

Effect of Orientation of Porphyrin Single-Crystal Slices on Optoelectronic Properties

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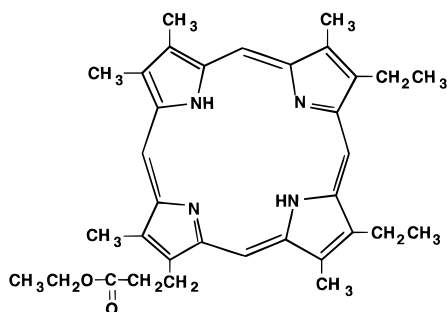
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Millimeter-sized organic single-crystal slices of methylpyrroporphyrin XXI ethyl ester (MPPEE) have been prepared by capillary filling at its melting point (~ 250 °C) between two parallel pieces of glass coated with indium–tin oxide (ITO) and separated by about $2\text{--}3$ μm . Crystal orientation was characterized with polarized light under an optical microscope. MPPEE single-crystal slices with different orientations appeared as dramatically different colors between two crossed polarizers. The relationship between crystal orientation and optoelectronic properties was investigated by monitoring the photocurrent flow through ITO/MPPEE/ITO symmetrical sandwich cells. The short-circuit photocurrent strongly depended on crystal orientation, varying by more than 1 order of magnitude. When a light spot (~ 150 μm in diameter) was scanned across adjacent MPPEE single-crystal domains with different orientations, short-circuit photocurrents generated at different spots within the same crystal domain were essentially constant, but they changed substantially among different domains. The photocurrent changed abruptly at domain boundaries.

Introduction

We report here experimental studies showing orientational effects on the optoelectronic properties of thin layers of the organic molecular crystal methylpyrroporphyrin XXI ethyl ester (MPPEE). Films (~ 2 μm thick) consisting of millimeter-sized



Methylpyrroporphyrin XXI ethyl ester

single crystals with a variety of orientations were produced in symmetrical sandwich cells between two pieces of indium–tin oxide (ITO)-coated glass by capillary filling with the melt. Polarized light was used to determine the crystal orientations under a light microscope. Photocurrents generated with unpolarized light impinging on the ITO/MPPEE/ITO cells strongly depended on the crystal orientation. These results were interpreted with a model based on the degree of overlap between orbitals of neighboring MPPEE molecules. A strong influence of the grain boundaries on the photocurrent was also found.

Organic molecular crystals differ from inorganic solids in that they are made up of discrete molecules;^{1–3} while intramolecular forces are strong, intermolecular interactions are generally weaker and of shorter range. This mixture of strong and weak forces leads to a configuration of electronic structure within the organic crystal where molecules in the lattice essentially retain their individual identity and charge carriers and excitons are mainly localized on individual molecules of the organic crystals.^{1,2} This is different than covalent or ionic inorganic solids with strongly bonded rigid atomic or ionic lattices characterized by a practically complete loss of individual

properties of the constituent particles in the crystal. Therefore, for studies of charge carrier transport, the well-established theory for inorganic semiconductors, such as the band model describing delocalized charge carriers, cannot be applied to organic molecular crystals without great caution.^{1,2} This leaves the theory of electronic conduction at an essentially qualitative level for a large number of organic systems, although much progress has been made in recent years.

Organic molecular crystals often show anisotropic properties (e.g., electrical conduction).^{1,2,4,5} The low symmetry of organic molecules is the main cause of a large lattice anisotropy, leading to anisotropic optical, electrical, magnetic, mechanical, and other physical properties of the crystal. Because of applications in areas like liquid crystal display technology,⁶ nonlinear optical materials,⁷ and potential electronic and optoelectronic devices,^{8–10} numerous efforts have been made to fabricate highly anisotropic systems, such as multilayer molecular systems by Langmuir–Blodgett or molecular beam techniques.¹¹ Another approach involves assembling molecules synthesized by design into well-defined organic crystals that show quasi-one-dimensional conductivity.^{12–15} For example, liquid crystal porphyrins¹² form regularly stacked crystals where the individual molecular columns behave as molecular wires with a higher conductivity along the columns than between columns due to the better intermolecular π – π overlap perpendicular to the molecular plane. The effect of temperature on the formation of porphyrin molecular columns or conduction channels between two parallel ITO electrodes has recently been probed in situ by comparing current flow in the solid, liquid crystal, and isotropic phases.¹⁶ An electronic switch effect corresponding to the “on” and “off” states of the molecular conduction channels was observed.¹⁶ Due to the low dimensionality of the electronic conduction pathway, crystal orientation should have a significant effect on the photoelectric properties of these porphyrin crystals. We describe here a study on the effect of crystal orientation on the photocurrent in cells of the asymmetric porphyrin molecule MPPEE.

