreflectance signal simultaneously at multiple wavelengths yields an improved signal-to-noise ratio compared to single-wavelength measurements that rely on lock-in amplification. These advantages allow fs-TTR to measure both the thermal conductivity and thermal boundary conductance with an accuracy comparable to or slightly exceeding that of conventional TDTR, making it well suited for chemically-doped polymer thin-film systems.

Chapter 4 of this thesis presents preliminary fs-TTR measurements of P3HT films doped with dodecaborane clusters functionalized with 3,5-bis(trifluoromethyl)benzyloxy functional groups (referred to as DDB-F₇₂), a bulkier and much stronger oxidizing dopant than F₄TCNQ. The

use of DDB-F₇₂ as a dopant not only improves carrier mobility, but also may achieve very low cross-plane thermal conductivity and higher thermoelectric figure of merit values compared to F₄TCNQ-doped P3HT. Preliminary results suggest that the cross-plane thermal conductivity of DDB-F₇₂-doped P3HT films monotonically decreases by an order of magnitude by high doping levels under the assumption that the volumetric heat capacity remains the same as the undoped polymer. Preliminary density measurements show that the film density monotonically increases upon doping with DDB-F₇₂, suggesting that the volumetric heat capacity of these composite systems differs from that of the undoped polymer, although specific heat measurements are still needed to confirm this. The thermorefective decays of DDB-F₇₂-doped P3HT films show a large-amplitude damped oscillation of unknown origin that dominates the signal during the timeframe needed to extract information about heat transfer within the doped polymer film. This means that thermal conductivity values for these doped P3HT systems cannot be defined until the damped oscillation is fully understood, a subject for future work. However, combining our preliminary thermal conductivity results with measured power factors reveal that DDB-F₇₂-doped P3HT may reach zT values of up to 0.18.

The dissertation of Reid William Wilson is approved.

Justin R. Caram

Alexander M. Spokoyny

Yves F. Rubin

Benjamin J. Schwartz, Committee Chair

University of California, Los Angeles

2026

To my twin sister, Olivia.
To my younger brother, Will.
To my beautiful girlfriend, Sarah.

“Pick a flower on Earth and you move the farthest star.”

– Paul A.M. Dirac

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The text portion of Chapter 2 of this dissertation is an adaption of the material as it appears in Wilson et al. *Adv Funct Materials* **2026**, e76788. DOI: 10.1002/adfm.76788, used with permission from Wiley. The dissertation author is also the first author and primary researcher of this publication. The co-authors listed in this publication are Xinping Shi, Diego Garcia Vidales, Abigail Slimp, Zerina Mehmedović, Alexander F. Simafranca, Eric C. Wu, Sarah H. Tolbert, Richard B. Wilson, and Benjamin J. Schwartz. Benjamin J. Schwartz directed and supervised the research in this article (and dissertation as a whole). Chapter 3 of this dissertation is an adaption of the material as it appears in Wilson et al. *Chem. Mater.* **2026**. DOI: 10.1021/acs.chemmater.6c01465. The dissertation author is co-first author (with Jack Kelleher-Ferguson) and the primary researcher of this publication. The co-authors listed in this publication are Jack Kelleher-Ferguson, Eric C. Wu, and Benjamin J. Schwartz. Benjamin J. Schwartz directed and supervised the research in this article. Chapter 4 is unpublished work directed and supervised by Benjamin J. Schwartz. Jack Kelleher-Ferguson, Xinyu Liu (co-advised by Prof. Sarah H. Tolbert and Prof. Yves Rubin) and Hashim Al Khunaizi (advised by Prof. Alexander M. Spokoyny) directly contributed to portions of this chapter in the form of materials synthesis, fabricating samples, performing experiments, and working up data.

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VITA

- 2022 Michael E. Jung Excellence in Teaching Award, UCLA
- 2020–2022 M.S. in Chemistry, UCLA
- 2020 Graduate Dean’s Scholar Award, UCLA Division of Graduate Education
- 2016–2019 B.S. in Chemistry, University of Connecticut

PUBLICATIONS

Wilson, R.W.; Kelleher-Ferguson, J.; Wu, E. C.; Schwartz, B. J. Transient Thermoreflectance with an Amplified Laser Simplifies Heat Transfer Modeling to Determine the Thermal Transport Properties of Materials. *Chem. Mater.* **2026**. <https://doi.org/10.1021/acs.chemmater.6c01465>.

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Chapter 1: Introduction

1.1 Chemically-doped conjugated polymers as thermoelectric materials

Chemically-doped conjugated polymers have become widely implemented in modern organic electronics as semiconducting materials because they provide a solution-processable means to tune electrical properties while preserving the fabrication and mechanical property advantages of ubiquitously-used polymeric materials.¹⁻⁵ For instance, while inorganic semiconducting materials such as Si require high-purity, energy-intensive processing and sometimes doping with scarce trace elements, semiconducting polymers are typically comprised of Earth-abundant, affordable, low-molecular weight carbon-, nitrogen-, oxygen-, sulfur- and hydrogen-containing monomers. Furthermore, semiconducting polymers are mechanically flexible materials that can conform to a variety of curved,³ a significant advantage over rigid inorganic semiconductors for many applications. Having mechanical flexibility allows semiconducting polymers to be used for unique electronic applications such as wearable devices with biocompatibility,^{6,7} curved light-emitting diode (LED) displays,⁸ organic photovoltaics (OPVs),⁹ and shape-conforming thermoelectric devices,¹⁰ the latter of which convert captured waste heat to electricity (Seebeck effect) or generate a temperature gradient from an applied potential (Peltier effect).

To improve the electrical properties of semiconducting polymer systems, the process of chemical doping is used to control the density of charge carriers on the conjugated backbone through redox or charge-transfer interactions. When the backbone is reduced and an electron is the charge carrier, the semiconductor is *n*-type. Conversely, when the polymer is oxidized and a hole serves as the charge carrier, the semiconductor is *p*-type. Collectively, these charge carriers and their associated lattice distortions are referred to as polarons.

As a thermoelectric material, semiconducting polymers are tuned in various ways (choice of dopant molecule, the molecular structure of the polymer, processing techniques, etc.) to maximize the figure of merit, zT , described by Eq. 1.1 below:¹⁰

$$zT = \frac{\sigma S^2}{\kappa} T, \quad (1.1)$$

where σ is the electrical conductivity, S is the Seebeck coefficient, κ is the thermal conductivity, and T is the absolute temperature, which appears on both sides of the equation to make zT unitless. When zT is high, the thermoelectric efficiency (the capacity to convert energy between a voltage potential and a temperature gradient, or vice versa) of a material is greater, and values of about 1 are necessary for many applications in practical devices.¹⁰ At present, doped semiconducting polymers typically have zT values that are substantially (one to several orders of magnitude) below those of inorganic semiconducting materials,¹⁰ although efforts to improve the capabilities of semiconducting polymers are underway. The past few decades of research on semiconducting polymers have largely focused on the numerator of Eq. 1.1, σS^2 , which is referred to as the power factor.¹¹⁻²⁹ This previous work has shown that generating charge carriers through chemical doping reshapes the electronic structure, microstructure, morphology and thermodynamic stability of polymer systems, increasing σ at the expense of decreasing S . Often, there is a ‘sweet spot’ where the power factor reaches a maximum as a function of the number of charge carriers, as seen in **Figure 1.1**.

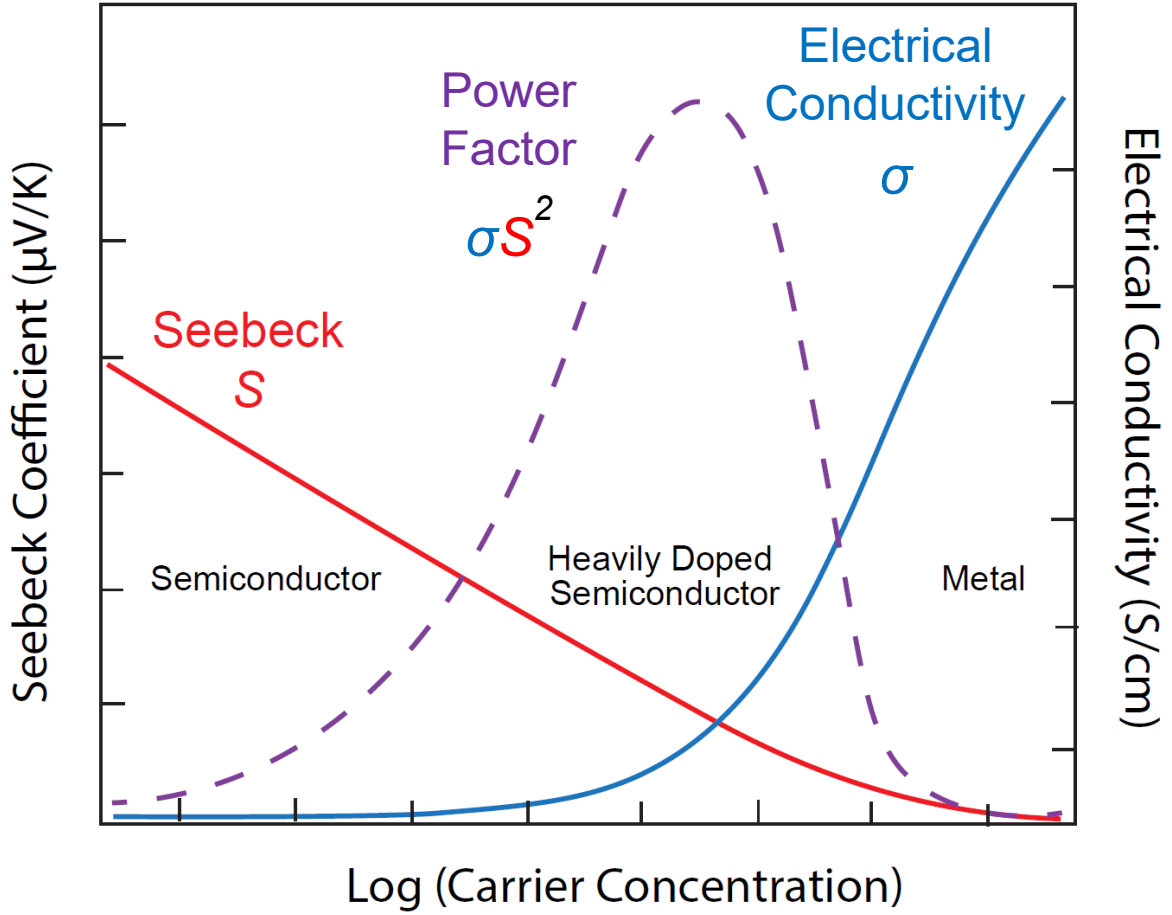


Figure 1.1. Schematic showing that as the carrier concentration (x -axis) increases, the electrical conductivity (in blue) increases at the expense of the Seebeck coefficient (in red). A ‘sweet spot’ or peak thus exists for the power factor, σS^2 (in purple).

However, Eq. 1.1 shows that optimizing the power factor alone is insufficient to maximize zT without a thorough understanding of how κ responds to doping and changes in the carrier density. Heat transfer within materials tends to be driven by either electronic (κ_{el}) or lattice vibrational (κ_{lat}) contributions, or by a combination of the two, as described by Eq. 2:³⁰

$$\kappa = \kappa_{\text{el}} + \kappa_{\text{lat}}. \quad (1.2)$$

In doped conjugated polymer systems, it is unclear to what extent charge carriers (electrons or hole polarons) contribute to heat transport through κ_{el} , which is related to the electrical conductivity

through the Wiedemann-Franz law (which is typically applied for materials with metal-like electronic transport).³⁰⁻³²

$$\kappa_{\text{el}} = L\sigma T, \quad (1.3)$$

where L is the Lorenz number. It is generally reported that doped conjugated polymers with $\sigma < 10 \text{ S cm}^{-1}$ have thermal conductivities that are dominated by κ_{lat} .³³⁻³⁵ However, polymer-dopant systems with σ in the 10's to 100's of S cm^{-1} can be readily achieved so κ_{el} may become a non-negligible contribution to the total κ in those systems, potentially limiting thermoelectric performance. Despite this, κ is vastly understudied across both p - and n -type semiconducting polymers, with only a few dozen total studies across the entire literature.^{33,36-62} Consequently, many researchers assume that the κ of a doped polymer system is equivalent to that of the undoped polymer in calculations of zT , an assumption that we will show below introduces significant systematic error given that doping-induced changes in microstructure, charge carrier density, and molecular packing all meaningfully alter heat transport.

The lack of studies on the κ of doped conjugated polymers is due to a plethora of issues related to limits imposed by the experimental techniques available and by the nature of the samples. Firstly, there is a general challenge in reliably measuring thermal conductivities that are $< 1 \text{ W m}^{-1} \text{ K}^{-1}$ ($0.1\text{--}1 \text{ W m}^{-1} \text{ K}^{-1}$ is typically the regime of undoped conjugated polymers), as poor thermal conductors yield small signals. Additionally, conjugated polymers are typically studied as thin films (only tens to hundreds of nm thick), which eliminates most steady-state methods for determining the thermal conductivity. High-frequency methods work better in this regime, but require knowledge of the volumetric heat capacity, C_v , to determine κ . This is because these methods typically probe thermal diffusivities, α , or effusivities, r , which are related to κ through Eq. 1.4:

$$\kappa = \alpha\rho C_p = \alpha C_v = \frac{r^2}{C_v}, \quad (1.4)$$

where the product of mass density, ρ , and the specific heat at constant pressure, C_p , are equal to C_v . The C_v 's of dopant-polymer composite systems are severely understudied, again because they are not easily measurable due to the fact that instruments that measure C_p require many mg of sample, which is orders of magnitude more mass than typically present in a doped conjugated polymer thin film). In addition to the issue of needing C_v for κ measurements, most methods for determining thermal conductivity also require the placement of metals and/or a dielectric layer on top of the thin film. Exposing films to heat during metal deposition and to easily oxidizable metals can de-dope *p*-type conjugated polymers, altering the sample being measured.

As an example of the issues with thermal measurements on doped conjugated polymer systems, we focus on thermal conductivity studies involving poly(3-hexylthiophene-2,5-diyl) (P3HT) doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F₄TCNQ), the molecular structures of which are shown in **Figure 1.2**.

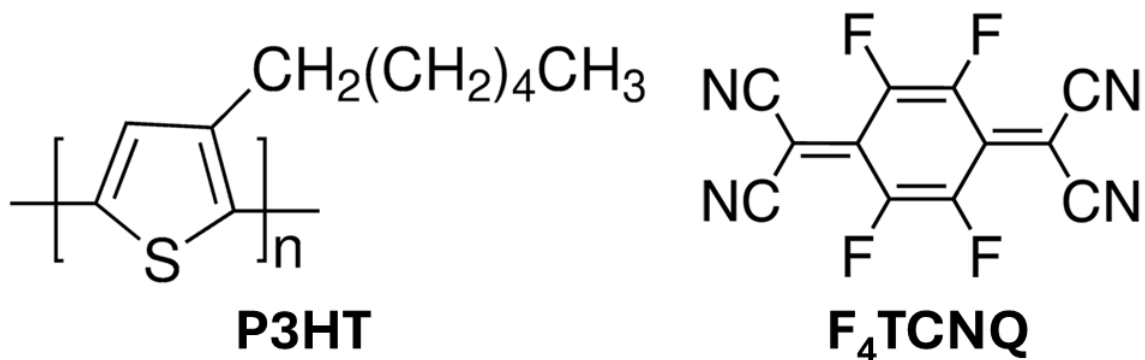


Figure 1.2 Molecular structures of poly(3-hexylthiophene-2,5-diyl) (P3HT), at left and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F₄TCNQ), at right.

P3HT is the most extensively studied *p*-type conjugated polymer, and its power factor, microstructure, and charge transport properties have been well-characterized across a wide range of doping conditions.^{11-29,63-66} This makes this material the natural model system for investigating how κ changes as a function of doping. However, the few studies that have probed the cross-plane

thermal conductivity of F₄TCNQ-doped P3HT thin films not only disagree as to the value of κ after doping,⁴⁸⁻⁵¹ but also do not even agree as to whether doping with F₄TCNQ increases or decreases κ relative to undoped P3HT. Resolving this conflict requires understanding how doping-induced changes in crystal structure, carrier density, dopant density and volumetric heat capacity all influence heat transport. It is for this reason that chemically-doped P3HT is the conjugated polymer of focus throughout this thesis.

The unanswered questions that are pertinent to developing energetically efficient thermoelectric materials, which we study through the lens of chemically-doped P3HT and that we address, include: 1) What factors control heat transport in doped semiconducting polymers? 2) How does the process of chemical doping influence heat transport in conjugated polymers? 3) How do charge carriers contribute to the thermal conductivity in doped conjugated polymers, and is the Wiedemann-Franz approximation appropriate for these systems? 4) How can the thermal conductivity of chemically-doped conjugated polymers be tuned (minimized) to maximize the figure of merit, zT , of thermoelectric devices based on these materials?

1.2 Experimental methods to determine the κ of different materials

Thermal conductivity measurement techniques can be categorized into three groups: steady-state, low-frequency, and transient methods.^{67,68} Steady-state methods, such as steady-state thermoreflectance (SSTR),^{69,70} Raman thermometry,⁷¹ and scanning thermal microscopy (SThM),^{72,73} establish a time-invariant temperature gradient across the sample and directly measure the resulting heat flux, from which κ is extracted. This type of measurement does not require knowledge of C_v . Low-frequency methods, which include 3ω ,^{74,75} Ångström technique,⁷⁶ and certain modulated frequency ranges of frequency-domain thermoreflectance (FDTR),^{77,78} rely on the sinusoidal heating and cooling of the sample to extract relevant thermal properties using a quasi-steady-state thermal model, and similarly do not require C_v as thermal resistances are

directly measured. Transient techniques, such as conventional forms of time-domain (TDTR) and transient thermoreflectance (TTR),⁷⁹⁻⁸² transient grating spectroscopy (TGS),⁸³ transient electro-thermal (TET),^{84,85} transient hot-wire (THW),^{86,87} and flash-differential scanning calorimetry (Flash-DSC),^{88,89} instead utilize the time-evolution of the sample's thermal response to a laser pulse or electrical current pulse to deduce κ , and consequently (due to their high-frequency nature) require knowledge of C_v to do so.

At first glance, steady-state and low-frequency methods appear advantageous over transient methods for doped conjugated polymers because they typically do not require C_v . As stated, it is difficult and thus rare for C_v to be experimentally determined for chemically-doped conjugated polymer thin-film materials, and groups using transient methods have consequently been forced to either: 1) assume that C_v of the dopant-polymer composite is equivalent to that of the undoped polymer,^{48,60,90-92} or 2) extrapolate how C_v changes with doping from isolated one-off measurements.⁴⁹ Since $\kappa = \alpha C_v$, as shown in Eq. 4, any error in C_v propagates directly into the extracted κ , representing a potentially significant and often unacknowledged source of error in the reported values. In fact, we argue below that much of the inconsistency in the different reported values of the κ of F₄TCNQ-doped P3HT films^{48,49} mentioned is due to differences in how C_v is treated, as most groups do not experimentally measure the C_v of their F₄TCNQ-doped P3HT samples.

Despite the potential advantage of using methods that do not require knowledge of C_v , quasi-steady-state and low-frequency electrothermal techniques such as 3ω and Ångström's method impose sample preparation requirements that are problematic for chemically-doped conjugated polymer thin-films. Because these techniques pass electrical current through a patterned metal electrode, an electrically insulating layer must be present between the electrode and the film as doped polymer films are also electrically conductive. Additionally, the electrode geometries required by these methods demand sufficiently flat samples over large lateral

dimensions, and usually require photolithographic patterning. Both the deposition of insulating layers and photolithographic processing involve chemical and thermal exposures that risk de-doping the polymer film, thus altering the material properties under investigation.

Among the transient techniques, not all are well-suited to thin-film geometries. TET and THW are designed for freestanding films or samples with wire-like geometries and cannot easily be applied to thin polymer films supported on a substrate. Flash-DSC operates on bulk powders or small bulk specimens rather than thin films. Optical laser-based transient techniques, specifically TDTR and TTR (as well as high-frequency-regime FDTR), are the most naturally suited methods for cross-plane measurements of thin-film samples, and require only the deposition of a uniform, sufficiently-thick metal transducer atop the film, a comparatively simple preparation step that (with an appropriately selected metal) minimizes chemical and thermal exposure to the doped polymer. For these reasons, TDTR and TTR will be the techniques implemented in this thesis to measure the thermal properties of chemically-doped polymer thin-films.

1.3 TDTR as a method to determine the κ of thin-film devices

Time-domain thermoreflectance (TDTR) is a pump-probe optical technique that measures the thermal properties of materials by monitoring the time-resolved thermoreflective signal of a metal transducer following laser pulse heating.⁸⁰⁻⁸² The nature of the decay of the thermoreflective signal as a function of time is directly related to the change in temperature of the transducer because the reflectivity of the metal is temperature dependent. Therefore, how heat diffuses within the transducer layer, and by extension the adjacent material layers that are in thermal contact with the transducer, as the heated sample cools can be monitored via changes in the temperature and thus reflectance of the transducer via a probe pulse.

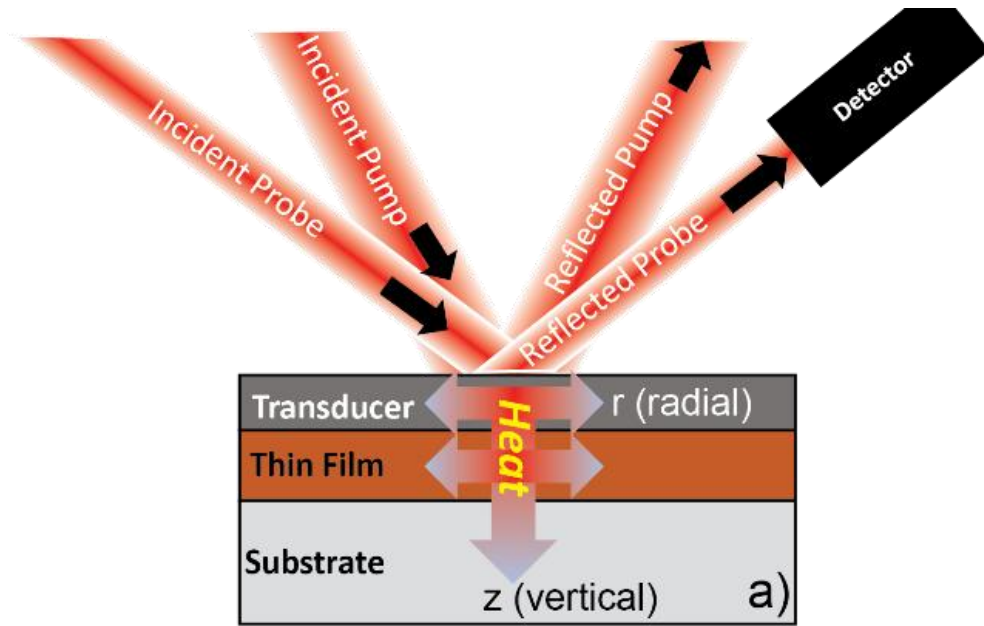


Figure 1.3. A cartoon of the pump-probe interactions with a multi-layer sample in a conventional TDTR experiment. A pulsed incident pump beam first deposits heat to the sample through the absorption of light by the metal transducer. At a controlled time after, the probe pulse monitors the change in reflectivity of the transducer; the reflectivity depends on the transducer temperature, which in turn depends on the rate at which the underlying material layers transport heat away.

In a typical TDTR setup, which uses a high-repetition-rate oscillator-type laser, the pulsed laser source is split into a high-intensity pump beam and a low-intensity probe beam. The pump beam is modulated at a fixed frequency (typically 1–20 MHz) and focused onto the sample surface, where it is absorbed by the transducer, as shown in **Figure 1.3**. The probe beam timing is controlled by a variable mechanical delay stage and the reflected signal is detected by a lock-in amplifier referenced to the pump modulation frequency, which isolates the thermally-induced reflectance change from background noise. This yields both in-phase and out-of-phase signal components as a function of pump-probe delay time.

The thermal conductivity of the sample is extracted by fitting a thermal model to the measured thermorefectance decay. The most widely used model treats the sample as a stack of

homogeneous, thermally isotropic layers and solves the heat diffusion equation in the frequency domain using a thermal transfer matrix approach,⁹³⁻⁹⁵ accounting for the Gaussian spatial profile of the pump and probe beams and the pump modulation frequency. Each layer in the sample is characterized by its thermal diffusivity, α , (or effusivity, r), volumetric heat capacity, C_v , and thickness. Special consideration must be given for the pump/probe spot sizes and modulation frequency, as different spot size geometries can have different sensitivities to heat diffusion in the radial and vertical directions of the sample. In the high modulation frequency/large pump beam regime, heat diffusion is quasi-1-D, allowing access to the cross-plane thermal conductivity of the material layer, while the low modulation frequency/small beam limit requires fitting both in-plane and out-of-plane thermal diffusion components. Additionally, the interfaces between material layers must also be modeled as heat moves from one layer to another during heat diffusion, as modeled using a thermal boundary conductance (TBC).

The thermal model is fitted to the measured thermoreflectance decay curve, which is comprised of the ratio of the in-phase to out-of-phase lock-in signals, $-V_{in}/V_{out}$, in conventional TDTR.⁸⁰⁻⁸² For a multilayer system, such as a metal transducer on a polymer thin film on a substrate, the sensitivity of the measurement to each of the individual layer's properties depends on the relative magnitude of that layer's thermal resistance compared to the total stack resistance, the modulation frequency, and the pump and probe beam sizes,⁸⁰⁻⁸² all of these influences must be considered to maximize sensitivity to the parameter of interest (usually the cross-plane κ of the polymer thin film layer) while minimizing correlation between the other free parameters in the fit. Unfortunately, in the case of low- κ thin film samples, conventional TDTR cannot simultaneously determine multiple unknown fitting parameters (κ and TBC).^{80,96} For instance, polymeric thin-films are typically sandwiched between high- κ transducer and substrate layers. The thickness of the polymer thin-film layer must be appropriately tuned to minimize substrate-dominated effects to reliably determine values for κ . This often means that choosing sample parameters to optimize

extraction of κ leads to having poor sensitivity to determining the TBC. Solving this problem will be the topic of the third chapter of this thesis, described briefly below.

1.4 Overview of this Thesis

The remainder of this thesis is comprised of three chapters. Two of the chapters implement transient varieties of thermoreflectance methods to measure the thermal properties of chemically-doped conjugated polymers, while the remaining chapter improves upon TTR by developing a novel instrumental method around a transient absorption-configured amplified ultrafast system to more simply and accurately measure the thermal properties of low- κ thin-film samples.

1.4.1 Chapter 2: Non-monotonic changes of the thermal conductivity of conjugated polymer films with increasing levels of chemical doping

The work in this chapter has been adopted from the following published article: Wilson, R. W.; Shi, X.; Vidales, D. G.; Slimp, A.; Mehmedović, Z.; Simafranca, A. F.; Wu, E. C.; Tolbert, S. H.; Wilson, R. B.; Schwartz, B. J. Non-Monotonic Changes in the Thermal Conductivity of Conjugated Polymer Films with Increasing Levels of Chemical Doping. *Adv Funct Materials* **2026**, e76788.⁹⁷ The performance of thermoelectric materials is characterized by the figure of merit (zT), which depends on knowing the thermal conductivity (κ). Poly(3-hexylthiophene-2,5-diyl) (P3HT) films doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ) are a prototypical conjugated polymer system studied for potential use in thermoelectrics. However, the few reports for this system disagree as to whether κ increases or decreases upon doping. This disagreement is partly due to the use of measurement techniques that rely on knowing the volumetric heat capacity (C_v) to determine κ , even though the C_v of conjugated polymers has not been systematically investigated as a function of doping. Here, we experimentally determine both C_v , using differential scanning calorimetry and careful density

measurements, and thermal effusivity, using time-domain thermoreflectance (TDTR), to reveal how the κ of both regioregular and regiorandom P3HT changes as a function of doping with F₄TCNQ. Our results show that both C_v and κ change non-monotonically with the intercalated F₄TCNQ:thiophene monomer ratio. At low doping ratios, κ increases because of doping-induced crystal structure changes, while at higher doping ratios, κ decreases because of the increasing density of F₄TCNQ[−] counterions in the crystal lattice. We find that F₄TCNQ-doped P3HT films can achieve zT values of 5.2×10^{-3} .

1.4.2 Chapter 3: Transient thermoreflectance with an amplified laser simplifies heat transfer modeling to determine the thermal transport properties of materials

The work in this chapter has been adopted from the following published Method/Protocols article: Wilson, R. W.; Kelleher-Ferguson, J.; Wu, E. C.; Schwartz, B. J. Transient Thermoreflectance with an Amplified Laser Simplifies Heat Transfer Modeling to Determine the Thermal Transport Properties of Materials. *Chem. Mater.* **2026**. <https://doi.org/10.1021/acs.chemmater.6c01465>.⁹⁸ Time-domain thermoreflectance (TDTR) is a pump-probe method typically used to measure both the cross-plane thermal conductivity (κ) of thin films and bulk materials and the thermal boundary conductance (σ) of material interfaces. Conventional TDTR relies on high-repetition-rate (MHz) ultrafast oscillators with low per-pulse energy, which require tightly-focused pump beams to generate measurable thermoreflectance signals. This tight focusing necessitates thermal models with both lateral and cross-plane heat diffusion components that have strong sensitivity to the exact pump size. High repetition rates also cause heat buildup (pulse accumulation), requiring periodic steady-state thermal modeling, and for thin films, modeling of heat flow into the substrate. This can be challenging for polymeric materials that exhibit anisotropic transport and often have very low κ and high surface roughness. Here, we introduce a new approach built around a standard kHz rep-rate amplified ultrafast laser

transient absorption set-up, which we call femtosecond transient thermoreflectance (fs-TTR). The orders-of-magnitude higher per-pulse energy and lower repetition rate enable a simplified one-dimensional cross-plane heat transport model without pulse accumulation. The fs-TTR thermal model permits simultaneous fitting of κ and σ , which we demonstrate for materials spanning four orders of magnitude in thermal conductivity, including very low- κ polymer thin films. The direct measure of pump-on/pump-off changes in reflectivity, along with probing transient reflectance simultaneously at multiple wavelengths, makes fs-TTR an equal, or in some cases, an improved alternative to conventional oscillator-only TDTR.

1.4.3 Chapter 4: Using fs-TTR to determine the thermal properties of DDB-F₇₂-Doped RR-P3HT Films

The work in this chapter focuses on a collection of preliminary, unpublished results that investigate how the cross-plane thermal conductivity changes as a function of doping level in DDB-F₇₂-doped P3HT thin-film systems. It implements our new fs-TTR method, described in Chapter 3, to measure the thermoreflective decay traces of these systems in an attempt to directly measure the cross-plane thermal diffusivity. However, damped oscillations of unknown origin dominate the thermoreflective traces within the same probe delay time window as the region needed to extract thermal diffusivity. Thus, accurate thermal diffusivity values cannot be resolved until the physical origins of the damped oscillation are understood so that this aspect of the signal can be incorporated into our fs-TTR model. However, a crudely modified fs-TTR model that incorporates a damped harmonic oscillation is used to extract information about the oscillation itself and to determine preliminary values for cross-plane thermal conductivity. This section also investigates how the film mass density, electrical conductivity, Seebeck coefficient, and film crystal structure (using X-ray diffraction techniques) of P3HT changes as a function of doping

with DDB-F₇₂ and applies preliminary thermal conductivity results to calculate figure of merit values.

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Chapter 2: Non-monotonic changes in the thermal conductivity of conjugated polymer films with increasing levels of chemical doping

2.1 Introduction

Doped semiconducting polymers are being developed as materials for thermoelectric applications due to their chemical tunability, mechanical flexibility, and material affordability.^[1,2] The thermoelectric energy conversion efficiency is typically quantified using the figure of merit, zT , which involves the electrical conductivity, σ , the Seebeck coefficient, S , and the thermal conductivity, κ , of a material via:^[3-5]

$$zT = \frac{\sigma S^2}{\kappa} T, \quad (2.1)$$

where T is the absolute temperature, introduced into Eq. 2.1 to make zT dimensionless. Much of the last few decades of work on doped conjugated polymer-based systems has focused on strategies to improve the power factor,^[6,7] σS^2 . Since increased doping levels tend to increase σ and reduce S , there is typically a doping level ‘sweet spot’ that maximizes the power factor. However, there are very few studies that have examined the κ of either p - or n -doped conjugated polymers,^[8-35] so there is relatively little knowledge of how zT changes with doping for this promising class of materials.

The thermal conductivity is an intrinsic property of a material primarily composed of electronic (κ_{el}) and lattice (κ_{lat}) contributions,^[36] $\kappa = \kappa_{\text{el}} + \kappa_{\text{lat}}$, where charge carriers and lattice vibrations, respectively, serve as vehicles for heat transfer. Thermal conductivities of pristine (undoped) polymeric materials typically fall in the range of $0.1 - 1.0 \text{ W m}^{-1} \text{ K}^{-1}$,^[37,38] and processing techniques that enhance polymer chain alignment, such as mechanical stretching or nanoscale templating, can increase κ by multiple orders of magnitude.^[37,39,40] Depending on the experimental method used,^[41] thermal conductivity measurements typically

determine κ either in the cross-plane (perpendicular to the film) or in-plane (parallel to the film) direction. Although advanced techniques can be employed to determine both directions if in-plane values for κ are sufficiently high,^[42-46] this is not true for most polymer thin films. Because the polymer chains in both spin-coated and drop-cast films tend to lie in-plane,^[47,48] polymers usually show a higher κ , or more efficient heat transfer, in the in-plane (along the chain) direction than in the cross-plane (perpendicular to the chain) direction.^[49-53]

One of the workhorse doped conjugated polymer systems studied for potential thermoelectric applications is poly(3-hexylthiophene-2,5-diyl) (P3HT) doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F₄TCNQ).^[54-56] Within the relatively few measurements of κ performed on chemically-doped conjugated polymer systems,^[8-62] several have focused on F₄TCNQ-doped P3HT.^[48-54] Most of the work on F₄TCNQ-doped P3HT measured the cross-plane κ .^[48-51] Disturbingly, the results from different groups not only do not agree as to the value of κ , but also do not agree as to whether doped P3HT has a higher^[48,51] or a lower^[49,50] κ compared to that of pristine P3HT. Among the few studies^[52-54] that report an in-plane κ measurement for F₄TCNQ-doped P3HT, only Degousée *et al.*^[52] compared the thermal conductivity of doped films to a pristine film, where an increase in κ upon doping was observed.

We believe that one of the main issues in determining accurate thermal conductivities for doped conjugated polymer films is that laser-based measurement methods directly probe either the thermal effusivity, r , or the thermal diffusivity, α . Both of these quantities are related to κ through the volumetric heat capacity, C_v :

$$r = \sqrt{\kappa \rho C_p} = \sqrt{\kappa C_v} = \frac{\kappa}{\sqrt{\alpha}}, \quad (2.2)$$

where C_v is the product of the mass density, ρ , and the specific heat measured under constant pressure, C_p . Although published data on ρ and C_p exist for various types of pristine P3HT

samples,^[50,50,52,57-66] there has been no systematic study of how C_v (or even how either ρ or C_p) change in P3HT films as a function of the extent of F₄TCNQ doping. As far as we are aware, Ref. 50 provides the only reported C_p measurement in the literature for F₄TCNQ-doped P3HT, and there is no experimental data on how ρ changes with doping for P3HT films.

This lack of C_p and ρ measurements means that different groups measuring r or α have had to make differing assumptions regarding how C_v changes with doping to extract values of κ . For example, some studies^[41-43,48,60] made the assumption that doped P3HT films (or various other doped semiconducting polymer systems) have identical C_v values to that of pristine P3HT (or to the pristine polymer at hand). Another study^[49] approximated the C_v of F₄TCNQ-doped P3HT by extrapolating increases in C_p based on the measured increase in C_p reported in Ref. 50; these workers also estimating doped film densities by assuming that there was one F₄TCNQ dopant for every two P3HT unit cells. Still other studies^[51-54] employed modeling to fit thermal resistivities (as opposed to r or α) in order to avoid the issue of how to treat C_v as a function of doping. Overall, we believe that the conflicting data in the literature about how the κ of conjugated polymers changes with doping arises because of the many different assumptions made about how C_v changes with doping.

To address both the conflicting reports of κ and the lack of C_v data in the literature, in this paper we combine values of cross-plane r , measured by time-domain thermoreflectance (TDTR),^[42,67-70] C_p , measured by differential scanning calorimetry (DSC) on samples of known mass, and ρ , determined directly as the mass/volume ratio, to accurately determine values for the cross-plane κ and zT for P3HT films as a function of the extent of doping by F₄TCNQ. Since regioregularity is known to influence the crystallinity, electronic structure, and thermoelectric properties of conjugated polymers,^[71-75] we also explore how κ changes for both regioregular (RR) and regiorandom (RRa) P3HT films over a wide range of doping levels.

Additionally, we use grazing-incident wide-angle x-ray scattering (GIWAXS) to correlate doping-induced changes to C_v and κ with changes in the polymer crystal structure.

We find that the way C_v changes as a function of the extent of doping depends on the regioregularity of P3HT. For RR-P3HT films, C_v values of lightly-doped films start slightly lower than pristine RR-P3HT but gradually increase with higher doping levels, eventually surpassing the value of the pristine polymer. In contrast, RRa-P3HT films show a significant decrease in C_v upon doping because of the doping-induced conversion of amorphous polymer to more-ordered crystalline domains. When these C_v values are combined with TDTR measurements, we find that κ changes non-monotonically with F₄TCNQ doping, first increasing relative to that of pure P3HT upon light-to-moderate doping followed by a subsequent decrease in κ with heavier doping. By also measuring the electrical conductivity, σ , of the doped films, we determine that the non-monotonic changes in κ with doping result from changes that occur to κ_{lat} as opposed to κ_{el} , a direct result of doping-induced changes to the crystal structure of the P3HT films. Finally, we also measure the Seebeck coefficient, S , to monitor how zT changes with doping, which we find can reach values of 5.2×10^{-3} in F₄TCNQ-doped RR-P3HT films.

2.2 Results and Discussion

The overarching goal of this paper is to rigorously determine, using TDTR, how the cross-plane κ and zT of F₄TCNQ-doped P3HT films changes with the extent of F₄TCNQ doping. To accomplish this, accurate values for C_v of doped films must be determined to extract values of κ from the thermal effusivities measured with TDTR. The rest of this paper is organized as follows. With GIWAXS, we first articulate how doping with F₄TCNQ changes the crystal structure of P3HT films in Section 2.2.1. We then discuss in Sections 2.2.2 and

2.2.3 how C_p , ρ , C_v and κ vary as a function of doping, and to what extent the changes in these quantities are driven by structural and nonstructural factors. We find that in both RR-P3HT and RRa-P3HT films, the thermal conductivity changes non-monotonically, increasing at low doping concentrations compared to undoped films, followed by a subsequent decrease at higher doping concentrations. The highest zT value achieved was 5.2×10^{-3} for highly-F₄TCNQ-doped RR-P3HT, as discussed in Section 2.2.4. Overall, the results allow us to better understand the intertwined effects of how doping-induced changes to crystal structure and the introduction of molecular dopants impact thermal transport and the thermoelectric properties of F₄TCNQ-doped P3HT films.

Polymer films for GIWAXS, density measurements, TDTR, electrical conductivity measurements, and Seebeck measurements were prepared by spin-casting and doped via the sequential processing (SqP) method,^[76] a two-step process where the polymer film is cast onto a substrate prior to doping. The doping step involves exposing a pre-cast film to a dopant solution where the extent of doping can be controlled by the dopant concentration. The SqP doping method has been shown to yield films with more optimal thermoelectric properties than films prepared via the blend-doping method,^[76] where both polymer and dopant are cast from a single solution. To reach the minimum sample mass required for DSC measurements, polymer films for C_p determination were drop-cast rather than spin-cast. In drop-casting, films are made by allowing the solvent of a polymer solution to evaporate; this allows films to be made that are orders of magnitude thicker than spin-cast films. Doped films for C_p measurements were prepared via the blend-doping method in order to precisely control the amount of F₄TCNQ. See Section 2.4.1, below, as well as Section 1.2 of Appendix A for additional sample preparation details.

Alongside direct measurements of mass and volume that were used to determine film densities, mass measurements of films taken before and after doping allowed us to also directly determine the amount of F₄TCNQ that intercalates within films doped via the SqP method (see Sections 1.3 and 1.4 of Appendix A for measurement details). This allowed for direct quantification of the mole ratio of F₄TCNQ-to-polymer thiophene monomer unit (3HT), as summarized in Table A.1 of Appendix A. For doped RRa-P3HT films, due to the loss of polymer during the SqP doping process (see Figure A.2 of Appendix A), we used a spectroscopy-based calibration method where measured film densities were used to determine the dopant:monomer mole ratios (see Section 1.4 and Figure A.3 and A.4 of Appendix A).

2.2.1 Measuring crystal structure changes in F₄TCNQ-doped RR- and RRa-P3HT films via GIWAXS

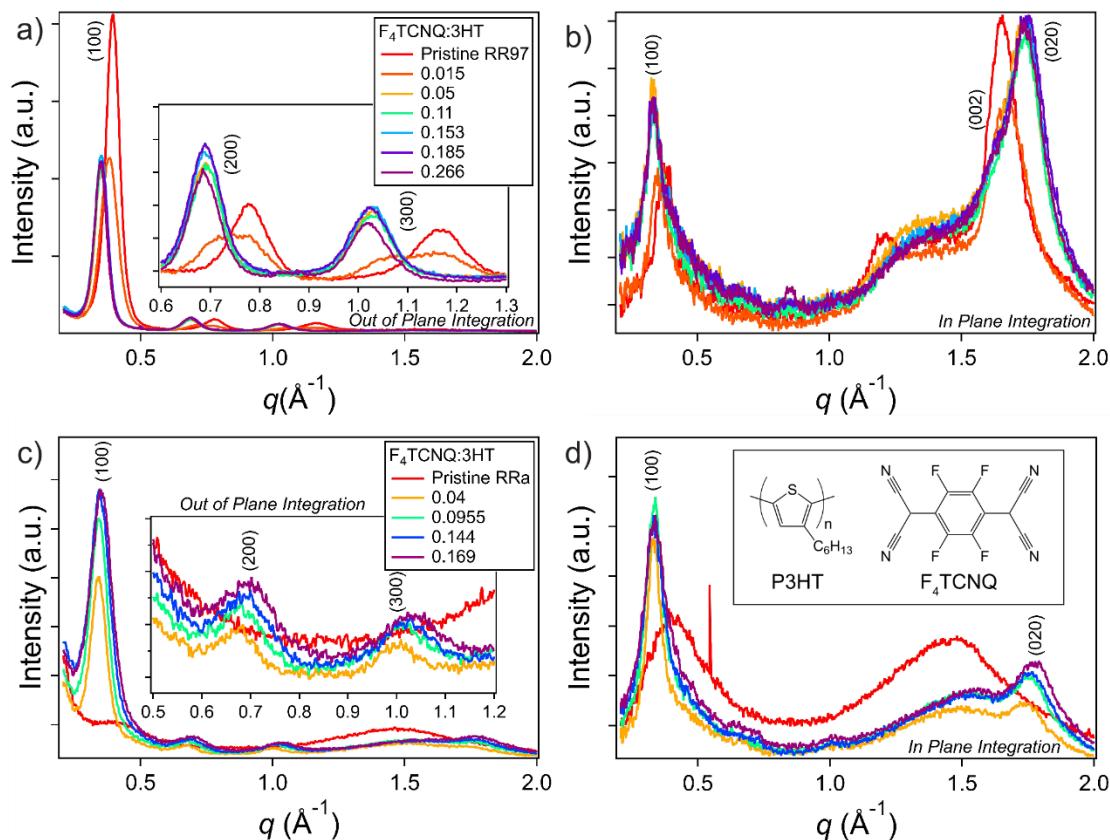


Figure 2.1: Integrated pristine-film-thickness-normalized GIWAXS patterns for pristine and F₄TCNQ-doped RR-P3HT (a-b) and RRa-P3HT (c-d) films (see Figure A.11 in Appendix A for the raw 2-D GIWAXS data). Figures 1a and 1c show out-of-plane integrations, which are dominated by the lamellar ($h00$) diffraction peaks, while Figures 1b and 1d show in-plane integrations, which show the (100) diffraction peaks with reduced intensity, as well as the monomer and π -stacking peaks, ($00l$) and ($0k0$), respectively. The data show that doping changes the crystal structure of the RR-P3HT films, and induces crystallization of the initially amorphous RRa-P3HT films.

Pristine RR-P3HT films are known to be semicrystalline, containing domains of ordered, π -stacked polymer, and more amorphous regions with less regular polymer stacking between the ordered domains. The presence of crystalline domains in both pristine and doped RR-P3HT films is apparent from the intense ($h00$) peaks in **Figure 2.1a**, which shows the out-of-plane integrated GIWAXS diffraction (for measurement details, see Section 1.9 of Appendix A). In contrast, pristine RRa-P3HT shows only a weak (100) peak with no overtones, as seen in Figure 2.1c, indicating a film structure that is mostly amorphous. In the in-plane integrations (Figures 2.1b and 2.1d), the ($h00$) diffraction intensity is dramatically reduced, and peaks corresponding to the periodicity along the π -stacks (labeled (020)) and along the backbone of the polymer chain (monomer peak labeled (002)) appear. The facts that the out-of-plane (100) peak (Figure 2.1a) is significantly more intense than the in-plane (100) peak (Figure 2.1b) and that the (020) π -stacking peak and (002) monomer peaks lie primarily in-plane (Figure 2.1b) indicates that for RR-P3HT, the crystalline domains lie predominantly edge-on with respect to the substrate. The difference between in-plane and out-of-plane diffraction is slightly reduced for RRa-P3HT (Figures 2.1c and 2.1d), indicating reduced edge-on texture.

As RR-P3HT films are doped with F₄TCNQ, Figure 2.1a shows that the lamellar peaks shift to lower q , indicating an increase in the lamellar spacing and thus a volume expansion of the unit cell. This is because F₄TCNQ[−] sits in the lamellar region of the crystallites between the side chains, so the crystal lattice must expand in this direction to make space for the counterion.^[77-82] Indeed, for the lowest doping level (0.015:1 F₄TCNQ:3HT ratio) the (200) and (300) peaks are both clearly split in two, indicating a first-order phase transition and the co-existence of two distinct structures corresponding to doped and undoped crystallite populations.^[82] As the doping level increases, the phase transition rapidly becomes complete, and the lamellar spacing then remains roughly constant as the doping level increases over a broad range (see Figure A.12 of Appendix A).^[77] Additionally, Figures 2.1b and 2.1d show that the initial doping-induced phase transition also causes the (020) π -stacking peak to shift to larger q (or smaller spacing – see Figure A.13 of Appendix A), the result of a change in chain tilt of the expanded unit cell.^[82] The distance decrease in the π -stacking direction is much less than the increase in the lamellar direction, resulting in an overall increase in the unit cell volume. This means that the density of initially-doped P3HT should be smaller than that of pristine P3HT because of the large increase in unit cell volume caused by the doping-induced phase transition, as we detail further below.

The situation is somewhat different for RRa-P3HT, where doping induces crystallization of the initially-amorphous polymer.^[83,84] This doping-induced crystallization is easy to observe from the increase in diffraction intensity of both the lamellar and π -stacking diffraction peaks in the doped material, as seen Figure 2.1c and 2.1d. Doping-induced crystallization increases throughout the low- to moderate-doping regime before gradually reaching a limit at the highest doping levels tested, as seen by the growth of the integrated (100) peak area in Figure 2.1c and Fig. A.14 of Appendix A. The doped lamellar and π -stack spacing

distances for RRa-P3HT are quite similar to those of doped RR-P3HT (see Figures A1.12 and A.13 of Appendix A), with peaks that do not change position significantly with doping level, again indicating that the doped polymer structure is fixed with F₄TCNQ[−] filling in open sites in the polymer lattice. This indicates that the doped film density should increase with doping level, as also discussed further below. It is worth noting that despite the doping-induced crystallization, the film-thickness-normalized integrated (100) peak areas are much smaller for RRa-P3HT than RR-P3HT across all doping levels (Figure A.14 in Appendix A), indicating net lower overall crystallinity in doped RRa-P3HT films. We expect that this difference in the crystalline-to-amorphous ratio of the two doped P3HT varieties will directly impact both the capacity of the respective polymer films to store heat (C_v) and transport it (κ).

2.2.2 Determining C_v of RR- and RRa-P3HT as a function of the extent of F₄TCNQ-doping

As mentioned above, to understand how doping-induced structural changes connect to the thermal conductivity, we need to have access to the volumetric heat capacity, C_v , to extract κ from the thermal effusivities measured by TDTR. Determining experimental values for C_v , in turn, requires taking the product of measured values for C_p and ρ , as per Eq. 2.2.

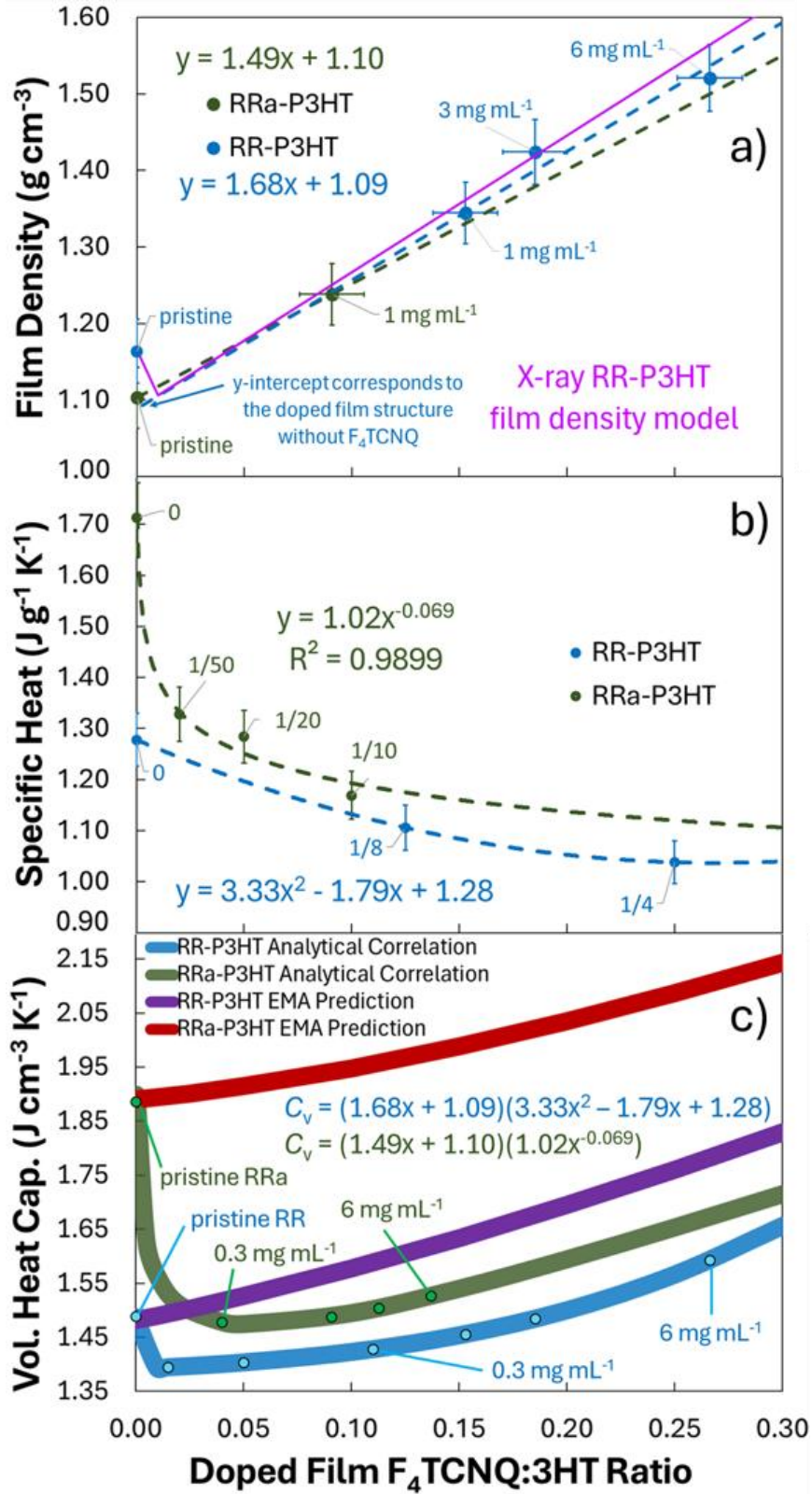


Figure 2.2: (a) Measured bulk film densities of pristine and doped RR-P3HT (blue) and RRa-P3HT (green) films as a function of $F_4TCNQ:3HT$ mole ratio; the dashed lines are fits to the data points; the

F₄TCNQ doping concentrations used for the SqP doping method are indicated for each point. The purple solid line is a theoretical construct based on a model using the unit cell volume of the pristine and doped crystal structures from x-ray scattering. The blue dashed line is a fit to the measured data points assuming that the y -intercept has the expanded unit cell volume of the doped crystal structure rather than the higher-density pristine crystal structure (see Section 1.4 of Appendix A for details). (b) Measured specific heat, C_p , of pristine and doped RR- and RRa-P3HT films as a function F₄TCNQ:3HT doping ratio, along with analytic fits (dashed curves) to the data points. (c) Analytically-determined volumetric heat capacities, using the product of the fitting functions from panels (a) and (b), for RR- and RRa-P3HT films as a function of F₄TCNQ:3HT doping ratio. F₄TCNQ doping concentrations used in the SqP doping method are indicated for some points, with full data in Table A.3 of Appendix A. Effective medium approximation (EMA) calculations for doped RR-P3HT (purple curve) and RRa-P3HT (red curve) films using mole-fraction-weighted contributions of the bulk C_v values of F₄TCNQ and pristine RR- or RRa-P3HT. Clearly, the EMA fails to correctly predict the C_v of F₄TCNQ-doped P3HT, a direct result of the doping-induced structural changes that alter the heat capacity of the composite doped systems.

2.2.2.1 Measured pristine and F₄TCNQ-doped RR- and RRa-P3HT film densities

As mentioned in the introduction, the way the density of F₄TCNQ-doped P3HT films changes with doping level has not been systematically studied in the literature, leaving κ studies that require C_v to either assume^[48] pristine P3HT density values for doped films or extrapolate^[49] increases in density based on estimated amounts of intercalated F₄TCNQ within the unit cell. The density of pristine P3HT, in contrast, has been examined in the literature using both experimental and computational methods,^[57-59] and most studies agree that the crystalline regions of RR-P3HT films have a density between 1.10–1.14 g cm⁻³.^[57] Given that the volumetric crystalline fraction of RR-P3HT samples has been estimated to be between 30%

and 90%,^[58,60,61] and that non-crystalline material should have a slightly lower density, overall film densities in the 1.10's g cm⁻³ are expected for RR material.^[58,59] Additionally, Refs. 58 and 59 suggest that the mass density remains practically constant for RR-P3HT as the molecular weight is varied. RRa-P3HT densities have been reported to be between 1.09–1.11 g cm⁻³,^[57-59] which is consistent with the idea that amorphous P3HT has a marginally lower density than the more crystalline RR-P3HT.

Direct measurements of mass and volume (see the experimental procedure in Section 1.3 of Appendix A) resulted in density values for pristine films of RR- and RRa-P3HT of $1.16(3) \pm 0.04$ and $1.10(3) \pm 0.04$ g cm⁻³, respectively, which are the left-most points in **Figure 2.2a** (see also Figure A.1 of Appendix A), in good agreement with the literature described above. We also measured the bulk film density as a function of F₄TCNQ:3HT mole ratio for doped RR- and RRa-P3HT films by measuring the net gain in mass and increase in thickness of the films after doping. Since the solvent used in the doping solution can dissolve some of the pre-cast polymer, particularly with RRa-P3HT, we performed a calibration procedure that involved soak-doping and UV-Vis-NIR spectroscopy to approximate the F₄TCNQ:3HT mole ratio for RRa-P3HT films doped using the SqP method, which is described in detail in Section 1.4 of Appendix A. The data show that for F₄TCNQ-doped RR- and RRa-P3HT films (see also Figure A.1 of Appendix A), there is a roughly linear increase in density as additional dopant is incorporated into the polymer films. F₄TCNQ (molecular weight ~276 g mol⁻¹) is heavier than a 3HT repeat unit (molecular weight ~168 g mol⁻¹), so it is not surprising that a composite doped film that is ~25% by mole dopant has a significantly higher density than a pristine polymer film.

We can understand the density changes upon doping in more detail by considering the doping-induced structural changes seen in the x-ray scattering data presented above. Based on

its x-ray-determined unit cell volume of $466 \text{ \AA}^3$, the crystalline fraction of pristine RR-P3HT should have a density of 1.20 g cm^{-3} (see Section 1.4 of Appendix A for details). Since the measured density is 1.16 g cm^{-3} , this suggests that our pristine RR-P3HT films are $\sim 60\%$ crystalline and $\sim 40\%$ amorphous, presuming that the amorphous fraction has the same 1.10 g cm^{-3} density as RRa-P3HT. Given that we also know from x-ray scattering that the unit cell volume of the crystalline fraction of the RR-P3HT film increases to $518 \text{ \AA}^3$ upon doping (as also detailed in Section 1.4 of Appendix A) and that crystalline material is doped preferentially, the x-ray measurements thus predict an initial decrease in density upon doping. Then, as F₄TCNQ molecules begin to fill the expanded unit cell upon increased doping, the purple solid line in Fig. 2.2a shows how the density would change given that there are no further structural changes and assuming that the crystalline fraction does not change upon doping. Clearly, our measured doped film densities agree well within error with the X-ray-predicted model, indicating that we have a good molecular understanding of the density of F₄TCNQ-doped RR-P3HT films. The fact that the density of the highest-doped sample we studied is a bit below the predicted value from the X-ray diffraction-based model is likely due to the fact that some lower-density amorphous material is also doped at this concentration.

To better estimate the density of the doped RR-P3HT films at lower doping levels, where it is hard to measure the mass change by direct weighing, we linearly fit the measured points in Fig. 2.2a, but forced the y-intercept to have a value that would correspond to the density of a hypothetical expanded (doped) structure, as determined from the x-ray model (see Section 1.4 of Appendix A), but without any F₄TCNQ in the lattice; this fit is shown as the blue dashed line. We then used the measured 1.16 g cm^{-3} density value of the pristine sample and the densities calculated using the blue dashed line for the doped RR-P3HT samples to determine C_v from C_p , as described further below.

We note that for P3HT, the doping efficiency (the ability of a dopant to generate a mobile carrier) of F₄TCNQ is 5–18%,^[85–87] so that the F₄TCNQ:P3HT ratio we measure is not equivalent to the carrier density. Instead, the ratio includes both intercalated F₄TCNQ[−] ions that generate mobile carriers and F₄TCNQ species that form charge-transfer complexes or that produce carriers that are otherwise trapped in the film. We also note that RRa-P3HT is several hundred mV harder to dope than RR-P3HT, as it has a deeper valance band. As a result, we cannot achieve the same doping levels with RRa-P3HT as RR-P3HT; this can be seen in Figure 2.2a by noting how different the F₄TCNQ:P3HT ratios are when doping with the same F₄TCNQ solution (1 mg mL^{−1}). However, since the doped crystal structures of the two materials are similar, the way the density of the two materials changes with increasing doping level should also be similar, as we observe.

2.2.2.2 Measured pristine and F₄TCNQ-doped RR- and RRa-P3HT C_p values

Specific heat measurements show that pristine P3HT samples with higher degrees of crystallinity tend to have lower specific heats.^[60,62] For example, a compilation of RR-P3HT samples of varying M_w (10.5–87 kg mol^{−1}) and polydispersity index (PDI) measured with DSC at 20 °C shows that C_p values fall between a range of 1.3–1.6 J g^{−1} K^{−1},^[50,52,60–65] whereas RRa-P3HT has C_p values between 1.72–1.95 J g^{−1} K^{−1}.^[60,62,66] Apart from a single measurement by Kiefer *et al.*,^[50] who studied cold-pressed P3HT pellets and found a 12.8% increase in C_p upon doping with 20 mol% F₄TCNQ, C_p values for F₄TCNQ-doped P3HT have not been presented in the literature. The lack of data has led groups either to assume that C_p does not change from its pristine value upon doping,^[48] or to extrapolate^[49] the result presented by Kiefer *et al.*^[50]

To remedy this situation, we performed DSC measurements on drop-cast pristine RR- and RRa-P3HT films of known mass, shown as the left-most points in Figure 2.2b and the

calorimetric traces in Figure A.5 in Section 1.5 of Appendix A. The values we obtained fall within the ranges found in the literature.^[50,52,60-66] The fact that RRa-P3HT has a higher C_p than RR-P3HT, and knowing that each material has: 1) a similar number density of atoms per unit volume (a proxy to ρ , as discussed above); and 2) the same average mass per atom, reinforces the idea that having more structural disorder allows for a higher number of molecular degrees of freedom and thus a higher specific heat.

We then performed DSC on blend-cast F₄TCNQ-doped RR-P3HT films with varying amounts of dopant at controlled F₄TCNQ:3HT mole ratios, as shown in the calorimetric traces in Figure A.6 and A.7 of Appendix A. We find that C_p decreases with increasing F₄TCNQ:3HT mole ratio, as seen in Figure 2.2b, a result that stands in contrast to that reported in Ref. 50. We measured bulk F₄TCNQ to have a C_p that is the same, within error, as RR-P3HT (see Figure A.5 of Appendix A), which suggests that the C_p drop in the doped films is not directly caused by F₄TCNQ having a different specific heat, but instead due to changes in the crystal structure that reduce the number of thermally-excitable degrees of freedom relative to the pristine polymer. We also see in Figure 2.2b that the C_p of F₄TCNQ-doped RRa-P3HT rapidly decreases upon initial doping and then decreases more slowly at higher doping concentrations. We believe that the larger initial drop in C_p of RRa-P3HT films upon doping is due to doping-induced crystallization (cf. Figs. 2.1c and 2.1d),^[83,84] as the creation of new crystallites should lower the number of thermally accessible degrees of freedom available to the material.

2.2.2.3 Pristine and F₄TCNQ-doped RR- and RRa-P3HT C_v values

Most studies in the literature that required C_v values for pristine P3HT films in order to extract thermal conductivities typically either referenced outside measurements^[49,88,89] for ρ and C_p or performed measurements of only one or the other of these two variables (see Table

A.6 of Appendix A for a compilation of studies).^[48,50,50,52,64] The fact that nearly every such study utilized inconsistent ρ and/or C_p values for pristine RR-P3HT resulted in values for C_v that ranged from 1.22–2.08 J cm⁻³ K⁻¹ (see Table A.6 in Appendix A). On the other hand, as far as we are aware, the C_v of pristine RRa-P3HT has only been presented once in the literature, at 1.84 J cm⁻³ K⁻¹, based on external ρ and C_p values.^[49] For F₄TCNQ-doped P3HT films, Zhao *et al.*^[48] assumed that the C_v of doped P3HT remained unchanged from the pristine polymer, while Kiefer *et al.*^[50] and Plunkett *et al.*^[49] both suggested that C_v increases upon doping (see Section 2.1 of Appendix A for a detailed description of the C_v assignments made in Refs. 49 and 50).

