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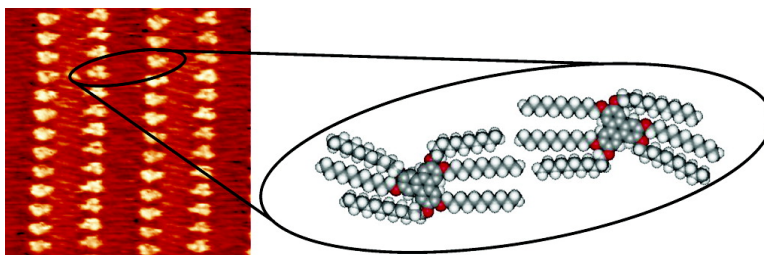
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Substrate-Induced Pairing in 2,3,6,7,10,11-Hexakis-undecalkoxy-triphenylene Self-Assembled Monolayers on Au(111)

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Self-assembled monolayers (SAMs) of liquid crystals (LCs) have been intensely investigated in surface science because of their applications in devices such as flat screens in computers, video screens, and instrument panels.[1] Their remarkable feature is their ability to change structure and optical properties in response to an electric or magnetic field. Such field-induced phase transitions are determined not only by the chemical structure of the molecules but also by their anchoring mode to the metal electrodes.

Among many types of LCs, planar disklike molecules such as triphenylenes are known to exhibit columnar mesophases. An example of such compounds are 2,3,6,7,10,11-hexakis-alkoxy-substituted triphenylenes, hereafter noted T_n, where n indicates the number of carbon atoms in the alkyl chains. T_n molecules consist of flat polyaromatic cores symmetrically surrounded by flexible n-carbon side chains. When deposited on a surface, T_n molecules stack upon each other to form hexagonally packed columns with a $\pi-\pi$ stacking configuration.[2] Triphenylene LC mesophases present a quasi-1D transport of charge carriers along these vertical columns which make them attractive for electronic devices applications.[3]

However, to control the 3D arrangement of T_n molecules on a metal surface, it is necessary to control the structure of the first T_n monolayer. A number of studies have been devoted to T_n self-assemblies on graphite,[4−6] but we found no report on metal surfaces although they are of great technological interest. We report here on in-situ STM investigations of T_{11} ($n = 11$, Figure 1a) self-assembled monolayers (SAMs) at the n-tetradecane/Au(111) interface[7] with the essential aim to elucidate the interplay between substrate−molecule and molecule−molecule interactions. We in particular show that T_{11} molecules on Au(111) associate in dimers and form self-assemblies with parallel rows of molecules.

Experiments are performed using a Pico SPM (Molecular Imaging) equipped with a home-built liquid cell. Au(111) surfaces on mica are commercial samples. The T_{11} powder is dissolved in n-tetradecane (Aldrich), with a concentration of approximately 0.05 mg/mL. A droplet of this solution is then deposited onto a reconstructed Au(111) sample. STM images are recorded in the constant-current mode. All preparations are carried out at room temperature. STM tips are mechanically cut from the 250 μm Pt/Ir (80:20) wire and tested on cleaved graphite. Typical imaging conditions are $10-500$ mV in bias tip voltage and $10-500$ pA in tunneling current. The error in measured distances is within 5%, and no filtering procedure is used.

Figure 1b shows a typical large-scale STM image of a T_{11} monolayer on an Au(111) atomically flat terrace. T_{11} molecules self-organize in domains which exhibit an ordered structure formed by double rows of aligned bright spots having an approximate diameter of 0.5 nm. Because π-conjugated systems are well-known to give large contributions to STM contrast,[8] we identify the bright rows as being constituted by the aromatic cores of T_{11} while the

darker rows would correspond to the alkyl chains. The ordered domains are aligned along two directions, forming an angle close to 30°. One of these directions is perpendicular to the straight Au step edge which is usually parallel to $\langle 110 \rangle$ (see AB in lower left corner in Figure 1b). These two preferential directions of growth are consequently parallel to the $\langle 110 \rangle$ and $\langle 112 \rangle$ directions of Au(111). This conclusion is also supported by the respective orientation of the T_{11} rows and the underlying reconstruction lines which were observable at appropriate experimental conditions. Thus, the two ordered domains marked α and β in Figure 1b are in epitaxy with the underlying gold substrate. The geometry of both types of domains is similar. In α-domains, the molecular rows run along the $\langle 112 \rangle$ direction, while in β-domains they are parallel to $\langle 110 \rangle$.

