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Evidence for a discotic smectic-nematic phase induced in Langmuir-Blodgett films

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Langmuir-Blodgett (LB) films are reported for an amphiphilic disklike mesogene with a nematic liquid crystalline phase in bulk. The molecular arrangement of a discotic smectic-nematic phase, induced in the LB films, is evidenced by means of x-ray diffraction, atomic force microscopy, and UV-VIS (visible) absorption spectroscopy. The disklike molecules are "edge-on" arranged with a bilayer periodicity of 4.45 nm normal to the solid substrate and with a nematic arrangement in the monolayer planes. This structure results in extremely smooth top film surfaces.

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Intermolecular interactions affect the phase state and the molecular arrangement of thin films. The phase state determines the general physical properties of the thin layers, while the specific film's features are dominated by molecular peculiarities. Changes in the phase state of thin liquid crystalline films may influence essentially their optical and electrical properties. A variety of aromatic disk-shaped molecules have been synthesized for microelectronics, low-dimensional physics, and optics. Disklike molecules (e.g., porphyrins, vitamins) play a significant role in living systems as well. However, the general diagram of the possible discotic phases is still incomplete [1].

The interest for the study of Langmuir-Blodgett (LB) films originates from their scientific and technological significance [2,3]. LB films may be utilized as insulating layers, sensors, and standards in optics and microelectronics [2,3], nonlinear optical structures [4], model systems to study membranes [2,5], phase transitions [3], and intermolecular interactions [2,3,6]. The research on LB films, as well as on liquid crystals, has been concentrated predominantly on rodlike molecules. Recently, films of disklike mesogenes [1] have indicated new opportunities for sensor [7] and optical display application [8], modeling of π-π and steric interactions in artificial low-dimensional [9] and biological systems.

The ability of the LB technique to alter the discotic phases has been proven only for compounds possessing a bulk hexagonal columnar liquid crystalline phase [8–12]. The LB technique has the advantage of both macroscopical and microscopical influence on the molecular arrangement (e.g., by means of the surface pressure variations and interactions with the aqueous subphase). π-π and steric intermolecular interactions also influence the molecular organization of the discotic LB films. With discotic mesogenes, the effects of these interactions on the LB film structures are stronger as compared to the case of the classical rodlike amphiphiles.

The molecular arrangements reported for discotic LB films so far correspond to low-ordered nematic [11] or columnar [8–10] phases obtained in the solid or liquid state temperature region. Atomic force microscopy (AFM) studies of LB films exhibiting a columnar phase have revealed a surface morphology periodically modulated by columns [8,13]. The mean surface roughness has been higher than 0.4 nm. Evidence has been presented recently [12] for a square-lattice discotic structure induced by means of the LB technique. This structure seems to be the two-dimensional analog of the cubatic discotic phase predicted by molecular modeling experiments [14]. The opportunity to induce, by mens of the LB technique, a higher-ordered discotic phase (e.g., smectic or columnar) in thin multilayers of compounds possessing a low-ordered nematic bulk phase appears to be an attractive perspective.

Langmuir monolayers of disk-shaped compound 1 (Fig. 1) were formed by spreading of its $10^{-3}M$ chloroform solution at the air-water interface. A typical surface pressure-area isotherm of the monolayers of 1, used for the preparation of LB films, is shown in Fig. 1. The area per molecule of 0.85 nm^2 at a surface pressure of 25 mN m^{-1} indicates that the disklike molecular planes are oriented normally to the air-water interface ("edge-on" orientation). This molecular arrangement could be transferred to a solid support if the deposition ratios are close to unity. The isotherms of the amphiphile 1 are very sensitive to the subphase pH and counterion type (e.g., Pb^{2+}, Cd^{2+}, Ba^{2+}, Na^{+}). The maxi-

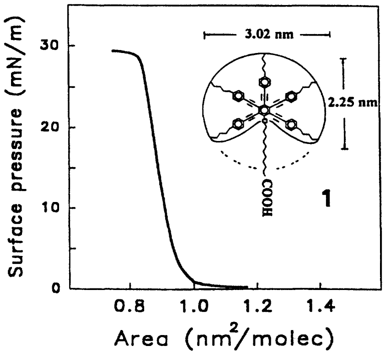

FIG. 1. Surface pressure-area isotherm of a monolayer of the disklike 11-[(4-pentylphenyl)ethynyl]-phenoxy undecanoic acid (compound 1) on $2\times10^{-4}M$ BaBr$_2$ subphase of pH 10.0. The compound 1 (designed by Praefcke *et al.* [15]) consists of an aromatic core, five flexible alkyl wings, and one alkoxy tail. It should be noted that the flexible long tail exceeds, in an extended state, the disk radius by about 0.5 nm and has a relative freedom to orient in the open triangular segment of the disk-shaped molecule. The bulk compound 1 is in a crystalline state at room temperature and exhibits a nematic liquid crystalline phase in the region 84–91° C [15].

