I. Lab of Organic Optoelectronics - Research Themes

Our research is focused on deciphering the physical properties that govern behavior of nanostructured materials and applying the findings to development of practical, active technologies. With focus on organic and inorganic-nanocrystal 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.
II. Integrated Materials Growth System

SPONSOR
Defense University Research Instrumentation Program (DURIP) - Air Force Office of Scientific Research
NSF Center for Materials Science and Engineering SEED Grant

PROJECT STAFF
Seth Coe, Conor Madigan, Debbie Mascaro, Sung Hoon Kang, Jonathan Tischler, Professor Vladimir Bulović

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.

In the past three years we developed 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.
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. 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.

III. Exciton Physics in Organic Optoelectronics

SPONSOR
National Science Foundation CAREER Award
National Defense Science and Engineering Graduate Fellowship – Department of Defense

PROJECT STAFF
Conor Madigan, Professor Vladimir Bulović

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. Photodetectors with collection efficiencies as high as 75%, and solar cells with power conversion efficiencies as high as 4% 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-(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 solvation 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 ($\mu\sim6$D 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.

![Figure 2](image_url)  
*Figure 2*  
(a) Evolution of peak PL spectra of DCM2 in films of Alq$_3$, TPD and $\alpha$-NPD.; (b) chemical structures of molecules used in this work.”.
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 

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

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**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.
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 solvation 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.


\[ E \downarrow = C - A\Lambda \]

where

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

and \( A \) and \( C \) are constants. In Fig. 5(a) 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(b) 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 solid state solvation 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 solid state solvation process can strongly determine the dispersion and position of molecular energy levels in organic solids. Additionally, solvation could be used as a new method for engineering of thin film energy

**FIGURE 5**  (a) Fits of OLM theory to observed evolution of DCM2 peak PL energy; (b) OLM fit to DCM2 PL data in solution.
structures, both for excitonic levels (as studied in this work) and for charge 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.

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 Förster energy transfer between DCM2 molecules.

![Figure 6](image_url)

**Figure 6** (a) Normalized DCM2 PL spectra, following ultrafast excitation; (b) Evolution of peak PL of DCM2 doped in films of Alq₃. Grey lines denote simulation results optimized for each data set.
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

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

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,

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

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 (i.e. that there exists some dispersion in exciton energies in our film), we obtain a straightforward explanation of the observed time-resolved spectral shifts: diffusion by Förster energy transfer progressively drives the excitons in the film towards the lowest energy sites.

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 $g_{ex}(E)$ distribution. We have assumed that $g_{ex}(E)$ has a Gaussian form, with a full-width-half-max (FWHM) of $w_{DOS}$. Once the system of sites has been created, each site is populated with an exciton, yielding an exciton population, $n_{ex}(E,t)$, such that,

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

where $t=0$ refers to the time immediately following the arrival of the PL excitation pulse. Then for each time step of length $\tau_{step}$ 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 $w_{DOS}$ and $R_F$. The values for $w_{DOS}$ decrease from $\sim0.260$ eV for 0.5% DCM2 doping to $\sim0.205$ 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 $w_{DOS}$ for polaron levels in amorphous organic materials, where the polaron $w_{DOS} \sim 0.1 eV$. 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 non-destructive 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 $R_F \sim 12 \text{ Å}$ and $\omega_{DOS} \sim 0.075 \text{ eV}$, 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 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 solid state solvation 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.
IV. Inorganic Quantum Dots in Organic Host Matrices for Efficient LEDs

SPONSOR
National Science Foundation MRSEC Program
MIT Institute for Soldier Nanotechnologies

PROJECT STAFF
Seth Coe, Jonny Steckel, Wing Woo, Professor Moungi Bawendi, Professor Vladimir Bulović

The luminescence of inorganic core-shell semiconductor nanocrystal quantum dots (QDs) can be tuned through the visible and near infrared spectral range by changing the size and material of the QDs while preserving a narrowband, gaussian emission spectrum and photoluminescence efficiency of 25%. Organic capping groups, surrounding the QD lumophores, facilitate processing in organic solvents and their incorporation into organic thin film light emitting device (LED) structures. Recent reports have shown that hybrid organic/inorganic QD-LEDs can be fabricated with high brightness and small spectral FWHM, utilizing a phase segregation process which self-assembles QDs onto an organic thin film surface [Coe et al., Nature 420, 800 (2002)]. The phase segregation process can be generally applied to the fabrication of QD-LEDs containing a wide range of particle sizes and materials. QD-LEDs emitting from 540nm to 1550nm have been demonstrated to date, with external quantum efficiencies as high as 2%.

