

Communications to the Editor

Enhanced Quantum Efficiencies and Short-Circuit Photocurrents in Solid Porphyrin Thin Film Cells by Internal Electric Fields

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We describe here dramatic increases in the observed photocurrents in cells composed of a thin ($\sim 1\text{--}2\ \mu\text{m}$) solid film of zinc octakis(β -decoxyethyl)porphyrin (ZnODEP) sandwiched between two pieces of indium–tin oxide (ITO)-coated glass by applying an electric field to (i.e., poling) the ZnODEP during cell preparation from the molten material. Photovoltaic cells composed of organic molecular crystals, such as porphyrins, phthalocyanines, and dye molecules, generally show low ($\ll 1\%$) quantum efficiencies (Φ , electrons per incident photon) even though these materials have high optical absorption coefficients ($a \approx 10^5$).¹ This low efficiency, compared to cells of inorganic materials, can be traced to inefficient dissociation of photo-generated excitons into electron/hole pairs and to the lower mobility of the carriers. We have found, however, that an internal electric field can be produced within the organic crystal film by solidifying it from the molten state in the presence of an applied electric field thus freezing-in trapped space charges or ions and aligning polar molecules and that this field promotes charge separation and transport. The short-circuit photocurrent (I_{sc}) with poled samples was increased by >1 order of magnitude and Φ values of up to 8.4% were attained.

Photovoltaic cells of ITO/ZnODEP/ITO were first described by Gregg et al.² and are prepared in an oven by capillary filling of ZnODEP in its molten state into the empty ITO cells separated by about $1.5\text{--}2.5\ \mu\text{m}$ followed by a slow cooling to room temperature. Detailed procedures for the cell fabrication were reported previously.^{2,3} The steady-state I_{sc} observed with ZnODEP cells occurs by the preferential photoinjection of electrons at the illuminated interface into the ITO.² The measured Φ for the cells produced in this study by this procedure was $0.5\text{--}0.7\%$ under $400\ \text{nm}$ irradiation with an intensity of about $10^{13}\ \text{photon cm}^{-2}\ \text{s}^{-1}$, close to values obtained previously with porphyrins with shorter hydrocarbon chains.² When a bias voltage was applied between the two ITO electrodes during the cell preparation, the Φ of I_{sc} increased substantially.⁴ Since cells with different organic layer thicknesses produced different photocurrent levels, the same cell was used in comparative measurements with and without poling. For example, a $1.5\ \mu\text{m}$ thick cell prepared without an electric field yielded a Φ of 0.7% (irradiation at $400\ \text{nm}$ at an intensity of $4.9\ \mu\text{W/cm}^2$). However, when this cell was reheated to its molten state and held at $160\ ^\circ\text{C}$ for about 20 min under a bias of $0.3\ \text{V}$, corresponding to an electric field of about $2000\ \text{V/cm}$, its Φ increased 12 times and reached 8.4% measured under identical conditions (Figure 1). In these measurements, the cell was short-circuited in the dark for 30 s before the

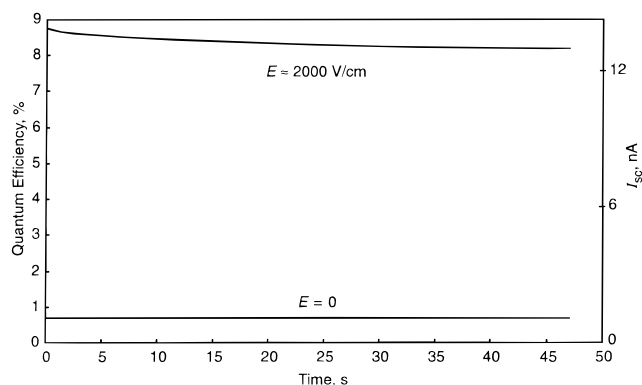


Figure 1. Comparison of quantum efficiency (left scale) and short-circuit photocurrent (right scale) as a function of time for an ITO/ZnODEP/ITO symmetrical sandwich cell ($9\ \text{mm}^2$ and $1.5\ \mu\text{m}$ thick) prepared with and without an electric field ($2000\ \text{V/cm}$). Calculated quantum efficiency based on incident light intensity, $4.9\ \mu\text{W/cm}^2$.

Table 1. Quantum Efficiencies of Short-Circuit Photocurrent from ITO/ZnODEP/ITO Cells^a

| cell | thickness (μm) | area (cm^2) | Φ (%) | |
|------|-----------------------------|------------------------|------------|----------|
| | | | field off | field on |
| 1 | 1.5 ± 0.1 | 0.09 | 0.69 | 8.4 |
| 2 | 1.9 ± 0.2 | 0.14 | 0.56 | 6.3 |
| 3 | 2.4 ± 0.3 | 0.36 | 0.45 | 4.1 |

^a Cells were prepared with and without an electric field ($\sim 2000\ \text{V/cm}$) under irradiation at $400\ \text{nm}$ ($4.9\ \mu\text{W/cm}^2$).

irradiation and no current was seen in the dark state when the light was chopped. Cells of different thickness showed similar enhancements in Φ upon poling as shown in Table 1. As seen in previous studies,^{2,5} Φ increased with decreasing cell thickness. Many heating and cooling cycles with a number of different cells following the same procedure have further confirmed that Φ increased by ~ 1 order of magnitude with an electric field of $\sim 2000\ \text{V/cm}$. Φ might be expected to increase even more with a larger field. However, the cells often became shorted under a larger bias. These shorted cells looked the same as unshorted ones under an optical microscope and could be repaired in many cases by heating again to their molten states in the absence of a field. Cells could be repaired a number of times after shorting without apparent damage. This suggests that the shorts occurred only at isolated points probably caused by impurities or dust rather than by breakdown of the ZnODEP, leading to chemical change and irreversible damage.

