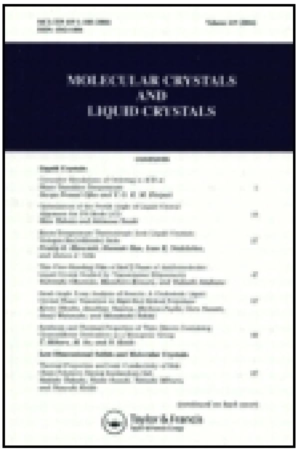

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Twofold Orientation of Triphenylene-Based Discotic Liquid Crystals on Gold

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Twofold Orientation of Triphenylene-Based Discotic Liquid Crystals on Gold

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Self-organization of first adsorbed monolayer of discotic liquid crystal, 2,3,6,7,10,11-hexapentyloxytriphenylene on the Au(111) surface was investigated by scanning tunneling microscopy at a solid/liquid interface. Visualizing the structure of the interface between organic molecules and the surface of the electrode is crucial for understanding the physics of potential devices, like organic light-emitting diodes or organic photovoltaic cells. We present images recorded with molecular resolution that reveal presence of ordered domains of hexagonal symmetry. Mutual distances between the centers of H5T lattice, combined with the orientation of the unit-cell suggest commensurability with the underneath metal surface. Two types of H5T lattices have been evidenced, coexisting on the same Au(111) substrate. They correspond to (7 × 7)R30 and (7 × 7)R44 structure of H5T molecules.

Keywords Discotic liquid crystals; scanning tunneling microscope; self-assembled monolayers; triphenylenes

1. Introduction

Discotic liquid crystals (DLCs) are interesting for their substantial potential in the frame of organic electronic devices where they can be used as active layers [1]. The origin of their semi-conducting properties lies in their ability to form columnar mesophases (Col), where the π-electrons of the central polyaromatic cores interact with the one of the neighboring molecules of the same column by π-π stacking. Due to the self-healing property the size of materials monodomain can reach tens to hundreds of microns [2], thus ensuring undisturbed charge transport along the defect-free molecular wires formed by the columnar stacks. Although the self-assembly [3], photophysical [4] and charge transport properties [5] of various groups of DLCs have been reported, investigations on the interface between the organic film and the surface of the electrode are still scarce, despite the fact that

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the boundary layer of liquid crystals often defines the organization of molecules in the bulk [6] and in the particular case of DLC molecules, they may influence the transport properties as well. Our focus is on the anchoring of hexaalkoxy-substituted-triphenylene molecules, which can be considered as models for DLCs. Previous investigations on the self-assembling properties of branched triphenylenes have aimed at investigating the influence of the length of the peripheral side-chains [7,8]. These studies resulted in discovering interesting effects, e.g. appearance of surface-induced chirality of the non-chiral system [7] or surface-induced pairing of the molecular components [9]. However, less attention has been given to the orientation of self-assemblies of H5T mesogen with respect to the substrate. Here, we report on the structure of the first monolayer of a triphenylene-based discotic liquid crystal anchored on a gold surface. By using scanning tunneling microscopy (STM) at the Au(111)/*n*-tetradecane interface we show that H5T molecules form two different types of domains, mutually rotated by 14°.

2. Experimental

Sample Preparation

2,3,6,7,10,11-hexapentyloxytriphenylene (H5T, Fig. 1) is a discotic liquid crystal, that exhibits a hexagonal columnar mesophase between 69°C and 122°C [10]. H5T was dissolved in *n*-tetradecane (Sigma Aldrich, pure >99%, used as received) with a concentration of 1,67 mmol/L. It was heated up to ~70°C for 15 min prior to deposition onto freshly flame-annealed gold. The Au(111) substrate was purchased from Neyco. Annealing with gas flame (propane-air) was performed until signs of glowing appeared on the sample. The STM tip was mechanically cut from a Pt/Ir wire (90/10 wt%, GoodFellow Inc.) and was immersed in the droplet of solution during the scanning process.

