Soft Semiconductor Devices

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Our group works with soft semiconductors. These are materials comprised of molecules held together by weak van der Waals bonds. In comparison, the atoms in conventional semiconductors are held together by strong covalent bonds. Weak intermolecular bonds offer a tradeoff to engineers. Their disadvantage is an enhancement of disorder and charge localization, yielding relatively poor charge transport properties.

But the advantage of soft semiconductors is that they are uniquely suited for large area electronics such as video displays, and solar cells. In contrast with the painstaking growth requirements of conventional semiconductors, films of soft semiconductors are readily deposited on a variety of materials at room temperature. Most importantly, the optical properties of the molecules within a soft semiconductor are relatively immune to structural defects and disorder in the bulk. Thus, soft semiconductors are tolerant of the defects that inevitably occur in the fabrication of large area applications.

Figure 1: Two examples of van der Waals bonded semiconductors. (Left) The structure of a molecular crystal of pentacene. Pentacene has a hole mobility of approximately 2 cm2/Vs and is widely used in organic electronics. Data is from Mattheus, et al. Acta Crystallographica C. 57, 939 (2001). (Right) The structure of the photosynthetic reaction center of Rhodobacter sphaeroides. Evolved over two billion years, this molecular circuit is the backbone of photosynthesis. The protein scaffold has been removed for clarity. Data is from Ermler, et al. Structure 2, 925 (1994).

This is a young field, with much promise and significant challenges. In our work, we have successfully integrated complex structures from photosynthesis with solid-state electronics. We also work in two of the major controversies in thin film soft semiconductors: the fundamental efficiency limit of organic light emitting devices, where we have questioned accepted models of

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excited-state formation; and charge injection, where we have developed a theory centered on structural and energetic disorder in these soft materials.

1. Extrafluorescent Electroluminescence in Organic Light Emitting Devices

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Organic light emitting devices (OLEDs) are a promising technology for flat panel displays and solid-state lighting due to their low cost, low power consumption, and mechanical flexibility. They can produce two kinds of light: fluorescence, the result of an allowed transition, and phosphorescence, the result of a partly forbidden transition [1]. Fluorescent OLEDs represent the vast majority of all OLEDs and have better stability in certain colors but have efficiencies that are usually limited by spin conservation to one fourth of phosphorescent efficiencies [1]. We have demonstrated a technology for raising the efficiency of fluorescent OLEDs to approach that of phosphorescent OLEDs [2]. This technology should prove to be a major step forward in producing stable and high-efficiency OLEDs across all colors.

The efficiency of fluorescent OLEDs is limited by the process in which a neutral molecular excited state, or exciton, is created from oppositely-charged neighboring molecules. Excitons can have triplet or singlet spin symmetry. Typically only singlet excitons are luminescent, and they represent only 25% of all excitons formed. We demonstrate that this percentage can be increased to nearly 100% by mixing the spins of exciton precursor states. We have calculated that the singlet exciton precursor state is lower in energy than the triplet precursor state, which will favor singlet precursors and excitons if mixing of the precursor states is introduced (Figure 1). If at the same time excessive mixing of the exciton state to dark triplets is avoided, an overall efficiency enhancement can result. We demonstrate such an efficiency enhancement using the mixing molecule FIrpic and the fluorescent material DCM2 (Figure 2).

Figure 1: Rate diagram for exciton formation. Triplet (\(1^\text{CT}\)) and singlet (\(1^\text{CT}\)) exciton precursor states form triplet (T) and singlet (S) excitons at rates \(k_T\) and \(k_S\). Extrafluorescence occurs when the CT state mixing rate \(k_T^\text{TS}\) is made large with respect to \(k_T\), and the exciton mixing rate \(k_S^\text{ST}\) is low. While \(\Delta E_{\text{EX}} > 0\), we have calculated and measured \(\Delta E_{\text{CT}} < 0\), so that \(k_T^\text{ST} > k_T^\text{TS}\), favoring singlet production.

