Organic and Nanostructured Materials in Optoelectronic Applications: Physical Processes and Active Devices

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1. **Lab of Organic Optoelectronics - Research Themes**

Our research is focused on deciphering the physical properties that govern behavior of nanostructured organic materials and applying the findings to development of practical, active organic technologies. With focus on electronic and optoelectronic structures, to date we demonstrated efficient LEDs, lasers, solar cells, photodetectors, transistors, memory cells, and chemical sensors. In addition to working on small-molecular-weight van-der-Waals-bonded organic thin films, we also examine hybrid organic/inorganic structures, polymer solids, and self-assembled materials. Our work tends towards the nano-scale where through development of new patterning and materials growth techniques we aim to reduce the size of active device layers from the present nano-scale thickness of organic thin films to that of single molecules or atomic clusters. Our ultimate goal is to utilize the nano-scale functionality of molecules, polymers, and inorganic/organic hybrid assemblies in practical nano-scale devices and both small- and large-area integrated systems.
2. Integrated Materials Growth System

**SPONSOR**
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Vacuum growth of organic materials can generate atomically flat thin films of high purity, facilitating fabrication of complex multi-layer devices with excellent uniformity and sharp interfaces between adjacent layers. Such vacuum grown devices are highly reproducible from run to run, and can have complex structures containing thin layers of precisely controlled composition. Increased control over the growth parameter is essential for the better performance devices. Additionally, flexibility of van der Waal bonds in the organic thin films facilitate their integration with both conventional technologies and less conventional materials such as flexible, self-assembled, or conformable substrates.

We are in the process of developing a versatile materials growth system (see Fig. 1) that combines conventional materials growth techniques with novel deposition methods developed in our laboratories. The completed growth system will integrate the method for physical and vapor phase deposition of hybrid organic/inorganic thin-films with a low-pressure RF/DC sputtering chamber, an evaporative growth chamber, and a chemical vapor deposition chamber. The completed vacuum system will be capable of depositing molecular organics, polymers, metals, metal oxides, inorganic nanodots, and colloids in a controlled layer-by-layer fashion. An in-situ shadow masking system enables fabrication of complex patterned structures inside a vacuum.

**Figure 1** Integrated Materials Growth System. Both present and projected chambers are indicated. Projected chambers and chambers in construction are labeled as “TO BE BUILT.”
environment, while the integrated N₂-filled, dry glove box facilitates handling, measuring, and packaging of organic thin film samples that are susceptible to reactions with atmospheric oxygen and water vapor. When the analysis chamber is built, the completed samples will be in-situ tested by contacting them with an electrical probe attached to an X-Y-Z manipulator. Optical ports on the analysis chamber allow for a telescopic view of the devices and facilitate optical excitation of probed samples. Optoelectronic properties of the hybrid materials and structures will be investigated at a range of temperatures from 5 K to 600 K, generated by the liquid helium cryostat and the boron-nitride heater situated behind the sample stage. Existing chambers are presently connected to the central transfer system that has linear degrees of freedom. Maximum substrate size is 10 cm with a 5% variation in the thickness and composition of deposited films over the substrate area. The integrated growth system is the centerpiece of our materials growth effort, as in its completed form it will accommodate solvent-free deposition and co-deposition of polymers, colloids, and molecular organic materials in vacuum. Its versatility is unsurpassed in the field of organic/inorganic materials deposition, and it is among the first to integrate organic and inorganic material deposition methods.

3. **Exciton Physics in Organic Optoelectronics**

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Over the last decade, enormous strides have been made in the field of organic optoelectronic devices. A first generation of visible organic light emitting devices has been commercialized. Optically pumped lasers have been demonstrated at UV, visible, and IR wavelengths. Groups have fabricated photodetectors with collection efficiencies as high as 75%. And solar cells with power conversion efficiencies as high as 3% have been reported.

As a whole, these results represent an extraordinary technological achievement, but often lost in this torrential development of new devices has been a complete physical understanding of their operation. Specifically, the factors determining the properties and behavior of molecular excitons, the fundamental excitation operating in all organic optoelectronic devices, are only imprecisely understood. In this project we study the influence of disorder in amorphous molecular organic materials on the excitonic energy structure of constituent molecules. We highlight two excitonic processes which are general to all amorphous organic thin film structures and which strongly determine organic device operation.

(a) **Solid State Solvation**

Emission and absorption spectra of many organic dyes in liquid solutions depend on the local electric fields generated by the surrounding polar solvent molecules and the response of the electronic charge on the solvent molecules to the excitation dynamics of the solute. This "solvation effect" is a result of intermolecular solute-solvent interaction forces (such as dipole-dipole or dipole-induced dipole) that tend to stretch molecular bonds and shift charge distribution on molecules, altering the energy difference between the ground and excited states of the solute. Our earlier experiments [Bulović, et al., Chem. Phys. Lett. 287 (1998) 455; 308 (1999) 317] suggested that the solvation effect is also present in molecular solids where closely packed polar molecules can generate large local electric fields. In these first studies we examined the Solid State Solvation (SSS) induced luminescence red shifts of amorphous organic thin films doped with the red laser dye [2-methyl-6-[(2,3,6,7-tetrahydro-1H, 5H-benzo [i,j] quinolizin-9-yl)-ethenyl]-4H-pyran-4-ylidene] propane-dinitrile (DCM2). By changing the concentration of
DCM2 present in a film of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) from 0.9% to 11%, the peak electroluminescence emission wavelength shifted from $\lambda=570$ nm to $\lambda=645$ nm (see Fig. 1). (In these measurements, the DCM2:TPD film comprised the active layer of an OLED.) Because DCM2 is a highly polar molecule (with $\mu\sim11$ D in ground state), and TPD is nearly nonpolar (with $\mu\sim1$ D in ground state), increasing the DCM2 concentration was thought to increase the strength of the local electric fields present in the film, and that this increase in the local fields was the cause of the spectral shift. The authors viewed the mechanism as a solid state realization of solvation, and so termed it “Solid State Solvation”. Similar results were also observed for DCM2 in aluminum tris-(8-hydroxyquinoline) (Alq$_3$) and Alq$_3$ in TPD (see Fig. 2). Further quantification of this mechanism, however, was complicated by a subsequent report, which argued that as the DCM2 doping increased in these systems, the DCM2 quantum efficiency dropped, which is generally considered an indicator of dopant aggregation [Baldo et al., Chem. Phys. Lett. 347 (2001) 297]. Such aggregation, by implying substantial local inhomogeneity in doping, would make it difficult to specify the environment surrounding each molecule. We therefore developed an alternative system in which to study the SSS phenomenon.

