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Control of the orientation of thin open supported columnar liquid crystal films by the kinetics of growth

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Abstract. – We report a study of the growth and of the orientation of thin open supported columnar liquid crystal films by thermal annealing. We show that there is a competition between planar and homeotropic orientations (columns respectively oriented parallel and perpendicular to the solid substrate) of the liquid crystal, which can be controlled by the kinetics of annealing. A model based on the different surface tensions of the system is proposed to account for the experimental observations. Such a control of the alignment opens the way towards discotics based optoelectronic devices.

Introduction. – Columnar liquid crystals (colLC) made of disc-shaped aromatics surrounded by flexible side chains are known to be good charge and exciton transporters, with mobilities approaching those of aromatic single crystals [1], but with the added capacity to self-assemble in large, oriented domains [2]. Such semiconducting materials may be used in devices such as solar cells [3]. In order to be able to benefit from the good uniaxial charge and exciton mobilities in the columnar mesophase, it is necessary to control the structure and the organization of the material in oriented sub-micron thin films. Whereas a uniaxial planar orientation (in which the molecules are edge-on to the solid substrate) is needed for applications such as field effect transistors, homeotropic alignment (columns perpendicular to the electrodes) is required in light-emitting diodes and solar cells.

In contrast to liquid crystal (LC) devices such as twisted nematic LC displays where the LC is switched between different orientations in an electric field, which have a thickness of several micrometers and which are filled by capillarity, cells that have a thickness of only a few hundred nanometers cannot be fabricated by capillarity. Organic light-emitting diodes and solar cells are in general made by sequential deposition of the organic layers on the anodic substrate, and the cathode is added by vacuum deposition afterwards [4]. If we want to use

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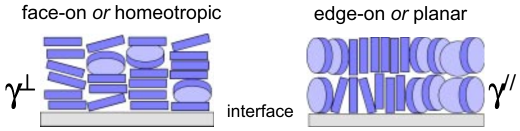

Fig. 1 – Schematic representation of the different orientations of a columnar liquid crystal with its associated surface tensions.

oriented films of discotic materials, it is therefore necessary to orient the film as an open layer in the face-on configuration of the molecules (fig. 1), prior to the deposition of the cathode. This creates a challenge in view of their application in optoelectronic devices: the control of the orientation of columnar liquid crystals in open films. Indeed, a well-aligned material in homeotropic orientation would largely improve the conductivity. In this paper, a study of the alignment of open supported sub-micron thick films of a hexagonal columnar mesophase is reported, and the conditions of the control between homeotropic and planar orientations are determined and explained in terms of the involved surface tensions.

Materials and methods. – Two discotic materials have been used to investigate the behavior of columnar liquid crystals in thin open films: ethylhexyl pyrene tetracarboxylate [5], and ethylhexyl triphenylene tetracarboxylate [6] (fig. 2). Their two principal features are the existence of a disordered hexagonal columnar mesophase from the isotropic liquid phase (Iso) down to ambient temperature [7] and a low isotropization temperature. Indeed, the pyrene and triphenylene derivatives have $T_{\mathrm{colLC\text{-}Iso}} = 92\,^{\circ}\mathrm{C}$ and $T_{\mathrm{colLC\text{-}Iso}} = 125\,^{\circ}\mathrm{C}$, respectively, allowing thermal processing at convenient temperatures.

