

Molecular Symmetry Breaking and Chiral Expression of Discotic Liquid Crystals in Two-Dimensional Systems

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We have studied the self-assembled monolayers from a series of discotic liquid crystal molecules on graphite substrate using scanning tunneling microscopy. An emergence of chirality in 1,7,13-trialkanoyldecacyclene (with n -carbon side chains, $n = 14$) monolayers was observed in the assembly. The driving force of the assembling behavior could be related to a cooperative interaction mechanism, possibly due to intermolecular steric hindrance, two-dimensional crystallization of alkyl substituents.

Introduction

The microscopic ordering in molecular assemblies has attracted general interests because molecular arrangement structure plays a significant role in the properties, such as optical, electrical, or enantioselective heterogeneous catalysis, of molecular materials.^{1,2} A number of interesting phenomena have been revealed through recent studies on various two-dimensional (2D) materials of the self-assembled and L–B films, such as the spontaneous separation of enantiomers from a racemic mixture, the formation of chiral domains from nonchiral molecules, and so on.^{3–15}

It has been generally known that the molecular self-assembly process at surfaces is controlled by the subtle balance between molecule–substrate and intermolecular interactions. Experimental observations have indicated that substrate materials such as noble metals could help fine tune molecule–substrate interactions.³ Weak nonbonding intermolecular forces, such as van der Waals forces and hydrogen bonds, are prevalent in the molecular self-assemblies. It is therefore of general interest to gain deeper insight of the effects due to nonbonding forces in order to understand the self-assembled molecular structures.

The self-assembled molecular structures through hydrogen bonding displaying supramolecular chirality have already been reported.³ Böhringer et al. observed a real space chiral phase transition on Au substrate.^{5,6} Yokoyama et al. reported the formation of surface-supported supramolecular structures whose size and aggregation patterns are rationally controlled by tuning the noncovalent interactions between individually absorbed molecules.¹⁶ It is plausible to anticipate that the behavior of the pattern transformation would correspond to the joint intermolecular interactions as reflected in the real-space images observed with scanning tunneling microscopy.

Earlier studies revealed that the cooperative interaction in the self-assembly of discotic liquid crystal molecules might result in remarkable changes of molecular arrangement. Charra et al. studied the 2,3,6,7,10,11-alkoxytriphenylene with alkoxy side chains containing nine and 11 carbons, finding molecular

symmetry breaking and a chiral unit cell.⁷ One could envision that the discotic liquid crystal molecules, having typically a rigid polycyclic aromatic core surrounded by equatorial flexible aliphatic side chains, could provide a variety of model systems to study the effect of intermolecular interaction on molecular assembling processes. The specific structures of molecules imply that there would be strong core steric hindrance and 2D crystallization of alkyl chains in the self-assembly process. These interactions could probably result in an interesting cooperative effect of steric hindrance and 2D crystallization.

Here, we present the results on 1,7,13-trialkanoyldecacyclene (with n -carbon side chains, $n = 14, 18$, named as TTD and TOD, respectively), on the surface of highly ordered pyrolytic graphite (HOPG) by using scanning tunneling microscopy (STM). To comprehend the cooperative forces and self-assembly process, comparison studies on 2,3,6,7,10,11-hexakisalkoxy-substituted triphenylenes with n -carbon side chains ($n = 12, 18$) (with small cores and more side chains, denoted as HTTP and HOTP, respectively) were also carried out. It is observed in the study that with only three side chains the space around the core can be filled up in two-dimensions with a close-packing fashion at the interface. This observation could provide a complementary example to the previous studies that tended to conclude that three elongated chains would insufficiently fill the space around the core and therefore could not allow the existence of columnar mesophase.¹⁷

Experimental Section

The materials used in the experiments, decacyclene, tetradecanoyl chloride, octadecanoyl chloride, were purchased from Acros and used without further purification. 1,7,13-Trialkanoyldecacyclenes with n -carbon side chains ($n = 14, 18$) were prepared as described in an earlier paper.¹⁸ The synthetic process involves a Friedel–Crafts acylation as illustrated in Scheme 1. The decacyclene derivatives, with large cores and only three side chains, have been shown to form columnar structures over a broad temperature range.¹⁸

