Self-Assembly and Odd−Even Effects of cis-Unsaturated Carboxylic Acids on Highly Oriented Pyrolytic Graphite

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The self-assembly of several cis-unsaturated carboxylic acids of the structure $cis\text{-}CH_3(CH_2)_{p-1}CH{=}CH(CH_2)_{m-1}\text{-}COOH$ on highly oriented pyrolytic graphite (HOPG) was studied. The impact of the interior $cis\text{-}CH{=}CH$ group and the molecular chain length on their self-assembled structures was considered. Due to the cis conformation of the $-HC{=}CH-$ group in the interior of these molecules, they display self-assembled structures significantly different from saturated acids with all-trans configurations. As an example of the class of molecules $cis\text{-}CH_3(CH_2)_{p-1}CH{=}CH(CH_2)_{2n-1}COOH$ ($p \neq 2n$) ($p = 8$, $n = 7$), $cis\text{-}CH_3(CH_2)_7CH{=}CH(CH_2)_{13}COOH$ self-assembles into two kinds of enantiomer domains with opposite 2-D chirality. Due to the steric restriction of the interior $cis\text{-}HC{=}CH$ group, all chains with acid groups are packed at the same side of a lamella, a head-to-head arrangement which is different from the head-to-tail packing of saturated all-trans acids. However, $cis\text{-}CH_3(CH_2)_7CH{=}CH(CH_2)_8COOH$, considered as one example of the group $cis\text{-}CH_3(CH_2)_{p-1}\text{-}CH{=}CH(CH_2)_{2n-2}COOH$ ($p \neq 2n - 1$) ($p = 8$, $n = 5$), does not form any stable self-assembled domain, consistent with the molecular arrangement model. This difference in self-assembly behavior between $cis\text{-}CH_3(CH_2)_{p-1}CH{=}CH(CH_2)_{2n-1}COOH$ ($p \neq 2n$) and $cis\text{-}CH_3(CH_2)_{p-1}CH{=}CHC_{2n-2}COOH$ ($p \neq 2n - 1$) shows an odd−even chain-length effect of $cis\text{-}CH_3(CH_2)_{p-1}CH{=}CH(CH_2)_{m-1}COOH$ ($p \neq m$, $m = 2n$ or $2n - 1$). For another category of molecules, cis-unsaturated acids with equal numbers of all-trans carbon atoms on both sides of the $cis\text{-}CH{=}CH$ group, $cis\text{-}CH_3(CH_2)_{m-1}CH{=}CH(CH_2)_{m-1}COOH$ ($m = 2n$ or $2n - 1$), display another odd−even effect. $cis\text{-}CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$, one example of $cis\text{-}CH_3(CH_2)_{2n-1}\text{-}CH{=}CH(CH_2)_{2n-1}COOH$ ($n = 4$), is predicted to form both an enantiomer and a nonchiral racemic structure, which is in accordance with the experimental observation of its self-assembled monolayer. However, $cis\text{-}CH_3(CH_2)_{2n-2}CH{=}CH(CH_2)_{2n-2}COOH$ does not form a stable self-assembled domain due to the same steric repulsion as that seen in the $cis\text{-}CH_3(CH_2)_7CH{=}CH(CH_2)_8COOH$ structure. These odd−even effects demonstrate that molecular self-assembly can be significantly tailored by slightly changing the molecular chain length.

1. Introduction

The invention of the scanning tunneling microscope 20 years ago opened a new door for the exploration of surface phenomena at the molecular and atomic scale.[1] Particularly, it has significantly fostered studies of the self-assembly of organic and biological systems on solid surfaces, even though the self-assembly phenomena of hydrocarbons had been revealed previously, as in work from the early 1970s.[2] Studies of organic self-assembled thin films have attracted an enormous amount of attention due to technological needs in enantioselective catalysis, enantiomeric selectivity in optical activity, and the development of molecular devices and sensors based on the construction of patterned surfaces. In addition, controlling the surface stereochemistry of molecular self-assembled monolayers on solid surfaces could display promising applications in the fabrication of 2-D nanostructural thin film materials and the development of substrates for molecular chiral recognition.

The self-assembly of saturated all-trans carboxylic acids on highly oriented pyrolytic graphite (HOPG) has been well studied.[3−7] Systematic investigations of the self-assembled monolayers of myristic, palmitic, stearic, arachidic, behenic, heptadecanoic, and nonadecanoic acids revealed an odd−even effect in the molecular packing pattern and chirality of the monolayers.[5−7] Fatty acid molecules with even-numbered all-

trans carbon atoms spontaneously separate to form two enantiomer domains with opposite chiralities when they self-assemble on HOPG. Conversely, acid molecules with an odd number of carbon atoms form racemic mixture structures. Figure 1 schematically presents this odd−even effect using decanoic and nonanoic acids as examples of saturated all-trans acids with an even and odd number of carbon atoms, $CH_3(CH_2)_{2n-2}COOH$ and $CH_3(CH_2)_{2n-3}COOH$, respectively.[8] In each lamella of Figure 1, two adjacent molecules pack together with a head-to-tail packing in which the CH_3 of one molecule packs with the COOH of its adjacent molecule on the same side of a lamella. As seen in Figure 1b, the absence of a racemic structure in the self-assembled monolayer of $CH_3(CH_2)_{2n-2}COOH$ is due to the fact that one hydrogen atom of the terminal CH_3 of one molecule is too close to the hydrogen atom of the COOH of its adjacent molecule in the same lamella. This steric repulsion between CH_3 and COOH makes the racemic mixture unstable. By reducing the chain length of the acid molecule by one carbon atom, this large repulsion is relaxed for acids with an odd number of carbon atoms ($CH_3(CH_2)_{2n-3}COOH$), allowing the formation of a stable racemic structure (Figure 1d). However, due to the large repulsion between the CH_3 of one molecule and the COOH of its adjacent molecule in a lamella of $CH_3(CH_2)_{2n-3}COOH$, it cannot form an enantiomer (Figure 1c).
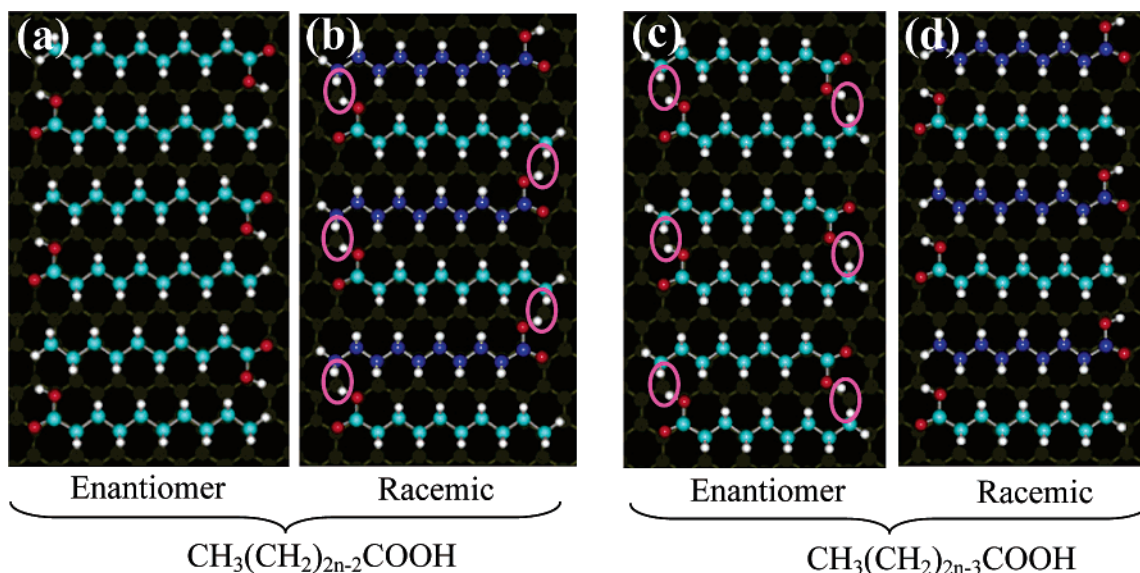
Figure 1. Schemes of the molecular arrangements of self-assembled carboxylic acids with an even number of all-trans carbon atoms, *cis*-CH$_3$-(CH$_2$)$_{2n-2}$COOH (a and b) and an odd number of all-trans carbon atoms, *cis*-CH$_3$(CH$_2$)$_{2n-3}$COOH (c and d). Due to the existence of a large repulsion (marked with pink rings) between two adjacent molecules in a lamella (b and c), only enantiomer (a) and racemic structures (d) were observed for *cis*-CH$_3$(CH$_2$)$_{2n-2}$COOH and *cis*-CH$_3$(CH$_2$)$_{2n-3}$COOH, respectively. The two faces used to adsorb on HOPG are differentiated by cyan and blue colors of the carbon skeleton. CH$_3$(CH$_2$)$_8$COOH and CH$_3$(CH$_2$)$_7$COOH represent *cis*-CH$_3$(CH$_2$)$_{2n-2}$COOH and *cis*-CH$_3$(CH$_2$)$_{2n-3}$COOH, respectively.