The integration of QDs into organic LEDs has the potential to enhance the performance of thin film light emitters. Organic light emitting devices (OLEDs) have been identified as a dominant new technology poised to realize the next generation of flat panel displays. OLED performance is exemplified by wide viewing angles, high color contrast, and low power consumption as compared to emissive liquid crystal displays. Indeed, internal quantum efficiencies can approach 100% when organic phosphorescent molecules are used as the emitting materials. A significant challenge of today’s OLED technology remains the identification and synthesis of organic lumophores compatible with electrically pumped device structures. Only a handful of efficient and long-lived organic phosphors have been incorporated into laboratory devices, while the ongoing research is aimed at the chemical design of new molecules, especially in the blue part of the spectrum[8]. As such, inorganic quantum dots have generated interest in the OLED community as efficient alternative lumophores, whose saturated color emission can be tuned across the

![Figure 8](image-url)  
*Figure 8* - Hybrid organic/inorganic light emitting device contain inorganic QDs. (left) QD-LED cross section. Luminescence spectra of QDs and QD-LEDs compared to the electroluminescence spectrum of efficient phosphorescent organic LEDs. The spectrally narrow luminescence of QDs results in saturated color emission.
visible spectrum. Additionally QD-LEDs provide an accessible platform for investigating physical processes in hybrid organic/inorganic structures.

(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.

In CdSe nanocrystals, quantum confinement increases the exciton energy from a bulk bandgap of 1.7 eV (corresponding to wavelength, \( \lambda = 730 \) nm and the red edge of the visible spectrum) to any value up to 2.75eV (corresponding to \( \lambda = 450 \) nm and blue luminescence). The CdSe cores can be chemically synthesized with a surrounding shell of a wider band-gap semiconductor that passivates the surface states of the nanocrystal (see Fig. 9), with a consequent increase in the QD photoluminescence quantum efficiency (\( \eta_{PL} \)). For example, \( \eta_{PL} \) of CdSe QDs can increase from below 20% for bare QDs in solution to 50% for QDs overcoated with several monolayers of ZnS. To achieve a narrow QD luminescence spectrum, the size distribution of CdSe(ZnS) QDs in a solution sample can be narrowed through selective precipitation to have a standard deviation of 5-8% in diameter, which translates to a spectral full width at half of maximum (FWHM) in solution of <30nm.

In the case of infrared QD-LEDs, colloidally grown PbSe quantum dots (QDs) are used. By changing the PbSe core size the electroluminescence is tuned from \( \lambda = 1.33 \) to 1.56 \( \mu \)m 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 $\lambda = 1.1 \, \mu m$ and 2.6 nm diameter QDs) to 0.56 eV ($\lambda = 2.2 \, \mu m$, 9.5 nm diameter). Our light emitting device fabrication combines the thin film processing techniques available to organic materials with the tunable optical properties of PbSe QDs. Formation of double heterojunction devices is enabled by material phase segregation during the spin-coating step. Such large area emitters in the near infrared have been identified as technologically useful for chemical spectroscopy and sensing, and could be incorporated into on-chip optoelectronic integrated circuits. Solution processing of inorganic nanocrystals is facilitated by the organic capping groups that dress the surface of the QDs. The capping layer may be tailored to control solubility, external chemistry, and particle spacing in a QD thin film. All of these independent controls make for a versatile material set for the creation of lumophores that could be imbedded within organic LEDs.

(b) Fabrication

Device fabrication uses QDs processed air-free and dispersed in anhydrous chloroform in a nitrogen environment (<10 ppm $O_2$ and $H_2O$). The QD solution is added to a chloroform solution of a hole transporting organic semiconductor, N,N’-diphenyl-N,N’-bis(3-methylphenyl)-(1,1’-biphenyl)-4,4’-diamine (TPD), and is spin cast onto a clean ITO coated glass substrate. The QDs phase segregate into a monolayer (or sub-monolayer) on the surface of the organic film (Fig. 10). The substrate is then transported into a thermal evaporator without exposure to air where the electron transporting layers (ETL), tris-(8 hydroxyquinoline)aluminum ($Alq_3$) and/or bathocuproine (BCP), are deposited at $<5x10^{-6}$ torr. Finally the metal cathode (50 nm thick Mg:Ag, 50:1 by weight, 50 nm Ag cap) is thermally evaporated through a shadow mask to define 1mm diameter devices. The assembled device structure is shown in the inset of Fig. 4(a). High device yields and consistent LED performance are standard for devices fabricated in this manner.

Figure 10- Steps in the phase segregation process responsible for the formation of organic/QD bilayer. The AFM micrograph on the right shows an incomplete monolayer of PbSe QDs on top of a smooth TPD film.
In device in Fig. 8, holes are injected from the indium tin oxide (ITO) contact into the TPD host matrix and are transported towards the single QD monolayer. Similarly, electrons are injected from the Mg:Ag cathode into the Alq3 and are transported to the QDs. Exciton generation on QDs 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 TPD, Alq3 and the QDs. For these charged QDs the barrier to hole injection from the 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 monolayer. These excitons can then energy transfer to the lower energy QD sites, where they recombine radiatively.

(c) Phase segregation as a fabrication method

Fabrication of organic/QD bilayers by phase segregation during spin-casting is in essence a very simple process, and is depicted in Fig. 10. It relies upon the solvation of both the organically capped inorganic QD and the organic material to be used as an underlayer in a compatible solvent system. A known quantity of the organic material is weighed out dry, solvated in the chosen solvent, and stirred until completely dissolved. Some quantity of QD solution is then added to this, to yield both the desired organic to QD ratio, as well as overall concentration of solution. For example, in the bilayers used in refs ORGELE and Nature, the final solution contained 10mg/mL of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD), and a 1:10 dilution of our prepared QD stock solutions. For consistency, all of our CdSe QD stock solutions are formulated to have the same absorbance at their band edge absorption peak. The final concentration of particles in the spin-casting solution is determined by accurately measuring out a volume of this QD stock solution into the mixed TPD/Chloroform solution.