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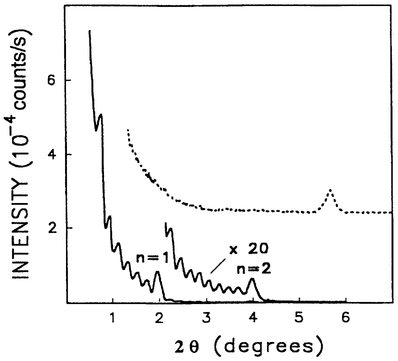

FIG. 2. Typical small-angle x-ray diffraction patterns of 20 monolayer LB films of 1 deposited on a hydrophobized [17] glass support from $2\times10^{-4}M$ $BaBr_2$ subsolution. The dashed line refers to an average transfer ratio of 0.35 at a surface pressure of 10 mN m^{-1} and pH 3.5. The solid line refers to an average transfer ratio close to unity at a surface pressure of 25 mN m^{-1} and pH 10.0. The two Bragg peaks (n) are well resolved on the background of many fringes of equal inclination (Kiessig fringes). X-ray diffractometer "Siemens-500D" operating at a wavelength of 0.154 nm was utilized in a reflection geometry [18]. The reported data have been reproducible over a period of 18 months. The samples were stored in clean closed boxes under room conditions [relative humidity (RH) = (48±10)%; temperature $t=(20\pm10)$ °C].

mum surface pressures, attained on monolayer compression in the acidic pH region, were typically less than 15 mN m^{-1}. In the alkaline pH region, the maximum pressures rose up to 40 mN m^{-1} depending on the counterion used [16]. Maximum transfer ratios of the monolayers of 1 were achieved in the presence of Ba^{2+} counterions in the subsolutions of pH values above 9.5.

Out-of-plane molecular arrangement of the deposited discotic films. The structure of the films in a direction normal to the substrate was analyzed by means of small-angle x-ray diffraction (Fig. 2). X-ray results are compared for LB films deposited at low (<0.5) and high (close to 1) transfer ratios. The films deposited at transfer ratios less than 0.5 (from pure water subphase or in the acidic pH region) showed the same single crystalline x-ray peak at 5.68° as the bulk compound 1. On increase of the transfer ratios, the crystalline peak disappears. The Bragg peaks, observed for the discotic multilayers deposited in the presence of Ba^{2+} counterions and with transfer ratios close to unity, evidence the appearance of a different structural arrangement with a periodicity of 4.45 nm normal to the substrate. This spacing fits the molecular dimensions (Fig. 1) for bilayers of "edge-on" oriented molecules.

The large number of observed Kiessig fringes (fringes of equal inclination) is indicative of an extremely smooth film surface over a relatively large area (several mm^2 typical for the x-ray diffraction measurements). In principle, mean roughness exceeding 0.2 nm reduces the total number of fringes, while roughness higher than 2 nm results in their disappearance [19]. From these fringes, the total thickness of the multilayer can be determined [20]. The refractive index of the film is defined as $n=1-\delta-i\beta$. The imaginary part (β) plays an important role at grazing angles of incidence, while the real part $(1-\delta)$ indicates that a total reflection with a critical angle $\theta_c=(2\delta)^{1/2}$ occurs at the air-film interface. For $\theta\gg\theta_c$, the Kiessig equation, which takes into account the correction for the refractive index, is given by [20] $2L(1-\delta/\sin^2\theta)\sin\theta=m\lambda$, where m is the interference order and L is the total thickness.

The total film thickness of 44.1 nm, calculated form the positions of the Kiessig fringes, yields a monolayer thickness of 2.2 nm. The obtained value is in agreement with that of 10 deposited bilayers (estimated from the Bragg peaks positions). The value obtained for δ ($=9.8\times10^{-6}$) is close to those evaluated for other organic amphiphiles (e.g., $\delta=7.6\times10^{-6}$ for behenic acid LB films [20]) and determines a critical angle of total reflection of $2\theta_c=0.508°$.