Notably, whether the odd−even effect of the saturated all-trans acids can be applied to unsaturated acids with one or more interior *trans*-HC═CH groups is not clear, though the trans conformation of the interior −HC═CH− group does not alter the zigzag extension of the carbon skeleton of the all-trans alkyl chain. This type of unsaturated acid may not adopt the head-to-tail packing of saturated acids in a lamella. For example, brassidic acid self-assembles on HOPG via a head-to-head arrangement.[9]

A common feature of molecular arrangements of these saturated acids with all-trans carbon atoms is the head-to-tail packing. Thus, each trough is made up of an alternate bright bar and dim region corresponding to two CH$_3$ groups and two COOH groups, respectively. Every lamella is equivalent in structure and chirality. The reason for selecting the head-to-tail packing in a lamella is to avoid the large steric repulsion between two neighboring −COOH groups on the same side of a lamella.

However, the cis conformation of the interior −HC═CH− group switches the extension direction of the carbon skeleton by 120°. The nonlinear extension of the carbon skeleton in *cis*-CH$_3$(CH$_2$)$_{p-1}$CH═CH(CH$_2$)$_{m-1}$COOH possibly induces different odd−even effects and molecular packing in a lamella, as well as the selection of a particular molecular rotamer for the adsorption in the structure.

Molecules with a nonlinear extension of the molecular skeleton comprise a large category of organic molecules. However, few studies of their self-assembly have been carried out for these molecules, which include esters and cis-unsaturated acids. Our recent study of carboxylic esters whose two alkyl chains are bent at the interior ester group shows that the original bent molecular skeleton can distort into a linear extension upon adsorption to facilitate matching between the surface lattice of the HOPG and maximizing the interaction between the molecule and the substrate.[10]

In this paper, we investigate the self-assembled structures of various unsaturated acids containing a *cis*-HC═CH group in their interior. On the basis of the observed scanning tunneling microscopy (STM) images and molecular packing models on HOPG resolved at the level of the molecular rotamer, we observed two odd−even chain-length effects for the self-assembly of various cis-unsaturated carboxylic acids.

2. Experimental Section

All of the studies described here were performed with a laboratory-built scanning tunneling microscope operating at the liquid−solid interface under ambient conditions.[9] The single-tube scanner and tip were horizontally mounted and used for scanning. The tip was fabricated by mechanically cutting 0.25 mm platinum/iridium wire (Pt/Ir = 90/10) from Goodfellow. HOPG of ZYB grade was obtained from Advanced Ceramics Corporation. *cis*-15-Tetracosenoic acid (98%), *cis*-10-nonadecenoic acid (99%), and *cis*-9-octadecenoic acid (99%) were purchased from Aldrich and used without further purification.

cis-Unsaturated acid was dissolved in 1-phenyloctane (99%, Aldrich) to produce a nearly saturated solution. The HOPG surface was freshly prepared by cleaving the graphite crystal to expose a mirrorlike surface before imaging. Samples were prepared by gently depositing one drop of the prepared solution (3−5 μL) onto the HOPG surface. Samples were positively biased. All images were collected in a constant current mode. All of the samples prepared here were fully covered by one organic self-assembled monolayer. It is possible to form the multilayer on the HOPG substrate using higher solution concentrations. However, our preparation and tunneling conditions favor imaging of the self-assembled monolayer. Generally, the multilayer is difficult to observe by STM due to the disorder in the multilayer structure resulting from the absence of lattice match with the graphite surface. Experiments were repeated with different tips and samples to check for reproducibility and to ensure that the images were not influenced by tip and sample artifacts.

In this work, the structural modeling of a self-assembled domain was carried out as follows. To make the structural model of the monolayer, the two-dimensional lattice of the HOPG substrate was first constructed on the basis of the crystallographic parameters of the HOPG crystal. The structure of the adsorbate molecule was optimized using HyperChem 7.0. Then, the optimized molecules were superimposed onto the modeled

HOPG substrate by matching the carbon skeleton of the adsorbate molecule with the zigzag lattice of the underlying HOPG substrate and making the plane of the molecular carbon skeleton lie parallel to the HOPG substrate. Then, additional adjacent molecules were added to the monolayer by leaving a space of two unit cells between the molecules to give a molecule−molecule distance of 4.26 Å in the direction perpendicular to the molecular long axis. This molecular arrangement method was confirmed by the measured chain−chain distance in a lamella obtained from the STM image. This approach has been widely used to analyze and assign the self-assembled structures of monolayers on HOPG imaged by STM.

