

ILLUMINATING DYNAMIC PHENOMENA WITHIN ORGANIC MICROSTRUCTURES
WITH TIME RESOLVED BROADBAND MICROSCOPIES

by

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DEDICATION

To my family who gave me life, love, and the drive to never yield to indifference.

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ABSTRACT

Materials derived from organic chromophore subunits are currently at the forefront of academic and industrial interest. This strong interest is driven in part by the tunability of their extant properties through engineering of both the intra-molecular and inter-molecular structure. The structure of organic materials affects optoelectronic properties because organic chromophores are sensitive to dipole-dipole and charge-transfer coupling interactions. This sensitivity presents both opportunities for tuning functional properties through designing specific packing geometries, and liabilities arising from the disruptive effects of structural disorder. Many organic materials are built from weak noncovalent interactions between chromophores, leading solid-state deposition, and crystallization to be susceptible to microscopic variations in environmental conditions. Structural heterogeneity is regularly intrinsic to organic materials, and even self-assembled systems of covalently linked chromophores exhibit defects. Ergo, in order to disentangle the effects of structural heterogeneity from the inherent properties of the material, the study of organic materials must be anchored with techniques that are capable of correlating optoelectronic properties and excited state evolution with microscale morphological characteristics. We have employed broadband pump-probe microscopies, in conjunction with steady-state and time resolved fluorescence techniques, to examine the effects of structure and coupling on excited state dynamics in solid-state organic microstructures. The study of perylene diimide (PDI) materials revealed that kinetically trapping PDI (KT-PDI) enhanced long-range ordering and led to distinct excited state evolution, delocalized charge-transfer states and long-lived charge separated species. In the MOF PCN-222, excitation energy dependent excited state behavior was observed. Pumping the first excited state (Q-band) led to immobile excited states that were relatively unaffected by local defect densities, whereas pumping the second excited state (Soret-band) led to mobile subdiffusive excited state species whose lifetimes are significantly impacted by morphologically correlated defect sites. Finally, we present progress made toward the construction and utilization of a frequency modulated-femtosecond stimulated Raman microscope, yielding spectra that resolve the location of photoinduced anion formation in KT-PDI. The work presented herein highlights broadband time-resolved microscopy as a potent tool for studying the structure-function relationship and photophysical behavior in molecular solids, deepening our understanding of how structural characteristics influence excited state evolution.

CHAPTER ONE

INTRODUCTION

1.1 Introductory Remarks

Materials derived from organic constituents are a burgeoning topic for semiconductor and light harvesting technologies, and yet still contain potential that is untapped due to poor understanding of the microscopic scale structure-function relationship. The strong academic and industrial interest is focused on organic aggregates and thin films with pronounced π conjugation because these systems often exhibit strong absorption in the visible regions of the electromagnetic spectrum as well as efficient excited state transport properties, making them useful for optoelectronic or light harvesting applications. Conjugated organic materials are highly sensitive to dipole-dipole coupling and charge-transfer coupling, leading to the functional and optoelectronic properties depending heavily on molecular arrangement and solid-state packing geometry. The strong coupling interactions enable impressive functional tuning possibilities through engineering of solid-state molecular arrangements, but they also make organic materials exceptionally sensitive to structural heterogeneity. Microscopic techniques capable of resolving microscale structural characteristics and correlating them with optoelectronic functionality could provide valuable insights into the structure-function relationship and the mechanisms governing energetic evolution in conjugated organic materials, potentially improving material design principles.

Organic semiconductors have garnered significant attention in industry and research recently due to their distinct and desirable characteristics relative to inorganic materials. Many

advantages of organic aggregate semiconductors arise from their solution processability, enabling facile, low-cost, large-area manufacturing. The primary weakness of solid thin film deposition from solution is structural heterogeneity arising from variations in microscale crystallization conditions, which has a significant impact on the extant energetic and optoelectronic properties of the resulting material.¹⁻³ On the other hand, the sensitivity of organic materials to packing geometry also presents a unique opportunity where the properties of the material can be tuned through modification of the constituent molecular subunits. For π -stacked systems this is commonly achieved through modification of solubilizing side chain functional groups to affect the molecular packing during self-assembly.⁴⁻⁷ Organic chromophores can also be covalently bound in targeted conformations to achieve the desired electronic coupling.^{1, 8-11} This tunability at both intramolecular and intermolecular levels enables the possibility for precise manipulation of electrical properties, allowing for customized semiconductor materials tailored to specific application requirements. However, because organic semiconductors are sensitive to even small changes in packing geometry, localized structural heterogeneity can complicate accurate characterization of functional properties. Crucially, the impact of modification efforts needs to be identified with a high degree of both spatial and temporal precision in the solid state in order to correlate optoelectronic characteristics with morphology and delineate the influence of the inherent structural heterogeneity.

Broadband microscopes encompass a diverse array of techniques, each offering unique insights into the microscale properties of materials that are well suited to aid in the understanding of microscale structural heterogeneity and the structure function relationship. In the case of materials suited for optoelectronic applications, time resolved techniques such as transient

optical microscopy and femtosecond stimulated Raman microscopy (FSRM) have valuable utility because they directly probe the electronic states responsible for optoelectronic functionality. Because the performance of all optoelectronic materials is critically tied to the nature of excited state species and their efficient transport, the direct measurement of these species is essential to describe their behavior with a high degree of accuracy. Indirect measurements of transport, such as photoluminescence quenching^{12, 13}, terahertz photoconductivity and time-of-flight techniques¹⁴, are effective at describing materials with homogenous morphology; however, as mentioned above, organic materials consistently exhibit structural heterogeneity. Therefore, the direct measurement of excited state species with pump-probe microscopy is imperative to reveal microscopic morphologically correlated transport characteristics at the length scale of structural heterogeneity^{15, 16}. Furthermore, the addition of spectral resolution to time resolved microscopy facilitates the elucidation of more complex excited state evolution through spectral feature analysis. Despite the favorable capabilities, broadband pump-probe techniques are relatively sparse in published literature. This scarcity can be attributed to the intricate experimental setups and specialized expertise required for their implementation, as well as the associated costs and time investments.

This body of work summarizes the development and utilization of broadband microscopies to probe the excited state electronic and vibration properties of morphologically complex organic and hybrid systems. Theoretical background and relevant literature will be presented in the following sections of Chapter 1 to provide context and motivation for the following chapters. Chapter 2 describes a spectral comparison of the excited state evolution between two distinct morphologies of a perylene diimide molecular aggregate and the discovery

of unique delocalized charge-transfer exciton formation that progresses into a charge separated state in the morphologically controlled aggregate. Chapter 3 highlights the use of a range of time resolved and ensemble techniques in concert with broadband pump-probe to reveal how defect density and excitation energy manifests in divergent relaxation pathways for photoexcited species in the metal organic framework PCN-222. Chapter 4 discusses the extensive work in designing and testing a frequency modulated femtosecond stimulated Raman microscope (FM-FSRM). A discussion of perovskite nanoparticle synthesis and efforts to facilitate exciton delocalization with energetically aligned ligand exchange is included in Appendix A. Ultimately, Chapter 5 summarizes the progress present herein and provides pathways for future work to build on this foundation.

1.2 Coupling and the Nature of Electronic Excitations

Coulomb Coupling.

Within the solid state, intermolecular coupling plays an important role in determining the optoelectronic properties of organic materials^{17, 18}. In both aggregated molecular solids, and structured organic frameworks, the packing geometry shapes intermolecular coupling interactions and hence the nature and evolution of electronic excitation as well as the efficiency of excited state transport. In Chapter 2 we show how improved long-range order enhances coupling interactions in a perylene diimide aggregate and alters the ultimate trajectory of the excited state. Then, in Chapter 3 we are able to better understand the nature of excited state transport in a porphyrinic metal organic framework (MOF) by examining the influence of coupling interactions. To provide context for these findings, a general understanding of the dominant types of intermolecular coupling must be established.

An early theoretical treatment of molecular coupling was described by Michael Kasha, who presented a comprehensive description of molecular excitons based on long range Coulomb coupling in 1965 which was built from the framework of Frenkel exciton theory¹⁸. Kasha's theory describes how the relative orientation and distance between transition dipole moments in molecular aggregates affects the energy of exciton states. Fifty-three years later, Spano and Hestand outlined and summarized the advances made toward the goal of describing the relationship between molecular aggregate structure and photophysics¹⁹. Their contribution introduced consideration of vibronic coupling and short-range charge-transfer states facilitated through wave function overlap¹⁸. Though an in-depth analysis of these relevant theories is beyond the scope of this dissertation, a brief discussion beginning with Kasha's work and touching on Spano and Hestand's contribution will follow to provide context for the discussion of organic material tunability.

Kasha's model of a molecular exciton is built as a state interaction theory based in the Frenkel exciton model. In the Frenkel model, excitation is considered to be a neutral transition on an individual molecule but with coupling allowed between the ground and excited states of neighboring molecules²⁰. A strong dipole coupling case is assumed, and to satisfy the requirements of perturbation theory, intermolecular electron overlap is assumed to be small, allowing chromophores to retain individuality in the aggregate. In this way, the composite wavefunction and Hamiltonian eigenfunctions (Eq. 1.1 for a dimer, Eq. 1.4 for a 1D aggregate) can be described in terms of the electronic states of the components, where H_{ij} is the dimer Hamiltonian operator, H_i , and H_j , are the Hamiltonian operators for isolated molecules i , and j , and V_{ij} is the intermolecular perturbation potential.

Eq. 1.1

$$H_{ij} = H_i + H_j + V_{ij}$$

The van der Waals interaction energy between molecule i, and j leads to exchange of excitation energy. Taking the difference of these terms in the ground state and excited state Hamiltonian, Kasha extracts the exciton splitting term. The exciton splitting term describes the energetic effects of Coulombic dipole coupling (J_C), and has magnitude determined by the transition moment (μ) of the molecules, the displacement vector ($\vec{R} = R\hat{R}$) where R is the magnitude of displacement and $\hat{R}$ is the unit vector of the displacement, and the local static dielectric constant (ϵ).

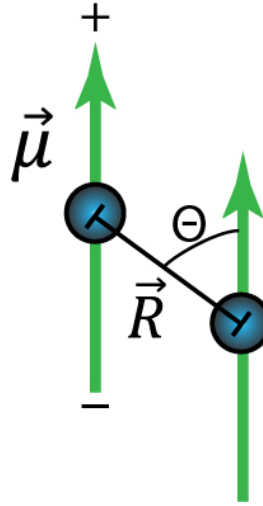


Figure 1.1: Point dipole moment approximation showing relevant variables in Eq 1.1.

In the case of a point-dipole dimer (Fig. 1.1) the vector-transition moment product from Eq. 1.2 can be simplified, and J_C is described by Eq. 1.3^{19, 21}.

Eq. 1.2:

$$J_C = \frac{\mu_1 \cdot \mu_2 - 3(\mu_1 \cdot \hat{R})(\mu_2 \cdot \hat{R})}{4\pi\epsilon R^3}$$

Eq. 1.3:

$$J_C = \frac{\mu^2(1 - 3\cos^2\theta)}{4\pi\epsilon R^3}$$

From this description, it is apparent that the sign and magnitude of the exciton splitting term between molecules is a function of not only the distance, R , but also the relative angle between dipole moments (θ).

In a molecular dimer two delocalized excited states composed of in and out-of-phase linear combinations of two localized excited states are split by $4|J_C|$. The in-phase (symmetric) state shows an enhanced transition dipole moment of up to $\sqrt{2}$ relative to the monomer. On the other hand, the out-of-phase (antisymmetric) state is optically dark due to a cancellation of transition dipole moments. J_C is stabilizing and negative, known as J-coupling, at angles of θ from 0° (head to tail configuration) to the so called “magic angle” of 54.7° . In J-type aggregates the symmetric state energy is reduced, leading to a redshift in the monomer absorption spectra. At the magic angle, the molecular coulombic coupling is zero and has no effect on the excitation energy or absorption intensity. At larger angles of θ , J_C becomes positive (H-coupling) for the in-phase delocalized state, reaching its maximum when the dipole moments are side by side at $\theta=90^\circ$. These configurations are termed H-type aggregates, and the optically allowed transition is elevated to a higher energy and blue shifted relative to the monomer and antisymmetric state. The radiative decay rate is likewise strongly affected by the exciton splitting term. In, J-aggregates the symmetric state is lower in energy than the out-of-phase state resulting in enhanced radiative coupling and superradiance²². Conversely, in H-aggregates due to symmetry constraints, the lower energy out-of-phase state has no direct radiative coupling to the ground state. Rapid intraband relaxation from the optically allowed in-phase state to the optically dark out-of-phase state results in a strongly reduced radiative rate. This effect is limited to the radiative rate, and H-aggregates have been shown to have high fluorescence quantum yields

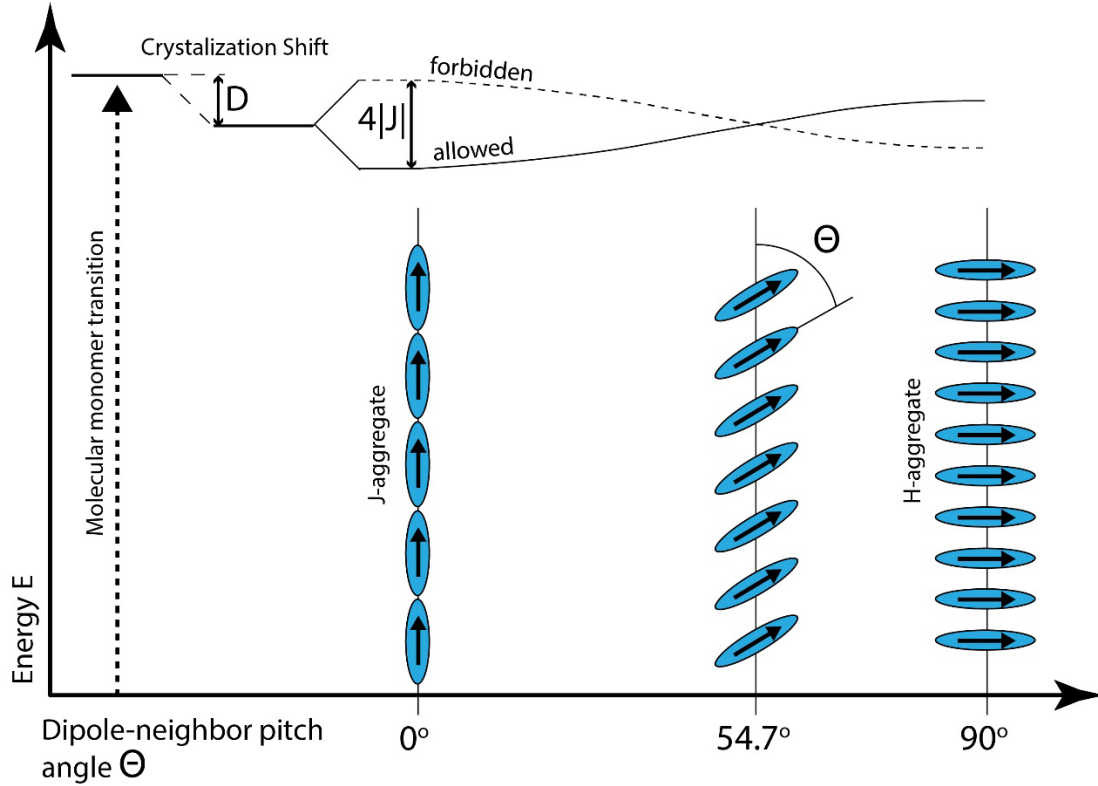


Figure 1.2: Representation of the energetic effects of monomer aggregation and crystallization showing the energetic effects and spectral shift arising from the relative dipole pitch angle. The energetic crystallization offset D is representative of the changing dielectric background from the gaseous and crystal environment.

when the radiative decay rate is large relative to the non-radiative decay rate.²³

Moving beyond the simplest case of the molecular dimer, we consider the Frenkel molecular exciton Hamiltonian for a linear aggregate of N -coupled chromophores. The energetic effects as a function of the intermolecular pitch angle and crystallization are shown pictorially in Figure 1.2. The Hamiltonian can be expressed with Eq. 1.4, where $\hbar$ is taken to be unity so energy and frequency can have equivalent units^{19, 21}.

Eq. 1.4:
$$H_{ex} = E_m + D + \sum_{m,n} J_{m,n} |m\rangle \langle n|$$

E_m is the gas-phase monomer $S_0 \rightarrow S_1$ transition energy, and D is the gas to crystal energy shift resulting from nonresonant excited state stabilization from neighboring molecules. $J_{m,n}$ is the resonant Coulomb coupling between molecules m and n , where the ket $|n\rangle$ represents a local excited state, in which the n th chromophore is excited to the S_1 singlet state with all other molecules remaining in the ground state S_0 (ie. $|n\rangle \equiv |g_1, g_2, \dots, e_n, \dots, g_N\rangle$, where g is a ground state molecule and e represents a molecule excited to the singlet state).

The eigenstates of this Hamiltonian are wavelike and can be described with a dimensionless wavevector $|k\rangle = \frac{1}{\sqrt{N}} \sum_n e^{ikn} |n\rangle$ with allowed k values of $0, \pm \frac{2\pi}{N}, \pm \frac{4\pi}{N}, \dots, \pi$. The Fourier component of the Coulombic coupling (J_k) is therefore described by Eq. 1.5 where under periodic boundary conditions the sum is independent of m and considering only nearest neighbor interactions reduces to Eq. 6.

$$\text{Eq. 1.5} \quad J_k \equiv \sum_n J_{m,n} \cos(k(n - m))$$

$$\text{Eq. 1.6} \quad J_k = 2J_c \cos(k)$$

The spectral phenomena predicted by Kasha's theory of Coulomb coupling (J_c) are clear from the energy dispersion curves that result from Eq. 1.5. J-aggregates which have a negative exciton splitting term will have a minimum energy exciton at $k=0$ and H-aggregates, with positive J_c , will have the minimum excitonic energy at $k=\pi$. The $k=0$ exciton is optically bright leading to J-aggregate and rapid radiative decay due to superradiance which manifests because the radiative decay rate scales as the square of the transition dipole moment, and in J-aggregates the transition dipole moment scales as $N^{1/2}$ (N =number of chromophores in the aggregate).¹⁹ The photoluminescence of H-aggregates from $k=\pi$ excitons is suppressed due to conservation of momentum requirements. Emission in H-aggregates must therefore be phonon mediated and this

constraint results in their characteristic emission and absorption profile where the 0-0 transition is weak relative to the 0-1 and other vibronic transitions. The presence of the low amplitude nominally forbidden 0-0 transition is a result of disorder effects and thermal activation which leads to the transition becoming partially allowed. The actual temperature dependence of the 0-0 transition amplitude depends on the exciton bandwidth, and also the aggregate order, via the exciton coherence length and correlation length²⁴.

Charge-Transfer Coupling.

In addition to vibronic coupling, further intermolecular coupling interactions can result in perturbation of excitonic energy and appreciable impact on photophysical properties¹⁹.

Wavefunction overlap can lead to charge-transfer-mediated intermolecular coupling, which is a result of a two-step process whereby a charge is transferred from one molecule to another through a higher energy virtual charge-separated state (Fig. 1.3). Also called superexchange coupling, the coupling arises from a linear combination of probabilistic state distributions that facilitate the dissociation of local excitations into charge-transfer (CT) states, described in detail by Spano and Hestand in 2017.¹⁸ Wavefunction overlap decreases exponentially with distance; however, aggregate systems, built from π -stacked monomers, are often close enough (~ 3.5 Å) that electronic wavefunction overlap is significant and the magnitude can be comparable to or even exceed Coulombic coupling¹⁸. With the assumption that the Frenkel and CT exciton states are energetically well-separated the superexchange interactions can be treated perturbatively. The charge transfer integrals give rise to effective short-range exciton coupling described in Eq. 1.7.

$$\text{Eq. 1.7} \quad J_{CT} = -2 \frac{t_e t_h}{E_{CT} - E_{S_1}}, \quad |E_{CT} - E_{S_1}| \gg |J_C|, |t_e|, |t_h|$$

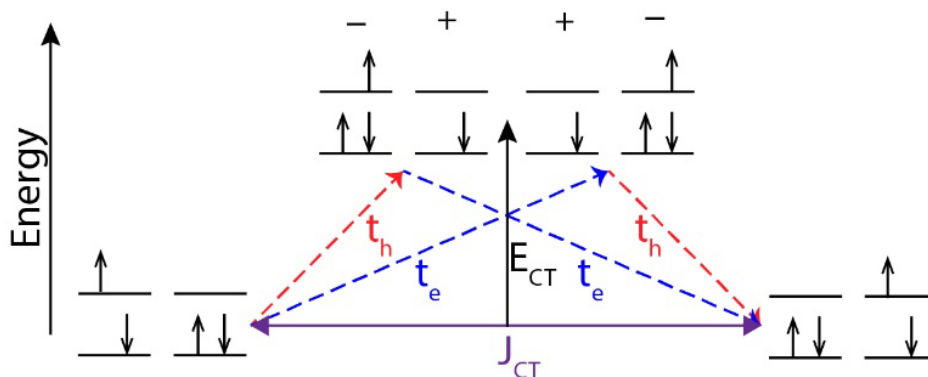


Figure 1.3: Simplified energy level diagram showing charge transfer interactions between neighboring chromophores. Superexchange coupling arises from a sum of the two virtual CT pathways.

Where E_{CT} is the energy of the charge transfer exciton, t_h and t_e are the hole and electron transfer integrals respectively, and E_{S_1} is the energy of the singlet localized Frenkel exciton. A simplified energy level diagram showing the CT pathways through a virtual CT intermediate state is shown in Figure 1.3. The values of t_e and t_h are hypersensitive to the transverse registry of π -stacked chromophores, because they are derived from the spatial overlap of neighboring LUMOs and HOMOs respectively.²⁵ The sign of charge transfer coupling is dependent on t_e , t_h , and $E_{CT} - E_{S_1}$, but if we assume that the CT state is higher in energy than the singlet state then J_{CT} is negative or “J-like” when $t_e t_h > 0$ and positive or “H-like” when $t_e t_h < 0$.¹⁹ The intense spatial sensitivity results in J_{CT} having strong nodal dependence. For instance, in perylene diimide the nodal distribution of the HOMO and LUMO results in 4 sign changes of J_{CT} from both transverse and longitudinal displacement where J_C only changes sign once, transitioning from H to J coupling through longitudinal displacement.

The fundamentals of intermolecular coupling theory form the basis for the tunability of organic material beyond direct chemical modification and informs design decisions for the

engineering of specific use cases. For instance, in light harvesting and solar cell applications, an ideal material would be a strong absorber in the visible, and rapidly transport energy to a charge separation interface with minimal radiative loss. For this application, aggregates dominated by H-type interactions, with strong excitonic coupling 0-but suppressed emission rates would be ideal. H-type aggregates with sufficiently strong CT exciton character to favor spontaneous charge separation and enough coupling to facilitate long range transport could be of particular benefit. On the other hand, for OLED applications, materials dominated by J-type interactions are preferable for emissivity with strong excitonic coupling to improve conductivity.²⁶ The application of organic semiconductors for device applications necessitates the use of solid thin films which is where the primary challenge for this goal emerges. Due to the complex interplay between J_C , J_{CT} , the changing dielectric background and the effects of structural heterogeneity, on the properties of an engineered material are impossible to predict with perfect accuracy and must be characterized experimentally.

1.3 Tuning Organic Materials

The established importance of intermolecular coupling and solid-state packing configurations has motivated extensive research on how adjustment of synthetic and deposition strategies affect the resulting properties of an organic material²⁷⁻³⁰. In contrast to inorganic semiconductors where the interconnecting bonds are primarily covalent or ionic in nature, organic materials and semiconductors are held together with weak noncovalent interactions. The weaker attraction between constituents enables facile tuning of packing geometries through perturbation of the energetic landscape of crystallization. Yet the weak binding forces also lead to prevalent structural heterogeneity and variability of function within solid thin films which can

introduce trap states and severely affect material functionality³¹. The solid-state assembly and ordering of molecules with neutral π -conjugated cores, relevant to semiconducting materials, are driven by the interplay of London dispersion, Pauli repulsion and electrostatic interactions³². These forces are also deeply related to the charge transport and energetic properties of a material³³. In this section we will briefly discuss synthetic strategies utilized to affect intermolecular assembly and coupling and examine their measurable effects.

The room temperature solubility properties of organic material precursors allow for rapid, facile deposition of material in large areas, reducing energy needs, and improving efficiency for manufacturing. These deposition techniques and the specific parameters used to convert organic precursors from the solvated or suspended state into solid state thin films, have a major impact on film morphology and performance.

Process Optimization.

Parameters such as precursor concentration, precursor solubility, and solvent volatility affect nucleation densities and crystal growth rates which in turn define grain boundary densities and the homogeneity of crystal morphology³⁴. High grain boundary density and regions with variable morphologies often limit excited state transport properties in organic thin films.³⁵ Throughout the evaporation of solvent, varying conditions and forces exist which can also result in regions nonequilibrium molecular packing geometries and structural heterogeneity. The contact line of the solvent front can affect experience pinning which gives rise to capillary flows transporting non-volatile precursors to the contact line (“coffee ring effect”). This flow and increased concentration at the solvent front can affect the overall performance of various evaporative processes.³⁶ In drop casting techniques, the concentration of the precursor solution

increases as solvent evaporates, which can lead to different levels of aggregation in the solvated phase and differing crystallization conditions.³³ Interaction of the solvent, precursor and the substrate is often what determines the overall orientation of the non-centrosymmetric crystal structures relative to the substrate, as well as the interfacial environment. The selection of the substrate material and roughness, or the introduction of surfactant interfacial layers can affect these interactions and dynamics.^{33, 37} Some techniques utilize electrostatic interactions to bias packing geometries³⁸, and others use phase separation surfaces facilitate meniscus guided assembly in order to remove substrate interaction considerations and encourage specific orientations of precursor molecules.³³ These techniques all have a different effects on the structural properties of a film, including structural heterogeneity, film thickness, grain boundary alignment, crystalline domain size, and molecular orientation.^{33, 34, 37, 39} The goal of process optimization is to permit specific patterning and primarily to improve homogeneity of the resulting organic material; however each organic precursor is unique and responds differently to different deposition techniques. The understanding of the effects of these efforts are often derived from bulk spectroscopic or device level measurements.

Molecular Functionalization.

One of the most effective methods to improve electronic and charge-transport properties of organic molecular aggregates is functionalization of the molecular subunits. Electron donating and electron withdrawing groups can be introduced to a conjugated core to affect the relative HOMO and LUMO positions.⁴⁰⁻⁴³ The resulting energetic alignments can encourage interfacial charge separation or generate n(p)-type semiconductor systems, but also will inevitably impact intermolecular coupling interactions. Hydrophilic or hydrophobic functionalization can also be

used to affect the solubility of the subunits.^{5, 44} Additionally, sterically bulky functionalization can be introduced with the aim of controlling and optimizing the energetic landscape of self-assembly.^{4, 6, 45, 46} One example is that, in the interest of increasing conductivity, the highest coupling in aggregate materials is to be expected for π -stacked monomers with cofacial stacking geometry. This coordination also maximizes the destabilizing exchange interaction. Thus, steric hindrance is introduced through functionalization with large aliphatic species to impose an energetically less favorable geometry^{28, 32}. The resulting materials are therefore more sensitive to localized crystallization conditions during evaporative assembly leading to significant structural heterogeneity. We present in Chapter 2 a microscopic investigation of a solid-state material where an alternative approach was taken. Cofacial π -stacking was encouraged through reductive titration followed by kinetic trapping of aggregates in solution prior to deposition. Our results reveal unique excited state evolution in this material that would be extremely difficult to detect without microscopic spectral characterization. Chemical modification of molecular building blocks of organic materials commonly has wide reaching impacts, where solubility, electronic energy, packing geometry and long-range structural order are often all affected simultaneously. This reality highlights the complexity of tuning organic material properties. Our results show that fundamental understanding of molecular materials is benefited by robust, specific characterization using techniques with spatial resolution on a length scale that can disentangle local heterogeneity and its effects.

Covalent Molecular Tethering.

Given the protean and sometimes unpredictable nature of self-assembly, a strategy that is employed to control the conformation of organic chromophores more robustly is the covalent

tethering of monomers to enforce a well-defined crystal structure.^{47, 48} Molecules can be covalently crosslinked in equilibrium or non-equilibrium conditions to lock in desired conformations and achieve novel supramolecular assembly architectures. A variety of different strategies are used to link organic chromophores^{47, 49} including click chemistry to structurally tether supramolecular aggregate structures¹, photochemical stitching of self-assembled nanostructures.⁵⁰ And by far the most successful strategy has been the synthesis of metal organic frameworks (MOF).

MOFs are built from organic chromophores with functional groups coordinated to metal nodes, forming large porous structures that have shown significant promise in catalytic and light harvesting applications.^{29, 51, 52} More than 90,000 different MOF structures have been reported with a wide range of different organic linkers and metal nodes, resulting in variable surface area, pore size and chemical functionality⁵¹. Several organic frameworks have shown promise in modulating interchromophore coupling by controlling structural geometry^{3, 53, 54}. Layered conductive MOFs has been synthesized with chromophore layer spacing of 3.4 to 3.7 Å where orbital overlap is significant and charge-transfer coupling is relevant.⁵⁵ A promising approach for photoswitchable MOFs has been demonstrated where incorporation of spiropyran photoswitches into the framework modulates the HOMO and LUMO electronic coupling between linkers, showing potential for the photoswitching of electron and hole conductivity.⁵⁶ In general, electronic conductivity and excited state transport in MOFs are driven by interchromophore coupling.⁵⁴ However, even the most carefully synthesized materials contain defects, and these defects, have significant effects on the stability, reactivity, and excited state lifetimes of bulk materials.^{15, 37} Thus, developing a robust understanding of the nature and impacts of defects in

covalently bound assemblies can inform synthetic strategies and perhaps even enable specialized properties for catalytic activity or chemical sensing.⁵⁷

The richness and diversity of the approaches available to tune the structural properties and coupling in organic materials permit extensive manipulation of electronic structure and yet structural heterogeneity and defects are pervasive issues that affect all organic and self-assembled materials. Accordingly, the methodologies used to characterize these organic systems need to be equally rich and diverse and should especially include microscopic measurements with temporal, spatial and spectral resolution. This thesis describes the use and development of broadband time resolved microscopy, alongside a suite of other spectroscopic techniques, to fill the gaps in the understanding of solid self-assembled structures left by bulk spectroscopic techniques.

Yet, when optical characterization techniques are used in concert, the ensemble of information yields the most complete description of a material's characteristics and functional properties. The next section discusses some of the more common spectroscopic techniques and what insight they provide as well as introducing the theory behind femtosecond pump probe microscopy and the challenges that arise with the introduction of spectral resolution.

1.4 Material Characterization

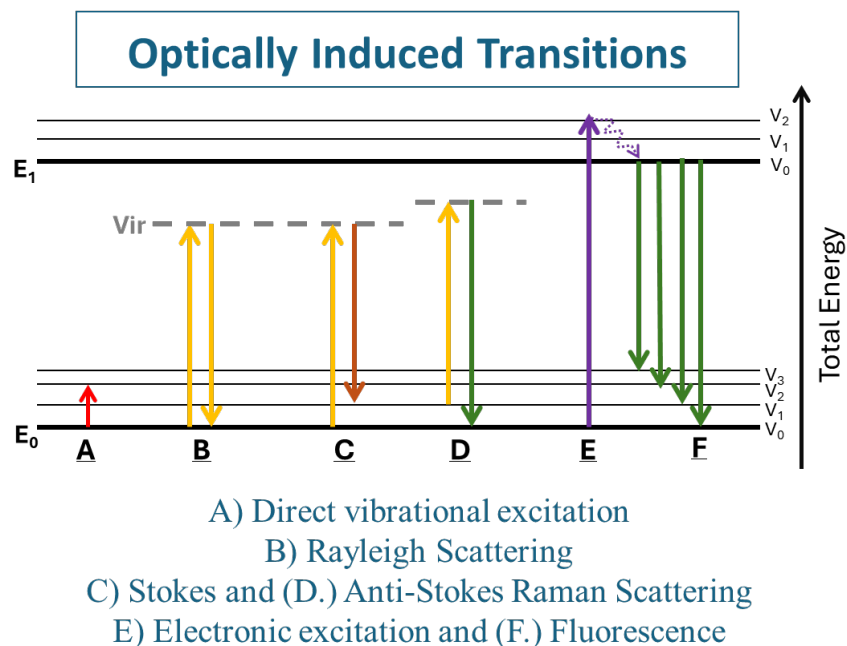


Figure 1.4: Energy diagram showing the optically induced state transitions in a two electronic state (E_n) system with V_n representing vibrational states and Vir the virtual transition state.

In the subsequent chapters of this dissertation, we employ diverse steady state and time resolved spectroscopic probes to characterize the optoelectronic and vibrational properties of self-assembled materials. Optically induced transitions of vibrational energy states (Fig 1.4(A, C, and D)) are explored in greater depth in Chapter 4 and appendix B, so we present a limited examination of these subjects here. Chapter 2 and 3 highlight the capabilities of microscopic steady state electronic measurements for the characterization of molecular coupling and structural ordering of organic chromophores in solid state materials. With this understanding in hand, ultrafast characterization of excited state dynamics and evolution help to elucidate how the structure and coupling of organic chromophores affects the trajectory of excited state species. Chapters 2 and 3 rely on the characterization of electronic transitions from either ground state

species or excited state species (Fig. 1.4(E and F)). Ergo, the discussion of the spectroscopic techniques utilized in our investigation is warranted to provide context on their capabilities.

Steady State Measurements.

UV-vis Absorbance. Measurements of absorption and optical density in the visible and UV inform the electronic structure of the sample by quantifying the resonant frequency and intensity of transitions from ground state to excited state electronic configurations (Fig. 1.4E). In molecular systems the transition is generally from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The spectral features and line shapes of UV-vis can elucidate important light matter interactions. Figure 1.5, shows the absorption spectrum of the perylene diimide aggregate control examined in Chapter 2 where the line shape is a result of H-aggregate interactions.

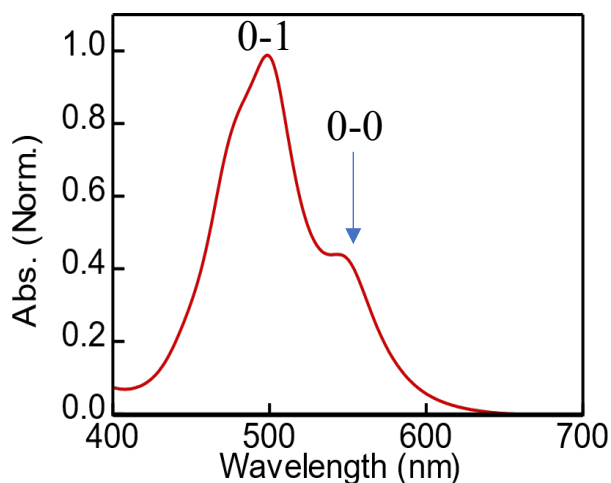


Figure 1.5: Normalized UV-vis absorption of aggregated perylene diimide in water. 0-0 and 0-1 vibronic transitions are labeled.

The 0-0 vibronic transition is suppressed and leads to strongest absorption peak being the 0-1 vibronic transition. Additionally the free exciton bandwidth ($W \equiv |J_{k=0} - J_{k=\pi}|$) which is

proportional to Coulombic intermolecular coupling was calculated to be 290meV evolving to 395meV through redox mediated kinetic trapping.¹⁹ In this way the steady state absorbance sheds light on the effects of synthetic strategies aimed at directing the degree of intermolecular coupling.

In another example, the chromophore tetrakis (4-carboxyphenyl) porphyrin (TCPP), relevant to the MOFs studied in Chapter 3, has unusual absorption spectra where the absorption profile is shaped by symmetry constraints and interacting antiparallel dipole transition moment vectors (Fig 1.6). The HOMO $\rightarrow$ LUMO and HOMO-1 $\rightarrow$ LUMO absorption peaks are the lowest energy transitions (π - π^*), termed the Q-band absorptions⁵⁸. TCPP is a free base porphyrin with an aromatic heterocyclic macrocycle core composed of four pyrrole subunits where two pyrroles are protonated resulting in a splitting of the nominally degenerate orthogonal dipole transition moments. The Q_x absorption is lower in energy and along the axis with protonated nitrogen atoms, and Q_y absorption is higher in energy corresponds to the perpendicular transition along the non-protonated axis.⁵⁹ These absorption peaks are split further by vibronic coupling resulting in four clear peaks and a small shoulder of $Q_{y(0,2)}$ near 490nm. Though, as is evident in panel A of Fig. 1.6, relative to the peak at 418nm the Q-bands are only weakly absorbing. This reduced transition intensity is because the transition is pseudoparity-forbidden.

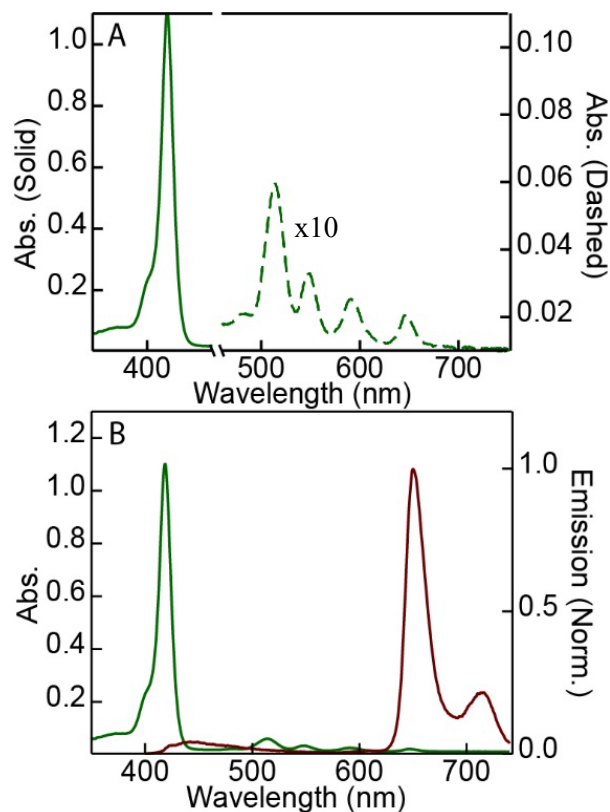


Figure 1.6: (A) Absorption of TCPP showing Soret band abs. (left axis) and Q band abs. (right axis). (B) Absorption (green) and emission (red) of TCPP with 375nm excitation.

