Electrically Pumped Polariton Emission in a J-Aggregate Organic Light Emitting Device

by

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Submitted to the Department of Electrical Engineering and Computer Science in Partial Fulfillment of the Requirements for the Degree of Master of Science in Electrical Engineering at the Massachusetts Institute of Technology

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Abstract

We present the first demonstration of polariton emission from an electrically pumped structure. Our demonstration is enabled by the high absorption constant (~$10^6 \text{ cm}^{-1}$), and narrow absorption spectra ($\lambda_{\text{max}} = 590 \text{ nm}$, FWHM $= 20 \text{ nm}$) of ordered J-Aggregate monolayers inserted into a planar microcavity. The strong coupling between the J-Aggregate excitons and the optical modes of the microcavity drastically alters the light matter interaction, giving rise to the polariton emission. The angularly resolved EL spectrum exhibits the characteristic anti-crossing of polariton energy bands, and we observe Rabi-splitting in excess of 200 meV, corresponding to a Rabi frequency of more than 48 THz. Due to the large Rabi-splitting (an order of magnitude larger than for any inorganic system) polariton emission peaks are pronounced even at room temperature.

This all-organic active device is the first to enable electrical pumping of polaritons in any material system. A typical layered structure contains a 4 to 10 monolayers thick film of J-Aggregates of the cyanine dye 5,6-Dichloro-2-[3-[5,6-dichloro-1-ethyl-3-(3-sulfopropyl)-2(3H)-benzimidazolylidene]-1-propenyl]-1-ethyl-3-(3-sulfopropyl) benzimidazolium hydroxide sodium salt, sandwiched between hole and electron transporting layers with metallic mirrors forming the microcavity. Although the quality factor of the microcavity is less than 100, polariton emission is still observed because of the high oscillator strength of the J-Aggregate monolayers. This demonstration could enable practical implementations of previously proposed polariton based optoelectronic devices such as low threshold polariton lasers and sub-picosecond optical clocks.

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II. Introduction

A. Purpose and Theme
The general theme of this project is strong coupling of quantized systems. Our specific goal is to demonstrate polariton emission in electrically excited devices. A polariton is a quantum mechanical state in which a photon is coupled to an exciton (light-matter coupling). The exciton participating in this state is a unique aggregate of dye molecules, in which the dipoles of individual dye molecules couple (dipole-dipole coupling) to form a high oscillator strength chromophore known as the J-Aggregate state of the dye. These two forms of dynamic coupling are discussed throughout the thesis. Since most of the preceding investigations of polariton physics were conducted using inorganic semiconductors, this project also represents a coupling of ideas and concepts, in which the practical concepts in the field of organics materials, organic light emitting devices (OLEDs), amorphous thin-film deposition, and Förster energy transfer are connected to the theories developed for crystalline, lattice-matched, low defect-density, high refractive-index inorganic semiconductors. A second theme that runs throughout the project is engineering systems to control the strength of couplings. Since any coupling mechanism must compete with loss processes, engineering couplings consists of the dual task of enhancing the coupling process while minimizing the loss processes, i.e. enhancing the relative rate at which the component systems exchange energy compared to the rates at which the component systems lose this energy. To that aim, we developed fabrication methods to integrate thin films of dissimilar materials (organics, metals, metal-oxides) into precisely tuned electrically active structures. Special emphasis is placed on developing methods for preparation of J-Aggregate thin films as these enable all of the described work.

B. Proposed Idea
Our goal for this project was to demonstrate the first electrically pumped polariton light-emitting device (LED). Our idea was to develop an organic LED (OLED) using J-Aggregates of cyanine dyes as the emitter material, and then incorporate a similar device structure in a resonant optical microcavity (RC-OLED) for demonstrating polariton emission. We chose J-Aggregates as the active element because this class of materials
has the highest oscillator strengths ever recorded (even relative to traditional inorganic semiconductors), which facilitates observation of polariton effects even at room temperature in low Q optical microcavities, and increases the chance that passing current will not adversely affect the polariton states of the J-Aggregate.

C. Significance
Demonstration of electrically pumped exciton-polariton emission has both scientific and technological significance. It is the first demonstration of electrically pumped polariton emission in any material system. It underscores the importance of considering J-Aggregates in the realization of future integrated polariton devices and their potential role in ultrafast non-linear optoelectronics applications. It may also be a first step towards implementing an electrically pumped organic laser, since polariton effects are predicted to significantly reduce the lasing threshold current density\(^1\).

D. Organization of Thesis
The thesis is structured in the following way. First, the physics of polaritons is reviewed, and the connection between oscillator strength and polaritons is clarified. Then J-Aggregates are introduced as good candidate materials for the polariton LED because of their very high oscillator strength, including an explanation of J-Aggregates’ oscillator strength and optical properties. From there, the methodology for forming J-Aggregates is described, particularly the methods we use in this project, and the structures of our J-Aggregate LED and polariton LED are explained. This leads to the results section where we describe the measurements of polariton effects in reflectivity and photoluminescence that led us to choose a specific J-Aggregate dye. Then, data for our J-Aggregate OLED structures are presented, and the steps needed to insure emission was predominantly from J-Aggregates are recounted. Lastly, electroluminescent spectra of the J-Aggregate resonant cavity OLED is presented as a function of cavity thickness and angle, proving electrically pumped polariton emission. The thesis concludes with a discussion of future experiments, all of which take full advantage of the J-Aggregate deposition technique we developed in the course of this project.
III. Polariton Principles

A polariton is a quantum mechanical state in which a semiconductor exciton (bound electron-hole pair) and the photon field of an optical microcavity act as a single coupled harmonic oscillator\(^2\). In the polariton state, the exciton exchanges energy periodically with the photon field at a rate determined by the interaction strength between exciton and photon, which can be on the order of THz. (This rate is referred to as the Rabi oscillation frequency.) The polariton state can be achieved if the energy and momentum of the uncoupled exciton match the energy and momentum of the photons in the bare microcavity, and if the rate of energy exchange is faster than dephasing processes that act on the exciton and photon\(^3\).