The x-ray diffraction results from the periodical distribution of the electron density within the multilayers studied. It is well known [21] that the LB transfer of amphiphilic monolayers with ionized carboxylic head groups is accompanied by inclusion of multivalent counterions from the aqueous subphase into the LB films. Despite the very high electron density of the barium ions included in the multilayers of 1, only two Bragg peaks were observed in the x-ray patterns. This indicates the existence of fluctuations of the positions of the barium ions in the bilayers. If these fluctuations were related to interdigitation of the disks from the adjacent layers, this would contribute to an increase of the surface roughness and to a reduction of the number of Kiessig fringes. The wriggle [Fig. 4(b)] of the long tails of the disks into the open triangular segments of the neighboring molecules can explain simultaneously both the large number of Kiessig fringes observed and the fluctuations of the positions of the barium ions. The latter are randomly distributed within the interfacial head groups region of the bilayers without disturbing the periodicity normal to the substrate. Therefore the small-angle x-ray diffraction in a reflection mode reveals a smecticlike arrangement of the mesogenic molecules in the discotic multilayers [Fig. 4(b)]. This arrangement is determined predominantly by the electrostatic interactions between the dissociated carboxylic groups and the barium ions in the bilayers. It is different from the bulk structure of compound 1 [15].

In-plane molecular arrangement of the deposited discotic films. The LB deposition performed with transfer ratios close to unity indicates that the disklike molecules are densely in-plane packed. Both nematic or columnar in-plane arrangement could be possible. However, the absence of columnar arrangement in the bulk compound 1 [15] implies that the intermolecular interactions disfavor it. Indeed, both the steric constraints between the hydrocarbon tails and the electrostatic interactions between the aromatic cores contribute to the "offset" arrangement. The electrostatic model [22] of the π-π electron interactions between aromatic cores predicts an "offset" π-stacking of relatively large disk-shaped π-electron systems polarized by an electron donating atom. According to this model, the attractive van der Waals interactions (proportional to the area of the molecular overlap) favor a columnar arrangement. However, the electrostatic repulsion between the π-electron clouds of nonpolar or electron-rich π systems causes distortion of the columnar arrangement, and favors an "offset" molecular arrangement [22,23]. The alkoxy oxygen atom attached to the aromatic core (Fig. 1) has been evidenced to be electron-donating [22,24]. The resulting repulsion between the π-electron rich cores favors a nematic in-plane arrangement of the disks [22].

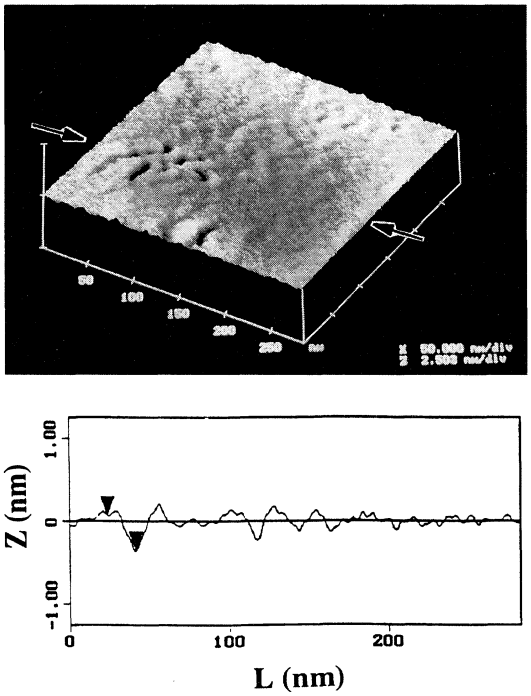

FIG. 3. AFM image (top) and cross-sectional profile Z vs L (bottom) of the LB sample studied by means of x-ray diffraction (Fig. 2, solid line). The arrows indicate the cross-section line L. Note that the few defects show small peak-to-valley values along the Z axis. The surface smoothness of the investigated discotic films distinguishes them from the morphologically rough fatty acid methylester LB films studied by means of AFM previously [17]. The images were obtained by means of a Nanoscope III AFM (Digital Instruments, Santa Barbara, CA) at 22 °C and RH of about 48% using a Si_3N_4 tip. The presented image was representative of eight different areas on the substrate surface. The images were stable for hours and were not filtered or processed.

The problem concerning the in-plane molecular arrangement in the discotic monolayers was addressed by applying transmission x-ray diffraction (TXD), AFM, and UV-VIS (visible) spectroscopy.

