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Dynamics of vacancy defects in 2-D crystalline monolayers under chiral smectic thin films studied by scanning tunnelling microscopy

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Scanning tunnelling microscopy (STM) can be used to image adsorbed organic molecules in real space and real time. The technique seems especially well suited for imaging 2-D crystalline monolayers formed under liquid crystal films. In addition to observing perfect 2-D crystals, STM provides the ability to observe crystal defects, and to observe how these defects evolve over time. In this study two different vacancy defects in 2-D lamellar monolayers of chiral liquid crystal molecules under bulk smectic films were observed *in situ*. Both vacancies showed dynamic behaviour and an unexpected transport anisotropy.

1. Introduction

In scanning tunnelling microscopy (STM), an atomically sharp metal tip is scanned over a conducting surface while a voltage is applied between the tip and the surface. In typical experiments, the tip height is adjusted during scanning to maintain the current at a constant value. In this way, an atomic-scale map of surface conductivity and topography can be obtained. Furthermore, it has been found that if a smooth, flat, conducting surface is covered with an organic compound, the molecules sometimes adsorb to the surface, forming a monolayer of 2-D crystal. This adsorbed monolayer typically modulates the tunnelling current, and images of individual adsorbed organic molecules at up to atomic resolution can be obtained [1, 2]. By allowing observation of adsorbates at molecular resolution and in real space, STM provides a unique opportunity to study surface structure.

We are particularly interested in studying the interactions of liquid crystals (LCs) with solid surfaces, as surface interactions are critical for making useful ferroelectric liquid crystal devices [3]. STM observations of adsorbed LC molecules can provide information about the nature of the interactions of the liquid crystal with surfaces and with other molecules. Furthermore, the real-space nature of STM allows observation of defects, polydomains, and partially disordered monolayers with molecular resolution. In monolayers of adsorbed molecules it is widely accepted that aromatic moieties image brighter (that is, exhibit more efficient tunnelling) by STM than aliphatic regions [4, 5].

Although large defect-free monolayers are sometimes observed, it is also common for the monolayers to contain line defects and domain walls. Several published studies have dealt with the dynamic behaviour of domain boundaries [6, 7], but point defects are much less common. In hundreds of sessions and thousands of STM images, we have observed vacancy defects or point dislocations only a few times. Defects can contain information about the adsorbed monolayer that is difficult to obtain from images of perfectly ordered monolayers.

2. Experimental

The liquid crystals observed are biphenylyl benzoates (figure 1), used as pure compounds and as mixtures. The saturated parent compound **1** [8, 9] is crystalline at room temperature, while the unsaturated isomers **2** and **3** [10] have smectic phases at room temperature. Mixtures of the saturated compound and unsaturated isomers also showed liquid crystal phases at room temperature. We have previously reported the general characteristics of monolayers of these molecules [11] both pure and as saturated/unsaturated mixtures. Like most monolayers of liquid crystals, these consist of

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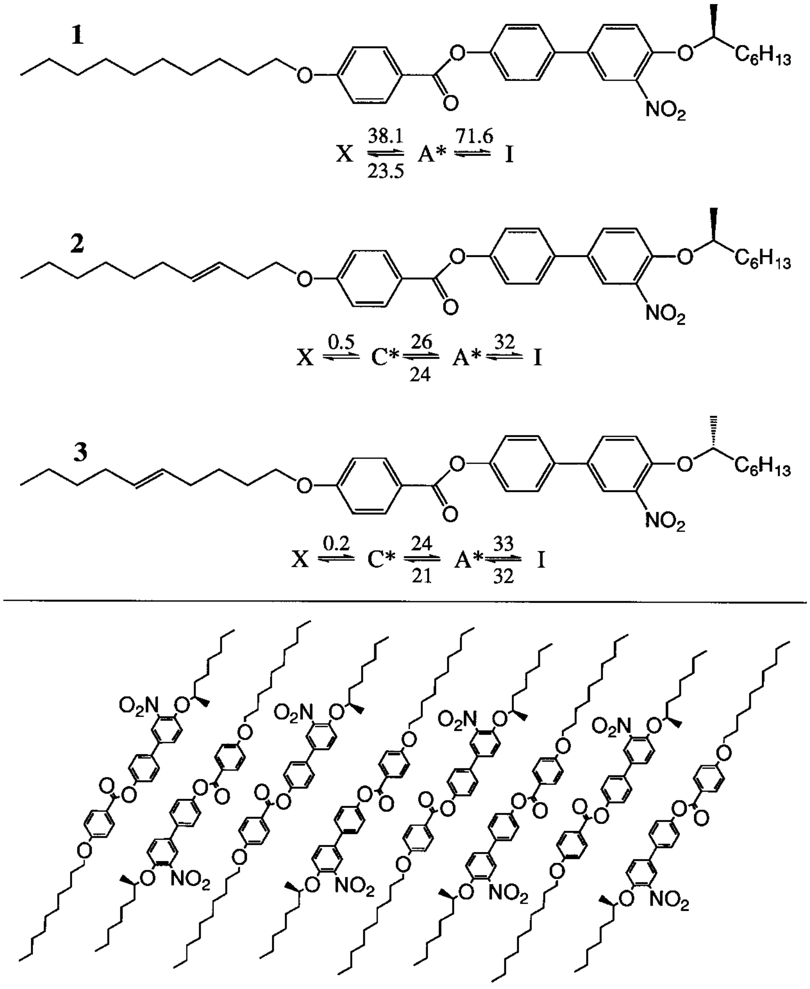

