Organic Materials in Optoelectronic Applications: Physical Processes and Active Devices

ACADEMIC AND RESEARCH STAFF

Professor Vladimir Bulovic

GRADUATE STUDENTS

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Research Themes

We are a new group at MIT. We study physical properties of organic thin films, structures, and devices. Our fundamental findings are applied to the development of optoelectronic, electronic, and photonic organic devices of nano-scale thickness, including visible LEDs, lasers, solar cells, photodetectors, transistors, flexible and transparent optoelectronics. In addition to working on small-molecular-weight van-der-Waals-bonded organic thin films, in the future we will also examine polymer solids, self-assembled materials, and hybrid organic/inorganic structures. We aim to reduce the size of active organic layers from the present nano-scale thickness of organic thin films to that of single molecules, with the ultimate goal of probing functionality of single molecules or polymer strands.

The present strong interest in use of organic thin films in optoelectronics stems from many technological benefits intrinsic to these materials. Organic thin film are simple to grow over both small and large areas, and easy to integrate with both conventional technologies and less conventional materials such as flexible, self assembled, or conformable substrates. Although functional use of organics has been demonstrated in the form of light emitters, photodetectors, optical elements, and active electronic logic components, many basic electronic and optical properties of these solids are not well understood. Much research is needed. Similarities with conventional inorganic semiconductors provide a physical framework for further investigations. However, a large number of phenomena in organic materials have no analog and require development of novel physical concepts.

For example, in contrast to conventional inorganic semiconductors the majority of processes in organic structures involve exciton formation. Design of optoelectronic and photonic devices with active organic layers therefore necessitates tracking and tailoring of excitonic processes. The group's research efforts are directed towards resolving some of the open questions in this field. Clarification of the fundamental physical processes in organic thin films will directly influence the development of practical organic optoelectronic components.

Recent research of Prof. Bulovic and his colleagues at Princeton University and Universal Display Corporation led to development of both active and passive organic devices. The application of their findings on fundamental properties of organic materials led to a number of practical inventions, such as demonstration of transparent organic light emitting devices (OLEDs) (see Fig. 1) [i,ii], temperature-insensitive low-threshold organic semiconductor lasers [iii,iv,v], broadly-spectrally-tunable luminescent layers [vi,vii], control of microcavity effects in layered organic structures [viii], stacked [ix] and inverted OLEDs [x], organic solar cells [xi] and multilayer photodetectors [xii]. The sum of this research indicates that the field of organic materials is abundant in novel physical phenomena unique to molecular organic and polymer systems.
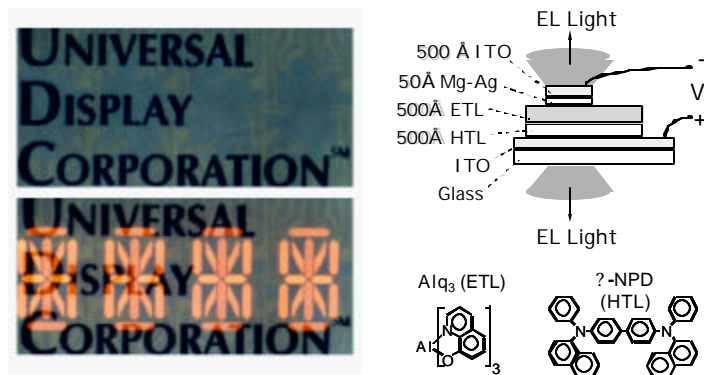
FIGURE 1   Transparent organic light-emitting device (TOLED) in off (top left) and on (bottom left) state. In the off state the device is more than 70% transparent, so we can look through it and see the logo of the Universal Display Corporation.   TOLED layer structure is shown in the upper right with typical electron transport layer (ETL) and hole transport layer (HTL) molecules in the bottom right of the figure.

With the present rapid pace of scientific discovery, the use of organic electronic and photonic devices in our everyday lives appears inevitable, although a great deal of research and development still must be accomplished. Development of each new organic device demonstrates the immense versatility of these materials, but simultaneously opens new questions into the origins of the observed physical processes. Hopefully, our research efforts will answer some of these riddles and lead to new venues of scientific endeavor.