Experimental Section

Methylpyrroporphyrin XXI ethyl ester (MPPEE, Aldrich) was purified by sublimation. ITO-coated glass was obtained from

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Donnelly Applied Film Corporation (Boulder, CO) and was cut into 1 cm \times 2 cm pieces. Symmetrical sandwich cells of ITO/MPPEE/ITO were fabricated according to a previously described method.^{12b,16} Briefly, MPPEE was filled by capillary action into ITO cells placed in an oven at \sim 250 $^{\circ}$ C, slightly above the melting point of the porphyrin material. The thickness of the MPPEE thin layer within the cells was about 2–3 μ m, as estimated by their interference pattern. Electrical contacts to the cells were made on ITO surfaces with silver paint for optoelectrical measurements. An optical microscope (Olympus Model BHTU), coupled with two Polaroid film polarizers, was employed for the determination of crystal orientation.

In general, about 85% of the area of a cell consisted of millimeter-sized crystal domains that could be seen with the naked eye. Under an optical microscope, all of these domains had the same color in the absence of polarizers. However, between two crossed polarizers, each crystal domain within the same cell showed a different color due to its different orientation relative to the polarizers. Moreover, the color changed upon sample rotation (with respect to fixed polarizers); this was useful in the comparison of different crystal orientations in the different domains.

In the photocurrent measurements, the porphyrin sandwich cell was fixed on the stage of a microscope, an individual crystal domain was selected, the polarizers were removed, and the photocurrent at that domain was measured. In this case, the optical system in the microscope provided the light source for illumination, and no external lamp was used. The light spot (top irradiation) was adjusted from 150 to 800 μ m in diameter for the photocurrent measurements. No bias voltage was applied to the cells, and therefore no dark current flowed. The short-circuit photocurrent was generated only at the irradiated area. The light intensity and spot size were kept constant for the comparison of photocurrent obtained from different positions within the same crystal domain or from various domains with different orientations. The short-circuit photocurrent was generally small (approximately picoamperes), because of the weak light source, and thus shielding with aluminum foil was necessary to prevent electrical interference and the effects from external stray light. A home-built high-sensitivity amplifier circuit was employed to measure the photocurrent. Polarized light was used only for determination of crystal orientation, and photocurrent was always generated with unpolarized irradiation.

Results and Discussion

Microscopy. After filling with molten porphyrin and cooling to room temperature, the organic layer in the ITO/MPPEE/ITO sandwich cells consisted of many millimeter-sized crystal domains which could be seen with the naked eye. Each domain was a single crystal that extended across the 2–3 μ m gap between the two pieces of ITO-coated glass (rather than the disordered array of small crystal particles frequently seen in polycrystalline layers fabricated by vacuum deposition or as mechanically pressed powder disks). This was confirmed with an optical microscope as shown in Figure 1. The pictures in Figure 1a,b were taken from different sides of the sandwich cell at the same location and show the same geometrical features. This was true for every crystal domain examined in both the transmission and reflection modes. The crystallinity of the sample was further determined with polarized light microscopy. Note that most of the crystal domains were too large, even at the lowest magnification of the microscope, to fit within the picture frame; so only smaller domains and portions of the larger ones could be shown in the photomicrographs. Since the thickness of the porphyrin thin layer was over 1000 times

