PHYSICAL REVIEW E **78**, 041707 (2008)

Anisotropic light absorption, refractive indices, and orientational order parameter of unidirectionally aligned columnar liquid crystal films

Emilie Charlet and Eric Grelet*
Centre de Recherche Paul Pascal, CNRS-Université Bordeaux 1, 115 avenue Schweitzer, 33600 Pessac, France

(Received 4 June 2008; published 21 October 2008)

The anisotropic optical properties of thermotropic columnar liquid crystals absorbing in the visible range are investigated for different discotic compounds unidirectionally oriented in open supported thin films. Two methods to monitor the alignment of columnar mesophases in thin films are reported, making possible to achieve either homeotropic anchoring (columns normal to the substrate) by a specific thermal annealing, or unidirectional planar orientation (columns parallel to the substrate) by using a rubbed Teflon coating. The columnar liquid crystal anchoring is found to depend on the nature of the compound, either parallel or perpendicular to the Teflon orientation. Based on this control of the mesophase alignment, the dichroic ratio and the orientational order parameter of oriented samples are measured, and a high order parameter of 0.9 is found in the case of parallel alignment. From the polarized absorption data of the columnar liquid crystal films, the light wavelength dependence of the birefringence and of the real and imaginary parts (refractive index and extinction coefficient, respectively) of the anisotropic optical indices are determined over the whole visible range.

DOI: 10.1103/PhysRevE.78.041707　　PACS number(s): 42.70.Df, 61.30.Hn

I. INTRODUCTION

Columnar liquid crystals (CLCs) have attracted considerable interest for their outstanding optical and electronic properties. These mesogens, consisting of an aromatic core substituted with flexible side chains, self-organize into columns which in turn form a two-dimensional lattice [1]. These materials exhibit high charge mobilities and large exciton diffusion lengths [2] along the column direction [3]. Such properties stem from the overlapping of π orbitals of adjacent molecules inside a column, providing a one-dimensional pathway for charge migration. Thus, CLCs can be used as active layers in optoelectronic devices if the columnar stacks are properly aligned between electrodes. While unidirectional planar anchoring, where columns are parallel to the substrate (Fig. 1), is needed for organic field effect transistors [4,5], homeotropic orientation, for which columns are normal to the interfaces (Fig. 1), is required for photovoltaic cells [6,7] and organic light-emitting diodes [8].

However, despite the growing interest in CLCs, a detailed characterization of their optical properties remains challenging and experimental values are scarce to date [1,9]. Progress in this field has been hindered by difficulties in *unidirectional alignment* of columnar liquid crystals in thin layers over large areas. While a competition between homeotropic and planar orientations has recently been shown in the geometry of open supported thin films [10], unidirectional planar alignment of columnar mesophases corresponding to a given direction of the CLC optical axis in the observation plane is hard to achieve. Indeed, in the absence of specific surface treatment, columnar liquid crystals preferentially adopt a *degenerate* planar orientation, characterized in polarizing microscopy by developable domains [11], which are known to be a distinctive texture of columnar mesophases. In this case, the rotation of the optical axis, associated with the column curvature, does not allow the determination of the optical properties. Among the different methods developed for CLC orientation [12–18], one of the most efficient alignment procedures to obtain unidirectional planar anchoring involves the use of a friction transferred Teflon orientation layer [19–23]. Taking advantage of the control of the CLC alignment in the geometry of open supported thin films, we report a complete optical study of two discotic compounds, which exhibit a hexagonal columnar liquid-crystalline phase at room temperature. From their polarized absorption spectra, we have determined the anisotropic complex optical indices as a function of the light wavelength λ, denoted the extraordinary $\tilde{n}_e(\lambda)=n_e+ik_e$ and ordinary $\tilde{n}_o(\lambda)=n_o+ik_o$ complex indices, respectively [24]. The real parts define the refractive indices of the material and the imaginary parts the extinction coefficients. The sign and the light wavelength dependence over the whole visible range of the birefringence, defined as $\Delta n(\lambda)=n_e-n_o$, have been independently obtained. Finally, the orientational order parameter deduced from the dichroic ratio is evaluated, and the CLC anchoring onto the Teflon layer is discussed.

II. EXPERIMENTAL SECTION

A. Materials

Two different CLCs have been studied (Fig. 2), namely, pyrene-1,3,6,8-tetracarboxylic tetra(2-ethylhexyl)ester (Py)

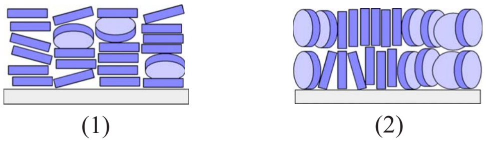


FIG. 1. (Color online) Schematic representation of the homeotropic (1) and unidirectional planar (2) alignments of a uniaxial columnar liquid crystal. The CLC optical axis is defined along the column direction.

---

*Corresponding author. grelet@crpp-bordeaux.cnrs.fr

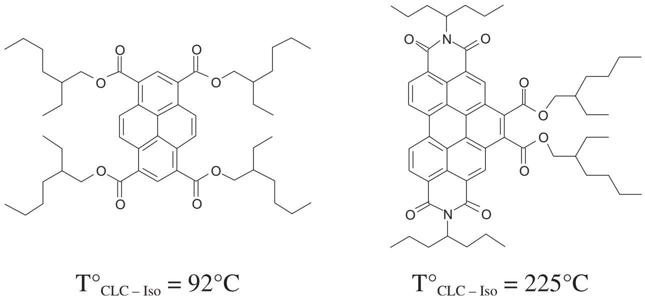


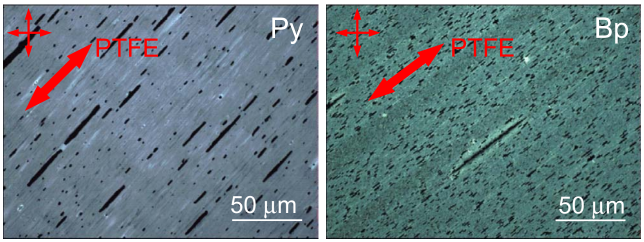
FIG. 2. Molecular structure of the two studied discotic compounds: the pyrene (Py) and benzoperylene (Bp) derivatives. These two materials exhibit a hexagonal columnar liquid crystalline phase from the isotropic liquid phase (Iso) at $T_{\text{CLC-Iso}}$ down to ambient temperature.