Integrated Materials Growth System

PROJECT STAFF

Seth Coe, Conor Madigan, Debbie Mascaro, Professor Vladimir Bulovic

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

We are in the process of developing a versatile materials growth system (see Fig. 1) that combines conventional materials growth techniques with novel deposition methods developed in our laboratories. The completed growth system will integrate the method for physical and vapor phase deposition of hybrid organic/inorganic thin-films with a low-pressure RF/DC sputtering chamber, an evaporative growth chamber, and a chemical vapor deposition chamber. The completed vacuum system will be capable of depositing molecular organics, polymers, metals, metal oxides, inorganic nanodots, and colloids in a controlled layer-by-layer fashion. An in-situ shadow masking system will enable fabrication of complex patterned structures inside a vacuum environment, while the integrated N_2-filled, dry glove box will facilitate handling, measuring, and packaging of organic thin film samples that are susceptible to reactions with atmospheric oxygen and water vapor. Completed samples will be in-situ tested in the analysis chamber by contacting them with an electrical probe attached to an X-Y-Z manipulator. Optical ports on the chamber allow for a telescopic view of the devices and facilitate optical excitation of probed samples. Optoelectronic properties of the hybrid materials and structures will be investigated at a range of temperatures form 5K to 600 K, generated by the liquid helium cryostat and the boron-nitride heater situated behind the sample stage. The AFM/STM chamber will facilitate in-situ atomic scale microscopy for evaluating morphology and electronic properties of hybrid materials.

All chambers are connected to the central transfer system that has linear degrees of freedom. Each chamber is isolated form the others by a gate valve resulting in typical base and operating pressures as indicated below.
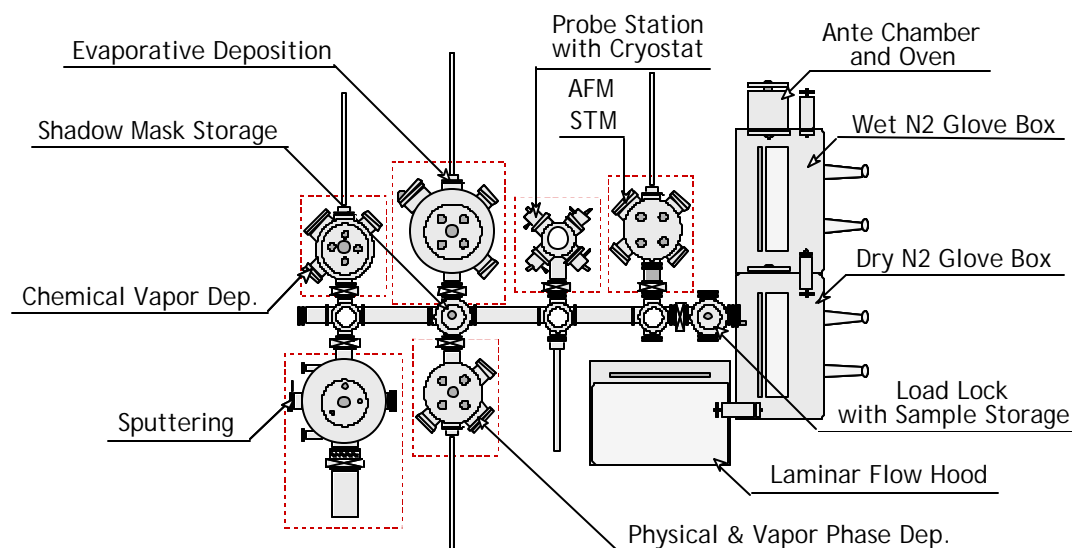

FIGURE 1 *Integrated materials and devices growth system consisting of the materials growth chambers based on physical and vapor phase deposition, sputtering, chemical vapor deposition, and evaporative deposition with in-situ shadow masking. Samples are analyzed in the analytical and AFM/STM chambers, and all connected to the central transfer line with load lock and an integrated, nitrogen-filled glove box.*

SYSTEM	Base Pressure [Torr]	Operating Pressure [Torr]
PVPD	10^{-8}	1 to 10
Sputtering	10^{-9}	10^{-3} to 10^{-2}
Evaporative	10^{-10}	10^{-10}
CVD	10^{-8}	1 to 10
Central Transfer	10^{-9}	10^{-7} to 10^{-9}
Probe Station	10^{-10}	10^{-10}
AFM/STM	10^{-10}	10^{-10}
Load Lock	10^{-7}	10^{-7} to atmosphere

