

**Experiment title:**

Homeotropic Alignment of Columnar Liquid Crystals in Open Films via Surface Nano-Patterning

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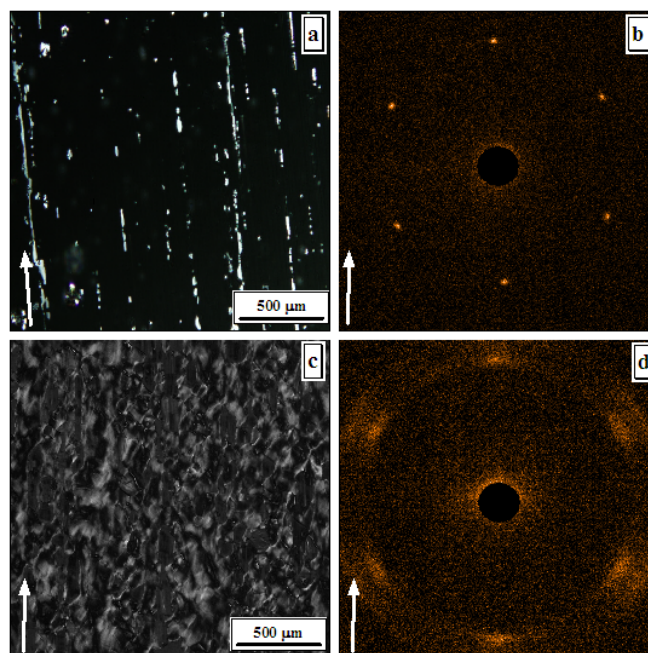
**Shifts:**

3

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Among various organic semiconductors, liquid crystals (LC) forming 2D columnar structures<sup>1-3</sup> are promising materials for electronic applications such as light emitting diodes<sup>4</sup> (LED), photovoltaic<sup>5</sup> (PV) cells or field effect transistors (FET)<sup>6</sup>. However, different device applications require specific orientation of the mesophase columns. For instance, in LED's and PV cells the columns should be orthogonal or homeotropically aligned between the two electrodes.

Since these devices are generally made by deposition of the organic active layer on one of the electrodes followed by deposition of the second electrode, it is necessary to obtain homeotropic orientation in open films (i.e. with one interface of the film being in contact with the air). Although it is quite usual to have homeotropic alignment of LC's squeezed between two substrates, the general strategy for achieving such an alignment in open films is missing yet, and studies of LC alignment in this geometry are very scarce to date<sup>7-9</sup>. Here we report on the possibility of using nano-patterned surfaces obtained via friction transfer of poly(tetrafluoroethylene) (PTFE) to homeotropically align columnar LC's in open films of variable thickness. The robustness of this method is demonstrated using two LC's with very different molecular architectures: a discotic molecule (phthalocyanine derivative<sup>10</sup>) denoted hereafter as **1a** and a star-shaped mesogen with a semiflexible core<sup>11</sup> (**1b**). The PTFE rubbing was carried out according to the published procedure<sup>12</sup>. LC films were prepared by solution casting followed by slow evaporation of the solvent. The columnar alignment in the films was examined as a function of temperature (i.e., during thermal cycling between the



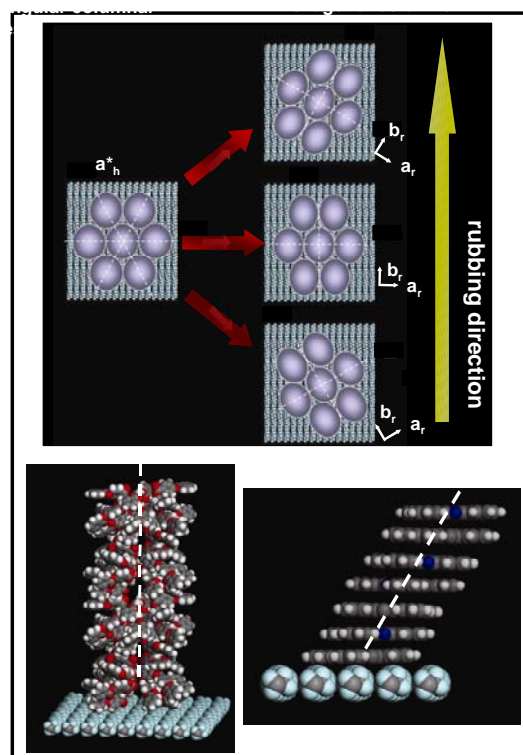
**Fig.1** Polarized optical micrographs of approx. 10 μm thick fresh (a) and annelaed (b) films at RT of molecule **1b** deposited PTFE surface. Black regions correspond to the homeotropically aligned material, while the white lines are indicative of defects in the film. (c) and (d) are the corresponding X-ray diffraction patterns. The rubbing direction is indicated by the arrows.

