Using Isotropic, Nematic, and Smectic Fluids for the Study of Self-Assembled Monolayers Formed from Alkanethiols on Gold

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The wetting of isotropic fluids is one of the oldest analytical methods[1] used for the study of surfaces. Although the balance of microscopic forces governing contact angles of isotropic fluids on surfaces is not yet fully understood,[2] this method enjoys great acceptance because it is surface-sensitive, simple to perform, and nondestructive to organic surfaces.[3] Herein we contrast the use of isotropic and anisotropic fluids (Figure 1) for the study of self-assembled monolayers (SAMs) formed by chemisorption of alkanethiols on films of gold.[4] We demonstrate that a fluid with long-range orientational order—a nematic liquid crystal—can be used to distinguish between pairs of surfaces that differ in molecular-level organization, mesoscale structure, or both, whereas isotropic fluids with the chemical functional groups of the nematic liquid crystal report these pairs of surfaces to be the same. A fluid with long-range positional and orientational order—a smectic liquid crystal—was found to be a more sensitive probe of molecular-level "imperfection" in a surface than a nematic fluid. These results can form the basis of strategies that use anisotropic fluids for the study of molecular-level and mesoscale structures on self-assembled surfaces.

We formed densely packed, quasi-crystalline SAMs on the surfaces of two types of thin, semitransparent films of gold (~100 Å of gold on 10 Å of Ti on glass) by immersion of the gold films in 1 mM ethanolic solutions of $CH_3(CH_2)_{15}SH$. "Uniformly" deposited films of gold were prepared by changing the angle and direction of incidence of the gold during deposition of the film, whereas "obliquely" deposited films of gold were prepared with an angle of incidence of 50° and a fixed direction of incidence.[5] Past studies have demonstrated
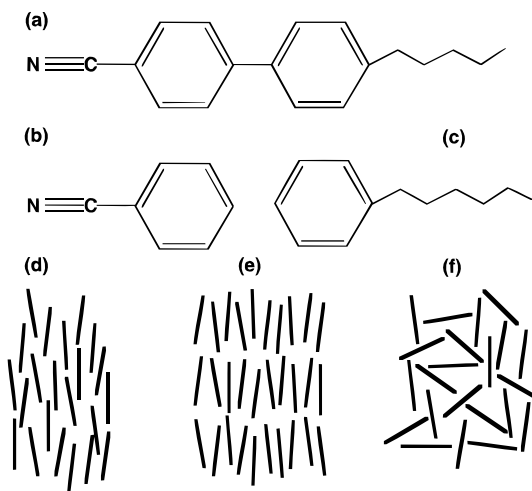
Figure 1. Chemical structures: (a) 4-cyano-4′-pentylbiphenyl (5CB). The structure of 8CB is the same as 5CB except the aliphatic chain of 8CB has 7 methylenes. (b) Benzonitrile. (c) Phenylhexane. At room temperature 5CB is a nematic fluid (d), 8CB is a smectic A fluid (e), and benzonitrile and phenylhexane are isotropic fluids (f).

that obliquely deposited films of metals or metal oxides can be statistically grooved or formed of "columnar" deposits, the details of which depend on factors such as rate and angle of deposition as well as the lateral mobility of adatoms.[6,7] Anisotropy in the shapes of grains (~250 Å in size) within our obliquely deposited films of gold was below the threshold detectable by scanning tunneling microscopy, plausibly because of the high mobility of adatoms of gold and the low rate of deposition (~0.2 Å/s). Furthermore, the contact angles (advancing and receding) of hexadecane, phenylhexane, and benzonitrile were (i) indistinguishable when measured on SAMs prepared on gold deposited uniformly or obliquely and (ii) indistinguishable when measured in orthogonal directions (AA′, AB) on SAMs on obliquely deposited gold (Table 1). We also prepared SAMs from $CH_3(CH_2)_{15}SH$ on obliquely deposited films of gold as thick as 2000 Å (deposited at 1 Å/s); although the hysteresis in the contact angle of hexadecane increased to 9°, no anisotropy was measured.