[25] and benzo[*g*,*h*,*i*]perylene-1,2,4,5,10,11-hexacarboxylic 1,2-di-(2-ethylhexyl)ester 4:5,10:11-di-(4-heptyl)imide (Bp) [26]. These molecules are composed of an aromatic core surrounded by aliphatic chains, and absorb light in the visible part of the spectrum (blue and green absorption, respectively). Both compounds exhibit a hexagonal columnar mesophase from the isotropic liquid phase down to ambient temperature [27].

B. Preparation of oriented samples

In order to obtain a unidirectionally planar aligned film, a Teflon [poly(tetra)fluoroethylene or PTFE] coating is deposited on a glass substrate by the method described in Ref. [28]. The glass slides are previously cleaned with three successive ultrasound baths of distilled water, acetone, and ethanol. They are then dipped in sulfochromic acid before being rinsed with distilled water, and dried with nitrogen. A cylindrical bar of Teflon, heated up to 270 °C, is slid with a controlled force of about 30 N on the cleaned glass plates at a constant speed of 0.5 mm/s. The PTFE obtained coating is a thin layer ($\leqslant$50 nm thick) made of stripes of different widths and heights, parallel to the rubbing direction. The birefringence of the Teflon layer is too weak to be detected by polarizing microscopy. A solution of columnar liquid crystal, of 2 wt % in chloroform, is spin-coated at 2000 rpm during 30 s on the Teflon-covered substrates. The resulting CLC thin film exhibits a significant degree of orientation characterized by a uniform birefringence between crossed polarizers (Fig. 3).

Homeotropically oriented open supported thin films of columnar mesophase are obtained by applying the procedure described in Refs. [7,10]. A liquid crystal solution of 3 wt % is spin-coated on cleaned substrates (see above) without any additional coating. A heating stage is then used for thermal annealing of the discotic compound in the isotropic liquid phase, followed by a cooling (10 °C/min) down to room temperature. This thermal process induces a homeotropic orientation of the columnar mesophase, which is thermodynamically metastable in the geometry of open film, but which can be preserved during a few days at room temperature [10].



(a) (b)

FIG. 3. (Color online) Optical textures observed after thermal annealing by polarizing microscopy of pyrene (a) and benzoperylene (b) CLC films, respectively. The Teflon stripes (indicated by a double arrow) form an angle of about 45° with respect to the direction of the crossed polarizers. The black regions correspond to CLC dewetted zones.

C. Techniques

The thickness *d* of the different films is measured by using an atomic force microscope (AFM, Digital Instruments, Nanoscope Dimension 3000) in tapping mode acting as a mechanical profilometer. A zone free of CLC is made on the sample surface with a razor edge to create a step with the film. In the case of CLC films with homeotropic anchoring, the film thickness, corresponding to the step height, is 257 ± 10 nm and 217 ± 10 nm for the pyrene and the benzoperylene derivatives, respectively. In the case of unidirectionally planar aligned films, the thickness is 176 ± 10 nm and 162 ± 10 nm for the Py and Bp compounds, respectively.

A heating stage (Linkam, THM600) and a camera (JAI, CV-M7) are combined with a polarizing microscope (Olympus, BX51) to perform thermal annealing while visualizing the CLC alignment. In order to measure the absolute value of the birefringence, a Berek compensator, which quantitatively determines the optical retardation [29], is used with three different monochromatic interference filters of 490, 550, and 602 nm transmitted wavelength.

The sign of the birefringence is determined by the interference figures obtained by conoscopy [30]. This method consists of the observation of an anisotropic material viewed in the focal plane of the microscope objective lens under convergent polarized light. The interference figures are modified by inserting a full wave retardation plate (λ-plate) in the optical path, and different colors appear revealing the sign of the birefringence [30]. For this specific measurement, the CLC material is studied between cover slip and slide in order to conveniently obtain a homeotropically aligned sample free of dewetting. For this sample thickness of about a few micrometers, the phase retardation is large enough to be observed by conoscopy.

Nulling ellipsometry (Nanofilm Technologies GmbH, EP-MW) is carried out for the evaluation of the mean refractive index n_{mean} of an open supported thin film without any surface treatment or thermal process. After spin coating, it has been shown that open CLC film exhibit a degenerate planar orientation [31] with a typical domain size of a few micrometers. The mean refractive index of this *two-dimensional* powder can then be defined as an average over all the orientations in the sample plan: $n_{\text{mean}}(\lambda) = (n_e + n_o)/2$.

