Photodimerization of Organic Semiconductors in the Strong Coupling Regime

By Richard Puro

An undergraduate thesis advised by Dr. Oksana Ostroverkhova.

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Abstract

Organic semiconducting materials have emerged in the last few decades as viable alternatives to inorganics in broad applications from field effect transistors to LEDs to solar cells. Organics provide many benefits over inorganics such as flexibility, sustainability, and reduced cost. However, these materials are more susceptible to degradation in the presence of light and oxygen, which prevents them from fully replacing silicon in electronics. Recently, techniques from polariton chemistry have been utilized in condensed matter physics research to tune material properties, such as chemical reaction rates, using interactions between light and matter. Light-matter interactions have been shown to reduce rates of oxidation in two organic semiconductors, P3HT and TDBC. This thesis explores the effects of strong light-matter interactions on photochemical reactions in acene-based semiconductors. The photodegradation of soluble derivatives of pentacene and tetracene, two benchmark organic semiconducting materials capable of singlet exciton fission, are explored under the influence of strong light-matter coupling in optical microcavities.

The dominant degradation process in cavities is determined to be photon-induced dimerization, a process possible even in anaerobic conditions. Despite well over a century of research into the dimerization of acene-based molecules, a novel photodimerization reaction in 5,12-Bis((triisopropylsilyl) ethynyl) tetracene films is reported, resulting in an alkyne dimer as opposed to the butterfly dimer that, in tetracene, had been observed exclusively prior to this report. Optical properties and chemical structure of this new dimer species are presented. Rates of both alkyne photodimerization in tetracene films and photodimerization in pentacene films are found to increase under the influence of strong coupling. The ability to enhance chemical reaction rates in organic semiconductors, which often proceed through charge or energy transfer, with optical microcavities may enable enhanced photogeneration efficiency in solar cells, which proceeds through similar processes. Better understanding polaritonics in singlet fission materials could also allow for benefits in the efficiency of solar cells and photodetectors. Furthermore, investigating chemical reactions of acene-based molecules in the strong coupling regime yields new insights into how polariton states interact with molecular states. Techniques presented can be utilized to probe the effects of light-matter coupling on the dynamics of various exciton reservoirs, which could have broad applications in future research of these and other materials.
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Section 1. Introduction

1.1 Motivation and Objectives

Organic semiconductors have begun to replace silicon in many applications from field effect transistors to LED displays to solar cells. They are cheaper, easier to work with, and more sustainable than inorganics, but they are also considerably less stable in the presence of light and oxygen. When exposed to light and oxygen, organics undergo chemical reactions that deactivate them optically and electronically, which leads to device failure. Currently, degradation is avoided by keeping organic semiconducting films in vacuum during device fabrication and encapsulation before device use. However, requiring these materials to be kept in vacuum is difficult and detracts from the benefits presented by organics. Furthermore, this does not protect them from anaerobic decay processes activated through interactions with light. Finding new ways to make organics more stable has the potential to significantly improve their marketability.

The goal of this thesis is to better understand the degradation pathways in common organic semiconductors, which may lead to methods of making these materials more stable. Increasing the photostability of organic semiconductors will allow them to replace silicon in many electronic devices that do not require high charge carrier mobility. The project focuses on the effects of strong light-matter interactions in optical microcavities, called exciton-photon coupling, in which a resonant photon interacts with excitons (excited molecules) trapped inside the cavity leading to formation of light-matter hybrid states called polaritons. Strong light-matter coupling has already been shown to influence chemical reaction rates in organic semiconductors, including reactions with oxygen, which facilitate molecular degradation [1,2,36-38]. Certain excitonic states, particularly the singlet and triplet exciton states, facilitate the reactions that are responsible for photodegradation. The polariton states introduced by strong coupling may or may not participate in chemical reaction processes, but these states do influence the populations of singlet and triplet states and thus may reduce or enhance degradation rates.

Previous studies have investigated the effects of strong light-matter coupling in systems that do not exhibit a property referred to as singlet fission [1,2]. In singlet fission materials, molecules in the excited singlet state can transfer some of their energy to a neighboring ground
state molecule to create two triplet states from one photoexcitation [3,7]. This process drastically shifts the equilibrium concentrations of molecular excited states, and thus should have an impact on photodegradation rates. For this reason, organic semiconducting materials that exhibit efficient singlet fission have been chosen for this study. Singlet fission is a common property of many high-performance organic semiconductors, and is beneficial in the efficiency of solar cells, so studying systems capable of singlet fission is essential for many practical device applications.

Different systems also have different photobleaching pathways. These pathways each depend on different excited states, and thus could be affected by strong coupling differently. The photobleaching pathways of the materials studied here are common in other semiconducting materials, making it possible to use results for the decay pathways studied to infer what the effects of strong coupling will be on other materials decaying through similar processes. The results of this thesis will allow researchers and engineers to determine if strong coupling will enhance the stability of many other organic semiconducting materials.
1.2 The Acenes

Organic semiconductors (OSCs) are materials composed of pi-bonded carbon and hydrogen bases, which form either crystalline structures or amorphous (non-crystalline) films. These materials are commonly synthesized in labs, but in some cases can occur naturally; for example, the organic semiconductor Xylindein can be extracted from certain fungi [39]. Though reported as early as the 1910’s, research into the practical applications of such materials has exploded in only the last two decades [3]. They have become prevalent in broad electronic applications such as field effect transistors (OFETs), light emitting diodes (OLEDs), solar cells, and many more. Motivation to use OSCs over their inorganic counterparts comes from their low cost, as well as relaxed requirements for large-scale molecular order and substrate structure. Whereas silicon fails if not fabricated in pristine crystalline structures, many organic materials naturally pack together in ways that facilitate charge transportation. This allows manufacturers to make semiconductor thin films using fast, cheap solution deposition techniques, such as spin casting and drop casting (discussed in Section 2.1.2), which are far more efficient than fabricating flawless crystalline structures. Moreover, since crystallinity in OSC films is not required for many applications, devices made from these materials are flexible and hence more durable. Samsung has recently used this quality to make phones with bendable OLED displays [4].

The materials explored in this thesis are structured around backbones of acene molecules, shown in Figure 1.1. Acenes are a class of organic semiconducting materials composed of linearly fused benzene rings in the form of a backbone structure. The alternating single and double bonds between carbon atoms allow for high electron mobility, which is why these materials are useful as semiconductors. Acenes are also known to be capable of exhibiting polariton formation at room temperature due to their high oscillator strength, discussed in Section 1.3. This thesis utilizes the medium length acenes tetracene (Tc) and pentacene (Pn).

![Fig 1.1. Chemical structures of the acenes. All hexagonal shapes represent benzene rings, composed of six carbon atoms bonded in alternating double and single bonds. Figure from Ref. [27].](image-url)
1.2.1. Side groups

The excited state energies and packing structures of acenes can be manipulated by adding side groups to acene backbones. In Figure 1.2, two (triisopropylsilyl)ethynyl (TIPS) side groups have been added to the central benzene ring of a pentacene backbone. This molecule is denoted as TIPS-Pn; in general, if a side group R is added to an OSC, like Pn or Tc, then the resulting molecule is denoted R-Pn or R-Tc.

![Chemical structure of 6,13-Bis((triisopropylsilyl) ethynyl) pentacene (TIPS-Pn), composed of a pentacene backbone with two TIPS side groups attached through triple bonds to the central benzene ring of the pentacene parent molecule. Figure from ChemSpider.](image)

The addition of side groups affects the molecule’s excited state energies and how the molecule interacts with its environment. The effects depend on the side group and the molecule used as the backbone. In the case of TIPS-Pn, the addition of the TIPS side group increases the stability of pentacene in solution, lowers the triplet energy level, and promotes solubility in organic solvents. Similarly, in the case of TIPS-Tc, the addition of the TIPS side group increases the molecule’s solubility. Different side groups can be added to tune material properties in different ways.
1.2.2. Singlet Fission

Molecular excitons are quasiparticles composed of a negatively charged electron in an excited energy state and the positively charged electron hole left behind but can essentially be thought of as molecules with an excited electron. These electronic excitations come in different types depending on electron spin; excitons can also transition between different excited states by changing spin. When a molecule absorbs a photon, an electron in its valence shell is initially excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) without changing spin. This excited state is referred to as a singlet, shown in Figure 1.3.a. Singlets are spin-0 states that are very short lived with lifetimes around 10 ns and fluorescence in the visible range. The excited electron can change spin through either a process called intersystem crossing (ISC), which is not relevant to this thesis, or through singlet fission (SF), which is far more efficient. This spin-1 exciton is referred to as a triplet. Triplets are much longer lived with lifetimes on the order of 10 µs and fluorescence in the IR range.

![Figure 1.3](image)

**Fig 1.3.** a) Energy level diagram showing electron spins in singlet and triplet exciton states. b) Singlet fission process in TIPS-Tc, in which a singlet exciton reacts with a ground state molecule to form a triplet-pair state. The triplet-pair state then evolves into two separate triplet states through spin evolution and spin dephasing. Figure from Ref [12].