In contrast to the isotropic fluids and STM, the use of nematic liquid crystals did reveal differences between obliquely and uniformly deposited films of gold, and SAMs supported on these films. Optical textures[8,9] of nematic liquid crystals were near-planar and azimuthally degenerate when liquid crystals were in contact with "bare", uniformly deposited gold but showed a uniform orientation, normal to the direction of incidence of gold, on obliquely deposited gold. Similar behavior

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(5) The procedure used for the deposition of the films of gold as well as their characterization by scanning tunneling microscopy is reported elsewhere (see Gupta and Abbott, *Langmuir* **1996**, *12*, 2587.

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(7) Obliquely deposited films of silicon oxide (300−3200 Å thick, deposited at 15−20 Å/s) can have, for example, columnar deposits arranged with periods of hundreds of angstroms[6a] whereas grains within films of copper deposited obliquely (500 Å thick, deposited at 2 Å/s) have no measurable elongation (see: Nakahara, S.; Kuwahara, K.; Nishimura, A. *Thin Solid Films* **1980**, *72*, 297.).

(8) Liquid crystals were sandwiched between two SAMs spaced apart by using a 2 μm thick film of mylar.[9] The optical textures under cross-polars were formed by light transmitted through the gold films, SAMs, and liquid crystal.

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Table 1. Advancing (θ_a) and Receding (θ_r) Contact Angles of Hexadecane (HD), Phenylhexane (PH), and Benzonitrile (BN) Measured on SAMs Formed from Alkanethiols on Films of Gold Deposited "Uniformly" or "Obliquely" (See Text for Details)[a]

	θ_a (θ_r) along direction AA′			θ_a (θ_r) along direction AB		
type of surface	HD	PH	BN	HD	PH	BN
$CH_3(CH_2)_{15}SH$ on uniformly deposited gold	46 ± 1 (42 ± 1)	52 ± 1 (50 ± 1)	67 ± 1 (62 ± 1)	46 ± 1 (41 ± 1)	52 ± 1 (50 ± 1)	67 ± 1 (62 ± 1)
$CH_3(CH_2)_{15}SH$ on obliquely deposited gold	46 ± 1 (42 ± 1)	52 ± 1 (50 ± 1)	66 ± 1 (63 ± 1)	46 ± 1 (42 ± 1)	52 ± 1 (50 ± 1)	66 ± 1 (63 ± 1)
mixed SAM C ($X_{16} = 25 \pm 5\%$)	36 ± 1 (33 ± 1)	42 ± 1 (38 ± 1)	59 ± 1 (56 ± 1)	36 ± 1 (33 ± 1)	42 ± 1 (38 ± 1)	59 ± 1 (57 ± 1)
mixed SAM D ($X_{16} = 61 \pm 8\%$)	37 ± 1 (34 ± 1)	42 ± 1 (39 ± 1)	59 ± 1 (56 ± 1)	37 ± 1 (34 ± 1)	42 ± 1 (40 ± 1)	38 ± 1 (55 ± 1)

