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**Final Report**  
**October 2004 – December 2007**

S. Forrest  
*Princeton University*  
*Princeton, New Jersey*

**Subcontract Report**  
**NREL/SR-520-42381**  
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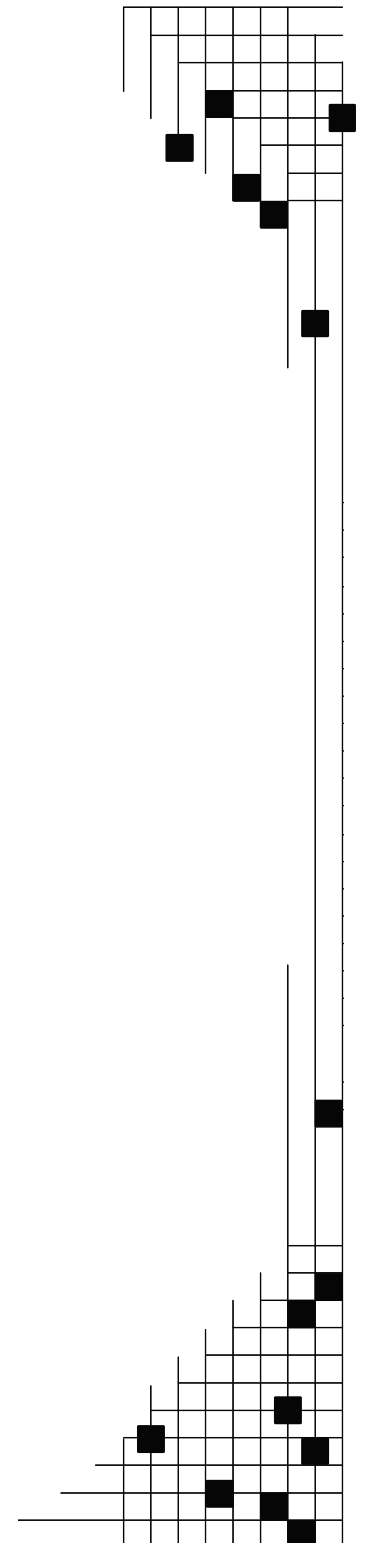
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## **Project Objectives:**

To find routes to achieving nearly 10% power conversion efficiency based on a new generation of organic photovoltaic cells based on vapor-deposited, small-molecular-weight organic materials.

## **Approaches:**

Our primary approaches to achieving our objective were as follows:

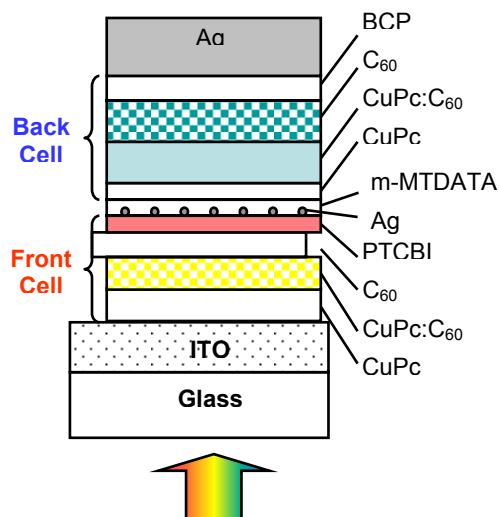
1. Employing tandem organic thin-film solar cells containing Ag nanoclusters that increase the efficiency of the individual cells comprising the structure through surface plasmon optical field enhancement. Each cell in the tandem stack will employ our innovative double-heterojunction architecture to maximize external quantum efficiency.
2. Employing different material compositions in each stacked sub-device to provide solar spectral coverage from the blue to the infrared (IR) at a wavelength of 1.1  $\mu\text{m}$ .
3. Exploring the use of small-molecular-weight bulk heterojunctions grown by the process of vacuum thermal evaporation and organic vapor-phase deposition.
4. Understanding sources of losses, particularly in the low open-circuit voltage often observed in organic donor-acceptor heterojunctions.