As a result of the strong light-matter coupling, the optical properties of the polaritons are distinctly different than those of uncoupled excitons. As in a classical system of coupled harmonic oscillators, the coupling between exciton and photon alters the eigenmodes of the system. This effect is readily manifest as two new photoluminescence emission peaks form\(^4\), with one at higher energy and with another at lower energy relative to the uncoupled exciton emission energy. Another consequence of the coupling is that the energy band dispersion relation associated with the excitons is modified with a corresponding change in the particle effective mass. Also, since the polariton only radiates when a scattering process disrupts the periodic energy exchange between exciton and photon, the radiative lifetime can be very different than that of the uncoupled exciton\(^5\), and can be as short as the reciprocal of the Rabi frequency, leading to very efficient light emission\(^6\). We expect that upon electrical excitation our polariton OLEDs will exhibit some of the same unique optical properties that are manifest when polaritons are optically excited\(^7\).

To gain intuition of the physics of strong coupling, one can model the exciton-photon interaction as a two level system (exciton) that is coupled to a simple harmonic oscillator (photon)\(^8\). 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 transition: \(E_2 - E_1 = h\omega_{ex}\).
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\(^9\), the coupling is due to dipole radiation, which can be represented by the perturbation Hamiltonian \( H^{(1)} = -\vec{\mu} \cdot \vec{E} \), where \( \vec{\mu} = \int \phi^* \vec{r} \phi dV \) 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 \( \phi_1 \) and \( \phi_2 \). Similarly, because the action of the exciton corresponds to the creation or annihilation of a photon, the perturbation \( H^{(1)} \) only couples states of different quantum number. We can capture this physics in our simplified model by representing \( H^{(1)} \) as \( H^{(1)} = V_0 \left( \hat{a}' + \hat{a} \right)^* (|\phi_1 \rangle \langle \phi_2| + |\phi_2 \rangle \langle \phi_1|) \), where \( \hat{a}' \) and \( \hat{a} \) are creation and annihilation operators for photons of energy \( \hbar \omega_0 \), and \( V_0 \) depends on the dipole moment and field strength both of which we can engineer in the RC-OLED. Applying this perturbation to \( \Psi_n \), we see that \( \Psi_1 \) and \( \Psi_2 \) couple to each other, while \( \Psi_0 \) couples to \( \Psi_3 = \phi_2 |1\rangle \).

Because of the coupling, the eigenstates of the system are no longer \( \Psi_n \), but rather are superpositions of the states involved in the coupling. Let’s denote the new stationary states as \( \Phi_n \). The ground state is \( \Phi_0 = c_1 \Phi_0 + c_2 \Phi_3 \), while the first and second excited states, \( \Phi_1 \) and \( \Phi_2 \), are rotational superpositions of \( \Psi_1 \) and \( \Psi_2 \), which can be compactly expressed as follows\(^8\):

\[
\begin{pmatrix}
\Phi_1 \\
\Phi_2
\end{pmatrix} = \begin{pmatrix}
\cos \theta & \sin \theta \\
-\sin \theta & \cos \theta
\end{pmatrix} \begin{pmatrix}
\Psi_1 \\
\Psi_2
\end{pmatrix}
\]
By applying first order perturbation theory, we can determine the energy levels of the states \( \Phi_0, \Phi_1, \) and \( \Phi_2, \) and therefore the dynamics of the coupled system. The energies of ground state, \( H_0, \) and first two excited states, \( H_1 \) and \( H_2, \) are given by:

\[
H_0 = \hbar \omega_0 + \frac{1}{2} (E_1 + E_2) - \frac{1}{2} \sqrt{(E_2 - E_1 + \hbar \omega_0)^2 + 4V_0^2}
\]

and

\[
H_1 = \hbar \omega_0 + \frac{1}{2} (E_1 + E_2) - \frac{1}{2} \sqrt{(E_2 - E_1 - \hbar \omega_0)^2 + 4V_0^2}
\]

\[
H_2 = \hbar \omega_0 + \frac{1}{2} (E_1 + E_2) + \frac{1}{2} \sqrt{(E_2 - E_1 - \hbar \omega_0)^2 + 4V_0^2}
\]

Figure 1 plots the energy levels of the coupled system as a function of the energy of an uncoupled photon (photon in a bare cavity without exciton). The energy levels of the uncoupled two state system are \( E_1 = 1eV \) and \( E_2 = 3eV, \) corresponding to a 2eV exciton (620 nm light) and the interaction energy \( V_0 = 0.1eV. \) Physically, we tune the photon energy by changing the length of the microcavity, and for a half-wavelength microcavity: \( \hbar \omega_0 = \hbar (\pi c/nL). \) The graph shows two effects. First, the ground state energy of the coupled system is lower relative to the ground state of the uncoupled system. It also shows that around the point where the photon energy equals the exciton energy, \( 2eV, \) the excited state energy-lines \( H_1 \) and \( H_2 \) change slope.

![Figure 1 Energy levels of ground state and first two excited states as a function of bare cavity photon energy in coupled model of polaritons](image)
This transition leads to a logical division of the dynamics into the following three regimes: negative detuning, resonance, and positive detuning. Negative detuning is the regime where the bare cavity photon mode is tuned to energy lower than the exciton energy, resonance is where the photon and exciton energies are equal, and positive detuning is the case where the photon mode is tuned to higher energies.

To gain more insight into how the coupled state energies relate to the underlying exciton and photon, Figure 2 graphs the photon and exciton fractions of the lower energy excited state, i.e. the $\Psi_1$ and $\Psi_2$ portions of $\Phi_1$. Mathematically, this is $\cos^2 \theta$ and $\sin^2 \theta$ respectively, where:

$$\cos \theta = \frac{1}{\sqrt{1 + \left( \frac{V_0}{H_1 - (\hbar \omega_0/2 + E_2)} \right)^2}}$$

At negative detuning, $\Phi_1$ is mostly photonic. As the cavity is tuned closer to resonance, the exciton fraction of the lower branch increases and at resonance the exciton and photon fractions are equally 50%. At positive detuning, the exciton fraction in the lower polariton branch continues to increase towards 100%. A similar description applies to the higher energy excited state $\Phi_2$, in that the photonic fraction increases from 0% to 50% at resonance, and then becomes almost completely photonic at positive detuning.