The two transitions that yield the lower component of the Q band ($a_u \rightarrow b_{3g}$, and $b_{1u} \rightarrow b_{2g}$) are antisymmetric, as are the two transitions that yield the upper component of the Q band ($a_u \rightarrow b_{2g}$, and $b_{1u} \rightarrow b_{3g}$). The mixing of these transition dipoles leads to cancellation of both transitions. On the other hand, the Soret band transition dipoles HOMO $\rightarrow$ LUMO+1 reinforce each other resulting in an intense absorption.⁶⁰ Aggregation and interchromophore coupling in porphyrin relaxes this alternancy symmetry constraint and leads to a conversion of transition intensity from a redshifted and split Soret-band to the Q-band.⁶⁰

In the interest of obtaining absorption measurements with better spatial resolution, we have built both a LED based and laser-generated supercontinuum based microscopic spectrometer to overcome some of the challenges that solid-state ensemble measurements face. We have had success in measuring the absorbance and polarization dichroism of individual microstructures as is shown in Chapter 2 and 3, expanding the information that solid state absorption spectroscopy can obtain.

Fluorescence. Because fluorescence spectroscopy measures the wavelengths of emitted photons following photoexcitation (Fig. 1.4E), it can be used to provide some insight into the branching ratios and fate of excited state species. Careful emission measurements can quantify the ratio of radiative and nonradiative recombination events through calculation of fluorescence quantum yield⁶¹. The PDI aggregate in Fig. 1.5 has no measurable emission, confirming the H-aggregate assignment and dominant non-radiative relaxation in the aggregate. In the TCPP spectra shown in Fig. 1.6B emission occurs at wavelengths redder than 600nm when pumped at 375nm, indicating that relaxation from the LUMO+1 state is rapid resulting in emission that is nearly entirely from the Q_x transition.⁵⁸ The fluorescence peak position shows the state from which emission occurs and the rough magnitude of the stabilizing excited state reorganization energy through the associated Stokes shift of the emission peak. Steady state emission does not reveal dynamic information, but the ease of the measurement relative to time resolved techniques can provide a starting point for understanding subsequent time-resolved spectroscopic measurements. In Chapter 3, it is shown that the fluorescence profile of TCPP chromophore linkers in solid state MOF-222 differs significantly from the TCPP monomer. Significant emission from the Soret-band in PCN-222 indicates that interband relaxation is much slower

than is generally expected for porphyrin systems. Understanding the mechanism of perturbation that drives changes in photophysical behavior like those shown by PCN-222 and the perovskite nanoparticles discussed in appendix B is challenging without knowledge of state dynamics. As such, we turn to time resolved techniques to help elucidate the rates and lifetimes of excited state species and their dynamical evolution.

Temporally Resolved Fluorescence Measurements.

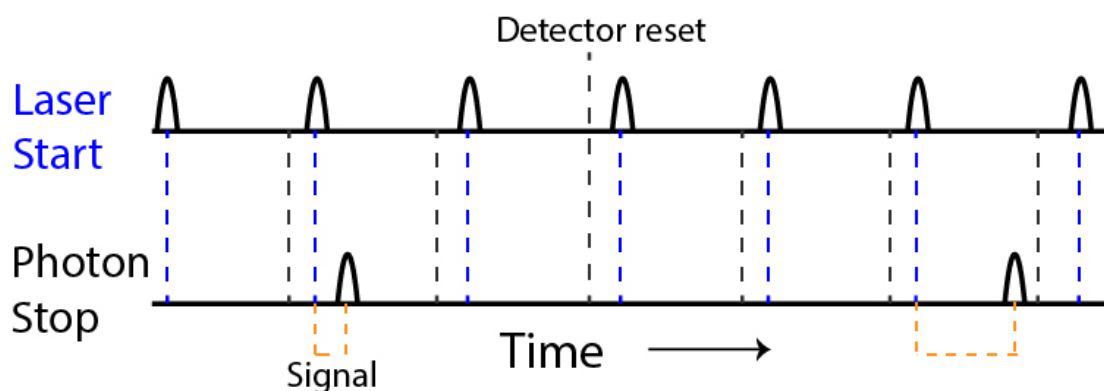


Figure 1.7: Illustration of pulse collection in TCSPC where electronic pulses from the laser start the viewing window and sample emission is the stop signal. If no stop signal is detected within the window the detector is reset.

The response time for electronic detection is generally too slow to observe excited state dynamics directly. Electronic relaxation and evolution commonly occurs on a time scale of femtoseconds or picoseconds and some of the fastest acquisition line cameras have a sampling interval of 8 microseconds. In light of this limitation, to capture the dynamics of excited-state species and their temporal evolution with the requisite precision, supplementary methodologies must be introduced. Time correlated single photon counting (TCSPC) is a temporally resolved fluorescence technique that employs a short excitation pulse and relies on the fact that the detection probability of an emitted photon is proportional to the fluorescence intensity.

Photomultiplier tubes and avalanche photodiodes (APDs) with enough sensitivity to detect single photons, a time-to-amplitude converter and low excitation densities permit the correlation of the time difference between an emitted photon and the electronic reference pulses provided by a pulsed excitation laser (Figure 1.7). The temporal resolution of TCSPC is limited by the instrument response function (IRF), which is measured by scattering the excitation pulse and measuring the recorded profile at the excitation wavelength. The IRF represents the pulse width of the excitation pulse, the width of the detector response, electronic jitter, and the monochromator's temporal dispersion. The typical temporal resolution of TCSPC is often in the 10s to 100s of picosecond range.⁶² This time resolution allows TCSPC to reveal fluorescence decay rates and inform excited state quenching phenomena that occur in hundreds of picoseconds to nanoseconds, but it does not have the temporal resolution to resolve rapid evolution events such as electron and hole transfer that often occur on the femtosecond to picosecond time scale.⁶³

Nevertheless, TCSPC has proven to be a valuable investigatory strategy in the solid-state characterization of organic materials. Time resolved fluorescence provided a useful approach for investigating the dynamics in solid state MOF PCN-222 in Chapter 3. TCSPC allowed us to examine a surprising emission feature, detected with fluorescence spectroscopy, and determine its relaxation dynamics. This emission band showed a long-lived population of emissive species when the responsible state is expected to relax on the femtosecond time scale. When fit to a biexponential decay TCSPC data revealed that one of the lifetime components was on the nanosecond timescale, as opposed to the previously reported femtosecond scale lifetime.^{3, 64} This insight into relaxation pathways for excited state species with long lifetimes is a helpful

component to the diverse optical toolbelt necessary for characterizing engineered self-assembled materials, but while TCSPC provides a facile and effective approach for resolving PL dynamics on the 100s of ps to ns timescale, there are disadvantages.

As an ensemble technique, TCSPC suffers from the same averaging biases of other bulk measurements. Also, fluorescence decay measures excitonic relaxation, through the radiative recombination of an electron and hole so resolving different nonradiative relaxation mechanisms and charge separation is challenging. Therefore, separating and determining the mechanisms of relaxation for excited state species often requires the incorporation of other techniques. Additionally, obtaining information from samples with low fluorescence quantum yields or very short lifetimes is challenging. The combination of pump-probe microscopy with time resolved emission measurements can be especially beneficial because optically dark states can be measured with generally finer temporal resolution to produce a more complete picture of the evolution and relaxation of nonequilibrium states.

1.4 Pump-Probe Microscopy

Pump-Probe Theory.

ump-probe microscopy which is a nonlinear experiment used to monitor the time-dependent evolution and relaxation of photoexcited species. Pump-probe experiments utilize laser pulses separated by a delay τ , where the pump pulse (E_{pump}) creates a nonequilibrium state and the time dependent evolution is measured with the probe pulse (E_{probe}). Figure 1.8 shows a simplified schematic of transient transmission pump probe microscopy which is the configuration of pump-probe that we utilize in this work. Pump-probe

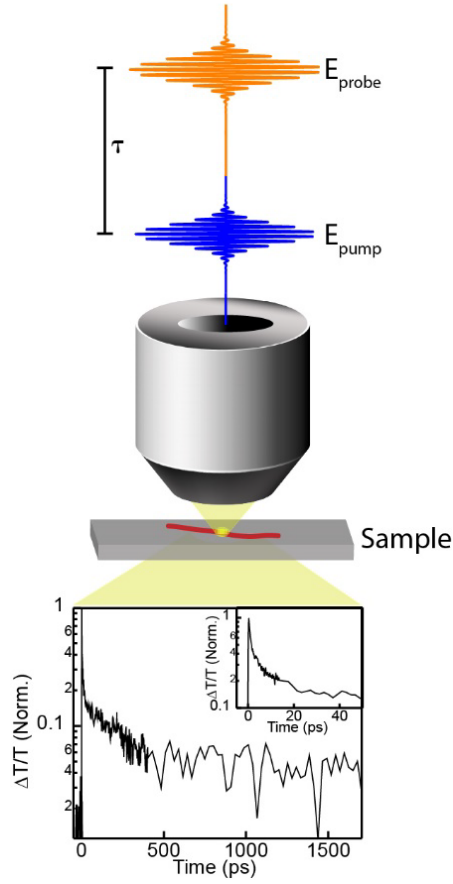


Figure 1.8: Pump-probe microscopy schematic with representative kinetic trace of perylene diimide thin film. τ is the time delay between pulses. E_{pump} , and E_{probe} are the pump and probe pulses respectively.

microscopy is a third-order coherent spectroscopy where there are two interactions with the pump field and a third interaction with the probe. The time ordering of the pump interactions are not distinguishable ($k_{\text{sig}} = \pm k_{\text{pump}} \mp k_{\text{pump}} + k_{\text{probe}}$), so multiple correlation functions can be used to describe the electronic pump-probe measurement (one of the valid Feynman diagrams is shown in Fig, 1.9). After the sample, a detector is used to measure the intensity of the transmitted probe and the nonlinear signal (Eq. 1.7).

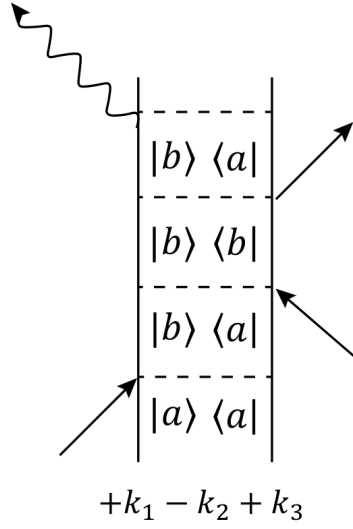


Figure 1.9: One possible Feynman diagram for electronic transient transmission measurements

The signal is extracted by comparing the intensity of the probe pulse in the “pump on” and “pump off” condition. Assuming a weak signal relative to the probe intensity, the differential intensity is dominated by the cross term and can be simplified from Eq. 1.8 to Eq. 1.9.

$$\text{Eq. 1.7} \quad I(\lambda) = \frac{n(\lambda)c}{4\pi} |E'_{probe} + E_{sig}|^2$$

$$\text{Eq. 1.8} \quad \Delta I(\lambda) = \frac{n(\lambda)c}{4\pi} (|E'_{probe} + E_{sig}|^2 - |E'_{probe}|^2)$$

$$\text{Eq. 1.9} \quad I(\lambda) = \frac{n(\lambda)c}{2\pi} \text{Re} |E'_{probe} E_{sig}^*(\tau)|^2$$

$I(\lambda)$ is the detected probe pulse intensity as a function of wavelength, c is the speed of light, and E_{sig} is the nonequilibrium state signal field intensity. The wavelength dependent refractive index is determined empirically and can be specified using the Sellmeier dispersion formula (Eq. 1.8), accurate for wavelength regions where resonant absorption is negligible.⁶⁵

$$\text{Eq. 1.8} \quad n(\lambda) = \sqrt{1 + \sum_j \frac{A_j \lambda^2}{\lambda^2 - B_j}}$$

The coefficients A_j and B_j arise from a simple damped oscillator model driven by an optical field and are obtained through fitting experimental data. The fact that the refractive index is wavelength dependent will be relevant in Section 1.6 when we cover broadband microscopic measurements. The pump-probe signal (E_{sig}) is directly proportional to the imaginary component of the polarizability and can therefore be used to directly measure the relaxation of nonequilibrium states in the sample volume.

The change in the imaginary component of polarizability in pump-probe spectroscopy occurs because the pump beam pumps electronic transitions and alters the electronic structure of the sample. The response of the probe to these changes in electronic structure manifests as an increase or decrease in transmitted light and is often most useful when it is related to more tangible photophysical phenomena. Figure 1.10 shows a simplified summary of the signals that are observed and their respective physical interpretations. After the pump is absorbed, shown in the first panel, a population of nonequilibrium states is formed consisting of excited electrons and holes. In molecular solids these charge carriers are largely Coulombically bound together, forming charge neutral excitons. Two of the resulting photophysical phenomena, known as ground state bleach (GSB) and stimulated emission (SE), result in an increase of transmitted light. GSB is a decrease in the optical density of the sample material in wavelength regions that are resonant with electronic transitions from the ground state and can be understood through the

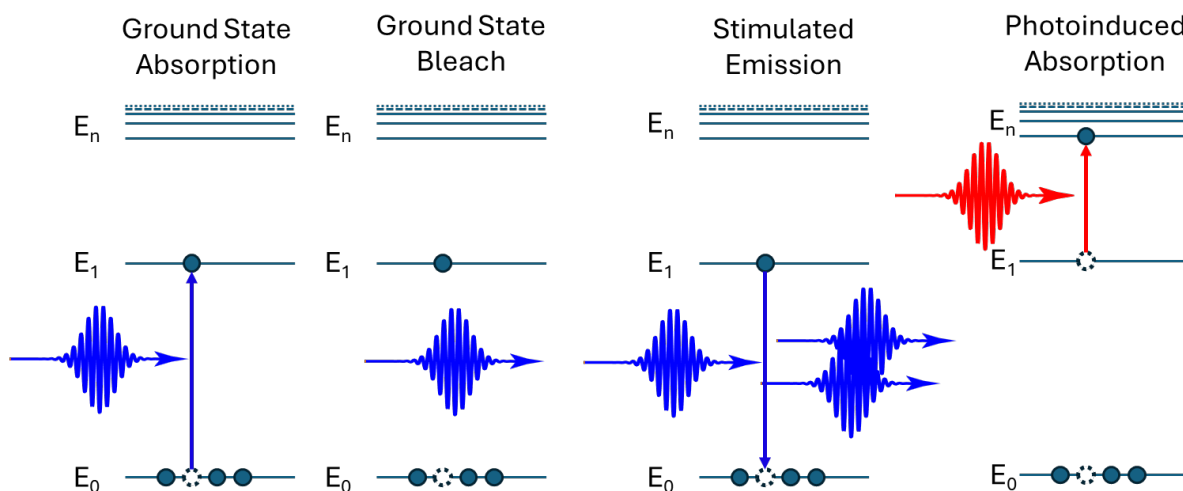


Figure 1.10: Visual representation of the different electronic pump probe signals. Ground state (E_0) electrons are pumped into the excited state (E_1) when the pump is absorbed creating a population of excitons or free charge carriers. Ground state bleach results from a reduction in optical density at frequencies resonant with the ground state absorption due to depletion of electron density. Stimulated emission is the photoinduced emission of a coherent photon by a probe photon that is resonant with the electronic transition from E_1 to E_0 . Photoinduced absorption results from an increase in optical density at frequencies resonant with electronic transitions of excited state species to higher lying states (E_n).

Einstein B_{12} coefficient. The decrease in optical density is due to a depletion of the number of species with ground state electron configurations. Stimulated emission also results in an increase of transmitted photons, and can be described by the Einstein B_{21} coefficient, where transition rate from state E_1 to E_0 is proportional to the number density of species in E_1 state and the energy density of the incident radiation. Stimulated emission is coherent with the probe pulse and therefore results in a signal that is colinear with the probe. Because the sign of GSB and SE is the same, if there is spectral overlap in the two signals it can be particularly difficult to distinguish between them. The absorption of light by excited state species is known as photoinduced absorption (PIA) and is commonly observed as an increase of optical density at longer wavelengths. PIA arises because the probe photoexcites excited state species to higher

lying states where the energy spacing is typically smaller. In organic materials, absorption resonances are typically quite broad resulting in overlapping signals. Broadband spectral information is extremely useful in these situations to help understand what phenomenon are being observed and how they evolve over time.

Pump-Probe Instrumentation.

Two-Color Pump-Probe Instrument. Relevant to Chapter 3, herein we describe the two-color pump-probe microscope with the ability to tune the photoexcitation wavelength. The microscope (Fig 1.11) is driven by a mode-locked Titanium Sapphire oscillator (Spectra Physics MaiTai) with tunable output frequency between 690 and 1040 nm. The nominal pulse width is ~70 femtoseconds with a repetition rate of 80 Megahertz. To produce the separate pump and probe pulses, the fundamental beam is split with a 50:50 beam splitter and modulated with two acousto-optic modulators (AOM). The pump is modulated at 4 MHz and probe is modulated at 8MHz. A Beta-Barium borate crystal is used to frequency double the pump beam. In addition to the tuning capability of the Ti:Sapphire Oscillator two mirrors can be introduced to direct the fundamental on the pump line into a photonic crystal fiber where a bandpass filter selects specific pump wavelengths that are resonant with the electronic transitions of the sample material. The pump then travels through a translation stage mounted with a reflective corner cube to achieve temporal resolution for the experiments. A set of galvanometer mirrors (Galvo) coupled with a 4f lens system are used to spatially raster the pump beam relative to the probe beam. The two beams are recombined with a dichroic mirror, and then enter a second Galvo and 4f system to provide spatially overlapped raster scans of the sample, before filling the back aperture of an Olympus 100x microscope objective, where the pump and probe beams are

focused onto the solid-state sample. Transmitted light is collimated, and the pump beam is removed with a hard coated edgepass filter. The probe is then focused onto an amplified photodiode detector to measure the intensity of transmitted light. A lock-in amplifier is used to isolate pump probe signal at the modulation frequency of the pump AOM to detect pump induced changes to the transmittance of the sample. The experiments performed with this configuration are termed transient transmission experiments. Figure 1.11 shows a diagram of the two-color pump-probe microscope.

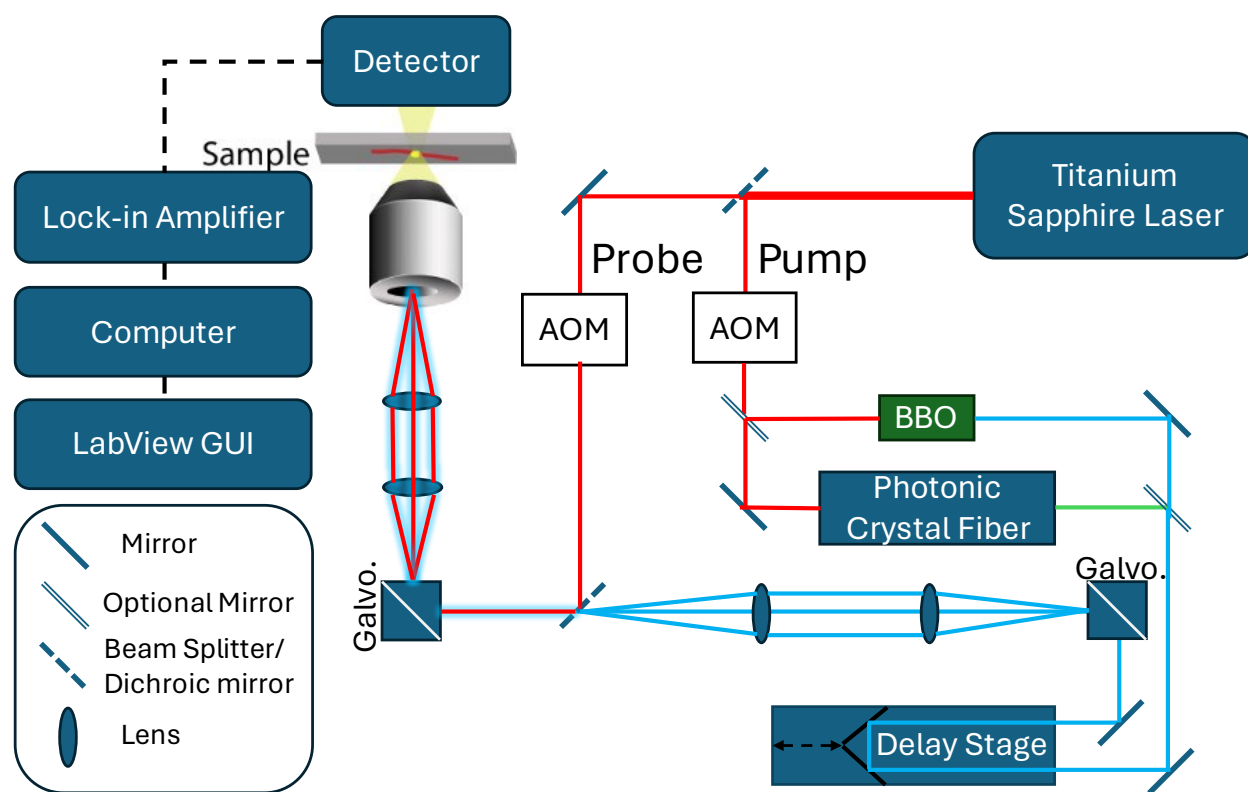
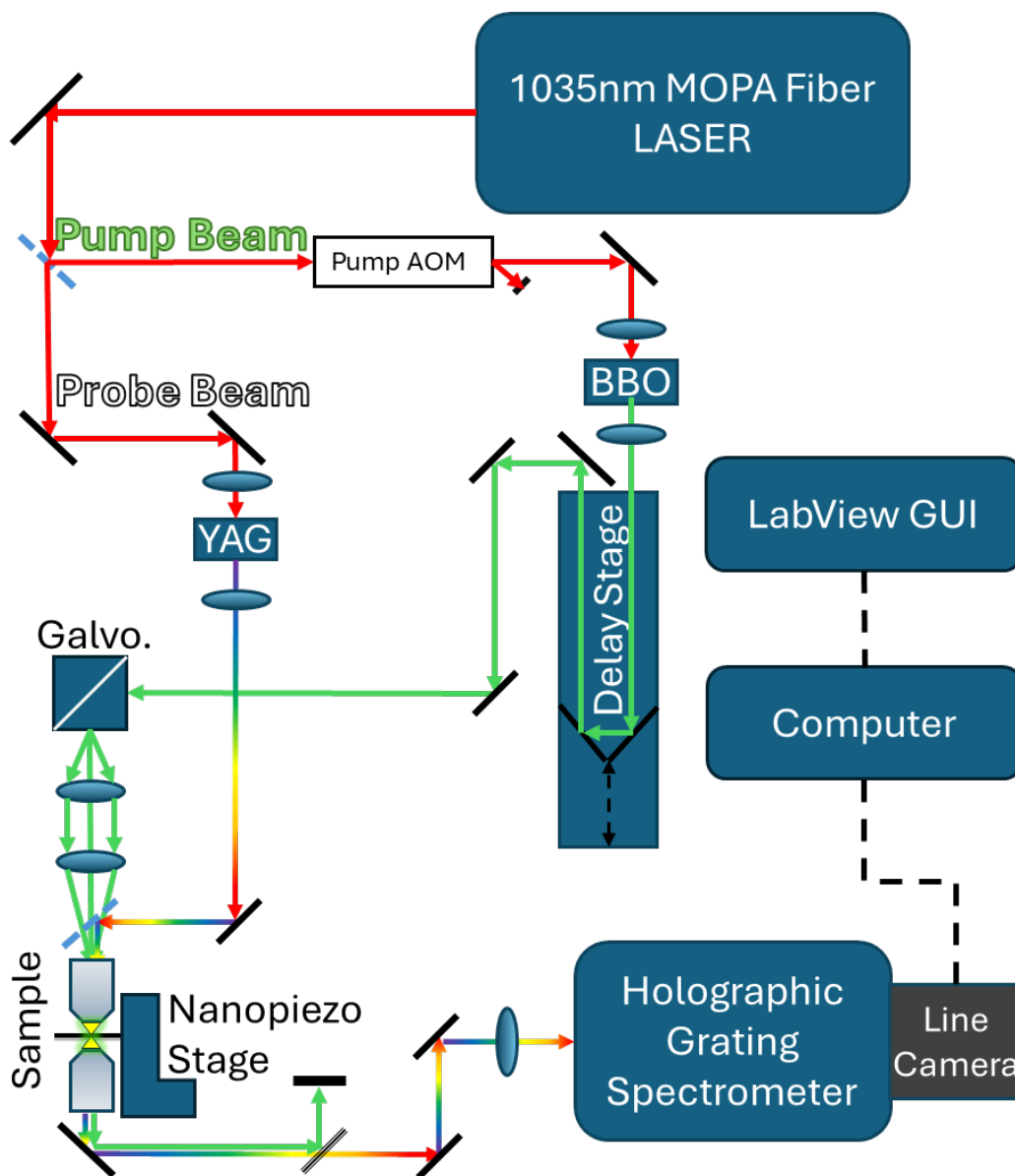


Figure 1.11: Schematic of the two-color pump-probe microscope. The red line is the fundamental wavelength, the blue line is the frequency doubled pump and the green line an optional photonic crystal fiber derived pump with tunable wavelength. Transient transmission signal is detected by the Si photodiode detector and amplified through the lock-in amplifier tuned to the pump modulation frequency. A custom LabView Guided User Interface (GUI) controls the instrument function and records experimental data.

Broadband pump-probe. The second pump-probe microscope is a broadband instrument, and it is the workhorse of the research presented in this dissertation. The extensive capabilities of this instrument enable comprehensive experiments that highlight structural effects on excited state spectra and their evolution. The Broadband pump-probe microscope is powered by a Coherent Monaco 1035 femtosecond laser. The laser produces 40W of pulsed 1035 nm light with a pulse width of ~ 300 fs. A 50:50 beam splitter is used to direct half of the fundamental to a solution phase transient absorption spectrometer. The remaining light is split by a 30:70 (R:T) beamsplitter and the reflected pump beam is reduced in diameter with a telescope and sent through an AA Opto Electronic AOM running at 15.56kHz with a 50:50 duty cycle. The pump beam is focused into a 1mm type 1 BBO to generate the second harmonic and the remaining fundamental beam is removed with a 1000nm short-pass filter. The pump is then sent onto a translation stage with a range corresponding to ~ 2 ns of pump-probe delay. A half-wave plate is used to control the polarization of the beam. The pump beam is sent into a Galvo, that is coupled to a 4f lens system with the output plane at the back aperture of the microscope objective, to control the position of the pump in the focal plane of the objective. The light transmitted by the 30:70 beamsplitter is further split by a 10:90 beam splitter to produce the probe. The remaining transmitted light is relevant in chapter 4. The reflected probe beam is unmodulated. A half-wave plate combined with a polarizing beamsplitting cube is used to control the power and polarization of the beam. The probe ($\sim 1\mu\text{J}$) is focused with a 75mm focal length into a Yttrium Aluminum Garnet crystal to generate the white light continuum (WLC), and then collimated with a 75mm achromatic lens. The fundamental 1035 nm component is filtered with a shortpass filter and no other transmissive optics are placed in the probe beam path before the microscope

objective to minimize temporal chirp. The beams are combined with a 70:30 beam splitter and sent into the back aperture of a 100X Olympus MPlanFL-N. After the sample, the pump beam is rejected with a longpass filter, and the probe is sent into spectrometer to disperse the wavelength components for spectral resolution. A custom-built spectrometer is used for data presented in Chapter 3 consisting of two 50mm 1.8F camera lenses and a 600 g/mm volume phase holographic grating. In Chapter 2 a SpectraPro 2200i Czerny-Turner spectrograph is used to disperse the probe in frequency space. The dispersed probe is focused onto a Teledyne DALSA OctoPlus E2V line CMOS camera with 2048 pixels and a maximum line rate of 125 kHz. Two pixels are binned together to increase the number of integrated photons resulting in spectral resolution of 0.58nm/pix and 0.43nm/pixel for the homebuilt spectrometer and Czerny-Turner spectrometer respectively. Spatial resolution of the sample is obtained with 0.2 nm positional precision, using a Mad City Labs, Nano-H100 piezoelectric stage. The camera interfaces with a computer and dumps frames of collected line data where data acquisition and control are provided by a homebuilt LabVIEW guided user interface (GUI). Line acquisition is triggered at a rate of 62.25kHz and frames are triggered at a rate of 77.8Hz. Line acquisition for the OctoPlus line camera is modulated in this way because the signal from sequential lines is binned by two different ADCs which have slightly different noise characteristics. Collecting two lines with the pump on and two with the pump off averages the noise of the two ADCs and limits the introduction of artifacts. Additionally, the maximum line rate of the camera is not used because of the sensitivity of samples to photodegradation. A lower line rate enables the integration of a greater number of pulses per line of data and utilizes more of the dynamic range which reduces

the relative amplitude of the instrument's electronic noise. A custom LabVIEW GUI allows for the consolidated control of transient transmission experiments.



1.12: Schematic of the broadband pump-probe microscope. The fundamental 1035 nm beam is split into the pump and probe beam lines. The pump beam is modulated at 15.6kHz with an AOM and the first order diffraction is frequency doubled in beta-Barium borate (BBO) crystal to generate the second harmonic. The probe white light supercontinuum is generated in an Yttrium Aluminum Garnet (YAG) crystal. Lenses are represented by blue ovals, beamsplitters by dashed blue lines, and interference mirrors by a triple line.

Frequency Modulated Femtosecond Stimulated Raman Microscopy. In the pursuit of advancing the frontiers of broadband microscopic spectroscopy research in solid state organic systems, this dissertation presents efforts undertaken toward the ambitious task of developing a femtosecond stimulated Raman microscope (FSRM) in Chapter 4. By introducing a third beam and harnessing the capabilities of broadband pump-probe we aimed to acquire time resolved Raman spectra and explore the effect of photoexcitation on vibrational resonances in these organic systems. Observation of these vibrational dynamics would provide an insightful perspective of the structure function relationship and assist with the optimization of organic material design by determining which molecular axes and vibrational modes participate in important photochemical reactions such as charge transfer and excitonic nonradiative relaxation. The culmination of our efforts materialized in the construction and validation of a functioning femtosecond stimulated Raman microscope. This endeavor necessitated meticulous optimization strategies, including the integration of frequency modulation methodologies, and the engineering of a noncollinear parametric amplifier. The theory and instrumentation are discussed in detail in Chapter 4 so we will not go into them here. Ultimately, aside from the short lifetime of excited state species in organic materials, the largest obstacle that was faced in the FSRM work was the high-power density required for significant Raman signal and photosensitivity of solid organic samples. While the outcomes of our work did not manifest in immediate publications, substantial progress was made in refining the technique, improving the signal amplitude, and disentangling Raman signal from parasitic electronic and thermal background signals.

1.5 Pump-Probe Measurements

Spatially Separated Raster Scans.

Scans in which the pump beam is raster scanned relative to the probe beam are achieved in the same manner for both pump-probe microscopes. The pump galvanometer mirror set is in the input plane of the 4f lens system, so that as the exit angle of the pump beam from the Galvo is controlled from the LabVIEW GUI, the beam is translated in the image plane of the system, but not at the output plane where only the incident angle into the back aperture of the objective is affected. The entrance angle of the pump into the microscope objective translates to a spatial displacement of the focused beam at the sample. The transient transmission intensity signal in the probe is measured as a function of the pump position yielding a convolution profile of the pump and probe beams. First, these scans facilitate the precise and accurate alignment and syzygy of the pump and probe beams in the sample which is imperative for maximizing pump-probe signal, but more importantly, by taking spatially separated scans at a series of delay times, a direct measurement of the spatial evolution of excited state species is generated. The temporal evolution of the signal profile results from the effects of excited state diffusion and therefore the diffusion coefficient can be extracted. The process used to extract the excited state diffusion constant has been described previously by Afrin et al. and in previous dissertations presented by the Grumstrup research group.^{15, 66}

Spatially Overlapped Raster Scans.

Images of the sample with the overlap of pump and probe beams maximized are collected differently between the two-color and broadband instruments. The two-color pump probe, after the two beams are combined, uses a subsequent Galvo coupled to a 4f lens system to

translate the focused beams at the sample in the same manner as spatially separated scans raster scans are taken. The broadband pump-probe instrument on the other hand translates the sample underneath the focused beams with a piezoelectric translation stage with nanometer spatial precision. The spatial resolution of the image is not limited by the stage but by the product of the pump and probe beam intensities. In this way hyperspectral images of the probed region can be built with the transient transmission spectra. The nanopiezo images reveal heterogenous signal in sample domains, and with careful experimental design correlations can be made between morphological characteristics and specific ultrafast spectroscopic observables.

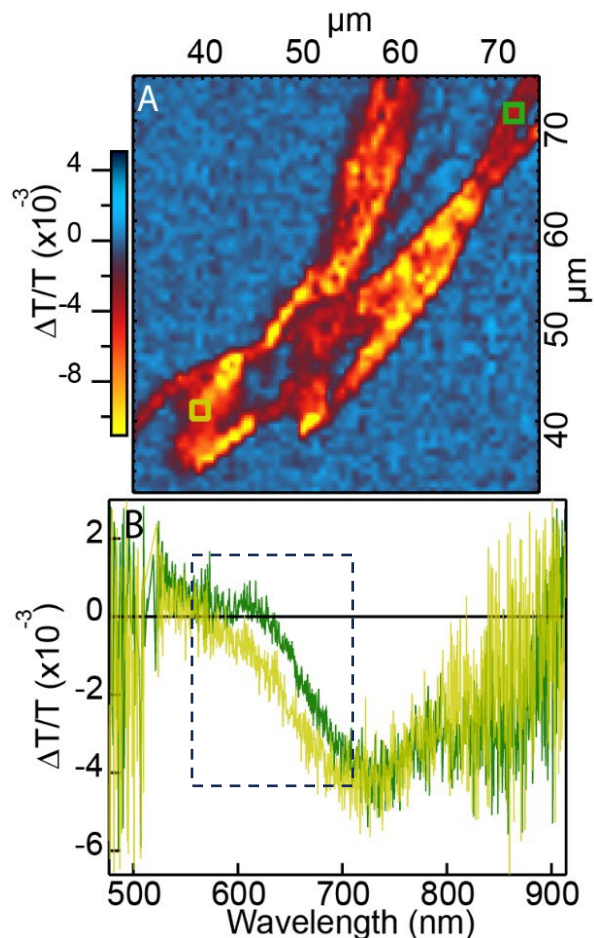


Figure 1.13: Spatially overlapped image and spectral correlation. Panel A shows a spatially overlapped nanopiezo (NP) scan of a PDI domain showing regions with microrod geometries as well as more amorphous regions. The transient transmission spectra 1ps after photoexcitation are shown in panel B. The green spectrum is from the green box shown in the NP image, and the yellow spectrum is from within the yellow box.

Figure 1.13A shows an example nanopiezo scan of the perylene diimide microstructure that is investigated in more depth in chapter 2. The scan shows the average transient transmission signal (ΔT) from 690 to 708 nm, 1 ps after photoexcitation by the pump normalized to the intensity of the probe without the pump present ($\Delta T/T$). The heterogeneity in morphology and signal intensity is evident in the image, and furthermore the raw image is a hyper spectral image where each pixel in the heat map is a full transient transmission spectrum. Panel B of Figure

1.13B shows transient transmission spectra taken from the regions shown by the rectangles shown in Panel A. The green spectrum was taken from a region of the sample that exhibited rod like morphology, whereas the yellow spectrum was taken from a region with seemingly less structure where the sample exhibited thin film morphology. The spectra taken in these two regions show variation in the zero-point crossing with the rod like structure exhibiting a red shifted positive GSB signal. In Chapter 3 this spectral feature is explored in greater detail and reveals unique structurally correlated excited state evolution relevant for light harvesting device applications.

Kinetic Dynamics Scans.

The final class of measurements enabled by the two pump-probe instruments kinetic decay experiments showing the relaxation of excited state species. Kinetic traces are collected in the same manner for the two-color and broadband microscopes and an example decay trace of normalized PIA in PDI can be found in Fig. 1.8. The path length of the probe is matched to the pump to obtain t_0 with the delay stage positioned near the back of its travel range. During a kinetics scan the stage is translated forward shortening the pump line and advancing the arrival of the pulse in time relative to the probe. The transient transmission signal is recorded at a series of steps corresponding to specific pump-probe delay times, and in this way the excited state decay dynamics can be measured and fit to better understand the mechanisms facilitating excited state relaxation. The temporal resolution of the measured relaxation dynamics is limited by the temporal convolution of the pump and probe pulses in the time domain, and thus the temporal resolution afforded by lasers with ultrashort pulse widths represents a major advancement for the

exploration of ultrafast photo physics and the foundation of the direct measurement of excited state relaxation and evolution.

The lifetime of photogenerated excited state species is of great interest to light harvesting industries and is an important consideration for optoelectronic materials. The dynamics shown in Chapter 3 reveal that photogenerated excited state species created from Soret-band and Q-band absorption within PCN-222 microstructures exhibit different relaxation dynamics and therefore have different relaxation pathways available to them. As mentioned in the time resolved fluorescence section, this result is of note because the common expectation was for Soret-band excitation to result in rapid relaxation into the Q-band.^{3, 67} Broadband pump-probe microscope introduces a new capability to kinetic measurements where morphologically correlated evolution of excited state spectra can be used to interpret how the evolution of the excited state is affected by local structural characteristics. Chapter 2 compares the relaxation dynamics and time resolved spectra in PDI aggregates that show differences in long range packing order and excitonic coupling. Through this examination the mechanism of long-lived charge carrier generation was determined, where to elucidate said mechanism with single wavelength kinetics alone would be very difficult due to overlapping GSB and PIA signal contributions. Deploying a polyspectral probe to microscopic applications is not as straightforward as generating a WLC and sending it into a microscope objective, however. As described in detail below, there are several significant challenges and complications that arise in microscopic time resolved spectroscopy that must be carefully navigated.

1.6 Challenges in Application and Detection

Chromatic Aberration.