Our work follows both analytical and experimental paths to ensure that our observations are fully understood. This approach provides the highest probability for achieving the efficiencies that we anticipate are within reach using our tandem cell approach.

## **Results:**

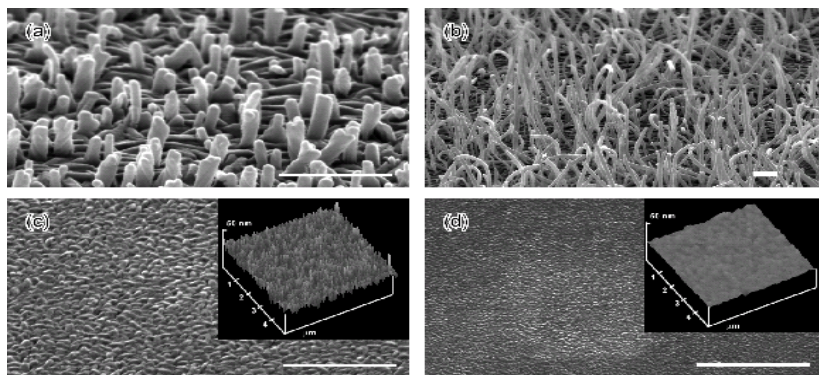
This was an exceptionally successful program that ended early due to my move from Princeton University to the University of Michigan in January, 2006. Nevertheless, the output consisted of 12 publications in scholarly journals, including *Nature Materials*, *Appl. Phys. Lett.*, *J. Appl. Phys.*, *Org. Electronics*, *Physical Review B*, and *Adv. Mater.*, as well as about 20 presentations (invited, contributed, and plenary) at numerous international conferences. The primary results are presented in the following publications:

1. "Asymmetric tandem organic photovoltaic cells with hybrid planar-mixed molecular heterojunctions," J. Xue, B. P. Rand, S. Uchida, and S. R. Forrest, *Appl. Phys. Lett.* **85**, 5757 (2004).



This paper describes a high-efficiency CuPc/C<sub>60</sub>, 2-element tandem cell tuned to optimize efficiency in the blue and red spectral regions. It employs a silver nanoparticle charge recombination layer and a pair of double-heterojunction cells. It demonstrated doubling of the output voltage of a single element in the stack, and achieved a 5.7% power conversion efficiency at 1 sun, AM1.5 illumination (not solar corrected) due to its increased thickness over a single planar-mixed element.

2. "Controlled growth of a molecular bulk heterojunction photovoltaic cell," F. Yang, M. Shtein, and S. R. Forrest, *Nat. Mater.* **4**, 39 (2005).



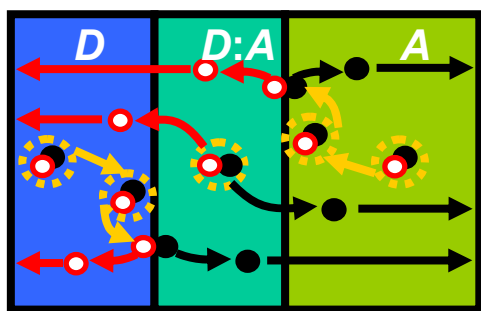
This represents the first controlled structure for a bulk heterojunction solar cell. The principle was to use organic vapor - phase deposition of CuPc on the ITO anode, adjusting the growth conditions to

introduce strain into the thin film. By optimizing the degree of strain, crystalline needles of CuPc were formed. This was then filled in by the acceptor, PTCBI grown in the OVPD "diffusive regime." The outcome was a heterojunction with controlled interface area far greater than that obtained using a planar interface. There were no bottlenecks or cul-de-sacs for charge transport either, reducing cell internal resistance. The result was a cell efficiency improvement of 2.7 times that of an analogous planar junction.

3. “The limits to organic photovoltaic cell efficiency,” S. R. Forrest, *invited*, *MRS Bulletin* **30**, 28 (2005).