In all of the simulated structural models of the cis-unsaturated carboxylic acids studied here, the space between two adjacent methyl groups of two neighboring lamellae is taken to be two unit cells along the direction of the molecular alkyl chain. We cannot completely exclude the possibility that the lamella−lamella space could be reduced by one graphite surface unit cell distance along the molecular long axis (2.4 Å), without modifying the molecular packing pattern. However, it is noted that such a reduction would produce a larger repulsion between the two end methyl groups of two adjacent lamellae due to steric crowding. In fact, the measurement of molecular length and lamella width in the images is consistent with this space of two unit cells in the structural models.

The space between two adjacent carboxylic acid groups in all proposed models is also reasonable, consistent with expected hydrogen-bonding distances, and supported by experimental measurements. This space is consistent with previous studies of all-trans carboxylic acid monolayer structures.

3. Results and Discussion

Figure 2 shows two representative domains of the self-assembled monolayer of *cis*-15-tetracosenoic acid (*cis*-CH$_3$(CH$_2$)$_7$-CH=CH(CH$_2$)$_{13}$COOH) which represents the class of molecules *cis*-CH$_3$(CH$_2$)$_{p-1}$CH=CH(CH$_2$)$_{2n-1}$COOH ($p \neq 2n$) ($p = 8$, $n = 7$). Two kinds of lamellae, **A** and **B**, pack alternately in this domain. Each lamella has a slightly brighter stripe ascribed to the C=C group, and marked with a light-yellow dashed line on this image. In lamella **A**, the left band is wider than the right one. However, the left band is narrower than the right one in lamella **B**. Because the carboxylic group is at the end of the longer chain, −(CH$_2$)$_{13}$COOH, trough **1** is assigned to the area of a hydrogen-bonding network. Trough **2** corresponds to the uncovered area between two terminal CH$_3$ groups. The two hydrogen-bonded molecules marked with yellow bars in Figure 2b comprise one unit cell of the self-assembled domain. The measured angle between the long and short chains of one molecule is ~125°, close to the 120° obtained in the optimized gas phase molecular structure for the cis conformation. The slight deviation may result from the inaccuracy of measurement in the less-than-atomic-resolution STM image here.

As is well-known, the HOPG surface has a 3-fold symmetry. This symmetry allows the molecular skeleton of two all-trans alkyl chains with an angle of ~120° to match with the substrate lattice (Figure 3). This is one of the driving forces for the formation of stable self-assembled monolayers from cis-unsaturated acids. Another driving force is the hydrogen-bonding network of trough **1** which stabilizes two adjacent lamellae. Notably, trough **1** only consists of acid groups. This trough is different from that of the saturated acid with an all-trans configuration, where terminal COOH (head) and CH$_3$ (tail) groups alternately pack in a trough and thereby form a structure with a trough-to-chain angle of 90° (Figure 1). This head-to-
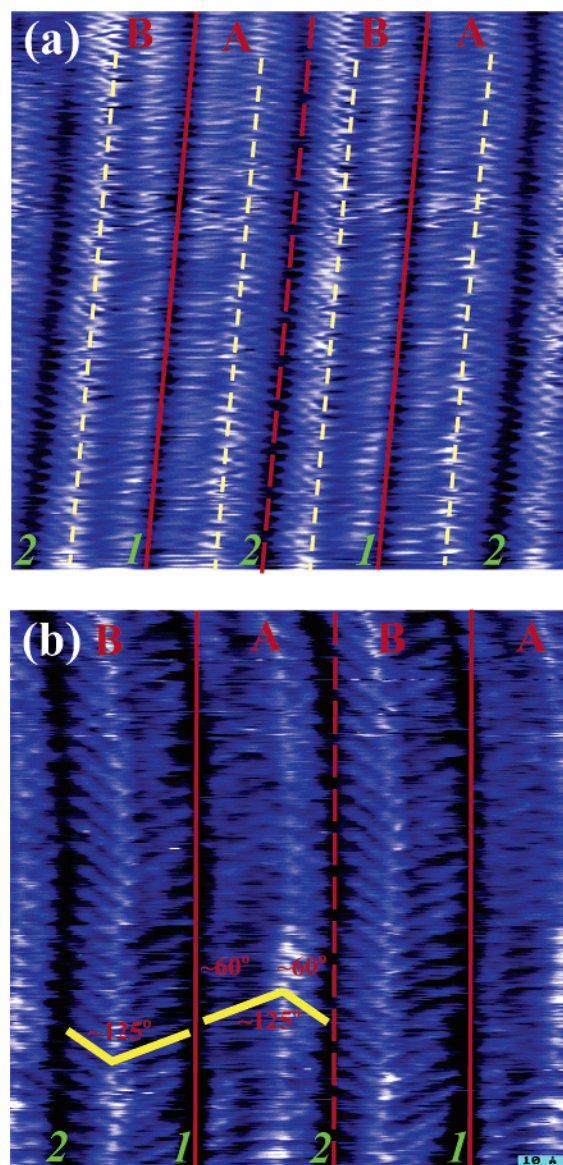

Figure 2. STM images of *cis*-CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_{13}$COOH on HOPG: (a) 135 Å × 135 Å, $V_b = 0.71$ V, $I_t = 0.75$ nA; (b) 121 Å × 121 Å, $V_b = 0.76$ V, $I_t = 0.75$ nA. The letters **A** and **B** on the two images represent two adjacent lamellae. The numbers **1** and **2** represent two adjacent but different troughs. Trough **1** is the area of the hydrogen-bonding network made of pure COOH groups. Trough **2** is the uncovered area between two terminal CH$_3$ groups. The light-yellow dashed line marks the interior C=C groups of a lamella. The yellow bar in part b schematically shows one packed molecule on HOPG. The two adjacent yellow bars in image b combine into a unit cell of this domain.

tail packing minimizes the molecule−molecule repulsion in a lamella. However, for *cis*-CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_{13}$COOH, all of the acid groups or all of the methyl groups are packed on one side of a lamella. No steric repulsion at either side of a lamella is expected because the COOH group of one molecule shifts from the COOH group of its adjacent molecule in a lamella by one unit (~2.52 Å) along the direction of the alkyl chain, forming a chain−trough angle of ~60° (Figure 2b). This shift forms a new hydrogen-bonding network, as shown in trough **1** of Figure 3, different from that of the saturated acid with an all-trans configuration.

