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Comparison of the anchoring of nematic liquid crystals on self-assembled monolayers formed from semifluorinated thiols and alkanethiols

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The anchoring of nematic liquid crystals on self-assembled monolayers (SAMs) formed by the chemisorption of semifluorinated thiols or alkanethiols on gold is compared and contrasted. The planar anchoring of 4-*n*-pentyl-4′-cyanobiphenyl (5CB) observed in the past on SAMs formed from alkanethiols is also observed on SAMs formed from semifluorinated thiols. The azimuthal anchoring of 5CB, however, differs on these two types of surfaces: nematic 5CB anchored on SAMs formed from alkanethiols has a grainy appearance due to the formation of domains with sizes $<10\,\mu$m whereas 5CB forms large domains ($\sim 100\,\mu$m) with diffuse branches emerging from defects of strength 1/2 when anchored on SAMs formed from semifluorinated thiols. Mixed (two-component) SAMs formed from either short and long semifluorinated thiols or short and long alkanethiols cause homeotropic anchoring of 5CB. We discuss these results in light of the known differences in the structure of SAMs formed from alkanethiols and semifluorinated thiols, i.e. the tilt of the chains and conformational freedom (flexibility) of the chains within these SAMs.

1. Introduction

The anchoring of liquid crystals by monolayers of organic molecules supported on solid substrates has been extensively investigated because, in principle, manipulation of the structure of the monolayer provides a means to control alignment of the contacting liquid crystal [1, 2]. The relationship between the structure of monolayers supported on solids and the anchoring of liquid crystals remains tenuous, however, largely because experimental systems studied in the past have not permitted the synthesis of surfaces with the precision and control necessary to test theories of the anchoring of liquid crystals by organic surfaces.

Past studies of the anchoring of liquid crystals on monolayers of organic molecules have correlated changes in the structures of the monolayers with changes in anchoring [3–6]. Unambiguous assignment of the molecular-level mechanisms responsible for the alignment of the liquid crystals has, in general, not been possible. For example, planar (optical axis of the liquid crystal parallel to surface) to homeotropic (optical axis of the liquid crystal normal to surface) anchoring transitions have been correlated with the packing density of the aliphatic chains of amphiphiles within monolayers formed by physisorption or deposition using the Langmuir–Blodgett (LB) method [3, 6]. Because these monolayers were formed from amphiphiles with charged or zwitterionic head groups, assignment of the planar to homeotropic anchoring transition to the change in density of the aliphatic chains within the monolayer (steric interaction) is not possible. It is equally plausible that the planar to homeotropic anchoring transition is caused by interactions of the dipoles and quadrupoles of the mesogens with the electric fields associated with the polar head groups of the amphiphiles that form the monolayer. Furthermore, because these monolayers are physisorbed to their substrates, the states of the monolayers after contact with liquid crystal (and heating) are largely unknown. Monolayer films prepared by spontaneous adsorption or LB deposition are known to change irreversibly upon heating [7].

Silanized surfaces have also been used to study the anchoring of liquid crystals [1, 8]. Surfaces prepared by

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the spin coating of solutions of silanes do not lead to monolayer surfaces. The structures of such surfaces are unknown and, therefore, not useful for fundamental studies of the anchoring of liquid crystals. Since the early work of Sagiv and coworkers [9], a great deal of work has focused on the use of silane *monolayers* (prepared by the reaction of organosilanes onto silicon oxide) for the anchoring of liquid crystals [10]. Poor reproducibility from laboratory to laboratory, however, has hindered the past usefulness of this system [11]. It is only recently that experimental conditions leading to the formation of densely packed monolayers formed from alkyltrichlorosilanes have been clearly established [12]. We note also that a relatively small number of functional groups can be introduced into monolayers formed from ω-substituted alkyltrichlorosilanes [7, 11, 13].

This paper reports the use of self-assembled monolayers (SAMs) formed by chemisorption of organosulfur compounds (for example, dialkyldisulfides, alkanethiols, semifluorinated thiols) on surfaces of gold as the basis of a simple, robust and versatile method for the preparation of surfaces for the anchoring of liquid crystals. These chemisorbed monolayers are thermally stable, form spontaneously and are, therefore, distinguished from physisorbed monolayers used in the past for the anchoring of liquid crystals. The physicochemical properties of SAMs formed from organosulfur compounds can be easily manipulated by using ω-functionalized alkanethiols, $X(CH_2)_nSH$, where X can be CH_3, COOH, OH, CH, Br, CF_3, OCH_3, ferrocene, azobenzene and other functional groups [7, 11, 14–16]. These surfaces have been successfully used as models for a variety of fundamental studies of interfacial phenomena in the physical, chemical and biological sciences [7].

Self-assembled monolayers formed by the chemisorption of alkanethiols on gold are now likely to be the most intensively characterized synthetic organic monolayers [7, 14]. These monolayers form spontaneously upon immersion of evaporated films of gold in solutions of alkanethiols. The sulphur head groups of the alkanethiols chemisorb and form a commensurate $\sqrt{3}\times\sqrt{3}R30°$ lattice on the surface of Au(111) [17–20].† The aliphatic chains within monolayers formed from $CH_3(CH_2)_nSH$, $n \geqslant 9$, are extended in the all-*trans* conformation. Because the spacing between sulphur groups on the $\sqrt{3}\times\sqrt{3}R30°$ lattice is 4·9 Å, whereas the van der Waals diameter of an aliphatic chain is only ~4 Å, the aliphatic chains of alkanethiols chemisorbed on Au(111) are tilted from the normal by approximately 30° so as to come into van der Waals contact and maximize cohesive dispersion interactions. Studies of the lateral structure within monolayers using X-ray diffraction reveal the existence of domains of ~100 Å, where each domain has one of six different tilt directions relative to the Au(111) face [19, 20].