This paper explores the fundamental limitations to photovoltaic efficiency. Here, the concept of the “exciton bottleneck”—that is, the tradeoff that exists between exciton diffusion length and optical absorption length that fundamentally governs organic cell layer thickness—was defined and discussed. A clear conclusion of this work is that organic solar cells must have two features to be highly efficient, and therefore competitive, for use as a means for solar energy generation. These features are a double heterojunction and a tandem-cell geometry.

4. “A hybrid planar-mixed molecular heterojunction photovoltaic cell,” J. Xue, B. P. Rand, S. Uchida and S. R. Forrest, *Adv. Mater.* **17**, 66 (2005).



This paper introduces a new and highly promising concept to achieve high efficiency using an organic thin-film structure. It is a hybrid between a donor-acceptor mixed region, and a standard planar double heterojunction. The two active materials are the donor, CuPc, and the acceptor, C<sub>60</sub>. By placing a 1:2 CuPc:C<sub>60</sub> mixture between two homogeneous films of the individual

components, the active region of the cell can be increased to equal the sum of the exciton diffusion lengths of the two materials, plus the charge-collection length of the mixture. Here, the charge-collection length was defined as the distance that a free electron or hole can travel in the mixed region before recombining with the opposite charge. By using the mixed layer, the total thickness of the active region increased by about 30%, leading to an increase in efficiency from 3.6% for the planar junction, to 5% (uncorrected for solar spectral differences with a 1 sun, AM1.5 solar simulator spectrum) for the planar-mixed hybrid. This particular junction design was used in the high-efficiency tandem in Ref. 2.

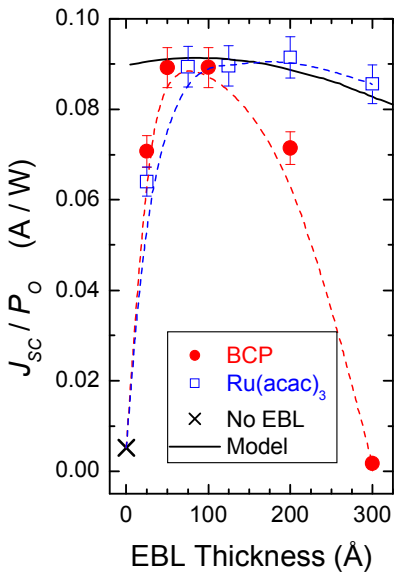
5. “Morphology control and material mixing by high-temperature organic vapor phase deposition and its application to thin-film solar cells,” F. Yang, M. Shtein, and S. R. Forrest, *J. Appl. Phys.* **98**, 014906 (2005).

This paper details the thermodynamics of organic vapor-phase deposition that leads to the growth of suitable materials for organic solar cell applications. OVPD is a proprietary growth technique employed by our laboratory to grow small-molecular-weight thin-film layers. The use of an inert carrier gas and hot-walled reactor characteristic of OVPD gives unprecedented control over thin-film morphology as is needed to obtain high-quality bulk heterojunctions. This paper introduces and studies the conditions required to deposit the high-temperature materials required in solar cell applications.



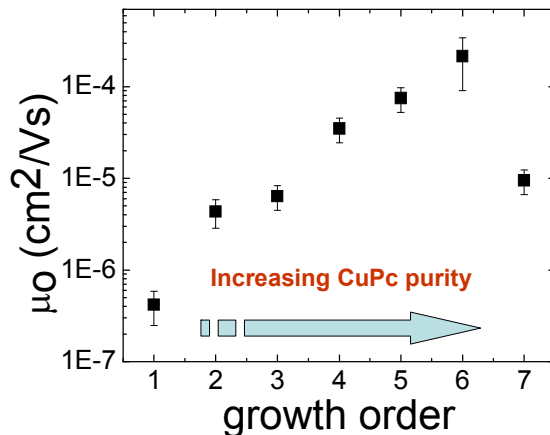
6. “Organic double-heterostructure photovoltaic cells employing thick tris(acetylacetonato) ruthenium(III) exciton blocking layers,” B. P. Rand, J. Li, J. Xue, R. J. Holmes, M. E. Thompson, and S. R. Forrest, *Adv. Mat.* **17**, 2714 (2005).