To form this hydrogen-bonding network, the orientation of the molecules in lamella **B** is obtained by rotating the molecules in lamella **A** around the normal to the substrate by 180°. All of
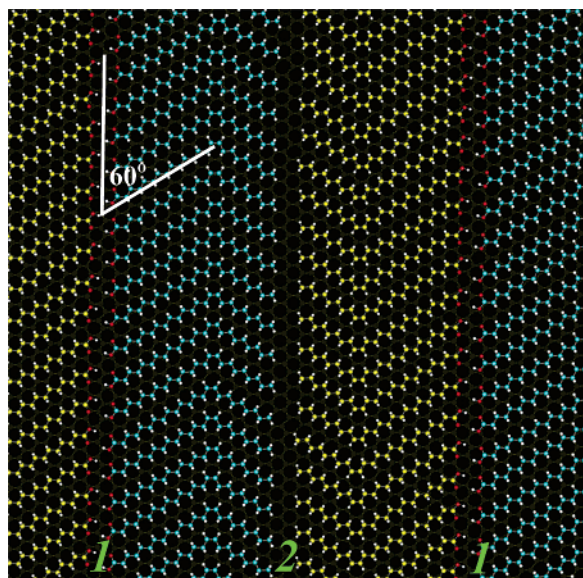
Figure 3. Molecular arrangement corresponding to the domains of Figure 2. All molecules pack on HOPG with face **1** which is defined as the face with an angle of ~120° from the short chain to the long chain along the clockwise direction.
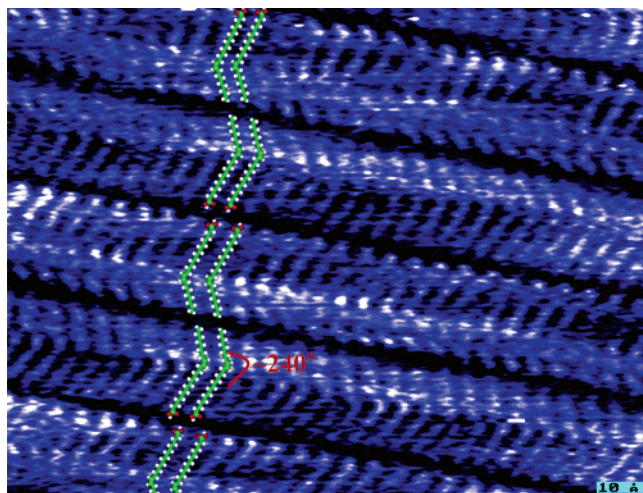

Figure 4. STM image of another kind of domain of *cis*-CH$_3$(CH$_2$)$_7$-CH=CH(CH$_2$)$_{13}$COOH (138 Å × 102 Å, V_b = 0.70 V, I_t = 0.75 nA). All of the molecules in this domain use face **2** to pack on HOPG. Face **2** is defined as the face with an angle of ~240° from the short chain to the long chain along the clockwise direction.

the molecules in the domains of Figure 2 use the same face to adsorb on the HOPG surface, demonstrating that these domains are the same type of enantiomer. The measured angle from short chain to long chain along the clockwise direction in these images is ~125° which is the characteristic parameter of this enantiomer. When *cis*-CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_{13}$COOH uses the other face to adsorb, the angle is ~240°, as is seen in the domain of Figure 4. Thus, this acid uses its opposite face to self-assemble into another enantiomer with opposite 2-D chirality. Due to the absence of images with very high resolution, the selection of rotamers cannot be completely identified here, though rotamer **II** is used to build a structural model in Figure 3 for the observed self-assembled domains.

On the basis of the structural model and the observed images of *cis*-CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_{13}$COOH, it is expected that cis-unsaturated acids with an even number of carbon atoms on the acid side, *cis*-CH$_3$(CH$_2$)$_{p-1}$CH=CH(CH$_2$)$_{2n-1}$COOH ($p \neq 2n$), can simultaneously self-assemble into two enantiomers on
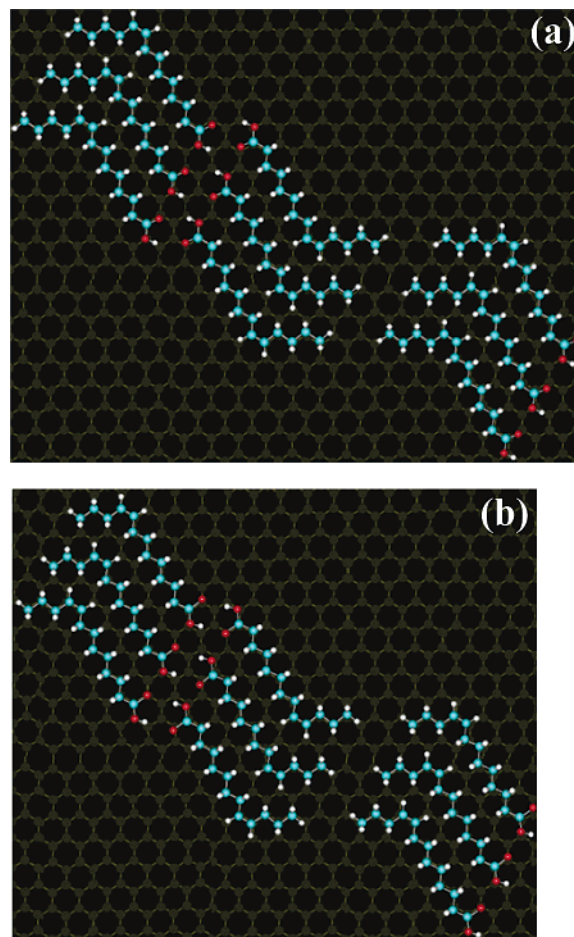
Figure 5. Molecular arrangements of *cis*-CH$_3$(CH$_2$)$_{p-1}$CH=CH-(CH$_2$)$_{m-1}$COOH ($p \neq m$, $p = 2n$ or $2n - 1$). The two structures show that the number of carbon atoms on the methyl side does not make a difference in the self-assembled structure of cis-unsaturated acids. *cis*-CH$_3$(CH$_2$)$_3$CH=CH(CH$_2$)$_7$COOH and *cis*-CH$_3$(CH$_2$)$_2$CH=CH(CH$_2$)$_7$-COOH represent *cis*-CH$_3$(CH$_2$)$_{p-1}$CH=CH(CH$_2$)$_{m-1}$COOH ($p = 2n$) and *cis*-CH$_3$(CH$_2$)$_{p-1}$CH=CH(CH$_2$)$_{m-1}$COOH ($p = 2n - 1$), respectively.

HOPG. In addition, *cis*-CH$_3$(CH$_2$)$_{p-1}$CH=CH(CH$_2$)$_{2n-1}$COOH ($p \neq 2n$) molecules such as *cis*-CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_{13}$-COOH ($p = 8, n = 7$) cannot alternately pack their two opposite faces in a lamella to form a racemic mixture because the numbers of carbon atoms on the two sides of the *cis*-HC=CH group are not equal. Therefore, no racemic structure can be predicted, nor was one observed for *cis*-CH$_3$(CH$_2$)$_{p-1}$CH=CH-(CH$_2$)$_{2n-1}$COOH ($p \neq 2n$).

