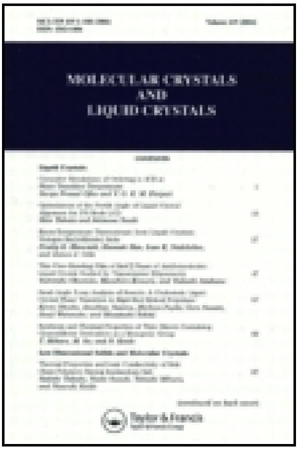

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Triphenylene Based Discotic Liquid Crystals as Self-Assembled Monolayers

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A side chain ω-thiol substituted triphenylene derivative was synthesised to investigate self-organisation of the triphenylene head group within a self-assembled monolayer (SAM). Scanning tunneling microscopy (STM) was used to characterise the ordering within the monolayer and the mesogenic head groups were found to orient with the discotic plane normal to the substrate forming columnar structures with the principal axis in plane of the monolayer. The overall degree of ordering within the monolayer and the persistence length of the columnar structures was increased by insertion of the SAM into trinitrofluorenone (TNF) solution. By altering the imaging parameters, the STM tip could be used to perturb the ordering in the monolayer and subsequent re-annealing of some of the columns was observed on a time scale of about a minute.

Keywords: SAM; STM; Triphenylene

INTRODUCTION

Self-assembled monolayers (SAMs) are widely viewed as the successor to Langmuir-Blodgett films, providing a surface with fewer defects, possessing actual covalent binding to the substrate and a variable functionality at the terminus[1].

The focus for this present study was to create surfaces able to impart columnar ordering to bulk samples of discotic liquid crystal applied to that surface. Recently, the detailed work of Evans *et al* on the alignment of a calamitic liquid crystal (8-cyanobiphenyl 8CB) using alkyl-thiol SAMs showed that control over the orientation of the bulk sample could be affected by the modification of the terminal head group.[2,3,4] However, the orientation of discotic liquid crystals by monolayer surface treatments has only just begun to receive attention.[5,,6,7]

By tailoring the end functional group of a SAM to the shape and nature of the discotic adlayer, it was hoped that any form of self-assembly within the monolayer would impart a similar alignment to the bulk sample.

Using thiol functionalised triphenylene derivatives to form SAMs two types of head-group packing can be envisaged. A symmetric tri-(2,6,10)-substitution of ω-thiol terminated side-chains around the triphenylene core should produce a parallel orientation of the discogen core relative to the gold substrate due to the three point tethering. Equivalent unsymmetrical one-point or 2,3-two-point substitution of the core should result in an "edge-on" tethering of the discogen producing a columnar phase[8] with the principal symmetry axis in the plane of the monolayer.

In this article we presents our scanning tunneling microscopy (STM) studies of the "edge-on" tethered discogens formed on a freshly annealed gold(111) surfaces. The "edge-on" SAM material chosen was *2-(5-mercaptopentyloxy)-3,6,7,10,11-pentahexyloxytriphenylene*[9] (Figure 1). In this article we show STM images of a 2D columnar phase and the effect that exposure of the SAM to trinitrofluorenone (TNF) solution has on the ordering observed. We present preliminary data which appears to show rupture of the columnar structures due to the interactions with the STM tip and re-annealing of the columns on the time scale of minutes.

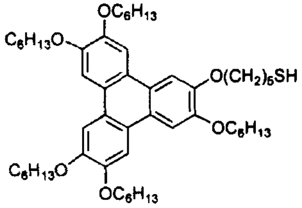

FIGURE 1, 2-(5-Mercaptopentyloxy)-3,6,7,10,11-pentahexyloxytriphenylene

EXPERIMENTAL

Flat gold surfaces for thiol self-assembly were prepared in two ways. The gold was either evaporated on to freshly cleaved mica to a thickness of 200nm at 10^{-6} Torr then hydrogen flamed annealed and quenched in pure methanol or it was epitaxially grown to the same thickness on pyrex and annealed at 450°C for two hours at 10^{-11} Torr. Both methods produced large flat gold terraces.

The SAM was prepared by immersing the gold substrate in a 1mM solution of the triphenylene in dry, distilled dichloromethane solvent for at least 5 hours to ensure complete SAM formation. All slides were washed copiously with distilled dichloromethane both before and after exposure to the solution.

It is known that trinitrofluorenone (TNF) forms donor-acceptor complexes with triphenylene derivatives[10]. The pre-formed SAM was immersed in a saturated solution of TNF in dichloromethane, to investigate the effect of formation of charge transfer complexes on the columnar ordering within the monolayer.

The STM images were acquired using a Digital Instruments (DI) IIIa STM with a low current boaster box and also with a Molecular Imaging (MI) STM with cold stage. Images were obtained with a tunneling current set point of 30-100pA, a tip bias of 800-1000 mV, in ambient conditions and using mechanically cut tips. Those obtained on the MI were acquired with a tunnel current of 300pA, with a tip bias of 300mV, at 3°C, using wax-coated tips.

