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Efficient photon harvesting at high optical intensities in ultrathin organic double-heterostructure photovoltaic diodes

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We demonstrate a method for efficient photon harvesting in organic thin films, thereby increasing the efficiency of organic photovoltaic cells. By incorporating an exciton-blocking layer (EBL) inserted between the photoactive organic layers and the metal cathode, we achieved an external power conversion efficiency of $2.4\% \pm 0.3\%$ in vacuum-deposited ultrathin organic bilayer photovoltaic (PV) cells employed in a simple light trapping geometry. Ultrathin (~ 100 Å) cells incorporating the transparent, conductive EBL have an *internal* quantum efficiency as high as $33\% \pm 4\%$ over a spectral region matched to the solar spectrum. The very thin organic layers have a low series resistance, allowing for efficient power conversion in organic PV cells under intense (>15 suns) AM1.5 illumination. This device structure demonstrates that control of exciton diffusion in solid-state organic devices leads to a significant increase in the photon-to-carrier conversion efficiency. © 2000 American Institute of Physics. [S0003-6951(00)03419-7]

Organic photodetectors and photovoltaic (PV) cells have the potential advantages of being light weight, economical in materials use, and can be deposited on low-cost substrates such as flexible plastic foils which are compatible with continuous roll-to-roll processing.¹ Unfortunately, the solar energy conversion efficiencies of organic PV cells^{2–7} have been quite poor, with few significant improvements made since the demonstration by Tang⁷ in 1986 of a bilayer cell with a 0.95% efficiency to AM2 illumination at an intensity of approximately 1 sun.

The low efficiency of organic PVs arises from the fundamental nature of charge photogeneration and transport in organic materials, which occurs as follows: A photon is absorbed by a molecule forming a molecular exciton. This exciton must be generated near to a donor–acceptor (DA) interface such that dissociation occurs prior to dissipative recombination. However, the diffusion length of an exciton ($L_D \sim 50$ Å) is typically much less than the optical absorption length (~ 500 Å), requiring a trade off between using a thick, resistive cell with multiple or highly folded interfaces,^{2–6} or a thin cell with a low optical absorption efficiency. To date, none of these proposals has led to a significant improvement in overall cell performance, particularly at high illumination intensities.

Using a thin cell geometry where the incident photons make multiple passes through the light absorbing organic films can offer a solution to both the exciton diffusion length/optical absorption length mismatch, and at the same time reduce cell series resistance. Here, we present a double-heterostructure organic PV cell structure where a large band gap (>3 eV) and, therefore, transparent, organic exciton-blocking layer (EBL) is inserted between the photoactive region and the metal cathode. Inserting such a layer prevents damage due to cathode evaporation⁸ and eliminates parasitic exciton quenching at the electron–acceptor/cathode interface.⁹ Since the EBL provides a spacer between the photoactive region and the cathode, the optical intensity at the

DA interface is increased, thereby increasing the light absorption efficiency.¹⁰ By virtue of the low series resistance of the modified thin cells, we demonstrate the linear operation of an organic PV cell under very high (>15 sun) solar illumination intensities. Employing a simple and practical light trapping structure, we measure external power conversion efficiencies as high as $\eta_P = 2.4\% \pm 0.3\%$ to AM1.5 illumination.

The PV cell structures are fabricated on precleaned¹¹ glass substrates coated with a ~ 1500 -Å-thick transparent, conducting indium–tin–oxide (ITO) anode (with a sheet resistance of $40 \Omega/\text{sq}$). Prior to deposition, the organic materials were purified using thermal gradient sublimation. Films are grown onto the ITO employing ultra-high-vacuum (1×10^{-10} Torr) organic molecular-beam deposition¹² in the following sequence: 30- to 600-Å-thick films of donor-like Cu–phthalocyanine (CuPc) are followed by a 30- to 600-Å-thick films of acceptor-like 3,4,9,10-perylenetetracarboxylic-bis-benzimidazole (PTCBI). Next, a 100- to 200-Å-thick film of the bathocuproine (BCP) EBL is deposited. Here, BCP has previously been shown to form an effective EBL,¹³ which easily transports electrons to the 800-Å-thick Ag cathode (evaporated at 1×10^{-6} Torr, through a shadow mask with 1-mm-diam circular openings) from the adjoining PTCBI layer.