Figure 2: Demonstration of an extrafluorescent OLED, or X-OLED ("X-DCM2"). The mixing molecule iridium(III) bis [(4,6-difluoro-phenyl)pyridinato-N,C\text{2}']picolinate (FIrpic) is used as an electron transport layer, so that exciton precursor states are preferentially mixed. The laser dye 4-(dicyanomethylene)-2-methyl-6-[(4-dimethylaminostyryl)-4-H-pyran] (DCM2) is used as an emissive material in a host of 4,4'-N,N'-dicarbazolyl-biphenyl (CBP). A control device ("DCM2") where FIrpic is replaced with 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), which has low mixing rates, shows a 2.7x lower efficiency. A second control device ("DCM2 w/ spacer") wherein the FIrpic layer is moved away from the emissive zone by 100 Å of BCP, shows no efficiency enhancement.
2. Saturated and Efficient Blue Phosphorescent Organic Light Emitting Devices with Lambertian Angular Emission

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The realization of stable blue phosphorescent organic light-emitting devices (OLEDs) has proved challenging. An important limitation is the broad photoluminescent (PL) spectrum characteristic of organic dyes. For example, greenish-blue or “sky-blue” phosphors have strong emission in the blue [1]. But optical transitions to higher vibrational modes of the electronic ground state extend their emission spectrum deep into the green. Because the eye responds strongly at green wavelengths, this broad emission spectrum yields an unsaturated color that is ill suited for most display applications.

In this work a strong microcavity is employed to optimize the color of a phosphorescent organic light emitting device (OLED) based on the sky blue phosphor FIrpic. The usual disadvantages of a strong microcavity, namely the introduction of an angular dependence to the OLED’s color and a non-Lambertian angular emission profile [2], are overcome by scattering the emitted radiation. As scattering sources, frosted glass, opal glass, and holographic diffusers are studied. With a holographic diffuser as the scattering medium, the microcavity OLED achieves an external quantum efficiency of (5.5±0.6)%, as compared to (3.8±0.4)% for a conventional structure. The color coordinates of the microcavity OLED with holographic diffuser are \((x,y) = (0.116±0.004, 0.136±0.010)\), with minimal angular color shift and a nearly ideal Lambertian angular emission profile.

![Figure 1: In the strong microcavity, the anode is a thin, semitransparent layer of Ag. The cathode is Al/LIF. Devices were grown directly on the smooth back surface of frosted glass and opal glass diffusers. The holographic diffuser was employed external to devices grown on regular glass.](image)

![Figure 2: (a) Electroluminescent spectra of the strong microcavity FIrpic OLED as a function of angle from the surface normal with the holographic diffuser. A color shift with increasing angle is barely perceptible. For comparison we plot the intrinsic photoluminescent spectrum of FIrpic (dotted line). (b) The color coordinates of the strong microcavity devices with and without holographic diffusers. Inset: the full CIE diagram identifying the expanded blue region.](image)
3. Optical Models of Organic Light Emitting Devices

We calculate the dipole energy propagation in a multilayer stack by analytically extending the theoretical model of Chance, Prock and Silbey [1], which calculates the field pattern and lifetime of a dipole in this geometry. This analytical extension [2] facilitates numerical calculations to predict the outcoupling and optical dissipation mechanisms of an organic light emitting device (OLED), where the excitons can be modeled as dipoles. We have applied this approach to a previous experimental measurement of an OLED outcoupling by Segal et al. [3] The model predictions agree with the experiment, yielding a similar outcoupling efficiency and in addition shows the mode-resolved spatial dipole energy dissipation of the same device (Figure 1). Thus we conclude that the surface-parallel oriented dipoles generate most of the emitted light, and the main optical loss mechanisms are the waveguiding in the glass and organic layers, along with a smaller loss to the plasmon modes of the cathode. Our method can be used for designing low-loss OLED structures and efficient cavity designs.

