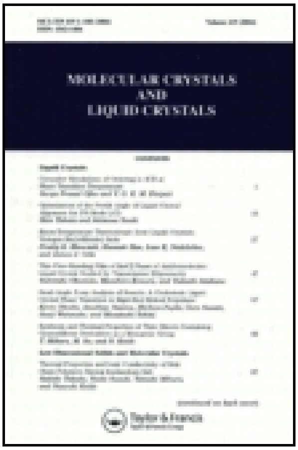

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Photocurrent Action Spectra of the Photoconductive Cell with a Mesogenic Long-Chain Tetraphenylporphyrin

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Photocurrent Action Spectra of the Photoconductive Cell with a Mesogenic Long-Chain Tetraphenylporphyrin

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Photocurrent action spectra for the cell in which 5,10,15,20-tetrakis(4-*n*-pentadecylphenyl)porphyrin ($C_{15}TPPH_2$) is sandwiched by ITO electrodes were measured and the phase dependence of the action spectra indicated a variable combination of the extrinsic and intrinsic carrier generation processes on the mesomorphic phase transitions. This results is in agreement with that deduced by the illumination intensity dependence of photocurrent.

Keywords: photoconductivity; discotic liquid crystal; tetraphenylporphyrin

INTRODUCTION

Discotic liquid crystals are one of the most interesting organic materials for a new application of liquid crystals because of the molecular stacks of columnar mesophases [1]. In the field of molecular conductors itt is well-known that such molecular stacks are quite suitable for the quasi-one-dimensional electronic conduction[2]. In fact, photoconductivity and electronic conductivity of discotic liquid crystals have been extensively studied so far[3-7]. In particular, fast hole mobility in a columnar mesophase (0.1 cm $V^{-1}s^{-1}$) was recently reported for a plastic crystalline phase of a triphenylene discotic mesogen [8].

On the other hand, tetraphenylporphyrin is an interesting class of discotic liquid crystalline compounds as a candidate for a material applicable to thin film photonic devices because of its electronic structure and metallation-derived functional properties [9]. It was found that a tetraphenylporphyrin having an alkyl chain attached at *p*-site of the phenyl rings (totally, four tails per molecule) and its metal complexes show lamellar mesomorphism [10]. From the results of powder X-ray diffractions and fluorescence lifetime measurements, the low-temperature phase (D_{LC} phase) was proposed to have a columnar structure in comparison with a broken columnar one proposed for the high-temperature

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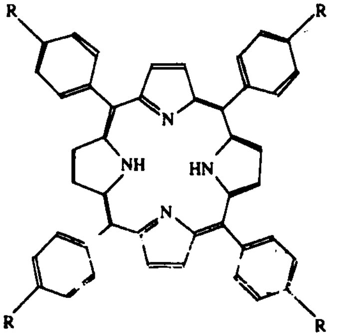
lamellar phase (D_L phase) as depicted in Fig. 1 [11].

In addition, it was found for a sandwich-type cell using the pentadecyl homologue ($C_{15}TPPH_2$) that the V-I characteristic for steady-state photocurrent is strongly affected by the mesomorphic phase transitions [12]. A drastic change of the photocurrent rectification behaviour at D_{LC} to D_L phase transition was observed. The phase transition parameters of $C_{15}TPPH_2$ are summarized in Table 1.



$C_{15}TPPH_2$
$R=(CH_2)_{14}CH_3$

Table 1 Phase transition temperatures and enthalpies of $C_{15}TPPH_2$.

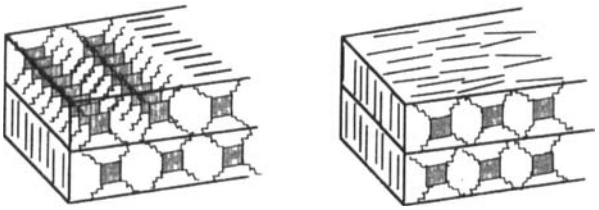
	crystal		D_{LC}		D_L		iso
T / °C		56		66		135	
ΔH / kJ mol^{-1}		92		31		27	

The studies on the illumination light intensity dependence of the photocurrent indicated that two photocarrier generation processes are involved and the degree of contribution of each process to the observed photocurrent is quite variant by the phase transitions [13].

