

The Pennsylvania State University

The Graduate School

The Eberly College of Science

**RELATING NANOSCALE STRUCTURE TO ELECTRONIC FUNCTION IN
ORGANIC SEMICONDUCTORS USING TIME-RESOLVED SPECTROSCOPY**

A Dissertation in

Chemistry

by

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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

December 2017

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ABSTRACT

Molecular packing arrangements at the nanoscale level significantly contribute to the ultimate photophysical properties of organic semiconducting materials used in solar energy conversion applications. Understanding their precise structure-function relationships will provide insights that can lead to chemical and structural design rules for the next generation of organic solar cell materials. In this work, two major classes of materials were investigated: Singlet fission sensitizers and semiconducting block-copolymers. By exploiting chemical design and film processing techniques, a variety of controllable nanoscale structures could be developed and related to their subsequent photophysical properties, including triplet and charge transport. Time-resolved optical spectroscopies, including both absorption and emission techniques, were used to measure the population dynamics of excited states and charge carriers following photoexcitation of the semiconducting materials.

Singlet fission, an exciton multiplication reaction that promises to boost solar cell efficiency by overcoming thermalization loss, has been characterized in several organic molecules. If the energetics are such that the excited state singlet energy is at least twice the triplet energy, then a singlet exciton may split into two triplet excitons through an intermolecular energy-sharing process. The thin film structure of a model singlet fission compound was exploited by modulating its crystallinity and controlling polymorphism. A combination of visible, near-infrared, and mid-infrared transient absorption spectroscopies were used to investigate the precise singlet fission reaction mechanism. It was determined that the reaction intermediates consist of bound triplet pairs that must physically separate in order to complete the reaction, which results in multiplied, independent triplet excitations. Triplet transfer, which is modulated by molecular packing arrangements that control orbital overlap coupling, was found

to determine the efficacy of triplet pair separation. Furthermore, the formation of these independent triplets was found to occur on longer (picosecond) timescales than previously believed, indicating that any kinetically competing relaxation processes, such as internal conversion, need to be controlled. Last, it was found that the diffusion of the multiplied triplet excitons, and thus their harvestability in devices, is highly influenced by the crystallinity of the material. In particular, the presence of even a small amount of “contaminant” amorphous phase was determined to be detrimental to the ultimate triplet diffusion length. Future research directions are outlined, which will be used to develop further chemical and structural design rules for the next generation of singlet fission chromophores.

Semiconducting block-copolymers, because of their natural tendency to self-assemble into ordered nanoscale structures, offer an appealing strategy for controlling phase segregation between the hole and electron transport materials in organic solar cells. Such phase segregation is important for both ensuring efficient conversion of the photogenerated excitons into charge carriers, and for creating percolation pathways for efficient transport of the charges to the device electrodes. Time-resolved mid-infrared spectroscopy was developed for monitoring charge recombination kinetics in a series of block-copolymer and polymer blend films possessing distinct, controlled nanoscale morphologies. In addition to explaining previous work that correlated film structure to device efficiency, it was revealed how the covalent linkage in block-copolymers can be carefully designed to prevent rapid recombination losses. Furthermore, novel solution-phase systems of block-copolymer aggregates and nanoparticles were developed for future fundamental spectroscopic work. Future studies promise to explain precisely how polymer chain organization, including intrachain and interchain interactions, governs their ultimate charge photogeneration and transport properties in solar cells.

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LIST OF ABBREVIATIONS

Polymers

BCP	block-copolymer
P3HT	poly(3-hexylthiophene)
PFTBT	poly-((9,9-bis(2-octyl)fluorene-2,7-diyl)-alt-(4,7-di(thiophene-2-yl)-2,1,3-benzothiadiazole)-5',5''-diyl)
PFT6BT	poly((9,9-bis(2-octyl)fluorene-2,7-diyl)-alt-(4,7-di(4-hexylthiophene-2-yl)-2,1,3-benzothiadiazole)-5',5''-diyl)
P3HT-b-PFTBT	poly(3-hexylthiophene-2,5-diyl)-block-poly-((9,9-bis(2-octyl)fluorene-2,7-diyl)-alt-(4,7-di(thiophene-2-yl)-2,1,3-benzothiadiazole)-5',5''diyl)
P3HT-b-PFT6BT	poly(3-hexylthiophene-2,5-diyl)-block- poly((9,9-bis(2-octyl)fluorene-2,7-diyl)-alt-(4,7-di(4-hexylthiophene-2-yl)-2,1,3-benzothiadiazole)-5',5''-diyl)
PS	polystyrene
PEDOT:PSS	poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)

Molecules

PC ₆₁ BM	[6,6]-phenyl C ₆₁ butyric acid methyl ester
Pn	pentacene
TIPS	triisopropylsilylethynyl
TIPS-Pn	6,13-bis(triisopropylsilylethynyl)pentacene
TIBS-Pn	6,13-bis(triisobutylsilylethynyl)pentacene
TES-Pn	6,13-bis(triethylsilylethynyl)pentacene
TSBS-Pn	6,13-bis(trisecbutylsilylethynyl)pentacene
2-CN-TCPS-Pn	2-cyano-6,13-bis-(tricyclopentylsilylethynyl)pentacene
F8-NODIPS-Pn	1,2,3,4,8,9,10,11-octafluoro-6,13-bis(n-octyldiisopropylsilylethynyl)pentacene
Cl2-TIPS-Pn	statistical mixture of 2,9- and 2,10-dichloro-6,13-bis-(triisopropylsilylethynyl)pentacene
Cl4-TIPS-Pn	2,4,9,10-tetrachloro-6,13-bis(triisopropylsilylethynyl)pentacene
Br2-TIPS-Pn	statistical mixture of 2,9- and 2,10-dibromo-6,13-bis-(triisopropylsilylethynyl)pentacene

Solvents

CF	chloroform
Tol	toluene
IPA	isopropyl alcohol

DCM	dichloromethane
THF	tetrahydrofuran

Other Materials

ITO	indium tin oxide
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Quantum Chemistry & Excited State Processes

S	singlet
T	triplet
CTP	correlated triplet pair
D	donor
A	acceptor
MO	molecular orbital
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital
SSA	singlet-singlet annihilation
TTA	triplet-triplet annihilation
CT	charge transfer
CS	charge separated
ET	energy transfer
eT	electron transfer
SF	singlet fission

Quantum Chemistry Computational Terms

DFT	density functional theory
TDDFT	time-dependent density functional theory
PCM	polarizable continuum model

Instrumentation & Measurement Techniques

FTIR	Fourier transform infrared
UV	ultraviolet
VIS	visible
NIR	near-infrared
MIR	mid-infrared
IR	infrared

O.D.	optical density
TRIR	time-resolved infrared
XRD	x-ray diffraction
GIXRD	grazing-incidence x-ray diffraction
GIWAX	grazing-incidence wide-angle x-ray
MCT	mercury cadmium telluride
TA	transient absorption
PL	photoluminescence
TRPL	time-resolved photoluminescence
FWHM	full-width at half-maximum
YAG	yttrium aluminum garnet
DLS	dynamic light scattering
IRF	instrument response function
UF	ultrafast
GSB	ground state bleach
ESA	excited state absorption
PIA	photo-induced absorption
TEM	transmission electron microscopy
SEM	scanning electron microscopy
SS	steady-state

Other

OPV	organic photovoltaic
LED	light-emitting diode
NP	nanoparticle
AC	as-cast
TA	thermally-annealed
SA	solvent-annealed
WPF	whole pattern fitting

ACKNOWLEDGMENTS

The most important component of the success throughout my journey through graduate school was the support of my family, friends, and coworkers. I express deepest gratitude to everyone in my life during this most challenging part of my education. Without you all, I would not have been able to accomplish everything I have leading to my doctoral degree. I deeply apologize to anyone that I might have mistakenly omitted in the following.

First and foremost, I would like to thank my undergraduate research advisor, Dr. Christopher Collison, for encouraging me to pursue a doctorate degree. Through his mentorship, he has instilled in my heart scientific obligations, imperatives, ethics, and skills that have and will carry throughout my career as a scientist. Without his support, I would not be who I am today.

I would like to thank my Ph.D. advisor, Dr. John Asbury, who has continuously inspired me to challenge myself in my pursuit of science, which lead to the completion of a strong doctorate degree. Such challenges have helped me develop into the bold, ardent scientist I am today. I would like to especially thank him for giving me the freedom to investigate science independently, and in a way I could personally relate to; he always gave me the freedom to and encouraged me to follow my passions in scientific research. I also thank him for giving me countless opportunities to expose myself to the scientific community and present my research at several professional conferences. Last, I thank him for providing financial support for my research throughout my graduate career. At this point I would like to also thank the financial support provided by the Office of Naval Research, the DOW Chemical Company, and the Department of Energy, which have enabled my research.

I extend sincerest gratitude to Dr. Ryan Pensack, who has been a mentor during most of my time during graduate school. Without him, I would not be as successful of a scientist as I am today. From him, I learned so much about scientific research, including experimental detail, scientific reasoning, collaboration, writing, and presentation. He has always been there whenever I needed help and guidance.

I would like to thank the members of my Ph.D. committee: Professors Enrique Gomez, Lasse Jensen, and Mark Maroncelli (in no particular order) for support in my research endeavors. They have each and all contributed to my research success in some form, including providing guidance, suggestions, and feedback on challenges I have faced.

I would like to thank all the members of the Asbury lab family for constant support. With you all, I have grown and experienced so much both inside and outside the lab. I've also learned so much about science from you all. I learned that we can accomplish so much by putting our heads together. I would like to thank the following people in particular (in no specific order): Chris Averill, Rob Stewart, Adam Rimshaw, Alec Larsen, Eric Kennehan, Grayson Doucette, and Kyle Munson. I also thank my mentee, Mike Kellogg, for his great help in the lab.

I would like to thank all of my collaborators, who have significantly contributed to my research in many different ways. They include (in no specific order): Brandon Smith, Changhe Guo, Thinh Le, Youngmin Lee, Melissa Aplan, Brooke Kuei, Dan Ye, Alyssa Brigeman, Jason Munro, Hwon Kim, Anatoliy (Tony) Sokolov, Mark McAdon, John Anthony, Greg Scholes, Chris Giebink, Ismaila Dabo.

I would like to thank the Materials Research Institute staff who have assisted me throughout my time during graduate school. They include (in no specific order): Tim Tighe, Jennifer

Grey, Josh Stapleton, and Gino Tambourine. I also want to especially thank Nichole Wonderling for teaching me almost everything I know about x-ray diffractometry. She has continuously provided advice and assistance in my research throughout graduate school.

I would like to thank the following people for helpful discussions that have assisted my research (in no particular order): Derek Keefer, Chris Rumble, Geoff Purdum, Dan Oblinsky, Tom Jackson, and James Anderson.

I would like to extend thanks to my colleagues whom I've taught with, including (in no specific order): Jenn, Jovan, Steve, and Brian. I also want to especially thank my teaching advisor, Dr. Bratoljub Milosavljevic (Dr. M), not only for his teaching advice, but also for teaching me invaluable hands-on skills and scientific thinking that have carried with me throughout my research in graduate school.

Last, I would like to thank my family for constant, unconditional support throughout life and throughout my time during graduate school. I would like to thank my love, Kate, for always being there for me during good and rough times in my graduate school experience. She and I have grown so much together in our endeavors leading to our graduate degrees. I sincerely thank her for being an invaluable part of this journey.



CHAPTER 1

Motivation and Background

Global energy demands ~ 13 terawatts of energy per year, of which 85% is provided from fossil energy.¹ On the other hand, renewable forms of energy only provide 2% of the total energy, largely because of economic reasons.¹ A combination of population growth and fossil fuel depletion motivates further improvements to renewable energy technologies.

In about one hour, the sun provides $\sim 4.6 \times 10^{20}$ J of energy to the Earth, which is approximately the amount of energy that people used annually in 2007.² As such, solar energy is a particularly appealing, renewable source of energy. Solar cells, particularly silicon-based devices, have already been industrialized. However, in order to make solar cells more marketable and widespread, there is a need to lower their production and installation costs.¹⁻³ As such, a strategy for approaching this problem is to develop alternate solar cell materials that are either much more efficient, or that can be produced more cheaply.

In this chapter, the limits of solar cell efficiency will first be discussed, providing motivation to search for alternate materials. Then, new strategies for exceeding these theoretical limits to boost device efficiencies will be discussed. Both of these topics are experimentally addressed in the work presented in the rest of this dissertation

1.1. Approaches to Reaching Widespread Commercialization of Solar Cells

In order to develop approaches for improving solar cell technologies for commercialization, it is important to consider theoretical limits to their efficiencies, as well as other realistic limitations. To this day, the generally accepted theoretical framework relies upon the principle of detailed balance of the absorption flux of photons from the sunlight and the emission flux

from radiative recombination of charge carriers in the solar cell. Originally established in 1961, this model is referred to as the Shockley-Queisser (S-Q) limit, or the detailed balance limit,⁴ which is illustrated in **Figure 1-1**. The SQ limit considers the maximum efficiency attainable as a function of solar cell energy gap, or bandgap (E_g), which is the energy above which photons can be absorbed by the device. Under this model, and for a single absorptive material with a given bandgap with a unit probability of an incident photon resulting in an electron-hole pair, the maximum theoretical efficiency is 32%. Several key assumptions^{4,5} are made under the SQ limit: (1) Unity probability that an absorbed photon results in the formation of an electron-hole pair, (2) only photons with energy higher than the bandgap are absorbed, (3) hot charge carriers relax to the band-edge, and (4) only radiative recombination of charge carriers can occur.

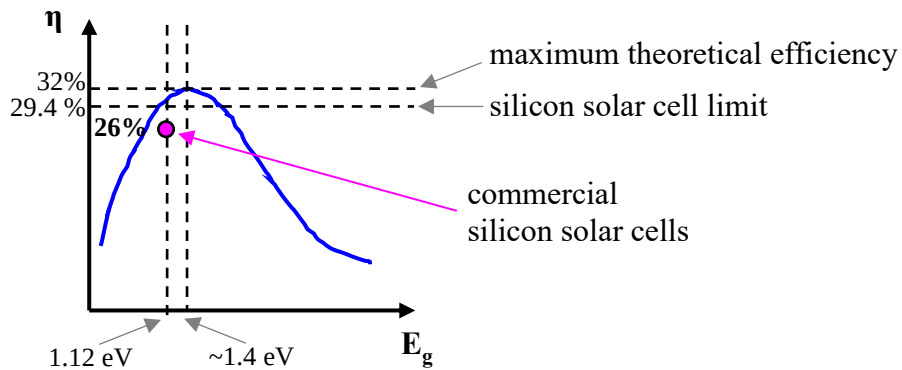


Figure 1-1: Shockley-Queisser limit (detailed balance limit) for solar cell efficiency.

Silicon is the most prominent active material of industrial solar cells because of its non-toxicity, stability, abundance, and high attainable device efficiencies.^{6,7} The highest certified efficiencies of silicon solar cells, achieved by companies like Panasonic, SunPower, and Kaneka, have been around 25-26%.³ The theoretical limit for silicon in particular is 29.4%,⁶ and so there an improvement of only about 3-4% is possible (see **Figure 1-1**). In addition to

continuing to boost efficiencies, companies seek to improve commercialization by lowering the solar cell module production and installations costs.³

The above considerations lead us to two general approaches for more widespread solar cell commercialization: (1) Make efficient solar cells cheaper, and (2) make cheap solar cells efficient. The latter issue has received widespread academic and industrial attention and includes the development of new types of devices, such as organic solar cells (OSCs)⁸ and quantum dot (QD) solar cells.⁹ The maximum efficiency of such devices has only reached around 11%.¹⁰ Much more recently, organohalide perovskite photovoltaics have been developed, resulting in certified efficiencies as high as 22.1%.¹¹ However, these perovskite devices have major stability issues that are currently being addressed.¹² Because these types of solar cells may be solution-processed at low temperatures, the prospect of roll-to-roll printing methods for solar cell fabrication offers a cheap solution to the commercialization problem.¹³

A third general approach opens up if the limitations within the S-Q limit model are overcome: (3) Make efficient solar cells more efficient. The most significant limitation to solar cell efficiency captured in the S-Q limit is the thermalization loss of energy that occurs when the absorbed photon energy exceeds the bandgap of the absorber. In this process, the charge carriers relax to the band edges, losing kinetic energy in the form of heat (**Figure 1-2**). If the excess energy can be captured and converted into charge carriers, then this loss mechanism can be overcome. Among several strategies for doing so,⁵ carrier multiplication has received a lot of attention as of late in organic materials, in which a high-energy photon (at least twice the bandgap energy of a device) produces an exciton that can fission into two lower-energy excitons. The multiplied excitation is then converted into two electron-hole pairs. In

this case, the maximum theoretical efficiency is 42%.² This process will be discussed in further detail later.

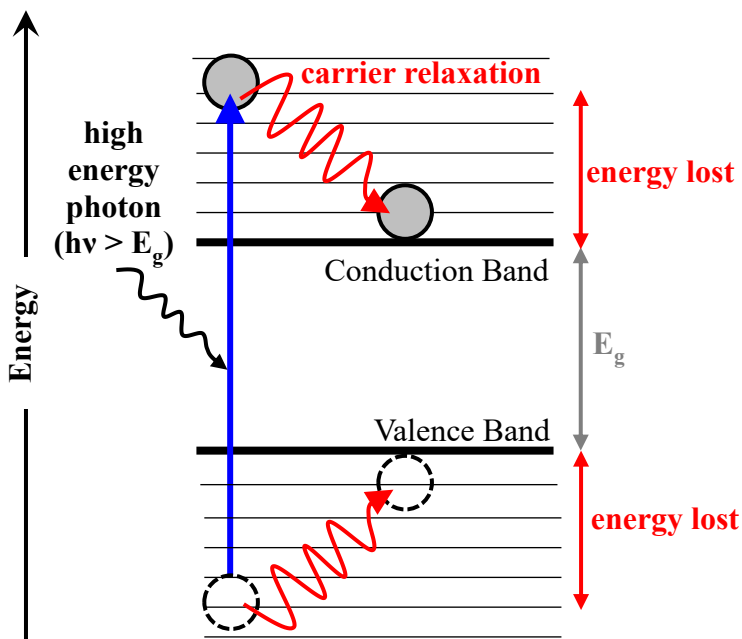


Figure 1-2: Absorption of a high-energy photon in an inorganic semiconductor, showing thermalization loss.

Two major topics, involving the second and third approach toward more widespread solar cell commercialization, will be covered in this dissertation. The first is organic semiconducting polymers and the second is singlet fission sensitizers. The background for each topic will be presented in the following sections.

1.2. Organic Semiconducting Materials and Molecular-Level Structure

1.2.1. Organic and inorganic semiconducting materials

Organic solids are composed of non-covalent interactions between molecules (and polymer chains), while inorganic solids, such as silicon, are often composed of a covalent network of

atoms. This is illustrated in **Figure 1-3** for silicon and an organic crystal of a pentacene derivative.

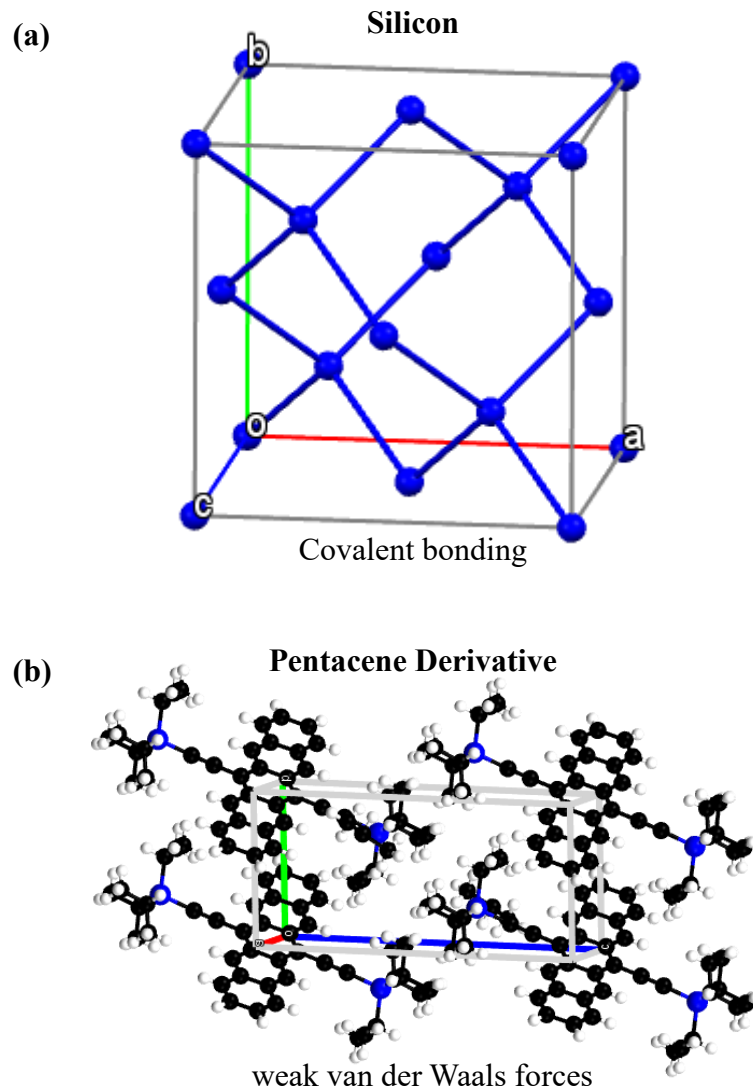


Figure 1-3: (a) Unit cell structure of silicon. (b) Crystal packing structure of a pentacene derivative.

Because weak van der Waals forces hold molecules together in organic solids, they very weakly electronically interact, resulting in excitations that tend to localize on single molecules. This is illustrated in **Figure 1-4**, which shows the nature of an exciton in inorganic versus organic semiconductors.

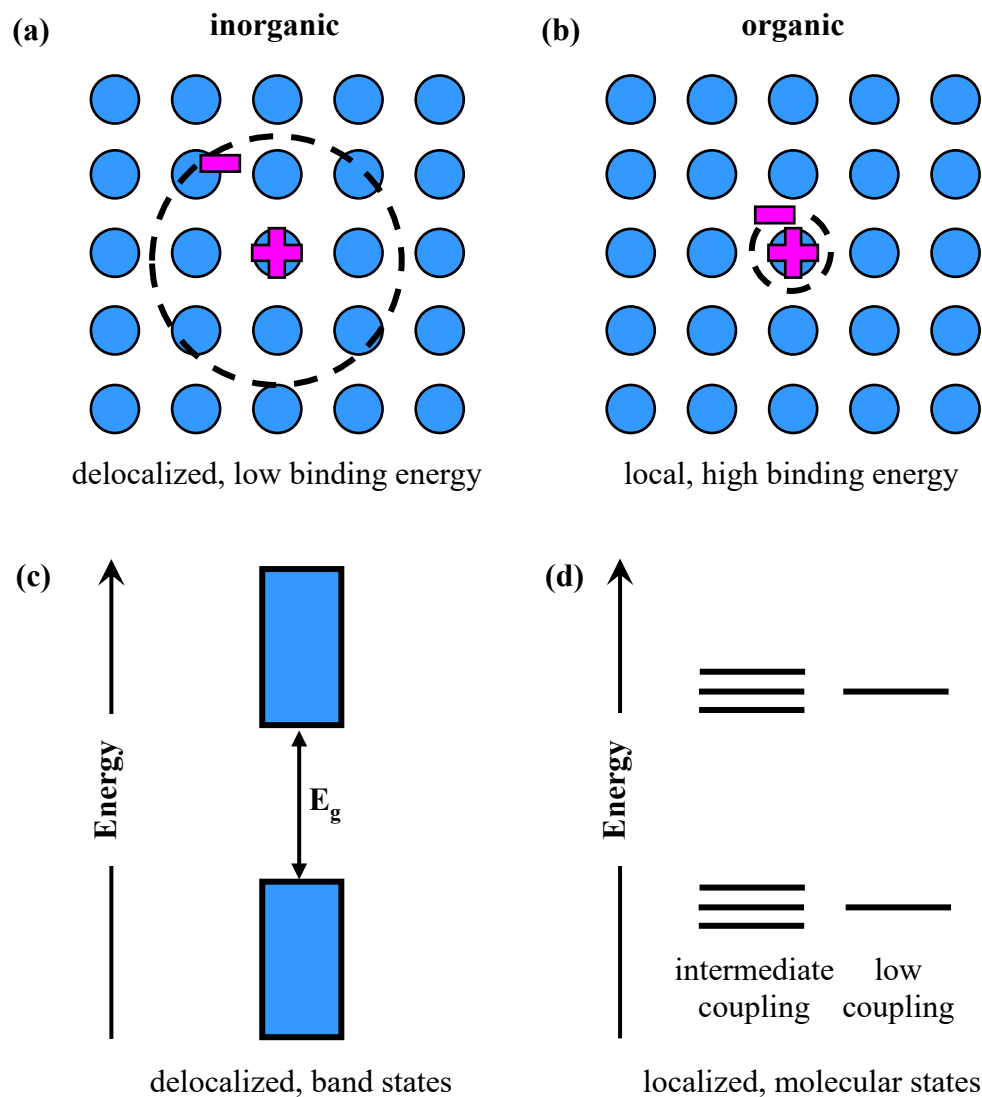


Figure 1-4: Nature of excitons in **(a)** inorganic and **(b)** organic materials. Blue circles represent lattice sites. Dashed black lines represent the spatial extent of the delocalization of charge within the exciton. Energy level diagrams for the electronic states in **(c)** inorganic and **(d)** organic materials.

In the case of inorganic materials, photoexcitation results in a weakly-bound electron-hole pair with a large excitonic radius, spanning several lattice sites (Wannier-Mott exciton).¹⁴ On the other hand, photoexcitation of organic materials typically results in strongly-bound electron-hole pairs with small excitonic radii, typically localized to a single lattice site (Frenkel exciton).¹⁴ The large excitons that form in inorganic materials can easily dissociate if the

Coulombic binding energy holding the charges together is on the order of thermal energy, making charge photogeneration very efficient. However, an additional driving force is often required in organic materials in order to split apart the electron-hole pair into dissociated charges that can be collected.¹⁵

In inorganic materials, strong coupling interactions between atoms in the lattice result in long-range delocalization of the electronic wavefunction, giving rise to band states. On the other hand, weak coupling interactions between organic molecules in the lattice result in localization of the electronic wavefunction, resulting in discrete states (see **Figure 1-4**). Because of this, charge transport in organic materials is controlled by a local hopping mechanism from site to site, or often, chromophore to chromophore.

Conjugated organic polymers have been developed in effort to extend the delocalization of excitons along their large conjugated frameworks. However, polymer solids typically contain a large extent of static and dynamical site disorder, which modulates the coupling strength between chromophore units and can reduce the rate of exciton and charge transport. Static disorder is usually characterized by positional disorder, whereby the positions of chromophore units of the polymer are imperfectly oriented within the solid-state lattice. On the other hand, dynamical disorder is created from low-frequency dynamical motions of the polymer chains, such as torsional and bending motions.

1.2.2. Singlet exciton fission

Singlet fission is a type of multiple exciton generation (MEG) mechanism characteristic to organic molecules.¹⁶ The singlet fission reaction is characterized by the fission of a singlet exciton into two triplet excitons by:



where S_1 is the first excited singlet state resulting from photoexcitation, S_0 is a singlet ground state, and T_1 is the first excited triplet state. Two major criteria must be met for the reaction to occur. The first is the energetic requirement, for which the energy of the singlet exciton is close to or larger than twice the energy of the triplet exciton ($E_{S_1} \gtrsim E_{T_1}$). The second is the coupling requirement, for which two molecules involved in the fission event are electronically coupled. These are illustrated in **Figure 1-5**. Further extensive details are provided in Chapter 3.

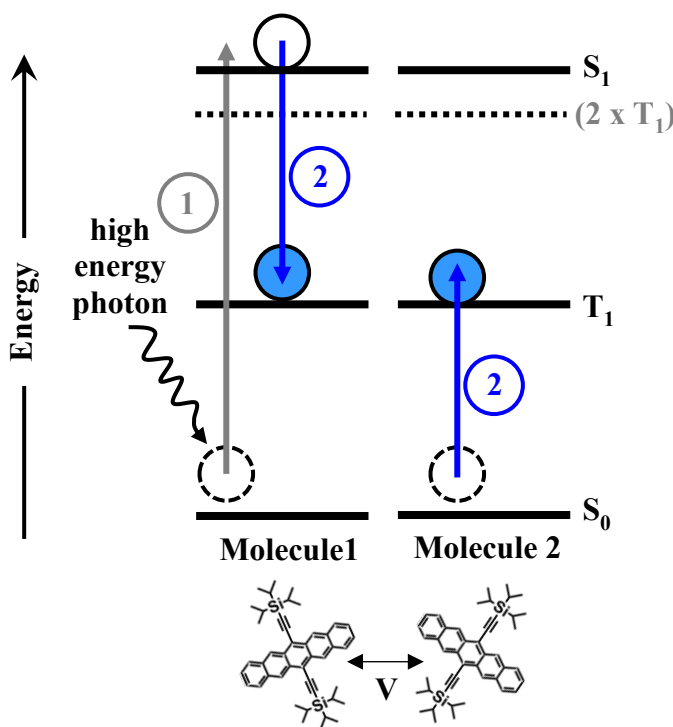


Figure 1-5: Singlet fission in organic molecules. First, a high energy photon is absorbed, creating a first excited singlet state (S_1) on a molecule. Second, the excited molecule shares its energy with a nearby ground state molecule (S_0), simultaneously relaxing to the first triplet excited state (T_1) and promoting an electron to T_1 on the other molecule. The electronic coupling between the two molecules involved is labeled as V .

In singlet fission, the absorption of a high-energy photon results in multiplied triplet excitons that must be further dissociated into charge carriers. Because the singlet fission material itself generally cannot undergo this process, it is desirable to transfer the multiplied

excitations to a material that can convert them to charges, such as an inorganic semiconductor. This procedure is called singlet fission sensitization. Notably, it may not be economically feasible to incorporate singlet fission sensitizer components into the fabrication of practical solar cells, since this could require major modifications to current infrastructure. As such, for this strategy, it is desirable to search for molecules that are not only compatible with practical solar cells, but also possess flexibility in how they may be processed.

With the need to transfer triplet excitations to another material, the ability to transport triplets efficiently through the singlet fission material becomes a necessary quality of the sensitizer. Like charge carriers, triplet transfer occurs through local coupling interactions, and the excitation must hop from site to site in the solid-state lattice.

1.3. Transport of Charges and Triplet Excitations

To this point, both charge and triplet transport in organic solids has been understood to occur via a hopping mechanism from site to site. In the following, the elementary transfer events are discussed in detail, which reveal that intermolecular coupling strength is critical to control in order to maximize transport of charges and excitations.

1.3.1. Quantum mechanical treatment of elementary transfer events

The transfer rate of a charge or excitation between two weakly-interacting chromophores (such as non-covalently interacting molecules in a solid) can be approximated using Fermi's Golden Rule (FGR).¹⁶⁻¹⁹

$$k_{if} = \frac{2\pi}{\hbar} |V_{if}^2| (DWFC) \quad (\text{eqn. 2})$$

where k_{if} is the rate of transfer involved between the initial, i , and final states, f , of the transfer event, V_{if} is the electronic coupling between the initial and final states of the transfer event,

and DWFC is the density-weighted Franck-Condon factors. The coupling term is expressed as:

$$V_{if} = \langle D^*A | H | DA^* \rangle \quad (\text{eqn. 3})$$

where D is the donor and A is the acceptor of charge or excitation, * represents either a charge or excitation, and H is the electronic Hamiltonian containing the Hamiltonian for the donor, acceptor, and their interactions. The initial state is $|D^*A\rangle$ and the final state is $|DA^*\rangle$. Sometimes V_{if} is referred to as a transfer integral, t . The charge transfer event can be expressed as:



The triplet transfer event can be expressed as:



An electron configuration diagram of the initial and final states involved in each type of transfer event is provided in **Figure 1-6**. For charge and triplet transfer, orbital coupling is a dominant component of the total coupling.²⁰ As such, the relative orientation and distance of the molecules involved in the transfer control the rate of transfer. The molecular (or polymer chain) packing arrangements in the solid state are important to consider when optimizing charge and/or triplet transport.

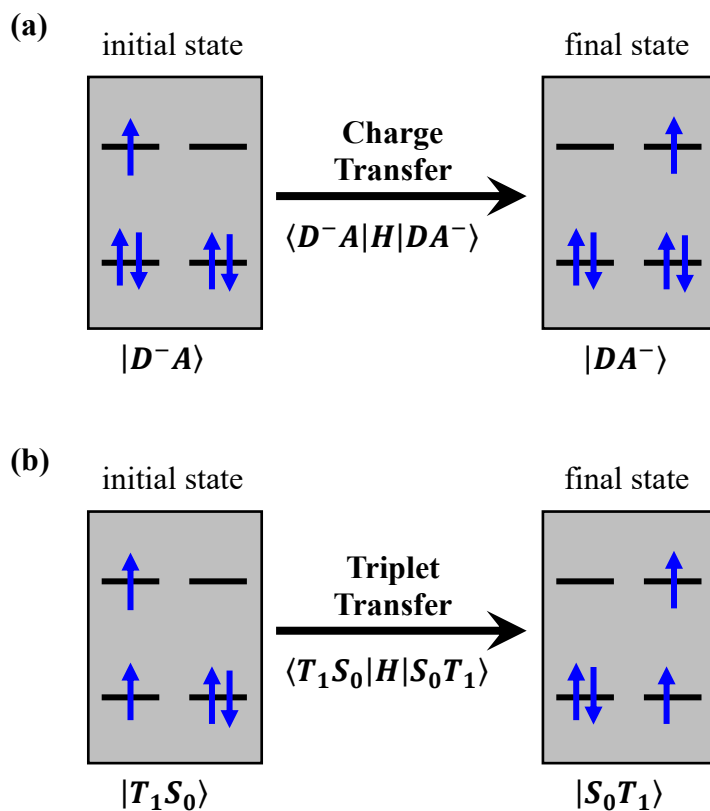


Figure 1-6: Electron configurations of the states involved for (a) charge transfer and (b) triplet transfer.

At this point, it is helpful to define what is meant by “orbital interactions” and “Dexter interactions” with regard to triplet transfer. Although triplet transfer (see definition in **Figure 1-6**) is an overall spin-conserved process, its occurrence by a dipole-dipole mechanism would require a simultaneous change in electronic state and spin for both the donor and acceptor and is therefore not a likely process. On the other hand, triplet transfer may be visualized as an exchange of electrons between the donor and acceptor, or a “simultaneous transfer” of two electrons. This “Dexter exchange interaction” would require that the donor and acceptor are close enough for their electronic orbitals to overlap in order to complete an exchange of electrons, and that the energy gaps of the electronic states involved are comparable. Hence, the “orbital interactions” between the donor and acceptor play a large role in the ability to

transfer a triplet. For more detailed information, the reader is encouraged to refer to the book: Modern Molecular Photochemistry by Nicholas J. Turro.

1.3.2. Polaron transport

Charge carriers in organic molecules and polymers are transported much more slowly compared to inorganic materials like silicon. For example, the highest charge mobilities measured for organic materials is $\sim 1 \text{ cm}^2/\text{Vs}$, while that of single crystal silicon is $10^2\text{-}10^3 \text{ cm}^2/\text{Vs}$.²¹ As such, the nuclear framework surrounding a charge in organic materials has sufficient amount of time to respond to the presence of a charge, polarizing against it. Such a charge entity is described as a polaron, which is illustrated in **Figure 1-7**. Because the lattice in the vicinity of the charge is able to distort to stabilize it, the site positions and energies are changed and transfer of the polaron becomes a thermally-activated process.

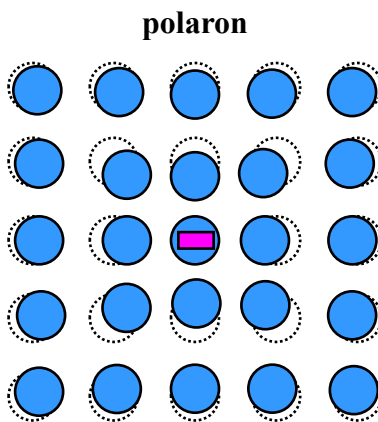


Figure 1-7: Illustration of a polaron. Blue circles represent molecules at each lattice site. Dashed circles represent the positions of the molecules in the neutral state.

1.4. Thesis: Structure Controls Transport at the Molecular Level

The thesis of this dissertation is that nanoscale structure affects transport of charge and excitation at the molecular level. Furthermore, the elementary transfer events between molecules determines their ultimate electronic properties in devices. Controlling the rates of

these elementary transfer events by careful design of the molecular and polymer chain packing arrangements ultimately affects their performance as semiconducting materials. This is illustrated in **Figure 1-8**, which exemplifies this thesis in the context of a polycrystalline film. It must be noted that for long range transport, static and dynamic disorder play a large role and must also be considered. This includes interfaces between crystalline domains or amorphous phases (featuring different orientation and energetics of the molecules and/or crystal planes) and dynamical motions (e.g. polymer chain bending and torsions) that modulate the coupling between chromophores. In this dissertation, the impact of chemical and structural organization of molecules and polymers on charge and triplet transport characteristics will be studied using a collection of time-resolved optical spectroscopic techniques. Structure-function relationships will be determined, leading to new chemical and structural design rules for developing more efficient organic semiconducting materials for solar cell applications.

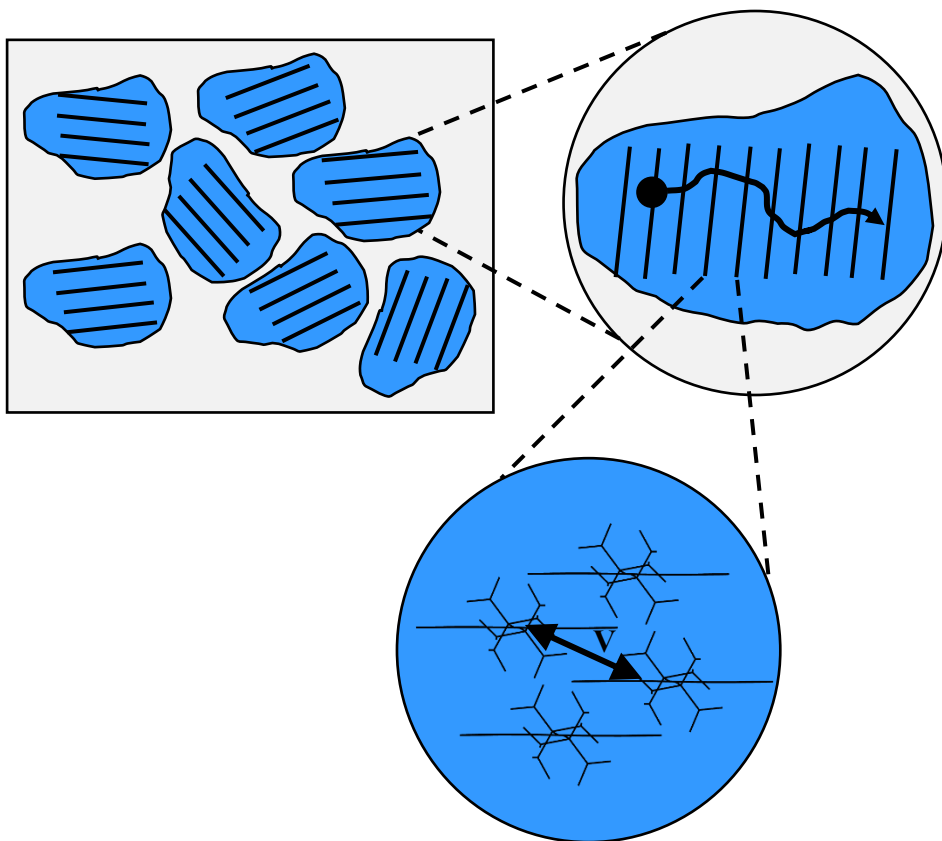


Figure 1-8: Illustration of a polycrystalline film, showing charge or triplet excitation transport within a crystalline domain. Intermolecular coupling is emphasized as an important parameter for charge or triplet excitation transport.

1.5. Thesis Overview

This chapter provides the background and motivation for the work presented in all following chapters of this dissertation. The ability to command function of electronic devices by exploiting nanoscopic structure will be a recurring theme. The work presented in this thesis not only uncovers structure-function relationships in organic and inorganic materials, but also offers new design criteria for the future development of high-efficiency semiconductors. A brief summary of the remaining chapters is provided below.

Chapter 2 discusses principles and instrumentation of various spectroscopic techniques, and provides an overview on sample preparation methods. First, the principles and instrumentation

behind steady state and time-resolved optical spectroscopies are presented, including spectrophotometry, flash photolysis (transient absorption and photoluminescence), and pump-probe techniques. Special attention is given to visible/near-IR flash photolysis instrumentation as its development and construction was a major part of the work of this dissertation. Next, general principles and instrumentation of X-ray diffractometry will be discussed. Then, spectral and kinetic analysis procedures of time-resolved optical spectroscopy will be detailed. Last, sample preparation and processing methods will be presented, including liquid sample cell design and film fabrication techniques.

Chapter 3 introduces the general principles of singlet fission, including a quantum mechanical description of the rate of reaction and its relation to intermolecular structure. Pentacene derivatives are then introduced as model systems for studying the singlet fission reaction. Methods for controlling crystallization and isolating and identifying crystal polymorphs in organic films of pentacene derivatives are detailed extensively, demonstrating control over intermolecular packing arrangements that are important for the studies of singlet fission presented in Chapters 4-7.

Chapter 4 begins by relating the extent of crystallization to singlet fission and triplet diffusion characteristics in a pentacene derivative. A method is then developed for determining triplet diffusion coefficients and diffusion lengths in polycrystalline films of singlet fission materials. The diffusivity of triplets in the films is examined, showing the occurrence of triplet transfer among mixtures of amorphous and crystalline phases. It was found that over time, triplets migrate to amorphous domains, in which they transport very slowly. The presence of an amorphous phase in polycrystalline films was found to be significantly detrimental to the

overall triplet diffusion length. From the study presented in this chapter, a pair of design rules for singlet fission sensitizers was developed.

Chapter 5 presents the first account of the application of time-resolved mid-infrared spectroscopy to the study of singlet fission materials. In particular, mid-infrared electronic transitions were discovered in solutions and films of a pentacene derivative that are useful for studying the singlet fission reaction from a new perspective. Most importantly, it was discovered that singlet fission intermediates absorb mid-infrared light, which can be used to directly track their time-evolution during the reaction. Kinetic modeling of the mid-infrared absorption signals associated with singlet excitons and reaction intermediates provides a new method for studying the singlet fission reaction. The work presented in this chapter leads to the determination that the reaction is not actually complete until a late picosecond timescale, contrary to the previously accepted belief that the reaction is completed by the early picosecond timescale.

Chapter 6 presents the first account of the application of time-resolved vibrational absorption spectroscopy to the study of singlet fission materials. In particular, the vibrational dynamics of the alkyne stretch probe for a pentacene derivative were measured during the singlet fission reaction. This vibrational signature was used to directly probe separated triplet excitations, useful for reporting on the dissociation time of the correlated triplet pair intermediates of singlet fission. Through vibrational dynamics, it was determined that triplet pair dissociation was mediated on a picosecond timescale, explaining the existence of the long-lived intermediate species that were monitored using time-resolved mid-IR absorption spectroscopy in Chapter 5. Furthermore, it was shown that molecular packing arrangements

are important to control in order to ensure rapid, efficient formation of multiplied triplet excitons.

Chapter 7 presents the determination of the crystal packing structure in polymorphs of a pentacene derivative, and relates changes in intermolecular orbital overlap interactions to singlet fission characteristics. In particular, it was found using visible transient absorption spectroscopy on the ultrafast and nanosecond timescales that the mechanism for the separation of correlated triplet pair intermediate species was triplet transfer. The triplet transfer mechanism was then related to changes in intermolecular packing arrangements of the two crystal polymorphs studied, explaining the observed differences in singlet fission rates. Based on these findings, this chapter then closes by suggesting a new *a priori* computational approach for identifying singlet fission sensitizers that can efficiently separate triplet pair excitations.

Chapter 8 serves to present various procedures for identifying and measuring triplet excitation spectra in potential singlet fission sensitizers. These methods will be particularly useful for carefully identifying transient absorption features that are characteristic of independent triplet excitations in candidate singlet fission molecules. Establishing these spectral assignments will be critical for discrimination between other potential transient species that may form during singlet fission, but cannot produce multiplied triplet excitations.

Chapter 9 begins by introducing organic polymer solar cells and providing the motivation for developing block-copolymer materials. Then, mid-infrared transient absorption spectroscopy is used to track the formation and recombination of charge separated polarons that form in films of a block-copolymer and its corresponding polymer blend, possessing different nanoscale morphologies. The presence of the covalent linkage between polymer segments in the block-copolymer system studied was determined to not impact charge

recombination. Based on this work, chemical design rules for block-copolymers were developed that would ensure that the intrachain interface resulting from covalent linkage does not introduce deleterious recombination centers in solar cell devices.

Chapter 10 represents the first report of transient absorption spectroscopy of semiconducting block-copolymer aggregates and nanoparticles in the solution phase. Such systems promise to serve as platforms for fundamental investigations into how polymer ordering and morphology ultimately determine their charge generation and recombination properties. The chapter begins with a detailed description of the methods developed for preparing aggregates and nanoparticles of block-copolymers. Then, transient absorption spectroscopy is used to track their polaron recombination kinetics. Several preliminary studies are presented, from which two major findings emerged: (1) Polymer chain flexibility modulates the branching ratio between polaron and triplet generation upon photoexcitation, and (2) intrachain charge transport mediates bimolecular recombination in block-copolymers. The chapter closes by presenting a future research direction: A study of how charge transport depends on the type of polymer aggregation, which would be exploited to controllably modulate the coupling interactions between and along polymer chains.

Chapter 11 presents the utility of time-resolved photoluminescence spectroscopy to study energy transfer dynamics preceding emission in inorganic carbide phosphors, which are being developed for in solid-state lighting applications. Changes in energy transfer rate between emissive sites in the crystal lattice were related to perturbations of its structure associated with carbon substitution, and optical and thermal stress (aging). Both the mechanism of energy transfer and color stability were determined for carbide phosphors.

phosphors. This work was a collaborative effort between the Pennsylvania State University and the Dow Chemical Company.

Chapter 12 discusses several future research directions that have sprung from the work of this dissertation and/or were not yet completed but warrant further investigation. These include: (1) The development of vibrational thermometers for studying internal conversion of singlet fission intermediates, (2) uncovering structural origins of thermal artifacts that arise in transient absorption spectroscopy, (3) development of a theoretical approach for predicting triplet diffusivity in singlet fission materials, (4) using vibrational spectroscopy to understand (non-electronic) molecular aggregation in “dilute” and concentrated solutions, (5) determination of the role of intermolecular electronic coupling on charge separation in polymer:pentacene photovoltaic materials, and (6) the role of transport dimensionality in triplet separation in singlet fission materials.

Chapter 13, the final chapter, concludes the work of this dissertation and provides further outlook.

In the Appendix, two sets of useful information for optical spectroscopists are presented: (1) Proper experimental measurement of transient species that decay bimolecularly, and (2) How to identify the inner filter effect artifact in emission spectroscopy of concentrated solutions. The Appendix then presents miscellaneous spectroscopic details for pentacene derivatives that will be helpful for researchers studying pentacene derivatives.

1.6. References

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CHAPTER 2

Instrumentation and Methods

In this chapter, the spectroscopic techniques used for the work in Chapters 3-12 will be discussed. Of particular focus is the development of visible/near-IR flash photolysis spectroscopy, which was a major part of the work presented in this dissertation. Last, basic sample preparation methods used in Chapters 3-10 and Chapter 12 will be overviewed. This chapter further provides a motivation for using population spectroscopy (e.g. time-resolved optical spectroscopy) for studying excitations and charges in organic semiconducting materials.

2.1. Optical Spectroscopy and Instrumentation

2.1.1. Absorption-based techniques

In absorbance spectroscopy,^{1,2} a light beam is passed through an absorptive medium and the transmitted light is detected (see **Figure 2-1**).

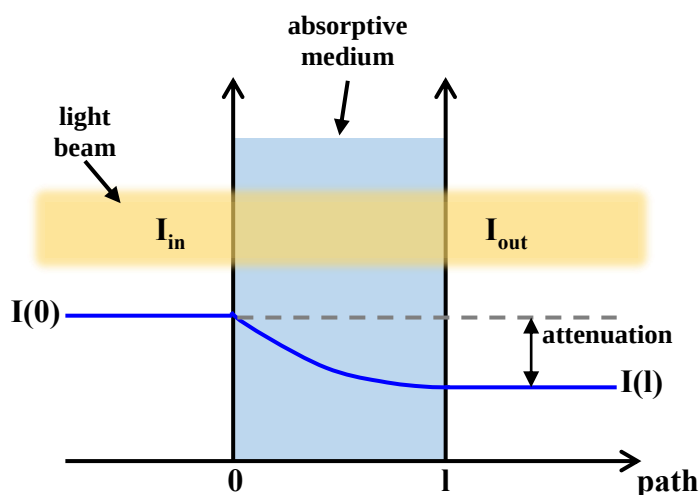


Figure 2-1: Light passing through an absorptive medium and principles behind absorption spectroscopy.

The intensity of the beam, $I(x)$, as a function of distance, x , through the medium is given as:

$$\frac{dI(x)}{dx} = -\alpha I(x) \quad (\text{eqn. 1})$$

where α is the efficiency of light absorption of the medium. Solving equation 1, and taking $I(0)=I_0$ gives:

$$I(x) = I_0 e^{-\alpha x} \quad (\text{eqn. 2})$$

which is Beer's Law. Immediately after the light is transmitted, which is at $I(l)$, the transmission is derived:

$$T = \frac{I_{out}}{I_{in}} = e^{-\alpha l} \quad (\text{eqn. 3})$$

where I_{in} is the intensity of the beam before the absorptive medium, I_{out} is the intensity of the beam exiting the absorptive medium, and l is the length of the absorptive medium. Additionally, the proportion of light absorbed, a , is given by:

$$a = \frac{I_{in}-I_{out}}{I_{in}} = 1 - T \quad (\text{eqn. 4})$$

Equation 4 will be particularly useful for transient experiments, in which the fraction of photons in the excitation pulse can be used to calculate the excited state concentration.

It is useful to express the absorbance, A , of the absorptive medium as:

$$A = -\log(T) = -\log\left(\frac{I_{out}}{I_{in}}\right) \quad (\text{eqn. 5})$$

Note that the base change to base 10 occurs if the molar concentration of absorbers, rather than number, is considered. For molecular absorption, the absorbance is expressed as:

$$A = \epsilon c l \quad (\text{eqn. 6})$$

where ϵ is the molar absorptivity, and c is the concentration. If multiple absorbers are present in the medium, and they are non-interacting, then Beer's Law gives:

$$A = \sum_{i=1}^N A_i \quad (\text{eqn. 7})$$

where the absorbance of each species, i , is A_i , and the total number of species is N . Equation 7 will be important later for the spectral analysis of steady-state and transient absorption spectra.

Beer's Law (equation 1) emphasizes the need for using low concentrations for transient absorption spectroscopy measurements. An example of the absorption profile through a medium of absorbers is provided in **Figure 2-2** for a variety of concentrations. After absorption, a non-uniform concentration density of excited states can result for solutions having high concentrations (or films having large thickness). This is particularly important to avoid in experiments in which the decay of the transient species is concentration dependent.

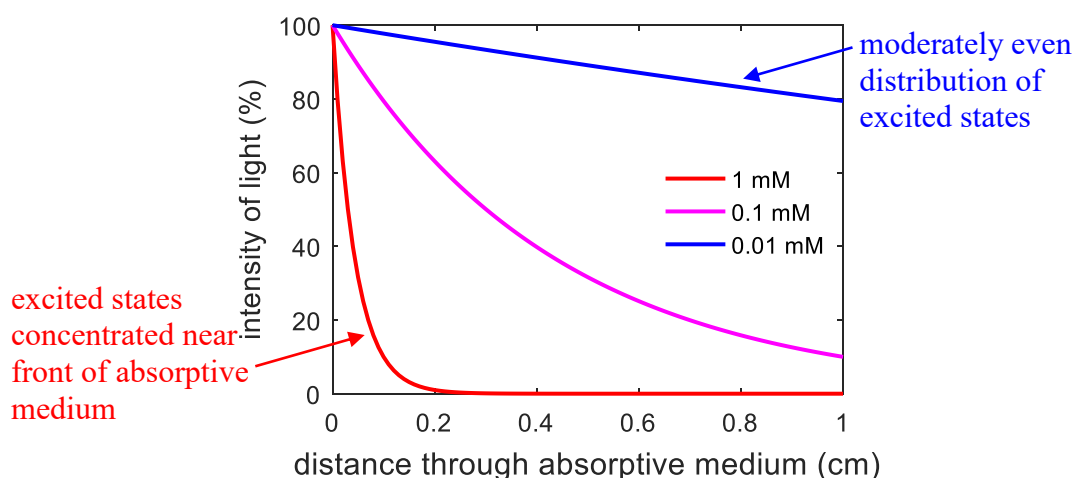


Figure 2-2: Examples of absorption profiles for solutions with 1 cm pathlength and a molar extinction coefficient of $10,000 \text{ M}^{-1} \text{ cm}^{-1}$.

A schematic for a basic steady-state absorbance spectrometer set-up is provided in **Figure 2-3**. The monitoring beam is produced from a light source, such as a tungsten-halogen lamp. After the beam transmits the sample, it passes through some type of wavelength selector, such as a diffraction monochromator or optical filters in order to obtain wavelength information. When using a diffraction monochromator, higher orders of diffracted light must be carefully removed from the exiting beam using optical filters, for example. After wavelength selection,

the beam is detected using a photodetector, which produces a voltage signal based on the intensity of light detected. The signal is then amplified (optional) and measured; for measurement, it may be digitized using an oscilloscope.

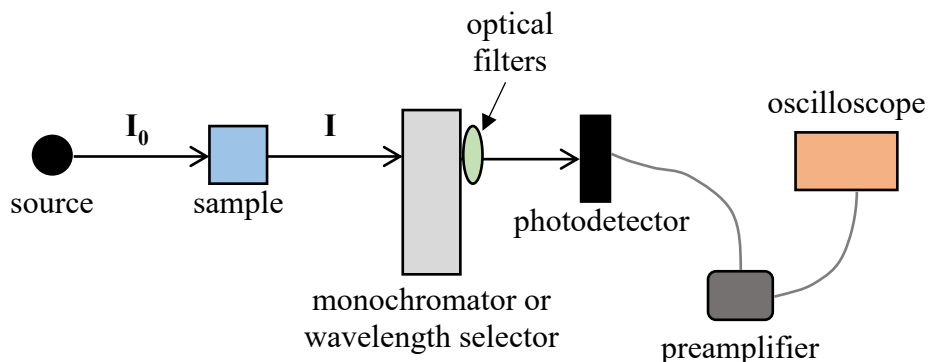


Figure 2-3: Simple schematic for an absorbance spectrometer

The light source can be of various types, such as lamps or lasers, and can emit various wavelengths of light depending on the needs of the experiment. Depending on the wavelength range of interest, collecting and focusing optics, diffraction gratings, and photodetectors must be carefully chosen in order to maximize the efficiency of the system. Additionally, it is desirable that the detector responds linearly to the incident light intensity (i.e. $V \propto I$). It is of note that absorbance spectroscopy is a self-normalized technique (the transmitted light intensity is considered relative to the incident light intensity), and so there is no need to correct for the wavelength-dependent efficiency of the spectrometer system (i.e. optic transmission, spectral efficiency of the wavelength selector, and detector spectral sensitivity).

In steady-state absorption spectroscopy, the sample of interest is often placed in a liquid medium, or on a solid surface, and so any changes in light intensity from such materials must be corrected for. As such, the absorbance of a “blank”, A_B , consisting of all materials other than the sample of interest, is subtracted (using Beer’s Law; equation 7) from the absorbance of the sample + blank material, (A_{S+B}):

$$A_S = A_{S+B} - A_B \quad (\text{eqn. 8})$$

Substitution using equation 5 eventually gives:

$$A_S = -\log\left(\frac{I_{S+B}}{I_B}\right) \quad (\text{eqn. 9})$$

where I_{S+B} is the output intensity of the beam for the sample + blank material, and I_B is the output intensity of the beam for the blank. Taking transmission of the blank and sample + blank as $T_B = \frac{I_B}{I_0}$ and $T_{S+B} = \frac{I_{S+B}}{I_0}$, respectively, equivalently leads to:

$$A_S = -\log\left(\frac{T_{S+B}}{T_B}\right) \quad (\text{eqn. 10})$$

which is the more common form of the expression.

Absorbance of light corresponds to a transition between two states of different energy (e.g. electronic or vibrational), and having a particular strength of transition (oscillator strength, f , or molar extinction coefficient, ϵ). Additionally, it requires the resonance condition, $\Delta E = hc/\lambda$. **Figure 2-4** shows a basic energy level diagram describing the absorption process. At steady-state conditions, the excited state concentration resulting from exposure to the light source is negligible under such low photon flux. As such, any excited state population may be neglected, and only the ground state is measured. The monitoring beam is then effectively “filtered” by the absorbance associated with the states, $|0\rangle \rightarrow |1\rangle$.

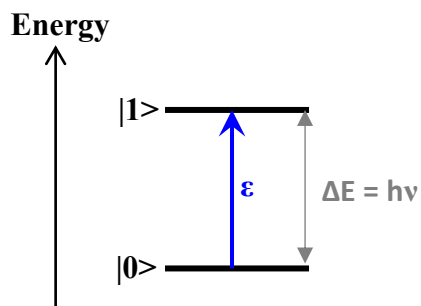


Figure 2-4: Basic energy level diagram showing an absorption transition. The molar extinction coefficient is represented as ϵ , which indicates the strength of the transition. The resonance condition is indicated. The ground state is indicated by $|0\rangle$ and a higher energy state is indicated by $|1\rangle$.

In certain cases, it is desirable to measure excited state absorption. For this, a significant concentration of excited states must be prepared using a significantly higher photon flux than is provided from a lamp. By compressing a large number of photons into a short pulse of light (e.g. pulsed laser source), a substantial number of photons can be delivered to the sample in a short amount of time, resulting in a substantive excited state population. This is illustrated in **Figure 2-5**.

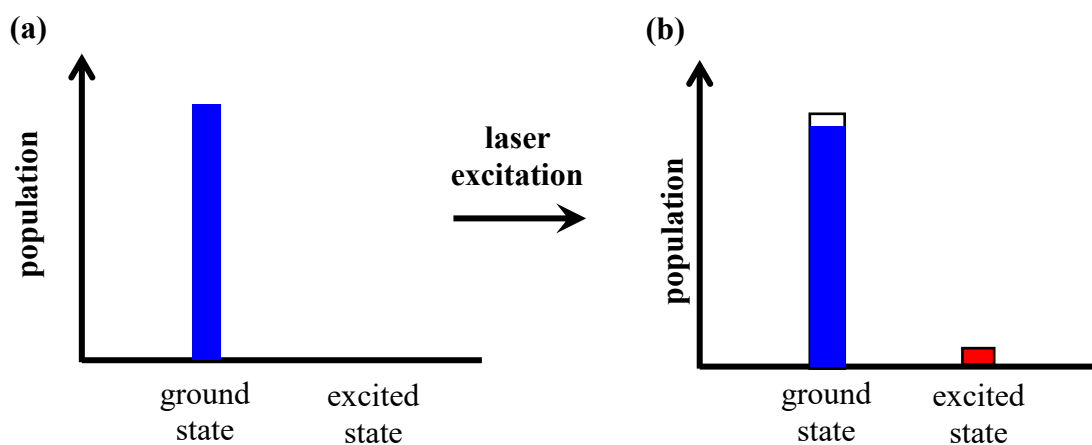


Figure 2-5: Population histograms for a sample **(a)** before and **(b)** after laser excitation in a transient absorption experiment.

In this situation, a combination of ground state and excited state populations are probed, for which the ground state population has been slightly depleted in the process of forming a small

population of excited states. Now, additional transitions associated with the excited state population are available to be probed, as shown in **Figure 2-6**.

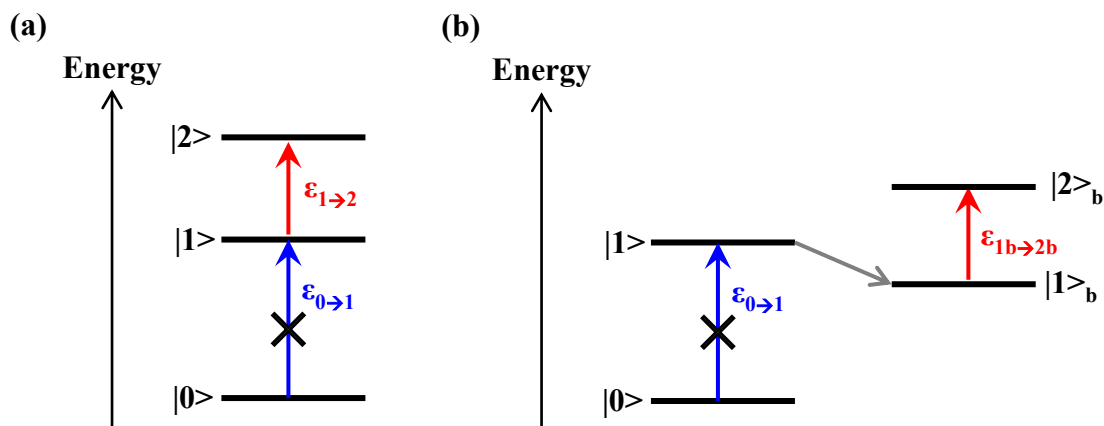


Figure 2-6: Simple energy level diagrams for transient absorption spectroscopy, showing a ground state bleach (blue arrows) and (a) an excited state absorption or (b) an absorption of a new transient species.

Furthermore, because a small fraction of the ground state population was depleted, less absorption associated with $|0\rangle \rightarrow |1\rangle$ would be observed. This concept forms the basis of the transient absorption spectroscopy technique called laser flash photolysis.

The basic design for a laser flash photolysis (transient absorption) instrument is shown in **Figure 2-7**, in which a laser excitation source was added to the design of a steady-state absorbance spectrometer. The pulsed laser beam is overlapped with the monitoring beam (from the lamp) on the sample. The voltage produced by the photodetector is measured over time after the laser pulse has interacted with the sample. A change in transmission, associated with new species that form upon sample absorption of the laser pulse, is tracked over time. Transient absorption spectroscopy is also a self-normalizing technique and does not need to take into account the wavelength-dependent spectrometer efficiency.

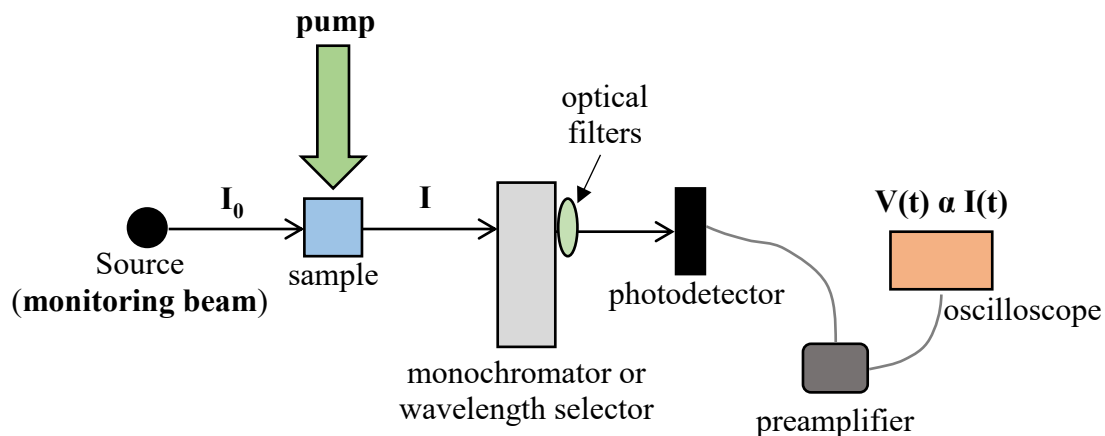


Figure 2-7: Simple schematic for a laser flash photolysis spectrometer.

In transient absorption measurements, the change of absorbance, $\Delta A(t, \lambda)$, is expressed as:

$$\Delta A(t, \lambda) = A(t, \lambda) - A_0(\lambda) \quad (\text{eqn. 11})$$

where t is time and A_0 is the absorbance in the absence of laser excitation. Using $I(t, \lambda) = I_{\text{in}}(\lambda)10^{-A(t, \lambda)}$, the change of absorbance can be expressed in terms of the measureable signals:

$$\Delta A(t, \lambda) = -\log \left(1 + \frac{\Delta I(t, \lambda)}{I_0(\lambda)} \right) \quad (\text{eqn. 12})$$

$$\Delta I(t, \lambda) = I_0(\lambda) - I(t, \lambda) \quad (\text{eqn. 13})$$

where ΔI is the change in transmission intensity associated with the presence of laser excitation, I is the transmission intensity due to laser excitation, and I_0 is the transmission intensity in the absence of laser excitation. Commonly, the transmission, “ T ”, is used in place of the transmission intensity, “ I ”.

The sign of the change in absorption observed in the transient measurement depends on the species being probed. In the case of a new species, a new absorption is measured as a result of the laser excitation, and so $\Delta A > 0$ ($\Delta T/T < 0$). In the case of ground state depletion, less absorption is measured as a result of laser excitation, and so $\Delta A < 0$ ($\Delta T/T > 0$). This is illustrated

in **Figure 2-8**. Additionally, the change in absorbance can be measured over time following laser excitation, providing information about how excited state populations (or ground state bleach recovery) evolve over time. For example, the relaxation rate constant for an excited state may be determined by monitoring the decay in its absorbance over time. It must be noted that the laser repetition rate must be slow enough for the ground state to fully-recover before a second pulse is absorbed by the sample, or else accumulation of excited state will occur.

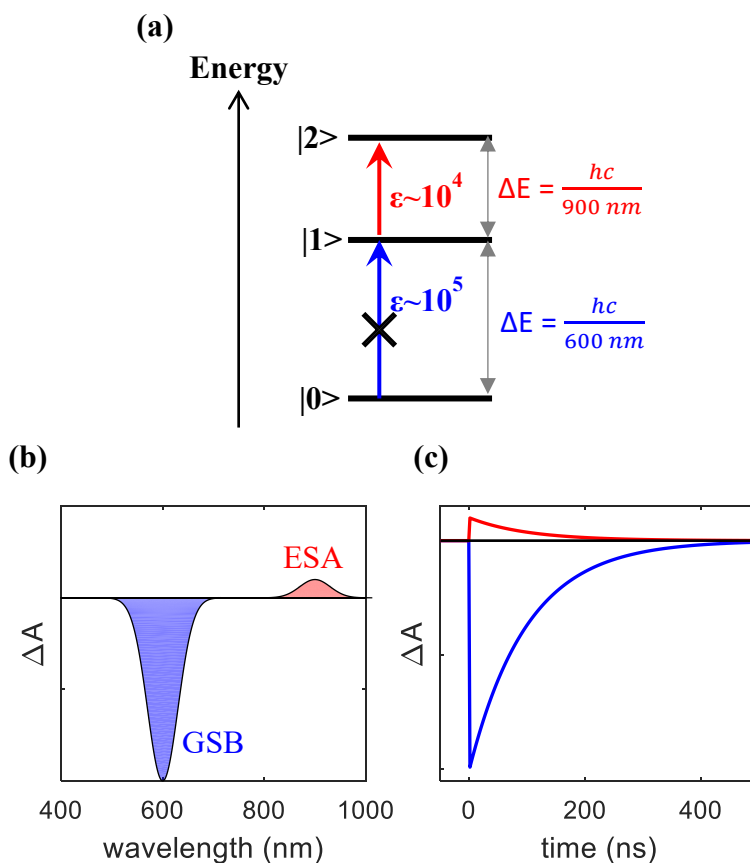


Figure 2-8: Illustration of transient absorption spectroscopy showing (a) energy level diagrams, (b) the corresponding transient absorption spectra, and (c) their kinetic decays. The examples have arbitrarily been shown for transitions possessing different transition energies and extinction coefficients.

In laser flash photolysis, the transmitted light signals are electronically resolved, and so the time resolution is fundamentally limited by the electronics used. Because the laser pulses can be as short as femtoseconds, the detector response time, in addition to the bandwidth of the

remaining electronics (e.g. preamplifiers and digitizers), usually limits the time resolution. Because the best detector and digitizer bandwidths are around 1 GHz, the time resolution can be at best around 0.68 ns. A measure of the time resolution of the instrumentation is called the instrument response function (IRF). The instrument response may be determined by measuring a signal that forms and decays instantaneously relative to the instrument response (e.g. faster than 0.68 ns for a system with 1 GHz detectors and electronics). This can be achieved, for example, by measuring laser scatter. In the limit of ultrashort laser pulses and high-bandwidth electronics, the instrument response function is typically determined by the rise and fall time of the photodetector response.

If faster time resolution is required by the experiment, pump-probe transient absorption spectroscopy may be used, which is no-longer an electronically time-resolved technique, thus avoiding the need to rely on high-speed electronics. In pump-probe spectroscopy (**Figure 2-9**), two ultrashort (~ 100 fs) laser pulses are used as the pump (excitation pulse) and probe (monitoring pulse). In order to obtain time resolution, one pulse is mechanically delayed in time relative to the other using a delay stage, which makes one pulse travel farther through space than the other. A precision of $1\text{ }\mu\text{m}$ in distance of the delay stage would correspond to a precision of ~ 30 fs in delay time for light propagating in air. The combination of this precision and the cross-correlation of the laser pulses (related to their pulse duration) defines the time resolution. The detector response to the probe pulse is integrated at each time delay (in the presence and absence of the pump pulse) to determine $I(t,\lambda)$ and $I_0(\lambda)$.

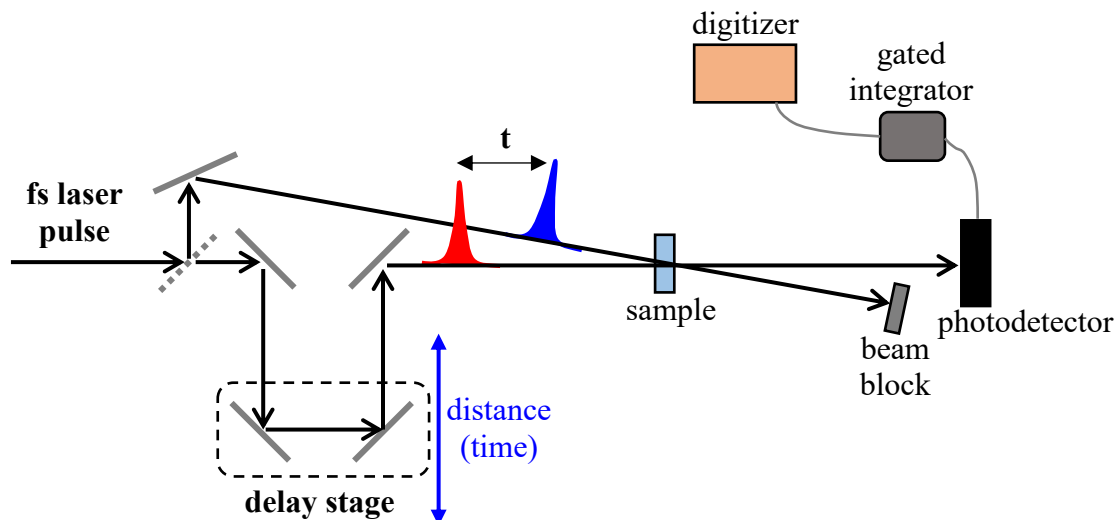


Figure 2-9: Simple schematic of a femtosecond pump-probe transient absorption spectrometer.

For both flash photolysis and pump-probe, the excitation density or photon density of the excitation or pump beam is often useful to calculate. This can be done by measuring the pulse energy, E , and dividing by the laser spot area, A , at the sample position:

$$\tilde{E} = \frac{E}{A} \quad (\text{eqn. 14})$$

where $\tilde{E}$ is the energy density, typically reported in $\mu\text{J}/\text{cm}^2$. The photon density may be calculated from the energy density by dividing it by the energy of the photons corresponding to the wavelength of light used.

2.1.2. Emission-based techniques

In the case of electronic states, it is possible that after the absorption of a photon, the energy of the excited state can be emitted (**Figure 2-10**). Because the number of photons emitted is proportional (1:1) to the number of states excited, it is therefore possible to monitor an excited state through its emission.

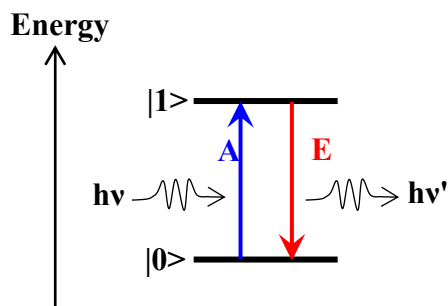


Figure 2-10: Basic energy level diagram showing emission following absorption of a photon. The ground state is indicated by $|0\rangle$ and a higher energy state is indicated by $|1\rangle$. Absorption is indicated by “A”, and emission is indicated by “E”.

In the work presented in this dissertation, steady-state measurements were not possible since a very sensitive detector (e.g. photomultiplier tube) is required in order to detect emission from extremely low steady-state concentrations of excited states generated from lamp excitation. However, if a substantial number of excited states are generated, as in transient absorption spectroscopy, enough signal could be produced for the less sensitive photodiode photodetectors available. As such, the work presented in this dissertation relies on the laser flash photolysis method for performing time-resolved emission spectroscopy. This method is essentially conducted like the transient absorption variety, except with removal of the monitoring light source (see **Figure 2-11**). In this way, photoluminescence may be measured with a time resolution as fast as ~ 0.68 ns (assuming an electronic bandwidth of 1GHz). It is of note that photoluminescence spectroscopy is not a self-normalizing technique like absorption spectroscopy, and so the wavelength-dependent spectrometer efficiency should be corrected for if quantitative assessment of the emission spectrum lineshape and absolute peak positions are required by the experiment.

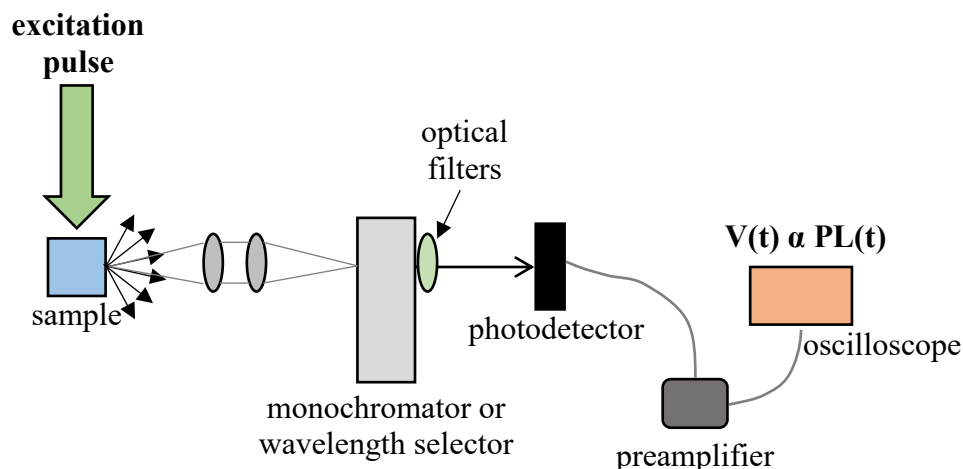


Figure 2-11: Simple schematic for a laser flash photolysis spectrometer designed for measuring time-resolved photoluminescence (PL).

In time-resolved emission spectroscopy, the relaxation of a transient species can be tracked indirectly through its emission:



where A represents a ground state molecule, $h\nu$ represents a photon, and B represents an emissive excited state. The relaxation of excited state, B, may be monitored by measuring the emission decay over time, $Em(t)$, following laser excitation. Because the emitted light intensity is proportional to the concentration of emitters, this provides a way to measure the relaxation of B over time, $B(t)$.

It must be noted that reabsorption artifacts may occur if the concentration of the sample is too high. The concept of reabsorption is illustrated in **Figure 2-12**. If the concentration is high, then it is possible for emitted light to be reabsorbed by different molecules in the sample. If the emission quantum yield is not unity (generally the case), then this process can decrease the true emission signal near the absorption band. This phenomenon is known as the “inner

filter effect” because the sample itself filters its own emission. This artifact is discussed in detail in the Appendix section of this dissertation.

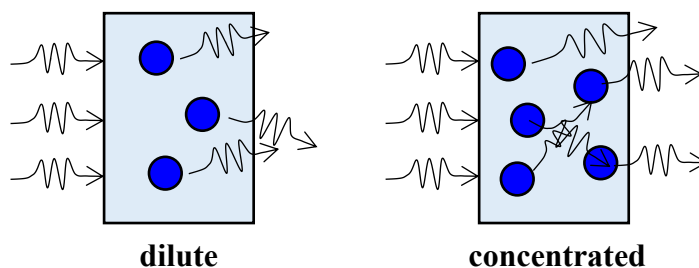


Figure 2-12: Illustration of a reabsorption artifact in concentrated solutions. Circles indicate chromophores and squiggly arrows indicate photons.

2.1.3. Laser flash photolysis instrumentation

A laser flash photolysis system using a visible to near-infrared (near-IR) monitoring beam was developed, constructed, and programmed. The details of the instrument are provided in the schematic in **Figure 2-13**.

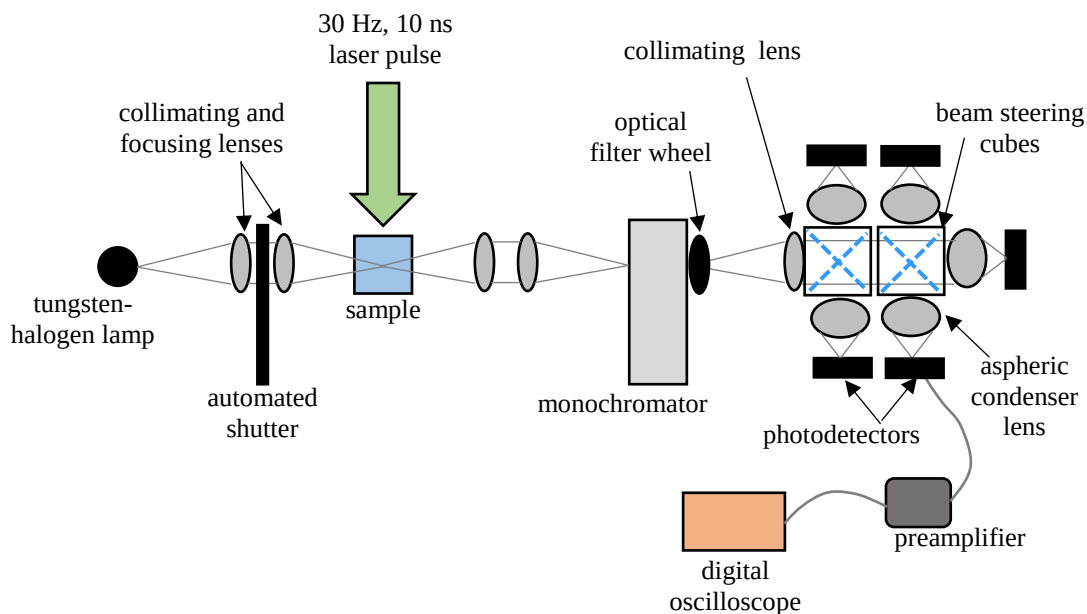


Figure 2-13: Schematic of the visible to near-infrared laser flash photolysis instrument.

A photograph of the system is provided in **Figure 2-14**.

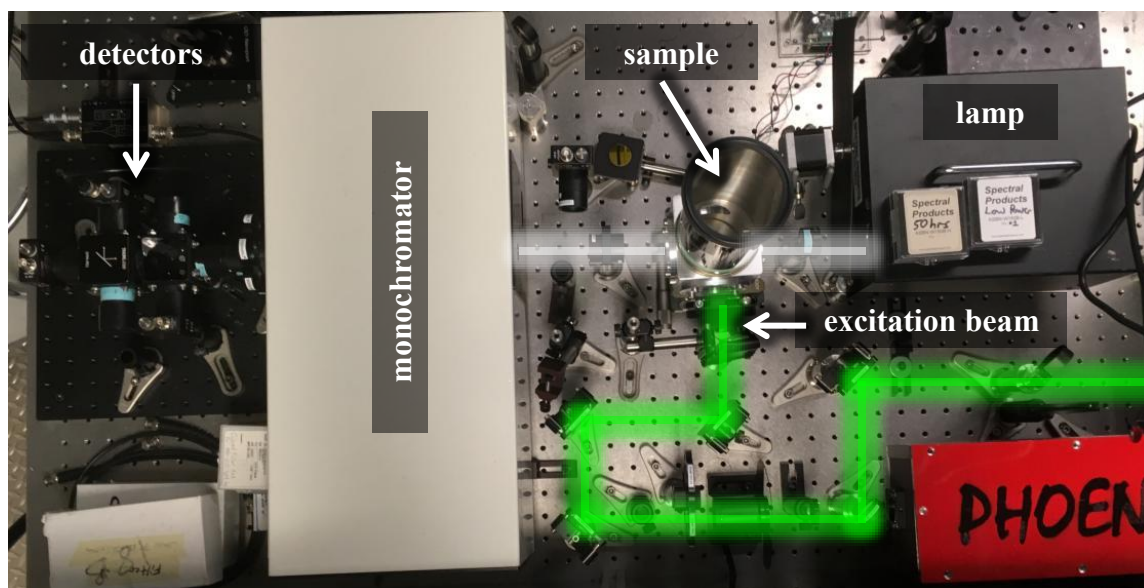


Figure 2-14: Photograph of the visible to near-infrared laser flash photolysis instrument. The monochromator is placed after the sample to reduce the detection of scatter and photoluminescence.

The excitation source was a frequency-doubled Nd:YAG laser (532 nm) with a ~ 10 ns pulse duration and a 30 Hz repetition rate. In many cases, the Nd:YAG laser was used to pump a dye laser cavity to produce longer wavelength excitation. The light source was a tungsten-halogen lamp, which is a blackbody emitter that produces ~ 400 – 2500 nm light. Before interacting with the sample, the monitoring beam is filtered using optical bandpass and longpass filters in order to limit the amount of optical power exposed to the sample. N-BK7 glass best form lenses are used to collimate and focus a portion of the lamp emission onto the sample. After transiting the sample, the beam is recollimated and focused onto the entrance slit of a monochromator, which contains a set of 3 gratings that each efficiently diffract different portions of the lamp emission spectrum. Upon exiting the monochromator, a filter wheel containing a collection of optical longpass filters is used to prevent the detection of higher orders of diffraction. The light exiting the monochromator is then collimated and sent into a beam-steering cube system that allows the choice of different photodiode detectors, each

having different wavelength sensitivities. Before each photodiode is an aspheric condenser lens used to tightly focus the light down to ~ 1 mm, which is the approximate element size for most of the photodiodes. All optics used (except the condenser lenses) have an F# of 4 to match the F# of the monochromator. The condenser lens has an F# of about 0.6, and so the focused image of the light source was minimized by ~ 6.7 times. The assortment of photodiodes includes a 1 ns rise-time MHz silicon photodiode (sensitive from 400–1100 nm), a 5 ns rise-time InGaAs photodiode (sensitive from 500–1700 nm), and a 17 ns rise-time InGaAs photodiode (sensitive from 800–2600 nm). The detected signal is further amplified using a 200 MHz preamplifier before it is digitized using a 200 MHz oscilloscope. The instrument is controlled by a computer using MATLAB.

An optical chopper is used to chop the laser pulse at 15 Hz in a noise suppression scheme reported previously.³ A home-built automated shutter is used to block and unblock the monitoring beam during experiments in order to subtract contaminant photoluminescence from the measured signals. If not careful, scatter and/or photoluminescence artifacts can result in attenuation of the transient absorption signal, as illustrated in **Figure 2-15**. Even in spectral regions in which scatter and/or photoluminescence is negligible, an extremely low amount can still contaminate the measured signal since the transient absorption signal is typically orders of magnitude smaller than the scatter and/or photoluminescence signals.

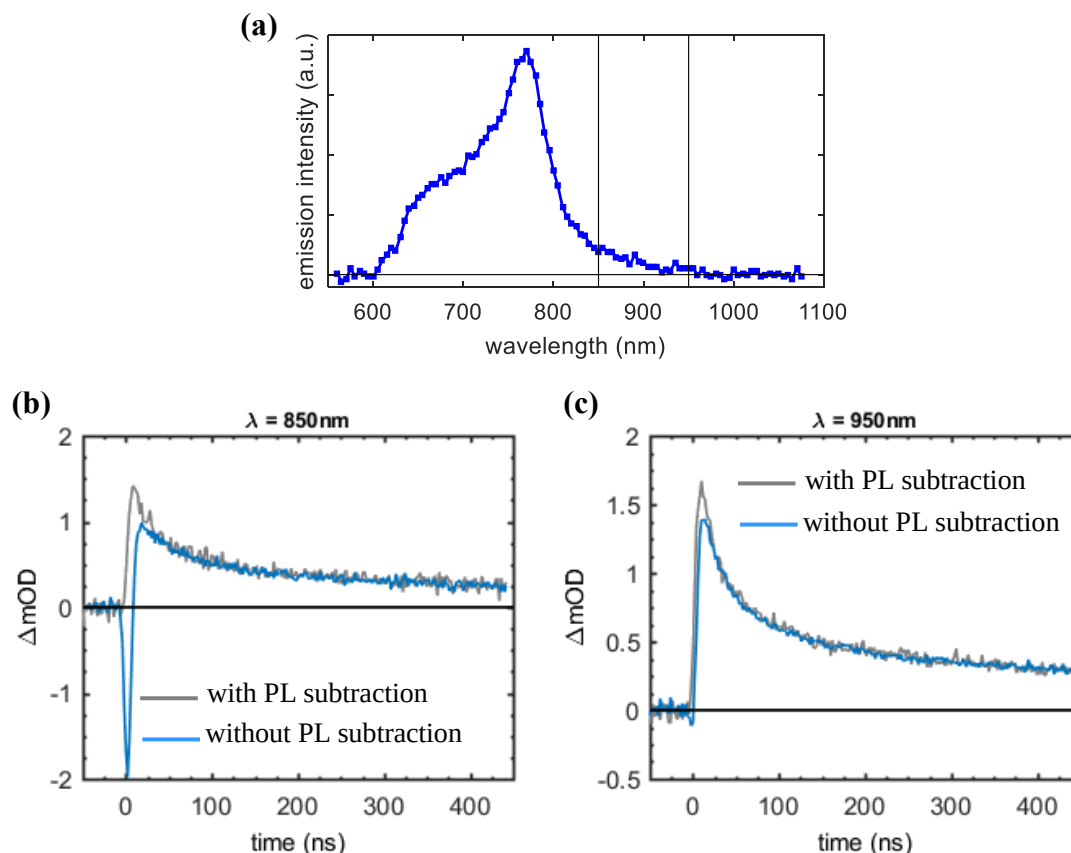


Figure 2-15: (a) Photoluminescence (PL) spectrum of a P3HT:PC₆₁BM blend film excited using 532 nm. Comparison of photoluminescence signals measured at (b) 850 nm and (c) 950 nm with and without PL subtraction. As seen in (c), even in a spectral region where PL seems negligible, it can still have an effect on the measured transient absorption signal.

For measuring samples that are sensitive to broadband visible light exposure, the monochromator is better positioned before the sample in order to limit the photon flux incident. As a result, a second laser flash photolysis system was also built for measuring transient absorption signals occurring within the visible spectral region. A detailed schematic of this instrument is provided in **Figure 2-16**, and a photograph of the set-up is shown in **Figure 2-17**.

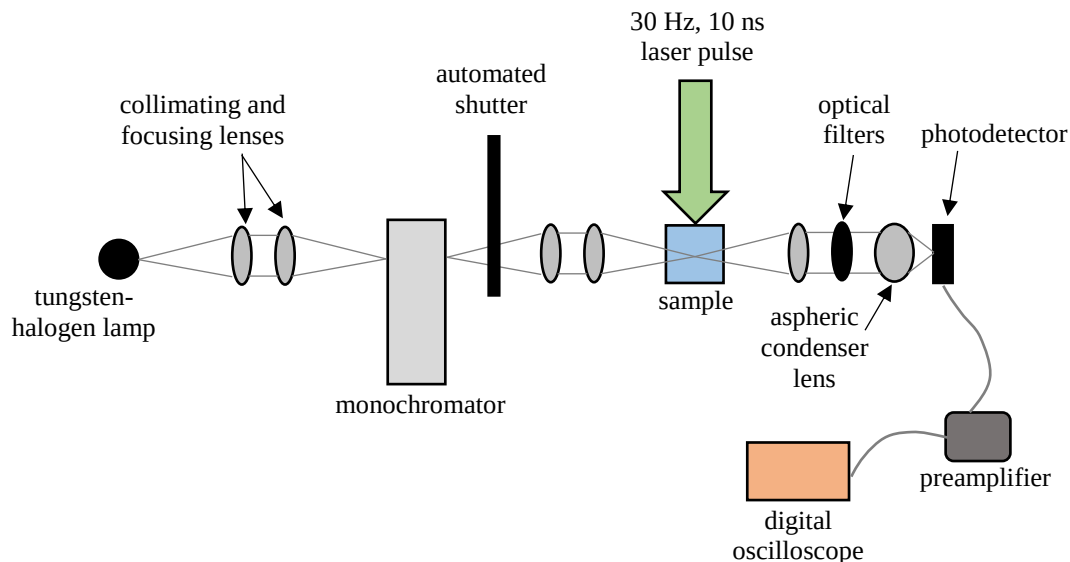


Figure 2-16: Schematic of the visible laser flash photolysis instrument.

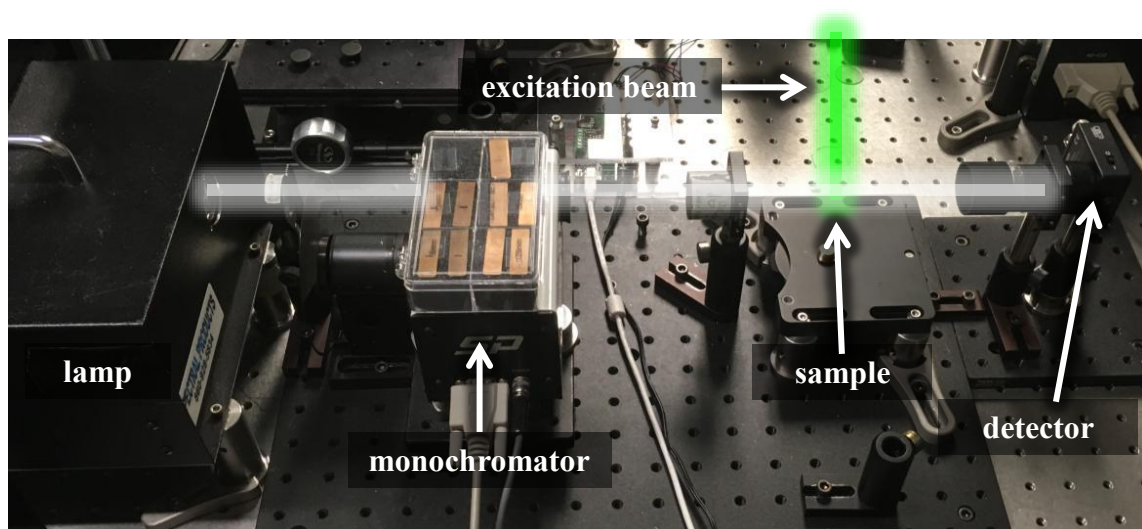


Figure 2-17: Photograph of the visible laser flash photolysis instrument. The monochromator is placed before the sample in order to reduce the level of exposure of the sample to the incident light. Note that the box on top of the monochromator contains an assortment of slits and is not actually part of the monochromator. The detector is a silicon photodiode.

In this case, an optical longpass filter was placed after the sample in order to prevent as much laser scatter and photoluminescence from being detected as possible. Because the photoluminescence detected is no longer wavelength dependent (since the monochromator is before the sample), the instrument software was modified so that the photoluminescence signal

is not collected at each wavelength, but is only collected once at the beginning of each scan, speeding up data acquisition. The detector used at the time was a 14 ns rise-time silicon photodiode.

The measured signals are exemplified in **Figure 2-18**. The transmission before the laser pulse ($t < 0$) is $T_0(\lambda)$, and the transmission change immediately following the laser pulse is $\Delta T(t, \lambda) = T_0(\lambda) - T(t, \lambda)$. The change in transmission eventually decays over time, resulting in $T_0(\lambda)$ again. In the system developed here, the change in transmission is actually collected using AC coupling, and the $T_0(\lambda)$ signal is collected in DC coupling. Because the change in transmission is typically very small (~ 10 's– 100 's μV) and $T_0(\lambda)$ is typically very large (~ 100 – 1 V), the use of a large voltage range for the digitizer to capture both signals would result in very low voltage resolution, raising the detection limit. For example, for a 8-bit digitizer and a 2 V range, the voltage resolution would be ~ 7.8 mV, which is much larger than the expected change in transmission signal. As such, the change in transmission is measured using AC coupling, which eliminates the “low frequency” $T_0(\lambda)$ from being detected and allows the use of much smaller voltage ranges, such as 20 mV. In this case, the voltage resolution would be ~ 78 μV for 8-bit digitization. At each wavelength probed, the signal is measured using both AC and DC coupling to determine $\Delta T(t, \lambda)$ and $T_0(\lambda)$, respectively.

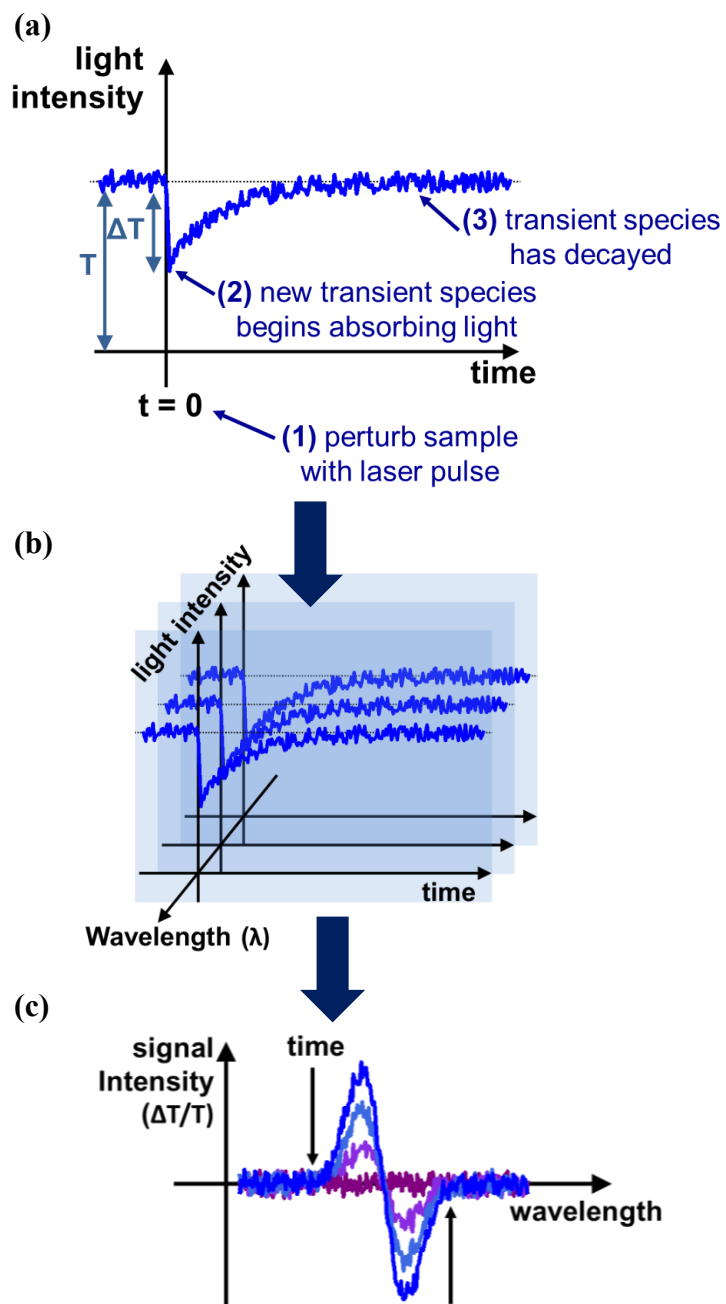


Figure 2-18: (a) Illustration of the detected transient absorption signal at a particular probe wavelength. (b) Illustration of the stacking of transient absorption traces on the wavelength scale. (c) Illustration of the resulting transient absorption spectrum.

2.1.4. Miscellaneous instrumentation

An absorption spectrometer was built using a CCD array detector in order to produce a rapid-scanning, high-throughput instrument for measuring steady-state visible absorption

spectra (400 – 800 nm sensitivity). A schematic and photograph of the instrument is provided in **Figure 2-19**. A stabilized tungsten-halogen lamp is used as the light source, which is filtered using optical filters. A fraction of the emitted light is collimated using a N-BK7 glass best-form lens. The beam then transmits the sample before being collected by a spectrometer containing a CCD array detector. The instrument can be used to perform *in-situ* absorbance measurements of films during thermal annealing if a temperature-controlled cryostat is used. In this case, the absorbance of a film can be measured at ~ 1 spectrum per second as the film is heated and cooled.

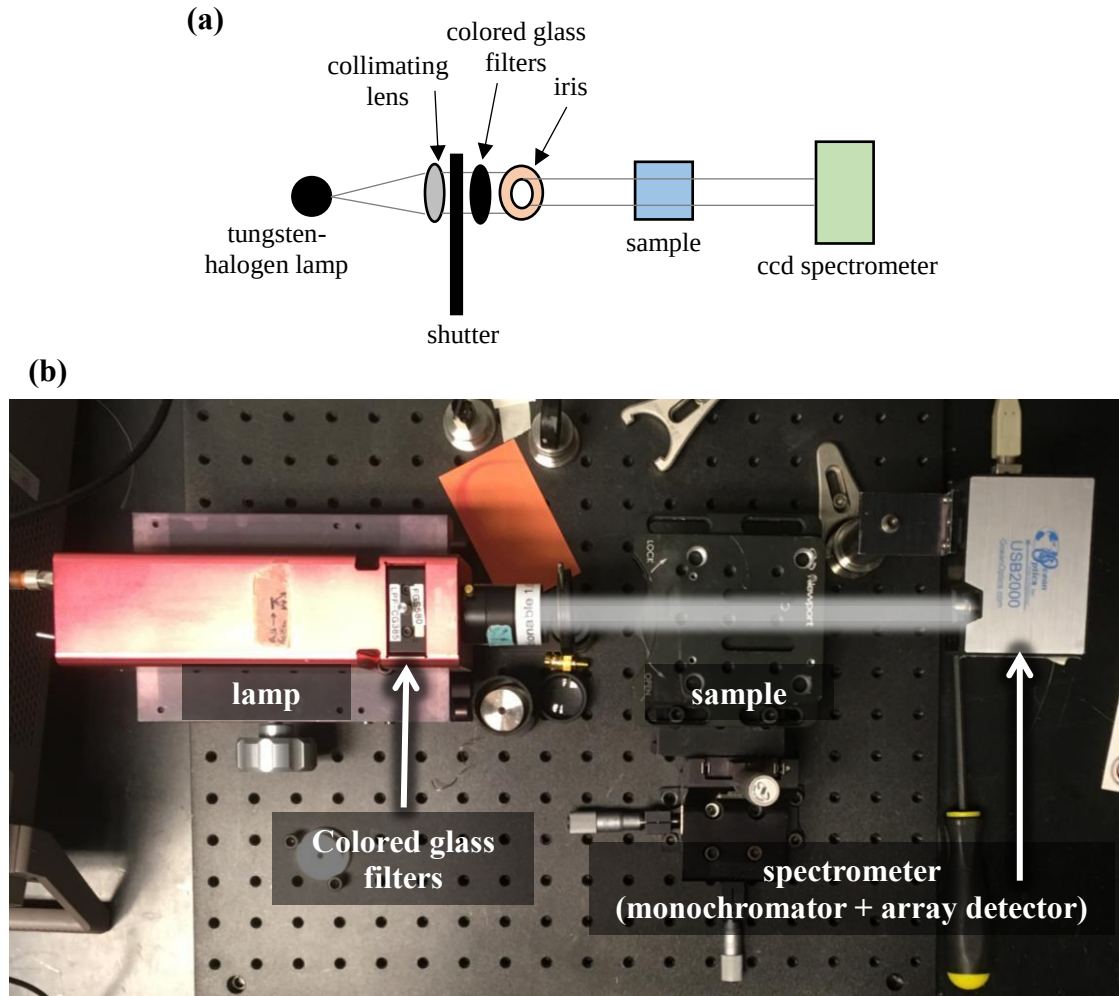


Figure 2-19: (a) Schematic and (b) photograph of the broadband visible absorbance spectrometer.

2.2. X-ray Diffractometry

Much of the work presented in this dissertation relied on X-ray diffraction (XRD) measurements, and so a brief overview⁴ of the principles and techniques used are provided here. Crystals consist of repeating or periodic units of its lattice, which creates repeating crystal planes, hkl, with spacings, d_{hkl} . The hkl are the Laue indices for the crystal planes. When light interacts with these repeating planes, it can diffract off of them and result in interference (see **Figure 2-20**).

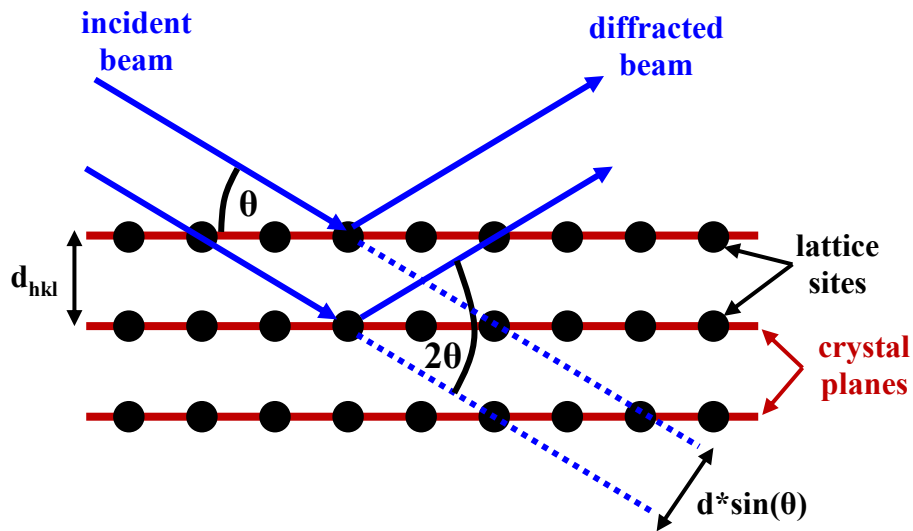


Figure 2-20: Illustration of the interference of light that is diffracted off of crystal planes in X-ray diffraction.

Maximum constructive interference (“reflection”) occurs when:

$$n\lambda = 2d_{hkl}\sin(\theta_{hkl}) \quad (\text{eqn. 17})$$

which is Bragg’s Law, where n is an integer representing the order of diffraction and θ_{hkl} is the Bragg angle (scattering angle).

Powder diffractometry is performed using a “ θ - 2θ ” scan, or “Bragg-Brentano” scan, in which the detected angle is always twice the incident angle (see **Figure 2-21**). In this way, the

Bragg condition (equation 17) is satisfied. A crystalline powder consists of an isotropic distribution of crystal planes, and so the entire set of crystal planes can be sampled.

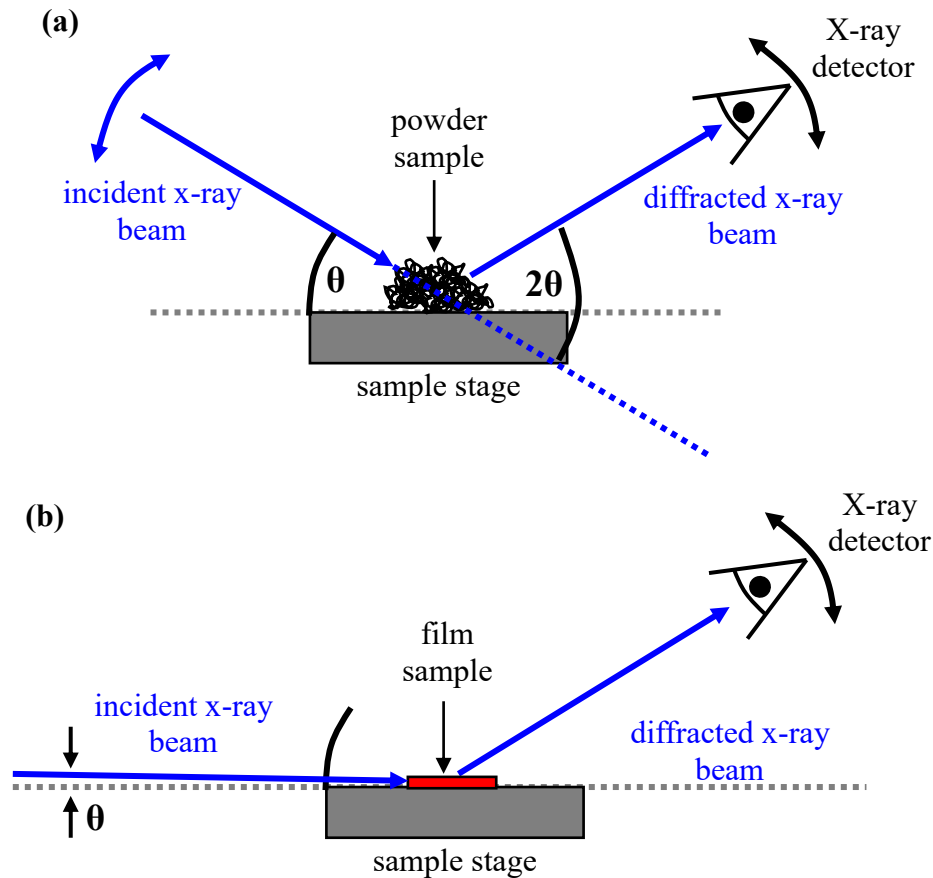


Figure 2-21: Simple diagrams for (a) powder (Bragg-Brentano) and (b) grazing-incidence X-ray diffractometry.

In crystalline films, crystal planes are often preferentially aligned on the substrate, and so not all of the planes may be sampled using a Bragg-Brentano scan. In addition, the film may be extremely thin, for which only a small number of crystal planes are available to be sampled, leading to low diffraction signals. A convenient technique for studying thin films is grazing-incidence X-ray diffraction (GIXRD), in which a fixed, grazing incidence angle is used (see **Figure 2-21**). Using conventional diffractometers, an angle of incidence as low as 1° can be used. In this way, the x-rays may sample through a larger number and set of crystal planes in the sample, and may be able to sample planes that are perpendicular to the substrate. However,

in this technique the Bragg condition is not satisfied, and so it is good for qualitative measurements. In particular, light interference cannot be described using Bragg's Law, and so this can lead to incorrect relative peak intensities and peak positions in the diffraction patterns.

2.3. Kinetic and Spectral Analysis of Time-Resolved Optical Spectroscopy

Next, methods for analyzing time-resolved optical spectroscopy will be briefly reviewed. These methods have been frequently used throughout the work presented in this dissertation.

2.3.1. Chemical kinetic theory

Chemical kinetic theory is often convenient for modeling the kinetic behavior of electronic states or other transient species measured in time-resolved optical spectroscopy. It is generally useful to use simple chemical kinetic theory to describe the photophysical reactions of excited states. A few examples of these reaction pathways will be described, the first of which is unimolecular decay:



In this example, the first excited singlet state (S_1) relaxes to the ground state (S_0) upon emission of a photon ($h\nu$) with rate constant, k_{uni} . The rate law can be expressed as:

$$\frac{d[S_1]}{dt} = -k_{uni}[S_1] \quad (\text{eqn. 19})$$

where square brackets indicate concentration, and t is time. Solving this expression gives:

$$[S_1] = [S_1]_0 e^{-k_{uni}t} \quad (\text{eqn. 20})$$

where $[S_1]_0$ is the initial concentration of excited singlet states. In transient absorption spectroscopy, ΔA is linearly proportional to $[S_1]$ by Beer's law. In photoluminescence spectroscopy, photoluminescence, PL, is also linearly proportional to $[S_1]$ since $[S_1]$ is proportional to the number of emitted photons. This gives:

$$\Delta A(t) = \Delta A_0 e^{-k_{uni}t} \quad (\text{eqn. 21})$$

$$PL(t) = PL_0 e^{-k_{uni}t} \quad (\text{eqn. 22})$$

where ΔA_0 and PL_0 are the original change in absorption and photoluminescence signals, respectively. As such, exponential decay of the measured signal is expected for unimolecular relaxation.

The next example is for unimolecular growth, which can be described using:



In this example, an excited singlet state, S_1 , undergoes intersystem crossing to form a triplet state, T_1 . The rate law can be expressed as:

$$\frac{d[T_1]}{dt} = +k_{uni'}[S_1] \quad (\text{eqn. 24})$$

If singlet relaxation is the only decay pathway for S_1 , the equation 20 may be substituted into equation 24. Using the initial condition of $[T_1]_0=0$ (no triplets exist preceding intersystem crossing), the solution is:

$$[T_1] = [S_1]_0(1 - e^{-k_{uni'}t}) \quad (\text{eqn. 25})$$

Thus the transient absorption signal for the population of triplet states would follow an exponential (1-e) growth. Note that in this representation, it is assumed that the S_1 state does not decay via any other paths.

The next example is for bimolecular decay, which can be described using:



In this example, triplet states diffuse and annihilate upon collision (triplet-triplet annihilation). The rate of reaction for the triplet-triplet complex that results from collision is assumed to be much faster than diffusion. The rate law is then expressed as:

$$\frac{d[T_1]}{dt} = -\frac{1}{2}k_{bi}[T_1]^2 \quad (\text{eqn. 27})$$

The solution is:

$$\frac{1}{[T_1]} = \frac{1}{[T_1]_0} + \frac{1}{2}k_{bi}t \quad (\text{eqn. 28})$$

Using Beer's Law, the transient absorption signal for the triplet population would be described by:

$$\frac{1}{\Delta A} = \frac{1}{\Delta A_0} + \frac{kt}{2\epsilon l} \quad (\text{eqn. 29})$$

If plotted as $1/\Delta A$ against t , this gives a linear dependence of the data on time, with a slope equal to $k/(2\epsilon l)$.

The bimolecular recombination⁵ of polarons in polymer films are often described using the following:



where p represents a hole polaron, n represents an electron polaron, and CT represents a charge-transfer complex. If the number of hole and electron polarons are taken to be equal, and if their mobilities are comparable, then p is indistinguishable from n , giving a similar scenario as in equation 26. The dependence of polaron concentration on time is then:

$$\frac{1}{n} = \frac{1}{n_0} + \gamma_{eh}t \quad (\text{eqn. 31})$$

where n_0 is the initial polaron concentration or number density, and γ_{eh} is the bimolecular recombination coefficient. Often this expression is generalized for transient absorption experiments in the form of an empirical power law⁶ as follows:

$$\Delta A = N(1 + at)^{-\alpha} \quad (\text{eqn. 32})$$

where N and a are empirical constants, and α is the power, which is related to the order of the reaction. Because polaron diffusion is influenced by charge trapping, their recombination is

not an ideal process (reaction order is less than two) and polaron absorption kinetics often have a power dependence of $0 < \alpha < 1$ (reaction order is between 1 and 2). Low values of α are a good indication of a low and/or broad trap distributions.⁷

For other, more complicated sets of coupled rate equations, numerical methods would be used to solve for the population kinetics. This was especially important for the work in Chapter 5, for example.

2.3.2. Kinetic modeling

Now that kinetic models have been established for describing time-resolved spectroscopic data, the finite temporal response of the instruments used must be considered. Because the instrument electronics (in the case of flash photolysis) or finite pulse durations (in the case for pump-probe) define their time resolution, they do not have infinitely fast responses to a signal. As a result, the measured signal is always a convolution of the true signal with the instrument response function (IRF). The IRF can be experimentally determined by measuring a signal that is expected to form and decay much faster than the expected response time. Time zero can be defined at the peak position of the IRF in time. Kinetic modeling of the data is then performed using:

$$S(t) = M(t) * IRF(t) \quad (\text{eqn. 33})$$

where $S(t)$ is the measured signal and $M(t)$ is the kinetic model for the true signal. An example of this process is illustrated in **Figure 2-22**. If time zero is set correctly, there is no need to adjust the time axis between the data and the IRF. After performing the convolution to obtain $S(t)$, the result is then compared to the data and the quality of fit is assessed. If the quality of fit is not as high as desired, the process may be repeated using a different set of parameters that define $M(t)$, or a different model may be selected.

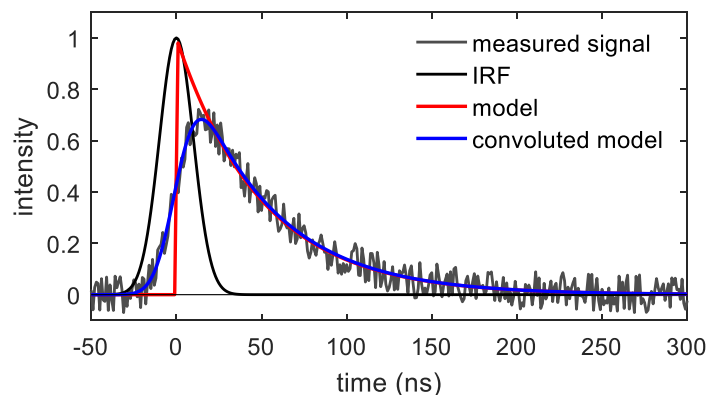


Figure 2-22: Illustration of a convolution-fit to a measured signal.

The need to convolute the IRF with the model function is most important if the changes modeled for in the measured signal are close to the IRF time. This process gives much more accurate values for the rate constants and other parameters used in the fitting process. If the changes in the kinetics that are being modeled occur on a much later timescale than the IRF, this convolution process may be neglected and the model itself may be fit directly to the data.

2.3.3. Spectral modeling

Often spectra measured using steady-state or time-resolved optical spectroscopies are composed of multiple overlapping peaks. If these peaks represent species that are non-interacting (i.e. Beer's Law is satisfied), then the spectrum may be decomposed into its components using equation 7. As a result, the spectrum may be modeled using a linear combination of the proposed underlying spectra:

$$S(t, \lambda) = c_1 M_1(t, \lambda) + c_2 M_2(t, \lambda) + \dots + c_n M_n(t, \lambda) \quad (\text{eqn. 34})$$

where c_i are scaling factors, and M_i are the modeled or measured spectra that underlie the overall observed spectrum, S . In cases where M cannot be measured, it is often approximated using a Gaussian (G), Lorentzian (L), or Pseudo-Voigt function.⁸ An illustration of spectral decomposition is provided in **Figure 2-23**.

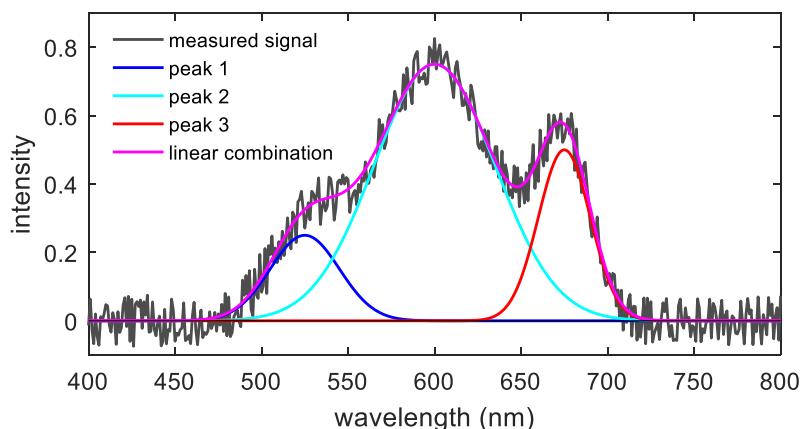


Figure 2-23: Illustration of spectral modeling.

2.4. Sample Preparation and Processing Methods

For the rest of the chapter, a brief overview of the sample preparation and processing methods used in this dissertation will be provided.