![Figure 1](image)

**Figure 1:** (a) Absorption of the parallel dipole energy as a function of the position and normalized surface-parallel wavevector. The dipole is located at the middle of the Alq3 layer and the emission wavelength is \( \lambda = 535 \) nm. Bright features correspond to a higher absorption. The green curve shows the outcoupled energy flux. (b) Same absorption as in part (a) but for perpendicular dipole. Perpendicular dashed lines divide this flux into air-outcoupled, glass-waveguided, organics-waveguided and surface plasmon polariton (SPP) portions. At \( \lambda = 535 \) nm, the dielectric constants for Mg, BCP, Alq3, TPD, PEDOT and ITO are the following: \( \varepsilon = 1.908 + 0.265i \), \( \varepsilon = 2.985 + (4.11 \times 10^{-5})i \), \( \varepsilon = 2.962 \), \( \varepsilon = 2.985 + (4.11 \times 10^{-5})i \), \( \varepsilon = 2.304 + (3.33 \times 10^{-2})i \) and \( \varepsilon = 3.296 + (3.63 \times 10^{-3})i \), respectively. Note that the dielectric constant of TPD was assumed to be equal that of BCP. (Figure is taken from [2]).
References


4. Surface Plasmon Polariton Mediated Energy Transfer in Organic Photovoltaic Devices

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With a theoretical efficiency similar to conventional inorganic photovoltaics (PVs) [1] and the potential to be manufactured inexpensively, organic semiconductor technology offers a promising route to ubiquitous solar energy generation. Organic PVs, however, are constrained by a tradeoff between exciton diffusion and optical absorption. The short exciton diffusion length within organic semiconductors demands the use of extremely absorptive materials[2]. Unfortunately, the excitonic character of most organic materials yields highly structured absorption spectra, with regions of strong and weak absorption.

We propose a device architecture that boosts the performance of a phthalocyanine-based PV in the absorption gap between the phthalocyanine Q and Soret bands. Light absorption is decoupled from exciton diffusion using a light-absorbing "antenna" layer external to the conventional charge generating layers (Figure 1). Radiation absorbed by the antenna is transferred into the charge generating layers via surface plasmon polaritons (SPP) in an interfacial thin silver contact. Off resonance, the antenna cavity operates as a reflector and all devices exhibit identical performance. However, in the region where the cavity is tuned to absorb light strongly, the devices with antennas have exhibited increased quantum efficiency of up to 200% compared to those with non-functioning antennas. Peak increases in external quantum efficiency of approximately 80% have been measured for devices with external light absorbing antennas compared to those without.

Energy coupling from external antenna layers into thin film organic PV provides a flexible route to higher efficiency devices. While the introduction of the antenna necessarily adds a step into the energy transduction process, it can be successfully employed in spectral regions where the absorption fraction of the PV cell drops below the SPP-mediated energy transfer efficiency. We measured this latter efficiency to be at least (51±10)%. It is possible to increase the quantum efficiency of an antenna to nearly 100% by optimizing the orientation and position of a luminescent dye with respect to a thin Ag film. Targeting resonant antennas to regions of poor absorption promises to solve a characteristic deficiency of organic PVs.
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Figure 1: Structure of organic photovoltaic devices with external resonant antenna cavities. We fabricate identical charge generation structures with antennas of varying PL efficiency consisting of isotropic mixtures of AlQ3 and either 1% of the quenching material CuPC or 1% of the laser dye DCM. Comparing the performance of these devices allows us to isolate the photocurrent originating from light absorbed in the antenna while avoiding interference effects due to changing device structures.

Figure 2: External quantum efficiency (EQE) for resonant antenna devices with functional external AlQ3-based antenna layers exhibits an increase in EQE over the wavelength range where AlQ3 absorption occurs and cavity reflectivity decreases. The functional antenna (□) shows a significant performance enhancement versus both the quenched antenna (○) and devices fabricated without any antenna (△). Comparison with modeling (—) indicates that the energy transfer efficiency is approximately 46%.

References

5. Reduction of self-absorption in luminescent solar concentrators (LSC) using energy transfer in guest/host thin films

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Due to the rapid rise in global demand for photovoltaics, silicon feedstock providers are racing to keep pace. By concentrating the sun’s light, energy conversion systems can be deployed that use just a fraction of silicon required by typical photovoltaic. The LSC system has the added benefit of having a large acceptance angle for sunlight, thereby reducing the need for expensive tracking equipment.

