Photostabilization of J-aggregate Cyanine Dyes for Exciton-Polariton Based Devices

by

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Photostabilization of J-aggregate Cyanine Dyes for
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Abstract

Organic molecules are becoming a commonly used material in strongly coupled systems as they possess large exciton binding energies and huge oscillator strengths that have allowed for the creation of room temperature polariton condensates, superfluids, and other exotic phenomena. Using J-aggregates, the aggregated form of cyanine organic dyes, we have previously fabricated light-emitting devices that demonstrated the first ever electrically pumped polariton emission, as well as critically coupled resonators with record high effective absorption constants. Although there are many promising applications for organic exciton-polariton devices, state-of-the-art devices suffer from rapid photodegradation at higher photon densities, which presently limits their eventual implementation into a viable technology.

To achieve stable devices, we need to isolate the causes of photodegradation. Specifically, we studied the photoluminescence stability of J-aggregate thin films under different atmospheric conditions. Our results indicated that J-aggregates maintain both better emission and stability in high humidity environments in comparison to oxygen-rich atmospheres. Furthermore, we show an order of magnitude improvement in the photostability via encapsulation of the film with a hygroscopic sugar encapsulant. These results are highly promising and suggest future pathways for the realization of functional and stable polariton-based devices which we will explore in this thesis.

Thesis Supervisor: Vladimir Bulović
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Chapter 1

Introduction

The goal of this thesis is to demonstrate stabilized excitonic materials suitable for the application of new optoelectronic devices that use coupled states between Frenkel excitonic resonances and microcavity confined photons. These strongly coupled states are referred to as exciton-polaritons. These quasiparticles have attracted waves of scientists from condensed matter physics and device physics fields because of their unique hybrid light/matter states. The matter component gives polaritons its intrinsic nonlinearities while the photon component gives it a very light effective mass. The physics community have studied polaritons for its fascinating effects including but not limited to: polariton lasing and condensation [1], superfluidity [2, 5], quantum vortices [13, 8], large TE-TM splitting [16, 33, 17], long-range spacial coherence [10], magnetic monopole analogues [14], and more. In 2005, our group was the first to demonstrate emissive electrically pumped exciton-polariton devices [30] and have since motivated interest in room-temperature polariton devices through exploration of new materials. Only recently have strong coupling [31], polariton condensation [20, 15] and superfluidity [9] been shown at room temperature. This has opened up opportunities for possible functional polaritonic devices such as single-photon switches [7], electrical spin-switches [6], all-optical logics [23] and control of chemical reactivity [19].
1.1 Exciton-Polariton Based Devices

Quantum electrodynamics (QED) is the quantum mechanical description of atom-vacuum interactions in cavities. This thesis studies the exchange in energy between Frenkel excitons and confined photos. Strong coupling regime is achieved if this rate of energy exchange is much greater than the rate that energy escapes the system through photons leaving the cavity or the matter wave function losing its phase information [27, 21]. In this limit, the microcavity and matter component form a composite quantum system with two new eigenstates that are superpositions of the initially uncoupled states.

Polaritons are especially interesting to study as it exhibits both qualities of light and matter. They behave as bosons with low in-plane effective mass from part-photon characteristics and can also be interacting from the nonlinear exciton components. The photon and exciton fractions can be easily tuned by the detuning of the cavity resonance around the excitonic resonance. This is done by changing the resonant modes of the cavity through wedged cavity structures [26] or angle resolved measurements. Cavity polaritons have the advantage over polaritons in bulk materials as the exciton-polariton properties can be easily optically probed by utilizing leaked photons from the cavity.

1.2 Motivation for J-aggregates

Realization of polariton lasing and condensation in solid state systems are limited to the exciton binding energy of materials. For most inorganics, this would mean cryogenic temperatures in addition to the inherent sophistication of epitaxial techniques. Organics on the other hand allow for much larger exciton binding energies to realize polariton emission and condensation at room-temperature with easily scalable manufacturing techniques. Nevertheless, photodegradation is common in organics and light exposure causes decays of absorption and photoluminescence of the material over time. In this part of the project we recognize the importance of the dye molecule
and its self assembled form of J-aggregates in the field of strong coupling of light and matter, and address systematically the photobleaching of the molecular assemblies to achieve photostability in the films.

![Chemical structure of an archetypical J-Aggregate forming C2S4 molecule.](image)

Our approach to developing these devices involves excitons in nanoscale thin films of J-aggregated molecules from a class of cyanine-based dyes. A distinct advantage in utilizing photo-active J-aggregates films in these devices is their facile solution processing for low cost, large-scale manufacturing. In turn, we avoid many complex deposition techniques such as epitaxial growth or labor intensive "flake hunting" required for transition metal dichalcogenides and other two-dimensional materials. Figure 1-1 shows the chemical structure of the dye molecule used in this thesis: 5,6-Dichloro-2-[[5,6-dichloro-1-ethyl-3-(4-sulfobutyl)-benzimidazol-2-ylidene[propenyl]-1-ethyl-3-(4-sulfobutyl)-benzimidazolium hydroxide, inner salt, sodium salt molecule, colloquially known as C2S4, that we have deployed for our study, as well as its absorption and emission spectra. J-aggregates are molecules that undergo supramolecular self-organization into structures in which the transition dipole moments of each molecule are aligned head to tail, along the molecular polymethine backbones. Coherent coupling between neighboring molecules due to interference of their transition dipole moments leads to delocalized excitonic states associated with H- and J-aggregation. J-aggregation is associated with the lower energy excited state, and is optically active. These J-aggregates enable strong light-matter interaction at room temperature due to their large exciton binding energies, huge oscillator strength, small Stokes shift, and narrow linewidth shown in Figure 1-2.
Figure 1-2: Absorption and emission spectra of the J-Aggregates studied in this report, demonstrating the narrow linewidth and small Stokes shift of the aggregated molecules.

Using J-aggregates, we have previously fabricated light-emitting devices that demonstrated the first ever electrically pumped polariton emission [30], as well as critically coupled resonators with record high effective absorption constants of $6.8 \times 10^6 \text{cm}^{-1}$ [29]. Although there are several promising applications in integrated exciton-polariton devices, state-of-the-art devices suffer from rapid photodegradation at higher photon densities, which presently limits their eventual implementation into a viable technology. Therefore, our primary objective has been extending the life of J-aggregate molecular films under experimental conditions.

