	Experiment title: STRUCTURAL STUDY BY X-RAY SURFACE SCATTERING OF COLUMNAR LIQUID CRYSTAL THIN FILMS FOR ORGANIC ELECTRONIC DEVICES	**Experiment number:** SC-1695
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Report:

STRUCTURAL STUDY BY X-RAY SURFACE SCATTERING OF THIN OPEN SUPPORTED COLUMNAR LIQUID CRYSTAL FILMS

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 (Fig. 1).

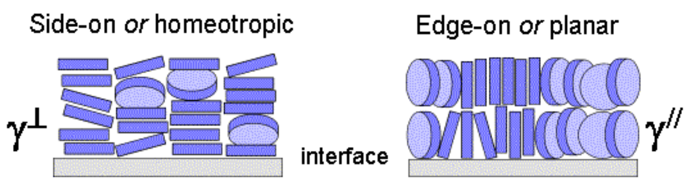
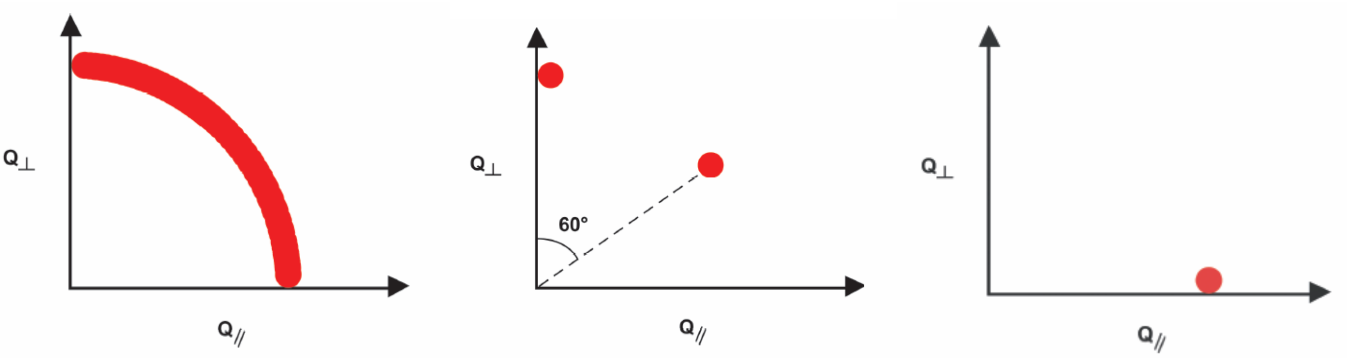


Fig. 1: Schematic representation of the different orientations of a columnar liquid crystal made of discotic molecules.

Usually, discotic materials are used in optoelectronic devices without any treatment after their preparation (by vacuum deposition or spin coating) in thin films. Therefore, we have investigated by Grazing Incidence X-ray Diffraction (GIXD) the alignment of such native thin films as a function of different parameters (film thickness, nature of the solid substrates, crystalline or liquid crystalline phases,…). Additionally, the effect of thermal annealing on the control of film orientation has been studied.

Experimental setup: The ESRF-BM02 beam line has been used in the goniometer configuration, with the CCD camera as a 2D-detector which was at a distance of about 550mm of the sample. The X-ray beam had an energy of 9 keV (corresponding to a wavelength of λ=1.38Å), and its size was 40µm × 1mm (V × H). The main studied discotic materials exhibit their columnar liquid crystal mesophase at room temperature [4], with a typical intercolumnar Bragg peak of about q_{100}=0.35Å^{-1}.

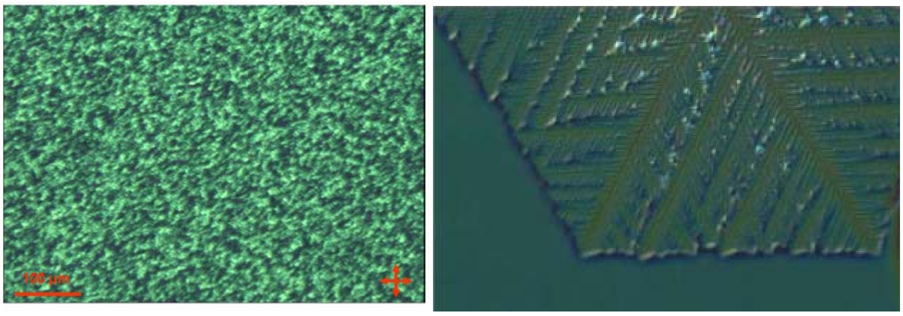
Results and discussion: The different schematic x-ray scattering patterns depending on the columnar orientation with respect to the solid substrate are shown in Fig. 2.



(a) (b) (c)

