

Odd/Even Effect in Self-Assembly of Chiral Molecules at the Liquid–Solid Interface: An STM Investigation of Coadsorbate Control of Self-Assembly

Dalia G. Yablon, David Wintgens, and George W. Flynn*

Department of Chemistry and Columbia Center for Integrated Science and Engineering, Columbia University, New York, New York 10027

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Manipulation of the self-assembly of chiral 2-bromohexadecanoic acid by templates composed of coadsorbed achiral molecules has been investigated at the liquid–solid interface using scanning tunneling microscopy (STM). The template formed by the odd-numbered saturated fatty acid heptadecanoic acid induces coadsorption of *R*-2-bromo-hexadecanoic acid and *S*-2-bromo-hexadecanoic acid within a single domain. Specifically, heptadecanoic acid effects an intra-lamellar alternation of *R* and *S*-2-bromo-hexadecanoic acid molecules, which is further confirmed by studies of heptadecanoic acid with pure *R*-2-bromo-hexadecanoic acid. Templates formed by even-numbered acids such as hexadecanoic acid induce the segregation of *R*- and *S*-2-bromo-hexadecanoic acid into separate (*R* or *S*) domains.

Introduction

Chirality is a subtle property, important in biological activity and pharmaceutical drug manufacturing, that plays an extremely important role in molecular functionality. One of the latest additions to the growing roster of techniques used to study chirality is scanning probe microscopy (SPM), which includes scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Given the difficulty of identifying chiral structures, the high-resolution imaging capability of SPM makes it an attractive technique to study chiral molecules on solid surfaces. Many systems have already been successfully explored with SPM including chiral phases in Langmuir–Blodgett films,¹ liquid crystals,^{2,3} mixtures of chiral and achiral components,^{4,5} and other self-assembled films.^{6,7} Recent reports of the direct determination of chirality for individual molecules by STM^{8,9} indicate that these SPM techniques provide an especially powerful tool for the advancement of studies of chiral systems.

Surfaces are a useful medium with which to resolve, separate, and manipulate chiral molecules. The symmetry breaking properties of surfaces can induce racemates to form enantiomorphous domains^{2,5,8} or impart a pseudochirality to achiral molecules.^{10–12} Furthermore, surfaces themselves can be inherently chiral as in the case of high Miller index surfaces of single metal crystals.¹³ Electrochemical studies have further demonstrated enantiospecific reactivity on such chiral surfaces.^{14,15}

Achiral surfaces that can be modified to manipulate and resolve chiral molecules are particularly desirable because of their low cost and ready availability. One of the most popular chiral separation techniques, high-pressure liquid chromatography, relies on the use of a chiral stationary phase (CSP) where an achiral surface is derivatized by a chiral constituent to effect enantiomeric resolution. Separation of a racemate is achieved through formation of energetically different diastereomeric complexes between the *R*- and *S*-solutes and the CSP.¹⁶ Chiral chromatography is an especially valuable technique because it allows simultaneous detection and collection of both enantiomers, a feature that has important implications for the detection of enantiomeric impurities and the measurement of enantiomeric excess. One surface that has received recent attention in chiral

chromatography is porous graphitic carbon, which has been chirally modified to effect the separation of enantiomers of chiral epoxides¹⁷ and amino acids.¹⁸

Here we describe another form of graphite surface that can be modified by the adsorption of achiral molecules, which themselves adopt a pseudo 2D chirality when adsorbed onto the graphite substrate.¹⁰ In this work, templates of different-length fatty acids formed at the liquid–solid interface on a highly ordered pyrolytic graphite surface are used to affect the self-assembly of the chiral molecule 2-bromo-hexadecanoic acid (2-BrHA). These fatty acid templates are shown to induce interfacial domains either with enantiomeric purity⁵ or domains with both enantiomers simultaneously present. In the latter case, a template can be chosen to create alternating lamellae of *R*- and *S*-2-bromo-hexadecanoic acid allowing for the simultaneous detection of both enantiomers within one interfacial domain.

Experimental Section

Methods. All the studies described were performed under ambient conditions at room temperature (16 °C) using a Nanoscope III scanning tunneling microscope (Digital Instruments). The experiments were conducted at the liquid–solid interface by immersing an STM tip, mechanically cut from a 0.25 mm diameter platinum/rhodium (87/13) wire (Omega), into a droplet of solution. The small (10 μ L) droplet of solution is applied directly to the surface of a freshly cleaved piece of highly oriented pyrolytic graphite, HOPG (Advanced Ceramics, ZYB grade).