[a] The direction AA′ is parallel to the direction of deposition of the gold for obliquely deposited films, and the direction AB is perpendicular to the direction of deposition.
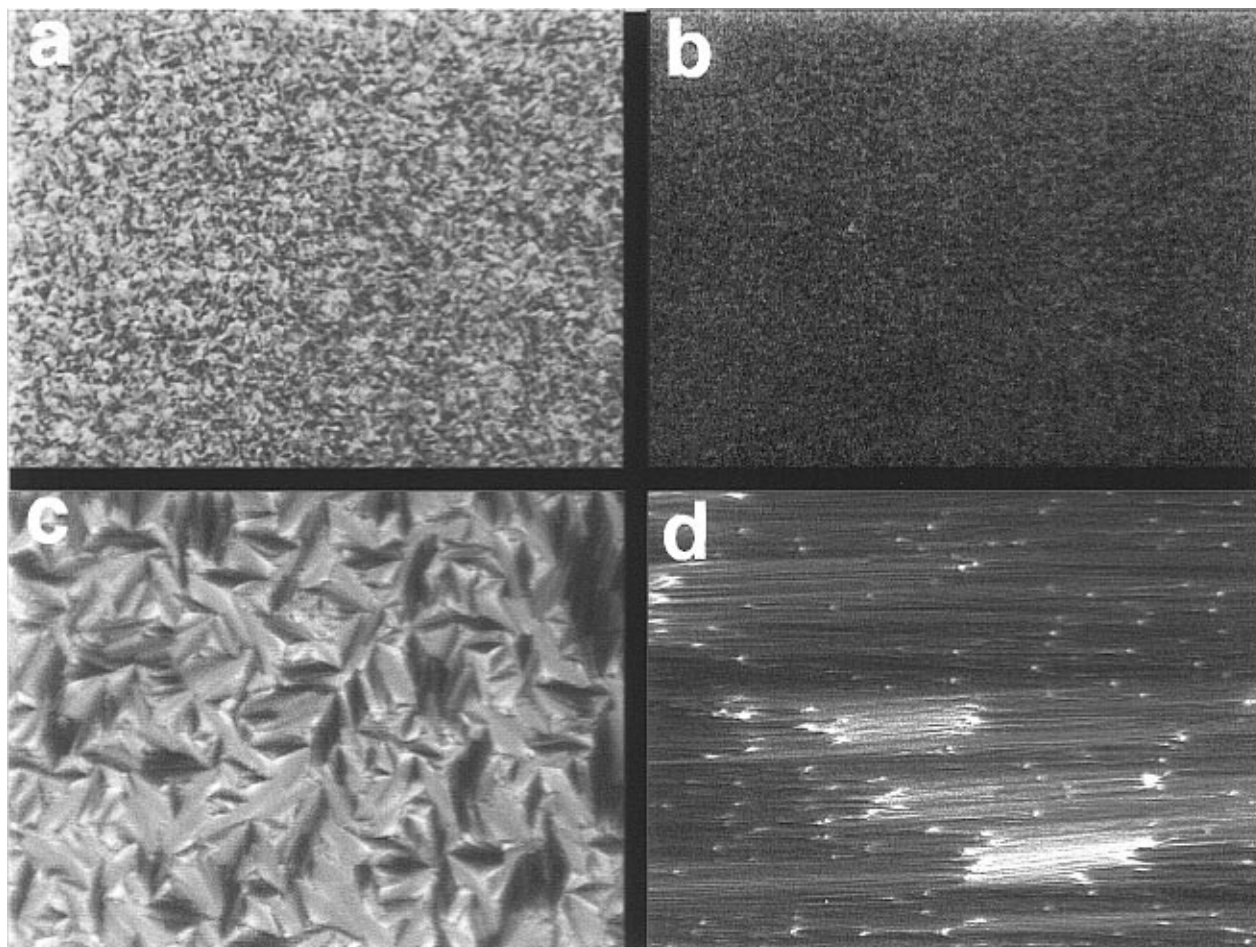

Figure 2. Optical textures (crossed polars) of 5CB and 8CB in contact with SAMs formed from $CH_3(CH_2)_{15}SH$ on the surface of uniformly or obliquely deposited films of gold: (a) uniformly deposited gold and 5CB; (b) obliquely deposited gold and 5CB; (c) uniformly deposited gold and 8CB; (d) obliquely deposited gold and 8CB. The horizontal dimension of each image is 550 μm. The uniformly oriented samples (b and d) did not transmit light when the optical axis (long axis of the rodlike nematic molecule) was parallel to either the polarizer or analyzer. The nonuniformly oriented samples (a and c) did not show complete extinction of light; these samples exhibited dark and bright domains at all orientations relative to the polars.

has been observed on obliquely deposited films of SiO and can be plausibly described by an elastic mechanism of anchoring.[6a,10] This change in anchoring of the nematic liquid crystal from azimuthally degenerate on uniformly deposited gold to uniform on obliquely deposited gold was also observed when the films of gold supported SAMs. Figure 2a,b shows the optical textures of 5CB on films of gold that support SAMs formed from $CH_3(CH_2)_{15}SH$. Self-assembled monolayers formed from alkanethiols with an odd number of methylenes on

obliquely deposited gold, however, caused the nematic liquid crystal to orient parallel to the direction of incidence of gold whereas alkanethiols with an even number of methylenes caused the orientation of the liquid crystal to be perpendicular to the direction of incidence of gold. Because FTIR spectra of SAMs formed from alkanethiols with odd and even number of methylenes show the orientation of the methyl group

(10) Elastic distortion of the director of the liquid crystal (for example, caused by columnar deposits on a surface) can determine the alignment of a liquid crystal on a surface, and is referred to as an "elastic mechanism" of anchoring.

