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Effects of Long Range Order, Temperature and Phase on the Photoconversion Properties of Liquid Crystal Porphyrin Films

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Effects of Long Range Order, Temperature and Phase on the Photoconversion Properties of Liquid Crystal Porphyrin Films

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Photocurrent and photovoltage measurements on thin films of a liquid crystal zinc porphyrin are described. The film order exerts a pronounced effect on the magnitude of the photocurrent in these quasi-1-dimensional semiconductors, and can be the predominant limitation to charge transfer in highly disordered films. The changes in photocurrent and photovoltage as the temperature is increased through the solid phase to the discotic liquid crystalline phase are measured and explained as resulting from changes in exciton diffusion length, charge carrier mobilities and the relative rates of exciton dissociation by electron and hole injection into the electrode. The greater disorder of the liquid crystalline phase relative to the solid phase is apparently responsible for the sudden decrease in photocurrent and photovoltage at the crystal to liquid crystal phase transition.

INTRODUCTION

In electronic applications, a crystalline material almost always has superior properties compared to the same material in an amorphous phase. There are a number of areas in which crystalline thin films of semiconductors are highly desirable, such as for thin film transistors and for solar energy conversion systems, but the growth and processing of large area single crystals of electroactive materials is often difficult and expensive. Partly for these reasons, the inherent tendency of liquid crystals to spontaneously self-order at moderate temperatures has generated increasing interest in the synthesis and characterization of electroactive liquid crystals. A number of electroactive and photoactive materials have been synthesized as liquid crystals including phthalocyanines,[1–4] porphyrins,[5–7] porphyrazines,[8] hexacyclens,[9] and various metal dithiolates,[10] diketonates,[11] tetracarboxylates[12] and dipyranylidenes.[13] The electronic and catalytic properties of these new materials are just beginning to be examined.[14–22] This report describes the changes in photoconversion properties observed in thin films of the discotic liquid crystal (LC) zinc 2, 3, 7, 8, 12, 13, 17, 18-octakis(β-octyloxyethyl)porphyrin[7,17,18] as the long range film order is varied, and as the temperature is increased through the crystal → discotic mesophase transition.

Test cells consisted of the LC porphyrin capillary-filled between two ITO (indium tin oxide) conducting glass electrodes. Although a photovoltaic effect in such symmetrical

cells (both electrodes have identical work functions) may seem unusual, it has been explained[18,19] as resulting from two simple processes: 1) the incident light is strongly absorbed by the porphyrin, thus the concentration of excitons is much higher at the illuminated electrode interface than at the dark electrode, and 2) exciton dissociation at the porphyrin/ITO interface is inherently asymmetric, electron injection into the ITO is more facile than hole injection. Taken together these two processes lead to a strong and persistent photovoltaic effect. These results show that band bending and space charge layers are not necessary to achieve charge separation in molecular semiconductors, and that molecular materials can operate by mechanisms unavailable to the better understood inorganic semiconductors. At the light intensities used in this work ($I > 1\,mW/cm^2$), photovoltages are primarily limited by the asymmetry of the interfacial exciton dissociation process[18], and thus are not greatly affected by the bulk film order. Photocurrents, on the other hand, are limited by the low conductivity of the relatively thick and undoped porphyrin films, and are thus strongly influenced by film order.

It has rarely been possible to measure the change in a photovoltaic effect as the semiconductor is heated through a reversible phase transition. Thus some preliminary results from such measurements are reported here and compared to the recent measurements of the variations in charge carrier mobility in the LC porphyrins as a function of temperature and phase.[22]

EXPERIMENTAL

The test cells consisted of two parallel ITO electrodes separated by 3–4 μm spacers.[18] The ITO was patterned into stripes about 2.5 mm wide by spin-coating a thin film of poly(ethylene vinyl acetate) onto the surface, scribing thin lines through the polymer film and then electroetching (0.5 N HCl at − 1.2 V vs. SCE) the ITO. The stripes on the two electrodes were placed perpendicular to each other thus forming a grid of "pexels" that could be individually addressed. In this fashion the differences in crystallinity between pexels could be examined in a single cell, thereby reducing or eliminating the variability from cell to cell caused by factors such as changes in layer thickness and the length of time the LCP was in its molten phase (see below). The LCP was then capillary-filled into the cell in its isotropic phase ($T > 162°C$)[7] and cooled to the solid state where most measurements were performed.