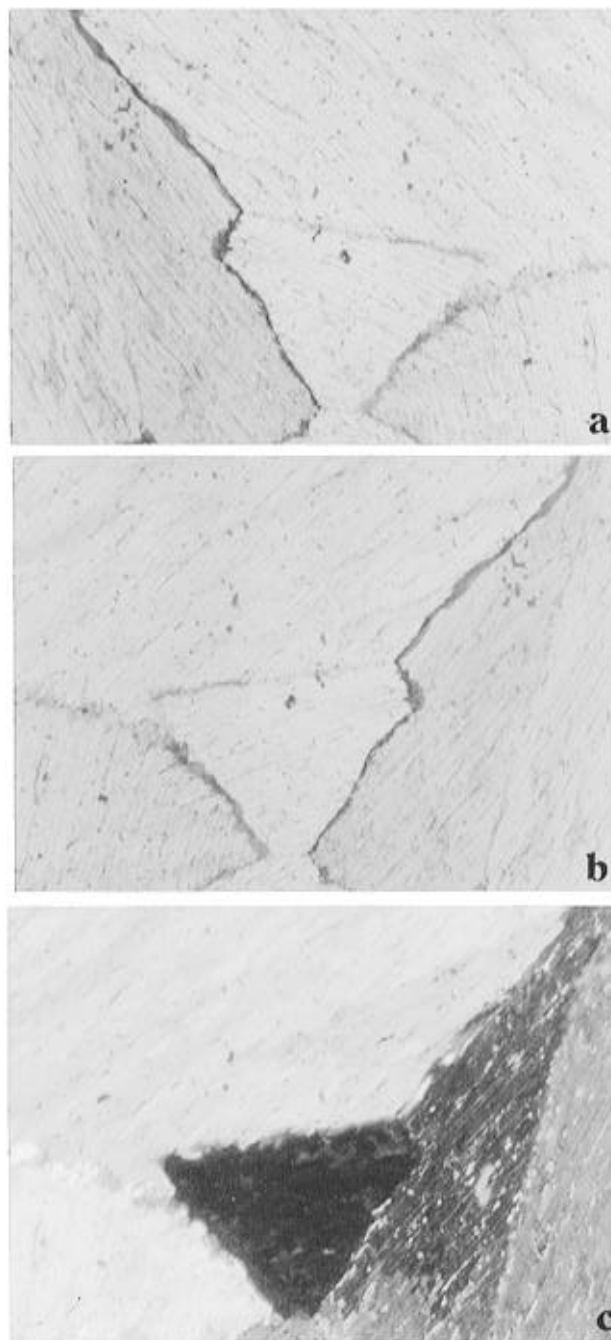


Figure 1. Micrographs of MPPEE single crystals between two pieces of ITO-coated glass (\sim 2 μ m thick; area of view, 1 mm \times 0.7 mm). Micrographs a and b were taken at the same location, but from different sides of the cell without polarizers. The same geometric structure shown in these two images indicates that the single crystals extend from one ITO surface to the other. Micrograph c was taken between two crossed polarizers at the same location as in (a) and (b). Five single-crystal domains with different orientations are clearly distinguished by their different colors.

smaller than the lateral dimension of the crystal domains, the sample is comprised of thin slices of single crystals that can be readily examined optically. This method of growing single crystals is simple and quick and eliminates the difficulties of cutting crystals.

The fine parallel straight lines that appear in each crystal domain are believed to be slip lines, a typical feature of plastic deformation occurring primarily by sliding along certain planes with one part of a crystal moving relative to another.¹⁷ Such planar glides result from crystal shrinkage during the cooling process after the cell is capillary filled at high temperature. In

general, the gliding occurs by translations along widely spaced planes in whole multiples of the displacement vector, so the relative orientation of different regions remains unchanged.¹⁷ Thus, these slip lines serve as a practical indicator of a particular crystal plane under certain conditions. For example, when straight lines are seen in two different crystal domains that run along different directions, these two domains must necessarily have different orientations.

