Adsorption-Induced Asymmetric Assembly from an Achiral Adsorbate

Yuguang Cai[†] and Steven L. Bernasek*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540

Received July 14, 2004; E-mail: sberna@princeton.edu

Abstract: Symmetry breaking in the self-assembled monolayer (SAM) structure of 1-octadecanol on highly ordered pyrolytic graphite (HOPG) is observed. Due to the slight mismatch of the octadecanol molecule with the graphite lattice, the alkane chain undergoes distortion upon adsorption on the surface. The asymmetric distortion of the octadecanol SAM unit cell pair is observed by scanning tunneling microscopy at the liquid/solid interface. Asymmetric distortion is due to the requirement for planarity of the hydrogen bond connecting the two octadecanol molecules in the chevron-shaped unit cell. This very simple structure provides the first example of an adsorption-induced distortion to form a supramolecular asymmetric structure, which is formed by achiral molecules adsorbed on an achiral surface. What makes this system interesting and different from other examples of adsorption-induced chirality is that the adsorbate itself undergoes asymmetric distortion due to the existence of the substrate and the adsorbate conformation is different from the molecule in solution.

Chirality is an important phenomenon in nature. Chiral structures can be formed not only from pure chiral molecules but also by the asymmetric assembly of molecules. At the supramolecular level, chiral structures induced by hydrogen bonding have been well studied. Successful design and synthesis of asymmetric assemblies involving hydrogen bonding have been reported in solution[1,2] and in the solid state,[3−5] with different shapes being observed.[4,5] Some researchers have even succeeded in forming enantio-pure chiral assemblies.[6−8] In the two-dimensional realm, potential applications such as enantioselective heterogeneous catalysts[9,10] have drawn a lot of interest in the study of chiral structures on surfaces.[9−16,18−26,33−39]

Using a chiral "modifier", i.e., depositing chiral molecules on the surface, is a typical way of generating a chiral surface.[10−12] Enantio-pure molecules such as (*R*,*R*)-tartaric acid have been successfully used as surface modifiers in enantioselective heterogeneous catalysis.[10,11] Achiral materials may also be used as chiral modifiers to create chiral surface structures. For example, racemic mixtures of certain chiral molecules spontaneously separate on the surface to form chiral domains.[13−16] This behavior is the two-dimensional analogue of Pasteur's separation in 1848 of the optical isomers of sodium ammonium tartrate.[17] Such racemic mixtures can also be used as surface modifiers, though they chirally modify the surface only in their respective chiral domains. At the supramolecular level, chiral structures may be formed by asymmetric assembly, which also serves as a chiral modifier. Hydrogen bonded chains[11,18,19] have been reported to show chiral structures on the surface. An achiral surface itself can induce an achiral adsorbate to form chiral adsorbate structures as well. Studies of adsorption-induced chirality reveal that the interaction between the substrate and the adsorbate play a key role in inducing structural changes and the symmetry breaking which results in chirality.[16,20,25,35−39]

[†] Present address: Physics Department, Brookhaven National Laboratory, Upton, New York 11973.