2.4.1. Solution samples

For the measurement of solutions, a sample cell must be used. The choice of cell window material is critical depending on the spectral range being measured. For visible and near-IR spectroscopy, cuvettes may be used, which are typically composed of quartz, glass, or infrasil. The pathlengths available are typically 1–10 mm, with larger pathlengths also available. For mid-IR spectroscopy, it is necessary to use different materials, such as CaF_2 , KBr, NaCl, or sapphire. However, cuvettes composed of these materials are not available, and instead, liquid cells must be constructed. The basic design of a liquid cell is the sandwiching of two optical windows using a chemically resistant spacer (see **Figure 2-24**). Typical spacers result in pathlengths as small as 12 μm and as large as 1–2 mm. For many of the transient absorption measurements used in this dissertation, sapphire or KBr windows were used and a Teflon or Viton o-ring was used as the spacer, resulting in a ~ 1.7 mm pathlength. Notably, the

pathlengths used in the mid-IR spectral region are often much smaller than those used in the visible spectral region because significant solvent vibrational absorption reduces the amount of light that may transmit the sample cell in mid-IR spectroscopy.

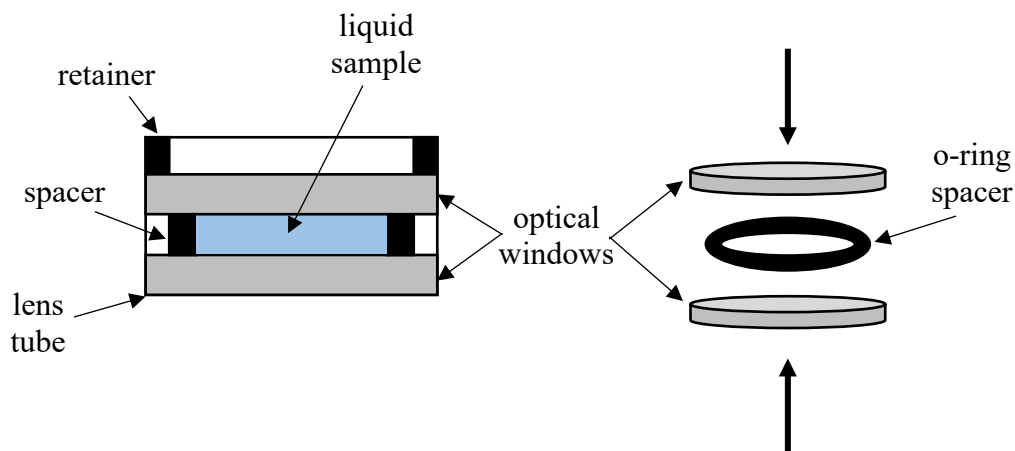


Figure 2-24: Diagram of the liquid cell used for optical spectroscopy measurements. The liquid is sandwiched between two optical windows separated using an o-ring spacer. This cell was enclosed using an optical lens tube.

In cases in which samples must be flowed during measurements, flow-cells may be used. For some of the work presented in this dissertation, flow-through cuvettes were used for visible and near-IR spectroscopic measurements. This was especially important for samples that were not very photostable because without flowing, the probed volume would otherwise contain a build-up of photoproducts. The flow rate needed depends on the degradation rate and the repetition rate of the laser. In some cases, the transient state lifetime may be exceedingly long. If the sample is not flowed in this case, a second excitation pulse may interact with the sample before the ground state has fully-recovered, resulting in a gradual build-up of a population of transient species.

2.4.2. Film samples and processing methods

Most of the films used in the work presented in this dissertation were prepared using spin-coating. Quickly after depositing a concentrated solution of polymers and/or molecules onto

a substrate, it is typically spun between 800–2000 rpm. Most of the solution is flung off of the substrate, leaving behind a thin liquid film on the substrate that then dries over time. Depending on the spin speed and solution concentration, this process usually results in films having thicknesses of tens to hundreds of nanometers. In some cases, films are instead produced by drop-coating, for which the solution is allowed to dry on the substrate without spinning. This typically results in much thicker, non-uniform films that are useful for testing.

The substrate material is important to consider depending on the measurement, and depending on how the molecules and/or polymers in the deposited films orient. In optical spectroscopy, the wavelength region of light transmitted determines what types of substrate materials can be used, which typically include quartz, glass, sapphire, CaF_2 , or silicon. Additionally, in transient spectroscopies that use high photon flux, thermal artifacts can occur as excited states relax and cause the film temperature to rise. In cases that this is particularly problematic, it is helpful to use substrates with high thermal conductivities to reduce this effect.⁹ These include sapphire and CaF_2 , in particular. In XRD measurements, crystalline substrates can lead to background signals that overlap with the diffraction pattern of the sample, often overwhelming the signals of interest. It is important to select substrates that are either amorphous (e.g. glass) or are crystalline with peaks appearing outside the range of measurement.

After deposition, the films may be further processed using annealing techniques, which assist the crystallization or organization of the polymers and/or molecules. The first technique, thermal annealing, is performed by placing the film onto a hotplate at a particular temperature and time duration. The second technique, solvent vapor annealing, relies on the interaction between solvent vapor and the polymers and/or molecules in the film. The film is exposed to

solvent vapor for a certain amount of time. A simple solvent annealer is illustrated in **Figure 2-25**.

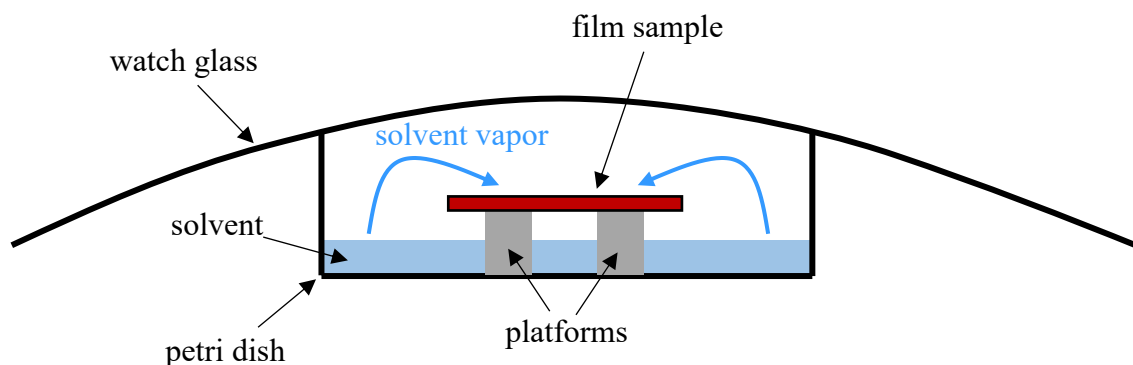


Figure 2-25: Diagram of a petri dish solvent vapor annealer.

2.5. References

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CHAPTER 3

General Principles of Singlet Fission and Morphological Characterization Methods for Singlet Fission Materials

Singlet fission is the conversion of a single singlet exciton into two triplet excitons, thus representing a type of multiple exciton generation mechanism potentially useful for solar cell applications. Because of the mechanistic requirement of discretized energy levels, singlet fission is a photophysical pathway characteristic to some organic molecules and polymers. It is hoped that these materials will serve as “singlet fission sensitizers” for either inorganic or organic solar cells that enable the complete utilization of high-energy photons, thereby overcoming thermalization loss. Because of the general requirement of at least two adjacent molecules for the reaction to occur (supporting the creation of two independent triplet excitations), the singlet fission reaction has been repeatedly shown to be controlled by intermolecular interactions, and hence, solid-state molecular packing arrangements.

Singlet fission is generally described as 2-step consecutive reaction, in which the reactant is a singlet exciton, the intermediate is a biexciton species (whose physical nature remains poorly-understood), and the product is a pair of independent triplet excitons. The first reaction step has been extensively studied and has been related very strongly to intermolecular arrangements of the organic molecules. However, as will be recurrently discussed, there is a great lack of understanding of how the second step is controlled. This conversion of the intermediate species into the product species is significant to the actual duplication of excitation, and hence, has practical bearing on the application of singlet fission sensitizers. This topic is examined and discussed in depth in Chapter 6 and Chapter 7. The diffusion of the product species, independent triplet excitations, and their relation to molecular packing

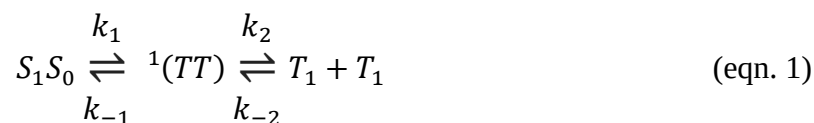
arrangements and sample morphology, are investigated in Chapter 4 and Chapter 7. Prior to these investigations, however, it was crucial to first develop methods for characterizing molecular packing and thin film morphology of singlet fission materials. This chapter serves to introduce to the reader to singlet fission in greater detail, after which the development of methods for characterizing structure and morphology of thin films of singlet fission sensitizers is presented, which will be important for the work presented in Chapters 4 – 7.

This chapter partially contains work reported in the following publications: Grieco, C., Kennehan, E.R., Pensack, R.D., Brigeman, A., Kim, H., Rimshaw, A., Payne, M.M., Scholes, G.D., Anthony, J.E., Giebink, N.C., Asbury, J.B., “Direct Observation of Correlated Triplet Pair Dynamics during Singlet Fission using Ultrafast Mid-IR Spectroscopy”, *submitted*; Grieco, C., Doucette, G.S., Munro, J.M., Kennehan, E.R., Lee, Y., Rimshaw, A., Payne, M.M., Wonderling, N., Anthony, J.E., Dabo, I., Gomez, E.D., and Asbury, J.B., “Triplet Transfer Mediates Triplet Pair Separation during Singlet Fission in 6,13-Bis(triisopropylsilylethynyl)-Pentacene”, *Adv. Func. Mater.*, **2017**, 1703929; and Grieco, C., Doucette, G.S., Pensack, R.D., Payne, M.M., Rimshaw, A., Scholes, G.D., Anthony, J.E., and Asbury, J.B., “Dynamic Exchange During Triplet Transport in Nanocrystalline TIPS-Pentacene Films”, *JACS*, **2016**, 138, 16069-16080.

3.1. Singlet Exciton Fission: General Principles

3.1.1. Kinetic model

The general singlet fission mechanism was first introduced in Chapter 1. This mechanism can be further expanded¹ into a set of two consecutive elementary reaction steps:



where S_1S_0 represents two adjacent molecules, one in the ground singlet state and the other in the first singlet excited state, ${}^1(TT)$ represents the “correlated triplet pair” intermediate state, and T_1 represents an independent triplet excitation. It is useful to represent each reaction step using a rate constant, k_i , with positive integers, i , corresponding to forward directions, and with negative integers, $-i$, corresponding to reverse directions. This formulation is the most generally accepted model, well-supported by optical spectroscopy measurements for a variety of organic molecules.²⁻¹⁰ Although the mechanism expressed in this form is well-established, it remains as an approximation.¹

In the first reaction step, the reactant species is represented as a singlet exciton localized on one molecule, which shares its energy with an adjacent ground state molecule to form the intermediate species. This intermediate correlated triplet pair species, as written, represents two triplet excitations on adjacent molecules, which possess spin functions that are coupled into a pure singlet. During this reaction step, the spin multiplicity does not change, making the process quantum mechanically “spin-allowed”. Consequently, this step can be very rapid, with experimental rate constants as high as $\sim 1 \times 10^{13} \text{ s}^{-1}$ for pentacene derivatives.¹¹ As such, the nature of this first reaction step leads to its categorization as a special case of internal conversion.

In the second reaction step, the correlated triplet pair converts into two kinetically independent triplet excitations by spin-decoherence.^{12,13} This conversion involves the mixing of two states with different multiplicity, and so it can be a much longer process. The specific pathways occurring during this process, such as exciton migration or physical separation of the

triplet pair, are debated, possibly being system-dependent. However, spin-decoherence is agreed to be a common characteristic of the overall process. Altogether, the nature of this second reaction step leads to its categorization as a special case of intersystem crossing.

In the literature, the use of the term, “singlet fission”, can be ambiguous: It is sometimes defined as the overall process, the first step, or the second step. Herein, the term “singlet fission” is used to describe the overall process, and the “first step” and “second step” are explicitly used to describe the general reaction steps involved during singlet fission.

The fission of a singlet exciton into two triplet excitons, from a thermodynamic standpoint, requires that the energy of the singlet is at least twice the energy of the triplet. This forms an important, but incomprehensive, criterion for the organic molecule candidate for singlet fission. In this perspective, there are two major regimes of singlet fission: (1) endergonic (“thermally-activated”) and (2) exergonic. In endergonic singlet fission, the energy of the singlet state is slightly less than twice the energy of the triplet state ($E_{S1} < 2 \times E_{T1}$). As a result, singlet fission is thought to be a thermally activated process, and so fission rates tend to occur on a late picosecond timescale or even a nanosecond timescale.^{4,14,15} Examples of molecules falling in this regime are tetracene^{14,15}, rubrene¹⁶⁻¹⁸, and perylenes⁴. In exergonic singlet fission, the energy of the singlet state is more than or equal to twice the energy of the triplet state ($E_{S1} \geq 2 \times E_{T1}$). In this case, fission is energetically favorable and so rates tend to occur much more rapidly, often on the early-picosecond and sub-picosecond timescale. Examples of molecules include pentacene and pentacene derivatives, which have singlet fission (first step) time constants of ~ 80 fs.^{19,20} Examples of singlet fission molecules are shown in **Figure 3-1**.

It is also possible for singlet fission to occur from higher-lying singlet excited states (above S_1).¹ Especially in cases in which fission may occur extremely rapidly, it is possible that singlet fission can kinetically out-compete internal conversion from $S_n \rightarrow S_1$.

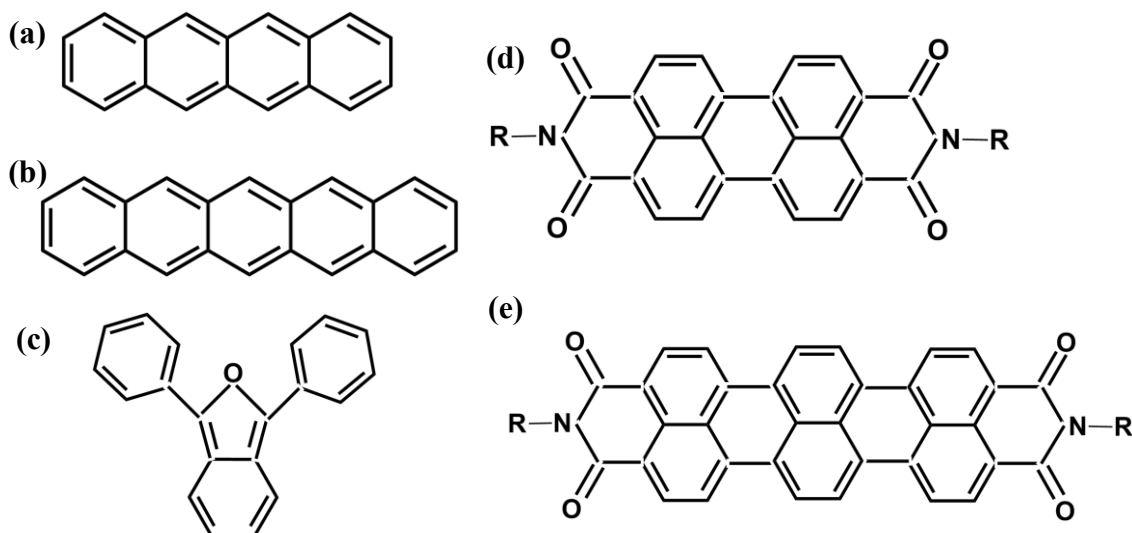


Figure 3-1: Examples of organic molecules that can undergo singlet fission. (a) tetracene, (b) pentacene, (c) 1,3-diphenylisobenzofuran, (d) perylenediimide, and (e) terrylenediimide

Exergonic singlet fission, from a kinetic perspective, is particularly appealing because of the prospect of occurring with high efficiency. High reaction rates pose singlet fission to be kinetically competitive with other excited state relaxation processes, thereby predisposing fission as the more favorable, and thus efficient, pathway. It is instructive to illustrate this attribute using a simple argument. Consider the simple expression for the quantum efficiency of singlet fission:

$$\Phi_{\text{singlet fission}}^{\text{singlet}} = \frac{k_{\text{singlet fission}}}{k_{\text{singlet fission}} + k_{\text{fluorescence}} + k_{\text{internal conversion}} + k_{\text{intersystem crossing}}} \quad (\text{eqn. 2})$$

The efficiency of the singlet fission reaction can be maximized if the rate is exceedingly fast compared to all other relaxation processes ($k_{\text{singlet fission}} \gg k_{\text{other}}$). Additionally, efficient singlet

fission would be kinetically competitive with other deleterious processes, such as excimer or charge formation.

Alone, the energetic requirement of singlet fission, while significant, does not guarantee that singlet fission will occur despite the potential of kinetic favorability. As will be discussed in the next section, a quantum mechanical description must be considered, which introduces the importance of intermolecular coupling for the first step of singlet fission reaction.

3.1.2. Quantum mechanical model and role of intermolecular coupling

Naturally, singlet fission is not universally intrinsic to any molecule that satisfies the condition, $E_{S1} \approx 2 \times E_{T1}$. Because the reaction involves the sharing of electronic energy between multiple adjacent chromophores, the rate depends on their electronic interactions. When two molecules are close enough to weakly interact, the total electronic Hamiltonian contains contributions from both the individual molecule Hamiltonians in addition to an interaction term. If the interaction between molecules is taken to be weak (e.g. noncovalent interactions present between molecules in an organic solid), the rate of singlet fission can be expressed using perturbation theory as Fermi's golden rule:

$$k_{I \rightarrow F} = \frac{2\pi}{\hbar} |\langle F | H_{el} | I \rangle|^2 \rho(E_I = E_F) \quad (\text{eqn. 3})$$

where I and F are the initial and final states, respectively, $\hbar$ is Planck's constant, H_{el} is the electronic Hamiltonian, and ρ is the Franck-Condon weighted density of final states, and E is energy.

In describing the two-molecule system, the basis states are described using molecular orbitals localized to each molecule. The electron configurations for each basis state and the off-diagonal coupling terms are illustrated in **Figure 3-2**.

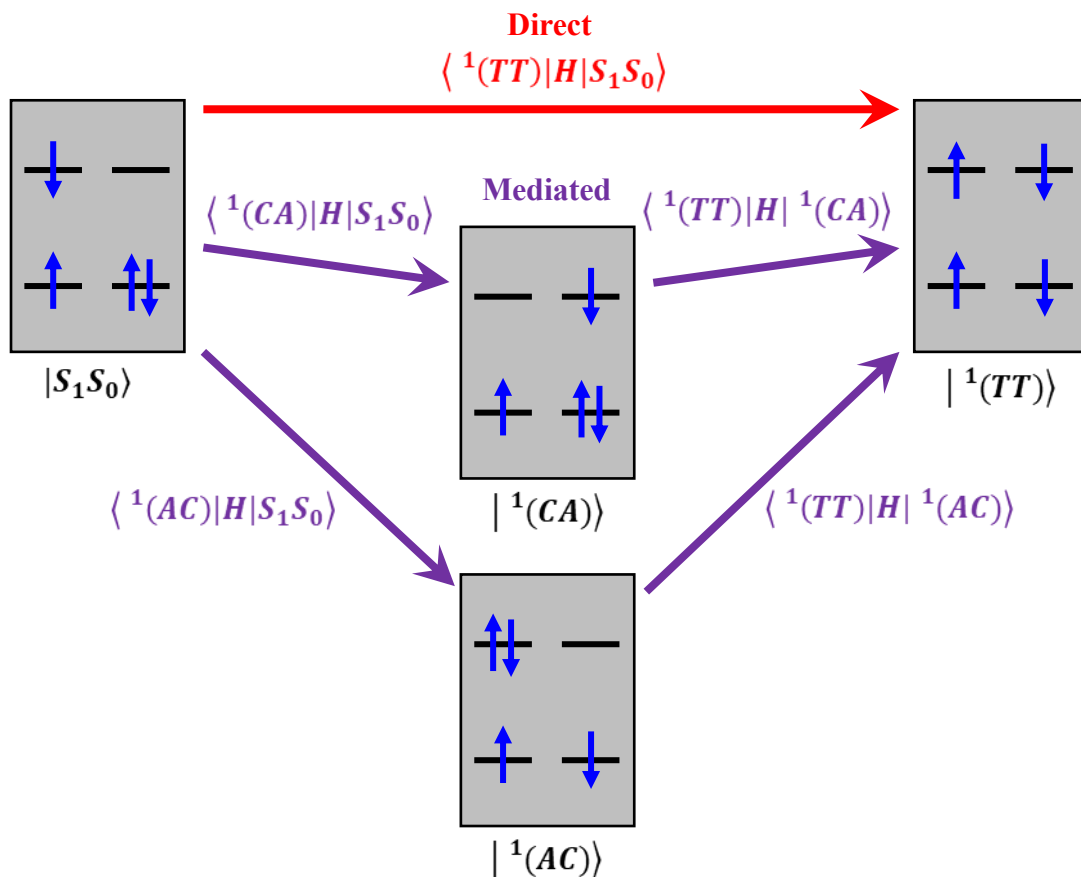


Figure 3-2: Perturbation theory description of the first step of singlet fission for a weakly coupled molecular pair, showing off-diagonal couplings for both the direct and mediated mechanisms. The electronic configurations are shown for each molecular pair state, or basis state.

The states are commonly defined based on their electronic configurations as: (1) a localized singlet exciton, S_1S_0 , (2) the correlated triplet pair, $^1(TT)$, and (3) singlet charge-transfer states, $^1(CA)$ or $^1(AC)$. Note that “C” represents a “cationic” species, and “A” represents an “anionic” species. In accordance to the model in **Figure 3-2**, the intrinsic singlet fission rate is described using equation 3 and the S_1S_0 and $^1(TT)$ basis states:

$$k_{singlet\ fission} \sim |\langle S_1S_0 | H_{el} | ^1(TT) \rangle|^2 \quad (\text{eqn. 4})$$

This term is also commonly referred to as the “direct coupling”, and singlet fission mechanism is said to occur “directly”. If the direct coupling term is small, or if the charge-transfer state

energy is close to the singlet exciton state energy, then it is possible for mixing of the singlet and charge-transfer states. In this case, singlet fission is said to be “mediated” via the charge transfer states, and higher-order perturbation theory is used to describe the rate. These mechanisms are summarized in **Figure 3-3**.

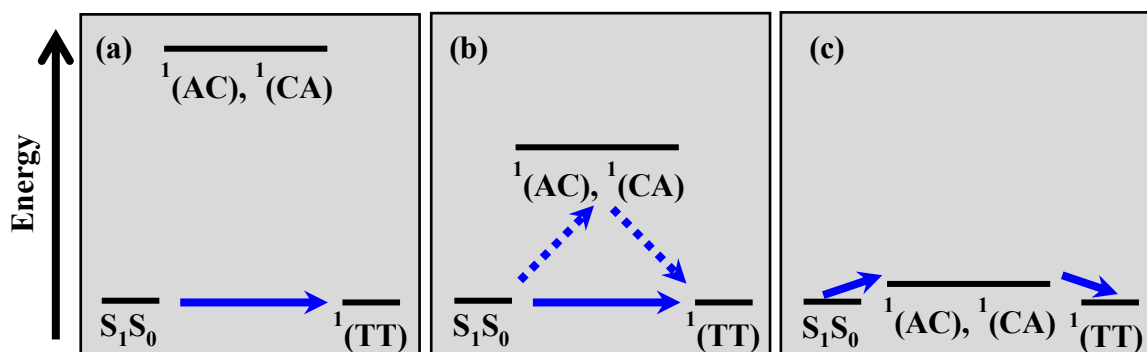


Figure 3-3: Simple energy level diagrams depicting the (a) direct, (b) mediated (virtual charge-transfer states), and (c) mediated (populated charge-transfer states) singlet fission mechanisms. Dashed arrows signify that coupling is significant, but the final state, indicated by the arrowhead, is not populated.

While the case of singlet fission proceeding via direct coupling has been supported in the past¹¹, the mediated mechanism is actually generally accepted to dominate.²¹ In particular, direct couplings have been found to be particularly weak compared to the couplings between singlet excitons and charge-transfer states.

The specific role of charge-transfer states is under current investigation. For instance, they may either serve as virtual (not populated) or real (populated) states in the singlet fission reaction.⁶ For example, in recent work by Margulies and coworkers^{6,22}, it was found that if the CA energy is too low, CA is populated/has too much excimer character, and singlet fission rate is low. On the other hand, some reports^{23,24} actually indicate that excimer states may in fact mediate singlet fission. In this case, the charge-transfer state is populated, but importantly, is substantially mixed with localized singlet excitations of each molecule in the pair state (S_1S_0 and S_0S_1).

Because singlet fission may occur at very high rates (e.g. faster than 1 ps), it is possible that phonon motions of the molecules are important for controlling the precise excited state pathway. For example, the dynamical motions of the molecules in a solid occur much more slowly than the preparation of the singlet exciton and its subsequent fission process. This would predetermine a distribution of intermolecular geometries that may be important to consider. In particular, the couplings between molecules in the excited state may depend on the types of phonon modes present, and so these phonons may play a role in singlet fission. Additionally, the static energetic disorder often present in molecular solids may modulate both intermolecular couplings and energetic driving forces that determine the rate of singlet fission.

3.1.3. Perspective: Unifying the quantum mechanical picture and molecular packing

The couplings involved in singlet fission (**Figure 3-2**) contain weakly interacting molecular pair states, and so the singlet fission rate intrinsically depends on the intermolecular geometry. In organic solids, the molecules interact through space via weak non-covalent interactions, and so the couplings are strongly influenced via orbital overlap interactions. Changing the intermolecular geometries result in different orbital overlap interactions, and so the packing or arrangements of the molecules in solids, such as amorphous films or crystals, will determine the ability or rate of singlet fission by modulating the couplings described in **Figure 3-2**. For example, the slip-stacked packing structure (illustrated in **Figure 3-4**) has been empirically related to highly efficient singlet fission. In addition, certain geometries may actually favor the population of charge-transfer states or excimer states, changing the apparent singlet fission mechanism and/or rate.

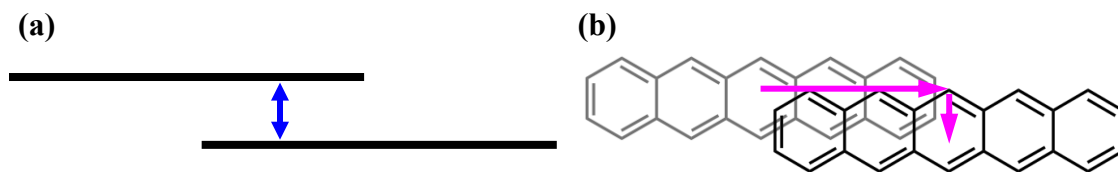


Figure 3-4: Example of a hypothetical slip-stacked geometry for a pair of molecules, showing a **(a)** side view, and **(b)** top-down view. Blue arrow indicates distance in the pi-pi stacking direction. Magenta arrows indicate directions of slippage.

Importantly, the quantum mechanical treatment of singlet fission thus far pertains to the first step of the reaction (i.e. formation of the correlated triplet pair intermediate). Minor attention has been given to what determines the second step of the reaction (i.e. formation of independent triplet excitations), which is illustrated in **Figure 3-5**.

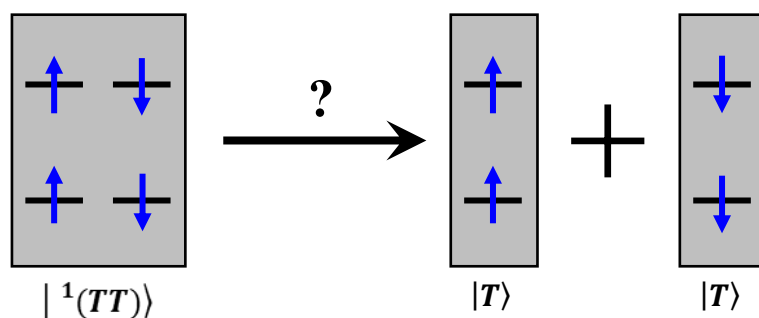
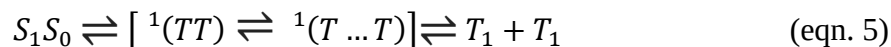


Figure 3-5: The second step of singlet fission for a weakly coupled molecular pair, showing the electronic configurations for each state involved.

The rate of this process has a strong bearing over the overall yield of independent triplet excitons, and consequently, is intimately related to the exciton multiplication aspect of singlet fission. Recently, physical separation of the spin-correlated triplet excitations has been observed spectroscopically²⁵, reviving the following (expanded) kinetic model originally proposed in 1978:²⁶



where ${}^1(T \dots T)$ is a spatially-separated correlated triplet pair intermediate. In this kinetic model, the separation of triplet excitations accompanies the formation of independent triplets,

$T_1 + T_1$. In another view, the correlated triplet pair state “splits” before it undergoes spin decoherence. Spin decoherence, which can occur on timescales exceeding nanoseconds,²⁷ limits the rate at which independent triplet excitations can be formed. Therefore, relaxation processes, such as internal conversion of the correlated triplet pair (or reformed singlet exciton), may become kinetically competitive for the second step of singlet fission. It is thought that physical separation of the triplets prevents rapid internal conversion, thereby allowing efficient formation of multiplied, independent triplet excitations. Further discussion on this point is provided in Chapter 12, in which future research directions are presented.

In theory, the mechanism by which triplet states may physically separate is triplet excitation energy transfer. This process depends very strongly on orbital overlap interactions since it is mediated via short-range Dexter interactions. Therefore, like in the first step of singlet fission, the efficiency of the second step also may be intimately connected to intermolecular packing arrangements. In Chapter 7, the first experimental account of this process is described in detail.

3.2. Pentacene Derivatives: Model Systems for Singlet Fission

3.2.1. General characteristics of pentacene derivatives

In this work, the pentacene derivative, 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-Pn), is taken as an exemplar for efficient singlet fission. Countless reports^{3,24,28-35} of this molecule as a singlet fission material have been published, and so much is known of its electronic structure, spectroscopic signatures, crystal packing structure, and photo- and chemical stability. The chemical structure of TIPS-Pn is provided in **Figure 3-6**. This pentacene derivative was designed^{35,36} with silylethynyl side groups placed at the 6 and 13 carbon positions of pentacene in order to improve chemical stability. These carbon positions

are reactive sites for oxygen, but can also serve as sites for highly-efficient cycloaddition reactions, forming what are called “butterfly dimers”.³⁷ Additionally the addition of side groups with bulky alkyl side chains improves the solubility of the compound dramatically,³⁶ which facilitates the use of cheap solution-processing techniques that are often employed in organic solar cell fabrication.

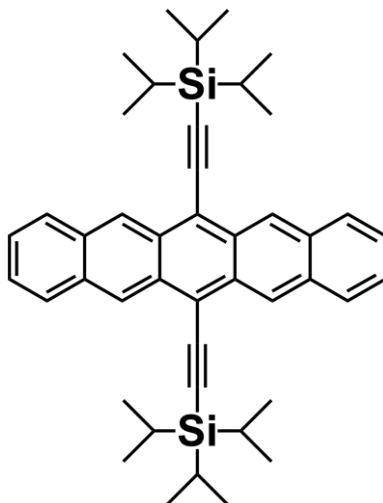


Figure 3-6: Chemical structure of TIPS-Pn.

Like in pentacene, singlet fission in TIPS-Pn is highly exergonic and results in a sub-picosecond (first step) reaction time constant.¹¹ Unlike pentacene, which forms a “herringbone” packing structure, TIPS-Pn forms a “2D-brickwork” arrangement, both of which are illustrated in **Figure 3-7**.³⁶

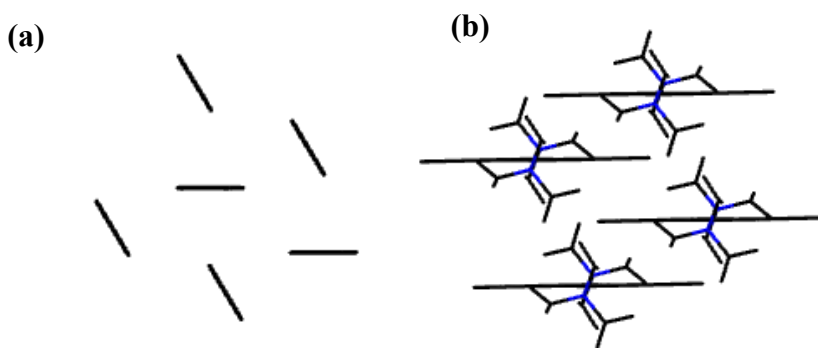


Figure 3-7: Comparison of the crystal packing structures for (a) pentacene (herringbone) and (b) TIPS-Pn (2D-brickwork).

This arrangement prominently displays slipped-stack intermolecular geometries. In addition to TIPS-Pn, many other pentacene derivatives have been shown to undergo rapid singlet fission, including, but not limited to: 6,13-bis(triethylsilylethynyl)pentacene (TES-Pn), 6,13-bis(triisobutylsilylethynyl)pentacene (TIBS-Pn), 6,13-bis(trisecbutylsilylethynyl)pentacene (TSBS-Pn), 2,9- and 2,10-dichloro-6,13-bis-(triisopropylsilylethynyl)pentacene (Cl2-TIPS-Pn), and 2,4,9,10-tetrachloro-6,13-bis(triisopropylsilylethynyl)pentacene (Cl4-TIPS-Pn).^{25,38} The crystal packing geometries of pentacene derivatives are highly dependent on small changes in the chemical composition of the side groups,³⁶ or functionalization of the pentacene core.^{39,40} The influence of alkyl substituents on crystal packing structure are exemplified in **Figure 3-8**.

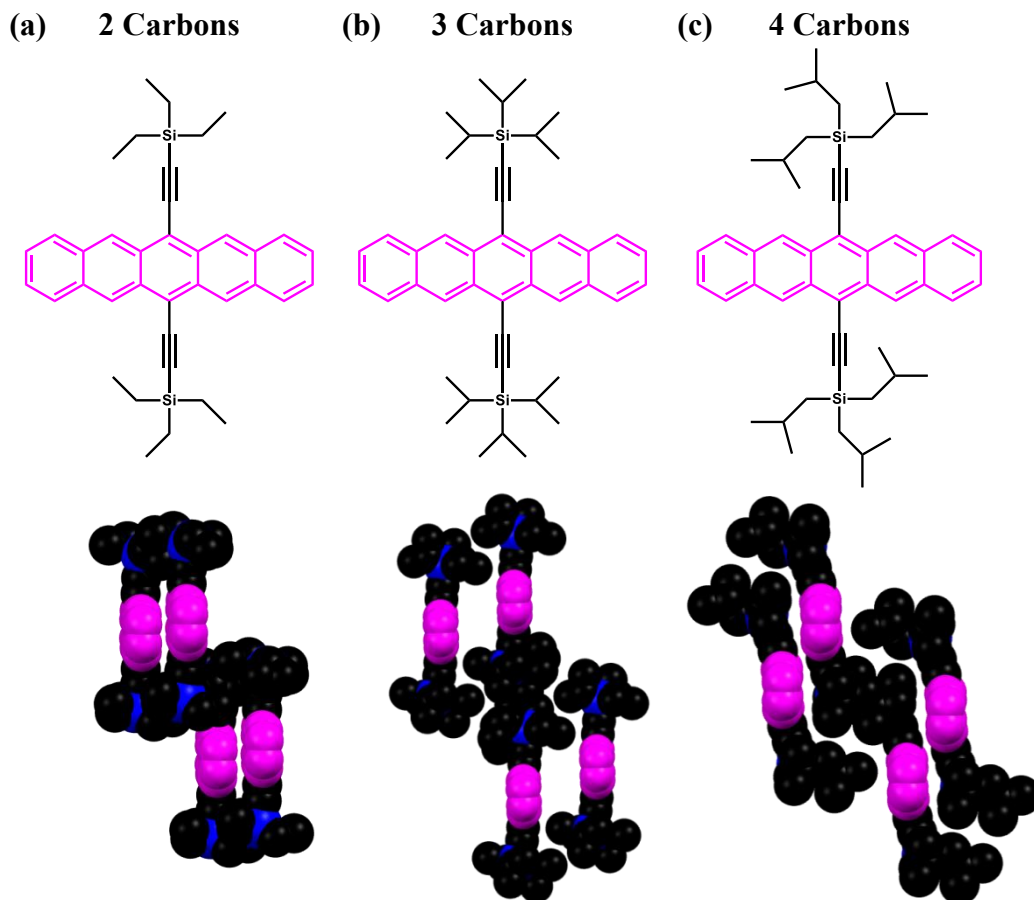


Figure 3-8: Comparison of the chemical structures and corresponding space-filled crystal packing structures for (a) TES-Pn, (b) TIPS-Pn, and (c) TIBS-Pn.

This tunability in molecular packing arrangements is enabled by weak noncovalent interactions between molecules in the crystal lattice.⁴¹ In particular, the van der Waals interactions between the alkyl side chains of different molecules, in addition to their electron densities, have been shown to control the crystal packing motifs in a recent report comparing TES-Pn to TIPS-Pn.⁴²

The ability to control crystal packing motifs offers a way to develop design principles for future singlet fission materials (see Chapter 12 for some examples). Because the molecular packing arrangements are modulated by changes in crystal packing motif, the impact of the accompanying changes in intermolecular interactions on singlet fission and triplet diffusion

may be directly studied. The results would provide information that could be used to help direct the development of molecular packing design rules for singlet fission sensitizers.

3.2.2. Energetics and spectroscopic characteristics of TIPS-Pn

The time-resolved spectroscopic signatures of pentacene derivatives, useful for studying singlet fission, are well-represented in solution samples. When sufficiently dilute, the molecules in solution are said to be electronically “isolated” from each other, surrounded by solvent molecules. The observed solute photophysics, assuming there are no significant solute-solvent interactions, therefore represent those of isolated molecules. The states participating in excited state dynamics are composed of molecular orbitals, and so typical decay pathways (illustrated in the Jablonski diagram in **Figure 3-9**) after photoexcitation include internal conversion (IC), fluorescence (fluor.), intersystem crossing (ISC), and phosphorescence (phos.). In time-resolved transient absorption spectroscopy, absorptions typically correspond to transitions from $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$. Such transitions can have a variety of transition energies depending on ordering and spacing of the energy levels. The corresponding absorptions measured (for a given excited state concentration) can have different extinction coefficients depending on the allowedness of each transition.

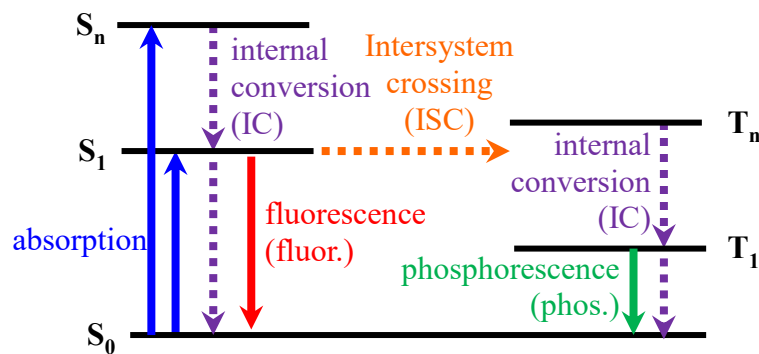


Figure 3-9: Jablonski diagram for isolated molecules. Solid arrows indicate radiative transitions and dashed arrows indicate nonradiative transitions between electronic states.

In organic molecules, because spin-orbit coupling is typically weak, transitions involving a change in spin state are often forbidden. For example, forward ISC from $S_1 \rightarrow T_n$ and relaxation from $T_1 \rightarrow S_0$ are slow compared to $S_1 \rightarrow S_0$. This results in T_1 having a much longer lifetime than S_1 . This characteristic enables the discrimination of excited singlet and triplet state absorptions through measurement of their decay times. Thus, monitoring the time-dependence of transient absorption signals also provides a potential method for assigning the spin of the excited states.

Steady-state absorption spectra of TIPS-Pn solutions reveal the allowed $S_1 \rightarrow S_n$ transitions. The transition energies are estimated as the central frequency of the 0-0 absorption bands. The extinction coefficients are determined using Beer's law, with the concentration of ground state equal to the known solution concentration (excited state concentration under weak, continuous illumination is negligible). The absorption spectrum is shown in **Figure 3-10**.

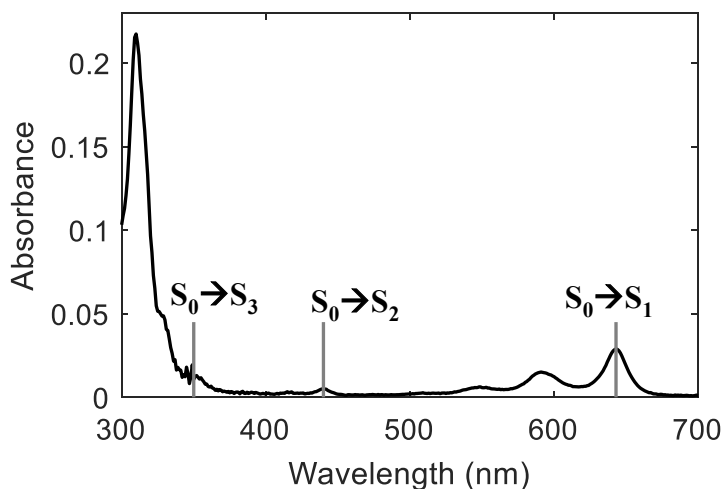


Figure 3-10: UV-Vis absorption spectrum of a dilute solution of TIPS-Pn dissolved in toluene. Transitions corresponding to each absorption band are indicated.

Several transient absorption spectra were measured for TIPS-Pn solutions using pulsed visible photoexcitation (~ 642 nm, ~ 10 ns pulse width) across the visible-to-near-IR spectral ranges. The excited singlet state lifetime is known from time-resolved fluorescence measurements (see Chapter 5) to be ~ 12 ns, and so S_1 absorption was identified by matching its decay time to that of fluorescence decay. The excited triplet state, because it is formed via ISC, exhibits a slow formation time and a slow decay time (~ 10 μ s). All time-resolved absorption spectra and kinetics are shown in **Figure 3-11**. Note that in this work, it was discovered that diatomic oxygen sensitizes intersystem crossing via spin-orbital perturbation, and so careful elimination of oxygen is needed in order to measure the intersystem crossing rate, and thus, the actual triplet yield. More information is provided in Chapter 8.

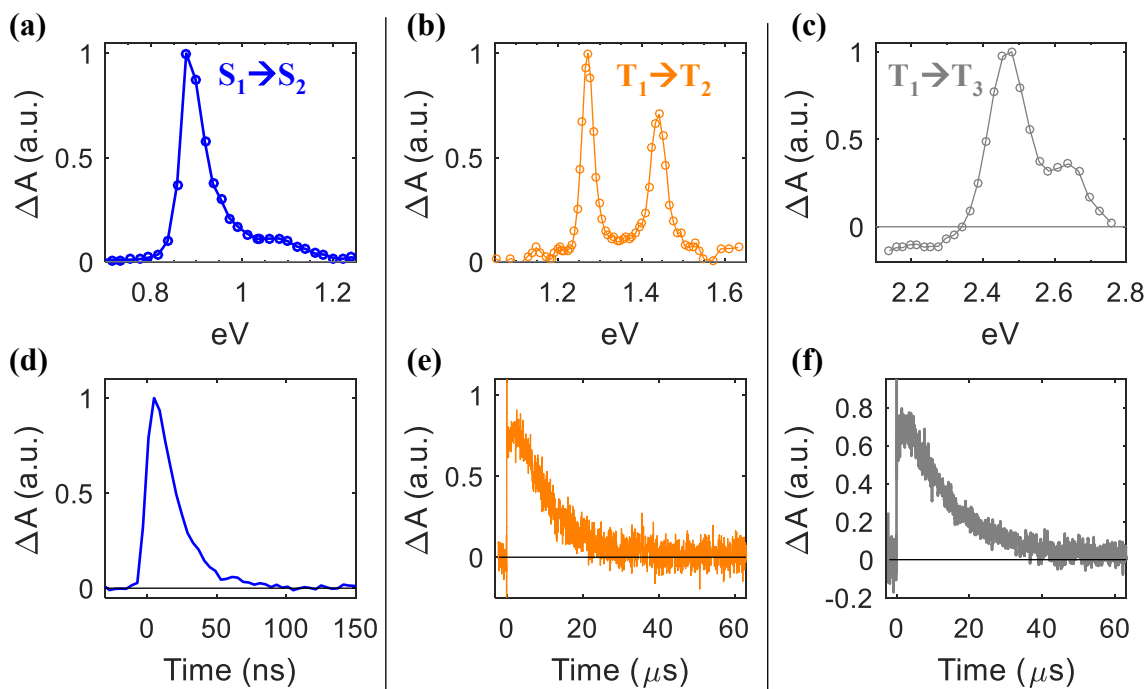


Figure 3-11: Transient absorption spectra for the (a) $S_1 \rightarrow S_2$, (b) $T_1 \rightarrow T_2$, and (c) $T_1 \rightarrow T_3$ transitions of dilute TIPS-Pn solutions. The corresponding kinetic traces are provided in (d), (e), and (f), respectively. Solvents used were either toluene or carbon tetrachloride. All samples were purged of oxygen by bubbling nitrogen gas prior to measurement. The instrument response functions varied for each spectral range, but was no longer than ~ 15 ns in FWHM.

In order to estimate the extinction coefficient for each transient absorption feature, it is necessary to first calculate the initial excited state singlet concentration. This concentration was calculated as follows: First, it was considered that the number of singlet excited states should be equal to the number of absorbed photons:



where S_0 is the ground state singlet, S_1 is the excited state singlet, and $h\nu$ represents a photon.

From the experiment, the number of excited state molecules (n_{S_1}) is:

$$n_{S_1} = n_{S_0} * (1 - 10^{-A_{642nm}}) \quad (\text{eqn. 7})$$

where n_{S_0} is the number of ground state molecules in the volume of excitation, and A_{642nm} is the absorbance of the sample at the excitation wavelength (642 nm). The initial number of

singlet excited states was converted to concentration (c_{S1}) using Avogadro's constant (N_A) and the volume of the excitation spot (V_{ex}):

$$c_{S1} = \frac{n_{S1}}{N_A * V_{ex}} \quad (\text{eqn. 8})$$

To calculate the molar extinction coefficient (ϵ_λ) of a singlet state absorption, Beer's Law was used as follows:

$$\epsilon_\lambda = \frac{\Delta A_\lambda}{b * c_{S1}} \quad (\text{eqn. 9})$$

where ΔA_λ is the initial transient absorption signal at probe wavelength, λ , and b is the pathlength. For the molar extinction coefficient values reported below, the 0-0 vibronic peaks were used, and so λ was taken at the maximum absorption of the 0-0 band for each transition. In solution, the singlet population has not significantly decayed in the first few nanoseconds, and so the kinetic signal at time zero was used as an approximate value of the true absorbance of the initial singlet excited state population.

To calculate the molar extinction coefficient for the triplet excited states, it was necessary to first calculate the initial triplet state concentration. Because ISC was relied upon to generate the triplet population in the solutions, its initial concentration depends directly on quantum yield of ISC (Φ_{ISC}). This quantum yield was approximated based on a report of triplet generation of TIPS-Pn in chloroform solutions by Walker and coworkers.²⁴ The initial triplet concentration (c_{T1}) was then calculated using:

$$c_{T1} = c_{S1} * \Phi_{ISC} \quad (\text{eqn. 10})$$

Once the initial triplet concentration was obtained, its molar extinction coefficient was calculated using equations 9, except with parameter values now associated with the triplet state absorption.

An energy level diagram was constructed for TIPS-Pn solutions using the experimentally determined transition energies (see **Figure 3-12**).

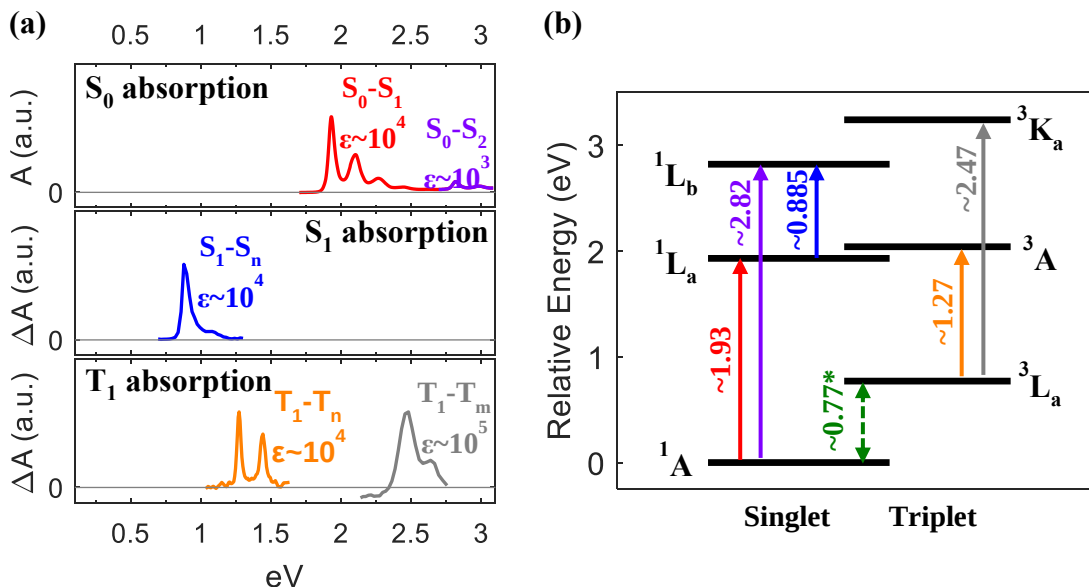


Figure 3-12: (a) Absorption spectra of dilute TIPS-Pn solutions showing S₀, S₁, and T₁ absorption bands. For transient absorption spectra, peaks were assigned based on their decay times in addition to their transition energies. The molar absorption coefficients for each transition is provided in M⁻¹cm⁻¹ units. (b) Experimentally determined energy level diagram for TIPS-Pn solutions based on the absorption spectra shown in (a). The transition energies are indicated in eV units. All states are labeled in accordance to the perimeter-free electron orbital model (PFE0) for pentacene. *The S₀-T₁ energy gap was taken from: Zirzmeier, J.; Lehnerr, D.; Coto, P.B.; Chernick, E.T.; Casillas, R.; Basel, B.S.; Thoss, M.; Tykwinski, R.R.; Guldi, M. *PNAS*. **2015**. 112, 5325-5330 (see supporting information section).

Because the transition S₀→T₁ is extremely forbidden (~10⁻⁷-10⁻⁹ for pi-pi* transitions⁴³), the energy gap is better estimated using phosphorescence spectroscopy. The transition energy was reported for TIPS-Pn measured in methyl-THF at cryogenic temperature to be ~0.77 eV.⁴⁴ All states in **Figure 3-12(b)** have been labeled in accordance to the perimeter free electron orbital (PFE0) model for pentacene⁴⁵, and excitation energies are also provided for convenience. Molar absorption coefficients were calculated (in M⁻¹cm⁻¹ units) and are provided next to each spectrum. For reference, a list of experimentally determined transition energies is provided in

Table 3-1. Notably, the energy levels are set up for exergonic singlet fission, since $E_{S1} > 2 \times E_{T1}$.

Table 3-1. Approximate excitation energies for dilute TIPS-Pn solutions determined from steady state and transient absorption experiments

Transition	Energy (ev)	Transition	Energy (ev)	Transition	Energy (ev)
$S_0 \rightarrow S_3$	3.54	---	---	---	---
$S_0 \rightarrow S_2$	2.82	---	---	$T_1 \rightarrow T_3^*$	1.27
$S_0 \rightarrow S_1$	1.93	$S_1 \rightarrow S_2$	0.89	$T_1 \rightarrow T_2^*$	2.47

*It is unclear whether there are additional triplet states available, and so the assignment of the 2nd and 3rd states in the triplet manifold is only tentative.

The singlet fission reaction occurring in pentacene derivatives is typically tracked using ultrafast transient absorption spectroscopy. The absorption of singlet excited states is observed to decay concurrently with the growth of the absorption of triplet excited states. The measurement is typically performed by monitoring the time-evolution of the visible absorption bands of both singlets (data not shown) and triplets, since they provide convenient, intense signals. However, more and more attention has been given to the near-IR absorption bands^{3,25} because of their spectral distance from the location of signals associated with ground state bleaching and stimulated emission, reducing the level of spectral overlap between multiple signals.

3.3. Isolation and Identification of Crystal Polymorphs in TIPS-Pentacene Films

Through this work, a method for isolating two crystal polymorphs of TIPS-Pn in polycrystalline solution-cast films was discovered. Small differences in molecular packing arrangements predisposed by each polymorph allowed the investigation into how changes in orbital overlap interactions affect both singlet fission and triplet diffusion. The remainder of

this chapter serves to establish methods for preparing and characterizing amorphous and polycrystalline films of TIPS-Pn, including the two polymorphs. Determining the detailed crystal packing structure of the polymorphs requires more extensive work, which is presented in Chapter 7.

3.3.1. Film preparation and characterization methods

Thin films of TIPS-Pn, produced either via evaporation⁴⁶ or solution casting methods⁴⁷, typically result in polycrystalline films possessing the 2D-brickwork packing structure characteristic of single crystals (see **Figure 3-7**). However, in this work, it was discovered that spin-casting films using solutions of TIPS-Pn dissolved dichloromethane (DCM) results in amorphous TIPS-Pn films containing weakly coupled chromophores. This is evidenced by comparing the absorption spectrum of these “as-cast” films with that of a dilute solution (see **Figure 3-13**). The film spectrum resembles that of the solution, with modestly broadened and redshifted vibronic peaks. This is indicative of very weak electronic coupling between disordered molecules. In particular, to fabricate amorphous (“as-cast”) films, 20 mg of TIPS-Pn was dissolved in 1 mL of dichloromethane before spin-coating onto 1 inch diameter sapphire, glass, or CaF₂ optical flats at 800-1600 rpm. For all substrates, the absorption spectra were nearly identical to that shown in **Figure 3-13**.

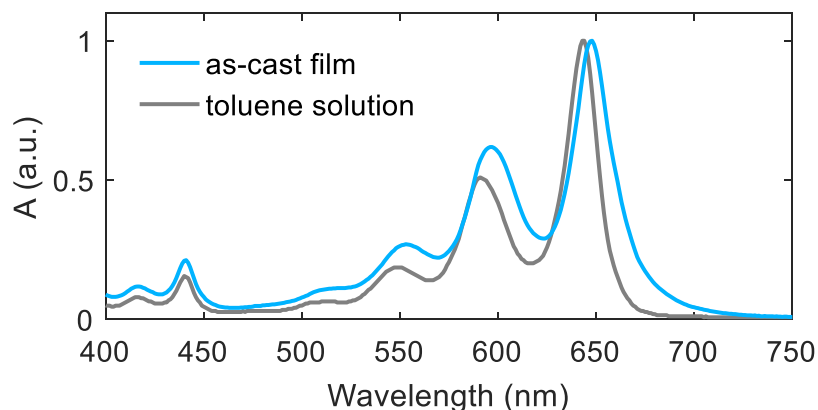


Figure 3-13: Normalized absorption spectrum of an amorphous TIPS-Pn film spin-cast from dichloromethane (“as-cast”). A spectrum of a dilute solution of TIPS-Pn in toluene is provided for comparison.

It was then found that annealing the amorphous films of TIPS-Pn resulted in crystallization. For annealing, films were either heated on a hot plate (“thermally annealed”), or were exposed to solvent vapor (“solvent annealed”). For thermal annealing, typical temperatures used were in the range of $\sim 80 - 120$ °C and the annealing times were usually 1 – 5 min. A color change from blue to green occurred almost instantly after a period of temperature equilibration time of several seconds. For solvent annealing, either toluene or isopropanol (IPA) was used. Using a petri dish annealer (see Chapter 2), the solvent vapor exposure time was typically 1 – 5 min. A color change from blue to gray was observed almost immediately. Using the graduated cylinder annealer (see Chapter 4), the solvent vapor exposure time was typically 0 – 2.5 hours. The absorption spectra (shown in **Figure 3-14**) for the as-cast, thermally-annealed, and solvent-annealed were all distinct, showing differences in the relative vibronic band intensities and peak widths. In accordance to the molecular exciton model⁴⁸, the annealed films contain molecules with different “intermediate” coupling interactions, suggesting that the molecules experience different intermolecular interactions. From this, it is inferred that the packing interactions in the thermal and solvent annealed films are likely distinct.

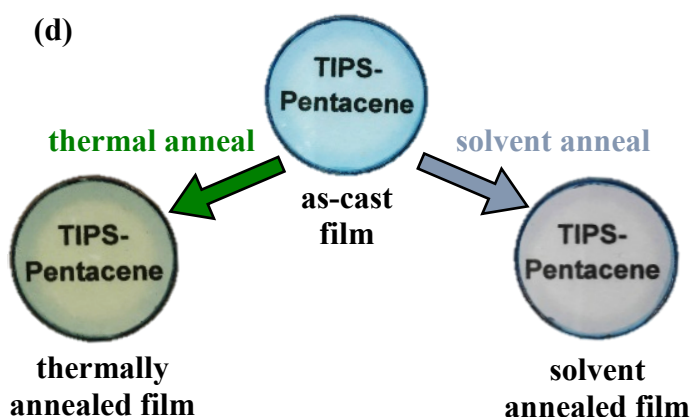
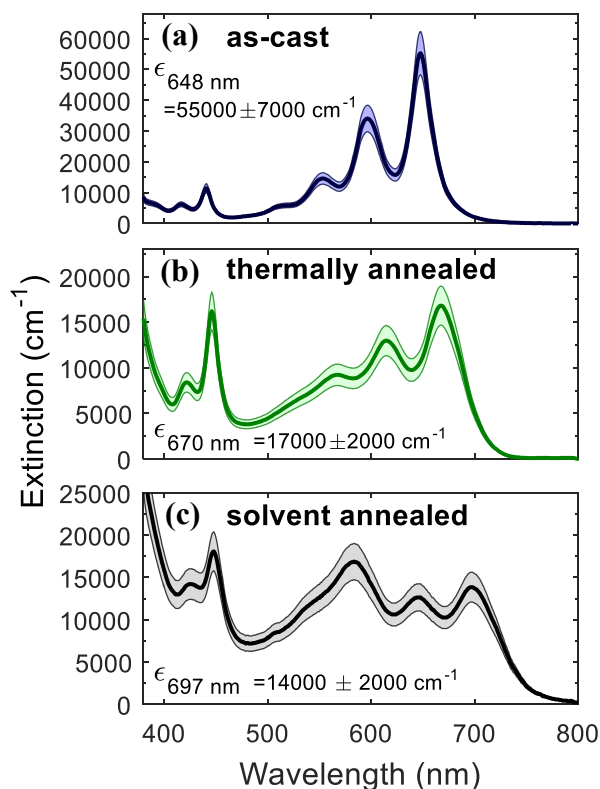


Figure 3-14: Extinction spectrum of an (a) as-cast, (b) thermally-annealed, and (c) solvent-annealed film of TIPS-Pn. The extinction coefficients were calculated by dividing the absorption by the film thicknesses determined from cross-sectional scanning electron microscopy (SEM) images. The shaded regions show the uncertainty limits, which were dominated by uncertainty in the film thicknesses. (d) Photographs of representative films of TIPS-Pn, illustrating the processing methods used.

The absorption spectrum of the solvent annealed film contains vibronic structure that is different than that of the amorphous film and the thermally annealed film (i.e. vibronic peak intensity ratios are not monotonically decreasing toward shorter wavelength). It is possible

that the orientations of the molecules in the solvent-annealed film are set in a way that creates H- and J-like absorption bands in its absorption spectrum. This would imply that the intensity of the vibronic bands may be modulated as a result of breaking of symmetry on the coupled dipole moments of molecular aggregates in the film. Inspection of the molecular packing structure for the single crystal structure of TIPS-Pn suggests that both types of aggregate interactions may exist for TIPS-Pn in the solvent-annealed film. On the other hand, the intermolecular orientations in the thermally annealed film may not contain such symmetry-breaking coupled dipole moments, implying that this film contains a different molecular packing structure. Further details of the molecular packing structures present in both types of films are provided in Chapter 7.

Several crystal polymorphs of TIPS-Pn have been demonstrated recently using solution-sheared films.⁴⁹ In a particular report, Diao et al. successfully isolated three TIPS-Pn polymorphs in extremely thin films (~30 nm), which were characterized using differential scanning calorimetry, x-ray diffractometry, and absorbance spectroscopy.³³ Comparison of the absorption spectra reported in that work with the thermal and solvent annealed films suggests that they consist of different crystal polymorphs. Extensive characterization of the packing structures is provided in Chapter 7.

The amorphous, thermally-annealed, and solvent-annealed TIPS-Pn films were characterized using grazing-incidence X-ray diffraction (GIXRD). All scans were made using a PANalytical X'Pert Pro MPD diffractometer (PANalytical; Almelo, Netherlands), with a 1° incident angle and Cu K α radiation. To avoid biasing the thick, crystalline regions of the sample that formed on the edges of the circular substrates from spin-coating, the x-ray spot size was reduced to about 1 cm x 1 cm using an assortment of x-ray optics and a beam mask.

The tradeoff for this was significant reduction of the intensity of the x-ray beam, and consequently the detected diffraction signals. **Figure 3-15** shows the X-ray diffraction patterns measured for the as-cast, thermally-annealed, and solvent-annealed films. The calculated powder diffraction pattern is shown in gray for reference. The as-cast film exhibited no discernible diffraction peaks indicating it was amorphous. In contrast, a diffraction pattern is clearly observed in the solvent-annealed film, which closely matches patterns reported in TIPS-Pn films and powders in which the molecules adopt the 2D-brickwork crystal packing structure.⁴⁷ To ensure the diffraction patterns were representative of the films and not biased due to epitaxial growth on the single crystal sapphire substrates, GIXRD measurements were performed using multiple sample rotations (see **Figure 3-15**). Preferential orientations of the crystallites in the lateral plane (parallel to the substrate surface) were not observed, since all patterns showed similar peak intensities and without the appearances of different reflections.

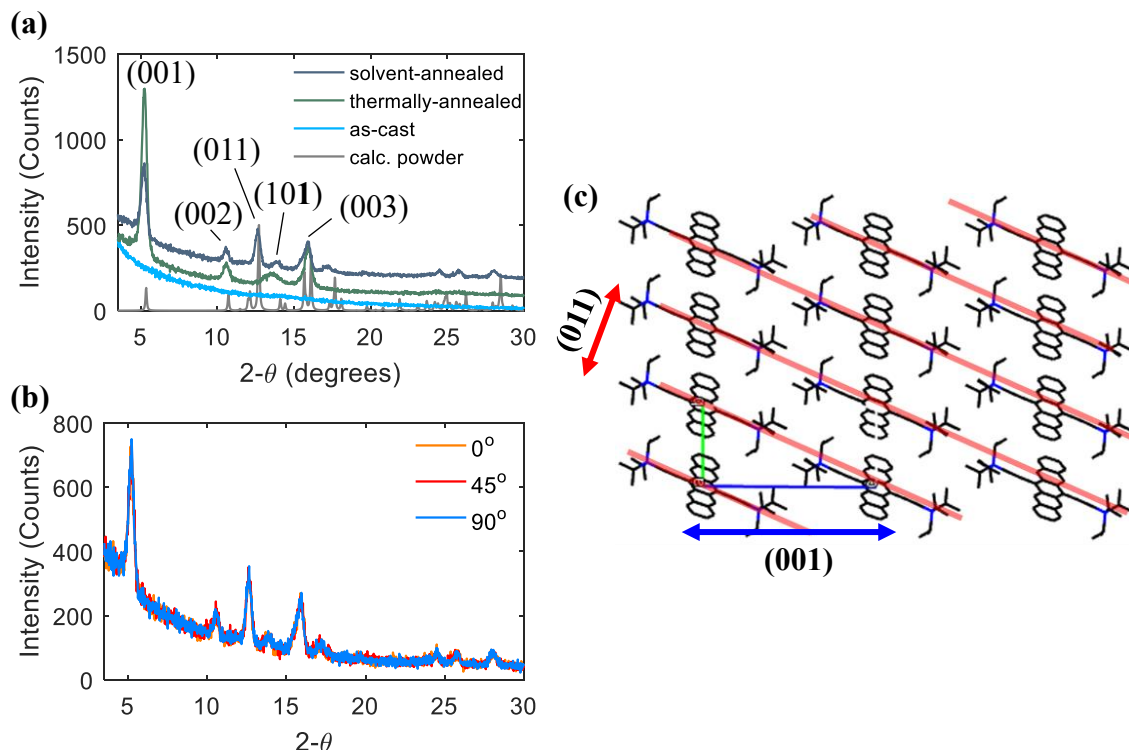


Figure 3-15: (a) Grazing-incidence x-ray diffraction (GIXRD) for TIPS-Pn films on sapphire substrates. The calculated powder pattern is provided for reference. (b) GIXRD patterns for a solvent-annealed TIPS-Pn film on sapphire collected for various sample rotation angles. (c) Illustration of the single crystal packing structure of TIPS-Pn, highlighting the (00l) and (011) directions.

The thermally-annealed film exhibited (00 l) reflections like the solvent-annealed film suggesting that the crystal planes in the crystallographic c-direction are similar in both films (see **Figure 3-15** for an illustration). However, a broad peak appeared around 13.5° 2θ for the thermally-annealed film that was missing in the solvent annealed film, indicating differences in molecular packing along other crystallographic directions. Changes in these diffraction peaks have been associated in prior reports with formation of different polymorphs of TIPS-Pn.^{33,34,49} In particular, the Form-II brickwork structure identified by Diao et al.³³ most closely resembles the structure present in the thermally annealed films, based on similar diffraction peaks in conjunction with similar vibronic peak locations in its absorption spectrum. It is noted that the different absorption spectra of the thermally- and solvent-annealed films (**Figure 3-**

14) are consistent with different molecular packing structures within the (001) plane that features pi-pi stacking, which strongly affects the electronic interactions between molecules. Consequently, the polymorph formed by thermal annealing most likely possessed the Form-II brickwork packing structure. On the other hand, the polymorph formed by solvent annealing possessed the Form-I brickwork packing structure. The specific structures of each polymorph obtained via thermal and solvent annealing are investigated in Chapter 7.

3.3.2. In-situ spectroscopic measurements of thermal annealing

In order to determine the crystallization temperature of amorphous TIPS-Pn films, an instrument was constructed such that absorption spectra could be measured during heating and cooling cycles. A diagram and photograph of the instrument is shown in **Figure 3-16**. A home-built visible spectrometer was assembled using a low power, stabilized tungsten-halogen light source (SLS-201, Thorlabs; Newton, NJ), and a CCD spectrometer (USB-2000, Ocean Optics; Dunedin, FL). Optical filters (colored glass and neutral density) were placed before the sample in order to limit it from too intense of light exposure. In addition, shorter wavelengths (below ~400 nm) were blocked in order to prevent detection of their higher orders of diffraction. Lenses were used to collimate the beam before transmitting through the sample. A cryostat equipped with a heating element was used to control the sample temperature during absorption measurements. The temperature was controlled using a digital and computer-programmable temperature controller unit (331 Temperature Controller, Lake Shore; Westerville, OH).

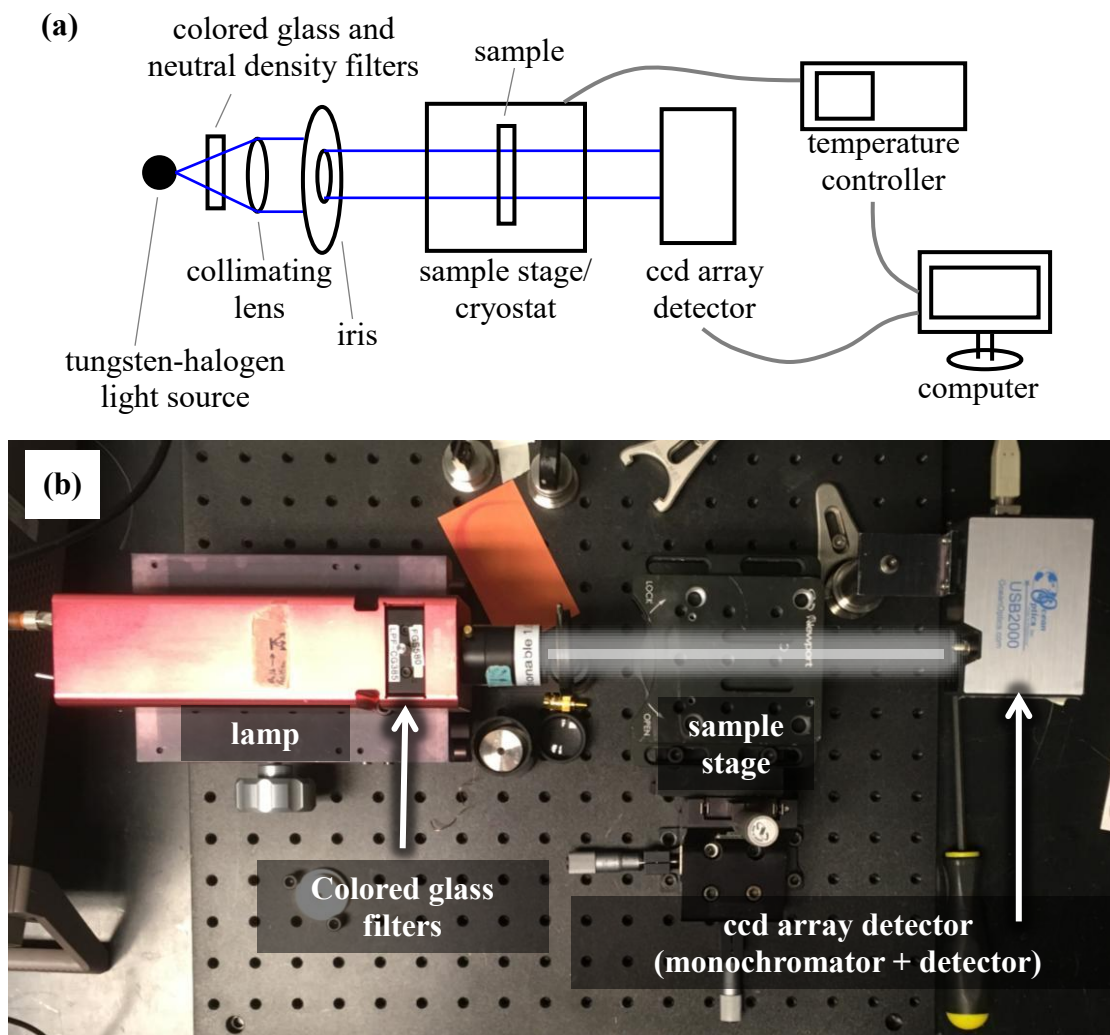


Figure 3-16: (a) Instrument schematic for the temperature-controlled absorption spectrometer. (b) Photograph of the instrument (cryostat not shown).

Software for controlling the instrument was written using MATLAB. A high-level pseudocode is provided in **Figure 3-17**. Initially, a dark offset is recorded by blocking the monitoring beam. Next, the light transmitting through a bare substrate (blank measurement) is recorded. Last, a temperature-dependent absorption spectrum is calculated for the sample after measuring the light transmitted through the sample as it is heated and/or cooled. If necessary, a temperature-dependent blank spectrum may be measured when the changes in the transmission of the blank with temperature are significant.

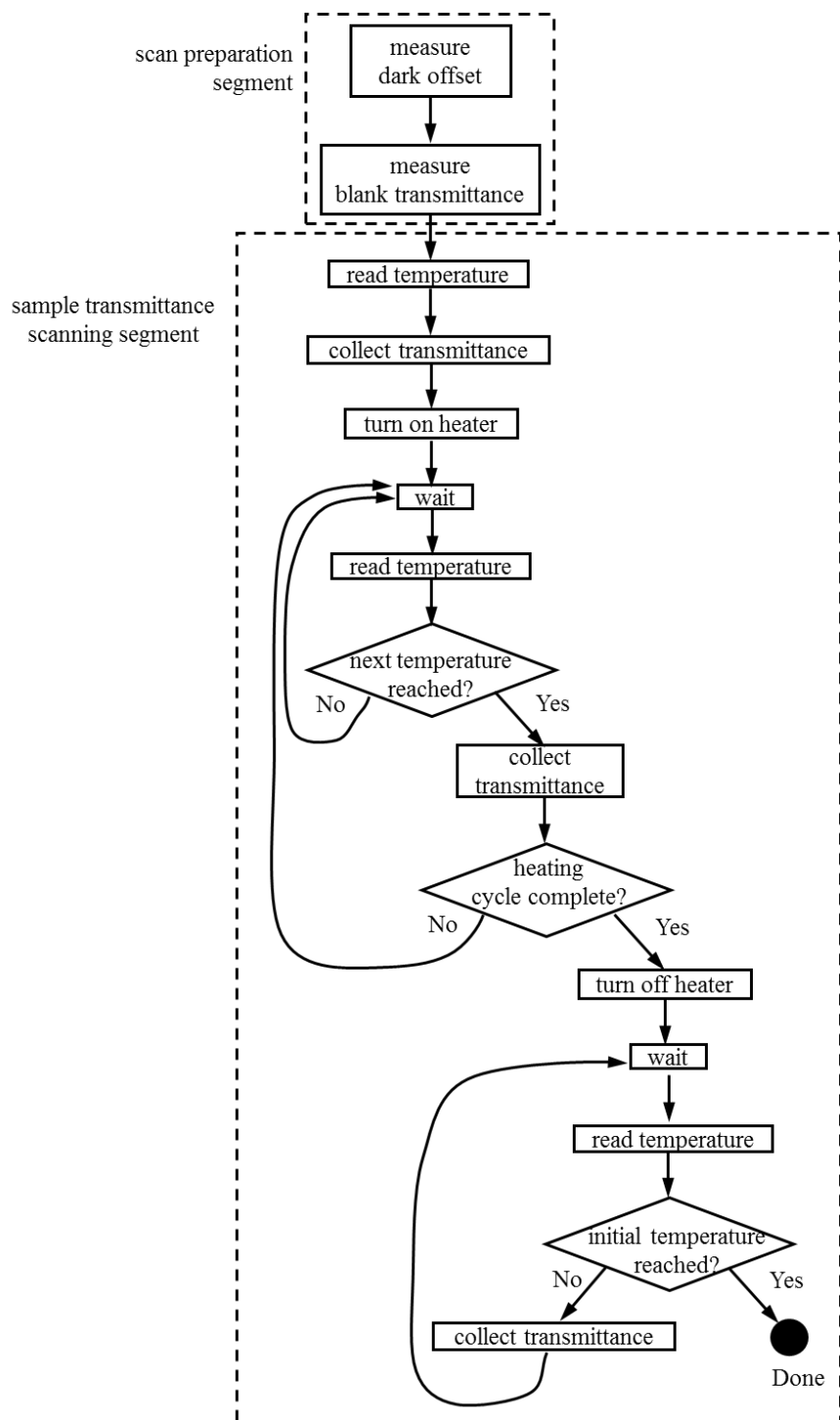


Figure 3-17: Pseudocode for temperature-dependent absorption instrument. Only the pseudocode for the heating-cooling cycle is shown for conciseness.

The absorption spectrum of an amorphous TIPS-Pn film was recorded during heating/cooling, which is shown in **Figure 3-18**. The absorption spectrum does not change

until the crystallization temperature ($\sim 84^\circ\text{C}$) is reached, after which the spectrum converts to that of a thermally-annealed film. Upon cooling the sample back to room temperature, the absorption spectrum does not change, indicating that the crystallization process was not reversible. The crystallization process can be tracked by analyzing the change in absorption at the wavelength (670 nm) corresponding to the 0-0 absorption band of the “thermally-annealed polymorph”.

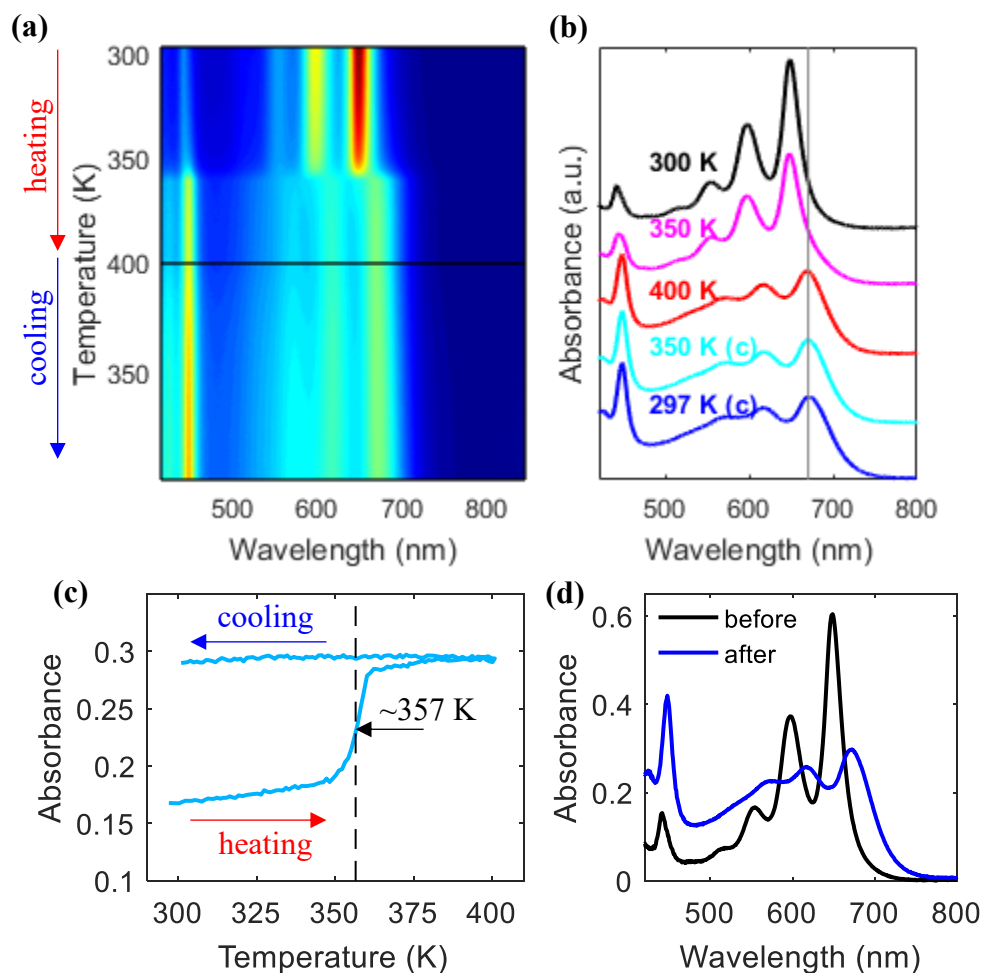


Figure 3-18: (a) Temperature-dependent absorption spectrum of an amorphous TIPS-Pn film as it is heated and cooled. (b) Spectral slices of the data at select temperatures during heating and cooling. Temperatures for which the spectra are shown during the cooling cycle are indicated using “(c)”. (c) Absorbance monitored at 670 nm during the heating-cooling cycles, showing a crystallization temperature around 375 K for TIPS-Pn. (d) Room temperature absorption spectrum of the film before and after the experiment.

3.3.3. Reversible and irreversible interconversion between crystal polymorphs

The temperature-dependent absorption spectrometer was useful for understanding the effects of heating on the molecular packing arrangements in polycrystalline films. This work was important for uncovering structural changes that are responsible for ambiguous thermal artifacts that often arise in transient absorption experiments⁴ of singlet fission materials (see Chapter 12 for specific details). A general description of the data is provided here.

The absorption spectrum of a solvent-annealed film of TIPS-Pn was recorded during a heating-cooling cycle, which is shown in **Figure 3-19**. Most notably, a reversible temperature-induced phase transition was observed, reminiscent of a previous report on drop-cast TIPS-Pn films.⁴⁷ The vibronic band positions in the absorption spectrum of the “high temperature polymorph” matched that of a thermally annealed (room temperature) film. This suggests that the packing structure of the thermally annealed film is similar to that of the high-temperature polymorph.

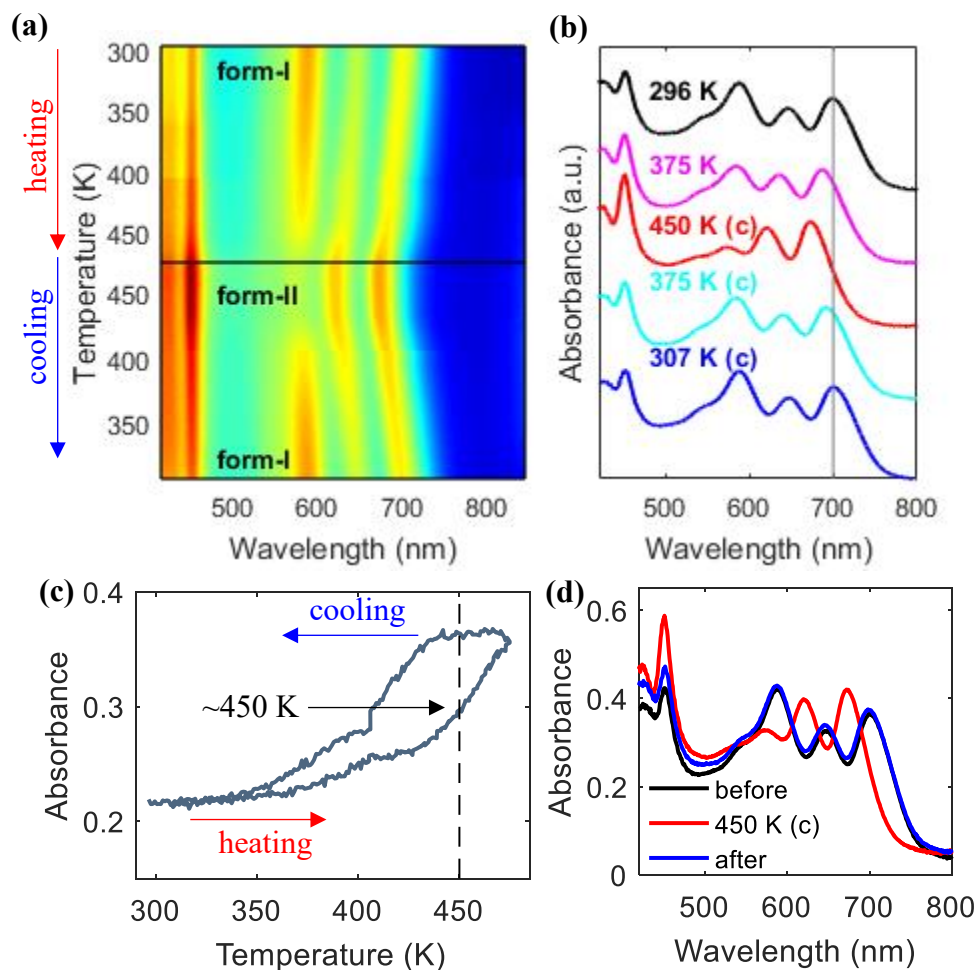


Figure 3-19: (a) Temperature-dependent absorption spectrum of a solvent-annealed (using toluene for 1 min in a petri dish annealer) TIPS-Pn film as it is heated and cooled. (b) Spectral slices of the data at select temperatures during heating and cooling. Temperatures for which the spectra are shown during the cooling cycle are indicated using “(c)”. (c) Absorption monitored at 670 nm during the heating-cooling cycles, showing a reversible phase transition around 450-470 K. (d) Room temperature absorption spectrum of the film before and after the experiment compared to the 450 K spectrum.

In some cases, heating and cooling of solvent-annealed films were not fully reversible. For example, for TIPS-Pn films annealed using IPA under the same conditions, the final absorption spectrum more closely resembles that of a thermally annealed film (see **Figure 3-20**). The current hypothesis is that because IPA is a much weaker solvent than toluene, the crystallites that form are much smaller. In the past, nanoconfinement has been shown to favor the

formation of the Form-II polymorph in solution-sheared films.³³ As such, it is hypothesized that the polymorph irreversibility of films annealed using IPA arises from a nanoconfinement effect.

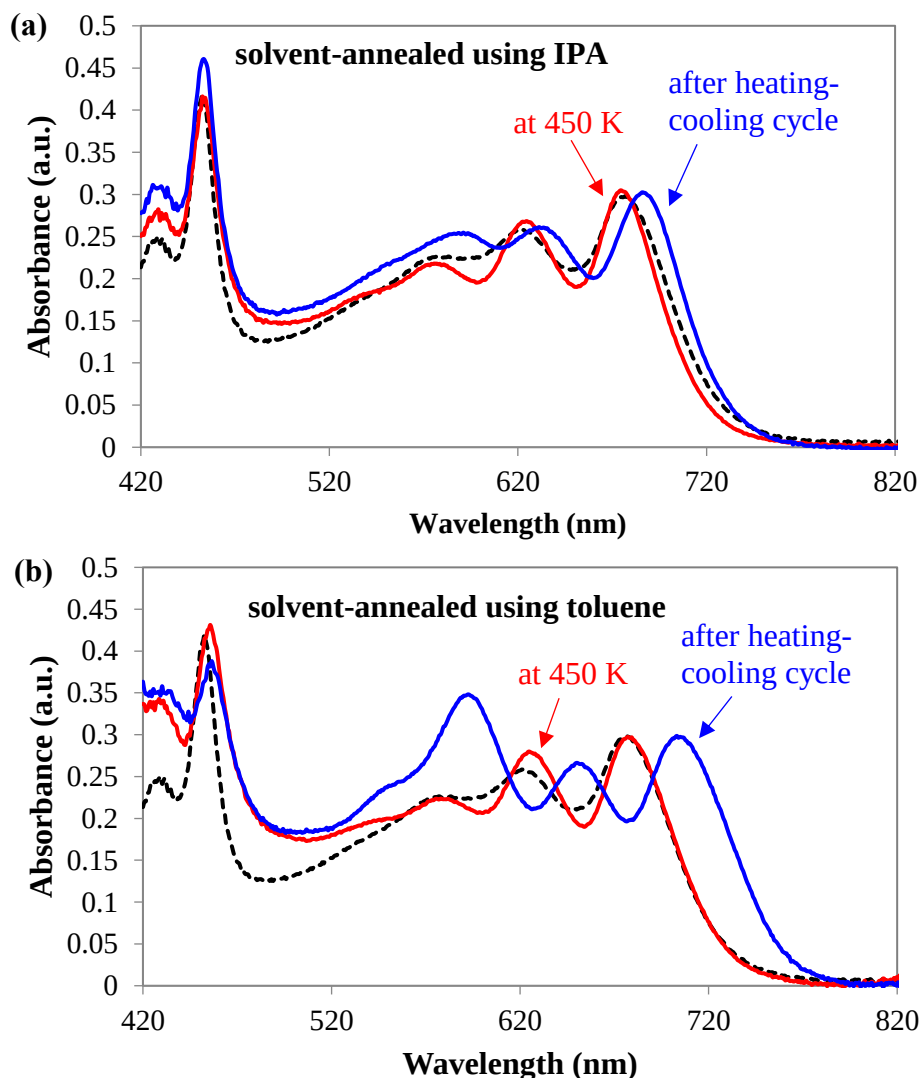


Figure 3-20: (a) Absorption spectra of a film of TIPS-Pn annealed using IPA for 1 minute in a petri dish annealer. The film was then thermally annealed. The spectra are shown at 450 K (red line) and after cooling (blue line). An absorption spectrum of a thermally-annealed (previously amorphous) film at room temperature is shown for reference (black dashed line). (b) Absorption spectra of a film of TIPS-Pn annealed using toluene for 1 minute in a petri dish annealer. The film was then thermally annealed. The spectra are shown at 450 K (red line) and after cooling (blue line). An absorption spectrum of a thermally-annealed (previously amorphous) film at room temperature is shown for reference (black dashed line).

Last, it was found that the polymorph structure formed by thermally annealing amorphous films could be converted into that of a solvent-annealed film. **Figure 3-21** shows the absorption spectrum of a thermally annealed film before and after exposure to toluene vapor, indicating that there was an irreversible phase transition. Altogether, these results suggest that the crystal structure originally obtained by solvent annealing amorphous films is more thermodynamically favorable. However, the thermally-annealed films were found to be incredibly stable in the absence of (good) solvent vapor.

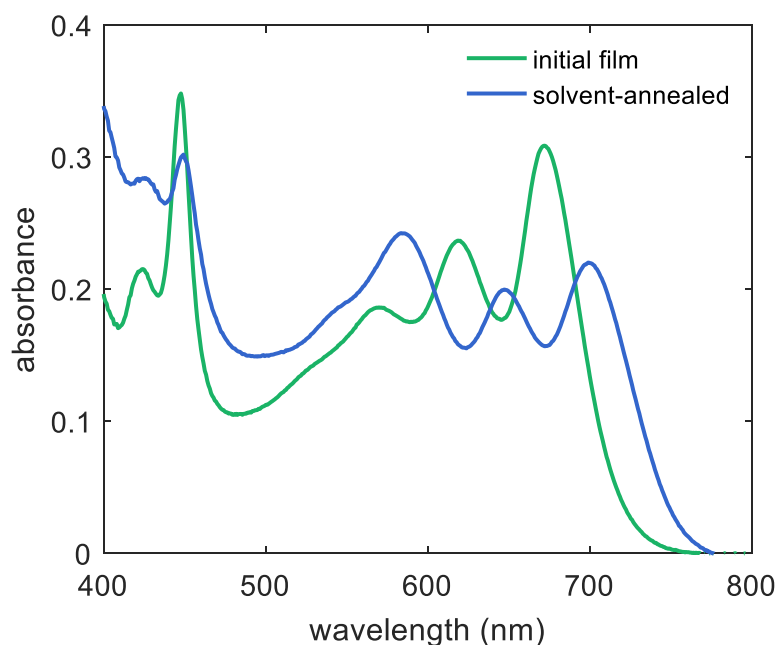


Figure 3-21: Absorption spectrum for a thermally annealed film before and after solvent-annealing using toluene vapor.

3.4. Method for Controlling and Characterizing Crystallization of Solvent Vapor Annealed TIPS-Pentacene Films

3.4.1. Preparation and characterization of partially-annealed films

A method for controlling the extent of crystallization in TIPS-Pn films was developed using gentle solvent annealing. Because IPA is a poor solvent for TIPS-Pn, the annealing process is

slow and can be used to gradually change the molecular-level packing and crystallinity of the films. In this case, films were annealed using a graduated cylinder apparatus shown in **Figure 3-22**. The films were held in a lens tube placed in a graduated cylinder and suspended over a pool of solvent. Upon removing the films from the solvent vapor, the annealing process was arrested, resulting in films that were stable for days to weeks.

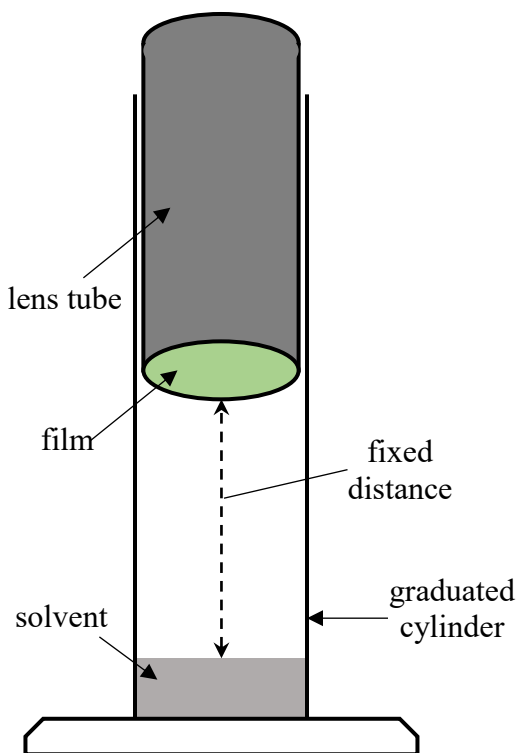


Figure 3-22: Schematic of the graduated cylinder solvent-annealing apparatus.

Annealing with a better solvent for TIPS-Pn, such as toluene, causes the crystallization to occur very rapidly, making these samples not well-controlled. In addition, the samples were not very suitable for spectroscopic measurements because the rapid crystallization resulted in rougher films, causing intense scatter features in the absorption spectrum (see **Figure 3-23**). As such, it is hypothesized that annealing using toluene results in larger crystallites. GIXRD measurements showed that films annealed with either IPA or toluene both resulted in

crystalline films possessing the 2D-brickwork packing structure, although films annealed with toluene appear to orient slightly differently on the substrate (evident from changes in relative peak intensities in **Figure 3-23**).

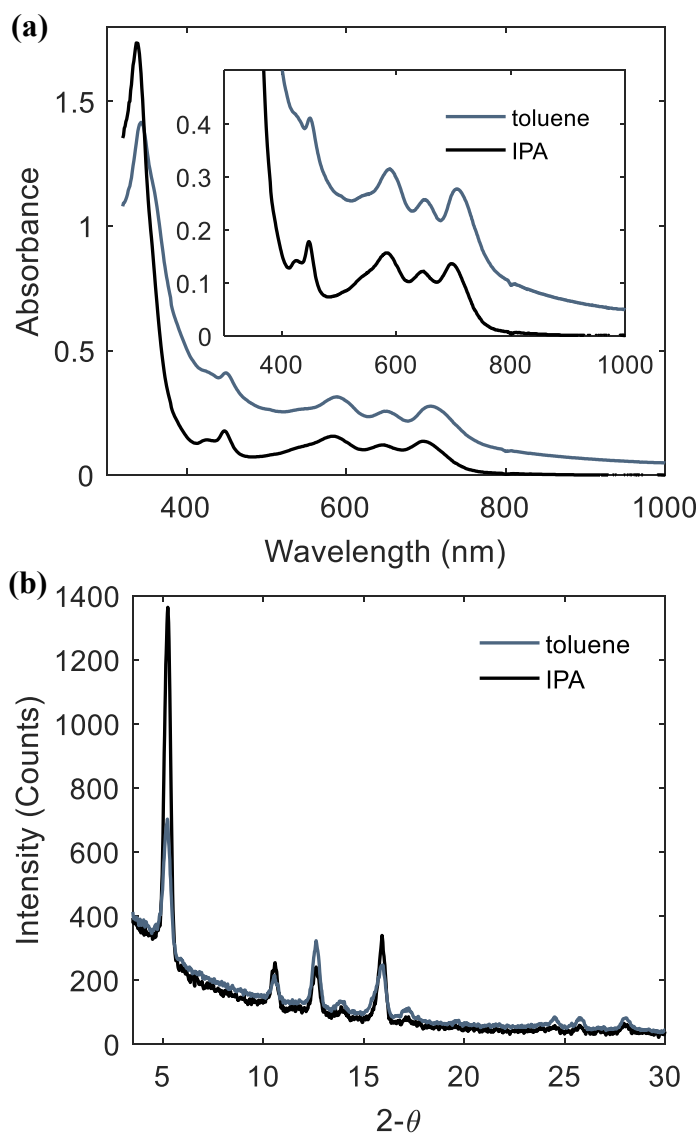


Figure 3-23: (a) Absorption spectra of solvent annealed TIPS-Pn films made using 60 minutes of exposure time to either IPA or toluene. (b) Grazing-incidence X-ray diffraction patterns for the same films.

A series of films were annealed to various extents using IPA. The absorption spectrum was measured for each film, showing that during annealing, the films evolve from weakly-coupled, disordered molecules into an ordered 2D-brickwork phase (see **Figure 3-24**).

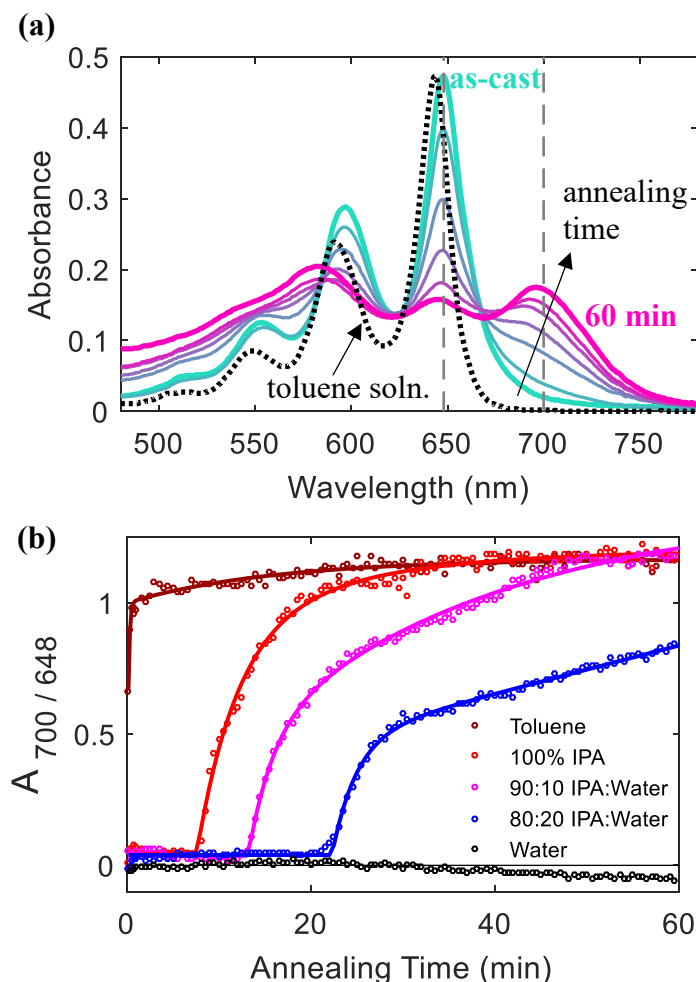


Figure 3-24: (a) Evolution of the absorption spectrum of TIPS-Pn films upon solvent annealing using IPA. Annealing times ranged from 0 – 60 minutes. A spectrum for a dilute solution of TIPS-Pn in toluene is provided for reference (dashed black line). (b) Solvent annealing kinetics for TIPS-Pn films using different solvents and solvent volume ratios. The metric for extent of annealing was taken as the 700:648 nm absorption ratio. Solid lines are biexponential growth fits to the data.

The extent of annealing was quantified by taking the ratio of absorption at the 0-0 transition of annealed films (700 nm) and the absorption at the 0-0 peak of disordered molecules (648 nm). The time-dependence of the extent of annealing could be determined using a method detailed in the next section. An example of such kinetics is provided in **Figure 3-24** for a variety of annealing solvents. The extent of annealing completes after about 60 min of continuous solvent exposure, and so films annealed in this way are referred to as “fully-annealed”. Films

annealed for shorter amounts of time are referred to as “partially-annealed”. Photographs of examples of these films are provided in **Figure 3-25**.

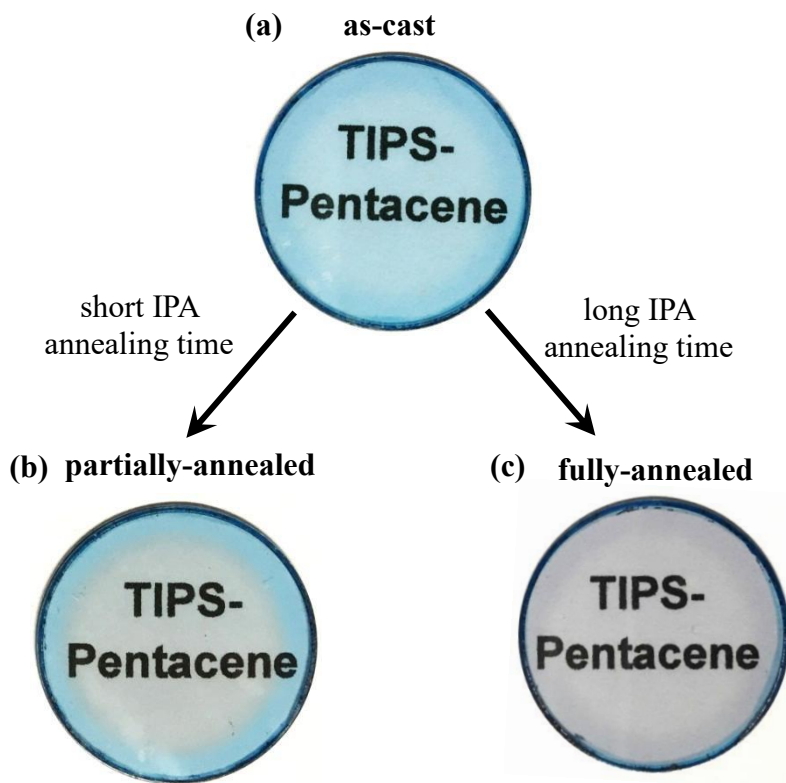


Figure 3-25: Photographs of (a) as-cast (amorphous), (b) partially-annealed, and (c) fully-annealed films of TIPS-Pn. The films were annealed using IPA in a graduated cylinder annealing apparatus. The light blue ring in (b) was part of the film not exposed to solvent vapor.

In order to confirm that crystallization occurs during gradual solvent annealing, GIXRD was performed for films that were as-cast, partially-annealed, and fully-annealed (see **Figure 3-26**).

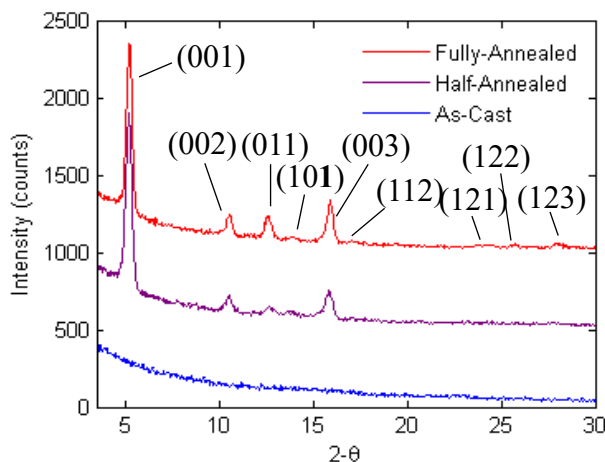


Figure 3-26: Grazing-incidence X-ray diffraction for TIPS-Pn films on sapphire made using different solvent annealing times. The angle of incidence was 1° . The patterns are offset by 500 units for clarity (without any additional scaling).

The diffraction pattern of the partially-annealed film resembled that of a fully-annealed film, qualitatively suggesting that they contain a similar crystal structure. To determine whether the crystallite size in the films changes with annealing extent, 2D-diffraction patterns were measured for films annealed for different amounts of time. During the scans, the films were rocked over the (001) peak, which enabled the quantification of differences in the crystal packing along the crystallographic c-direction without biasing particular crystallite orientations. The 2D diffraction patterns along with the integrated (001) diffraction peaks are shown in **Figure 3-27**.

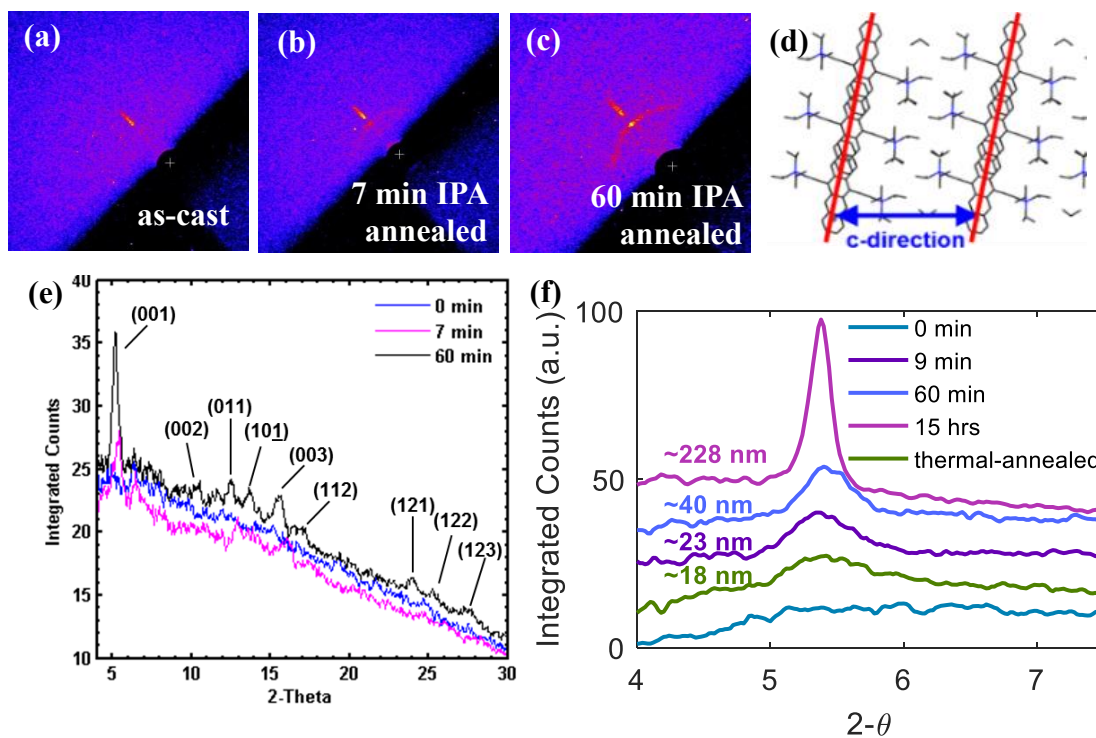


Figure 3-27: Examples of 2D X-ray diffraction patterns for TIPS-Pn films that were (a) as-cast from dichloromethane, (b) solvent annealed using IPA for 7 min, and (c) solvent annealed using IPA for 60 min. The samples were rocked over the (001) peak. (f) Illustration of the crystallographic c-direction in TIPS-Pn. (e) The corresponding integrated patterns, labeled by annealing time. (f) Integrated patterns for films annealed for different amounts of time using IPA. Data were offset of clarity. The partially-annealed sample in this case had an extent of annealing of $A_{700}/A_{648} = 0.7$. The pattern for a thermally annealed film is included for reference. The average crystallite sizes determined from the Scherrer equation are provided. For all X-ray diffraction measurements, Cu K α radiation was used.

The integrated rocking scan for the fully-annealed film resulted in a peak center at $\sim 5.4^\circ$ 2- θ , with the smaller full-width at half-maximum (FWHM) indicating a larger average crystallite size. The integrated rocking curve for the partially-annealed film (with $A_{700}/A_{648} = 0.7$) showed a larger FWHM, indicating that the crystallites were smaller than those in the fully solvent-annealed film.

The Scherrer equation was used to estimate the average crystallite sizes in the partially- and fully-annealed films:

$$\tau = \frac{\kappa\lambda}{(\beta_{\text{sample}} - \beta_{\text{standard}})\cos(\theta)} \quad (\text{eqn. 11})$$

where τ is the average size of the crystallites, κ is the shape factor, λ is the x-ray wavelength, β_{sample} is the FWHM of the sample peak, β_{standard} is the FWHM of the standard peak (limited by the detector resolution), and θ is the diffraction angle. The FWHMs of the (001) peaks, determined by fitting a Gaussian function to each set of data, were corrected for the finite angular resolution of the diffractometer in this way. Assuming minimal differences in crystallite strain between the two films, the average crystallite sizes were determined to be 23 ± 3 nm and 40 ± 10 nm in the partially- and fully-annealed films, respectively. A shape factor of 0.96 ± 0.09 was assumed for the calculation.⁵⁰ The confidence limits were obtained using the uncertainties in the fits and the shape factor. For reference, a thermally-annealed film was also measured, which had an average crystallite size of 18 ± 2 nm.

3.4.2. *In-situ spectroscopic measurements of solvent vapor annealing*

For *in-situ* absorbance measurements of TIPS-Pn films during solvent annealing, a home-built instrument was used. The light source was a fiber-coupled stabilized tungsten-halogen lamp (Thorlabs, SLS-201; Newton, NJ). A lens was used to collimate the light, which travelled through the bottom of the graduated cylinder. After transmission through the annealing solvent and the sample, the light was collected by a fiber, which was coupled to a CCD spectrometer (Ocean Optics, USB-2000; Dunedin, FL). A schematic and photograph of the instrument is provided in **Figure 3-28**.

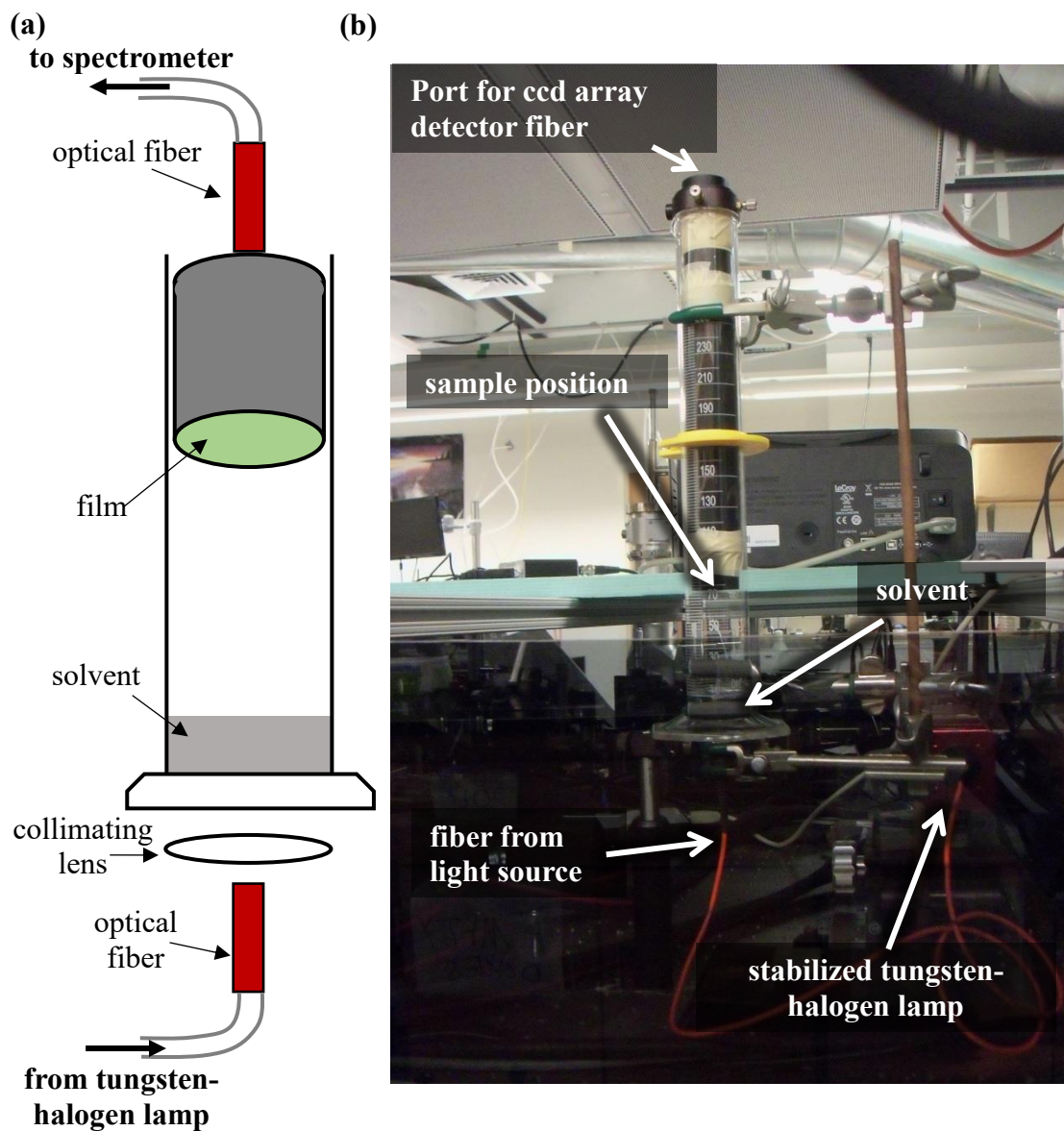


Figure 3-28: (a) Schematic of the instrument constructed to measure sample absorption during solvent annealing. (b) Photograph of the instrument.

Using this instrument, absorption spectra could be collected over time as the films were annealed, with an acquisition rate as fast as 1 scan per second depending on the signal-to-noise ratio (S/N). The kinetics of annealing were determined by plotting the extent of annealing, as defined above (A_{700}/A_{648}), over solvent exposure time. Several examples of time-dependent spectra collected are shown in **Figure 3-29**.

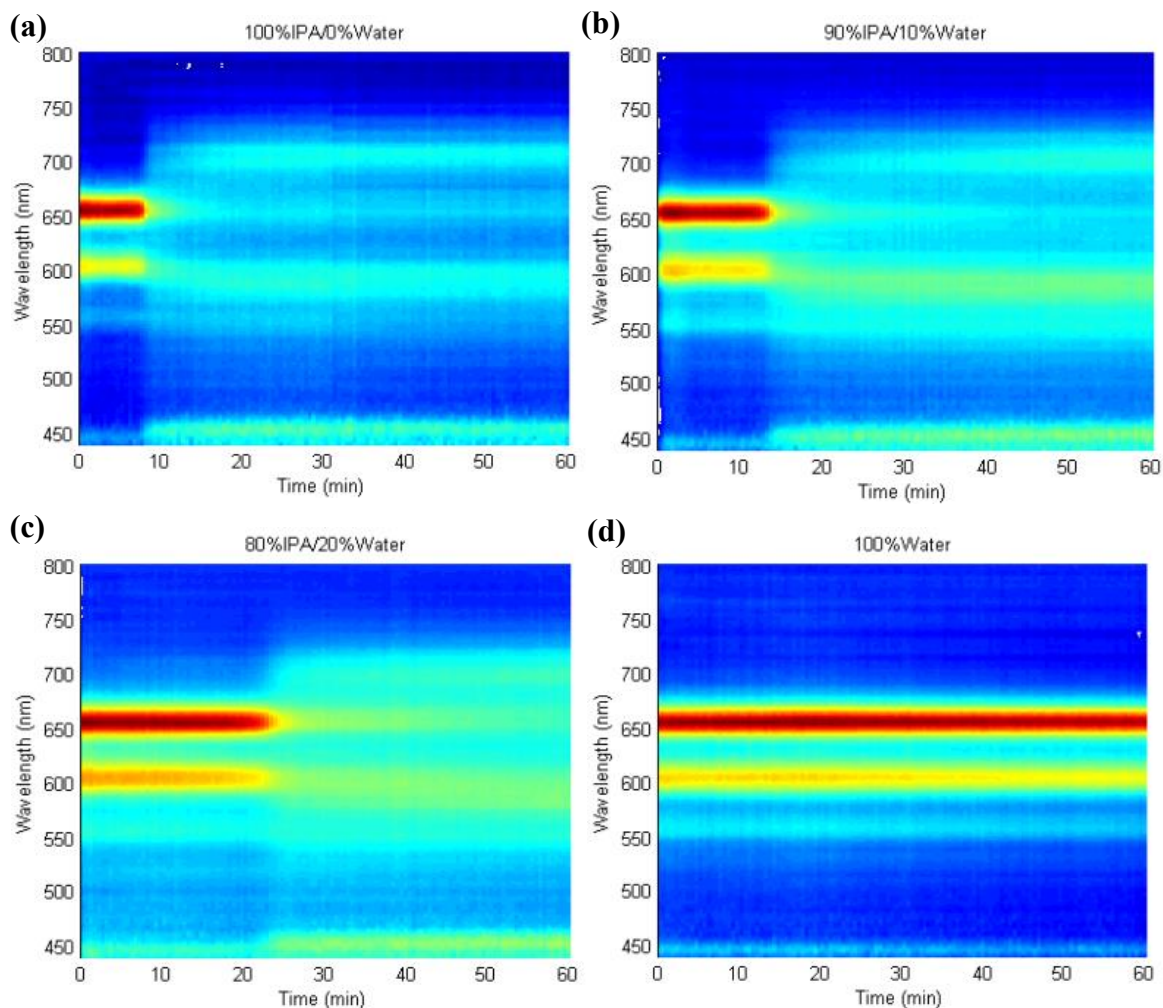


Figure 3-29: Examples of absorption spectra for TIPS-Pn films during solvent annealing using (a) IPA, (b) IPA:H₂O (90:10 v/v), (c) IPA:H₂O (80:20 v/v), and (d) H₂O.

3.4.3. Identifying and quantifying the composition of partially-annealed films

Based on changes in the absorption spectrum during solvent annealing, the composition of the partially annealed films appeared to be described by a mixture of various proportions of crystalline and amorphous phases. To describe the absorption spectra of the partially annealed films, a spectral model was developed consisting of basis spectra corresponding to the absorption spectrum of amorphous and crystalline phases. First, the simplest two-phase model was considered, consisting of the absorption spectrum of amorphous (as-cast film) and 2D-

brickwork (fully-annealed film) phases. This “two-phase model” predicts that the evolution of the absorption spectrum upon annealing can be described by the linear combination of these two basis spectra. An example of the best fit to the data for a partially-annealed film based on this model is shown in **Figure 3-30**. The residual spectrum indicated that the partially annealed film contained absorption that was not properly described by the selected basis spectra. The absorption spectrum of a thermally-annealed film (Form-II brickwork phase) is compared to the residual spectrum, which show matching vibronic peaks. This indicates that the absorption not accounted for using the 2-phase spectral model in the partially-annealed films likely arises from Form-II brickwork phase.