Film instability may result from several different origins, including the photooxidative degradation of the J-aggregates through chain scission, crosslinking, and oxidative reactions initiated through radical processes [32]. To further understand these degradation mechanisms, we study both the impact of solution processing on J-aggregate
film formation and probe the effect of different environments on J-aggregate thin film stability. Through our findings, we can begin to rationalize the operational stability of J-aggregates in working optoelectronic devices and started to explore encapsulation methods to effectively prevent the photodegradation process from manifesting.
Chapter 2

Exciton-Polaritons

2.1 Review of Quantum Electrodynamics

Quantum electrodynamics (QED) is the quantum mechanical description of atom-vacuum interactions in cavities. In free space, spontaneous emission in the simplest case refers to the emission of a photon due an initially excited energy state transitioning to a lower energy state separated by the energy interval $E_e = E_f = \hbar \omega$. This emission is not an intrinsic property of matter but rather the coupling with the electromagnetic field in its vacuum state, whereby altering the vacuum electromagnetic field can affect spontaneous emission of these excitations. One example of this is when excited states are localized in a cavity where it is designed so that the cavity length ($L$), where when $L$ is on the order of magnitude of the wavelength, there cannot be a mode such that $\lambda/2 > L$ such that this becomes the lowest-order mode cut off. The cavity allows for control of spontaneous emission of excited states and facilitates the study of the regime of cavity QED. A resonant cavity allows for enhancement of vacuum fluctuations and the interaction can be described by the Rabi frequency ($\Omega$) of the vacuum, which is the frequency at which the atom and the field would exchange energy if there were only a single mode of the field. The physics explained in this chapter is all review derived 20 years ago so this chapter is in no means new physics. For comprehensive review of this field please refer to M. S. Skolnick (1998) et al [27]. The excited states studied in this thesis are quantum systems of excitons in molecules.
2.2 Design of Semiconductor Microcavities

A semiconductor microcavity is made of three different components: the emissive semiconductor material, the cavity, and two highly reflective mirrors on either side of the cavity to confine light. The characteristic transmission through a resonator cavity exhibits sharp resonances, with the only allowed modes inside the cavity resonating with the cavity modes.

Photon inside the cavity are quantized perpendicular to the plane of the cavity, whereas in-plane photon states remain unaffected by the confinement of the cavity[27]. Therefore, cavity photon dispersion is modified from that of the linear dispersion relation in free space. To design cavity to a specific cavity mode (\( \lambda \)), the optical cavity length must be an integer multiple of the half the wavelength in the cavity medium (\( L_{\text{cav}} = \frac{n\lambda}{2n} \)). In this thesis, the cavity resonance is design to be on or with negative detuning with exciton emission resonance in order to achieve anti-crossing of energy levels.

Confining the cavity on either sides are the highly reflective distributed Bragg reflectivity (DBR) mirrors. Theses mirrors act as stop band high reflectivity optical filters where it is highly reflective across a band of wavelengths centered around \( \lambda_{\text{center}} \). The design consist of alternating high and low refractive index dielectric layers of thickness \( \frac{\lambda_{\text{center}}}{4n} \). The reflectivity at the center frequency is given by

\[
R = 1 - 4 \frac{n_{\text{air}}}{n_{\text{cav}}} \left( \frac{n_L}{n_H} \right)^{2N}
\]  

(2.1)

where \( n_{\text{air}}, n_{\text{cav}}, n_L \) and \( n_H \) are the index of refraction for air, the cavity medium, the low and high index layers respectively, and \( N \) represents the number of pairs of the alternating layers. For outside the stop band, the reflection and transmission for
the entire spectrum, optical interference and absorption in multilayer stacks need to be calculated. Standard transfer matrix method, where transmission and reflection are calculated for each interface in the stack as well as attenuation in each layer, can be used to simulate the reflection and transmission shown in Figure 2-1.

Figure 2-1: (left) DBR consisting of SiO₂ and TiO₂ as the low and high index materials respectively with thickness of the layer designed for the center wavelength $\lambda = 588$ nm. (right) Simulation of the reflectance and the transmittance of the DBR.

The combination of a cavity sandwiched between two DBR’s results in a high quality factor (high-Q) microcavity, and is very similar to a simple planar fabry-perot with the similar derivation for cavity linewidth ($\kappa$) for $R \to 1$ but with an increased effective cavity length ($L_{\text{eff}}$) given by

$$L_{\text{eff}} = L_{\text{cav}} + \frac{\lambda_{\text{cav}}}{2n_{\text{cav}}} \frac{n_L n_H}{n_H - n_L}$$  \hspace{1cm} (2.2)

$$\hbar \kappa = \frac{\hbar c (1 - R)}{n_{\text{cav}} L_{\text{eff}}}$$  \hspace{1cm} (2.3)

where the $\lambda_{\text{cav}}$ is is the wavelength of light inside the cavity. From the above parameters we can derive the photon dispersion inside a cavity, given that the wavevectors inside the cavity can be split into the perpendicular and the in-plane components($k^2 = $
\( \tilde{k}_\perp + \tilde{k}_\parallel \) where \( \tilde{k}_\perp \) is the perpendicular wavevector that is confined by the cavity mode given by \( \tilde{k}_\perp = \frac{2\pi}{\lambda_{\text{cav}}} \).

\[
E_c(\tilde{k}_\parallel) = \frac{\hbar c}{n_{\text{cav}}} \sqrt{k^2_\perp + k^2_\parallel} = E_0 \sqrt{1 + \left( \frac{\hbar c}{E_0 n_{\text{cav}} k_\parallel} \right)^2}
\] (2.4)

where \( E_0 = E_c(\theta = 0) = \frac{\hbar c}{n_{\text{cav}} \lambda_{\text{cav}}} \) is the photon energy when in-pane wavevector is 0. At small \( \tilde{k}_\parallel \), using Taylor series expansion, the dispersion is parabolic and can be described by a very small effective mass \( M_{\text{eff}} = \frac{\hbar n_{\text{cav}}}{c \lambda_{\text{cav}}} \). Now we can plug in the relation between wavevector and the external angle \( \tilde{k}_\parallel = \frac{E(k)}{\hbar c} \sin \theta \) into Eq. 2.4 to give the angle dependent cavity photon dispersion relation [27] given by

\[
E_c(\theta) = E_0 \left( 1 - \frac{\sin^2 \theta}{n_{\text{eff}}^2} \right)^{-\frac{1}{2}}
\] (2.5)

This cavity photon dispersion relation cavity mode energy \( E_c \) can be tuned by varying the external angle of incidence. This has the important implication that without having to changing cavity length, the interaction of the exciton with cavity photon can be tuned.