We prepared spun-cast films consisting of polystyrene (PS), a small concentration of the laser dye DCM2 (< 0.005% by mass), and a range of concentrations of the polar small molecule material camphoric anhydride (CA). This material system was chosen so that the DCM2 concentration could be kept constant (and very low), thereby fixing (and limiting) DCM2 aggregation effects, while still allowing for the modification of the strength of the local fields in the film. We modified these fields by changing the concentration of CA, which has a large dipole moment ($\mu\sim6D$ in ground state) relative to its molecular weight and is optically inactive over the range of wavelengths relevant for studying the properties of DCM2. The polymer host material polystyrene was selected because it provides a transparent, non-polar background for the system.

For a fixed DCM2 concentration of 0.005%, we found that the DCM2 emission spectrum shifts continuously from 2.20 eV (563 nm) to 2.05 eV (605 nm) for CA concentrations ranging from 0% to 25% (see Fig. 3). We also performed the same measurements on films with DCM2 concentrations up to 0.05%, and observed no change in the results, demonstrating that
aggregation does not play a role. Measurement of the electronic susceptibility of the films (see Fig. 3) shows a marked increase with CA concentration, following a linear relationship given by

\[ \varepsilon = 2.44 + 0.131 \times (\text{CA} \%) \]

Our results show that the DCM2 emission red shifts as the concentration of dipoles (i.e. CA molecules) increases in the film, and that this phenomenon not related to DCM2 aggregation but is consistent with the SSS mechanism sketched in Fig. 4. By employing a system free of aggregation and then measuring the electronic susceptibility, however, we can take the model a step further and apply the theory of liquid solvation quantitatively to our films.

**Figure 3** (left) PL spectra of 0.005% DCM2 in PS:CA films. The spectrum red-shifts as the CA concentration is changed from 0 to 25%. (middle) Chemical structures of CA, DCM2, and PS. (right) Change of the peak luminescence energy and the dielectric constant as a function of CA doping.

**Figure 4** Equilibrium and non-equilibrium states of the solvation process

\[ E_i = C - A\Lambda \]

(1)

where

\[ \Lambda = \frac{2(\varepsilon - 1)}{2\varepsilon + 1} \]

and \( A \) and \( C \) are constants. In Fig. 5 we plot three different fits to the spectral data, indicating the sensitivity of the fit to the choice of \( A \). We find that the trend in the spectral shift is in excellent agreement with the solvation theory, with the optimal fit obtained for \( A = 0.57 \) eV.

It is difficult to determine how plausible this value is based on the definition for \( A \) because of inherent arbitrariness in the specification of the OLM parameters. However, we can look at solvation in solutions, where the solvation mechanism is known to operate. A plot of the peak emission energy for DCM2 in different solvents is shown in Fig. 5 against each solvent’s value for \( \varepsilon \). We find that the OLM theory again works quite well, and obtain an optimal fit for \( A = 0.55 \) eV.

The SSS mechanism can, therefore, comprehensively describe the observed spectral shifts, and the model parameter is consistent with known values for DCM2 in solution. A priori, this result is not surprising as one could argue that dielectric relaxation in amorphous organic solids should be similar to that of liquids. Indeed, the SSS process can strongly determining the dispersion and position of molecular energy levels in organic solids. Additionally, SSS could be used as a new method for the engineering of energy structures, both for excitonic levels (as studied in this work) and for conduction levels (which are also subject to solvation).

(b) Exciton Diffusion

The second process we have studied is Exciton Diffusion, and refers to the migration of excitons between molecules. Though the presence of exciton diffusion is well-known, the details of the phenomenon have not been studied in a disordered solid. Specifically, the impact on this process of dispersion in molecular energy levels has been previously ignored and we find plays a controlling role.

![Figure 5](image_url)
Time resolved photoluminescence measurements of disordered molecular organic thin films of Alq3 doped with DCM2 show an emission spectrum that significantly red shifts as a function of time following excitation by a 100 fs laser pulse (see Fig. 6). (The spectral measurements were performed using a Hamamatsu streak camera.) Spectral shifts of ~ 0.10 eV over a time window of ~ 10 ns, are observed for doping levels ranging between 0.5% and 5%, in addition to significant spectral narrowing over that same period. We show that this previously unreported phenomenon can be attributed to the diffusion of excitons through the film by means of Forster energy transfer between DCM2 molecules.

This site-to-site transfer rate is governed by the emission and absorption spectra of the exciton donating and the exciton accepting molecule. From Förster's original formulation, the rate of exciton transfer, $\Gamma_F$, is given as

$$\Gamma_F = \frac{1}{\tau_{rad}} \left( \frac{R_F}{R} \right)^6$$

(3)

where $R$ is the distance separating the donor and acceptor, $\tau_{rad}$ is the intrinsic radiative lifetime of the donor, and $R_F$ is the Förster radius, given by,

$$R_F^6 = \frac{3 \, c^4 \, \kappa^2}{4\pi \, n^4} \int S_D(\omega) \sigma_A(\omega) \frac{d\omega}{\omega^4}$$

(4)

where $\kappa^2$ reflects the relative orientation of the donor and acceptor, $n$ is the index of refraction of the medium, $S_D$ is the normalized donor fluorescence spectrum, and $\sigma_A$ is the acceptor molar absorption cross section (in units of cm$^2$).

As indicated by the rate expression, the Förster energy transfer occurs more readily when the acceptor molecule has lower energy spectra than the donor. In other words, the Förster mechanism preferentially transfers excitons towards lower energy sites. If we combine this observation with an assumption that the excitonic density of states, $g_{ex}(E)$, has a non-zero width.
We developed a Monte Carlo simulation of this diffusion process. The simulation tracks the emission and Förster energy transfer of excitons in a large lattice of molecular sites, with each site characterized by its position and peak emission energy. The lattice spacing corresponds to the mean molecular inter-site spacing. The histogram of all the site energies reproduces the shape of the $g_{\text{ex}}(E)$ distribution. We have assumed that $g_{\text{ex}}(E)$ has a Gaussian form, with a full-width-half-max (FWHM) of $w_{\text{DOS}}$. Once the system of sites has been created, each site is populated with an exciton, yielding an exciton population, $n_{\text{ex}}(E,t)$, such that,

$$n_{\text{ex}}(E,t=0) \propto g_{\text{ex}}(E)$$

where $t=0$ refers to the time immediately following the arrival of the PL excitation pulse. Then for each time step of length $\tau_{\text{step}}$, each exciton has the opportunity to Förster transfer to another site or to emit.