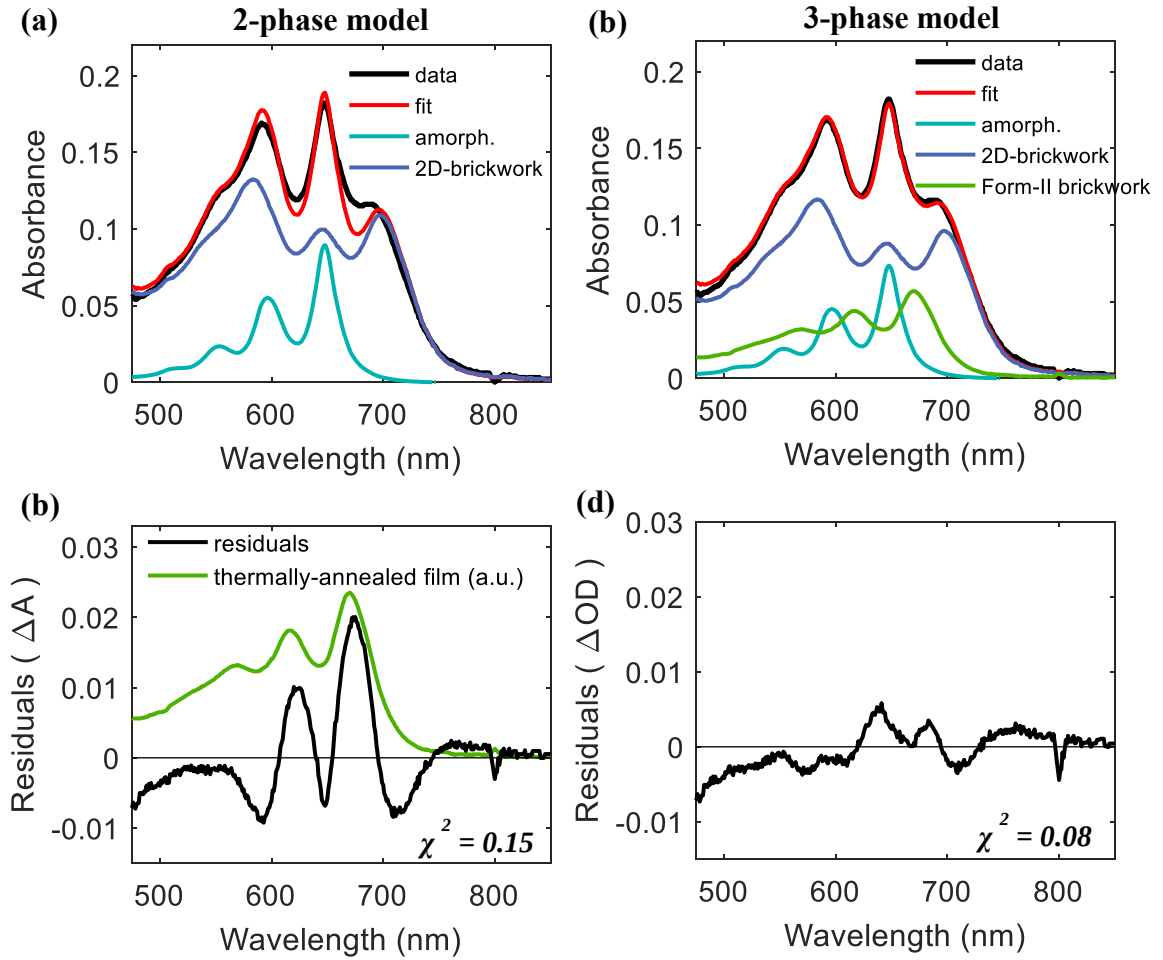


Figure 3-30: (a) Result of the spectral decomposition using the 2-phase model for the absorption spectrum of a partially-annealed film ($A_{700}/A_{648} = 0.6$). The basis spectra used to fit the data are shown. (b) Residuals of the fit using the 2-phase model shown in comparison to an absorption spectrum of a thermally-annealed film. (c) Result of the spectral decomposition of the same absorption spectrum using the 3-phase model. The basis spectra used to fit the data are shown, now with the inclusion of the Form-II brickwork phase. (d) Residuals of the fit using the 3-phase model.

Next, a three-phase spectral model was constructed, consisting of the absorption spectrum of amorphous, Form-II brickwork, and 2D-brickwork phases as the basis spectra. The best fit to the data for the same partially-annealed film is also shown in **Figure 3-30**, showing a $\sim 10\times$ reduction of the residual spectrum. Examples of this comparison for a variety of partially-annealed films with different extents of annealing are provided in **Figure 3-31**. In all cases, the three-phase model described the absorption spectra with high fidelity.

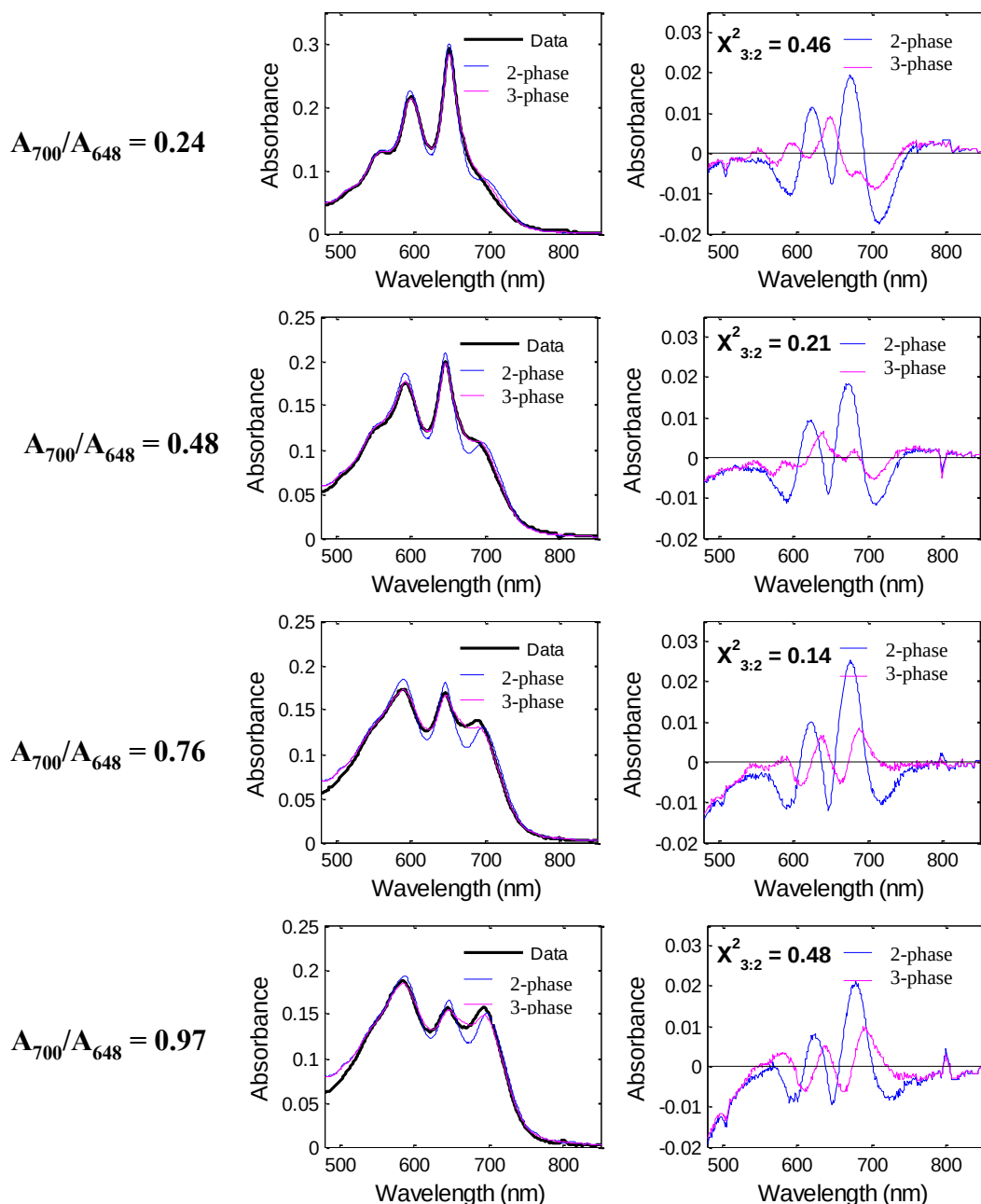


Figure 3-31: Examples of spectral modeling of partially-annealed TIPS-Pn films, shown for different extents of annealing (A_{700}/A_{648}) using IPA. The left graphs show an overlay of the data with the fit results using the 2-phase and 3-phase model. The right graphs show the corresponding residual spectra. The relative quality of the 3-phase model fits is expressed as the χ^2 ratios ($\chi^2_{3:2}$) for the 3-phase : 2-phase fits.

It is possible that there may be more than three sets of packing arrangements present in the partially-annealed films, such as those discovered in solution-sheared films.³³ If crystalline

phases containing these structures are present in the films, they would have mole fractions below the uncertainty of the measurements (< 5% mole fraction). Thus, the presence of alternate phases is neglected in the spectral modeling.

Because singlet fission and triplet diffusion depend intimately on molecular-level packing and morphology, we used the three-phase model to quantify the mole fractions of the molecules in each of the amorphous, Form-II brickwork, and 2D-brickwork phases. Specifically, the model can be expressed as:

$$f(\lambda) = N[w_{AC}A_{AC}(\lambda) + w_{TA}A_{TA}(\lambda) + w_{SA}A_{SA}(\lambda)] \quad (\text{eqn. 12})$$

$$w_{AC} + w_{TA} + w_{SA} = 1 \quad (\text{eqn. 13})$$

where N is a normalization factor, λ is wavelength, w_i are weighting factors for each phase, and $A_{AC}(\lambda)$, $A_{TA}(\lambda)$, and $A_{SA}(\lambda)$ are the basis spectra corresponding to the absorptions of the as-cast, thermally-annealed and solvent-annealed TIPS-Pn films, respectively. The sum of the weighting factors for each phase was constrained to unity. This satisfies the physical constraint that all TIPS-Pn molecules in the films must exist in only one of three phases. By scaling the basis spectra by the relative absorption coefficients of the respective phases, the weighting factors become the mole fractions of TIPS-Pn molecules in each phase. The mole fractions of the molecules present in each phase are plotted against the extent of annealing (A_{700}/A_{648}) in **Figure 3-32**. As the TIPS-Pn films were solvent annealed, there was a monotonic decrease of the amorphous phase and a concurrent monotonic increase of the total crystalline phase, as expected. The 2D-brickwork phase showed a monotonic growth upon solvent annealing, while a growth and decay of the Form-II brickwork phase resulted. This spectral modeling approach was significant for the work presented in Chapter 4, which shows how the composition of polycrystalline films of TIPS-Pn affects singlet fission and triplet diffusion.

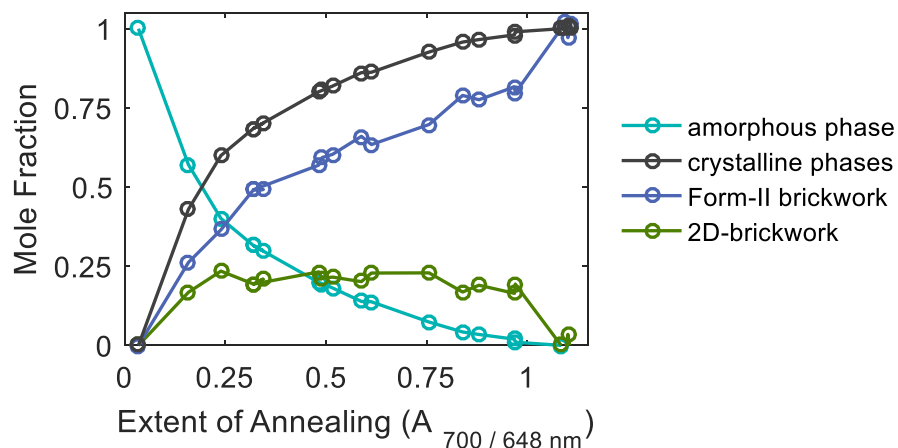


Figure 3-32: Spectral decomposition using the 3-phase model for the absorption spectrum of TIPS-Pn films made using a variety of extents of annealing.

3.5. Conclusions and Significance

This chapter discussed singlet fission as a special type of multiple exciton generation mechanism that can occur in organic molecules. A simple kinetic model was presented, which expresses singlet fission as a series of two consecutive reactions. The first step involves the spin-allowed formation of a correlated triplet pair state from a singlet exciton, a special case of internal conversion. The second step involves spin-decoherence of the correlated triplet pair, a special case of intersystem crossing. It is proposed that spin-decoherence is accompanied by physical separation of the triplets within the correlated pair state, which is thought to prevent kinetic competition of other relaxation processes. The rate of the first step of singlet fission was described using a simple quantum mechanical description, which indicates that intermolecular coupling has significant bearing on the efficiency of the reaction. The role of charge transfer states were assessed, which may participated in mediated singlet fission.

Pentacene derivatives were introduced as a model system for singlet fission. TIPS-Pn was selected as an exemplar for studying rapid singlet fission. General characteristics of this molecule were discussed, including crystal packing arrangements, energy level alignments, and spectroscopic signatures of singlet and triplet excitons. Methods for preparing amorphous films of TIPS-Pn, in addition to isolating two different crystal polymorphs, were detailed. *In-situ* methods for measuring film absorption during thermal and solvent annealing were presented in detail. A gradual solvent annealing method was developed, providing a route to controlling the extent of crystallinity of TIPS-Pn films for spectroscopic studies of singlet fission and triplet diffusion. A spectral model was constructed in order to calculate the mole fractions of molecules present in different amorphous or crystalline phases in the polycrystalline films.

3.6. References

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CHAPTER 4

Triplet Diffusion and Interphase Exchange in Polycrystalline Films of a Pentacene Derivative

This chapter focuses on how molecular packing arrangements impact the diffusion of multiplied triplet excitations following singlet fission in polycrystalline films. This work provides insight into how structural disorder, which naturally results from solution-casting organic films, impacts the harvestability of the multiplied excitons. In particular, the diffusivity of triplets was found to strongly depend on film composition, leading to a new structural design rule. Although highly efficient singlet fission can occur in disordered molecular systems, such as amorphous and polycrystalline films, there is a need to maximize structural order in order to efficiently transport triplets to other elements of solar cell devices.

The work presented in this chapter also revealed that triplets may exchange between both amorphous and crystalline domains in solution-cast films of organic materials. This led to a dramatic decrease in triplet diffusivity, because the presence of disordered packing arrangements of molecules in the amorphous phase limits the rate of triplet diffusion. A pair of design rules emerges for systems in which amorphous domains are inevitably formed: (1) Singlet fission should occur primarily in highly ordered regions of the film; (2) Energy level mismatch between amorphous and crystalline phases may be necessary to prevent triplets from transferring to amorphous regions of the film.

This chapter was adapted from the publication: Grieco, C., Doucette, G.S., Pensack, R.D., Payne, M.M., Rimshaw, A., Scholes, G.D., Anthony, J.E., and Asbury, J.B., “Dynamic Exchange During Triplet Transport in Nanocrystalline TIPS-Pentacene Films”, *JACS*, **2016**, 138, 16069-16080, which has been rephrased in the context of this dissertation.

4.1. Introduction

Singlet fission (SF) is an exciton multiplication mechanism observed in some organic molecules¹ that promises to improve solar cell efficiency by overcoming the Shockley-Queisser limit.² Singlet fission quantum efficiencies as high as 200% have been reported.^{3,4} However, applying singlet fission sensitizers to enhance device efficiency requires energy or electron transfer of the multiplied excitations to other elements of the solar cell.⁵⁻⁸ Therefore, highly efficient exciton multiplication is a necessary but incomplete criterion for employing singlet fission sensitizers. In particular, the transport of the triplet excitons following the singlet fission process must also be considered.⁹ Recent attention has been drawn to developing highly efficient compounds, the first step toward their employment in solar cells, and so the harvestability of the multiplied excitons has been underexplored.

Although SF sensitization has been shown in principle to push the thermodynamic limits of solar cell power conversion efficiency through recent device studies^{8,10}, device engineering is far from practical. With the exception of these discoveries, the prominence of singlet fission sensitized solar cells is lacking because of a scarcity of design rules for materials that are efficient at transferring excitation to solar cells. In particular, only few studies have related triplet exciton dynamics to solid state properties.^{11,12} In fact, studies of SF in solution^{3,4,13-15} have become very popular as of late because of their usefulness for studying fundamental properties of the formation of triplet excitons in SF materials. Despite these developments, understanding solid-state interactions remains critical in order to fully exploit processing conditions of SF-based devices.

Most reports on SF molecules in the solid-state have focused on how gross changes in molecular coupling arising from chemical modifications affect SF rates in effort to develop

rules for improving SF efficiency.^{16,17} Other reports consider how large changes in crystal structure affect SF rates.^{11,12} However, only a few studies have investigated the influence solid-state morphology have on the triplet exciton harvesting ability.¹¹ Hence there remains the need for understanding how changes in solid-state morphology, ultimately determined by variations in molecular packing arrangements, influence triplet exciton decay dynamics. This is very important because it would form a generalized model for the effect that morphology has on triplet population formation and decay behaviors that can foster both chemical and device engineering of new singlet fission sensitizers.

In this work, a new solvent annealing method (see Chapter 3) is used to systematically tune the molecular-level packing in polycrystalline films of a model singlet fission material, 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-Pn). Using this method, the strength of intermolecular coupling interactions in the films are tuned without the need to modify its chemical structure.^{18,19} A series of films containing different mixtures of amorphous and nanocrystalline domains was used to systematically investigate the diffusion of the multiplied triplet excitons following singlet fission.

The rates of singlet fission measured in TIPS-Pn films were found to depend on their molecular-level packing and crystallinity, similar to prior observations.^{11,12,18-23} However, the most dramatic changes were observed for diffusion-controlled triplet annihilation, suggesting that triplet transport depended sensitively on both molecular-level and crystalline order and composition. A combination of structural and spectroscopic characterizations revealed that triplet excitons experienced annihilation processes that reflected the average properties of the films consisting of mixtures of nanocrystalline and amorphous phases. This implied that the triplets were able to diffuse over distances far enough to experience both the types of phases

in the polycrystalline films. Using the exciton-exciton annihilation method,²⁴ the triplet diffusion lengths were estimated for films containing varying mole fractions of the amorphous versus crystalline phases. The results suggest that triplet excitons undergo dynamic exchange between amorphous and crystalline domains of TIPS-Pn. Ultimately it was found that even small amounts of an amorphous (“impurity”) phase in films of singlet fission sensitizers can significantly decrease the ultimate triplet diffusion length. This led to a new structural design rule for singlet fission sensitizers: Highly ordered, crystalline materials are needed to efficiently harvest multiplied excitons even when singlet fission can occur efficiently.

4.2. Experimental Methods

Methods for preparing and annealing TIPS-Pn films are detailed in Chapter 3. Briefly, solutions were made by dissolving 20 mg of TIPS-Pn in 1 mL of dichloromethane before spin-casting onto 1 inch diameter sapphire substrates at 1600 rpm. These “as-cast films” were the starting point for further annealing. Isopropyl alcohol (IPA) vapor was used for solvent annealing. Films were heated at ~100 °C for 1 minute for thermal annealing.

UV-Visible spectrometry was performed using a commercially available spectrophotometer (Beckman, DU 520; Brea, CA). For time-dependent absorption spectroscopy, a home-built spectrophotometer was used, which is detailed in Chapter 3.

Grazing-incidence x-ray diffraction (GIXRD) measurements were made using a PANalytical X’Pert Pro MPD diffractometer (PANalytical; Almelo, Netherlands). All scans used a 1° incidence angle and Cu K α radiation. To avoid biasing the thick crystalline areas of the films that formed on the edges of the circular substrates (artifact from spin-coating), the x-ray spot size was reduced to about 1 cm x 1 cm.

Two-dimensional x-ray diffraction (2D-XRD) measurements were made using a Rigaku DMAX-Rapid II Microdiffractometer (Rigaku; Tokyo, Japan) in the reflective geometry. Like in GIXRD, all films were measured using Cu K α radiation. A 1 hour exposure time was used while the films were rocked from 4.5–6° 2-theta. All data were processed using the AreaMax software package.

Scanning electron microscopy (SEM) was performed using a Zeiss Merlin FE-SEM (Zeiss; Jena, Germany). The films were first coated with 30 Å of iridium to provide a conductive layer necessary for preventing charge build-up during scans. All images were collected with acceleration voltages between 0.5 and 2.0 keV to limit electron penetration. For cross sectional images, films were made on glass substrates coated with 40 nm gold, using identical casting conditions as those used for sapphire substrates. These samples were cleaved at room temperature across the center of the substrate.

Ultrafast 2-color visible-pump/visible-probe spectroscopy was performed using a home-built system. In particular, a regenerative Ti:Sapphire laser amplifier (Integra, Continuum; San Jose, CA), which was seeded by a Ti:Sapphire oscillator (Vitesse, Coherent; Santa Clara, CA), was used as the source for both the pump and the probe pulses. For the pump, the laser drove an OPA (TOPAS, Light Conversion Ltd; Vilnius, Lithuania) that was tuned to 655 nm. For all samples, the incident energy density used was $\sim 40 \mu\text{J}/\text{cm}^2$. For the probe, a small portion of the fundamental of the Ti:Sapphire laser was focused onto a sapphire window (WG30530, Thorlabs; Newton, NJ) to create a white-light supercontinuum. It was then optically filtered before the sample position using colored glass filters for the spectral range of interest. A motorized delay stage (IMS600CCHA, Newport; Irvine, CA) was used to mechanically delay the pump relative to the probe beams. After transmitting the sample, the

probe beams were filtered using 10 nm FWHM dielectric bandpass filters, and was tuned by rotating the filters. The resulting beams were detected using a balanced silicon photodetector (PDB210A, Thorlabs; Newton, NJ). The instrument response was estimated to be ~150 fs in FWHM.

Nanosecond visible-pump/visible-probe transient absorption spectroscopy was performed using a home-built laser flash-photolysis instrument, which was a modified version of one previously reported.²⁵ A home-built dye cavity was pumped using a 30 Hz, 10 ns Nd:YAG laser (Surelite, Continuum; San Jose, CA) to generate the excitation source (~649 nm). The absorbed excitation density range used for all film samples was within ~5–50 $\mu\text{J}/\text{cm}^2$. A high-power tungsten-halogen lamp (ASBN-W, Spectral Products; Putnam, CT) was used as the probe source, which was dispersed using a monochromator (CM110, Spectral Products; Putnam, CT) before encountering the sample. The transmitted light was detected using a silicon photodiode (DET36A, Thorlabs; Newton, NJ) after passing through a 600 nm dielectric longpass filter (FELH0600, Thorlabs; Newton, NJ), which was used to block laser scatter. A 200 MHz preamplifier (HVA-200M-40-B, Femto; Berlin, Germany) was used to amplify the detected signal, which was digitized using a 200 MHz PC oscilloscope (Pico-5000, Pico Technology; Cambridgeshire, United Kingdom).

4.3. Morphology Dependence of Singlet Fission in TIPS-Pn Films

In Chapter 3, the molecular-level and long-range order in TIPS-Pn films was examined as a function of solvent and thermal annealing conditions. The remainder of this chapter relates the film structures to the transport characteristics of triplet excitons generated by singlet fission. First, singlet fission was verified to occur on ultrafast timescales in amorphous,

thermally-annealed, and solvent-annealed TIPS-Pn films, suggesting that the triplet excitons measured were formed principally from singlet fission and not intersystem crossing.

In order to monitor singlet fission (via measurement of triplet absorption) across all films studied, the specific positions of the triplet absorption bands were first needed. For this, nanosecond transient absorption spectroscopy was used to measure the absorption of independent triplet excitations. **Figure 4-1** displays visible transient absorption spectra of TIPS-Pn films made using various annealing conditions. All spectra were measured 10 ns following photoexcitation of each film with 649 nm and 30 $\mu\text{J}/\text{cm}^2$ absorbed energy density. The resulting transient absorption spectrum probed in the visible spectral region around 520 nm has been assigned to a $T_1 \rightarrow T_n$ absorption, which is commonly referred to in the literature as “ $T_1 \rightarrow T_3$ ”.^{26,27} This absorption band was redshifted and broadened upon solvent annealing, consistent with the increased average intermolecular interactions between TIPS-Pn molecules that are present in crystalline films (see Chapter 3 for details).

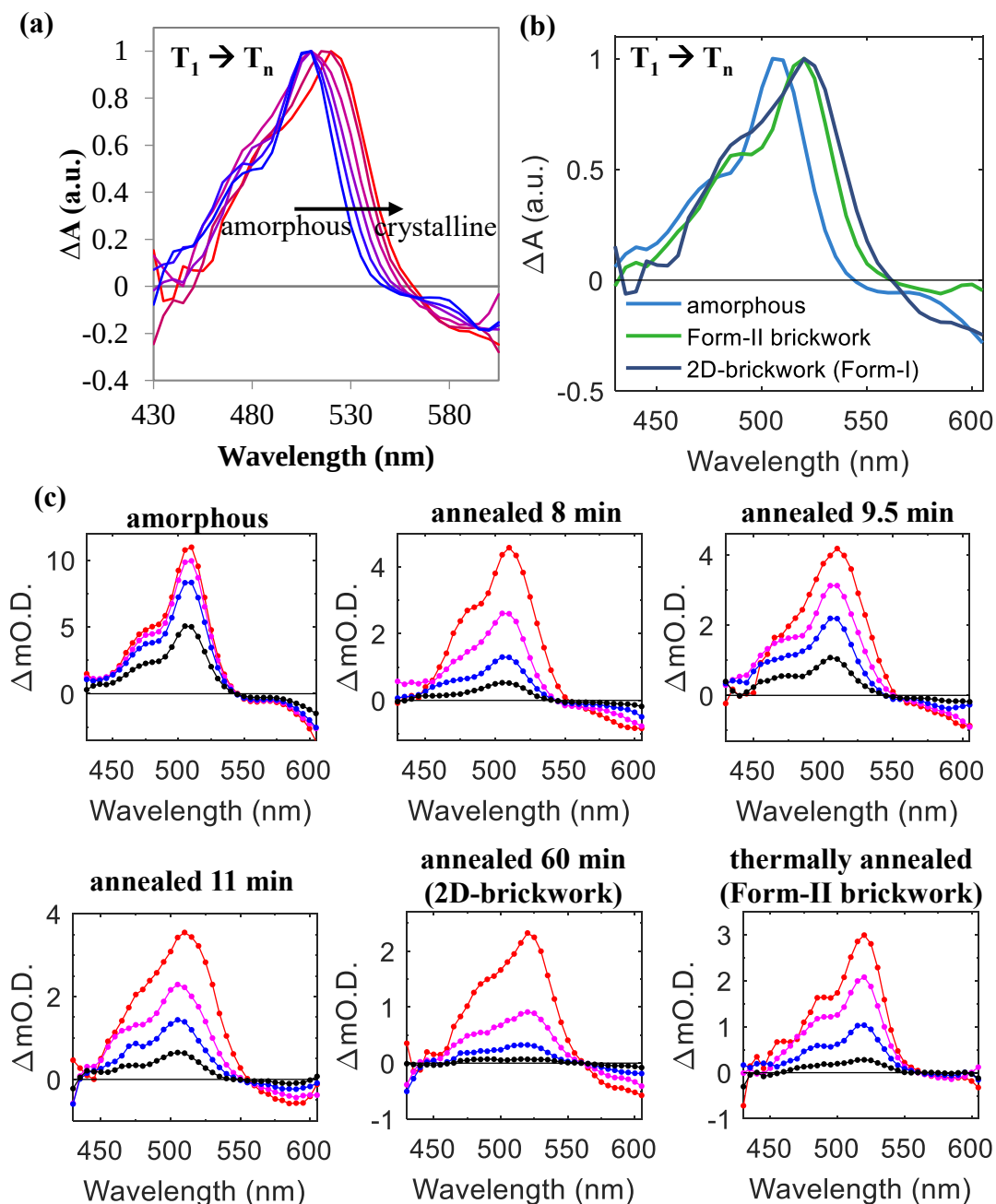


Figure 4-1: (a) Triplet photo-induced absorption ($T_1 \rightarrow T_n$) spectra measured at 10 ns time delay in TIPS-Pn films solvent annealed to varying extents. (b) Triplet absorption spectra taken at 10 ns time delay for TIPS-Pn films representing amorphous, Form-II brickwork, and 2D-brickwork (Form-I) phases. (c) Time-dependent transient absorption spectra for various TIPS-Pn films. For all plots, the spectra were temporally averaged between 0–10 ns (red), 10–50 ns (magenta), 50–100 ns (blue), and 100–500 ns (black). For solvent annealed films, IPA was used as the solvent.

Triplet formation kinetics (representing the singlet fission kinetics) were measured on the femtosecond to picosecond time scale for each film, probed at the λ_{max} of the corresponding triplet absorption bands. The kinetics traces are shown in **Figure 4-2**, which were all measured following photoexcitation at 655 nm and 20 $\mu\text{J}/\text{cm}^2$ absorbed energy density.

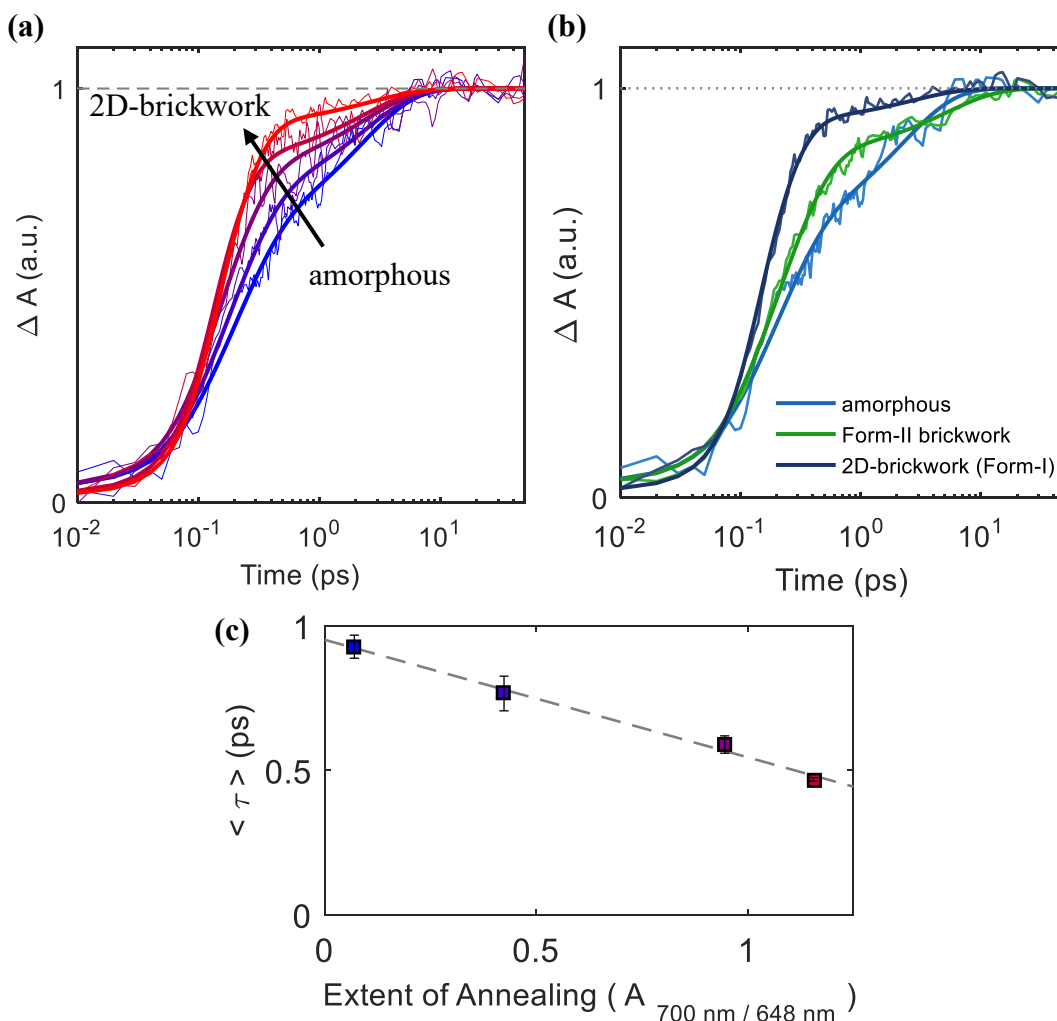


Figure 4-2: (a) Ultrafast transient absorption of triplets ($T_1 \rightarrow T_n$) in TIPS-Pn films that were solvent annealed to varying extents. (b) Ultrafast transient absorption for TIPS-Pn films representing amorphous, Form-II brickwork, and 2D-brickwork (Form-I) phases. All kinetics were probed at the λ_{max} of the appropriate triplet photoinduced absorption spectrum. (c) Dependence of the average singlet fission time constant on extent of solvent annealing. Errors were determined from fitting a sum of two exponential growth (1-e) functions to the ultrafast growth kinetics. Dashed gray line is an empirical linear fit to the data.

Singlet fission was complete within the first 20 ps across all types of annealing, which is characteristic of pentacene derivatives in general.^{19,28} All singlet fission kinetics were well-described using a sum of two exponential growth functions.^{19,28} The results of the fits are summarized in **Table 4-1**.

Table 4-1. Fit results for ultrafast triplet state absorption growth kinetics of TIPS-Pn films

Sample Name	a_1^*	$\tau_1^\dagger$ (ps)	a_2^*	$\tau_2^\dagger$ (ps)	$\langle \tau \rangle^\ddagger$ (ps)
As-Cast	0.64	0.19	0.36	2.26	0.93
Partially-annealed ($A_{700}/A_{648} = 0.6$)	0.79	0.14	0.21	2.30	0.59
Fully solvent-annealed	0.92	0.11	0.08	2.60	0.32
Thermally-annealed	0.84	0.21	0.16	5.10	1.00

* a_1 and a_2 are amplitude factors for the fast and slow exponential growth functions, respectively

$\tau_1^\dagger$ and $\tau_2^\dagger$ are the time constants for the fast and slow exponential growth functions, respectively

$\langle \tau \rangle^\ddagger$ is the weighted average time constant

The specific model, $F(t)$, that was used to fit the data was:

$$F(t) = f(t) * g(t)$$

$$f(t) = N_1 \left[a_1 \left(1 - e^{-t/\tau_1} \right) + (1 - a_2) \left(1 - e^{-t/\tau_2} \right) \right] \quad (\text{eqn. 1})$$

$$a_1 + a_2 = 1 \quad (\text{eqn. 2})$$

$$g(t) = N_2 \exp \left[-\frac{1}{4} \left(\frac{t}{FWHM/2\ln(2)} \right)^2 \right] \quad (\text{eqn. 3})$$

where $f(t)$ is a double exponential growth function and $g(t)$ is an area-normalized Gaussian function, t is time, N_1 and N_2 are a normalization constants, a_1 and a_2 are scaling factors (or weights) for exponential terms 1 and 2, respectively, τ_1 and τ_2 are lifetimes for exponential terms 1 and 2, respectively, and FWHM is the full-width at half-maximum. The Gaussian function is used to represent the instrument response function (IRF). The time resolution was estimated to be at least 100 fs, which was Gaussian FWHM that best described the kinetic rise in the data across the entire series.

The triplet formation dynamics were found to depend on the strength of intermolecular interactions in the films, consistent with results of prior investigations.^{11,12,18,20-23,29} The origin of the bimolecular growth of the triplet kinetics in pentacene derivatives has been previously analyzed in detail.¹⁹ In amorphous films, singlet fission may occur via diffusion of singlet excitation to “singlet fission centers”, or sites in the material that contain intermolecular arrangements favorable for the reaction to occur.¹¹ This form of heterogeneity gives rise to multi-exponential growth of the triplet population. In highly ordered crystalline films, however, the multi-exponential growth has been attributed to the sequential nature of the singlet fission reaction (i.e. formation and separation of correlated triplet pair intermediates).²⁸ In the case of partially annealed films, the multi-exponential growth of the triplet population probably arises from a combination of both.

4.4. Morphology Dependence of Triplet-Triplet Annihilation in TIPS-Pn Films

After formation of multiplied triplets from singlet fission, the excitations migrate through the material until they relax to the ground state. If the concentration of triplets is high, they may encounter each other (nongeminately) within their natural lifetime in a collision

event, causing a dissipation of energy. This triplet-triplet annihilation pathway is thus a diffusion-controlled bimolecular process that is controlled by the rate of transfer from molecule to molecule. The triplet transfer mechanism involves Dexter exchange interactions, and so this process is strongly mediated by electronic orbital overlap coupling.³⁰ As a result, the rate of triplet transport through a material, measured through annihilation kinetics, should sensitively depend on the types of intermolecular packing arrangements in the TIPS-Pn films. In the remainder of this chapter, triplet-triplet annihilation rate constants are quantified for films solvent annealed to different extents in order to relate triplet transport rate to changes in molecular and structural order. In addition, the triplet-triplet annihilation method^{7,31,32} was used to estimate their triplet diffusion length for each film.

4.4.1. Triplet absorption dynamics and kinetic model for bimolecular annihilation

The triplet decay kinetics (**Figure 4-3**) were measured on the nanosecond to microsecond timescale in the solvent annealed films by probing the $T_1 \rightarrow T_n$ peak (**Figure 4-1**) following 649 nm excitation, with an absorbed energy density set to $\sim 20 \mu\text{J}/\text{cm}^2$ for each film. The compositions of the films were determined using absorption spectroscopy (see Chapter 3 for all details). The mole fraction of the crystalline phase was defined as the sum of the mole fractions of the Form-II brickwork and 2D-brickwork phases. The triplet decay kinetics traces are labeled accordingly. Henceforth, the partially-annealed films are referred to by their crystalline phase mole ratio.

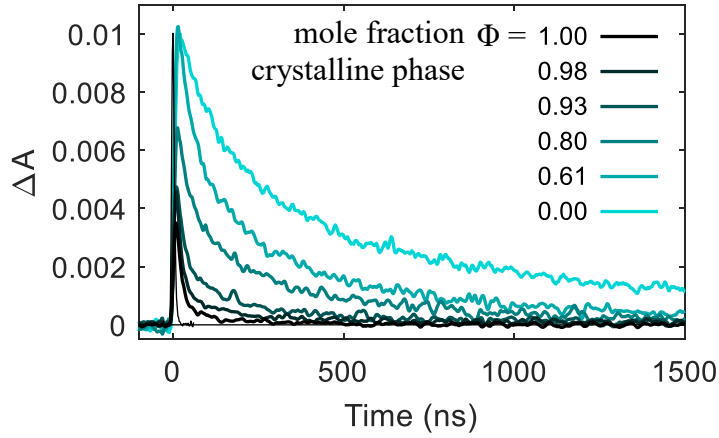
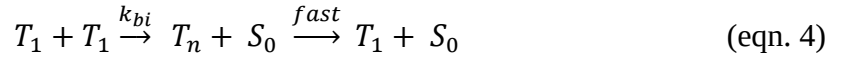


Figure 4-3: Nanosecond-microsecond transient absorption kinetics of triplets ($T_1 \rightarrow T_n$) in TIPS-Pn films that were solvent annealed to varying extents (identified using mole fraction of crystalline phase).

The time decay of the triplet excitons may be described using chemical kinetic theory as follows:



where T_1 and T_n are excited triplet states, S_0 is the ground state, k_{bi} is the bimolecular rate constant, and k_{uni} is the unimolecular rate constant. From these expressions, the triplet-triplet annihilation model^{7,31,32} is derived, which describes the time-evolution of the triplet concentration by the rate equation:

$$\frac{d[T]}{dt} = -\frac{[T]}{\tau} - \frac{1}{2}k_{bi}[T]^2 \quad (\text{eqn. 6})$$

where $[T]$ is the triplet concentration, τ is the natural (unimolecular) triplet lifetime, and t is time. Note that $\tau = 1/k_{uni}$ in this representation. In the case of TIPS-Pn, triplet-triplet annihilation is believed to predominantly form one highly excited T_n state from two T_1 states, and not an excited singlet state because reformation of the S_1 state via triplet fusion is endergonic.¹⁴

When the triplet concentration is high (particularly at early time delays, and at moderate excitation densities) and when $1/\tau \ll k_{bi}[T]$, the second-order term dominates and the first term may be neglected. To illustrate the validity of this assumption, as-cast films are used as an example because they have the slowest triplet decay, and consequently, the clearest kinetic behavior. The triplet absorption decay is shown in **Figure 4-4** in a semi-logarithmic plot, in addition to a $1/\Delta A$ vs. t plot for convenience.

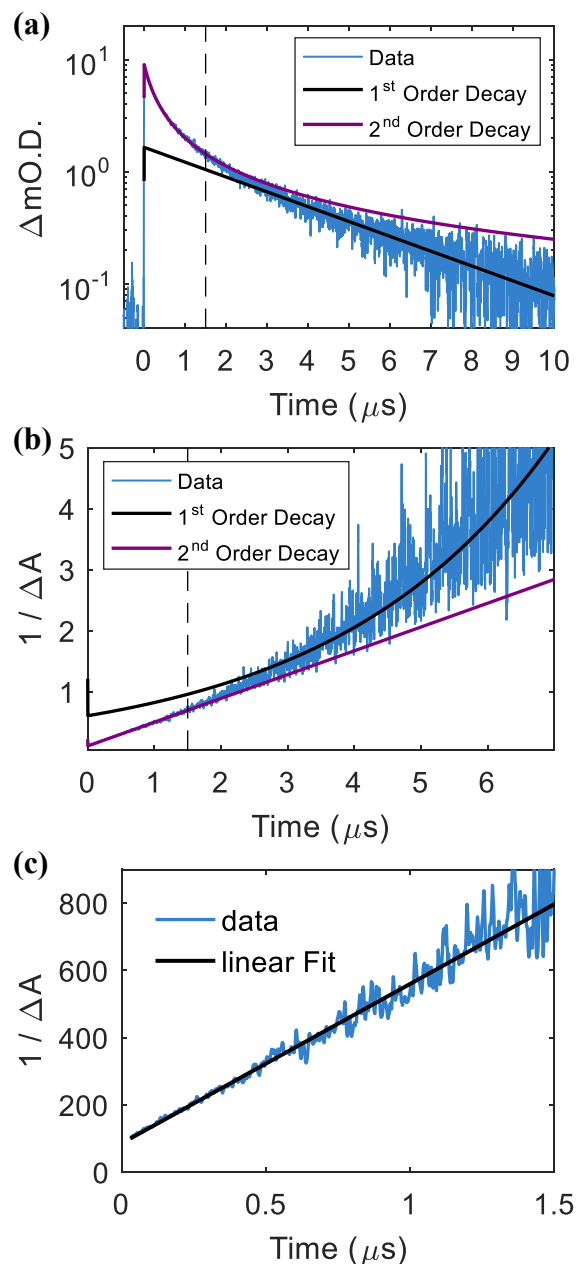


Figure 4-4: (a) Semi-logarithmic plot of the triplet absorption kinetics for an amorphous TIPS-Pn film. Examples of 1st and 2nd order decays are overlaid, showing a conversion of the data from bimolecular to unimolecular over time. (b) The data represented in a $1/\Delta A$ versus time plot illustrating that the decay before $\sim 1.5 \mu\text{s}$ (indicated by dashed vertical line) is well-described as bimolecular reaction kinetics. (c) Close-up view of the kinetics showing a linear fit to the data below 1.5 μs time delay.

The kinetics are well-described using 2nd order decay kinetics on the early microsecond timescale (0–1.5 μs), and 1st order decay kinetics on a later timescale (1.5–10 μs).

Consequently, the kinetics on the early microsecond ($< 1.5 \mu\text{s}$) are approximated as 2nd order bimolecular decay, and the first order term is negligible. In this case, the simplified rate expression is solved to be:

$$\frac{1}{[T]} = \frac{1}{[T_0]} + \frac{1}{2}k_{bi}t \quad (\text{eqn. 7})$$

which predicts that the inverse of triplet concentration should depend linearly on time with a slope equal to the $\frac{1}{2}k_{bi}$. Unlike in single exponential decay kinetics, the rate constant cannot be immediately determined from a ΔA vs t kinetics trace. The relation of the triplet state absorbance, ΔA , to the triplet concentration, $[T]$, can be approximated using the Beer-Lambert law as:

$$\Delta A = \varepsilon b[T] \quad (\text{eqn. 8})$$

where ε is the molar extinction coefficient of the triplet absorption at the probe wavelength, and b is the sample pathlength. Therefore, the change in absorbance can be related to concentration if both ε and b are known. Substituting this relation into eqn. 7 gives:

$$\frac{1}{\Delta A} = \frac{1}{\Delta A_0} + \frac{1}{2\varepsilon b}k_{bi}t \quad (\text{eqn. 9})$$

where ΔA_0 is the transient absorption signal at time zero. It is convenient in this case to rearrange the expression as:

$$\frac{2\varepsilon b}{\Delta A} = \frac{2\varepsilon b}{\Delta A_0} + k_{bi}t \quad (\text{eqn. 10})$$

In this way, the bimolecular decay constant is equivalent to the slope of a linear fit to the transient absorption data plotted as $2\varepsilon b/\Delta A$ vs. t . In order to determine the rate constant, it first is necessary to quantify both ε and b . To calculate b , the film thicknesses was measured using cross-sectional SEM, which were reproducibly ~ 100 nm (see **Figure 4-5** for an example).

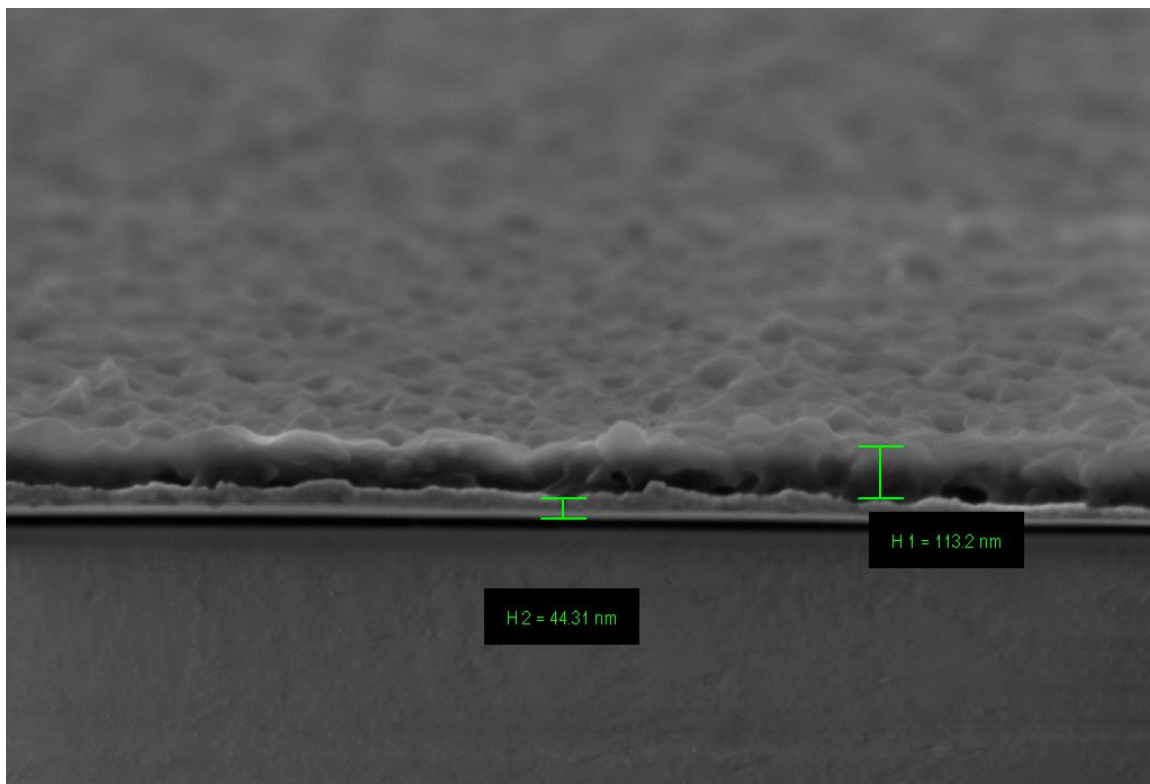


Figure 4-5: Example of a cross-sectional SEM image of a partially-annealed TIPS-Pn film on a (~ 40 nm thick) gold layer showing a film thickness of ~ 100 nm.

Calculating ϵ for each film is much less straightforward because it would depend on the annealing conditions. The following section describes the method that was developed for determining ϵ for each film.

4.4.2. Determining extinction coefficients for triplet absorption in TIPS-Pn films

The value of the triplet absorption extinction coefficient was taken from a report by Ramanan et al.²⁷ for a disordered TIPS-Pn film. However, this value cannot be assumed to be independent of the extent of annealing, especially since the extinction coefficient of the ground state absorbance ($S_0 \rightarrow S_1$) is observed to very strongly depend on the extent of annealing. If the relative extinction coefficients for the triplet absorptions are known for each film, the values of ϵ may be calculated using the known absolute value.

The method used for determining relative triplet absorption ($T_1 \rightarrow T_n$) extinction coefficients is as follows: (1) Measure the absorption change of the initial triplet population, ΔA_0 , as a function of triplet concentration, $[T]_0$; (2) Fit a line to a plot of ΔA_0 vs. $[T]_0$, the slope of which is proportional to the extinction coefficient. Power-dependent measurements were performed on the same film in order to generate different initial triplet concentrations. Even if the triplet yield is dependent on the annealing condition, the relative extinction coefficients calculated in this way still hold. In other words, $d(\Delta A_0)/d[T]_0 = \text{slope}$ for each individual film irrespective of the triplet yield. Several assumptions must first be tested in order to use this method:

(1) The bimolecular constant is independent of pump fluence. From the rate expression, the bimolecular rate constant is defined to be independent of time and concentration. Because it has units of $M^{-1}s^{-1}$, the rate of decay of the triplets is actually dependent on its initial triplet concentration. In other words, $[T]_t$ depends on $[T]_0$, but k_{bi} does not depend on $[T]_0$. As a result, plotting ΔA vs. t would yield power-dependent decays, while plotting $1/\Delta A$ vs. t would yield power-independent kinetics. To test this, the dependence of the $1/\Delta A$ vs. t kinetics trace on absorbed energy density was considered for each film. Representative results are shown for an as-cast film in **Figure 4-6** over an absorbed energy density range of $\sim 6\text{--}76 \mu J/cm^2$.

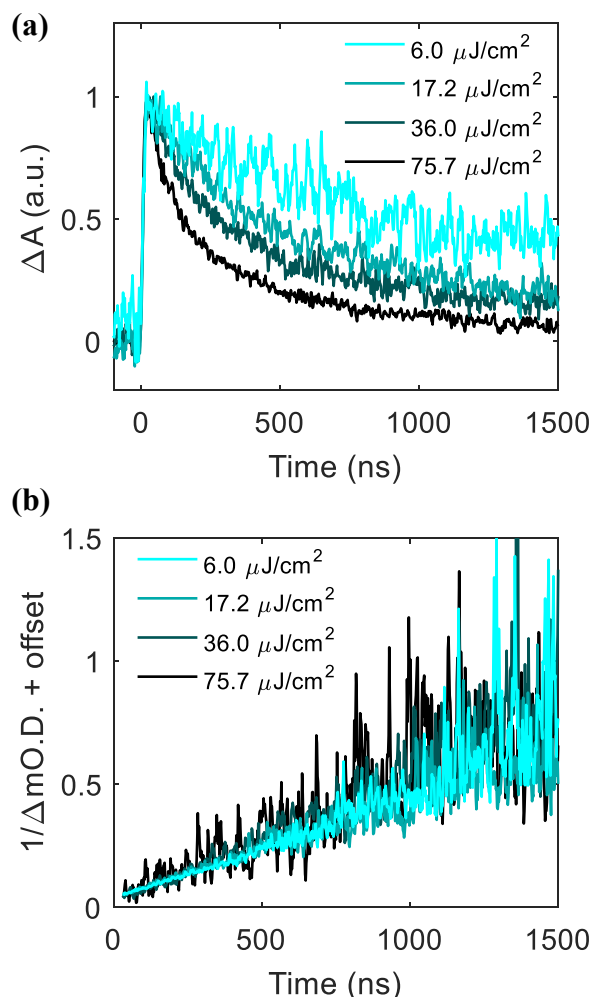


Figure 4-6: (a) Normalized transient absorption corresponding to $T_1 \rightarrow T_n$ for an amorphous film showing strong dependence of the decay on energy density absorbed. (b) Non-normalized version of the same kinetics plotted in the form of $1/\Delta A$ versus time. The slope of the data was invariant with energy density absorbed in this representation. Data were offset since the initial triplet concentration was not equal for all energy densities used.

(2) The initial triplet concentration, $[T]_0$, can be represented as the maximum kinetic intensity of the nanosecond kinetics (around time zero), which were actually measured with a ~ 10 ns time response. If this was valid, then there would be a linear dependence of triplet absorption amplitude, ΔA_0 , on absorbed energy density, E_{abs} . This was true for films annealed to different extents, which is evident in **Figure 4-7**.

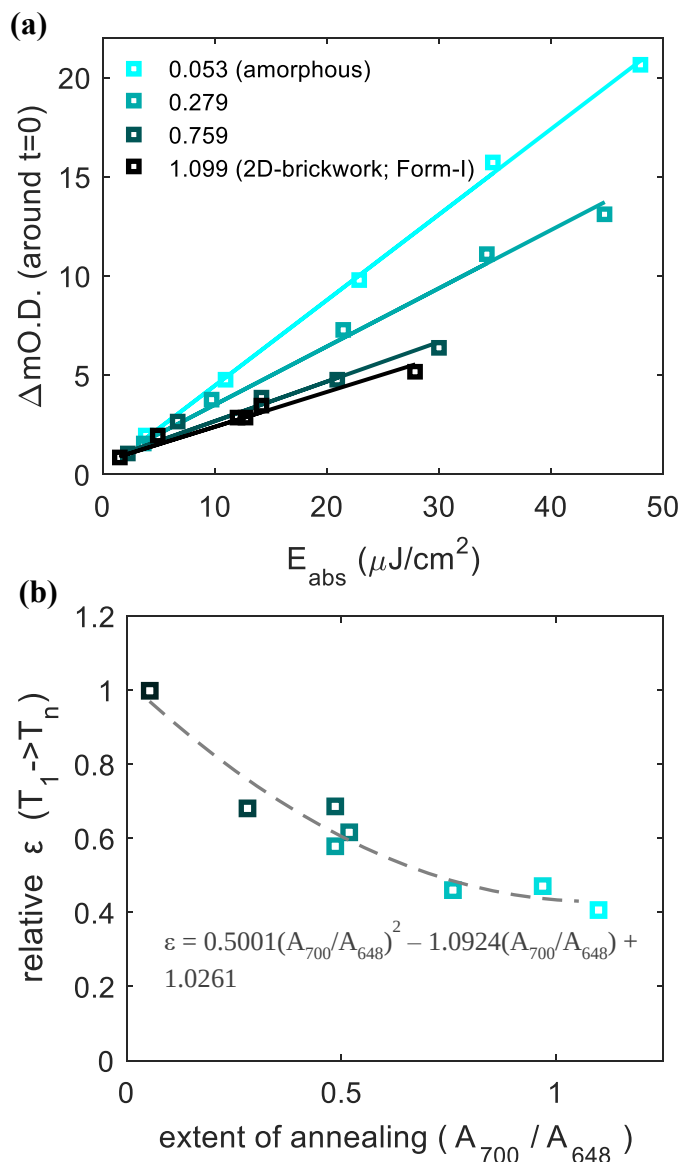


Figure 4-7: (a) Power dependence of the triplet absorption ($T_1 \rightarrow T_n$) signals around time zero for TIPS-Pn films solvent annealed to various extents (represented using A_{700}/A_{648} values in the legend). E_{abs} is the absorbed energy density used. The straight lines are linear fits to the data, with slopes equal to the relative extinction coefficients. **(b)** Empirical relation between relative triplet extinction coefficients and extent of annealing. The dashed gray fit line is a 2nd order polynomial, serving as a calibration curve.

(3) The absorbed energy density is linearly related to the initial concentration of triplets.

This is already proven because the ΔA_0 and E_{abs} are linearly related for all films in **Figure 4-**

7. This condition would not be satisfied if other nonlinear deactivation mechanisms began to

compete with singlet fission, such as singlet-singlet annihilation. Pensack and coworkers have shown that singlet fission is sufficiently fast in pentacene derivatives to outcompete even singlet-singlet annihilation.¹⁹

Now, the relative extinction coefficients were determined as the ratio of the slopes of the ΔA_0 vs. E_{abs} data in **Figure 4-7**. The variation of relative extinction coefficients on extent of annealing was related and empirically fit using a second order polynomial (see **Figure 4-7**). The bimolecular rate constants could be determined for all films reported as the triplet extinction coefficients were determined using:

$$\varepsilon = \varepsilon_{\text{relative}} \varepsilon_{\text{disordered}} \quad (\text{eqn. 11})$$

Examples of extinction coefficients calculated for films annealed to various extents are tabulated in **Table 4-2**.

Table 4-2: $T_1 \rightarrow T_n$ extinction coefficients for solvent annealed TIPS-Pn films

A_{700}/A_{648}	Mole Frac. 2D-brickwork	Mole Frac. Crystalline	$\varepsilon \text{ (M}^{-1} \text{cm}^{-1})$
0.053	0	0.00	$64\,000 \pm 1\,000$
0.485	0.55	0.80	$44\,000 \pm 1\,000$
0.759	0.69	0.92	$29\,400 \pm 700$
1.099	1	1.00	$26\,200 \pm 600$

This process was repeated for the thermally annealed film as well and the results are shown in **Figure 4-8**.

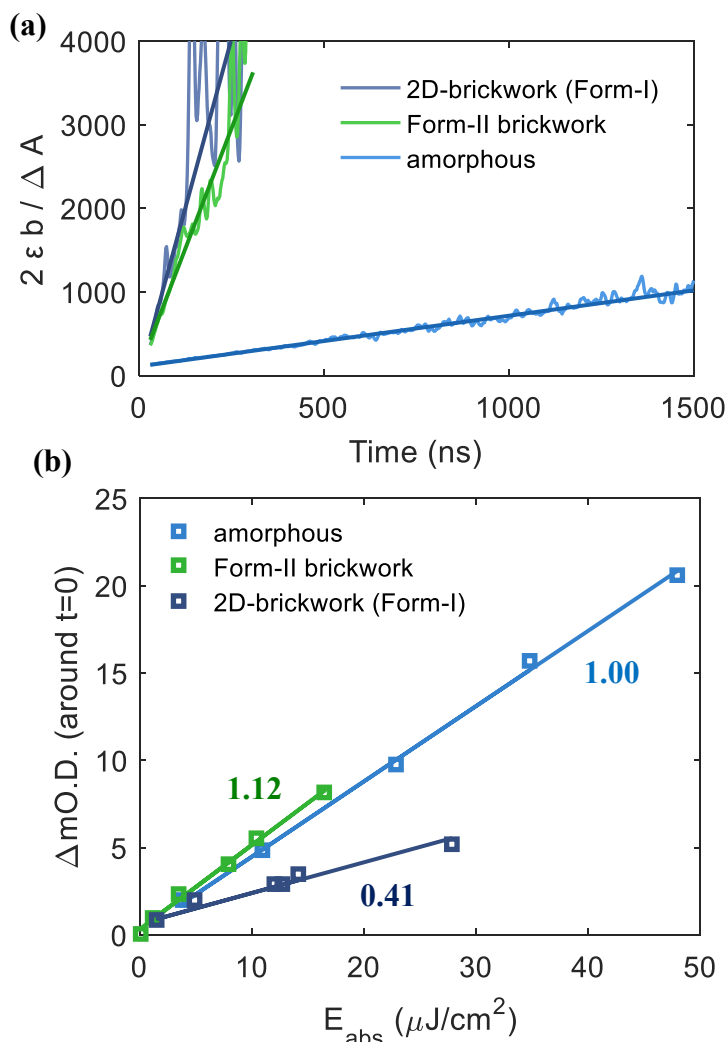


Figure 4-8: (a) Triplet absorption decays represented as $2\epsilon b / \Delta A$ versus time. The straight lines are the linear fits to the data, with slopes equal to the bimolecular rate constants for triplet-triplet annihilation. (b) Power dependence of the triplet absorption ($T_1 \rightarrow T_n$) signals around time zero for TIPS-Pn films representing amorphous, Form-II brickwork, and 2D-brickwork (Form-I) phases. The labels are the relative triplet extinction coefficients. E_{abs} is the absorbed energy density used.

Triplet absorption extinction coefficients are provided in **Table 4-3** for reference.

Table 4-3: $T_1 \rightarrow T_n$ extinction coefficients for TIPS-Pn films with different molecular packing structures.

Packing Type	ϵ ($M^{-1} cm^{-1}$)
Disordered	$64\,000 \pm 1\,000$
Form-II brickwork	$72\,000 \pm 2\,000$
2D-brickwork (Form-I)	$26\,200 \pm 600$

There are significant sources of error that must be addressed; the uncertainties in the values were estimated as follows: The value of the extinction coefficient for the as-cast film was taken as that reported for TIPS-Pn solutions²⁷ because the absorption spectrum of the as-cast film most closely resembles that of a solution. However, spectral overlap of the steady-state absorption the transient absorption of triplets is not negligible in annealed films; this signifies that it is possible that an overlapping ground state bleach signal may be slightly attenuating the measured absorption intensity of the triplet spectrum for the annealed films. The attenuation factor was estimated using data reported in Figure 7a in the paper by Ramanan et al.²⁷ as follows: Using a conservative assumption, the maximum bleach intensity overlapping the triplet absorption signal was taken as the 33.3 ps bleach intensity of the 590 nm peak (after which the only excited state population remaining is expected to be triplets). In this way, the maximum error of the triplet absorption intensity was estimated to be 0.89%. Next, the linear absorption extinction coefficient at 590 nm of our films was considered to vary at most by 39%. Compounding these errors, the variation in the calculated triplet extinction coefficients was estimated to be ~2.3 %.

4.4.3. Bimolecular rate constants for triplet-triplet annihilation

The triplet decay kinetics shown in **Figure 4-3** are plotted as $2\epsilon b/\Delta A$ versus time in **Figure 4-9** because the slopes of linear fits to the data now represent the bimolecular (triplet-triplet annihilation) decay constants.

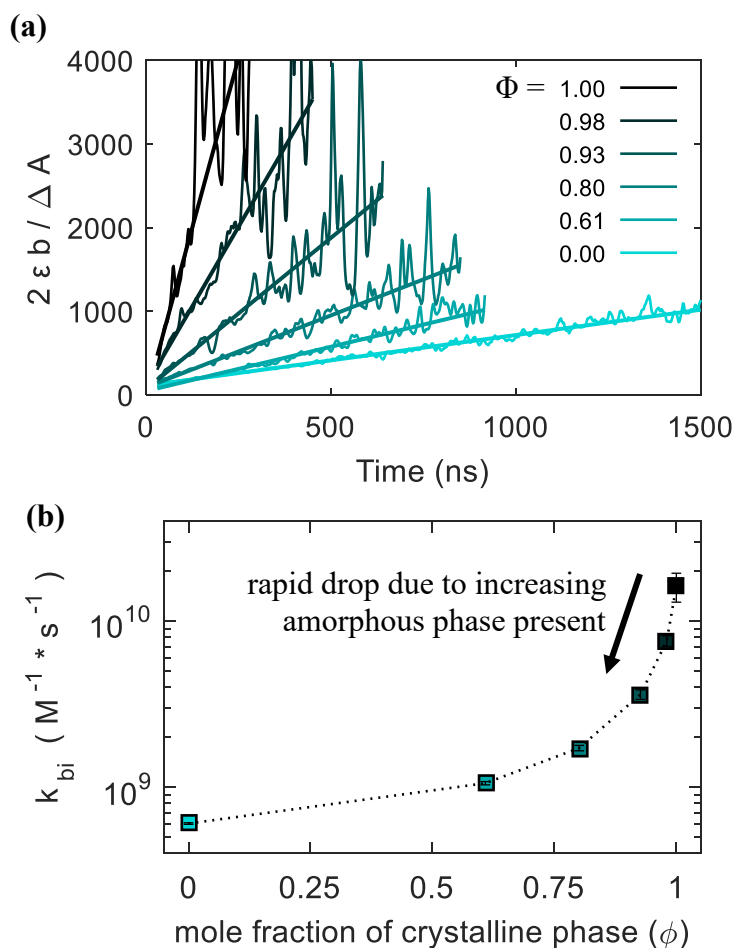


Figure 4-9: (a) Nanosecond-microsecond transient absorption kinetics of triplets ($T_1 \rightarrow T_n$) in TIPS-Pn films that were solvent annealed to varying extents (identified using mole fraction of crystalline phase). The kinetics are represented as $2\epsilon b/\Delta A$ versus time. The straight lines are the linear fits to the data, with slopes equal to the bimolecular rate constants for triplet-triplet annihilation. (b) Dependence of the corresponding bimolecular rate constants on the mole fraction of crystalline phase in the films.

The linearity of the data indicated that the kinetics measured for each TIPS-Pn film were well-described by a bimolecular decay process with a single decay constant k_{bi} , even though they were composed of mixtures of amorphous, Form-II brickwork, and 2D-brickwork phases. The

data were fit with a linear function to determine the bimolecular decay rate constants for each film. The uncertainties in the values were found to be dominated by the uncertainties associated with the linear fits to the data. The bimolecular decay rate constants were plotted on a logarithmic scale in **Figure 4-9** against the mole fraction of the crystalline phase of the corresponding films. Over an order of magnitude change in the rate constants was measured in films ranging from amorphous to crystalline, and so the triplet diffusivity is expected to depend similarly. Notably, such an observation is reminiscent of that for tetracene.³³ The rate constants are tabulated in **Table 4-4** for reference.

Table 4-4: Bimolecular (triplet-triplet annihilation) rate constants for TIPS-Pn films.

Sample	$k_{bi} (M^{-1} s^{-1})$
Disordered (As-Cast)	$(6.06 \pm 0.03) \times 10^8$
0.43 mass frac. 2D-brickwork	$(1.06 \pm 0.01) \times 10^9$
0.58 mass frac. 2D-brickwork	$(1.72 \pm 0.03) \times 10^9$
0.70 mass frac. 2D-brickwork	$(3.6 \pm 0.10) \times 10^9$
0.82 mass frac. 2D-brickwork	$(7.6 \pm 0.30) \times 10^9$
2D-brickwork (Form-I)	$(1.6 \pm 0.10) \times 10^{10}$
Form-II brickwork (Thermally-annealed)	$(6.00 \pm 3.00) \times 10^9$

4.4.4. Interphase diffusion of triplet excitons

Herein, a few kinetic models will be developed in attempt to describe the triplet annihilation characteristics in TIPS-Pn films with varying crystallinities. A “Confined Triplet” kinetic model was first constructed to describe the diffusion of triplet excitons among the amorphous and crystalline phases in partially-annealed TIPS-Pn films. In this model, it was assumed that triplet excitons were formed in each phase, but did not transfer to other phases. The total

population of triplet excitons, $[T]_{Total}$, were described by three populations of triplets: One in the amorphous phase, $[T]_{amorph}$, one in the Form-II brickwork phase, $[T]_{F2}$, and one in the 2D-brickwork phase, $[T]_{2D}$.

$$[T]_{Total} = [T]_{amorph} + [T]_{F2} + [T]_{2D} \quad (\text{eqn. 12})$$

Square brackets indicate concentration. Because the model assumes that triplet excitons are confined within the phases in which they were generated, three independent rate equations described their time-evolution:

$$\frac{d[T]_{amorph}}{dt} = -\frac{1}{2}k_{amorph}([T]_{amorph})^2 \quad (\text{eqn. 13})$$

$$\frac{d[T]_{F2}}{dt} = -\frac{1}{2}k_{F2}([T]_{F2})^2 \quad (\text{eqn. 14})$$

$$\frac{d[T]_{2D}}{dt} = -\frac{1}{2}k_{2D}([T]_{2D})^2 \quad (\text{eqn. 15})$$

where k_i is the bimolecular decay rate constants for phase i . Solving each rate equation and substitution into eqn. 12 results in the time-dependent triplet concentration:

$$[T]_{Total} = \frac{[T]_{0,dis}}{1 + \frac{1}{2}[T]_{0,dis}k_{dis}t} + \frac{[T]_{0,F2}}{1 + \frac{1}{2}[T]_{0,F2}k_{F2}t} + \frac{[T]_{0,2D}}{1 + \frac{1}{2}[T]_{0,2D}k_{2D}t} \quad (\text{eqn. 16})$$

where the $[T]_{0,i}$ is the initial concentration of triplets in phase i immediately following the pulsed excitation. This expression could be converted to absorbance units by using Beer's Law, with the known molar extinction coefficients of triplet absorption for each type of phase.

The bimolecular rate constants, k_i , were determined using measurements of films consisting of the pure amorphous, Form-II brickwork, and 2D-brickwork phases (as shown in **Figure 4-8**). To calculate the initial triplet concentrations, $[T]_{0,i}$, in each phase for a given partially-annealed film, knowledge of the number of photons absorbed by each phase (providing the concentration of singlet excitons) and the triplet quantum yields were required. The relative extinction coefficients of the $S_0 \rightarrow S_1$ transitions (see Chapter 3) and the phase compositions of

the partially-annealed films (see Chapter 3) were used together to calculate the proportion of incident photons absorbed by each phase, and therefore, the initial number of singlet excitons.

Next, the triplet exciton quantum yields were estimated for each of the three phases to calculate their initial triplet exciton concentrations from the initial concentration of singlet excitons. As discussed above, since the triplet absorption was linearly proportional to the absorbed energy density in the range studied, the kinetic amplitudes around time zero represent the initial concentration of triplets. As such, the triplet exciton yields were calculated by taking the ΔA_0 value at the same given absorbed energy density for each film (arbitrarily, $10 \mu\text{J}/\text{cm}^2$) and scaling these values by the appropriate relative extinction coefficients. Using a known triplet quantum yield of $\sim 200\%$ for the 2D-brickwork crystal structure, the quantum yields could then be determined for the other phases.

The triplet-triplet annihilation kinetics for a partially-annealed TIPS-Pn film with 90% mole fraction ordered phase is reproduced in **Figure 4-10**. The data were compared to the kinetics predicted using the Confined Triplet kinetic model. Because it was assumed that triplets do not leave their respective phases, the predicted kinetics consisted of a fast decay due to rapid annihilation in the ordered phases, followed by slower annihilation kinetics, characteristic of amorphous phase. As such, the Confined Triplet model failed to describe the measured annihilation kinetics.

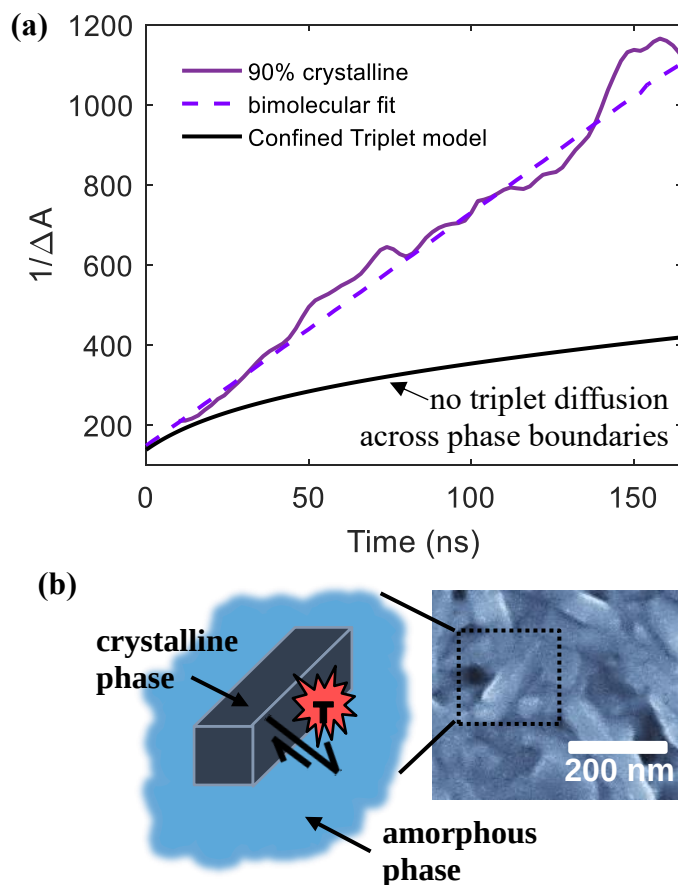


Figure 4-10: (a) Transient absorption kinetics of triplets in a partially solvent-annealed film containing 90% mole fraction of crystalline phase. The bimolecular fit to the data is included as a dashed purple line. The solid black trace represents the kinetics as predicted by the Confined Triplet model. (b) A cartoon illustrating the exchange of triplets between crystalline and amorphous phases. An (artificially colored) SEM image is included, showing the approximate length scale of triplet diffusion.

Next, the possibility of inter-phase diffusion was considered, such that a triplet can sample different domains within its lifetime. Like in the Confined Triplet model, triplet-triplet annihilation occurring within each respective domain has a characteristic rate constant that is described by the pure phases. Neglecting differences in triplet diffusion rate in these phases, the triplet exciton can experience the “average phase” as follows:

$$k_{net} = \frac{w_1 k_{amorph} + w_2 k_{F2} + w_3 k_{2D}}{w_1 + w_2 + w_3} \quad (\text{eqn. 17})$$

$$w_i = [T]_{0,i} \quad (\text{eqn. 18})$$

$$[T]_{Total} = \frac{[T]_0}{1 + \frac{1}{2}[T]_0 k_{net} t} \quad (\text{eqn. 19})$$

where w_i is a weight for phase i , which is either amorphous (“amorph.”), Form-II brickwork (“F2”), or 2D-brickwork (“2D”). In this way, the bimolecular rate constant is represented as a weighted average of the bimolecular rate constants of the three phases. The combination of the diffusion rates and domain sizes corresponding to each of the three phases would determine more explicitly the weighting coefficients. Since not all of these values were known, the weighting factors were merely taken as the initial triplet populations (eqn. 18) as an approximation. In this representation, the intradomain diffusion of triplets is taken to be equal for all phases.

Using the “Averaged 3-Phase” kinetic model, the total triplet absorption decay was predicted and is shown in **Figure 4-11** (along with the prediction of the Confined Triplet model).

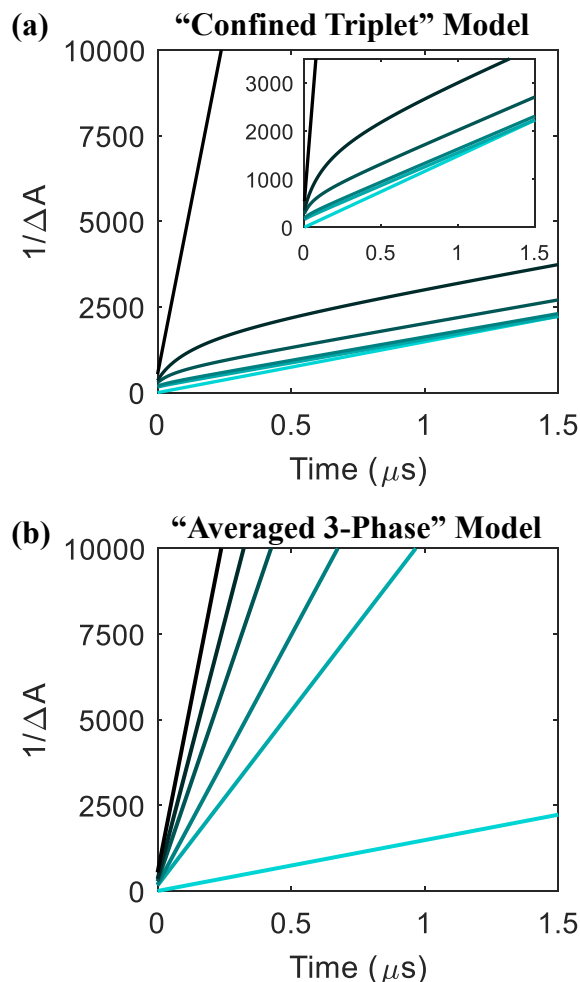


Figure 4-11: (a) Triplet kinetics predicted using the Confined Triplet model for a variety of extents of annealing. The inset shows a close-up of the kinetics. (b) Triplet kinetics predicted using the Averaged 3-Phase model for the same extents of annealing. Differences in diffusion constants among the phases was neglected in this model.

Again, the initial change in absorbance, ΔA_0 , was calculated using the experimentally determined parameters of fraction of photons absorbed, extinction coefficient of $T_1 \rightarrow T_n$, triplet yield, and bimolecular rate constants for each phase. The Averaged 3-State model qualitatively describes the behavior observed in the transient absorption data presented in **Figure 4-9**. This suggests that triplets undergo annihilation processes that reflect the average composition of the films. Furthermore, a gradual change in the bimolecular decay rate constants over a significant change in film composition indicated that triplets are able to diffuse over large distances such

that they can sample both amorphous and crystalline domains. The cartoon in **Figure 4-10** illustrates interphase exchange of triplet excitons. An SEM image of a TIPS-Pn film with 90% mole fraction of crystalline phase is included to show the approximate length scale over which triplets must diffuse in order to exhibit decay kinetics reflective of the average film composition. This implies that triplets must be able to diffuse over tens of nanometers during their lifetime in order to sample multiple phases in the films.

Last, another alternate explanation of the data was considered: Since the triplet concentration in the amorphous phase is the primary contributor to the overall observed triplet absorption signal, the total observed kinetic behavior could be dominated by signal arising from triplets present in amorphous phase that changes upon solvent-annealing. There are 2 major possibilities:

(1) Gradual increase of intermolecular order among the TIPS-Pn molecules within the amorphous phase give rise to the observed triplet-triplet annihilation kinetics. The absorption spectra presented in Chapter 3 were well described using a linear combination of static basis spectra. In particular, the sharp vibronic peaks of the amorphous phase did not appear to shift to longer wavelength or broaden, but rather monotonically decreased in amplitude with increased annealing time. This suggests that solvent-annealing caused a discrete conversion of amorphous to crystalline phases (including either Form-II brickwork or 2D-brickwork), rather than a gradual increase of intermolecular coupling within the amorphous phase.

(2) The intermolecular interactions within the amorphous phase do not change; rather, the volume of the amorphous domains gradually decreases in size. This would cause the local triplet concentration within amorphous phase to increase upon annealing. Since triplet-triplet annihilation is a bimolecular process that depends on the initial triplet concentration, the rate

constant should therefore increase as the domain size decreases. This phenomenon has been observed for triplet-triplet annihilation in micellar solutions, in which molecules were trapped inside micelles of varying size.³⁴ Photoexcitation led to the formation of triplet states, which underwent annihilation within the micelles. As the size of the micelles was decreased, triplet-triplet annihilation was found to increase in rate.

4.5. Determination of Triplet Diffusion Lengths of Polycrystalline Films of TIPS-Pn using the Exciton Annihilation Method

Triplet-triplet annihilation models have often been used in the light emitting diode (LED) literature to determine triplet diffusion lengths in crystalline organic materials.^{7,24,31,32} From the Smoluchowski theory of diffusion-limited reactions, the bimolecular decay constant, k_{bi} , can be related to the triplet diffusion constant, D , of the triplets using:

$$k_{bi} = 8\pi R_C D \quad (\text{eqn. 20})$$

where R_C is the capture radius, which corresponds to the encounter distance at which triplet-triplet annihilation has unit probability.³⁵ The diffusion constant is related to the triplet diffusion length L_D using:

$$L_D = \sqrt{\tau D} \quad (\text{eqn. 21})$$

where τ is the natural (unimolecular) triplet lifetime, determined by the intersystem crossing relaxation time from $T_1 \rightarrow S_0$. Using this procedure for calculating diffusion length is known as the “exciton-exciton annihilation method”.²⁴ Because the bimolecular decay constants are proportional to the diffusion constants, the data in **Figure 4-9** suggest that triplet diffusion could be described by a single effective diffusion constant, reflecting the weighted average of the polycrystalline TIPS-Pn films.

The exciton-exciton annihilation method^{7,31,32} was adopted to estimate the triplet diffusion lengths as determined using their annihilation kinetics to confirm that triplet diffusion occurs over many tens of nanometers in polycrystalline TIPS-Pn films. From eqn. 20 and eqn. 21, the natural triplet lifetime and a triplet capture radius are required in order to calculate the diffusion length. The natural triplet lifetime in TIPS-Pn films was determined by using transient absorption kinetics measurements. At the lowest excitation densities for which bimolecular decay is suppressed, the triplet decay was found to be well-described as a first order decay process, indicative of intersystem crossing. Fitting the exponential decay of the triplets in an amorphous film led to a natural lifetime of $2.1 \pm 0.3 \mu\text{s}$. For crystalline films, it was not experimentally practical to lower the excitation energy density enough to observe a first order decay, indicating that annihilation occurs even at relatively low triplet concentrations. However, it was safely assumed that the natural lifetimes would be invariant across all films tested based on the energy gap law in the following argument: The lifetime of T_1 depends on the coupling between the T_1 and S_0 states, which can be gauged using the change in their energy gap. The change in energy gap between the amorphous and fully-annealed films was approximated to be $\sim 0.01 \text{ eV}$, based on the following observations: In another singlet fission molecule, 1,6-diphenyl-1,3,5-hexatriene, the triplet energies shift only modestly compared to shifts in the S_0 - S_1 transition.³⁶ In particular, from solution to crystal, a 2000 cm^{-1} change in the S_0 - S_1 transition energy corresponded to a shift in the S_0 - T_1 gap of only $\sim 200 \text{ cm}^{-1}$. Assuming the same trend for TIPS-Pn, and assuming a S_0 - T_1 energy gap in TIPS-Pn solutions of $\sim 0.77 \text{ eV}$,¹⁵ the change in the S_0 - T_1 energy gap for films (amorphous vs. crystalline) would be at most $\sim 0.01 \text{ eV}$. Therefore according to the energy gap law, it is assumed that the change in natural triplet lifetime in TIPS-Pn films would be negligible.

Next, the triplet capture radius needed to be determined. Because a measurement of the triplet capture radius for TIPS-Pn films was not available, a range of possible values were considered to estimate the triplet diffusion lengths. **Figure 4-12** provides the correlation between the estimated triplet diffusion lengths and the mole fraction of the amorphous phase ($1 - \Phi$), where Φ was defined earlier as the mole fraction of the ordered phases.

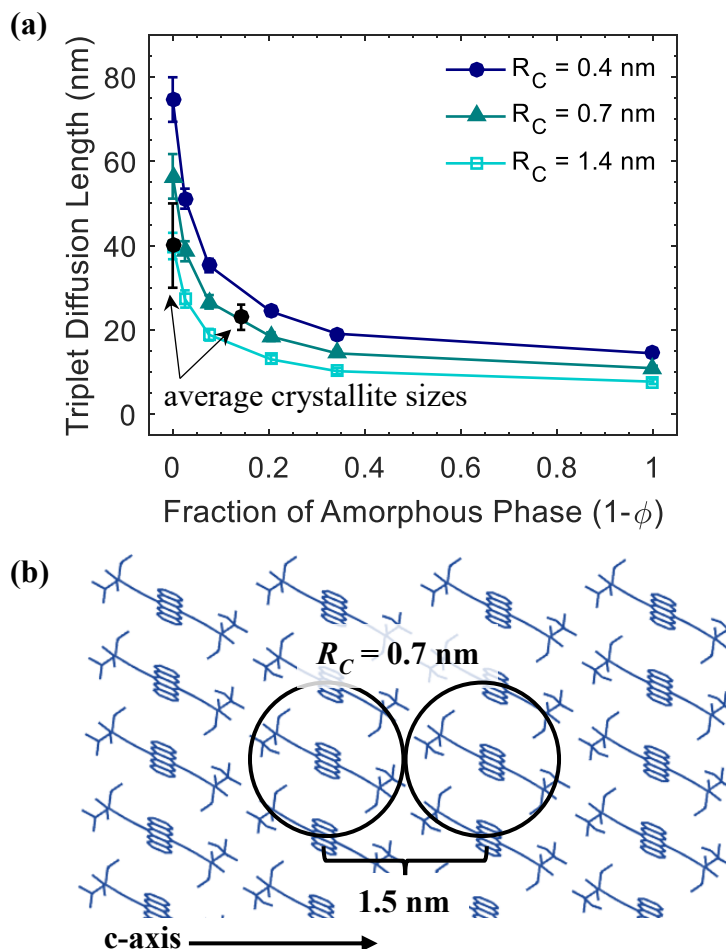


Figure 4-12: (a) Relationship between triplet diffusion length and mole fraction of amorphous phase in TIPS-Pn films, for various triplet capture radii. Average crystallite sizes are shown as black data points, which were determined from 2D-XRD measurements. (b) Illustration of the intermolecular distance along the crystallographic c-direction of the 2D-brickwork packing structure corresponding to a triplet capture radius of 0.7 nm.

Diffusion lengths were determined using three possible values of R_C : 0.4 nm, 0.7 nm and 1.4 nm. The two smaller values were proposed based on the distances between neighboring TIPS-

Pn molecules within the 2D-brickwork packing motif. Notably, the value of $R_C = 0.4$ nm is similar to the 0.41 nm spin confinement length recently reported in TIPS-Pn films using both microwave susceptibility and light-induced electron spin resonance measurements.³⁷ In addition, this radius is close to the pi-pi stacking distance of any two molecules in the 2D-brickwork packing structure.^{18,38-40} Using the capture radius value of 0.4, the triplet diffusion lengths for the TIPS-Pn films varied from ~14 to ~75 nm, as shown in **Figure 4-12**. This corresponded to a range of diffusion constants from $(1.00 \pm 0.03) \times 10^{-6}$ cm²/s to $(2.7 \pm 0.2) \times 10^{-5}$ cm²/s. Tables providing the triplet diffusion constants and diffusion lengths calculated for all samples and for all considered capture radii are provided in **Tables 4-5, 4-6, 4-7, and 4-8**.

Table 4-5: Triplet diffusion coefficients and lengths for TIPS-Pn films for $R_C = 0.4$ nm.

Sample	D (cm ² /s)	L _D (nm)
Amorphous (as-cast)	$(1.00 \pm 0.03) \times 10^{-6}$	14 ± 1
0.43 mole frac. 2D-brickwork	$(1.75 \pm 0.05) \times 10^{-6}$	19 ± 1
0.58 mole frac. 2D-brickwork	$(2.85 \pm 0.9) \times 10^{-6}$	24 ± 1
0.70 mole frac. 2D-brickwork	$(6.00 \pm 0.20) \times 10^{-6}$	35 ± 2
0.82 mole frac. 2D-brickwork	$(1.25 \pm 0.06) \times 10^{-5}$	51 ± 2
1.00 mole frac. 2D-brickwork (Form-I)	$(2.70 \pm 0.20) \times 10^{-5}$	75 ± 5
Form-II brickwork (thermally-annealed)	$(1.00 \pm 0.50) \times 10^{-5}$	40 ± 10

D is triplet diffusion coefficient and L_D is triplet diffusion length

Table 4-6: Triplet diffusion coefficients and lengths for TIPS-Pn films for $R_C = 0.7$ nm.

Sample	D (cm ² /s)	L _D (nm)
Amorphous (as-cast)	$(5.72 \pm 0.09) \times 10^{-7}$	11 ± 1
0.43 mole frac. 2D-brickwork	$(1.00 \pm 0.02) \times 10^{-6}$	14 ± 1
0.58 mole frac. 2D-brickwork	$(1.63 \pm 0.04) \times 10^{-6}$	18 ± 1
0.70 mole frac. 2D-brickwork	$(3.40 \pm 0.10) \times 10^{-6}$	27 ± 2
0.82 mole frac. 2D-brickwork	$(7.20 \pm 0.30) \times 10^{-6}$	39 ± 2
1.00 mole frac. 2D-brickwork (Form-I)	$(1.50 \pm 0.10) \times 10^{-5}$	56 ± 5
Form-II brickwork (thermally-annealed)	$(5.00 \pm 3.00) \times 10^{-6}$	34 ± 9

D is triplet diffusion coefficient and L_D is triplet diffusion length

Table 4-7: Triplet diffusion coefficients and lengths for TIPS-Pn films for $R_C = 1.4$ nm.

Sample	D (cm ² /s)	L _D (nm)
Amorphous (as-cast)	$(2.86 \pm 0.02) \times 10^{-7}$	7.7 ± 0.6
0.43 mole frac. 2D-brickwork	$(5.00 \pm 0.06) \times 10^{-7}$	10.2 ± 0.7
0.58 mole frac. 2D-brickwork	$(8.10 \pm 0.20) \times 10^{-7}$	13.0 ± 0.9
0.70 mole frac. 2D-brickwork	$(1.71 \pm 0.05) \times 10^{-6}$	18.9 ± 1.4
0.82 mole frac. 2D-brickwork	$(3.60 \pm 0.10) \times 10^{-6}$	27.0 ± 2.0
1.00 mole frac. 2D-brickwork (Form-I)	$(7.60 \pm 0.50) \times 10^{-6}$	39.9 ± 3.2
Form-II brickwork (thermally-annealed)	$(3.00 \pm 1.00) \times 10^{-6}$	24.0 ± 6.0

D is triplet diffusion coefficient and L_D is triplet diffusion length

Table 4-8: Triplet diffusion coefficients and lengths for TIPS-Pn films for $R_C = 3.0$ nm.

Sample	D (cm ² /s)	L _D (nm)
Amorphous (as-cast)	$(1.33 \pm 0.01) \times 10^{-7}$	5.3 ± 0.4
0.43 mole frac. 2D-brickwork	$(2.33 \pm 0.02) \times 10^{-7}$	7.0 ± 0.5
0.58 mole frac. 2D-brickwork	$(3.79 \pm 0.07) \times 10^{-7}$	8.9 ± 0.6
0.70 mole frac. 2D-brickwork	$(8.00 \pm 0.20) \times 10^{-7}$	12.9 ± 0.9
0.82 mole frac. 2D-brickwork	$(1.67 \pm 0.07) \times 10^{-6}$	18.7 ± 1.0
1.00 mole frac. 2D-brickwork (Form-I)	$(3.60 \pm 0.20) \times 10^{-6}$	27.3 ± 2.0
Form-II brickwork (thermally-annealed)	$(1.30 \pm 0.70) \times 10^{-6}$	16 ± 4.0

D is triplet diffusion coefficient and L_D is triplet diffusion length

A capture radius of $R_C = 0.7$ nm was also considered because this distance was approximately half of the core-to-core spacing among the pentacene rings of the TIPS-Pn molecules along the crystallographic c-vector (the direction separated by the TIPS side groups). Adoption this capture radius implies that two triplets residing on neighboring molecules along this axis would have unit probability to annihilate, despite the presence of electronically insulating side groups. Along the other two crystallographic directions, this distance implies that triplets on next-nearest neighbors having unit probability to annihilate. For this value of R_C , the range of triplet diffusion lengths varied from ~ 11 nm to ~ 56 nm.

The precise molecular packing structure of the TIPS-Pn molecules, which vary during solvent annealing, may actually control the triplet capture radius. For example, the Form-II and 2D-brickwork packing structures have been shown to have $\sim 5\%$ difference in their average pi-pi stacking distance.³⁸ Additionally, amorphous films consisting of disordered molecules may be less dense, having even larger average intermolecular separations. Assuming the film density does not significantly change from amorphous to crystalline films, the largest intermolecular spacing for disordered molecules would roughly be the length of two TIPS side groups. This approximately corresponds to the crystallographic c-vector, giving a radius of ~ 0.7 nm. Thus it is considered that the range of capture radii considered to this point ($R_C = 0.4$ nm to $R_C = 0.7$ nm) encompass any potential variations of intermolecular distances that may occur in the set of films studied.

Finally, the capture radius that would be needed to predict triplet exciton diffusion lengths that matched the average crystallite sizes were considered. See Chapter 3 for crystallite size determination. This calculation was motivated by the argument that triplets may be confined within the crystallites in which they were generated. The average crystallite sizes of two of

the crystalline films are included in the plot in **Figure 4-12**. It was necessary to use a value of 1.4 nm for the triplet capture radius in order for the calculated triplet diffusion lengths to match the average crystallite sizes. Similar sizes of triplet capture radii have been reported in organic molecules like rubrene⁴¹ that undergo delayed fluorescence, or phosphorescent organic LED materials containing heavy atoms like iridium.³¹ In rubrene (and tetracene)^{42,43}, delayed fluorescence is observed since reformation of S_1 upon triplet-triplet annihilation (or “fusion”) is exergonic. In fact, in tetracene crystals, dynamic conversion between triplet and singlet states has been observed^{36,44} on long time scales, giving rise to enhanced triplet diffusion distances. Additionally, large triplet capture radii have been observed in molecules like rubrene since triplet-triplet annihilation may involve Forster-type triplet interactions.⁴⁵ A larger triplet capture radius would be supported in such systems due to the long-range nature of Forster energy transfer.

In the following discussion, it will be argued why $R_C = 1.4$ nm is unreasonable for TIPS-Pn triplets. In functionalized pentacenes, singlet fission is exergonic,¹⁴ which implies that reformation of singlet excitons from triplet fusion is endergonic. It is therefore more likely that triplets annihilate in TIPS-Pn by forming a highly excited T_n state⁴⁶ as shown in eqn. 4. However, in this case, triplet states are unable to possess Forster interactions because the relaxation of one triplet to the singlet ground state involves a spin-forbidden de-excitation event.³⁰ Delayed fluorescence due S_1 reformation from triplet fusion has not been observed in TIPS-Pn, consistent with the mechanism proposed in eqn. 4. This implies that the triplet capture radius in TIPS-Pn is expected to be much smaller than 1.4 nm, consistent with a Dexter-type interaction. Such a smaller distance would also be consistent with the spin-confinement length of 0.41 nm recently reported for TIPS-Pn, which indicates that the triplet-triplet

interactions are highly localized. These considerations led us to conclude that triplets in the TIPS-Pn films have diffusion lengths ranging from ~14 nm to ~75 nm, as estimated using an R_C value of 0.4 nm.

The estimated ~75 nm triplet diffusion length in the fully solvent-annealed (2D-brickwork) TIPS-Pn film was significantly larger than the ~40 nm average crystallite size (see Chapter 3). This observation suggested that grain boundaries between crystallites do not necessarily impede triplet diffusion, which is consistent with recent reports of ultrafast microscopy measurements that found grain boundaries to not be molecularly sharp.^{18,29,47} The authors of those works showed that the crystalline grain boundaries actually consist of small nanocrystalline domains of molecules. These interfaces may provide enough electronic wavefunction overlap for triplets to transfer between grain boundaries, which is consistent with the triplet-triplet annihilation behavior reported in this work.

The measurement of triplet diffusion constants in the amorphous and crystalline films can be used to consider how triplets may be partitioned as they undergo dynamic exchange between amorphous and crystalline phases. Assuming equal populations of triplet excitons generated near the phase boundaries, and using the diffusion coefficients, Fick's law would predict that the initial flux of triplets diffusing into the amorphous phase from the crystalline phase would be ~27 times higher than from crystalline to amorphous. Under solar irradiation conditions, annihilation of triplet excitons is a negligible decay pathway⁷, and so the lifetime of triplets in the amorphous phase would not be limited by concentration-dependent bimolecular decay. As such, a positive net transfer of triplets from the crystalline to the amorphous phases would result until the concentration of triplets in the amorphous phases is high enough to balance the flux in the opposing direction. If the probability of triplet transfer across an inter-phase

boundary is assumed to be unity, then ~97% of the initial triplet population would end up in the amorphous phase over time.

A tendency for net transfer of triplets into amorphous phase explains why the presence of even a minute amount of amorphous (“impurity”) material has a significant detrimental impact on the ultimate triplet diffusion length. This result has significant implications for the design of new singlet fission sensitizers,⁴⁸ especially polymeric systems.⁴⁹⁻⁵² For example, even highly ordered polymers (e.g. polyethylene) can contain significant fractions of an amorphous phase.⁵³ The work in this chapter leads to design rules for systems in which the formation of amorphous phase is inevitable: (1) Singlet fission should occur only in the crystalline phase; (2) Triplet transfer from crystalline to amorphous domains should be energetically unfavorable.

As evident from absorption spectroscopy (see Chapter 3), TIPS-Pn exhibits some degree of energetic change of the S_1 state upon crystallization. However, because triplet excitons are more localized than singlet excitons, the change in T_1 energy between the amorphous and crystalline phase is not high enough to prevent triplets from transferring between phases. In fact, the estimated change in $S_0 \rightarrow T_1$ energy gap from amorphous to crystalline film was ~0.01 eV. This implies that in polymeric materials, it may be necessary to search for singlet fission sensitizers that undergo significant changes of their electronic energy levels upon crystallization,²⁹ such as poly(3-hexylthiophene).⁵⁴ In these cases, large differences in energy level mismatch between the crystalline and amorphous phases may be important for confining triplets to crystalline domains. Maintaining high triplet diffusivity would then be possible despite the presence of amorphous domains.

4.6. Conclusions and Significance

By controlling the crystallization of TIPS-Pn, the rates of singlet fission and triplet-triplet annihilation were related to molecular packing arrangements using a transient absorption spectroscopy. The triplet-triplet annihilation rate constants varied by over an order of magnitude, spanning a range of morphologies from amorphous to crystalline. Films falling within this range were composed of mixtures comprising both amorphous and crystalline phases. The triplet-triplet annihilation kinetics were well-described by single bimolecular rate constants even in films consisting of mixtures of amorphous and crystalline phases. Furthermore, triplets were found to transfer across phase boundaries between the amorphous and crystalline phases during their lifetime. Using the exciton-exciton annihilation method for determining diffusion length, the triplet diffusion lengths were determined to vary from ~14 to ~75 nm depending amorphous phase content in the films.

Overall, the results of this work suggest that controlling intermolecular packing of singlet fission molecules is important for maximizing triplet diffusion lengths, which can be significantly reduced by the presence of small amounts of amorphous material. This finding implied that new semi-crystalline singlet fission materials, in which the formation of amorphous phases is inevitable, should possess large energy level differences between amorphous and crystalline phases. This may create a barrier to triplet transfer from crystalline to amorphous phases, confining triplets to highly-diffusive, ordered regions of the films.

4.7. References

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CHAPTER 5

Long-Lived Singlet Fission Intermediates Discovered Using Mid-Infrared Spectroscopy

Typically, spectroscopists have applied visible and near-infrared pump-probe transient absorption techniques for monitoring the singlet fission reaction by tracking the growth in absorption of the “product” triplet states over time. Using these measurements, assessments of singlet fission chromophores have been made, often leading to the conclusions of sub-picosecond reaction rates and 200% quantum yield of triplets. However, it was recently proposed that spectroscopic distinction between the intermediate correlated triplet pair states and the product independent triplet excitons is very challenging. As such, the formation of the intermediate species of the singlet fission reaction is often misinterpreted as the product species, leading to incorrect conclusions about the reaction mechanism and the ultimate triplet yields. This chapter presents a new spectroscopic approach to measuring intermediate states during the singlet fission reaction in a model pentacene derivative compound.

Using ultrafast visible-pump mid-infrared-probe transient absorption spectroscopy, new absorption bands associated with the singlets reactants and the correlated triplet pair intermediates were discovered. With a method for directly probing intermediate states of the singlet fission, it was realized that the reaction takes orders-of-magnitude longer to complete than previously believed in a model singlet fission compound. In particular, it was found that the intermediate species actually persist on a tens to hundreds of picoseconds timescale. This observation implies that any kinetically competing excited state pathway (e.g. excimer formation) would decrease the ultimate yield of triplets and must be suppressed in order to optimize the efficacy of singlet fission sensitizers in practical applications.

This chapter was adapted from the work: Grieco, C., Kennehan, E.R., Pensack, R.D., Brigeman, A.N., Rimshaw, A., Payne, M.M., Scholes, G.D., Anthony, J.E., Giebink, N.C., and Asbury, J.B., “Direct Observation of Correlated Triplet Pair Dynamics during Singlet Fission using Ultrafast Mid-IR Spectroscopy”, *submitted*, which has been rephrased in the context of this dissertation.

5.1. Introduction

Singlet exciton fission is an excited state multiplication process in which a singlet exciton converts into two independent triplet excitons with triplet quantum yields thought to approach 200%.¹⁻⁴ The reaction has been demonstrated in a few organic molecules and polymers,⁵⁻¹² which may potentially serve as sensitizers for solar cells by eliminating thermalization losses associated with absorption of high energy solar emission.^{13,14} Proof-of-principle studies have already demonstrated solar cell external quantum efficiencies exceeding 100%,¹⁴⁻¹⁷ however, enhancements in power conversion efficiency have been very limited. The role and dynamics of intermediate states in the singlet fission reaction remain ambiguous, which potentially impede their successful application because they may decrease the overall yield of triplet excitons. Thus, in order to ensure the multiplication and harvestability of the triplet excitons, it is necessary to determine the nature of the reaction intermediates.

Singlet fission is commonly measured using ultrafast pump-probe spectroscopy to monitor the absorption of singlet and triplet excitons over time using their characteristic absorption bands appearing in the visible and near-infrared (near-IR) spectral regions.^{3,18-22} However, the spin-correlated triplet pair (CTP) intermediate states have been challenging to spectroscopically distinguish from independent triplet states since both have similar triplet

electronic character.²³ As a result, the singlet fission reaction is typically tracked by measuring triplet absorption kinetics in the visible and near-IR spectral range.^{21,23,24} It is therefore desired to develop an alternate approach for directly measuring singlet fission intermediates.

In this chapter, it was determined that ultrafast mid-infrared (mid-IR) spectroscopy can be used to directly probe CTP intermediate state dynamics using crystalline films of a model singlet fission chromophore, 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-Pn). New mid-IR electronic transitions were discovered, which were kinetically distinct for both the initially photogenerated singlet excitons and the CTP intermediates. In particular, the mid-IR absorption kinetics were used to monitor the formation and decay of CTP intermediates. It is shown that mid-IR spectroscopy offers an unambiguous method for probing CTP intermediates, avoiding problems associated with overlapping triplet spectral features.

Combining ultrafast mid-IR and visible transient absorption measurements, it was found that the formation of independent triplet excitons via CTP dissociation occurs on the hundreds of picoseconds timescale in crystalline films of TIPS-Pn. This timescale, which marks the completion of the singlet fission reaction, is orders of magnitude longer than previously believed for TIPS-Pn and other pentacene derivatives.^{18,21,24} Furthermore, this finding suggests that excited state deactivation pathways that may kinetically compete with singlet fission, such as excimer formation,²⁵ must be suppressed on timescales far longer than previously expected. Such competing excited state pathways would impede efficient multiplication of triplet excitons, and subsequently limit the ability to harvest triplets even in systems that undergo exergonic singlet fission.

5.2. Experimental

Solution samples were prepared by dissolving TIPS-pentacene in organic solvents, such as carbon tetrachloride (CCl_4) or toluene. Concentrations in the range of 2×10^{-5} M to 2×10^{-4} M were used depending on the spectroscopy measurement performed. Solutions were loaded into a homemade liquid cell having potassium bromide or sapphire optical windows that sandwiched a ~ 1.7 mm thick Viton o-ring. For more dilute solutions, and in spectral regions with high solvent transmittance, spectroscopy measurements were performed using a 1 cm pathlength quartz cuvette.

Films were prepared by spin-casting 20 mg/mL solutions of TIPS-Pn dissolved in dichloromethane (DCM) at ~ 800 rpm onto CaF_2 substrates. The resulting amorphous films were crystallized using solvent vapor annealing for ~ 2.5 hours in an apparatus described previously.²⁶

Some steady-state absorbance spectrometry was performed using a commercially available instrument (Beckman, DU 520; Brea, CA). Other steady-state absorption spectra were measured using a home-built instrument. For this, a stabilized tungsten-halogen lamp (SLS-201, Thorlabs; Newton, NJ) was used as the light source, which was collimated and transmitted through the sample. The transmitted beam was then detected using a CCD spectrometer (USB-2000, Ocean Optics; Dunedin, FL).

FTIR spectroscopy was carried out using a commercially available instrument (Madison Instruments, Mattson Research Series; Middleton, WI). A liquid nitrogen cooled MCT detector was used.

Nanosecond mid-IR transient absorption spectroscopy was performed using a home-built flash photolysis instrument as described previously.^{27,28} For solution measurements, the

visible excitation was 649 nm and the excitation energy density was $\sim 200 \mu\text{J}/\text{cm}^2$. A 100 MHz MCT photodiode detector (Kolmar Technologies, KV104; Newburyport, MA) was used for measuring kinetic decays, which were measured over $\sim 2.5 - 5.6 \mu\text{m}$. For spectral measurements, a 16 MHz MCT photodiode detector (Kolmar Technologies, KMPV11-1-J1; Newburyport, MA) was used, and spectra were collected using a 40 nm effective spectral bandwidth.

Nanosecond visible and near-IR transient absorption spectroscopy was performed using other home-built flash photolysis instruments, similar to those described previously.²⁸ The excitation source was the same one used in the mid-IR transient absorption measurements. A silicon photodiode (DET36A, Thorlabs; Newton, NJ) was used for the visible spectral region. InGaAs photodiode detectors (DET10N and DET05D, Thorlabs; Newton, NJ) were used, having a 5 ns and 17 ns rise time, respectively, for near-IR spectral regions.

Ultrafast visible-pump/mid-IR probe spectroscopy was performed using a home-built system.²⁹ The visible pump was 655 nm, and the mid-IR probe beam was tuned over a $\sim 4.4 - 4.9 \mu\text{m}$ range.

Ultrafast 2-color visible-pump/visible-probe transient absorption spectroscopy was performed using a home-built instrument. For solution samples the excitation wavelength was 642 nm and probe wavelength was $\sim 505 \text{ nm}$. For film samples the excitation wavelength was 655 nm and the probe wavelength was $\sim 520 \text{ nm}$.

For ultrafast time-resolved photoluminescence spectroscopy, a high-speed streak camera with ps time resolution (C10910, Hamamatsu; Bridgewater, NJ) synced to a mode-locked picosecond tunable laser (PL2210A laser and PG403 optical parametric generator, EKSPLA; Bozeman, MT) was used. Laser excitation was tuned to 633 nm and the absorbed energy

density of the films samples was $\sim 92 \mu\text{J}/\text{cm}^2$. Photoluminescence data were collected over the 640 to 1000 nm wavelength range.

Nanosecond time-resolved fluorescence spectroscopy was performed using a homebuilt flash photolysis instrument.³⁰ Specifically, a 30 Hz frequency-doubled (532 nm) Nd:YAG laser (Surelite, Continuum; San Jose, CA) pumped a modified dye laser cavity (GL-302, photon technology international; Edison, NJ), resulting in an output of 642 nm and ~ 10 ns pulse duration. Sample emission was dispersed using a monochromator (DK240, Spectral Products; Putnam, CT) and detected using a 350 MHz silicon photodiode (DET210, Thorlabs; Newton, NJ). A 2.5 nm effective spectral bandwidth was used for all measurements. An excitation energy density of $\sim 200 \mu\text{J}/\text{cm}^2$ was used for all solution samples.

5.3. Mid-Infrared Electronic Transitions in TIPS-Pn

Searching for absorption features of triplet pair intermediates in the mid-IR region was motivated by previous discovery of low-energy absorption transitions associated with molecular pair states, such as excimers.³¹⁻³⁴ In these accounts, long absorption tails extending into the deep near-IR region have been reported. In fact it has been recently uncovered by Mauck et al. that low-energy excimer absorption bands appear for Perylene-3,4:9,10-bis(dicarboximide) derivatives in the wavelength range of $1.2 - 4.0 \mu\text{m}$ ($\sim 1 - 0.31$ eV) depending on the type of aggregate formed.³⁴ In addition to these findings, broad, low-energy absorptions of triplet pair intermediates have been reported in functionalized pentacenes²³ extending from ~ 1 eV and continuing toward the mid-IR region. Another possible low-energy transition corresponds to the dark “multi-exciton” (ME) state that is often reported for singlet

fission in crystalline pentacene.³⁵ Calculations suggest that the energy gap between the relaxed ME state and the parent singlet exciton state in pentacene is ~ 0.18 eV.^{35,36}

Ultrafast mid-IR transient absorption measurements of singlet fission materials have not been previously reported. As such, in the following, mid-IR spectral features are measured and assigned first for solutions and then films.

5.3.1. Solution samples

Concentration-dependent steady-state absorption spectra of TIPS-Pn molecules in CCl_4 were measured (**Figure 5-1**), which show negligible change between concentrations of 2×10^{-5} and 2×10^{-4} M.

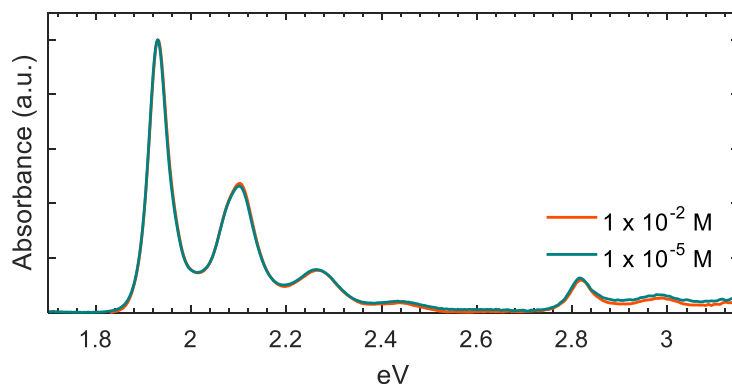


Figure 5-1: Absorption spectra of solutions of TIPS-Pn dissolved in CCl_4 .

This suggests that the molecules do not electronically interact in this concentration range. Additionally, similar concentrations ($\sim 1 \times 10^{-3}$ M and lower) of TIPS-Pn solutions have been shown to not undergo diffusion-limited singlet fission.³ Time-dependent fluorescence spectra were measured for a 2×10^{-4} M solution using 642 nm excitation (**Figure 5-2**).

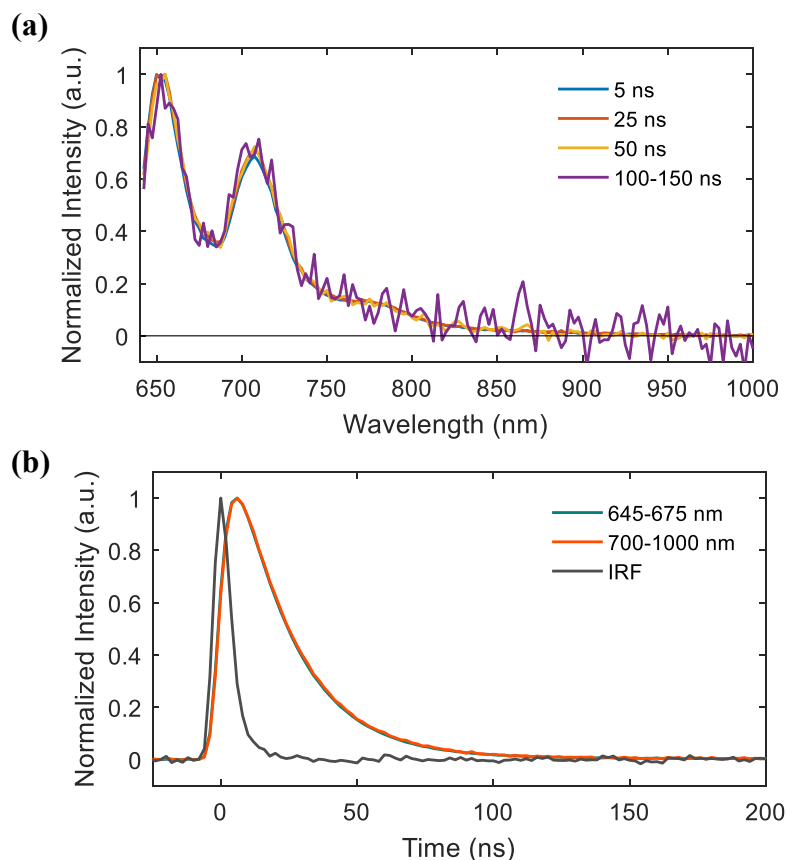


Figure 5-2: (a) Time-resolved photoluminescence spectrum for a 0.2 mM solution of TIPS-Pn in CCl₄. The spectrum is shown for several time ranges. (b) Kinetic decays that were integrated over short and long wavelength ranges. The instrument response function (IRF) is included for reference.

Both the spectral and kinetic data show a lack of excimer emission. Specifically, no broad, longer wavelength emission features were found to grow in over time. Additionally, the kinetic analysis presented in **Figure 5-2** shows that the kinetics at longer wavelengths matches exactly those at shorter wavelengths. Altogether, it can be concluded that TIPS-Pn solutions within this concentration range did not form electronic aggregates or excimers.

Using TIPS-Pn solutions, consisting of electronically isolated molecules, spectral features associated with the first singlet excited state were determined using transient absorption and emission spectroscopy. The transient absorption spectrum in the mid-IR region was measured for a 2×10^{-4} M solution of TIPS-Pn in CCl₄ that was excited at 642 nm with ~ 200 $\mu\text{J}/\text{cm}^2$

excitation energy density (**Figure 5-3**). A mid-IR absorption band featuring vibronic structure was observed, with the first vibronic peak appearing at ~ 0.21 eV. Such vibronic structure is characteristic of the electronic transitions observed in both absorbance and fluorescence spectra.

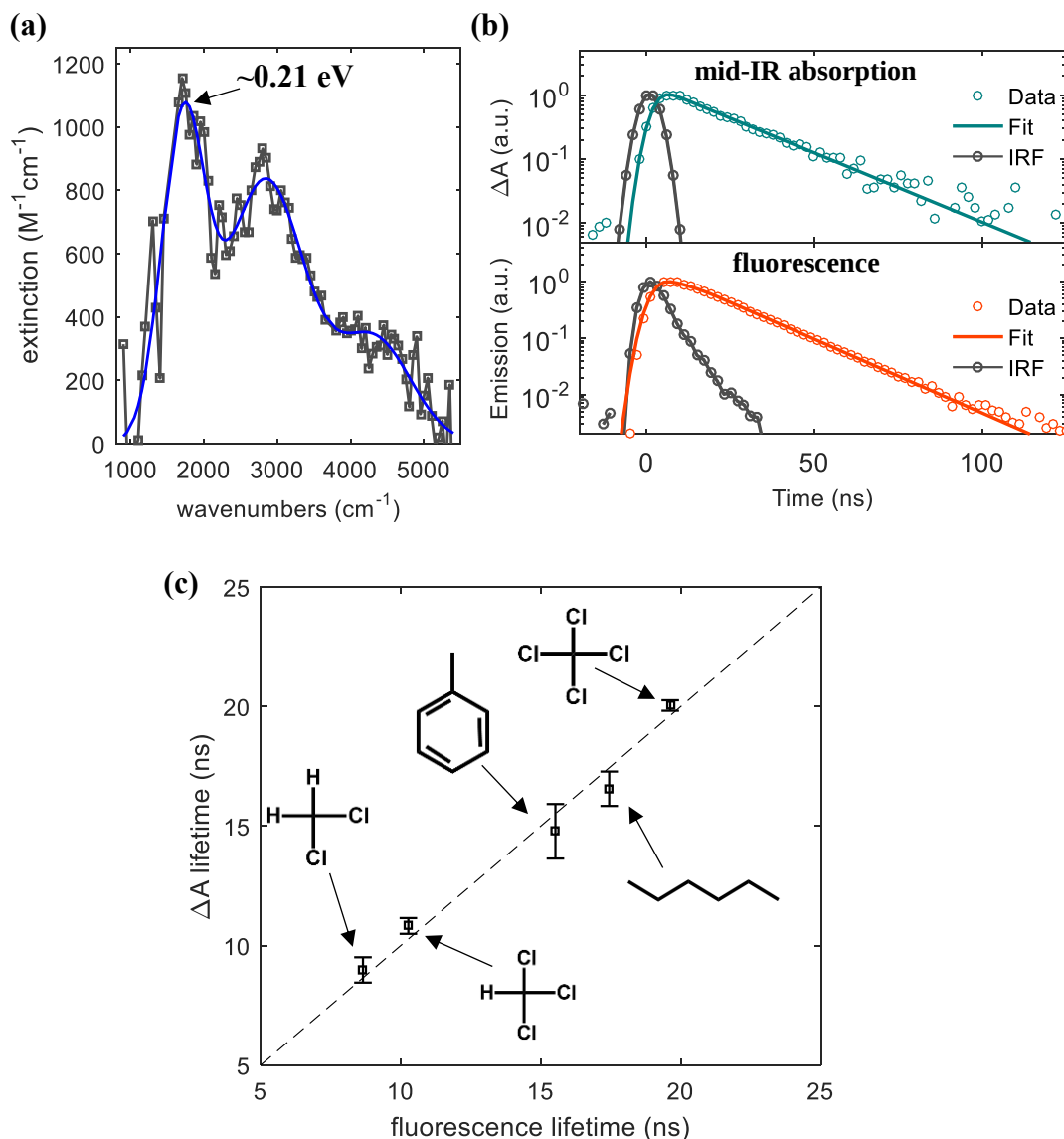


Figure 5-3: (a) Extinction spectrum for the mid-IR absorption of a dilute solution of TIPS-Pn in CCl_4 . The blue line is a fit to the data using an unconstrained 3-Gaussian fit. (b) Normalized time-resolved absorption (top) and fluorescence (bottom) of a TIPS-Pn solution in toluene (0.2 mM). The excitation wavelength was 642 nm and the incident energy density was $\sim 200 \mu\text{J}/\text{cm}^2$. The instrument response functions (IRFs) are included. The solid lines are fits to the data using single exponential decay functions convoluted with the appropriate IRFs. (c) Correlation between the lifetimes determined for the mid-IR absorption and fluorescence decays. The dashed line represented a 1:1 relationship. Error bars reflect the standard errors of the fits to the data.