Self-assembled monolayers formed from fluorinated organosulphur compounds on the surface of gold have also been reported [21, 22]. These surfaces can be highly ordered. The origin of the order within these SAMs is largely *intramolecular* and contrasts, therefore, to SAMs formed from alkanethiols where the order largely reflects a cohesive *intermolecular* dispersion force. Steric interactions between adjacent fluorine atoms on the same perfluorinated chain cause the chain to twist into a rigid, helical conformation. An isolated perfluorinated chain is stiff when compared to an aliphatic chain. Because perfluorinated chains have larger cross-sectional areas than alkanethiols, SAMs formed on gold from semifluorinated thiols are not tilted from the normal to the same degree as alkanethiols [22]. Estimates made by using grazing incidence Fourier transform infrared (FTIR) spectroscopy report the tilt of the perfluorinated chains to be 0–10°. Because perfluorinated chains within SAMs are not tilted to the same degree as the chains of alkanethiols, SAMs formed from semifluorinated thiols are not expected to possess tilt domains of the type found in SAMs formed from alkanethiols (see above).

Several recent papers have reported the use of SAMs formed from alkanethiols on gold in experimental studies of the anchoring of liquid crystals on surfaces [23–27]. The principal results of these studies are threefold:

First, the anchoring of nematic phases of 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA), and smectic A phases of 4-*n*-octyl-4′-cyanobiphenyl (8CB), on SAMs formed from alkanethiols ($CH_3(CH_2)_nSH$, $n \leqslant 17$) on gold was observed to be planar [24–27]. These observations are surprising and contrast with past reports of homeotropic anchoring of nematic phases of 5CB anchored on SAMs formed from alkyltrichlorosilanes (for example, octadecyltrichlorosilane, OTS) on fused silica [10]. Anisotropic dispersion forces acting between mesogens and gold (through a SAM) likely cause the planar anchoring of liquid crystals on SAMs supported on gold [26]. Although the anchoring of 5CB was observed to be planar on SAMs on gold, the optical textures appeared grainy on micrometer length scales when the SAMs were supported on films of gold deposited without a preferred direction (achieved by rotation of the substrate during deposition of the gold film). Diffuse meandering branches characteristic of degenerate azimuthal anchoring† of 5CB [1, 2] were not generally

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† Recent studies have shown the existence of a c(4 × 2) superlattice, the cause of which remains unresolved (see [20]).

† The term 'azimuthal anchoring' refers to the azimuthal orientation of the liquid crystal within the plane defined by the surface.

observed on SAMs formed from alkanethiols on gold [23–26].

Second, nematic and smectic liquid crystals were reported to align with uniform azimuthal orientations on SAMs supported on gold deposited with a preferred direction (oblique deposition of gold) [24, 25, 27]. The azimuthal orientations of the liquid crystals were parallel to the direction of incidence of the gold when the SAMs were formed from $CH_3(CH_2)_nSH$ with n being an odd integer and perpendicular to the direction of incidence of the gold for even values of n [27]. Because the aliphatic chains of SAMs formed from alkanethiols are tilted by 30° from the normal of the surface, the orientation of the methyl groups (CH_3) at the outer surface of these SAMs differs for SAMs formed from alkanethiols with odd and even numbers of methylene groups (CH_2). This structural difference is known to cause an odd–even effect in contact angles of fluids measured on these surfaces [28].

Thirdly, whereas single component SAMs formed from alkanethiols on gold cause planar anchoring of nematic and smectic liquid crystals, mixed SAMs formed from short and long alkanethiols can cause homeotropic anchoring [23–25]. The protruding outer segments of the long chains within mixed SAMs formed from short and long chains are conformationally disordered and loosely-packed when characterized prior to contact with the liquid crystal. The low number density of long aliphatic chains within mixed SAMs was proposed to lead to the homeotropic anchoring of liquid crystals through a steric mechanism of interaction (interdigitation) [6, 25].

In this paper the anchoring of liquid crystals on SAMs formed from semifluorinated thiols is reported. Past reports do not describe the anchoring of liquid crystals on *densely packed* monolayers formed from semifluorinated chains. Past investigations of fluorocarbon surfaces have focused on surfaces coated with films of fluorinated polymers such as poly(tetrafluoroethylene) (Teflon^{TM}) and poly(vinylidene fluoride) (Tedlar^{TM}), or fluorine-containing surface-active agents that pack loosely and host polar/charged groups [1, 8, 29]. Results reported in the past for the anchoring of liquid crystals on fluorinated surfaces are variable, probably reflecting differences in the methods of preparation of the surfaces (for example, plasma polymerization of teflon versus sliding contact of a teflon block). In general, the fluorocarbon surface, which is a low energy surface, is reported to cause homeotropic anchoring [8, 29]. However, anchoring transitions from homeotropic to planar as a function of decreasing temperature have also been reported [29, 30].

The use of SAMs formed from semifluorinated thiols permits the preparation of well-defined fluorocarbon surfaces for studies of the anchoring of liquid crystals. Furthermore, comparison of the anchoring of liquid crystals on SAMs formed from either alkanethiols or semifluorinated thiols permits three fundamental questions to be addressed:

Question 1: Does the 30° tilt of the aliphatic chains within SAMs formed from alkanethiols on gold influence the orientation of liquid crystals on these surfaces? Chains within SAMs formed from alkanethiols on Au(111) are tilted by 30° from the normal [14] whereas SAMs formed from alkyltrichlorosilanes are tilted by 10° [12]. Differences in the tilts of chains within these SAMs can plausibly explain the planar anchoring of 5CB observed on the former surfaces and the homeotropic anchoring observed on the latter ones. Herein the question of whether the tilt of chains within SAMs influences the anchoring of liquid crystals is addressed by forming SAMs from the following semifluorinated thiols: $CF_3(CF_2)_7CONH(CH_2)_2SH$ (**1**), $CF_3(CF_2)_7(CH_2)_2SH$ (**2**) and $CF_3(CF_2)_7(CH_2)_{11}SH$ (**3**). Chains within SAMs formed from these semifluorinated thiols tilt less than chains within SAMs formed from alkanethiols when both types of SAMs are supported on evaporated films of gold [22, 24, 31].

