

## Polarized ATR-IR Studies of Surface-Field-Induced Anchoring of Alkyl Cyanobiphenyls

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We report initial studies of the use of polarized ATR-IR spectroscopy to obtain information on molecular alignment, on the mesoscopic scale, in the interfacial region of alkyl cyanobiphenyl liquid crystals in contact with self-assembled monolayers (SAMs). Specific mesoscopic alignment was induced by variation of the surface field, via the  $\omega$ -functional group of self-assembled monolayers of alkanethiol derivatives. Our experimental approach involved the deposition of a thin gold layer onto a ZnSe prism. The presence of this layer strongly attenuates the s-polarized field leading to an “effective surface selection rule”, which can be used to determine the average orientation of the liquid crystal molecules within the attenuation depth of the evanescent field. A frequency shift of the  $\text{C}\equiv\text{N}$  stretching band was seen in the case of homeotropic anchoring.

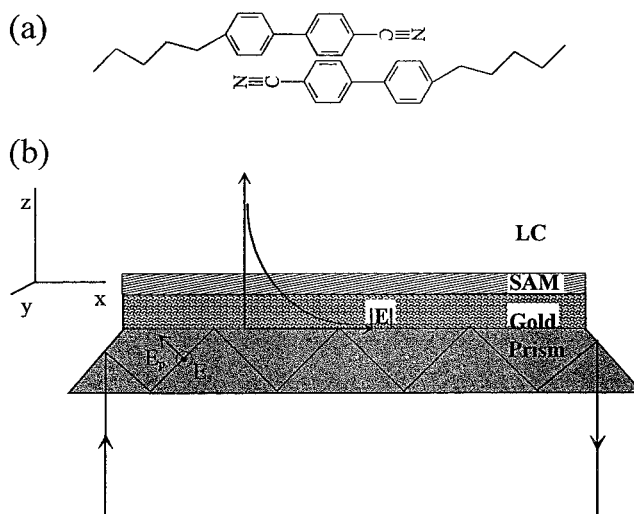
## Introduction

Nematic (N) liquid crystals (LC) are representative of a class of fluids that interact anisotropically with surfaces. In the absence of an applied external field, or surface field, the nematic director will take up an arbitrary orientation. The introduction of a surface can lead to mesoscopic alignment of the molecules via a pinning of the orientation of the nematic director at the surface. This ability of a surface to anchor the nematic director is of interest from both the practical perspective of liquid crystal devices as well as from the purely scientific viewpoint of developing our understanding of adsorption and wetting phenomena in anisotropic fluids.<sup>1–8</sup>

Self-assembled monolayers (SAMs), of alkanethiols adsorbed onto gold-coated substrates, have become widely established as a means for producing chemically designed substrates.<sup>4,9–11</sup> These systems combine reasonable chemical and mechanical stability with an ease of production and a high degree of reproducibility. Variation of the  $\omega$ -functional group, presented at the SAM–ambient interface, provides a controlled method for studying adsorption and wetting phenomena as a function of surface field.

In this paper, we report on the characterization of ordered liquid crystalline phases of alkyl cyanobiphenyls, in contact with SAM modified substrates, using polarized attenuated-total-reflection infrared (ATR-IR) spectroscopy. In the ATR mode the interface is probed, from the substrate side, by an evanescent field that decays exponentially into the liquid crystal phase (penetration depth ca. 500 nm). This technique is, therefore, sensitive to changes occurring within a mesoscopic distance from the surface.

It is widely believed that the nematogens studied here have a propensity to associate in an antiparallel “dimer” arrangement in which the biphenyl cores overlap significantly with the alkyl chains pointing roughly in opposite directions (Figure 1a). Structural evidence for such an arrangement has been obtained from X-ray and neutron diffraction studies and from Raman spectroscopy.<sup>12–14</sup> In the latter work it was proposed that while the  $\text{C}\equiv\text{N}$  bond lies parallel to the long molecular axis for



**Figure 1.** (a) 5CB (4-*n'*-pentyl-4'-cyanobiphenyl) dimer (cf. refs 12 and 13). (b) Polarized ATR-IR experimental setup.  $E_p$  and  $E_s$  are the components of the electric field parallel and perpendicular to the plane of incidence.