RESULTS AND DISCUSSION

a) Observation of 2-D columnar ordering in the SAM and the effect of a TNF insertion on the degree of ordering

Figures 2(a)-(e) are constant current images obtained on the DI IIIa. Figure 2(a) shows a 300nm area of the SAM. Columnar structures running from the bottom to the top of the image can just be seen in this large scale, low resolution image but more easily seen in the enlarged region of this image shown in figure 2(b). The large feature in the bottom right hand corner of image 2(a) is due to triangular gold terraces beneath the SAM. The constant height image of figure 2(c) shows a higher resolution image of 40nm square area of the sample. Some small columnar features 2.2-2.5nm wide with a length of a few nm can be seen, however, a great deal of disorder is also apparent in the SAM. The measured width of the columnar structure agrees well with the diameter of the triphenylene head group (2.2nm) strongly supporting our interpretation of these features. Images of the samples which have been subsequently immersed in TNF solution are shown in figures 2(d)-(e). Columnar structures are clearly visible in both images. The addition of TNF appears to have increased the degree of columnar ordering of the triphenylene head groups in the SAM which can be seen by comparing

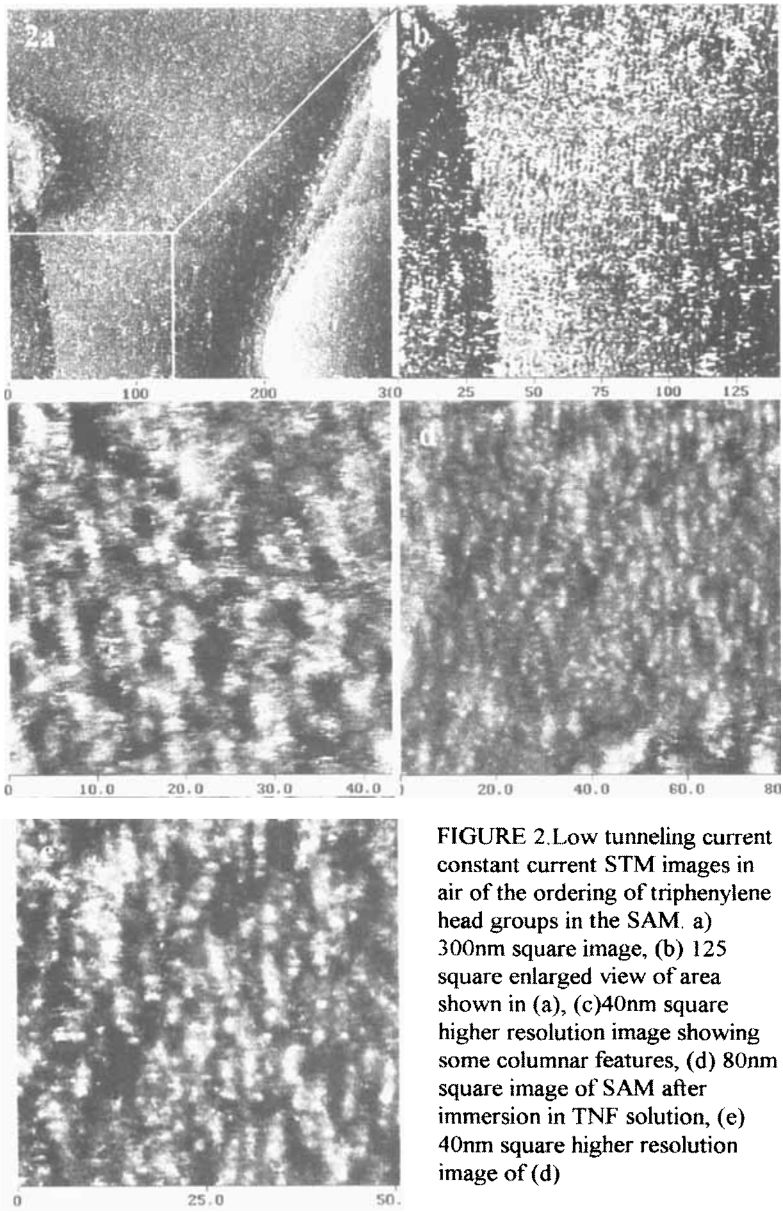

FIGURE 2.Low tunneling current constant current STM images in air of the ordering of triphenylene head groups in the SAM. a) 300nm square image, (b) 125 square enlarged view of area shown in (a), (c)40nm square higher resolution image showing some columnar features, (d) 80nm square image of SAM after immersion in TNF solution, (e) 40nm square higher resolution image of (d)

figures 2(c) and 2(e). This increase in average persistence length most probably arises from a stiffening of the structures due to insertion of the TNF molecules between the discotic head groups reducing the room temperature disorder.

b) Observation of columnar dynamics induced by the STM tip.