The samples were dissolved in toluene (HPLC grade, Aldrich) with a concentration of less than 1%. A droplet of the solution was deposited onto a freshly cleaved surface of HOPG (quality ZYB, Digital Instruments, Santa Barbara, CA). The experiments

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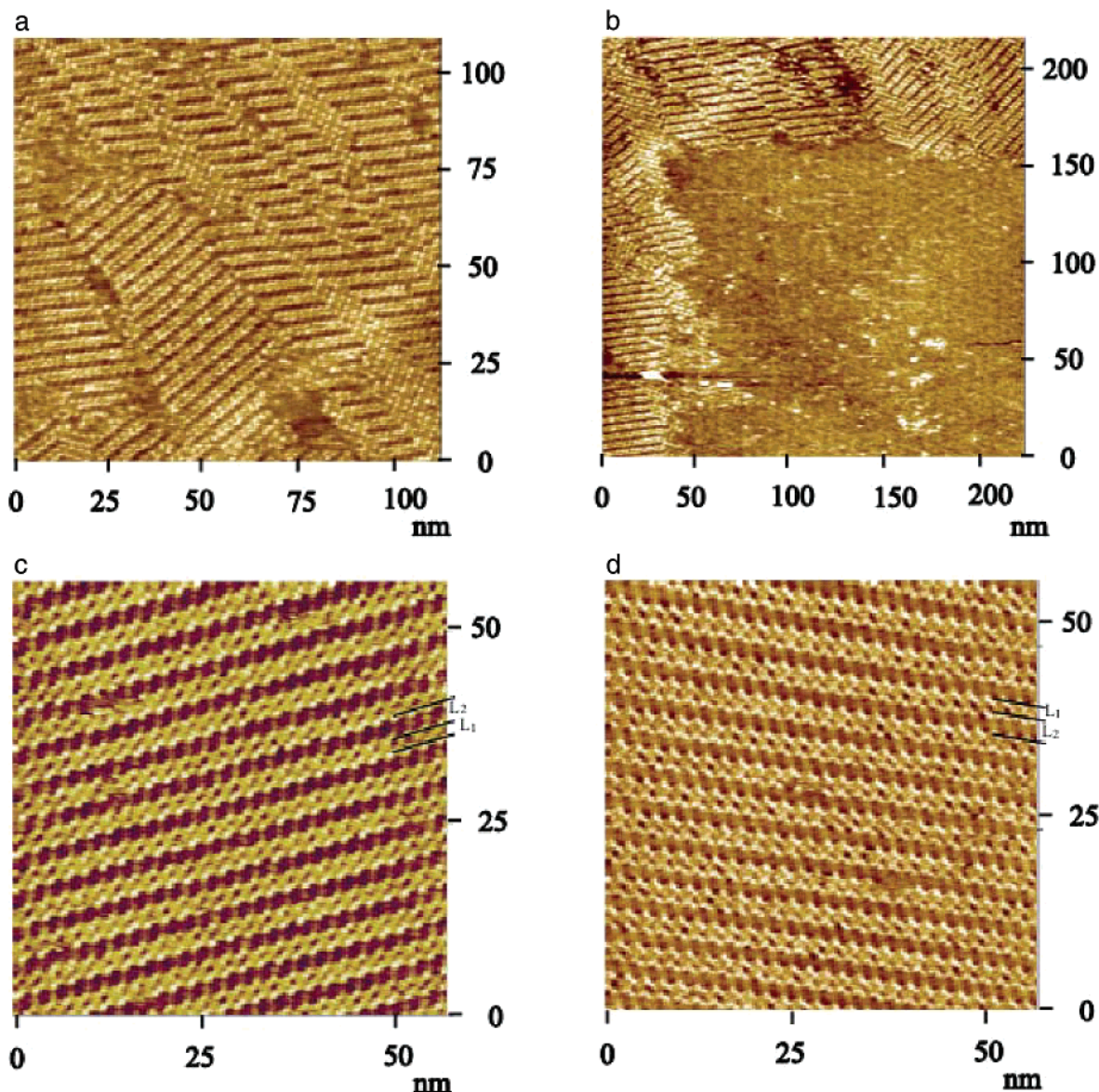
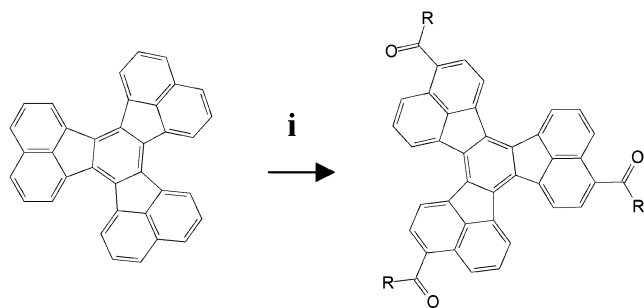