This mixed solution is then spin-cast onto a substrate. The entire substrate surface must be wetted by the solution before spin casting begins. The process is observed for a wide range of spin-casting parameters such as speed, acceleration, spinning time, and atmosphere (gas, temperature, solvent content). However, it is noted that for the best control and reproducibility in our bilayers, we have found it useful to maximize acceleration (10,000 rpm/s), to use a single spin speed (3000 rpm), and to use a suitably long spinning time (60s) to insure complete evaporation of the solvent. All property tuning could then be performed by changing the solution composition, and run to run reproducibility was achieved. During solvent drying, the QDs phase segregate from the organic underlayer material, and rise towards the surface of the solution. When drying is complete, the organic material has formed a homogenous underlayer, which is coated in a layer of QDs. The exact structure and composition of this layer is completely determined by the composition of the spin-casting solution.

Figure 11 – 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.
Some statement of generality is necessary to assess the utility of such a fabrication technique. While it is of course impossible for any thin film fabrication method to be universally applicable, we have demonstrated that this process is not dependant on any one component of the system. We have observed phase segregation and assembly of QD monolayers while varying the substrate, solvent, organic underlayer materials, QD core material, QD organic capping group, QD diameter, QD size aspect ratio, and the spin-casting parameters and environment. The only known constraint on the process is that there is a solvent or solvent system which will dissolve both QDs and organics for the concentrations which are necessary.

Another important aspect of this fabrication process is the formation of self-assembled, hexagonally ordered, large area arrays of nanometer sized objects on a two dimensional surface. The ability to control the extent to which this ordering occurs, and to push the limits of such ordering to larger area grains, could have technologically interesting applications. To date, we have learned to control the self-assembly process through QD sample size distribution, QD aspect ratio (eccentricity), and solvent drying time (vapor pressure) (Fig. 12).

The degree of hexagonal packing that is observed on a QD monolayer is directly related to the QD sample diameter monodispersity. Figure 12(a) shows a bilayer formed from a QD sample with 5% size monodispersity. While it is clear that the QDs have assembled into the hexagonal close packed monolayer structure, the grains remain small, containing at most a few hundred QDs per grain. It is noted that this size distribution is already adequate for forming high coverage monolayers, that are sufficient for the fabrication of monochromatic emitting QD-LEDs.

Through recent advances in QD synthetic techniques, size distributions of even smaller than 5% are now achievable. This in turn allows us to probe the ultimate limits of the effect that size distribution can have on this self-assembly process. Figure 12(b) shows an AFM image of a bilayer created with such a sample, in this case PbSe QDs on a TPD surface. The high degree of spatial periodicity of the sample allows extremely clear imaging of each individual QD in the hexagonally close packed array. In addition, one can see that this array is now ‘large area’, with average grain size exceeding 1µm². There are few examples of such a simple technique for the creation of <10nm period 2D arrays that are perfect over 10,000’s of repeat units.

Figure 12 - QD monolayer packing is influenced by QD size distribution (with standard deviation indicated) and QD aspect ratio.
26-15

Chapter 26. Organic and Nanostructured Materials in Optoelectronic Applications

(d) Impact and Applications

Incorporation of nanoscale active elements into OLEDs enables the creation of a new set of devices, the properties of which can be tailored at the quantum mechanical level. However, attaining such levels of control necessitates a separation of the creation of the nanoscale elements (QDS, J-aggregates) and the macro-device fabrication. In the case of QDs, it is the colloidal chemical growth process that enables the nanometer scale control over the material properties. The phase segregation process then controls the precise positioning of these nano-elements with a large area device. It is the combination of these two distinct nano-fabrication processes that enable creation and control of the QD-LED properties. Importantly, once we learn to manipulate these two material sets to make hybrid structures, other possible applications open up as well. Use of the nanometer period pattern that results from phase segregation as a patterning template is a foreseeable application that is now on the horizon.

In addition, the properties of known devices are improved through the use of this nanotechnology. The color gamut that is accessible to QD-LEDs far exceeds that of conventional OLEDs, due to the narrow FWHM of emission of the QDs themselves. In addition, power savings are also likely due to the narrow QD emission profile. Comparing a 2% external quantum efficient red QD-LED to a 20% red phosphorescent LED, it is clear that more electrons per photon are wasted in the QD-LED. However, for display applications, it is the perceived quantum efficiency [cd/A] that is most important, as the human eye response is all that is of consequence for commercial display applications. In Adachi et al., a 7% EQE device has a power efficiency of 4.5 lm/W, at an operating voltage of ~6V, or 27 lm/A. A QD-LED that is 2% EQE has a recorded power efficiency of 1 lm/W, for an operating voltage of 13V, or 13 lm/A. Thus, assuming that device operating voltages and external quantum efficiencies will converge for the two technology platforms, a QD-LED device has the potential to be 50% more power efficient than the equivalent PhOLED, based upon the spectral purity of the QD emission profile.