The high stability of the T_{11} adlayer allows one to obtain intramolecular resolution which reveals details of the molecular packing (Figure 1c). Molecular rows appear to have a paired structure composed of rows R1 and R2. These rows are not equidistant but are alternatively separated by ∼2.9 and ∼3.2 nm. Furthermore, the troughs between R1 and R2 rows present, respectively, bright and dark STM contrast, which is another argument in favor of a pairing association of T_{11} molecules. Finally, Figure 1c clearly shows that molecules of R1 and R2 rows are in an antiparallel position (rotation by 180°).

The observation of dimers in T_{11} monolayers on Au(111) is surprising. Usually, pairing is observed with nonsymmetrical (amphiphilic) molecules such as alcohols[9] or organic salts.[10] For such molecules, the formation of dimers occurs directly in solution or in the gas phase without participation of the substrate. In contrast to polar molecules, T_{11} does not form dimers in solution.[2] One can then assume that the unexpected formation of dimers on Au(111) is a substrate-induced process. This assumption is also supported by the fact that we observed no T_{11} dimers on graphite under the same experimental conditions, in agreement with previous studies.[4,5] A pairing phenomenon has already been observed on symmetrical molecules by Ito et al. with peri-hexabenzocoronene adlayers on graphite.[11] However, in this latter case, the role of the substrate in the pairing mechanism is not fully understood.

In light of our results, we can now propose a possible explanation of T_{11} pairing on Au(111). Self-assembly processes are governed by the interplay of intermolecular and interfacial interactions. Upon deposition, these interactions drive the system toward a minimum of the overall free energy. In addition to the conjugated core, long alkyl chains of T_{11} bring another important contribution to the substrate−molecules interaction. It has been recently shown that adsorption of long alkanes at the liquid/Au(111) interface always occurs in second-neighbor furrows of gold with their main molecular axis parallel to the $\langle 110 \rangle$ direction.[12] Such an adsorption is a direct consequence of the strong anisotropy of the Au(111) surface.

As can be seen in Figure 1c, due to this orientational effect of the gold substrate, the alkyl chains of each T_{11} molecule adopt two