Figure 1. STM images of the assembly of TTD. (a) An STM image ($120 \times 120 \text{ nm}^2$). Tunneling conditions: 830 mV, 0.97 nA. (b) A larger-scale image ($238 \times 238 \text{ nm}^2$). Tunneling conditions: 830 mV, 0.97 nA. (c) A large-scale image of one of two orientated stripes ($57 \times 57 \text{ nm}^2$). Tunneling conditions: 800 mV, 1.10 nA. (d) A large-scale image of the other of two orientated stripes ($57 \times 57 \text{ nm}^2$). Tunneling conditions: 880 mV, 0.99 nA.

SCHEME 1: Schematic of Trialkanoyldecacyclenes^a



^a (i) AlCl_3 , RCOCl ($\text{R} = \text{C}_{13}\text{H}_{27}$, $\text{C}_{17}\text{H}_{35}$).

were performed on a Nanoscope IIIa SPM (Digital Instruments, Santa Barbara, CA) at room temperature in ambient conditions. The tunneling tip was mechanically formed Pt/Ir (90:10) wire. All STM images were recorded using constant current mode of operation. The specific tunneling conditions are given in the figure captions.

Results and Discussion

Figure 1a presents an STM image of a monolayer of TTD physisorbed on a HOPG surface. The 2D array of TTD is clearly visible with the zig-zig patterns corresponding to two orientation stripes. The consideration of the monolayer structure is supported by the simultaneous observation of the molecular layer and the HOPG surface in uncovered regions at domain boundaries, as shown in Figure 1b. The high-resolution images of the monolayer of the two differently orientated stripes are shown in Figure 1c,d. The observed domains are characterized by darker bands, which correspond to the locations of interdigitated alkyl chains, and the brighter zones, which coincide with the location of the decacycene core moieties. The nearest neighboring molecules form twin supramolecular chains, which are the basic periodical unit in a domain. In the twin supramolecular chains, the constituent molecular cores are antiparallel to each other. The diameter of the brighter parts is approximately $1.70 \pm 0.10 \text{ nm}$, in good agreement with the theoretical value ($\sim 1.54 \text{ nm}$). The distances of intra- and intertwin supramolecular

chains are $L_1 = 1.60 \pm 0.10$ nm and $L_2 = 3.0 \pm 0.2$ nm, respectively. The distance between adjacent molecules within each chain is $d = 2.35 \pm 0.15$ nm (as denoted in Figure 2a), and the rows of TTD within the twin chains are shifted by $s = 0.75 \pm 0.05$ nm (as denoted in Figure 2a). High-resolution images are presented in Figure 2. It can be identified that one of the three side chains of a molecule is located within twin supramolecules and the rest of the two side chains is between twin supramolecules. This assignment is illustrated by the cross-sectional profile shown in Figure 2b. The width of the contour line is about $z \approx 0.42$ nm (as denoted in Figure 2b), being equal to the width of alkyl chains. Although TTD is achiral with D_{3h} symmetry, we can discern that the carbon chains of the molecule are divided into two orientation groups, leading to the loss of the original molecular symmetry. Two molecular patterns were assigned according to the geometrical arrangement of TTD from high-resolution STM images, designated as α and β , respectively, in Figure 2c. It can be concluded that α , β species cannot be superimposed by rotation and translation operation within the surface plane. This observation indicates that TTD of α and β species in planar adsorption geometry on HOPG possesses chiral characteristics, and for the transformation of α into β species, a mirror operation is mandatory.