Question 2: Do the ~100 Å-scale domains of uniform molecular tilt within SAMs formed from alkanethiols on Au(111) cause the graininess and absence of diffuse meandering branches in textures of nematic phases of 5CB anchored on these surfaces [23–25]? Because perfluorinated chains within SAMs formed from semifluorinated thiols (**1** or **2**) on Au(111) are oriented almost normal to the surface of the gold, these SAMs cannot possess the small domains of uniform tilt that characterize alkanethiols on Au(111). By comparing and contrasting the azimuthal anchoring of 5CB on single component SAMs formed from semifluorinated thiols, this paper reports the effect of the tilt of chains within SAMs on the azimuthal anchoring of liquid crystals.

Question 3: What structural characteristics of SAMs are responsible for the transition from planar to homeotropic anchoring observed on mixed SAMs formed from short and long chains? The long protruding chains in SAMs formed from short and long alkanethiols are flexible and conformationally disordered and can, therefore, reorganize upon contact with the liquid crystals [25]. Herein, the role of the restructuring of the SAM upon contact with liquid crystals is addressed by studying the anchoring of 5CB on mixed SAMs formed from short and long semifluorinated thiols (**1** and **3**). The long protruding (stiff) perfluorinated chains within these SAMs are restricted in their ability to reorganize upon contact with the liquid crystal.

2. Materials and experimental methods

2.1. *Materials*

Hexadecane was purchased from Aldrich and passed through a column of neutral alumina before use. The semifluorinated thiols $CF_3(CF_2)_7CONH(CH_2)_2SH$ (**1**), $CF_3(CF_2)_7(CH_2)_2SH$ (**2**) and $CF_3(CF_2)_7(CH_2)_{11}SH$ (**3**) were available from previous studies [22, 31]. Decanethiol (**4**), dodecanethiol (**5**) and hexadecanethiol (**6**) were purchased from Aldrich, and 4-*n*-pentyl-4′-cyanobiphenyl (5CB, $T_{NI} = 35°C$, $T_{CrN} = 24°C$) was purchased from EM Sciences. Anhydrous ethanol was purchased from Quantum.

2.2. *Sample preparation*

Glass microscope slides were cleaned in 'piranha' solution (70:30 concentrated H_2SO_4/30 per cent H_2O_2, **WARNING:** *Piranha solution reacts strongly with organic compounds and should be handled with extreme caution; do not store the solution in closed containers*) for 30 min at 90°C. Substrates of gold were prepared by evaporation (100 Å at 0·2 Å s^{-1}, $P < 5 \times 10^{-6}$ torr, with epicyclic rotation of sample relative to the incident flux of gold) onto microscope slides [24]. Approximately 10 Å of titanium was used to promote adhesion between the gold and glass microscope slides. Self-assembled monolayers were formed for 2 h in ethanolic solutions that contained 1 mM total concentration of organothiol. Ellipsometry ($\lambda = 633$ nm, $\theta = 70°$) was used to measure the thickness of each SAM. Binary mixed SAMs were formed by coadsorption of the thiols such that the compositions of SAMs were 1 : 1 for SAMs formed from **1** and **2** and from **1** and **3**†. The compositions of mixed SAMs formed under these conditions were controlled largely by the kinetics of the chemisorption.

2.3. *Contact angles*

Advancing and receding contact angles of hexadecane were measured using a Rame–Hart goniometer and environmental chamber. A drop of hexadecane was placed in contact with the surface using the needle of a syringe. By increasing or decreasing the volume of the drop, the advancing and receding contact angles were measured. The environmental chamber was purged with nitrogen during measurements of the contact angles to avoid contamination of the SAMs. All contact angles reported are the averages of at least 12 measurements at four different places on the sample.

2.4. *Polarized light microscopy*

Self-assembled monolayers supported on films of gold were paired and spaced apart by 2 or 25 μm thick spacers of mylar to form optical cells. A drop of 5CB was heated into the isotropic phase, drawn between the surfaces of the optical cells by capillary action, and then cooled into the nematic phase (~1°C min^{-1}). A polarized light microscope (Olympus) was used to observe the optical textures of the liquid crystals at room temperature [23–25]. Conoscopic interference figures [23–25] were used to confirm the orientation of the director of the liquid crystal relative to the substrate in a uniformly anchored sample.

3. Results

3.1. *Single component SAMs formed from semifluorinated thiols*

The cartoons presented in figure 1 summarize our understanding of the structure of SAMs formed from **1**–**3** and **5**. These cartoons are largely based on the results of investigations using X-ray photoelectron spectroscopy (XPS), grazing incidence FTIR spectroscopy and near edge X-ray absorption fine structure (NEXAFS) spectroscopy [22, 31]. All four compounds form densely packed and highly ordered SAMs. The semifluorinated chains are, in general, tilted away from the normal less than the chains of alkanethiols; the semifluorinated chains appear to be nearly normal to the surface when they contain short CH_2 sequences (for example, **1** and **2**) [22, 31]. The perfluorinated chains (outer region) within SAMs formed from **3** are tilted away from the normal more than the perfluorinated chains within SAMs formed from **1** and **2** [31]. The tilt of the aliphatic chains (inner region) in SAMs formed from **3** is less than the tilt of the aliphatic chains of **5** [31]. Evidence for hydrogen bonding between C=O and NH within SAMs formed from **1** has been observed in grazing incidence FTIR spectra. The hydrogen bonding does not appear to alter the packing density of the chains on the surface [22, 31].