In this work, photocurrent action spectra of the symmetrical sandwich-type cell containing a mesogenic tetraphenylporphyrin ($C_{15}TPPH_2$) was investigated in order to discuss the photocarrier generation process and the mechanism of the mesomorphologically dependent rectification behavior.

EXPERIMENTAL

The synthetic procedures for $C_{15}TPPH_2$ were on the basis of the literature



D_{LC} mesophase
(the low-temperature phase)

D_L mesophase
(the high-temperature phase)

Figure 1 Schematic representations of two types of lamellar phases.

with slight modifications. The details were described elsewhere [13]. The purity of compound synthesised was finally checked before use by evaluating the darkcurrent conductivity which should be less than 10^{-14} S cm^{-1} at room temperature (in a crystal phase).

The dark- and photo-currents were measured as steady-state ones for a sandwich-type cell consisting of two ITO-coated glasses, spacer (polyimide film or silica microparticles) and $C_{15}TPPH_2$.

The cells were prepared to have a sandwich-type configuration which was fixed using a silicone cement. The empty space between both electrodes (the effective area:1 cm^{-2}) was filled with $C_{15}TPPH_2$ on heating above the clearing point (*ca.* 150 °C) by capillarity and the cell was cooled down slowly to room temperature. The polarised microscopic observations revealed polydomain structures of the sandwiched film of $C_{15}TPPH_2$.

A Xenon-lamp was used as a light source (Ushio WUXL-500D-O) and the light was monochromated by JASCO CT-25N to illuminate the cell set in a temperature-controllable cryostat. The steady-state current was detected by a digital multimeter (Advantest digital electrometer TR8652) as closed-circuit currents under an applied field. The illumination light intensity was fixed to be 0.33 mW cm^{-2} at 620 nm. The action spectra shown in this work are not normalised for the Xenon-lamp characteristic and all measurements were carried out in nitrogen atomosphere.

RESULTS AND DISCUSSION

Fig. 2, 3 and 4 show photocurrent action spectra of the cells with the thickness of 25, 8 and 4 μm, respectively. For the positive electrode illumination of the crystalline cell with 25 μm-thickness, the spectral pattern in the longer wavelength region (Q band) does not coincide with the absorption spectrum, showing an antibatic relation and, in the shorter wavelength region corresponding to Soret band, the photocurrent is very small. This indicates most of the hole carriers generated near the interface are trapped or recombined during the transportation because of the polydomain film. Thus, the photocurrent observed is derived from the carriers generated in the bulk region. This could explain the antibatic relation between the action and absorption spectra in the

