Novel Photocurrent Rectification Behaviour for a Photoconductive Cell using the Mesogenic 5,10,15,20-Tetrakis(4-n-pentadecylphenyl)porphyrin

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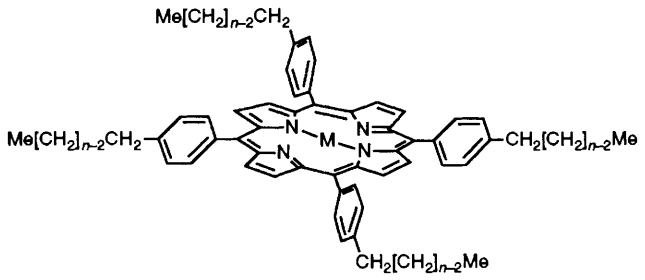
A novel photocurrent rectification behaviour associated with mesomorphic phase transitions was found for a symmetrical cell in which the mesogenic 5,10,15,20-tetrakis(4-n-pentadecylphenyl)porphyrin (C15TPP) was sandwiched between two indium–tin oxide electrodes; the rectification properties shown by the crystalline C15TPP cell disappears in the mesomorphic cell (discotic lamellar phase).

Mesomorphic states, located between the crystalline and isotropic liquid states, are interesting in view of their relevance to advanced materials.[1] It may not be easy to distinguish between their chemical and physical properties and those in the crystalline solid and the isotropic liquid phases. The particular molecular ordering of discotic liquid crystals is interesting; their molecules are aligned parallel to the molecular plane in columnar stacking[2] and the extended π-conjugated electron system for the rigid core, and thus a variety of electronic properties such as photoconductivity,[3] electric conductivity,[4] pulse-irradiation induced conductivity[5] as well as energy migration[6] in mesophases have been intensively studied.

Porphyrin analogues are particularly attractive mesogenic materials for studies of the photo and electronic properties of mesophases.

We now report the first example of photocurrent rectification behaviour achieved *via* phase transitions between the mesophase and crystalline phase in the symmetrical indium–tin oxide/5,10,15,20-tetrakis(4-n-pentadecylphenylporphyrin/



C15TPP (n = 15)

indium–tin oxide (ITO/C15TPP/ITO) cell. The temperature dependence of the dark- and photo-currents (positive electrode illumination) has already been reported for such a symmetrical cell;[3] the crystal C15TPP cell generates a larger photocurrent with positive electrode illumination than with negative electrode illumination. Gregg *et al.*[7] also reported similar results for photovoltaic effect studies of a similar type of ITO symmetrical cell including porphyrin mesogens, octa-substituted porphyrins, only in the crystalline state.[7]

The synthesis and purification of C15TPP have been described elsewhere.[8] The phase transition sequence of C15TPP is as follows:[3]

	crystal	D_L'	D_L	isotropic
T/°C	56	66	135	
ΔH/kJ mol^{-1}	92	31	27	

This mesogen shows two somewhat softened phases between the brittle crystal and isotropic phases. The higher temperature phase is a discotic lamellar (D_L) phase and the lower one seems to be a crystal phase with a lamellar structure (D_L' phase), as shown by X-ray diffraction studies. In the D_L and D_L' phases, molecules are aligned parallel to the molecular planes to form a layer structure with random positioning, and somewhat ordered positioning of molecules within the layer, respectively.

The photoconductive cell we used consists of two ITO coated glass plates and a polyimide film as a spacer (25 μm thick). The cell was heated to 150 °C, at which temperature C15TPP melts to the isotropic liquid, and C15TPP was injected into the cell space between the two ITO glass plates by capillarity; the cell was then carefully cooled to room temperature.

Photoconduction measurements were carried out for a closed circuit and the photocurrent was detected by an electrometer. Monochromated light (620 nm) from a xenon lamp (500 W) was used to illuminate the cell. The cell was placed on a temperature-controllable stage of a cryostat and all measurements were done under an inert atmosphere (Ar or N_2).

Fig. 1(*a*) shows the photocurrent–applied voltage characteristics of the cell for the crystalline, D_L' and D_L phases of C15TPP. Marked rectification of photocurrent is apparent for the crystal C15TPP cell, positive electrode illumination causing a larger photocurrent which increases with bias. For the D_L mesophase, however, the photocurrent generated by positive electrode illumination is much reduced and comparable with that resulting from negative electrode illumination, photocurrent rectification disappearing. For the D_L' phase, rectification occurs, as for the crystalline phase, but somewhat reduced. This rectification of the D_L' phase, occurring at a higher temperature than for the crystalline state, is consistent with the X-ray diffraction results which show that the D_L' phase is a slightly softened crystalline phase.[8]

Fig. 1(*b*) shows the (dark)current–applied voltage characteristics of the cell for the crystalline, D_L' and D_L phases. Symmetrical features are clearly shown.

