INTRODUCTION

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.
Chapter 29. Organic and Nanostructured Materials in Optoelectronic Applications

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

Sponsors
Sponsorship: National Science Foundation, MARCO Materials Structures and Devices Center

Project Staff
D. Mascaro, R. Tabone, V. Bulovic

The challenge of generating crystals of organic materials has been pursued by many research groups who aim to develop materials sets for active electronic and optoelectronic devices, including field-effect transistors, photodetectors and optical modulators. We developed a method for in-plane growth of millimeter-scale crystalline organic needles from initially amorphous thin films of the molecular organic semiconductor tris(8 hydroxyquinoline)aluminum (Alq3). The needles form when the vacuum-deposited amorphous films are exposed to chloroform vapor at room temperature and pressure, and can be as large as several microns thick, several microns wide, and one centimeter long (limited in length by the substrate dimensions). As such, the Alq3 needles are more than 100 times longer than any previously reported organic crystals formed in the plane of the substrate. Moreover, the Alq3 needles are spatially separated from one another and oriented with their long axes parallel to lithographically pre-defined periodic submicron grooves in the substrate surface.

The distinct facets (Fig. 1(b)) and diamond-shaped cross sections (Fig. 1(c)) of the fabricated Alq3 needles are indicative of crystallinity. The optical smoothness of the needle facets is evidenced in fluorescence micrographs that show waveguiding of the Alq3 fluorescence with outcoupling occurring at the needle edges and defects (Fig. 1(a)). Polarized fluorescence measurements show a change in luminescence intensity with polarization angle, with a maximum at ~15 degrees from the long axis of the needle (Fig. 2(a)). Fluorescence spectra of the crystal needles, obtained via confocal microscopy, peak at energy of 2.36 eV (peak wavelength of 525 nm) in agreement with the previously reported spectrum of polycrystalline α-Alq3 (Fig. 2(b)).

![Figure 1: Alq3 crystalline needles formed by exposure of amorphous Alq3 thin films to chloroform vapor at room temperature. (a) Optical micrograph (left) and fluorescence micrograph (right, 365 nm excitation wavelength) of an Alq3 needle that extends ~35 µm beyond the substrate edge. (b) SEM micrograph (top view) showing the distinct facets of an Alq3 needle. (c) SEM micrograph showing the typical diamond-shaped cross section of an Alq3 needle.](image)

![Figure 2: Fluorescence of Alq3 needles. (a) Plot of the normalized photoluminescence (PL) intensity (365 nm excitation wavelength) as a function of polarizer angle, where 0 degrees corresponds to the polarizer aligned with the long axis of the needle. The decrease in fluorescence intensity from 0 to 180 degrees is due to gradual photooxidation of the Alq3 during the measurement as indicated by the straight dashed line. The sinusoidal response of PL with polarizer angle and the composite of the PL response and the gradual oxidation are plotted in dashed and solid lines, respectively. (b) Fluorescence spectra (365 nm excitation wavelength) of an as-deposited Alq3 thin film and an Alq3 crystal needle, obtained via confocal microscopy. The solution fluorescence spectrum (408 nm excitation wavelength) of Alq3 in chloroform is also plotted.](image)
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2. Quantum Dot Light-Emitting Devices

Sponsors
Sponsorship: Presidential Early Career Award for Scientists and Engineers, MIT Institute for Soldier Nanotechnologies, MIT National Science Foundation MRSEC, MIT Deshpande Center

Project Staff
S. Coe-Sullivan, P. Anikeeva, J. Steckel, M. Bawendi, and V. Bulović

Hybrid organic/inorganic light-emitting devices (QD-LEDs) combine stability and color clarity of semiconductor nanoparticles and low-cost processing procedures of organic materials with the aim to generate a flat-panel-display technology. Semiconductor quantum dots (QDs) are nanocrystals that are of smaller diameter than the Bohr exciton in a bulk crystal of the same material. By reducing the size of the nanocrystal, quantum confinement effects lead to an increase in the band-edge, exciton energy. Changing QD sizes and materials can produce luminescence wavelength from UV, through visible spectrum, and near-IR.