Figure 1. *Top* Structures of the liquid crystals observed by STM. **1**: (*S*)-[4′-(1-methylheptyloxy)-3′-nitrobiphenyl-4yl] 4-decyloxybenzoate, **2**: (*S*)-[4′-(1-methylheptyloxy)-3′-nitrobiphenyl-4yl] 4-(*trans*-3-decenyloxy)benzoate, **3**: (*R*)-[4′-(1-methylheptyloxy)-3′-nitrobiphenyl-4yl] 4-(*trans*-5-decenyloxy)benzoate. *Bottom* General structure of the 2-D monolayers formed on graphite by the liquid crystals.

anti-dimers of liquid crystal molecules arranged in rows (figure 1). Although molecules are not clearly resolved in these STM images (figures 2 and 3), the bright bands correspond to the sideways-packed aromatic cores of the molecules, while the dark bands correspond to the packed alkyl tails. While the STM images are lamellar, the adsorbed crystal differs from the smectic phase both by being a true crystal and in having a significant amount of interdigitation between the layers.

Each STM sample was prepared by placing a small amount (<1 mg) of the LC on a freshly cleaved surface of highly oriented pyrolytic graphite. The sample was heated to about 60°C to melt the LC into the isotropic phase, then allowed to cool slowly to room temperature. Scanning tips were prepared from mechanically cut 0·25 mm platinum/iridium (80:20) wire. Typical scanning conditions were 1·0 nA and −0·4 V (tip positive), constant current mode, 5·8 Hz (scan lines/s; 400 lines/image). Images were taken in air using a commercial STM (Nanoscope II, Digital Instruments, Inc.).

3. Results

The dark spots observed in figures 2 and 3 could represent vacancies (areas where molecules are missing from the crystal) or inclusions (incorporation into the crystal of other molecules which appear dark by STM). The behaviour of the dark areas suggests that they are vacancies, as they are observed to grow and shrink over time. A vacancy may change size as molecules adsorb to or desorb from the surface, but an inclusion would be expected to be static. Apart from the change in size of the vacancies, another dynamic process can be observed in the monolayer as a misregistered domain to the right of the vacancy in figure 2 shifts into alignment with the rest of the domain (figure 2A, B, H).

While it is not surprising that the vacancies can change size, the nature of the change is unexpected. In both cases the change in size of the vacancies occurs across the rows of molecules, rather than along them. This is surprising, because the molecule next to the vacancy in the same row is in contact with the crystal

