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## Morphology of open films of discotic hexagonal columnar liquid crystals as probed by grazing incidence X-ray diffraction

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# Morphology of open films of discotic hexagonal columnar liquid crystals as probed by grazing incidence X-ray diffraction

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**Abstract.** The structure and the orientation of thermotropic hexagonal columnar liquid crystals are studied by grazing incidence X-ray diffraction (GIXD) for different discotic compounds in the geometry of open supported thin films. Whatever the film deposition mode (either spin-coating or vacuum evaporation) and the film thickness, a degenerate planar alignment with the liquid crystalline columns parallel to the substrate is found. However, if a specific thermal process is applied to the liquid crystal film, homeotropic anchoring (columns normal to the interface) can be stabilized in a metastable state.

## 1 Introduction

Columnar liquid crystals (CLC) made of flat aromatic discs surrounded by flexible peripheral chains can form thermotropic mesophases where discs are stacked into columns, which in turn arrange into a two-dimensional crystal lattice [1]. Because of their highly anisotropic absorption and charge carrier properties, these self-assembled conjugated molecules represent a promising system as active layer in organic devices [2,3], such as field-effect transistors and photovoltaic cells [4,5]. An important issue to achieve high mobilities in the columnar mesophase is to control the structure and the organization of the discotic semiconducting material in oriented thin films: homeotropic alignment is required in solar cells [3,6], whereas unidirectional planar alignment is needed for organic field-effect transistors (fig. 1(a)) [7, 8]. The range of CLC film thicknesses suitable for optoelectronic applications is about 100 nm, which is between self-assembled monolayers and conventional liquid crystal cells made of two solid surfaces [3,9–11]. One of the main advantages of discotics-based liquid crystals is that they are either solution-processable like polymers into large-area thin devices [12], or can be prepared in thin films by vacuum deposition like most small molecules [13]. We have previously shown, based on anchoring energy arguments and microscopy observations, that if the homeotropic alignment of discotic mesophases can be kinetically favored in open supported thin films, the planar alignment should be the thermodynamically stable state [14]. In this work, the structure and the alignment of hexagonal

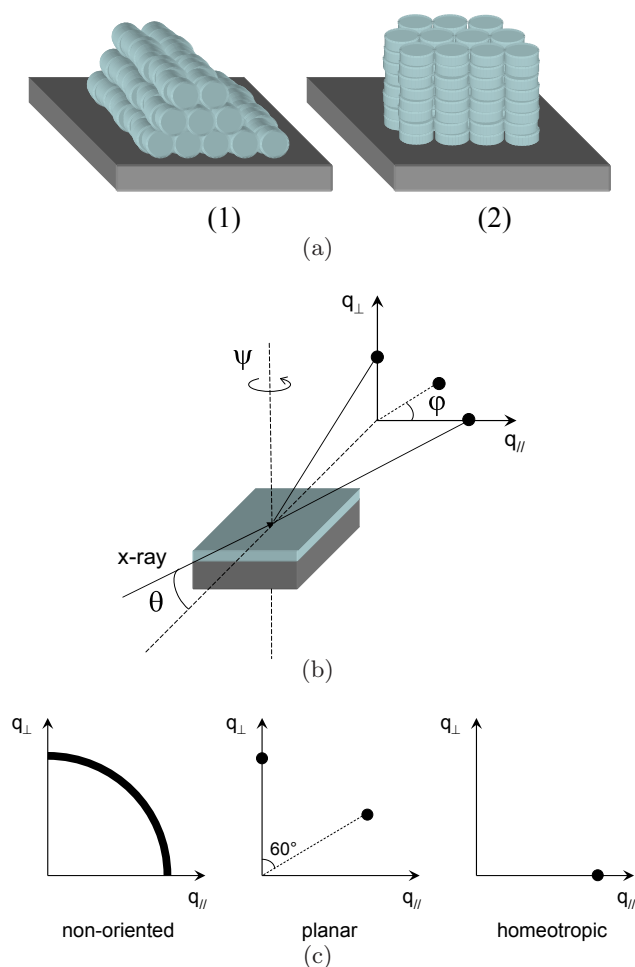
CLC films as a function of the deposition mode, the film thickness, and the nature of the solid substrate have been investigated for different discotic compounds by grazing incidence X-ray diffraction (GIXD) (fig. 1(b)). The GIXD measurements demonstrate an edge-on orientation of the discotic molecules within the layer, corresponding to a degenerate planar alignment. Only such investigations by GIXD allow the discrimination between a degenerate planar alignment and a completely non-oriented sample (corresponding to an isotropic average of the orientation of CLC microdomains). After a specific thermal annealing, we also show that the homeotropic alignment can be stabilized in thin open films. The results shown in this work constitute the experimental validation of the theoretical considerations [14] on the CLC anchoring energy in open supported films.