We would like to point out that it appears that TTD molecules in Figure 2a lost the 3-fold symmetry. This observation is reproducible in the experiments. The possible explanation could be qualitatively accounted for according to the optimized molecular conformation using HyperChem version 5.02. The TTD molecular core is not a perfect plane, with limited tilt when adsorbed on the substrate as illustrated in the side view of the adsorbed molecular structure, Figure 2d. As a result, the images of the cores of TTD molecules displayed certain distortion from ideally 3-fold symmetry.

The observed assembly structures could be interpreted by the joint effect of frustrated 2D alkane lamella and steric hindrance interaction with respect to the adsorbate–substrate interaction. The steric hindrance of core molecules would favor antiparallel molecular orientations, and alkyl substitution is beneficial in stabilizing molecules on solid surfaces. In a previous work,^{19–22} we reported that 2D crystallization of alkyl parts is important to immobilize molecules within the assembly. In the case of nonchiral molecules, this could lead to a reduction in symmetry and thus a limitation of symmetry elements required for generating a stabilized 2D array. In the current study, the TTD molecules are self-assembled into supramolecular twin chains and stabilized by 2D alkyl crystallization. The three side chains have diverse orientation arrangements. Molecules of α and β species are enantiomers and form supramolecules separately through self-assembly, related by a mirror symmetry.

When the number of the methylene units reaches 18 to 1,7,13-trioctadecyldecacylene (TOD), the molecular arrangement is fundamentally the same, as shown in Figure 3a. From the high-resolution image in Figure 3b, it can be seen that the molecules are antiparallel to each other and form twin supramolecular chains. As denoted in Figure 3b, the value of the relative displacement is about $s = 1.40 \pm 0.10$ nm and the distance between the same points in adjacent molecules within each chain is $d = 3.20 \pm 0.30$ nm, more than that of TTD. The distances of intra- and intertwin supramolecular chains are $L_1 = 3.00 \pm 0.30$ nm and $L_2 = 3.09 \pm 0.30$ nm, respectively. Although we can also discern that the alkyl chains of the molecules are divided into two orientation groups, which lead to the loss of the original molecular symmetry, no chirality is observed in the assembly. The analogy arrangement behavior was first

observed in an earlier study of Charra and Cousty,⁷ who have tuned the alkoxy side chain length and observed that a chiral ordering transition appears when increasing the triangular aspect ratio of molecules.

In addition, HDTP and HOTP were studied as comparison experiments. Figure 4a is a high-resolution STM image of HDTP, showing a unit cell of a near hexagon containing seven molecules. There are two kinds of molecules that can be assigned in the assembly. The central molecule displaying 6-fold symmetry is marked as the red triangle in Figure 4a. The molecules located at the corners of the hexagon appear as 3-fold and are marked as green triangles in Figure 4a. It can be seen that the alkyl chains are separated into three groups and the angle, α , between every two side chain groups is about 120° . Figure 4b is the suggested molecular arrangement model.

When the number of the methylene units reaches 18 (HOTP), as shown in Figure 4c, the intermolecular spacing within the triphenylene arrays becomes nonuniform. The aromatic cores are no longer uniformly spaced along the array, as displayed in the histogram in Figure 4d showing a spread of spacing between adjacent molecular cores with an average spacing around 2.4 nm. This arrangement can be accounted by the consideration that the 2D alkyl crystallization becomes dominant due to long side chains.

Discussion

The structural transformations such as emergence of chirality and molecular symmetry breaking described above are the result of specific geometries favored energetically. They may be interpreted with respect to three driving forces. First is to achieve optimal commensuration with the substrate lattice. In the self-assembly process, the graphite substrate acts as a template for the formation of the monolayers in which the hydrogen atoms of the alkyl chains are believed to be in registry in the hollow sites of the graphite lattice.²³ The molecule–substrate interactions would lead to commensurate packing of the assembly. In the situation of molecules with long side chains, molecular symmetry is reduced in order to achieve optimal commensuration with the substrate lattice. If the interaction between the aromatic cores and the underneath substrate becomes the dominant factor, the molecular assembly structure could develop commensurate packing patterns. Contrarily, if the intermolecular interactions within the assembly are dominant, the adsorbate assembly could develop incommensurate packing. Therefore, the substrate could have a tuning effect on the symmetry and 2D assembly pattern of molecular adsorbate consisting of aromatic cores and side chains.