The simulation yields results consistent with the experimentally observed shifts (see fits in Fig. 6), and through fitting of the available parameters, provides a probe of $w_{\text{DOS}}$ and $R_F$. The values for $w_{\text{DOS}}$ decrease from $\sim 0.260$ eV for 0.5% DCM2 doping to $\sim 0.205$ eV for 5% doping. In addition we find that $R_F$ falls with increasing doping, from 38 Å for 0.5% to 20 Å for 5%. We can not turn to any published results for a direct comparison of these fitted values. However, there do exist calculations of $w_{\text{DOS}}$ for polaron levels in amorphous organic materials, where the polaron $w_{\text{DOS}} \sim 0.1 eV$. Though it is not necessary that polaron levels and excitonic levels should experience identical energy dispersion, it is reasonable to expect that they are comparably dispersed, which is what we observe.

We know of no other method for measuring the energy dispersion in exciton energies in the literature. For this reason, this technique potentially represents a major breakthrough in the analysis of energy structure in amorphous organic solids. We have also demonstrated this modeling method with neat films; we studied time-dependence of PL in films of Alq3 and Ir(ppy)3. The evolution of the peak PL for these two films is shown in Fig. 7, along with fits from our simulation. Note that spectral shifts just like those observed in the DCM2:Alq3 system are observed. In both cases, we obtain $R_F \sim 12$ Å and $w_{\text{DOS}} \sim 0.075$ eV, which, as per the arguments made above, have reasonable magnitudes. The similarity between the two systems should not be surprising as they have similar molecular ground state dipole moments and bulk spectral

![Figure 7](image-url)  

**Figure 7**  
(a) Evolution peak PL of Alq3 with simulation fit; (b) evolution of peak PL of Ir(ppy)3 with simulation fit.
overlaps.

By extension, this technique should apply to any pure organic thin film material in which Förster energy transfer occurs. Experimentally, all that is required is a film with thickness of at least 20 nm and an ultrafast source operating at a wavelength for which the film is absorptive. Thus we find that this technique is not only of great value in analyzing excitonic properties in organic thin films, but its application is also straightforward and general.

(c) Conclusions

In inorganic, crystalline semiconductors, accurate physical models have been invaluable in assisting technological improvement. Currently, however, very few physical models describe electronic and excitonic behavior in organic optoelectronic devices. The larger aim of this work is the development of a practically useful model of electronic and optoelectronic processes in amorphous organic solids, which might then be used to predict the behavior of new organic device structures.

The quantification of SSS helps us towards this goal in identifying one of the primary mechanisms by which solid state energy levels are altered from their gas phase values. In addition, it identifies an additional lever with which one can modify energy levels through the modification of bulk property (i.e. electronic susceptibility). The development of a more comprehensive theory of exciton diffusion aids us by providing a building block for a total model of electronic and optoelectronic processes in organic thin films. Combined with a carrier transport model and a microcavity model, one can already imagine constructing a simulation of a working OLED. And as indicated above, applying the exciton diffusion model to dynamic spectral shifts allows us to obtain previously inaccessible information about the excitonic energy level dispersion. While much work remains in developing physical models of processes in organic optoelectronic devices, these results already represent a significant step forward.

4. Inorganic Quantum Dots in Organic Host Matrices for Efficient LEDs

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We recently demonstrated the first efficient hybrid organic/inorganic light emitting devices (LEDs), with saturated color emission, whose performance reaches that of the all-organic LED technology (Fig. 8) [Coe et al., Nature 420, 800 (2002)]. The hybrid LEDs are large-area, efficient light emitters consisting of luminescent inorganic nanocrystals (quantum dots) embedded in organic LED structures. They represent a completely new technology platform for development of the flat-panel displays and the flat-panel lighting. Their greatest benefit is in the ease of tuning their saturated emission color across the visible spectrum (by changing the size of the nanocrystal), and in their potentially longer operating lifetimes as compared to the all-organic LEDs.

(a) CdSe Quantum Dots

Nanocrystal quantum dots (QDs) are semiconductor nanoparticles that are chemically synthesized using simple benchtop techniques. Their sizes can be precisely controlled in a range from 1 to 10 nanometers. Electrons and holes are delocalized in QDs in states that are reminiscent of atomic wavefunctions. The energy of these states is strongly size-dependent: emission from CdSe QDs can be tuned across the entire visible spectrum by changing the size of
the nanocrystals. Nanocrystal QDs can be synthesized with narrow size distributions so that the bandwidth of the emission can be < 30 nm. The dots are grown in organic solvents. Their surface is covered with a ligand shell that can be easily exchanged, giving the dots the potential for broad chemical and electronic flexibility (Fig. 9). The combination of broad spectral tunability and chemical flexibility make nanocrystal QDs ideal chromophores for opto-electronic applications in organic/inorganic hybrid structures such as QD-LEDs.

QD’s have unique advantages over other classes of common (small molecule or inorganic phosphor) chromophores. The emission wavelength of a QD depends on its size, and can be controlled by varying the diameter of the particle. The excitation band is very broad, requiring only that the excitation light, or energy transferred excitations be above the band gap of the semiconductor; and it is independent of the emission, so that the same energy can be used to excite QDs with different emissions. A size series of QDs represents a family of fluorophores with different emissions that can be excited with the same light source. Furthermore, QDs are significantly less susceptible to photobleaching than dye molecules, making them ideal candidates as the chromophore in organic/inorganic hybrid structures. The energy level structure of QDs also differs substantially from most organic chromophores. The emission from QDs is from a lowest transition that is thought to be partly spin forbidden, leading to long (10-100 nsec) emission lifetimes at room temperature (and microseconds at cryogenic temperatures). The density of states above this emissive state becomes dense with both spin allowed (equivalent to singlet states of organics) and spin forbidden states (equivalent to the triplet states in organics). This high density of states should make QDs ideal in both Förster and Dexter transfer schemes of coupling excitons from organics to the QD.

(b) Performance of Layered Structures Containing QDs

The demonstration of quantum dot LEDs (QD-LEDs) is a direct result of a cross-disciplinary merge of the nanocrystal chemistry of Prof. Bawendi’s lab and Prof. Bulović’s lab expertise in the development of active organic optoelectronics. The devices incorporate CdSe nanocrystals in a molecular organic host via spin-on deposition of solvated materials. Spin-casting results in
the formation of an organic/nanocrystal bilayer film due to the alkyl/phenyl phase segregation, where by alkyl-coated nanocrystals form a densely packed single monolayer on top of the conjugated organic film (see Fig. 10 and device cross section in Fig. 8). The devices are completed by thermally evaporating thin organic films and a metal cathode on top of the organic/nanocrystal layers. These first devices operate with a quantum efficiency of 0.4%, they have a saturated color, and brightness of 1500 cd/m² at current density of 120 mA/cm², corresponding to luminescence efficiency of 1.25 cd/A, as compared to the best previous results for nanocrystal-LEDs of 600 cd/m² at 1 A/cm², corresponding to 0.06 cd/A.