A typical QD-LED consists of a transparent inorganic anode deposited on a glass substrate followed by organic electron (ETL) and hole transport layers (HTL) with a QD monolayer in between. A metal cathode is deposited on top of the structure as Figs. 1 and 2 (left) show. We are presently investigating physical mechanisms that govern light generation in QD-LEDs. Time-resolved optical methods allow us to study charge and exciton transport in organic films and at organic/QD interfaces, as in Fig. 2 (right). Physical insights lead to an optimized design and improved performance of QD-LEDs.

Fig. 1: Current-Voltage (IV) characteristics of QD-LEDs with monolayers of red, green, and blue QDs as the recombination layers. Top left corner: structure of the device.

Fig. 2: On the left: level diagram of a typical QD-LED. On the right: time-resolved photoluminescence measurement of the structure on the top right corner.
3. Layer-by-Layer, J-aggregate Thin Films with an Absorption Constant of $10^6$ cm$^{-1}$ in Optoelectronic Applications

**Sponsors**
DARPA Optocenter, NDSEG, MIT NSF MRSEC

**Project Staff**
J.R. Tischler, M.S. Bradley, and V. Bulović

Thin films of J-aggregate cyanine dyes deposited by layer-by-layer (LBL) assembly exhibit exciton-polariton dynamics when incorporated in an optical microcavity. Such LBL, J-aggregate thin films can be precisely deposited in a specific location in an optical microcavity, enabling the development of previously unachievable optoelectronic devices, as for example, the recently demonstrated resonant-cavity exciton-polariton organic light-emitting device [1].

To gain insight into the physical properties of these films, we investigate the optical and morphological properties of 5,6-dichloro-2-[3-[5,6-dichloro-1-ethyl-3-(3-sulfopropyl)-2(3H)-benzimidazolene]-1-propenyl]-1-ethyl-3-(3-sulfopropyl) benzimidazolium hydroxide, inner salt, sodium salt (TDBC) J-aggregates, alternately adsorbed with poly-(diallyldimethylammonium chloride) (PDAC) on glass substrates. Atomic force microscopy (AFM) shows that the first few sequential immersions in cationic and anionic solutions (SICAS) form layered structures, which give way to Stransky-Krastanov-type growth in subsequent SICAS. We combine thickness measurements from AFM and spectroscopic data to determine the optical constants of the films and find that at the peak absorption wavelength of 596 nm, the films possess an absorption coefficient of $\alpha = 1.05 \pm 0.1 \times 10^6$ cm$^{-1}$, among the highest ever measured for a neat thin film. The optical constants were calculated by fitting spectroscopic data for films in the layered growth regime to a model based on propagation and matching matrices (Fig. 1).

The presented method is a general approach to generating thin films with very large absorption constant, an enabling step in the fabrication of novel devices that utilize strong coupling of light and matter, such as light emitting devices (shown in Fig. 2) and polariton lasers.

Reference:
4. Excitons in Organic Optoelectronic Devices

Sponsors
NSF Career Grant, NDSEG

Project Staff
C. Madigan, V. Bulović

Sponsorship: Most of the published physical studies on disordered molecular organic materials investigate charge conduction mechanisms, specifically the microscopic and macroscopic behavior of polarons. While consensus remains elusive, in part because of the continuing uncertainty over the role of interfaces as compared to the bulk in determining device performance, there has been considerable progress. By comparison, very few studies have been published on exciton dynamics in organic optoelectronic devices (where excitons are the dominant optical excitations in amorphous organic materials). Exciton modeling studies are often qualitative, reduced to parameters such as the exciton diffusion length and exciton lifetime, leaving significant questions unanswered about the detailed microscopic processes and how to develop models capable of yielding quantitative device properties on the macro-scale.