QD-LEDs are a versatile test-bed for studying the electrical and optical behavior of QDs in the solid state. Active devices allow us to probe the electrical properties of single monolayers of QD solids. Furthermore, there is evidence that such devices could satisfy the technological requirements of flat panel displays and imaging applications which require the narrowband emission characteristic of QDs, as well as the efficient creation of visible light in the blue and red regions of the spectrum. In a span of eight years QD-LED efficiency has improved over two orders of magnitude reaching the luminous and quantum efficiencies of fluorescent OLEDs. This

![CdSe(ZnS)/TOPO and PbSe/Oleic Acid](image)

**Figure 13** - Electroluminescence spectra from the visible to the near infrared of (left) CdSe, CdS, and (right) PbSe based QD-LEDs.
rapid advance was facilitated by the expanding knowledge of the OLED community whose developments are largely applicable to the QD-LED structures. Indeed, we identify QD-LEDs as a kin technology to OLEDs, potentially complementing their performance when highly saturated color emission is desirable. It is conceivable that with further development, QD-LEDs could reach the efficiencies of phosphorescent OLEDs through incorporation of QDs in organic triplet generating hosts. The combination of inorganic luminescent properties, with the advantages of organic processing techniques, suggest the possibility of creating robust, large area emitters with physical properties that are tailored on the nanoscale. The present pursuit of QD-LEDs has the potential for near term scientific and technological impact, as the fabrication and synthetic processes are perfected.

V. Smart Active-Matrix Display Drivers For Organic Light Emitting Devices

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PROJECT STAFF
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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.

![OLED Diagram](image)

**Figure 14** (top right) 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. (bottom left) Pixel design in integrated circuit implementation. (bottom right) Result of the external feedback.
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 (Fig. 14). 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 constant brightness output. Figure 14 shows a typical integrated structure in which a 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. Notice that six transistors control each pixel (Fig. 14). 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 integrated circuit layout of the mini-display is shown in Fig. 15 together with an SEM on a pixel cross-section.

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 brightness in ~5000 hours. As a human eye can distinguish brightness change of less than 10% the 90% operating point overestimates the useful lifetime of a pixel in a display.

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. 16 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.

From the data of Fig. 16 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.

VI. Nanopattern-Assisted Growth of Organic Materials for Device Applications

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PROJECT STAFF
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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. 17. 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 (\(T_g=175 °C\)) 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 Alq\textsubscript{3} 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 Alq\textsubscript{3} and thereby generate such oriented needle crystals in the plane of the substrate. The optical micrograph in Figures 18 shows a portion of nano-patterned substrates with Alq\textsubscript{3} crystals that are predominantly aligned with the underlying nano-grooves.

To generate the crystal needles Alq\textsubscript{3} is deposited onto nano-patterned Si or SiO\textsubscript{2} substrates by thermal evaporation in vacuum (<10\textsuperscript{-6} Torr). The Alq\textsubscript{3} 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 Alq\textsubscript{3} 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 crucible containing n-octadecyltrichlorosilane (OTS). The vessel is evacuated to a pressure of <1 Torr and heated to 120 °C for ~2 hours. Substrates treated in this manner are hydrophobic.
Following the evaporation of Alq₃, the substrates are placed in a glass jar 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, SiOₓ interlayer, or photoresist. After the wafers are diced into ~cm² pieces, these pieces are further cleaned and processed as described above.

Figure 19 summarizes all of the fabrication steps, beginning with the nano-lithography, necessary to form oriented crystals of Alq₃.

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 thicknesss 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 20 shows two SEM micrographs of different Alq$_3$ 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 Alq$_3$ needles is polarized, which is expected if the Alq$_3$ is crystalline. The graph in Figure 21 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 measurements.

![Figure 21](image)

**Figure 21** (left) Polarized fluorescence micrographs (UV excitation at 449 nm) for two orthogonal polarizer angles. (right) The graph plots the normalized photoluminescence intensity as a function of polarizer angle.

The formation of the Alq$_3$ crystals, such as that in Fig. 22, is traced to the exposure of the evaporated thin films to the chloroform vapor. We observe that formed Alq$_3$ crystals are surrounded by what appear to be amorphous an 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 22 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 Alq$_3$ 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. $T_g$ of Alq$_3$ 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 Alq$_3$ is able to incorporate enough chloroform to become fluid at room temperature.
Chapter 26. Organic and Nanostructured Materials in Optoelectronic Applications

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 Alq₃. The crystal in Figure 22 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 Alq₃ to widen.

In some cases extended nano-films (exceeding several microns in length) are present in the grooves immediately adjacent to an Alq₃ crystal. This implies that the crystal was in a very active stage of growth—having a plentiful supply of fluid Alq₃ close by—when the vapor treatment was terminated. In fact, the crystals likely grow up out of the Alq₃ 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 22.

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 18 is a region with crystallite clusters. The rest of the substrate surrounding the crystals has experienced flow of chloroform-rich Alq₃.

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 Alq₃ crystals. What has been emphasized up to this point is that the incorporation of enough (~25% by volume) chloroform can cause Alq₃ 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 Alq₃ on the crystal surface. It is also likely that chloroform is excluded as Alq₃ 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

![Figure 22](left) SEM and (right) AFM micrograph of a Alq₃ crystal and vicinity.
nano-grooves of the patterned substrate. As it flows down the grooves, it encounters and permeates Alq3, 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 Alq3 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 Alq3 flow and crystal formation, such as the substrate shown in Figure 18. The distance traveled by Alq3 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 Alq3 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.