The remarkable 20-fold improvement in the electroluminescence efficiency of our QD-LEDs is attributed to the optimized device structures and improved photoluminescence efficiency and chemical stability of nanocrystals. The technologically innovative step of generating the self-assembled nanocrystal monolayer through phase segregation, allows us to position the nanocrystals in the recombination zone of the multilayer active organic EL device. Their confinement to the device active region maximizes the efficiency of nanocrystal usage. Furthermore, the use of alkane/phenyl phase segregation to create spin-cast heterostructures provides a new general method for the fabrication of organic or hybrid devices.

The layer design of our QD-LEDs deliberately isolates the role of QDs in the luminescence processes from their participation in charge conduction by containing only a single monolayer of QDs within the structure. The organic layers transport charge carriers to the vicinity of the QD monolayer from which the luminescence originates. This is in contrast to previous studies that utilized QD multilayer films, on the order of 10-20 layers thick, which had the dual function of both transporting electrons and serving as the emissive layer. Poor conduction through these QD multilayers lead to an injected charge imbalance, and consequently luminescence efficiency of these early devices never exceeded 0.10 cd/A. Furthermore, a high density of pinhole defects in QD multilayers resulted in low device yields and inconsistent device performance. These technological shortcomings are avoided in our new structures that use only a single monolayer of QDs as the emissive layer. High device yields and consistent LED performance are standard for our devices.

Figure 10 - AFM images showing the surface morphology of various organic/nanocrystal films. (A) Phase image of a partial monolayer of nanocrystals on top of organic thin film after phase segregation during spin-coating. Nanocrystal surface coverage is 21%. (B) Height image of a close-up of (A) showing both an island of nanocrystals as well as individual nanocrystals (QDs) on a flat organic background. (C) Phase image of a complete, hexagonally packed monolayer of nanocrystals phase segregated from the underlying organics. Grain boundaries between ordered domains of nanocrystals are observable.
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(c) Charge Transport and Energy Transfer in Hybrid Structures

Generation of excitons on QDs in our LED structures occurs via two parallel processes: direct charge injection and exciton energy transfer from organic molecules. For direct charge injection, electrons may be trapped at the QDs due to the relative energy alignment of the lowest unoccupied molecular orbital (LUMO) levels of the electron transporting organic layer (Alq3) and the QDs (see the energy diagram in Fig. 11). For these charged QDs the barrier to hole injection from the hole transporting organic (TPD) is reduced. Upon acceptance of holes from TPD, excitons form on the QDs, and can subsequently recombine radiatively. Alternatively, excitons can be formed on organic molecules that are near grain boundaries, interstitial spaces, and voids in the single QD mono-layer. These excitons can then energy transfer to the lower energy QD sites, where they recombine radiatively.

In this program we are studying the relative importance of the direct charge injection in comparison to energy transfer processes for exciton generation on QDs. For example, by increasing the thickness of the shell structure of the dot we can preferentially inhibit the short range charge tunneling processes into the dot (Fig. 12). The longer range (up to 50 Å transfer radius) Förster energy transfer is still be able to take place. Similarly, we are able to evaluate relative importance of Auger processes in quenching the emission of the QDs.

The quantum dot structure strongly affects the QD-LED performance. For example, the semi-log plot of the spectral emission intensity as a function of drive current is shown in Fig. 13 for (a) ZnS coated CdSe nanodots and (b) uncoated CdSe nano-dots. Synthetic step for the coating process

**Figure 11** - Proposed energy level diagram of device in Fig. 8. Values for ionization energy (IE) of all materials except QDs are taken from photoemission spectroscopy measurements. Electron affinity levels (EA) were then calculated using optical absorption data. QD levels shown are from calculated values. 

**Figure 12** – Excited states of QDs can be generated by either direct charge injection or exciton transfer from an organic material. Determining the relative importance of the two processes will be essential in optimizing QD-LEDs.
organic materials can be of either singlet and triplet type, with their ratio corresponding to their characteristics. In other material systems, such mixed states facilitate capture of both singlet and triplet excitons on the lumophore. Rapid exciton recombination that follows can lead to nearly 100% internally quantum efficient LEDs. It remains an open question as to whether or not complete even at higher device currents, so its luminescence steadily increases with the number of defect states on uncoated dot devices is significantly larger and cannot be filled as the luminescence from the confined states of the dot can start as the current is increased.

We are also interested in tailoring exciton generation processes and exciton energy transfer under electrical pumping conditions in the hybrid thin films. Electrically generated excitons in organic materials can be of either singlet and triplet type, with their ratio corresponding to their spin multiplicities. In contrast, excited states of QDs mix the spin-triplet and spin-singlet exciton characteristics. In other material systems, such mixed states facilitate capture of both singlet and triplet excitons on the lumophore. Rapid exciton recombination that follows can lead to nearly 100% internally quantum efficient LEDs. It remains an open question as to whether or not analogously efficient exciton harvesting is possible in QD-LEDs.

The fundamental limits of QD-LED performance are different than those of all organic LEDs. The discrete energy structure of QDs gives rise to a narrow emission spectrum, which in our electroluminescent devices is as small as 32 nm at full-width-half-maximum (FWHM). In contrast, molecular organic LEDs have a typical FWHM of between 50 and 100 nm, although emission of
some polymers and phosphorescent molecules was shown to be as narrow as 26 nm FWHM but with long, low energy tails. The vibrational structure of structurally flexible organics typically generates broad single molecule emission spectra at room temperature. The same is not true of the rigid, covalently bonded inorganic QD, for which single QD spectroscopy shows that the fundamental FWHM linewidth at room temperature is 14 nm with a symmetrical, gaussian shape. It is the combination of spectral diffusion and size distribution of QDs in a specific sample that yields further line broadening. However, it is reasonable to expect that current techniques in QD preparation and processing could yield QD-LED line widths that are as narrow as 25 nm, a feat that has already been accomplished in solution. Such true color saturation would benefit applications where efficient production of narrowband light is desired. In particular, the creation of high luminous efficiency red and blue LEDs requires both high external quantum efficiency as well as narrowband emission, to prevent the bulk of emission from occurring in the infrared or ultraviolet, respectively, where our eyes have minimal response.