In this project, we aim to develop detailed exciton dynamics models to enable and implement device-level simulations. Three considerations motivate this work. First, as has long been recognized in the inorganic semiconductor industry, designing a device on paper and simulating it using a computer is far more efficient than designing, fabricating and testing a device. Second, good models of both polarons and excitons are necessary to accurately simulate optoelectronic device behavior, but at this stage, comparatively little attention has been given to excitons. Finally, since few studies simultaneously consider polaron and exciton simulations to treat the behavior of these devices, it is significant to determine the specific ways to efficiently and accurately combine existing models of polarons with improved models of excitons in a combined simulation.

To date we demonstrated that exciton energy levels are altered through interaction with neighboring molecules by the mechanism of solid-state solvation. We continue to investigate other electric-field-induced, excitonic energy-level shifts. We have also demonstrated that ultra-fast, time-resolved, fluorescence spectroscopy can be used to probe exciton diffusion in our materials, as previously demonstrated for polymer films. We have developed a complete Monte Carlo simulation of exciton diffusion in disordered molecular solids by treating spatial and energetic disorder and diffusion by either Dexter or Forster energy transfer. This simulation models homogenous, continuous solids as well as doped and structured materials, as required for treating devices. Existing analytical models for treating the general excitation diffusion in disordered media have been evaluated and found to be generally inapplicable to this project. Current work develops additional experimental methods for monitoring exciton diffusion, namely site-selective fluorescence and fluorescence-polarization anisotropy, and modifies the exciton Monte Carlo simulation to incorporate polarons.

Figure 1: Series of DCM2:AlQ3 fluorescing films showing DCM2 excitonic energy shifts (i.e., different colors) due to intermolecular interactions. The leftmost film shows AlQ3 PL, and the remaining films show DCM2 PL for different DCM2 dopings.

Figure 2: Example of ultra-fast, time-resolved, fluorescence data. The vertical axis denotes wavelength; the horizontal axis, time. In this example, DCM2 is the photo-luminescing material, doped into an AlQ3 host.
5. Quantum Dot Photodetectors

Sponsors
MIT, Institute for Soldier Nanotechnologies

Project Staff
A. C. Arango, D. C. Oertel, M. G. Bawendi, and V. Bulovic

Solution-processable colloidal quantum-dot systems exhibit many of the special optical and electronic properties associated with epitaxially grown, quantum confined systems. Their tunable band gap and higher absorption relative to the bulk make quantum dots particularly attractive as photo-generation materials. At the same time, colloidal quantum dots offer much greater material system flexibility than epitaxial quantum dots because deposition on any substrate is possible.

Efficient photoconductivity has previously been observed in lateral device structures consisting of single thin quantum dot films [1]. Response time of this device was limited by charge transport, suggesting that a vertical photodetector structure could both decrease the response time and support higher currents due to the larger contact cross-sections. That motivates our present project, in which we study the photo-response of quantum dot thin films in a vertical sandwich structure. We engineer a multilayer thin film device with a colloidal quantum dot film inserted into the middle of a wide bandgap structure forming a double heterojunction device that functions as a rectified diode (Figure 1). The rectifying behavior ensures suppression of the shunt current in the reverse-biased structure that can arise from the mechanical imperfections in the quantum dot film. Additionally, the photo-generative quantum dot film can be positioned in the peak of the optical field, increasing the device efficacy. Changing the size and material properties of the quantum dots tunes the response spectrum of the device across visible and near infra-red spectra.

With current-voltage measurements (not shown), we have achieved low dark current and have identified high internal resistance of the cadmium selenide (CdSe) quantum-dot film as a major limitation to the device performance. The quantum efficiency (number of generated electrons per incident photon) is shown in Figure 2. At present we focus on improving the device performance and optimizing the photodetection response in the 1um-to-2um wavelength region by using lead selenide quantum-dot films.