## 2 Experimental part

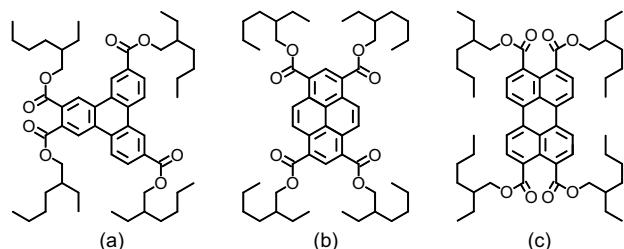
### 2.1 Materials

Several arene tetracarboxylic tetra-*rac*-2-ethylhexyl esters with different aromatic cores (triphenylene, pyrene, and perylene, see fig. 2) have been investigated [15,16]. The use of racemic branched alkoxy carbonyl chains has been shown to lead, with a variety of aromatic cores, to a columnar mesophase with accessible clearing temperatures, subambient melting points, absence of mesophase-to-mesophase transitions within the liquid crystalline temperature range and reasonably good chemical stability at elevated temperatures under illumination. The suppression of crystallization is due to the disorder induced within

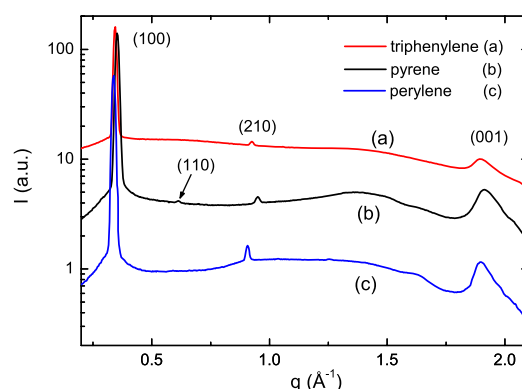
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**Fig. 1.** (Colour on-line) (a) Schematic representation of the *unidirectional* planar (or edge-on) 1) and the homeotropic (or face-on) 2) alignments of a hexagonal columnar liquid crystal made of discotic molecules. (b) Schematic geometry of the GIXD experimental setup. (c) Expected X-ray diffraction pattern of the first-order intercolumnar Bragg peak (100) in the cases of non-oriented (or three-dimensional powder), planar and homeotropically aligned samples. The scattering vector range is limited to positive values.



**Fig. 2.** Molecular structure of the room temperature liquid crystalline compounds used in this work: (a) triphenylene, (b) pyrene, and (c) perylene derivatives.



**Fig. 3.** (Colour on-line) Powder X-ray diffractogram at room temperature of the triphenylene (a), pyrene (b) and perylene (c) derivatives showing the Bragg reflections as the typical signature of a hexagonal packing of columns. The (001) broad peak is characteristic of the liquid-like  $\pi$ -stacking of the discotic molecules within the columns. The diffuse scattering around  $1.4 \text{ \AA}^{-1}$  represents the signal of the disordered aliphatic chains.

the alkyl periphery by the chiral racemic branching and the resulting elevated number of stereoisomers present. The columnar mesophase exhibited by this class of discotic materials is invariably of hexagonal symmetry, as shown in fig. 3 by powder X-ray scattering on the three derivatives [15,16]. The transition temperature from the hexagonal columnar liquid crystalline phase to the isotropic liquid phase is  $125^\circ\text{C}$ ,  $92^\circ\text{C}$ , and  $260^\circ\text{C}$  for the triphenylene, pyrene, and perylene derivatives, respectively.