### 2.3 Microcavity Exciton-Polaritons

Now that we have treated the optical properties of the empty cavity, we can now move on to understanding the same microcavity structure with excitonic materials placed at the antinode of the cavity for maximum field intensity. For this structure, it is important to understand the coupling between the cavity mode and the excitonic states. This thesis is interested in studying the strongly coupled regime which is the limit where the exchange of energy between matter and light (the Rabi splitting) is significantly greater than the decay rate due to light escaping the cavity and matter loosing polarization (cavity and exciton linewidths: \( \kappa \) and \( \gamma \)). The new eigenstates of the coupled system in the strong coupling regime are called polariton modes or branches.
Experimentally, we can directly collect polariton dispersion curves through reflectivity and photoluminescence measurements from leaked photons from the cavity. The strong coupling limit of a single photon mode and a single exciton mode manifests itself in the reflectivity spectra in the form of two dips representing the two new eigenstates from the coupling. The splitting at the anticrossing is vacuum Rabi splitting (analogy with atom-cavity coupling in atomic physics) which can be controlled by cavity and exciton properties.

The system can be modeled as the coupling of a two level system (exciton) to a harmonic oscillator (photon) and quantum mechanically described by a combined Hamiltonian in the second quantization notation:

\[
H = H_c + H_e + H_{int} \\
= \sum E_c(k)\hat{a}_{k\parallel}^\dagger \hat{a}_{k\parallel} + \sum E_e\hat{b}^\dagger \hat{b} + \sum \hbar g_0(\hat{a}_{k\parallel}^\dagger \hat{b} + \hat{b}^\dagger \hat{a}_{k\parallel})
\]

In Eq. 2.7, \(E_c(k)\) and \(E_e\) are the uncoupled cavity and exciton eigenstates respectively. Notice for simplicity, the exciton eigenstate is assumed not a function of wave-vector \(k\) because compared to the cavity photon, it has a much larger effective mass therefore the curvature of the exciton dispersion would be small enough to be approximated as zero; this shows up in Figure 2-2 as a straight line. \(\hat{a}^\dagger\) and \(\hat{a}\) are the creation and annihilation operators in-plane photons in the cavity, where as \(\hat{b}^\dagger\) and \(\hat{b}\) are the creation and annihilation operators for exciton. The last term is the interaction term with \(g_o\) as the interaction rate given by

\[
g_0 = \sqrt{\frac{N\mu^2E_c}{2\hbar^2\epsilon_0V_m}}
\]

where \(N\) is number of dipoles, \(\mu\) is the transition dipole moment and \(V_m\) is the mode volume of the cavity. We can see that an increase in dipole volume density \(\left(\frac{N}{V_m}\right)\) would increase the interaction rate \(g_0\). The interaction rate is the rate of the
exchange in energy between the exciton and photon where the time it takes for one full cycle of exciton and photon energy exchange is \( \frac{2\pi}{\gamma} \).

New eigenstates can be derived from diagonalizing the Hamiltonian in Eq. 2.7 with the following eigenvalues in terms of the uncoupled exciton and photon energy levels \( E_e \) and \( E_c \)

\[
E_{\pm} = \frac{E_e + E_c}{2} \pm \frac{1}{2} \sqrt{(\hbar \Omega)^2 + (E_e - E_c)^2} \\
E_{\pm} = \frac{E_e + E_c}{2} \pm \frac{1}{2} \sqrt{(\hbar \Omega)^2 + \Delta^2}
\]

In the semiclassical regime [3], the vacuum Rabi coupling frequency has an upper-limit of twice the strength of the exciton-photon interaction and can be smaller due to broadening \((\Omega = \sqrt{4g_0^2 - (\gamma - \kappa)^2})\). Eq. 2.10 represent the energy levels of the polaritons, more specifically in this case the upper polariton branch (UPB) and the lower polariton branch (LPB). Figure 2-2 shows the calculated polariton dispersion for a sample semiconductor microcavity with a slight cavity detuning \( \Delta \) defined by the difference in energy between the cavity resonance and the exciton resonance at \( k=0 \) (\( \theta = 0 \)) controlled by tuning the cavity length since the exciton resonance is constant due to material of choice. In this specific cavity simulation example, the detuning of the cavity is \( \Delta = 50\text{meV} \) from exciton resonance at \( k=0 \). The uncoupled cavity mode reaching resonance with the exciton mode towards 20°. Beyond 20°, the system moves once again away from resonance.

Contribution to the polariton branches from the uncoupled exciton or photon eigenstates can be expressed by the exciton and photon fractions \((X(\theta) \text{ and } C(\theta)) \) given by

\[
|X(\theta)|^2 = \frac{1}{2} \left( 1 + \frac{\Delta E(\theta)}{\sqrt{\Delta E(\theta)^2 + 4g_0^2}} \right), \quad |C(\theta)|^2 = \frac{1}{2} \left( 1 - \frac{\Delta E(\theta)}{\sqrt{\Delta E(\theta)^2 + 4g_0^2}} \right)
\]

(2.11)
Figure 2-2: Calculated polariton dispersion of up to $40^\circ$ from perpendicular to the sample cavity. The uncoupled excitonic (dashed) and cavity (solid) dispersions are shown in black. The new coupled eigenstates are shown as dots with the lower polariton branch (LPB) in blue and upper polariton branch (UPB) in red. At high angles, the UPB is more photon like and the LPB is more massive and exciton like.
where $\Delta E(\theta)$ is the energy difference between the uncoupled excitonic and photonic states.

Chapter 4 will go into detail the experimental results of strong coupling experiments inside of organic semiconductor microcavities. Traditionally experimental data of the dispersion of the polariton modes was collected using angle tuning experiments (Houdre Weisbuch stanley phys rev lett 1994). In this thesis, a k-space imaging (Appendix D) setup is used that allows for direct wide angle imaging of the polariton dispersion.
Chapter 3

Stability of Aggregates

This chapter first motivates films of J-aggregates of cyanine dyes as key to realizing polariton devices at room temperature, given the rich exciton dynamics. The rabi-splitting of organic materials due to Frenkel excitons typically can be from 0.1-1 eV, compared to that of inorganics of 0.003-0.1 eV due to Wannier-Mott excitons [25]. Specifically for the excitonic material studied in this thesis, the large rabi-splitting is due to the inherently large optical transition dipole of C2S4 as a monomer and enhanced oscillator strength derived from J-aggregated molecules. This section also addresses the process of aggregation of the molecule in solution, the photochemistry of the dye molecule and aggregates, and solution processed deposition of nano-scale controlled thin films.