Singlet fission is a process whereby a molecule in the excited singlet state and a molecule in the ground state exchange energy to form two triplet excitons. Generally, singlet fission is only possible if the singlet energy is greater than twice the triplet energy so that energy is conserved in the process, but this is not always required. In TIPS-Tc for example, the singlet energy is 2.3 eV, and the triplet energy is 1.25 eV. Even though the singlet energy is 200 meV lower than twice the triplet energy, these molecules undergo singlet fission very efficiently. As shown in Fig. 1.3.b, intermediate states are necessary for endothermic singlet fission. In TIPS-Tc, the intermediate states are bound triplet-pairs, which have energies lower than the singlet energy, but can still convert into two separate triplets through spin dephasing. Reference [23] argues these triplet-pairs
are the intermediates in singlet fission, but others have argued that it is excimers, not triplet-pairs, that enable endothermic singlet fission [12-14]. Excimers are states composed of two molecules that are bonded together only when there is an electronic excitation but are not bonded when both molecules are in the ground state. Excimer states have a distinct emission spectrum, but do not appear different from monomers in absorption because the molecules are not bonded until they absorb a photon.

The efficiency of singlet fission depends strongly on the spacing of molecules that have not undergone photobleaching reactions (referred to here as active molecules) in semiconductor films. Molecules with many active neighbors undergo singlet fission efficiently, but isolated molecules cannot because they need a nearby ground state molecule with which to exchange energy. The average spacing between active molecules grows as the film bleaches, since many molecules are deactivated through photobleaching reactions and act as spacers between active molecules. This leads to a decrease in singlet fission efficiency throughout the bleach. A process of long-distance singlet fission through an oxygen intermediary has been proposed for TIPS-Pn [24], but in general singlet fission is not possible if the average spacing between molecules is high.

In practical applications, singlet fission is important in the efficiency of solar energy production. In solar cells, singlet fission allows one absorbed photon to induce two charge carriers, which can double the efficiency of energy production. This provides a possible route to overcome the Shockley-Queisser limit on the efficiency of singlet-junction solar cells [14]. Endothermic singlet fission is even more exciting because it allows the molecules to essentially harvest energy from their environments. This is the reason we will focus on two efficient singlet fission materials, TIPS-Pn and TIPS-Tc.
1.2.3. Photodegradation

All organic semiconductors degrade in the presence of light and oxygen through chemical reactions with $O_2$. In many OSCs, anaerobic photodegradation processes have also been reported [8,10,11], although oxidation is generally dominant when oxygen is present. Oxidation in acenes is a triplet activated process where a triplet exciton sensitizes singlet oxygen ($^1O_2$) through direct energy transfer, then $^1O_2$ reacts with another triplet exciton to form endoperoxide (EPO), shown in the left path of Figure 1.4.a. In pentacene and higher acenes, there is also a singlet activated EPO formation process, shown in the right path of Figure 1.4.a, where an electron is transferred from the excited singlet state of Pn to $O_2$ creating a Pn$^+$ cation and an $O_2^-$ anion. In either case, $O_2$ fuses to the central benzene ring of the acene backbone to form endoperoxide (EPO). The addition of $O_2$ to the acene backbone breaks the alternating single and double bond structure that allows the acenes to act as semiconductors, resulting in either one or two naphthalene chromophores (acenes composed of two benzene rings) as opposed to the desired pentacene or tetracene chromophores. This results in deterioration of electronic properties and effectively deactivates the parent molecule.

Fig 1.4. a) Two mechanisms of endoperoxide (EPO) formation. The left path is a triplet-activated mechanism in which acenes sensitize and react with $^1O_2$ to form EPO. The right path is a singlet-activated mechanism proceeding through electron transfer. The electron transfer process is only possible in Pn and higher acenes. b) Photon-induced dimerization, referred to as photodimerization. Figure from Ref. [25].

EPO can be reversed through thermolysis or even by simply letting the photobleached molecules rest in the dark; if recovery does not happen quickly enough, the molecule will cleave irreversibly. Oxidation can be limited in practice once films have been fabricated by encapsulating the films between two solid layers of polymer or metal. We show in Section 3.2 that TIPS-Tc films
between 45-nm thick silver mirrors have no oxygen available to them and do not undergo oxidation. In devices such as solar cells, active OSC films are regularly a middle layer between many other solid films, so oxygen availability should be negligible. Because of this, oxidation is mainly a concern in the device fabrication process as it can degrade OSCs rapidly in solution before film fabrication, or in the solid phase before other solid layers are deposited on top.

While EPO formation in acenes can be eliminated once devices have been fabricated, photon-induced dimerization, where two monomers bond to form a dimer (Figure 1.4.b), is always a prevalent decay mechanism. Since dimerization is activated solely through interactions with light, it cannot be mitigated in solar cells or organic light emitting diode (OLED) displays since these devices cannot be kept in the dark. Dimerization in pentacene has been shown to occur primarily when excitation is in the UV range [25], but in tetracene rapid dimerization is observed even with excitation in the visible range. The butterfly dimer shown in Figure 1.4.b is the standard dimer reported in the literature [8,10,11]. An equivalent dimer structure is also generally reported for tetracene. Here, conjugation of the acene backbones in each parent molecule is broken in the same way as in EPO, which again leads to deactivation of optical and electrical properties. The singlet state has been reported as the catalyst of photodimerization in the acenes, with dimerization proceeding either through reactions between singlet excitons or through the singlet-fed excimer state [11,15,21].
1.3 Strong Coupling

Strong light-matter coupling is a process induced by interactions between a strong oscillating electric field and molecular excitons with high oscillator strengths. If the energy of the electric field, induced by a photon, is near the transition energy of the molecules, then the light and matter interact so strongly that they must be treated as a single light-matter state with energy levels that differ from the energies of the photon or the exciton. This coupled state can be treated as a single quasiparticle and is referred to as a polariton. The energy levels of the polariton are called the upper and lower polariton branches, shown in Figure 1.5. In the case of many exciton systems, there will be additional polariton branches called middle polaritons. OSCs have uniquely high oscillator strengths enabling strong coupling even at room temperature, which is true for few other classes of materials. Strong coupling has been shown to influence scores of material properties from resonance energy transfer [32,33] and exciton transfer [34,35] to chemical reaction rates [1,2,36-38].

Fig 1.5. Energy level diagram of coupled states. Optical cavity mode refers to the energy of the photon resonant in the cavity. Exciton absorption transition refers to the electronic transition energy of the coupled molecule.

Much of the data presented in this thesis come from semiconductor thin films inside Fabry-Perot microcavities, illustrated in Figure 1.6. These cavities consist of two planar mirrors with a thin film separating them. Film thickness is on the order of 100 nm, which corresponds to half the wavelength of visible light in dielectrics with high indices of refraction. When light is incident on the cavities, only light with an appropriate wavelength to resonate in the cavity penetrates the silver mirrors. This light then creates a standing electromagnetic wave inside the cavity, referred to as a cavity photon or cavity photon mode, which interacts with molecules in the cavity more strongly than a photon passing through a bare film. As discussed above, when the energy of the cavity
photon is near the energy of the electronic transitions of the molecules, the molecular excitons couple to the cavity photon mode creating polariton states.

![Fig.1.6. Fabry-Perot microcavity composed of two silver mirrors separated by a thin film of optically active material. Mirror spacing is on the order of 100 nm. Figure from Ref. [26].](image)

The strength of the interaction between the excitons and cavity photons is characterized by taking reflectance measurements at various angles of incidence. As the angle of incidence of light used to illuminate the cavities is increased, the in-plane wavevector $k$ increases, as does the cavity photon energy $\hbar\omega_c$. Plotting the photon energy or wavevector against the energy of reflectance dips, which show the energy levels of the coupled system, gives a dispersion curve for the cavity. In Figure 1.7, the dark black curves correspond to the dips in the reflectance spectra from the cavity at various angles. Grey curves correspond to the exciton (flat line) and cavity photon energies. The coupled systems produce a reflectance dip above the energy of the exciton/photon, and a dip below the energy of the exciton/photon. The difference in energy between these two dips when the exciton and photon energies are equal is called the Rabi splitting. Large Rabi splittings (typically above 100 meV in OSCs) correspond to strong light-matter interactions. If the polariton and exciton did not interact whatsoever, the upper and lower branches would hug the exciton and photon energies, giving zero splitting. The dispersion curve in Figure 1.7. displays avoided crossing behavior, whereby the energy curves appear to avoid crossing each other, which is characteristic of a strongly coupled system.
Fig 1.7. Dispersion curve of a strongly coupled exciton-polariton system. Energy of absorbance peaks (y-axis) is plotted against the energy difference between the cavity photon and molecular excitons (x-axis). The separation between the upper branch and lower branch at $h\omega_c - h\omega_0 = 0$ is referred to as the Rabi splitting. Figure from Ref. [28].
1.4 Optical Measurement techniques

Optical properties of fluorescent thin films, such as the quantity and wavelength of light absorbed and emitted, can reveal much about the film’s molecular excited states. The main optical measurements utilized in this thesis are absorbance, reflectance, and photoluminescence (PL) measurements. In absorbance and reflectance measurements, white light is passed through the films and collected on the opposite side or the same side to determine what wavelength of light is absorbed or reflected. In PL measurements, the film is excited by a laser and the fluorescence is collected. Examples of absorbance and PL spectra for TIPS-Tc are given in Figure 1.8. The peaks in the absorbance curve show the energy of each electronic transition. Peaks are spaced by similar energy gaps with each successive gap absorbing less light. The energy progression of absorbance peaks shown here is referred to as a vibronic progression, with the lowest energy absorbance band corresponding to the 0-0 electronic transition, the second corresponding to the 0-1 transition, and so on. A similar trend can be seen in the PL spectrum, but is obscured by a large bell-shaped emission band centered at 1.9 eV. The vibronic progression in the PL corresponds to emissions from singlet excitons and the broad bell-shaped curve corresponds to the emissions of excimers. Tracking how the areas of excimer emissions and singlet emissions change as the sample bleaches is one example of excited state dynamics being revealed by PL. The absorbance of the film as the molecules bleach will decay since fewer molecules are actively absorbing, which allows us to track the concentration of molecules as the samples bleach. Reflectance measurements are generally only used to track cavity dispersion as described in Section 1.3.