## 2.2 Preparation of open CLC films

Different solid interfaces such as microscope glass slides (Thermo Scientific), silicon wafers with their oxide (Siltronix), and graphite substrates, have been investigated. All were first cleaned with three successive ultrasound baths of distilled water, acetone and ethanol. Glass slides and silicon wafers were then dipped in sulfochromic acid used as powerful oxidizing agent, before being rinsed with distilled water, and dried with nitrogen. The substrates were then coated with a discotic material, either by spin-coating or by vacuum evaporation. In the former deposition mode, a liquid crystal solution of a few wt% in chloroform is spin-coated at 2000 r.p.m. during 30 seconds on the previously cleaned substrates. The film thicknesses were measured by using an atomic force microscope in tapping mode acting as a mechanical profilometer, leading to values ranging from 20 nm to  $1 \mu\text{m}$ , with an accuracy of  $\pm 10 \text{ nm}$ . In the latter deposition mode, the organic films were prepared by vacuum evaporation at a pressure of  $10^{-6} \text{ mbar}$ . The CLCs were initially placed in flat silica cupels located 25 cm below the substrate. The deposition rate of the evaporated materials was of about  $1 \text{ \AA/s}$  and the thickness of each layer was controlled by a quartz crystal thickness monitor placed near the samples. In both cases, the resulting CLC thin film exhibits

a mosaic texture formed by birefringent domains of about a few  $\mu\text{m}$  in size (fig. 4(a)). These observations were done with an optical microscope (Olympus, BX51), combined with both a color CCD camera (JAI, CV-M7) and a heating stage (Linkam, THM600) when a thermal annealing was applied. Two contrast modes were used to study the orientation of the CLC films, either between crossed polarizers or by differential interference contrast (DIC). The DIC technique is sensitive to the refractive index gradient, and therefore improves the contrast of optically isotropic samples by enhancing all interfaces such as grain boundaries between CLC domains and dendrites (fig. 4(c)).

