

Solvent Effects on the Chirality in Two-Dimensional Molecular Assemblies

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In this work we reported the observations, using scanning tunneling microscopy (STM), on the solvent effects upon the expression of supramolecular chirality on the graphite surface in the two-dimensional assembly of 3,5-di(4-*n*-tetradecyloxyphenyl) pyrazole (DTPP). It was observed that DTPP dissolved in a 1:3 solvent mixture of toluene and chloroform can form chiral lamellae, while no chiral characteristics can be found when DTPP is dissolved in toluene alone. Rod-shaped molecular cores are observed in the assembly from toluene solution, while bent-shaped molecules are observed in the solvent mixture of toluene and chloroform. The observation suggests that surface-stabilized supramolecular chiral lamellae may be appreciably affected by solvents through tuning of intermolecular hydrogen-bond configuration.

Introduction

Determination and manipulation of supramolecular chirality have general interests since chirality plays a significant role in fields such as heterogeneous, asymmetric catalysis and chemical sensors.¹ A number of recent studies have reported on the 2-dimensional (2D) supramolecular chiral structures within the adsorbed molecular monolayer by deposition of chiral or achiral molecules onto achiral surfaces.² A number of studies are specifically focused on the expression of supramolecular chirality by the self-assembly of achiral molecules in monolayers. Yet to be reported are the solvent effects on the expression of supramolecular chirality in two dimensions.

It has been demonstrated that from nonpolar organic solvents, long-chain alkanes, alcohols, fatty acids, etc., can assemble on the basal plane of graphite.³ In polar solvents, long-chain molecules modified with desired functional groups such as diacetylene and azobenzene can also form ordered lamella monolayers.⁴ Flynn et al reported previously that solvents could play an appreciable role in the adsorption and mobility of molecules adsorbed on the graphite surface.⁵ In this work, a typical ferroelectric smectic liquid crystal⁶ molecule, namely, banana-shaped achiral molecules of 3,5-di(4-*n*-tetradecyloxyphenyl) pyrazole (DTPP) were studied. The study is aimed at understanding the arrangement of bent-core molecules and polar ordering induced in a 2D system.

In this work we studied a model system, 3,5-di(4-*n*-tetradecyloxyphenyl) pyrazole (DTPP), being prepared as described in an earlier paper,⁸ and report direct observations of the dependence of supramolecular chirality on the solvent mixture used. Using scanning tunneling microscopy (STM), it was observed that DTPP dissolved in 1:3 solvent mixtures of toluene and chloroform and physisorbed on the graphite surface can form chiral lamellae, which is a consequence of polar ordering by the bent-core shaped molecules. In contrast, no apparent

chiral ordering can be found for DTPP assemblies prepared from toluene solution.

Experimental Section

The experiment was performed on Nanoscope IIIa SPM (Digital Instruments, Santa Barbara, CA) at room temperature in ambient conditions. STM tips were mechanically formed Pt/Ir wires (90/10). 3,5-di(4-*n*-tetradecyloxyphenyl) pyrazole (DTPP) was prepared as described in the literature.⁸ The molecules were dissolved in toluene and in 1:3 solvent mixtures of toluene and chloroform (HPLC grade, Aldrich), respectively, with a concentration of less than 1 mM. The DTPP SAM was prepared by depositing a droplet of this solution onto a freshly cleaved surface of highly oriented pyrolytic graphite (HOPG, quality ZYB, Digital Instruments). All STM images were recorded using constant current mode. The specific tunneling conditions were given in the figure captions. The preliminary simulations were performed using a Hyperchem software package.

Results and Discussion

DTPP is an achiral bent-core molecule with the molecular structure shown in Figure 1a.⁹ The molecular core is composed of two benzene rings and a pyrazole ring labeled **1**, **2**, **3**, respectively. The optimized results indicate that dihedral angle between **1** and **2** is about 8° and the dihedral angle between **3** and **2** is about -13° using Hyperchem software. It can be seen that DTPP can provide functional groups for hydrogen bonding. In theory, it is possible that the N-H moieties of the pyrazole could form dimers through N-H...N (Figure 1b). However, Barbera et al. proposed that hydrogen bonding of the former (dimer) is not sufficient for the formation of discotic phases.⁸ Our STM results indicate that the molecular assembly on the HOPG surface cannot form dimer structures but rather forms a well-ordered 2D lamella structure with densely packing, which is supportive to the results of Barbera et al.

