

## Soft Semiconductor Devices

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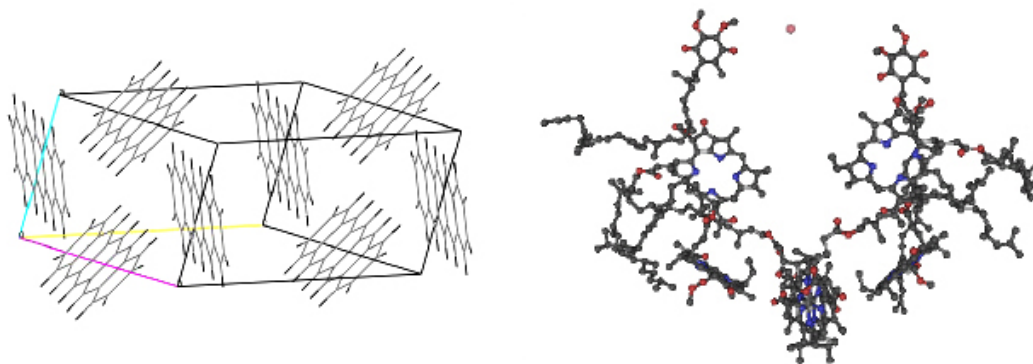
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Our group works with soft semiconductors. These are materials comprised of molecules held together by weak *van der Waals* bonds. In comparison, the atoms in conventional semiconductors are held together by strong covalent bonds. Weak intermolecular 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  $2 \text{ cm}^2/\text{Vs}$  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. Extrafluorescent Electroluminescence in Organic Light Emitting Devices

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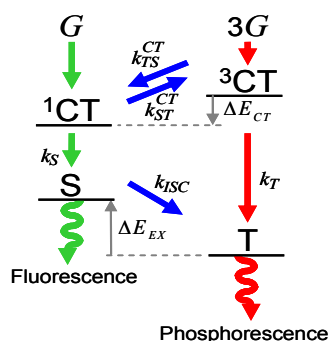
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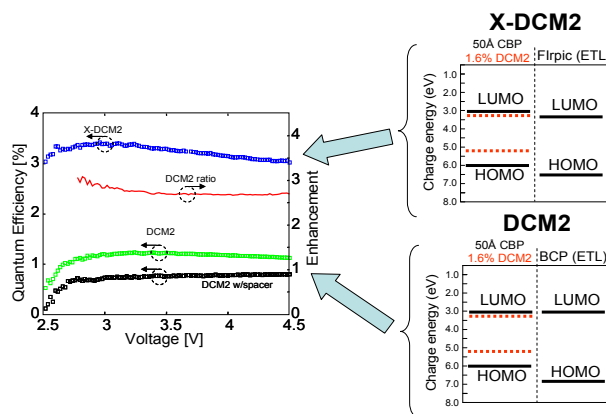
M. Segal, M. Singh, K. Rivoire, S. Difley, T. Van Voorhis, M.A. Baldo

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<sup>1</sup>. 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<sup>1</sup>. We have demonstrated a technology for raising the efficiency of fluorescent OLEDs to approach that of phosphorescent OLEDs<sup>2</sup>. 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 Flrpic and the fluorescent material DCM2 (Figure 2).



**Figure 1:** Rate diagram for exciton formation. Triplet ( $^3CT$ ) and singlet ( $^1CT$ ) exciton precursor states form triplet (T) and singlet (S) excitons at rates  $k_S$  and  $k_T$ . Extrafluorescence occurs when the CT state mixing rate  $k_{TS}^{CT}$  is made large with respect to  $k_T$ , and the exciton mixing rate  $k_{ST}^{CT}$  is low. While  $\Delta E_{EX} > 0$ , we have calculated and measured  $\Delta E_{CT} < 0$ , so that  $k_{TS}^{CT} > k_{ST}^{CT}$ , favoring singlet production.



**Figure 2:** Demonstration of an extrafluorescent OLED, or X-OLED ("X-DCM2"). The mixing molecule iridium(III) bis [(4,6-difluorophenyl)pyridinato-N,C<sup>2'</sup>] picolinate (Flrpic) is used as an electron transport layer, so that exciton precursor states are preferentially mixed. The laser dye 4-(dicyanomethylene)-2-methyl-6-[(4-dimethylaninostyryl)-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 Flrpic is replaced with 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), which has low mixing rates, shows a 2.7 $\times$  lower efficiency. A second control device ("DCM2 w/ spacer"), wherein the Flrpic layer is moved away from the emissive zone by 100 Å of BCP, shows no efficiency enhancement.

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## 2. High Efficiency Organic Solar Concentrators

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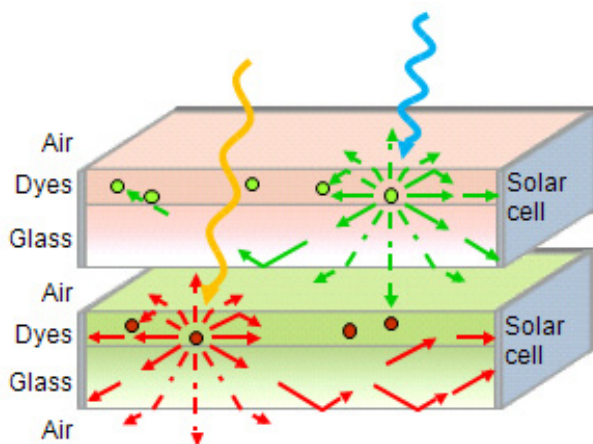
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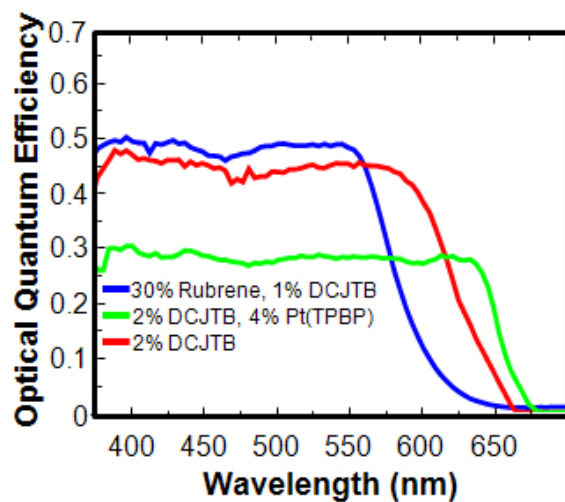
J.K. Mapel, M.J. Currie, T.D. Heidel, S. Goffri, M.A. Baldo