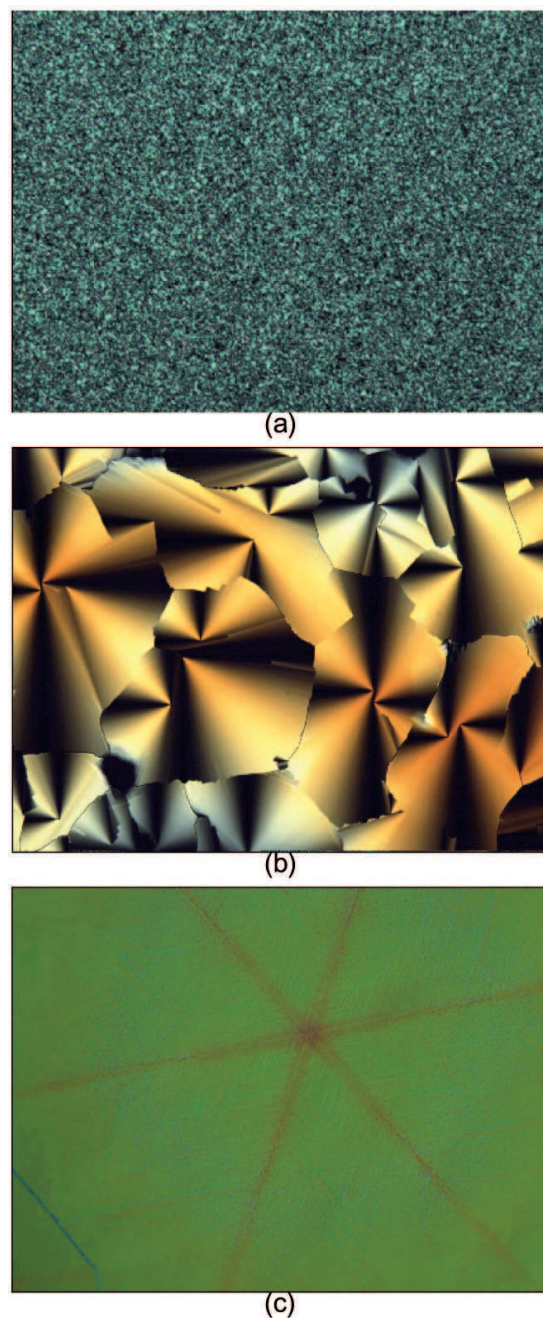
### 2.3 X-ray scattering setup

The ESRF-BM02 beam line was used in the GIXD goniometer configuration as shown in fig. 1(b), with the CCD camera as a two-dimensional detector which was at a distance of about 550 mm (fig. 5) or 120 mm (figs. 6 and 7) of the sample depending on the configuration. The X-ray beam had an energy of 9 keV (corresponding to a wavelength of  $1.38 \text{ \AA}$ ), and its size was  $40 \mu\text{m} \times 1 \text{ mm}$  ( $V \times H$ ). The GIXD studies were performed with the X-ray beam probing the sample surface at a grazing incidence angle of  $\theta = 0.17^\circ$  (fig. 1(b)) providing a total reflection from the solid substrate. Therefore, the background scattering from the solid substrate is reduced, enhancing the signal from the thin organic film. In these conditions, the sample area exposed to the incident X-ray beam is of about  $3.3 \text{ mm} \times 1 \text{ mm}$ . The scattering vector can be defined on the detector along two components,  $q_{\parallel}$  and  $q_{\perp}$ , for the directions parallel and perpendicular to the sample surface, respectively (fig. 1(b)). In order to reduce the diffuse scattering by the air, vacuum tubes with Kapton polymer windows were used in the path of the scattered X-ray signal. Such polymer windows generate an additional signal on the CCD detector, which is characterized by a uniform broad ring at  $q \simeq 0.67 \text{ \AA}^{-1}$  in figs. 6(a) and 7.