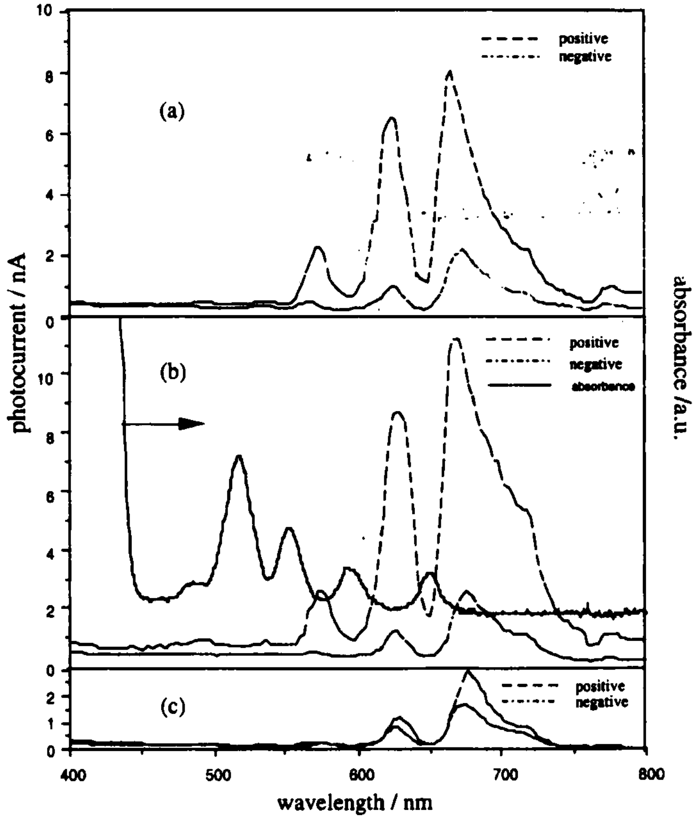


FIGURE 2 Absorption and action spectra of ITO/$C_{15}TPPH_2$/ITO cell. Photoconductive layer thickness : 25 μm. Applied field : 8000 V/cm. (a) Crystal at 25 °C, (b) D_{LC} phase at 60 °C, and (c) D_L phase at 80 °C for $C_{15}TPPH_2$. Positive and negative mean polarity of the electrode illuminated.

longer wavelength region where the compound has a lower absorption coefficient. In addition, the spectral pattern for the negative electrode illumination of the crystalline cell resembles that for the positive electrode illumination.

In D_{LC} to D_L phases, the same patterns were seen except for the enhanced photocurrent in the former phase and the diminished one in the latter.

As for the action spectra of 8 μm-thick cell, the complexity of spectral patterns were obtained as shown in Fig. 3. Though the spectra for the negative

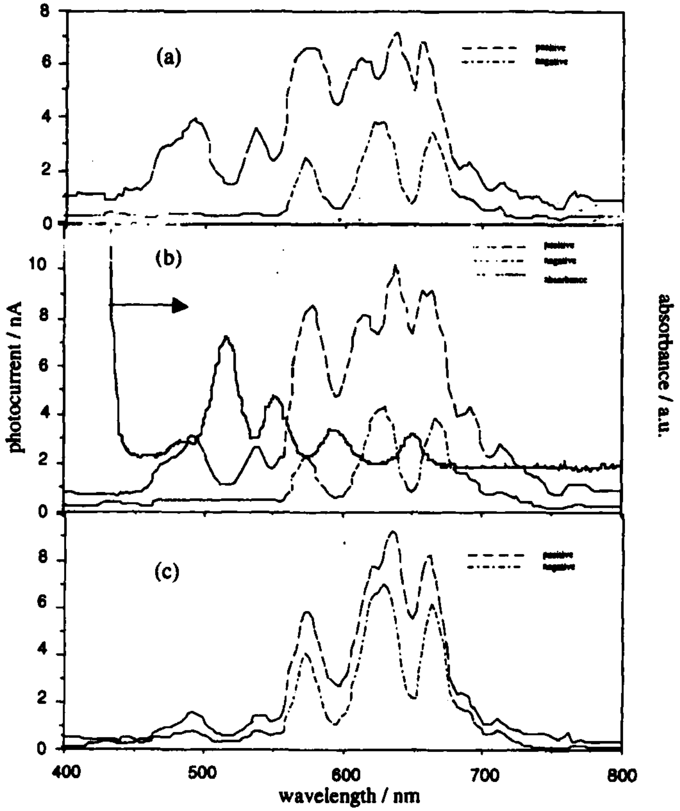


FIGURE 3 Absorption and action spectra of ITO/$C_{15}TPPH_2$/ITO cell. Photoconductive layer thickness : 8 μm. Applied field : 8000 V/cm. (a) Crystal at 25 °C, (b) D_{LC} phase at 60 °C, and (c) D_L phase at 80 °C for $C_{15}TPPH_2$. Positive and negative mean polarity of the electrode illuminated.

electrode illumination are almost in symbatic relation to the absorption one in all phases, those for the positive electrode illumination look like an overlapped spectra of symbatic and antibatic ones in both crystal and D_{LC} phases. In D_L phase, the spectral patterns for both polarities of illumination are similar to each other, symbatic. These results indicate that an extrinsic mechanism contributes to the observed photocurrent for the positive electrode illumination in crystal and D_{LC} phases in addition to an intrinsic one. In D_L phase, however, it could be inferred that only an intrinsic mechanism contributes to the photocurrent.