With the demonstrated improvement in the luminescent power efficiency of QD-LEDs, we still have not reached the fundamental limits of device performance in both quantum efficiency and color saturation. We expect that with our development of the new methods for growth of QD-films in vacuum, higher material purity will be obtained. Performance of such vacuum-grown QD-LEDs could match and potentially exceed that of conventional organic thin-film LEDs, resulting in durable, integratable, highly-efficient light sources of nano-scale thickness. By changing the diameter of the CdSe core from 22 to 65Å, the peak luminescence wavelength can be precisely tuned from $\lambda=470$ nm to $\lambda=640$ nm with a typical spectral full width at half of maximum of less than 35nm. Fig. 14 shows the electroluminescence spectra of a series of visible and infra-red emitting QD-LEDs. Such broadly tunable, saturated color emission of quantum dots is unmatched by any class of organic chromophores. Furthermore, environmental stability of covalently bonded inorganic nanocrystals suggests that device lifetimes of hybrid-LEDs should match or exceed that of all-organic LEDs.

(d) QD Monolayer Formation via Material Phase Segregation

QD-LEDs demonstrate that sheets of single QD monolayers, square centimeters in size, can be employed in electrically active devices. This minimizes QD material use to the active device
region. The material phase segregation that governs formation of the organic/QD spin-cast thin film bilayers is a general and, we expect, widely applicable fabrication process. The process is governed by the physical size and chemical character of the two solvated constituents; the organic molecules in our devices are small (~1 nm) and have aromatic character, while the QDs are large in comparison (>3 nm) and present a surface that consists of mostly alkane chains. In general, phase segregation is not limited to aromatic/aliphatic pairs, but governs the interaction between any pair of materials with disparate chemical functionality. To date, the phase segregation phenomenon has been observed in spin cast solutions of (CdSe)ZnS core-shell/TOPO capped QDs and PbSe/oleic acid capped QDs with both α-NPD and TPD in chloroform and chlorobenzene.

(e) Infra-Red QD-LEDs

We also demonstrate large area (mm$^2$ in size) infrared electroluminescent devices using colloidally grown PbSe quantum dots (QDs) in organic host materials (Fig. 14). By changing the QD size the electroluminescence is tuned from 1.33 µm-1.56 µm with a full width at half maximum of <160 nm (< 0.11 eV). This represents only a portion of the accessible QD tuning range, as the lowest energy optical absorption peak of our PbSe solutions can be tuned from 1.1 eV (corresponding to wavelength $\lambda = 1.1$ µm and 2.6 nm diameter QDs) to 0.56 eV ($\lambda = 2.2$ µm, 9.5 nm diameter). Such large area emitters in the near infrared have been identified as technologically useful for chemical spectroscopy and sensing, night vision applications, and could be incorporated into an on-chip optoelectronic integrated circuit.

PbSe is a convenient choice for inorganic semiconductor QDs for NIR applications ($\lambda > 1$ µm), as the colloidal synthesis is reproducible and yields highly monodisperse nanocrystals. In addition, the exciton Bohr radius is large (46 nm), leading to strong confinement of QD excitons throughout the synthetically accessible range of 2 nm to >10 nm (corresponding to absorption peaks $\lambda = 1.0$ µm (1.2 eV) to >2.4 µm (<0.5 eV), respectively). Figure 15(a) shows typical absorption and emission spectra for 5.0±0.5 nm diameter PbSe QDs, while Fig. 15(b) depicts an ordered layer of 4.0±0.5 nm diameter QDs imaged by high resolution transmission electron microscopy, showing their highly crystalline structure in the inset.

The NIR EL spectrum of QD-LEDs closely resembles the PL spectrum of the corresponding QD solution (see Fig. 15(a)). The tunability of QD-LED emission as a function of the QD diameter is shown in Fig. 14(a), with EL spectral peaks at 1.33, 1.42, 1.50, and 1.56 µm. The FWHM of all four devices is <160 nm (< 0.11 eV). The devices also have an emission peak at 530 nm (not shown) due to exciton recombination within the Alq$_3$ ETL (or 405 nm corresponding to TPD EL when BCP is used as the ETL). We note that the InGaAs photodiode array used to record all of these spectra has low detection efficiency for $\lambda > 1.6$ µm, modifying the apparent shape of the 1.56 µm emission peak.

The electrical characteristics of all the QD-LEDs of this study are similar, with a linear ($J$) versus voltage ($V$) dependence for $V<3$ V, and power law dependence, $J \propto V^0$, when light is emitted. This is consistent with the properties of an Alq$_3$/TPD device, though the operating voltage is a few volts higher, possibly due to QD charge trapping or interface dipole realignment. The PbSe QD-LED NIR external quantum efficiency is measured to be 0.001%, using a Silicon wafer to filter out visible emission from organic EL. The visible emission originates from Alq$_3$ and TPD and has an external EL quantum efficiency of 0.1-0.3%. These QD-LEDs demonstrate the feasibility of generating controllably tunable $\lambda >1.3$ µm EL in a large area device, and give us a starting point in the creation of higher efficiency devices in the spectral range of 1.2 µm < $\lambda$ < 2.2 µm.
5. Smart Active-Matrix Display Drivers For Organic Light Emitting Devices

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PROJECT STAFF
Eko Lisuwandi, Matthew Powell, Jennifer Yu, Professor Charles Sodini, Professor Vladimir Bulović

In this project we are developing pixilated active matrix “smart drivers” for displays consisting of organic light emitting devices (OLEDs). Organic LEDs are perhaps the most promising novel technology for development of efficient, pixilated, and brightly emissive, flat-panel displays. They naturally emit over large areas, and offer the advantage of growth on lightweight and rugged substrates such as metal foils and plastic, with no requirement for lattice-matching.

Organic LED devices, however, exhibit non-linear light output responses that complicate their implementation in an application requiring a fine control of the output light intensity. Specifically, the I-V characteristics of OLEDs depend on the cathode/anode type, device layer thickness, and operating temperature. The power efficiency of pixels in a display will drift over time due to operational degradation. The individual pixels in a display can then exhibit different aging, in accordance with their use. The brightness non-uniformities due to the differential aging will reduce the useful display lifetime.