Organic solar concentrators (OSC) are a class of luminescent solar concentrators<sup>1</sup> that exploit advances in thin film organic semiconductor technology and low cost manufacturing processes to create efficient, large area optical concentrators for inorganic solar cells. OSCs are dye-based light concentrators that operate through successive absorption and emission of light into confined modes of a light guide to a photovoltaic cell for electrical conversion; see Figure 1. OSCs hold the potential to reduce the cost per generated watt of power for solar power transduction systems by separating the optical and electrical parts of a solar cell. Previous demonstrations have shown limited performance due to the high probability of re-absorption of confined light, which lowers the guided transport efficiency<sup>2</sup>.

We have fabricated single and tandem waveguide organic solar concentrators with quantum efficiencies exceeding 50% and projected power efficiencies up to 6.8%. Near field energy transfer,<sup>3</sup> solid state solvation,<sup>4</sup> and phosphorescence<sup>5</sup> are employed within a thin film organic coating on glass to substantially reduce self absorption losses, enabling flux gains exceeding  $F = 10$ , meaning that a photovoltaic cell attached to the concentrator generates approximately  $10 \times$  the power of the photovoltaic cell without optical concentration. Flux gains of  $F > 10$  in organic solar concentrators should enable the economical use of high performance photovoltaic cells in low cost systems.



**Figure 1:** Physical processes leading to energy conversion in an OSC. Photons are absorbed by a luminescent chromophore embedded within or coating a waveguide. The chromophore can re-radiate a photon of equal or lesser energy, and some portion of the emitted radiation will be confined in the waveguide by total internal reflection. Some fraction of the trapped light will travel to another face of the guide which has a smaller cross sectional area, where a photovoltaic element resides for the collection of the concentrated light.



**Figure 2:** Optical quantum efficiency (OQE) spectra at a geometric gain of 3. The OQE is the fraction of incident photons that are emitted from the edges of the single waveguide OSC. In blue, the OSC utilizes near field energy transfer from the AIQ3 matrix and rubrene dopants to pump emission through DCJTJB, a laser dye. In green, light is absorbed by AIQ3, rubrene, and Pt(TBTP) and phosphoresces from Pt(TBTP). The energetic separation between absorption and emission in these OSCs enable higher flux gains than single materials systems.

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### 3. Luminescent Solar Concentrators Employing Phycobilisomes

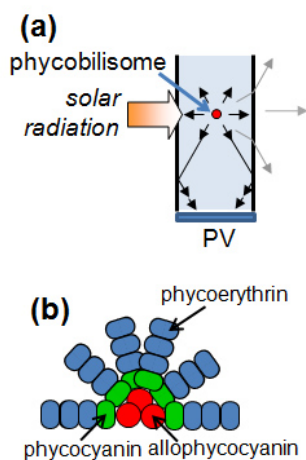
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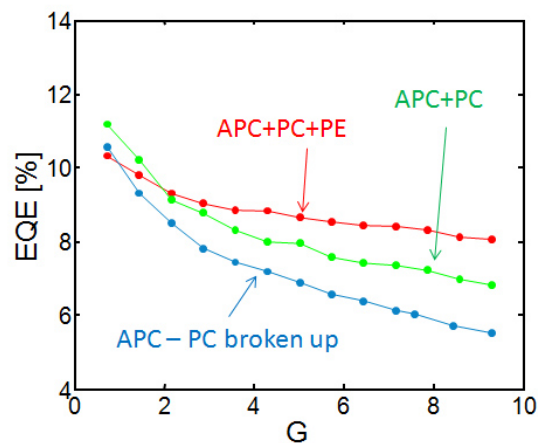
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We present luminescent solar concentrators (LSCs) employing phycobilisomes from cyanobacteria. Luminescent solar concentrators are non-tracking optical collectors that increase the effective light capture area of a solar energy conversion device, while reducing the size of the expensive photovoltaic (Figure 1a)<sup>1</sup>. The geometric gain,  $G$ , is an important metric of LSC performance. It is defined as the ratio of the light collection area to that of the photovoltaic. By increasing  $G$ , the total power per unit cost can be increased. But at large geometric gains, photons trapped in the LSC are subject to self-absorption losses that degrade performance. In this work we employ a biological photosynthetic system to study and circumvent the effects of self-absorption.



**Figure 1:** (a) A schematic representation of a luminescent solar concentrator. (b) A schematic representation of a phycobilisome. These antenna complexes consist of a core of allophycocyanin (APC) that is connected to radial rods of phycocyanin (PC) billins and/or phycoerythrin (PE) billins.



**Figure 2:** External quantum efficiency at the peak absorption wavelength vs. geometric gain of LSCs employing phycobilisomes as the optical dye system. The complexes having the largest Stokes' shift, the phycobilisomes with APC, PC and PE (red), showed the least roll-off with increasing  $G$ . The complexes with APC and short rods of PC exhibited a larger roll-off, while the dye system for which the internal Förster transfer was shut off (blue) had the poorest performance with increasing  $G$ .

Phycobilisomes are macromolecular antenna complexes that are responsible for collecting light in photosynthetic systems<sup>2</sup> (see Figure 2b for a schematic representation). Each of these proteins serves as a scaffold for antenna pigment molecules, also known as chromophores. The chromophores are arranged through self-assembly in cascading Förster energy transfer pathways that couple short wavelength chromophores at the extremities of the complex to long wavelength chromophores at the core of the complex, thereby enhancing the Stokes shift between absorption and emission. We have characterized the optical absorbance and photoluminescence spectra and efficiencies of several different types of phycobilisomes, and compared their performance when used as the active dye in a liquid or solid state LSC.