Two techniques were employed to obtain variations in film order. Method 1: cells were capillary-filled with LCP under vacuum, cooled into the liquid crystalline phase ($107° < T < 162°C$) where the vacuum was released. The sudden increase in pressure crushed the crystals that had formed as the LCP cooled from the isotropic liquid into the discotic mesophase. This procedure resulted in a relatively uniform distribution of crystallites 2–5 μm in diameter. The cells could be recordered by heating to the isotropic phase and slow cooling, resulting in crystallites approximately 30–100 μm in diameter. Method 2: rapid thermal quenching of one part of a cell (a few pexels) was achieved by contacting it with a metal rod immediately after capillary-filling. This resulted in small crystallites in the quenched part of the cell, and normal sized crystallites in the rest (see Figure 2). The photovoltaic effect in each area could be assessed by measurements of the individual pexels. In no case has it been possible to

prepare amorphous films in these capillary-filled LC porphyrin cells, thus even the "disordered" films are much more highly ordered than the evaporated films of porphyrins commonly used in photovoltaic studies[23–25] (see below).

The LC porphyrin cells were illuminated by a 150 W Xe-lamp (Photon Technologies Inc.) through a 15 cm water filter. Calibrated screens were employed to decrease the light intensity. The photocurrent was measured at 25 mV intervals with a Keithley 236 Source Measure Unit allowing 1 s for the current to stabilize at each voltage. Dark currents were measured similarly. The optical characteristics of the cells were examined and photomicrographs were taken through crossed polarizers with a Nikon Labophot 2 Pol microscope equipped with a Leitz 350 hot stage and a Nikon AFXDX camera system.

During the thermal experiments the LC porphyrin cells were secured to the hot stage with Omegatherm 201 high temperature thermally conductive paste. The temperature was increased at ca. 5°/min while current-voltage measurements were performed. The accuracy of the temperature measurements in this experiment was approximately ± 4°C.

RESULTS AND DISCUSSION

Effects of Order

The photocurrent vs. voltage behaviour of a cell prepared by method 1 is shown in Figure 1, both as-filled (2–5 μm diameter crystallites) and after subsequent reordering (30–100 μm diameter crystallites). The incident white light intensity was approximately 10 mW/cm^2. The short circuit photocurrent density increased from 0.4 μA/cm^2 in the relatively disordered films to 7.7 μA/cm^2 after ordering. This 19 fold increase in

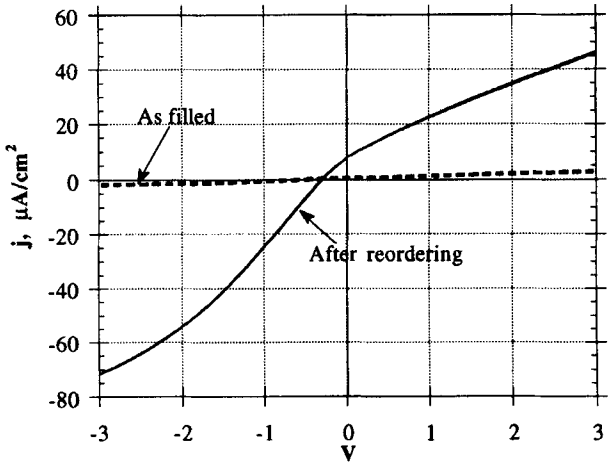

FIGURE 1 Photocurrent-voltage characteristics of a cell prepared by method 1 with crystallites of 2–5 μm diameter (dashed line). The cell was then heated back to the isotropic liquid and cooled slowly resulting in crystallites of ca. 30–100 μm in diameter (solid line). Light intensity was 10 mW/cm^2. Cell was 3.5 μm thick.