Self-assembled monolayers formed from **1**–**3** were also characterized by ellipsometry and contact angles of hexadecane (see the table). The ellipsometric thicknesses of SAMs formed from **1**–**3** were measured to be 17 Å, 15 Å and 26 Å. These thicknesses are consistent with the formation of densely packed monolayers [31]. The advancing and receding contact angles of hexadecane were 75–76° and 71–73°, respectively, for all samples with the exception of the advancing contact angle measured on SAMs formed from **3**. All contact angles are consistent with presentation of CF_3 and CF_2 groups at the outer surface of each SAM [7]. The advancing contact angle of hexadecane measured on SAMs formed from **3** was 79°, suggesting that the outer regions of these SAMs were structured differently than SAMs formed from **1** or **2** (see comment above regarding tilt of chains). Optical cells assembled with surfaces formed from **3** could not be filled with liquid crystal by using capillary action when 2 μm thick mylar was used to separate the surfaces of the cell. We report, therefore,

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† Solution compositions of 1 : 1 and 3 : 1 were needed to form mixed SAMs with compositions of 1 : 1 of **1** and **2**, and **1** and **3**, respectively.

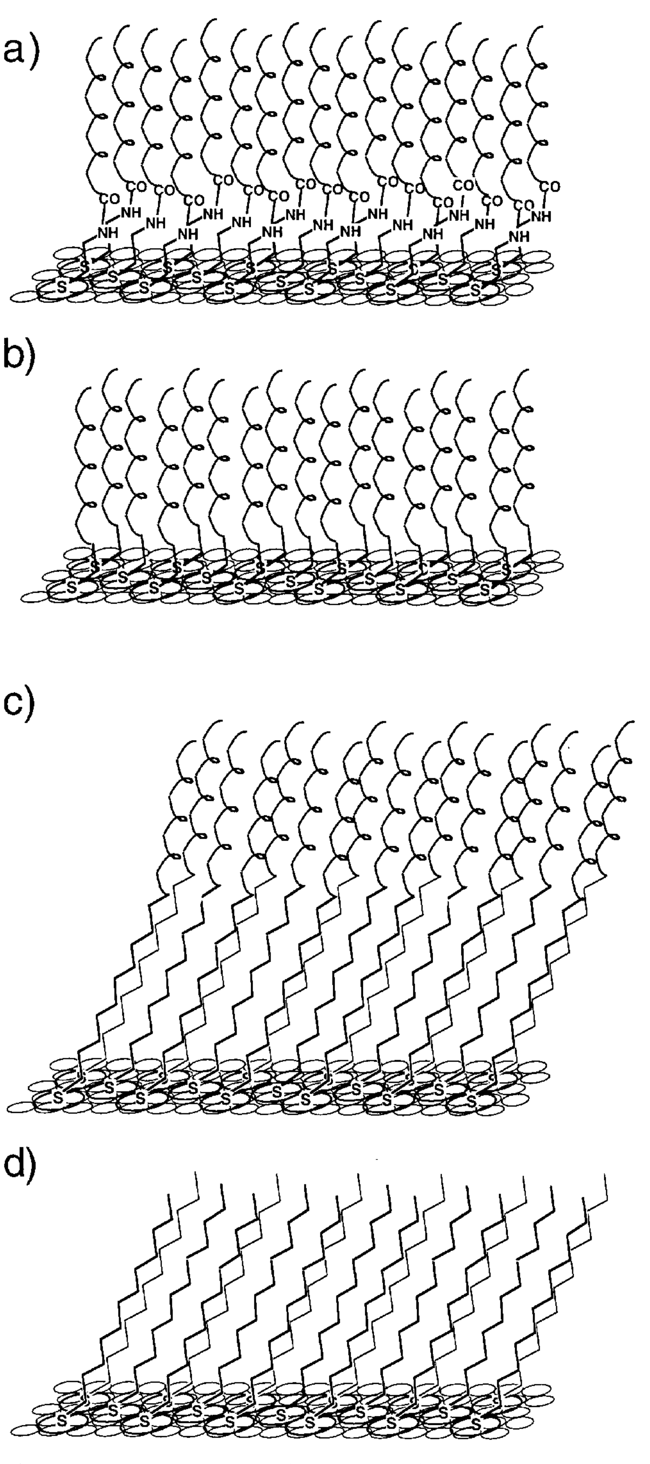


Figure 1. Cartoons of SAMs formed from (*a*) **1**: $CF_3(CF_2)_7CONH(CH_2)_2SH$, (*b*) **2**: $CF_3(CF_2)_7(CH_2)_2SH$, (*c*) **3**: $CF_3(CF_2)_7(CH_2)_{11}SH$, and (*d*) **5**: $CH_3(CH_2)_{11}SH$. The semifluorinated chains form a helical confirmation within the SAM; the axis of the helix is almost normal to the surface for SAMs formed from either **1** or **2** and slightly tilted from the normal for SAMs formed from **3**. In comparison, the alkanethiols are tilted 30° from the normal to the surface. The sulphur headgroups are arranged in a lattice commensurate with a (111) surface of gold. The superlattice [19–21] is not shown.