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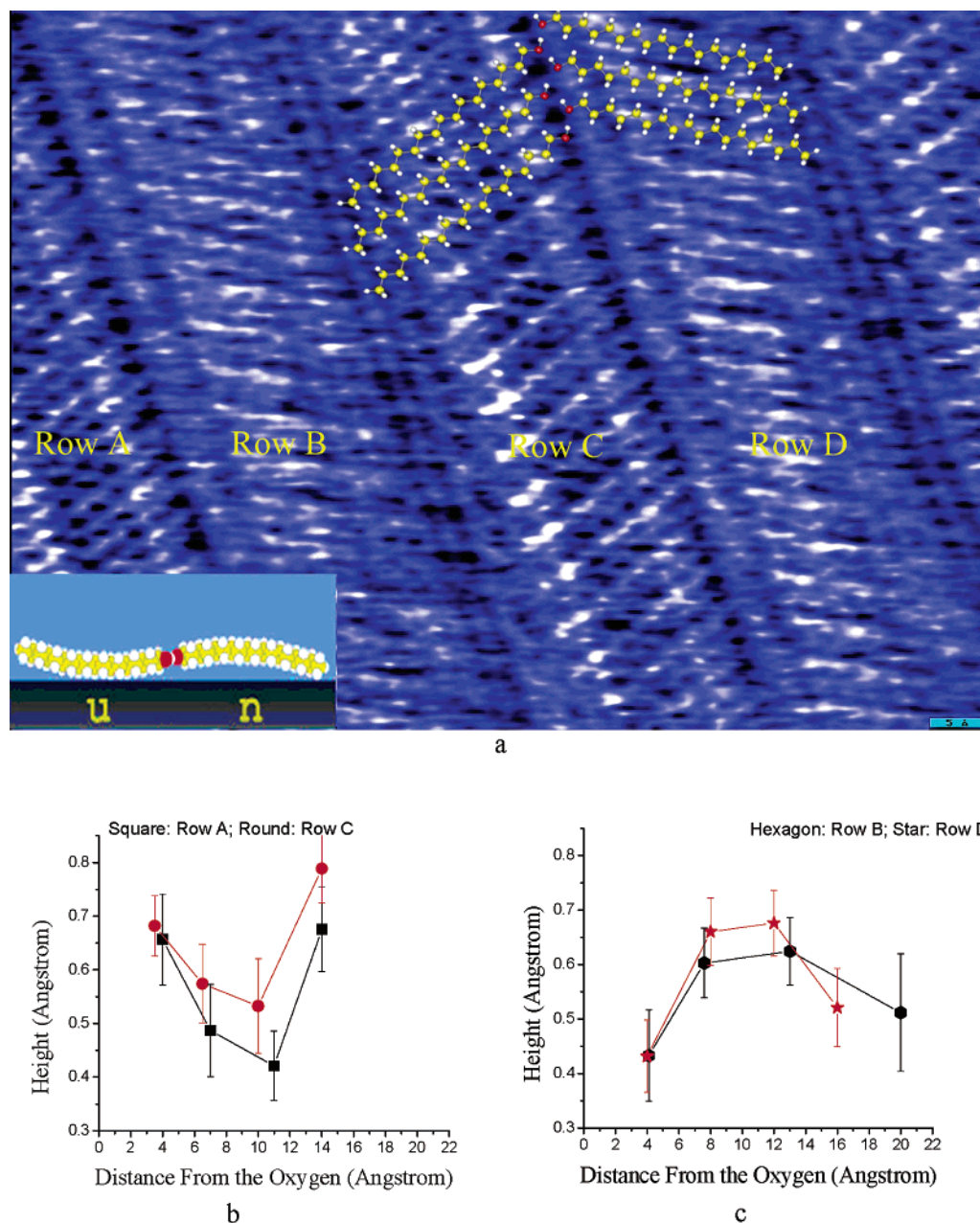(25) Qian, P.; Nanjo, H.; Yokoyama, T.; Suzuki, T. M. *Chem. Commun.* **1999**, *13*, 1197−1198.

Figure 1. (a) Octadecanol SAM. Scan area 86.0 Å × 85.0 Å, $V_b = 1.17$ V, $I_t = 0.63$ nA. Upper right shows model of octadecanol chevron structure overlaid on the STM image. The inset illustrates the asymmetric distortion in the chevron pair. (b and c) The averaged height profiles along the chain direction of octadecanol molecules in row A, B, C, D, respectively. The "u" rows (row A and C) or "n" rows (row B and D) have a similar shape but not exactly the same height variation.

High-resolution scanning probe microscopy (SPM) makes the study of chiral structures on the surface possible. Self-assembled monolayers of long chain alkane derivatives on the HOPG surface are ideal systems for SPM studies of asymmetric structures on surfaces. Significant progress has been made in this area, including the observation of spontaneous separation of a racemic mixture,[14–16] direct identification of the chirality of homochiral domains,[15] the discovery of the formation of

heterochiral domains,[21] and the observation of surface-induced chirality.[20,25,35–39]

In this paper, an example of the formation of an asymmetric structure on the surface, which involves both supramolecular assembly through hydrogen bonding and adsorption-induced