Figure 1 shows the external quantum efficiency (η_{EXT}) of several ITO/CuPc/PTCBI/BCP/Ag devices measured in air under zero bias. For devices with 300 Å CuPc and 100 Å BCP (filled squares), an *increase* in η_{EXT} is observed as the PTCBI layer thickness is *reduced*. If the BCP EBL is omitted, the PV cell photocurrent response is significantly reduced for the thinnest cells, as shown for devices with 300 Å CuPc and PTCBI layers of various thicknesses (open squares). This indicates that the BCP layer prevents exciton diffusion to and subsequent quenching at the Ag cathode/organic interface. While the 3.5 eV optical energy gap of BCP would be sufficiently large to block electron as well as

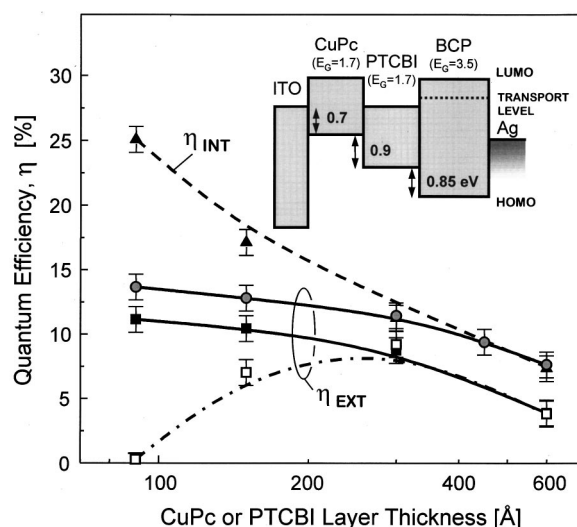


FIG. 1. Dependence of the external and internal quantum efficiencies (η_{EXT} and η_{INT} , respectively) of ITO/CuPc/PTCBI/BCP/Ag PV cells at a power density of $\leq 3 \text{ mW/cm}^2$ on layer thickness. Filled squares correspond to η_{EXT} measured at $\lambda=540 \text{ nm}$ (corresponding to the peak absorption of PTCBI) of cells with a variable thickness of the PTCBI. Open squares correspond to η_{EXT} of similar PV cells without the BCP layer. Filled circles correspond to η_{EXT} measured at $\lambda=620 \text{ nm}$ (corresponding to a peak absorption of CuPc) of cells with a variable thickness of the CuPc layer. The triangles are calculations of η_{INT} at $\lambda=620 \text{ nm}$ for devices with equal CuPc and PTCBI layers and a 100-Å-thick BCP layer. Inset: energy-level diagram obtained from ultraviolet photoemission spectroscopy measurements (courtesy of I. G. Hill and A. Kahn). The energy gap (E_g) corresponds to the onset of optical absorption.

exciton transport (inset, Fig. 1), the ready collection of electrons in our devices suggests that the electron conducting level in BCP is not accurately determined by this parameter. The same trend is observed for the external quantum efficiency of ITO/CuPc/PTCBI/BCP/Ag devices with 300 Å PTCBI and 100 Å BCP (filled circles). The monotonic increase in η_{EXT} , and the even greater increase in the internal quantum efficiency (η_{INT} , solid triangles) with decreasing photoactive layer thicknesses, confirms that excitons must diffuse to the heterointerface for efficient dissociation and subsequent charge collection. The decreasing external quantum efficiency for thicker films is due to the increased absorption in inactive regions.