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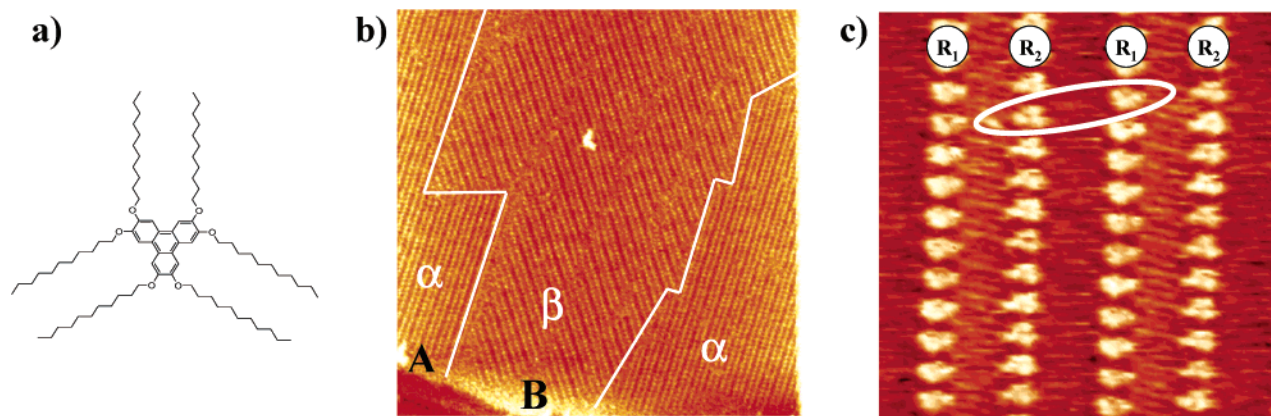
Figure 1. (a) Chemical structure of T_{11}. (b) Large-scale STM image (140×140 nm^2, $U_t = 0.20$ V, $I_t = 71$ pA) of a T_{11} self-assembled monolayer at the n-tetradecane/Au(111) interface. In the α-domains, molecular rows are perpendicular to the Au step edge (AB, lower left corner) and form an angle close to 30° with molecular rows of β-domains. (c) High-resolution STM image of an α-domain (17×17 nm^2, $U_t = 0.26$ V, $I_t = 96$ pA) revealing the triangular shape of the T_{11} aromatic cores and the alkyl-chains positions. Molecular rows R1 and R2 associate through T_{11} pairs (or dimers) as delimited by the white ellipse.
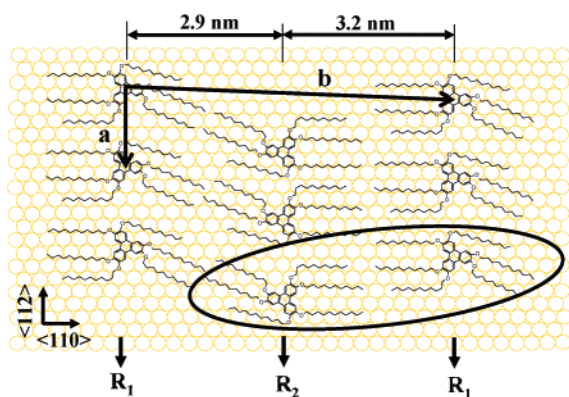
Figure 2. Possible model for the packing of T_{11} on Au(111). A T_{11} dimer is identified by an ellipse. Inside each dimer, T_{11} molecules are in an antiparallel position.

different orientations between R1 and R2 rows. In the bright contrast troughs, alkyl chains are tilted, while in the dark contrast troughs they are horizontal and parallel to the $\langle 110 \rangle$ direction. The average separation between horizontal alkyl chains as measured on STM images is ~0.5 nm, which corresponds to a minimum of the chain–substrate interaction.[12] Because of steric restrictions, the three tilted side chains cannot be directed along $\langle 110 \rangle$. They are tilted by an angle of ~20° to minimize the mean interchain distance down to the optimum value of ~0.48 nm.[13] The noncommensurability of these tilted chains is at the origin of their flexibility on the substrate and thus of the bright contrast generated in STM images (Figure 1c). A possible model for this surface arrangement is presented in Figure 2. It takes into account intermolecular distances and the observed overlayer symmetry. The parameters of the unit cell are $a = 6.3$ nm, $b = 1.5$ nm, and the angle between a and b is $86 \pm 1°$.

A T_{11} dimer is defined as two T_{11} molecules stacking in neighboring R1 and R2 rows and having their three respective alkyl chains parallel to the $\langle 110 \rangle$ direction close to each other (see ellipse in Figure 1c and Figure 2). Pairing through tilted side chains can be excluded because it would occur without any orientational action of the Au(111) substrate. In this case, dimers would form in solution and would be observed on other substrates, which is not the case.

As we define it, the T_{11} dimer constitutes a building block for the T_{11} adlayer which further self-assembles in a lamellar packing similarly to linear liquid crystals.[14]

In contrast to the hexagonal packing found on graphite for triphenylenes, T_{11} molecules deposited on Au(111) are epitaxially ordered in rows and form dimers. This pairing association of T_{11} is governed by the strong interaction between the alkyl chains and the Au(111) substrate. Preliminary results show that T_n molecules with various alkyl chain lengths self-assemble in different geometries. Modulation of the T_n alkyl chain length appears then as an efficient way to control their 3D arrangement in columnar discotic LCs on atomically flat metal surfaces.

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