The mid-IR transition was determined to originate from first excited singlet states of TIPS-Pn by comparing its decay form with fluorescence decay (**Figure 5-3**). The fluorescence decay

represented the relaxation of the first excited singlet states of TIPS-Pn solutions. Because the mid-IR transient absorption decay quantitatively matched that of fluorescence, it was also assigned to singlet excited states. For completeness, such comparisons were also made using other solvents (**Figure 5-4**) with varying solvent polarity functions to verify this assignment.

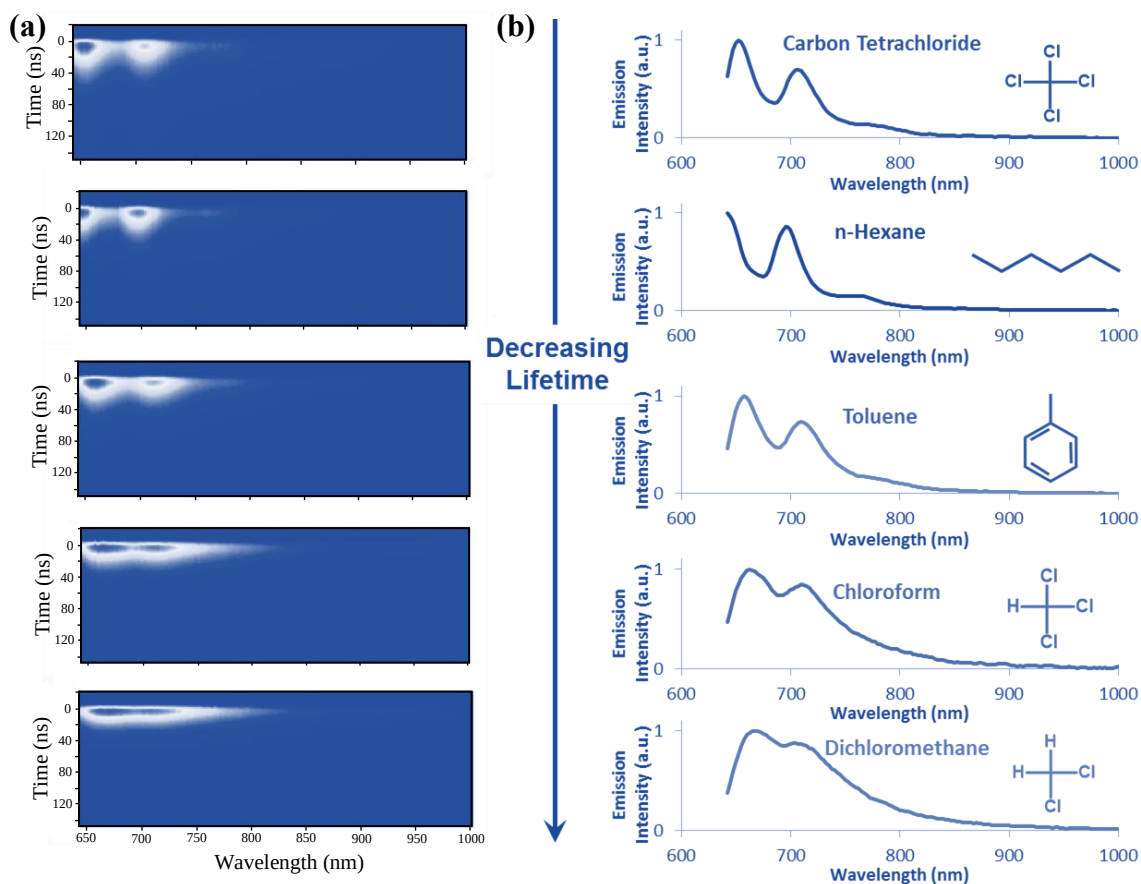


Figure 5-4: Time-resolved fluorescence spectra measured for 0.2 mM solutions of TIPS-Pn dissolved in a variety of solvents displayed as (a) time-wavelength plots and (b) time-integrated spectra.

The kinetic decays of the fluorescence and mid-IR absorption were measured for 0.2 mM solutions in solvents with a variety of polarities. The instrument response was measured for both measurement techniques, and were used to fit each set of data in order to obtain accurate decay time constants. For the fits, the model, $M(t)$, was:

$$M(t) = F(t) * IRF(t) \quad (\text{eqn. 1})$$

$$F(t) = N * e^{-kt} \quad (\text{eqn. 2})$$

where t is time, $F(t)$ is an exponential function describing the singlet excited state population, $IRF(t)$ is the instrument response function, k is the first order (unimolecular) decay rate constant for the singlet excited state population, and N is a scaling factor. All of the fit results are shown in **Figure 5-5** for both fluorescence and mid-IR absorption decays.

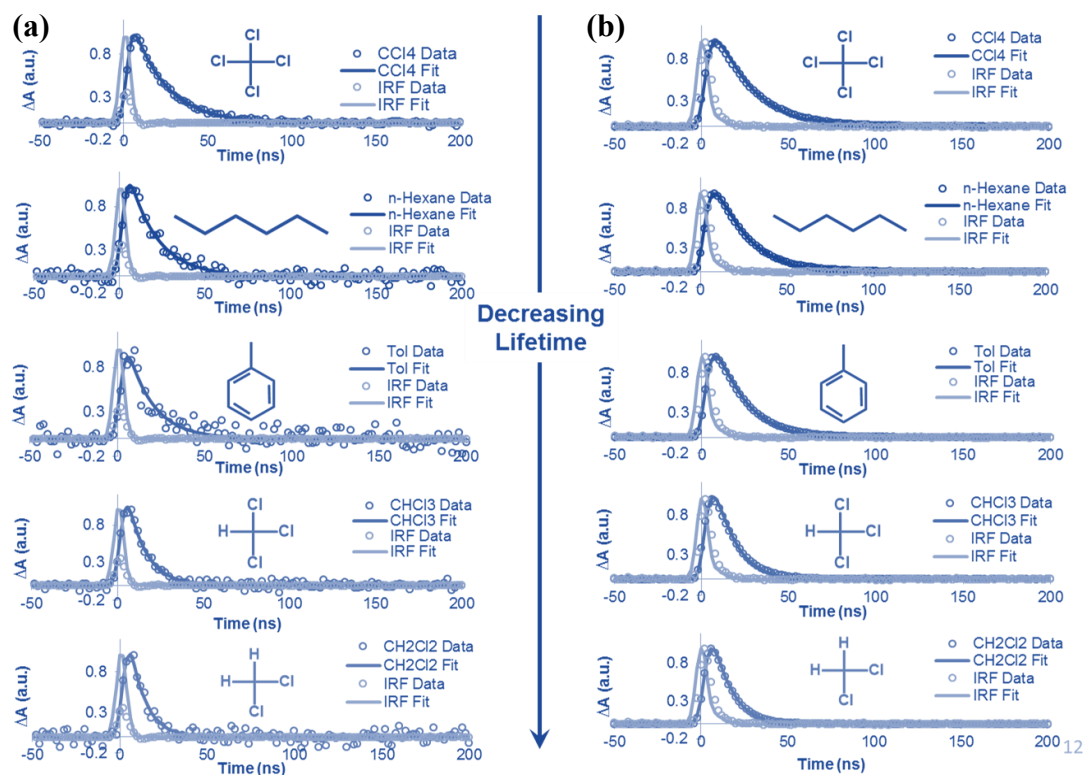
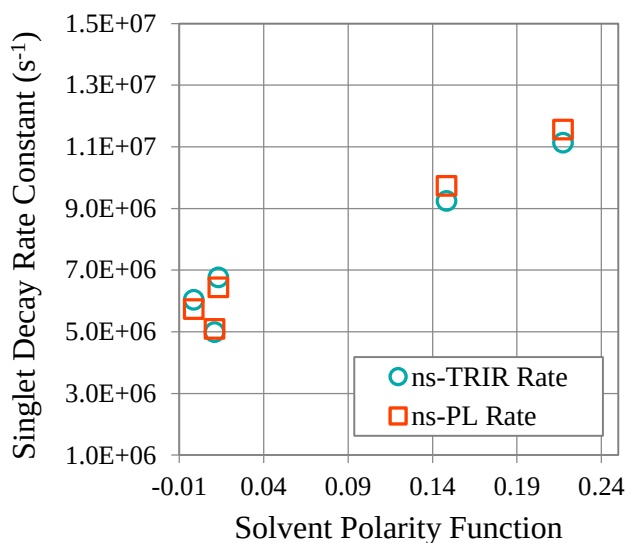


Figure 5-5: Decay kinetics for the first excited singlet state of 0.2 mM TIPS-Pn solutions measured using time-resolved (a) mid-IR absorption and (b) fluorescence spectroscopy. Data are plotted as circles and the fits are displayed as solid lines. All fits were generated by convoluting a single exponential decay function with the appropriate instrument response function (IRF). The solvents used for the solutions are indicated in the plots.

The lifetimes determined from the fits are shown in **Figure 5-3**, which demonstrate a 1:1 correlation between fluorescence and mid-IR absorption decay time constants for all solvents investigated. This confirmed that the mid-IR transition originates from the first singlet excited

states of non-interacting TIPS-Pn molecules. For reference, the singlet decay rate constants were related to the solvent polarity function³⁷ in **Figure 5-6**.



$$\Delta f = \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right)$$

Figure 5-6: Decay time constants for the first excited singlet population measured in 0.2 mM solutions of TIPS-Pn using either time-resolved photoluminescence (ns-PL) or time-resolved mid-IR absorption (ns-TRIR) spectroscopy. The equation is the solvent polarity function.

Next, the molar extinction coefficient of the mid-IR excited singlet transition was experimentally determined by measuring the transient absorption for a variety of TIPS-Pn solution concentrations (**Figure 5-7**). The absorption intensity was taken as the average signal over the first 25 ps, before the singlet population is able to start decaying. In this way, these intensities correspond to the initial absorption of the excited singlet state population immediately generated upon photoexcitation. The initial singlet excited state concentration was calculated as described in Chapter 3. Using Beer's law, a plot of the transient absorption signal, ΔA , relative to the appropriate pathlength, b , against excited singlet state concentration resulted in a linear relationship. The resulting slope is equal to the molar extinction coefficient (see **Figure 5-7**), which was found to be $\sim 6.6 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$ at $\sim 0.27 \text{ eV}$ ($\sim 2177 \text{ cm}^{-1}$).

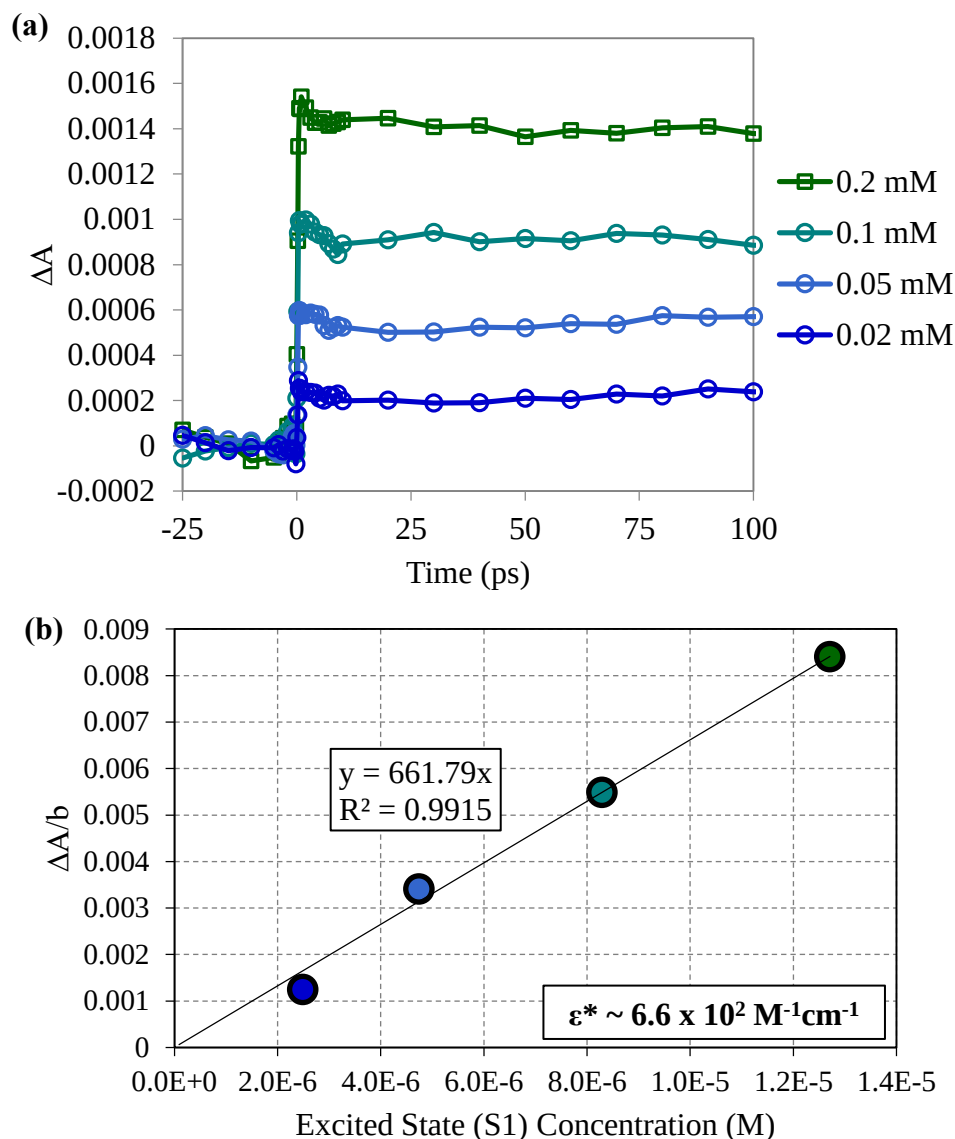


Figure 5-7: (a) Mid-IR transient absorption kinetics measured at ~ 0.27 eV for various concentrations of solutions of TIPS-Pn dissolved in CCl_4 . (b) Determination of the molar absorption coefficient of the mid-IR signal at ~ 0.27 eV ($\sim 2177 \text{ cm}^{-1}$).

In order to deduce the final state of the mid-IR absorption transition, other optically bright states having transitions present in the visible, near-IR and mid-IR spectral ranges were experimentally determined using either steady-state or time-resolved absorption spectroscopy. The results of this investigation are summarized in Chapter 3 as an energy level diagram. Because the energy level diagram corresponded to electronically isolated TIPS-Pn molecules

in dilute solution, the mid-IR transition could not involve multiple chromophores. Consequently, the final state of the mid-IR absorption transition was first considered to be a close-lying singlet or triplet state.

With a moderate oscillator strength of $\sim 6.6 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$, the most probable final state of the mid-IR absorption transition is a singlet excited state that is $\sim 0.2 \text{ eV}$ higher in energy than the S_1 state. The perimeter-free electronic orbital (PFEO) model applied to pentacene does not predict states falling between the S_1 (1L_a) and S_2 (1L_b). However, it was considered that the alkynyl substituents in TIPS-Pn might contribute additional singlet states to its electronic manifold. To determine whether additional singlet states are present for TIPS-Pn, density functional theory (DFT) computations were performed to determine the first few singlet excitation energies. The geometry of the TIPS-Pn molecule was first optimized using the B3LYP functional, after which excitation energies were calculated using time-dependent DFT (TD-DFT) with either the B3LYP or the long-range corrected (LCR) wPBE functional (LCR-wPBE). All calculations employed the cc-PVTZ basis set³⁸ and the polarized continuum model (PCM) for carbon tetrachloride as the solvent. This DFT strategy was adapted from previous studies on pentacene reported by Richard and Herbert, who investigated why certain functionals are better at predicting specific singlet excitation energies based on the quantum mechanical nature of the excited states.³⁹ The results the calculations for TIPS-Pn are summarized in **Table 5-1**. Bolded values correspond to the excitation energies predicted using functionals that are known to accurately describe the corresponding states in pentacene.^{39,40} In all cases, the calculated singlet excitation energies did not indicate that singlet states fall in-between 1L_a and 1L_b , suggesting that the mid-IR absorption transition of TIPS-Pn was not $S_1 \rightarrow S_n$.

Table 5-1: Calculated and experimental $S_1 \rightarrow S_n$ excitation energies of TIPS-Pn in eV

Final State	Experimental	LC-wPBE	B3LYP
S_4	-	4.1165	3.1119
$S_3 (^1B_b)$	3.54	3.5351	3.0636
$S_2 (^1L_b)$	2.82	3.3591	2.6617
$S_1 (^1L_a)$	1.93	2.0466	1.6077

It was improbable that the mid-IR absorption corresponds to $S_1 \rightarrow T_n$ since such a transition is typically extremely forbidden in organic molecules. However, as seen in Chapter 3, the energy gap between the $S_1 (^1L_a)$ and $T_n (^3A)$ states was ~ 0.1 eV, which is close to the value for the measured transition energy (~ 0.21 eV). Additionally, the spin-orbit coupling in TIPS-Pn may be enhanced due to the presence of heavy Si atoms and alkynyl groups (containing orthogonal orbitals) in the TIPS side groups.

Last, the mid-IR transition was considered to possibly involve an intramolecular CT state³⁹ or intramolecular multi-exciton states.³⁵ Previous computational work by Richard and Herbert suggested that the 1L_a (S_1) state of pentacene contains charge-separated (diradical) character.³⁹ Thus it is possible that the S_1 state mixes with another excited state having charge-transfer character. On the other hand, computational studies by Zimmerman et al. suggested that the S_1 states in pentacene dimers relax rapidly into dark multi-exciton, D, states that have an energy ~ 0.2 eV lower than the S_1 state energy.³⁵

Closer analysis of the absorption spectrum of a dilute solution of TIPS-Pn dissolved in octane (**Figure 5-8**) reveals odd splitting in its vibronic structure that is not typically associated with isolated molecules. The vibronic progression of TIPS-Pn contains a spacing of ~ 1427 cm^{-1} , which corresponds to C=C ring deformations. This implies that the electronic transition is strongly coupled to the pentacene ring deformations. However, there is an additional

splitting of the vibronic peaks present in the absorbance spectrum. Such splitting have often been observed in molecular solids, such as perylenes,^{41,42} and are generally described as charge-transfer (CT) excitations resulting from intermolecular electronic interactions. Based on this observation, it is hypothesized that CT absorptions may occur in the monomer of TIPS-Pn, implying that the first excited singlet state has CT character (possibly via excited state mixing effects). An alternative hypothesis is that TIPS-Pn contains two nearly-degenerate HOMOs with an energy gap comparable to thermal energy at room temperature (0-0 “splitting” seen in **Figure 5-8** was 34 meV). From this viewpoint, TIPS-Pn in the ground state may possibly possess diradical character. Last, it should be noted that the splitting may merely be a result of another low frequency vibrational mode that may significantly couple to the electronic transition.

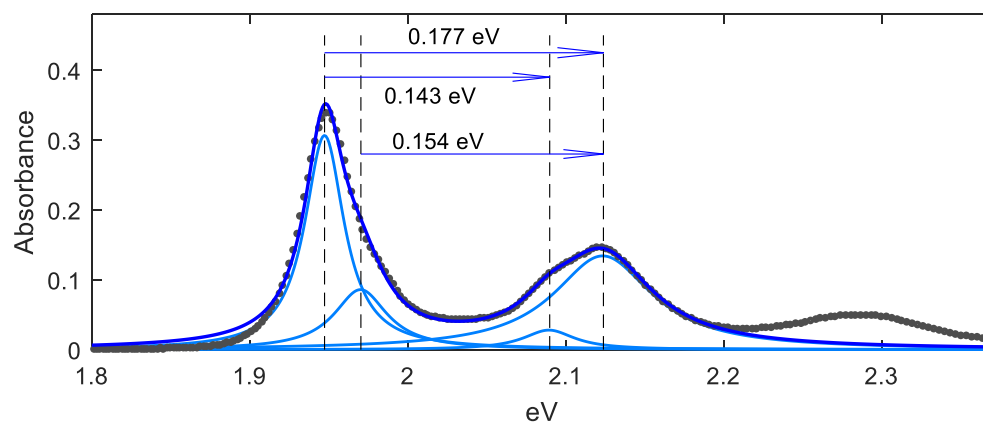


Figure 5-8: Steady-state absorption spectrum of a 0.02 mM solution of TIPS-Pn dissolved in octane. Data are shown as gray circles and the total fit is shown as a dark blue line. The first two vibronic peaks were fit using Lorentzian functions (light blue lines) to illustrate the peak splitting.

Ultimately, regardless of the identity of the final state of the mid-IR absorption transition, it is clear that the absorption corresponds to the first excited state of TIPS-Pn. In the following, the mid-IR absorption kinetics measured for crystalline films of TIPS-Pn will be investigated during singlet fission.

5.3.2. *Film samples*

Having assigned the mid-IR absorption band to the S_1 state in TIPS-Pn, the transition was next used to study the singlet fission reaction in a crystalline film. A 2-dimensional wavenumber-time plot of the ultrafast mid-IR transient absorption spectrum of a crystalline TIPS-Pn film excited using 655 nm with a $\sim 65 \mu\text{J}/\text{cm}^2$ absorbed energy density is shown in **Figure 5-9**. Similar to the solution measurements, an electronic transition was observed immediately upon photoexcitation. A vibrational feature, arising from the depletion of the ground state population of TIPS-Pn molecules (ground state bleach, GSB), was also observed. This vibrational feature is investigated in detail in Chapter 6. The remainder of the work presented in this chapter focuses on the electronic transition.

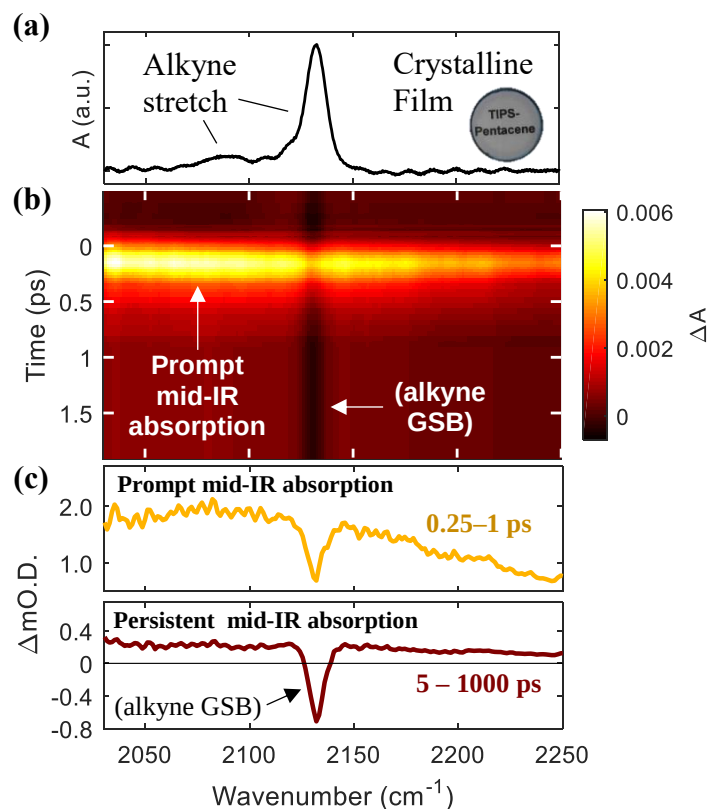


Figure 5-9: (a) FTIR spectrum of the alkyne stretching modes in a crystalline TIPS-Pn film. (b) Transient absorption spectrum measured in the mid-IR spectral region showing a prompt photoinduced absorption in addition to the vibrational ground state bleach (GSB). (c) Spectral slices obtained by time-integrating the spectra from either 0.25–1 ps or 5–1000 ps.

Unlike in dilute solutions, TIPS-Pn molecules in crystalline films are electronically coupled and consequently undergo singlet fission. This would lead to the rapid decay of the S_1 absorption band on the sub-picosecond time scale. As seen in **Figure 5-9**, the initial mid-IR absorption signal decayed well before 1 ps time delay, confirming its assignment to S_1 states in the film. However, a persistent, weak absorption signal was observed following 1 ps and surviving to the nanosecond timescale. Comparing the spectra of the prompt and persistent mid-IR absorption signals in **Figure 5-9** reveals a change in spectral shape and signal strength. Notably, the GSB of the vibrational feature provides an internal reference that indicates the concentration of TIPS-Pn molecules that have not yet relaxed back to the ground state. As a

result, the absorption transition giving rise to the persistent signal has a significantly smaller cross section compared to the S_1 absorption.

Next, the singlet fission reaction was characterized in the TIPS-Pn film in order to verify the assignment of the sub-picosecond decay of the S_1 mid-IR absorption. The kinetics of the triplet absorption transition ($T_1 \rightarrow T_n$) in the visible spectral range were measured using ultrafast 2-color pump-probe spectroscopy (see **Figure 5-10**). The comparison of the mid-IR and visible absorption kinetics indicated that the sub-picosecond decay of the S_1 mid-IR absorption signal occurs concurrently with the growth of the absorption signal. This was an indication that the rapid loss of excited singlet states results from singlet fission.

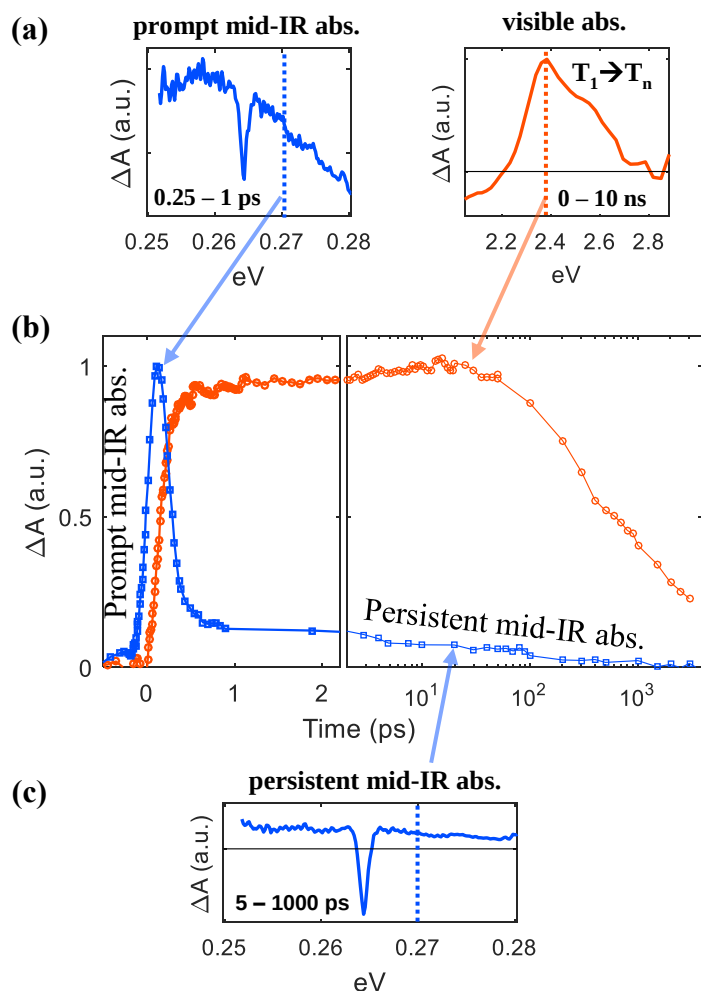


Figure 5-10: (a) (Left) mid-IR transient absorption spectrum measured over ~ 0.25 – 0.28 eV and averaged from 0.25–1 ps, and (right) visible transient absorption spectrum measured over ~ 2 – 3 eV and averaged from 0–10 ns for a crystalline film of TIPS-Pn. The dotted lines show the energies probed for the kinetic traces. (b) Comparison of mid-IR and visible absorption kinetics on the ultrafast timescale shown on two different x-axes. (c) Persistent mid-IR transient absorption averaged from 5–1000 ps.

Although singlet fission is expected to occur on the 100 fs timescale and with unit quantum yield in pentacene and its derivatives,^{18,43,44} the persistent mid-IR absorption signal did not decay completely until the nanosecond timescale. This suggests that the species responsible for this absorption is not the S_1 state. The comparison of the kinetic decays of the persistent mid-IR absorption to the visible triplet absorption in **Figure 5-11** shows that the mid-IR absorption cannot arise from triplet excitons. In particular, the average time constants

(empirically obtained from biexponential fits) that are associated with their decays were distinct. As will be discussed below using detailed kinetic modeling, the persistent mid-IR absorption was attributable to CTP intermediates that feed into the final independent triplet population.

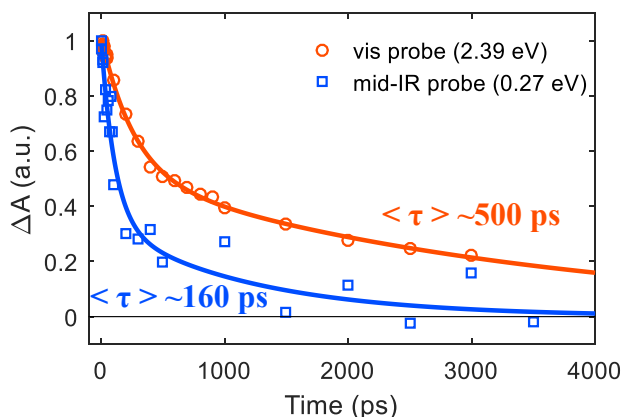


Figure 5-11: Decay kinetics normalized at 5 ps for transient absorption features measured using either visible (2.39 eV) or mid-IR (0.27 eV) light. The (weighted) average time constants obtained from biexponential fits to the data are included for reference. The fits are presented as solid lines, and the data are presented as symbols.

5.3.3. Alternate explanation of persistent mid-IR absorption in TIPS-Pn films

In the following discussion, several alternative hypotheses for the origin of the persistent mid-IR absorption signal are considered. Each is then eliminated as a possibility, revealing that the signal likely arises from CTP intermediates.

5.3.3.1. Residual singlet exciton hypothesis

It is possible that the persistent mid-IR absorption signal arose from a residual population of excited singlet states that could not undergo singlet fission (because of singlet trapping, for example).¹⁹ The persistent mid-IR absorption signal (at 10 ps) was ~10% of the intensity of the prompt S_1 signal (around time zero). This would indicate that ~10% of the initial concentration of S_1 states could not undergo singlet fission. This hypothesis was tested using

ultrafast fluorescence spectroscopy, from which a fluorescence signal should be observed from this ~10% population of singlets if they indeed cannot undergo fission.

It was first verified that fluorescence could be measured using an amorphous film of TIPS-Pn that was not expected to undergo singlet fission with unit quantum efficiency.²⁶ A comparison of the steady-state absorption spectrum of the amorphous and crystalline films of TIPS-Pn used is shown in **Figure 5-12**.

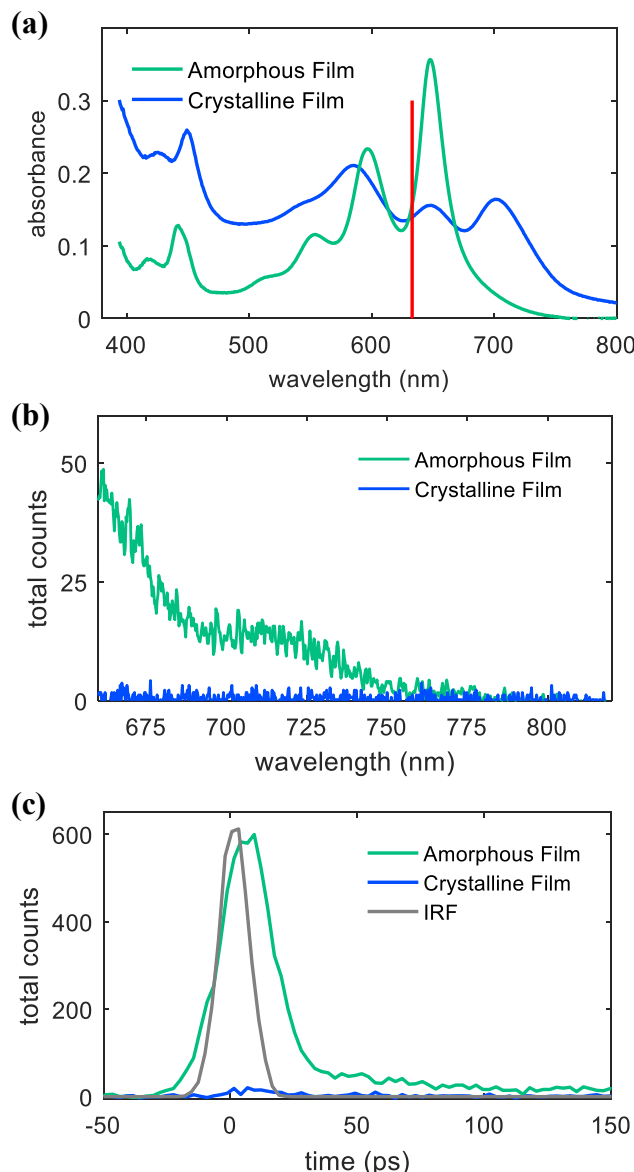


Figure 5-12: (a) Steady-state absorption spectra for a crystalline and amorphous film of TIPS-Pn. The red line represents the excitation wavelength (633 nm) used in time-resolved photoluminescence measurements. (b) Ultrafast fluorescence spectra for the same films obtained by time-integration from 0–150 ps. The absorbed energy density used for each film was $\sim 92 \mu\text{J}/\text{cm}^2$. (c) Spectrally-integrated fluorescence decay traces for the same films. The instrument response function (IRF) is included.

The ultrafast fluorescence spectra that were time-integrated from 0–150 ps for both films are shown in **Figure 5-12**. The amorphous film exhibited fluorescence that was characteristic of S_1 emission. The decay kinetics for the spectrally-integrated fluorescence signal revealed a prompt (< 50 ps) and delayed signal. The prompt signal may have arisen from singlet emission

that competes with slower singlet fission,²⁶ which has been reported to occur as a diffusion-mediated reaction in amorphous solids.⁴⁵ The delayed fluorescence (beyond ~50 ps) likely arose from singlet trapping since its lifetime matched that of isolated TIPS-Pn molecules dispersed in a polystyrene matrix (see **Figure 5-13**).

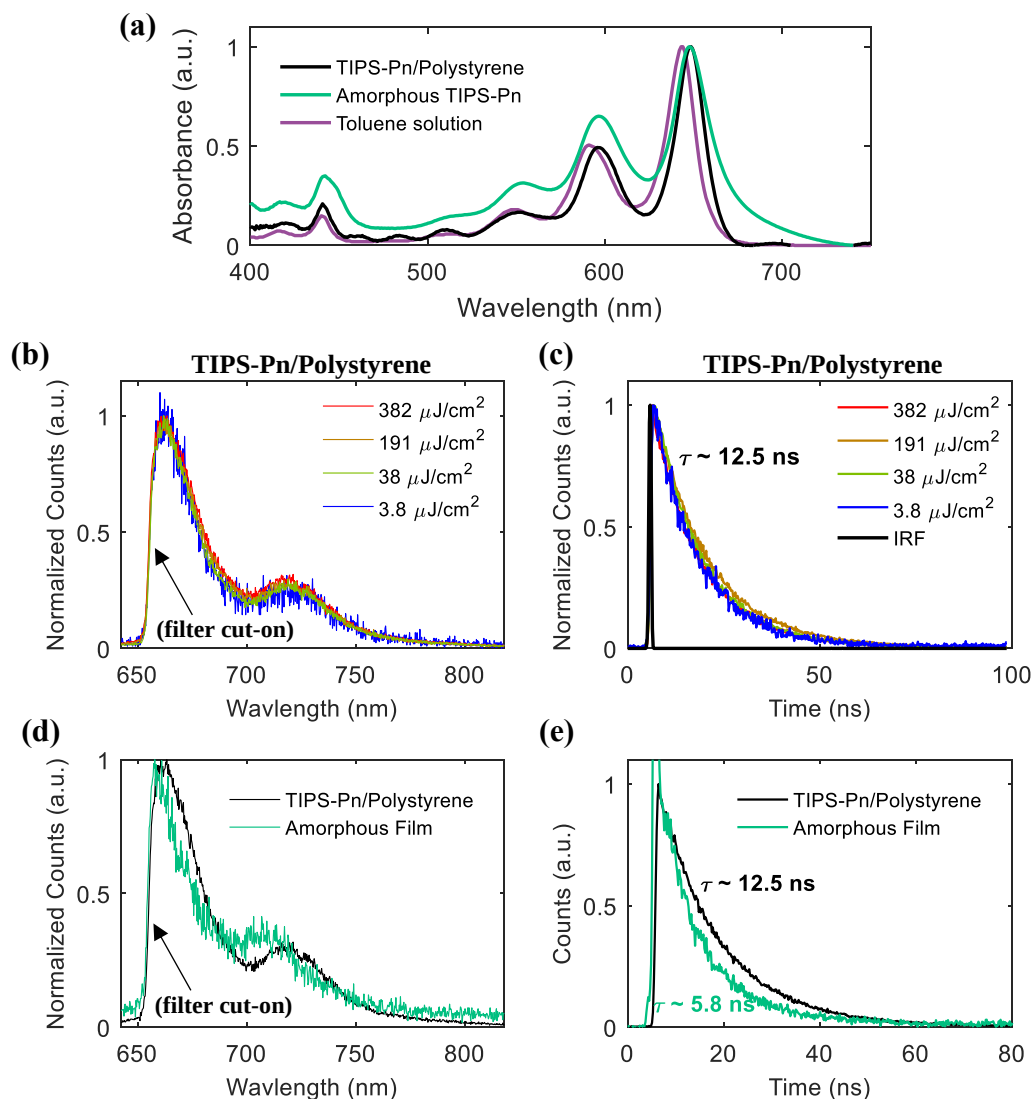


Figure 5-13: (a) Steady-state absorption spectra for TIPS-Pn dissolved in toluene, dispersed in a polystyrene matrix (solid-state solution), or as an amorphous film. (b) Fluorescence spectrum (averaged over time) for the solid-state solution of TIPS-Pn in polystyrene for a variety of incident excitation energy densities. (c) Spectrally-integrated fluorescence decay traces for the TIPS-Pn/polystyrene sample for the same energy densities. The kinetics were fit using a single exponential, which gave a time constant of ~ 12.5 ns. (d) Comparison of the fluorescence spectrum (averaged over time) for the solid-state solution and the amorphous film of TIPS-Pn measured at $383 \mu\text{J}/\text{cm}^2$ excitation. (e) The corresponding fluorescence decay traces, which were fit using single exponential decays. The time constants are provided.

To specifically determine if the singlet excitons in the amorphous TIPS-Pn film instead underwent bimolecular reformation (from triplet fusion) a “solid state solution” of TIPS-Pn

dispersed in a polystyrene matrix was investigated. The recipe²² previously reported by Lukman and coworkers was adopted. The absorption spectrum (**Figure 5-13**) measured for the TIPS-Pn/polystyrene film was very similar to that of a dilute solution of TIPS-Pn dissolved in toluene, indicating that the majority of TIPS-Pn molecules were electronically isolated and therefore cannot undergo singlet fission. Its fluorescence spectrum and kinetics were found to be independent of excitation energy density from ~ 3.8 – $382 \mu\text{J}/\text{cm}^2$. The fluorescence decay kinetics was describable using a single exponential decay function, which had a time constant of ~ 12.5 ns, close to that of the dilute solution (~ 15 ns). It was therefore concluded that the TIPS-Pn molecules were successfully isolated in the polystyrene matrix. The fluorescence spectrum of the amorphous film resembled that of the solid-state solution, and its kinetic decay was also well-described using a single exponential decay function. The time constant for the amorphous film was ~ 5.8 ns, which was close to that of the solid-state solution, indicating that the delayed fluorescence signal did not arise from triplet fusion.

Returning to the crystalline film, no discernible fluorescence signal was resolved, indicating that singlet fission occurs very efficiently, kinetically out-competing fluorescence decay. Additionally, this suggests that the persistent mid-IR transient absorption signal observed after 10 ps could not arise from a residual singlet excited state population that cannot undergo singlet fission.

5.3.3.2. Singlet reformation via triplet fusion hypothesis

Next, the hypothesis that the persistent mid-IR absorption signal arose from reformation of singlet excitons from triplet fusion (giving rise to a delayed signal) was tested. The excitation energy density dependence of the persistent mid-IR signal was investigated to test if singlets were regenerated from bimolecular reformation due to triplet fusion. The intensity of the

persistent mid-IR absorption signal measured at 10 ps was plotted against excitation density in **Figure 5-14**, which shows a linear relationship. For triplet fusion in the “weak annihilation regime”, this dependence would be quadratic, and in the “strong annihilation regime”, this dependence would be linear.⁴⁶ The excitation energy dependence of the triplet absorption signal in **Figure 5-14** shows a linear dependence at 10 ps time delay, which indicates that any triplet fusion occurring at 10 ps falls within the weak annihilation regime.⁴⁶ Therefore, the mid-IR absorption appearing at 10 ps time delay cannot arise from singlet reformation from triplet fusion.

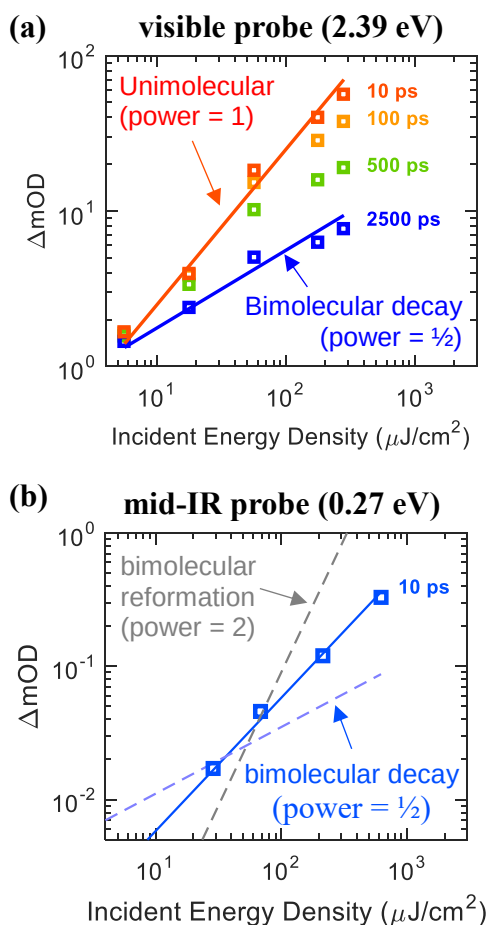


Figure 5-14: (a) Excitation energy dependence of the visible transient absorption signal at various time delays. Linear (power = 1) and square-root (power = $1/2$) functions are overlaid for reference. **(b)** Excitation energy dependence of the mid-IR transient absorption signal at 10 ps time delay. Square (power = 2), linear (power = 1), and square-root (power = $1/2$) functions are overlaid for reference.

It is possible that the mid-IR signal at 10 ps arose not from bimolecular recombination of independent triplet excitons, but actually from geminate recombination of CTP states. However, this hypothesis is not supported based on previous discussion of the time-resolved fluorescence data. If geminate recombination of CTPs was able to reform singlet excitons, then ~10% of the original singlet exciton concentration should be restored by 10 ps. Furthermore, if this was a dominant pathway, then a dynamic equilibrium between S_1 and CTP states would exist over a time scale long enough for fluorescence to be able to kinetically compete. However, no fluorescence was detectable in the crystalline TIPS-Pn film.

Finally, it is noted that triplet excitons do indeed undergo bimolecular annihilation under the excitation energy densities used,²⁶ which is evident at later time delays in **Figure 5-14**. This likely led to reformation of CTPs on a hundreds of picoseconds timescale. However, this cannot explain the mid-IR absorption signal appearing on the tens of picoseconds timescale.

5.3.4. Review of the assignment of CTP mid-IR absorption

Having eliminated alternate hypotheses for the persistent mid-IR absorption signal, it is concluded that it likely arises from CTP intermediates that form from the photogenerated singlet excitons. Although the absorption signal was assigned to CTP states, the states involved in the transition remain unknown. It is possible that the initial (S_1) and final states involved in the singlet exciton absorption transition can mix with the states of the CTP intermediates since both excited states possess singlet character. In this situation, the CTP states may borrow oscillator strength from the bright S_1 state. If this occurred, then the absorption coefficient of the persistent absorption transition could be used to estimate the excited state mixing. The corresponding time dependence in absorption coefficient would then be a direct probe of such mixing, which could be monitored over time to assess the decoherence

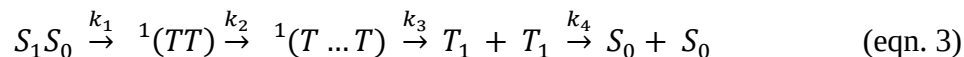
of the triplet pairs as they dissociate and form independent triplets excitations. In an alternate view, the mid-IR absorption transition of the CTPs may be similar in nature to the low energy near-IR transitions observed for excimer species in perylene diimides^{31-34,47} or for the triplet pair intermediates measured in nanoparticle dispersions of pentacene derivatives.²³ Last, the mid-IR CTP absorption transition may involve dark “multi-exciton” states previously calculated for crystalline pentacene.^{35,36} Ultimately, understanding the specific nature of the CTP absorption transition would provide new insight into the mechanism of CTP dissociation and would be the subject of future work.

5.4. Kinetic Modeling of Ultrafast Mid-Infrared Absorptions in TIPS-Pn Films

5.4.1. Two-intermediate state model

Having established a method to probe CTP intermediates during singlet fission, the mechanism of formation of independent triplet excitons from the CTP intermediates is now considered. Combining the mid-IR absorption kinetics of the CTP intermediates along with the visible absorption kinetics of triplets, kinetic models for singlet fission were tested.

Using kinetic modeling of the singlet fission reaction, the population dynamics of singlets, CTP intermediates, and independent triplets were extracted for the crystalline TIPS-Pn film. A system of coupled rate equations was adapted from previous reports^{23,48,49} for the following sequential reaction:



where S_1S_0 represents a singlet exciton, ${}^1(TT)$ and ${}^1(T \dots T)$ are the proximal and separated CTP intermediates, respectively, and $T_1 + T_1$ represents independent triplet excitons. In this model, ${}^1(TT)$ represents triplet pair states in which the excitation is delocalized over two neighboring

molecules with net singlet character. For the $^1(T...T)$ states, the triplet pairs have started to physically separate but retain spin coherence, resulting in net singlet character. In accordance with equation 3, the coupled rate equations are then:

$$\frac{d[S_1S_0]}{dt} = -k_1[S_1S_0] \quad (\text{eqn. 4})$$

$$\frac{d[^1(TT)]}{dt} = +k_1[S_1S_0] - k_2[^1(TT)] \quad (\text{eqn. 5})$$

$$\frac{d[^1(T...T)]}{dt} = +k_2[^1(TT)] - \frac{1}{2}k_3[^1(T...T)] \quad (\text{eqn. 6})$$

$$\frac{d[T_1]}{dt} = +2k_3[^1(T...T)] - \frac{1}{2}k_4[T_1]^2 \quad (\text{eqn. 7})$$

where the brackets indicate concentration, k_i are rate constants, and t is time. The coefficients account for differences in stoichiometry. These equations could be solved numerically using the following initial conditions: $[S_1S_0]_{t=0}=1$, $[^1(TT)]_{t=0}=0$, $[^1(T...T)]_{t=0}=0$, and $[T_1]_{t=0}=0$. The (normalized) observed kinetics could then be described using a linear combination of the kinetics of the appropriate absorbing populations according to:

$$\frac{\Delta A_{mid-IR}(t)}{\Delta A_{mid-IR}^{max}} = a_1[S_1S_0](t) + a_2[^1(TT)](t) + a_3[^1(T...T)](t) \quad (\text{eqn. 8})$$

$$\frac{\Delta A_{Vis}(t)}{\Delta A_{Vis}^{max}} = a_4[^1(TT)](t) + a_5[^1(T...T)](t) + a_6[T_1](t) \quad (\text{eqn. 9})$$

where a_i are scaling factors related to the absorption coefficients of each state, i.

The result of the kinetic modeling of both the mid-IR and visible transient absorption data are shown in **Figure 5-15**.

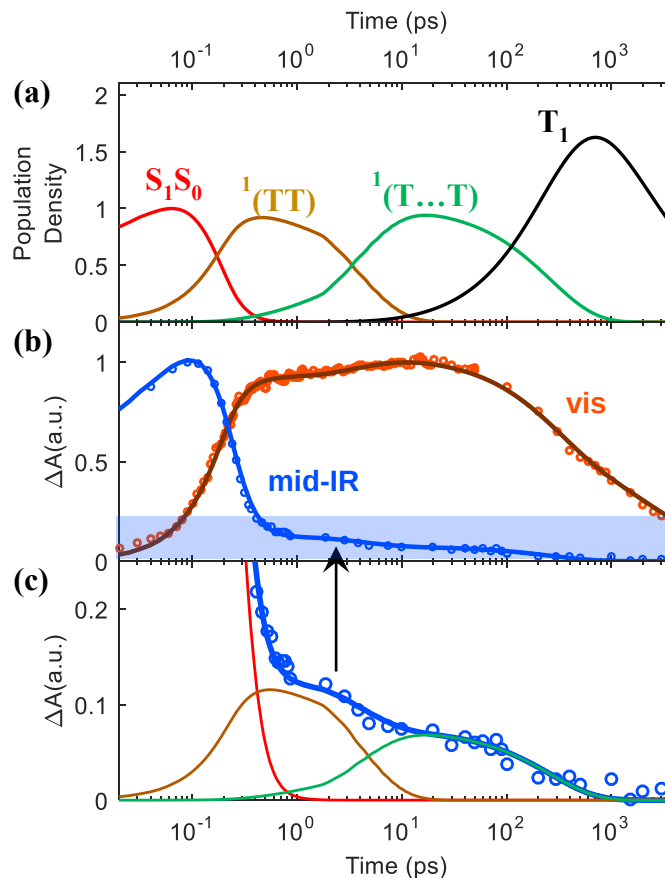


Figure 5-15: (a) Population kinetics corresponding to the best fit of the 2-intermediate state model to the mid-IR and visible absorption data. (b) The best fits to the mid-IR and visible transient absorption kinetics. Data are shown as symbols and the fits are shown as lines. (c) Close-up of the mid-IR decay trace along with the total fit and the fit components for each population. All of the modeled kinetics were convoluted with the instrument response function prior to fitting the data.

In accordance with previous reports on pentacene derivatives, the sub-picosecond rise component of the visible absorption kinetics corresponds to the initial step of singlet fission, $S_1S_0 \rightarrow ^1(TT)$, while the picosecond rise component corresponds to the second step of singlet fission, $^1(TT) \rightarrow ^1(T...T)$.^{20,23} As such, the values of k_1 and k_2 obtained from the best fit to the visible absorption kinetics were fixed when fitting the mid-IR kinetics. The values of all the resulting fit parameters are provided in **Table 5-2**.

Table 5-2. Parameters for the 2-intermediate state kinetic model for crystalline TIPS-Pn

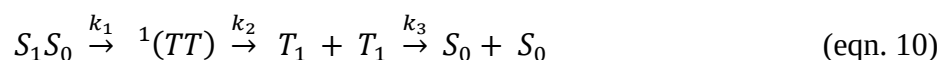
Amplitude (a.u.)	Value	Rate Constant	Value (ps ⁻¹)
a ₁	0.9809	k ₁	12.5
a ₂	0.1256	k ₂	0.264
a ₃	0.0724	k ₃	0.0038
a ₄	0.9039	k ₄	0.0004
a ₅	1.0180		
a ₆	0.2506		

The population dynamics solved by kinetic modeling of the ultrafast kinetics are shown in **Figure 5-15** along with the best fits to the data. The results show that the decay of the CTP intermediates, ¹(TT) and (T...T) is not complete until the nanosecond timescale, suggesting that the formation of independent triplet excitons occurs over a much longer time period than previously believed.^{18,21,24}

5.4.2. Alternate models

Next, alternate kinetic models are considered, including the simpler, 1-intermediate state model^{1,50}, and the 1- and 2-intermediate state models in which reverse reactions are considered. While the best fits to the data could not accurately describe the curvature of the mid-IR or visible transient absorption data, the errors were close to experimental precision. Furthermore, it was found that the inclusion of the triplet in the 2-intermediate state kinetic model did not have a significant effect on the resulting fit.

The 1-intermediate state model, commonly invoked in the literature,¹ is written as:



The coupled rate equations rate equations are therefore expressed as:

$$\frac{d[S_1S_2]}{dt} = -k_1[S_1S_0] + k_{-1}[{}^1(TT)] \quad (\text{eqn. 11})$$

$$\frac{d[{}^1(TT)]}{dt} = +k_1[S_1S_0] - k_{-1}[{}^1(TT)] - k_2[{}^1(TT)] + \frac{1}{2}k_{-2}[T_1]^2 \quad (\text{eqn. 12})$$

$$\frac{d[T_1]}{dt} = +2k_2[{}^1(TT)] - k_3[T_1]^2 - \frac{1}{2}k_{-2}[T_1]^2 \quad (\text{eqn. 13})$$

This system of equations could then be numerically solved using the initial conditions: $[S_1S_0]_{t=0}=1$, $[{}^1(TT)]_{t=0}=0$, and $[T_1]_{t=0}=0$. The total kinetics could then be described using a linear combination of the appropriate absorbing populations. Since the absorption coefficients for each state were not known, the normalized absorption kinetics were fit using:

$$\frac{\Delta A_{mid-IR}(t)}{\Delta A_{mid-IR}^{max}} = a_1[S_1S_0](t) + a_2[{}^1(TT)](t) \quad (\text{eqn. 14})$$

$$\frac{\Delta A_{Vis}(t)}{\Delta A_{Vis}^{max}} = a_3[{}^1(TT)](t) + a_4[T_1](t) \quad (\text{eqn. 15})$$

Like in the 2-intermediate state model, the values of k_1 and k_2 obtained from fitting the visible absorption kinetics were fixed. The resulting fits are shown in **Figure 5-16**. The mid-IR kinetics were poorly described using this model since the rate constant, k_2 , was too fast to describe signal beyond a few picoseconds. Next, it was considered if the model could be improved by allowing k_2 to vary. The corresponding results are shown in **Figure 5-16**. Again, the model failed to describe the curvature in the data. Last, the effect of considering reverse reactions was assessed. It was found that turning on the reverse of k_1 modified the initial decay of the model below 1 ps trivially, with no effect at later time delays. Next, the reverse of k_2 was considered. In this case, it is known that reformation of the CTPs (reverse of k_2) would occur with a rate constant of $\sim 1/3$ the rate of the forward reaction: $k_{-2}=1/3*k_2$.⁴⁸ It was found that this model described the data very well at late time delays, albeit the curvature of the data was not accurately reproduced (see **Figure 5-16**).

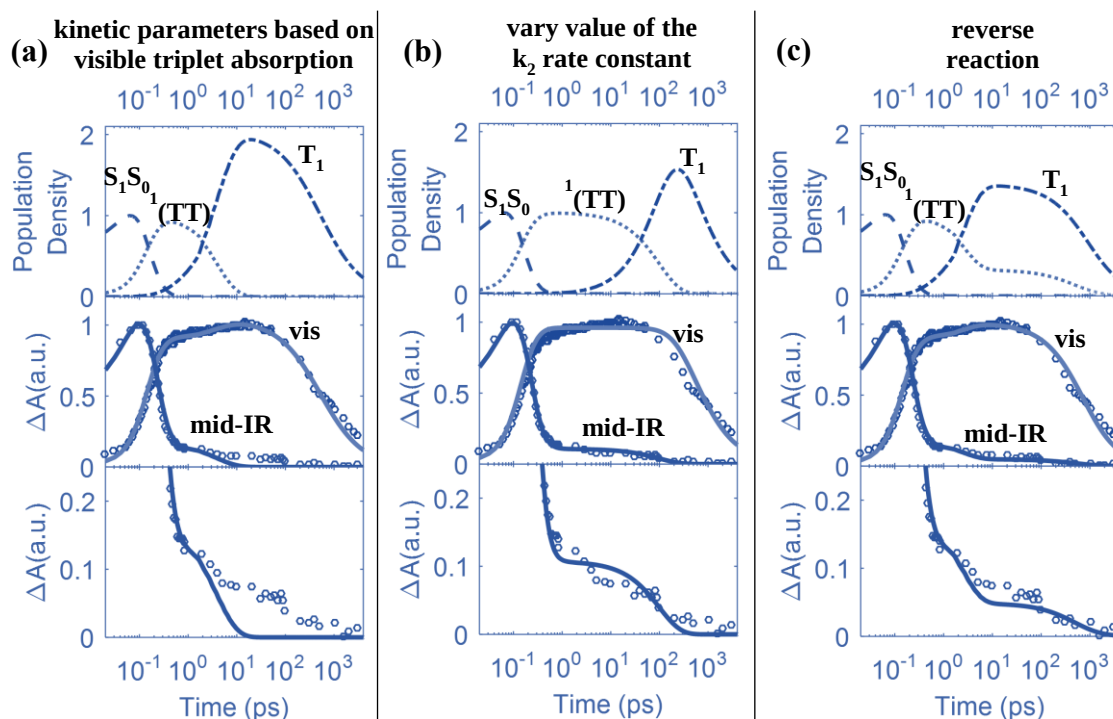


Figure 5-16: (a) Best fit for the 1-intermediate state model to the kinetic data for the mid-IR and visible absorptions. The rate constants (k_1 and k_2) obtained from modeling the visible kinetics independently were used. (b) Best fit if k_2 was allowed to vary. (c) Best fit if the reverse of k_2 was varied. For all panels, data are shown as symbols and the kinetic models are shown as lines.

Last, the effect of including reverse reactions in the 2-intermediate state model was assessed. Again, the values of k_1 and k_2 obtained from kinetic analysis of the visible absorption data were fixed. Variations of each reverse rate constant (k_{1-} , k_{2-} , and k_{3-}) were tested one at a time in **Figure 5-17**. In each case, turning on reverse reactions changed the yields of each population. Since the absorption coefficients for each species was not known, the scaling parameters, a_i , must be varied. Consequently, varying the scaling parameters compensates for the differences in yields determined for each population (a trivial exception occurs when varying k_{1-}). Therefore, the reverse reactions of the 2-intermediate state model merely affected the apparent yields of each population, without affecting the rate constants. Therefore, the

conclusion of this work about long-lived singlet fission intermediate states still holds true, although the reverse reactions may still be important for the singlet fission reaction.

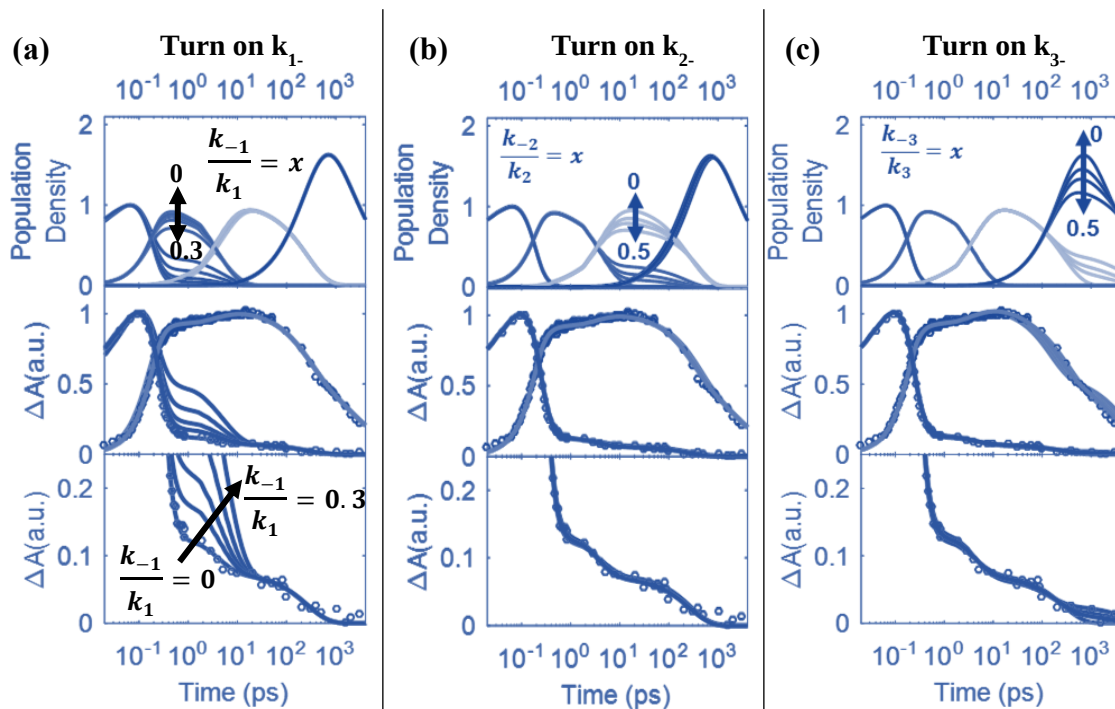


Figure 5-17: Best fits for the 2-intermediate model to the visible and mid-IR transient absorption kinetics. The effects of turning on reverse reactions was investigated for (a) k_{1-} , (b) k_{2-} , and (c) k_{3-} . For all the panels, data are presented as symbols, and the kinetic models are presented as lines.

5.5. Conclusions and Significance

Ultrafast mid-IR spectroscopy was used directly measure the dynamics of CTP intermediates that formed during singlet fission in a crystalline TIPS-Pn film. The assignment of the mid-IR electronic transition was assessed using spectroscopic measurements of isolated molecules of TIPS-Pn in dilute solutions. Singlet excited states were found to possess a mid-IR absorption band with decay time constants that matched those determined from time-resolved fluorescence measurements. In films, this absorption decayed on a sub-picosecond timescale due to singlet fission, which was confirmed by monitoring the kinetic growth of the

triplet absorption feature in the visible spectral range. Following the decay of the S_1 mid-IR absorption feature, a residual signal persisting into the nanosecond timescale was observed and assigned to CTP state absorption. From the CTP absorption decay kinetics, it was found that independent triplet excitons form on the hundreds of picoseconds to nanoseconds timescale, orders of magnitude longer than previously believed. Notably, the transport of the triplet states, whether they are entangled or not, is what is important for singlet fission sensitizers. As such, the occurrence of long-lived CTP states does not necessarily mean that the triplets cannot be effectively transported through a device. However, any kinetically competing relaxation processes (e.g. internal conversion or excimer formation), may need to be suppressed in order to ensure efficient triplet harvesting.

Detailed kinetic modeling of the ultrafast mid-IR (S_1 and CTP states) and visible (CTP and T_1 states) transient absorption kinetics revealed the true formation time of independent triplet excitations. The new ability to directly measure CTP state absorption offers a new approach to monitoring the singlet fission reaction and studying its specific mechanisms. Insights gained from mid-IR measurements can be used to help identify design rules for guiding the development of new singlet fission sensitizers by uncovering specific details about the reaction mechanism. These details, in turn, would explain how to properly maximize the quantum efficiency and harvesting of multiplied triplet excitons in practical applications.

5.6. References

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CHAPTER 6

Ultrafast Vibrational Dynamics Reveal Slow Triplet Pair Separation during Singlet Fission in a Pentacene Derivative

This chapter presents the first account of the application of time-resolved vibrational spectroscopy for studying the evolution of electronic states involved in the singlet fission reaction. Studying the singlet fission mechanism using traditional time-resolved electronic absorption spectroscopies has been challenging because it is extremely difficult to spectroscopically distinguish triplet pair intermediates from multiplied, independent triplet excitons. Using the alkyne stretching vibration of TIPS-Pn, the formation of the independent triplet excitons was able to be monitored during singlet fission. This unprecedented result establishes a new method for determining the true formation time of independent triplet excitons, which is critical for assessing the quality of new singlet fission materials, and of specific molecular packing structures. Additionally, by monitoring independent triplet exciton formation, the separation rate of the triplet pair intermediates is indirectly determined. As a result, this work confirms previous reports that concluded that triplet pair separation is an important pathway required for singlet fission to complete.

This chapter was adapted from the publication: Grieco, C., Kennehan, E.R., Rimshaw, A., Payne, M.M., Anthony, J.E., and Asbury, J.B., “Harnessing Molecular Vibrations to Probe Triplet Dynamics during Singlet Fission”, *J. Phys. Chem. Lett.*, **2017**, 8, 5700–5706, which has been rephrased in the context of this dissertation.

6.1. Introduction

Singlet fission is a multiple exciton generation process that occurs in some organic molecules, for which an excited singlet state fissions into two triplet states.^{1,2} Because this reaction is capable of producing a 200% yield of triplets,^{3,4} singlet fission may be used to enhance solar cell power conversion efficiency by overcoming thermalization losses associated with absorption of high-energy photons emitted by the sun.⁵⁻⁸ Despite high singlet fission efficiencies that occur in crystalline materials, such as tetracene, rubrene, pentacene, and some others,⁹⁻²⁰ the reported enhancements in performance of solar cells utilizing such singlet fission sensitizers have been only modest.

A better understanding of the singlet fission reaction, from photogenerated singlet excitations to independent, multiplied triplets, would assist in the development of high performance solar cells (taking proof-of-principle to in-practice). Although the precise singlet fission mechanism is still a topic of debate^{9,21-23} it is agreed upon that in order to form independent triplet excitons, an intermediate state, known as the correlated triplet pair (CTP), must first dissociate.²⁴ Unfortunately, it is challenging to unambiguously distinguish CTP intermediates from independent triplet excitons using time-resolved electronic spectroscopy. This is because both species have similar electronic character and both possess triplet character, resulting in significantly overlapping transient absorption bands.^{25,26}

In the following work, it is proposed that the discovery of direct spectroscopic probes of independent triplet excitons would reveal opportunities to investigate the precise singlet fission mechanism. Motivated by prior work,^{27,28} an ultrafast vibrational spectroscopy investigation was performed to study the singlet fission reaction in crystalline films of 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-Pn). It was shown that monitoring the

vibrational modes of organic molecules during singlet fission is a new approach to more directly measure the dissociation of the CTP. In addition, unique vibrational signatures were discovered that report on the deposition of thermal energy via triplet-triplet annihilation. Since all organic singlet fission sensitizers possess measurable vibrational modes, this spectroscopic approach may be universally applied to study the singlet fission mechanism.

6.2. Ultrafast Vibrational Dynamics in TIPS-Pn Films

Crystalline (Form-I brickwork) TIPS-Pn films were prepared using solution-processing methods previously reported (see Chapter 3).²⁹ An absorption spectrum and grazing-incidence X-ray diffraction (GIXRD) pattern for a representative film is displayed in **Figure 6-1**. In particular, films were made by spin-coating a solution containing 20 mg of TIPS-Pn dissolved in 1 mL of dichloromethane at ~800 rpm onto CaF₂ substrates. After this, the films were crystallized using solvent-vapor annealing with isopropanol.

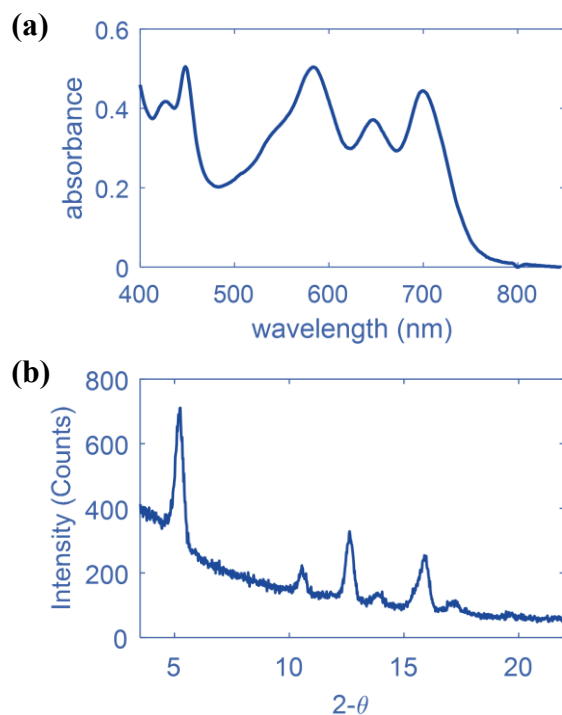


Figure 6-1: (a) Absorption spectrum and (b) grazing-incidence X-ray diffraction (GIXRD) pattern measured for a crystalline TIPS-Pn film.

Conventional transient absorption spectroscopy in the visible spectral region^{2,30} was first used to measure the triplet dynamics in crystalline TIPS-Pn films. The $T_1 \rightarrow T_n$ excitation spectrum was measured for a film using laser flash photolysis with a 645 nm excitation wavelength (see **Figure 6-2**). Transient absorption kinetics measured at 520 nm were well-described using a biexponential growth model in accordance with the literature.^{15,26,29} In particular, the primary growth of the triplet absorption signal occurred with a ~ 100 fs time-constant, followed by continued growth on a few picosecond timescale. The subsequent decay of the signal resulted from bimolecular triplet-triplet annihilation,^{7,31} which is known to occur in crystalline TIPS-Pn when excitation energy densities in the 5 - 300 $\mu\text{J}/\text{cm}^2$ range are used.²⁹ In particular, the transient absorption decays were found to be dependent on excitation energy density (**Figure 6-2**). Furthermore, triplet-triplet annihilation was found to become activated

during the 10's of picoseconds timescale for the energy density used in the vibrational dynamics measurements ($\sim 150 \mu\text{J}/\text{cm}^2$).

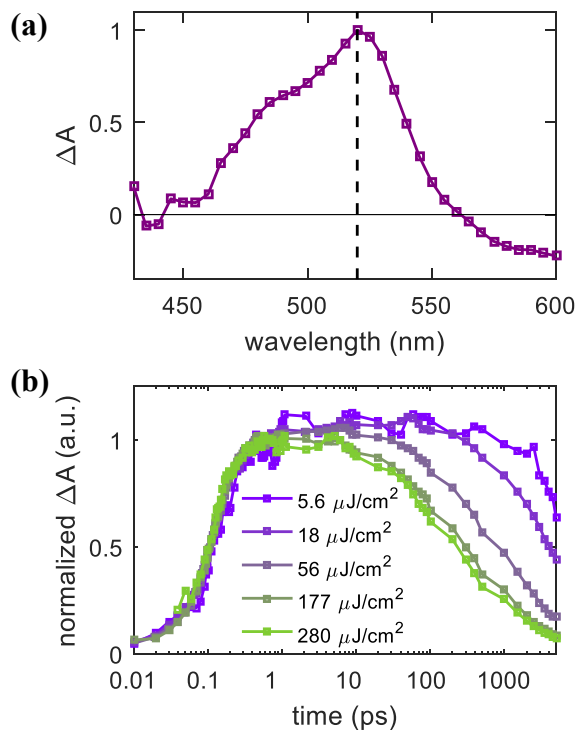


Figure 6-2: (a) Triplet excitation spectrum ($T_1 \rightarrow T_n$) measured in the visible spectral region for a crystalline TIPS-Pn film excited at 645 nm. (b) Dependence of ultrafast triplet absorption kinetics on excitation energy measured for a film pumped at 655 nm and probed at 520 nm. The dashed line in (a) indicates the probed wavelength.

The vibrational dynamics occurring during singlet fission in a crystalline TIPS-Pn film were measured using ultrafast visible-pump mid-IR-probe spectroscopy with an excitation at 655 nm with $150 \mu\text{J}/\text{cm}^2$ energy density (see **Figure 6-3**). The spectra showed a combination of a broad photo-induced absorption (PIA) feature and narrow vibrational features in the vicinity of 2132 cm^{-1} . The vibrational peaks corresponded to the symmetric and asymmetric alkyne stretch modes of TIPS-Pn. The broad PIA feature was previously assigned to the absorption of singlet excitons and CTP intermediates (see Chapter 5). In this work, the vibrational dynamics occurring during singlet fission are followed in particular. As such, a spectral

modeling procedure was developed (discussed later), which includes the removal of this broad PIA feature in order to isolate the time-resolved vibrational spectrum at each delay time. This process is exemplified in **Figure 6-3**, which shows the best fits of the broad PIA “baseline” signal prior to its subtraction.

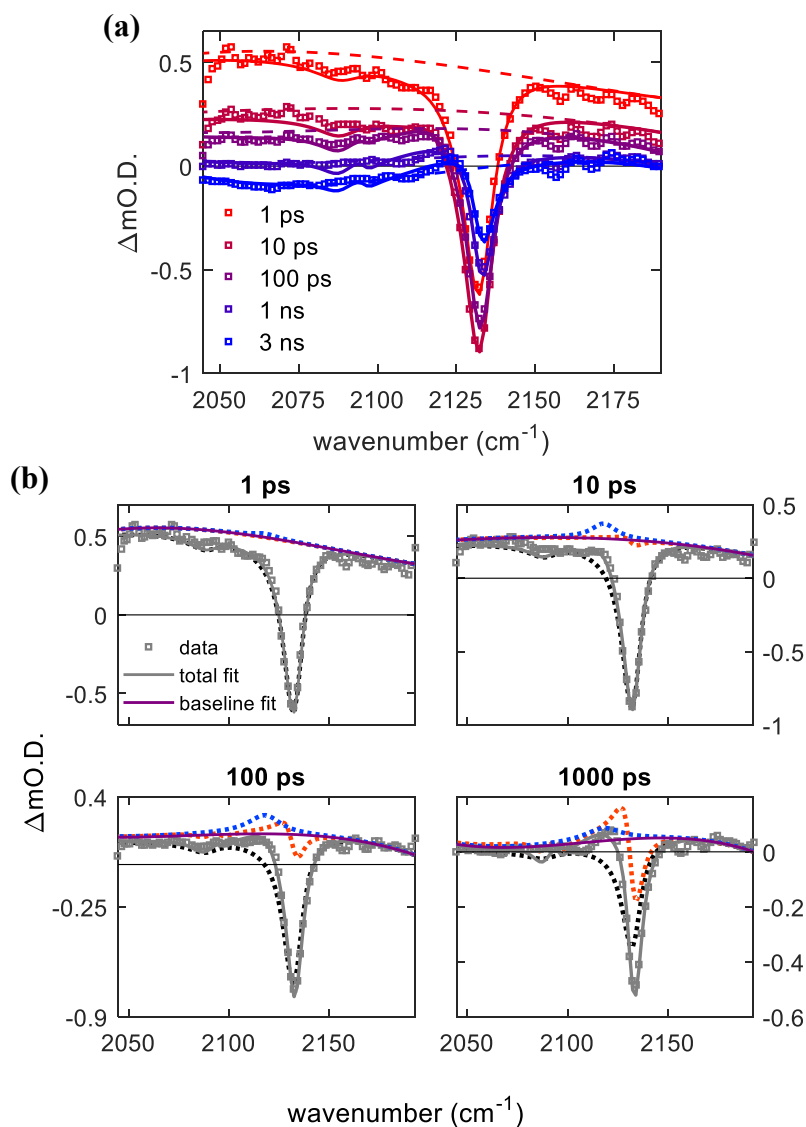


Figure 6-3: (a) Ultrafast transient absorption spectra measured in the mid-IR spectral region for a crystalline TIPS-Pn film. The excitation wavelength was 655 nm and the incident energy density was $\sim 150 \mu\text{J}/\text{cm}^2$. The spectra collected for several key time delays are shown (squares), and the total fits (solid lines) and fits to the baseline (dashed lines) are included. (b) The baseline correction procedure shown for the spectrum at several key time delays. The ground state bleach (black dotted lines), triplet absorption (blue dotted lines), and thermal effect (orange dotted lines) components are included.

A frequency-time plot of the baseline-corrected time-resolved vibrational spectrum is shown in **Figure 6-4**. Photoexcitation resulted in a reduced ground state population of TIPS-Pn molecules, producing a ground state bleach (GSB) signal, which was prominent at 1 ps time delay. A positive feature was found at lower frequency ($\sim 2116\text{ cm}^{-1}$) that grew in on an early picosecond timescale. An additional positive feature was found to grow in on a hundreds of picoseconds timescale having a peak position around 2124 cm^{-1} .

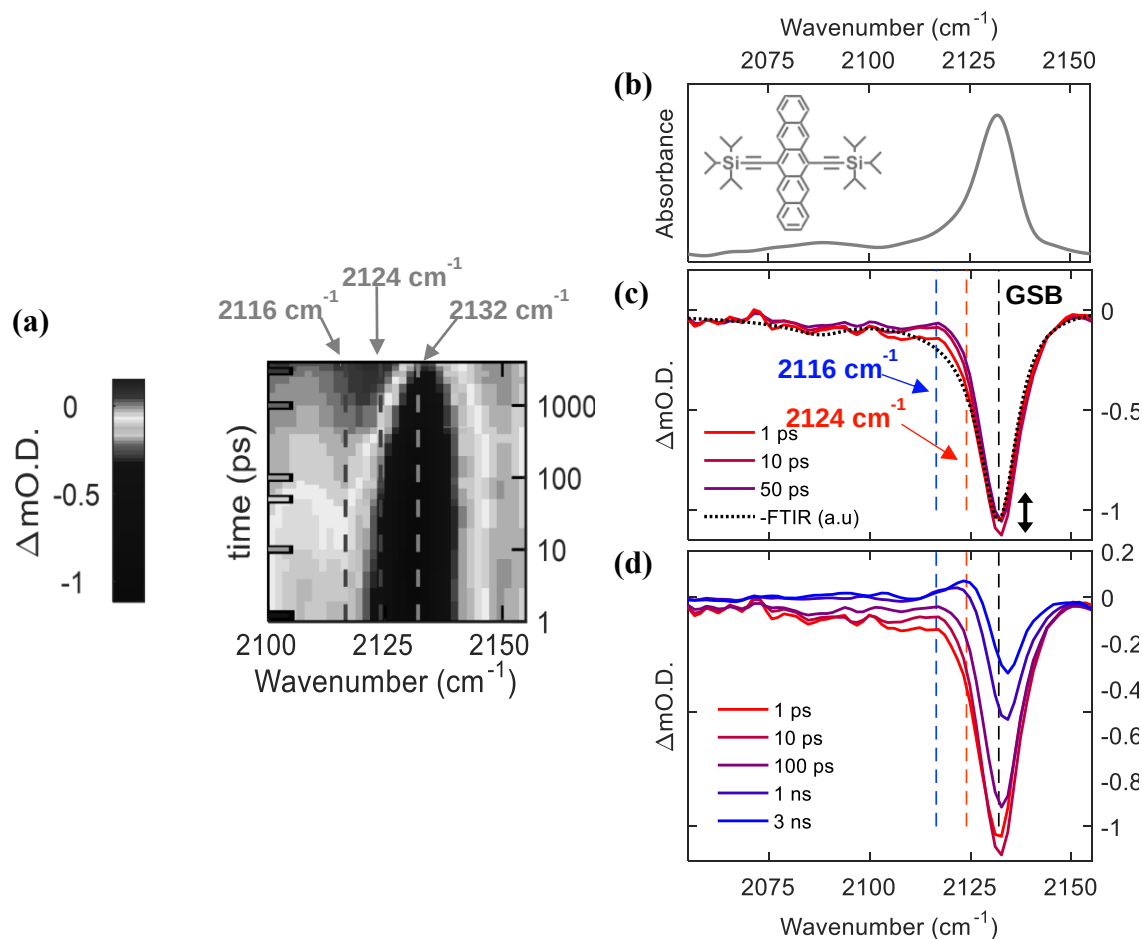


Figure 6-4: (a) Wavenumber-time plot of the time-resolved vibrational spectrum of a crystalline TIPS-Pn film excited at 655 nm with an incident energy density of $\sim 150 \mu\text{J}/\text{cm}^2$. (b) FTIR spectrum showing the alkyne stretching modes for a crystalline TIPS-Pn film. A chemical structure of TIPS-Pn is included. (c) Ultrafast transient absorption spectra for the film shown at 1, 10, and 50 ps time delays. (d) Spectra shown over a larger timescale, which includes singlet fission and triplet-triplet annihilation. The dashed lines highlight different features, corresponding to triplet excitons (2126 cm^{-1}), the thermal effect (2124 cm^{-1}), and the ground state bleach (GSB, 2132 cm^{-1}).

Spectral slices were taken at several key time delays to illustrate the evolution of the vibrational features (see **Figure 6-4**). The inverted FTIR spectrum was found to match the transient absorption spectrum at 1 ps, indicating that the full distribution of TIPS-Pn molecules were perturbed upon photoexcitation. The positive feature at 2116 cm^{-1} prominently grew on the few picosecond time scale. In addition, the amplitude of the GSB signal increased

synchronously with the growth of the positive feature at 2116 cm^{-1} from 1 to 10 ps. Importantly, the peak position of the GSB peak did not shift during this timescale. Over a longer timescale (100's of picoseconds to nanoseconds), there was a peak shift of the GSB and the positive feature (to $\sim 2124\text{ cm}^{-1}$). From electronic spectroscopy measurements of TIPS-Pn, one would predict that the positive feature at 2116 cm^{-1} corresponds to independent triplet excitons, and that the 2124 cm^{-1} feature grows in on the timescale of triplet-triplet annihilation. In the following, each feature will be identified using independent measurements.

6.3. Identification of Dynamic Vibrational Signatures of TIPS-Pn Films

Temperature-dependent FTIR spectroscopy and nanosecond mid-IR transient absorption spectroscopy were used to assign the ultrafast vibrational (positive) features appearing in **Figure 6-4**.

6.3.1. Thermal effects on transient absorption spectra

Triplet-triplet annihilation^{7,31} is known to occur on the late picosecond to nanosecond timescale, and so the vibrational spectrum is likely dominated by thermal effects on these timescales. For example, thermal effects have been previously reported to contaminate transient absorption spectra in perylene diimide films, complicating spectral analysis and leading to false conclusions about singlet fission kinetics.³² In order to characterize thermal effects on the time-resolved vibrational spectrum of TIPS-Pn, temperature-dependent FTIR spectra of the crystalline TIPS-Pn were measured.

The FTIR spectra of a crystalline TIPS-Pn film were measured over the 295 to 395 K temperature range (see **Figure 6-5**). The spectra were found to red-shift and broaden as temperature was increased. To illustrate the thermal effect that would appear in transient

absorption measurements, the temperature-difference spectra were calculated and are also shown in **Figure 6-5**. Following an analysis method discussed by Rao et al.,³³ and using the specific heat measured for TIPS-Pn³⁴ along with the absorbed photon energy used in the ultrafast measurement, the maximum expected temperature change during the transient absorption experiment was estimated to be ~ 3 K. The 320 – 295 K temperature difference spectrum was used to approximately represent the thermal effect under such a temperature change. This spectrum, including a positive feature appearing around 2125 cm^{-1} , closely matched the transient absorption spectrum at 3 ns time-delay. This suggests that on the 100's of picoseconds timescale, the vibrational spectrum is dominated by the growth of a thermal effect that corresponds to a thermal energy dump arising from triplet-triplet annihilation.

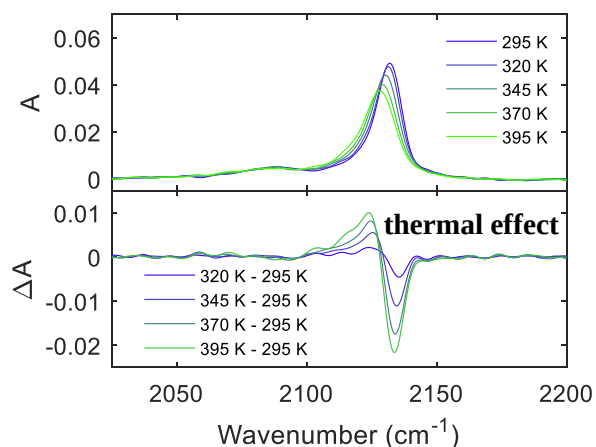


Figure 6-5: Temperature-dependent FTIR spectra of the alkyne stretch modes in a crystalline TIPS-Pn film shown as absorption spectra (top) or difference spectra (bottom).

6.3.2. Triplet exciton alkyne vibrational spectrum

In order to establish that the triplet excitons feature a vibrational feature around 2116 cm^{-1} in the ultrafast vibrational spectra, nanosecond transient absorption spectra were collected for solutions of TIPS-Pn dissolved in CCl_4 at either 1 mM or 25 mM. From concentration-

dependent absorbance spectroscopy, TIPS-Pn molecules were not found to electronically interact (see **Figure 6-6**).

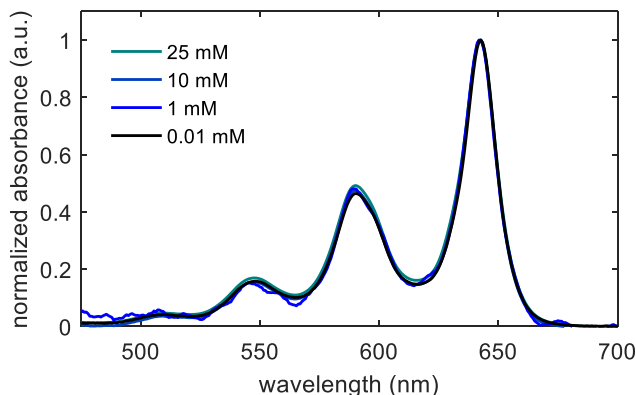


Figure 6-6: Normalized steady-state absorption spectra for different concentrations of solutions of TIPS-Pn dissolved in carbon tetrachloride.

Note that to avoid experimental artifacts, the most concentrated samples (1–25 mM) were measured as liquid films. At 1 mM concentration, only a small fraction of excited states undergo intersystem crossing to form triplet excited states. However, at 25 mM concentration, TIPS-Pn molecules efficiently undergo diffusion-limited singlet fission and can produce triplets in much higher yields.³ As seen in **Figure 6-7**, rapid triplet generation occurs for the 25 mM sample, as indicated by the fast growth of a transient absorption feature at the lower frequency side of the GSB.

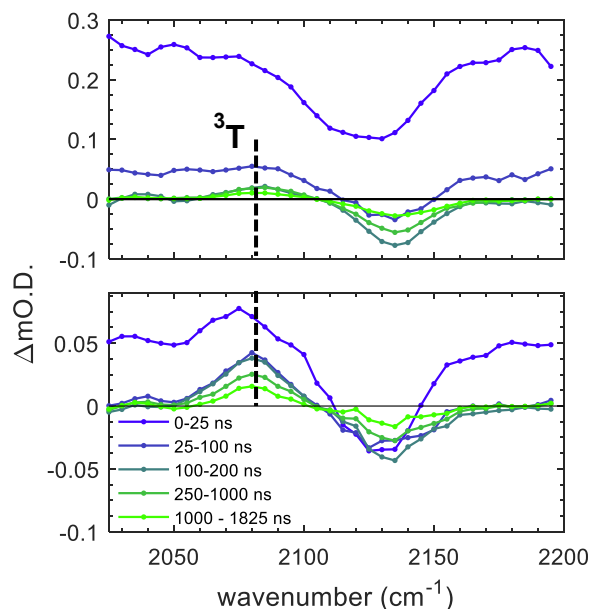


Figure 6-7: Nanosecond transient absorption spectroscopy of the alkyne stretching modes for a dilute (1 mM; top) and more concentrated (25 mM; bottom) solution of TIPS-Pn dissolved in carbon tetrachloride. The dashed black line indicated the vibrational absorption of the triplet states.

As such, triplet excited states of TIPS-Pn solutions were found to have an alkyne stretching mode appearing around 2080 cm^{-1} , redshifted from the ground state peak appearing at 2134 cm^{-1} .

The triplet vibrational spectra in **Figure 6-7** were measured in TIPS-Pn solutions, and so the vibration is not expected to have the same frequency as that in crystalline films due to a difference in solvent environment. As such, in order to quantitatively assign the 2116 cm^{-1} feature observed in the ultrafast spectra to triplet excitons, nanosecond transient absorption spectroscopy was next performed for a crystalline film (see **Figure 6-8**).

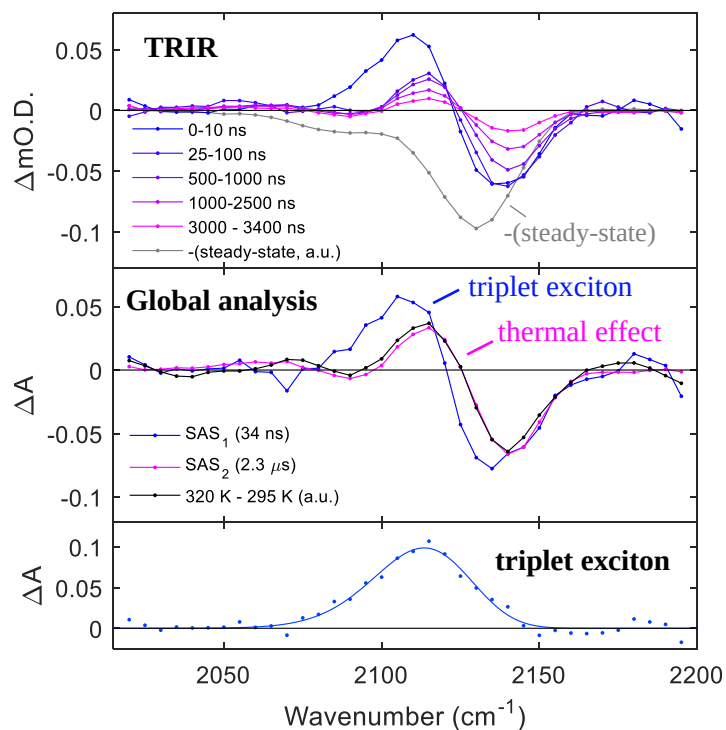


Figure 6-8: (Top) nanosecond transient absorption spectra measured for the alkyne stretching modes of a crystalline film of TIPS-Pn using 642 nm excitation. (Middle) convolution-fitted global analysis results, which employed a sequential kinetic model. The species-associated spectra (SAS) are provided along with their associated time constants. A 320 K – 295 K difference spectrum that was collected using identical wavenumber resolution is included for reference. (Bottom) the positive component of SAS1 (triplet absorption) is included, showing a peak center at $\sim 2116\text{ cm}^{-1}$.

Discernable features in the spectrum were observed, one from 0-10 ns and one after 25 ns, each featuring a positive peak having a different peak center. Global target analysis was performed for the data using a simplistic sequential (unimolecular) kinetic model representing: $T+T \rightarrow S_0+S_0^* \rightarrow S_0+S_0$, where S_0^* is a hot electronic ground state. Two species-associated spectra (SAS) were extracted, one of which corresponded to triplets, and second of which corresponded to a thermal effect. These results were confirmed by showing that the thermal effect (SAS2) matched a 320–295 K temperature difference spectrum of the steady-state absorption spectrum, measured using identical spectral bandwidth. Next, the positive feature

associated with triplets (in SAS1) was extracted by subtracting the GSB component, which revealed that the triplet vibrational frequency was $\sim 2116\text{ cm}^{-1}$. This quantitatively matched the transient absorption feature observed in the ultrafast measurement that was prominent on the early picosecond timescale.

To summarize the analysis of the temperature-dependent FTIR spectroscopy and the nanosecond transient absorption spectroscopy, it is concluded that the lower frequency feature (2116 cm^{-1}) arises from triplets that form on an early picosecond timescale. On the other hand, the higher frequency feature (2124 cm^{-1}) arises from a thermal effect that likely results from sample heating caused by triplet-triplet annihilation.

6.4. Spectral Modeling of the Ultrafast Vibrational Dynamics in TIPS-Pn Films

A spectral modeling procedure was developed to determine the population kinetics of the electronic species during singlet fission in crystalline TIPS-Pn films using their distinct vibrational features. The three basis spectra that were established for the spectral modeling are shown in **Figure 6-9**. The inverted (295 K) FTIR spectrum represented the GSB, and the 320–295 K difference spectrum represented the thermal effect. In order to describe the transient absorption feature of triplets, a third basis spectrum was introduced for which the peak width and peak center were allowed to vary, since this peak was not able to be determined at the spectral resolution of the ultrafast experiment. A skewed Lorentzian lineshape was used to describe the triplet vibrational spectrum since such a lineshape was found to best fit both the ground and the triplet vibrational peaks measured for crystalline TIPS-Pn in the FTIR and nanosecond transient absorption spectroscopy, respectively.

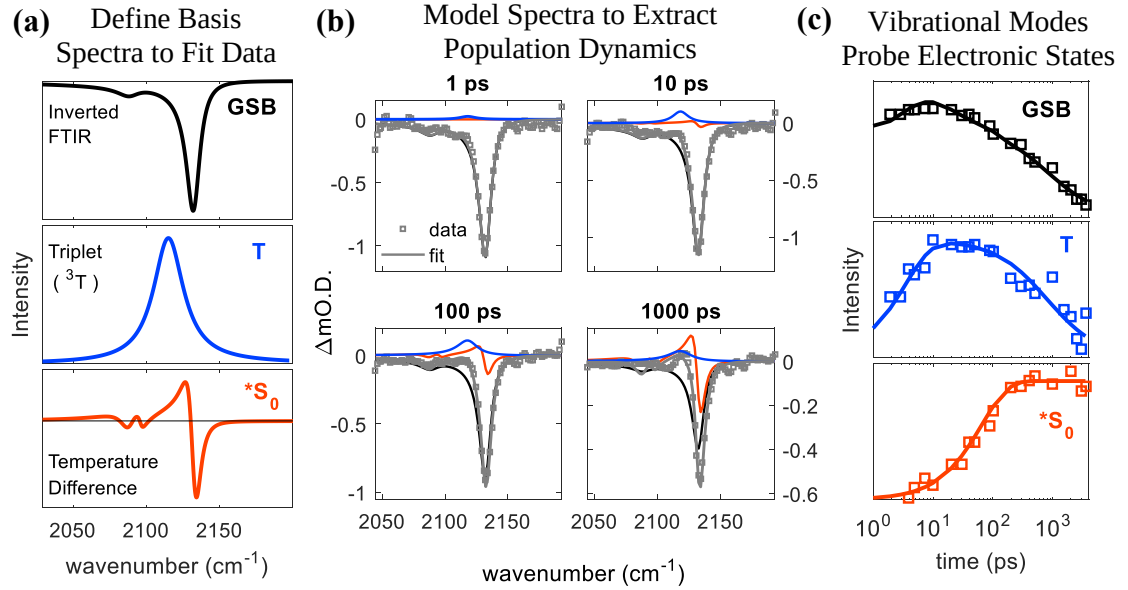


Figure 6-9: (a) Basis spectra that were used to describe the ultrafast transient absorption spectra of the asymmetric alkyne stretching mode in a crystalline TIPS-Pn film. (b) Examples of fits to the transient absorption spectra for a variety of time delays using a linear combination of the basis spectra. (c) Fit kinetics for the ground state bleach (GSB), triplet excitons (T), and thermal effect (*S_0) determined by fitting the spectrum at each time delay.

A nonlinear least squares method was used to fit the transient absorption spectrum at each time delay. The following spectral model was developed:

$$F(\tilde{\nu}) = n_1 P(\tilde{\nu}) + n_2 GSB(\tilde{\nu}) + n_3 \Delta A_{Temp}(\tilde{\nu}) + n_4 L(\tilde{\nu}) \quad (\text{eqn. 1})$$

$$P(\tilde{\nu}) = p_1 \tilde{\nu}^3 + p_2 \tilde{\nu}^2 + p_3 \tilde{\nu} + p_4 \quad (\text{eqn. 2})$$

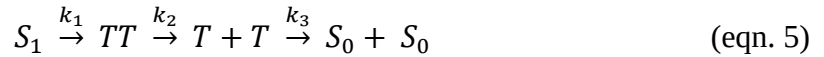
$$L(\tilde{\nu}) = \frac{2A}{\pi\gamma} \left(\frac{1}{1 + 4 \left[\frac{(\tilde{\nu} - \tilde{\nu}_0)}{\gamma} \right]^2} \right) \quad (\text{eqn. 3})$$

where $\tilde{\nu}$ is wavenumber, $P(\tilde{\nu})$ is a third-order polynomial, $GSB(\tilde{\nu})$ is taken as the inverted FTIR spectrum, $F(\tilde{\nu})$ is the total fit, ΔA_{Temp} is the FTIR temperature-difference spectrum (320 K - 298 K), $L(\tilde{\nu})$ is a skewed Lorentzian function³⁵ representing the triplet vibrational absorption spectrum, p_i are polynomial coefficients, n_i are scaling factors, $\tilde{\nu}_0$ is the peak center of the skewed Lorentzian, A is its area, and γ is its width determined by³⁵:

$$\gamma(\tilde{\nu}) = \frac{2\gamma_0}{1 + \exp[s(\tilde{\nu} - \tilde{\nu}_0)]} \quad (\text{eqn. 4})$$

where s is the skew parameter representing the degree of asymmetry in the Lorentzian peak, and γ_0 is the peak width.

The cubic polynomial represents the broad PIA “baseline” signal that overlaps with the vibrational feature. This baseline is fit concurrently with all other components, as seen in equation 1. After fitting each spectrum, the data are effectively “baseline-corrected” by subtracting the polynomial fit at each time delay. This process is exemplified in **Figure 6-3**. After baseline-correcting the transient absorption spectrum at each time delay, the areas of the remaining fit components were calculated and plotted against time (see **Figure 6-9**). The resulting fit kinetics are shown for the ground state bleach (GSB), the skewed Lorentzian (3T), and the thermal effect (*S_0). They were each fit using the following simplistic sequential kinetic model:



The population kinetics could then be modeled using the following coupled rate equations:

$$\frac{dS_1}{dt} = -k_1 S_1 \quad (\text{eqn. 6})$$

$$\frac{dTT}{dt} = +k_1 S_1 - \frac{1}{2} k_2 TT \quad (\text{eqn. 7})$$

$$\frac{dT}{dt} = +2k_2 TT - k_3 T^2 \quad (\text{eqn. 8})$$

where t is time. The spectral components could then be described as:

$$GSB(t) = S_1(t) + TT(t) + T(t) \quad (\text{eqn. 9})$$

$$L(t) = T(t) \quad (\text{eqn. 10})$$

A simple exponential growth model was used to describe the thermal effect:

$$\Delta A_{Temp}(t) = 1 - \exp(-kt) \quad (\text{eqn. 11})$$

where k is an exponential factor.

Examples of the transient absorption data and the best fit spectra, taken at 1, 10, 100, and 1000 ps time delays, are shown in **Figure 6-9**. The fitted basis spectra are also included for comparison. The population kinetics obtained from the spectral modeling procedure are also shown in **Figure 6-9**. The GSB kinetics exhibited a pulse-limited growth (not shown), followed by small continued growth in intensity over the early picosecond timescale. After this, the GSB intensity decayed on the time scale of triplet-triplet annihilation, indicating ground state recovery.^{36,37} The hot electronic ground state feature, *S_0 , was found to grow in slowly on the timescale of triplet-triplet annihilation. The triplet exciton feature, T, was found to grow in during an early picoseconds timescale. It then was found to decay over a similar time range as the loss of the GSB, due to triplet-triplet annihilation.

Triplet exciton absorption, as probed using the alkyne stretching vibration, did not appear until the few-picosecond timescale, unlike measurements in the visible spectral range that rely on the $T_1 \rightarrow T_n$ electronic transition (see **Figure 6-10**). Since both CTP intermediates and independent triplets have overlapping electronic transitions,^{25,26} the growth of the “triplet absorption signal” in the visible spectral region does not necessarily represent the true triplet population kinetics. Recently, it was shown using ultrafast near-IR spectroscopy that the singlet fission mechanism includes two CTP intermediate states, the interacting $^1(TT)$ and non-interacting $^1(T...T)$ CTPs.²⁶ In this study, it was concluded that CTP states form on a sub-picosecond timescale, after which the triplet pair spatially separates on the few picoseconds timescale. This kinetic scheme is highlighted in **Figure 6-10**.

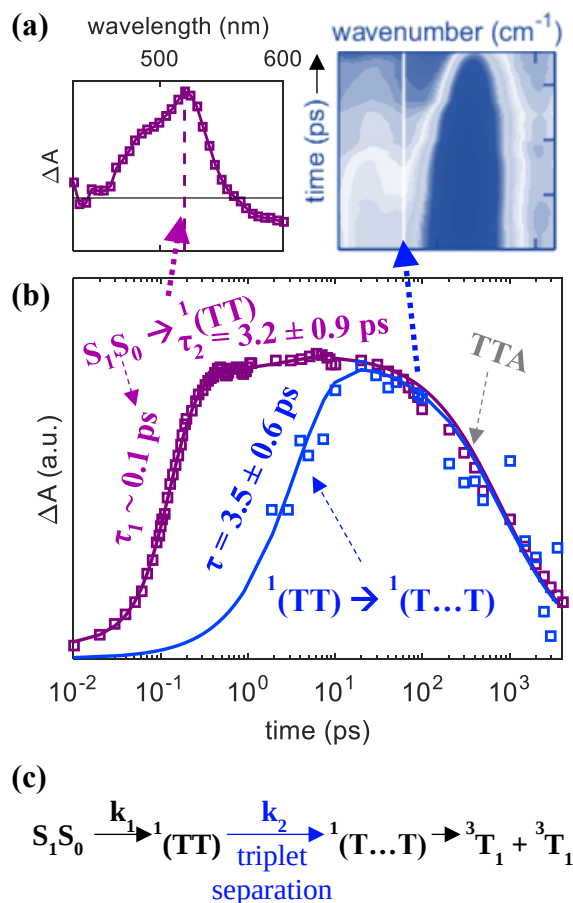


Figure 6-10: (a) Transient absorption spectra for a crystalline TIPS-Pn film probed in the (left) visible and (right) mid-IR spectral regions. (b) Transient absorption kinetics corresponding to the triplet absorption features in either the visible (electronic signal) or mid-IR (vibrational signal) spectral regions. Time constants are provided for reference. (c) Kinetic model for singlet fission. The second rate constant, k_2 , describes the triplet pair separation step, which is captured by the kinetics of the vibrational signal, and the second component of the electronic signal.

Although CTP formation is known to occur in crystalline TIPS-Pn on a sub-picosecond timescale, the time-resolved vibrational spectrum at 1 ps did not contain evidence of triplet excitations. The GSB indicates the concentration of ground state molecules that have been perturbed by photoexcitation. Using the GSB, it was determined that the concentration of perturbed ground state molecules has already reached its highest value by 1 ps, consistent with rapid conversion of singlet excitons into CTP states. As a result, CTP formation cannot explain the continued growth of the GSB signal on the few picoseconds timescale. In recent work (see

Chapter 5), it was shown that a residual population of singlet excitons that cannot undergo singlet fission does not form in crystalline films of TIPS-Pn. Therefore, the observation of continued GSB growth on a few picoseconds timescale suggests that there is an overlapping positive feature at the same frequency and that decays on this timescale. This GSB growth occurs concurrently with the growth of the positive feature at 2116 cm^{-1} arising from triplets, and with the slow growth component of the triplet electronic absorption. This latter observation was clarified in previous work, which showed that the absorption band of CTP states either have a small redshift in absorption maximum or an increase in oscillator strength.¹⁵

The TIPS-Pn solution data could be used to determine the vibrational spectrum of singlet excited states. As seen in **Figure 6-11**, the bleach intensity measured for the 1 mM sample is not as large as expected. Since the triplet yield should be very low (a few %) in this solution, the decay of the GSB should be much larger in magnitude as the singlet excited states relax. In particular, 99% of the excited singlet population relaxes by $\sim 50\text{ ns}$, and so the GSB intensity should, as a result, decay very strongly. Since this was not true, a positive feature must have been present at early times before the singlet excited states have decayed. From this observation, it is concluded that singlet excited states must have a vibrational absorption peak with the same peak center as that of the GSB.

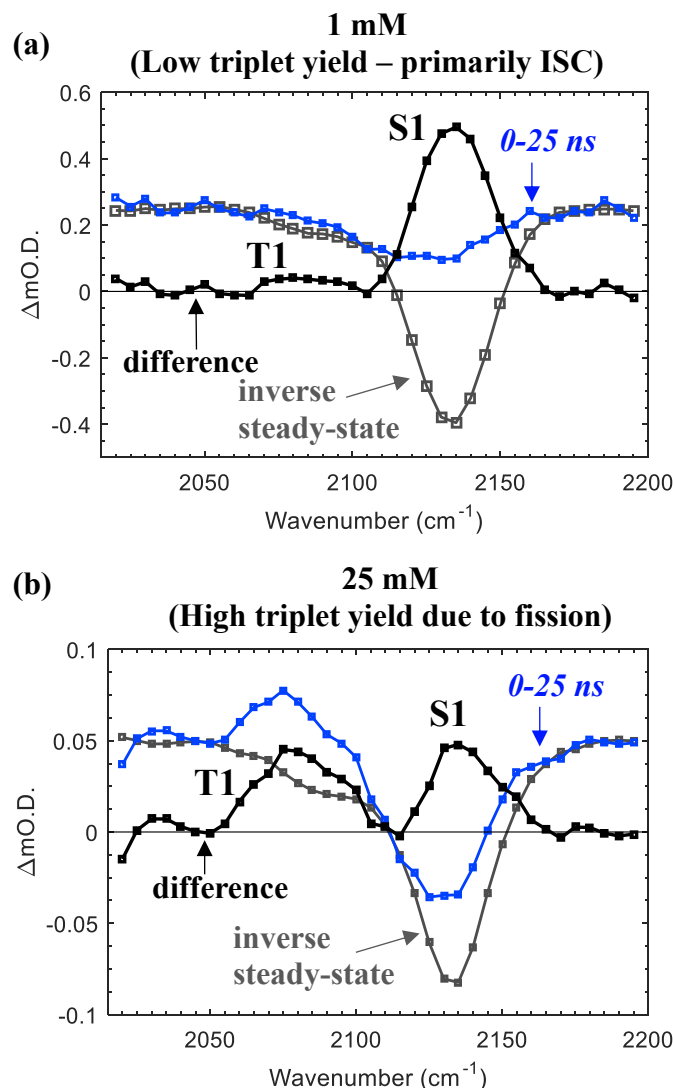


Figure 6-11: Determining the vibrational absorption spectrum of the S_1 state for a **(a)** dilute (1 mM) and **(b)** concentrated (25 mM) TIPS-Pn solution with carbon tetrachloride as the solvent. The S_1 vibrational spectrum is obtained by taking the difference between the transient absorption spectrum (integrated between 0–25 ns) and the inverse steady state absorption spectrum (arbitrarily scaled).

The positive part of the vibrational spectrum of the singlet excited states (and triplet states) was approximated for the TIPS-Pn solutions. In particular, the inverted steady-state absorption spectrum was scaled and subtracted from the transient absorption spectrum averaged between 0–25 ns. The results revealed that the singlet excited state (S_1) had a peak at 2135 cm^{-1} , which was very close to the ground state bleach (2134 cm^{-1}). In addition, the triplet (T_1) peak was

again identified with a peak center at 2080 cm^{-1} . A summary of these results and the results for a crystalline TIPS-Pn film is provided in **Table 6-1**.

Table 6-1: Experimentally determined peak positions for transient absorption features corresponding to the asymmetric stretch mode of the alkyne in TIPS-Pn solutions and films

electronic state	CCl_4 solution	crystalline film
S0 (GSB)	2134 cm^{-1}	2132 cm^{-1}
S1	2135 cm^{-1}	---
T1	2080 cm^{-1}	$\sim 2116\text{ cm}^{-1}$

6.5. Conclusions and Significance

CTP state separation during singlet fission was monitored using time-resolved vibrational spectroscopy to directly probe independent triplet excitons. In addition, this process was observed to occur on a few picosecond timescale in crystalline TIPS-Pn films. Comparing the triplet kinetics monitored using vibrational and electronic absorptions, it was confirmed that the slower growth component of the $T_1 \rightarrow T_n$ absorption kinetics reported in the literature arises from dissociation of CTPs. After CTP separation, triplet-triplet annihilation was measured, which resulted in formation of hot electronic ground states. The alkyne stretch frequency was found to depend sensitively on temperature, and so the time-resolved vibrational spectroscopy measurements were also able to monitor the deposition of thermal energy accompanying triplet-triplet annihilation.

Ultimately, this work suggests that ultrafast vibrational spectroscopy provides a new approach for examining the dynamics of electronic states during singlet fission. Most importantly, it was shown using TIPS-Pn that time-resolved vibrational spectroscopy can be

used to monitor the separation of CTPs. Since all organic molecules possess measurable vibrational modes, time-resolved vibrational spectroscopy offers to be a useful method for examining the singlet fission mechanism in general. This work showed that vibrational spectroscopy can provide insights into how CTPs evolve into independent, multiplied triplet excitons in new singlet fission sensitizers that are currently under development.

6.6. Outlook: Slow Triplet Separation in Amorphous Materials

The work presented in this chapter provides a new method for monitoring independent triplet excitons during singlet fission. Importantly, the separation of the CTP intermediates can be indirectly probed by monitoring the time-dependence of the independent triplet state absorption. As shown later in Chapter 7, triplet transfer is the mechanism for CTP separation in crystalline TIPS-Pn films. In amorphous materials consisting of disordered molecules, triplet transfer would occur at a much slower rate because the average intermolecular orbital overlap coupling would be much weaker. Because of this, it is hypothesized that CTP separation occurs at a much slower rate in amorphous films of TIPS-Pn.

The ultrafast vibrational spectrum was measured for an amorphous and a crystalline film of TIPS-Pn (see **Figure 6-12**). The electronic absorption of triplets is also shown for comparison. From the electronic absorption kinetics, it appears that the triplet excitons are formed in both amorphous and crystalline films by about 20 ps. However, analysis of the time-resolved vibrational spectrum for the amorphous film (using the same analysis method as presented in this chapter) reveals that independent triplet excitons do not form until a much later timescale (hundreds of picoseconds to nanoseconds). This preliminary result suggests that amorphous materials take a much longer time to dissociate CTPs, and so the ultimate triplet yield may be

lessened if there are other kinetically-competing excited state pathways available. It is the hope of this chapter that future work will also use time-resolved vibrational spectroscopy to study amorphous films further.

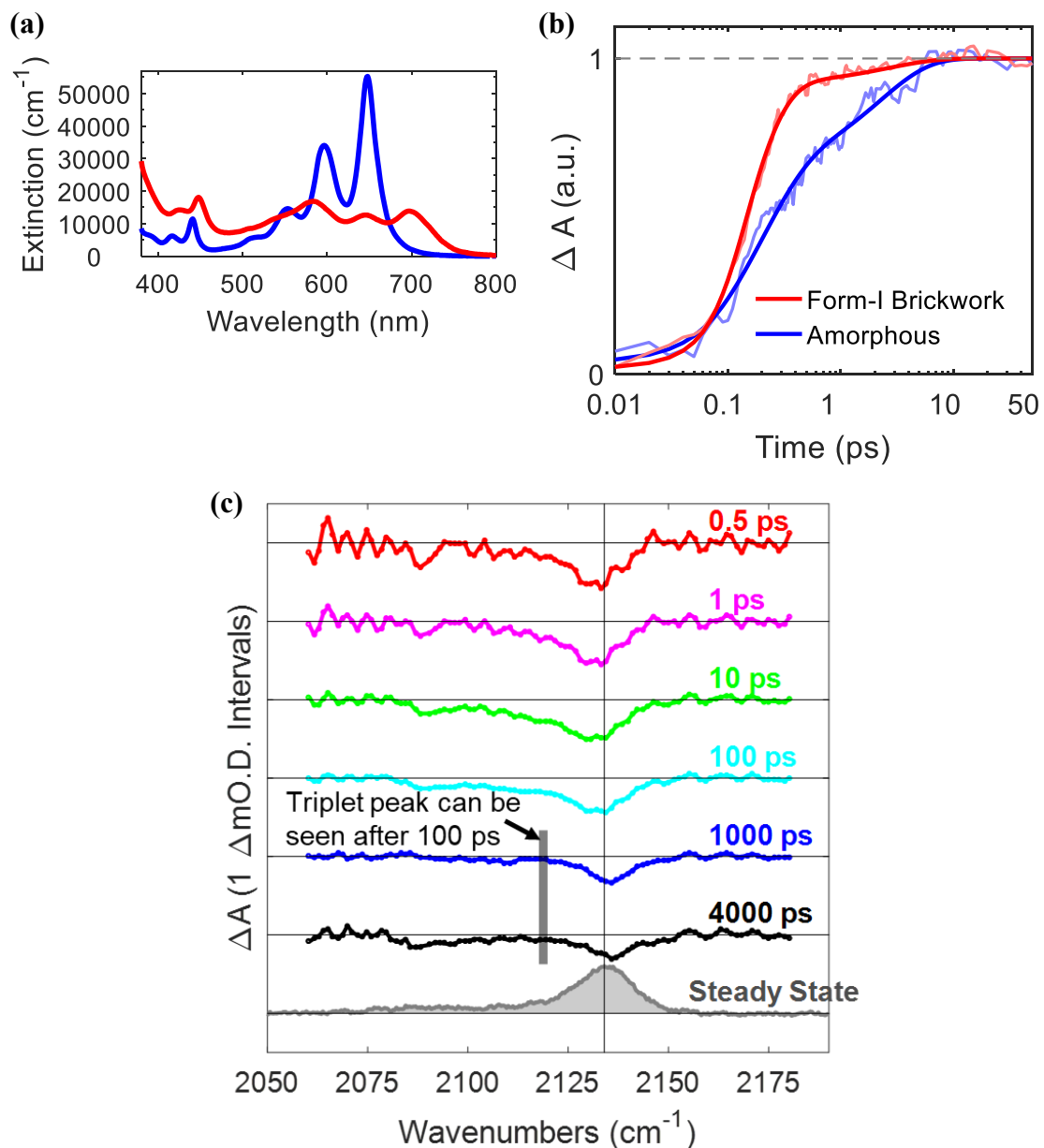


Figure 6-12: (a) Absorption spectra for an amorphous and crystalline (form-I brickwork) film of TIPS-Pn. (b) Ultrafast triplet state absorption ($T_1 \rightarrow T_n$) kinetics measured in the visible spectral region at 508 nm and 520 nm for the amorphous and crystalline films, respectively. (c) Ultrafast vibrational absorption spectra for the amorphous film shown at several time delays. The expected location of the triplet vibrational absorption feature is indicated.

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CHAPTER 7

Triplet Transfer Mediates Triplet Pair Separation during Singlet Fission in a Pentacene Derivative

This chapter focuses on how the second step of singlet fission, dissociation of correlated triplet pair (CTP) intermediates, is influenced by specific molecular packing arrangements. Recently, it has been theoretically¹ and experimentally² suggested that the rate of triplet excitation transfer is important for the physical separation of CTPs. This implies that electronic orbital overlap interactions play a significant role in CTP dissociation. As a consequence, molecular packing arrangements not only influence the first step of singlet fission (see Chapter 3 for discussion), but also the second step. However, further experimental proof of triplet transfer as the mechanism for CTP dissociation is needed. This chapter satisfies this need using crystal polymorphs of a pentacene derivative, and provides structural insight into how this process is controlled by molecular packing arrangements.

Most theoretical and experimental work to date investigates how intermolecular packing geometries influence the first step of singlet fission, formation of the CTP. However, an understanding of how packing structures influence the second step is lacking. A universal understanding of how a given molecular packing structure influences both steps is critical for the developing new singlet fission sensitizers, since the first step alone does not guarantee the multiplication of excitation. In another view, it is feasible that certain packing structures favor the first step, but prevent the second step. The results of the work presented herein motivate the inclusion of calculating triplet transfer couplings when considering which packing structures are favorable for efficient singlet fission.

This chapter was adapted from the publication: Grieco, C., Doucette, G.S., Munro, J.M., Kennehan, E.R., Lee, Y., Rimshaw, A., Payne, M.M., Wonderling, N., Anthony, J.E., Dabo, I., Gomez, E.D., and Asbury, J.B., “Triplet Transfer Mediates Triplet Pair Separation During Singlet Fission in TIPS-Pentacene”, *Adv. Func. Mater.*, **2017**, 1703929, which has been rephrased in the context of this dissertation.