On the other hand, the spectral behaviour appears to be simple for the 4 μm-thick cell (Fig.4). All spectra for the positive electrode illumination are almost in symbatic relation to the absorption one except for those in the wavelength region of Soret band. In contrast, the spectra for the negative electrode illumination show some complexity in which the patterns consist of

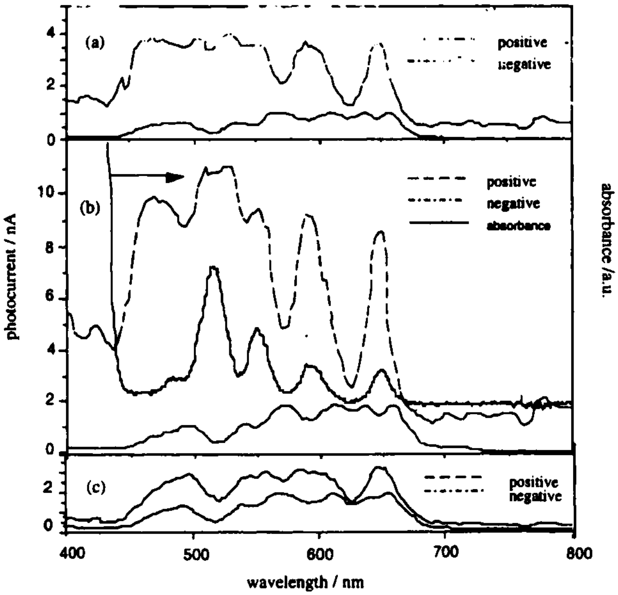


FIGURE 4 Absorption and action spectra of ITO/$C_{15}TPPH_2$/ITO cell. Photoconductive layer thickness : 4 μm. Applied field : 8000 V/cm. (a) Crystal at 25 °C, (b) D_{LC} phase at 60 °C, and (c) D_L phase at 80 °C for $C_{15}TPPH_2$. Positive and negative mean polarity of the electrode illuminated.

mainly antibatic and a little of symbatic ones. Especially, a maximum of photocurrent was observed between minima and maxima in the absorption spectrum, indicating that the illuminated light from the negative side can reach to the interface on the counter electrode to generate carriers in an extrinsic way.

The common characteristic property seen in these cells is the almost same degree of photocurrent for D_L mesophase. This behaviour is also observed in the photocurrent V-I characteristics previously reported[12].

The photocurrent behaviour against the illumination light intensity indicated that the intrinsic mechanism is predominant in the D_L phase, while in crystal and D_{LC} phases both extrinsic and intrinsic mechanisms can provide charged carriers into the system (Table 2)[13].

TABLE 2 Phase transitions and charged carrier generation.

Phase	charged carrier generation process	
	extrinsic	intrinsic
crystal, D_{LC} phase	limited	limited
D_L phase	negligible	limited

The present results of photocurrent action spectra are well explained by variable mechanisms of charged carrier generation depending on the phases shown above.

Generally, hopping migration of charged carrier in a molecular aggregation is thought to be very sensitive to the molecular ordering in the system. However, in a mesophase, dynamics should be also considered in addition to the molecular orientational order.

The action spectra of D_L phase showed a difference between photocurrents for the positive and negative electrode illuminations. The photocurrent of the positive electrode illumination is larger than that of the negative one. Such a difference of the photocurrent, thus, indicates a differnce of carrier mobilities. In this way, it seems to be implied that the hole mobility is quite sensitive to the phase transitions, though the electron mobility does not depend so much on the phase type. The mobility measurements are now in progress in order to explain the mechanism change of carrier generation on the mesomorphic phase transitions.

CONCLUSION

An ITO/C_{15}TPPH$_2$/ITO photoconductive cell was investigated, measuring the dependence of photocurrent action spectra on the phase type and photoconductive layer thickness. The results obtained support the variable mechanisms of charged carrier generation depending on the phase type. The photocurrent for D_L mesophase is contributed by almost only an intrinsic mechanism of carrier generation, whilst extrinsic as well as intrinsic ones relate to the photocurrent observed in the crystal and D_{LC} phases.

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