

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.

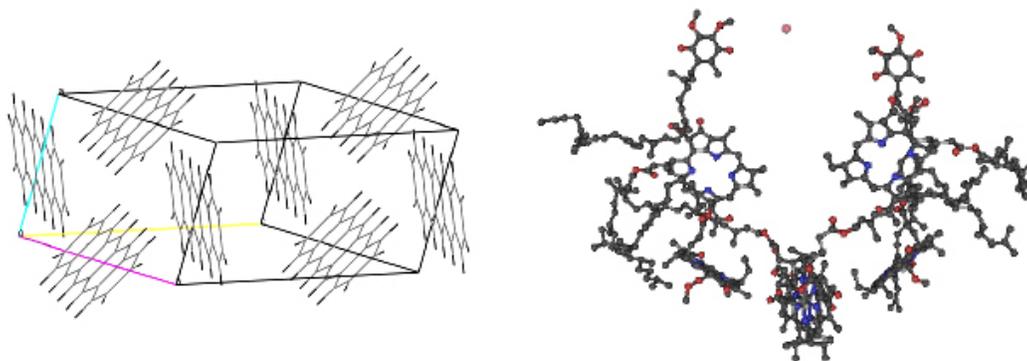


Figure 1: Two examples of van der Waals bonded semiconductors. **(Left)** The structure of a molecular crystal of pentacene. Pentacene has a hole mobility of approximately 2 cm²/Vs and is widely used in organic electronics. Data is from Mattheus, et al. *Acta Crystallographica C*. 57, 939 (2001). **(Right)** The structure of the photosynthetic reaction center of *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).

Biological electronics is the other main application for soft semiconductors. In biology, complex circuits are fabricated by ‘bottom-up’ self-assembly from molecular components. For example, photosynthesis relies on self-assembled complexes of a handful of weakly interacting molecules positioned by a protein scaffold. These structures are perhaps the smallest electronic circuits known. But they harvest photons with nearly 100% quantum yield and an expected power conversion efficiency exceeding 20%. Biological photosynthetic complexes are perhaps the ultimate demonstration of the promise of soft semiconductors.

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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.

1. Organic Photovoltaics with External Antennas

Sponsors

DARPA/AFOSR F49620-02-1-0399, National Science Foundation NIRT

Project Staff

Jonathan Mapel, Timothy Heidel, Kemal Celebi, Madhusudan Singh, Marc Baldo

The structures and processes of photosynthesis are evolved, highly efficient, robust, and possess high power density. We attempt to leverage these characteristics in solar cells by incorporating photosynthetic architectural motifs in organic solar cells. We adapt the organization of processes in photosynthesis and introduce a synthetic light harvesting structure into organic PV which couples light energy to the active device area by near field energy transfer. Light energy absorbed in an artificial antenna layer is transferred to an artificial reaction center in the interior of the solar cell. The energy transfer is of the Förster type, mediated by surface plasmons polaritons. While the introduction of the antenna necessarily adds a step into the energy transduction process, decoupling photon absorption and exciton dissociation can be exploited to increase each separately.

We have theoretically and experimentally examined the efficiency of energy transfer for this process by adapting a method developed by Chance et al¹. We utilize a film of photoluminescent chromophores placed immediately adjacent to an organic solar cell with dual silver electrodes as an antenna layer. We predict and verify that energy transfer can occur in technically relevant device structures with energy transfer efficiencies of approximately 50% and demonstrate this transfer results in increased quantum efficiency.