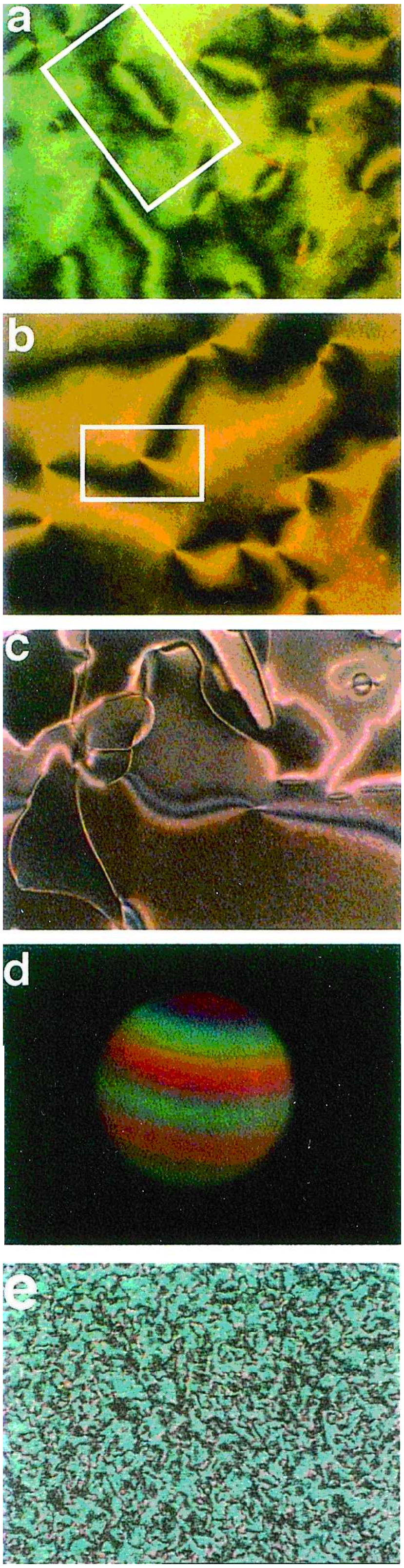
Table. Contact angles of hexadecane and descriptions of the anchoring of 5CB on SAMs formed from single component semifluorinated thiols and by coadsorption of semifluorinated thiols.

SAM	θ_a	θ_r	Anchoring of 5CB
1	75	71	schlieren, planar, 1/2 defects
2	75	73	schlieren, planar, 1/2 defects
3	79	73	‘marbled’, tilted
1 and **2**	75	72	schlieren, tilted, no 1/2 defects
1 and **3**	76	68	uniform, homeotropic

results for SAMs formed from **3** in cells with surfaces spaced apart by 25 μm thick mylar.

Optical textures of 5CB anchored on SAMs formed from **1**–**3** and **5** are shown in figure 2. Optical textures of 5CB anchored on SAMs formed from **6** have been published elsewhere and are similar to the optical textures of SAMs formed from **5** [23–25]. The table summarizes the salient features of the optical textures reported in figure 2. The diffuse, meandering branches emerging from defects of strength 1/2 (two branches) within nematic phases of 5CB supported on SAMs formed from either **1** or **2** (see figures 2 (*a*) and (*b*)) are consistent with planar, azimuthally degenerate anchoring of 5CB. In contrast, the optical textures of 5CB anchored on SAMs formed from **5** (see figure 2 (*e*)) have a grainy appearance with characteristic dimensions that are much smaller than observed with SAMs formed from either **1** or **2**. Although meandering branches and 1/2 defects are not generally observed when 5CB is anchored on SAMs formed from alkanethiols, measurements of the anchoring of 5CB on SAMs formed from $CH_3(CH_2)_{11}SH$ (an alkanethiol that forms a SAM of similar thickness to **1** or **2**) confirm planar anchoring [24, 26, 27]. Thus, the anchoring of 5CB is planar on SAMs formed from **1**, **2** and alkanethiols. We note also that the spatial correlation of the azimuthal alignment of the director of 5CB is greater for 5CB anchored on SAMs formed from semifluorinated thiols than for SAMs formed from alkanethiols.

The optical textures of 5CB anchored on SAMs formed from **3** were different from **1** or **2**. The textures observed on SAMs formed from **3** were not schlieren, but ‘marbled’ (see figure 2 (*c*)). The domains of 5CB were larger on SAMs formed from **3** than for 5CB on SAMs formed from $CH_3(CH_2)_{15}SH$ (a monolayer of similar thickness to **3**). Some domains were sufficiently large that a conoscopic image could be obtained (see figure 2 (*d*)). The position of the interference fringes indicated a tilt of the optical axis ($\gg 15°$) away from the surface normal.



