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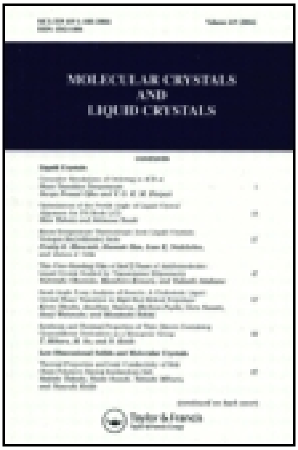

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Photoconductivity Measurements in the Discotic Columnar Phase of a few Anthraquinone Derivatives

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PHOTOCONDUCTIVITY MEASUREMENTS IN THE DISCOTIC COLUMNAR PHASE OF A FEW ANTHRAQUINONE DERIVATIVES

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It has recently been shown that the structure of the columnar phase of discotic liquid crystals is suitable for fast transport of photogenerated charge carriers. Although the magnitude of the charge carrier mobility exhibited by these systems is still small compared to those in organic single crystals, the fluidity and the resulting self-healing nature of the liquid crystalline columnar phases hold promises for potential applications. In this paper we report on steady-state photoconductivity measurements carried out on three anthraquinone derivatives exhibiting the columnar phase. Upon illumination of the sample with UV light the current through the sample increases abruptly and reaches a photostationary value within a short span; the fastest observed response time is 17 ms. It was found that the anisotropy of the photoconductivity, defined as the ratio of the photocurrent along and perpendicular to the column axis, reaches a value of about 450. We also discuss the relation between the chemical structure of the molecule and the maximum value of the photocurrent observed.

Keywords: photoconductivity; columnar phase; anthraquinone; derivatives.

INTRODUCTION

Conventional organic photoconductive materials have been successfully used as photoreceptors in photocopiers and laser printers [1]. The large area films needed for this purpose are prepared by polymerization, vacuum evaporation, etc., which result in the amorphous nature of the films [2]. Therefore, their performance is much less than that which can be obtained from single crystals of the same materials. On the other hand, liquid

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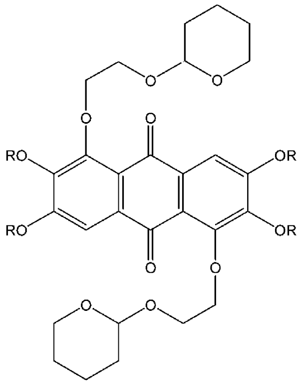
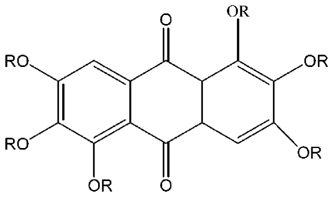
crystals which have seen outstanding success in the area of display devices are being proposed as suitable candidates due to their ability to self assemble into large area uniform films. Both discotic and calamitic liquid crystals have been investigated for this purpose and have been shown to exhibit high charge carrier mobilities of up to 0.7 $\mathrm{cm}^2\,\mathrm{V}^{-1}\mathrm{s}^{-1}$ [3–8]. Further, liquid crystalline materials also exhibit significant photoconductivity anisotropy. For example, in calamitic materials, using high energy pulsed laser [7] or steady-state [9] sources anisotropic values as high as $\sim$1000 have been achieved. In this paper we report on steady-state photoconductivity measurements carried out on three anthraquinone derivatives exhibiting the columnar phase.

EXPERIMENTAL

The structural formulae and the transition temperatures of the three anthraquinone derivatives used for the experiments are shown in Figure 1. All of them exhibit a single columnar phase, which Xray studies show to be of the hexagonal type. A schematic diagram of the experimental set up used for the photoconductivity measurements is given in Figure 2. Samples were filled in cells fabricated with ITO-coated glass plates treated with a polyimide solution but unrubbed, to obtain a homeotropic alignment, i.e., the column axis normal to the substrates. The sample thickness was





II: R= C_5H_{11}

Iso 114.8°C $\mathrm{Col_h}$ 63°C Cr

Ia: R=$C_{10}H_{21}$
Iso 62.5°C $\mathrm{Col_h}$ 52°C Cr

Ib: R= C_5H_{11}
Iso 101.5°C $\mathrm{Col_h}$ 79.5°C Cr

FIGURE 1 Molecular structures and transitions temperatures of the compounds used in this study.