Typical STM image of the monolayer of DTPP dissolved in toluene is shown in Figure 2a. The monolayer consists of two types of domains (I, II) with different lamella orientations. Well-ordered lamella patterns with parallel bright ridges and dark troughs can be resolved. The height of the lamella monolayer

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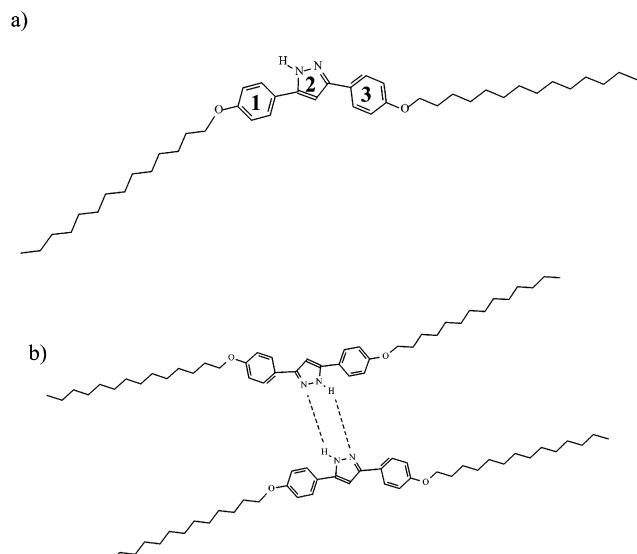


Figure 1. (a) Optimized conformation of DTTP molecule. (b) Dimer structure formed by intermolecular N—H...N.

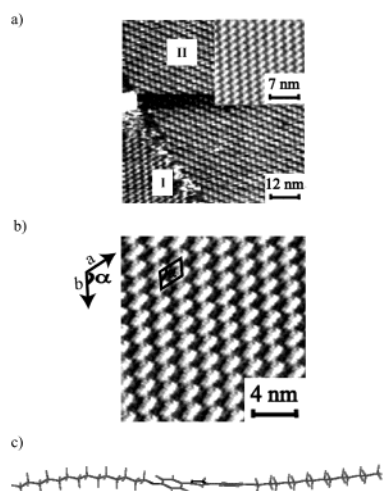


Figure 2. (a) A larger-scale STM image of self-assembled monolayer of DTTP dissolved in toluene adsorbed on the HOPG surface. Scanning area is $70 \text{ nm} \times 70 \text{ nm}$. The imaging condition is 0.932 nA, 691 mV. The insert is a magnified image. (b) STM image of a lamellae with a unit cell schematic. Scanning area is $20 \text{ nm} \times 20 \text{ nm}$. The imaging condition is 1.15 nA, 600 mV. (c) Side view of the adsorbed molecular structure.

is about 1.5 \AA , corresponding to the height of a single molecule layer on the graphite surface. Careful observation indicates that the molecular arrangements within two domains show the same molecular orientation seen in the magnified image in the insert of Figure 2a. The high-resolution image of the lamella structure with individual molecular chains clearly resolved is shown in Figure 2b. From the molecular structures, the brighter parts can be attributed to the core moieties containing conjugated π -electron systems and the surrounding zigzag lines interconnecting the bright ring correspond to the linear alkyl substitutes. It can be observed that the character of the core moieties is rod-shaped, different from originally molecular bent-core. The long-chain molecular axes are parallel to each other. In addition, the observed molecular images could be accounted for by the proposition that the molecular backbone may be tilted sideways and make the molecule non parallel to the substrate surface. The tilt of the molecules can be verified by the side view of optimized molecular structure (Figure 2c). The unit cell is

TABLE 1: Comparison between Lattice Parameters of Unit Cell for Assembly in Toluene and Mixed Solution^a

parameter	in mixed-solvent system		
	in toluene system	in Figure 3b	in Figure 3c
a (nm)	2.80	2.83	2.83
b (nm)	2.10	2.30	2.30
α ($^\circ$)	130	130	130

^a Ridge-to-ridge distance, molecule-to-molecule spacing, and the angle between the long molecular axis and the lamella direction are denoted with a , b , α , respectively. Errors on distance are $\pm 0.05 \text{ nm}$; errors on angles are $\pm 5^\circ$.

indicated in Figure 2b (the parameters of unit cell are listed in Table 1). The molecular rows show relative displacements and the rows of adjacent DTTP are shifted by ca. 1.34 nm, in contrast to the perpendicular geometry in alkane layers. The shift of the molecules leads to the tilt angle between the molecular chains and the lamellae, illustrated by the relative angle α of about 130° between the molecular axis and the lamellae.