Lens induced aberrations are a particularly important consideration in microscopic applications because they can compromise the signal profile and spatial resolution. Spatial beam aberrations can be minimized through careful optical design and beam alignment, however chromatic aberrations are an intrinsic challenge of polychromatic probes transmissive lenses and objectives. Chromatic aberrations stem from the differential dispersion of different wavelengths of light and result in two imaging effects, axial aberration, and transverse aberration. Both effects arise because different wavelengths of light will experience different degrees of refraction through a lens as a consequence of dispersion, where the phase velocity of different wavelengths differs when passing through refractive materials.⁶⁵ We have introduced the wavelength dependent nature of the refractive index and the Sellmeier equation above, but we shall reintroduce it now alongside Snell's law in Fig. 1.14 to better facilitate discussion of chromatic aberration. Transverse aberrations occur perpendicular to the optic axis of a lens and result in different wavelength components of light focusing at different locations of the focal plane.

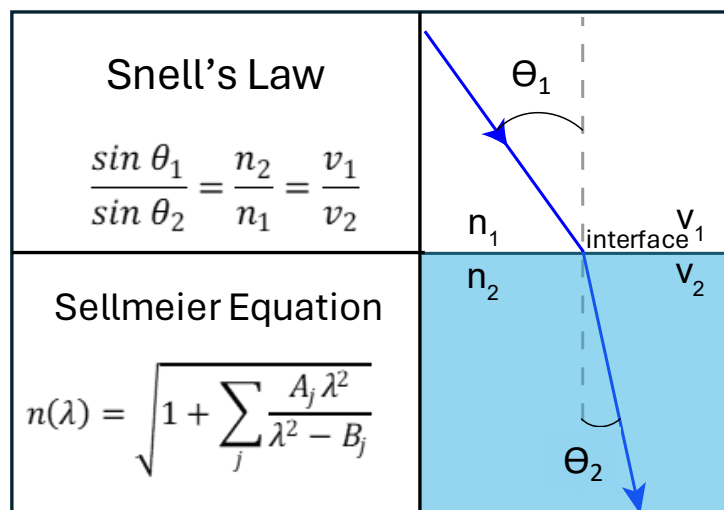


Figure 1.14: Visual depiction of light refraction. Snell's law describes the refraction of light at an interface between refractive materials. θ_1 and θ_2 are the angles relative to the surface normal vector (grey dashed line), n_1 and n_2 are the refractive indexes of the two environments (where $n_2 > n_1$ in the case shown) and v_1 and v_2 are the respective phase velocities. The Sellmeier equation is included to describe highlight how the refractive index changes with the wavelength of light.

This aberration is most significant for light that is not incident parallel to the optical axis of a lens because θ_2 in Fig. 1.14 will be different for different wavelengths of light with common θ_1 . Axial chromatic aberrations, depicted in Figure 1.15A, also arise from the wavelength variation of θ_2 where the optical power or diopter of a lens will vary with the wavelength of incident light. The result is a variation in focal length or depth of field of a lens (Δf). For broadband microscopic measurements this is a serious limitation because the various spectral components of the WLC probe will not be in focus in the same z-position and the depth of organic thin film samples is often only a few microns. Figure 1.15B shows an example of how much the focal length can vary in a 100mm focal length N-BK7 lens over a spectroscopically relevant wavelength range.

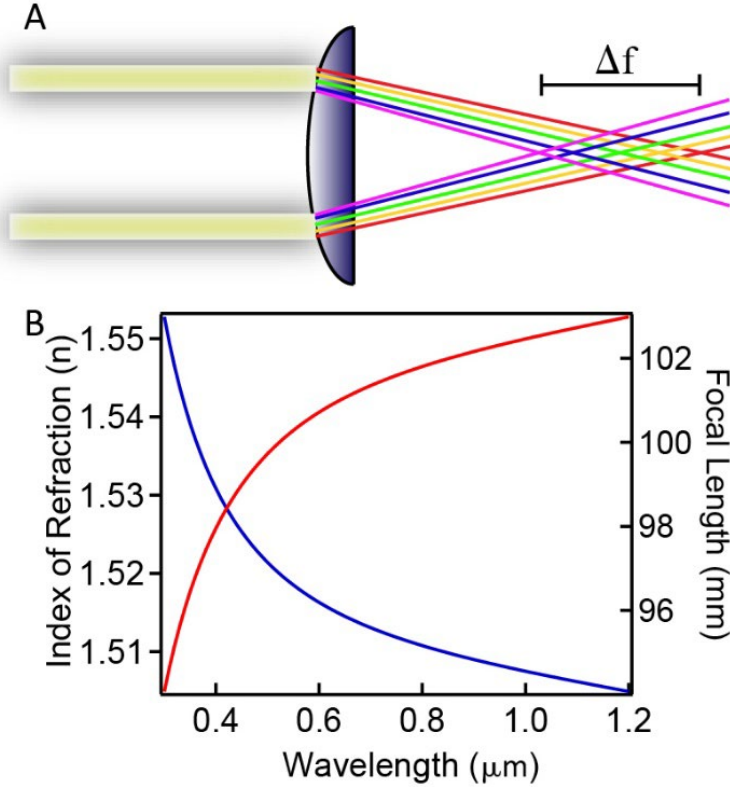


Figure 1.15: Example of chromatic aberration through a Planoconvex N-BK7 lens with a nominal focal length of 100mm (A). The Sellmeier equation (Eq. 1.8) with a three-term expansion, was used to calculate the wavelength dependent refractive index and corresponding focal length shown in panel B. The Sellmeier coefficients are $A_1=1.03961$, $A_2=0.23179$, $A_3=1.01046$, $B_1=6.00069 \times 10^{-3} \mu\text{m}^2$, $B_2=2.00179 \times 10^{-2} \mu\text{m}^2$, and $B_3=1.03560 \times 10^2 \mu\text{m}^2$.

Between the 517nm pump and 1035nm fundamental of the broadband microscope Δf is roughly 2mm. This difference in focal length also affects the magnification of the lens resulting in different image dimensions of spectral components in the image plane.

The complications arising from chromatic aberrations are some of the most insidious obstacles to application of broadband pump-probe microscopy. Though it is impossible to completely eliminate the effects of dispersion in refractive optics, efforts have been made to minimize the impacts and standardize the comparisons made in this dissertation. One of the most straightforward and worthwhile efforts is simply good fastidious attention to optical alignment.

The effects of transverse chromatic aberrations can mostly be eliminated if the broad-spectrum probe is carefully aligned through the optical axis of any refractive optics. To this end, the incident angle-based beam rastering capabilities of the Galvo and 4f system are only utilized for the quasi-monochromatic pump. Addressing axial aberrations is less straightforward. The objectives used to focus and collimate the beams in the broadband pump-probe microscope (Olympus MPlanFL-N and Nikon plan apo 100x 0.9 NA) are apochromatic lenses where different optics consisting of lens materials with different dispersion properties are combined to minimize chromatic aberration. We explored the use of a reflective objective to help eliminate dispersion in the focusing objective; however, scattering from spider mount arms and transmission efficiency resulted in poor image quality and spatial resolution. Additionally, the only other refractive optic in the probe beam path prior to the sample is an achromatic doublet on a translation stage used to collimate the WLC generated by focusing the probe into a YAG crystal. This lens is translated to optimize the focal overlap of the spectral region of interest with the pump in the sample plane. The careful alignment and selection of optics helps to minimize the effects of chromatic aberrations, but it is impossible to eliminate them. To ensure data was not corrupted by these effects spectral phenomena were investigated by focusing different wavelength components of the probe with the pump and examining the result. Also, importantly any comparisons made between spectra and kinetics were made with the broadband microscope in identical configurations to ensure the efficacy of the comparison.

Temporal Chirp.

As we mentioned above and can be seen through Snell's law, the change in refractive index of a sample results from a wavelength dependent change in group velocity. The change in

group velocity of different wavelengths also results in the temporal chirp of spectral components through refractive materials.⁶⁸ We mitigate these effects by limiting the number of refractive optics in the probe beam path, and in previous configurations negative group dispersion delay(GDD) optical assemblies were utilized to address the positive GDD induced by the microscope objective and other transmissive optics.⁶⁹ Ultimately, we elected to remove these components as the spatial chirp and beam distortion effects compromised imaging capabilities. Instead, we utilized a custom-built LabVIEW based chirp correction software that fits the temporal chirp and then adjusts the different spectral components of a scan in time, matching dimensionality with linear interpolation. An example of excited state spectra from PDI and the result of chirp correction is shown in Fig. 1.16.

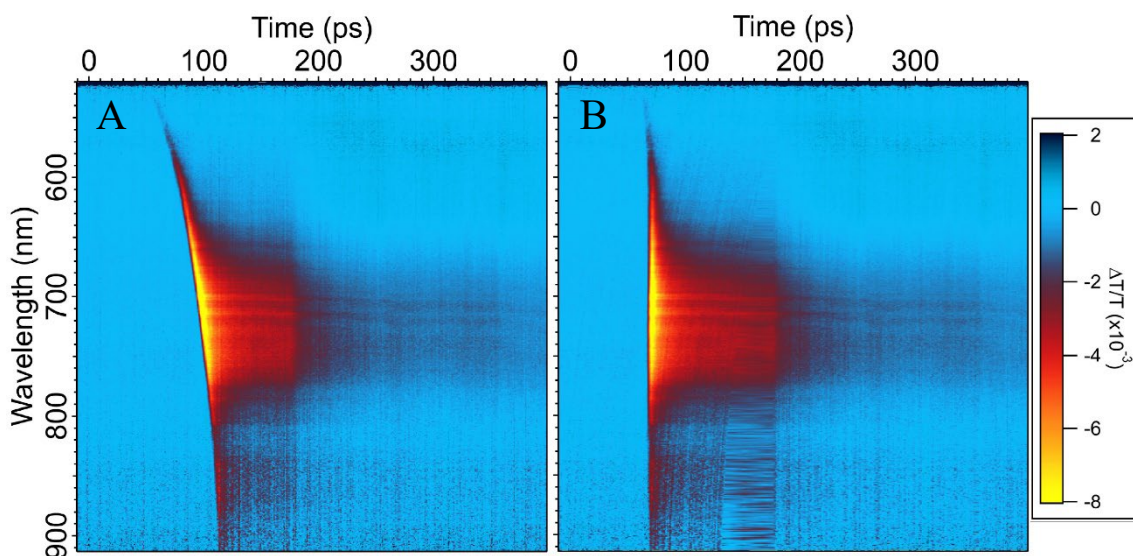


Figure 1.16: An example of chirp correction. Panel A shows raw excited state spectral evolution of KT-PDI and Panel B shows the same spectral evolution post chirp correction.

The correction of temporal chirp in our spectra through post processing also has the added advantage of reducing the instantaneous power density of the probe focused into the sample.

Photodegradation of organic materials is a significant issue so reducing the photon flux is a benefit.

Power Density.

The most significant limitation affecting signal to noise in broadband pump-probe microscopy is the photodegradation of samples. To obtain information regarding GSB of sample materials the WLC probe necessarily contains frequencies resonant to the ground state transitions. Moreover, the probe is intentionally overlapping with PIA transitions that are generally broad and redshifted. The resulting probe induced photoexcitation events must relax generally resulting in significant thermalization of the sample. With a high repetition rate detection scheme in an insulative environment such as air the dissipation of this thermal energy may not be fast enough to prevent heating and thermal degradation of weakly bound aggregate systems. We have tested a temperature-controlled substrate mounting device cooled with a Peltier circuit to attempt to address possible thermal degradation. However, we saw no significant improvement of the probe power density tolerance in the PDI sample studied in Chapter 2. Additionally, we have encapsulated samples to prevent photoactivated reactions with oxygen. However, the only unequivocally effective approach to prevent photodegradation is to reduce the power of the incident beams. We therefore routinely operate with nano watts of pump power and a few μW of probe power. Because of the small volume probed with broadband pump-probe these powers correspond to relatively high energy densities at the sample. The signal to noise limitation emerges at the detector where the intensity of the probe when dispersed spectrally often only utilizes 2.5% of the dynamic range of the line camera. Thus, the absolute electronic noise is a major detrimental factor in the signal to noise of microscopic transient

measurements with spectral resolution. We have begun work aiming to address this limitation through the use of a ultrasensitive sCMOS camera paired with a novel mechanical approach to obtain high repetition temporally resolved spectra.

1.7 Conclusion and Objectives

The sensitivity of molecular chromophores to dipole-dipole and charge-transfer coupling presents both challenges due to the disruptive effects of structural heterogeneity and exciting opportunities for functional tuning and through solid-state molecular arrangements. Self-assembled materials derived from organic chromophores are often held together by weak noncovalent interactions resulting in heterogeneous solid state structural characteristics. Even covalently linked assemblies exhibit defects that have a significant impact on excited state properties introduced during self-assembly. Ergo, in order to discover materials that are innately suited to specific processes and applications, and to understand the true effects of defects and heterogeneity our investigation must be rooted in techniques that allow us to correlate optoelectronic properties and excited state evolution with morphological characteristics. We show two cases where the employing microscopic spectroscopy and specifically broadband pump-probe microscopy has enabled the exploration of previously undescribed and uncharacterized excited state evolution in solid state organic chromophores. Additionally, we present progress made toward the development of a time resolved Raman microscope and its application. Despite the challenges posed by challenging instrumental design and specialized expertise required for implementation, this body of work endeavors to summarize the progress made in probing the excited state properties of morphologically complex systems with

broadband microscopies and lay the groundwork for future exploration and development in this field.

CHAPTER TWO

PROBING EXCITED STATE DELOCALIZATION AND
CHARGE SEPARATION IN HIERARCHICAL PERYLENE
DIIMIDE MATERIALS WITH TIME-RESOLVED
BROADBAND MICROSCOPY

Contribution of Authors and Co-Authors

Manuscript in Chapter Two

Author: Skyler R. Hollinbeck

Contributions: Designed experiments and built broadband pump-probe microscope. Collected and analyzed all time resolved and solid-state data.

Co-Author: Kaixuan Liu

Contributions: Synthesized structures investigated in the work and provided solution phase measurements.

Co-Author: Jean-Hubert Olivier

Contributions: Provided perylene diimide materials. reviewed and provided feedback of the manuscript.

Co-Author: Erik Grumstrup

Contributions: Assisted with analysis and editing of the manuscript for final submission

Manuscript Information

Hollinbeck, Skyler; Liu, Kaixuan; Olivier, Jean-Hubert ; Grumstrup, Erik

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- ☒ Accepted by a peer-reviewed journal
- ☐ Published in a peer-reviewed journal

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2.1 Abstract

Using a variety of steady state and time-resolved microscopies, this work directly compares the excited state dynamics of two distinct morphologies of a hierarchical perylene diimide material: a kinetically-trapped 1D mesoscale aggregate produced with a redox-assisted self-assembly process, and a thin film produced via conventional solution-processing techniques. Although the constituent monomer is identical for both materials, linear dichroism studies indicate that the kinetically-trapped structures possess significantly higher long-range order than the conventional thin film. A comparison of the two systems with broadband pump-probe microscopy reveals distinct differences in their excited state dynamics. In the kinetically-trapped structures, polarization-resolved kinetics, as well as a picosecond redshift of the ground state bleach provide evidence for rapid excited state delocalization, which is absent in the thin film. A comparison of transient spectra collected at 1 μ s indicates the presence of long-lived charge separated states in redox treated samples, but not in the thin film. These results provide direct evidence that control of the supramolecular assembly process can be leveraged to affect the long-range order of derived PDI materials, thus enabling increased yield and lifetime of charge separated states for light harvesting applications. Furthermore, these results highlight the need for microscale broadband probes of organic materials to accurately capture the influence of local morphology on excited state functionality.

2.2 Introduction

Organic materials comprise a class of semiconductors with significant advantages, including low-cost solution-based fabrication and synthesis methods, low environmental impact, mechanical

flexibility, and versatile chemical tunability.⁷⁰⁻⁷² The application potential arising from the tunability of organic materials is well exemplified by π -conjugated molecular aggregates, where the optical and electronic properties can, in principle, be tuned not only by the *intra-molecular* structure determined by chemical design, but also by the *inter-molecular* structure and long-range ordering of the constituent monomers.^{7, 73, 74} Early work by Kasha serves as the foundational guide to understanding how electronic coupling between paired monomers affects absorption energy, vibronic ratios, vibrational energy redistribution and emission efficiencies through molecular dipole coupling.²¹ Kasha's early theoretical work has been expanded by Spano and others,^{28, 75, 76} showing that in addition to the dipole coupling described by Kasha's exciton model, the optical properties of π -stacked aromatic aggregates are strongly influenced by charge-transfer superexchange interactions.^{18, 19} Strongly interacting frontier molecular orbitals and consistent long-range order are central to these intermolecular coupling mechanisms, that can give rise to a host of functionalities applicable to light harvesting applications. For example, coupling can facilitate the formation of delocalized charge transfer excitons with an increased propensity to charge separate.^{77, 78}

The experimental description of intermolecular coupling and how it gives rise to the optoelectronic properties in π -stacked systems, derives in large part from extensive spectroscopic comparisons of monomers to their aggregates in the solution-phase.^{4, 5, 7, 46, 79-84} Perylene diimide (PDI) derivatives are an especially promising class of organic materials⁷⁴ because of their thermal and chemical stability, high electron affinity, and strong optical absorption.⁸⁵ H-aggregated complexes of PDI derivatives represent a powerful testbed for probing optical and electronic tunability through modulation of interchromophore π orbital overlap, as chemical modification of

side groups can be utilized to change the lowest energy stacking conformation.^{4, 5, 46, 86} The advent of such strategies to influence aggregation pathways has enabled exploration of the structure-function relationship and the emergent optoelectronic properties of supramolecular structures, as well as provided a means to design novel materials with properties targeted to specific applications.^{6, 45, 73, 81}

While spectroscopic studies of solvated aggregates are critical for establishing a fundamental understanding of intermolecular coupling, practical devices generally require condensation of the solvated precursors into a solid-state material. In the solid state, the characteristic low dielectric constant, which is in large part responsible for the superb tunability of organic materials,^{18, 78} can be especially disadvantageous, underpinning high exciton binding energies, strongly localized charge carriers, and sensitivity of excited state transport to vibrational coupling.²⁰ The parasitic effects of these properties are reflected in slow excited state transport, short lifetimes, and low device efficiencies.⁸⁵ While enhancing intermolecular orbital overlap^{18, 27} and facilitating delocalized excited states⁸⁷⁻⁸⁹ can mitigate these deficiencies^{63, 90-92}, structural disorder introduced upon solid-state deposition begets additional difficulties in the context of both fundamental studies and in potential applications. Indeed, because the electronic coupling is highly sensitive to small perturbations in π -stacking geometry, even localized regions of structural variability can give rise to significant functional heterogeneity.^{27, 75} This localized morphological (and perhaps functional) heterogeneity is especially concerning given that the crystallization of most organic materials is driven by relatively weak non-covalent interactions. Thus, if the characterization methods employed for organic materials average over the intrinsic microscale variations in morphology, they are likely to provide an incomplete picture of the structure-function relationship.^{2, 70}

In this work, we utilize broadband pump-probe microscopy with micron scale spatial resolution and femtosecond time resolution to compare the optoelectronic properties of two chemically identical PDI-derived materials with differing morphology (Fig. 2.1). The first sample, used as a baseline for comparison, is a thin film formed by drop-casting solvated molecular assemblies onto a substrate and allowing the solvent to slowly evaporate under near-equilibrium conditions (EQ-PDI). In the second sample, referred to as kinetically-trapped PDI (KT-PDI), the solid-state sample is formed from a solution of precursor assemblies whose stacking geometry is perturbed via a redox-assisted self-assembly approach.⁷³ While the modified structure of the KT-PDI assemblies has been shown to form hierarchical microscale structures and enhance exciton coupling relative to the EQ-PDI assembly in solution, it is unclear how these traits translate to the character and dynamical evolution of the excited electronic states in solid-state materials.

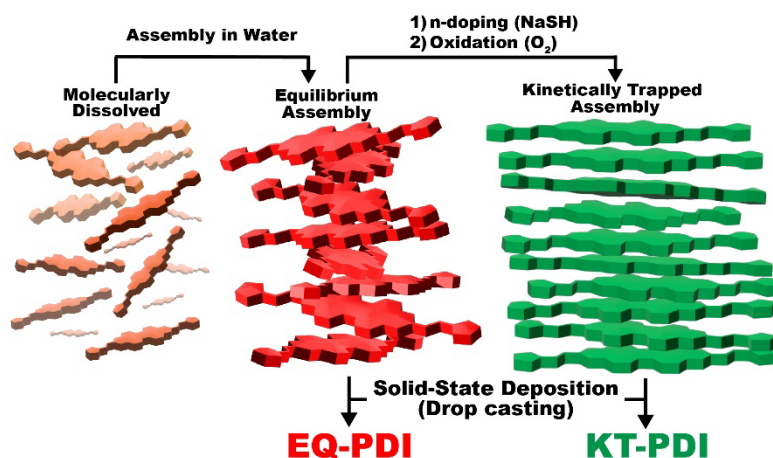


Figure 2.1: Depiction of the two divergent aggregation pathways of the amphiphilic PDI monomer units leading to the morphologically distinct equilibrium (EQ-PDI) and kinetically trapped (KT-PDI) solid state materials.

The direct comparison of the two materials presents a unique opportunity to study the excited state behavior of materials that feature identical molecular building blocks but evolve into

morphologically distinct molecular aggregates in the solid state. In addition, this strategy allows us to determine the extent to which nanoscale assembly ordering, controlled via redox-assisted assembly in the solvated state, regulates the optoelectronic properties of solid-state hierarchical materials. We find distinct differences in both ground and excited state spectroscopies of the two materials. Relative to EQ-PDI, KT-PDI exhibits significantly enhanced linear dichroism and a distinctly red-shifted absorption spectrum, consistent with increased long-range packing order. In contrast to EQ-PDI, broadband time-resolved measurements of KT-PDI reveal a rapid redshift of the excited state spectra and anisotropy in polarization-resolved kinetics. At long times, spectroscopic signatures in KT-PDI are consistent with charge separated states persisting up to the μs timescale. In sum, this comparative study unambiguously demonstrates that tuning intermolecular interactions of solution phase precursors can be leveraged to enhance long-range order and intermolecular coupling in the derived solid-state materials, giving rise to greater delocalization of the initially formed excited state and influencing the branching ratio of photogenerated species. These distinctions and their sources would be exceptionally difficult to disentangle using more conventional single wavelength approaches, highlighting the importance of broadband spectroscopic microscopies for the characterization of organic optoelectronic materials.

2.3 Materials and Methods

Synthesis.

Synthetic methods and characterization details of the perylene assemblies used as precursors for the solid-state samples studied here have been described in detail elsewhere.⁷³ Briefly, EQ-PDI assemblies were prepared by allowing 1-(2-hydroxyethyl)-3-propyl-1H-imidazolium bromide

functionalized Perylene-3,4:9,10-bis(dicarboximide) (PDI-C₃Im-C₂OH) monomers (Fig. 2.2A) to aggregate in D₂O under ambient environmental conditions. KT-PDI assemblies were produced through a reductive treatment of the D₂O suspended PDI-C₃ImC₂OH assemblies in which NaSH was incrementally added up to 2 molar equivalents (relative to initial PDI monomer concentration), followed by a single addition of NaSH solution resulting in a 5-molar equivalence of NaSH. The reduced assemblies are then oxygen-neutralized and allowed to age for 18hrs. Solid-state samples were prepared by drop casting precursor suspensions of the KT-PDI and the EQ-PDI assemblies onto fused quartz substrates. No solvent is present on the samples for any of the reported measurements.

Photophysical Measurements.

Polarization-resolved brightfield microscope images are collected using an Olympus BX51 microscope equipped with a plate polarizer. Ground state extinction spectra are collected on a custom-built microspectrometer, with the broadband light source generated by focusing 300 fs 1035 nm laser pulses into a yttrium aluminum garnet (YAG) crystal. The spot size of the continuum at the sample plane is 1.7 μm . Note that we are unable to quantify scattering or reflection signal contributions, so extinction is defined simply as $A = 1 - \frac{T}{T_0}$. Extinction of the sample is determined by dividing the spectrum transmitted through the sample (T) by a background spectrum obtained in a region of the substrate with no sample (T₀).

Time-resolved measurements of the solid-state PDI samples were collected with a broadband pump-probe instrument previously described.⁶⁹ Briefly, the instrument is pumped by a 1035nm fiber laser with a 1 MHz repetition rate and a standard pulse width of 300 fs. The fundamental beam is split to form pump and probe beams, which are independently modulated with acousto-

optic modulators. The pump is modulated at 31.25 kHz signal with a 50% duty cycle. The probe beam is focused into a YAG crystal to generate the supercontinuum, and the pump beam is focused into a Beta-Barium Borate crystal to produce the second harmonic 517.5 nm excitation pulse (power density limited to 58 $\mu\text{J}/\text{cm}^2$). At the fluence levels used, decay kinetics are independent of excitation density and the materials showed no sign of photodamage from the excitation or probe beams. Note also that because the probe is tightly focused, excited state diffusion out of the probe spot can contribute to the kinetic trace decay. However, calculations using standard methods show that for the measurements reported below, this effect is negligible, even under conditions of an exceptionally large excited state diffusion coefficient ($D_{\text{est}} = 1.0 \text{ cm}^2/\text{s}$).⁹³ A translation stage in the pump line provides the pump-probe delay and a set of galvanometer mirrors are used to spatially scan the pump relative to the probe. Spatially overlapped (pump and probe) scans of the sample are collected using a closed loop piezo stage (Mad City Labs, Nano-H100). Spatial resolution is limited by the focused beam convolution to approximately 1.7 μm . The beams are combined with an 80/20 beam splitter before being focused onto the sample with an Olympus MPlanFL N 100X 0.9 NA objective. The transmitted light is collected with a Nikon 100x TU Plan Apo 0.9 NA objective, dispersed in a grating spectrometer, and focused onto a Teledyne Octopus line-camera with 2048 pixels operating at 125 kHz.

2.4 Results and Discussion

Morphology.

Figures 2.2B and 2.2C show brightfield microscopy images of EQ-PDI thin films and KT-PDI microstructures, respectively. The EQ-PDI precursor forms thin films with variations in optical density and complex structure determined by the evaporating solvent front. Spectroscopic

measurements are performed near the edge of the “coffee ring” region of the dropcast sample, seen in the top right corner of Fig. 2.2B. The KT-PDI precursor forms long microstructures with large aspect ratios. The morphology of the KT-PDI microstructures varies between isolated long rods to crossed or bundled rods, which have been shown with transmission electron microscopy to be hierarchical superstructures of the nanoscale assemblies initially formed in solution.⁷³ These mesoscale materials, which spontaneously assemble on a substrate, enable us to carefully isolate and interrogate rod-like structures like those shown in Fig. 2.2C to compare with the EQ-PDI film. We were unable to measure X-ray diffraction patterns from either sample while maintaining the morphologies shown in Fig. 2.2, however materials derived from structurally similar monomeric precursors show π - π stacking distances of 3.45 Å in drop cast films.⁹⁴

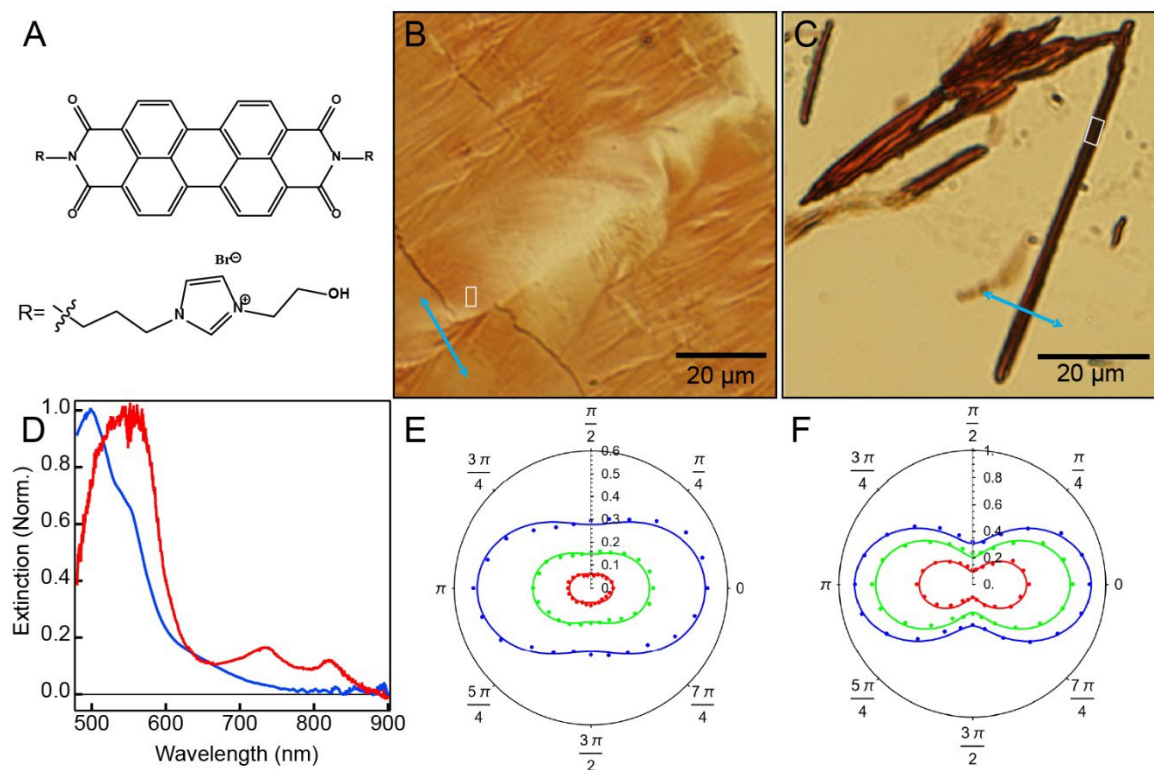


Figure 2.2: Steady state characterization of solid-state samples. (A) Both EQ-PDI and KT-PDI are composed of PDI-C₃Im-C₂OH monomer units. (B) Brightfield image of a dropcast film of EQ-PDI. (C) Brightfield image of the microstructures formed from KT-PDI precursors. In (B) and (C), the blue arrow indicates the polarization of the brightfield illumination. (D) Steady state extinction spectra of KT-PDI (red) and EQ-PDI (blue). Panels (E) and (F) show polarization-resolved extinction (measured in white boxes indicated in panels (B) and (C)) isolating the red, green, and blue camera channels of EQ-PDI, and KT-PDI, respectively. Solid lines are fits from Malus' law.

Ground State Extinction.

Figure 2.2D shows a comparison of the normalized extinction spectra collected from a region $\sim 1.7 \mu\text{m}$ in diameter on each sample. The EQ-PDI spectrum shows good agreement with previously reported absorption spectra of PDI derivatives in the solid-state.^{4,95} The solid-state EQ-PDI spectrum is similar to that of the EQ-PDI precursor suspension (Fig. S1), although the solid-state spectrum exhibits broadened vibronic peaks and a shoulder feature near 650 nm that is absent in the suspension. The similarity of the spectra suggests that condensation has a mild effect on the

electronic coupling between chromophores, with the 650 nm band perhaps indicating regions of structural disorder that lead to lower energy sites. In contrast, the KT-PDI sample shows a prominent redshifted absorption peak at 550 nm, which extends beyond 600 nm. While these lower energy transitions could be seen as evidence of low energy states arising from structural defects, linear dichroism measurements, described below, indicate that the KT-PDI sample is structurally more ordered than the EQ-PDI sample. We therefore attribute the redshifted absorption to delocalized electronic states perhaps made accessible by the altered packing geometry and stronger electron coupling in the KT-PDI microstructures. Also present in the KT-PDI spectrum are two peaks at 735 nm and 820 nm, that are also observed in solution-phase measurements (Fig. S2) of the aggregate upon electrochemical reduction. These two peaks are assigned to vibronic transitions of the electron polaron⁹⁶ and indicate the presence of persistent reduced species from the redox-assisted self-assembly or alternatively self n-doping behavior that has been previously shown in solid-state PDI with similar imide functionalizations.^{97, 98}

Polarization Dichroism.

To provide insight into the microscale order of the two samples, we next turned to polarization-resolved brightfield microscopy. Examination of Fig. 2B shows large variations in the optical density with $\sim 10 - 20 \mu\text{m}$ long channels aligned approximately orthogonally to the edge of the film. These variations in extinction are a result of linear dichroism and show inverted contrast if the polarization of light is rotated by 90° (Fig. S3). Such polarization dichroism has been previously correlated to the long-range alignment of PDI cores, achieved, for example, through a layer-by-layer electrostatic assembly method.^{38, 99} Given their shape and orientation relative to the film edge, we suspect the channels are local regions where alignment of the precursor assemblies

was perturbed during deposition, presumably due to local differences in the solvent evaporation rate. Qualitatively, this polarization-resolved brightfield image demonstrates the need for spatially resolved spectroscopic probes, as the local structure is clearly sensitive to microscale variations in the environment during crystallization.

Malus' law can be used to evaluate long-range chromophore ordering by quantifying extinction as a function of the angle between the polarization of the light and the electronic transition dipole moment.^{100, 101} For PDI, the largest electronic transition dipole moment is oriented along the long axis of the aromatic core of the molecule.¹⁰² Figure 2.2E shows polarization-dependent extinction ($1-T/T_0$) collected from a $8\text{ }\mu\text{m}^2$ ($2\times 4\text{ }\mu\text{m}$, drawn as a white box on Fig. 2.2B) region of the EQ-PDI film with homogeneous polarization response. The blue channel of the image sensor shows the strongest polarization anisotropy and is resonant with the primary excitation band in PDI.¹⁰³ For the data shown in Fig. 2.2E, the dichroism³⁸ ($D = \frac{A_{max}-A_{min}}{A_{max}+A_{min}}$, where A_{min} and A_{max} are the minimum and maximum extinction values) is found to be $D = 0.29 (\pm 0.01)$ for the blue channel. We note that despite using a simple drop casting procedure for the EQ-PDI film, this dichroism value is comparable to that observed in previously reported PDI films intentionally oriented with an electric field.³⁸ The high dichroism we observe here likely reflects a combination of the local alignment achieved by the coffee ring effect³⁶, as well as the fact that the precursor solution is comprised of molecular assemblies rather than solvated monomers.³⁸ We find that for the EQ-PDI film, A_{max} is oriented parallel to the edge of the film, and A_{min} is oriented perpendicular to the film edge. However, as can be seen in Fig. 2.2B, there is significant microscopic heterogeneity, where nearby regions form features with differing anisotropy from each other and the spatially averaged behavior.

Whereas the EQ-PDI film has microscale regions in which the assembly orientation is altered relative to the bulk, the KT-PDI microstructures show consistent linear dichroism throughout (Fig. 2.2C). In Fig. 2.2F we show the polarization-resolved extinction from the region highlighted in Fig. 2.2C. In comparison to the EQ-PDI film, the KT-PDI microstructure shows even greater polarization anisotropy, with a dichroism value of $0.48 (\pm 0.01)$ on the blue channel. For KT-PDI, A_{min} is oriented parallel to the long axis of the microstructure, and A_{max} is perpendicular. Without a detailed crystal structure, it is difficult to evaluate the extent to which the dichroism value we measure in KT-PDI microstructures reflects the intrinsic packing geometry vs. conformational disorder. In the simplest case in which the plane of the PDI aromatic core is orthogonal to the long axis of the microstructure, and there are no electronic states with a transition dipole moment with a finite projection parallel to the structure's long axis, we would expect to measure a dichroism value of 1. However, more complicated stacking geometries (i.e. a slip-stack arrangement) and/or new electronic states with transition dipoles along the long axis (due perhaps to interchromophore coupling) would reduce this value from its ideal limit. Nevertheless, as a relative measure of long-range order, the greater polarization anisotropy clearly indicates that the ordering in the KT-PDI sample is significantly higher than even the locally homogeneous regions of the EQ-PDI film.

Transient Microscopy.

To probe how the morphological differences of the two PDI samples affect their excited state functional properties, we next turned to broadband pump-probe microscopy. The spectral resolution of broadband transient transmission measurements are useful in interpreting excited state behavior of solid organic materials where spectral resonances are 100s of nanometers broad, with strongly overlapping signals from singlet exciton absorption,¹⁰⁴ charge-transfer

excimer absorption,^{82, 83, 105} and triplet absorption.^{84, 86, 106-108} Figure 2.3 summarizes the transient response of the EQ-PDI thin film up to a pump-probe delay (Δt) of 400 ps. The $\Delta t = 0$ ps pump-probe image shown in panel A is representative of the film, with spatial variation in signal intensity reflecting the microscale domains noted in the polarization-resolved brightfield images (Fig. 2.2B), as well as local variation in sample thickness. Although the pump polarization does not affect the shape of the transient spectra, the amplitudes of the spectral features are reduced by a factor of approximately two when the pump is polarized along the direction of minimum extinction ($A_{\min}$). For all the pump-probe data presented here (for both EQ-PDI and KT-PDI), the pump is polarized along the direction of maximum extinction ($A_{\max}$).