The second half of the chapter addresses the degradation processes of the material is solution and solid state. Stability of the solution addresses the need for solution to remain in steady state during one deposition and potentially allowing for recycling of materials for multiple depositions, allowing for scalability of solution processing. Stability of the solid state thin films is key to achieve reproducible experiments for the realization of polariton devices at room temperature.
3.1 Motivation of J-aggregates of Cyanine Dyes

C2S4 is the cyanine dye molecule used as the J-aggregating material in this thesis and the chemical structure is shown in Figure 1-1. Even as a monomer, the molecule has a relatively narrow absorption band which corresponds to an already large optical transition dipole. Upon reaching ultralow concentrations of $10^{-5}M$ in water, the molecules can already readily form aggregates. At specific orientations, the molecule can couple so that the transition dipole moment of the aggregate is enhanced from that of the monomer, allowing for strengthened strong coupling to light in the light-matter interaction experiments. Additionally, intensive study has been done to reproducibly produce self-assembled films of J-aggregates using solution processing first explored in 1998 [18]. These films, with a slightly have since then been the first to demonstrate electrically pumped excitonic polariton device [30].

3.1.1 Photochemistry of Dye Molecules

The C2S4 cyanine dye is a molecule that processes high oscillator strength, high absorption coefficient and allows for these molecules, even as monomers, to interact even strongly with cavity photons even at room temperature for our strong coupling experiments.

![Figure 3-1: Transition dipole moment is in the direction of the polymethine and interacts most strongly with light polarized parallel to this direction.](image)

The monomer molecule is highly polar thus having a large transition dipole. This rod-like organic salt has a lumophore that consists of a conjugated poly-methine...
bridge subtended by two highly polar nitrogen rich end-groups. The positive Nitrogen end is electron deficient and electron accepting whereas the uncharged Nitrogen group is electron rich and electron donating. The polymethine bridge acts as a one-dimensional optical dipole antenna and the transition dipole moment points in the direction of the polymethine and interacts most strongly with with light polarized parallel to this direction.

3.1.2 Photochemistry of Aggregates

Although the cyanine dyes are fluorescent even as a monomer, the absorption and fluorescence spectra of the aggregated form of the molecules can be narrowed and shifted significantly. When monomers closely assemble and align, coherently coupling of the transition dipoles of the molecules can be achieved, resulting in a mixing of the excited states of the uncoupled molecules. This interaction between the two dipoles is very orientation dependent so that only at specific angles, where the uncharged Nitrogen groups of one molecule overlaps with the positively charged Nitrogen groups of the other molecule, can the transition dipole moments be enhanced by a factor proportional to the square root of the number of coherently coupled molecules \( N \). This specific orientation of the overlap of the dipoles is referred to as J-aggregation.

Based on known crystal structures, the energy levels of the aggregates can be calculated with the application of Kuhn’s model for a two-dimensional crystal. Point dipole approximation can be used to present transition dipole moments of two arbitrarily oriented molecules. The exchange matrix elements are calculated by summing the Coulomb interactions of the charges. The extended dipole model [22] gives insight to the energy spectrum of crystals where energy difference relative to the monomer transition energy can be found as a function of the orientation of the molecules on one unit cell. This analysis allows for the understanding of J- and H-aggregates, also known as head-to-tail/brickstone and card-staking arrangements respectively, two distinct orientations shown in Figure. 3-2 out of the many possible arrangements. The energy bands and the absorption and fluorescence spectra of the monomer and
aggregates are significantly changed due to the coupling of the electronic transition dipole moments of the molecules. The J- and H-aggregates show red and blue shifted absorption bands from the monomeric absorption, respectively due to this shift in their energy band.

![Figure 3-2: J- and H-aggregates](image)

Specifically for the J-aggregate configuration, the absorption spectrum is not only redshifted but also narrowed due to the coupling of the oscillator strength. In the approximation for large $N$ of participating J-aggregated molecules, the oscillator strength $\mu$ can be calculated based on tight-binding model [28] and is given by

$$\mu^2 \approx 0.81(N + 1)\mu_0^2$$  \hspace{1cm} (3.1)

where $\mu_0$ is the transition dipole of a monomer.

Aggregation of dye molecules was highly dependent on dye concentration and solvent. Specifically in water, the molecule readily forms J-aggregates at ultra low concentrations of $\leq 10^{-5}$ M. In the past, it was believed that raising pH of dye growth solution also promotes J-aggregation [28]. However, absorption measurements show that despite having different pH’s, as long as the ionic strength of the solution is kept constant, the absorption spectrum can be can be the same. In fact, adjusting the pH of the solution produced better films not because of a change in aggregation in the
solution, but and improvement in the deposition process discussed in 3.1.3

In the past, solutions of J-aggregates used for dip-coating were adjusted to pH=9 with sodium hydroxide. However, this solution was found to be non-reusable, meaning over time the solution is not stable. This is a big problem for us as the depositions require up to 500 mL of solution and a lot of solution is wasted if it needs to be disposed of after each dip-coating run. Figure 3-3 shows that the pH=9 solution used in [29] does not seem to be in aggregate stability. The goal is to achieve a stabilized aggregated solution to be used and reused for the deposition of the films.

![Figure 3-3](image)

Figure 3-3: Over a period of 8 hours, the pH (dashed) of the recipe used previously for J-aggregate deposition decreases from 9.5 to below 8.5. The particle size of the aggregates were also monitored (solid), and is also unstable, increasing from 180 nm to around 230 nm. This suggests instability of the solution used for dip-coating, especially through the typical duration of a dip-coating run (Appendix A) of around 2 hours.
3.1.3 Thin Films

Reproducible high quality films are deposited through the dip-coating technique where monolayers are deposited with nanometer-scale thickness control. This control if deposition is extremely important for coherent strong coupling as it requires that the molecules J-aggregates and assemble as single crystal with translational symmetry.