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(31) Figure 3 also shows an example of this. In Figure 3, starting from the right, for the four rows A, B, C, D, the apparent height profiles across these four rows has a "unnu" style, which is different from their neighbouring rows. In the whole image, the height variation across different rows does not have any recognizable pattern.
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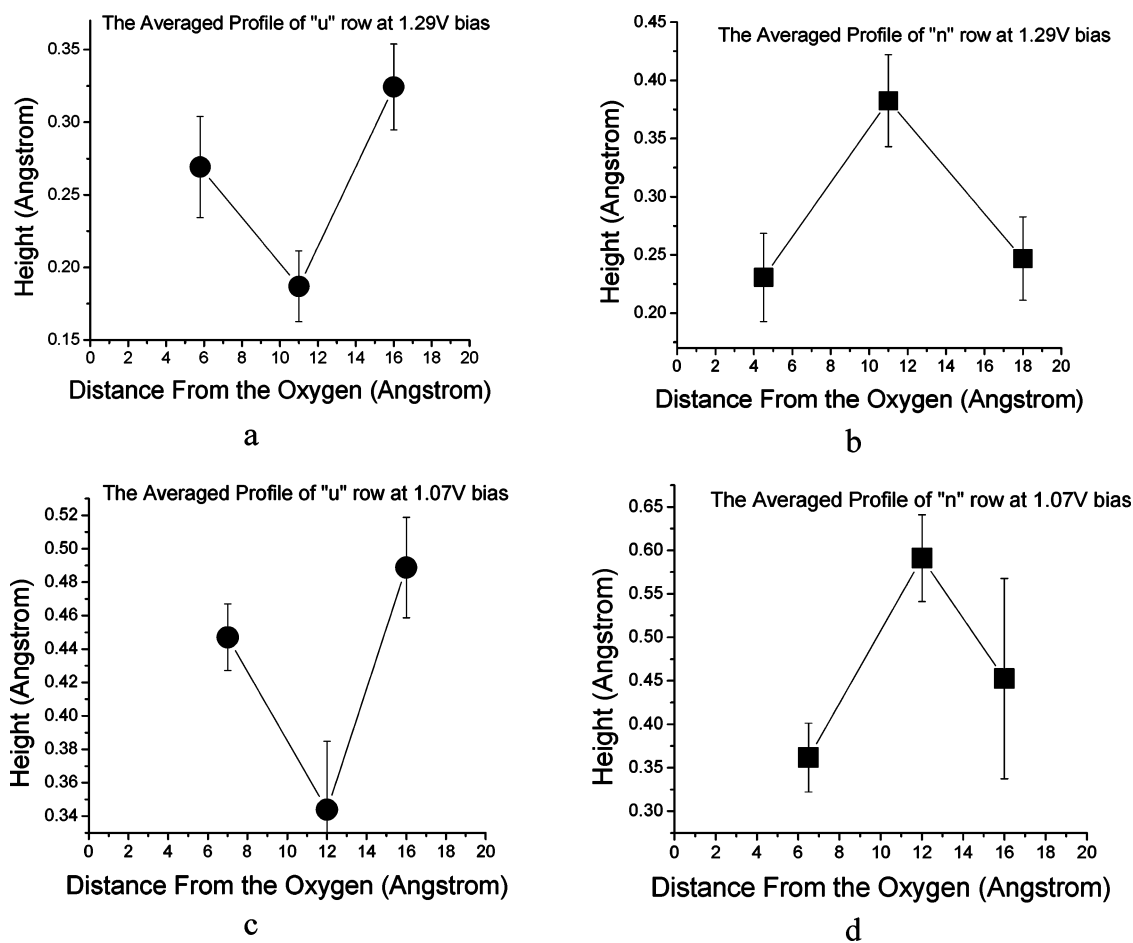(35) Yablon, D. G.; Giancarlo, L. C. Flynn, G. W. *J. Phys. Chem. B* **2000**, *104*, 7627–7635.