![Figure 1: Alignment of energy bands in a conceptual tri-layered p-i-n-like quantum dot hetero-junction photo-detector. The contact layers (indicated in green and blue) serve to transport charge out of the device, block charge from entering the device, and transmit light to the absorbing quantum dot layer. Under applied bias, the proposed device exhibits rectification because charge is blocked at both electrodes under reverse bias yet allowed to enter under forward bias.](image1)

![Figure 2: The photo-detector device structure (a) consists of a solution-deposited, colloidal CdSe, quantum-dot layer sandwiched between n-type TiO2 and a p-type organic semiconductor TPD. At zero bias and under illumination (b), an excited electron can exit the device via the TiO2 layer, while the corresponding hole can exit via the TPD. The resulting quantum efficiency spectrum at zero bias (c) tracks the shape of the CdSe absorption. An important metric for photo-detectors (especially infrared detectors) is the detectivity D* (d), a measure of a device sensitivity to background noise.](image2)
References:

6. Patterned Quantum Dot Monolayers in QD-LEDs

**Sponsors**
Presidential Early Career Award for Scientists and Engineers, MIT Institute for Soldier Nanotechnologies, MIT National Science Foundation MRSEC, and MIT Deshpande Center

**Project Staff**
S. Coe-Sullivan, L. Kim, J. Steckel, R. Tabone, M.G. Bawendi, and V. Bulović

Hybrid organic/inorganic quantum dot light-emitting devices (QD-LEDs) contain luminescent nanocrystal quantum dots (QDs) imbedded in an organic thin film structure. The QDs are nanometer-size particles of inorganic semiconductors that exhibit efficient luminescence; their emission colors can be tuned by changing the size of the nanocrystals. For example, the luminescence of QDs of CdSe is tuned from blue to red by changing the QD diameter from 2 nm to 12 nm. By further changing the material system, saturated color emission can be tuned from the UV, through the visible, and into the IR. The inorganic emissive component provides potential for a long operating lifetime of QD-LEDs. The room temperature fabrication method ensures compatibility of the QD-LED technology with the established all-organic LEDs (OLEDs).

The optimized QD-LED device structure contains a single monolayer of QDs embedded within the layered, organic thin-film structure. The technology is enabled by the self-assembly of the QDs as a densely packed monolayer on top of a conjugated organic film. The QD film is positioned with nanometer precision in the recombination zone of the device. [1] Most recently, by using a microcontact printing (stamping) process, we demonstrated that neat layers of QDs can be placed independently of the organic layers and in-plane patterned, allowing for the pixel formation necessary for display technology (Fig. 1). To date, we demonstrated QD-LED color emission across the visible part of the spectrum and from 1.3 um to 1.6 um in the near infra-red (Fig. 2).
References:


**Figure 1:** (A) A 25-um-wide, lined, red QD-LED, patterned by microcontact printing (stamping). (B) Stamped red QD-LED, stamped green QD-LED, and blue organic LED. (C) Stamped, patterned, green/red QD-LED. (D) Stamped blue QD-LED.

**Figure 2:** Electroluminescence spectra of QD-LEDs in visible and infra-red.
7. Chemo-sensing Optoelectronic Structures

Sponsors
MIT Institute for Soldier Nanotechnologies, MIT National Science Foundation MRSEC

Project Staff
J. Ho, A. Arango, T. Swager, and V. Bulović

We are developing solid-state, organic device structures capable of efficiently converting analyte detection into an electrical signal. The main advantage to using organic materials is that they are synthetically flexible and can be tailored to respond in a distinct manner to specific analytes. Our proposed device structure is a heterostructure consisting of an optically active, chemo-sensing layer and a charge transport layer. Physically separating the sensing and transport functions in chemical sensors has two significant advantages. First, we can optimize both the sensing and the transport layers independently to maximize chemical sensitivity. Second, we can tailor materials in the sensing layer to detect specific materials, allowing us to reuse the same device structure for a variety of applications.