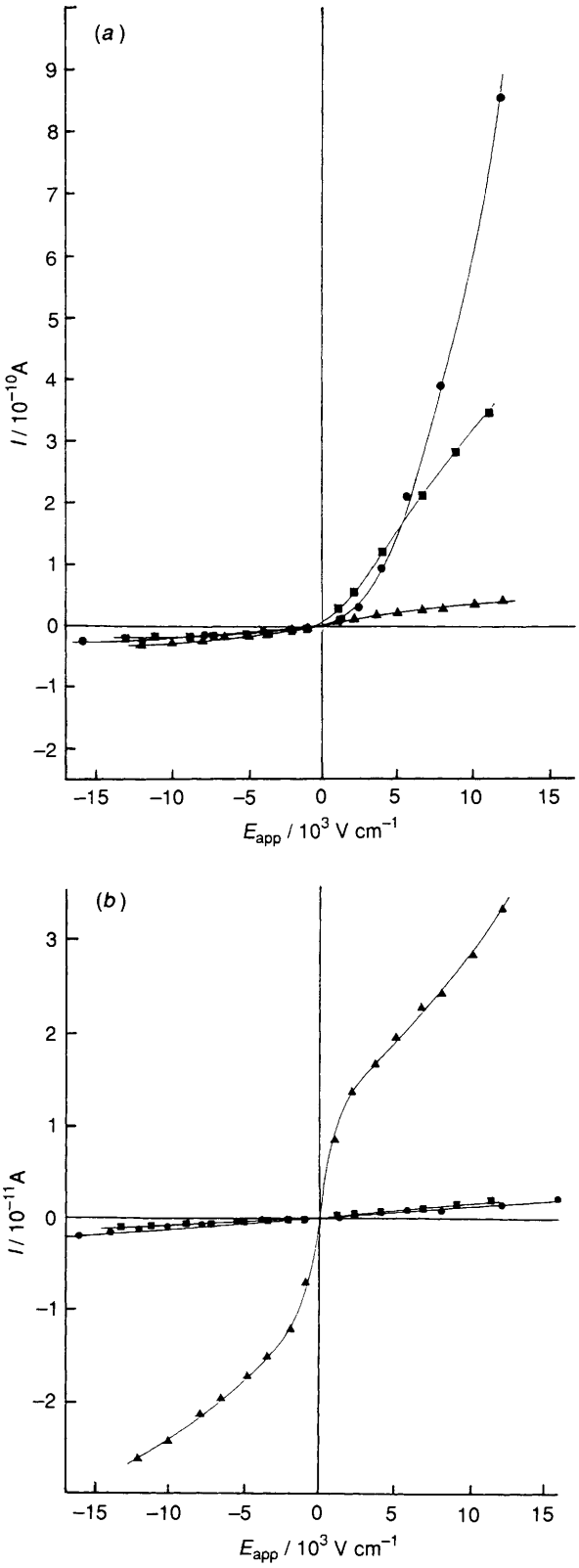


Fig. 1 Applied field (E_{app}) dependence of (*a*) photocurrent and (*b*) darkcurrent in an ITO/C15TPP/ITO (25 μm-thick) cell for the crystalline (30 °C; ●), D_L' (58 °C; ■) and D_L (80 °C; ▲) phases of C15TPP under 620 nm light illumination with an intensity of 0.33 mW cm^{-2}

A similar rectification behaviour was also observed for a cell using SnO_2 electrodes instead of ITO.

Tanimura *et al.*[9] reported that electrons were injected to the conduction band of SnO_2 through the tetraphenylporphyrin–

SnO_2 interface, when tetraphenylporphyrin evaporated on an ITO glass was excited by light illumination.[9] These studies show similar phenomena to those in the present work, as a result of the extrinsic process of carrier generation; the rectification in the crystal C15TPP cell is mainly due to the extrinsic photocurrent at the C15TPP–ITO interface. The mechanism of the carrier generation process and its relationship to the rectification behaviour (drastic change at the phase transition between the meso- and crystalline phases) will be discussed elsewhere.[10]

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