Examination of porphyrin single crystal slices between two crossed polarizers provides clear evidence of crystal orientation (Figures 1 and 2). Single-crystal domains with different orientation show up as dramatically different colors. For example, the two adjacent crystal domains shown on the right of Figure 2a are barely distinguishable, but appear with two completely different colors under polarized light, as shown in Figure 2b,c. Normally no light emerges from crossed polarizers, because the light emerging from the first polarizer is completely blocked by the second. The insertion of an isotropic material between the polarizers does not change this, because the polarization of light is unchanged as it travels through this material. Figures 1c and 2b,c are therefore evidence that the porphyrin molecular crystal under study here is anisotropic, leading to birefringence.^{18,19}

The color in each crystal domain changed with sample rotation between the two crossed polarizers (Figure 2c). Rotation of the sample was thus an effective way to compare the porphyrin crystal orientations among different domains. This is illustrated in Figure 3, a schematic diagram of a porphyrin molecular stack. If the x - y plane is taken for the ITO surface, ϕ represents the tilt angle of the porphyrin column relative to the z axis. At a given ϕ , the molecular columns still have all of the possible (360°) orientations within the x - y plane. These different orientations are distinguished by the polarized light. When the samples were rotated, the crystal domains showed systematic changes in color, and the sequence of color changes was reproduced in some other domains. These domains, with apparently different orientations in the x - y plane, may have the same orientation relative to the z axis, in which case each crystal domain has the same opportunity to show the same color tints upon rotation. However, crystal domains showing a different sequence of color change with sample rotation may have different orientations with respect to the z axis.

The anisotropic molecular crystal of the porphyrin propagates the two different light polarizations at different velocities, causing a phase difference between the two polarizations as the light travels through the porphyrin crystal slice.¹⁹ Since every crystal domain in the sample has the same thickness, the progressive separation in the phase of the two waves for each wavelength depends only on the difference in their velocities, which is sensitive to the crystal orientation at each domain.¹⁹ For example, when the orientation of a crystal domain is such that both polarizations propagate with the same velocity, no phase difference would be expected. In other words, that particular crystal domain would appear dark at all sample rotations between two crossed polarizers. Such a special crystal orientation, however, was not observed at any of the domains in the porphyrin crystal thin-layer cells.

Photocurrents. The optical properties affecting the polarization characteristics of the propagating wave originate from crystal structure anisotropy. Such anisotropies can also influence the electronic properties of organic molecular crystals. Electronic conductivity has been found to be higher along porphyrin molecular columns (Figure 3) because of better intermolecular π - π overlap in a direction perpendicular to the molecular plane.^{12b,c,16} The term "quasi-one-dimensional con-