As shown in the inset of Fig. 2, the cell photocurrent exhibits a good match to the solar spectrum over wavelengths from 400 to 800 nm, and can be described by the sum of the absorption spectra of the organic films weighted by the optical flux incident on each absorbing layer.¹⁴

Current versus voltage (I - V) measurements of a thin device incorporating an EBL (ITO/150 Å CuPc/60 Å PTCBI/150 Å BCP:PTCBI/800 Å Ag) under different intensities of AM1.5 spectral illumination obtained under a nitrogen ambient are shown in Fig. 2. The BCP was doped with $\sim 10\%$ (by weight) of PTCBI to prevent film recrystallization, which is especially rapid under high illumination intensities. We observe no changes in I - V characteristics or quantum efficiency upon doping of the EBL with PTCBI. The measured shunt resistance is $(20 \pm 2) \text{ k}\Omega \text{ cm}^2$, and the series resistance is $(30 \pm 10) \Omega \text{ cm}^2$. The dark current follows the expression for a classical p - n junction diode with an ideality factor of $n=1.4$ - 1.7 and rectification ratios of $\sim 1 \times 10^5$ at $\pm 1 \text{ V}$.

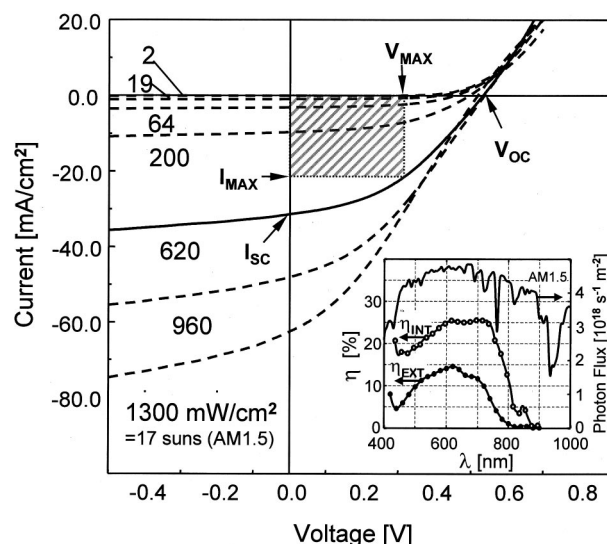


FIG. 2. Current-voltage characteristics of an ITO/150 Å CuPc/60 Å PTCBI/150 Å BCP:PTCBI/800 Å Ag PV cell under varying illumination intensity of up to 17 suns. A 150 W Xe arc lamp equipped with AM1.5 and neutral density filters was used for simulated spectral illumination. Inset: monochromatic internal (η_{INT} , solid line) and external (η_{EXT} , dashed line) quantum efficiency of an ITO/150 Å CuPc/60 Å PTCBI/150 Å BCP:PTCBI/800 Å Ag cell as a function of wavelength. The solar spectrum (AM1.5) is plotted for comparison (dotted line).

The short-circuit current is linear with illumination intensity under an AM1.5 spectrum. Even at the highest illumination levels of ~ 17 suns, no significant space-charge buildup occurs. The open-circuit voltage (V_{OC}) increases monotonically until it reaches a plateau of $V_{\text{OC}}=0.54 \text{ V}$ for illumination intensities >10 suns. The fill factor (FF) approaches 0.57 at low intensities, and exceeds $\text{FF} < 0.35$ found in other organic PVs,²⁻⁴ even at the highest illumination intensities considered. In Fig. 3, the external power conversion efficiency (η_p) of this device is plotted versus the illumina-