## 3 Results and discussion

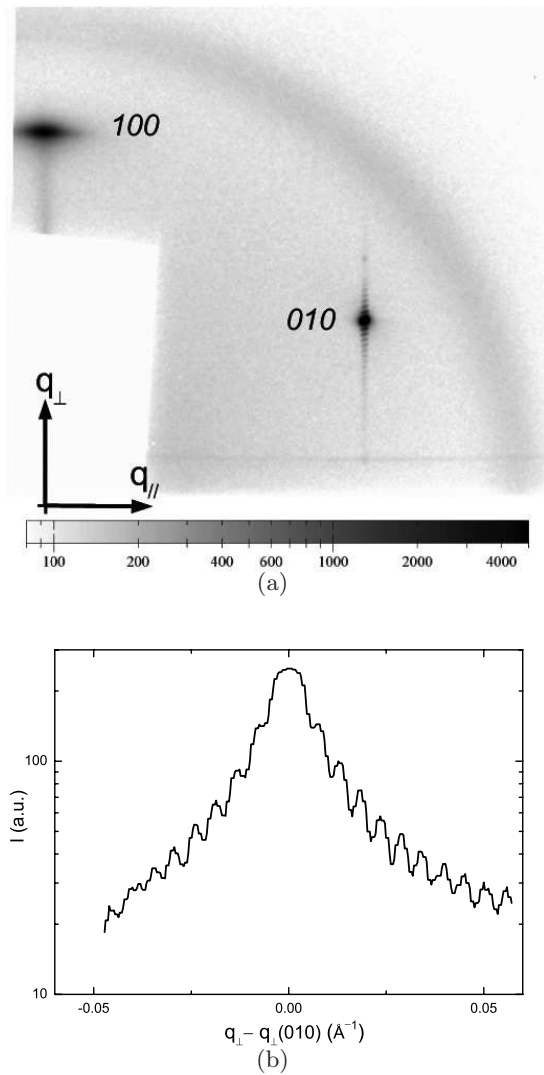
### 3.1 CLC planar orientation

The dependence of the GIXD patterns on the columnar orientation with respect to the solid substrate is shown in fig. 1(c) for the first-order Bragg peak. A three-dimensional powder, that can be defined as an orientational average of CLC domains in all the directions of space, gives rise to a uniform ring as GIXD pattern. Such an alignment could be expected for the CLC film presented in fig. 4(a) which exhibits a birefringent mosaic texture characteristic of a powder. Surprisingly, X-ray scattering experiments on this sample reveal a remarkably well-defined *planar* orientation of the CLC layer (fig. 5(a)), according to fig. 1(c). The presence of fringes, called Laue oscillations, around the first-order Bragg peak  $010$ , is related to the coherently ordered film thickness via  $2\pi/\Delta q_{\perp}$ ,



**Fig. 4.** (Colour on-line) (a) Optical texture observed between crossed polarizers of a hexagonal columnar liquid crystal (perylene derivative) in an open supported thin film prepared either by spin-coating or by vacuum deposition. The CLC film exhibits a birefringent mosaic texture characteristic of a powder. (b) Developable domains featuring a degenerate planar orientation of a hexagonal columnar liquid crystal obtained after a thermal annealing of the sample below the isotropic liquid-CLC phase transition (triphenylene derivative). The observation is between crossed polarizers. (c) Single columnar liquid crystal domain observed by differential interference contrast microscopy in the geometry of an open supported film. The sixfold symmetry is the signature of the homeotropic alignment, which has been obtained after a specific thermal process on the pyrene derivative. In each case, the image size is  $880 \mu\text{m} \times 650 \mu\text{m}$ .





**Fig. 5.** (a) GIXD pattern of a planarly aligned CLC film at small angles (pyrene derivative). The scale is given by the length of the two arrows ( $q_{\parallel}$  and  $q_{\perp}$ ), which corresponds to  $0.10 \text{ \AA}^{-1}$ . (b) Laue oscillations corresponding to an integration along  $q_{\perp}$  of the scattered intensity of the first-order Bragg reflection  $010$ .

which gives  $1200 \text{ \AA}$  [13]. This value is in agreement with the thickness measurement performed during the CLC film preparation, showing that the CLC layer is coherently ordered throughout its whole thickness. Note that we did not perform any  $\theta$ - $2\theta$  scan (the grazing incidence angle  $\theta$  being fixed, see sect. 2.3), therefore no Kiessig or Laue fringes should be observed. However, the presence of Laue oscillations is probably due to both sample mosaicity and the fact that such fringes are not very sensitive to the quality of the interface. Indeed, Laue oscillations only depend on the number of lattice planes which scatter coherently in the film thickness.

At larger angles, the GIXD pattern characteristic of a planar anchoring of the columnar mesophase is shown in fig. 6(a). The azimuthal integration of the scattered inten-

**Table 1.** Set of film thicknesses probed by GIXD for the three different discotic compounds deposited either on silicon wafers or on glass slides.

Film thickness (nm)	Spin-coating	Vacuum evaporation
Pyrene	10, 70, 380, 440 630, 820, 1075	50, 120, 250
Triphenylene	330	-
Perylene	600 <sup>a</sup> , 630	-

<sup>a</sup> Deposited on graphite substrate.