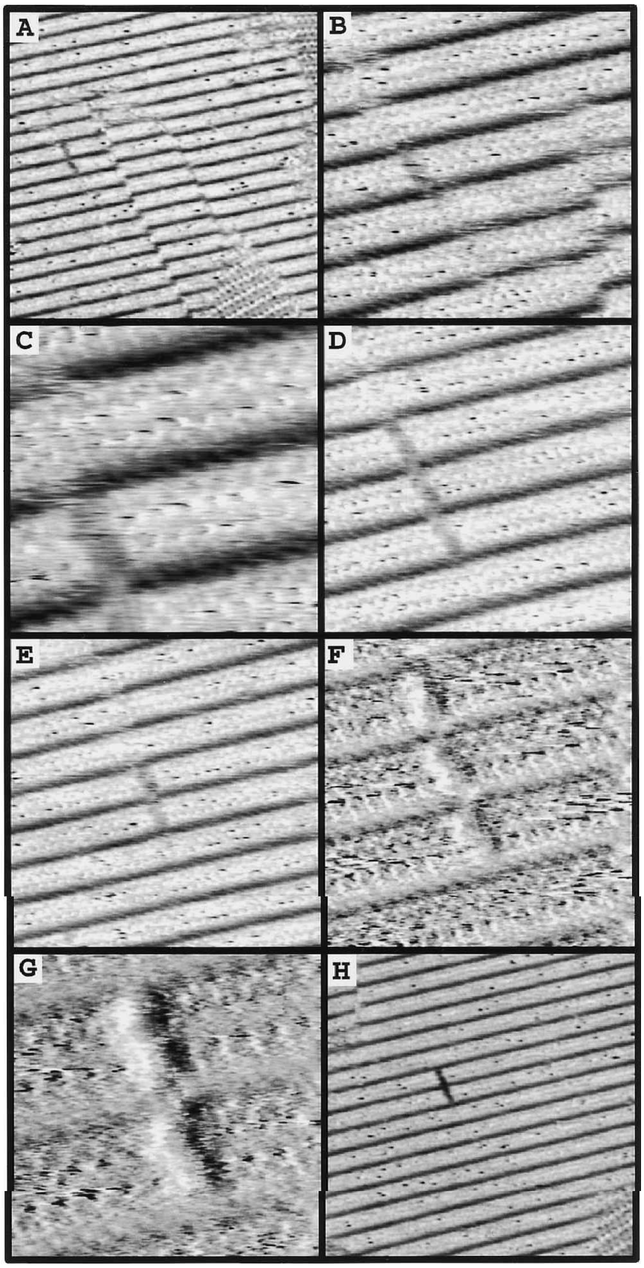

Figure 2. STM images of first vacancy observed for a mixture of **1** and **2** (1:1). All images were taken at 1·0 nA, −500 mV (tip positive); F–G taken in constant height mode and others in constant current mode. Scan sizes and time elapsed (min:s) from first image: A 75 nm, 0:0; B 30 nm, 1:55; C 14·4 nm, 2:22; D 30 nm, 6:37; E 40 nm, 8:16; F 20 nm, 9:07; G 12·2 nm, 13:24; H 75 nm, 16:12.

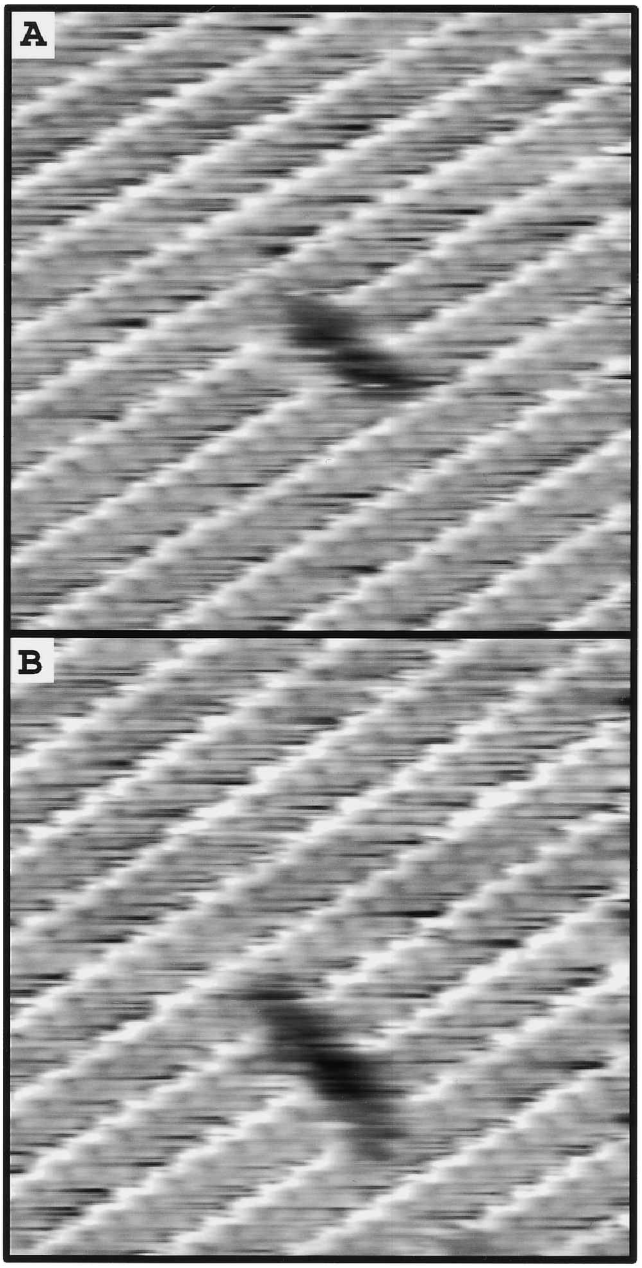

Figure 3. STM images of second vacancy observed for pure **3**. Both images were taken at 1·0 nA, −500 mV (tip positive), 8·7 Hz, 30 nm. Second image taken 0:49 (min:s) after first image.