Prior to this paper, the only high-quality exciton blocking layers applicable to organic solar cells was bathocuproine (BCP). It was assumed that damage induced in BCP by the cathode metal deposition led to defect states that allowed for electron transport through the film. This material has proven central to all double-heterojunction cells as first introduced by our laboratory, but its thickness was limited by the depth to which damage can be induced by contact deposition, or about 10 nm. In this work, we introduce Ru(acac)<sub>3</sub> as a second, highly effective exciton blocking layer (EBL) material. Interestingly, it was found that Ru(acac)<sub>3</sub> could be deposited at thicknesses much larger



than could be explained by the extent of cathode-induced damage. A measurement of the ionization potential energy of Ru(acac)<sub>3</sub> indicated that the highest-occupied molecular orbital energy was comparable to the lowest unoccupied molecular orbital energy of the adjacent acceptor layer of C<sub>60</sub>. This suggested that holes were transported in Ru(acac)<sub>3</sub> to recombine with electrons generated in C<sub>60</sub>, quite the contrary of our previous understanding of the action of BCP. Indeed, in a second set of experiments, it was found that BCP, too, was effective at transporting holes and not electrons, although that transport once again could only occur along defect-induced trap states. This set of experiments significantly clarified our understanding of the operation of the EBL, and introduced a new and important material for this purpose.

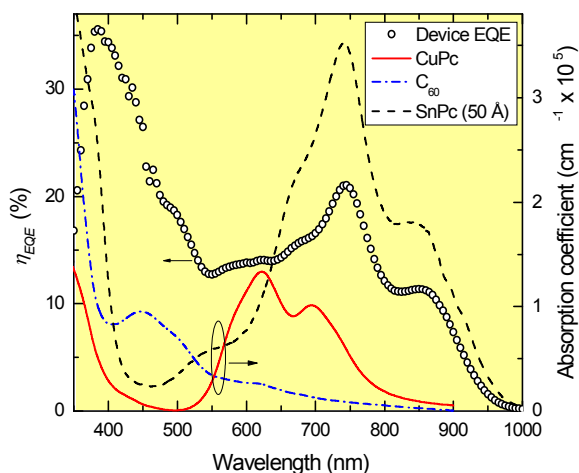
7. “The effects of copper phthalocyanine purity on organic solar cell performance,” R. F. Salzman, J. Xue, B. P. Rand, A. Alexander, M. E. Thompson, and S. R. Forrest, *Org. Electron. Lett.* **6**, 242 (2005).



There is considerable variability in the literature regarding efficiencies quoted for various materials combinations. For example, in the CuPc/C<sub>60</sub> system, power conversion efficiencies vary from 0.5% to 3.5%. This range encompasses several different heterostructure and layer thickness combinations, as well as different efficiency measurement calibrations. Nevertheless, the variability is beyond the range that can simply be explained by these factors. For this reason, we suspected that variations in

material purity could also account for these differences. In this study, we investigated several CuPc/PTCBI/BCP double-heterojunction cells as a function of CuPc purity, as inferred from the number of times the material was outgassed in vacuum at high temperature. We also studied the effects of deposition in high vs. ultrahigh vacuum, and measured the IR and other spectral properties of the material to identify various impurities. It was found that the cell efficiency was a strong function of material purity, but not conditions of deposition. Furthermore, the mobility of CuPc films closely tracked the cell efficiency. The primary impurity identified in the unpurified CuPc source material was the free-base phthalocyanine, H<sub>2</sub>Pc. To our knowledge, this was the first systematic study of the effects of material purity on cell efficiency.

8. “Organic solar cells with sensitivity extending into the near-infrared,” B. P. Rand, J. Xue, F. Yang and S. R. Forrest, *Appl. Phys. Lett.* **87**, 233508 (2005).



A significant problem of organic thin-film cells is their lack of absorption in the near-infrared (IR) spectral range. In this work, we demonstrated a cell with sensitivity extending to 1.1  $\mu\text{m}$  wavelength based on a combination donor material consisting of CuPc (absorbing in the yellow and red) and SnPc, absorbing into the IR. The efficiency of this cell, using C<sub>60</sub> as the acceptor, was 1.1% under 1 sun, AM1.5 simulated illumination.