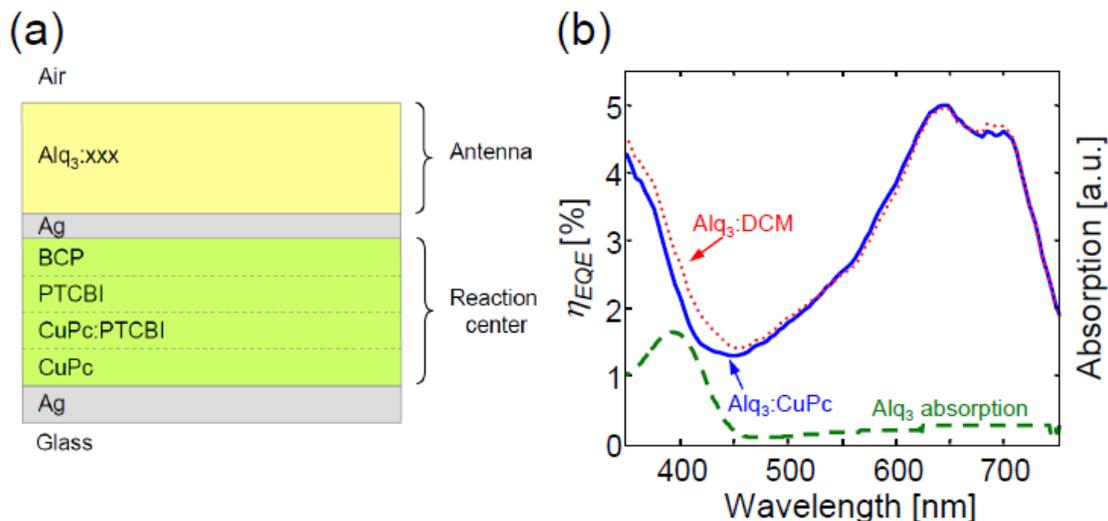


Figure 1: (a) The device structure utilized in these studies is comprised of aluminum tris(8-hydroxyquinoline), bathocuproine, copper phthalocyanine, 3,4,9,10-perylenetetracarboxylicbis-benzimidazole, 4-dicyanomethylene-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran, and silver. To tune the emission of the Alq₃ antenna it was doped with either CuPc or DCM at 1% weight ratio. (b) The comparison of devices with functional (dotted line) and nonfunctional (solid line) antennas demonstrate external energy transfer. Devices with functional external Alq₃ antenna layers (dotted line) exhibit an increase in external quantum efficiency over the wavelength range where Alq₃ absorption occurs (dashed line). The photocurrent spectra are identical outside the spectral range where Alq₃ absorbs. Functional antennas employ the laser dye, X = DCM, whereas nonfunctional antennas employ the quencher X = CuPc).

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2. Optical Models of Organic Photovoltaic Cells

Sponsor

DARPA, NSF NIRT

Project Staff

Kemal Celebi, Madhusudan Singh, Marc Baldo

Organic semiconductors generate excitons when exposed to sunlight. However, the limited diffusion length of excitons results in a trade off between the absorption and charge generation by exciton diffusion to the interface^[1]; thin devices efficiently separate excitons into charge, but do not absorb sufficient radiation. We have recently demonstrated a separation of the absorption and charge generation processes in organic photovoltaics by absorbing the sunlight in an external antenna and then transferring the energy across a metal contact to a charge generation component. Determining the efficiency of energy transfer requires calculation of the near field of the antenna excitons since the distances involved on the order of the wavelength of the radiation absorbed. To solve this problem we extend a previously established dyadic Green's functions model^[3] to calculate the z-component of the Poynting vector, thus determining the spatial absorption of energy transferred from the antenna throughout the multilayer stack (Figure 2). Using these calculations we calculate optimum layer thicknesses for maximum efficiencies. We find that for excitons located approximately 20nm from the cathode interface, energy transfer to the charge generating layers exceeds 80%. Future work in modeling will concentrate on far-field emission for OLED outcoupling studies and collective dipole behavior.