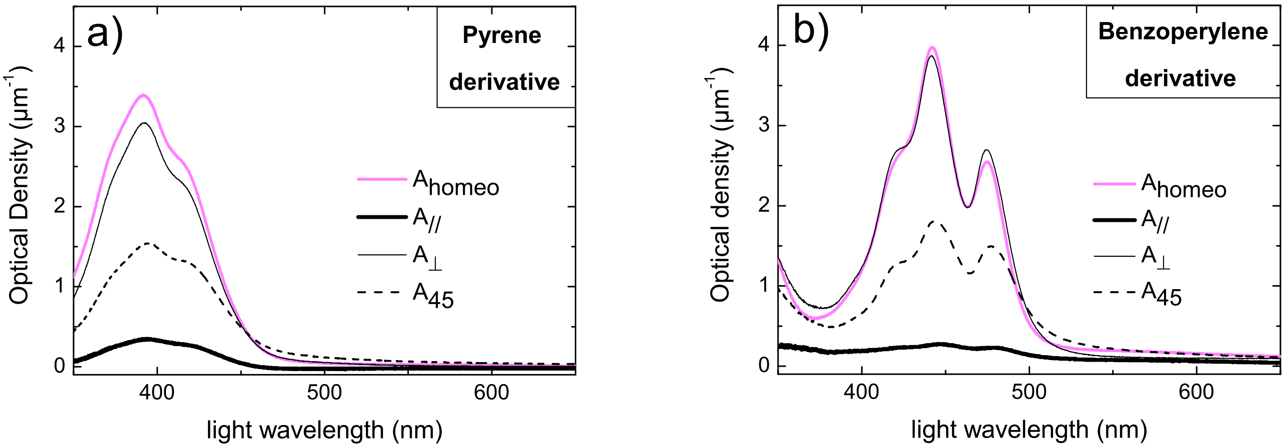


FIG. 4. (Color online) Polarized absorption spectra of pyrene (a) and benzoperylene (b) CLC films in homeotropic (pink lines) and unidirectional planar (black lines) orientations. For the planar alignment, the spectra are measured after thermal annealing, with the incident light polarization parallel ($A_{\parallel}$), perpendicular ($A_{\perp}$), and at 45° (A_{45}) with respect to the optical axis of the sample. Each absorbance is normalized by the corresponding film thickness.

The measurements have been performed at ambient temperature with a light wavelength of $\lambda = 635$ nm.

Polarized absorption spectra are obtained between a pair of parallel polarizers using a spectrophotometer (Unicam UV-Vis spectrometer, UV4-500). All spectra are recorded in the visible range from 350 to 650 nm, with a scan speed of 30 nm/min. The illuminated area on the sample by the light source is about 1 cm^2. In order to remove the substrate effects, a baseline is achieved with a Teflon-coated glass slide.

III. RESULTS AND DISCUSSION

A. Influence of thermal annealing

Due to the rubbed Teflon coating, the columnar liquid crystal film exhibits a uniform birefringence between crossed polarizers, which features a unidirectional planar alignment (Fig. 3). Nevertheless, a more detailed observation indicates some inhomogeneities in the CLC orientation. A thermal annealing is then applied to improve the unidirectional orientation of the columnar mesophase [20] by removing defects, such as grain boundaries between CLC domains. This annealing is performed during about three hours at a temperature of 60 and 180 °C for the pyrene and the benzoperylene compounds, respectively (Fig. 2). At theses temperatures, the viscosity of the columnar mesophases substantially decreases allowing an easier column rearrangement in the Teflon stripes. However, some dewetting is also promoted due to the low surface tension ($\gamma_{\text{Teflon-air}} = 20$ mJ m^{-2}) of the Teflon layer. A compromise has thus to be found between the alignment improvement and the increase of dewetted zones, as shown in Fig. 3.

B. Dichroic ratio

The obtention of CLC films exhibiting a unidirectional planar anchoring, i.e., having the optical axis lying in a given direction in the plan of the film, allows the investigation of the anisotropic optical properties. An opposite direction of the optical axis with respect to the Teflon rubbing direction has been found for the two studied compounds and will be discussed in Sec. III E.

Polarized absorption spectra have been measured with the incident light polarized both parallel and perpendicular to the optical axis of the uniaxial sample, corresponding to the absorbances $A_{\parallel}$ and $A_{\perp}$, respectively. The spectra of both CLC materials (Fig. 4) reveal a significant polarized absorption anisotropy, with a higher absorption for the light polarized perpendicularly to the optical axis ($A_{\perp}$). This anisotropy is characterized by the dichroic ratio A_{OD} defined as [32]

$$A_{\text{OD}} = \frac{A_{\perp}}{A_{\parallel}} \tag{1}$$

at the light wavelength corresponding to the maximum of absorbance. The measured dichroic ratio is $A_{\text{OD}} = 14.3$ at $\lambda = 442$ nm for the Bp compound (Fig. 4). This dichroic ratio is one of the highest values reported for thermotropic discotic compounds [20,22,23]. Note that, before thermal annealing, the dichroic ratio was only $A_{\text{OD}} = 2.5$, demonstrating thus the efficiency of such a thermal process for the unidirectional columnar organization. The dichroic ratio, which quantifies the performance of a polarizer, shows that the benzoperylene derivative is a promising material to be used as a selective polarizer in the green part of the visible range [33].

For the pyrene derivative, the dichroic ratio is $A_{\text{OD}} = 8.9$ at $\lambda = 392$ nm (Fig. 4). The lower value might stem from the larger dewetted area appearing during thermal annealing, as shown in Fig. 3.

C. Birefringence: Values and sign

The birefringence is an important feature of liquid crystals for their use in optical devices. Taking advantage of the unidirectional alignment of CLC films, the birefringence Δn is first determined from the spectroscopic data over the whole visible range according to the method developed in Ref. [34]. The intensity transmitted by a uniaxial material with its optical axis oriented at the angle α with respect to the two parallel polarizers is