monomer units, in the case of dimers it may make an angle of approximately  $25^\circ$  with respect to the long axis of the dimer.<sup>14</sup> On approaching the isotropic–nematic phase transition boundary from the isotropic phase, it was established that the molar concentration of dimers (and perhaps also larger associations of antiparallel molecules) increases to approximately 0.4. This association, as dimers or larger aggregates, has little effect on the  $\langle P_2 \rangle$  order parameter but probably lowers the  $\langle P_4 \rangle$  order parameter.<sup>14</sup>

The polarized ATR-IR experimental setup used here is illustrated in Figure 1b. The presence of the thin gold film on the ATR crystal modifies the electric field distribution of the evanescent wave at the substrate–sample interface. In particular, only the p-polarized light has a significant E-field component within the LC phase.<sup>15</sup> To measure the average molecular orientation of the liquid crystal molecules, we have used the  $\text{C}\equiv\text{N}$  stretching vibration mode. This is a strong band, occurring at about  $2223\text{ cm}^{-1}$ , which lies in a region of the spectrum relatively free from other vibrations and has its

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transition moment lying almost parallel to the long molecular axis. Since the only significant component of the electric field within the LC phase is perpendicular to the surface, this effectively gives rise to a "surface selection rule" similar to that more usually associated with reflection-absorption experiments.<sup>15,16</sup> That is, IR active vibrations that are oriented parallel to the plane of the surface will not be detected. The average orientation of a particular bond can be calculated using eq 1.<sup>16</sup>

$$\langle \cos^2 \theta \rangle = \frac{I_{\text{obs}}}{3I_{\text{iso}}} \quad (1)$$

in which  $\theta$  is defined as the angle of the transition dipole moment with respect to the substrate normal,  $I_{\text{obs}}$  is the observed spectral intensity found for a liquid crystal phase, and  $I_{\text{iso}}$  is the intensity found for the isotropic phase.