Thin columnar LC films have been prepared by vacuum deposition or by spin-coating from an organic solvent (chloroform). The organic layers are deposited on a silicon wafer (with its oxide) or on a piece of glass which have been previously cleaned with sulfochromic acid. The layer thickness varies from 50 nm up to 1000 nm. Optical experiments have been performed in a heating stage by polarizing and differential interference contrast microscopy. By heating up to the temperature of the isotropic liquid phase, a uniform isotropic layer is obtained, which is stable for film thicknesses higher than $\sim$ 100 nm. Dewetting occurs with thinner films in the isotropic liquid phase. After complete isotropization, the temperature is lowered and the mesophase is allowed to form. The formation of the mesophase is observed by optical

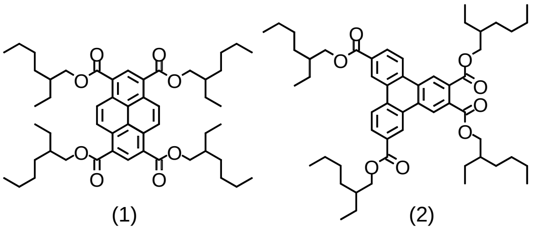

Fig. 2 – Molecular structures of the two discotic molecules studied in this paper: (1) pyrene-1,3,6,8-tetracarboxylic tetra(2-ethylhexyl)ester and (2) triphenylene-2,3,6,10-tetracarboxylic tetra(2-ethylhexyl)ester. The main feature of these two compounds is a hexagonal columnar liquid crystalline phase at ambient temperature.

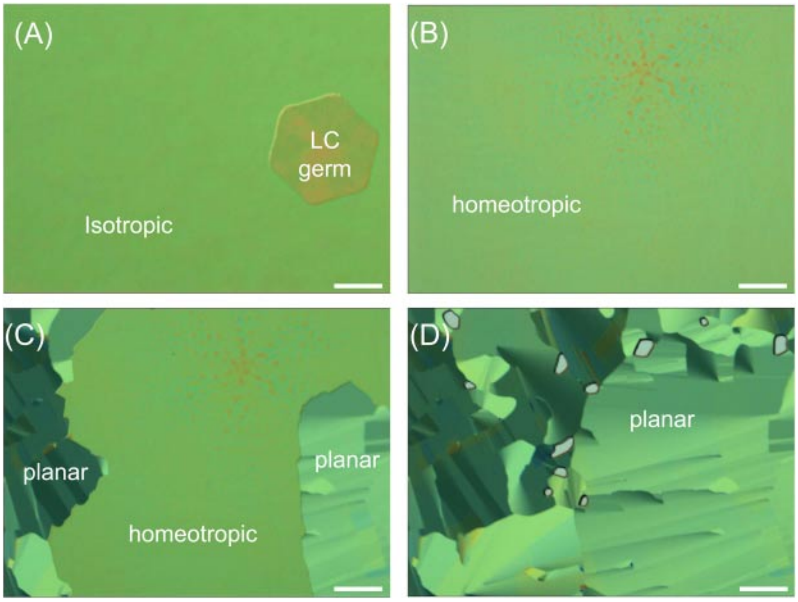

Fig. 3 – Nucleation and growth ((A) and (B)) of a hexagonal liquid crystal germ and evolution of the columnar discotic film during thermal annealing slightly below $T_{\text{colLC-Iso}}$ ((C) and (D)), observed by differential interference contrast microscopy. The film thickness is about 400 nm. The scale bar indicates 50 μm.

microscopy. Edge-on orientation of the molecules is easily established by the induced birefringence seen between crossed polarizers. Inversely, the lack of birefringence is characteristic of homeotropic anchoring, where the column orientation, corresponding to the optical axis of the liquid crystal, coincides with the direction of light propagation perpendicular to the substrate. In this latter case where there is no optical anisotropy detectable by polarizing microscopy, differential interference contrast (DIC) is suitable to visualize the growth of the mesophase, especially to enhance the boundaries of the LC domains. The initial thicknesses of the films are measured by ellipsometry, and are corroborated by their Newton interference color [8].

Experimental results. – A competition between planar and homeotropic alignments of the columnar mesophase is observed when the sample is cooled down to room temperature. At a given cooling rate (typically between 1 and 10 °C/min), the homeotropic anchoring is favored in relatively thick films ($\gtrsim$ 300 or 400 nm for the faster cooling rates). At same cooling rate, the planar orientation of the liquid crystal appears for thinner films.