An integral part of this research is to demonstrate efficient, organic photo-transistors and to physically model their behavior. By building upon models developed for organic transistors we can begin to explain the behavior or organic photo-transistors. In the photo-transistor structure, light acts as a gate pseudo-electrode by changing the conductivity in the transistor channel to modulate current. Once the photo-transistor model has been developed and the material set has been optimized, the next challenge will be to introduce chemically sensitive materials into the structure of the device to modulate the photo-detection ability of the sensing layer. In this way we can detect the presence of any analyte. By transducing the sensing response of an analyte into the transport of charge, we can observe a bulk change in the system with only a small number of binding events, thereby increasing the sensitivity of the devices.

![Figure 1](image1.png)
**Figure 1:** A) Schematic structure of a phototransistor. B) Schematic of phototransistor operation. C) Microscope pictures of photoresistors under 40X magnification.

![Figure 2](image2.png)
**Figure 2:** Linear I-V plots of A) 50 Å CuPc, B) 50 Å TiOPc, C) 50 Å CuPc, and 50 Å TiOPc. The dotted red lines represent I-V curves in the absence of light for gate voltages ranging from 0 V to -100 V in steps of -20 V. The dashed black lines represent the same curves in the presence of white illumination. Notice that the heterostructure improves the photo-transistor action.
8. Sensitivity Gains in Chemosensing by Lasing Action in Organic Optoelectronic Structures

Sponsors
NASA, MIT Institute for Soldier Nanotechnologies, MIT National Science Foundation MRSEC

Project Staff
A. Rose, C. Madigan, J. Ho, T. Swager, and V. Bulović

Societal needs for greater security require dramatic improvements in the sensitivity of chemical and biological sensors for weapons detection. To meet this challenge, increased attention has been directed at materials and devices with highly non-linear characteristics. Semiconductive organic polymers (SOPs) (Fig. 1) exemplify a class of amplifying materials which have also been recognized as promising lasing materials, although their susceptibility to optical damage due to photo-oxidation has thus far limited applications.

We recently demonstrated that for photostable SOPs, attenuated lasing in optically-pumped SOP thin films can exhibit more than 30-times higher sensitivity to explosive vapors than can be observed from spontaneous emission [1]. Through optical pumping, amplified stimulated emission was readily observed at sufficiently low pump power so as to prevent SOP bleaching during operation in ambient air. Ambient operation is necessary for applications involving the detection of explosives in the field. Upon exposure of the lasing SOP thin film to vapors of 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene, cessation of the lasing action is observed and recorded. Associated enhancement of sensitivity is most pronounced when the films are pumped at intensities near their lasing threshold (Fig. 2). The responses at low analyte-exposure levels are detectable in the lasing peak before any attenuation appears in the spontaneous emission peak. The strong binding of these nitro-aromatic analytes to electron-rich SOPs and their ease of reduction produce a selective response that is relatively immune to other airborne analytes (no response was observed upon exposure to benzene or naphthalene). Present efforts focus on incorporating SOPs into open, high-Q, optical-feedback structures that will reduce the lasing threshold as well as enhance sensitivity by using thinner active layers.

**Figure 1:** Fluorescence of the SOP in solution and in a thin film (before and after DNT exposure).

**Figure 2:** Spectral response of a ring-mode structure consisting of a 25-um-diameter, silica fiber dip-coated with an SOP thin film. The ASE attenuation in the absence of spontaneous emission attenuation after 1.5 min of exposure to saturated TNT vapor pressure. Right inset, plots of ASE peak-emission intensity (wavelength of 535 nm) as a function of excitation power. Left inset pictures a chemo-sensitive SOP thin-film laser.
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Reference:


Sponsors
MARCO Focus Research Center for Circuit and Systems Solutions (C2S2)