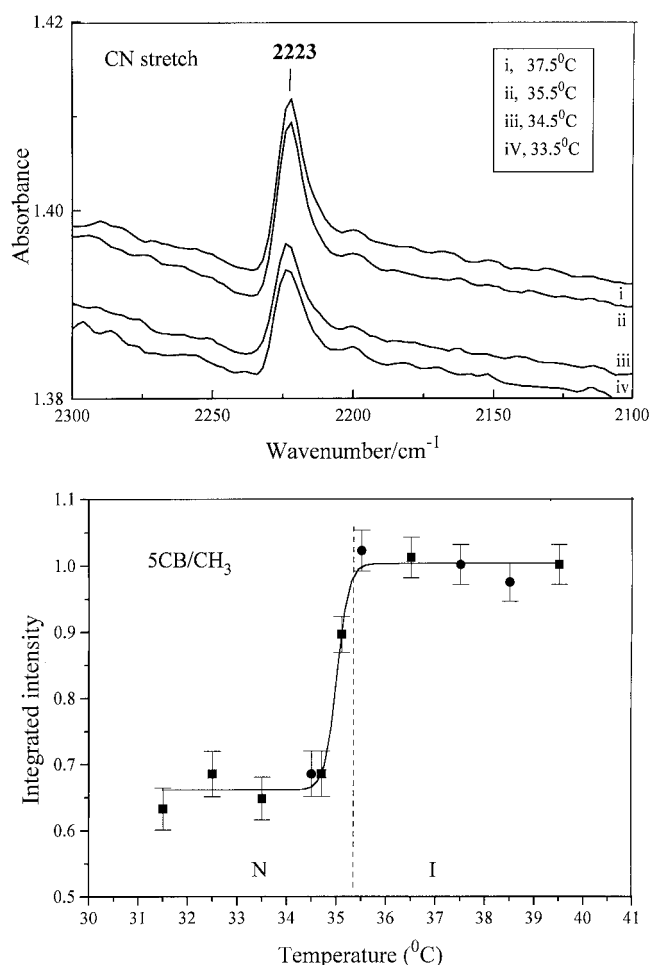
## Experimental Section

**Surface Preparation.** A gold film (17 nm thick 99.99% purity) was deposited onto one side of a ZnSe ATR crystal, using an Edwards Auto 306 TMP evaporator. SAMs were formed by placing the freshly prepared gold-coated ATR crystal directly into a  $10^{-3}$  M solution of alkanethiol derivative, in HPLC grade dichloromethane, for 1 h. The samples were then rinsed repeatedly with dichloromethane to remove excess thiol and dried in a stream of filtered  $\text{N}_2$ . The alkanethiol derivatives used were  $\text{HS}-(\text{CH}_2)_{10}-\text{COOH}$  and  $\text{HS}-(\text{CH}_2)_{17}-\text{CH}_3$  (purchased from Aldrich) and  $\text{HS}-(\text{CH}_2)_4-\text{O}-\text{C}_6\text{H}_4-\text{S}-\text{CH}_2-(\text{CF}_2)_9-\text{CF}_3$  (available from previous studies<sup>11</sup>). Note that the perfluorothiol is known to form closely packed monolayer on gold substrate.<sup>17,18</sup>

**Polarized ATR-IR Spectroscopy.** Polarized ATR-IR spectra were recorded on a Perkin-Elmer spectrometer (1760X) equipped with a gold-grid polarizer on a KRs-5 substrate (Specac, U.K.). A Specac variable-angle ATR attachment in conjunction with a 45°-cut ZnSe crystal was used to give 14 reflections. Liquid crystal molecules 5CB and 8CB, obtained from Merck Ltd. with a stated purity level of 99.7%, were injected into an airtight, thermostated liquid cell with a 0.8 mm viton spacer (Goodfellow, U.K.). The cell temperature was controlled by circulating water, from a Colar water bath, to an accuracy of 0.1 °C and was calibrated with a known compound. Each spectrum represents an average of 200 scans taken with an instrumental resolution of 4  $\text{cm}^{-1}$ .

## Results

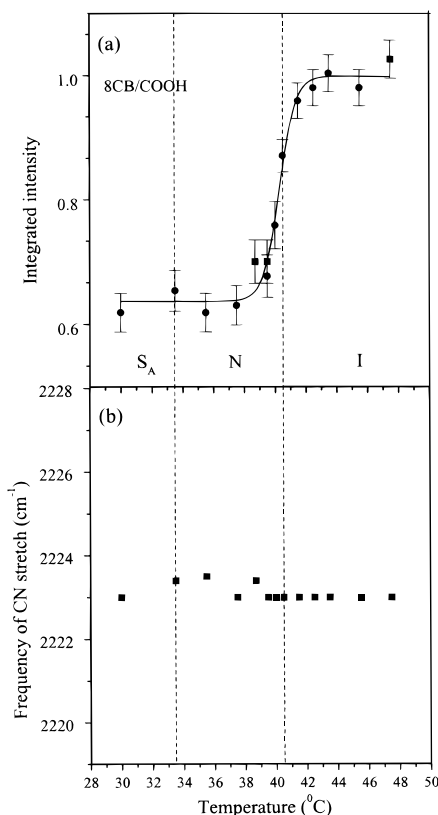
**Interaction of 5CB with a  $\text{CH}_3$  Surface.** A p-polarized ATR-IR spectrum of 5CB shows three bands in the spectral region between 3000 and 2000  $\text{cm}^{-1}$ . Two of these, at 2917 and 2850  $\text{cm}^{-1}$ , belong to the asymmetric and symmetric stretching vibrations of the  $\text{CH}_2$  units in the pentyl chain. The third band at 2223  $\text{cm}^{-1}$  is the stretching vibration of the  $\text{C}\equiv\text{N}$  group.<sup>19</sup> Figure 2a shows p-polarized ATR-IR spectra of 5CB in contact with a  $\text{CH}_3$  surface, obtained during heating and cooling through the isotropic-nematic phase transition ( $T_{\text{IN}} \approx 35.0\text{--}35.3$  °C).<sup>20,21</sup> Figure 2b shows the variation of the integrated intensity of the  $\text{C}\equiv\text{N}$  band, normalized to the average integrated intensity of the  $\text{C}\equiv\text{N}$  band in the isotropic phase, during cooling and heating through the isotropic-nematic phase transition. The abrupt decrease in the area under the  $\text{C}\equiv\text{N}$  peak implies that the  $\text{C}\equiv\text{N}$  bonds are oriented preferentially in the plane of the surface, at temperatures below  $T_{\text{IN}}$ ; i.e., we have a planar alignment. Using eq 1, we estimate a value for  $\langle \cos^2(\theta) \rangle$  of  $0.22 \pm 0.03$ ; i.e., the average angle of the  $\text{C}\equiv\text{N}$  bond