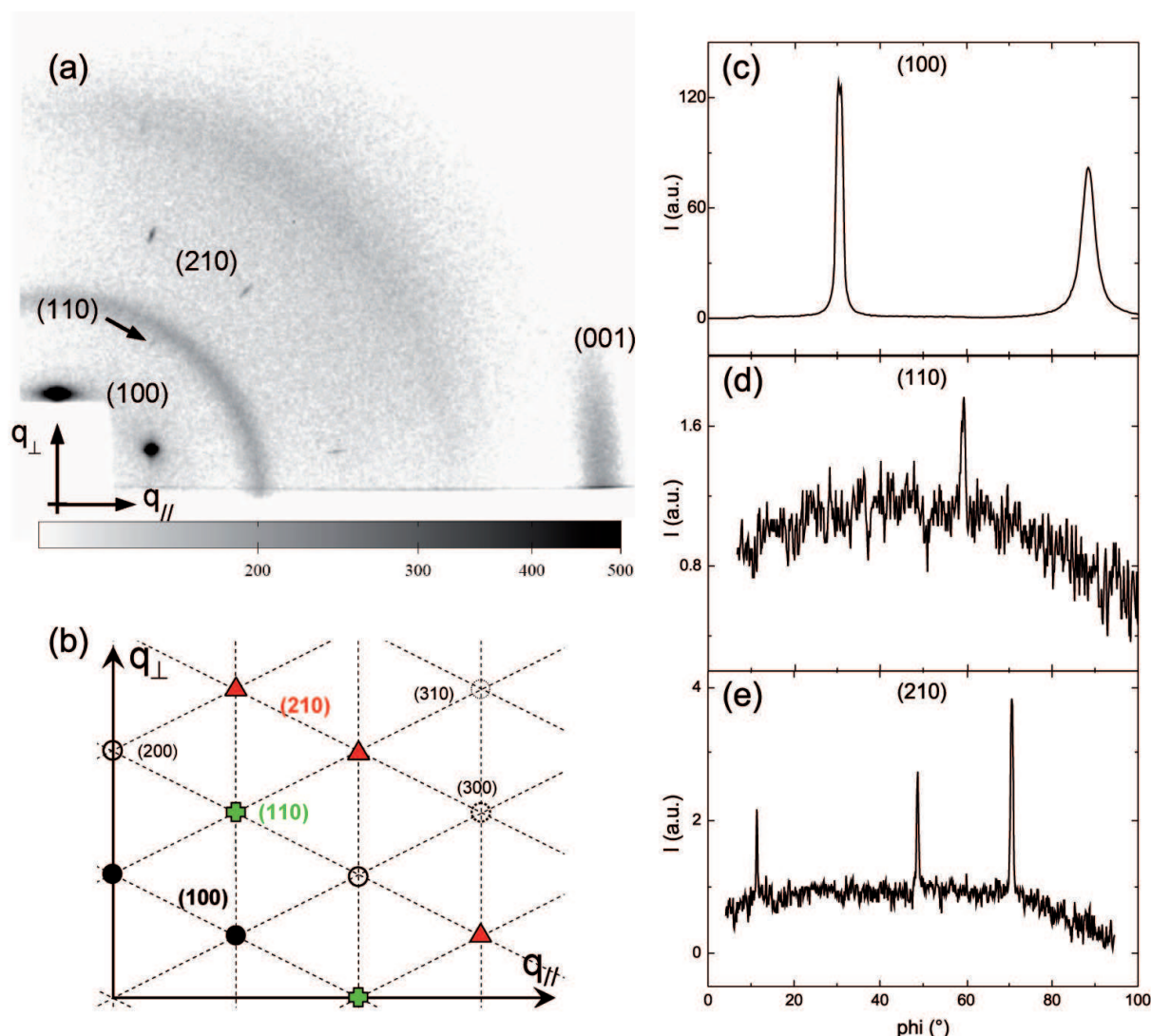
sity along the angle  $\varphi$  (fig. 1(b)) of the  $(100)$ ,  $(110)$  and  $(210)$  Bragg reflections is consistent with the structure of a hexagonal lattice [17]. Moreover, this GIXD pattern is shown to be independent of the sample rotation with respect to the angle  $\psi$  (fig. 1(b)) indicating a *degenerate* (*i.e.* not unidirectional) planar orientation [18]. In this edge-on arrangement of the discotic molecules, the CLC domains are randomly oriented within the sample plane, corresponding to a planar *two-dimensional* powder. This degenerate planar alignment of the columns is found for all the materials studied (fig. 2), whatever the film preparation mode, either by spin-coating or by vacuum deposition, and no influence of the film thickness (from a few nm up to  $1 \mu\text{m}$ ) has been observed (table 1).