The first type of phycobilisomes consisted of allophycocyanin (APC) with short rods of phycocyanin (PC) proteins (green). The second type consisted of APC with long rods of PC and PE proteins (red), which showed an increased Stokes shift in comparison to the first type of phycobilisomes. This increase in rod length was accompanied by a better performance with geometric scaling, reflecting the suppression of the self absorbance losses achieved by reducing the overlap between the emission and absorption spectra. When the internal Förster energy transfer was shut off by breaking up the phycobilisomes into their loose protein complexes, the LSC showed an even larger drop in efficiency with increasing geometric gain (blue). At  $G=9.3$ , the efficiency was 50% lower in the broken complexes than the complete APC + PC + PE phycobilisomes. These results suggest that using resonant energy transfer from higher to lower energy chromophores might provide a route to reducing self-absorption losses in LSCs.

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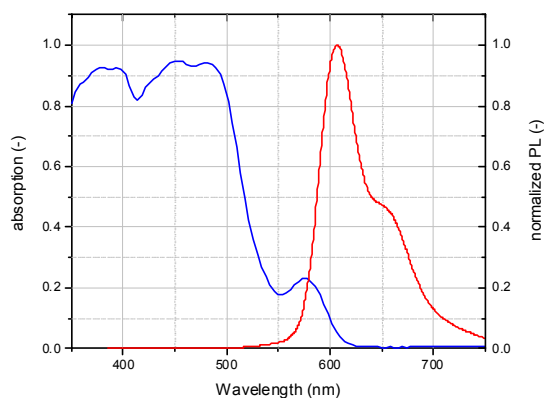
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## 4. Solution processed organic solar concentrators

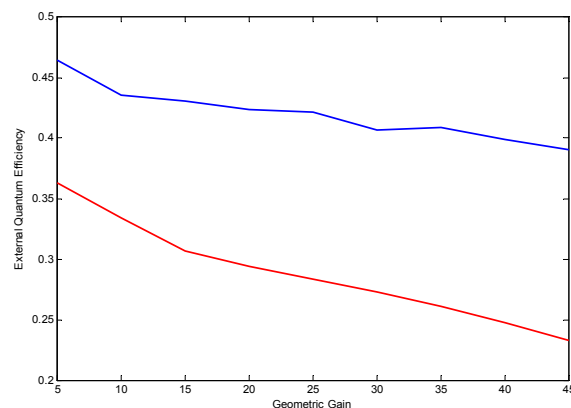
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S. Goffri, M. Currie, J. Mapel, M. Baldo

Solar energy is a clean and abundant energy source that promises to provide sustainable and economical sources of renewable power. Solar power generation is growing; however it is still more expensive than fossil fuel based electricity sources. To address the cost of solar power we are developing organic solar concentrators (OSCs) as an alternative to conventional solar concentrators. OSCs do not require tracking of the sun or cooling of the solar cells and they require a smaller area of photovoltaic (PV) cells for the same power output.



**Figure 1: Normalized absorption and emission spectra of perylene-based OSC film.** The ratio between the peak absorption coefficient and the absorption coefficient at the emission wavelength provides a measure of the self absorption in an OSC film.



**Figure 2: OSC efficiency as a function of geometric gain,  $G$ .** With increasing  $G$ , photons must take a longer path to the edge-attached PV, increasing the probability of self absorption losses. Blue: perylene composite system, red: single DCJT based system

An OSC is comprised of organic chromophores to absorb sunlight and re-emit photons into a planar waveguide with PV cells attached to the edges<sup>1-4</sup>. The performance of an OSC is largely limited by self absorption of the emitted photons by organic chromophores due to an overlap between their absorption and emission. We have investigated the used of novel chromophores and their compositions to reduce the overlap between emission and absorption. We coat glass flat plate collectors using solution processing resulting in low cost thin film solar collectors. This enables us to use recent advances in

organic optoelectronics and apply near field energy transfer to reduce the required concentration, and hence the self absorption of the emissive dye<sup>5</sup> (Figure 1).

The ratio of the area of the concentrator to the area of the PV cell is the geometric gain,  $G$ . Figure 2 shows the external quantum efficiency (EQE) as a function of geometric gain for different system measured at  $\lambda = 489$  nm for the composite perylene based fluorescent system compared to the conventional 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran(16) (DCJTB)-based fluorescent system, measured at  $\lambda = 532$  nm. The DCJTB-based OSC shows the strong self absorption. The self absorption is lower in the composite perylene based OSC, consistent with the spectroscopic data in Figure 1.

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## 5. Self-absorption measurements of photoluminescent efficiency of thin film organic semiconductors

### Sponsorship

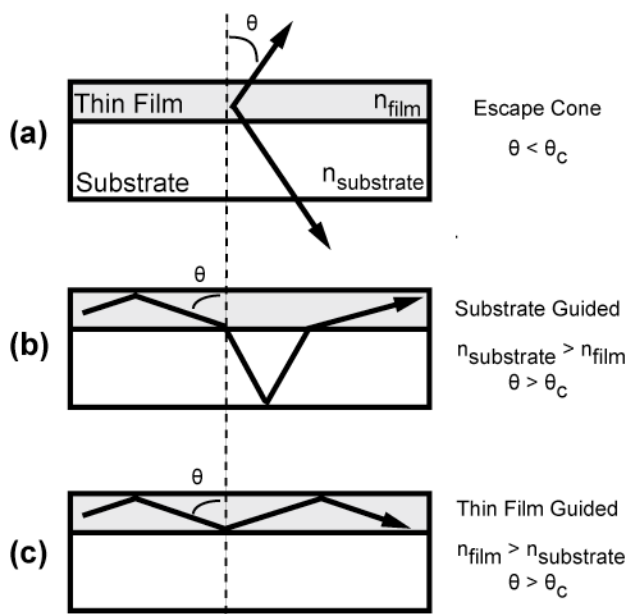
DARPA/AFOSR, NSF Nanoscale Interdisciplinary Research Team