Here, we analytically determine C_v values for pristine and F₄TCNQ-doped P3HT films by fitting our measured ρ and C_p data to analytic functions, as seen in Figures 2.2a-b, and then multiplying the two functions, as summarized in Figure 2.2c and Section 1.6 of Appendix A. We find that the C_v 's of pristine RR- and RRa-P3HT films are 1.49 and 1.89 J cm⁻³ K⁻¹, respectively, as seen via the left-most points in Figure 2.2c. The higher C_v of RRa-P3HT is due to the intrinsic disorder of the amorphous film, while in RR-P3HT films, the presence of crystalline domains results in a comparatively lower number of thermally excited degrees of freedom per unit volume. As RR-P3HT is doped with F₄TCNQ, C_v immediately decreases slightly due to the volume expansion that occurs within the crystalline domains of the film, the result of the doping-induced phase transition described above. C_v then slowly increases as more F₄TCNQ enters the film at higher doping levels, eventually surpassing the value of pristine RR-P3HT at roughly the 1:5 F₄TCNQ:3HT ratio. As RRa-P3HT is doped, however, a much more significant decrease in C_v occurs at low F₄TCNQ:3HT mole ratios due to doping-induced crystallization, as discussed above. The small increases in C_v at the highest doping

levels of both P3HT varieties is believed to be driven by additional thermally-excitabile degrees of freedom introduced by the increasing number of dopant molecules within the unit cell.

We can also compare our experimentally-derived C_v values to those expected from the effective medium approximation (EMA), which is commonly used to estimate the physical properties of composite materials. In the EMA, the C_v of doped P3HT can be estimated using the mole-fraction-weighted contributions of the C_v 's of bulk F₄TCNQ ($2.3 \text{ J cm}^{-3} \text{ K}^{-1}$, which is the product of ρ , 1.57 g cm^{-3} ,^[90] and our measured C_p) and the pristine polymer; these estimates are shown as the purple and red curves in Figure 2.2c for RR- and RRa-P3HT, respectively. Since the C_v of bulk F₄TCNQ is larger than that of both P3HT varieties, the EMA predicts an increase in C_v as the F₄TCNQ:3HT ratio increases, thus significantly overestimating C_v across nearly all doping levels. This is because the EMA does not account for doping-induced changes to the polymer's crystal structure, which leads to significant changes in C_p (for RR- and RRa-P3HT) and ρ (for RR-P3HT only). Therefore, the use of the EMA to estimate C_v in doped conjugated polymers, as was done in Ref. 49, is likely to lead to significant errors.

2.2.3 Determination of κ as a function of RR- and RRa-P3HT and F₄TCNQ-doping

With experimentally-derived C_v values in-hand, we next determine cross-plane thermal conductivities using time-domain thermoreflectance for films of pristine and F₄TCNQ-doped RR- and RRa-P3HT. The thermal modeling implemented (see Section 1.7 of Appendix A for details) combines TDTR-measured thermal effusivities (r) with the above-determined volumetric heat capacities (C_v) to back out values for κ .

2.2.3.1 Measured pristine RR- and RRa-P3HT κ values

In the literature, cross-plane κ measurements on non-aligned pristine P3HT have been performed using thermoreflective (TDTR/FDTR),^[49,88,89,91] photoacoustic (PA),^[92] and electro-thermal (3ω , TET/PLTR2, TWA, Hot Disk TPS, Flash-DSC)^[48,50,51,50-52,64,93,94] techniques. Although high-frequency laser-based and electro-thermal methods require a C_v value, techniques in the low-frequency regime (particularly 3ω)^[51,52,51,93] do not require C_v to be known as thermal resistivities are directly measured.^[95,96] We note, however, that electro-thermal methods such as 3ω do not work well when the material of interest is electrically conductive, as is the case for doped conjugated polymers; they require an electrical insulator between the electrode and thin-film, which can then affect the resulting thermal measurement. In Table A.6 of Appendix A, we provide a list of cross-plane κ studies on pristine P3HT films tabulated by measurement technique, film processing method, P3HT type, the value of C_v used in extracting κ (if any) and the final estimated κ value. The range of published cross-plane κ values for pristine P3HT films spans 0.05–0.83 W m⁻¹ K⁻¹, well over an order of magnitude, and the reasons for the wide range in κ are not entirely easy to decipher (see Section 2.2 of Appendix A for an analysis of how polymer properties and film processing techniques may impact κ and, beyond C_v assignments, likely contribute to the wide range of reported values).

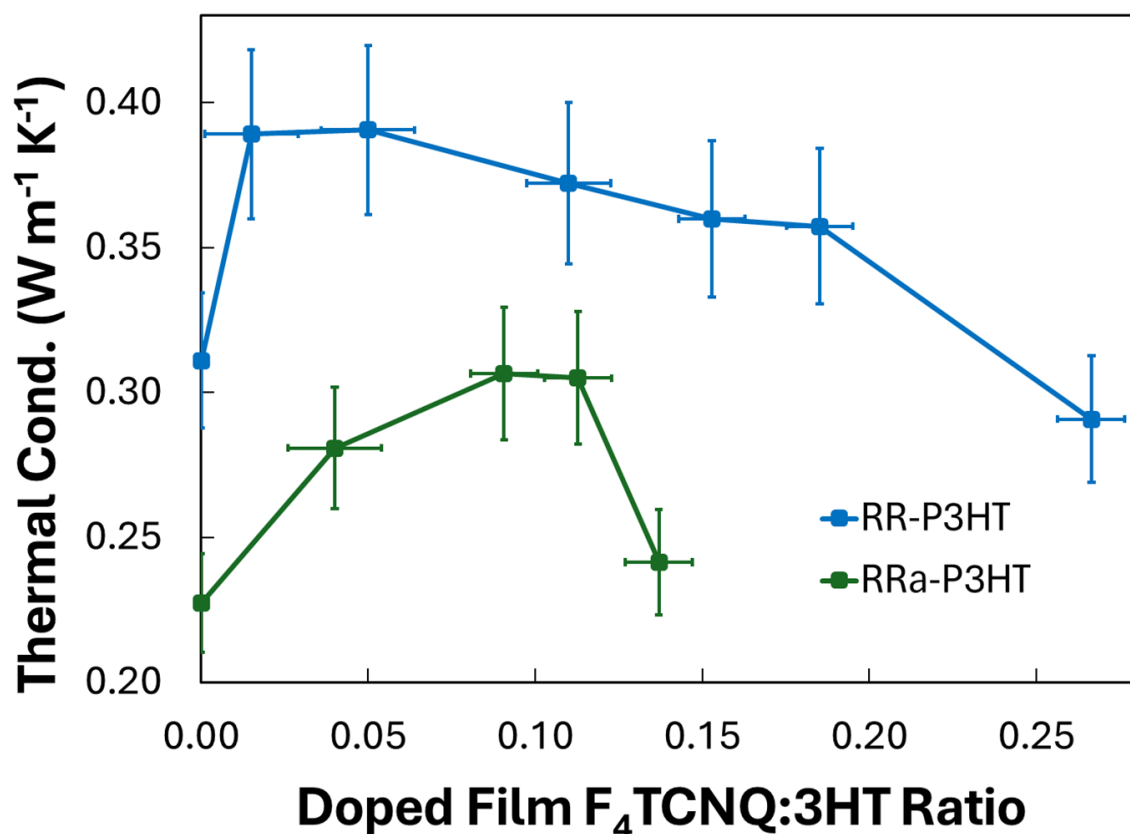


Figure 2.3: Thermal conductivities, determined from effusivities (see Figure A.9 of Appendix A) measured via TDTR and the C_v values in Figure 2.2c, of doped RR- and RRa-P3HT films as a function of F₄TCNQ:3HT doping ratio. Non-monotonic changes to the thermal conductivity are observed with increasing doping level, with κ increasing upon light doping and then decreasing upon further doping. Thermal diffusivities plotted as a function of F₄TCNQ:3HT ratio are also displayed in Figure A.10 of Appendix A.

Here, we measure a higher cross-plane κ for pristine RR-P3HT films, $0.31(1) \pm 0.02(3)$ W m⁻¹ K⁻¹, than for pristine RRa-P3HT, $0.22(7) \pm 0.01(7)$ W m⁻¹ K⁻¹, as shown by the left-most points in **Figure 2.3** (Fig. A.8b of Appendix A shows an example of the thermal model fitted to data). We selected both P3HT varieties to have roughly the same molecular weight (see Section 2.4.1) to ensure that the percent regioregularity alone is the reason behind differences in the κ . Our measurements agree with reports in the literature that show that κ

increases with the degree of polymer regioregularity.^[49,93] Since undoped P3HT has no charge carriers to transport heat, the changes to κ with regioregularity must be vibrational in nature, indicating that κ_{lat} increases with greater film crystallinity, as shown by our GIWAXS data for pristine RR- and RRa-P3HT in Section 2.2.1.

2.2.3.2 Measured F₄TCNQ-doped RR- and RRa-P3HT κ values

Cross-plane κ measurements on F₄TCNQ-doped P3HT in the literature have been performed much less frequently than pristine P3HT samples, although both thermoreflective (TDTR)^[49] and electro-thermal (3ω , Flash-DSC, Hot Disk/TPS)^[48,50,51] measurements have been presented (see Table A.7 of Appendix A for a summary of the reported data). Refs. 49 and 50, both of which published results on films doped to a single level alongside pristine films, reported a doping-induced 20–50% decrease in κ . In contrast, Refs. 48 and 51, which measured κ across a variety of doping levels, reported a roughly 60% initial increase in κ upon doping compared to pristine P3HT samples. Additionally, Ref. 48 saw κ decrease as higher doping levels were reached, while Ref. 51 did not see any drop in κ at the highest doping levels investigated.

The results of our TDTR measurements show that the κ of both F₄TCNQ-doped RR- and RRa-P3HT changes non-monotonically as a function of the extent of doping, as seen in Figure 2.3. Both P3HT varieties show a rise in κ at low doping levels compared to their respective pristine films, followed by a lowering of κ at the highest doping levels tested. The non-monotonic trends of κ with doping level strongly suggests that there are at least two competing factors affecting thermal transport in doped P3HT films.

One possible explanation could involve competing changes in the electrical and lattice contributions underlying κ . The Weidmann-Franz law,^[97,98] $\kappa_{\text{el}} = \sigma L_0 T$, where L_0 is the

Lorenz number assigned as the Sommerfeld value, $2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$, can be used to approximate the electronic contribution (κ_{el}) to the overall κ if the electrical conductivity, σ , is known. We measured the electrical conductivities of our doped P3HT samples, shown in **Figure 2.4a**, with additional details presented in Section 1.8 of Appendix A. The highest σ we measured across all of our doped P3HT films was 7.9 S cm^{-1} , which means, based on the Weidmann-Franz law, that κ_{el} can be no more than $0.006 \text{ W m}^{-1} \text{ K}^{-1}$ (see Table A.4 of Appendix A for κ_{el} approximations at each doping level). This value represents less than 10% of the observed increases in κ with doping, which leads us to conclude that the changes in κ across all doping levels must come from changes in κ_{lat} . This idea also agrees with literature claims that the κ of doped semiconducting polymers with low σ ($<10 \text{ S cm}^{-1}$) is entirely influenced by κ_{lat} .^[33,99,100]

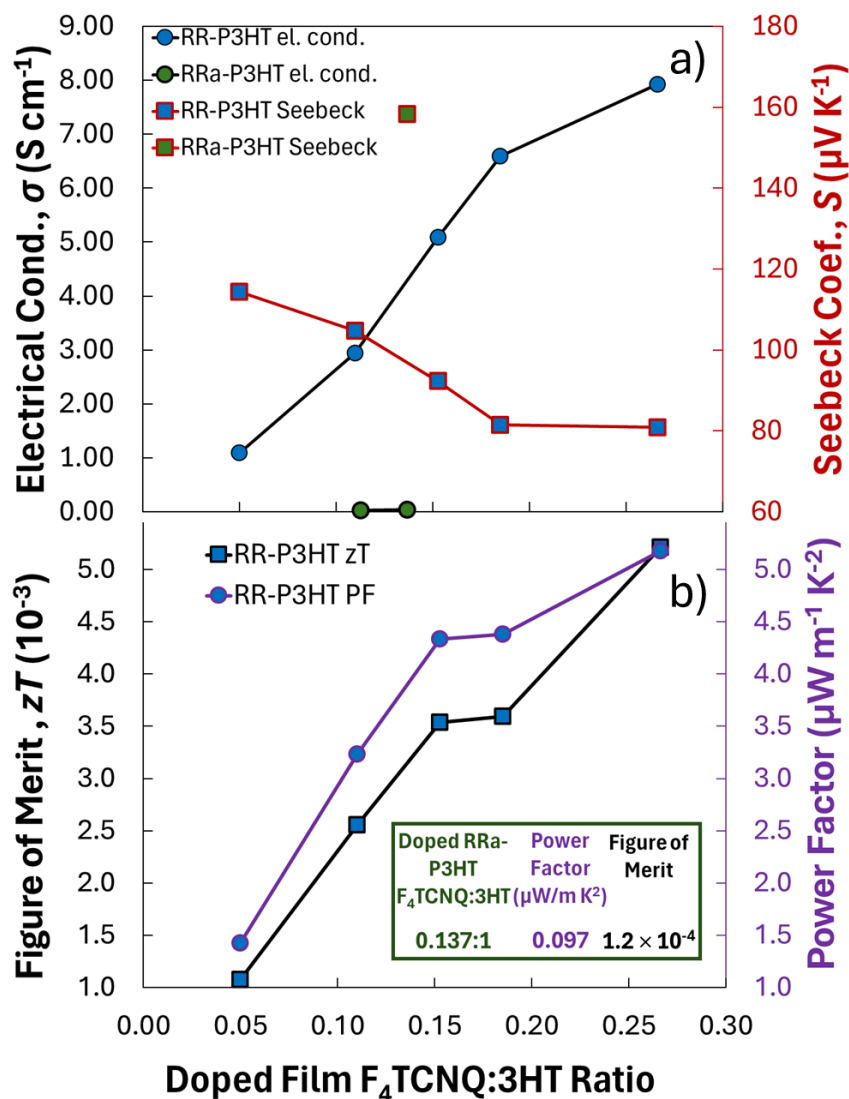


Figure 2.4: (a) Electrical conductivity (black lines connected to circular data points) and Seebeck coefficient (red lines connected to square data points) plotted as a function of $F_4TCNQ:3HT$ mole ratio for RR-P3HT (blue data points) and RRa-P3HT (green data points). (b) Figure of merit zT (black lines connected to square data points) and power factor values (purple lines connected to circular data points) for F_4TCNQ -doped RR-P3HT (blue data points). Only the most-doped RRa-P3HT film had a measurable Seebeck coefficient, so only this film has a reported power factor and zT value (see inset table outlined in green).

Thus, the initial increases in κ we observe at low F₄TCNQ:3HT mole ratios in RR-P3HT films and low-to-moderate ratios in RRa-P3HT films are due to doping-induced crystal structure changes that alter κ_{lat} . For RR-P3HT, the initial increase in κ with doping through the 0.05:1 F₄TCNQ:3HT mole ratio level is correlated with the doping-induced phase transition that occurs within the same doping regime, as mentioned above and documented in Figures A.12 and A.13 of Appendix A. This phase transition also decreases the film paracrystallinity and increases the crystalline coherence length (Figure A.16 of Appendix A). For RRa-P3HT, the increase of κ with doping through the 0.1:1 F₄TCNQ:3HT mole ratio tracks closely with increasing levels of doping-induced crystallization, as also discussed above and shown in Figure A.14 of Appendix A. To understand the non-monotonic dependence of cross-plane κ on doping level, we consider different theories of thermal transport.

In kinetic-gas theory, κ depends on the number of thermally excited vibrational modes, their velocities, and their scattering rates. One interpretation of our results in Fig. 2.3 is that pristine P3HT lies at or near the amorphous minimum-thermal conductivity limit described by the Cahill-Pohl model.^[101-104] Low levels of doping increase structural order and coherence, as supported by the GIWAXS in Section 2.2.1, allowing vibrational modes with longer wavelengths than the minimum mean-free-path limit to propagate. Once RR- and RRa-P3HT films take on doped structures, the lack of decrease in C_v across varying doping levels, as seen in Fig. 2.2c, rules out a large decrease in thermally populated vibrational degrees of freedom. Therefore, within kinetic-gas theory, the κ trend from low to high film F₄TCNQ:3HT ratios must primarily reflect changes in vibrational velocities, scattering rates, or both. In the absence of structural changes at high doping levels (as seen in Section 2.2.1), heavier doping adds local mass and force constant disorder through F₄TCNQ⁻ incorporation. This local disorder increases

scattering rates and pushes mean-free-paths back toward the amorphous minimum-conductivity limit.

The Allen-Feldman framework for transport in amorphous solids yields a similar microscopic explanation for the non-monotonic cross-plane κ trend. In the Allen-Feldman framework,^[105,106] heat-carrying vibrations are classified along a spectrum from highly mobile, extended modes to strongly localized ones. Our results imply that the structure changes that occur as pristine P3HT films are lightly doped with F₄TCNQ allow modes to have greater diffusivities and/or longer propagation distances. Then, increases in the F₄TCNQ:3HT ratio at higher doping levels cause vibrational modes to become more localized. It makes sense that incorporating F₄TCNQ dopant anions into the P3HT crystallites, which have very different vibrational frequencies than the surrounding polymer (e.g., the exterior of the dopant molecule consists of C-F and C $\equiv$ N bonds), serve to further localize the vibrational modes that are responsible for thermal transport. For RRa-P3HT, the decrease in κ only occurs after doping-induced crystallization is complete, which occurs at roughly 0.11:1 F₄TCNQ:3HT, as seen in Figure A.15 of Appendix A.

We note that our view of increased mode scattering (kinetic-gas theory) or increased mode localization (Allen-Feldman framework) caused by the presence of dopant counterions stands in contrast to that of Guo *et al.*,^[60] who claimed that the cross-plane κ decrease seen upon doping conjugated polymers is due entirely to the lattice expansion of the unit cell within crystalline regions. Here, however, we see in Fig. 2.3 that the doping-induced lattice expansion actually enhances the cross-plane κ .

Overall, we believe that the conflicting literature reports of increases and decreases to κ upon doping P3HT can be understood based on our finding of non-monotonic changes in thermal transport with doping. The competing effects are: 1) doping-induced changes to the

crystal structure, which occur at low doping levels leading to increases in κ); and 2) increased mode localization due to the increasing number of F₄TCNQ[−] ions in the lattice at high doping levels, resulting in a decrease in κ . For example, when Zhao *et al.*'s κ data on doped RR-P3HT is plotted as a function of F₄TCNQ:3HT ratio,^[48] as seen in Figure A.17 of Appendix A, the rise and fall in κ closely resembles the nonmonotonic trend observed in our measurements in Figure 2.3. In addition, Takayama *et al.*'s data on doped RR-P3HT,^[51] which saw an increase in κ upon doping without any decrease at higher doping levels, also mirrors our data in Figure 2.3 because all of their samples remained in the low-doping regime (based on their reported σ). Both Keifer *et al.* and Plunkett *et al.* found that κ decreases when RR-P3HT was doped with F₄TCNQ,^[49,50] but the samples in these works were all heavily doped ($\geq 0.2:1$ F₄TCNQ:3HT mole ratios), at the high end of what we show in Figure 2.3. If Ref. 49's value for κ is adjusted to reflect the film C_v we report in Figure 2.2c, then our κ data and those in Refs. 49 and 50 all converge to about $0.3 \text{ W m}^{-1} \text{ K}^{-1}$ for heavily-F₄TCNQ-doped RR-P3HT. In Section 2.3 of Appendix A, we present a more detailed comparison of literature-based κ results and our findings.

2.2.4 Determination of zT for F₄TCNQ-doped RR- and RRa-P3HT films

The thermoelectric figure of merit zT (Eq. 2.1) allows a comparison of the efficiency of different thermoelectric systems. Most studies on doped polymers only report power factors, σS^2 , due to the inherent difficulties of measuring κ . Maximizing only the power factor is equivalent to the assumption that the thermal conductivities of doped polymer films do not change with doping level. With our well-characterized values for cross-plane κ 's in-hand, we can calculate values of zT for F₄TCNQ-doped P3HT films as a function of doping level. These calculations are upper bounds due to the fact that our measurements of σ and S are in-plane

while our measurements of κ are cross-plane, and we expect in-plane values of κ to be higher than cross-plane values.^[52,49-52]

Electrical conductivities (circles) and Seebeck coefficients (squares) of our F₄TCNQ-doped P3HT samples are plotted in Figure 2.4a, with additional details described in Section 1.8 of Appendix A. As expected, σ increases while S decreases as P3HT films become more doped. In Figure 2.4b, the power factor of doped RR-P3HT (circles) shows an increase with increasing doping level. Figure 2.4b also shows zT (squares) as a function of F₄TCNQ:3HT ratio for doped RR-P3HT films, with the numerical data presented in Table A.5 of Appendix A. We are able to report zT only for the most heavily-doped RRa-P3HT film due to limitations in being able to reliably measure σ and S for the lower-doped samples. We find that the zT of doped RR-P3HT films is over an order of magnitude larger than that of the most-doped RRa film, primarily because RR-P3HT is significantly easier to dope.

The highest zT for F₄TCNQ-doped RR-P3HT that we found, 5.2×10^{-3} , which corresponds to the most heavily-doped film that we tested, is either comparable to or higher than the very few published zT values found in the literature for this polymer-dopant combination (see Table A.8 of Appendix A). For example, if one combines Chabinyk and colleagues' reported thermopower values¹⁰⁷ for vapor-doped RR-P3HT with the κ measured for vapor-doped high- M_w RR-P3HT in Ref. 49, one obtains a comparable zT of $\sim 5 \times 10^{-3}$. Drop-cast RR-P3HT films that were blend-doped with F₄TCNQ by Zhao *et al.* and Kiefer *et al.* yielded zT values of 5×10^{-4} and 1×10^{-4} , respectively.^[48,50] Compared to our zT results for doped RR-P3HT, the fact that the zT values reported in Refs. 48 and 50 are lower by an order of magnitude due is likely due to their utilization of the blend-doping method, which has been shown to yield films with poorer thermoelectric properties than those that prepared using the SqP doping method.^[76]

2.3 Conclusions

With well-characterized film densities and specific heats and thus volumetric heat capacities, we have shown that the ambiguity in the literature regarding whether the thermal conductivity of F₄TCNQ-doped P3HT films increases or decreases upon doping relative to pristine P3HT can be understood in the context of: 1) ambiguities in the values of C_v chosen to determine κ from measured thermal diffusivity or effusivity data; 2) the extent to which the film has been doped; and, 3) the competing influences of doping-induced changes to the P3HT crystal structure and the mode localization effects of F₄TCNQ[−] ion intercalation. We conclude that changes in the cross-plane κ of P3HT films as a function of doping are entirely vibrational in nature. The increase in κ at light-to-moderate doping concentrations in both RR- and RRa-P3HT is due to doping-induced crystal structural changes, specifically the doping-induced phase change of the unit cell for RR-P3HT and doping-induced crystallization in RRa-P3HT, that each enhance cross-plane heat transport. The subsequent decrease in κ at the highest doping levels result from intercalated F₄TCNQ[−] ions further localizing vibrational modes within the P3HT crystallites. Finally, with accurate values for cross-plane κ , we were able to determine zT upper limits for F₄TCNQ-doped P3HT as a function of doping level. A peak zT value of 5.2×10^{-3} was determined for RR-P3HT doped with 6 mg mL^{−1} F₄TCNQ via the SqP method. Further studies are needed to map changes of C_v and κ for P3HT films doped with other molecular dopants to optimize these systems for thermoelectric applications.

2.4 Experimental Section

2.4.1 Poly(3-hexylthiophene) (P3HT) materials

We used RR-P3HT (97.6% regioregularity (RR), $M_n = 28.65 \text{ kg mol}^{-1}$, $M_w = 60.15 \text{ kg mol}^{-1}$, PDI = 2.1, sourced from Ossila) and RRa-P3HT ($M_n = 19\text{--}34 \text{ kg mol}^{-1}$, $M_w = 60\text{--}95 \text{ kg mol}^{-1}$).

mol⁻¹, PDI = 2.8–3.1, sourced from Rieke Metals) to make films for TDTR, electrical conductivity, Seebeck coefficient, DSC and GIWAXS measurements. We used RR-P3HT (91–94% regioregularity, $M_n = 20\text{--}35\text{ kg mol}^{-1}$, $M_w = 50\text{--}70\text{ kg mol}^{-1}$, PDI = 2.0–2.5, sourced from Rieke Metals) and RRa-P3HT (same as above) for bulk film density and F₄TCNQ:3HT mole ratio measurements. All of the above values for M_n , M_w , PDI and %RR were provided by the supplier and were not independently verified. The range in values of M_n and M_w were also provided by supplier Rieke Metals. Any density difference between films made from 97.6% and 91–94% RR P3HT fall well within the density measurement error of our experiments ($\pm 0.04\text{ g cm}^{-3}$). In addition to the measurements described earlier in this chapter, we also performed DSC measurements using the aforementioned 91–94% RR-P3HT to test for any regioregularity dependence on C_p . We found no discernable difference in C_p between 97.6% and 91–94% RR-P3HT in their bulk-powder morphology. However, as drop-cast films, we found that the C_p of 97.6% RR-P3HT is ~10% lower than 91–94% RR (see Table A.2 of Appendix A). See Section 1.1 of Appendix A for details on how we sourced all solvents, substrates and deposited metals.

2.4.2 Instrumental methods

We utilized a PerkinElmer DSC 8000 instrument to perform differential scanning calorimetry, a thermoanalytical technique used to measure how much energy is required to heat sample material, to determine C_p ; this experiment is described in detail in Section 1.5 of Appendix A and the standard operating procedure (SOP) implemented is described in Appendix E. We utilized an amplitude-modulated, low-pulse energy ultrafast laser system to perform time-domain thermoreflectance (TDTR), a pump-probe optical technique used to measure thermal effusivity; this experiment is described in detail in Section 1.7 of Appendix A. We

utilized a Lakeshore MeasureReady M91 FastHall system in the Van der Pauw configuration to perform four-point-probe measurements to determine electrical conductivities and a custom-built instrument that applies thermal gradients to determine Seebeck coefficients; both of these experiments are described in detail in Section 1.8 of Appendix A. We utilized the Synchrotron Radiation Lightsource (SSRL) at SLAC National Accelerator Laboratory to perform grazing-incidence wide-angle x-ray scattering (GIWAXS) experiments, an x-ray diffraction technique, to characterize the nanoscale structure and morphology of polymeric thin-films; this experiment is described in detail in Section 1.9 of Appendix A.

2.5 Supporting Information

See Appendix A for the Supporting Information.

2.6 Acknowledgements

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Chapter 3: Transient thermorefectance with an amplified laser simplifies heat transfer modeling to determine the thermal transport properties of materials

3.1 Introduction

Pump-probe thermorefectance (TR) techniques, such as the time-domain (TDTR)^{1,2} and frequency-domain (FDTR)³ methods, are used in many fields to characterize the thermal properties of materials as well as the thermal behavior at interfaces. These non-contact, non-destructive methods for determining the thermal properties of thin films and their interfaces were first developed in the 1980's by research groups led by Eesley,⁴⁻⁶ Rosencwaig^{7,8} and Maris.^{9,10} Subsequent efforts lead by Cahill¹¹⁻¹⁴ and Schmidt^{15,16} in the 2000's resulted in significant improvements to TR techniques that have since become widely implemented to accurately thermally model a variety of material types, including within multi-layer sample geometries.

Both TDTR and FDTR methods operate by utilizing a periodically-modulated pump beam to deposit heat into a metal transducer and a probe beam to monitor the thermal response via the temperature-dependent reflectivity of the transducer. The TDTR method probes transient changes in surface reflectivity by controlling the time difference between pump and probe pulses,^{1,2} whereas FDTR probes changes in the phase lag between periodic heating and the reflective thermal response of the transducer as a function of the modulation frequency of the pump.³ The pump modulation frequency can be held constant in TDTR, but the specific frequency must be carefully selected to produce a thermal wave with the necessary penetration depth to probe the sample;^{1,2} for example, probing nm-scale thin-films requires MHz pump modulation frequencies.

In transient TR methods, the change in probe reflectivity as a function of time monitors how heat leaves the transducer. At the earliest times, this depends on how heat diffuses within the transducer, but at longer timescales, the reflected probe signal is a function of how heat is transferred away from the transducer by the underlying material that is in thermal contact. The thermal models employed to fit thermorefective decay data rely on either the thermal diffusivity, α , or the thermal effusivity, r , of the underlying material, as well as the thermal boundary conductance, σ , at the interface of the two materials. One can then use the value of α or r extracted from the TDTR measurement with a separately-measured value of the volumetric heat capacity, C_v , to determine the thermal conductivity, κ , of the underlying material via Equation 3.1:¹

$$\kappa = \alpha \cdot C_v = \frac{r^2}{C_v}. \quad (3.1)$$

Sometimes, it is also possible to simultaneously fit values for C_v and κ if α (or r) is sufficiently uncorrelated to C_v .^{16–19}

Although TR methods are capable of reliably determining the thermal properties of a vast array of materials, polymers and other low thermal conductivity ($< 1 \text{ W m}^{-1} \text{ K}^{-1}$) materials are more difficult to thermally characterize due to inherently small changes in the thermorefectance. Additionally, polymeric materials are often studied as thin (tens to hundreds of nm thick) films that are usually deposited onto substrates that have much higher thermal conductivities. This means that the study of polymeric materials often requires tri-layer heat modeling to capture the heat diffusion through each of the transducer, polymer film, and substrate layers.²⁰ For conventional TDTR methods to be sensitive to σ , a sample must have a thickness similar to the Kapitza length, which is in the range of 1–10 nm for very low- κ polymers.^{21,22} However, films this thin often have their TDTR signals dominated by the

substrate response when the thermal penetration depth (determined by the modulation frequency) exceeds that of the film thickness.¹ Thus, the inability to probe both κ and σ in low thermal conductivity thin-film materials lead many researchers to choose a constant value for σ (rather than treat it as a parameterized variable) when determining κ is the measurement priority,^{23–25} or to treat the thin film and both interfaces as a single in-series thermal resistor.^{21,22}

Some limitations of the TDTR method stem from its use of ultrafast ‘oscillator’-type lasers, which have high repetition rates (a few MHz) and low per-pulse energies ($\sim$ nJ). This means that the pump and probe pulses are focused to a small (typically a few tens of μ m) spot size to generate signals that are measured with a lock-in amplifier. As a result, the modeling of the data needed to extract the thermal parameters of interest is complicated as it must account for both:^{11,12,15} 1) the heat built-up within the sample due to pulse accumulation, because the high repetition rate exceeds the kinetics of heat loss out of the sample and into the substrate; and 2) the radial and vertical diffusion of heat in the sample, because the small pump spot leads to both radial and vertical heat loss. Thus, TDTR experiments require precisely characterizing the pump beam radius, r_0 , and also must differentiate the radial (κ_r , or a combination of in-plane κ_{xx} and κ_{yy}) and the vertical (cross-plane, κ_{zz}) thermal conductivity components when the probe is sensitive to radial heat diffusion. For conventional TDTR to assume 1-D (cross-plane) heat transport, both the modulation frequency and the pump/probe diameter ratio must be sufficiently high or large, respectively, depending on the thermal diffusivity of the underlying material.²⁶ Conversely, in the opposite limit, conventional TDTR may be utilized to resolve both radial and vertical thermal conductivity components with variable-spot-size or modulation-frequency-dependent studies.^{26–28}

In this paper, we present a new thermoreflectance method, femtosecond transient thermoreflectance (fs-TTR), that utilizes a chirped pulse-amplified^{29–32} (hereafter referred to

as just ‘amplified’), kHz repetition-rate, femtosecond pulse duration laser system instead of a MHz repetition-rate oscillator-type laser to simultaneously extract κ_{zz} and σ using a universal bi-layer model for both bulk and thin-film materials beneath the transducer. Our new method takes advantage of a simple retrofitting of standard ultrafast transient absorption (TA) setups that utilize amplified femtosecond lasers to probe reflectance instead of absorbance. Such TA set-ups usually can probe absorbance changes on the order of $10^{-4} \Delta OD$,^{33–37} and here we use them to perform similarly sensitive thermoreflectance measurements that yield robust information about 1-D vertical heat diffusion.

As with standard TA set-ups,^{33–37} our method directly probes pump-on, pump-off changes in reflectivity, $\Delta R = (R_{\text{pump on}} - R_{\text{pump off}})$, as a function of probe delay time using a mechanical delay stage. Although the low repetition rate is not conducive to lock-in amplification, the high pulse energies allow generation of a white-light continuum for the probe beam,^{38,39} allowing the TR signal to be acquired at multiple wavelengths simultaneously to improve the signal-to-noise ratio. The lower repetition rate (typically a few kHz) and higher pulse energies (typically a few mJ) of amplified lasers allow for complete thermal equilibration between pulses and permit the use of a much larger pump spot size, which greatly simplifies the thermal modeling of the TDTR signals. The ability to isolate κ_{zz} relies on the fact that we can pump a much larger region than is probed, so that radial heat transport does not take place on the ns time scales of the overall fs-TTR measurement.

Our fs-TTR method builds on but goes beyond the low repetition rate TDTR method presented by Larkin *et al.*,⁴⁰ which utilized a 250 kHz repetition-rate amplified laser system with a 4 μJ pulse energy, and detected the TR signal using lock-in amplification. Unlike the thermal model we present below, that used by Larkin *et al.* is sensitive only to the substrate and not to any thin-film samples of interest underneath the transducer in tri-layer samples.⁴⁰ Our

fs-TTR method is also distinct from previous ns- and ps-transient thermoreflectance experiments that utilize tens of kHz pulse repetition rates for exciting the samples of interest but employ a continuous-wave (CW) laser as the probe.^{41–43} However, all of these previous TDTR and TTR methods, as well as our new fs-TTR method, share similar advantages over oscillator-type TDTR, such as the elimination of heat build-up from pulse accumulation and more strict 1-D vertical heat diffusion sensitivity.^{41,43}

In what follows, we show that performing transient thermoreflectance with an amplified transient absorption laser system (which is what we refer to as ‘fs-TTR’) and using a correspondingly-derived simplified thermal model allows accurate determination of both κ_{zz} for different materials that span four orders of magnitude in thermal conductivity (~ 0.10 – 100 $\text{W m}^{-1} \text{K}^{-1}$) and the σ of the transducer-underlying material interface, even for low- κ_{zz} polymer thin-film samples. Furthermore, we show that fs-TTR provides a multi-wavelength detection advantage such that the signal can be integrated over a spectral range of wavelengths rather than the single wavelength available to oscillator-type TDTR. Fs-TTR is capable of simultaneously determining values for both κ_{zz} and σ with equal or slightly higher certainty than measurements taken with oscillator-type TDTR. This is primarily due to simplifications of the thermal model afforded by using an amplified laser system, the minimization of noise-related uncertainty in fitted values of κ_{zz} and σ , and the dual-sensitivity of the model to locate solutions for both κ_{zz} and σ , which are anti-correlated, in the 2-D parameter space.

3.2 Thermal Model for fs-TTR Utilizing an Amplified Ultrafast Transient Absorption System

TDTR was originally developed utilizing oscillator-type laser systems that operate at pulse repetition rates of single to tens of MHz with pulses energies of ~ 1 nJ, necessitating focused beam diameters on the order of tens or hundreds of μm .⁶ The modeling of oscillator-

driven TDTR data thus utilizes heat diffusion equations written in cylindrical coordinates to account for radial and vertical heat diffusion within the multilayer sample.^{11,12,15} If the beam spot size, r_0 , is well characterized, the heat diffusion equations, including α and σ as fitting parameters, are solved using the thermal quadrupole approach:^{1,44} the radial dependence of heat diffusion is converted to radial modes, with each radial mode becoming a separate vertical 1-D heat diffusion problem within the multi-layered sample.

To our knowledge, TR measurements performed using an amplified ultrafast transient absorption system with a pump-on, pump-off detection method have not been presented in the literature. Thus, as mentioned above, our fs-TTR scheme differs from the low-rep-rate TDTR with an amplified laser demonstrated in Ref. 40; we also note that single-pulse TR measurements like fs-TTR are not the same as baseline-subtraction of the in-phase signal of conventional TDTR responses (see Ref. 45). In what follows, we present a new thermal model for fs-TTR that incorporates the unique physics of amplified lasers with pulse energies in the mJ regime at a repetition rate of a few kHz. The high pulse energy allows the use of pump spot sizes on the order of many mm in diameter, while the low repetition rate prevents heat build-up in the sample between pulses. If the probe beam diameter remains small (less than hundreds of μm in comparison to the mm-sized pump), then the area around the probe is uniformly heated so that the temperature response of the probe is no longer sensitive to lateral heat diffusion. This means that only cross-plane heat diffusion modifies the temperature of the transducer in the probed area. The pump/probe beam size differences between oscillator-type TDTR and our fs-TTR method are qualitatively shown in **Figures. 3.1a-b**.

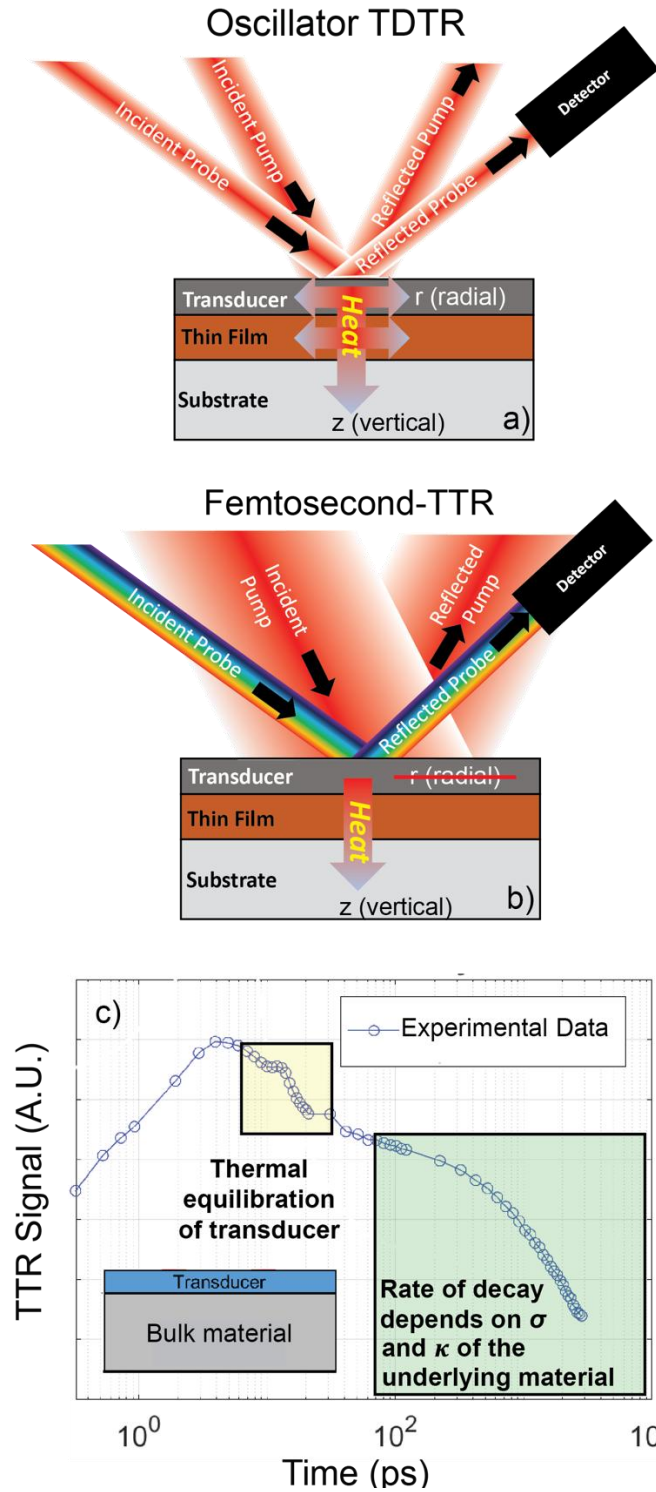


Figure 3.1. (a) Schematic of the common oscillator-based TDTR method. The small pump/probe spot size ratio results in the thermal response of the probe being sensitive not only to the laser spot size but also to heat diffusion in both the radial and vertical directions. (b) Schematic of the new proposed

amplified fs-TTR method presented in this work. The significantly larger pump/probe spot size ratio results in the thermal response of the probe being sensitive only to 1-D vertical heat diffusion. The rainbow coloring of the probe beam represents the ability of fs-TTR to have the thermoreflectance signal measured simultaneously at multiple wavelengths, as is typical in ultrafast transient absorption experiments, providing a signal-to-noise ratio advantage. (c) An example of fs-TTR data for an Al transducer on bulk silicon. The signal from 0 until ~ 120 ps is dominated by thermalization of the transducer. After ~ 120 ps, the signal depends only on the κ_{zz} and σ of the underlying material of interest, allowing the model described below to be fit to this portion of the data with a high degree of precision.

TR methods rely on pumping an interband transition or plasmon resonance to deposit heat into the selected metal transducer. Modeling the heat delivered to the transducer by the pump is done by applying a variation of Beer-Lambert law, Equation 3.2, adapted here from the work of Zhang *et al.*⁴⁶ To model temperature along a 1-D vertical grid, as depicted in Figure 2, the transducer is comprised of spatial depth points indexed at positions $i = 1$ to k , where $z_i = i \cdot \Delta z$, and at time-steps indexed by j , where $t_j = j \cdot \Delta t$ and $j = 0$ is the initial condition:

$$T_i^{j=0} = \frac{J(1 - R^{\text{pump}})}{C_v^{\text{met}} \delta^{\text{pump}}} \exp\left(-\frac{z_i}{\delta^{\text{pump}}}\right). \quad (3.2)$$

In Eq. 3.2, T is the absolute temperature at position z_i at time zero, J is the laser fluence of the pump beam, R^{pump} is the reflectance of the transducer at the pump wavelength, C_v^{met} is the volumetric heat capacity of the metal transducer, and δ^{pump} is the optical penetration depth of the pump wavelength. Throughout, we use the superscripts ‘met’ and ‘sam’ to denote that a particular variable is associated with the metal transducer or the underlying sample material of interest, respectively. Eq. 3.2 also assumes that no light interacts with the material beneath the transducer. Therefore, it is important that the transducer thickness is greater than roughly three

optical penetration depths to ensure that $\geq 95\%$ of the pump light is attenuated by the transducer.

Due to the sufficiently large pump-probe spot size ratio afforded by amplified systems, heat diffusion within the transducer and underlying material can be described using Fourier's equations for one-dimensional heat transport along direction z :

$$\frac{\partial T^{\text{met}}}{\partial t} = \alpha^{\text{met}} \frac{\partial^2 T^{\text{met}}}{\partial z^2} = \frac{\kappa^{\text{met}}}{C_v^{\text{met}}} \frac{\partial^2 T^{\text{met}}}{\partial z^2} \quad (3.3)$$

$$\frac{\partial T^{\text{sam}}}{\partial t} = \alpha_{zz}^{\text{sam}} \frac{\partial^2 T^{\text{sam}}}{\partial z^2} = \frac{\kappa_{zz}^{\text{sam}}}{C_v^{\text{sam}}} \frac{\partial^2 T^{\text{sam}}}{\partial z^2}, \quad (3.4)$$

where t is the time after the pump pulse is incident on the transducer and T is the temperature. The cross-plane thermal diffusivity of the underlying sample material, α_{zz}^{sam} , is used as a fitting parameter to the fs-TTR data, which in turn yields the cross-plane thermal conductivity, κ_{zz}^{sam} , if the volumetric heat capacity of the sample material, C_v^{sam} , is known. We assume that the metal transducer is thermally isotropic and thus do not place a 'zz' subscript on α^{met} and κ^{met} .

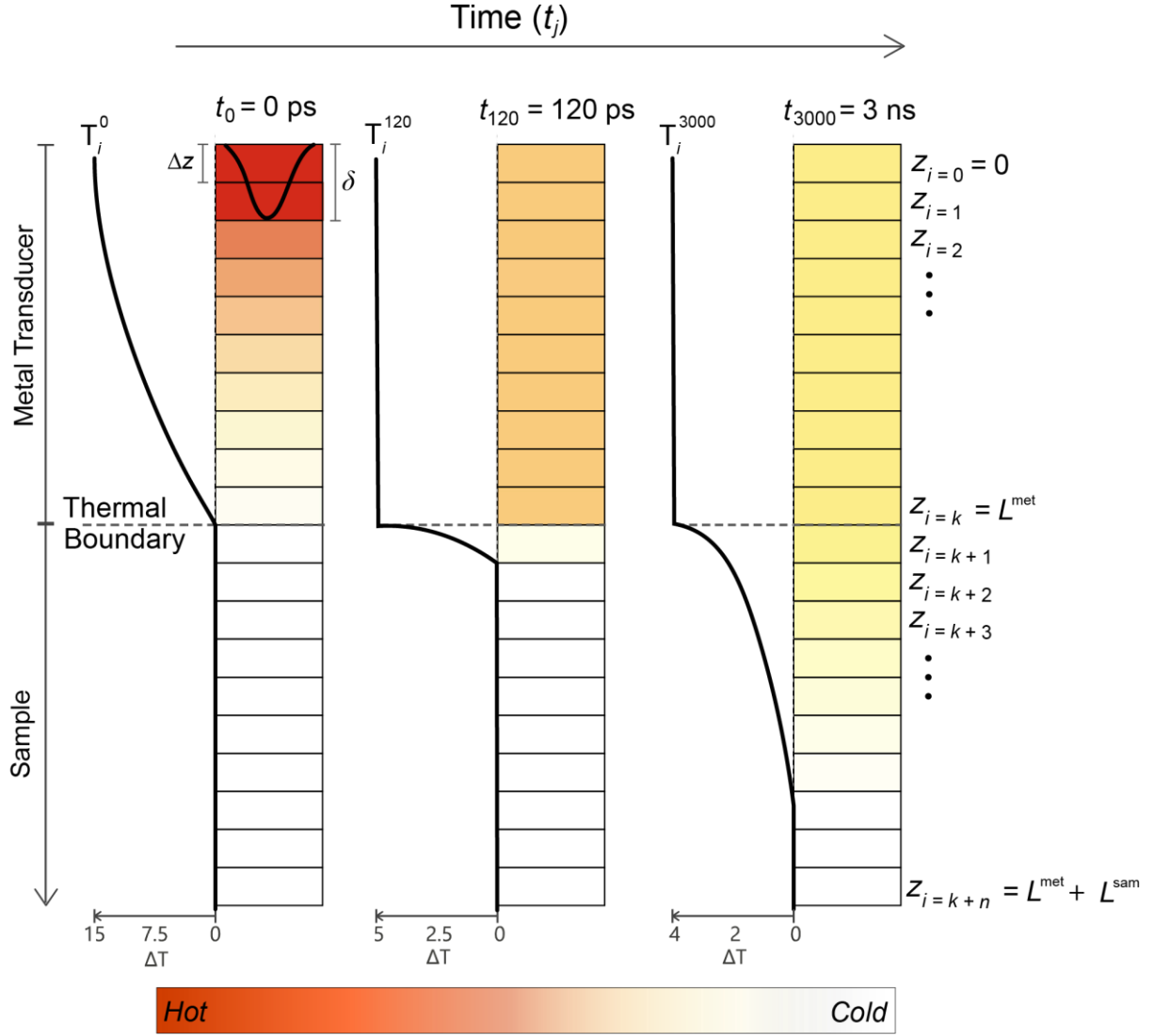


Figure 3.2. Discretized depiction of the 1-D thermal model for fs-TTR at different time stages. From left to right, $t_0 = 0$ ps corresponds to the point at which the transducer absorbs heat from the pump pulse, t_{120} corresponds to a time delay of 120 ps when the transducer has thermalized across its entire depth and heat is just beginning to enter the sample of interest, and t_{3000} corresponds to time delay of 3 ns where heat has diffused a significant distance into the underlying sample layer. The fitting parameters of the model include the thermal boundary conductance, σ , located at $z = L^{\text{met}}$, which quantifies the transfer of heat across the interface between the transducer and sample material, as well as α_{zz}^{sam} , which is the rate at which heat diffuses within the ‘zz’ direction of the underlying sample material (cf. Eq. 3.1).

To solve Eqs. 3.3 and 3.4, we rewrite the equations so that space and time are discretized, as in Eq. 3.2, in a Crank-Nicolson finite differences formalism:⁴⁷

$$\begin{aligned} & -\alpha^{\text{met}} \frac{\Delta t}{\Delta z^2} T_{i-1}^{(j+1)} + 2 \left(1 + \alpha^{\text{met}} \frac{\Delta t}{\Delta z^2} \right) T_i^{(j+1)} - \alpha^{\text{met}} \frac{\Delta t}{\Delta z^2} T_{i+1}^{(j+1)} \\ & = \alpha^{\text{met}} \frac{\Delta t}{\Delta z^2} T_{i-1}^{(j)} + 2 \left(1 - \alpha^{\text{met}} \frac{\Delta t}{\Delta z^2} \right) T_i^{(j)} + \alpha^{\text{met}} \frac{\Delta t}{\Delta z^2} T_{i+1}^{(j)} \end{aligned} \quad (3.5)$$

$$\begin{aligned} & -\alpha_{\text{zz}}^{\text{sam}} \frac{\Delta t}{\Delta z^2} T_{i-1}^{(j+1)} + 2 \left(1 + \alpha_{\text{zz}}^{\text{sam}} \frac{\Delta t}{\Delta z^2} \right) T_i^{(j+1)} - \alpha_{\text{zz}}^{\text{sam}} \frac{\Delta t}{\Delta z^2} T_{i+1}^{(j+1)} \\ & = \alpha_{\text{zz}}^{\text{sam}} \frac{\Delta t}{\Delta z^2} T_{i-1}^{(j)} + 2 \left(1 - \alpha_{\text{zz}}^{\text{sam}} \frac{\Delta t}{\Delta z^2} \right) T_i^{(j)} + \alpha_{\text{zz}}^{\text{sam}} \frac{\Delta t}{\Delta z^2} T_{i+1}^{(j)} \end{aligned} \quad (3.6)$$

where i indexes a particular z location with $z = 0$ at the top of the transducer, and j indexes a particular time after excitation, as shown in **Fig. 3.2**. Heat transfer across the interface of the transducer-underlying material, located at thickness $z = L^{\text{met}}$, is then described by:

$$-\kappa^{\text{met}} \frac{\partial T^{\text{met}}}{\partial z} \Big|_{z=L^{\text{met}}} = \sigma [T^{\text{met}}(L^{\text{met}}, t) - T^{\text{sam}}(L^{\text{met}}, t)] = -\kappa_{\text{zz}}^{\text{sam}} \frac{\partial T^{\text{sam}}}{\partial z} \Big|_{z=L^{\text{met}}}, \quad (3.7)$$

where σ is the thermal boundary conductance, also typically used as a fitting parameter. In its discretized Crank-Nicolson form, Equation 3.7 is written as:

$$\begin{aligned} -\kappa^{\text{met}} \frac{-3T_k + 4T_{k-1} - T_{k-2}}{2\Delta z} &= \sigma \left(\frac{4T_{k-1} - T_{k-2}}{3} - \frac{4T_{k+2} - T_{k+3}}{3} \right) \\ &= -\kappa_{\text{zz}}^{\text{sam}} \frac{3T_{k+1} - 4T_{k+2} + T_{k+3}}{2\Delta z}, \end{aligned} \quad (3.8)$$

where the index k denotes the depth of the interface between the metal transducer and the underlying film, so that the spatial depth points representing the underlying sample run from $k + 1$ to $k + n$, as also depicted in Fig. 3.2.

Due to the low repetition rate of amplified laser systems and the corresponding lack of pulse accumulation-induced heat build-up, we can safely assume in our model for most materials and thicknesses that: 1) heat fully dissipates throughout the material layer(s) underneath the transducer in both bi- and tri-layer sample geometries before the next pump

pulse arrives, and 2) heat does not reach the back of the underlying film or substrate within the few-ns time window of the probe delay. This is specified mathematically by the adiabatic boundary condition:

$$\left. \frac{\partial T^{\text{sam}}}{\partial z} \right|_{z=L^{\text{sam}}} = 0, \quad (3.9)$$

where $z = L^{\text{sam}}$ is the distance coordinate of the backside of the underlying material layer. We show in Fig. B.8 in Appendix B that assumption (1) is easily tested by checking that the transient signal has fully recovered to baseline before the next pulse. We also discuss in Section 4 in Appendix B that assumption (2) can be verified by using our thermal model to predict the extent of heating through the underlying layer as a function of depth and time if rough values for κ_{zz}^{sam} are known (see Fig. B.13 in Appendix B).

The integrated probed temperature of the transducer, θ , is then modeled using Equation 3.10, which is rewritten as Equation 3.11 in discretized form:

$$\theta(t; \kappa_{zz}^{\text{sam}}, \sigma) = \int_0^{L^{\text{met}}} \exp\left(-\frac{z}{\delta^{\text{probe}}}\right) \cdot T^{\text{met}}(z, t) dz \quad (3.10)$$

$$\theta(t_j; \kappa_{zz}^{\text{sam}}, \sigma) \approx \sum_{i=1}^k \exp\left(-\frac{z_i}{\delta^{\text{probe}}}\right) \cdot T_i^{(j)} \cdot \Delta z. \quad (3.11)$$

This time-dependent spatially-integrated transducer temperature is directly proportional to the fs-TTR signal, which is based on how the reflectance changes with the transducer temperature. The optical penetration depth of the probe light, δ^{probe} , determines how sensitive the probe is to the transducer temperature at a particular depth:

$$\left(R_{\text{pump on}}^{\text{probe}} - R_{\text{pump off}}^{\text{probe}}\right) = \Delta R^{\text{probe}}(t_j) \approx \left(\frac{dR^{\text{probe}}}{dT^{\text{met}}}\right) \theta(t_j; \kappa_{zz}^{\text{sam}}, \sigma). \quad (3.12)$$

Thus, the change in reflectivity of the probe as a function of time, $\Delta R^{\text{probe}}(t_j)$, is proportional to $\theta(t_j; \kappa_{zz}^{\text{sam}}, \sigma)$ through the thermorefectance coefficient of the metal transducer, $dR^{\text{probe}}/dT^{\text{met}}$.

To fit this thermal model to experimental fs-TTR data, we implement a nonlinear least-squares fitting algorithm (lsqnonlin in MATLAB) that optimizes the model fit via residual minimization:

$$\min \text{RSS}(\kappa_{zz}^{\text{sam}}, \sigma, c) = \sum_{j=1}^N [c \cdot y_j^{\text{data}} - \theta(t_j; \kappa_{zz}^{\text{sam}}, \sigma)]^2, \quad (3.13)$$

where min RSS is the minimized square residual, N is the number of experimental time points and y_j^{data} is the amplitude of an experimental thermoreflective signal at the j^{th} time point. The fitting parameters are κ_{zz}^{sam} and σ , plus a scaling parameter c that normalizes the amplitude of the fs-TTR signal. The scaling factor avoids having to know precise numerical values for the laser fluence, J , and the thermorefectance coefficient as model inputs, both of which would be necessary only to predict the magnitude of the signal. Because the fs-TTR signal amplitude scales linearly with pump power (see Fig. B.7 in Appendix B), we can use this simple scaling factor to match the signal amplitude generated by the model with experimentally-acquired thermoreflective data.

To fit the thermal model to data, as is also necessary in conventional TDTR modeling, we must specify properties of the metal transducer, such as κ^{met} , C_v^{met} , the optical penetration depth, the percent reflectivity and the transducer thickness. For tri-layer thin-film samples, the use of a universal bi-layer model in performing fs-TTR necessitates that the thickness of the underlying material must be precisely measured to ensure that heat does not reach the substrate

(or the second interface) within the $\sim$ ns time window of the probe delay. The MATLAB code that fits the model to data and solves for κ_{zz}^{sam} and σ is included in the SI/repository link.

We note that the fs-TTR model we present above is not designed to accurately account for short-time thermal phenomena such as acoustic echoes or hot electron carrier dynamics,^{48,49} neither of which are required for studying the thermal behavior of the underlying material. Therefore, we fit our thermal model to thermorefective data starting at $\sim$ 120 ps time delay, after these more rapid processes are fully complete. Our model also does not need to account for radiative cooling, which can play a role in thermorefectance measurements that take place on μ s time scales,^{41,43} because this type of heat transfer is negligible on the few ns-timescale of a fs-TTR experiment.

3.3 Noise and Sensitivity Analysis of the fs-TTR Thermal Model

In this section, we analyze how well the 1-D thermal model can extract κ_{zz}^{sam} and σ from fs-TTR data that has varying levels of noise. We do this by generating simulated signal data with pre-selected κ_{zz}^{sam} and σ values, adding selected amounts of Gaussian noise to the simulated signal, and then fitting the thermal model to this noisy data to test how well the model extracts the original values of κ_{zz}^{sam} and σ . We also perform a sensitivity analysis to understand correlations between the fit parameters, which we find differs from how these parameters behave in oscillator-type TDTR thermal models.

We investigated the model's sensitivity to noise across materials with a four-order-of-magnitude range of κ 's, similar to what we measure experimentally with fs-TTR in Section 3.4, below. For the sensitivity testing, we chose parameters to model the thermorefectance signals of silicon, sapphire, fused silica and polystyrene (see Table B.2 of Appendix B), each with a 75-nm-thick Al transducer. After simulating the signals, we added Gaussian noise to

the simulated data and then quantified the noise percentage (see Table B.3 of Appendix B) as the average magnitude of root-mean-square (RMS) residuals relative to the noiseless simulated fs-TTR trace with the input values of κ_{zz}^{sam} and σ . In total, we generated 100 data sets for each simulated material at each of the multiple noise levels using data sets with the same time intervals and number of data points that we use experimentally below in Section 3.4. To test the reliability of the fs-TTR model as a function of noise level, we fit the model to the simulated noisy data and extracted κ_{zz}^{sam} and σ as the fitting parameters (see Fig. B.15 of Appendix B for a distribution of fitting results for a given sample at a single noise level).

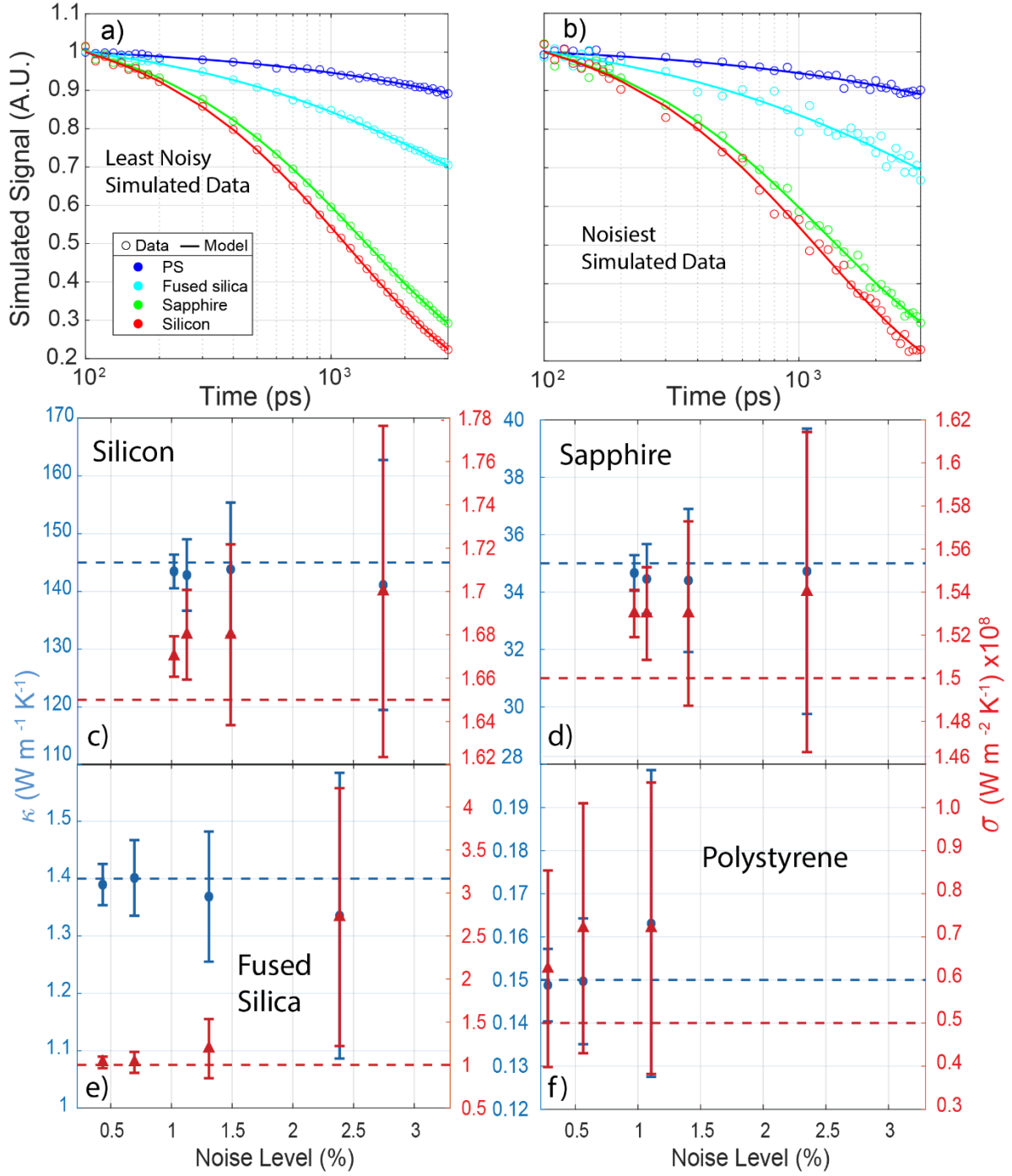


Figure 3.3. a) Decay trace examples of simulated noisy data for four materials of interest at the lowest noise levels analyzed. b) Similar examples of simulated noisy data at the highest noise levels tested. c-f) κ_{zz}^{sam} and σ determined from fitting the fs-TTR thermal model for simulated noisy data emulating silicon (c), sapphire (d), fused silica (e) and polystyrene (f), each as a function of increasing percentage of added gaussian noise. The noisy data was generated with a time interval of 10 ps between 120 ps

and 200 ps and a time interval of 100 ps between 200 ps and 3 ns, respectively, as used in the experiments presented below in Section 3.4. The red and blue dashed lines represent the initially simulated, ‘correct’ values for κ_{zz}^{sam} and σ , respectively, whereas the error bars represent the standard deviation of the parameters extracted from 100 fitted data sets.