9. “Mixed Donor-Acceptor Heterojunctions for Photovoltaic Applications. I. Materials Properties,” B. P. Rand, J. Xue, S. Uchida, and S. R. Forrest, *J. Appl. Phys.* **98**, 124902, (2005).
10. “Mixed Donor-Acceptor Heterojunctions for Photovoltaic Applications. II. Device Applications,” B. P. Rand, J. Xue, S. Uchida, and S. R. Forrest, *J. Appl. Phys.* **98**, 124903 (2005).

Both papers 9 and 10 provide a detailed study of the properties of mixed CuPc:C<sub>60</sub> layers used in planar mixed junctions such as in Ref. 4. Among other parameters, the carrier transport length and the charge mobility are measured as functions of mixture fraction. The study determines both analytically and experimentally the optimum mixtures and layer thicknesses required to achieve high-efficiency solar cells based on the hybrid planar-mixed structure.



11. “Semitransparent Organic Photovoltaic Cells,” R. Bailey-Salzman, B. P. Rand, and S. R. Forrest, *Appl. Phys. Lett.* **88**, 233502 (2006).

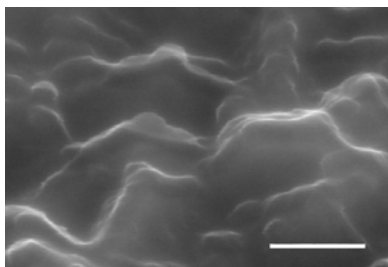
An intriguing possibility of our work has been that the solar cells are very thin. For this reason, the optimum structures are semitransparent. In earlier work on organic light-emitting diodes, we demonstrated that sputtered indium tin oxide can be used both as an anode and a cathode. We applied this same technology to organic solar cells,



demonstrating the first semitransparent organic photovoltaic. The cathode consisted of a very thin (~10 nm) Ag layer, followed by a thicker layer of ITO. Cell efficiencies were not degraded from their values using a metal contact, provided that the optical absorption through only a single pass of the light through the device (as opposed to the reflective, double pass of thick metallic cathodes) was taken into account. These devices have

potential as energy-generating window coatings and other applications where semitransparency is required. Analysis of the device also indicates that the use of transparent cathodes in tandem cells significantly increases the layer thickness design flexibility of that structure.

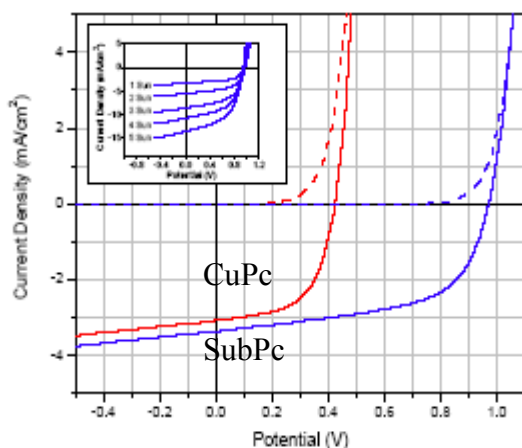
12. “Organic solar cells using transparent  $\text{SnO}_2\text{:F}$  anodes,” F. Yang and S. R. Forrest, *Adv. Mater.* **18**, 2018 (2006).



Indium tin oxide is known to be a very expensive anode material. However,  $\text{SnO}_2\text{:F}$  is finding uses in solar cells, particularly those based on thin-film group II-VI compounds. One significant drawback of  $\text{SnO}_2\text{:F}$ , however, is that it is quite rough. Given the very thin nature of organic solar cells, roughness tends to introduce shorts across the organic active region. However, organic vapor-phase deposition

has been shown, under some growth conditions, to lead to a highly conformal film that can follow large variations in roughness of a substrate. In this work, we grew controlled bulk heterojunctions consisting of strained CuPc followed by conformal layers of  $\text{C}_{60}$  to result in a very efficient PV cell as compared to a planar control consisting of these same materials on ITO. This work opens the door to the use of this lower-cost  $\text{SnO}_2\text{:F}$  anode in place of ITO.