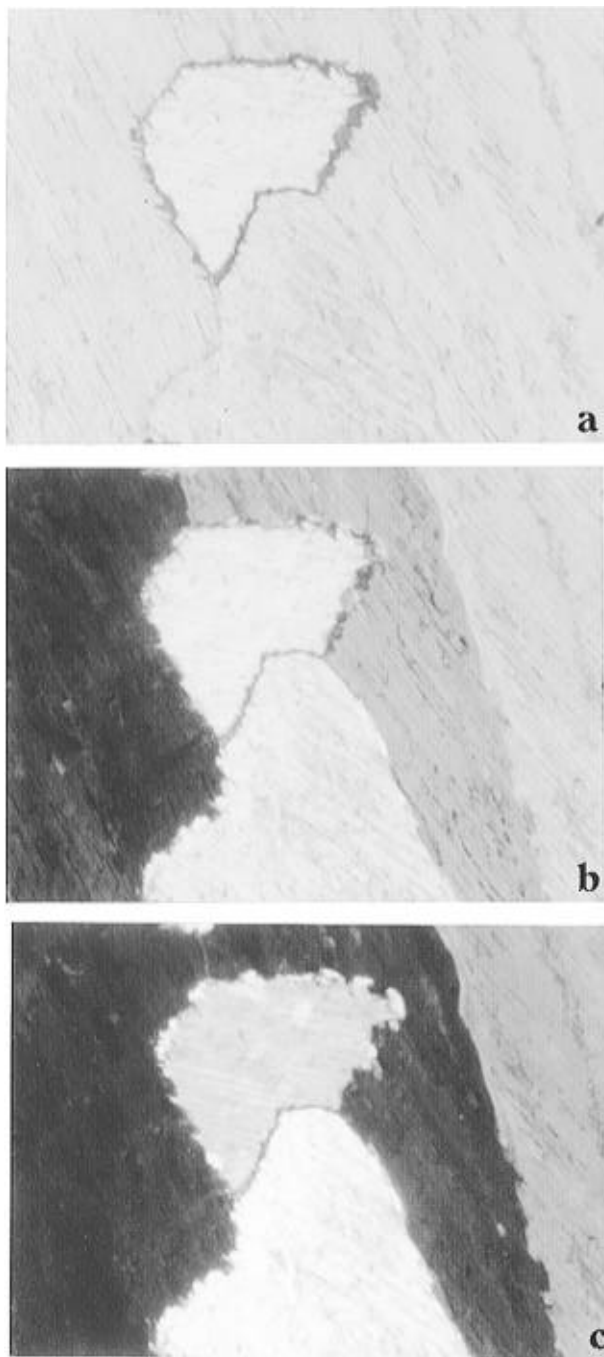


Figure 2. Micrographs of MPPEE single crystals between two pieces of ITO-coated glass ($\sim 2 \mu\text{m}$ thick; area of view, $1 \text{ mm} \times 0.7 \text{ mm}$) (a) without polarizers, (b) between two crossed polarizers, and (c) after sample rotation from (b). The change in color with sample rotation allows recognition of crystal domains with slightly different orientation.

ductor" has been adopted to characterize such electronic properties in certain organic molecular crystals, such as the porphyrins, phthalocyanines, and triphenylenes.¹²⁻¹⁶ Unfortunately, previous studies were based on polycrystalline samples containing small crystals oriented in an essentially random manner, making it impossible to distinguish experimentally a quasi-one-dimensional crystal from a three-dimensional system as far as optoelectronic properties are concerned. Consequently, this interesting characteristic of the porphyrin crystals has not been investigated. With the capability of growing single-crystal sheets, we can now examine directly the orientational effect on optoelectronic properties. Since the conduction of a quasi-one-dimensional system must be sensitive to crystal orientation, if the x - y plane was parallel to the ITO surfaces in Figure 3,

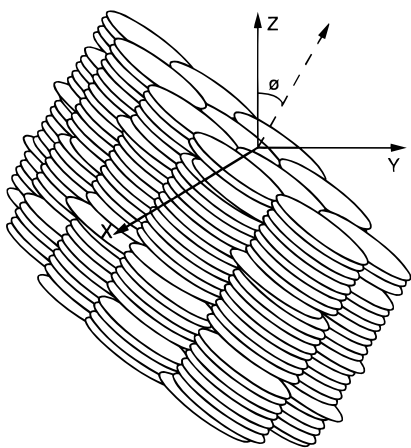


Figure 3. Schematic diagram of porphyrin columnar structure with crystal defects.

then $\phi = 0^\circ$ would represent an orientation with the highest conductance between the ITO surfaces, because the porphyrin molecular columns would be perpendicular to the ITO, while $\phi = 90^\circ$ would yield the lowest conductance. Between these two extremes there are many possible crystal orientations with intermediate conductances.