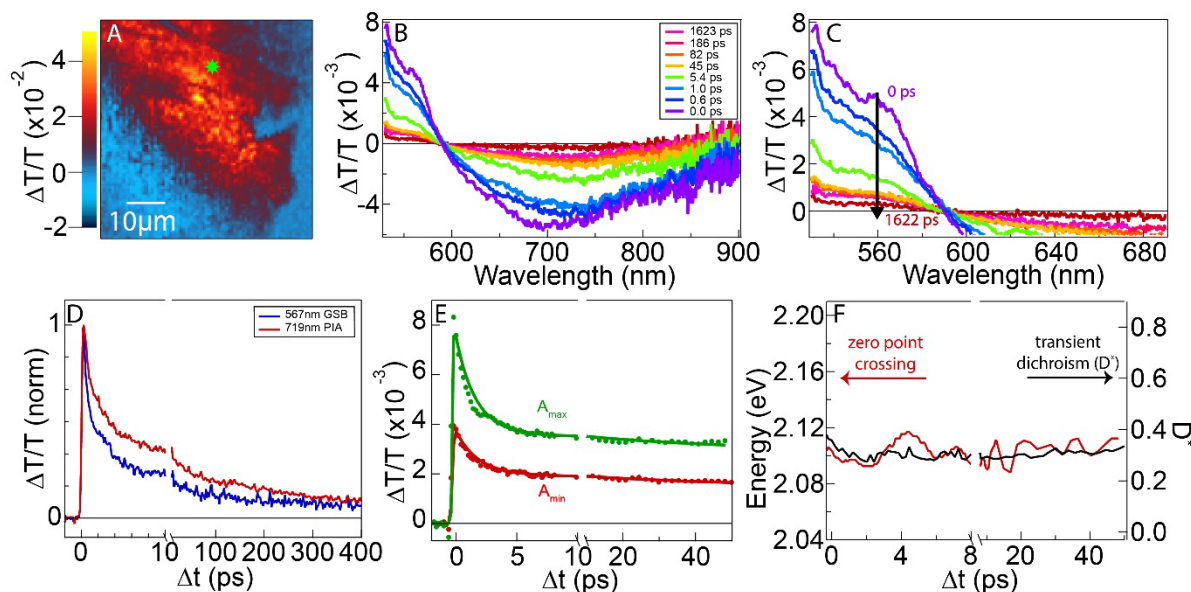


Figure 2.3: Excited state microscopy of EQ-PDI. (A) Spatially resolved pump-probe images of EQ-PDI (540-567nm) collected at $\Delta t = 0.1$ ps. (B) Broadband $\Delta T/T$ spectra for delay times $\Delta t = 0, 0.6, 1.01, 5.42, 82, 186,$ and 1622 ps collected from the location indicated by the green star in panel A. (C) Detailed view of the ground state bleach region. (D) Comparison of normalized decay kinetics of the GSB ($\lambda = 567$ nm in blue) and the PIA ($\lambda = 719$ nm in red). (E) comparison of early time kinetics at $\lambda = 542$ nm for $A_{\max}$ and $A_{\min}$ probe polarizations. The solid traces show biexponential fits to the data. (F) Early time zero-point crossing of the transient spectra (red) and time dependent linear dichroism (black).

Figures 2.3B and 2.3C show chirp-corrected transient transmission spectra ($\Delta T/T$), collected from the location on the EQ-PDI sample indicated by the green star in panel A. The spectra are collected with both the pump and the broadband probe polarized along $A_{\max}$ and are generally characterized by a ground state bleach (GSB) on the blue edge of the spectrum and a broad, nearly featureless photoinduced absorption (PIA) that spans 590-900 nm. The GSB closely matches the ground state absorption shown in Fig. 2.2D and is consistent with bleach features previously reported for other solid-state PDI films.⁹⁵ The PIA maximum undergoes a slight redshift from 706 nm to 727 nm in the first few picoseconds, which we attribute to structural reorganization associated with the excited state electron configuration. The PIA and the GSB relax with similar kinetics, resulting in a nearly ideal isosbestic point at 590 nm, as can be seen in the magnified view of the bleach region shown in Fig. 2.3C. Normalized kinetic traces of the GSB ($\lambda = 567$ nm) and PIA ($\lambda = 719$ nm) are shown in Fig. 2.3D, and while the kinetics at 719 nm decay slightly slower at early times due to the PIA spectral redshift, the PIA and GSB kinetics are identical after 10 ps (Fig. S4), consistent with a two level model in which the excited state population (described by the PIA) decays directly back to the ground state.

Recent solution-phase transient absorption measurements of similar PDI aggregates assign a PIA peak at $\lambda = 600$ nm to the singlet exciton and, based on spectroelectrochemical comparisons, a second PIA band with a peak at $\lambda = 720$ nm to the radical anion absorption.^{8, 109} The broadband spectra shown in Fig. 2.3 show no evidence of a PIA near 600 nm immediately after photoexcitation, suggesting that the initially formed singlet excitons rapidly convert¹¹⁰ (within the instrument response time of ~ 300 fs) into a charge transfer excimer or charge separated state with strong anionic character.^{111, 112} We note that independently probing the evolution of PBI

radical cation is hindered by its low extinction, strongly overlapping spectrum with both the radical anion and excitonic transient spectra.¹¹³⁻¹¹⁵ Early time kinetics (Fig. 2.3D) of the bleach region ($\lambda = 542$ nm) with the probe polarized parallel ($A_{\max}$, green) and perpendicular ($A_{\min}$, red) to the pump show nearly identical decay kinetics, with initial lifetimes that are the same within error ($A_{\max}$: $\tau = 1.6 (\pm 0.2)$ ps and $A_{\min}$: $\tau = 1.8 (\pm 0.2)$ ps). In analogy to the ground state linear dichroism discussed above, we can also calculate the transient linear dichroism, defined by $D^*(\Delta t) = [(\Delta T/T)_{A_{\max}} - (\Delta T/T)_{A_{\min}}]/[(\Delta T/T)_{A_{\max}} + (\Delta T/T)_{A_{\min}}]$, which provides a measure of the linear dichroism of the excited state. As can be seen in Fig. 2.3F, $D^*(\Delta t)$ is delay independent and is closely comparable to the ground state dichroism (of the RGB green channel), $D = 0.27$. This static behavior indicates that the excited state of the EQ-PDI sample is localized with little or no evolution of the dipole along the PDI stacking axis.¹¹⁶ Instead, the anisotropy observed in both the ground and excited state spectra likely reflects structural disorder (i.e. differently oriented PDI monomers) introduced during film fabrication. Together, the excited state polarization anisotropy, the well-defined isosbestic point, and the similar relaxation profiles of the GSB and PIA strongly suggest that excitation of the EQ-PDI film rapidly results in a localized charge transfer excimer that directly relaxes back to the ground state.^{88, 117}

Figure 2.4 summarizes the time-resolved microscopy results for the KT-PDI sample. The pump-probe image in Fig. 2.4A shows a region of the sample with two larger crossed microstructures and a small, isolated microrod. The kinetics and spectra shown in the other panels of Fig. 2.4 were collected on the isolated rod at the location indicated by the green star. The polarization of the pump was adjusted to be parallel to $A_{\max}$ or perpendicular to the long axis of the crystal, and unless otherwise indicated (Fig. 2.4E), the probe polarization is along $A_{\max}$ for the data shown in Fig. 2.4.

Broadband pump-probe spectra of the KT-PDI sample, collected from $\Delta t = 0$ ps to $\Delta t = 1600$ ps, are shown in Fig. 2.4B and Fig. 2.4C. Qualitatively, the transient spectra are similar to EQ-PDI, with a GSB on the blue edge of the spectrum and broad photoinduced absorption from $\lambda \sim 600$ nm to $\lambda = 900$ nm. Closer inspection, however, reveals distinct differences between the excited state dynamics of the two samples. First, while the GSB initially looks similar to that of EQ-PDI, the bleach in KT-PDI rapidly broadens and redshifts (Fig. 2.4F), with a peak that moves from 570 nm to 600 nm in the first 6 ps after photoexcitation. The bleach then continues to slowly grow for ~ 200 ps before decaying on the nanosecond timescale. As a result of this spectral evolution, there is no clear isosbestic point in the transient spectra, with the zero-crossing point shifting from 590 nm at $\Delta t = 0$ ps to 660 nm at $\Delta t = 1600$ ps. The growth of the redshifted bleach feature is clearly visible in Fig. 2.4D, which shows a comparison between the GSB kinetics at $\lambda = 567$ nm and the PIA kinetics at $\lambda = 719$ nm. While the kinetics traces decay at comparable rates for the initial 10-20 ps, the superimposed growth and redshift of the bleach as well as overlapping PIA relaxation results in a clear rise over the next 200 ps.

A second important difference is revealed in the polarization-resolved kinetics. Whereas in EQ-PDI the early time kinetics collected at $\lambda = 542$ nm measured with the two orthogonal probe polarizations were highly similar (Fig. 2.3E), in KT-PDI they differ substantially. For the kinetics collected with probe polarization along $A_{\max}$ (Fig. 2.4E, green), fits to the data recover an early decay lifetime of $\tau = 0.8 (\pm 0.1)$ ps, slightly shorter than the lifetimes observed in EQ-PDI for both $A_{\max}$ and $A_{\min}$ polarizations. However, as shown by the red trace in panel E, the kinetics measured along $A_{\min}$ grow in with a time constant of $265 (\pm 15)$ fs and decay on much slower timescales. This difference in polarization response leads to distinct transient dichroism behavior, as plotted

in Fig. 2.4F. Immediately after photoexcitation, $D^*(\Delta t = 0) = 0.65$ is slightly larger than the ground state green-channel dichroism ($D = 0.56$), before decaying to nearly 0.0 within 10 ps. The rapid decay of $D^*(\Delta t)$ implies that, in contrast to EQ-PDI where the transient dichroism simply reflected the film morphology and was therefore time independent, in KT-PDI the excited state evolves from a state whose transition dipole projects in the same orientation as the ground state absorption to one in which the transition dipole is more strongly polarized along the π -stacking direction (long axis of the microrod).

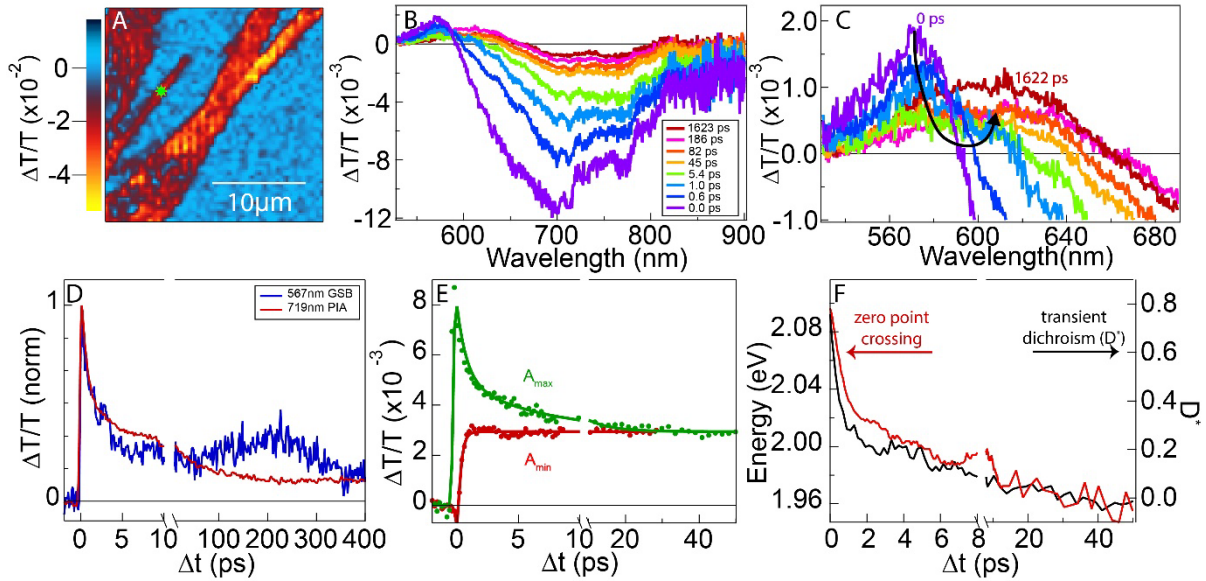


Figure 2.4: Excited state microscopy of EQ-PDI. (A) Spatially resolved pump-probe images of KT-PDI (670-711nm) collected at $\Delta t = 0.1$ ps. (B) Broadband $\Delta T/T$ spectra for delay times $\Delta t = 0, 0.6, 1.01, 5.42, 82, 186,$ and 1622 ps collected from the location indicated by the green star in panel A, with (C) a detailed view of the ground state bleach region. (D) Comparison of normalized decay kinetics of the GSB ($\lambda = 567$ nm in blue) and the PIA ($\lambda = 719$ nm in red). (E) comparison of early time kinetics at $\lambda = 542$ nm for A_{max} and A_{min} probe polarizations. The solid traces show biexponential fits of the data. (F) Comparison between the transient spectral zero-point crossing (red) and time dependent linear dichroism (black).

When compared with EQ-PDI, the distinct excited state spectral evolution of KT-PDI strongly suggests that its increased long-range ordering enables access to a manifold of lower energy excited states with substantial oscillator strength along the π -stacking direction. While the PIAs of both samples have anionic features which are characteristic of an excited state with charge transfer character, the redshifting GSB and the time-dependent excited state polarization dichroism show that the excited state in KT-PDI is not immediately trapped like in EQ-PDI, but evolves for 10s – 100s of ps. A comparative plot of the spectral redshift of the GSB and the transient linear dichroism (Fig. 2.4F) shows that the time evolution of the two spectroscopic signatures is nearly identical, indicating that the two processes are reporting on the same excited state relaxation process. Together, these spectroscopic observables suggest that after photoexcitation of KT-PDI, the initially photogenerated state relaxes on the picosecond timescale to form a delocalized charge-transfer exciton.^{95, 110} Although the susceptibility to photodamage and the broad spectral resonances of these solid state materials make it difficult to estimate a delocalization length¹¹⁸⁻¹²⁰, similar delocalization behavior has been observed in analogous non-covalent organic solids, where increased molecular ordering has been correlated with delocalization of charge-transfer excitons over multiple molecular pairs.^{27, 121} It is especially noteworthy that because the two films are assembled from the same monomer subunit, this distinct difference in photophysical behavior can only be a result of the different assembly conditions and morphologies of the two samples.

Delocalized charge transfer excitons are known to help facilitate higher rates of charge separation^{27, 63, 78} and lead to better efficiencies in light-harvesting devices.¹²² To test whether the enhanced delocalization observed on the ps-ns timescale in KT-PDI resulted in any difference in excited state evolution and charge carrier formation, we next measured transient spectra from both

samples at a delay time of $\Delta t = 1 \mu\text{s}$. To achieve this long pump-probe delay we adjusted the acousto-optic modulator timing values to select pump and probe pulses with a $1 \mu\text{s}$ separation. Figure 2.5A shows a comparison of these long-lived spectral signatures for both EQ-PDI (blue) and KT-PDI (black). For EQ-PDI (blue) the transient spectra are characterized by a low amplitude signal ($\sim$ one hundredth of $\Delta t = 0 \text{ ps}$ signal) that closely resembles the early time transient transmission spectra (Fig. 2.3). This similarity of the early and late time spectra suggests that a small subpopulation of long-lived excimers persist even to μs timescales. Given the spectral similarity of the early and late time populations, it is difficult to precisely explain the origin of this long-lived portion of the population. However, it may be that microscopic structural heterogeneities facilitate the formation of the long-lived states that are decoupled from the dominant relaxation pathways.

In contrast to EQ-PDI, the $1 \mu\text{s}$ KT-PDI transient spectra has significant amplitude ($\sim$ one tenth of $\Delta t = 0 \text{ ps}$ signal) and is distinct from the early time transient transmission spectra, with sharp positive peaks at 818 nm and at 726 nm overlaying a broad PIA. The distinctive peaks closely align with the monoanionic vibronic absorption features observed in ground state extinction spectra of KT-PDI.^{73, 97, 98, 123} Comparison of the transient spectra with the ground state extinction spectra shows the transient features do not arise from a simple bleaching of the ground state spectrum. Whereas the band near 720 nm is stronger than that near 820 nm in the ground state extinction spectrum (Fig. 2.2D), the relative intensities are reversed in the transient spectrum, with the band at 818 nm nearly a factor of three more intense than that at 726 nm. Instead, we assign the long-lived transient spectrum to an electron polaron, resulting from charge separation of the delocalized charge-transfer exciton. Comparison of the $1 \mu\text{s}$ KT-PDI transient transmission

spectrum to a calculated difference spectrum obtained from chemical reduction supports this assignment (Fig. 2.5b). Shown in red in Fig. 2.5b is the differential spectrum determined by subtracting the solution-phase transmission spectrum of KT-PDI assemblies at 0.3 equivalents sacrificial electron donor (NaSH) concentration from that obtained at 0.5 equivalents. The difference spectrum shows that as the electron concentration in the assemblies increases, the features associated with monoanion absorption bleach and transmission near 650 nm decreases. Although not a perfect match, the simulated spectral evolution is consistent with the spectral features observed in pump-probe data. Differences between the two spectra likely arise from radical cation contributions, including ground state bleaching (particularly around 600 nm) and the broad PIA evident in the $\Delta t \sim 1$ ns transient spectra (Fig. 2.4D). Moreover, aromatic dianion stabilization or the formation of negative trions may also be contributing to the prolonged existence of anionic spectral signatures.^{98, 124}

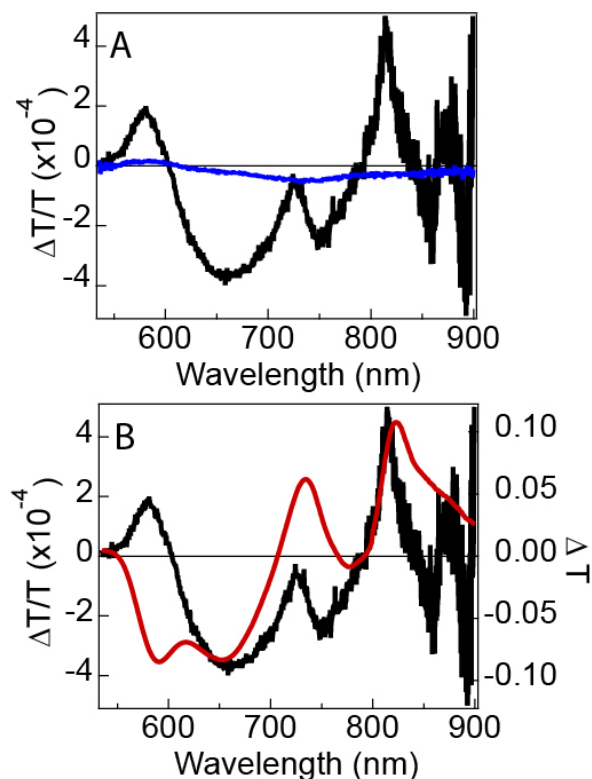


Figure 2.5: Long lived transient transmission signal $\Delta t = 1 \mu s$ after photoexcitation (Panel A). The blue trace corresponds to EQ-PDI ($A_{\max}$) and black to KT-PDI ($A_{\max}$). Panel B compares the long-lived KT-PDI spectra (black) to the differential spectrum (red) calculated from steady state spectra collected for different levels of PDI-C₃Im-C₂OH chemical reduction ($T_{0.5eq.NaSH} - T_{0.3eq.NaSH}$).

The spectroscopic evidence of long-lived electron polarons in KT-PDI and its absence in EQ-PDI can be understood by considering the differences in early time excited state evolution for the two samples. For EQ-PDI, we observe no evidence of excited state delocalization (Fig. 2.3) in the early time dynamics. It appears that in EQ-PDI, the reduced crystalline order (Fig. 2.2E) results in localized excited states, which directly relax to the ground state. In contrast, for KT-PDI we observe spectral redshifting and evolution of the polarization dichroism (Fig. 2.4), both of which indicate that initially photogenerated states undergo rapid relaxation to form delocalized charge-transfer states. Because delocalization will reduce the Coulomb coupling between charges, these

states are more likely to charge separate to form polarons.^{17, 19, 27, 122} Delocalization will also reduce phonon coupling, which may make the nascent polarons more mobile. Thus, the formation and perhaps greater mobility of delocalized polarons leads to a long-lived population that persists on timescales greater than 1 μ s.

2.5 Conclusion

This work highlights the importance of non-covalent assembly processes in determining the solid-state morphology of derived molecular aggregate materials. Using both steady state and time-resolved microscopies, fundamental differences in the nature and evolution of excited state species are identified in morphologically distinct PDI-C₃ImC₂OH aggregates. Brightfield microscopy and linear dichroism indicate that relative to EQ-PDI, the long-range ordering of KT-PDI is significantly enhanced. Broadband transient spectra, collected using a pump-probe microscope to ensure that the probed regions of both samples are structurally homogeneous, are consistent with formation of an initial excited state population with significant charge transfer character. However, in KT-PDI, increased electronic coupling and greater long-range order result in excited state evolution on the 1s – 100s of ps timescale to a delocalized charge-transfer state poised for charge separation. At long times ($\Delta t = 1 \mu$ s), only KT-PDI exhibits transient spectral features that are characteristic of electron polaron formation, highlighting the importance of delocalization in charge-separated excited state formation. These results confirm the potential of controlling solution-phase aggregation pathways to affect the nature and trajectory of photoexcited species in solid-state organic materials derived from molecular aggregate precursors. These approaches may provide a reliable approach for the formation of solid state materials that facilitate charge separation, with substantive implications for both photovoltaic and photocatalytic applications.^{78,}

^{92, 122} Finally, we note that the combination of structural heterogeneity and broad spectral resonances that are characteristic of solid-state molecular solids pose a significant barrier to photophysical understanding of these challenging systems. Ensemble spectroscopies necessarily integrate over structural variation, and single wavelength microscopies can miss important spectral dynamics. In this respect, broadband time-resolved microscopy offers enormous potential as a tool to elucidate the particularly sensitive structure-function relationship in molecular solids.

CHAPTER THREE

ENERGETICALLY DEPENDENT TRANSPORT AND
RELAXATION DYNAMICS WITHIN A SINGLE
PORPHYRINIC METAL ORGANIC FRAMEWORK
MICROCRYSTAL

Contribution of Authors and Co-Authors

Manuscript in Chapter 3

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Contributions: Designed experiments collected and analyzed steady-state and time resolved data.

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Contributions: Designed experiments collected and analyzed steady-state, and time resolved data.

Co-Author: Amanda J. Morris

Contributions: Provided PCN-222 material and review of manuscript

Co-Author: Erik M. Grumstrup

Contributions: Assisted with analysis and editing of the manuscript for final submission

Manuscript Information

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3.1 Abstract

Spectroscopic characterization of porphyrinic metal-organic frameworks has primarily been performed through ensemble measurements in the suspended phase. These measurements only reveal structurally averaged functional properties. In this work, broadband and two-color time-resolved pump-probe microscopy measurements are presented to elucidate the ultrafast dynamics within individual PCN-222 MOF single crystals. The simultaneous high spatial, temporal, and spectral resolution of these microscopic techniques facilitates the observations of time-resolved spectroscopic evolution within single microcrystals. The transient broadband spectra from PCN-222 microrods exhibit ground-state bleach of the Q bands, stimulated emission peaks and transient absorption features, and their relaxation dynamics. A significant red shift in the broadband spectra was observed in the bent regions relative to the straight regions in the microrods, which was attributed to microscale structural defects introduced during crystallization. Two-color pump-probe microscopy enables direct measurement of excited state transport and the imaging of exciton diffusion with the Soret band and Q band excitation on the same MOF crystal. The results show that Soret band excitation causes rapid but sub-diffusive exciton transport where hot carriers are rapidly transported through the porphyrin network of PCN-222 before becoming trapped. In contrast, Q band excitation yields no evidence of exciton transport, and excited states do not travel far through the porphyrin network of PCN-222. Collectively, these measurements offer valuable new perspectives on light harvesting MOF system functionality by defining the influence of excitation energy and structural heterogeneity on the excited state characteristics and dynamics within a single structure.

3.2 Introduction

Metal-organic frameworks (MOFs) comprise a category of molecular assemblies where organic linkers connect metal clusters, forming an ordered porous network of chromophores.¹²⁵ This structural arrangement in MOFs is the foundation of their strong potential in light harvesting and photochemical applications, achieving advantageous photophysical properties, such as high extinction coefficients and efficient energy transfer, with highly organized and densely packed chromophores.¹²⁶⁻¹²⁸ Zr-TCPP-based MOFs have gained enormous attention due to their exceptional chemical stability even under harsh experimental conditions and their diverse range of functionalities, including catalysis, light harvesting, gas storage, and sensing.¹²⁹⁻¹³²

While the existing comprehension of excited state dynamics in MOFs is mainly derived from ensemble spectroscopic studies, recent research suggests that employing single-structure probes can reveal undiscovered relations between the structure and photophysical function within MOF crystals.^{128, 133, 134} Ensemble measurements have only provided structure-averaged spectroscopic observables, which conceal the impact of structural heterogeneity in determining the photophysical properties of MOF microstructures. Our previous work has utilized two-color pump-probe microscopy to explore transport properties and relaxation dynamics in individual porphyrinic MOF microstructures. Rapid sub-diffusive exciton transport was observed, and relaxation dynamics have significant lifetime variation which was correlated with structural heterogeneity. However, the experimentally measured values of the time-averaged diffusion coefficient were a factor of 20 larger than those predicted by Forester theory. To achieve a comprehensive understanding of the excited state dynamics in porphyrinic MOF microstructures, broadband transient absorption microscopy can be a substantial tool. With broadband transient

absorption microscopy, the time-resolved spectral and spatial evolution of the Q bands can be observed to explain the exciton transport more clearly.

We have employed broadband transient absorption microscopy to study the spectral intricacies of individual microrods in the PCN-222 MOF. PCN-222 (or MOF-545), based on Tetrakis (4-carboxyphenyl)-porphyrin (H_2TCPP) is a highly stable mesoporous zirconium–porphyrin MOF where the H_2TCPP ligand in PCN-222 functions as a visible-light-harvesting unit.^{130, 135} The spectroscopic measurements unveil some crucial understanding regarding the excited state dynamics in this porphyrin-based MOF. Initially, we directly measure the transient absorption spectra of an individual structure that align with the steady-state spectra of the H_2TCPP ligand monomer. The transient absorption spectrum relaxes without significant transformation biexponentially with a long lived offset. Secondly, we observe significant spatial variations in transient spectral peak positions within each PCN-222 microrod. The spatial shift in spectra is particularly pronounced in regions where the microrods exhibit bending. It is hypothesized that these bent regions result from defects that accumulate during growth, leading to a reoriented preferential growth direction. Previous work exciting with 400nm light, has correlated variation in relaxation dynamics with structural heterogeneity.¹³³ However, we observe spatially homogenous relaxation dynamics within a microstructure when pumping with 517nm light. Finally, to understand this phenomenon we compare excited state relaxation and transport arising from 400nm and 520nm excitation within a single domain. The results show that the nature of excited state transport and the relaxation dynamics in PCN-222 microrods depend strongly on excitation energy and reveal valuable insight for the future design of PCN-222 based light harvesting systems.

3.3 Synthesis PCN-222

PCN-222 microrods were synthesized by suspending $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, TCPP, and DFA in DMF within a scintillation vial. The suspension was placed in an oven set at 120°C for 18 hours. The resulting violet powder underwent centrifugation and was then washed with DMF and acetone. Subsequently, the microrod powder was dried under vacuum at 60°C overnight.^{134, 136} For microscopy sample preparation, PCN-222 microrods were dispersed in ethanol, spin-coated onto a glass substrate, and heated at 200°C for 10 minutes on a hot plate to ensure complete solvent evaporation. Then the annealed PCN-222 thin film was encapsulated with a Styrene Ethylene Butylene Styrene (SEBS) bead coating to prevent photodegradation.

3.4 Result and Discussion

Figure 3.1, panel A, shows a representative scanning electron microscopy (SEM) image of a straight PCN-222 microrod. The rods are faceted with hexagonal cross-sections and show few structural defects visible on the surface. The hexagonal microstructures can have bent structures or can bundle to form complex superstructures. In Fig. 3.1 panel B, we show a PPM image of a typical PCN-222 rod collected on a homebuilt transient broadband pump-probe microscope. The transient transmission ($\Delta T/T$) image is collected by scanning overlapped pump ($\lambda = 517 \text{ nm}$) and probe (626 nm) beams with a spatial convolution of $\sim 1 \mu\text{m}$ at a pump-probe delay time of $\Delta t = 1 \text{ ps}$. The negative $\Delta T/T$ signal arises from a combination of Q-band photo-induced absorption ($S_1 \rightarrow S_n$).¹³⁷ Figure 3.1C illustrates the normalized absorption spectra of solid-state PCN-222 microstructures (red trace) and H_2TCPP suspended in THF (blue trace). Normalized emission

spectra of solid state PCN-222 (red trace) and H₂TCPP suspended in THF (blue trace) are shown in Fig. 3.1D.

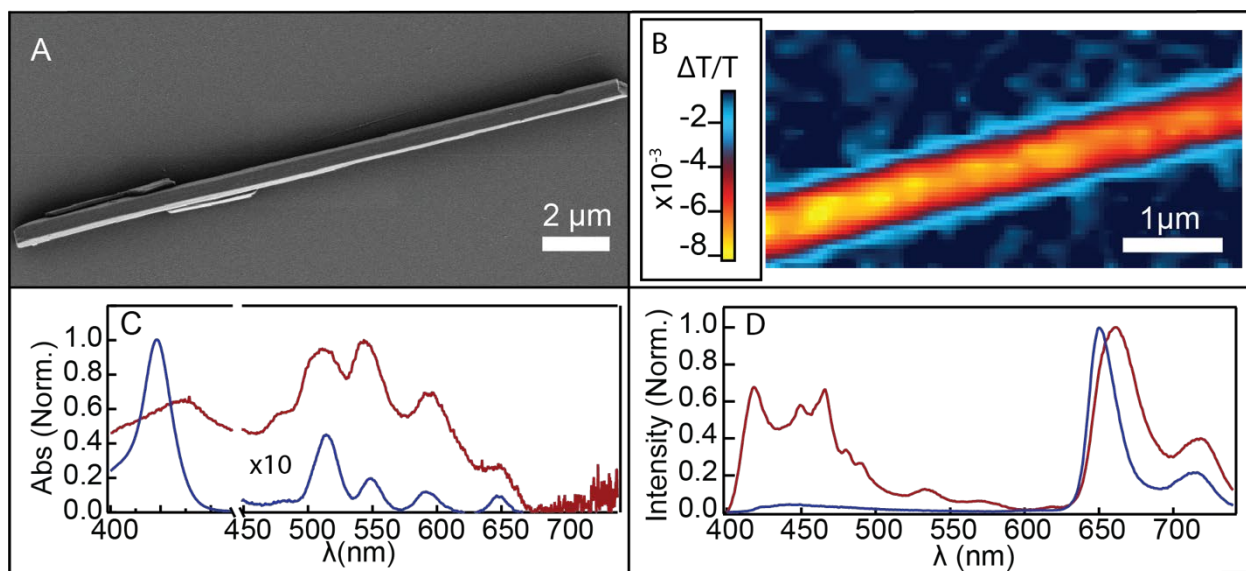


Figure 3.1. PCN-222 microrod. (A) SEM image of a straight rod. (C) Transient transmission image of a single rod (B) Normalized absorption spectra of PCN-222 (red trace) and H₂TCPP (blue trace) (D) Normalized emission spectra of PCN-222 (red trace) and H₂TCPP (blue trace).

The spectroscopic character of PCN-222 in the visible is defined by the organic ligand TCPP, and the absorption bands of TCPP, shown in blue in Fig. 3.1C, arise from π - π^* electronic transitions on the porphyrin macrocycle.^{58, 60} The solid state PCN-222 absorbance shown in red (Fig. 3.1C) highlights some important differences from the suspended TCPP monomer, but first a discussion of the theory behind TCPP photophysics is warranted. The lower energy absorption peaks (450nm-660nm) are called Q-band transitions ($\text{HOMO}(\text{HOMO}-1) \rightarrow \text{LUMO}$) and are split by vibronic coupling and macrocycle protonation in free base porphyrin. The higher energy transition at 418nm ($\text{HOMO} \rightarrow \text{LUMO}+1$) is termed the Soret (or B) band. The relative intensity of these absorption bands is strongly affected by molecular symmetry and dipole moment

interactions, where the two transition dipole moments that give rise to the Q-band transitions exhibit alternancy symmetry. The two dipole moments of opposite sign mix, leading to the cancellation of their intensities.⁶⁰ The two analogous transitions for the Soret-band have synchronous symmetry and reinforce each other leading to a strong transition dipole moment.⁶⁰,
 138 Because the Q-band transitions are pseudo-forbidden the absorption is weak relative to the Soret-band absorbance (Fig 3.1). The assembly of TCPP into the MOF PCN-222 shifts the observed Soret-band absorption by 83meV, however the Q-band absorptions do not significantly shift in energy but gain significant intensity relative to the Soret-band³. In PCN-222 microrods, Q-band and Soret-band absorption are on the same order of magnitude indicating incorporation of the ligand into the framework may relax the parity constraints (Fig 3.1 Panel C). We believe the spectroscopic changes of TCPP that occur from monomer to PCN-222 are a consequence of electronic coupling between the chromophore linkers particularly affecting Soret-band excitation. The stronger energetic effect shown by the Soret-band can be interpreted through the lens dipole-dipole coupling where coupling energy is proportional to product of the interacting dipole moments.²¹ A theoretical analysis of porphyrin aggregation presented by Zimmerman et. al in 2003 and supports the hypothesis that the spectral effects we have observed in PCN-222 likely arise from excitonic coupling between TCPP linkers.¹³⁸ Similarly enhanced absorption of the Q-bands has been reported in aggregated free base porphyrin and in covalent organic frameworks(COF) with enforced J-aggregate conformations. ^{53, 139} In the J-aggregate COF molecular coupling led to lengthened excited state lifetimes as well as facilitation of excited state delocalization.⁵³ The changes in ground state absorption between TCPP monomers to PCN-222

evidence coupling between TCPP linkers, and inform how the structural properties of the framework affects the electronic properties of the material.

Another important difference between the TCPP monomer in isolation and PCN-222 is found in the steady state fluorescence profile (Fig. 3.1D). In TCPP, 400nm excitation into the Soret-band is followed by rapid, femtosecond time scale, relaxation to the Q-bands where vibrational cooling and fluorescence occurs.^{58, 59} Thus, very little emission is observed from the Soret-band or any other band but the Qx(0,0) and Qx(0,1) transitions shown by the blue spectrum in Fig 3.1D. On the other hand, solid-state PCN-222 (red spectrum in Fig. 3.1D) shows considerable emission intensity from the Soret-band and subtle emission from higher vibrational energy Q-band transitions. The reason for the enhancement of Soret-band emission is not fully elucidated, but the lifetime of these emissive states is investigated further below, and the presence of appreciable emission intensity suggests that the transfer of the excited state from the Soret-band to the Q-band is significantly slower in PCN-222.

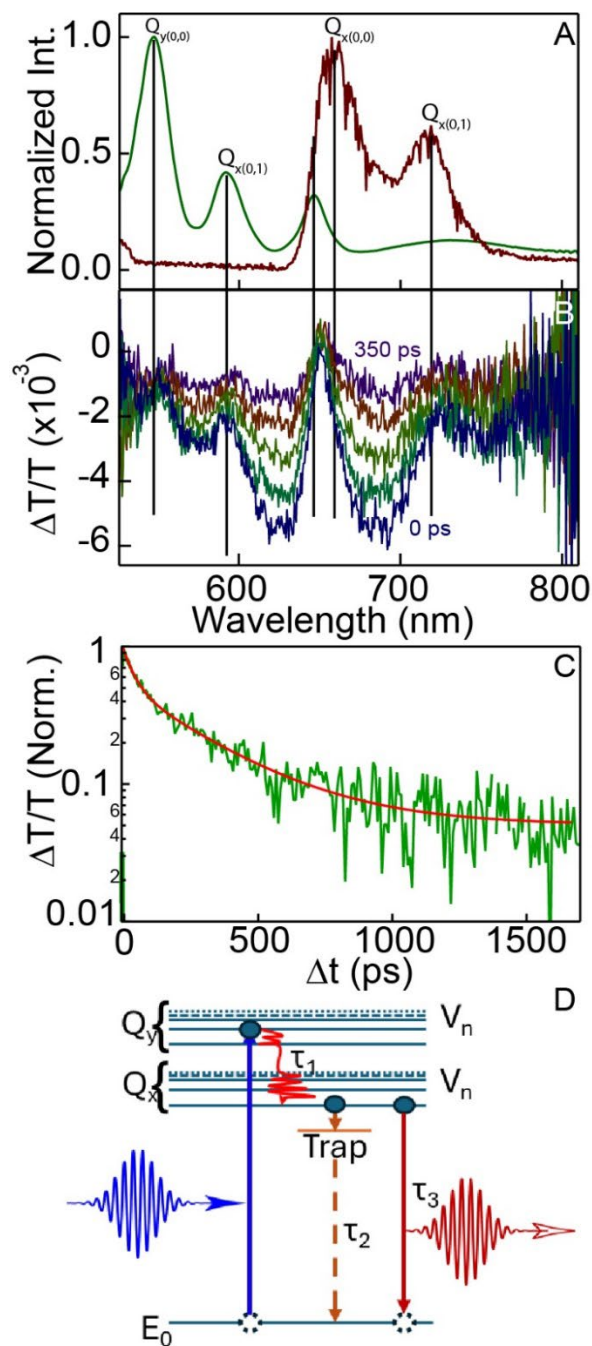


Figure 3.2: PCN-222 Spectroscopic and dynamic characterization. A) Normalized steady state absorbance(green) and emission(red) of single PCN-222 microstructure. Lines are drawn highlighting the alignment of the main spectral features in the steady state spectra and features in pump-probe spectra (Panel B). Time resolved spectra shows the temporal progression of 1, 11.3, 21.6, 46.7, 83.4, 145.5, 248.6, and 351.6ps. C) Kinetic trace of normalized PIA signal at 526nm with biexponential decay fit ($\tau_1=41.245\pm3.56\text{ps}$, $\tau_2=306.81\pm21.2\text{ps}$). D) Energy level diagram lifetime assignments of relaxation dynamics.

We next turn to transient transmission microscopy to investigate how the electronic coupling of the TCPP liners, shown in steady state spectra, affects the evolution of photogenerated excited state species. To establish a microscopic steady state baseline, we first measure the extinction of an individual straight microrod by comparing the transmission of our white light continuum (WLC) probe through the glass substrate and through the sampled domain, as well as the spontaneous emission arising from excitation of the domain with our 517nm pump. The spectral window of our WLC encompasses the $Q_{y(0,0)}$, $Q_{x(0,1)}$, $Q_{x(0,0)}$ absorption and the Q_x emission bands that are also shown in the steady state spectra (Fig. 3.2 panel A).⁵⁹ Figure 3.2 Panel B shows the temporal progression of transient transmission ($\Delta T/T$) after photoexcitation of the 517nm pump. The positive-shaped spectral features are overlaid with a broad photoinduced absorption (PIA), resulting in a net negative signal. The positive shaped peaks can be assigned to ground state bleach (GSB) of $Q_{y(0,0)}$ and $Q_{x(0,1)}$, as they align with the steady state features. The peak positions do not appear to shift over the 350ps time frame examined. The positive shaped peak at 651nm is red of the $Q_{x(0,0)}$ absorption feature by 7nm. We attribute this peak position to a convolution of the GSB and the Stokes shifted $Q_{x(0,0)}$ stimulated emission (SE). The $Q_{x(0,1)}$ SE peak is also visible near 725nm. The transient transmission spectra show features that relax without any noticeable shift in peak position, indicating that the nature of the observable excited state in the spectral window does not evolve after photoexcitation. However, the positions of the Q band features vary between different microrods, revealing the presence of structural heterogeneity within different structures.

