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Thermal switching of the optical anisotropy of a macroscopically aligned film of a discotic liquid crystal

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We have studied the temperature dependence of anisotropy in the optical absorption and charge transport properties of an aligned film of hexakis-dodecyl-hexa-*peri*-hexabenzocoronene (HBC-C12) formed by zone-casting on a quartz substrate. At room temperature the film displays a large anisotropy in (photo)conductivity, as determined using the flash photolysis time-resolved microwave conductivity technique, with charge transport in the casting direction favoured by a factor of at least 10. The anisotropy in the optical absorption is however negligible. At the temperature corresponding to the transition from the crystalline solid to the liquid crystalline mesophase (*c.* 110°C), the optical anisotropy increases abruptly, with absorption of light polarized in the direction perpendicular to the alignment direction favoured by a factor of *c.* 3. On cooling, the dichroism reverts to its initial very low value with a hysteresis of *c.* 30°C. The results are explained in terms of a reversible change in the orientation of the molecules with respect to the axis of the aligned columnar stacks from tilted (at *c.* 45°) in the crystalline phase to close to orthogonal in the liquid crystalline phase.

1. Introduction

The alignment of liquid crystals is a prerequisite to the exploitation their self-organizing properties for practical opto-electronic materials and devices. While well established techniques are available for calamitic liquid crystals, the alignment of discotic mesogens is still at an early stage of development. Sophisticated methods have resulted in aligned discotic nematic phases that are already commercially exploited as optical compensation films for thin film transistor liquid crystalline displays [1]. However little success has been achieved in the past with more ordered and viscous discotic compounds, as discussed in a review by Eichhorn *et al.* [2].

Recently in-plane columnar alignment of discotic triphenylene and hexabenzocoronene (HBC) derivatives was achieved by solution processing on a primer layer of friction-deposited polytetrafluoroethylene (PTFE) [3, 4], or by zone-casting onto a bare glass substrate [5]. We have shown that charge transport in PTFE-aligned films of HBCs is highly anisotropic [6]. In contrast, the *optical* anisotropy was found to depend on whether the particular HBC derivative was crystalline or liquid crystalline at room temperature. In the former case the molecules adopt a herringbone structure in which they are tilted at an angle close to 45° with respect to the columnar axis, resulting in no net optical anisotropy. In the latter case the molecules stack with their planes orthogonal to the columnar axis and a large optical anisotropy is observed. In the present work we demonstrate that the optical anisotropy of a zone-cast film of an HBC derivative can be reversibly switched on or off by varying the temperature in the region of the crystal-to-mesophase transition where the molecules reorient from a tilted to an orthogonal stacking arrangement. This effect could possibly be applied in optical switching or memory storage devices.

2. Experimental

A *c.* 40 nm thick film of hexakis-dodecyl-hexa-*peri*-hexabenzocoronene (see figure 1 for molecular structure) was deposited on a $24 \times 12\,\mathrm{mm}^2$, 1 mm thick quartz substrate by zone-casting a $0.25\,\mathrm{mg\,ml}^{-1}$ solution in tetrahydrofuran as described previously [5]. Optical micrographs of the film were taken using a

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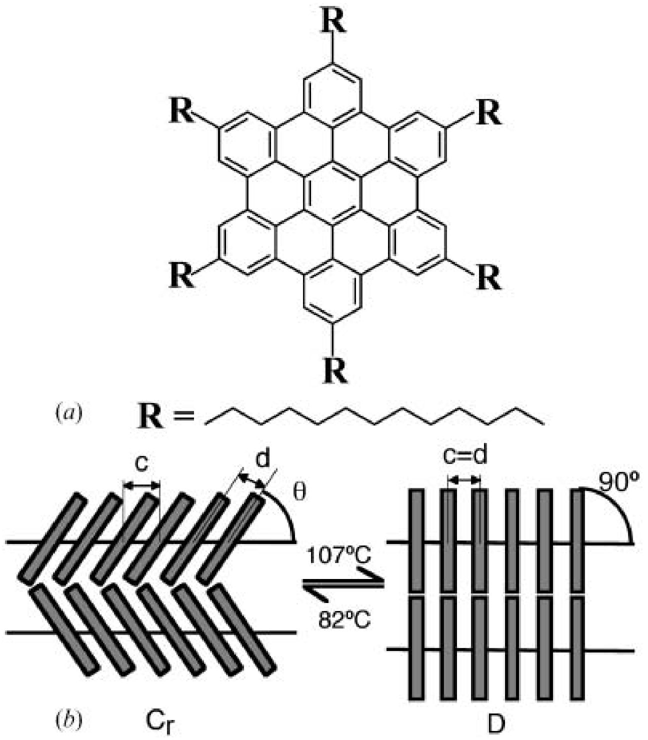