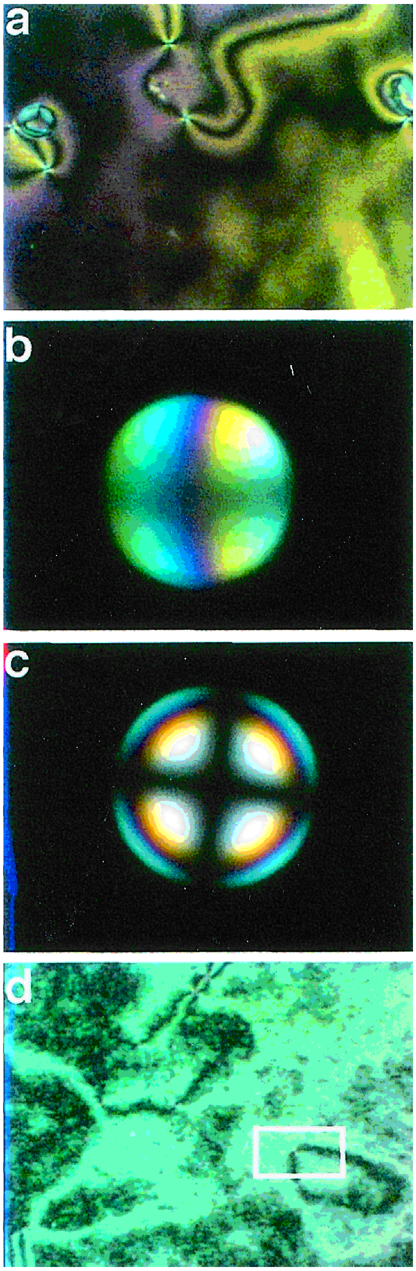


Figure 4. Optical textures of 5CB supported on SAMs formed by coadsorption of (*a*) **1**: $CF_3(CF_2)_7CONH(CH_2)_2SH$ and **2**: $CF_3(CF_2)_7(CH_2)_2SH$ (orthoscopic observation), (*b*) **1**: $CF_3(CF_2)_7CONH(CH_2)_2SH$ and **2**: $CF_3(CF_2)_7(CH_2)_2SH$ (conoscopic observation), (*c*) **1**: $CF_3(CF_2)_7CONH(CH_2)_2SH$ and **3**: $CF_3(CF_2)_7(CH_2)_{11}SH$ (conoscopic observation) and (*d*) **4**: $CH_3(CH_2)_9SH$ and **5**: $CH_3(CH_2)_{11}SH$ (orthoscopic observation). The rectangle in (*d*) encloses a 1/2 defect. The lateral dimension of each orthoscopic figure is 550 μm.

Figure 2. Optical textures of 5CB supported on SAMs formed from (*a*) **1**: $CF_3(CF_2)_7CONH(CH_2)_2SH$, (*b*) **2**: $CF_3(CF_2)_7(CH_2)_2SH$, (*c*) **3**: $CF_3(CF_2)_7(CH_2)_{11}SH$ (all orthoscopic observation) (*d*) **3**: $CF_3(CF_2)_7(CH_2)_{11}SH$ (conoscopic observation) (*e*) **5**: $CH_3(CH_2)_{11}SH$ (orthoscopic). The rectangles in (*a*) and (*b*) enclose 1/2 defects. The lateral dimension of each orthoscopic figure is 550 μm.

3.2. *Mixed SAMs formed by coadsorption of semifluorinated thiols*

Mixed self-assembled monolayers were formed by coadsorption of either **1** and **2** or **1** and **3**. The compositions of the mixed SAMs were confirmed to be 1:1 by XPS [31]. Figure 3 shows schematic illustrations of the mixed SAMs formed from the semifluorinated thiols and a mixed SAM formed from **5** and **6**. In the discussion that follows we use the variable Δ_t to denote the difference between the lengths of the short and long chains within these mixed SAMs.

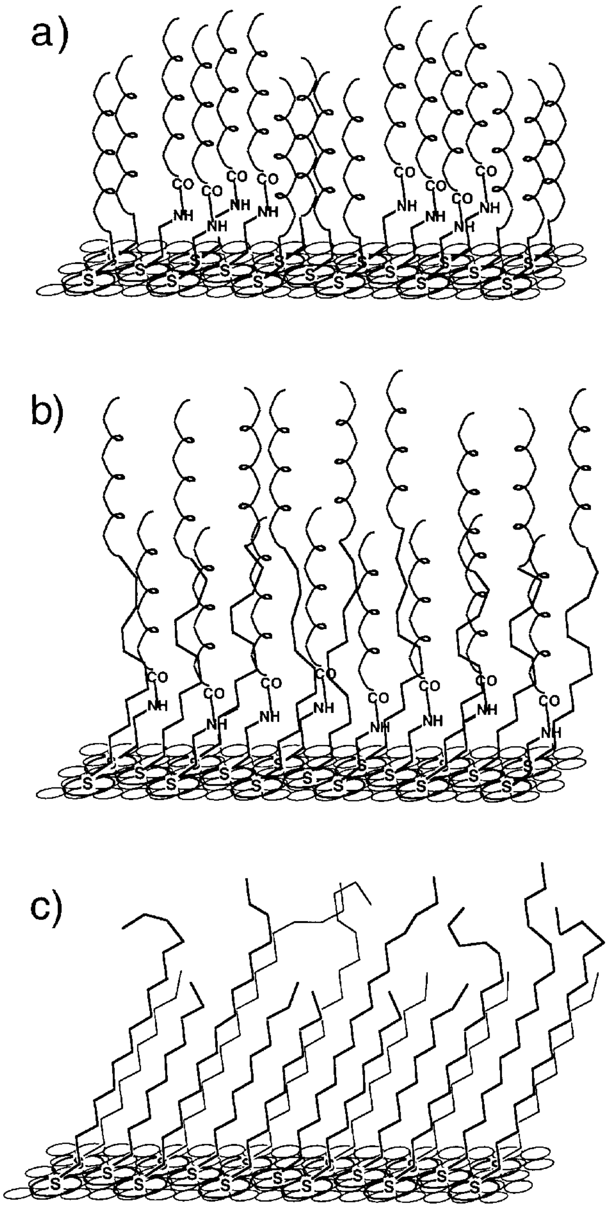


Figure 3. Cartoons of mixed SAMs formed by coadsorption of (*a*) **1**: $CF_3(CF_2)_7CONH(CH_2)_2SH$ and **2**: $CF_3(CF_2)_7(CH_2)_2SH$ ($\Delta_t = 2$ Å), (*b*) **1**: $CF_3(CF_2)_7CONH(CH_2)_2SH$ and **3**: $CF_3(CF_2)_7(CH_2)_{11}SH$ ($\Delta_t = 9$ Å) and (*c*) **4**: $CH_3(CH_2)_9SH$ and **6**: $CH_3(CH_2)_{15}SH$ ($\Delta_t = 9$ Å). These cartoons illustrate differences in the height of the chains within the mixed SAMs, and their relative degrees of conformational freedom.

Contact angles of hexadecane measured on the mixed SAMs are shown in the table. The contact angles are consistent with the presentation of CF_2 and CF_3 groups at the surface of the SAM, except perhaps for the receding contact angle of SAMs formed from **1** and **3** (68°, see below).