The images obtained at 200pA and 300 mV using the MI system are displayed in figures 3(a)-(c). These are a sequence of images of the same position of the surface, the acquisition of which, was separated in time by approximately one minute. Large, curved columnar structures can be seen extending many tens of nanometers across the images, however, in the top right hand corner of each figure, but most clearly observed in figure 3(a), an area of closely packed columnar structures can be seen running from upper left to lower right. The columnar widths in this highly ordered region are of the order 2.2 - 2.6nm and the inter-column spacing is approximately 2.6 - 3.2nm, dimensions which are comparable with those measured in bulk triphenylene columnar phases[11]. The larger, curved columns have widths of approximately 2.3 -2.9nm in figures 3(a) and (b) increasing to 3.6nm in figure 3(c).

The high tunnel current and lower bias used means that the tip would have been much closer to the surface than in the images in figure 2 and may well be penetrating the SAM. Rupturing of columns can clearly be observed between figures 3(a) and (b) (centre-left of the image) which can be attributed to the influence of the STM tip. Some of these ruptured columns appear to have re-annealed in figure (c), presumably driven by the self-organising property of the triphenylene head groups. The increase in observed column width from figure 3(a) - (c) is also probably due to tip becoming contaminated during the imaging process - a well known cause of increasing feature size in scanning probe microscopy.

An observation which is difficult to explain is that the columnar structures move over greater distances when ruptured by the tip than the length of the alkyl tether should allow. One explanation of this is that the

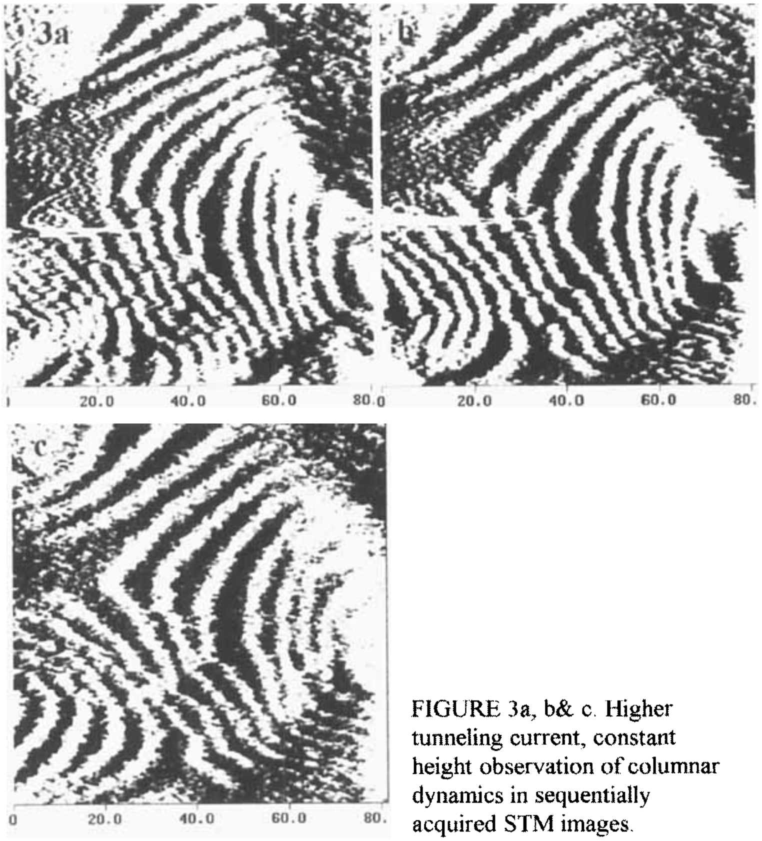

FIGURE 3a, b& c. Higher tunneling current, constant height observation of columnar dynamics in sequentially acquired STM images.

gold-sulphur bond is in fact being broken during the imaging process permitting the head group and tether to move over distances greater than the tether length. However, a rupture of a covalent bond by the imaging process seems highly unlikely indeed. A second possibility is that the gold-sulphur bond does not break but that the metal atom moves with the tethering unit across the surface. This migration of metal atoms across a surface is known to occur[12], however, since there is no independent evidence in the present work to support this rationalisation of the large scale motion of the triphenylene head groups, the phenomenon remains unexplained.

CONCLUSIONS

Low current STM images showing columnar structures within a self-assembled monolayers of a triphenylene based discotic liquid crystal have been presented. Although columnar ordering is observed in unmodified SAMs the insertion of the preformed SAM into a solution of TNF in dichloromethane was shown to increase the overall degree of columnar ordering and to increase the average persistence length of the columns. This is believed to occur due insertion of TNF molecules between the discotic mesogens in the columns which results in increased stiffness and reduced thermal disordering.

When the tunnel current is increased bringing the tip closer to, and in all probability penetrating the SAM, rupturing of the columnar structures by the tip is observed. In a few cases the ruptured columns are seen to re-anneal on a time scale of about a minute.

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