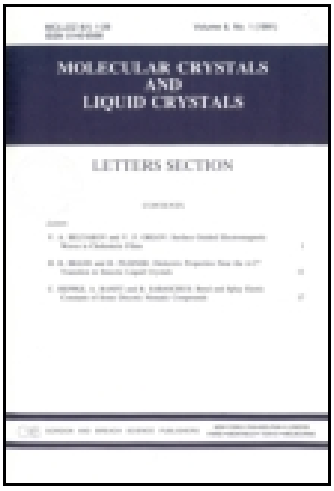


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# STM Study of Self-Organization of 10CB Molecules on Au(111) Surface

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*We report the scanning tunnelling microscopy (STM) observation of a self-organization of* 4-*cyano-4′-n*-decylbiphenyl *(10CB) molecules on the reconstructed Au(111) surface. The self-organized monolayers were obtained by the deposition from a liquid. We revealed a row-like dimer structure with regularly arranged kinks within each dimer row. The separation between neighbor kinks is equal to 4 or 5 intermolecular distances. STM-images with intramolecular resolution showed that the association of molecules in dimers is due to the interaction between cyano groups. The obtained results are discussed in terms of the balance between the molecule-molecule and molecule-substrate interactions and are supported by the results of DFT calculations.*

**Keywords** STM; self-assembled monolayers; reconstructed Au(111) surface; 10CB; 4-cyano-*4′*-n-decylbiphenyl; alignment; alkyl chain.

## Introduction

There have been a lot of microscopic studies of a 10CB molecule alignment on the HOPG (highly ordered pyrolytic graphite - semimetal) [1–4] and $MoS_2$ (semiconductor) [4–6] substrates carried out up to now. Differences in the lattice constants and electronic nature of these substrates have to present a relevant impact onto the formation of different types of molecular packing. However, 10CB molecules deposited onto HOPG and $MoS_2$ display the equivalent double-row type of molecular alignment with unit cells consisting of 10 molecules [5]. It was found that the alkyl chains of 10CB molecules on the hexagonal lattice of sulphur atoms of $MoS_2$ are parallel to each other and inclined at an angle of 60° with respect to the interplanar packing [6]. In the case of cleaved HOPG, the hydrogen orbitals of alkyl chains of 10CB fit into the holes of carbon rings on the (0001) plane of graphite [4]. As a result, the most stable monolayer on HOPG can be obtained in three equivalent crystallographic directions different to 60°. These observations suggest that the 10CB molecular anchoring on the surface is driven by molecular chain-surface interactions,

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while the driving force for forming a 2D self-assembled structure is the intermolecular dipole-dipole interaction. This led us to suspect that the 2D self-assembled structure of 10CB as well as the number of molecules in a unit cell should not depend on the lattice parameter that lies from 2.74 Å (HOPG) to 3.16Å ($MoS_2$).

In this paper, we represent, for the first time, an experimental observation of the 10CB alignment on the Au(111) surface with lattice constants equal to 2.88 Å. The STM observations revealed the formation of a double-row molecular alignment on Au(111), which is similar to HOPG and $MoS_2$, but with the number of molecules in the unit cells different to that for HOPG and $MoS_2$.

## Experimental Section

For the deposition on the Au(111) surface, a fresh solution of 10CB in ethanol (∼2·10-5 M) was used. For the deposition by the melting method, a small grain of 10CB was placed directly on the flamed Au(111) surface at the controlled temperature.

The Au(111) substrates are Neyco gold films (thickness ∼150 nm) carefully annealed in a gas flame (propane+air) in order to obtain a reconstructed surface. The monolayers were investigated using a commercial STM equipped by a low-current head ("Veeco", Digital Instruments, Inc., USA). The STM tip was prepared by the mechanical cutting of a Pt/Ir (80:20) wire. For each monolayer, several STM-images recorded in the constant-current mode with a current ranging from 5 to 30pA and a tip bias from ±100 to ±1500 mV were obtained with different samples and tips to check the reproducibility and to ensure that the results are free from artefacts. All STM images presented here were recorded under ambient conditions without any further image processing.