### VII. Efficient Electrically Pumped Polariton Emission in a J-Aggregate OLED at Room Temperature

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DARPA Optocenter

**PROJECT STAFF**

Jonathan Tischler, Scott Bradley, Professor Vladimir Bulović

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**

J-aggregates are ordered arrangements of highly polar cyanine dye molecules (Fig. 23) in which the transition dipole moments of the individual molecules add to form a giant dipole oscillator and a new optical transition called a J-band. Relative to the monomer, the J-band
absorption/fluorescence is red-shifted, weakly Stokes shifted, and considerably narrower in energy (50 meV at room temperature). The lifetime of the J-band transition is also much faster (~ps) which can lead to an efficient fluorescence process (see Fig 23). 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. We have recently demonstrated that the exceptionally large optical cross section (\(\alpha \sim 10^6 \text{ cm}^{-1}\)) and narrow absorption spectra (e.g. FWHM = 20 nm) of ordered J-Aggregate monolayers results in the strong coupling between the J-Aggregate excitons and the optical modes of the microcavity. This drastically enhances light matter interaction, giving rise to the observed exciton-polariton emission. Within this proposal we will utilize exciton-polaritons to demonstrate ultra-fast optical switches and nanometer scale intense optical sources, such as threshold-less exciton-polariton lasers.

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.

We previously used all of the above approaches to make J-Aggregate light emitting devices, but we prefer 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. 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 possessing much greater translational symmetry than in amorphous systems, 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.

**J-Aggregate Linear Optical Properties:** Figure 23 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^{-5} 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 6 x 10^5 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 κ = 5.3. The absorption coefficient of TDBC-PDAC bi-layers significantly increases in more alkaline environments (pH > 7).

High reflectivity and polarization dependence of TDBC are demonstrated in Figure 24. The two photographs are 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.
(b) J-Aggregate LEDs

We developed a light emitting device (LED) using J-Aggregates of cyanine dyes as the emitter material, and then we incorporated a similar device structure in a resonant optical microcavity to demonstrate polariton emission. Figure 25 illustrates the two structures that are differentiated only by 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. The electroluminescence (EL) spectra, of J-aggregate LED (Fig. 26) show 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 ~10nm thick J-Aggregate layer.

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. 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. 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
Figure 27  Linear optical properties of J-Aggregate polaritons: angularly resolved reflectivity, photoluminescence, and polariton dispersion curves. Rabi-splitting of 200 meV based on fit to reflectivity data.

(c) Polariton Electroluminescence

Figure 28 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 600 nm.

Figure 29 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.

Next, polariton properties were established for dip-coated TDBC coupled to a metal mirror microcavity (Fig. 27) 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 Fig. 13 was generated and fit using the model described above, 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 28  Normal direction electroluminescence of five polariton OLEDs tuned through the J-Aggregate resonance by changing the poly-TPD layer thickness.
Fitting the data to a dispersion curve 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 the Rabi-splitting is proportional to the square root of the absorbance.

![Graph showing EL intensity vs. wavelength and energy](image)

**Figure 29** Angularly resolved electroluminescence of J-Aggregate polariton OLED.
Chapter 26. Organic and Nanostructured Materials in Optoelectronic Applications

VIII. Integrated Organic Field Effect Transistors

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Dr. Ioannis Kymissis, Professor Akintunde I. Akinwande, Professor Vladimir Bulović

Organic field effect transistors (OFETs) have been considered for a number of applications including display backplanes, force sensing, radiofrequency identification, and logic. OFETs are processed at temperatures below 100ºC, which allows fabrication on virtually any substrate. A number of strategies have been used in the past to create integrated arrays of organic transistors including photolithography, stamping, and shadow masking. Even the best of the processes, however, fabricate devices that operate in depletion mode, which necessitates the use of level shifting stages to form self-sustaining combinatorial logic.

We are developing a process for fabricating organic field effect transistors which is fully photolithographic, provides two layers of metal with arbitrary via placement, and reliably delivers enhancement mode p-type OFETs (i.e. with a negative threshold voltage, \(V_T\)). We can repeatably fabricate integrated OFETs with \(V_T \approx 6\) V and field effect mobility of \(\mu = 0.05\text{cm}^2(\text{Vs})^{-1}\) using pentacene as the semiconductor active layer and parylene-C as the gate dielectric and encapsulation layer. This process is unique because it uses parylene in a lithographic process flow. Parylene-C gate dielectric films are easily processed, facilitate ordered semiconductor crystal growth (which is necessary for a good transistor performance), and do not dope the semiconductor film allowing formation of enhancement mode devices. The process flow used is summarized in Figure 30.

The substrate used is a 100 mm glass wafer made with Schott D-263 unpolished borosilicate float glass. The glass is initially cleaned using a piranha bath to remove particles from the scribing process and any residual organic residue. Four lithographic steps are then used to define the structure. First, the gate layer is defined using an image reversal lift-off step. A 3 nm chrome adhesion layer is used, followed by 30 nm of platinum.