Figure 3.3 displays examples of simulated data with the lowest and highest tested noise levels for each material (panels a,b) as well as the average κ_{zz}^{sam} and σ parameters extracted from 100 fitted data sets at each noise level for each material, with the raw standard deviation used as the error bars (panels c-f); see Section 5 in Appendix B for further details on how the noisy simulated data was generated and analyzed. For high- κ_{zz}^{sam} , high- σ samples (silicon and sapphire, Figs. 3.3c-d), our results show that correct values (within 3% of the initially simulated input) for both κ_{zz}^{sam} and σ are obtained even through the 2–3% noise regime. As the noise percentage level gets smaller, the variability (the standard deviation or error bars) in our extracted values also gets smaller and closer to the initially-simulated ‘correct’ values. This indicates that the model remains consistent even at elevated noise levels for high- κ_{zz}^{sam} materials, although we suggest using data with $< 1.5\%$ noise to remain in the most accurate regime to fit κ_{zz}^{sam} and σ . We also observe an anticorrelation between the extracted values: if the average κ_{zz}^{sam} is slightly underestimated compared to the simulated value, then the average σ is slightly overestimated. This anticorrelation between the κ_{zz}^{sam} and σ parameters occurs with materials that have high thermal conductivities because both parameters affect the fs-TTR signal on similar time scales.

For simulated fused silica, which has a κ_{zz}^{sam} that is two orders of magnitude lower than silicon, the accuracy and reliability of the model fit is more impacted by noise. Above the 2% noise level, the model consistently yields values of σ that are higher than the initially-simulated

value, as seen in Figure 3.3e. Despite the overestimated average, however, the average fitted κ_{zz}^{sam} at the same noise level is $< 5\%$ below the simulated value. This is because κ_{zz}^{sam} and σ become less correlated (more orthogonal) in lower- κ_{zz}^{sam} materials: as we show below, σ is more determined by the early-time part of the transient signal in fs-TTR, while κ_{zz}^{sam} is more reflected in the longer-time part of the decay. We suggest only using data with $< 1\%$ noise to remain in the most accurate regime to fit the κ_{zz}^{sam} and σ of low κ_{zz}^{sam} materials.

Finally, for simulated polystyrene, a polymeric material with an order of magnitude lower κ_{zz}^{sam} than fused silica, even relatively low ($< 1\%$) noise levels inhibit the ability of the model to accurately extract σ , as seen in Figure 3.3f. Like with fused silica, however, the fitted κ_{zz}^{sam} is less than 1% different from the simulated value below the 0.6% noise level and is less than 10% different at the $\sim 1\%$ noise level. This observation reinforces the idea that with fs-TTR, κ_{zz}^{sam} and σ become increasingly decorrelated as the thermal conductivity of the sample material decreases. This means that fs-TTR can obtain accurate fitted values for κ_{zz}^{sam} even if it is difficult to reliably extract σ due to high noise. If experimental data pertaining to very low- κ_{zz}^{sam} ($< 1 \text{ W m}^{-1} \text{ K}^{-1}$) materials has too high of a noise level (above 0.5%) to reliably determine σ , one may choose to simply keep σ as a pre-selected input value that is held constant, as the choice of σ negligibly influences the fit of κ_{zz}^{sam} . This alternative approach, as mentioned above, is already the standard when performing oscillator-type TDTR measurements on very low- κ_{zz}^{sam} materials.^{23–25}

Another way to show the dependence of the κ_{zz}^{sam} and σ fitting parameters in the 1-D fs-TTR model is by calculating sensitivity ratios. The sensitivity ratio, Equation 3.14, quantitatively reveals the influence that a specific parameter has on the model fit with respect to the measured signal:

$$S_x(t_j) = \frac{\theta_{x+\Delta x}(t_j) - \theta_x(t_j)}{\frac{\Delta x}{x} \theta_x(t_j)} = \frac{\Delta \theta_x(t_j)}{\theta_x(t_j)} \left(\frac{\Delta x}{x} \right)^{-1}, \quad (3.14)$$

where $S_x(t_j)$ is the sensitivity ratio of model parameter x at the j^{th} time-step point and Δx is a small perturbation (usually single percentages). We normalized the sensitivity ratios, which are shown in **Figure 3.4a-d**, to allow better comparison of the relative sensitivity ratios for each parameter for the different simulated materials.

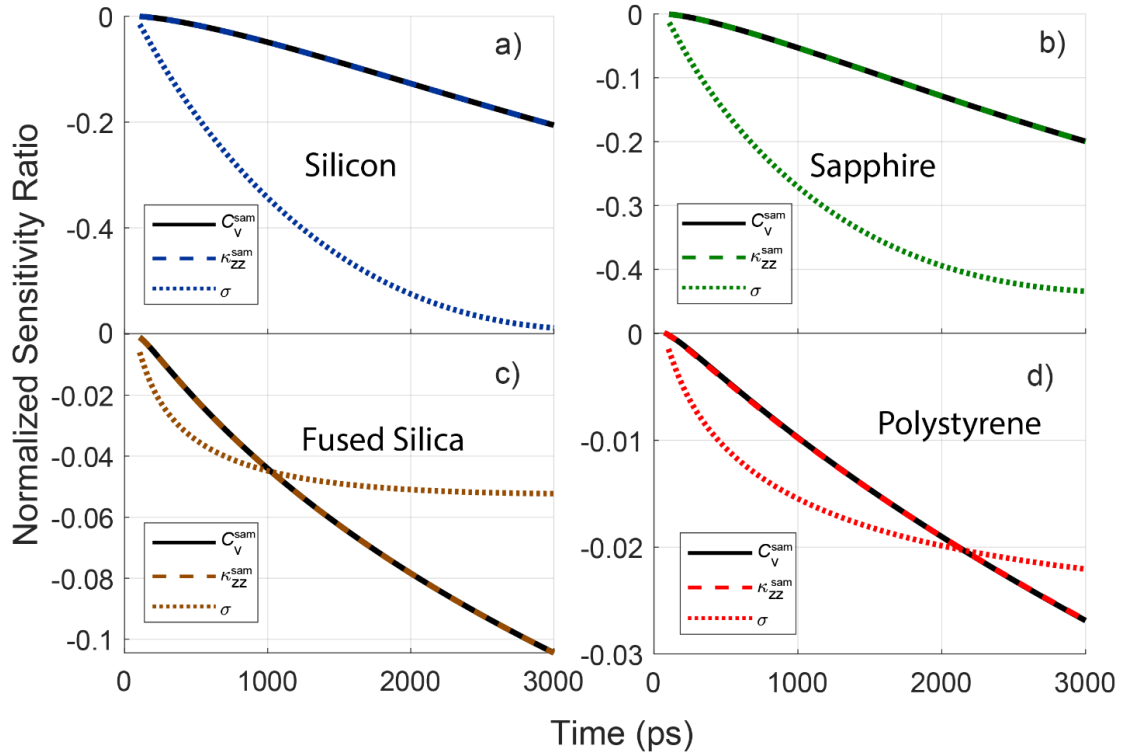


Figure 3.4. Sensitivity ratios, calculated using Eq. 3.14, for the thermal properties of C_v^{sam} , κ_{zz}^{sam} , and σ corresponding to the fs-TTR-simulated systems in Fig. 3.3, including: (a) Al/silicon, (b) Al/sapphire, (c) Al/fused silica, and (d) Al/polystyrene. The sensitivity ratios for C_v^{sam} and κ_{zz}^{sam} are identical as fs-TTR measures the thermal diffusivity, which is composed of these two parameters (cf. Eq. 3.1). For lower- κ_{zz}^{sam} fused silica and polystyrene samples, the thermal boundary conductance, σ , has the most influence on the thermoreflectance signal at early delay times, while κ_{zz}^{sam} more strongly controls the fs-TTR decay at longer delay times. Conversely, for higher- κ_{zz}^{sam} silicon and sapphire samples, the

thermal boundary conductance more strongly controls the thermoreflectance decay compared to κ_{zz}^{sam} across the entire selected probe delay range. See Fig. B.16 of Appendix B for additional sensitivity ratio curves for all other model input parameters.

The sensitivity ratios we calculated using Eq. 3.14 show that, as an absolute value, $|S_k^{\text{sam}}|$ increases as a function of fs-TTR delay time for all simulated materials. This is very different from oscillator-type TDTR where $|S_k^{\text{sam}}|$ peaks at early delay times and then decreases as a function of time.^{1,50–53} Additionally, $S_k^{\text{sam}}(t_j)$ is negative in fs-TTR but is typically positive in traditional oscillator-type TDTR.^{1,52} This difference means that in fs-TTR, a faster decay of the signal with time is directly correlated with higher κ_{zz}^{sam} values, so that longer delay times are more important for fitting accurate values of κ_{zz}^{sam} than shorter delay times. This also means that fs-TTR provides less sensitivity for lower- κ_{zz}^{sam} materials due to shallower signal decays, as is reflected in the S_k^{sam} and S_σ for polystyrene, both of which are smaller in absolute value compared to materials with higher heat conduction. However, as demonstrated in Section 3.4 below, with sufficiently low-noise data, we are still able to resolve both fitted values of κ_{zz}^{sam} and σ to reasonable certainties for very low- κ_{zz}^{sam} polymeric materials.

In the thermal model for fs-TTR, the sensitivities of the thermal conductivity and volumetric heat capacity, S_k^{sam} and $S_{C_v}^{\text{sam}}$, are equal because the ratio of κ_{zz}^{sam} and σ are equal to α_{zz}^{sam} , as shown in Eq. 3.1. This fact means that fs-TTR requires C_v^{sam} to determine κ_{zz}^{sam} , as is also the case for high-modulation-frequency TDTR measurements.^{1,2} For example, the modulated pump frequencies typically used in conventional TDTR cause S_k^{sam} to match $S_{C_v}^{\text{sam}}$ as a function of probe delay time,¹ although the sensitivities of the two parameters begin to deviate below the 1–10 MHz regime.^{1,18} Due to the nonzero $S_{C_v}^{\text{sam}}$ present in both fs-TTR and

TDTR, any uncertainty in the measured value of C_v^{sam} will be propagated directly to the extracted fit values of κ_{zz}^{sam} and σ .

Since the real-value sensitivity ratios S_{κ}^{sam} and S_{σ} are both negative as a function of probe delay time in fs-TTR, an overestimation of one parameter results in the other parameter being underestimated, as shown by the spread of fitting results for κ_{zz}^{sam} and σ in Figure B.15 in Appendix B as well as above in Fig. 3.3. However, in conventional TDTR, an overestimation of κ_{zz}^{sam} results in an overestimation in σ , as shown by Jiang *et al.*¹ This is because there is a difference in the behavior of the sensitivity ratios of the two methods: in conventional TDTR, S_{κ}^{sam} is a positive value that decreases towards 0 over time and S_{σ} is a decreasing value that turns from positive to negative as a function of time,¹ whereas these ratios are both negative and become more negative over time in fs-TTR.

We should note that both TDTR and fs-TTR share the requirement of having well-characterized transducer properties (L^{met} , C_v^{met} and κ^{met}) as model input parameters. This is because the thermoreflective signals measured by both methods are sensitive to the transducer properties, as shown by the fact that the transducer property sensitivity ratio values are on the same order or even larger than the sensitivity ratios for κ_{zz}^{sam} and σ . We provide a complete comparison of sensitivity ratios in Fig. B.16 of Appendix B for fs-TTR, while a similar analysis for oscillatory-type TDTR has been presented in work by both Jiang *et al.*²⁷ and Zhang *et al.*⁵⁴

Overall, our sensitivity analysis shows that the ability to simultaneously extract both κ_{zz}^{sam} and σ is robust with the fs-TTR model. For fs-TTR, the fitting parameter σ has much greater influence on the overall signal (larger sensitivity) than κ_{zz}^{sam} at early times (≤ 1 ns), regardless of how well the system/underlying material transports heat. $|S_{\kappa}^{\text{sam}}|$ and $|S_{\sigma}|$ are larger in materials with higher κ_{zz}^{sam} and σ , whereas with lower thermal conductivity materials, S_{σ} has a smaller magnitude, reaching its plateau at earlier times. This results in $|S_{\kappa}^{\text{sam}}| > |S_{\sigma}|$

at longer delay times for our simulated fused silica and polystyrene systems. These differences, along with the fact that there are fewer fitting parameters and input values that can contribute to error, is what allows extracted values of κ_{zz}^{sam} and σ from fs-TTR to have similar or even lower uncertainty compared to conventional TDTR, as demonstrated in Section 3.4 below.

3.4 Experimental Validation of fs-TTR Using Samples that Span Four Orders of Magnitude in Thermal Conductivity

To verify that the model developed in Section 3.2 and an amplified laser can perform accurate thermal measurements, we fabricated six samples that span four orders of magnitude in thermal conductivity (~ 0.10 to hundreds of $\text{W m}^{-1} \text{K}^{-1}$). Simple bi-layer (transducer/underlying material) samples of silicon (Si), sapphire (Al_2O_3), and fused silica (SiO_2) were fabricated by evaporating $100. \pm 1$ nm thick Al transducers directly on top of the material (see Section 1.2 in Appendix B for details). We also prepared thin-film, tri-layer samples of polystyrene (PS) and poly(methyl methacrylate) (PMMA) by spin-casting these polymers onto silicon substrates followed by evaporation of a $100. \pm 1$ Al transducer (also see Section 1.2 in Appendix B for details).

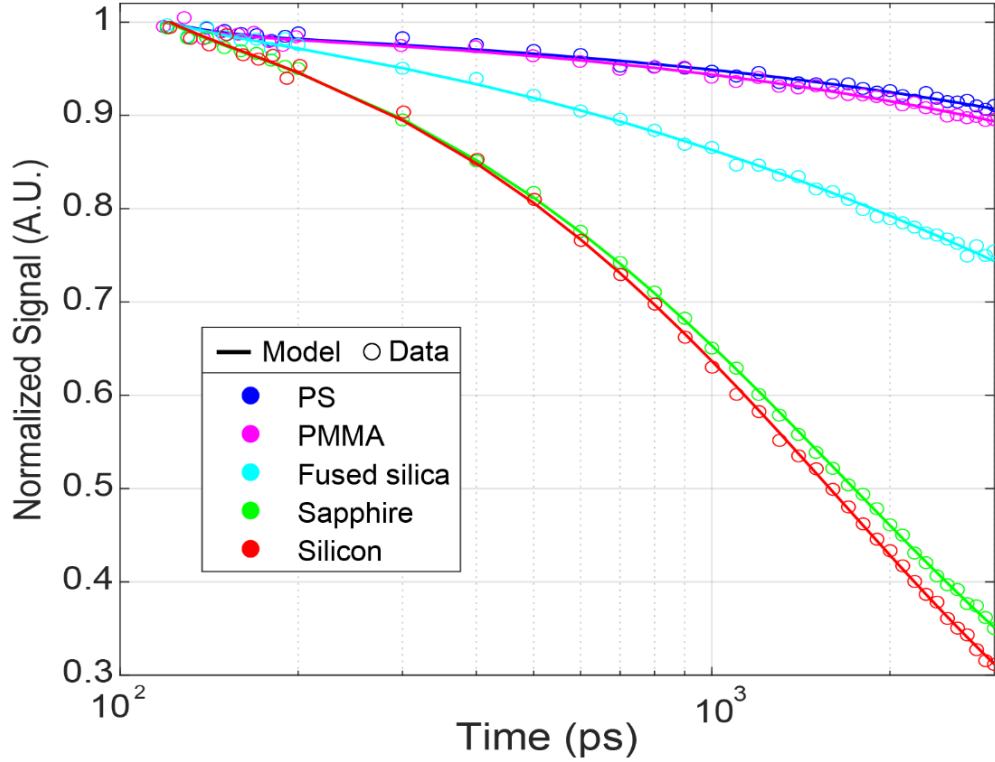


Figure 3.5. Experimental fs-TTR signal traces for silicon (red), sapphire (green), fused silica (aquamarine), PMMA (magenta), and PS (dark blue) samples, each with an evaporated 100-nm-thick Al transducer. The pump wavelength was 800 nm and the integrated probe wavelength range was 900–915 nm. The pump/probe spot size ratio was 70.5:1. The experimental data are the circles and the corresponding model fits are the solid curves. The percentage noise of each dataset, given in Table 3.1, was calculated using the RMS residuals of the data and the final model fit, the same way as in Fig. 3.3. Fs-TTR traces that include the early probe time-delay window (not included in model fits) are shown in Fig. B.9 in Appendix B. The minimized square residuals of the model fits are shown in Fig. B.12 in Appendix B.

Table 3.1. Fitted values of κ_{zz}^{sam} and σ for various materials in contact with Al transducers determined by fitting the data taken with fs-TTR shown in Fig. 3.5 to the model in Section 3.2, along with literature values for these same materials.

Material	C_v^{sam} Input (J cm ⁻³ K ⁻¹)	Extracted κ_{zz}^{sam} (W m ⁻¹ K ⁻¹) ^c	Lit. κ_{zz}^{sam} (W m ⁻¹ K ⁻¹)	Extracted σ (MW m ⁻² K ⁻¹) ^c	Lit. σ (MW m ⁻² K ⁻¹)	Calculated %Noise ^c
Silicon (100)	1.66 ^{18,54}	143 ± 10	130–152 ^{18,19,55–57}	161 ± 2	115–200 ^{57–61}	0.78%

Sapphire (0001; $\parallel$ to c -axis) ^a	3.09 ^{16,62,63}	41.4 $\pm$ 1.4	38–42 ^{64,65}	164 $\pm$ 2	134–350 ^{10,16,66} –68	0.46%
Fused Silica	1.65 ^{18,69,70}	1.31 $\pm$ 0.05	1.27–1.39 ^{20,70–72}	136 $\pm$ 9	100–150 ²⁰	0.52%
PMMA	1.61 ^{23,24,73–75}	0.18(8) $\pm$ 0.02(2)	0.18–0.22 ^{23,24,73–81}	30 $\pm$ 4	No reports on Al/PMMA ^b	0.39%
PS	1.25 ^{82,83}	0.15(3) $\pm$ 0.01(7)	0.14–16 ^{24,82–86}	35 $\pm$ 7	$\sim$ 20 ^{82,84,85}	0.41%

^a The thermal conductivity anisotropy ratio range for sapphire in Ref. 64 was converted to values of κ_{zz}^{sam} by assigning 35 W m^{–1} K^{–1} to the direction perpendicular to the c -axis.

^b See Section 6.4 in Appendix B for details on TBC measurements of PMMA and non-Al metals.

^c This work; values extracted from fitting the data in Fig. 3.5 to the model in Section 3.2.

The fs-TTR experiments we performed pumped the Al transducer at the 1.5-eV^{87,88} peak of the interband transition and integrated the reflected white-light probe wavelengths over the range 900–915 nm; the results are shown as the circles in **Fig. 3.5**. We determined that the probe wavelength range of 900–915 nm was optimal for our set-up due to a convolution of the stability of the white-light continuum generated with our laser at different wavelengths and the high thermoreflective response of Al; we explore the use of this and other probe wavelength ranges in Section 3.1 in Appendix B (see Figs. B.10 and B.11). In Fig. 3.5, each sample was measured at one spot and the extracted values of the fitting parameters in Table 3.1 are from a single measurement. Our integrated signals averaged 30,000 or 60,000 shots per data point for samples with $\kappa_{zz}^{\text{sam}} > 1 \text{ W m}^{-1} \text{ K}^{-1}$ or $\kappa_{zz}^{\text{sam}} < 1 \text{ W m}^{-1} \text{ K}^{-1}$, respectively, across the selected probe delay time window of 120 ps to 3 ns, with a time interval of 10 ps between 120–200 ps and a time interval of 100 ps between 200–3000 ps. This time window and data point interval selection is identical to the simulated data generated for the noise analysis of the thermal model discussed above in Section 3.3.

The solid curves through the fs-TTR data points in Fig. 3.5 are fits to the thermal model described in Section 3.2 (for all model input parameters, see Table B.1 in Appendix B), and the extracted fit parameter values of κ_{zz}^{sam} and σ for each material, which are all consistent with

values found in the literature, are given in Table 3.1. We calculated the uncertainty ($\pm$ error) pertaining to fitted κ_{zz}^{sam} and σ values using the covariance of the Jacobian (which accounts for both noise in data as well as how many unknown variables are parameterized in the thermal model) from MATLAB's `lsqnonlin` fitting algorithm. For underlying materials with $\kappa_{zz}^{\text{sam}} > 1 \text{ W m}^{-1} \text{ K}^{-1}$ and $\sigma > 100 \text{ MW m}^{-2} \text{ K}^{-1}$, our errors in κ_{zz}^{sam} and σ are 3–7% and 1–7%, respectively, which is an improvement over the 7–12% error typically found in traditional oscillator-type TDTR methods.^{50,89} In Table B.4 and Fig. B.17 in Section 6.2 of Appendix B, we perform a detailed error propagation analysis for the fitted values of κ_{zz}^{sam} and σ based on uncertainty in the fs-TTR model input parameters. Additionally, we show in Table B.5 in Section 6.3 of Appendix B that the fitted values of κ_{zz}^{sam} and σ for our samples are anticorrelated. Finally, we show in Fig. B.18 of Appendix B that large deviations in the fitted values of κ_{zz}^{sam} for the Al/Si and Al/sapphire samples only marginally changed the fitted values of σ , whereas for the Al/PMMA/Si and Al/PS/Si samples, multiplicative changes in σ cause κ_{zz}^{sam} to change by only a relatively tiny amount.

Our fs-TTR measurements on the very low- κ_{zz}^{sam} thin-film polymer samples, PS and PMMA, yielded errors in κ_{zz}^{sam} just above 10%, which is comparable to conventional TDTR,^{50,89} and errors in σ as high as 20%. However, our ability to determine both parameters simultaneously at these uncertainty levels is also an improvement over conventional oscillator-type TDTR (where different modulation frequencies would be required to achieve different thermal penetration depths that are sensitive to the different parameters, effectively requiring κ_{zz}^{sam} and σ to be probed independently through separate measurements). We also note that with the signal averaging we implemented above, the noise percentage of our experimental data (calculated using the RMS residuals of the data and the final model fit) falls between 0.4–0.8% for all five materials (see Table 3.1); these noise levels are low enough to provide very good

fitting results based on the analysis in Section 3.3.

Silicon (cubic crystal structure) and fused silica (amorphous SiO₂ network) are thermally isotropic bulk materials,^{65,90} which means that our measurements of κ_{zz}^{sam} are numerically equivalent to κ measurements that involve heat transfer through multiple axes of the material. On the other hand, single-crystal sapphire is thermally anisotropic ($\kappa_{xx} = \kappa_{yy} \neq \kappa_{zz}$),^{64–66} which means that our measurement results depend on the orientation of the sapphire crystal. Here, we used a crystal cut along the 0001 plane, so that the transducer surface is perpendicular to the c -axis, meaning that our fs-TTR experiments report only on heat transfer along the c -axis. In the literature, κ measurements of bulk sapphire fall between 32–38 W m⁻¹ K⁻¹,^{16,62,63,91–96} and the thermal conductivity anisotropy ratio between the c and a axes ranges from 1.08:1–1.18:1.⁶⁴ Our κ_{zz}^{sam} measurement along the c -axis of sapphire, 41.4 ± 1.4 W m⁻¹ K⁻¹, is thus consistent with the literature, as it is higher than reported bulk values by 10–20%, supporting the idea that our fs-TTR method is sensitive only to 1-D vertical heat transfer.

To validate the efficacy of our 1-D model and the use of fs-TTR on tri-layer thin-film samples with low thermal conductivities, we examined two amorphous polymeric materials: PS and PMMA, shown as the blue and magenta curves in Fig. 3.5, respectively. As spin-cast thin-films, PS and PMMA also display thermal anisotropy with in-plane thermal conductivities that are greater than those in the cross-plane direction.^{81,86,97} Our extracted κ_{zz}^{sam} values for both materials fall well within error of values in the literature, as shown in Table 3.1. Our fitted value for the σ of Al/PS interface, in the 30's MW m⁻² K⁻¹, is slightly higher than literature values (~ 20 MW m⁻² K⁻¹),^{82,84,85} although variability in polymer surface roughness and/or metal deposition conditions can change the boundary conductance of metal-polymer interfaces by 10's MW m⁻² K⁻¹.^{21,22,98} To our knowledge, there is no reported thermal conductance measurement for Al/PMMA (see Section 6.4 in Appendix B for other studies performed on

non-Al-metal/PMMA interfaces). However, our inclusion of PMMA as a sample to compare to PS shows with fs-TTR, the κ_{zz}^{sam} of polymeric thin-films can be resolved down to hundredths of $\text{W m}^{-1} \text{K}^{-1}$. The ability of fs-TTR to extract values for σ with $\leq 20\%$ uncertainty is a particularly notable result as our polymer films have thicknesses that are $\sim 10\times$ their Kapitza lengths, so that σ would not be measurable in conventional oscillator-type TDTR. Overall, fs-TTR allows κ_{zz}^{sam} and σ values to be extracted with equal or lower uncertainty compared to conventional TDTR over at least four-orders-of-magnitude range in thermal conductivity.

3.5 Experimental Details for fs-TTR

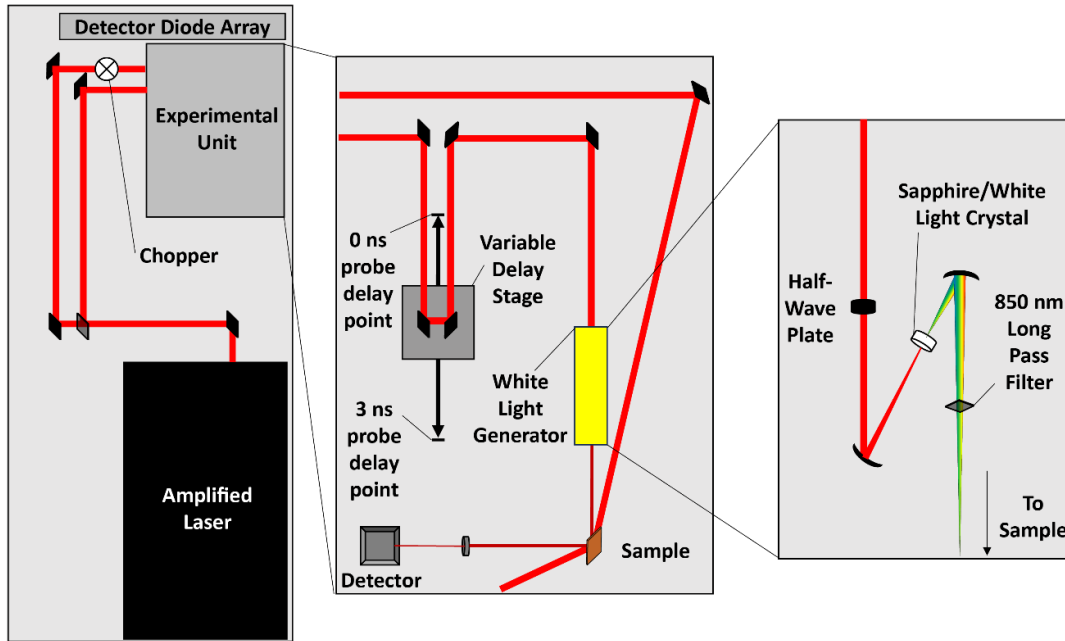


Figure 3.6. Schematic of a standard amplified ultrafast laser transient absorption system that was modified to perform measurements of fs-TTR signal in this work. The amplified laser beam is steered to a beam splitter to generate separate pump and probe beams. Both beams are steered into the experimental unit, although the pump beam goes through an optical chopper that only passes every other pulse. The only change to the set-up from performing transient absorption is that the probe light is collected in reflection instead of transmission. Within the experimental unit, the probe beam is

steered onto a variable delay stage to control the time delay. The probe beam is also steered through a half wave plate – its polarization relative to the pump beam is set to the magic angle (54.7°) and then focused into a sapphire plate to generate a white-light supercontinuum. This white-light probe is then focused tightly onto the sample where it is overlapped with the center of chopped large-diameter pump beam. The transducer on the sample acts as a mirror to steer the probe beam through a focusing lens and into the multiwavelength detector. The signal is collected as the difference between pump-on and pump-off spectra on consecutive laser shots.

One of the main advantages of fs-TTR is that it can use a standard amplified laser TA set-up, where the only modification required is to collect the signal in reflection rather than transmission. We show a schematic of such a system in **Figure 3.6**, with specific details of our particular set-up given in further detail in Section 1.3 in Appendix B. As with many TA systems, our amplified laser produces ~ 3 mJ pulses of ~ 40 -fs duration at 800 nm at a 2 kHz repetition rate; the pulse energy and duration are sufficient to allow the use of non-linear optics for generating other excitation wavelengths and for producing a white-light supercontinuum for probing multiple wavelengths simultaneously. The 800-nm output naturally generated by amplified Ti:Sapphire systems is perfect for heating aluminum transducers as the interband transition for Al is located at 800 nm.^{87,88} Additionally, the white-light probe in amplified systems can be tuned to spectrally overlap with aluminum's optimally-high thermorefectance region located in the near-infrared (850–1500 nm).^{99,100} The time between the pump and probe pulses is controlled mechanically with a variable delay stage, allowing for time delays of up to 3 ns in our setup, which is still sufficient for TDTR even with low κ_{zz}^{sam} materials, as demonstrated in Section 3.4.

An important distinction between conventional TDTR and the fs-TTR method we present is the way that signal is detected. Conventional TDTR uses a lock-in amplifier to resolve both in-phase and out-of-phase signals at the chosen MHz modulation frequency; the ratio of the signals ($V_{\text{in}}/V_{\text{out}}$) yields a TDTR signal as a function of pump-probe delay.^{1,2} Conversely, fs-TTR directly measures the reflected probe intensity for adjacent pump-on and pump-off shots and the signal directly measured is the change in reflectance, $\Delta R = (R_{\text{pump on}} - R_{\text{pump off}})$, as a function of pump-probe delay. The low repetition rate of the pump pulse (which is optically chopped at 1 kHz to be 50% of the probe repetition rate of 2 kHz) allows nearly every sample to return to ambient temperature equilibrium between the pump-on and pump-off probe pulses. The high energy of each pump pulse induces large enough changes in reflectivity, with single ΔmOD signals, that a lock-in amplifier is not necessary.

As mentioned above, the main advantage of having high amplified pulse energies is that the pump spot size can be large enough (many mm) to easily achieve 1-D vertical heat transport, as modeled above in Section 3.2 and demonstrated experimentally on both bulk (sapphire) and thin-film (PS and PMMA) thermally anisotropic materials in Section 3.4. To detect the point at lower pump/probe spot size ratios at which heat transport can no longer be treated with the 1-D model described in Section 3.2, we performed a series of fs-TTR measurements with different spot size ratios, as shown in **Figure 3.7**. Details of how we measured our pump and probe spot sizes are given in Sections 2.1 and 2.2 of Appendix B (see Figs. B.1–B.5). For the measurements in Fig. 3.7, we chose a very low- $\kappa_{\text{zz}}^{\text{sam}}$ sample consisting of an Al transducer on thin-film PMMA on a Si substrate and found that the best-performing (largest signal) pump/probe spot area ratio was 70.5:1 (or 8.4:1 diameter ratio; red points in Fig. 3.7). Since this ratio yielded an accurate value of $\kappa_{\text{zz}}^{\text{sam}}$ for PMMA,⁷⁶ we performed fs-TTR using this ratio for each material studied in Section 3.4. We also found that the 1-D

amplified fs-TTR model breaks down for the PMMA sample when the spot size ratio is $\leq 6.4:1$ (or $\leq 2.5:1$ diameter ratio). The blue points in Figure 3.7 show that at this 6.4:1 spot area ratio, the fs-TTR signal decays faster in time, producing an unphysically high fitted value for κ_{zz}^{sam} compared to the measurement at the 70.5:1 spot size ratio. Failure of the 1-D thermal model at smaller spot area ratios is expected when the probe is large enough to sample the thermal gradient caused by the Gaussian spatial profile of the pump beam.

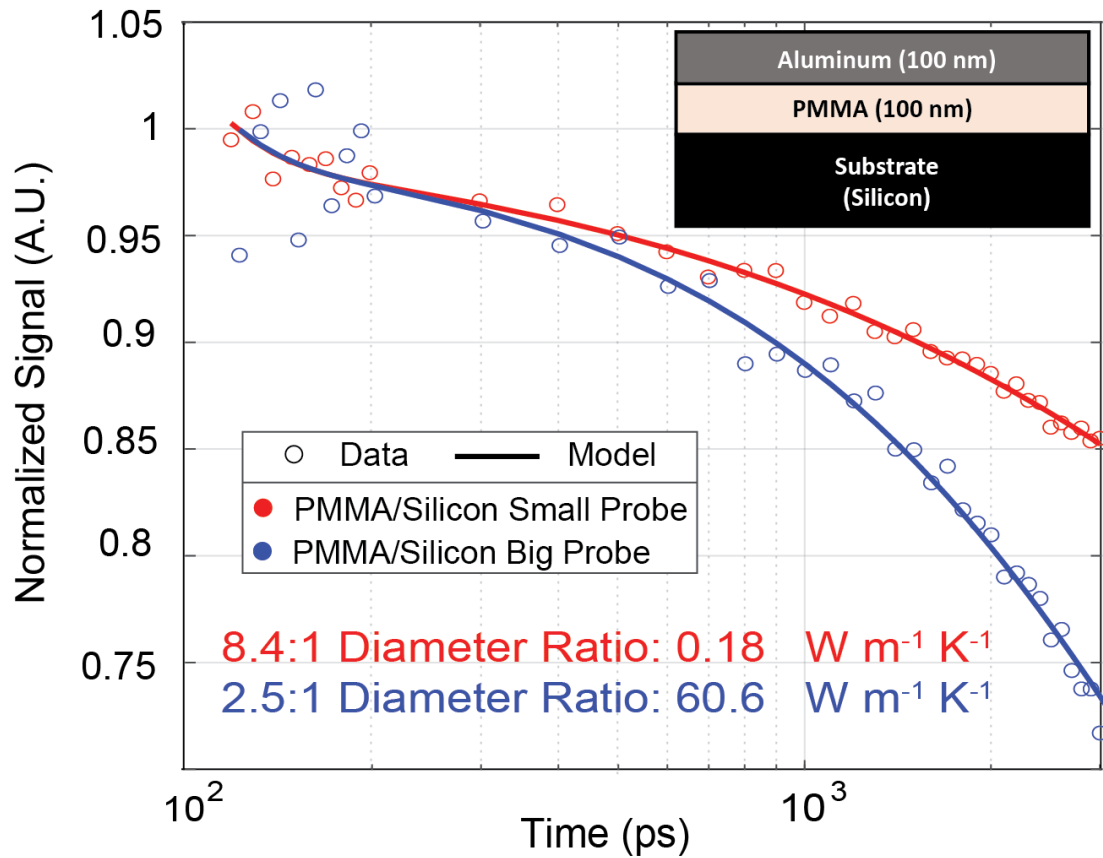


Figure 3.7. Experimental fs-TTR traces of an Al/PMMA/Si sample collected with different pump/probe diameter ratios; the red data is taken at the best-performing (for high signal intensity and signal-to-noise) diameter ratio of 8.4:1, whereas the blue data is taken using a pump/probe diameter ratio of 2.5:1, where the probe is large enough to experience non-flat portions of the Gaussian spatial profile of the pump beam. Our fs-TTR thermal model, which assumes 1-D vertical heat diffusion, can only fit correct values for κ_{zz}^{sam} if the pump/probe diameter ratio is $> 2.5:1$. Note that the y-axis scale is highly expanded

so that the absolute signal differences seen are relatively small. In both of these experiments, we pumped the Al transducer at 800 nm and probed the reflected response integrated between 900 and 915 nm. The pump diameter was fixed at 2952 μm and the diameter ratio was controlled by changing the size of the probe.

Of course, the spot size ratio at which the 1-D model breaks down will also depend on the thermal properties of the sample being studied, as samples with faster in-plane heat transport will need larger pump spot sizes. In Section 2.3 of Appendix B, we derive a model that allows one to predict pump-probe beam size ratios that are compatible with the 1-D thermal model from Section 3.2:

$$y = \frac{(r_{\text{probe}})^2}{[(r_{\text{pump}})^2 + (r_{\text{probe}})^2 + 8\alpha_{\text{radial}}t_{\text{max}}]}. \quad (3.15)$$

In Eq. 3.15, y is the probe spatial averaging error fraction (i.e., the fraction of the temperature response being probed that is not experiencing the maximum pump intensity), r_{probe} and r_{pump} are the $1/e^2$ radii of the probe and pump beams, respectively, α_{radial} is the radial thermal diffusivity of the material/transducer being probed, and t_{max} is the maximum probe delay time. The larger the value of y , the worse the induced error from the heat distribution being non-uniform in the radial direction over the size of the probe.

As the probe beam is more tightly focused on the top of the Gaussian profile of the pump beam, and thus more strictly samples the peak power density of the pump, the value of y decreases to 0. Our 1-D thermal model breaks down if the probe: 1) becomes sensitive to lateral heat diffusion; or 2) begins sampling thermal gradients due to the Gaussian spatial profile of the pump beam. If the pump spot radius is larger than hundreds of μm , then the lateral heat diffusion term, $8\alpha_{\text{radial}}t_{\text{max}}$, will be small compared to $(r_{\text{pump}})^2$ and thus will be

negligible on the few-ns time scale for materials with $\alpha_{\text{radial}} < 100 \text{ mm s}^{-2}$. Therefore, in the large pump diameter regime, the probe spatial averaging error fraction y is entirely dependent on the size of the probe beam. In Figure B.6 of Appendix B, we show that the probe spatial averaging error fraction reaches the 10% threshold that we consider acceptable for fs-TTR measurements at a pump/probe diameter ratio of about 3:1. This is consistent with the $\sim 2.5:1$ breakdown diameter ratio that we observed experimentally in Fig. 3.7.

Another advantage of the low amplified laser repetition rate is that it allows the bi-layer thermal model in Section 3.2 to be applied to thin-film (tens to hundreds of nm thick) samples without having to consider heat flow into the substrate. With the lack of pulse accumulation, a fs-TTR experiment can be tuned to prevent heat from a single pump pulse reaching the backside of the thin-film layer in a tri-layer sample by either controlling the film thickness or selecting an appropriate probe delay time window. Ensuring that heat does not reach the backside of a thin-film sample within the probe delay window means that substrate effects will not influence the observed signal decay. In Section 4 of Appendix B (see Figs. B.13a-b), we show that for very low- $\kappa_{\text{zz}}^{\text{sam}}$ polymer samples, a minimum thickness of only 50 nm is necessary to prevent heat from reaching the substrate within the 3-ns probe delay of our system. Higher $\kappa_{\text{zz}}^{\text{sam}}$ film samples will require larger thicknesses, but as long as this is achieved, our bi-layer fs-TTR model does not require fitting the thermal boundary conductance of the thin-film/substrate interface.

3.6 Conclusions

In summary, we presented a novel method for thermoreflectance measurements that is designed around a standard amplified ultrafast laser transient absorption system, rather than the traditionally-used oscillator-type system. Fs-TTR provides the same time resolution as

traditional oscillator-type TDTR, but the higher per-pulse pump energies and lower repetition rate provide significant benefits in the thermal modeling in terms of extracting the thermal conductivity and boundary conductance from the signals. The high pulse energies of amplified lasers allow for significantly greater pump/probe spot size ratios, which makes the heat transport under the probed region effectively one-dimensional, avoiding the need to incorporate both vertical and radial heat diffusion into the model. Furthermore, the use of a white-light probe allows the change in thermorefectance to be integrated spectrally across a wavelength range, providing a signal-to-noise advantage that helps compensate for the lower repetition rate. The low repetition rate, however, provides the advantage that even thin-film samples with very low κ still have enough time to reach ambient equilibrium before the next pump pulse, so that there is no heat build-up due to pulse accumulation. This also reduces the number of interfaces and material layers that need to be thermally modeled in thin-film sample architectures.

To test the robustness of the simplified 1-D model for fitting fs-TTR data, we simulated Gaussian-noise-embedded data for a variety of materials with differing κ_{zz}^{sam} and σ across a range of noise levels. The model allows simultaneous fitting of κ_{zz}^{sam} and σ with an equal or lower uncertainty than conventional TDTR because in fs-TTR, each of these parameters relies on distinct probe time windows, as demonstrated by sensitivity analysis. We also verified that the assumptions of the 1-D model are easily met experimentally, and that we can readily measure values of κ_{zz}^{sam} and σ for materials with values spanning over four orders of magnitude. Overall, we believe that fs-TTR, an experimental set-up that can be constructed trivially from a lab that is already set-up to do ultrafast transient absorption spectroscopy, provides a great alternative with potential advantages over the oscillator-type version of this experiment.

3.7 Supporting Information

See Appendix B for the Supporting Information.

3.8 Acknowledgements

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Chapter 4: Using fs-TTR to measure the thermal properties of DDB-F₇₂-Doped RR-P3HT Films

4.1 Introduction

The ability to tune the thermal and electrical properties of chemically-doped conjugated polymer thin films is central to the development of organic semiconductors as thermoelectric materials. Both thermal and electrical properties influence the energetic conversion efficiency of such materials, which can be quantified via the thermoelectric figure of merit, zT ; see Chapter 1 Equation 1.1. Thermoelectric materials need to have zT values ≥ 1 for their practical use in devices.¹ The last few decades of research on doped polymers for thermoelectrics have largely focused on maximizing zT through tuning of the power factor,²⁻²⁰ σS^2 , comprised of the electrical conductivity (σ) and Seebeck coefficient (S). However, significantly less research has been published on tuning the zT of chemically-doped conjugated polymers through the thermal conductivity,²¹⁻²⁹ κ .

As discussed in Chapters 1 and 2, chemically-doped poly(3-hexylthiophene-2,5-diyl) (P3HT) has served as an important model system for studying structure-property relationships in conjugated polymers because of its electronic tunability, semicrystalline morphology, and relatively well-defined chain packing.³⁰⁻³³ In fact, the choice of dopant can significantly enhance the electrical properties of P3HT.^{15,19,34,35} However, it has also been shown that through the process of doping, κ may also increase, which is not beneficial to zT , due to dopant-induced crystal structure changes (see Chapter 2).^{24,26,29} Perhaps the most robust way to maximize zT is through the choice of dopant: one that both substantially improves the power factor while also substantially decreasing κ .

This chapter outlines preliminary investigations into the way the thermal properties of P3HT change when doped with dodecaborane clusters that are functionalized with 3,5-bis(trifluoromethyl)benzyloxy groups (referred to as DDB-F₇₂, Fig. 4.1),³⁶ which we believe may serve as an optimal dopant to enhance the zT of P3HT.

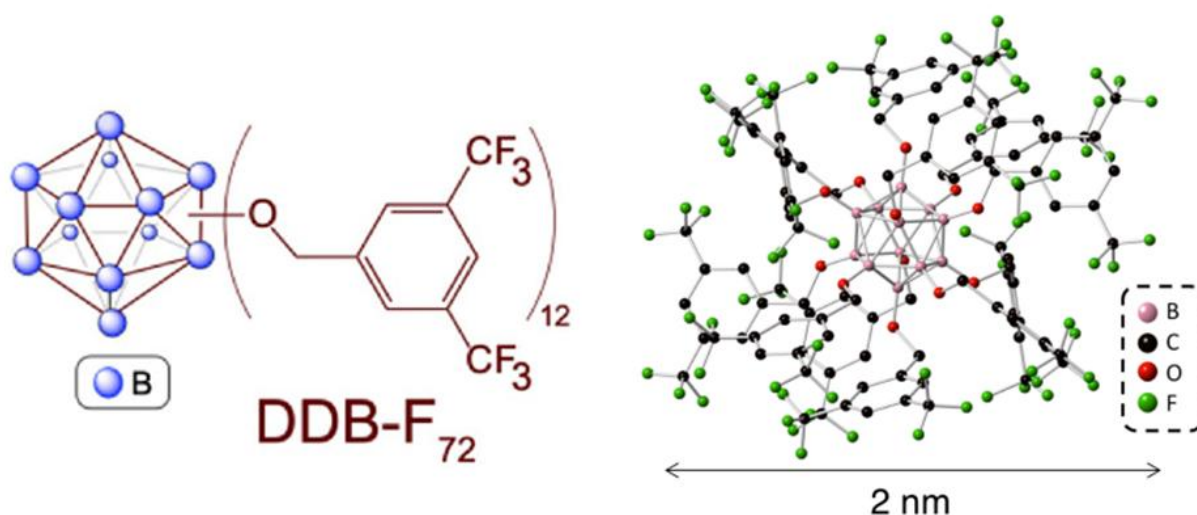


Figure 4.1. At left is the molecular structure of a 3,5-bis(trifluoromethyl)benzyloxy-functionalized dodecaborane cluster, referred to as DDB-F₇₂. At right is the X-ray crystal structure of DDB-F₇₂; image credit:¹⁹ Aubry et al. *Advanced Materials* **2019**, 31 (11), 1805647.

Compared to the F₄TCNQ dopant studied in Chapter 2, DDB-F₇₂ is a bulkier and much more oxidizing dopant, one that has been shown to significantly improve carrier mobility^{5,7,9,15,19} and lead to higher power factors.⁵ This is because its large size insulates the Coulomb attraction of the dopant anion from the polaron on the polymer backbone, and because the higher redox strength provides doping efficiencies near 100%.^{9,15,19} How this dopant impacts the thermal properties of P3HT, however, has never been investigated, although we hypothesize that DDB-F₇₂ may achieve extraordinarily low cross-plane thermal conductivities and thus higher thermoelectric figure of merit values compared to other dopants. We expect that the facts that

the large size of DDB-F₇₂ (~2-nm diameter) causes disruption of P3HT's crystallinity at high doping, as well as the many C-F bonds on the surface of the molecule that are vibrationally mismatched with those of P3HT, may both contribute to hindering thermal transport within P3HT-DDB-F₇₂ doped composite systems.

Here, we utilize femtosecond transient thermoreflectance (fs-TTR), described in detail in Chapter 3, to measure the cross-plane thermal diffusivity, $\alpha_{\perp}$, of DDB-F₇₂-doped P3HT thin film samples. We can combine $\alpha_{\perp}$ values from fs-TTR with experimentally-measured volumetric heat capacity, C_v , values to determine the cross-plane thermal conductivity, $\kappa_{\perp}$, as shown in Equation 1.4 in Chapter 1. We can determine C_v by taking the product of experimental measurements of mass density, ρ , and specific heat at constant pressure, C_p . Additionally, we can combine values of $\kappa_{\perp}$ with in-plane electrical conductivity, σ , and Seebeck coefficient, S , measurements to determine upper limits to values of the thermoelectric figure of merit, zT , as shown in Equation 1.1 in Chapter 1. These are upper limit zT calculations because spin-cast P3HT films tend to have a lower $\kappa_{\perp}$ compared to their in-plane direction,^{27,37–40} and zT calculations should incorporate the in-plane thermal conductivity as our electrical measurements are taken in-plane. Experiments have been completed to determine all these variables except for the C_p of DDB-F₇₂-doped films (to preliminarily fit data from fs-TTR measurements in this chapter, we apply the C_v value of undoped P3HT to our doped films).

We exclusively use P3HT that is 97.6% regioregular (RR) throughout this chapter. We first present UV-vis-NIR spectra on P3HT samples doped from different concentrations of DDB-F₇₂ in *n*-butyl acetate (*n*-BA) to achieve a range of doping levels. We then show X-ray diffraction studies on DDB-F₇₂-doped P3HT films via grazing incidence wide-angle x-ray scattering (GIWAXS) and small-angle X-ray scattering (SAXS) measurements to characterize how the crystal structure and film morphology evolve across our samples. Next, we

experimentally measure the film mass density as a function of the ratio of DDB-F₇₂ dopant molecules to P3HT monomer unit (3HT), which we refer to as the DDB-F₇₂:3HT ratio; this data will support calculations of C_v and allow us to monitor changes in $\alpha_{\perp}$, $\kappa_{\perp}$, σ , S and zT as a function of DDB-F₇₂:3HT ratio rather than the concentration of DDB-F₇₂ in solution used in the sequential process (SqP)⁴¹ method. Then, we present fs-TTR results on DDB-F₇₂-doped P3HT films. Unfortunately, the thermoreflectance signals from our doped films are dominated by a large-amplitude damped oscillation of unknown origin that occurs across the same timeframe needed to extract information about heat transport within the doped polymer film. Until the nature of the oscillation is fully understood and it can be rigorously incorporated into our thermal model, values of $\alpha_{\perp}$ cannot be precisely determined. To obtain preliminary values for $\alpha_{\perp}$, and thus $\kappa_{\perp}$, as well as to investigate the nature of the oscillation itself, we perform a simple fit of the oscillation as an approximate way to separate the amplitudes originating from both the oscillation and the underlying thermal transport component. Finally, we present in-plane electrical conductivity and Seebeck coefficient measurements on our doped film series to combine with $\kappa_{\perp}$ results to determine zT values.

We find that monotonic changes in ρ occur upon doping P3HT with DDB-F₇₂, which suggests that changes also occur to C_v (noting that C_p has not yet been quantified). Assuming a C_v for doped films that is equal to that of undoped P3HT, our rudimentary fits of $\alpha_{\perp}$ reveal that $\kappa_{\perp}$ likely monotonically decreases with increasing doping level (i.e. with increasing amounts of DDB-F₇₂ in the film), and that $\kappa_{\perp}$ may be an order of magnitude lower at the highest doping levels compared to that of the undoped polymer. If we combine these preliminary results for $\kappa_{\perp}$ with measured power factors, we show that zT values approaching that of the record for solid organic films may be possible with DDB-F₇₂-doped RR-P3HT.

4.2 Monitoring the Extent of Doping in DDB-F₇₂-doped P3HT Films using UV-vis-NIR Spectroscopy

Doping P3HT with strong oxidants generates charge carriers by removing an electron from the backbone of the polymer. In P3HT and other *p*-type systems, these charge carriers, called polarons, occupy intergap energy states between the valance and conduction bands; transitions to and from these states can be used spectrally to monitor the extent to which the polymer film is doped.^{7,42,43} Undoped P3HT consists only of the bandgap transition, as shown by the black spectra in **Figure 4.2**. In the doped state, the formation of intergap states allows for an electronic transition between the valance band (VB) and the lower intergap state (called P1) as well as a transition between the two intergap states (P2), as shown in the energy diagram on the right side of Fig. 4.2. If the polaron delocalizes across more than one polymer chain, a transition between the valance band and the upper intergap state (P3) is also possible. As the extent of doping increases with higher DDB-F₇₂ solution concentration, we see in Fig. 4.2 an increase in the intensity of the P1 and P2 transitions due to the greater number of polarons formed.

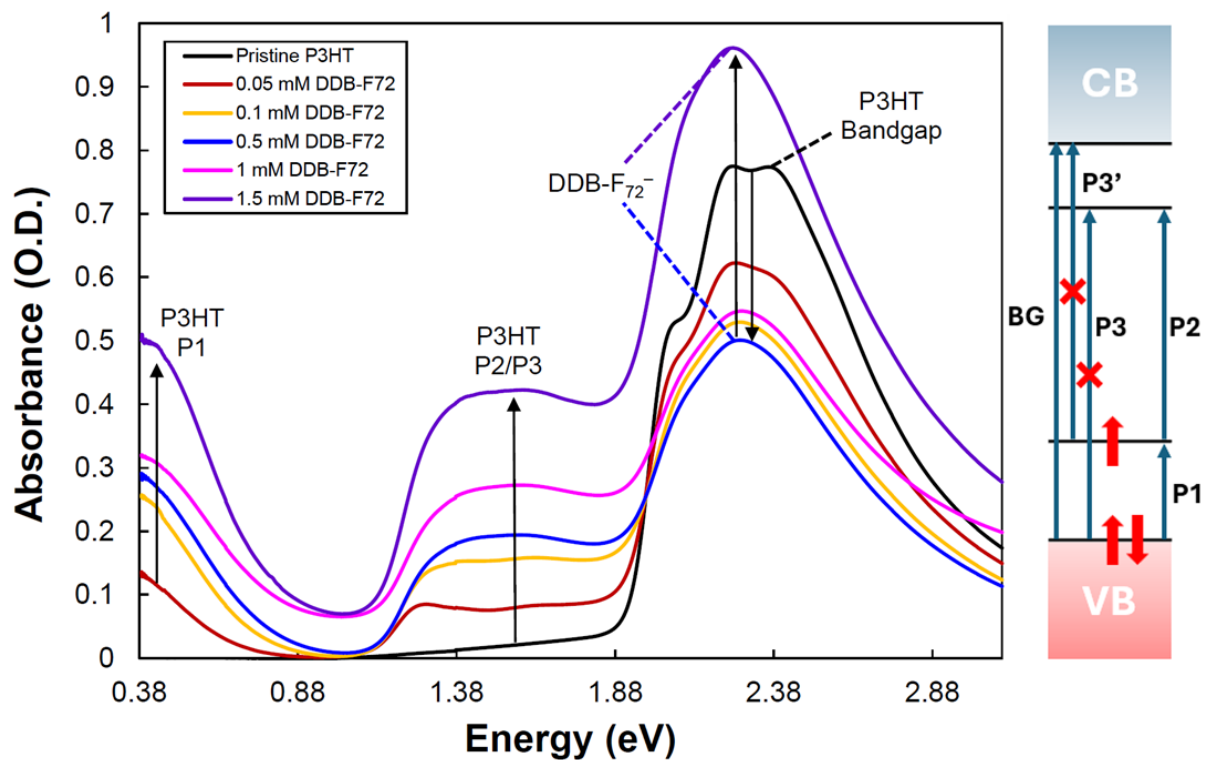


Figure 4.2. UV-vis-NIR spectra of undoped RR-P3HT (in black) and DDB-F₇₂-doped P3HT films as a function of DDB-F₇₂ doping concentration (using *n*-BA as the solvent) using the SqP method. Pristine P3HT shows only the bandgap transition, whereas doped P3HT has new electronic transitions involving the polaronic intergap states (see the right-side energy diagram for a doped *p*-type polymer with a polaron). The lower-energy transition between the valance band (VB) and the lower intergap state is called P1. The transition between the two intergap states is called P2. If the polaron is delocalized between more than one polymer chain, a transition between the conduction band and different chain's upper intergap state, called P3, may be allowed. The growth in the intensity of both P1 and P2 across the entire sample series indicates that higher doping levels are achieved with higher solution concentrations of DDB-F₇₂.

Across the entire sample series tested (0.05 – 1.5 mM DDB-F₇₂), we observe steady increases in P1 and P2 intensities. We note that previously published work using DDB-F₇₂ to dope RR-P3HT utilized either dichloromethane (DCM) or *n*-BA as the choice of solvent for

the doping solution.^{5,7,9,15,19} Compared to *n*-BA, DCM is a better swelling solvent that allows DDB-F₇₂ to more easily intercalate into the crystal structure.^{20,44,45} Due to this doping solvent difference, P3HT doped with DDB-F₇₂ using DCM reaches higher doping levels at lower solution doping concentrations compared to using *n*-BA. In this study, however, the use of *n*-BA was necessary as this solvent is more orthogonal to P3HT than DCM. Our method of determining the DDB-F₇₂:3HT ratio in doped films, discussed later in Section 4.4, requires that no P3HT polymer is redissolved during the SqP doping step, something that is not possible when DCM is used as the doping solvent.

We note that both the absorption of the P3HT bandgap and the DDB-F₇₂⁻ ion largely overlap with each other. Between 0.05–0.5 mM DDB-F₇₂, we see a bleach of the bandgap due to the removal of electrons in the valance band as doping increases. At higher doping levels, we would expect to see further bleaching of the bandgap, but this is overshadowed by the growing absorption intensity from DDB-F₇₂⁻ ions.

4.3 X-ray Diffraction of Undoped and DDB-F₇₂-doped P3HT Films

We performed grazing-incidence wide-angle X-ray scattering (GIWAXS) and small-angle X-ray scattering (SAXS) to monitor changes in the crystal lattice structure and mesoscale film morphology, respectively, as a function of the extent to which P3HT is doped with DDB-F₇₂. It was previously demonstrated that doping RR-P3HT with DDB-F₇₂ from DCM induces: 1) the undoped crystal structure to undergo a volume expansion of the unit cell, greatly increasing the lamellar distance, and 2) a substantial decrease in the overall film crystallinity as the doping level increases.^{5,7,15,19} It was also shown that for the regiorandom (RRa) variety of P3HT, which is completely amorphous as a pristine film, doping with DDB-F₇₂ from *n*-BA induces the formation of isotropically-oriented doped crystallites.⁹ These doping-induced

crystalline regions have lamellar and π -stacking distances that are identical to those of DDB- F_{72} -doped RR-P3HT.⁹

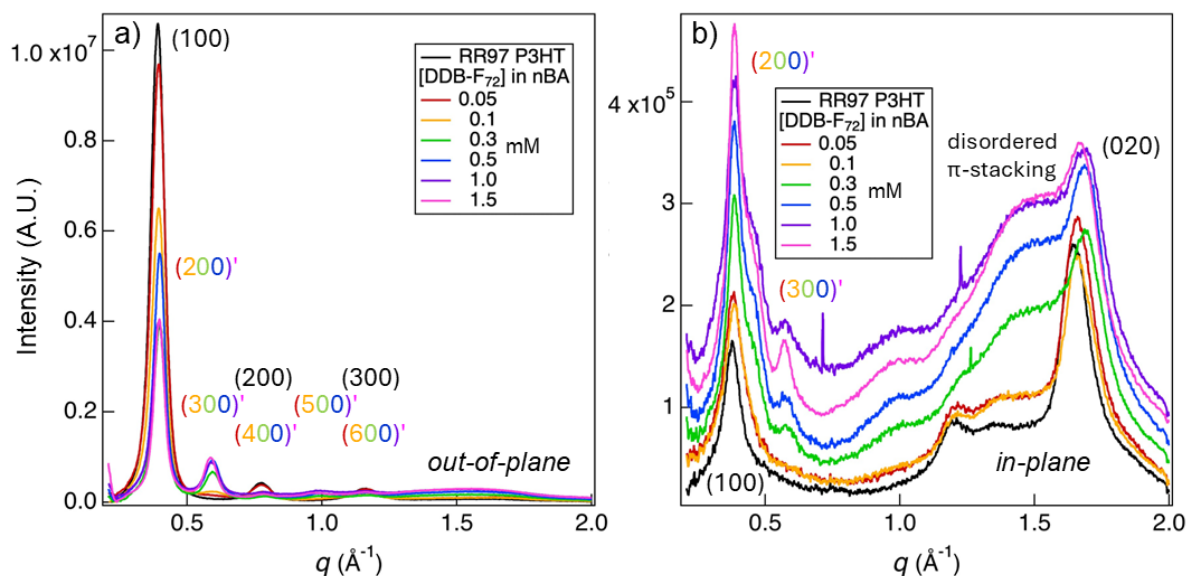


Figure 4.3. Integrated pristine-film-thickness-normalized GIWAXS patterns for pristine and DDB- F_{72} -doped RR-P3HT. (a) Out-of-plane integrations, which are dominated by the lamellar ($h00$) diffraction peaks and the ($h00$)' overtones of doped crystallites. (b) In-plane integrations, which show the (100) and ($h00$)' diffraction peaks with decreased intensity (note the different y-axis scale from panel (a)), as well as the π -stacking peak, (020). The data show that doping significantly changes the crystal structure of RR-P3HT films, nearly doubling the lamellar distance, as shown in Figure C.1 in Appendix C. The in-plane (200)' peak intensity increases with doping level, due to the formation of isotropically-oriented doped crystallites created by doping previously amorphous regions.⁹ Because of the overlap of the lamellar peaks of the pristine and doped structures, we use the (020) integrated peak area to show that doped films see a large reduction in overall crystallinity by the 0.3 mM doping level, as seen in Figure 4.4a below.

Our integrated pristine-film-thickness-normalized GIWAXS patterns for pristine and DDB- F_{72} -doped RR-P3HT, shown in **Figure 4.3a-b**, suggest that doping from n -BA induces

structure changes that resemble a mix of what occurs when both RR-P3HT is doped with DDB-F₇₂ from DCM,^{5,7,15,19} and RRa-P3HT is doped with DDB-F₇₂ from *n*-BA.⁹ For instance, the locations of the (*h*00) overtones of the doped structure for DDB-F₇₂-doped P3HT using *n*-BA as the solvent, which are marked with a prime symbol after the parentheses and labeled in rainbow colors, reveal that the lamellar distance of doped crystallites nearly doubles (see the 0.3 mM point onward in Figure C.1a in Appendix C). The magnitude of the lamellar distance expansion in our samples is the same as that determined by both a previous study that investigated the crystal structures of RR- and RRa-P3HT doped with DDB-F₇₂ from *n*-BA,⁹ as well as other studies that investigated the doped structure of RR-P3HT doped with DDB-F₇₂ from DCM.^{5,7,15} The expansion in lamellar spacing occurs because DDB-F₇₂ must create new space between polymer chains to accommodate its large molecular size.^{5,7,9,15} Furthermore, Figure C.1b in Appendix C reveals that the π -stacking (020) distance slightly decreases (again, by the 0.3 mM point onward), reflecting a change in the tilt of the P3HT backbones that accompanies the lamellar expansion of the unit cell, which is also similar to that of P3HT films doped from both DCM and *n*-BA.^{5,7,9,15}

There are also doping-induced crystal structure changes that we observe in our films doped from *n*-BA that are slightly different from what has been observed in previous studies. For example, in our RR-P3HT films DDB-F₇₂-doped using *n*-BA, signs of the doped structure are not as prominent at lower doping concentrations (0.05 mM and 0.1 mM) compared to RR-P3HT films doped using DCM at equally-low concentrations (0.05 mM).¹⁵ Additionally, we see in our RR-P3HT films doped with DDB-F₇₂ from *n*-BA that the in-plane (200)' peak becomes narrower and increasingly intense with increasing doping level. This result, similar to that observed after doping RRa-P3HT with DDB-F₇₂ using *n*-BA,⁹ is consistent with the creation of isotropically-oriented crystallites, which is the result of doping-induced

crystallization of amorphous regions. Previous studies that investigated the crystal structure of RR-P3HT doped with DDB-F₇₂ using DCM observed the growth of a broadening (200)' peak rather than a narrowing one.^{15,19}

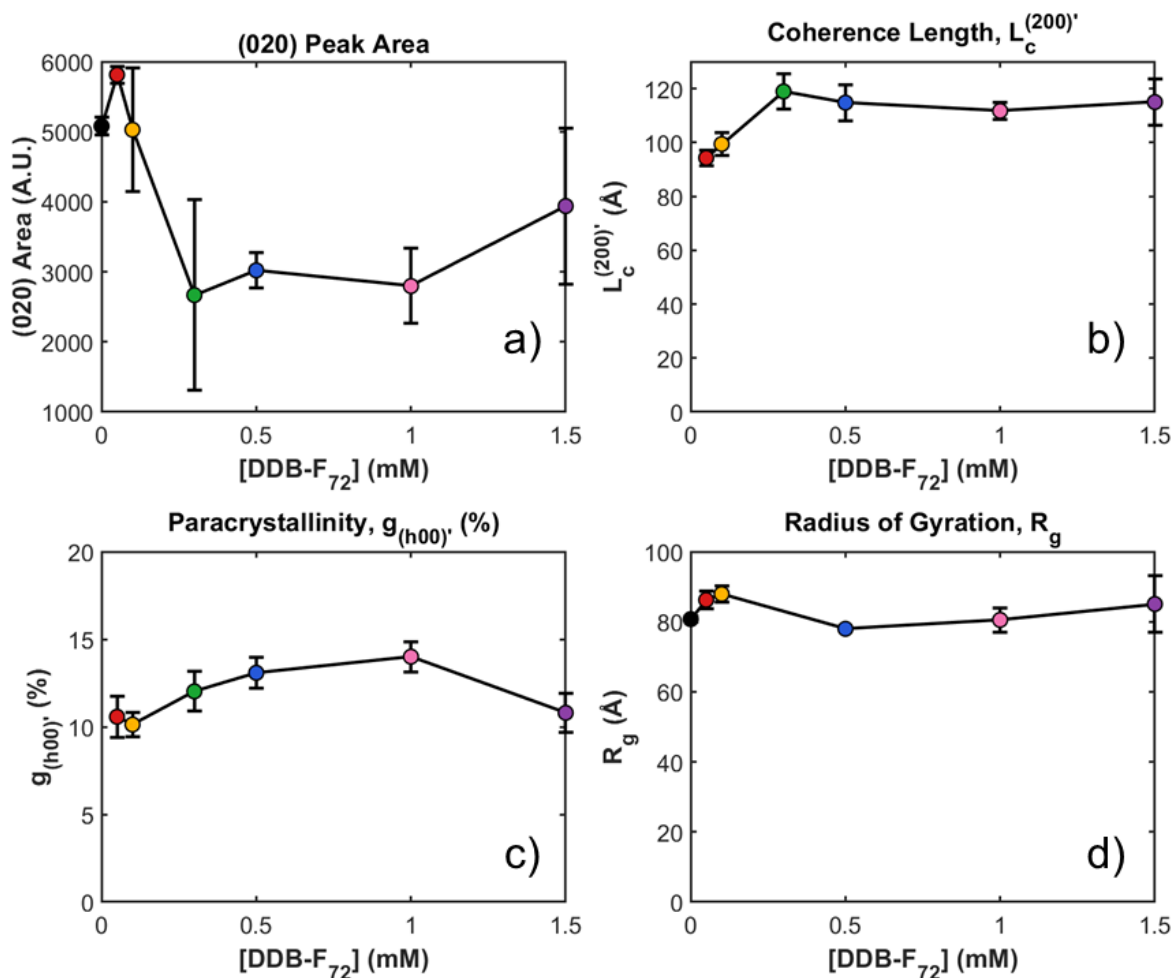


Figure 4.4. Structural evolution of DDB-F₇₂-doped P3HT films as a function of the concentration of DDB-F₇₂. The results in panels a–c are extracted from analyzing the integrated, pristine-film-thickness-normalized GIWAXS patterns shown in Figure 4.3a–b, whereas panel (d) is determined from the GISAXS data in Figure C.1 of Appendix C. All films were doped using the SqP method with *n*-BA as the doping solvent. Y-axis error bars represent the standard deviation in peak-fitting across three separate samples. a) The peak-fitted, integrated (020) peak areas taken from the in-plane diffraction pattern. The decrease in overall (020) peak intensity suggests a loss of film crystallinity with heavier doping.^{15,19} b) The crystalline coherence length, L_c , calculated from (200)' peak widths via the Scherrer

equation, representing the average size of a coherently-ordered crystalline domain along the lamellar stacking direction. (note: the prime symbol marks that it is related to the doped structure). c) The paracrystallinity of the lamellar stacking, $g_{(h00)'}$, which quantifies the fraction of imperfect molecular ordering in the crystalline domain and is determined from the increase in $(h00)'$ peak broadening with increasing diffraction order.⁴⁶⁻⁴⁸ d) The radius of gyration, R_g , determined from a Guinier analysis of the low- q GISAXS scattering intensity,⁴⁹ capturing structural correlations on mesoscopic length scales that are larger than the atomic-scale lattice spacings probed by GIWAXS in panels a–c.