All geometrical configurations and molecular wave functions were obtained for an isolated 10CB molecule in the neutral form using the quantum-chemical calculations. The calculations of the full geometry relaxation, electron density (HOMO and LUMO levels), and energies are performed at the density functional theory (DFT) level with a hybrid B3LYP functional and the standard 6-31G* basis set using the Gaussian'03 program package.

## Results and Discussion

10CB molecules deposited from a solution onto the Au(111) surface form epitaxial monodomains vary in size and in the direction of rows. The angle of 60° between rows of molecules in domains was expected, since the Au(111) has six-fold symmetry. When the rows of neighboring domains have an angle of 60° between each other, the domains are separated by disordered regions, while the rows in co-directed domains are only slightly shifted (Fig. 1a). These observations suggest that the rows are co-directed with <110> or <112> crystallographic directions of the Au(111) lattice. However, the angle between the rows and the step edges of Au(111), which are known to be parallel to <110>, is equal to 109° ± 5°. This mismatch was referred to a specific intrarow molecular packing, since the domains do not show any long range Moiré pattern, which appears when molecules come into and out of phase with underlying substrate [7].

The STM image in Fig. 1b shows the intrarow structure formed by groups containing 8 molecules with orientation to each other by –C≡N groups. The bright contrast areas on the STM images correspond to the $\pi$-conjugated biphenyl cores of 10CB with a length, which agrees well with the calculated core length, and the profile of frontier wave functions (Fig. 1c), which is mainly defined by phenyl rings. The investigations of different domains revealed that this type of packing (8 molecules in a group) is more favorable than the

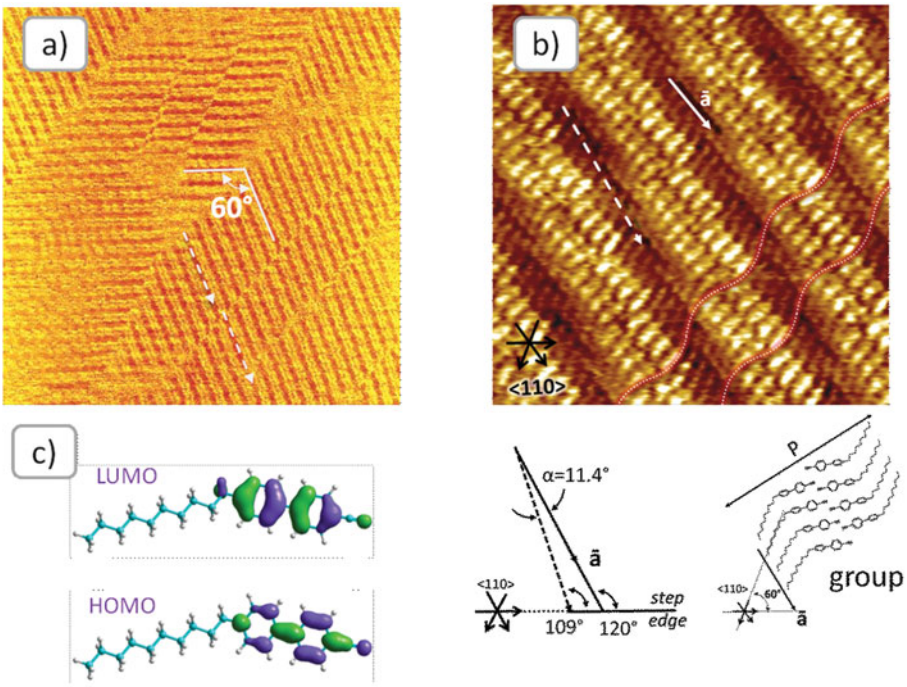


**Figure 1.** STM images of SAM of 10CB molecules on Au(111) surface in **a)** large scale (200×200 nm$^2$) and **b)** small scale (16.8×16.8 nm$^2$), with the graphic explanation of the appearance of angle $\alpha$. Dotted wavy lines denote the boundary between 4–to–4 and 5–to–5 arranged molecules. The STM parameters are $I_t = 2$ pA, $U_t = 280$ mV. Part **c)** represents the DFT/B3LYP/6-31G* calculated profiles of LUMO and HOMO levels of 10CB with energies –1.6 and –6.3 eV, correspondingly.