The images displayed were obtained in either constant height or constant current mode of operation. A zeroth-order flattening procedure has been utilized to normalize the vertical offset produced in the constant current operating mode. Typical tunneling parameters used in the experiments include a bias voltage of 1.5V (sample negative) and a tunneling current of 250–600 pA. The resulting images display tunneling current between STM tip and surface (constant height mode) or relative distance between the STM tip and the surface (constant current mode) where “bright” corresponds to topographically higher

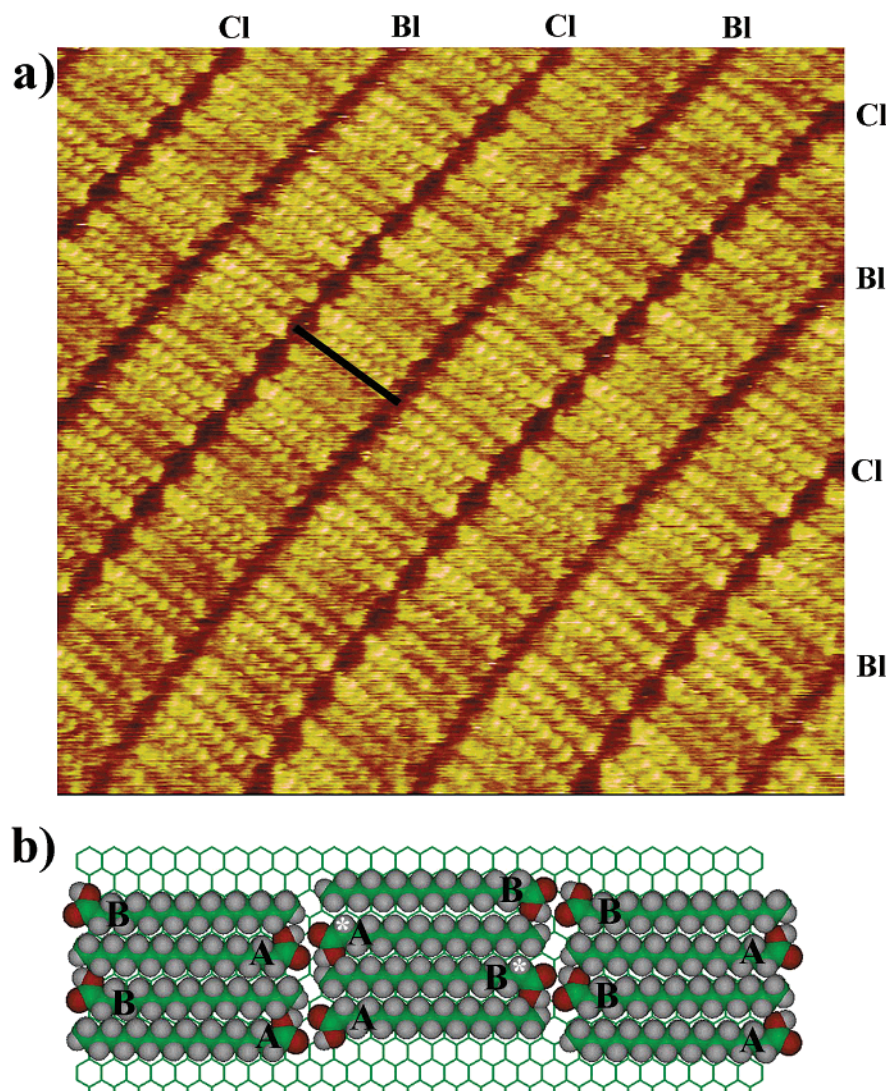


Figure 1. (a) A $15 \times 15 \text{ nm}^2$ STM constant current image of heptadecanoic acid ($\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{COOH}$) physisorbed onto a graphite substrate taken at 1.5V (sample negative) and 350 pA. A black bar represents a single molecular length. Heptadecanoic acid forms organized lamellae separated by troughs that are composed of individual hydrogen-bonding carboxylic acid groups. Half of the troughs consist of distinct round dark groups (marked by a CI) while others (marked by a BI) are composed of blurred dark spots. (b) A model representing a typical domain of heptadecanoic acid where the lamellae are composed of heptadecanoic acid molecules alternately configured in A and B, two-dimensional chiral conformations. The white asterisks on the hydrogen of the carbon atom alpha to the COOH group highlight the differences between A and B conformations of heptadecanoic acid on graphite. In two dimensions the A and B conformers are mirror images of each other and are referred to as two-dimensional chiral conformations.

areas on the surface and “dark” corresponds to topographically lower regions on the surface.