**Figure 2.** (a, top) p-polarized ATR-IR spectra of 5CB in contact with a  $\text{CH}_3$  functionalized surface. The spectra were obtained at temperatures spanning  $T_{\text{IN}}$ . (b, bottom) Normalized integrated intensity of the  $\text{C}\equiv\text{N}$  stretching vibration of 5CB on a  $\text{CH}_3$  surface as a function of temperature, on heating (●) and cooling (■). The dashed line indicates the transition temperature between the nematic (N) and the isotropic (I) phase. The solid curve is a guide to the eye only.

with respect to the surface normal is  $62 \pm 2^\circ$ . If we assume that the director of the liquid crystal is pinned in the plane of the surface, then this value would correspond to a bond order parameter of  $0.67 \pm 0.04$ .<sup>22</sup> This result is in agreement with our previous qualitative studies based on evanescent wave ellipsometry and surface plasmon resonance, in which it was found that 5CB was planar aligned on methyl, carboxylic acid, and hydroxyl functionalized surfaces.<sup>5</sup>

**Interaction of 8CB with  $\text{COOH}$  and  $\text{CF}_3$  Surfaces.** Our ellipsometric studies of nCB molecules on SAM surfaces have characterized an orientational phase diagram in which the alkyl chain length and surface field are the dimensions of phase space. Namely, we have mapped out a line of orientational anchoring transitions between planar and homeotropic alignment.<sup>5,23</sup> Our choice of 8CB on  $-\text{COOH}$  and  $-\text{CF}_3$  functionalized surfaces has been made for our ATR-IR study because these two systems lie on either side of this line; i.e., they should give rise to planar and homeotropic alignment, respectively. Figure 3a,b shows the integrated intensity and frequency, as a function of temperature, of the  $\text{C}\equiv\text{N}$  band for 8CB molecules in contact with the hydrophilic  $-\text{COOH}$  functionalized surface. It is evident that we find a similar intensity profile to that obtained for 5CB in contact with a  $\text{CH}_3$  surface, indicative of planar alignment. The average orientation of the 8CB molecules is again calculated to be  $62 \pm 2^\circ$ , which would correspond to a bond order

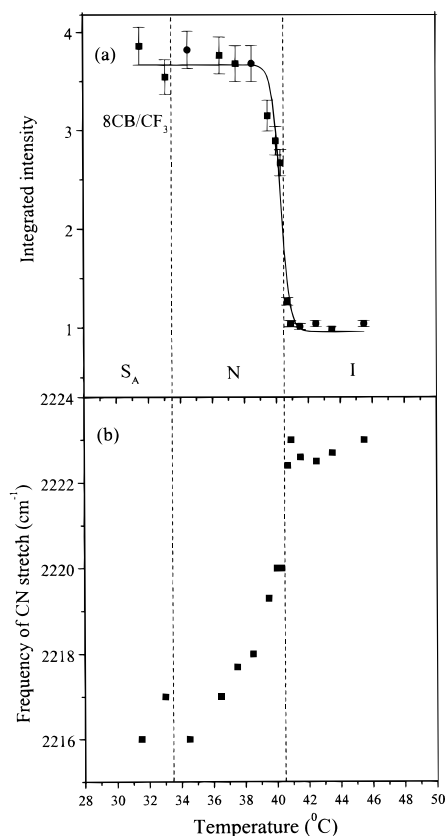


**Figure 3.** (a) Normalized integrated intensity and (b) the frequency of the C≡N stretching vibration, of 8CB on -COOH functionalized surface. Data are shown as a function of temperature, on heating (●) and cooling (■) through isotropic–nematic–smectic phases. The dashed lines indicate the transition temperatures between smectic–A (S<sub>A</sub>) and nematic (N) and between nematic and isotropic (I). The solid curve is a guide to the eye only.