![Figure 2 Photon fraction and exciton fraction of lower energy first excited state, as a function of bare cavity photon energy](image)

Figure 2: Photon fraction and exciton fraction of lower energy first excited state, as a function of bare cavity photon energy.
At resonance, the stationary states are exclusively neither exciton nor photon but rather equal parts exciton and photon. This equal division is only true when averaged over time. The system actually oscillates back and forth between being excitonic or photonic. If the system was purely excitonic at time $t = 0$, then the probability of remaining excitonic is given by

$$P_{\text{ex}} = \cos^2 \left( \frac{|V_0|}{\hbar} t \right)$$

Similarly the probability of being photonic is

$$P_{\text{ph}} = \sin^2 \left( \frac{|V_0|}{\hbar} t \right)$$

A subtle point to be aware of is that even at times $t = 0, \pi \hbar / |V_0|, 2\pi \hbar / |V_0|, \ldots$ when the first excited state is instantaneously purely excitonic, the energy of state is still $H_1 = 3.9\text{eV}$ and not the $4\text{eV}$ one would calculate on the basis of having an exciton and no photon ($3\text{eV} + 1\text{eV}$). The reason for this is that being “excitonic” is not a steady state of the system and does not have an energy value associated with it alone. Another point is that the oscillation between exciton and photon occur within a single excited state of the coupled system. No energy is exchanged between $\Phi_1$ and $\Phi_2$, because these are eigenstates of the system. When the energies of the uncoupled exciton and bare cavity photon are not exactly matched, Rabi’s Formula gives the general expression for the probability of transitioning between exciton and photon as:

$$P_{\text{trans}} = \frac{4|V_0|^2}{(H_2 - H_1)^2} \sin^2 \left( \frac{(H_2 - H_1)t}{2\hbar} \right)$$

Figure 3 is a graph of the prefactor of this equation, which is a measure of the extent of the transition between exciton and photon. Only on resonance does the system completely switch between the exciton and photon.
Figure 3 Magnitude of transition probability from exciton to photon portion of first excited state, as a function of bare cavity photon energy.

Figure 4 plots $H_2 - H_1$, the energy separation between upper and lower energy levels, which is often referred as the Rabi Splitting energy. The energy separation measures how fast the system oscillates between exciton and photon components. This is sometimes a point of confusion, because the energy levels of the eigenstates are used to calculate the oscillation rate of the non-stationary states. Note that the coupled system transfers energy more quickly off-resonance, however the extent of the energy transfer is not as complete. (In a pump-probe experiment this subtlety would present itself in that the relaxation time would be faster off resonance but the change in transmission signal would be much stronger on resonance.)

Figure 4 Rabi splitting energy for the interaction energy $V_0$ of $0.1 \text{ eV}$, as a function of photon tuning; the minimum splitting is $0.2 \text{ eV}$.
The first excited states of the coupled system, $\Phi_1$ and $\Phi_2$, represent the polariton states of the semiconductor microcavity. From the model, we see that 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 5 plots these energy differences: $\hbar\omega(-) = H_1 - H_0$ and $\hbar\omega(+) = H_2 - H_0$. 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 is referred as the lower (upper) branch polariton curve. We see that 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 which is twice the interaction energy $V_0$ (0.1 eV). 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.

From the polariton dispersion curve, we are able to relate our model directly to the optical and dynamical properties of polaritons. At any given cavity tuning, $\hbar\omega_0$, we see that 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.

![Graph: Polariton Dispersion Curve](image)

**Figure 5** Upper and lower branches of polariton dispersion curve, as a function of photon tuning, with anti-crossing energy equal to the Rabi-splitting $2V_0=0.2$ eV

In the model so far, the cavity and exciton energies were assumed to be infinitely well-defined, which is obviously unrealistic. The impact of accounting for 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.

![Graph: Power Spectrum](image)

**Figure 6** 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 $(\gamma_{ph}+\gamma_{ex}) = 80$ meV
We can model the line broadening in the frequency domain by first thinking about what the finite line widths of the cavity and exciton mean in the time domain. A finite line width 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:

\[
s_{\pm}(t) = A \cos(\omega_{ex} \pm \Omega) t,
\]

where \(\Omega = V_0 / \hbar\).

Given the cavity photon mode damping \(\gamma_{ph}\) and the exciton damping \(\gamma_{ex}\), the two normal modes are now damped oscillations in time:

\[
S_{\pm} = Ae^{-\left(\frac{\gamma_{ph} + \gamma_{ex}}{2}\right) t} \cos(\omega_{ex} \pm \Omega') t,
\]

where now \(\Omega' = \sqrt{\left(\frac{V_0}{\hbar}\right)^2 - \frac{1}{4} \left(\frac{\gamma_{ph} - \gamma_{ex}}{2}\right)^2}\).

Parenthetically, we see from the \(\Omega'\) expression that matching \(\gamma_{ex}\) and \(\gamma_{ex}\), 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, we have an expression for the polariton “power” spectrum:

\[
S(\omega) = \frac{A_+}{\left(\frac{\gamma_{ph} + \gamma_{ex}}{2}\right)^2 + (\omega - (\omega_{ex} + \Omega'))^2} + \frac{A_-}{\left(\frac{\gamma_{ph} + \gamma_{ex}}{2}\right)^2 + (\omega - (\omega_{ex} - \Omega'))^2}.
\]

From a plot of this expression in Figure 6, it is clear that the polariton spectrum is double peaked so long as the Rabi splitting \(2\Omega'\) satisfies the following condition:

\[
2\Omega' > 0.5\left(\frac{\gamma_{ph} + \gamma_{ex}}{2}\right).
\]

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

Extending this linear system analysis of the polariton spectrum, we see that the frequency domain representation of the polaritons is simply two offset damped sinusoids. Therefore, if a broadband pulse excites both of the polariton normal modes simultaneously, then the linear response of the polaritons will be the sum of \(S_{\pm}(t)\):

\[
S(t) = S_{+}(t) + S_{-}(t) = Ae^{-\left(\frac{\gamma_{ph} + \gamma_{ex}}{2}\right) t} [\cos(\omega_{ex} + \Omega') t + \cos(\omega_{ex} - \Omega') t]
\]

The two normal modes beat against one another, and by trigonometric identity the beat signal, which is just like an amplitude-modulated (AM) signal, is equivalent to:

\[
S(t) = Ae^{-\left(\frac{\gamma_{ph} + \gamma_{ex}}{2}\right) t} \cos(\Omega') \cos(\omega_{ex} t)
\]
The intensity of the response is:

\[ I(t) \propto |S(t)|^2 = Be^{-\left(r_0 + r_c\right)} \begin{bmatrix} \cos^2(\Omega' t) \cos^2(\omega_c t) \end{bmatrix} \]

This is a very important result of our model. When both polariton modes are excited simultaneously, the intensity of the radiation response beats with a frequency \( 2\Omega' \). Surprisingly, this conclusion is consistent with our original Quantum Mechanical model in which exciting a single polariton state exhibited a Rabi oscillation of the same frequency. The consistency comes because there is physically no way of distinguishing between the two scenarios, since attempting to excite a single polariton state fast enough to observe the Rabi oscillation in the time domain unavoidably requires an excitation pulse that is sufficiently broad in frequency so as to excite both polariton normal modes simultaneously.