(i) The TXD studies [10,11,25] of columnar structures have shown two typical Bragg peaks: one, determined by the intercolumnar spacing, in the low-angle region ($2\theta = 0.8$–$7.0°$ for x-ray wavelength $\lambda = 0.154$ nm); and the second one, determined by the "face-to-face" distance between the disklike molecules within the columns, in the high-angle region ($2\theta = 20$–$27°$). The intensity of both peaks has been of the same order of magnitude or the intensity of the low-angle peak has been higher if the intracolumnar arrangement was disordered [26]. The TXD of a nematic in-plane molecular arrangement would result in the observation of only a high-angle peak (determined by the face-to-face distance) and absence of the low-angle peak (due to the absence of columns). The low intensity of the transmission x-ray diffraction requires the use of very thin substrates. Twenty monolayers of 1 were deposited onto 20 μm thick silicon substrate with transfer ratios close to unity under the same conditions as for the sample in Fig. 2, solid line. The TXD of this sample showed a single peak corresponding to a Bragg spacing of 0.37 nm, and an absence of a peak in the low-angle region. This experiment evidences the nematic in-plane arrangement of the molecules studied [Fig. 4(b)].

(ii) Important information about the in-plane structure of the thin LB films can be provided by means of AFM [8,17,27]. The top of the film surface should be periodically modulated by columns for columnar in-plane arrangement [8,13]. Typical AFM images of iscotic LB samples, deposited at transfer ratios close to unity, are presented in Fig. 3. The absence of periodical morphological modulations, expected for a discotic columnar structure, supports the conclusion about a nematic in-plane molecular arrangement. However, one should have in mind that the flexible nature of the molecules studied could also influence the AFM images. Owing to the extreme smoothness of the investigated surfaces and the flexible nature of the molecules, the imaging over smaller scales (down to 15×15 nm^2) did not yield further information about the molecular cross-sectional features of the disks (3.0×0.3 nm^2, Fig. 1).

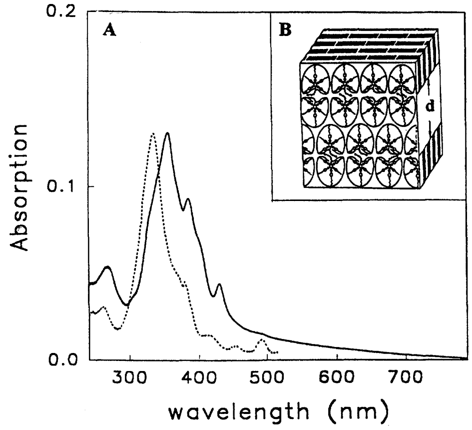

FIG. 4. (a) UV-VIS absorption spectra of the compound 1 in $1\times 10^{-6} M$ hexane-chloroform (4:1 molar ratio) solution (dashed line) and of an alternating multilayer structure of the compound 1 and barium arachidate (solid line) with transfer ratios close to unity. Thirty monolayers were deposited. The maximum of the main absorption transition of the alternative LB multilayer is strongly "redshifted" about 1780 cm^{-1} with respect to the monomer band position in solution. Its transitional dipole moment orientation in the alternating film was experimentally determined by means of polarized absorption spectroscopy to be in a dipping direction and parallel to the substrate. The spectra were obtained using a "Perkin-Elmer Lambda 19" double beam UV-VIS spectrometer. An identical quartz plate or a quartz cuvette, containing the same hexane-chloroform solvent mixture, were placed in the reference beam. (b) Schematic structural model of a smectic-nematic phase of disklike molecules in LB films. The periodic ($d = 4.45$ nm) lamellar arrangement normal to the substrate resembles a smectic phase. The "offset" in-plane arrangement of the disklike molecules resembles a nematic phase in the monolayer planes.

The AFM image on Fig. 3 demonstrates a remarkably smooth top surface. The few corrugations seen on all of the images, taken from different surface areas of the sample, show low peak-to-valley values. This AFM result is in good agreement with the observation of a lot of Kiessig fringes in the nondestructive x-ray measurements. Homogeneous, free of optical defects, surfaces were observed also upon scanning the LB samples by means of the optical microscopy technique [17] over scales larger than 1 μm^2. Therefore all results indicate that the extremely smooth LB film surface spreads over the entire substrate area covered (4.0×2.5 cm^2).