7.1. Introduction

Singlet fission promises to increase the performance of low bandgap solar cells by preventing thermalization losses associated with high energy photons.³⁻⁸ Although an understanding of the singlet fission mechanism continues to improve, the development of practical design criteria for new singlet fission sensitizers is needed. In particular, knowledge of the interplay between sensitizer structure and photophysical properties is necessary to ensure material compatibility with other components of the devices.⁹⁻¹¹ In Chapter 4, singlet fission and triplet-triplet annihilation was shown to sensitively depend on the morphology of the films. Quantum mechanical theory discussed in Chapter 1 and Chapter 3 predicts that singlet fission and triplet transport depend on the types of intermolecular interactions among organic molecules like TIPS-Pn. In particular, the rates depend on intermolecular electronic coupling, which significantly includes orbital overlap interactions.^{12,13}

The singlet fission mechanism, consisting of multiple steps leading to mobile triplet excitons, has been recently described both experimentally² and theoretically¹⁴. The first step, correlated triplet pair formation, has been studied extensively and the dependency on exciton delocalization and exergonicity are well-understood.¹³ However, the second step, the formation of independent triplet excitons via triplet pair separation, has only recently been

addressed, despite having influence on the ultimate yield of the multiplied excitons. Recently, it has been theorized¹⁴ that triplet pair separation is driven by triplet excitation energy transfer, which may be sensitive to short-range solid-state morphology. However, there lacks experimental evidence for this mechanism, and how different solid-state molecular packing arrangements can influence its efficiency.

To assess the relationship between singlet fission and triplet transport with molecular packing structure, 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-Pn) was used as a model system because it has been shown to form multiple polymorphic crystal structures that are spectroscopically distinguishable.^{15,16} In addition, the exergonic nature of singlet fission in TIPS-Pn temporally separates the multiple reaction steps involved, facilitating spectroscopic measurement.² Two particular useful polymorphs of TIPS-Pn, termed Form-I and Form-II brickwork, were reported by Diao et al. in solution-sheered films.^{15,17} However, such films were significantly thinner than the ~100 nm thickness desirable for optical spectroscopy measurements. In Chapter 3, an alternate spin-coating method for isolating similar crystal polymorphs in thicker films was discussed.

In this work, crystalline films consisting of the Form-I and Form-II brickwork polymorphs were studied, providing experimental evidence that the dominant mechanism of correlated triplet pair (CTP) separation in TIPS-Pn is triplet transfer. Grazing incidence wide angle X-ray scattering (GIWAXS) was performed for both types of films in order to solve the crystal structure of each polymorph. Using whole pattern fitting and molecular mechanics, the unit cell parameters and crystal packing structures were solved. Density functional theory (DFT) calculations on molecular pair states in the crystal structures were used to explain their differences in CTP separation and triplet diffusion. Such analyses motivate the use of simple

computations for any conceived molecular packing structure as an *a priori* screening procedure for new singlet fission sensitizer materials.

7.2. Experimental Methods

Film Preparation. For all ultrafast spectroscopy measurements, films were spin-cast for 1 min at 1600 rpm onto 2.5 cm diameter sapphire substrates from 20 mg/mL solutions of TIPS-Pn in dichloromethane. The amorphous films that formed were subsequently annealed using either solvent or thermal annealing to produce nanocrystalline films consisting of the Form-I or Form-II brickwork polymorphs, respectively. For solvent annealing, the films were exposed to isopropylalcohol (IPA) vapor for 2.5 hrs in the apparatus detailed in Chapter 3. For thermal annealing, amorphous films were heated for 1 min at 80°C.

Optical Spectroscopy. Ultrafast 2-color visible-pump/visible-probe spectroscopy was performed.¹² Briefly, the excitation pulse was 650 nm, with an absorbed energy density set to $\sim 12 \mu\text{J}/\text{cm}^2$ for each sample. For the probe pulse, a white-light supercontinuum was generated and filtered to limit spectral range exposed to the films. After transmitting the films, the probe was filtered using a 10 nm FWHM dielectric bandpass filter to obtain spectral resolution. The filter angle was adjusted to achieve a transmitted wavelength of ~ 520 nm. The instrument response function had a FWHM of ~ 170 fs.

Nanosecond visible-pump/visible-probe transient absorption spectroscopy was performed using a laser flash photolysis system.^{12,18} Briefly, the excitation was tuned to 650 nm, with a pulse energy adjusted so that each film had $\sim 10 \mu\text{J}/\text{cm}^2$ absorbed energy density. The probe was set to 517 nm using a monochromator with slits adjusted to achieve a 10 nm effective spectral bandwidth.

Steady-state UV-visible spectrometry was performed using a commercial instrument (Beckman, DU 520; Brea, CA).

X-ray Diffractometry. Grazing-incidence wide angle X-ray scattering (GIWAXS) measurements were performed at beamline 7.3.3 of Advanced Light Source in Lawrence Berkeley National Laboratory, operating at an X-ray energy of 10.0 keV ($\lambda = 1.2398 \text{ \AA}$). Scattering data were acquired using a 0.15° incident angle. For all measurements, films were prepared on silicon substrates.

Molecular packing structure optimizations. Molecular packing structures were determined using an iterative geometry optimization using BIOVIA Materials Studio Forcite software. The unit cell geometries were optimized using the Compass force-field,¹⁹⁻²¹ similar to a previous report on TIPS-Pn.¹⁶ The unit cell parameters were fixed during all optimizations.

Charge Transfer Integral Computations. The TIPS-Pn monomer was optimized using the Gaussian 09 software with B3LYP/cc-pVTZ, adapting from previous computational studies of pentacene.^{22,23} Molecular pair structures were produced using the optimized monomers with the long- and short-axis intermolecular slippages obtained from the unit cell optimizations. Charge transfer integrals were calculated using the energy splitting method, with the HOMO and LUMO energies as computed using DFT calculations at the LRC- ω PBE/cc-PVTZ level.

7.3. Transient Absorption Spectroscopy of TIPS-Pn Polymorphs

Solvent and thermal annealing methods were used to isolate distinct polymorphs of TIPS-Pn in spin-coated films thick enough for ultrafast spectroscopic measurements. The thickness limit for thermally annealed films was tested using absorbance spectroscopy, which was used to determine if the “thermally-annealed polymorph” was formed in isolation. The extinction

coefficients of the films (see Chapter 3) were used to calculate the film thickness from their absorption spectra (**Figure 7-1**).

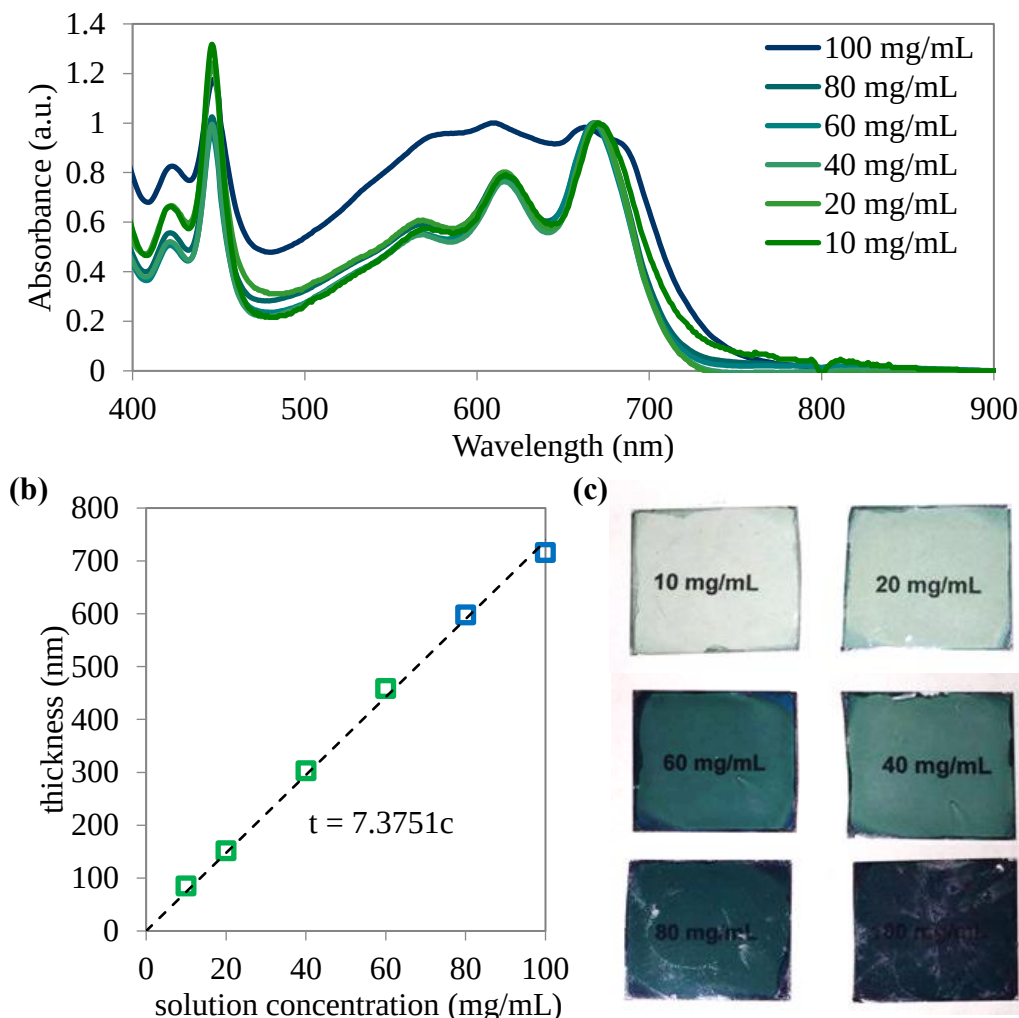


Figure 7-1: **(a)** Absorption spectra of thermally-annealed TIPS-Pn films. Films were spin-cast from solutions of TIPS-Pn in dichloromethane at 1000 rpm and annealed at 80° C for 10 min. **(b)** Dependence of the film thickness on concentration used for spin-casting. Thicknesses were determined using the extinction coefficient at 550 nm. Blue data points represent films that did not contain isolated Form-II brickwork polymorph. **(c)** Photographs of all of the films.

All of these films were made by spin-coating TIPS-Pn onto glass slides at 1000 rpm for a variety of concentrations ranging from 10 – 60 mg/mL. Slower spin speeds resulted in thicker, but non-uniform films, and so 1000 rpm was used as a standard spin speed. All films were

thermally annealed at 80°C for 10 minutes. The thickest film made consisting of pure Form-II polymorph was ~460 nm, which appeared to be limited by the solubility. Using higher concentrations resulted in a mixture of polymorphs, which can be seen visibly (photographs in **Figure 7-1**). Crystallization was observed to occur at the liquid-air interface immediately before spinning the substrate, which then became deposited on the film. Grazing-incidence X-ray diffractometry (GIXRD), displayed in **Figure 7-2**, was performed using a PANalytical X'Pert Pro MPD diffractometer (PANalytical; Almelo, Netherlands) with a 1° incidence angle and Cu K α radiation.

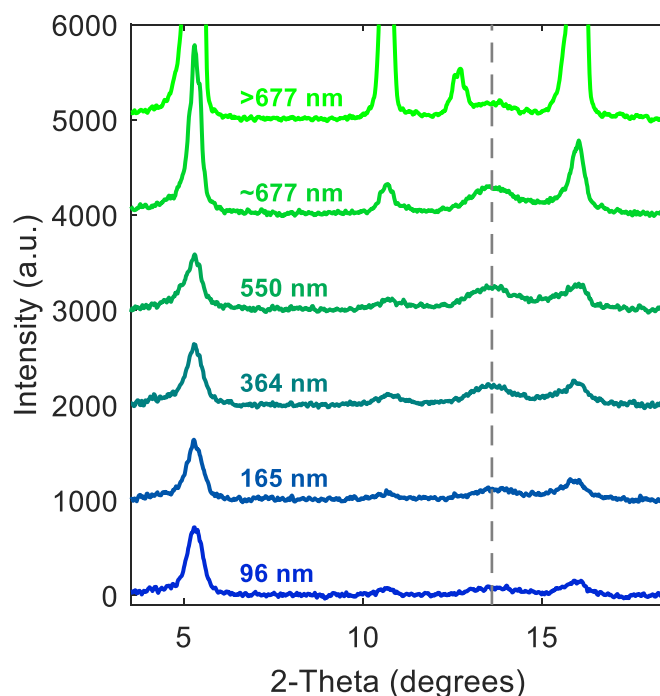


Figure 7-2: (a) GIXRD patterns for thermally annealed TIPS-Pn films with different thicknesses, which are labeled by each trace. The peak characteristic of the Form-II brickwork is indicated by the gray dashed line. The baseline was removed from all of the patterns. The substrates used were glass slides.

The x-ray beam spot size was reduced to approximately 1 cm x 1 cm using an assortment of optics. Consistent with the results from absorption spectroscopy, the Form-II brickwork polymorph was formed in isolation for thicknesses up to ~460 nm.

The absorption spectra of thermally annealed (TA) and solvent annealed (SA) films (see Chapter 3) show that the 0-0 absorption of the SA annealed is redshifted. This suggests that the molecules in the SA film experience stronger intermolecular coupling interactions. Triplet transfer is strongly controlled by orbital overlap interactions between molecules because it involves Dexter exchange interactions that require short-range direct wavefunction overlap between the molecules involved.²⁴ A quantitative analysis of the short-range intermolecular interactions between the TIPS-Pn molecules in each polymorph structure would lead to the prediction of their singlet fission and triplet transport characteristics.^{25,26} Notably, controlling polymorphism simplifies this process because intermolecular interactions can be modified without changing the chemical structure of the molecules.

Using transient absorption spectroscopy, the $T_1 \rightarrow T_n$ transition was used to track the formation of triplets (**Figure 7-3**) in the TA and SA films of TIPS-Pn. Kinetics traces measured at the λ_{max} of the peak (~ 520 nm) were used to track triplet absorption growth (singlet fission) and decay (triplet-triplet annihilation).

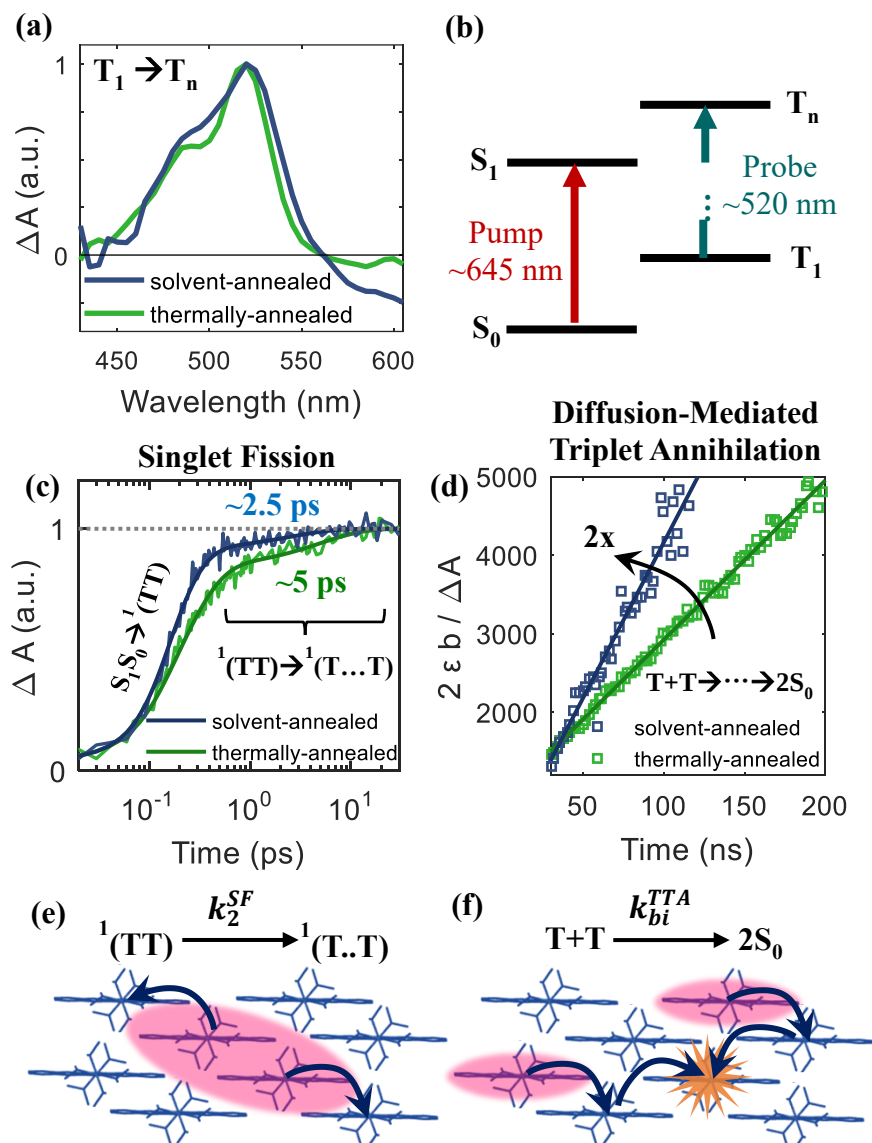


Figure 7-3: (a) Triplet transient absorption spectra ($T_1 \rightarrow T_n$) for TIPS-Pn films. (b) Simple energy level diagram for TIPS-Pn, highlighting the pumped and probed transitions used in the transient absorption measurements. (c) Ultrafast singlet fission dynamics measured through triplet absorption growth kinetics for the solvent and thermally annealed films. The two steps of singlet fission are indicated and the time constants for the second reaction step are labeled for each kinetics trace. The solid lines are fits to the data consisting of a sum of two exponential growth functions. (d) Nanosecond triplet decay kinetics plotted in the $2\epsilon b / \Delta A$ versus time form for both films. The solid lines are linear fits to the data, with slopes equivalent to the bimolecular rate constants. (e) Illustration of the dissociation mechanism of the correlated triplet pair intermediate. (f) Illustration of the triplet diffusion process that mediates triplet-triplet annihilation.

The pump wavelength used was ~ 645 nm, which excited the molecules from $S_0 \rightarrow S_1$. The ultrafast triplet absorption kinetics exhibited biexponential growth, consisting of a <100 fs time

constant component and a slower component with a few picosecond time constant. These time constants have been associated with the two sequential steps of singlet fission. The triplet growth kinetics were fit using a biexponential growth function to determine the time constants for each film to assess their singlet fission kinetics (see Chapter 4 for more details). **Table 7-1** summarizes the resulting fit parameters in terms of rate constants (inverse time constants).

Table 7-1: Comparison of rate constants for the second step of singlet fission and for triplet-triplet annihilation for the solvent and thermally annealed TIPS-Pn films

Rate Constant	Solvent Annealed Film (Form-I)	Thermally Annealed Film (Form-II)	Relative Rate Constant (Form-I:Form-II)
Singlet Fission $k_2^{SF} \text{ (s}^{-1}\text{)}$	$(3.9 \pm 0.5) \times 10^{11}$	$(2.02 \pm 0.08) \times 10^{11}$	1.9 ± 0.1
Triplet annihilation $k_{bi}^{TTA} \text{ (M}^{-1} \text{s}^{-1}\text{)}$	$(4.0 \pm 0.2) \times 10^{10}$	$(2.0 \pm 0.1) \times 10^{10}$	2.0 ± 0.1

Most importantly, the timescale of the slower, picosecond component has been related to the spatial separation of CTP intermediates.^{2,13,14} Between the TA and SA films, there was a difference in time constant of about a factor of two, implying slower CTP separation in the TA film.

Following singlet fission, the multiplied triplet excitons are able to diffuse independently.^{8,14} Under the excitation energy densities used in this study ($\sim 10 \text{ } \mu\text{J}/\text{cm}^2$ absorbed by the samples), the triplets are known to undergo triplet-triplet annihilation, which occurs on the nanosecond time scale.¹² When plotted in $2\epsilon b/\Delta A$ versus time t form, the triplet decay kinetics exhibit linearity, which is characteristic of a bimolecular decay process, such as

exciton-exciton annihilation. A bimolecular decay kinetic model^{8,27-29} has been used in the context of singlet fission to describe triplet-triplet annihilation, which is expressed as:

$$\frac{d[T]}{dt} = -\frac{[T]}{\tau} - \frac{1}{2}k_{bi}^{TTA}[T]^2 \quad (\text{eqn. 1})$$

where [T] is the concentration of triplets, τ is the natural triplet lifetime, k_{bi}^{TTA} is the second-order decay constant, and t is time (see Chapter 4 for more details). As a result, the slope of the $2\epsilon b/\Delta A$ versus t plot of the transient absorption data is equivalent to the bimolecular decay constant. The results of linear fits to the nanosecond kinetics in **Figure 7-3** are tabulated in **Table 7-1** for both the TA and SA films. Under the Smoluchowski theory of diffusion-limited reactions (see Chapter 4 for details) the bimolecular decay constant is directly proportional to the triplet diffusion constant. As a result, the ratio of the bimolecular rate constants between the SA and TA films qualitatively provides their relative triplet diffusion constants (assuming they possess the same triplet capture radius). It was found that triplets in the TA films diffused at a rate twice as slow as those in the SA films.

The comparison of the singlet fission and triplet-triplet annihilation rate constants in **Table 7-1** provides insight into the assignment of the second step of singlet fission. The <100 fs component of the triplet growth kinetics has been assigned to formation of correlated triplet pair (CTP) intermediates in TIPS-Pn and other pentacene derivatives.² The precise mechanism of the picosecond component has been debated. The relative rate constant for the SA and TA films was identical to the relative rate constant for triplet-triplet annihilation, indicating that CTP separation and triplet diffusion have a common elementary mechanism. Because triplet-triplet annihilation is a diffusion-mediated reaction, it is controlled by the rate of triplet transfer between molecules. Since this and CTP separation share a common elementary mechanism, it is concluded that CTP separation must also occur via triplet transfer.

The assignment of the second component of the triplet growth kinetics to triplet pair separation via triplet transfer is now rationalized through an analysis of the triplet diffusion coefficients determined from the triplet-triplet annihilation results. Since the triplet-triplet annihilation process depends on elementary triplet transfer events, the triplet transfer rate may be approximated using the annihilation rate constants. Using eqn. 20 from Chapter 4, the triplet diffusion coefficient may be determined if the triplet-triplet annihilation (bimolecular) rate constant and triplet capture radius are known. Taking the bimolecular rate constants obtained from analysis of the nanosecond transient absorption kinetics, and assuming a capture radius of 0.4 nm (see Chapter 4 for details), the triplet diffusion coefficient for the SA and TA films are approximated to be $6.6 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$ and $3.3 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$, respectively. Assuming an elementary triplet transfer event results in an area traveled equal to the square of the approximate pi-pi distance ($\sim 0.32 \text{ nm}$), then the elementary triplet transfer rates for the SA and TA films are approximated to be $6.6 \times 10^{10} \text{ s}^{-1}$ and $3.3 \times 10^{10} \text{ s}^{-1}$, respectively. These values are close to the second rate constants determined for the triplet growth kinetics (see **Table7-1**). Note that the calculation of the bimolecular rate constants is sensitive to the precise quantification of the molar absorption coefficients of the $T_1 \rightarrow T_n$ transition probed (see Chapter 4 for details), and so the precise values for the elementary triplet transfer event are very closely dependent on how accurate the values of the molar absorption coefficients were. In the future, it is desirable to more accurately quantify the molar extinction coefficients for $T_1 \rightarrow T_n$ for the SA and TA films.

7.4. Determining the Crystal Packing Structure of TIPS-Pn Polymorphs

7.4.1. Determining unit cell parameters for TIPS-Pn polymorphs

GIWAXS measurements were performed for both SA and TA TIPS-Pn films. **Figure 7-4** shows geometrically-corrected diffraction patterns for both films measured at 0.15° incidence angle.

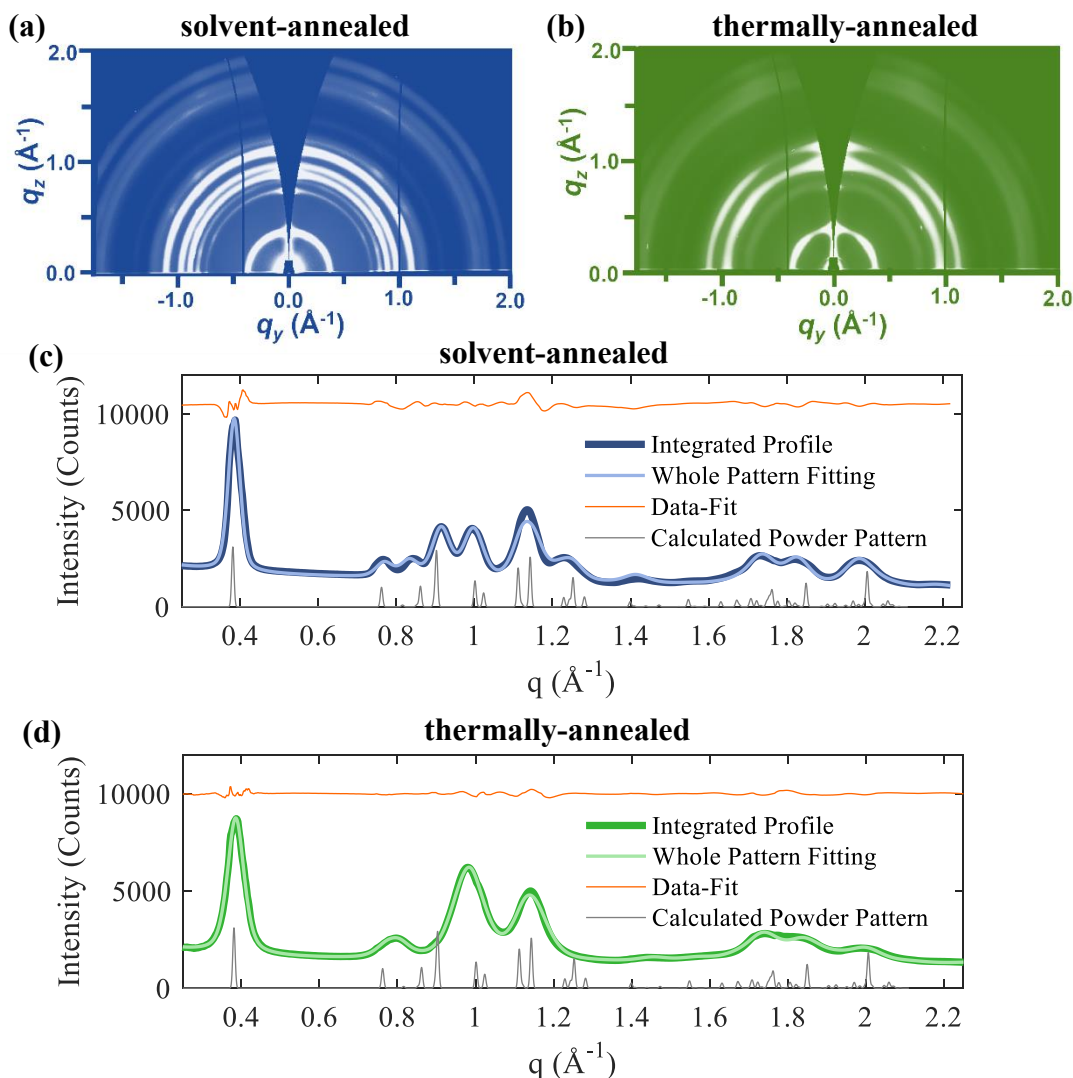


Figure 7-4: (a) GIWAX diffraction patterns for (a) solvent annealed and (b) thermally annealed TIPS-Pn films. The corresponding angularly-integrated patterns for the (c) solvent annealed and (d) thermally-annealed films.

The patterns were circularly-integrated and subsequently corrected in q -space using an AgBe standard that was measured in the Bragg-Brentano geometry. The MDI JADE XRD Analysis

Software was used to fit the integrated patterns. The whole pattern fitting (WPF) tool with Rietveld refinement was utilized to extract the unit cell parameters for both the TA and SA films. The results of the WPF procedure and the residuals of the fit are included in **Figure 7-4**. The calculated powder pattern is included for reference. The solved unit cell parameters are provided in **Table 7-2** for both films in comparison to those of the single-crystal structure.³⁰

Table 7-2: Crystal lattice parameters determined from whole pattern fitting of the integrated GIWAX patterns for TIPS-Pn polymorphs

Parameter	Single Crystal	Solvent Annealed Film	Thermally Annealed Film
a	7.565 Å	7.81 ± 0.01 Å	8.62 ± 0.03 Å
b	7.750 Å	7.69 ± 0.01 Å	7.28 ± 0.04 Å
c	16.835 Å	16.86 ± 0.01 Å	17.03 ± 0.04 Å
α	89.15°	88.57 ± 0.07°	85.90 ± 0.20°
β	78.42°	76.00 ± 0.10°	73.50 ± 0.30°
γ	83.63°	81.60 ± 0.10°	67.90 ± 0.20°

The Rietveld goodness of fit estimate, χ^2 , was 2.63 and 1.07 for the SA and TA films, respectively. The low values of χ^2 (approaching unity) indicate that the data are fitted without over-parameterization. Comparing the unit cell parameters, the SA film shows similar parameters to the single crystal structure, consistent with previous assignments to the “2D-brickwork” structure (see Chapter 3). On the other hand, the TA film showed significant differences in the a and γ parameters, suggesting there was a change in the molecular packing structure. Below, molecular mechanics were used to solve the specific crystal packing structures for the polymorphs isolated in the TA and SA films. Afterwards, the solved packing

structures are assessed and related to the differences in singlet fission and triplet-triplet annihilation rate constants.

7.4.2. Determining crystal packing structures of TIPS-Pn polymorphs

To determine the packing structures of the crystal polymorphs isolated in the SA and TA films, unit cell geometry optimizations were performed using molecular mechanics calculations with the Compass force field.¹⁹⁻²¹ Such an optimization procedure was adapted from that reported by Chen et al., who determined changes in TIPS-Pn crystal packing structures in drop-cast films that were associated with a solid-state phase transition.¹⁶ The single crystal packing structure was used as a starting point for all optimizations. The unit cell parameters determined from WPF of the GIWAXS data were imposed and restrained for each polymorph. A series of two minimization steps was developed to allow the side groups and pentacene cores to reach their lowest energy conformations. All optimizations were performed using the Compass force field using the Forcite molecular mechanics extension of the Materials Studio (BIOVIA) package.

First, several optimization routines were analyzed to determine the optimal procedure for solving the crystal packing structures. The procedures were tested by reproducing the known single crystal packing structure made available through reference 30. A two-stage optimization was developed: (1) Side group coordinates were fixed and the pentacene core atoms were optimized; (2) All atomic coordinates were varied to obtain the final structure. Using this process, the two molecular pair states of the single crystal structure were reproduced successfully, which are shown in **Figure 7-5**. From this analysis, a maximum slip error of be $\sim 0.2 \text{ \AA}$ ($< 22\%$ error) was estimated.

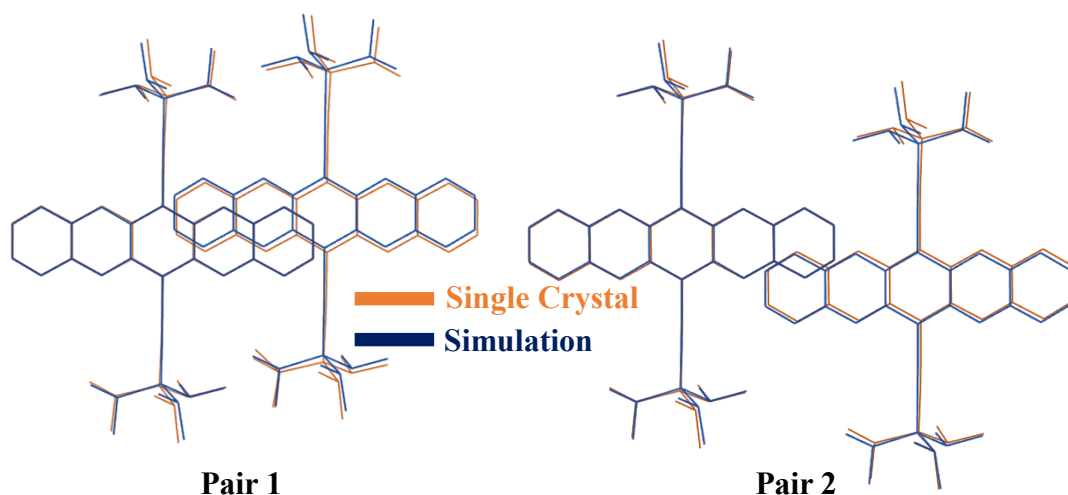


Figure 7-5: Unit cell optimization results for both molecular pair states of the single crystal packing structure. The results are compared to the known packing structures obtained from single crystal data made available through reference 30.

The unit cell optimization routine was then performed for the SA and TA films. The resulting structures are presented in **Figure 7-6**.

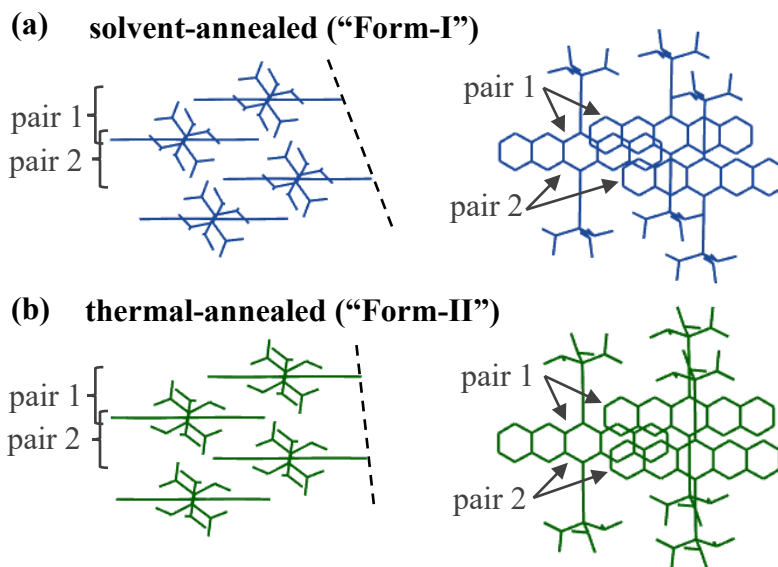


Figure 7-6: Crystal packing structures determined for the **(a)** Form-I and **(b)** Form-II polymorphs.

The packing structure of the SA film resembled the single crystal structure very closely, consistent with the observation of similar unit cell parameters. However, the TA film had a significantly different packing structure, reflective of the changes in the a and γ cell parameters.

These results are in qualitative agreement with those reported by Diao et al. in solution-sheared films of TIPS-Pn.¹⁵ As such, the crystal polymorphs isolated in the SA and TA films are henceforth identified by the names established by those authors as “Form-I” and “Form-II” brickwork, respectively. For reference, several packing structure parameters were determined and tabulated (**Table 7-3**), including π - π stacking, long- and short-axis slippage distances, center-of-mass (COM), and side-group tilt angle. The definitions of each parameter are illustrated in **Figure 7-7**.

Table 7-3: Distance and angle parameters for optimized unit cell packing arrangements for TIPS-Pn polymorphs. Parameters for the single crystal packing structure are provided for reference

	Single Crystal		Form-I		Form-II	
	pair 1	pair 2	pair 1	pair 2	pair 1	pair 2
COM distance	7.565 Å	10.212 Å	7.814 Å	10.134 Å	8.615 Å	8.940 Å
π-π distance	3.479 Å	3.168 Å	3.410 Å	3.115 Å	3.199 Å	3.338 Å
Long-axis slip	6.659 Å	9.537 Å	6.970 Å	9.515 Å	7.955 Å	8.444 Å
Short-axis slip	0.950 Å	-1.625 Å	1.248 Å	-1.10 Å	1.989 Å	-1.239 Å
Side group tilt angle	174.61°		176.80°		176.18°	

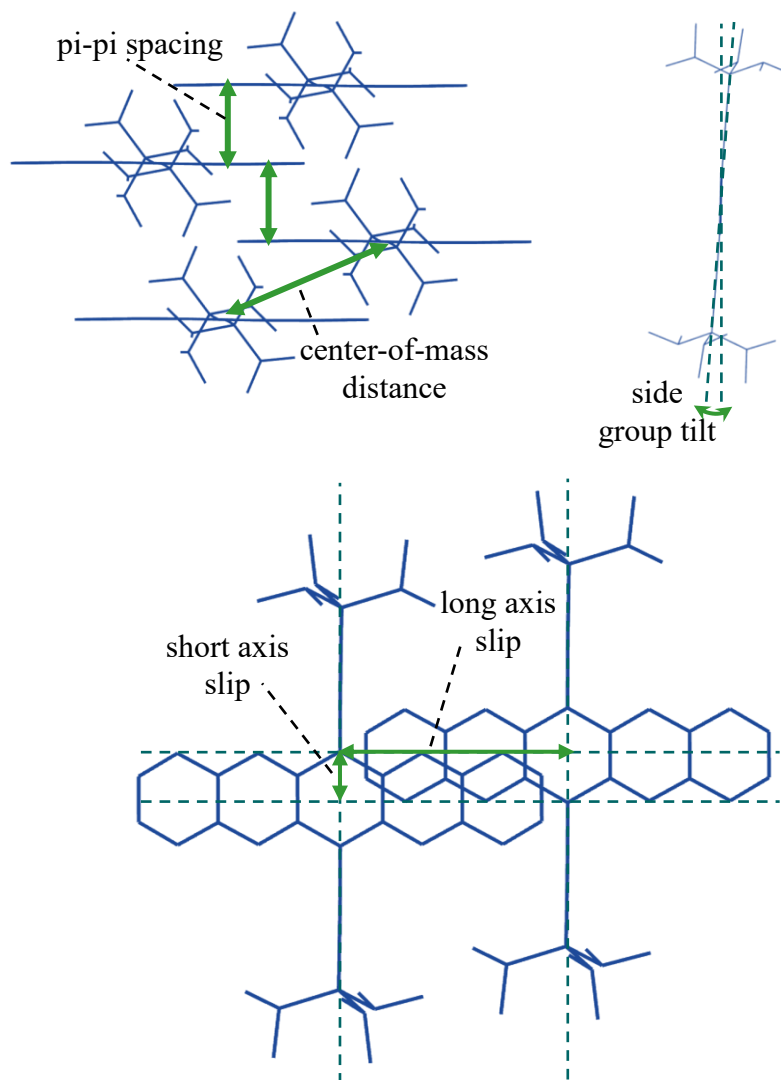


Figure 7-7: Definitions of the parameters for molecular packing in TIPS-Pn.

It is of note that the occurrence of two distinct molecular pair sites in the crystal structures could, in principle, lead to two sets of CTP formation and decay rates for the two polymorphs studied. However, it is not known if (1) the formation of one particular CPT state (e.g. over a single molecular pair) kinetically outcompetes the other, or if (2) rapid localization of the CTP wavefunction to a specific molecular pair site occurs, or if (3) the CTP is delocalized over more than two molecules (e.g. involving both molecular pair sites). As such, each molecular pair site individually is considered in the following without loss of generality. It is acknowledged

that a simple treatment of interactions between pairs of molecules may be an oversimplification with regards to understanding what governs CTP separation.

7.5. Charge Transfer Integrals of Molecular Pair States of TIPS-Pn Polymorphs

Electronic orbital overlap is known to be a dominant contributor to the overall triplet transfer coupling between molecules.^{24,26,31-33} The Form-I and Form-II polymorphs of TIPS-Pn, which feature significant changes in intermolecular geometries, inevitably correspond to differences in orbital overlap between molecules.³⁴⁻³⁶ In this framework, it was considered how the changes in the molecular packing between the Form-I and Form-II structures can affect their singlet fission and triplet diffusion characteristics. However, basing analysis on their molecular pair geometries alone is too indirect since the locations of the molecular orbitals themselves, and not necessarily the relative positions of the atoms, determine orbital overlap.³⁴⁻³⁶ Since molecular orbital locations are not immediately known from geometric structures, a computational method was sought for determining how the specific molecular packing arrangements in TIPS-Pn polymorphs control their triplet transfer behaviors.

Charge transfer integrals have been used to evaluate the electronic coupling of organic semiconducting molecules and polymers by methods reported by Bredas and coworkers.^{32,34-37} In particular, a simplistic approach, the energy splitting method,³³ can be used to accurately compute transfer integrals for molecular pairs.³⁸ Under the one-electron approximation, the charge transfer integral, t , is equal to half the energy splitting of the orbitals involved:

$$t_{eT} = \frac{\epsilon_{LUMO+1} - \epsilon_{LUMO}}{2} \quad (\text{eqn. 2})$$

where ϵ_i represents the LUMO+1 and LUMO energies. Similarly, the hole transfer coupling can be expressed using the HOMO and HOMO-1 energies. For a given molecular pair, the

energy splitting can be visualized by considering how strongly spatially overlapped their orbitals are; significant overlapping interactions would result in larger energy splittings, and thus, higher coupling values. In the energy splitting method, a major breakdown often results when the site energies of the molecules within the pair are not equal, which occurs, for instance, in the molecular pair states of the herringbone crystal structure in pentacene.³² However, the equal site energy assumption was valid for the molecular pairs in TIPS-Pn because their relative orientations are all face-on.

To calculate the energy splittings for TIPS-Pn pairs in the Form-I and Form-II brickwork polymorphs, a TIPS-Pn molecule was first optimized using DFT at the B3LYP/cc-PVTZ level of theory. The molecule was optimized in a toluene environment using the polarizable continuum model (PCM). The molecular pair structures obtained from the unit cell optimizations were then reconstructed using the DFT-optimized monomer structure (**Figure 7-8**).

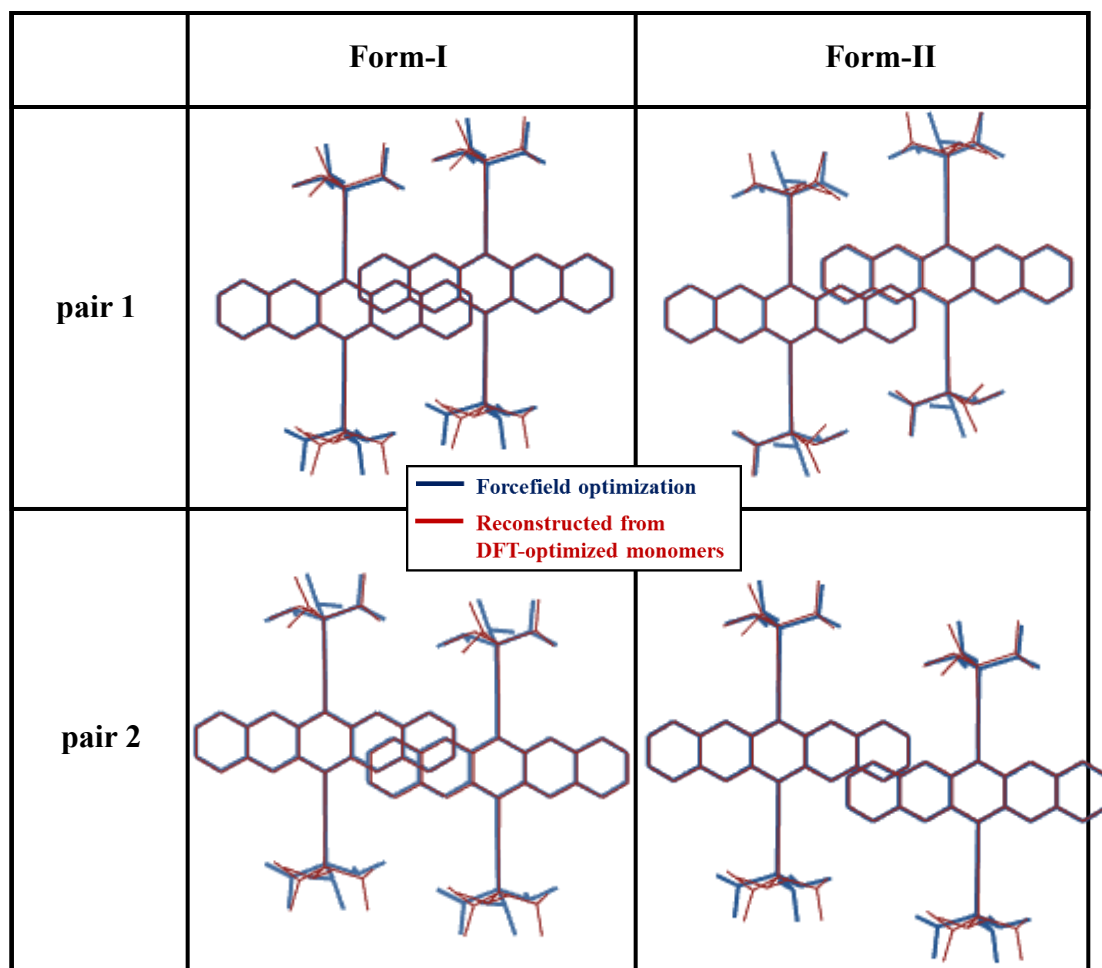


Figure 7-8: (a) Overlay of the molecular pair states resulting from the forcefield optimizations in comparison to the structures reconstructed using DFT-optimized monomers. Small changes in the side group rotational angles occurred, which are not expected to have an effect on the HOMO and LUMO splittings.

To calculate the HOMO and LUMO energy splittings for the charge transfer integrals, additional DFT calculations were made for each pair structure using the long-range corrected ω PBE functional^{34,35,39} with $\omega = 0.3$. This functional was chosen since it has been shown to successfully describe the ground and excited state properties of pentacene,²² including asymptotic regions of the molecular orbitals that greatly affect electronic coupling.⁴⁰ **Table 7-4** summarizes the resulting energy splitting values in addition to the energies calculated for the HOMO-1, HOMO, LUMO, and LUMO+1 levels.

Table 7-4: Energy levels calculated using LRC- ω PBE/cc-PVTZ calculations for the molecular pair states in the solved polymorph structures for TIPS-Pn. All values are reported in eV

Orbital	Form-I		Form-II	
	pair 1	pair 2	pair 1	pair 2
LUMO+1	-1.3867	-1.4759	-1.5320	-1.4629
LUMO	-1.6740	-1.6596	-1.5516	-1.6204
HOMO	-6.6684	-6.6929	-6.6815	-6.6344
HOMO-1	-6.6837	-6.7329	-6.7139	-6.7672
LUMO Splitting	0.2873	0.1837	0.0196	0.1575
HOMO Splitting	0.0153	0.04	0.0324	0.1328

Using the energy splittings, the charge transfer integrals were calculated for each molecular pair state of each TIPS-Pn polymorph (**Figure 7-9**). These results are consistent with the couplings computed for comparative polymorph structures by Diao et al. using the projective method.¹⁵ From these values, it was found that on average, the transfer integrals were significantly larger for the Form-I brickwork structure, suggesting stronger orbital overlap interactions for this polymorph. The stronger interactions in this polymorph are likely associated with the factor of two higher triplet transfer rate inferred from the analysis of the transient absorption kinetics.

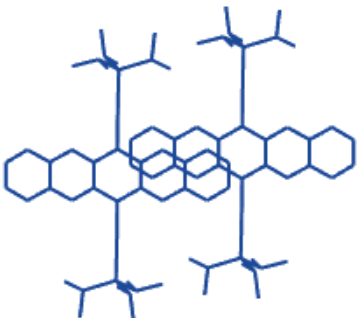
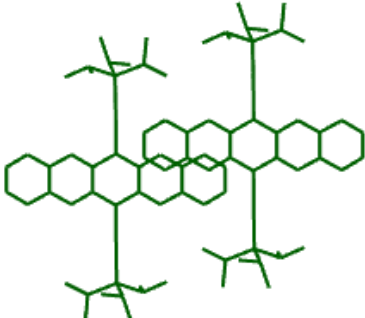
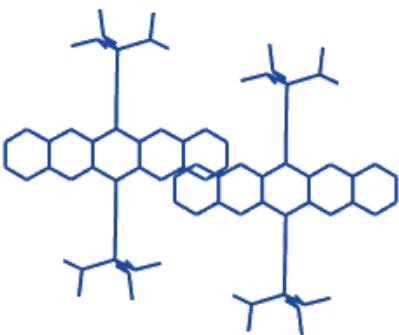
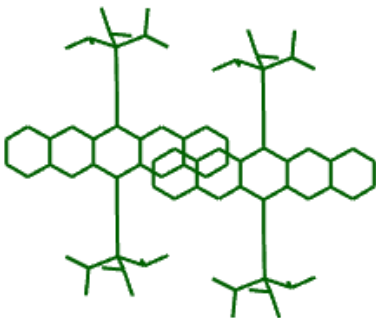
	Form I	Form II
Pair 1	$\pi\text{-}\pi = 3.410 \text{ \AA}$  $t_{\text{elec}} = 144 \text{ meV}$ $t_{\text{hole}} = 8 \text{ meV}$	$\pi\text{-}\pi = 3.199 \text{ \AA}$  $t_{\text{elec}} = 10 \text{ meV}$ $t_{\text{hole}} = 16 \text{ meV}$
Pair 2	$\pi\text{-}\pi = 3.115 \text{ \AA}$  $t_{\text{elec}} = 92 \text{ meV}$ $t_{\text{hole}} = 20 \text{ meV}$	$\pi\text{-}\pi = 3.338 \text{ \AA}$  $t_{\text{elec}} = 79 \text{ meV}$ $t_{\text{hole}} = 66 \text{ meV}$

Figure 7-9: (a) Electron and hole transfer integrals calculated for both molecular pair states present in each of the Form-I and Form-II polymorphs. The pi-pi stacking distances are provided for reference.

These findings suggest that intermolecular packing interactions that are able to produce charge transfer integrals on the order of 10 to 100 meV may be associated with rapid CTP separation. Furthermore, the results confirm that simple visual inspection of the intermolecular packing geometries of molecules cannot predict differences in orbital couplings; their complex

orbital nodal structure, in addition to their relative distances (in this case, determined by π - π stacking), both contribute to the ultimate orbital overlap. Notably, the excitonic redshifts apparent in the steady-state visible absorption spectra of the two polymorphs (see Chapter 3) qualitatively reflect differences in the electronic interactions of TIPS-Pn molecules. This may be considered as the easiest, albeit superficial, metric for predicting fast CTP separation in circumstances in which the origin of the redshift is well-understood.

The charge transfer integral approach reported here should only be used as a qualitative predictor of triplet transfer rate. However, these relatively simple calculations can be performed on large sets of molecular systems that are potential candidates for singlet fission.⁴¹⁻
⁴⁹ Since triplet transfer and charge transfer are both determined by short-range orbital overlap,^{31,50} charge transfer integrals may provide a valuable metric for screening potential singlet fission sensitizers through their ability to undergo rapid CTP separation. It is the hope that in the future, triplet transfer integrals may replace charge transfer integrals in this procedure to form a direct analysis of triplet transfer rate in singlet fission materials. The computational resources were not available at the time of this study to perform such computations. For future studies, the reader is referred to the work by Van Voorhis and coworkers,⁵¹ which outlines the use of constrained DFT for effectively calculating triplet transfer integrals in organic compounds.

7.6. Conclusions & Significance

Ultrafast and nanosecond transient absorption spectroscopy was used to follow the triplet formation kinetics during singlet fission, and subsequent triplet-triplet annihilation decay kinetics, in crystalline films of TIPS-Pn. These processes were compared for two crystal

polymorphs, which were identified using optical absorption and X-ray diffraction measurements as possessing Form-I and Form-II brickwork packing structures. The relative rate constant for CTP separation matched the relative rate constant for triplet-triplet annihilation between the two polymorphs, which indicated that triplet transfer is the mechanism of CTP separation.

It was investigated whether the combination of structural analysis and quantum chemical computations of the resulting electronic couplings might be useful for predicting efficient singlet fission molecules *a priori*. The packing arrangements of the TIPS-Pn molecules in the spin-casted films consisting of the Form-I and Form-II polymorphs were determined using a combination of GIWAX measurements and molecular mechanics simulations. Charge transfer integrals, which reflect electronic orbital overlap interactions, were computed to assess how these packing arrangements may control triplet transfer rates. The results of this study illustrate how the calculation of the triplet transfer integrals for a conceived set of molecular packing arrangements may form a method for predicting the efficacy of CTP separation in the search for the next generation of singlet fission sensitizers.

7.7. Perspective: A General *a priori* Method for Searching for Materials that Undergo Efficient Correlated Triplet Pair Separation

The work presented in this chapter motivates the consideration of the second step of singlet fission, CTP separation, when computing molecular packing structures favorable for efficient singlet fission. Recently, computational screening methods have been developed to search for packing structures that favor efficient formation of CTPs for a given chemical structure.⁵² These methods have relied on calculating direct and mediated couplings for predicting the efficacy of the first step of singlet fission (see Chapter 3 for details). However, when triplet

transfer is the mechanism of CTP separation (as is the case for TIPS-Pn), the application of triplet transfer integral calculations on the molecular packing geometries output by the current screening methods would provide further insight into structures that are also efficient at separating the triplet excitations. As an alternative, triplet transfer integrals may also be incorporated side-by-side into the current screening methods, as illustrated by **Figure 7-10**. For a given molecule, a proposed packing structure is conceived (experimentally or hypothetically) and the singlet fission and triplet transfer couplings are evaluated. A decision is then made based on the results of the computations of whether the molecule and its packing structure are viable for efficient singlet fission. The process is then repeated for another packing arrangement or another chemical structure. This *a priori* screening approach would facilitate the search for new singlet fission materials, allowing the synthetic chemist to focus on a select, reduced number of molecules. In the process, universal packing structures may also be discovered that favor efficient singlet fission, irrespective of the chemical identity of the molecule.

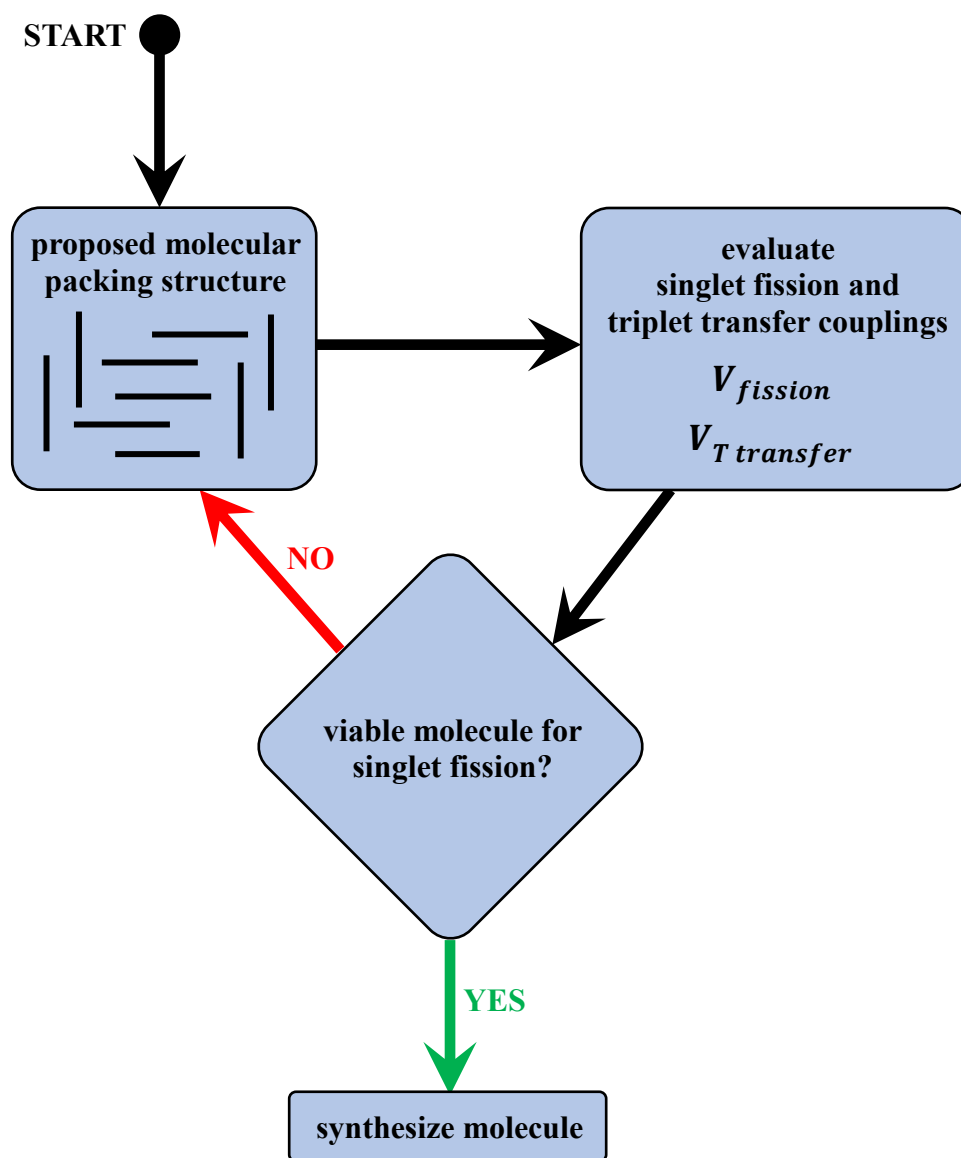


Figure 7-10: Proposed *a priori* strategy for searching for new singlet fission molecules. A molecule with energy levels satisfying the condition, $E_{S1} \sim 2x E_{T1}$, and its expected packing structure is conceived. The triplet transfer couplings are calculated in addition to single fission couplings for each molecular pair state. Based on the results, the structure and/or molecule is screened as a viable singlet fission material. This process may also be used instead to generate a generic set of packing interactions that are favorable to both steps of singlet fission, relying on the singlet fission and triplet transfer couplings, respectively.

It is also hoped that the work presented in this chapter serves as a platform for future studies of correlated triplet pair separation in pentacene derivatives, as well as new singlet fission sensitizers being developed. In particular, a deeper understanding of how intermolecular

packing arrangements determine the nature of correlated triplet pair intermediates, and the ability for the pair state to separate effectively, is needed. The work presented in this chapter also leads to the development of future research directions, which are detailed in Chapter 12.

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CHAPTER 8

Methods for Measuring and Identifying Triplet Excitation Spectra in Singlet Fission Materials

Practical concerns for applying singlet fission sensitizers to solar cells primarily involve meeting the materials compatibility requirements of the active layers of the devices. In order to engineer such devices, a large collection of singlet fission sensitizers with different optical, energetic, and structural properties must be first developed. With the drive to search for new singlet fission compounds, careful spectroscopic assignment of triplet excitation is necessary in order to properly characterize singlet fission and accurately quantify their triplet yields. This chapter serves to identify different methods for determining the excitation spectra of triplets using transient absorption spectroscopy in the visible and near-IR spectral ranges. Each method has been applied for studying model compounds and candidates for singlet fission.

This chapter includes work that contributed to the following publications: Pensack, R.D., Ostroumov, E.E., Tilley, A.J., Mazza, S., Grieco, C., Thorley, K.J., Asbury, J.B., Seferos, D.S., Anthony, J.E., and Scholes, G.D., “Observation of Two Triplet-Pair Intermediates in Singlet Exciton Fission”, *J. Phys. Chem. Lett.*, **2016**, 7, 2370-2375; Pensack, R.D., Grieco, C., Purdum, G.E., Mazza, S.M., Tilley, A.J., Ostroumov, E.E., Seferos, D.S., Loo, Y., Asbury, J.B., Anthony, J.E., Scholes, G.D., “Solution-processable, crystalline material for quantitative singlet fission”, *Materials Horizons*, **2017**, 4, 915-923. Ryan D. Pensack is acknowledged for supplying all nanoparticle dispersions.

8.1. Introduction

Currently, there is a minimal number of classes of singlet fission materials, which includes tetracene, pentacene, and 1,3-diphenylisobenzofuran.¹⁻⁴ Recently, perylene⁵ and terylene⁶ derivatives have also been shown to undergo fission. The expansion of this set of materials is important for their application to the active materials of photovoltaic devices, which impose restrictions on the choice of sensitizer based on their chemical and energetic compatibility. In the search for new singlet fission materials, there is a need to identify triplet excitation spectra in order to properly assign features present in the measured transient absorption spectra evolving during singlet fission. For example, the intermediate states of singlet fission, the correlated triplet pairs (CTPs), spectroscopically resemble independent triplet excitations. It has been shown (work submitted by Ryan D. Pensack) that the excitonic nature of the intermediate states determines whether or not they may dissociate, and so the precise excitation spectrum is needed in order to distinguish bound triplet from free triplets.

In addition to CTPs, other transient species may form on the timescale of singlet fission, such as excimers or charge transfer states. The formation of such excitations may kinetically compete with singlet fission, decreasing triplet yields, and so their clear spectroscopic assignment is essential for studying new compounds. For example, the confusion of triplet absorption for excimer absorption could lead to false or misleading conclusions about the singlet fission efficiency of a new molecular system.

Both the visible and near-IR spectral regions, featuring triplet absorption bands in pentacene derivatives, have been useful for studying the singlet fission mechanism.⁷⁻¹¹ For instance, the near-IR band has been shown to be sensitive to whether the triplets are electronically

interacting (as in CTP states) or not (spatially separated triplet pairs).⁷ In the following, methods for identifying triplet absorption appearing in both spectral ranges will be detailed.

8.2. Singlet Fission Method

The first method for identifying triplet excitation spectra is the measurement of the independent triplet excitons produced by singlet fission. This method, however, requires that triplet are indeed separated efficiently, which may be supported by the observation of absorption signals that persist on a nanosecond to microsecond timescale. In this case, the photophysics may be described by the following sets of reactions:



where S_1S_0 represents a singlet exciton adjacent to a ground state molecule, T_1 represents the independent triplet exciton, S_0 represents the ground state, and k_i are the rate constants for singlet fission (**eqn. 1**), triplet-triplet annihilation (**eqn. 2**), and triplet relaxation to the ground state (**eqn. 3**). The transient absorption is measured on a nanosecond to millisecond timescale, before which it is hoped that the product triplet excitons have already been formed. In other words, it is assumed that $k_{\text{fission}} \gg k_{\text{annihilation}}$. This, in turn, leads to the following rate expression:

$$\frac{d[T_1]}{dt} = -\frac{1}{2}k_{TTA}[T_1]^2 - k_{relax}[T_1] \quad (\text{eqn. 4})$$

The first expression, a second order term, would dominate at high triplet concentrations. At later times when the triplet concentration is low, the second expression, a first order term, would dominate. As such, the expected triplet kinetics would feature bimolecular decay at

early time delays (due to triplet-triplet annihilation) and unimolecular decay at later time delays (due relaxation to the ground state).

The singlet fission method for determining triplet excitation spectra is demonstrated for nanoparticles of a series of pentacene derivatives.⁷ In the nanoparticles, the molecules are aggregated and so singlet fission occurs efficiently, producing an appreciable triplet yield.^{8,12,13} Transient absorption features and their associated kinetic decays in the visible spectral region are shown for several pentacene derivatives in **Figure 8-1**. The kinetic decay behavior for all the nanoparticles matched the predictions of **eqn. 4**, with clear bimolecular decay occurring at early time delays ($<1 \mu\text{s}$) after which the signal decayed exponentially (at a $\sim 1 - 100 \mu\text{s}$ timescale).

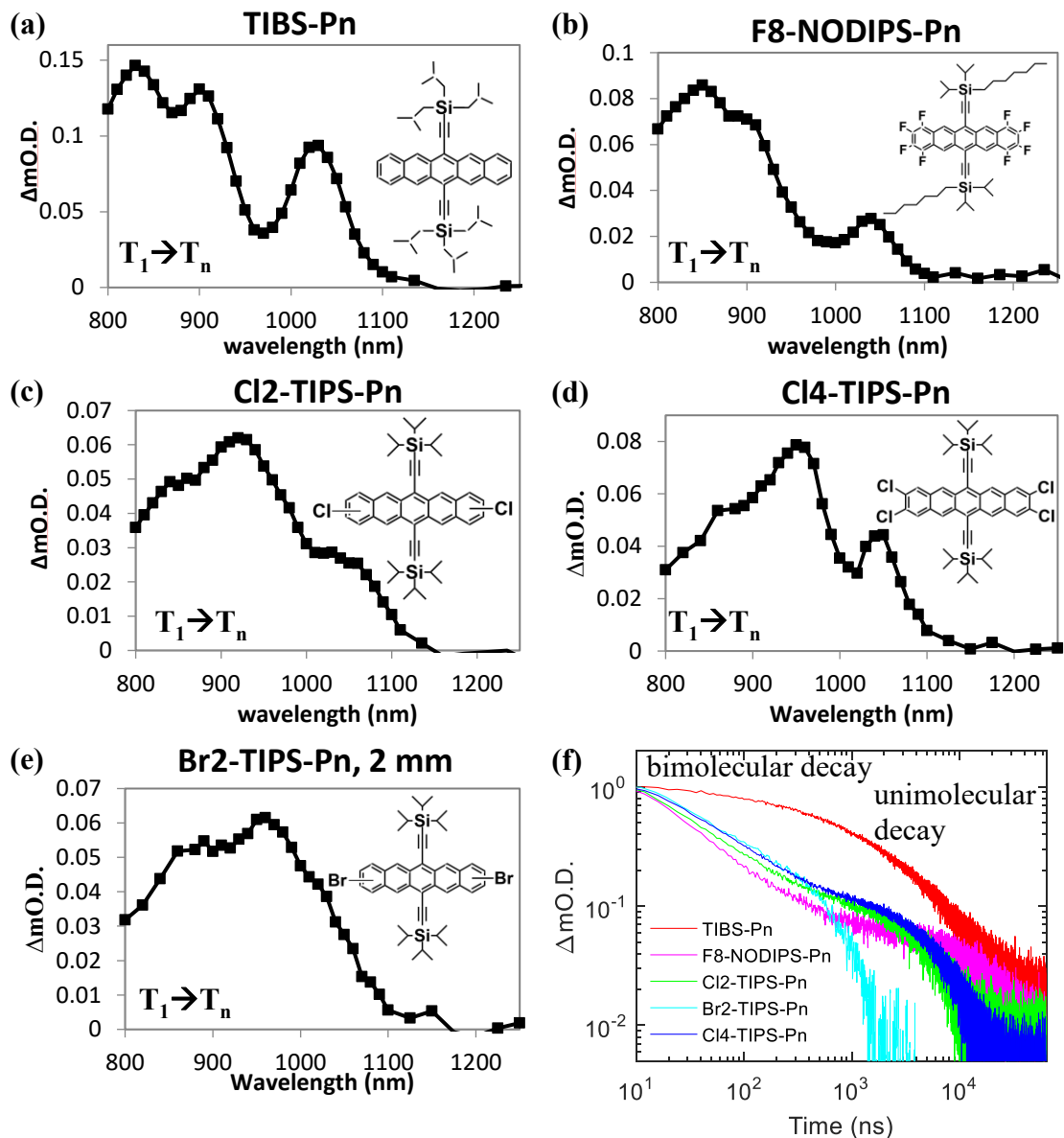


Figure 8-1: (a-e) Transient absorption spectra of triplets for nanoparticle dispersions of pentacene derivatives. The excitation wavelength used was 642 nm. All spectra were integrated from 1-10 μs except for the Br2-TIPS-Pn, which was integrated from 0.5-1 μs . (f) Kinetic decays for the same samples probed at 890 nm, 840 nm, 910 nm, 950 nm, and 950 nm for the TIBS-Pn, F8-NODIPS-Pn, Cl2-TIPS-Pn, Br2-TIPS-Pn, and Cl4-TIPS-Pn samples, respectively.

In cases in which the formation of independent triplet excitations before the nanosecond to microsecond timescale cannot be safely assumed, alternate methods must be sought to determine triplet excitation spectra. In dilute solutions, the deactivation channels of

photogenerated singlet excited states are simplified because intermolecular interactions are turned off. This leads to two major decay pathways of the excited singlets: Relaxation (radiative and nonradiative) and intersystem crossing (forming triplets, which subsequently relax). The first approach is to rely on intersystem crossing to produce the triplet excitations. In cases in which the intersystem crossing efficiency is low, a second approach, triplet excitation energy transfer (TEET) using a triplet sensitizer, is employed.

8.3. Intersystem Crossing Method

8.3.1. Identifying triplet absorption in solutions of pentacene derivatives

For the intersystem crossing method, dilute solutions are prepared for the compound of interest and the molecules are photoexcited to produce a population of S_1 states. The decay pathways involving triplet excitations are then expressed as:



which are sequential reactions consisting of $S \rightarrow T$ intersystem crossing followed by triplet relaxation to the ground state. In singlet fission sensitizers, it is possible for intersystem crossing to instead generate higher-lying triplet states (T_n) since the triplet manifold is characteristically lowered. In accordance with Kasha's rule, it is assumed that the relaxation of $T_n \rightarrow T_1$ is fast. Therefore, in these cases the mechanism can be reduced to **eqn. 5**, resulting in the same expected kinetic behavior. In this case, the rate expression is:

$$\frac{d[T_1]}{dt} = +k_{ISC}[T_1] - k_{relax}[T_1] \quad (\text{eqn. 7})$$

which predicts unimolecular growth of a triplet population, followed by unimolecular decay. This intersystem crossing method for generating a triplet state population works well for

molecules that have intersystem crossing rates high enough to compete with fluorescence decay rates ($k_{\text{ISC}} \sim k_{\text{fluor}}$).

The transient absorption spectra for a variety of pentacene derivatives are shown in **Figure 8-2** and **Figure 8-3** for the near-IR and visible spectral regions, respectively. The spectra were assigned to triplet absorption based on their kinetic behavior, which was in qualitative agreement with the expected kinetics as predicted by **eqn. 7**.

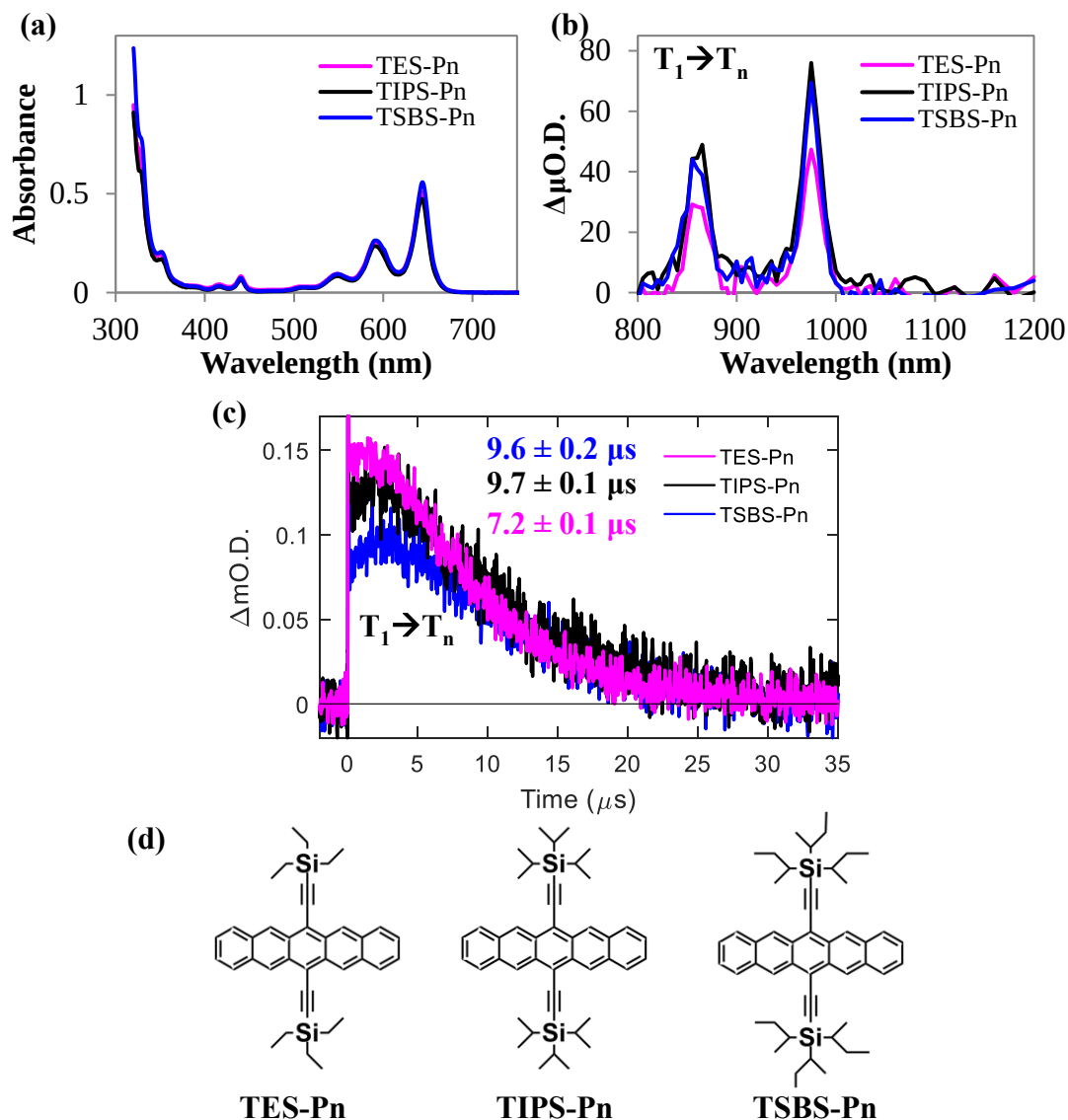


Figure 8-2: (a) Absorption spectra of 0.02 mM solutions of pentacene derivatives dissolved in toluene. (b) Corresponding transient absorption spectra of triplets that were time-integrated from 100-500 ns. The excitation wavelength was 649 nm and incident energy density was $\sim 100 \mu\text{J}/\text{cm}^2$. All solutions were flowed during measurements. (c) Kinetic decays measured at 975 nm. The lifetimes determined from single exponential fits to the data are included. (d) Chemical structures of the molecules used.

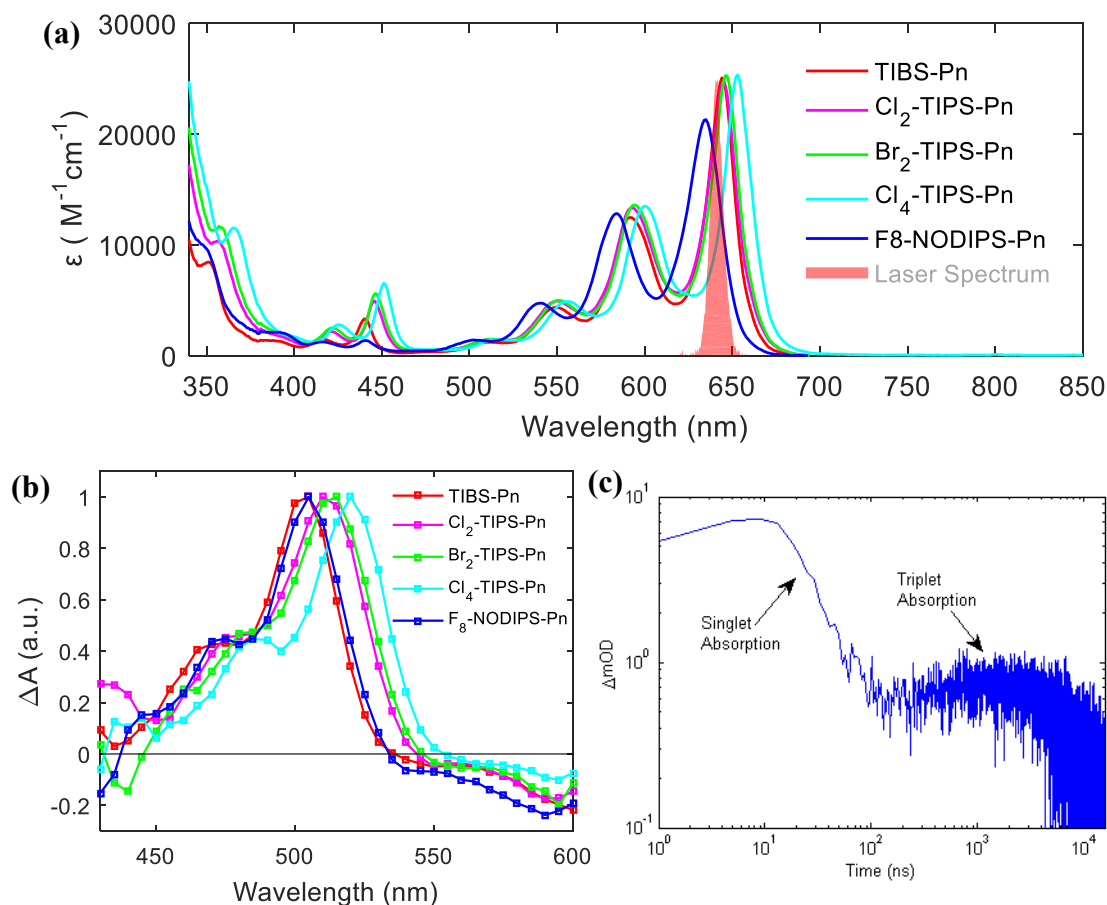


Figure 8-3: (a) Extinction spectra measured for pentacene derivatives dissolved in toluene at 0.04 mM. The chemical structures are provided in an earlier figure. The emission spectrum of the pump laser used for the transient absorption measurements is included for reference. (b) Triplet excitation spectrum measured using transient absorption spectroscopy for the same solutions with excitation at 642 nm. The spectra were obtained by integrating the data from 250 – 10,000 ns. (c) Example of the transient absorption kinetics measured for the Br_2 -TIPS-Pn solution, showing singlet absorption at early time and triplet absorption at late time.

8.3.2. Triplet sensitization by oxygen

While measuring triplet absorption spectra in pentacene derivatives, it was discovered that dissolved oxygen enhances their intersystem crossing rate. As a result, oxygen has the ability to further sensitize triplet production via spin-orbit perturbation¹⁴ in solutions of pentacene derivatives. Spectroscopic evidence for this is provided in two measurements of 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-Pn) (**Figure 8-4**). In the first, the singlet decay

rate was found to be kinetically quenched by the presence of oxygen. For this experiment, the concentration of dissolved oxygen was varied by measuring the solutions as prepared (partial pressure of oxygen at atmospheric pressure), after bubbling using oxygen (partial pressure ~ 1), and after bubbling using nitrogen (partial pressure ~ 0). Oxygen concentrations were calculated using Henry's Law. As the oxygen concentration was increased, the singlet decay rate was enhanced. This indirectly indicates that the intersystem crossing rate may have increased in the presence of oxygen (provided no other deactivation pathways, such as photo-oxidation, are present).

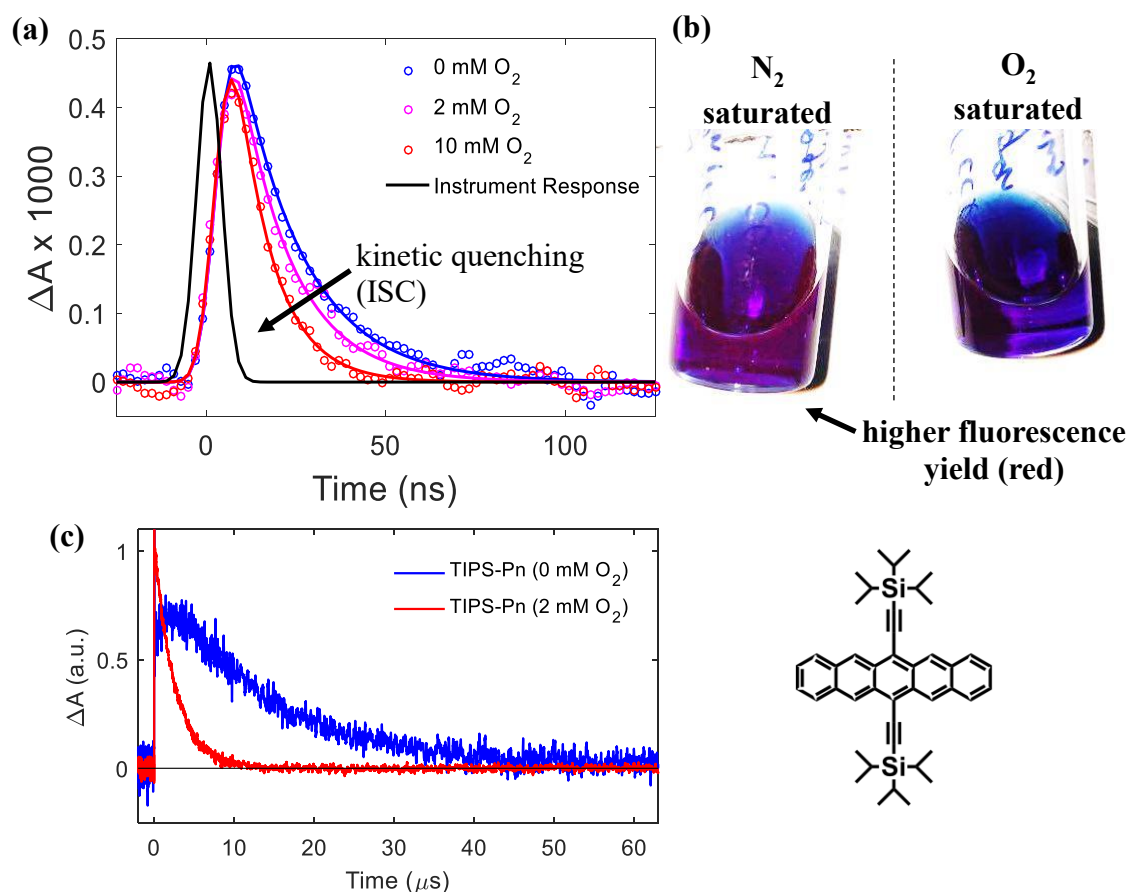


Figure 8-4: (a) Singlet absorption decays (measured in the mid-IR) for a 1 mM TIPS-Pn solution in carbon tetrachloride with different concentrations of dissolved oxygen. (b) Photographs of the TIPS-Pn solutions bubbled either with nitrogen (“nitrogen saturated”) or oxygen (“oxygen saturated”) gas. (c) Triplet absorption kinetics measured in the near-IR.

In the second experiment, the effect of oxygen on the triplet absorption kinetics was determined (**Figure 8-4**). In solutions containing an appreciable amount of dissolved oxygen (atmospheric pressure conditions), the triplet absorption growth and decay rates were much faster. This indicated that oxygen does indeed enhance intersystem crossing in TIPS-Pn. As a result, if absolute values for the natural ISC rate, ISC quantum yield, or triplet lifetime are required, it is essential to eliminate any dissolved oxygen in the solutions. Caution is recommended, especially in nonpolar organic solvents in which oxygen is highly soluble. In cases in which higher signal levels are demanded by the experiment, and quantitative determination of the rate constants is not needed, purposely incorporating dissolved oxygen can be advantageous.

8.3.3. Note: Triplet enhancement in concentrated solutions via singlet fission

It is also possible to enhance triplet generation in solutions of singlet fission molecules via singlet fission. This was first discovered by Walker and coworkers in 2013, who reported diffusion-mediated singlet fission in concentrated TIPS-Pn solutions.¹⁵ The conclusions of the paper pertaining to emissive excimer intermediates are actually proven to be incorrect in the Appendix of this dissertation; using the concentrations and pathlengths reported in that study, the so-called “excimer” emission spectrum is actually an experimental artifact, proven to originate from the inner filter effect. Regardless, the conclusions made in that work regarding singlet fission occurring in concentrated solutions was found to be reproducible.

The TIPS-Pn concentration dependence of the near-IR transient absorption kinetics of both singlets and triplets is shown in **Figure 8-5**. Kinetic quenching of the singlet absorption occurred as concentration of TIPS-Pn was increased, suggesting that a diffusion-mediated photophysical pathway was present. The triplet absorption kinetics showed faster growth

kinetics upon increasing concentration, consistent with the faster observed singlet decay rates. Together, these results are indicative of some type of diffusion-limited singlet fission. In Chapter 12, it is shown that molecular aggregation (via side-group interactions) may actually lead to the enhancement of singlet fission in concentrated solutions.

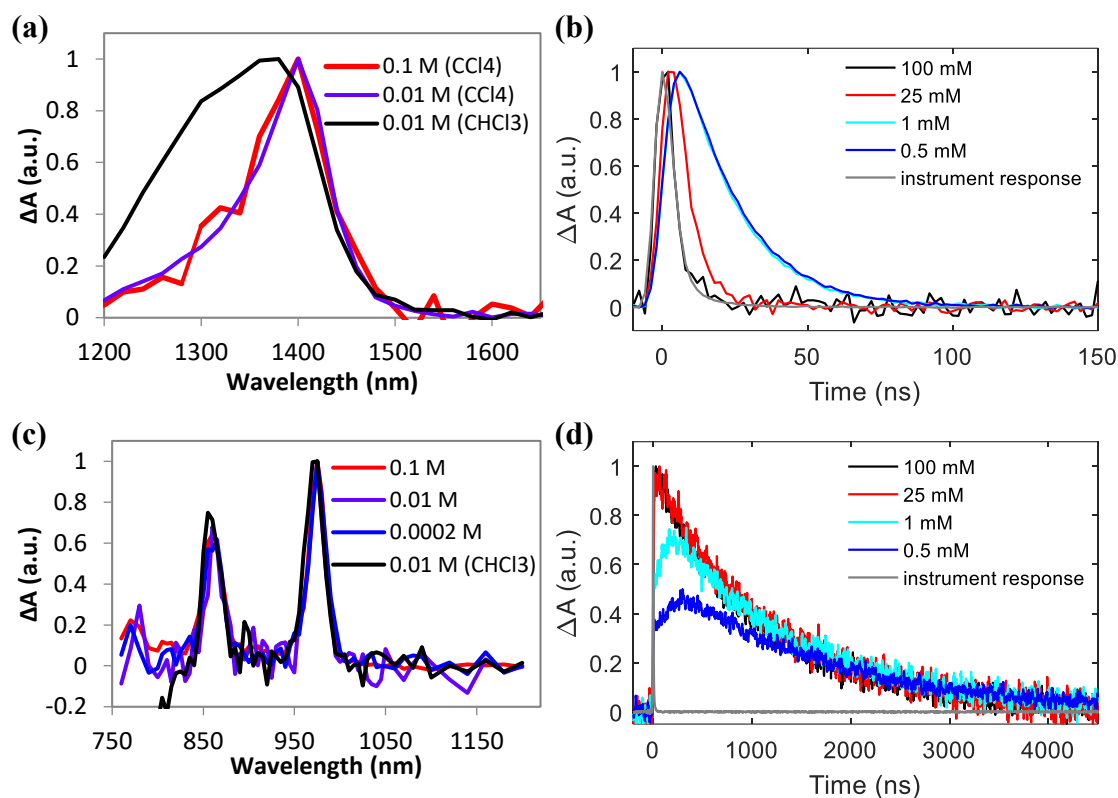


Figure 8-5: (a) Singlet excitation spectra measured for TIPS-Pn solutions using transient absorption spectra integrated from 0–25 ns. (b) Concentration dependence of the normalized singlet absorption kinetics for TIPS-Pn dissolved in carbon tetrachloride. (c) Triplet excitation spectra measured for TIPS-Pn solutions (in carbon tetrachloride) using transient absorption spectra integrated from 100–500 ns. (d) Concentration dependence of the normalized triplet absorption kinetics for TIPS-Pn dissolved in carbon tetrachloride. All samples were bubbled with nitrogen gas before measurement.

8.4. Triplet Excitation Energy Transfer Method

For compounds that do not undergo efficient intersystem crossing in solution, the triplet excitation energy transfer (TEET) approach may be useful for generating an appreciable triplet

concentration. In this method a triplet photosensitizer, such as fullerene,¹⁶⁻¹⁹ is used to efficiently generate triplets that can be transferred to the compound of interest as follows:



where Sens is the triplet sensitizer. After photoexciting the triplet sensitizer, it diffuses until it encounters a singlet fission candidate molecule and transfers its triplet excitation. TEET can occur very efficiently since it is a spin-conserved process.

Because of limitations of the excitation wavelengths available at the time (532 nm and longer), PC₆₁BM was used as the triplet sensitizer.¹⁹ The transient absorption spectrum was measured, featuring a broad absorption associated with photogenerated triplet states extending into the deep near-IR (**Figure 8-6**). The associated kinetics featured a unimolecular decay occurring on an early microsecond timescale, consistent with a previous report by Chow and coworkers.¹⁶

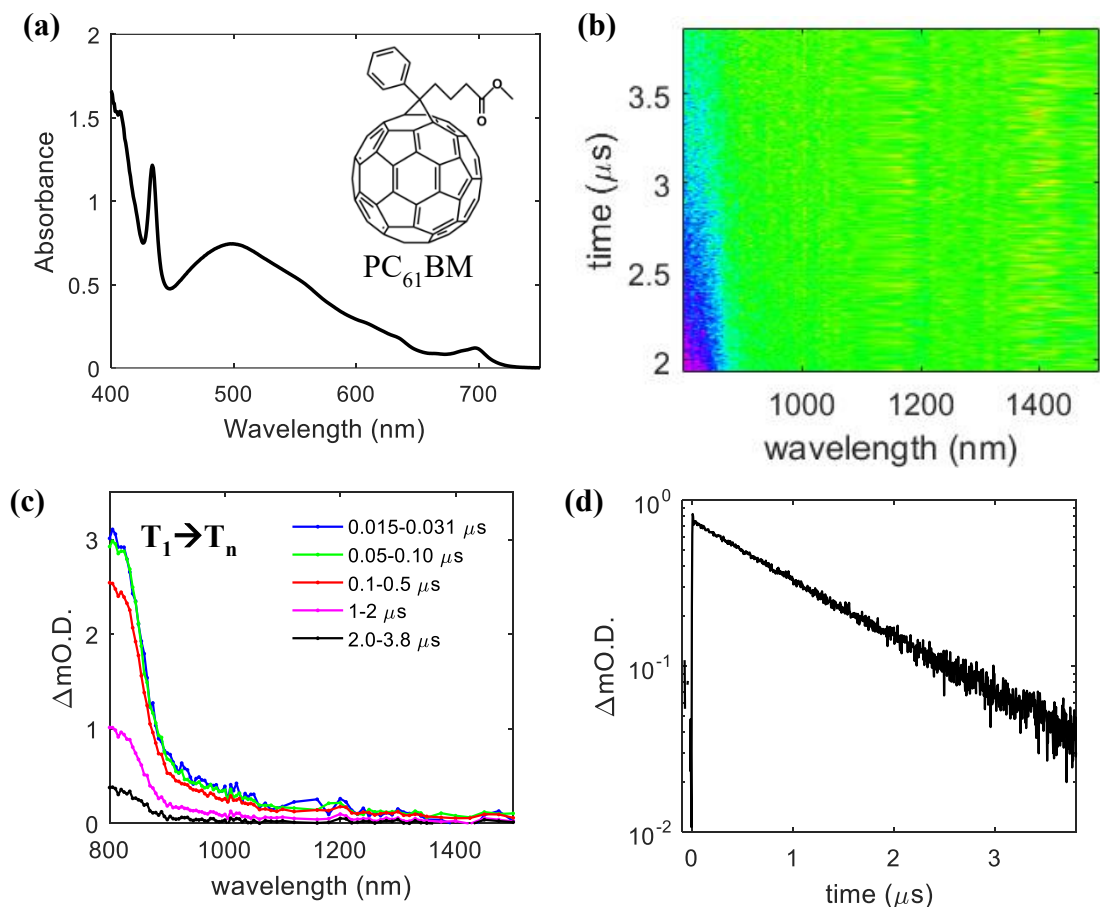


Figure 8-6: (a) Absorption spectrum of PC₆₁BM dissolved in toluene at a 0.4 mg/mL concentration. (b) Transient absorption spectrum (of triplets) measured for the same solution using 532 nm excitation. (c) Time-evolution of the transient absorption spectrum for select time delays. (d) Transient absorption kinetics spectrally-integrated from 800–1500 nm. The solution was bubbled with nitrogen gas prior to measurements.

The triplet excitation spectrum in the near-IR spectral region was determined using the TEET method with PC₆₁BM for two singlet fission candidates (**Figure 8-7** and **Figure 8-8**). The absorption spectra and decay kinetics were distinct from that of PC₆₁BM triplets, indicating that energy transfer occurred. The kinetics were fit with single exponential decay functions, indicating that the decays represented unimolecular relaxation. The PC₆₁BM concentration used was particularly high in order to ensure an appreciable amount of excitation at 532 nm and to ensure rapid transfer of energy to the singlet fission candidates.

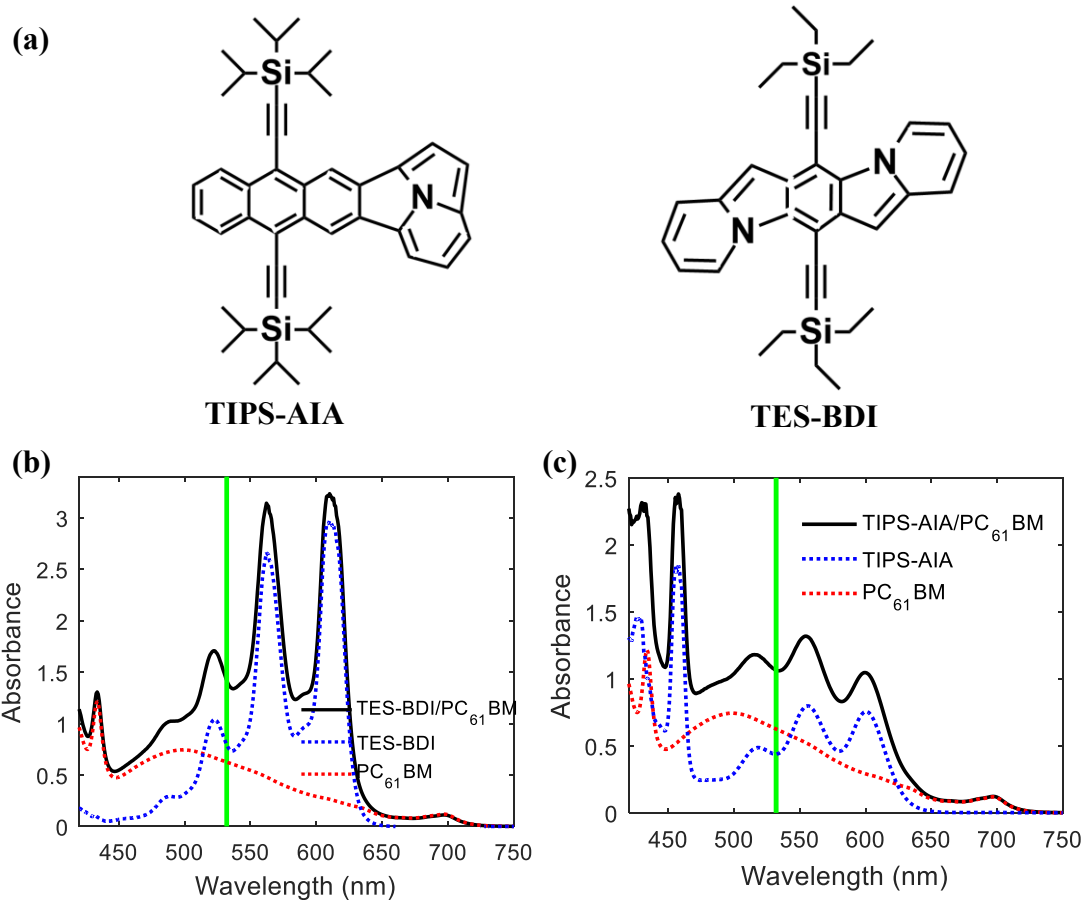


Figure 8-7: (a) Chemical structures for TIPS-AIA and TES-BDI. (b) Absorption spectra for solutions of 1 mM TIPS-AIA, ~3-4 mg/mL PC₆₁BM, and the mixture in toluene. (c) Absorption spectra for 1 mM TES-BDI, ~3-4 mg/mL PC₆₁BM, and the mixture in toluene. The green vertical lines indicate the excitation wavelength (532 nm) used for the transient absorption experiments.

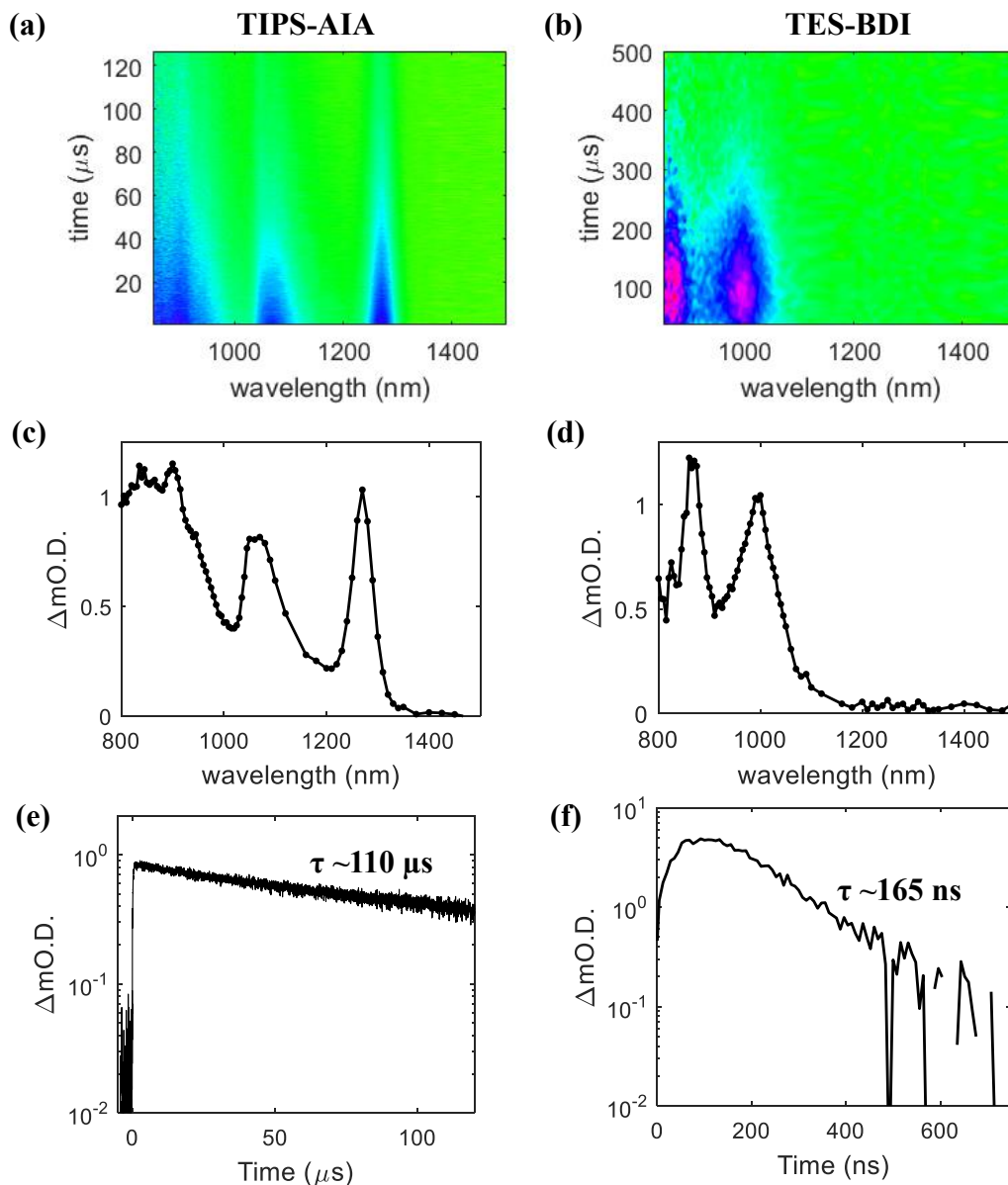


Figure 8-8: Transient absorption spectra collected for **(a)** TIPS-AIA and **(b)** TES-BDI 1 mM solutions containing $\sim 3\text{--}4 \text{ mg/mL}$ of PC₆₁BM in toluene. The samples were excited using 532 nm excitation at $\sim 200 \mu\text{J/cm}^2$ incident energy density. The transient absorption spectra were averaged from **(c)** 10–100 μs for TIPS-AIA/PC₆₁BM, and **(d)** 10–500 ns for TES-BDI/PC₆₁BM. Transient absorption kinetics measured using **(e)** 1270 nm probe wavelength and $\sim 40 \mu\text{J/cm}^2$ excitation for TIPS-AIA/PC₆₁BM, and **(f)** 995 nm and $\sim 200 \mu\text{J/cm}^2$ excitation for TES-BDI/PC₆₁BM. The lifetimes obtained from single exponential fits are included for reference. All samples were bubbled with nitrogen gas prior to measurement.

8.5. Conclusions and Significance

Methods for measuring triplet excitation spectra in singlet fission candidates were presented. The singlet fission method was demonstrated in nanoparticle dispersions of pentacene derivatives, for which transient absorption was measured for independent triplet excitons that formed on an ultrafast timescale via singlet fission. The intersystem crossing method was demonstrated for solutions of pentacene derivatives, in which intersystem crossing was a competitive relaxation pathway with fluorescence decay. Oxygen was shown to sensitize intersystem crossing via spin-orbit perturbation. The triplet excitation energy transfer method was demonstrated using the triplet sensitizer, PC₆₁BM, for solutions of singlet fission candidates.

Independent measurements of triplet excitation spectra are important in the search for new singlet fission compounds in order to carefully assign transient absorption features arising during the ultrafast timescale. Transient species, such as excimers or charge-transfer states that may not lead to formation of multiplied triplets, may be confused spectroscopically for triplet excitons and lead to false conclusions about singlet fission.

8.6. References

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CHAPTER 9

Developing Chemical Design Rules for Covalent Linkages in Semiconducting Block-Copolymers

Several previous chapters investigated in detail how molecular packing structure controls triplet exciton dynamics in singlet fission materials. In this and the following chapter, the effects that chemical modification has on the morphology of organic semiconducting polymers will be studied. In particular, the changes in the nanoscale structure of polymer films and aggregates will be related to their charge carrier dynamics. As discussed in Chapter 1, local intermolecular interactions influence the rate of both triplet and charge transfer. Therefore, like triplet transport in organic molecules, charge transport is expected to be sensitive to the arrangement of the polymers.

Developing commercially-viable organic solar cells requires two major improvements: (1) lowered cost of fabrication and/or installation, and (2) increased photoconversion efficiency. The use of widespread solution-processable organic materials promises to satisfy the former. However, boosting photoconversion efficiency has been particularly challenging for the past ~20 years. A significant roadblock for boosting device performance is the ability to transport photogenerated charges to the electrodes, which is hindered by disorganized thin film morphologies leading to poor percolation pathways. Controlling thin film morphology, without compromising charge transport, is especially difficult for solution-processed polymers that intrinsically tend to form disordered structures. Recently, this problem has been addressed by using block-copolymers, for which two polymer materials are covalently tethered together. If the blocks of polymers are not chemical compatible, the block-copolymer can self-assemble

into ordered structures that may improve charge percolation pathways for efficient transport to the electrodes of the device.

The covalent linkage in block-copolymers offers a method to control nanoscale morphology, which promises to boost device performance. However, to this date block-copolymer photovoltaics have produced very low efficiencies compared to other types of organic materials. Consequently, a better understanding of how the chemical structure and covalent linkage of block-copolymers affect photogeneration and transport of charges is needed. This and the following chapter serve to investigate how block-copolymer materials can be better designed by relating changes in nanoscale structure to charge generation and transport characteristics. Through the work presented in this chapter, chemical design rules were developed that promise to improve block-copolymer photovoltaics.

This chapter was adapted from the publication: Grieco, C., Aplan, M.P., Rimshaw, A., Lee, Y., Zhang, W., Wang, Q., Milner, S.T., Gomez, E.D., and Asbury, J.B., “Molecular Rectification in Conjugated Block Copolymer Photovoltaics”, *J. Phys. Chem. C*, **2016**, 120, 6978-6988, which has been rephrased in the context of this dissertation.

The Gomez lab at The Pennsylvania State University Department of Chemical Engineering is acknowledged for the synthesis and characterization of all polymers presented in this chapter. Youngmin Lee is acknowledged for preparing all film samples and devices, and for performing all device testing. Thinh Le is acknowledged for performing the RSOX measurements. Melissa Aplan is acknowledged for steady-state optical spectroscopy of all polymer solutions. Wenlin Zhang is acknowledged for all DFT calculations.

9.1. Background: Polymer Photovoltaics

9.1.1. Principles of organic photovoltaics

Charge photogeneration, the primary process of solar cells, is the conversion of light energy to charge carriers that can subsequently be collected at the device electrodes. A simple scheme of this process is illustrated in **Figure 9-1**. In organic materials, photoexcitation creates a spatially separated electron-hole (e/h) pair. However, this e/h pair is intrinsically difficult to split apart and separate from each other.¹ Organic materials typically have low dielectric constants (~ 3) and high localization of charges following photoexcitation. This creates Coulombic barriers to charge separation (CS) of ~ 0.5 - 0.1 eV, which are much larger than thermal energy (0.025 eV).¹ Thus in general, tightly-bound excitons are created upon photoexcitation in organic molecules and polymers.

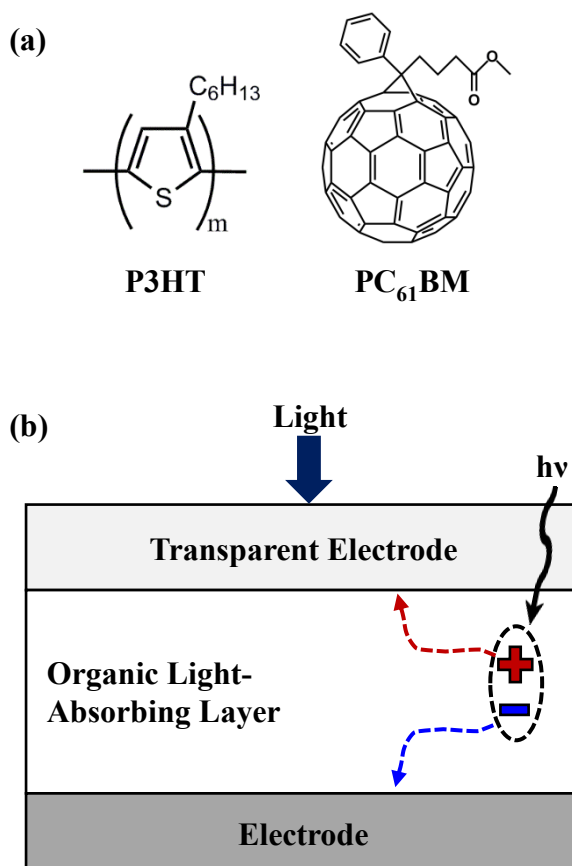


Figure 9-1: (a) Example of prototypical molecules used in organic solar cells. (b) Simple diagram of an organic solar cell, highlighting the formation/splitting of excitons and the subsequent diffusion of charges to the electrodes.

An additional driving force to split excitons in OSCs is needed in order to attain efficient charge photogeneration. This is accomplished by creating an interface across which excitons can split via electron-transfer between two materials differing in electron affinity. This “interfacial charge transfer” creates a Coulombically-bound e/h pair over a larger spatial extent than an exciton, with localization of the hole on the electron-donating material and localization of the electron on the electron-accepting material. From this point forward, this is referred to as a charge-transfer (CT) state. Once an exciton splits at an interface between an electron donor (D) and an electron acceptor (A), it may be able to separate into free charges that can subsequently travel through their respective phases and be collected at the electrodes. This

constitutes the general charge photogeneration mechanism of OSCs, which is illustrated for a simple device geometry in **Figure 9-2**.

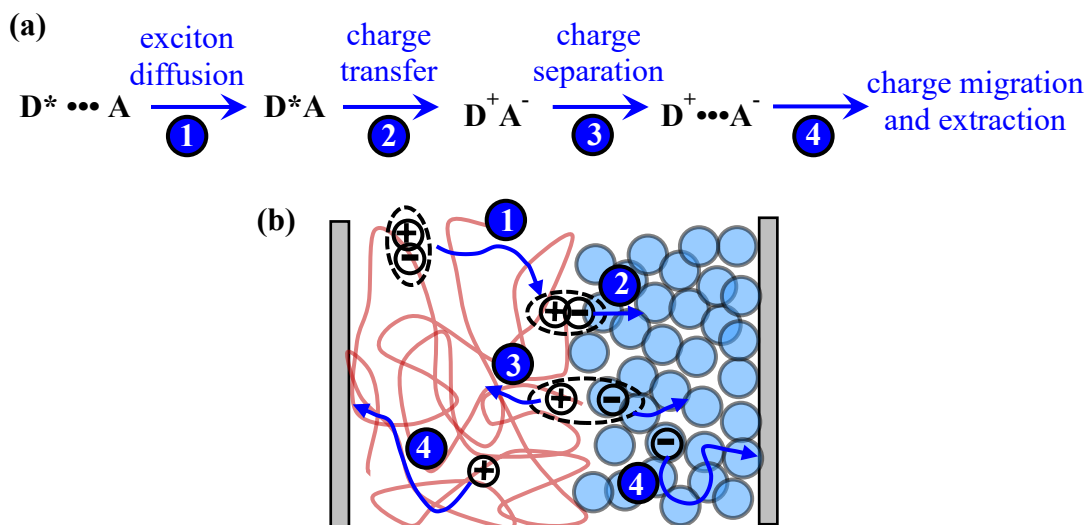


Figure 9-2: (a) Simple scheme for the current photogeneration mechanism in organic solar cells. (b) Illustration of the mechanism.

Though interfacial charge transfer can lower the barrier to CS and enable OSC function, the addition of the second material actually introduces photocurrent loss routes.² First, photoexcitation creates a tightly-bound exciton, which must diffuse to a D-A interface. Exciton loss can occur if the exciton does not encounter an interface within its excited-state lifetime, or does not undergo CT. Photon loss occurs when the organic photogenerating layer thickness of the device must be limited (smaller absorptive path) in order to accommodate finite exciton diffusion lengths. CT state loss occurs if they do not dissociate within the CT state lifetime, which results in geminate e/h recombination. Charge carrier loss occurs if charge carriers encounter each other at a D-A interface and recombine before reaching the electrodes.

Some of these photocurrent losses have been reduced by using bulk-heterojunction (B-H) devices, which are made by either mixing a D and A material together and solution-casting them, or by coevaporation of D and A solids. The ideas behind intermixed D and A domains

are: To decrease the average length that an exciton must diffuse so that the active layer thickness may be larger (increasing absorption); and to create a larger interfacial area to enhance the probability for CT to occur. In fact, B-H OSCs for polymer-fullerene blends have historically resulted in the highest efficiencies.³ However, the challenges to improving B-H devices originate from the lack of control of the miscibility of the D and A material. This directly impacts the B-H interfacial area, D/A domain size, and availability of bicontinuous percolation pathways for charge migration to electrodes. Manipulation of these characteristics is significant to device optimization, and so the lamellar heterojunction device (see **Figure 9-3**) is often thought to be ideal. However, this nanoscale morphology has been very difficult to attain and is usually not self-assembled, but requires expensive patterning techniques.⁴ Consequently, B-H layer fabrication typically involves solution-casting a D and A material (and often thermal or solvent treatment) and relying on satisfactory phase-separation that balances both interfacial area with domain size. Because of difficult control of these numerous active layer parameters, successful OSC materials are often found by serendipity more than by design.

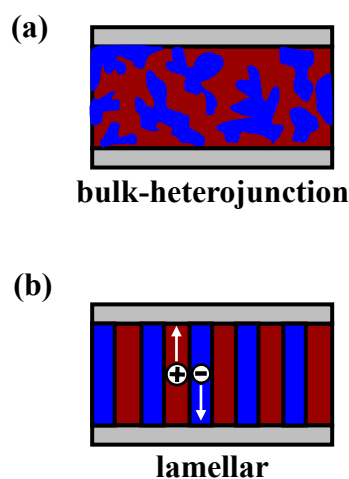


Figure 9-3: Examples of the (a) bulk-heterojunction, and (b) lamellar geometries for the active layer in organic photovoltaics.

To characterize device performance, a current-voltage (J-V) characteristic is measured under solar illumination. The photocurrent is measured over a range of applied biases, forming a J-V curve, as exemplified in **Figure 9-4**.

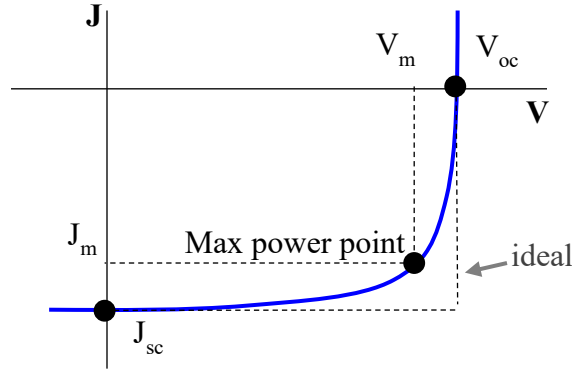


Figure 9-4: Illustration of a current-voltage (J-V) characteristic of photovoltaic devices.

The short circuit current, J_{SC} , is the current that is generated at no applied bias. The open circuit voltage, V_{OC} , is the bias that is required to reduce the photocurrent to zero. The maximum power point is the position on the J-V curve that produces the highest power. The fill factor, FF, is the ratio of the maximum power to the product of the J_{SC} and V_{OC} :

$$FF = \frac{J_m V_m}{J_{SC} V_{OC}} \quad (\text{eqn. 1})$$

In an ideal diode, the FF approaches a value of unity, producing a rectangular-like J-V characteristic. The power conversion efficiency (PCE), η_P , is defined as:

$$\eta_P = \frac{J_{SC} V_{OC} FF}{P_{in}} \quad (\text{eqn. 2})$$

where P_{in} is the input power of the light. Thus, in general increasing the J_{SC} , V_{OC} , and FF will all improve the device performance. The V_{OC} is typically limited by the energetics of the materials used in the device, which is typically controlled by chemical composition. The J_{SC} and FF is typically limited by the efficacy of charge migration through the device.

9.1.2. Motivation for block-copolymer photovoltaics

Block-copolymers (BCPs) enable thermodynamically-favored self-assembly of a nanoscale lamellar heterojunction (among many others).^{4,6} An illustration of a block-copolymer is shown in **Figure 9-5**. The idea behind enabling nanophase separation is to covalently link two chemically incompatible polymers, which prevents their macrophase segregation.^{4,5} In fact, the synthesis of a variety of all-conjugated diblock copolymers has recently been developed for use as active materials in OSCs. These block copolymers include an electron-donor (D) block and an electron-acceptor (A) block that can be chosen to form thermodynamically self-assembled lamellar structures.^{4,7} An illustration of this goal is shown in **Figure 9-5**.

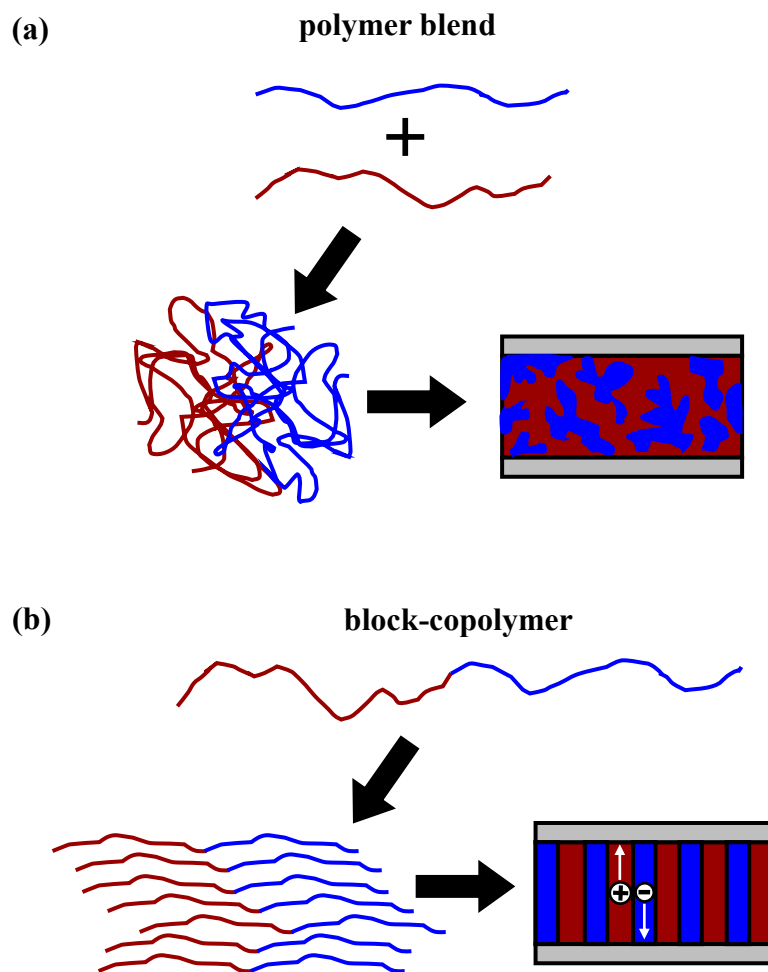


Figure 9-5: Illustration of solution-processed polymer materials for photovoltaic devices comparing a **(a)** polymer blend system to a **(b)** block-copolymer system.