Lift-off is performed in acetone, and a second acetone rinse followed by a water rinse and a spin/rinse/dry is used to remove any additional photoresist residue.

FIGURE 30 Overview of process flow for organic field effect transistor process. A transistor and gate/source drain layer via is shown.
Section 26. Organic and Nanostructured Materials in Optoelectronic Applications

Next, the substrates are coated with 170-210 nm of parylene-C. Parylene-C is a well explored dielectric for organic transistors. It is a fully cross-linked polymer which is deposited at room temperature and is conformal. 1 µm thick photoresist is spun onto parylene, exposed and developed, and the parylene is etched using an oxygen reactive ion etching system.

The substrate is then coated with 30 nm of gold, which is lithographically patterned to define the source/drain layer. The semiconductor, pentacene, is then deposited. The substrate is unheated in the evaporation system. 30 nm of pentacene is deposited, at a rate of 1.5 nm/min.

If patterning of the semiconductor is desired, a passivating layer of parylene (1 µm) is then deposited on top of the semiconductor, photolithographically defined, and etched in an oxygen plasma. A final parylene coating passivates the transistor structure (Fig. 30).

Figure 31: Micrographs of several structures formed using this process. (a) shows individual transistors (b) shows an array of transistors and pixel electrodes (c) shows a ring oscillator circuit and (d) shows part of a logic gate. The transistor in (d) has a channel length of 25 microns, and the via connects the gate and source/drain levels.

Figure 32: Typical transistor characteristics for 25x1000 µm transistors. The transistor shown here has a linear region mobility of 0.16 cm² (V s)⁻¹ and saturation region mobility of 0.14 cm² (V s)⁻¹.
Both resistors and capacitors can easily be formed in this process. Resistors can be formed using long runs of interconnect metal of either layer. Capacitors are formed across the source/drain and gate metal layers through the gate dielectric layer. The current leakage through parylene-C is negligible (in the fA range), even for large capacitors (300µm x 300µm) at 20 V. The gate capacitance is typically about 2.4 x 10⁻⁸ F/cm². Figure 31 shows several micrographs of the patterned transistor and circuit structures.

Current-voltage (I-V) curves for a 25x1000µm transistor are shown in Fig. 32. Applying the standard transistor model we extrapolate the field effect mobility of 0.16 cm²/(V s)⁻¹ in the linear region and 0.14 cm²/(V s)⁻¹ in the saturation region. The gate capacitance for the used dielectric thickness is 2.7x10⁻⁸ F/cm², and the threshold voltage is approximately 8V.

Table 1 summarizes the performance results for ten devices of each of several sizes fabricated on a single process run (different from the run of Fig. 32). The field effect mobility remains constant down to channel lengths of approximately 8µm. At shorter channel lengths contact resistance becomes a larger fraction of the channel resistance and decreases the apparent mobility extracted from the I-V parameters.

### IX. Quantum Dot Photodetectors

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MIT Institute for Soldier Nanotechnologies

**PROJECT STAFF**
Alexi Arango, David Oertel, Professor Moungi Bawendi, Professor Vladimir Bulović

To date, organic based photodetectors have achieved fast response times (2ns) and high external quantum efficiencies (70%) in the visible part of the spectrum. Organic photovoltaics are approaching 4% conversion efficiencies. Many ionorganic photodetectors operate at near infrared and middle infrared wavelengths, a wavelength range important for applications like infrared imaging and automotive sensors. In this work, we are attempting to extend the sensitivity of organic based photodetectors into the infrared by imbedding inorganic quantum dot sensitizers in large area, room temperature deposited organic structures. Such a device may help lower costs, cooling requirements and enable tuning of the peak detection wavelength.

In high performance photodetectors, low dark current is an essential figure of merit determining the limits of detectivity at long wavelengths where thermal generation at room temperature can

<table>
<thead>
<tr>
<th>Size (width x length) [µm]</th>
<th>Mobility [cm²/(V s)⁻¹]</th>
<th>Threshold Voltage [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 x 25</td>
<td>0.048 ± 0.015</td>
<td>6.4 ± 0.54</td>
</tr>
<tr>
<td>1000 x 20</td>
<td>0.053 ± 0.013</td>
<td>6.3 ± 0.46</td>
</tr>
<tr>
<td>1000 x 15</td>
<td>0.036 ± 0.009</td>
<td>6.1 ± 0.47</td>
</tr>
<tr>
<td>1000 x 8</td>
<td>0.053 ± 0.013</td>
<td>6.3 ± 0.44</td>
</tr>
</tbody>
</table>

*Table 1: Performance summary for wafer 040122, showing average mobility and threshold voltage, and the standard deviation of these parameters measured across 10 transistors. Both mobility and threshold voltage were determined by curve-fitting the I-V curves in the linear region of operation.*
overwhelm detected signal intensities. Conventional infrared detectors often require cooling systems to reduce dark currents. In a good device, dark current is limited by the thermal generation rate $G$ in the absorber species. The metric for signal to noise performance is the detectivity $D^*$. For an optimized photodetector,

$$D^* = 0.31 \frac{\lambda}{hc} \sqrt{\frac{\alpha}{G}}$$

where $\lambda$ is the wavelength, $h$ is Planck’s constant, $c$ is the velocity of light and $\alpha$ is the absorption coefficient. The figure of merit is then ($\omega/G$), meaning that high quantum efficiency should be combined with a thin device. To raise operating temperatures, one must increase this ratio. To this end, we employ a film of quantum dots, whose confined states are known to have increased oscillator strengths and therefore higher absorption relative to the bulk material. In conjunction with the quantum dot film, we use a wide band gap organic/inorganic diode structure designed to combine low dark current with good rectification.