A short-circuit photocurrent is obtainable from these symmetrical sandwich cells as reported previously.^{9,12b,16} The primary driving force is believed to be the preferential photo-injection of electrons from the excited porphyrin molecules into the ITO electrode and holes into the organic layer.^{12b} Photoconduction through the porphyrin single-crystal slice is essential to maintain a steady-state photocurrent flow. Thus, the conductivity of the porphyrin molecular crystal has a direct effect on the steady-state photocurrent. The relation between crystal orientation and electronic conductance was probed experimentally by photocurrent measurements in which unpolarized light was focused to a spot of about $150\ \mu\text{m}$ diameter, which is much smaller than the dimensions of the crystal domains (approximately millimeters). No bias voltage was applied to the sandwich cell, and the photocurrent was generated only at the irradiated spot. The short-circuit photocurrents produced at different spots within the same crystal domain were essentially identical, which confirms that the crystal orientation determined with polarized light did not change from spot to spot within the same domain. However, the photocurrents generated in different crystal domains were dramatically different, as shown in Figure 4 in which the short-circuit photocurrents obtained from nine different crystal domains are compared; these differed by more than 1 order of magnitude. Polarized light microscopy showed that these nine domains had different crystal orientations. In these experiments, the light intensity and spot were fixed, and the sample stage was moved on the microscope to select the irradiated domain. When the light beam was scanned across a number of adjacent domains with different crystal orientations, the photocurrent showed sharp changes at the boundaries (Figure 5). These experiments provide direct evidence for the effect of orientation of the porphyrin crystals on the optoelectronic properties. Note that the photocurrents produced from those crystal domains with the same ϕ , oriented differently only at the x - y plane, were about the same. This implies that at a given ϕ the crystal domains with different orientations distinguishable between crossed polarizers showed equivalent electrical conduction and that the crystal orientation relative to the z axis is the determining factor for photocurrent generation.

Effect of Grain Boundaries. While our samples were generally dominated by millimeter-sized crystal domains ($\sim 85\%$

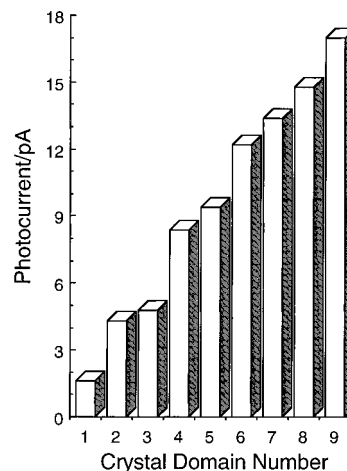


Figure 4. Short-circuit photocurrents generated at nine different crystal domains with different orientations. The crystal domains are numbered arbitrarily.

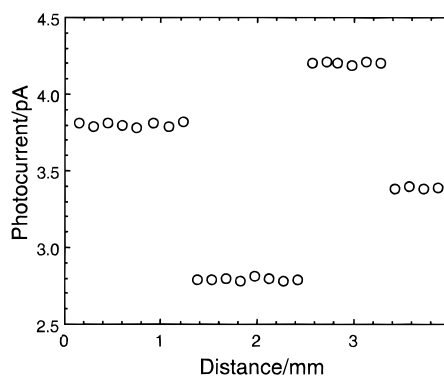


Figure 5. Short-circuit photocurrents produced by scanning a light spot ($\sim 150\ \mu\text{m}$ in diameter) across four adjacent crystal domains with different orientations. The photocurrent is essentially constant within a given crystal domain but varies considerably from domain to domain and changes sharply at domain boundaries.

of the total area), smaller crystals also appeared at very few spots (Figure 6a). In these, the crystal domains had so many different orientations that it was difficult to recognize all of the different domains in the image with the polarized light (Figure 6b). This illustrates again how powerful the use of polarized light is in the determination and comparison of molecular orientations within specific crystal domains. Note that the black spot shown at the center of Figure 6b did not represent a special crystal orientation in which both polarizations traveled at the same velocity, as discussed above, because the color of this domain changed with sample rotation. Compared to the large single-crystal domains, the location shown in Figure 6 is a "boundary-rich" area. Crystal (grain) boundaries are often invoked at sites of charge trapping, recombination centers for photochemical or photoelectric processes, and as luminescence quenchers. It was thus of interest to compare the boundary-rich area with boundary-free single-crystal domains in terms of photocurrent production. In this experiment, the light spot was adjusted to $\sim 800\ \mu\text{m}$ in diameter so that it was large enough to cover most of the boundary-rich area shown in Figure 6 but was still small enough to be confined within some of the single-crystal domains. The photocurrent transients obtained at these two different areas, shown in Figure 7, are representative of a number of experiments at different times with different domains. In general, the photocurrent generated within a single crystal was essentially constant over time, while in the boundary-rich area the photocurrent decayed (Figure 7a). We believe this represents the effect of the accumulation (trapping) of charge