only along one side, and might be expected to be more easily removed than the molecule in the next row, which contacts the crystal along both sides and touches the vacancy at only one end.

In figure 2, the vacancy appears to lie along a slight row mismatch in the crystal (figure 2B, D, E) which may account for the tendency to grow across the molecular rows, as molecules along a defect might be particularly mobile. However, figure 3 shows no defects apart from the vacancy, but this vacancy also grows across the rows. Since the vacancies are dynamic, it is somewhat surprising that molecules from the bulk do not immediately adsorb into the vacancy, causing the vacancy to disappear. Indeed, the vacancy in figure 3 could be observed for only two scans before it vanished, but the vacancy in figure 2 was observed in many scans over 16 minutes. The long lifetime of the vacancy in figure 2 may also be related to the slight row mismatch defect along which it appears to lie. It is possible that the row mismatch has created a point defect where the vacancy is observed, and due to this defect, there is not enough space to adsorb enough molecules to fill in the vacancy. Although this would explain the persistence of the vacancy, it is not clear why the vacancy would grow.

Although the images of the vacancies do not show molecular resolution, the width of the vacancies and the known unit cell [11] of the monolayers can be used to estimate the number of molecules missing. In the case of figure 2, the monolayer has a unit cell of 1·2 nm by 4·6 nm (two molecules per unit cell) and the vacancies are 1·0–1·8 nm wide, so there are 2–3 molecules (1–1·5 pairs) missing from each row. In figure 3 the unit cell is 1·0 nm by 3·9 nm (two molecules per unit cell) and the vacancies are 2·8–3·2 nm wide, so there are 6 molecules (3 pairs) missing per row. Since figure 2 shows the vacancy extending across 1–3 rows, the number of molecules missing from the crystal varies between 2–3 and 6–9. Likewise, figure 3 shows a 2–3 row long vacancy, so there are 12 or 18 molecules missing from the crystal.

The molecules seem to be missing from the rows in pairs (though some images in figure 2 may show 3 molecules missing) which may indicate strong pair interactions in the monolayer. It is also interesting that the vacancy stays essentially the same width while changing the number of rows that it extends across. In other words, not only do the vacancies grow preferentially across the rows rather than along them, but the preference seems quite strong. The molecular rows in the monolayer are actually interdigitated more than the general representation of a monolayer structure shown in figure 1, and interdigitation should decrease the preference for the vacancies to grow along the rows, but it is still not at all clear why the preference of the vacancies to grow across the rows is so strong.

If the vacancies are truly ‘empty’ then they would be expected to have topography lower than the dark bands in the monolayer (since at the dark bands the surface is covered by alkyl tail groups, while vacancies are bare graphite). This is the case for the second vacancy observed (figure 3) but the first shows topography the same or slightly higher than the dark bands in the monolayer (figure 2). In figure 2C especially, the vacancy is clearly lighter (enhanced tunnelling or higher topography) than the dark bands. Although tip shape could cause the vacancy depth to read as shallower than it actually is, where the vacancy crosses the dark rows it should still show up darker than the dark rows. In figure 2C and D the dark rows are actually brighter as they cross the vacancy, so we propose that the vacancy was ‘partially occupied’ by molecules which adsorbed and desorbed too rapidly to be resolved by the STM. The partial occupancy appears to have been non-selective, with some molecules briefly adsorbing such that the aromatic cores cut across the dark rows usually occupied by molecular tails, causing the dark rows to appear brighter in the vacancy. The observation that the vacancies can change size rapidly implies that molecules can adsorb to and desorb from the vacancy readily, in agreement with the vacancies showing ‘partial occupancy’.

4. Conclusion

Vacancies in monolayers of some liquid crystal molecules behave in unexpected ways. In particular, vacancy mobility across rows in the lamellar 2-D crystal is higher than mobility within rows. This seems very counter-intuitive, since disruption of intermolecular packing forces induced by the vacancy should be greater within a row than across rows.

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