Figure 1. (*a*) Molecular structure of the hexa-*peri*-hexabenzocoronene derivative, HBC-C12, studied. (*b*) A schematic representation of the columnar arrangement in the room temperature crystalline phase, Cr, and the high temperature hexagonal mesophase, D, with the intercolumnar distance *c*, cofacial distance *d*, and tilt angle θ. The Cr↔D phase transition temperatures indicated were determined by differential scanning calorimetry (DSC) on bulk material [9].

Zeiss microscope equipped with polarizing filters and a Hitachi KP-D50 digital CCD camera. The samples were heated on a Linkam hot stage with a Linkam TMS 91 temperature controller.

Optical transmission, $F_T(\lambda)$, and reflection, $F_R(\lambda)$, spectra of the film were recorded at room temperature using a Perkin-Elmer Lambda 900 spectrophotometer equipped with an integrating sphere ('Labsphere'). The optical density, *OD*, was determined from $OD = -\log_{10}[F_T/(1-F_R)]$. For measurements at elevated temperatures the sample was contained in a nitrogen-filled, thermostated cell which was placed at the entrance port of the integrating sphere. The temperature could be varied from room to a maximum of 130°C with an accuracy of ±1°C. For the high temperature measurements $F_R(\lambda)$ could not be directly measured but was taken to have the same spectral dependence as at room temperature normalized to the value of $(1-F_T)$ determined at 500 nm, i.e. a wavelength at which the absorption of HBC is negligible. The plane of polariztion of the incident light could be controlled to within 0.2° by means of a double polarizer driver fitted with Glan–Taylor prisms.

For flash photolysis time-resolved microwave conductivity (FP-TRMC) measurements of the anisotropy of the photoconductivity, the coated substrate was divided into two $12\times12\,\mathrm{mm}^2$ plates. These could be placed in the microwave cavity with the casting direction of the film either parallel or perpendicular to the electric field vector of the microwaves. In addition, the plane of polarization of the laser beam used to photoexcite the sample could be oriented parallel or perpendicular to the casting direction. The transient photoconductivity of the sample was monitored as a reduction in the microwave power reflected by the cavity as described in detail in previous publications [7, 8].

3. Results and discussion

In a previous study of a zone-cast film of HBC-C12 the molecules were shown to be macroscopically aligned in columnar stacks with the axes of the columns parallel to the casting direction [5]. Despite this, the films were found to exhibit negligible birefringence in optical micrographs taken with crossed polarizers. A lack of significant optical anisotropy was also apparent for the present sample at room temperature, as shown by the similarity of the optical absorption spectra obtained for light polarized parallel or perpendicular to the casting direction, figure 2 (*a*). This apparent anomaly has been attributed to a tilted, herringbone arrangement of the molecules in the columns with a tilt angle (θ in figure 1) close to 45° as found in an X-ray diffraction study of the bulk material [9]. Since the transition dipole of the first absorption band of the aromatic cores lies in the plane of the core, this configuration should lead to a lack of optical anisotropy, as observed.

To confirm that the present sample was in fact macroscopically aligned we measured the anisotropy of the photoconductivity using FP-TRMC, which was applied recently to films of HBC derivatives self-assembled from solution on friction-deposited PTFE [6]. As can be seen from the results in figure 3, the photoconductivity transients with the casting direction parallel to the electric field vector of the microwaves are much larger than for a perpendicular orientation. The latter transients are in fact close to the noise level of detection, and the anisotropy in the conductivity is estimated to be at least a factor of 10 in favour of charge transport in the casting direction, i.e. along the axis of the columnar stacks. In agreement with the lack of optical anisotropy found in the absorption spectra, the photoconductivity is found to be almost independent of the relative orientation of the polarization of the laser beam used to photoexcite the sample. The photoconductivity