Project Staff
K. Ryu, I. Kymissis, V. Bulovic, C.G. Sodini

The field of organic semiconductor materials and devices is rapidly expanding due to the commercialization of novel organic electronic technologies such as organic light emitting diodes (OLEDs), and organic photovoltaic cells. Among the organic devices that have been actively studied are organic field effect transistors (OFETs) because of their compatibility with low temperature substrates such as plastic foils, enabling design of large-area circuits. The number of papers published each year pertaining to OFETs is increasing rapidly, and a new conference titled Organic Field-Effect Transistors has been organized in 2002 under the Society of Photo-Optical Instrumentation Engineers (SPIE).

We are developing OFET arrays as sensors and switches for OLEDs. Today’s displays using OLEDs consume less power, have higher contrast, and better hue/saturation compared to liquid crystal displays, suggesting OLEDs may be the next generation of flat panel displays. However, OLEDs have a severe problem of degradation with usage. OLED display image quality degrades over time as not all pixels are used equally leading to undesirable burn-in artifacts. One solution to this problem is to use optical feedback to correct for the change in OLED pixel brightness. Optical sensors are placed behind each pixels and the signal captured by these sensors are used to control the corresponding OLED pixel. In our implementation the sensor/switch arrays are fabricated in OFETs because of their compatibility with OLED fabrication.

In this project, we are modeling OFET response by investigating the governing physical processes with the aim to aid the design of OFET circuits such as the ones used in OLED display panels. Parameters such as mobility, threshold voltage, and contact resistance are extracted, and peculiarities like mobility change due to charge trapping are explored. Mobility and contact resistance has been extracted via various methods, and charge storage in the channel and the effect of charge trapping are being investigated primarily through I-V and C-V measurements (Fig. 1) and specialized structures (Fig. 2).

![Figure 1: Capacitance vs. channel length measured directly in 1000 µm wide OFETs.](image1.png)

![Figure 2: Array of lithographically patterned OFETs fabricated at MTL.](image2.png)
10. Integrated Organic Electronics

Sponsors
MARCO MSD Center, NSF

Project Staff
I. Kymissis, K. Ryu, A.I. Akinwande, C. G. Sodini, V. Bulovic

Organic electronics hold promise for a wide range of applications. Using organic materials it is possible to fabricate transistors, organic light emitting devices (OLEDs), and photodetector elements, all at low process temperatures (<90° C). While many of these individual devices have been extensively studied and optimized, technologies which are able to produce a large number of devices as well as different types of devices together in integrated circuits are not well developed.

The goal of this project is to make a fully lithographic modular platform for organic electronics which is capable of supporting organic field effect transistors (OFETs) or other related amorphous thin film transistors together with organic photodetectors and OLEDs. Because these systems can be fabricated at low temperatures, they are compatible with a wide range of substrates, including flexible polymeric foils.

To date the project has achieved several milestones, including the development of a fully lithographic OFET backplane process, a self-aligned OFET process (Fig. 1), and the demonstration of an active matrix organic integrated photodetector array (Fig. 2). Work continues on refinement of these modular elements and their integration with organic light emitting devices (OLEDs) to create a full feedback controlled OLED display system which compensates for degradation in OLED devices as well as nonlinearities in the driving circuitry.

Figure 1: A summary of the technologies which we have developed to enable the lithographic fabrication of OFET backplanes and control their characteristics. The wafer shown is a typical 100mm wafer processed using our lithographic process.

Figure 2: (a) Shows a micrograph of the low temperature active matrix photodetector presented in [1] (b) details the structure of the photodetector, and (c) schematically shows the device cross section. The transistor backplane is fabricated first, it is isolated using a layer of parylene, and a vias cut into parylene allow the photoconductor access to the interdigitated electrode structure.
References:


Publications

Journal Articles


Meeting Papers


**Theses**


**Doctoral**