Fig. 1.8. Absorbance and emission (PL) spectra for TIPS-Tc; molecular structure in upper left inset.
1.5 Polymer-Host Matrix

Highly concentrated films of TIPS-Pn have a tendency to form aggregates, a process by which clusters of molecules experience intermolecular interactions that alter optical and electronic properties of films. For our investigation, it is beneficial to spread out TIPS-Pn molecules in films to minimize the chance of aggregation. This can be done by embedding the active molecules in a polymer-host matrix composed of poly(methyl methacrylate) (PMMA), a polymer with minimal absorbance and PL in the visible range. A polymer-host matrix can be thought of as a film made of spaghetti and meatballs, where the meatballs are TIPS-Pn molecules spaced out randomly among PMMA spaghetti. This contrasts with a pristine film, which would be made entirely of TIPS-Pn meatballs mashed together into a meatloaf-like film. This allows for measurements on “isolated” molecules, as opposed to more complex aggregated ones, and results in more rapid photodegradation. TIPS-Tc molecules do not generally aggregate, so embedding them in a polymer-host matrix is not necessary.

Films composed of TIPS-Pn in PMMA are characterized by their average intermolecular spacing. The lower the average spacing, the more likely it is for the films to contain aggregates. If the average intermolecular spacing is too low, there will not be enough molecules absorbing and emitting photons to detect and there will not be enough excitons to observe strong coupling, so the intermolecular spacing needs to be optimized. Spacings of either 1 nm or 2 nm are generally chosen. A formula for the average spacing of molecules in a polymer-host matrix can be derived using the model shown in Figure 1.9.

![Figure 1.9. Model for the average intermolecular spacing (d) of TIPS-Pn molecules. Figure from Ref. [25].](image-url)
The TIPS-Pn molecule is treated as a point particle surrounded by some number of PMMA molecules. It is assumed that there is considerably more PMMA than TIPS-Pn so that neglecting the volume of the TIPS-Pn molecule does not significantly affect the volume of the unit spheres. Let the ratio of PMMA molecules to TIPS-Pn molecules be defined as

$$f \equiv \frac{N_H}{N_{Pn}} = \frac{C_H}{C_{Pn}},$$  \hspace{1cm} (1.1)$$

where $N$ is the number of molecules, and $C$ is the concentration in solution. Each unit sphere contains $f$ PMMA molecules, each of which has volume

$$V_H = \frac{M_H}{N_A \rho_H},$$  \hspace{1cm} (1.2)$$

where $M_H$ is the molar mass of the host molecule PMMA, $\rho_H$ is the mass density of PMMA, and $N_A$ is Avogadro’s number. The total volume of each sphere is then

$$V = f \cdot V_H = \frac{4\pi}{3} \left(\frac{d}{2}\right)^3,$$  \hspace{1cm} (1.3)$$

After some algebra, the formula for average intermolecular spacing in a polymer-host matrix is found to be

$$d = \sqrt[3]{\frac{6M_H}{N_A \rho_H \pi f}}.$$  \hspace{1cm} (1.4)$$
Section 2. Methods

2.1 Sample Fabrication

2.1.1 Summary

Glass slides are coated with a 45-nm Ag film through silver evaporation. Thin films of organic semiconductors (~100-200 nm) are then deposited from solution onto the silvered slides through spin-casting. Some organic semiconductors, like tetracene and its derivatives (R-Tc), are deposited from solutions containing only R-Tc and the organic solvent, resulting in pristine R-Tc films. Other semiconductors, like pentacene and its derivatives (R-Pn), are easier to measure optically when they are deposited in a polymer-host matrix of poly(methyl methacrylate) (PMMA) so that the molecular concentration is much lower. These are deposited from solutions containing both TIPS-Pn and PMMA in appropriate relative concentrations to create films with average intermolecular spacings from 1-2 nm. These films are then capped with an additional 45-nm Ag layer to create a Fabry-Perot microcavity. Ag layers are deposited such that only half of the slide is coated by each layer in an offset pattern to create four distinct regions with or without silver above and below OSC films; non-cavity regions serve as control samples in this report.

After sample fabrication, absorbance and photoluminescence (PL) measurements are performed on each region as the film is irradiated with laser light (generally 633 nm or 532 nm light) to induce photodegradation. White light is used in addition to laser light to measure the absorbance of films over the course of the bleach. As the films degrade, the number of active molecules absorbing incident photons and emitting PL decays, so photodegradation is tracked using either total integrated PL or total integrated absorbance. The total amount of light emitted or absorbed over time then gives the dynamics of the concentration of active molecules. Using an electronic shutter, each sample can be bleached for specific periods of time and the films can be allowed to recover in the dark between bleaches to track recovery.
2.1.2. Cavity Fabrication

Rectangular glass slides are cut into 25 mm × 25 mm squares using a carbide rolling cutter blade. Slides are then cleaned by rinsing with acetone, isopropyl alcohol, and deionized water, then dried with compressed air to remove all particulates. A 45-nm Ag layer is deposited onto each slide through silver evaporation, in which an electric current heats Ag in vacuum causing it to sublimate. The Ag gas then condenses onto the glass slide. By placing a metal plate, called a shadow mask, over half of each slide, deposition can be blocked from certain regions of the slide. This is implemented so that each slide is only half covered in Ag with the rest bare.

Silvered glass slides are then placed in a spin caster (WS-400-6NPP/LITE) and suctioned to the center of the spinner, shown in Figure 2.1.a. The silvered glass slides are spun at angular velocities between 1000 RPM and 6000 RPM. Approximately 80 μL of solution is dropped from a pipette onto the silvered slide immediately after it begins to spin. The solution evenly coats the slide and dries into a solid film, like that shown in Figure 2.1.d. Solution preparation is outlined in Section 2.1.3. The spin casting speed can be varied to alter the thickness of the resulting film. Faster spin casting speeds correspond to thinner films according to

\[ t \propto \frac{1}{\omega} \]  

for \( t \) the film thickness and \( \omega \) the spin casting speed. Film thickness is intentionally varied by manipulating spin casting speed across different samples to produce a range of cavity thicknesses.

Fig 2.1. Diagram of spin-casting procedure. The glass slide is first suctioned to the spin-caster (a), then as it begins to spin either solution containing R-Tc or solution containing both PMMA and R-Pn is dropped onto the slide (b). The solution spreads out (c) and dries into a solid film (d). Figure from Ref. [25].
During the spinning process, all solvent from the deposited solution evaporates, leaving a solid film of either pure semiconducting material, or semiconducting material embedded homogeneously in a polymer film. Films are allowed to dry, then are removed from the spin caster. Due to low photostability, films of TIPS-Tc degrade in a matter of hours from exposure to ambient room light. Therefore, these films must be wrapped in tin foil to prevent light exposure so they can be used over the span of several weeks. This precaution is not required for TIPS-Pn films, but keeping TIPS-Pn films covered between uses still prolongs their lifetimes.

Finally, an additional 45-nm silver layer is deposited on top of the semiconducting film using the same type of shadow mask described previously but offset from the first mask. This results in three regions of interest, each with a 45-nm Ag layer above and/or below the semiconducting film. Regions with no Ag above or below semiconducting films are not discussed in this thesis. The three important sample types for this report are depicted in Figure 2.2. Films capped with Ag are denoted T (top mirror samples); films on top of Ag are denoted B (bottom mirror samples); films between Ag layers are denoted C (cavity samples). Strong coupling is present only in C samples. Oxygen availability is greatly reduced in T and C samples due to the Ag cap.

![Diagram of sample types](image)

Fig. 2.2. Diagram of sample types. a) Top mirror sample, denoted T. b) Bottom mirror sample, denoted B. c) Cavity sample, denoted C.
2.1.3. Solution Preparation

All materials used dissolve readily in organic solvents. Dry shards or powders of TIPS-Pn or TIPS-Tc are weighed, then added to 1 mL of toluene in a 4 mL vial. Solutions are sonicated in warm water for 20 minutes to make sure they are adequately mixed. In TIPS-Pn films, where low concentration films are desired, poly(methyl methacrylate) (PMMA) is weighed separately and added to the solution. The relative concentration of R-Pn to PMMA is chosen to result in films with a specific average intermolecular spacing, generally either 1 nm or 2 nm. Lower average spacings result in more aggregation in films, which changes the optical properties, but also leads to larger absorbance and PL signals and higher coupling to cavity photon modes (the coupling strength is proportional to $\sqrt{N}$ for $N$ the number of molecules). Since in the case of TIPS-Pn, aggregated molecules behave differently from non-aggregated “isolated” molecules, aggregation is minimized to study the behavior of only isolated molecules. For TIPS-Tc, molecules do not aggregate even in pristine films, so this is not necessary.