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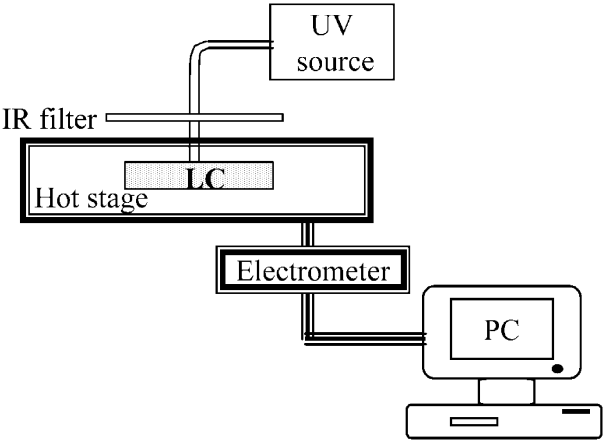

FIGURE 2 Schematic diagram of the experimental setup used for the photoconductivity measurements.

defined using Mylar spacers and was ~2.5 μm. To obtain information about the photoconductivity anisotropy measurements were also done such that the column axis is in the plane of the substrates. For this purpose thicker cells (~25 μm) were used and the samples were cooled from the isotropic phase in the presence a 2 Tesla magnetic field. Due to the negative diamagnetic anisotropy of the sample, the column axis would prefer to be orthogonal to the direction of the applied magnetic field. The light source used was a 365-nm-enhanced intensity-stabilized Mercury-Xenon source (Hamamatsu L7212-01, Japan). An IR-block filter was inserted in the beam path just before the sample to eliminate any local heating effects. The actual power of the radiation falling on the sample was measured using a power meter (Hamamatsu C6080-03) kept in the sample position. The photocurrent was measured using an electrometer (Keithley 6517A) in the force-voltage-measure-current (FVMI) mode. In this mode the built-in bipolar 1 W voltage source was used to apply a bias voltage to the sample.

RESULTS AND DISCUSSION

Figure 2 shows the photo current response to an UV illumination of 272 mW/cm^2 in the homeotropic ($\mathbf{I}_{\|}$) and in-plane ($I_{\perp}$) geometries for compound **Ia** (here $\|$ and $\perp$ refer to the cases where the applied bias field is along and perpendicular to the column axis respectively.). In the homeotropic geometry, turning the UV illumination ON results in an abrupt and substantial increase in the current density. In contrast, with the sample

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in the in-plane geometry the magnitude of the current density remains practically the same irrespective of the presence or absence of the radiation, and is comparable to the value of the dark current in the homeotropic geometry. The calculated photocurrent anisotropy $\delta I (= I_{\|}/I_{\perp})$ turns out to be value of ~ 450. This may be compared with a value of ~ 850 that we have recently observed in the crystal E phase of a calamitic system. Thus at present it appears that the columnar structure is a more efficient system for charge transport. However, it should be borne in mind that the columnar phase exhibited by compound **Ia** has only a short-range correlation of the molecular discs within the same column. In contrast the crystal E phases possesses a three-dimensional positional ordering of the molecules.

Figure 3 presents the current-voltage (I-V) characteristics of the photo- and dark currents in both the homeotropic and in-plane cells. The dark current remains approximately the same in both the cells; the calculated conductivity turns out to be 5×10^{-13} S/cm. Large changes are seen in the photocurrent for the homeotropic configuration, displaying a rectifier type of I-V characteristics, with the photoconductivity anisotropy clearly depending on the applied bias voltage.

It is well known that decreasing the length of the peripheral alkyl chains enhances the effective interaction between the molecular cores within the same column, a parameter that can be quantified by the corresponding correlation length. It is also known that the charge transport mechanism in the columnar phase is, to a large extent, controlled by the overlapping of the molecular orbitals of the neighbouring discs in the same column. Hence, by decreasing the length of the alkyl chain attached to the central

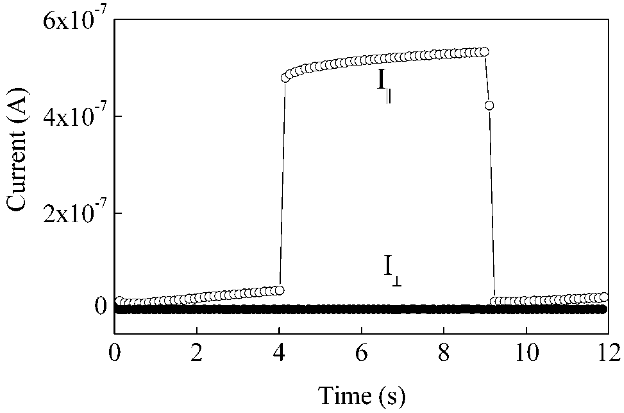

FIGURE 3 Photocurrent response under steady-state UV illumination in the $\mathrm{Col_h}$ phase of compound **Ia** with the molecules aligned in the homeotropic (○) and planar (●) configurations.

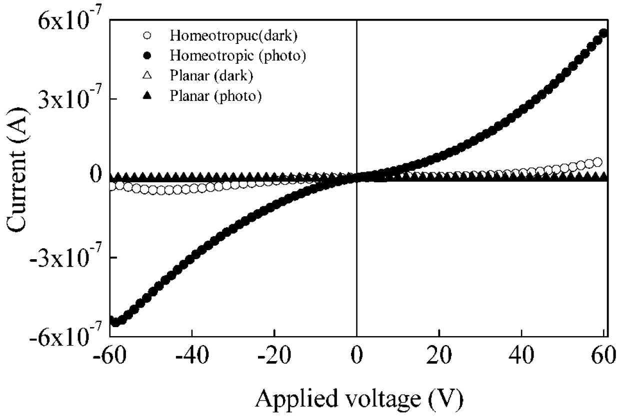

FIGURE 4 I-V characteristics of the dark (open symbols) and photocurrents (filled symbols) in the homeotropic (○ and •) and planar (Δ and ▲) configurations in the Col$_h$ phase of compound **Ia**. In the planar configuration the dark and photocurrents are nearly indistinguishable from one another.