Molecular models were created with the molecular modeling software package Biosym (InsightII, Molecular Simulations, Inc.) running on a Silicon Graphics workstation.

Materials. Stock solutions of heptadecanoic acid, racemic 2-bromo-hexadecanoic acid, and *R*-2-bromo-hexadecanoic acid were prepared separately and then mixed in various ratios. Heptadecanoic acid ($\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{COOH}$) and racemic 2-bromo-hexadecanoic acid ($\text{CH}_3(\text{CH}_2)_{13}\text{CHBrCOOH}$) were procured from Aldrich and dissolved separately in 1-phenyloctane (Aldrich) to produce saturated solutions. *R*-2-Bromo-hexadecanoic acid (synthesis described elsewhere¹⁹) was dissolved in 1-phenyloctane to produce a solution with $\sim 100 \text{ mg/mL}$ concentration. The heptadecanoic acid and racemic 2-bromo-hexadecanoic acid solutions were mixed in a 1:1 ratio by volume. Heptadecanoic acid and *R*-2-bromo-hexadecanoic acid solutions were mixed in a 1:6 ratio by volume.

Results

Heptadecanoic Acid. Heptadecanoic acid forms an organized two-dimensional structure at the phenyloctane–graphite interface similar to that of other odd-numbered fatty acids.¹⁰ Stable, well-ordered domains, such as the one depicted in the representative STM image of Figure 1a, are formed that span hundreds of nanometers in width. The length of one molecule is marked by a black bar, 2.38 nm, and corresponds exactly to the expected 2.38 nm length of heptadecanoic acid when the molecule is configured in an all-trans conformation lying flat on the basal plane of graphite. The dark (topographically depressed) red troughs in the STM image of Figure 1a are comprised of individual dark spots that are assigned to the locations of individual COOH groups.^{20,21} The troughs in Figure 1a are dissimilar and alternate between clear troughs (marked by a CI) comprised of distinct dark red spots, and blurry troughs (delineated by a BI) where the dark red spots constituting the troughs have poorly defined edges and blend into one another.