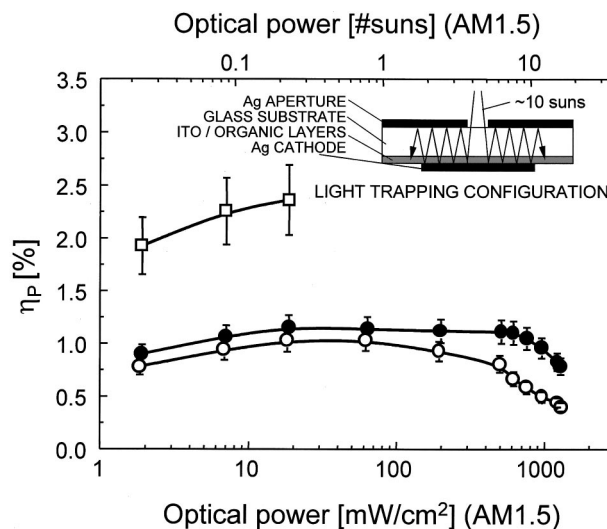


FIG. 3. Dependence of the power conversion efficiency on the incident optical power density of an ITO/150 Å CuPc/60 Å PTCBI/150 Å BCP:PTCBI/800 Å Ag (filled circles) and an ITO/300 Å CuPc/300 Å PTCBI/150 Å BCP:PTCBI/800 Å Ag (open circles) PV cell. The open squares are the measured efficiencies of a ITO/60 Å CuPc/60 Å PTCBI/150 Å BCP:PTCBI/800 Å Ag PV cell with light trapping. The optical power was calculated as the average power over the total device area. Inset: schematic illustration of the PV cell used in the light trapping configuration.

tion intensity (filled circles), reaching a maximum of $\eta_P = (1.1 \pm 0.1)\%$ over a broad plateau extending from 0.1 to 10 suns. The external efficiency of a device with a thicker photoactive region (ITO/300 Å CuPc/300 Å PTCBI/150 Å BCP:PTCBI/800 Å Ag) is plotted for comparison (open circles). The lower maximum efficiency is in agreement with the trend in peak external quantum efficiency (Fig. 1, filled circles) and with earlier work.⁷ The falloff in efficiency for illumination intensities >1 sun for this thicker device is attributed to a larger internal series resistance.

Since only a limited fraction of the incident light is absorbed in a single pass through a thin device, efficiencies approaching the *internal* efficiency can be achieved in a multiple-pass configuration. To demonstrate this principle, we placed a reflective Ag layer with a small aperture (with $\sim 1\%$ of the area of the entire cell) on the substrate surface of the cell. The concentrated radiation (~ 10 suns at AM1.5) on this aperture then forms a near-normal incidence beam which reflects several times between the cathode and Ag-coated reflecting substrate surface, with each pass undergoing additional absorption in the CuPc/PTCBI bilayer (inset, Fig. 3). Using this technique, the external power efficiency increases from $\eta_P = 1.0\% \pm 0.1\%$ to $\eta_P = 2.4\% \pm 0.3\%$ for a cell with 60 Å CuPc and 60 Å PTCBI. This is plotted as a function of the incident optical power normalized to the *total* device area (Fig. 3, open squares).

Due to the small top electrode, not all of the incident radiation was trapped, and hence, η_P represents a lower limit. This scheme can be extended to a more efficient and practical light trapping configuration for flexible, low-cost, large-area organic PV cells based on the injection molding and reflective coating of multiple small polymeric Winston-type¹⁵ collectors placed on the substrate surface (inset, Fig. 4). Ray optics calculations using this light trapping scheme predict that $\eta_P = 2.7\% \pm 0.3\%$ can be achieved,¹⁶ comparing well to the ideal value of $3.0\% \pm 0.3\%$ obtained by integrating η_{INT} (peaking at $33\% \pm 4\%$ for this device) with the solar spectrum. Further, using this approach, the optical intensity at the PV cell is distributed due to the multiple collectors, such that the local intensity never exceeds ~ 10 suns, compatible with the linear performance region of our thin-film cells.

Higher-power conversion efficiencies can be achieved by further optimizing the device structure. In Fig. 4 we calculate η_{INT} versus the thickness of the photoactive layers with the exciton diffusion length L_D as a parameter (solid lines). The measured η_{INT} of our cells (open circles) are well described by this simple theory. Moreover, the value for L_D required to fit the data (~ 30 Å) is in agreement with an independent measurement of L_D (30 ± 3 Å in PTCBI).¹⁶ Optimized growth conditions may lead to enhanced L_D , providing an additional route for optimization. It has been shown that CuPc grown on layers of perylene derivatives (and vice versa) can result in amorphous thin films,¹¹ which presumably would result in the very low values of L_D measured for our present cells. Indeed, L_D in 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), a material similar to PTCBI, was measured¹⁷ to be (880 ± 60) Å, in sharp contrast with the value measured here. From our re-