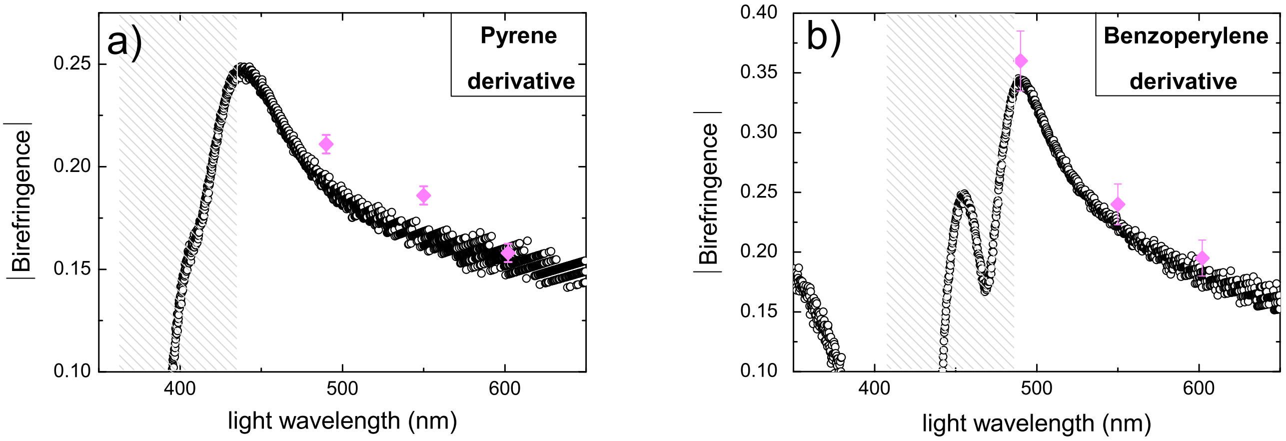


FIG. 5. (Color online) Absolute value of the CLC birefringence as a function of the light wavelength for Py (a) and Bp (b) compounds, respectively, obtained from Eq. (4) (black open circles) and obtained from a direct measurement with a Berek compensator at three wavelengths ($\lambda=490$, 550, and 602 nm) (pink solid circles). The dashed regions indicate the wavelength range of the CLC absorption band.

$$t = t_{\parallel}\cos^4\alpha + t_{\perp}\sin^4\alpha + \frac{\sqrt{t_{\perp}t_{\parallel}}}{2}\cos(\Delta\varphi)\sin^2(2\alpha) \tag{2}$$

with $\Delta\varphi$ the phase retardation given by

$$\Delta\varphi = \frac{2\pi\Delta n d}{\lambda}, \tag{3}$$

where d is the sample thickness and λ the light wavelength. In order to determine $\Delta\varphi$, and therefore Δn, an additional measurement is required, which is performed at $\alpha=45°$, where the best accuracy is achieved for Eq. (2), which can then be reduced to

$$\cos(\Delta\varphi) = \frac{4t_{45} - (t_{\parallel} + t_{\perp})}{2\sqrt{t_{\parallel}t_{\perp}}}. \tag{4}$$

The transmittances $t_{\parallel}$, $t_{\perp}$, and t_{45} are obtained from the optical absorption by the relation

$$t = 10^{-A}. \tag{5}$$

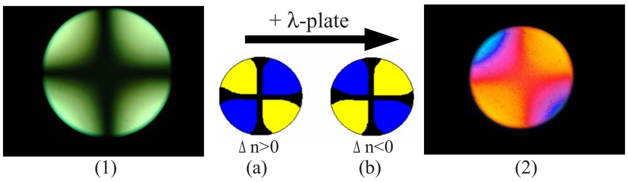
The calculated birefringence spectra are presented in Fig. 5. In the two graphs, the dashed regions represent the CLC absorption bands. Their width is defined by the full width at half maximum of the corresponding absorption peak (Fig. 4). Note that the nonmonotonic behavior of $\Delta n(\lambda)$ near the absorption bands can be attributed to the effect of anomalous dispersion [24].

In order to confirm the birefringence values obtained from absorption data, the birefringence has also been measured according to a more classical technique with the use of a Berek compensator. The results are shown in Fig. 5. In general, there is a good agreement between the two methods. However, it has to be noted that, for the pyrene compound, the birefringence measured by the Berek technique is slightly larger than the one calculated from the spectroscopic data. The Berek compensator provides a local measurement of the birefringence: a highly aligned zone, free of defects, with a typical area of a few μm^2 is chosen under the microscope to perform the measurement. Conversely, the birefringence based on the absorbance data is the mean value over the area ($\sim$1 cm^2) probed by the light beam of the spectrophotometer, which includes orientational topological defects. The difference between the two measurements probably stems from some misalignment of the CLC film. For the benzoperylene derivative, no significant difference is observed between the two methods, which reveals in this case the high degree of columnar organization. Only a few studies of the birefringence of columnar liquid crystal have been reported, mainly on triphenylene derivatives which do not absorb in the visible part of the spectrum [1,35]. The birefringence of these compounds is very similar to the value found for our materials far from their absorption band. The great advantage of the method based on the absorbance is the determination of the birefringence over all the visible range, and not only at few discrete wavelengths.

However, none of these techniques provides the sign of the birefringence, which can be determined by using conoscopy on a homeotropically oriented sample (Fig. 6) [30]. The birefringence is found to be negative for both compounds, in agreement with previous measurements [1,35], and as expected for discotic materials for symmetry reasons.

D. Anisotropic refractive indices

From the absorption data, the anisotropic refractive indices n_e and n_o are calculated using the Kramers-Kronig rela-



(1) (a) (b) (2)

FIG. 6. (Color online) Determination by conoscopy of the sign of the birefringence for an optically uniaxial material. (1) Interference figure observed for homeotropically aligned CLC samples between cover slip and slide. (2) After insertion of the full wave retardation plate, the birefringence is defined as positive (a) or negative (b) according to the relative positions of the blue and yellow colors in the interference figure. The birefringence of both discotic materials is therefore negative.