To capture the changes in overall film crystallinity between our pristine and DDB-F₇₂-doped P3HT films, we compare the integrated area of the in-plane (020) peaks, shown in **Figure 4.4a**. We cannot use the integrated areas of the $(200)'$ peaks to track film crystallinity because the films, particularly at low doping levels, may have both undoped crystallite (100) and doped crystallite $(200)'$ populations contributing to the intensity of the out-of-plane peak at $0.4 \text{ \AA}^{-1}$; the contributions are unfortunately not separable. Overall, we see that our films doped from *n*-BA experience a significant reduction in overall crystallinity as the doping level is increased from 0.1 mM to 0.3 mM. The general reduction in film crystallinity is also visible by the growth in the intensity of the broad amorphous π -stacking peak centered near $1.4 \text{ \AA}^{-1}$, shown in the in-plane diffraction patterns in Fig. 4.3b. As discussed earlier, a reduction in overall film crystallinity also occurs in films doped from DCM,^{5,7,15,19} although the onset of the loss in crystallinity occurs at lower doping concentrations in DCM,¹⁵ likely due to the greater swelling power of DCM compared to *n*-BA.

We also performed GISAXS measurements, shown in Figure C.2 of Appendix C, on RR-P3HT films doped with DDB-F₇₂ using *n*-BA as the doping solvent. From the GISAXS patterns, we can extract the radius of gyration,⁴⁹ R_g , shown in Fig. 4.4d, which is a measure of

the domain size based on regions of similar electron density. Across varying doping levels, R_g remains constant within error. Despite changes in overall crystallinity across doping levels, the lack of significant change in the longer-ranged contrast in electron density implies that doping RR-P3HT with DDB-F₇₂ using *n*-BA is uniform across the film as opposed to the dopant preferentially selecting either crystalline or amorphous regions.

4.4 Measuring the Mass Density and DDB-F₇₂:3HT Ratio of DDB-F₇₂-doped P3HT Films

To experimentally determine the volumetric heat capacity, C_v , which is required to determine values of $\kappa_{\perp}$ from fs-TTR, the film mass density, ρ , and the specific heat at constant pressure, C_p , must both be measured. This section investigates how the total film mass, total film volume, and ρ change as a function of doping level. Using the methods discussed in Section 1.4 of Appendix A pertaining to the work in Chapter 2, we also quantify the ratio of DDB-F₇₂ dopant to P3HT monomer unit (3HT) as a function of doping level. In brief, we measured the DDB-F₇₂:3HT ratio at each doping level based on differences in the film mass before and after doping.

We first present the normalized average total film mass and film volume of samples at each doping level, shown in **Figure 4.5**. To account for differences in the average initial P3HT mass between samples measured at each doping level, we normalized the total film mass by the average initial P3HT mass and applied this normalization scaling factor to the appropriate average total film volume. At low doping levels (0.05 mM and 0.1 mM), we see relatively small increases in film mass (which is assumed to be entirely from intercalated DDB-F₇₂) that are accompanied by relatively small increases in total film volume. Then, between the 0.1 mM and 0.5 mM doping levels, a significant jump in both additional DDB-F₇₂ mass and total film volume occurs. The significant change in mass and volume by 0.5 mM occurs across the same

doping regime where we observe a significant degree of the doped structure appearing via GIWAXS (see the 0.3 mM and 0.5 mM samples in Figure 4.3). At doping concentrations above 0.5 mM, we observe both smaller increases in total film mass (i.e. smaller amounts of additional DDB-F₇₂, and thus smaller increases in DDB-F₇₂:3HT ratio) and total film volume. This suggests that doping RR-P3HT with DDB-F₇₂ from *n*-BA at 1 mM and 1.5 mM concentrations may be approaching a doping saturation point. Furthermore, across the whole doping range tested, the film volume proportionally increases less as a function of DDB-F₇₂:3HT ratio than the film mass, as shown by the shallower orange curve in Fig. 4.5 (note that the y-axes increase proportionally). Therefore, we can expect that the film density will steadily increase as a function of DDB-F₇₂:3HT ratio.

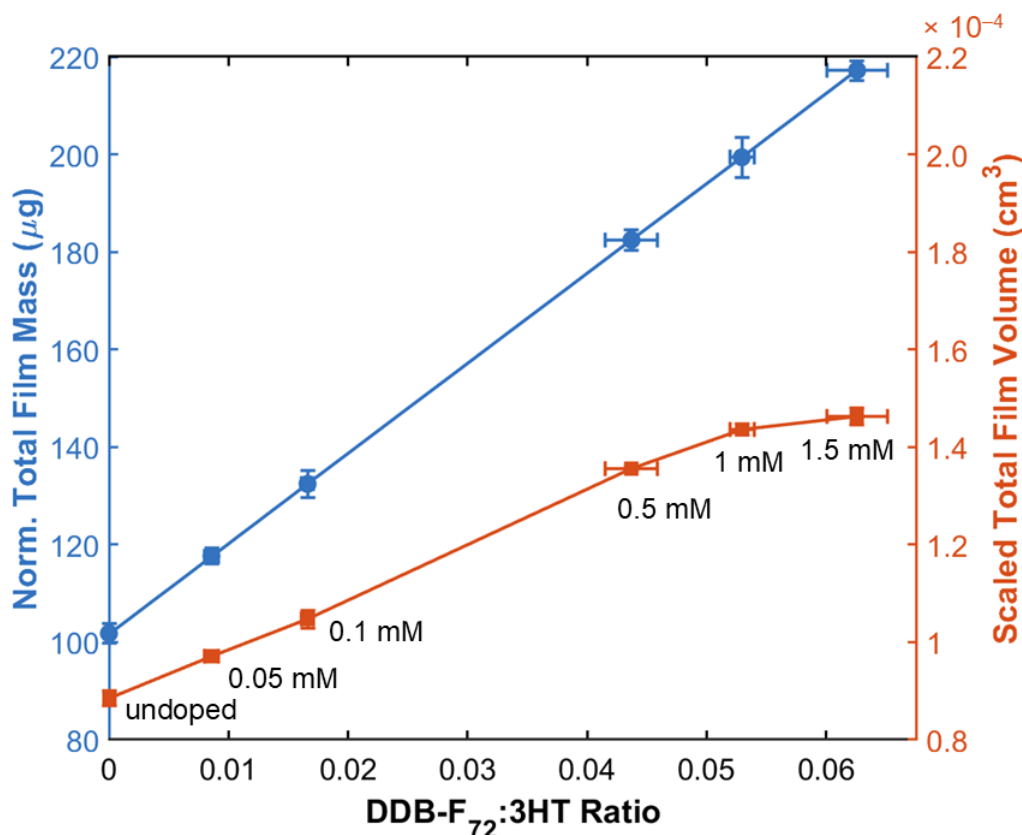


Figure 4.5. Normalized average total film mass (in blue) and total film volume (in orange) as a function of DDB-F₇₂:3HT ratio. We normalized the average total film mass at each doping level to the average P3HT mass in order to account for small differences in initial P3HT mass between samples. We then

applied our normalization scaling factor to adjust the total film volume accordingly. Our total film mass and volume measurements were used to determine the film densities of DDB-F₇₂-doped RR-P3HT films, shown in Fig. 4.6. The SqP dopant solution concentrations, ranging from 0.05 – 1.5 mM in *n*-BA, are labeled. The data show that the film mass increases proportionally faster than the film volume as a function of DDB-F₇₂:3HT ratio across our entire doping range tested, which means that the film density steadily increases with DDB-F₇₂:3HT ratio.

In **Figure 4.6**, we show how the film density of our DDB-F₇₂-doped P3HT films monotonically increases as a function of DDB-F₇₂:3HT ratio. The linear (within error) increase in film density with DDB-F₇₂:3HT ratio suggests that doping with DDB-F₇₂ from *n*-BA locally converts both pristine crystallites and amorphous regions to the expanded doped structure up to a doping saturation point. This behavior deviates from what we saw in Chapter 2 when RR-P3HT was F₄TCNQ-doped from *n*-BA, where the P3HT crystallites all converted to the doped structure during a phase transition at very low doping levels.²⁹ Our general picture of how DDB-F₇₂ dopes RR-P3HT using *n*-BA is consistent with the GISAXS data in Section 4.3 that shows that R_g remains the same within error across doping level and thus DDB-F₇₂ dopes the polymer uniformly.

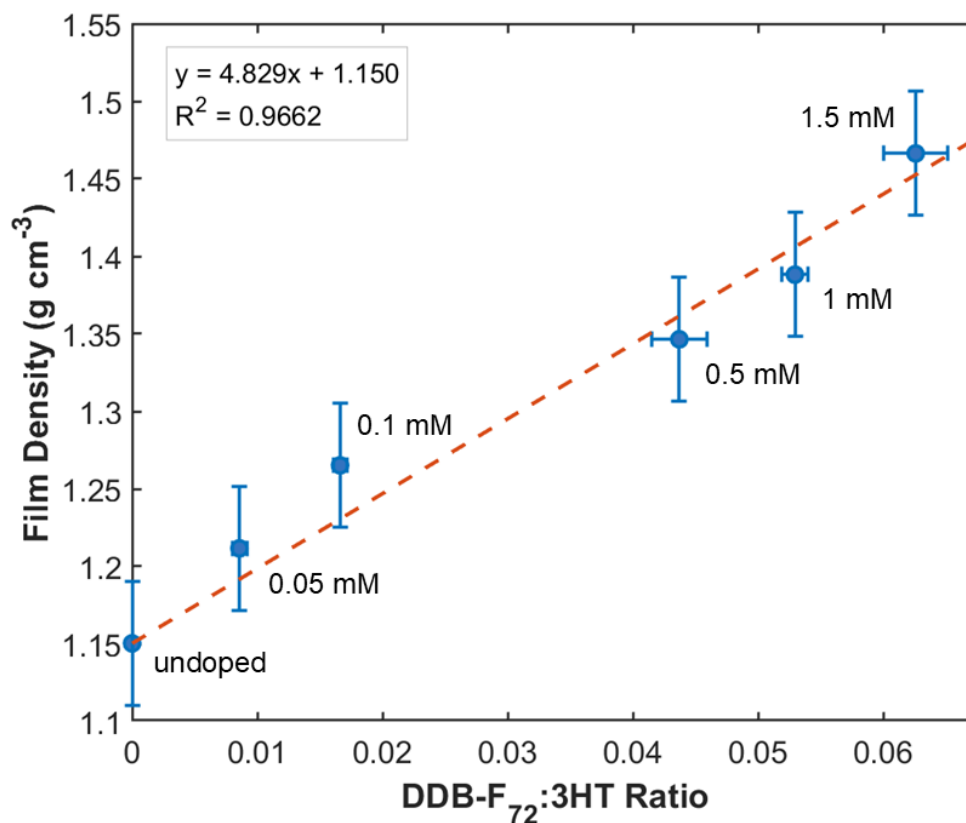


Figure 4.6. Film densities, calculated using the data presented in Fig. 4.5, of DDB-F₇₂-doped RR-P3HT films as a function of DDB-F₇₂:3HT ratio. The SqP dopant solution concentrations, ranging from 0.05 – 1.5 mM in *n*-BA, are labeled. A monotonic increase in film density occurs across the entire doping range tested. Fitting a linear trendline (see upper left corner for the equation) through the data, forced through the *y*-intercept data point, results in a R^2 value of 0.9662 and suggests that the density of doped films depends primarily on the degree of doping with DDB-F₇₂ (quantified here using the DDB-F₇₂:3HT ratio). Note that changes in the DDB-F₇₂:3HT ratio do not scale linearly with the SqP doping concentration because higher SqP concentrations of dopant result in smaller amounts of additional DDB-F₇₂ as the doping saturation level is approached.

It is worth noting that the DDB-F₇₂:3HT ratios are not as high as those achieved by doping RR-P3HT with F₄TCNQ (see Fig. 2.2a in Chapter 2).²⁹ This is because the doping efficiency of DDB-F₇₂ is nearly 100%,^{9,15,19} a significant increase over the 5–18% doping

efficiency of F₄TCNQ.^{19,50,51} Furthermore, DDB-F₇₂ is considerably larger than F₄TCNQ, which limits the number of dopant molecules that can physically fit into the lattice. Additionally, at the 0.062:1 DDB-F₇₂:3HT doping level (achieved with 1.5 mM DDB-F₇₂ in *n*-BA), the doped polymer film is comprised 54% by weight of DDB-F₇₂. The significant mass fraction of dopant at these high doping levels suggests that these composite systems are likely to have greatly varied thermal properties compared to undoped P3HT.

4.5 Fs-TTR Measurements on DDB-F₇₂-doped P3HT Films

We utilize femtosecond transient thermoreflectance (fs-TTR), described in detail in Chapter 3, to measure the cross-plane thermal diffusivity, $\alpha_{\perp}$, of P3HT films as a function of the extent of doping with DDB-F₇₂. Combining $\alpha_{\perp}$ values with volumetric heat capacity values would allow the determination of cross-plane thermal conductivity, as discussed in Section 4.1.

We first performed measurements on three separate pristine RR-P3HT films to determine the cross-plane thermal conductivity of the undoped polymer. Data was taken from 120 ps to 3 ns using the same exact experimental and data work-up methods described in Chapter 3 with the exception that we integrated across a probe wavelength range of 900–950 nm instead of 900–915 nm to generate the averaged thermoreflective trace for each sample; this choice was made because it yielded the best signal-to-noise. As a model input parameter, we utilized our experimental volumetric heat capacity value for undoped RR-P3HT, 1.48(9) J cm⁻³ K⁻¹, as shown in Figure 2.2c in Chapter 2; all other input parameters we utilized for fitting the thermal model are exactly as described in Table B.1 of Appendix B for the polystyrene and poly(methyl methacrylate) (PMMA) thin-film polymer samples (including the transducer, time-step, and distance-step parameters). We should note that the transducer we placed on the DDB-F₇₂-doped P3HT samples for fs-TTR included depositing 10 nm of Ag on

the P3HT film prior to depositing an additional 90 nm of Al, although this 100-nm-thick transducer was modeled as a single layer of 100 nm of Al. The small layer of Ag placed atop the P3HT film served to protect the P3HT from de-doping by low-work function Al for samples that were deeply doped with DDB-F₇₂, which we discuss below in Section 4.4.

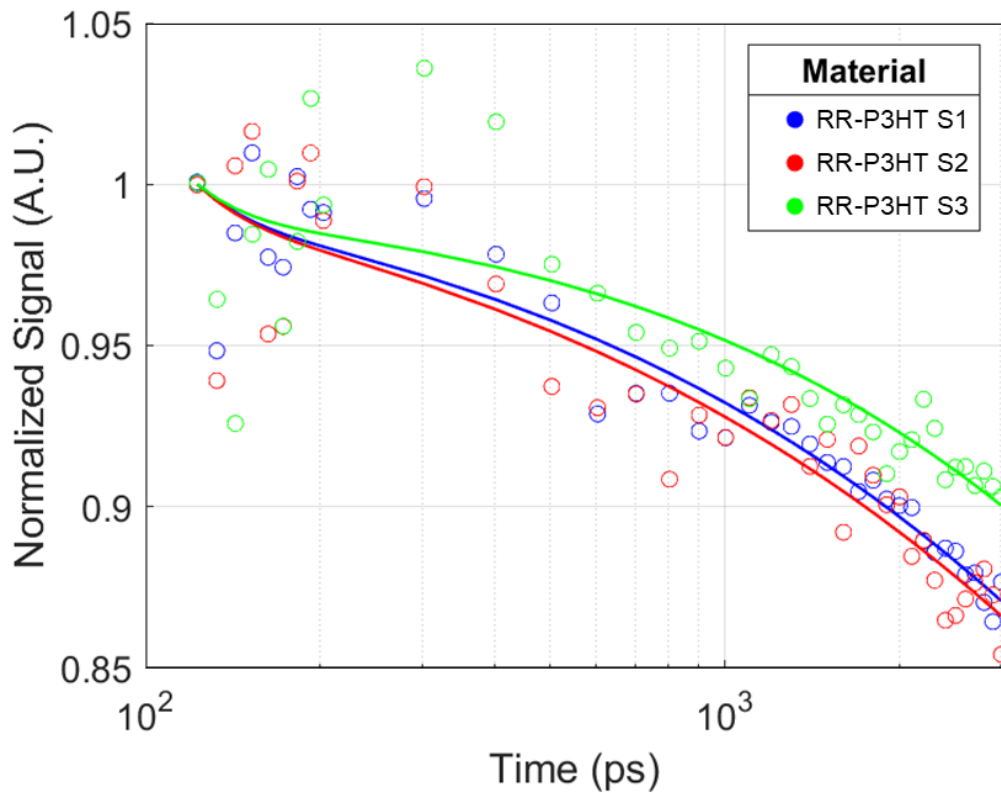


Figure 4.7. Fs-TTR traces of three separate samples of pristine RR-P3HT thin film tri-layer samples, each with 100-nm-thick transducers (10 nm Ag plus 90 nm Al) on Si substrates. The thermal model fits are shown as solid curves and the data are shown as colored circles; note that the y-axis is greatly expanded to better show subtle differences between the datasets. The $\kappa_{\perp}$ and σ fitting results are tabulated in Table 4.1. The green sample yielded a fitted value for $\kappa_{\perp}$ that is roughly 5–10% lower than that of the red and blue samples; this difference is believed to be the result of small morphological differences between separate spin-cast films.

Table 4.1. Fitting Results for $\kappa_{\perp}$ and the Thermal Boundary Conductance (G) of Al/RR-P3HT from fs-TTR Measurements on Three Pristine RR-P3HT Thin Film Tri-Layer Samples

Undoped RR-P3HT Sample	Fitted $\kappa_{\perp}$ (W m ⁻¹ K ⁻¹) ^a	Fitted G (MW m ⁻² K ⁻¹) ^a	Calculated Noise from Fit (%)
S1	0.29(7) $\pm$ 0.04(1)	48 $\pm$ 20	1.43
S2	0.30(3) $\pm$ 0.04(5)	68 $\pm$ 42	1.95
S3	0.28(0) $\pm$ 0.04(7)	19 $\pm$ 11	2.14
Averages	0.29(3) $\pm$ 0.04(4)	45 $\pm$ 20	--

^a Error bars are generated from the covariance of the Jacobian from the model fits.

The $\kappa_{\perp}$ and G fitting results of our undoped RR-P3HT films are displayed as the solid curves in **Figure 4.7** with the parameters tabulated in **Table 4.1**. The average $\kappa_{\perp}$ value measured with fs-TTR is the same within error as that measured using TDTR in Chapter 2: 0.31(1) $\pm$ 0.02(3).²⁹ This is to be expected as both the variety of RR-P3HT and the casting procedure are the same in both Chapter 2 and the measurements discussed here.

Thermal diffusivity measurements using the DDB-F₇₂ dopant have never previously been performed on any *p*-type polymer. After using the SqP method to dope RR-P3HT films with DDB-F₇₂, as per the previous sections, significant changes to the thermoreflective decay occur when compared to pristine RR-P3HT. As seen in **Figure 4.8** below, the most obvious feature is the presence of a damped oscillation that becomes larger in amplitude as the doping level increases. Unfortunately, we do not know the origin of this oscillation, which means we cannot use the fs-TTR thermal model discussed in Chapter 3 to rigorously extract $\alpha_{\perp}$ values as the oscillation overlaps with the exact region of the TTR trace used to extract thermal properties.

To investigate the nature of the damped oscillation, we crudely modified the fs-TTR thermal model to incorporate a damped harmonic oscillator (DHO), $\ddot{x} + 2\gamma\dot{x} + \omega_0^2x = 0$, as a separate feature of the amplitude of the overall TTR signal, as shown in Eq. 4.1:

$$\Delta R^{\text{probe}}(t_j) \cdot c = \left(\frac{dR^{\text{probe}}}{dT^{\text{met}}} \right) \theta(t_j; \kappa_{\perp}) + \text{DHO}(t_j; \gamma, \omega_d, A_1, A_2). \quad (4.1)$$

The DHO has a general solution of the following form:

$$x(t_j) = e^{-\gamma \cdot t_j} [A_1 \cdot \sin(\omega_d \cdot t_j) + A_2 \cdot \cos(\omega_d \cdot t_j)], \quad (4.2)$$

where $\omega_d = \sqrt{\omega_0^2 - \gamma^2}$ is the damped frequency, $A = \sqrt{A_1^2 + A_2^2}$ is the oscillation amplitude, $\tau = 1/\gamma$ is the damping decay constant, and $\phi = \text{atan}^2(A_1, A_2)$ is the initial phase.

We use the model described by Eq. 4.1 to fit the TTR traces in Figure 4.8 using the following routine (see Section 1 of Appendix D for the MATLAB script). First, an appropriate scaling factor, c , was determined in order to provide the thermal model with a starting seed value for $\kappa_{\perp}$. Next, a 2D grid was generated to scan for appropriate seed values for both ω_d and γ . Next, we utilized variable projection (VARPRO), an algorithm that solves separable nonlinear least squares problems,⁵² to refine the fit of ω_d and γ using VARPRO projected residuals. Finally, all nonlinear fitting variables ($\kappa_{\perp}$, ω_d and γ) were simultaneously globally fit. During this final step, the linear variables (A_1 and A_2) were computed directly from the least-squares solution pertaining to the nonlinear variables.

As a quick test of the ability of the thermal + DHO model to accurately resolve the thermal component from the DHO, we extracted the $\kappa_{\perp}$ of our undoped P3HT samples that we initially presented in Figure 4.7. Although the amplitude of the oscillation is small in undoped films (and thus somewhat ignorable) compared to doped films, the thermal + DHO model resolves a peak from the oscillation at around 300 ps delay time, as shown by the black curve

in Figure 4.8. Fitted values of $\kappa_{\perp}$ using our modified model for all three undoped films, as tabulated in **Table 4.2**, are $< 2\%$ different compared to the fits using our standard fs-TTR thermal model; this suggests that the modified model works as intended, and that it may be possible to reliably extract thermal diffusivities from the data despite the oscillations. We also note that the percentage noise values calculated from the residuals of the model fit are much lower when we use the thermal + DHO model; this suggests that some of the ‘noise’ that our standard fs-TTR model detects is actually coming from the oscillation.

We should note that Eq. 4.1 does not parameterize the thermal boundary conductance, G , which we assumed to be constant at $50 \text{ MW m}^{-2} \text{ K}^{-1}$ for the doped films. Furthermore, these fits also assume a volumetric heat capacity of the doped films that is equal to that of undoped P3HT, an assumption that we argued in Chapter 2 is insufficient, but one we make for now until an accurate value for C_p can be obtained. We should also note that our use of this thermal + DHO model alongside the VARPRO fitting algorithm is primarily to extract information about the damped oscillation. The amplitudes of the damped oscillation and that of the thermal decay, $\theta(t_j; \kappa_{\perp})$, cannot always be accurately separated using VARPRO alone (i.e. we would need to know more about the nature of the oscillation to correctly model it) and, therefore, the resulting fit results for $\kappa_{\perp}$ are subject to error. This is because the amplitude of the thermal component is smaller than that of the oscillation, especially in the highly-doped films. In Figure 4.8, we show the fitted thermal component from the modified TTR model in Eq. 4.1 (dashed colored curves) after subtracting out the DHO component. This allows us to preliminarily comment about the possible trend in thermal diffusion for our DDB-F₇₂-doped RR-P3HT films.

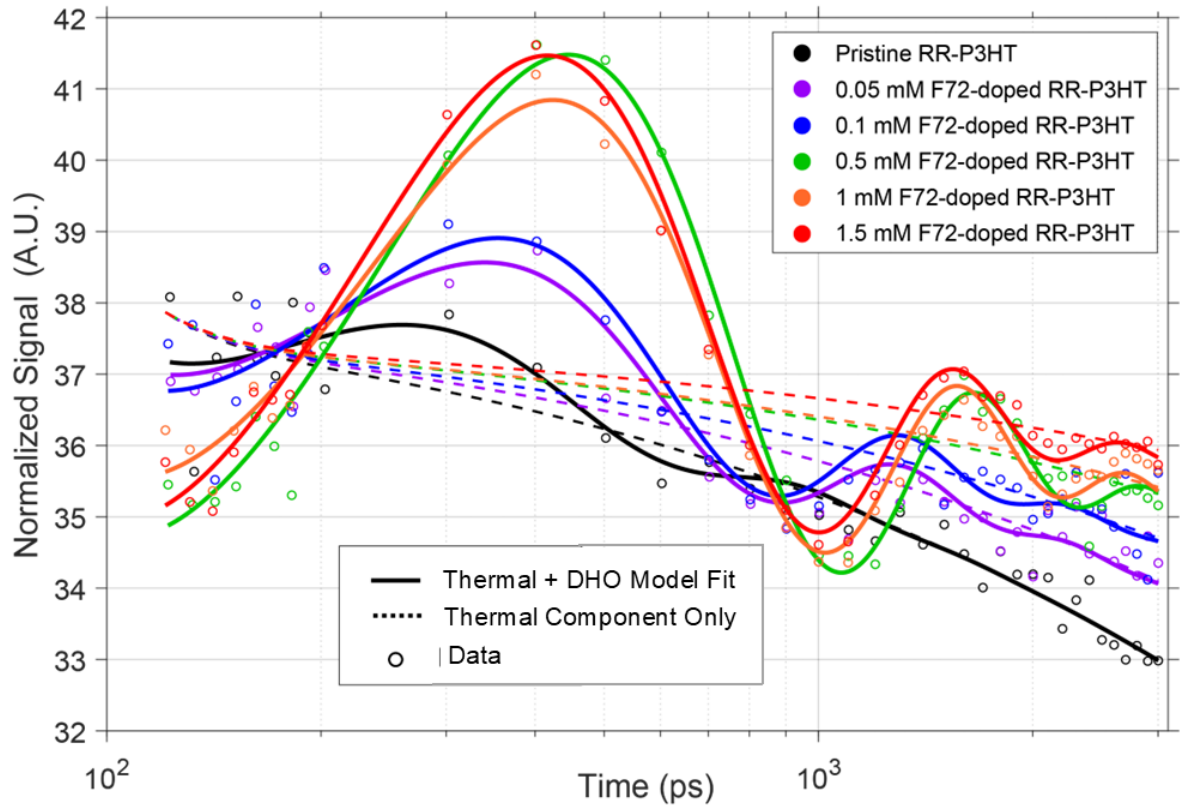


Figure 4.8. Fs-TTR data on pristine (black) and DDB- F_{72} -doped (colored) P3HT thin-film tri-layer samples fitted using a modified version of the fs-TTR model described in Chapter 3, Eqs. 4.1 and 4.2, that incorporates a damped harmonic oscillation (DHO) component (solids lines). The fitting results related to the oscillation from the thermal + DHO fs-TTR model, the code of which is provided in Section 2.0 in Appendix C, are shown in Table 4.2. The heat diffusion component of the solid curve fits are displayed as dashed curves that have corresponding $\kappa_{\perp}$ fits shown in Table 4.3. There is a monotonic trend in the thermal component as the decay of the dashed curve becomes shallower with increasing doping level, which suggests that cross-plane heat transfer becomes increasingly hindered.

Table 4.2. Values for $\kappa_{\perp}$ from the Thermal + Damped Harmonic Oscillator (DHO) Model Fitted to the Fs-TTR Data on Undoped and DDB-F₇₂-Doped P3HT Film Samples

RR-P3HT Sample	Fitted $\kappa_{\perp}$ (W m ⁻¹ K ⁻¹) ^a	Fixed G Input (MW m ⁻² K ⁻¹)	Calculated Noise from Fit (%)
Undoped S1	0.29(9) $\pm$ 0.02(3)	48 ^b	1.24
Undoped S2	0.30(5) $\pm$ 0.02(8)	68 ^b	1.76
Undoped S3	0.27(6) $\pm$ 0.04(9)	19 ^b	1.50
Average	0.29(4) $\pm$ 0.03(3)	--	--
0.05 mM DDB-F ₇₂ S1	0.10(9) $\pm$ 0.01(1)	50	1.26
0.05 mM DDB-F₇₂ S2	0.14(5) $\pm$ 0.01(2)	50	1.38
0.05 mM DDB-F ₇₂ S3	0.11(9) $\pm$ 0.01(5)	50	1.62
Average	0.12(4) $\pm$ 0.01(3)	--	--
0.1 mM DDB-F₇₂ S1	0.09(1) $\pm$ 0.01(1)	50	1.45
0.1 mM DDB-F ₇₂ S2	0.07(0) $\pm$ 0.00(8)	50	1.25
Average	0.08(0) $\pm$ 0.01(0)	--	--
0.5 mM DDB-F ₇₂ S1	0.05(1) $\pm$ 0.00(8)	50	1.52
0.5 mM DDB-F₇₂ S2	0.05(5) $\pm$ 0.00(5)	50	0.95
Average	0.05(3) $\pm$ 0.00(7)	--	--
1 mM DDB-F ₇₂ S1	0.04(6) $\pm$ 0.00(4)	50	0.79
1 mM DDB-F ₇₂ S2	0.05(3) $\pm$ 0.00(4)	50	0.80
1 mM DDB-F₇₂ S3	0.04(9) $\pm$ 0.00(4)	50	0.76
Average	0.04(9) $\pm$ 0.00(4)	--	--
1.5 mM DDB-F ₇₂ S1	0.02(5) $\pm$ 0.00(3)	50	0.72
1.5 mM DDB-F₇₂ S2	0.02(7) $\pm$ 0.00(3)	50	0.69
1.5 mM DDB-F ₇₂ S3	0.03(5) $\pm$ 0.00(3)	50	0.79
Average	0.02(9) $\pm$ 0.00(3)	--	--

^a All error bars are generated from the covariance of the Jacobian from the model fits.

^b Values for G that we extracted from fitting the fs-TTR data, as shown in Table 4.1, using the thermal model described in Section 3.2 of Chapter 3.

Table 4.3. Average Amplitude (A), Frequency (ω_d), Initial Phase (ϕ), Decay Constant (τ) and Period from the Thermal + Damped Harmonic Oscillator (DHO) Model Fitted to the Fs-TTR Data on Undoped and DDB-F₇₂-Doped P3HT Films*

P3HT Film	Avg. A (A.U.)	Avg. ω_d (GHz)	Avg. ϕ (rad)	Avg. τ (ps)	Avg. Period (ps)
Undoped	3.23 ± 1.85	1.30 ± 0.12	-1.35 ± 0.11	531 ± 342	822 ± 102
0.05 mM DDB-F ₇₂	2.61 ± 0.82	1.04 ± 0.03	-1.08 ± 0.01	870 ± 242	987 ± 18
0.1 mM DDB-F ₇₂	5.62 ± 1.49	1.07 ± 0.01	-1.12 ± 0.01	569 ± 1	971 ± 9
0.5 mM DDB-F ₇₂	8.97 ± 0.02	0.88 ± 0.03	-1.02 ± 0.01	645 ± 88	1194 ± 25
1 mM DDB-F ₇₂	7.91 ± 0.50	0.89 ± 0.01	-1.03 ± 0.01	734 ± 16	1160 ± 6
1.5 mM DDB-F ₇₂	9.35 ± 0.72	0.92 ± 0.01	-1.04 ± 0.01	636 ± 23	1135 ± 4

*All error bars are standard deviations.

As shown in Fig. 4.8 and tabulated in **Table 4.3**, the amplitude of the oscillation clearly increases as a function of increasing doping level. The average decay rate appears to be constant within error across the undoped and DDB-F₇₂-doped P3HT films. Furthermore, the average frequency of the oscillation appears to decrease with increasing doping level. This change in the frequency of the oscillation with doping suggests that the process of doping alters the underlying mechanism. In fact, changes in the frequency are somewhat correlated to structure changes that we show in the GIWAXS data discussed in Section 4.3; the decrease in the frequency in lightly-to-moderately-doped (0.05–0.5 mM DDB-F₇₂) films parallels the significant conversion of undoped crystallites and amorphous regions to the expanded doped structure across the same concentrations. Closer to the doping saturation level (1+ mM DDB-F₇₂), the frequency of the oscillation appears to remain constant within error.

Unfortunately, a literature search of oscillatory mechanical or acoustic phenomena with 0.9–1.1 GHz frequencies related to polymeric materials returned no insights into the origin of what fs-TTR might be detecting. We note that the frequency of the oscillation is incompatible

with an acoustic echo pertaining to either the transducer or the polymer film due to the thickness of our material layers and what is known about reasonable speeds of sound in polymeric materials.

The dashed curves in Fig. 4.8 reveal a likely monotonic decrease in $\kappa_{\perp}$ with doping, as the more highly DDB-F₇₂-doped samples have shallower TTR traces than lightly-doped or pristine films (see Table 4.2 for the $\kappa_{\perp}$ results from individual samples and the averages across different samples, which support this trend). In fact, our preliminary fitting results suggest a drop in $\kappa_{\perp}$ by an order of magnitude between undoped P3HT and the most-doped sample. Fully elucidating more definitive values of $\kappa_{\perp}$ requires experimental values for C_v as a function of DDB-F₇₂:3HT ratio and a fully understood (and modeled) origin for the damped oscillation. However, based on the analysis above, we expect to see a significant decrease in $\kappa_{\perp}$ as films are increasingly doped with DDB-F₇₂.

4.6 Calculating Preliminary zT Values for DDB-F₇₂-doped RR-P3HT Films

We performed electrical conductivity and Seebeck coefficient measurements on DDB-F₇₂-doped RR-P3HT films, the averaged results of which are shown in **Figure 4.9a**, to calculate power factor values, shown in Figure 4.9b, as a function of DDB-F₇₂:3HT ratio. These results are ultimately intended to determine values for the thermoelectric figure of merit, zT , pending the refinement of $\kappa_{\perp}$. Our σ measurements are generally in-line with published values that involved the DDB-F₇₂-doping of different varieties of RR-P3HT using either DCM or *n*-BA as the doping solvent.^{5,7,9,15,19} We note that doping RR-P3HT with DDB-F₇₂ from DCM yields slightly higher σ as a function of DDB-F₇₂ concentration compared to doping from *n*-BA; this is because DCM is a better swelling solvent,^{20,44,45} as previously stated. Our S measurements (and calculated power factors) are also in-line with published values that utilized DCM as the

doping solvent.⁵ Our measurements were performed using the methodologies described in Section 1.8 of Appendix A.

Across the DDB-F₇₂:3HT ratios achieved in this sample series, the power factor appears to reach a plateau between a DDB-F₇₂:3HT ratio of 0.04–0.07:1. Given that the power factor is maximized within this DDB-F₇₂:3HT ratio range and that $\kappa_{\perp}$ appears to monotonically decrease as a function of DDB-F₇₂:3HT ratio (presuming that there isn't a strongly compensating change in C_v with doping), then zT values for this polymer-dopant system should monotonically increase at these doping levels. Using our preliminary $\kappa_{\perp}$ results and assuming a 50% uncertainty in these values for error propagation, RR-P3HT films doped with DDB-F₇₂ may reach zT values as high as 0.18 at room temperature, as shown in Figure 4.9b. A zT value this large would be record-breaking for doped P3HT films (and 36× larger than F₄TCNQ-doped RR-P3HT, $zT = 0.0052$,²⁹ as determined in Chapter 2) and on the same order as the record for organic solid films (PEDOT:PSS with added rhodamine zwitterions have achieved $zT = 0.46$).⁵³

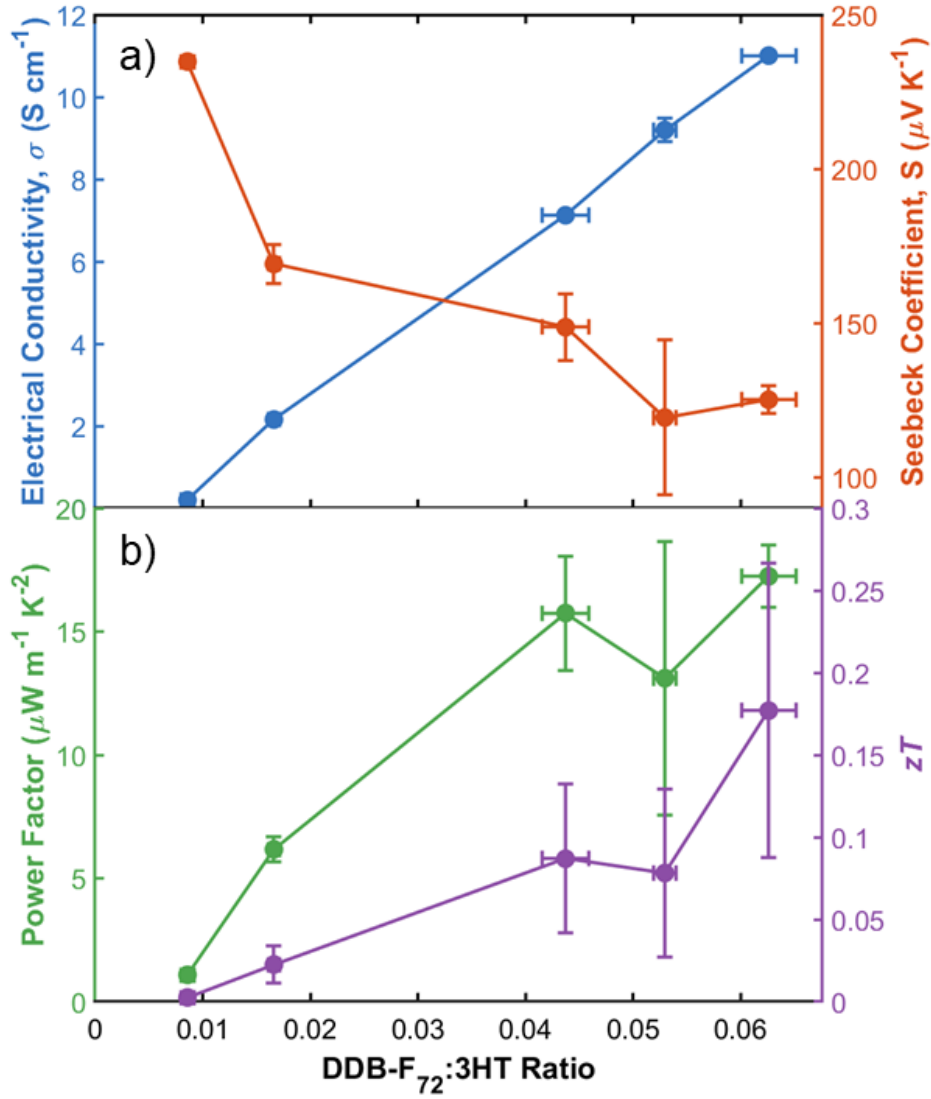


Figure 4.9. a) Averaged electrical conductivity and Seebeck coefficient measurements of DDB-F₇₂-doped P3HT films as a function of DDB-F₇₂:3HT ratio. The Seebeck coefficient decreases at the expense of increasing electrical conductivity. b) Power factor values, σS^2 , calculated from the electrical conductivity and Seebeck coefficient data presented in (a), and zT values calculated using preliminary $\kappa_{\perp}$ results from fs-TTR in Section 4.4, for DDB-F₇₂-doped P3HT films as a function of DDB-F₇₂:3HT ratio. For error propagation purposes, values for $\kappa_{\perp}$ carry 50% uncertainty due to our assumption that doped films have a C_v value equal to that of undoped RR-P3HT and the difficulty in accurately separating the amplitudes of the damped oscillation and thermal decay components using a modified TTR model.

4.7 Conclusions

In this chapter, we investigated how doping RR-P3HT with the bulky, strongly-oxidizing dopant DDB-F₇₂ alters the crystal structure of the polymer, film mass density, thermal transport properties and electrical properties as a function of the extent of doping. Although the thermal conductivity (and, by extension, the thermoelectric figure of merit) results are preliminary, we demonstrate that DDB-F₇₂ is a promising dopant for enhancing the thermoelectric performance of RR-P3HT and potentially other *p*-type polymer systems. We showed with UV-vis-NIR spectroscopy that polaron formation increases monotonically with increasing DDB-F₇₂ dopant concentrations using *n*-BA as a solvent with the SqP method. We showed with GIWAXS that doping creates a new crystallite structure that nearly doubles the lamellar (*h*00) spacing. Our GIWAXS data also shows, using the integrated area of the in-plane (020) peak, that doping with DDB-F₇₂ decreases the overall crystallinity of the film. Direct measurements of pristine and doped film mass and volume reveal that film mass grows proportionally faster than film volume as a function of DDB-F₇₂:3HT ratio. Thus, the film density steadily and linearly increases with increasing DDB-F₇₂:3HT ratio. The trends in both the X-ray diffraction experiments and density measurements are consistent with the general picture that DDB-F₇₂ dopes RR-P3HT films uniformly and locally converts either undoped crystallites or amorphous regions to the expanded doped structure, and that this continues until the doping saturation point is reached. Electrical conductivity increases substantially with doping while the Seebeck coefficient decreases, yielding a power factor that plateaus at DDB-F₇₂:3HT ratios of 0.04–0.07:1.

The main result of this chapter is the apparent monotonic, order-of-magnitude decrease in cross-plane thermal conductivity, extracted from fs-TTR measurements using approximate fits of the thermal decays, with increasing DDB-F₇₂:3HT ratio. Our preliminary thermal

conductivity results, when combined with our power factor values, reveal that thermoelectric figure of merit values of up to ~ 0.18 are possible with DDB-F₇₂-doped RR-P3HT, a record high for P3HT and of the same magnitude as the highest zT reported for any organic solid film. These results should be regarded as preliminary rather than definitive given that there are two open questions that limit the certainty in $\kappa_{\perp}$, which future work must resolve. First, the physical origin of the damped oscillation is necessary to accurately separate its amplitude from the thermal component used to fit $\kappa_{\perp}$. Second, the volumetric heat capacity values as a function of DDB-F₇₂:3HT ratio must be well-defined to accurately fit $\kappa_{\perp}$; specific heat at constant pressure measurements would resolve this.

4.8 References

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APPENDIX A: Supporting Information for Chapter 2

1.0 Experimental methods

1.1 Sourced materials

As stated in Section 2.4.1 in Chapter 2, 97.6% RR-P3HT was sourced from Ossila and both 91–94% RR- and RRa-P3HT were sourced from Rieke Metals. Additionally, we sourced the polymer casting solvents, *ortho*-dichlorobenzene (*o*DCB) and chloroform (CF), and the doping solution solvents, *n*-butyl acetate (*n*-BA) and acetonitrile (MeCN), as well as the dichloromethane (DCM) used in cleaning, from either Sigma-Aldrich or OmniSolv and stored them over molecular sieves in an N₂ atmosphere. We sourced the glass substrates (white borosilicate glass) and silicon substrates from VWR and University Wafer, respectively. We sourced the platinum and aluminum for sputtering, and gold for thermal deposition, from AJA International and Kurt J. Lesker, respectively.

1.2 Sample film preparation

We prepared separate film samples for each of the different experiments that we performed – mass/volume for determining ρ , net gain in mass for determining the F₄TCNQ:3HT mole ratio, DSC for determining C_p , Van der Pauw four-point-probe for measuring electrical conductivity (σ), the application of thermal gradients for determining the Seebeck coefficient (S), TDTR for determination of κ , and GIWAXS for measuring the film structure. The reason we had to use separate samples is due to a combination of experimental limitations concerning the required sample masses, electrode geometries and/or substrate material requirements. Details on how we processed each sample are included in the methods section for each experiment (see Sections 1.3–1.5 and 1.7–1.9 in Appendix A below). For all experiments except for DSC measurements, we spin-cast the polymer films and doped them

using the sequential processing (SqP) method. We prepared films for DSC measurements by drop-casting and doped them using the blend-doping method, largely because it is not possible to spin-coat a polymer film with the requisite mg mass. SqP is a procedure that separates the polymer film casting and solution doping into different steps, whereas putting the polymer and dopant into a single solution for casting is referred to as blend-doping. The SqP doping method is known to achieve films of higher quality than the blend-doping method,¹ which is why we chose it for samples where the mass of the film is not a limiting factor.

1.3 Bulk film density measurements of pristine and F4TCNQ-doped P3HT processed via SqP

We measured spin-cast film densities, shown in Figure A.1, for both pristine and F4TCNQ-doped RR- and RRa-P3HT films following a series of mass and volume measurements. We measured the polymer films' mass first and then the polymer films' volume, as described below, to avoid artifacts that might arise due to the scratching of the film that occurs when taking thickness measurements to determine the volume.

We prepared substrates for bulk film density measurements by first cutting $\sim 1.9 \times 1.9$ cm² glass squares and cleaning the glass through a sonication cycle of soapy water, deionized water, and acetone, in that order. Afterward, we dried glass substrates with air and then plasma-etched them. We then recorded the mass of these bare clean glass substrates. We performed all mass determinations using a Sartorius Cubis II Microbalance that can measure to single micrograms. We exclusively used tweezers without teeth to handle the substrates after the plasma etching step to prevent any microchipping of the glass substrate after our initial weighing. This is because any loss of substrate mass via chipping could result in an

underestimated film mass. Our use of clean tweezers also prevented any contaminants during handling from adding non-polymer mass to the substrate.

To prepare the polymer solutions, we dissolved RR- or RRa-P3HT in *o*DCB at a concentration of 5% wt/volume (50 mg mL⁻¹). We utilized 5% wt/volume solutions to make films thick enough to have at least 100 µg mass so that we could determine density values to three significant figures ($\leq 1\%$ error). When we used 2% wt/volume (20 mg mL⁻¹) polymer solutions (the same as what we utilized to make films for other thermoelectric measurements), we obtained similar density values but with only two significant figures due to the smaller overall mass. We filtered the RRa-P3HT solution using a polytetrafluoroethylene (PTFE) 0.22 µm pore-size filter prior to casting the films to remove any polymer aggregates, dust, or other impurities that negatively impact film uniformity and quality by leaving behind visible-to-the-eye particle features on the film. We did not investigate how this filtration impacted the M_n , M_w , PDI or %RR of RRa-P3HT, although we expect that any impact would be minimal given that the polymer does not have segments with higher and lower regioregularities. We did not filter the RR-P3HT solutions because the film quality was high without filtration, indicating a lack of polymer aggregates or impurities present after dissolution.

We spin-cast polymer films in a N₂ atmosphere at 1000 rpm for 60 seconds, then at 3000 rpm for 5 seconds. We then placed these films under vacuum for two hours to ensure that no residual solvent remained after spin-casting. Because polymer can get onto the backside and sides of the substrate during spin-casting, we wiped these surfaces with a Kimwipe that was wet with DCM and then dried the DCM with pressurized air before measuring the mass of the substrate plus polymer. We found that if the wiping step was not performed, additional polymer mass from the underside or substrate edges could lead to an overestimation of the film density as there is no way to account for volume of this material.

We prepared F₄TCNQ-doped RR- and RRa-P3HT films via the SqP method by first casting pristine polymer films as described above and then doping them with solutions of F₄TCNQ dissolved in *n*-BA. To dope the films, we dropped the dopant solution on top of a pre-cast film, held the solution there for 80 seconds, and then removed it by spin-casting at 4000 rpm for 10 seconds. We then placed these doped films under vacuum to remove residual solvent after the dopant step. We note that it is known that placing F₄TCNQ-doped P3HT films under vacuum does not cause changes in electrical conductivity;² thus, it is safe to assume that any F₄TCNQ molecules taking part in doping remain in the film following this step. As with the pristine P3HT films, we wiped the sides and underside of doped film substrates using a Kimwipe wet with DCM, then further dried the substrate itself with pressurized air to remove DCM. To calculate the mass of the doped polymer films, we subtracted the recorded mass of the substrate from that of the substrate plus doped polymer sample.

We then measured the volume of our pristine and doped P3HT films. To do so, we measured the substrate area and thickness using a digital caliper and a Veeco Dektak 150 profilometer, respectively. Measuring the length and width of each substrate with the digital caliper afforded a substrate area that is accurate down to 1/1000th of a cm². To measure the polymer film thickness, we cut a minimum of three cross sections into the film by manually dragging a blade across the sample at different locations. To test film uniformity, we measured the height of each scored line with the profilometer at least three different points, assuming that the bottom of the measured trench was the surface of the glass substrate. By averaging the thickness measurements for each type of sample, we could obtain thickness values accurate to ± 2 nm (<1% error). We should note that spin-casting can lead to beading of the polymer around the substrate's perimeter, so we used profilometry to measure these beads to determine the volume of this thicker part of the film. We calculated final film volumes for each sample by

multiplying the film area by the average film thickness and then adding a volume representative of the height and width of the bead that was in excess of the average thickness. We note that not incorporating the ridge volume could result in an overestimation of film density as the total volume would be underestimated.

To obtain the density of each polymer film, we divided a polymer film's measured mass by its measured volume. We performed these density measurements across a multitude of films (five films at a minimum) for each film type (both pristine RR- and RRa-P3HT and each of the doping concentrations in Figure A.1). We then averaged the densities across like samples to obtain the final bulk film density values. The error bars associated with the bulk density values are propagated errors.

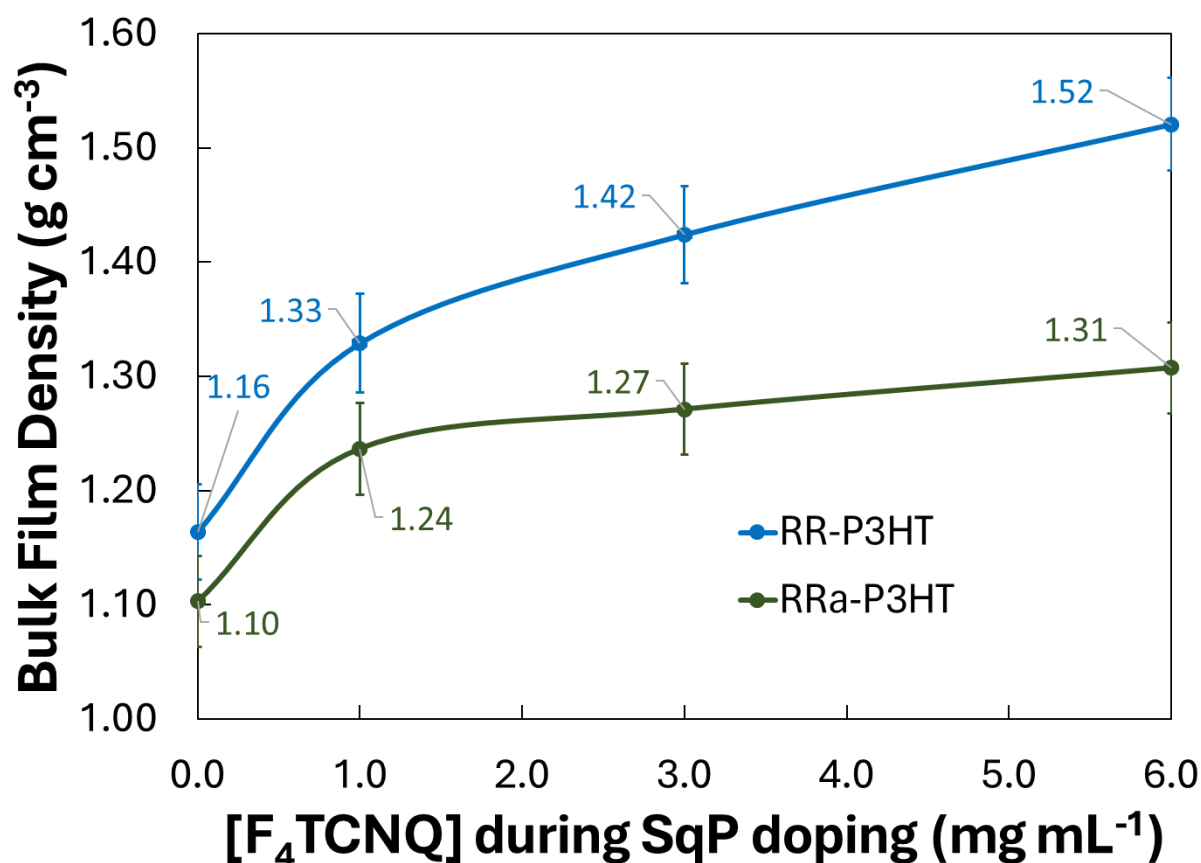


Figure A.1: Measured bulk film density of RR- and RRa-P3HT films as a function of the concentration of F₄TCNQ in the *n*-BA solution used for SqP doping. The amount of F₄TCNQ deposited into the P3HT

films is not linear with the doping solution concentration, saturating at the highest-concentration solutions used.

As both RR- and RRa-P3HT films are doped with F₄TCNQ, we find that the film densities increase rapidly at low F₄TCNQ-doping concentrations, followed by more gradual increases at higher concentrations. The sharp rise in film density at low doping concentrations is the result of a large influx of dopant molecules that intercalate within the lamellae of crystalline regions, in the case of RR-P3HT, or which cause amorphous regions to become more crystalline, in the case of RRa-P3HT. The shallower increase in film density at dopant solution concentrations above 1 mg/mL shows that higher doping concentrations only add marginal amounts of additional F₄TCNQ to the films. The fact that F₄TCNQ-doped RRa-P3HT films have lower densities than RR-P3HT films when doped with the same solution stems from the fact that there is less F₄TCNQ intercalated into the RRa-P3HT film compared to RR-P3HT. The reason for this is that it is harder to dope RRa-P3HT due to its deeper HOMO; the energy difference between the HOMO of RRa-P3HT and the LUMO of F₄TCNQ is smaller compared to that of RR-P3HT, so the same doping solution is less able to dope RRa-P3HT. This is why we went to the effort to determine the F₄TCNQ:3HT ratio for our samples, as described in the next section.

1.4 F₄TCNQ:3HT mole ratio measurements on F₄TCNQ-doped P3HT films processed via SqP

Although the data in Figure A.1 show that the density of P3HT films increases upon doping, the SqP method does not provide an easily measurable way to determine how much dopant intercalates into a given doped film. It is worth noting that the doping efficiency of

F₄TCNQ with P3HT is well below 100%,³⁻⁵ and also likely not constant with doping level, which means that it is not appropriate to use a measured carrier density to estimate the number of dopant molecules within a film. Thus, we developed a method to determine the F₄TCNQ:thiophene monomer unit (3HT) mole ratio of P3HT films doped via the SqP method.

To prepare doped RR-P3HT films for F₄TCNQ:3HT mole ratio measurements, we followed a procedure identical to the one described above to measure bulk film densities (Section 1.3 of Appendix A) except that we measured masses at three separate points: 1) the bare substrate, 2) the undoped polymer film plus substrate, and 3) the SqP-doped polymer film plus substrate. We performed these measurements on films SqP-doped with 1 mg mL⁻¹, 3 mg mL⁻¹, and 6 mg mL⁻¹ F₄TCNQ/*n*-BA solutions. As with the bulk film density procedure, we placed films under vacuum after both spin-casting the polymer and again after the polymer film was doped. We then determined the mass of the F₄TCNQ molecules intercalated into a given RR-P3HT film as the difference in mass before and after the doping step. We then used this mass and the mass of the polymer film to calculate the ratio of F₄TCNQ:3HT monomer units at a particular dopant concentration.

The mole fraction solubility (χ) of RR-P3HT has been reported to be 4.1×10^{-9} in *n*-BA,^{6,7} so a negligible (< 2% by mass) amount of polymer should be removed from the substrate during the doping step. We verified this by exposing pristine RR-P3HT films to pure *n*-BA in volumes typically used for the doping step of SqP, and measured no significant loss of polymer mass (which is < 2% of the initial mass of the polymer film given our mass sensitivity). However, for RRa-P3HT films, we were unable to use the procedure outlined above because the dopant solution solvent (*n*-BA) does remove a significant fraction of RRa-P3HT polymer films, so that we cannot properly determine the mass of the polymer after doping. As an example, after exposing a pristine RRa-P3HT film to pure *n*-BA in amounts and times typically

used to solution dope with SqP, roughly 26% of the absorption intensity is lost (see Figure A.2), indicating that a significant fraction of the RRa-P3HT dissolved away during exposure. The fact that the bandgap peak doesn't shift after *n*-BA exposure, however, indicates that there is no significant change in the M_w , M_n , or PDI of the RRa-P3HT that is left behind.

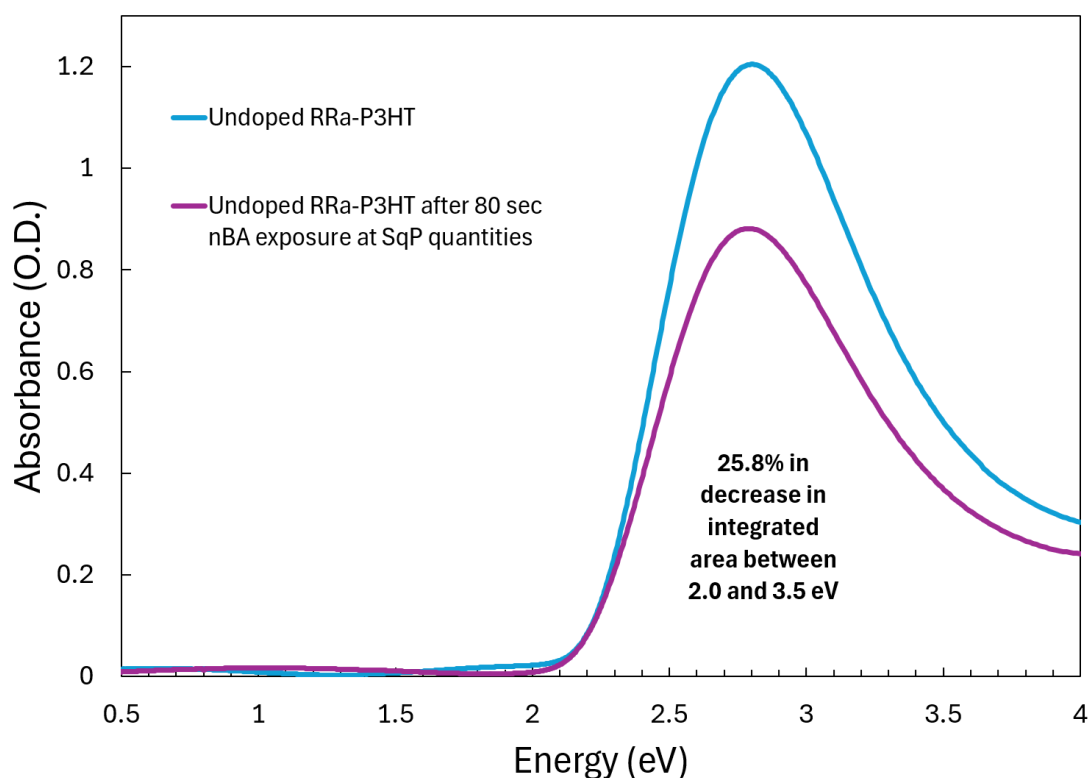


Figure A.2: UV-Vis-NIR absorption spectrum of a pristine RRa-P3HT film spin-cast from *o*DCB (blue curve) and the same film after soaking in 100 μ L of *n*-BA for 80 s (magenta curve) and spinning under similar conditions to SqP doping. The data show that there is a $\sim 26\%$ decrease in the integrated absorption area after *n*-BA exposure, indicating that RRa-P3HT is partially soluble in this solvent, so that the polymer mass is not constant before and after the doping step.