Spin casting results in films containing only PMMA and TIPS-Pn after all the solvent has evaporated. This means the average intermolecular spacing depends only on the relative concentrations of PMMA and TIPS-Pn, not their concentrations relative to the solvent. Their concentrations relevant to the solvent influence the film thickness though, so PMMA concentrations of 0.4 M, 0.2 M, or 0.1 M are chosen to create thick, medium, or thin films, respectively (all are referred to as “thin films”). Varying PMMA concentration has a larger influence on film thickness than varying spin casting rate, so it is used for bulk changes, such as halving or doubling film thickness. For cavity fabrication, 0.4 M PMMA solutions are used, so in 1 mL of solution, $4 \times 10^{-4}$ moles of PMMA are added. Thinner films may be desired for special cases and other applications, so in these cases solutions of either 0.1 M or 0.2 M PMMA can be used. The amount of TIPS-Pn to be added is calculated using equation 1.4,

$$d = \sqrt[3]{\frac{6M_H}{N_A\rho_H\pi}} \left(\frac{mol_H}{mol_{PN}}\right).$$  \hspace{1cm} (1.4)

In equation 1.4, derived in Section 1.5, $M_H$ and $\rho_H$ are the molar mass and mass density of the host polymer, $N_A$ is Avogadro’s number, and $mol_H$ is known to be $4 \times 10^{-4}$ mol in solutions for fabricating cavities. Choosing $d$ (in units of nanometers) allows the equation to be solved for
$mol_{Pn}$. The molar masses of PMMA and TIPS-Pn are used to determine the weights of each to add to the organic solvent. Sonication in warm water is especially important for solutions containing PMMA because the polymer is not as easily dissolved in organic solvents as TIPS-Pn and TIPS-Tc. Before sonication, the solutions contain large PMMA granules.
2.2 Optical Measurements

Photoluminescence (PL) and reflectance measurements are used to determine the concentration of active molecules over time as films bleach and to probe the recovery of molecules when films are allowed to rest in the dark. In PL measurements, films are irradiated with laser light from either a 532 nm frequency-doubled Nd:YVO$_4$ laser (Verdi-5, Coherent, Inc.) or a 633 nm HeNe laser. Excitation wavelength is chosen based on which wavelength is best absorbed by films, which maximizes fluorescence and degradation. Films of TIPS-Pn are irradiated with 633 nm excitation, whereas films of TIPS-Tc are irradiated with 532 nm excitation. Fluorescence is directed into an optical fiber, which leads to an Ocean Optics spectrometer. The spectrometer generates PL spectra every 50-250 ms depending on integration time. The integration time is optimized to maximize PL signature while avoiding spectrometer saturation. Over time, the total PL emitted decreases, which indicates the relative concentration of active molecules has decayed. In practice, materials that are capable of singlet fission, like Pn and Tc, exhibit a rise in PL before the total PL begins to decay, as is shown in the inset of Figure 2.3.a. Fluorescence is quenched at low intermolecular spacings by singlet fission, which converts emissive singlet excitons into less emissive triplet excitons. Figure 2.3.a illustrates an example of a PL trace from TIPS-Pn. The result of integrating each of these traces and plotting the integrated PL against time is shown in the inset.

![Fig 2.3.](image)

Fig 2.3. a) Photoluminescence (PL) trace of dilute (2-nm intermolecular spacing) TIPS-Pn film at an arbitrary time. Inset: integrated PL over time as the film bleaches. b) Absorbance of pristine TIPS-Tc film at an arbitrary time. Inset: integrated absorbance over time as the film bleaches.

Absorbance measurements are taken using a white light source. White light is reflected off a 45-nm Ag film with no semiconducting layer on top as a reference spectrum. The silver slide is then replaced by an OSC thin film, which is also illuminated by the white light source. The
reflectance is calculated using equation (2.3), where \( R_X \) is the light spectrum reflected from the plain silver slide or the TIPS-Pn film on top of a silver slide, and \( B_g \) is the background spectrum in the dark.

\[
R = \frac{R_{PN} - B_g}{R_{Ag} - B_g}
\]  

(2.4)

Absorbance is then calculated as \( \text{Abs} = -\log R \). The full definition of absorbance requires knowledge of both \( R \) and transmission \( T \). However, since all white light is reflected from the rear Ag layer, what has been referred to as the reflectance is really what has transmitted through the semiconducting film and reflected off the rear Ag layer. Therefore, in this case \( T=0 \). Absorbance is a reliable indicator of molecular concentration and is relied on heavily for this purpose in Sections 3.2 and 3.4. The effects of singlet fission that produce an initial rise in PL do not apply to absorbance, so integrated absorbance measurements provide monotonic decays, like what is expected from the concentration of molecules over the course of a bleach (see inset in Figure 2.3.b).

Reflectance measurements are also used to quantify the strength of light-matter interactions in cavities. More specifically, varying the angle of incidence of white light changes the photon energy resonant in the cavity. By sweeping over a range of angles, a dispersion curve like the one shown in Section 1.3 can be generated. The coupling strengths between the cavity photon and each exciton are extracted from these dispersion curves. If no coupling were present, the reflectance dip corresponding to the molecular absorbance would not move as the cavity photon energy changes. In the presence of coupling the two reflectance dips appear to avoid crossing each other. The difference in energy between the two peaks at the point where the photon and exciton energies are equal is called the Rabi splitting of the system and characterizes the exciton-photon interaction strength.
Section 3. Results

3.1 Proof of Strong Coupling

Microcavities containing either pristine films of TIPS-tetracene (TIPS-Tc) or dilute films of TIPS-pentacene (TIPS-Pn) with average intermolecular spacings of 2 nm were fabricated as described in Section 2. Reflectance measurements were taken at varying angles of incidence (AOI) on a custom-built optical assembly, which allowed for angles of incidence of white light ranging from 20° to 80°. Varying the AOI changes the in-plane wavevector of the light, allowing dispersion curves to be generated by plotting the reflectance dips against the \( k \)-vector of the photons. Two such dispersion curves are shown in Figure 3.1 for films of TIPS-Pn (a) and TIPS-Tc (b). Colored points on each plot correspond to exact dip locations from reflectance measurements at each AOI. Horizontal dotted lines show the exciton energies; curved purple line shows the photon energy as the AOI increases. Reflectance peaks appear to avoid crossing one-another or the exciton energies, which is the anti-crossing behavior expected from strongly coupled systems.

![Fig. 3.1. Dispersion curves for a) TIPS-Pn cavity and b) TIPS-Tc cavity. Dispersion curves are generated by taking reflectance measurements at various angles of incidence (various cavity photon \( k \)-vectors) and plotting the reflectance dips (colored data points) against cavity photon \( k \)-vector. Right insets: Absorbance traces from bare films to show exciton energies.](image)

Angular reflectance measurements were fit with a coupled oscillator Hamiltonian python script written by Jonathan Van Schenck, a graduate student at Oregon State. Interaction strengths are shown as an inset in both figures. Generally, interaction strengths of >100 meV are considered to be in the strong coupling regime. All microcavities of TIPS-Tc are well into the strong coupling regime, but TIPS-Pn cavities are near the boundary between the weak coupling and strong coupling...
regimes. Coupling of 85 meV is likely high enough to observe strong coupling effects, but not effects as pronounced as in TIPS-Tc cavities.
3.2 Photobleaching of Tetracene in Microcavities

3.2.1. Photobleaching of Uncoupled Samples

Pristine, poly-crystalline films of TIPS-Tc were fabricated as outlined in Section 2, with a 45-nm Ag layer either between the film and glass substrate ($B$ samples), between the film and air ($T$ samples), or both ($C$ samples). Absorbance and emission spectra of unbleached $B$ samples are presented in Figure 3.2. The absorbance exhibits sharp peaks and is similar to the absorbance spectra presented for TIPS-Tc thin films in other reports [3,9-14]. Emissions exhibit a small vibronic progression, attributed to emissions from singlets, obscured by a broad single bell curve, attributed to excimers (pairs of molecules emitting as dimers). Considerable excimer emissions are expected from highly concentrated samples of TIPS-Tc [13,14], especially in poly-crystalline films with high intermolecular interaction.

![Emissions and Absorbance Spectra](image)

Fig. 3.2. PL and absorbance spectra for unbleached TIPS-Tc thin films. Inset: Chemical structure of TIPS-Tc. The emission spectrum is initially dominated by a broad single emission peak centered at 1.9eV, attributed to excimer emissions.

Endoperoxide (EPO) formation and photon-induced dimerization (photodimerization) have been demonstrated as the dominant, if not the only, two photodegradation processes in tetracene and other acenes [8,10,11,15-19]. The relative contributions from each decay process to the total photodegradation of films can vary greatly depending on molecular concentration, side-groups, parent molecule, etc. [11,19]. For this reason, the photodegradation rates of $B$ samples in air and in vacuum were measured, as outlined in Section 2. Samples bleached in air are denoted as $B^A$ and samples bleached in vacuum are denoted as $B^V$. In addition to allowing us to determine the relative contributions of each process to the total degradation of the films, this also allows us
to determine the dominant decay mechanism in $T$ and hence also $C$ samples, since $C$ samples will have the same oxygen availability as $T$ samples. We assume that EPO formation is impossible in vacuum (because it requires bonding to oxygen) and that both EPO formation and photodimerization are active when films are exposed to air.

![Image](Fig. 3.3. a) Absorbance of $B^A$ sample over time. Left inset: Cross section of $B^A$ sample. Right inset: Total integrated absorbance of $B^A$ sample plotted against $B^V$ sample. b) Absorbance of $T$ sample over time. Left inset: Cross section of $T$ sample. Right inset: Total integrated absorbance of $T$ sample plotted against $B^V$ sample.)