Scanning Tunneling Microscopy (STM)

All the measurements have been performed in ambient conditions (room temperature). In order to minimize the influence of thermal drift all figures presented have been collected

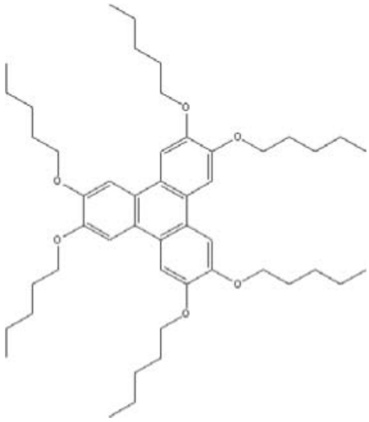
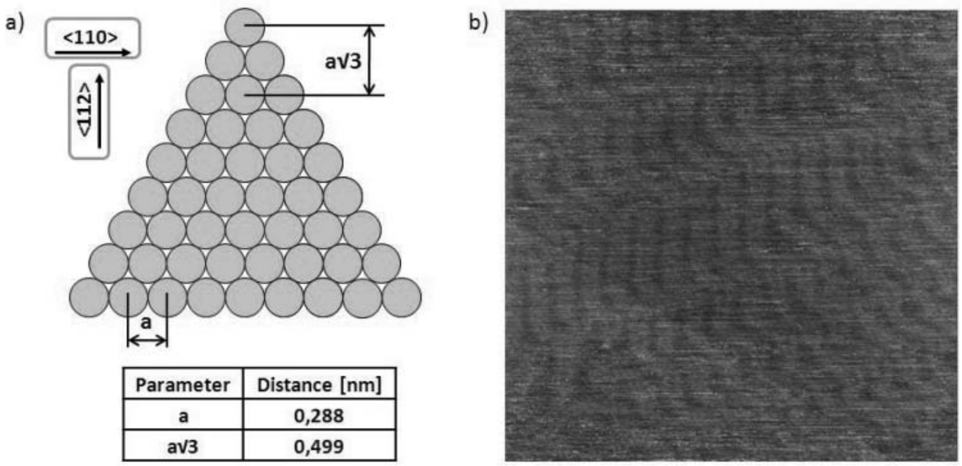


Figure 1. Molecular structure of the discotic liquid crystal 2,3,6,7,10,11-hexapentyloxytriphenylene (H5T).



Parameter	Distance [nm]
a	0,288
a√3	0,499

Figure 2. (a) Hard-sphere representation of non-reconstructed Au(111) surface with indicated crystallographic directions and distance parameters; (b) STM constant current image of Au(111) reconstructed surface, 150 × 150 nm^2, I_t = 1,2 pA, V_t = -200 mV.

after sufficient time of scanning, when both upward and downward scans were identical. The images were obtained in the constant current mode.

The Au(111) Surface

Bulk crystal of gold corresponds to a face-centered cubic (fcc) crystallographic structure. The (111) face of gold, denoted as Au(111), is one of its three low-index planes and represents the situation when surface atoms are hexagonally packed with the distance between the centers of closest neighbors equal to 0,288 nm (Fig. 2(a)). However, this ideally flat facet is a highly unfavorable state. Since surface atoms are lacking of neighbors, to minimize the surface energy, they reorganize the bonding among themselves. This leads to formation of reconstructions of periodicities different from bulk-terminated surface (Fig. 2(b)). Appearance of reconstruction is, firstly, the evidence of purity of the surface, which is crucial for self-assembled monolayers (SAMs) formation. Secondly, it is well-established that lines of surface reconstructions on Au(111) are formed along <112> crystallographic direction, thus making them reference for finding orientation of molecules of adsorbates with respect to underneath substrate. In this work, lines of reconstruction helped us to answer if H5T self-assemblies on gold reveal any features of commensurability with Au(111).

3. Results and Discussion

Upon absorption of H5T molecules on Au(111), the molecules self-organize into well-ordered domains on the large atomically flat gold terraces (Fig. 3(a)). The monolayers were stable for several days, within a large range of voltages (−0,5; 0,5)V associated with STM measurements. This observation is in agreement with previous reports on the two-dimensional self-assembly of H5T on graphite (HOPG) [7] and on Au(111) [11]. On Fig. 3(a), first feature that should be noticed are the bright stripes of gold reconstruction, oriented preferentially with ∼10° deflection anti-clockwise from the vertical,