Second, to achieve maximal local 2D crystallization, alkyl chains would pack highly parallel regardless of the core molecular symmetries. As a result, molecules might undergo a spontaneous symmetry breaking and lose the original symmetry. Finally, the existence of steric hindrance would favor the molecules to adopt antiparallel orientations such as a frustrated antiferromagnetic-like triangular Ising net.⁷

In our present experiments with discotic liquid crystal molecules, the decacylene derivations would have stronger steric hindrance induced by larger cores than triphenylene derivatives, while the longer side chain corresponds to stronger 2D crystallization. As a consequence of these factors, the molecular arrangement is varied when methylene units of the alkyl compound of molecules are added or rigid units of the core moieties are enlarged. In the case of decacylene derivatives, TTD possesses a large core and three side chains each with 13 methylene units. The strong interaction of core and substrate

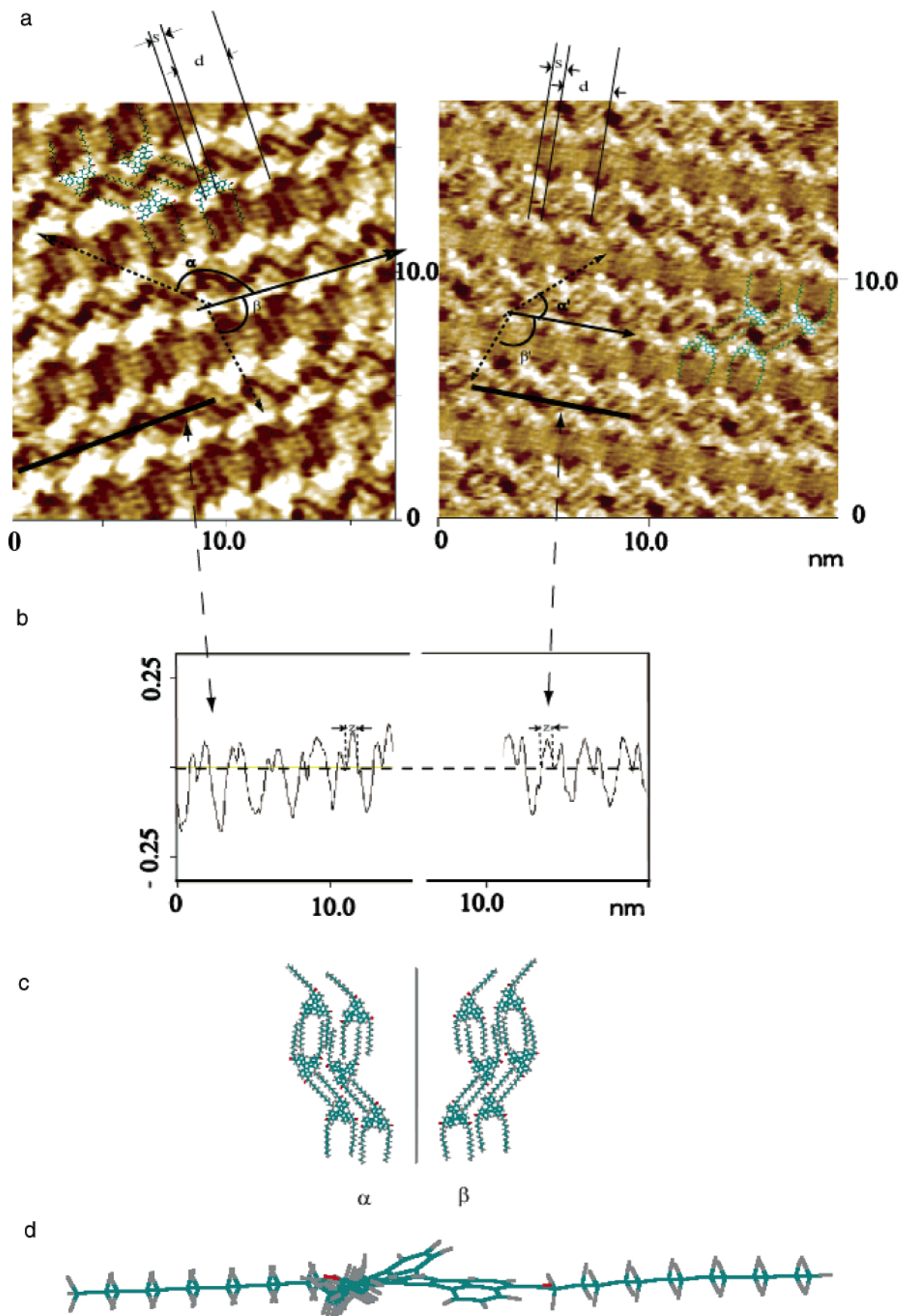


Figure 2. High-resolution STM images of the TTD assembly. (a) Left: scale of $17 \times 17 \text{ nm}^2$. Tunneling conditions: -692 mV , 1.23 nA . Right: scale of $26 \times 26 \text{ nm}^2$. Tunneling conditions: 880 mV , 1.06 nA . (b) The sectional profiles along the lines indicated in (a) demonstrate