D-A BCPs have recently been shown to form working OSCs.^{8,9} In particular, Guo et al.⁹ have demonstrated improved OSC performance when switching from an all-polymer mixture to its corresponding BCP by almost 3-fold. As the thermal treatment of the BCP device was increased, the authors showed the formation of nanoscale lamellar structures that correlated with a substantial increase in device performance. However, despite this enhancement of morphological control, the device efficiency still remains low compared to the polymer-fullerene B-H OSCs, which typically have efficiencies around 7-10%.¹⁰⁻¹³ This suggests that

in addition to controlling the nanomorphology of BCP OSCs, optimization of their interfacial charge photogeneration characteristics is needed.

D-A BCPs feature (by definition) at least one D-A interface for every polymer chain. This suggests that as opposed to conventional B-H OSCs, intramolecular charge transfer is a viable pathway involved in charge photogeneration in BCP OSCs. For example, the BCP lamellar device described above shows that although there is a significant reduction in intermolecular interfaces, charges are still efficiently separated. Thus, the intramolecular interface is new potential site for CT that can involve different mechanisms of charge photogeneration and charge recombination. Therefore in order to better engineer BCP OSC materials, it is important to understand how the molecular structure that is imposed using a linkage between D and A affects charge generation and recombination characteristics.

9.1.3. Challenges imposed by covalent linkages in block-copolymers

With the recent emergence of BCPs as a viable OSC material, Johnson et al. investigated the impact of electronic coupling between the D and A blocks in a model BCP system in 2013.¹⁴ The authors used a monomer (F8-TBT) as the electron-accepting unit and the polymer (P3HT) as the electron-donating block (see **Figure 9-6**). The F8-TBT was linked to P3HT through either the F8 or TBT moiety. The idea was to photoexcite P3HT and follow charge transfer to/from the TBT unit. By doing this, the electronic coupling between the LUMOs of P3HT and TBT were changed. As shown in **Figure 9-6**, when electronic coupling is very strong, a tightly-bound and localized CT state forms between D and A, which makes CS improbable. On the other hand, increasing the D-A distance via a “bridging unit” reduces their electronic coupling, resulting in the formation of more weakly-bound and delocalized CT states

that have a higher probability to separate. The results of this work highlight the importance of tailoring the covalent linkage in order to favor charge generation.

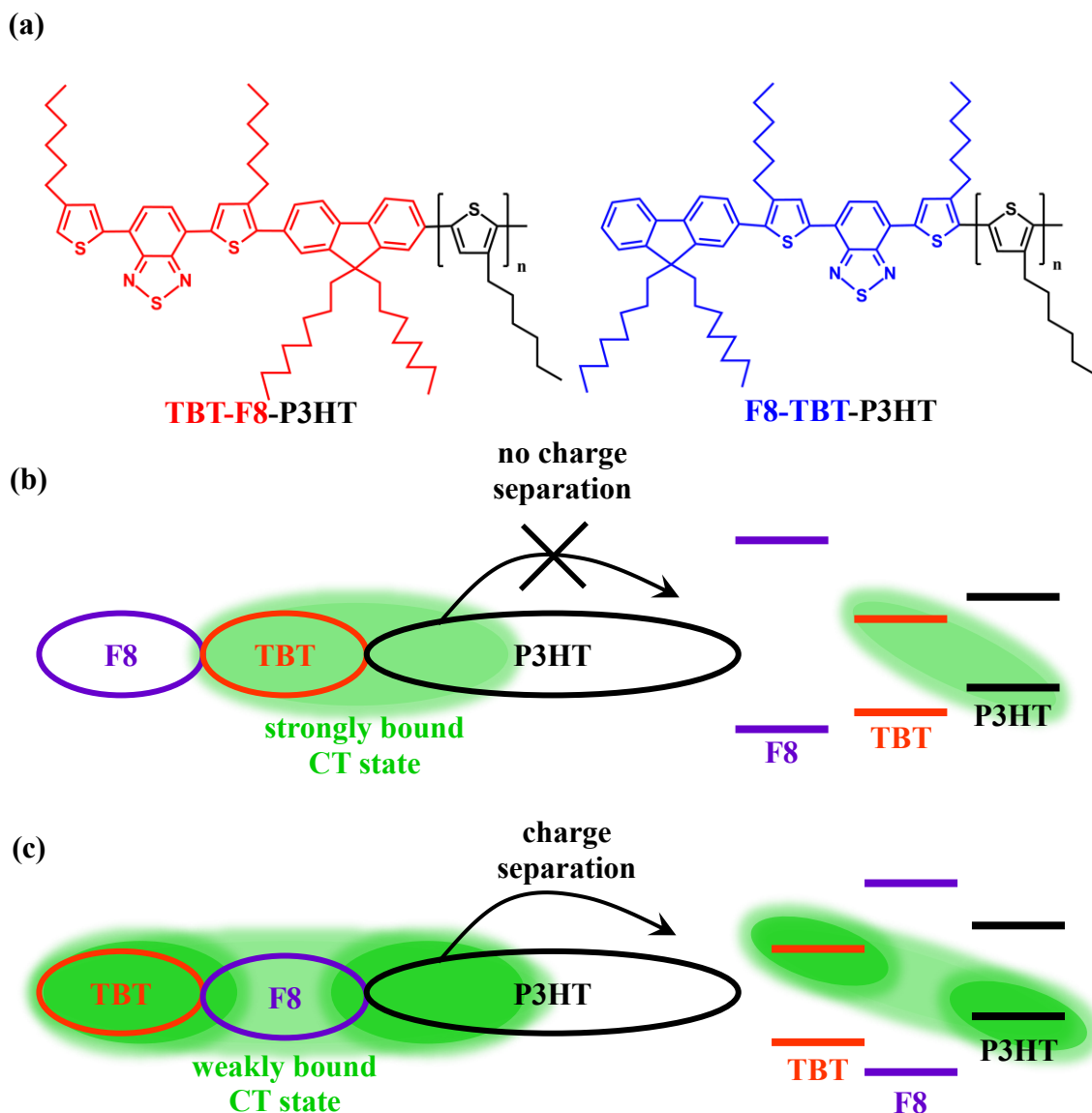


Figure 9-6: (a) Chemical structures of TBT-F8-P3HT and F8-TBT-P3HT. (b) Cartoon illustrating strongly bound CT states that form in F8-TBT-P3HT that cannot charge separate. Energy level diagram showing the HOMOs and LUMOs of each moiety. (c) Cartoon illustrating weakly bound CT states that form in TBT-F8-P3HT that can charge separate. Energy level diagram showing the HOMOs and LUMOs of each moiety.

9.2 Introduction

Semiconducting block-copolymers provide a route to controlling electron donor and acceptor phase separation on the nanoscale level for organic photovoltaics.^{4,9,15-18} For example, changing the volume fractions, interaction energies, and total molecular weight of each polymer block enables the formation of lamellar or other bicontinuous mesoscale structures,^{19,20} creating continuous paths for charge transport and extraction. Previous reports on block-copolymer films demonstrated phase separation on length scales comparable to the ~10 nm exciton diffusion length of organic molecules.^{4,9,15-18} However, when applied to photovoltaics, such systems have failed to achieve photovoltaic power conversion efficiencies (PCEs) over 1%.^{18,21} It was thought that block-copolymers may undergo rapid charge recombination since the covalent linkage between the donor and acceptor polymer blocks turns on strong electronic coupling via wavefunction overlap interactions.²²⁻²⁹

Recently, block-copolymer photovoltaics have reached as high as ~3% PCE using poly(3-hexylthiophene-2,5-diyl)-block-poly((9,9-bis-(2-octyl)fluorene-2,7-diyl)-alt-(4,7-di(thiophene-2-yl)-2,1,3-benzothiadiazole)-5',5''-diyl) (P3HT-b-PFTBT).⁹ This particular block-copolymer system demonstrated about a three-fold higher PCE in comparison to their polymer blend counterpart (lacking a covalent linkage). The chemical structures of these systems are provided in **Figure 9-7**. The enhancement of the photovoltaic efficiency was associated with the formation of a favorable mesoscale morphology having ~20 nm periodicity, consisting of lamellar phases of donor and acceptor polymer. Altogether, these results suggested that charge transport and extraction became kinetically competitive with charge recombination. However, direct spectroscopic evidence for this hypothesis has not yet been provided.

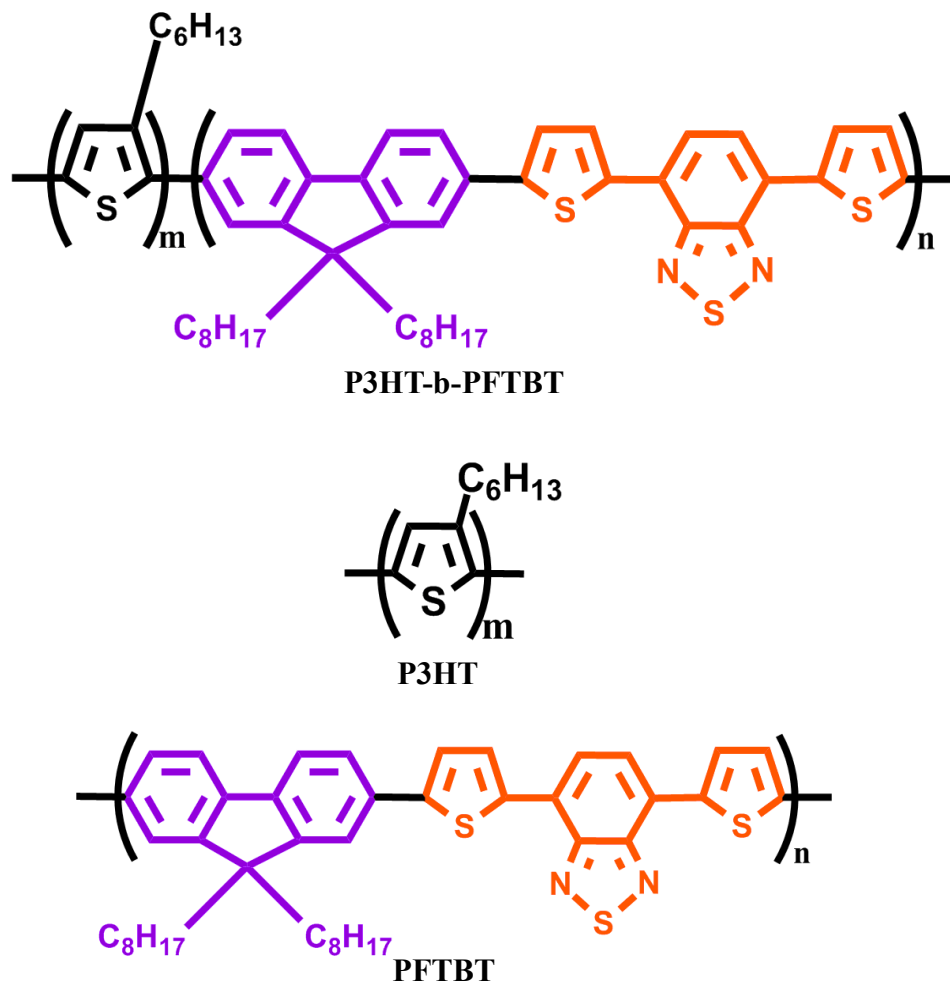


Figure 9-7: Chemical structures of the block-copolymer and homopolymers used.

In this work, charge carrier kinetics are measured in films of P3HT-b-PFTBT in comparison to the P3HT/PFTBT homopolymer blend counterparts to assess the role that the covalent linkage in the block-copolymer has on charge recombination. Charge generation and recombination were measured through absorptions found in the mid-infrared region on timescales ranging from picoseconds to microseconds. These measurements demonstrated that the covalent linkage does not have any significant impact on charge recombination in the block-copolymer films. Charge recombination was found to occur at similar rates in both the P3HT-b-PFTBT and the P3HT/PFTBT blend films. Additionally, it was shown that transient

absorption measurements in the mid-infrared region are critical for accurately measuring charge carrier kinetics, since this region contains signals associated with separated charge carriers absorption features uncontaminated from other transient species. Time-resolved spectroscopy, combined with morphology and device characterization, led to the development of design rules for guiding the future development of block-copolymer materials for organic photovoltaics.

9.3. Experimental Methods

9.3.1. Photovoltaic device fabrication and characterization

Photovoltaic devices were fabricated using a conventional architecture of ITO/PEDOT:PSS (70 nm)/active layer (80 – 100 nm)/Al electrode (75 nm). The film thicknesses were measured using a TENCOR P-10 surface profiler. PEDOT:PSS (Clevios P, Heraeus) was spin-coated onto ITO-coated glass substrates (20 ohm/sq, Xin Yan Technology, Hong Kong) at 4000 rpm for 2 min, followed by drying on a hotplate at 165 °C for 10 min. The substrates were transferred into a nitrogen glove box for all other processing. Solutions of P3HT/PFTBT mixtures (5.0 mg/mL, 1:1 in weight) and P3HT-b-PFTBT (5.0 mg/mL) were made in anhydrous chloroform ($\geq 99\%$, amylenes as stabilizer, Sigma-Aldrich) and were heated with stirring at 90 °C for about 20–22 hr in a tightly sealed vial. The solutions were spin-coated at 1000 rpm for 60 sec onto the device substrates. Vacuum thermal evaporation was carried out at 10^{-6} Torr to deposit aluminum on top of the active layer using a shadow mask, with a device area of 16.2 mm². The completed solar cells were then further annealed at 100 °C for 20 min or at 165 °C for 10 min.

Device characteristics were measured in nitrogen atmosphere under simulated AM 1.5G illumination (97 mW/cm^2) using a xenon lamp solar simulator (Newport Model SP92250A-1000). The intensity was calibrated using a power meter and NREL certified Si reference photocell (Newport). A Keithley 2636A Sourcemeter was used for the device measurements.

9.3.2. RSOXS sample preparation and measurement

Thin films of either P3HT-b-PFTBT or P3HT/PFTBT mixtures were spin-coated in nitrogen atmosphere from 7 mg/mL chloroform solutions onto PEDOT:PSS-coated silicon wafers. The silicon wafers were previously cleaned by sonicating in acetone and isopropanol followed by UV ozonation. The as cast polymer films were floated off in deionized water and lifted with 5 mm $\times$ 5 mm silicon frames containing a 1 mm $\times$ 1 mm, 100 nm thick Si_3N_4 window. The film samples were dried for 24 hrs at room temperature under vacuum before they were thermally annealed under nitrogen atmosphere. RSOXS measurements were performed in vacuum using transmission geometry at beamline 11.0.1.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory. The scattering patterns were obtained using polarized X-rays with an energy of 285.4 eV. Dark currents were taken into account. The patterns were then radially integrated for analysis.

9.3.3. Optical spectroscopy

Sample preparation for solution measurements: Polymers were dissolved in anhydrous chloroform (Sigma Aldrich) at a concentration of 1 mg/mL in nitrogen atmosphere and stirred overnight. The solutions were then diluted to 1 $\mu\text{g/mL}$ and sealed inside 1 cm pathlength quartz cuvettes. Measurements were taken within 30 minutes upon removing from nitrogen atmosphere.

Sample preparation for film measurements: P3HT/PFTBT mixtures (5.0 mg/mL, 1:1 in weight) and P3HT-b-PFTBT (5.0 mg/mL) were dissolved in anhydrous chloroform ($\geq 99\%$, amylene as stabilizer, Sigma-Aldrich) and stirred for about 20–22 hrs at 90 °C in a tightly sealed vial under nitrogen atmosphere. Films were made on CaF₂ substrates by spin-coating the solutions at 1000 rpm, followed by thermal annealing at either 100 °C for 20 min or at 165 °C for 10 min.

Ultrafast mid-IR transient absorption spectroscopy of films: Ultrafast visible-pump/mid-IR-probe spectroscopy was carried out using a home-built system.³⁰ Briefly, a Ti:Sapphire regenerative laser amplifier (Integra, Quantronix), was seeded by a Ti:Sapphire laser (Coherent). The laser drove an OPA (TOPAS, Light Conversion Ltd) that was tuned to 532 nm to generate the visible pump pulse. A second OPA was used and tuned to ~ 4000 nm to generate the mid-IR probe pulse. The pump energy density was kept below $\sim 30 \mu\text{J}/\text{cm}^2$ to avoid measuring a nonlinear sample response.

Nanosecond mid-IR transient absorption spectroscopy: Nanosecond mid-IR transient absorption measurements were performed using a home-built flash photolysis system.^{31,32} A silicon nitride emitter (Spectral Products) was used as the monitoring probe beam. A 30 Hz frequency-doubled (532 nm) Nd:YAG laser (Continuum) with ~ 10 ns pulse duration was used as the excitation source. Spectral resolution was obtained using a monochromator (Spectral Products) with slits set to achieve a 40 nm effective bandwidth. For all kinetic measurements, the probe beam was filtered using a combination of a 2.5 μm longpass filter and a 10 μm shortpass filter before it was detected using a 100 MHz MCT photodiode (Kolmar Technologies, KV104). For spectral measurements the probe was detected using a 16 MHz MCT photodiode (Kolmar Technologies, KMPV11-1-J1). The detected signal was digitized

using a 100 MHz PC oscilloscope (Pico Technology). The excitation energy density was kept around $\sim 30 \mu\text{J}/\text{cm}^2$ for all kinetic measurements in order to match that used in the ultrafast measurements. All spectra were measured using a higher energy density ($\sim 50 - 60 \mu\text{J}/\text{cm}^2$) in order to achieve satisfactory S/N.

Nanosecond vis/near-IR transient absorption spectroscopy: Nanosecond vis/near-IR transient absorption measurements were carried out using a home-built vis/near-IR flash photolysis system.³¹ A tungsten halogen light source (Spectral Products) was used as the monitoring probe beam. Before encountering the sample, it was filtered using an assortment of longpass dielectric filters. The excitation source was the same as that used in the nanosecond mid-IR measurements. Spectral resolution was attained using a monochromator (Spectral Products) with slits set to achieve 10 nm effective bandwidth. The transmitted beam was measured using a variety of photodiode detectors, each having similar rise-times depending on the spectral region measured. A silicon photodiode (Thorlabs, DET10A) was used for the range of $\sim 575-800$ nm. An InGaAs photodiode (DET10N, Thorlabs) was used for the range of $\sim 800-1300$ nm. An InGaAs transimpedance amplified photodiode (PDA10D, Thorlabs) was used for the range $\sim 1300-2300$ nm. For the former two photodiodes, the detected signal was amplified using a 200 MHz preamplifier (Femto). The signal was then digitized using a 200 MHz PC oscilloscope (Pico Technology). The pump energy densities used were the same as those used in the nanosecond mid-IR measurements.

Steady-state absorbance and photoluminescence spectroscopy: For solution measurements, absorption spectra were collected using a UV-Vis spectrometer (Agilent Technologies, Cary60). Steady-state photoluminescence spectra were collected using a fluorometer (Photon

Technology International) using 470 nm excitation and spectral resolution of 2 nm. For films, absorption spectra were measured using a different UV-Vis spectrometer (Beckman, DU 520).

9.3.4. Quantum chemical calculations

Density functional theory (DFT) calculations were performed at the B3LYP 6-31G* level using the Gaussian 09 software package. The geometry of the α -sexithiophene and 7-(5-thienyl)-2,1,3-benzothiadiazole-4-(2-fluorene-5-thienyl) molecules were optimized, and the resulting HOMOs and LUMOs were rendered using the VMD software package.

9.4. Block-Copolymer Device Characteristics and Thin Film Structure

In the original report of P3HT-b-PFTBT and P3HT/PFTBT blend photovoltaic devices, significant enhancement in block-copolymer device performance was associated with the formation of a lamellar mesophase via thermal annealing at 165 °C.⁹ In the present report, in which it is desired to relate charge recombination characteristics to such device performance, a different set of polymer batches were studied. It is critical to study block-copolymer material systems on a batch-by-batch basis since their synthesis remains a challenge.^{17,18,23} Consequently, the morphological and device characterization was necessarily repeated on the current batch of P3HT-b-PFTBT, P3HT, and PFTBT that were used in the spectroscopic measurements.

The morphological and device characterizations are represented in **Figure 9-8** and **Figure 9-9**.

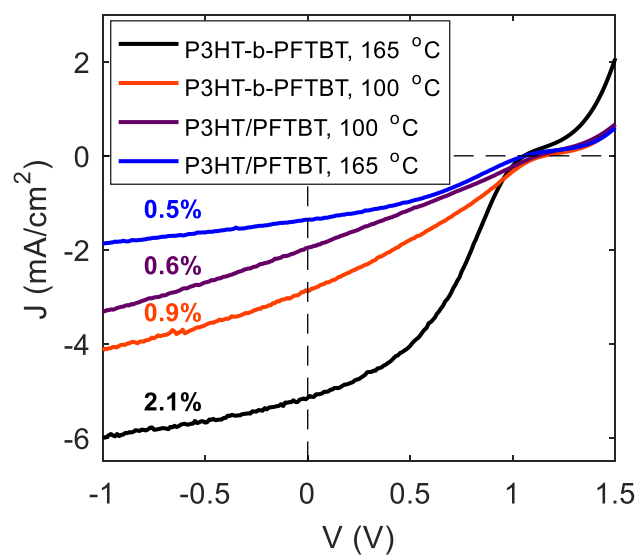


Figure 9-8: Current-voltage characteristic for block-copolymer and homopolymer blend devices. The power conversion efficiencies are labeled for reference.

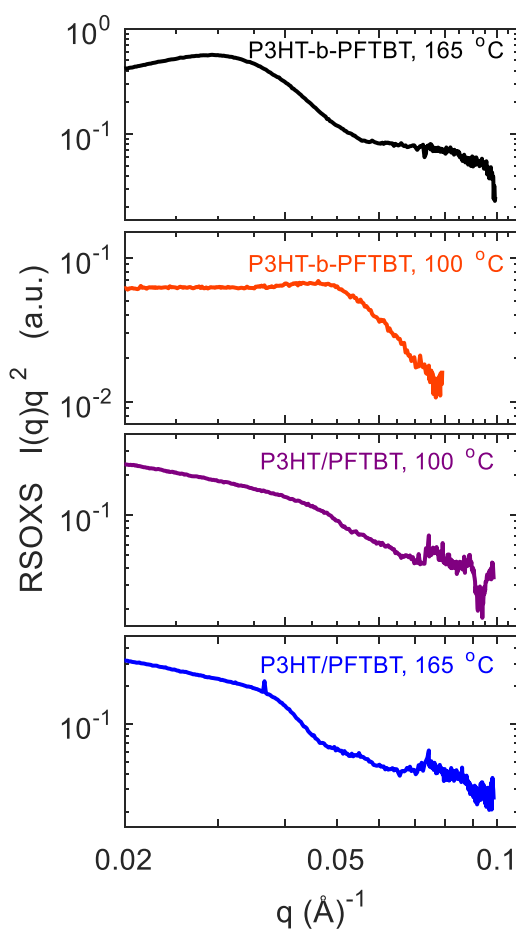


Figure 9-9: RSOXS patterns collected for P3HT-b-PFTBT and P3HT/PFTBT blend films, presented as $I(q)q^2$ versus scattering vector, q .

Figure 9-8 displays J-V characteristics measured in P3HT-b-PFTBT devices and P3HT/PFTBT blend control devices, thermally annealed at either 100 °C or 165 °C. **Table 9-1** lists the detailed device results (PCE, J_{sc} , V_{oc} , FF).

Table 9-1. J-V characteristics for polymer photovoltaics

Sample	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
P3HT-b-PFTBT, 165 °C	4.9 ± 0.4	1.07 ± 0.02	0.40 ± 0.01	2.14 ± 0.07
P3HT-b-PFTBT, 100 °C	2.9 ± 0.1	1.16 ± 0.01	0.27 ± 0.01	0.94 ± 0.02
P3HT/PFTBT, 100 °C	1.9 ± 0.1	1.12 ± 0.01	0.27 ± 0.01	0.59 ± 0.03
P3HT/PFTBT, 165 °C	1.3 ± 0.1	1.06 ± 0.05	0.36 ± 0.01	0.51 ± 0.03

Device results are the average of at least 5 devices.

Blend films (P3HT/PFTBT) were 1:1 wt/wt.

The temperatures listed are the thermal annealing temperatures.

The molecular weights and polydispersity of the polymers used to form the P3HT/PFTBT blends were matched those used in the P3HT-b-PFTBT block copolymer. The results matched, in trend, those reported previously.⁹

The improvement in the P3HT-b-PFTBT photovoltaic performance was then associated with formation of mesoscale ordering as in the previous report.⁹ Kratky plots are displayed for P3HT-b-PFTBT and P3HT/PFTBT blend films in **Figure 9-9**, for which resonant soft X-ray scattering (RSOXS) intensities, $I(q)$, are plotted in the form, $I(q)q^2$ versus scattering vector, q , in order to clarify the scattering features.^{12,33-36} The P3HT-b-PFTBT film that was annealed at 165 °C exhibited a peak around $q = 0.03 \text{ \AA}^{-1}$ in addition to a shoulder around $3q = 0.09 \text{ \AA}^{-1}$, which corresponds to a ~20 nm repeating domain size. As previously observed, this size corresponds to the end-to-end distance of the polymers.⁹ On the other hand, the P3HT/PFTBT blend film that was annealed at 165 °C exhibited a shoulder around $q = 0.04 \text{ \AA}^{-1}$, indicating that a ~15 nm structure was formed, possibly associated with P3HT fibrils.

Consideration of the differences in mesoscale structure of the P3HT-b-PFTBT and P3HT/PFTBT blend films that were thermally annealed at 100 °C explains how device

performance of the block-copolymer annealed at 165 °C was improved. Scattering from the blend films annealed at 165 °C or 100 °C and from the block-copolymer film annealed at 100 °C all share a similar scattering feature around $q = 0.04\text{--}0.05 \text{ \AA}^{-1}$. This is attributed to the occurrence of P3HT fibrils, since the features are present in both the blend and block-copolymer films. Regardless, there are additional differences in the scattering from these films: The data for the blend film at low q shows a negative slope, which indicates the presence of large ($>50 \text{ nm}$) features, consistent with uncontrolled, macrophase separation. On the other hand, block copolymer exhibits scattering that is either independent of q or decreases at low q (positive slope). For the 165 °C annealed film, the scattering at low q has a positive slope, indicating further coarsening of the morphology compared to the 100 °C annealed film.

9.5. Identifying Spectroscopic Signatures of Charge Carriers in Polymer Films

9.5.1. Nanosecond transient absorption spectra of polarons

Ultrafast and nanosecond transient absorption spectroscopy was used to measure charge recombination kinetics in the P3HT-*b*-PFTBT and P3HT/PFTBT blend films, which were fabricated similarly to the samples used in the device and RSOXS studies. First, nanosecond transient absorption spectra were collected, spanning the visible to mid-IR spectral regions in order to identify the cleanest spectroscopic location for measuring the photogenerated charge carrier kinetics.³⁷⁻³⁹ **Figure 9-10** shows the transient absorption spectra obtained for each film following photoexcitation at 532 nm with absorbed excitation densities at $\sim 50 \text{ \mu J/cm}^2$. The spectra shown were averaged between either 25 and 50 ns or between 1 and 2 μs time delays.

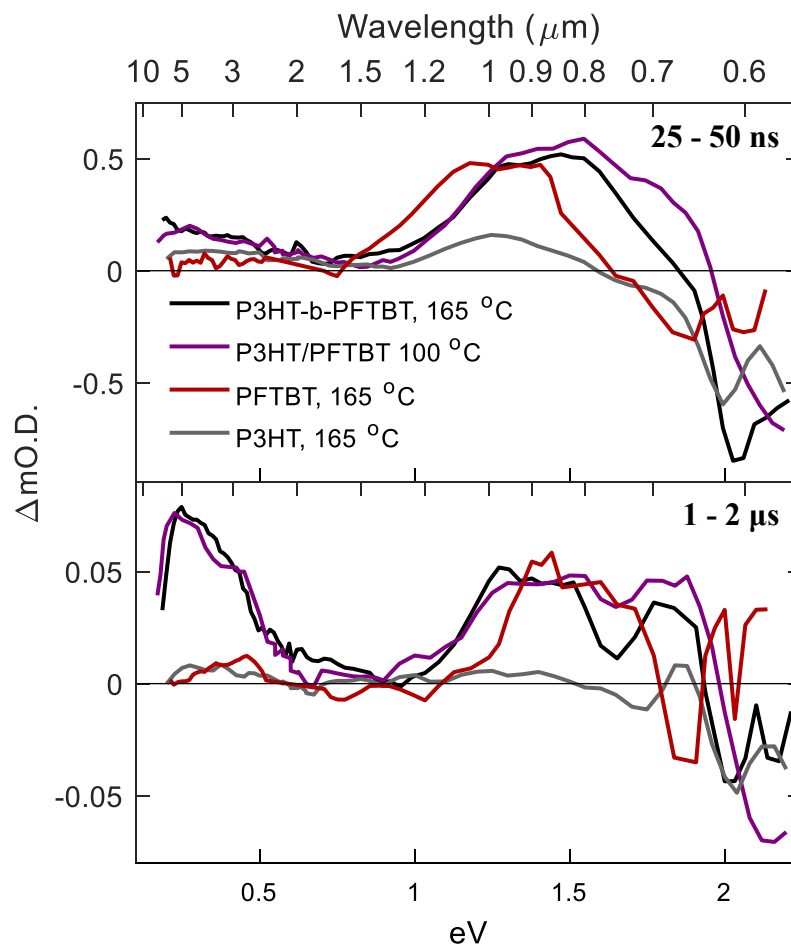


Figure 9-10: Transient absorption spectra for the P3HT-b-PFTBT film annealed at 165 °C, the P3HT/PFTBT blend film annealed at 100 °C, and the homopolymer films annealed at 165 °C. The top panel shows the spectra averaged between 25 and 50 nanoseconds, while the bottom panel shows the spectra averaged between 1 and 2 microseconds. All films were excited using 532 nm excitation, and their spectra were normalized for slight differences in fraction of photons absorbed by the pump.

The nomenclature used in the literature to describe charge carriers in polymer photovoltaics is highly varied. The following naming conventions are used: Photogenerated charge carriers (electrons and holes) that arise from charge separation from a donor-acceptor interface are termed “charge separated polarons” in accordance with Durrant and coworkers.³⁸ Such polarons primarily contribute to the photocurrent measured in photovoltaic devices.³⁹ Polaronic species that form in P3HT homopolymer films (or P3HT domains within polymer blend films) are termed “polaron pairs” in accordance with other researchers.^{37,40,41} While

polaron pairs exhibit spectroscopic features similar to or identical to those arising from charge separated polarons, they contribute insignificantly to device photocurrent.⁴² Finally, distinct excited electronic states are generated in PFTBT having intramolecular charge transfer character since it is, by design, a “push-pull” (or “donor-acceptor”) copolymer.^{43,44} In this work, such electronic species are called “pseudo charge transfer states” in accordance with Chen and coworkers.⁴⁵ In the literature, these species have also been called “intramolecular polaron pairs”.^{43,44}

The transient absorption spectra reveal substantial signals in both the visible and near-IR regions for all the films. In addition, the signals appearing in the near-IR for the PFTBT control sample are equal in amplitude to those measured in either block-copolymer or polymer blend samples on both sets of timescales. Such PFTBT absorption signals may include contributions from pseudo charge transfer states and/or triplet excitons.⁴⁴ It is therefore challenging to discriminate the absorptions of these species from those of charge separated polarons in the block copolymer and polymer blend films.

Unlike the visible and near-IR spectral regions, the mid-IR region features distinct spectral signatures of charge separated polarons. Polaron absorption was observed spanning ~0.1-0.5 eV that is present on the nanosecond timescale and persists into the microsecond timescale only when both P3HT and PFTBT are present in the films (block-copolymer or blends). As a result, the absorption feature that persists into the microsecond timescale is assigned to charge separated polarons.

9.5.2. Selection of the mid-IR region for measuring polaron absorption kinetics

Further support of the mid-IR spectral assignment of the charge separated polarons is provided by kinetic analysis (**Figure 9-11**). For the following discussion, an as-cast

P3HT/PFTBT blend film is used as a representative sample. Transient species possessing a unimolecular decay in PFTBT have absorptions in the near-IR that significantly overlap polaron absorption. The “contaminant” signal that arises is often attributed to triplets that often form in high yields in amorphous polymer films.³⁸ In contrast, the mid-IR region seems to feature only polaron absorption, based on the clear observation of power law decay for both homopolymers (P3HT or PFTBT) and the P3HT/PFTBT blend films. The homopolymer films show weak signals, signifying that a very low population of polarons is formed, consistent with a previous report.⁴⁶ The additional signal arising in the P3HT/PFTBT blend film is assigned to polarons that have formed as a result of charge separation at an electron donor-acceptor interface (i.e. charge separated polarons). In summary, these data suggest that the mid-IR spectral region exclusively features polaron absorption for the P3HT/PFTBT polymer blend film on the nanosecond to millisecond timescale. Consequently, mid-IR transient absorption spectroscopy can be used to most clearly track the polaron kinetics for the P3HT-b-PFTBT and P3HT/PFTBT films.

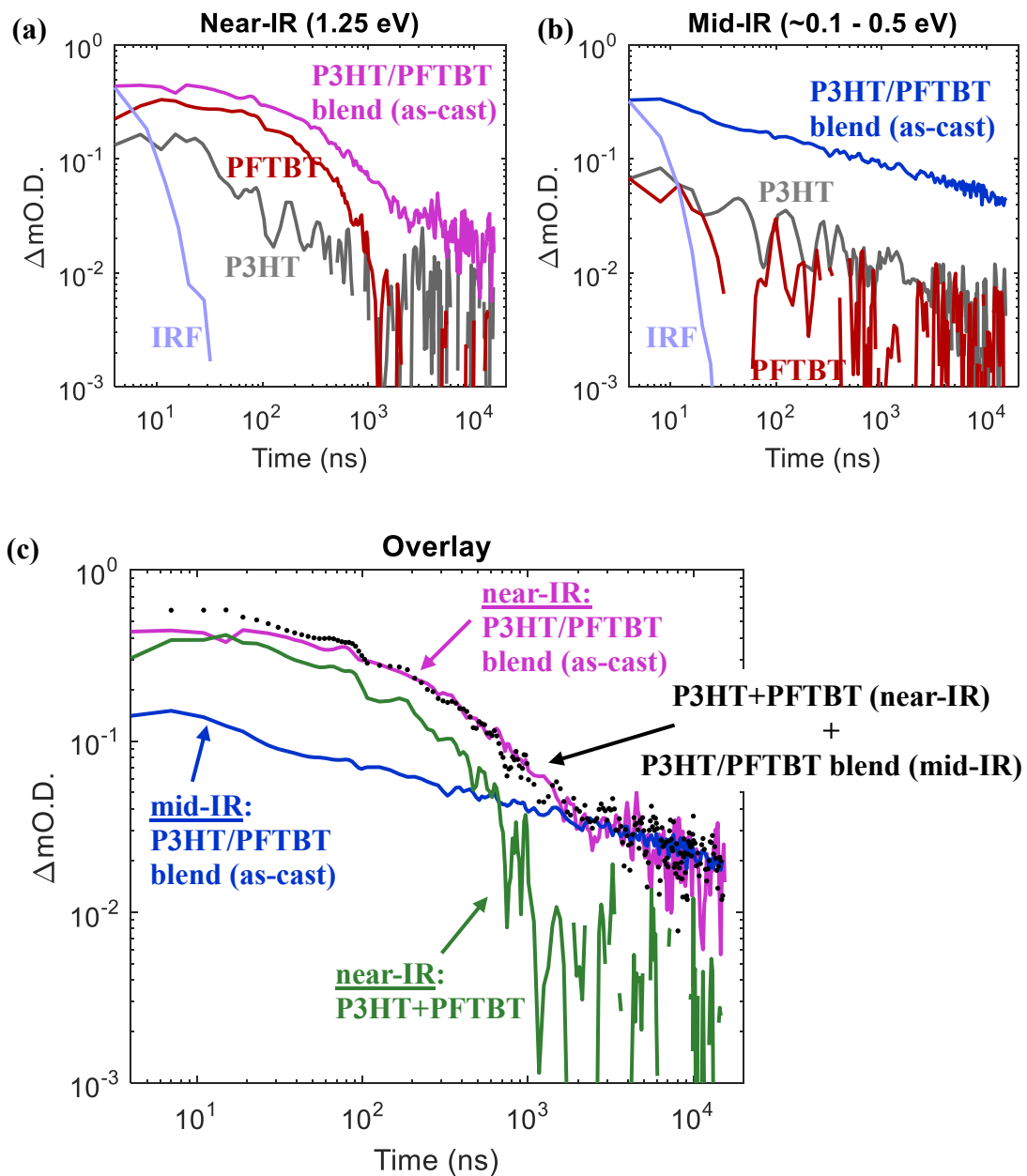


Figure 9-11: Nanosecond-microsecond transient absorption kinetics measured for an as-cast P3HT/PFTBT blend film and P3HT and PFTBT homopolymer films in the (a) near-IR and (b) mid-IR regions. A 532 nm excitation with $\sim 30 \mu\text{J}/\text{cm}^2$ incident energy density was used for all samples. The kinetics were each normalized to the fraction of absorbed photons by each sample. (c) Demonstration that the near-IR kinetics for the polymer blend is well-described using a linear combination of its mid-IR kinetics and the near-IR kinetics of the homopolymer films.

9.6. Charge Carrier Dynamics in Block-Copolymer and Polymer Blend Films

The charge recombination kinetics were measured in the mid-IR in P3HT-b-PFTBT and P3HT/PFTBT blend films to determine the effect that the covalent linkage in the block-copolymer has on charge recombination. In particular, if the covalent linkage enhances charge recombination due to stronger intramolecular donor-acceptor wavefunction overlap between the P3HT and PFTBT units,^{22,28} then there would be a faster loss of the polaron absorption signal in the block-copolymer films.

The transient absorption kinetics for the same series of P3HT-b-PFTBT and P3HT/PFTBT blend films used in the device and RSOXS studies is shown in **Figure 9-12**. The kinetics traces were produced by connecting ultrafast transient absorption data with nanosecond-microsecond transient absorption data that were measured using separate instruments under similar excitation conditions. However, the spectral ranges for the kinetics measured using the ultrafast and nanosecond instruments were not identical. This was warranted due to two experimental constraints: (1) The ultrafast probe pulse, which was generated by an OPA, had an emission range with only $\sim 200\text{ cm}^{-1}$ FWHM before dispersion; and (2) in nanosecond spectroscopy, it was necessary to sacrifice spectral resolution to obtain higher light levels required to measure the sub- $\Delta\text{mO.D.}$ absorption signals. In order to optimize the time resolution in the nanosecond measurements, the probe beam was focused onto the miniscule 0.1 mm diameter element of a 100 MHz MCT detector without using a monochromator. It was impossible to focus the incoherent probe light enough to achieve appreciable light levels required to measure the expected low signals ($\ll 1\text{ }\Delta\text{mO.D.}$). Eliminating the monochromator, and alternatively using a longpass filter, resulted in enough light to focus onto the detector

element. As a result, the spectral range measured for the nanosecond instrument was ~ 0.1 - 0.5 eV, while that of the ultrafast instrument was ~ 0.30 - 0.32 eV.

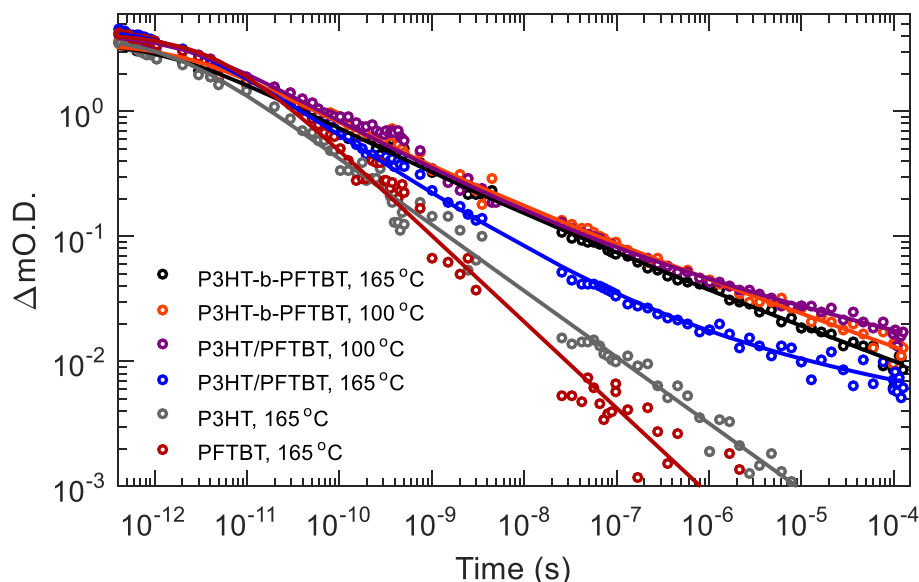


Figure 9-12: Mid-IR transient absorption kinetics measured in films of P3HT-b-PFTBT, P3HT/PFTBT blends, and the P3HT and PFTBT homopolymers. The excitation wavelength was 532 nm. All traces were scaled by the fraction of photons absorbed by each sample. The solid lines represent fits made using a sum of two empirical power laws.

A large discrepancy in spectral range can lead to experimental artifacts if multiple absorbers with different kinetics are present, or if there is a dynamic shift in absorption band. The primary absorbing species has been assigned to delocalized polarons in P3HT in the past.³⁷ Only a minimal contribution from localized polaron absorption was expected since its peak is known to be centered at ~ 0.5 eV in P3HT.³⁷ In addition, regioregular P3HT has been shown to produce minimal absorption of localized polarons³⁷ due to its nature to pi-stack when it crystallizes in thin films. The suppression of the localized polaron absorption peak was shown for the P3HT/PFTBT blend system upon thermal annealing, which is expected because P3HT (and possibly also PFTBT) crystallized as it anneals (see **Figure 9-13**). As a result, the mid-IR kinetics as measured using the nanosecond instrument primarily arise from delocalized

polaron absorption, with minimal spectral contamination from localized polaron absorption. Likewise, the transient absorption kinetics measured using the ultrafast instrument is assigned primarily to delocalized polarons since the probe wavelength (~ 4000 nm; ~ 0.31 eV) is far from 0.5 eV. Therefore, the data collected using both ultrafast and nanosecond instruments could be connected despite the difference in the wavelength used.

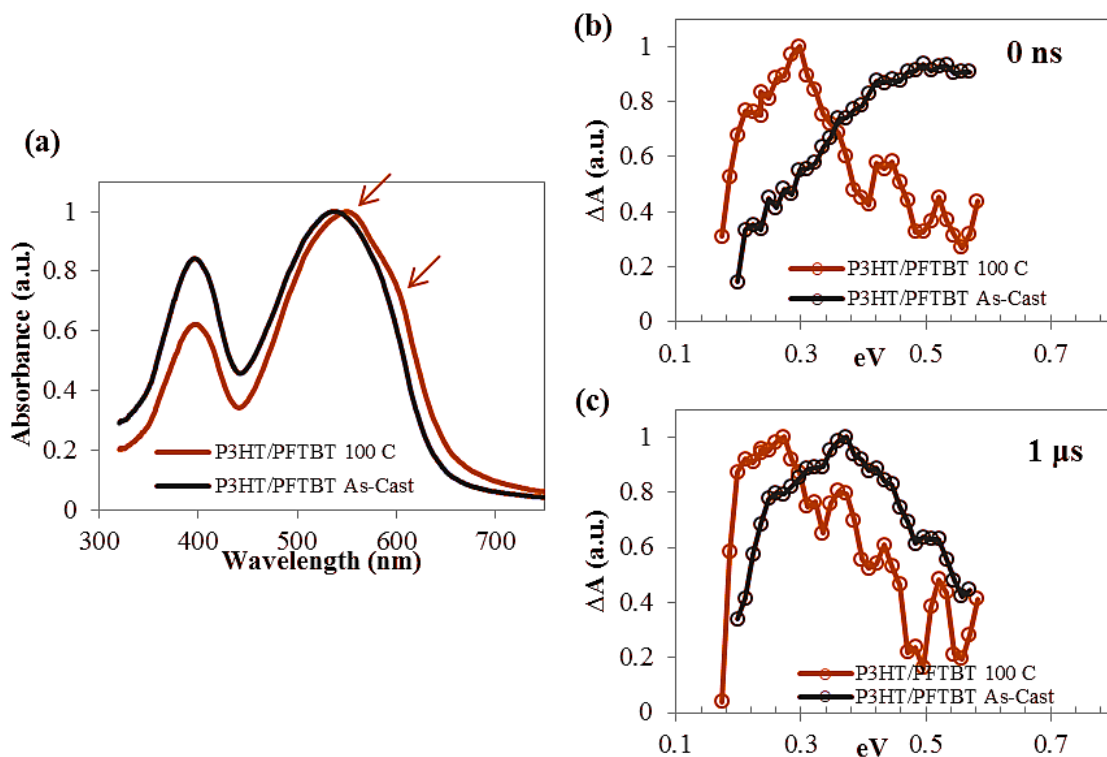


Figure 9-13: (a) Normalized absorption spectra of P3HT/PFTBT blend films with (100 °C) and without (“as-cast”) thermal annealing. (b) Mid-IR transient absorption spectra measured at (b) 0 ns and (c) 1 μ s time delays using 523 nm excitation with an energy density of ~ 50 μ J/cm². The as-cast film features a transient absorbance peak at 0 ns time delay around 0.5 eV, which is assigned to localized polaron absorption. At later time, the peak resembles that of delocalized polaron absorption.

The signal strength of transient absorption measured by the nanosecond instrument should not accurately describe the true polaron absorption intensity at ~ 0.31 eV because the kinetics are spectrally integrated over a range of ~ 0.1 – 0.5 eV, in which the polaron absorption intensity is dependent on wavelength. Provided that the lineshape of the polaron absorption spectrum

is invariant across the series of samples measured, applying a single scaling factor should correct for the small discrepancy in signal magnitude. This assumption is valid because the transient absorption spectrum is nearly identical between the P3HT/PFTBT (100 °C) and P3HT-b-PFTBT (165 °C) films (see **Figure 9-10**). Consequently, the kinetics were corrected using the following steps: (1) Normalize the data by the proportion of photons absorbed for each sample; (2) truncate the data at the earliest resolvable time-delay (starting at 20 ns); and (3) apply a single scaling factor to the kinetic traces for every sample until the kinetics line-up with the ultrafast kinetics. The scaling procedure is exemplified in **Figure 9-14**, in which the transient absorption kinetics are shown for a variety of scaling factors for every film tested. Power law fits to the data are shown for the 0.2 scaling factor as solid gray curves.

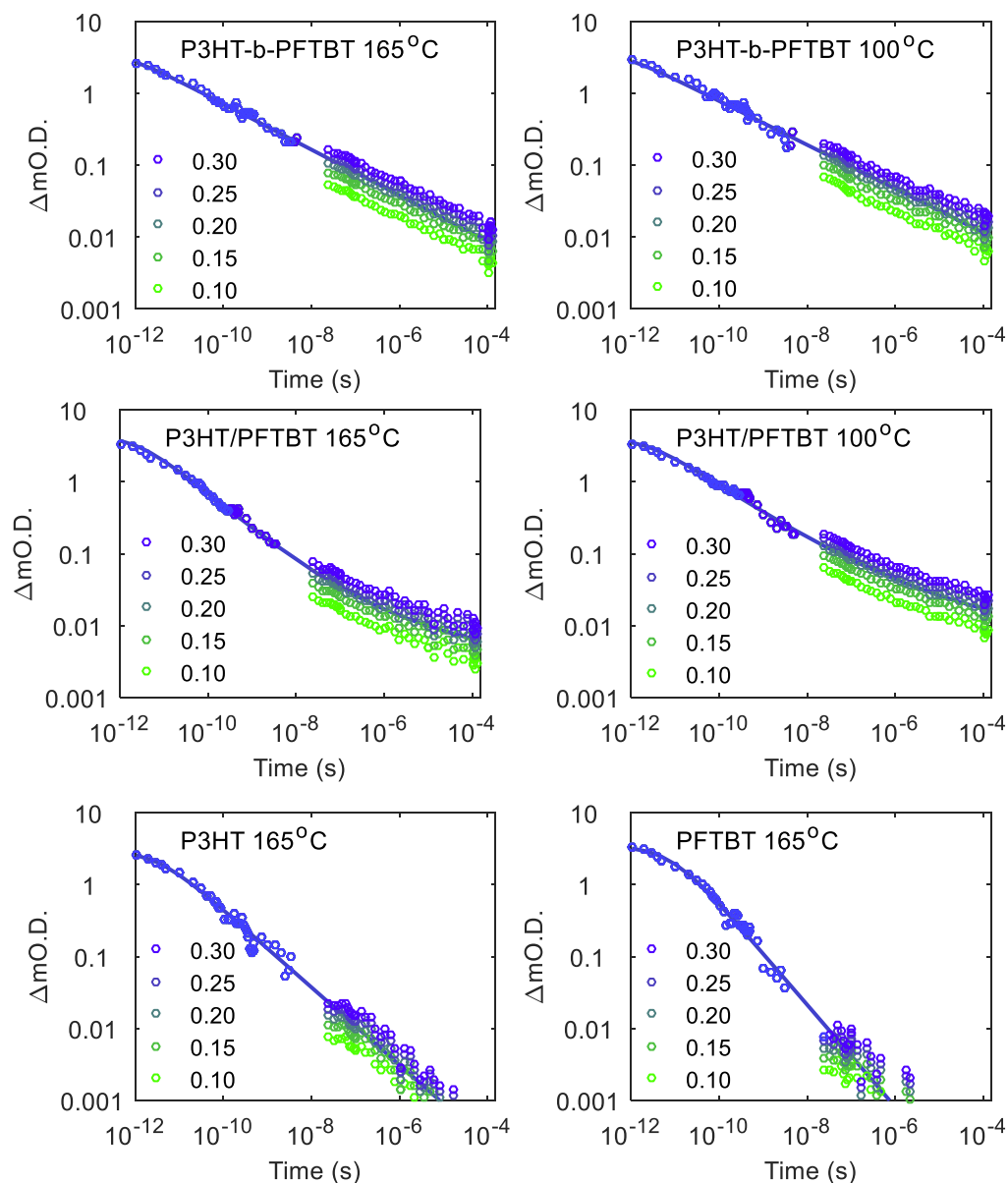


Figure 9-14: Connected mid-IR transient absorption kinetics measured using ultrafast and nanosecond instruments. The blue data points represent the data collected using the ultrafast instrument, and the solid blue lines represent single power law fit functions. The other data points are the scaled kinetics measured using the nanosecond instrument. The specific scaling factor values are included in the legend.

The scaling factor was selected qualitatively, and so the error associated with the fits due to the choice of scaling factor needed to be considered as a major source of error. Each set of kinetics was fit for different scaling factors in the range of 0.175 – 0.225, over which the resulting fit parameters changed moderately and systematically for all of the samples. The

associated errors (taken as the standard deviations) were then calculated for each fit parameter. More details on the power law fits are discussed later.

The kinetic data collected for each sample (shown in **Figure 9-12**) have been scaled by the energy density of the excitation pulse that was absorbed in the films ($\sim 15 \mu\text{J}/\text{cm}^2$). To ensure suppression of nonlinear effects on either polaron generation and/or recombination in the data, a pump laser energy dependence study was performed for one of the film samples (P3HT-b-PFTBT, 100°C). The results are shown in **Figure 9-15**, which shows linear response by the sample using $<50 \mu\text{J}/\text{cm}^2$ excitation.

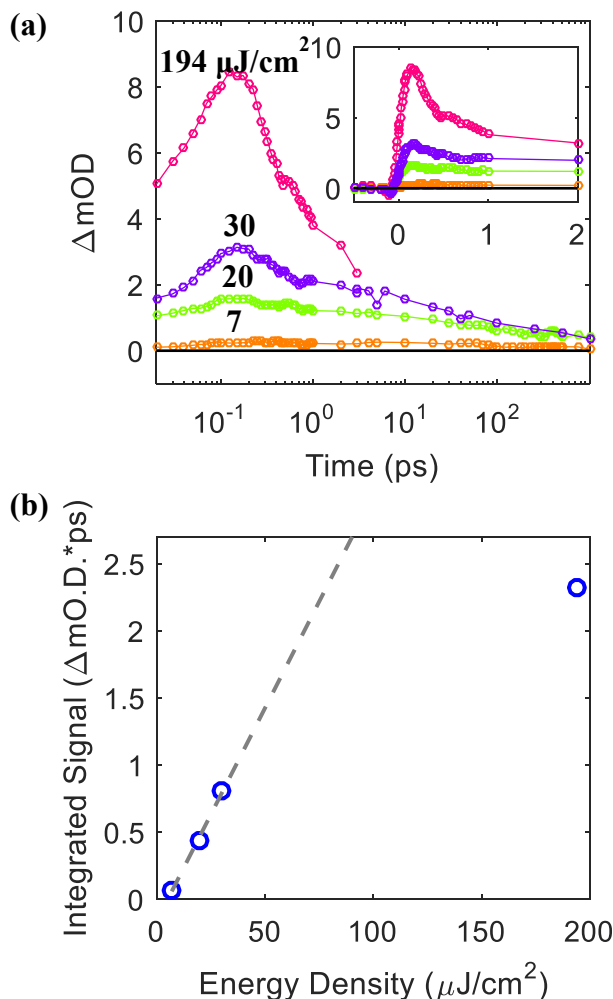


Figure 9-15: (a) Excitation energy dependence of the mid-IR transient absorption kinetics for a P3HT/PFTBT film annealed at 100 °C. The excitation wavelength was 532 nm. The energy densities used are included as labels in units of $\mu J/cm^2$. (b) Plot of the integrated transient absorption signal (from -0.3 to 0.3 ps) against the energy density of the pump pulse. The dashed gray line shows a linear fit to the data in the linear response region.

The charge recombination kinetics for both P3HT-b-PFTBT films were indistinguishable from those measured for the P3HT/PFTBT blend film annealed at 100 °C. In contrast, the P3HT/PFTBT blend film annealed at 165 °C had a faster decay, with a lower signal intensity on the nanosecond to microsecond timescale. Thermally annealing the P3HT/PFTBT blend film at 165 °C is known promote phase separation of the P3HT and PFTBT phases.⁹ Consequently, a substantial fraction of the excitons formed in the resulting large domains

cannot reach a donor-acceptor interface in order to split into charge separated polarons. This was reflective of the lower observed short-circuit current measured in the corresponding photovoltaic device.

The similar charge recombination kinetics measured in the P3HT-b-PFTBT and the P3HT/PFTBT blend film that was annealed at 100 °C indicate that the covalent linkage of the block copolymer does not lead to rapid recombination of charges. This further suggests that through-bond back electron transfer is not a dominant charge recombination pathway in the block-copolymer films, unlike previous reports in other block-copolymer systems.^{22,24-27} Other prior work showed that covalent linkage of the electron donor and acceptor blocks having an electron-deficient unit, such as a benzothiadiazole,²² fullerene,²⁴⁻²⁶ or perylenediimide,²⁷ led to the formation of tightly bound charge-transfer states and/or rapid charge recombination. The P3HT/PFTBT block-copolymer system is the first that does not exhibit such enhanced charge recombination behavior.

The polaron absorption kinetics of the P3HT-b-PFTBT and the P3HT/PFTBT blend films were analyzed more closely using kinetic modeling in order to relate charge recombination to the underlying chemical and mesoscale morphologies. The kinetic decays are reproduced individually in **Figure 9-16** to more clearly illustrate the kinetic modeling process.

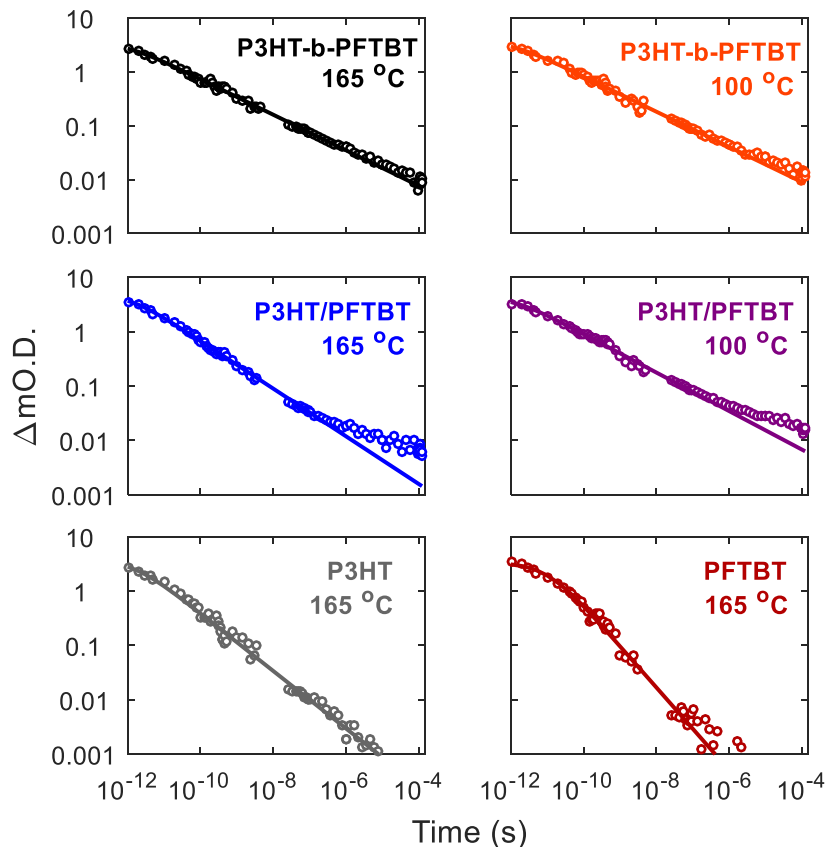


Figure 9-16: Mid-IR transient absorption kinetics for P3HT-b-PFTBT block copolymer films, P3HT/PFTBT blend films, and P3HT and PFTBT homopolymer films. The solid lines represent single power law fit functions to each trace.

Power law functions, which are the solutions to second order (bimolecular) decay processes, were fit to the data. It is customary to modify the power law function using an empirical exponent, α , leading to:

$$\Delta A(t) = n(1 + at)^{-\alpha} \quad (\text{eqn. 3})$$

where ΔA is the transient absorption signal, t is time, n is a scaling factor related to the number density of polarons, and a is an empirical factor. In this form, this expression is known as the “empirical power law”.³⁹ In the past, this model has been used for organic semiconducting polymers to describe trap-assisted bimolecular polaron recombination, for which the exponent tends to vary between zero and unity.³⁹

To further understand the power law fit results, it is instructive to consider how each parameter changes the power law decay shape. **Figure 9-17** shows how variations in n , a , and α influence the resulting the power law function. Plotted on a logarithmic intensity axis and time axis, the exponent controls the “slope” of the decay trace. Lower exponent values are associated with shallower slopes, reflective of slower decays that result from wider trap distributions and/or deeper trap energies.⁴⁷⁻⁴⁹ In particular, ideal behavior ($\alpha = 1$) results in the steepest decay profile, while trap-limited bimolecular recombination results in shallower decay (e.g. $\alpha = 0.3$). The “time constant”, a , in the power law function, unlike in exponential decays functions, does not influence the “steepness” of the decays. Instead, the a parameter affects the onset of the decay.

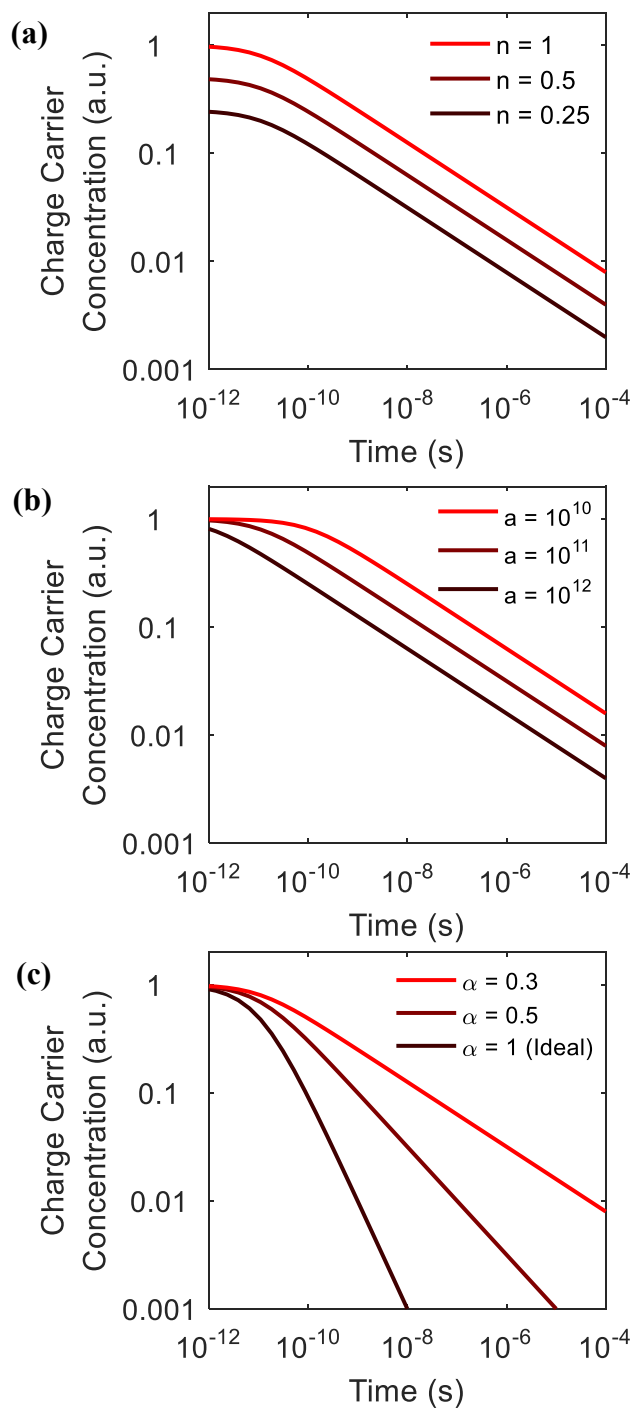


Figure 9-17: Power law decay functions shown for a different of parameter values with variations in **(a)** n , **(b)** a , and **(c)** α . The default values were $n=1$, $a=10^{11}$, and $\alpha=0.3$.

Comparing the fit results to the measured kinetic decays for the P3HT-b-PFTBT films thermally annealed at both 100 °C and 165 °C (**Figure 9-16**) shows that charge recombination

is well-described by a single power law function. An exponent of $\alpha = 0.33$ was determined for both of the P3HT-b-PFTBT films, indicating trap-assisted bimolecular recombination of charges. The fit results for all films tested are provided in **Table 9-2** for reference. A single power law fit was used to describe the kinetics in both block copolymer films, indicating that their photophysics are relatively simple: Charge separated polarons form in the block-copolymer films on the ultrafast timescale before undergoing trap-assisted bimolecular recombination.

Table 9-2. Power law fit parameters for mid-IR transient absorption kinetics

Sample	n	a	α
P3HT-b-PFTBT, 165 °C	3.3 ± 0.3	$(1.1 \pm 0.5) \times 10^{12}$	0.33 ± 0.01
P3HT-b-PFTBT, 100 °C	3.6 ± 0.3	$(1.0 \pm 0.5) \times 10^{12}$	0.33 ± 0.02
P3HT/PFTBT, 100 °C	4.4 ± 0.2	$(0.9 \pm 0.3) \times 10^{12}$	0.35 ± 0.02
P3HT/PFTBT, 165 °C	5.0 ± 0.2	$(1.0 \pm 0.3) \times 10^{12}$	0.44 ± 0.02
P3HT, 165 °C	3.8 ± 0.4	$(0.8 \pm 0.3) \times 10^{12}$	0.53 ± 0.02
PFTBT, 165 °C	3.3 ± 0.1	$(1.1 \pm 0.1) \times 10^{11}$	0.76 ± 0.02

Similar to the P3HT-b-PFTBT films, the kinetic decays of the P3HT and PFTBT homopolymer films are well-described using single power law functions. Accordingly, the photogenerated polaron pairs (or pseudo charge-transfer states) undergo bimolecular recombination with exponents of $\alpha = 0.53$ ($\alpha = 0.76$) for the P3HT (PFTBT) homopolymer films. Unlike in the block-copolymer films, these species do not lead to the generation of separated charges surviving into the nanosecond timescale that can be extracted by electrodes in photovoltaic devices.

The kinetic decays for the P3HT/PFTBT blend films showed more complex photophysics. In particular, the decay measured for the P3HT/PFTBT blend that was annealed at 100 °C

exhibits deviations from the single power law function at longer time delays. Such deviations are present to a larger extent for the P3HT/PFTBT blend annealed at 165 °C. This indicated that a more complex physical model should be applied to the data measured for these films. However, ~95% of the kinetic decay signal measured for each of these films was well-described using a single power law decay, with exponents of $\alpha = 0.35$ ($\alpha = 0.44$) for the P3HT/PFTBT blend films thermally annealed at 100 °C (165 °C). Coarser film morphologies may result in the blend films (in comparison to the block-copolymer films) because they lack a covalent linkage, leading to a higher tendency to phase-separate. As a result, domains of P3HT (PFTBT) may form that are too large for every photogenerated exciton to reach an acceptor (donor) interface during its lifetime. Such excitonic loss would lead to a reduced yield of charge separated polarons. The lower yield of charge separated polarons in the P3HT/PFTBT blend film annealed at 165 °C is consistent with both the observation of increased phase separation and the lower J_{SC} measured in the corresponding device.

Because the bimolecular decay process is characterized by a reaction order greater than one, the decay rate depends on concentration in addition to time. As a result, the substantially lower yield of charge separated polarons in the P3HT/PFTBT blend film annealed at 165 °C would lead to a slower decay rate at longer time delays (i.e. nanosecond-microsecond timescale). This, in turn, partially explains the significant deviation from a single power law at late time delays. In another interpretation, the slower decay component at late time delay may also arise from photogenerated carriers that become spatially trapped in large domains of P3HT or PFTBT that form in both P3HT/PFTBT blend films. Such domains are not likely to form in the block-copolymer films because the covalent linkage prevents macroscopic phase separation.

Ultimately, the similarity of the kinetics measured for the P3HT/PFTBT blend annealed at 100 °C to those obtained for the P3HT-b-PFTBT films confirms that the covalent linkage of the block-copolymer does not enhance rapid charge recombination.

9.7. Assessing the Covalent Linkage of P3HT-b-PFTBT

Having established that the covalent linkage in P3HT-b-PFTBT does not influence charge recombination behavior, the molecular structure was further analyzed in an effort to explain this phenomenon. A recent report of the solution photophysics of P3HT that was end-capped with a fluorene and dithianylbenzodiathi-azole (TBT) unit demonstrated the formation of a strongly bound and emissive charge-transfer (CT) state when the TBT was covalently bonded directly to the P3HT.²² On the other hand, when the fluorene unit was covalently bound to the P3HT, as in the case of P3HT-b-PFTBT, such a CT state was suppressed, and instead, separated charges were formed. Similar discoveries were reported in block-copolymer film study, in which the TBT or the fluorene unit were bonded directly to P3HT.²¹ In that work, covalently linking the TBT moiety to the P3HT decreased photovoltaic device performance, probably due to formation of strongly bound CT states that could not separate into charges.

The results presented in this chapter suggest that the fluorene moiety has an additional effect: It can prevent the back electron transfer across the covalent linkage, suppressing intrachain recombination. Interchain charge recombination between donor and acceptor blocks (in different polymer chains) is likely the primary recombination mechanism in both block-copolymer and blends of the P3HT/PFTBT system. In other words, the fluorene serves as an inert bridging unit in P3HT-b-PFTBT that reduces the likelihood of intrachain recombination by preventing it from kinetically competing with interchain recombination. The mechanistic

hypothesis is that the fluorene moiety decreases the electronic coupling between the P3HT and the PFTBT blocks in the block-copolymer.

To test the hypothesis that intrachain coupling between the P3HT and PFTBT blocks in P3HT-b-PFTBT is weak (due to the covalent linkage to the fluorene moiety), steady-state absorbance and emission spectroscopy of was performed. A solution study is warranted since it would eliminate any interchain interactions. Because the P3HT-b-PFTBT polymer is highly insoluble in most organic solvents, it was necessary to synthesize alternate polymers containing solubilizing alkyl side groups. The chemical structure of such polymers, P3HT-b-PFT6BT and PFT6BT, are provided in **Figure 9-18**. The UV-visible absorption spectrum of a dilute solution of P3HT-b-PFT6BT in chloroform (1.0 $\mu\text{g/mL}$) was compared to the corresponding spectra of homopolymer solutions of P3HT or PFT6BT (see **Figure 9-18**). A mass-weighted linear combination of the homopolymer spectra was compared to the measured spectrum of P3HT-b-PFT6BT. The exact match of the linear combination spectrum and the P3HT-b-PFT6BT spectrum indicated that the absorption spectrum of the block-copolymer could be described as a combination of non-interacting P3HT and PFT6BT absorption spectra (obeying Beer's Law). In other words, the covalent linkage between the P3HT and PFT6BT blocks must cause negligible effects on the electronic structure of the corresponding block-copolymer.

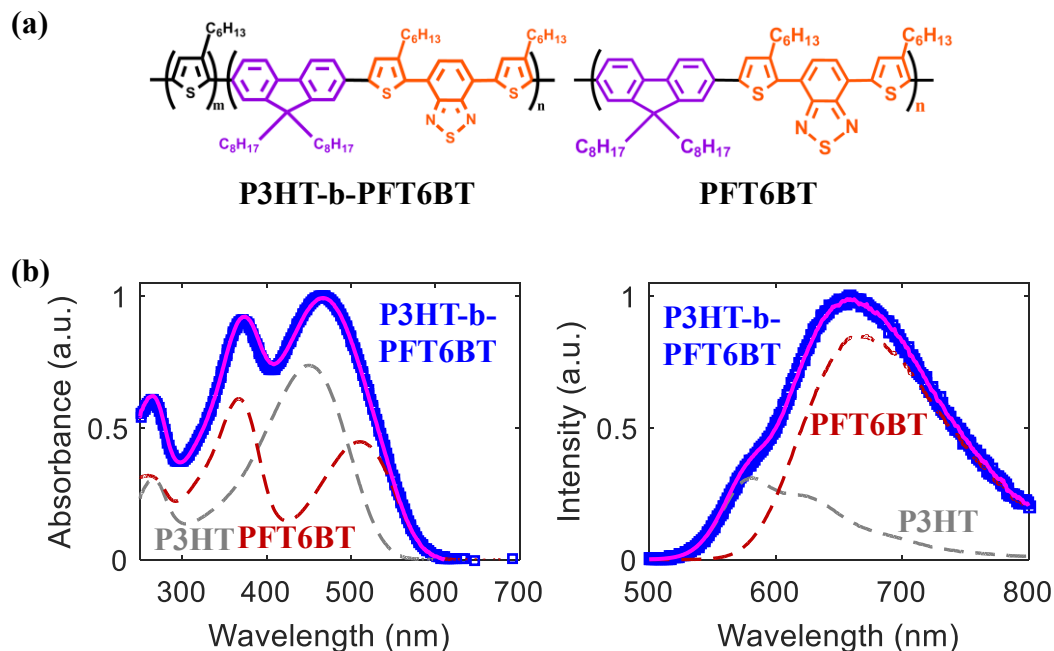


Figure 9-18: (a) Chemical structures of P3HT-b-PFT6BT and PFT6BT used for solution measurements. (b) Absorbance and (c) emission spectra (blue squares) of a dilute P3HT-b-PFT6BT solution in chloroform. The mass-weighted spectra of the homopolymer solutions (dashed lines), and the linear combination spectra (solid magenta lines) are included.

The photoluminescence spectra (shown in **Figure 9-18**) of same solutions of P3HT-b-PFT6BT, P3HT, and PFT6BT, were also measured. Like the absorption spectra, the linear combination spectrum composed of the emission from both the P3HT and PFT6BT homopolymers cannot be distinguished from the measured block-copolymer spectrum. This further supports the conclusion that the covalent linkage does not modify the electronic structure of the P3HT/PFT6BT system. In addition, there was a lack of new emission bands (e.g. from CT state emission).

It is important also to eliminate the possibility that CT state interactions are induced in the block-copolymer samples in the solid state due to polymer chain planarization, which is known to change their electronic structure significantly. It is possible that changes in the energy levels of either P3HT or PFTBT can affect their intrachain coupling strength in the block-copolymer.

The UV-visible absorption and photoluminescence spectroscopy of blend and block-copolymer films for the P3HT/PFTBT system are provided in **Figure 9-19**. It was found that the photoluminescence spectrum of the P3HT/PFTBT blend film annealed at 165 °C can be well-described by a linear combination of the corresponding homopolymer film emission spectra. However, the block-copolymer films made using either annealing temperatures have significantly different emission spectral shapes (“rounded” and broadened) that may occur due to the presence of amorphous polymer and/or differences in peak position resulting from variations in molecular weight. Consequently, the possibility of CT state emission cannot be determined from the data. It is thought that the presence of amorphous domains lead to such emission spectrum characteristics because the P3HT/PFTBT blend film annealed at 100 °C (which lacks an intrachain interface) also exhibits emission peak broadening.

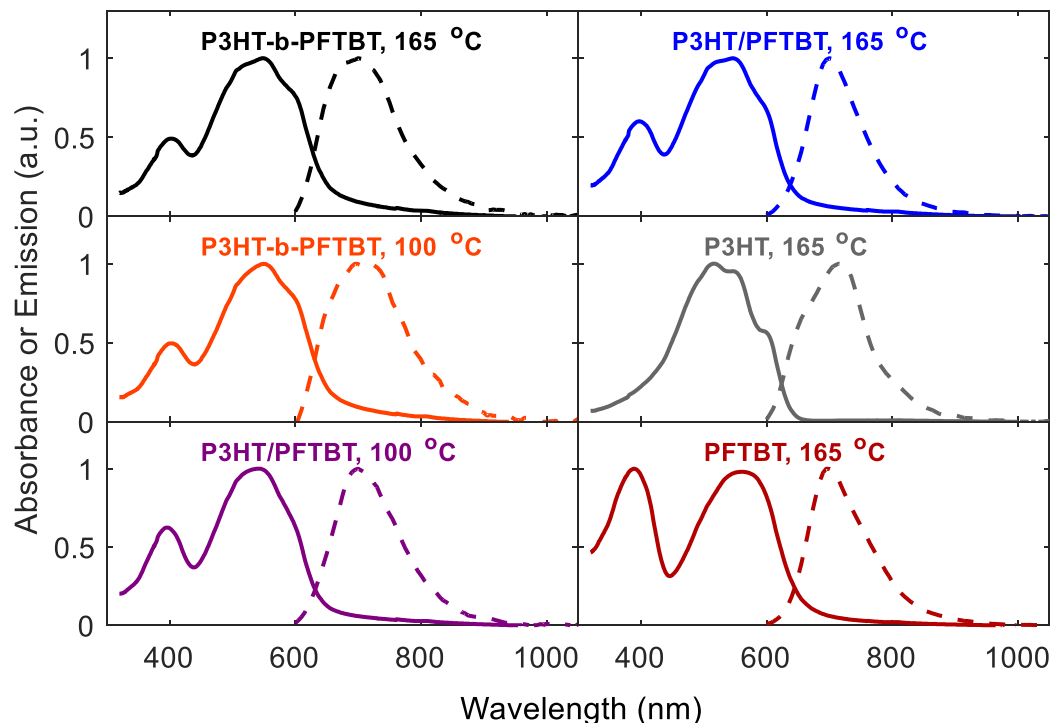


Figure 9-19: Normalized steady-state absorption (solid lines) and emission (dashed lines) spectra for all the block-copolymer, blend, and homopolymer films studied. For the emission spectra, the excitation wavelength was 532 nm. Each emission spectrum was determined by time-integrating the time-resolved emission over the entire decay kinetics. These spectra were not corrected for the efficiency of the spectrometer used.

The absence of intrachain coupling between P3HT and PFTBT in P3HT-b-PFTBT could be explained by considering the frontier orbitals corresponding to the states of P3HT and PFTBT involved in charge transfer. For quantum chemical calculations, the P3HT block was modeled as α -sexithiophene (6T) and the PFTBT block as 4-(thiophene-2-yl)-7-(5-(fluorene-2-yl)-thiophene-2-yl)-2,1,3-benzothiadiazole (FTBT). The frontier orbitals were determined following geometry optimization using density functional theory (DFT).⁵⁰ The results (**Figure 9-20**) showed that the HOMO of FTBT was delocalized over the entire molecule. However, the LUMO was largely localized on the dithienylben-zothiadiazole moiety.^{21,51}

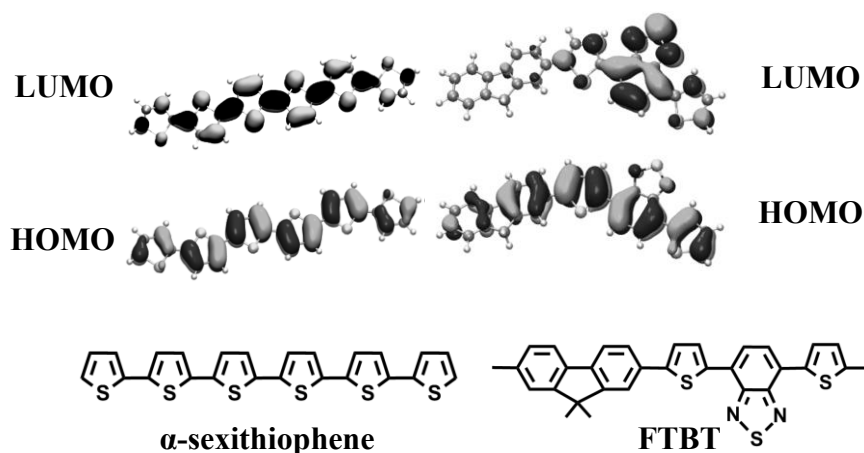


Figure 9-20: Frontier molecular orbitals for α -sexithiophene and FTBT, which represent P3HT and PFTBT, respectively. The orbitals are shown for both the HOMO and the LUMO of each compound.

Extrapolating these results to P3HT-b-PFTBT, the HOMO of the PFTBT block would be coupled to the P3HT, but the LUMO of the PFTBT would couple much more weakly to the P3HT. This is because the LUMO would be localized on the TBT unit fluorene unit, separated from the P3HT by the fluorene moiety. Notably, the LUMO is likely to be representative of the anionic state of the PFTBT block. Consequently, intrachain charge recombination, which involves the transfer of an electron from PFTBT back to P3HT, is expected to be slow. Additionally, this back electron transfer would occur in the Marcus inverted region, which was previously reported in the P3HT-b-PFTBT system using DFT calculations.⁵⁰

Interchain charge recombination may still occur between neighboring block-copolymer chains. In this case, the rate would be determined by through-space electronic orbital overlap of the P3HT and PFTBT blocks, which would depend on their relative alignment and orientation. Ultimately, the results of this chapter suggest that block-copolymers, if engineered carefully at the molecular level, can offer mesoscale structural control beneficial to improving charge transport in photovoltaic devices, without introducing deleterious intrachain charge recombination centers.

9.8. Conclusions and Significance

Charge recombination kinetics were measured for block-copolymer and polymer blend films using ultrafast and nanosecond transient absorption spectroscopy. These kinetics were compared in order to test how the covalent linkage between electron donating and accepting polymers impacts the resulting polaron recombination characteristics. Transient absorption spectra were measured over a wide spectral window to identify the location most suitable for unambiguously measuring charge recombination kinetics. The mid-infrared region was found to contain polaron absorption features ascribable to the same type of charges that contribute to photocurrent in photovoltaic devices. The covalent linkage between donor and acceptor polymer blocks in P3HT-b-PFTBT films was not found to lead to enhanced charge recombination compared to the P3HT/PFTBT polymer blends films.

The results of this work lead to a new design rule for designing block-copolymer systems for photovoltaics: The inclusion of a push-pull copolymer as either the electron donor or acceptor polymer block may be necessary to prevent deleterious recombination centers. For example, if the acceptor block is a push-pull (“donor-acceptor”) copolymer, such as PFTBT, then the LUMO should be preferentially localized to the acceptor moiety. In addition, the donor moiety should be positioned between the donor block and the acceptor moiety to inhibit the enhancement of intrachain (“intramolecular”) charge recombination. As an alternative rule, disrupting the intrachain electronic coupling using a short non-conjugated bridge, such as an alkyne chain, may achieve the same functionality.

9.9. Perspective: Chemical Design Rules for Block-Copolymer Photovoltaics

The results presented in this chapter suggested that block-copolymer materials can be designed to enable solid-state morphological control through their tendency to self-assemble, without creating intrachain recombination centers. The chemical design of the covalent linkage controls whether the electronic coupling between donor and acceptor polymer blocks is too strong, favoring tightly-bound intrachain CT state formation and/or facilitating rapid intrachain recombination. It was found through the P3HT-b-PFTBT system that the location of the orbitals is important for determining the electronic coupling between the blocks comprising the block-copolymer. This leads to new design rules: (1) at least one of the polymer blocks should be a push-pull (donor-acceptor) copolymer; and (2) the electron- (hole-) rich moiety of the electron acceptor (donor) block should not be covalently linked to the electron donor (acceptor) block. This set of rules is illustrated in **Figure 9-21** using simple molecular orbital theory.

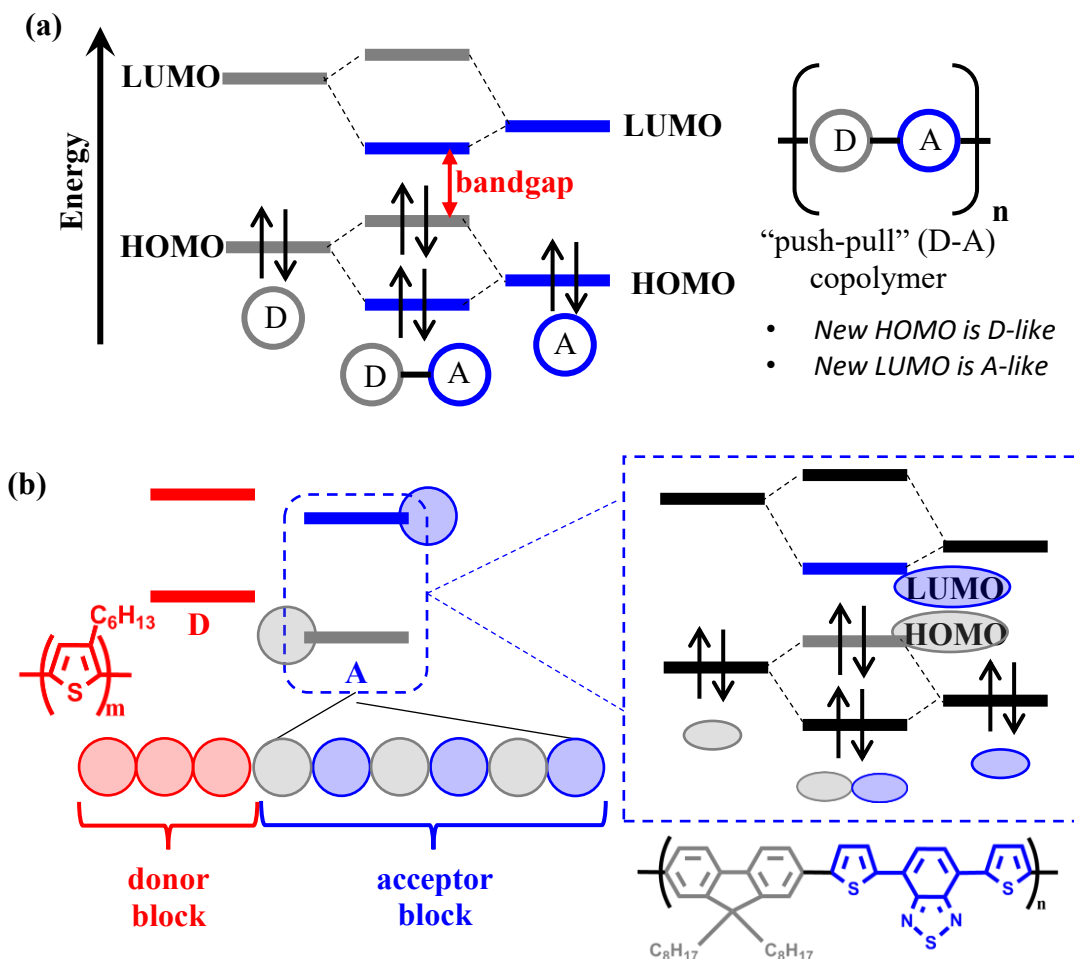


Figure 9-21: (a) Design of push-pull (Donor-Acceptor, "D-A") copolymers, illustrating the introduction of a low energy bandgap used for absorbing low-energy photons from the sunlight. As a result, the new HOMO has more "D-character" and the new LUMO has more "A-character". (b) Chemical design of a block-copolymer for photovoltaic applications, for which the electron acceptor block is a D-A copolymer. The "D" moiety of the electron acceptor block is covalently linked to the electron donor block of the block-copolymer in order to spatially separate the LUMO of the electron accepting block from the HOMO of the electron donating block.

The design of a push-pull polymer is as follows: An electron donor moiety (D) is covalently bound to an electron acceptor moiety (A) in an alternating fashion, producing a D-A copolymer. This design, often used in polymers for photovoltaics, purposely introduces strong, low-energy CT state interactions in the polymer so that it can absorb low-energy photons from the sunlight. The creation of CT state absorption in a D-A copolymer can be understood

through a simple molecular orbital diagram (see **Figure 9-21**). From the diagram, it can be seen that the new HOMO has more D character, while the new LUMO has more A character.

Naturally, every D-A copolymer will have a HOMO that more closely reflects the D moiety, and a LUMO that more closely reflects the A moiety. As such, this simple molecular orbital description of D-A copolymers can be used to decide *a priori* which moiety should be linked to the second polymer block. This is also illustrated in **Figure 9-21**. It is the hope that the set of rules outlined here may lead to the design of new block-copolymer materials for improving organic solar cell performance beyond the P3HT-b-PFTBT system. For example, it may be possible to covalently link select polymers that have been shown to produce the highest reported device efficiencies to date. Covalent linkage of these high performance polymers could improve their device performance even further through the addition of morphological control.

9.10. Outlook

Understanding charge transport and recombination pathways in block-copolymer films is challenged by a variety of factors that are intrinsic to the solid-state. In particular, both interchain and intrachain interactions between the two polymer blocks are present and are poorly controlled in thin films. This is a result that inevitably occurs using solution-casting techniques. As such, alternate methods for controlling the structure and morphology of block-copolymer materials are under development. Exploitation of the self-assembling nature of block-copolymers may enable the development of new systems for studying specifically how molecular-level structure and nanoscale organization directly influences charge transport and separation in block-copolymer materials. In Chapter 10, the development of semiconducting

block-copolymer nanoparticle systems is discussed for the first time, for which experiments of charge recombination dynamics are made. This work is hoped to serve as the foundation for future structure-photophysics studies of block-copolymer materials that will lead to further chemical and structural design rules for block-copolymer photovoltaics.

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CHAPTER 10

Developing Solution-Phase Systems for Studying Charge Carrier Dynamics in Semiconducting Block-Copolymer Materials

Control over polymer chain ordering, including both intrachain and interchain structure, is known to determine charge generation and transport in polymer photovoltaics. However, relationships between solid-state interactions and the corresponding photophysics, which may be manipulated to optimize device efficiency, are not well-understood. Thin films of organic semiconducting materials inevitably form heterogeneous structures that complicate spectroscopic analysis. As a result, it is desirable to simplify such systems, isolating certain nanoscale structures in order to associate specific morphological properties to the resulting photophysics. Block-copolymers, because of their intrinsic ability to self-assemble in the solution-phase, promise to serve as a well-controlled platform for studying fundamental relationships between structure and function in organic photovoltaics. This chapter focuses on the development of solution-phase block-copolymer nanoparticle systems that will be utilized in future work.

Polaron generation and recombination have been spectroscopically investigated in the past for nanoparticles consisting of blends of electron donating and accepting materials.^{1,2} However, like in films, these nanoparticle systems consist of disordered domains of polymers and/or small molecules that are difficult to control. This chapter presents the first account of the preparation and spectroscopic measurement of semiconducting block-copolymer aggregates and nanoparticles in the solution-phase. It is the hope that the work presented herein will lead to future fundamental studies of charge photogeneration and charge transport in

block-copolymers, which will be used to better understand the photophysics occurring in the solid-state of photovoltaic materials in general.

Brooke Kuei and Jennifer Grey are acknowledged for collecting dry TEM and liquid TEM images, respectively, which are presented in this chapter.

10.1. Introduction

The charge photogeneration event occurring in organic photovoltaics requires that charge-transfer (CT) states, which form at an interface between an electron donating (D) and accepting (A) materials, are able to efficiently separate into charge carriers (see Chapter 9 for more details). Although this process is generally understood, the precise mechanism is still debated. In particular, electronic delocalization of the CT state, favored in systems possessing strong intermolecular coupling, is believed by some to facilitate the separation of charges.³ On the other hand, others believe energetic disorder actually plays a dominant role in facilitating charge separation, which is prominent in systems possessing weak intermolecular coupling and short-range electronic delocalization.⁴

After photogeneration, the charges migrate through the organic material in photovoltaics to their respective electrodes. In devices incorporating polymer materials, the charges are known to be able to transport both along chains (intrachain transport) and between chains (interchain transport).⁵ However, it is unclear which type of transport mechanism is important for devices, and if one or the other should be suppressed. Intrachain transport is believed to be highly efficient if there is extensive electronic delocalization, supported by structural order, within a single chain. On the other hand, interchain transport requires favorable through-space electronic coupling, which is strongly modulated by dynamical motions of the polymers.⁶

The block-copolymer system, consisting of covalently linked D and A polymer blocks, is a promising model platform for studying how intramolecular and intermolecular delocalization play a role in both charge generation and transport in organic photovoltaics. Because block-copolymers tend to self-assemble into ordered nanoscopic structures⁷, they potentially offer a means of fabricating systems with control over intrachain and interchain structure. The ideal block-copolymer structure is the micelle (depicted in **Figure 10-1**), in which the polymer blocks self-assemble into phase-segregated domains of D and A.

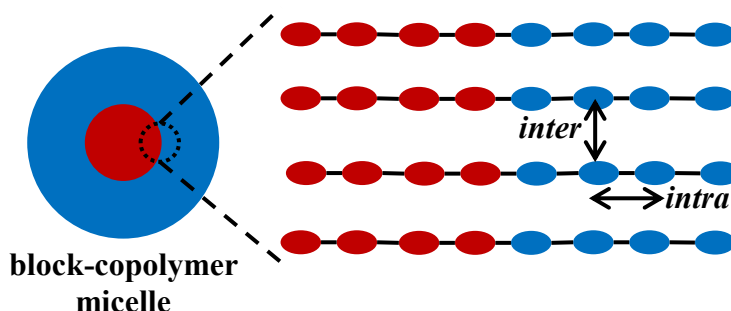


Figure 10-1: Illustration of an ideal block-copolymer aggregate (micelle) structure, where the red and blue phases represent the electron donating and accepting polymer blocks. The polymer chains are highly ordered, where each chromophore unit is represented as an oval. The arrows indicate intrachain and interchain interactions.

In the following, the terms “aggregate” and “nanoparticle” are distinguished based on the following definitions: An “aggregate” consists of an interaction between at least two molecules or polymers in solution that are formed through attractive forces or energetic stabilization. Extended aggregate structures, such as P3HT nanofibers having lengths as long as microns, may form spontaneously in certain types of solutions.⁸ On the other hand, “nanoparticles” represent aggregated structures that are not necessarily formed due to attractive forces or self-assembly. For example, and as will be exemplified below, nanoparticles may be clusters of polymer chains that have formed due to hydrophobic interactions. Additionally,

the term “nanoparticle” will be used for systems in which the structure is not well-identified. This can include clusters of aggregated domains, for example.

10.2. Preparing and Controlling Block-Copolymer Nanoparticles

The block-copolymer system chosen was P3HT-b-PFT6BT (the chemical structure is shown in **Figure 9-18**), due to its superior solubility in comparison with P3HT-b-PFTBT, the subject of Chapter 9. The preparation of aggregates and nanoparticles was motivated by widespread reports of P3HT aggregation,⁸⁻¹¹ since it was one of the polymer blocks. Methods for forming P3HT aggregates were adapted for the block-copolymer, with the hypothesis that inducing P3HT aggregation would drive total aggregation of the block-copolymer.

10.2.1. Binary solvent approach

A common method for inducing P3HT aggregation is to use binary solvent systems.^{12,13} In particular, the polymer is first dissolved in a “good” solvent, in which it is highly soluble. A “bad” solvent, in which the polymer is much less soluble, is introduced into the solution. Aggregates of P3HT chains form spontaneously, typically resulting in the growth of nanofibers. The rate of bad solvent addition and the volume ratio of good:bad solvents determines the ultimate structure and size of the aggregates that form.¹³ An illustration of the binary solvent method is provided in **Figure 10-2**. While this method is relatively simple to carry out, it does not result in a complete conversion of unimers to aggregates, and so further purification is often necessary.¹¹

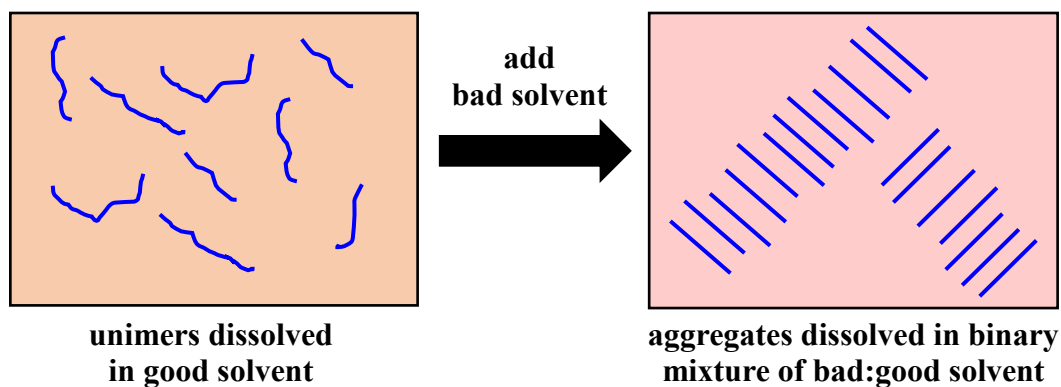


Figure 10-2: Binary solvent method for preparing polymer aggregates.

10.2.2. Good solvent evaporation approach

Fabrication of nanoparticles consisting of molecules and/or polymers have been extensively reported for a handful of organic photovoltaic material systems.² Nanoparticles are typically formed using the flash reprecipitation method, in which a small quantity of solution is injected rapidly into a bath of antisolvent. This process is illustrated in **Figure 10-3**. THF is often used to prepare solutions because it is highly miscible in water, which is an effective antisolvent for organic molecules and polymers in general. Upon injection of the organic material, the THF immediately mixes into the bath of water, forcing the solute to cluster together. The THF, which has a relatively low boiling temperature, is then evaporated out of the water, resulting in a stable dispersion of nanoparticles in water with typical diameters of tens of nanometers.²

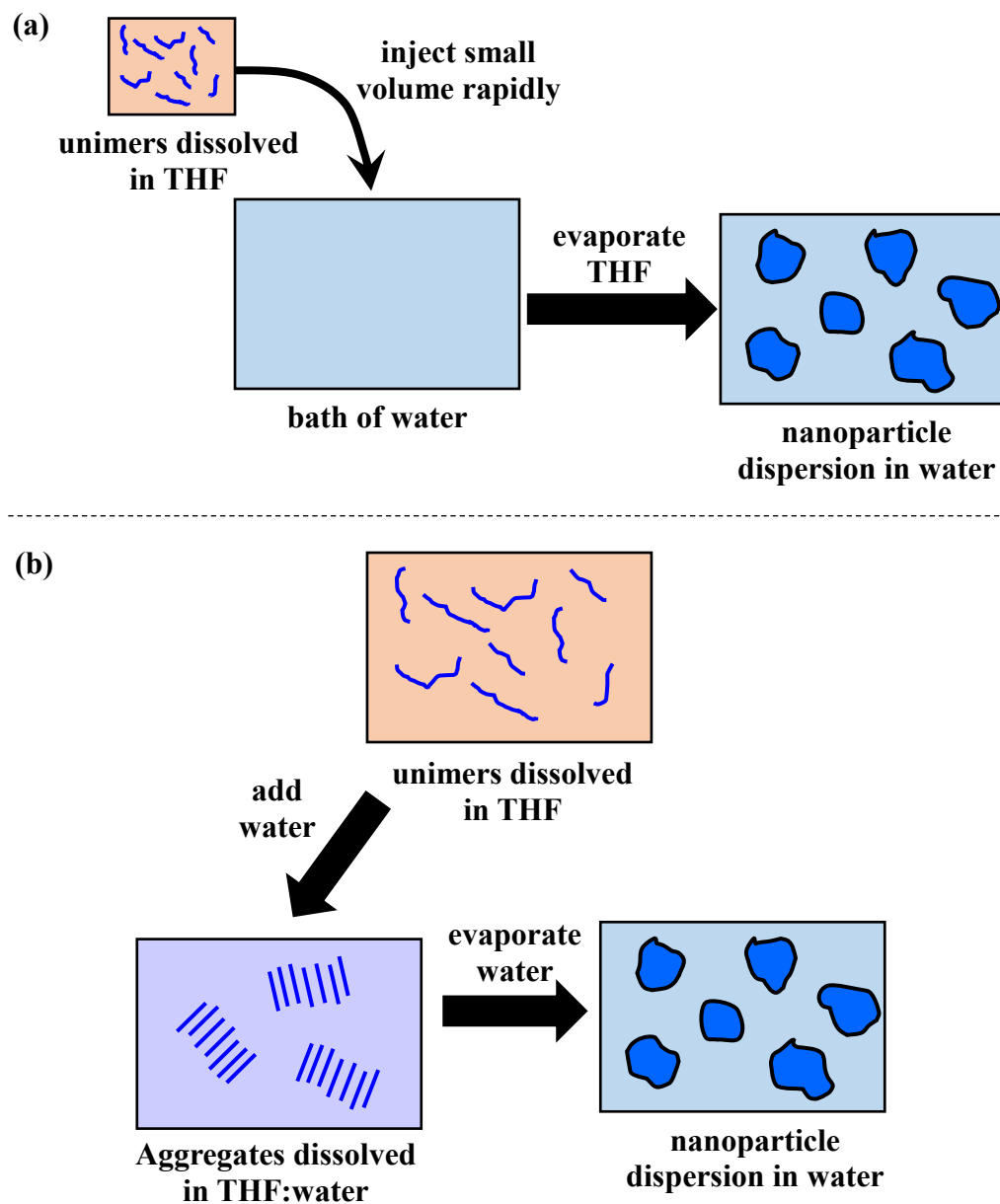


Figure 10-3: Polymer nanoparticle preparation methods, featuring (a) flash reprecipitation and (b) good solvent evaporation.

An alternate method has been developed for block-copolymer systems consisting of two hydrophobic blocks. Typically, block-copolymer micelles are prepared using the “selective solvent method”, in which a solvent that dissolves only one of the polymer blocks is used. This results in the spontaneous formation of micelles, in which the block-copolymer forms a spherical, phase-segregated structure with the soluble polymer on the exterior. For example,

block-copolymers consisting of hydrophobic and hydrophilic blocks are mixed into water.^{14,15} However, semiconducting polymers useful for photovoltaics often always consist of two hydrophobic blocks, and so an alternate method is required. One particularly useful procedure, termed the “good solvent evaporation” method, has been demonstrated for the model (non-semiconducting) hydrophobic system, poly(styrene-block-isoprene) (PSt-b-PI).¹⁶ In particular, the polymer is dissolved in a large volume of THF, after which a comparable volume of water is added dropwise. After the addition of water, the THF is then evaporated slowly over time, resulting in the formation of highly organized nanoparticles. This process is illustrated in **Figure 10-3**.

The good solvent evaporation method was adapted for P3HT-b-PFT6BT, which is demonstrated in **Figure 10-4** through photographs taken during the process. The water addition step resulted in aggregation, while the THF evaporation step resulted in nanoparticle growth. As discussed in depth later, the rate of addition of water was found to control the extent of order of the aggregates of P3HT-b-PFT6BT prior to nanoparticle formation. The rate of THF evaporation was found to control the final size of the nanoparticles.

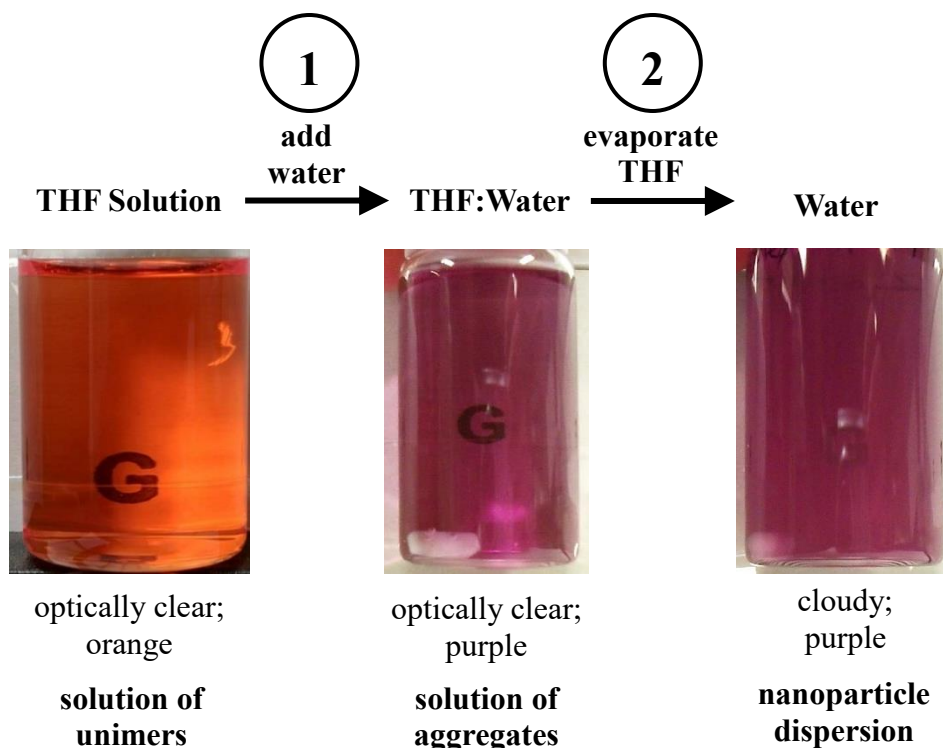


Figure 10-4: Illustration of the good solvent evaporation method for preparing block-copolymer nanoparticles using P3HT-b-PFT6BT.

10.3. Monitoring Aggregation in Block-Copolymer Solutions

Having selected methods for preparing nanoparticles of block-copolymers, it is important to characterize their structural order. The electronic structure of P3HT is known to be very sensitive to its arrangement of the polymer chains, giving rise to clear spectroscopic changes.^{9,17} Consequently, the aggregation of the P3HT-b-PFT6BT block-copolymer was monitored indirectly using measurements of changes experience by the P3HT domains. In particular, evolution of spectroscopic features associated with P3HT block will be used to indirectly assess changes in the block-copolymers as a whole.

10.3.1. Structural and optical characteristics of P3HT aggregates

The structure of P3HT aggregates has been studied extensively in both solutions (nanofibers) and films.¹⁸ P3HT is known to form a mixture of amorphous and crystalline domains in thin films and nanofibers. The polymer chains have a natural tendency to planarize and pi-pi stack during aggregation, forming extended lamellae structures. The terminals of the lamellae are typically portions of the chains that do not planarize, resulting in disordered domains that are free to bend and twist. This is depicted in **Figure 10-5**.

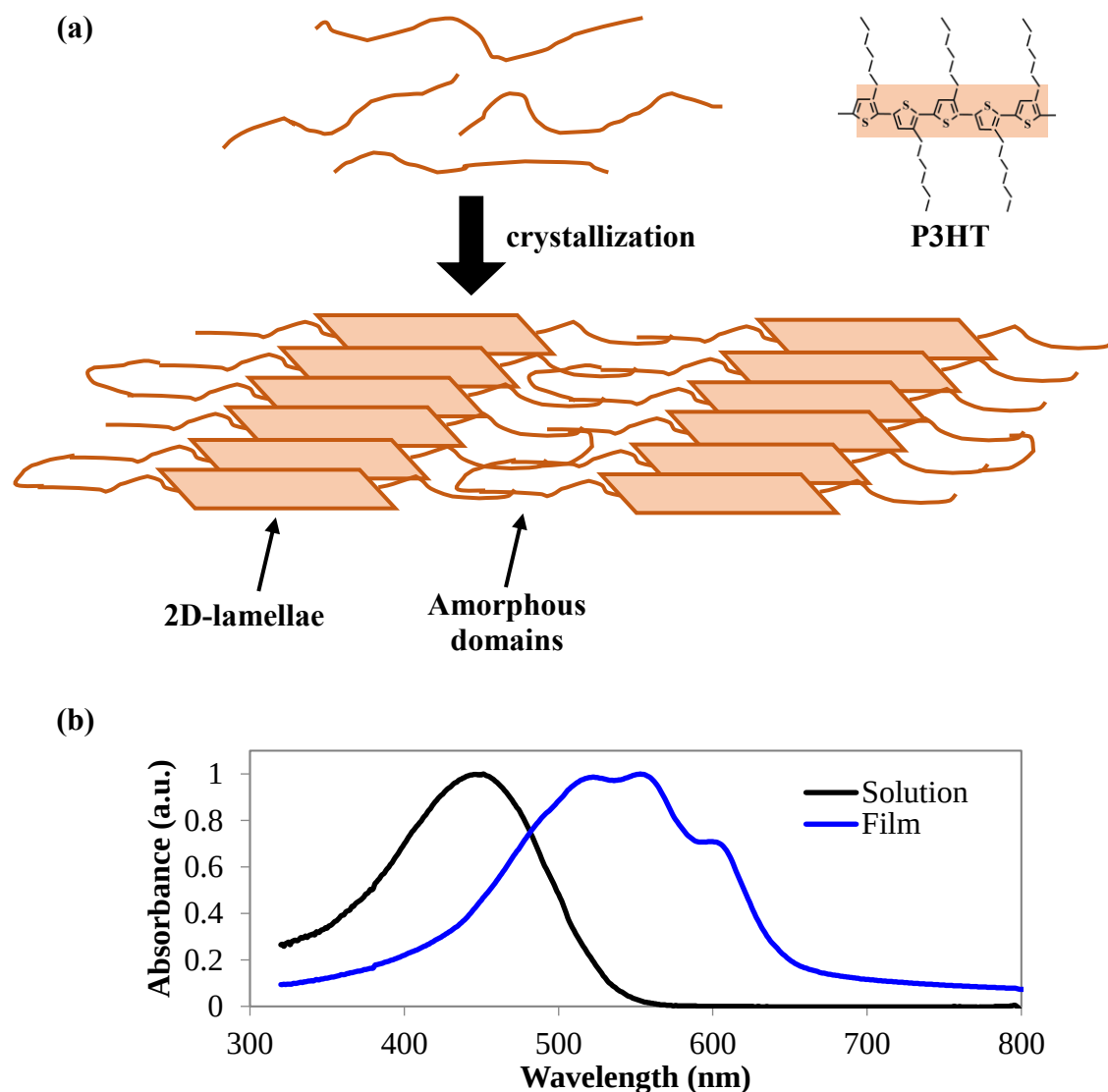


Figure 10-5: (a) Illustration of the crystallization of P3HT, forming a mixture of crystalline 2D-lamellae and amorphous phases. (b) Comparison of the absorption spectra of a P3HT solution and film.

Due to its intrinsic nature to form lamellae structures, P3HT typically forms mixed morphologies consisting of different energetics. In particular, the planarization that occurs during aggregation elongates the conjugation length, lowering its optical bandgap and causing a redshift of its absorption spectrum. In addition, the aggregation of the chains introduces interchain electronic coupling interactions that lead to further perturbations of its absorption spectrum. An example of the changes of the absorption spectrum of a P3HT film upon

crystallization is shown in **Figure 10-5**. When P3HT crystallizes, the absorption spectrum evolves, featuring a red-shifted band with the growth of vibronic peaks (typically) indicative of H-aggregation.^{17,19} The ratio of the absorbance of the 0-0 and 0-1 bands for H-aggregates of (regioregular) P3HT has been associated with the strength of interchain coupling using a model developed by Spano and coworkers.¹⁷

In transient absorption spectroscopy, the mixture of amorphous and crystalline states in P3HT films leads to multiple polaron absorption features. These features have been identified by Vardeny and coworkers using charge modulation spectroscopy experiments.²⁰⁻²² In the charged state of a single P3HT chain, two possible electronic transitions exist, which correspond to “localized polaron” (LP) absorption. In this case, the polaron is electronically localized on a single chain. Under a molecular orbital theory description, the formation of lamellae of P3HT chains leads to energy level splittings, which are shown in **Figure 10-6**. The splittings give rise to new transitions for the P3HT lamellae, corresponding to “delocalized polaron” (DP) absorption. In this case, the polaron is electronically delocalized among multiple polymer chains. In a film of P3HT, the two sets of transitions are present, giving rise to a LP and DP absorption band in both the near-IR and mid-IR spectral regions.

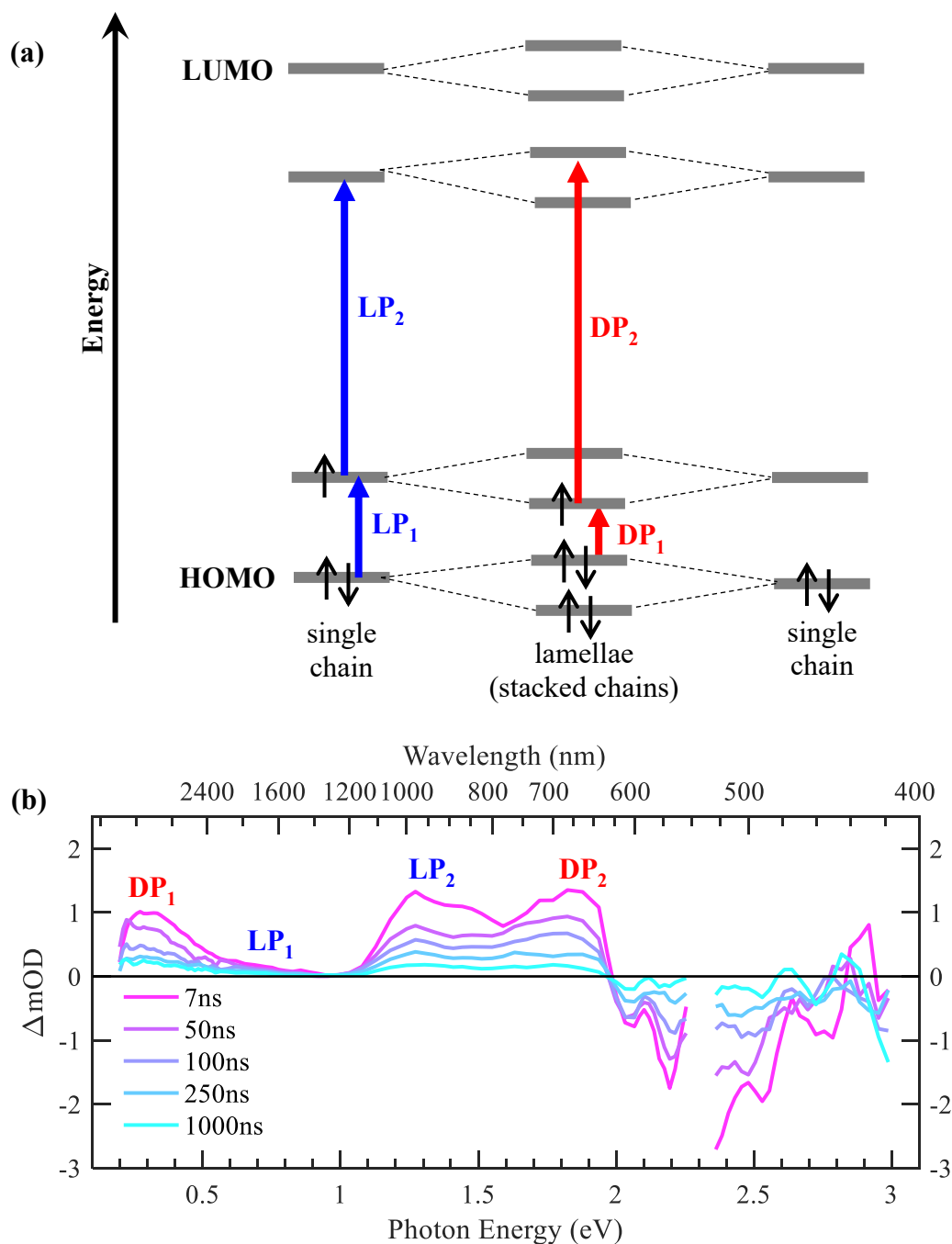


Figure 10-6: (a) Energy level diagram for the P3HT polymer as either isolated chains, or interacting chains. Energy level splitting occurs when the P3HT chains pack together, forming lamellae. Transition arrows correspond to the possible absorptions associated with localized polarons (LP) and delocalized polarons (DP). (b) Transient absorption spectrum of a P3HT:PC₆₁BM blend film, featuring absorption bands associated with the localized and delocalized polarons that form in P3HT domains.

The polaron absorption bands of P3HT can be exemplified using the nanosecond transient absorption spectrum of the prototypical P3HT:PC₆₁BM blend film system (**Figure 10-6**). For this sample, photoexcited P3HT results in excitons that diffuse to and split at a P3HT-PC₆₁BM (D-A) interface on an ultrafast timescale. On the nanosecond timescale, polarons diffuse through the P3HT and PC₆₁BM domains before they recombine bimolecularly at a D-A interface. The absorption of PC₆₁BM anions is known to contribute minimally to the total transient absorption spectrum.²³ Consequently, the spectrum corresponds predominantly to the hole polarons in P3HT domains.

It is desirable to have the ability to measure both LPs and DPs in block-copolymer aggregates and nanoparticles. However, the measurement of the DPs is particularly challenging in the solution-phase because of two major experimental limitations: (1) mid-IR light does not transmit most solvents (especially water), requiring extremely small pathlengths and/or high concentrations of polymer; and (2) the DP band in the near-IR typically overlaps CT state bleaching in addition to photoluminescence and/or stimulated emission. As discussed in Chapter 2, photoluminescence significantly complicates flash photolysis measurements, potentially leading to experimental artifacts.

The measurement of near-IR absorption of either LPs or DPs is additionally challenged in systems in which triplet yields are high. This is because the triplet photo-induced absorption (PIA) spectrum of P3HT, centered at ~850 nm, overlaps both the LP and DP peaks (see **Figure 10-7**). Triplets are known to form in high yields in amorphous polymer films or dilute polymer solutions, in which the polymer chains are flexible. This is because the out of plane bending and torsions of chromophore units within the chains increases spin-orbit coupling via the orthogonal orbital effect.²⁴ Triplet PIA signals may be distinguished from that of polaron

absorption by performing an oxygen quenching experiment. As seen in **Figure 10-7**, kinetic quenching by diatomic oxygen is easily observed for triplet populations, while polarons exhibit no change in decay rate.