The technique used to deposit J-aggregate thin films in this thesis is layer-by-layer (LBL) deposition, first reported by Fukumoto and Yonezawa [18], where monolayers of cationic polyelectrolyte and monolayers of the cyanine dye (with anionic lumophores) can be sequentially deposited on a crystalline substrate to make the J-aggregate thin films. We opted to use layer-by-layer deposition because of its ability to create highly uniform macroscopic films with sub-nanometer surface roughness and because it offers sub-nanometer thickness control. We deposited J-aggregate films by sequential immersions of a charged substrate into aqueous cationic and anionic solutions containing polydiallyldimethylammonium chloride (PDAC) and J-aggregate forming cyanine dyes, respectively. By reversing the sign of the charged species in solution, we deposited single molecular layers onto our substrate via Coulomb attraction. This dip-coating technique can be found in detail in Appendix A.

Deposition of weak J aggregates polyelectrolytes is highly dependent on the pH of the aqueous solution. The weak dissociation constant renders a fractional charge rather than all J-aggregates being full charged in solution. In order to better facilitate interaction of the negatively charged J-aggregate sulfonate moieties with the PDAC polycations, the pH of the solution is made alkaline to prevent protonation of these anchoring groups. Changes were made to the conventional dip-coating method used previously by using buffers for the J-aggregate solution (Chapter 3.2.2) and improving the sample holder, which was previously designed for microscope slide sized sample, to hold up to 10 half inch samples per deposition. Additionally, a new encapsulation layer is explored (Chapter 3.2.1) for the photo-stability of the J-aggregate film. This
extra step involves a saturated solution of 50:50 trehalose:sucrose sugar matrix that is deposited as the last step on top of the J-aggregate film, then dried off with compressed nitrogen.

The optical properties of the J-aggregate films are characterized in comparison to the J-aggregates in solution to show that we indeed have deposited J-aggregates on our films. And indeed the absorption spectrum of solution and film do match, as we would expect. The morphology of the J-aggregate films are characterized using Atomic Force Microscope (AFM) and both bare and encapsulated films show very low roughness.

Figure 3-4: Absorption measurements using Cary UV-Vis using cuvette (solution) and thin film configurations. Film aggregates only slightly redshifted around 3 nm which is likely due to thin film packing, where intermolecular forces change the conformation of the molecules thus energetics of the transitions. The two figures present the same set of data with the raw absorbance (left) and normalized absorbance (right). From the raw absorbance data, we can see the peak absorption peak for the monomers (black) is a lot weaker and blue-shifted the J-aggregates, which conforms to theory presented in Chapter 3.1.2. The aggregates in pH=9 buffer (blue) also show a lower absorption coefficient than the aggregates in water (green) because the ionic strength of the solution changed. If the ionic strength of the solutions were matched the J-aggregates in the two solutions should have the same absorption, despite having different pH’s. The absorption spectrum for the J-aggregate films (red) and films with encapsulation (magneta) show very similar distinctive narrow band absorption spectrum as the aggregates in solution.
3.2 Stability

3.2.1 Colloidal Stability in Solution

During deposition, the stability of the colloidal solution is of high importance as the formation of J-aggregates is a nanoscale process and is extremely sensitive to its environmental conditions, such as the intermolecular forces from Coulomb interactions between charged species and Van der Waals forces due to induced dipoles. Consequently, the charge and deposition of the weak J-aggregate polyelectrolytes is highly dependent on pH of the solvent. Typically, the anionicity of the J-aggregate solution is controlled by dissolving the molecules in an alkaline solution of NaOH with a pH greater than 9.0. Surprisingly, we recently found that under ambient conditions, the solution pH decreases as a function of time (Figure 3-6) and over the course of the deposition, indicating acidification of the solution which reduces the interaction of the aggregates with the positively charged PDAC molecules. In order to counter this effect, Figures 2 shows the stabilization of the pH through the utilization of a borate buffer solution, which resists changes in pH. We are now further investigating the role
of the buffer solution in film formation and stability as the supramolecular chemistry is dependent on the presence of ionic species in solution.

Figure 3-6: pH of J-aggregate solutions as a function of time. The red trace shows the pH of J-aggregates suspended in a basic solution of NaOH, which steadily decreases over the course of 300 minutes. The black trace shows the stabilization of the pH through utilization of a borate buffer solution.

When the buffer concentration is too high, it seems to affect the aggregation of the molecules at the same C2S4 molecule concentration. This is shown by looking at the absorption spectrum of the molecules in solution suspended in water, and in different concentrations of the buffer. We see that if the concentration is high, the absorption peak is redshifted and broader. However at lower buffer concentrations, we reach a point where pH can be maintained and the aggregation of the molecules can be preserved and controlled to be the same as if it were in water shown in Figure 3-7.

The ability to deposit films with reproducible aggregation, composition, uniformity, and thickness is not only critical for systematically studying the film stability, but it is essential for reliable fabrication of high-quality polaritonic devices. By creating buffered solutions of J-aggregates that maintain their pH, we have demonstrated steady progress toward achieving these goals.
3.2.2 Photostability in Film

Preliminary experiments yielded early insights into the formation and long term air stability of J-aggregates embedded in a sugar matrix. For at the time, unknown reasons, the stability of the absorption peak of drop-casted J-aggregate films was improved by over 50 fold with a sugar encapsulation layer as shown in Figure 3-8. The results from our early experiments suggest that the sugar matrix is preventing degradation of the J-aggregate molecules. We observe the absorption as a function of time for J-aggregate molecular films, for the J-aggregate films with sugar encapsulation, we see a long term stability that is not seen in the bare J-aggregate films.

To answer why the sugar seems to increase photostability in films, to design the optimized encapsulant for the film and to isolate the potential mechanisms facilitating photodegradation, further studies of photostability measurements of the J-aggregate films in different atmospheres need to be conducted. Specifically, we probed the room-temperature fluorescence stability of the films in ambient air, nitrogen, oxygen, vacuum, and high humidity under constant laser illumination. We investigated the
Figure 3-8: (a) Absorption and emission spectrum of dropcasted J-aggregate films with sugar encapsulant; (b) The stability of peak absorption of the J-aggregate films and the sugar (50:50 trehalose:sucrose sugar matrix) encapsulated films over time in air.

time evolution of the J-aggregate films for up to 30 minutes or until ultimate photobleaching of the sample as shown in Figure 3-9b, signaled by depletion of emission signal to noise. We excite the film with 533 nm pulsed laser with an energy density of 24μJ/cm² and the photoluminescence (PL) is imaged on a CCD spectrometer.

Figure 3-9: (a) Size of laser beam (533 nm, 24μJ/cm²) in comparison to TEM grid; (b) Ultimate photobleaching of film beyond sample damage threshold causing defect.
The position of the PL maxima, the integrated intensity and the full width at half-maximum (FWHM) of the emission were determined by fitting the temporally resolved spectra to a Voigtian function, accounting for the intrinsic and doppler broadening of the emission shown in Figure 3-10.