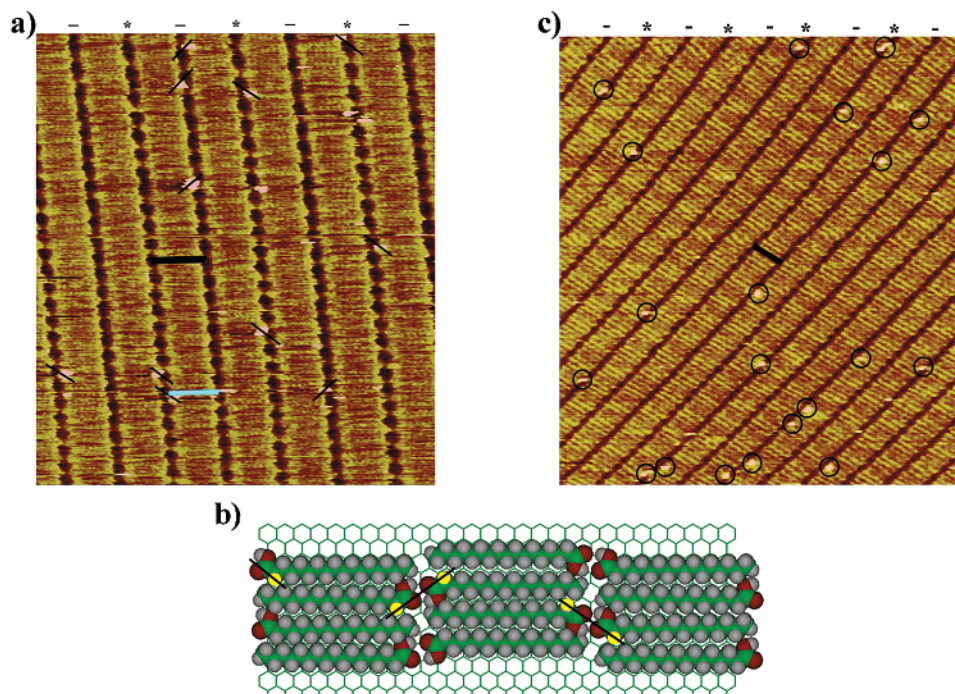


Figure 2. (a) An $18 \times 18 \text{ nm}^2$ STM constant-current topograph of a 1:1 mixture by volume of heptadecanoic acid with racemic 2-bromo-hexadecanoic acid ($\text{CH}_3(\text{CH}_2)_{13}\text{CHBrCOOH}$) imaged at 1.5 V (sample negative) and 588 pA. One molecular length of heptadecanoic acid is marked by a black bar and one molecular length of 2-bromo-hexadecanoic acid is marked in blue. Individual dark round regions (topographical depressions) in the troughs are typical of a pair of hydrogen-bonded carboxylic acid groups and the bright spots (topographical protrusions) that sporadically accompany the troughs are assigned to the locations of bromine atoms and hence coadsorbed brominated molecules. Superimposed black lines highlight the bromine/COOH orientations and reflect a mirror-image pattern along alternating troughs. The brominated molecules in the (*) troughs are identified as *R*-2-bromo-hexadecanoic acid while those in the (−) troughs are *S*-2-bromo-hexadecanoic acid. (b) A molecular model depicts a typical domain of a heptadecanoic acid/racemic 2-bromo-hexadecanoic acid mixture. The alternating *R*-, *S*-bromine/COOH configuration, which is highlighted by superimposed black bars, is obtained by substituting Br atoms for the alpha hydrogen atoms of heptadecanoic acid and shortening the chain length by one CH_2 unit. (c) A $26 \times 26 \text{ nm}^2$ STM constant-current image of a 6:1 mixture by volume of *R*-2-bromo-hexadecanoic acid with heptadecanoic acid collected at 1.5V (sample negative) and 300pA is shown. One molecular length is marked by a black bar. All the bright spots in this image are circled and appear only in the troughs that are marked by (*). All the (−) troughs are devoid of any brominated molecules.

The origin of the clear/blurry alternation in trough identity is not obvious but provides the first experimental suggestion that alternate troughs might have different properties related in some way to the existence of two possible configurations of the molecule. This suggestion is borne out below in studies of mixtures of heptadecanoic acid with 2-bromo-hexadecanoic acid. Further efforts to explain the origin of the clear/blurry effect with both theoretical modeling and temperature-dependent experiments are in progress.

Though heptadecanoic acid is achiral in three dimensions, it adopts a two-dimensional chirality when adsorbed onto the graphite surface, similar to other fatty acids.¹⁰ The two-dimensionally chiral configurations that heptadecanoic acid can adopt on a surface have been arbitrarily labeled “A” and “B” in the molecular model in Figure 1b. Molecules A and B are referred to as two-dimensional chiral configurations because no amount of in-planar rotation will convert the configuration of an A molecule into that of a B molecule. Molecule A can only be superimposed on molecule B by lifting it off the surface and flipping it over. The difference between these two configurations on a surface is highlighted by white asterisks marking the relative positioning of the hydrogen on the carbon alpha to the COOH group, which further help in identifying these configurations as mirror images of each other. This model (Figure 1b) of heptadecanoic acid on graphite depicts a classic interdigitating pattern commonly found among self-assembled fatty acids, which facilitates hydrogen bonding between the carboxylic acid end groups. Figure 1b further suggests an intra-

lamellar alternation of molecules in the A and B configurations whose carboxylic acid groups comprise the troughs, a pattern proposed by Hibino et al.¹⁰ for odd-numbered fatty acids.

Heptadecanoic Acid and Racemic 2-Bromo-hexadecanoic Acid.

A mixture of heptadecanoic acid with racemic 2-bromo-hexadecanoic acid forms well-ordered domains when physisorbed onto a graphite surface at the liquid–solid interface. A representative STM topograph is shown in Figure 2a where a single molecular length of heptadecanoic acid is depicted by a black bar and a single molecular length of 2-BrHA is marked by a blue bar (the distinction in the image between the two chemical moieties is explained below). The lamellae are perpendicular to the molecular axis in this self-assembled structure. The measured length of a given molecule in this STM image (heptadecanoic acid or 2-bromo-hexadecanoic acid), 2.23 nm, is close to the expected length of an all-trans conformation of either heptadecanoic acid, 2.38 nm, or 2-bromo-hexadecanoic acid, 2.24 nm, lying flat on the basal plane of graphite. The difference in molecular lengths between these two molecules is too small to be measured reliably by our STM under ambient conditions, and without the benefit of additional identifying features, the length measured in the STM image may be attributed to either a heptadecanoic acid molecule or a 2-bromo-hexadecanoic acid molecule.

