

## Soft Semiconductor Devices

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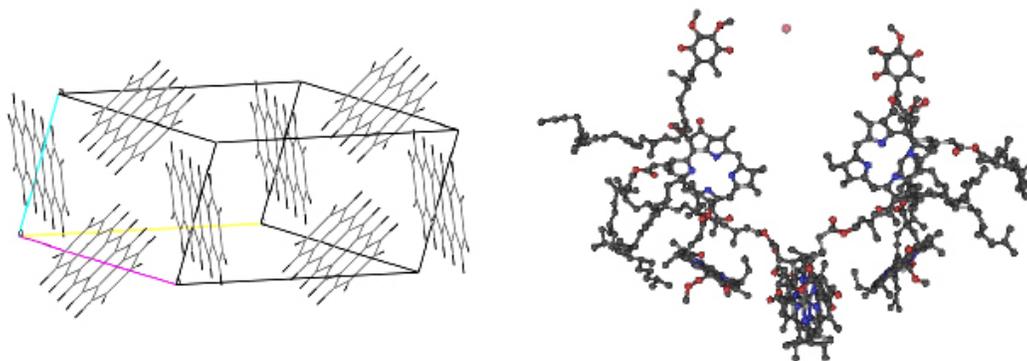
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Our group works with soft semiconductors. These are materials comprised of molecules held together by weak *van der Waals* bonds. In comparison, the atoms in conventional semiconductors are held together by strong covalent bonds. Weak intermolecular 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 cm<sup>2</sup>/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 *Rhodospirillum rubrum*. 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 excited-state formation; and charge injection, where we have developed a theory centered on structural and energetic disorder in these soft materials.

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## 1. Neodymium for Infrared Luminescent Solar Concentrator

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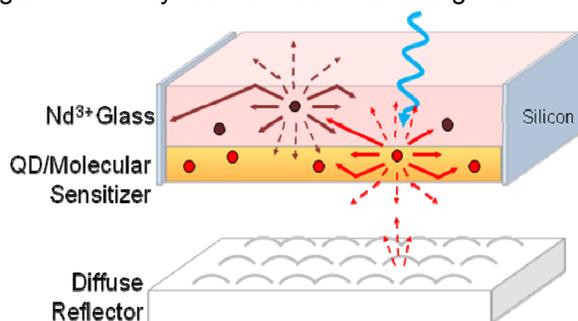
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P.D. Reusswig, C. Rotschild and M.A. Baldo

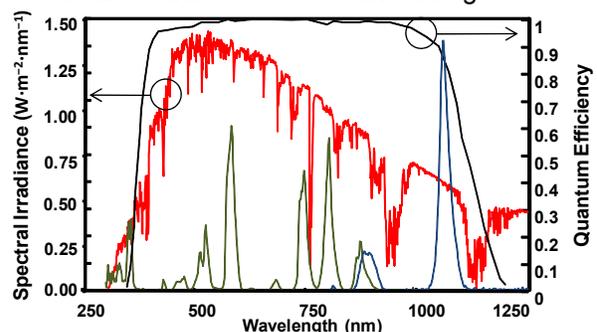
Photovoltaic solar concentrators aim to increase the electrical power obtained from solar cells. Conventional solar concentrators track the Sun to generate high optical intensities, often by using large mobile mirrors that are expensive to deploy and maintain. Solar cells at the focal point of the mirrors must be cooled and the entire assembly wastes space around the perimeter to avoid shadowing neighboring concentrators.

High optical concentrations without excess heating in a stationary system can be achieved with a luminescent solar concentrator (LSC) [1]. LSCs consist of a dye dispersed in a transparent waveguide. Incident light is absorbed by the dye and then reemitted into a waveguide mode. The energy difference between absorption and emission prevents reabsorption of light by the dye, isolating the concentrated photon population in the waveguide. Unfortunately, the performance of LSCs has been limited by two factors: self-absorption losses, and scarcity of dyes that absorb and emit efficiently in the infrared. We have previously made significant progress on the problem of self-absorption losses [2]. Now we address operation in the infrared.