Comparison of $B^A$ and $B^V$ bleaches is shown in the right inset of Figure 3.3.a. The bleaches measured are not exponential decays or linear decays like have been presented in other studies [1,2] but are closer to power law decays, particularly in $T$ and $B^V$ bleaches. The effective decay rates for $B^A$ and $B^V$ bleaches, after correcting for excitation intensity (see Appendix II), are $1.10 \text{s}^{-1}$ and $9.42 \times 10^{-3} \text{s}^{-1}$ respectively. The photodimerization rate should not be affected by the presence of oxygen, so none of the increase in bleach rate can be attributed to photodimerization. Because of this, the $117 \times$ more rapid decay in the presence of oxygen can be attributed entirely to EPO formation being this amount more rapid than photodimerization.

In contrast to the significant difference in decay rate between $B^A$ and $B^V$ samples, the right inset in Figure 3.3.b shows there is negligible difference in bleach rate between $T$ and $B^V$ samples, which were bleached at the same excitation intensity. Were oxygen able to reach the TIPS-Tc film through the Ag cap or through the sides of the sample, or if some remainder oxygen were trapped in the film from the fabrication process, we would expect the bleach in $T$ samples to be more rapid than in $B^V$ samples. It is not unreasonable that $T$ samples would be isolated from oxygen as the top Ag layer was deposited in vacuum, so no oxygen should remain in the films after fabrication.
We conclude that EPO formation is impossible in $T$ and therefore also $C$ samples due to a lack of oxygen availability.

As additional confirmation that EPO formation is the dominant decay mechanism in $B^A$ samples while photodimerization is the only active mechanism in $B^V$, $T$, and $C$ samples, the recovery of each sample after bleaching was measured. When bleached films are allowed to rest in the dark for a period after bleaching, some of the molecules that went through photobleaching reactions “recover” by going through the reverse reaction. This means either molecules in EPO separate from the $O_2$ bonded to them, or molecules in dimers split back into monomers. Photoluminescence (PL) spectra of each sample immediately after bleaching (dotted lines) and after 10 minutes of recovery in the dark (solid lines) are shown in Figure 3.4. In $B^A$ samples, large recovery of singlet emissions was observed; in $B^V$ and $T$ samples, no recovery of singlet emissions was observed, but slight recovery of excimer emissions was present. It has been shown that EPOs are highly recoverable photoproducts [19], while dimers recover negligibly [15,19]. Slight recovery of excimer emissions in $T$ and $B^V$ samples, where photodimerization is likely the dominant decay mechanism, can be attributed to dimers separating into near-neighbor monomers, which then emit as excimers. The lack of singlet recovery and the similarity between $T$ and $B^V$ bleach rates imply that dimerization is the only significant decay mechanism in $T$ and $C$ samples.

![Fig. 3.4. Comparison of PL recovery in $B^A$, $B^V$, and $T$ samples respectively. Dotted spectra are taken after 5-15 minutes of constant irradiation. Solid spectra are taken immediately after an additional 10 minutes of relaxation in the dark.](image-url)
3.2.2. The Emergence of a New Dimer Species

Photodimerization of the acenes is one of the earliest known chemical reactions, reported as early as the mid-19th century [22]. Photodimerization in the acenes generally proceeds through a [4+4] cycloaddition, resulting in a butterfly-shaped dimer with the parent molecules bonded at two of their central benzene rings [8,10,11,15-17,19]. Formation of these butterfly dimers in tetracene results in a large (>100 nm) blue shift in the absorbance of the films [17]. Increased absorbance in the UV range is then generally reported for photodimerization of tetracene and higher acenes [8]. Butterfly dimerization does not produce new absorbance peaks in the visible range, like is shown in red in the bleached absorbance spectrum of Figure 3.5.a.

In stark contrast to the disappearance of absorbance in the visible range generally reported for photodimers of acenes, we report the emergence of an absorbance shoulder blue shifted by only ~10 nm. This is illustrated in Figure 3.5.a, which shows the unbleached absorbance spectrum for T samples fit with a single vibronic progression, compared with the bleached absorbance spectrum fit by the sum of two vibronic progressions separated by 49 meV. The proposed chemical structure for dimers resulting in such an absorbance spectrum is given as an inset in Figure 3.5.a and is similar to hexacene dimers reported by Anthony et al. [18]. This novel alkyne dimer species is the product of bonding between the TIPS side group of one TIPS-Tc monomer and the Tc
backbone of the other monomer. This results in conjugation being broken in the tetracene backbone of one parent molecule, like in a typical photodegradation product, and the other parent molecule being relatively unaffected. Computational simulations for this chemical structure in Gaussian predict a singlet energy 93 meV higher than that of unbleached TIPS-Tc. This energy difference qualitatively matches with the small observed blue shift of 49 meV.

Figure 3.5.a provides clear evidence that irradiation of T samples induces the formation of some photoproduct. The dimer described above is predicted to have the correct excited state energy to result in such an absorbance signature, though this could also be true for other photoproducts. Figure 3.5.b provides additional evidence that this photoproduct is indeed the dimer we have described. Throughout the bleach, excimer emissions from T samples decay rapidly. A comparison of the decay of isolated molecule absorbance with that of excimer emissions is presented in Figure 3.6 and shows the two have similar features in their kinetics. This may imply it is the pairs of molecules emitting as excimers that are most likely to convert into this photoproduct. It has been reported previously that dimers of acenes generally form through an excimer intermediate state [11,15,20,21], which supports dimers as the photoproduct in question. We conclude that we have observed the formation of a dimer species that has never been reported in TIPS-Tc.

![Normalized absorbance of isolated molecules (green) compared to normalized emissions from excimers (purple) in T sample over the course of a bleach.](image)

Fig. 3.6. Normalized absorbance of isolated molecules (green) compared to normalized emissions from excimers (purple) in T sample over the course of a bleach.
3.2.3. Photodegradation of Microcavity Samples

Microcavities containing TIPS-Tc thin films were fabricated as described in Section 2. Cavities with thicknesses ranging from 100 nm to 120 nm were made so a range of detunings could be tested. Detuning is the frequency difference between the cavity photon and molecular exciton \( (\omega_p - \omega_{ex}) \), which determines how much exciton and photon characteristic the lower polariton and upper polariton states have. The observed detunings range from zero detuned, meaning equal exciton and photon characteristics in the upper and lower branches, to highly red detuned, meaning mostly photonic characteristics with some excitonic characteristics in the lower branch and the opposite in the upper branch.

Strong coupling for these cavities was justified in Section 3.1.1. Interaction strengths were determined to be between 250 meV and 300 meV for all cavities. These interaction strengths are well within the strong coupling regime. Figure 3.7 shows the reflectance of a zero-detuned cavity over a 30-minute bleach period with the peak locations plotted against time as an inset. Little change was observed in the peak locations for the two middle polariton branches, whereas the lower polariton reflectance peak blue shifted by nearly 100 meV.

![Reflectance of 100 nm cavity over time. Vertical black bars represent exciton energies. Inset: Peak locations plotted against time. Horizontal black bars represent exciton energies, towards which the peaks trend as the films bleach.](image)

Though small, it should be noted that the highest middle polariton branch shown in the inset of Figure 3.7 rises over the course of the bleach after dropping initially. This behavior was observed in most bleaches in one or both middle polariton branches. The middle polariton branches are initially at slightly higher energy than the nearest exciton energy level, but over the course of
the bleach should red shift to approach the nearest exciton energy. This unexpected rise indicates the photodimer forming throughout the bleach can couple to the cavity photon modes just like the unreacted TIPS-Tc molecules. The addition of a new set of exciton energies slightly blue shifted from the original ones would add new middle polariton branches above those observed initially. Since the middle polariton peaks are somewhat shallow and broad, the sum of the two peaks would likely be resolved as a single peak with energy between that of the exciton from TIPS-Tc monomers and the exciton from TIPS-Tc dimers. The oscillator strength of the dimer excitons rises as more dimers form, causing the observed peak to appear to blue shift as the higher energy component of the peak becomes more prominent. This evidence that dimers couple to cavities allows Rabi splitting to be used to extract the concentration of all optically active molecules, whether or not they are part of a dimer.

Peak shifts were fit with a coupled oscillator Hamiltonian python script to extract the Rabi splitting of the coupled system as a function of time. The number $N$ of active molecules can then be determined from the Rabi splitting $\Omega$ as

$$\Omega \propto \sqrt{N}.$$  \hfill (3.1)

Bleaches of strongly coupled $C$ samples at various detunings are compared to the bleach of uncoupled $T$ samples in Figure 3.8.a. Due to interference effects, electric field strength and therefore excitation intensity varied based on cavity thickness. *Plots in Figure 3.8.a do not account for this effect.* Electric field intensity in each sample was determined using a python script. This was used to correct for excitation intensity as described in Appendix II.

Effective "destabilization factors", defined as

$$D := \frac{C\text{ bleach rate}}{T\text{ bleach rate}},$$  \hfill (3.2)

are plotted against detuning in Figure 3.8.b., with bleach rates corrected for excitation intensity. A clear dependence on detuning is observed. It is found that $C$ samples bleach $1.5 - 5 \times$ more rapidly than $T$ samples, with red detuned cavities bleaching at a higher rate than zero-detuned cavities. These destabilization factors are similar in magnitude to the stabilization factor of $3 \times$ reported by Peters *et al.* in strongly coupled P3HT cavities [1].
Fig. 3.8. a) Concentration of active molecules plotted against time for $T$ and $C$ samples. Excitation intensity varies across bleaches due to cavity effects, with the lowest in the most red detuned cavity and highest in the zero detuned cavity. b) Destabilization factor plotted against detuning for each cavity. Destabilization factors are reversed from the order they appear in (a) due to variable excitation intensity, which is corrected for in (b) but not in (a). Orange and red triangles both correspond to highly red detuned cavities.
3.3 Photobleaching of Pentacene in Microcavities

3.3.1 Photobleaching PL Dynamics

Thin films of TIPS-Pn embedded in a polymer-host matrix of poly(methyl methacrylate) (PMMA) were fabricated as outlined in Section 2. Average intermolecular spacings of 2 nm were chosen to minimize aggregation effects while keeping exciton density relatively high. Films with average intermolecular spacings of 1 nm exhibit highly aggregated absorbance characteristics and films with average spacings of 3 nm are too dilute to strongly couple to microcavity systems.