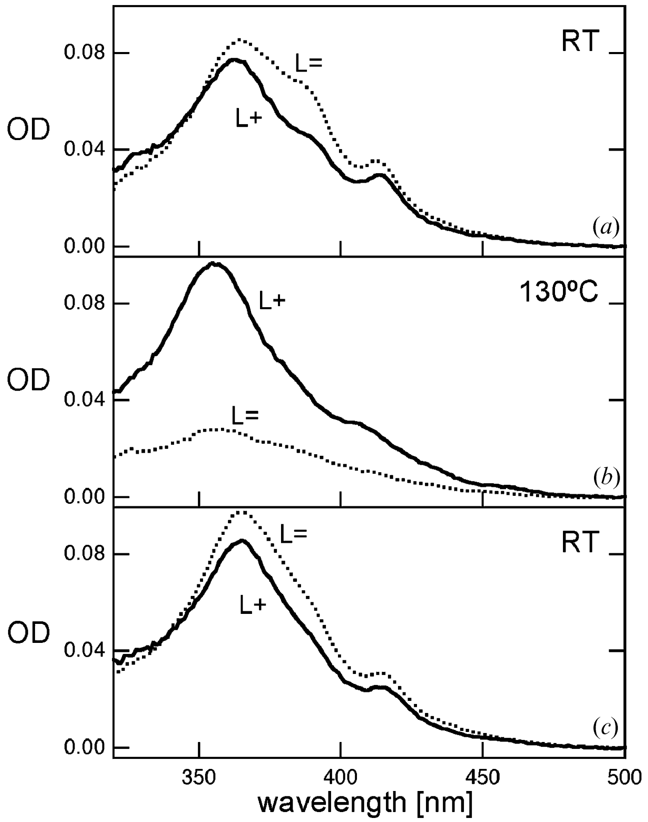

Figure 2. The optical density of a zone-cast film of HBC-C12 for light polarized perpendicular, L+, or parallel, L=, to the casting direction. (*a*) Pristine sample at room temperature; (*b*) on heating to 130°C; (*c*) on cooling back to room temperature.

results confirm therefore the high degree of columnar alignment of the discotic molecules in the present sample and the tilted, herringbone arrangement of the molecules in the columnar stacks at room temperature.

X-ray diffraction and DSC measurements on bulk HBC-C12 have shown that a transition from the crystalline phase, Cr, to a discotic mesophase, D, occurs at 107°C on heating [9]. The transition is accompanied by a reorientation of the molecules within the columnar stacks from a tilted to an orthogonal arrangement as illustrated in figure 1. The Cr phase was found to be re-entered at 82°C on cooling. On the basis of these results we concluded that, if reorientation of the molecules is possible within the present aligned film, then this should be apparent as a reversible change in the optical anisotropy on raising and lowering the temperature in the region of the Cr–D phase transition.

That a reversible change in anisotropy does indeed occur for the present film is shown by the absorption spectra in figure 2, which were taken for light polarised parallel and perpendicular to the casting direction for (*a*) the pristine sample at room temperature, (*b*) on heating to 130°C, and (*c*) on cooling back to room temperature. The reversible change from almost no anisotropy at room temperature to a highly anisotropic medium above the temperature of the phase transition is apparent. The actual ratios of the maximum optical density for perpendicular to that for parallel excitation, $OD_{\max}(+)/OD_{\max}(=)$, are 0.91, 3.30 and 0.87, respectively. Clearly, a considerable rotation of the molecules from their tilted, room temperature configuration has taken place at the elevated temperature.

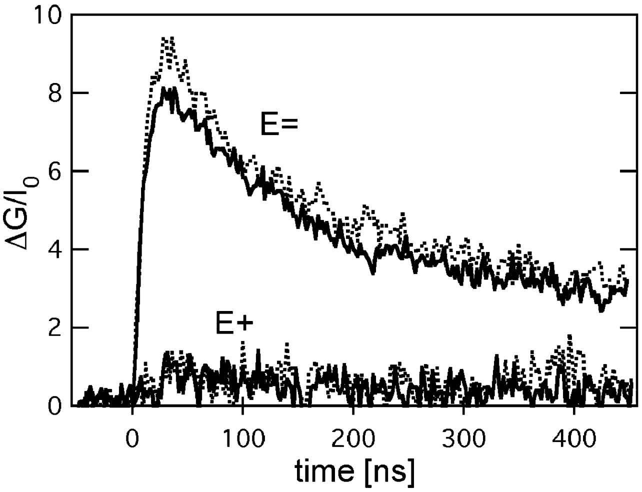

Figure 3. Intensity normalized photoconductivity transients, $\Delta G/I_0$ in units of $10^{-24}\,\mathrm{S\,cm^{-2}}$ per incident-photon, obtained by flash-photolysis of a zone-cast film of HBC-C12. The full and dashed traces are for light polarized perpendicular or parallel to the alignment direction of the discotic columns respectively. The two upper, $E=$, and two lower, $E+$, traces are for the casting direction (columnar alignment) parallel or perpendicular to the electric field vector of the microwaves, respectively.