that one of three side chains of a molecule is located within twin supramolecules. (c) Possible alignment of TTD deduced from the STM images. The respective species are designated α and β ; the mirror symmetry is reflected by a real line. (d) Side view of the adsorbed molecular structure.

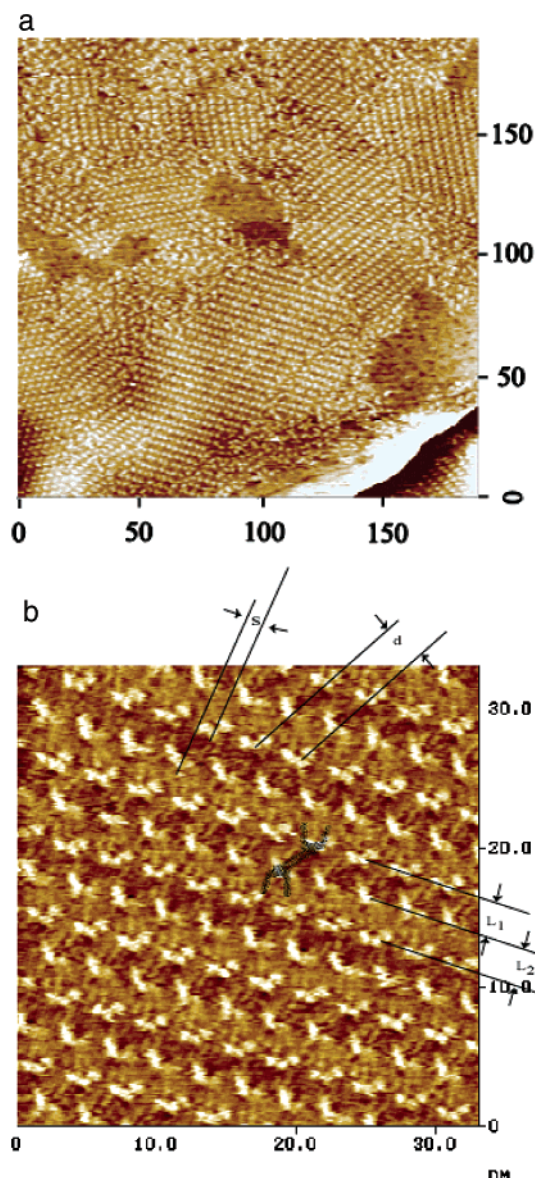


Figure 3. STM images of the TOD. (a) A large-scale image ($190 \times 190 \text{ nm}^2$). Tunneling conditions: 713 mV, 1.18 nA. (b) Scale image of $33 \times 33 \text{ nm}^2$. Tunneling conditions: -561 mV, 1.17 nA.

would favor retaining its symmetry. However, it is obvious that the arrangement of symmetry maintaining in the 2D system would result in much larger voids because the number of side chains is not suffice to fill the space around the cores. Such large voids will lead to the reduction of surface coverage, thus increasing surface free energy and being energetically unfavorable. Therefore, Figure 2c is the favored configuration for the observed molecular assembly shown in Figure 2a. The arrangement of TTD in the 2D system is apparently a compromise of the interaction forces of cores with substrate and the minimization of the surface free energy. When four additional methylene units are added, TOD adopts a similar arrangement, while only the separation and the angle are changed due to lengthened side chains.