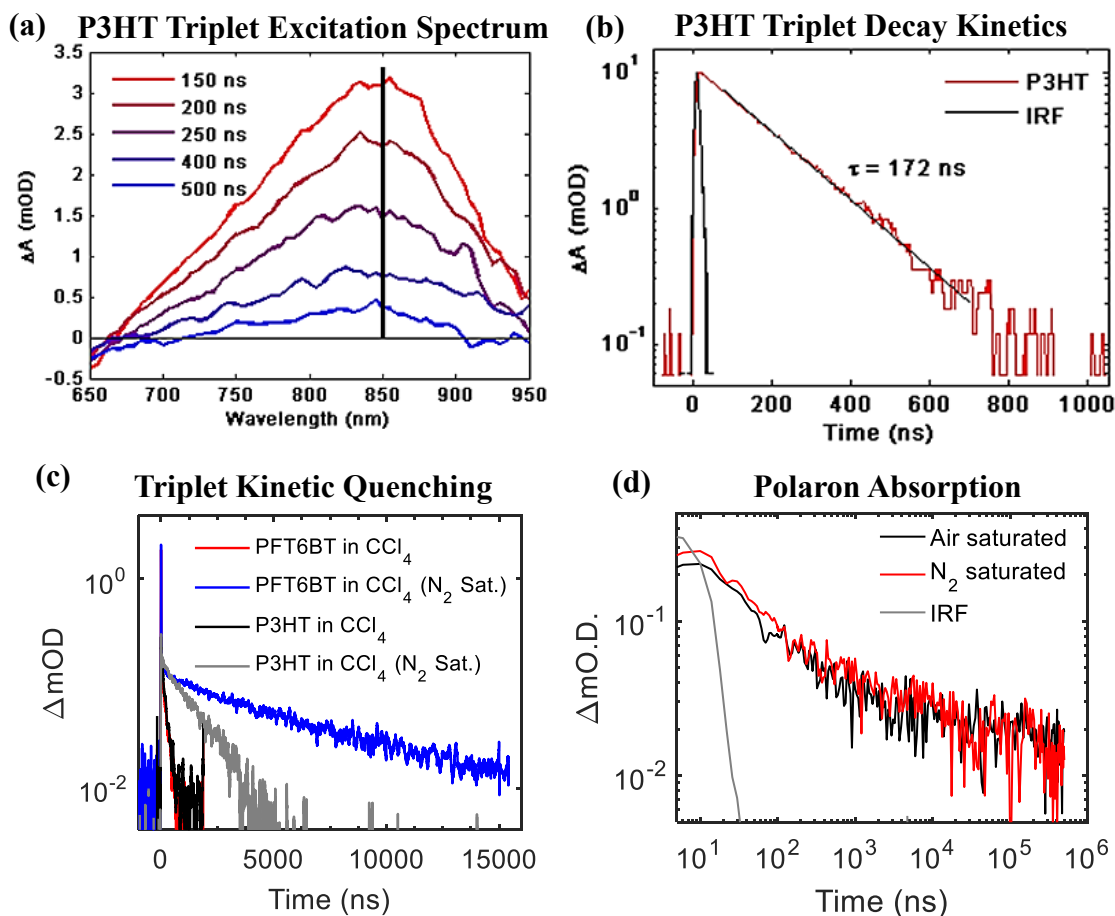


Figure 10-7: (a) Triplet excitation spectrum of a dilute P3HT solution measured using 532 nm excitation. (b) The triplet absorption kinetics at 850 nm for the same solution, showing a single exponential decay with a time constant of ~ 172 ns. Oxygen was not purged from the sample. (c) Triplet kinetic quenching by oxygen, as shown for P3HT and PFT6BT solutions in carbon tetrachloride excited using 532 nm. (d) Example of polaron absorption kinetics measured for a P3HT-b-PFT6BT nanoparticle dispersion in water. The excitation wavelength was 532 nm and the probe wavelength was 992 nm. No kinetic quenching by oxygen was observed.

10.3.2. Block-copolymer aggregation: Binary solvent system

It is known that n-hexane is an effective “bad” solvent for preparing P3HT aggregates.¹³

As such, P3HT-b-PFT6BT was dissolved in carbon tetrachloride (CCl_4) and different volumes

of n-hexane were added ranging from 0-90% volume ratio. The absorption spectra for these solutions are shown in **Figure 10-8**. Upon addition of n-hexane, there was a gradual decrease of absorption around 450 nm, which is peak location of isolated P3HT chain absorption. This indicated that there was a gradual conversion of population from isolated chains to aggregates. Additionally, there was a redshift of the P3HT absorption, with the growth of vibronic peaks. This indicated that the degree of order of the P3HT chains increased. In particular, the increase in its 0-0/0-1 peak ratio indicated that the interchain coupling strength of the aggregated P3HT increased gradually. Dynamic light scattering (DLS) was also performed for several of the solutions to determine the average hydrodynamic diameter upon adding n-hexane (**Figure 10-8**). Particle sizes of the aggregates were found to vary from ~10-500 nm.

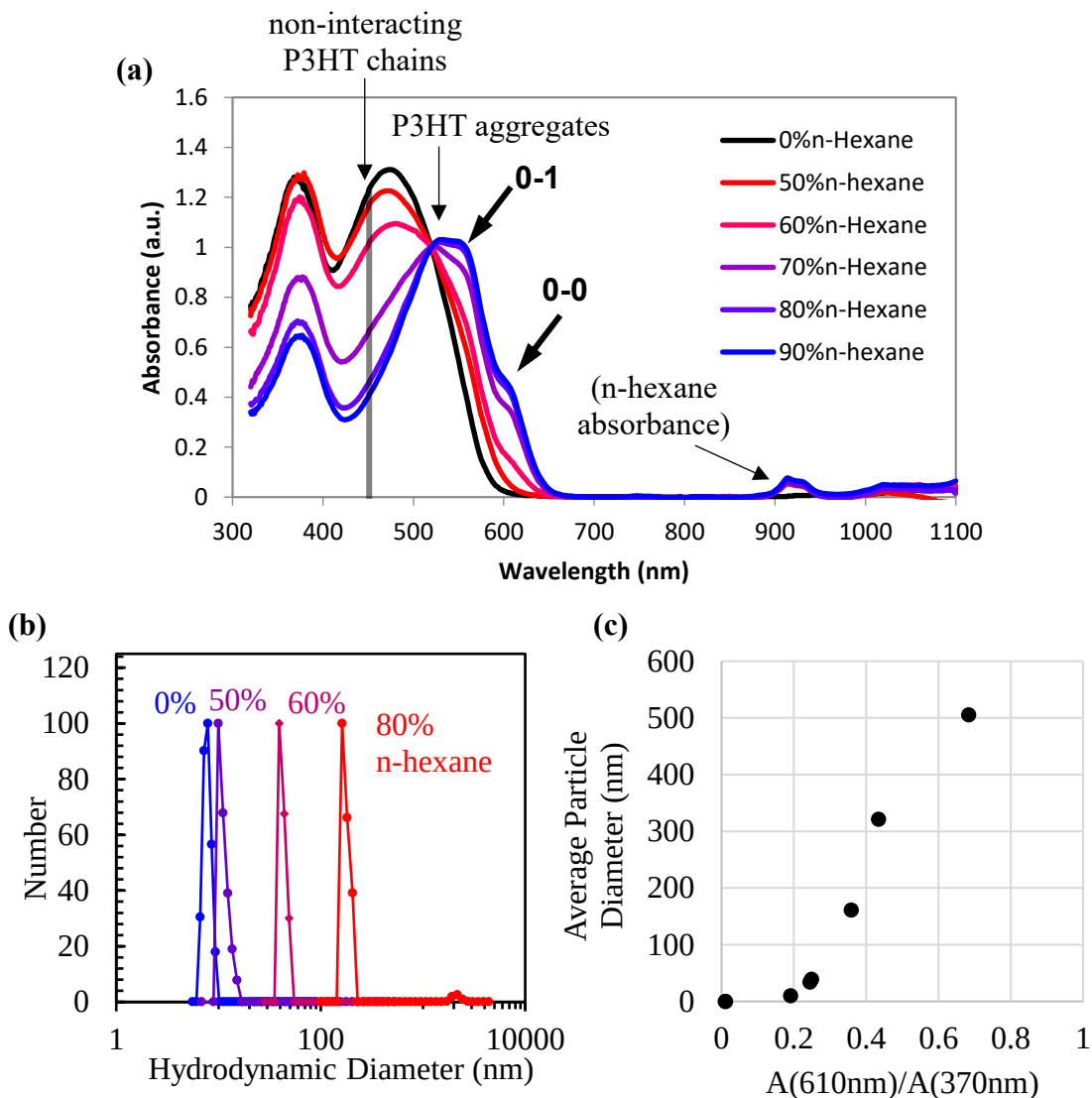


Figure 10-8: (a) Evolution of the P3HT-b-PFT6BT absorption spectrum for carbon tetrachloride solutions with different volume percents of n-hexane added. (b) Particle size distribution for 0.1 mg/mL solutions of P3HT-b-PFT6BT in binary mixtures of CCl_4 :n-hexane. (c) Relationship between the average particle hydrodynamic diameter and the 610:370 nm absorption ratio, serving as a calibration curve.

From the absorption spectrum, it is noticed that the interchain coupling of the P3HT is quite weak. Additionally, the absorption round 370 nm, originating from the PFT6BT polymer block, did not appear to change lineshape relative to the unimer solution (0% sample), suggesting that the PFT6BT may not be experiencing a large change in electronic coupling from interchain interactions. Altogether, the changes in the absorption spectrum suggest that

the block-copolymers are aggregating, but experience weak interchain coupling interactions. Notably, this sample set is complicated by an incomplete conversion to aggregates in most of the samples tested. However, by 80-90% n-hexane, it appeared that most of the polymer had become aggregated.

10.3.3. Block-copolymer aggregation: Water system

In attempt to improve the yield of aggregates formed in P3HT-b-PFT6BT solutions, the good solvent evaporation method was used, since unlike in n-hexane, the block-copolymer is completely insoluble in water and so no unimers are expected to persist. The absorption spectrum was measured for a THF solution as water was slowly added (see **Figure 10-9**). Even upon adding 1 mL of water (9% in volume), a complete conversion from unimers to aggregates was observed. Specifically, the absorbance around 450 nm decreased immediately, and to the limit of 10 mL water (50% in volume). The appearance of vibronic peaks of P3HT also occurred rapidly, with much higher 0-0/0-1 ratios than in the n-hexane series. This indicated that the interchain coupling of the P3HT domains were much stronger, also suggesting that they were highly ordered.

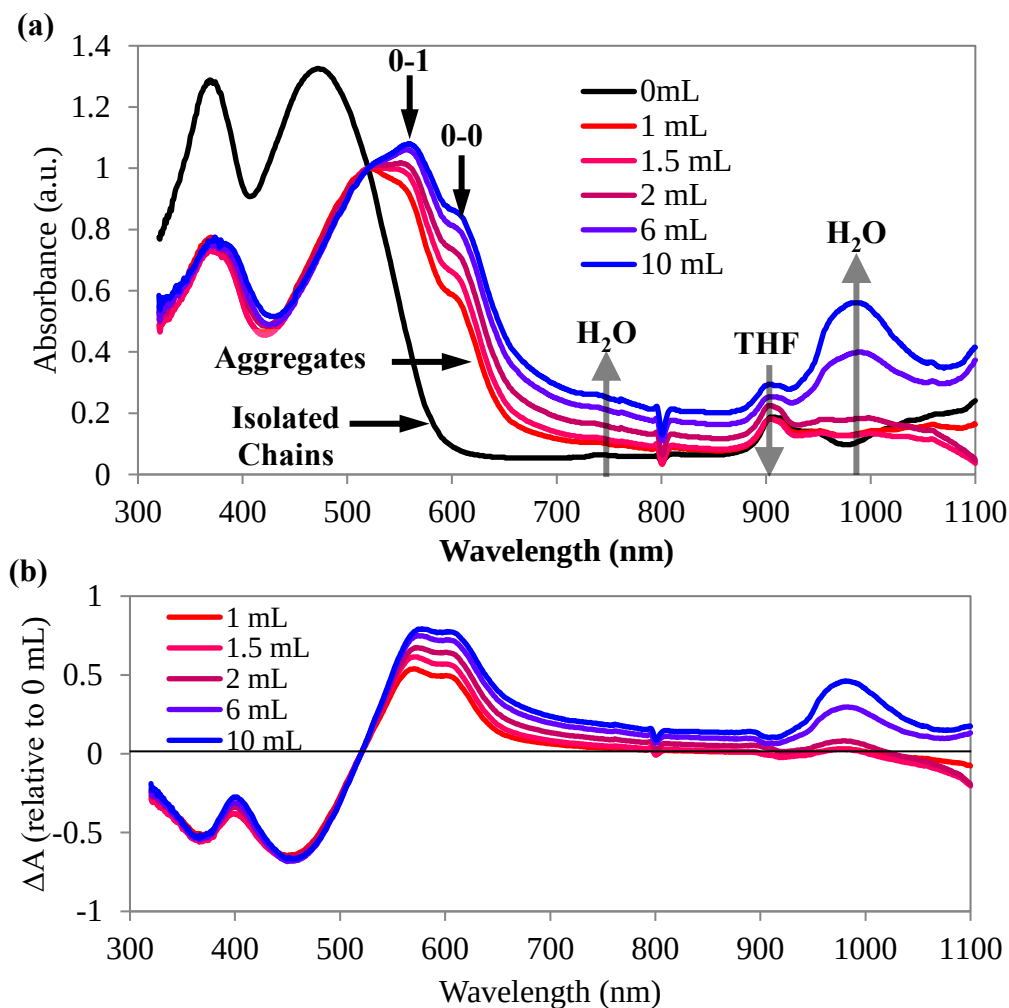


Figure 10-9: (a) Evolution of the normalized absorption spectrum for P3HT-b-PFT6BT solutions in 10 mL of THF after different amounts of water were added. (b) Difference spectra for each sample relative to the solution without water.

Upon evaporation of THF, the absorption spectrum did not exhibit much further change, except there was a significant amount of scattering present, indicating that the aggregates grew into larger nanoparticle structures. Both liquid and dry TEM was performed on the nanoparticles in order to determine their shapes and sizes (see **Figure 10-10**). For dry TEM, nanoparticle dispersions were drop-cast onto lacey carbon TEM grids. The particles were spherical-like, and with a diameter of ~ 200 nm.

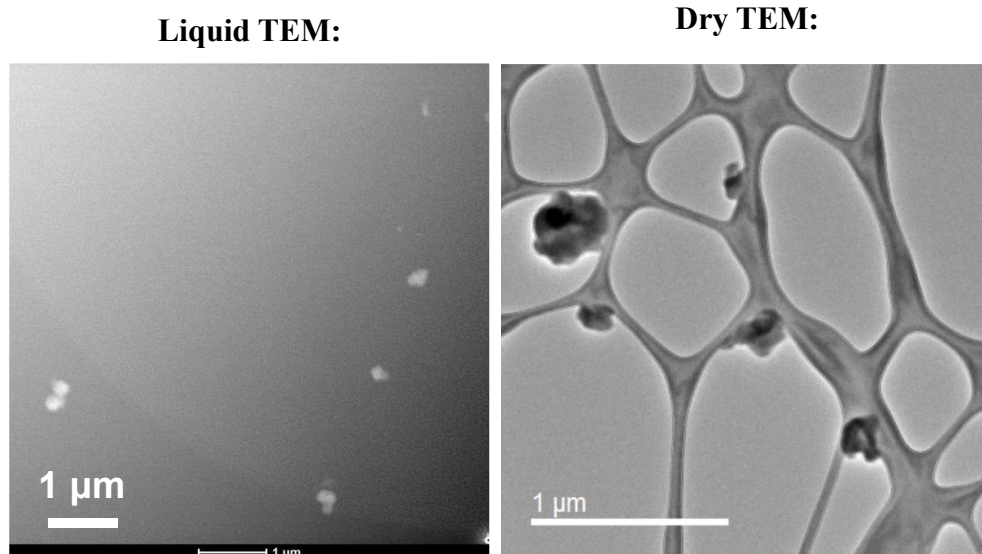


Figure 10-10: Example of TEM images collected for P3HT-b-PFT6BT nanoparticles made using the good solvent evaporation method.

10.4. Polaron Generation and Decay Kinetics in Block-Copolymer Nanoparticles

In this section, general characteristics of polaron absorption in aggregates and nanoparticles of P3HT-b-PFT6BT will be described. In the following section, further details of how their specific structure affects their photophysics will be detailed.

10.4.1. Polymer aggregation turns on polaron generation

A representative nanosecond to microsecond transient absorption spectrum is shown for a nanoparticle dispersion of P3HT-b-PFT6BT in **Figure 10-11**. A P3HT DP and LP band was observed as expected. There was an additional peak present, which may be attributed to triplet absorbance, or may originate from the absorption of polarons in PFT6BT domains. The transient absorption kinetics at the peak of the LP band, ~ 1.25 eV, is shown for both a solution of unimers (in THF) and the nanoparticle dispersion in water. From the kinetics it was determined that the unimer solution forms singlet and triplet excitons, each of which experience unimolecular decay (exponential decay fits are overlaid on the data). On the other

hand, the nanoparticles featured a much different kinetic decay form, which was well-described using an empirical power law function. Details on the power law expression are provided in Chapter 9. From the kinetic data, it can be concluded that the addition of interchain interactions present in the nanoparticles turns on polaron generation in P3HT-b-PFT6BT. Two explanations are possible: (1) The energetic changes in the P3HT upon planarization are necessary for driving the initial charge transfer event preceding polaron formation; or (2) electronic delocalization (either intrachain or interchain) of excitons is important for polaron formation.

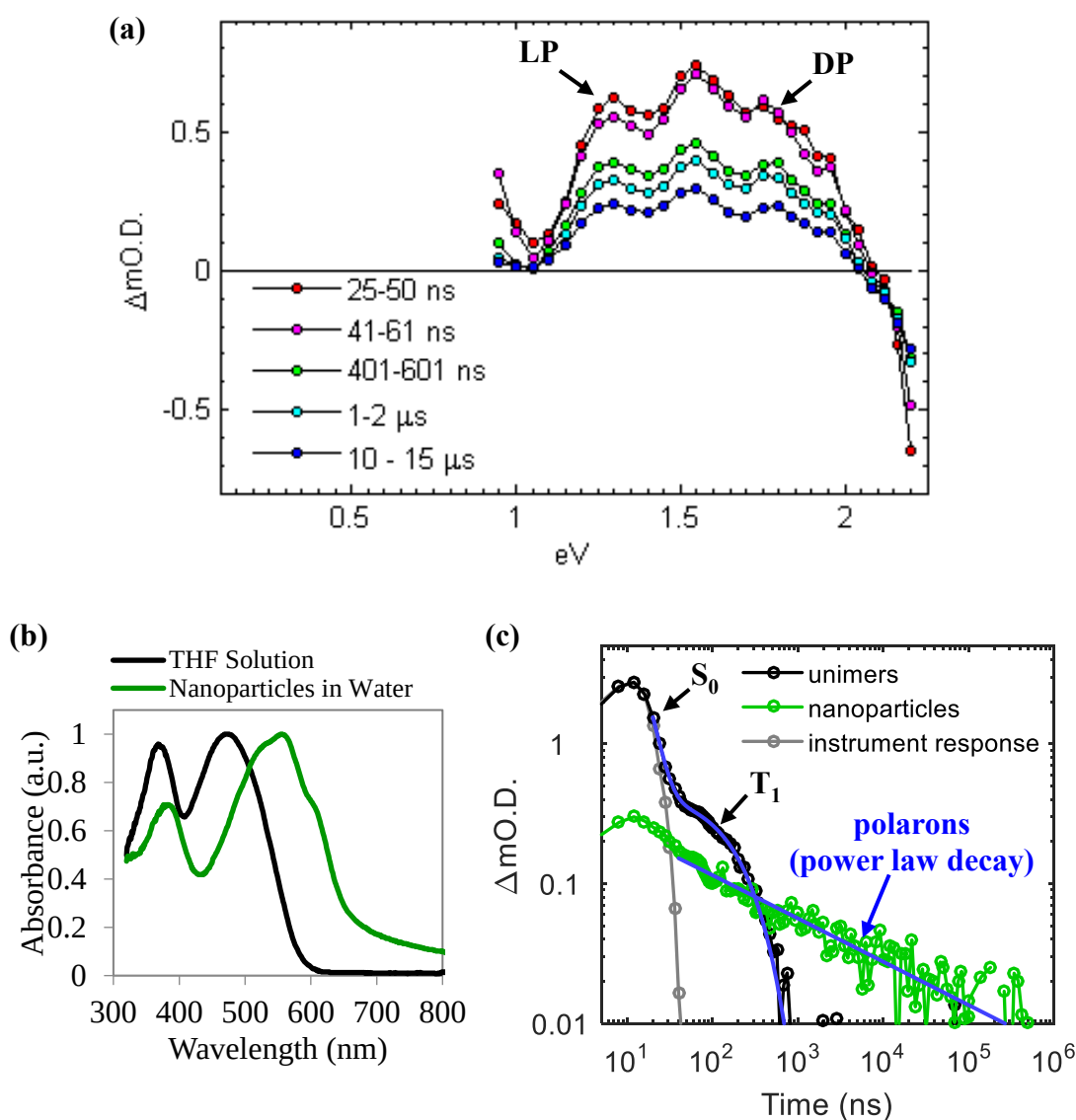


Figure 10-11: (a) Example of a transient absorption spectrum of P3HT-b-PFT6BT nanoparticles excited using 532 nm excitation. Due to limited transmission of water, the spectrum could not be collected below ~ 0.9 eV. (b) Absorption spectrum of P3HT-b-PFT6BT in solution or nanoparticle form at concentrations of ~ 0.05 mg/mL. (c) Transient absorption kinetics measured for the same samples. The excitation was 532 nm and the absorbed energy density was $\sim 38 \mu J/cm^2$. The probe wavelength was 992 nm (1.25 eV).

10.4.2. Photophysics is determined at the aggregate level

As previously discussed for the good solvent evaporation method, addition of water induces aggregation, while evaporation of the THF results in nanoparticle growth (see **Figure 10-12**

for an illustration). Comparison of their transient absorption kinetics at ~ 1.25 eV (992 nm) shows that nanoparticle growth does not change polaron formation or recombination behavior. As such, the interchain interactions present in small aggregates are sufficient for turning on charge formation and transport. Assembling aggregates into larger structures does not significantly affect their polaron dynamics.

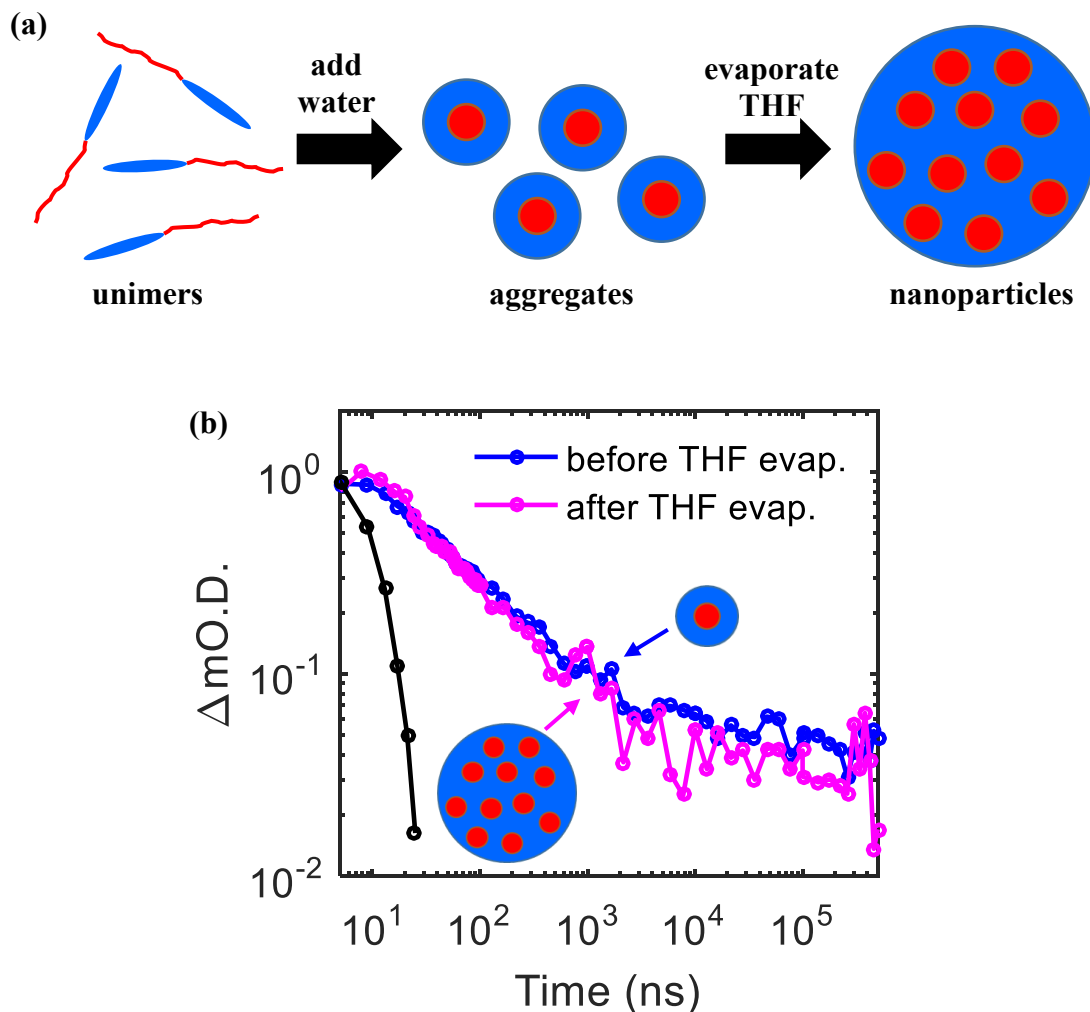


Figure 10-12: (a) Illustration of aggregate and nanoparticle growth during the good solvent evaporation method. (b) Localized polaron absorption decay kinetics for P3HT-b-PFTBT before and after THF evaporation. The excitation wavelength was 532 nm and the polarons were probed at 1.25 eV (992 nm).

10.5. Effect of Polymer Ordering on Polaron Kinetics in Block-Copolymer Nanoparticles

10.5.1. Polymer chain flexibility modulates the branching ratio between triplet and polaron generation

Comparison of the transient absorption kinetics of unimers, aggregates formed using n-hexane, and nanoparticles dispersions formed in water, reveals the importance for polymer chain packing on maximizing polaron yield (see **Figure 10-13**). As previously discussed, the solution of unimers produces triplet excitons upon photoexcitation, without showing any evidence of polaron formation. The nanoparticle dispersion shows the formation of polarons, as evidenced by their power law (bimolecular) decay. However, the aggregates formed using n-hexane appear to show features associated with both triplets and polarons. This suggests that the initial photogenerated singlet excitons bifurcate into two relaxation pathways that produce either triplets or polarons.

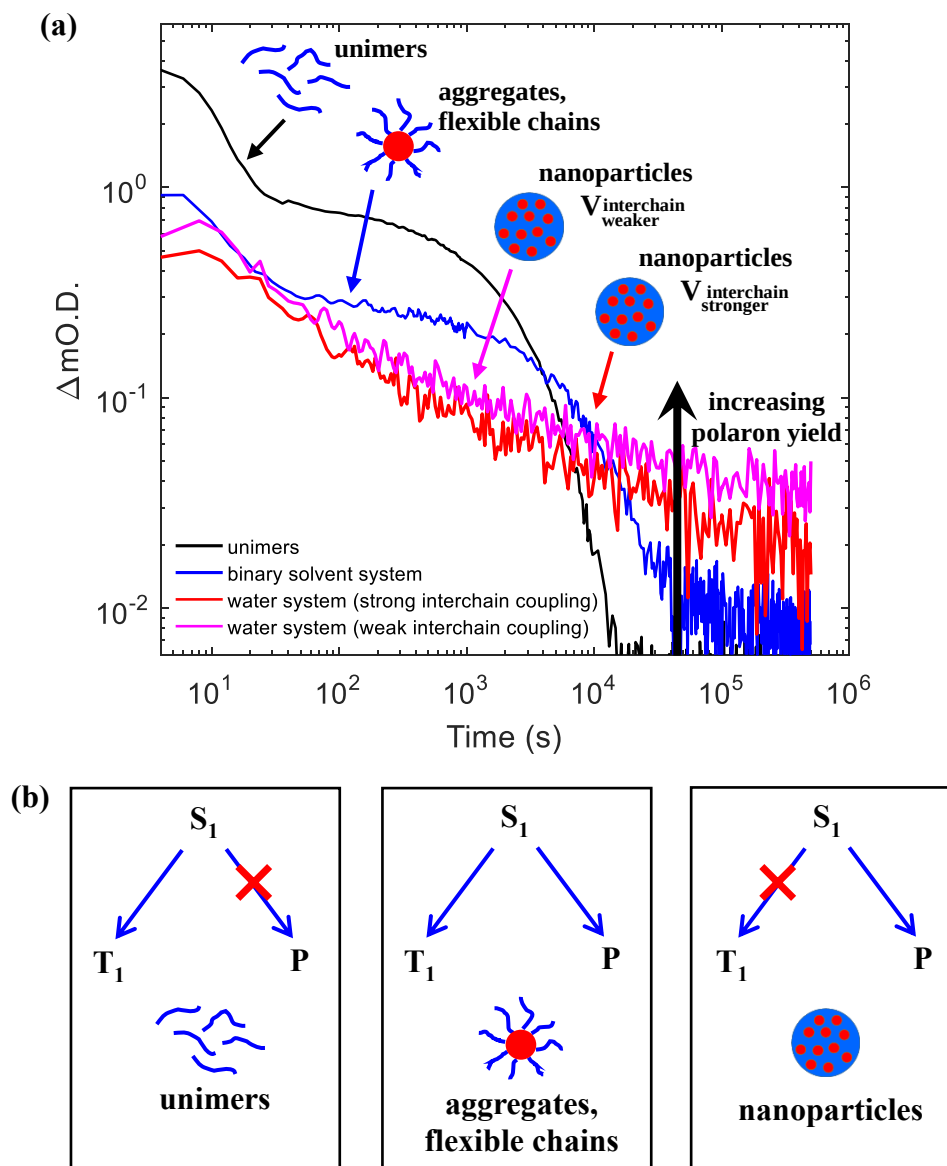


Figure 10-13: (a) Transient absorption kinetics measured for different types P3HT-b-PFT6BT samples in the solution-phase. The excitation wavelength was 532 nm and the probe wavelength was 992 nm (~ 1.25 eV), the position of the LP band of P3HT. All signals were corrected for slight differences in absorption of the pump. (b) Proposed bifurcation model for triplet and polaron formation, and its association with the structure of the block-copolymer solution-phase systems.

As discussed earlier, triplets are known to form in high yields in polymer solutions and amorphous polymer films for which the polymer chains can bend and twist. This observation, combined with the fact the P3HT domains are ordered (as evident from the 90% n-hexane

absorption spectrum), suggests that the PFT6BT domains are disordered and produce a significant amount of triplet excitons. As such, it is hypothesized that the aggregate structure of P3HT-b-PFT6BT in the CCl₄:n-hexane solutions consists of spherical or cylindrical micelles, with the PFT6BT on the exterior. The PFT6BT is hypothesized to be unpacked and disordered, as illustrated in **Figure 10-13**.

Altogether, the kinetic data presented in **Figure 10-13** suggests that the packing of polymer chains is important for decreasing the efficiency of triplet exciton formation pathway, irrespective of the strength of interchain coupling. In an alternate view, conformational flexibility of the polymer chains favors the triplet formation pathway, lowering the yield of polarons. As a result, it is proposed that rigid polymers in general may be more beneficial for photovoltaics.

10.5.2. Intrachain charge transport mediates bimolecular recombination

Interchain interactions were controlled in nanoparticle dispersions by changing the water addition rate to P3HT-b-PFT6BT solutions in THF. **Figure 10-14** shows the absorption spectrum for samples made using fast and slow water addition, confirming modulation of the P3HT interchain coupling strength.

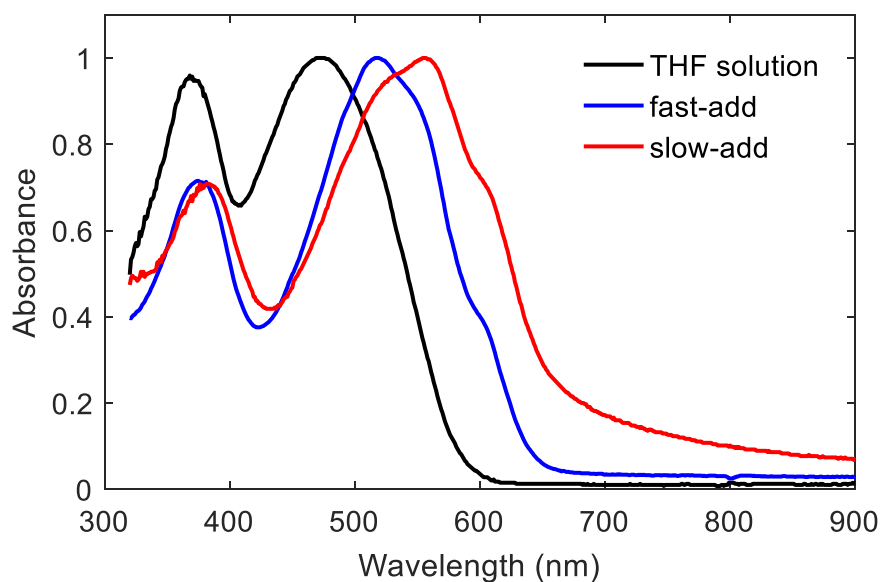


Figure 10-14: Normalized absorption spectra for P3HT-b-PFT6BT in the solution-phase, featuring a dilute THF solution and nanoparticle dispersions made by either injecting water very quickly or very slowly into THF solutions.

The THF evaporation rate was (arbitrarily) fast and slow for the fast and slow water addition, respectively. Both liquid and dry TEM was performed for each nanoparticle dispersion, revealing that there was an order-of-magnitude different in particle size (**Figure 10-15**).

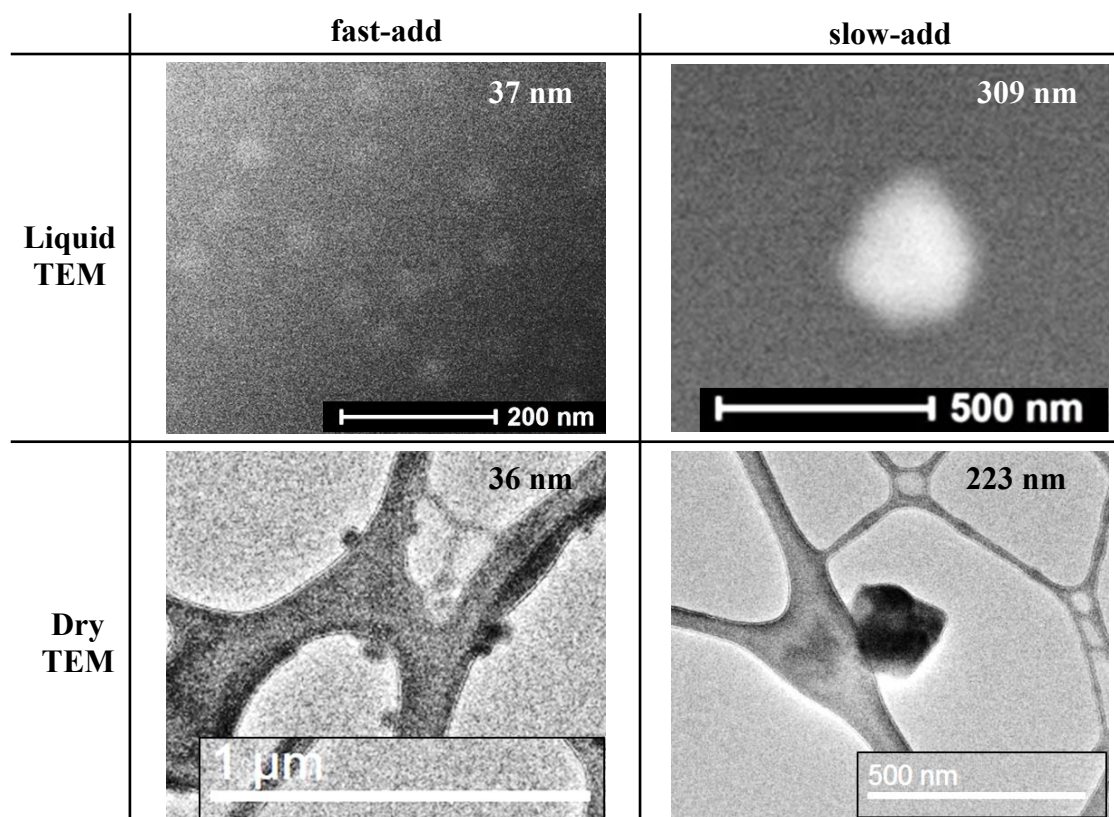


Figure 10-15: TEM images collected for P3HT-b-PFT6BT nanoparticles prepared using fast and slow addition of water, with fast and slow evaporation of THF, respectively. The approximate particle sizes are labeled for each image.

The transient absorption kinetics of the LP and DP bands of P3HT in the block-copolymer nanoparticles are shown in **Figure 10-16**. There was little difference in both sets of kinetics, suggesting that bimolecular recombination of polarons did not depend on the interchain coupling strength of P3HT. This leads to two possible explanations: (1) The diffusion of charges in PFT6BT limits recombination; or (2) Intrachain transport mediates charge recombination. Unpublished data, reported by the Gomez lab in the Chemical Engineering lab at Penn State University, suggests that the electron mobility of PFT6BT is comparable to the hole mobility of P3HT. This suggests that the first explanation is less likely, since the charge diffusion through both the P3HT and PFT6BT domains would be expected to occur at comparable rates. As a result, it is proposed that intrachain transport mediates polaron

recombination in block-copolymer nanoparticles. This can be explained by either of the following two possibilities: (1) The P3HT and PFT6BT domains are well phase-separated and have few interdomain interfaces in comparison to the number of intrachain interfaces; or (2) intrachain transport occurs much more slowly than interchain transport, resulting from dynamical torsional motions in the polymer chains that interrupt through-bond coupling.

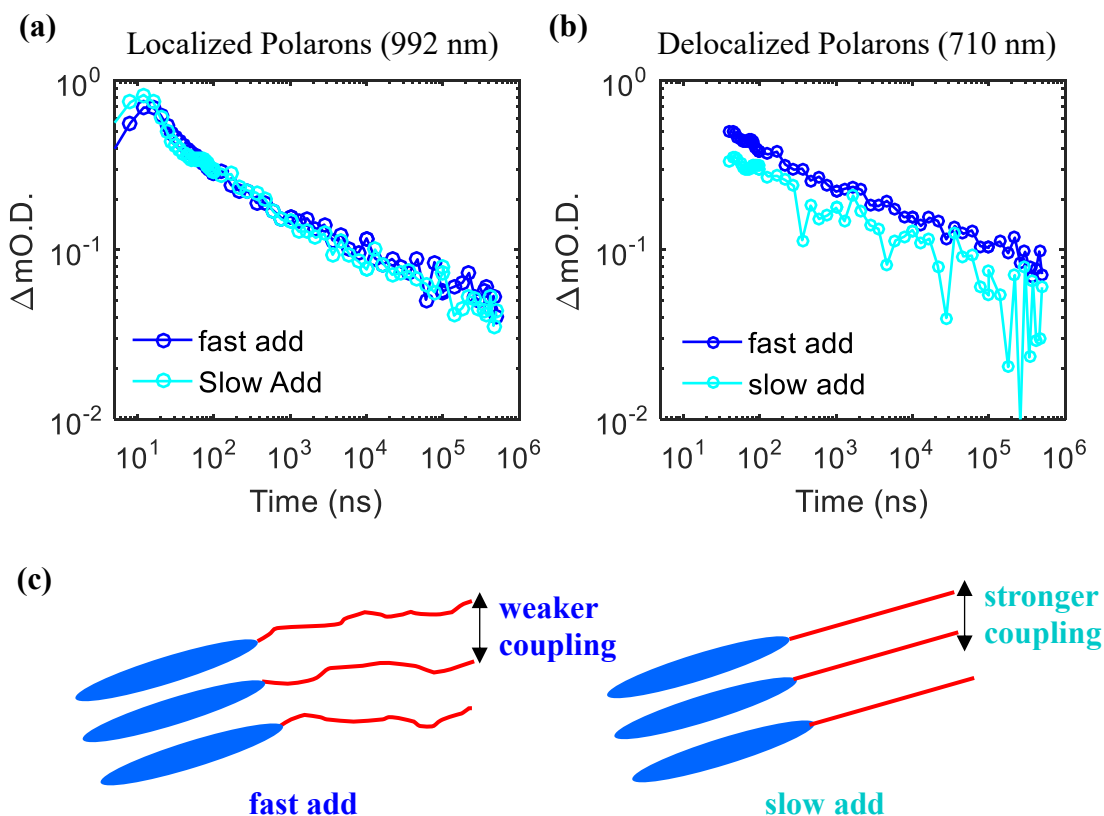


Figure 10-16: Transient absorption kinetics of (a) localized and (b) delocalized polarons in P3HT-b-PFT6BT nanoparticle dispersions prepared using either fast or slow addition of water. (c) Hypothesized aggregate structures within the nanoparticles, illustrating how weaker interchain coupling interactions result from fast water addition.

The lower intensity observed for the DP absorption kinetics may be due to either a lower DP yield in the disordered nanoparticles, or a change in the absorption coefficient between the two nanoparticle dispersions. Spano and coworkers have reported that the strength of interchain coupling is related to the absorption coefficients of the LP and DP bands in the mid-

IR spectral region.²⁵ As a result, the difference in DP absorption intensity may not be significant enough to conclude that there was a difference in DP yield between the two samples.

10.6. Future Directions: Block-Copolymer H- and J-Aggregate Studies

Exploiting the nature of the aggregation of P3HT offers another method for investigating the role of interchain versus intrachain charge transport. In particular, P3HT is known to form both H-like and J-like aggregates in solution. A proposed representation of the packing structures¹⁹ of the polymer chains in both forms of aggregates is shown in **Figure 10-17**. In the J-like aggregate, the thiophene rings in P3HT are fully-planarized, resulting in enhanced conjugation and enhancing their intrachain coupling strength. On the other hand, the thiophene rings in the H-like aggregates have nonzero torsional angles, allowing the polymer chains to stack closer together and enhancing their interchain coupling interactions. As a result, charge transport in J-like aggregates is expected to be more efficient along chains, while that in H-like aggregates is expected to be more efficient between chains.

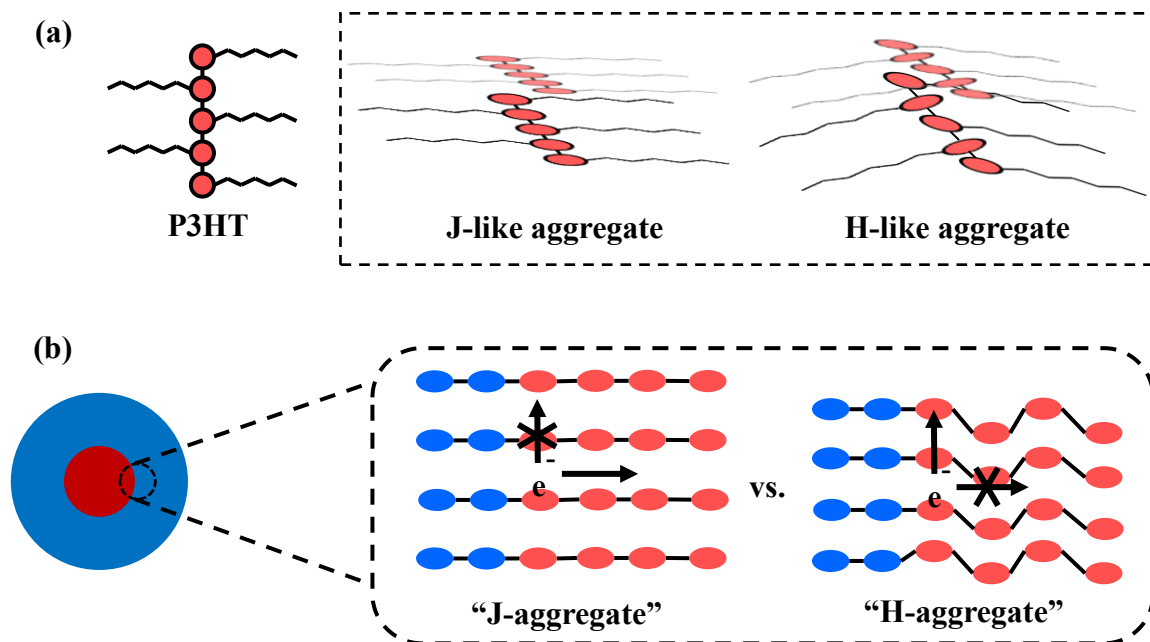


Figure 10-17: (a) Packing structure of J-like and H-like aggregates of P3HT. (b) Depiction of a block-copolymer aggregate, featuring J-like and H-like aggregation of the P3HT polymer block.

Applying these principles to P3HT-b-PFT6BT aggregates could offer a new way to control which type of interactions, intrachain versus interchain, dominate. An illustration of this system is provided in **Figure 10-17**. Such block-copolymer systems could be used to independently test how interchain and intrachain coupling impacts charge generation and recombination behavior.

10.7. Conclusions and Significance

In this chapter, new methods for producing block-copolymer aggregates and nanoparticles in the solution-phase were developed using the P3HT-b-PFT6BT system. The structure of the aggregates/nanoparticles was modulated depending on the solvent system chosen. Evolution of the absorption spectrum of the P3HT polymer block was used to assess changes in the block-copolymer during aggregation and/or nanoparticle growth. It was found that aggregation turns

on polaron generation in P3HT-b-PFT6BT, and that further nanoparticle growth does not significantly change their photophysics. The flexibility of polymer chains within the aggregates was found to modulate the branching ratio of triplet versus polaron formation. More rigid and packed structures resulted in higher yields of polarons. Last, it was found that the intrachain charge transport pathway limits the bimolecular recombination of charges in P3HT-b-PFT6BT nanoparticles.

The results presented in this chapter are preliminary and require further testing. Nonetheless, this work serves in developing a new block-copolymer platform for studying charge generation and recombination processes in organic materials. It is the hope that future fundamental studies on block-copolymer solution-phase systems will spring from this work, leading to better understandings of the complex photophysical mechanisms that occur in organic photovoltaics in general.

10.8. References

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CHAPTER 11

Uncovering the Roots of Color Degradation in an Inorganic Phosphor Material for Solid State Lighting

In the previous chapters, the effect of intermolecular and intramolecular structure on triplet and charge transport was investigated. The triplet transfer and charge transfer coupling of molecules and polymers was controlled through local orbital overlap interactions. In this chapter a different type of structural change is investigated, whereby modulation of interchromophore distance is shown to control energy transfer rates in inorganic phosphorescent materials.

The crystal lattice structure of inorganic carbidonitride phosphors used in solid-state lighting applications was found to be important to control. In particular, specific changes in the lattice were found to impact the resulting energy transfer characteristics between emissive sites. Aging of the materials under optical and thermal stress conditions present during device operation resulted in changes of the lattice that led to poor color stability. It was determined that pre-setting the interchromophore distance via synthesis is a method for preventing a change in the lattice structure over device operation time, leading to improved color stability.

The work presented in this chapter was a joint effort between the Dow Chemical Company and the Pennsylvania State University. The Dow Chemical Company designed, synthesized, and fabricated film samples of the inorganic phosphors. This included designing and constructing an accelerated aging apparatus, performing x-ray diffraction powder measurements. In addition, the Dow Chemical Company performed all density functional theory computations.

This chapter was adapted from the publication: Grieco, C., Hirsekorn, K.F., Heitsch, A.T., Thomas, A.C., McAdon, M.H., Vanchura, B.A., Romanelli, M.M., Brehm, L.L., Leugers, A., Sokolov, A.N., and Asbury, J.B., “Mechanisms of Energy Transfer and Enhanced Stability of Carbide Nitride Phosphors for Solid-State Lighting”, *ACS Appl. Mater. Interfaces*, **2017**, 9, 12547-12555, which has been rephrased in the context of this dissertation.

11.1. Introduction

Phosphor-converted light-emitting devices (pcLED), which rely on down-conversion to produce visible light from UV near-UV excitation, are being developed for solid state lighting applications.¹⁻⁴ In particular, green and red phosphors are deposited onto GaN LED chips, which emit 450 nm blue light. The phosphors then absorb a fraction of the blue light, allowing the color of total pcLED emission to match the emission from incandescent light sources.¹⁻⁵ However, in this design, the phosphors experience significant optical and thermal stress because they are necessarily subject to intense ($0.1 - 1 \text{ W/mm}^2$) excitation, resulting in high temperatures (exceeding 150°C).^{4,6}

A variety of inorganic materials, such as nitrides, oxynitrides, and garnets, are typically doped with rare earth ions in order to produce visible phosphors.^{3,4,7,8} Red phosphors are particularly challenging to implement because they lack long-term photostability related to high-energy UV excitation, and their luminescent efficiency typically suffers at elevated temperatures.⁴ The $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor is a particularly promising red phosphor candidate because of its broad absorption spectrum, low thermal quenching of phosphorescence, and emission tunability. Unlike in oxides, the N^{3-} ions in the crystal lattice of the $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$

phosphor provide it with a higher degree of covalency, which enables the absorbance of blue light.³

While the luminous efficacy of radiation (lumens/W) has been optimized, the long-term emission stability under thermal and optical stress is an active area of investigation.^{4,9} Incorporating new phosphors into the pcLED market requires fulfillment of the initial optical performance criteria (total LED lumens at a specific color temperature) and reliability, which are requested by the manufacturer. Both the initial and long-term performances are critical to optimize in order to maintain high color stability. In white light pcLEDs, subtle changes in the brightness and emission spectrum of the phosphor can change the color rendering index, degrading the “visual quality” of the light. Understanding the phosphor aging process, or how the initial optical properties degrade under device operation, is therefore significant to the commercialization of pcLEDs.^{3,4}

Phosphors have been developed for pcLEDs to achieve high emission quantum efficiency by minimizing non-radiative relaxation processes.¹⁰⁻¹⁹ A new set of proprietary phosphors have been designed by activating carbide nitride $\text{Sr}_2\text{Si}_5\text{N}_8\text{C}_x\text{O}_{3z/2}$ host crystals using Eu^{2+} ions, which produce the radiative centers in the lattice.^{11,12} Recently, these carbide nitride phosphors, developed by Lightscape Materials Inc. (wholly owned by The Dow Chemical Company), were recently studied under thermal stress.²⁰ In study, it was found that incorporation of carbon and oxygen into the $\text{Sr}_2\text{Si}_5\text{N}_8\text{Eu}^{2+}$ lattice created distortions, resulting in contraction of the (010) direction and expansion in the other two directions.²⁰ Such changes in crystal lattice structure was shown to stabilize the emission intensity at elevated operational temperatures.²⁰ Such reduced thermal quenching was hypothesized to be attributed to the

reduction of the coupling strength of the electronic transition involved in phosphorescence to excited phonon modes.²¹

In this work, the mechanism of lattice stabilization of $\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ phosphors by incorporation of carbon (and oxygen), and its associated photophysical properties were investigated using time-resolved photoluminescence spectroscopy (TRPL). In addition, the influence of realistic optical and thermal stress conditions on the phosphorescence was tested using an accelerated aging apparatus. Using TRPL, the mechanism of degradation was determined, leading to the conclusion that during aging, the accumulation of lattice strain in materials lacking carbon is responsible for their low color stability.

11.2. Experimental Methods

All measurements were performed using phosphor materials that were dispersed within silicone films (OE-6351, Dow Corning) at 5 wt. %. An accelerated aging apparatus developed by the Dow Chemical Company was used to test the reliability performance of thin films of the phosphors. For these tests, the films were placed on glass cover slips directly above a 100 W blue LED array and were subsequently aged in ambient laboratory conditions. The glass cover slip (GOLD Seal Cover Glass 22mm x 22mm No. 2 – 220 μm thickness) prevented any exceedingly, unnaturally high temperatures exposed to the phosphor silicone. The films were then exposed to blue light for a pre-set amount of time. The film position on the LED was changed from time-to-time to ensure uniform exposure to different portions of the 100 W LED array.

Time-resolved photoluminescence (TRPL) spectroscopy was carried out using home-built flash photolysis instrumentation.²² For the pulsed excitation source, a 20 Hz nitrogen laser

(GL-3300, Photon Technology International) was used to pump a dye cavity (GL-302, Photon Technology International) that was tuned to 450 nm. The emission had a full-width at half-maximum less than 1 nm, and ~1 ns pulse duration. The sample was measured in the L-geometry. The emission was dispersed by a monochromator (DK240, Spectral Products) before it was detected using an unamplified 350 MHz silicon photodetector (DET210, Thorlabs). The signal was amplified using a preamplifier (HVA-200M-40-B, FEMTO) and was then digitized using a 200 MHz oscilloscope (Picoscope-5244A, Pico Technology). The time resolution was limited by the oscilloscope bandwidth, and the instrument response function (IRF) had a FWHM of ~3.5 ns. The monochromator slits were adjusted to achieve a 5 nm effective spectral bandwidth.

The incident excitation energy density was $\sim 100 \mu\text{J}/\text{cm}^2$ and the illuminated area was $\sim 0.5 \text{ cm}^2$. The film samples were positioned at a $\sim 45^\circ$ angle relative to the direction of excitation. Different spots of each film were measured to test for spot-to-spot variation, and the averages of three scans were used to generate all the reported spectra.

Non-local density functional theory (DFT; generalized gradient approximation) was used to optimize three crystal structure models developed by the Dow Chemical Company. The atomic coordinates and the unit cell parameters were optimized. The first model optimized was the $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor. Two models were selected for the carbidonitrides based on a separate computational study containing 0.47 weight percent (wt. %) carbon ($\text{Sr}_2\text{Si}_5\text{O}_{0.17}\text{N}_{7.66}\text{C}_{0.17}$). The Mercury software package (version 3.5.1) was used to generate all crystal structure graphics. The CrystalMaker software package (version 9.1.1) was used to calculate the distributions of Sr-Sr distances.

11.3. Emission Characteristics of $\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ Phosphors

Carbidonitride phosphors ($\text{Sr}_2\text{Si}_5\text{N}_{8-[(4x/3)+z]}\text{C}_x\text{O}_{3z/2}$) contain carbon and oxygen, which substitute nitrogen ions in the host lattice ($\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$).²³ A fraction of the Sr^{2+} ions in the lattice are substituted for Eu^{2+} ions, which form the radiative centers.^{11,12} The electronic transition corresponding to the absorption and emission corresponds to a $4f^7-4f^65d^1$ transition of Eu^{2+} .²⁴ Crystal-field splitting causes the emission to appear in the visible spectral region.²⁰ Previous studies reported that the $\text{Sr}_2\text{Si}_5\text{N}_8$ host lattice contains two energetically distinct Sr^{2+} sites that differ in their Sr-N coordination.^{24,25} In the first site (“Sr1”), the Sr^{2+} is coordinated to ten nitrogen ions having an average Sr-N distance of 2.969 Å. In the second site (“Sr2”), the Sr^{2+} is also coordinated by ten nitrogen ions, but has a slightly smaller average Sr-N distance of 2.928 Å. The difference in average Sr-N distance causes Eu^{2+} ions at the Sr2 site to have a lower emission energy than Sr2 site.²⁵ An energy level diagram and the photoluminescence spectrum of a carbidonitride phosphor is provided in **Figure 11-1**. The representative photoluminescence spectrum is shown for a phosphor containing 0.044 wt. % Eu^{2+} and 0.05 wt. % carbon.

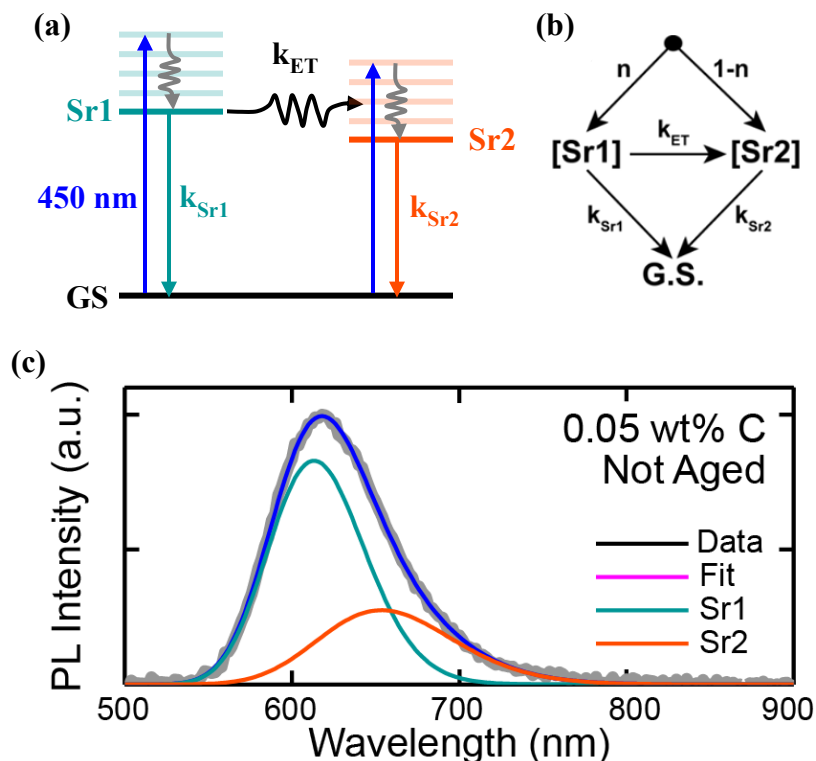


Figure 11-1: (a) Simple energy level diagram for $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor, showing the Sr1 and Sr2 emissive sites and energy transfer from Sr1 to Sr2. Nonradiative relaxation arrows to the ground state have been omitted. The excitation is indicated by the blue lines, which corresponds to the laser wavelength used in this work. (b) Kinetic model for emission in the $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphor after photoexciting Sr1 and Sr2 sites. (c) Photoluminescence (PL) spectrum for a pristine phosphor containing 0.05 wt. % carbon. The spectrum was decomposed into Sr1 and Sr2 emission bands.

The Eu^{2+} ions at both Sr^{2+} sites could be excited using 450 nm light, giving rise to Sr1 and Sr2 phosphorescence. The total phosphorescence spectrum is composed of individual emission bands of both the Sr1 and Sr2 sites. Because the Eu^{2+} ions at the Sr2 sites have a lower transition energy, efficient energy transfer (ET) can occur between Eu^{2+} ions from Sr1 to Sr2 sites.²⁶ The rate of energy transfer determines the shape of the ultimate photoluminescence spectrum since it controls the relative intensity of emission at Sr2 sites. For example, faster energy transfer from Sr1 to Sr2 sites would lead to higher emission intensity at longer wavelengths, giving rise to a redshift.

11.4. Carbon Substitution and Impact on Emission Characteristics and Color Stability

The normalized (time-integrated) phosphorescence spectra of carbidonitride phosphors containing 0.05, 0.10, 0.20 and 0.30 wt. % carbon are shown in **Figure 11-2**.

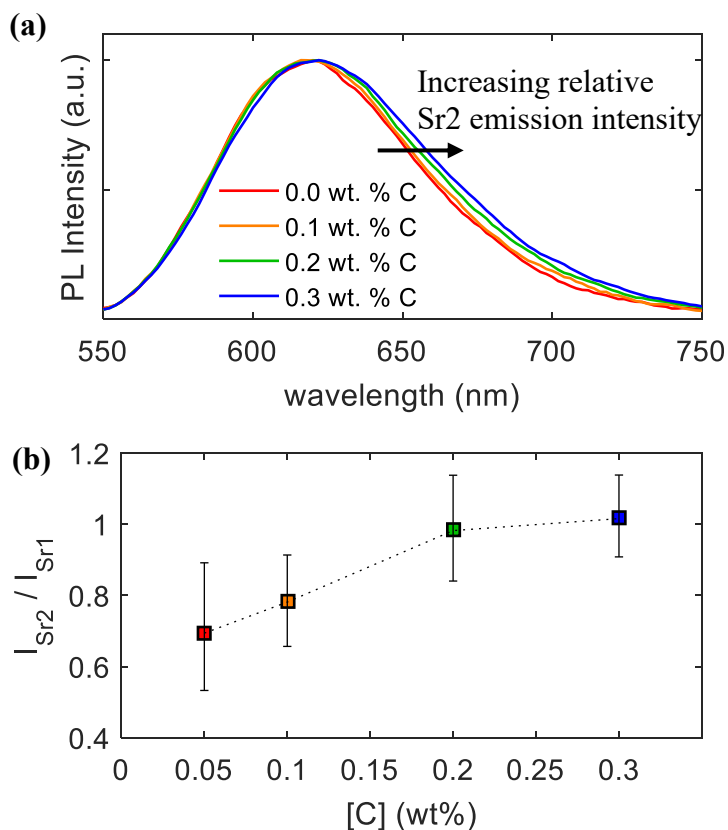


Figure 11-2: (a) Photoluminescence (PL) spectra of carbidonitride phosphors containing different amounts of carbon. (b) Dependence of Sr2/Sr1 emission intensity ratios on wt. % carbon.

The relative emission intensity at longer wavelengths increases for the phosphors incorporating higher amounts of carbon. The emission spectra were all fit using a linear combination of Sr1 and Sr2 bands in order to determine the relative intensity originating from each site. Taking the ratio of the integrated emission bands ($I_{\text{Sr2}}/I_{\text{Sr1}}$) gives the relative emission at Sr1 and Sr2 sites. The comparison of relative Sr1:Sr2 emission to the amount of carbon content in the carbidonitride phosphors suggested that the energy transfer rate from Sr1 to Sr2 sites may be modulated. In particular, increased carbon content may lead to faster Sr1 to Sr2 energy

transfer. The (time-integrated) photoluminescence spectra for each sample before and after accelerated aging are shown in **Figure 11-3**.

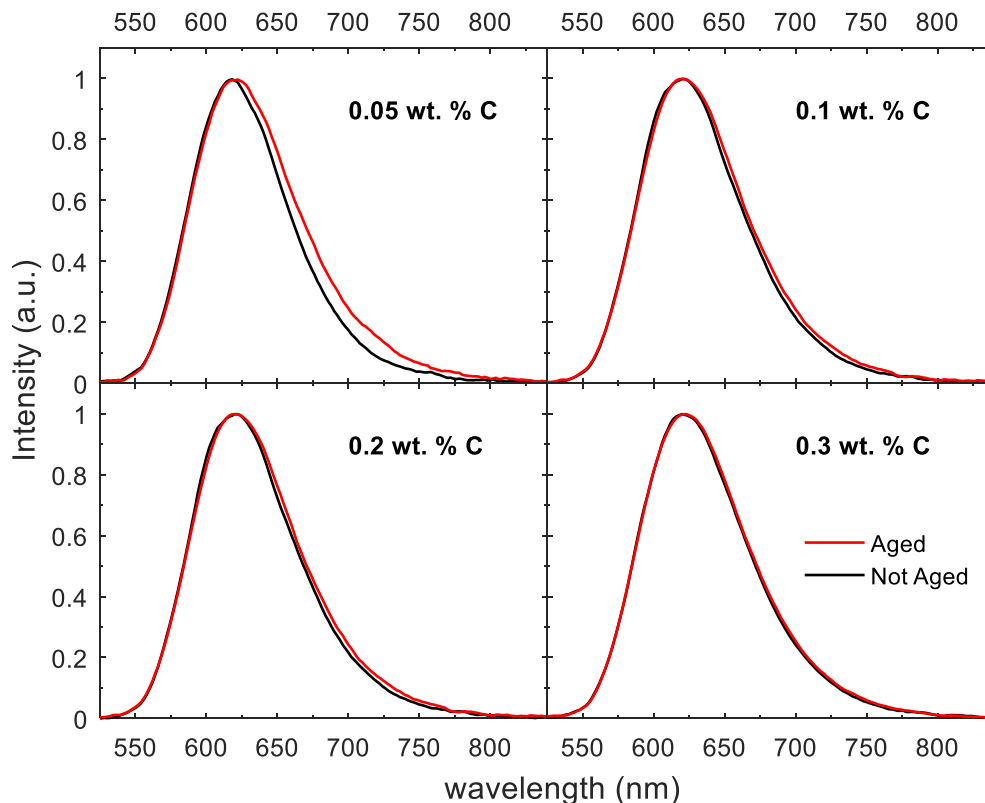


Figure 11-3: Time-integrated photoluminescence spectra collected for carbidonitride phosphors containing different amounts of wt. % carbon before (black lines) and after (red lines) accelerated aging.

As carbon loading is increased, there was a reduction in changes of relative Sr1-Sr2 emission intensity associated with aging. As such, it appeared that incorporation of carbon into the $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ lattice prevents a change in the rate of energy transfer between Sr1 and Sr2 sites upon aging.

A representative (two-dimensional) TRPL spectrum for a carbidonitride phosphor containing 0.05 wt. % carbon is provided in **Figure 11-4**, showing a dynamic red-shift.

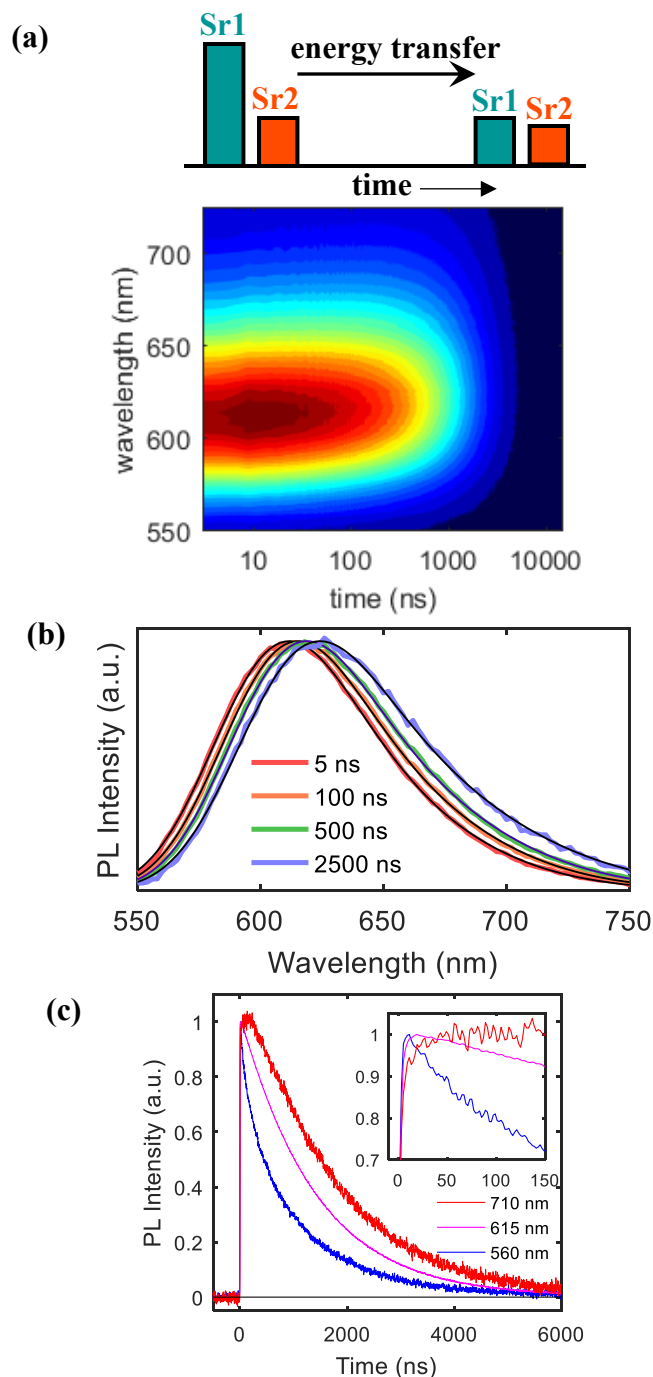


Figure 11-4: (a) Time-resolved photoluminescence (PL) spectrum for a carbidonitride phosphor containing 0.05 wt. % carbon after photoexcitation using 450 nm. The schematic illustrates the energy transfer process between Sr1 and Sr2 sites that causes the observed dynamic redshift. (b) Spectra selected at several time delays showing the dynamic redshift. The data are represented as thick, colored lines. The fits are shown as thinner, black lines.

Following 450 nm excitation, emission occurs from both Sr1 and Sr2 sites, proportional to the concentration of Eu^{2+} ions present at each site, and the oscillator strength of each transition. At later time, the spectrum red-shifts, indicative of energy transfer from Sr1 to Sr2 sites. It is possible that the dynamic red-shift actually originates from a shorter excited state lifetime of Eu^{2+} ions at Sr1 sites. However, a previous study²⁴ on $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphors showed that the excited state lifetimes of both Sr1 and Sr2 sites (in the absence of Sr1 to Sr2 energy transfer) are equivalent. The validity of this conclusion was tested for the carbidonitride phosphors in this study. The TRPL data were spectrally-integrated for each phosphor to determine the kinetic decay of the total excited state population. In this treatment of the data, the influence of energy transfer on the kinetics was eliminated. **Figure 11-5** shows a representative decay trace for a carbidonitride phosphor containing 0.05 wt. % carbon.

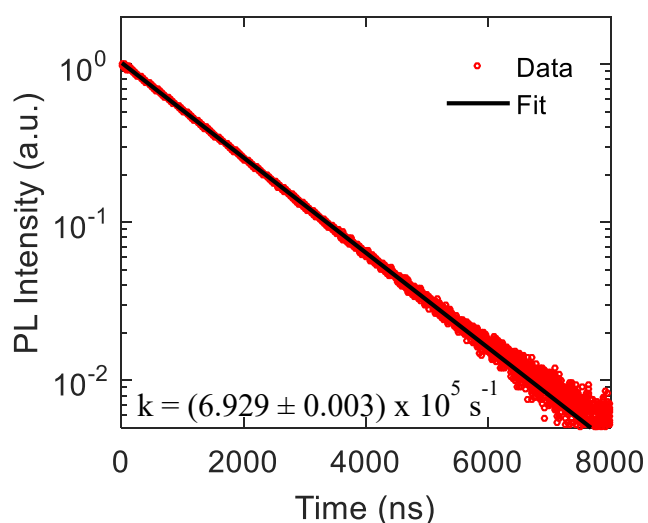


Figure 11-5: Photoluminescence (PL) decay obtained by spectrally-integrating the time-resolved spectrum for a carbon carbidonitride phosphor containing 0.05 wt. % carbon. The data was fit using an exponential decay function.

The phosphorescence decay was well-described using a single exponential function, which suggests that the phosphorescence decay rates for both the Sr1 and the Sr2 sites must be the same. If this was not true, then the spectrally-integrated kinetics would be described by a sum

of two exponential decay functions. In the process, the phosphorescence decay rates ($k_{\text{Sr1}}=k_{\text{Sr2}}$) were determined for each sample, which were used in kinetic modeling described later. These values are tabulated in **Table 11-1**.

Table 11-1: Rate constant values obtained from TRPL spectroscopy for carbidonitride phosphors containing various amounts of carbon

Sample (%wt C)	$k_{\text{Sr1}} (\text{s}^{-1})$	$k_{\text{obs}} (\text{s}^{-1})$	$k_{\text{ET}} (\text{s}^{-1})$
0.05	$(6.929 \pm 0.003) \times 10^5$	$(7.508 \pm 0.009) \times 10^5$	$(5.79 \pm 0.09) \times 10^4$
0.1	$(6.947 \pm 0.003) \times 10^5$	$(7.710 \pm 0.010) \times 10^5$	$(7.60 \pm 0.10) \times 10^4$
0.2	$(6.953 \pm 0.002) \times 10^5$	$(8.110 \pm 0.020) \times 10^5$	$(1.15 \pm 0.02) \times 10^5$
0.3	$(7.017 \pm 0.003) \times 10^5$	$(8.440 \pm 0.020) \times 10^5$	$(1.42 \pm 0.02) \times 10^5$
0.05 (aged)	$(7.306 \pm 0.006) \times 10^5$	$(8.86 \pm 0.04) \times 10^5$	$(1.56 \pm 0.04) \times 10^5$
0.1 (aged)	$(7.434 \pm 0.007) \times 10^5$	$(8.88 \pm 0.04) \times 10^5$	$(1.45 \pm 0.04) \times 10^5$
0.2 (aged)	$(7.199 \pm 0.005) \times 10^5$	$(8.71 \pm 0.03) \times 10^5$	$(1.51 \pm 0.03) \times 10^5$
0.3 (aged)	$(7.314 \pm 0.005) \times 10^5$	$(8.96 \pm 0.03) \times 10^5$	$(1.64 \pm 0.03) \times 10^5$

Next, it must be determined if the changes of the emission spectra (**Figure 11-2**) observed upon increasing carbon content results from changes in differences in occupation of Eu^{2+} at Sr1 versus Sr2 sites. **Figure 11-6** compares the normalized phosphorescence spectra for all the carbidonitride phosphors measured at 5 ns following photoexcitation. The spectra were found to show insignificant changes in lineshape, indicating that the amount of carbon content does not modulate the relative occupation of Eu^{2+} at Sr1 versus Sr2 sites. This result was found to be consistent with a previous report on $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ phosphors.²⁴

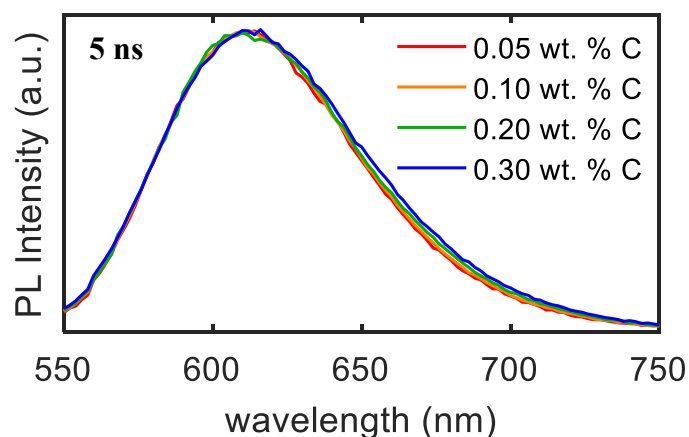


Figure 11-6: Photoluminescence (PL) spectrum at 5 ns for carbide phosphors containing different wt. % carbon excited using 450 nm.

Altogether, these analyses suggest that comparing the dynamic redshift across the series of carbide phosphors studied would reveal differences in the energy transfer rate from Sr1 to Sr2 sites. The time-dependence of the emission peak location and full-width at half-maximum (FWHM) for each phosphor would help reveal how carbon content affects the energy transfer rates. To determine these parameters, simple algorithms were developed using MATLAB (version 2012b). A search algorithm, which located the wavelength corresponding to 50% of the maximum intensity of each PL spectrum, was used to determine the FWHMs. The peak locations were found by first fitting an n^{th} degree polynomial to each 1^{st} derivative emission spectrum, and then solving for its zero. An example of this procedure is provided in **Figure 11-7**.

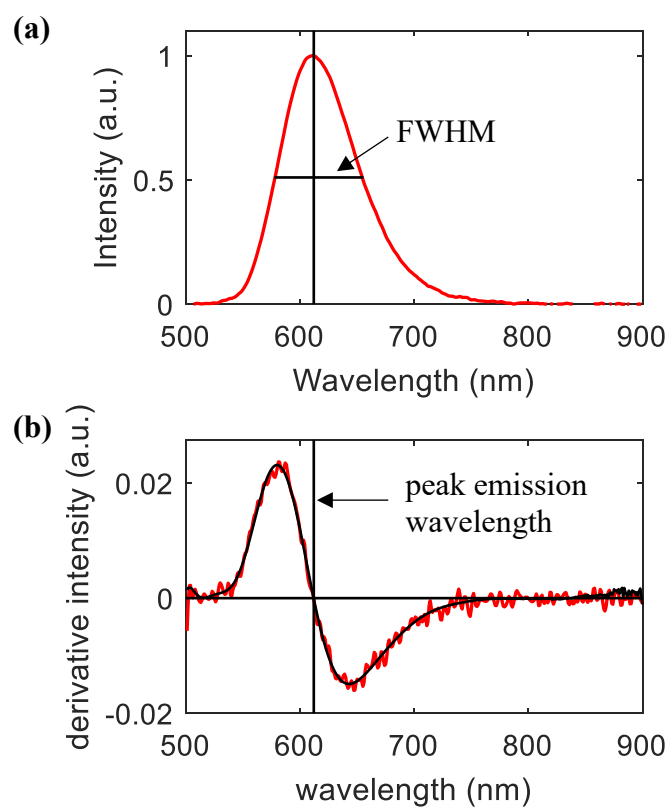


Figure 11-7: Illustration of the methods used to extract **(a)** full-width at half maxima (FWHM) and **(b)** peak emission wavelengths for the photoluminescence spectra of the carbide nitride phosphors.

Figure 11-8 shows the time-dependence of the peak position and FWHM for each carbide nitride sample.

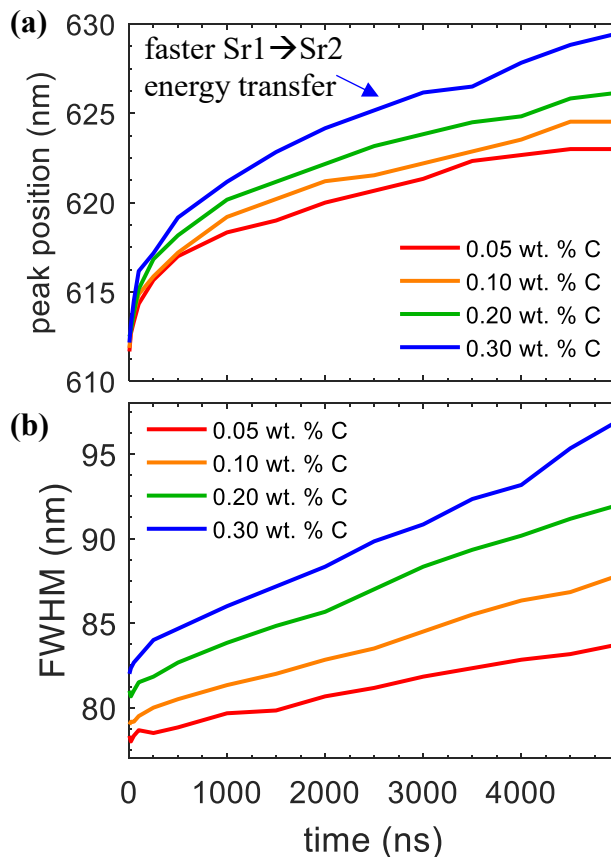


Figure 11-8: (a) Time-dependence of the (a) peak positions and (b) full-width at half-maxima (FWHM) of the photoluminescence of carbide nitride phosphors containing different amounts of carbon.

The largest shift in peak position to longer wavelengths for the phosphor containing 0.30 wt. % carbon suggests that this sample had the fastest Sr1 to Sr2 energy transfer rate. Similarly, the comparison of the time-dependent FWHMs shows that Sr2 emission contributes more to the total emission spectrum for phosphors with the highest carbon content.

11.5. Quantifying Rate Constants for Energy Transfer between Sr1 and Sr2 Sites

A kinetic model (see **Figure 11-1**) was used to quantify the changes in Sr1 to Sr2 energy transfer rate for the series of carbido-nitride phosphors tested. The initial population of excited Eu^{2+} ions at Sr1 sites was taken as $[\text{Sr1}]_{t=0}=n$, while the initial population at Sr2 sites was taken as $[\text{Sr2}]_{t=0}=1-n$, where n is concentration. In other words, n is the fraction of the initial population of Eu^{2+} ions excited at Sr1 versus Sr2 sites. The phosphorescence decay rates for the Sr1 and Sr2 sites are written as k_{Sr1} and k_{Sr2} , respectively. The initial ratio of the excited populations, $[\text{Sr1}]/[\text{Sr2}]$, was determined using the spectral fit to the emission spectrum of each sample at the earliest resolvable time (5 ns). The energy transfer rate (from Sr1 to Sr2) was written as k_{ET} . Since the Sr2 site emission energy is ~ 100 meV lower than that of Sr1 sites,²⁴ it was assumed that the reverse energy transfer rate (Sr2 to Sr1 sites) was negligible at room temperature. In other words, unidirectional energy transfer (from Sr1 to Sr2 sites) was assumed in the model.

From the kinetic model depicted in **Figure 11-1**, the coupled rate expressions could be represented as:

$$\frac{d[\text{Sr1}]}{dt} = -k_{\text{Sr1}}[\text{Sr1}] - k_{\text{ET}}[\text{Sr1}] \quad (\text{eqn. 1})$$

$$\frac{d[\text{Sr2}]}{dt} = -k_{\text{Sr2}}[\text{Sr2}] - k_{\text{ET}}[\text{Sr2}] \quad (\text{eqn. 2})$$

The exact solution of the coupled rate equations is then:

$$[\text{Sr1}] = n * e^{-(k_{\text{Sr1}}+k_{\text{ET}})*t} \quad (\text{eqn. 3})$$

$$[\text{Sr2}] = e^{-(k_{\text{Sr1}}+k_{\text{ET}})*t} * e^{-k_{\text{Sr2}}t} * \left(\frac{e^{(k_{\text{Sr1}}+k_{\text{ET}})*t} (k_{\text{Sr1}}-k_{\text{Sr2}}+k_{\text{ET}}-n(k_{\text{Sr1}}-k_{\text{Sr2}}))}{(k_{\text{Sr1}}-k_{\text{Sr2}}+k_{\text{ET}})} - \frac{nk_{\text{ET}}e^{k_{\text{Sr2}}t}}{(k_{\text{Sr1}}-k_{\text{Sr2}}+k_{\text{ET}})} \right) \quad (\text{eqn. 4})$$

The initial conditions were taken as $[\text{Sr1}]_{t=0}=n$ and $[\text{Sr2}]_{t=0}=(1-n)$. A single exponential decay is obtained using $n=1$ or $n=0$, corresponding to unimolecular decays of Sr1 and Sr2 sites,

respectively. Since it was shown that $k_{Sr1}=k_{Sr2}$, the expression for [Sr2] could be simplified to give:

$$[Sr2] = e^{-(k_{Sr1}+k_{ET}) * t} * e^{-k_{Sr2}t} * (e^{+(k_{Sr1}+k_{ET}) * t} - n * e^{k_{Sr1} * t}) \quad (\text{eqn. 5})$$

To apply the kinetic model to the TRPL spectra, the spectra were first spectrally fit using normalized Gaussian functions, $C_{Sr1}(\lambda, t)$ and $C_{Sr2}(\lambda, t)$. These spectra represented the emission of Eu^{2+} ions at the Sr1 and Sr2 sites, respectively. All fits were performed on an energy axis and the results are displayed on a wavelength axis. At time zero, the emission spectrum is described by:

$$PL(\lambda, t = 0) = n * C_{Sr1}(\lambda, t = 0) + (1 - n) * C_{Sr2}(\lambda, t = 0) \quad (\text{eqn. 6})$$

This two-state spectral model was used to fit the TRPL spectra for each phosphor at each time point. **Figure 11-9** shows a representation of this procedure for the carbidonitride phosphor containing 0.05 wt. % carbon. To account for dispersive energy transport of the excitations, the peak centers and widths were allowed to slightly vary with increasing time.

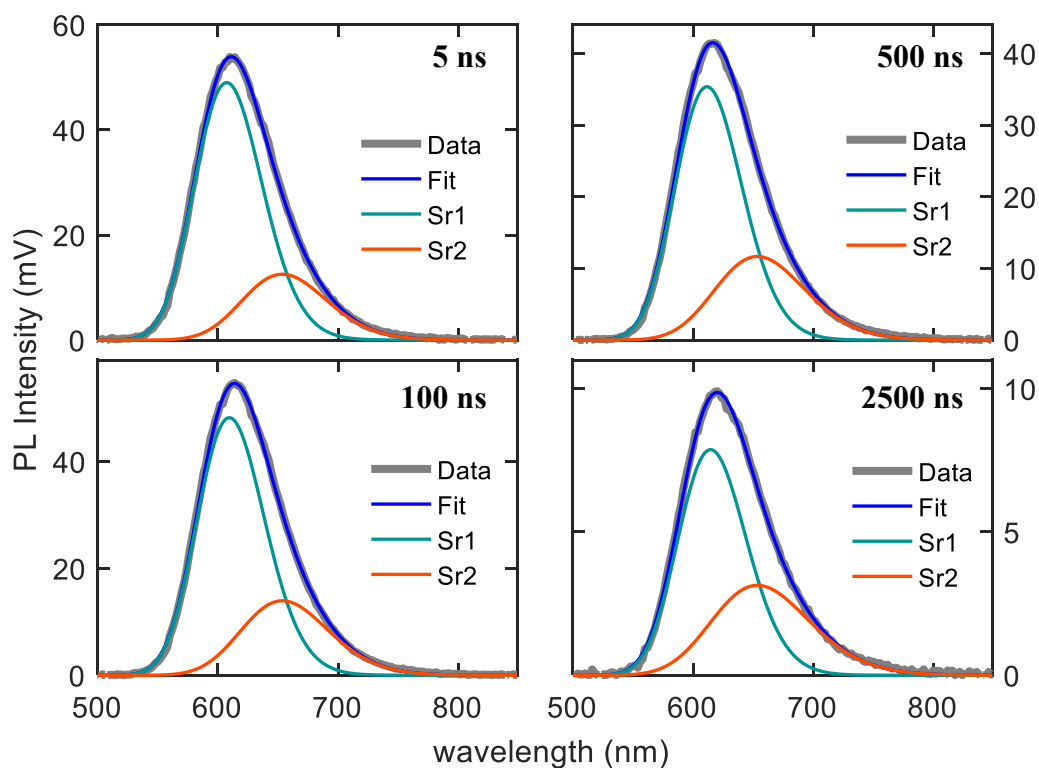


Figure 11-9: Time-resolved photoluminescence (PL) spectra at select time delays for a 0.05 wt. % carbon carbidonitride phosphor after accelerated aging. The excitation wavelength was 450 nm. All of the spectra are decomposed into Sr1 and Sr2 emission bands.

Using the spectral fitting procedure, the emission kinetics for both the Sr1 and Sr2 sites could be determined. The decomposed Sr1 peak was integrated at each time point in order to obtain its decay kinetics. **Figure 11-10** shows the normalized Sr1 emission kinetic decays along with their single exponential decay fits for each of the carbidonitride phosphors tested.

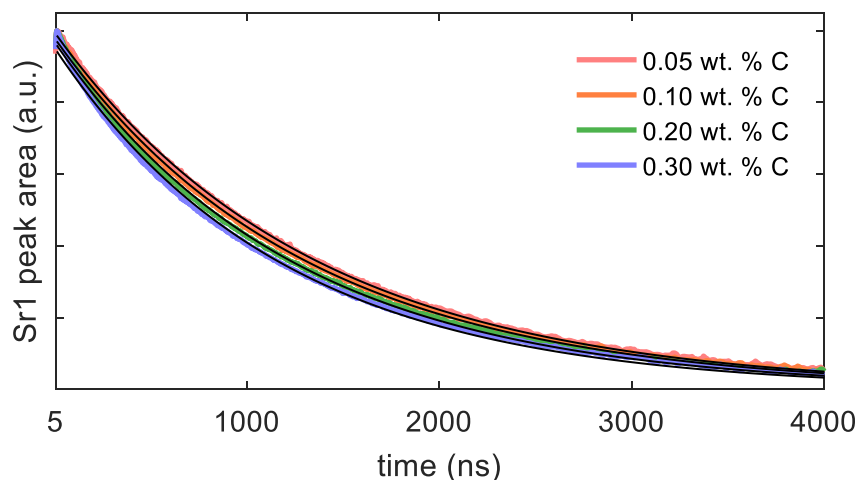


Figure 11-10: Kinetic decays of the Sr1 state, represented by the Sr1 emission peak areas determined from spectral modeling of the photoluminescence data for carbide phosphors containing different amounts of carbon. Data are displayed as thicker colored lines, and the exponential fits are displayed as thinner black lines.

Equation 3 shows that the decay rate constant of Sr1 in the presence of energy transfer depends on both the natural phosphorescence decay rate and the energy transfer rate. The observed rate constant for the Sr1 kinetic decays is therefore:

$$k_{obs} = k_{Sr1} + k_{ET} \quad (\text{eqn. 7})$$

The decomposed Sr1 decays were fit using single exponentials to obtain k_{obs} . These values, combined with the k_{Sr1} values determined from fitting the spectrally-integrated kinetic data, were used to determine the energy transfer rate constants for each sample (**Table 11-1**). The energy transfer rate constants are also plotted against wt. % carbon in **Figure 11-11**.

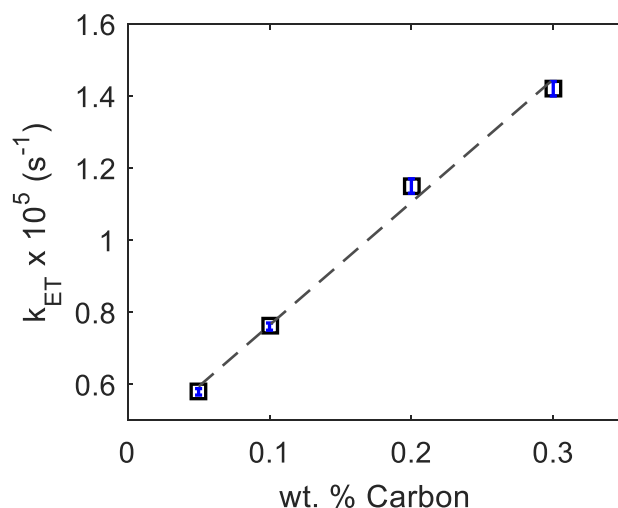


Figure 11-11: Dependence of energy transfer rate constants ($\text{Sr1} \rightarrow \text{Sr2}$) on wt. % carbon content in carbidonitride phosphors. The dashed gray line is an empirical linear fit to the data.

The error bars reflect the uncertainty limits obtained from nonlinear least-squares fits of the kinetic data. The uncertainty values for k_{ET} were obtained via error propagation using equation 7. Uncertainty values for k_{Sr1} and k_{Obs} were determined from nonlinear least squares fits to the appropriate set of kinetic data. **Figure 11-11** shows that incorporating 0.30 wt. % carbon into the phosphor results in a nearly 3-times increase of the energy transfer rate constant compared to 0.05 wt. % carbon.

11.6. Changes in the $\text{Sr}_2\text{Si}_5\text{N}_8$ Crystal Lattice and Energy Transfer Mechanism

11.6.1. Crystal lattice structure and dependence on carbon substitution

The rate of energy transfer from Sr1 to Sr2 sites in the carbidonitride lattice should depend on their distance, regardless of the specific mechanism. Structure models of the lattice of $\text{Sr}_2\text{Si}_5\text{N}_8$ and carbidonitride were optimized using Density Function Theory (DFT) by the Dow Chemical Company. Specifically, the PW91 DFT method and the DNP double numerical basis set were implemented using the Materials Studio DMol³ (version 8.0) software package.^{27,28}

The results are shown in **Figure 11-12**, which shows the unit cell of the phosphor with no carbon substitution, and the supercell of the carbidonitride having 0.47 wt. % carbon and oxygen. The lattice constants calculated for $\text{Sr}_2\text{Si}_5\text{N}_8$ agreed with the experimentally determined values ($a = 5.76 \text{ \AA}$, $b = 6.86 \text{ \AA}$, and $c = 9.43 \text{ \AA}$).^{24,25} Furthermore, the average Sr-N distances for the Sr1 and Sr2 sites were 2.9931 and 2.9537 $\text{\AA}$, respectively. These were close to the experimental values of 2.969 and 2.928 $\text{\AA}$, respectively, and reproduced the difference in average of 0.04 $\text{\AA}$.^{24,25} The results for the carbidonitride supercell ($\text{Sr}_2\text{Si}_5\text{O}_{0.17}\text{N}_{7.66}\text{C}_{0.17}$) with 0.47 wt. % carbon resulted in a 0.023 $\text{\AA}$ (0.34%) contraction along the (010) direction, which agreed closely with the experimental value.²⁰

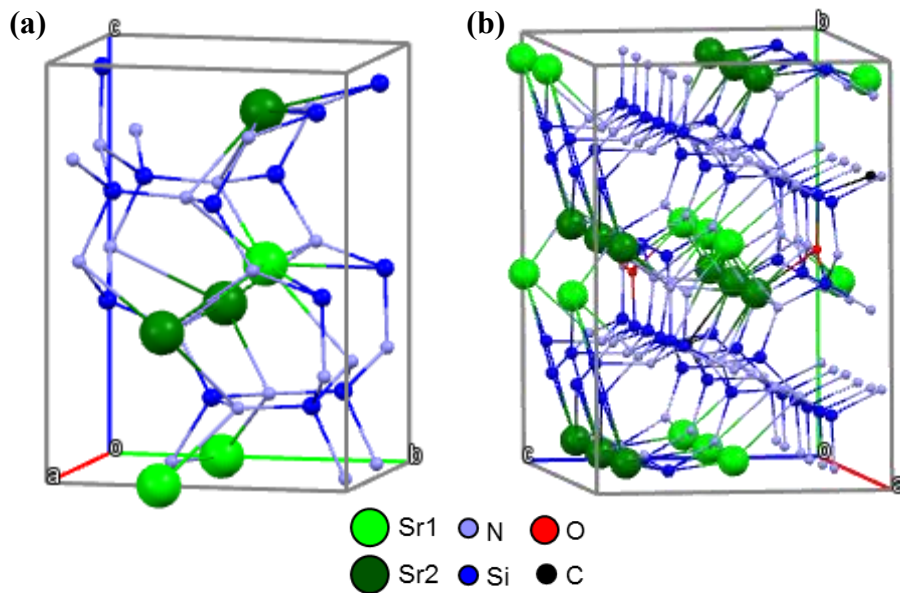


Figure 11-12: (a) DFT-optimized unit cell structure of $\text{Sr}_2\text{Si}_5\text{N}_8$. (b) DFT-optimized supercell of the carbidonitride containing 0.47 wt. % carbon ($\text{Sr}_2\text{Si}_5\text{O}_{0.17}\text{N}_{7.66}\text{C}_{0.17}$).

The Sr-N clusters for the optimized $\text{Sr}_2\text{Si}_5\text{O}_{0.17}\text{N}_{7.66}\text{C}_{0.17}$ supercell are shown in **Figure 11-**

13.

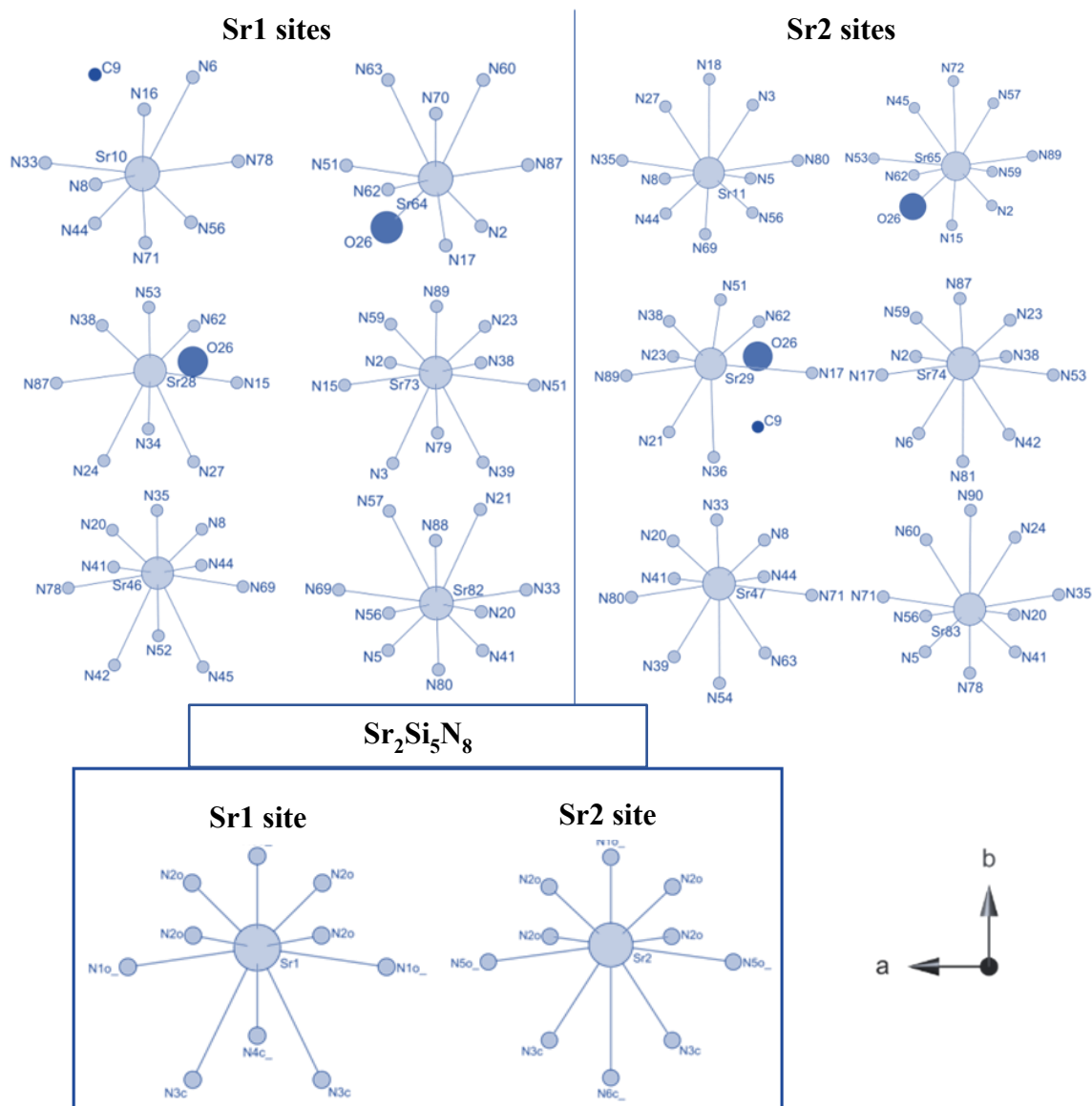


Figure 11-13: Sr-N clusters in the supercell of the 0.47 wt. % carbon carbidonitride ($\text{Sr}_2\text{Si}_5\text{O}_{0.17}\text{N}_{7.66}\text{C}_{0.17}$). Both Sr1 and Sr2 sites are identified. The clusters are also shown for the carbidonitride containing no carbon ($\text{Sr}_2\text{Si}_5\text{N}_8$) for reference.

Based on the coordination, each cluster was identified as either a Sr1 or Sr2 site. The distributions of Sr-N distances (nearest 10 nitrogen ions) are shown in **Figure 11-14** as box-and-whisker plots.

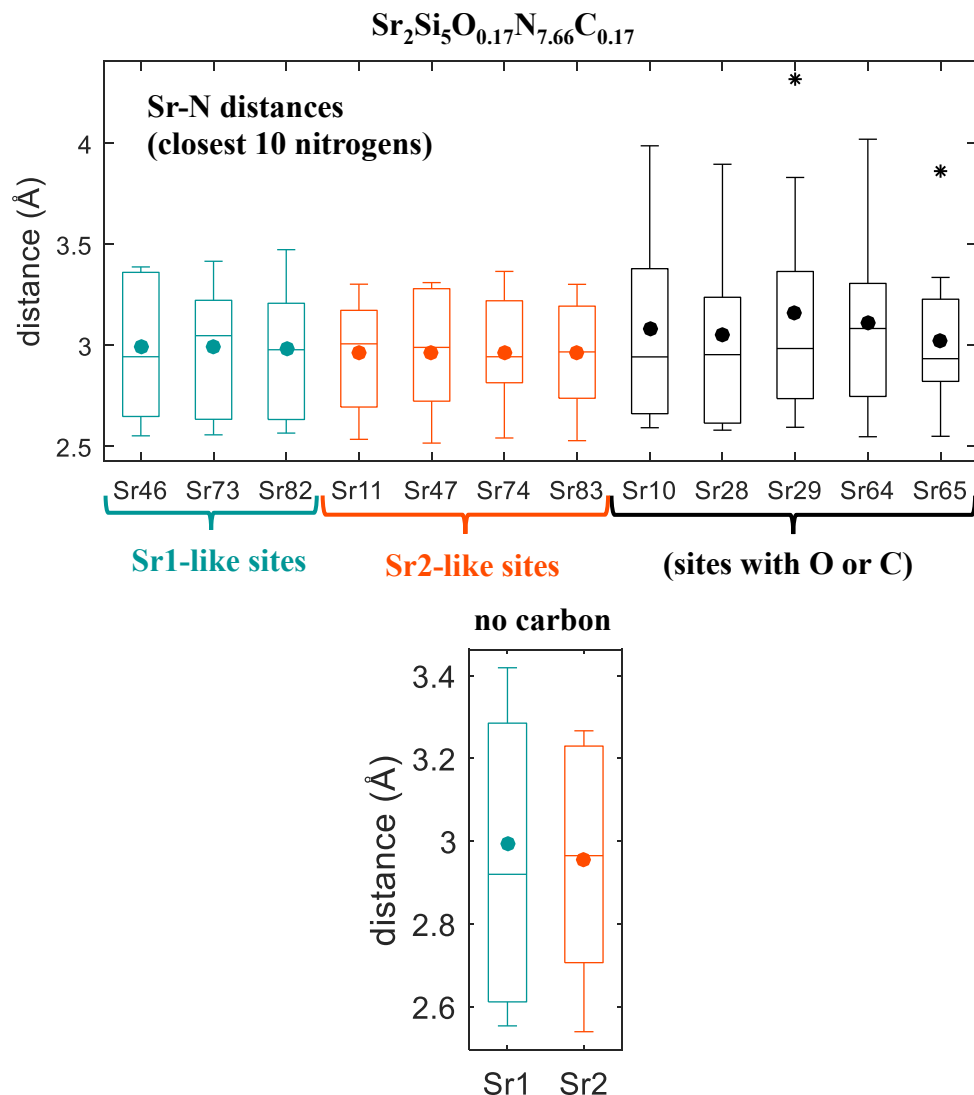


Figure 11-14: Distributions of Sr-N distances for the Sr-N clusters resulting from the optimized supercell for the 0.47 wt. % carbon carbidonitride ($\text{Sr}_2\text{Si}_5\text{O}_{0.17}\text{N}_{7.66}\text{C}_{0.17}$). For reference, the distance distributions for the $\text{Sr}_2\text{Si}_5\text{N}_8$ structure are also provided.

Sites with very large distance distributions contained Oxygen and/or Carbon in their coordination shells. The clusters were separated into three Sr sites: “Sr1-like” sites, “Sr2-like” sites, and Sr sites containing coordinated oxygen or carbon. The latter clusters were excluded from the analysis of Sr1-Sr2 site distances.

The average Sr1-Sr2 site distances were determined for both the $\text{Sr}_2\text{Si}_5\text{N}_8$ and the $\text{Sr}_2\text{Si}_5\text{O}_{0.17}\text{N}_{7.66}\text{C}_{0.17}$ lattice. The distribution of these distances were determined for the

$\text{Sr}_2\text{Si}_5\text{N}_8$ unit cell (“no Carbon”) and the $\text{Sr}_2\text{Si}_5\text{O}_{0.17}\text{N}_{7.66}\text{C}_{0.17}$ supercell (“0.47 wt. % Carbon”). They were then scaled to determine the number density of Sr1(2) sites at each radius, r , from Sr2(1) sites by the volume of spheres of radius, r . The distance distribution of Sr1-Sr2 pairs over a 50 Å range is shown in **Figure 11-15**. The weighted average distance between Sr1 and Sr2 sites was then calculated for the two structure models. From this analysis, incorporation of 0.47 wt. % carbon led to a decrease of the average Sr1-Sr2 distance of 3.9%. Next, this analysis was extended to the experimentally measured phosphors. Because the lattice constants of the carbidonitride phosphors was previously shown to vary linearly with wt. % carbon content,²⁰ the average Sr1-Sr2 distances are expected to change with linear proportionality. As such, the average Sr1-Sr2 site distance is expected to decrease by ~2.5% in the carbidonitride phosphors containing 0.30 wt. % carbon.

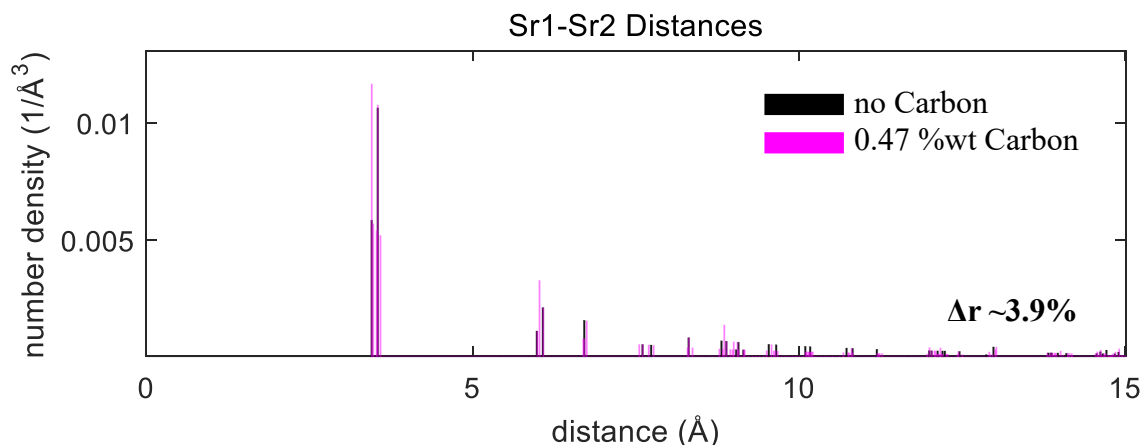


Figure 11-15: Distribution of Sr1-Sr2 distances weighted by number density for the optimized carbidonitride structures containing no carbon or 0.47 wt. % carbon. The carbidonitride containing 0.47 wt. % carbon was calculated to have a 3.9% shorter weighted average Sr1-Sr2 distance.

11.6.2. Energy transfer mechanism

A variety of different energy transfer mechanisms was considered for explaining how changes in carbidonitride structure affect the variation of Sr1 to Sr2 energy transfer rates. It was revealed that an expected 2.5% decrease in the average Sr1-Sr2 distance results in a three-

fold increase in energy transfer rate from Sr1 to Sr2. Using Eu^{2+} concentration dependent measurements, previous work identified dipole-dipole or higher-order multi-polar energy transfer as the specific mechanism in activated phosphors.²⁹⁻³³ The dipole-dipole energy transfer mechanism³⁴ predicts a $1/r^6$ distance dependence on rate of transfer. In this case, a ~15% decrease in average Sr1-Sr2 energy transfer distance must occur in order to explain the three-fold change in energy transfer rate observed in the carbidonitride phosphors. Multi-polar energy transfer has higher-order distance dependence, such as $1/r^8$ and $1/r^{10}$, which would predict distortions of 11% and 9% for the 0.05 wt. % and 0.30 wt. % samples, respectively. Consequently, an energy transfer mechanism that has a more sensitive distance dependence is required to in order to explain the change in the measured energy transfer rates.

In other cases, energy transfer via tunneling is known to occur,³⁵ which predicts a steep, exponential dependence of energy transfer rate upon distance. For the tunneling mechanism, the energy transfer rate, k , is expressed as:

$$k = \frac{2\pi}{\hbar} H_{\text{DA}}^2 \sqrt{\frac{1}{4\pi\lambda k_B T}} \exp\left(\frac{(\Delta G + \lambda)^2}{4\lambda k_B T}\right) \exp(-\beta r) \quad (\text{eqn. 8})$$

Where $\hbar$ is Planck's constant, H_{DA} is the electronic coupling between Eu^{2+} ions in nearest neighboring Sr1 and Sr2 sites, λ is the reorganization energy associated with energy transfer from Sr1 to Sr2 sites, k_B is Boltzmann's constant, T is temperature, ΔG is the change in free energy associated with the energy transfer event, β an exponential factor, and r is distance between the Eu^{2+} -occupied Sr1 and Sr2 sites. The exponential distance dependence is produced by the last term in equation 8.

Using the tunneling model in equation 8, the ratio of energy transfer rates for the carbidonitride phosphors containing 0.05 wt. % and 0.3 wt. % leads to the following expression for the reduction in transfer distance, Δr :

$$\Delta r = 1 - \frac{r_{0.3}}{r_{0.05}} = \ln \left(\frac{(k_{0.3} - k_{0.05}) \hbar \sqrt{4\pi\lambda k_B T}}{2\pi H^2 FCWD} \right) \quad (\text{eqn. 9})$$

where $r_{0.30}$ and $r_{0.05}$ are the energy transfer distances for the 0.30 wt. % and 0.05 wt. % phosphors, respectively, $k_{0.30}$ and $k_{0.05}$ are the energy transfer rates for the 0.30 wt. % and 0.05 wt. % phosphors, respectively, and the FCWD term is the Franck-Condon weighted density of states, corresponding to the Gaussian term in equation 8. Using the values for energy transfer rate determined experimentally using TRPL, the decrease in Δr was determined for a variety of possible coupling values and reorganization energies (see **Table 11-2**).

Table 11-2: Reduction of the predicted energy transfer distances (Δr) upon carbon substitution into the $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ crystal lattice

λ H_{DA}	0.025 eV	0.05 eV	0.075 eV	0.10 eV
0.02 eV	5.0%	4.6%	4.6%	4.6%
0.05 eV	4.7%	4.3%	4.3%	4.3%
0.10 eV	4.4%	4.1%	4.0%	4.0%
0.20 eV	4.1%	3.8%	3.8%	3.8%
0.50 eV	3.8%	3.6%	3.5%	3.5%
1.00 eV	3.6%	3.4%	3.3%	3.3%

A variety of parameters were considered because their values have not been previously determined for carbidonitride phosphors. From this, it is shown that the tunneling mechanism predicts a reduction of Sr1-Sr2 distance of only 3-5% to explain the three-fold change in measured energy transfer rate between the 0.30 wt. % and 0.05 wt. % samples. This change in distance is close to the ~2.5% change predicted from the analysis of the optimized

carbide nitride supercell. This suggests (albeit does not prove) that the tunneling mechanism explains the observed changes in energy transfer rate in carbide nitride phosphors.

11.6.3. Carbon substitution effects on energy transfer and aging

Next, the origin of the enhanced color stability of the carbide nitride phosphors was investigated. **Figure 11-16** compares the normalized (time-integrated) emission spectrum of a carbide nitride phosphor containing 0.05 wt. % carbon before and after accelerated aging. The emission intensity on the longer-wavelength side of the band had a higher relative intensity. On the other hand, the emission spectrum of the carbide nitride phosphor containing 0.3 wt. % did not change upon aging. Comparing the emission spectrum of the aged 0.05 wt. % sample to the 0.3 wt. % sample shows that incorporating carbon into the carbide nitride lattice has the same effect as aging on the emission spectrum. As a result, it is hypothesized that aging caused some change in the lattice leading to the reduction of the average Sr1-Sr2 site distances in the phosphor containing 0.05 wt. % carbon.

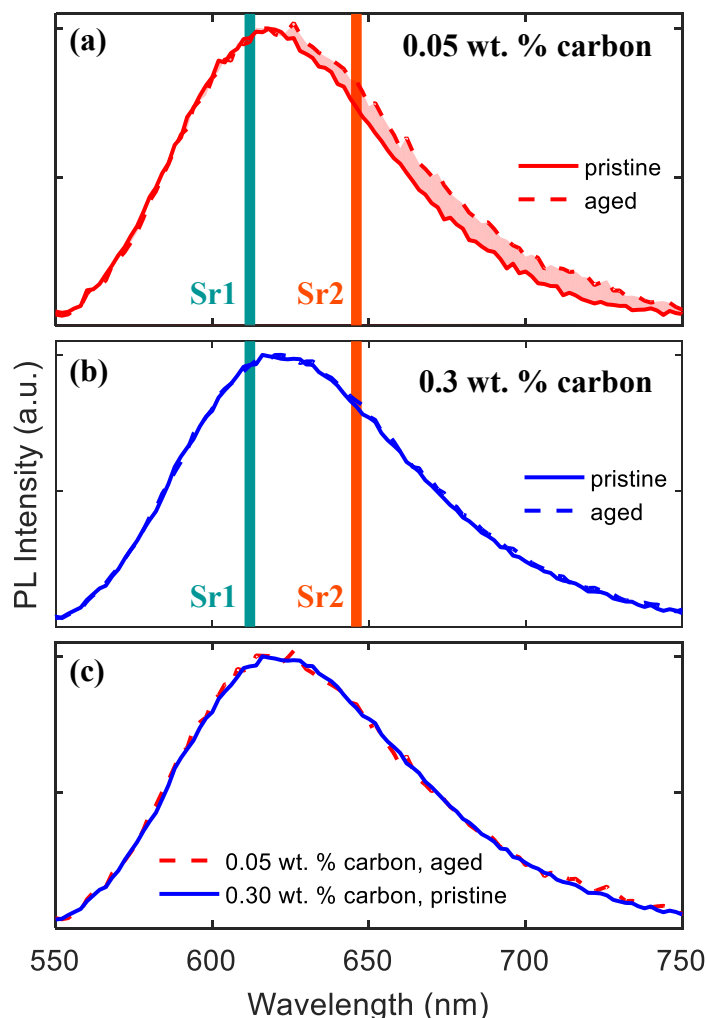


Figure 11-16: (a) Photoluminescence (PL) spectra for a carbide phosphor containing 0.05 wt. % carbon before and after accelerated aging. (b) Photoluminescence spectra for a carbide phosphor containing 0.3 wt. % carbon before and after accelerated aging. (c) Comparison of the spectrum for the 0.05 wt. % sample (aged) and the 0.3 wt. % sample (pristine), showing invariance in the emission profile.

TRPL spectroscopy was also used to measure the carbide phosphors after accelerated aging. The time dependence of the emission peak position and FWHM are shown in **Figure 11-17**. The observed red-shifts and FWHM broadening were indicative of faster energy transfer from Sr1 to Sr2 sites upon aging. These results suggest that the sample containing 0.05 wt. % carbon exhibited the largest change in energy transfer, while the sample containing 0.30 wt. % carbon underwent a negligible change in energy transfer rate upon aging.

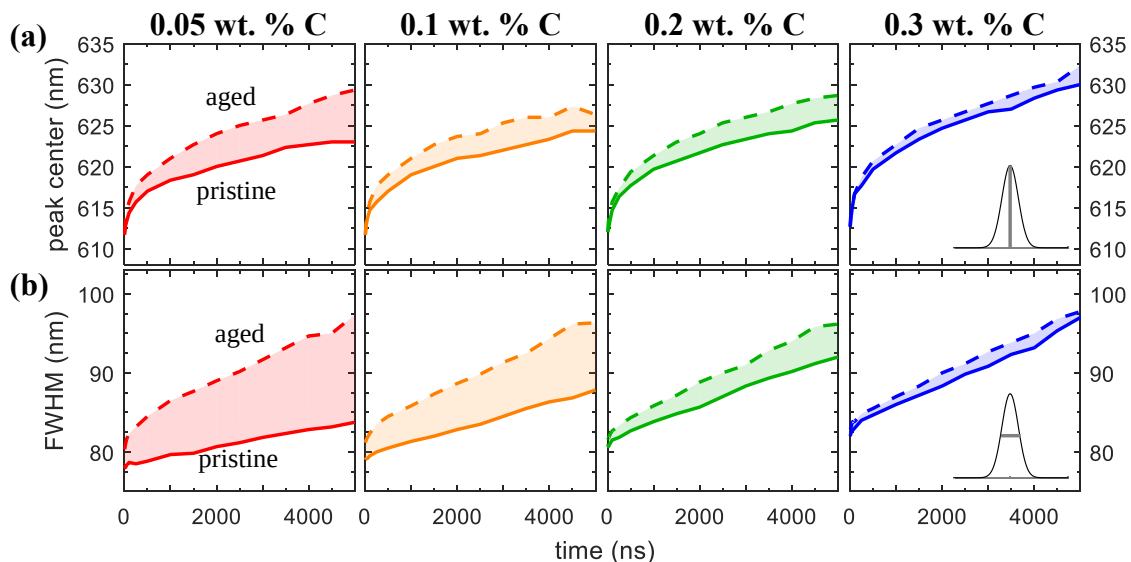


Figure 11-17: (a) Time-dependence of the (a) peak centers and (b) full-width at half-maxima (FWHM) of the emission spectra for carbide phosphors containing different amounts of carbon. The pristine phosphor data are shown as solid lines, while the data of the aged phosphors are shown as dashed lines. The shading in-between the data highlights the changes associated with accelerated aging.

Next, the energy transfer rates from Sr1 to Sr2 sites were quantified. **Figure 11-18** shows the Sr1 emission decay determined from the spectral modeling for all the carbide phosphors investigated before and after accelerated aging.