packing with 10 molecules (marked by a dotted envelope in Fig. 1b). It is clearly seen that each group of a molecule is slightly shifted with respect to its neighbor. In consequence, this shift forms a specific row structure of the domains observed on the large scale (marked by a dashed arrow). If we consider, for example, vector $\bar{\mathbf{a}}$ as the axis of the 10CB groups, which is parallel to the group border (Fig. 1b), its tilt angle $\alpha$ with respect to the row direction is equal to 11.4° ± 2.3°. With respect to the measured angle of 109° between rows and the step edge, we may deduce that the angle between axis $\bar{\boldsymbol{a}}$ and the step edge is equal to 60° (Fig. 1b). This means that axis $\bar{\boldsymbol{a}}$ runs along <110>, the main crystallographic direction of Au(111). These observations allowed us to define the main crystallographic directions of the underlying substrate.

The lateral repeated distances along <110> between the biphenyl rings (heads) and the alkyl chains of molecules within the molecular group were quantified from cross-sections and are equal to 7.34 ± 1 Å and to 5.86 ± 0.41 Å, respectively. In fact, the heads of neighboring molecules are separated by a distance which is not multiple to interatomic distance $T_{Au}$ ($T_{Au} = 2.88$Å) of Au(111) along <110>. Meanwhile, the separation between the terminal groups of the alkyl chains of molecules was found to be close to the value of 5.76Å or to $2{\cdot}T_{Au}$. The value of the period $\boldsymbol{P}$ along <112> is equal to 49.8 ± 2Å or $10{\cdot}T_{Au}\sqrt{3}$, revealing the commensuration of 10CB molecules on Au(111). Moreover, the

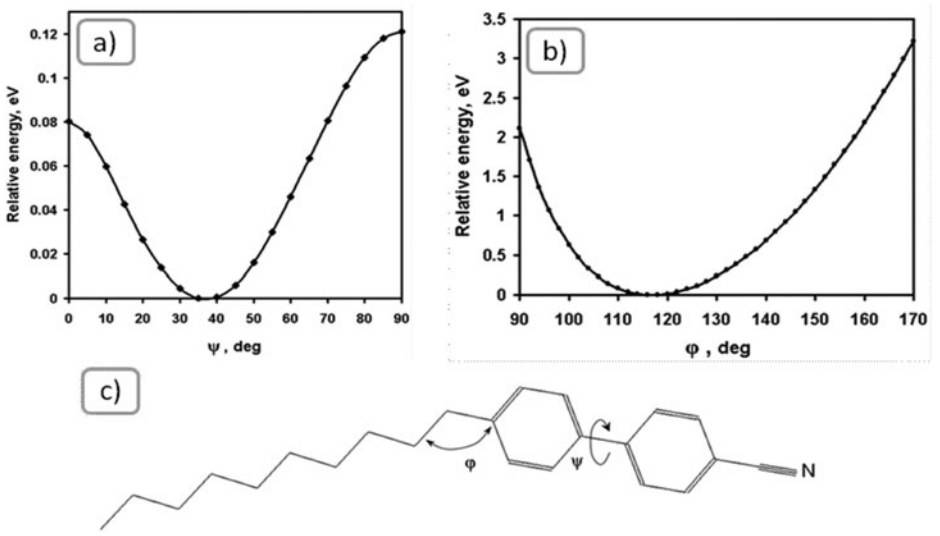


**Figure 2.** Energy profiles of conformational changes for 10CB calculated at DFT level: **a)** potential for a single phenyl rotation related to the torsion angle $\psi$ and **b)** bending potential related to the angle $\phi$ (lowest energy structure assigned as being at 0 eV). Part **c)** represents a structure of 10CB molecule with definition of the torsion, $\psi$, and bending, $\phi$, angles.

value of the shift of a molecular group with respect to the neighboring one along <110> was found to be equal to $2 \cdot T_{Au}$.