Our smart active matrix circuitry compensates for the OLED non-uniformities by monitoring light output and adjusting the driving conditions according to the OLED performance. The adjusted output provides a defect-free picture. In the final design a Si $p$-$n$ detector integrated behind each pixel will give feedback to the driver circuits that will adjust the proper current level to derive a

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**Figure 15** - (a) Typical absorption (peak at 1.456 µm), photoluminescence (peak at 1.500 µm), and electroluminescence spectra (peak at 1.495 µm) of 5.0±0.5 nm diameter PbSe particles; (b) HRTEM Image of 4.0±0.5 nm diameter PbSe particles with two enlarged images (inset).
constant brightness output. Figure 16 shows a typical integrated structure in which our patented transparent OLED is used. In this design both OLED electrodes are capable of transmitting the emitted light, which is mostly observed on the top, but is also partially absorbed in the detector. The integrated circuit layout of the mini-display is shown in Fig. 17. Notice that six transistors control each pixel (Fig. 16). Also, each column shares one feedback circuitry. The integrator type of compensation is used for each feedback circuitry to ensure that the light output is matched to the reference input. The values of discrete components were so chosen to stabilize the feedback loop.

The present state of the art of OLED display technology uses a constant current to drive an oled pixel. In this driving scheme even the most efficient of OLEDs will drop their luminescent output to 90% of the 100 Cd/m² initial brightens in ~ 5000 hours. As a human eye can distinguish brightness change of less than 10% the 90% operating point indicates the longest useful lifetime of a pixel in a display.

**FIGURE 16** (left) An OLED pixel integrated with a “smart” Si active matrix driver. The Si photodetector monitors the intensity of the OLED pixel during the on state and provides feedback to the driving circuit to keep the light output intensity constant as the device efficiency changes with operation. (right) Pixel design in integrated circuit implementation
With the circuit developed in this project we compensate for the loss of brightness of an aging OLED pixel by increasing the operating (driving) voltage as a function of time. The lifetime of such compensated pixel is now primarily limited by the maximum voltage that the driving circuit can deliver. From the data of Fig. 18 we project that for the maximum driving circuit voltage of 10V the constant pixel brightness can be sustained for 30,000 hours by doubling the initial drive current, and for the maximum driving voltage of 12V the constant pixel brightness can be sustained for 50,000 hours by tripling the initial drive current. Such long projected lifetimes would enable the use of OLEDs in commercially viable displays.

**Figure 17** 128 x 16 pixel integrated circuit layout.

**Figure 18** Driving circuit voltage increase the proposed display driving scheme that compensates for the aging of an OLED.

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While optoelectronic devices based on organic small molecules have recently become commercially available, electronic devices such as field-effect transistors are less well developed. Typical organic field-effect transistors utilize polycrystalline thin films of evaporated organic materials such as pentacene as the semiconducting layer. The charge carrier mobility, and hence performance, in pentacene OFETs is primarily determined by the molecular ordering within the thin film, where the best OFET (with highest mobility) are made from single crystals of organic materials. As previous research shows that growing large single crystals of molecular organic materials directly on a substrate is a difficult task we developed a new approach to the formation of such crystals.

Our work to date has focused on tris-(8-hydroxyquinoline)aluminum (Alq₃), which is commonly used as the emitting layer in organic LEDs. The crystal structures of the Alq₃ α-phase and β-phase [from Brinkmann, et al., J. Am. Chem. Soc., 122, 5147 (2000)] is shown in Fig. 19. The widespread use of Alq₃ in OLEDs—including products on the market—results from the amorphous nature of as-deposited films and the high glass transition temperature \( T_g = 175 \, ^\circ C \) of Alq₃. These properties yield efficient and durable devices, yet several studies suggest that device failure can result from crystallization of the Alq₃ film during device operation. Indeed, it has been demonstrated that needle-like crystals form when Alq₃ thin films are thermally annealed at temperatures above \( T_g \). The formation of crystals upon exposure to organic solvent vapors has also been observed. This is likely due to the reduction of \( T_g \) by the permeation of solvent molecules into the film, which is a well-known effect—that of plasticization—in the field of polymers.

The crystallization of Alq₃ thin films is detrimental to OLED performance, but it suggests that generating large thin single crystals of organic materials in the plane of the substrate could be possible. A technique that could form such crystals and also direct them along pre-determined substrate directions would be especially useful for OFET use and also for forming single crystals of organic non-linear materials for optoelectronic applications.

We recently demonstrated that nano-patterned substrates can, indeed, be used to direct the flow of solvent-rich thin films of Alq₃ and thereby generate such oriented needle crystals in the plane of the substrate. The optical micrograph in Figures 20 shows a portions of a nano-patterned substrates with Alq₃ crystals that are predominantly aligned with the underlying nano-grooves.
To generate the crystal needles Alq₃ is deposited onto nano-patterned Si or SiO₂ substrates by thermal evaporation in vacuum (<10⁻⁶ Torr). The Alq₃ films are typically 10-20 nm thick and are deposited at rates of 1-3 Å/s (as measured by a quartz crystal thickness monitor) onto room temperature substrates. Prior to Alq₃ deposition, the nano-patterned substrates are cleaned via a sequence of steps involving either sonication in a solution/solvent or immersion in a boiling solvent. Following the final boiling 2-propanol step, the substrates are dried in a stream of nitrogen and further cleaned by UV-ozone treatment for 5 to 30 minutes. In the case of chemical surface modification, the substrates are placed in a vessel together with a beaker of chloroform, and the jar is sealed with a Teflon-lined cap. Exposure of the Alq₃ films to chloroform vapor for times ranging from a few hours to two days results in the formation of elongated Alq₃ crystals that are oriented parallel to the underlying nano-grating. The crystals are characterized by a variety of techniques, including optical microscopy, fluorescence microscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM).

The nano-patterned substrates are fabricated via interference lithography in the Nanostructures Laboratory (NSL) at MIT. Interference lithography is a maskless lithography in which photoresist is exposed by the optical standing wave generated by the interference of two coherent beams of light. Using the Lloyd’s Mirror setup in the NSL, we can generate periodic patterns over square centimeters with feature sizes ranging from 100 to 500 nm. The patterns are transferred to Si or SiO₂ via etching, resulting in surface relief gratings with depths up to 150 nm. After etching, the wafers are cleaned in 5:1:1 H₂O:H₂O₂:NH₄OH at 80 °C for ~10 minutes to remove any remaining anti-reflection coating, SiO₂ interlayer, or photoresist. After the wafers are dined into ~cm² pieces, these pieces are further cleaned and processed as described above. Figure 21 summarizes all of the fabrication steps, beginning with the nano-lithography, necessary to form oriented crystals of Alq₃. The final step depicted is the evaporation of metal electrodes to enable electrical characterization.
The Alq3 crystal needles formed in this process vary in size from experiment to experiment, with thicknesses and widths ranging from hundreds of nanometers to a few microns and lengths ranging from a few hundred microns up to one centimeter (the size of the substrate). The needle length can exceed the needle thickness and needle width by a factor of 1000 or more. Needle thicknesses exceed the initial Alq3 amorphous film thickness (typically 10-20 nm) by as much as 200 times. The total volume of a 10 nm thick film on a centimeter square substrate is $10^{-12}$ m$^3$. A needle with dimensions 1 µm by 1 µm by 1 cm has a volume of $10^{-14}$ m$^3$. Hence, 100 such needles could be formed from the initial thin film, and these needles would be separated by approximately 100 microns. Such a perfect sample has never been produced, but the sizes of the needles formed are consistent with this simple volume analysis. With respect to the nano-pattern dimensions, the needles can be as narrow as one nano-groove or as wide as tens of grooves, and the needle thickness can exceed the groove depth by a factor of 50 or more.