A normalized kinetic trace of PIA relaxation for solid-state PCN-222 at 626nm is shown in Fig. 3.2C. Biexponential fitting yielded decay lifetimes of 41ps and 307ps with an unresolved

long-lived component approximated with an offset accounting for roughly 10 percent of the excited population. Several different relaxation mechanisms have been reported for porphyrin-based MOFs suspended in various solvents, with the first and second lifetimes attributed to solvent-induced vibrational reorganization and vibrational cooling respectively³ as well as shallow trap states¹⁴⁰, and the longest lifetime to fluorescence¹³⁹ and deep trap states¹⁴⁰. We have assigned the shortest lifetime to vibrational cooling of the excited state from the photoexcited $Q_{y(1)}$ to the $Q_{x(0)}$ state affecting Frank-Condon overlap between the excited state and higher lying states and decreasing PIA intensity. We assign the live-lived population to a stable radiative state that relaxes to the ground state without further transformation. The ~10 percent quantum yield of TCPP³ and the ~10 percent long-lived signal in pump-probe measurements led to the investigation of this excited state population with Time Correlated Single Photon Counting (TCSPC). TCSPC yielded single exponential decay kinetics from Q_x emission at 652nm with a lifetime of 832ps (Fig. 3.6).¹³³ Fits of kinetic taken in different location and on different microrods yield variation in lifetimes, but despite limitations in signal to noise imposed by sample photosensitivity and instrument limitations reveal a trend. Figure 3.2D summarizes our hypotheses that photoexcitation into the Q_{y1} state results in an excited state that relaxes vibrationally to the Q_{x0} state in tens of picoseconds followed by trap mediated relaxation with lifetimes that range from 100 to 300ps (Table S1). The remaining excited state species then relax radiatively with a lifetime of ~800ps. The contradictory reported assignments of relaxation mechanisms in PCN-222^{139, 140} and the subtle variability in early relaxation dynamics necessitate investigation with alternative techniques.

Broadband transient spectra exhibited distinct spectral shifts in Q band ground-state bleach (GSB) and stimulated emission (SE) features across various microstructures. A plausible explanation for the spectral shift is attributed to microscale structural heterogeneity in PCN-222 rods. Two-color pump-probe study on PCN-222 bend rods indicated that bends are correlated to higher defect density.¹⁴¹

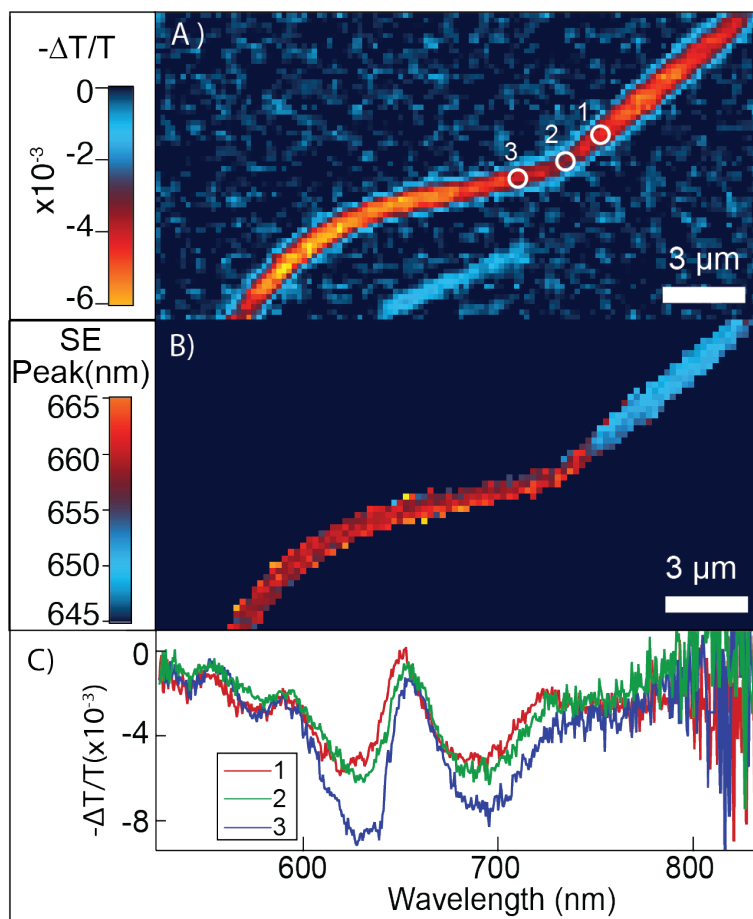


Figure 3.3: Spectral evolution within a bent structure. (A) Transient transmission image of a bent rod. (B) transient transmission spectra collected on marked spots shown in panel (A). (C) Stimulated emission peak position image of the bent rod shown in panel (A).

To investigate the correlation between the spectral shift and local microscale structural heterogeneity, we obtained hyperspectral transient transmission images of bent single crystals. Figure 3.3 Panel A illustrates a transient transmission image of a bent domain captured at $\Delta t = 1$ ps (probed at 626nm). Every pixel within the transient transmission image captures a broadband spectrum, illustrating how local microscale structural heterogeneity manifests via spatial variations in the spectral shift. To quantify the spectral shift in a single structure, each spectrum has been analyzed through background subtraction and a Gaussian fitting function to identify the SE ($Q_{x(0,0)}$) peak position precisely. Upon plotting the SE ($Q_{x(0,0)}$) peak positions, we observe an energetic distribution that illustrates a redshift (up to 19 nm) as the microstructure deviates from its straight to a bent trajectory (Fig. 3.3B). The transient spectra 1, 2, and 3 in Fig. 3.3 Panel C illustrate the apparent spectral shifts. The locations where transient spectra were collected along the length of the wire are indicated in Fig. 3.3, panel A, with white circles. The spectral red shift in the bent regions where we expect structural defects to be higher suggests that defects facilitate the change in peak position, perhaps due to peak broadening and low energy trap states. The presence of structural heterogeneity in a bent rod will supposedly impact the relaxation dynamics of the transient spectra. Our hypothesis was that the excited state would relax faster because of the low-energy trap states. Therefore, Spectra 3 (blue trace Fig. 3.3 Panel C) was expected to show the fastest relaxation lifetime, while Spectra 4 (red trace Fig. 3.3 Panel C) would exhibit a longer relaxation lifetime. The average relaxation lifetime does not show any trend to support our hypothesis. The kinetic traces collected along the length of the rod exhibit very subtle variation in the averaged relaxation lifetime (based on double exponential fit in SI). Even though we

observe a distinct red shift due to local defect sites, the impact of local structural heterogeneity on the relaxation dynamics remains elusive.

The fact that a two-color pump-probe study on PCN-222 bent rod with 400 nm excitation has shown a ~ 100 ps variation of averaged relaxation lifetime suggests that the structural heterogeneity influences the excited state relaxation dynamic.¹⁴¹ However, this behavior is not consistent with the relaxation dynamics observed in the broadband transient spectra. To investigate this inconsistency between broadband (at 517 nm) and two-color (at 400 nm) relaxation dynamics, we made a direct comparison of the excited state relaxation on a bent rod excited at 400 nm and 530 nm using two-color pump-probe microscopy. We hypothesized that exciting at 400 nm, which excites into the Soret band, would create excited states that are delocalized due to enhanced coupling, resulting in more mobile excited states that are likely to access the defect sites, where trap-mediated recombination results in shorter lifetimes in highly defect-concentrated locations.⁵⁴ On the contrary, exciting at 530 nm, which excites into the Q bands, yields excited states with much lower mobility due to reduced coupling, which has a low probability of encountering local defect sites.

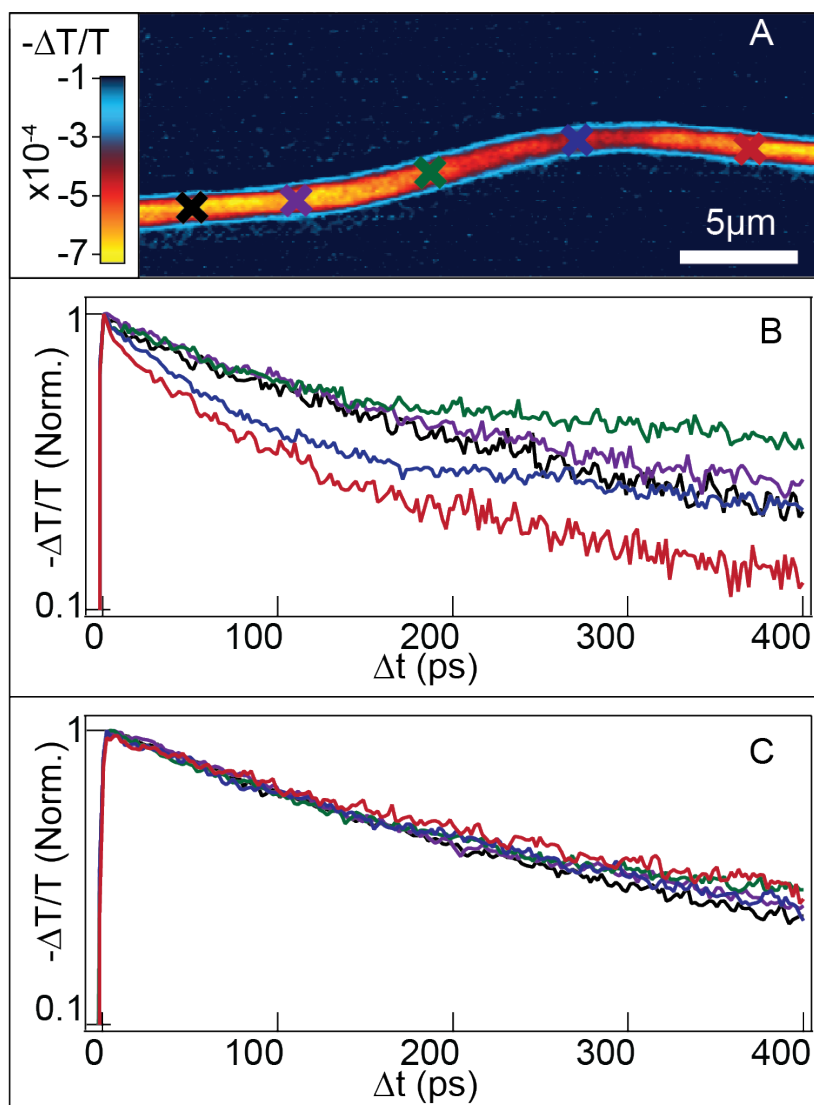


Figure 3.4:(A) Pump-probe image of a bent rod, cross marks are where relaxation kinetics are collected (B) relaxation kinetics from Soret band excitation. (C) relaxation kinetics from Q band excitation.

To test this hypothesis, we used two-color pump-probe microscopy to measure kinetics on a bent PCN-222 rod at the same location upon photoexcitation at the Soret band (400 nm) and Q band (530 nm), probing at 800 nm. The transient transmission image in Fig. 3.4 panel A shows the microrod, where the kinetics shown in Fig. 3.4B and 3.4C were collected. In the straight part of

the rod, the kinetics from both 400 nm and 530 nm excitation show similar relaxation (black and purple trace in panels B and C), suggesting that the straight region have lower defect density. On the contrary, in the bent region, kinetics from 400 nm excitation exhibit a significant variation in lifetime (green, blue, and red traces in Fig. 3.4 panel B). The kinetics from 530 nm excitation do not show this variability and closely match the kinetics collected in the straight regions, as shown in Fig. 3.4C. The subtle variation in relaxation within a microrod observed in dual color pump-probe with Q band excitation is consistent with our observation made in broadband pump-probe microscopy. Perhaps Q band excitation creates excited states that are spatially separated from defects, and therefore, Q band excited states never encounter them, resulting in small variations in relaxation. The comparison of kinetics relaxation for Soret and Q band excitation supports our theory that excitation into the Soret band produces excited states that are more likely to transport and encounter local trap sites, resulting in heterogeneous relaxation.

The excited state transport measurement from the Soret band and Q band excitation can provide concrete evidence of the mobility of the excited state resulting from enhanced or reduced coupling. Soret band excitation has shown power-independent lifetimes below power densities of $41 \mu\text{J}/\text{cm}^2$ (8.25×10^{13} photons/ cm^2), whereas the Q band excitation shows power independence up to $80.5 \mu\text{J}/\text{cm}^2$ (2.09×10^{14} photons/ cm^2) (Power study shown in the appendix). The power studies strongly support our hypothesis that Soret band excitation yields more mobile excited state species than Q band excitation. Excited state transport in PCN-222 microstructures has been reported to be rapid (0.27 to 1 cm^2/s) and sub-diffusive, consistent with the cooling and subsequent trapping of hot carriers¹⁴². We measured the transport properties of the excited state from the Soret band and Q band excitation to prove our hypothesis.

In order to measure exciton transport, we used spatially separated pump-probe microscopy. The probe beam was fixed at a certain location on the rod (Fig. 3.5A) while the pump beam was scanned over the probe. Since the microrod width is narrow, we could only measure transport along the long (c) axis. The resulting profiles, collected at various pump-probe delay times, allowed us to directly probe excited state transport in real space. In the case of diffusive transport, the mean square deviation (MSD) of the profile increases linearly with delay time, Δt . In Fig. 3.5 panel B, the MSD is increasing sublinearly, resulting in subdiffusive transport from the Soret band excitation (blue trace).¹⁴³ In Fig. 3.5 panel B the green trace is representing the transport measurement from Q band excitation, where the MSD is not showing any increase with delay time resulting in no evidence of exciton transport. These two transport measurements were conducted at the locations indicated in Fig. 3.5 4A. The plot in Fig. 3.5C illustrates the distribution of time-averaged diffusion coefficients, resulting from three measurements each for Soret (blue) and Q band excitation (green). Q band excitation generates carriers that show no detectable transport, yet the excited state generated from Soret band excitation displays rapid sub-diffusive transport.

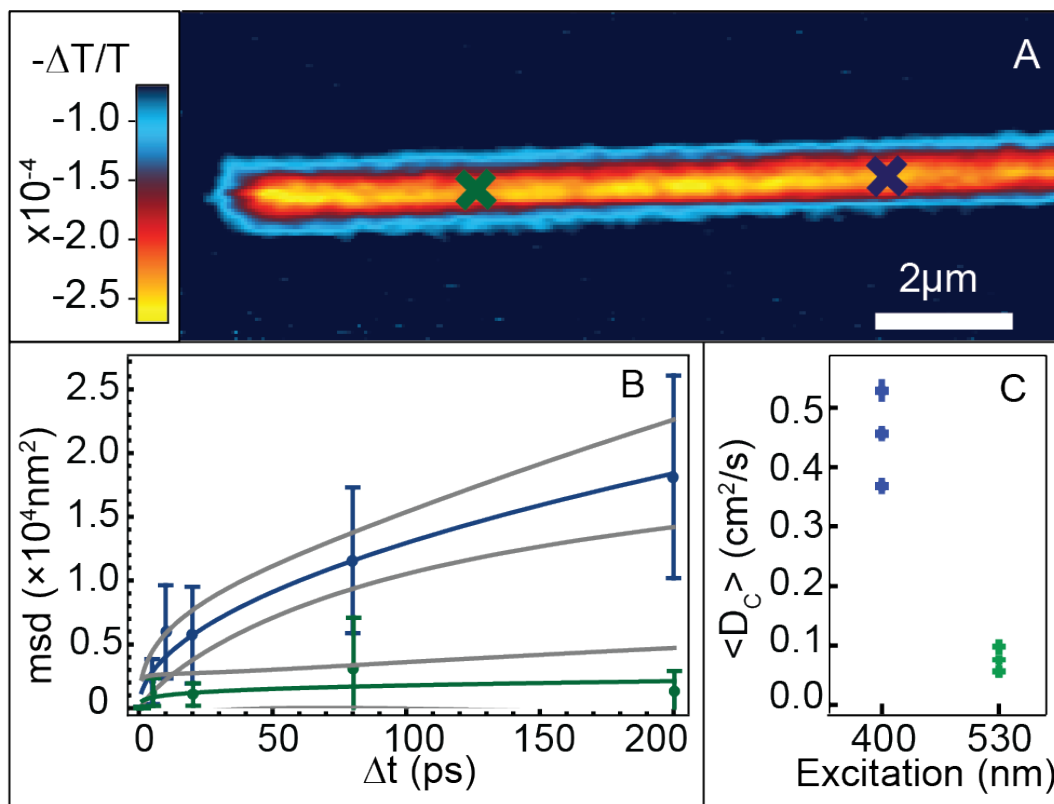


Figure 3.5 (A) Pump-probe image of a microrod the transport measurements are conducted (B) MSD vs. Δt for 400nm (blue) and 520nm (green) excitation, blue and green line are the fits with confidence intervals in gray (C) Exciton dependent time averaged diffusion coefficients for 400nm (blue) and 520nm (green) excitation collected on a same domain.

The results presented above lead to several important conclusions. Firstly, the transport of excitons in PCN-222 is rapid and sub-diffusive when carriers are excited with excess energy into the Soret band. As shown by the exciton transport measurements shown in Fig. 3.5, excitons are highly mobile after photogeneration using 400 nm light. The diffusion length of these excitons varies from crystal to crystal but generally is around 100 nm. This large diffusion length means that the excitons are likely to sample many sites in the crystal structure and are likely to encounter relatively low-concentration defect sites and relax by getting trapped into the defect sites (relaxation shown in Fig.3.4 panel B). Secondly, Q band excitation generates fewer mobile

excitons that do not show any measurable transport, as shown in Fig. 3.5, and they are also less likely to encounter the local defect sites and show very small variation in relaxation in Fig. 3.4 panel C. The difference in excited state behavior between 400 nm excitation and 530 nm excitation is surprising because previous reports have shown that porphyrin MOFs have exhibited relaxation from the Soret band into the Q band in the femtosecond timescale.^{128, 144, 145} In such conditions, we would not observe any difference between the Soret band and the Q band relaxation and transport properties. Our fluorescence measurements show strong Soret band emission (Fig. 3.1 panel D), which is not possible according to Kasha's rule as the Soret band is not the lowest excited state.¹⁴⁶ The lifetime of the fluorescence measured by TCSPC is shown in Fig. 3.6. The Soret band fluorescence lifetime is evident that the Soret band excited state does not relax into the Q band within the femtosecond timescale. Hence, we observe the difference in excited state behavior between the Soret band excitation and the Q band excitation.

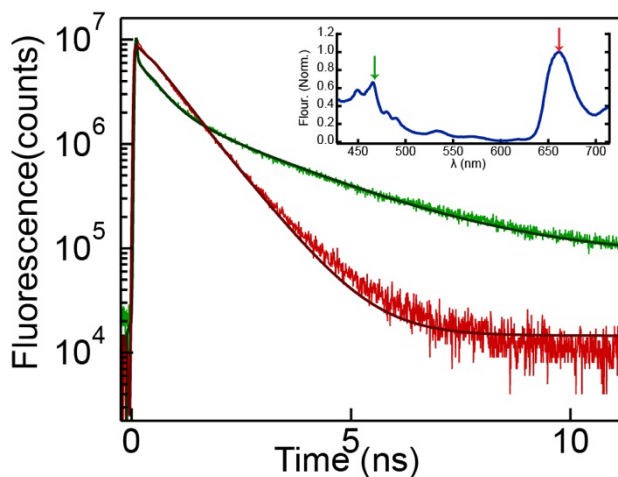


Figure 3.6: Time-correlated single photon counting (TCSPC) measurements showing time-resolved Soret-band emission (466nm) in green and Q_x-band emission (650nm) in red. Q_x-band emission was fit with a single exponential decay (dark red) with a lifetime of 832 ± 9 ps. Soret band emission was fit with a biexponential decay shown in dark green ($\tau_1 = 443 \pm 11$ ps, $\tau_2 = 2.4 \pm 0.1$ ns).

3.4 Conclusion

In summary, we have investigated the excited state dynamics of single-crystal PCN-222 microrods using broadband and dual-color pump-probe microscopy. Microscopic steady-state and the first broadband pump-probe spectra demonstrate the spectroscopic features with minimal scattering effects on a single PCN-222 microrod. The hyperspectral broadband imaging illustrates a ~ 19 nm spectral shift of the $Q_{x(0,0)}$ peak in a microstructure due to local structural heterogeneity. We have revealed that the Soret band and Q band excitation determine the coupling of the chromophores, resulting into more or less mobile excited states. The ability of the excitons to access local trap sites depends on the excitation energy. Rapid ($0.3\text{-}0.5\text{ cm}^2/\text{s}$) and subdiffusive behavior in transport properties stem from excitons getting trapped in local defect sites when excited into the Soret band. Excited state relaxation also exhibits $\sim 100\text{ ps}$ variation in lifetime for Soret band excitation. Q band excited states do not exhibit the long-range influence of structural heterogeneity in transport and relaxation. These results highlight the unique transport and relaxation properties of MOF structures arising from different photoexcitation energies and the impact of structural heterogeneity on the excited state dynamics.

CHAPTER FOUR

PROGRESS MADE TOWARD TIME RESOLVED RAMAN

MICROSCOPY OF PERYLENE DIIMIDE

MICROSTRUCTURES

Femtosecond Stimulated Raman Microscopy Progression

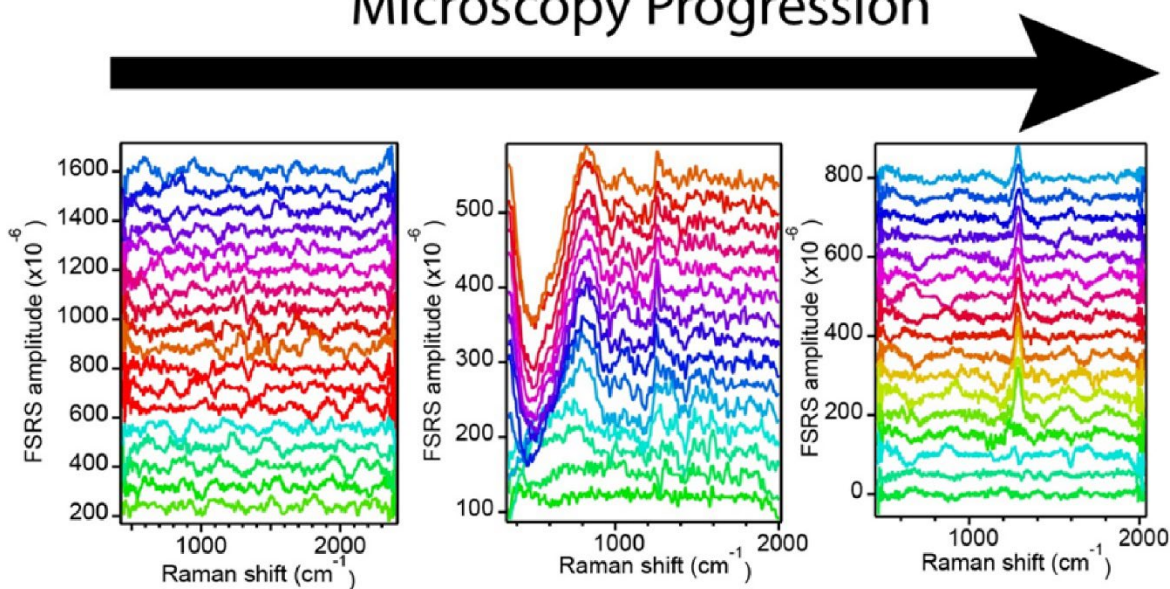


Figure 4.1: The progression of femtosecond stimulated Raman microscopy measurements as spectroscopic and computational techniques were improved. Panels are waterfall plots of the time resolved change in stimulated Raman spectra of a perylene diimide (PDI) aggregate resulting from photoexcitation.

4.1 Introduction

The previous two chapters have demonstrated the capability of broadband pump-probe microscopy to produce valuable spectral information that enables the characterization of excited state evolution in solid state self-assembled organic materials. Taking time resolved broadband microscopy a step further in the investigation of the structure-function relationship, femtosecond stimulated Raman microscopy (FSRM) emerges as a cutting-edge technique offering unprecedented insight into the excited state evolution of organic material through the lens of Raman-active vibrational resonances. Spontaneous Raman spectroscopy probes vibrational resonances through inelastic scattering of light without direct absorption. The difference in energy between incident photons and Stokes or anti-Stokes scattered photons informs the vibrational energy levels that exist in a sample. Unlike spontaneous Raman spectroscopy which generally utilizes high intensity continuous wave (CW) lasers, stimulated Raman Scattering (SRS) harnesses ultrafast laser pulses to induce coherent stimulated Raman scattering. SRS significantly amplifies the Raman signal ($\sim 10^7$ time larger).^{147, 148} SRS also assists detection because Raman scattered photons are coincident with the beam that stimulates Raman scattering. FSRS introduces a third electronic pump beam to photoexcite the sample. Similar to the electronic pump-probe, the difference of SRS signal, with, and without the pump present is calculated, enabling the observation of the effects of photoexcitation on vibrational modes with femtosecond temporal resolution.

Viewing excited state phenomena through vibrational resonances has several advantages. Detailed molecular structural information offers insight into how specific chemical bonds and molecular conformations are coupled to excited state species. The bleaching, enhancement or

shifting of ground state Raman signals allows for the elucidation of nuclear rearrangements and the evolution of vibronic coupling within molecular systems in the excited state.^{149, 150 151}

Determination of excited state structural dynamics inform the nuclear coordinates that facilitate important processes, such as singlet fission¹⁵¹ and charge transfer reactions, and can provide guidance for the design of materials that optimize these processes.^{150, 152, 153} The incorporation of optical microscopy enables the isolation of the effects of micrometer and nanometer structural features, such as grain boundaries, and defects on localized coupling, as well as vibrational and electronic processes.¹⁵² Molecular crystal axes can be related to the structural character of constituent monomers, intermolecular distances and packing geometries. Thus, the correlation of excited state angular anisotropy with these crystal axes facilitates a better understanding of anisotropic energy and charge carrier transport phenomena.^{152, 154, 155} As can be seen, FSRM is the ideal tool to investigate the structure-function relationship and how electronic coupling affects excited state evolution; however, its implementation in material science and solid-state characterization has been limited.¹⁵²

Implementing FSRM in the characterization of solid-state organic semiconductors poses several challenges. Achieving sufficient signal-to-noise ratios while maintaining sample integrity remains a significant hurdle. Typical stimulated Raman scattering cross-sections are roughly 10^{-23} cm² per molecule, resulting in relatively small signal amplitudes.^{147, 148, 156} FSRS is a measurement that takes the difference in intensity of these SRS signals and hence has even smaller signal amplitude, requiring raw data with high signal to noise. Additionally, due to complicating parasitic background signal contributions, data analysis and interpretation demands innovative signal isolation strategies to extract meaningful information from the datasets

generated by FSRM experiments.^{152, 155, 157, 158} Herein, we outline the efforts and progress made in the development of a high-repetition-rate femtosecond stimulated Raman microscope with the aim of aiding in the implementation and furthered development of the technique and instrument.

4.2 Raman Spectroscopy

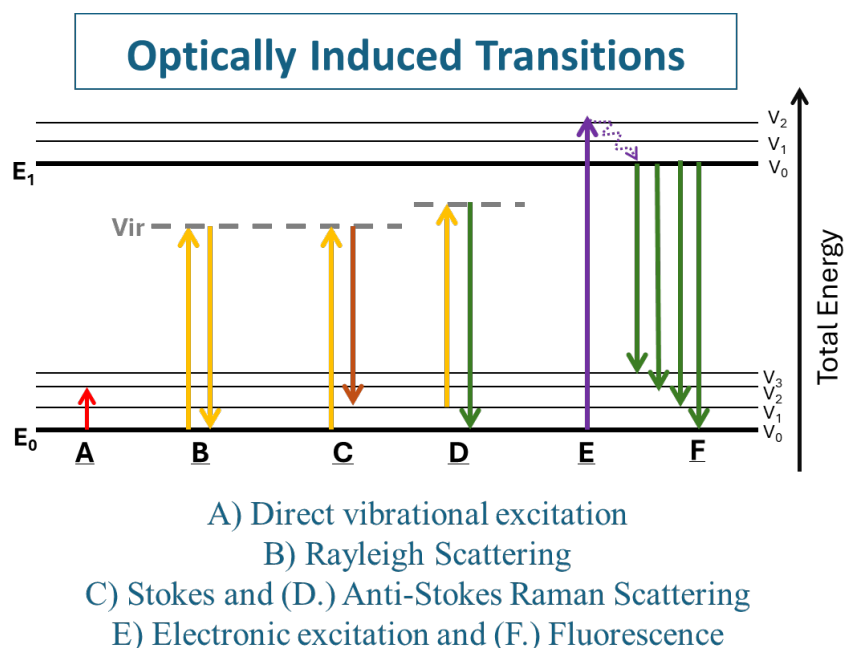


Figure 4.2: Energy diagram showing optically induced state transitions in a two electronic state (E_n) system with V_n representing vibrational states and Vir a virtual state.

Spontaneous Raman Spectroscopy

Raman scattering was discovered by physicist Chandrasekhara V. Raman, who had a fascination with the vibrational dynamics of string and percussive instruments as well as the scattering of light. He proved that the ocean's blue coloration arises, not from the reflection of the sky, but from the Rayleigh scattering of sunlight by water molecules. In 1928, C. V. Raman presented his groundbreaking work relevant to the methodology used in this chapter. He had

discovered the inelastic scattering process that bears his name.¹⁵⁹ In spontaneous Raman spectroscopy, a high intensity Raman pump beam (ω_p) scatters inelastically off of a molecule or material. Most often light will scatter elastically without changing its energy, known as Rayleigh scattering. In Raman scattering, light incident on a sample couples to a vibrational mode leading to the annihilation of the incident photon ($\hbar\omega_p$), a vibrational energy level transition, and the generation of a new photon with energy $\hbar\omega_s$. The molecule transitions from a state with energy E_i to a state with energy E_f in this process. Conservation of energy necessitates that $\Delta E_{fi} = \hbar(\omega_p - \omega_s)$. If the energy of the inelastically scattered photon is lower than the incident photon, the process is called Stokes Raman scattering, and the sample is promoted to a higher vibrational energy. Anti-Stokes Raman scattering occurs when the scattered photon is higher in energy than the incident photon, leaving the sample in a lower vibrational energy state. It is important to reemphasize that $\hbar\omega_p$ does not necessarily correspond to an electronic transition energy, but rather, scattering off of a perturbative virtual state that opens the possibility of spectroscopic transitions other than direct absorption.¹⁶⁰ The source of the scattered radiation can be thought of as induced oscillating electric dipoles. In order for a vibration mode to be Raman active the atomic motion must correspond to a change in polarizability of a molecule or material, whereas for a vibrational mode to be active in infrared absorption spectroscopy, the vibration must correspond to a change in the dipole moment of the sample. Polarizability is a measure of the susceptibility of the electron cloud to distortion by an external electric field. When stretching or bending motions change the volume and therefore the electronic density of a molecule or material the polarizability is affected.¹⁶⁰ Although primarily employed for molecular vibrational and rotational analysis, Raman spectroscopy can also capture phonon modes, rendering it a

versatile tool in the realm materials characterization. However, spontaneous Raman scattering is a scarce occurrence with only ~ 1 in every 10 million incident photons being inelastically scattered. Because of the infrequency of inelastic scattering, the measurement of spectra requires long integration times to overcome noise and makes microscopic spontaneous Raman imaging challenging.^{148, 161}

Stimulated Raman Spectroscopy

A particularly effective technique to amplify Raman signal is through the introduction of a second coherent laser beam to stimulate Raman scattering (SRS). In this experimental framework, an incident photon scatters off of a virtual state by a Raman pump (RP) pulse, and instead of relying on spontaneous Raman scattering, photons in the probe pulse with energy corresponding to the difference between the RP and Raman active vibrational modes stimulate inelastic scattering and vibrational transitions. Stimulated Raman spectroscopy, like pump-probe spectroscopy, is a third-order nonlinear spectroscopy. Figure 4.3 shows a Feynmann diagram for this process, where $\vec{k}_{sig}$ is colinear with $\vec{k}_{probe}$. In contrast to the omnidirectional scattering and emission of spontaneous Raman scattering and fluorescence, the Raman signal is coherent with the probe the entire Raman signal can be directed towards the detector along the path of the probe beam. Thus, as is shown in Fig. 4.4, the SRS signal appears as gain in the probe spectrum at frequencies shifted by the energy of a sample's Raman active modes relative to the RP pulse. The directed and coherent nature of the SRS photons significantly enhances the efficiency of signal collection, and in combination with the amplified signal SRS, significantly improves the detection of Raman scattering.

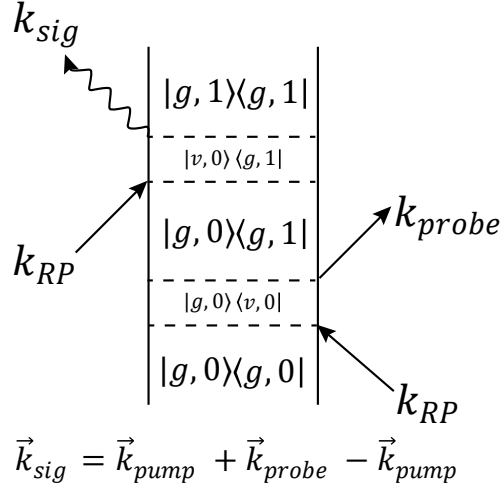


Figure 4.3: Double-sided Feynmann diagram showing stimulated Raman Scattering. The RP pulse excites the bra to a virtual state which is brought to $\langle g, 1|$ by the Raman probe. The second interaction with the RP promotes the ket $|g, 0\rangle$ to the virtual state and a photon is scattered out when the system returns to the ground electronic state.

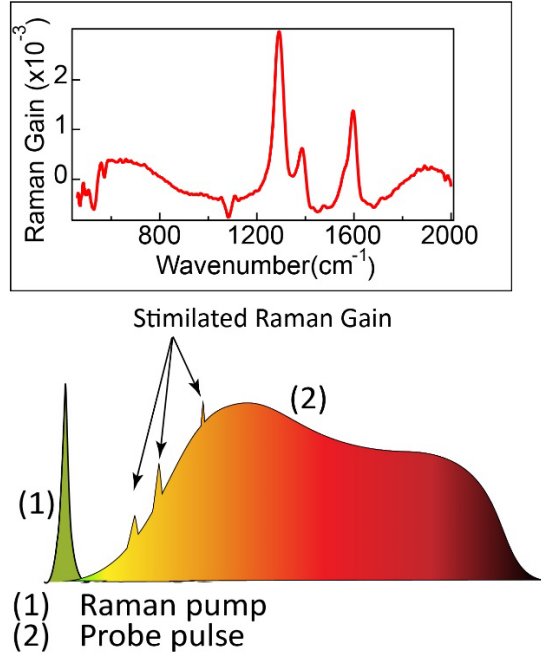


Figure 4.4: Diagram of stimulated Raman process showing a narrow frequency RP pulse (1) that scatters off of a virtual state and a broad-spectrum probe pulse that stimulates Stokes Raman scattering. Raman signal appears as gain in probe photon intensity at wavelengths corresponding to the difference in energy between the RP pulse and Raman active vibrational modes ($\hbar\omega_{RP} - \hbar\omega_{n_{vib}}$). The inset shows an SRS spectra collected with our microscope from a KT-PDI microrod described in Chapter 2.

Because SRS is a nonlinear spectroscopic technique that requires two RP pump wave interactions and is subject to the time-bandwidth product limit, achieving high spectral resolution requires employing an ensemble with a narrow spectral bandwidth RP pulse with long temporal duration and a broad-spectrum probe pulse with short duration. The fundamental spectral resolution of SRS is limited by the Raman pump's spectral linewidth, the spectral resolution of the spectrometer set up, and can also be affected by the time-bandwidth limit. This limit means if the Raman pump pulse's duration is shorter than the vibrational dephasing time of the target vibrational mode(s), the measured Raman line widths will be broadened. Typical pulse durations are picoseconds, longer than most ground-state vibrational dephasing times, and so do not limit the spectral resolution of SRS. However, with the introduction of the time domain in the case of FSRS the vibrational dephasing time can affect the maximum achievable temporal resolution.^{149,}

152, 162

Femtosecond Stimulated Raman Spectroscopy

Examining the temporal evolution of vibrations in the excited state is achieved through a process similar to electronic pump-probe spectroscopy. A resonant pump is used to promote species to an excited state and a Raman pump and probe ensemble measure the stimulated Raman gain, with, and without the pump present.

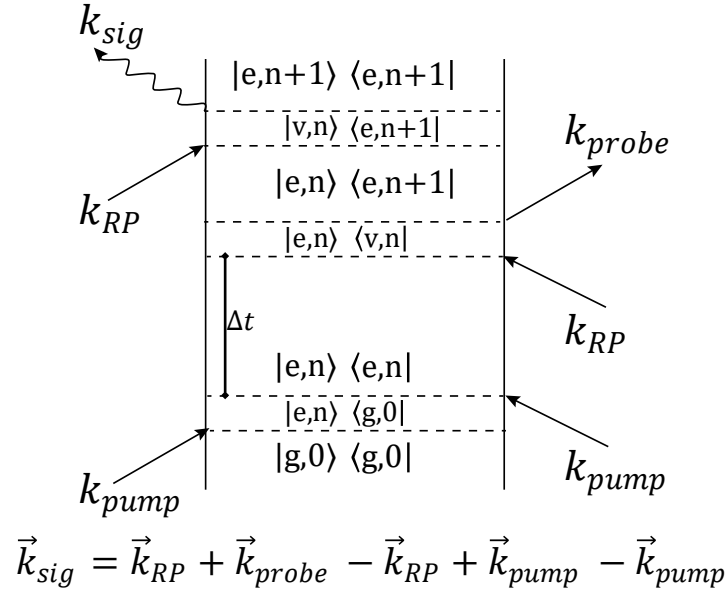


Figure 4.5: Double-sided Feynmann diagram incorporating photoexcitation and stimulated Raman Scattering. The pump pulse photoexcites the system from ground state (g) to an excited electronic state (e), after the specified delay time Δt and stimulated Raman scattering interactions occur changing the vibrational quantum state of the sample and generating Raman scattering signal from the excited state (described in Fig 4.3). These signals are compared with ground state SRS signal to obtain temporally resolved Raman signal.