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 will be the centerpiece of our materials growth effort, as it will accommodate solvent-free deposition and co-deposition of polymers, colloids, and molecular organic materials in vacuum. We expect that our solvent-free vacuum growth will produce polymer thin films of superior electronic grade compared to those previously grown. Furthermore, elimination of solvents from the deposition process should allow for the growth of multilayer polymer structures with precisely controlled thickness and a much expanded choice of heterojunction interfaces. Versatility of the integrated growth system will allow for development of active optoelectronic devices based on previously unachievable materials and material multilayers, which should lead to both technological breakthroughs and investigations of new physical concepts.

Solid State Solvation Effect

PROJECT STAFF

Conor Madigan, Professor Vladimir Bulovic

Emission and absorption spectra of many organic dyes in *liquid solutions* depend on the local electric fields generated by the surrounding polar solvent molecules [xiii]. 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 experiments recently confirmed that the solvation effect is also present in *molecular solids* where closely packed polar molecules can generate large local electric fields. By adjusting the strength of local electric fields inside the organic films with intermolecular dipole-dipole interactions, the solid state solvation (SSS) can be used as a new general method for tuning the energy level structure of organic materials. Using SSS we demonstrated that luminescence of some polar laser dyes can be wavelength shifted by as much as 75 nm (from red to yellow and

green to blue) when doped into less polar molecular hosts [vi,vii]. Remarkably, with judicious control of SSS effect, a single device structure was designed to produce an efficient blue, green, yellow, orange, red, or white emission while utilizing an identical set of molecular organic materials [vii].

(a)   Physical Origins of the Solvation Effect

Theories describing the solvation process principally assume that the chemical states of the isolated and solvated molecules are the same, and processes such as solvent-solute charge transfer, solvent-dependent aggregation, ionization, complexation, or isomerization do not occur. Simply, solvation is considered as a physical perturbation of the relevant molecular states of the solute due to the presence of the solvent. Spectroscopic studies on solutions of polar molecules in polar solvents show that the peak luminescence (λ_{max}) and absorption wavelength of a solute can undergo both bathochromic (red) and hypsochromic (blue) shifts in λ_{max} as the solvent polarity increases [xiii].

Theoretical modelings of the solvation effect are generally limited by the complexity of the solute-solvent system that involves dipole-dipole, dipole-induced dipole, higher order multipole, and hydrogen bonding interactions. Qualitative treatments of the problem, however, give a reasonable agreement with experimental measurements. In essence, it is found that the polar solvent strongly influences the more polar state of the molecule. Since molecular electronic transitions lead to redistribution of charge, the dipole moment of the ground state (ρ_0) and an excited state (λ_1) of a molecule will, in general, be different. If the excited state of the molecule has a larger dipole moment than the ground state, an increase in solvent polarity will more strongly stabilize the excited state (Fig. 2(a)), lowering its energy, and red shifting λ_{max} [xiii]. Conversely, if $\lambda_0 > \lambda_1$ (Fig. 2(b)) the ground state is more stabilized upon increase in solvent polarity, and a blue shift in λ_{max} is observed.
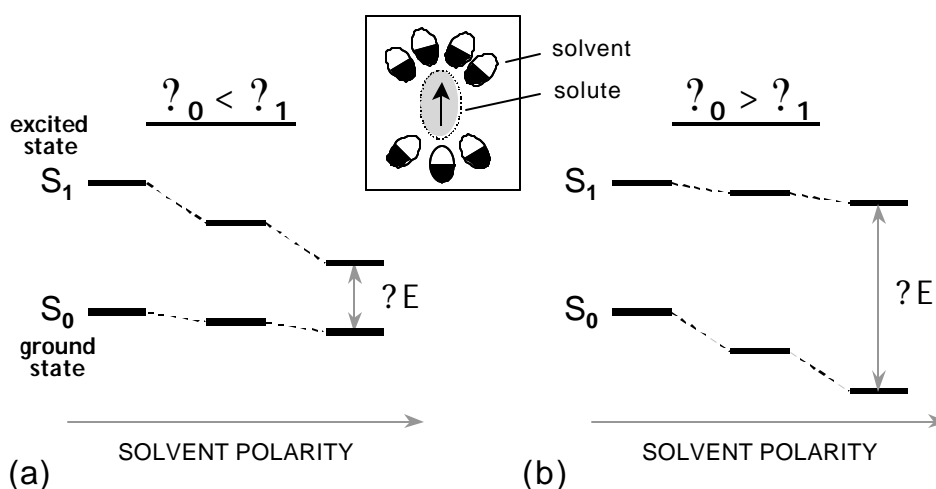

