Solid State Cavity QED: Practical Applications of Strong Coupling of Light and Matter

by

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ABSTRACT: J-aggregates of cyanine dyes are the excitonic materials of choice for realizing polariton devices that operate in strong coupling at room temperature. Since the earliest days of cavity QED, there has been a major desire to construct solid state optical devices that operate in the limit where strong light-matter interactions dominate the dynamics. Such devices have been successfully constructed, but their operation is usually limited to cryogenic temperatures, because of the small binding energies for the excitonic materials typically used. It has been demonstrated that when J-aggregates are used as the excitonic material, it is possible to achieve strong coupling in solid state even at room temperature. J-aggregates are a unique choice of materials because their central feature, a very large optical transitional dipole, is itself the result of strong coupling amongst monomeric dye elements. The strong coupling amongst dye molecules produces a well-defined cooperative optical transition possessing oscillator strength derived from all of the aggregated monomers that is capable of interacting strongly with the cavity confined electromagnetic field even at room temperature. There are different materials and methods for assembling J-aggregates which are capable of producing strong coupling. This thesis argues in favor of a particular dye and method of assembly which are then thoroughly characterized. With this dye and assembly technique, the first demonstration of electrically pumped polariton emission is reported as is the largest optical absorption coefficient for a solid thin film at room temperature not contained in a full microcavity. This combination is then used to demonstrate strong coupling at room temperature, as characterized by a light-matter coupling strength, Rabi-splitting, that significantly exceeds the dephasing processes competing against the coherence of the interaction. Finally, prospects of this approach for realizing a polariton laser at room temperature are considered, and improved microcavity architectures are demonstrated as a path towards its realization.

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1 Introduction

1.1 Background

Quantum electrodynamics (QED) is the quantum mechanical description of electromagnetic radiation, matter, and the interaction of the two. Cavity QED is the study and utilization of the quantum interactions between light and matter inside a microcavity optical resonator. When matter inserted inside a microcavity exchanges energy with a resonant mode of the cavity more rapidly than the combined rate at which energy escapes the system either in the form of photons leaving the cavity or the matter wave function losing its phase information [1, 2], the strong coupling limit of cavity QED is reached. 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. The coupled system is governed by quantum effects that rely on or leverage quantum coherence.

The matter component of the coupled system can be a gas of atoms trapped inside the cavity [3], a superconducting qubit [4], or a thin film containing excitons, 2-level-system-like light-absorbers, in the form of an inorganic quantum well [5], quantum dot [6, 7] or organic material [8]. When excitons are used, the superposition states are referred to as exciton-polaritons, as in the experiments discussed in this thesis.

Applications of strong coupling in atomic and semiconductor systems have led to one-atom zero-threshold lasers [9], high gain polariton parametric amplifiers [10], and predictions that strong coupling may play a key role in future quantum information processors [11].

Within cavity QED, the study of strong coupling is taken up in the atomic optics community, the quantum optics community, and the semiconductor research communities. Historically, the antecedents date back to work on Masers in the 1960's [12] through 1980's [13]. Within the atomic optics community, the push starting in the 1980's has been towards single atom devices, a goal that was finally reached in the year 1991 [14]. For such devices the optical properties can be modified dramatically with a single photon. Within the semiconductor communities, the first observation of vacuum Rabi-splitting in the year 1992 [5], set the community moving towards realizing the semiconductor analogues of the atomic systems [15]. The semiconductor research focused primarily on quantum well based devices, inherently not single exciton systems. Eventually this field split into two, with one group embracing the quantum optics single exciton roadmap [16] and the second embracing the many body Bose-Einstein condensate vision [17]. The former continued the push towards single exciton strong coupling optics, using quantum dots, typically expitaxially grown, which in 2005 culminated in the first demonstration of strong coupling for a single semiconductor quantum dot [6, 7], performed at cryogenic temperatures. The second group continued to work on quantum well devices, recognizing that a single incident photon is not sufficient.
to modulate the optical properties such structures. However, the fascinating possibility of realizing a polariton condensate in such systems has kept the field burning. In the early part of this decade, resonantly pumped coherent emission was observed even at relatively high temperatures [10]. The first report of non-resonantly pumped polariton (matter) condensation was reported in Sept. 2006 [18], and in 2007 a second group reported polariton lasing although evidence of condensation in the form of spontaneous polarization build-up was not presented [19].

1.2 Research Objectives

The goal of this research effort is to develop solid state integrated devices that operate in the strong coupling limit of cavity quantum electrodynamics (QED) for high speed optical switching, optical computing, and quantum computing applications. The materials that are utilized for this purpose are J-aggregates of (organic) cyanine dyes which, by virtue of their molecular arrangement and strong dipolar coupling, exhibit a collective narrow linewidth high oscillator strength optical transition. These materials can be deposited over large area and engineered at the nanoscale and enable strong coupling of light and matter at room temperature. It is also the objective of this research to demonstrate in solid state the non-intuitive consequences of strong coupling: lasing without population inversion, electroluminescent (polariton) lasing in organic devices, and stimulated long range coherent energy transfer.

Building solid state devices based on strong coupling that use J-aggregates and operate at room temperature will potentially have both scientific and technological significance. The laser device would be one of the first solid state cavity QED lasers operating in the strong coupling limit. Lasing in the strong limit has been demonstrated using atomic beams and even single atoms in optical resonators possessing quality-factors (Q) exceeding $10^6$, and recently in semiconductor polaritonic systems [18, 19]. A demonstration of lasing in the strong coupling limit with considerably more modest Q's of several thousand could alleviate the need for some of the heroic processing constraints. Experimental demonstration of a stimulated Forster energy transfer process, (similar to Raman lasing) could lead to compact electrically generated sources of non-classical light. Likewise, a low threshold energy ultra fast thin-film integrated optical switch, and the ability to modulate the switch electrically could make extremely large scale optical computing possible.

1.3 Structure of Thesis

The thesis is structured in the following order. In Chapter 2, it begins with an explanation of the interactions between light and matter, in a general sense, and then transitions to a description of strong coupling in solid state systems, where the fundamental quasi-particle which describes strong coupling is the exciton-polariton or polariton for short. In Chapter 3, J-aggregates of cyanine dyes are introduced as the material set used for realizing strong coupling at room temperature. First, the
photophysics of J-aggregates is developed, and then methods of formation and deposition in thin film are discussed. The need for a more powerful method of formation and deposition is argued, proposed, and demonstrated. The resultant films are thoroughly characterized, highlighting their unique optical and morphological properties. In Chapter 4, J-aggregates are incorporated into microcavity structures and strong coupling is demonstrated with giant coupling strengths but also with correspondingly fast dephasing processes. This becomes the spring board for developing electroluminescent OLEDs in Chapter 5, based on the J-aggregate films. In Chapter 6, electrically pumped polariton emission is demonstrated and discussed, as well as other electrically interrogated strongly coupled devices. Critically coupled resonators (CCR’s) are then discussed in Chapter 7 as an intermediate and illuminating step towards higher Q cavity devices. From there, in Chapter 8, results are reported of strong coupling with large ratios of the coupling strength relative to dephasing processes. In Chapter 9, a more elaborate microresonator architecture consisting of an all-dielectric planar microcavity is presented. In this chapter, a strategy for realizing a room temperature optically pumped polariton laser based on direct excitation is developed and the unique physics that becomes testable in such a device is presented. In Chapter 10, a short conclusion follows.

Chapters will have an introduction, some background material, a theoretical or experimental component, a conclusion section, and then a bibliography. I will do my best throughout the thesis to strike some kind of balance between writing about experimental data and writing about other peoples work. This is not meant to be a review article of other peoples’ work, but it also is not intended to be entirely self-centric. Lastly, at the beginning of each chapter, a few quotations will be provided to spice up lessons learned along the experimental trail and whet the appetite of the reader.
2 Physics of Strong Coupling

"Who forms light and creates darkness, Who makes harmony, and creates everything."
(Benediction excerpted from Judaic morning prayers)

Anectdotal Introduction

As the “Men of the Great Assembly” said, light and darkness are actually in harmony, and this coherence is a fundamental property of the natural world.
2.1 Introduction

What happens when light is trapped in an optical resonator filled with matter (in the form of atoms, excitons or other two level systems) that can exchange energy resonantly with that light? The type of dynamical behavior that is produced depends on the relative rates of the fundamental processes involved. Fundamentally, there are three rates to consider (using notation from Kimble [1]):

1. The rate at which the light and matter transfer energy: \( g \).
2. The rate at which light escapes the cavity: \( \kappa \).
3. The rate at which matter looses its polarization: \( \gamma \).

When the rate of energy transfer, \( g \), is considerably larger than \( \kappa \) and \( \gamma \) (\( g \gg \kappa, \gamma \)) then strong coupling of the light and matter occurs. In this limit, the light and matter exchange energy periodically (with period \( 2\pi/g \)), for a number of periods before the energy escapes the system. To first order, there is direct analogy between strong coupling and an underdamped LRC (inductor-resistor-capacitor) circuit. The periodic exchange of energy between light and matter is akin to the underdamped LRC circuit exhibiting oscillations in current and voltage before the energy is dissipated in the resistor. The opposite limit, where \( g \ll \kappa, \gamma \) is called the weak coupling limit, because the light and matter trapped in the resonator interact not much more strongly with each other than with light or matter outside the system. By way of analogy, this limit is likened to an overdamped LRC circuit, where no ringing occurs because of heavy damping. The main limitation of the analogy is that the LRC circuit is linear while the light matter system is not. Nevertheless, whenever the number of excitations is low, the analogy applies and it can be used to guide intuition.

The physical process responsible for the energy transfer between light and matter is to first order a coupling between dipole and electric field. The energy, \( E \), associated with this coupling is given by \( E = \bar{\mu} \cdot \bar{E} \), where \( \bar{\mu} \) is the transition dipole (matrix element) of the matter component and \( \bar{E} \) is the vacuum electric field inside the cavity. Mathematically, the vacuum \( \bar{E} \) field is given by:

\[
\bar{E} = \sqrt{\frac{\hbar \omega_{\text{cav}}}{2\varepsilon_0 V_m}}
\]

Where \( \omega_{\text{cav}} \) is the resonant frequency of the cavity mode and \( V_m \) is the modal volume. The transfer rate, \( g \), is proportional to \( E \), with \( g = E / \hbar \). A model of the strong coupling limit is depicted in Figure 2-1 for the case of a single exciton and single photon.
Figure 2-1 The underdamped case. Single exciton in microcavity interacting with a single photon. Energy is exchanged periodically between the two constituents, at rate "g" while it gradually decays out the system with rate $\Gamma = (\kappa+\gamma)/2$. The “phase angle” is a representation of the phase of the transition dipole associated with the exciton.

The periodic exchange of energy between light and matter, at the rate $g$, directly affects the transmittance and reflectance of the microcavity structure. In particular, in the case where the frequencies of the microcavity resonances, $\omega_{\text{cav}}$, and matter resonance, $\omega_{\text{ex}}$, are equal, ($\omega_{\text{cav}} = \omega_{\text{ex}} = \omega_0$), the transmittance and reflectance spectra both show two new resonances, $\omega_\pm$, at frequencies $\omega_\pm = \omega_0 \pm g$. This situation is illustrated in Figure 2-2 for reflectance. Applying the analogy of the underdamped LRC circuit, the two new resonances correspond to the beating of the underdamped (light-matter) oscillator superimposed on the fundamental carrier frequency, $\omega_0$.
2.2 Quantitative Model

To gain insight into the physics of strong coupling, the light-matter interaction can be modeled as a two level system (exciton) that is coupled to a simple harmonic oscillator (photon) [20]. The two level system has states: $\phi_1$ and $\phi_2$ with energies $E_1$ and $E_2$, such that the energy difference equals the energy of the exciton’s optical transition: $E_2 - E_1 = \hbar \omega_{ex}$. Similarly, the simple harmonic oscillator has states: $|n\rangle$ where $n = 0, 1, 2, \ldots$ with energies of $\hbar \omega_0 (n + 1/2)$. Without coupling, the stationary states of the combined system $\Psi_n$ are simply product wavefunctions. The ground state is $\Psi_0 = \phi_1 |0\rangle$, and there are two states with one excitation of either one photon $\Psi_1 = \phi_1 |1\rangle$ or one exciton $\Psi_2 = \phi_2 |0\rangle$, respectively.

Which states, $\Psi_n$, couple depends on the nature of the coupling interaction. In the case of light-matter interactions, to first order [21], the coupling is due to dipole radiation,
which can be represented by the perturbation Hamiltonian $H^{(i)} = -\vec{\mu} \cdot \vec{E}$, where

$$\vec{\mu} = e \int \phi^* \vec{r} \phi dV$$

is the transition dipole moment of the radiator and $\vec{E}$ is the electric field strength of the photon mode, with $\vec{r}$ being the spatial location of the state integrated over the volume $V$. Since $\vec{r}$ is an odd-parity operator, the perturbation only acts between orthogonal states $\phi_i$ and $\phi_2$. Similarly, because the action of the exciton corresponds to the creation or annihilation of a photon, the perturbation $H^{(i)}$ only couples states of different quantum number. To capture this physics, $H^{(i)}$ is represented as

$$H^{(i)} = V_o (\hat{a}^* + \hat{a}) \phi_i \phi_j + |\phi_i \phi_j| \Psi_a \Psi_b \rho \Psi_{a'} \Psi_{b'}$$

[20], where $\hat{a}'$ and $\hat{a}$ are creation and annihilation operators, respectively, for photons of energy $\hbar \omega_0$ and $V_o$ is the magnitude of $H^{(i)}$, which can be tuned by engineering dipole moment and field strength, and is related to $g$, by $V_o = \hbar g$. Applying the perturbation $H^{(i)}$ to $\Psi_a$, it is clear that $\Psi_1$ and $\Psi_2$ couple to each other, while $\Psi_0$ couples to $\Psi_3 = \phi_2 |\Psi\rangle$.

Because of the coupling, the eigenstates of the system are no longer $\Psi_a$, but rather are superpositions of the states involved in the coupling. Denoting the new stationary states as $\Phi_n$, the ground state is $\Phi_0 = c_1 * \Psi_0 + c_2 * \Psi_3$, while the first and second excited states, $\Phi_1$ and $\Phi_2$, are rotational superpositions of $\Psi_1$ and $\Psi_2$ [20].

Solving for the eigenstates determines the energy levels of the states $\Phi_0$, $\Phi_1$, and $\Phi_2$. The energies of the ground state, $H_0$, and first two excited states, $H_1$ and $H_2$, are given by [20]:

$$H_0 = \hbar \omega_0 + \frac{1}{2} (E_1 + E_2) - \frac{1}{2} \sqrt{(E_2 - E_1 + \hbar \omega_0)^2 + 4V^2}$$

and

$$H_1 = \hbar \omega_0 + \frac{1}{2} (E_1 + E_2) - \frac{1}{2} \sqrt{(E_2 - E_1 - \hbar \omega_0)^2 + 4V^2}$$

$$H_2 = \hbar \omega_0 + \frac{1}{2} (E_1 + E_2) + \frac{1}{2} \sqrt{(E_2 - E_1 - \hbar \omega_0)^2 + 4V^2}$$

The first excited states of the coupled system, $\Phi_1$ and $\Phi_2$, represent the polariton states of the semiconductor microcavity. The polaritons have both exciton and photon character only near the resonance condition where the exciton and photon energies match. Far away from resonance, the two excited states are essentially equivalent to the first two excited states of the uncoupled exciton photon system.
To generate one of the polariton states, i.e. either $\Phi_1$ or $\Phi_2$, a quantum of energy equal to the difference in energy between the ground state and excited state must be delivered to the coupled system. Figure 2-3 plots these energy differences: $E_- = H_1 - H_0$ and $E_+ = H_2 - H_0$, where:

$$E_+ = \frac{1}{2} \sqrt{(E_2 - E_1 + \hbar \omega_0)^2 + 4V_0^2} - \frac{1}{2} \sqrt{(E_2 - E_1 - \hbar \omega_0)^2 + 4V_0^2}$$

This plot is sometimes referred to as a polariton dispersion curve since the bare cavity photon mode energy $\hbar \omega_0$ is related to k-space via the component of the photon mode wave vector perpendicular to the mirrors. The curve representing the amount of energy needed to generate the lower (higher) energy polariton state, $E_-$ ($E_+$), is referred as the lower (upper) branch polariton curve. The two branches do not cross at the exciton photon resonance, but instead "repel" each other. The difference in energy between the polariton branches at resonance is the Rabi splitting, $\hbar \Omega_R$, which is twice the interaction energy $V_0$, i.e. $\hbar \Omega_R = 2V_0$. Creating the upper polariton requires a quantum of energy at negative detuning approximately equal to the exciton energy since at this detuning, $\Phi_2$ is mostly excitonic, while at positive detuning the energy required is approximately the bare cavity photon energy since at this detuning $\Phi_2$ is mostly photonic.

![Figure 2-3 Upper and lower branches of polariton dispersion curve, as a function of photon tuning, with anti-crossing energy equal to the Rabi-splitting of $\hbar \Omega_R = 2V_0 = 0.2$ eV.](image)

The polariton dispersion curve relates the model to the optical properties of polaritons. At any given cavity tuning, $h\omega_0$, the coupled system responds to two photon energies, and therefore has two absorption peaks. As the system is tuned through resonance these peaks approach each other until the resonance condition at which point they begin to move further away in energy. These absorption peaks also correspond to peaks in the
photoluminescent response of the system when the coupled microcavity is excited, and to resonant dips in the reflectivity spectrum as in Figure 2-2.

The expressions for $E_{\pm}$ are greatly simplified by recognizing that the square root term containing the square sum of $\hbar\omega_0$ and $E_2 - E_1$ in the expression for $H_0$ reduces to:

$$\frac{1}{2} \sqrt{(E_2 - E_1 + \hbar\omega_0)^2 + 4|V_0|^2} \rightarrow \frac{1}{2} (E_2 - E_1 + \hbar\omega_0)$$

since the $4|V_0|^2$ term is comparatively small for realistically attainable values of $V_0$. With this simplification, $E_{\pm}$ is expressed as:

$$E_{\pm} = \frac{1}{2} (E_2 - E_1 + \hbar\omega_0) \pm \frac{1}{2} \sqrt{(E_2 - E_1 - \hbar\omega_0)^2 + 4|V_0|^2}.$$  

In the polariton literature, the expression for $E_{\pm}$ is typically written as:

$$E_{\pm} = \frac{1}{2} (E_2 + E_1) \pm \frac{1}{2} \sqrt{\left(\hbar\omega_0\right)^2 + (E_2 - E_1)^2}$$

where $\hbar\omega_0 = E_{ph}$ is the photon energy, $E_2 - E_1 = E_{ex}$ is the energy difference between the uncoupled levels 1 and 2, which equals the exciton energy, and $2V_0 = \hbar\Omega_R$ is the Rabi-splitting discussed earlier.

In the model so far, the cavity and exciton energies were assumed to be infinitely well-defined, which is unphysical. The impact of the finite linewidths of both the excitonic transition and the photon mode is to broaden the polariton absorption peaks, making observation of the Rabi splitting more difficult.

Figure 2-4 Power spectrum envelope of upper and lower polariton branches for Rabi-splitting ($2V_0$) of (a) 40 meV and (b) 200 meV in the case of $(\kappa+\gamma) = 80$ meV

The line broadening in the frequency domain can be modeled by considering the impact of the finite linewidths of the cavity and exciton in the time domain. A finite linewidth is
simply the result of a finite lifetime due to damping of the oscillation in the time domain. On resonance, the two normal modes of the system without damping are:

\[ s_{\pm}(t) = A \cos(\omega_{ex} \pm g)t, \text{ where } g = \frac{V_0}{\hbar} \]

Given the cavity photon mode damping \( \kappa \) and the exciton damping \( \gamma \), the two normal modes are now damped oscillations in time [22]:

\[ S_{\pm}(t) = Ae^{-\frac{1}{2}(\kappa + \gamma)/t} \cos(\omega_{ex} \pm g')t \text{ where now } g' = \sqrt{\left(\frac{V_0}{\hbar}\right)^2 - \frac{1}{4}(\kappa - \gamma)^2} \]

Parenthetically, from the \( g' \) expression it is clear that matching \( \kappa \) and \( \gamma \), which is analogous to impedance matching, maximizes the coupling and therefore the Rabi-splitting.

By Fourier transforming \( S_{\pm}(t) \) and then taking the magnitude squared, the polariton "power" spectrum is given by [22]:

\[ S_{\pm}(\omega) = \frac{A_{\pm}}{\left(\frac{\kappa + \gamma}{2}\right)^2 + (\omega - (\omega_{ex} + g'))^2 + (\omega - (\omega_{ex} - g'))^2} \]

It is clear from this expression that the polariton spectrum is double peaked so long as the Rabi splitting \( \Omega_R = 2g' \) satisfies the following condition [23]:

\[ \Omega_R = 2g' > 0.5(\kappa + \gamma). \]

This condition determines what coupling strength is needed to observe polariton splitting.

Thus far, the model accounts for the splitting between the polariton branches, the dynamics of the Rabi-oscillation and the interaction strength needed to overcome cavity and exciton finite lifetimes. Once an actual microcavity is fabricated and the mirror spacing is fixed, the polariton dispersion can still be probed through angularly resolved transmission, reflection, and photoluminescence measurements, because at any angle of the incident light, only a single frequency will satisfy the bare cavity (no-excitons) resonant condition. Physically, this frequency is given by [2]:

\[ \omega = c|\vec{k}| = \frac{c|\vec{k}_\perp|}{\sqrt{1 - \sin^2 \theta}} \]

Where \( |\vec{k}_\perp| = (\pi/nL) \) for a \( \lambda/2 \) cavity, and \( \theta \) is the angle of incidence measured relative to the normal of the cavity. This equation applies to the general case of refractive index mismatch between air and the medium of the microcavity.
Ultimately, the degree of polariton coupling depends on the magnitude of the transition dipole moment $\bar{\mu}$. The quantity $|\bar{\mu}|^2$, however, is experimentally the more accessible metric, since for light-matter interactions where strong coupling does not apply, the quantity $|\bar{\mu}|^2$ governs the relaxation dynamics and linear optical properties. Fermi's Golden Rule gives the rate of decay of the excited state (of the exciton), which is proportional to $|\bar{\mu}|^2$, as [24]:

$$R_{\text{FGR}} = \frac{2\pi}{\hbar} |\bar{\mu} \cdot \vec{E}|^2 \rho_{ph}(\hbar \omega_\nu)$$

with the lifetime of the excited state, $\tau_{\text{FGR}} = 1/R_{\text{FGR}}$ being inversely proportional to $|\bar{\mu}|^2$. Similarly, if the absorption spectrum of the exciton is given by $\alpha(\omega)$ [cm$^{-1}$], then it can be shown that [24]:

$$|\bar{\mu}|^2 = 3e_0 \hbar c \frac{\pi N}{\omega} \int \alpha(\omega) \, d\omega$$

Where $N$ is the density of absorbing excitons per unit volume. Fundamentally, $|\bar{\mu}|^2$ represents the variance of the charge distribution of the exciton, and by the Fluctuation-Dissipation Theorem, the fluctuation directly determines the dissipative response of the system [24] (in the perturbative limit of light matter coupling, radiation is indeed dissipative).

It is worth reflecting upon the relation between $|\bar{\mu}|^2$ and the absorption coefficient $\alpha(\omega)$. It says that highly absorptive materials make the best candidates for strong coupling, since $V_0 \propto |\bar{\mu}| \propto \sqrt{\alpha_{\text{max}}}$. At first glance this concept appears at odds with the notion that in the strong-coupling limit the radiation process is periodic. The consistency comes because, in actuality, the higher the absorption constant of a material the less light intensity is actually lost in the film. The higher $\alpha(\omega)$ is, the more closely the material resembles an ideal radiator (at the frequency $\omega$) with infinitely fast response time to incident electric field of the light, so that the material can in very short space reflect the light and reject it from penetrating into the film. Thus, the enhanced optical response due to high oscillator strength makes the exciton to photon energy transfer process more persistent and the light matter coupling more complete.

### 2.3 Conclusion

To achieve strong coupling of light and matter, the energy transfer rate between an exciton and photon, $g$, must exceed the dephasing processes acting on the system. Hence the desire to construct a system where the matter component has a large dipole moment, $\mu$. In a system where $g$ for a single exciton is low compared to $\kappa$ and $\gamma$, the number of excitons coupled to the cavity mode, $N_{\text{ex}}$, must be increased since for $N_{\text{ex}}$ excitons, the
coupling [1]: \( g(N_{ex}) = g_0 \sqrt{N_{ex}} \). Ideally, the excitonic material should also have a very small \( \gamma \), since the non-radiative dephasing processes from the exciton give an upper limit on how long coherent quantum phenomena will last before dissipation scrambles the phase information.
3 J-aggregate Films for Realizing Strong Coupling

“It usually takes 5 years for a film to self-assemble.” (Musings on nano-assembly)

Anecdotal Introduction:

My first day as a grad-student at MIT, July 2\textsuperscript{nd} 2001, Vladimir gave me Prof. David Lidzey’s Physical Review Letter article on photoluminescence from exciton-polaritons at room temperature. The paper talked about cyanine dyes, J-aggregates, and PVA. What was a cyanine dye? What was a J-aggregate? What was PVA? What was a polymer? The answer I got to the last question (not from a professor) was simply this, “any compound that starts with the word poly is a polymer”. It was a correct answer, but left a lot to be understood. In the fall of 2003, Scott Bradley and I began collaborating on the project of strong coupling. Scott quickly became an expert at characterizing the morphology and optical properties of the J-aggregate films (amongst many other aspects to this project) and over time more in-depth answers began materializing to those early questions.
3.1 Introduction

J-aggregates of cyanine dyes are a unique choice of materials for realizing strong coupling because their central feature, a very large optical transitional dipole, is itself the result of strong coupling amongst monomeric dye elements. The strong coupling amongst dye molecules produces a well-defined cooperative optical transition possessing oscillator strength derived from all of the aggregated monomers. Thin films of J-aggregates are capable of interacting strongly with cavity confined electromagnetic fields even at room temperature. There are different materials and methods for assembling films of J-aggregates that are capable of producing strong coupling. This space of possibilities is described, but ultimately a particular dye and method of assembly are chosen for realizing strong coupling.

This chapter is structured as follows. First, the photophysics of J-aggregates is developed. Then methods of formation and deposition in thin film are discussed. Finally, the optical properties of the thin films used for strong coupling applications are characterized.

3.2 Photophysics of J-aggregates

J-aggregates are luminescent nano-structured ordered arrangements of highly polar cyanine dye molecules that enable strong light-matter interactions to be observed at room temperature [8, 25] due to their high oscillator, high absorption coefficient ($\alpha_{\text{max}} \approx 10^6 \text{cm}^{-1}$), and room temperature stability. The Rabi-splitting due to thin films of J-aggregate excitons typically exceeds 100 meV, compared to 10 meV or less using excitons of most inorganic exciton based material systems.

Figure 3-1 illustrates the chemical structure of an archetypical J-aggregate forming cyanine dye called TDBC.

![Chemical structure of TDBC](image)

Figure 3-1 Chemical structure of TDBC, an anionic cyanine dye that readily forms J-aggregates in solution and solid state. The chemical formula of TDBC is (5,6-dichloro-2-[3-[5,6-dichloro-1-ethyl-3-(3-sulfopropyl)-2(3H)-benzimidazolidene]-1-propenyl]-1-ethyl-3-(3-sulfopropyl) benzimidazolium hydroxide, inner salt).