Thus far our model of polaritons 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\(^{11}\):

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

Where \(|k|=(\pi/nL)\) for \(\lambda/2\) 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.

Figure 7 is an example of angularly resolved polariton dispersion curve for the case where the photon mode is resonantly matched to the exciton transition at \(\theta = 0^\circ\).
Figure 7 Angularly Resolved Polariton Dispersion Curve

In generating this simulation, it is assumed that the matrix element for the coupling interaction is angle dependent on the grounds that the transition dipole is oriented in the plane of the microcavity:

\[ V_0(\theta) = -\bar{\mu} \cdot \bar{E} \approx V_0(0^\circ) \frac{\cos \theta}{\sqrt{1 - \frac{\sin^2 \theta}{n^2}}} \]

The \( \cos \theta \) term captures the projection aspect of the coupling, while the denominator accounts for the electric field strength dependence on energy \( n \):

\[ \left| \bar{E} \right| \propto \left( \frac{\hbar \omega / 2\varepsilon_0 L}{n^2} \right)^{1/2} \]

Ultimately, the magnitude of the transition dipole moment, \( \bar{\mu} \), determines the degree of the polariton coupling, however, the quantity \( |\bar{\mu}|^2 \) is the metric which is more easily measured. In fact, for most light-matter interactions—where strong coupling does not apply, the quantity \( |\bar{\mu}|^2 \) is in several ways more fundamental. Fermi’s Golden Rule gives the rate of decay of the excited state (of the exciton), which is proportional to \( |\bar{\mu}|^2 \), as

\[ R_{PGR} = \frac{2\pi}{\hbar} \left| \bar{\mu} \cdot \bar{E} \right|^2 \rho_{pp} \left( \hbar \omega_f \right) \]
Similarly, the lifetime of the excited state, $\tau_{FGK} = 1/R_{FGK}$ is inversely proportional to $|\vec{\mu}|^2$. Another reason $|\vec{\mu}|^2$ is considered fundamental is it can be thought of as 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\(^{12}\) (in the perturbative limit of light matter coupling, radiation is indeed dissipative). This concept is embodied in the quantity called the oscillator strength, $f$, which is defined as the ratio of the variance of the charge density of the exciton, $|\vec{\mu}_x|^2$, relative to the variance of the charge density of a single electron, $|\mu_e|^2$, in an idealized 3-dimensional simple harmonic oscillator potential\(^{12}\):

$$f = \frac{|\vec{\mu}_x|^2}{|\mu_e|^2}, \text{ where } |\mu_e|^2 = e^2 (\Delta x^2) = 3 e^2 \frac{h}{2 m_e \omega}$$

The term $\Delta x^2$ is the positional variance of the electron in a 1-dimensional simple harmonic oscillator potential, and the factor of 3 takes account for all three dimensions. Higher oscillator strength translates directly into a shorter radiative lifetime. In addition to lifetime measurements, $|\vec{\mu}|^2$ and $f$ can be directly calculated from the absorption spectrum of the exciton. If the absorption spectrum of the exciton is given by $\alpha(\omega) \text{ [cm}^{-1}]$, then it can be shown that\(^{12}\)

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

Where $N$ is the density of absorbing excitons per unit volume. This expression can also be applied to a semiconductor crystal by making the identification that $N = \int \rho_{xc}(E) dE$ where $\rho_{xc}$ is the semiconductor reduced density of states for the conduction and valence bands. Similarly, the oscillator strength is related to the absorption spectrum by\(^{12}\):

$$f = \frac{2 m_e e^2 \omega_{ex}}{\pi e^2 N} \int \frac{\alpha(\omega)}{\omega} d\omega$$

Where $\omega_{ex}$ is the frequency of the exciton transition.
For a thin-film of thickness $d$ and surface exciton density $\sigma$, then the volume density $N = \sigma/d$, and

$$\frac{\alpha}{N} = \frac{\alpha \cdot d}{\sigma} = \frac{abs}{\sigma}$$

Where $abs$ is the (dimensionless) absorbance of the film. Then for a thin-film\(^{13}\):

$$|\bar{\mu}|^2 = \frac{3\varepsilon_0 hc}{\pi \sigma} \int \frac{abs(\omega)}{\omega} d\omega \quad \text{and} \quad f = \frac{2m_e e^2 c \omega \alpha}{\pi e^2 \sigma} \int \frac{abs(\omega)}{\omega} d\omega$$

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 $V_0 \propto |\bar{\mu}| \propto \sqrt{abs_{\text{max}}}$. 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 absorbed by the film. The higher $\alpha(\omega)$ is, the more closely the material resembles an ideal metal (at the frequency $\omega$) with infinitely fast response time to incident electric field of the light, so that the material can in very short distance reject the light from penetrating into the film. Mathematically, the percentage surface reflectivity at such an interface is\(^{14}\):

$$R = \left| \frac{n_2 - n_1}{n_2 + n_1} \right|^2, \quad \text{where} \quad \tilde{n}_i = n_0 + i \frac{c \alpha(\omega)}{\omega} = n_0 + i \kappa$$

Where the imaginary term in $\tilde{n}_i$ is traditionally called the extinction coefficient $\kappa$. For very large $\alpha(\omega)$ or $\kappa$, $R \rightarrow 1$ and 100% of the light is reflected, with no light being transmitted or absorbed. In the strong coupling limit, higher oscillator strength, due to large absorption, enables the film to respond to it's own (virtual) radiation more quickly then the time it takes for that radiation to escape the cavity, and to retransmit this energy back to the photon field before the energy is dissipated via non-radiative pathways. Thus, the enhanced optical response due to high oscillator strength makes the exciton photon energy transfer process more persistent and the light matter coupling more complete.
IV. J-Aggregates

J-Aggregates in Polariton Experiments

J-Aggregates are a unique material set for observing strong light matter interactions because the Rabi-splitting due to J-Aggregate excitons is typically an order of magnitude higher than those using excitons of most other material systems. For example, when J-Aggregates were incorporated in a metal mirror microcavity, polariton emission peaks were separated in energy by more than 300 meV, which corresponds to record high coupling strengths an order of magnitude larger than any Rabi splitting achieved with inorganic semiconductors. Also, the only reported observation of room temperature polariton photoluminescence utilized J-Aggregates as the exciton material in the microcavity. This observation was possible because the Rabi splittings are much larger than room temperature thermal noise (~26meV), and because J-Aggregate excitons remain bound at 300K, unlike inorganic excitons, which ionize into free electrons and holes well below this temperature.