Neodymium ( $\text{Nd}^{3+}$ ) is nearly the optimal infrared LSC material: inexpensive, abundant, efficient, and spectrally well matched to high performance silicon solar cells. It is a natural four level system, reasonably transparent to its own radiation, and therefore capable of generating high optical concentrations. Neodymium is stable and well-understood, because of its extensive application to high power lasers. Neodymium's one disadvantage is its relatively poor overlap with the visible spectrum, meaning that it will require sensitization in the visible spectrum as seen in Figure 2. There are numerous possibilities for sensitizing Neodymium including inorganic nanocrystals for a fully inorganic LSC or organic dye molecules as used in conventional LSC technology. A schematic of the system is shown in Figure 1. Neodymium should enable single LSC matched to silicon with efficiencies exceeding 10%.



**Figure 1:** A schematic representation of a LSC. The LSC consists of  $\text{Nd}^{3+}$  doped glass coated with a thin film sensitization layer of organic dye or quantum dot molecules and a diffuse back reflector. Solar radiation incident on the LSC is absorbed by the  $\text{Nd}^{3+}$  and reemitted as infrared radiation. The solar spectrum not absorbed by  $\text{Nd}^{3+}$  is captured and collected by the sensitization layer through radiative energy transfer to the  $\text{Nd}^{3+}$ .



**Figure 2:** A comparison between the emission and absorption spectra (a.u.) of  $\text{Nd}^{3+}$  (green and blue respectively), the AM1.5 solar radiation spectrum (red), and the external quantum efficiency of a Sunpower photovoltaic cell (black) [3].

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## 2. Luminescent Solar Concentrators for Energy Harvesting in Displays

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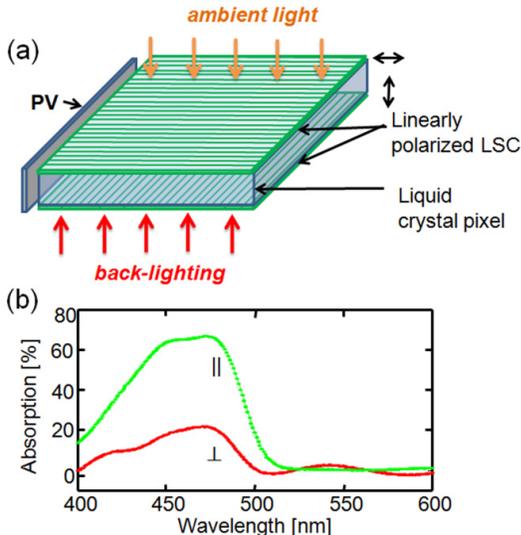
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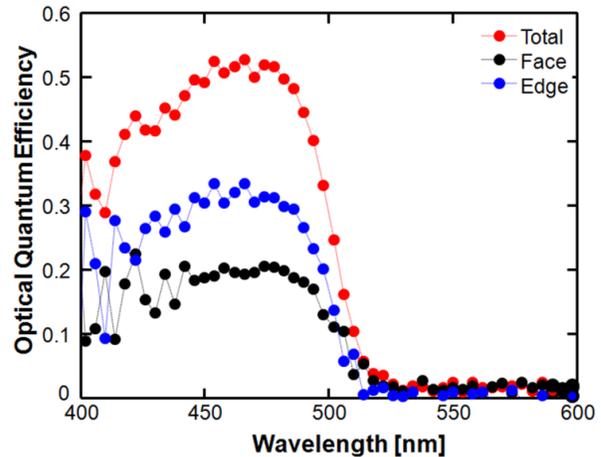
C.L. Mulder, H. Kim and M.A. Baldo

We present linearly polarized luminescent solar concentrators (LSCs) optimized for energy harvesting in displays. Current methods to increase the contrast ratio of liquid crystal and organic light emitting displays use combinations of linear polarizers to absorb and dissipate incident light. The polarizers also absorb 50% of the light emitted by the display. The inherently absorptive surface of a display, together with the trend to larger area of televisions and displays in mobile electronics, makes displays attractive candidates for energy harvesting [1]. In this project, we propose to replace the purely absorptive polarizers in displays with two linearly polarized luminescent concentrators (LSCs) [2] (Figure 1a). Conventional polarizers employ aligned molecules that absorb strongly along the long axis of the molecules or polymer strands (see for instance Figure 1b for aligned Coumarin 6 dye molecules). In our device, light emitting molecules are introduced in the polarizer that re-emit the captured photons into a waveguide. These photons travel to the edges of the waveguide by total internal reflection where they are collected by solar cells. This geometry will allow for the solar cells to be placed only in the frame of the display, leaving the entire front surface available for the display.