photocurrent occurs despite the fact that the LC porphyrin is not entirely stable at its melting point and heating the film usually reduces the photocurrent. In this case, the increase in crystallinity more than compensates for the slight decomposition of the LC porphyrin at high temperatures. The relative increase in photocurrent density with order is most prominent at low incident light intensity. At ca. 170 mW/cm^2 the ordered film shows a photocurrent only 2.1 times greater than the relatively disordered film. The diminution of the influence of film order on the photocurrent is caused by the

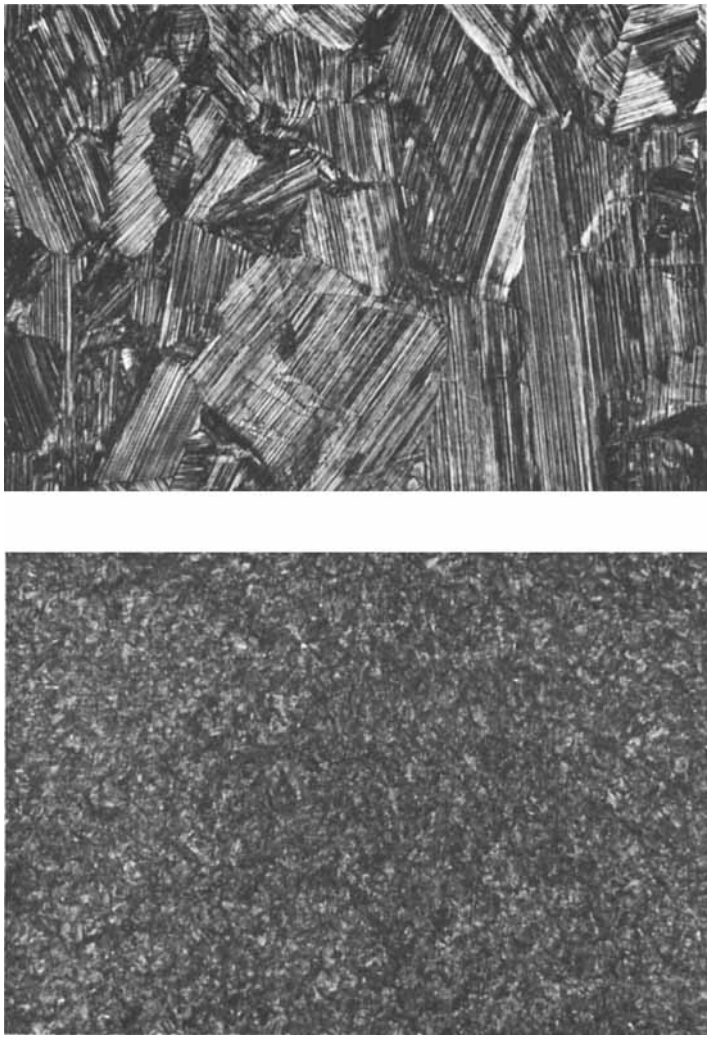

FIGURE 2 Photomicrographs through crossed polarizers of two pexels (individually addressable areas), a) ordered and b) disordered, of a single cell prepared by method 2. The area shown is 1.6 × 1.1 mm^2. Note that the "disordered" region is still much more highly ordered than a typical evaporated film of porphyrin which would transmit no light under these conditions. It has not been possible to generate amorphous film of the LC porphyrin. [See color plate I]

greater prevalence of charge carrier recombination at higher light intensity,[18] thus the rate of charge transfer through the film is no longer the only factor limiting the magnitude of the photocurrent.