The values of the ratio $OD_{\max}(+)/OD_{\max}(=)$ over the full heating and cooling cycle are shown in figure 4. As can be seen, the increase in the optical density ratio occurs abruptly at close to 110°C on heating and returns to the initial value at close to 85°C on cooling, i.e. close to the transition temperatures found in DSC measurements for the phase transition in bulk samples. Also shown in figure 4 are polarization microscopy images under crossed polarizers taken at different temperatures in the heating and cooling cycle. These images provide an additional illustration of the reversible change in anisotropy occurring at the phase transition. They furthermore demonstrate the high degree of alignment that is retained in the mesophase.

Thermally induced rotation of the molecules along an axis perpendicular to the substrate apparently occurs in the present thin film sample despite the fact that this requires a considerable adjustment in the lattice geometry of the material, i.e. a longitudinal contraction

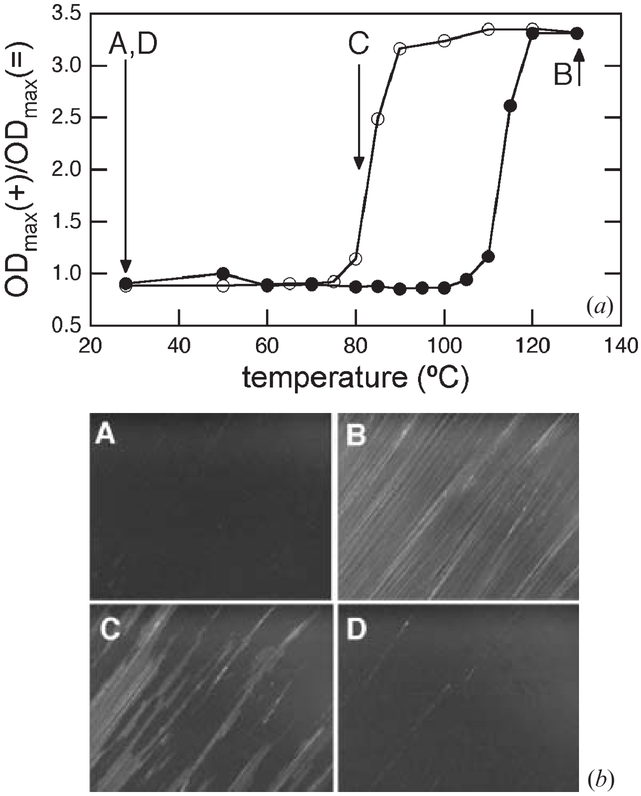

Figure 4. (*a*) Temperature dependence of the ratio of the optical density of a zone-cast film of HBC-C12 at the absorption maximum for the incident light polarized perpendicular and parallel with respect to the casting direction. (*b*) Optical micrographs obtained under crossed polarisers: A, pristine sample at room temperature; B, liquid crystalline phase at 130°; C, at close to the phase transition temperature on cooling; D, the crystalline phase on returning to room temperature.

and lateral expansion with respect to the direction of the columns. That reorientation is in fact restricted in the film, i.e. complete orthogonal stacking is not achieved in the mesophase, is indicated by the fact that the optical density ratio of 3.3 in the mesophase is still considerably lower than expected on the basis of the anisotropy factor of 10 or more found for the conductivity. The value of *c.* 3 is also considerably smaller than the optical anisotropy factor of 12 found for an aligned film of HBC-PhC12 on friction-deposited PTFE [6, 10]. This HBC derivative is liquid crystalline at room temperature and is expected to adopt a close to perfect orthogonal stacking arrangement on self-assembly from solution.

4. Summary

We have shown how a thermally induced change in the intracolumnar tilt angle of discotic molecules in a macroscopically aligned film causes the optical properties of the film to change abruptly from isotropic to highly anisotropic at the crystal-to-liquid crystal phase transition. When combined with the highly anisotropic conductive properties, this phenomenon opens up the possibility of creating optoelectronic switching devices that could be actuated by external influences such as temperature or magnetic field. In addition, there are known examples of discotic compounds, such as peripherally substituted *n*-alkoxyphenylphthalocyanines, for which the transition from a tilted crystalline phase, formed on precipitation at room temperature, to an orthogonal mesophase is irreversible [11]. Such compounds would be potential candidates for optical data storage media based on the present phenomenon. The advantage over previously reported mechanisms for switching the optical properties of columnar discotics [12, 13] is that the columnar arrangement remains intact, and therefore their excellent semiconductive properties [11] could be exploited together with their unique optical behaviour.

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