Figure 2 shows preliminary results for a linearly polarized LSC based on a rod-shaped dye molecule, Coumarin 6, that is aligned in the plane of the substrate using a nematic-liquid-crystal matrix. As can be observed, the optical quantum efficiency of these films, defined as the fraction of the photons incident on the face of the waveguide versus the number of photons emitted from the edges, is 30%, limited presently by relatively weak absorption. Another 20% of the photons are emitted from the face of the sample, which might hamper the contrast ratio of a display. We propose to use infrared dyes to circumvent this effect.



**Figure 1:** (a) A schematic representation of linearly polarized luminescent solar concentrators (LSC) for energy harvesting in displays. (b) Preliminary results for the absorption of aligned rod-shaped Coumarin 6 dye molecules showing a strong anisotropy between the absorption along the long axis (green) of the molecule and the short axis (red).



**Figure 2:** The Optical Quantum Efficiency, defined as the fraction of the photons incident on the face of the luminescent concentrator that is emitted from the edge for a linearly aligned system. Only 70% of the incident photons was absorbed for this device.

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### 3. High Efficiency Organic Multilayer Photodetectors based on Singlet Fission

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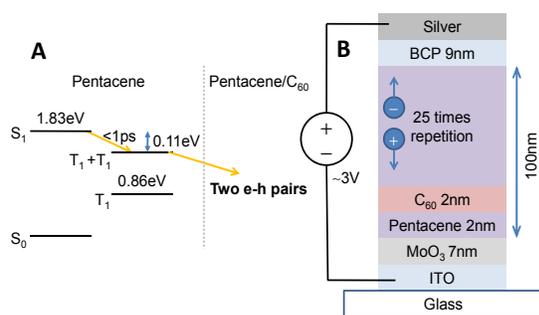
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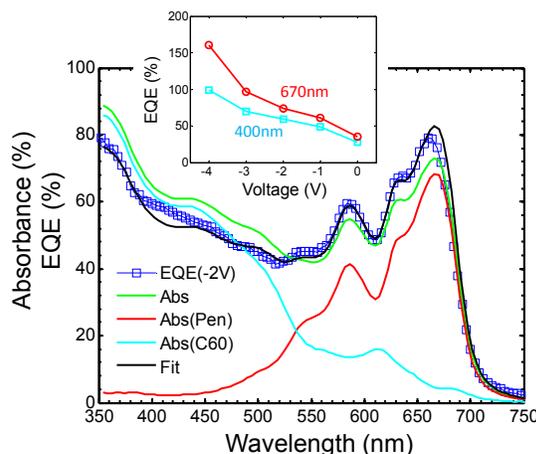
Organic optoelectronic devices are favorable for applications that require low-cost manufacturing processes or compatibility with flexible plastic substrates. For example, efficient organic photodetectors may find application in integrated organic optoelectronic circuits. Peumans *et al.* reported multilayer organic photodetectors with external quantum efficiencies of 75% across visible spectrum using an ultrathin ( $\sim 10\text{\AA}$ ) donor-acceptor (DA) junction [1]. In multilayer photodetectors, photogenerated excitons efficiently dissociate via rapid charge transfer at a close DA interface. Photogenerated carriers escape via tunneling or percolating pathways before recombination, achieving high efficiency.

We aim to enhance the efficiency of an organic multilayer photodetector by exploiting exciton fission. In pentacene, the energy of a singlet exciton (an excited state with a total spin of 0) is higher than two triplets (with a total spin of 1). Thus the spin-allowed transition of a singlet into two triplets, called singlet fission, is energetically possible and occurs rapidly ( $<1\text{ps}$ ) (See Figure 1A) [2]. If charge transfer takes place after singlet fission, one photon can lead to two carriers, doubling the efficiency.

To implement this idea, we built a multilayer photodetector composed of pentacene and  $C_{60}$  for donor and acceptor, respectively. Each layer thickness is 2nm, thin enough to allow efficient exciton separation and charge extraction. Figure 2 shows the external quantum efficiency (EQE) at a voltage bias of -2V. We fitted the EQE spectrum using optical interference modeling, obtaining the charge collection efficiencies of 1.15 and 0.85 for pentacene and  $C_{60}$ , respectively. This suggests that the EQE enhancement from singlet fission is  $\sim 30\%$ . Furthermore, photocurrent due to selective illumination of pentacene decreases by up to  $\sim 3\%$  under a magnetic field, which suppresses singlet fission. The magnetic field dependence confirms that the efficiency enhancement is due to singlet fission in pentacene/ $C_{60}$  multilayer photodetectors, widening the feasibility of exciton fission to improve various organic photodiodes such as organic light-emitting diodes, small-molecule and dye-sensitized solar cells.