A representation of the pulse configuration and an example spectral progression are shown in

Fig. 4.6. FSRS is formally a six-wave mixing spectroscopy requiring five light matter

interactions.^{149, 162} The wave interactions are depicted in the Feynman diagram presented in Fig.

4.5. The pump pulse interacts with the sample promoting excited state species, and then after a

delay Δt the SRS beam ensemble consisting of a picosecond Raman pump and a femtosecond probe pulse act to induce vibrational coherences and subsequently stimulate Raman scattering.

When mapping the temporal evolution of the photoexcited state, at most time delays the pump

and RP pulses are not temporally overlapped in the sample and the pump and SRS wave

interactions can be treated independently; however measuring extremely short-lived dynamics

where the pump and RP pulses overlap necessitates consideration of all the potential wave interaction orders which significantly complicates the calculation of temporal resolution.¹⁶²

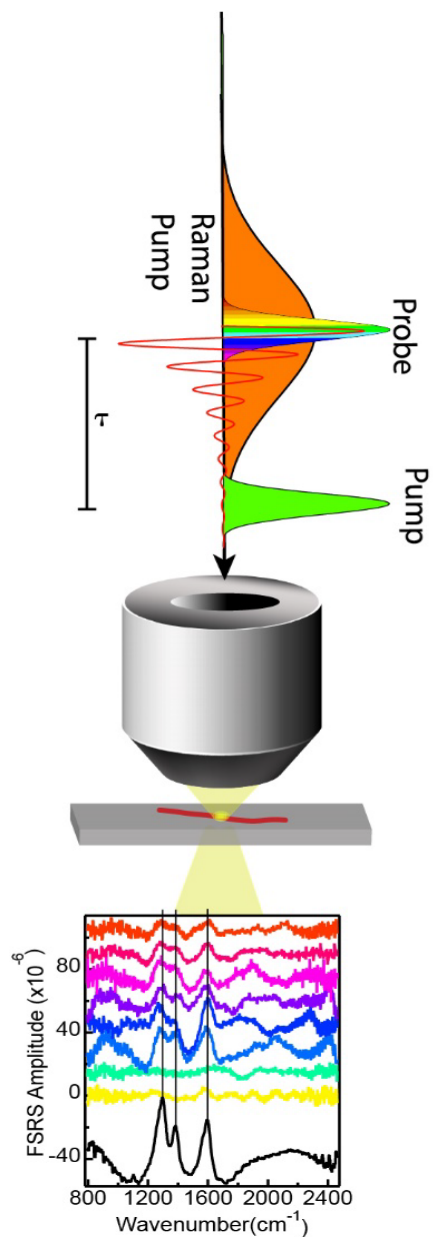


Figure 4.6: FSRM experiment depicted in the time domain. A femtosecond pump pulse excites the sample, followed by a SRS ensemble composed of a narrow bandwidth, picosecond Raman pump pulse and a broadspectrum femtosecond probe pulse. The vibrational dephasing time is depicted in red, and the inset shows a FSRM spectra collected on a KT-PDI microrod.

Determining the exact time resolution of a FSRS experiment is complicated because it not only depends on the product of probe and pump pulses, the time-bandwidth limit, but also the vibrational dephasing time of the molecule under investigation, which is commonly not known in advance.¹⁵² However, impressive time resolutions of less than 25 fs have been reported with the use of global fitting of full FSRS data sets.¹⁶³

In FSRS, the ground state Raman spectrum serves as a reference baseline and is obtained with the photoexcitation pump turned off. The Raman gain is calculated using Eq. 4.1 where the difference in transmitted probe intensity with the RP on and off is divided by the probe intensity without the RP to normalize the data and reduce the effects of shot-to-shot probe fluctuations.

$$\text{Eq. 4.1} \quad \text{Raman Gain} = \frac{I_{\text{Probe (RPon)}} - I_{\text{probe (RPoff)}}}{I_{\text{probe (RPoff)}}$$

Following the excitation of molecules by the pump beam, the collected Raman spectra contain contributions from both ground and excited state molecules. The excited state Raman scattering contributions will be weak, since the pump intensity is carefully controlled to limit the number of photoexcited molecules. The power of pump pulses is limited in order to prevent Auger recombination and photodamage of the sample. To extract the effect of photoexcitation on the vibrational modes of a sample and the resulting Raman spectra, ground state Raman spectra are subtracted from the Raman spectra acquired after pump excitation. Microscopic FSRS in solid state samples is exceptionally difficult because the small volume being investigated means that high probe and RP power densities are required to overcome electronic and detector noise contributions to resolve small differences in weak Raman signals. Additionally, there are significant parasitic signal contributions in FSRM measurements like transient transmission effects and cross phase modulation.^{157, 158, 164}

The hurdles that exist in the implementation of FSRM are worthy of surmounting because it is perhaps the most well-suited technique available to resolve the structure-function relationships in organic self-assembled materials. FSRM presents distinct advantages for studying how structural characteristics affect ultrafast excited state dynamics owing to its exceptional temporal resolution (~ 300 fs), and high spectral resolution (up to 10 cm^{-1}).¹⁵⁵ FSRS can also directly probe excited singlet to triplet state transitions, eliminating the need to solely rely on Electron Paramagnetic Resonance or accompanying processes such as phosphorescence.¹⁵¹ Additionally, the direct probing of vibrational modes enables the investigation of the relationship between exciton transport and structural coordinates, where excited state perturbations of Raman modes corresponding to vibrations with a particular molecular orientation can inform how an excited state is moving through the material and what vibrational modes couple with that motion.¹⁵⁵ Moreover, the FSRM setup acquires all the information to produce transient transmission spectra alongside the time resolved Raman spectra, enabling a comprehensive analysis of the system's dynamics.

4.3 Outline of Efforts

As a three-beam nonlinear spectroscopy with both spatial and temporal resolution, FSRM is a complicated technique with multiple degrees of freedom affecting its performance and the quality of data. The remainder of this chapter delves into the efforts and configurations that were implemented to obtain time resolved Raman spectra of solid-state superstructures. Raman scattering is rare, so producing enough events to observe a discernable signal in FSRM requires a high-power Raman pump. Initially we implemented a near IR based Raman pump using the fundamental 1035nm MOPA laser output and explored both Raman gain and Raman loss

configurations for the probe. This initial exploration focused on probing the behavior of perovskite nanoparticles and their interaction with energetically aligned passivating ligands, detailed in Appendix B. However, the scattering cross-section of the ligands relative to the nanoparticles proved inadequate to obtain meaningful spectra.

Subsequently, our study shifted to PDI aggregates, because of the homogenous chemical composition and robust resistance to photodamage and oxidation. The study of PDI employed a visible RP. To obtain an RP with both high power and tunable frequency, a BBO-based noncolinear optical parametric amplifier (NOPA) was constructed. At this stage we achieved consistent observation of FSRS signal, but those signals were overlayed with background signal and artifacts. To further improve the resolution of Raman peaks and clarify the origin of ambiguous FSRS features we implemented frequency modulation of the RP. Frequency modulation enabled facile removal of background signal and the extraction of clear high amplitude Raman signatures. Ultimately, we present the final state of the FSR microscope, examine the meaning of the FSRS signals in PDI that we obtained, and discuss directions for further optimization and samples to investigate.

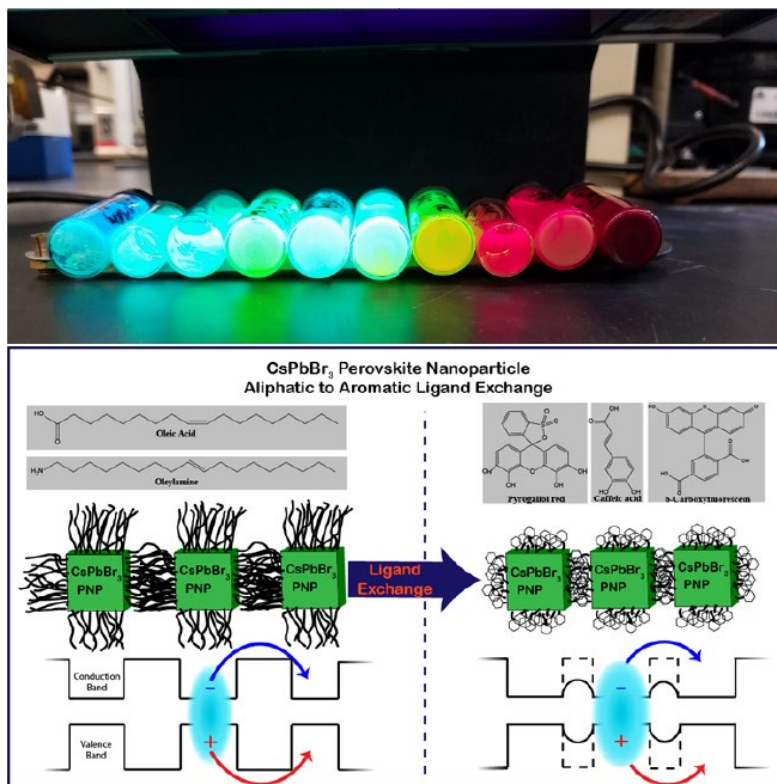


Figure 4.7: Perovskite nanoparticles initially investigated using the stimulated Raman microscope. The top panel shows conventionally grown nanoparticles with oleic acid and oleylamine passivating ligands. The color difference in emission is a result of varying the halide of the perovskite and different levels of quantum confinement. The bottom panel is the summary figure for the ligand exchange project. More information about the project can be found in Appendix B of this dissertation.

4.4 Near Infrared SRS Pump

The initial system that was to be studied using FSRM was quantum confined CsPbBr₃ perovskite nanoparticles, where the aim was to measure the Raman spectra of the organic passivating ligand brush. Ligand exchange with aromatic chromophores that are energetically aligned with the conduction and valence band of the perovskite nanoparticles has been hypothesized to allow delocalization of perovskite excitons into the brush and allow for more rapid excited state transport.^{165, 166} With Raman spectra of the ligand, FSRM could directly

determine if this hypothesis is correct and explore the dynamics. Figure 4.7 shows an image of the nanoparticles and a cartoon representation of the process and the hypothesis.

Because perovskite nanoparticles have a large two-photon absorption cross section, the fundamental 1035nm beam from the Coherent Monaco MOPA laser was used as the RP.¹⁶⁷ Also, to reduce the two photon absorption of the probe and resolve Raman gain, we utilized the supercontinuum red of the 1035nm fundamental generated in the YAG crystal. The RP is sent into a diffraction grating spectral filter that narrows the bandwidth to ~ 1.5 nm full width half maximum (fwhm) and broadens it in time to over 1ps. This configuration required the replacement of the OctoPlus line camera described in the instrumentation section of the introduction with a Linea SWIR 512 GigE Indium Gallium Arsenide (InGaAs) camera with a 40 kHz maximum line rate. The line trigger was set at 38.3 kHz and the frame trigger at 95 Hz. The transmission of our apochromatic microscope objectives drops off into the near IR so a reflective objective was used to focus the beam onto the sample, and InGaAs line camera was mounted to a SpectroPro 2300i Czerny-Turner spectrometer. Though strong Raman scatter could be seen from control samples such as PDMS, the combination of weak probe intensity in the >1035 nm spectral region and poor image quality arising from high amount of scattering in the reflective objective prevented the acquisition of meaningful Raman gain spectra from nanoparticle samples. We then pivoted to a stimulated Raman loss configuration, shown in Fig. 4.8, to mitigate these problems.

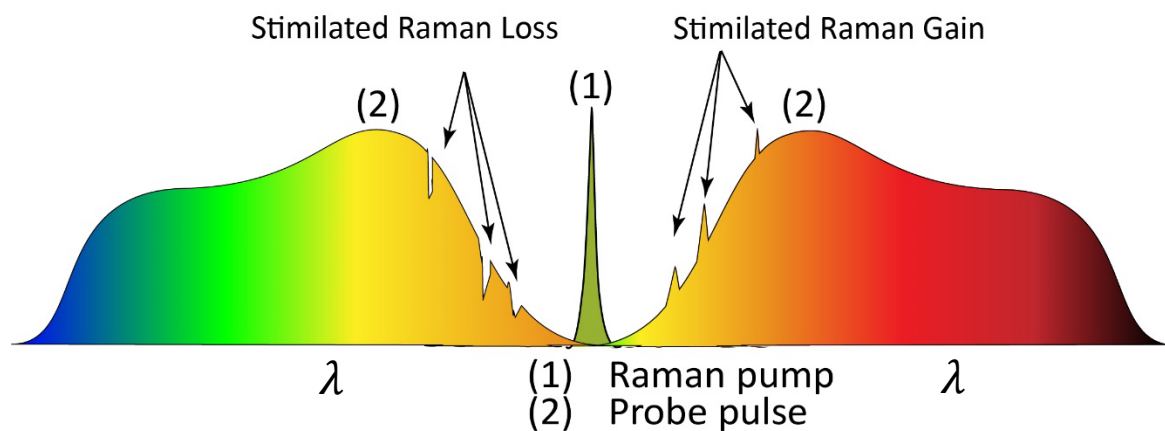


Figure 4.8: Frequency domain depiction of stimulated Raman gain vs stimulated Raman loss SRS configurations.

The Octoplus line camera was remounted, and the reflective objective replaced by the Olympus MPlanFLN. In this configuration SRS manifests as a loss in probe photons, and we were able to obtain SRS spectra of the pure ligands in solid state shown in Fig 4.9A.

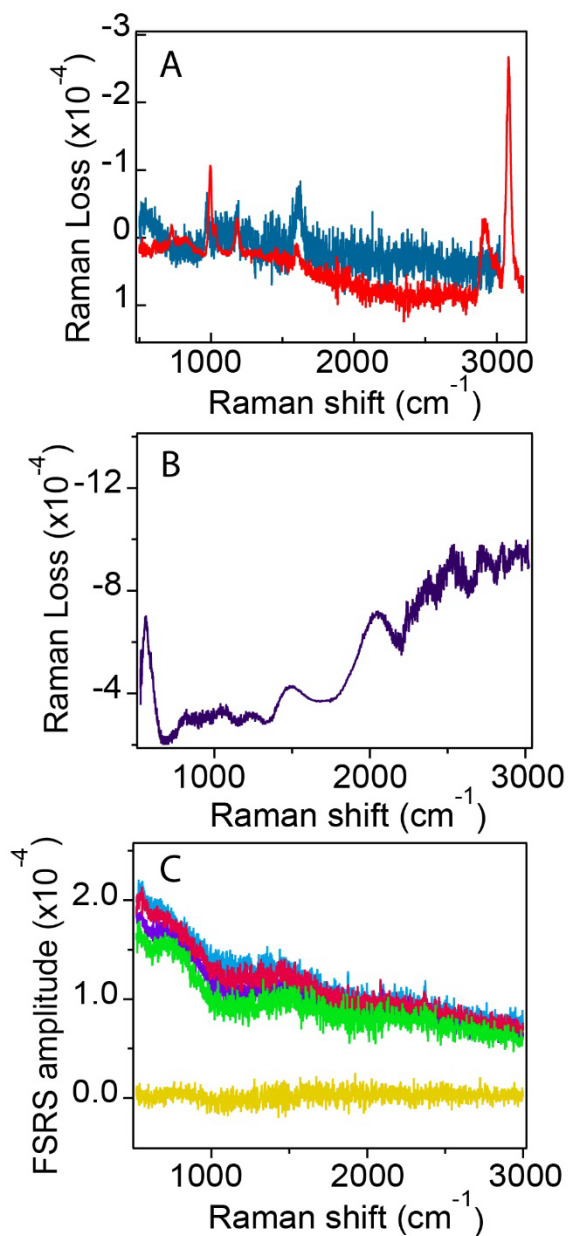


Figure 4.9: Summary of perovskite nanoparticle SRS and FSRM data. Pannel A shows the SRS signal from the pure ligands. The blue spectrum is trans-cinnamic acid (TCA) and the red spectrum is 3,3-Diphenylpropylamine. The purple trace in Pannel B is the SRS signal from CsPbBr_3 nanoparticles ligated with the two ligands shown above. Pannel C shows a FSRS progression from 0 to 300 ps.

Yet the perovskite nanoparticle did not show clear Raman peaks corresponding to the Raman peaks of the ligands. The spectrum in red is the Raman spectrum of 3,3-diphenylpropylamine

(DPA), and the spectrum in blue is the spectrum of solid trans-cinnamic acid (TCA). Also, the presence of the large baseline indicates that the signal observed is likely arising from electronic background. Although we did not see any clear Raman peaks in a salt made from a 1 to 1 mixture of the ligands either. Regardless, it is unsurprising that the FSRS spectra shown in panel C do not show any clear evidence of defined Raman peaks corresponding to the resonance of the passivating ligands. While our configuration successfully yielded SRS spectra of pure ligands in the solid state, the perovskite nanoparticle failed to exhibit clear Raman peaks corresponding to those of the ligands. We believe one possible reason for this lack of ligand Raman signal is high amounts of scattering from the perovskite nanoparticles themselves obscuring the Raman signal of the smaller ligand species.

Motivated by the hypothesis that the ligand concentration was too low in the perovskite QD system to produce sufficient Raman signal, we pivoted to studying a conjugated organic material in order to benchmark the FSRM. This material was the kinetically trapped perylene diimide (KT-PDI) studied with broadband transient transmission spectroscopy in Chapter 2. The molecular monomer that makes up the KT-PDI aggregate microstructures and a microscope image of the structures are shown in Fig. 4.10A and C. The SRS spectrum of the microstructures is shown in Fig. 4.10B. with three clearly defined peaks. The three Raman active vibrations at 1278 cm^{-1} , 1364 cm^{-1} , and 1579 cm^{-1} have been assigned to ring breathing modes of the core perylene species.¹⁵⁰

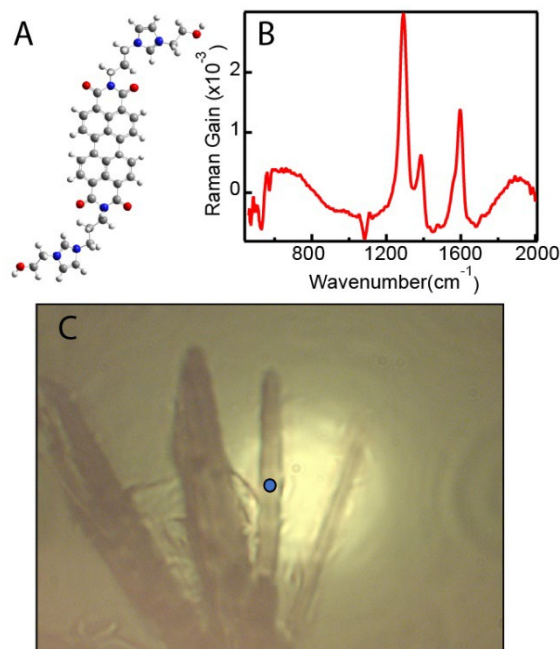


Figure 4.10: Perylene diimide microstructures studied with FSRM. (KT-PDI) Molecular monomer of KT-PDI (A). The SRS spectrum of KT-PDI (B). A brightfield microscope image of the KT-PDI microstructures(C).

4.5 Frequency Modulation

Despite the unmistakable SRS signal observed in the all-organic KT-PDI sample, the issue of high amplitude background signal persisted, as illustrated in Fig. 4.11. We employed several post-processing techniques, such as subtracting a 4th order least squares fit of the background, median and Butterworth filtering, aimed at isolating the Raman signature, yet distinguishing Raman peaks from high-frequency artifacts proved challenging.

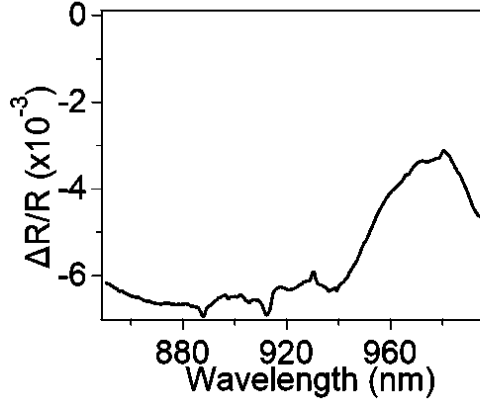


Figure 4.11: Example of SRS spectrum without post processing. The signal is the difference in intensity of the probe with the RP present and without normalized by the probe in absent the RP pulse. The spectrum shows a large background signal and multiple features that are not canonic PDI Raman peaks.

In order to overcome this obstacle, we introduced frequency modulation of the RP beam. In the frequency modulation configuration we collect two SRS spectra with the center frequency of the RP (ω_{RP}) in each spectrum offset from each other ($\Delta\omega_{RP} \approx 40 \text{ cm}^{-1}$). One of the spectra is subtracted from the other producing an SRS difference spectrum. The Raman scattering peak positions are much more sensitive to the RP frequency than the electronic background features and thus much of the background signal is removed through the subtraction. The SRS spectrum is then reconstructed using a simple numerical algorithm. Our initial method for frequency modulation of the RP leveraged the 0th and 1st order diffraction of an acousto-optic modulator (AOM). By running the AOM at maximum radio frequency (RF), our goal was to achieve a nearly equal distribution of light between the two diffraction modes. Subsequently, both beams were directed into the grating-based spectral filter with two narrow slits in the Fourier plane and then combined with a beam splitter. In this way two spectrally separated and narrow RP beams were obtained. Figure 4.12 shows a representation of how the AOM based frequency modulation

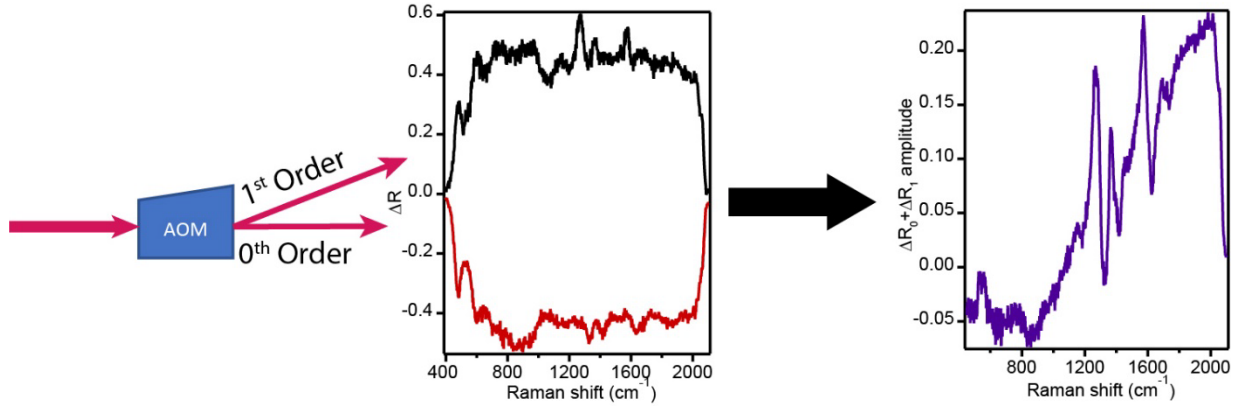


Figure 4.12: Diagram showing the acousto-optic modulator (AOM) based frequency modulation set-up. The fundamental 1035nm beam was split into 1st and 0th order diffraction beam lines which were used to generate the black and red SRS spectra respectively. The addition of these two spectra resulted in the frequency modulated SRS spectrum shown in purple.

set up obtained SRS spectra. This AOM frequency modulation set up is advantageous because SRS spectra can be collected at high repetition rates and the signal from the different RP frequencies is opposite in sign allowing for direct addition to generate the difference spectrum. The separation and recombination of the diffraction orders can require tight tolerance optical alignments but is achievable without specialized optics. The frequency modulated stimulated Raman spectrum (FM-FRS) resembles a derivative spectrum, but unlike EPR it is not a true derivative. It is a difference spectrum meaning as opposed to direct integration, the reconstruction is achieved using Eq. 4.2

$$\text{Eq. 4.2} \quad SRS_n(\nu) = SRS_{n-\delta} + D_n(\nu)$$

SRS_n is the reconstructed signal at pixel n , δ is the number of detector pixels separating RP_{0th} and RP_{1st} , $SRS_{n-\delta}$ is the reconstructed at pixel $n-\delta$, and D_n is the difference signal at the pixel n .

Prior to reconstruction, any remaining background signal is removed through the fitting and subtraction of a 3rd or 2nd order polynomial in the region of interest. After reconstruction the spectrum is Fourier transformed and a notch filter is applied at n/δ to remove any high frequency

oscillations resulting from the recursive nature of Eq. 4.2.¹⁵⁸ Although the reconstructed SRS signal was drastically improved by this process oscillations still plagued the FSRS spectra produced in experiments. After extensive investigation the source of these artifacts was discovered and is shown in Fig. 4.13.

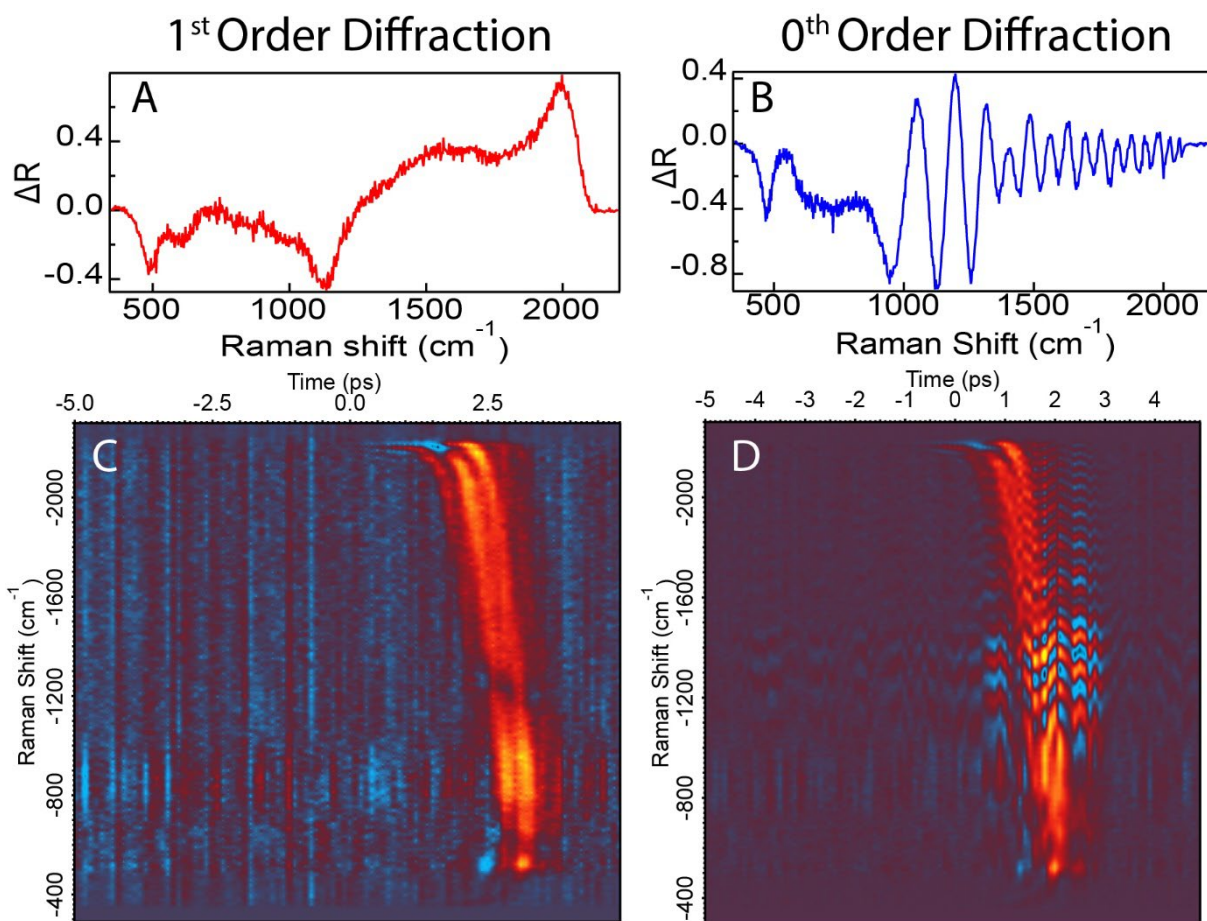


Figure 4.13: Examination of the source of oscillations in AOM based FM-FSRS data. The 1st and 0th SRS spectra collected at high Raman pump power in a glass coverslip are shown (A, and B respectively) Above the corresponding 2D time, Raman shift images (C and D) from which they were taken.

The SRS produced from the 0th order diffraction of the AOM resulted in peculiar oscillations in the intensity of transmitted probe beam when the two beams were overlapped in the glass

sample. This phenomenon was only clearly visible at very high RP powers, but even when not discernable the hypersensitive FSRS data were affected. AOM diffraction efficiency is less than 100% efficient and though we were able to obtain exceptional splitting ratios (48% 1st Order: 52%, 0th order) one possible source of the oscillation in the 0th order SRS spectrum could be interference effects between undiffracted and pulses doubly diffracted back to the 0th order path and shifted in frequency by the AOM. However, the true source of this complication to AOM frequency modulation is unknown and warrants further investigation.

In the interest of progressing the project, a less elegant and simpler approach was adopted to accomplish frequency modulation shown in Fig 4.14.

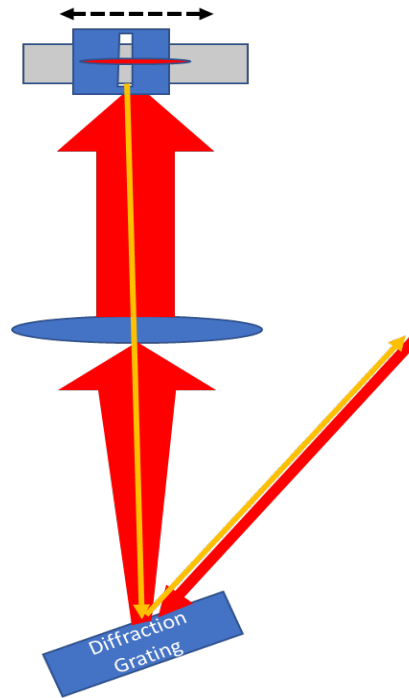


Figure 4.14: Schematic of the frequency modulation configuration using a motorized stage actuating a slit in the fourier plane with a worm gear actuation.

In this configuration the 1st order diffraction of the AOM was passed into the same grating spectral filter used previously. However, a motorized stage was introduced to actuate the slit in the Fourier plane to obtain the spectrally separated RP pulses. Because motorized actuation is slow in this configuration, at one time point, 100 camera frames were collected and average at each of the RP frequencies. A representative FM-SRS spectrum and the process used to generate it is shown in Figure 4.15, alongside an SRS spectrum for comparison.

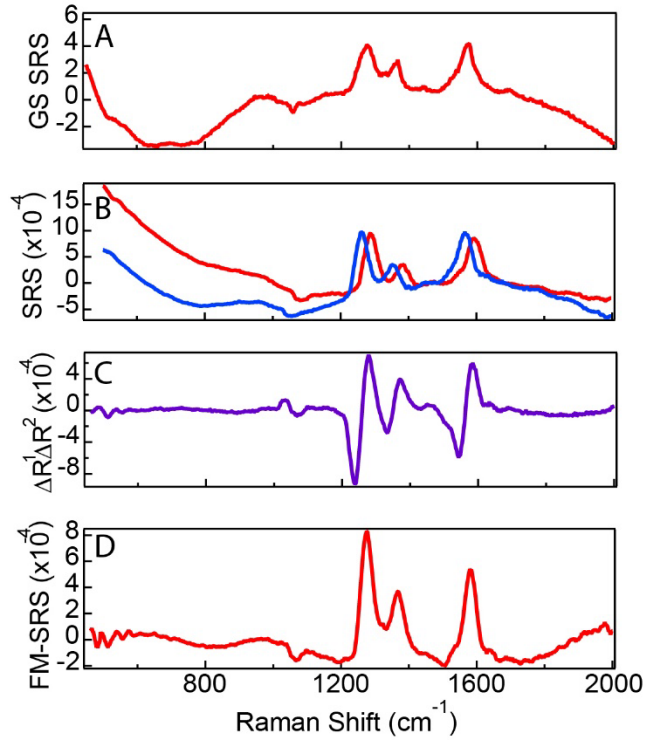


Figure 4.15: Comparison of SRS spectrum with FM-SRS spectrum. A nominal SRS spectrum of KT-PDI is shown in Panel A. SRS spectra taken with two spectrally separated RP configurations and their difference (Panel B and C respectively). Panel D shows the reconstructed FM-SRS spectrum.

The MOPA laser's fundamental frequency has insufficient spectral bandwidth to separate RP pulse energies sufficiently, and so prompted the construction of a noncolinear optical parametric

amplifier (NOPA). With this final development amplification of ~50nm of visible light allowed well separated RP pulses pulse energies and reconstruction of FM-SRS spectra with minimal broadening or artifact introduction. Below we will briefly cover the configuration of the NOPA we constructed.

4.6 Parametric Amplifier

An optical parametric amplifier (OPA) is an optical device that uses the difference frequency process to convert energy from a pump photon (ω_p) to a signal photon (ω_s) and also produces an idler photon (ω_i) in the process. The amplification is achieved by using a photon resonant with the desired signal photon energy to preferentially stimulate its generation over other signal-idler combinations. Within our NOPA device shown in Fig. 4.16 multiple parametric processes contribute to its operation. A parametric process is one in which the light matter interaction leaves the quantum state of the material unchanged. Some of the most common examples of linear parametric processes are refraction and elastic scattering events. In nonlinear materials multiple useful nonlinear parametric processes such as sum frequency and difference frequency generation (SHG and DFG), optical parametric fluorescence (OPF), and optical parametric amplification (a form of DFG) can be achieved. In nonlinear materials there is not a normal dispersion where the index of refraction changes monotonically with the wavelength of light as was discussed in the chromatic aberration section. Instead, in birefringent materials for example, the two polarization dependent indices of refraction can be leveraged by adjusting the direction that light passes through the material relative to the crystal axes achieving the same wave vector for different wavelengths of light. This is known as the phase matching condition and enables the nonlinear parametric processes mentioned above. Our NOPA is driven by the 1st

order diffraction of the Raman AOM. The 1035 nm light is split by a 90:10 beamsplitter where 90 percent is reflected and focused into a type 1 BBO crystal to generate our pump frequency through second harmonic generation (a form of SFG). The remaining ten percent is transmitted to drive OPF and create a supercontinuum in a YAG crystal. A half waveplate and polarizing cube beamsplitter are used to obtain the correct polarization conditions ($\omega_p=e$, $\omega_s=o$, $\omega_i=e$) and attenuate the pump. The optical parametric amplification occurs in a 5mm type 1 BBO, where there are six parameters that affect the device's performance: temporal overlap, crystal angle, signal wavelength, the angular offset of the pump and signal beams and x, and y position of the beams. First and most intuitively the pulses of light involved must be overlapping in the crystal. Achieving overlap is not a trivial task however, because the beams are focused to tight spots to maximize power density, and amplification is a delta function like process where all conditions must be met before noticeable gain is generated.

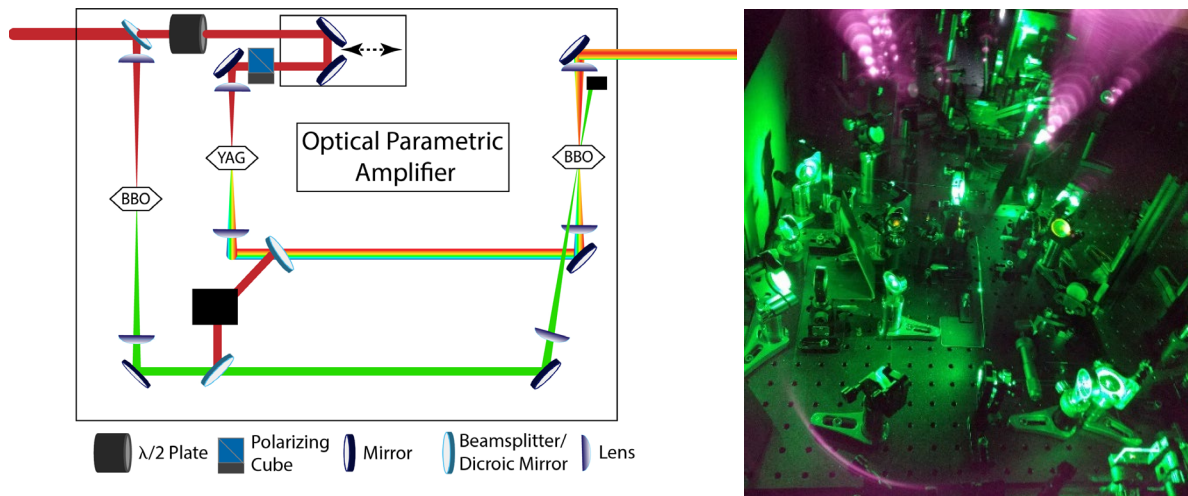


Figure 4.16: Schematic of the Noncolinear optical parametric amplifier (left) we constructed. Image of the device on the laser table (right).

A delay stage in the probe path is used to match path lengths for temporal overlap and kinematic mirrors are used to spatially overlap the beams in the BBO. In order to amplify more than a single center wavelength of light the angles of incidence of the signal and pump must be offset. For our purposes a pump tilt of $\sim 2.5^\circ$ relative to the signal beam allowed us to amplify up to 50 nm spectral range of the supercontinuum from 700 to 800nm. The final parameter is the angle of tilt of the BBO crystal which was nominally 22° relative to the crystal axis. The NOPA allowed us to amplify light over a broad spectral range while preserving the coherence properties of the input signal. One of the key advantages of a NOPA is its ability to amplify ultrashort pulses without significant distortion. This configuration enables the generation of amplified RP pulses with tunable energies making NOPAs invaluable the FSRM instrument.