The troughs in Figure 2a primarily contain dark circular regions that are sporadically accompanied by bright spots. The individual dark regions (topographical depressions) are assigned to the positions of pairs of hydrogen-bonding carboxylic acid

groups,^{20,21} whereas the bright spots (topographical protrusions) correspond to bromine atoms, which appear bright when they are located at a nonterminal position along the hydrocarbon chain.^{22,23} The presence or absence of the chemical marker bromine (bright) near the COOH (dark) group provides a straightforward and facile differentiation of the two chemical species in this mixture despite their similar lengths.

The relative orientation of the bromine atoms to the carboxylic acid groups is identical in *alternating* troughs of this self-assembly pattern; black bars have been superimposed over the COOH/bromine orientation to highlight this configuration. For example the bromine atoms (bright spots) in the troughs arbitrarily marked by (*) are either below and to the right or above and to the left of the carboxylic acid group (dark round region). In contrast, the bromine atoms in the troughs arbitrarily marked by (−) are all either below and to the left or above and to the right of the carboxylic acid groups. The assignment of a bromine atom to a particular carboxyl group is achieved by carefully comparing distances between the bromine atom and neighboring carboxyl groups within a given trough. This assignment is further facilitated by taking advantage of the interdigitation patterning of the hexadecanoic acid molecules that separates neighboring carboxyl groups. When this procedure is followed, over 90% of the time the bromine atom (bright spot) is found to be closest (directly adjacent) to only one carboxyl group (dark region).

The relative positioning of the bromine atoms to the carboxylic acid groups in the * troughs in Figure 2a is the *mirror image* of the positioning of the bromine atoms to the carboxylic acid groups in the (−) troughs. Figure 2b provides a molecular model based on a typical region of the self-assembled monolayer where the orientation of the carboxylic acid group with respect to the accompanying bromine in the alternating troughs is accordingly reflected. Thus, in these mixtures, each lamella is composed of alternating *R*- and *S*-2-bromo-hexadecanoic acid molecules giving rise to the enantiomeric alternation along the starred (*) and minus (−) troughs.

Determination of the absolute chirality of individual 2-bromo-hexadecanoic acid molecules has been described in detail elsewhere^{8,22} and can be assigned from the relative orientations of the three dissimilar groups on the chiral carbon center that are all clearly present in the STM image — the bromine atom, carboxylic acid group, and the remainder of the alkyl chain. Thus, the brominated molecules that appear in those troughs arbitrarily marked by a (*) are identified as *R*-2-bromo-hexadecanoic acid, while the brominated molecules in the troughs arbitrarily marked by a (−) are readily recognizable as *S*-2-bromo-hexadecanoic acid.

Heptadecanoic Acid and *R*-2-Bromo-hexadecanoic Acid. Mixtures of heptadecanoic acid with *R*-2-bromo-hexadecanoic acid form organized, stable domains extending hundreds of nanometers in width. Figure 2c shows a representative STM constant current image where one molecular length of heptadecanoic acid is marked by a black bar. The measured length of a given molecule in this STM image (heptadecanoic acid or *R*-2-bromo-hexadecanoic acid), 2.19 nm, is close to the expected length of an all-trans conformation of either heptadecanoic acid, 2.38 nm, or *R*-2-bromo-hexadecanoic acid, 2.24 nm, lying flat on the basal plane of graphite.

The surface structure formed by this mixture is similar to the one described in Figure 2a for heptadecanoic acid and racemic 2-bromo-hexadecanoic acid but with the notable exception that only half of the troughs are dotted by bright spots or bromine atoms. Alternating troughs in Figure 2c have been

accordingly labeled with either a (*) or (−). All the (−) troughs are totally devoid of any accompanying bright spots and, therefore, lack any brominated molecules. In contrast, the (*) troughs in this STM image are dotted by encircled bright spots indicating the coadsorption of some brominated molecules into this particular set of troughs. The identity of all the brominated molecules is known a priori to be *R*-2-bromo-hexadecanoic acid. Therefore, in a mixture of *R*-2-bromo-hexadecanoic acid with heptadecanoic acid, *R*-2-bromo-hexadecanoic acid is observed only in *every other* trough in the STM images.

Discussion

Odd–Even Effect in Formation of Achiral Templates.