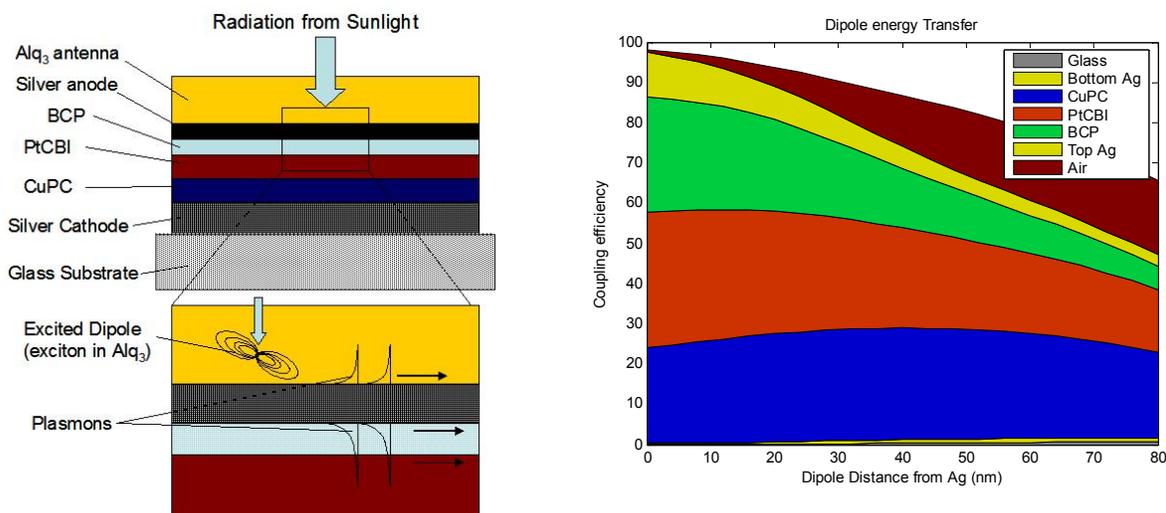


Figure 1: Working principle of the organic PVs with external antennas. Energy is first absorbed by the excitons in the antenna and then these excited excitons transfer their energy to the excitons in the active layers (PtCBI & CuPC) mainly through surface plasmon polariton modes. Structure used is Air/ 800Alq₃/ 80Ag/ 100BCP/ 180PtCBI/ 240CuPC/ 400Ag/ Glass (thicknesses are in Angstroms).

Figure 2: Percentage of power transferred from the excitons in the antenna to different layers in the structure of Figure 1 as a function of exciton distance from the Alq₃-Ag interface. White space on the top shows internal damping in the Alq₃ molecules, which is assumed to be lightly doped with a laser dye that is 70% efficient. As the exciton distance from silver film increases efficiency decreases due to the reduction in plasmon coupling.

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3. Characterization of Electrical and Optical Properties of Photosynthetic Complexes

Sponsors

DARPA/AFOSR, NSF Nanoscale Interdisciplinary Research Team

Project Staff

Michael Currie, Marc Baldo

The molecular components within photosynthetic protein complexes are precisely oriented to achieve near 100% quantum efficiency and create electron/hole pairs that exhibit low recombination rates.[1] These complexes, along with the protein scaffolds that preserve their specific orientation, cannot be duplicated by current fabrication technologies. Because of their excellent optoelectronic properties, photosynthetic protein complexes are a strong candidate for integration into solid-state devices.

We are investigating the reaction center complex from *Rhodobacter sphaeroides*. The complexes are self-assembled into nanofabricated structures by selective binding of polyhistidine tags, expressed by the bacterium, to gold via nickel chromatography techniques[2]. To create two-terminal devices, we are exploring soft lithography methods that minimally deform the reaction center structure and hence preserve functional viability. The current device relies on Van der Waals contact between gold coated poly(dimethylsiloxane) and the reaction center. We are conducting pump and pump-probe measurements of the self-assembled complexes under electrical bias. These measurements should yield the open circuit voltage and fill factor of these biological photovoltaic structures.