In order to confirm this result, a sample exhibiting developable domains (fig. 4(b)) known to be a distinctive optical texture of columnar mesophases has been studied [19]. In the developable domains obtained with a thermal annealing below the isotropic liquid-CLC phase transition, the columns are bent, forming then a degenerate planar orientation. As expected, a similar GIXD pattern compared to fig. 6(a) has been found.

Many experimental parameters such as the film preparation process, the film thickness, and the discotic compound, have been probed and varied and neither a three-dimensional powder, nor a hybrid alignment involving column distortion within the film thickness have been evidenced. Instead, the two-dimensional planar orientation of CLC films has been found to be a very robust configuration, and this result has been also shown to be independent of the nature of the investigated solid substrates, as summarized in table 1. In particular, even with a graphite substrate known for its strong affinity for discotic molecules, a planar alignment of the CLC layer has been confirmed.

### 3.2 CLC homeotropic alignment

The planar orientation obtained after the film deposition can be overcome by applying a specific thermal process, by which it is possible to kinetically stabilize the homeotropic alignment [6,14]. The discotic compound is in a first step heated up to the isotropic liquid phase, followed in a second step by a thermal quenching down to room temperature with the nucleation and the growth of CLC germs. This thermal process induces a homeotropic orientation



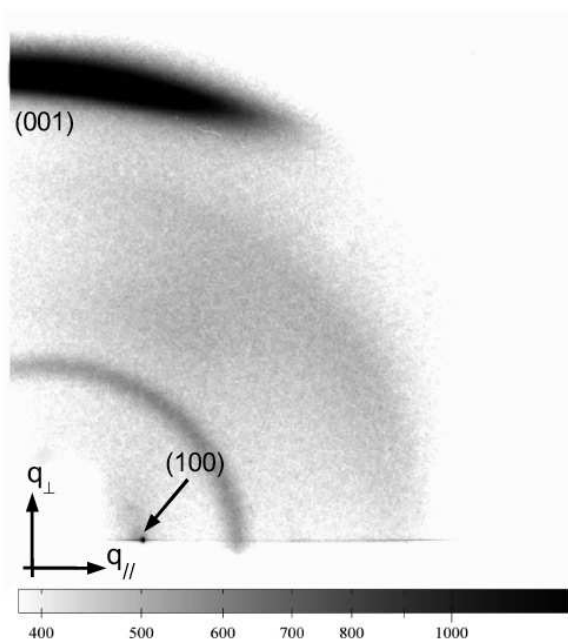
**Fig. 6.** (Colour on-line) (a) GIXD pattern of a hexagonal columnar liquid crystal film of the pyrene derivative indicating a degenerate planar orientation according to the positions of the Bragg reflections. Note that some reflections are experimentally hidden by the horizon. The scale is given by the length of the two arrows ( $q_{\parallel}$  and  $q_{\perp}$ ), which corresponds to  $0.25 \text{ \AA}^{-1}$ . (b) Expected X-ray diffraction pattern of the different Bragg peaks ((100): black solid circles, (110): green crosses, (200): open circles, (210): red triangles, (300): dashed circles, (310): dotted circles) for a hexagonal columnar mesophase exhibiting a degenerate planar orientation. Right: azimuthal integration of the scattered intensity of the (100) (c), (110) (d) and (210) (e) Bragg reflections shown in panel (a), characteristic of a hexagonal lattice according to panel (b).

of the hexagonal columnar mesophase on solid substrates such as glass, ITO, or silicon oxide. This face-on alignment of the molecules is thermodynamically metastable in the geometry of an open film, but it can be preserved until the deposition of an electrode for instance. The homeotropic anchoring is evidenced by optical microscopy with the sixfold symmetry observed during the dendritic growth of CLC germs (fig. 4(c)), and confirmed by X-ray scattering in fig. 7. As expected for a homeotropic alignment (fig. 1(c)), the intercolumnar Bragg peaks lie along  $q_{\parallel}$ , while the scattered intensity corresponding of the  $\pi$ -stacking of the discotic molecules is oriented at  $90^\circ$ , along  $q_{\perp}$ . This homeotropic alignment extends over a remarkably large surface area of several  $\text{mm}^2$ .