J-Aggregate Materials

The materials that most readily form J-Aggregates are cyanine dyes. Figure 8 illustrates the chemical structure of TTBC, an archetypical J-Aggregate forming cyanine dye.

Like TTBC, 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\textsuperscript{18}.

**J-Aggregate Formation**

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\textsuperscript{19}. 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.

**J-Aggregate Optical Properties**

J-Aggregates exhibit a number of optical properties, which make these materials uniquely suitable for observing polariton dynamics. As an excitonic transition, J-Aggregates possess very high oscillator strength ($\alpha_{\text{max}} \approx 10^6 \text{cm}^{-1}$) and correspondingly very short radiative lifetimes. For organic systems, they also have very narrow absorption and photoluminescence (PL) spectra—with FWHM of between 10-20nm. Finally, the Frank-Condon shift between absorption and emission is typically less than 2 nm if at all observable, making it easier to strongly couple the absorption and emission of the J-Aggregates simultaneously to the microcavity.

The photophysical basis for these optical properties comes from the fact that cyanine dyes in the J-Aggregate state act as a single giant harmonic oscillator with the combined oscillator strength of all the aggregated dye monomers. Proof that J-Aggregates are coupled oscillators of monomer organic molecules is apparent in a comparison of the optical properties of the monomer to the J-Aggregate. Compared to the monomer, J-Aggregates absorb and emit photons in a lower energy band because the oscillator coupling makes new lower energy eigenmodes available to the aggregate\textsuperscript{20}. Furthermore,
since radiation rates are proportional to oscillator strength, the J-Aggregate radiative lifetime is much shorter than that of the monomer, which has a noticeable effect on the photoluminescence quantum efficiency. For example\textsuperscript{21}, for THIA, the dye’s quantum efficiency increases from 0.8\% to 48.0\% (in solution), a factor of 60, as the radiative rate becomes 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.

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. This situation is depicted qualitatively in Figure 9. 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 $\sqrt{2}$.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure9.png}
\caption{Energy levels of two molecules interacting via dipole-dipole coupling, with the arrows representing the orientation of the molecular dipoles}
\end{figure}

\textbf{2 Molecules}

\begin{itemize}
  \item $S_0 \rightarrow (\uparrow \downarrow)$ \quad $\hat{\mu} = 0$
  \item $S_1 \rightarrow (\uparrow \uparrow)$ \quad $\hat{\mu} = \sqrt{2} \mu_0$
  \item $S_0 \rightarrow (\rightarrow)$ \quad $\hat{\mu} = \sqrt{2} \mu_0$
\end{itemize}
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\(^\text{22}\). 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: \( H_M (|1\rangle_n - |0\rangle_n) = E_M (|1\rangle_n - |0\rangle_n) \). 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 1\(^{st}\) 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\(^{14,22}\):
\[
H |\Psi^1_n\rangle = E_M |\Psi^1_n\rangle + J (|\Psi^1_{n-1}\rangle + |\Psi^1_{n+1}\rangle)
\]
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\(^\text{22}\):
\[
|\Phi^1_k\rangle = \sum_{n=1}^{N} c_{n,k} |\Psi^1_n\rangle = \sum_{n=1}^{N} \sqrt{\frac{2}{N+1}} \sin \left( \frac{k \pi n}{N+1} \right) |\Psi^1_n\rangle, \quad k = 1, 2, \ldots, N
\]
With corresponding energies (note the degeneracy is broken)\(^\text{22}\):
\[
E(k) = E_M + 2J \cos \left( \frac{k \pi}{N+1} \right), \quad k = 1, 2, \ldots, N
\]
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:

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

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 \( x = nd, \quad n = 1, 2, \ldots, N \).

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:

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

Then the dipole moment from an excited state of the J-Aggregate to the ground state is:

\[ \mu_{g,k} = \langle \psi^0 \lvert \hat{P} \lvert \psi^1_k \rangle = \mu_0 \sqrt{\frac{2}{N + 1}} \sum_{n=1}^{N} \sin \left( \frac{k \pi n}{N + 1} \right) \]

Using trigonometric identities the dipole moment can be rewritten in closed form as:

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

This expression shows that the oscillator strength \( \sim \lvert \mu_{g,k} \rvert^2 \) 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, \( \hbar \omega_j \approx \hbar \omega_m - 2|J| \), typically 50-60nm, and also why the absorption spectrum tails out asymmetrically towards higher energy. For large \( N \):

\[ \mu_{g,k=1}^2 \rightarrow 8(N + 1)\mu_0^2 / \pi^2 \approx 0.81(N + 1)\mu_0^2 \]
It is interesting to note that in the J-Aggregate the dipole moments of the dye molecules do not add, which would have yielded $|\mu_{\text{dye}}|^2 \propto N^2$. 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 $\text{Var}(\bar{x}_i) = |\mu|^2$, then the variance of a sum of dipoles equals the sum of the variances of the individual dipoles:

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

Because oscillator strength is conceptually a variance, the total oscillator strength is proportional to $N$ and not $N^2$. In a J-Aggregate this dependence can be interpreted to mean that there is cooperation amongst the dye molecules but it is not complete. Nevertheless, since numerous molecules participate when a J-Aggregate absorbs a photon, the exciton created on the J-Aggregate is considered shared or delocalized over the molecules that form the coupled oscillator state.

The 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. But most likely, most of the observable width 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 $\Delta\omega_j = \Delta\omega_M/\sqrt{N}$.