Like TDBC, cyanine dyes are rod-like organic salts in which the lumophore consists of a conjugated poly-methine bridge subtended by two highly polar nitrogen rich end-groups.
The nitrogen possessing positive charge is equivalently described as electron deficient, acidic or electron accepting and the uncharged nitrogen group as electron rich, alkaline or electron donating. Optically, the poly-methine bridge acts as a 1-dimensional quantum-wire optical dipole antenna, with the end groups donating (accepting) electron density to (from) the lumophore. Consistent with this description, the transition dipole moment is directed along the polymethine backbone and the dye interacts most strongly with light polarized parallel to this direction, as depicted in Figure 3-2a [26].

In the J-aggregate state, the cyanine dye monomers are closely assembled and specially aligned so that the electron rich nitrogen group of one molecule partially overlaps with the electron deficient nitrogen group of another [27]. This overlap enables the oscillating electron density in one molecule, setup by an optical excitation, to induce similar oscillations in the electron density of nearest neighbor molecules. In this respect, the overlap of side groups can be thought of as the near-field optical-interconnect that couples adjacent molecular oscillators in the J-aggregate.

When the molecules couple, the transition dipole moments of the individual molecules add to form a giant dipole oscillator and a new optical transition called a J-band [28]. Relative to the monomer, the J-band absorption/fluorescence is red-shifted, weakly Stokes shifted, and considerably narrower in energy. Figure 3-2c illustrates the absorption shift and narrowed absorption spectrum for the J-band of a dye similar to TDBC. The data, taken for monomeric solutions and J-aggregate thin films of the dye, show a shift of approximately 300 meV and a J-band with FWHM of ~50 meV at room temperature. The lifetime of the J-band transition is also much faster (10-100 ps) which can lead to an efficient fluorescence process [29]. For example for the J-aggregating dye THIATS, the dye’s quantum efficiency increases from 0.8% to 48.0% (in solution), a factor of 60. This boost is the result of the radiative rate’s in the aggregate becoming as fast as the non-radiative scattering rates that had hampered the luminescence pathway of the monomer. The fact that the aggregate form of these cyanine dyes is more fluorescent than the monomer runs contrary to the usually accepted rule for organics, which is that aggregates do not fluoresce. As will be described in the subsequent paragraphs, the discrepancy in quantum efficiency between J-aggregates and ordinary amorphous organic aggregates is in the distribution of the oscillator strengths among the energy levels available to the aggregate.

3.3 Detailed Physical Model

The physical model explaining the optical properties of J-aggregates can be built up from an understanding of the interaction of just two dye molecules. When two cyanine dye molecules are in close proximity their transition dipoles will couple, producing a perturbation to the energy levels of the system and causing a mixing of the excited states of the uncoupled molecules. The interaction energy for two dipoles is predictably orientation dependent [30]. This situation is depicted in Figure 3-2. When the two molecules are aligned tip to tail, then if the transition dipoles are out of phase the energy
is higher and the dipole moments cancel, but if the transition dipoles are in phase, the energy is lower and the net transition dipole moment is enhanced by a factor of $\sqrt{2}$.

**Figure 3-2** Physical model describing the origin of the J-aggregate states. (a) Single TDBC molecule with transition dipole, $\mu_0(t)$, aligned parallel to the poly-methine backbone. (b) Orientation dependent coupling between two dipoles. The locations of the arrows represent the orientation and physical position of the molecular dipoles. The direction in which the arrows point represent the phase of the transition dipole. (c) Energy levels for $N$ molecules coupled together in chain, along with $E-k$ dispersion relation and oscillator strength. Absorption spectra are actual data for three different samples indicating the shift from monomer to J-aggregate absorption. The two monomeric samples are solutions of dye in methanol (MeOH) and chloroform (CHCl$_3$). The thin film is of poly vinyl alcohol (PVA) doped with dye. The dye used here is the cationic version of TDBC.

A similar picture emerges for a J-aggregate where there are $N$ molecules in a row. The lowest energy excited state corresponds to all $N$ molecules coupling in phase and this state also possesses an enhanced transition dipole moment [31]. For $N$ molecules in a row, a model based on tight-binding has been developed which predicts the $k$-space dispersion relation and oscillator strength distribution. This model illustrates several key properties of J-aggregates that hold even in more elaborate descriptions of the physics. The classic derivation [31] is presented with modifications below. The results of which are plotted in Figure 3-2c.
Each molecule (labeled with subscript $n$) can be represented as a two state system consisting of ground state $|0\rangle_n$ and excited state $|1\rangle_n$, where the energy difference between them equals the monomer absorption energy: $E_n = E_1 - E_0$. For the system as a whole, the ground state is given by the product wavefunction: $|\Psi^0\rangle = |0\rangle_1 |0\rangle_2 \ldots |0\rangle_n \ldots |0\rangle_N$, and if there were no interaction between the monomers, the 1st excited states would be product wavefunctions: $|\Psi^1_n\rangle = |0\rangle_1 |0\rangle_2 \ldots |1\rangle_n \ldots |0\rangle_N$ of $N$-fold degeneracy. In J-aggregates however, transition dipoles couple strongly, which is not surprising considering cyanine dyes are very high oscillator strength, so the excited state product wavefunctions $|\Psi^1_n\rangle$ are no longer stationary. If the coupling interaction is represented as $J = \langle \Psi^1_n | H^{(1)} | \Psi^1_{n+1} \rangle$, which for dipoles aligned tip to tail reduces the energy of the system, then the Hamiltonian for the J-aggregate can be modeled as [31, 32]:

$$H|\Psi^1_n\rangle = E_M|\Psi^1_n\rangle + J(|\Psi^1_{n-1}\rangle + |\Psi^1_{n+1}\rangle)$$

Which says that if the $n^{th}$ molecule is excited, that excitation has some probability of transferring to the nearest neighbor dye molecules via the interaction $H^{(1)}$. The stationary states for a single excitation of the J-aggregate are instead superpositions of the single molecule excitations [31]:

$$|\Phi^1_k\rangle = \sum_{n=1}^{N} c_{n,k} |\Psi^1_n\rangle = \sqrt{\frac{2}{N+1}} \sin \left( \frac{k\pi n}{N+1} \right) |\Psi^1_n\rangle, \quad k = 1, 2, \ldots, N$$

With corresponding energies (note the degeneracy is broken) [31]:

$$E(k) = E_M + 2J \cos \left( \frac{k\pi}{N+1} \right), \quad k = 1, 2, \ldots, N$$

The coefficients weighting the $|\Psi^1_n\rangle$ in the superposition $c_{n,k}$ can be thought of as an envelope function that modulates the single molecule wavefunctions.

The sinusoidal standing wave nature of the envelope function closely resembles the expression for a 1-dimensional particle in a box where [21]:

$$\psi_k = |k\rangle = \sqrt{\frac{2}{L}} \sin \left( \frac{k\pi x}{L} \right), \quad k = 1, 2, \ldots, N$$

The connection comes because the J-aggregate (in the model) is also 1-dimensional and is of finite extent. The analogy is completed by recognizing that the length of the box, $L$, for the J-aggregate is $L = (N+1)d$, where $d$ is the spacing between dye molecules and the position of any molecule along the J-aggregate is $x = nd$, $n = 1, 2, \ldots N$. 

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Just like for a single emitter, the optical properties of the J-aggregate depend on the matrix element for the transition dipole moment. The dipole moment operator for the collection of molecules can be represented as [31]:

\[
\hat{P} = \mu_0 \sum_{n=1}^{N} \left( |\Psi_n^1\rangle \langle \Psi^0 | + |\Psi^0 \rangle \langle \Psi_n^1| \right)
\]

Where \( \mu_0 \) is the transition dipole of a monomer. Then the dipole moment from an excited state of the J-aggregate to the ground state is [31]:

\[
\mu_{g,k} = \mu_0 \sqrt{\frac{2}{N+1}} \sum_{n=1}^{N} \sin \left( \frac{k \pi n}{N+1} \right)
\]

Using trigonometric identities, the dipole moment can be rewritten in closed form as [31]:

\[
\mu_{g,k} = \mu_0 \sqrt{\frac{2}{N+1}} \left( \frac{1 - (-1)^k}{2} \right) \cot \left( \frac{k \pi}{2(N+1)} \right)
\]

This expression shows that the oscillator strength \( \sim |\mu_{g,k}|^2 \) is distributed over all the even function envelopes \((k = 1, 3, 5, \ldots)\), but mostly is concentrated in the \( k = 1 \) to ground state transition, which is consistent with the initial qualitative picture derived from the two molecule case. This distribution of oscillator strength explains why the J-aggregate absorption peak is significantly red-shifted relative to the monomer, \( \hbar \omega_j = \hbar \omega_m - 2|J| \), typically 50 nm to 60 nm, and also why the absorption spectrum tails out asymmetrically towards higher energy. For large \( N \) [31]:

\[
\mu_{g,k=1}^2 \rightarrow 8(N+1)\mu_0^2/\pi^2 \approx 0.81(N+1)\mu_0^2
\]

This means that even when a single excitation is created on the J-aggregate it will radiate approximately \( N \) times faster than a single monomer. The J-aggregate is therefore super-radiant, by virtue of the dipole-dipole coupling. Numerous molecules participate when a J-aggregate absorbs a photon and the exciton created on the J-aggregate is shared or delocalized over the molecules that form the coupled oscillator state [33].

Although the oscillator strength increases like \( N \), the energy level of the J-band is independent of \( N \) for large \( N \) as captured in the expression: \( \hbar \omega_j = \hbar \omega_m - 2|J| \). This independence is the result of the dipole-dipole coupling interaction being very short range. To a very good approximation, only nearest neighbor molecules affect the shifted new energy levels which is captured in the "\(-2|J|\)" term.

The model of the dipole-dipole coupling in J-aggregates is to be contrasted with the light-matter coupling interaction when excitons are strongly coupled to the vacuum electric field in a microcavity. There the energy level splitting goes like \( \sqrt{N} \) even for large \( N \) because all \( N \) excitons that are in the modal volume of the cavity interact with the
electric field (the extent of which depends on location within the cavity). The interaction
distance is much longer range on the order of $\lambda$, i.e. 300 nm to 600 nm, for light matter
coupling, compared to $\sim 1$ nm for the dipole-dipole coupling in J-aggregates. In light
matter coupling, a molecule couples to its image dipole which is located $\lambda/2$ away ($\sim 300$

nm). In a J-aggregate, a molecule couples to another molecule which is only $\sim 1$ nm
away. Not surprisingly, the interaction amongst dipoles in a J-aggregate is much stronger
than the light matter coupling strength observed for a single molecule. Nevertheless,
strong coupling of light and matter is similar to strong dipole-dipole coupling in a
J-aggregate in that for $N$ excitons in a microcavity, the square of the total transition dipole
moment is proportional to: $\mu_{\text{tot}}^2 = N\mu^2_0$.

It is also interesting to note that in the J-aggregate, the dipole moments of the dye
molecules do not add, which would have yielded $|\mu_{\text{tot}}|^2 \propto N^2$. This means that the
oscillators are coupled but not coherently coupled so as to be in phase in a classical sense.
Earlier in defining oscillator strength, the connection was made between $|\mu|^2$ and variance
of a charge distribution. Thinking statistically, if $\bar{x}_i$ represents a single dipole with
$Var(\bar{x}_i) = |\mu|^2$, then the variance of a sum of dipoles equals the sum of the variances of
the individual dipoles:

$$Var(\sum \bar{x}_i) = \sum Var(\bar{x}_i) = N|\mu|^2$$

Because oscillator strength is conceptually a variance, the total oscillator strength is
proportional to $N$ and not $N^2$.

The linear chain model also explains the narrowed spectrum of the J-aggregate absorption
band. The linewidth can be decomposed into homogeneous and inhomogeneous
broadening. Higher oscillator strength means the radiative pathway will compete $N$
times better against the non-radiative pathways. This means that the homogeneous
linewidth of the J-aggregate is actually $N$ times broader than the linewidth of a monomer.
However, most of the observable width in the monomer and J-aggregate absorption bands
is due to inhomogeneous broadening, i.e. the variation of the energy levels of the $N$
coupled dye molecules. In that case, if the monomer exciton transition frequency is $\omega_m$
with error $\Delta\omega_m$ (FWHM), the spread in the average energy $\langle \omega_m \rangle$ is statistically reduced
to $\Delta\omega_m / \sqrt{N}$, which is the energy spread seen by the J-aggregate since it involves all
$N$ molecules simultaneously. The linewidth of the J-aggregate absorption band is
therefore $\Delta\omega_j = \Delta\omega_m / \sqrt{N}$ [34].

The linewidth expression can also be inverted to yield an estimate of the size of the J-
aggregate involved in the coupling [34]:

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\[ N = (\Delta \omega_M / \Delta \omega_J)^2 \]

With typical numbers for \( \Delta \omega_M = 40 \text{nm} \) and \( \Delta \omega_J = 10 \text{nm} \), a typical size J-aggregate is \( N = (40 \text{nm} / 10 \text{nm})^2 = 16 \). The physical size of the J-aggregate may be much larger, but only 16 molecules cooperate in the molecular dipole coupling. Using \( N = 16 \), if the radiative lifetime of the monomer is 1 ns, then the radiative lifetime of the J-aggregate becomes 63 ps, and if the monomer were 6\% PL quantum efficient, then assuming no change in the non-radiative decay rate, the J-aggregate would be 50\% PL quantum efficient.

Similarly, the Frank-Condon shift is reduced perhaps because each dye molecule nuclear rearrangement is \( 1/N \) of what it was before. If the monomer shift is 32 nm, then for \( N = 16 \), the J-aggregate Frank-Condon shift is 2 nm, which appears consistent with experiment.
3.4 J-aggregates in Thin-Film

3.4.1 Background

J-aggregate thin films are commonly formed using one of three techniques: Langmuir-Blodgett, spin-casting in a polymer matrix, and layer-by-layer (LBL) deposition.[35-37] The last technique is the newest, having first been reported by Fukumoto and Yonezawa in 1998. To form J-aggregates in thin film, dye molecules (while in solution) are brought in contact with a crystalline substrate like mica or with a polymer template that has highly polar constituents. These deposition techniques take advantage of the electrostatic attractive sites on the monomer to concentrate dye molecules with the proper alignment. The two general strategies for aligning cyanine dye using polymers are to disperse the dye into a suitable polymer host matrix or deposit the dye on top of the surface of a polyelectrolyte monolayer via the dip-coating method developed by Fukumoto and Yonezawa [38]. A common method is to mix dye in a poly vinyl alcohol (PVA) matrix, and spin cast the composite into a thin film [36]. PVA is semi-crystalline and forms very strong hydrogen bonds to the nitrogen groups of the cyanine dye. The cyanine dye can also be dispersed in semi-crystalline aromatic polymer matrix and then the solution heat cycled to nucleate the J-aggregate formation [39, 40]. In the dip-coating technique, a monolayer of cationic polyelectrolyte such as PDAC (poly-diallyl-dimethyl-ammonium chloride) is adsorbed onto the substrate and then in a second dip cycle, a monolayer of cyanine dye with an anionic lumophore like TDBC is adsorbed on top.

3.4.2 J-aggregates via Dip-Coating

For the purpose of realizing strong coupling at room temperature, the LBL deposition method is adopted for forming thin films of J-aggregates [41]. This decision is based on the following considerations. In general, analysis indicates that LBL J-aggregate thin films combine high absorption with low optical scattering and nanometer-scale thickness control [42]. Specific considerations relating to strong coupling are as follows. Using the dip-coating technique, a large number of bi-layers of polyelectrolyte and J-aggregate could be stacked together [38] to provide the absorption strength required to achieve a given Rabi-splitting. It could also be possible to layer several J-aggregating dyes together [43]. Given sufficient time to nucleate, monolayers of J-aggregate could form with no detectable monomer signature. These monolayers can potentially assemble as single crystal [27] possessing much greater translational symmetry than in amorphous systems [44], which is considered an important precondition for making the exciton photon coupling more coherent. The ability to process the polyelectrolyte and dye layers from separate solutions allows the pH of the dye to be better controlled, which directly affects the degree of aggregation and the photoluminescence quantum efficiency of the J-aggregates.
The LBL deposition method has been an active field of materials science research in the past decade since it was first reported by Decher et al.[37, 45-51]. A basic LBL process consists of dipping a substrate in alternating polycation and polyanion solutions. Substrates undergo sequential immersions in cationic and anionic solutions (SICAS) in order to build up a thin film, one layer of polymer at a time. The polycations and polyanions can be either strong or weak: strong polyelectrolytes are not pH sensitive, whereas the charge on weak polyelectrolytes depends on the pH of the solvent. The substrates are rinsed between immersions in the polyelectrolytes in order to remove excess polymer. Prior to the deposition, the substrate must be prepared in some manner that allows the first adsorption step to occur.

While the LBL process was developed initially using polyelectrolytes as both of the charge carrying constituents, further work in the 1990s showed that one of the polyelectrolytes could be replaced by a dye molecule or other small, charged component [51]. The only requirement of the charged component was that enough of the component adsorb in the LBL process to reverse the charge on the surface of the substrate. Fukumoto and Yonezawa showed that, by using J-aggregating cyanine dyes as one of the charged components, thin films of J-aggregates could be built using the LBL process [37]. A schematic of the charge reversal and dye double layer formation is depicted in Figure 3-3. The aggregation of the dye molecules, which results in the charge reversal, is likely the result of the dye attempting to shield the hydrophobic poly-methine bridge portion of the “backbone” from the aqueous environment.

Figure 3-3 Representation of charge reversal and dye double layer formation in the LBL process developed and described by Fukumoto and Yonezawa. The aggregation of dye molecules results in charge reversal allowing for multilayer assembly. The aggregation of dye shields the hydrophobic poly-methine bridge “dye backbone” from the aqueous environment.
The dye chosen for demonstrating polaritonic devices and realizing strong coupling at room temperature is TDBC. It is fluorescent even as a monomer, readily forms J-aggregates at ultra low concentrations ($<10^{-5}$ M in water) and has been studied in the photographic industry as a membrane potential sensitive dye, and for its rich exciton dynamics [52-58].

A schematic of a typical LBL PDAC/TDBC film grown on glass is shown in Figure 3-4, along with the structural formulas of the film constituents. First, a glass substrate is treated with oxygen plasma to provide a negative surface charge and undergoes multiple immersions in cationic PDAC and anionic TDBC. Then, to assemble a bi-layer, the substrate is immersed in 20% (w/v) PDAC solution in deionized water (DI) for 15 min, and then rinsed 3 times with DI (2, 2, and 1 min) to remove all but the first monolayer of PDAC. The substrate is then immersed into 50 µM TDBC solution for 15 min, followed by three additional rinses (2 min, 2 min, and 1 min) to remove excess dye. The process is repeated to assemble multiple bi-layers. Often, the pH of the dye solution is raised to pH = 9.0 (using aliquots of sodium hydroxide) to promote J-aggregation in the growth solution. Also, the step time in the PDAC and TDBC solutions is often decreased from 15 minutes to 5 minutes.

![Layer of PDAC/TDBC](image)

**Figure 3-4** Layer-by-layer (LBL) J-aggregate thin film layer constituents. LBL J-aggregate thin films are grown on glass using the polycation PDAC and the anionic, J-aggregating cyanine dye TDBC. Optical measurements are taken with the LBL-film side of the sample facing the light beam at a specified angle $\theta$ away from the normal [42].

LBL PDAC/TDBC J-aggregate films, when grown on glass, possess remarkable morphological properties, including a layered structure which allows for nanometer-scale thickness variation. These properties are revealed through atomic force microscopy (AFM), which also allows one to gauge the film thickness for optical analysis. Figure 3-5 shows the evolution of thin film morphology as substrates undergo increasing numbers of SICAS.

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Figure 3-5 Atomic force microscope (AFM) images of LBL PDAC/TDBC J-aggregate growth with histograms of thickness frequency. Each SICAS consists of a PDAC adsorption step followed by a TDBC adsorption step. N.5 SICAS refers to N SICAS followed by an additional PDAC adsorption step. The AFM images show samples that underwent the indicated number of SICAS. The top three images show that significant PDAC/TDBC layered growth is not evident until 2.0 SICAS. The bottom three images show the build-up of thick layers. The histograms are lined up at the dominant film thicknesses to show that each layer is about 1.7 nm thick, which is the thickness per layer used when modeling the optical constants of the films. The histograms are created from the full 1 μm² and 16 μm² images for the first three and last three films shown, respectively. The layer numbers indicated in the histograms are based on the progression of layer growth observed in the AFM images. The plot shows the roughness profile of films from 3.5 to 10.5 SICAS. At 6.5 SICAS, the dominant growth regime changes from layered to Stransky-Krastanov (SK) type. All images have a vertical scale of 50 nm [42].

As indicated by the 1.5 SICAS and 2.0 SICAS AFM images in Figure 3-5, the surface treatment of a substrate can have significant effects on the build-up of the first few layers in an LBL process. The layered structure of the LBL PDAC/TDBC films does not appear until after the second dye immersion, likely in part due to using oxygen plasma as a surface treatment as opposed to functionalizing with other molecules. Another notable feature of the film growth progression shown in Figure 3-5 is the increase in roughness in the 6.5 and higher SICAS samples. This increase suggests a range in which LBL J-aggregate thin films can be grown without significant roughness and with nanometer-scale thickness control.

The optical properties of the LBL J-aggregate thin films shown in Figure 3-4 can be analyzed through reflectance and transmittance measurements together with film thickness estimates provided by AFM measurements. From this data, the optical constants of the thin films can be calculated. Various methods can be used to obtain the complex index of refraction of the thin film ($\tilde{n} = n + j\kappa$), which is related to the linear thin film absorption constant by the formula $\alpha = 4\pi\kappa(\lambda)/\lambda$. Two such methods were discussed in a previous study [42].

Generally, some of the most reliable $(n,\kappa)$ values are derived by fitting optical data to a model that is compatible with the constraints of the Kramers-Kronig relations. The Kramers-Kronig relations are based on the causality of an optically excited system. Causality implies that the linear dielectric function, and therefore the complex index of refraction, is analytic on the upper complex frequency plane. This condition allows for the application of Cauchy’s Theorem, which in the end results in a relation between the real part of the index of refraction, $n$, and the imaginary part (extinction coefficient), $\kappa$ [59]. Ultimately, to be exact, the Kramers-Kronig relations require integration to infinite frequency, for which data collection is impossible. Therefore, the contributions outside of the measured frequency range are frequently lumped into a background index of refraction. One of the resulting approximations of the Kramers-Kronig relations is shown in the following equation for $n(\omega_j)$ [60]:

$$n(\omega_j) = n_{\text{offset}} + \frac{2}{\pi} P \int_{\omega_j}^{\omega_u} \frac{\omega\kappa(\omega)}{\omega^2 - \omega_j^2} d\omega, \quad \omega_k \leq \omega_j \leq \omega_u$$
\( n_{\text{offset}} \) refers to the lumped background index due to contributions from outside the measured frequency range, \( \omega_L \) to \( \omega_U \), and \( P \) signifies that the integral is the Cauchy Principal value. This expression can be used in a model-free Kramers-Kronig regression algorithm as proposed by Nitsche and Fritz [60]. The advantage of such an algorithm is that it requires no initial model and instead determines the \((n,K)\) that match the optical data provided. Frequent use is made of the model-free Kramers-Kronig regression algorithm in analyzing LBL J-aggregate thin films. The results of one such analysis are shown in Figure 3-6 along with the optical reflectance and transmittance data used to perform and verify the regression. The peak value of \( \kappa \) from the analyzed sample corresponds to an absorption constant of nearly \( 10^6 \) cm\(^{-1} \) (at wavelength \( \lambda = 593 \) nm, \( \kappa = 4.5 \), hence \( \alpha = 4\pi \kappa \lambda = 0.96 \times 10^6 \) cm\(^{-1} \)) [42].

Figure 3-6 Optical data and characterization of optical properties for LBL PDAC/TDBC J-aggregate films. Plots (a) and (b) show reflectance at \( \theta = 70^\circ \) and transmittance at \( \theta = 0^\circ \) for a series of samples that underwent different numbers of SICAS. Plot (a, inset) shows the FWHM of the reflectance peak as a function of the number of SICAS. Plot (c) shows measured reflectance and transmittance for 4.5 SICAS (5.1 nm thick film, 3 layers with 1.7 nm per layer) and calculated spectra using the \((n,K)\)
shown in Plot (d). Plot (d) shows \((n,\kappa)\) for the 4.5 SICAS film in (c) obtained through a Kramers-Kronig (KK) regression based on the reflectance data [42].

Aside from the high peak thin film absorption constant, LBL films of PDAC/TDBC have other notable optical properties as indicated by Figure 3-6. The reflectance data shown in Figure 3-6a indicate that as thicker films are grown, the full-width at half-maximum (FWHM) of the reflectance band increases, potentially indicating the onset of a superradiance effect observed with inorganic semiconductor quantum well stacks [61] or increased inhomogeneous broadening of the J-aggregate resonant peak. This linewidth growth is examined in greater detail in Chapter 9. Additionally, the higher energy feature that is visible in the transmittance data in Figure 3-6b, as discussed in our previous study, may be due to a J-aggregate vibronic level [42], residual monomer or the onset of the upper branch of a bulk-polariton mode. As the thickness of a thin film of strongly coupled molecules grows, the excitonic optical properties change from super-radiant excitons to radiationless bulk-polariton crystal [62]. In subsequent chapters and experiments, the film thickness is always kept very much less than \(0.37\lambda\) (\(\lambda \sim 595\) nm), the crossover point from super-radiant to radiationless in Knoester's analysis [62]. Hence, the LBL films for used for strong coupling are treated as being in the super-radiant limit.

The good agreement of the calculated fits in Figure 3-6c with the measured data, besides indicating the accuracy of the Kramers-Kronig-derived \((n,\kappa)\) values, also shows that there is remarkably low scattering in the 4.5 SICAS film. Scattering would be particularly noticeable in the correspondence of the calculated to the measured transmittance since the Kramers-Kronig regressions for these films were based on reflectance data, which would not be as affected by scattering as transmittance data.

Further evidence that the increase in the FWHM of the J-aggregate reflectance peak is in part due to a superradiance effect can be seen as thicker LBL J-aggregate films are formed. Figure 3-7 shows the reflectance of a 6 SICAS PDAC/TDBC compared to that of a 31 SICAS film along with photographs of the 31 SICAS film. The 31 SICAS reflectance shows that as the reflectance saturates, two resonant peaks appear, which suggests that two resonances may have been produced by the coupling of the photons of the weak cavity of the thick film to the excitons of the J-aggregates in the film. It may also suggest the crossover point discussed by Knoester [62]. The 31 SICAS film is about 50 nm thick. In the context of Knoester's metric, at \(\lambda = 595\) nm, \(0.37\lambda = 220.2\) nm. If this number is scaled by the background refractive index \(n = 1.7\), then the metric \(0.37\lambda/n = 129.5\) nm. If instead it is scaled by the peak \(n = 4.25\) of Figure 3-6d to account for dispersion effects in the film, the metric works out to be \(0.37\lambda/n = 51.8\) nm. This value is close to the thickness of the 31 SICAS film, indicating the reflectance doublet signifies the onset of the bulk polariton regime.
Figure 3-7 Reflectance measurements of a 6 SICAS and 31 SICAS PDAC/TDBC LBL J-aggregate thin film on glass. The 31 SICAS reflectance shows that broadening of the FWHM eventually leads to the appearance of two resonant peaks in reflection, suggesting that the broadening of the FWHM is due in part to polaritonic effects caused by the formation of a weak cavity in the LBL J-aggregate thin film. The inset photographs show the 31 SICAS film in transmission and reflection, exhibiting the strong reflectance around $\lambda = 595$ nm.