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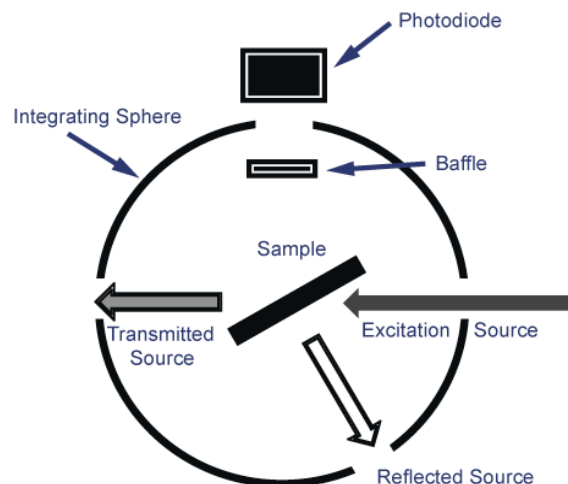
M. Currie, J. Mapel, S. Goffri and M. Baldo

Characterizing the photoluminescent (PL) efficiency of thin films is essential to ascertaining the performance limits of light-emitting devices. The PL efficiency is the fraction of photons emitted per photon absorbed. Integrating sphere measurements are a common method used to measure PL efficiencies, but we show that the substrate must possess an index of refraction greater than that of the thin film to be valid<sup>1-3</sup>. The substrate index restriction is demonstrated by measuring the PL of commonly used organic materials on low and high index substrates. Measurements on low index substrates exhibit optical losses due to thin film waveguiding that result in an errors up to 50%. This effect is pronounced for low Stokes-shift films with large self absorption. Figure 1 depicts the three light-paths for a thin film deposited on a transparent substrate, and Figure 2 shows the measurement set-up.

To illustrate substrate effects on PL measurements, three films were prepared on high ( $n = 1.80$ ) and low ( $n = 1.52$ ) index glass substrates that are 25mm x 25mm x 2mm in size. A neat 200-nm-thick film of tris (8-hydroxyquinoline) aluminum (AlQ<sub>3</sub>), and a 200-nm-thick film of AlQ<sub>3</sub> and rubrene at (50% v/v) were thermally deposited. The PL efficiency of AlQ<sub>3</sub> is 29.2% and 28.1% on high and low index substrates respectively. The error due to thin film waveguiding on the low index substrate is low due to the large Stokes shift and low self absorption in AlQ<sub>3</sub>. The PL efficiency of rubrene, however, is 43.3% and 30.2% on high and low index substrates, demonstrating a significant error if the PL efficiency measurement is performed on low index substrates.



**Figure 1:** Light-paths for a thin film on a transparent substrate: There are three potential pathways for light to travel within, and eventually leave, a thin film deposited on a transparent substrate: (a) escape cone light, (b) substrate guided light and (c) thin-film guided light. Light that is guided in the thin-film will largely be reabsorbed and underestimate PL in these measurements.



**Figure 2: Schematic of Integrating Sphere Measurement:** Shown is the configuration used to measure PL within an integrating sphere. The sphere and sample are aligned such that the transmitted and reflected beam of the excitation source leave the sphere through an outlet port. The baffle within the integrating sphere prevents the photodiode from sensing direct photoluminescence from the sample.

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## 6. Monochromatic Organic Solar Cells

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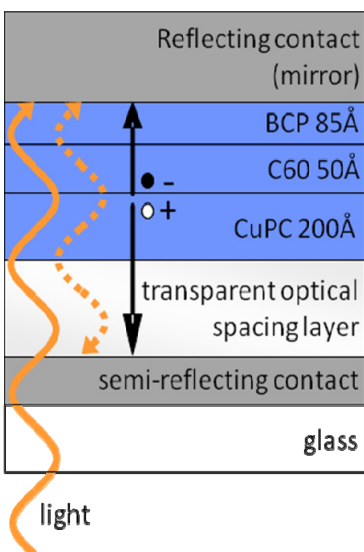
T.D. Heidel, M.A. Baldo

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. However, organic PVs are constrained by a tradeoff between exciton diffusion and optical absorption: as absorption is increased by fabricating thicker devices, the efficiency of charge separation decreases since excitons cannot reach the charge separation interface. Ultimately, this tradeoff limits the portion of the solar spectrum that an optimized organic PVs can harness.

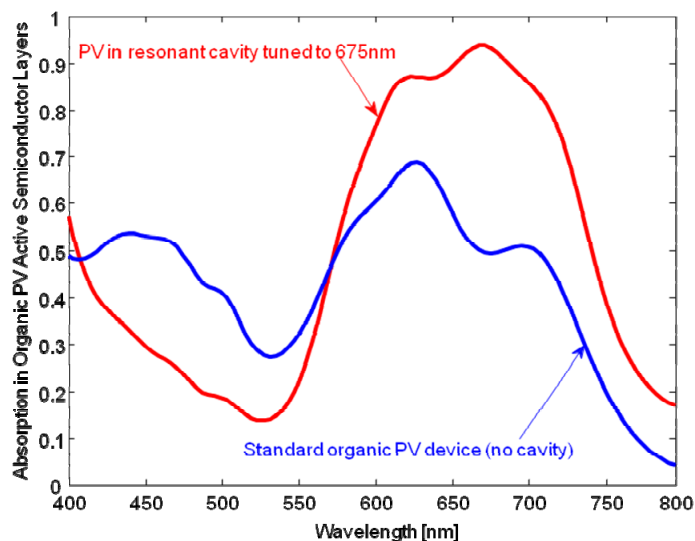
In our work, we increase absorption in organic solar cells within the limits of exciton diffusion by fabricating cells inside a resonant microcavity. As illustrated in Fig. 1, the resonant cavity devices have a semi-reflecting bottom contact and a fully reflecting mirror contact on the back. The layers between the contacts consist of a transparent optical spacing layer and a thin organic solar cell. Modulating the thickness of the transparent spacing layer allows the increase in absorption to be tuned across the entire visible spectrum. The reflectivity of the contacts can also be engineered to modulate the width of the absorption resonance. Fabricating a thin organic solar cell within the cavity allows charge separation efficiencies to reach 100%. Modeling indicates absorption in the organic semiconductor layers can be

increased as much as 91% relative to absorption in optimized organic PVs with no resonant cavity, see Fig. 2.

Resonant cavity monochromatic organic solar cells have applications in tandem organic solar cells and advanced solar concentrator designs. Organic tandem solar cells attempt to overcome the tradeoff between exciton diffusion and absorption by utilizing multiple heterojunctions that absorb strongest in different regions of the solar spectrum. High efficiency, monochromatic solar cells could increase the efficiency of these individual multiple heterojunctions. The efficiency of many solar concentrator designs could also be maximized by using solar cells optimized for specific regions of the solar spectrum.