The position of the grazing incidence FTIR absorbance frequency corresponding to the amide II stretch (NH in-plane bending, $1545\,cm^{-1}$) measured using SAMs formed from **1** and **2** is similar to the position of the amide II stretch measured using SAMs formed from **1** only [31]. This observation indicates hydrogen bonding takes place within the mixed SAM which, in turn, suggests incomplete mixing—and possibly islanding—of **1** and **2** within the mixed SAMs; that is, ideal mixing of species within the mixed SAM formed from **1** and **2** has not occurred. In contrast, the grazing incidence FTIR spectra measured using SAMs formed from **1** and **3** does show a shift of the amide II frequency to lower wave numbers, from which it can be inferred that there is substantial mixing of the two species within the SAM. The influence of the level of molecular mixing within the mixed SAMs on the anchoring of liquid crystals (and contact angles) is unknown. The degree of mixedness could, however, account for the lower receding contact angles of hexadecane measured on SAMs formed from **1** and **3** (see above).

The optical textures of 5CB anchored on mixed SAMs formed from **1** and **2** ($\Delta_t = 2$ Å) were schlieren (see figure 4(*a*)), although no defects with strength 1/2 could be found. Conoscopic images obtained from regions removed from defects showed interference fringes consistent with a tilt of the director (≈15°–20°) away from the surface (see figure 4(*b*)). In contrast, mixed SAMs formed from **1** and **3** ($\Delta_t = 9$ Å) caused homeotropic anchoring of 5CB (see figure 4(*c*)). Mixed SAMs formed from **4** and **5** ($\Delta_t = 3$ Å) caused near-planar anchoring (see figure 4(*d*)) while past studies have shown that homeotropic anchoring is obtained on mixed SAMs formed from **4** and **6** ($\Delta_t = 9$ Å) [23].

4. Discussion

This paper reports the anchoring of 5CB on densely packed SAMs formed from semifluorinated thiols **1** or **2** to be planar. Self-assembled monolayers formed from alkanethiols on Au(111) also cause planar anchoring of 5CB [23–27]. Because the chains within SAMs formed from either **1** or **2** are oriented almost normal to the surface of the gold whereas alkanethiols are tilted away from the normal by approximately 30°, we conclude that differences in the tilt of chains within these SAMs do not influence the out-of-plane orientation of 5CB. Furthermore, these results suggest that differences in the anchoring of 5CB on SAMs formed from alkanethiols on gold (planar) and SAMs formed from OTS on silica (homeotropic) are unlikely to result from the different tilts of chains within these SAMs. We believe anisotropic dispersion interactions cause the planar anchoring of liquid crystals observed on SAMs supported on gold [26]. Differences in the anchoring of 5CB on SAMs formed from alkanethiols and OTS likely reflect differences in the polarizability (permittivity) of the substrates (silica versus gold) supporting these SAMs.

Although the anchoring of 5CB was found to be planar on SAMs formed from **1**, **2**, **5** or **6**, the optical textures in figure 2 clearly demonstrate that the azimuthal anchoring of 5CB on SAMs formed from semifluorinated thiols differs from that observed on SAMs formed from alkanethiols. Diffuse meandering branches were observed in the textures of liquid crystals anchored on SAMs formed from either **1** or **2** but not alkanethiols. Furthermore, the azimuthal orientation of 5CB anchored on the SAMs formed from **1** or **2** was correlated over spatial scales of approximately 100 μm whereas correlations in the azimuthal anchoring were lost within 10 μm on SAMs formed from akanethiols.

Here we consider how known differences in the structure and properties of SAMs formed from alkanethiols and SAMs formed from semifluorinated thiols may lead to the optical textures of 5CB described in the paragraph above. Because chains within SAMs formed from alkanethiols tilt by approximately 30° from the normal whereas perfluorinated chains orient along the normal, the azimuthal symmetry of SAMs formed from alkanethiols and semifluorinated thiols differ on scales of ~100 Å. Alkanethiols within SAMs on Au(111) form domains of uniform tilt—thus breaking the azimuthal symmetry of the surface and likely imposing a local bias in the azimuthal direction of anchoring (at least over spatial length scales a few times the size of the tilt domains)—whereas perfluorinated SAMs formed from either **1** or **2** do not. Differences in the symmery of these surfaces on scales of tens of nanometers may be reflected in the micrometre-scale structure of the textures of 5CB observed on SAMs formed from alkanethiols and SAMs formed from semifluorinated thiols. We cannot, however, rule out the possibility that differences in the permittivity (polarizability) of perfluorinated and hydrogenated materials may also influence the anchoring energy of 5CB on their surfaces. Differences in the permittivity (polarizability) of alkanethiols and semifluorinated thiols may influence the strength of the anisotropic dispersion interactions between 5CB and the gold substrate supporting the SAMs. For example, the widths of branches and threads in optical textures of liquid crystals increase with decreasing anchoring energy [32]. The longer range of the azimuthal alignment of 5CB on SAMs formed from either **1** or **2** as compared to SAMs formed from either **5** or **6** may reflect differences in the strength of the anchoring on these surfaces. These results suggest that the anchoring may be weaker on SAMs formed from semifluorinated thiols than alkanethiols (see below). Measurements of the strength of anchoring on SAMs formed from semifluorinated thiols and alkanethiols would allow this hypothesis to be tested.