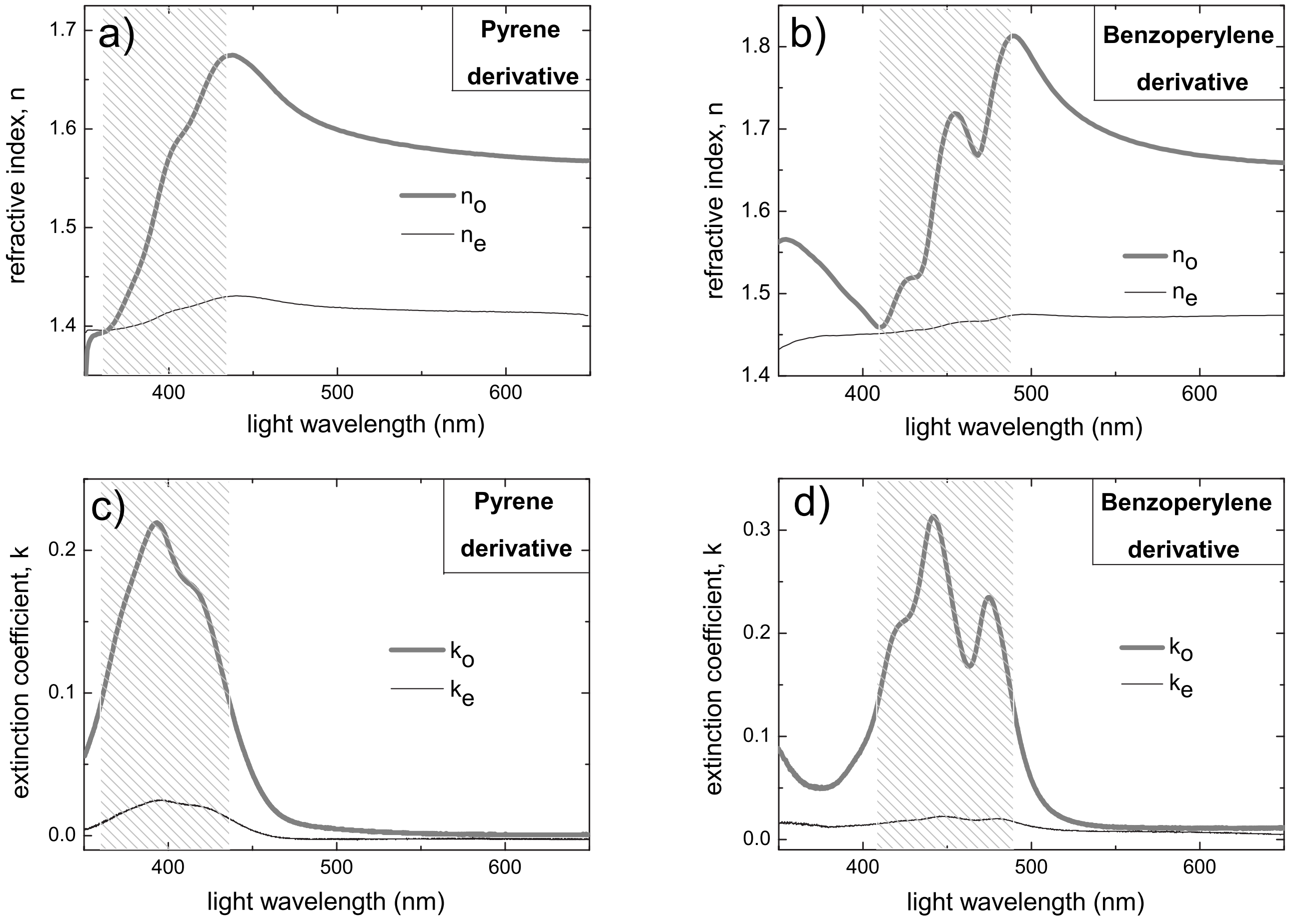


FIG. 7. Dependence on the light wavelength of the anisotropic refractive indices n_e and n_o and of the extinction coefficients k_e and k_o for the Py (a),(c) and Bp (b),(d) compounds, respectively. The dashed regions indicate the wavelength range of the CLC absorption band.

tion, which interconnects the real and the imaginary components n and k of the complex optical index [36]:

$$n(\lambda_i) = n_\infty + \frac{2}{\pi} \mathrm{P} \int_0^\infty \frac{\lambda_i^2 k(\lambda)}{\lambda(\lambda_i^2 - \lambda^2)} d\lambda, \tag{6}$$

where P is the Cauchy principal value of the integral. The quantity n_∞ is defined as the offset of the refractive index generated by the Kramers-Kronig relation, if the wavelength range from zero to infinity is used for the evaluation of the integral. Experimentally, the absorbance is measured only on a finite wavelength interval corresponding to the visible range. It has been recently shown [37] that this restriction does not prevent the use of Eq. (6), which can be approximated by

$$n(\lambda_i) = n^{\mathrm{offset}} + \frac{2}{\pi} \mathrm{P} \int_{\lambda_L}^{\lambda_U} \frac{\lambda_i^2 k(\lambda)}{\lambda(\lambda_i^2 - \lambda^2)} d\lambda, \quad \lambda_L \leqslant \lambda_i \leqslant \lambda_U, \tag{7}$$

with n^{offset} a constant. The extinction coefficient $k(\lambda)$ is extracted from the optical absorption A (Fig. 4) by [29]

$$k(\lambda) = \frac{A\lambda \ln 10}{4\pi d}. \tag{8}$$

The Cauchy integral has been numerically determined over the entire visible range (350–650 nm) by using the MATLAB software (The MathWorks, Inc.). In order to estimate n^{offset} of each anisotropic refractive index for both discotic compounds, two relations connecting n_e and n_o at a given wavelength have to be known, such as the birefringence $\Delta n = n_e - n_o$ (Fig. 5) and the mean refractive index $n_{\mathrm{mean}} = (n_e + n_o)/2$ measured by ellipsometry. This index is found to be $n_{\mathrm{mean}} = 1.49$ and 1.57 for the films of pyrene and benzoperylene compounds, respectively. Thus, the anisotropic refractive indices n_e and n_o have been calculated according to the Kramers-Kronig relation [Eq. (7)], and the results are shown in Fig. 7.