Thus, to precisely determine how much F₄TCNQ resides in doped RRa-P3HT films (and thus the F₄TCNQ:3HT ratio), we selected a different solvent (one that negligibly removes the RRa-P3HT polymer) for the SqP dopant solution, acetonitrile (MeCN). This is because

RRa-P3HT has an extremely low solubility in MeCN ($\chi = 6.2 \times 10^{-10}$).⁶ Then, we correlated (see below for detailed procedure) RRa-P3HT films doped with F₄TCNQ using MeCN as the doping solvent to RRa-P3HT films doped with F₄TCNQ using *n*-BA as the doping solvent. To verify that MeCN was a good choice, we took a pristine spin-cast RRa-P3HT film (Figure A.3, black curve) and then washed it by soaking in MeCN for 60 minutes (Figure A.3, green curve) before proceeding to the doping step; soaking the film for an hour in MeCN led only to a 1.6% absorption intensity loss. The slight red-shift of the absorption peak after 60 minutes of soaking suggests that only a small amount of low-*M_w* RRa components were preferentially removed from the film by MeCN. We also verified that an additional 30-minute soak in MeCN resulted in no further loss of absorption, as seen by the red curve in Figure A.3. We did not further investigate how soaking RRa-P3HT films in MeCN changed the *M_n*, *M_w*, or PDI of the remaining polymer; we operate under the assumption that the observed marginal changes do not affect the overall findings of this study.

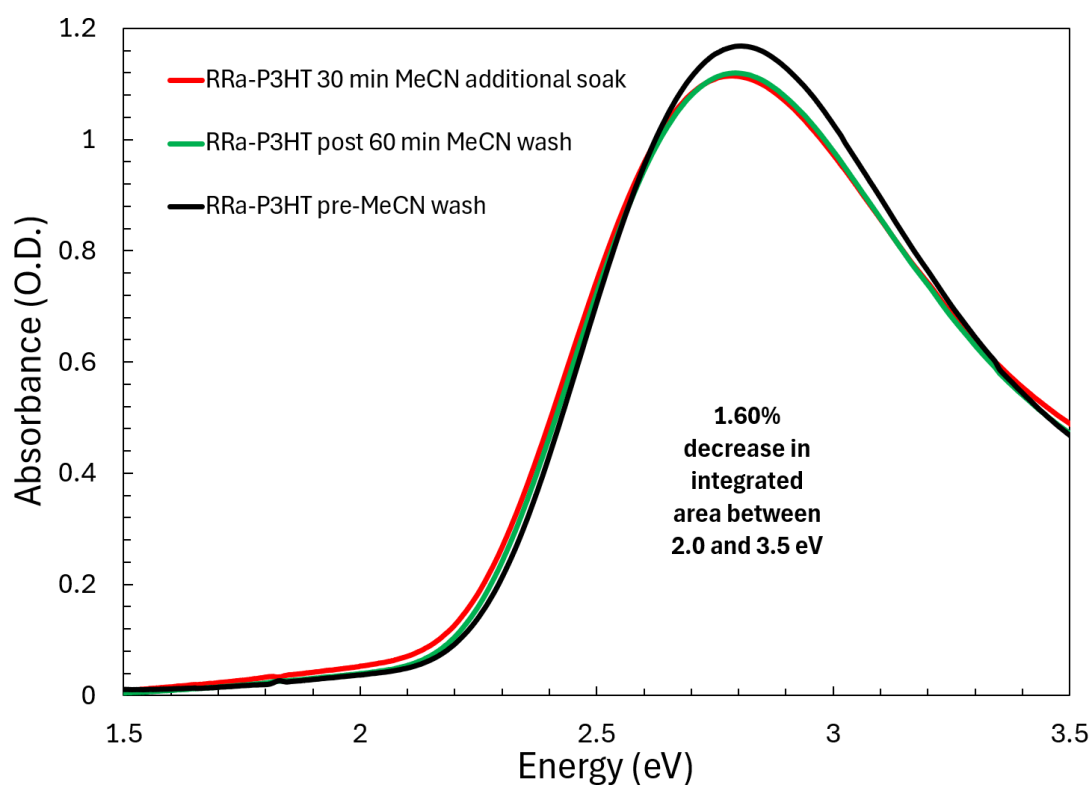


Figure A.3: UV-Vis-NIR absorption spectrum of pristine RRa-P3HT after being spin-cast from *o*DCB (black curve) and the same film after being soaked in 10 mL of MeCN for 60 minutes (green curve). The 1-hr soaking step leads to only a small loss in absorption area (1.6%). The soaking step induces a slight red-shift of the absorption spectrum, which indicates that some low- M_w RRa-P3HT polymer chains were redissolved. The red curve shows the spectrum of the same film after an additional 30 minutes of soaking in MeCN, where no further loss of absorption area occurred. This suggests that if RRa-P3HT films that are spin-cast from *o*DCB receive a 60-minute soaking in MeCN, any further exposure to MeCN (such as during SqP doping) after the initial 60-minute MeCN wash does not result in a loss of polymer.

With validation that we can use MeCN as the dopant solution solvent for RRa-P3HT films in F₄TCNQ:3HT mole ratio experiments, we prepared films as follows. Through the polymer spin-casting step, we fabricated pre-cast RRa-P3HT films for F₄TCNQ:3HT mole ratio experiments in the exact same way as outlined in experiments for bulk film density measurements (Section 1.3 of Appendix A). Then, we soaked the pre-cast RRa-P3HT films in MeCN solvent for 60 minutes prior to placing them under vacuum and then weighing them. To dope the MeCN-washed RRa-P3HT films, we submerged them in separate solutions of 5 mg mL⁻¹ F₄TCNQ/MeCN for 30 minutes. After 30 minutes, we removed the films from the dopant solution and immediately spin-cast them at 4000 rpm for 10 seconds to remove any residual dopant solution and prevent excess solution from drying on the surface of the film, which would have deposited additional neutral F₄TCNQ on the film surface. After we wiped the substrate underside and edges to remove any excess polymer and/or dopant, as performed above, we measured the mass of the doped films. Final mass measurements yielded a 1:11 F₄TCNQ:3HT mole ratio for RRa-P3HT films submerged in 5 mg mL⁻¹ F₄TCNQ/MeCN solutions for 30

minutes. We note that longer soaking times are required for MeCN than *n*-BA because MeCN does not significantly swell the polymer to allow for facile dopant intercalation.

In order to correlate the 1:11 F₄TCNQ:3HT mole ratio value to those of RRa-P3HT films SqP-doped with F₄TCNQ/*n*-BA solutions, we matched the doping levels of films doped with the two solvents in two different ways. First, we developed a spectroscopic doping level matching procedure that involved comparing the absorption of the band-gap (normalized to the frequency-weighted, integrated P1 absorption area) of the film doped via the F₄TCNQ/MeCN solution to a series of RRa-P3HT films SqP-doped using solutions of F₄TCNQ/*n*-BA with concentrations of 0.5 mg mL⁻¹, 0.8 mg mL⁻¹ and 1.0 mg mL⁻¹. Our sample preparation for films doped with F₄TCNQ/*n*-BA solutions in this concentration series followed a procedure identical to that of the bulk film density experiments described above in Section 1.3 of Appendix A. After we wiped the backside of the substrate to remove any excess polymer or dopant, we took the UV-Vis-NIR absorption spectra of each film and normalized the spectra to their frequency-weighted, integrated P1 area, as shown in Figure A.4. The overlap of the band-gap absorption intensities between the 1.0 mg mL⁻¹ F₄TCNQ/*n*-BA-doped RRa-P3HT film and the 5 mg mL⁻¹ F₄TCNQ/MeCN-doped film suggests that these films have matched doping levels. Thus, we assigned an F₄TCNQ:3HT mole ratio of 1:11 to RRa-P3HT films SqP-doped with 1.0 mg mL⁻¹ of F₄TCNQ/*n*-BA, as seen plotted in Figure 2.2a in Chapter 2.

One piece of evidence that supports our assumption that equivalent doping levels were reached between RRa-P3HT films doped with 1.0 mg mL⁻¹ F₄TCNQ/*n*-BA and 5 mg mL⁻¹ F₄TCNQ/MeCN solutions is that we found that both of these films have identical densities within error: our measured film densities (using the method described above in Section 1.3 of Appendix A) were $1.23(7) \pm 0.04 \text{ g cm}^{-3}$ and $1.23(9) \pm 0.04 \text{ g cm}^{-3}$ for 1.0 mg mL⁻¹ F₄TCNQ/*n*-BA-doped and 5 mg mL⁻¹ F₄TCNQ/MeCN-doped RRa-P3HT films, respectively. In Figure

2.2a of Chapter 2, the film density value corresponding to RRa-P3HT doped with 1 mg mL^{-1} F₄TCNQ/*n*-BA is an average of these two measured densities.

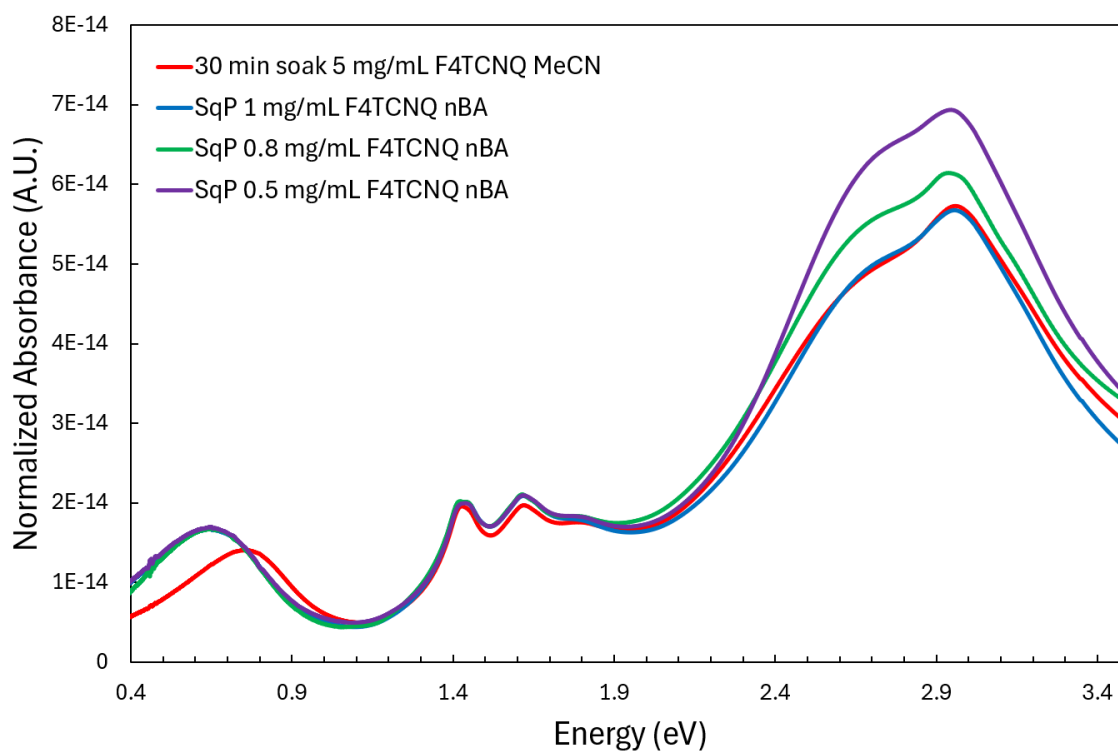


Figure A.4: UV-Vis-NIR absorption spectra of F₄TCNQ-doped RRa-P3HT films normalized to the frequency-weighted integrated P1 area in the region of 0.4–1.0 eV. Absorption spectra of RRa-P3HT films doped at increasing F₄TCNQ/*n*-BA concentrations (0.5 mg mL^{-1} in purple, 0.8 mg mL^{-1} in green, and 1 mg mL^{-1} in blue) show a smaller relative remaining bandgap absorption spanning 2.4–3.2 eV due to the increased doping achieved at higher solution dopant concentrations. The alternative doping method of soaking a film in 5 mg mL^{-1} F₄TCNQ/MeCN for 30 minutes (red curve) yields the same degree of doping as SqP with 1 mg mL^{-1} F₄TCNQ/*n*-BA (blue curve), as seen by the matching bandgap absorption intensities and shape of the bandgap region. We note that the sharp peak at 2.9 eV superimposed on the bandgap peak is due to excess neutral F₄TCNQ on the sample.

To correlate F₄TCNQ:3HT mole ratios to density values for various SqP-doped P3HT films, we utilized fits to the ρ -versus-F₄TCNQ:3HT data (dashed lines with linear equations

colored blue and green in Figure 2.2a of Chapter 2), where x is the F₄TCNQ:3HT mole ratio and y is the bulk film density. For RR-P3HT films doped with solutions of 1 mg mL⁻¹, 3 mg mL⁻¹ and 6 mg mL⁻¹ F₄TCNQ/*n*-BA, we used our measured F₄TCNQ:3HT ratios to determine film densities from the blue trendline fit in Figure 2.2a, but forcing the y -intercept to match the density of the (empty) doped structure from the x-ray model, described below. For RRa-P3HT films doped with solutions of 3 mg mL⁻¹ and 6 mg mL⁻¹ F₄TCNQ/*n*-BA, we used our direct measurements of bulk film density at these concentrations (see the labeled points in Figure A.1) to calculate the F₄TCNQ:3HT mole ratio using the green trendline fit in Figure 2.2a. For RR-P3HT films doped with solutions of 0.01 mg mL⁻¹, 0.1 mg mL⁻¹, and 0.3 mg mL⁻¹ F₄TCNQ/*n*-BA, and RRa-P3HT films doped with 0.3 mg mL⁻¹ F₄TCNQ/*n*-BA, we interpolated values for F₄TCNQ:3HT using the trends in Figure A.1 from Appendix A and Figure 2.2a of Chapter 2 and estimated values for density using the appropriate trendlines in Figure 2.2a.

Table A.1: Film densities and F₄TCNQ:3HT ratios for F₄TCNQ-doped RR- and RRa-P3HT

Polymer	[F ₄ TCNQ/ <i>n</i> -BA] in SqP (mg mL ⁻¹)	Measured Bulk Film Density (g cm ⁻³)	F ₄ TCNQ:3HT mole ratio	Film Density Utilized for C_v calculations (g cm ⁻³)
RR-P3HT	none	1.16(3) ± 0.04	0	1.16(3)
RR-P3HT	0.01	--	0.015 ^[a]	1.11(4) ^[c]
RR-P3HT	0.1	--	0.05 ^[a]	1.17(3) ^[c]
RR-P3HT	0.3	--	0.11 ^[a]	1.27(4) ^[c]
RR-P3HT	1	1.32(9) ± 0.04	0.152(9)	1.34(6) ^[d]
RR-P3HT	3	1.42(4) ± 0.04	0.185(2)	1.40(0) ^[d]
RR-P3HT	6	1.52(1) ± 0.04	0.266(4)	1.53(7) ^[d]
RRa-P3HT	none	1.10(3) ± 0.04	0	1.10(3)
RRa-P3HT	0.3	--	0.04 ^[a]	1.16(3) ^[e]
RRa-P3HT	1	1.23(8) ± 0.04	0.090(7)	1.23(8)
RRa-P3HT	3	1.27(1) ± 0.04	0.112(8) ^[b]	1.27(1)
RRa-P3HT	6	1.30(7) ± 0.04	0.137(0) ^[b]	1.30(7)

^[a] We interpolated F₄TCNQ:3HT mole ratios using Figure A.1 of Appendix A and Figure 2.2a from Chapter 2

^[b] We calculated F₄TCNQ:3HT ratios from bulk densities using the linear RRa-P3HT equation in Figure 2.2a

^[c] We calculated film densities from interpolated ratios using the linear RR-P3HT equation in Figure 2.2a

^[d] We calculated film densities from the measured ratios using the linear RR-P3HT equation in Figure 2.2a

^[e] We calculated film density from the interpolated ratio using the linear RRa-P3HT equation in Figure 2.2a

In Figure 2.2a, rather than fitting the slope through the measured film density of pristine RR-P3HT (the blue data point on the y-axis) to generate the fitted linear correlation for F₄TCNQ-doped RR-P3HT, we forced the fit through the calculated x-ray-derived density value (see below) of 1.08(9) g cm⁻³ at $x = 0$ (i.e., assuming that the crystalline fraction of the film had the density of the doped structure containing no F₄TCNQ); this is because this point incorporates the doping-induced volume expansion of the unit cell within the ~60% of the crystalline regions within the film. This is needed to account for the drop in density that occurs following the doping-induced phase transition at low F₄TCNQ:3HT mole ratios.

To derive a model for the density of doped RR-P3HT films that is based on what we known from x-ray scattering about the doping-induced volume expansion within the crystalline regions, we first had to approximate the crystalline:amorphous ratio. To do this, we calculated the density for the crystalline regions of pristine RR-P3HT films based on our x-ray data. Using the lamellar (16.110 Å) and π -stacking (3.648 Å) distances from our GIWAXS data (see Figure A.12 & A.13), we calculated the volume of a two-monomer-inclusive unit cell to be 466 Å³, which given the molecular weight of two 3HT monomers yields a density of 1.20(0) g cm⁻³. Assuming the amorphous regions of RR-P3HT films have a density equivalent to that of our measured bulk film density for RRa-P3HT (1.10(3) g cm⁻³), volume-weighting each region to match our measured pristine RR-P3HT film density of 1.16(3) g cm⁻³ yields a crystalline:amorphous ratio of ~60:40, which is in agreement with literature estimates for RR-P3HT.⁸⁻¹⁰ Next, we calculated the density of the volume-expanded crystalline regions in RR-P3HT using our x-ray data, as above. With doped lamellar (18.125 Å) and π -stacking (3.605 Å) distances from our GIWAXS data (see Figure A.12 & A.13), we calculate the volume of a two-monomer-inclusive unit cell to be 518 Å³, yielding a density of 1.07(9) g cm⁻³. Therefore,

a RR-P3HT film with doping-induced volume-expanded crystalline regions and an assumed a 60:40 crystalline:amorphous ratio should have a film density of 1.08(9) g cm⁻³.

To verify the accuracy of our use of x-ray data to approximate the density of crystalline regions in doped RR-P3HT films, we constructed a model to predict density values as a function of F₄TCNQ:3HT ratio simply adding the molar mass of F₄TCNQ by the fractional occupancy of the dopant in the unit cell; this is what leads to the purple solid line in Fig. 2.2a of Chapter 2. The model is:

$$\rho(x, \phi_c) = \left(1 + x \frac{m_{\text{F}_4\text{TCNQ}}}{m_{\text{3HT}}}\right) \left(\frac{\phi_a}{\rho_a^0} + \frac{\phi_c}{\rho_c^0}\right)^{-1}, \quad (\text{A. 1})$$

where x is the F₄TCNQ:3HT ratio, ϕ_c is the crystalline polymer volume fraction, ϕ_a is the amorphous polymer volume fraction, $m_{\text{F}_4\text{TCNQ}}$ is the mass of F₄TCNQ, m_{3HT} is the mass of a 3HT monomer unit, ρ_a^0 is the density of amorphous polymer (without F₄TCNQ) and ρ_c^0 is the density of crystalline polymer (also without F₄TCNQ). If we assume that the crystalline:amorphous volume ratio for all F₄TCNQ-doped RR-P3HT films is 60:40, as estimated for the pristine film, and that ρ_a^0 and ρ_c^0 are each 1.10(3) g cm⁻³ and 1.07(9) g cm⁻³, respectively, then Equation A.1 can be simplified to:

$$\rho(x) = 1.78597x + 1.08847. \quad (\text{A. 2})$$

Eq. A.2 is what is plotted above the vertex in the purple line in Figure 2.2a, and the intercept value of 1.08847 is what was used for the fit to the data in the blue dashed line in that figure. We numerically compare density values estimated from our x-ray model to our measured density and F₄TCNQ:3HT ratio values for 1 mg mL⁻¹, 3 mg mL⁻¹, and 6 mg mL⁻¹ F₄TCNQ-doped RR-P3HT films in Table A.1. The good agreement gives us confidence in our understanding of how P3HT bulk film density changes with F₄TCNQ:3HT upon doping given what we know about the doping-induced volume-expansion of crystallites.

1.5 Measuring film C_p using differential scanning calorimetry (DSC)

Our DSC instrument – a double-furnace, power-compensating PerkinElmer DSC 8000 – requires samples with masses of at least 5–10 mg for accurate measurements. This makes spin-cast films unfeasible to use for measuring C_p : for example, pristine P3HT films spin-cast from 5% wt/volume solutions on our standard size substrates typically mass only 100 to 200 μg . Therefore, only for our C_p measurements, we prepared films via the drop-casting and blend-doping methods, as films with the needed masses can be routinely made using these methods.

To prepare drop-cast films of pristine RR- and RRa-P3HT for C_p measurements, we weighed out 5–10 mg of each polymer and then fully dissolved that polymer in chloroform (CF). We then transferred these polymer solutions to flat-bottom vials and let the solutions dry under a N_2 atmosphere until the solvent fully evaporated. We selected CF as it readily evaporates at room temperature due to its high vapor pressure. We then removed the dried films from the vials and placed them under vacuum to remove any remaining solvent. We then placed film samples into aluminum pans and crimped the pans with aluminum lids.

To prepare drop-cast, blend-doped RR- and RRa-P3HT films for C_p measurements, we weighed out 5–10 mg of each polymer alongside separately-weighed F_4TCNQ . Then, we made polymer solutions using CF for both P3HT varieties alongside F_4TCNQ solutions made also with CF. For blend-doped RR-P3HT samples, we added the required amount of F_4TCNQ solution to the polymer solution to achieve F_4TCNQ :3HT mole ratios of 1:8 and 1:4. We prepared blend-doped RRa-P3HT samples with F_4TCNQ :3HT mole ratios of 1:50, 1:20, and 1:10. We then transferred these polymer-dopant solutions to flat-bottom vials and evaporated them under a N_2 atmosphere. Once dry, we removed the films from the vials, placed them under vacuum, and then into aluminum pans (which we crimped with aluminum lids after).

In order to determine C_p from DSC, the mass of the material-of-interest as well as the mass of the crimped aluminum pan must both be known. Therefore, before measurements, we weighed out a specific amount of polymer sample using the pre-crimped aluminum pan and then re-weighed the crimped aluminum pan (with polymer sample inside). We subtracted the mass of polymer sample from the total mass of the crimped pan to determine the mass of the aluminum pan.

During DSC measurements, we performed scans under a purging N_2 atmosphere and we used Pt lids to cover the sample and reference chambers. We calculated C_p curves, as seen in Figures A.5, A.6 and A.7, using the traditional two-curve method across a temperature range of 15 to 40 °C. The baseline/reference pan used was aluminum. We obtained all C_p values for drop-cast pristine and F₄TCNQ-blend-doped RR- and RRa-P3HT films – listed in Table A.2 as well as plotted in Figure 2.2b in Chapter 2 – at 20 °C. As a control sample, we reproduced the literature C_p value for bulk polystyrene ($M_w = 258 \text{ kg mol}^{-1}$, $C_p = 1.2275 \text{ J g}^{-1} \text{ K}^{-1}$ at 300 K) with our instrument:¹¹ $C_p = 1.24 \text{ J g}^{-1} \text{ K}^{-1}$ for a sample with $M_w = 280 \text{ kg mol}^{-1}$.

Table A.2: C_p data for drop-cast pristine and F₄TCNQ-blend-doped RR- and RRa-P3HT films

Polymer	F ₄ TCNQ:3HT blend-doped mole ratio	$C_p \text{ (J g}^{-1} \text{ K}^{-1})$ at 293.15 K
91–94% RR-P3HT (bulk-powder)	none (pristine)	1.46
97.6% RR-P3HT (bulk-powder)	none (pristine)	1.45
91–94% RR-P3HT (drop-cast)	none (pristine)	1.41
97.6% RR-P3HT (drop-cast)	none (pristine)	1.28
97.6% RR-P3HT (blend-doped)	1:8	1.11
97.6% RR-P3HT (blend-doped)	1:4	1.04
RRa-P3HT (drop-cast)	none (pristine)	1.71
RRa-P3HT (blend-doped)	1:50	1.33
RRa-P3HT (blend-doped)	1:20	1.28
RRa-P3HT (blend-doped)	1:10	1.17

We also performed C_p measurements on two varieties (91–94% and 97.6%) of pristine RR-P3HT to examine: 1) if there is any regioregularity dependence on C_p and 2) if there is any C_p difference between bulk powder polymer and drop-cast polymer film samples. For bulk powder samples, we used the polymer directly as received from the respective vendors for DSC measurements. We found that there appears to be no measurable difference in the C_p of the different RR-P3HT varieties in their bulk powder morphology. However, as RR-P3HT is drop-cast into films, the C_p drops, which suggests that the process of drop-casting orders the polymer. We also see that the 97.6% RR-P3HT variety has a larger drop in C_p upon drop-casting than the 91–94% RR-P3HT variety, indicating that C_p does depend on polymer regioregularity in their film morphology.

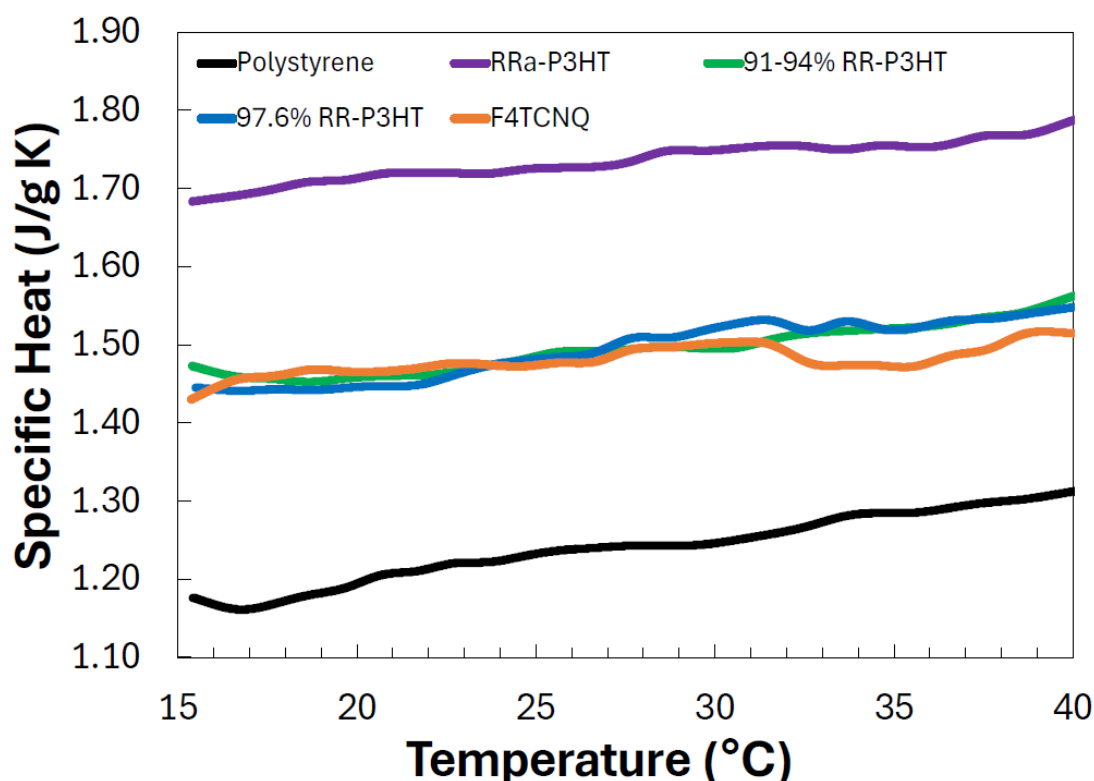


Figure A.5: C_p values, measured with DSC between 258–313 K (15–40 °C), for pristine (undoped) bulk powder polystyrene (black), bulk powder 91–94% RR-P3HT (green), bulk powder 97.6% RR-P3HT (blue), drop-cast RRa-P3HT (purple), and bulk powder F4TCNQ (orange). Both bulk powder RR-P3HT

samples, which have regioregularity >90%, have identical C_p within error. Our measurement on the polystyrene control sample agrees with published literature values to better than 1%.¹¹

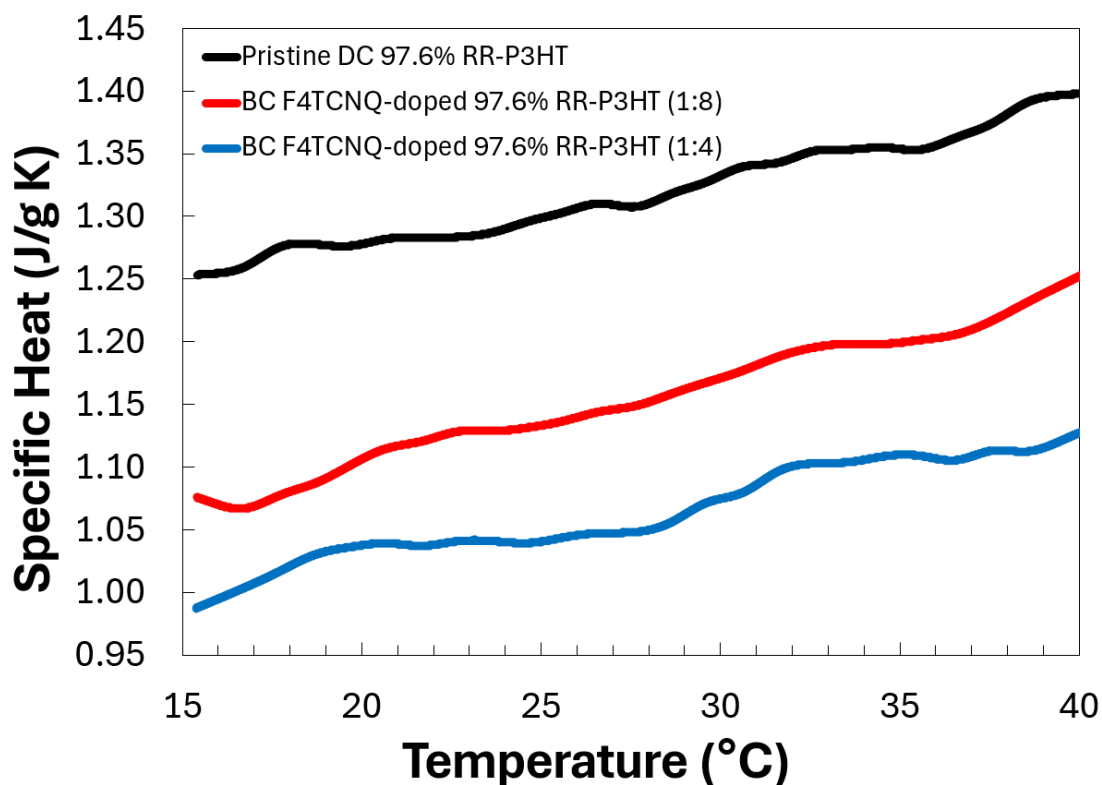


Figure A.6: C_p values, measured with DSC between 258–313 K (15–40 °C), for pristine drop-cast 97.6% RR-P3HT (black) and F₄TCNQ-blend-doped 97.6% RR-P3HT films doped at F₄TCNQ:3HT ratios of 1:8 (red) and 1:4 (blue). Clearly, C_p decreases as P3HT films are blend-doped with greater amounts of F₄TCNQ.

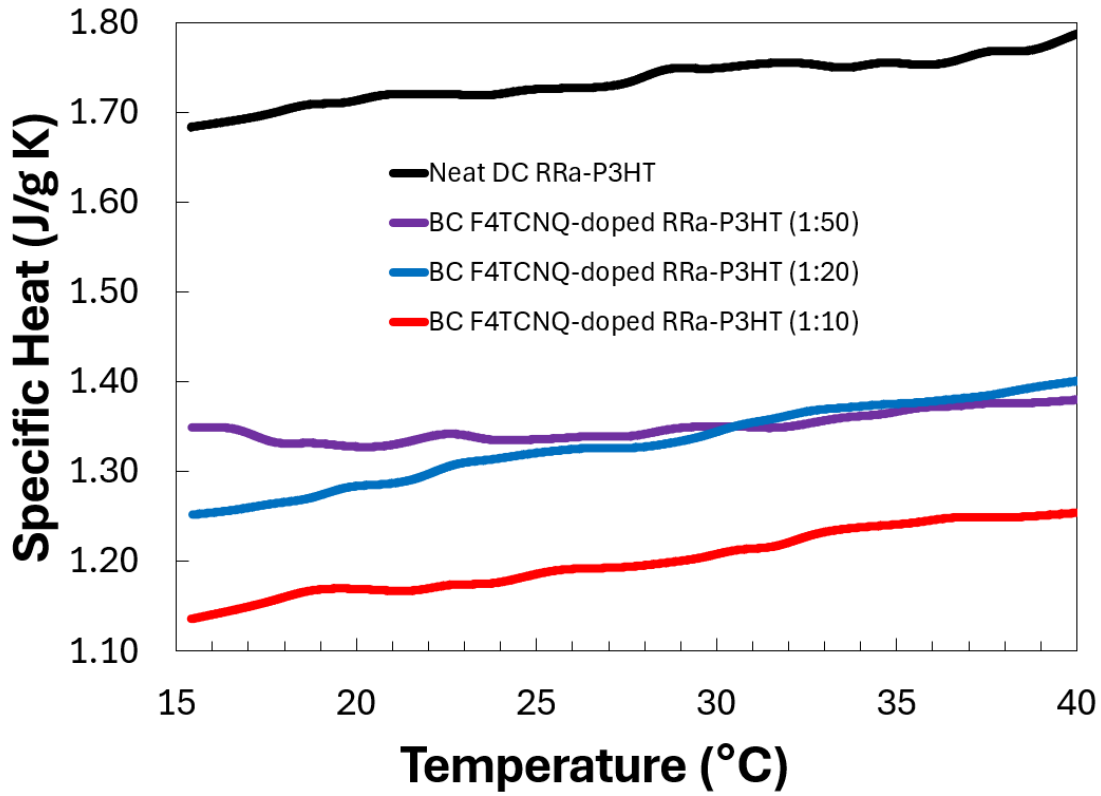


Figure A.7: C_p values, measured with DSC between 258–313 K (15–40 °C), for pristine drop-cast RRa-P3HT (black) and F₄TCNQ-blend-doped RRa-P3HT films doped at F₄TCNQ:3HT ratios of 1:50 (purple), 1:20 (blue) and 1:10 (red). As with RR-P3HT, the C_p of RRa-P3HT decreases as the films are blend-doped with greater amounts of F₄TCNQ.

1.6 Calculating C_v values for F₄TCNQ-doped RR- and RRa-P3HT films

We developed analytical functions to calculate C_v values for F₄TCNQ-doped RR- and RRa-P3HT films across a range of F₄TCNQ:3HT mole ratios by multiplying the best-fit equations for the density (Figure 2.2a in Chapter 2) and C_p (Figure 2.2b in Chapter 2), as summarized in Equation A.3 and A.4 below as well as in Figure 2.2c in Chapter 2:

$$C_{v,RR-P3HT} = (1.6817x + 1.0886)(3.3286x^2 - 1.7922x + 1.278), \quad (\text{A.3})$$

$$C_{v,RRa-P3HT} = (1.4901x + 1.1029)(1.0182x^{(-0.069)}), \quad (\text{A.4})$$

where x is the F₄TCNQ:3HT mole ratio. We chose to analytically determine C_v values because it best interpolates the data given that different films were used for the C_p and ρ experiments.

The C_v values we used to fit κ values in TDTR for F₄TCNQ-doped RR- and RRa-P3HT films are listed in Table A.3. We calculated the pristine C_v values for RR- and RRa-P3HT using the directly measured values for ρ and C_p as our analytical expression is not usable at $x = 0$. We note that the F₄TCNQ-doped RR- and RRa-P3HT films for which we interpolated F₄TCNQ:3HT mole ratios values for (these include RR-P3HT doped with 0.01 mg mL⁻¹, 0.1 mg mL⁻¹, and 0.3 mg mL⁻¹, and RRa-P3HT doped with 0.3 mg mL⁻¹) have well-defined C_v values due to the fact that, for these particular films, there is little dependence of the value of C_v on the F₄TCNQ:3HT mole ratio, as seen in Figure 2.2c of Chapter 2.

Table A.3: Analytically determined C_v values for F₄TCNQ-doped RR- and RRa-P3HT films

Polymer	[F ₄ TCNQ] doping (SqP) (mg mL ⁻¹)	F ₄ TCNQ:3HT mole ratio	C_v (J cm ⁻³ K ⁻¹)
RR-P3HT	None (pristine)	0	1.48(9)
RR-P3HT	0.01	0.015 ^[a]	1.39(4)
RR-P3HT	0.1	0.05 ^[a]	1.40(3)
RR-P3HT	0.3	0.11 ^[a]	1.42(8)
RR-P3HT	1	0.152(9)	1.45(6)
RR-P3HT	3	0.185(2)	1.48(4)
RR-P3HT	6	0.266(4)	1.59(3)
RRa-P3HT	None (pristine)	0	1.88(6)
RRa-P3HT	0.3	0.04 ^[a]	1.47(8)
RRa-P3HT	1	0.090(7)	1.48(8)
RRa-P3HT	3	0.112(8)	1.50(4)
RRa-P3HT	6	0.137(0)	1.52(6)

^[a]These F₄TCNQ:3HT mole ratios are interpolated as described in Section 1.4 of Appendix A.

1.7 Measuring thermal effusivity with time-domain thermoreflectance (TDTR)

We prepared pristine and F₄TCNQ-doped RR- and RRa-P3HT films for TDTR using the SqP doping method. Before spin-casting the polymer, we first cut glass substrates into 1.5

$\times 1.5 \text{ cm}^2$ squares and then cleaned them via a sonication cycle of soapy water, deionized water, and acetone, in that order. Afterward, we plasma-etched the substrates. As above, we prepared polymer solutions by dissolving 2 %wt/volume (20 mg mL^{-1}) RR-P3HT in *o*DCB and RRa-P3HT in CF. We filtered the RRa-P3HT solution using a polytetrafluoroethylene (PTFE) $0.22 \text{ }\mu\text{m}$ pore-size filter.

With these solutions, we spin-cast polymer films in a N_2 atmosphere at 1000 rpm for 60 seconds, then at 3000 rpm for 5 seconds. We doped the pre-cast P3HT films using the following SqP doping concentrations of $\text{F}_4\text{TCNQ}/n\text{-BA}$: RR-P3HT with 0.01 mg mL^{-1} , 0.1 mg mL^{-1} , 0.3 mg mL^{-1} , 1 mg mL^{-1} , 3 mg mL^{-1} , 6 mg mL^{-1} solutions, and RRa with 0.3 mg mL^{-1} , 1 mg mL^{-1} , 3 mg mL^{-1} and 6 mg mL^{-1} solutions. We did not perform TDTR measurements on RRa-P3HT films doped with 0.01 mg mL^{-1} or 0.1 mg mL^{-1} because RRa-P3HT requires higher dopant concentrations for doping to occur. To dope the films, we placed the dopant solution on top of the pre-cast film, held it there for 80 seconds, and then removed it by spin-casting the film at 4000 rpm for 10 seconds.

To prepare these films for TDTR experiments, we then sputtered an Al (70 nm)/Pt (10 nm) bilayer transducer on top of the polymer film. We deposited the transducer using an AJA magnetron sputtering chamber at a sputtering pressure of 3.5 mTorr. We deposited the Pt layer on the polymer before the Al layer to prevent chemical de-doping by Al, the latter metal of which readily serves as a reducing agent to fill holes on the F_4TCNQ -doped P3HT backbone.

We conducted TDTR experiments using an amplitude-modulated, low pulse-energy laser system to measure the cross-plane thermal effusivity of our pristine and doped P3HT films. TDTR is a well-established pump/probe technique used for measuring the thermal properties of thin films;^{12–14} the system used is illustrated in Figure A.8a. In this method, the pump beam deposits energy into the thermal transducer on the surface of the film and causes

the temperature to rise; the temperature then subsequently decays due to heat conduction into the polymer sample. The probe beam measures the reflectance of the transducer, which is directly related to the temperature. The beam path length difference is changed by a linear delay stage. During TDTR experiments, we maintained a low laser power to avoid a significant temperature rise (<30 K) in the polymer films, using a pump power of approximately 5 mW and a probe power of approximately 2 mW. Both the pump and probe wavelengths were 783 nm. We measured the spot size to be about $10.5\ \mu\text{m}$ and modulated the pump beam at 10.7 MHz.

We analyzed the TDTR data using a thermal model based on a multi-layer heat diffusion equation.¹⁵ This model incorporates the thermal parameters of the transducer, polymer film, and substrate. It calculates the in-phase and out-of-phase temperature responses from pump laser heating. The ratio of the in- and out-of-phase signals was analyzed to determine the thermal properties of the underlying P3HT films. The thickness of the transducer is determined by performing TDTR measurements on an Al-Pt/Sapphire control sample that had the bilayer transducer deposited at the same time as the polymer samples. This leaves the only unknown parameter as the thermal effusivity of the polymer. We thus extract the thermal effusivity by fitting the thermal model to experimental data, an example of which is shown in Figure A.8b, using an algorithm that minimizes the sum of the squares of the residuals.

When modelling the data, we fixed the interface thermal boundary conductance (TBC) between the transducer and polymer to be constant at $50\ \text{MW m}^{-2}\ \text{K}^{-1}$ for all of the pristine and doped P3HT films we tested. We did this because the best-fit thermal effusivity was not sensitive to the chosen value of the TBC parameter because all our films' thermal resistance was much greater than the transducer/film boundary resistance. The κ and C_v of the substrate (glass) in the model were set to literature values of $1.3\ \text{W m}^{-1}\ \text{K}^{-1}$ and $1.65\ \text{MJ m}^{-3}\ \text{K}^{-1}$,

respectively. At short times, as shown in Figure A.8b, the TDTR data show two kinds of oscillations: (1) acoustic echoes generated at the transducer/polymer interface (times < 100 ps) and (2) a larger sinusoidal-like signal with a period of approximately 800 ps. We believe that the slower oscillations may result from surface displacement of the polymer due to its relatively soft mechanical properties. The red solid line represents the thermal model prediction, while the red dashed line is the thermal model prediction with a damped harmonic function added to it. Since the slower oscillations have a lesser effect on the signals after ≈ 1000 ps, we analyze the data from 1000—9000 ps and fit the P3HT film thermal effusivities, which are listed in Table A.4. The thermal conductivities we report are based on the best-fit effusivity values from our TDTR experiments and our experimentally-determined C_v values, listed in Table A.3. We also report thermal diffusivities in Table A.4 from Equation 2.2 of Chapter 2.

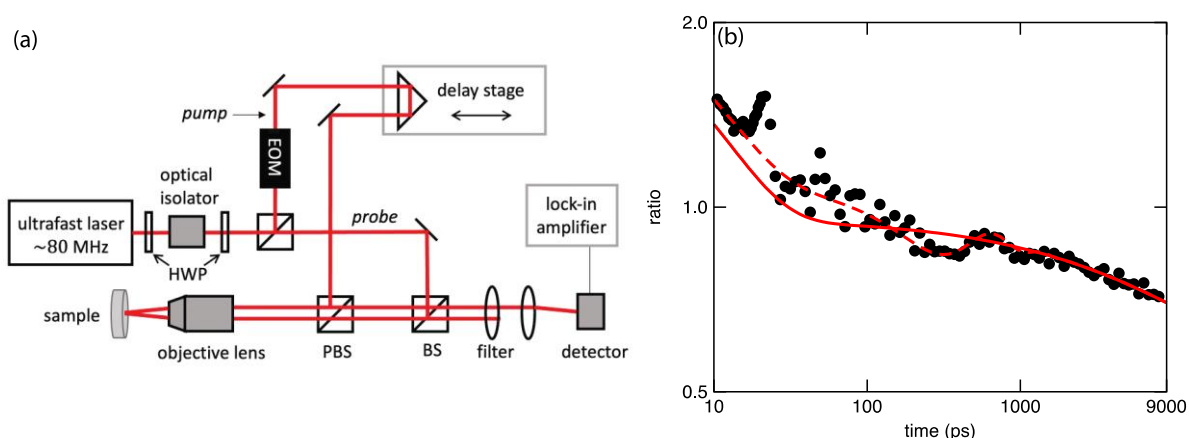


Figure A.8: (a) Schematic of pump/probe laser system used for TDTR measurements. (b) Experimental TDTR data and thermal model prediction for a RR-P3HT film SqP-doped with 0.3 mg mL^{-1} $\text{F}_4\text{TCNQ}/n$ -BA. The red solid curve represents the fitted thermal model prediction; the red dashed curve includes a sinusoidal function with decayed amplitude. We used only the data at times ≥ 1000 ps to determine the thermal effusivities of our samples.

Table A.4: Fitted thermal effusivity (e) measured with TDTR, alongside determined thermal conductivity (κ), thermal diffusivity (α), and Weidmann-Franz predicted κ_{el} (using electrical conductivities from Table A.5) for pristine and F₄TCNQ-doped RR-P3HT and RRa-P3HT films at 20 °C.

Polymer	F ₄ TCNQ/ <i>n</i> -BA in SqP (mg mL ⁻¹)	e (W s ^{1/2} m ⁻² K ⁻¹)	κ (W m ⁻¹ K ⁻¹)	α (mm ² s ⁻¹)	κ_{el} (W m ⁻¹ K ⁻¹) per Weidmann-Franz
RR-P3HT	--	680	0.31(1)	0.20(9)	σ not measured
RR-P3HT	0.01	737	0.38(9)	0.27(9)	σ not measured
RR-P3HT	0.1	740	0.39(1)	0.27(8)	0.0007(8)
RR-P3HT	0.3	729	0.37(2)	0.26(1)	0.002(1)
RR-P3HT	1	724	0.36(0)	0.24(7)	0.003(6)
RR-P3HT	3	728	0.35(7)	0.24(1)	0.004(7)
RR-P3HT	6	681	0.29(1)	0.18(3)	0.005(7)
RRa-P3HT	--	655	0.22(7)	0.12(1)	σ not measured
RRa-P3HT	0.3	644	0.28(1)	0.19(0)	σ not measured
RRa-P3HT	1	675	0.30(6)	0.20(6)	σ not measured
RRa-P3HT	3	677	0.30(5)	0.20(3)	0.00001(7)
RRa-P3HT	6	607	0.24(1)	0.15(8)	0.00002(8)

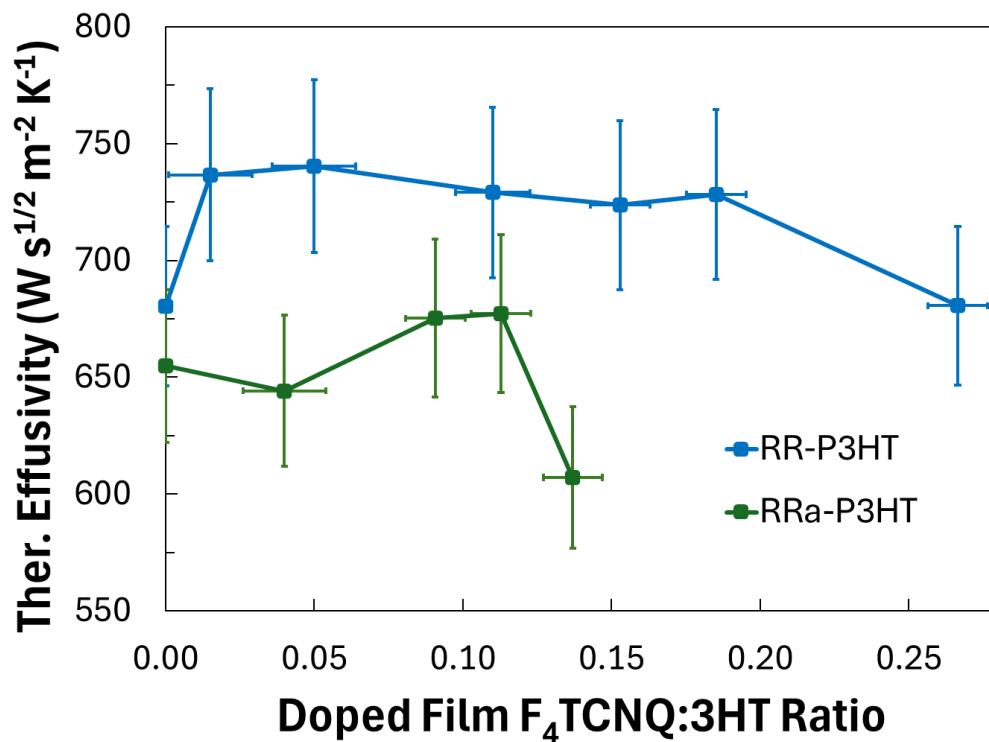


Figure A.9: Thermal effusivity values for F₄TCNQ-doped RR-P3HT and RRa-P3HT films as a function of F₄TCNQ:3HT ratio determined by TDTR.

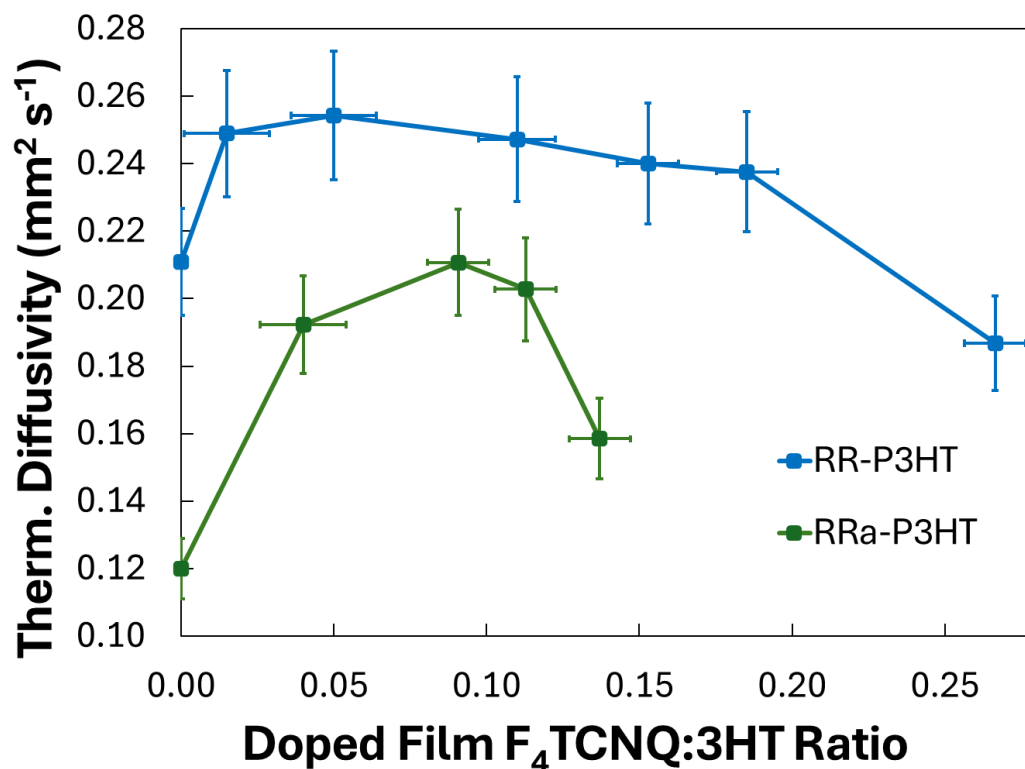


Figure A.10: Calculated thermal diffusivity values for F₄TCNQ-doped RR-P3HT and RRa-P3HT films as a function of F₄TCNQ:3HT ratio. We calculated diffusivity values using experimental thermal effusivity, C_p and density data discussed above and in Chapter 2.

1.8 Measuring electrical conductivity, Seebeck coefficient, and zT values for F₄TCNQ-doped P3HT

We prepared F₄TCNQ-doped RR- and RRa-P3HT films for electrical conductivity and Seebeck coefficient measurements by the SqP method in the exact same way as films prepared for TDTR, except that the substrates were $1.2 \times 1.2 \text{ cm}^2$ in size. After casting the films, we deposited gold electrodes (45 nm thick, $1 \times 1 \text{ mm}^2$) using an Angstrom Engineering Nexdep thermal evaporator under high vacuum (below 1×10^{-6} torr) at a deposition rate of 0.5 Å s^{-1} on

to the corners of the film using a custom shadow mask. We determined values for electrical conductivity by measuring the sheet resistance using a Lakeshore MeasureReady M91 FastHall system in the Van der Pauw configuration.¹⁶ We then measured film thickness using a Veeco Dektak 150 stylus profilometer by scoring the film at three different locations, measuring multiple locations for each score, and then taking an average, as described above.

To prepare doped P3HT films for Seebeck coefficient measurements, we deposited in the same manner as above two parallel gold electrodes (45 nm thick, $10 \times 1 \text{ mm}^2$) that were spaced 10 mm apart. We performed the measurements using a custom-built set-up with two Peltier plates used to apply a temperature gradient. We used two RTD sensors to monitor the temperature of different points on the film.

We performed electrical conductivity and Seebeck coefficient measurements on samples prepared identically to those for which we performed TDTR in order to determine values for zT across a range of F₄TCNQ:3HT mole ratios. We note that some of the films we used for TDTR were too lightly doped to reach the minimum sensitivity of our electrical conductivity and/or Seebeck coefficient measurements, resulting in the ‘missing’ data in Figure 2.4 of Chapter and Table A.5 of Appendix A. We calculated zT values using Equation 2.1.

Table A.5: Measurements of σ and S alongside calculated power factors (σS^2) and zT values for F₄TCNQ-doped RR-P3HT and RRa-P3HT films

Polymer	F ₄ TCNQ/ <i>n</i> -BA (mg mL ⁻¹)	σ (S cm ⁻¹)	S (μV K ⁻¹)	σS^2 (μW m ⁻¹ K ⁻²)	zT (20 °C)
RR-P3HT	0.01	Not measurable	Not measurable	Not measurable	Not measurable
RR-P3HT	0.1	1.0(9)	$1.1(4) \times 10^2$	1.4(2)	$1.0(7) \times 10^{-3}$
RR-P3HT	0.3	2.9(4)	$1.0(5) \times 10^2$	3.2(3)	$2.5(4) \times 10^{-3}$
RR-P3HT	1	5.0(9)	$9.2(3) \times 10^1$	4.3(3)	$3.5(3) \times 10^{-3}$
RR-P3HT	3	6.5(9)	$8.1(5) \times 10^1$	4.3(8)	$3.5(9) \times 10^{-3}$
RR-P3HT	6	7.9(2)	$8.0(8) \times 10^1$	5.1(8)	$5.2(2) \times 10^{-3}$
RRa-P3HT	0.3	Not measurable	Not measurable	Not measurable	Not measurable
RRa-P3HT	1	Not measurable	Not measurable	Not measurable	Not measurable

RRa-P3HT	3	$2.4(3) \times 10^{-2}$	Not measurable	Not measurable	Not measurable
RRa-P3HT	6	$3.8(6) \times 10^{-2}$	$1.5(8) \times 10^2$	$9.6(7) \times 10^{-2}$	$1.1(8) \times 10^{-4}$

1.9 Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements

We prepared pristine and F₄TCNQ-doped RR- and RRa-P3HT films for GIWAXS experiments using the same methods employed for the TDTR experiments, described above, except that we used $1.5 \times 1.5 \text{ cm}^2$ silicon substrates instead of glass substrates.

GIWAXS measurements were conducted at the Synchrotron Radiation Lightsource (SSRL) at SLAC National Accelerator Laboratory on beamline 11-37.3.3 with a 12.7 keV X-ray beam incident at 0.12° and a detector distance of approximately 240 mm. GIWAXS samples were held in a helium atmosphere to reduce air scattering. Data analysis (including baselining and peak fitting) was performed using IgorPro, and calibration used the Irena and Nika packages with LaB₆ as the calibrant. Raw, calibrated data is shown in Figure A.11. The WAXStools package was used for radial integrations. Out-of-plane integrations utilized a radial range of 0° – 10° with respect to the positive q_z axis. Similarly, in-plane integrations used the radial range of 78° – 88° with respect to the positive q_z axis. Lamellar and π -stacking peak positions, peak widths, and peak areas (Figures A.12–A.14) were calculated by fitting a baseline function to the 1D integrated GIWAXS data to account for diffuse sample scattering, and then fitting each diffraction peak with a Voight function.

The crystalline coherence length (Figure A.15) was calculated from the peak width of the (100) diffraction peak for each sample using the Scherrer equation: $L_C = 2\pi K / \Delta q$,^{17–19} where, Δq is the full-width half-max (FWHM) of the (100) diffraction peak and K is the shape factor, which was approximated as 0.89, assuming quasi-spherical domains.¹⁹ Error bars in all plots come from the standard deviation of duplicate samples. The crystalline coherence length increased slightly upon the initial doping and was then roughly constant across higher doping

levels for RR-P3HT. Interestingly, the fractional domain size change was approximately the same as the fractional expansion of the lamellar structure, suggesting that changes in crystalline coherence length were dominated by simple changes in the lattice constant. The crystalline coherence length was observed to decrease with increasing doping level for RRa-P3HT. The decrease for RRa-P3HT can be correlated with the gradual process of dopant-induced crystallization, shown in Fig. 2.1 of Chapter 2. As the crystallinity increases with doping, new crystallites with variable size and degrees of order are created within the film.

Although the crystalline coherence length is dominated by the crystalline domain size, it also contains a component of paracrystalline disorder, which can further broaden the diffraction peaks. To quantify the percent of the peak broadening that stems from paracrystallinity, we looked at peak broadening across the lamellar overtones, using a linear fit of the FWHM of each overtone versus the overtone number squared. The slope of the linear fit is equivalent to $\pi^2 g^2 / d_{(100)}$, where $d_{(100)}$ is the lamellar spacing and g is the paracrystalline disorder.^{20,21} Figure A.16 indicates that the paracrystalline disorder drops slightly upon doping in RR-P3HT, and then remains constant with doping level for both RR- and RRa-P3HT, indicating that lattice disorder does not change significantly with doping level. Together, these results indicate that crystallite size and disorder should have little effect on the thermal conductivity across doping level. As a result, the observed changes can be ascribed to intrinsic doping-induced changes in thermal conductivity.

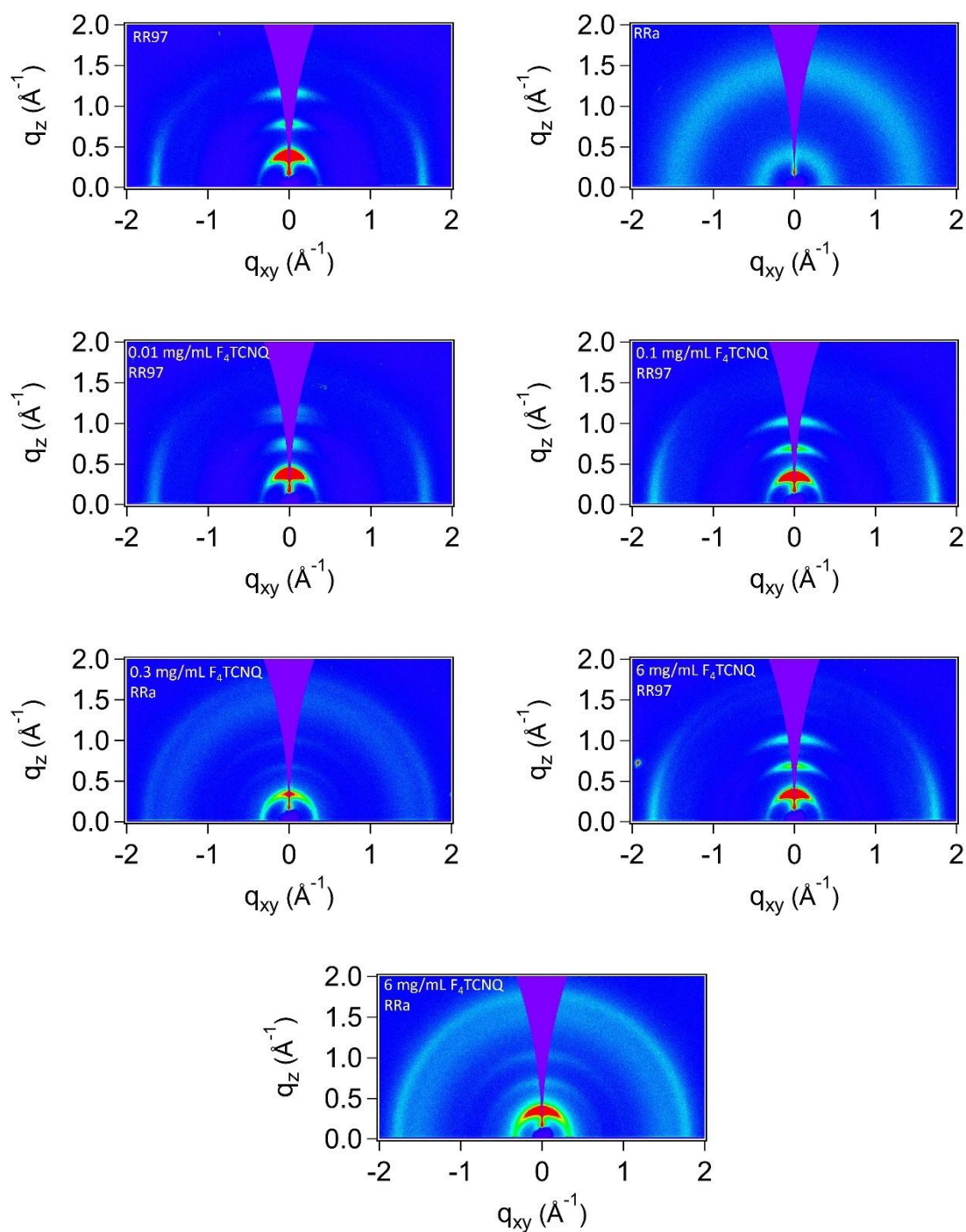


Figure A.11. 2D GIWAXS data for RR- and RRa-P3HT films. Data from undoped films is shown on the first line, followed by a selection of F₄TCNQ-doped samples. For all samples, both the polymer (RR- or RRa-P3HT) and the concentration of F₄TCNQ used for SqP doping are shown on the panel. It

is worth pointing out that the double peak pattern seen in the 0.01 mg mL^{-1} F₄TCNQ doped RR-P3HT sample shows the midpoint of the phase transition between the doped and undoped crystal structures.²²

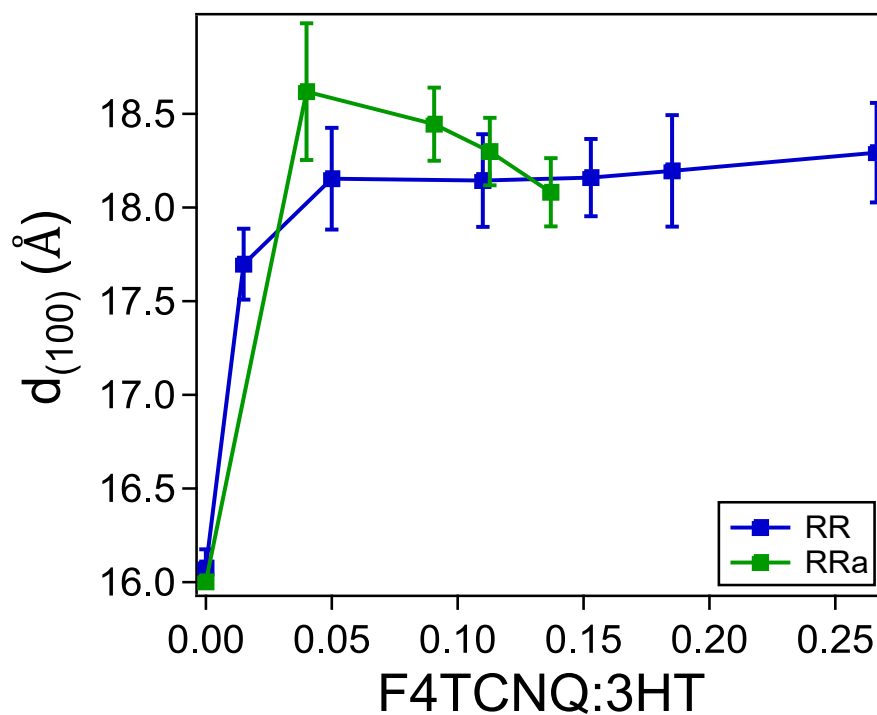


Figure A.12. Calculated lamellar spacings for doped P3HT films based on the average lattice constant obtained from the (100), (200), and (300) diffraction peaks. Error bars are the standard deviation of the lamellar spacings calculated from the three peaks.