Photomicrographs of two pexels in a cell prepared by method 2 are shown in Figure 2. The two pexels are separated by one pexel (2.5 mm) that shows the transition in crystallinity between these two and exhibits photoelectrical characteristics intermediate between them. Photocurrent-voltage curves of the two pexels are shown in Figure 3 at an illumination intensity of ca. 170 mW/cm^2. The short circuit photocurrent density increases about seven fold from 9.7 to 67 μA/cm^2 from the disordered to the ordered pexel while both show an open circuit voltage of −280 mV. The greater magnitude of the increase in photocurrent with order seen in this cell compared to the previous cell at the same light intensity may be caused by the greater change in crystallinity in the present case and by the fact that the LC porphyrin was heated only once (during filling) rather than twice.

The strong effect of film order on the photocurrent is expected in porphyrins and similar molecular semiconductors. These quasi-1-dimensional materials conduct much better along the pi–pi stacking direction than perpendicular to the stacks.[26,27] Thus crystallites of a size at least on the same order as the film thickness are required to ensure a conducting pathway from one electrode to the other.[18] When this condition is not met, the observed photoelectronic effects may be dominated by various processes occurring at the grain boundaries, rather than by the inherent characteristics of the molecular semiconductor. Disordered films are also known to exhibit strongly quenched fluorescence relative to ordered films.[17] Sublimation, the most common way to prepare films of porphyrins, leads to either amorphous films or to films containing extremely small crystallites.[23–25] Solar cells prepared from such films commonly show photocurrent densities of less than 1 μA/cm^2 for film thicknesses of several hundred

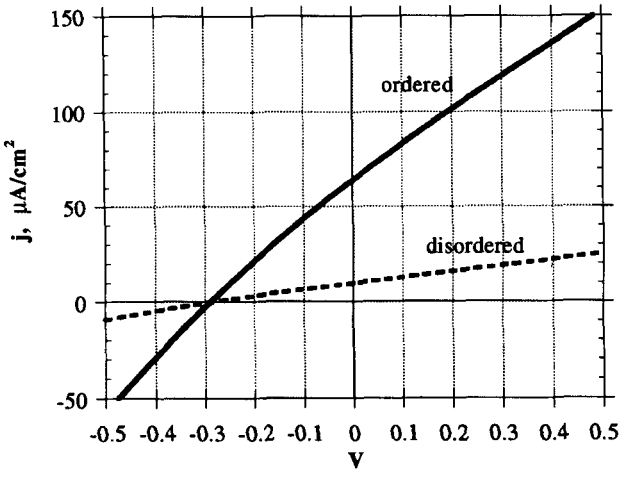

FIGURE 3 Photocurrent-voltage characteristics of the two pexels shown in Figure 2 at a light intensity 170 mW/cm^2. Cell was 4.0 μm thick

nanometers.[23] Under similar illumination, the ordered LC porphyrin films show photocurrents about 100 fold greater in films that are 3–4 μm thick. We have previously shown that the photocurrents are inversely proportional to the square of the film thickness.[18] Correcting for this difference, the photocurrents in the ordered films are estimated to be approximately 4 orders of magnitude higher than in the disordered (sublimed) films. This is consistent with our previous results showing that the corresponding free base of the LC porphyrin, which forms very small crystallites (< 0.4 μm) in capillary-filled cells, generates photocurrents about 1000 fold smaller than the highly ordered films of zinc-containing LC porphyrin.[18]

The dark current density in these symmetrical cells is extremely low, ca. 10–100 pA/cm^2 at 5 V, and is only slightly affected by the film order, increasing 20–50% in an ordered film. Highly purified and undoped molecular semiconductors, such as the LC porphyrins, are usually insulators in the dark, having a very low density of free charge carriers.[18,28,29] The dark current is thus often limited by the rate of carrier injection from the electrodes into the molecular semiconductor, not by the rate of charge transfer through the material. The dark currents are therefore not greatly influenced by changes in the bulk film order.