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

$$N = \left(\Delta\omega_M/\Delta\omega_j\right)^2$$
With typical numbers for $\Delta \omega_m = 40\text{nm}$ and $\Delta \omega_f = 10\text{nm}$, a typical size J-Aggregate is $N = \left(\frac{40\text{nm}}{10\text{nm}}\right)^2 = 16$. 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 $1\text{ns}$, then the radiative lifetime of the J-Aggregate becomes $63\text{ps}$, 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 $32\text{nm}$, then for $N = 16$, the J-Aggregate Frank-Condon shift is $2\text{nm}$, which appears consistent with experiment.

**J-Aggregates in Thin-Film**

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. A common method is to mix dye in a poly vinyl alcohol (PVA) matrix, and spin cast the composite into a thin film. 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. 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 anionic lumophore is adsorbed on top. All of these approaches have been used to make J-Aggregate OLEDs.
J-Aggregates via Dip-Coating

The approach adopted in making the J-Aggregate polariton OLEDs is the dip-coating technique, based on the following considerations. Using the dip-coating technique, practically an unlimited number of bi-layers of polyelectrolyte and J-Aggregate can be stacked together\textsuperscript{25}. Because the dip-coating method is a thermodynamic equilibrium driven process, given sufficient time to nucleate, monolayers of J-Aggregate will form with no detectable monomer signature. These monolayers can potentially assemble as single crystal\textsuperscript{30} possessing much greater translational symmetry than in amorphous systems\textsuperscript{31}, which is considered an important precondition for making the exciton photon coupling more complete. The ability to process the polyelectrolyte and dye layers from separate solutions allows the pH of the dye to be better controlled, which directly effects the degree of aggregation and the photoluminescence quantum efficiency of the J-Aggregates.

V. Experimental

Proposed Structures

We first develop an OLED using J-Aggregates of cyanine dyes as the emitter material, and then incorporate a similar device structure in a resonant optical microcavity (RC-OLED) to demonstrate polariton emission. The basis for the J-Aggregate OLED architecture comes from the work of Era, et al\textsuperscript{32}. In their structure, the molecular hole transport layer material TAD is first evaporated on an indium tin oxide (ITO) coated glass substrate. Then, 2 bi-layers of J-Aggregate and polyelectrolyte are deposited via the Langmuir-Blodgett technique, and are capped by the molecular hole blocking material PBD. The authors reported that the 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.” Reading their assessment led to two simple ideas for improving their approach. First, use a polymer for the hole transport material instead of a small molecule, since polymers are less likely to dissolve or be “polluted” in water. Second, use the dip-coating technique instead of Langmuir Blodgett, so that multi-layers could be formed in a reproducible fashion.

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Figure 10 illustrates the structure of our J-Aggregate OLED and polariton LED, where the only structural difference between them is in the electrical contacts. In the OLED structure the anode is transparent conducting indium tin oxide (ITO), whereas in the polariton LED the anode is a thin film of silver forming one mirror of the optical microcavity. The hole transport layer (HTL) is a polymer film spin-cast on top of the anode. The J-Aggregate layers are then solution deposited from water. The electron transport layers (ETL), composed of small molecule organics, are thermally evaporated on top of the J-Aggregates. In this design, the J-Aggregate layers are concentrated at the cavity antinode, in order to maximize the exciton-photon coupling. Additionally, by not having dispersed dye throughout the device, which can act as electron traps, the electron and hole transport properties of the device are better maintained.

Hole Transport Layer
An aromatic polymer is used to make the HTL, instead of a polar conducting polymer, since such films are least likely to be damaged or dissolved during the dip-coating of the J-Aggregate layers. The polymer chosen is the semiconducting wide-bandgap fluorescent polymer Poly-TPD, which is essentially the polymeric form of TAD. Poly
vinyl carbazole (PVK) was also tried but it was determined that the morphology of PVK disrupted the J-Aggregate formation. Inserting the HTL between the anode and J-Aggregate layers improves hole injection and current balance, reduces exciton quenching by the anode contact, and enables placement of the exciton recombination region precisely at the cavity anti-node.

**J-Aggregate Layers**

Dip-coating 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 electrostatically charged via surface treatment techniques like UV-ozone or oxygen-plasma in order for the polyelectrolytes to adsorb. Applying such methods would most likely have damaged the fluorescence of Poly-TPD. Fortunately, such methods were not necessary because the polymer readily oxidizes forming polar sites that promote polyelectrolyte adsorption. In fact, we found in the course of our experiments that the polyelectrolytes adsorbed even onto Teflon; they just didn’t adhere when run through a sonication cycle.

**Electron Transport Layers**

The ETL consists of BCP, which also performs the function of a hole blocking layer that confines excitons electrically generated in the J-Aggregate layers. High Vacuum Sublimation of BCP is performed with angstrom thickness, enabling the optical cavity to be fine tuned to the J-Aggregate resonance. An additional benefit of exposing the structure to ultra high vacuum ($10^{-7}$ torr) is that it drives off any residual water from the polyelectrolytes, improving device current-voltage characteristics.

**Electrical-Contact/Mirror Layers**

Different materials are used for the electrical contacts of the J-Aggregate and polartion OLED. For the J-Aggregate OLED, the cathode consists of magnesium-silver alloy (Mg:Ag) which provides better electrical injection to the BCP, a property attributed to the low work function of magnesium. For the polariton OLED, the cathode consists only of silver since it is about 10%-15% more reflective than magnesium throughout the visible
spectrum. In the polariton OLED, the cathode mirror is opaque, serving as the strong reflector, while the anode mirror is semitransparent to allow some light to escape the cavity for detection.

**Choice of Dye**

TDBC is the cyanine dye used as the J-Aggregating material in the polariton LED\(^1\) (See Figure 11). It is efficiently fluorescent even as a monomer, readily forms J-Agregates at ultra low concentrations \((10^{-5} \text{ M in water})\) and has been studied in the photographic industry, as a membrane potential sensitive dye, and for its rich exciton dynamics\(^{33-39}\). It is similar to TTBC, except that the lumophore is anionic, which makes it suitable for dip-coating.