The Averaged Profile of "u" row at 1.29V bias

The Averaged Profile of "n" row at 1.29V bias

The Averaged Profile of "u" row at 1.07V bias

The Averaged Profile of "n" row at 1.07V bias

a

b

c

d

Figure 2. Averaged height profiles along the chain direction of octadecanol molecules in "u" rows and "n" rows at different bias voltages. (a and b) Height profiles of "u" row and "n" row at bias voltage of 1.29 V, tunneling current 0.72 nA. (c and d) Height profiles of "u" row and "n" row at bias voltage of 1.07 V, tunneling current 0.72 nA.

chirality, is reported. What makes this system interesting and different from other examples of adsorption-induced chirality is that the adsorbate itself undergoes asymmetric distortion due to the existence of the substrate. The adsorbate conformation is different from the conformation of the molecule in solution. The molecule pair in the self-assembled monolayer of octade-canol is observed to bend asymmetrically in the unit cell due to adsorbate−substrate interactions and hydrogen bonding in the unit cell, resulting in symmetry breaking in the unit cell and the generation of an asymmetric structure on an achiral surface.

The scanning tunneling microscope (STM) used in these studies is a home-built ultrahigh vacuum variable temperature STM. The tip is cut from 0.01″ diameter platinum iridium wire (Pt/Ir = 90:10) from Goodfellow. Samples are positively biased, and all scans were carried out under ambient condition at the liquid/solid interface. Different tips and HOPG samples are used to ensure reproducibility. Octadecanol (99%+) and phenyloctane are purchased from Sigma-Aldrich and used without further purification. HOPG is from Union Carbide, ZYA grade. One drop of a saturated solution of octadecanol in phenyloctane was applied on a newly cleaved HOPG surface, and then the STM images were acquired. All image dimensions are calibrated by using the bare HOPG hexagonal lattice.

One reason that long chain alkanes and their derivatives form stable self-assembled monolayers on HOPG is the good match of the HOPG lattice unit (2.46 Å) and the H−H distance on adjacent methylene groups (2.52 Å) in the hydrocarbon chain. Even so there is a 2.5% difference in this repeat distance. To keep good registry with the substrate, a compression of 2.5% of the alkane chain length is needed. In long chain alkane SAMs on HOPG,[27−30] small apparent height variations along the molecule chain have been observed. These observed variations have the same pattern along the same row in the alkane SAMs, and the variations are not the same in different rows.[31] If such variation was the result of a Moiré pattern due to the interaction between the alkane SAM lattice and the graphite lattice, there would be two possibilities. First, if the mismatch of the two sets of lattices is translational, then the Moiré pattern would appear in the translation direction. Thus, there would be periodic apparent height variations in only one direction. Second, if the mismatch of the two sets of lattices is rotational, then the Moiré pattern would have the hexagonal symmetry of the graphite substrate lattice. Since the observed height variation is not exactly the same for every row, which means literally there is not a height variation across the rows, the variation cannot be the result of a translational Moiré pattern. Also, within each