**Figure 1:** Resonant cavity organic solar cells consist of a thin organic PV and transparent optical spacing layer fabricated between reflecting contacts.



**Figure 2:** The resonant cavity enhances absorption strongly in one region of the solar spectrum. The absorption peak can be tuned across the entire visible spectrum. Combining two or more cavity organic PVs will allow for enhancement across the entire visible.

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## 7. Charge Recombination in Small Molecular Weight Organic Solar Cells

### Sponsorship

MARCO MSD

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J. Lee, M. Segal, M.A. Baldo

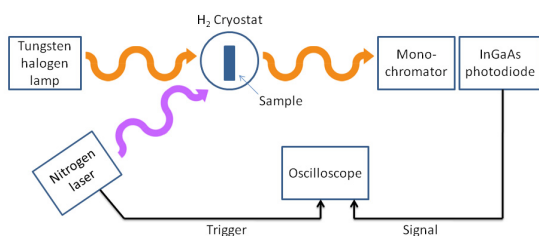
Organic solar cells promise efficient and cost-effective solar energy generation from low-cost materials and a low-temperature manufacturing process compatible with flexible plastic substrates. In organic photovoltaic cells, photon absorption creates a bound electron-hole pair, or exciton. The excitons diffuse toward the donor-acceptor (DA) heterojunction. The energy offset at the DA interface dissociates the strongly bound excitons in organic molecules with near unity efficiency. Excitons are separated into charge transfer (CT) states, which are bound electron-hole pairs across the DA junction<sup>1</sup>. The CT states can be dissociated into free carriers which ultimately generate photocurrent or they may recombine into low-energy states such as ground states or triplet excitons. The recombination of CT states can cause a



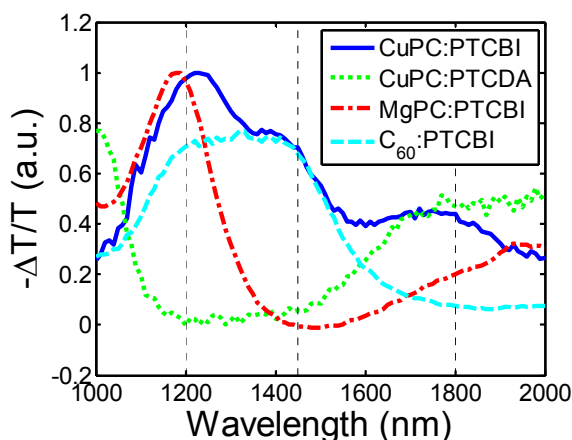
substantial loss in the photovoltaic efficiency depending on the CT state lifetime and the operating voltage bias.

We perform transient absorption spectroscopy to study the charge recombination dynamics of small molecular weight organic solar cells. The transient absorption setup was built as illustrated in Figure 1. The samples are held at the temperature of 50K. We investigate thin film bulk heterojunction of the archetype organic solar cell molecules, copper phthalocyanine (CuPC) and 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PTCBI). To assign the absorption wavelength of CuPC cations and PTCBI anions, the photoinduced absorption (PIA) spectra of related organic molecules are compared as shown in Figure 2. The CT states in CuPC/PTCBI live up to milliseconds. Also, we found that the states featuring the broad peak at 1450nm decay much faster than the CT states with the lifetime of  $\sim 150\mu\text{s}$ . We tentatively assign the state at 1450nm to the PTCBI triplet exciton. The evidence of triplet excitons implies that PTCBI triplet formation is an importance source of recombination loss in CuPC/PTCBI photovoltaic cells.

Further study of organic heterojunction thin films is expected to reveal the physical origin of charge recombination and should contribute to reducing the recombination loss in organic photovoltaic cells.



**Figure 1:** Schematic diagram of the transient absorption setup. The nitrogen laser creates excitons which we subsequently dissociated into CT states. Then, the CT states absorb the white light provided by the tungsten halogen lamp. The photodiode detects the change of the transmitted light at the selected wavelength. The setup probes the decay dynamics of CT states.



**Figure 2:** The PIA spectrum of organic bulk heterojunction thin films that are studied in this work. PTCDA: 3,4,9,10-perylenetetracarboxylic dianhydride, MgPC: magnesium phthalocyanine.

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## 8. The density of states in thin film copper phthalocyanine (CuPC) as measured by alternating current Kelvin Force Probe Microscopy (AC-KFPM)

### Sponsorship:

DuPont-MIT Alliance

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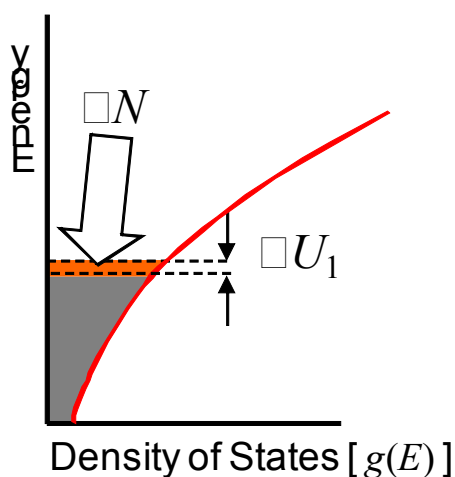
Kemal Celebi, Kaveh Milaninia, Priya Jadhav and Marc Baldo

The rational design of organic electronic devices is presently complicated by our inability to directly measure the energetic disorder in the semiconductor. Consequently, many studies have sought to obtain the density of states (DOS) in organic semiconductors. Unfortunately, existing techniques such as ultraviolet photoelectron spectroscopy or thermally stimulated luminescence either lack sufficient