![Figure 11 TDBC, anionic cyanine dye sodium salt that readily forms J-Aggregates via dip-coating](image)

**Equipment**

Completing this experiment required a unique set of thin-film deposition equipment and measurement instruments. A programmable slide-stainer was purchased to systematize the bi-layer deposition of the polyelectrolytes and J-Agregates, and the stainer’s substrate-racks were customized to hold 1” square substrates, a size compatible with the

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\(^1\) A major challenge was finding a dye company that supplies J-Aggregate forming cyanine dyes at affordable prices. The companies that publicize their J-Aggregate dye portfolios charge in excess of 200 dollars for 5-milligram lots, since they typically market to biologists who need only very small quantities. But at this exorbitant price, we simply could not purchase the quantities that our experiments require. In time, we discovered that dye companies that cater instead to the photographic film industry, manufacture high purity J-Aggregating cyanine dyes in very large quantities at very affordable prices, typically 200 dollars or less for 1 gram, since the most common application of J-Agregates is sensitizing silver halide based film to narrow regions of the visible spectrum. This find has enabled us to purchase the dyes and the quantities needed to conduct our polariton experiments now and in the future.
rest of our integrated growth system. To determine polariton dispersion curves, spectrally resolved surface reflectivity was measured as a function of the angle of the incident beam. This measurement was in part carried out at MIT’s Center for Material Science and Engineering (CMSE) Shared Facilities Lab. A spectroscopy set-up has also been assembled to measure polariton photoluminescence and electroluminescence emission spectra as a function of angle, consisting of micropositioners, and a custom holder for the optical-fiber of the spectrometer.

V. Results and Analysis

J-Aggregate Linear Optical Properties

Figure 12 shows absorption and photoluminescence spectra of dip-coated (layer-by-layer) J-aggregates of TDBC and the polyelectrolyte PDAC on a glass substrate where four bilayers were adsorbed on each side of the glass. (Both sides of the substrate contribute to the absorbance values.) The dip-coating procedure consisted of 15 minute soak in PDAC (5x10^{-3} M), then 3 rinses in deionized water (DI) of durations 2 min., 2 min, and 1 min, followed by similar steps using TDBC (5x10^{-3} M). The pH was not deliberately controlled, and is estimated to be pH ~ 6.0. Spectral data indicate peak absorption at 588 nm, FWHM of approximately 20.0 nm and 21.4 nm for absorption and photoluminescence respectively, a Frank-Condon shift of less than 2 nm (comparable to the measurement error of the spectrometer), and thin-film photoluminescence quantum efficiency of 8% ± 2%.

From the absorption spectra, a peak absorption coefficient of \(5.7 \times 10^5 \text{cm}^{-1}\) is calculated, assuming the thickness per bi-layer is approximately 1 nm, a typical thickness for PDAC based polyelectrolyte multilayers. The extinction coefficient \(\kappa = 5.3\). These calculations are considered estimates since they do not account for reflection off the dye interfaces.
The absorption coefficient of TDBC-PDAC bi-layers significantly increases in more alkaline environments (pH > 7), as demonstrated in Figure 13. Five bi-layers were deposited on each side of the glass using the same preparation conditions as in Figure 12, except that the troughs containing the dye and dye rinses were adjusted to pH 11.5 (using NaOH as the base). The peak absorption is located at 594nm with a FWHM of 16.5 nm, and a peak absorption coefficient is calculated to be $3.5 \times 10^6 \text{ cm}^{-1}$, assuming total dye thickness of 10nm, and a peak absorbance of 1.51 (0.11 subtracted as background). The extinction coefficient $\kappa = 32.9$. This represents a 6-fold increase in absorption for a pH change of approximately 5.5.
Qualitative demonstrations of the high reflectivity and polarization dependence of TDBC are depicted in Figure 14. Figure 14 shows two photographs of surface reflection from TTBC crystallites suspended in a PVA water-methanol colloid that were taken using an optical microscope operated in reflectance mode, without and with a polarized white light source. Comparing photographs it is clear that the reflection from some of the crystals disappears when the polarizer is inserted, indicating the reflectivity is highly pronounced but only with light polarized parallel to their optical axis. Figure 15 shows the pronounced reflection off the surface of crystals of PIC (pseudo-isocyanine) when illuminated by a white-light halogen source.
Figure 14 Reflection Micrographs of TTBC J-Aggregate crystalites, TTBC J-Aggregates in solution, and PIC crystals
**J-Aggregate OLEDs**

With the dip coating technique established for TDBC J-aggregates, we proceeded to develop J-aggregate OLED structures. Poly-TPD was dissolved at a concentration of 10 mg/ml in chlorobenzene and spin-cast on pre-cleaned ITO substrates at the spin speed of 3000 rpm, with an acceleration of 10,000 rpm/sec for 60 sec. After baking out residual solvent for 30 min at 60°C, between 2 and 8 bi-layers of J-aggregates were absorbed, and then capped with BCP and the cathode layers. Current-Voltage (I-V) characteristics and optical power measurements were taken, as well as electroluminescence (EL) spectra, showing emission peaked at 600 nm with a 16.5 nm FWHM. It is significant to note that the EL spectra are independent of current level, which indicates that the exciton recombination region is entirely in the J-Aggregate layer. A typical I-V curve and external EL quantum efficiency plot are depicted in Figure 16. The maximum EQE is 0.035%.

![Figure 15 TDBC J-Aggregate OLED electroluminescence spectrum](image)
Resonant Microcavity Optical Properties

The next step was designing the optical microcavity, given that it was going to be made of silver mirrors. The two parameters that we concentrated on simulating were the overall thickness of the cavity and the linewidth or quality (Q) of the cavity. We simulated an empty (no J-Aggregate) cavity using a T-matrix model, with complex index of refraction values for silver taken from the CRC handbook\(^40\). The empty cavity consisted of 1200Å Ag mirror, a \(n = 1.7\) spacer (like Poly-TPD), and 300Å Ag mirror. For a cavity tuned to 586 nm, the Q is about 10 and the thickness of the spacer is 123nm. This thickness is considerably less than 172nm, which is the half-wavelength value assuming perfect mirrors, because some fraction of the wave penetrates into the silver layers. We confirmed the Q calculation with reflectivity measurements of an actual microcavity.