The photoluminescence (PL) of PDAC/TDBC J-aggregate thin films exhibits a narrow FWHM and small Stokes’ shift from the absorption, as shown in Figure 3-8. The small Stokes’ shift is important for use of such films in strong-coupling since a large Stokes’ shift will contribute to the dephasing of the strongly coupled states.
3.5 Conclusion

The matter component used to achieve strong coupling at room temperature are nanoscale SICAS assembled thin films of J-aggregated dye. The dye selected is TDBC. The deposition technique was originally developed by Fukumoto and Yonezawa for other J-aggregating cyanine dyes. TDBC is used because of its high absorption coefficient, narrow linewidth, ability to J-aggregate at ultra low concentrations, and high quantum yield. The optical and morphological properties of thin films of PDAC/TDBC are characterized in detail using AFM, and transmission and reflection measurements. The complex refractive index is modeled using KK regression, and the peak absorption coefficient for a 4.5 SICAS film was determined to be $\alpha = 0.96 \times 10^6 \text{ cm}^{-1}$. 

Figure 3-8 Photoluminescence (PL) of a LBL PDAC/TDBC J-aggregate thin film from excitation at $\lambda=500$ nm. An absorbance measurement from the same film is shown. Absorbance is defined as $\log_{10}(1/T)$, where T is the measured transmittance. The two plots show the small Stokes’ shift of the LBL PDAC/TDBC film and narrow FWHM of the PL.
4 Rabi-Splitting in a Metal-Mirror Low Q Microcavity

“If I fail, I’m not going down without the fight of my life.” (My feeling when the only thing working was me.)

“I’ve come too far!” (What I shouted in lab, when the Polariton RC-OLEDs still showed no sign of Rabi-splitting, even after switching to dip-coating.)

Anecdotal Introduction:

One night, I had just completed testing yet another round of very low efficiency PVA-based J-aggregate OLEDs. I decided then on my way back to the office that if J-aggregate OLEDs were going to be good for something, it had better be related to strong coupling, because that’s what differentiated the material set. I was walking from 26-lab back to Building 13, when I met Vladimir and Aimee Rose in the hall, on their way to test lasing of TNT sensitive fluorescent polymers. Vladimir asked how the OLEDs were going, and that’s when I told him the only J-aggregate OLEDs that I thought were worth building were ones for strong coupling. He said to do that. First, Vladimir thought we could just put the same OLED structure between two mirrors, demonstrate Rabi-splitting, and then apply voltage. It was a sound approach, and to a degree it worked. The PVA based J-aggregate films finally did show Rabi-splitting, after reoptimizing the spin-conditions for the film, and results were similar to David Lidzey’s. The only problem was that when I tried to use those films in J-aggregate OLEDs, the devices didn’t turn on.

Soon after, I started been working on ion-exchanging the iodide to chloride to make the TTBC salt more water-soluble. I knew part of the difficulty with the J-aggregate OLEDs was simply that the dye precipitated before the film could be cast. I was using PIC as my test dye for doing the ion-exchange chemistry, a procedure that the chief scientist of American Dye Source, Dr. Nguyen, gave me over the phone. One night in lab, shortly after adding HCl to the DMF solution, I noticed a large pool of water overtaking the floor of the lab. I called the office for all to help cleanup. Even Vladimir came. When mopping the floor he looked to the corner of the lab at the dip-coater, which had been idle since I purchased it and asked if I was ever going to use it. The idea of dip-coating devices was a pipe-dream. It was a dream I had, and until that moment it was pure fantasy. Making devices out of water was simply sacrilege in the OLED world. Of course, to some extent, that’s exactly why the contrarian in me wanted to try it. That night, I finally gained the resolve to follow through. Soon after, I spoke with Vladimir about moving away from PVA. A lot of time had been committed to PVA, yet he was supportive of the switch. He said it would take 2 months to transition, and that turned out to be accurate, despite my incredulity. But in the end, the pudding was edible and the proof was in the eating. As I worked out the dip-coating procedure, the PIC cocktail sat in the hood for weeks, until it was brought to my attention that I had left a flask unlabeled in the hood. To my surprise, the ion exchange had worked astoundingly well and large crystals had formed—easily 3 mm x 4 mm. Evidently, the night of that flood, the dye began to crystallize and as did our thinking...
4.1 Introduction

A first step towards realizing polariton devices that operate in true strong coupling at room temperature is establishing that the selected excitonic material exhibits Rabi-splitting and polaritonic dispersion when coupled to an optical microcavity. To that aim, thin films of PDAC/TDBC SICAS with high absorption coefficient (5.1 ± 0.5 nm thick with $a = 1.0 \times 10^6$ cm$^{-1}$) are assembled in a metal mirror low Q microcavity. Reflectivity measurements are performed at room temperature as a function of cavity thickness and as a function of angle. From the reflectance data, across multiple devices and angle, polaritonic dispersion is established and Rabi splitting is demonstrated, with a coupling strength (Rabi-splitting) of $\Omega_R = 265 \pm 15$ meV.

4.2 Background

When designing a cavity QED device, an important decision is whether to use metal or dielectric materials for the mirror components. Both materials have their strengths and weaknesses in terms of performance. Dielectrics produce the highest reflectivity mirrors, with planar cavity Q's exceeding 5500 [63], but poorly confine light, with light penetrating usually much more than $\lambda/2$ into the mirror structure, depending on refractive index contrast (See Chapter 8.2). Metal mirrors produce the best light-confinement by virtue of their large extinction coefficient but have a maximum reflectance of only about 94.0% (for a thick silver film) at wavelength $\lambda = 620$ nm.

Nevertheless, metals are an effective choice of material for QED experiments and polariton devices where ultra high reflectivity can be “traded” for greater confinement or ease of deposition. A famous example of their use is the work by K. Drexhage on weak coupling cavity QED effects [64]. In 1970, he positioned a monolayer of Europium chelate a variable distance from a silver mirror and measured changes in radiative lifetime and emission wavelength. In terms of strong coupling, Hobson, Barnes, Lidzey, et al. in 2002 demonstrated Rabi-splitting greater than 300 meV when J-aggregate doped PVA films were inserted in an all-metal microcavity consisting of two silver mirrors [65]. They posit that the giant coupling strength is due to the superior light confinement afforded by metal.

Here, the cavity is constructed using metal mirrors instead of dielectrics for the following reasons. The focus of this experiment is the dip-coated PDAC/TDBC, not the microcavity, so a simplified microcavity design is better. Furthermore, using metal mirrors means the device design can also function for an OLED, with appropriate patterning of the metal layers into electrical contacts. Reflectivity measurements on a device exhibiting Rabi-splitting serve as a baseline for determining the presence of strong coupling in the corresponding OLED’s emission. Finally, as mentioned in the paragraph above, metal mirrors provide better light confinement than dielectrics, and therefore yield greater degree of exciton-photon coupling for the same density of excitons, making strong coupling is easier to realize and verify.
4.3 Device Design

The device design used to demonstrate Rabi-splitting is illustrated in Figure 4-1.

As mentioned above, the microcavity consists of two metal mirrors. The “top” mirror, which is the final layer deposited in the device, is a 110 nm thick layer of silver (Ag). As indicated in the simulation of Figure 4-2, such a layer produces reflectivity of approximately 94% at wavelength \( \lambda = 620 \text{ nm} \) \( (E = 2.0 \text{ eV}) \). An additional 10 nm thick layer of magnesium-silver (Mg:Ag) alloy is deposited immediately before the Ag film so the device more accurately baselines the polaritonic dispersion in a resonant cavity OLED (RC-OLED) where the presence of such a layer improves electrical injection into the BCP layer. The “bottom” mirror is a 50 nm thick Ag film, which produces a reflectivity exceeding 90%, according to simulation in Figure 4-2a. Reflectivity measurements are performed with light incident on the “bottom” mirror (substrate) side of the device, by virtue of this layer’s semi-transparency. The cavity spacer layers are a thermally evaporated thin film of BCP and a spin-cast film of Poly-TPD. The refractive indexes of these layers are both \( n \sim 1.7 \) in the wavelength region of interest: \( \lambda = 600 \text{ nm} \).

![Figure 4-1 Low Q Polaritonic device structure consisting of metal-mirror microcavity containing SICAS assembled PDAC/TDBC J-aggregate exciton layer. A 10 nm thick Mg:Ag (50:1) alloy layer followed by thick Ag film acts as high-reflectance “top mirror”. (If part of a resonant cavity OLED, the alloy layer facilitates electron injection.) A semi-transparent 50 nm thick Ag film serves as a “bottom” mirror, allowing for angular reflectivity measurements with light incident from the glass substrate side of the device. A variable thickness spin-cast Poly-TPD layer tunes the microcavity resonance through the exciton resonance of the J-aggregate film.](image-url)

T-matrix simulation of an “empty cavity”, i.e. a cavity with only the \( n = 1.7 \) spacers and mirror layers is depicted in Figure 4-2b. When the combined thickness of the spacer layers equals 123 nm, a resonant dip in reflectance is produced at wavelength \( \lambda = 586 \text{ nm} \). The FWHM of this dip is 31 nm, yielding a cavity \( Q \sim 18.9 \) \( (Q = \lambda / \Delta \lambda = 586 / 31) \). It should be emphasized that this resonant dip corresponds to a “\( \lambda/2n \)” cavity. Although
for \( \lambda = 586 \text{ nm} \) with an \( n = 1.7 \) spacer, a total thickness of 172 nm might be expected for a "\( \lambda/2n \)" cavity, in actuality a 123 nm thick layer is sufficient because of optical field penetration into the metal layers (The plots of reflectance vs. thickness in Figure 4-2a also show this penetration.)

![Figure 4-2 Linear optical properties of metal layer and optical cavity. (a) Reflection, Transmission, and Absorption for a metal layer as a function of thickness. Calculations performed for silver, gold, and aluminum, which are typical mirror materials, at \( \lambda = 620 \text{ nm} \) (E = 2 eV). Parameters, (\( n, k \)) are incorporated into a T-matrix model of the film. (b) T-matrix simulation of reflectance of a microcavity consisting of "bottom" 50 nm Ag mirror, transparent spacer of refractive index \( n = 1.7 \) and thickness \( L = 123 \text{ nm} \), and "top" 120 nm Ag mirror. The cavity produces a resonant dip in reflectance at \( \lambda = 586 \text{ nm} \) with a FWHM = 31 nm.

The matter component of the device is a 5 ± 1 nm thick film of J-aggregated dye consisting of 4.5 SICAS of cationic polyelectrolyte PDAC and J-aggregates of the anionic cyanine dye TDBC.
4.4 Experimental Methods

The experimental methods used here to establish that the devices exhibit polaritonic dispersion consist of varying the photon energy and observing the impact on the eigenmodes of the exciton-photon composite system. The photon energy is directly changed by adjusting the thickness of the microcavity. For a $\lambda/2n$ cavity with idealized reflectors, the resonant (standing) wavelength of the cavity is given by:

$$\lambda_{\text{cav}} = 2nL$$

Where $L$ and $n$ are the length and refractive index of the cavity spacer layer separating the reflectors. Hence, changes in cavity length lead to proportional changes resonant wavelength:

$$\Delta \lambda_{\text{cav}} = 2n\Delta L$$

And with $n \sim 1.7$, the proportionality constant is $2n = 3.4$. A precise relationship between cavity thickness and resonant photon energy is established through a T-matrix simulation. For an “empty” cavity, consisting of no J-band absorption, Figure 4-3a shows how the resonant dip in reflectivity (%R) varies as a function of cavity thickness (D). The wavelength position ($\lambda$) of the reflectivity dip changes linearly with D, as expressed in the equations above and as illustrated in Figure 4-3b.

![Figure 4-3](image)

**Figure 4-3** Results of T-matrix simulation for “empty” $\lambda/2n$ metal-mirror microcavity. (a) Reflectivity vs. Wavelength ($\lambda$) as a function of spacer layer thickness (D). (b) Two dimensional rendition of (a) with resonant dip in reflectance corresponding to blue line in plot. Resonance of $\lambda = 586$ nm corresponds to $D = 123$ nm.

Experimentally, the cavity thickness is varied by changing the thickness of the Poly-TPD layer. This layer is varied instead of BCP for process considerations. The Poly-TPD film is spin-cast instead of thermally evaporated. The spin-casting method allows the
thickness to be adjusted by simply reprogramming the spin-coater recipe, which takes about 1 minute, compared to evaporating a different thickness BCP film, which takes more than 20 minutes for each film. Several substrates can be processed within minutes, and the remainder of the device layers fabricated on all the substrates simultaneously.

In order to insure that the thickness is being varied over a meaningful range, a spin-curve measuring thickness as function of spin-speed was generated for a fixed concentration of 15.3 mg/ml Poly-TPD in chlorobenzene. All films were spun at 10,000 rpm/sec acceleration and all thickness measurements were carried out by profilometry on films spun on glass substrates (using P10 Tencor Surface Profiler). It was determined (Figure 4-4) that by varying spin-speed between 1000 to 2250 rpm (in 250 rpm steps), the thickness could be adjusted from 45 nm to 65 nm. Hence for a typical device, the spacer and PDAC/TDBC layers total a thickness of between 112 nm to 135 nm thick.

![Figure 4-4 Spin curve for Poly-TPD to determine film thickness as a function of spin speed, for a concentration of 15.3 mg/ml Poly-TPD in chlorobenzene spun at an acceleration of 10,000 rpm/s. The second order polynomial fit is displayed in the figure, with an $R^2$ of 99.7%.](image)

Experimental techniques used to assemble the remaining layers are discussed in Chapter 5 on J-aggregate OLEDs.

For any single device and device-thickness, a second experimental method is used to extract a value for the Rabi-splitting. This method consists of measuring reflectance as a function of angle, and observing the change in eigenmodes of the exciton-photon composite system.
4.5 Experimental Set-up

Reflectance measurements were performed using a Cary 5E UV-Vis-NIR spectrophotometer using the following two accessories. Absolute reflectance measurements were taken using the Specular Reflectance Accessory (SRA) with light incident on the sample at $\theta = 7^\circ$ from normal (See Figure 4-1 for "working definition" of $\theta$). Angular reflectance measurements are taken with the Variable Angle Specular Reflectance Accessory (VASRA) with $\theta$ varying from 20° to 70°. With the SRA, data were taken in "in a V-W setup" with the instrument set to "Absolute Reflectivity" mode. With the VASRA, incident light was TE-polarized and individual baseline scans were taken at each angle. For the baselines, an aluminum coated glass microscope slide served as a best approximation of broadband "perfect 100%" reflector.
4.6 Results and Discussion

Figure 4-5a plots the normal mode reflectance for a series of microcavities with different thickness Poly-TPD layers ranging from 42 nm to 65 nm thick. In each of the spectra, two resonant dips are evident, one each at energies that are higher and lower than the energy of the uncoupled J-aggregate exciton resonance, $E_{ex}$. These resonant dips correspond to the resonances of the combined metal-microcavity PDAC/TDBC system. The depths of the two dips depend on the thickness of the microcavity. In the thickest sample, with Poly-TPD thickness of 65 nm, the lower energy dip is more pronounced than the higher energy one, while in the thinnest sample, with Poly-TPD thickness of 42 nm, the higher energy peak is more pronounced. For the sample with the intermediate Poly TPD layer thickness of 54 nm, the reflectance dips appear almost equal in depth.

From a plot of the resonant dips vs. bare photon energy a dispersion relation is created. In Figure 4-5b, a dispersion relation is constructed from these resonant dips. The energy positions of the resonances are plotted as a function of the “empty cavity” bare photon energy, i.e. the simulated position of the resonance of the cavity sans J-aggregate excitonic layer. From these data, it is appears that the resonances of the coupled system anti-cross and exhibit oppositely signed curvature.

The data is fit to the standard two level model of strong coupling, where polaritonic eigenstates with energy levels, $E_{\pm}$, are separated from the uncoupled exciton and photon energy levels, $E_{ex}$ and $E_{ph}$, respectively by:

$$E_{\pm} = \frac{E_{ex} + E_{ph}}{2} \pm \frac{1}{2}\sqrt{\left(\hbar\Omega_R\right)^2 + \left|E_{ex} - E_{ph}\right|^2}$$

The energy separation, $E_+ - E_-$, is dependent on the degree of energy matching between the exciton and photon modes, and has a minimum of $\hbar\Omega_R$ when the exciton and photon are resonant, $E_{ex} = E_{ph}$. The dependence of polariton energy levels $E_{\pm}$ on $E_{ph}$ described by this equation is evidenced in the dispersion relation of Figure 4-5b. As the Poly-TPD layer thickness is varied from 65 nm to 42 nm, $E_{ph}$ is tuned between 1.98 eV and 2.26 eV, spanning the energy range that encompasses the J-aggregate exciton resonance, $E_{ex} = 2.08$ eV ($\lambda_{ex} = 595$ nm). As a result, the energy separation between resonant dips in reflectivity varies from more than 300 meV (Figure 4-5b), when the exciton and photon are far off-resonance to a minimum of $\hbar\Omega_R = 265$ meV, when $E_{ex} = E_{ph}$, which corresponds to a Poly-TPD layer thickness of 56 nm.

Agreement between the strong coupling model and the normal mode reflectance data confirms that the PDAC/TDBC films enable strong coupling to be realized.
Figure 4-5 Normal mode reflectance spectra for a series of polaritonic structures with different Poly-TPD spacer thickness and hence different microcavity resonance. The empty cavity resonance is tuned across a 250 meV band, by adjusting the thickness of the Poly-TPD layer from 42 nm to 65 nm.

(a) Reflectivity at $\theta = 7^\circ$ for a series of polaritonic structures taken with SRA. Data of successive measurements are offset by 50 percentage points.

(b) Polaritonic dispersion relation. Resonant dips in reflectivity (solid data points) plotted as a function of the bare (cavity) photon energy exhibit anticrossing. Fits are generated by the two-state model of Chapter 2, with a Rabi-splitting of $\hbar \Omega_x = 265$ meV. Uncoupled bare exciton and photon lines are displayed as a guide to the eye. The right vertical-axis plots the energy separation between the fit generated $E_+$ and $E_-$ resonances ($E_+ - E_-$). The minimum separation obtained is Rabi-splitting $\hbar \Omega_x = 265$ meV, which occurs at cavity tuning of approximately 2.08 eV ($\lambda \sim 595$ nm).
To further confirm the existence of strong coupling, reflectance spectra are analyzed as a function of angle for the coupled structures. In Figure 4-6, VASRA data is plotted for the devices with Poly-TPD thickness of 54 nm (a) and 59 nm (b). These samples are chosen because they correspond to tuning conditions close to the point of matching between exciton and photon resonance. The uncoupled bare cavity photon resonance of the device in Figure 4-6a is at $E_{ph}(\theta = 0^\circ) = 2.11$ eV and at $E_{ph}(\theta = 0^\circ) = 2.05$ eV, for the device in Figure 4-6b. The differences in microcavity tuning are evident in the reflectance spectra. For instance, at $\theta = 70^\circ$, the higher energy reflectance dip appears at a higher energy for the device in Figure 4-6a than for the device in Figure 4-6b.

![Figure 4-6 Angularly resolved reflectance measurements for the polaritonic structures of Figure 4-1.](image)

(a) Device with Poly-TPD thickness of 54 nm, with $E_{ph}(\theta = 0^\circ)=2.11$ eV. (b) Device with Poly-TPD thickness of 59 nm, $E_{ph}(\theta = 0^\circ) = 2.05$ eV. Uncoupled bare photon energy is depicted by green dashed line in the plot. Reflectance measurements are taken in 5 degree increments from $\theta = 20^\circ$ to $70^\circ$. The data for $\theta = 20^\circ$ is offset by 50 percentage points to distinguish it from the $\theta = 7^\circ$ data taken with the SRA. Values for successive angles are offset by an additional 25$^\circ$ increment. The reflectivity at $\theta = 7^\circ$ of a 4.5 SICAS PDAC/TDBC film, is shown for comparison.
From the reflectance data, angular dispersion relations are generated for the coupled systems that again display the characteristics of strong coupling. As a function of angle \( \theta \), the energy positions of the resonant dips are plotted in Figure 4-7. Again, the resonances fit to the two-state model of strong coupling used above, with modification made to account for the \( \theta \) dependence of \( E_{ph} \).

Figure 4-7: Angularly resolved polariton dispersion relations in (a) and (b) for polaritonic structures with Poly-TPD thicknesses of (a) 54 nm and (b) 59 nm respectively. Resonant dips in reflectance are derived from spectra of Figure 6 and are plotted as a function of angle. Dispersion relations are generated assuming two-state model with bare exciton energy \( E_{ex} = 2.08 \text{ eV} \). In (a) the bare (empty cavity) photon energy \( E_{ph}(\theta = 0^\circ) = 2.11 \text{ eV} \) and in (b) \( E_{ph}(\theta = 0^\circ) = 2.05 \text{ eV} \). For both fits, the same angle independent coupling interaction is used, a Rabi-splitting of \( \hbar \Omega_k = 265 \text{ meV} \).

For an uncoupled "bare" cavity, the photon resonance, as a function of \( \theta \) is given by [2]:

\[
E_{ph}(\theta) = E_0 \left(1 - \sin^2 \theta/n^2 \right)^{-1/2}
\]

Where \( E_0 \) is the "empty" cavity bare photon resonance at \( \theta = 0^\circ \) and \( n \) is the refractive index of the cavity spacer layers. (For the devices here, with \( n = 1.7 \) for the Poly-TPD and BCP layers, \( E_{ph} \) increases by 23% as angle is increased from \( \theta = 0^\circ \) to \( \theta = 80^\circ \)).

This angular dependence means the polaritonic energy levels in the two-state model become functions of \( \theta \), with \( E_z \rightarrow E_z(\theta) \). Figure 4-7 plots the calculated dispersion relations for the polariton states \( E_z(\theta) \). The same value for the vacuum Rabi splitting, \( \hbar \Omega_k = 265 \text{ meV} \), used to fit the normal mode data of Figure 4-5 is applied to fit the
angular data of both devices, with Poly-TPD layer thickness of 54 nm and 59 nm in Figure 4-7a and Figure 4-7b respectively. The only difference between the fits is the value for the parameter $E_0$, 2.11 eV and 2.05 eV, in Figure 4-7a and Figure 4-7b respectively. Figure 4-7 plots $E_{ph}(\theta)$ in addition to the polariton dispersion relations, $E_z(\theta)$, to emphasize this point. In Figure 4-7a, the cavity photon mode is slightly over-tuned relative to the J-aggregate resonance, while it is slightly under-tuned in Figure 4-7b. In both plots, at $\theta = 0^\circ$, near resonance for $E_{ph}(\theta)$ and $E_{ex}$, the polariton branches of the dispersion relation $E_z(\theta)$ anti-cross in energy, while at larger $\theta$, far away from the resonance condition, they devolve into uncoupled exciton and photon dispersion curves.

Consistent agreement of the reflectance data across multiple devices and collection angles further confirms that these devices are in the strong coupling limit. The resulting dispersion relations are fit with a single value of $\hbar \Omega_R$. Also, the values for $E_0$ in the angular dispersion relation are identical to the values used in the normal mode dispersion relation. Since the same two parameters, $E_0$ and $E_{ex}$, are used to fit two different sets of data, there are no free parameters in the model to explain away the quality of the fits.

Consistency across SRA and VASRA data and different devices with the same fit parameter confirms that the two level model characteristic of strong coupling works to describe the linear optical properties of these devices. This in turn demonstrates that thin films of PDAC/TDBC produce strong coupling even in low Q all metal microcavities.
4.7 Conclusion and Future Work

The coupled system consisting of dip-coated films of J-aggregated TDBC integrated into a low Q all metal optical microcavities exhibits strong coupling at room temperature. Strong coupling is manifest as normal mode splitting in reflectance measurements, and polariton dispersion as a function of tuning $E_{ph}$ through $E_{ex}$. The characteristic dependence of the polaritonic states on $E_{ph}$ is observed both as a function of cavity thickness and in the angular reflectance spectra of the microcavity/bi-layer structures. The polaritonic dips in the reflectance spectra are most balanced and equally pronounced when the microcavity is resonantly tuned near to the TDBC peak reflection wavelength $\lambda = 595$ nm. The observed room temperature Rabi-splitting between exciton-polariton peaks is $\hbar \Omega_p = 265$ meV, an order of magnitude larger than in inorganic quantum well structures, which is a consequence of the high absorption coefficient of the PDAC/TDBC films.

For the coupled structure with 54 nm thick Poly-TPD layer, the reflectance (Figure 4-5) spectrum exhibits two resonant dips at $\lambda = 554$ nm and $\lambda = 625$ nm. In contrast, a thin film of 4.5 SICAS of PDAC/TDBC on glass have a single resonance at $\lambda = 595$ nm (FWHM = 19 nm), and the bare microcavity would produce a resonant dip at $\lambda = 587$ nm. The depth of the resonant dips in reflectance is large because the cavity linewidth effectively matches the overall linewidth of the PDAC/TDBC film’s reflectance.

This structure is designed to act as a resonant cavity OLED (RC-OLED) as well, where correspondence between polariton dispersion observed in the reflectance spectra and RC-OLED emission is used to establish the existence of electrically pumped polariton emission.

Further improvements to the device structure could be made by replacing the silver mirrors with DBRs, which would increase the Q of the resulting cavity and thus reduce dephasing due to losses in the mirrors, and allow for the use of an anode that can better inject holes into the Poly-TPD HTL, such as ITO, which has a higher work function than silver. The trade-off would be a decrease in Rabi-splitting due to reduced modal confinement.
5 J-aggregate Organic Light Emitting Device (OLED)

"If you can make an OLED, then you can make a device" (Vladimir Bulović on importance of being able to make an OLED.)

"What do I have to do to make sure this never happens again?" (My feeling after the N\textsuperscript{th} PVA based J-aggregate failed to turn on)

"Let's imagine doing this totally differently." (My response to the words above.)

Anecdotal Introduction:

In my first year at MIT, after learning about Lidzey’s work on using J-aggregates for producing giant Rabi-splitting at room temperature, the question was could J-aggregates be used as an OLED material. The motivations were straightforward. J-aggregate PL spectra can exhibit linewidths as narrow as 11 nm, about a factor of 3 narrower than a nanocrystal quantum dot (QD). At the time, QD-LED’s hadn’t yet broken the 0.1% external quantum efficiency (EQE) barrier, so it was tempting to consider how J-aggregates might perform as an alternative to conventional OLED materials. Vladimir had pointed out that by aligning the J-aggregate crystallites, a process that had been documented in the scientific literature, a polarized light source could be made that would lead, \textit{ceteris paribus}, to higher power efficiency LCD displays because 50% of the backlight would no longer be wasted through the first polarizer. Another motivation was that in the context of an electrically pumped laser. At the time, there was still great interest in developing a solid-state electrically pumped thin film organic laser, considering Jan Hendrik Schönh had just claimed to have made one. Steve Forrest’s group at Princeton University, which had worked extensively on the problem, had determined run-away polaron losses as the primary process preventing lasing action, and Vladimir hypothesized that with J-aggregate crystallites polaron losses would be smaller than with typical amorphous organic small molecule host-guest electrically pumped laser prototypes. Furthermore, the process of making an OLED that had a respectable EQE was a right of passage not only for the researcher, but for the materials in question. Ultimately, the process of making J-aggregate OLEDs did bear fruit. The final design came about through the influence of Shoshana Gordon who had been a big proponent of dip-coating, and from the reviewer on Seth Coe-Sullivan’s Nature paper, Chihaya Adachi, who brought to the group’s attention that in the early 90’s, he and co-workers had made a “Double-heterostructure electroluminescent device with cyanine-dye bimolecular layer as an emitter”, where the emitter was a J-aggregated cyanine-dye. To date, the best J-aggregate OLEDs built in our group have $\text{EQE} = 0.035\%$, with great prospects for improvement, particularly through the use of energy transfer and more compatible hole-transport materials. More importantly, the process forced a redesign of the J-aggregate layers, which has lead to development of a new class of J-aggregate based polariton devices.
5.1 Introduction

Historically, the “killer” application for J-aggregates has been photographic sensitization of silver halide crystallites [66], and experimentally, these materials have been widely studied for $\chi^{(3)}$ based non-linear optical properties [31] and cell-staining [67], and somewhat for photovoltaics [68]. Only a small number of research groups have reported attempts to utilize J-aggregates as emissive elements in an organic electroluminescence device (OLED) [69-72].