FIGURE 2 *Schematic illustration of solvatochromism.   Decrease [increase] in the luminescence energy of molecules with excited state dipole moment (λ_1) larger [smaller] than the ground state moment (ρ_0) as a function of solvent molecule dipole moment (polarity) is shown in (a) [(b)]. INSET: Solvent molecules organize around the polar solute to minimize total system energy.*

(b)   Photoluminescence of Polar Lumophore DCM2

The solvation effect is pronounced for laser dye DCM2 dissolved in solvents of different dielectric susceptibility (Fig. 3).   The DCM2 peak luminescence wavelength (ℓ_{max}) varies from 565 nm for the nonpolar solvent, benzene, with a low frequency dielectric constant of $? = 2.27$ in solution, to 675 nm for dimethylsufoxide (DMSO) with a molecular dipole moment of 3.9 D and $? = 46.7$ (solvent dipole moments are indicated in the figure).   From these data we conclude that the dipole moment of the excited DCM2 molecule is higher than that of the ground state, consistent with earlier measurements and calculations of the dipole moment of DCM1 [xiv].
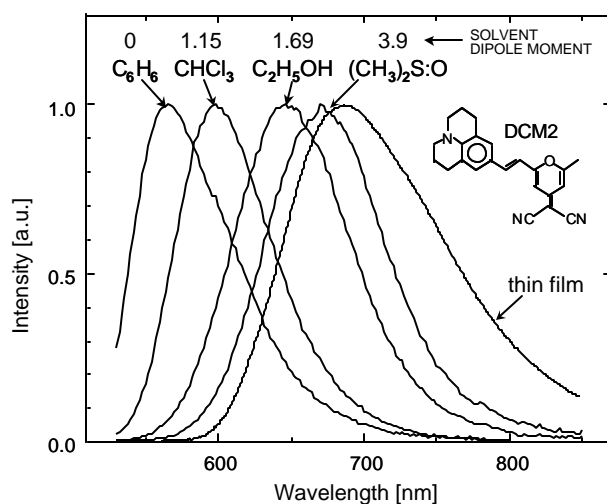

FIGURE 3   *Normalized photoluminescence spectra of dilute DCM2 solutions in benzene (C_6H_6), chloroform ($CHCl_3$), ethanol (C_2H_5OH), and DMSO ((CH_3)$_2$S:O).   Solvent dielectric constant and molecular dipole moment are also indicated.   Photoluminescence spectrum of DCM2 thin film is also shown.   The solutions were very dilute (~1/1000 of the saturated solution concentration), ensuring that the spectra observed are due to monomer fluorescence, and that the contribution from aggregates is negligible.   There is no significant difference in the quantum yield from DCM2 in any of the solutions used.*
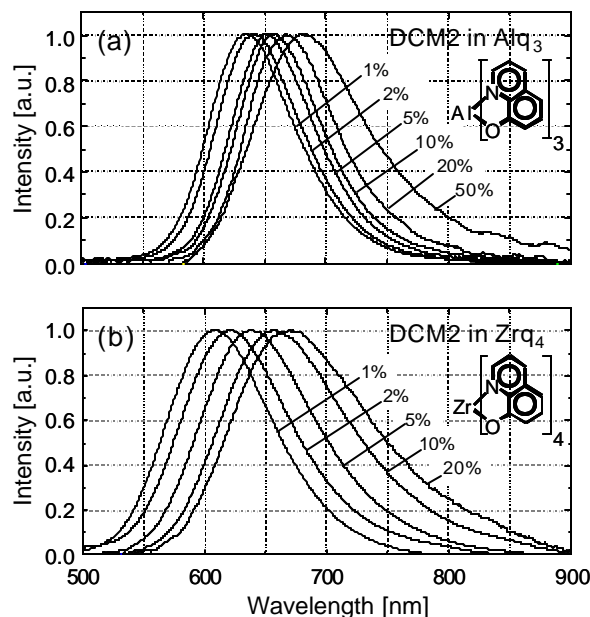
FIGURE 4   *Normalized photoluminescence spectra of 400 Å thick vacuum-deposited thin films of (a) Alq_3:DCM2 and (b) Zrq_4:DCM2 as a function of DCM2 concentration.*