**Figure 1:** A: Energy transfer process in the pentacene/ $C_{60}$  photodetector. A singlet exciton created upon photoexcitation on pentacene undergoes singlet fission, leading to two triplets. They are separated at the pentacene/ $C_{60}$  heterojunction, generating photocurrent. B: Multilayer device structure.



**Figure 2:** The external quantum efficiency (EQE) spectrum at a voltage of -2V and the absorbance of pentacene,  $C_{60}$  layers and both. The EQE was modeled with assuming the charge collection efficiencies are 1.15 and 0.85 for pentacene and  $C_{60}$ , respectively. The inset shows the EQE at 400nm and 670nm as a function of voltage.

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## 4. Exciplex Transistors

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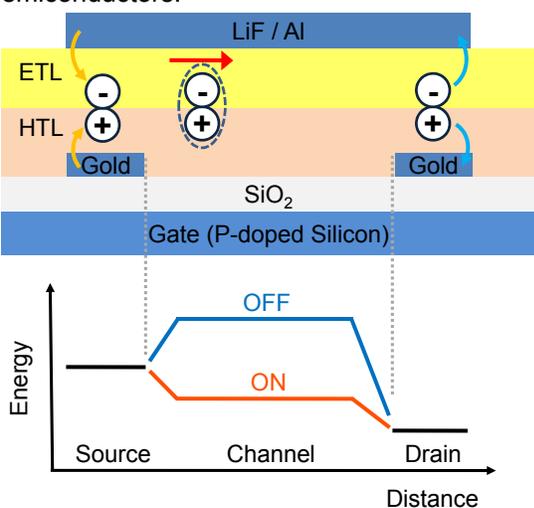
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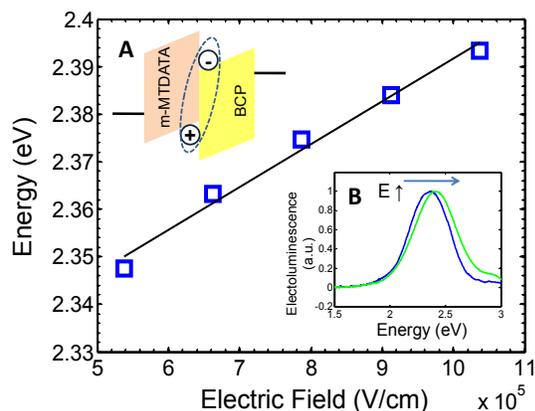
J. Lee, C.L. Mulder, M.A. Baldo

Excitons, bound pairs of electrons and holes, mediate the interconversion of charges and photons and thus can be used for an efficient interconnect between electronic circuits and optical communication. The ability to guide excitons in space can lead to an excitonic switch that directly routes an optical signal. Recently, High et al. demonstrated an excitonic transistor using indirect excitons formed in AlGaAs/GaAs coupled quantum wells at a temperature of 1.4K [1]. The much larger binding energy of excitons in organic semiconductors could enable excitonic transistors at room temperature. Furthermore, by exploiting spin-disallowed transitions in organic materials, room temperature excitons can last up to milliseconds, more than sufficient to enable exciton propagation over large distances and the operation of sample circuits.

In this work we aim to demonstrate an exciton transistor based on organic semiconductors that can operate at room temperature. Exciplexes, indirect electron-hole pairs situated on adjacent molecules, are interesting because they are spatially oriented with a defined electron-hole spacing. The exciplex energy can be controlled by applying electric fields. We propose to guide exciplexes using the energy gradient determined by external electric fields (See Figure 1). In Figure 2, we show that by changing the voltage bias over a 4,4',4''-tris-(3-methylphenylphenylamino)triphenylamine (m-MTDATA)/bathocuproine (BCP) heterojunction the energy of the exciplexes can be changed over 40meV, well above thermal energy at room temperature. We also observe that long-lived exciplexes can be created with a lifetime of several microseconds at room temperature in the phosphorescent system of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD)/ iridium(III) bis(4,6-difluorophenylpyridinato-N,C2')-picolinate (Firpic). These results open a promising route toward the spatial manipulation of exciplexes in organic semiconductors.