Achiral fatty acid molecules form a template for the interfacial self-assembly of chiral brominated molecules in all the mixtures described above, similar to mixtures of 2-bromo-hexadecanoic acid with hexadecanoic acid.⁵ All the resultant self-assembled structures of the mixtures shown in Figures 2 exhibit a perpendicular angle between the lamellar and molecular axes that maximizes hydrogen bonding between carboxylic acid end groups. This right-angle arrangement is typical for pure fatty acids self-assembled at the liquid–solid interface.¹⁰ Pure racemic 2-bromo-hexadecanoic acid on the other hand organizes into a structure where bromine–bromine van der Waals attraction can be maximized in addition to hydrogen bonding between carboxylic acid groups, resulting in a 45° angle between molecular and lamellar axes.⁸ Introducing a template composed of nonbrominated fatty acid molecules manipulates the intermolecular interactions (the Br–Br interactions are frustrated) to effect patterns of brominated molecules that are different from those 2-bromo-hexadecanoic acid forms as a sole adsorbate on the graphite substrate.

The subtle geometric difference caused by the odd–even chain length of the fatty acid is critical to the formation of different templates in these mixtures. Figure 3 depicts schematic diagrams of self-assembly structures of an even-length chain fatty acid (a) and an odd-length chain fatty acid (b) and (c). The carboxylic acid group and terminal methyl unit lie on opposite sides of the molecular axis in fatty acids with an even number of carbons in the hydrocarbon backbone, as depicted by the arrows in Figure 3a for the case of hexadecanoic acid. Hexadecanoic acid self-assembles into a surface pattern shown by the diagram in Figure 3a where all the molecules are oriented in the same two-dimensional chiral configuration, which has been arbitrarily labeled A.¹⁰

In direct contrast, the carboxylic acid group and terminal methyl unit lie on the same side of the molecular axis in fatty acids with an odd number of carbons in the hydrocarbon backbone such as heptadecanoic acid, as depicted by the arrows in Figure 3b. The schematic of a self-assembled monolayer of heptadecanoic acid shown in Figure 3b contains an intralamellar alternation of molecules oriented in the two-dimensional chiral configurations A and B, which avoids steric interactions between the carboxylic acid group of one molecule with a terminal methyl of a neighboring molecule within the lamella. For comparison, Figure 3c shows a schematic of heptadecanoic acid molecules all configured in the “A” orientation with the encircled problematic interaction between the terminal methyl group of one molecule with a carboxylic acid group of a neighboring molecule. Such a self-assembly pattern is not observed experimentally for odd-numbered fatty acids.

The effect of the fatty acid template on the self-assembly of the chiral molecules depends greatly on the chain length of the fatty acid. In work previously described,⁵ the even-numbered