The advantages afforded by J-aggregates are straightforward. J-aggregates exhibit PL spectra with linewidths as narrow as 11 nm, about a factor of 3 narrower than nanocrystal quantum dots (QDs) [73], so color saturation at all viewing angles could be exceptional. J-aggregating cyanine dyes exist with PL spectra in the near infrared (NIR), at wavelengths longer than 800 nm, that could be useful in photonic IR applications, as needed by the military. Chemically, they are organic dye salts that as a general class of fluorophores are very optically and chemically stable materials. Aligning the J-aggregate crystallites to produce polarized light sources could lead to higher power efficiency LCD backlights. These crystallites might also exhibit smaller polaron losses than typical amorphous organic small molecule host-guest emissive layers, because vibrations would be distributed over many molecules and would generally be better damped. In the context of an electrically pumped thin-film organic laser, this would mean that run-away polaron losses preventing lasing action could be arrested. J-aggregate OLEDs could also be integrated into microcavities to form electrically actuated polaritonic devices with low power switching and lasing thresholds.

The challenges presented with using J-aggregate materials are essentially that the dyes must be solution processed and typically combined with a polymeric host matrix that promotes J-aggregation. Moreover, J-aggregation is achieved most thoroughly in aqueous-based solutions, conditions frequently considered fatal for OLED performance. Finally, J-aggregates are very polar organic salts that phase segregate out of most OLED or PLED materials, so interface quality is also an issue to be addressed.

To date, the best J-aggregate OLEDs have EQE = 0.2% [74], with great prospects for improvement, particularly through the use of energy transfer and more compatible hole-transport materials.

5.2 Background

The first reports of a successful J-aggregate OLED came in 1991/1992 from Era, et al. [69, 70]. Their device architecture became the basis for the structure developed to demonstrate strong coupling in a microcavity LED [75]. Their device consists of thermally evaporated wide-bandgap hole transport layer (HTL) and wide-bandgap electron transport layer (ETL) that together form a double heterostructure for the J-
aggregate emissive layer sandwiched in between. In their structure, the molecular HTL material TAD is first evaporated on an indium tin oxide (ITO) coated glass substrate. Then, 2 bi-layers of an oxacyanine J-aggregate and polyelectrolyte (polyvinyl N-methyl pyridinium iodide) are deposited via the Langmuir-Blodgett (LB) technique from the air-water interface of an LB trough. The bi-layers are then capped with a film of a hole-blocking ETL material, either PBD or OXD1. The authors initially reported that device efficiency was considerably lower than typical OLEDs “most likely due to the pollution of the interfaces of organic layers caused by the exposure of the EL cell to water and air in the fabrication process of the EL cell” [69]. In [70], they reported IV curves and a luminance of $\sim 4 \text{ cd/m}^2$ at a current density of $5 \text{ mA/cm}^2$, which corresponds to an external quantum efficiency (EQE) of $\sim 0.023\%$.

Era et al.’s device is remarkable for a number of reasons. It combines thermal evaporation and aqueous-based LB deposition. Their device produces saturated J-aggregate emission peaked at wavelength $\lambda = 560 \text{ nm}$, with a FWHM that appears to be $\sim 25 \text{ nm}$. Moreover, the emissive region is only about 2 monolayers thick.

In 1998, Mal’tsev et al. began reporting on a series of experiments carried out of the next four years, involving a single layer J-aggregate doped polymer LED (PLED) [71]. The polymer used was an ambipolar semiconducting polyimide dissolved in chloroform. A J-aggregate forming cyanine dye was then added to the solution, and the mixture was temperature-cycled in order to grow the promote growth of the J-aggregate crystallites. Crystal growth was observed by periodic measurements of the solution absorption spectrum. Once the J-aggregates were considered ripened, an aliquot was spin-cast onto an ITO coated glass substrate, and metal cathode deposited to complete the device. According to the researchers, this architecture yields an EQE as high as EQE = 0.2\% for a device with EL peak at $\lambda = 675 \text{ nm}$ [74], although no $I-V$ curves are shown. For a different cyanine dye, emission in the near IR is observed, with EL peak at $\lambda = 815 \text{ nm}$ and EQE = 0.01\% [39].

Their approach is novel in a number of ways. Era et al.’s well-defined double heterostructure is abandoned in favor of a distributed polymer-aggregate interface. Water is no longer required to assemble the J-aggregate layers. The J-aggregates are not grown before being mated with the polyimid material, as they are on the LB trough. On the contrary, the polyimid may serve as a template for promoting crystallite formation. Furthermore, this approach is suitable for polarizing the J-aggregate emission, because stretching and hence aligning polymer films and as well as their matrix constituents is a an established operation [36, 76].

In 1999, Bourbon and coworkers [72] reported a different approach utilizing a different kind of polymer/dye blend to achieve J-aggregate electroluminescence. Their approach consists of growing in water a polyelectrolyte/J-aggregate multilayer onto an ITO coated substrate, followed by a thermally evaporated Aluminum cathode. While the device is similar to Mal’tsev et al.’s in that there are only two organic (active) materials and no double-heterostructure, it is also similar to Era et al.’s in that the J-aggregate layers are
assembled in water in a manner that is in principle similar to LB. The polyelectrolyte used is the polycationic PPV precursor, poly(p-xylene tetrahydrothiophenium chloride) (pre-PPV), and the cyanine dye used in the multilayer is (5,6-dichloro-2-[3-[5,6-dichloro-1-ethyl-3-(3-sulfobutyl)-2(3H)-benzimidazolidene]-1-propenyl]-1-ethyl-3-(3-sulfobutyl) benzimidazolium hydroxide, inner salt), which is referred to in the text as TDBC. After assembling the film, the pre-PPV is thermally converted to the conjugated polymer, PPV, by heating the combined film to $130^\circ C$ for 12 hours at $10^{-4}$ mbar. EL spectrum peaks at approximately $\lambda = 590$ nm. The paper, while novel and noteworthy, is somewhat incomplete. $I-V$ curves are not presented and EQE is not reported. The authors write that emission could be seen with the naked eye in a dark room; experience indicates that this statement can correspond to an EQE $\approx 0.001\%$.

At MIT, in 2002, a new J-aggregate OLED development effort began. The initial approach consisted of spin-casting a polyvinyl alcohol (PVA) film doped with J-aggregates, from a water-methanol solution. This approach was subsequently modified and the same two constituents were deposited sequentially. PVA was first spin cast from water on ITO, followed by the J-aggregating dye spin-cast from methanol. In this case, the PVA acted as a solid state template for promoting J-aggregation. The “double spun” layers where then capped with a 10 nm thermally evaporated film of Bathocuparin (BCP), a wide bandgap ETL material meant to restrict exciton recombination to the J-aggregate containing layer. A 40 nm thick film of aluminum tris-quinolate (Alq$_3$) was then thermally evaporated on top along with metal cathode layers. EL spectrum of one such device is shown in Figure 5-1. The cyanine dye used is 1,1',3,3'-tetraethyl-5,5',6,6'-tetrachlorobenzimidazolocarbocyanine Iodide (TTBC-I), and the (80% hydrolyzed) PVA layer is approximately 30 nm thick based on profilometry measurements of similar films. EL peaks at $\lambda = 593$ nm with a FWHM of 10 nm. A slight shoulder appears in the EL spectrum peaked around $\lambda = 510$ nm that is likely due to Alq$_3$ emission in regions of the device where TTBC-I coverage is incomplete. Typical values for EQE are $\approx 0.001\%$.

This initial approach built off the work of Mal’tsev in that a polymer layer was spin cast directly onto the ITO contact, and combined some of Era’s thinking by localizing a thin region of J-aggregate dye near the physical and operational “center” of the device. The main fabrication drawbacks arose from the PVA being a poor semiconductor and the TTBC-I layers being incomplete.

Consequently, a new device design was sought that would yield higher EQE and a more saturated J-aggregate EL spectrum. It was also desirable for this design to be compatible with potential polaritonic structures. To that aim, in the current design, PVA is abandoned entirely in favor of a proven polymeric HTL material and a polyelectrolyte template for promoting J-aggregation.
5.3 Device Design

The basis for this J-aggregate OLED architecture comes from the work of Era, et al. [69] (and in hindsight Bourbon [72]), in which the small-molecule HTL material TAD is first evaporated before J-aggregates and polyelectrolytes are deposited via LB. Reading their self-assessment led to two simple ideas for improving upon their design. First, a polymer could be used for the HTL instead of a small molecule, since polymers are less likely to dissolve or be “polluted” in water. Second, the dip-coating technique could be used instead of LB, so that multi-layers could be formed in reproducible fashion.

The structure for this J-aggregate OLED design is illustrated in Figure 5-2. The anode is transparent conducting ITO sputter-coated onto a glass substrate and the HTL is a 60 nm thick film of Poly-TPD spin-cast on top. The polyelectrolyte PDAC and J-aggregating cyanine dye TDBC are then deposited by sequential immersion into cationic and anionic solutions (SICAS) from water. A 60 nm thick film of BCP is then thermally evaporated...
on top of these films, followed by a 10nm thick Mg:Ag alloy (50:1) layer to improve electron injection and a 110 nm thick Ag cap-contact. This design locates the J-aggregate layers at approximately the first cavity anti-node relative to the metal cathode layers, in order to maximize microcavity effects. Additionally, isolating the dye, which can act as an electron trap, away from other device layers, may better maintain electron transport through the device.

![Diagram of device structure](image)

Figure 5-2 J-aggregate OLED. The device structure consists of 150 nm thick sputter-coated ITO film as the anode, 60 nm thick spin-cast Poly-TPD film, several SICAS of PDAC/TDBC, a 60 nm thick film of thermally evaporated BCP, a 10nm thick Mg:Ag alloy (50:1) electron injection layer, and a 110 nm thick Ag contact. Chemical structures are shown for Poly-TPD, PDAC, TDBC, and BCP.

### 5.4 Experiment Methods

The polymer material chosen for the HTL is Poly-TPD, poly(N,N’-bis(4-butylphenyl)-N,N’-bis(phenyl)-benzidine). Poly-TPD is a semiconducting wide-bandgap (blue emitting) fluorescent polymer that is chemically the polymeric form of TAD, the HTL used by Era et al. [69, 70]. An aromatic polymer was opted for instead of a polar conducting polymer composite such as PEDOT-PSS, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) aqueous dispersion, because aromatics are less likely to dissolve or suffer damage during subsequent aqueous dip-coating processes. Parenthetically,

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1 Poly-TPD purchased from American Dye Source, Inc.
polyvinyl carbazole (PVK) was also examined, but evidently the morphology of PVK disrupts J-aggregate formation.

To process the films, Poly-TPD is first dissolved in chlorobenzene at a concentration of 10 mg/ml and then spin-cast onto UV-ozone treated ITO coated glass substrates at a spin speed of 3000 rpm and an acceleration of 10,000 rpm/sec for 60 sec. Chlorobenzene was chosen as the solvent over chloroform and toluene for stability and solubility considerations, respectively. Chloroform produces trace amounts of photo-initiated hydrochloric acid (HCl) when exposed to UV light, which then attacks the Poly-TPD in solution, and toluene does not possess a very electronegative atom, like chlorine, to adequately solvate Poly-TPD. (See Chapter 4 for details on the spin-curve used to determine experimental parameters for spin-casting films with thickness in the range of 45 nm to 65 nm.) Weighing of the material is performed in a lab-environment, while adding solvent and spin-casting are performed in nitrogen in a glove box. After spin-casting, the substrates are placed on a hot-plate set to ~100°C for 30 minutes to bake out residual chlorobenzene and crosslink the Poly-TPD. Time and temperature settings were determined empirically. Baking is performed in dim light to reduce the possibility of photobleaching.

After baking, the Poly-TPD coated substrates are sent through the dip-coater for deposition of the PDAC/TDBC film. Assembly of the polyelectrolyte and J-aggregate layers on top of Poly-TPD relies on the ability of the polyelectrolytes to adsorb to the polymer surface. Typically, a glass or silicon substrate is modified via surface treatment techniques like UV-ozone or oxygen plasma to facilitate polyelectrolyte adsorption. Applying such methods would most likely have damaged the fluorescence of Poly-TPD. Fortunately, such methods are not necessary because the polymer readily oxidizes, forming polar sites that promote polyelectrolyte adsorption.

The deposition cycle for each SICAS consisted of immersion for 15 min. in 20% (w/v) PDAC solution in deionized water (DI), three rinses in DI (2 min, 2 min, and 1 min), followed by immersion into 50 μM (pH = 9.0) TDBC solution for 15 min and three additional (pH = 9.0) rinses (2 min, 2 min, and 1 min). The pH of the TDBC solution and dye rinses was adjusted to pH = 9.0 by addition of sodium hydroxide pellets.

The substrates are cut to 0.992” squares to be compatible with the width of the dip-coater’s racks, which are designed to hold 1” wide x 3” long microscope slides, and the size of the substrate holders used in the thermal evaporator of the integrated growth system. The racks also needed to be modified to hold the 0.992” square substrates instead of 1”x3” rectangular microscope slides. This modification was accomplished by inserting a Teflon block into the racks.

After the SICAS deposition, the substrates are carefully extracted from the racks and the films are blown dry using a nitrogen gun. Then they are inserted into the integrated growth system and exposed to high vacuum (10⁻⁷ torr), which drives off any residual water from the polyelectrolytes.
The BCP layer used for the ETL is thermally evaporated because the alternative of spin-casting would dissolve the Poly-TPD under-layer. BCP also functions as a hole blocking layer that confines holes and by extension exciton-recombination to the PDAC/TDBC layers. This helps to insure the EL spectra are dominated by emission from the J-aggregate layer of the device. The BCP is carefully sublimed (in high vacuum) at low deposition rates, less than 0.05 nm/s, in order to achieve precise layer thickness, which enables fine tuning of the optical cavity to the J-aggregate resonance.

Following BCP deposition, the substrates are shadow-masked and metals are thermally evaporated through the mask to form the top-contacting cathode. The first 10 nm of the cathode consists of a magnesium-silver alloy of atomic ratio 50:1 (Mg:Ag). Magnesium serves to lower the work function and therefore promote electron injection into the BCP layer [77]. The silver fraction serves to promote adhesion of the metal to the organics [77]. A relatively thick 110 nm silver layer is then evaporated on top to complete the contact, additionally acting as an encapsulation layer and a mirror surface.

5.5 Results and Analysis

Figure 5-3 shows an EL spectrum for the device architecture of Figure 5-2, with 8.5 SICAS of PDAC/TDBC as the J-aggregate layer. The spectrum peaks at $\lambda_{EL} = 600$ nm (corresponding to energy $E_{EL} = 2.067$ eV) with a FWHM = 16.5 nm (57 meV). It is significant to note that the EL spectra for this device are independent of the current level, indicating that the exciton recombination region is well-confined to the J-aggregate layer.

For comparison, normalized PL spectrum of an 8.5 SICAS film is also plotted in Figure 5-3. The PL peaks at wavelength $\lambda_{PL} = 596$ nm ($E_{PL} = 2.081$ eV) with a FWHM = 19.0 nm (66 meV). The film was excited with nearly monochromatic light of wavelength $\lambda_{ex} = 500$ nm ($E_{ex} = 2.480$ eV). This film was prepared after the device growth using similar assembly conditions of 5 minutes in the PDAC and TDBC solutions at pH = 5.5 (DI water).

Overall, the EL and PL spectra are quite similar, with some noteworthy differences. In terms of peak wavelength and linewidth, the discrepancies between EL and PL spectra may be due to slight differences in the growth conditions or due to weak microcavity effects that are capable of shifting the EL peak by 20 nm [78]. To various degrees, both EL and PL exhibit similarly shaped spectral shoulders on the low energy side of the J-band, near $\lambda = 635$ nm ($E = 1.953$ eV). This feature is therefore likely due to disorder in the J-aggregate crystallites. The higher energy shoulder present in EL at $\lambda = 545$nm ($E = 2.275$ eV) is likely from uncoupled TDBC monomer. This monomeric shoulder is absent in PL of the neat film because the SICAS grow more uniformly on glass than on Poly-TPD.
Figure 5-3 J-aggregate OLED EL spectrum with TDBC as the J-aggregate emitter. 8.5 SICAS of PDAC/TDBC form the J-aggregate film. The EL spectrum (in orange) peaks at $\lambda_{EL} = 600$ nm ($E_{EL} = 2.067$ eV), with a FWHM = 16.5 nm (57 meV). For comparison, PL spectrum is also shown (in blue) of an 8.5 SICAS PDAC/TDBC film, excited at $\lambda_{ex} = 500$ nm ($E_{ex} = 2.480$ eV).

This spectrum is about a factor of two narrower than QD-LED spectra in [73]: $\lambda_{EL} = 562$ nm and FWHM = 32 nm. It is on par with some of the narrowest organic emitters, such as PtOX, (platinum(II)-2,8,12,17-tetraethyl-3,7,13,18-tetramethylporphyrin): $\lambda_{EL} = 656$ nm and FWHM = 18 nm [79]. It is still a factor of 4.7 broader than Europium chelate based OLEDs, which produce the most saturated unfiltered EL spectra, such as in [80]: $\lambda_{EL} = 612$ nm and FWHM = 3.5 nm.
A typical $I-V$ curve and external EL external quantum efficiency plot are depicted in Figure 5-4, with the maximum efficiency of 0.035%. I-V traces were taken with an HP 4156 Semiconductor Parameter Analyzer. Optical power measurements were made with a Newport calibrated photodiode. A geometric factor was used to scale-up the measured optical power to account for incomplete light capture with a planar photodiode.

Figure 5-4 Current-voltage (I-V) and external quantum efficiency (EQE) results for TDBC J-aggregate OLED.
5.6 Future Work

Future work will focus on improving EQE and narrowing EL linewidth. Several straightforward modifications could yield significant increases in device performance, particularly through the use of energy transfer, more compatible hole-transport materials, and other J-aggregating dyes.

J-aggregated dyes can and do interact with small molecules and polymers participate in Förster resonant energy transfer (FRET) [81]. The current design locates the exciton recombination region on the J-aggregate side of the device. If the recombination region was instead located on a highly fluorescent donor inserted into one of the adjacent layers, it would be possible to boost EQE through FRET injection. By incorporating a phosphorescent emitter layer it could be possible to generate four times the excitons (ceteris paribus) which could then excite the J-aggregate layer via triplet mediated FRET [82]. This again assumes that the exciton recombination region could be redesigned to coincide with the phosphorescent material [83]. An alternative for accomplishing FRET would be to include a multi-valent phosphorescent dye that exhibits high efficiency EL such as Ruthenium complexes [84] directly into the SICAS in high proportion relative to the J-aggregating dye. The majority of exciton formation would occur on the phosphor and then FRET to the J-aggregate. Still a third approach could involve doping the Poly-TPD layer with a phosphor [85], although a small molecule compatible with subsequent emersion in water would need to be found.

A better choice for HTL might be an inorganic semiconducting metal oxide film. Recent work by Caruge et al. [86] has shown that sputter-coated Nickel Oxide (NiO) films can substitute for organic HTL materials in QD-LEDs, yielding EQE as high as of $\text{EQE} = 0.18\%$. In J-aggregate OLEDs, the benefit metal-oxides would bring is that in all likelihood they would not dissolve in water. A potential problem could be insuring the correct oxygen doping during dip-coating, but alternatively, immersion of the oxide in solutions with the proper electrolyte-chemistry could actually improve performance of the film. In photovoltaic cells, J-aggregate films have been assembled successfully onto titanium dioxide [68], and similar success may be realized in EL devices.

The use of metal oxides as the HTL would also enable experimentation with different J-aggregate deposition techniques such as ink-jetting the dye. This approach is reminiscent of the “double spun” approach discussed previously, but with many added benefits. With a metal oxide film, it would be possible to lithographically pattern the HTL in such ways that would promote aligned crystal growth [87] or simply functionalize the oxide with a J-aggregation promoting surface treatment [88].

Another strategy for increasing EQE would be to select a different J-aggregate dye system. This could involve using different cyanine dyes. It could involve choosing a better polyelectrolyte, one that produces smoother films and hence better interfaces or one that templates J-aggregation better. In the past few years, a number of aromatic conjugated semiconducting polyelectrolytes have been synthesized that could yield
surprisingly good EQE. Research is on-going to chemically attach J-aggregates on the surface of QD’s, which together emit saturated J-aggregate photoluminescence by virtue of high efficiency FRET between the constituents. These hybrid materials could also yield a significant boost in EQE when integrated in standard QD-LED structures as phase-segregation drives monolayer formation [89] and perhaps J-aggregate formation.

Finally, a study to determine the HOMO and LUMO levels of the J-aggregate films would assist in optimizing charge injection, exciton recombination, and electron-hole current balance, and further improve EQE.

5.7 Conclusion

A new design for a J-aggregate OLED was presented, developed, and analyzed. This design combines key features of previous reports on J-aggregate EL experiments such as the double heterostructure and thermally evaporated ETL of Era’s work [69, 70], the use of polymer HTL as in Mal’tsev’s [39, 71, 74], and the use of dip-coated J-aggregate layers as in Bourbon’s report [72]. These various assembly techniques were successfully combined to yield J-aggregate OLEDs with EQE = 0.035%. The EL spectrum of these devices has a single saturated EL peak due to J-aggregate emission at wavelength $\lambda_{\text{EL}} = 600$ nm (2.067 eV) with a FWHM = 16.5 nm (57 meV). Great prospects exist for improvement of EQE, particularly through the use of energy transfer, triplet-sensitization, and more compatible hole-transport materials. Revisiting the choice of cyanine dye and template materials used to form the J-aggregate layers would also be promising. It should be possible to assemble a J-aggregate OLED with EQE greater than 1%. Depending on the level of polaron losses in J-aggregate OLED, such a device integrated into a polaritonic structure could prove promising as a path for realizing lower threshold lasing action.
6 Electrically Pumped Polariton Emission (EPPE)

"A man without a goal is like a ship without a rudder." (Thomas Carlyle)

Anecdotal Introduction:

The goal was electrically pumped polariton emission, i.e. EPPE. I was keen on achieving it. I felt this was the kind of goal that would force me to be better, as an engineer and as a person, in order to achieve it. It would also force me to relearn the process of growing an OLED. I had spent so long working on the PVA based J-aggregate OLED that I really didn’t have a feel for making a regular OLED. Making a regular OLED in our lab involves shadow masking, evaporating dual boats of metal at a precise doping level, transferring substrates in ultra high vacuum, testing samples, and being vigilant against device contamination. To me it was simply a matter of getting back to basics, “Blocking and Tackling”, as football coaches say. If you can’t make a TPD-Alq₃ OLED with respectable quantum yield, how can you expect to make an exotic experimental device that functions? If nothing else, it’s a question of confidence. Once I had relearned how to make a decent OLED, it was on to EPPE.
6.1 Introduction:

Thin films of PDAC/TDBC with high absorption coefficient (6 nm thick with $\alpha \sim 1.0 \times 10^6$ cm$^{-1}$) inserted in an optical microcavity exhibit polaritonic dispersion and Rabi-splitting with a coupling strength of $\Omega_R = 265 \pm 15$ meV. The metallic reflector elements can be patterned such that the structure functions as a resonant cavity OLED (RC-OLED). The thinness of the excitonic layer allows for active spacer elements to be integrated within the device that enable electroluminescence to be generated. When electrically excited, the RC-OLED emits light at the wavelengths corresponding to the strongly coupled states of the unpatterned polaritonic structures of Chapter 4. Strong coupling is maintained even when the films are electrically excited. This marks the first demonstration of electrically pumped polariton emission (EPPE).

6.2 Background

Solid state devices based on semiconductor quantum wells, quantum dots, and colloidal quantum dots or organic semiconductors afford the possibility of electrically exciting or probing strongly coupled states of light and matter.

The first reports of utilizing electrical excitation to probe exciton-polaritons were made by Fisher et al. [90, 91] in 1995 and 1996. In these studies, an electric field is applied across the InGaAs quantum wells that constitute the excitonic portion of the device. By varying the field strength, the exciton resonance is modulated via the quantum confined Stark effect and is tuned through the resonance associated with the microcavity. Moreover, with light incident on the device, a photo-current response is measured as a function of wavelength that shows two peaks in photo-current at the polaritonic resonances.

In 1997, Klimovitch, Bjørk, Cao, and Yamamoto [92] proposed electrically exciting the exciton-polariton states of a GaAs quantum well based micropillar device. They argued that photon confinement was necessary in three spatial dimensions to insure that the dominant pathway for exciton recombination was into the lower branch polariton states. With optimized device design, it was argued that EQE of about 50% would be achievable. The lifetime of the polariton states would be only a few picoseconds compared to the observed lifetime of the excitonic bath which is several nanoseconds, the relative rates suggesting that the overwhelming majority of excitons created would be formed as polaritonic states. In a resonantly tuned system, the polaritonic states are 50% photonic, hence 50% of the excitonic energy should scatter out of the device as light. In addition to high EQE, polaritonic LED’s would exhibit very fast lifetimes of only several picoseconds. Such devices would mark a new generation of monolithic light sources that could be directly modulated at rates approaching 500 GHz.

In the related field of single photon sources, Zrenner et al. demonstrated that the photocurrent response of a quantum dot photodiode exhibits Rabi-oscillations when the
device is excited with a laser [93]. Their device is essentially a single-photon LED [94] operated in reverse bias. This study is similar to Fisher et al.'s in that they both use photocurrent response to probe Rabi-splitting. They differ, however, in that in this study there is no cavity and therefore no vacuum Rabi-splitting. In the study by Zrenner et al., the strong coupling is generated via the coherent pump laser beam. Also, this study is focused on single quantum dots as a single photon source. In contrast, Fisher et al. are investigating vacuum Rabi-splitting in an optical microcavity wherein a collective of 2-dimensional quantum well excitons couple to the confined optical field.

These demonstrations of electrically probing the strongly coupled states of light and matter, whether such states are manifestations of vacuum Rabi-splitting or laser driven Rabi-oscillation, have all consisted of reverse biasing the structure and optically pumping the device. In contrast, in this chapter the strongly coupled states are electrically excited via forward biasing the RC-OLED layers of the polaritonic structure, showing that the coherently coupled polaritonic states can be generated via a non-coherent applied bias voltage source.

### 6.3 Device Design

The RC-OLED design used to demonstrate EPPE is illustrated in Figure 4-1. The design is almost identical to that of the Low Q cavity polaritonic structures of Chapter 4, where layer considerations are discussed in detail.

![RC-OLED structure](image)

Figure 6-1 RC-OLED structure consisting of metal-mirror microcavity containing LBL SICAS assembled PDAC/TDBC J-aggregate exciton layer. A 10 nm thick Mg:Ag (50:1) alloy layer followed by a 110 nm thick Ag film acts as high-reflectance “top mirror”. A semi-transparent 50 nm thick Ag film serves as the “bottom” mirror. Angularly-resolved electroluminescence measurements are performed from the glass substrate side of the device. A variable thickness spin-cast Poly-TPD layer tunes the microcavity resonance.
The primary differences relate to the “top” mirror. In particular, the metallic layers that form the “top” mirror are patterned into ~1 mm diameter circles to delineate individual devices. The “top” mirror, which is the final layer deposited in the device, is a 120 nm thick layer of consisting of a 110 nm thick silver (Ag) film on top of a 10 nm thick layer of Magnesium-Silver (Mg:Ag) alloy. The alloy layer is deposited on top of the BCP layer immediately before the Ag film to improve electrical injection into the BCP. (See Chapter 5 on J-aggregate OLEDs for further details). Together, these layers form the cathode of the RC-OLED.