Effects of Temperature and Phase

The measurement of the change in photovoltaic properties, exciton diffusion lengths, charge carrier mobilities, etc. as a semiconductor is heated through the phase transitions from crystal (K) to liquid crystal (LC) and from liquid crystal to isotropic liquid (I) is a topic of great interest. Here I present preliminary data on such effects in the LC porphyrin cells. Unfortunately, the LC porphyrin is not completely stable in the photovoltaic cells at the high temperatures of its phase transitions ($T_{K \to LC} = 107°$, $T_{LC \to I} = 162°$).[7] There is apparently some irreversible degradation of the porphyrin

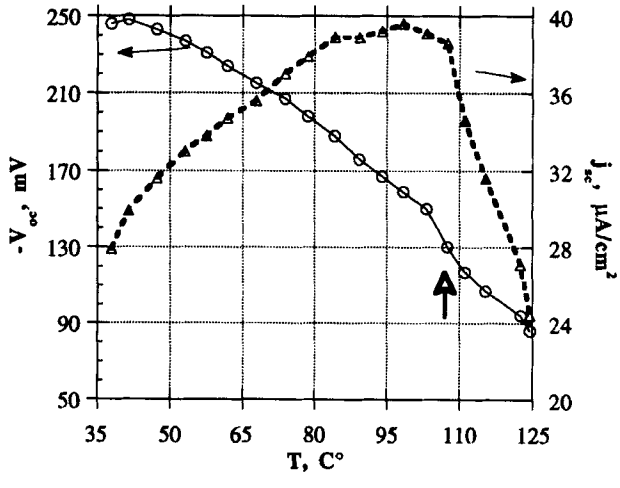

FIGURE 4 Open circuit photovoltage and short circuit photocurrent density vs. temperature as an LC porphyrin cell is heated (ca. 5°/min) through the solid phase into the discotic liquid crystalline phase. The arrow shows the phase transition temperature at 107°C. Light intensity was 170 mW/cm^2

caused by such thermal excursions, thus these results are necessarily qualitative. Nevertheless, the qualitative behavior described below did not change when one cell was repeatedly heated, nor were any qualitative differences between cells observed. A careful study of these effects must await the synthesis (in progress) of a material with lower phase transition temperatures.

The cells were heated quite rapidly (5°/min) in these experiments to minimize thermal degradation. Under such conditions the change (decrease) in photocurrent and photovoltage from one experiment to the next on a single cell was ca. 10%. The accuracy of the temperature measurements was estimated as $\pm 4\%$. No attempt was made to perform measurements in the isotropic liquid phase. Figure 4 shows the changes in open circuit photovoltage (V_{oc}) and short circuit photocurrent density (j_{sc}) as the temperature (T) is increased from 37° to 125°. The photovoltage decreases monotonically with increasing temperature, but decreases noticeably faster after the K → LC transition. The monotonic decrease is consistent with the postulated mechanism for photovoltage generation, i.e., V_{oc} is governed by the relative rates of exciton dissociation by electron injection vs. hole injection into the ITO electrode. Since the ratio of the (Arrhenius) rates of two competing processes is expected to approach one as T increases, and since in our case this would result in zero photovoltage, the reversible decrease in V_{oc} with temperature is reasonable. The change in slope at $T_{K \to LC}$ may result from a decrease in exciton flux to the surface caused by a decrease in exciton diffusion length in the LC phase relative to the solid phase.