Figures 3 and 4 summarize the growth and the evolution of an open supported columnar liquid crystal film observed during thermal annealing. During the cooling-down from the liquid isotropic phase, a LC germ nucleates in which the discotic molecules initially arrange face-on towards the substrate, leading to a homeotropic domain of hexagonal symmetry (figs. 3A and 4a). In these experimental conditions, the growth of the colLC is dentritic, as illustrated in fig. 4a. The result of thermal quenching is a liquid crystalline film in homeotropic anchoring (fig. 3B). Note that the trace of the initial colLC germ can still be observed by the presence of small orange (see the on-line version) zones, corresponding to inter-dendritic regions of slightly lower thickness. The structure of such an aligned layer is maintained down to ambient temperature. This room temperature stability of uniformly aligned homeotropic films opens

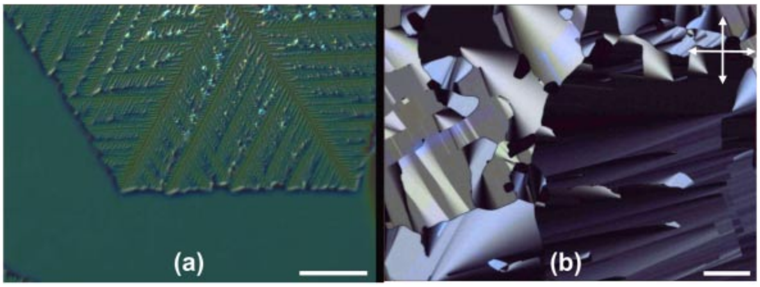

Fig. 4 – (a) Dendritic growth of a columnar LC germ observed by DIC. The appearance of some bright spots indicates the beginning of the transition to planar orientation. The film thickness is about 300 nm. (b) Same sample as shown in fig. 3D, observed by polarizing optical microscopy. The typical fan-shaped texture is the signature of planar orientation. The scale bar represents 50 μm.

the way to their incorporation into devices such as solar cells, that have to be fabricated by sequential deposition of open layers [4].

However, if a thermal annealing process is performed at elevated temperature inside the colLC temperature range, the homeotropic orientation switches to a planar alignment after a few hours (fig. 3C). This anchoring transition takes place more quickly if the annealing temperature is close to the isotropization temperature ($T \sim T_{\text{colLC-Iso}} - 10\,^\circ\text{C}$) because the colLC viscosity is then weak. The planar alignment finally covers all the sample surface, as depicted in fig. 3D. In the case of thinner films, the transient homeotropic state can be sometimes difficult to detect because the discotic LC switches almost instantly to the edge-on orientation, as shown in fig. 4a.

Anchoring transitions of colLC between two solid interfaces (*i.e.* inside cells) have already been reported [9, 10], and an empirical film thickness dependence has also been mentioned for thin open colLC layers [11, 12], where homeotropic orientation is seen in thick films whereas a planar anchoring is observed at lower thickness, but no phenomenological explanation has been provided. To account for the competition between homeotropic and planar anchorings, a model based on the different surface tensions existing in thin open colLC film is proposed in the following.

Discussion: surface tensions of columnar liquid crystals. – Only few data of colLC surface tensions have been reported in the literature due to the difficulties in determining all the anisotropic components. Part of such measurements has been performed for discotic compounds (hexaalkoxy-triphenylenes) which are structurally close to the materials studied here (fig. 2). The key feature is that the air-LC interface strongly prevails over the two other interfaces (solid-LC and isotropic liquid phase - LC) and this can be summarized by

$$\gamma_{\text{LC-air}} \gg \gamma_{\text{LC-solid}} > \gamma_{\text{LC-Iso}} \tag{1}$$