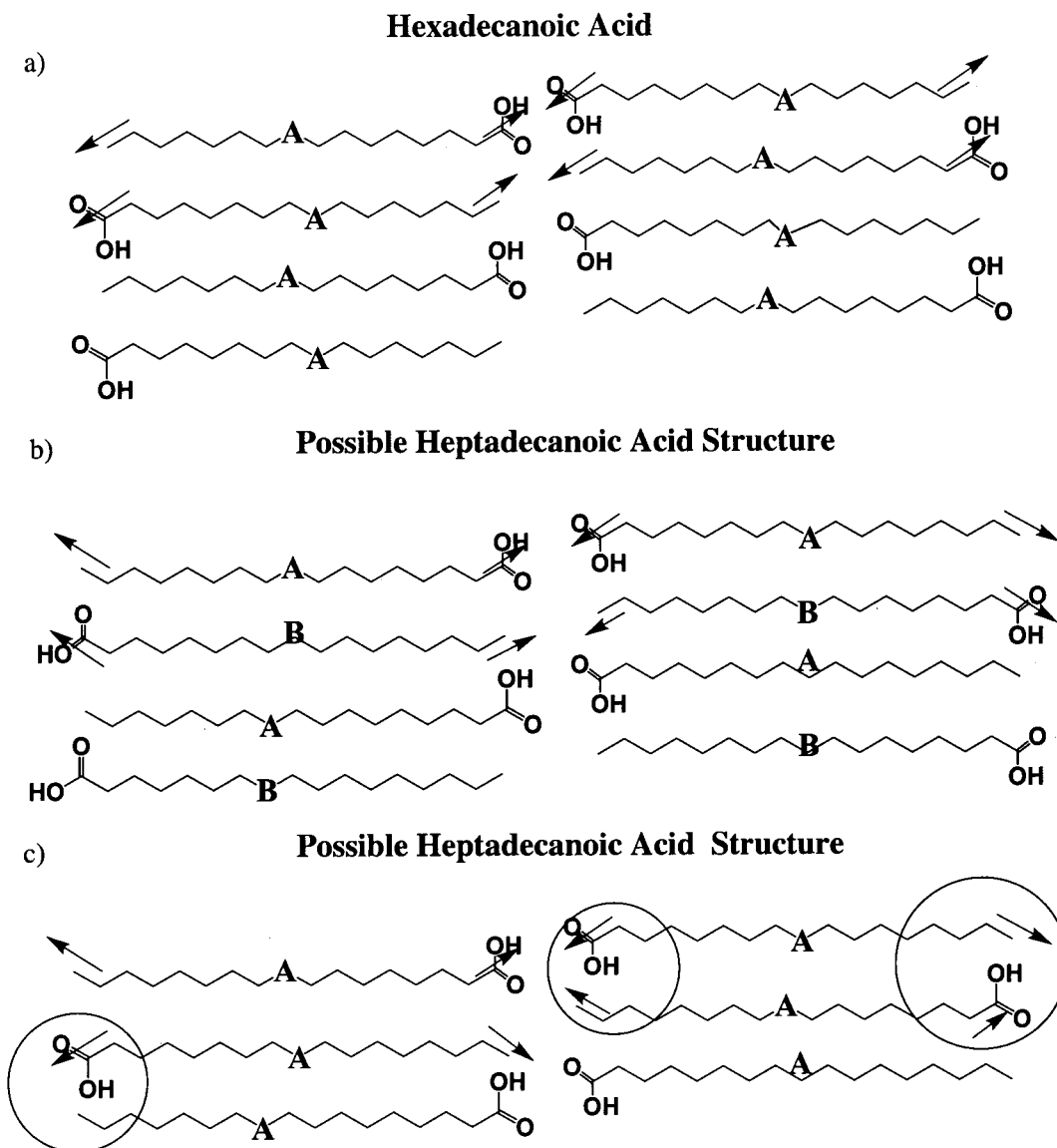


Figure 3. A series of schematic diagrams representing different possible self-assembly patterns for fatty acid molecules. (a) Array of hexadecanoic acid molecules where each molecule is in the all-trans conformation. The carboxylic acid group and terminal methyl group that lie on opposite sides of the hydrocarbon chain are indicated by the arrows. All the molecules here are configured in the two-dimensional chiral "A" conformation shown in Figure 1b. (b) Array of heptadecanoic acid molecules where each molecule is in the all-trans conformation. The carboxylic acid group and terminal methyl group lie on the same side of the hydrocarbon chain as indicated by the arrows. The molecules here are alternately arranged in two different two-dimensional chiral configurations arbitrarily labeled "A" and "B" (see Figure 1b). A self-assembled arrangement of heptadecanoic acid consisting of molecules all oriented in the same two-dimensional chiral configuration (e.g., the "A" conformation of Figure 1b) is included in (c) for comparison. The structure in (c) is not observed experimentally and reveals unfavorable intermolecular steric interactions that have been circled.

coadsorbate hexadecanoic acid separates racemic 2-bromohexadecanoic acid molecules into domains of enantiomeric purity. In the present work, a new template composed of heptadecanoic acid induces enantiomeric mixing of *R*- and *S*-2-bromohexadecanoic acid within one domain. Templates formed by longer-chain acids such as nonadecanoic acid and eicosanoic acid have also been explored.²⁴ Mixtures of 2-bromohexadecanoic acid with these longer fatty acid templates form surface structures with domains composed predominantly of fatty acid with the shorter chained brominated molecules banding together into "stripes" as they quasi phase-segregate from the unsubstituted fatty acid molecules. In mixtures with odd-length acids, both *R*-2-bromo-hexadecanoic acid and *S*-2-bromo-hexadecanoic acid stripes are found within a single domain. In mixtures with even-length acids, only a single kind of brominated stripe (e.g., all *R*-2-bromo-hexadecanoic acid or *S*-2-bromo-hexadecanoic acid) is found within a domain. Therefore, even-numbered acids

(such as hexadecanoic acid and eicosanoic acid²⁴) induce domains of enantiomeric purity while odd-numbered acids (such as heptadecanoic acid and nonadecanoic acid²⁴) cause co-adsorption of both enantiomers within one domain.