The 50 nm Ag film, which serves as the “bottom” mirror of the microcavity, also acts as the anode of the device.

6.4 Experimental Methods

The methods for assembling the RC-OLEDs are nearly identical to those used for the Low Q cavity polaritonic structures of Chapter 4. The primary difference is that following BCP deposition, the substrates are shadow-masked and the metal layers are thermally evaporated through the mask to form patterned top-contacting cathodes.

6.5 Experimental Setup

The setup constructed for taking EL spectra as a function of angle is illustrated in Figure 6-2 below. EL is collected with an optical fiber (bundle) which is attached to rotational stage. For a given device, to measure emission at a given angle \( \theta \), the fiber and stage are rotated while keeping the substrate fixed. Translational stages are used to reposition the substrate as necessary. The electrical probes can also be independently positioned to contact one device at a time. Care is taken to insure that the stage is locked during measurement and that the device is aligned centrally relative to the stage’s axis of rotation.
Figure 6-2 Experimental setup for measuring electroluminescence (EL) spectra as a function of angle. The device substrate is positioned in a mount that is connected to a translational stage. Electrical probes contact the substrate to complete the circuit. The anode probe connects at the edge of substrate to the ITO coating. The cathode probe has a thin gold wire at the edge of the tip which contacts the Ag cathode of a single device. The translational stage is used to align the device to the center of the rotational stage, and to translate the substrate from one device to the next as testing proceeds. The optical fiber bundle is mounted on a shaft that is connected to the rotation stage at the stage’s axis of rotation. The fiber-shaft apparatus is rotated by turning the rotational stage to the desired angle. The optical fiber is coupled to a spectrometer with charged coupled device (CCD) detector.

6.6 Results and Discussion

When electrically excited, the RC-OLEDs exhibit strong coupling with exciton-polariton electroluminescence (EL) peaks observed at room temperature. The exciton-polariton peaks in EL coincide with the polaritonic resonant dips in the reflectivity spectra discussed in Chapter 4. The EL peaks and reflectivity dips are most pronounced when the microcavity is resonantly tuned to the TDBC peak reflection wavelength $\lambda = 595$ nm. The observed room temperature Rabi-splitting between exciton-polariton peaks is $\hbar\Omega_R = 265 \pm 15$ meV, which is a consequence of the high absorption coefficient of the PDAC/TDBC films.
Figure 6-3 plots the spectral properties of such an RC-OLED exhibiting Rabi-splitting. Figure 6-3 shows that the reflectance, photoluminescence, and EL spectra of the device noticeably differ from the spectra of an uncoupled OLED, one with the same organic layer thicknesses but without the 50 nm thick Ag anode mirror. For the RC-OLED with 54 nm thick Poly-TPD film, the reflectance (Figure 6-3a) spectrum exhibits resonant dips at $\lambda = 554$ nm and at $\lambda = 625$ nm. In contrast, the 4.5 SICAS assembled PDAC/TDBC film on glass have a single resonance at $\lambda = 595$ nm (FWHM = 19 nm), and the bare microcavity corresponding to this cavity thickness would produce a resonant dip at $\lambda = 587$ nm. Similarly, this splitting is observed in the PL measurements of the structure (Figure 6-3b), with resonant PL peaks at $\lambda = 543$ nm and $\lambda = 619$ nm. In contrast, the thin film has a single PL peak at $\lambda = 596$ nm (FWHM = 13 nm). Finally, in EL (Figure 6-3c), the forward ($\theta = 0^\circ$) spectrum of the uncoupled OLED has one emission peak at $\lambda = 602$ nm (FWHM = 23 nm), corresponding to the resonance of the uncoupled TDBC J-aggregate exciton, while in the RC-OLED, the single emission peak splits into two peaks located at $\lambda = 546$ nm and $\lambda = 622$ nm.

The large splitting between the resonances of the Figure 6-3c RC-OLED is due to strong coupling between the J-aggregate exciton ($\lambda = 595$ nm) and photon field of the near resonantly tuned microcavity ($\lambda = 587$ nm). Because of the strong coupling, the exciton and photon are exchanging energy at a faster rate than the respective dephasing processes, namely dephasing due to spontaneous emission and non-radiative relaxation of
the J-aggregate exciton and photon dephasing due to light leakage from the cavity. Consequently, new eigenstates form with energy levels, $E_z$, separated from the uncoupled exciton and photon energy levels, $E_{ex}$ and $E_{ph}$, respectively:

$$E_z = \frac{E_{ex} + E_{ph}}{2} \pm \frac{1}{2} \sqrt{\left(\hbar \Omega_R \right)^2 + \left(E_{ex} - E_{ph} \right)^2}$$

In addition to splitting of the normal mode emission, the RC-OLEDs exhibit polaritonic anti-crossing characteristic of the strong coupling limit, which is also described by the above equation. This approach to confirming strong coupling is identical in spirit to the approach taken in Chapter 4.

Although the EL $E_z$ peaks are not equally pronounced as are the resonant dips in reflectivity, the dispersion's dependence on $E_{ph}$ via cavity thickness and angle tuning follows the same relation.
To illustrate the evolution of the anti-crossing as a function cavity tuning, the EL spectra for a series of different thickness RC-OLEDs is resolved as a function of angle. Angular EL spectra are plotted in Figure 6-4a-e for cavities of uncoupled bare cavity photon energies of 2.22 eV through 1.98 eV. Tuning is achieved by spin-casting the Poly-TPD layer at speeds ranging from 2.0k rpm to 1.0k rpm, which in turn produces nominal thicknesses between 45 nm and 65 nm, based on the spin-curve of the Chapter 4. The series of EL spectra at $\theta = 0^\circ$ are analyzed in Figure 6-5 and compared to normal mode reflectance data of Chapter 4. The spectra of Figure 6-4c and Figure 6-4d, two structures for which the cavity is closely tuned to the TDBC J-aggregate exciton resonance, are then examined in greater detail. Their EL dispersion data are compared to the reflectance measurements and dispersion relations based on the corresponding un-patterned polaritonic structures.

Figure 6-4 EL Spectra as a function of angle for RC-OLED devices of different cavity tuning. (a) through (e) The bare cavity at $\theta = 0^\circ$ is nominally tuned to 2.22 eV, 2.17 eV, 2.11 eV, 2.05 eV and 1.98 eV, respectively. Tuning is achieved by spin-casting Poly-TPD layer at spin-speeds of 2.0k rpm, 1.75k rpm, 1.5k rpm, 1.25k rpm, and 1.0k rpm, respectively, which in turn produce nominal layer thicknesses of 45 nm, 49 nm, 54 nm, 59 nm, and 65 nm. EL spectra are normalized to lower energy polariton peak, $E_c(0)$. Inset: expanded view of higher energy portion of the EL spectra, normalized to emission maximum corresponding to the higher energy polariton peak, $E_c(0)$, in the $\lambda = 450$ nm to $\lambda = 575$ nm range. Figure 6-4 continues on the next 2 pages.
(B) $E_c = 2.17 \text{ eV}$
$\lambda_c = 571.3 \text{ nm}$

(C) $E_c = 2.11 \text{ eV}$
$\lambda_c = 587.0 \text{ nm}$
(D) $E_c = 2.05 \text{ eV}$  
$\lambda_c = 605.5 \text{ nm}$

(E) $E_c = 1.98 \text{ eV}$  
$\lambda_c = 626.6 \text{ nm}$
The series of EL spectra in Figure 6-4 reveal several trends:

1. The lower energy EL peaks, \( E_- \), asymptotically approach the uncoupled J-aggregate OLED emission peak, as the angle of observation increases.
2. At the same time, the higher energy EL peaks, \( E_+ \), do not show an asymptote at larger angles. Instead, the \( E_+ \) peaks at large angle appear to tune as would the emission of a weakly coupled resonant cavity LED.
3. When the cavity is tuned to higher energy, as in Figure 6-4a and Figure 6-4b, the \( E_+ \) states have higher relative intensity than in the devices where the cavity is tuned to lower energy.
4. In all cases, the \( E_+ \) states are less pronounced than the \( E_- \) states.
5. When the cavity is tuned to lower energies, as in Figure 6-4d and Figure 6-4e, a spectral shoulder at \( \lambda = 610 \text{ nm} \) is apparent, at small angles.

These trends are qualitatively indicative of the RC-OLEDs exhibiting emission from the strongly coupled states.

Figure 6-5 shows quantitatively that emission is coming from polaritonic states, as the EL peaks at \( \theta = 0^\circ \) follow a similar dispersion relation as the resonant dips in reflectivity of same thickness un-patterned polaritonic structures (reflectance measured at \( \theta = 7^\circ \) for experimental reasons). In particular, as the Poly-TPD layer thickness is varied from 65 nm to 42 nm, \( E_{ph} \) is tuned between 1.98 eV and 2.26 eV, spanning the energy range that encompasses the J-aggregate exciton resonance, \( E_{ex} = 2.08 \text{ eV} (\lambda = 595 \text{ nm}) \). As a result, the energy separation between resonant dips in reflectivity varies from more than 300 meV (Figure 6-5c), when the exciton and photon are far off-resonance to a minimum of \( \hbar \Omega_R = 265 \text{ meV} \), when \( E_{ex} = E_{ph} \), which corresponds to a thickness of 56 nm for the Poly-TPD layer. Similarly in EL, the \( E_\pm \) spectral peaks (Figure 6-5a,b) are greatly separated off-resonance and then approach each other as the microcavity is tuned through \( E_{ex} \).

In the EL of Figure 6-5a, a spectral shoulder at \( \lambda = 610 \text{ nm} \) appears superimposed on the emission spectrum of the \( E_- \) state. This emission could be from J-aggregates that are not strongly coupled to the microcavity due to disorder in the bi-layers. The shoulder is absent in reflectivity (Figure 6-5c). One explanation is that optical excitation selects the J-aggregates with transition dipoles oriented parallel to the mirrors and therefore only J-aggregates contributing to strong coupling are excited. However, close examination of the reflectance spectra indicates roughened spectral features in the same spectral vicinity, indicating that disorder of the film may be affecting both reflectivity and EL, but in different ways.
Figure 6-5 Normal mode polariton EL and reflectivity for series of RC-OLED structures with different microcavity resonance, tuned by adjusting the thickness of the Poly-TPD layer from 42 nm to 65 nm. (a) EL spectra at $\theta = 0^\circ$, normalized to the lowest energy peak, $E_-$. (b) Expanded view of high-energy portion of EL spectra, normalized to emission of the higher energy polariton peak, $E_+$. (c) Reflectivity at $\theta = 7^\circ$ from similar un-patterned devices. (d) Polaritonic dispersion data from resonant peaks in EL (brown data points) and reflectance (black data points) as a function of bare (cavity) photon energy. The fit is based on reflectance data with Rabi-splitting of $\hbar \Omega_R = 265$ meV.
The characteristic dependence of $E_\pm$ on $E_{ph}$ is also observed in the angular EL spectra of the RC-OLEDs, since changing $\theta$ affects the tuning of $E_{ph}$. As $\theta$ increases, $E_{ph}$ tunes towards higher energy according to the dispersion relation [2]:

$$E_{ph}(\theta) = E_0 \left(1 - \sin^2 \theta / n^2 \right)^{1/2}.$$  

Figure 6-6 Angularly resolved polariton electroluminescence dispersion relations in (a) and (b) for polaritonic structures with Poly-TPD thicknesses of (a) 54 nm and (b) 59 nm respectively. Resonant peaks in EL (brown circles) are derived from spectra of Figure 6-4 and are plotted as a function of angle. For comparison, resonant dips in reflectance (black circles) for similar un-patterned structures are also plotted. Dispersion relations are generated based on a fit of the reflectance data, assuming two-state model with bare exciton energy $E_0 = 2.08$ eV. In (a) the bare (empty cavity) photon energy $E_{ph}(\theta = 0^\circ) = 2.11$ eV and in (b) $E_{ph}(\theta = 0^\circ) = 2.05$ eV. For both fits, the same angle independent Rabi-splitting of $\hbar \Omega_R = 265$ meV is used.

As a result of the angular dependence, the polariton energy levels become functions of $\theta$ with $E_\pm \rightarrow E_\pm(\theta)$. Figure 6-6 plots the angular dependence of the EL peaks and reflectivity dips together with the calculated dispersion relations for $E_{ph}(\theta)$ and the polariton states $E_\pm(\theta)$. At $\theta = 0^\circ$, near resonance for $E_{ph}(\theta)$ and $E_{ex}$, the polariton branches of the dispersion relation $E_\pm(\theta)$ anti-cross in energy, while at larger $\theta$, far away from the resonance condition, they devolve into uncoupled exciton and photon dispersion curves.

The EL spectra of Figure 6-4 and in particular Figure 6-5a show that in the normal direction the intensity of the upper branch, $E_+ \left(\theta \right)$, is significantly attenuated compared to
that of the lower branch, $E_-(\theta)$, in contrast to reflectivity (Figure 6-5c) where the resonant dips are of similar magnitude. Lower PL emission intensity of the $E_-$ states is commonly observed in polaritonic systems. Lidzey et al. have studied the PL phenomenon in depth for dye doped PVA-filled microcavities [25]. They argue that optical phonon mediated fast energy transfer contribute to redistribution of the polariton population. Similarly in EL, thermalization of the polaritons could account for the lower intensity of $E_-(\theta)$ in the EL spectra.

A single value for the vacuum Rabi splitting, $\hbar \Omega_R = 265$ meV, is used to generate the fits in Figure 6-5d and Figure 6-6a,b, which plot normal mode and angular dispersion of the RC-OLEDs. Consistent agreement of the RC-OLED data, across multiple devices and collection angles, with a single value of $\hbar \Omega_R$ in the dispersion relation defined by Eq. 1, further confirms that the RC-OLEDs operate in the strong coupling limit.

EL and reflectivity measurements yield similar dispersion relations, as they are both linear optical probes of the polariton energy levels, confirming that electrical excitation, at the applied field ($\sim 10^6$ V cm$^{-1}$) and current density ($\sim 0.1$ A cm$^{-2}$), does not change the optical energy levels of the polariton states. Possibly, the applied field does not perturb the Rabi-splitting since the dipoles contributing most to strong coupling lay in plane perpendicular to the direction of the applied E-field. Also likely, the linewidths of the coupled system are too broad to resolve any effect that a change in absorption and dispersion might have as a function of applied voltage.

Although the dispersion relations mostly coincide, in EL the $E_-$ branch follows the polariton dispersion relation less closely than the $E_-$ branch. The EL of $E_-$ appears to be shifted 75 meV above the fit generated from reflectivity and appears to increase in intensity at larger $\theta$. These trends are likely due to residual EL from the Poly-TPD hole transport layer that is optically filtered through the $E_-$ polariton resonance. At larger $\theta$, as $E_+$ tunes to higher energy, it overlaps with the more intense portion of the Poly-TPD luminescence spectrum, with a consequent increase in EL of the $E_+$ branch, and a blue-shift in the observed EL peak of $E_+$ towards higher energies.
6.7 Future Work

So far, the discussion of the physics has focused on the optical properties of the device, demonstrating that the EL emission stems from polaritonic states that exhibit Rabi-splitting and anti-crossing. Further study is needed to formulate the physical mechanisms behind polariton formation from free electrons and holes. One open question is whether the polariton states, which correspond to new resonances in an optical sense, also correspond to new energy levels in an excitonic sense.

When polaritons are formed, is it the case that new energy levels with new HOMO and LUMO have been created? In single photon optics, when a single atom is in strong coupling with a microcavity, the description given is that the energy levels of the atom actually change [95]. In this limit, when such an EL device is realized, the voltage required to excite emission from the different energy levels would show distinct thresholds.

Another possible description of electrical polariton formation is that electrons and holes recombine on the J-aggregate, which then fluoresces into every available mode. However, since the J-aggregate layer induces vacuum Rabi-splitting which changes the modes of the coupled system, the only bright modes available are the polaritonic modes. Therefore, the emission can only come from the polaritonic states. In this picture, the homo and lumo of the J-aggregate are not necessarily modified.

Perhaps, this question can be answered experimentally by sensitively measuring the EL as a function of applied voltage, compared to EL of an uncoupled J-aggregate OLED. If it could be determined that the threshold voltage for emission was in fact lowered, this would support the new energy level model. Likely, the drop in threshold would be by an amount on the order of half the Rabi-splitting ($\sim \hbar \Omega_R / 2$).

6.8 Further Device Optimization

Future work will focus on improving the Q of the cavity and EQE of the embedded J-aggregate OLED. Both the Q and the EQE of the device can be improved by following the suggestions outlined in Chapters 8 and 5 of this thesis, namely adopting dielectric mirrors, confining light in all 3 dimensions, and optimizing electron-hole current balance, energy transfer effects, and morphology of the J-aggregate layers.
Larger Q’s can enable Rabi-splitting to be observed with thinner J-aggregate films. In that case, fewer dye-layers would be necessary and the overall time spent dip-coating in water could be reduced, which would minimize the possibility of water-born impurities inadvertently contaminating the device.

With a dielectric mirror, the anode electrical contact can be made of ITO instead of silver. ITO will improve hole injection into the Poly-TPD layer since it has a higher work function than silver. The ITO film can also be integrated into the DBR as the last layer of the Bragg stack (of thickness $\lambda/4n_{\text{ITO}}$). The cavity will still be “$\lambda/2n$”, as determined by the lower refractive index organic spacers, and the electric field and hence coupling strength will be larger than if an ITO layer of thickness $\lambda/2n_{\text{ITO}}$ were incorporated within the cavity.

With improved Q and EQE, it may be possible to discern changes in the optical properties of the device as a function of applied voltage. Forward bias may shift the wavelengths of the EL spectrum. Likewise, applied bias may shift the reflectance (and transmittance) spectrum of the device, forming the basis for a family of electrically actuated optical switches.

With improved Q and EQE, it should also be possible to determine whether energy transfer dopants have a different impact on EQE in polaritonic devices compared to non-cavity J-aggregate OLEDs. Although such a measurement likely will not discriminate between non-radiative and “trivial” energy transfer to the J-aggregate layer, it may nevertheless give insight into approaches for optimizing strongly coupled RC-OLEDs.

More work is needed to characterize the electrical and optical properties of better more efficient renditions of polaritonic RC-OLEDs. In particular, intensity vs. angle and current-voltage profiles, EQE, and relaxation lifetime of emitted light should be measured, and compared to data from uncoupled J-aggregate OLEDs.
6.9 Conclusion

It is possible to electrically excite strongly coupled states of light and matter. Furthermore, electrical excitation preserves the energy levels of the polariton states, at least for the polaritonic structures of this chapter. Using bi-layer assembly, a Rabi-splittting of $\hbar\Omega_z = 265 \text{meV}$ is achieved with 5 nm thick films of PDAC/TDBC. This development demonstrates that electrical excitation can be used as a general approach towards accessing polariton effects. This may serve as a stepping-stone towards making integrated polariton based optical switches and electrically pumped organic lasers that operate by coherent spontaneous emission, a process that does not require full population inversion. This could be an enabling step in the design of electrically pumped polariton lasers [96], electrically pumped polariton parametric amplifiers [10] or other cavity QED devices where engineering the occupancy of a particular polariton state [17] is critical for device operation.
7 Critically Coupled Resonator (CCR)

“Remember, the enemy has only images and illusions behind which he hides his true motives. Destroy the image and you will break the enemy.” (Bruce Lee’s Teacher in Enter the Dragon)

“G-d’s Kindness Is Infinite.” (My words when I measured our first CCR.)

Anecdotal Introduction:

After demonstrating electrically pumped polariton emission, the logical next step was to integrate the nanoscale thin films of PDAC/TDBC into a more reflective microcavity, one containing at least one dielectric mirror, i.e. dielectric Bragg reflector (DBR). Prof. Nurmikko had been pressing for a full dielectric cavity that would be suitable for transmission based optical switches. For the specifics of the methodology and our tool set for constructing DBR’s in-house, see Chapter 8 on higher Q cavities. Originally, thermal evaporation of exotic oxides was attempted in Prof. Baldo’s evaporator with the hope that the programming capabilities of his system would permit full DBR automation; those oxides turned out to be unstable when exposed to moisture. The alternative was to sputter coat oxides, which requires two targets, one of high refractive index and a second of low refractive index. The materials available for high and low index were Titanium Dioxide (TiO$_2$) and Aluminum Oxide (Al$_2$O$_3$) respectively. With the help of Erin Boyd, who worked out the idiosyncrasies of the sputterer, the DBR’s were successfully grown. The next step was integrating the PDAC/TDBC layers, which involved sputtering another low-index Al$_2$O$_3$ layer as the bottom spacer of the cavity, and then dip-coating. It became evident after about 6 months that these two processes were incompatible, because during dip-coating the Al$_2$O$_3$ layer was being wet-etched by the dye solution, which at the time was slightly alkaline (pH = 9.0 by addition of sodium hydroxide). To overcome this problem, deionized water was used instead, which has pH = 5.5, a change that not only prevented rapid etching but also produced smoother PDAC/TDBC films. Until this dilemma had stymied progress, no one had ever reported measurements of the optical properties of a thin film structure consisting DBR, bottom spacer, plus nanoscale thin-film J-aggregate layer. Once it became clear that the Al$_2$O$_3$ layer was being wet-etched, pure curiosity dictated that we measure the optical properties of the half structure, since evidently even this was posing a challenge. This chapter covers the results that this structure yields, reinforcing the uniqueness of the PDAC/TDBC film optical properties. It also demonstrates that in principle, similar results could be achieved with other materials if greater thickness films are used.
7.1 Introduction

When constructing a system for demonstrating strong coupling, the natural tendency is to focus primarily on the optical properties of the components, i.e. the excitonic layer and the microcavity, and on the fully integrated composite system to check for Rabi-splitting. Understandably, optical measurements of the half cavity structure consisting of just one of the two mirrors from the microcavity, one of the cavity spacer layers, and the excitonic layer are routinely not reported. Linear optical measurements of the half cavity structure reveal interesting properties of a sub-structure nestled inside almost every exciton polariton device. The central point is that such a structure is capable of producing critical coupling between the reflective mirror element and excitonic layer, yielding a device that absorbs nearly 100% of the light incident at normal from the exciton layer side of the device [97]. The general conditions for satisfying the critically coupled resonator (CCR) phenomenon are developed and it is shown that many materials would be suitable for such CCR devices. That a film of PDAC/TDBC only (5.1 ± 0.5) nm thick satisfies these conditions, absorbing more than 97% of incident $\lambda = 591$ nm light, with an effective peak absorption coefficient of $\alpha_{\text{eff}} = (6.9 \pm 0.7) \times 10^6$ cm$^{-1}$, underscores the uniqueness of the J-aggregate layers as a material with an extraordinarily large absorption coefficient. Applications of the CCR as a standalone device are also discussed.

7.2 Background

Critical coupling is a general phenomenon in optical systems whereby impedance matching is utilized to eliminate reflection and achieve either complete transmission or absorption of optical power of a specific wavelength across some dielectric interface [98]. The principal is utilized to couple optical power efficiently from waveguides and optical fibers into ring mode and whispering gallery mode based high $Q$ resonators [99-102]. In addition, critical coupling can lead to greater switching contrast [100]. In this chapter, the concept refers to a planar thin film structure wherein none of the incident optical power is reflected from the structure without the use of an anti-reflection coating deposited on top of the absorber layer [97]. In this context, the critically coupled resonator (CCR) is a thin film structure that can absorb nearly all the incident light of a given wavelength in a few nanometers thick absorbing film. Impedance matching applies to the interface between air and the front face of the absorber layer of the structure.

7.3 Device

The CCR, sketched in Figure 7-1, consists of a dielectric Bragg reflector (DBR) as the mirror, a (5.1 ± 0.5) nm thick film of PDAC/TDBC as the absorbing layer, and a spacer layer of transparent material that separates the mirror and absorber layer by the correct distance needed for critical coupling. In the CCR of Figure 7-1, the absorbing thin film
consists of 4.5 SICAS of the cationic polyelectrolyte PDAC and J-aggregates of the anionic cyanine dye TDBC.

![Diagram of CCR structure](image)

**Figure 7-1** Critically coupled resonator (CCR) structure. The device consists of a dielectric Bragg reflector (DBR), a transparent spacer layer, and a layer of J-aggregate cyanine dye. The DBR consists of 8.5 pairs of sputter coated TiO$_2$ and Al$_2$O$_3$ layers, ending on TiO$_2$. The spacer layer is an additional sputter coated layer of Al$_2$O$_3$. The J-aggregate layer consists of 4.5 SICAS of the cationic polyelectrolyte PDAC and the anionic cyanine dye TDBC deposited at pH = 5.5. Reflection and transmission measurements are made with light incident from the J-aggregate side of the device.

### 7.4 Experimental Result

When light of wavelength $\lambda_c = 591$ nm is incident on the CCR of Figure 7-1 from the absorber layer side of the device, the measured reflectance is $R = 2\%$ (Figure 7-2). In contrast, for the DBR with spacer but without the absorbing layer, the reflectance at $\lambda_c = 591$ nm exceeds 95%, showing the dramatic change due to critical coupling. A similar structure has been discussed in the context of microwave engineering to eliminate wave reflections from conducting surfaces [103]. For the same CCR, the transmittance at $\lambda_c$ is $T = 1\%$. Consequently, 97% of the incident light is absorbed within the $(5.1 \pm 0.5)$ nm thick absorber layer, corresponding to a peak effective absorption coefficient of $\alpha_{eff} = (6.9 \pm 0.7) \times 10^6$ cm$^{-1}$. 
Figure 7-2 Measured reflectance and transmittance for the CCR with \( d_s = (90 \pm 1) \) nm, along with reflectance data for the neat PDAC/TDBC film and for the dielectric stack consisting of DBR with spacer layer. At \( \lambda_c = 591 \) nm, the CCR absorbs 97% of incident light.

7.5 Numerical Simulation

A wavelength resolved T-matrix simulation [104] numerically confirms the experimentally observed critical coupling phenomenon. To simulate the CCR's reflectance, T matrices were first constructed corresponding to the PDAC/TDBC film and the DBR. For the PDAC/TDBC film, with thickness \( d_a = 5.1 \) nm, the real and imaginary components of the refractive index \( (n + j \kappa = \tilde{n}) \) were obtained via a Kramers-Kronig regression of the neat film reflectance data, which as shown previously reproduces the neat film transmittance spectrum [42]. The DBR was modeled as consisting of 8.5 pairs of TiO\(_2\) and Al\(_3\)O\(_3\) layers, with refractive indices of \( n = 2.39 \) and \( n = 1.62 \) respectively, with the layer thickness adjusted to satisfy the Bragg condition \( (d_l = \lambda/4n_i) \) for \( \lambda = 565 \) nm. These models were combined with a model of the spacer layer with \( n_s = 1.62 \) and thickness \( d_s \) left as a free parameter. The simulation reproduces critical coupling at \( \lambda_c = 591 \) nm (Figure 7-3) for a spacer layer thickness \( d_s = 90 \) nm and odd multiples thereof. When \( d_s \) is set to a value greater or less than 90 nm, critical coupling does not occur at another wavelength.
Figure 7-3 Measured and calculated reflectance for the CCR device and DBR spacer stack. The calculated reflectance is based on the T-matrix formalism described in the text. The calculated fit matches the experimentally observed reflectance minimum at \( \lambda = 591 \text{ nm} \).