In most studies, as in Section 3.2 of this report, absorbance is used to track molecular concentration over the course of a bleach. However, this is not feasible in films that are too thin or too dilute to register a clear absorbance signal. In these cases, it could be advantageous to use the emissions (PL) signal to track molecular concentration, though this method has not been implemented before. Films used here are dilute enough that this novel method of tracking molecular concentration is necessary, so instead of tracking absorbance of films over time, we track the total PL emissions. An issue with using this technique for singlet fission capable materials, like TIPS-Pn, is that neighboring molecules do not radiate efficiently. Molecules close together undergo singlet fission and quickly become a pair of triplets. The lifetime of triplets is three orders of magnitude longer than that of singlets, so neighboring molecules emit negligibly compared to isolated molecules. For this reason, the total integrated PL of these films rises before beginning to fall. This is illustrated in Figure 3.9, which shows the evolution of the PL spectrum over time with the integrated PL as an inset.

![Figure 3.9](image)

Fig. 3.9. a) Emissions from B sample for the first 8 s of irradiation, during which the PL signal increases. b) Emissions for \( t > 8 \) s, during which the PL decreases. Insets: Integrated PL over time.
After the total integrated PL reaches its maximum and begins to decrease, the decay is very close to an ideal power law. This is similar to what was observed in bleaches of TIPS-Tc films. Figure 3.10 shows the integrated PL curves at various excitation intensities for a $B$ sample exposed to air plotted on a log-log scale. Straight lines on log-log plots indicate power law dynamics, i.e.

$$PL(t) = At^{-k}$$

(3.2)

for some constants $A$ and $k$. The decay constant $k$ gives the slope of the straight line and the scaling factor $A$ gives the height of the curve. It can be seen in Figure 3.10 that the slope of the decay curves, and therefore the exponent of the power laws, does not increase with increasing excitation intensity. It is the constant factor $A$ that increases with excitation intensity. This indicates that the exponent cannot be used to quantify bleach rates across different samples, since clearly a sample bleached at excitation intensity $I_0$ decays more rapidly than one bleached at intensity $I_0/10$.

![Fig. 3.10. Integrated photoluminescence for $B$ samples bleached at various laser intensities. Decays approximate a power law (linear on log-log axes) after 10-100 seconds of bleaching.](image)

To compare decay rates across different sample types quantitatively, we model the bleach with a Gamma distribution of decay rates. This model is derived in Appendix III, where we find the concentration of active molecules as a function of time will be given by

$$C(t) = A \int_0^m \beta^{k-1} e^{-\beta t} d\beta,$$

(3.3)

for $A$ a scaling factor, $k$ the power law exponent of the bleach, $\beta$ all possible decay rates, and $m$ the maximum decay rate of any population of molecules in the film. To account for the effects of singlet fission, which lead to an initial rise in PL, we subtract an exponential term from equation 3.3 giving

$$PL(t) = A \int_0^m \beta^{k-1} e^{-\beta t} d\beta - B e^{-\gamma t},$$

(3.4)
where $B$ and $\gamma$ are arbitrary constants. This model allows us to fit integrated PL curves with equation 3.4, then remove the exponential term to be left with equation 3.3, the concentration of active molecules over time.
3.3.2. Photodegradation of TIPS-Pn Films and Cavities

Microcavities containing films of TIPS-Pn in a polymer-host matrix of PMMA were fabricated as outlined in Section 2. Film thickness was measured to be 173 nm through ellipsometry. Since fabrication of TIPS-Pn samples was identical to fabrication of TIPS-Tc samples, we assume that no oxygen is present in these T and C samples either. This implies that photodimerization is the only active decay process in these samples, while both photodimerization and EPO formation are present in B samples. Strong coupling in the TIPS-Pn microcavity system was demonstrated in section 3.1.1 with an interaction strength of 84 meV.

Samples were photobleached with 633 nm laser excitation from a helium-neon (He-Ne) laser. Excitation in T and B samples came from the exposed side of the TIPS-Pn film. This resulted in similar excitation intensities in T and B samples, but lower excitation intensity in C samples where laser light passed through a 45-nm Ag layer. Raw bleach data from each sample type at equal laser intensity (but unequal excitation intensity) is shown in Figure 3.11.a. overlaid by fits of equation (3.4). Dotted lines show the concentration of molecules as a function of time with the effects of singlet fission removed, given by equation (3.3). Figure 3.11.b compares the normalized concentrations of active molecules over time in each sample.

![Fig. 3.11. a) Raw data with fit by equation (3.4) overlayed (solid lines) and corresponding fit by equation (3.3) (dotted lines). b) Normalized concentrations of active molecules over time for each sample type. Excitation intensity in T and B samples are equal, but excitation intensity in C sample is slightly reduced.](image)

We observe that the decay of active molecules in B samples is far more rapid than in C samples, which in turn is more rapid than in T samples. This is exactly what was observed in TIPS-Tc films, which have similar photophysics to non-aggregated TIPS-Pn films. The bleach rates in each sample are given in Table 3.1, corrected for excitation intensity. Correcting for excitation...
intensity makes the numerical value of the decay rate somewhat arbitrary, but the values relative to each other are significant.

<table>
<thead>
<tr>
<th>Sample</th>
<th>B</th>
<th>T</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decay Rate ($s^{-1}I_0^{-1}$)</td>
<td>4.476</td>
<td>0.026</td>
<td>0.470</td>
</tr>
</tbody>
</table>

Table 3.1. Bleach rates of $B$, $T$, and $C$ samples corrected for excitation intensity.

Decay rates given in Table 3.1 imply that EPO formation (in $B$ samples) is $172 \times$ more rapid than photodimerization when strong coupling is not present (in $T$ samples). This difference is on the same order of magnitude as the $117 \times$ difference between rates of EPO formation and photodimerization in TIPS-Tc films. Previous studies have reported low photodimerization rates in TIPS-Pn films under 633 nm excitation [25], so a large difference between the rate of EPO formation and the rate of photodimerization is expected. What is significant is that $C$ samples decay $18 \times$ more rapidly than $T$ samples. This strong coupling induced destabilization is within an order of magnitude of the destabilization observed in TIPS-Tc films. The effects of detuning were not investigated for TIPS-Pn films in this report.
Section 4. Discussion

4.1 Effects of Strong Coupling on Dimerization

We have observed that strong coupling enhances the rate of photodimerization in thin films of both pentacene and tetracene. In this section, we will justify this enhancement using rate equations. The argument provided is for TIPS-Tc because all relevant rates for TIPS-Tc are provided by Ref. [12]. The same argument applies to TIPS-Pn but will not apply to molecules that cannot undergo singlet fission. Since singlet fission is highly efficient in both pentacene and tetracene, the two molecules should have similar equilibrium excited state populations.

![Diagram](image)

Fig. 4.1. Connections between excited states in TIPS-Tc cavities used to model equilibrium excited state populations. Model from Ref. [12].

Photodimerization of acenes is known to be a singlet activated process, proceeding through the singlet-fed excimer state [11,15,20,21]. This implies a higher steady-state concentration of singlets in films will result in a higher rate of photodimerization. Figure 4.1 shows the rate model used to determine the steady-state population of each exciton reservoir. The relevant excited states are summarized below.

- **Excited singlet state** \( (S_1) \); spin-0 exciton state, into which all molecules are initially excited after photon absorption. The singlet lifetime is \( \sim 10 \, ns \).
- **Triplet-pair states** \( (TT_B) \) and \( (TT_D) \); bound states between two spin-1 triplet excitons. Singlet fission leads to an emissive (bright) triplet pair \( (TT_B) \), which can evolve into a non-emissive (dark) triplet pair \( (TT_D) \).
- **Excited triplet state** \( (T) \); spin-1 exciton state formed from triplet-pair states through spin dephasing or from singlets through intersystem-crossing. The triplet lifetime is \( \sim 10 \, \mu s \).
- **Lower polariton state** \( (LP) \); polariton state only present in microcavities.
Figure 4.1 does not include relaxation pathways for excited states, which are represented by rates $k_r$ (radiative relaxation) or $k_{nr}$ (nonradiative relaxation). The rate at which molecules are excited is given by $\Phi_{exc}$ and is only relevant in the $S'$ equation since all molecules are initially excited into the singlet state. All other relevant rate constants are shown in Figure 4.1. The set of differential equations yielded by this model for a strongly coupled system is as follows:

$$S' = \Phi_{exc} + k_{sf} (TT_B) - (k_{sf} + k_{pol-b} + S_1 k_r + S_1 k_{nr})S$$  \hspace{1cm} (4.1)

$$TT'_B = k_{sf} S + k_{-spin} T + k_{-dark}(TT_D) - (k_{-sf} + k_{dark} + k_{spin} + k_{pol-b} + TT_B k_r + TT_B k_{nr})(TT_B)$$ \hspace{1cm} (4.2)

$$TT'_D = k_{dark}(TT_B) + k_{-spin} T - (k_{pol-d} + k_{spin} + k_{-dark} + TT_B k_{nr})(TT_D)$$ \hspace{1cm} (4.3)

$$T' = k_{spin}(TT_B) + k_{spin}(TT_D) - (2k_{-spin} + Tk_{nr})T$$ \hspace{1cm} (4.4)

$$LP' = k_{pol-S} S + k_{pol-b} (TT_B) + k_{pol-d} (TT_D) - (LP k_r) LP$$ \hspace{1cm} (4.5)

Setting all derivatives equal to zero allows the equilibrium concentrations of each exciton reservoir to be determined. All rate constants are taken from the Supporting Information of Ref. [12]. The same set of differential equations can be corrected to apply to the uncoupled case by setting all $k_{pol-x}$ equal to zero and removing equation 4.5 (i.e., removing the $LP$ state from the model). Equilibrium solutions to the above set of differential equations in both the coupled and uncoupled cases at zero-detuning, with the total excited state concentration normalized to $10^4$, are presented in Table 4.1. The predicted equilibrium concentration of singlet molecules in the coupled system is a factor of 1.69 higher than for the uncoupled system, which matches well with the $1.5 - 1.8 \times$ higher photodimerization rate reported for strongly coupled TIPS-Tc films near zero-detuning.