13. “Enhanced Open Circuit Voltage in Subphthalocyanine/ $C_{60}$  Organic Photovoltaic Cells,” K.L. Mutolo, E. I. Mayo, B. P. Rand, S. R. Forrest, and M. E. Thompson, *J. Am. Chem. Soc.* **128**, 8108 (2006).

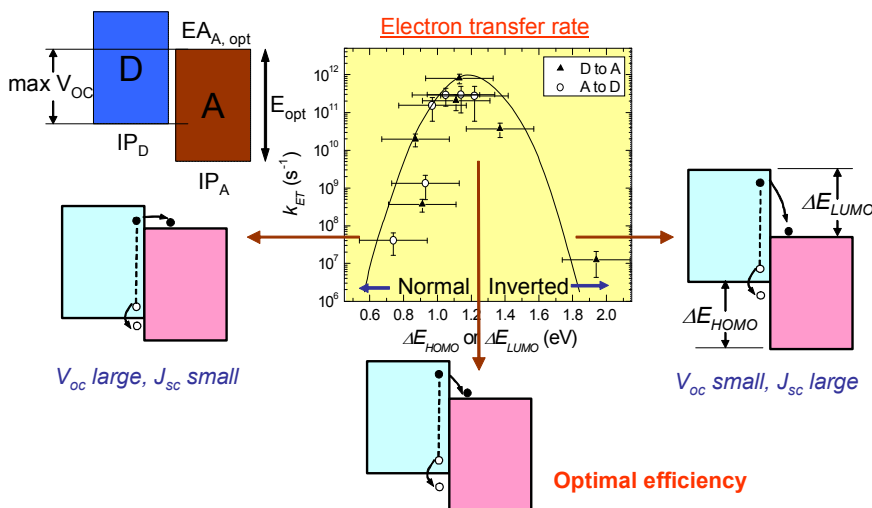


In collaboration with Prof. Mark Thompson’s group at the University of Southern California, we demonstrated a high open-circuit voltage organic photovoltaic cell based on the new donor, boron subphthalocyanine. This work showed that the interface gap, that is the energy difference between the lowest-unoccupied molecular orbital of the acceptor as determined by optical absorption and the ionization potential of the donor, is responsible for the open-circuit voltage of the devices. The subPc devices had

open-circuit voltages approaching 1 V, as compared to analogous CuPc devices where the voltage is consistently 0.5 V. This is a very important finding as the subPc’s represent a large class of donors that may find use in organic solar cell applications.

14. “Offset energies at organic semiconductor heterojunctions and their influence on the open-circuit voltage of thin-film solar cells,” B. P. Rand, D. P. Burk, and S. R. Forrest, *Phys. Rev. B* **75**, 115327 (2007).

This final study attempts to systematically determine the source of the open-circuit voltage ( $V_{OC}$ ) in organic solar cells. In this work, we relate both the modified Shockley Equation and Marcus Theory of Charge Transfer to understand the large energy losses in the processes of exciton generation and photoinduced charge-transfer characteristic of



organic solar cells. We emphasize that the origin of  $V_{OC}$  can only be found by comparing the *maximum* value of this parameter that is obtained either at low temperature or high incident power density. We determine the maximum value of  $V_{OC}$  for 14 donor and acceptor

material combinations, and find that its value is fundamentally limited by the size of the interface energy gap (see Ref. 13 description for definition), which takes into account the

large binding energy of the Frenkel-like excitons characteristic of most organic materials used in photovoltaic cell applications. We clearly show that CuPc/C60 cell efficiencies can be as high as 4.5% (compared to the maximum of 3.6% currently reported), but that planar double-heterojunction cells optimized with analogously absorbing materials combinations can extend to about 11%. This, to our knowledge, is the first systematic study of the fundamental origin of the limitations to organic heterojunction cells.

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