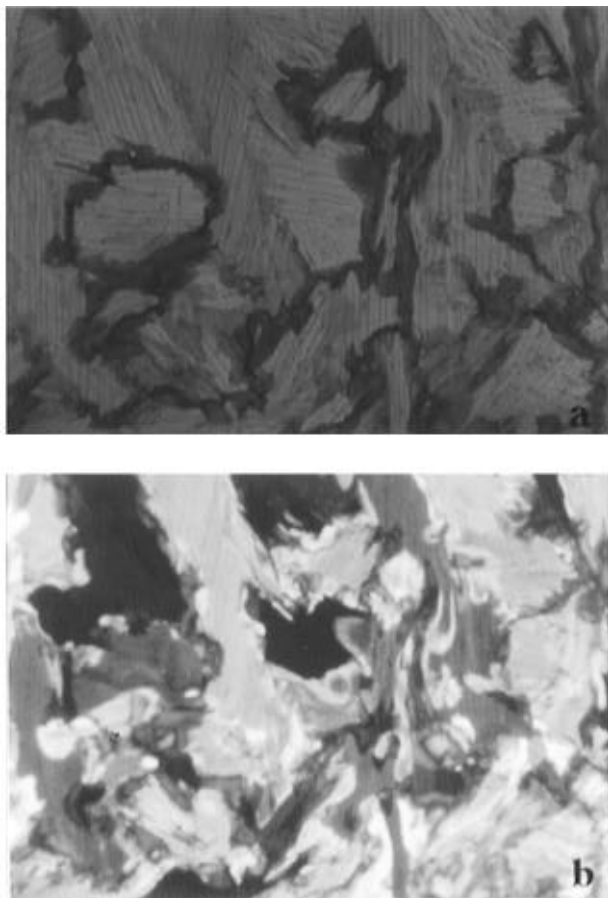


Figure 6. Micrographs of MPPEE in a location with smaller crystal domains ($\sim 2 \mu\text{m}$ thick; area of view, $1 \text{ mm} \times 0.7 \text{ mm}$) (a) without polarizers and (b) between two crossed polarizers.

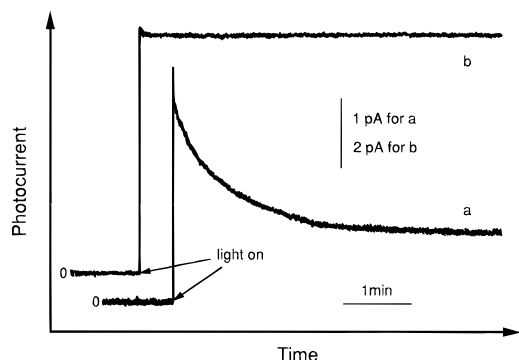


Figure 7. Short-circuit photocurrents as a function of time with a light spot $\sim 0.8 \text{ mm}$ in diameter. The zero-current location is shifted for clarity, and the current scale is different for the two curves. (a) Taken from a boundary-rich area shown in Figure 6. (b) Taken within a single-crystal domain with the same illumination as in (a).

at grain boundaries, with the photocurrent attaining a steady state when the charge trapping and detrapping rates are the same. Moreover, the steady-state photocurrent in the boundary-rich area is significantly smaller than that found in all single crystals. Although the photocurrent generated in the boundary-rich area represents the average for many crystal domains with different orientations, we conclude that the grain boundaries act as trapping or recombination centers, leading to a reduction in the photocurrent.

Conclusions

Large (millimeter-sized) porphyrin single crystals spanning the micrometer gap between parallel ITO-coated glass slides form on crystallization from the melt. The orientation of these crystals can be determined by polarized light microscopy. The short-circuit photocurrent varied from one domain to another and was larger with single-crystal domains than in areas with many grain boundaries. Taken together, these results illustrate the importance of molecular orientation and grain boundaries on photovoltaic and charge-trapping processes in such thin-layer cells.