The molecular packing models of *cis*-CH$_3$(CH$_2$)$_3$CH=CH-(CH$_2$)$_7$COOH ($p = 4, m = 8$) and *cis*-CH$_3$(CH$_2$)$_2$CH=CH-(CH$_2$)$_7$COOH ($p = 3, m = 8$), two examples of the class of molecules *cis*-CH$_3$(CH$_2$)$_{p-1}$CH=CH(CH$_2$)$_{m-1}$COOH ($p \neq m$), in Figure 5 suggest that the number of carbon atoms on the methyl side should not affect the packing pattern of *cis*-CH$_3$-(CH$_2$)$_{p-1}$CH=CH(CH$_2$)$_{m-1}$COOH ($p \neq m$). Thus, for *cis*-CH$_3$-(CH$_2$)$_{p-1}$CH=CH(CH$_2$)$_{m-1}$COOH cis-unsaturated acids, we only discuss how the number of carbon atoms on the acid side induces a difference in the self-assembled structure.

As discussed above for *cis*-CH$_3$(CH$_2$)$_{p-1}$CH=CH(CH$_2$)$_{2n-1}$-COOH ($p \neq 2n$) molecules such as *cis*-CH$_3$(CH$_2$)$_7$CH=CH-(CH$_2$)$_{13}$COOH ($p \neq 2n$), two enantiomers with opposite 2-D chiralities can be formed (Figure 6a and b). For *cis*-CH$_3$-(CH$_2$)$_{p-1}$CH=CH(CH$_2$)$_{2n-2}$COOH ($p \neq 2n - 1$), however, there is a large steric repulsion between the hydrogen atom of the COOH group of one molecule and one hydrogen atom of the
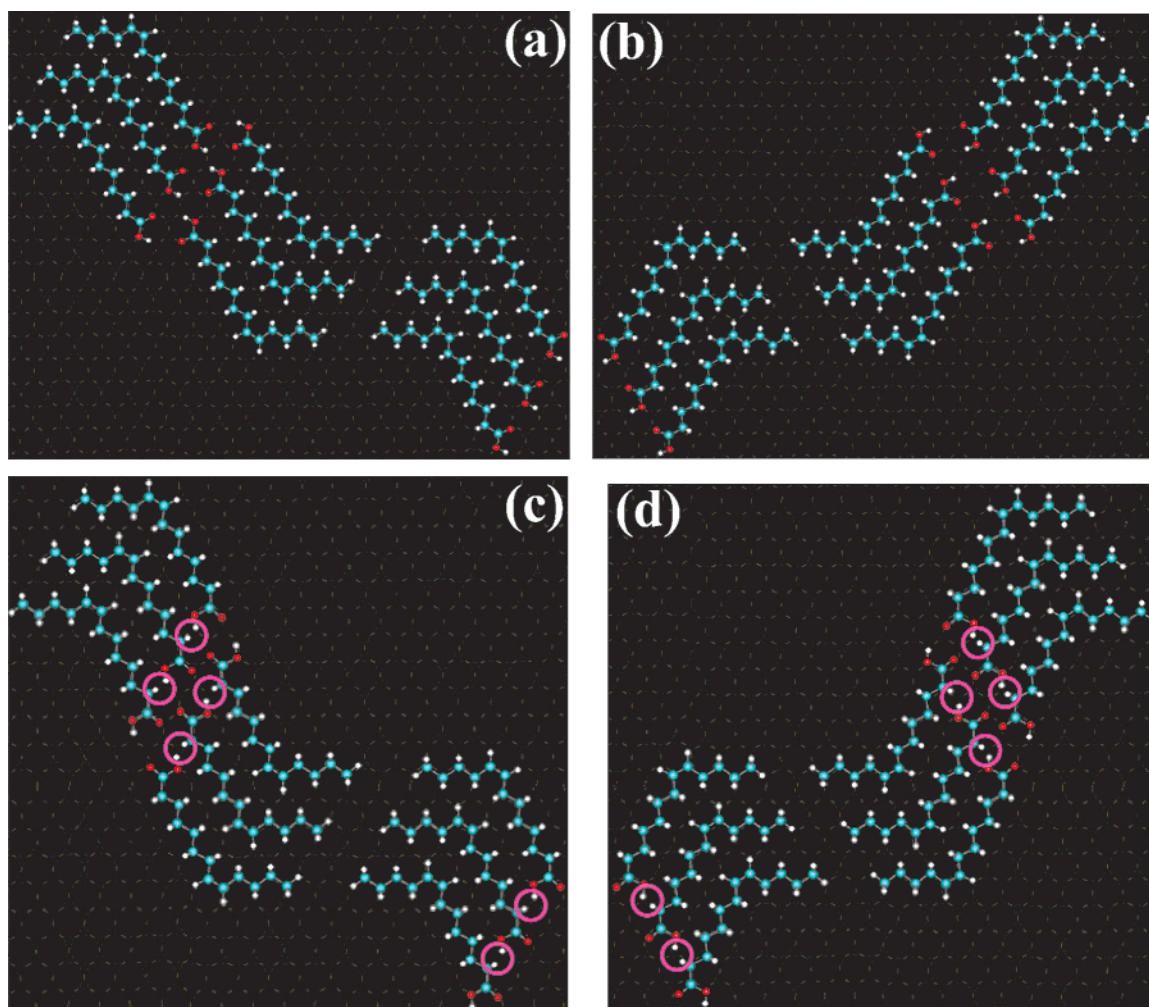
Figure 6. Molecular arrangements of two enantiomers (a and b) of *cis*-unsaturated acid with even numbers of all-trans carbon atoms on the side of the acid group, $cis\text{-}CH_3(CH_2)_{p-1}CH=CH(CH_2)_{2n-1}COOH$ ($p \neq 2n$). Molecular arrangements of two enantiomers (c and d) of *cis*-unsaturated acid with odd numbers of all-trans carbon atoms on the side of the acid group, $cis\text{-}CH_3(CH_2)_{p-1}CH=CH(CH_2)_{2n-2}COOH$ ($p \neq 2n-1$). Each pink ring in parts c and d shows a large repulsion between the hydrogen atom of the COOH group of one molecule and one hydrogen atom of the $\alpha\text{-}CH_2$ group of its adjacent molecule in a lamella. $cis\text{-}CH_3(CH_2)_4CH=CH(CH_2)_7COOH$ and $cis\text{-}CH_3(CH_2)_4CH=CH(CH_2)_6COOH$ represent $cis\text{-}CH_3(CH_2)_{p-1}CH=CH(CH_2)_{2n-1}COOH$ and $cis\text{-}CH_3(CH_2)_{p-1}CH=CH(CH_2)_{2n-2}COOH$, respectively.