An error bar of about ±0.03 is estimated for all the refractive indices of both compounds. It mainly stems from the n_{mean} measurement used in the n^{offset} calculation. For the Py derivative, some misalignment of the columnar liquid crystal in the Teflon layer can also be invoked. The birefringence obtained from the refractive indices calculated by the Kramers-Kronig relation is found to be similar to the birefringence experimentally measured for each CLC derivative (Fig. 5), which evidences the self-consistency of the results.

E. Alignment on the Teflon coating

1. Comparison with a homeotropically aligned film

As previously shown, the Teflon coating is an efficient method to unidirectionally orient columnar liquid crystals. In order to evaluate the quality of the obtained alignment for each compound, the absorption of homeotropically aligned samples, A_{homeo}, is measured. Indeed, the unidirectionality of the homeotropic anchoring with the columns normal to the substrate can be considered as almost perfect (Fig. 1). Therefore the incident light is sensitive only to the ordinary optical index $\tilde{n}_o = n_o + ik_o$, and the absorption A_{homeo} can be used as a reference (Fig. 4). In the case of the benzoperylene derivative, the absorbances A_{homeo} and $A_\perp$ (normalized by the corresponding film thickness) are very similar (Fig. 4). The good superposition of the two spectra demonstrates the high degree of alignment of the Bp liquid crystal on the Teflon layer. Consequently, the measured dichroic ratio is close to the highest value which can be reached on this kind of substrate for this specific molecule. On the contrary, for the pyrene compound, a small shift exists between the two spectra A_{homeo} and $A_\perp$, revealing an alignment of lower quality on the rubbed Teflon layer. This is confirmed by the presence of weakly extended developable domains in polarizing microscopy at high magnification, where columns are only slightly bent. The same optical texture has been observed in Ref. [16] for a phthalocyanine derivative prepared as a thin film by the zone-casting process, where the columns have been found to be normal to the deposit direction.

2. Orientational order parameter

To quantify the degree of alignment of the columnar mesophase, the scalar order parameter is obtained from the orientational distribution of the short axis of the discotic molecules by

$$S = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle \qquad (9)$$

where the angular brackets represent an average over all molecular orientations [38]. For dichroic molecules, the orientational distribution is experimentally connected to the molecular transition moment, with the corresponding order parameter S_T. According to Ref. [39], the general expression between S and S_T is

$$S_T = S\left(1 - \frac{3}{2}\sin^2\beta\right) \qquad (10)$$

with β the angle between the transition moment and the liquid crystal director. For the discotic molecules studied here, the transition moment is in the plane of the molecule, i.e., normal to the column long axis ($\beta = 90°$), reducing Eq. (10) to

$$S = -2S_T. \qquad (11)$$

Thus, when no orientational order exists, as in the isotropic liquid phase, $S_T = 0$ and $A_\perp = A_\parallel$. For a perfectly oriented system with the strict alignment of all the columns and of the discs in the columns, $S_T = -\frac{1}{2}$ (or equivalently $S = 1$) because the orientation of the transition moment of such discotic molecules is degenerated in the plane normal to the columns. Consequently, the absorption parallel to the optical axis, i.e., along the columns, is null ($A_\parallel = 0$). Therefore, the scalar order parameter of the transition moment S_T can be expressed as a function of the absorbances $A_\parallel$ and $A_\perp$ [39,40]:

$$S_T = \frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp} = \frac{1 - A_{\text{OD}}}{1 + 2A_{\text{OD}}}. \qquad (12)$$

Using Eqs. (11) and (12), an orientational order parameter of $S_{\text{Bp}} = 0.90$ and $S_{\text{Py}} = 0.84$ is found for the benzoperylene and the pyrene derivatives, respectively. These values evidence the high degree of alignment obtained for columnar liquid crystals with a rubbed PTFE coating. For highly birefringent materials, the effect of the internal field can be taken into account [39,41], with a corrected expression of the order parameter:

$$S^{\text{corr}} = -2 \times \frac{n_e A_\parallel - n_o A_\perp}{n_e A_\parallel + 2n_o A_\perp}. \qquad (13)$$

The values obtained are $S^{\text{corr}}_{\text{Bp}} = 0.91$ and $S^{\text{corr}}_{\text{Py}} = 0.85$, showing therefore that the correction is negligible for both compounds studied.

3. CLC anchoring with respect to the PTFE stripes

By measuring the polarized absorption spectra parallel and perpendicular to the optical axis of the CLC thin films, a different column orientation has been observed for each compound with respect to the PTFE stripes. In order to prove the change of the columnar anchoring, a full wave retardation plate has been used to localize the position of the slow and fast vibration axes of uniaxial birefringent materials [30]. If the slow vibration axis of the sample is superimposed over the corresponding axis of the λ-plate, the additive retardation effects give higher-order interference colors (blue color). However, if the fast vibration axis is parallel to the slow axis of the retardation plate, it results in lower-order interference colors (yellow color). For both discotic compounds, the birefringence is negative, i.e., $n_e < n_o$, which implies $v_e > v_o$, where v is the corresponding speed of light in the medium. For a uniaxial material exhibiting a negative birefringence, the slow axis therefore corresponds to the ordinary axis and the fast vibration axis to the extraordinary index. For the benzoperylene derivative, when the Teflon orientation is parallel to the slow axis of the λ-plate, a yellow color appears (Fig. 8): the direction of the extraordinary index, which has been defined along the columns, is parallel to the PTFE stripes. Conversely, a blue color appears in the case of the pyrene derivative (Fig. 8) for the same Teflon orientation with respect to the retardation plate slow axis, showing thus that Py columns are normal to the PTFE stripes. The pyrene derivative exhibits an unconventional behavior: for most discotic molecules, rubbed Teflon coatings have been reported to induce homogeneous planar alignment with columns parallel to the PTFE stripes [21,23]. This optical method also validates that the main transition moment of the Bp and Py discotic molecules is in the plane of the disc, i.e., normal to the columns.