![Figure 3-10: Example PL Spectrum for one sample at one time with the corresponding Voigtian fit.](image)

We monitored the time evolution of the room-temperature emission spectra of the J-aggregate films until the emission signal nearly reached a steady-state value. The integrated emission intensity and position of the fluorescence maximum were determined by fitting the temporally-resolved spectra to a Voigt function, accounting for homogeneous and inhomogeneous broadening. Figure 3-11 shows the normalized integrated intensity in each atmosphere as well as the evolution of center emission energy as a function of time. We observed a more rapid decay in PL from samples exposed to pure oxygen compared to those exposed to atmospheric conditions, which suggests that oxygen plays a significant role in the photodegradation process. Our results from conducting cyclic voltammetry (CV) on C2S4 molecules in a range of electrolytes, we indeed observe such irreversible oxidation. Our result corroborates the results of a similar study, which attributed photodegradation of J-aggregates in
solution to an irreversible oxidation and dimerization of cyanine molecules [24].

![Graph](image)

**Figure 3-11:** (Left) Normalized integrated PL intensity of the J-aggregates in time in different environments with data points and their respective biexponential fits. (Right) Emission energy as a function of time for different environments with their data point and fits.

We also see that in all environmental conditions, some degree of degradation occurs, signified by a decay in PL intensity over time. The blueshift in PL spectrum, also seen in all environmental conditions, similarly suggests a photodegradation mechanism. Curiously, the film measured in the high humidity environment demonstrated not only the smallest reduction in emission intensity, but also the slowest emission decay, suggesting that water molecules could potentially help stabilize J-aggregates in solid-state films. Based on these findings, we next seek to rationally engineer a method of encapsulation to prevent further photodegradation of the films. Overall the most effective encapsulant would be one that prevents oxygen from reaching the J-aggregates, but is able to retain moisture on the sample.

In this regard, we explored a hygroscopic sugar matrix, which may prevent oxygen diffusion. Previous studies have specifically utilized a 50:50 trehalose:sucrose sugar matrix to realize long term air stability of a different set of J-aggregates [11].
enhanced stability was attributed to the encapsulation of the J-aggregates in a solid sugar matrix. To investigate whether this method also applies to our structures, we deposited films of J-aggregate molecules and encapsulated one sample in a sugar matrix, while leaving the other exposed to ambient conditions.

Figure 3-12 shows the normalized integrated photoluminescence (PL) intensity as a function of time from films with and without sugar encapsulation. Under continuous laser illumination, we observed a five-fold increase in the photostability lifetime of encapsulated films over the bare films. We find that the PL intensity is best fit by a biexponential decay, which suggests that there are possibly two separate photodegradation mechanisms. Interestingly, the longer lifetime component of the bare film trace matches the shorter lifetime component of the encapsulated film trace, suggesting a possible shared degradation pathway that is not affected by the encapsulant.

Based on our environmental study that suggested water molecules may act a stabilizing agent for J-aggregate films, we took a thermogravimetric analysis (TGA) of the encapsulated films and discovered that indeed water was present. Sugar is well known to be a hygroscopic material, and one of our hypotheses is that by trapping water in these films, it is stabilizing them against photodegradation; however, further investigation is required to confirm this theory. Additional steps will be taken to assess other forms of encapsulation as well as the potential of different molecules in slowing the photooxidation process through radical scavengers, hydroperoxide decomposers, and antioxidants.
Figure 3-12: (a) Normalized integrated PL intensity of J-aggregate thin films in air as a function of time. The decay of the molecules are depicted for the bare films (blue) and encapsulated films (red) and their biexponential fits are shown. (Right) Lifetimes of the biexponential fits of the normalized PL intensity curves. The two films seem to have one common lifetime component and the second component is much longer for the encapsulated films.
Chapter 4

Polaritons in J-Cavity

This chapter displays the experimental results and discussion of the work done so far in strong coupling of excitons and cavity photons in J-aggregate microcavity (J-cavity). Exciton-polariton are studied in low-Q cavities. These semitransparent metallic cavity are easily fabricated and sufficient device structure to show the promise of polaritonic devices in organic structures at room temperature. These cavities have one highly reflective metallic mirror on one side and a thin semi-transparent layer on the other side to allow light into the cavity. Further work is explored to improve fabrication of J-cavity with high-Q cavities.

4.1 Semitransparent Metallic Cavity

4.1.1 Cavity Characterization

The empty cavity can be grown bottom up on glass all in the thermal evaporator and the sputterer. The device structure is shown in Figure C-1 and the fabrication process is detailed in (Appendix B). The optical spacer layer for the empty cavity is silicon oxide, and the thickness of this layer determines the cavity length hence the cavity modes. The disadvantage of metallic mirrors is that it is broadband reflective which means when used as the material for the mirrors of a microcavity, one of the mirrors need to be decreased in thickness so that it can become semitransparent to
allow pump photons in. Therefore on one side of the cavity is a thin layer of silver and at 16 nm, the transmission through this silver layer is around 50% so that 50% of light can enter the cavity and 50% of light can be contained in the cavity. The other side of the cavity is a bulk silver film which is broadband reflective.

The device stack of the metallic J-cavity is slightly more complicated due to the additional dip-coating step for the excitonic materials located at the antinode of the cavity and a change in the cavity spacer layer material on top of the organic layer. This is because organics do not do well sputtered directly on top of. Therefore, another optically transparent spacer layer with an index of refraction close to SiO$_2$, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine or BCP), is chosen and is evaporated on top of the organic layer.

![Schematic diagram of semitransparent λ/2 microcavity consisting of a bottom semitransparent silver layer (16 nm) and a bulk silver top layer (120 nm) and the optical spacer layer of SiO$_2$. Empty cavity is shown top and J-Aggregate cavity is shown on the bottom. The emissive material consists of 4.5 SICAS of dipcoated J-Aggregates designed to be located at the antinode of the cavity. The optical spacer layers are vacuum sputtered SiO$_2$ and evaporated BCP. These are different because sputtering on top of organics in unfavorable and damages the film.](image-url)
Each J-cavity sample run involves making samples of empty cavities and J-cavities to allow for direct characterization of the empty cavity to determine the cavity length for each device run. The angle-resolved k-space spectroscopy is able to image up to 60° from normal incidence, so it is important to characterize the cavity at a number of angles to reflection measurements using the ellipsometer. Sample data for this cavity characterization can be shown in Figure 4-2 at angles of 18°–33°.