Preliminary electron diffraction data indicates that the needles are single crystals. Other characterization of the needles supports this as well. Figure 22 shows two SEM micrographs of different Alq3 needles. Micrograph A is a top view of one end of a several micron wide needle, and micrograph B shows the cross section of a smaller needle (the substrate was cleaved in the middle of the needle). Both micrographs show that the needles have distinct crystal facets and tend to be diamond-shaped in cross section. In addition, the fluorescence of the Alq3 needles is polarized, which is expected if the Alq3 is crystalline. The graph in Figure 23 plots normalized photoluminescence intensity as a function of polarizer angle, while the fluorescence micrographs shown below the plot correspond to the brightest and dimmest data points. The discrepancy between the 0° and 180° data points is a result of photobleaching of the needle during the course of the experiment.
The formation of the Alq₃ crystals, such as that in Fig. 24, is traced to the exposure of the evaporated thin films to the chloroform vapor. We observe that formed Alq₃ crystals are surrounded by what appear to be amorphous and flowing organic films. The flowing segments are confined by the substrate grooves and are characterized by menisci at both ends in the plane of the substrate and also in cross section. Several of these segments can be seen in the middle of the SEM micrograph of Figure 24 and also surrounding the AFM image inset in the same figure. The menisci of the amorphous segments lend evidence towards a fluid-like state of the Alq₃ thin film in the presence of chloroform. This fluidity can be understood in terms of a plasticization effect, whereby the $T_g$ of a glassy material (typically a polymer) is reduced by the presence of low molecular weight additives. The effect of plasticization on $T_g$ can be roughly estimated by the following semi-empirical equations:

$$T_g \approx \frac{T_{gp}}{1 + (X - 1)(1 - \Phi_p)}$$  \hspace{1cm} (6)

$$X \approx \frac{T_{gs}}{T_{gs}}$$  \hspace{1cm} (7)

$$T_{gs} \approx \frac{2}{3} T_{ms}$$  \hspace{1cm} (8)

These equations are based on free-volume considerations. $T_{gp}$ and $T_{gs}$ are the glass transition temperatures of the pure polymer and pure solvent, respectively, and $T_{ms}$ is the melting temperature of the solvent. Equation 8 is used to estimate $T_{gs}$ based on $T_{ms}$ because $T_{gs}$ has been measured for only a few solvents. $\Phi_p$ is the volume fraction of the polymer. Using $T_{gp}=175 \degree C$ for Alq₃ and $T_{ms}=-63 \degree C$ for chloroform in the above equations, the predicted effect of chloroform permeation on the $T_g$ of Alq₃ is plotted in Figure 25. As can be seen from the plot, the $T_g$ of Alq₃ is significantly reduced by the presence of the chloroform, dropping to 40 °C when the film is 20% chloroform and falling below room temperature when the films is 25% chloroform by volume. Hence, it is reasonable to suggest that the Alq₃ is able to incorporate enough chloroform to become fluid at room temperature.

It is curious, however, that the amorphous segments, which are the signature of fluid Alq₃, are only observed adjacent to Alq₃ crystals, suggesting that there is a higher concentration of chloroform in the vicinity of the crystals. This could result from a rapid exclusion of chloroform in liquid form as Alq₃ molecules are incorporated into the growing crystal. Another possible explanation is based on the apparent affinity between chloroform and Alq₃, and assumes that the surface of each crystal is coated with a thin layer of fluid, chloroform-rich Alq₃. The large surface...
area of the crystal relative to that of the crystallite clusters would therefore result in a higher concentration of chloroform near the crystal. Indeed, a correlation exists between the size of the crystal and the width of the surrounding region that has experienced flow of chloroform-rich Alq$_3$. The crystal in Figure 24 is ~300 nm thick and ~600 nm wide, and nano-films are observed in a strip that extends ~2.5 microns to the right of the crystal (similarly on the other side of the crystal). For comparison, for a smaller needle that is ~130 nm thick and ~400 nm wide the width of the strip containing nano-films is only one to two grating periods (300-600 nm). Therefore, as a crystal grows, an increasing concentration of chloroform at the crystal surface (due to increasing surface area) causes the surrounding region of flowing Alq$_3$ to widen.

In some cases extended nano-films (exceeding several microns in length) are present in the grooves immediately adjacent to an Alq$_3$ crystal. This implies that the crystal was in a very active stage of growth—having a plentiful supply of fluid Alq$_3$ close by—when the vapor treatment was terminated. In fact, the crystals likely grow up out of the Alq$_3$ that flows in the nano-grooves as evidenced by the nano-films that are protruding out from underneath the crystal tip in the AFM micrograph of Figure 24.

Although the individual amorphous segments and crystallite clusters are too small to be resolved by optical microscopy, the regions of the substrate with clusters can be distinguished from amorphous flow regions in optical micrographs. For example, the darker, speckled region of the substrate on the left in Figure 20 is a region with crystallite clusters. The rest of the substrate surrounding the crystals has experienced flow of chloroform-rich Alq$_3$.

What is astonishing about the flow regions of Figure 20 is the extent to which they extend beyond the ends of the crystals in the direction parallel to the underlying nano-grooves. This sheds light on the critical role played by the substrate nano-pattern in the formation of the Alq$_3$ crystals. What has been emphasized up to this point is that the incorporation of enough (~25% by volume) chloroform can cause Alq$_3$ to become fluid at room temperature, but this seems to happen only near crystals. As was mentioned before, this suggests that there is extra chloroform associated with the crystals, possibly due to a thin fluid layer of chloroform-rich Alq$_3$ on the crystal surface. It is also likely that chloroform is excluded as Alq$_3$ molecules are incorporated into a crystal. Since the atmosphere in the vapor treatment jar is already saturated with chloroform vapor, it is reasonable to assume that the excluded chloroform will remain on the substrate as a liquid. The chloroform can then flow on the substrate, but due to capillary effects it prefers to flow down the nano-grooves of the patterned substrate. As it flows down the grooves, it encounters and permeates Alq$_3$, reducing its $T_g$ and allowing it to flow down the grooves as well. It is in this way that the nano-grooves aid the transport of Alq$_3$ to the forming crystals, and this also explains the elongation of the flow regions parallel to the nano-grooves.