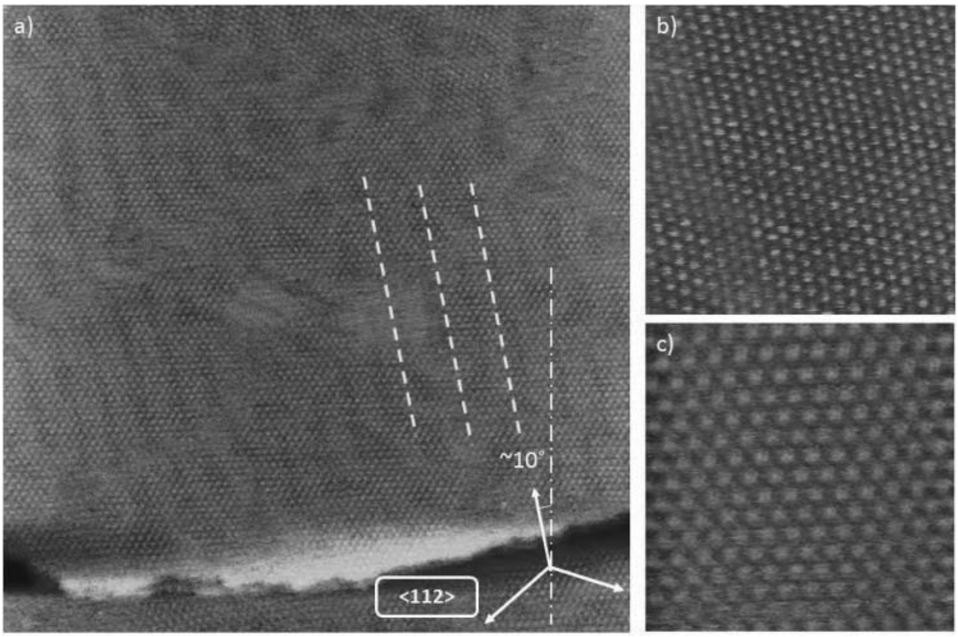


Figure 3. STM images of H5T molecules self-assembled at the Au(111)/*n*-tetradecane interface. (a) 195 × 195 nm^2, $I_t = 5$ pA, $V_t = 100$ mV; (b) 40,6 × 40,6 nm^2, $I_t = 5$ pA, $V_t = 100$ mV; (c) 23 × 23 nm^2, $I_t = 20$ pA, $V_t = 280$ mV.

which corresponds to the <112> crystallographic axis on the gold surface. The fact that Au(111) reconstruction is not lifted as a result of monolayer formation suggests that the discotic molecules are physisorbed. On the STM image, each bright spot is attributed to a triphenylene aromatic core since it is well-known that conjugated π-electron systems exhibit a large contribution to the STM contrast [12]. Those spots form ordered domains of hexagonal symmetry, which is seen more clearly in higher resolution images (Figs. 3(b) and 3(c)). On both large- and small-scale images all bright spots exhibit the same contrast, which suggests that the molecules occupy energetically equal adsorption sites. This situation was preserved throughout subsequent scans, for different scan directions, tip-sample polarities and tunneling current parameters and could constitute an indirect evidence of commensurability of the adlayer with respect to the symmetry of substrate.

H5T has been involved previously in reports where the influence of the alkyl chain length was systematically investigated. However, no structural details of its self-assemblies on gold has been underlined. This is partially due to the fact that H5T molecules are usually visualized as diffuse spots, with hardly obtainable intra-molecular resolution, which is not the case for e.g. H11T and other long-tail analogues. The reason lies in the fact that interdigitation of side-chains from neighboring molecules occurs for the mesogens with peripheral alkyl-tails longer than five carbon atoms, what results in increased monolayer stability [9].

Using our data which provided the precision necessary for accurate measurements, the center-to-center distance between two spots has been calculated to be 2,0 ± 0,1 nm for several samples. This value, together with the fact of possible commensurability of H5T monolayer has driven us to study this system in details. If one considers the lattice parameters of Au(111) (Fig. 2(a)) it is straightforward to find two possible ways of simple