parameter of  $0.67 \pm 0.04$ . The intensity of the C≡N band does not alter as the temperature is reduced below the nematic-to-smectic-A bulk phase transition ( $33.5\text{ }^{\circ}\text{C}$ )<sup>24</sup> showing that the planar anchoring remains when the adsorbed phase is smectic. We note from Figure 3b that there is no temperature dependence of the position of the C≡N stretch. In complete contrast, for the case of 8CB on a CF<sub>3</sub> functionalized surface, Figure 4a shows that the absorbance associated with the C≡N band increases as  $T$  drops below  $T_{\text{IN}}$ , implying that the molecules are anchored homeotropically by the low-energy surface, and from Figure 4b we observe that the C≡N band shifts gradually to a lower frequency as temperature decreases below  $T_{\text{IN}}$ . The transition from nematic to smectic shows no further change in structure. The frequency shift of the C≡N vibration implies that the effective mass (or spring constant) is changing, thus making estimation of the molecular orientation problematic.<sup>15</sup> Notwithstanding this, such a calculation yields an average molecular tilt of  $0^{\circ}$  with respect to the surface normal.

## Discussion and Conclusions

We have demonstrated the use of polarized ATR-IR spectroscopy as a method of investigating anchoring phenomena of liquid crystals at SAM modified surfaces. To our knowledge, this is the first such study. The optical properties of our system are strongly influenced by the presence of the gold film, which yields a “surface selection rule” allowing the determination of the average molecular alignment within a mesoscopic distance from the substrate/liquid crystal interface. The results presented



**Figure 4.** (a) Normalized integrated intensity and (b) the frequency of the C≡N stretching vibration, of 8CB on -CF<sub>3</sub> functionalized surface. Data are shown as a function of temperature, on heating (●) and cooling (■) through isotropic–nematic–smectic phases. The dashed lines indicate the transition temperatures between smectic–A (S<sub>A</sub>) and nematic (N) and between nematic and isotropic (I). The solid curve is a guide to the eye only.

here are in agreement with our earlier ellipsometric and surface plasmon resonance experiments.<sup>5,6</sup> The bond order parameter for planar alignment is estimated to be  $0.67 \pm 0.04$ , which is similar to that found for bulk nCB molecules measured using polarized Raman and carbon-13 NMR spectroscopy.<sup>14,25</sup> The molecular picture implied by our studies is in general agreement with experiments using the surface forces apparatus (SFA).<sup>24,26</sup> Briefly, with smooth high-energy surfaces, the SFA experiments observe layering in the nematic and smectic phases appropriate to planar alignment. In contrast much greater layer spacings, corresponding to the length of a dimer (Figure 1a), were observed between low-energy surfaces, implying homeotropic anchoring of the nCB pairs. Our ellipsometric study gave the additional result that for homeotropic anchoring the interface between the low-energy surface and isotropic phase is completely wet by a nematic film as  $T$  tends to  $T_{\text{IN}}$  from above.<sup>5</sup> This interesting case of complete wetting, not induced by surface energy, has been presumed to be associated with a growth of pseudo-smectic layers at the substrate surface. Even in bulk isotropic phase, there is believed to exist a significant amount of short-range smectic order, known as cybotactic clusters.<sup>27</sup> It would thus be of some interest to carry out detailed ATR-IR experiments close to the isotropic–nematic transition of 8CB on a CF<sub>3</sub> surface, where complete orientational wetting has been observed.<sup>5</sup> This, however, requires an order of magnitude better temperature control than used in these preliminary studies. Finally, we note that there is a frequency shift associated with homeotropic anchoring but not with planar anchoring. Recent

transmission IR experiments and theoretical calculations based on the GAMESS program suite have shown that this shift is associated with the formation of dimers.<sup>28–30</sup> This correlates well with the observation of complete orientational wetting by homeotropic nematic molecules at the substrate–isotropic interface, when the substrate is very low energy. Namely, such a class of complete wetting would have to be driven by nCB–nCB interactions and/or structural entropy.

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## References and Notes

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