The triphenylene derivative, HDTP, holding short side chains of only 12 methylenes, maintains the molecular symmetry in the self-assembly structure. Probably, the interaction of aromatic cores and substrate is prominent. However, with long side chains, the 2D crystallization of HOTP alkyl chains is the dominating factor. Thus, the steric hindrance of aromatic cores is less important, and the aromatic cores could be either in

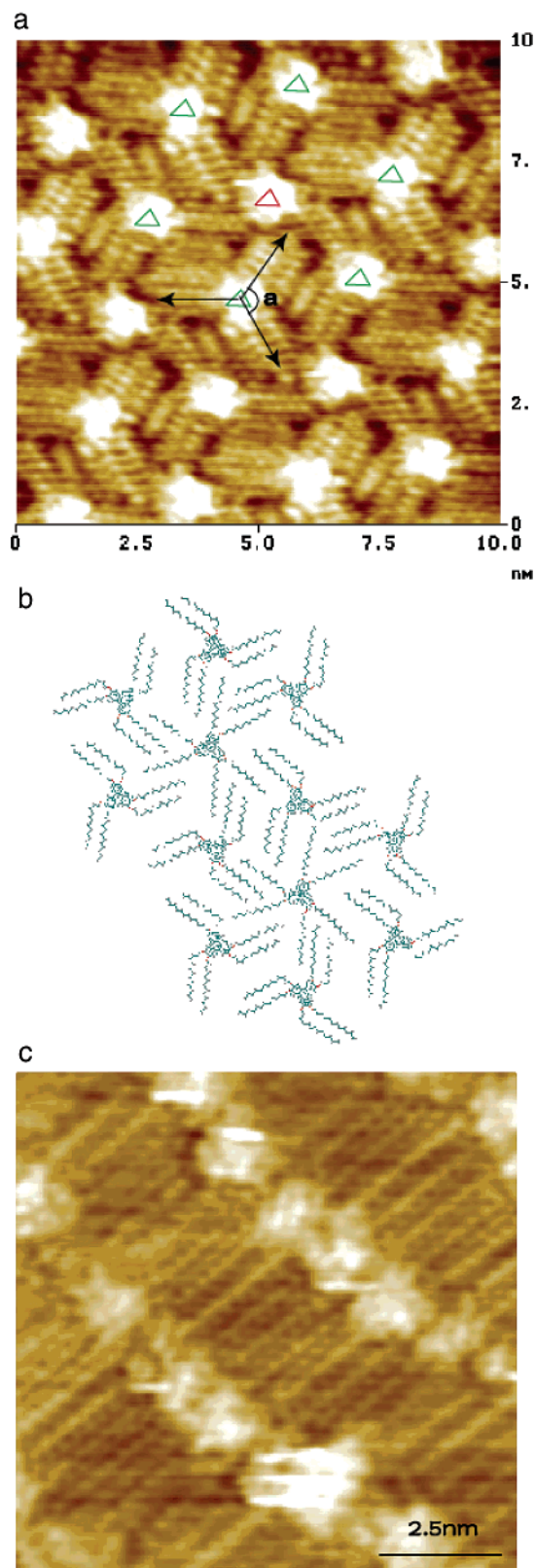


Figure 4. (a) STM image of the HDTP. Tunneling conditions: -774 mV, 1.08 nA. (b) Proposed arrangement of HDTP deduced from the STM images. (c) STM image of the HOTP assembly. Tunneling conditions: -799 mV, 1.13 nA. (d) Histogram of the spacing between HOTP molecular cores in the assembled structure.

parallel or in antiparallel arrangement, evidenced by the STM observation of nonuniform spacing between aromatic cores.²²

It is worth pointing out that even if molecules are successfully immobilized, they might still undergo rapid conformational

changes since the long alkyl side chains are flexible and mobile at the interface. Molecules that could be successfully imaged with STM should have thermal dynamics on the time scale of the STM measurement.

Conclusion

It is demonstrated that discotic liquid crystal molecules may undergo symmetry breaking, losing their original symmetry such as spontaneous emergence of chirality in 2D assemblies. The cooperative interactions between cores and side chains dominate the process of self-assembly, together with the tuning effect of substrate. Further studies would be needed on achieving rationally controlled 2D assembly patterns.

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