room temperature mesophase and the isotropic phase) by polarized optical microscopy and synchrotron X-ray diffraction in transmission geometry. The thermotropic behavior was preliminarily studied by differential scanning calorimetry and X-ray diffraction. During heating, molecule **1a** exhibits a transition from a columnar rectangular ( $\text{Col}_r$ ) to a columnar hexagonal mesophase ( $\text{Col}_h$ ) at  $49^\circ\text{C}$  followed by the isotropisation at  $166^\circ\text{C}$ <sup>10</sup>. X-ray diffraction measurements on oriented samples of **1a** showed that, in the  $\text{Col}_r$  phase, the molecules adopt an angle of about  $18^\circ$  between the normal to the molecular core and the columnar axis. Importantly, in the  $\text{Col}_h$  phase the molecules are not tilted. Molecule **1b** exhibits a more complex phase diagram<sup>11,13</sup> as compared to that of **1a**. The sample prepared by cooling from the isotropic phase firstly forms a hexagonal disordered columnar mesophase ( $\text{Col}_{hd}$ ). This phase is metastable, or monotropic, and converts into a stable crystalline columnar phase (Cr) after several hours annealing at room temperature<sup>13</sup>. The constitutive element of the column for the **1a** derivative is a single molecule. Based on density data and simulations of fiber diffractograms a cluster built up of six molecules in an E-shaped conformation seems to be the constitutive element of the columns for the molecule

**1b**. It should be noted that when deposited on flat surfaces such as Si wafers or carbon coated substrates, the columns tend to lie with their axes in the plane of the substrate.

The orientation of the columns changes when deposited on PTFE ribbed surfaces. When viewed between at  $100^\circ\text{C}$ , i.e. in the  $\text{Col}_h$  phase, the film of **1b** appears black (cf. Fig. 1a), which indicates that the columns are oriented parallel to the optical axis of the microscope, or perpendicular to the substrate. Some defects in the PTFE film deposition appear as bright spots. X-ray diffraction measurements performed on such films show six-spot patterns (Fig.1b) corresponding to hexagonal packing of vertically standing columns. It can be seen that the PTFE chain direction coincides with the direction of the reciprocal vector  $\mathbf{a}^*$  of the mesophase lattice. The point-like appearance of reflections indicates that not only the columns are homeotropically oriented but also they are characterized by a single-crystal-like arrangement. The span of the LC mono-domain was examined by laterally scanning the sample stage with stepper motors while simultaneously performing X-ray diffraction. No variation of the LC lattice orientation or of the quality of the columnar alignment could be observed over the entire sample size (10-20 mm). The results presented in Fig. 1 were obtained on films of several microns thickness, which are perfectly suited for synchrotron X-ray diffraction measurements in transmission. Similar results were also obtained with POM on much thinner films. Similar observations have been made also for molecule **1a**. We discovered that the type of the columnar phase is crucial for achieving the homeotropic orientation on PTFE-rubbed substrates. Thus, during thermal cycling, the homeotropic columnar alignment was recovered

each time the sample was in the  $\text{Col}_h$  phase. By contrast, a change in the mesophase structure immediately affected the LC alignment. Thus cooling the **1a** sample to ambient temperature into the  $\text{Col}_r$  phase results in the appearance of a birefringent texture in the POM images. The same holds for the films of **1b** after several hours of annealing at room temperature when the transition to the Cr phase is at a sufficiently advanced stage (Fig. 1c). In both cases, the ideal six spot patterns observed in the  $\text{Col}_h$  phase undergo substantial change (Fig. 1d). The pattern of sample **1b** after transformation to  $\text{Col}_r$  phase shows six broad doubled peaks as in can be seen in Fig. 1d. One can suggest that the single mono-domain initially present in the homeotropically-aligned hexagonal phase splits into small domains with different orientations of the rectangular unit cell as shown in Fig. 2. The organization of the molecules in respect to the PTFE layers is shown in the bottom left panel of Fig. 2. Upon transformation to the Cr phase, the hexagonal lattice slightly shrinks in one direction



**Fig.2** Model showing (top panel) the change in the lattice orientation during phase transition from hexagonal to rectangular unit cell. The lattice can shrink along the main three directions with the same probability, which explains the appearance of additional peaks in the X-ray pattern. Representation of the columnar organization with respect to the PTFE layer for molecule **1b** in the Cr phase (left, bottom) and molecule **1a** in the  $\text{Col}_r$  phase (right, bottom).

and dilates in the other. Since it is improbable that the film changes its lateral size, all the three orientations of the rectangular lattice should be equally probable, which explains the  $C_6$  symmetry of the pattern. Similar, when passing into the rectangular phase, the molecules **1a** adopt a small tilt about one of the lattice axes, according to the  $C_{2mm}$  unit cell symmetry<sup>10</sup>. If one suggests that the cores of the molecules stay parallel to the substrate, this tilt will make the columns incline with respect to the substrate normal (Fig.2, low panel, right). Then the reflection conditions cannot be respected simultaneously for all the equatorial reflections, and the fact that the reflections are still visible can only be due to their angular spread, which allows for a part of the intensity distributed in reciprocal space to be intersected by the detector plane. This also explains the unequal apparent intensity of different reflections. By scanning the sample, it was possible to see differently oriented domains having different axes of columnar inclination. The almost instantaneous reorganization of columns upon transition to  $Col_h$  phase can be accounted for by the low viscosity of the mesophase at the temperatures of the experiment. However, understanding the reasons for the homeotropic alignment has not been achieved yet. It may be related to the necessity of the lateral alkyl chains to minimize their contact with the PTFE substrate, which could be more difficult for the case of the in-plane columnar orientation.

In conclusion, it is shown that homeotropic columnar alignment in open LC films can be obtained via nano-patterning of the substrate for discotic and semi-flexible mesogens. The main requirement for producing macroscopic homeotropically-aligned LC mono-domains is that the sample is in the hexagonal columnar mesophase. These findings can open new perspectives for the use of columnar liquid crystals for solar cell applications.

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