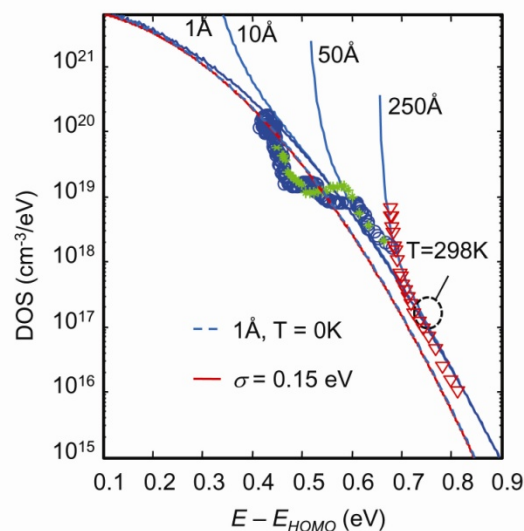
resolution or require complicated models for interpretation. The KPFM technique can measure DOS at a resolution of at least 1:1000. We improve upon the original KPFM technique of Tal *et al.*<sup>1</sup> and investigate its limitations. We employ alternating current (AC-KPFM) to reduce noise, and minimize hysteresis due to charge trapping at the semiconductor/insulator interface. Finally, we model space charge phenomena that distort the data and we demonstrate that the AC-KPFM technique is applicable beyond the low inversion density regime analyzed by Tal *et al.*

Kelvin probe force microscopy (KPFM) employs a scanning probe to measure the local surface potential difference between the probe tip and a substrate. We perform the measurements on CuPC (hole transporter) organic thin film transistors (OTFT). The source and drain were grounded to maintain equilibrium and a constant Fermi level in the channel. Then, the gate voltage is modulated, shifting the energy levels in the semiconductor. If the DOS at the Fermi level changes, the charge density in the channel must also change. Measurements of the surface potential detect this charging, and in turn the DOS.

Devices were made with and without octadecyltrichlorosilane (OTS) passivation of the oxide surface. Consistent with previous observations, the magnitude of the threshold voltage was significantly reduced by OTS passivation. OTS treatment also substantially reduces hysteresis suggesting that passivation of the oxide surface reduces the trap density at the SiO<sub>2</sub>-CuPC interface.



**Figure 1:** Changes in the charge density in the channel change the surface potential  $U$  by an amount determined by the density of states.



**Figure 2:** The density of states calculated from AC and/or DC measurements on OTFTs of various thicknesses. The sharp increase in the DOS is due to the screening effect of accumulated charge. The solid lines are the result of simulations for a Gaussian density of states for films of the thicknesses shown.

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## 9. Cathode metal diffusion and doping in organic light emitting devices

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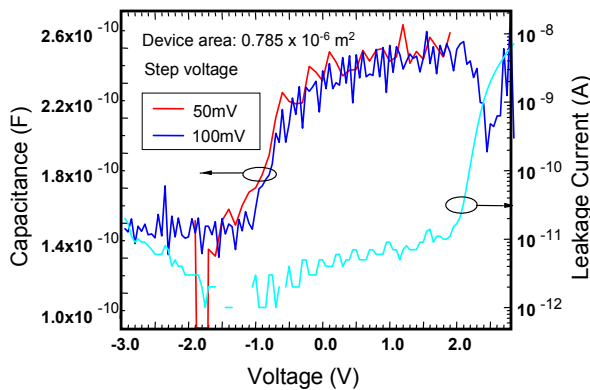
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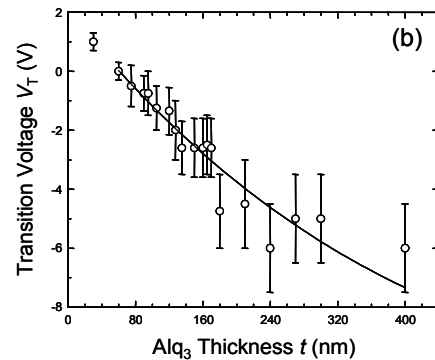
Priya Jadhav, Benjie Limketkai and Marc Baldo

Organic semiconductors employed in organic light emitting devices (OLEDs) are typically assumed to be intrinsic. There are suggestions, however, that organic semiconductors may actually be doped within OLEDs<sup>1</sup>. It is important to resolve the origin of the apparent doping phenomena because: (i) doping apparently determines the operating voltage and quantum efficiency, and (ii) compositional control is a prerequisite for the rational design of stable OLEDs. Indeed, one notable characteristic – the retained negative charge in tris(8-hydroxyquinoline) aluminum (AlQ<sub>3</sub>)-based OLEDs – has been directly correlated to degradation<sup>1</sup>. The retained charge undergoes a transition from negative to positive that is linearly related to the loss of luminance.

We demonstrate that one significant origin of impurities is cathode metal diffusion. Cathode materials diffuse into the bulk of the AlQ<sub>3</sub>, introducing free charges if the cathode material reacts with neighboring AlQ<sub>3</sub> molecules. In addition, the presence of reactive cathode materials stabilizes electrons on other nearby AlQ<sub>3</sub> molecules, forming electron traps. Thus, the diffusion of cathode species is associated with both free charge and traps in AlQ<sub>3</sub>. We probe charge stored in electron traps using capacitance-voltage<sup>2</sup>. In bilayer OLEDs consisting of AlQ<sub>3</sub> and a hole transport layer (HTL), holes are confined at the AlQ<sub>3</sub>/HTL interface. Thus, the capacitance is determined by the thickness of the AlQ<sub>3</sub>. Under reverse bias, the holes are extracted and the capacitance is determined by the thickness of the entire OLED. In the absence of stored charge, the transition in the observed capacitance should occur at the built-in potential,  $V_{Bi}$ . But we observe transitions at more negative potentials, confirming the presence of fixed negative charge. The negative charge density calculated from these measurements decreases with cathode distance from the interface and exhibits a clear dependence on the cathode material, confirming that the cathode is the origin of the fixed charge.



**Figure 1:** Quasi-static capacitance-voltage measurement for hetero-layer AlQ<sub>3</sub>/HTL device. As the biasing voltage is reduced from forward to reverse bias the capacitance changes from  $C_{AlQ_3}$  to that of the series sum of  $C_{AlQ_3}$  and  $C_{HTL}$ . This transition would be expected to occur at  $V = V_{Bi}$ , which is the difference in work functions of the two electrodes. But instead, it occurs at a voltage further into reverse bias, revealing the existence of trapped negative charge in the AlQ<sub>3</sub> layer.



**Figure 2:** The thickness dependence of the capacitive transition voltage. It is fit by a model assuming that the fixed charge density decreases exponentially with distance from the cathode.