![Figure 4-2](image)

Figure 4-2: Empty cavity reflection over many angles measured with ellipsometer, with the smallest measurable angle at 18° constrained by the ellipsometer. This specific cavity corresponds to a semitransparent metallic (Ag) microcavity with a cavity length of 352 nm. The quality factor of this cavity is $\sim 15$, hence low-Q cavity.

From the location of the minima of the angle resolved reflection data point, we can construct the cavity photon dispersion relation. Standard transfer matrix method is used to simulate the cavity and fit the appropriate/corresponding cavity length of the device.
4.1.2 Strong Coupling in Semitransparent Metallic J-Cavity

The k-space imaging setup (Appendix D) is used to measure the angle-resolved reflectivity spectrum of the polaritonic modes. The resolution in angle is limited only by the resolution of the k-space image and the size of the pixels on the CCD camera of the spectrometer. A sample polariton dispersion raw data is shown in Figure 4-3.

![Figure 4-3: Polariton dispersion (Right) and example spectrum cross-sections of the dispersion at 5 different angles (left).](image)

The dispersion clearly depicts the UPB and the LPB. Interestingly, a third branch is evident in all of the dispersion curves, at the monomer absorption that is not angle dependent. This dip is blue shifted from the LPB at large angles (mostly excitonic, J-aggregate absorption), as expected. This may suggest that we still have some monomers in our film that is not strongly coupling to the cavity photons and require further attention.

A fitting algorithm is applied to the k-space image that fits the upper and lower branches of the dispersion at each angle (each row of pixels in Figure 4-3) to produce the UPB and LPB as a function of angle. Care was taken to deconvolve the
Figure 4-4: Comparison of the third branch possibly due to uncoupled J-aggregates in the film shown by the matching of the wavelength of the angle independent peak at 50° with the absorption of J-aggregates. The slight blue shifting is due to the upper polariton branch that has not been deconvolved from this raw data.

UPB from the angle independent monomer band to find the reflectivity minima of the upper branch. This data can be fitted with Equation 2.10 to produce Figure 4-5. This fit is able to give a rabi splitting of $\hbar \Omega = 2V_A = 97.3\text{meV}$.

Figure 4-5: Polariton dispersion experimental fitted with theory. Uncoupled states in black: exciton (dashed) and cavity (solid). UPB in red and LPB in blue. Fitted Parameters $E_c = 2.11\text{eV}$, $V_A = 48.7\text{meV}$ and $E_c(\theta = 0) = 2.04\text{eV}$

At a low $Q$ of 15, the semitransparent cavity is easily deposited and offers ability to study the strong coupling of light and matter at room temperature in air.
4.2 High-Q Cavities

Fabrication of high-Q cavities are much more time intensive and can take up to ten hours of deposition. Work has been done to deposit DBR coating consists of 8 pairs of SiO$_2$ and TiO$_2$ layers, and has a reflectivity at the designed center wavelength of 588 nm higher than 99.9%. A SiO$_2$ layer of 89.1 nm thickness is subsequently sputtered on these DBR coated substrates to serve as an optically transparent spacer layer.

Figure 4-6: Schematic diagram of DBR $\lambda/2$ microcavity consisting of 16 pairs of high index contrast materials TiO$_2$ (61 nm) and SiO$_2$ (100.8 nm) sputtered in vacuum.

This cavity offers Q-factor of more than two orders of magnitude better than the Q-factor of the metallic cavity. Figure 4-7 shows the reflectance of the DBR cavity. We can see a significantly narrower resonance in comparison to the reflection measurements for the semitransparent cavity shown in Figure 4-2.
Figure 4-7: Reflectance of a DBR λ/2 microcavity consisting of 16 pairs of high index contrast materials $TiO_2$ (61 nm) and $SiO_2$ (100.8 nm) sputtered in vacuum with a Q-factor of 1200.
Chapter 5

Conclusion

In this thesis we have addressed the works leading up to the demonstration of polaritonic devices. We have captured the importance of having room temperature operational, and scalability of functional devices by exploring organic excitonic materials with large coupling to light at room temperature and can be solution processed. We have learned a great deal in this process about the photostability of the molecules and aggregates of molecules in both pre-deposition solution form and post-deposition thin film, knowledge that will aid us in producing polaritons in stabilized structures. To our initial surprise, it seems that the J-aggregate film measured in the high humidity environment demonstrated the slowest emission decay, suggesting that water molecules could potentially help stabilize J-aggregates in solid-state. The greatly improves our ability to encapsulate the devices to have sustainable experimental measurements and hope for functional devices.

From our lessons learned about the film stability and deposition of high-Q cavities, future work will be conducted in making photostabilized organic excitonic-polariton based devices. We would like to explore polariton and condensation physics demonstrated in conventionally complicated experiments and to seek promising applications of polaritonic devices in the field of optical switching at ultra-low energy levels. We are also interested in exploring high-Q resonators outside of planar microcavity structures including photonic crystal waveguides, micropillars and ring resonators in combina-
tion of utilizing organic active layers. Overall, we see J-aggregates as a promising material given its narrow linewidth and high-oscillator strength that should be used for demonstration of exciton-polariton phenomena at room temperature and incorporated into practical optoelectronics.
Appendix A

Method: LBL Deposition of J-Aggregates

The layer-by-layer (LBL) deposition method [28] described in this section lays the fundamental method of which all J-aggregate thin films in this thesis are deposited, allowing for nanometer scale thickness control of monolayers of aggregated cyanine dye molecules. The dip-coater used for the LBL deposition is the Leica AutoStainer XL - Automated slide stainer. The C2S4 cyanine dye molecules were purchased from FEW Chemicals and the polycations (PDAC 20% w/v) was purchased from Sigma-Aldrich.

In this dip-coating routing, there are eight participating solution buckets as shown in Figure A-1: the polycation solution, the polyanion dip-coating solutions, and three rinse solutions for each, consisting of pure DI water. The glass substrates are prepared by oxygen plasma to provide negative surface charges for the absorption of the first polycation layer. In one cycle, the substrate undergo sequential immersions in cationic and anionic solutions (SICAS) with rinse steps in between to rid of excess dye and PDAC to ensure one bilayer/SICAS only consist of monolayers of the alternating materials as shown in Figure A-2.