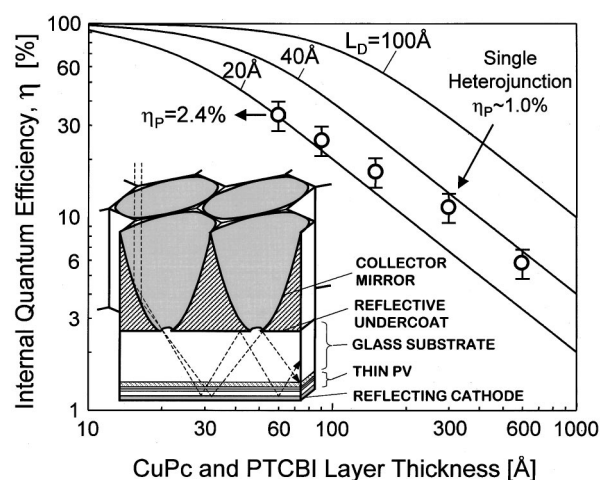


FIG. 4. Internal quantum efficiency as a function of the thickness of the photoactive layers. The open circles correspond to measurements at $\lambda = 620$ nm. The solid lines are solutions to the steady-state diffusion equation for exciton diffusion lengths L_D of 20, 40, and 100 Å. The discrepancy between theory and experiment for the thinnest devices is due to microcavity effects and parasitic absorption. For comparison, the performance of an optimized single heterojunction device from Ref. 7 is indicated. Inset: potential realization of an efficient light trapping scheme. On the substrate are placed multiple Winston-type collectors fabricated by a low-cost, high-throughput, large-area injection molding process. The top and collector mirror are obtained by metal coating both top and bottom collector surfaces.

sults, we anticipate that $\sim 80\%$ internal quantum efficiencies, corresponding to $\sim 8\%$ external power conversion efficiencies are within the reach of such optimized organic solar cells.

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- ¹A. Shah, P. Torres, R. Tschamer, N. Wyrsh, and H. Keppner, *Science* **285**, 692 (1999).
- ²J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, and A. B. Holmes, *Nature (London)* **376**, 498 (1995).
- ³M. Granström, K. Petritsch, A. C. Arias, A. Lux, M. R. Andersson, and R. H. Friend, *Nature (London)* **395**, 257 (1998).
- ⁴G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science* **270**, 1789 (1995).
- ⁵U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, and M. Grätzel, *Nature (London)* **395**, 583 (1998).
- ⁶J. Rostalski and D. Meissner, *Proceedings of the European Conference on Organic Solar Cells, ECOS'98*, Cadarache (1998).
- ⁷C. W. Tang, *Appl. Phys. Lett.* **48**, 183 (1986).
- ⁸C. Arbour, N. R. Armstrong, R. Brina, G. Collins, J. Danziger, J.-P. Dodellet, P. Lee, K. W. Nebesny, J. Pankow, and S. Waite, *Mol. Cryst. Liq. Cryst.* **183**, 307 (1990).
- ⁹Y. Hirose, A. Kahn, V. Aristov, P. Soukiasian, V. Bulović, and S. R. Forrest, *Phys. Rev. B* **54**, 13748 (1996).
- ¹⁰S. E. Burns, N. Pfeffer, J. Guner, M. Remmers, T. Javoreck, D. Neher, and R. H. Friend, *Adv. Mater.* **9**, 395 (1997).
- ¹¹P. E. Burrows, Z. Shen, V. Bulović, D. M. McCarty, S. R. Forrest, J. A. Cronin, and M. E. Thompson, *J. Appl. Phys.* **79**, 7991 (1996).
- ¹²S. R. Forrest, *Chem. Rev.* **97**, 1793 (1997).
- ¹³D. F. O'Brien, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.* **74**, 442 (1999).
- ¹⁴S. R. Forrest, L. Y. Leu, F. F. So, and W. Y. Yoon, *J. Appl. Phys.* **66**, 5908 (1989).
- ¹⁵R. Winston, *Sol. Energy* **17**, 255 (1974).
- ¹⁶P. Peumans, V. Bulović, and S. R. Forrest (unpublished).
- ¹⁷V. Bulović and S. R. Forrest, *Chem. Phys.* **210**, 13 (1996).