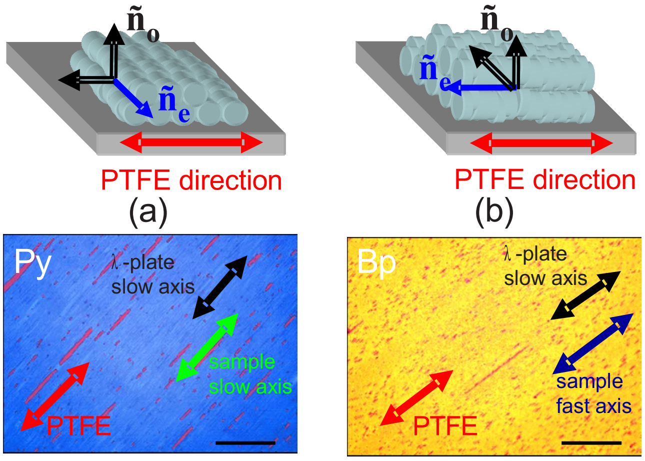


FIG. 8. (Color online) Schematic representation of the different orientation of the columns for a unidirectional planar alignment onto a Teflon coating and the corresponding optical pictures observed by polarizing microscopy after the insertion of the full wave retardation plate into the optical path in the case of pyrene (a) and benzoperylene (b) derivatives, respectively. The scale bar indicates 50 μm.

4. Origin of the different columnar orientations

Various rotational orientations of crystals have been reported on the Teflon layer in Ref. [42]. The explanation of this behavior is based on an adequate interlocking of the substrate and the deposit contact planes. If an acceptable substrate-deposit lattice matching is observed in most cases where the PTFE interchain distance can be slightly distorted to accommodate the material periodicity, the cost in energy of the lattice distortion is sometimes too high [42,43]. Consequently, a different crystal orientation with tilted molecules can be observed. However, such an explanation seems not suitable in the case of these columnar liquid crystals, given that both materials exhibit the same hexagonal lattice parameter (q_{100}=0.35 Å^{-1}) [25,26], as shown by x-ray diffraction.

The change in column orientation could stem from the polar-apolar feature of the studied discotic molecule. Indeed, the Bp derivative is more polar than the Py molecule (Fig. 2). Depending on the polarity, repulsive (attractive) van der Waals interactions with the Teflon layer can be created for an apolar (polar) molecule originating from the different sign of the Hamaker constant [44]. This variation of the intermolecular interactions based on the compound polarity, which can moreover be associated with an epitaxial mechanism as described above, could lead to a different alignment of the discotic mesophases with respect to the PTFE stripes. This assessment needs to be further supported by more experimental investigations, such as a systematic study of columnar liquid crystals with varied aromatic cores.

IV. CONCLUSION

By achieving highly aligned columnar liquid crystal samples, we have measured polarized absorbance spectra, and determined the maximum anisotropy of absorption (dichroic ratio). From this measurement, the orientational order parameter has been calculated, showing the efficiency of the rubbed Teflon layer in orienting discotic compounds in open supported thin films. A different orientation of the columns with respect to the PTFE stripes (parallel and perpendicular) has been revealed. The birefringence over the whole visible range has been deduced from absorption data, and its sign has been found to be negative by conoscopy. Finally, all the complex optical indices have been calculated, especially the anisotropic refractive indices n_e and n_o by use of the Kramers-Kronig relation. The method developed in this work not only is relevant for columnar liquid crystals, but can be extended to any optically uniaxial material exhibiting well-defined absorption bands in the visible range and for which the orientation can be controlled.

ACKNOWLEDGMENTS

This work is supported by CNRS and Region Aquitaine. We thank Harald Bock and Anne Hochedez for the synthesis of the chemical compounds, Hassan Saadaoui for the film thickness measurements, and Christophe Blanc and Maurizio Nobili for their help in the preparation of PTFE-covered glass substrates.

---

[1] P. Oswald and P. Pieranski, *Smectic and Columnar Liquid Crystals: Concepts and Physical Properties Illustrated by Experiments* (Taylor and Francis/CRC Press, London, 2005).
[2] S. Sergeyev, W. Pisula, and Y. H. Geerts, Chem. Soc. Rev. **36**, 1902 (2007).
[3] D. Adam, P. Schumacher, J. Simmerer, L. Häusslinger, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf, and D. Haarer, Nature (London) **371**, 141 (1994).
[4] I. O. Shklyarevskiy, P. Jonkheijm, N. Stutzmann, D. Wasserberg, H. J. Wondergem, P. C. M. Christianen, A. P. H. J. Schenning, D. M. de Leeuw, Z. Tomovic, J. Wu, K. Müllen, and J. C. Maan, J. Am. Chem. Soc. **127**, 16233 (2005).
[5] W. Pisula, A. Menon, M. Stepputat, I. Lieberwirth, U. Kolb, A. Tracz, H. Sirringhaus, T. Pakula, and K. Müllen, Adv. Mater. (Weinheim, Ger.) **17**, 684 (2005).
[6] L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, and J. D. MacKenzie, Science **293**, 1119 (2001).
[7] E. Charlet, E. Grelet, P. Brettes, H. Bock, H. Saadaoui, L. Cisse, P. Destruel, N. Gherardi, and I. Seguy, Appl. Phys. Lett. **92**, 024107 (2008).
[8] G. Lüssem and J. H. Wendorff, Polym. Adv. Technol. **9**, 443 (1998).
[9] S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, and M. Tosoni, Angew. Chem., Int. Ed. **46**, 4832 (2007).
[10] E. Grelet and H. Bock, Europhys. Lett. **73**, 712 (2006).
[11] Y. Bouligand, J. Phys. (France) **41**, 1307 (1980).
[12] W. Pisula, Z. Tomovic, M. Stepputat, B. El Hamaoui, M. D.