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## 10. Excitonic Surface Plasmon Resonance Biosensor

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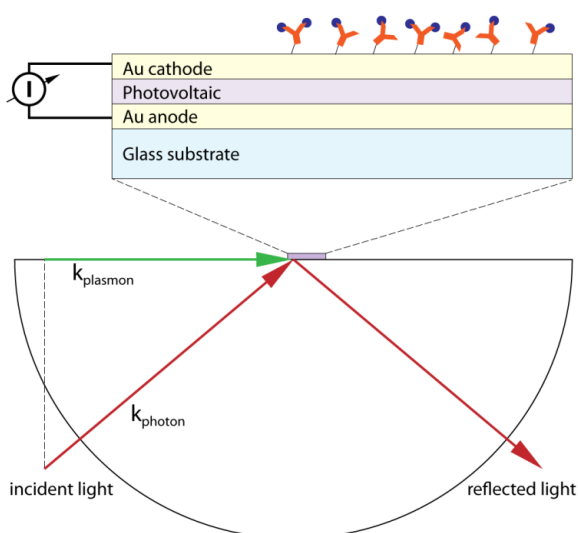
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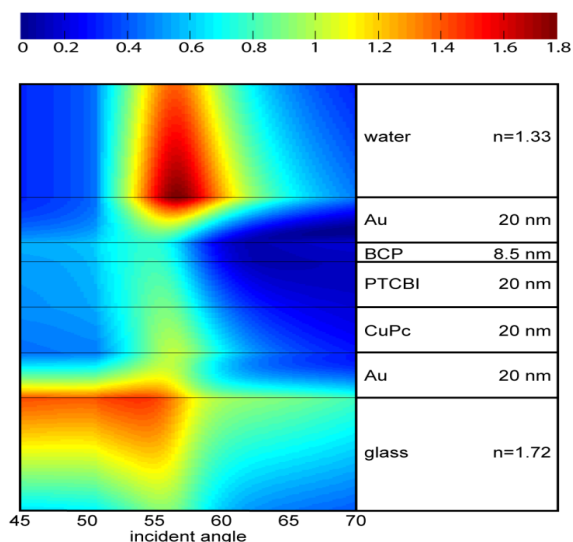
M. Bora, K. Celebi, M. A. Baldo

The main disadvantages of surface plasmon resonance (SPR) biosensors are their high cost and lack of portability. We propose to solve these deficiencies by integrating a plasmon source and detector with microfluidic components for a compact, inexpensive instrument. Surface plasmons are electromagnetic waves that propagate along a metal dielectric interface. SPR biosensors exploit the sensitivity of surface plasmons to changes in the dielectric constant immediately adjacent to a metal surface. The angular reflectivity of the metal film has a sharp plasmon resonance feature that shifts when higher dielectric constant biomolecules bind to the surface. The high sensitivity of the SPR is complemented by real time, label free detection that provides additional information on the chemical kinetics of the interaction.

Here, we propose a novel surface plasmon biosensor that uses a plasmonic mode bound to the anode and cathode of a thin film organic photovoltaic (PV). The sensor design combines the sensitivity of SPR with a novel plasmon conversion mechanism in the thin film organic PV. The plasmon resonance is detected directly in the near field by coupling the electric field of the plasmon modes with exciton formation within the adjacent PV cell. The splitting of excitons into holes and electrons at the organic heterojunction interface of the PV cell generates a short circuit photocurrent modulated by the plasmon resonance condition set by the electric properties of the thin film structure and adjacent medium. Measurements of reflected power and photocurrent have a strong dependence on incident light angle similar to typical plasmon resonance curve. Agreement between this data and numerical simulations, prove the existence of plasmon modes bound to the metal layers. The photocurrent generated by plasmon absorption in the photovoltaic is considerably larger than the optical absorption background. For sensing purposes, the photocurrent measured in our devices and reflectivity measured in standard SPR instrumentation are interchangeable and yield comparable sensitivity upon binding of biological species on the surface. We expect that this approach may replace large bench top SPR sensors by sub  $1\text{mm}^2$  devices compatible with array processing of biological samples.



**Figure 1:** Device structure and experimental setup. P-polarized light falls on the photovoltaic structure at an angle controlled by the rotation of a hemi-cylindrical prism. Reflected power and current generated between the gold anode and cathode are monitored with respect to either incident angle or time for binding events on the top gold surface.



**Figure 2:** Relative amplitude of the electric field for the transverse magnetic mode. Numerical simulations highlight the existence of a bound mode spanning the whole device structure. Plasmon excitations have the highest amplitude on the top surface of the cathode layer and extend in the organic layers of the photovoltaic.

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## 11. Carbon Nano-Switches for Low-Leakage Circuit Applications

### Sponsorship

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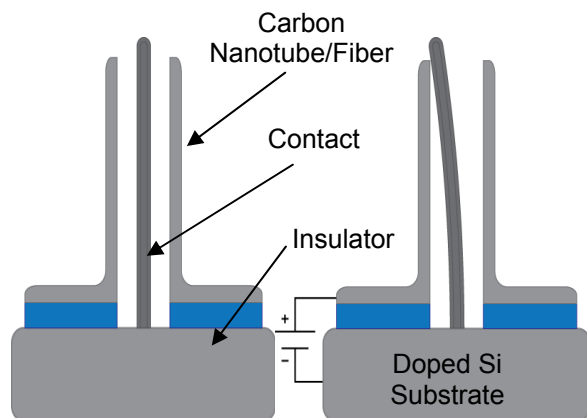
### Project staff