with $\gamma^{\parallel}_{\text{LC-air}} \approx 7 \cdot 10^{-2}\,\text{J/m}^2$ [13], $\gamma^{\parallel}_{\text{LC-Iso}} \approx 5 \cdot 10^{-4}\,\text{J/m}^2$ [14]. The molecular similarity between the columnar liquid crystal and its own isotropic liquid phase leads to the low surface tension $\gamma_{\text{LC-Iso}}$. It has been experimentally shown that the ends of columns are energetically favored at the isotropic-liquid interface [15], with $\gamma^{\parallel}_{\text{LC-Iso}} - \gamma^{\perp}_{\text{LC-Iso}} \approx 10^{-4}\,\text{J/m}^2$. Contrary to solid substrates like glass or silicon, it is highly unfavorable to expose to air (or vacuum) the polarizable π electron system of the discotic molecules [10, 16]. Only one estimation of anchoring energy at the solid interface has been reported: $\gamma^{\parallel}_{\text{LC-solid}} - \gamma^{\perp}_{\text{LC-solid}} \approx 10^{-5}\,\text{J/m}^2$ [17].

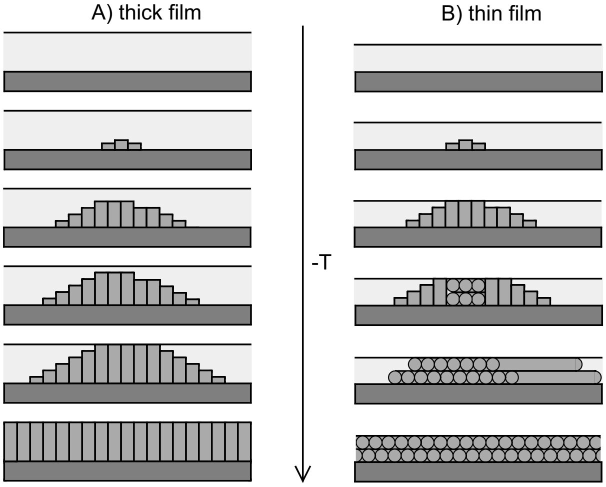

Fig. 5 – Scenario illustrating the lower stability of the homeotropic alignment in a thin film: at a *given cooling rate*, the nucleation of the columnar mesophase (depicted in medium gray) from its isotropic liquid phase (shown in light gray) first occurs on the solid substrate (drawn in dark), leading to a face-on arrangement of the molecules. If the homeotropic domains quickly grow up to the liquid crystal air interface in the case of a thin film (B), a transition to the planar anchoring takes place more easily than at lower temperature where a thicker film (A) can be maintained in a metastable homeotropic state by its high viscosity.

Consequently, the following relations can be written by taking into account the anisotropic parts of the surface tensions (fig. 1):

$$\gamma^{\parallel}_{\text{LC-Iso}} > \gamma^{\perp}_{\text{LC-Iso}} \tag{2}$$

$$\gamma^{\perp}_{\text{LC-air}} > \gamma^{\parallel}_{\text{LC-air}} \tag{3}$$

$$\gamma^{\parallel}_{\text{LC-solid}} > \gamma^{\perp}_{\text{LC-solid}}\ . \tag{4}$$

A model can then be developed from these surface tension considerations. The nucleation of the discotic mesophase first occurs on the solid substrate, leading to a face-on arrangement of the molecules (eq. (4))(fig. 3A). The studied compounds (fig. 2) exhibit similar morphological behavior: in both cases, the colLC crystallites adopt a face-on configuration with respect to the solid substrate. The presence of polar ester groups in the molecules certainly increases their affinity towards polar surfaces like glass or silicon oxide. The preferential nucleation of LC germs on the solid interface is probably reinforced by the rugosity of the substrate (which is higher than at the air-LC interface) and by temperature gradients in the heating stage [18]. The very large aspect ratio (diameter over thickness) of the hexagonal LC germs, where the homeotropic area in contact with the liquid isotropic phase is dominant, promotes also the minimization of the surface energy (eq. (2))(fig. 3A) [19]. At a given cooling rate, and therefore at a fixed growth velocity, the LC domains reach more rapidly, *i.e.* at *higher temperature*, the air interface for a *thin* film: consequently, the anchoring transition takes place, leading to a planar alignment (eqs. (1) and (3)). However, in the case of a *thick* film, homeotropic domains attain the free air interface in contact with air at a *lower temperature* where the colLC viscosity is high enough to inhibit the anchoring transition. The homeotropic orientation can thus be maintained in a metastable state (fig. 3B). To experimentally confirm this scenario where the disjoining pressure and defects have been neglected, a thermal annealing (figs. 3C and D) of a homeotropically aligned film has been performed at a temperature close to $T_{\text{colLC-Iso}}$: the system becomes more fluid and consequently it adopts with time the planar orientation corresponding to the configuration of minimal energy (fig. 5).