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References and Notes

- (1) Silinsh, E. A.; Capek, V. *Organic Molecular Crystals: Interaction, Localization, and Transport Phenomena*; American Institute of Physics: New York, 1994.
- (2) Silinsh, E. A. *Organic Molecular Crystals: Their Electronic States*; Springer-Verlag: Berlin, 1980.
- (3) Wright, J. D. *Molecular Crystals*; Cambridge University Press: Cambridge, 1987.
- (4) (a) Gutmann, F.; Lyons, L. E. *Organic Semiconductors, Part A*; Krieger: Malabar, FL, 1981. (b) Gutmann, F.; Keyser, H.; Lyons, L. E. *Organic Semiconductors, Part B*; Krieger: Malabar, FL, 1983.
- (5) Meier, H. *Organic Semiconductors: Dark- and Photoconductivity of Organic Solids*; Verlag Chemie: Weinheim, 1974.
- (6) (a) Castellano, J. A. *Handbook of Display Technology*; Academic Press: San Diego, 1992. (b) Collings, P. J. *Liquid Crystals: Nature's Delicate Phase of Matter*; Princeton University Press: Princeton, 1990.
- (7) Garito, A.; Shi, R. F.; Wu, M. *Phys. Today* **May 1994**, 51.
- (8) Forrest, S. R. *IEEE Circuits Devices Mag.* **May 1989**, 33.
- (9) Liu, C.-Y.; Pan, H.-L.; Fox, M. A.; Bard, A. J. *Science* **1993**, *261*, 897.
- (10) Simon, J. In *Nanostructures Based on Molecular Materials*; Gopel, W., Ziegler, Ch., Eds.; VCH: Weinheim, 1992, p 267.
- (11) Kobayashi, T. In *Organic Crystals I: Characterization*; Karl, N., Ed.; Springer-Verlag: Berlin, 1991; pp 1–63.
- (12) (a) Gregg, B. A.; Fox, M. A.; Bard, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 3024. (b) Gregg, B. A.; Fox, M. A.; Bard, A. J. *J. Phys. Chem.* **1990**, *94*, 1586. (c) Gregg, B. A.; Fox, M. A.; Bard, A. J. *J. Phys. Chem.* **1989**, *93*, 4227.
- (13) (a) Chandrasekhar, S.; Sadashiva, B. K.; Suresh, K. A. *Pramana* **1977**, *9*, 471. (b) Tinh, N. H.; Dubois, J. C.; Malthete, J.; Destrade, C. *C.R. Acad. Sci., Paris* **1978**, *286C*, 463. (c) Billard, J.; Dubois, J. C.; Tinh, N. H.; Zann, A. *Nouv. J. Chim.* **1978**, *2*, 535. (d) Destrade, C.; Mondon, M. C.; Malthete, J. *J. Phys.* **1979**, *40-C3*, 17. (e) Destrade, C.; Foucher, P.; Gasparous, H.; Tinh, N. H.; Levelut, A. M.; Malthete, J. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 121. (f) Goodby, J. W.; Robinson, P. S.; Teo, B.-K.; Clad, P. E. *Mol. Cryst. Liq. Cryst. Lett.* **1980**, *56*, 303–309. (g) Morelli, G.; Ricciardi, G.; Roviello, A. *Chem. Phys. Lett.* **1991**, *185*, 468.
- (14) Simon, J.; Bassoul, P. In *Phthalocyanines, Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1989; Vol. 2, p 223 and references therein.
- (15) (a) Boden, N.; Bushby, R. J.; Clements, J. *J. Chem. Phys.* **1993**, *98*, 5920. (b) Boden, N.; Borner, R. C.; Bushby, R. J.; Clements, J. *J. Am. Chem. Soc.* **1994**, *116*, 10807.
- (16) Liu, C.-Y.; Pan, H.-L.; Tang, H.; Fox, M. A.; Bard, A. J. *J. Phys. Chem.* **1995**, *99*, 7632.
- (17) Hertzberg, R. W. *Deformation and Fracture Mechanics of Engineering Materials*, 2nd ed.; John Wiley & Sons: New York, 1983.
- (18) Bousfield, B. *Surface Preparation and Microscopy of Materials*; John Wiley & Sons: New York, 1992.
- (19) Pankove, J. I. *Optical Processes in Semiconductors*; Dover: New York, 1975.