Two device structures are presented here: a transparent pn diode structure and the same structure with a cadmium selenide (CdSe) quantum dot layer inserted at the interface between the p and n layers (Fig. 35). Since wide band gap n-type organic semiconductors with high carrier mobilities are rare, we use an n-type titanium dioxide (TiO$_2$) layer (Fig. 33). The p-type contact is the hole transporting organic small molecule N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) and is deposited by thermal evaporation and is approximately 100 nm thick.

The CdSe nanocrystals utilized here, with their high structural quality and associated organic capping groups, have recently been utilized in a photoresponsive layer across laterally spaced bar electrodes [Bawendi group, to be published]. In the first stage of this project, we have demonstrated visible sensitization by CdSe of an otherwise transparent photodiode. The 40 nm thick CdSe multiplayer is spun directly on the TiO$_2$. 

**Figure 33** TiO$_2$ thin film deposition process via sol-gel and AFM image of the surface of the resulting film.
TiO$_2$ has been used for some time as an electron-accepting layer in dye-sensitized photovoltaics. For our purposes, we are interested in a thin, smooth, dense and transparent n-type film. TiO$_2$, deposited from a sol gel precursor solution, satisfies these requirements. By volume, 4 parts of the TiO$_2$ precursor Titanium ethoxide, C$_8$H$_{20}$O$_4$Ti (Gelest), is added to a stirring solution of 40 parts ethyl alcohol, which contains 1 part water and two drops of hydrochloric acid. The TiO$_2$ precursor reacts with water to form the reactive monomer (RO)$_3$TiOH that in turn reacts with other monomers to form a sol. Heating the solution for 45 min. at 60°C aids the gelation (cross-linking) process, during which the viscosity gradually increases. The TiO$_2$ precursor is spin coated at 1000 rpm onto a patterned ITO glass substrate that is masked with scotch tape. After deposition, the tape is removed and the sample is heated at 100°C for 30 min. to allow further cross-linking and dehydration of the TiO$_2$ matrix. Annealing under vacuum at 450°C for 30 min. allows the growth of crystalline regions of the anatase phase (densification). The resulting films are transparent, smooth and approximately 100 nm thick, with surface features less than 8 nm.

To evaluate the dark current and wavelength dependent response of quantum dot photodetectors, we have built a current-voltage apparatus and a photocurrent spectrum setup (Fig. 34). Photocurrent action spectra are measured with a xenon white light source, monochrometer, chopper and lock-in amplifier as shown in (a). The measurement setup for current voltage characteristic under white light illumination at varying intensities is depicted in (b). We employ a patterned electrode structure (c) and an associated probe fixture (d).

**FIGURE 34** Schematic of our testing apparatus. Photocurrent action spectra are measured with a xenon white light source, monochrometer, chopper and lock-in amplifier as shown in (a). The measurement setup for current voltage characteristic under white light illumination at varying intensities is depicted in (b). We employ a patterned electrode structure (c) and an associated probe fixture (d).
Energy level alignment of our CdSe photodetector device (Fig. 35a) is designed to allow photogenerated charge to exit the device when illuminated while blocking charge injection from the electrodes under reverse bias and in the dark. In reverse bias, hole injection from the ITO electrode into TiO₂ is suppressed because of the large potential step at the interface. Likewise, electron injection from the gold electrode into TPD is limited due to the potential barrier at that interface. Therefore, dark current in reverse bias should be largely due to generated carriers in CdSe. Note that in this structure electron transfer from CdSe to TiO₂ is not energetically favorable limiting the efficiency.

In Fig. 35c, we plot the current-voltage characteristics of the CdSe device and control in white light (intensity on the order of 1mW/cm²) and in dark. The dark current traces the instrument noise floor in reverse bias for both devices. In forward bias, the current magnitude in dark for the CdSe device is lower than that of the control, most likely due to the added serial resistance of the CdSe layer. In light, the CdSe device displays a significant photocurrent, although the reverse bias photocurrent does not saturate. The minimal photo-response of the control device is due to absorption in the UV. In Fig. 35d, we plot the photocurrent action spectra of a CdSe device (red) and control (blue) at zero bias. The absorption profile of the CdSe quantum dots is shown in the inset.

In summary, we have demonstrated a reliable quantum dot based platform with which we can explore operating principles of quantum dot photodetectors.
X. Memory Effect from Charge Trapping in Layered Organic Structures

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Structural disorder in amorphous organic thin films can result in the presence of localized electronic states which can trap and store charge in an equilibrium. Because of a relatively low density of intrinsic free charge carriers in organic solids, the presence of the trapped charges can dominate the current voltage (I-V) characteristics of organic devices. It is evident that developing models of charge trapping and charge conduction and by devising means for controlling the energy of the trap distribution we can optimize performance of organic electronic devices.