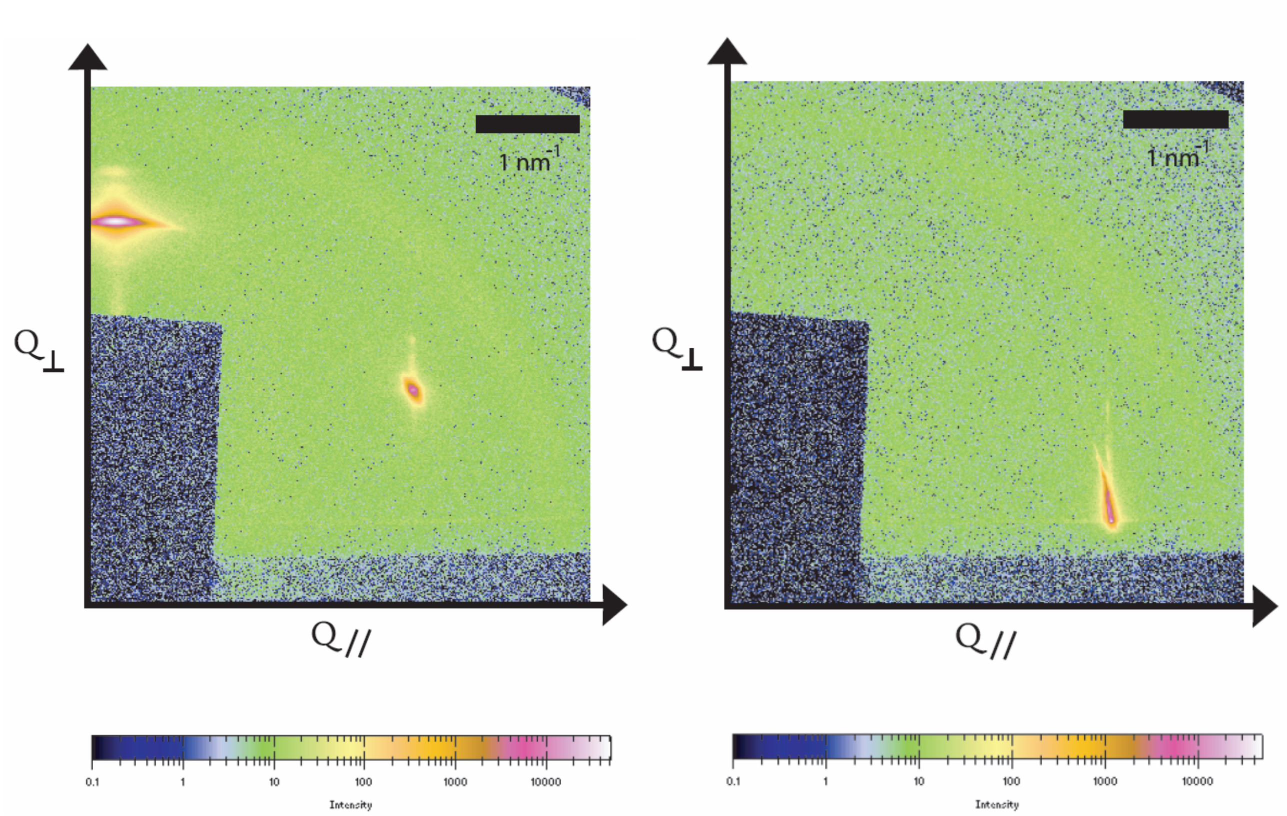
Fig. 2: Expected X-ray scattering patterns of the first order intercolumnar Bragg peak q_{100} (restricted to the positive scattering wave vectors) in plane and perpendicular to the plane of the colLC film in the case of a: (a) 3D powder, (b): 2D powder in planar orientation (c) hometropic orientation of the columns with respect to the substrate.

The optical texture of native colLC films observed just after their preparation by spin-coating or vacuum deposition is presented in Fig. 3-a: they both look like a 3D powder (orientational average of small colLC domains in the three dimensional space). However, the result of grazing incidence x-ray scattering of such colLC films shown Fig. 4-a is surprising: the colLC layer exhibits a well defined orientation which is a *planar alignment* of the columns (See Fig. 2). This planar alignment is degenerated (i.e. not uniaxial) in the plane of the sample, corresponding to a *planar 2D powder*. Many experimental parameters have been varied and a 3D powder has in no case been detected. Indeed, the 2D planar orientation of native films has been found to be a very robust anchoring and this result has been shown to be independent of: the film preparation process (vacuum deposition or spin coating), the film thickness (from a few nm up to 1µm), the nature of the phase (crystal or liquid crystal), the solid substrate and (silicon oxide or graphite). The planar anchoring of thin open supported columnar liquid crystal films can be explained by looking at the different interfaces involved in this system.



(a) (b)

Fig. 3: Optical texture of thin colLC films observed by polarizing (a) and differential interference contrast (b) microscopy respectively. The image (a) corresponds to a typical birefringent texture observed after vacuum deposition or spin coating. The picture (b) shows a dendritic growth in homeotropic orientation of a colLC germ during thermal annealing.



(a) (b)

Fig. 4: Experimental X-ray scattering patterns of the intercolumnar Bragg peak q_{100} of a colLC thin film, (a) which exhibits a planar orientation, whatever its preparation process (spin coating or vacuum deposition) (b) showing a homeotropic alignment after some specific thermal annealing.

Indeed, the key feature is that the air-liquid crystal (LC) interface strongly prevails over the two other interfaces (solid to LC and isotropic liquid phase to LC), and that it is highly unfavorable to expose to air the polarizable π electron system of a discotic molecule [5]. However, this native planar orientation can be overcome by applying a thermal annealing, by which it is possible to kinetically stabilize the homeotropic alignment of colLC thin films [5], as shown in Fig. 3-b and Fig. 4-b.

Conclusion: The grazing incidence x-ray scattering experiment has shown that a strong planar orientation is found for thin open supported colLC films, and this result is independent of the main experimental parameters as the film preparation process, film thickness, and nature of the phase and of the solid substrate.
Thus, the planar alignment of native colLC thin films corresponds to the worst orientation for carrying charges and excitons in solar cells. Therefore, the control of the orientation of colLC thin films, such as thermal annealing, is absolutely necessary in order to benefit from the high uniaxial charge and exciton mobilities, and then to increase the efficiency of organic solar cells based on discotic materials.

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