The solution luminescence shift can be compared to the change in the photoluminescence spectrum of DCM2 doped into different vacuum deposited thin films. The photoluminescence (PL) of 1% DCM2 in aluminum *tris*-(8-hydroxyquinoline) (Alq_3) (λ_{max} = 635 nm) is red-shifted with respect to that of 1% DCM2 in zirconium 8-hydroxyquinoline (Zrq_4) (λ_{max} = 605 nm) (Fig. 4). This is consistent with the trend found in the solution studies since the ground state dipole moment of Alq_3 (μ_0 = 5.5 D) is larger than that of the more symmetric Zrq_4 ($\mu_0 \sim 0$ D). The dipole moments of molecules in organic thin films are obtained from semi-empirical molecular orbital calculations based on an intermediate neglect of the differential overlap algorithm [xv], parameterized from solution of electronic spectra for the optimized molecular geometries.

As the concentration of DCM2 changes in both Alq_3 and Zrq_4, the luminescence red-shifts. The similarity of the spectral widths, and the magnitudes of the peak shifts in both Figs. 3 and 4 suggests that DCM2 suspended in solid matrices of Alq_3 and Zrq_4 undergoes an energy shift due to self-polarization. That is, as the concentration of highly polar (μ_0 = 11.3 D) DCM2 molecules in the relatively non-polar Alq_3 and Zrq_4 is increased, the distance between nearest neighbor DCM2 molecules decreases, thereby increasing the local electric field. This field perturbation tends to red-shift the DCM2 emission spectrum. The effect is increased until the concentration is 100% in an undiluted DCM2 film, where λ_{max} = 685 nm is close to that attained in the polar solvent, DMSO. By comparison, the most dilute films of 1% DCM2 in Alq_3 and 1% DCM2 in Zrq_4 are both red-shifted from DCM2 PL in $CHCl_3$ (with μ_0 = 1.15 D and ε = 4.81). This suggests that even at such low concentrations, the DCM2 emission spectrum is influenced by the presence of other DCM2 molecules, given that a smaller shift than that observed would be expected from interactions with only the non-polar Zrq_4.
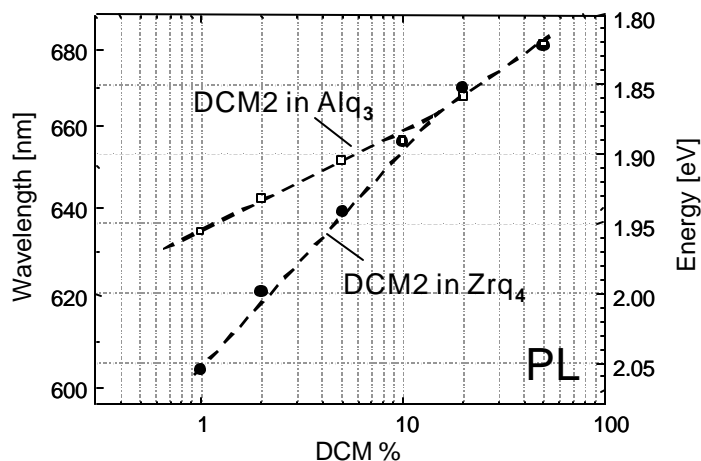
FIGURE 5   *Peak photoluminescence (PL) wavelengths of films from Fig. 4 as a function of DCM2 concentration.*

The self-polarization of DCM2 due to dipole-dipole interactions can thus strongly influence the energy levels of the lumophore.   Indeed, for DCM2 concentrations above 10%, λ_{max} is independent of the host material (Fig. 5) as the local fields are overwhelmingly determined by the highly polar DCM2 molecules.   At concentrations below 10% emission from Alq_3 is always red-shifted from that of Zrq_4 since the local field is largely determined by the host.