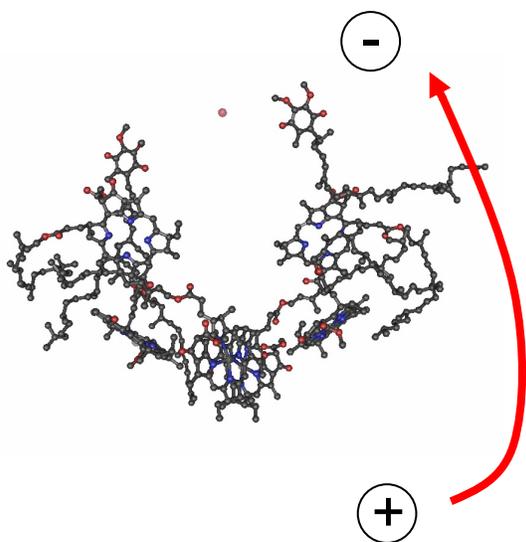


Figure 1: The internal molecular circuitry of the photosynthetic bacterial reaction center with the protein scaffold removed. The complex is only a few nanometers top-to-bottom. After photoexcitation, an electron is transferred from the special pair (bottom of complex), to the quinone (top of complex). The process occurs within 200 ps, at nearly 100% quantum efficiency.

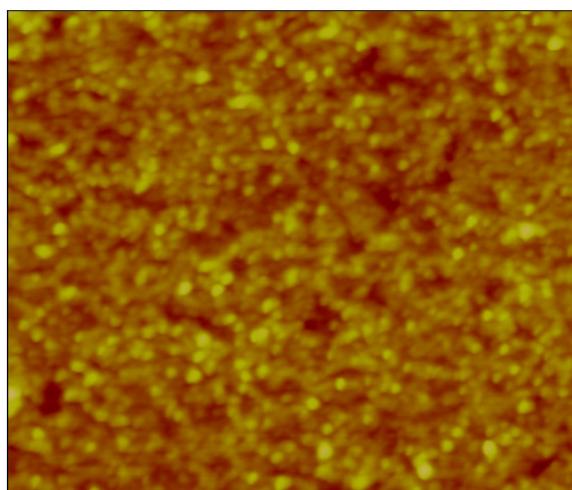


Figure 2: AFM image of a photosynthetic reaction center monolayer. Each small dot represents a bound protein complex.

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4. Extrafluorescent OLEDs: Achieving OLED Fluorescent Efficiency Enhancement Through Spin-Orbit Coupling

Sponsors

National Science Foundation

Project Staff

Michael Segal, Madhusudan Singh, Kelley Rivoire, Troy Van Voorhis, Marc 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. OLEDs can produce two kinds of light: fluorescence, the result of an allowed excited state relaxation, and phosphorescence, the result of a forbidden excited state relaxation.¹ Phosphorescent OLEDs have high efficiency, but are currently unable to achieve stable emission in the deep blue. 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 equal that of phosphorescent OLEDs. This 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 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, so that singlet precursors and excitons will be preferentially formed 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 DCM. (Figure 2).