$\alpha\text{-}CH_2$ group of the adjacent molecule in a lamella, marked with a pink ring in Figure 6c and d. This model is consistent with the fact that no ordered domain of $cis\text{-}CH_3(CH_2)_7CH=CH(CH_2)_8COOH$ ($p = 8$, $n = 5$) was experimentally observed, suggesting that $cis\text{-}CH_3(CH_2)_{p-1}CH=CH(CH_2)_{2n-2}COOH$ ($p \neq 2n-1$) cannot form a stable self-assembled structure. Therefore, the $cis\text{-}CH_3(CH_2)_{p-1}CH=CH(CH_2)_{m-1}COOH$ ($p \neq m$, $m = 2n$ or $2n-1$) molecule, called category **I**, exhibits an odd−even effect which is different from that of the saturated acids with all-trans carbon atoms.[5−7]

For the cis-unsaturated acid containing chains with equal numbers of all-trans carbon atoms on the alkyl side and acid side of the $cis\text{-}HC=CH$ group, $cis\text{-}CH_3(CH_2)_{m-1}CH=CH(CH_2)_{m-1}COOH$ ($m = 2n$ or $2n-1$), called category **II**, there is another odd−even effect. *cis*-10-Nonadecenonic acid, $cis\text{-}CH_3(CH_2)_7CH=CH(CH_2)_7COOH$, is one example of this class of molecules, $cis\text{-}CH_3(CH_2)_{2n-1}CH=CH(CH_2)_{2n-1}COOH$ ($n = 4$). Figure 7 is one type of domain observed from the self-assembled monolayer of $cis\text{-}CH_3(CH_2)_7CH=CH(CH_2)_7COOH$, as an example of this class ($cis\text{-}CH_3(CH_2)_{2n-1}CH=CH(CH_2)_{2n-1}COOH$ ($n = 4$)). This structure shows alternate bright, wide molecular lamella and dim, narrow troughs between two adjacent lamellae. Notably, the packing style of the chains at both sides of trough **1** is completely different from that of trough

2. Every two nearest chains from two sides of trough **1** can be aligned on the same line, called *on-line* packing. However, the two closest chains from two sides of trough **2** are not on a line and they are packed via an *interdigitated* packing.

Figure 8a reveals another kind of domain of $cis\text{-}CH_3(CH_2)_7CH=CH(CH_2)_7COOH$. Notably, the trough between two neighboring lamellae is significantly different from that of Figure 7. Each trough of Figure 8 is identical and made of alternating bright bars and dim regions. The feature of the troughs of Figure 8 is the same as those of the enantiomer and racemic domains of the all-trans saturated carboxylic acid,[5−7] in which two adjacent molecules in a lamella pack together via a head-to-tail arrangement. Thus, the molecules in each lamella of Figure 8 also adopt the head-to-tail packing pattern.

However, no alternately packed bright bars and dim regions were observed in the troughs of Figure 7, showing that two adjacent $cis\text{-}CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ molecules in a trough use another packing mode, a head-to-head arrangement. Figure 9 shows four expected packing models for the domain of Figure 7 based on the head-to-head packing. Parts a1 and a2 of Figure 9 correspond to molecules using face **I** or **II** of rotamer **I**, respectively. Rotamer **I** is defined as that with the carbonyl at the same side as the hydrogen atoms of the $\alpha\text{-}CH_2$ group. If they are on the opposite side of the carbon skeleton, this model
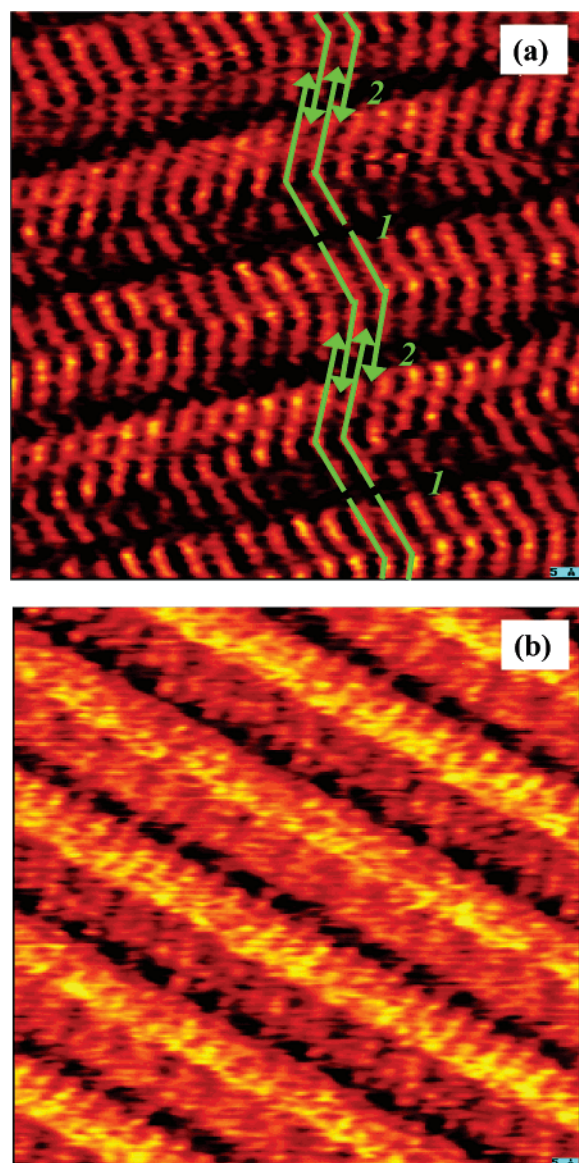
Figure 7. Two domains of a *cis*-CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$COOH monolayer with different self-assembled structures. They have a similar resolution. (a) 100 Å × 100 Å, V_b = 0.79 V, I_t = 0.75 nA. The numbers **1** and **2** are used to differentiate two adjacent troughs. The green arrows and green lines mark the extended direction of the chains on the two sides of troughs **2** and **1**, respectively. (b) 115 Å × 115 Å, V_b = 0.71 V, I_t = 0.74 nA. Each trough of part b is made of an alternating bright bar and dim region.

Figure 8. Another kind of domain of a *cis*-CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$-COOH monolayer: (a) 200 Å × 200 Å, V_b = 0.71 V, I_t = 0.74 nA; (b) 115 Å × 115 Å, V_b = 0.71 V, I_t = 0.74 nA. All troughs of the two domains are identical. Each trough is made of an alternating bright bar and dim region.

is rotamer **II**. Parts b1 and b2 of Figure 9 are the self-assembly structures of rotamer **II** with faces **I** and **II**, respectively. In the structures of rotamer **II**, the two chains at the two sides of any trough align via an *on-line* model. However, for the structures of rotamer **I**, one of two adjacent troughs uses an *interdigitated* pattern and the other uses an *on-line* model. Thus, the molecules in the domain of Figure 7 choose rotamer **I** to self-assemble. According to the packing model of rotamer **I**, troughs **1** and **2** in Figure 7 are made of pure CH$_3$ groups and COOH groups, respectively.