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Figure 16 TDBC J-Aggregate OLED current-voltage and external quantum efficiency results
Polariton Optical Properties
From our estimate of the Q of the cavity and our data on the linewidth of the J-Aggregate we estimated that a Rabi-splitting of about 130 meV would be needed for it to be observable, and approximately 8 bi-layers of J-Aggregate would be needed to provide this splitting. This estimate is based on data of Lidzey et al\textsuperscript{41}. Their graph showed that for $\sqrt{abs} \approx 0.7$, a Rabi-splitting of 120 meV was observed in a cavity consisting of a DBR and Ag mirror. From our absorption data, 8 bi-layers produce an $\sqrt{abs} \approx 0.68$, and since all-metal mirror microcavities exhibit greater Rabi-splitting due to the higher degree of optical confinement, we surmised that 8 bi-layers would be sufficient.

![Figure 17 T-Matrix simulation results for 123 nm thick spacer with index of refraction n = 1.7, where cavity is tuned to 586 nm light with a quality factor of approximately 10](image)

Next polariton properties were established for dip-coated TDBC coupled to a metal mirror microcavity. Figure 18 shows the angular dependent reflectivity and photoluminescence data for a sample consisting of 1200Å Ag, poly-TPD, 8 J-Aggregate bi-layers, BCP, and 300Å Ag. From the reflectivity resonance dips, the polariton dispersion curve in Figure 18 was generated and fit using the model developed in section III, and a Rabi splitting of 200 meV was determined. In the PL experiment, a Gallium
Nitride 408 nm laser was used as the excitation. The PL peaks exhibit similar anti-crossing behavior as observed in the reflectivity spectra characteristic of polaritons.

Figure 18 Linear optical properties of J-Aggregate polaritons: angularly resolved reflectivity, photoluminescence, and polariton dispersion curves. Rabi-splitting of 200meV based on fit to reflectivity data
Polariton Electroluminescence

Similar results were to be expected in electroluminescence. However, tuning the cavity to the J-Aggregate peak turned out to be difficult to control. To solve this problem, a series of Poly-TPD films of different thickness were prepared, with the remainder of the devices fabricated on all the substrates simultaneously. In order to insure that the thickness was 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 at 10,000 rpm/sec acceleration. Thickness measurements were carried out by profilometry. It was determined (Figure 19) that by varying spin-speed between 1000-2000 rpm, the thickness could be adjusted from 450Å-650Å.

Figure 19 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.
Figure 20 shows EL spectra at normal incidence for 5 microcavities of different cavity thickness, and hence different photon energy tuning. As the cavity thickness is tuned through the exciton resonance, the J-Aggregate peak splits into a higher energy peak and a lower energy shoulder, in addition to the bare exciton peak near 600nm.

Figure 20 Normal direction electroluminescence of five polariton OLEDs tuned through the J-Aggregate resonance by changing the poly-TPD layer thickness. Poly-TPD spin-cast speeds are indicated and they correspond to the data of Figure 19.

Figure 21 plots angularly resolved EL spectra for the most strongly coupled device (2000 rpm). The two polariton branches are clearly distinguishable, as two additional peaks at higher and lower energy relative to the bare J-Aggregate emission. The lower polariton branch moves to higher energy until about 60°, where it becomes almost completely excitonic, while the upper branch peak becomes photonic as it tunes towards higher energy. Although the lower energy peak appears only as a shoulder, it is clearly a
polariton state and not simply the bare cavity peak, since based on the thickness curve of the cavity the bare photon mode is at 581 nm.

![Energy vs Wavelength Graph](image)

**Figure 21** Angularly resolved electroluminescence of J-Aggregate polariton OLED

Fitting the data to a dispersion curve (Figure 22), a Rabi-splitting of 240 meV is calculated compared to the 200 meV from the reflectivity data. The splitting is higher because 12 bi-layers were adsorbed for the polariton OLED, while only 8 were for the reflectivity measurement. The ratio of the Rabi-splitting’s (240/200 = 1.2) is approximately the square root of the ratio of the bi-layers (√(12/8) = 1.22), which is expected since as derived in Section III, the Rabi-splitting is proportional to the square root of the absorbance.
VII. Future Work

A serious limitation with our device is the design of the anode, which currently is simply a 300Å layer of silver. The major problems are cavity line-width, electrical injection, and silver migration. Using a DBR instead of a metal mirror will likely improve the Q of the cavity by a factor of 10-100. Larger Q will mean the Rabi-splitting will become observable with lower oscillator strength. Consequently, fewer dye-layers will be necessary, and the overall efficiency should improve since less material will need to be excited. With a DBR serving as the mirror, ITO can be used as the anode electrical contact instead of silver. ITO will also improve hole injection into the poly-TPD layer since it has a higher work function than silver. If the ITO film is integrated into the DBR as the last dielectric layer, the cavity will still be $\lambda/2$, the field strength will be high and the coupling will be larger, then if the ITO and DBR are treated as separate entities.
Also, by optimizing the pH of the J-Aggregate solution, the absorbance per bi-layer will increase, and the total number of layers that are needed can be further reduced, perhaps to the point where only one or two layers will be needed. With fewer layers, the formation time per layer can be increased without extending the overall deposition time for the dip-coating steps, which should improve the morphology of the dye layers, perhaps enabling the formation of larger crystal domains. Limiting the overall time of deposition is desired because it minimizes the possibility of impurities inadvertently contaminating the device.

We are also eager to investigate energy transfer from small molecule organics to the J-Aggregate exciton and directly to the polariton states. Since the polariton states occupy a greater portion of the cavity, long-range energy transfer may be possible. Energy transfer could also improve the quantum efficiency of the devices, if the host is more quantum efficient in generating excitons than poly-TPD or BCP.

VIII. Conclusion

The goal for this thesis was to develop the first polariton LED—the first demonstration of electrically pumped polariton emission, and initial results indicate a Rabi-splitting of 240meV at room temperature. We used J-Aggregates of the cyanine dye TDBC as the exciton layer and an RC-OLED as the test structure to complete this objective. J-Aggregates were used as the excitonic material because of their very high oscillator strengths, which can be almost as large as the combined oscillator strength of the dye molecules that make up the aggregate. Nanoscale thick films of J-Aggregates were formed using a layer-by-layer dip coating technique that enabled us to engineer the oscillator strength of the J-Aggregates with monolayer precision. Incorporating these layers in the OLED microcavity was a challenge since it required synthesis of three different deposition techniques—spin-coating, dip-coating, and thermal evaporation, but it proved to be an effective approach in achieving polariton emission in an LED. This development demonstrates that polariton states persist even when excited electrically, and 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 will operate by coherent spontaneous emission, a process that does not require full population inversion.

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