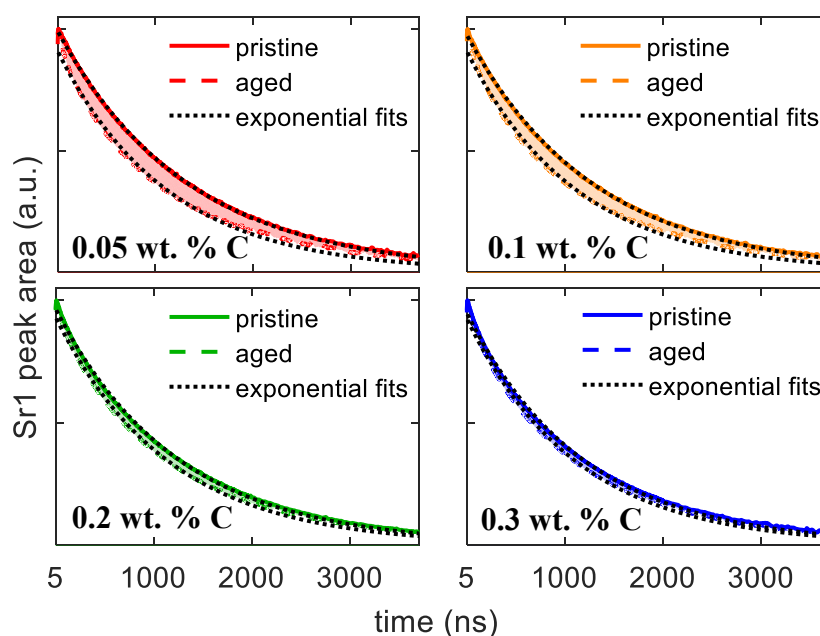


Figure 11-18: Kinetic decays of the Sr1 state, represented by the peak area obtained from spectral modeling of the photoluminescence spectra of the carbide phosphors containing varying amounts of carbon. The results for the pristine samples are provided as solid colored lines, while the results for the aged samples are provided as dashed colored lines. The exponential fit curves are provided as dotted black lines.

The exponential decay fits, which were used to determine k_{obs} for each trace, are included. Identical to the previous analysis for the phosphors before aging, the rate of energy transfer k_{ET} was determined for the aged phosphors and the values are tabulated in **Table 11-1**. These rate constants are also plotted against wt. % carbon in **Figure 11-19** for phosphors before and after aging.

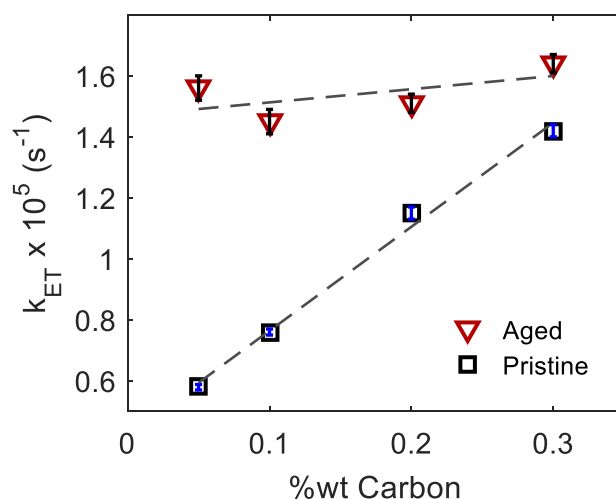


Figure 11-19: Rate constants for energy transfer from Sr1 → Sr2 sites in pristine or aged carbide phosphors containing different amounts of carbon. The dashed gray lines are empirical linear fits to the data.

The data suggest that the energy transfer rates were related to structural changes of the carbide lattice. Furthermore, the data suggest that the carbide phosphor containing 0.30 wt. % carbon possesses average Sr1-Sr2 site distances that are achieved in all other samples upon accelerated aging. It is hypothesized that the structure attained by the 0.30 wt. % sample upon its initial synthesis does not change upon aging, and it is similar to the aged structure of all other phosphors tested with lower carbon content.

Substitution of carbon into the carbide lattice required high temperature synthesis, during which the lattice may accommodate the strain associated with compression of the (010) axis. In samples with lower carbon content, the accelerated aging resulted in similar compression in the (010) axis, but such structural changes occurred at much lower temperatures (only ~170 °C). In this case, the crystal lattice may not be able to reorganize in response to the contraction along the (010) direction and concurrent expansion along the other directions. On the other hand, the lattice structure of the phosphor containing 0.30 wt. %

carbon was already changed upon its synthesis, and so aging caused minimal further distortions, improving its color stability.

11.7. Conclusions and Significance

In this work, the impact of carbon substitution and accelerated aging on carbide nitride phosphor emission was investigated using TRPL spectroscopy. Previous measurements demonstrated that incorporating carbon into the $\text{Sr}_2\text{Si}_5\text{N}_8\text{:Eu}^{2+}$ crystal lattice exhibited significantly improved luminescent maintenance at 150 °C.²⁰ This was attributed to the contraction of the (010) direction, which decreased the coupling of phonon modes to the radiative transition. These structural changes also modulated the average distances between the Sr1 and Sr2 sites by about 2.5% for a carbon content of 0.3 wt. %. Long-range tunneling was found to be the mechanism of energy transfer from Sr1 to Sr2 sites in the carbide nitride phosphors. The increase in energy transfer rate leads to higher emission at longer-wavelengths of the band. The aging of phosphors with the lowest carbon content was found to induce structural changes in the crystal lattice that increased the rate of energy transfer between Sr1 and Sr2 sites, causing its emission color to change. Furthermore, the energy transfer rates of all the phosphors after aging approached that of the sample containing 0.30 wt. % carbon. From this observation, it was concluded that aging resulted in similar structural changes that resulted from substitution of carbon and oxygen into the crystal lattice.

The observation that lattice strain can be controlled during synthesis to mimic the aging process reveals new opportunities for stabilizing the color of other red-emitting phosphors. These findings, including the mechanism of aging, inform ongoing work for improving the color stability of phosphors in pc-LEDs for solid state lighting applications.

11.8. References

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CHAPTER 12

Future Directions

This chapter serves to present future research directions that stem from the work discussed in this dissertation, or present incomplete work that warrants further attention. Several studies relating to major topics of this dissertation will be outlined, including singlet fission, and organic solar cells. It is the hope that these studies will provide the scientific communities better understandings about how nanoscale packing arrangements affect function in solar cell materials.

12.1. Vibrational Thermometer of Singlet Fission: Monitoring Internal Conversion of Reaction Intermediates

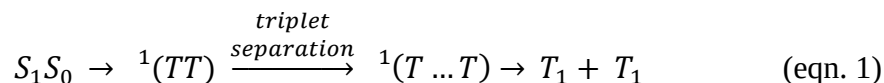
In this section, a new research direction is proposed for studying singlet fission materials. In particular, new photophysical insights into overcoming obstacles to quantitative multiplication of triplet excitons during singlet fission will be revealed. Additionally, crystal packing structure design principles for efficient singlet fission sensitizers will be established as a result of this proposed work.

12.1.1. Problem, background, and hypothesis

Solar cells employing singlet fission sensitizers thus far have been very inefficient, although proof-of-principle studies have demonstrated internal quantum efficiencies (IQEs) exceeding 100%.^{1,2} It is likely that a lack of control over the thin film structure of the sensitizer challenges device efficiency. For example, the IQE spectrum of a device studied using TIPS-Pn as the sensitizer showed evidence of amorphous film structure; the authors either had not noticed, or chose to not discuss this.² In fact, this even led to the potentially incorrect use of a crystalline

film absorption spectrum for calculating the IQE spectrum. The presence of an amorphous sensitizer layer (among other types of potential morphologies) may be detrimental to the overall device performance, especially since triplet transport has been shown to be very slow in amorphous films of TIPS-Pn (see Chapter 4).³ Additionally, it has been previously implied that amorphous materials lead to lower singlet fission efficiencies.³

Recently, the singlet fission mechanism has become better understood, providing further insights into how solid-state structure affects the ultimate yield of multiplied triplet excitons. In particular, it was found that triplet pair separation of the correlated triplet pair intermediates is a critical step of the singlet fission reaction to control. This was also shown in Chapters 5, 6, and 7. The singlet fission reaction may be described using:^{4,5}



where S_1S_0 is a singlet exciton, ${}^1(TT)$ is a proximal correlated triplet pair, ${}^1(T \dots T)$ is a separated correlated triplet pair, and T_1 is an independent triplet exciton.

Most transient absorption spectroscopists monitor the “triplet” photoinduced absorption (PIA) appearing in the visible or near-infrared (near-IR) spectral regions to calculate the rate of formation of triplets and their quantum yields during singlet fission. However, it has been shown that the PIA spectrum of the independent triplets (T_1) can be nearly indistinguishable from that of correlated triplet pairs,⁴ and so the calculated triplet yields may in fact be grossly overestimated. For example, it was recently found that amorphous films of TIPS-Pn may actually produce a 140% yield of independent triplet excitons, despite the observation of rapid growth in its PIA signal on an early picosecond timescale.^{3,6} It was shown in that work⁶ that the reason the triplet yield does not approach 200% is because a significant fraction of the

triplet pair intermediates are unable to separate, allowing alternate relaxation processes like internal conversion to kinetically compete with singlet fission.

Recent published and unpublished work on the new idea that triplet pair separation plays a significant role in singlet fission offers a possible explanation of why devices thus far have produced low power conversion efficiencies (PCEs). For example, weak and short range intermolecular coupling is thought to inhibit the separation of triplets in amorphous films, since triplet separation is mediated by triplet transfer (see Chapters 6 and 7). A branching ratio of the excited state pathways can be deduced, which is shown in **Figure 12-1** for pentacene derivatives. First, the proximal correlated triplet pairs are formed very rapidly from singlet excitons. Next, these triplet pairs may either separate into independent triplet excitons, or may not be able to separate, nonradiatively relaxing back to the ground state via internal conversion. Because the correlated triplet pairs possess overall singlet spin multiplicity, internal conversion may be an efficient relaxation process, especially if its electronic nature favors strong coupling to the ground state. This was shown in (currently) unpublished collaborative work with Ryan D. Pensack at Princeton University.

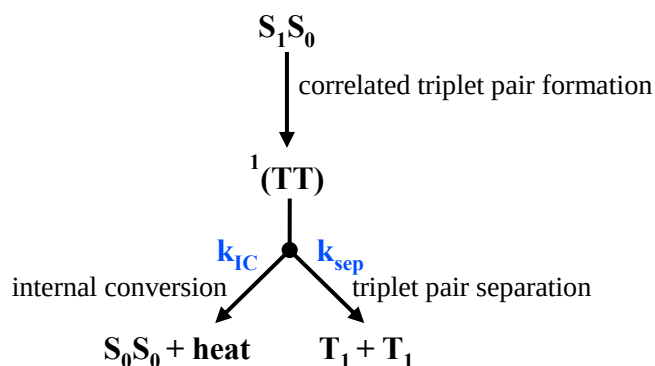


Figure 12-1: Proposed kinetic model for excited state pathways in a singlet fission material, highlighting a bifurcation in relaxation pathway of the correlated triplet pair, the branching between internal conversion and triplet pair separation.

A seemingly obvious solution to the triplet pair separation problem is to avoid the use of amorphous materials. However, not only weak intermolecular coupling in amorphous films prevent triplet pair separation, but also certain molecular packing arrangements in crystalline films result in strongly bound triplet pairs that efficiently internally convert to the ground state (from currently unpublished collaborative work with R.D. Pensack). Specific molecular packing arrangements, such as the cofacial/sandwich geometry, may favor the formation of strongly bound correlated triplet pairs with “excimer-like” character that cannot separate. This was shown in recent collaborative work with R.D. Pensack for a series of pentacene derivatives (manuscript in review).

Ultimately, the electronic nature of the correlated triplet pair states, and their relation to specific molecular packing arrangements, requires further investigation. In particular, these new findings motivate the development of a spectroscopic method for directly measuring internal conversion during singlet fission for a variety of molecular packing arrangements in order to target structures that lead to efficient triplet pair separation. Using this method, systematic investigations can be made to identify solid state morphologies and crystal packing structures that are ideal for efficient triplet pair separation during singlet fission. In the following proposal, the development of a new spectroscopic thermometer will be discussed. Heat dumped due to internal conversion of correlated triplet pair intermediates that cannot separate into independent triplet excitons will be measured and related to molecular packing structure (see concept illustration shown in **Figure 12-2**).

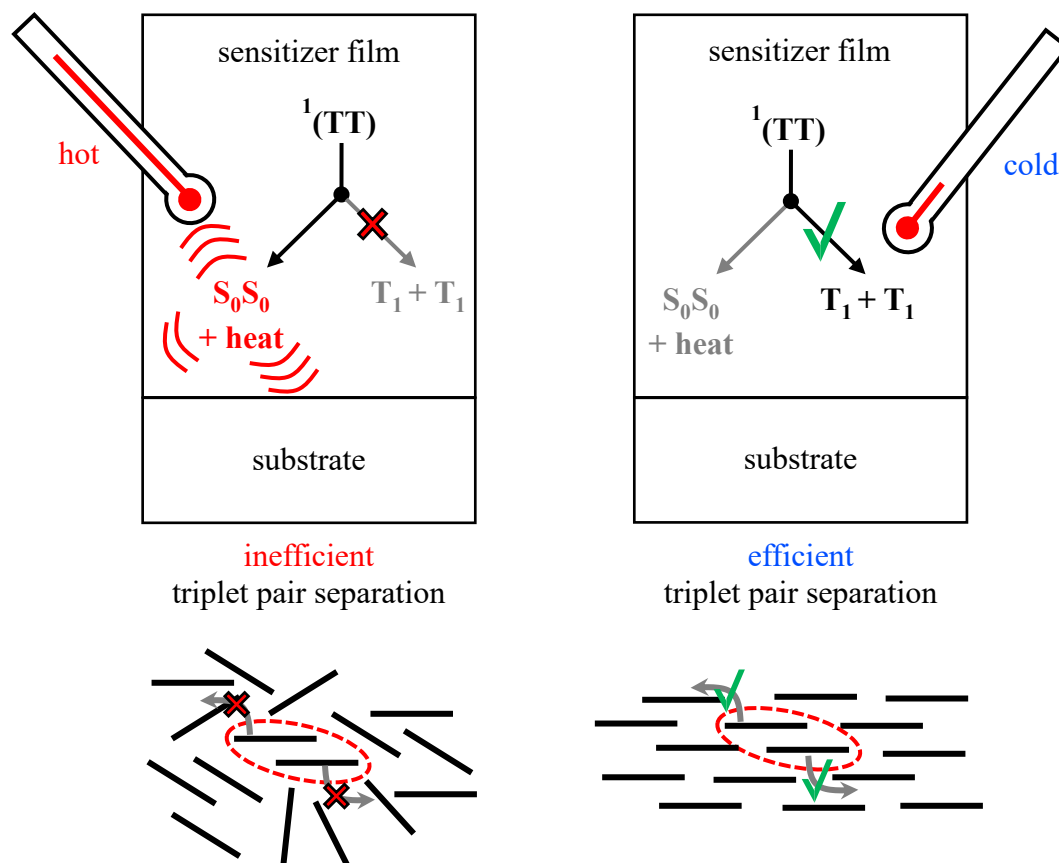


Figure 12-2: Illustration of the concept of a spectroscopic thermometer for measuring heat dumping in a film of a singlet fission sensitizer. Samples for which internal conversion is the dominant relaxation pathway will result in heating of the sample.

12.1.2. Primary goals

The primary goals of the following proposed work are to: (1) Develop a method (“ultrafast thermometer”) for tracking energetic losses (in form of heat) occurring during singlet fission that arise from rapid, efficient internal conversion of triplet pair intermediates; (2) relate the efficiency of internal conversion to a variety of specific crystal packing structures and film morphologies in order to identify molecular packing structures that should be avoided when designing new singlet fission sensitizers; (3) in the process, develop new design rules for types of molecular packing structures that enable efficient singlet fission. The latter goal would, in turn, expand the current set of design rules that relate packing structure to efficient formation

of correlated triplet pairs. In this way, the results of this proposal would form a complete set of design rules that encompasses the entire singlet fission reaction, necessary for pushing singlet fission sensitization toward real application

12.1.3. Proposed research strategy

(1) *Development of “vibrational thermometer”*: Vibrational motion in organic molecules is known to be very sensitive to changes in temperature (thermochromism). This has been previously demonstrated in crystalline TIPS-Pn films (Chapter 6), for which the alkyne stretching frequency was used to monitor heat dumping from annihilation of triplet excitons following singlet fission. In transient absorption spectroscopy, heat may be detected using the thermal effect for vibrational spectra (**Figure 12-3**).

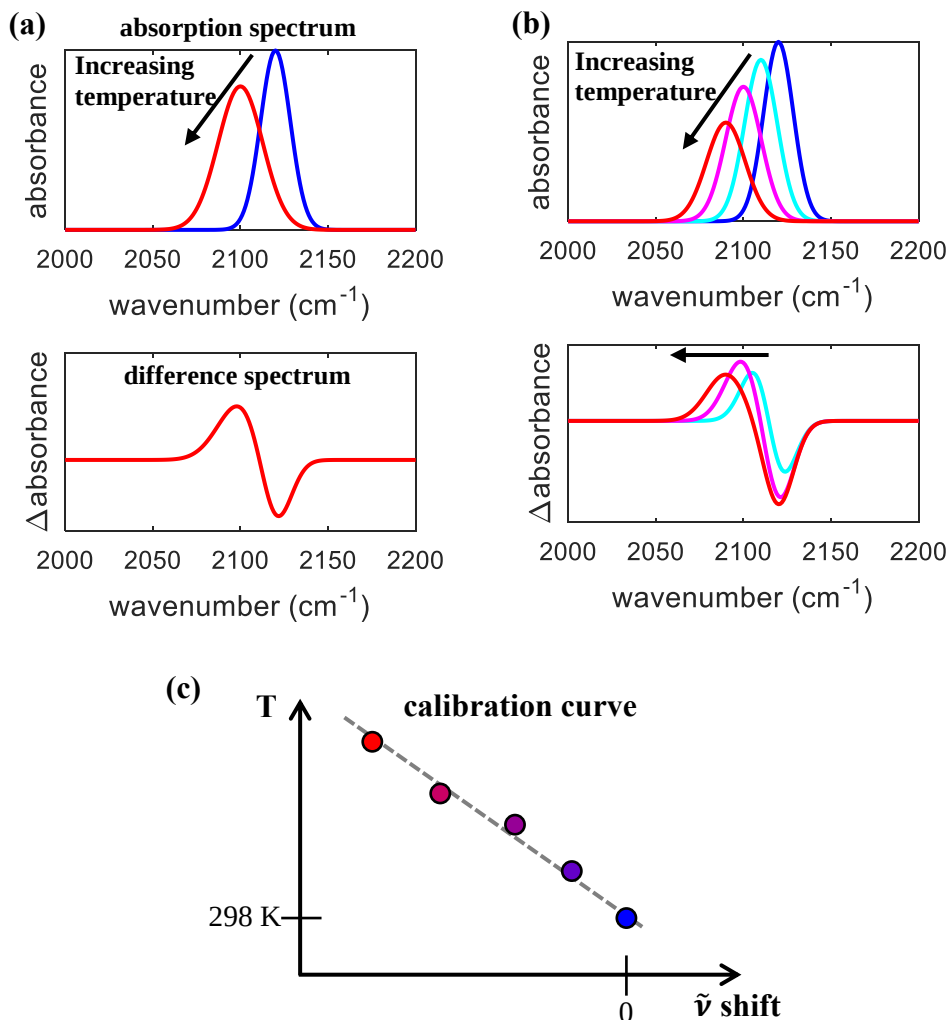


Figure 12-3: (a) Illustration of the temperature dependence of a vibrational absorption spectrum (top) and its difference spectrum (bottom). (b) Illustration of the changes in absorption spectrum and difference spectrum of a vibrational mode for a range of temperatures. (c) Illustration of a temperature-frequency shift calibration curve for a vibrational mode (“calibrating the thermometer”).

The shift of the absorption peak (arising from a change in bond vibration frequency) accompanying an increase in temperature results in a difference spectrum possessing a derivative-like shape. This difference spectrum is often manifested in transient absorption experiments, which is described as having a “thermal effect” on the measured spectrum that originates from a change in sample temperature. The change in vibrational frequency may be related to the change in temperature of the sample by generating a temperature-frequency shift

calibration curve (see **Figure 12-3**). This will be referred to as “calibrating the vibrational thermometer”. The amount of energy, E , deposited into the spot of the film being sampled in the transient absorption measurement can be approximated using:⁷

$$E = nC_p\Delta T \quad (\text{eqn. 2})$$

where n is the number of moles of molecules in the probed volume, C_p is the specific heat of the sample, and ΔT is the change in temperature in the probed volume. If the energy gap involved in internal conversion is known, then the concentration of molecules undergoing internal conversion may be determined. In addition, evolution of the dynamic shift in the vibrational peak can also be tracked in time to determine information about when the heat was deposited.

(2) Development of a set of singlet fission molecules with vibrational probes that assume several different types of molecular packing arrangements and crystal packing structures: In a collaborative effort with John E. Anthony at the University of Kentucky, several new pentacene derivatives containing vibrational probes could be developed for the transient absorption measurements. Requirements for the vibrational probe are: (1) The probe should be electronically isolated from the conjugated organic framework to avoid changes in frequency associated with the formation of excited electronic states, such as singlet and triplet excitons; (2) The probe should possess high oscillator strength and narrow peak linewidth, such as high frequency vibrations of $\text{C}\equiv\text{N}$ and $\text{C}=\text{O}$ bonds, in order to ensure maximal signal strength and temperature resolution, respectively. Other bonds prone to hydrogen-bonding interactions, such as $\text{O}-\text{H}$, should be avoided since hydrogen-bonding would broaden the vibrational linewidth and subsequently decrease temperature resolution. Several proposed

chemical structures and possible crystal packing arrangements of pentacene derivatives are illustrated in **Figure 12-4**.

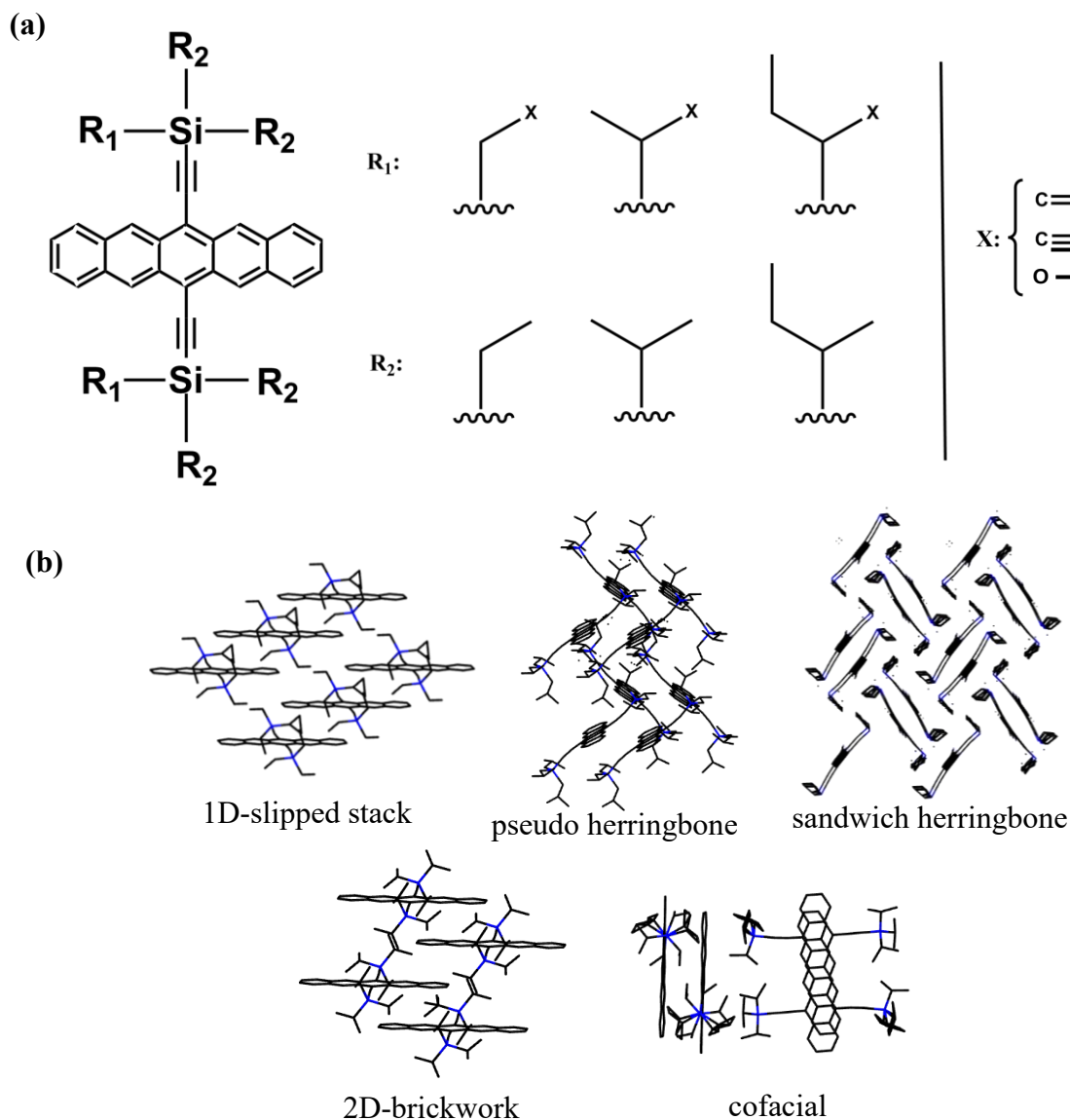


Figure 12-4: (a) Proposed chemical structures of pentacene derivatives with vibrational probes for use in vibrational thermometer measurements of singlet fission. (b) Possible crystal packing structures attainable by pentacene derivatives.

(3) *Determine molecular packing arrangements that favor efficient triplet pair separation:*

The first step is to verify that the vibrational thermometer technique for measuring internal conversion works. For proof-of-principle demonstration, the technique will be applied to

crystalline and amorphous films, in which low and high yields of internal conversion are expected as previously discussed. After establishing the technique, it will be used to determine which molecular packing structures favor efficient triplet pair separation and minimize internal conversion of the correlated triplet pair. This can be approached in two overall ways: (1) Perform a wide survey of crystal structures to generate general design rules for singlet fission sensitizers; (2) perform a close analysis of how specific changes in intermolecular slippage and rotation, including the degree of sandwiching, affect triplet pair separation (prevent internal conversion). A particularly useful comparison is TIPS-Pn versus offset-TIPS-Pn, which contain the same chemical formula, but form either the slipped-stack or cofacial crystal packing geometries, respectively.

12.2. Exploring Structural Origins of Thermal Effects in Organic Polycrystalline Films

Thermal artifacts frequently plague transient absorption spectroscopy measurements of thin film materials since energy dissipated from excited electronic states via nonradiative decay channels can cause heating of the sample. Poor thermal conductivities of the film and and/or substrate can cause heat to build up in the sample, causing its temperature to increase.⁷ Because the ground state absorption of films is typically particularly sensitive to temperature (thermochromism), heating of the sample during time-resolved spectroscopic experiments leads to artificial signals that resemble transient absorption features occurring at the ground state bleach (GSB) location. The transient signals associated with sample heating have growth and decay times that are often confused with the signal arising from the excited states of interest.⁷ This often leads to misinterpretation of the true excited state dynamics of solar cell materials like singlet fission sensitizers, leading to incorrect conclusions about their

photophysical behavior.⁸ Notably, this has been a particular challenge observed for polycrystalline films, but not in single crystals.¹² Importantly, this remains an outstanding issue often invoked by the singlet fission community. Concerns about such thermal artifacts skewing the conclusions made for singlet fission sensitizers⁸ have also been raised at the 2017 Singlet Fission Workshop (Lyons, CO).

The microscopic origins for such spectroscopic thermal artifacts were discovered in polycrystalline films of TIPS-Pn. It is the hope that this work will be published as a communication after a few more experiments are carried out. With the recent concerns raised by the singlet fission community, this work would be released at an opportune time.

A temperature-dependent absorption spectrum (**Figure 12-5**) of a crystalline (Form-I brickwork) film of TIPS-Pn was measured as previously discussed in Chapter 3. As the film was heated, there was a gradual blueshift in the vibronic peak positions.

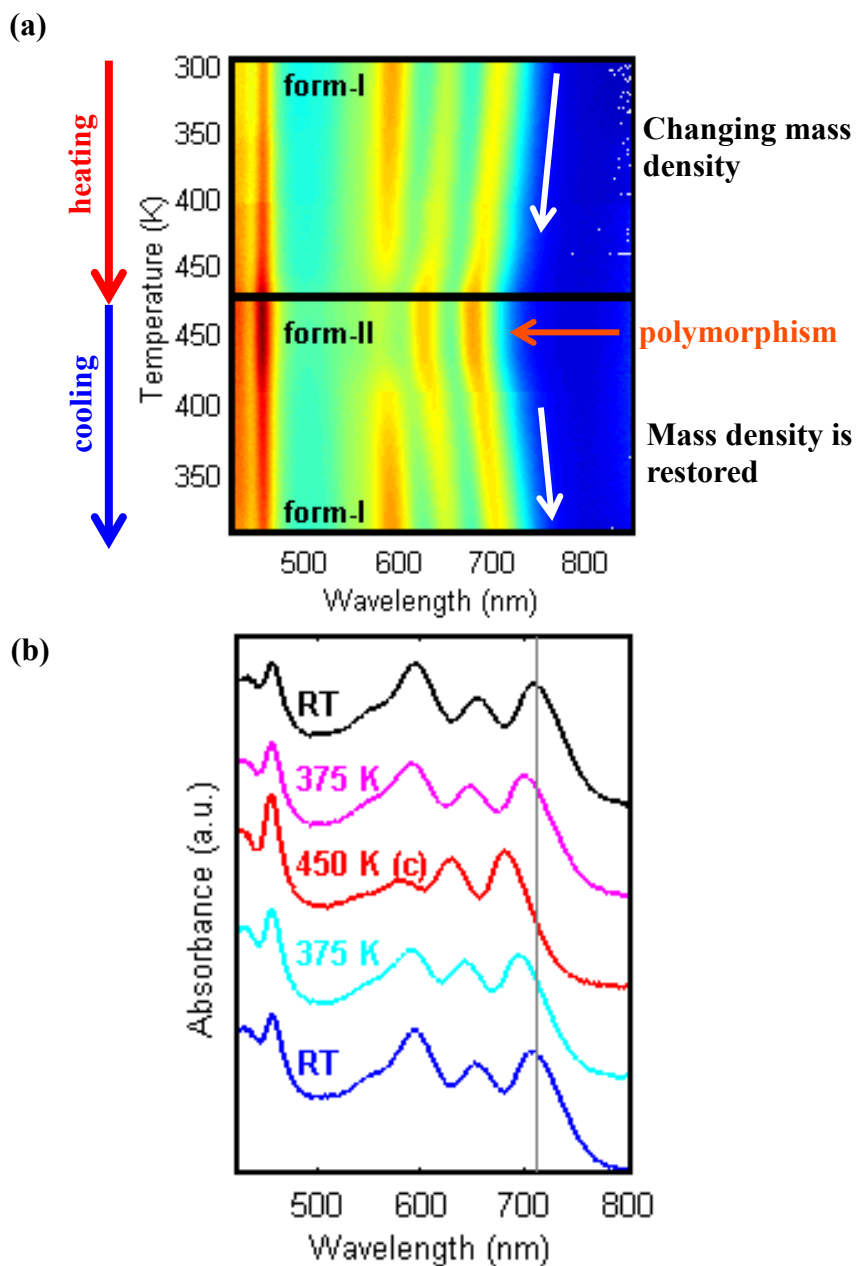


Figure 12-5: (a) Temperature dependence of the absorption spectrum of a crystalline (Form-I brickwork) film of TIPS-Pn during a heating/cooling cycle. (b) Absorption spectrum taken at a variety of temperature points during the heating/cooling cycle. “RT” represents room temperature, which was approximately 298 K.

After 450 K, there was an abrupt change in the absorption spectrum, in which a rapid blueshift of the vibronic peaks occurred. After this change, the absorption spectrum at resembled that of a film consisting of the Form-II brickwork polymorph at room temperature (see **Figure 3-**

20). This was reminiscent of the thermally-induced phase transition previously reported in drop-cast films of TIPS-Pn.⁹ Upon cooling, there was first rapid redshift in the vibronic peaks, followed by a gradual redshift, which mirrored the changes observed during the heating cycle.

The temperature-dependent shifts of the vibronic bands indicate that the molecular packing structure was sensitive to temperature. As discussed in Chapter 7 and in a recent report by Pensack et al.,¹⁰ as well as deduction from the observations reported by Kasha,¹¹ the redshift of the absorption spectrum in pentacene derivatives is associated with the strength of electronic coupling between the TIPS-Pn molecules. Therefore, as the film was heated, the average electronic coupling strength of the molecules may have decreased gradually. It is proposed that there was a change in mass density of the molecules that caused this change in coupling interactions. Upon reaching 450 K, it is proposed that the molecular packing structure evolved into that of the Form-II brickwork motif, which is known to exhibit lower coupling strength than the Form-I brickwork structure.³ Importantly, these observations were originally noted in 2005 by Ostroverkhova et al., who reported temperature-dependent changes in the absorption spectrum of thermally-evaporated films of pentacene and TIPS-Pn.¹²

To obtain further insight into the temperature-dependent changes in the molecular packing of TIPS-Pn films, hot-stage grazing-incidence x-ray diffraction (GIXRD) measurements were performed. The diffraction patterns shown in **Figure 12-6** indicate that there was indeed a thermally-induced polymorphism that occurred by 450 K. In particular, the 450 K pattern resembled that of a film consisting of the isolated Form-II brickwork polymorph, which was measured at room temperature. Additionally, it was found that the (001) reflections shifted to lower 2- θ as temperature increased, while the (011) reflection shifted to higher 2- θ . This indicated that the crystal lattice expanded in the (001) direction and contracted in the (011)

direction. The (00l) direction is characterized primarily by alkyl side group interactions, which are proposed to expand in volume with increasing temperature, causing an increase of the c unit cell parameter. On the other hand, the (011) spacing decreased, indicating that there was a change in the intermolecular slippage of the chromophore units that is related to the observed changes in their average electronic coupling strength. Notably, in polycrystalline films, unlike single crystals, there would be space available to accommodate such thermal expansion.

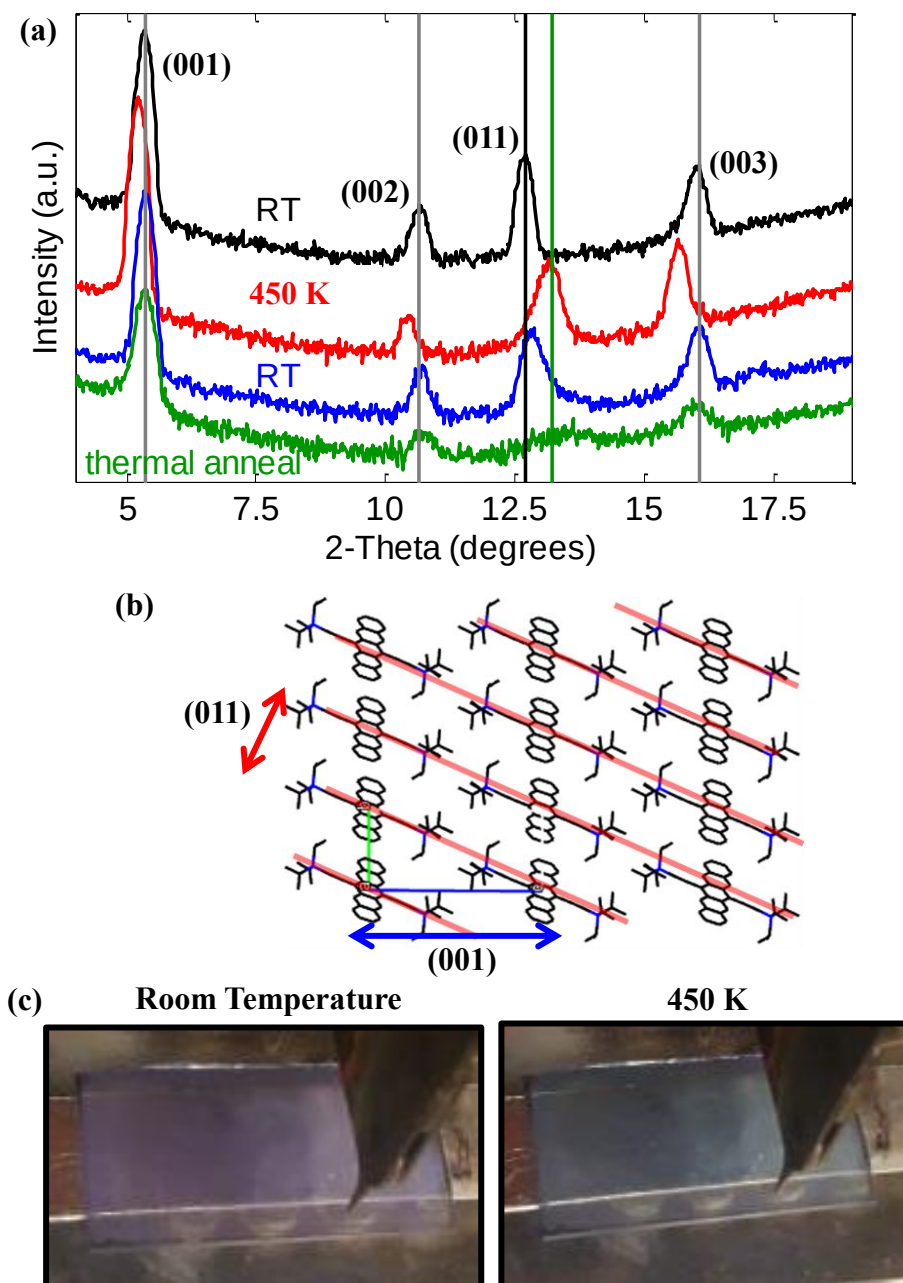


Figure 12-6: (a) Hot-stage grazing-incidence X-ray diffraction (GIXRD) pattern for a crystalline (Form-I brickwork) TIPS-Pn film on glass. “RT” represents room temperature, which was approximately 298 K. The pattern is compared to that measured for a “thermally-annealed film” (Form-II brickwork) measured at room temperature. (b) Crystal lattice for the Form-I brickwork structure highlighting the (001) and (011) crystal plane spacings that are changed when the sample is heated/cooled. (c) Photographs of the film during the measurement at room temperature and at 450 K.

It must be noted that the reversibility of the GIXRD pattern was not perfect. It is hypothesized that the partial irreversibility results from a small fraction of crystallites that

retain in the Form-II brickwork packing motif upon cooling down to room temperature due to a nanoconfinement effect. Such an effect has been observed in ultrathin films of TIPS-Pn prepared using solution-shearing methods.¹³

From the results from temperature-dependent absorbance and GIXRD measurements, the following structural changes in the crystal packing structures are proposed, which are illustrated in **Figure 12-7**. It is proposed that there are two regimes for the evolution of the crystal packing structure: (1) gradual intermolecular slippage accompanying thermal expansion and contraction of the crystal lattice, and (2) abrupt polymorphism, during which the molecules are able to “snap into place”.

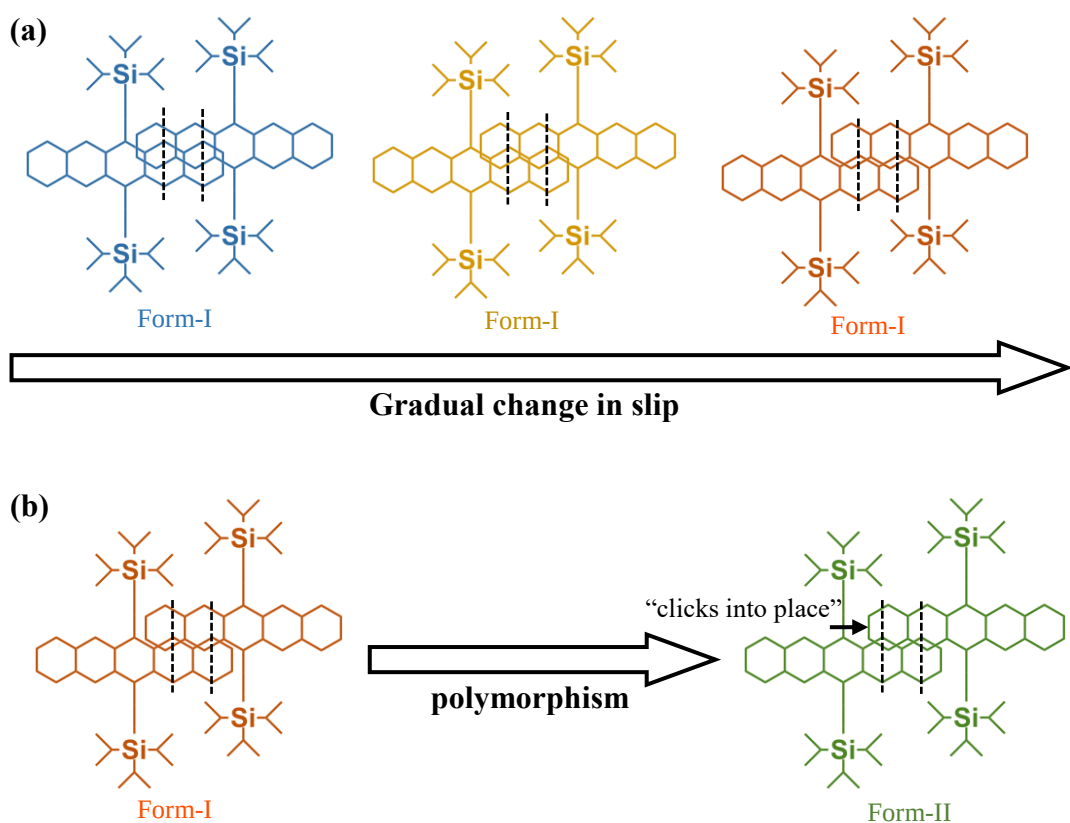


Figure 12-7: Proposed changes in TIPS-Pn packing structure upon heating a crystalline (Form-I brickwork) film. Changes in the slippages between molecules for the pair 1 state only are shown.

The gradual changes in the intermolecular coupling of TIPS-Pn molecules observed upon heating have significant implications on transient absorption measurements that are not only related to thermal artifacts. A particular experiment prone to such changes in coupling involves activation energy measurements. In an activation energy experiment, the temperature of the sample is varied and some photophysical process is measured. The temperature dependence is related to activation energy associated with that process using an Arrhenius plot. For example, energetic barriers to triplet (charge) transport may be determined by measuring the rate of triplet (charge) transfer over a certain temperature range. However, as discussed in Chapter 1, the rate of triplet or charge transfer is strongly dependent on the electronic coupling strength of the molecules involved in the transfer event. Since the electronic coupling of the molecules in TIPS-Pn films was shown to be sensitively dependent on temperature, the measured activation energy for triplet (charge) transfer may be skewed by static changes in electronic coupling that accompany the change in mass density of the molecules as they are heated or cooled. Thus, the measured activation energy no longer represents the true barrier to triplet or charge transfer for a given set of intermolecular interactions (e.g. room temperature), even if the temperature range is far from the polymorph transition temperature.

The hot-stage GIXRD measurements need to be repeated using several temperature points in between room temperature and 450 K to ensure a gradual shift occurs in the (00l) reflections, and that polymorphism occurs discretely. If this was found to be true, then sufficient evidence has been collected to support the conclusions made in this section.

12.3. Development of Approaches for Predicting Triplet Transport in Potential Singlet Fission Materials

As discussed in Chapter 7, triplet transfer was found to mediate triplet pair separation in crystalline TIPS-Pn films. In particular, an enhancement of electronic overlap coupling between molecules was found to favor triplet pair separation and triplet transport. Furthermore, the combination of calculations of singlet fission couplings and triplet transfer integrals was proposed for determining new structural design rules for singlet fission sensitizers that efficiently undergo both the first and second steps of the reaction. See Chapter 7 for more details of the proposal.

An additional consideration for designing materials with high triplet diffusivities is energetic disorder, which may be manifested, for example, through grain boundaries that form between disordered crystallites in polycrystalline films. Such morphologies would affect long-range transport of triplets following singlet fission, but not necessarily separation of the correlated triplet pairs. A systematic study may be performed on pentacene derivatives assuming a variety of crystal packing arrangements. Triplet pair separation and triplet-triplet annihilation (a measure of triplet diffusivity) would be assessed for a series of pentacene derivatives that assume a variety of crystal packing structures, such as those presented in **Figure 12-8**.

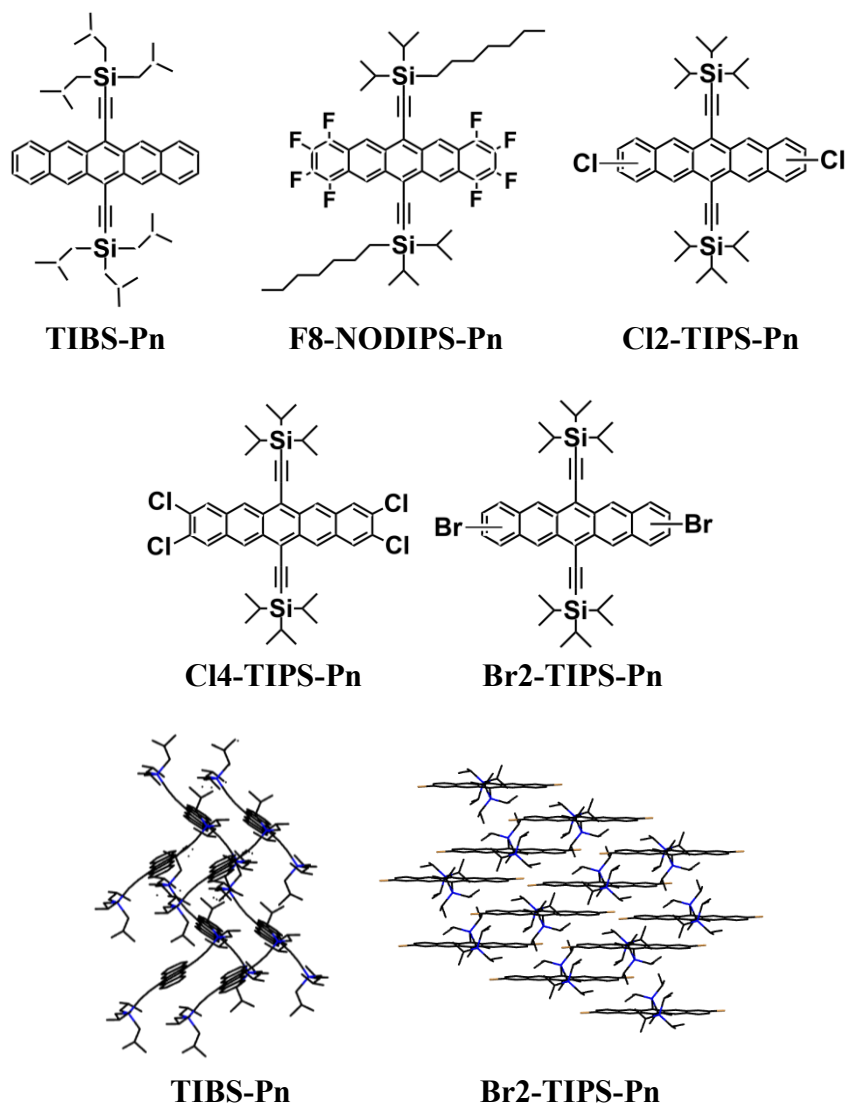


Figure 12-8: Examples of pentacene derivatives and crystal packing structures used in triplet transient absorption measurements.

In particular, rapid triplet pair separation, but slow triplet-triplet annihilation, would indicate that its crystal structure contains molecular packing arrangements that favor efficient triplet transfer, but result in polycrystalline films that do not favor long-range transport of triplets. This has been discovered in preliminary measurements of the pentacene derivative, TIBS-Pn, which is known to undergo rapid singlet fission⁴, but exhibits very slow triplet-triplet annihilation compared to other derivatives (see **Figure 12-9**).

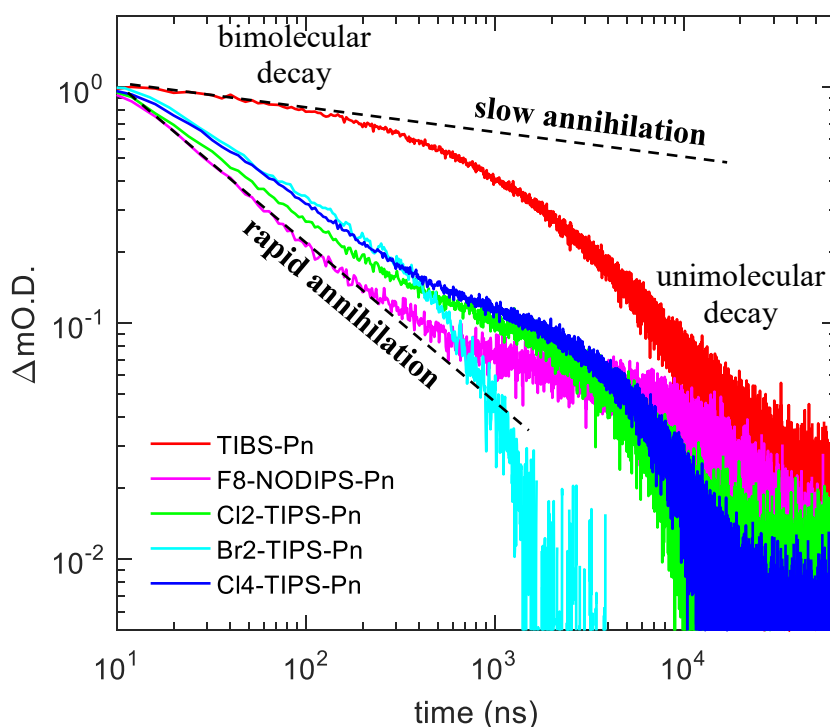


Figure 12-9: Nanosecond-to-microsecond transient absorption kinetics of triplet excitons in nanoparticle dispersions of pentacene derivatives in water. The excitation wavelength was 642 and the probe wavelength was 890 nm, 840 nm, 910 nm, 950 nm, and 950 nm for TIBS-Pn, F8-NODIPS-Pn, Cl2-TIPS-Pn, Br2-TIPS-Pn, and Cl4-TIPS-Pn, respectively.

12.4. Molecular Packing Arrangements in Concentrated Solutions of a Pentacene Derivative: Insights from Vibrational Spectroscopy

In this section, vibrational absorption spectroscopy is used to identify molecular aggregation in solutions of TIPS-Pn, for which electronic absorption spectroscopy actually reveals no aggregation. It was found that although molecules may not electronically couple in the ground state of both dilute and concentrated solutions, they may aggregate via side groups interactions that do not perturb the electronic absorption spectrum. This discovery was particularly important in the context of the precise singlet fission mechanism that occurs in concentrated solutions. It is the hope that this work will serve as the foundation for future

work investigating aggregation in solutions of singlet fission sensitizers, and their impact on singlet fission in solution. These studies can lead to fundamental insights into how molecular structure within the aggregates controls the rate and efficiency of singlet fission.

In 2013, Walker et al. reported that singlet fission occurs in concentrated TIPS-Pn via diffusion-mediated formation of emissive excimer intermediates.¹⁴ This method had then been adapted by others for quantifying singlet fission efficiency in new compounds.¹⁵ However, the conclusion about emissive excimer formation in concentrated TIPS-Pn solutions can be easily proven incorrect by careful analysis of the emission data for the most concentrated solutions, which are prone to the inner filter effect (see Chapter 2 for description), especially when using 1 mm cuvettes (see Appendix for proof). As such, this result led to false conclusions about the intermediate state of singlet fission for TIPS-Pn. Furthermore, the precise mechanism of singlet fission in solution has been challenged by careful analysis of molecular aggregation in both dilute and concentrated solutions.

An additional concern about using concentrated solutions to quantify the yield of singlet fission is that if not careful about the inner filter effect, a process that is referred to here as “triplet amplification” may occur. In very concentrated solutions measured in pathlengths larger than that of liquid films (in some cases liquid films are not even sufficiently thin), any photon that is emitted by a molecule that cannot undergo singlet fission may be reabsorbed by another (inner filter effect). This multiplies the chances for a single incident excitation to be converted into triplet excitons, leading to an amplification of the true triplet quantum yield.

In the study presented herein, vibrational spectroscopy is performed for various concentrations of TIPS-Pn dissolved in CCl₄ to assess its degree of aggregation of non-electronically interacting molecules. In addition, the triplet yield was determined using a

method similar to that developed by Walker et al using near-IR transient absorption spectroscopy.¹⁴ Chapter 8 discusses the changes in transient absorption features associated with singlet fission in concentrated solutions of TIPS-Pn. From the structural insight gained from vibrational spectroscopy, it is proposed that molecular rotations are responsible for mediating singlet fission in solutions of TIPS-Pn, and not translational diffusion of the molecules. The specific structure of the molecular aggregates is proposed for a large range of concentrations, and two general aggregation behaviors are hypothesized: Short-range 1-dimensional aggregation between multiple molecules, and large-range multi-dimensional aggregation. These hypotheses were supported by the results of degradation experiments, which showed that in solutions with extremely high concentrations, the TIPS-Pn molecules undergo a different type of chemical reaction than those with extremely low concentrations.

The concentration-dependent vibrational spectrum of C-H stretching vibrations in solutions of TIPS-Pn dissolved in CCl₄ are shown in **Figure 12-10**. The spectra were found to evolve starting with concentrations as low as 6.35×10^{-6} M. The most significant changes in the absorption spectrum were associated with changes in the frequency of C-H stretching modes of the triisopropyl side groups of the TIPS-Pn molecules. These changes indicated that the environment of the C-H bonds varied with concentration, suggesting that the molecules were aggregating. Because the molecules under these concentrations are known to not electronically interact (see Chapters 5 and 6), it is proposed that they can aggregate through side chain interactions. Furthermore, as the solution concentration was increased, the shape of the absorption spectrum approached that of an amorphous film of TIPS-Pn, which contain side group interactions (see crystal structure in Chapter 3). The changes in the spectrum were quantified using the relative peak ratio between the peaks at 2944 cm^{-1} and 2929 cm^{-1}

(A_{2944}/A_{2929}), which was surprisingly found to increase at concentrations as low as 10^{-5} M (see **Figure 12-10**).

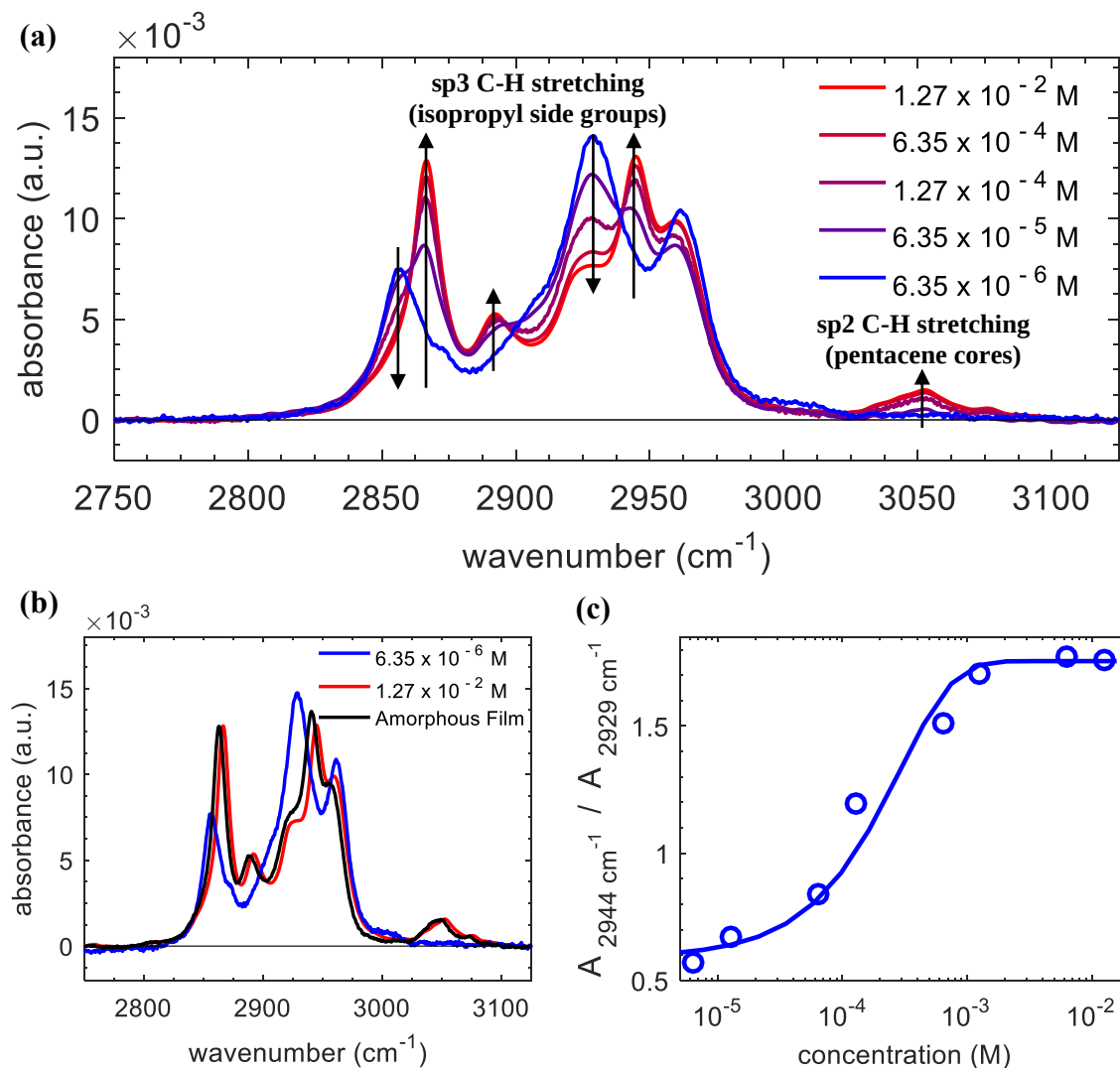


Figure 12-10: (a) Concentration-dependent evolution of the C-H stretching (area-normalized) vibrational absorption spectrum of TIPS-Pn dissolved in CCl_4 . (b) Comparison of dilute and concentrated solution spectra with that of an amorphous film of TIPS-Pn. (c) Dependence of the absorption ratio of the peaks at 2944 cm^{-1} and 2929 cm^{-1} on solution concentration.

The singlet decay rate was determined using fluorescence spectroscopy and transient absorption spectroscopy (probing S_1 near-IR absorption at 1400 nm), which is shown in **Figure 12-11**. As expected, the decay rate was enhanced as concentration was increased due to kinetic

quenching from singlet fission. Interestingly, a linear relationship between singlet decay rate and solution concentration was observed. The triplet yield was additionally determined and related to solution concentration in **Figure 12-11**, also showing a linear dependence on concentration. These results suggest that the concentration of a certain type of aggregate structure favorable for singlet fission is increasing with total solution concentration.

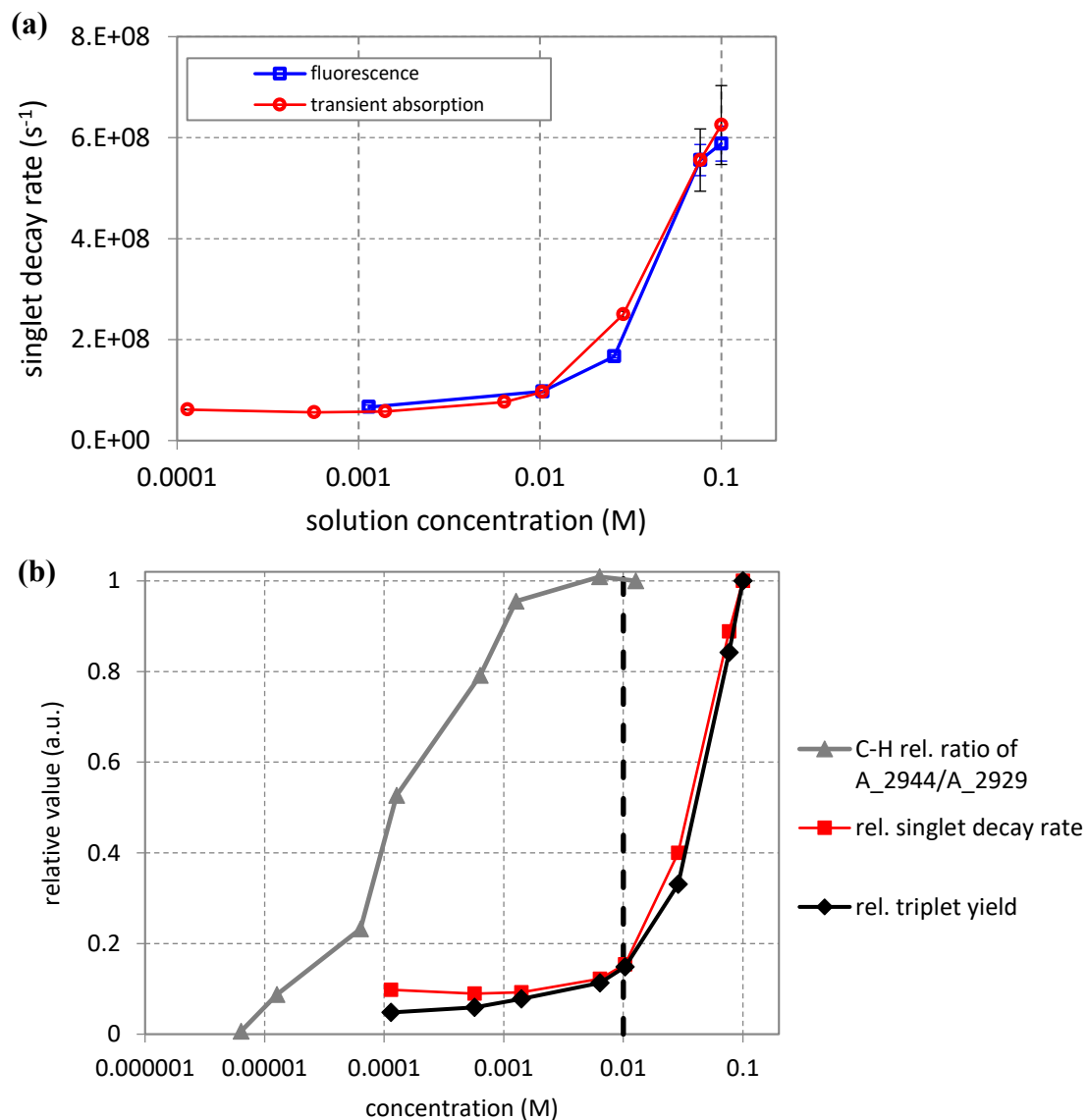


Figure 12-11: (a) Comparison of the singlet decay rate constants determined from fluorescence and transient absorption measurements over a large range of concentrations of TIPS-Pn solutions. The excitation wavelength was 642 nm. The transient absorption kinetics of the $S_1 \rightarrow S_2$ band were measured at 1400 nm. (b) Comparison of the relative singlet decay rates, triplet yield, and A_{2944}/A_{2929} over a large range of concentrations of TIPS-Pn solutions. Carbon tetrachloride was used as the solvent for all samples.

Next, the absorption ratio of the C-H stretching peaks defined earlier (A_{2944}/A_{2929}) was compared to solution concentration, which did not reveal a linear relationship. In fact, the onset of singlet fission quenching appears to occur as soon as the changes in the vibrational

spectrum reach their asymptotic limit. From this, it is proposed that two mechanisms of aggregations occur: (1) One-dimensional aggregation of a few TIPS-Pn molecules (up to 10^{-5} M), and (2) multi-dimensional growth forming extended aggregate structures of TIPS-Pn molecules (beyond $\sim 6 \times 10^{-3}$ M). See **Figure 12-12** for an illustration. It is proposed that extended aggregate structures are necessary for efficient singlet fission to occur in TIPS-Pn solutions, and aggregate growth results in faster singlet fission. This could explain the abrupt increase in singlet decay rate and triplet yield observed for concentrations beyond 10^{-3} M.

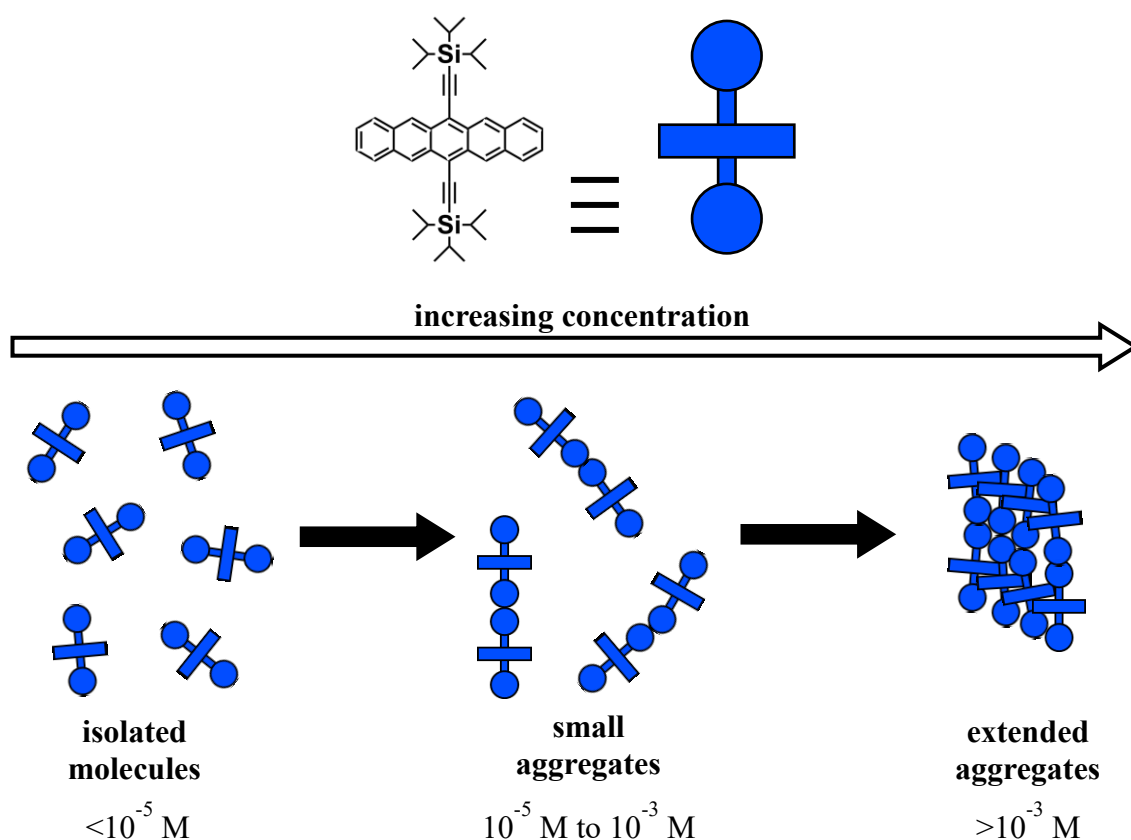


Figure 12-12: Illustration of the proposed aggregation behavior of TIPS-Pn in solution as concentration is increased.

Last, further support for the proposed aggregation mechanism was provided by analysis of degradation of TIPS-Pn solutions having different concentrations (see **Figure 12-13**). For these experiments, TIPS-Pn was dissolved in dichloromethane at either 1 mg/mL (1.6×10^{-3}

M) or 60 mg/mL (9.3×10^{-2} M). The absorption spectra of diluted aliquots of each solution were measured after storage in the dark for several months (**Figure 12-13**). The spectrum of the 1 mg/mL solution was similar to pristine TIPS-Pn. Dilute solutions of TIPS-Pn are known to degrade via oxidation or butterfly dimerization (cycloaddition of the pentacene cores), which results in a decrease of the intensity of the visible absorption bands and the formation of UV and near-UV absorption bands. The growth of these latter bands are associated with the break in conjugation of the pentacene cores into benzene-like and anthracene-like units. On the other hand, the 60 mg/mL solution exhibited a completely different absorption spectrum, indicating that it degraded to form a completely different chemical structure. Comparing this spectrum to that reported previously in a study of TIPS-Pn degradation revealed that the structure likely formed via a cycloaddition between the pentacene core of one molecule and the alkyne bond of another.¹⁶ As such, the structure of the aggregates in the 60 mg/mL (9.3×10^{-2} M) solution must have been different than those in the 1 mg/mL (1.6×10^{-3} M) solution. These results are consistent with the observation that singlet fission rate increases dramatically for concentrations exceeding $\sim 6 \times 10^{-3}$ M.

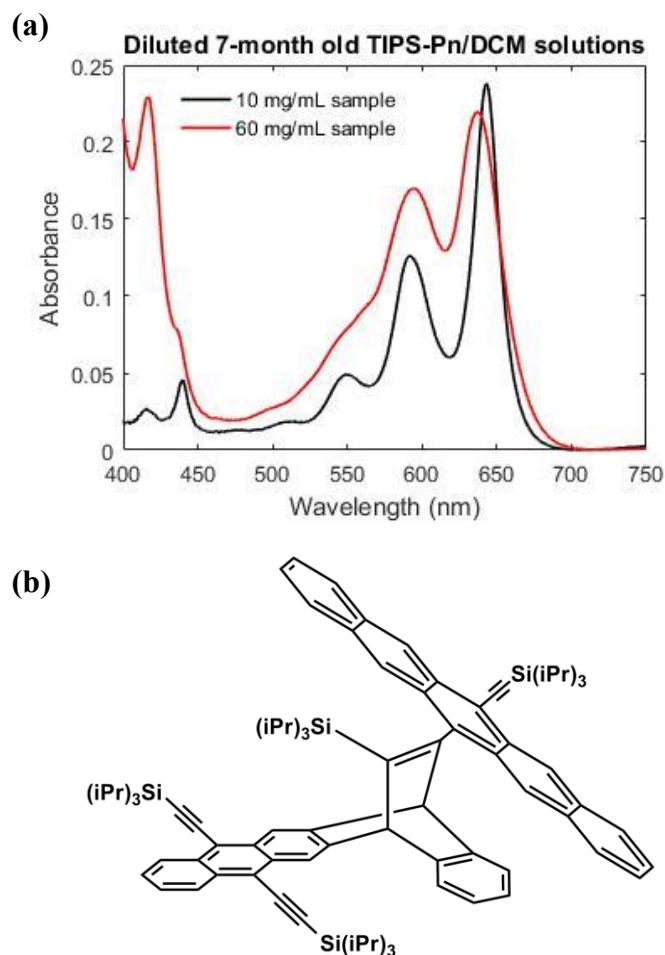


Figure 12-13: (a) Absorption spectrum of diluted aliquots of solutions of TIPS-Pn dissolved in dichloromethane after aging for 7 months in the dark. (b) Potential structure of the degraded product produced in the more concentrated (60 mg/mL) sample.

12.5. Role of Electronic Coupling on Charge Separation in Polymer:Pentacene Photovoltaics

As discussed in Chapter 10, the role of electronic delocalization at electron donor-acceptor interfaces on charge generation in organic solar cells is debated. As such, a platform for selectively modulating the electronic coupling in electron acceptors in a polymer:molecule blend was developed. It is the hope that this work serves as a foundation for future studies that

investigate how the modulation of such coupling impacts charge separation of charge transfer excitons at donor-acceptor interfaces.

Polymer:molecule blends have been frequently employed in organic solar cells, in which charge separation must occur at the interface between polymer and molecular domains. Commonly, poly(3-hexylthiophene) (P3HT), an exemplar electron donating material, is blended with a small molecule that serves as the electron acceptor. In the case of this work, P3HT was blended with a pentacene derivative, 2-CN-TCPS-Pn^{17,18} (see structures in **Figure 12-14**).

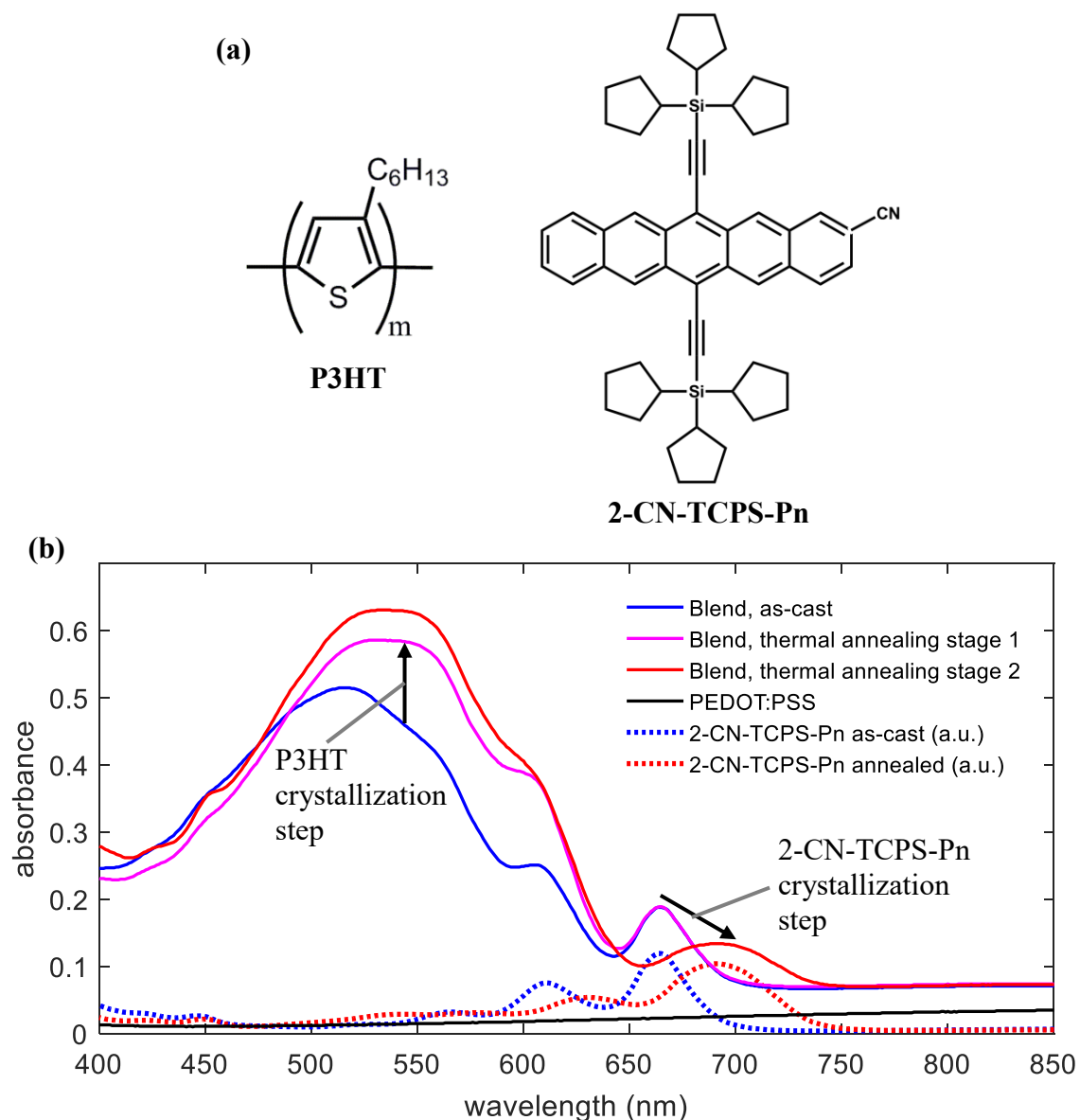


Figure 12-14: (a) Chemical structures of the electron donor and acceptor materials used in the polymer:molecule blend study. (b) Absorption spectra of a blend film cast onto PEDOT:PSS after several steps of thermal annealing. The first stage was annealing at $\sim 37^\circ\text{C}$ overnight. The second stage was annealing at 60°C for 20 minutes, although this can be performed for shorter amounts of time.

From the discovery that amorphous films of pentacene derivatives can be produced via spin-coating, it was found that casting solutions of P3HT:2-CN-TCPS-Pn (1:1 mass ratio, 40 mg/mL total volume) from chloroform results in films consisting of amorphous domains of P3HT and 2-CN-TCPS-Pn. This was indicated by their characteristic absorption spectra shown in **Figure**

12-14. In order to ensure that the P3HT was crystallized, which is known to be important for dramatically improving its hole mobility,¹⁹ the P3HT was selectively annealed without causing the 2-CN-TCPS-Pn to crystallize. This was achieved by thermal annealing the blend film overnight at a low temperature (~40 °C), which was below the crystallization temperature of 2-CN-TCPS-Pn. The absorption spectrum of the resulting film shows that the P3HT was successfully annealed without inducing crystallization of the pentacene derivative. Last, the crystallization of the pentacene derivative can be induced by thermal annealing at a temperature above its crystallization temperature (e.g. 80 °C) for a brief amount of time (e.g. 10 seconds). Because the crystallization occurs almost instantaneously, the P3HT does not have enough time to undergo further large-scale rearrangements or diffusion, and the pentacene derivative does not have enough time to diffuse any further into or out of the polymer phases.

12.6. Role of Transport Dimensionality in Triplet Separation in Pentacene Derivatives

An outstanding question for singlet fission sensitizers is the role of transport dimensionality on the separation of the triplet pair states, and the corresponding effectiveness of triplet transport. While triplet diffusion constant is known to scale inversely with dimensionality²⁰, it is not clear if lower dimensional transporters are actually beneficial for survival of triplets. In particular, it is known that limiting the dimensionality in which triplets may transport can enhance their annihilation rates (through a confinement effect, which increases their effective concentration).²¹⁻²⁵

A model pentacene derivative system was recently developed that can be used to test how transport dimensionality affects singlet fission. Both TIBS-Pn and THS-Pn have similar crystal packing structures, but with different numbers of transport directions. The TIBS-Pn

molecule has relatively compact isobutyl side chains that allows the pentacene cores to electronically interact in two crystal directions (See **Figure 12-15**).

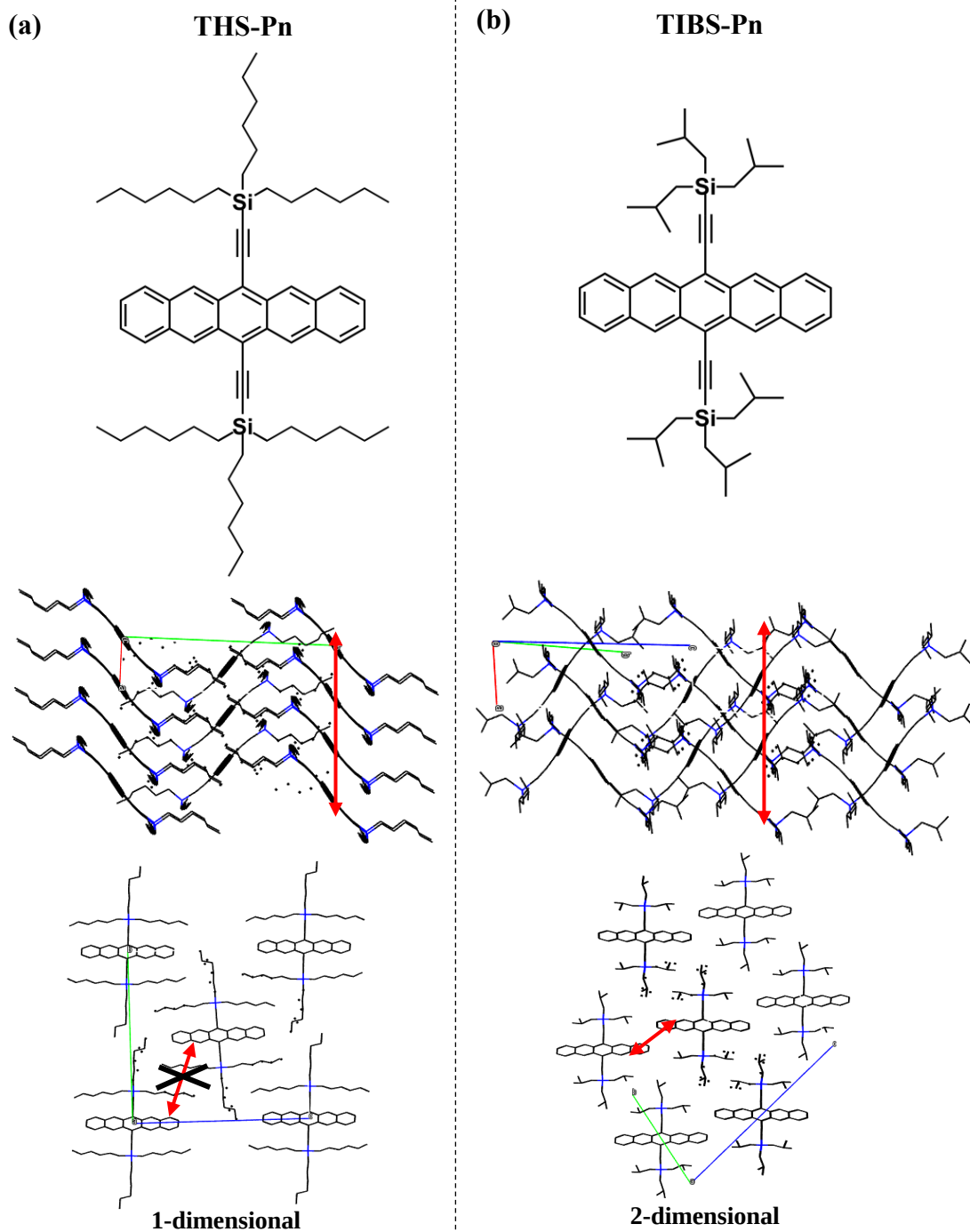


Figure 12-15: Chemical structure and crystal packing structures for **(a)** THS-Pn and **(b)** TIBS-Pn.

On the other hand, the THS-Pn molecule has larger hexyl side chains that prevent the pentacene cores from electronically coupling in two crystal directions. The ultrafast triplet state absorption kinetics measured in the visible spectral region (**Figure 12-16**) show that the triplet pairs (unclear if they are separated or bound) in THS-Pn very rapidly recombine or annihilate well before 1 ns. On the other hand, TIPS-Pn, which is expected to behave spectroscopically like TIPS-Pn based on previous published¹⁰ and unpublished data, results in much longer-lived triplet absorption kinetics. These preliminary results will hopefully serve as a starting point for a future study.

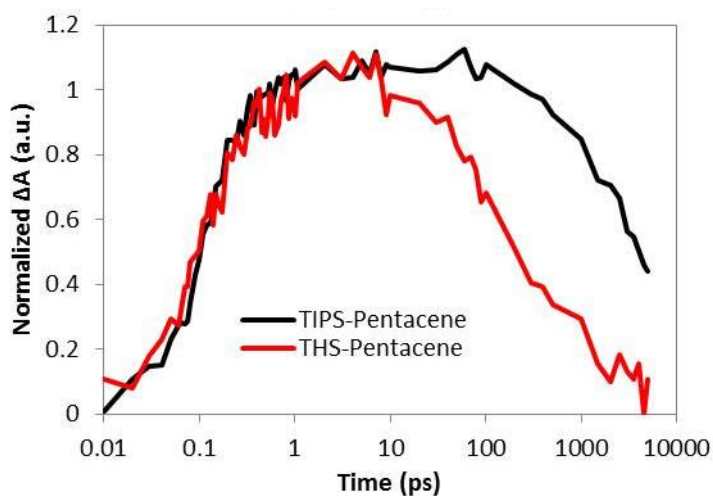


Figure 12-16: Ultrafast transient absorption kinetics of the $T_1 \rightarrow T_n$ transition in the visible spectral region for TIPS-Pn and THS-Pn crystalline films. The excitation was 642 nm and had a $18 \mu\text{J}/\text{cm}^2$ energy density. The transient absorption was monitored at 520 nm.

12.7. References

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CHAPTER 13

Conclusions and Outlook

In this dissertation, structure-function relationships in organic solar cell materials were investigated using time-resolved optical spectroscopy. Changes in solid-state packing interactions between molecules or polymers were found to determine their overall photophysical characteristics, including their ability to transport excitation or charge. Two major systems were studied in this work: Singlet fission sensitizers, and semiconducting block-copolymers. Each is summarized in the following, after which a general outlook on these materials is offered.

13.1. Singlet Fission

Singlet fission is an exciton multiplication mechanism manifested by some organic materials by which a singlet exciton is split into two triplet excitons. Intermolecular coupling interactions allows an excited electronic singlet state on one molecule to share its energy with an adjacent ground electronic state on another in a special way that results in the formation of two excited triplet states. The specific molecular packing arrangements, which influence intermolecular orbital overlap couplings, determines the efficiency of singlet fission, including both the formation of correlated triplet pair intermediates and their subsequent separation into independent triplet excitations. Because the singlet fission reaction can produce a triplet yield as high as 200%, it offers a strategy for improving the power conversion efficiency of solar cells by overcoming thermalization loss and pushing beyond the Shockley-Queisser limit for maximum theoretical efficiency.

Through the work presented in this dissertation, the impact of molecular packing arrangements and film crystallinity on the photophysical properties of a model singlet fission chromophore, TIPS-Pn, was investigated in depth. It was shown that triplet transfer mediates triplet pair separation of the intermediate states of the singlet fission reaction. Furthermore, structures that prevent strong intermolecular orbital overlap coupling, such as amorphous solids, lead to much slower formation of multiplied, independent triplet excitons. In these cases, kinetically competing mechanisms, such as excimer formation and internal conversion, are proposed to limit the ultimate yield of triplets. In addition, correlated triplet pair intermediates have been observed to persist in time much longer than previously believed during spin decoherence, even in crystalline materials in which the triplet pairs may be efficiently separated. An ultrafast vibrational spectroscopy technique was developed for studying the singlet fission reaction; unlike in electronic spectroscopy, it was shown that vibrational probes may be used to selectively track separated triplet excitations, enabling spectroscopic discrimination of separated triplets from the proximal, bound triplet pairs. Last, it was found that the presence of amorphous phase in polycrystalline films is significantly detrimental to their ultimate triplet diffusion lengths. This led to the practical conclusion that highly crystalline singlet fission sensitizer layers in solar cells should be ensured in order to optimize the triplet diffusion length, increasing the ability to harvest the multiplied triplet excitons.

13.2. Block-Copolymer Photovoltaics

Semiconducting block-copolymers are appealing materials for organic solar cells since they can have the ability to self-assemble into phase-separated nanoscale structures that are believed

to be optimal for device performance. Their design consists of two polymer blocks that are covalently linked together, including an electron donating and an electron accepting polymer. Nanoscale ordering of the electron donor and acceptor would optimize the ability to both photogenerate charges, and facilitate rapid transport of the charges via organized percolation pathways to the device electrodes.

Through the work presented in this dissertation, the photophysical role of the covalent linkage in a model semiconducting block-copolymer system, P3HT-b-PFTBT, was investigated. It was found that careful design of the covalent linkage between polymer blocks may lead to favorable nanoscale structure, while preventing the introduction of widespread charge-trapping centers that would reduce the amount of current produced by the solar cell. Design rules were implicated, which promise to prevent rapid charge recombination in the next generation of block-copolymer materials. In addition, solution-phase systems of semiconducting block-copolymer materials were developed for the first time for enabling well-controlled photophysical studies that can be performed in the future to understand fundamental charge photogeneration and transport mechanisms in organic solar cell materials.

13.3. Outlook

For singlet fission sensitizers, it is the hope that future work continues to develop our understanding of the precise singlet fission mechanism, and how it can be controlled by careful selection of chemical and structural properties. Uncovering further structure-function relationships in singlet fission sensitizers will hopefully push their application to solar cells from proof-of-principle to practical. Or, on the other hand, it will be determined if singlet fission sensitized solar cells would be practical at all. New chemical and structural design rules

will hopefully continue to be established using the work presented in this dissertation as a foundation for future investigations.

For block-copolymer solar cells, it is the hope that the work presented in this dissertation provides a foundation for future studies, which seek to develop further chemical and structural design rules that ensure maximal device performance. Additionally, the design rules developed herein will be tested for newly designed polymer systems that are being synthesized. Future work on solution-phase block-copolymer systems, such as aggregates and nanoparticles, will lead to better fundamental understandings of photocurrent generation and charge transport mechanisms in organic solar cells, and how they are related to both nanoscale and larger-scale structure.

APPENDIX

Herein, some important sets of experimental considerations will be discussed. Furthermore, additional sets of spectroscopic data of pentacene derivatives will be provided for reference for future research.

A.1. Experimental Considerations for Properly Measuring Bimolecular Decay

The rates of bimolecular decay processes, including polaron recombination and triplet-triplet annihilation, depend not only on time but also concentration. As a result, extra caution must be taken when measuring and comparing decay rates between different samples, or samples measured on different days. In particular, the concentration of the transient species photogenerated in the experiment and/or formed via other excited state species must be controlled in order to properly assess their decay rates. In many cases, such as in polaron absorption, the decay rate is extremely sensitive to concentration (see **Figure A-1** for an example using a P3HT:PC₆₁BM blend film). In addition, because sample sets often have slight variations in absorption (due to variations in film thickness, for example), the amount of photons absorbed from the excitation pulse in time-resolved spectroscopy measurements is not equal across the set of samples even if the *incident* excitation energy density is fixed. As such, the excitation energy density should be adjusted for each sample to ensure that the *absorbed* energy density is equal for all samples tested. This ensures that the initial photoexcited species has the same concentration for all samples. This of course does not eliminate the complication that the transient species being probed may have an unequal quantum yield for all samples tested. For example, different samples may have different quantum yields of polarons generated for every photon absorbed.

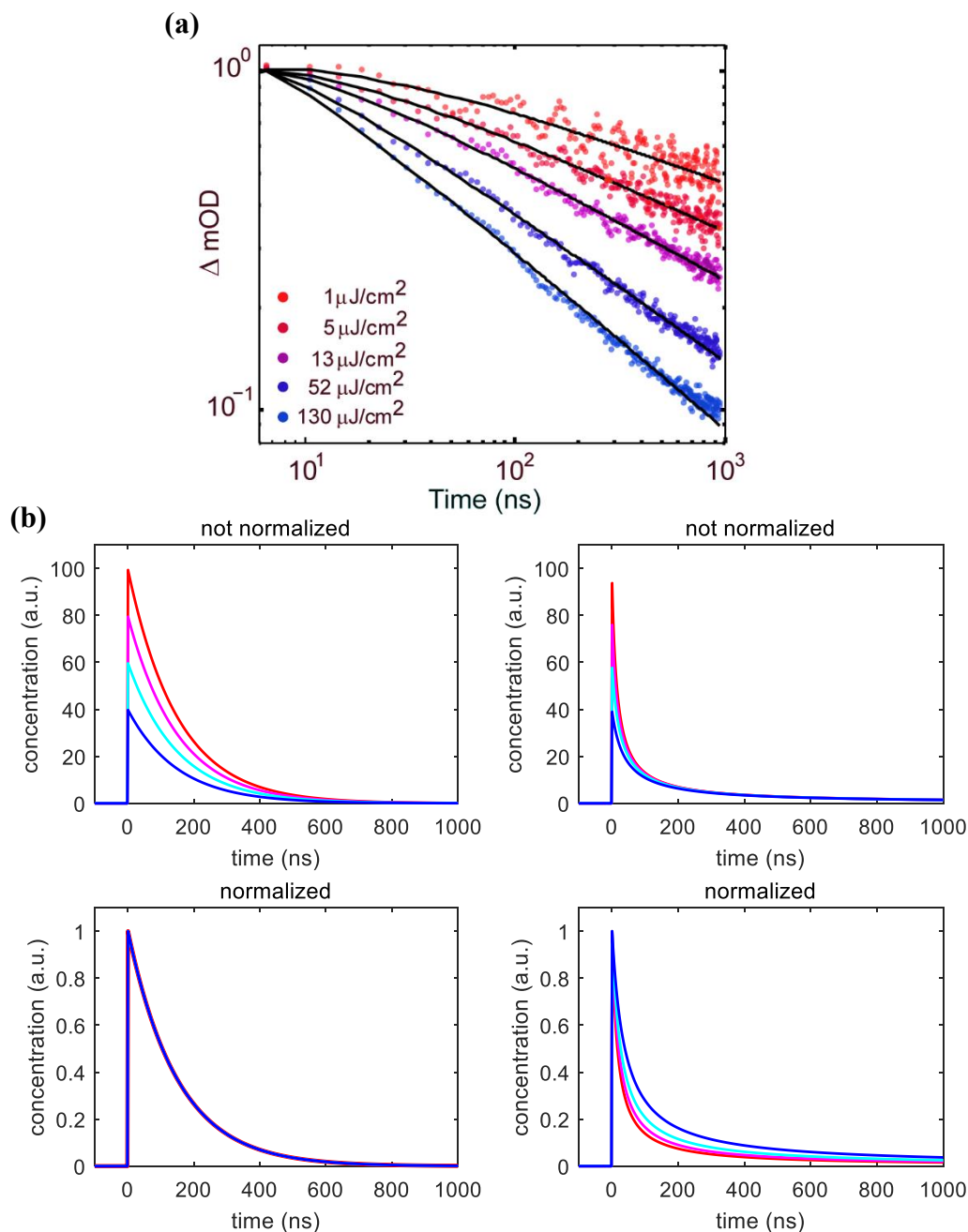


Figure A-1: (a) Polaron absorption kinetics for a blend film of P3HT:PC₆₁BM excited at 532 nm and over a range of incident energy densities. (b) Models of exponential and bimolecular decay kinetics for different initial concentrations plotted before and after normalizing. The rate constants were held constant for all traces and only initial concentration was changed.

Another consideration that must be made when measuring bimolecular decays is that the data being compared generally cannot be normalized. This results from the fact that the decay

rates depend not only on time, but also concentration. Typically, spectroscopists normalize kinetic data by dividing the kinetics trace by the value near the time origin of the measurement. This normalization procedure makes the assumption that the initial concentration of the transient species is equal across all samples tested. This is acceptable for species that decay unimolecularly (exponentially) because the decay rate depends only on time, and not on concentration. However, this normalization procedure would effectively skew the decay rates of bimolecularly decaying species, leading to incorrect interpretations. This is illustrated in **Figure A-1** for unimolecular and bimolecular decays.

A.2. Identification of the Inner Filter Effect in Emission Spectra of Concentrated Solutions of a Pentacene Derivative

The inner filter effect occurs when the absorptivity of a sample is high enough so that any emission may be reabsorbed before exiting the sample cell. This effect was illustrated in Chapter 2 (**Figure 2-12**). This results in the alteration of the emission spectrum measured, especially near the region where the sample absorbs, which can lead to incorrect interpretation of data (see discussion in Chapter 12 for an example). To demonstrate the inner filter effect, the emission spectrum of solutions of TIPS-Pn dissolved in CCl₄ are compared for a variety of concentrations (**Figure A-2**). All solutions were measured as liquid films. Upon increasing concentration, the shape of the emission spectrum changed, with a disappearance of the 0-0 emission peak. To test for the inner filter effect, a 25 mM solution was measured as both a liquid film, and in a 1 mm pathlength cuvette. Because the sample was unchanged, then the emission spectrum measured should not depend on the sample pathlength. As seen in **Figure A-2**, the emission spectrum was indeed dependent on the sample pathlength, which indicated that the inner filter effect explains the disappearance of the 0-0 emission peak.

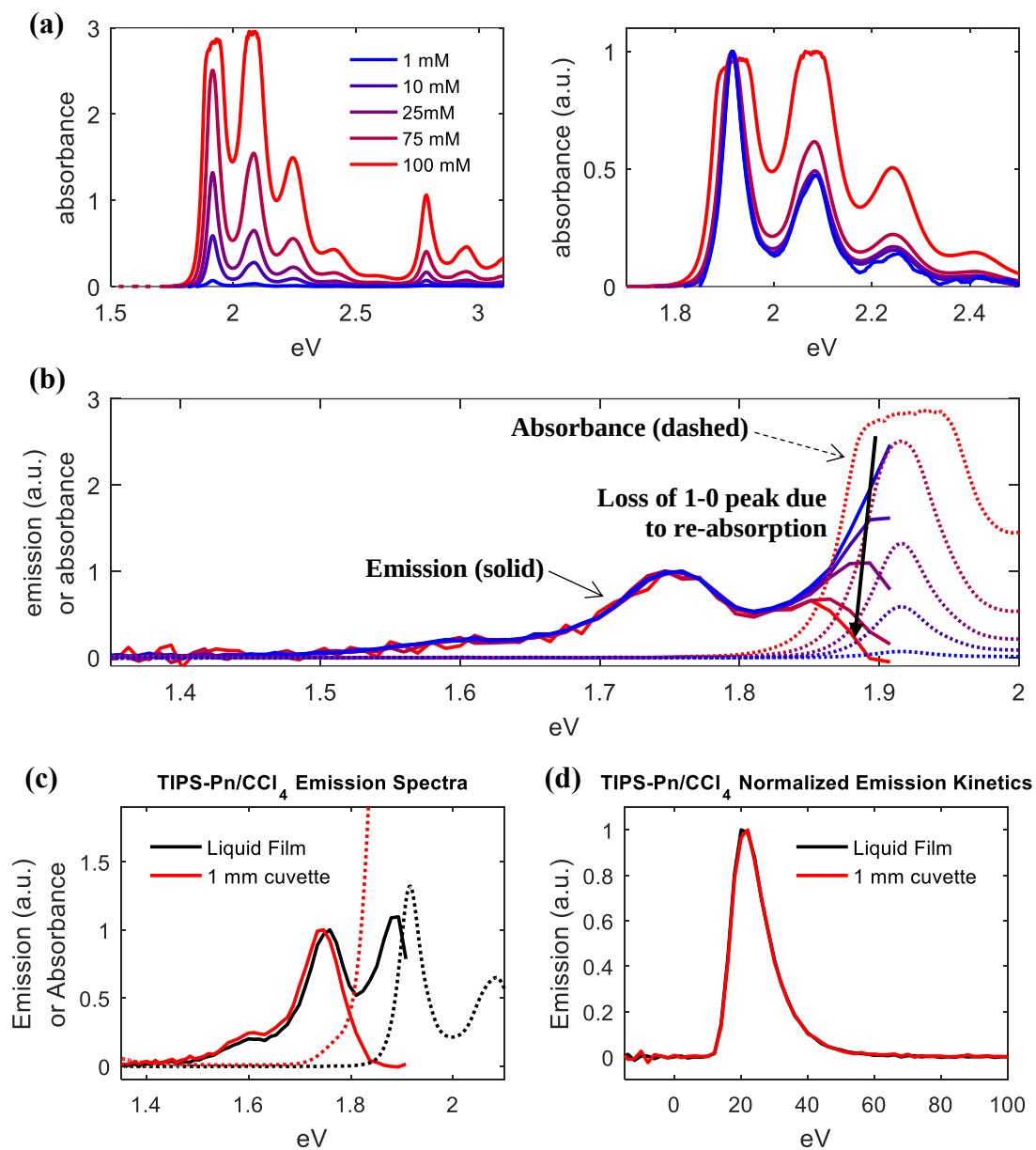
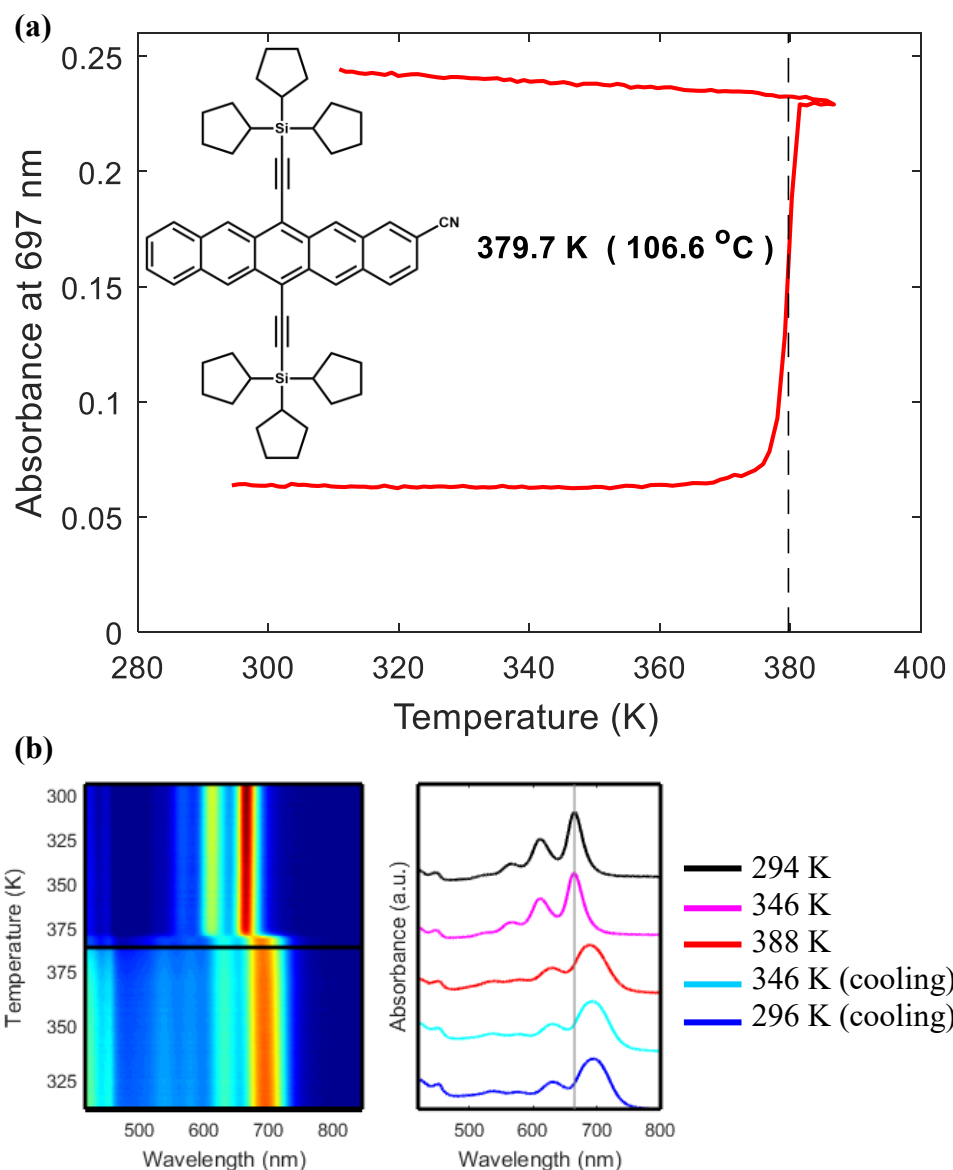


Figure A-2: (a) Absorption spectrum of solutions of TIPS-Pn dissolved in CCl_4 for a variety of concentrations. All samples were measured as liquid films. (b) Concentration-dependent emission spectrum for the sample solutions, measured as liquid films and using 532 nm excitation. (c) Testing for the inner filter effect using a 25 mM solution measured as a liquid film or in a 1 mm pathlength cuvette. (d) Emission decay kinetics for the same samples.

A.3. Thermally Annealing Amorphous Films of Other Pentacene Derivatives

In Chapter 3, it was shown that the pentacene derivative, TIPS-Pn, can be cast as amorphous films that can subsequently be thermally annealed to induce crystallization. While not a common aspect of all pentacene derivatives, this has been demonstrated in a few others, as shown in **Figure A-3** and **Figure A-4**. The ability to cast amorphous films seems to depend on the side groups, whose interaction energies may control how easily crystallizable the molecules are. In addition, the crystallization temperature is also dependent on the chemical structure of the pentacene derivative. Last, it was found (data not shown) that the presence of another material, such as P3HT, can influence the crystallization temperature of the pentacene derivative. It also must be noted that caution must be taken to ensure that heating the sample does not cause degradation.



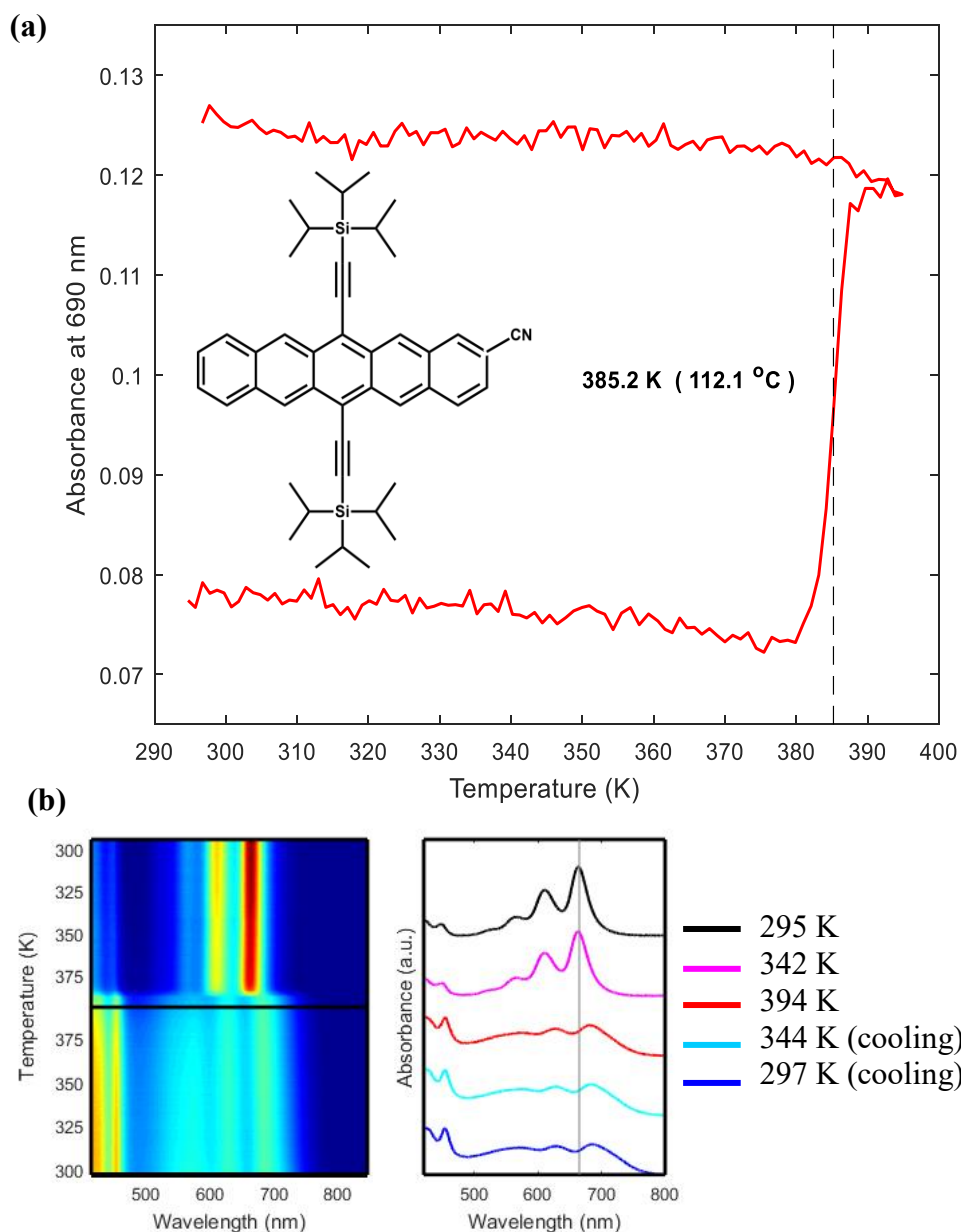


Figure A-4: (a) Absorption “thermogram” measured for an amorphous film of 2-CN-TIPS-Pn during a heating/cooling cycle. The crystallization temperature is indicated. (b) Temperature-dependent absorption spectrum during the heating/cooling cycle, including a plot of spectral slices taken at a variety of key temperature points.

A.4. Ultrafast Spectroscopic Characteristics of Other Pentacene Derivatives

In the singlet fission studies presented in this dissertation, the bulk of the work involved the model compound, TIPS-Pn. However, other functionalized pentacenes are also known to undergo rapid, efficient singlet fission. Here, additional data collected on TIPS-Pn and other pentacene derivatives are included for future reference (see **Figure A-5** and **Figure A-6**). It is the hope that these data will assist future researchers in ultrafast transient absorption measurements of TIPS-Pn and other compounds.

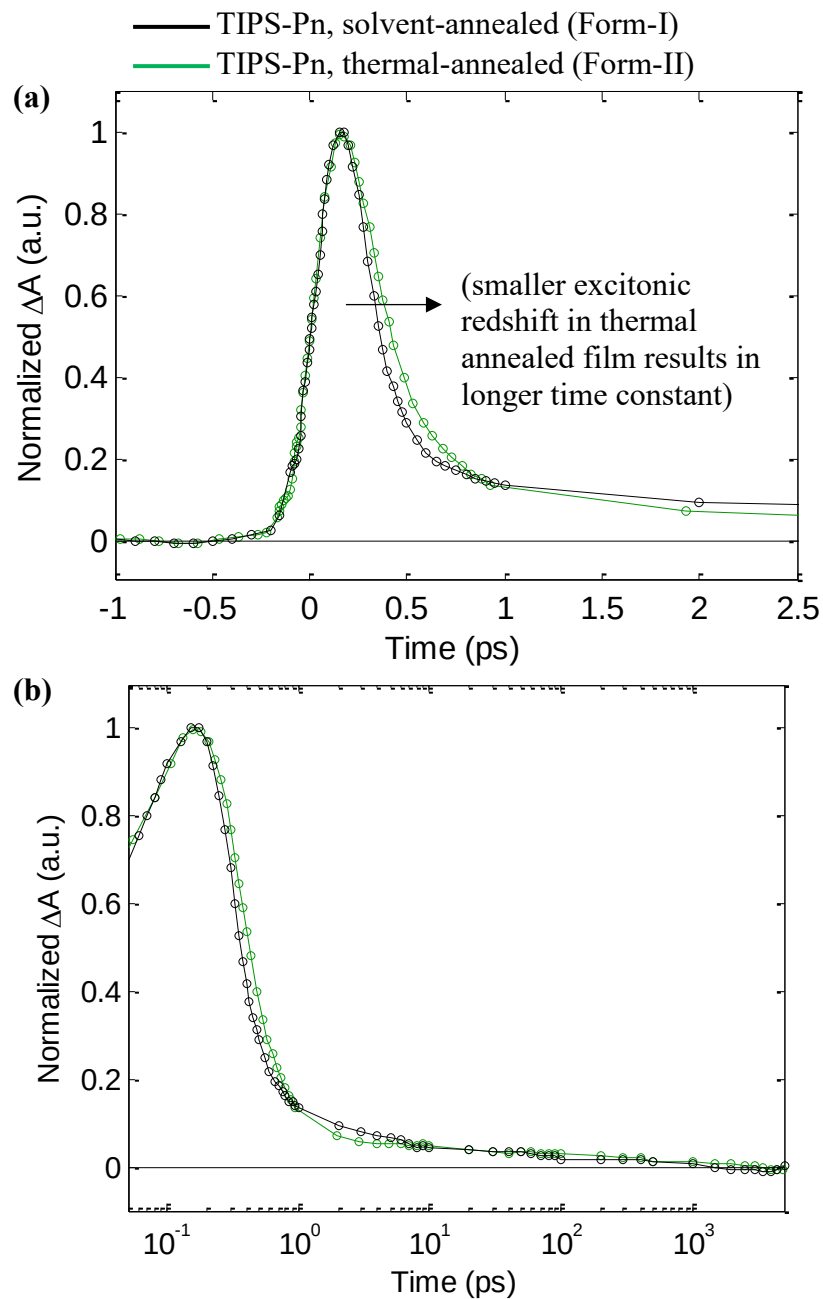


Figure A-5: Singlet decay kinetics in TIPS-Pn films measured using their mid-infrared absorption signals presented on a **(a)** linear time axis and on a short timescale and **(b)** logarithmic time axis and on a longer timescale.

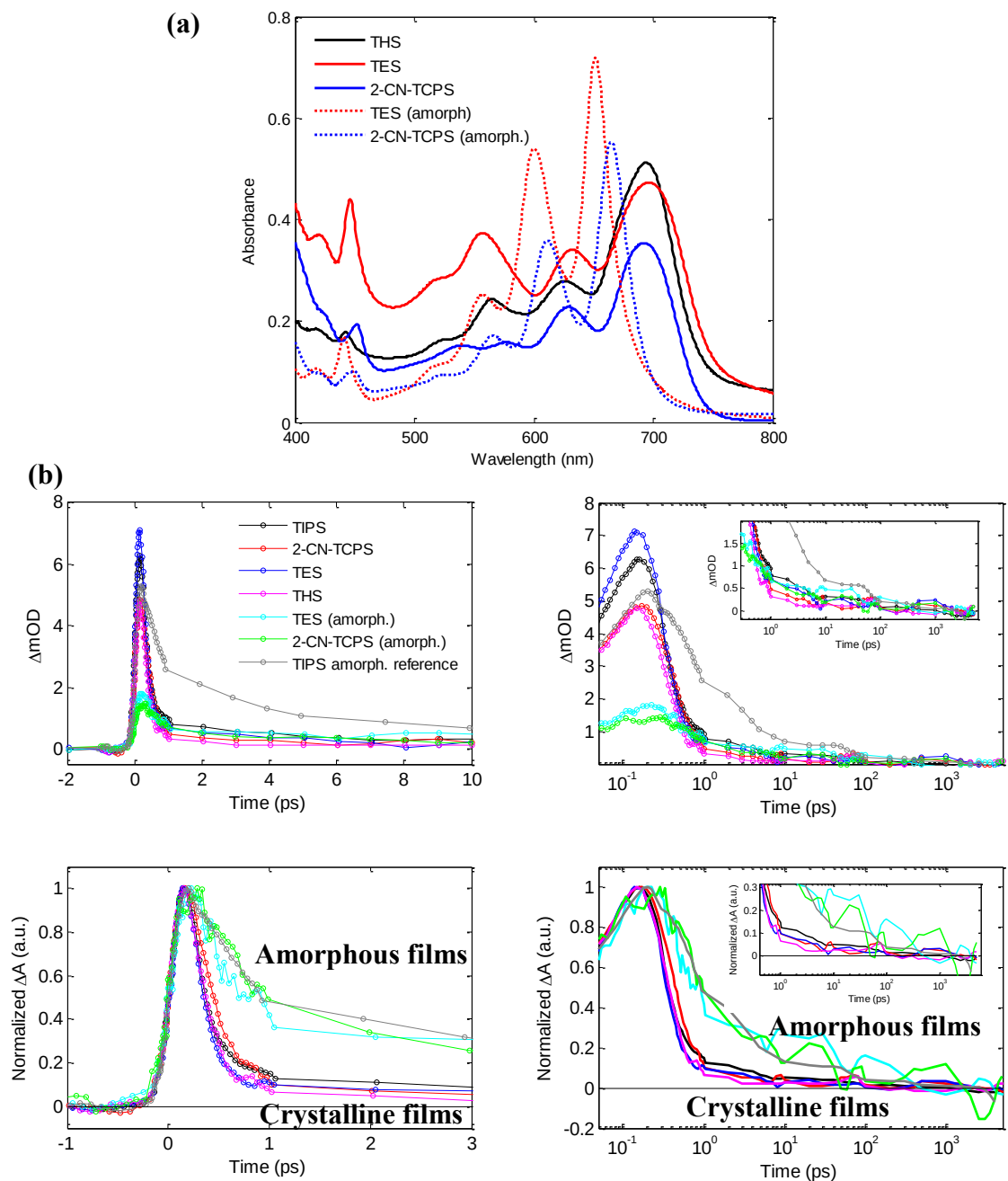


Figure A-6: (a) Film absorption spectra for a variety of pentacene derivatives. All films were crystalline unless noted. (b) Ultrafast mid-infrared absorption kinetics of singlet excitons in each film excited at ~ 650 nm and using an incident energy density of $\mu\text{J}/\text{cm}^2$. The kinetics are plotted on different time axes and as either raw data or normalized data.

Note that the data for the amorphous films in **Figure A-6** were particularly noisy because they become annealed from the laser very rapidly and so only a few scans were taken; it is necessary to change the probed spot on the sample frequently for amorphous films.

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Christopher Grieco earned a B.S. degree in Chemistry and a B.S. degree in Applied Mathematics at Rochester Institute of Technology in 2012. During his time there, he carried out research under the mentorship of Professor Christopher J. Collison on developing a polarization-resolved fluorometric method for optically characterizing nanoscale ordering of semiconducting polymers in thin films. While attending Rochester Institute of Technology, he had the opportunity to present a poster of his research at the Materials Research Society Fall Meeting & Exhibit (2011; Boston, MA).

In the summer of 2012, Christopher became a graduate student in Chemistry at the Pennsylvania State University, where he joined the research lab of Professor John B. Asbury. There, Christopher's research focused on time-resolved optical spectroscopic investigation into the fundamental photophysical processes underlying semiconducting device functionality, and their relationships to nanoscale structure. His work spanned several research fields focusing on organic photovoltaics, singlet fission sensitizers, and inorganic light-emitting diodes. While attending Penn State, he had the opportunity to present posters and seminar talks at several professional conferences including: American Chemical Society Central Regional Meeting (2014; Pittsburgh, PA), Time Resolved Vibrational Spectroscopy International Conference (2015; Madison, WI), American Chemical Society Mid-Atlantic Regional Meeting (2016; Riverdale, NY), American Chemical Society National Meeting & Exposition (2016; Philadelphia, PA), American Chemical Society Mid-Atlantic Regional Meeting (2017; Hershey, PA), and Singlet Fission Workshop (2017; Lyons, CO). In addition, his work at Penn State contributed to several publications:

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This dissertation serves to complete Christopher's work as a doctoral candidate at The Pennsylvania State University.