### 7.6 Generalized Model

The critical coupling phenomenon observed for the 5.1 \text{ nm} thick film of PDAC/TDBC spaced 90 \text{ nm} from the DBR of Figure 7-1 applies more generally to any thin film absorber layer of sufficient absorption strength (i.e. \( \kappa \)), providing \( d_a \) and \( d_s \) are set to the appropriate thicknesses. To demonstrate this, a generalized formalism for critical coupling was constructed for the CCR structure of Figure 7-1. To simplify the analysis, it is assumed that the mirror is a single layer of metal that is thick enough to neglect reflections from the mirror to substrate interface. The CCR structure then reduces to four regions of different refractive index: 1, air; 2, the absorber layer; 3, the spacer layer; and 4, the Ag mirror (See Figure 7-4a). These have three interfaces: 1-2, 2-3, and 3-4, with thicknesses for absorber and spacer layers, \( d_a \) and \( d_s \), represented as \( L_2 \) and \( L_3 \), respectively. The reflection coefficient, \( r \), of the structure for normal-incidence light is given by:

\[
r = \left[ \frac{r_{12} (1 + r_{23} r_{34} e^{2j \beta_{L_2}}) + e^{2j \beta_{L_2}} (r_{23} + r_{34} e^{2j \beta_{L_3}})}{(1 + r_{23} r_{34} e^{2j \beta_{L_2}}) + r_{23} e^{2j \beta_{L_2}} (r_{23} + r_{34} e^{2j \beta_{L_3}})} \right]
\]

where \( r_{ij} = (\vec{n}_i - \vec{n}_j) / (\vec{n}_i + \vec{n}_j) \) and \( \beta_i = 2 \pi \vec{n}_i / \lambda \) are the Fresnel coefficient for the interface \( ij \) and wavevector for the \( i^{th} \) layer, respectively. The percent reflectance, \( R \), is
given by $R = |r|^2$. Critical coupling occurs when parameters are chosen such that $R = 0\%$, since no light is transmitted through the CCR.

Figure 7-4b shows the absorber and spacer layer thicknesses that are needed to achieve critical coupling as function of the absorber layer $\kappa$. The result is plotted for three different values of the real part of the absorber layer refractive index, $n_a \in (1.55, 1.75, 2.0)$, $n_s = 1.7$ throughout, and the single mirror layer is assumed to be Ag, with complex refractive index derived from a fit to published data: $\bar{n} = 0.259 + j3.887$ at $\lambda = 584$ nm [105]. The thicknesses are normalized to $\lambda_c$ to emphasize the generality of this model. The model shows that as $\kappa$ increases, the absorber layer thickness must decrease to satisfy CCR conditions, with a corresponding increase in the spacer layer thickness. It also shows that for a given $\kappa$, as $n_a$ increases, $d_s$ decreases, as expected, while $d_a$ remains nearly constant. The model dictates that in order to critically couple the $d_a = 5.1$ nm thick PDAC/TDBC film of Figure 7-1 at $\lambda_c = 584$ nm ($d_a/\lambda_c = 0.87\%$) the extinction coefficient of the film must be $\kappa = 4.2$, which also sets $d_s/\lambda_c = 15\%$ or equivalently $d_s = 88$ nm for $n_a = 2.0$ and $n_s = 1.7$. These theoretical values agree well with the experimentally measured $\kappa = 4.2$ and $n_a = 2.1$ at 591 nm (for a 4.5 SICAS thin film of PDAC/TDBC) and $d_s = 90$ nm for the CCR structure in Figure 7-2 with $n_s = 1.62$.

Figure 7-4 Generalized structure and formalism for achieving critical coupling to absorber layer as a function of absorber $\kappa$. (a) General CCR structure consisting of 4 distinct media and 3 interfaces. (b) Model. Thicknesses for absorber and spacer layers are normalized to the CCR wavelength, $\lambda_c$. The reflectance plotted is at $\lambda_c$. For the spacer layer, $n_s = 1.7$, and for the absorber, the real component of the refractive index is set to $n_a \in (1.55, 1.75, 2.0)$.  

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7.7 Physical Explanation

Physically, critical coupling occurs when (1) all of the incident optical power is transferred through the front face of the CCR absorber layer and (2) the Poynting vector in the dielectric layers is purely imaginary. Consequently, two boundary conditions must be simultaneously satisfied to achieve critical coupling: that is, the magnitude of the Fresnel reflection coefficient, $\rho_F$, from air to the absorber layer front face must be zero, $|\rho_F|^2 = 0$, and the magnitude of the reflection coefficient, $\rho_B$, from the absorber layer back face to the dielectric spacer must be unity, $|\rho_B|^2 = 1$ (See Figure 7-5a). The first boundary condition is realized by impedance matching the CCR with air, and the second by mismatching the impedances across the absorber-spacer interface by a phase difference of $\pm \pi/2$. The second boundary condition also dictates that the Poynting vector is purely real on the absorber layer side of the interface. Figure 7-5b plots the real and imaginary components of the Poynting vector for the CCR structure simulated in Figure 7-3.

Mathematically, these boundary conditions can be expressed in compact form by recasting them in terms of impedances and applying appropriate impedance transformations. In general, for an electric field propagating (left to right) from a dielectric layer with impedance, $\eta_i$, to a second with impedance, $\eta_f$, the reflection coefficient across the interface is given by:

![Figure 7-5 Boundary conditions and Poynting vector for generating CCR. (a) Reflection coefficients across the air to absorber ($\rho_F$) and absorber to spacer ($\rho_B$) interfaces. (b) Magnitude of the real and imaginary components of the Poynting vector for actual CCR device of Figure 7-1.]
\[ \rho_y = \frac{\eta_y - \eta_i}{\eta_i + \eta_y} \]

where \( \eta_i \) is related to the complex refractive index, \( \tilde{\eta}_i \), by \( \eta_i = \eta_0 / \tilde{\eta}_i \), and \( \eta_0 \) is the impedance of free-space (377 Ω).

Using this notation, the back face reflection coefficient, \( \rho_B \), is given by:

\[ \rho_B = \frac{(\eta_2 - \eta_a)/(\eta_2 + \eta_a)}{1 + (\eta_2 - \eta_a)/(\eta_2 + \eta_a)} \]

where \( \eta_a \) is the impedance of the absorber layer and \( \eta_2 \) is the effective impedance of the spacer and mirror layers when evaluated at the back face to spacer interface. To satisfy the condition that \( |\rho_B|^2 = 1 \), one of three conditions must be met. Either letting \( \eta_a \to \infty \) or \( \eta_2 \to \infty \) will work mathematically, but these scenarios do not match the physics of the CCR. The third possibility, which matches the physics, is that the magnitude of the numerator and denominator in the \( \rho_B \) expression are equal, namely \( |\eta_2 + \eta_a| = |\eta_2 - \eta_a| \). Since impedances can be complex values, this condition is satisfied when the complex impedances, \( \eta_2 \) and \( \eta_a \), are mismatched by a phase difference of \( \pm \pi/2 \). Complex numbers map to vectors in 2-dimensions, hence this condition can be described graphically by considering the impedances, \( \eta_2 \) and \( \eta_a \), as vectors, \( \tilde{\eta}_2 \) and \( \tilde{\eta}_a \) in the plane. A specific example of this is given in Figure 7-6a, where \( \eta_2 \) is real and \( \eta_a \) is imaginary. In that case the sum \( \tilde{\eta}_2 + \tilde{\eta}_a \) and difference \( \tilde{\eta}_2 - \tilde{\eta}_a \) clearly have the same magnitude. More generally, even when both \( \eta_2 \) and \( \eta_a \) are complex, the same condition is satisfied, providing the \textbf{dot product} of their vectors is zero: \( \tilde{\eta}_2 \cdot \tilde{\eta}_a = 0 \) (See Figure 7-6b). This can be seen by applying a rotation to the vectors of the specific example, since rotations are length preserving operations.
Specific Example: If $\bar{\eta}_a$ is Imaginary and $\bar{\eta}_2$ is Real

When $\bar{\eta}_2 \cdot \bar{\eta}_a = 0$

**Figure 7-6** Vector description of Back Face CCR Condition. (a) Specific example of equal magnitudes of sum and differences of impedance vectors. (b) More general example of sum and difference vectors possessing equal magnitude, by virtue of orthogonality of the two complex impedances.

The physical significance of $\bar{\eta}_2 \cdot \bar{\eta}_a = 0$, beyond simply providing the conditions for achieving critical coupling, is that it dictates that, for a given mirror/spacer configuration, the real and imaginary components of the impedance and similarly the refractive index must scale linearly for critical coupling to be maintained. This scaling is evident in Figure 7-4b describing the generalized formalism for the CCR. For a given normalized spacer layer thickness of $d_0/\lambda = 0.11$, as $n_a$ changes from $n_a = 1.55$ to $n_a = 2.0$, a difference of 29.0%, the corresponding $\kappa_a$ changes from $\kappa_a = 1.49$ to $\kappa_a = 1.96$, for a difference of 31.5%. Similarly, at a spacer layer thickness of $d_0/\lambda = 0.16$, for the same changes in $n_a$, $\kappa_a$ changes from $\kappa_a = 4.10$ to $\kappa_a = 5.21$, for a difference of 27.1%. On average, $\kappa_a$ changes by 29.3% while $n_a$ changes 29.0%, numerically confirming the scaling described by: $\bar{\eta}_2 \cdot \bar{\eta}_a = 0$ derived from the CCR back face condition: $|\rho_b|^2 = 1$.

Recasting the front face condition, $\rho_r = 0$, in terms of impedances yields:

$$\rho_r = \frac{\eta_r - \eta_0}{\eta_r + \eta_0} = 0$$

where $\eta_r$ is the transformed impedance of the total CCR structure evaluated at the air front face interface, and $\eta_0$ is again the impedance of free-space. $\eta_r$ can be expressed in terms of the impedance of the absorber layer, $\eta_a$, modified by an impedance transformation to capture the effects of reflection from the back face of the absorber.
This transformation gives:

\[ \eta_l = \eta_a \left[ \frac{1 + \rho \beta e^{-2j\beta s}}{1 - \rho \beta e^{-2j\beta s}} \right] \]

where \( \beta = 2\pi (n_a - j\kappa_a) / \lambda \) and \( \rho \beta \) is defined as previously. Setting \( \eta_l = \eta_0 \), leads to:

\[ \frac{\eta_l}{\eta_a} = \left[ \frac{1 + \rho \beta e^{-2j\beta s}}{1 - \rho \beta e^{-2j\beta s}} \right] \]

from which an expression for \( \rho \beta \) is obtained in terms of \( \tilde{n}_a \):

\[ \left[ \frac{\tilde{n}_a - 1}{\tilde{n}_a + 1} \right] e^{2j\beta s} = \rho \beta \]

Since critical coupling simultaneously satisfies both the front and back face boundary conditions, it must be the case that \( |\rho \beta|^2 = 1 \), and the magnitude squared of the above expression is determined as:

\[ \left| \frac{\tilde{n}_a - 1}{\tilde{n}_a + 1} \right|^2 e^{2j\beta s} = |\rho \beta|^2 = 1 \]

Rewriting \( \tilde{n}_a \) in terms of real and imaginary components, the above expression becomes:

\[ \left( \frac{\tilde{n}_a - 1}{\tilde{n}_a + 1} \right)^2 e^{2j\beta s} = |\rho \beta|^2 = 1 \]

This expression captures the central behavior of the normalized absorber layer thickness curves, \( d_a/\lambda \), as a function of \( \kappa_a \) for a given value of \( n_a \). In particular, it elucidates the inverse relation between \( d_a \) and \( \kappa_a \), which is evident in the \( d_a/\lambda \) curves in Figure 7-4b.

### 7.8 PL Enhancement

If the absorbing films that satisfy the critical coupling conditions of Figure 7-4b were deposited on glass \( (n = 1.48) \) as neat films, T-matrix simulation shows that at \( \lambda_c \) they would absorb 32% of the incident light. The absorption gain from the CCR is therefore a factor of 3.1. Thus the CCR is essential for maximizing light absorption in a nanometer-scale thin-film single-mirror vertical geometry structure. In addition to increased absorption, the mirror element intrinsic to the CCR reflects the photoluminescence (PL) into the forward direction, thus boosting PL collection efficiency by about a factor of 2. From these calculations, an overall factor of 6 increase in collected PL can be expected, when optically exciting the CCR near the critical wavelength, \( \lambda_c \). This expectation is born out in the experiment. Figure 7-7a compares the normalized PL spectra of the CCR and a thin film witness sample, when excited at wavelength \( \lambda_{ex} = 500 \) nm. The spectra appear almost identical, with a 1.5 nm shift in PL peaks, and a 1 nm difference in FWHM. The structures where then excited with \( \lambda_{ex} = 590 \) nm light, nearly resonant with the critically coupled wavelength, and emission collected at wavelengths \( \lambda_{em} = 570 \) nm and \( \lambda_{em} = 605 \) nm. The ratio of PL intensity for the CCR and thin film sample are recorded at both of these wavelengths in Figure 7-7b. The ratio measures the increase in
collected PL for the CCR compared to thin film sample, and the average ratio computes
to 6.08, nearly the value of 6 expected based absorption and PL collection increases.

Figure 7-7 PL Spectrum from the CCR of Figure 1 and related table of PL counts. (a) Normalized
PL spectrum of CCR device and thin film witness sample. The samples were excited with $\lambda_{ex} = 500$
nm light and emission collected using a dual path intensity variation compensated SPEX
fluororimeter. PL intensity for the CCR is 9.45 times higher than for the thin film when excited at
$\lambda_{ex} = 500$ nm. The PL spectrum peaks at $\lambda = 596$ nm (2.081 eV) for the CCR and at $\lambda = 594.5$ nm
(2.086 eV) for the thin film, with FWHM of 15 nm (52 meV) and 14 nm (49 meV), respectively. (b)
Table of PL counts. PL emission is generated via excitation at the critically coupled wavelength $\lambda_{ex} = $
$\lambda_c = 590$ nm. Emission is collected at two different wavelengths offset from the critically coupled
wavelength for the CCR and thin film. Ratios are calculated and average 6.08, nearly as expected.

7.9 Applications

Looking beyond films of PDAC/TDBC and other J aggregates, one can envisage building
CCR’s with a variety of highly absorptive materials. Among non-epitaxially grown
materials, CCR structures can be implemented with organic polymers that are used in
biological assays and chemical sensors, with molecular materials that are used in
photodetectors and xerographic photoresistors, and in the emerging uses of colloidally
grown inorganic nanocrystal quantum dots (QDs), with the QD continuum states
providing the necessary absorption [106].

CCR’s, particularly with fast-relaxing chromophores like J-aggregated cyanine dyes or
porphyrins, could be used in non-linear optical switching and pulse generation
applications. In a review of Semiconductor Saturable Absorber Mirrors (SESAM)
technology [107], Keller, Weingarten, Kärtner, et al. assess the merits of an archetypical
“Thin anti-reflection (AR) coated SESAM”. CCR’s would be a specialized class of such
SESAMs, which would potentially exhibit very large modulation depth by virtue of the absorption occurring within thin films of only a few molecular layers.

In the CCR, separating the absorber layer from the mirror surface by the critical distance can increase light absorption in the absorber layer by a factor of 3.1. This boost could lead to photodetectors that are 3.1 times more power efficient. Similar design considerations have since been adopted by Heeger et al. in order to improve the power efficiency of their photovoltaic (PV) devices [108]. By introducing a TiO$_x$ optical spacer between their absorber layer and metallic contact, an increase of “incident photon-to-current collection efficiency (IPCE)” of ~ 40% is observed, which was attributed to the boost in absorption due to improved absorber layer placement relative to the optical field.

7.10 Conclusion

As mentioned at the beginning of this chapter, the CCR is an integral part of planar microcavity structures that exhibit strong coupling of light and matter in the form of exciton-polariton resonances [75]. Conceptually, PDAC/TDBC based polariton devices, where the absorber layer film is placed at the anti-node of the microcavity's optical field, are equivalent to a CCR plus a top mirror that is separated approximately $\lambda/4$ away from the PDAC/TDBC absorber film of the CCR. Measurement of the polaritonic bandgap observed as a high reflectance band centered about the uncoupled exciton resonance follows naturally since with the CCR in place there is no optical feedback from the bottom mirror to cause a resonant dip in reflectance in this wavelength band. Thus an understanding of the CCR phenomenon can assist in the development of future devices that operate in the strong coupling regime. Specifically, it can be used as diagnostic for determining whether the half cavity structure is being properly assembled. This diagnostic technique has since been utilized extensively in constructing more elaborate polaritonic devices.
8 Strong Coupling in Higher Q Cavities

“When you build a house, first you erect the walls, then you construct the furniture.”

(Remark by Betzalel, chief engineer of the Tabernacle’s construction to Moses on the proper sequence of assembling the Tabernacle.)

“He (Jacob) had a vision in a dream. A ladder standing on the ground, and its top reached up toward heaven. G-d’s angels were going up and down on it.”

(Genesis 28:12)

Anecdotal Introduction:

Growing DBR’s for the purpose of constructing higher Q cavities capable of generating true strong coupling has often seemed to be a task of Biblical proportions. It is, or at least it certainly seems that way. Growing a DBR is a long process that involves many variables and interdependencies, a fair number of which have malfunctioned along the way. So drawing on Biblical sources of guidance seemed natural and actually turned out to be quite helpful.

For the better part of 2 ½ years, I had been engaged in the process of growing DBR’s for J-aggregate based polaritonic devices. This effort began when Erin Boyd did a summer session in the lab, continued the next year with Stephanie Claussen in 2005, and then Scott and I worked on it regularly all of 2005-2006. In the summer of 2006 shortly after CLEO in Long Beach, California, Scott set about tackling the gargantuan task of automating the sputterer, which he finally tamed in September 2006. It would take 2 more months before we finally arrived at techniques for growing high quality DBR’s in the tight confines of the LOOE sputterer.

One may be tempted just to rely on commercially grown DBR’s. They serve a useful purpose. However, as this area of research is still in its infancy, having the flexibility to grow a DBR with exactly the right specifications is paramount.

With the help of Erin Boyd, who worked out some of the idiosyncrasies of sputterer, DBR’s were successfully grown for the first time. Her SEM image is shown in Figure 8-2d.
8.1 Introduction

In true strong coupling at room temperature, the light matter coupling strength, characterized by the Rabi-splitting, significantly exceeds the dephasing processes competing against the coherence of the interaction. With the aim of achieving true strong coupling at room temperature, polaritonic structures are constructed with narrower linewidths than those observed in the all metal mirror microcavities of Chapters 4 and 6. In the low Q metal mirror microcavities, large Rabi splitting of 265 meV is observed even under electrical excitation, however the linewidths of the resulting polaritonic resonances are quite large. In particular, the linewidth of the $E_\pm$ resonance in reflectance is $\Gamma = 77$ meV and $\Gamma = 105$ meV in EL, for the structure with empty cavity resonance $E_c = 2.11$ eV, closely tuned to the TDBC J-aggregate resonance (2.08 eV). Taken together, the strength of the coupling relative to dephasing, i.e. $\Omega_R/2\Gamma = 1.72$ in reflectance and $\Omega_R/2\Gamma = 1.27$ in EL. By decreasing the dephasing rate $\Gamma$, steps can be taken towards realizing $\Omega_R/2\Gamma >> 1$, either by improving the quality of the excitonic or photonic component of the polaritonic system. In this chapter, the quality of the cavity is improved by replacing the thinner 50 nm thick silver metal mirror of the devices in Chapters 4 and 6 with a dielectric Bragg reflector (DBR). The DBR is a highly reflective and low loss dielectric mirror element. As a result, a Q of 243.5 is achieved with a linewidth of 8.5 meV in an Alq$_3$ filled $\lambda/2n$ cavity. When a PDAC/TDBC film of 4.5 SICAS is situated at the anti-node of such a $\lambda/2n$ cavity, strong coupling is observed with a Rabi-splitting $\hbar\Omega_R \geq 125 \pm 7$ meV, average $\Gamma = 12.1$ meV, and $\Omega_R/2\Gamma \geq 5.1$.

The spacer separating the J-aggregate film from the silver mirror is comprised of a 65 nm thick film of Alq$_3$. Alq$_3$ is a fluorescent small-molecule organic compound with a broad-band photoluminescence (PL) spectrum that overlaps well with the polaritonic resonances of the device. By optically exciting the Alq$_3$ layer with a near UV laser, the polaritonic dispersion relation is probed using PL measurements. Agreement is demonstrated between PL results and the dispersion relation derived from angular reflectance data. Strong coupling is observed in reflection, transmission, and photoluminescence for the structure, with cleanly delineated $E_\pm$ resonances. For higher optical density excitations, as the J-aggregate layer photobleaches, the polariton resonances of the cavity are destroyed and are replaced by a single “empty” cavity resonance, which remains observable in PL until subsequent photobleaching of the Alq$_3$ layer. Deliberate photobleaching is exploited in order to determine the polaritonic resonances as a function of empty cavity resonance for spot sizes too small to be readily probed in reflectance measurements ($< \frac{1}{4}$"). PL probing samples with a number of thicknesses reveals Rabi-splitting as high as $\hbar\Omega_R = 140 \pm 7$ meV, and $\Omega_R/2\Gamma = 5.5$. 

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8.2 Background

Within the field of polaritonic devices based on organic semiconductors, the majority of the work reported utilizes microcavities that consist of a DBR and metal mirror [109]. These microcavities provide a compromise between the extremes of modal confinement of all metal mirror microcavities at one end and the high Quality factors of all dielectric cavities at the other. They possess reasonably high Q and modal confinement.

The increase in modal volume and therefore the expected decrease in Rabi-splitting can be quantified by considering the following formula for the effective penetration depth of optical field into a DBR [110]:

\[ L_{pen} = \frac{\lambda_c n_L n_H}{2n n_H - n_L} \]

Where \( \lambda_c \) is the center wavelength of the DBR, \( n \) is the refractive index of the cavity spacer, and \( n_L \) and \( n_H \) are the low and high refractive indexes of the two materials used to form the DBR. Typical values for refractive indices are \( n = 1.8 \), \( n_L = 1.46 \), and \( n_H = 2.34 \), which yields \( L_{pen} = 642 \) nm, assuming \( \lambda_c = 595 \) nm. This penetration is significantly larger than the penetration depth provided by silver in this wavelength range, where a 60 nm thick film of Ag attenuates the optical field by about 99%. The modal volume is increasing by about a factor of 3, from \( \sim \lambda / 2n \) to \( \sim 3\lambda / 2n \). The Rabi-splitting should therefore decrease by a factor of \( \sqrt{3} = 1.73 \). It is expected that the Rabi-splitting observed in the Low Q metal mirror cavities of \( h\Omega_R = 265 \pm 15 \) meV should decrease to \( h\Omega_R = 153 \pm 9 \) meV (assuming the PDAC/TDBC films are of similar optical properties). This prediction matches within experimental error, the maximum Rabi-splitting of \( h\Omega_R = 140 \pm 7 \) meV that is obtained in the higher Q metal-DBR microcavities.

The first investigations of strong coupling by Lidzey et al. [8, 25] were performed in such metal-DBR microcavities. He and coworkers spin-cast dye doped polymer films of controlled thickness onto DBR’s and then thermally evaporated a metal layer to complete the cavity. The Rabi-splitting achieved in such structures is about 80 meV to 160 meV [8]. Holmes and Forest used similar cavity architectures with thermally evaporated layers of small molecules such as NTCDA, PtOEP, and TPP as the excitonic component materials of the strongly coupled states [111, 112].

Investigating the characteristic polaritonic dispersion of such structures has been illuminating in a number of respects. In 1999, Lidzey showed the first room temperature PL spectra from such a cavity where a cyanine dye is doped into a PVA matrix [25]. Much effort was applied by his group and others to explain the details and peculiarities of the emission signatures. In particular, they wrestled with the problem of explaining the relative emission intensities from the upper and lower branch polariton states and uncoupled exciton states. They also worked to characterize a system where the excitons
were distributed throughout a matrix in a less than orderly fashion [44]. They postulate that optical phonons act rapidly to depopulate the upper branch states and induce energy transfer to the lower branch [113]. They also present experimental evidence based on Raman scattering supporting this model [114]. Holmes and Forrest used PL measurements to ascertain rate estimates for very fast molecular energy transfer processes based on the magnitude of the Rabi-splitting for their structures [112].

8.3 Device Design

The device design for the higher Q cavity polaritonic structures being investigated are illustrated in Figure 8-1. The DBR is deposited onto a float glass or polished quartz substrate, followed by inorganic oxide spacer layer, dip-coated PDAC/TDBC film, thermally evaporated organic spacer layer, and 100 nm Ag mirror layer. The DBR is designed to have a stop-band centered at the wavelength of the exciton resonance, i.e. a center wavelength \( \lambda_c \) between 590 nm to 595 nm. The high and low refractive index layers that constitute the DBR stack have thicknesses of \( \lambda_c/4n_i \) for the \( i^{th} \) layer. The two spacer layers need similar refractive index in the wavelength band of the J-aggregate resonance to maintain the integrity of the cavity. Large index mismatch leads to an undesired reflection at the layer interface which spoils the cavity. Hence, when Alq3 is the top spacer as for PL investigations, Al2O3 is selected as the bottom spacer since their refractive indexes are 1.7 and 1.62 respectively (measured at 632 nm), while when SiO2 is the bottom spacer (n = 1.46), TAZ is chosen as the top spacer (n = 1.55).

![Figure 8-1 Device design of higher Q polaritonic structure. The microcavity consists of a sputter-coated DBR and a silver (Ag) mirror layer. The Al2O3 spacer is approximately \( \lambda/4n \) thick, where \( \lambda = 595 \text{ nm} \) and \( n = 1.62 \). The J-aggregate layer is 4.5 SICAS of PDAC/TDBC assembled from Deionized (DI) H2O solutions. On top of the J-aggregate layer, a film of small molecule Alq3 is thermally evaporated. The Alq3 film is approximately 65 nm thick, which is less than \( \lambda/4n \) thick because the optical field penetrates more than 20 nm into the top reflector Ag layer. The DBR high refractive index material is either Hafnium dioxide (HfO2) or Titanium Dioxide (TiO2) and the low refractive index materials is usually SiO2 and sometimes Al2O3. Another configuration consists of SiO2 as the “bottom” sputter-coated oxide spacer layer and TAZ and the “top” organic thermally evaporated spacer layer.](image-url)
8.4 Experimental Methods

To construct higher $Q$ cavities, serious process development was required with respect to the following three areas:

1. Growing high quality DBR’s.
2. Integrating SICAS deposition of bi-layers onto DBR coated substrates
3. Matching the resonance of the cavity to that of the PDAC/TDBC film.

Figure 8-2 illustrates several aspects of the DBR growth process. The DBR’s are sputtered in the chamber of the integrated growth system of the lab. The sputterer was specifically fitted with a second RF power supply for the purpose of efficiently and safely sputtering two insulating oxide targets without swapping RF cables. Process gas of 20:1 mixture Argon to Oxygen at a pressure of 4 mT is used to sputter the targets at wattages between 180W to 350W yielding deposition rates less than 0.3 Å/s. Variation is measured in sputtered layer thickness from the center of the sputterer chamber towards the edge of the substrate, indicating that a maximum of four highly uniform 1” square substrates can be grown simultaneously. The SEM shows the smoothness of the sputtered DBRs, indicating a lack of roughness for the composite structure and lack of strain accumulation.