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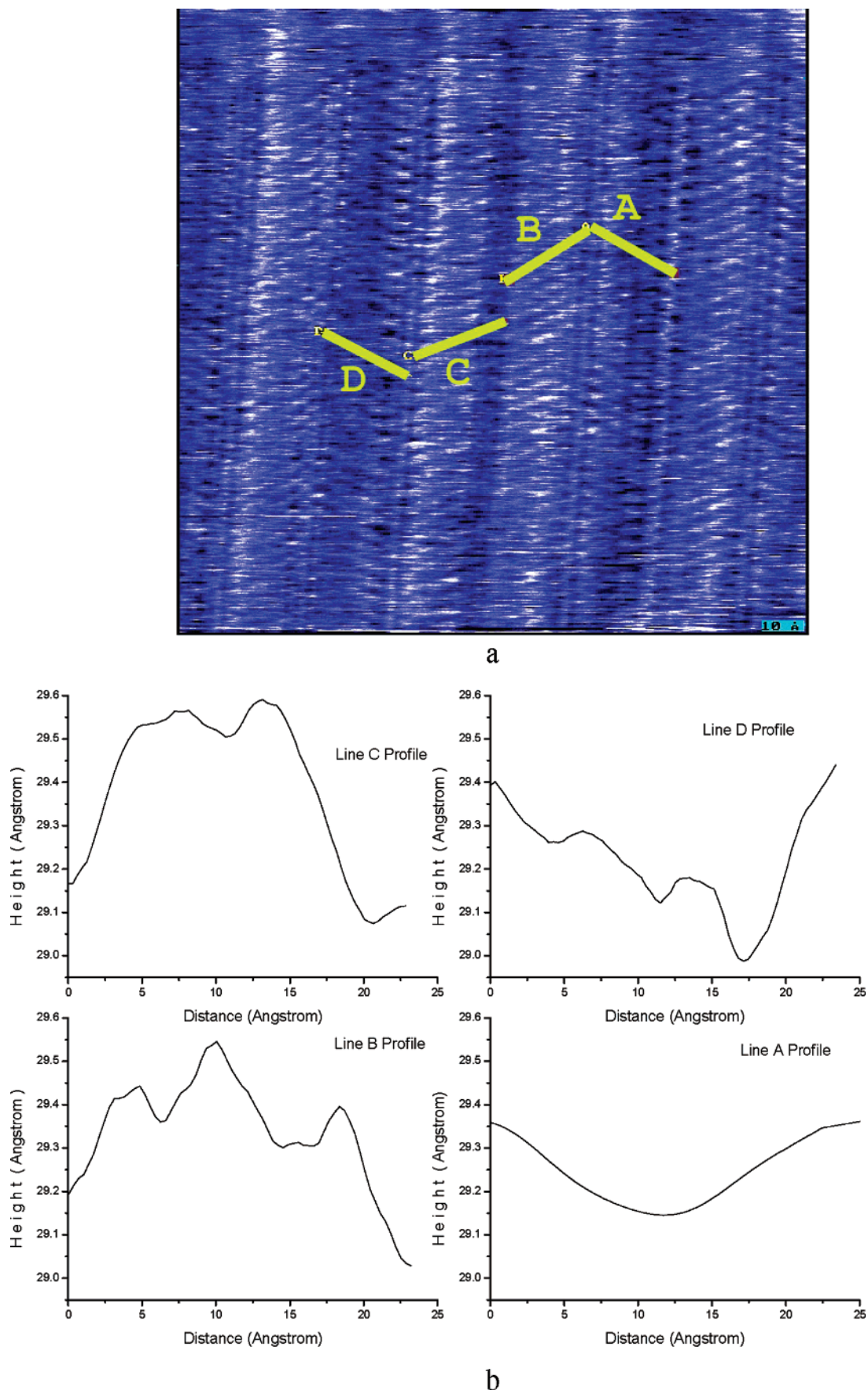(39) Chen, Q.; Frankel, D. J.; Richardson, N. V. *Surf. Sci.* **2002**, *497*, 37−46.

Figure 3. (a) A defect line in the octadecanol domains. Scan area 152 Å × 153 Å, $V_b = 0.86$ V, $I_t = 0.75$ nA. (b) Line profiles of line A to D in part a. From right (line A) to left (line D), four rows have "u", "n", "n", "u" shapes, respectively. Within a chevron pair, the two rows always distort in opposite directions.

row, the molecules have the same height variation, and no hexagonal symmetry is observed, which means it is also not the result of a rotational Moiré pattern. Thus, the observed height variations are likely to be true topographical variations due to the buckling of the alkane chain rather than due to a Moiré pattern. Of course, the compression in the chain length does not necessarily have to be 2.5% to exactly match the lattice. The deformation of the chain costs energy, while the reduced chain length lowers the overall energy due to better adsorbate−substrate interaction. The final change in chain length must be the balance of these two opposing energetic effects.

The octadecanol SAM on HOPG has been extensively studied.[28,32] Since the octadecanol chain is relatively short, the induced height variation along the chain is expected to be less obvious than in the case of the long alkane chains studied previously[27−30] and has not yet been reported.