**Figure 1:** The device structure of the organic exciplex transistor and its energy profile under the operating condition. We control exciplex fluxes by modulating the gate bias, and thus, the potential barrier. The source creates exciplexes by injecting electrons and holes. The drain detects the exciplex fluxes by separating and extracting them with high reverse biases.



**Figure 2:** The control of the exciplex energy by external electric field. The exciplex energy is changed over 40meV in an organic heterojunction of m-MTDATA and BCP. Inset (A): the organic heterojunction diode that exhibits exciplex emission. Inset (B): the electroluminescence spectra with low and high electric field.

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## 5. Organic Solar Cells with Graded Exciton-Dissociation Interfaces

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U.S. Department of Energy

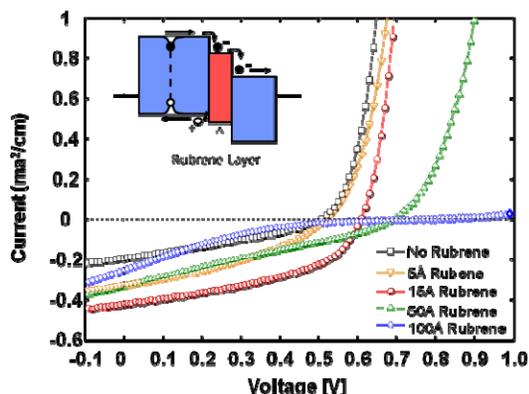
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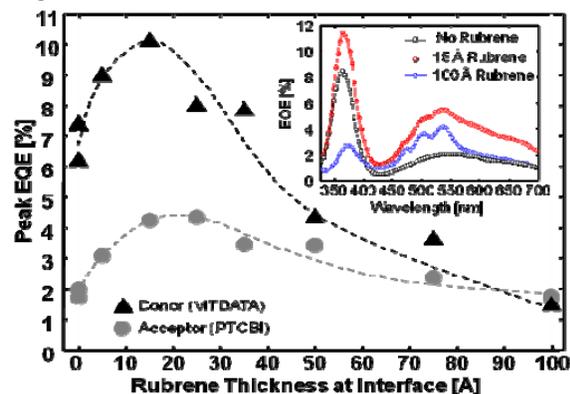
With a theoretical efficiency similar to conventional inorganic photovoltaics (PV) and the potential to be manufactured inexpensively over large areas, organic semiconductor technology offers a promising route to ubiquitous solar energy generation[1]. However, despite significant improvements in efficiency in recent years, additional progress is still needed before organic photovoltaics can compete with other photovoltaic technologies[2]. Organic heterojunction PVs suffer from recombination of separated charges at the exciton-dissociation interface[3]. Ultimately, this recombination limits the efficiency of organic PVs. Device structure modifications represent one of the most promising routes to higher efficiency.

In our work, we reduce the recombination of separated electrons and holes at the exciton-dissociation interface by introducing an additional, thin, interfacial layer sandwiched between the active semiconductor layers. The interfacial layer in this architecture creates a cascade energy structure at the exciton-dissociation interface as shown in the inset of Figure 1. Previous efforts to add an interfacial layer in organic PVs have suffered due to poor materials selection [4,5] Reducing recombination losses yields increases in both open circuit voltage ( $V_{OC}$ ) and short circuit current ( $J_{SC}$ ) leading to higher power conversion efficiencies as illustrated in Figure 1. We are studying how the energy level alignment of the interfacial layer impacts recombination and developing criteria for optimal interface material design and selection.

As illustrated in Figure 2, we find devices with too thin an interfacial layer demonstrate limited improvements in charge collection due to partial layer coverage. Devices with interfacial layers that are too thick suffer from carrier transport problems in the interfacial layers. Determining the optimal interfacial layer thickness promises to give greater insight into the physical mechanism of charge carrier recombination at the exciton dissociation interface in organic PVs.



**Figure 1:** Current–Voltage characteristics for devices with and without a Rubrene interfacial layer. Devices with a thin layer of Rubrene at the exciton-dissociation interface exhibit increased short circuit current and increased open circuit voltage. However, at large interfacial layer thicknesses, the current decreases.



**Figure 2:** Devices with thin interfacial layers exhibit higher external quantum efficiencies. The optimal layer thickness is approximately 15Å. The interfacial layer reduces recombination of separated charges at the exciton-dissociation interface.

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### Book Chapters

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