![DBR Deposition via Sputtering](image)

Figure 8-2 DBR Deposition via Sputtering. (a) 3-Gun Sputterer chamber and control panel. (b) Top down view of DBR consisting of Titania (TiO$_2$) and Alumina (Al$_2$O$_3$) as high and low refractive index oxide materials, respectively. Mirrors are reflective within stop-band (bright “gold” color) and transparent out of stop-band (“green region”). (c) Relative variation of layer properties as a function of distance from center of sputterer chamber: refractive index, layer thickness, and wavelength. Parameter shifts determined from Al$_2$O$_3$ calibration films grown on silicon substrate, measured via ellipsometry. (d) SEM image in cross-section of similarly grown DBR on silicon substrate. Dark gray regions correspond to 89.4 nm thick Al$_2$O$_3$ layers and light gray regions correspond to (more conductive) 61.7 nm thick TiO$_2$ layers.
In previous chapters (i.e., 3, 4, 5, and 6), PDAC/TDBC films were grown at pH = 9.0 (adjusted with sodium hydroxide) to promote J-aggregation in solution before subsequent adsorption into the film. However, when Al$_2$O$_3$ coated substrates are immersed in solutions at this pH, instead of PDAC/TDBC being deposited, the Al$_2$O$_3$ oxide layer is etched away. This result is illustrated in Figure 8-3. After immersing the substrate through a series of SICAS cycles (and the cavity completed with TAZ organic spacer and Ag top mirror), the cavity resonance is measured. It shifts to shorter wavelength upon additional SICAS because the Al$_2$O$_3$ layer is being thinned. The wavelength shift appears linear in SICAS as expected. To integrate SICAS deposition of the PDAC/TDBC films with the DBR coated substrates, plain deionized (DI) water is used (instead of pH = 9.0), which has a pH = 5.5. At this pH, the Al$_2$O$_3$ is not noticeably etched, and the PDAC/TDBC film adheres. The half structure that results is a CCR, which is discussed in Chapter 7. Changing to lower pH provides an additional benefit as it reduces surface roughness in the J-aggregate layer since nanocrystallites tend not to cluster in solution but form predominantly at the substrate-solution interface.

Figure 8-3 Effects of SICAS deposition in pH 9.0 Sodium Hydroxide (NaOH) on spacer layer thickness and thereby cavity resonance. (a) Device structure consists of sputter coated DBR and Al$_2$O$_3$ spacer layer, several SICAS, thermally evaporated organic TAZ, and Ag top mirror layers. (b) Reflectance of complete cavity indicates that at pH = 9.0, SICAS process etches Al$_2$O$_3$ layer, resulting in shortened cavity and therefore shorter wavelength cavity resonance. Layer thicknesses grown to coincide with λ ~ 590 nm. Inset shows Al$_2$O$_3$ layer is etched in linear increments, with resonant shift of 14.9 ± 0.5 nm per SICAS.
Matching the cavity resonance precisely to that of the J-aggregate film is of greater consequence than in lower Q cavities because the narrow bandwidth of the cavity windows a much more distinct portion of the J-aggregate (thin film) dispersion relation. Matching the cavity resonance translates into carefully controlling the thickness of the cavity layers. A 1 nm shift in spacer thickness translates into a 3 nm shift in resonance; hence the techniques for growing smooth uniform thickness DBR’s mentioned previously are crucial. Nevertheless, cavity tuning tends to be a single point of failure in the fabrication process unless a probabilistic approach is adopted. In particular, if several thicknesses are grown the chance of at least one of them having the correct thickness is greatly increased. The probability that after N trials, $p_N$, there is at least one success is given by:

$$p_N = 1 - (1 - p_T)^N$$

Where $p_T$ is the probability per trial of matching. Even with modest thickness control ($p_T \sim 0.3$), with 8 trials, $p_N \sim 95\%$. Several cavity thicknesses can be realized on a single substrate by growing the “discretized” wedge device of Figure 8-4b. A wedge with discrete increments in thickness is implemented instead of the traditional wedge architecture [115] achieved by sloping one of the cavity spacer layers so as to preserve the Q within each plateau of the structure.

![Figure 8-4 Probabilistic approach to matching cavity and exciton resonances](image)

Figure 8-4 Probabilistic approach to matching cavity and exciton resonances. (a) Total probability of matching both resonances after either 3, 8 or 16 trials are made, given a certain probability per trial. Blue range corresponds to a cumulative probability greater than 95%. (c) Up to 16 distinct cavity resonances are generated on a 1" substrate by implementing methods for growing 16 cavity thicknesses on a single substrate. The thickness of the Al₂O₃ spacer layer is varied incrementally.
8.5 Experimental Set-up

Transmission and reflection measurements are taken using the same apparatus as described in Chapter 4 on Rabi-splitting in low Q cavities. Transmission measurements are performed at $\theta = 0^\circ$, absolute reflectance measurements at $\theta = 7^\circ$ and angular TE polarized (relative) reflectance measurements at $\theta = 20^\circ$ to $70^\circ$.

The setup constructed for taking PL spectra as a function of angle is illustrated in Figure 8-5 below. The set-up is almost identical in concept and to the set-up for measuring EL spectra vs. angle (see Chapter 6). The main differences are the addition of lasers to excite the devices optically and the lack of electrical probes. Care is taken to insure that the excitation spot is located at the center of the axis of rotation for the rotational stage. In some cases an offset of several degrees ($\theta_{\text{offset}}$) is detected in the data and is accounted for in the analysis. A 4" focal length (FL) lens is used to collimate the laser beam and irises are used to reduce scattered or stray laser light. A near UV laser, either at $\lambda = 408$ nm or $\lambda = 414$ nm is used to excite polaritons off-resonances via excitation of the Alq$_3$ layer. A $\lambda = 532$ nm frequency-doubled Nd:Yag laser is used to excite samples within stop-band wavelength range of the DBR, Effectively exciting only the TDBC J-aggregate exciton layer. Unless specified otherwise, PL spectra are generated using the near UV laser.

408 or 414 nm Laser

<table>
<thead>
<tr>
<th>Laser Beam</th>
<th>Stop - Imit Flip</th>
<th>Fiber Tip</th>
<th>Spectrometer with CCD</th>
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<tbody>
<tr>
<td>Beam Stop</td>
<td>Optical Fiber</td>
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<tr>
<td>Mirror</td>
<td>Lens (4&quot; FL)</td>
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<td>Iris</td>
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<td>Device</td>
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<td>Beam Stop</td>
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<td>532 nm Laser</td>
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Figure 8-5 Experimental setup for measuring photoluminescence (PL) spectra as a function of angle. Lasers excite the sample from 70° off normal relative to the sample. Either a "green" $\lambda = 532$ nm laser excites the sample or a "blue" laser that is either a $\lambda = 408$ nm CW Gallium Nitride laser or a $\lambda = 414$ nm solid-state high-rep pulsed laser. One laser is used at a time, the choice controlled by a flip-up mirror. The device substrate is positioned in a mount that is connected to a translational stage. The translational stage is used to align the device to the center of the rotational stage, and to translate the substrate from cavity thickness to another, in the case of "discretized" wedge substrates. The optical fiber bundle is mounted on a shaft that is connected to the rotation stage at the stage's axis of rotation. The fiber-shaft apparatus is rotated by turning the rotational stage to the desired angle, which is restricted to the range or $\theta = \pm 55^\circ$ so as not to interfere with the laser beam path. The optical fiber is coupled to a spectrometer with charged coupled device (CCD) detector.
8.6 Results and Discussion

This section is structured as follows. First results of PL experiments on a cavity that does not contain a J-aggregate film are presented. From these results, properties of the “empty” cavity are derived and parameters are inferred that are subsequently applied in the analysis of the polaritonic structures. Then, a resonantly tuned polaritonic structure is investigated. Transmission and reflection are measured at normal and angular dispersion is characterized from which a Rabi-splitting is derived. PL is investigated and a PL dispersion relation is observed which matches that of reflection, establishing correspondence between PL and reflectance data. Then results of the photo-bleaching technique are presented for this initial device. Finally, a series of structures with different cavity tunings are investigated and it is demonstrated that the different polaritonic dispersions measured correspond to the shifts in the “bare” cavity resonance.

Figure 8-6 shows results of PL experiments on a cavity that does not contain a J-aggregate film. Figure 8-6a and Figure 8-6c plot normalized PL spectra versus angle (θ) using low resolution (Low Res.) and high resolution (High Res.) gratings (150 g/mm and 1200 g/mm, respectively). The spectra in Figure 8-6a show that the CCD saturates at large angle. The cavity resonance is at \( \lambda = 597.5 \) nm for small angles. The secondary peak at wavelengths shorter than \( \lambda = 500 \) nm is due to Alq3 fluorescence outside of the stop-band. At larger angles, the cavity resonant peak shifts to 534.6 nm, and a secondary peak at about 650 nm appears due to the long wavelength tail of the Alq3 fluorescence emitting outside of the DBR stop-band. Linewidths are considerably narrower in High Res. configuration (c) compared to Low Res. configuration (a). The High Res. spectra indicate structure at larger angles. Broadening of the PL peak is due to lowering of the reflectance of the DBR at large angle, which in turn reduces the cavity quality Q. Spikes in \( \theta = 66^\circ \) spectrum of (c) are due to fluorescence of the optical fiber. From the PL dispersion data (Figure 8-6b) it is clear that the fiber was offset from normal by about 7°. This is accounted for in the fit by introducing the variable \( \theta_{\text{offset}} \) in the model, yielding a dispersion relation of the form [2]:

\[
E_{\text{ph}}(\theta) = E_0 \left(1 - \sin^2(\theta - \theta_{\text{offset}})/n^2\right)^{1/2}.
\]

The refractive index, \( n = 1.9 \). This is interpreted as the average value of \( n \) over the band. This is higher than \( n = 1.7 \), the value typically ascribed to fluorescent organics, because the wavelength range under consideration is closer to the resonance of Alq3. The maximum \( Q = 243.5 \), demonstrating the improvement even a single DBR can make in reducing the photonic contribution to the polaritonic linewidth.

When a 4.5 SICAS film of PDAC/TDBC is situated at the cavity anti-node, strong coupling is produced. Figure 8-7a-d show the reflection and transmission spectra of the strongly coupled states. Both the \( E_+ \) and \( E_- \) polaritonic resonances are evident in both methods of measurement. The spectral feature associated with the \( E_- \) resonance is considerably narrower and more intense than that for \( E_+ \). It should be emphasized that this difference in lineshape is manifest even though the cavity is resonantly tuned to the J-aggregate resonance (See Figure 8-8b). This difference in lineshape is expected considering the n,k dispersion relation for such 4.5 SICAS PDAC/TDBC films is

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asymmetric and sharply peaked in refractive index on the lower energy side of the J-aggregate resonance. Note that only a tiny percentage of light is transmitted through the full structure because one of the mirrors is Ag.

Figure 8-6 Normalized PL spectra and dispersion relation for microcavity containing Alq3 spacer and no J-aggregate film. (a) PL spectra vs. θ, taken with low resolution (Low Res.) grating. (c) PL vs. θ with high resolution (High Res.) grating. (b) Dispersion relation. A single fit is used for both data sets, with $E_{ph} = 2.075$ eV ($\lambda = 597.6$ nm), background $n = 1.9$, and $\theta_{offset} = 7^\circ$. (d) Quality factor (Q) vs. θ, for High Res. and Low Res. data sets. The maximum measured $Q = 243.5$ at $\theta = 10^\circ$. 
Figure 8-7 Normal mode reflectance and transmittance spectra for higher Q microcavity resonantly tuned polaritonic structure with $E_{ph}(\theta = 0^\circ) = 2.10$ eV. (a) Absolute reflectance at $\theta = 7^\circ$ for polaritonic structure and 4.5 SICAS thin film. (b) Expanded view of reflectance indicating $E_\pm$ states. (c) Transmission from polaritonic structure and thin film at $\theta = 0^\circ$. Transmission of the cavity has been scaled up by 100 times (100x). (d) Expanded view of unscaled transmission data showing $E_\pm$ states. To reveal $E_\pm$ entirely, the top portion of the $E_\pm$ state data set was cropped from the figure.
Figure 8-8a shows the angularly resolved reflectance spectra for this same device. The resonance dips in reflectivity are plotted vs. \( \theta \) in Figure 8-8b and fit to the two state model of polaritonic dispersion. The results demonstrate good agreement with the fit, when \( E_{ex} = 2.1 \) eV, \( E_{ph} = 2.1 \) eV, and \( n = 1.8 \). Rabi-splitting of \( h\Omega_R = 125 \pm 7 \) meV is observed. The error bars in the dispersion correspond to the linewidths of the resonant spectral features, and not to an actual error in the resonance value.

Rabi-splitting of \( h\Omega_R = 125 \pm 7 \) meV is fit to Figure 8-8b, using background \( n = 1.8 \) and \( \theta_{off} = 0^\circ \).

When this polaritonic device is excited with a near UV laser, PL is observed that displays the characteristic polaritonic dispersion of strongly coupled states. The PL data and analysis are depicted in Figure 8-9a-d. Figure 8-9a shows the Low Res. PL spectra vs. \( \theta \). The \( E_- \) state is peaked at \( \theta = 0^\circ \) and then attenuates at larger angle while the opposite is true for the \( E_+ \) state. The \( E_- \) state is most intense at shallow angle where it is still highly photonic in character. The \( E_+ \) state becomes brighter at large angle where it is more photonic. In terms of spectral purity, these structures show very little emission from uncoupled J-aggregate states within the polaritonic bandgap. In this respect, these devices show marked improvement over the Low Q devices of Chapter 4 where stray emission from uncoupled J-aggregate was present. The dispersion relation of the PL
peaks vs. $\theta$, shown in Figure 8-9b, are fit with identical material parameters as the reflection data. However, $\theta_{\text{offset}} = 2^\circ$, to account for experimental misalignment.

Figure 8-9 PL Spectra vs. $\theta$ for resonantly tuned polaritonic structure. (a) PL vs. $\theta$. (b) PL polariton dispersion relation, fit with $\hbar\Omega_R = 125$ meV, $E_{\text{ex}} = 2.1$ eV, $E_{\text{ph}} = 2.1$ eV, background $n = 1.8$, and $\theta_{\text{offset}} = 2^\circ$. (c) Expanded view of PL spectra vs. $\theta$ for $E_-$ states. (d) Expanded view of PL spectra vs. $\theta$ for $E_+$ states.

The agreement between PL and reflection measurements in discerning the polaritonic dispersion points to PL as being an effective probe of polaritonic dispersion particularly
The PL spectrum at $\theta = 0^\circ$ of Figure 8-9a show that even when the 65 nm thick film of Alq$_3$ present in the cavity is optically excited, the emission intensity of the $E_+$ state is still significantly lower than that of the $E_-$ state. This is not surprising considering that the transmission through the polaritonic structure, while doubled-peaked (See Figure 8-7c,d), is less than 0.01% through $E_+$ at $\theta = 0^\circ$ while it is about 50 times higher through the $E_-$ state. Hence, much less emission is detected from the $E_+$ states, even though the resonant dip in reflectance for $E_+$ is several percent. It seems that the Alq$_3$ emission is being absorbed in the TDBC layer in a manner similar to the functioning of a CCR. After being absorbed in the TDBC layer, the energy is then funneled in to the $E_-$ states. However, the $E_-$ peak is not significantly brighter here than when the J-aggregate film and Alq$_3$ layers are excited together in a half-cavity structure with the DBR absent. Therefore, it may be that the Alq$_3$ emission is being “trapped” by the polaritonic states either by “trivial” transfer, i.e. far-field absorption, or non-radiatively by near field effects. Further investigation of the lifetime of the emission would probably be necessary to resolve this point.

As the TDBC layer is photobleached, the uncoupled cavity resonance is recovered. Figure 8-10b shows a time sequence of PL spectra from the polaritonic structure as the PDAC/TDBC film photobleaches. The PL peak of $E_-$ shifts towards $E_{ph}$, from a starting wavelength $\lambda_{PL} = 606.9$ nm ($E_{PL} = 2.043$ eV) with FWHM = 3.8 nm (13 meV) to $\lambda_{PL} = 591.8$ nm ($E_{PL} = 2.095$ eV) with a FWHM = 3.1 nm (11 meV), yielding an “empty” cavity quality $Q = 189.9$. The ending resonance, 2.095 eV, is almost exactly the value chosen for $E_{ph} = 2.1$ eV in the dispersion relation fits. Not all of the intensity from $E_-$ is bleached. Figure 8-10c shows that when an iris constricts the area of excitation the PL peaks for $E_-$ and $E_{ph}$ decrease by different amounts, suggesting that the photobleaching is non-uniform across the beam cross-section. Figure 8-10d shows that when a TDBC layer is photobleached outside of a polaritonic device (in this case a half-cavity structure), the PL intensity decreases without a shift in the $E_{ex}$ resonance. This suggests that shift in resonance towards $E_{ph}$ in the polaritonic structure is due to loss of absorption strength and not to a shift of $E_{ex}$.
Figure 8-10 Analysis of PL properties of resonantly tuned polaritonic and PDAC/TDBC J-aggregate constituent film. (a) PL spectrum of 4.5 SICAS film embedded in half-cavity consisting of J-aggregate film, 65 nm thick Alq3 spacer, and 100 nm thick Ag mirror. PL peaks at $\lambda_{PL} = 594.5$ nm ($E_{PL} = 2.086$ eV) with FWHM = 13.6 nm (48 meV) generated via laser excitation with $\lambda_{ex} = 532$ nm. (b) Time sequence of PL spectra of polaritonic structure as PDAC/TDBC film photobleaches. The PL peak of the E. state starts at $X_{PL} = 596.7$ nm ($E_{PL} = 2.078$ eV) initially and shifts $\Delta \lambda = 0.3$ nm. The PL spectra are generated via $\lambda_{ex} = 414$ nm, and plotted spectra are the 1st, 4th, 10th, 22nd, 36th, and 50th scans acquired. High energy shoulder is due to PL of Alq3.
The characteristic dispersion of strong coupling demonstrated in the resonantly tuned devices is also captured in the data of Figure 8-11, Figure 8-12, and Figure 8-13, which plot angular PL for three polaritonic structures of different $E_{ph}$. The PL peaks vs. $\theta$ are used to generate angular dispersion relations which are fit via the two state model used previously. The sample spots are labeled, F, K, M. There actually were 16 devices on the substrate, labeled A-P, each square about $\frac{1}{4}''$ x $\frac{1}{4}''$ on the substrate, grown using the “discretized” wedge approach described in the experimental methods section. For all three fits, $E_{ex} = 2.1$ eV, $n = 1.8$, and $\theta_{offset} = 5^\circ$. The values of $E_{ph}$ used in the fits are 2.16 eV, 2.12 eV, and 2.09 eV, for samples F, K, and M, respectively. The Rabi-splitting of spots F and K is 125 meV while it is 140 meV for spot M. With the photobleaching technique, the extracted value for the uncoupled $E_{ph}$ are 2.143 eV, 2.097 eV, and 2.072 eV, respectively. These values compare well with the fit parameters, although they are red-shifted about 20 meV from them.

Tuning $E_{ph}$ through $E_{ex}$ effects the energy levels and also the relative intensity of the strongly coupled states, $E_\pm$. In particular, $E_+$ is considerably higher intensity for spot F, which has a higher energy $E_{ph}$ than spots K and M. Tuning also effects the intensities of the $E_-$ polaritonic resonances relative to the photobleached $E_{ph}$ PL peak. In particular, $E_-$ is strongest intensity (and most red-shifted) in spot M where $E_{ph}$ is tuned to the longest wavelength of the three spots. These observations support the assertion that the probability of emission from a polaritonic state is proportional to its photon fraction.

For the 4 structures presented, linewidths of the $E_-$ state average 12.6 meV and the Rabi-splitting averages 129 meV. This yields an average $\Omega_R/2\Gamma$ of 5.1. The best $\Gamma$ is observed in the resonantly tuned sample of Figure 8-7. The largest Rabi-splitting and highest $\Omega_R/2\Gamma$ are observed in spot M, where $\hbar\Omega_R = 140$ meV and $\Omega_R/2\Gamma = 5.5$, respectively.
Figure 8-11 PL characterization of strong coupling at position F (Pos. F) on the substrate. (a) PL vs. \( \theta \). (b) PL polariton dispersion relation, fit with \( \hbar \Omega_p = 125 \) meV and \( E_{ph} = 2.16 \) eV, background \( n = 1.8 \), and \( \theta_{offset} = 5^\circ \). (c) High Res. PL spectra vs. \( \theta \) of E. states. (d) Time sequence of PL spectra as PDAC/TDBC film photobleaches. The PL peak of the E. state starts at \( \lambda_{PL} = 601.6 \) nm (\( E_{PL} = 2.061 \) eV) with FWHM = 3.9 nm (13 meV). As TDBC photobleaches, the resonance blue-shifts to \( \lambda_{PL} = 578.7 \) nm (\( E_{PL} = 2.143 \) eV) with a FWHM = 2.9 nm (11 meV), yielding an “empty” cavity quality \( Q = 200.2 \).
Figure 8-12 PL characterization of strong coupling at position K (Pos. K) on the substrate. (a) PL vs. θ. (b) PL polariton dispersion relation, fit with $\hbar \Omega_R = 125$ meV and $E_{ph} = 2.12$ eV, background $n = 1.8$, and $\theta_{offset} = 5^\circ$. (c) High Res. PL spectra vs. θ of E. states. (d) Time sequence of PL spectra as PDAC/TDBC film photobleaches. The PL peak of the E. state starts at $\lambda_{PL} = 606.7$ nm ($E_{PL} = 2.044$ eV) with FWHM = 4.3 nm (14 meV). As TDBC photobleaches, the resonance blue-shifts to $\lambda_{PL} = 591.3$ nm ($E_{PL} = 2.097$ eV) with a FWHM = 2.9 nm (10 meV), yielding an “empty” cavity quality $Q = 205.5$. 

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Figure 8-13 PL characterization of strong coupling at position M (Pos. M) on the substrate. (a) PL vs. \( \theta \). (b) PL polariton dispersion relation, fit with \( \hbar \omega_p = 140 \) meV and \( E_{ph} = 2.09 \) eV, background \( n = 1.8 \), and \( \theta_{offset} = 5^\circ \). (c) High Res. PL spectra vs. \( \theta \) of E. states. (d) Time sequence of PL spectra as PDAC/TDBC film photobleaches. The PL peak of the E. state starts at \( \lambda_{PL} = 612.9 \) nm (\( E_{PL} = 2.023 \) eV) with FWHM = 3.6 nm (12 meV). As TDBC photobleaches, the resonance blue-shifts to \( \lambda_{PL} = 598.4 \) nm (\( E_{PL} = 2.072 \) eV) with FWHM = 2.8 nm (10 meV), yielding an "empty" cavity quality \( Q = 211.8 \).
8.7 Conclusion and Future Work

Here metal-DBR microcavities are used to provide higher Q than the all metal mirror cavities of Chapters 4 and 6. The CCR's of Chapter 7 are completed as polaritonic structures by growing a 65 nm thick film of Alq3 on top of the PDAC/TDBC film followed by a silver layer. The devices are probed using transmission and reflection measurements as well as PL. In order to excite the polaritonic resonances, the Alq3 layer is excited at energy levels above the stopband of the DBR. Alq3 acts as an internal "white light" source for probing the strongly coupled states. Combining knowledge of the n,k dispersion of the PDAC/TDBC films as well as measurements of the transmission through the device yields insight into the relative intensity of the upper and lower branch polariton states.

Strong coupling is achieved using LBL assembled films of J-aggregated TDBC and PDAC. Rabi-splitting is observed in transmission, reflection, and PL, with coupling strengths of $\hbar\Omega_R \geq 125 \pm 7$ meV, average $\Gamma = 12.1$ meV, and $\Omega_R/2\Gamma \geq 5.1$. The Q of a $\lambda/2n$ cavity filled with Alq3 is measured to be $Q = 243.5$. Photobleaching the TDBC film reveals the uncoupled photon resonance. From these data it is inferred that the Alq3 emission is being funneled either radiatively or non-radiatively into the TDBC film as would be expected considering the similarities between the full device and the CCR.

Future work for these structures will focus on increasing the number of J-aggregate layers, decreasing the modal volume by creating a pillar device [116] which should increase Q and possibly increase the coupling strength. These points are further discussed in the Chapter 9. Energy transfer dynamics should be investigated. The Alq3 emission appears completely "quenched" compared to the J-aggregate free cavity. Fluorescence lifetime measurements should be investigated. Furthermore, several J-aggregates could be loaded into the cavity. Structures containing multiple J-aggregate layers were first investigated by Lidzey et al. [117] using thick polymer layers doped with different cyanine dyes. The relative PL intensity of the resulting polariton resonances could provide information on fast energy transfer processes if understood according to the model developed by Holmes and Forrest [112].
9 Towards a Room Temperature Polariton Laser

"Before you can do something, you must first be something."

"Take the first step and magic will happen."

(Johann Wolfgang von Goethe)

"Take off is actually the most dangerous point of flight. There's a point where you have to decide, 'either go or no go', before it's actually clear that you are going to make it."

(Paraphrasing Scott Bradley's description of pilots' decision process.)

Anecdotal Introduction:

A double DBR microcavity is an ultra high Q microcavity consisting of two dielectric mirrors. Such a cavity usually takes over 24 hours of continual material deposition to complete and often more than 48 hours. It can feel like embarking on a flight around the world excursion. Of course, there's also no guarantee the DBR is going to have exactly the properties specified and even if both DBRs grow with the correct stop-band, there's still the challenge of growing approximately a 187.5 nm thick cavity spacer with about 1 nm precision across the majority of a 1" square. To be sure, other researchers and commercial coating houses can accomplish such heroics. Our lab is able to do this, with repeatability thanks to the work of Scott Bradley, who automated the sputterer. Before then, by great exertions, such devices were successfully grown, however the growth was simply so taxing that it was usually beyond emotional capability to fully test the resulting devices. Automation increased throughput more than 200% and productivity by an even greater multiple because devices could now be characterized while a follow-on experiment was being started. In the airlines, all seats arrive at the same time, but not all passengers share the same flight experience. The same is true for the substrates grown inside the sputterer, and therefore great care was taken to characterize the variation such that it was ultimately reduced to less than 0.5% across a 1" square.
9.1 Introduction

The goal of this chapter is to describe the workings of a laser operating in the strong coupling limit and outline a path for constructing one. Conceptually, a laser operating in the strong coupling limit should act as both a traditional laser and traditional parametric oscillator simultaneously. A laser operating in strong coupling, which could be called a polariton laser in the solid state, by definition has $\beta = 1$ [118, 119]. Searching for a lasing threshold in a classical sense is therefore futile. Rather, such a laser should have markedly different dynamics than a regular laser, which should be manifest as a function of pump intensity. In order for these effects to materialize, losses characterized by $\Gamma$ must be reduced in absolute terms. Specifically, large Rabi splitting alone is an insufficient condition, as would be giant $\Omega_R/2\Gamma$. It is critical that small $\Gamma$ be achieved in absolute terms. This scenario can be accomplished by raising the Q of the cavity and by reducing the excitonic contribution of the coupled system’s linewidth to the homogeneously broadened value of the J-aggregate film. Results and simulation showing promise towards this aim are described in the chapter. Specifically, strong coupling is demonstrated in a $\lambda/2n$ an all-dielectric microcavity constructed of two sputtered DBR’s with a $\hbar\Omega_R = 105$ meV, with $\Omega_R/2\Gamma = 3.5$, and a path is presented for achieving $\hbar\Omega_R \geq 240$ meV, $\Omega_R/2\Gamma > 30$, and $\Gamma \sim 4$ meV.

In essence, every traditional laser or optical parametric oscillator is a resonator in which damping losses are compensated by some gain process. Using the LRC circuit analogy, either the resistance must become negative or the inductance or capacitance must become time dependent. The former case is referred to as a laser and is achieved by inverting the population of the matter component. The latter case is an optical parametric oscillator and is achieved through exciting a non-linearity in the polarization of the material. A laser operating in the strong coupling limit combines both effects.