In contrast to SAMs formed from either **1** or **2**, the anchoring of 5CB on SAMs formed from **3** is not planar; the director is tilted away from the surface. This is the first report of non-planar anchoring on SAMs formed from a single type of thiol on gold. Self-assembled monolayers formed from **3** differ from either **1** or **2** in a number of ways, all of which may influence the anchoring on these SAMs. First, the thickness of a SAM formed from **3** is greater than **1** or **2**, and thus the distance between the gold and 5CB is greater with **3**: dispersion interactions between the gold and 5CB decrease with increasing thickness of the SAM. Second, recent grazing incidence FTIR and NEXAFS measurements [31] indicate that chains within the SAMs formed from **3** are tilted away from the normal and that the tilt is complex; the perfluorinated chains in the outer region do not tilt to the same degree as the aliphatic chains in the inner region. Contact angles measured on SAMs formed from **3** and SAMs formed from either **1** or **2** confirm differences in the organization of the chains within the outer regions of these SAMs. Finally, we note that a direct comparison between the anchoring of 5CB on SAMs formed from **3** and those formed from **1** or **2** is complicated because the thickness of the cells differed in the two sets of experiments (≈25 μm versus ≈2 μm).

Whereas planar anchoring of 5CB is observed on densely packed SAMs formed from alkanethiols and semifluorinated thiols (**1** or **2**), mixed SAMs formed from short and long chains cause homeotropic anchoring of 5CB. Homeotropic alignment of 5CB is observed on mixed SAMs formed from semifluorinated thiols when the length of the chains differed by 9 Å but not 2 Å. Similarly, homeotropic anchoring is observed on mixed SAMs formed from short and long alkanethiols such as $CH_3(CH_2)_9SH$ and $CH_3(CH_2)_{15}SH$ ($\Delta_t = 9$ Å) but not on mixed SAMs formed from $CH_3(CH_2)_9SH$ and $CH_3(CH_2)_{11}SH$ ($\Delta_t = 3$ Å) or from $CH_3(CH_2)_{13}SH$ and $CH_3(CH_2)_{15}SH$ ($\Delta_t = 3$ Å). We conclude, therefore, that the lengths of short and long chains in mixed SAMs must differ by more than 3 Å to cause homeotropic alignment of 5CB (for both alkanethiols and semifluorinated thiols).

Mixed SAMs formed from short and long alkanethiols consist of a fluid-like overlayer formed by protruding ('waving') segments of the long chains supported on a densely packed foundation formed from the inner region of the long chains and short chains (see figure 3) [37]. Because the perfluorinated chains of the semifluorinated thiols are stiff in comparison to the alkanethiols, the outer regions of mixed SAMs formed from perfluorinated chains will not be fluid-like and mobile. The protruding segments of the long chains in the semifluorinated SAMs formed from **1** and **3** are expected to be 'spikes' protruding from a densely packed foundation. Because the 'spikes' are stiff and restricted in their ability to undergo reorganization when placed in contact with 5CB, and because homeotropic alignment of 5CB is observed on SAMs formed from short and long alkanethiols as well as short and long semifluorinated thiols, we conclude that reorganization of the outer regions of these SAMs is not necessary to achieve homeotropic anchoring. This conclusion supports the inference made by Drawhorn and Abbott [23] regarding the homeotropic anchoring of 5CB on SAMs formed from short and long alkanethiols. These authors concluded that the density of packing of the long aliphatic chains is important in determining the anchoring of 5CB in these systems. We speculate that mixed SAMs formed from short and long alkanethiols on gold may reorganize upon contact with the liquid crystal to form a structure that resembles the mixed semifluorinated SAMs formed from **1** and **3**.

5. Conclusions

We report a comparison of the anchoring of nematic 5CB on SAMs formed from semifluorinated thiols and alkanethiols on gold. Because planar anchoring is observed on single-component SAMs formed from both alkanethiols and semifluorinated thiols, we infer the cause of planar anchoring to be extrinsic to the structure of these SAMs: such a conclusion is consistent with the previously proposed influence of anisotropic dispersion interactions between 5CB and gold (through the SAMs) [26]. Differences in the tilts of chains within SAMs formed from alkanethiols and semifluorinated thiols do not change the out-of-plane orientation of 5CB on these surfaces. This result leads us to conclude that differences in the anchoring of 5CB on SAMs formed from alkanethiols on gold (planar) and SAMs formed from OTS on silica (homeotropic) are unlikely to result from differences in the tilts of the chains within these SAMs. The difference in anchoring of 5CB on these SAMs likely reflects the polarizability (permittivity) of the substrates (silica versus Au) that support the SAMs. We also report the azimuthal anchoring of 5CB to be different on SAMs formed from alkanethiols and semifluorinated thiols: 5CB is anchored on SAMs formed from alkanethiols in domains with sizes $<10\,\mu m$ whereas 5CB forms large domains ($\sim 100\,\mu m$) with diffuse branches on SAMs formed from semifluorinated thiols. Differences in the azimuthal anchoring of 5CB observed on semifluorinated thiols and alkanethiols may reflect the presence/absence of chain tilt and/or tilt domains within these SAMs. Homeotropic anchoring of 5CB is observed on mixed SAMs formed from semifluorinated compounds with short and long chains. Homeotropic anchoring of 5CB is also observed on surfaces formed by coadsorption of alkanethiols with short and long aliphatic chains. Differences in the conformational degrees of freedom (flexibility) of alkanethiols and semifluorinated thiols do not appear to influence the transition to homeotropic anchoring: we infer that flexibility of the protruding chains within mixed SAMs (and restructuring upon contact with the liquid crystal) is not a necessary condition to cause homeotropic anchoring of 5CB.

Note: (*added in proof*) Evans and coworkers [34] have recently reported measurements of the orientation of nematic 5CB within 1°C of the nematic–isotropic transition temperature (T_{NI}) on SAMs formed from CF_3–$(CF_2)_9$–CH_2–S–C_6H_4–O–$(CH_2)_4$–SH on gold. They also find planar anchoring of 5CB. In contrast, they report homeotropic anchoring of 8CB within 1°C of its T_{NI}. We find planar anchoring of smectic 8CB at room temperature on SAMs formed from either **1** or **2**.

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