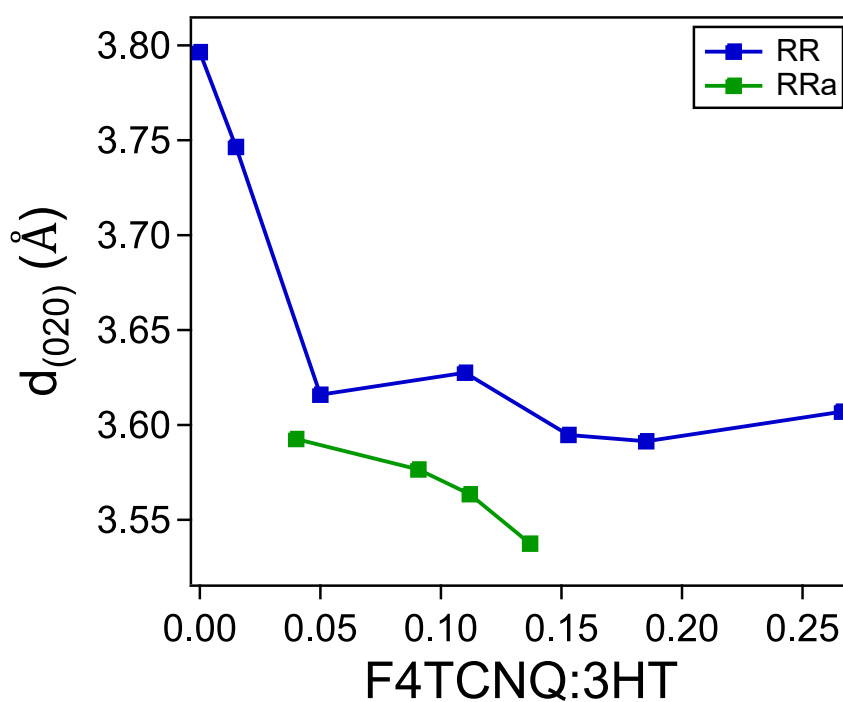


Figure A.13. Calculated π -stack distance based on the (020) peak position. No data is shown for undoped RRa-P3HT, as the (020) peak cannot be clearly observed in this sample due to the amorphous nature of undoped RRa-P3HT films.

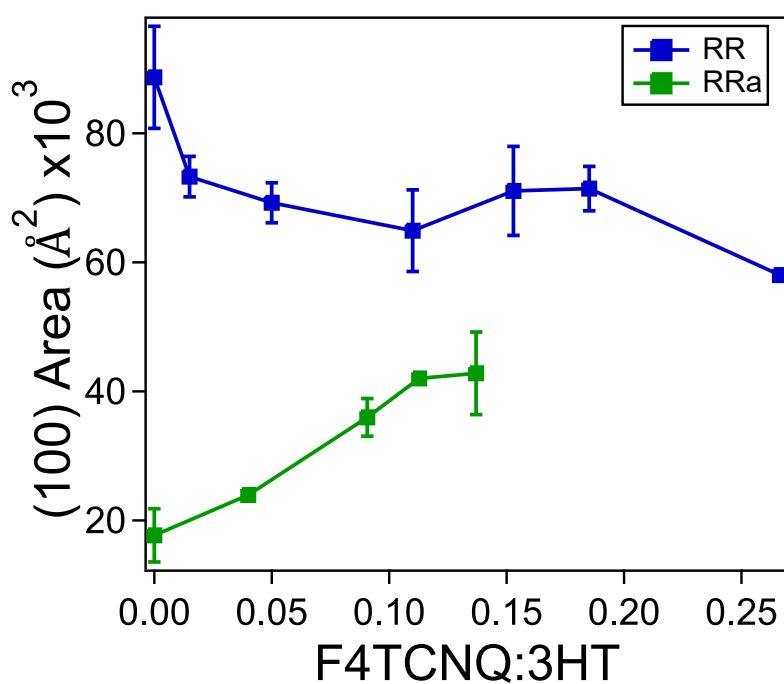


Figure A.14. Integrated (100) peak area as a function of F₄TCNQ:3HT mole ratio. The (100) area roughly correlates with the crystalline fraction in the polymer film. The (100) peak area marginally decreases upon doping in the initially highly crystalline RR-P3HT. In contrast, the area increases upon doping in the initially mostly amorphous RRa-P3HT due to doping induced crystallization.

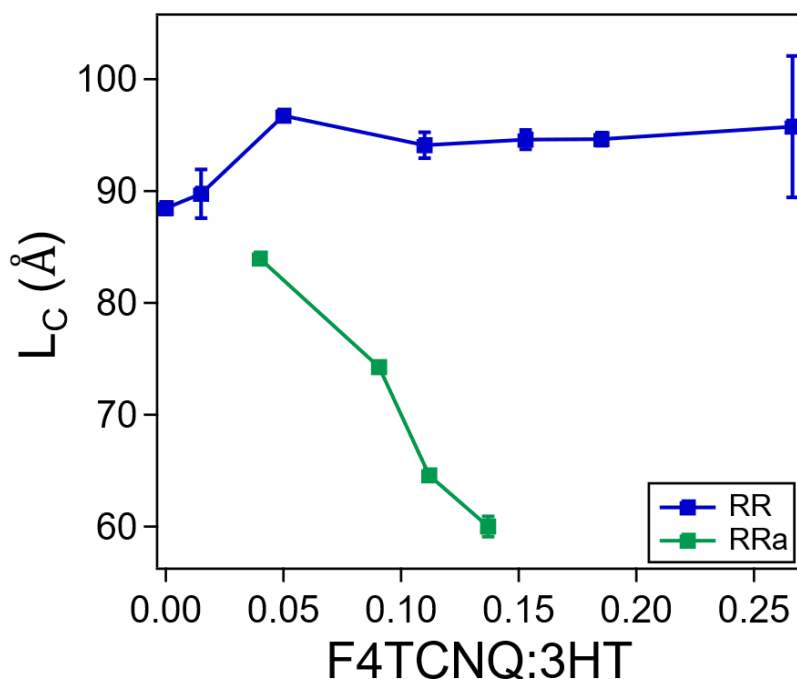


Figure A.15. Coherence length, L_c , as a function of F₄TCNQ:3HT mole ratio for doped RR- and RRa-P3HT films. Coherence length is roughly correlated to the crystalline domain size. Doping with F₄TCNQ increases the coherence length in RR-P3HT films, remaining elevated across doping regime. RRa-P3HT films see a decrease in coherence length as the extent of doping increases. RRa-P3HT does not have a pristine data point as its structure is fully amorphous in the undoped state.

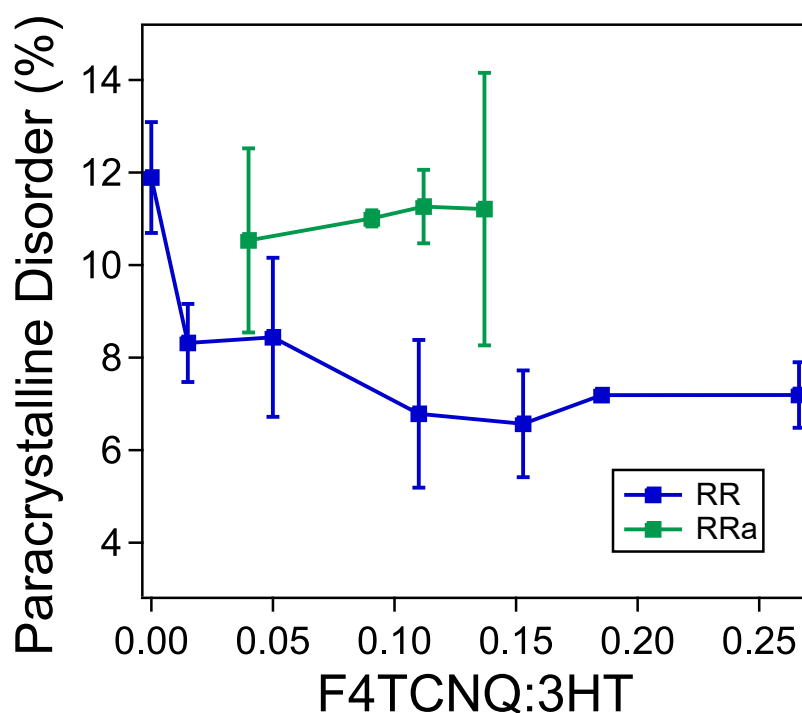


Figure A.16. Paracrystalline disorder percentage, which is inversely related to the degree of long-range crystalline order, as a function of F4TCNQ:3HT mole ratio. The paracrystalline disorder decreases upon doping RR-P3HT, which means that doping enhances long range crystalline order. After initial doping, the paracrystalline disorder is roughly constant for both P3HT systems. No data is shown for RRa-P3HT in the pristine state as the polymer film is too disordered to allow for calculation of paracrystalline disorder in the undoped state.

2.0 A review of C_v , cross-plane κ and zT results on F4TCNQ-doped P3HT samples in the literature

2.1 An analysis of literature assignments for ρ , C_p , and C_v for pristine and F4TCNQ-doped P3HT

Tables A.6–A.8, below, summarize the thermal properties of doped P3HT that have been presented to date in the literature. In general, most of the values do not agree with those presented in Chapter 2, largely because of different assumptions made for the values of ρ and C_p of P3HT films, which in turn affect the estimated values of C_v , which then affect the values

of κ extracted from thermal effusivity or diffusivity measurements. For example, many early studies^{23,24} that calculated C_v values for pristine RR-P3HT routinely referenced Erwin *et al.*'s²⁵ ρ value of 1.33 g cm^{-3} , a value notably higher than the 1.1 g cm^{-3} that is now standard in the literature (as well as our own measurements).^{8,26–28} A separate study implemented a value for ρ of 0.95 g cm^{-3} into C_v calculations.²⁹ Additional studies^{30,31} associated with measurements of κ have also chosen to parameterize both ρ and κ (α was measured while C_p was a cited, fixed value) to determine ‘effective’ C_v values that ranged between $1.5\text{--}2.6 \text{ J cm}^{-3} \text{ K}^{-1}$ for pristine RR-P3HT films and $0.82 \text{ J cm}^{-3} \text{ K}^{-1}$ for stretch-aligned films. We also note that the difference in C_p values between pristine RR- and RRa-P3HT has not been fully appreciated in the literature; for example, in assigning a C_p value for pristine RRa-P3HT (to be used in FDTR experiments), Rodríguez-Martínez *et al.*³² cited a value (from Ref. 33) that instead pertained to RR-P3HT.

Of the few C_v values in the literature assigned to F₄TCNQ-doped P3HT films, Plunkett *et al.*³⁴ and Kiefer *et al.*³⁵ both implied that C_v increases with doping compared to pristine films. However, Kiefer *et al.* did not report values for ρ , which they claimed to have measured, nor did they publish any numerical values for C_v . It is likely that the C_v values calculated by Kiefer *et al.* are higher for doped films due to their reported increase in C_p (F₄TCNQ-doped RR-P3HT was 12.8% higher than pristine polymer).³⁵ In turn, the C_v values reported by Plunkett *et al.*³⁴ rely on the C_p values reported by Kiefer *et al.* as well as the assumption in their density estimation that one F₄TCNQ molecule resides in every two P3HT unit cells at the doping level they investigated. For example, for high- M_w F₄TCNQ-doped RR-P3HT films, Plunkett *et al.* combined a calculated density, 1.51 g cm^{-3} , with Kiefer *et al.*'s measured C_p of $1.246 \text{ J g}^{-1} \text{ K}^{-1}$ to obtain a C_v of $1.88 \text{ J cm}^{-3} \text{ K}^{-1}$.³⁴ For low- M_w F₄TCNQ-doped RR-P3HT films, Plunkett *et al.* applied the C_p increase upon doping given by Kiefer *et al.* (12.8%) to the pristine C_p value

given in Ref. 36 ($1.42 \text{ J g}^{-1} \text{ K}^{-1}$, or $1.60 \text{ J g}^{-1} \text{ K}^{-1}$ after scaling to account for doping), which, when multiplied by an estimated density of 1.53 g cm^{-3} , yielded a C_v value of $2.45 \text{ J cm}^{-3} \text{ K}^{-1}$.³⁴ For F₄TCNQ-doped RRa-P3HT films, after scaling a separately referenced C_p value for pristine RRa-P3HT by the same 12.8% to account for doping, Plunkett *et al.* used an estimated density of 1.46 g cm^{-3} to yield a C_v value of $2.84 \text{ J cm}^{-3} \text{ K}^{-1}$.³⁴

Another potential issue with the literature discrepancy in C_v values for pristine and doped P3HT is that Kiefer *et al.*³⁵ took C_p measurements on P3HT samples that were cold-pressed into pellets. Their measured C_p for pristine RR-P3HT is quite low ($1.105 \text{ J g}^{-1} \text{ K}^{-1}$) compared to other values in the literature as well as those determined here for pristine RR-P3HT.³⁵ The lower C_p reported in Ref. 35 suggests that changes in how heat is stored, perhaps through changes in structure, might occur with the cold-pressing process. Our C_p measurements thus indicate that Kiefer *et al.*'s C_p results on cold-pressed samples should not be applied to cast P3HT films which are likely to have a different morphology.

2.2 An analysis of the values of κ for pristine P3HT reported in the literature

In regard to the wide range of measured values in the literature of the cross-plane κ of pristine P3HT discussed in Chapter 2, the numerous differences between studies that may have contributed to differences in κ include: 1) different assumptions (such as temperature and/or C_v) that are made with differing experimental methods to measure κ ; 2) differences between P3HT samples in different work (different degrees of regioregularity and/or molecular weight; 3) differing film processing methods (e.g. spin-coating, drop-casting, blade-coating, etc., in addition to thermal annealing); and, 4) different polymer casting solvents, which are known to impact the crystallinity of RR-P3HT films,^{37,38} can result in changes in thermal conductivity.

The influence of solvent used to make the polymer solution is nicely demonstrated in the work of Zhao *et al.*:³⁹ thermal conductivities of $0.05 \text{ W m}^{-1} \text{ K}^{-1}$ and $0.168 \text{ W m}^{-1} \text{ K}^{-1}$ were measured using the same RR-P3HT but with films cast from chloroform (CF) and chlorobenzene (CB), respectively. How various film processing conditions impact the κ of P3HT films has not been rigorously studied, although recent measurements on spin-cast and blade-coated P3HT films made from the same polymer yielded values that are roughly within error of each other.³² The impact on κ from the process of thermal annealing, which is known to increase P3HT crystallinity but decrease tie-chain intercrystallite connectivity,⁴⁰ also hasn't been systematically studied for P3HT (the few studies^{34,41,42} that implement thermal annealing also omitted testing non-annealed control films). However, studies on other conjugated polymer systems suggest that thermal annealing can change κ in an anisotropic way.^{43,44} For example, a study on dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT) showed that no change in cross-plane κ occurred following thermal annealing up to 140°C ,⁴³ whereas the in-plane κ increased following thermal annealing of films of poly[[1,2,3,6,7,8-hexahydro-2,7-bis(2-octyldodecyl)-1,3,6,8-dioxobenzo[lmn][3,8]phenanthroline-4,9-diyl][2,2'-bithiophene]-5,5'-diyl] (P(NDI2OD-T2)).⁴⁴

Concerning the influence of M_n or M_w on the κ of RR-P3HT, both Plunkett *et al.*³⁴ and Rodríguez-Martínez *et al.*³² reported increases in the cross-plane κ with increasing M_n or M_w , with both studies speculating that the increase in κ is the result of a higher degree of tie-chain intercrystallite connectivity. Conflictingly, however, Herrmann *et al.*⁴² effectively saw no increase in the κ of RR-P3HT across a large range of M_w tested. Even with the possible benefits to thermal transport that tie-chains may contribute to a high M_w polymer, Plunkett *et al.*'s³⁴ κ result ($0.83 \text{ W m}^{-1} \text{ K}^{-1}$) for pristine RR-P3HT remains notably higher than those reported in the rest of the literature, especially when compared to the values presented in Refs. 32, 42 and

this paper, which all utilized RR-P3HT with similar molecular weights and films cast using similar techniques and solvents. We note that Plunkett *et al.*'s unusually high κ value is likely not the result of a mistaken C_v value as only an overestimation of C_v would cause the κ to be overestimated, but the value of $1.22 \text{ J cm}^{-3} \text{ K}^{-1}$ assumed by these authors is lower than our measured C_v of $1.48 \text{ J cm}^{-3} \text{ K}^{-1}$. Thus, we believe that the main reason for the high value of κ in Ref. 34 is that these authors thermally annealed their P3HT films.

2.3 Comparing κ results on F₄TCNQ-doped P3HT in the literature to those presented in Chapter 2

When we display the κ values that Zhao *et al.*³⁹ measured for F₄TCNQ-doped RR-P3HT films as a function of F₄TCNQ:3HT mole ratio (their data was published as wt.% of dopant-to-polymer), the rise and fall in κ they report closely resembles the non-monotonic trend we observe, as shown in Figure A.17. However, it is apparent that the κ values reported in Ref. 39 are all lower than our results. The overall lower κ in Zhao *et al.*'s³⁹ experiments is likely due to a combination of their use of a lower regioregularity P3HT material (90% versus our 97.6%) and their use of the blend-doping method (as opposed to our use of the SqP-doping method). This is because the crystalline volume fraction of P3HT is known to decrease from 45% to 35% as the %RR decreases from 97% to 90%,⁴⁵ which is likely to lead to a reduction in overall κ . In addition, films doped via the SqP method tend to retain their pre-doped crystalline structures whereas blend-doping generates films with much lower crystallinity,¹ which may also contribute to lower values of κ . Based on our C_v measurements, we believe that Zhao *et al.*'s assumption that the C_v values of F₄TCNQ-doped RR-P3HT films are equal to that of pristine RR-P3HT is accurate across the F₄TCNQ:3HT ratios that they examined (see Figure 2.2c).

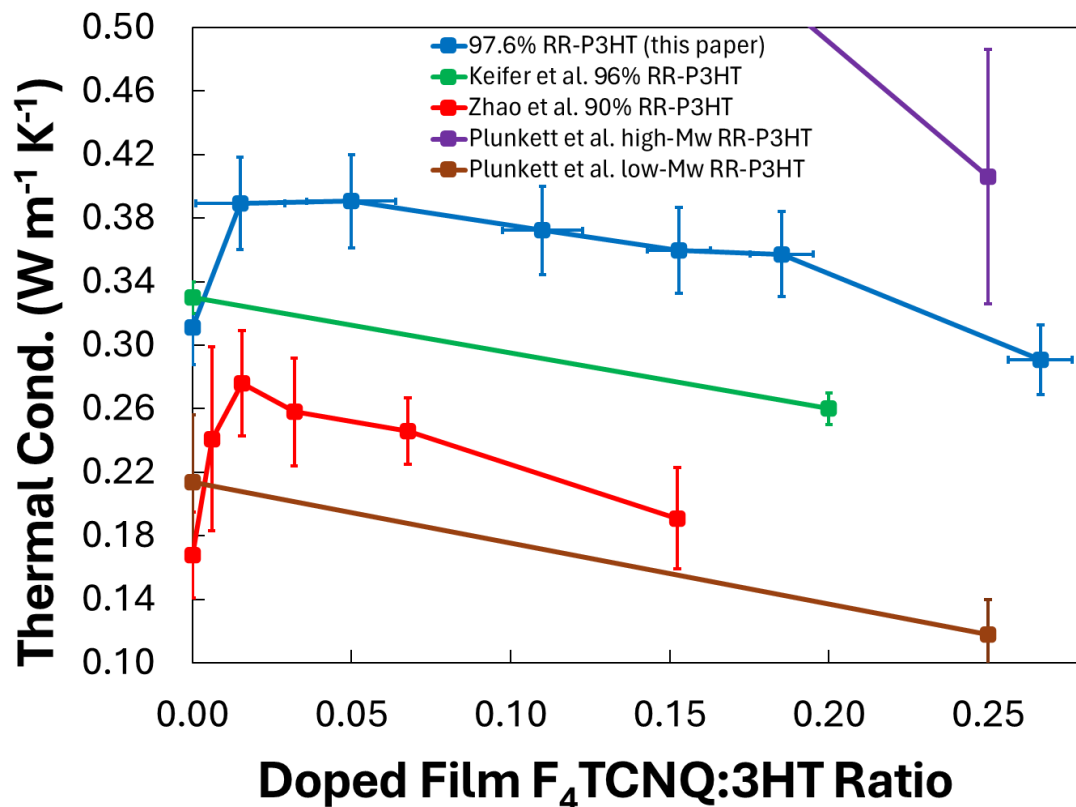


Figure A.17: Our thermal conductivity measurements on 97.6% RR-P3HT films doped via SqP with F₄TCNQ (blue) compared to Zhao *et al.*'s³⁹ 90% RR-P3HT films blend-doped with F₄TCNQ (in red), Keifer *et al.*'s³⁵ 96% RR-P3HT samples blend-doped with F₄TCNQ (in green), and Plunkett *et al.*'s³⁴ high-*M_w* (in purple) and low-*M_w* (in brown) RR-P3HT vapor-doped with F₄TCNQ, all plotted as a function of F₄TCNQ:3HT mole ratio. The increase in κ at low F₄TCNQ:3HT ratios is seen in our 97.6% RR-P3HT series and Zhao *et al.*'s 90% RR-P3HT series. A decrease in κ is then observed at higher F₄TCNQ:3HT ratios, now visible in data by Refs. 34 and 35, as well. Plunkett *et al.*'s measured κ value for pristine high-*M_w* RR-P3HT is off the y-axis (0.83 W m⁻¹ K⁻¹).³⁴ The absolute difference in values likely arises due to differences in the regioregularity of the P3HT, differences in film processing technique, and differing *C_v* assignments, although a clear non-monotonic change in κ occurs across the various doping regimes.

Takayama *et al.*⁴¹ saw κ increase upon doping RR-P3HT with F₄TCNQ at all SqP doping concentrations they tested except for one low-doping concentration point (see Table A.7). Both our data and that of Takayama *et al.* agree that a sharp increase in κ occurs at very low doping concentrations for RR-P3HT films, followed by a plateau through higher doping concentrations at an elevated κ value compared to undoped films. It is also encouraging that despite the fact that these authors measured κ using the 3ω method while we used TDTR, both of our studies report values for F₄TCNQ-doped RR-P3HT in the range of $0.3 \text{ W m}^{-1} \text{ K}^{-1}$ for films doped using SqP. We believe that Takayama *et al.* did not see a drop in κ at their highest doping concentration (10 mg mL^{-1}) because of their choice of MeCN as the doping solvent. As mentioned above, MeCN does not swell P3HT very well, making it harder to infiltrate F₄TCNQ to dope the films.⁴⁶ This means that the samples in Ref. 41 remained in the low-doping regime (as verified by the fact that the electrical conductivity of their most-doped film was only 3.0 S cm^{-1}).

Reports by Keifer *et al.*³⁵ and Plunkett *et al.*³⁴ argued that a decrease in κ occurs after heavily doping RR-P3HT with F₄TCNQ (Ref. 35 blend-doped using 20 mol% F₄TCNQ; Ref. 34 claimed to have doped to an estimated 0.25:1 F₄TCNQ:3HT mole ratio). Both results fall within the high ($\geq 0.2:1$) F₄TCNQ:3HT mole ratio doping regime, which is where we observed a reduction in κ . Despite differences in measurement technique and sample processing, both Keifer *et al.* and we agree that films doped to $\geq 0.2:1$ F₄TCNQ:3HT mole ratios have values for κ that are only slightly lower than pristine RR-P3HT films (see Table A.7 and Figure A.17 of Appendix A),³⁵ whereas Plunkett *et al.* reported a much more substantial (51%) decrease in κ after heavily doping.³⁴ However, if we modify Plunkett *et al.*'s κ result for heavily-F₄TCNQ-doped high- M_w RR-P3HT by using the C_v value based on our analytical function for C_v (at 0.25:1 F₄TCNQ:3HT mole ratio), we get a value of roughly $0.3 \text{ W m}^{-1} \text{ K}^{-1}$, in good agreement

with both our results and those in Ref. 35. The way we recalculated the κ value in Ref. 34 is as follows. First, we used Equation 2.2 to calculate Ref. 34's thermal diffusivity, obtaining a value of $0.215 \text{ mm}^2 \text{ s}^{-1}$. Then, we calculated C_v at 0.25:1 F₄TCNQ:3HT mole ratio to be $1.56 \text{ J cm}^{-3} \text{ K}^{-1}$ (Plunkett *et al.* used a C_v value of $1.88 \text{ J cm}^{-3} \text{ K}^{-1}$ to determine κ ,³⁴ which is 20% larger).³⁴ Thus, the recalculated κ with their thermal diffusivity and our C_v is $0.33 \text{ W m}^{-1} \text{ K}^{-1}$.

Plunkett *et al.* also witnessed a significant (33%) decrease in κ after doping RRa-P3HT to an estimated 0.25:1 F₄TCNQ:3HT mole ratio,³⁴ which is well within the doping regime that this paper suggests is negatively impacted by phonon scattering from intercalated F₄TCNQ. However, it should be noted that the κ value reported by Ref. 34 has some degree of error due to their highly inaccurate assumed C_v of $2.84 \text{ J cm}^{-3} \text{ K}^{-1}$, which is 77% larger than the value predicted by our analytical function for C_v . We also tried modifying Plunkett *et al.*'s κ result for F₄TCNQ-doped RRa-P3HT by first calculating their thermal diffusivity ($0.065 \text{ mm}^2 \text{ s}^{-1}$) and using the C_v predicted by our analytical function, $1.65 \text{ J cm}^{-3} \text{ K}^{-1}$ (at F₄TCNQ:3HT mole ratio of 0.25), to get $0.107 \text{ W m}^{-1} \text{ K}^{-1}$. Such a significant drop in κ may be due to Plunkett *et al.* reaching a much higher F₄TCNQ:3HT mole ratio through vapor-doping than we were able to achieve through SqP.

In summary, the doped P3HT thermal conductivity values reported by Zhao *et al.*,³⁹ Takayama *et al.*,⁴¹ and Keifer *et al.*³⁵ all agree with our finding of non-monotonic changes in thermal conductivity as P3HT is doped with increasing amounts of F₄TCNQ, as long as the literature data is properly viewed in the context of F₄TCNQ:3HT mole ratio. The numerical differences in the reported absolute thermal conductivity values between these previous studies and our measurements may be due to differences in P3HT type, film processing technique, and/or the value of C_v used to extract the thermal conductivity. In contrast, our results are not consistent with the data reported by Plunkett *et al.*,³⁴ which suggests that a significant (51%)

reduction in κ occurs upon heavily doping high- M_w P3HT; we note, however, that this reported drop is contingent on the accuracy of the authors' unusually high cross-plane κ reported for pristine RR-P3HT that is not in good agreement with the rest of the literature. The reported values of κ by Plunkett *et al.*'s³⁴ for highly doped high- M_w RR-P3HT film may be reconciled, however, if they are adjusted based on the value of C_v reported here, as the C_v value they choose is likely overestimated.^{35,41}

Table A.6: Literature cross-plane κ measurements on isotropic, non-aligned pristine P3HT

Polymer properties	Casting solvent	Film fab. methods	κ exp. method	C_p ($J g^{-1} K^{-1}$)	ρ ($g cm^{-3}$)	C_v ($J cm^{-3} K^{-1}$)	κ ($W m^{-1} K^{-1}$)	Ref.
??% RR (Sigma-Aldrich)	CF	Drop-casted	FA-FDTR (Nb)	1.2 (from lit.)	1.33 (from lit.)	1.60	0.17 ± 0.004	23
??% RR (Sigma-Aldrich)	CB	Spin-coated	TDTR (Al)	≈ 1.45 (from lit.)	1.33 (from lit.)	≈ 1.93	0.185 ± 0.011	24
94% RR; $M_n = 50-60 kg mol^{-1}$ (Reike Metals)	CB	Spin-coated	3ω	N/A	N/A	N/A	0.189 ± 0.023	47
??% RR (Sigma-Aldrich)	DCM	Drop-casted	TWA	1.6 (DSC measured)	1.3 (m/v measured)	2.0(8)	0.21	48
??% RR (Plextronics)	1:1 (v/v) CB:oDCB	Spin-coated	3ω	N/A	N/A	N/A	0.17 ± 0.026	49
??% RR	oDCB	Spin-coated	TDTR (Al)	N/A	N/A	1.5 (assumed by authors)	$0.32 \pm 0.02-0.04$	50
96% RR; $M_n = 29 kg mol^{-1}$	1:1 (v/v) CB:oDCB	Films drop-casted, pressed into pellets	Hot Disk/TPS	1.105 (DSC measured)	Value not in paper (m/v measured)	Unknown	0.33 ± 0.01	35
??% RR; $M_w = 44 kg mol^{-1}$ (Sigma-Aldrich)	CF	Drop-casted	TWA	1.32 (DSC measured)	1.10 (SFM measured)	1.45	0.158	51
??% RR; $M_w = 10.5 kg mol^{-1}$	CB	Spin-coated	3ω	1.53 (DSC measured)	0.95 (m/v measured)	1.45	0.27 ± 0.02	29
>90% RR; $M_w = 32.5 kg mol^{-1}$ (Sigma-Aldrich)	CB	Spin-coated, annealed 40 °C	PA	N/A	N/A	N/A	0.25	42
>90% RR; $M_w = 62.5 kg mol^{-1}$ (Sigma-Aldrich)				N/A	N/A	N/A	0.25	
>90% RR; $M_w = 92.5 kg mol^{-1}$ (Sigma-Aldrich)				N/A	N/A	N/A	0.23	
90% RR; $M_n = 26.5 kg mol^{-1}$ (Rieke Metals)	CB	Repeat drop-casted (>20)	Flash-DSC (In)	1.98 (DSC measured 156 °C)	1.03 (from lit. at 156 °C)	2.04	0.168 ± 0.027	39
	CF			Assumed to be 1.98 (above)	1.03 (from lit. at 156 °C)	2.04	0.05 ± 0.01	
??% RR; $M_w = 50-100 kg mol^{-1}$ (Sigma-Aldrich)	oDCB	Spin-coated, annealed 120 °C	3ω	N/A	N/A	N/A	0.20	41
RRa; $M_w = 60-95 kg mol^{-1}$ (Sigma-Aldrich)	CB	Blade-coated & spin-coated	3ω	N/A	N/A	N/A	Avg. = $0.50 \pm 0.02^{[a]}$	32
??% RR; $M_w = 20-45 kg mol^{-1}$ (Sigma-Aldrich)		Blade-coated & spin-coated					Avg. = $0.18 \pm 0.02^{[a]}$	
??% RR; $M_w = 100 kg mol^{-1}$ (Sigma-Aldrich)		Blade-coated					0.67 ± 0.04	
RRa; $M_n = 16.3 kg mol^{-1}$ (Sigma-Aldrich)	1:1 (v/v) CB/oDCB	Spin-coated, annealed 70 °C	TDTR (Al)	1.72 (from lit.)	1.08 (from lit.)	1.84	0.275 ± 0.053	34
??% RR; $M_n = 4.5 kg mol^{-1}$ (synthesized)				1.42 (from lit.)	1.11 (from lit.)	1.58	0.214 ± 0.042	
??% RR; $M_n = 23 kg mol^{-1}$ (Ossila)				1.105 (from lit.)	1.11 (from lit.)	1.22	0.830 ± 0.166	

^[a] Thermal conductivity values are an average of all listed film processing methods

Table A.7: Cross-plane thermal conductivity measurements on isotropic F₄TCNQ-doped P3HT samples presented in the literature

Polymer properties	Casting solvent	F ₄ TCNQ doping conc.	Film fab. methods	κ exp. method	C_p (J g ⁻¹ K ⁻¹)	ρ (g cm ⁻³)	C_v (J cm ⁻³ K ⁻¹)	κ (W m ⁻¹ K ⁻¹)	Ref.
96% RR; $M_n = 29$ kg mol ⁻¹	1:1 (v/v) CB:oD CB	20 mol%	Films blend-doped, drop-casted, pressed into pellets	Hot Disk/TPS	1.246 (DSC measur.)	Value not in paper (m/v measur.)	Unknown	0.26 ± 0.01	35
90% RR; $M_n = 26.5$ kg mol ⁻¹ (Rieke Metals)	CB	1% wt/P3HT	Films blend-doped, drop-casted	Flash-DSC	Authors assumed pristine 1.98 (DSC measur. 156 °C)	Authors assumed pristine 1.03 (from lit. at 156 °C)	Authors assumed pristine value 2.04	0.241 ± 0.058	39
		2.5% wt/P3HT						0.276 ± 0.033	
		5% wt/P3HT						0.258 ± 0.034	
		10% wt/P3HT						0.246 ± 0.021	
		20% wt/P3HT						0.191 ± 0.032	
??% RR; $M_w = 50$ - 100 kg mol ⁻¹ (Sigma-Aldrich)	oDCB (P3HT) ; MeCN (dopant)	0.01 mg mL ⁻¹	Films spun-cast, annealed 120 °C, doped SqP	3 ω	N/A	N/A	N/A	0.32	41
		0.1 mg mL ⁻¹						0.24	
		1 mg mL ⁻¹						0.33	
		10 mg mL ⁻¹						0.32	
RRa; $M_n = 16.3$ kg mol ⁻¹ (Sigma-Aldrich)	1:1 (v/v) CB/oD CB	vapor-doped	Films spun-cast, annealed 70 °C, vapor-doped	TDTR (Al)	1.94 (assumes 12.8% increase from 1.72 pristine)	1.46 (calc. assumes 1 dopant:2 unit cells)	2.84	0.188 ± 0.036	34
??% RR; $M_n = 4.5$ kg mol ⁻¹ (synthesize d)					1.60 (assumes 12.8% increase from 1.42 pristine)	1.53 (calc. assumes 1 dopant:2 unit cells)	2.45	0.118 ± 0.022	
??% RR; $M_n = 23$ kg mol ⁻¹ (Ossila)					1.246 (assumes 12.8% increase from 1.105)	1.51 (calc. assumes 1 dopant:2 unit cells)	1.88	0.406 ± 0.080	

Table A.8: Literature zT values for F4TCNQ-doped P3HT films using cross-plane κ values

Polymer	F4TCNQ doping	σ (S cm ⁻¹)	S (μ V K ⁻¹)	κ (W m ⁻¹ K ⁻¹)	zT	Ref.
90% RR; M_n = 26.5 kg mol ⁻¹ (Rieke Metals)	blend-doped 20% wt/P3HT	0.43	90.76	0.191	5.5×10^{-4}	39
96% RR; M_n = 29 kg mol ⁻¹	blend-doped 20% mol/P3HT, cold-pressed	0.07	110	0.26	1×10^{-4}	35
??% RR; M_n = 23 kg mol ⁻¹ (Ossila)	vapor-doped			0.406	$5.3 \times 10^{-3[a]}$	34
95% RR; M_n = 50 kg mol ⁻¹ (Merck)	vapor-doped	0.1	85			52

^[a] σ and S are not explicitly published for films made with only high- M_w RR-P3HT by Plunkett *et al.*³⁴ therefore, values from Lim *et al.*⁵² were used to calculate an approximate value for zT .

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APPENDIX B: Supporting Information for Chapter 3

1.0 Experimental methods

1.1 Materials

For all samples that used silicon as a substrate, we employed 1 mm-thick silicon wafers, cut to be $1.5 \times 1.5 \text{ cm}^2$ in area, sourced from University Wafer. The pre-polished silicon surface was cut along the (100) orientation. We used a 3-mm-thick, 25-mm-diameter sapphire optical window, the surface of which was cut along the *c*-plane or (0001) orientation, purchased from UQC Optics. For fused silica, we cut off and used one side of a 1-mm-thick spectroscopy-grade, IR-rated cuvette purchased from Thorlabs. For samples that had glass substrates, we sourced 1.2 mm-thick glass substrates, cut to be $1.5 \times 1.5 \text{ cm}^2$ in area, from VWR. We sourced the polystyrene (PS) ($M_n = 140,000 \text{ g mol}^{-1}$; $M_w = 230,000 \text{ g mol}^{-1}$) and poly(methyl methacrylate) (PMMA) ($M_w = 38,000 \text{ g mol}^{-1}$) from Sigma-Aldrich and *ortho*-dichlorobenzene (*o*-DCB), used to spin-coat the polymer films, from Fischer Scientific. We sourced the aluminum used for vapor deposition of the transducers from the Kurt J. Lesker Company.

1.2 Sample preparation

To prepare the silicon, sapphire and fused silica materials for fs-TTR experiments, we first cleaned the materials via serial sonicated washes using water with Alconox detergent, then deionized water, and finally acetone. We then dried the materials with nitrogen gas and prepared the surface for Al vapor deposition by plasma-etching for 60 minutes. The substrates we used to fabricate polymer thin-films of PS and PMMA, which were silicon and glass, underwent the same cleaning procedure described above. To make polymer thin-films of PS and PMMA, we first dissolved the polymer, used as received from the vendor, in *o*-DCB at a

concentration of 2% wt/volume (20 mg mL⁻¹). Using a spin-coater, we spin-cast the polymer solutions in a N₂ atmosphere at 1000 rpm for 60 s, then at 3000 rpm for 5 s. We then placed the thin-film polymer samples, along with the cleaned silicon, sapphire and fused silica substrate materials, into an Angstrom Engineering Nexdep thermal evaporator. We vapor-deposited a total of 100 nm of aluminum under high vacuum ($< 1 \times 10^{-6}$ torr) at a deposition rate of 0.5 Å s⁻¹. We confirmed the thicknesses of the polymer films and aluminum transducers using a Veeco Dektak 150 stylus profilometer (± 2 nm resolution) on sacrificial glass or silicon substrate samples. We took sample thicknesses on at least nine different sections of the film to ensure that the polymer and deposited transducer films were both uniform. Surface scans with the profilometer showed no unusual surface roughness texture outside of the error of the profilometer, which suggests that the surface of the pre-cast polymer films and the deposited transducers were smooth on a nm scale.

1.3 Chirped Pulse-Amplified (CPA) Ultrafast Laser System

The pump/probe ultrafast amplified laser system we utilized to perform fs-TTR in Chapter 3 is depicted in Figure 3.6 of that chapter. Our laser system is a Spectra Physics Solstice Ace that produces ~ 3 mJ pulses of ~ 40 fs duration at 800 nm with a 2 kHz repetition rate. The pulsed beam generated by the Solstice Ace is split to generate the pump and probe beams, respectively. The pump beam is sent down a certain distance of the table to match the length travelled by the probe beam and, along the way, is sent through an optical chopper that is synchronized to the output of the Solstice to precisely chop half the pulses to yield the most accurate measurement of ΔR . The probe beam, which starts out comprised of 5% of the pre-split beam, is sent through a variable delay stage from Newport Corporation that is 0.457 m in

length with a silver corner cube retroreflector. The delay stage is configured in a double-pass geometry, allowing for up to 3200 ps time delay. The probe beam is then passed through a $\frac{1}{2}$ waveplate and so that its polarization is set to the magic angle of 54.7° relative to the pump beam before being focused through a sapphire window to generate a white light continuum from 450 nm to 1300 nm. The white light continuum is then reflected and focused using a curved protected silver mirror onto the sample. For our choice of aluminum transducers, we used an 850 nm long-pass filter to select the desired NIR wavelength range to serve as the probe. The reflected probe beam was then directed into a focusing lens to focus into a fiberoptic cable that led to the multiwavelength diode array detector. Detection was performed using a Helios (Ultrafast Systems) transient absorption spectrometer and software suite.

2.0 Experimental characterization of pump & probe beams

2.1 Pump/Probe Beam Radii Characterization Under Best Performance

To measure the beam diameters of the pump and probe spots, we employed the razor-edge technique to block the beam at controlled step sizes and measured the resulting change in the transmitted beam intensity. The pump beam power (in mW as measured on a power meter) and the probe beam's signal (in mV as detected on a photodiode) were measured as a function of the blade position, as shown below in Figures B.1 and B.2, respectively. Since the beam profiles are Gaussian, we fit error functions to the resulting power curves to determine the beam radii. The functions used are shown in Eqs. B.1 and B.2:

$$P(x) = a \left(1 + \operatorname{erf} \left(\frac{x - x_0}{\sigma\sqrt{2}} \right) \right), \quad (B.1)$$

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt, \quad (B.2)$$

where x represents the position of the knife edge, x_0 represents the initial position of the knife edge, α is the amplitude scaling factor, and σ represents the beam radius. For the 70.5:1 spot area ratio (or 8.4:1 diameter ratio), the pump and probe beams had radii of 1476 μm and 176 μm , respectively. These pump and probe radii thus correspond to beam areas of 6.85 mm^2 and 0.0971 mm^2 , respectively. These pump/probe spot sizes are visually represented in Figures B.3 and B.4 as normalized gaussian profiles derived from our knife-edge radii measurements.

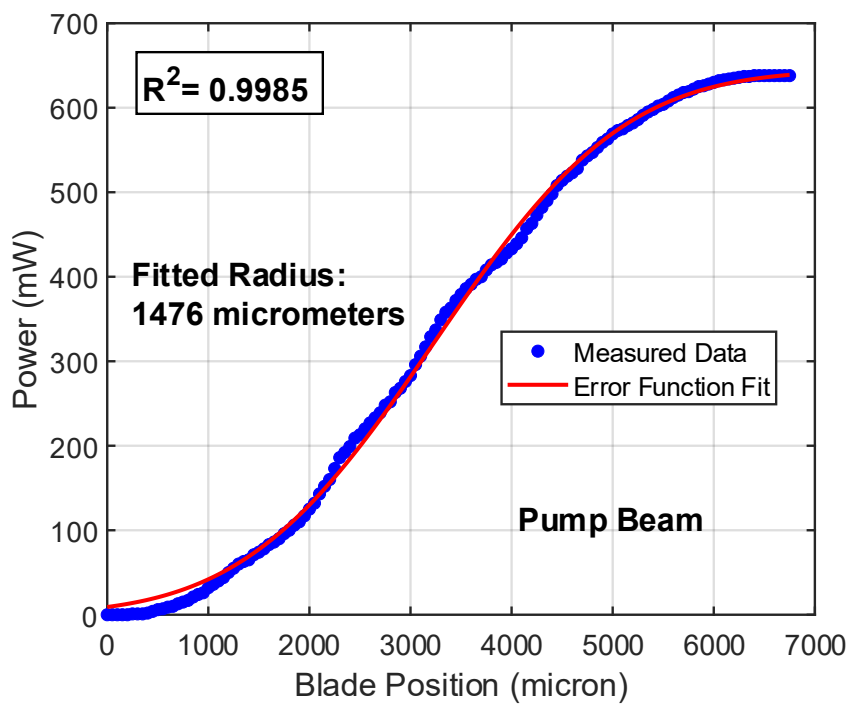


Figure B.1. Measurement of the spot size of the pump beam at the ideal radius for fs-TTR measurements. The blue dots represent the power, measured with a commercial power meter, as a function of the knife-edge position. The knife edge was placed at the same position on the laser table as the sample.

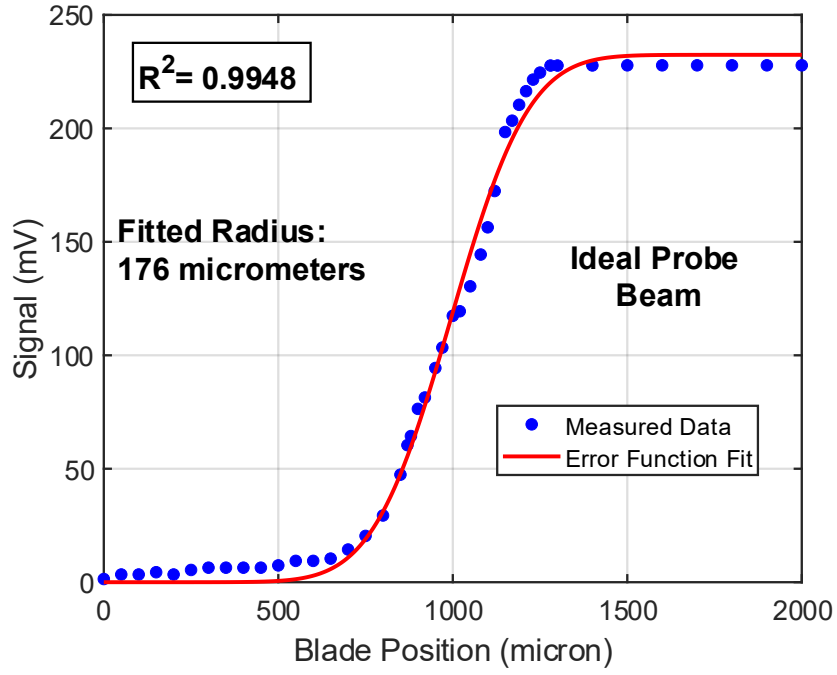


Figure B.2. Measurement of the spot size of the white light probe beam at the ideal radius for fs-TTR measurements. The blue dots represent the signal, measured with a Si photodiode (as the intensity was too low to be measured by a power meter), as a function of the knife-edge position.

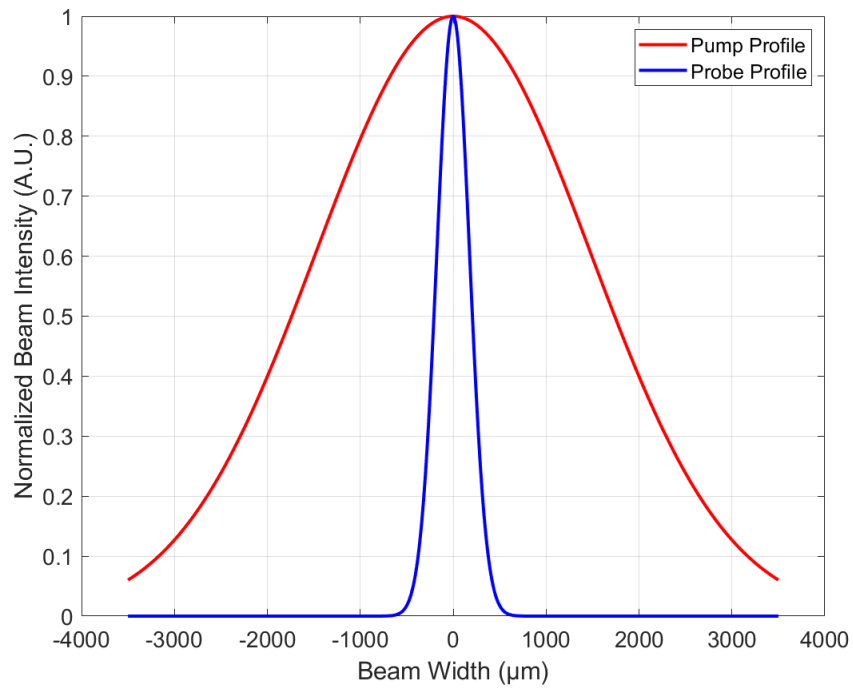


Figure B.3. 1-D representation of the normalized beam intensity of the 70.5:1 ‘ideal’ pump and probe beam area ratio showing the much larger size of the pump beam.

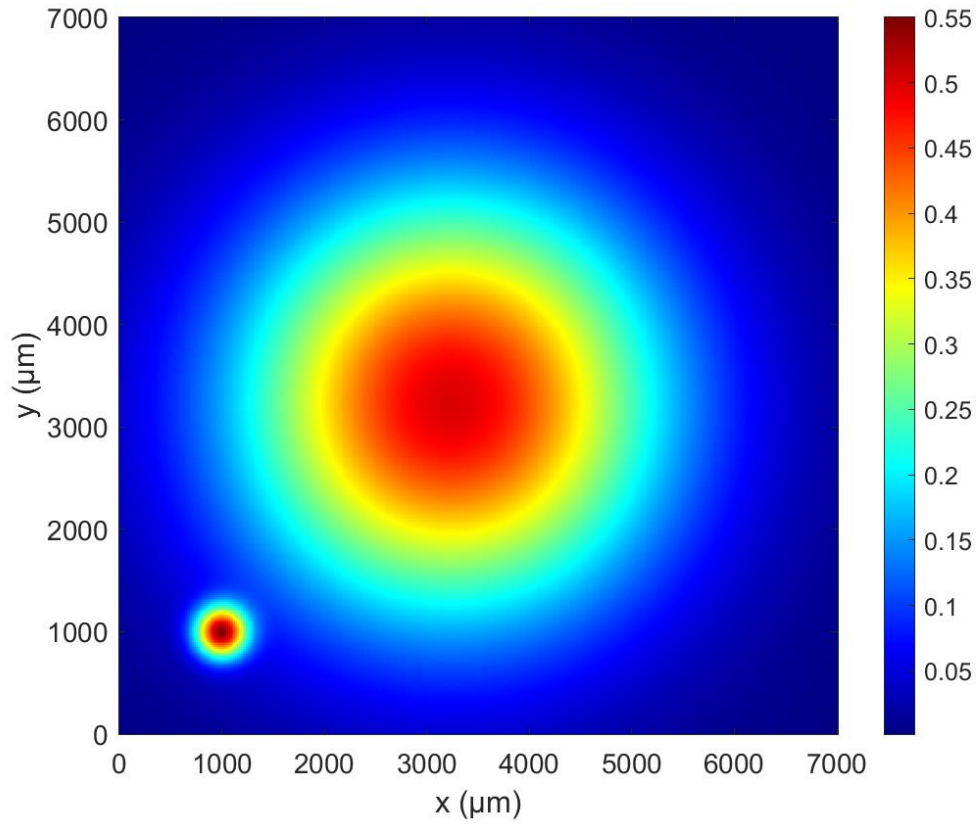


Figure B.4. 2-D heatmap representation of the normalized beam intensity of the pump beam (large circle) and probe beam (small circle) showing the large contrast in the areas of the pump and probe beams.

2.2 Beam Radii Characterization at 1-D Heat Diffusion Spot Size Ratio Breakdown

Our thermal model relies on the pump/probe spot size ratio to be sufficiently large to achieve 1-D vertical heat diffusion through the z -axis. As discussed in Section 3.5 of Chapter 3, a pump/probe spot size ratio of $\sim 70.5:1$ was determined to provide the best fs-TTR performance for our set-up. Here, we discuss how we determined the spot size ratio required

to keep the thermal response of the probe compatible with the 1-D thermal model. We did this by decreasing the pump/probe spot size ratio (making the pump and probe spot sizes closer in size) until the 1-D fs-TTR model could no longer accurately fit the κ_{zz}^{sam} of a control material.

We found that the breakdown point occurred at a pump/probe spot area ratio of 6.4:1 (or 2.5:1 diameter ratio). After increasing the size of the probe to 584 μm in radius or 0.342 mm^2 , as determined by the razor-edge experiment shown in Fig. B.5, the measured fs-TTR decay no longer accurately represented the control sample. As discussed and shown in Section 3.5 and Fig. 3.7 of Chapter 3, our Al/PMMA/Si sample yielded fitted values for κ_{zz}^{sam} and σ of 60.6 $\text{W m}^{-1} \text{K}^{-1}$ and 20 $\text{MW m}^{-2} \text{K}^{-1}$, respectively, at the 6.4:1 spot area ratio, which is an overestimation in κ_{zz}^{sam} by over two orders of magnitude.¹ The breakdown in the 1-D thermal model occurred because the probe was large enough to sample the thermal gradient of the Gaussian profile of the pump pulse.

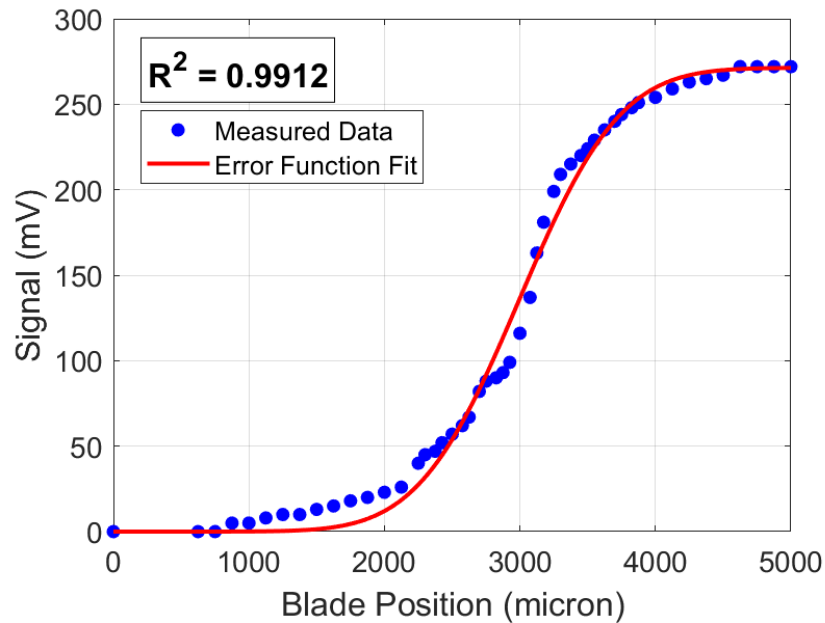


Figure B.5. Measurement of the spot size of the probe beam at the pump/probe spot area ratio breakdown of 6.4:1, performed in the same way as in Fig. B.2.

2.3 Optimizing the Pump/Probe Area Ratio via a Probe Spatial Averaging Error Model

Here, we derive the model presented as Eq. 3.15 in Section 3.5 of Chapter 3. We describe the heat energy deposited by the pump at the surface of the sample, centered radially at $r = 0$, with the following Gaussian intensity profile:

$$Q(r) \propto \exp\left(\frac{-2r^2}{r_{\text{pump}}^2}\right), \quad (\text{B.3})$$

where Q is heat and r_{pump} is the $1/e^2$ radius of the pump beam. Over time, heat diffuses laterally with a profile that remains Gaussian. This heat equation in cylindrical coordinates has the following Gaussian solution:²

$$T(r, t) \propto \frac{1}{r_{\text{pump}}^2 + 8\alpha t} \exp\left(\frac{-2r^2}{r_{\text{pump}}^2 + 8\alpha t}\right), \quad (\text{B.4})$$

there T is the temperature of the surface, t is probe delay time, and α is the thermal diffusivity of the surface material. We model the probe beam as also having the following Gaussian profile:

$$I_{\text{probe}}(r) \propto \exp\left(\frac{-2r^2}{r_{\text{probe}}^2}\right), \quad (\text{B.5})$$

where I_{probe} is the probe intensity and r_{probe} is the $1/e^2$ radius of the probe beam. We define the signal, ΔR , as being proportional to the probe-intensity-weighted average of ΔT across the surface:

$$\Delta R(t) \propto \int_0^\infty I_{\text{probe}}(r) \cdot T(r, t) \cdot r \, dr. \quad (\text{B.6})$$

After substituting Eq. B.4 and Eq. B.5 into Eq. B.6 and simplifying, the result is:

$$\Delta R(t) \propto \frac{1}{r_{\text{pump}}^2 + r_{\text{probe}}^2 + 8\alpha t}. \quad (\text{B.7})$$

Our 1-D thermal model assumes that the probe is only sensitive to vertical heat diffusion. This assumption only holds if the probe beam is sufficiently small compared to the pump beam and if the probe beam is spatially overlapped only with the flat peak of the Gaussian profile of the pump beam. Conversely, the 1-D thermal model breaks down if the probe beam is too large with respect to the pump because the probe now samples the lateral temperature gradient of the pump, which introduces a spatial averaging error that the 1-D model doesn't account for. The 1-D thermal model also breaks down if the probe becomes sensitive to lateral heat diffusion on the timescale of the probe delay, t .

Eq. B.8 below can be used as a rudimentary, quantitative way to calculate the probe spatial averaging error fraction, y :

$$y = \frac{r_{\text{probe}}^2}{r_{\text{pump}}^2 + r_{\text{probe}}^2 + 8\alpha t_{\text{max}}}, \quad (\text{B.8})$$

where t_{max} is the selected maximum probe delay time in a fs-TTR experiment. We note that with the use of a pump diameter of 2952 μm (this is pump size we use in Chapter 3 to perform fs-TTR on the samples), $8\alpha t \ll r_{\text{pump}}^2$ and lateral heat diffusion does not contribute any influence on y when $t_{\text{max}} = 3 \text{ ns}$ and $\alpha = 0.1\text{--}100 \text{ mm}^2 \text{ s}^{-1}$. Therefore, the probe spatial averaging error fraction, y , is entirely dependent on the pump/probe diameter ratio, as shown in Figure B.6. The term $8\alpha t_{\text{max}}$ only begins to influence the value of y (if $t_{\text{max}} = 3 \text{ ns}$ and $\alpha = 0.1\text{--}100 \text{ mm}^2 \text{ s}^{-1}$) when r_{pump}^2 is $< 10 \mu\text{m}$, which is a typical pump beam size in conventional oscillator-type TDTR.

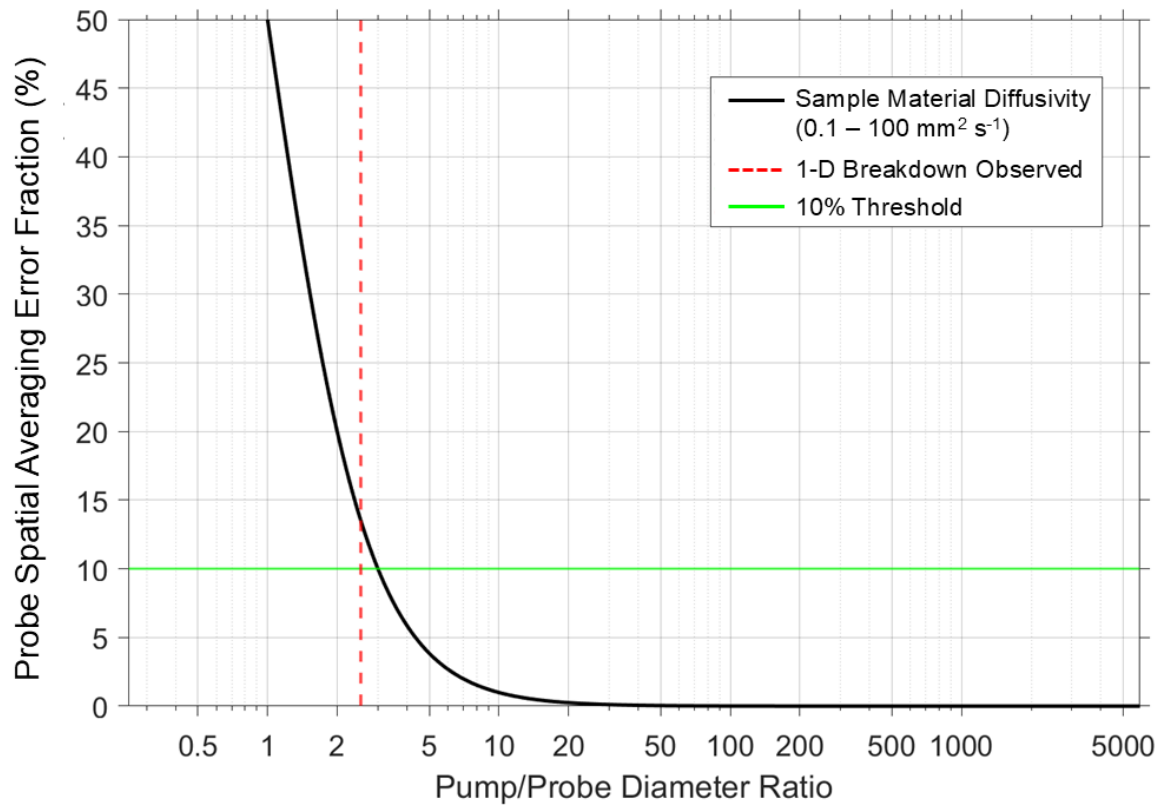


Figure B.6. Probe spatial averaging error fraction, y , plotted as a function of pump/probe diameter ratio. For the 1-D vertical heat diffusion model to work as intended, the probe beam must be sufficiently small with respect to the pump beam and the probe must be focused on the flat portion of the top of the Gaussian profile of the pump beam. If the probe beam is too large, the probe samples the temperature gradient along the edges of the Gaussian profile. This introduces a probe spatial averaging error that, if too large, breaks the 1-D thermal model. The probe spatial averaging error fraction grows to 10% at pump/probe diameter ratios of about 3:1. We experimentally observe a breakdown in the 1-D thermal model with the use of a pump/probe diameter ratio of 2.5:1. In this figure, the pump diameter is fixed at 2952 μm , which is the pump diameter implemented in Chapter 3 (unless otherwise noted). The black curve is calculated with a probe delay time of 3 ns, which is the maximum probe delay time implemented in Chapter 3.

2.4 Measuring the fs-TTR Signal as a Function of Pump Power

We measured the change in the fs-TTR signal at 1.2 ns as a function of pump power to show that the amplitude of the signal was in the linear response regime. Neutral density filters were used to control the power of the pump. As shown in Figure B.7, the fs-TTR signal is indeed highly linear with pump power, as expected. The optimal pump power is one that is maximized within the linear region without causing heat and/or ablation damage to the transducer or the rest of the sample. In the case of our amplified system, 710 mW average power, which is at the upper end of capabilities of our system, yielded the best SNR without causing sample damage. Since the linear response regime may be laser system-dependent, it is critical to independently quantify the usable pump power range by reproducing Figure B.7 before fs-TTR experiments are performed.

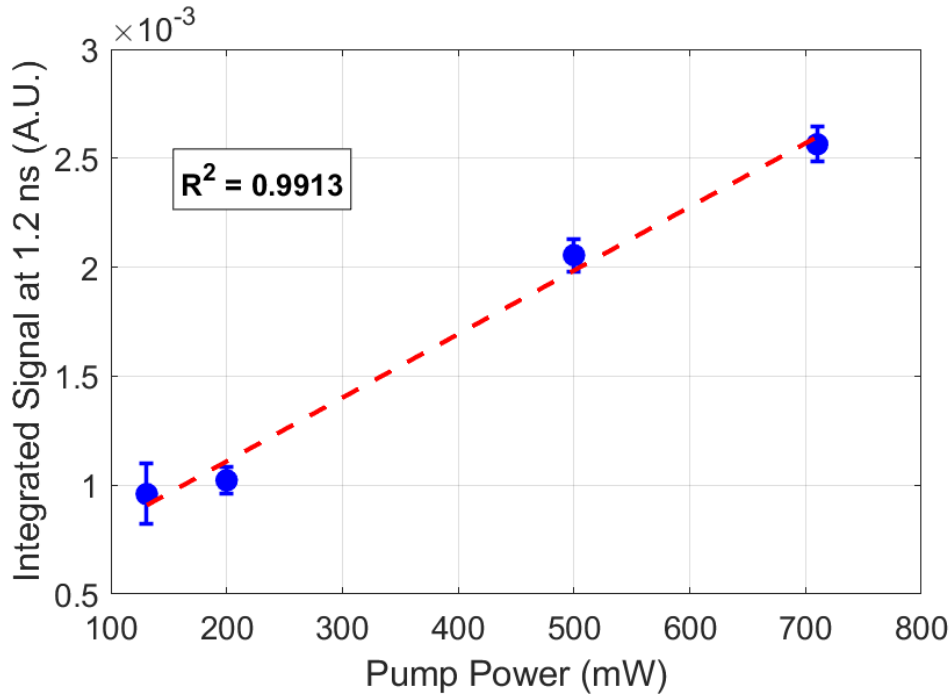


Figure B.7. Integrated spectral fs-TTR signal at the same 1.2 ns time delay for an Al/PMMA/Si sample at four different power levels. The pump power was controlled using neutral density filters. The

amplitude of the integrated signal scales linearly with pump power. Error bars were generated by calculating the standard deviation of the integrated areas for each of the 10 scans taken at each point.