Following the head-to-tail packing model of two adjacent molecules in a lamella, *cis*-CH$_3$(CH$_2$)$_{2n-1}$CH=CH(CH$_2$)$_{2n-1}$-COOH possibly selects rotamer **I** or **II** to form two self-assembled structures, as shown in parts a and b of Figure 10, respectively. If rotamer **II** is chosen, no alternate bright bar and dim region can be observed in the direction of the alkyl chain,
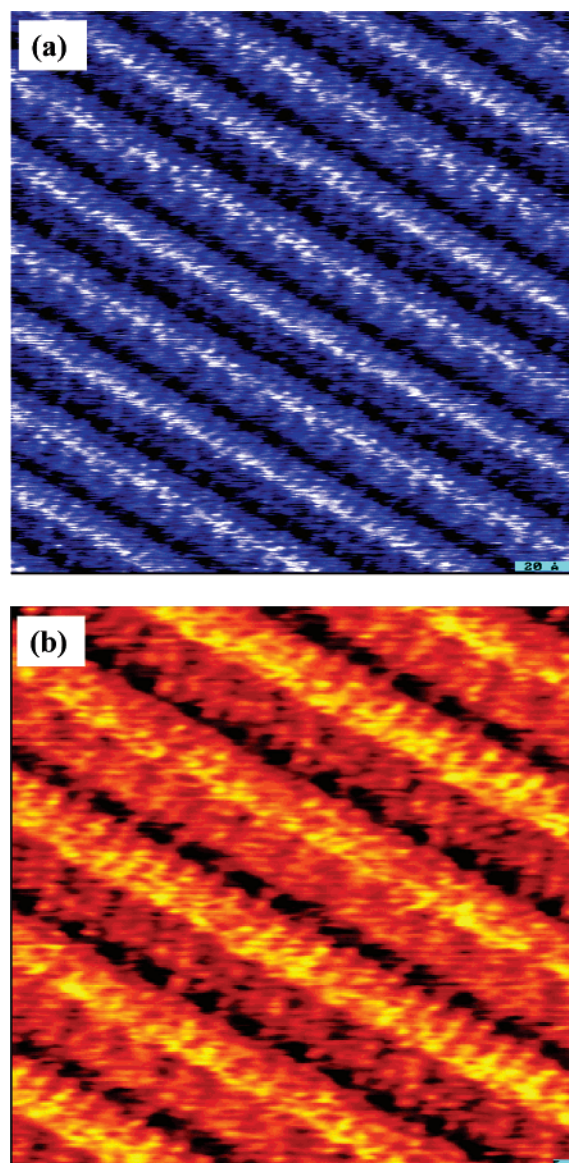
because each part of the trough is made of homogeneous pairs of CH$_3$ and COOH groups.

A pair of CH$_3$ and COOH groups along the chain direction is marked with red and green arrows in one white box of Figure 10b. For the structure of rotamer **I**, however, two adjacent parts of a trough along the direction of the alkyl chain are made of alternating pairs of CH$_3$ and COOH groups. These are marked with a pair of red arrows and a pair of green arrows in the two white boxes of Figure 10a. Thus, the trough of the structure using rotamer **I** appears as an alternating bright bar and dim region. Figure 10a thus shows the molecular packing model of the domains of Figure 8. The saturated acids also select rotamer **I** for self-assembly; otherwise, no alternate bright bar and dim region in a trough would be observed. Similar to the domain of Figure 7, *cis*-CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$COOH in its other class of domains (Figure 8) still chooses to use rotamer **I** to self-assemble. However, for molecules of the class *cis*-CH$_3$(CH$_2$)$_{p-1}$-CH=CH(CH$_2$)$_{m-1}$COOH ($p \neq m$) such as *cis*-CH$_3$(CH$_2$)$_7$-CH=CH(CH$_2$)$_{13}$COOH (p = 8, m = 14), a specific selection

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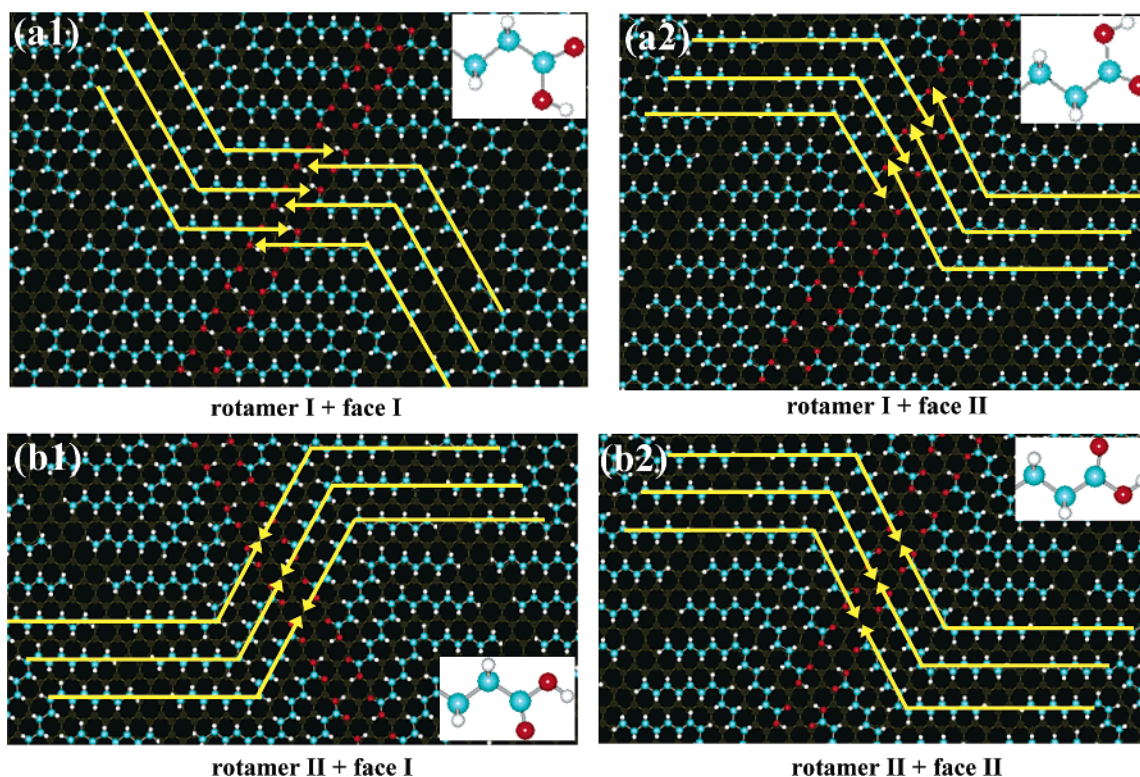*J. Phys. Chem. B, Vol. 110, No. 9, 2006* **4205**