<table>
<thead>
<tr>
<th>Excited state</th>
<th>$C_{coupled} \times 10^4$</th>
<th>$C_{uncoupled} \times 10^4$</th>
<th>$C_{coupled}/C_{uncoupled}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>1.38</td>
<td>0.82</td>
<td>1.69</td>
</tr>
<tr>
<td>$TT_B$</td>
<td>14.95</td>
<td>24.89</td>
<td>0.60</td>
</tr>
<tr>
<td>$TT_D$</td>
<td>6640.74</td>
<td>6651.16</td>
<td>1.00</td>
</tr>
<tr>
<td>$T$</td>
<td>3332.82</td>
<td>3333.05</td>
<td>1.00</td>
</tr>
<tr>
<td>$LP$</td>
<td>0.06</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 4.1. Equilibrium concentrations of relevant excited states in coupled and uncoupled systems.
The low equilibrium concentrations of $S_1$ excitons and $LP$ polaritons can be attributed to the incredibly efficient rate through which singlet fission proceeds and the short lifetime of polaritonic states. The rate constants for singlet fission and for the decay of $LP$ states dwarf all other rate constants by an order of magnitude or more, meaning $S_1$ and $LP$ states depopulate much faster than any others. The long lifetimes and inability to efficiently undergo reverse singlet fission allow dark triplet-pair excitons ($TT_D$) and triplet excitons ($T$) to dominate the steady-state concentration of the films.

The effects of strong coupling on oxidation, a triplet activated decay process, were not investigated in this report. The rate model proposed suggests that in singlet fission materials the addition of the $LP$ branch has a negligible effect on the steady-state concentration of triplets. This would imply that strong coupling would have no effect on the stability of these materials in oxygen-rich environments where oxidation is the dominant decay mechanism. However, as the films bleach and the average spacing between active molecules increases, the efficiency with which the material undergoes singlet fission will decrease, which will change the steady state concentration of each exciton reservoir. The effects of strong coupling on oxidation should be the subject of future investigations.
4.2 Effects of Detuning on Dimerization

The increase in singlet concentration allows us to explain why photodimerization — a singlet activated process — is enhanced in microcavities, but it does not explain why red-detuned cavities are less stable than zero-detuned cavities. The energy level diagram presented in Figure 4.2 shows the effects of detuning on connections between different exciton reservoirs.

$$\Delta = \hbar \omega_p - \hbar \omega_{ex}$$

In the case of zero detuning, the energy of the lower polariton branch is approximately $\Omega/2 = 125$ meV lower than the singlet energy of 2.3 eV. The energy of both triplet-pair states is $E_{TT} = 2.2$ eV [12], which closely matches the energy of the lower polariton branch. For red-detuned cavities where $\omega < \omega_0$, the energy of the lower polariton branch decreases to considerably less than $E_{TT}$, making transitions from these triplet-pair states to the $LP$ state much more efficient.

To add these effects to the model given above, we simply increase $k_{pot-b}$ and $k_{pot-d}$. It is expected that $k_{pot-s}$ would be negligibly affected since the energy difference between the $S_1$ state and the $LP$ state is large to begin with. By raising these two rate constants by only a factor of four (somewhat arbitrarily, but reasonably small) we find that $[S_1]_{coupled}/[S_1]_{uncoupled} = 3.79$, which matches well with our strongly red-detuned destabilization factors ranging from $3.0 - 5.0$. This small change in transition rate, within one order of magnitude, is not unreasonable for such a significant change in the energy difference between the $(TT)$ and $LP$ states. We conclude that in singlet fission materials, strong coupling increases the steady-state concentration of singlet.
excitons, which leads to enhanced photodimerization rates. The effects of detuning are likely unique to TIPS-Tc since in other systems the \((TT)\) energy and \(LP\) energy at zero detuning would not necessarily match so well. This enhancement may not apply to non-singlet fission materials, which should be the topic of future investigations.
Section 5. Conclusion

Electronic devices built around organic semiconductors are less expensive to buy and produce, less susceptible to damage, and more environmentally friendly than those built around inorganics. These materials have proven to be capable of replacing silicon, the current king of semiconductors, in applications ranging from field effect transistors to LEDs to solar cells. The major issues still preventing their widespread use include low charge carrier mobility and susceptibility to photo-chemical reactions with oxygen and with each other. With molecular instability still presenting a pressing bottleneck in the marketability of organic semiconductors, this thesis focused on understanding the mechanisms behind such instability and potential ways to mitigate them.

The field of polariton chemistry has recently emerged as a powerful tool in condensed matter physics, capable of manipulating scores of material properties from resonance energy transfer [32,33] and exciton transfer [34,35] to chemical reaction rates [1,2,36-38]. Light-matter interactions have even been used to protect two organic semiconductors, P3HT and TDBC, against oxidation [1,2]. The goal of this thesis was to explore how strong light-matter interactions affect the chemical reactions relevant to acene-based molecules, which have different photophysics from P3HT and TDBC. The interesting difference between the materials is the ability of pentacene and tetracene to undergo singlet fission, whereby two triplet excitons are generated from one singlet exciton. Singlet fission provides a possible route to overcome the Shockley-Queisser limit on singlet-junction solar cell efficiency [14], so research into materials with this property is of particular interest in sustainable energy applications.

It was determined that the chemical reaction leading to degradation in the strongly coupled microcavity systems studied was photon-induced dimerization, an anaerobic decay mechanism that has been well characterized in the acenes [8,10,11,15,21]. Despite the depth of research into the dimerization mechanisms of acenes, a novel dimerization product was reported in films of 5,12-Bis((triisopropylsilyl) ethynyl) tetracene (TIPS-Tc). The proposed photoproduct is an alkyne dimer resulting from bonding between the tetracene backbone of one parent molecule and the TIPS side group of the other. This dimer is unique in that conjugation is broken in only one of the two tetracene backbones, giving the dimer similar optical properties to the parent TIPS-Tc monomers.
Electrical properties and reactivity of the dimer were not investigated here but should be the topic of future research. With absorption in the visible range and one in-tact tetracene chromophore, this dimer could be useful in the same electronic applications as tetracene. However, having already undergone a photochemical reaction it may be less susceptible to further degradation than its parent molecules.

Strong coupling in optical microcavities was found to facilitate these dimerization reactions in both pentacene and tetracene films. This contrasts with the suppression of oxidation rates found in P3HT and TDBC, but the changes in rates were of the same order of magnitude. Dimerization reactions in the acenes are known to proceed through the singlet exciton state, while oxidation in P3HT and TDBC proceeds through the triplet exciton state. This is a major source of the difference between the effects of strong coupling in these two systems; strong coupling in non-singlet fission materials decreases the population of triplet excitons, whereas strong coupling in singlet fission materials increases the population of singlet excitons. The increase in singlet exciton population was confirmed in Section 4 through a rate equation argument, which showed the steady-state concentration of singlets in strongly coupled tetracene films is higher than in uncoupled films by the same factor as the increase in dimerization rate.

The techniques presented here can be utilized to probe the effects of polariton formation on various molecular excited states by observing rates of chemical reactions that depend on the excited state of interest. Just as the increase in photodimerization rates corresponded with the expected increase in singlet exciton population, measuring a change in oxidation rates could be used to determine the change in steady-state triplet exciton population. The same technique can also be utilized to explore excited state dependence of chemical reactions. For example, if strong coupling were known to increase singlet exciton population and decrease triplet exciton population in a given system, observing an increase in the rate of an unknown chemical reaction would suggest the reaction is catalyzed by singlets.

Going beyond the effects of strong coupling on photodimerization and other chemical reactions, what has been shown here is that polariton formation can be used to tune molecular excited state concentrations in pentacene and tetracene. The ability to manipulate the dynamics of molecular excited states with strong coupling may lead to enhanced exciton transfer and charge carrier mobility, photogeneration efficiency, singlet fission efficiency, and scores of other material
properties that depend on the molecular excited states explored in this thesis. Research into the effects of polaritonic states on many of these material properties have been conducted in other materials, but at this time properties of polaritons in pentacene and tetracene have been explored minimally; no studies on polaritonics in pristine pentacene films have yet been published. The results presented here suggest that cavity photochemistry in pentacene and tetracene, though largely overlooked until now, is an exciting area for future investigations.
References


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*ACS Omega*, **4** 13309-13318 (2019).
Appendix

I. Quantifying Decay Rates in Non-Exponential Decays

Non-exponential decay rates are commonly found in bulk photobleaching experiments [1,2]. These non-exponential dynamics can result from a spatial distribution of decay rates or from a time dependent decay rate. Spatial distributions of decay rates may arise from a non-uniform laser profile, randomly oriented molecular dipole moments causing preferential absorption in certain molecules, or effects of film depth on laser penetration to name a few [29]. Temporal distributions of decay rates may arise from depletion of oxygen or rapid bleaching of neighboring molecules leaving only isolated molecules that are not able to photo-dimerize. In any case, it is necessary to find ways of assigning numerical values of decay rates to non-exponential bleaches so that the effects of different environments on photostability can be compared quantitatively.