A transport ratio can also be calculated from substrates with much more extensive Alq$_3$ flow and crystal formation, such as the substrate shown in Figure 20. The distance traveled by Alq$_3$ perpendicular to the nano-grooves can be ascertained by the gap between the (speckled) crystallite cluster region on the left side of the micrograph and the leftmost crystal. This gap is ~200 microns wide. In contrast, the typical distance parallel to the nano-grooves separating the cross needles from the oriented needles ~2 mm, indicating that the Alq$_3$ was able to flow at least...
1 mm down the nano-grooves to reach a crystal. The calculated transport ratio in this case is only 1:5, but this is likely a conservative estimate since the flow is so widespread and may even have been limited by the size of the substrate. The large size of the cross crystals can be understood in terms of the large number of nano-grooves intersected by these crystals relative to the number of grooves that directly feed the oriented crystals.

While the proposed mechanism for crystal growth via capillary flow of chloroform-rich Alq3 down substrate nano-grooves in the vicinity of pre-existing crystals seems well-supported, the question remains as to how the crystals are formed initially. It is possible that crystallites present in the as-deposited films seed the growth, or that crystallite clusters (formed during exposure to chloroform vapor) of a certain size can act as a seed. Whatever the case may be, it seems that the requirement for crystal formation is a large enough concentration of chloroform to initiate significant flow of Alq3. Although the exact mechanism for the nucleation of the crystals is not fully understood at this time, the ease of formation of crystals of such large dimensions in the plane of a substrate is a technological breakthrough in the field of organic electronics.
7. Efficient Electrically Pumped Polariton Emission in a J-Aggregate OLED at Room Temperature

The goal of this project is to develop ultrafast active optoelectronic devices based on the unique physical properties of J-aggregates, and their interaction with light. The essential physics of J-aggregates underpinning this project is that the excited state of a J-aggregate is a delocalized Frenkel exciton of high oscillator strength, which enables it to couple strongly to the optical field inside a resonant cavity according to the principles of semiconductor cavity QED. We are using J-aggregates because J-aggregates exhibit the strong coupling regime of Cavity QED, even at room temperature, even in an all-metal cavity, and because their lifetime is extremely short. The ultimate goal is to realize the vision of the electrically pumped polariton laser and polariton optical switches at room temperature, using J-aggregates as our material platform. The first milestone is to develop a room temperature polariton LED.

J-aggregates are ordered arrangements of highly polar cyanine dye molecules (Fig. 26) in which the transition dipole moments of the individual molecules add to form a giant dipole oscillator. When dye molecules form a J-aggregate, a new optical transition develops called a J-band.

Relative to the monomer, this optical transition of the J-aggregate is red-shifted, minimally stokes shifted, and considerably narrower in energy, and the lifetime of this transition is also much faster. J-aggregates are therefore described anatomically and functionally. Anatomically, they are crystalline phase of the dye monomers, although not necessarily the lowest energy crystalline form, and functionally, they are quantum systems in which the excitons delocalize over several molecular sub-units of the aggregate, which gives rise to narrow absorption and emission spectra.

**Figure 26** Absorption spectrum, TEM Micrograph, and electron diffraction pattern of a J-aggregate dispersed in polyvinyl alcohol.
J-aggregates received their moniker in recognition of Edwin Jelly, who while working for Kodak in the 1930's discovered that the cyanine dye, pseudoisocyanine (PIC), at high concentrations became resonantly fluorescent [E. E. Jelly, Nature 138, 1009 (1936)]. This was surprising at the time because PIC at lower concentrations is not fluorescent. It is also contrary to the generally accepted rule of concentration quenching, which states that the higher the concentration is, the lower the quantum yield of fluorescence. From that point forward, J-Aggregates have been studied to understand the physics of excitons, their optical properties, and their crystallographic properties, and this understanding has been fruitfully applied to the science of sensitizing photographic active silver halide crystals to narrow bands of light in regions of the visible spectrum that the silver halides would otherwise not absorb.

The genesis for our research effort has come from the recent demonstration of room temperature polariton photoluminescence from J-aggregate Frenkel excitons coupled to the cavity photon mode [Lidzey et al., Nature 395, 53 (1999)]. Because of the high oscillator strength of the Frenkel exciton, Rabi Splitting exceeding 100meV was realized, an order of magnitude larger than the splitting achieved in inorganics even at ultralow temperature. This work laid the foundation for us to start imagining how we could access the strong coupling regime using J-aggregates in active optoelectronic devices.

To make these devices, J-aggregates must be formed in a thin film process. J-aggregates can be formed in solution and in solid state. In solution, particularly in water, the dye molecules form aggregates at high concentration and in an alkaline environment, while in solid state, J-aggregates form more readily when in contact with a polymer template. In our present studies we use polyvinyl alcohol (PVA) polymer layer. We have chosen JC-1 as the J-aggregate molecule (Fig. 27). JC-1 readily forms J-aggregates even at ultra low concentrations (10^-6 M) and has been well studied in the photographic industry, as a membrane potential sensitive dye, and for its rich exciton dynamics.
To investigate its applicability for strong coupling devices, we sought to demonstrate Rabi Splitting and measure the polariton dispersion curve for JC-1. We prepared a series of samples, consisting of silver mirror layer (1200Å), J-Aggregate/PVA matrix and a thin silver film on top (300Å). The thickness of the J-Aggregate layer was varied so as to tune the bare cavity mode through the J-Aggregate exciton resonance. From reflectivity measurements taken from 7° - 70°, we conclude that JC-1 does in fact exhibit a strong coupling to the photon mode as illustrated by the anti-crossing in the dispersion curves. From this data and other dispersion curves we calculate a Rabi Splitting of >95 meV.

Our current objective is to develop an efficient J-Aggregate OLED that we can then fabricate within an optical cavity to demonstrate electrically pumped polariton emission. Presently, we have successfully demonstrated EL from JC-1 in an exploratory structure consisting of a mixed film of PVA doped with JC-1 (Fig. 29).

**Figure 28** Angle dependent reflectivity and dispersion curve of a silver mirror metal microcavity containing J-aggregates of JC-1 in polyvinyl alcohol.

**Figure 29** Electroluminescence spectrum of a JC-1 OLED.
Publications, Presentations, and Thesis

PUBLICATIONS


PRESENTATIONS


Theses