Thus, the homeotropic or face-on orientation is kinetically favored, whereas the planar alignment is thermodynamically stable. This yields the following relation between the anisotropic parts of surface tensions:

$$\gamma^{\perp}_{\text{LC-air}} - \gamma^{\parallel}_{\text{LC-air}} > \gamma^{\parallel}_{\text{LC-solid}} - \gamma^{\perp}_{\text{LC-solid}} \,. \tag{5}$$

The planar orientation has been experimentally confirmed by grazing-incidence X-ray scattering [20] and by the existence of the typical fan-shaped texture of developable domains, observed by polarizing optical microscopy (fig. 4b). This texture is the consequence of elastic deformations of columns *in the plane* of the film, that bend without any distortion of the hexagonal lattice [21, 22].

A coexistence of antagonist anchorings is known from nematic or smectic open supported films: LC mesogens adopt opposite orientations at the solid and air interfaces, exhibiting a hybrid alignment [23–25]. This hybrid alignment only exists if the elastic energy associated with the LC deformation between the two surfaces is smaller than the smallest involved anchoring energy, otherwise the interface with the higher anchoring energy fixes the orientation throughout the whole of the film.

In the case of discotic liquid crystal films, the interface with the solid substrate has the lower anchoring energy (eq. (5)) and no such hybrid alignment has been observed, meaning that the colLC elasticity prevails over the surface tension. Therefore, by comparing the highest film thickness considered in this study ($e = 1\,\mu\text{m}$) with the anchoring extrapolation length $L = K/\Delta\gamma_{\text{LC-solid}}$, this yields

$$\gamma^{\parallel}_{\text{LC-solid}} - \gamma^{\perp}_{\text{LC-solid}} < K/e \sim 10^{-4}\,\text{N/m} \tag{6}$$

with $K \approx 7 \cdot 10^{-11}\,\text{N}$ the elastic constant of column bend curvature [15].

Having a planar alignment of the colLC film after the anchoring transition is not favorable at the solid-LC interface (eq. (4)). This induces dewetting to minimize the free energy by decreasing the contact area between the edge-on aligned LC and the solid substrate. Small dewetted zones can for instance be seen in fig. 3D. Investigations of the dewetting occurring during the growth or during the anchoring transition of colLC domains are currently in progress.

Conclusion. – In this study, highly ordered homeotropically aligned thin films have been successfully obtained using liquid crystalline discotic materials by controlling the kinetics of growth. Indeed, a columnar liquid crystal layer can be kinetically stabilized in a homeotropic state, even though we show that the planar alignment is thermodynamically stable. This result is of first importance for optoelectronic devices based on columnar mesophases in order to benefit from their good charge mobility.

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[8] The refractive index has been measured with an Abbe refractometer in the isotropic liquid phase close to $T_{\text{colLC-Iso}}$ and its value is: $n_{\text{Iso}} = 1.5390 \pm 0.0005$ for the pyrene derivative and $n_{\text{Iso}} = 1.5145 \pm 0.0005$ for the triphenylene derivative. For a vizualisation of Newton's colors, see: `http://home3.netcarrier.com/~chan/EM/PROGRAMS/THINFILM/`.

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