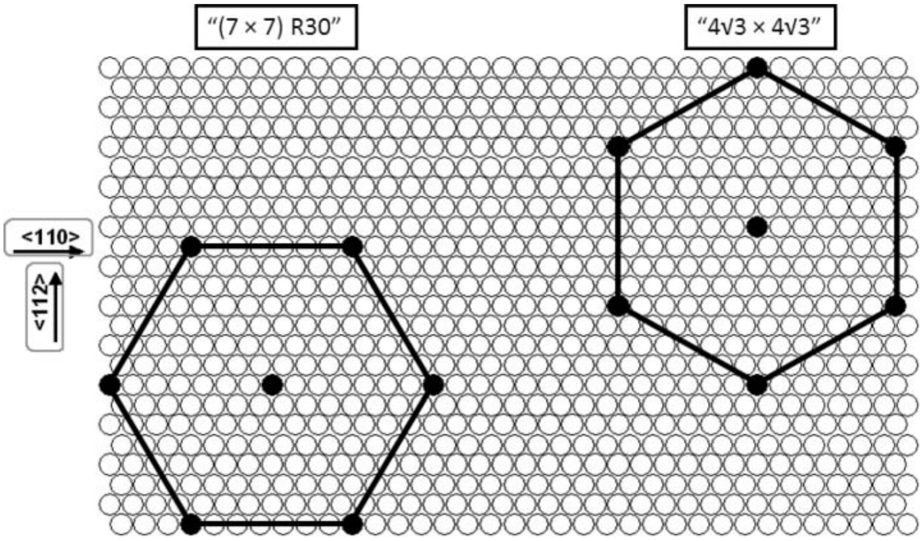


Figure 4. Schematic view of hexagons of two possible packing models of H5T on Au(111) with lattice parameters equal to: 2,02 nm and 2,00 nm for (7 × 7) R30 and ($4\sqrt{3} \times 4\sqrt{3}$) domains, respectively.

packing along main crystallographic directions that fullfill the condition of periodicity with 2,0 nm. Both of them are shown on Fig. 4.

The two hexagons correspond to two possible geometric arrangements for which H5T molecules are aligned along either the <110> or the <112> direction, respectively. Theoretical spacing between centers of neighboring discotics that was calculated on the basis of distance between gold atoms in Au(111) is equal to 2,02 nm for the $4\sqrt{3} \times 4\sqrt{3}$ case and to 2,00 nm for the (7 × 7)R30 case. Relative spatial difference between those two values equals to ~1%, which is not a sufficiently small difference to exclude the appearance of both structures-by self assembly. However, when analyzing STM images we have never found molecules aligned along the Au(111) reconstruction lines, which suggests that ($4\sqrt{3} \times 4\sqrt{3}$) are not formed. In contrast, the main axis of the hexagon created by bright dots is often tilted by ±30° from a reconstruction line, which corresponds to the <110> crystallographic direction, expected for (7 × 7)R30. Tilting from the reconstruction lines and lateral separation between H5T molecules both suggest that the (7 × 7)R30 surface structure is formed by H5T at Au(111)/*n*-tetradecane interface.

Suprisingly, STM images also reveal that another type of domain usually coexists with (7 × 7)R44 domains on Au(111). This second type of domains is highlighted in red (Fig. 5(a)). The mutual orientation between both types of domains is depicted by two vectors, and present rotation by 14° from one to another. What may be noticed on Fig. 5(a) is, again, stability of the monolayer, confirmed by a still perfect organization at the "screw-dislocation" defect in the top-left corner (red-bordered domain). Figure 5(b) represents mutual geometry of two domains of different orientation. The black line highlights the boundary between top (A) and bottom (B) domains, and yellow dashed-line corresponds to direction of gold reconstruction that served as reference. The symmetry axis of top domain creates angle equal to 30° with respect to <112> direction of underneath substrate, as predicted by (7 × 7)R30 model. The bottom domain, however, is tilted by 14° from the top one, as already shown on the large-scale Fig. 5(a). As in previous case, molecules

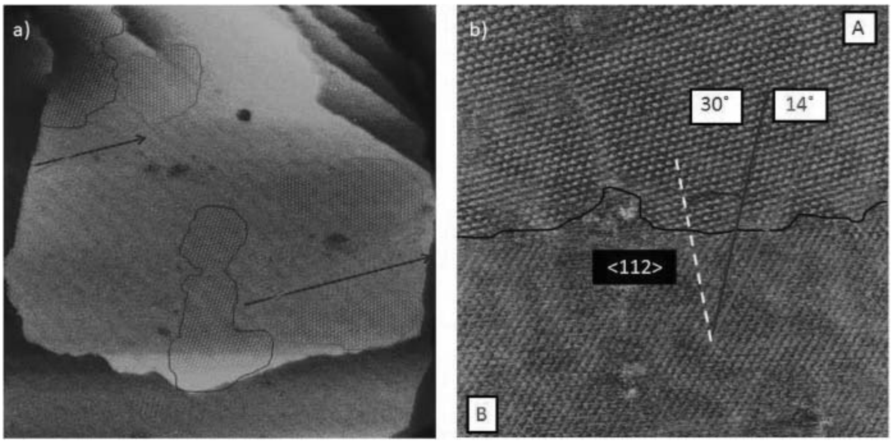


Figure 5. STM images of H5T molecules self-assembled at the Au(111)/*n*-tetradecane interface. (a) 210 × 210 nm^2; (b) 95 × 95 nm^2; both: $I_t = 10$ pA, $V_t = 100$ mV. Blue and red colors indicate two different types of domains. Black line at (b) underlines boundary between top and bottom domains, yellow dashed-line indicate direction of substrate reconstruction.

within a single domain do not exhibit any periodical contrast changes, with respect to their environment, which suggest commensurability of both structures.