### 3.3 Considerations on CLC surface tensions

In order to account for the dominant planar alignment of CLC in the geometry of open supported thin films, the role of air and solid interfaces of the CLC layers has to be invoked [14]. Although the solid substrate favors the preferred face-on alignment, the CLC-air interface strongly favors the edge-on alignment, because the aromatic molecular cores prefer to interact with each other and tend to avoid being exposed to air or vacuum. In terms of anchoring energy, that can be expressed by

$$\gamma_{\text{CLC-air}}^{\perp} - \gamma_{\text{CLC-air}}^{\parallel} > \gamma_{\text{CLC-solid}}^{\parallel} - \gamma_{\text{CLC-solid}}^{\perp}, \quad (1)$$



**Fig. 7.** GIXD pattern of a hexagonal CLC film of the pyrene derivative in homeotropic orientation. The (100) Bragg reflection is partially hidden by the horizon. The scale is given by the length of the two arrows ( $q_{\parallel}$  and  $q_{\perp}$ ), which corresponds to  $0.25 \text{ \AA}^{-1}$ .

where  $\gamma^{\perp}$  and  $\gamma^{\parallel}$  are the anisotropic surface tensions associated with the homeotropic and the planar orientations, respectively [14]. If the planar alignment is shown to be the thermodynamically stable anchoring, the homeotropic alignment can nevertheless be kinetically promoted and stabilized during its growth from the isotropic liquid phase, according to ref. [14]. The scenario of the CLC growth in homeotropic orientation is summarized in the following text: in a preliminary step, the CLC sample is heated up to the isotropic liquid phase and then cooled down. During the cooling-down, the nucleation of the mesophase first occurs on the solid substrate mainly due to temperature gradients in the heating stage, with a face-on arrangement of the molecules, according to  $\gamma_{\text{CLC-solid}}^{\parallel} > \gamma_{\text{CLC-solid}}^{\perp}$ . Because of the geometry of thin films, the very large aspect ratio (diameter over thickness) of the hexagonal CLC domains, where the homeotropic area in contact with the liquid isotropic phase is dominant, favors also the minimization of the surface energy, according to  $\gamma_{\text{CLC-Iso}}^{\parallel} > \gamma_{\text{CLC-Iso}}^{\perp}$  [20]. Depending on the cooling rate, and therefore on the growth velocity, the CLC domains can reach the air interface at temperatures where the CLC viscosity is high enough to freeze the system in the homeotropic alignment, which can thus be maintained in a metastable state at room temperature. However, this metastable homeotropic alignment will undergo *in fine* an anchoring transition to the planar orientation. This process, which is very slow at ambient temperature, can take up to a few weeks, but can be speeded up by a thermal annealing below the isotropic liquid-CLC phase transition,

where the CLC fluidity increases: the system then adopts the planar anchoring which is the configuration of minimal anchoring energy.

## 4 Conclusions

In this work, experiments demonstrate that a strong degenerate planar orientation is found for thin open supported hexagonal columnar liquid crystal films, and this result is independent of the main probed experimental parameters, such as the discotic compounds, the film preparation process, the film thickness, and the nature of the three investigated solid substrates. This degenerate planar alignment which has been unambiguously evidenced by grazing incidence X-ray diffraction corresponds to the worst orientation for carrying charges or excitons in organic devices. A thermal annealing is revealed as being a convenient way to achieve homeotropic anchoring of hexagonal columnar liquid crystal films. Therefore, the active control of the orientation of CLC thin films is shown to be an absolute necessity in order to benefit from the uniaxial CLC optoelectronic properties, *i.e.* to increase the efficiency of organic solar cells based on discotic materials.

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