Figure 9. Four packing structures of *cis*-$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ using a head-to-head packing of two adjacent molecules in a lamella and choosing rotamer **I** and face **I** (a), rotamer **I** and face **II** (b), rotamer **II** and face **I** (c), or rotamer **II** and face **II** (d). *cis*-$CH_3(CH_2)_5CH=CH$-$(CH_2)_5COOH$ represents *cis*-$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ for a clearer presentation.
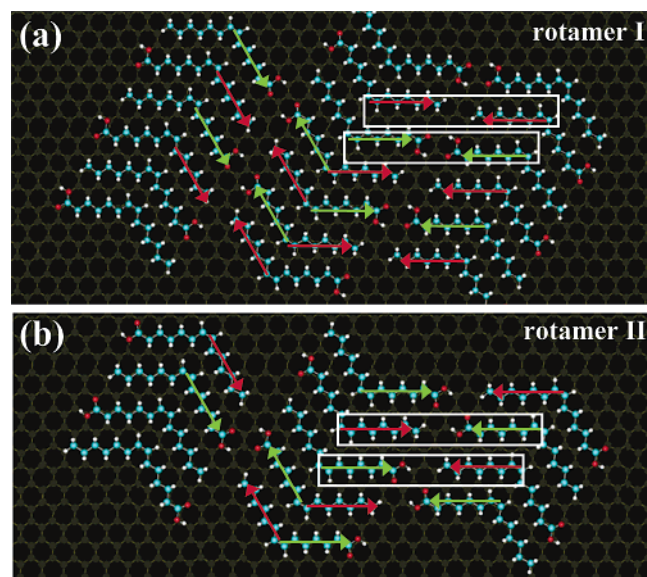

Figure 10. Two packing structures of *cis*-$CH_3(CH_2)_7CH=CH(CH_2)_7$-COOH using a head-to-tail arrangement selecting rotamer **I** (a) or rotamer **II** (b).

Figure 11. Packing structure of *cis*-$CH_3(CH_2)_4CH=CH(CH_2)_4COOH$, one example of *cis*-$CH_3(CH_2)_{2n-2}CH=CH(CH_2)_{2n-2}COOH$ ($n = 3$), on HOPG. In parts a and b, all molecules use face **1** or **2** to form two enantiomers, respectively. In part c, two adjacent molecules use opposite faces to adsorb on the HOPG surface in a lamella, forming a racemic structure.

for rotamers **I** and **II** is not needed because they do not give rise to a different self-assembled structure.

According to the packing model in Figures 9a and 10a, the domains of Figures 7 and 8 are enantiomer and racemic structures, respectively. Thus, it is expected that *cis*-CH_3-$(CH_2)_{2n-1}CH=CH(CH_2)_{2n-1}COOH$ forms both enantiomer and racemic domains on HOPG. This is the first example of a carboxylic acid which can simultaneously self-assemble into both enantiomer and racemic structures.

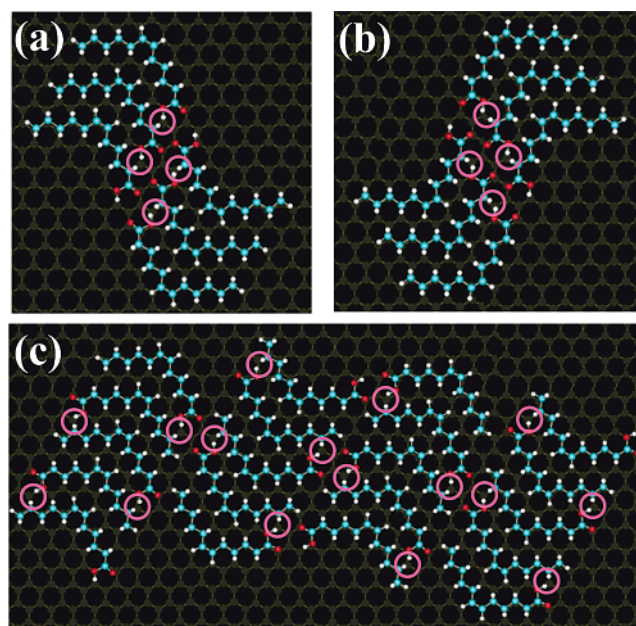To study the odd–even effect for a cis-unsaturated acid with an equal number of carbon atoms on both sides of the

cis-$HC=CH$ group, the expected molecular packing of enantiomer domains (a and b) and racemic domain (c) of *cis*-$CH_3(CH_2)_{2n-2}CH=CH(CH_2)_{2n-2}COOH$ are presented in Figure 11. In all three structures, there are large steric repulsions marked with pink rings similar to the expected structure of *cis*-$CH_3(CH_2)_7CH=CH(CH_2)_8COOH$ (Figure 6c and d) which cannot form stable ordered domains on HOPG. Thus, it is

reasonable to deduce that cis-$CH_3(CH_2)_{2n-2}CH=CH(CH_2)_{2n-2}$-COOH cannot self-assemble into stable ordered domains. Obviously, cis-unsaturated acids with equal numbers of carbon atoms on both sides of the cis-HC=CH group, cis-$CH_3(CH_2)_{m-1}CH=CH(CH_2)_{m-1}$COOH (category **II**), exhibit another odd−even effect for molecular self-assembly on HOPG.

4. Summary

Studies of the self-assembled monolayers of cis-$CH_3(CH_2)_{p-1}CH=CH(CH_2)_{m-1}$COOH on HOPG revealed new self-assembly behaviors different from what is observed for saturated acids with all-trans configurations. cis-$CH_3(CH_2)_7CH=CH(CH_2)_{13}$COOH acid, one example of the class of molecules cis-$CH_3(CH_2)_{p-1}CH=CH(CH_2)_{2n-1}$COOH, forms two enantiomers with opposite chiralities, in which every two adjacent lamellae are linked via a hydrogen-bonding network comprised of pure COOH groups. This hydrogen-bonding network is different from that of saturated acids with all-trans configurations. Both the simulated molecular packing structures and the STM studies of cis-$CH_3(CH_2)_7CH=CH(CH_2)_8$COOH suggest that cis-$CH_3(CH_2)_{p-1}CH=CH(CH_2)_{2n-2}$COOH cannot form a stable self-assembled structure due to the large repulsion between two adjacent molecules in a lamella. This difference indicates an odd−even effect for cis-$CH_3(CH_2)_{p-1}CH=CH(CH_2)_{m-1}$COOH ($p \neq m$) ($m = 2n$ or $2n - 1$). cis-Unsaturated acids containing two chains with equal numbers of carbon atoms on both sides of the cis-HC=CH group, cis-$CH_3(CH_2)_{m-1}CH=CH(CH_2)_{m-1}$COOH ($m = 2n$), can form both enantiomer and racemic structures. However, no stable domain is predicted to form on HOPG for cis-$CH_3(CH_2)_{m-1}CH=CH(CH_2)_{m-1}$COOH ($m = 2n - 1$). This odd−even effect is also ascribed to the steric repulsion between two adjacent molecules in a lamella.

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