K.M. Milaninia, C.E. Schmitt, A.I. Akinwande, M.A. Baldo, A.P. Chandrakasan

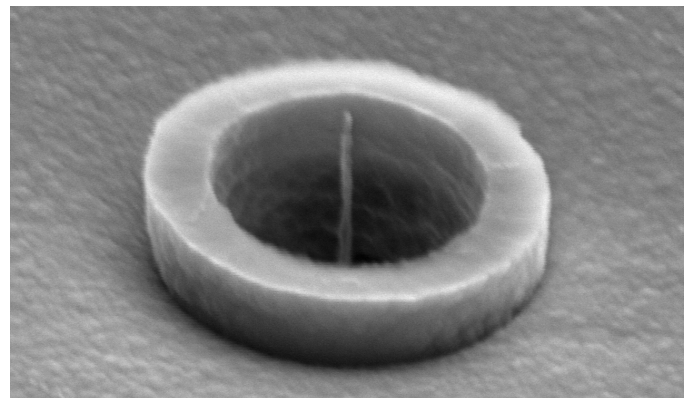
Nanoelectromechanical switches (NEMS) exhibit minimal leakage current in the off state. Consequently, they may find application in low power electronics. This work focuses on the fabrication of a vertically oriented nano-switch using a carbon fiber or nanotube as the active component. The device schematic is shown in Figure 1, and Figure 2 shows an SEM image of the self-aligned fabrication process used to create the nano-switch<sup>1</sup>. The device consists of a carbon nanotube/fiber grown directly on a highly doped silicon substrate between two contacts which are electrically isolated from the substrate by an insulator. The device is actuated when a voltage is applied between the substrate and one of the contacts. This causes the nanotube to be pulled into and eventually make physical contact with one of the contacts and allows current flow between the substrate and the contact.

One of the primary benefits of the nano-switch is that it has extremely low leakage current because a physical gap separates the nanotube from the contact during the off state. One possible application that takes advantage of the reduced leakage is power gating idle circuit blocks. The nano-switch is connected as a header switch between the power supply and the load circuit. During normal operation, the nano-switch acts as a short circuit and power is supplied to the load circuit. When the circuit is not in use, the nano-switch is opened and the supply voltage is disconnected to reduce power consumption. This technique is similar to power gating with a high threshold CMOS device, but the nano-switch provides extra power savings because it has even less leakage current.

A test chip has been designed to quantify the power savings of the nano-switch for this power gating application. The chip also implements proof-of-concept SRAM and reconfigurable interconnect circuits that explore other potential benefits of the nano-switch.



**Figure 1:** Left) Schematic of a vertically oriented carbon nano-switch. Right) Carbon nano-switch upon actuation using an applied voltage between the substrate, i.e. tube, and a contact.



**Figure 2:** SEM image of a carbon nano-based field emitter produced by the self-aligned fabrication process<sup>1</sup>.

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## 12. Inkjet Stimulation of Neurons

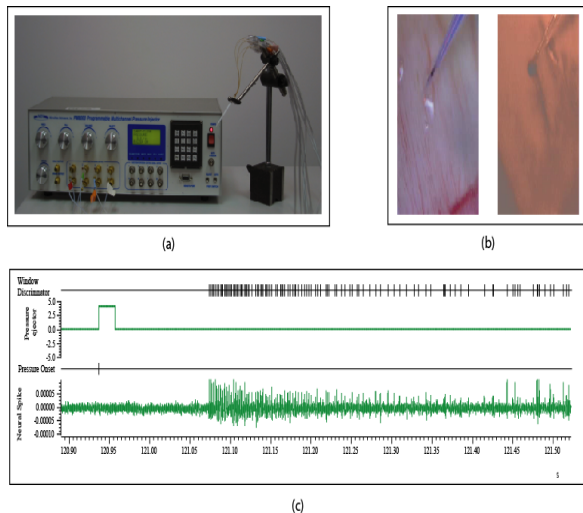
### Project Staff

L. Theogarajan and M. A. Baldo

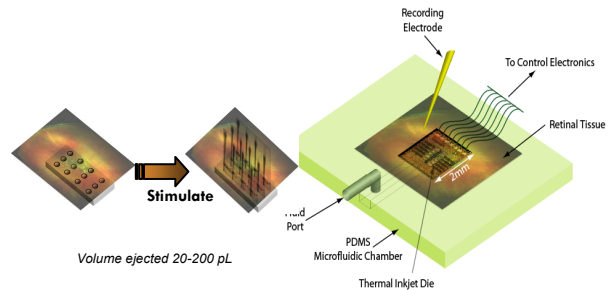
Electrical excitation is the standard method for stimulating neural tissue<sup>1</sup>. Though widely used, it is not the most efficient method. We have been investigating the use of potassium ions as a method of stimulating neural tissue. The use of ionic stimulation allows for a more biocompatible and low power method of stimulation. Initial in-vitro experiments on rabbit retina show that modest increase (~10mM) of extracellular potassium ion concentration elicits neural responses.

Our initial experiments were performed by pressure ejection of KCl using a multibarrel glass pipette and performed on the epi-retinal side of the retina<sup>2</sup>, see fig 1. However, the final envisioned device will be situated in the sub-retinal space. Furthermore, a different in-vitro experimental platform needs to be designed to overcome the limitations of the existing setup. Furthermore, a device that allows for ejection of very small volumes (pL compared to nL) and also allows for accurate estimation of volumes ejected would greatly enhance the development of a prosthetic device using this concept. An additional advantage of ionic stimulation over electrical stimulation, as an investigation tool for neuroscience, is that ionic stimulation does not induce a stimulus artifact which allows for simultaneous recording from multiple neurons.

Thus, it would be advantageous to build an ionic stimulation platform that has the capability of array stimulation. Inkjet printing technology naturally lends itself to this endeavor and is the platform of choice for our device. The scheme is illustrated in figure 2. However, our initial experiments using thermal inkjet technology met with failure for reasons including inkjet head construction and chamber size. Simple experiments performed using a piezoelectric inkjet head showed more promise and we are currently building a custom in-vitro stimulation platform using a piezoelectric inkjet head controlled by custom electronics and uses a software platform based on LabView.



**Figure 1:** a) Experimental setup used for the K<sup>+</sup> stimulation b) Snapshots of the pipette positioned over the retina, the figure with a red shading is the pipette under red light illumination and shows the KCl solution being ejected with the dark stain caused by the Azure B dye used for visualization. The red light was used to prevent the retina from responding to the ambient light since it is known that e rabbit retinae do not respond to red light. c) Typical response to K<sup>+</sup> stimulation. Shown is the response to concentration of 30mM KCl. The square pulse is the onset of the ejection.



**Figure 2:** Inkjet Stimulation platform for accurate determination of ejected volumes and multi-point stimulation (See text for more details)

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