(11) The transition dipole moment of the symmetric CH_3 stretching mode is parallel to the surface of the SAM for SAMs formed from alkanethiols with an even number of CH_2 groups but is perpendicular to the surface of the SAM for SAMs formed from alkanethiols with odd numbers of CH_2 groups (see: Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558.).
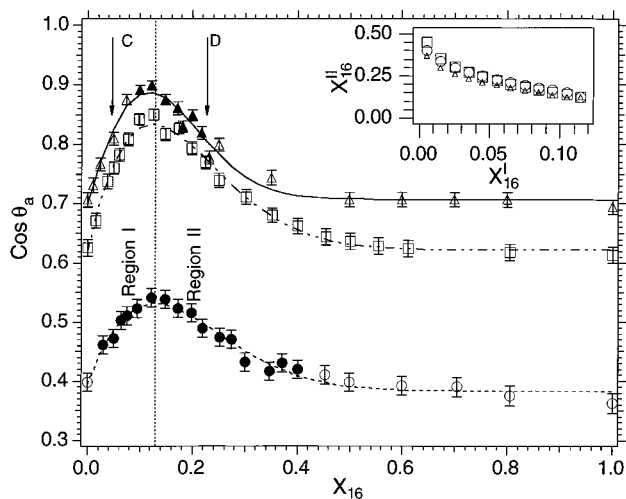
Figure 3. Cosine of the advancing contact angle (θ_a) of hexadecane ($\triangle$), phenylhexane ($\square$), and benzonitrile ($\bigcirc$) on mixed SAMs formed by coadsorption of $CH_3(CH_2)_{15}SH$ and $CH_3(CH_2)_9SH$. The abscissa is the fraction of $CH_3(CH_2)_{15}SH$ in the ethanolic solution from which the mixed SAMs were formed (1 mM total alkanethiol concentration; formed for 2 h). Mixed SAMs labeled C and D are discussed in the text. The inset shows the compositions of solutions from which SAMs with the same contact angles were formed: compositions from region I are shown on the abscissa and compositions from region II are shown on the ordinate. Filled triangles indicate SAMs on which 5CB was homeotropically anchored and filled circles indicate homeotropic anchoring of 8CB. Open symbols indicate tilted or planar anchoring of 5CB and 8CB.

of the SAMs to differ,[11] we infer that nematic liquid crystals can detect changes in SAMs, on obliquely deposited gold, that result from differences in the orientation of methyl groups. Optical textures of liquid crystals on the SAMs formed from alkanethiols with odd and even number of methylenes were, in contrast, not systematically different when supported on uniformly deposited gold. A full account of these odd−even effects is forthcoming.

Self-assembled monolayers prepared by coadsorption of long and short alkanethiols on gold permit the synthesis of surfaces that differ in conformational order.[12,13] Figure 3 shows contact angles of hexadecane, benzonitrile, and phenylhexane measured on mixed SAMs formed by coadsorption of $CH_3(CH_2)_{15}SH$ and $CH_3(CH_2)_9SH$. The contact angles on these mixed SAMs are less than single-component SAMs because the outer regions of the long alkane chains within these mixed SAMs are conformationally disordered.[12−15] In general, we observed there to be two SAMs—each with different compositions, e.g., SAMs C and D in Figure 3—that gave rise to the same contact angle (advancing and receding) of each fluid (Table 1). The inset in Figure 3 shows the relationship between the composition of solutions used to form SAMs on which contact angles were measured to be the same. We found the curve to be a "universal" one, independent of the fluid used to measure the contact angles.[16] Pairs of SAMs on which the contact angles (advancing and receding) were the same, such

as SAMs C and D in Figure 3, did, however, cause nematic phases to assume different orientations.[17,18] We observed a nematic phase of 5CB to anchor parallel to the surface of mixed SAM C but perpendicular to the surface (homeotropic) of mixed SAM D (Figure 3). The compositions of these mixed SAMs were determined by X-ray photoelectron spectroscopy[15] to be (C) $X_{16} = 25 \pm 5\%$ and (D) $X_{16} = 61 \pm 8\%$, where X_{16} is the mole fraction of $CH_3(CH_2)_{15}SH$ within the SAM (Table 1). The reflection absorption infrared spectra (RAIRS) of SAMs C and D were consistent with past studies;[13] the outer methylenes of SAM C are less densely packed and more disordered and mobile as compared to SAM D. The nematic phase can, therefore, be used to distinguish between pairs of SAMs that differ in the density of packing and degree of conformational disorder and that are indistinguishable when examined using isotropic fluids.