Over a large volume, the net DCM2 dipole moment averages to zero since the molecules in the solid solution should be randomly distributed.   However, considering that the dipole field decreases as $1/r^3$ where r is the distance between dipoles, only those molecules nearest the luminescent center contribute to the local electric field and hence influence the emission spectrum.   Local fields due to randomly oriented dopants would contribute equally to blue and red spectral shifts, broadening the overall spectrum, but would not change the peak wavelength. Polar dopants such as DCM2, however, tend to aggregate in oriented domains that minimize the overall energy of the system, causing the spectral red shift.

(c) Temporal Response of Luminescence

Our initial measurements of time resolved luminescence of polar luminescent dyes indicate that spectral shifts also take place during the luminescent process.   The lower panel of Fig. 6 shows a typical contour trace of luminescence intensity as a function of wavelength and time for DCM dye in Alq_3.   Most of the spectral shifting takes place during the first 2 ns and has tentatively been assigned to molecular reorganization induced by the sudden change in the lumophores' dipole moment upon excitation.   The remaining shift can be associated with an exciton thermalization process, due to exciton diffusion through the doped molecular structure.   The observed phenomenon is general in nature and provides insight into exciton dynamics during the luminescence process.   Such information is essential in tailoring optimal performance of organic LEDs and chemical sensors.   We are presently developing a comprehensive theoretical framework describing these luminescence phenomena.
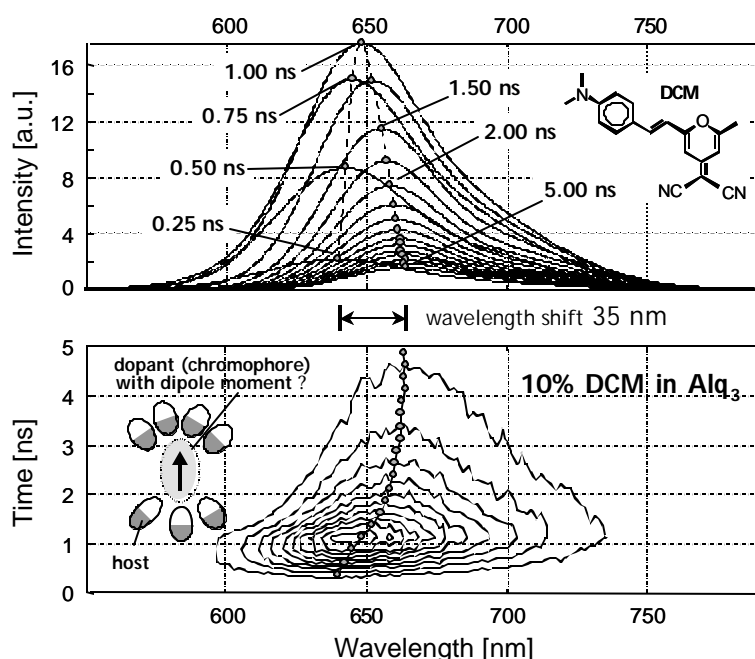
FIGURE 6 *(Bottom) Contour plot of photoluminescence intensity of 10% DCM in Alq 500 Å thick film as a function of wavelength and time. (Top) Time resolved spectra of the same sample, where each spectrum is integrated over 0.2 ns window, with an average time indicated in the figure.*

Appendix: Milestones

Dr. Vladimir Bulovic, Assistant Professor of Electrical Engineering and Computer Science received an award under the National Science Foundation's Faculty Early Career Development program. Professor Bulovic, a principal investigator in RLE's Organic Optoelectronics group, plans to investigate the physical principles underlying the solid state solvation effect he identified in molecular organic solids. Insights gained will be applied to improvement and development of organic optoelectronic devices. The CAREER program recognizes the outstanding new faculty members who intend to pursue academic careers that involve both research and education. Professor Bulovic's work has focused on development of both active and passive organic devices. His experimental findings to led development of a number of practical inventions, such as demonstration of transparent organic light emitting devices (OLEDs), temperature-insensitive low-threshold organic semiconductor lasers, broadly-spectrally-tunable luminescent layers, control of microcavity effects in layered organic structures, stacked and inverted OLEDs, organic solar cells and multilayer photodetectors. Professor Bulovic joined the MIT faculty in 2000.

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