The operation of the LSC is as follows: (1) Light is absorbed by the luminescent chromophores embedded within a waveguide. The chromophores luminesce, with some quantum yield, a photon of equal or lesser energy, and some portion of the emitted light will be confined in the waveguide by total internal reflection. Of the trapped light, a fraction will impinge on a properly placed energy conversion device such as a photovoltaic.
Our research applies advancements in burgeoning field of organic light emitting diodes (OLED) to the LSC. OLED fabrication techniques allow us to precisely control the phasing of chromophores in thin films. By engineering the physical distances between chromophores [1], we are able to achieve resonant energy transfer to a terminal chromophore that is optimized for quantum yield and self-absorption. This process is repeated with each additional chromophore with the goal of complete coverage of the solar spectrum for the visible to the near infrared.

References

6. Electric field and Temperature dependent Analytic Model of Charge carrier Mobility in Amorphous Organic Semiconductors

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Understanding the electric-field dependence of charge carrier mobility is central to the rational design of organic semiconductor devices [1]. Studies of charge transport in organic semiconductors have observed a \( \log \mu \sim \sqrt{F} \), or Poole-Frenkel, dependence of charge carrier mobility, \( \mu \), on electric field, \( F \). Numerical simulations have established that the Poole-Frenkel dependence is due to disorder, and analytic theories have continued to employ simulation-based empirical models in efforts to jointly summarize the electric-field, temperature-, and charge-density-dependencies [1].

In this research we present a complete analytic description of mobility by considering non-equilibrium carrier distributions within a percolation framework. Only three free parameters are required: the width of the density of states, the decay length of the charge carrier wave function, and the maximum conductivity, which depends in turn on the strength of the intermolecular...
interaction. The electric field dependence of charge carrier mobility is found to be well-modeled by an effective temperature, suggesting that the dominant effect of the electric field is to generate a nonequilibrium charge carrier distribution.

The theory is compared to measurements by Brütting, et al [1] of the current-voltage and mobility of the archetype small molecule tris (8-hydroxyquinoline) aluminum. The theory accurately reproduces the temperature, carrier density, and electric field dependencies of the experimental data over a wide range of temperatures, carrier densities, and electric fields. Most significantly, the mobility theory enables predictive models of organic semiconductor devices based on material parameters that may be determined by ab initio quantum chemical simulations. Consequently, we expect that the theory will allow the rational design of organic devices in important applications such as video displays and solar cells.

![Figure 1](image1.png)  
**Figure 1:** Temperature-dependence of the J-V characteristics of an Al/Alq3/Ca device with an Alq3 thickness of 300 nm. Solid lines show theoretical fits. Current-voltage curves were offset by a voltage $V_{off} = 2V$ to compensate for uncertainty in $V_{bi}$ and the contact resistances.

![Figure 2](image2.png)  
**Figure 2:** Temperature and electric field dependence of charge carrier mobility obtained from transient electroluminescence measurements. Theoretical fits are shown in solid lines.

**References**

7. Exciton-Coupled Surface Plasmon Resonance Biosensor

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The development of portable and cost-effective biological sensors promises benefits to medical care, pharmaceutical testing and the detection of biological warfare agents. Electronic devices are compact and readily integrated into microfluidic substrates, making them a promising alternative to today's bio-detection requirements.

Our sensor design aims to exploit the sensitivity of surface plasmon resonance (SPR). Unlike conventional SPR sensors, the plasmon is detected in the near field using a thin film organic photovoltaic (PV). High absorption coefficients make organic semiconductors ideal candidates for the detection of surface plasmons. They are also easily deposited on microfluidics, enabling use of these devices outside the laboratory environment in a convenient portable package.

In the initial demonstration, plasmon modes are excited in the top surface of the gold cathode by a p-polarized laser beam, when the horizontal component of the light wavevector matches the plasmon wavevector[1]. The plasmon is absorbed by the organic semiconductor and split into holes and electrons at the interface between the donor and acceptor layers composing the PV cell (Figure 1). The plasmon resonance measured indirectly as reflected power and photocurrent (Figure 2) has a strong angular location dependence on the adjacent layer's dielectric constant that is altered upon binding of bio-molecular species. The steep slope of the resonance enables sensitive detection as well as measurement of kinetic parameters of the binding event.