We should note that it is possible to damage samples if the peak power density per pump pulse is too high. For the samples we studied in Figure 3.5 of Chapter 3, we performed fs-TTR with a 710 mW average pump power, which converts to a peak power density of 273 GW cm^{-2} (assuming a Gaussian temporal pulse). Although this peak power density did not damage any of the control samples, we observed that an Al/PS/glass tri-layer sample was irreversibly damaged at a slightly higher peak power of 358 GW cm^{-2} . Each sample has a different damage threshold, depending on the material composition, so damage thresholds should be investigated before running fs-TTR experiments to determine κ_{zz}^{sam} and σ .

2.5 Checking t_0 to Verify Samples Reach Thermal Equilibrium Before Next Pump Pulse

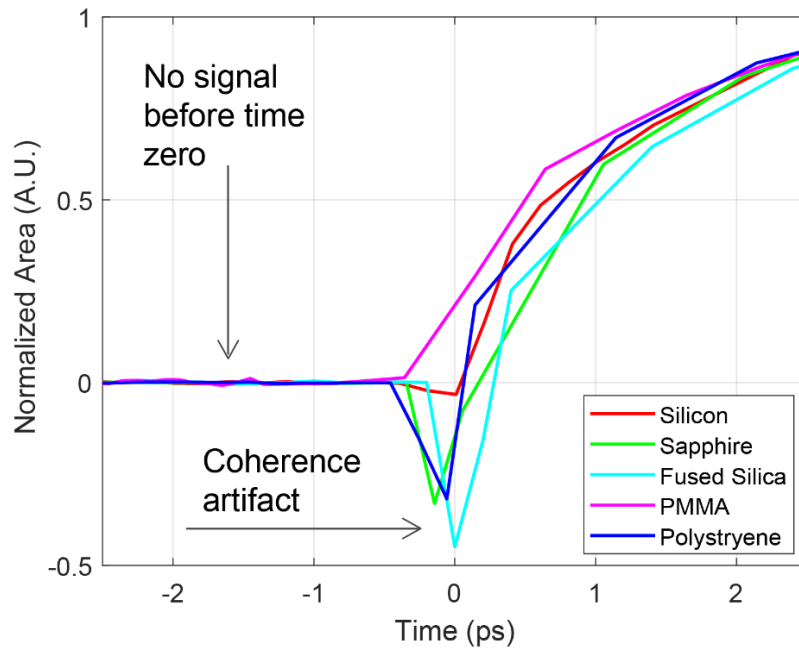


Figure S8. After time-zero (t_0), the fact that the pump pulse was absorbed by the metal transducer to induce heating is detected as a positive change in thermorefectance. Before time-zero, no signal is

detected as the transducer is at thermal equilibrium with the ambient environment. The lack of signal before time-zero in all sample materials is proof that the heat delivered by the prior pump pulse fully dissipated before the next pump pulse. A short-time coherence artifact that occurs only during the pump/probe temporal overlap is apparent in some of the traces. In this dataset, the PMMA and PS thin films were spin-cast onto Si substrates.

3.0 Obtaining fs-TTR Data & Optimization of Fitting the Thermal Model to Data

3.1 Data Acquisition Workflow & Selection of Spectral Region for Model Fitting

Here, we describe how we measure fs-TTR signals and how we chose the wavelengths of probe light that comprised the signal. After the pump pulse deposits heat onto the transducer, a probe pulse is sent to the transducer surface at a controlled time delay via a mechanical delay stage, as shown in Fig. 3.6 of Chapter 3. With an amplified laser transient absorption system, it is common practice to create a white light continuum and detect it dispersed with a grating onto a photodiode array to collect data over a wide spectral range on every laser shot. The sample transducer doubles as a mirror that directs the probe light into the detector.

The fs-TTR data we collect is a matrix with rows running over wavelengths and columns corresponding to different time slices. For each of the samples in this study, a minimum of 30 scans of the delay stage were taken with 1 second (consisting of 1000 shots) averaging intervals. The individual scans were averaged together to make one averaged data matrix. Spectra taken before t_0 were used to subtract background noise from all time slices. These pre- t_0 scans were also used to ensure the transient signal had fully recovered by the next pulse, as described above. We also corrected for the chirp in the probe beam, as standard for transient absorption, although we note that the chirp is not significant at NIR probe wavelengths on the time scales probed in fs-TTR. As stated in Section 3.4 of Chapter 3 and described below, we chose to only average the fs-TTR dynamics over the wavelength region from 900 nm to

915 nm, despite the fact that our system is capable of recording spectral data across a wavelength range of 800–1200 nm. Thus, while ultrafast oscillator systems achieve high SNR due to the large number of shots that are averaged at each time delay, amplified systems can achieve comparable SNR by both averaging a select wavelength range and simply taking more time to acquire more scans. Fs-TTR traces, with data across the full probe delay window of 1 ps to 3 ns, of all five control samples shown in Figure 3.5 of Ch. 3 are shown in Figure B.9.

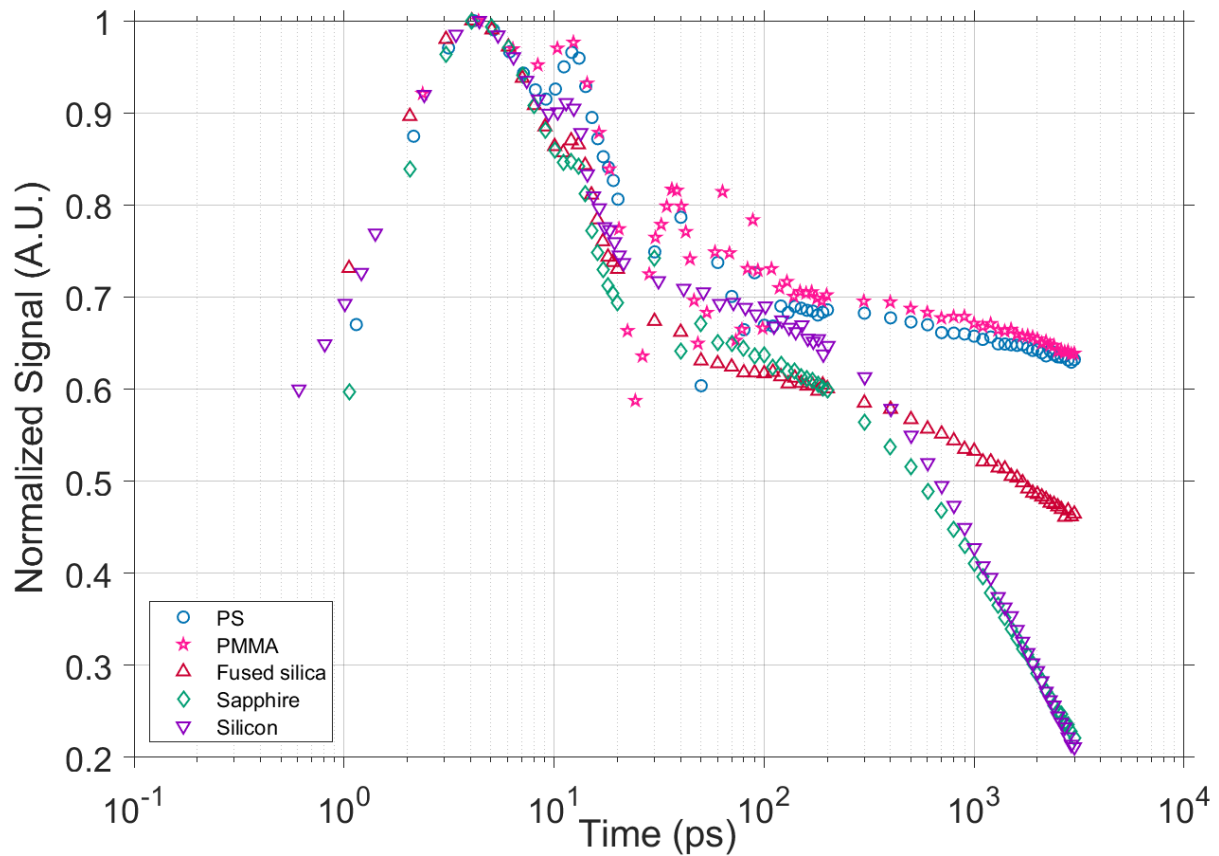


Figure B.9. Processed, uncropped fs-TTR traces from 1 ps to 3 ns of samples presented in Figure 3.5 of Chapter 3. Al/PS/Si is marked as a blue circle, Al/PMMA/Si is marked as a pink star, Al/SiO₂ is marked as a red triangle, Al/Al₂O₃ (sapphire) is marked as a green diamond, and Al/Si is marked as a purple inverted triangle. All traces were spectrally averaged across the selected 900–915 nm probe wavelength range to maximize SNR.

We selected the wavelength range of 900–915 nm to spectrally integrate as it yielded fs-TTR decays with the highest SNR compared to any other wavelength range or any single wavelength, as shown in Figs. B.10 and B.11. Since the transducer we chose was comprised of aluminum, this relatively narrow spectral region showed near-identical fs-TTR decay dynamics.³ The white light probe provides the ability to average over many independent single-wavelength fs-TTR decay traces to help improve SNR without any modification of the thermal model if the thermorefectance coefficient of Al remains the same within the selected wavelength range. The optimal wavelength window must be determined empirically for each laser system-transducer metal combination. It's also important to consider whether non-negligible wavelength-dependent spatial chirp and/or focus is present within the selected probe wavelength range as these could artificially alter the fs-TTR decay.

We should note that since the thermorefectance coefficient of metals may change as a function of wavelength, integrating across a wavelength range with variable thermorefectance coefficient will also distort the fs-TTR decay dynamics. In the case of aluminum, the reflectance steadily increases with wavelength across the NIR region; from 900–925 nm, the reflectance change is 1.7%.³ Using linear interpolation, the reflectance change across the wavelength range we selected for fs-TTR experiments in Chapter 3 (900–915 nm) is approximately 1%. The validation of our control experiments in Section 3.4 of Chapter 3 shows that a change of only 1% in reflectivity is well approximated by a constant reflectivity value.

In the context of our laser system, the white light continuum generated is weaker at redder wavelengths. Since the fs-TTR signals are typically around $\sim 2 \Delta \text{mOD}$ at maximum signal, even at pump fluences of $\sim 10 \text{ J m}^{-2}$, the lack of detectable light at redder wavelengths contributes additional noise if we average these redder wavelengths into the spectrally-

integrated fs-TTR signal, lowering the overall SNR. We did not use wavelengths below 900 nm because of spectral interference from the scattered 800-nm pump light.

Figs. B.10 and B.11 show that spectrally integrating the 900–915 nm probe region for both low and high thermal conductivity samples resulted in the most accurate fitting results for κ_{zz}^{sam} and σ as well as the highest SNR compared to using any single wavelength or using a different wavelength range. We note that in Figs. B.10 and B.11, using the redder probe wavelengths resulted in fitted values for κ_{zz}^{sam} and σ that are overestimated, likely because there were a greater number of noisy data points skewed in the direction of a faster signal decay. This is likely specific to our laser system and will differ for other laser/detector systems combinations.

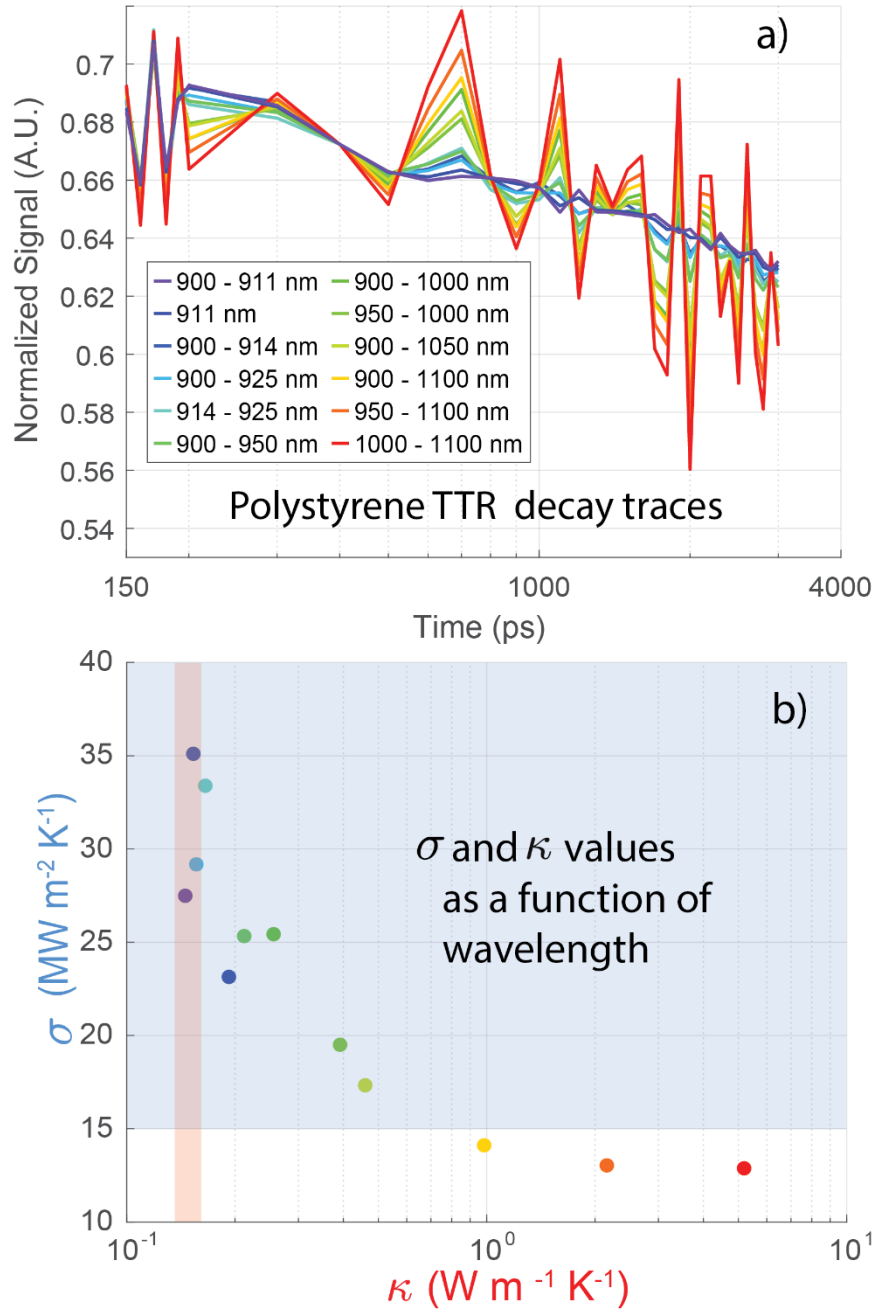


Figure B.10. a) Overlay of fs-TTR decay traces for an Al/PS/Si sample for a variety of selected integrated wavelength ranges. Although the decay for each wavelength range is roughly the same, the noise is accentuated at redder wavelengths due to the properties of the white light continuum. b) Fitted values for both σ (y-axis) and κ_{zz}^{sam} (x-axis) for each wavelength integration range, matched by color to the traces in (a). The blue highlighted region corresponds to accepted σ values for the interface Al/PS

while the red highlighted region corresponds to accepted κ_{zz}^{sam} values for PS (see Table 3.1 in Chapter 3 for literature references).

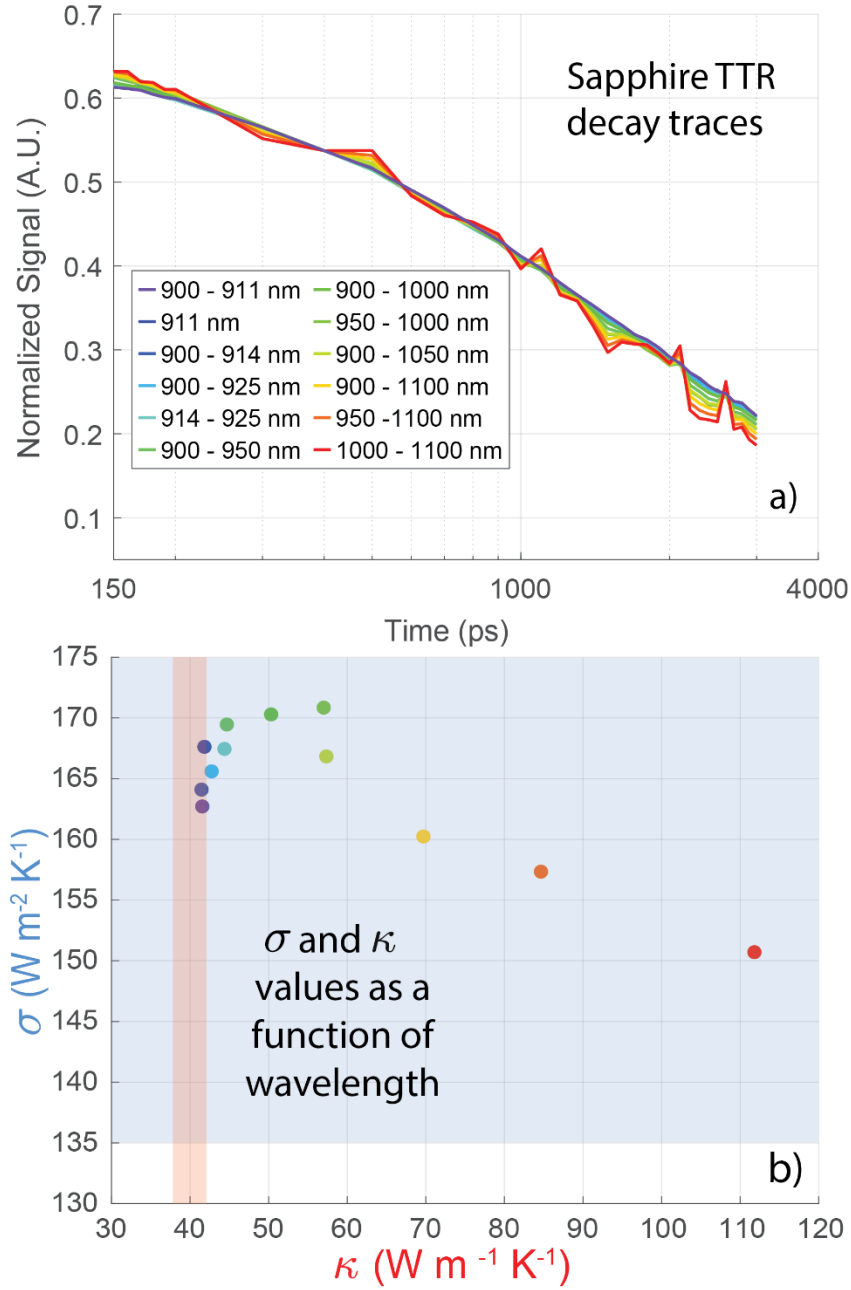


Figure B.11. a) Overlay of fs-TTR decay traces for an Al/sapphire sample for a variety of selected integrated wavelength ranges. Although the decay for each wavelength range is roughly the same, the noise is accentuated at redder wavelengths due to the properties of the white light continuum. b) Fitted values for both σ (y -axis) and κ_{zz}^{sam} (x -axis) for each wavelength integration range, matched by color to

the traces in (a). The light blue highlighted region corresponds to accepted σ values for the interface Al/sapphire while the light purple highlighted region corresponds to accepted κ_{zz}^{sam} values for sapphire (see Table 3.1 in Chapter 3 for literature references).

After selecting an appropriate probe wavelength range, we use numerical integration to average the raw fs-TTR data matrix to generate the fs-TTR signal at each time point. This signal vs time data were what we used in our fitting algorithm to extract both κ_{zz}^{sam} and σ . We fit the model to data by minimizing the square residual, each residual weighed equally regardless of probe delay time. The minimized square residuals of the control samples presented in Figure 3.5 of Chapter 3 are shown in Figure B.12 below.

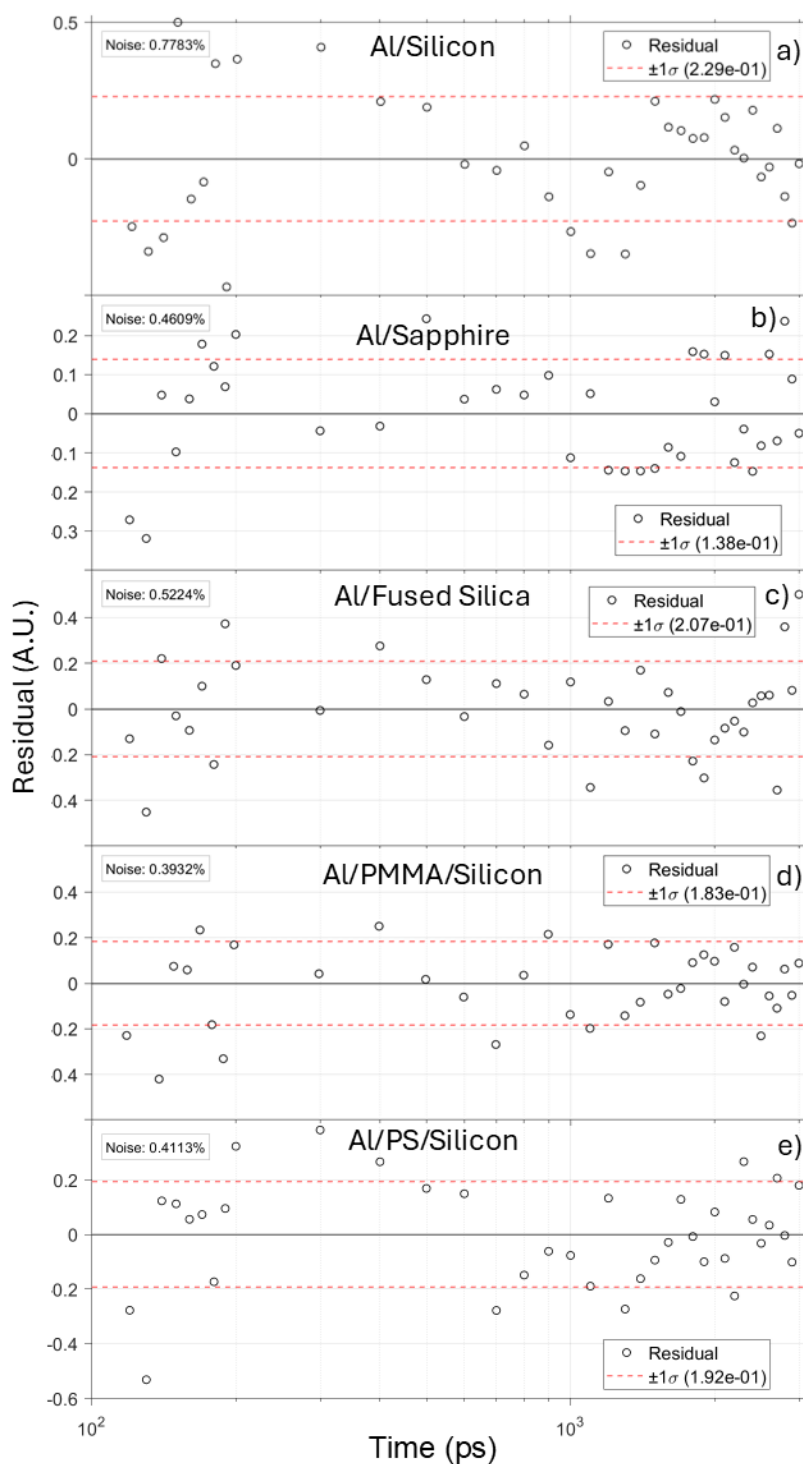


Figure B.12. Minimized square residuals of the model fit to the experimental fs-TTR sample data presented in Figure 3.5 of Chapter 3: a) Al/Si bi-layer sample; b) Al/Al₂O₃ (sapphire) bi-layer sample; c) Al/SiO₂ bi-layer sample; d) Al/PMMA/Si tri-layer sample; and, e) Al/PS/Si tri-layer sample. For each

sample, the minimized square residuals appear to be randomly distributed across the probe delay time window. This suggests that the minimized residuals are representative of noise.

3.2 Different Weighting of Residuals for Fitting the Model to fs-TTR Data

With our amplified transient absorption system and transducer quality, we can typically measure signals of singular ΔmOD or lower. The variability between the signal strength and embedded noise inspired us to check if there were different regions of the decay that would be better being weighted more heavily to achieve the most accurate fitting results. Since κ_{zz}^{sam} is increasingly more sensitive at later delay times, as shown in Section 3.3 of Chapter 3, we attempted to change the weighting of the data to more heavily weight the residuals at these later times. We tried residual weights including equal weighting of all time points, linear in time weighting, square-root of time weighting, logarithmic in time weighting, and squared time weighting. We found that any heavier weighting of data at later delay times negatively impacted the accuracy of the fitting results compared to simply weighing each data point equally. Therefore, we exclusively weighed each data point equally when using our fitting algorithm throughout this paper.

In the repository, we show the fitting results for κ_{zz}^{sam} and σ from our simulations of noisy data (see Section 3.3 of Chapter 3 and Section 5 of Appendix B) between data that received equal weighting of all time points vs linear in time weighting. Across all simulated materials (silicon, sapphire, fused silica and polystyrene) regardless of noise level, we found that the fitting results for κ_{zz}^{sam} and σ deviated from their ‘correct’ value to a greater extent when linear in time weighting was implemented compared to equally weighing all time points.

3.3 Input Parameters Used to Determine κ_{zz}^{sam} and σ for fs-TTR Experimental Samples

The control materials used to validate the efficacy of the fs-TTR experiments in Section 3.4 of Chapter 3 required a set of thermal model input parameters, listed below in Table B.1, to fit values for κ_{zz}^{sam} and σ . Since we are also using MATLAB's built-in lsqnonlin fitting algorithm, we can set upper and lower boundary limits that control how κ_{zz}^{sam} , σ and c float. Since our fitting algorithm did not show a susceptibility to getting stuck in local minima, we did not restrict the boundaries for either κ_{zz}^{sam} or σ for any of the materials we studied.

Table B.1. Thermal Model Input Parameters for fs-TTR Experiments on Different Samples

Input Parameter	Silicon	Sapphire	Fused Silica	PMMA	Polystyrene
Transducer Thickness (nm)	100	100	95	100	100
Film Thickness (m)	1×10^{-5}	1×10^{-5}	1×10^{-5}	100×10^{-9}	100×10^{-9}
Spatial Step (m)	1×10^{-9}	1×10^{-9}	1×10^{-9}	5×10^{-10}	5×10^{-10}
Time Step (s)	5×10^{-12}	5×10^{-12}	5×10^{-12}	1×10^{-12}	1×10^{-12}
C_v^{sam} (J cm ⁻³ K ⁻¹)	1.66	3.09	1.65	1.61	1.25

Additional thermal model input parameters that are not included in Table B.1 were constant for all five materials. These include: pump/probe reflectance = 87% (Al/800 nm); laser power = 5 J m⁻²; pump/probe optical penetration depth = 7.62 nm (Al/800 nm); thermal conductivity of the transducer = 100 W m⁻¹ K⁻¹; and, volumetric heat capacity of the aluminum transducer = 2.42 J cm⁻³ K⁻¹.⁴ In our fs-TTR experiments, we set the percent reflectance and optical penetration depth values for the pump and probe to be equal, which we found to be an accurate assumption for the Al transducer despite small differences in pump (800 nm) and

probe (900–915 nm) wavelengths. The laser power value is arbitrary as the scaling factor, c , in the thermal model adjusts the amplitude of the signal. The thermal conductivity of the physical vapor-deposited aluminum transducer was determined to be $\sim 100 \text{ W m}^{-1} \text{ K}^{-1}$ by performing electrical conductivity measurements and applying the Wiedmann-Franz law. This lower thermal conductivity of vapor-deposited aluminum thin films compared to bulk aluminum ($237 \text{ W m}^{-1} \text{ K}^{-1}$) is in line with other measurements reported in the literature.^{5,6} When using `lsqnonlin` to fit the thermal model to data, we selected an optimality tolerance of 10^{-5} . The MATLAB script we use for fitting the fs-TTR thermal model to data can be found in the repository link.

We note that modeling the true thickness of a mm-sized substrate in bi-layer samples is computationally inefficient. Since the fs-TTR signal decay is only concerned with heat flow up until the longest time delay point (a few nanoseconds), it is algorithmically more efficient to simply model the substrate layer with a thickness that is smaller than reality but which still safely exceeds the depth to which the material is heated within the time window of the probe delay. As an example, our bi-layer samples that had an underlying layer of at least 1 mm in thickness and with κ_{zz}^{sam} in the range of $1\text{--}200 \text{ W m}^{-1} \text{ K}^{-1}$ were suitably modeled with a thickness of just $10 \text{ }\mu\text{m}$.

4.0 Additional Thermal Model Simulations and fs-TTR Experiments on Thin-Film Samples

4.1 Thermal Model Simulations to Test Thin-Film Thickness Dependence

One limitation of the 1-D thermal model presented in Chapter 3 is that heat is assumed to not reach the backside of the underlying material layer within the time window of the probe delay. If the underlying material layer is a thin film (10s to 100s of nm thick) and the maximum

probe delay is in the regime of multiple ns, it is possible for heat to be transported to the backside of the underlying film (even very low- κ_{zz}^{sam} materials) within the probe delay time window. This would cause a breakdown in our thermal model as the model ignores heat transfer across the interface of the underlying film-supporting substrate and within the substrate.

Ways to prevent heat from reaching the backside of an underlying film include increasing the thickness of the film or reducing the time window of the probe delay. To gain insight into how these knobs can be controlled to optimize a fs-TTR experiment, we simulated heat transfer within an Al/PS sample using our 1-D thermal model as a function of time and vertical depth (see Figure B.13a below). We simulated this system using our thermal model with the input parameters listed for PS in Table B.1 and values for κ_{zz}^{sam} and σ equal to $0.15 \text{ W m}^{-1} \text{ K}^{-1}$ and $50 \text{ MW m}^{-2} \text{ K}^{-1}$, respectively.

Our simulations reveal that heat penetrates through a 100 nm-thick PS thin film in 8 ns. Therefore, a PS film of 100 nm affords no more than 8 ns of maximum probe delay time. Since our mechanical delay stage can probe delay times out to 3 ns, this requires that we use a polystyrene thin film of at least 50 nm to prevent heat from reaching the backside of the film. For materials that have higher κ_{zz}^{sam} than PS, thicker films would be required as the rate of heat transfer (thermal diffusivity) is proportional to the thermal conductivity.

Figure B.13b depicts the heat flow shown in Figure B.13a as a function of temperature differential (ΔT) versus vertical depth, with each trace showing the time evolution of ΔT within the sample. In this depiction, we can see that the transducer thermalizes across its entire vertical depth within the first ~ 100 ps. This helped contribute to our decision to only use the thermal model to fit data ≥ 120 ps.

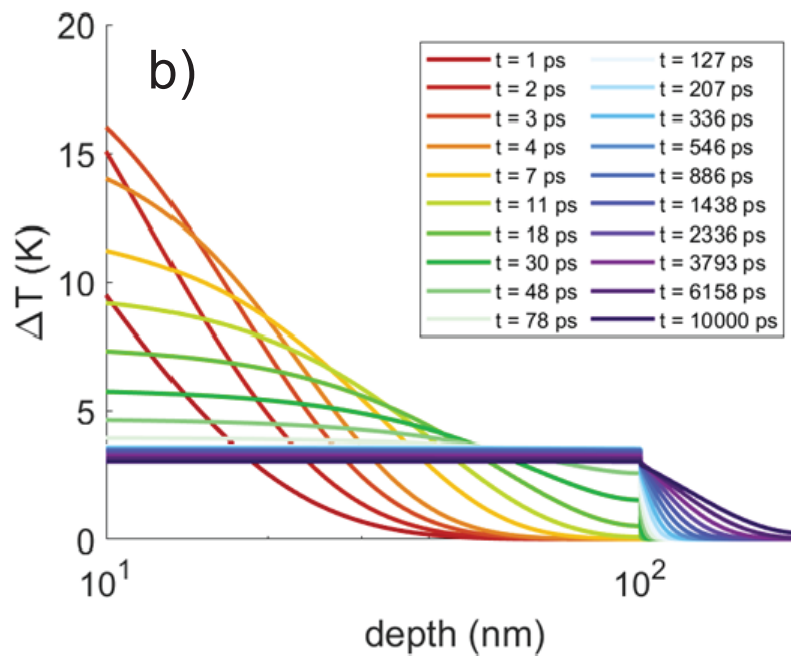
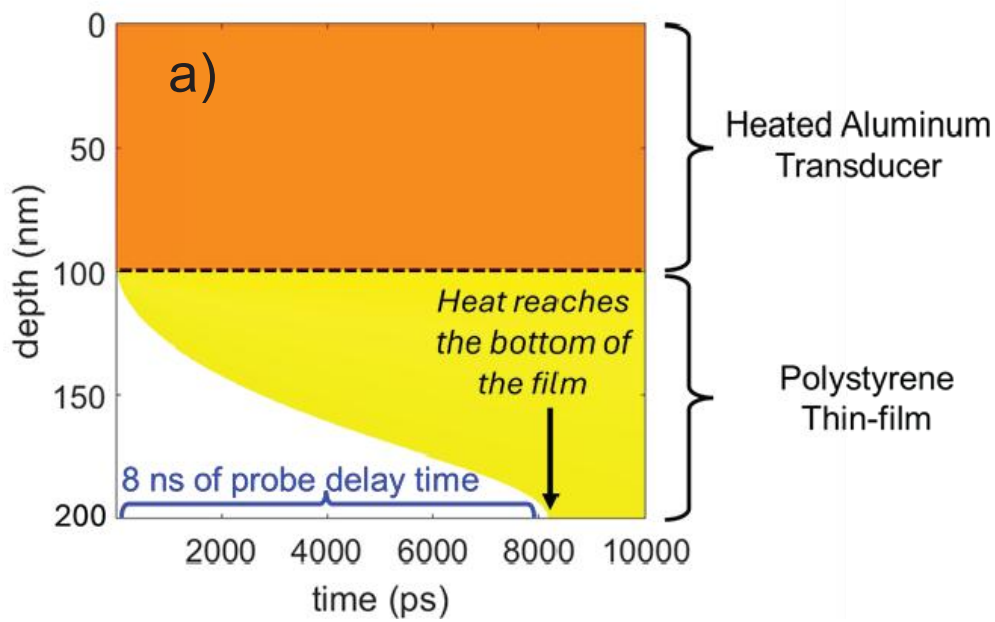


Figure B.13. a) Heatmap showing the flow of heat (starting in the upper left hand corner) as a function of time (x -axis) and depth (y -axis) for a bi-layer Al/PS sample architecture. The modeled system comprises of a 100 nm Al transducer and a 100 nm thin-film of PS. The yellow contour suggests that it takes 8 ns for heat to reach the backside of the PS thin-film. Since our 1-D thermal model omits heat transfer across the PS-supporting substrate interface and into the substrate, the probe delay must be shorter than 8 ns for the model to properly function. b) Plot showing the temperature differential as a

function of vertical sample depth where each trace represents a different probe delay time snapshot. The plot shows that by the very pale blue trace (127 ps after initial heating) the transducer has thermalized across its entire depth and any of the change in thermorefectance after this time point is representative of how well heat transfers across the Al/PS interface and through the polymer film.

4.2 Experimental Verification that Substrate Effects are not Important in fs-TTR

A primary point of Chapter 3 is that the substrate does not influence the fs-TTR decay of a tri-layer (transducer/thin film/substrate) sample if the thickness of the thin film material is sufficiently large and the probe delay time window is short enough to ensure that heat doesn't reach the back of the thin film (while still being long enough to characterize the decay). This allows a simplified bi-layer thermal model to be used to fit values for κ_{zz}^{sam} and σ . To verify that the substrate does not influence the fs-TTR signal, we compared fs-TTR traces taken on Al/PS/Si and Al/PS/glass tri-layer samples, as shown in Figure B.14 below. The Al/PS/Si sample in Fig. B.14 is the same sample presented in Fig. 3.5 of Chapter 3, while the fitting results for the Al/PS/glass sample in Fig. B.14 are $\kappa_{zz}^{\text{sam}} = 0.15(9) \pm 0.02(2) \text{ W m}^{-1} \text{ K}^{-1}$ and $\sigma = 35 \pm 12 \text{ W m}^{-2} \text{ K}^{-1}$. The fs-TTR traces are almost entirely overlapped and the fitted values of κ_{zz}^{sam} and σ are within error. This suggests that the Si and glass substrates have no influence on the fs-TTR decay of tri-layer samples that have sufficiently thick central layers.

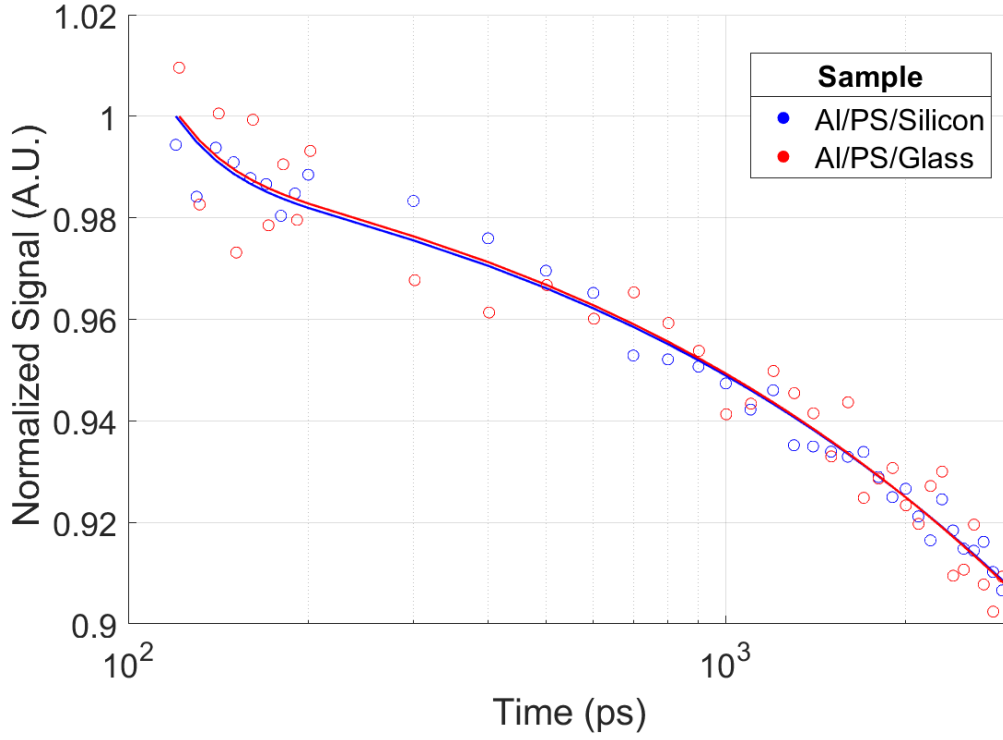


Figure B.14. Fs-TTR traces for Al/PS/Si (in blue, taken from Figure 3.5 of Chapter 3) and Al/PS/glass (in red). The fitting results for the Al/PS/Si sample are $\kappa_{zz}^{\text{sam}} = 0.15(3) \pm 0.01(7) \text{ W m}^{-1} \text{ K}^{-1}$ and $\sigma = 35 \pm 7 \text{ W m}^{-2} \text{ K}^{-1}$; the results for the Al/PS/glass sample are $\kappa_{zz}^{\text{sam}} = 0.15(9) \pm 0.02(2) \text{ W m}^{-1} \text{ K}^{-1}$ and $\sigma = 35 \pm 12 \text{ W m}^{-2} \text{ K}^{-1}$, which are within error to that of the Al/PS/Si sample. The fact that the fs-TTR traces overlap almost identically suggests that a difference in substrate has no effect on the fs-TTR decay of tri-layer samples that have sufficiently thick layers between the transducer and substrate.

5.0 Generation of Simulated Data with Embedded Noise

One objective in Chapter 3 was to assess the reliability of our thermal model to fit values for κ_{zz}^{sam} and σ from experimental fs-TTR data with noise. The SNR of data taken with ultrafast laser experiments can vary day-to-day from environmental factors and system-to-system from performance and alignment factors. To investigate the noise tolerance of our model, we generated noise-embedded simulated amplified thermorefective decay data across

a range of noise levels for silicon, sapphire, fused silica and polystyrene materials (spanning four orders of magnitude in thermal conductivity) and then refitted the data using our thermal model with the goal of comparing the resulting fitted values for κ_{zz}^{sam} and σ to their initially simulated inputs.

We first simulated a thermoreflective decay without noise using our thermal model with the input values listed in Table B.2:

Table B.2. Model input parameters to generate simulated fs-TTR data for various materials

Input Parameter	Silicon	Sapphire	Fused Silica	Polystyrene
Film Thickness (m)	1×10^{-6}	1×10^{-6}	1×10^{-6}	100×10^{-9}
Spatial Step Size (m)	1×10^{-10}	1×10^{-10}	1×10^{-10}	1×10^{-10}
Time Step Size (s)	1×10^{-11}	1×10^{-11}	1×10^{-11}	1×10^{-12}
Laser Fluence (J m^{-2})	10	5	5	2
C_v^{sam} ($\text{J cm}^{-3} \text{K}^{-1}$)	1.66	3.05	1.65	1.25
κ_{zz}^{sam} ($\text{W m}^{-1} \text{K}^{-1}$)	145	35	1.4	0.15
σ ($\text{MW m}^{-2} \text{K}^{-1}$)	165	150	100	50

Except for the Al transducer thickness, modeled as 75 nm in these simulations, all other model input parameters not listed in Table B.2 were identical to the values listed in Section 3.3 of Appendix B. The C_v^{sam} , κ_{zz}^{sam} and σ values for each material in Table B.2 are representative of the literature values referenced in Table 3.1 of Chapter 3.

Once we simulated the amplified thermoreflective decays, we added Gaussian noise as a function of the percentage noise standard deviation relative to the maximum normalized amplitude of the decay, which was at 120 ps. We generated simulated data with the same probe delay time window, with the same number of data points and respective time intervals, as the experimental data we took in Section 3.4 of Chapter 3. To gain insight into both the accuracy

and precision of fitting results for κ_{zz}^{sam} and σ as a function of added noise, we generated 100 total unique data sets for each material at each noise level.

Global averages of the fitted values for κ_{zz}^{sam} and σ at each noise level for each material, presented in Figs. 3.3c-f of Chapter 3, were calculated using the 100 separate data sets generated (after removing occasional outliers, representing less than 3% of the data sets, that fell beyond 3 standard deviations from the mean). When fitting the model to the simulated noisy data, each data point received equal weighting in the calculation of min RSS, as discussed above. An example of a κ_{zz}^{sam} vs σ heatmap plot, for Al/sapphire with added gaussian noise of 0.125% standard deviation of the y_{max} signal, is shown in Figure B.15 below.

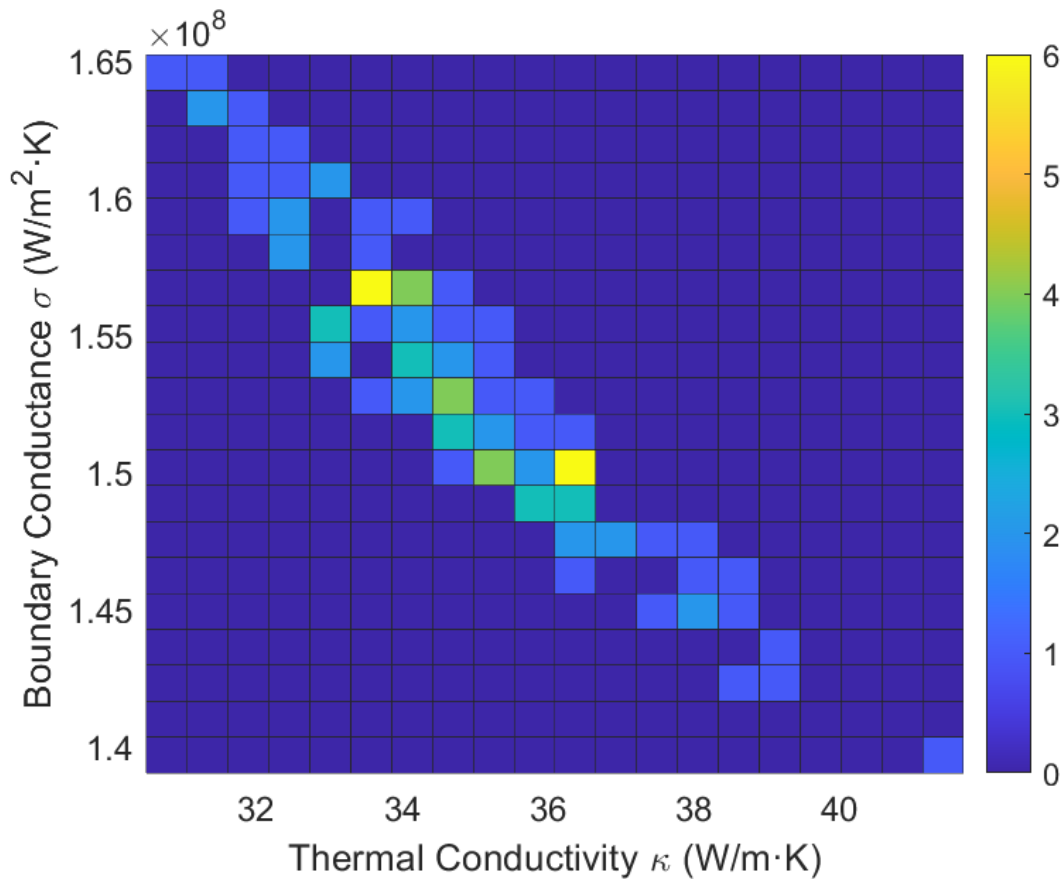


Figure B.15. Plotted is a κ_{zz}^{sam} vs σ heatmap for the fitting results of 100 data sets for Al/sapphire with added gaussian noise of 0.125% standard deviation of the y_{max} signal. Data was fit with equal weighting per point.

Using the 100 data sets for each material at each noise level, we also calculated the average percentage noise values, listed along the x -axis of Fig. 3.3c-f of Chapter 3 and in Table B.3 below, via the root-mean-square (RMS) residuals relative to the trace of the simulated fs-TTR decay using fixed, correct values for κ_{zz}^{sam} vs σ . Doing so allowed us to compare the noise percentage of our experimental results to the results from our simulations of noisy data.

Table B.3. Average Percentage Noise Across Simulated Noisy Data Sets for Each Material

Gaussian Noise Added (%STDV of y_{max})	Silicon (Resulting RMS residual %Noise)	Sapphire (Resulting RMS residual %Noise)	Fused Silica (Resulting RMS residual %Noise)	Polystyrene (Resulting RMS residual %Noise)
0.0625	1.0201%	0.9730%	0.4336%	0.2802%
0.125	1.1261%	1.0723%	0.6952%	0.5625%
0.25	1.4874%	1.4048%	1.3084%	1.1056%
0.5	2.7469%	2.3509%	2.3851%	--

6.0 Additional Discussion & Analysis

6.1 Additional Sensitivity Ratio Analysis

First, we compare transient changes in the absolute value of the sensitivity ratios for κ_{zz}^{sam} , $|S_{\kappa}^{\text{sam}}|$, and σ between our fs-TTR and oscillator-type TDTR. To do so, we compare our Al/Si sample from Figure 3.4a in Chapter 3 to sensitivity ratios calculated for an Al/GaN sample by Jiang *et al.*, chosen since GaN has a both a thermal conductivity and thermal interface conductance (with Al) that is similar to silicon.⁷ From our fs-TTR sensitivity ratio calculations, $|S_{\kappa}^{\text{sam}}|$ increases from 0.05 to 0.2 from 1 ns to 3 ns of time delay, whereas oscillator-type TDTR sees a decrease in $|S_{\kappa}^{\text{sam}}|$ from 0.3 to 0.2 across the same time range.⁷ Regarding the thermal interface conductance, $|S_{\sigma}|$ grows from 0.35 to 0.6 from 1 ns to 3 ns of time delay in fs-TTR, whereas oscillator-type TDTR sees an increase from 0 to 0.25 in $|S_{\sigma}|$.⁷ This comparison showcases that fs-TTR better leverages longer delay time data than oscillator-

type TDTR. Furthermore, the facts that: 1) S_σ is never 0 at longer delay times in fs-TTR and 2) $|S_\sigma|$ is consistently larger in value in fs-TTR, means that κ_{zz}^{sam} and σ are better decoupled as fitting parameters in fs-TTR compared to oscillator-type TDTR.

Next, to determine how pre-selected input values influence the signal decay in our 1-D thermal model for fs-TTR (beyond just C_v^{sam} , which is shown in Figure 3.4 of Chapter 3), we also show below in Figure B.16 sensitivity ratios calculated as a function of time for the transducer thickness (L^{met}), the underlying sample thickness (L^{sam}), the volumetric heat capacity of the transducer (C_v^{met}), the thermal conductivity of the transducer (κ^{met}) and the optical penetration depth of the pump and probe (δ). Across all sample types, L^{sam} has no influence on the fs-TTR signal as heat is assumed to not reach the backside of the underlying material within the probe delay time of 3 ns (the sample layer, plus any substrate underneath, serves as a heat-sink); this assumption is ensured in a fs-TTR experiment by selecting sufficient thick underlying sample materials. Furthermore, the optical penetration depth is shown to have a sensitivity ratio of 0.

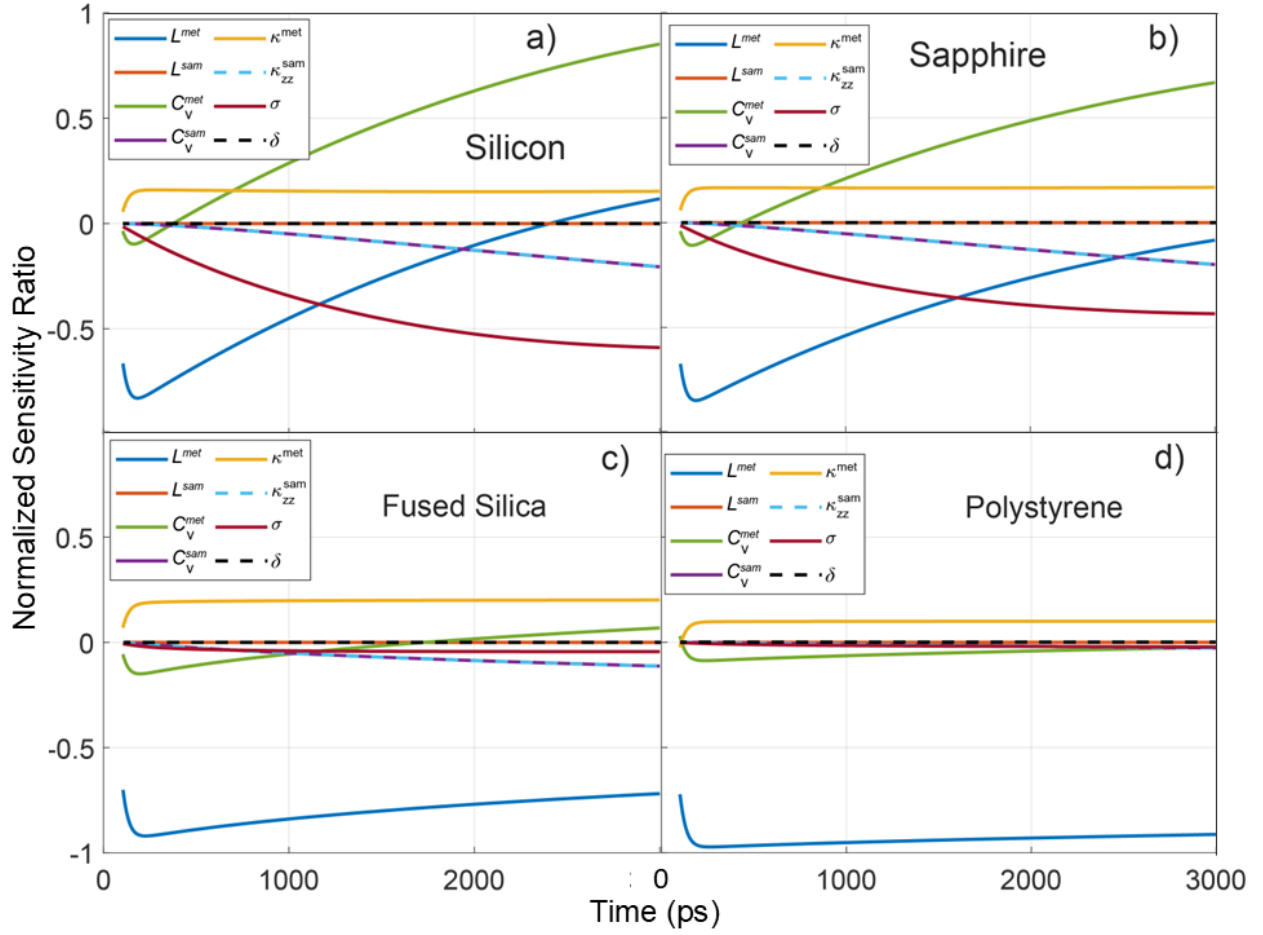


Figure B.16. Sensitivity ratios as a function of probe delay time for various model input parameters: L_{met} is the transducer thickness; L_{sam} is the underlying sample thickness; C_v^{met} is the volumetric heat capacity of the transducer; C_v^{sam} is the volumetric heat capacity of the underlying sample material, κ_{met} is the thermal conductivity of the transducer and δ is the optical penetration depth of the pump and probe. The thermal conductivity of the underlying sample material, κ_{zz}^{sam} , and the thermal boundary conductance, σ , are parameterized valuables determined with model fits.

6.2 Error Propagation Analysis Involving Uncertainty in Model Input Parameter

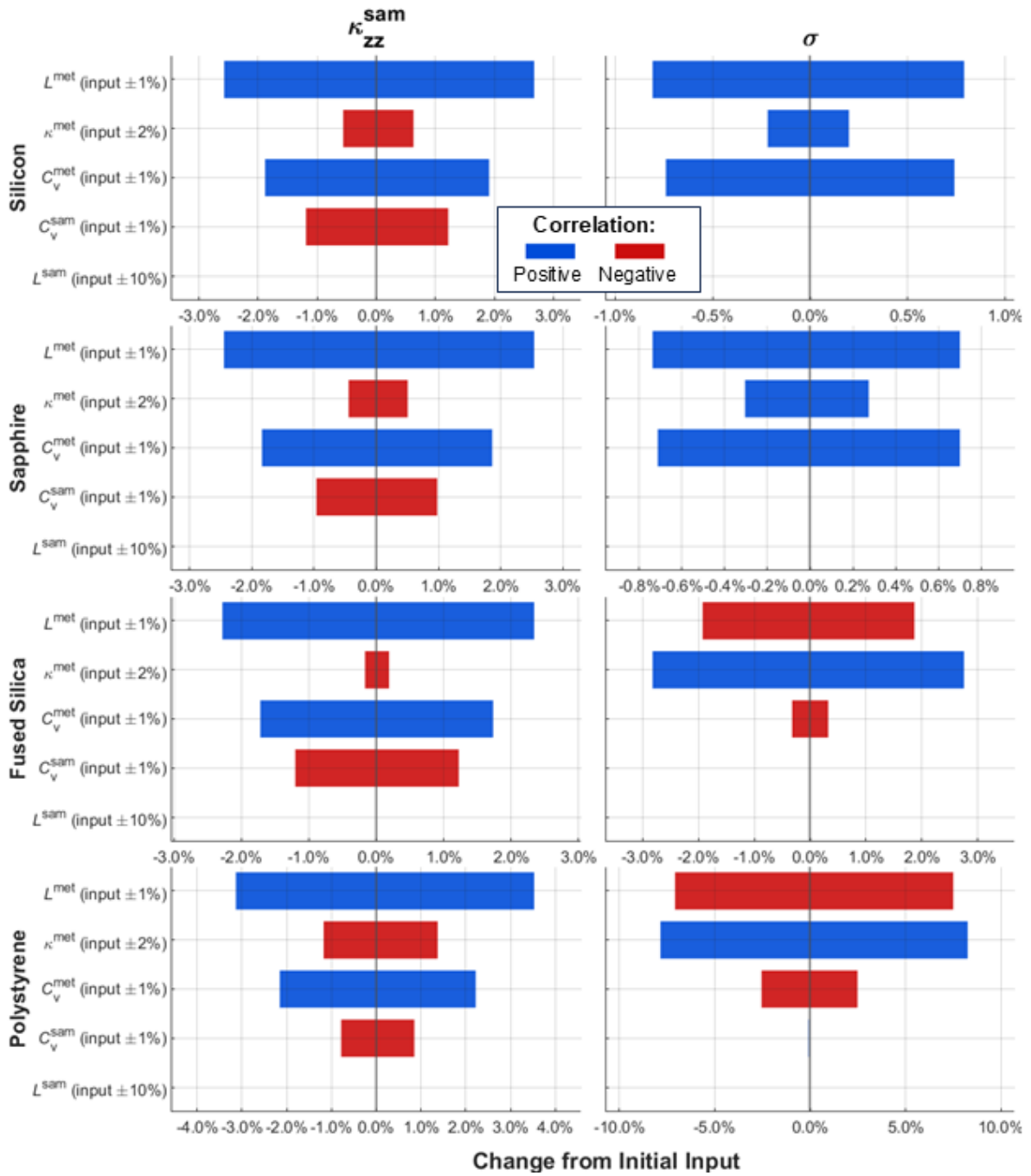


Figure B.17. Changes in the extracted values of κ_{zz}^{sam} (left side) and σ (right side) as a function of upper- and lower-bound uncertainties for various model input parameters (y-axis ticks) for the silicon, sapphire, fused silica and polystyrene experimental samples that are presented in Figure 3.5 of Chapter 3. Each model input parameter is perturbed with the others held constant at the stated values described

above in Section 3.3 of Appendix B (see Table B.1). The impact of each perturbation on κ_{zz}^{sam} and σ are shown as the colored bars that quantify how much the extracted κ_{zz}^{sam} and σ values, presented along the x -axis, change relative to the values in Table 3.1 of Chapter 3. Blue bars indicate a positive correlation (i.e., that an increase (or decrease) in the model input parameter results in an increase (or decrease) in the fitted parameter), while red bars indicate a negative correlation. For all samples, κ_{zz}^{sam} is most sensitive to uncertainties in L^{met} , the transducer thickness, and C_v^{met} , the volumetric heat capacity of the transducer, although no change in κ_{zz}^{sam} exceeds more than 3% for any one model input uncertainty. For polystyrene, the uncertainties of all model input parameters corresponding to the transducer each alter κ_{zz}^{sam} by $\pm 1\%$ to $\pm 3\%$ while σ is altered by $\pm 3\%$ to $\pm 8\%$. The extracted value of σ is most sensitive to uncertainties in L^{met} and C_v^{met} for the silicon and sapphire samples, and to uncertainties in L^{met} and κ^{met} for the fused silica and polystyrene samples. For all samples, κ_{zz}^{sam} and σ are not sensitive to uncertainty in L^{sam} , because heat does not reach the backside of the underlying sample layer during the time scale of the fs-TTR measurement, as shown above in Section 4.2 of Appendix B).

We determined uncertainties in fitted values of κ_{zz}^{sam} and σ propagated using both the covariance of the Jacobian output (i.e. based on the noise in the experimental data) and using uncertainties in the model input parameters, which are summarized in Table B.4. These uncertainties were calculated using the multivariate linear approach (first-order Taylor expansion) described by Yang *et al.*¹⁵ For our experimental samples, the uncertainties of the model input parameter are: L^{met} uncertainty = ± 1 nm; κ^{met} uncertainty = ± 1 W m⁻¹ K⁻¹; C_v^{met} uncertainty = ± 0.01 J cm⁻³ K⁻¹; and, C_v^{sam} uncertainty = ± 0.01 J cm⁻³ K⁻¹.

Table B.4. Predicted Uncertainties for Fitted κ_{zz}^{sam} and σ Values from the Experimental Samples Presented in Fig. 3.5 of Chapter 3 Propagated using both the Covariance of the Jacobian Output and Defined Error in the Model Input Parameters

Experimental Sample	Uncertainty in κ_{zz}^{sam} (W m ⁻¹ K ⁻¹)	Uncertainty in σ (MW m ⁻² K ⁻¹)
Silicon	143 ± 16	161 ± 5
Sapphire	41.4 ± 3.3	161 ± 5
Fused Silica	1.31 ± 0.08	136 ± 29
PMMA	0.19 ± 0.04	30 ± 12
Polystyrene	0.15 ± 0.03	35 ± 20

6.3 Correlation Matrices and 2D Uncertainty Ellipses for the Experimental Samples Presented in Figure 3.5 of Chapter 3

The parameter correlation matrices (see Table B.5, below) for the experimental samples presented in Figure 3.5 of Chapter 3 show that κ_{zz}^{sam} and σ have a negative correlation. In other words, if one of these variables is overestimated in the fitting process due to, for example, noise in the TR decay, the fit of the other variable will be underestimated. This fact reveals that the fitting process relies on minimizing parameter space along a linear trajectory, as shown by the distribution in the uncertainties in fitted values of κ_{zz}^{sam} and σ in Figure B.18 below. This is consistent with the linear trend in the fitting results for κ_{zz}^{sam} and σ in Figure B.15 of Appendix B, where we show the distribution of fitting results from 100 simulated data sets with embedded noise.