Figure 1a is an STM image of the octadecanol SAM on HOPG obtained in this study. As in previous studies, the alkanol molecules form a herringbone structure; the center dark trough is the position of the oxygen atoms. The octadecanol molecule in the image is measured to be 23.6 ± 0.4 Å, which is shorter than the 24.6 Å length of the all-trans model of the molecule.[32] The herringbone angle is 120°. In the upper left of the figure is a model structure overlaid on the actual image, showing the packing of the octadecanol molecules. There are additional features seen in this image. Inside each row, a height variation is observed. In the two rows on each side of the oxygen trough, the pattern of the height variation is different. In Figure 1a, rows A and C, which are the rows on the left side of the oxygen trough, show a "u" shape; i.e., the height of the octadecanol molecule at the center is lower than the heights at the two ends. For rows B and D, the rows on the right side of the oxygen trough, an "n" shape along the molecular axis is seen; i.e., the height of the octadecanol molecule at the center is higher than the heights at the two ends. While it is possible that the introduction of a few gauche defects along the chain could result in the observed distortion, it seems more likely due to a series of small deformations of all the bond angles along the chain. This effect is illustrated in Figure 1b and c.

Figure 1b and c are the averaged octadecanol height profiles along the chain direction in rows A, B, C, and D, respectively. Careful examination of the shape of the "u" row and "n" row shows that if the oxygen trough is used as the folding line, the "n" row can roughly fold into the "u" row. In other words, one row looks just like the other row after rotation of 180° along the oxygen trough position. One difference between the alkane molecule SAMs and the octadecanol SAM is that the unit cell of the alkane SAMs contains only one molecule, while the octadecanol SAM unit cell contains two molecules connected by hydrogen bonding across the trough in the chevron pattern. Once the two molecules bend differently, as in the octadecanol structure, they are not equal. The symmetry in the basal plane is broken. The mirror image of this pair cannot be superimposed on the pair in the same HOPG plane. Hence this pair becomes a chiral pair. The domain composed of such a chiral unit cell becomes a chiral domain.

This asymmetric distortion of the octadecanol chevron pair is not due to tip−substrate interaction. This is based on the fact that (a) STM images of the octadecanol SAM taken from opposite scanning directions during the same image acquisition process always show the same asymmetric pattern of height variation and, (b) imaging the same domain with different bias voltages while maintaining the same set tunneling current, the octadecanol molecules in the chevron pair always appear to be distorted asymmetrically. The distortion pattern is independent of the bias voltage over the range of 0.86 V to 1.29 V. This observation is illustrated in Figures 2 and 3. Figure 2 shows two averaged height profiles of "n" and "u" rows at different bias voltages. Each profile curve represents the averaged apparent height variation of a row of octadecanol molecules. At different bias voltages, the image contrast/height variations of the octadecanol rows are not exactly the same, but the distortion pattern (left "n", right "u" in this domain) remains the same as the bias voltage changes.

This bending in the opposite direction across the chevron pair is due to the hydrogen bonding that forms the chevron. Only when $C_u-O_u-H_u$ and $C_n-O_n-H_n$ are in the same plane, will the pair have the most stable hydrogen bond. Thus, if one molecule is bent in a "u" shape, the OH end would point upward; the other molecule must bend in the "n" shape to make the OH end point down, forming a stable coplanar hydrogen bond. If the pair were to bend as "nn" or "uu", the two OH groups would not be in the same plane, and the nonplanar hydrogen bond would be weakened.

STM images of these octadecanol SAMs were acquired using different tips, samples, and tunneling conditions to check the reproducibility. The bending of each molecule is not always exactly identical to those shown above, but the two molecules in the unit cell always bend in an opposite way. This is especially apparent when considering the image shown in Figure 3. In this case, a defect line between adjacent rows is seen. On the left of the defect line, an "n" row is paired with a "u" row. On the right side of the defect line, a "u" row is paired with an "n" row. This image reemphasizes the requirement for planarity of the hydrogen bond across the unit cell pair in this structure.

Asymmetric bending upon adsorption of the octadecanol molecule pair in the SAM unit cell has been observed. This asymmetric bending is explained by the requirement of the hydrogen bond connecting the two octadecanol molecules in the chevron-shaped unit cell to form a planar bond. This very simple structure provides the first example of the formation of an adsorption-induced supramolecular asymmetric structure, formed by achiral molecules adsorbed on an achiral surface.