References
8. Kelvin Probe Microscopy of Organic Electronic Devices

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Kelvin Probe Microscopy (KPM) may be used to determine the contact potential difference between different materials using scanning force microscopy. It has been employed previously in the study of organic semiconductor surfaces and interfaces [1]. We are applying KPM to the channel of an organic field effect transistor to determine the density of states [2]. The technique measures changes in the surface potential of the channel in response to changes in the gate potential relative to a grounded source and drain electrode. The measurement setup is shown in Figure 1. In an ordered semiconductor with energy bands and no states in the gap, the surface potential is expected to vary linearly with the gate before being pinned at threshold by the large density of states at the band edge. But in a disordered semiconductor with an energetic dispersion of localized states, the transition at the threshold voltage is expected to be blurred. Figure 2a shows the initial results for the hole transporting organic semiconductor copper phthalocyanine (CuPC). CuPC is observed to have a broad density of states that stretch well into the gap between its highest occupied molecular orbital (HOMO) and its lowest unoccupied molecular orbital (LUMO). In Figure 2b we plot the density of states as calculated from the relation:

\[ \text{DOS} = \frac{C_G q^2}{\varepsilon_0} \left( \frac{dV_{GS}}{dU} - 1 \right) \]

where DOS is the density of states per unit energy, CG is the gate-channel capacitance, VGS is the gate-source potential, U is the surface potential and q is the electronic charge. Because the technique offers previously unattainable resolution, it promises to yield new insights into electronic transport and degradation processes in organic semiconductors.

![Figure 1: Image of the VT-SPM (Omicron GmbH) inside the UHV chamber (3x10^-10 Torr). Surface potential measurements are recorded relative to a Pt-Ir coated Si tip. Measurement of the tail states requires equilibrium in the channel. However, the resistance of the channel is extremely large below the threshold. Further measurements are required to determine whether the measurement of the extreme tail states have indeed been made under equilibrium conditions.](image1)

![Figure 2(a): The OFET channel surface potential versus the gate bias. The blue dots represent the actual data and the green line is a cosh-fit of the data. The OFET consists of 50-nm-thick Au top-contacts with a 50-µm-wide, 20-nm-thick CuPC channel on Si-substrate with 300-nm thermal oxide. (b) The calculated density of states noting that the measured density of the extreme tail states remains subject to additional verification.](image2)

References

9. Nanoelectromechanical Switches and Memories

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The ability to change shape is a compelling attraction of molecular semiconductors. Compared to rigid inorganic materials, molecules are soft and malleable, and their conformational changes are essential to the functionality of biological systems. Applications of nano-electro-mechanical (NEM) molecular devices include memories and transistors: Information can be stored in the conformation of molecules, potentially leading to very high density memories, and molecular transistors that change shape under bias could exhibit sub-threshold slopes of \( \leq 60 \text{ mV/decade} \). Indeed, as an example of the potential of NEMs, voltage gated ion channels possess sub-threshold slopes of approximately 15 mV/decade [1].

Although many materials are available for NEM applications, carbon nanotubes exhibit low resistance and good mechanical properties. In this project, we are constructing an NEM testbed. The proposed design for our relay is shown in Figure 1. Nanotubes are directly grown at the bottom of an electron-beam defined trench etched in Si. Leaving tube growth to the final step gives us better control of the nanotube and removes the need for additional steps that are required for the removal of surfactants and organics from the surface of the nanotubes. Because the nanotubes are vertically oriented, we are able to take advantage of the smallest size feature of the carbon nanotube, its diameter, and enables us to create dense arrays of relays for applications such as memory or logic devices. The vertical orientation allows NEM structures with very large aspect ratios. Theoretical results [2] have shown that increasing the aspect ratio of a carbon nanotube reduces the voltage needed to pull in the nanotube, and thereby reducing the power consumption. Furthermore, because of the ability to easily functionalize the surface of nanotubes, we can functionalize the tube with multiple charges to lower the pull-in voltage even further.

![Figure 1: Testing is performed by introducing a probe-mounted CNT in between two gold contacts on silicon and then sweeping it from the center position (1), to the right contact (2), and subsequently to the third contact (3), and then back.](image)

![Figure 2: An I-V of the device being switched from State 1 to 2 by applying a bias between Contact 1 and CNT, then switched from state 2 to 3 by applying a bias between Contact 2 and CNT, and finally switched from state 3 to 2 by applying a bias between Contact 1 and CNT.](image)
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References


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