The short circuit photocurrent density appears to be thermally activated below $T_{K \to LC}$, but then decreases rapidly in the liquid crystal phase (Figure 4). The decrease is consistent with previous measurements of (a lower limit for) the charge carrier mobilities in the LC porphyrin. Thus changes in the radiation-induced conductivity were measured by a time-resolved microwave conductivity technique resulting in estimates of the charge carrier mobility $\mu > 2.6 \times 10^{-6}\,m^2\,V^{-1}\,s^{-1}$ in the solid phase and $\mu > 0.6 \times 10^{-6}\,m^2\,V^{-1}\,s^{-1}$ in the liquid crystal phase.[22] This change in carrier mobility, and the assumed diminution in exciton flux to the surface, can explain the rapid drop in photocurrent at $T_{K \to LC}$.

The changes in photocurrent density at applied biases of + 6 V and − 6 V are shown in Figure 5. The photocurrent under bias was less sensitive to the effects of thermal degradation than was the short circuit photocurrent. The differences in magnitude of the photocurrent at positive and negative applied bias is related to the difference in charge carrier mobilities, electrons having a higher mobility than holes.[18] The marked rise in photocurrent with temperature in the solid phase, followed by the sudden drop at the phase transition, is clearly seen in these data. The photocurrent is proportional to both the number of charge carriers in the material and their mobilities. Since the carrier mobilities in molecular crystals often decrease with increasing temperature,[28-30] and this was in fact observed in the LC porphyrins in the microwave conductivity measurements,[22] I tentatively conclude that the increase in photocurrent in the solid phase with increasing temperature is caused by an increase in the number of free charge carriers. This may result from enhanced charge carrier separation after exciton dissociation at the illuminated interface, from a greater number of carriers directly photogenerated in the bulk, or from thermal depopulation of traps. This question is being addressed in current studies.

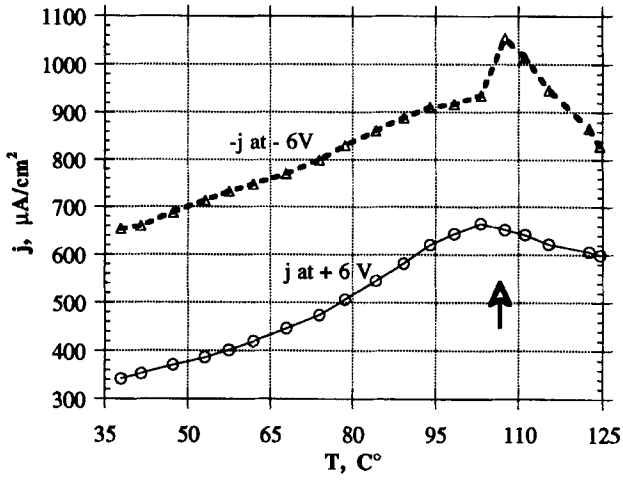

FIGURE 5 Photocurrent density at ± 6 V applied bias vs. temperature. Conditions as in Figure 4.

CONCLUSIONS

Photocurrents in liquid crystal porphyrin films are strong functions of the bulk film order. Highly ordered films of these quasi-1-dimensional semiconductors can support much greater photocurrents than disordered films. The greater disorder of the liquid crystalline phase relative to the solid phase is apparently responsible for the sudden decrease in photocurrent and photovoltage at the crystal to liquid crystal phase transition. The self-ordering properties of liquid crystals may be employed for the growth of ordered electroactive thin films of molecular materials.