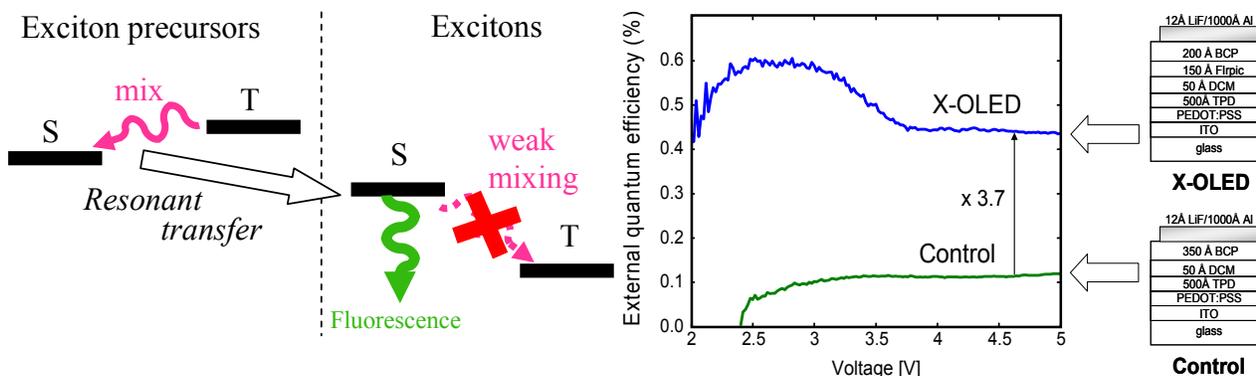


Figure 1: Scheme for increasing fluorescence efficiency. Exciton precursor states are spin mixed to preferentially form singlets. Mixing of final exciton states from singlet to triplet is avoided.

Figure 2: Demonstration of an extrafluorescent OLED or X-OLED. The mixing molecule iridium(III) bis [(4,6-difluorophenyl) pyridinato- N,C^2] 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] (DCM) is used as an emissive material. Without mixing, the efficiency is 3.7x lower.

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5. Percolation Models of Charge Transport in Organic Semiconductors

Sponsors

DuPont-MIT alliance

Project Staff

Benjie Limketkai, Marc Baldo

In this project, we study charge transport in organic semiconductors using percolation theory. A percolation model was first introduced by Ambegaokar *et al*¹ to explain the hopping conductivity in disordered systems. It was later incorporated in Vissenberg and Matters² for an exponential DOS to explain the field-effect mobility in amorphous organic transistors. This percolation model is further employed here, incorporating the effects of an applied electric field to the mobility and current-voltage (IV) characteristics of organic semiconductors. By modifying the percolation model to include the effect of applied electric field, the temperature and field dependence of mobility and IV characteristics are found. A universal IV characteristic for organic semiconductors is explained. The Miller-Abrahams expression for charge hopping between exponential trap distributions gives a master equation:³ $J = J_0(V/V_0)^m$, where J_0 and V_0 are constants and $m = 1 + kT_0/(qF/2\alpha + kT)$, where α is the tunneling decay rate, is the power-law slope. Characterization of IV measurements were done with the archetype organic semiconductor material, tris(8-hydroxyquinoline) aluminum, or Alq₃. Its molecular structure is shown in Fig. 1. To demonstrate the universality of the model, the IV characteristics of a number of Alq₃ devices are overlapped as shown in Fig. 2.

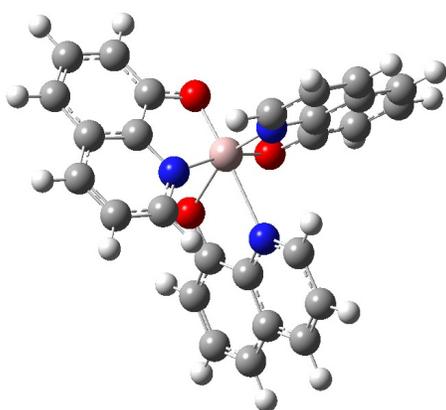


Figure 1: Molecular structure of the archetype organic semiconductor material, tris(8-hydroxyquinoline) aluminum (Alq₃).

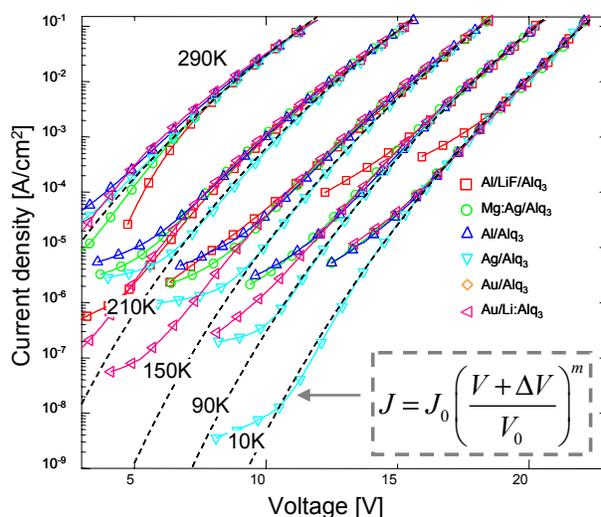


Figure 2: The temperature dependence of the universal IV characteristics of Alq₃ devices. A rigid voltage shift was applied to each IV characteristics to overlap on one another.