We investigated the charge trapping process by demonstrating a device (Fig. 36) that in forward bias performs a function of an organic LED, while in the reverse bias stores charge, that can be interpreted as a memory event. The charge is stored in a charge trapping layer that consists of either an organic or metallic dopant in an organic host structure.

Figure 36(a) shows the I-V characteristics of the doped organic light emitting device. We tested the device by starting the voltage sweep at different voltages. As we applied different negative biases, we used 'read' sweeps (i.e. without a negative bias phase) to ensure that the device is in the same initial state. By comparing the I-V characteristics we found that current spikes are only observed when the device is first subjected to a negative bias of at least -3V. For the control device, which has no doping layer but the same total thickness of the TPD layer, didn’t show the current spike after a negative bias. From series of experiments using different charging time, we observed that this turn-on voltage could be lowered to a certain degree if we apply a negative bias for longer time. If we fix the integration time of the semiconductor parameter analyzer and increase the magnitude of negative bias, the current observed increases. However, if we apply too much negative voltage, the current is reduced. We can therefore conclude that for the same integration time, the magnitude of applied reverse bias determines the amount of injected/stored
charge in the charge trapping layers, and hence influences the current response in the forward bias sweep. If no negative bias is applied, the doped device compared with a TPD-AIq3 OLED of same thickness, showed about 10% higher quantum efficiency due to a more balanced hole and electron transport, but the turn-on voltage was higher than a typical OLED and the current was two orders of magnitude smaller at the same voltage.

A schematic model shown in Fig. 37 illustrates the proposed operating mechanism of the device. When the device is reverse biased, electrons from the bottom electrode charge the doped layer. If the magnitude of this reverse bias is too small, no current spike is observed as we apply a forward bias because we do not have enough tunneling voltage to charge the doped layer. If we then apply a forward bias, holes from the bottom electrode annihilate trapped DCM2 electrons giving a current spike. The remainder of the injected holes combine with injected electrons from the top electrode and form excitons on AIq3. By changing the magnitude of the reverse bias, we can control the amount of stored charge in the organic layers and therefore the current output. If too great a voltage is applied, the net amount of stored charge is reduced due to hole injection. This leads to a smaller current response for reverse biases of –5 V and higher. We can set the device “on” by reverse bias, and we test whether the device stores charge or not from the I-V characteristic and/or light emission.

In order to verify that charges are stored in the trap layer, we measured photoluminescence (PL) of the DCM trap layer while applying voltage pulses. The PL measurement was performed by exciting the device by a 532 nm Nd:YAG laser while applying a square wave using an Agilent 33250A arbitrary waveform generator and reading the photocurrent from a Tektronix TDS 3000B oscilloscope through Stanford Research SR830 Lock-in amplifiers connected to a photodetector as shown in Fig. 38(a). When the device is charged, the PL intensity from DCM2 decreased due to the quenching of PL in trap layer as shown in Figure 38(b). This is strong evidence that the charges are stored in the trap layer. Assuming only charged molecules are quenched and there is no influence on the neighboring molecules, we calculated that the charge density of the trap layer from the PL intensity change (the density of the DCM2 is 1.1 g/cm³, and the molecular weight of DCM2 and TPD is 355.2 g/mol and 516.3 g/mol, respectively). The charge density is on the order of 10¹⁸ cm⁻³, or approximately 10% of the trap sites.

Based on the above model, we made a similar structure with a metal trap layer by depositing 5 nm of Ag instead of DCM2 doped TPD layer. Figure 36(b) shows the characteristics of metal trap layer devices. When a thin Ag film is deposited on top of the organic layer, it forms metal clusters. When organic traps were replaced with this very thin metal layer, the device still showed the memory behavior, but the peak spectrum shifted due to a microcavity effect.
Figure 39(a) shows the time resolved result I-V characteristic of the organic trap layer device. The write-read-erase-read cycles were recorded with an oscilloscope using an arbitrary waveform generator and a Keithley 428 current amplifier. The difference between the read and re-read currents demonstrates the "on" and "off" state of the bit stored in the doped organic light emitting device. We measured the retention time of the device by delaying discharge. After applying negative bias, we waited for varying period of time and performed additional I-V sweep to see if the device still shows a current spike. Using this method, the retention time exceeds two hours.

Finally, in order to see the effect of different doping concentrations, we fabricated samples with 10% and 20% DCM2 doped TPD trap layer, and compared the device characteristics with the 5% DCM2 doped device as shown in Figure 4 (b). If we increase the doping concentration, we need more voltage to extract trapped charges from the device. This phenomenon is consistent with our model the more trap states are in the doping layer, the harder they are to annihilate. The retention time of the device also increases as we increase the doping concentration. The more charges we have in the trapped layer, the longer it takes for carriers to escape from the doped layer. In such manner, the OLED display pixel arrays can be used as memory arrays that, for example, store information when the display is dormant.
XI. Publications, Presentations, and Thesis

PUBLICATIONS


PRESENTATIONS


XII. Publications, Presentations, and Thesis

PUBLICATIONS


PRESENTATIONS


Chapter 26. Organic and Nanostructured Materials in Optoelectronic Applications


THESIS


PATENTS AND PATENT APPLICATIONS