Table B.5. Parameter Correlation Matrices for the Experimental Samples Presented in Figure 3.5 of Chapter 3

Silicon							
	κ_{zz}^{sam}	σ	c	L^{met}	κ^{met}	C_v^{met}	C_v^{sam}
κ_{zz}^{sam}	1	-0.89432	0.06743	0.10528	0.092252	-0.01202	-0.04012
σ	-0.89432	1	-0.39668	0.12029	0.13458	0.015554	-3×10^{-6}
c	0.06743	-0.39668	1	-0.43283	-0.78350	0.28493	8×10^{-7}
L^{met}	0.10528	0.12029	-0.43283	1	0	0	0
κ^{met}	0.092252	0.13458	-0.78350	0	1	0	0
C_v^{met}	-0.01202	0.015554	0.28493	0	0	1	0
C_v^{sam}	-0.04012	-3×10^{-6}	8×10^{-7}	0	0	0	1
Sapphire							
	κ_{zz}^{sam}	σ	c	L^{met}	κ^{met}	C_v^{met}	C_v^{sam}
κ_{zz}^{sam}	1	-0.81258	-0.12324	0.20012	0.17922	-0.01942	-0.07990
σ	-0.81258	1	-0.36637	0.15353	0.18256	0.031401	-8×10^{-6}
c	-0.12324	-0.36637	1	-0.44851	-0.81402	0.29530	9×10^{-7}
L^{met}	0.20012	0.15353	-0.44851	1	0	0	0
κ^{met}	0.17922	0.18256	-0.81402	0	1	0	0
C_v^{met}	-0.01942	0.031401	0.29530	0	0	1	0
C_v^{sam}	-0.07990	-8×10^{-6}	9×10^{-7}	0	0	0	1
Fused Silica							
	κ_{zz}^{sam}	σ	c	L^{met}	κ^{met}	C_v^{met}	C_v^{sam}
κ_{zz}^{sam}	1	-0.88373	0.16760	0.14791	0.13838	-0.00766	-0.06538
σ	-0.88373	1	-0.42200	-0.03855	-0.00956	0.028443	-2×10^{-6}
c	0.16760	-0.42200	1	-0.40678	-0.72105	0.26518	6×10^{-5}
L^{met}	0.14791	-0.03855	-0.40678	1	0	0	0
κ^{met}	0.13838	-0.00956	-0.72105	0	1	0	0
C_v^{met}	-0.00766	0.028443	0.26518	0	0	1	0
C_v^{sam}	-0.06538	-2×10^{-6}	6×10^{-5}	0	0	0	1
PMMA							
	κ_{zz}^{sam}	σ	c	L^{met}	κ^{met}	C_v^{met}	C_v^{sam}
κ_{zz}^{sam}	1	-0.94543	0.14367	0.098123	0.068255	-0.02779	-0.02024
σ	-0.94543	1	-0.24451	-0.08120	-0.03279	0.045639	2×10^{-5}
c	0.14367	-0.24451	1	-0.54984	-0.73447	0.13040	2×10^{-5}
L^{met}	0.098123	-0.08120	-0.54984	1	0	0	0
κ^{met}	0.068255	-0.03279	-0.73447	0	1	0	0
C_v^{met}	-0.02779	0.045639	0.13040	0	0	1	0
C_v^{sam}	-0.02024	2×10^{-5}	2×10^{-5}	0	0	0	1
Polystyrene							
	κ_{zz}^{sam}	σ	c	L^{met}	κ^{met}	C_v^{met}	C_v^{sam}
κ_{zz}^{sam}	1	-0.93238	0.22524	0.089917	0.064579	-0.02353	-0.02052
σ	-0.93238	1	-0.33715	-0.08002	-0.03482	0.042584	6×10^{-6}
c	0.22524	-0.33715	1	-0.52432	-0.70619	0.12265	3×10^{-5}
L^{met}	0.089917	-0.08002	-0.52432	1	0	0	0
κ^{met}	0.064579	-0.03482	-0.70619	0	1	0	0
C_v^{met}	-0.02353	0.042584	0.12265	0	0	1	0
C_v^{sam}	-0.02052	6×10^{-6}	3×10^{-5}	0	0	0	1

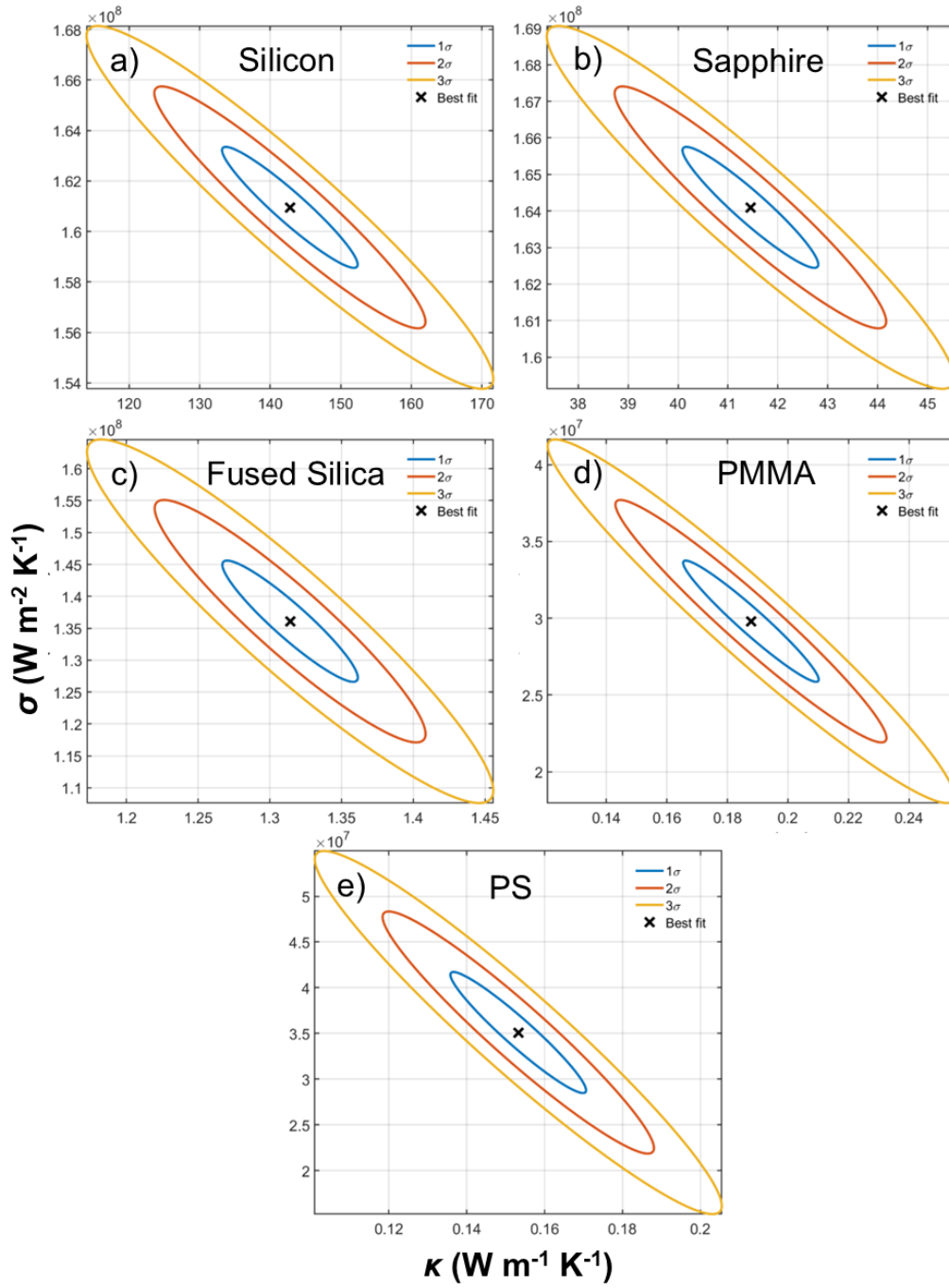


Figure B.18. Global uncertainty analysis for extracting κ_{zz}^{sam} and σ from the fs-TTR model described in Chapter 3. The 2D uncertainty ellipses fall along the anti-diagonal, indicating the negative correlation between these parameters (see also Table B.4). The ellipses were generated by first decomposing the covariance matrix of the Jacobian output into eigenvector and eigenvalue matrices and then scaling a unit circle by the magnitudes obtained from these matrices. The ellipses quantify how an overestimation

in one fitting parameter causes a high likelihood that the other parameter is underestimated. The confidence ellipses (1σ , 2σ , 3σ) for silicon, sapphire, fused silica PMMA and polystyrene (PS) are shown in panels (a), (b), (c), (d), and (e), respectively. The overall impact one variable has on another depends on the underlying sample material. For example, a $\pm 10\%$ deviation in the fitted value of κ_{zz}^{sam} from our Al/silicon bi-layer sample impacts the value of σ by $< \mp 2\%$.

6.4 Analysis of Measured σ Values for Al/PS and Al/PMMA

The similarity in thermal boundary conductance (TBC or σ) between the two polymers we studied in Chapter 3 and the Al transducer is expected as both polymers have similarly amorphous film structures. To our knowledge, there are no reported values for the TBC of the Al/PMMA interface in the literature. Instead, we found that either the TBC for Al/PMMA was pre-selected or was not used as a fitting parameter due to a lack of sensitivity,^{8,9} or the TBC was measured using metals other than aluminum.¹⁰ Also, Putnam *et al.* determined that the TBC of $\text{Al}_2\text{O}_3/\text{PMMA}$ was $30 \pm 10 \text{ MW m}^{-2} \text{ K}^{-1}$,¹¹ which is within error of our measurements in Chapter 3 for the Al/PMMA interface. Of the few TBC measurements pertaining to the Al/PS interface, most researchers report values close to $20 \text{ MW m}^{-2} \text{ K}^{-1}$.¹²⁻¹⁴ The slightly higher TBC value we measured for Al/PS may be due to differences in polymer film processing and/or thermal deposition conditions that contributed to the creation of a more thermally conductive interface.

7.0 References

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APPENDIX C: Supporting Information for Chapter 4

1.0 Additional X-ray Diffraction Data

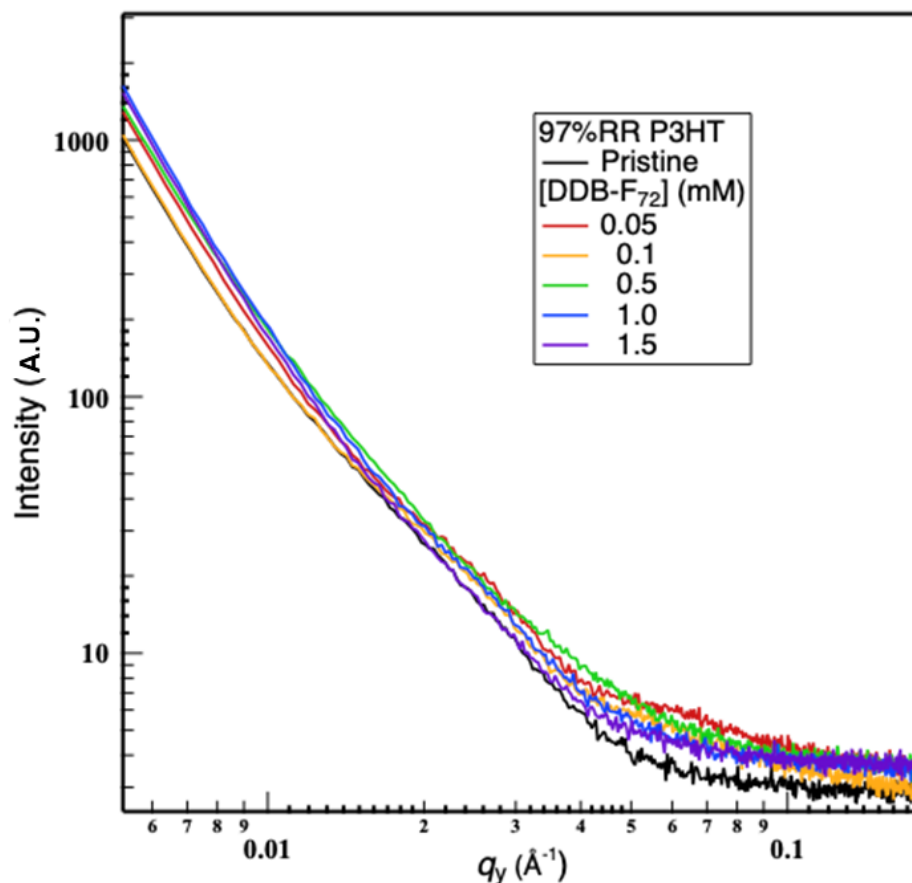


Figure C.1. Shows the GISAXS diffraction for pristine and DDB-F₇₂-doped RR-P3HT films across the doping series presented in Figure 4.3a-b (minus the 0.3 mM sample). The DDB-F₇₂ concentrations (in mM) reflect the concentrations of dopant in *n*-BA during the doping step of the SqP method.

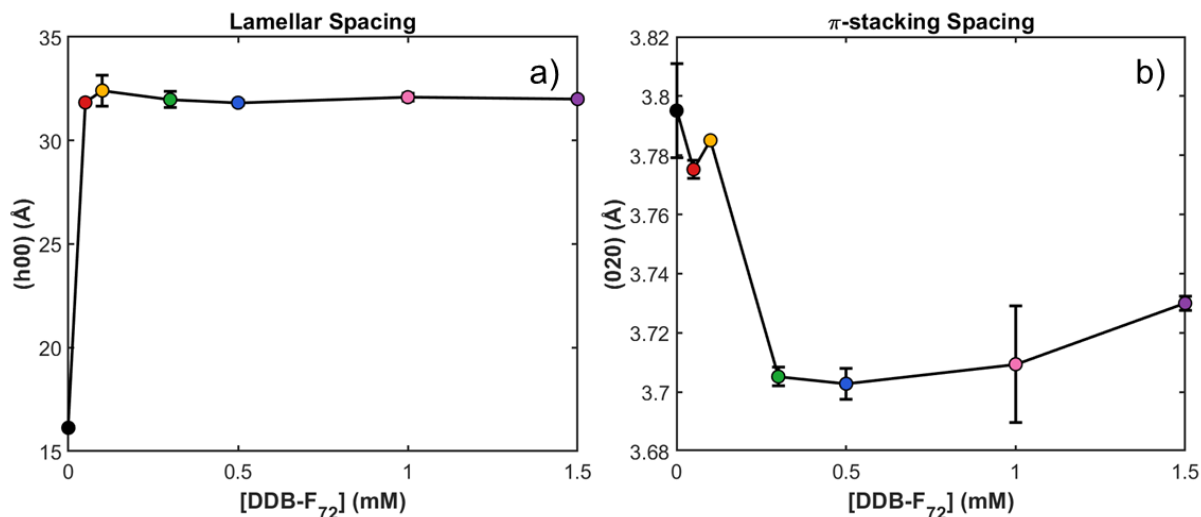


Figure C.2. Structural evolution of DDB-F₇₂-doped P3HT films as a function of the concentration of DDB-F₇₂. The results in panels a–b are extracted from analyzing the integrated, pristine-film-thickness-normalized GIWAXS patterns shown in Figure 4.3a–b. All films were doped using the SqP method with *n*-BA as the doping solvent. *Y*-axis error bars represent the standard deviation in the peak-fitting across three separate samples. a) The lamellar ($h00$) spacing, obtained from the position of the ($h00$) out-of-plane diffraction peak(s); this spacing reflects the periodicity of the alkyl side-chain stacking direction of the P3HT lattice and its expansion upon dopant intercalation. The red and orange-yellow points (0.05 mM and 0.1 mM, respectively) are calculated assuming the peak at $0.4 \text{ \AA}^{-1}$ is $(200)'$. b) The π -stacking (020) spacing, obtained from the position of the (020) diffraction peak, which sees only a modest decrease with doping due to the change in the tilt of the unit cell.

APPENDIX D: Fs-TTR Thermal Model Fitting Algorithm Scripts

1.0 MATLAB Script: Fs-TTR Thermal Model Fitting Algorithm for Sample κ_{zz} and

Thermal Boundary Conductance (σ)

```
%% FIT FS-TTR THERMAL MODEL TO DATA
clear; clc;

% Load experimental data
expt_data = dlmread('C:\Users\'); % [time, signal]

%% FIT KAPPA & SIGMA TO DETERMINE SCALING FACTOR C
% Initial guess for parameters: [k, sigma, c]
initial_params = [0.15, 30e6, 1]; % [W/m-K, W/m^2-K, scale factor]
% Lower and upper bounds
lb = [0.1, 1e6, 0.1];
ub = [400, 400e6, 10000];

% Options for lsqnonlin
options = optimoptions('lsqnonlin', ...
    'Display', 'iter', ...
    'MaxFunEvals', 4000, ...
    'MaxIter', 100, ...
    'OptimalityTolerance', 1e-5);

% Nonlinear least squares fitting
[opt_params, resnorm, residuals, exitflag, output, lambda, jacobian] = ...
    lsqnonlin(@(p) residuals_all_params(p, expt_data), initial_params, lb, ub,
    options);

% Extract optimized parameters
opt_k = opt_params(1);
opt_sigma = opt_params(2);
opt_c = opt_params(3);

fprintf('\n--- First Fit Results (k, sigma, c) ---\n');
fprintf('Opt. thermal conductivity k: %.4f W/m-K\n', opt_k);
fprintf('Opt. boundary conductance sigma: %.4e W/m^2-K\n', opt_sigma);
fprintf('Opt. scaling factor c: %.4f\n', opt_c);

%% FIT KAPPA & SIGMA USING FIXED SCALING FACTOR C
initial_params_2 = [opt_k, opt_sigma];
lb2 = [0.01, 1e6];
ub2 = [400, 400e6];

[opt_params_2, resnorm2, residuals2, exitflag2, output2, lambda2, jacobian2] = ...
    lsqnonlin(@(p) residuals_k_sigma_only(p, expt_data, opt_c), ...
    initial_params_2, lb2, ub2, options);

opt_k2 = opt_params_2(1);
opt_sigma2 = opt_params_2(2);

fprintf('\n--- Second Fit Results (k, sigma | c fixed) ---\n');
```

```

fprintf('Opt. thermal conductivity k: %.4f W/m-K\n', opt_k2);
fprintf('Opt. boundary conductance sigma: %.4e W/m^2-K\n', opt_sigma2);
fprintf('Fixed scaling factor c: %.4f\n', opt_c);

%% CALCULATE PERCENT NOISE
time_exp = expt_data(:,1);
signal_exp = expt_data(:,2);

calc_data_final = TDTR_func(opt_k2, opt_sigma2);
model_fit = interp1(calc_data_final(:,1), calc_data_final(:,2), ...
    time_exp, 'linear', 'extrap');

scaled_exp_signal = opt_c * signal_exp;
residuals_vec = scaled_exp_signal - model_fit;

% Absolute noise standard deviation from residuals
noise_std = std(residuals_vec);

% RMS-based percent noise
signal_rms = sqrt(mean(scaled_exp_signal.^2));
if isfinite(signal_rms) && signal_rms > 0
    noise_percent = 100 * noise_std / signal_rms;
else
    noise_percent = NaN;
end

fprintf('\n--- Noise Metrics (from second fit) ---\n');
fprintf('Residual norm: %.6f\n', resnorm2);
fprintf('Noise std: %.6e\n', noise_std);
fprintf('Signal RMS: %.6e\n', signal_rms);
fprintf('Percent noise (relative to signal RMS): %.4f%%\n', noise_percent);

%% CALCULATE PARAMETER UNCERTAINTIES

nparams2 = length(opt_params_2);
ndata2 = numel(residuals_vec);

% Basic residual variance (mean squared error):
residual_variance2 = sum(residuals_vec.^2) / (ndata2 - nparams2);

% Covariance from Jacobian: Cov(p) ≈ sigma^2 * (J^T J)^(-1)
JTJ = jacobian2' * jacobian2;
param_cov2 = residual_variance2 * inv(full(JTJ));

% 1-sigma standard uncertainties
param_std2 = sqrt(diag(param_cov2));

fprintf('\n--- Parameter Uncertainties, second fit (1-sigma, basic) ---\n');
fprintf(' k: %.4f W/m-K\n', param_std2(1));
fprintf(' sigma: %.4e W/m^2-K\n', param_std2(2));

%% PLOT FIT (Linear time)
figure;
plot(time_exp, model_fit, 'r-', 'LineWidth', 2, 'DisplayName', 'Model Fit (2-
param)');

```

```

hold on;
plot(time_exp, scaled_exp_signal, 'bo', 'DisplayName', 'Scaled Exp Data');
xlabel('Time (ps)');
ylabel('Signal (A.U.)');
title('TDTR Data Fit (Linear Time, c fixed from first fit)');
legend('Location', 'best');
grid on;

%% PLOT FIT (Logarithmic time)
figure;
semilogx(time_exp, model_fit, 'r-', 'LineWidth', 2, 'DisplayName', 'Model Fit (2-
param)');
hold on;
semilogx(time_exp, scaled_exp_signal, 'bo', 'DisplayName', 'Scaled Exp Data');
xlabel('Time (ps) [log scale]');
ylabel('Signal (A.U.)');
title('TDTR Data Fit (Log Time, c fixed from first fit)');
legend('Location', 'best');
grid on;

%% LOCAL FUNCTION: residuals vector for all parameters (k, sigma, c)
function residuals = residuals_all_params(params, expt_data)
    k = params(1);
    sigma = params(2);
    c = params(3);
    calc_data = TDTR_func(k, sigma);
    model_interp = interp1(calc_data(:,1), calc_data(:,2), expt_data(:,1),
'linear', 'extrap');
    residuals = c * expt_data(:,2) - model_interp;
end

%% LOCAL FUNCTION: residuals when only k, sigma are free; c fixed
function residuals = residuals_k_sigma_only(params, expt_data, c_fixed)
    k = params(1);
    sigma = params(2);
    calc_data = TDTR_func(k, sigma);
    model_interp = interp1(calc_data(:,1), calc_data(:,2), expt_data(:,1),
'linear', 'extrap');
    residuals = c_fixed * expt_data(:,2) - model_interp;
end

%% LOCAL FUNCTION: TTR thermal model
function output = TDTR_func(Kf, sigma)
    % Model parameters
    Lm = 100E-9; % metal thickness (m)
    Lf = 100E-9; % film thickness (m)
    total_t = 3E-9; % total simulation time (s)
    dx = 5E-10; % spatial step (m)
    dt = 1E-12; % time step (s)
    R = 0.87; % reflectance
    J = 5; % laser power (J/m^2)
    delta = 7.62E-9; % penetration depth (m)
    Cm = 2.42E6; % volumetric heat capacity metal [J/m^3K]
    Km = 100; % thermal conductivity metal [W/m-K]
    Cf = 1.25E6; % volumetric heat capacity film [J/m^3K]

```

```

k = round(Lm/dx);
n = k + round(Lf/dx);
steps = round(total_t/dt);

am = Km/Cm;
af = Kf/Cf;
gm = (am*dt) / (dx^2);
gf = (af*dt) / (dx^2);
pm = (2*sigma*dx)/Km;
pf = (2*sigma*dx)/Kf;

A = pm/(3+pf);
B = 3 + pm - pf*A;
C = pf/(3+pm);
D = 3 + pf - pm*C;

T = zeros(n, steps);
T(1:k,1) = J*(1-R)/(Cm*delta)*exp(-(1:k)*dx/delta);

Lx = spdiags([-gm*ones(k-2,1) 2*(1+gm)*ones(k-2,1) -gm*ones(k-2,1); ...
             -gf*ones(n-k-2,1) 2*(1+gf)*ones(n-k-2,1) -gf*ones(n-k-2,1)], ...
             [-1 0 1], n-4, n-4);

Lx(1,1) = 2 + 2/3*gm; Lx(1,2) = -2/3*gm;
Lx(k-2,k-3) = gm/B - gm; Lx(k-2,k-2) = 2*(1+gm) - 4*gm/B;
Lx(k-2,k-1) = -4*gm*A/B; Lx(k-2,k) = gm*A/B;
Lx(k-1,k-3) = gf*C/D; Lx(k-1,k-2) = -4*gf*C/D;
Lx(k-1,k-1) = 2*(1+gf) - 4*gf/D; Lx(k-1,k) = gf/D - gf;
Lx(n-4,n-5) = -2/3*gf; Lx(n-4,n-4) = 2 + 2/3*gf;

Rx1 = spdiags([gm*ones(k,1) 2*(1-gm)*ones(k,1) gm*ones(k,1)], [0 1 2], k-2,
k);
Rx2 = spdiags([gf*ones(n-k,1) 2*(1-gf)*ones(n-k,1) gf*ones(n-k,1)], [0 1 2],
n-k-2, n-k);

for i = 2:steps
    RHS = [Rx1*T(1:k,i-1); Rx2*T(k+1:n,i-1)];
    LHS = Lx\RHS;
    T(2:k-1,i) = LHS(1:k-2);
    T(k+2:n-1,i) = LHS(k-1:end);
    T(1,i) = 4/3*T(2,i) - 1/3*T(3,i);
    T(k,i) = -1/B*T(k-2,i) + 4/B*T(k-1,i) + 4*A/B*T(k+2,i) - A/B*T(k+3,i);
    T(k+1,i) = -C/D*T(k-2,i) + 4*C/D*T(k-1,i) + 4/D*T(k+2,i) - 1/D*T(k+3,i);
    T(n,i) = 4/3*T(n-1,i) - 1/3*T(n-2,i);
end

t = dt*(0:steps-1)*1e12; % time in ps

reflectance = zeros(steps,1);
for i = 1:steps
    reflectance(i) = trapz((1:k), exp(-(1:k)*dx/delta) .* T(1:k,i)');
end

output = [t', reflectance];
end

```

2.0 MATLAB Script: Modified Fs-TTR Thermal + Damped Harmonic Oscillator (DMO)

Model Fitting Algorithm for Sample κ and Oscillation Characteristics

```

%% FIT TTR THERMAL + DAMPED HARMONIC OSCILLATOR MODEL
%
% PHYSICAL MODEL
%
% The oscillatory component is treated as a general damped harmonic
% oscillator (DHO) – the impulse response of the equation of motion:
%
%       $\ddot{x} + 2\gamma\dot{x} + \omega_0^2x = 0$ 
%
% For the underdamped case ( $\gamma < \omega_0$ ), the solution is:
%
%       $x(t) = \exp(-\gamma t) \cdot [A1 \cdot \sin(\omega_d \cdot t) + A2 \cdot \cos(\omega_d \cdot t)]$ 
%
% where:
%       $\omega_d = \sqrt{\omega_0^2 - \gamma^2}$       damped angular frequency      (rad/ps)
%       $\gamma$       damping coefficient      (rad/ps = 1/ps)
%       $\omega_0 = \sqrt{\omega_d^2 + \gamma^2}$       natural angular frequency      (rad/ps)
%       $Q = \omega_0 / (2\gamma)$       quality factor      (dimensionless)
%       $\tau = 1/\gamma$       amplitude decay time      (ps)
%       $f_d = \omega_d / (2\pi)$       damped frequency      (THz)
%       $T_d = 1/f_d$       damped period      (ps)
%
% No assumptions are made about the physical origin of the oscillation.
%
% VARPRO STRUCTURE
%
% Parameterize by the two natural nonlinear quantities  $\{\gamma, \omega_d\}$  – which
% map one-to-one to  $\{\tau, f_d\}$  – and solve for  $\{A1, A2\}$  linearly:
%
%       $\Phi = [\exp(-\gamma t) \cdot \sin(\omega_d \cdot t), \exp(-\gamma t) \cdot \cos(\omega_d \cdot t)]$        $[n \times 2]$ 
%       $[A1; A2] = \Phi \backslash r_{osc}$ 
%
% Nonlinear params fitted by lsqnonlin:  $\{\gamma, \omega_d\}$ 
% Linear params solved analytically:  $\{A1, A2\}$ 
%
% Derived:
%       $\omega_0 = \sqrt{\omega_d^2 + \gamma^2}$ 
%       $Q = \omega_0 / (2\gamma)$ 
%       $A = \sqrt{A1^2 + A2^2}$       oscillation amplitude
%       $\phi = \text{atan2}(A2, A1)$       initial phase
%
% STAGE LAYOUT
%
% Stage 1 : TTR-only fit (full signal)      →  $k_0, c$  ( $c$  is final)
% Stage 2 : Period + damping scan on residuals → seed  $f_d, \gamma$ 
% Stage 3 : DHO fit on TTR residuals      →  $A1, A2, \gamma, \omega_d$ 
% Stage 4 : VARPRO re-fit for  $k$  ( $c$  fixed)      →  $k_{final}$ 

clear; clc;

%% — User settings —————

```

```

data_file = 'C:\Users\ ';
SIGMA_FIXED = 48e6; % W/m2·K – interface conductance, held fixed
osc_t0 = 0; % ps – oscillator onset (0 = present from t=0)

% k search bounds
k_lb = 0.001; k_ub = 5; % W/m·K

% DHO parameter bounds
% γ bounds (damping, 1/ps): lower = very lightly damped, upper = overdamped
limit
gamma_lb = 1e-5; gamma_ub = []; % gamma_ub set from data after load
% wd bounds (rad/ps): set from data after load
wd_lb = []; wd_ub = [];

% LUT resolution
N_lut = 80;

%% — Load data —————

expt_data = dlmread(data_file);
time_exp = expt_data(:,1);
signal_exp = expt_data(:,2);
n_pts = numel(time_exp);

if osc_t0 > 0
    osc_mask = time_exp >= osc_t0;
else
    osc_mask = true(n_pts, 1);
end
t_osc = time_exp(osc_mask);
t_span = t_osc(end) - t_osc(1);
dt_osc = mean(diff(t_osc));

% — Automatic parameter bounds derived from data —————
%
% γ upper bound: decay time τ = 1/γ must be at least one sampling
% interval, so γ_ub = 1/dt.
gamma_ub = 1 / dt_osc;

% wd bounds: Nyquist sets the upper limit; require at least 2 full cycles
% in the observation window to set the lower limit.
fd_nyq = 1 / (2 * dt_osc); % THz – Nyquist frequency
fd_min = 2 / t_span; % THz – at least 2 cycles visible
wd_lb = 2*pi * fd_min; % rad/ps
wd_ub = 2*pi * fd_nyq; % rad/ps

fprintf('Loaded %d points. Oscillator region: %d points\n', n_pts,
sum(osc_mask));
fprintf('Parameter bounds:\n');
fprintf(' gamma : [%.4e, %.4e] 1/ps\n', gamma_lb, gamma_ub);
fprintf(' wd : [%.4e, %.4e] rad/ps (fd: %.4e – %.4e THz)\n', ...
wd_lb, wd_ub, wd_lb/(2*pi), wd_ub/(2*pi));

% STAGE 1: TTR-only fit – recover c (and rough k seed)

```

```

fprintf('\n--- Stage 1: TDTR-only fit (recover c) ---\n');

options_tdtr = optimoptions('lsqnonlin','Display','off', ...
    'MaxFunEvals',4000,'MaxIter',150,'OptimalityTolerance',1e-8);

% 1a: joint k and c
[p1a, ~] = lsqnonlin( ...
    @(p) tdtr_resid(p(1), SIGMA_FIXED, p(2), time_exp, signal_exp), ...
    [0.3, 1], [k_lb, 0.01], [k_ub, 1e4], options_tdtr);
k0 = p1a(1);
c = p1a(2); % <<< final c, held fixed from here on

fprintf('Stage 1a: k0 = %.4f W/m-K c = %.4f (c is now fixed)\n', k0, c);

% 1b: fix c, refit k
[p1b, ~] = lsqnonlin( ...
    @(p) tdtr_resid(p(1), SIGMA_FIXED, c, time_exp, signal_exp), ...
    k0, k_lb, k_ub, options_tdtr);
k0 = p1b(1);
fprintf('Stage 1b: k0 = %.4f W/m-K c = %.4f (fixed)\n', k0, c);

% STAGE 2: Period + damping scan on TTR-subtracted residuals
%
% Scan a 2-D grid of {fd,  $\gamma$ } to seed the nonlinear optimizer.
% For each trial (fd,  $\gamma$ ), VARPRO solves {A1, A2} linearly and
% records the residual sum of squares. The grid minimum provides
% a robust starting point that does not require manual guessing.
%
% Grid design:
% fd : 300 points log-spaced from fd_min to fd_nyq
%  $\gamma$  : 20 points log-spaced from gamma_lb to gamma_ub/10

fprintf('\n--- Stage 2: 2-D {fd, gamma} scan ---\n');

calc0 = TDTR_func(k0, SIGMA_FIXED);
tdtr0 = interp1(calc0(:,1), calc0(:,2), time_exp, 'linear', 'extrap');
resid0 = c * signal_exp - tdtr0;
r_osc = resid0(osc_mask);

n_fd = 300;
n_gam = 20;
fd_grid = linspace(wd_lb/(2*pi), wd_ub/(2*pi), n_fd)';
gam_grid = logspace(log10(gamma_lb), log10(gamma_ub/10), n_gam)';

rss_2d = zeros(n_fd, n_gam);
for ifd = 1:n_fd
    wd_try = 2*pi * fd_grid(ifd);
    for ig = 1:n_gam
        gam_try = gam_grid(ig);
        Phi = dho_basis(t_osc, gam_try, wd_try);
        ab = Phi \ r_osc;
        rss_2d(ifd, ig) = sum((r_osc - Phi*ab).^2);
    end
end

[~, idx] = min(rss_2d(:));

```

```

[ifd_best, ig_best] = ind2sub([n_fd, n_gam], idx);
fd_seed = fd_grid(ifd_best);
gamma_seed = gam_grid(ig_best);
wd_seed = 2*pi * fd_seed;

fprintf('2-D scan: fd = %.4e THz Td = %.1f ps gamma = %.4e 1/ps tau = %.1f
ps\n', ...
    fd_seed, 1/fd_seed, gamma_seed, 1/gamma_seed);

% Derived seed quantities
w0_seed = sqrt(wd_seed^2 + gamma_seed^2);
Q_seed = w0_seed / (2*gamma_seed);
fprintf('          omega0 = %.4e rad/ps Q = %.2f\n', w0_seed, Q_seed);

% STAGE 3: DHO fit on TTR-subtracted residuals (c fixed)
%
% Nonlinear params: g = [gamma, wd] (2 params)
% Linear params: [A1, A2] (2 params, VARPRO)
%
% The 2-D scan provides a good seed so only a modest multi-start
% grid is needed around the scan minimum.

fprintf('\n--- Stage 3: DHO fit on oscillator residuals ---\n');

lb_s3 = [gamma_lb, wd_lb];
ub_s3 = [gamma_ub, wd_ub];

options_ms = optimoptions('lsqnonlin','Display','off', ...
    'MaxFunEvals',300,'MaxIter',60, ...
    'OptimalityTolerance',1e-5,'FunctionTolerance',1e-5);
options_pol = optimoptions('lsqnonlin','Display','off', ...
    'MaxFunEvals',6000,'MaxIter',500, ...
    'OptimalityTolerance',1e-11,'FunctionTolerance',1e-11,'StepTolerance',1e-11);

% Refine around scan minimum
gam_cands = gamma_seed * [0.3, 0.6, 1.0, 1.7, 3.0];
wd_cands = wd_seed * [0.7, 0.85, 1.0, 1.15, 1.3];

best_rn3 = Inf;
best_g3 = [gamma_seed, wd_seed];

for gi = 1:length(gam_cands)
for wi = 1:length(wd_cands)
    g0 = [gam_cands(gi), wd_cands(wi)];
    try
        [gt, rn] = lsqnonlin( ...
            @(g) dho_varpro_resid(g, t_osc, r_osc), ...
            g0, lb_s3, ub_s3, options_ms);
        if rn < best_rn3; best_rn3 = rn; best_g3 = gt; end
    catch; end
end; end

n_starts3 = length(gam_cands) * length(wd_cands);
fprintf(' Multi-start complete (%d starts). Best RSS = %.4e\n', n_starts3,
    best_rn3);

```

```

[g_s3, ~, ~, ~, ~, ~, ~] = lsqnonlin( ...
    @(g) dho_varpro_resid(g, t_osc, r_osc), ...
    best_g3, lb_s3, ub_s3, options_pol);

gamma_s3 = g_s3(1);
wd_s3    = g_s3(2);

Phi3 = dho_basis(t_osc, gamma_s3, wd_s3);
ab3   = Phi3 \ r_osc;
A_s3  = sqrt(ab3(1)^2 + ab3(2)^2);
w0_s3 = sqrt(wd_s3^2 + gamma_s3^2);
Q_s3  = w0_s3 / (2*gamma_s3);

fprintf('Stage 3:   fd = %.4e THz   tau = %.1f ps   A = %.4e   Q = %.2f\n', ...
    wd_s3/(2*pi), 1/gamma_s3, A_s3, Q_s3);

% STAGE 4: VARPRO re-fit for k (c fixed, DHO modelled jointly)
%
% Nonlinear params: g = [k, gamma, wd]   (3 params)
% Linear params:    [A1, A2]             (2 params, VARPRO)
%
% Model (scaled-signal space):
%   c·signal = TTR(k) + DHO(gamma, wd, A1, A2)
% → rearranged: c·signal - TTR(k) = Phi · [A1; A2]

fprintf('\n--- Stage 4: VARPRO k re-fit (c fixed, DHO joint) ---\n');

% Build LUT
fprintf('  Building LUT (%d points)...\n', N_lut);
k_lut = logspace(log10(k_lb), log10(k_ub), N_lut);
lut_tic = tic;
tmp     = TDTR_func(k_lut(1), SIGMA_FIXED);
t_lut   = tmp(:,1);
lut_refl = zeros(length(t_lut), N_lut);
lut_refl(:,1) = tmp(:,2);
for ik = 2:N_lut
    tmp = TDTR_func(k_lut(ik), SIGMA_FIXED);
    lut_refl(:,ik) = tmp(:,2);
end
lut_on_exp = zeros(n_pts, N_lut);
for ik = 1:N_lut
    lut_on_exp(:,ik) = interp1(t_lut, lut_refl(:,ik), time_exp, 'linear',
    'extrap');
end
fprintf('  LUT built in %.1f s\n', toc(lut_tic));

scaled_signal = c * signal_exp;

lb_n14 = [k_lb, gamma_lb, wd_lb];
ub_n14 = [k_ub, gamma_ub, wd_ub];

k_grid4 = k0 * [0.5, 1.0, 1.5, 2.0];
gam_grid4 = gamma_s3 * [0.6, 1.0, 1.5];
wd_grid4 = wd_s3 * [0.9, 1.0, 1.1];

options_vp_ms = optimoptions('lsqnonlin','Display','off', ...

```

```

    'MaxFunEvals',400,'MaxIter',70, ...
    'OptimalityTolerance',1e-6,'FunctionTolerance',1e-6, ...
    'FiniteDifferenceStepSize',1e-4);

best_rn4 = Inf;
best_n14 = [k0, gamma_s3, wd_s3];
n_ms4 = length(k_grid4)*length(gam_grid4)*length(wd_grid4);
fprintf(' Multi-start: %d starts...\n', n_ms4);

for ki = 1:length(k_grid4)
for gi = 1:length(gam_grid4)
for wi = 1:length(wd_grid4)
    g0 = [k_grid4(ki), gam_grid4(gi), wd_grid4(wi)];
    try
        [gt, rn] = lsqnonlin( ...
            @(g) varpro_k_resid_lut_dho(g, lut_on_exp, k_lut, ...
                scaled_signal, osc_mask, t_osc), ...
            g0, lb_n14, ub_n14, options_vp_ms);
        if rn < best_rn4; best_rn4 = rn; best_n14 = gt; end
    catch; end
end; end; end

options_vp_pol = optimoptions('lsqnonlin','Display','iter', ...
    'MaxFunEvals',6000,'MaxIter',500, ...
    'OptimalityTolerance',1e-11,'FunctionTolerance',1e-11,'StepTolerance',1e-11);

[g_opt, ~, resid_vp, ~, ~, ~, jac_vp] = lsqnonlin( ...
    @(g) varpro_k_resid_full_dho(g, SIGMA_FIXED, time_exp, ...
        scaled_signal, osc_mask, t_osc), ...
    best_n14, lb_n14, ub_n14, options_vp_pol);

opt_k = g_opt(1);
opt_gamma = g_opt(2);
opt_wd = g_opt(3);

% Recover final oscillator linear coefficients
calc_f = TDTR_func(opt_k, SIGMA_FIXED);
tdtr_f = interp1(calc_f(:,1), calc_f(:,2), time_exp, 'linear', 'extrap');
r_for_osc = scaled_signal - tdtr_f;

Phi_f = zeros(n_pts, 2);
Phi_f(osc_mask, :) = dho_basis(t_osc, opt_gamma, opt_wd);
ab_f = Phi_f \ r_for_osc;

opt_A = sqrt(ab_f(1)^2 + ab_f(2)^2);
opt_phi = atan2(ab_f(2), ab_f(1));

% Derived physical quantities
opt_tau = 1 / opt_gamma;
opt_fd = opt_wd / (2*pi);
opt_Td = 1 / opt_fd;
opt_w0 = sqrt(opt_wd^2 + opt_gamma^2);
opt_f0 = opt_w0 / (2*pi);
opt_Q = opt_w0 / (2*opt_gamma);

% Uncertainties + derived quantity propagation

```

```

%
% Full parameter vector: [k, gamma, wd, A1, A2] (5 params)
% Jacobian: [J_n1(n×3) | -Phi_f(n×2)]
%
% Derived quantities and their delta-method uncertainties:
%   tau = 1/gamma          → std_tau = std_gamma / gamma^2
%   fd  = wd/(2π)         → std_fd  = std_wd / (2π)
%   w0  = sqrt(wd^2 + gamma^2) → propagate cov(gamma,gamma), cov(wd,wd),
cov(gamma,wd)
%   Q   = w0/(2*gamma)     → propagate the same

n_obs = numel(resid_vp);
n_par = 5;
var_r = sum(resid_vp.^2) / max(n_obs - n_par, 1);

Jfull = [full(jac_vp), -Phi_f];
JTJ_full = Jfull' * Jfull;
if rcond(JTJ_full) > 1e-15
    cov_full = var_r * inv(JTJ_full);
    std_full = sqrt(abs(diag(cov_full)));
else
    cov_full = NaN(n_par); std_full = NaN(n_par, 1);
    warning('Jacobian near-singular – covariance unreliable.');
```

end

```

std_k      = std_full(1);
std_gamma  = std_full(2);
std_wd     = std_full(3);

if ~any(isnan(std_full))
    % tau = 1/gamma
    std_tau = std_gamma / opt_gamma^2;

    % fd = wd/(2*pi)
    std_fd = std_wd / (2*pi);

    % w0 = sqrt(wd^2 + gamma^2)
    dw0_dwd = opt_wd / opt_w0;
    dw0_dgam = opt_gamma / opt_w0;
    var_w0 = dw0_dwd^2 * cov_full(3,3) + ...
             dw0_dgam^2 * cov_full(2,2) + ...
             2*dw0_dwd*dw0_dgam * cov_full(2,3);
    std_w0 = sqrt(abs(var_w0));
    std_f0 = std_w0 / (2*pi);

    % Q = w0/(2*gamma) → dQ/dgamma = (dw0/dgamma*2*gamma - w0*2)/(4*gamma^2)
    %                  dQ/dwd   = dw0/dwd / (2*gamma)
    dQ_dgam = (dw0_dgam * 2*opt_gamma - opt_w0 * 2) / (4*opt_gamma^2);
    dQ_dwd  = dw0_dwd / (2*opt_gamma);
    var_Q = dQ_dgam^2 * cov_full(2,2) + ...
            dQ_dwd^2 * cov_full(3,3) + ...
            2*dQ_dgam*dQ_dwd * cov_full(2,3);
    std_Q = sqrt(abs(var_Q));

    % Amplitude and phase (linear params at indices 4,5)
    a1 = ab_f(1); a2 = ab_f(2);
```

```

    dA1 = a1/opt_A; dA2 = a2/opt_A;
    var_A = dA1^2*cov_full(4,4) + dA2^2*cov_full(5,5) + 2*dA1*dA2*cov_full(4,5);
    std_A = sqrt(abs(var_A));
    dp1 = a2/(a1^2+a2^2); dp2 = -a1/(a1^2+a2^2);
    var_phi = dp1^2*cov_full(4,4) + dp2^2*cov_full(5,5) + 2*dp1*dp2*cov_full(4,5);
    std_phi = sqrt(abs(var_phi));
else
    std_tau=NaN; std_fd=NaN; std_w0=NaN; std_f0=NaN;
    std_Q=NaN; std_A=NaN; std_phi=NaN;
end

%% — Reconstruct model curves —————

tdtr_curve = tdtr_f;

osc_curve = zeros(n_pts, 1);
if any(osc_mask)
    osc_curve(osc_mask) = ...
        ab_f(1) * exp(-opt_gamma*t_osc) .* sin(opt_wd*t_osc) + ...
        ab_f(2) * exp(-opt_gamma*t_osc) .* cos(opt_wd*t_osc);
end

model_total = tdtr_curve + osc_curve;
scaled_data = scaled_signal;
final_resid = scaled_data - model_total;

noise_std = std(final_resid);
signal_rms = sqrt(mean(scaled_data.^2));
noise_pct = 100 * noise_std / signal_rms;

%% — Print results —————

fprintf('\n=====');
fprintf(' FINAL RESULTS (sigma fixed = %.3e W/m^2.K)\n', SIGMA_FIXED);
fprintf(' DAMPED HARMONIC OSCILLATOR MODEL\n');
fprintf('=====');
fprintf('Thermal:\n');
fprintf(' k = %.4f +/- %.4f W/m.K\n', opt_k, std_k);
fprintf(' c = %.4f (fixed from Stage 1)\n', c);
fprintf('Oscillator – fitted parameters:\n');
fprintf(' gamma = %.4e +/- %.2e 1/ps (damping coefficient)\n', opt_gamma,
std_gamma);
fprintf(' wd = %.4e +/- %.2e rad/ps (damped ang. freq.)\n', opt_wd,
std_wd);
fprintf('Oscillator – derived quantities:\n');
fprintf(' tau = %.1f +/- %.1f ps (= 1/gamma, amplitude decay time)\n',
opt_tau, std_tau);
fprintf(' fd = %.4e +/- %.2e THz (damped frequency)\n', opt_fd, std_fd);
fprintf(' Td = %.1f ps (damped period)\n', opt_Td);
fprintf(' omega0 = %.4e +/- %.2e rad/ps (natural ang. freq.)\n', opt_w0,
std_w0);
fprintf(' f0 = %.4e +/- %.2e THz (natural frequency)\n', opt_f0, std_f0);
fprintf(' Q = %.3f +/- %.3f (quality factor = omega0/(2*gamma))\n',
opt_Q, std_Q);
fprintf(' A = %.4e +/- %.2e (oscillation amplitude)\n', opt_A, std_A);

```

```

fprintf(' phi      = %.4f +/- %.4f rad (initial phase)\n',    opt_phi,
std_phi);
if opt_Q < 0.5
    fprintf(' NOTE: Q < 0.5 – system is overdamped. DHO solution still
valid\n');
    fprintf('          but the oscillation may not be physically meaningful.\n');
elseif opt_Q < 3
    fprintf(' NOTE: Q = %.2f – moderately damped oscillator.\n', opt_Q);
else
    fprintf(' NOTE: Q = %.2f – lightly damped / high-Q resonance.\n', opt_Q);
end
fprintf('Noise:\n');
fprintf(' Residual std:  %.4e\n', noise_std);
fprintf(' Signal RMS:    %.4e\n', signal_rms);
fprintf(' Percent noise: %.4f%%\n', noise_pct);

% Plots

col_data = [0.15  0.40  0.70];
col_tdtr = [0.85  0.20  0.10];
col_osc   = [0.10  0.60  0.25];
col_env   = [0.70  0.40  0.00];
col_comb  = [0.10  0.10  0.10];
col_res   = [0.50  0.50  0.55];
col_scan  = [0.20  0.45  0.70];

t_fine    = linspace(max(min(t_osc), 1e-6), max(t_osc), 2000)';
env_fine  = exp(-opt_gamma * t_fine);
osc_fine  = ab_f(1)*env_fine.*sin(opt_wd*t_fine) + ...
            ab_f(2)*env_fine.*cos(opt_wd*t_fine);
env_pos   = opt_A * env_fine;
env_neg   = -opt_A * env_fine;

tdtr_fine = interp1(calc_f(:,1), calc_f(:,2), t_fine, 'linear', 'extrap');
osc_fine_all = ab_f(1)*exp(-opt_gamma*t_fine).*sin(opt_wd*t_fine) + ...
               ab_f(2)*exp(-opt_gamma*t_fine).*cos(opt_wd*t_fine);
model_fine = tdtr_fine + osc_fine_all;

% Figure 1: Full fit – linear
fh1 = figure('Name','Fit – linear','Units','inches','Position',[1 1 10
5.5], 'Color','w');
ax1 = axes('Parent',fh1);
plot(ax1, time_exp, scaled_data, 'o', 'Color', col_data, 'MarkerSize', 6, ...
'DisplayName', 'Data (c \times signal)');
hold(ax1, 'on');
plot(ax1, t_fine, model_fine, '-', 'Color', col_comb, 'LineWidth', 2.2, ...
'DisplayName', 'TDTR + DHO');
plot(ax1, t_fine, tdtr_fine, '--', 'Color', col_tdtr, 'LineWidth', 1.6, ...
'DisplayName', 'TDTR component');
if osc_t0 > 0
    xline(ax1, osc_t0, '--', 'Color', [.55 .55
.55], 'LineWidth', 1.2, 'HandleVisibility', 'off');
end
fmt(ax1);
xlabel(ax1, 'Time (ps)', 'FontSize', 12);
ylabel(ax1, 'c \times Signal (A.U.)', 'FontSize', 12);

```

```

title(ax1, sprintf('k = %.4f +/- %.4f W/m·K    f_d = %.4e THz    \\tau = %.0f ps
Q = %.2f', ...
    opt_k, std_k, opt_fd, opt_tau, opt_Q), 'FontSize',11);
lg1 = legend(ax1, 'Location', 'northeast', 'FontSize',10); lg1.Box='on';
lg1.Color='w';

% Figure 2: Full fit – log
fh2 = figure('Name','Fit – log','Units','inches','Position',[1.5 1.5 10
5.5], 'Color','w');
ax2 = axes('Parent',fh2);
semilogx(ax2, time_exp, scaled_data,
'o','Color',col_data,'MarkerSize',6,'DisplayName','Data');
hold(ax2,'on');
semilogx(ax2, t_fine, model_fine, '-
','Color',col_comb,'LineWidth',2.2,'DisplayName','TDTR + DHO');
semilogx(ax2, t_fine, tdtr_fine, '--
','Color',col_tdtr,'LineWidth',1.6,'DisplayName','TDTR component');
set(ax2,'XScale','log'); fmt(ax2);
xlabel(ax2,'Time (ps) [log scale]', 'FontSize',12);
ylabel(ax2,'c \\times Signal (A.U.)', 'FontSize',12);
title(ax2, sprintf('k = %.4f W/m·K    f_d = %.4e THz    Q = %.2f', opt_k, opt_fd,
opt_Q), 'FontSize',11);
lg2 = legend(ax2, 'Location', 'northeast', 'FontSize',10); lg2.Box='on';
lg2.Color='w';

% Figure 3: Isolated oscillator with envelope
fh3 = figure('Name','DHO component','Units','inches','Position',[2 2 10
5.5], 'Color','w');
ax3 = axes('Parent',fh3);
plot(ax3, time_exp(osc_mask), scaled_data(osc_mask)-tdtr_curve(osc_mask), ...
'o','Color',col_data,'MarkerSize',6,'DisplayName','Data minus TDTR');
hold(ax3,'on');
plot(ax3, t_fine, osc_fine, '-', 'Color',col_osc,'LineWidth',2.2, ...
'DisplayName',sprintf('DHO (A=%.3e, T_d=%.0f ps, Q=%.2f)', opt_A, opt_Td,
opt_Q));
plot(ax3, t_fine, env_pos, '--', 'Color',col_env,'LineWidth',1.4, ...
'DisplayName',sprintf('Envelope exp(-t/\\tau), \\tau = %.0f ps', opt_tau));
plot(ax3, t_fine, env_neg, '--
','Color',col_env,'LineWidth',1.4,'HandleVisibility','off');
yline(ax3, 0, '--', 'Color',[.6 .6 .6], 'LineWidth',1, 'HandleVisibility','off');
fmt(ax3);
xlabel(ax3,'Time (ps)', 'FontSize',12);
ylabel(ax3,'Oscillator amplitude (A.U.)', 'FontSize',12);
title(ax3, sprintf('Isolated DHO    \\omega_0 = %.4e rad/ps    \\omega_d = %.4e
rad/ps    Q = %.2f', ...
    opt_w0, opt_wd, opt_Q), 'FontSize',11);
lg3 = legend(ax3, 'Location', 'northeast', 'FontSize',10); lg3.Box='on';
lg3.Color='w';

% Figure 4: Final residuals
fh4 = figure('Name','Residuals','Units','inches','Position',[2.5 2.5 10
4.0], 'Color','w');
ax4 = axes('Parent',fh4);
plot(ax4, time_exp, final_resid, '-
','Color',col_res,'LineWidth',1.2,'DisplayName','Residuals');
yline(ax4, 0, 'k-', 'LineWidth',1, 'HandleVisibility','off');

```

```

yline(ax4, noise_std, 'r--','LineWidth',1,'HandleVisibility','off');
yline(ax4, -noise_std, 'r--','LineWidth',1,'HandleVisibility','off');
fmt(ax4);
xlabel(ax4,'Time (ps)','FontSize',12);
ylabel(ax4,'Residual (A.U.)','FontSize',12);
title(ax4, sprintf('Residuals (noise = %.3f%%)', noise_pct), 'FontSize',11);
lg4 = legend(ax4,'Location','northeast','FontSize',10); lg4.Box='on';
lg4.Color='w';

% Figure 5: 2-D scan heatmap (fd vs gamma)
fh5 = figure('Name','2-D scan','Units','inches','Position',[3 3 9 5],'Color','w');
ax5 = axes('Parent',fh5);
% log-transform RSS for better contrast
log_rss = log10(rss_2d + eps);
imagesc(ax5, log10(gam_grid), fd_grid*1e3, log_rss); % fd in GHz for readability
axis(ax5,'xy');
colormap(ax5, flipud(hot));
cb = colorbar(ax5);
cb.Label.String = 'log_{10}(RSS)';
hold(ax5,'on');
% Mark scan minimum and final solution
plot(ax5, log10(gamma_seed), fd_seed*1e3, 'c+','MarkerSize',14,'LineWidth',2, ...
'DisplayName','Scan minimum');
plot(ax5, log10(opt_gamma), opt_fd*1e3, 'g*','MarkerSize',14,'LineWidth',2, ...
'DisplayName','Final solution');
legend(ax5,'Location','northeast','FontSize',10,'Color','w');
xlabel(ax5,'log_{10}(\gamma) (1/ps)','FontSize',12);
ylabel(ax5,'f_d (GHz)','FontSize',12);
title(ax5,'2-D {f_d, \gamma} scan - RSS landscape','FontSize',11);
fmt(ax5);

% LOCAL FUNCTIONS

function fmt(ax)
    set(ax,'FontSize',11,'TickDir','out','Box','on','GridAlpha',0.25);
    grid(ax,'on');
end

% — DHO VARPRO basis: [exp(-gamma*t)*sin(wd*t), exp(-gamma*t)*cos(wd*t)] —
function Phi = dho_basis(t, gamma, wd)
    env = exp(-gamma * t);
    Phi = [env .* sin(wd * t), ...
           env .* cos(wd * t)];
end

% — Stage 3: VARPRO residuals for DHO on TTR residuals —————
function r = dho_varpro_resid(g, t_osc, r_osc)
    % g = [gamma, wd]; linear params [A1, A2] via backslash
    Phi = dho_basis(t_osc, g(1), g(2));
    ab = Phi \ r_osc;
    r = r_osc - Phi * ab;
end

% — Stage 4 multi-start: VARPRO k residuals using LUT —————
function r = varpro_k_resid_lut_dho(g, lut_on_exp, k_lut, ...
    scaled_signal, osc_mask, t_osc)

```

```

% g = [k, gamma, wd]
k = g(1); gamma = g(2); wd = g(3);
n = length(scaled_signal);
tdtr = interp1(k_lut, lut_on_exp', k, 'pchip');
rhs = scaled_signal - tdtr;
Phi = zeros(n, 2);
Phi(osc_mask, :) = dho_basis(t_osc, gamma, wd);
ab = Phi \ rhs;
r = rhs - Phi * ab;
end

% — Stage 4 polish: VARPRO k residuals using full PDE —————
function r = varpro_k_resid_full_dho(g, sigma, time_exp, ...
    scaled_signal, osc_mask, t_osc)

% g = [k, gamma, wd]
k = g(1); gamma = g(2); wd = g(3);
n = length(scaled_signal);
cd = TDTR_func(k, sigma);
tdtr = interp1(cd(:,1), cd(:,2), time_exp, 'linear', 'extrap');
rhs = scaled_signal - tdtr;
Phi = zeros(n, 2);
Phi(osc_mask, :) = dho_basis(t_osc, gamma, wd);
ab = Phi \ rhs;
r = rhs - Phi * ab;
end

% — Stage 1: TTR-only residuals —————
function r = tdtr_resid(k, sigma, c, t_exp, y_exp)
cd = TDTR_func(k, sigma);
mi = interp1(cd(:,1), cd(:,2), t_exp, 'linear', 'extrap');
r = c * y_exp - mi;
end

% — TTR PDE solver —————
function output = TDTR_func(Kf, sigma)
Lm=100E-9; Lf=110E-9; total_t=3.1E-9;
dx=5E-10; dt=1E-12; R=0.90; J=5; delta=7.62E-9;
Cm=2.42E6; Km=100; Cf=1.489E6;
k=round(Lm/dx); n=k+round(Lf/dx); steps=round(total_t/dt);
am=Km/Cm; af=Kf/Cf;
gm=(am*dt)/(dx^2); gf=(af*dt)/(dx^2);
pm=(2*sigma*dx)/Km; pf=(2*sigma*dx)/Kf;
A_bc=pm/(3+pf); B_bc=3+pm-pf*A_bc;
C_bc=pf/(3+pm); D_bc=3+pf-pm*C_bc;
T=zeros(n,steps);
T(1:k,1)=J*(1-R)/(Cm*delta)*exp(-(1:k)*dx/delta);
Lx=spdiags([-gm*ones(k-2,1) 2*(1+gm)*ones(k-2,1) -gm*ones(k-2,1);...
    -gf*ones(n-k-2,1) 2*(1+gf)*ones(n-k-2,1) -gf*ones(n-k-2,1)],...
    [-1 0 1],n-4,n-4);
Lx(1,1)=2+2/3*gm; Lx(1,2)=-2/3*gm;
Lx(k-2,k-3)=gm/B_bc-gm; Lx(k-2,k-2)=2*(1+gm)-4*gm/B_bc;
Lx(k-2,k-1)=-4*gm*A_bc/B_bc; Lx(k-2,k)=gm*A_bc/B_bc;
Lx(k-1,k-3)=gf*C_bc/D_bc; Lx(k-1,k-2)=-4*gf*C_bc/D_bc;
Lx(k-1,k-1)=2*(1+gf)-4*gf/D_bc; Lx(k-1,k)=gf/D_bc-gf;
Lx(n-4,n-5)=-2/3*gf; Lx(n-4,n-4)=2+2/3*gf;
Rx1=spdiags([gm*ones(k,1) 2*(1-gm)*ones(k,1) gm*ones(k,1)],[0 1 2],k-2,k);

```

```

    Rx2=spdiags([gf*ones(n-k,1) 2*(1-gf)*ones(n-k,1) gf*ones(n-k,1)],[0 1 2],n-k-
2,n-k);
    for i=2:steps
        RHS=[Rx1*T(1:k,i-1);Rx2*T(k+1:n,i-1)];
        LHS=Lx\RHS;
        T(2:k-1,i)=LHS(1:k-2); T(k+2:n-1,i)=LHS(k-1:end);
        T(1,i)=4/3*T(2,i)-1/3*T(3,i);
        T(k,i)=-1/B_bc*T(k-2,i)+4/B_bc*T(k-1,i)+4*A_bc/B_bc*T(k+2,i)-
A_bc/B_bc*T(k+3,i);
        T(k+1,i)=-C_bc/D_bc*T(k-2,i)+4*C_bc/D_bc*T(k-1,i)+4/D_bc*T(k+2,i)-
1/D_bc*T(k+3,i);
        T(n,i)=4/3*T(n-1,i)-1/3*T(n-2,i);
    end
    t_ps=dt*(0:steps-1)*1e12;
    refl=zeros(steps,1);
    for i=1:steps
        refl(i)=trapz((1:k),exp(-(1:k)*dx/delta).*T(1:k,i)');
    end
    output=[t_ps',refl];
end

```

APPENDIX E: Standard Operating Procedure (SOP) for Measuring the Specific Heat at Constant Pressure (C_p) using a PerkinElmer DSC 8000

PHASE 1 – Sample Preparation:

- 1) Mass the two pans (sample pan and the empty reference pan) that you want to use in order to correct the data for the difference in pan weights. All pans must be the same material.
- 2) Mass and place your sample material into a sample pan and place the pan in the sample holder with a top. Assemble a reference pan/top using the same material.
- 3) Crimp the sample in the sample pan, as normally done, and crimp the empty reference pan.
- 4) Mass the sample and reference pans, subtracting the mass of the sample material from the sample pan to determine the mass of sample material in the pan.
- 5) Crimp both pans.
- 6) Load the crimped sample and reference pans into the autosampler.

PHASE 2 – Calibration:

- 1) Calibrate the DSC in a normal manner, including an accurate two-point calibration bracketing the temp region of interest & an ordinate calibration using the indium metal melt. (2 °C per minute is suggested for melting standards)

PHASE 3 – Create the Method:

- 1) Open the default method.
- 2) Enter the weight of the sample material into the Sample Info page. Fill the other fields as required, such as the file name.

3) Click on the Program tab, click "Add a step" and select "StepScan Scan Iso" from the options box.

4) Populate the following fields on the Program tab:

- i) Start Temp: set start temp low enough to establish 10 °C or 20 °C of C_p baseline.
- ii) Heating Rate to the 2nd Temp: use low rate such as ≤ 2 °C per minute to allow scanning equilibrium.
- iii) 2nd Temp: Use +2 °C above the initial temp for survey scan without transition or +1 °C for high resolution work.
- iv) Isothermal: 1 min
- v) Reps: Once 2nd Temp is selected, the number of reps is set to achieve the desired ending temper.
- vi) Seconds between points: normally set in the range of 0.2-1.0 second per point.
- vii) Criteria: leave as default

5) Save the StepScan method to selected folder.

6) Load the Method into the Player Editor.

PHASE 4 – Running the Experiment & Taking the Baseline:

- 1) Run the sample by selecting “Start Method.”
- 2) After the sample run, proceed with the empty reference pan experiment.
- 3) Create baseline file by opening the default method for editing; the method should have the same values in each field, except for "Weight" and "File Name". The sample weight should be 0.00 mg.

- 3) Click on the Program tab and repeat steps 3 and 4 from "Create the Method" procedure. The fields should be entered identically.
- 4) Save the baseline StepScan method and click on "Start Method" to run the baseline.
- 5) Load the Method into the Player Editor.

PHASE 5 – Calculating C_p :

- 1) After collecting the baseline and sample data, enter Data Analysis and select the sample and baseline data files. Hold down the CTRL button to select both.
- 2) Click on "Calc" and hover over "Specific Heat" and select "StepScan C_p ".
- 3) Select the "Use a Baseline Curve" check box to utilize baseline data.
- 4) Enter the weights of the sample and reference pans and the pan material.
- 5) In the Algorithm fields, "StepScan From Area" is more robust than "StepScan From Delta Y" if thermal equilibrium is not being achieved/scan is too fast.
- 6) Click "Calculate" to compute the C_p curve. Data will be displayed as a function of temperature by default.
- 7) Save C_p data: Tools → Tables → Write to File