Figure 3a represents the typical STM image containing domain boundaries of monolayer of DTTP prepared from 1:3 solvent mixtures of toluene and chloroform. Two domains are clearly observed in a well-defined pattern. High-resolution images are shown in Figures 3b and 3c, respectively. The bent-core shape of the molecules is clearly seen. In Figure 3b, in the direction indicated by a bold black arrow, one can observe the next molecule shifts in clockwise orientation by a certain distance (indicated by a broken line with the arrow in Figure 3d). Owing to the bent-core shape of the molecules, in the molecular plane each molecule possesses a dipole moment (represented by an arrow with double black lines). Again, because of the bent-core molecular shape, a steric packing is favored in a domain where all molecules are oriented in the same direction, thereby defining a polar axis. The coordination consisting of a normal layer (dark line with arrow), the polar axis (an arrow with double black lines), and the shifting orientation (broken line with arrow) defines a left-handed coordinate system (denoted by black curve with glove) as shown in Figure 3d. The coordination of the vectors in Figure 3c defines a right-handed system as shown in Figure 3e. Each domain can be deemed as chiral, despite the fact that the individual molecules are achiral. This ordering means that, for a given shifting orientation (broken line with arrow), two equivalent layer structures with antiparallel polar axes can exist, such that they are mirror images of each other. This fact is reflected from parameters of the unit cell, which is indicated in Figures 3b and 3c (the parameters of unit cell are listed in Table 1). The angle is about 130° clockwise for molecules in Figure 3b, while it is 130° counterclockwise for molecules in Figure 3c. Two relative displacements are about 1.45 nm and -1.45 nm , respectively. The chirality in these materials is a consequence of the steric packing of the bent-core molecules. This is similar to the chiral phenomenon observed in thin films, in which achiral molecules were found to separate spontaneously into lamellae with chiral packing of opposite handedness.¹⁰ The proposed models are shown in Figures 3f and 3g.

As previously noted, different solvents could affect the molecular assembling structure in 2D system. Comparison between lattice parameters of unit cell for assembly in toluene and mixed solution are summarized in Table 1. The differences between the images of DTTP molecules in toluene and mixed solution are reflected in the appearance of the molecular core region and the lattice parameters of the unit cell. From the STM images of the molecules where toluene was used as solvent, rod-shaped molecules were clearly visible. In the mixed solution,