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References

1. C. Piechocki, J. Simon, A. Skoulios, D. Guillon and P. J. Weber, *J. Am. Chem. Soc.* **104**, 5245–5247 (1982).
2. J.-J. Andre, M. Bernard, C. Piechocki and J. Simon, *J. Phys. Chem.* **90**, 1327–1330 (1986).
3. M. J. Cook, N. B. McKeown and A. J. Thomson, *Chemistry of Materials*, **1**, 287–289 (1989).
4. J. F. van der Pol, E. Neeleman, J. W. van Miltenburg, J. W. Zwikker, R. J. M. Nolte and W. Drenth, *Macromolecules*, **23**, 155–162 (1990).
5. J. W. Goodby, P. S. Robinson, B. K. Teo and P. E. Cladis, *Mol. Cryst. Liq. Cryst.*, **56**, 303–309 (1980).
6. B. A. Gregg, M. A. Fox and A. J. Bard, *J. Chem. Soc., Chem Commun.*, 1134–1135 (1987).
7. B. A. Gregg, M. A. Fox and A. J. Bard, *J. Am. Chem. Soc.*, **111**, 3024–3029 (1989).
8. P. Doppelt and S. Huille, *New. J. Chem.*, **14**, 607–609 (1990)
9. S. H. J. Idziak, N. C. Maliszewskyj, G. B. M. Vaughn, P. A. Heiney, C. Mertesdorf, H. Ringsdorf, J. P. McCauley and A. B. Smith, *J. Chem. Soc., Chem. Commun.*, 98–99 (1992).
10. M. Veber, R. Fugnito and H. Strzelecka, *Mol. Cryst. Liq. Cryst.*, **96**, 221–227 (1983).
11. K. Ohta, A. Ishii, I. Yamamoto and K. Matsuzaki, *J. Chem. Soc., Chem. Commun.*, 1099–1101 (1984).

12. A.-M. Giroud-Godquin, J.-C. Marchon, D. Guillon and A. Skoulios, *J. Phys. Chem.*, **90**, 5502–5503 (1986).
13. V. Gionis, H. Strzelecka, M. Veber, R. Kormann and L. Zuppiroli, *Mol. Cryst. Liq. Cryst.*, **137**, 365–372 (1986).
14. D. Markovitsi, I. Lecuyer and J. Simon, *J. Phys. Chem.*, **95**, 3620–3626 (1991)
15. Z. Belarbi, C. Sirlin, J. Simon and J.-J. Andre, *J. Phys. Chem.*, **93**, 8105–8110 (1989).
16. Z. Belarbi, M. Maitrot, K. Ohta, J. Simon, J. J. Andre and P. Petit, *Chem. Phys. Lett.*, **143**, 400–403 (1988).
17. B. A. Gregg, M. A. Fox and A. J. Bard, *J. Phys. Chem.*, **93**, 4227–4234 (1989).
18. B. A. Gregg, M. A. Fox and A. J. Bard, *J. Phys. Chem.*, **94**, 1586–1598 (1990).
19. B. A. Gregg, M. A. Fox and A. J. Bard, *Mat. Res. Soc. Symp. Proc.*, **173**, 199–204 (1990).
20. J. F. van Der Pol, M. P. De Hass, J. M. Warman and W. Drenth, *Mol. Cryst. Liq. Cryst.*, **183**, 411–420 (1990).
21. G. Blasse, G. J. Dirksen, A. Meijerink, J. F. van der Pol, E. Neeleman and W. Drenth, *Chem. Phys. Lett.*, **154**, 420–424 (1989).
22. P. G. Schouten, J. M. Warman, M. P. de Haas, M. A. Fox, H.-L. Pan, *Nature*, **353**, 736–737 (1991).
23. F. J. Kampas and M. Gouterman, *J. Phys. Chem.*, **81**, 690–695 (1977).
24. F. J. Kampas, K. Yamashita and J. Fajer, *Nature*, **284**, 40–42 (1980).
25. K. Yamashita, Y. Harima and H. Iwashima, *J. Phys. Chem.*, **91**, 3055–3059 (1987).
26. B. M. Hoffman and J. A. Ibers, *Acc. Chem. Res.*, **16**, 15–21 (1983).
27. T. J. Marks, *Science*, **227**, 881–889 (1985).
28. M. Pope and C. E. Swenberg, *Ann. Rev. Phys. Chem.*, **35**, 613–55 (1984).
29. J. Simon and J.-J. Andre, *Molecular Semiconductors*, Springer Verlag: Berlin, 1985.
30. Y. Maruyama, *Mol. Cryst. Liq. Cryst.*, **171**, 287–303 (1989).