4.7 Final Instrumental Design

Herein we present the final instrumental design of our FSRM, illustrated in Fig 4.17. There are many commonalities with the broadband pump-probe microscope presented in the introduction with a few key additions. Note the beamsplitter that picks off $\sim 60\%$ of the fundamental beam and forms the RP beam. The Raman AOM then picks pulses in a complex multiplexed configuration with line acquisition of 4 lines on, 2 lines off, 4 lines on, 6 lines off, and 4 lines on, with a total repeating frequency of 7.8kHz. This pulse modulation scheme ensures the different RP conditions sample the analog to digital converters (ADCs) of the Octoplus E2V line camera evenly. The custom-built NOPA described above then amplifies the desired spectral region of a supercontinuum. The motorized actuator based spectral filter and frequency modulator creates the two narrow frequency picosecond RP beam configurations. The RP beam is then sent onto a motorized delay stage to allow temporal overlap of the probe and RP pulses to

be found. Finally, a beamsplitter combines the RP with the probe beam and the pump, probe and RP beams are all focused onto the sample with the 100x Olympus MPlanFLN objective, collimated with a 100x Nikon TU Plan Apo objective and sent to the 2300i Spectrapro Czerny-Turner Spectrometer, where the probe is dispersed and focused on to the line camera.

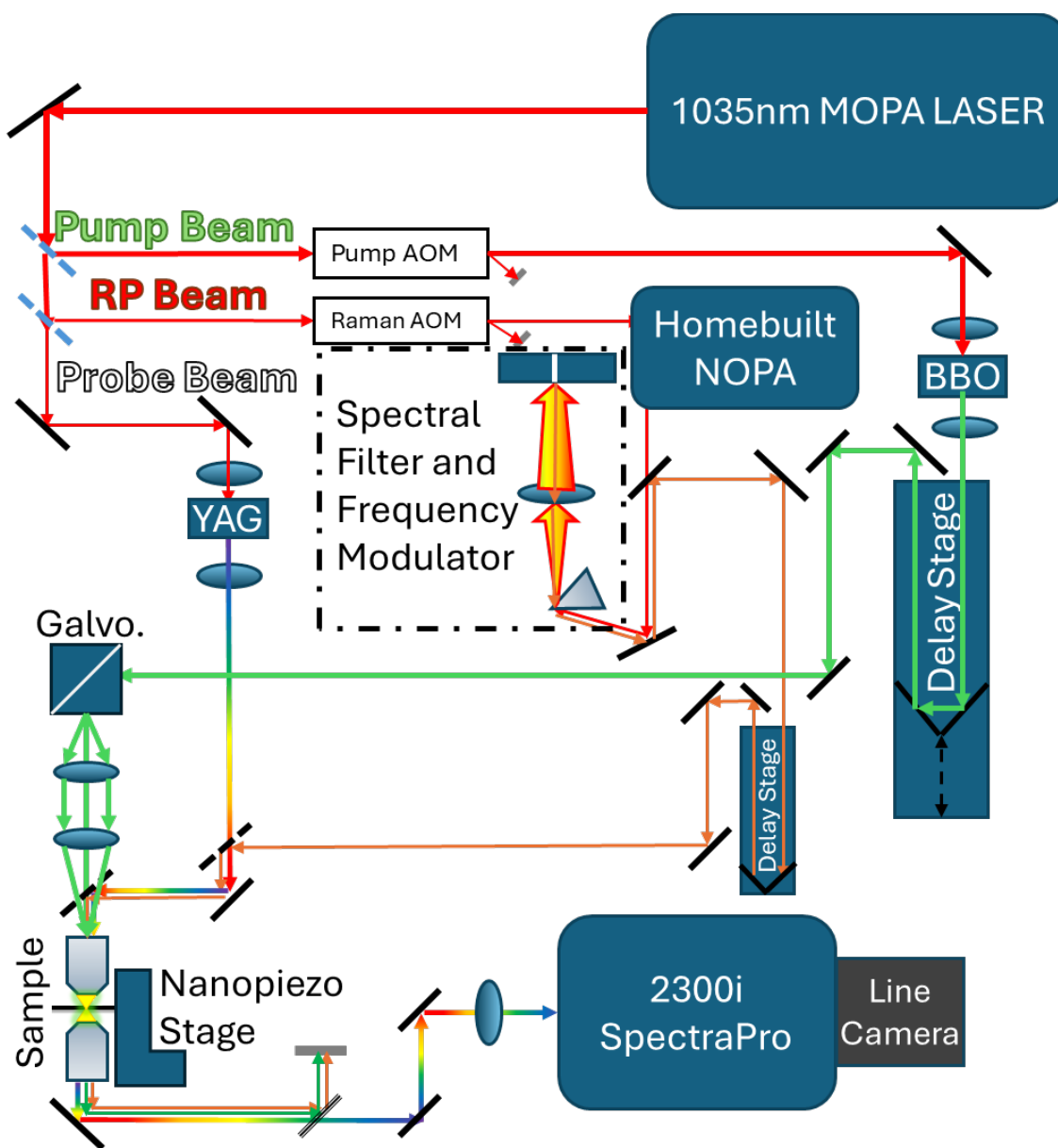


Figure 4.17: Frequency modulated-femtosecond stimulated Raman microscope. Blue ovals denote lenses, dashed lines are beamsplitters and dichroic mirrors and black lines are mirrors.

4.8 Perylene Diimide Aggregate Spectra

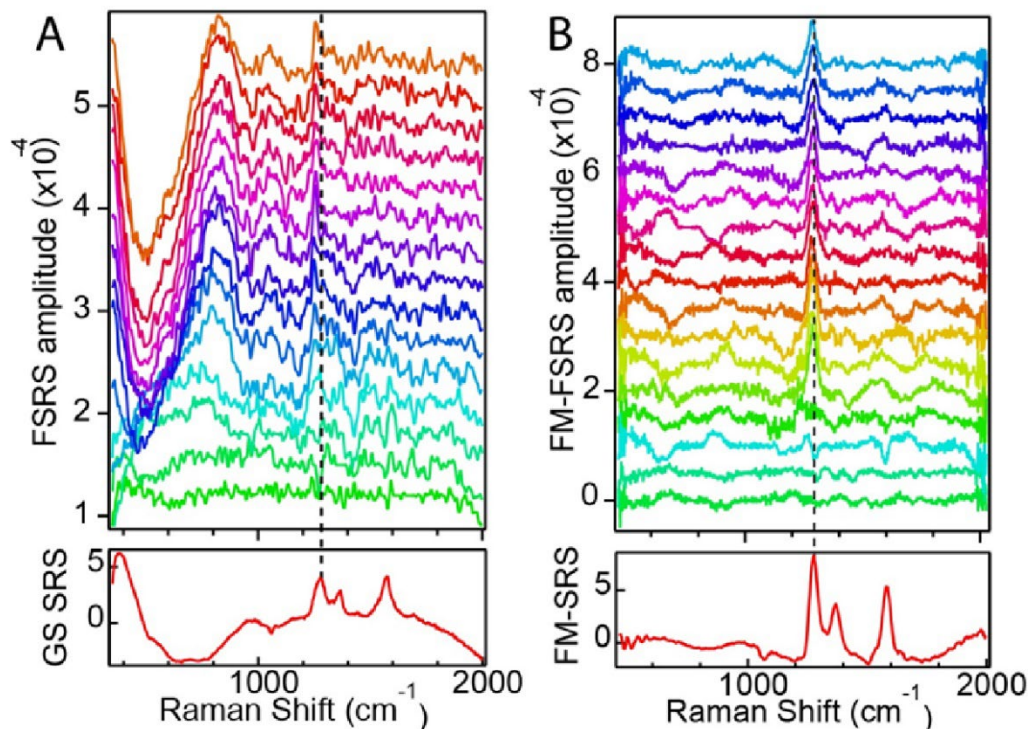


Figure 4.18: SRS and FSRM spectra taken on KT-PDI microstructures. Panel A: SRS, and FSRM spectra without frequency modulation showing both excited state Raman features and artifacts that arise from the background features. Panel B: SRS and FM-FSRM spectra (at Δt of -7.5, -0.5, 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6.5, 7.5, and 8 ps) where frequency modulation produced distinguished ground and excited state Raman peaks with very few artifacts or background signal.

The optimization of the FSRM instrument has made the interpretation of solid state FSRS spectra of a single microstructure significantly more robust. A comparison of the FSRS spectra and SRS spectrum in Fig. 4.18A before implementation of frequency modulation and Fig. 4.18B after clearly shows the improvement in feature clarity. Perylene diimide exhibits three clear peaks in solid state SRS spectra. The peak at 1585 cm^{-1} is an aromatic C-C stretch combined with a CH bend. The 1369 cm^{-1} peak is a pure aromatic C-C stretch of the core perylene, and the

1278 cm^{-1} peak with the shoulder between the 1369 cm^{-1} is heteroring deformation of and C-N stretching of the imide ring and is likely a combination of neutral (1308 cm^{-1}) and reduced species present in the KT-PDI microstructure sample volume (1288 cm^{-1}).¹⁶⁸

Both of the time resolved Raman spectral evolutions shown in Fig 4.18 have evidence of excited state Raman gain at 1285 cm^{-1} . The FSRS spectra show gain in the 1285 cm^{-1} and also a negative feature at 1200 cm^{-1} and a large amplitude broad negative signal at 500 cm^{-1} . In the FM-FSRS spectra the gain is clear at 1278 cm^{-1} and the other features from FSRS are not present indicating they were likely artifacts and not true Raman scattering features. At t_0 subtle dispersive features appear near 1288 and 1585 cm^{-1} indicating that photoexcitation disrupts these ring breathing vibrational modes of the perylene core. The peaks recover in less than a picosecond followed by the growth of a strong Raman gain feature at 1285 cm^{-1} . Steady state Raman spectroscopy of perylene diimide has shown that electrochemical reduction leads to the formation and growth of a peak at 1288 cm^{-1} and reduction of 1308 cm^{-1} Raman intensity. This blue shifted peak is assigned to a delocalized negative charge in the imide ring structures of porphyrin originating from radical anion carbonyl species. The formation of this peak occurs at electrode potentials well below where a noticeable change in UV-Vis could be observed (-0.7V for Raman and 1.05V for UV-vis, vs. $\text{Ag}/0.1 \text{ M Ag}^+$).¹⁶⁸

The fact that FSRS can resolve the location and identity of anionic species proves that FSRM can be a more effective approach than transient transmission microscopy for observing information about the ultrafast formation of charge separated species in organic materials/PDI. The KT-PDI material is kinetically trapped through reduction and since the first reduction of PDI has been shown to form a delocalized anion in the six membered imide ring position,¹⁶⁸ it is

likely that the stabilization of the nonequilibrium metastable stacking confirmation is directly related to this delocalized anion FSRS is a powerful tool to observe the formation and decay of this species to determine its role in excited state evolution. The Raman gain at 1288cm^{-1} does not decay significantly over the period of the 8 ps FSRS scan, where the transient transmission GSB signal measured with broadband pump-probe decays by roughly 50% over the same time frame. This longevity along with published theory and experiments¹⁶⁸, indicates that the state that is giving rise to the Raman scattering enhancement is likely due to formation of charge-transfer or separated species that is representative of longer lived excited states in KT-PDI. Indeed, we have observed in Chapter 2 exceptionally long-lived reduced state species that survive for over a microsecond. It appears, based on our FM-FSRS, this reduced species begins to form in roughly a picosecond. Additionally, our FM-FSRS has elucidated that photoexcitation results in the formation of this anion is in all probability on the imide ring of the porphyrin diimide. These results highlight the value of using electronic and vibrational pump-probe spectroscopies in concert for the determination of the trajectories of photoexcitation.

4.9 Conclusion and Future Work

The deployment of FSRM in solid-state organic semiconductor characterization presents formidable technical and analytical challenges. Achieving the requisite signal-to-noise ratios while preserving sample integrity is an ongoing struggle and requires innovative methodologies and meticulous experimental design. This chapter has covered the theoretical framework of Raman scattering, SRS and FSRS, as well as how these techniques can provide valuable information about the structure-function relationship in organic materials and molecular superstructures. We then outline the major aspects of the efforts undertaken to produce an

instrument capable of microscopic time resolved SRS investigations of organic and hybrid self-assembled superstructures. From the initial exploration of perovskite nanoparticle-ligand electronic coupling with an IR-based Raman pump to the subsequent shift towards PDI aggregates with a visible Raman pump, each step represents a deliberate progression aimed at overcoming the challenges inherent in this complex solid-state technique. The construction of a homebuilt NOPA and the implementation and troubleshooting of frequency modulation represent some of the most significant advancements in SRS signal quality and the ability to discern FSRM spectral features. The data acquired from the culmination of these efforts and the final state of the FSRM, offered valuable insights into excited state behavior in PDI aggregates and provided additional context for charge formation phenomenon observed with broadband electronic pump-probe microscopies.

Moving forward, there exist many opportunities for further optimization and exploration. First, further investigation of the PDI system is warranted. A direct comparison of EQ-PDI and KT-PDI could help elucidate if the anion formation observed in the KT-PDI is a unique process for the kinetically trapped aggregate that is directly leading to the long-lived charge separated state or if it is arising from a charge-transfer excimer that is common to both systems.^{17, 18, 28} Secondly these solid state investigations could be benefited by the understanding of how the vibrational dynamics of organic aggregate samples change from a solvated phase into the solid state. To achieve this capability microscopic resolution is not needed, and so a modular beam path circumventing the microscope apparatus could be added without disrupting the FSRM apparatus. Thirdly, the mechanical stage-based frequency modulator, despite its reliability drastically slows data acquisition. So further investigation into why the AOM based frequency

modulator was problematic or other high speed pulse picker options are some of the most pressing endeavors in the interest of obtaining valuable FSRM data. Finally, with the improvements in resolvable FSRS data that have been achieved, exploration of other samples could provide valuable insight into their behavior. For example, FSRM could help solve the mystery of porphyrinic metal organic framework PCN-222 excited state dynamics and why the solid-state lifetime of Soret-band relaxation is so different from TCPP monomer.

CHAPTER FIVE

CONCLUSION AND FUTURE WORK

5.1 Summary

The works presented in this dissertation explore the intricate relationship between the structural characteristics of self-assembled solid-state materials containing organic chromophores and their functional properties. The development and utilization of ultrafast broadband microscopies engendered a unique perspective enabling meaningful insights into excited state dynamics and the effects of intermolecular coupling. In Chapter 1 we introduced the spectroscopies and pump-probe microscopies employed throughout the rest of the dissertation along with the accompanying measurements. A discussion of the theoretical framework of intermolecular coupling and the synthetic considerations of self-assembly, was included to provide context for how time resolved microscopies are important for the characterization of solid-state materials with intrinsic structural heterogeneity.

Chapter 2 then detailed the study of PDI aggregates with an ensemble of steady state and time resolved microscopies. The findings emphasize the significance of the assembly environment in determining the solid-state properties of materials built from non-covalent interactions. Redox mediated assembly of the PDI monomer enabled the kinetic trapping of the aggregate (KT-PDI) and the formation of morphologically distinct materials in the solid-state. Relative to PDI assembled in equilibrium conditions (EQ-PDI), the kinetically trapped sample showed enhanced long-range order, increased electronic coupling, and the formation of reduced species that persist for microseconds within the sample. The detection of this long lived polaron

in KT-PDI and the elucidation of the exciton delocalization mechanism were made possible through the use of broadband pump-probe microscopies and highlight the exceptional potential of the tool to resolve the structure function relationship in molecular solids with intrinsic structural heterogeneity and broad spectral resonances.

The results presented in Chapter 3 show how time resolved broadband microscopy can be used in concert with other steady state and time resolved techniques such as two-color pump-probe and TCSPC to explore complex excited state dynamics and transport phenomena in covalently linked chromophore networks. The material that was studied, PCN-222, is a porous network of porphyrin chromophores (TCPP) bound to $\text{Zr}_6(\mu_3\text{O})_8(\text{OH})_8$ clusters. PCN-222 grows into large aspect ratio microrods with hexagonal crystal structure. We have uncovered distinct excited state behavior in PCN-222 between photoexcitation wavelengths and hypothesize that it arises from different sensitivities to defect density. We have correlated morphological features believed to arise from defects to variations in excited state spectral peaks positions, indicating that the chromatic shifts likely arise from higher defect densities. We have also shown that Soret-band excitation with 400nm light yields excited states with rapid subdiffusive transport properties in PCN-222, and also when pumping into the Soret-band we see marked variation in excited state lifetime as a function of position within PCN-222 microrods. However, when we excite the TCPP linker with 517nm light, resonant with the Q-band transitions, we see only small variations in excited state lifetimes and do not see any measurable transport. We hypothesize the difference in transport properties is a result of significant intermolecular coupling affecting the Soret-band. The steady state absorption of deposited single crystals shows evidence of J-type coupling and relaxation of the transition symmetry constraints. Additionally, we see significant

emission from the Soret-band and TCSPC measurements have shown an excited state population of Soret-band excitons that have nanosecond lifetimes. This microscopic investigation of solid state PCN-222 has ascertained that the excited state dynamics are more nuanced than expected proved that assumptions regarding Soret-band relaxation are not always applicable in solid state MOF systems.

Chapter 4 explores the theoretical underpinnings of Raman scattering techniques like SRS and FSRS before stepping into the efforts and progress we have made toward the development of a FM-FSRM instrument capable of acquiring excited state Raman spectra on individual solid-state superstructures. Time resolved Raman spectroscopy is a powerful tool for studying the structure-function relationship because it provides comprehension of the dynamic structural changes that occur upon excitation. This comprehension can help identify intermediate states and excited state-vibrational coupling, revealing specific information about the relaxation pathways and energy transfer processes of a material. The implementation of a microscopic FSR instrument is far from trivial and requires persistence and creativity to achieve. We have walked through the extensive iteration and improvement of our experimental set-up with the intent of aiding future efforts to develop solid state FSRM devices. Finally, we have also shown, through the study of KT-PDI microstructures and the observation of anion formation on the imide heteroatom ring in ~ 1 ps, that FSRM can provide meaningful insight into the trajectory of excited state species that may be opaque to electronic characterization techniques.

While the work presented in this dissertation represents substantial progress in the characterization of the structure-function relationship with the utilization and development of

broadband microscopic pump-probe techniques, there remains extensive work to be done, and questions to be answered.

5.2 Future Work

Metal Organic Framework PCN-222

The observation of unique transport properties and relaxation dynamics in PCN-222 microstructures as a function of excitation wavelength was a striking finding that requires further investigation. Notably, if the rapid ~ 200 fs relaxation observed in the Soret-band of TCPP monomer⁵⁹ were applicable to PCN-222, minimal Soret band emission would be expected. However, we observe Soret band emission and our TCSPC results show that the average lifetime of Soret-band excited state species in solid PCN-222 is much longer than generally expected for porphyrinic MOF systems³ and the TCPP^{59, 60, 169} monomer. This finding opens two possible explanations for the observed differences in transport and kinetic behavior. One possibly is hot-exciton diffusion in the Q-band, where excess thermal energy enables the excited state to overcome the potential energy barrier between TCPP linkers and move more freely through the MOF.¹⁴² Alternatively, the excitonic coupling observed in microscopic absorption measurements predominantly affecting the Soret-band could be facilitating delocalization of the excited state and facilitating rapid diffusion before the state localizes or relaxes. Indeed there is literature precedent showing that the charge-transfer integrals between TCPP linkers in the triangular pore of PCN-222 are substantial and are capable of facilitating charge hopping, charge transfer-exciton formation or exciton delocalization over the cluster of chromophores.⁵⁴ In order to better understand the mechanism of the distinct transport properties and relaxation dynamics in PCN-

222 microstructures, influenced by excitation wavelength, further investigation into the prolonged existence of Soret-band species and the influence of chromophore coupling is needed.

Computation analysis could be a powerful tool to elucidate the mechanism leading to the divergent excited state behaviors from the Soret-band and Q-band in PCN-222. Modeling the triangular cluster of TCPP monomers and the simulated excitation of one monomer to the S_1 or S_2 state could provide valuable insight into the evolution of the two excited state species and provide an anchor for our experimental data. The most significant challenge in this endeavor may be tuning the electronic coupling between the TCPP molecules in the cluster. However, there is established theoretical work detailing how excitonic coupling affects Soret-band and Q-band absorption in the aggregate of a similar porphyrin (β -Tetraethyl-tetrapyrrolyl,porphyrin) and we have experimental absorption measurements of single crystals of PCN-222 to provide and anchor for this process. Ultimately, the computational modeling of this porphyrin system is beyond the scope of the typical work of our lab, and so we turn to further experimental characterization techniques that could provide further understanding into the evolution of the Soret-band species.

The primary constraint of the broadband pump-probe microscope in characterizing the evolution of Soret-band excitation lies in the spectral bandwidth of our probe beam and the wavelength of the pump. Herein, we propose a potential alteration of our microscope configuration to overcome this limitation (Figure 5.1). In this setup, the probe would be generated within a calcium fluoride (CaF_2) crystal to achieve a spectral window that aligns with the Soret-band absorption and emission. Literature precedent has demonstrated the generation of a supercontinuum spanning from 300nm to 625nm by irradiating a CaF_2 crystal with 515nm

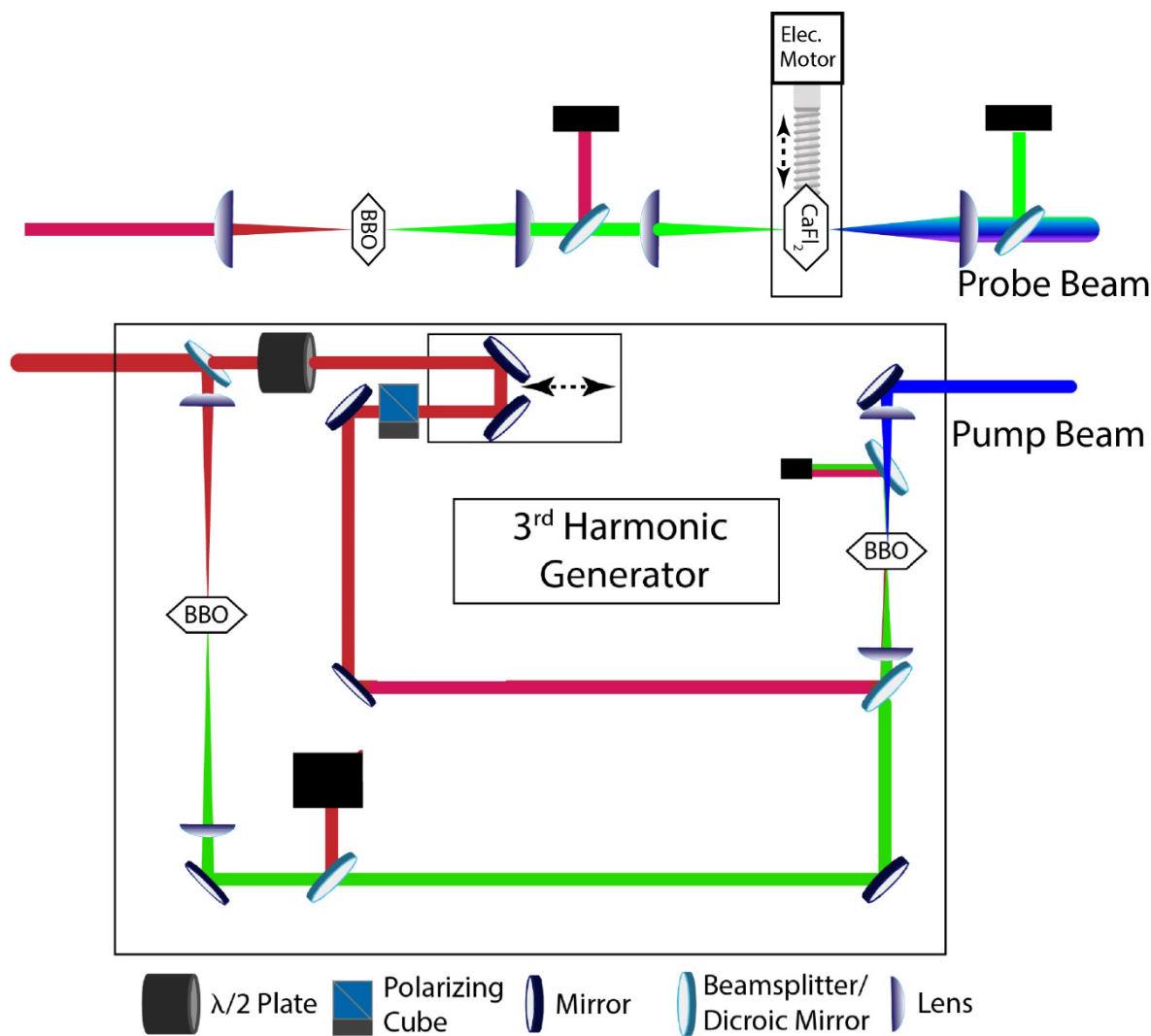


Figure 5.1: Diagram of the proposed optical construction to obtain the capabilities needed to explore PCN-222 Soret-band spectral dynamics. The top beam line shows the generation of the probe, where the fundamental 1035 nm beam from the Coherent Monaco laser is focused into a BBO to generate the second harmonic (517.5nm), which is then focused into a calcium fluoride (CaF_2) window to generate a supercontinuum blue of 517.5 nm. The CaF_2 window is translated using a worm gear and motor to prevent photodamage. The bottom beam shows the generation of the pump, where the NOPA discussed is repurposed to a 3rd harmonic generator. The fundamental is split by a 75:25 beam splitter, and the reflected beam is sent into a BBO (@23.3°) to generate the second harmonic. The transmitted beam is sent through a $\lambda/2$ waveplate and polarizing beamsplitter to obtain the correct polarization combination then both beams are recombined and focused into the 2nd Type 1 BBO (@32.3°) to generate the third harmonic (345nm) used as the Pump.

150fs pulsed light.¹⁷⁰ Thus, to achieve a suitable continuum, we would first frequency double the 1035nm fundamental to 517.5 nm, then focus it into the CaF₂ crystal. Continuous translation of the crystal to mitigate photodamage would be facilitated by a worm gear translation stage driven by an electric motor. For generating the pump, we propose repurposing the NOPA discussed in Chapter 4 into a 3rd harmonic generator. This setup utilizes two BBO crystals and the combination of 517.5 and 1035nm pulses to produce 335 nm light for use as the pump. The main unresolved challenge lies in the transmissivity of the pump in the microscope objectives; however, a reflective objective could potentially mitigate this issue, albeit with potential compromises to image quality.

Obtaining excited state spectra in this wavelength region could help answer some core questions. First, we would be able to examine the GSB features of the Soret-band and see if there is evolution of the spectral profile over time. We probed the capability of Broadband pump-probe microscopy to resolve excited state delocalization in Chapter 2, and there is a possibility similar information could be obtained for PCN-222. Second, our probe would overlap the Soret emission bands observed in the steady-state fluorescence measurements. The isolation of stimulated emission features and the evolution and dynamics of these features would provide higher resolution information than TCSPC regarding the rate of relaxation of the Soret band and may help resolve excited state branching ratios. Finally, we could examine MOFs exhibiting different molecular orientations in the framework such as PCN-221 and PCN-224 to determine how the molecular ordering and coupling is affected as a function of the interchromophore structural characteristics. This could provide insight into to what degree the electronic coupling of the Soret-band in PCN-222 is facilitating delocalization and transport.

Femtosecond Stimulated Raman Microscopy (FSRM)

Future work on the FSRM will initially prioritize improving the frequency modulation mechanism. The mechanically actuated spectral filter, though reliable, has significant disadvantages for measurement efficiency. The first approach would be further investigation of the AOM based configuration to identify the root cause of oscillations in the SRS spectra generated by the 0th order diffraction. Similar oscillations have been reported in FSRM and thoroughly investigated, with the purported source being spectral interference.¹⁷¹ Strategies are proposed for mitigating their effects, such as counter propagation of RP and probe pulses or adjusting the relative polarization of the RP and probe pulses, but the proposed strategies have the dual effect of reducing SRS signal intensity. Therefore, we introduce the alternative strategy of employing a digital micromirror device (DMD) based system to obtain the two frequencies of RP pulses. DMDs sport high repetition rates of up to 32kHz for binary patterns,¹⁷² which would allow for direct modulation of the frequency components.

Furthermore, with the optimization of FSRM, future research will delve into the exploration of time-resolved Raman spectra of additional conjugated organic samples. Investigation of equilibrium assembled Perylene diimide aggregates will inform the origin in the differences in excited state behavior for the solid state perylene diimide aggregates studied in Chapter 2 and provide a control to compare KT-PDI against. This investigation holds potential for uncovering valuable insights into the dynamic structural changes that facilitate charge separation in KT-PDI relative to EQ-PDI. Additionally, capturing SRS spectra and FSRS spectra of PCN-222 is an objective of the lab, shedding light on the coupling interactions and excited state structural transformations in the MOF. Raman spectroscopy has shown exceptional promise for the characterization of MOFs¹⁷³ and even steady state Raman microscopy measurements

could prove valuable to understand how assembly into the framework affects the nuclear degrees of freedom.

Ultimately, dower density serves as the primary constraint for microscopic applications of FSRS due to the delicate balance between signal amplitude and sample degradation. In the focal plane of the microscope, the probed volume is on the order of $1\ \mu\text{m}^3$, allowing for the high spatial resolution of the instrument while also limiting the maximum fluence possible before photodamage. The fluence limitation has a detrimental effect on the SNR, where spectral dispersion often results in underutilization of the dynamic range detectors and, in our case, the line camera. Therefore, the noise contribution from the camera and electronics is a major contributor to the SNR and can make resolving the extremely low signal FSRS measurements of FSRM very difficult.

5.3 Conclusion

The body of work compiled in this dissertation provides direct examples of how the structural properties of solid-state organic chromophore assemblies, resolved at the micron length scale, effect significant changes in excited state evolution by influencing intermolecular electronic coupling. The optoelectronic properties of organic materials exhibit dramatic sensitivity to dipole-dipole and charge-transfer coupling. Materials derived from organic chromophores are often interconnected with weak noncovalent interactions resulting in significant structural heterogeneity which can strongly affect their performance. In Chapter 2 we show that by directing the selfassembly process of perylene diimide aggregates using redox chemistry, the long-range order of the resulting solid-state material can be improved. With the unique advantages of broadband pump-probe microscopy, we were able to resolve excited state

evolution yielding long lived charge separated species, that resulted from this synthetic process and solid-state order. Chapter 3 explored the excited state dynamics of porphyrin chromophores linked in a porous MOF called PCN-222, uncovering distinctive excited state transport and dynamics between excitation into different energy states. One of the future aims of this research is to resolve how intermolecular coupling is affecting this difference in excited state behavior. Additionally, the FM-FSRM instrument will continue to be optimized and improved to augment electronic pump-probe spectroscopy with a vibrational perspective on excited state dynamics and structural evolution. This study underscores the effectiveness of broadband pump-probe microscopies, complemented by other spectroscopic methods, in resolving the intricacies of excited state properties at length scales comparable to intrinsic structural features and heterogeneity.

APPENDICES

APPENDIX A

SUPPORTING INFORMATION: STRUCTURE-FUNCTION
RELATIONSHIPS IN PERYLENE DIIMIDE POLYMORPHS:
EXPLORING EXCITED STATE DELOCALIZATION AND
CHARGE SEPARATION WITH BROADBAND PUMP-PROBE
MICROSCOPY

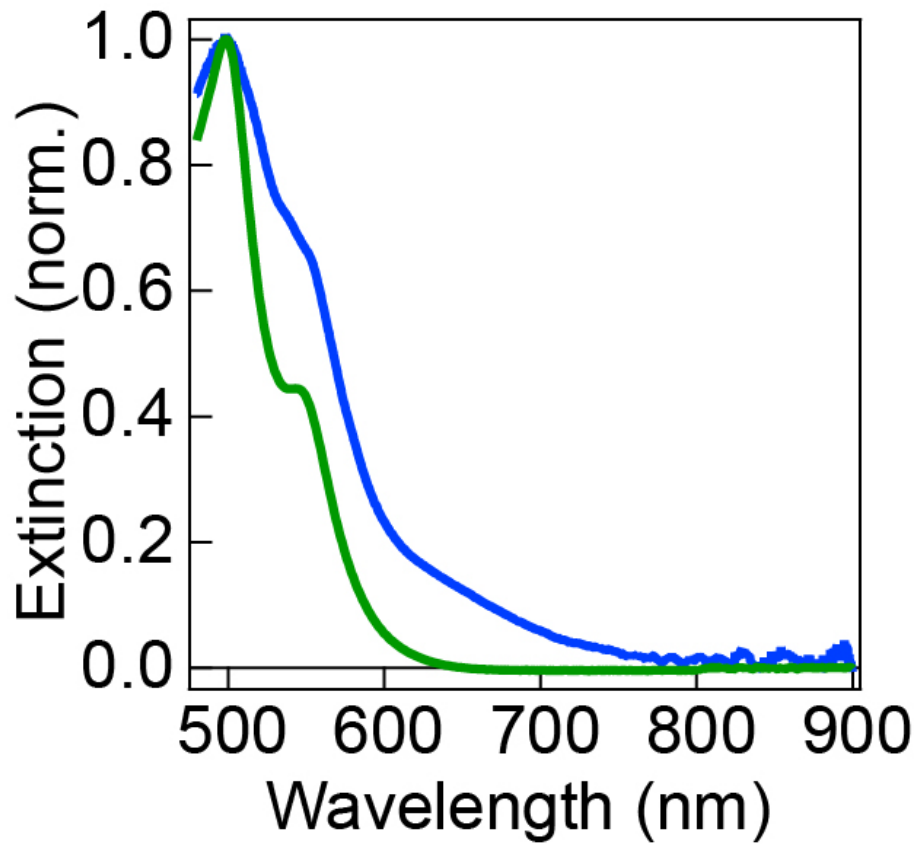


Figure A.S1: Spectral comparison between suspended neutral aggregate extinction (green) with thin film extinction of EQ-PDI(blue).

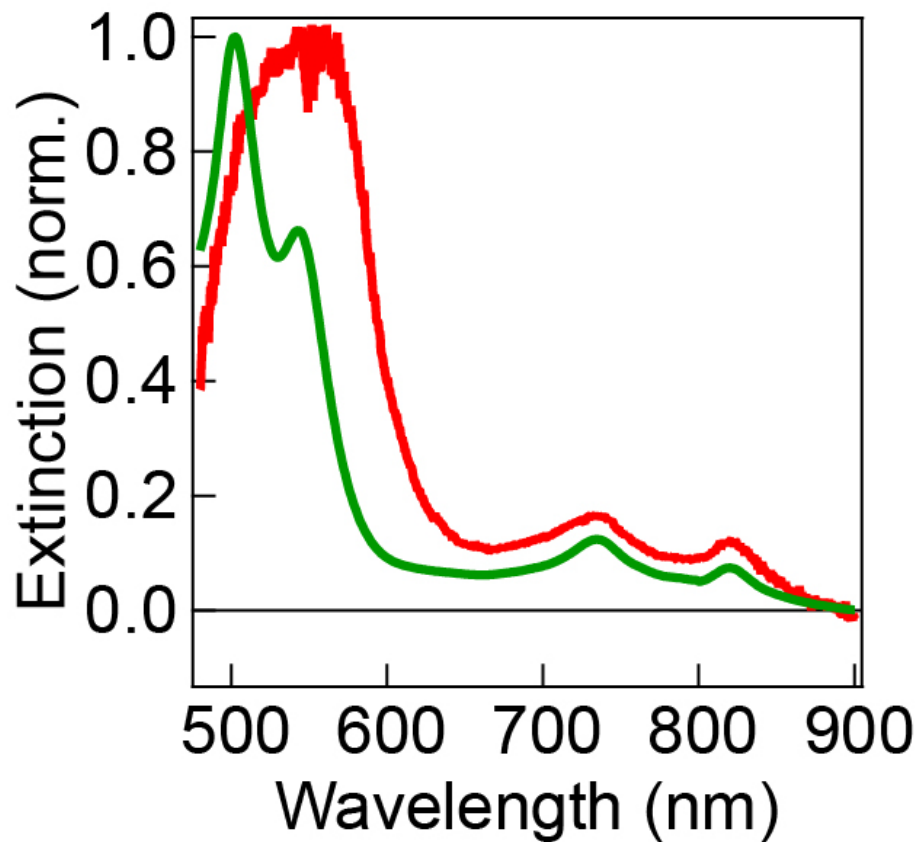


Figure A.S2: Comparison of the extinction of suspended chemically reduced PDI (0.1 equivalents of NaSH) in green, against the extinction of KT-PDI Microstructure measured in the solid state (red).

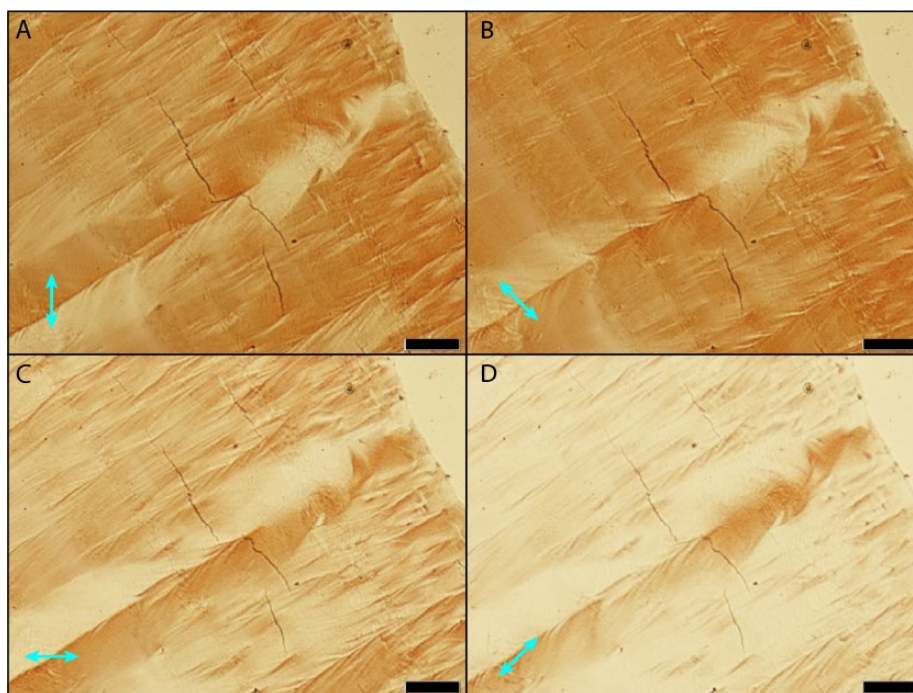


Figure A.S3: Brightfield microscope images of EQ-PDI thin film with the polarization of transmissive illumination shown by the blue arrow.