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6. Nanoelectromechanical Switches and Memories

Sponsors

MARCO Materials Structures and Devices Focus Center, Institute for Soldier Nanotechnologies

Project Staff

K.M. Milaninia, Marc A. Baldo

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 subthreshold slopes of $\ll 60$ mV/decade.[1] Indeed, as an example of the potential of NEMs, voltage gated ion channels possess subthreshold slopes of approximately 15 mV/decade.[2]

Although many materials are available for NEM applications, carbon nanotubes exhibit low resistance and good mechanical properties. In this project, we are constructing a 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. This offers better control over nanotube growth 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. This allows 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[3] have shown that increasing the aspect ratio of a carbon nanotube reduces the voltage needed to pull in the nanotube, and thereby power requirement. Furthermore, because of the ability to easily functionalize the surface of nanotubes, we can functionalize the tube with charge to lower the pull-in voltage even further.

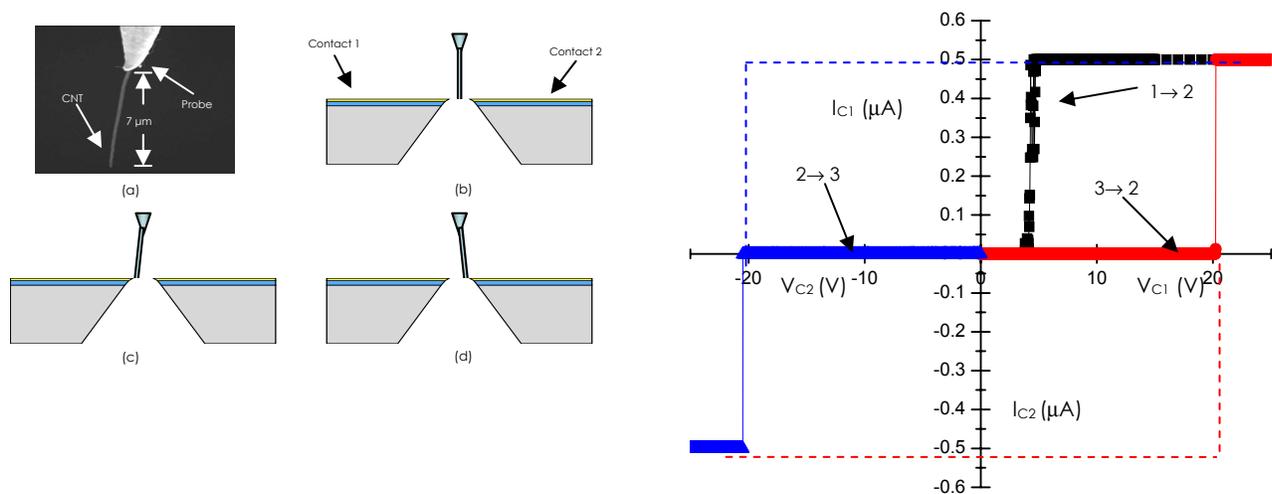


Figure 1: Initial results were obtained by introducing a (a) carbon nanotube mounted to a tungsten probe between two (Au/SiO₂/Si) contacts similar to the ones shown in Fig 8. (b),(c), and (d) are schematics of the device in state 1 (it's initial state), state 2, and state 3, respectively.