The observed effect of the electric field can be attributed to several factors. Impurity ions, almost inevitably present in these materials, could be displaced within the organic layer in the presence of the applied bias, causing the buildup of an internal electric field which would increase the probability of light-induced charge separation and charge movement. Polar molecules could also be oriented by the applied field and contribute to an internal one. ZnODEP is a symmetric molecule without a dipole moment and thus its orientation and crystal growth should not be affected by the field. In fact, no morphological difference was seen under an optical microscope between cells prepared with and without an electric field. However, dipoles of impurity molecules could

(1) Forrest, S. R. *Chem. Rev.* **1997**, *97*, 1793 and references therein.
(2) Gregg, B. A.; Fox, M. A.; Bard, A. J. *J. Phys. Chem.* **1990**, *94*, 1586.
(3) Liu, C.-Y.; Pan, H.-L.; Tang, H.; Fox, M. A.; Bard, A. J. *J. Phys. Chem.* **1995**, *99*, 7632.

(4) Some preliminary experiments of this type were performed, but the large enhancements shown here were not found. Gregg, B. A. Ph.D. Dissertation, University of Texas, 1988; p 181.

(5) Liu, C.-Y.; Bard, A. J. *Chem. Mater.* **1998**, *10*, 840.

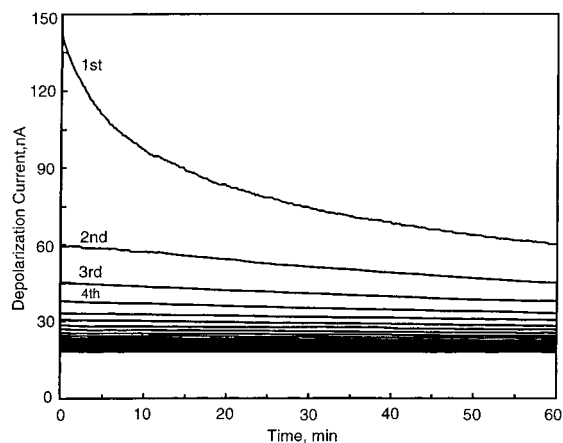


Figure 2. Photocurrent as a function of time for an ITO/ZnODEP/ITO cell (9 mm^2 and $1.5 \mu\text{m}$ thick) prepared with an electric field ($\sim 2000 \text{ V/cm}$). The continuous photocurrent curve is plotted in sections representing the first, second, third, etc. hours of operation.

form an internal electric field after poling. The direction of I_{sc} was determined by the polarity of the bias voltage applied to the ITO/ZnODEP/ITO cell during preparation; electrons moved from the irradiated ITO into the organic layer with cells prepared with a positive bias applied to the irradiated ITO electrode and from the ZnODEP to the irradiated ITO for cells prepared under a negative bias. This contrasts with the behavior of cells prepared without a bias^{2,3} where photogenerated electrons always moved from organic layer into the illuminated ITO electrode. This direction dependence of I_{sc} on the applied bias provides strong experimental evidence for the existence of an internal electric field or internal polarization. Indeed, the observed effect is similar to those when the electric field is applied to polymers at high temperature to generate electrets⁶ or to produce persistent internal polarization in a number of substances.^{7,8}

(6) Sessler, G. M. *Electrets*; Springer-Verlag: Berlin, 1987.

(7) Freeman, J. R.; Kallmann, H. P.; Silver, M. *Rev. Modern Phys.* **1961**, *33*, 553.

(8) Kallmann, H. P.; Rosenberg, B. *Phys. Rev.* **1955**, *97*, 1596.

The I_{sc} in a poled cell slowly decayed with time (Figure 1). The decay increased under continuous irradiation with white light at higher intensity, e.g., with the light adjusted to produce an initial I_{sc} value that was >1 order of magnitude larger than that in Figure 1. Figure 2 shows this decay over a 27 h period. I_{sc} decayed relatively quickly during the first hour and attained a near steady-state value close to that of the unpoled cell after about 27 h. The total charge in excess of that in an unpoled cell was determined by integration of I_{sc} with time, taking the steady state as a baseline to yield a total excess charge of $7.6 \times 10^{-4} \text{ C}$. This is well in excess of that obtainable with the bias if the field induced simple charging of the ITO/ZnODEP/ITO cell like a conventional capacitor which then discharged with irradiation at short-circuit condition. A total charge, Q , of $7.6 \times 10^{-4} \text{ C}$ would require a bias voltage, V , of $4.7 \times 10^{10} \text{ V/cm}$ for charge storage in a capacitor ($V = Qd/\epsilon\epsilon_0$, where d is the cell thickness, and ϵ is the dielectric constant, taken as 2 for ZnODEP). One can account for the decay of I_{sc} with continuous irradiation by the gradual neutralization of the internal field by trapped charges or relaxation of oriented dipoles. Obviously, the excess current on poling was not just the cancellation of an internal field established during the sample preparation but rather it resulted from the internal field assisting charge generation and separation in a way similar to space charge layer effects in inorganic semiconductors.

The apparent buildup of an electric field by poling produces symmetric sandwich cells of ITO/ZnODEP/ITO which show quantum efficiencies among the highest of those reported for organic-based (nonsensitized) photovoltaic cells. Such an internal electric field-induced amplification may have a great impact in the design of optoelectric devices based on organic materials. Further experiments are under way to explore this effect and optimize the cell performance. These include studies of the effect of high purification of the organic material and doping with ionic species.

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