Heptadecanoic Acid Template To Determine Enantiomeric Excess. Heptadecanoic acid forms a unique template that induces an organized segregation of *R*- and *S*-2-bromohexadecanoic acid along alternating troughs. An advantage of such a template in analytical studies of chiral purity is that both enantiomers are present simultaneously within one domain but side by side in alternating lamellar stripes, which can immediately reveal the presence of enantiomeric impurities. A quantitative study of enantiomers in adjacent lamellae can further provide a direct measure of enantiomeric excess. In the present experiments, the adsorption of *R* and *S*-2-bromo-hexadecanoic acid within a heptadecanoic acid template is expected to be governed by identical thermodynamic processes, so that the ratio

of these two enantiomers on the surface should reflect their ratio in solution. Thus, a control study of racemic 2-bromo-hexadecanoic acid with heptadecanoic acid should yield a 50%/50% enantiomeric ratio. Our STM images of racemic 2-bromo-hexadecanoic acid with heptadecanoic acid mixtures reveal a 45.3%/54.7% enantiomeric ratio as calculated from 15 constant current STM images collected on 4 different days and containing a total of 280 brominated molecules. These values are (within the experimental error $[(140 \pm \sqrt{140})/280]$ of $50 \pm 4.2\%$) those that would be expected for a statistical sampling of 280 molecules. Experimental error here arises primarily from those few cases in which it can be difficult to distinguish a Br atom from a hydrogen atom with enhanced contrast due to incommensurate registry with the surface (Moire pattern). In many cases of organic synthetic studies, a highly accurate *R/S* ratio is required. The accuracy of the STM sampling method is simply limited by the number of samples counted.

Clear/Blurry Alternation in Troughs of Odd-Numbered Fatty Acids. Further insight into the clear/blurry effect observed in alternating troughs of odd-numbered acids (see Figure 1) is provided by the marker molecule 2-bromo-hexadecanoic acid in studies of mixtures of heptadecanoic acid with 2-bromo-hexadecanoic acid. The brominated molecule serves as a marker for the various configurations of pure heptadecanoic acid on a surface where *R*-2-bromo-hexadecanoic acid is a marker for the B configuration of heptadecanoic acid (as defined in Figure 1a) and *S*-2-bromo-hexadecanoic acid is a marker for the A conformation (as defined in Figure 1a). This is similar to the use of *R*- and *S*-2-bromo-hexadecanoic acid molecules as marker molecules for the different two-dimensional chiral orientations of hexadecanoic acid.⁵ The observed alternation of *R* and *S*-2-bromo-hexadecanoic acid along troughs in mixtures with heptadecanoic acid (Figure 2a) strengthens the hypothesis¹⁰ that heptadecanoic acid self-assembles with an intra-lamellar alternation of molecules configured in the two-dimensional chiral "A" and "B" configurations.

The mixture of heptadecanoic acid with racemic 2-bromo-hexadecanoic acid further reveals that at times *R*-2-bromo-hexadecanoic acid is found in the clear troughs and at other times it is found in the blurry troughs, with identical observations for *S*-2-bromo-hexadecanoic acid. In other words, the clear/blurry troughs are not associated with any one configuration (A or B) of heptadecanoic acid, but instead result from the overall structure formed by a four-molecule unit cell, which contains two molecules in one two-dimensional chiral configuration and two molecules in the other two-dimensional configuration. One possible explanation for the clear/blurry troughs is that the physisorption of the unit cell onto the graphite surface "favors" one orientation (e.g., A) over the other (e.g., B) by optimizing the hydrogen bonding of molecules in one orientation at the expense of the hydrogen bonding of the molecules in the second configuration. Once this happens for the first set of molecules, the rest of the molecules will follow the same pattern. Which orientation (A or B) is favored is a random process since the molecules are absolutely identical and differ *only* in their conformation on the surface.

Conclusions

Scanning tunneling microscopy has been used to investigate the self-assembled surface patterns formed by mixtures of 2-bromohexadecanoic acid with various fatty acid molecules. Depending on the length and the presence of an odd/even number of carbons in the fatty acid chain, different templates are formed that affect the self-assembly of the chiral molecule

2-bromo-hexadecanoic acid at the liquid–solid interface. Fatty acids with an even chain length form enantiomerically pure domains, whereas fatty acids with an odd chain length induce coadsorption of both enantiomers (*R* and *S*) within one domain. These mixtures demonstrate the utility of templates formed by inexpensive, easily available achiral molecules in manipulating the self-assembly of chiral molecules on a surface. The odd-numbered fatty acid templates are especially interesting as they induce coadsorption of two enantiomers simultaneously within one domain and are being further explored as a method to determine the enantiomeric excess of a chiral molecule.

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