Figure 2: I-V of device being switched from state 1→2 by applying a bias between Contact 1 and CNT, then switched from state 2→3 by applying a bias between Contact 2 and CNT, and finally from state 3→2 by applying a bias between Contact 1 and CNT

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7. Combinatorial Sensing Arrays of Phthalocyanine-Based Field Effect Transistors

Project Staff

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Of the millions of molecular species floating in air or dissolved in water, a substantial fraction can be smelled and uniquely discriminated.[1] Biological systems achieve this functionality with a multitude of non-specific receptors. In this project, we are developing gas sensors based on combinatorial arrays of organic transistors. The combinatorial approach reduces the need to develop specific receptors for each and every molecule of interest. Rather, our sensors are based on exploiting the wide variation in interactions between molecules and metal ions,[2] an approach previously employed in colorimetric sensors.[3]

We have fabricated gas-sensitive organic transistors each consisting of an approximately 10nm-thick polycrystalline layer of a metallophthalocyanine (MPC) with gold source and drain contacts. The width and length of the channel for each transistor is 2mm and 50 μ m, respectively. The charge carrier mobility is typically between 10^{-3} and 10^{-4} cm²/Vs. But the transconductances of various MPC transistors (CoPC, CuPC, ZnPC, and NiPC) are observed to vary when exposed to different gases (acetonitrile, tetrahydrofuran, and toluene); channel current in MPC transistors decreases linearly with increasing solvent concentration (fig. 1). The transient response of the current modulation (fig. 2) is chemically selective and dependent on the interaction between the solvent and the central metal atom in the MPC. The linear dependence of channel current on solvent concentration, the steady state current modulation, and the transient response of the MPC transistors are all consistent with the disruption of percolation pathways leading to modulation of transistor channel currents. Since the sensors can be manufactured simply by inkjet printing on a patterned substrate, they may find application as single-use diagnostic aids.

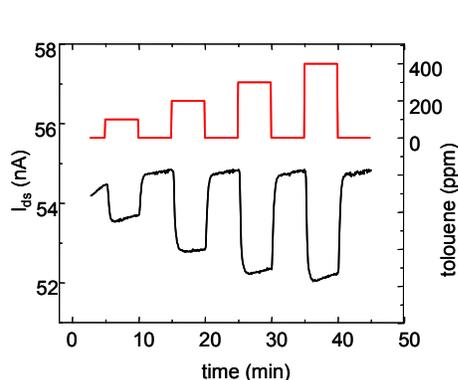


Figure 1: The linearity of MPC sensors is tested by modulating the solvent concentration ($V_{ds}=-20V$, $V_g=-20V$).

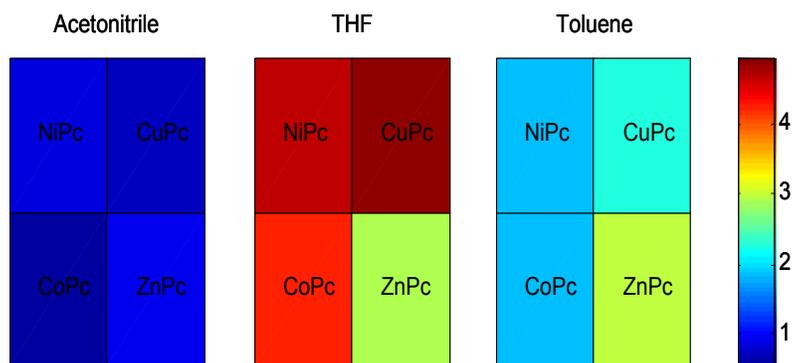


Figure 2: The transient rate of channel current recovery, k_{OFF} , after removal of solvent vapor in units of min^{-1} , summarized for various MPC-solvent combinations. Transistor bias conditions are $V_{ds}=-20V$, $V_g=-20V$.

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Book Chapters

- M.A. Baldo and M. Segal, "Phosphorescence as a Probe of Exciton Formation and Energy Transfer," in *Physics of Organic Semiconductors*, edited by W. Brütting. (Wiley VCH, 2005).