Optical textures of smectic 8CB were near-planar and azimuthally nonuniform on SAMs formed from $CH_3(CH_2)_{15}SH$ when supported on uniformly deposited gold but showed a preferred direction, parallel to the direction of incidence of gold, on obliquely deposited gold (Figure 2c,d). The introduction of only a few percent of $CH_3(CH_2)_9SH$ into a SAM formed from $CH_3(CH_2)_{15}SH$ (or vice versa) caused the anchoring of 8CB to change from planar to homeotropic (Figure 3). The smectic phase is, therefore, sensitive to the *onset* of disorder within SAMs caused by introduction of a minor species and can be used as a probe of imperfection within these types of highly organized (pseudocrystalline) organic surfaces.[19] The smectic 8CB, however, did not discriminate between mixed SAMs C and D and anchored homeotropically on both.

Methods for the study of surfaces that are based on the use of isotropic, nematic and smectic fluids differ in their sensitivity to the structure of surfaces for at least three reasons. First, contact angles (θ) depend on the excess free energies of *three* interfaces—solid−liquid (γ_{SL}), liquid−vapor (γ_{LV}), and solid−vapor (γ_{SV}); $\cos\theta = \gamma_{SV} - \gamma_{SL}/\gamma_{LV}$. Changes in γ_{SL} can be masked by γ_{SV} and γ_{LV}. In contrast, birefringence that results from long-range orientational order within liquid crystals makes possible measurements of the interactions of liquid crystals with a *single* type of interface. Second,

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(16) Because there exists such a "universal curve" to relate the solution compositions (and, therefore, surface compositions), we conclude that these SAMs reorganize similarly, or not at all, when placed in contact with either hexadecane, benzonitrile, or phenylhexane. We also measured the hysteresis in each contact angle ($\gamma_{lv}\Delta\cos\theta$) to be 1.5 ± 0.7 mN/m, independent of the fluid and composition of the SAM.

(17) An anchoring transition from near planar to homeotropic is also observed as a function of composition for mixed SAMs formed from (i) $CH_3(CH_2)_4SH$ and $CH_3(CH_2)_{15}SH$ (see ref 9) and (ii) $CH_3(CH_2)_{11}SH$ and $CH_3(CH_2)_{15}SH$ (Drawhorn, R. A.; Abbott, N. L., unpublished results).

(18) Past measurements of contact angles of polar and nonpolar fluids on SAMs formed from alkanethiols on gold have been interpreted to infer the interactions between fluids and these surfaces to be dispersive.[12,14] According to Naemura (Naemura, S. *Mol. Cryst. Liq. Cryst.* **1981**, *68*, 183), substrates with purely dispersive interactions obey the Creagh−Kmetz rule (Creagh, L. T.; Kmetz, A. R. *Mol. Cryst. Liq. Cryst.* **1973**, *24*, 59). This rule predicts the anchoring of 5CB to be homeotropic when the critical surface tension (γ_c) of the substrate is less than the surface tension of 5CB (γ_{LC}). The value of γ_c for single-component SAMs formed from alkanethiols is reported to be 19 mN/m,[14] which is less than the surface tension of 5CB (30−40 mN/m; Cognard, J. *Mol. Cryst. Liq. Cryst., Suppl. 1* **1982**, *78*, 1). Our observations do not agree with the rule of Creagh and Kmetz.

(19) We infer the onset of conformational disorder within the mixed SAMs by measurement of a decrease in the contact angle of hexadecane.

mesoscale structures on surfaces perturb long-range orientational and positional order within liquid crystals by causing bending, splaying, or twisting deformations. Isotropic fluids, in contrast, cannot experience these deformations on comparable spatial scales. Third, liquid crystals are known to induce large changes in the molecular-level organization within loosely-packed, conformationally disordered, organic surfaces[20] whereas, in general, isotropic fluids do not (in the absence of specific interactions with the SAM, such as H bonding[21]). Differences in the molecular-level organization within mixed SAMs such as SAMs C and D (Figure 3; as revealed by RAIRS prior to contact with liquid crystal) are likely amplified by restructuring upon contact with the nematic liquid crystal. A study to investigate the extent of restructuring of SAMs upon contact with liquid crystals is underway.

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