Watson, T. Pakula, and K. Müllen, Adv. Funct. Mater. **15**, 893 (2005).

[13] J.-H. Lee, H.-S. Kim, B. D. Pate, and S.-M. Choi, Physica B **385-386**, 798 (2006).

[14] Y. Zakrevskyy, C. F. J. Faul, Y. Guan, and J. Stumpe, Adv. Funct. Mater. **14**, 835 (2004).

[15] A. Tracz, J. K. Jeszka, M. D. Watson, W. Pisula, K. Müllen, and T. Pakula, J. Am. Chem. Soc. **125**, 1682 (2003); W. Pisula, Z. Tomovic, M. Stepputat, U. Kolb, T. Pakula, and K. Müllen, Chem. Mater. **17**, 2641 (2005).

[16] A. Tracz, T. Makowski, S. Masirek, W. Pisula, and Y. H. Geerts, Nanotechnology **18**, 485303 (2007).

[17] H. Monobe, K. Awazu, and Y. Shimizu, Adv. Mater. (Weinheim, Ger.) **12**, 1495 (2000).

[18] K. Ichimura, S. Furumi, S. Morino, M. Kidowaki, M. Nakagawa, M. Ogawa, and Y. Nishiura, Adv. Mater. (Weinheim, Ger.) **12**, 950 (2000).

[19] J. C. Wittmann and P. Smith, Nature (London) **352**, 414 (1991).

[20] S. Zimmermann, J. H. Wendorff, and C. Weder, Chem. Mater. **14**, 2218 (2002).

[21] A. M. Van de Craats, N. Stutzmann, O. Bunk, M. M. Nieslen, M. Watson, K. Müllen, H. D. Chanzy, H. Sirringhaus, and R. H. Friend, Adv. Mater. (Weinheim, Ger.) **15**, 495 (2003); O. Bunk, M. N. Nieslen, T. I. Sølling, A. M. Van de Craats, and N. Stutzmann, J. Am. Chem. Soc. **125**, 2252 (2003).

[22] J. Piris, M. G. Debije, N. Stutzmann, B. W. Laursen, W. Pisula, M. D. Watson, T. Bjørnholm, K. Müllen, and J. M. Warman, Adv. Funct. Mater. **14**, 1053 (2004).

[23] S. A. Benning, R. Oesterhaus, and H.-S. Kitzerow, Liq. Cryst. **31**, 201 (2004).

[24] E. Hecht, *Optics*, 4th ed. (Addison-Wesley, Reading, MA, 2001).

[25] T. Hassheider, S. A. Benning, H.-S. Kitzerow, M.-F. Achard, and H. Bock, Angew. Chem., Int. Ed. **40**, 2060 (2001).

[26] S. Alibert-Fouet, S. Dardel, H. Bock, M. Oukachmih, S. Archambeau, I. Seguy, P. Jolinat, and P. Destruel, ChemPhysChem **4**, 983 (2003).

[27] S. Saïdi-Besbes, E. Grelet, and H. Bock, Angew. Chem., Int. Ed. **45**, 1783 (2006).

[28] E. Campanelli, S. Faetti, and M. Nobili, Eur. Phys. J. E **11**, 199 (2003).

[29] M. Born and E. Wolf, *Principles of Optics*, 2nd ed. (Pergamon, New York, 1964).

[30] W. J. Patzelt, *Microscopie en Polarisation, Théorie, Instruments, Applications* (Ernst Leitz, Wetzlar, 1974) (in French).

[31] E. Grelet *et al.* (unpublished).

[32] C. D. West and R. Clark Jones, J. Opt. Soc. Am. **41**, 976 (1951).

[33] E. Peeters, J. Lub, J. A. M. Steenbakkers, and D. J. Broer, Adv. Mater. (Weinheim, Ger.) **18**, 2412 (2006).

[34] Y. A. Nastishin, H. Liu, T. Schneider, V. Nazarenko, R. Vasyuta, S. V. Shiyanovskii, and O. D. Lavrentovich, Phys. Rev. E **72**, 041711 (2005).

[35] V. A. Gunyakov, N. P. Shestakov, and S. M. Shibili, Liq. Cryst. **30**, 871 (2003).

[36] L. Landau and E. M. Lifchitz, *Electrodynamics of Continuous Media* (Pergamon, New York, 1960).

[37] R. Nitsche and T. Fritz, Phys. Rev. B **70**, 195432 (2004).

[38] M. Kleman and O. D. Lavrentovich, *Soft Matter Physics, an Introduction* (Springer, New York, 2003).

[39] B. Bahadur, *Handbook of Liquid Crystals* (Wiley-VCH, Weinheim, 1998), Vol. 2A.

[40] D. L. White and G. N. Taylor, J. Appl. Phys. **45**, 4718 (1974).

[41] V. R. Horowitz, L. A. Janowitz, A. L. Modic, P. A. Heiney, and P. J. Collings, Phys. Rev. E **72**, 041710 (2005).

[42] P. Damman, M. Dosière, M. Brunel, and J. C. Wittmann, J. Am. Chem. Soc. **119**, 4633 (1997).

[43] P. Damman, C. Fisher, and J. K. Krüger, J. Chem. Phys. **114**, 8196 (2001).

[44] A. Milling, P. Mulvaney, and I. Larson, J. Colloid Interface Sci. **180**, 460 (1996).