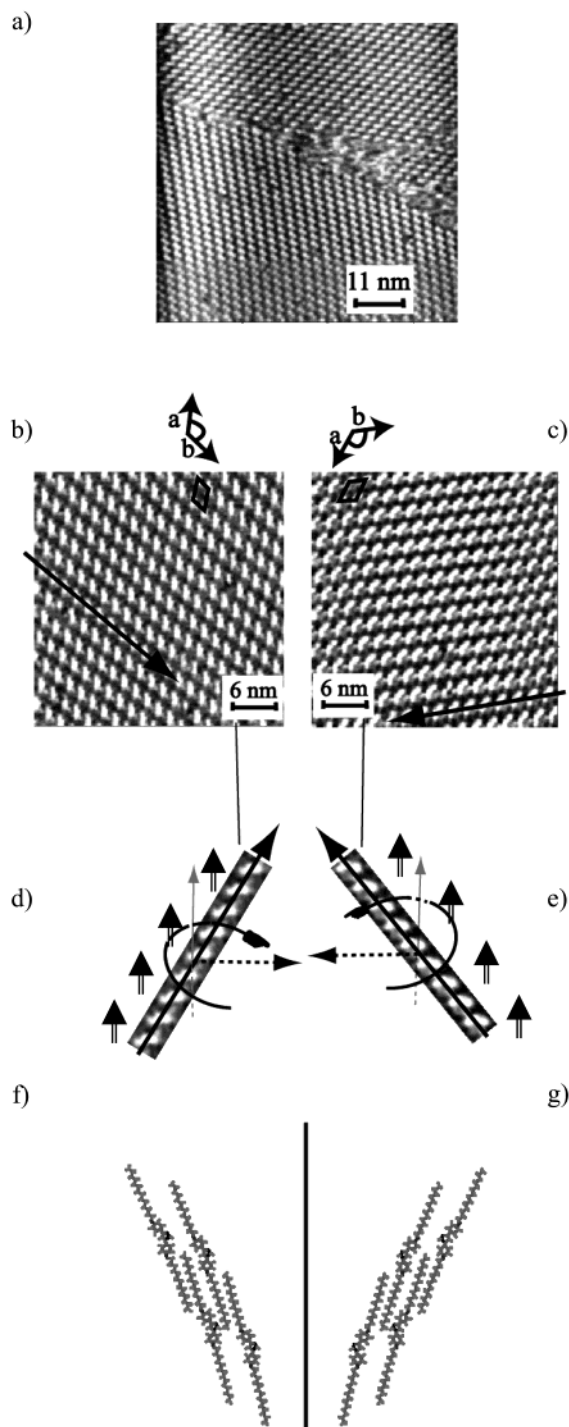


Figure 3. (a) STM image of DTTP dissolved in 1:3 solvent mixtures of benzene and chloroform adsorbed on the HOPG surface and a large-scale boundary of the two differently orientated lamellae domains. Scanning area is 65 nm \times 65 nm. The imaging condition is 0.967 nA, 845 mV. (b) STM image of left-handed orientated lamellae. Scanning area is 32 nm \times 32 nm. The imaging condition is 0.828 nA, 800 mV. The unit cell for the adsorbate lattice is indicated. (c) STM image of the right-handed orientated lamellae. Scanning area is 32 nm \times 32 nm. The imaging condition is 0.828 nA, 800 mV. The unit cell for the adsorbate lattice is indicated. (d) The alignments of DTTP along the bold black lines with arrow indicated in (b) and their left-handed coordination. (e) The alignments of DTTP along the bold black lines with arrow indicated in (c) and their right-handed coordination. (f) Left-handed molecular model of DTTP monolayer. (g) Right-handed molecular model of DTTP monolayer.

however, bent-shaped molecules were obtained, which define a dipole axis and eventually result in chiral domain. In addition,

according to the measured parameters of the unit cell, molecule-to-molecule spacing can be seen to be less in toluene than those in the mixed solution, which indicates molecules assemble more closely in toluene. These disparities most likely are due to the nature of the solvent and adsorption behavior of DTTP molecules as discussed below.

Usually, chloroform is considered to be a fairly good solvent for hydrogen bonding and is also a slightly polar solvent.¹¹ Chloroform is less acidic and thus less able to be involved in strong solvent hydrogen bond interactions, although chloroform might form a hydrogen bond to DTTP. On the other hand, it could reduce self-association of DTTP in solution. Such self-association is evident in a nonpolar, non-hydrogen bonding solvent such as toluene. Recent studies indicated that solutions at the onset of crystallization can form structure clusters that control the structure of the precipitating crystalline phase.¹² In the present experiment, with toluene evaporation and supersaturated solution formation, the formation of structured clusters of DTTP in toluene like self-association could play important roles in the assembly of DTTP molecules on the surface.

The adsorption behavior of DTTP on the graphite surface can be inferred from the energetics for physisorption of DTTP from solution onto a surface before the solvent evaporated. The interaction between the DTTP molecule and the solvent molecule could be considered different for the two solutions. As mentioned above, the DTTP molecules can provide functional groups for hydrogen bonding. In the mixed solvents, where one of the species is a hydrogen bonding solvent, the solute molecule can form a hydrogen bond to the solvent (chloroform in this study), resulting in an increased solvation heat. Therefore, the free energy of a DTTP molecule in the mixed solvent is expected to be lower than that of a molecule in toluene. In a similar manner, the solvent can affect the adsorption energy for solute on the surface. The most probable effect is a destabilization of the solute–surface interaction. Both of these effects would result in lower activation energy for a DTTP molecule in the mixed solvents than in toluene. Consequently, a molecule can adsorb or desorb from the surface with reduced barrier in the mixed solvents compared to those in toluene. The mobility provides a chance for a DTTP molecule to adopt a favorable conformation to match the graphite surface like the conformation in Figures 3b and 3c. However, it seems that the less mobility and self-association would make DTTP molecules adopt a tilted configuration and not be parallel to the substrate surface in toluene. Although this configuration would lead to instability, it could be compensated by close-packing assembling in the domain.

The observations presented suggest the effect of solvents in determining molecular self-assembly characteristics. The bent-core molecules studied show an unexpected assembling behavior from two different solvents. Although not possessing a chiral structure, the individual molecular chirality is here displayed by the chirality of the domain, now acting as a whole as a chiral object, which could be further applied in ferroelectric materials.

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