To first order, in strong coupling, a damped oscillator still exists. When the coupling, $g$, is large compared to polarization and photon decay, i.e. $\gamma$ and $\kappa$, the two eigenstates at $\omega_k$ decay exponentially at a rate of $(\kappa + \gamma)/2$. When the system is impedance matched ($\kappa = \gamma$), the decay rate per mode is just $\kappa$, the same parameter for photon decay one would use in a traditional cavity.

The primary differences between a regular laser and polariton laser as shown in Figure 9-1 is that because of the rapidity of the light matter interaction, in strong coupling the matter and light fields beat coherently with each other.
Figure 9-1 Comparison of lasers operating in weak and strong coupling, both cavities containing multiple excitons. (a) In a regular laser the decay rate for the exciton polarization is much larger than the light matter coupling. Therefore, the induced polarizations decay away before they can affect the dynamics. (b) In a polariton laser, the dipoles interact strongly with the photons in the cavity and the net polarization is large.
9.2 Physical Model

In order to achieve lasing in a traditional laser, the following equation must be satisfied for the threshold density of photons, \( N_t \), in the resonator [120]:

\[
N_t = \frac{1}{c \tau_c \sigma_{em}}
\]

where \( \tau_c \) is the lifetime of light in the cavity and \( \sigma_{em} \) is the emission cross section for optical transition of the excitons that are resonant with the cavity. \( N_t \) is generated by means of population inverting some density of excitons. If the excitons are "4-level" species, then the density of inverted excitons, \( N_0 \), is given by:

\[
N_0 = t_{sp} N_{ex} \sigma_{abs} \frac{I}{h \nu_{abs}}
\]

where \( t_{sp} \) is the lifetime of spontaneous emission, \( N_{ex} \) is the material density in the cavity, \( \sigma_{abs} \) is the absorption cross section for the excitons at the pump frequency \( \nu_{abs} \), and \( I \) is the intensity (W/cm\(^2\)) of pump light. By satisfying \( N_t = N_0 \), the threshold pump intensity \( I_t \) and pulse energy per unit area \( J_t = I_t t_{sp} \) are determined (assuming 100% photoluminescence quantum efficiency).

In the strong coupling limit, where \( \Omega_R^2/(\gamma \kappa) \gg 1 \), there is no laser threshold, because the rate of spontaneous emission into the mode is much greater than the decay of photons out of the cavity. This is quite different than in a traditional laser, where in CW pumping, the rate of emission (by combination of spontaneous and mostly stimulated emission) into the mode exactly balances the rate of decay out. In strong coupling, it is precisely because the spontaneous emission into the mode is faster than both \( \kappa \) and \( \gamma \) that strong coupling is observed at all. Thus the effect of strong coupling is to generate a scenario similar to a traditional laser that has \( \beta = 1 \) [118, 119]. The strong coupling case is still quite different because of the underdamped Rabi-oscillations via persistent polarization.

Qualitatively strong coupling modifies the spontaneous emission rate into the cavity mode (s), by boosting the emission cross section, \( \sigma_{em} \), by a factor of \( \Omega_R^2/(\gamma \kappa) \) (See Kimble [1, 118, 119]):

\[
\sigma_{em} \rightarrow \sigma_{em} \Omega_R^2/(\gamma \kappa)
\]
If the vacuum Rabi-splitting $\Omega_R = 125$ meV and the linewidths $\kappa = \gamma = 1$ meV, the cross section in the strong coupling limit would be about 15,625 times larger than in the conventional laser. This boost in emission cross section, $\sigma_{em}$, is plausible considering that in the light-matter interaction, the matter dipole and a number of its image dipoles radiate in phase. However, the number of image dipoles that cooperate must be normalized relative to the decay processes. It must be emphasized that it is not correct to make such a substitution in the threshold equation, since in the strong coupling limit, the "threshold" condition of balancing cavity decay by emission into the mode is satisfied for any density of photons in the mode.

Formally, the introduction of $\Omega_R^2$ in the equation for $\sigma_{em}$ makes the laser threshold equation look very similar to the threshold for an optical parametric oscillator (OPO): $g^2 = \alpha_1 \alpha_2$ [121] where subscripts "1" and "2" denote the signal and idler beams. In a traditional OPO, a third beam, beam "3", is the pump beam which passes straight through the OPO because the mirrors are transparent at the pump frequency. In the case of strong coupling, the signal beam and idler beam correspond to the strongly coupled states at $\omega_\pm$ and the pump beam is internal to the resonator. In an OPO, a non-linear material is needed. In strong coupling, the non-linear dependence between electric field and polarization is itself the result of the strong coupling of light and matter.

In a traditional laser, the linewidth of the laser light is determined by [121]:

$$\Delta \nu_{laser} = \frac{1}{2\pi \tau \bar{n}}$$

Where $\bar{n}$ is the average number of photons in the lasing mode and it is again assumed that the laser is comprised of excitons that are "4-level" species. This equation is very telling. First, it says that in a traditional laser the linewidth is inversely proportional to $\tau$, the lifetime of light in the cavity. This is quite reasonable since it was the photon decay that determined the loss of the resonator in the first place. Second, it says that the linewidth will decrease as $\bar{n}$ increases. This fact insures that the power loss, which is proportional to $\bar{n} \Delta \nu_{laser}$ is independent of the number of photons in the cavity. This equation also says that the laser light becomes more correlated as $\bar{n}$ increases, since the correlation time, $\tau$, for a laser is inversely proportional to $\bar{n}$ with $\tau = 4 \tau_c \bar{n}$ [121].

At first brush, one would think the same dependence would hold for the linewidth of a laser operating in the strong coupling limit. However, this is not true. To understand how the linewidth changes with $\bar{n}$, it is important to consider the eigenvalue equation for the light-matter system. For a system of N excitons interacting with a single mode resonantly tuned cavity [1]:

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\[ \lambda_\pm = \left( \frac{\kappa + \gamma}{2} \right) \pm \left[ \left( \frac{\kappa - \gamma}{2} \right)^2 - g_0^2 N \right]^{1/2} \]

Where \( g_0 \) is the interaction for a single exciton in the cavity and \( 2g_0 \sqrt{N} = \Omega_k \), the observed vacuum Rabi-splitting. When there are \( \bar{n} \) photons in the cavity, this equation needs to be modified in the following three ways:

\[
\begin{align*}
g_0^2 N &\rightarrow (\bar{n} + 1)g_0^2 N \quad \text{(Interaction Strength)} \\
\gamma &\rightarrow (\bar{n} + 1)\gamma_0 \quad \text{(Polarization Decay)} \\
\kappa &\rightarrow \frac{1}{(\bar{n} + 1)}\kappa_0 \quad \text{(Cavity Decay)}
\end{align*}
\]

The interaction strength increases because the number of photons and excitons both equally enhance energy transfer (between light and matter) in so far as the coupled system is concerned. The polarization decays more rapidly because of amplified spontaneous emission. The cavity decays at a slower rate as it does for a traditional laser because of stimulated emission.

When these substitutions are made in the equation for \( \lambda_\pm \) and the system is initially impedance matched, i.e. \( \gamma_0 = \kappa_0 \), and assuming \( (\bar{n} + 1) \approx \bar{n} \), the following relation holds:

\[
\lambda_\pm = \frac{\kappa_0}{2} \left( \frac{1}{\bar{n} + \bar{n}} \right) \pm \frac{\kappa_0}{2} \left[ \left( \frac{1}{\bar{n}} - \bar{n} \right)^2 - \frac{4g_0^2}{\kappa_0^2} \bar{n}N \right]^{1/2}
\]

Setting the Rabi-splitting to 125 meV and the linewdths \( \hbar \kappa = \hbar \gamma = 1 \) meV, as in the previous example, leads to:

\[
\frac{4g_0^2}{\kappa_0^2} = 125^2 = 15,625
\]

The imaginary component of \( \lambda_\pm \) corresponds to the sinusoidal component of the decaying exponential solutions and is the effective coupling: \( g(\bar{n}, \bar{n}) \). Unlike in the traditional laser, the magnitude of the linewidth increases for all \( \bar{n} \), as the impedance matching between the light and matter constituents is thrown out of balance.

Similar linear and square-root dependence regions of the laser linewidth on \( \bar{n} \) have been identified by Yamamoto [15] in his theoretical treatment of polariton lasing from the lower branch (LB) polariton state when excited via stimulated polariton-polariton scattering between LB states. The model presented here indicates that although the linewidth of the laser line increase linearly with \( \bar{n} \), the overall coupling and hence Rabi-splitting increase at a considerably faster rate for any realistic region of operation (i.e. \( \bar{n} \))
< 5x10^3). For the traditional laser, the power loss is constant for large \( \bar{n} \), because the laser linewidth is reciprocal in \( \bar{n} \) (\( \Delta \nu_{\text{laser}} \propto 1/\bar{n} \)). In strong coupling, since the linewidth is increasing with \( \bar{n} \), the power emitted goes as \( \bar{n}^2 \), and drains more quickly as more photons are injected into the mode. This laser is therefore super-radiant. Similar super-radiant phenomena are found in other non-linear optical systems [122].

A benefit of the device architecture being proposed here is the ability to incorporate additional materials in the cavity that can serve as energy transfer donors or acceptors that may modulate or simply probe the strong light matter interactions. Energy transfer could be important for at least three reasons: it allows the strongly coupled states to be excited resonantly within the cavity, by means of exciting the structure indirectly. It may be possible to generate higher intra-cavity photon numbers \( \bar{n} \) if the cross section of the donor molecule is higher than that of the J-aggregate at the off-resonant pump wavelength. Cooperation amongst the J-aggregates may enhance or suppress the energy transfer rate. Likewise, as the polarization of the J-aggregate oscillates, if the decay pathways are minimized this oscillation could induce phase locking of the donor dipoles and cause the transfer rate to increase super-radiantly. As a function of pump power, these non-linear effects would be manifest in the emission spectrum of the laser as greater Rabi-splitting and bandwidth expansion of the strongly coupled \( E_p \) polaritonic states.

In summary, a laser operating in the strong coupling limit has no threshold, much like a traditional laser with \( \beta = 1 \). The lack of threshold is the result of strong coupling boosting the spontaneous emission rate in the laser modes well above the photon decay rate, and not because of a fictitious “no loss” assumption. Such a laser emits light super-radiantly at a frequency that should be intensity dependent. The polarization of the emission should match that of the pump laser, similar to the behavior of a microcavity dye laser with large \( \beta \) [123]. This laser is qualitatively similar to traditional non-linear optical oscillators where non-linear polarization plays an important role in the power transfer process, e.g. optical parametric oscillators, Raman lasers and four-wave-mixers. To recover threshold behavior, one would have to decrease the density of molecules in the microcavity, making the coupling strength, \( g \), lower than both \( \kappa \) and \( \gamma \). Thus an electrically pumped laser in the strong coupling limit could be modified to exhibit extremely low threshold traditional laser behavior. Lastly the possible benefits of energy transfer need to be explored. The transient behavior of the laser when pulsed sources are used will also be considered as it promises to be rich territory for understanding and leveraging the coherent quantum (semi-classical) dynamics.
9.3 Device Design

The devices being proposed in this chapter operate in the strong coupling limit, where $g$ and hence $\Omega_R \gg \kappa$ and $\gamma$. The structure of these devices is shown in Figure 9-2. The optical resonator, which traps the light, is composed of two dielectric mirrors to provide higher $Q$ and the discretized ladder approach of Chapter 8 is used to generate structures of different cavity resonance. An optically thin layer of several SICAS is positioned at the center of the cavity where the electric field intensity is a maximum and an organic spacer such as TAZ is used as both a spacer layer and protective coating for sputtering the top DBR.

![Figure 9-2 Structure of optical microcavity resonator with SICAS deposited layer of J-aggregate positioned at the cavity anti-node. The device consists of a bottom DBR, spacer layer and the J-aggregate layer, followed by a top spacer layer and top DBR.](image)

For depositing the top DBR, sputtering is performed at low power without oxygen for the first few oxide layers in order to protect the J-aggregate layer. During sputtering, a process gas such as argon is introduced into the chamber and converted into plasma in order to generate the plume of target material which then deposits onto the substrate. This plasma reacts with the J-aggregate layer and causes it to photobleach, unless the J-aggregate layer is protected. If the J-aggregate layer is coated with a 90 nm thick oxidation-resistant layer before sputtering, such as an n-type organic material, the reflectivity and absorption properties of the J-aggregate layer are preserved to a great degree.
9.4 Cavity Characterization

Figure 9-3 shows PL spectra of such a cavity when no J-aggregate layer is present, and instead, the entire λ/2n layer is filled with Alq3. The bottom DBR consists of 5.5 pairs of TiO2 and SiO2 as the high n and low n materials of thickness “λ/4n”. The top DBR consists of 6.5 such pairs. Both DBR stacks begin and end with TiO2 layers. The PL spectra indicate that the Q = 734, which is considerably higher than in the metal DBR devices.

![Figure 9-3 PL spectra and angular dispersion relation of Alq3 filled double DBR microcavity. (a) PL spectrum generated via pump laser at λ = 408 nm. (b) High resolution PL spectrum revealing linewidth of 0.806 nm and Q = 734. (c) Angularly resolved PL. (d) Dispersion relation fit using E_{ph} = 2.095 eV and background n = 1.89, and plot of cavity Quality factor as a function of angle.](image-url)
9.5 Strong Coupling in Double DBR Microcavity

When a 4.5 SICAS film of PDAC/TDBC is inserted in such a cavity at the anti-node, strong coupling is achieved. The device consists of the same DBR’s as in the Alq$_3$ filled microcavity. A bottom spacer of SiO$_2$ and a top spacer of TAZ are used, each of which is approximately $\lambda/4n$ thick. Figure 9-4 illustrates the normal mode splitting and polaritonic dispersion for this device.

Figure 9-4a,b illustrates reflection at $\theta = 7^\circ$ and transmission at $\theta = 0^\circ$ for the device. Both data sets show two resonances that are split-off from the uncoupled J-aggregate peak. Figure 9-4c plots the TE polarized angular (relative) reflectance data. The data show that as $\theta$ increases, the higher energy reflectance dip continues to tune towards higher energy, while the lower energy dip asymptotes to the uncoupled J-aggregate resonance. The resonant dips in reflectance are used to generate the dispersion relation data in Figure 9-4d. The two state model of the light matter interaction of previous chapters was utilized to fit the data. The fit parameters were $E_{ex} = 2.1$ eV, $E_{ph} = 2.115$ eV, and a background $n = 1.7$. A Rabi-splitting of $\hbar\Omega_r = 105$ meV is determined, and $\Omega_r/2\Gamma = 3.5$.

From the fit parameters, a T-matrix simulation was performed on the full strongly coupled structures. The results of the simulation study are shown in Figure 9-4a,b along with the actual reflection and transmission data. The $(n,\kappa)$ values for the J-aggregate layer were determined using the Kramers-Kronig relations discussed in Chapter 3, and the peak $\kappa$ for this particular film was determined to be $\kappa = 4.75$. The simulated cavity has a “bare” cavity resonance at $E_{ph} = 2.115$ eV, just like the fit to the angular reflectance data. The simulated thickness of the J-aggregate layer is 3.5 nm. This is also the value chosen to fit the half cavity CCR structure consisting of bottom DBR, SiO$_2$ spacer and 4.5 SICAS, indicating that less than the usual amount of J-aggregate adsorbed to the sputter coated SiO$_2$ bottom spacer. In transmission, the simulated resonances $E_\pm$ match the energy positions of the data. In reflection, the simulated $E_-$ resonance is red shifted slightly from the measured dip. The simulated reflectance resonance is red-shifted because the simulation is performed at $\theta = 0^\circ$, while the reflectance is measured at $\theta = 0^\circ$. This slight red-shift is also captured in the dispersion relation in Figure 9-4d, where the $E_-$ data point at $\theta = 7^\circ$ is clearly above the lowest value for the $E_-$ state at $\theta = 0^\circ$. The simulated transmission and measured transmission for the $E_-$ state are of the same order of magnitude. Moreover, the simulated and measured linewidth for the $E_-$ state are the same, $\Gamma = 15.1$ meV.

The correspondence between T-matrix simulation and the observed polaritonic dispersion indicates that the $(n,\kappa)$ values determined for the thin film accurately describe the physics of the microcavity. This is remarkable considering the microcavity structure was subjected to a harsh sputtering environment. This indicates that the J-aggregate layer survives the sputtering process at least to the degree that the $(n,\kappa)$ values of the neat-film are still a valid description of the film’s optical properties. Therefore, T-matrix
simulations based on the \((n, \kappa)\) values of the neat-film can be used to extrapolate how the Rabi-splitting for such a structure might evolve if the thickness of the \(J\)-aggregate layer were increased.

\[\text{(A)}\]

\[\text{(B)}\]

\[\text{(C)}\]

\[\text{(D)}\]

Figure 9-4 Strong coupling in double DBR microcavity containing 4.5 SICAS. (a) Reflection at \(\theta = 7^\circ\), taken on SRA. (b) Transmission at \(\theta = 0^\circ\). (c) Angular reflectance data taken on VASRA apparatus. (d) Polariton dispersion relation. Fits are generated using \(E_{\text{ex}} = 2.1\) eV, \(E_{\text{ph}}(\theta = 0^\circ) = 2.115\) eV and a background \(n = 1.7\). A Rabi-splitting of \(\hbar \Omega_R = 105\) meV is determined.
The dephasing time, T$_{2}$, has not yet been determined for the LBL PDAC/TDBC films, yet knowledge of T$_{2}$ is critical for determining the smallest possible $\Gamma$. An accurate value for T$_{2}$ is also critical for the design of the cavity, since the exciton dephasing and cavity linewidths should be matched for optimum strong coupling. At first glance, the large and increasing FWHM of the reflectance spectra in Figure 3-6 would seem to indicate that the dephasing time, T$_{2}$ = 13.2 fs, corresponding to the observed spectral broadening of 50 meV. However, preliminary pump-probe measurements suggest a more gentle dephasing process of only 1 meV (T$_{2}$ ~ 5 psec), in line with the assumptions in the calculations presented earlier in the chapter. The dominant contribution to the reflectance FWHM would then be due to a super-radiant enhancement observed in semiconductor QW structures [61, 62] and/or inhomogeneities. Either possibility could explain the linear dependence of the FWHM on the number of SICAS, as shown in Chapter 3 on J-aggregate films.

It has been argued that in a system where the Rabi-splitting exceeds the inhomogeneously broadened exciton linewidth, the resulting strongly coupled states will have a linewidth corresponding to the homogeneous linewidths of the system [124]. To examine this limit and estimate the homogeneous T$_{2}$, the simulation for the actual device depicted in Figure 9-4 is extended to the case of thicker layers. The results of the T-matrix simulation are shown in Figure 9-5. The Rabi-splitting and $\Omega_R/2\Gamma$ increase, and the linewidth of the $E_2$ states in fact narrows. The asymptote for the linewidth appears to be at $\Gamma = 4$ meV. Using $2\Gamma = \kappa + \gamma$ (on resonance), and $\kappa = 2.3$ meV (dashed line in Figure 9-5b representing the empty cavity linewidth), $\gamma = 5.7$ meV. This is equivalent to a 1.6 nm linewidth or 115 fs, a factor of almost 9 less than predicted by the reflectance spectrum. This appears to be the lower bound on T$_{2}$ as determined for a large extended J-aggregate film. In isolated regions it would be expected to fluctuate and be as long as the values inferred from the pump-probe data.

A crucial assumption in this analysis is that the (n,\kappa) values of the 4.5 SICAS film applies for thicker films. This assumption needs to be tested in light of Knoester's analysis wherein he showed that thicker films loose their super-radiant properties and devolve into bulk polaritons [62]. A way to circumvent this cross-over and maintain the (n,\kappa) values would be to disrupt the J-aggregate layer with inserts of inert polyelectrolyte multilayers. The thick J-aggregate layer would be then be equivalent to a series of quantum wells, each assembled via 4.5 SICAS.
Figure 9.5 Analysis of Rabi-splitting and lower branch linewidth as a function of J-aggregate layer thickness, \( N \). (a) Simulated Reflection at normal (\( \theta = 0^\circ \)) based on (n,\( \chi \)) dispersion relation of 4.5 SICAS PDAC/TDBC film, along with empty cavity (E.C.) resonance. (b) Rabi-splitting, \( \hbar \Omega_R(N) \), and \( E_\gamma \) state linewidth \( \Gamma(N) \), as functions of PDAC/TDBC film thickness, \( N \), measured in nanometers. Rabi-splitting is fit to \( \hbar \Omega_R(N) = 80.7(N - 0.992)^{1.4} \) meV. The theoretical power would be \( \frac{1}{2} \) if all the molecules were situated at the cavity anti-node. Dashed line indicates E.C. linewidth, \( \kappa \). (c) Strength of coupling vs. number of layers, i.e. \( \frac{\hbar \Omega_R}{2 \Gamma} \) vs. \( N \), demonstrating that the device progresses further into strong coupling as the layer thickness increases with: \( \frac{\hbar \Omega_R(N)}{2 \Gamma(N)} = -3.88 + 1.86N \).

9.6 Method of Excitation

The simplest method of exciting the laser structures appears to be direct excitation of the J-aggregate films. This would be possible by designing a dielectric mirror so as to allow the high energy states of the J-aggregate in the region of \( \lambda = 500 \) nm to be optically pumped.

9.7 Testing and Measuring

The key experiment for the laser devices are optical excitation of the laser structures using both on-resonance and off-resonance laser sources of either CW or pulsed light emission. The measurements will be: determining polarization of the emitted light, observing changes in the emission spectrum and fraction of emitted power delivered in the forward direction as a function of excitation intensity. Since laser structures are being assembled with and without an added donor layer, in general several measurements will be made on each sample in determining whether laser action in the strong coupling limit has been achieved. Pump-probe spectroscopy will also be performed.
9.8 Conclusion

A polariton-laser is a laser that operates in the strong coupling limit with $\beta = 1$. The dynamics and spectral positions of the emission should be strong functions of intra-cavity photon number and hence pump intensity. In order to realize such dynamics, with minimal number of photons, it is necessary to construct a polaritonic structure with large $\Omega_R/2\Gamma$ and small $\Gamma$ in absolute terms. To that aim, all-dielectric microcavities were constructed with $Q = 734$. Strong coupling has been realized in such structures, using 4.5 SICAS of PDAC/TDBC, with $\hbar\Omega_R = 105$ meV, $\Omega_R/2\Gamma = 3.5$, and $\Gamma = 15.1$ meV. T-matrix simulation confirms that the LBL films survive the sputtering processes required to construct the top DBR. Simulation also shows that it should be possible to achieve $\hbar\Omega_R \geq 240$ meV, $\Omega_R/2\Gamma > 30$, and $\Gamma \sim 4$ meV as the thickness of the J-aggregate layer is increased. Ultimately, the threshold for observing the described dynamics will depend on the value for the homogeneous $T_2$ time.
10 Conclusion

It was shown than thin films of J-aggregates assembled via the LBL deposition technique enable strong coupling at room temperature. The experimental demonstrations focused on the cyanine dye TDBC, because of its narrow linewidth and high absorption coefficient ($\alpha \sim 10^6$ cm$^{-1}$) in thin film, even at room temperature. Nanoscale thin films of TDBC and the polyelectrolyte PDAC grown via LBL were characterized in terms of smoothness and it was determined that a 4.5 SICAS deposited film had the best morphological and optical properties for polaritonic applications. These films were deposited within active organic LED materials and used to realize the first demonstration of electrically pumped polariton emission. This demonstration was realized in Low Q all metal mirror microcavities that exhibited Rabi-splitting of $\hbar \Omega_R = 265$ meV. The linewidth $\Gamma$ of the lower energy polariton state $E_-$ in such devices was large, with $\Gamma \sim \hbar \Omega_R / 2$, indicating that theses devices are barely operating within strong coupling. In order to realize strong coupling with larger $\hbar \Omega_R / 2\Gamma$, higher Q cavities consisting of at least one dielectric low loss mirror were employed. Experimental issues forced changes to the growth of the J-aggregate layers, which in turned revealed that the half structure consisting of DBR, spacer, and PDAC/TDBC absorbed nearly 100% of the light incident from the absorber layer side of the device. The J-aggregate layer when situated within such a cavity exhibits strong coupling with narrower linewidths, and $\Omega_R / 2\Gamma$ as high as 5.5. These structures were investigated in transmission, reflection, and PL. The PDAC/TDBC films used to realize strong coupling are much thinner compared to the other means of realizing strong coupling with organic materials. It was therefore possible to integrate other films of fluorescent organics such as Alq3 that acted as an internal light source for intensely exciting the strongly coupled states. This technique can be used to probe the dispersion of very small spot sizes vs. angle, and conceivably could be applied to micropillar devices where the device diameter is only several microns. Furthermore, when the cavity resonance is generated statistically via a "ladder" or discretized wedge of states, photobleaching the J-aggregate film after inverting the dispersion can be used to determine the uncoupled cavity energy. Finally, steps taken towards realizing a room temperature polariton laser were reported, first developing a model of the dynamics of such a device and then arguing in favor of even higher Q cavities. Initial results of all dielectric microcavities were presented that to date exhibit $Q = 734$ and $\Omega_R / 2\Gamma = 3.5$. These devices were simulated using the T-matrix formalism and the n,$\kappa$ dispersion values determined for the PDAC/TDBC film. It was shown that the experimental linewidth of the lower branch and simulation matched. From there it was argued that to realize a polariton laser, narrower linewidth J-aggregate films would be needed to complement the higher Q dielectric cavities. Simulation showed that if the $(n, \kappa)$ of the 4.5 SICAS deposited film could be preserved in thicker films such a structure could be realized. Such a device would possess $\Omega_R / 2\Gamma = 30$ and should exhibit room temperature polariton lasing.
11 Personal Statement

This thesis is in part a personal statement. It is a statement of what I believe in that goes well beyond simply scientific pursuits. It is reflection and expression of beliefs and desires that run very deep inside. It is a snapshot of many of the learning experiences that I have undergone in the PhD program at MIT that I wish to share. Therefore, I want to make these connections concrete in writing.

Why have I chosen to work on strong coupling? I have chosen to work and continue work on the topic of strong coupling of light and matter for a few simple reasons. First, I really appreciate this branch of Physics. In college, “I wanted to be a quantum mechanic”, and light is fascinating to think about and work with and relate to. Second, strong coupling has great scientific interest and technological promise relating to Bose-Einstein condensates and optical/quantum computing respectively. Third, for me the concepts of strong coupling represent a physical model for different kinds of relationships: between people, things, people and things, etc. Moreover, it is a model that captures the basic point that there are always different degrees of connectedness or coupling strength in such relationships. Therefore in a not so abstract sense, the desire to realize strong coupling at room temperature is really the desire to see the promise of this physics manifest in realistic every day experience.

Quantum Mechanics teaches us that canonical variables like momentum and position, energy and time, cannot be simultaneously specified with absolute precision. In life, there are many canonical conjugate pairs of variables: seemingly contradicting and conflicting visions, pursuits, ideals, like the desire to be selfish and altruistic, etc. The principles of strong coupling take up the problem of emission and absorption, light and dark, outward and inward directions. The lesson is simple. These conjugate variables are actually part of a greater unity; in real-life systems they only appear uncorrelated. A basic tenet is that phase coherence can and often does exist in perfectly isolated systems (up to the limits of Planck’s constant). It is spoiled in real-life room-temperature systems, but it can nevertheless be recovered and strengthened through cooperative interactions amongst individual actors even in open systems. For the physicist engaged in realizing strong coupling, the quest is to create this cooperation, harmonize these conjugate attributes, and achieve this unity not only in quantum mechanical systems like the microcavity, one nanometer at a time, but in the very open yet-finite system that is life on Earth—for good.
References