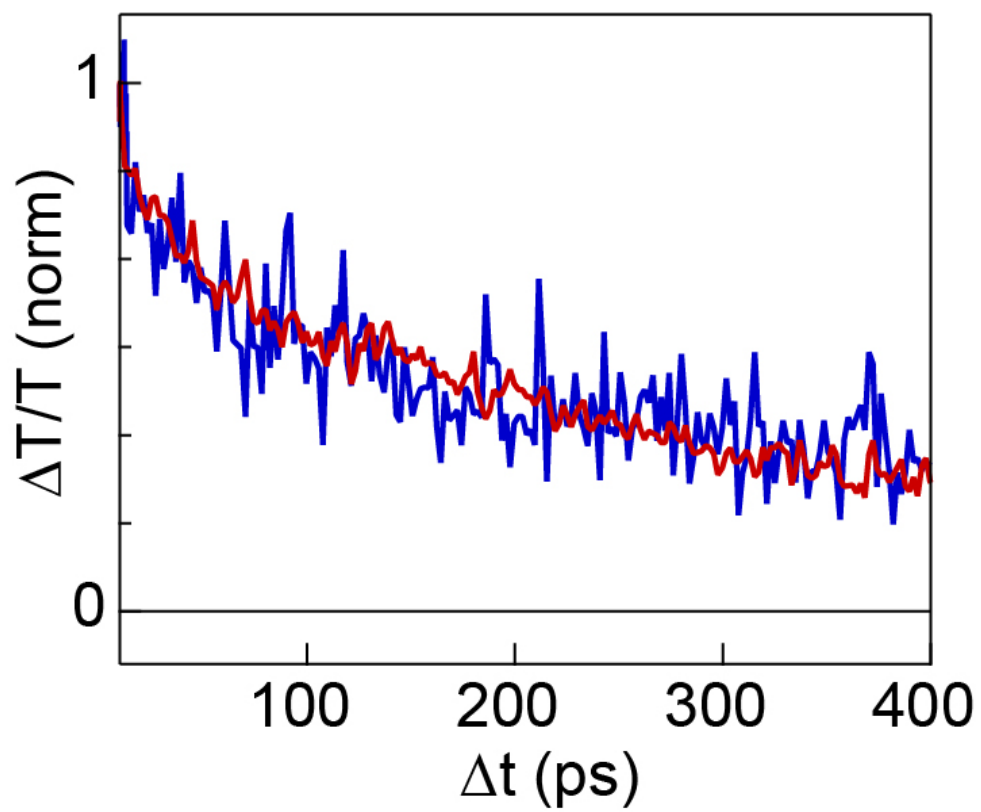


Figure A.S4: EQ-PDI Kinetics of the ground state bleach at 567nm (blue) and the photoinduced absorption 719nm (red) transient transmission signal normalized at 10ps.

APPENDIX B

TUNING ENERGY AND CHARGE TRANSFER IN CESIUM
LEAD TRIHALIDE NANOPARTICLES WITH LIGAND
EXCHANGE

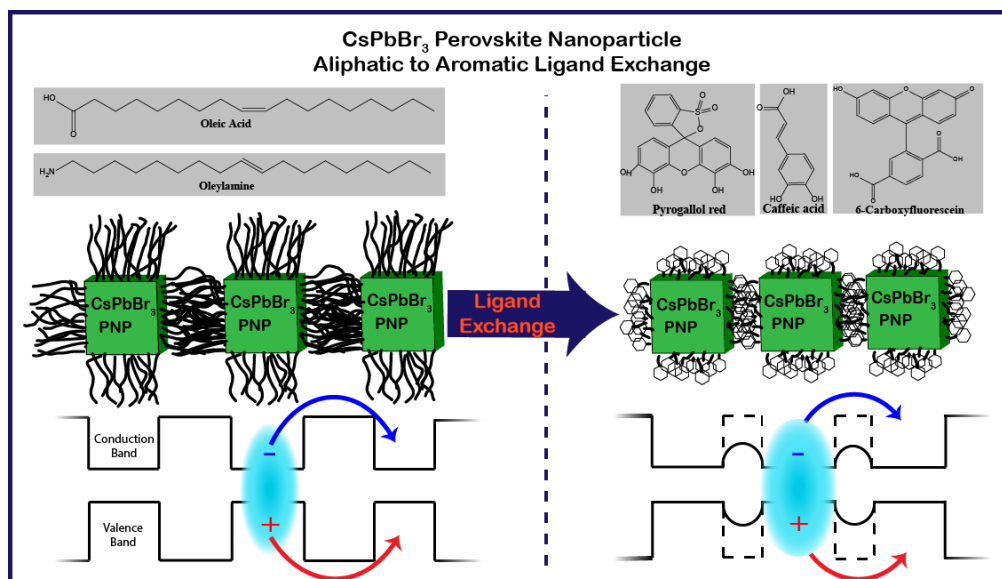


Figure B.1: Summary figure showing the conventional aliphatic passivating ligands and aromatic ligands that were investigated above. Below is a cartoon of the ligand exchange process and a visual representation of the hypothesis.

B.1 Introduction

Lead-halide perovskite materials are a class of direct band gap semiconductors that have benefitted from high visibility in materials science and chemistry research. The combination of high charge carrier mobility¹⁷⁴, large absorption coefficients¹⁷⁵, and a relatively facile and cheap synthesis has made them desirable for a variety of optoelectronic applications. In 2015 Protesescu et al. first synthesized colloidal inorganic perovskite nanoparticles (PNP), introducing the advantages of quantum confinement to the field and later revealing the exceptional defect tolerance of the PNPs¹⁷⁶. Since then, PNPs have shown promise in applications including photovoltaics (PV)¹⁷⁷⁻¹⁸¹, light emitting devices (LEDs)^{182, 183}, sensing devices¹⁸³⁻¹⁸⁵ and lasing^{186, 187}.

In the synthesis of PNPs aliphatic surfactant ligands are used to rapidly terminate precipitation induced perovskite crystal growth, producing monodisperse colloidal nanoparticles. A mature body of research has developed focused on improving PNP quantum yield and stability through more effective surface passivation. However, the strongly insulative natures of the most well-studied ligands, oleylamine (OAm) and oleic acid (OA), limit transport in solid films of the PNPs. The ligands interrupt the electronic band structure in the spatial dimension by introducing energy barriers into the lattice^{188, 189}. Photovoltaic efficiency requires a balance between total light absorption of the photon absorbing layer and excited state diffusion to charge separating interfaces¹⁷⁷. A higher diffusivity in the absorbing layer allows a greater film thickness to be used where generated carriers are reaching a charge separation interface or an electrode before relaxing. In the bulk, the optimal hybrid perovskite layer thickness for photo conversion efficiency (PCE) is 400 to 800nm¹⁹⁰, which maximizes light absorption. On the other hand, for a solar cell fabricated with CsPbI₃ quantum dots (QD), the optimal film thickness was found to be only 200nm. Exemplified by the lower maximum photoconversion efficiency (PCE) obtained by PNP PVs (16.6%) relative to bulk perovskite PVs (23.7%)[1], it is clear that excited state transport rates and diffusion lengths in solid films are major limiters for PNP PVs.

To address this shortcoming, we endeavored to facilitate energy and charge transport in arrays of PNPs through the incorporation of conjugated aromatic passivating ligands. We hypothesized that by tuning energetic alignment and spectral overlap of passivating ligands we could modify excited state transfer rates in thin films by affecting interparticle potential energy surfaces. CsPbBr₃ PNPs were synthesized through hot-injection and reprecipitation utilizing OA/OAm passivating ligands. Ligand exchange of OA/OAm with targeted energetically aligned

molecules was completed and refined through experimental iteration. Initially we exchanged oleic acid with caffeic acid because the catechol group of caffeic acid, was expected to outcompete the carboxylic acid species of oleic acid in binding to the surface lead species of the perovskite. Exchange with two other dye molecules, pyrogallol red, and 6-carboxyfluorescein were also explored, before turning to an established protocol using trans-cinnamic acid, and 3,3-diphenylpropylamine.^{166, 191} The resultant PNP-ligand complexes were spectroscopically and electronically probed in colloidal solution phase to understand how the coupling between the inorganic lattice and the organic ligands has affected the optoelectronic characteristics of the complex. Subsequently, solid-state interparticle coupling was examined by quantifying energy transport measurements and excited state with spatially and temporally resolved spectroscopic techniques.

B.2 Background

Stable PNPs with minimal surface defects are most easily and consistently created by capping crystal growth with aliphatic surfactant ligands. An added advantage of this strategy is that the hydrophobic tails of the capping ligands protect the PNPs from water and oxygen induced degradation. However, the insulating nature of these capping ligands limits electronic coupling between nanoparticles, which in turn inhibits exciton and charge carrier transport. With the aim of improving the capabilities of PNP complexes for PV applications, surface modification with energetically aligned aliphatic ligands was used to enhance excited state mobilities.

OA/OAM Capped CsPbBr₃ colloidal PNPs form a cubic superlattice upon deposition with evaporative assembly¹⁹². The close packed nature of the lattice enables Förster resonance

energy transfer (FRET) of excitons between neighboring cubic quantum dots. Unlike bulk perovskite semiconductor systems where energy is predominantly carried by charge particles, in quantum dot solids exciton diffusion represents the major contribution to energy transport through the material¹⁹³. The coulombic binding energy of the electron and hole are complemented by confinement energies, which minimize charge separation events. Therefore, the rate of exciton diffusion is highly dependent on the interparticle coupling strength. In OAm/OA PNP where the coupling is weak, FRET is widely accepted to be the dominant mechanism of exciton transport. The frequency of Donor-Acceptor hopping in FRET theory depends on the radius between point dipoles to the negative sixth power as is shown in Eq. B.1. Where τ_{DA} is the donor-acceptor hopping lifetime, $\mu_D^2\mu_A^2$ describes the donor/acceptor spectral overlap, r is the radius between point dipoles, and n is the index of refraction of the media.

Eq. B.1

$$\frac{1}{\tau_{DA}} = \frac{2\pi}{\hbar} \frac{\mu_D^2\mu_A^2 k^2}{r^6 n^4}$$

The substitution of the conventional OA and OAm passivating ligands with shorter aliphatic surfactants to has been shown to decrease the interparticle separation and the decrease FRET hopping lifetimes.¹⁹³⁻¹⁹⁵ Conductivity and exciton mobility have both been improved in this manner, however exciton lifetimes and diffusion lengths can be reduced in the process¹⁹⁵.

Another approach for enhancing interparticle coupling is manipulation of the exciton localization through incorporating aromatic molecules into the ligand brush. The use of conjugated ligands in semiconductor QDs is well established in literature¹⁹⁶⁻²⁰¹, with Vickers et al. notably reporting the use of exciton delocalizing ligands in organo-metal halide PNPs to improve conductivity in solid state films^{166, 191}. The first study in 2018 investigated benzylamine (BZA) and benzoic acid (BA), and the second study in 2020 looked at 10 different combinations

of aliphatic and energetically aligned aromatic ligands. The aromatic ligand-PNP complexes showed improved conductivity, higher photoluminescence quantum yield (PLQY), photocurrent densities and growth of the exciton localization radius. Although these findings are encouraging, there has been no attempt to disentangle charge carrier dynamics from excitonic dynamics and little insight has been gained into the excited state dynamics on the fs-ns timescales.

B.4 Synthesis and Ligand Exchange

Colloidal CsPbBr_3 nanoparticles were synthesized with two unmodified previously reported techniques: hot injection²⁰², and room temperature reprecipitation²⁰³. Hot injection consists of the combination of two precursor solutions in the temperature range of 140-200°C followed by immediate immersion in an ice bath. The solutions are Cs-Oleate in octadecene (ODE), and PbBr_2 solubilized with OA and OAm also in ODE.

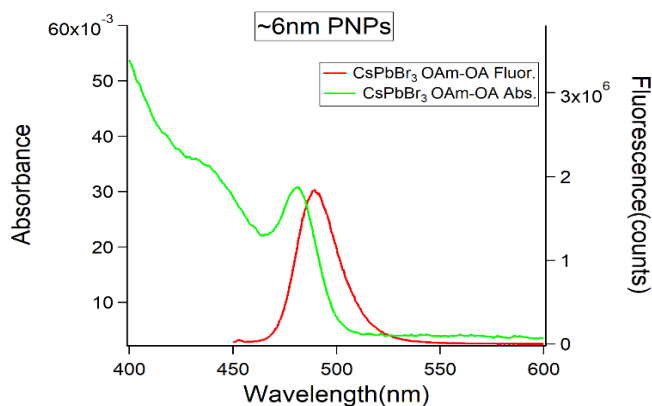


Figure B.2: Absorption and fluorescence of a typical CsPbBr_3 OAm-OA sample prepared through hot injection.

The room temperature reprecipitation technique consists of hybrid precursor solution (Cs-Oleate, PbBr_2 , OA, dodecylamine) in a good solvent (Dimethylformamide) being added to a poor solvent

for the inorganic components, resulting in ligand-mediated precipitation driven crystallization of nanoparticles. Example absorption and emission spectra from PNPs synthesized via hot injection are shown in Fig. B.2. Additional size purification steps are required to obtain a monodisperse sample, especially with the reprecipitation technique. To approximate the average size of the QD, Absorption profiles were compared against published data. Fig B.3 (taken from ref ²⁰⁴) shows a summary of the correlation between average PNP edge length and the optical band gap of the QD.

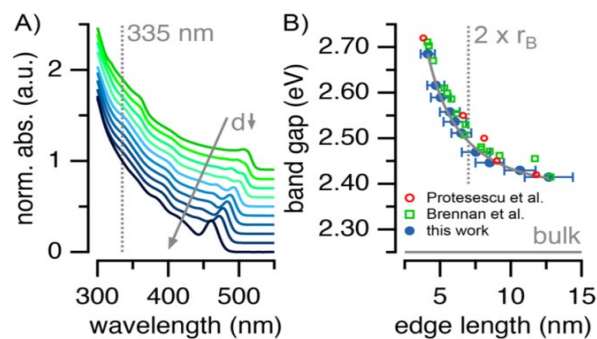


Figure B.3: From Maes et al.'s work, Band gap of CsPbBr₃ PNPs derived from UV-Vis spectra (panel A) correlated with average edge length (panel B) from their research and two others.

Although both hot injection and reprecipitation have been performed successfully, the hot injection technique was be the primary synthetic protocol used because monodisperse samples of specific edge lengths are more easily obtained.

Ligands of Interest.

We selected caffeic acid (CA), pyrogallol red (PGR) and 6-Carboxyfluorescein(6-FAM) as the initial ligands that we investigated to explore the effect of surface modification on interparticle coupling and transport in CsPbBr₃ PNPs. We aimed to tune the energetic and spectral alignment between the PNP and the ligand to modulate both ground and excited state electronic structure in

the confined complex as well as the excited state dynamics and interparticle coupling in thin film morphologies.

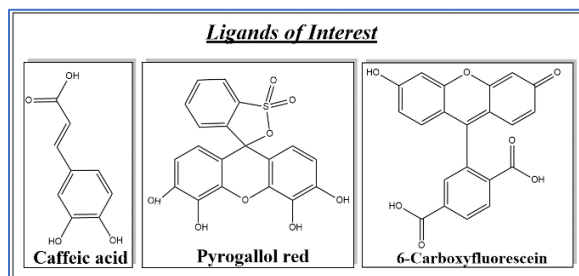


Figure B.4: Chemical structure of selected ligands

The delivery and absorption of the ligands of interest to colloidal PNPs was one of the most challenging aspects of this project. Ligands can have a major effect on the morphological characteristics of the QD, as has been demonstrated by Sun *et al.* where ligand-assisted reprecipitation results in spherical QD, nanoplatelets, nanorods or nanocubes depending on the ligand combination used²⁰³. Liang *et al.* also showed that that PNP morphologies can be engineered simply by varying the relative concentrations of OA and OAm in synthesis²⁰⁵. Currently there is no consensus as to the functional mechanism of organic ligands in CsPbBr₃ PNP synthesis^{61, 206-208}, although it is known that OA, and especially OAm, both exhibit highly dynamic²⁰⁶ binding. The dynamic nature of OA and OAm binding has enabled displacement and exchange in both the colloidal and solid states^{201, 209-213}. Ligand exchange techniques vary depending on the coordination group and whether they are performed with solid state or colloidal QDs. They generally involve introduction of the target ligand as a solid or, more commonly, dissolved in a miscible solvent to the PNP sample. In solid state ligand exchange, the solvent used is often designed to encourage the stripping of the native ligands as it introduces the target ligand²¹⁰. We

utilized simple concentration driven ligand exchange techniques in our work and successfully performed partial ligand exchange with caffeic acid.

The delocalization of electron density and relaxation of confinement from the QD has been shown to increase interparticle coupling and improve conductivity²¹⁴. The degree of delocalization was expected to be enhanced by PNP valence band(VB) and conduction band(CB) edge energetic alignment with the HOMO and LUMO of the ligands¹⁶⁶. Ground state delocalization results in a bathochromic shift of the absorption onset due to the corresponding relaxation of confinement.

Based on a qualitative comparison of energetic alignment (shown in figure B.5), we expect that 6-FAM would allow for the greatest delocalization of electron density, followed by PGR and CA.

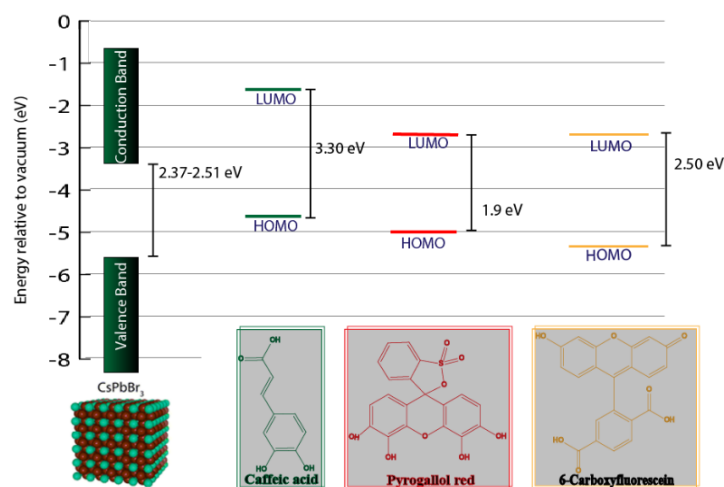


Figure B.5: Schematics of approximate energetic positions of ligands of interest relative to CsPbBr₃ (The range in band gap for CsPbBr₃ reflects available values from adjusting PNP size and therefore quantum confinement effects)

Interestingly, as we describe below, preliminary results show that even in the case of PNPs passivated with CA, a band gap redshift is observed, suggesting that partial delocalization of electron density occurs even with relatively poor energetic alignment. PGR and 6-FAM both have

better orbital alignment with the valence and conduction. However, synthetic challenges led to limitations in the exchange of these molecules.

While our goal is to enhance exciton transport via surface modification, ligand substitution may also enhance charge transfer as a competing pathway of exciton evolution. As can be seen in Fig. B.5, the HOMO energies, approximated from the formal redox potential in acetonitrile, indicates an uphill potential between an electron residing in the PNP VB and the HOMO of the aromatic ligands. Upon photoexcitation, the driving potential would favor a hole transfer from the VB of the PNP to the HOMO of the ligands, separating charges and destroying the exciton. This is consistent with the known reducing agent nature of CA and PGR^{215, 216}. 6-FAM has the smallest driving potential and the greatest alignment with PNP band edge positions, which could indicate that excitonic integrity could be maintained. These hypotheses are based on solvated ligands, and colloidal OA-OAm PNP energetics. Coordination and environmental interactions have a strong effect on the energetics of both organic molecules and confined semiconductors and could therefore significantly affect the energetics of the systems.

B.5 Electronic and Morphological Characterization of the Colloidal PNP-ligand Complex

One of the advantages of colloidal suspension is the low rate of interaction between suspended PNPs. Spectroscopic examination of colloidal PNPs allows for the properties of the QDs to be characterized where ligand-solvent interactions are the primary external perturbations to the semi-isolated complex. Solution phase measurements were used to determine if the surface environment was changed through the ligand exchange attempt. If PNP decomposition occurs through the interaction with the ligand, the distinct absorption profile of CsPbBr₃ PNPs would be

lost. The strong excitonic resonance peak would disappear, and the absorption would lose its distinct onset in the 400 to 500nm range. The presence of the excitonic peak is unique to quantum confined semiconductors and verifies that quantum confinement of the PNPs has been maintained.

The surface composition of the PNP complexes was explored with FT-IR absorption measurements. Although the ability of FTIR to probe surface bound molecules is limited, its use has been well established in the characterization of ligand exchange in quantum dot systems^{166, 179, 191, 201, 211, 213, 217-219}. An FTIR spectrum has been taken of both pure ligands and PNP-ligand complexes. The spectra can then be compared and correlated to determine if the target ligand was exchanged and to what degree it replaced the original stock ligand. The vibrational resonances of coordinating functional groups can also be affected by physisorption or chemisorption. This information, although convoluted with effects from the solvent and ligand-ligand interactions, can hint at the mechanism of ligand surface adsorption.

Steady state fluorescence spectroscopy measurements provide the first indication of how surface modification has affected the available excited state relaxation pathways. The PLQY of PNPs are highly dependent on the degree of ligand surface passivation and reduction of non-radiative surface trap sites²²⁰. Before examining the behavior of excited state species in thin films, we examined relaxation kinetics and PLQY of the PNP-ligand complex in colloidal suspension as a means of investigating the system in effective isolation. Fluorescence measurements of PNPs allowed for the calculation of relative PLQY and the determination of the fluorescence peak positions. Charge transfer to the ligand results in extensive fluorescence quenching, whereas ligands exhibiting only exciton delocalization have minimal effect on PLQY in colloidal

suspension. Figure B.6 shows a comparison of the fluorescence spectra of stock oleic acid/oleylamine PNPs compared with PNPs post CA ligand exchange. The quenching indicates CA could be encouraging a charge transfer to the ligand.

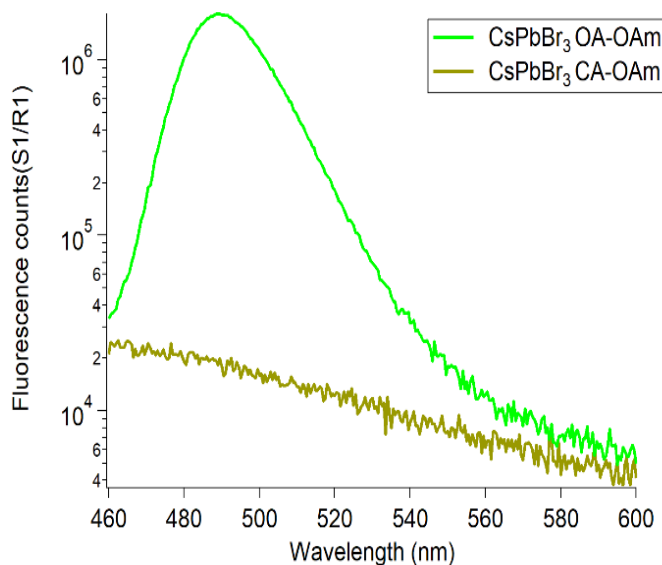


Figure B.6: Fluorescence spectra of CsPbBr₃ PNPs before and after ligand exchange. The OAm-OA NP were dispersed in hexane and the OAm-CA NP were dispersed in Acetone.

Time resolved photoluminescence (TRPL) measurements can be used to help quantify the fluorescence lifetime and clarify the mechanisms of fluorescence quenching. Time correlated single photon counting (TCSPC) and streak camera measurements have allowed for the collection of fluorescence kinetics, which can then be fit to an exponential decay function, to help identify decay pathways. The rate of exciton relaxation from radiative relaxation or interband surface trapping states can often be resolved with TRPL, but charge transfer processes are difficult to resolve (~500fs hole transfer, <150fs electron transfer in CdSe-PGR complex)²¹⁶. In order to obtain kinetics with better time resolution and to examine charge separation events within a PNP ligand complex, we have employed solid-state phase pump-probe measurements.

B.7 Results

Caffeic acid was selected as the first ligand to be investigated and several ligand exchange strategies have been tested. Ultimately an elevated temperature (50°C) concentration gradient exchange was employed. Colloidal CsPbBr₃ nanoparticles suspended in hexane were added to an equal volume of 0.4M CA in acetone. The resultant solution was then stirred at around 700rpm on a hot plate at 50°C for 24hrs, followed by centrifugation (10min at 3600rpm). The long duration exchange protocol was motivated by a continued redshift of the PNP's absorption band onset as well as improved resolution of the onset relative to shorter exchange procedures. The pellet was redispersed in hexane through sonication, centrifuged out, and then resuspended in acetone. Successful ligand exchange was evidenced by irreversible changes in the color, solubility, FTIR resonances, and a complete loss of fluorescence of CA-CsPbBr₃ PNPs.

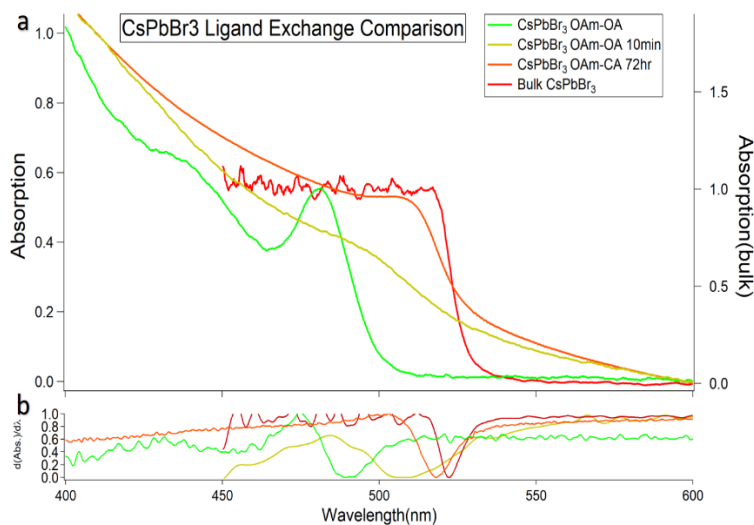


Figure B.8: a) Absorption spectra of bulk CsPbBr₃, nanoparticles with OA-OAm ligands after and after two different caffeic acid ligand exchange procedures. b) derivative of absorption measurements. First minima have been set to zero for ease of comparison.

UV-Vis absorption measurements for caffeic acid, shown in panel a of Fig. B.8, support successful ligand exchange. There is a bathochromic shift of 142 meV or 29 nm, which can be seen by comparing the first minima of the derivative of absorption, as shown in panel b of Fig. B.8. The presence of a subtle excitonic peak and the hypsochromic position of the absorption onset relative to bulk indicates that the nanoparticles are still present and have not fully agglomerated. The Brus equation for semiconductor QDs (Eq. B.2) indicates that the energy shift from caffeic acid exchange results in an increase of the effective radius of 3.07 nm.

Eq. B.2

$$E_{conf} = E_{gap} + \frac{h^2}{8r^2} \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right)$$

Where E_{conf} is the band gap energy of the quantum confined material, E_{gap} is the bulk band gap, h is Planck's constant, r is the radius of the box, and m_e^* (m_h^*) is the electron(hole) effective mass.²⁰² Currently it is not known how much of this shift is a result of delocalization versus agglomeration.

The FT-IR spectra for caffeic acid ligand exchange are shown in Fig B.9. The OAm-OA PNP spectra shown in Panel a is consistent with published literature²¹³.

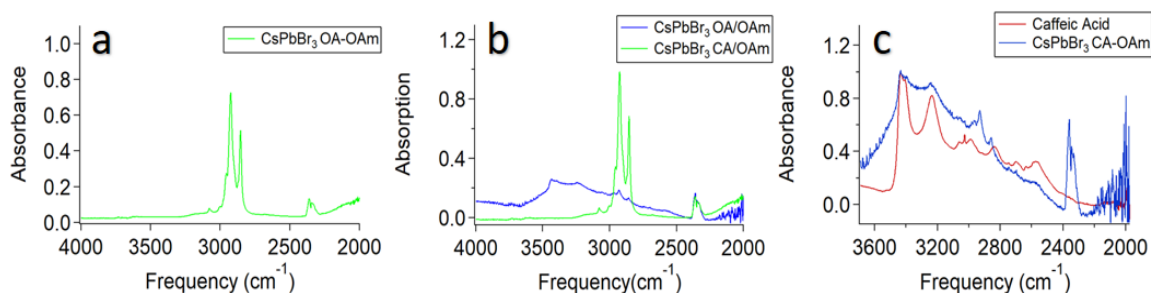


Figure B.9: FTIR spectra collected from solid state thin films deposited on a glass slide. a) as synthesized CsPbBr₃ OAm-OA PNP, b) normalized CsPbBr₃ PNPs before and after ligand exchange, c) Comparison of pure CA with OAm-CA.

The main features are likely CH₂ symmetric stretching (2925cm⁻¹), and asymmetric stretching of CH₃ (2872cm⁻¹). There is a broad OH stretching absorption peak that overlaps the CH stretching modes, but the twin peaks at 2361cm⁻¹ and 2343cm⁻¹ are from CO₂ contamination. Panel **b** compares the PNPs before and after ligand exchange. There is still a signature of the long aliphatic ligands present after the ligand exchange, however the intensity decreases from 0.8OD to 0.18OD and exhibits a very slight hypsochromic shift of 5cm⁻¹. The other features that are present can be attributed to caffeic acid, as can be seen in Panel **c** of Fig. B.9. The results of the FTIR support ligand exchange, but also indicate an overall loss of ligand concentration.

The introduction of CA in the polar solvent almost certainly leads to abstraction of Oleic acid and Olylamine, which could cause deshielding and exposure of surface defect sites since CA will replace OA and not OAm²²¹. The retention of the aliphatic peaks in FTIR spectroscopy (Fig B.9) after ligand exchange indicates that not all ligands are abstracted, however the weakness of the ligand peaks indicates a reduction of overall ligand concentration and surface passivation. OA and OAm adsorption in nonpolar solvents benefits from their surfactant nature, since its polar head is generally associated with the charged PNP surface and its lipid tail is exposed to the nonpolar solvent. CA's dynamic binding and polar nature could be leading to desorption due to the concentration gradient present when the nanoparticles are resuspended in pure polar solvent after the ligand exchange process. Recently we have explored solubilizing CA in non-polar solvents by performing an acid base reaction with Olylamine and performing the exchange procedure in hexane. A post exchange treatment of the PNPs with OAm was also explored. Vickers et al. reported that DPPA can stabilize aromatic ligands and improve conductivity, which

merits its investigation as a counter ligand for CA as well, since there could be π -stacking stabilization¹⁶⁶.

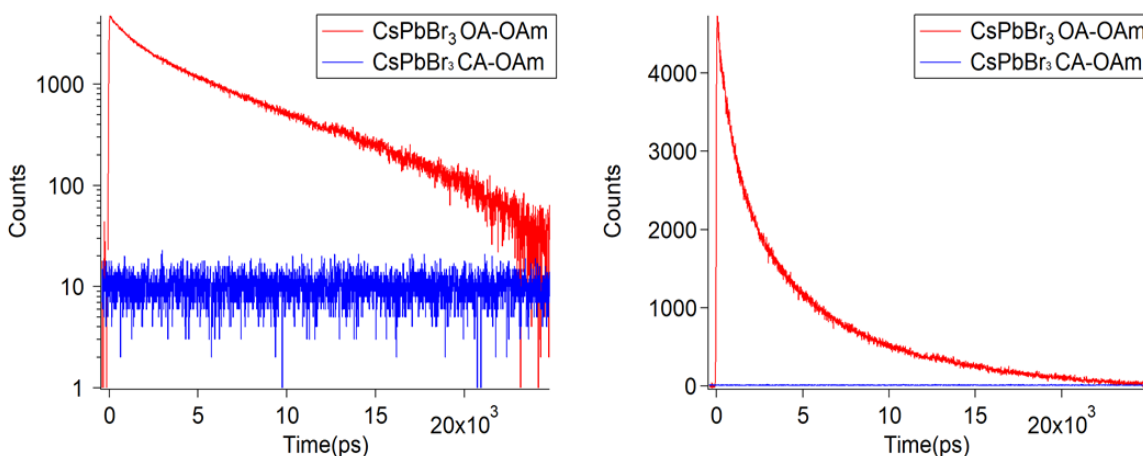


Figure B.10: Time correlated single photon counting of CsPbBr₃ PNPs before and after ligand exchange. The CsPbBr₃ OAm-OA sample was dispersed in hexane and the CsPbBr₃ OAm-CA was dispersed in acetone.

Caffeic acid coordinated CsPbBr₃ nanoparticles exhibited a complete loss of fluorescence visible to the naked eye after ligand exchange. The fluorescence quenching was confirmed through fluorimeter measurements, as shown in Fig. B.6. When the ligand exchange was performed in t-Butyl alcohol, there was a subtle signature of PNP fluorescence remaining, with a bathochromic shift of 14nm. The relative quantum yield of the OAm-CA nanoparticles in acetone was calculated to be 0.34% relative to Coumarin 152. When compared to 74.6% PLQY displayed by OAm-OA PNPs in hexane, effective quenching was evident.

TCSPC was performed to determine if there was any early emission from the OAm-CA PNPs that was not resolved with fluorimeter measurement. As can be seen in Fig. B.10 the TCSPC measurements also did not show any fluorescence from the OAm-CA nanoparticles. The instrument response function of the TCSPC device displayed a FWHM of 64ps, defining the

time resolution, but it is possible that the fluorescence quenching occurs before significant radiative recombination can occur.

The diffusivity of a material in solid thin films can be quantified with TRPL. Time resolved fluorescence was measured in OA-OAm capped PNPs as shown in Fig. B.7, with a Streak camera coupled to a monochromator configured for spatial resolution.

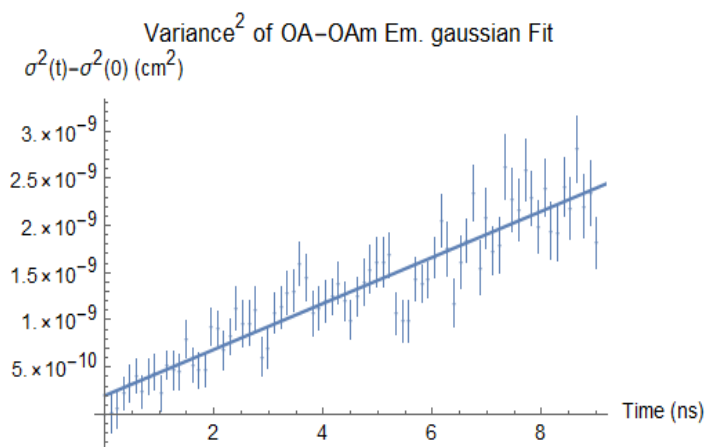


Figure B.7: Plot of the variance in Gaussian fit of Streak camera photoluminescence profiles as a function of time in nanoseconds.

The sample was excited with a short pulse ($\sim 200\text{fs}$) of 400nm light and emission from the sample was collected by a streak camera detector set up in such a way that time is projected along one axis and space along the other axis. The emission profile was then fit to a gaussian curve, and the variance of the curve was calculated and plotted as a function of time. The change in the square of the variance as a function of time is proportional to the diffusivity (Eq. B.3).

$$\text{Eq. B.3} \quad D(t) = \frac{\Delta(\sigma^2)}{\Delta t} = A * \alpha * t^{\alpha-1}$$

Where $D(t)$ is diffusivity as a function of time, σ is the variance of the gaussian fit, A is a proportionality constant, and α is the diffusion exponent. The slope of the linear fit Shown in Fig.

B.7 is $0.573 \pm 0.026 \text{ cm}^2 \text{ s}^{-1}$. This diffusion value is consistent with the value reported in literature for OA-OAm capped nanoparticles FRET exciton transport¹⁸⁹. Unfortunately the novel PNP-ligand complexes did not display adequate fluorescence in solid state assemblies to perform the same method.

The energetics of CsPbBr₃ and the ligand can be compared in Fig. B.5. The alignment of the PNP VBM with CA's HOMO indicates that exciton delocalization is possible but excited state hole transfer to CA is very likely. As a known hole acceptor, CA could accept the excited hole from PNP's VBM²¹⁵, but energetics also indicate possible electron transfer from CA to the PNP upon ligand excitation. We will pursue further TCSPC studies of the OAm-CA PNPs, in t-Butyl alcohol since a small fluorescence peak was preserved after ligand exchange. Rapid quenching was also observed in CdSe quantum dots though exchange with hole accepting ligands, but fluorescence was still observed by TCSPC²⁰¹, and CdTe fluorescence quenching has been reported utilizing caffeic acid¹⁹⁶. The results of our work with CA are encouraging, showing that exchange is possible and the effects on PNPs are significant, but the work also highlights some of the experimental challenges that we there are to overcome.

B.7 Conclusions

The goal of this research is to improve the versatility of PNPs by increasing interparticle coupling through surface modification with aromatic ligands. We chose ligands with HOMO energy that are increasingly electron donating but have relatively close alignment with the VB of CsPbBr₃ PNP. The ligands also had varying HOMO-LUMO gaps that range from slightly smaller to slightly larger than the band gap of the QDs. In this way we intended to test whether these

energetic properties encourage exciton delocalization, or charge transfer and how that affects excited state transport.

We have synthesized CsPbBr₃ PNPs and characterization measurements verify successful production of QDs with tunable size²⁰². Successful ligand exchange with our first ligand, CA, was evidenced by irreversible optical changes including extensive fluorescence quenching. It is suspected that CA induces charge separation by accepting a hole from the PNP, but further investigation is required to deconvolute solvent effect from the effects of ligand exchange. Ligand exchange with PGR and 6-FAM, was attempted and though the energetics of PGR and 6-FAM will be less likely to encourage charge separation the bulky steric nature of the chromophores may have prevented displacement of the aliphatic ligands in the brush.

Further work in this research will focus on effects of the direct synthesis route published by Vickers et. al¹⁶⁶ where aromatic passivating ligands are directly incorporated into the ligand brush. The effect of these aromatic ligands could be examined through TCSPC and pump-probe measurements to establish the effects of delocalization in a proven system before moving on to more experimental synthetic work. Ultimately this research proved the efficacy of spectroscopic characterization techniques in the quantification and examination of ligand exchange effects but was hindered by complications in synthetic outcomes.

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