core one expects the magnitude of the photoconductivity to increase. For this purpose we studied Compound **Ib**, the lower homologue of Compound **Ia**. Figure 4 shows the photocurrent response obtained in the homeotropic configuration for the two compounds. It is seen that for the compound with

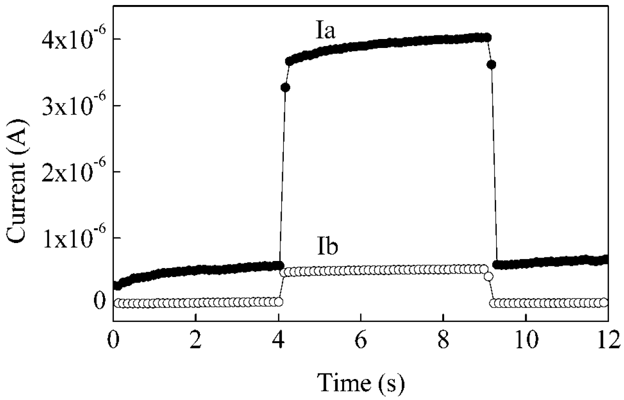

FIGURE 5 Photocurrents obtained in the Col$_h$ phase of compounds **Ia** (•) and **Ib** (○) for the homeotropic configuration. Notice that shortening the length of the alkyl chain increases the magnitude of the photocurrent significantly.

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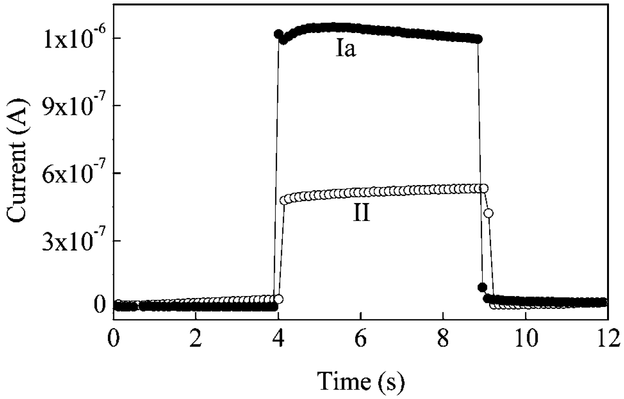

FIGURE 6 Plot showing the effect of the molecular core size on the magnitude of the photocurrent. Compound **Ia** (•) exhibits a larger photocurrent than compound **II** (○).

a shorter chain (Compound **Ib**) there is one of order of magnitude increase in the value of the photocurrent.

The strength of the core-core interaction also depends on the size of the molecular core; obviously, larger the core, higher is this strength. Charge carrier mobility studies have shown that changing the core from triphenylene (small core) to benzocoronene (larger core) enhances the value of the mobility significantly. To check the effect of the size of the core

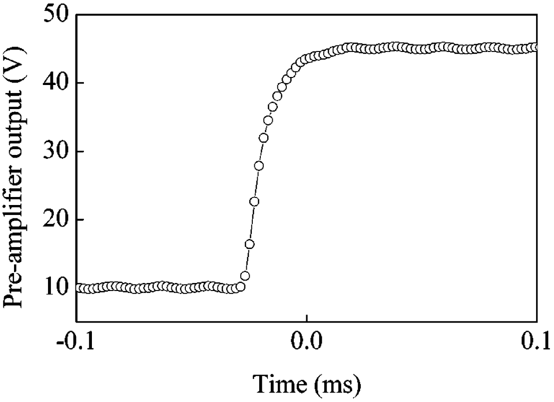

FIGURE 7 Dynamic response of the photocurrent response observed for compound **II** with the sample aligned in the homeotropic configuration. The response time, defined as the time taken for the current to change from 10% to 90% of the final photo-stationary value, is 17 ms.

on the magnitude of the photoconductivity we did measurements on Compound **II**, having a smaller core but the same chain length as for Compound **Ia**. The photocurrent response for the compounds **Ia** and **II** are given in Figure 5 showing a factor of three reduction in the value, when the core size is smaller.

We have also measured the dynamics of the photocurrent response observed for Compound **II** with the sample aligned in the homeotropic configuration. The time-resolved photocurrent data obtained with a bias voltage of 40V is shown in Figure 6. The response time, defined as the time taken for the current to change from 10% to 90% of the final photo-stationary value, is 17 ms (see Figure 7). This is quite a fast response considering the fact that a conventional source is used for photo excitation.

In summary, we have studied the photoconducting properties of three different anthraquinone derivatives. A large value (~450) of photocurrent anisotropy, as well as significant effects of the size of the molecular core and the length of the peripheral chain have been observed.

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