The J-aggregate solution (concentration: 50μM) is adjusted to a pH of 9 with
Figure A-1: A total of eight buckets in the dip-coating process with the time duration of the substrate spent in each bucket specified. The PDAC solution consists of 20 mL of PDAC 20%w/v with 380 mL of DI water. The J-aggregate solution was made with 15 mg of C2S4 molecule in 400 mL of DI water adjusted to a pH of 9 with sodium hydroxide.

Figure A-2: One SICAS of LBL J-aggregate of PDAC/C2S4 grown on glass.
sodium hydroxide to promote film growth. We found that this higher pH yielded films of better quality and peak absorption coefficient. The solutions were changed after each round of dip-coating, with each deposition run yielding up to ten 1/2 inch samples.

All J-aggregate films in this thesis consists of 4.5 SICAS. This was optimally chosen as previous work [28] show remarkably low scattering in the 4.5 SICAS film compared to a range of 1.5 to 10.5 SICAS films with the peak absorption coefficient determined to be $a = 0.96 \times 10^6 \text{cm}^{-1}$. 
Appendix B

Method: Fabrication of Semitransparent Metallic Cavity

The metallic J-cavity is composed of a stack of five material layers: chromium, silver, SiO$_2$, BCP and J-aggregates. The chromium, silver and BCP are thermally evaporated while the SiO$_2$ is sputtered. The chromium is not part of the cavity stack, however due to the solution processing of J-aggregate films and the fact that silver does not adhere to glass, 5 nm of chromium is first deposited on the glass as an adhesion layer. The J-aggregates are LBL dip-coated in air on the sputtered SiO$_2$ half cavity. The sample is returned to vacuum and chamber and the rest of the cavity (BCP) is evaporated followed by the bulk silver film.

Figure B-1: Material stack of semitransparent metallic J-cavity.

The bottom optical spacer material chosen out of SiO$_2$ and Al$_2$O$_3$. J-aggregates coated much better on sputtered SiO$_2$ with higher peak absorption coefficient. The top optical spacer material needs to be thermally evaporated, as sputtering on or-
ganic layers has shown to damage the films. BCP was chosen as it has comparable refraction of index to $SiO_2$.

The cavity thickness in deposition varies with distance from center, thus measures were taken to know the exact thickness of the cavity length across samples. The deposition ratio to thickness at center is tooled for both the sputterer and the evaporator in Figure. B-2.

![Figure B-2: Chemical structure of an archetypical J-Aggregate forming C2S4 molecule.](image-url)
Appendix C

Method: Fabrication of High-Q Cavity

A high-Q cavity is an optical oscillator that has a very narrow bandwidth, with the Q of the cavity calculated by ratio between the center frequency of the cavity mode and the FWHM bandwidth of the mode ($\nu_c/\Delta \nu$). There are many ways of achieving high-Q cavities including photonic crystal cavity[4] and whispering gallery resonators[12], however in the Fabry-Perot cavity configuration, we chose to go with the DBR cavity.

The DBR coating consists of 8 pairs of sputtered SiO$_2$ and TiO$_2$ layers, and has a reflectivity at the designed center wavelength of 588 nm higher than 99.9%. Each DBR has a half cavity of SiO$_2$ (89.1 nm thick) to serve as an optically transparent spacer layer. Two substrates with their respective DBR’s and half cavities are assembled to make a sandwich DBR microcavity.
Figure C-1: Schematic diagram of DBR $\lambda/2$ microcavity consisting of 16 pairs of high index contrast materials $TiO_2$ (61 nm) and $SiO_2$ (100.8 nm) sputtered in vacuum.
Appendix D

Setup: K-space Imaging of Polariton Dispersion

A common method for probing the light matter interactions between strongly-coupled light emitters and cavity photons is to measure the energy spectrum and angular distribution of light that escapes the cavity. In this way, we can directly observe the dispersion relation for polaritons in our devices, and by reconstructing the dispersion relation, we can extract the Rabi splitting.

The experimental method we use to measure the angular distribution of escaped cavity photons is called Fourier microscopy, also colloquially known as k-space imaging. Light from our sample is collected by an infinity corrected objective and is then refocused by a tube lens to form a magnified image plane on the output port of the microscope. We then place a Bertrand lens after the image plane, at a distance of the focal length away. A Bertrand lens acts to form a fourier transform of the image plane, giving us a new image where the spatial coordinates of this fourier plane correspond to the projection of the wavevector of the emitted light that is normal to the optical axis. By placing a CCD at this fourier image plane, we can directly measure the angular distribution of light.

To get energy spectrum information, we can replace the CCD with an imaging...
spectrometer. The fourier image plane is focused onto the entrance slit of the spectrometer. Inside the spectrometer, the slit is spatially separated by frequency using a grating and projected onto a CCD. Along the x axis of the spectrometer, we now have frequency information, and along the y axis is the projection of the wavevector.

Figure D-2 shows the details of our experimental setup. Between the Bertrand lens and the spectrometer slit, we have placed a pair of lenses that form a 4f imaging system to act as relay optics. This lens pair allows us to adjust the magnification of the fourier image to fit the size of the CCD of the spectrometer. To minimize aberrations of our image, we used long focal length lenses which have a large radius of curvature. We are also using achromatic doublets to minimize chromatic abberation. Finally, to ensure we are not getting interference from multiple points of the sample, we place a pinhole at the image plane, between the tube lens and the Bertrand lens.

Figure D-1: Schematic of the Fourier imaging microscopy setup used to measure cavity polariton dispersion. The back focal plane of the objective is imaged onto the spectrometer CCD directly measuring wavevector and energy along the two axis.
Fourier microscopy is an elegant method for collecting information about the angular distribution of emitted light simultaneously, compared with the relatively much slower alternative of sweeping the angle using a goniometer. The increased speed of measurement is useful not only from a logistical perspective, but it is critical for the measurement of J-aggregates which may photodegrade.

Currently, we are working to ensure the precise alignment of the system. The alignment of fourier planes is less intuitive than real space images due to the lack of a sharp focus, however we have identified several techniques that are very helpful in the alignment procedure. We use a collimated laser source that is aligned to the optical axis of the microscope along with a shear plate interferometer to precisely place the lenses following the microscope. The laser should be collimated after the Bertrand lens, and again after the second relay lens. We also use reference samples (empty cavities) to align the CCD and spectrometer to the Fourier planes.

Figure D-2: Sample dispersion images of empty cavity (left), J-aggregate film on glass (middle) and a J-cavity polariton dispersion (right).
Bibliography