After detailed analysis of lateral distances between triphenylene cores in both (A) and (B) areas of monolayers, value of 2,0 ± 0,1 nm has been established as periodicity of lattice nodes in both kinds of domains. Similar spacing in both regions, and repeatedly appearing of

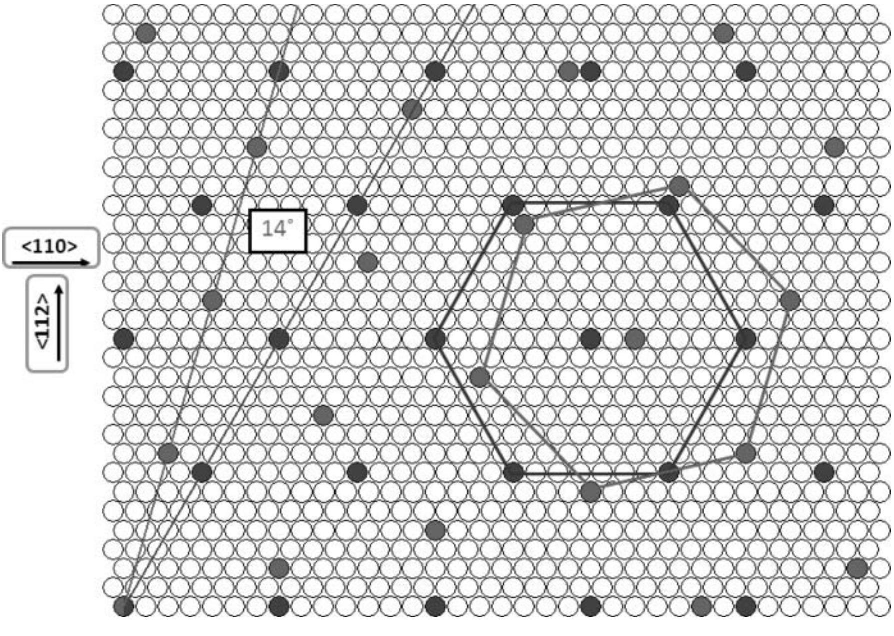


Figure 6. Proposed model of packing of twofold orientation of H5T molecules at the Au(111)/*n*-tetradecane interface. Blue mesh correspond to (7 × 7)R30 superstructure and red array show the 14°-rotated domain with lattice parameter equal to: 2,07 nm.

14° orientation of two domains resulted in the construction of geometrical model depicted on Fig. 6. While (7 × 7)R30 structure, proved to exist in the H5T/Au(111) system, is depicted by blue mesh of points, the red pattern represents schematically arrangement of second type of domain. It appears to correspond to a (7 × 7)R44 structure. (7 × 7)R44 domain calculations based on 0,288 nm lattice parameter of Au have given 2,07 nm center-to-center distance. This value, due to the thermal drift and non-instantaneous response of piezoelectric element of the microscope scanner, lies within the experimental error for STM measurements performed in the ambient conditions.

The structural features described here have been repeatedly obtained as result of multiple experimental trials and appear not to be connected with any peculiarities of measurements procedure, whatsoever. The reason of such twofold geometrical conformation of ad-layer with respect to gold substrate remains unclear, and so far was never observed by us on HOPG. One hypothesis connects it with multiple energetic local minima occurring for different conformation of alkyl tails on atomically flat surface of Au(111). This will be further examined with the help of theoretical calculations.

4. Conclusion

In conclusion, we have shown that H5T molecules form stable monolayers of hexagonal symmetry at Au(111)/*n*-tetradecane interface. Taking advantage of well-established directionality of reconstruction of gold we were able to show the orientation of H5T domains with respect to the substrate and to establish their commensurability. Two structures have been evidenced, (7 × 7)R30 and (7 × 7)R44. No report about twofold orientation of H5T on Au(111) can been found in literature. This observation raises new questions concerning the nature of monolayers formation. Results presented here will consequently be followed by temperature-dependent studies of monolayers behavior and theoretical simulations, to increase our understanding of the described system.

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