(iii) It is well known [3,28] that the "redshift" (toward longer wavelengths) of the UV-VIS absorption maximum with respect to the monomer band is typical for an "offset" (brickstone-work) arrangement of the parallel transitional dipoles of J aggregates. With H-type aggregation, the parallel transitional dipoles are arranged in columns which leads to a "blueshift" of the absorption band. All LB films of 1 studied show a "redshift" of the absorption bands. To eliminate the possible influence of the transitional dipoles of the adjacent discotic monolayers on the absorption and to consider only the in-plane molecular arrangement, the monolayers of 1 were separated by deposition of barium arachidate monolayers in an alternating LB multilayer structure The low-angle x-ray diffraction pattern of this structure shows eight Bragg peaks. This demonstrates a good bilayer periodicity of 5.2 nm normal to the substrate, determined by the sum of the thicknesses of the discotic and the barium arachidate monolayers. The "redshift" of the absorption band of about 1780 cm^{-1} for this structure [Fig. 4(a)] also evidences the nematic in-plane arrangement of the aromatic disks within the monolayers [Fig. 4(b)].

Therefore the established smecticlike structure normal to the substrate, and the nematiclike in-plane arrangement of the disklike molecules, resembles a discotic smectic-nematic phase in the LB films [Fig. 4(b)]. This discotic phase has been suggested previously [1] and here we present clear experimental evidence.

The molecular arrangement in the smectic-nematic phase appears to be a basis for anisotropic optical and electrical properties of the discotic films. The conductivity of some discotic compounds has been found to increase up to six orders of magnitude after doping by electron acceptors [29]. The large delocalized π-electron systems of the neighboring close-packed "edge-on" oriented disklike molecules can interact effectively in a direction normal to the disk plane. In this direction, the conductivity would be maximal for perfect domain-free films. The localization of the electron transport within the bilayers is expected to result in different electrical properties of the smectic-nematic phase as compared to the nematic and columnar ones.

The discotic smectic-nematic molecular arrangement [Fig. 4(b)] is related to the observation of smooth LB films surfaces (Fig. 3). While in the columnar discotic structures, the intercolumnar space contributes to an increase of the film's surface roughness, and the disposition of the disks in the nematiclike in-plane arrangement reduces the total mean film roughness. Additionally, the surfaces may be smoothed by the close-packed lamellar of large molecules, forming bridges [30] over the substrate concaves, and by the hydrocarbon wings that lie down parallel to the top film surface. It is energetically favorable for the hydrophobic flexible wings to expose minimum surface area in relatively moist air environment [relative humidity (RH) of about 48%]. This orientation of the wings at the outermost surface might explain the small difference of the total thicknesses estimated from the Kiessig fringes and the Bragg spacing multiplied by the number of bilayers. Such large, smooth hydrophobic surfaces are an essential need for molecular electronics and as substrates, suitable for organic and biological objects, in AFM experiments.

The opportunities to induce different structural arrangements in the LB films of disk-shaped molecules demonstrates the necessity of more in depth studies of the intra- and interlayer molecular interactions, and especially of the steric and π-π interactions. The defined experimental conditions of the LB technique make it suitable for a verification of the theoretical model predictions [22] of the π-π interactions. It is expected that these interactions would govern the structure and properties of thin films of many natural biological and artificial disk-shaped aromatic molecules [22]. The observation of large, smooth hydrophobic surfaces of discotic LB films with an anisotropic molecular arrangement, resembling liquid crystalline phases, and containing π-electron conjugated systems, is a promising result suggesting a potential for electronic and optical device applications.

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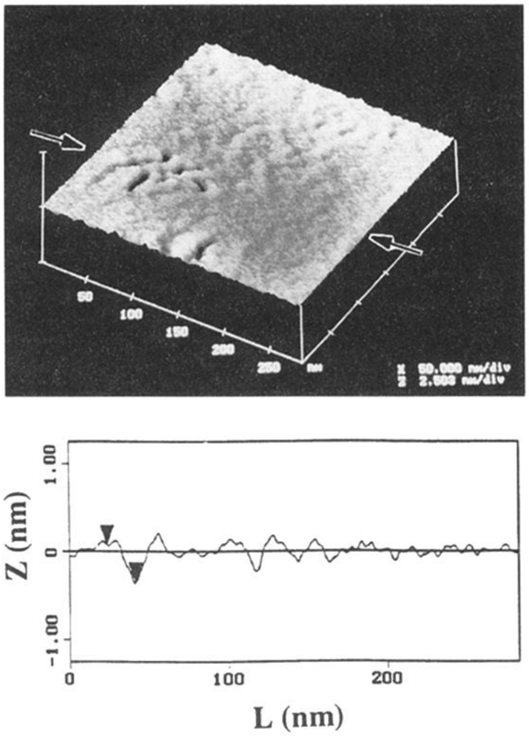

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