In exponential decays, decay “speed” is numerically described by either the material’s half-life or by its decay rate. Half-life is defined as the time it takes for a population to decay from its initial size to half its initial size, and decay rate is defined as the exponent $k$ in the equation

$$P(t) = P_0 e^{-kt},$$

which gives the size of the population at some later time $t$. What is useful about these values is that they scale linearly with the rate at which elements of the decaying population are lost; if a sample decaying exponentially were to lose twice as many elements in a given period (double in bleach “speed”), its half-life would be cut in half and its decay rate would double.

These same quantifiers cannot be applied to non-exponential decays. For example, in samples decaying according to a power law, given by

$$P(t) = P_0 t^{-k}$$

for $t \gg 0$, there is no well defined half-life because the time it takes for the sample to reach half its initial population is not the same as the time it then takes for the sample to reach one quarter its initial population. This implies the time it takes the sample to reach half its initial population does not scale with decay speed and is dependent on the initial size of the population. It was also shown in Section 3.3.1 that the decay factor $k$ does not scale linearly with decay speed either.

Using a top mirror ($T$) sample of pristine TIPS-tetracene, the bleach dynamics under various laser excitation intensities were measured and compared to determine the most accurate
way to compare non-exponential bleaches numerically. Relative laser intensities of 100%, 50%, and 20% power were tested. Laser intensity was measured by directing the beam through a beam splitter and optical chopper then into a photodiode. The peak-to-peak voltage was measured with an oscilloscope and laser intensity was tuned with a neutral density wheel to the desired relative intensities. Bleaches at each laser intensity are shown in Figure I.1. It was found that the slope of the bleach at any given time scales linearly with laser intensity. The beginning of each bleach was then fit by an exponential to give the initial decay rates. These initial decay rates come from the fits given by black dotted lines and are plotted in the inset of Figure I.1 against laser intensity. The initial decay rates scale linearly with laser intensity. These initial decay rates are used to quantify the effective bleach rate for all non-exponential decays in this thesis.

Fig. I.1. Bleach dynamics for T samples of pristine TIPS-Tc films excited at various laser intensities. The beginning of each bleach was fit with an exponential decay (black dotted lines) to extract the initial decay rates. Inset: Initial decay rates plotted against laser intensity.
II. Excitation Intensity Calculations

Exciting various sample types with equal laser intensities may result in unequal electric field intensities in semiconducting films due to enhancement in the vicinity of metal nanostructures. In microcavities, for example, multiple reflections from Ag mirrors results in interference effects, which can increase or decrease electric field strength in the cavity relative to if the second Ag mirror were not present. The same enhancement can be observed in metallic nanoholes or nanoparticles due to coherent oscillations of free electrons. It is therefore not valid to compare decay rates of different sample types even if the laser intensities used to bleach each sample are equal. This section describes how to correct for electric field enhancement in microcavities and near metallic nanostructures, as well as how to correct for varying absorption efficiencies at different wavelengths.

Reference [1] made similar calculations of excitation intensities in optical microcavities, so the procedure used here is adapted from their procedure. Three variables between sample types are believed to affect photodegradation rate: laser intensity, absorption efficiency, and electric field strength ($|E|^2$) in semiconducting films relative to if no Ag mirrors were present. Both absorption efficiency and $|E|^2$ in cavities are dependent on wavelength, but since excitation was always with either 532 nm or 633 nm laser light, only the absorption and $|E|^2$ at one particular wavelength need to be considered. The excitation intensity then simply becomes a product of the relative laser intensity, the absorption at the laser wavelength, and $|E|^2$ at the laser wavelength. The laser intensity is measured with a photodiode and optical chopper as described in Appendix I and the absorption of each film is measured directly as described in Methods. Only $|E|^2$ then needs to be determined theoretically.

Maxwell’s equations were solved for an electromagnetic wave incident on some geometry of Ag and semiconducting films with variable thicknesses using a python script written by Jonathan Van Schenck, a physics graduate student from Oregon State. Figure II.1.b shows the simulated electric field induced by 532 nm light (of intensity 1 arbitrary unit) in a 100 nm TIPS-Tc cavity with 45 nm thick Ag mirrors. The different colors represent photons with different phases. The electric field strength is determined by integrating $|E|^2$ across the cavity width.
Fig. II.1. a) Absorption of TIPS-Tc film with absorption at 532 nm marked. b) $|E|^2$ plotted against film depth in a 100 nm thick TIPS-Tc cavity for various photon phases.

The electric field intensity shown in Figure II.2.b is integrated over the cavity thickness to give the total electric field strength in the film. This is then multiplied by the absorption at the laser wavelength, shown in Figure II.1.a, and the relative laser intensity measured directly by a photodiode to give the relative excitation intensity, as defined in equation II.1. Bleach rates are then corrected through division by the excitation intensity.

$$\text{Excitation Intensity} \ := \ \text{Absorption coefficient} \times \int |E|^2 \ dx \times \text{Laser intensity}. \quad \text{(II.1)}$$
III. Modeling PL Dynamics in Pentacene Films

Power law fluorescence decay dynamics have been shown theoretically to arise from a spatial distribution of decay rates [29]. This distribution could come from such sources as a non-uniform laser profile, distribution of dipole orientations, or dependence of oxygen exposure on film depth. To model the distribution of decay rates, we choose to use a Gamma distribution. Gamma distributions of decay rates are commonly used to model product lifetimes in high-stress conditions [30], and result in power law dynamics. They are characterized by their probability density function (PDF)

$$f(t) = \frac{\beta^{\alpha}}{\Gamma(\alpha)} t^{\alpha-1} e^{-\beta t},$$  \hspace{1cm} (III.1)

where $\beta$ represents the decay rate and $\alpha$ will be treated as a fit parameter. The term $\Gamma(\alpha)$ is called the Gamma function and is just a normalization factor. We see from experimental data that our model should resemble a power law, so we manipulate the PDF to get such a model. Integrating equation III.1 over all possible decay rates gives

$$\int_0^\infty \beta^\alpha e^{-\beta t} d\beta = \frac{\alpha}{t^\alpha},$$ \hspace{1cm} (III.2)

Finally, by substituting $k = \alpha + 1$ into equation III.2, we obtain our model for the long-term behavior of the fluorescence decay:

$$PL(t) = A_1 \int_0^\infty \beta^{k-1} e^{-\beta t} d\beta = A_2 t^{-k},$$ \hspace{1cm} (III.3)

for some constants $A_1$ and $A_2$.

This derivation may seem unnecessary since we have arrived at a simple power law as our model. However, the integral over $\beta$ being unbounded implies that the distribution of decay rates in TIPS-Pn films goes to infinity, which is not the case. This can be corrected by adding an upper limit to the decay rates $m$, so that

$$PL(t) = A \int_0^m \beta^{k-1} e^{-\beta t} d\beta.$$ \hspace{1cm} (III.4)

The difference between equations (III.3) and (III.4) is shown in Figure III.1. Modeling the decay with a power law results in an asymptote near $t = 0$, but capping the distribution of decay rates at some finite value leads to more realistic behavior for the concentration of active molecules at values of time near $t = 0$. Modeling the behavior accurately at small values of time is especially
important since the initial decay rates for each bleach will be compared, as described in Appendix I. The decay modeled by equation (III.4) is similar in shape to the decays of absorbance observed in TIPS-Tc films.

Fig. III.1. Comparison of equation (III.3) and equation (III.4) showing the effects of capping the distribution of decay rates as a finite value. This change leads to more physically realistic behavior for small values of time.

To account for the initial rise in PL, we will subtract an exponential term from equation (III.4). The initial rise in PL is rapid enough that it can be modeled well by an exponential, even if the behavior is slightly non-exponential. This gives us our final equation for the PL as a function of time:

$$PL(t) = A \int_0^m \beta^{k-1} e^{-\beta t} d\beta - Be^{-\gamma t}. \quad (III.5)$$

In equation (III.5), the integral term represents the concentration of active molecules as a function of time and the exponential term represents the effects of singlet fission in inhibiting emissions near $t = 0$. Fits of equation (III.5) to bleaches of $B, C,$ and $T$ samples are shown in Figure III.2.

Fig. III.2. Fits of equation III.5 to experimental data from bleaches of $C, B,$ and $T$ samples. Inset: Blown-up fit to $B$ sample bleach.
This model allows for experimental data, including the initial rises in PL, to be fit by equation (III.5), then for the concentration of active molecules ($C(t)$) to be extracted by removing the exponential term. Our final model for this system is given by the set of equations

\[
PL(t) = A \int_{m}^{\infty} \beta^{k-1} e^{-\beta t} d\beta - Be^{-\gamma t}, \quad (\text{III.5})
\]

\[
C(t) = A \int_{0}^{m} \beta^{k-1} e^{-\beta t} d\beta. \quad (\text{III.6})
\]