In order to understand the nature of molecular ordering, the simplified model of 10CB packing on Au(111) was proposed. Note that the structure of 10CB molecule was not considered as a rigid one. DFT calculations reveal that the geometry of a molecule in vacuum can be changed under a minor variation of the full energy of the molecule (Fig. 2a). The potential for a single phenyl rotation related to the angle $\psi$ and the bending energy as a function of the plane angle $\phi$ for 10CB molecule (Fig. 2b) are calculated and compared with earlier obtained results for isolated biphenyl 4-cyanobiphenyl molecules to elucidate the steric effect of an alkyl chain and phenyl rings. The rotational biphenyl barriers (Fig. 2a) for 10CB found to be 0.080 eV at 0° angle (plane conformation) and 0.121 eV at 90° are generally consistent with the results of other *ab initio* calculations and experiments reported for isolated biphenyl and 4-cyanobiphenyl molecules [8,9].

The DFT results indicate that the most stable conformation of an isolated 10CB molecule is realized at the torsion angle $\psi = 37°$ and the bending angle $\phi = 117°$ (Fig. 2b). The relatively small deviations from this configuration produce only minor changes in the electronic properties (shapes and energies of frontier molecular orbitals) of the molecule. Due to the relatively small value of 10CB biphenyl rotational barrier, the molecule-substrate interaction is an origin of the conformational adaptation and can easily drive the phenyl rotation providing a nearly flat 10CB configuration on the gold substrate. In contrast, the bending potentials are characterized by relatively high values, thus a change of the bending angle $\phi$ is expected to be less sensitive to the influence of the substrate, and the molecules adapt their positions in the potential relief of a substrate with minor changes of the angle $\phi$. These experimental and theoretical findings were taken into account in the proposed model in Fig. 3a, which represents the packing of 10CB molecules with the 4-to-4 arrangement, since 5-to-5 on Au(111) was considered as less favorable.

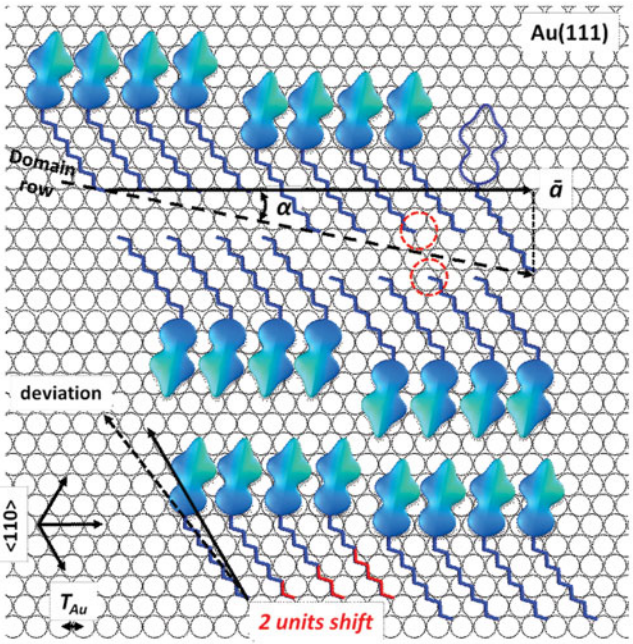


**Figure 3.** Proposed model of arrangement of 10CB on Au(111) surface. The model represents the 4-to-4 molecular alignment. The angle $\alpha$ between domain row and axis $\bar{\mathbf{a}}$ is measured from the relation $\tan(\alpha) = (2 \cdot T_{Au} \cdot \sqrt{3})/(18 \cdot T_{Au}) = \sqrt{3}/9$ and equal to 10.9°. Non-equivalent positions of the ends of terminal groups of alkyl chains are depicted by red dashed circles.

In the proposed model, 10CB molecules are oriented so that the alkyl chains backbones have slight deviation from the strict following to <110>. This effect has to be expected because a deviation appears when the interaction between an alkyl chain and gold is relatively weak. For the normal alkanes, this appears when a carbon chain becomes shorter resulting in the formation of a small angle between alkane backbones and <110> crystallographic direction on Au(111) [10]. The observed shift by 2 units of methylenes of the neighboring alkyl chain of 10CB within the group along <110> (marked by red colour) is recognized also as the packing of *n*-alkanes on Au(111) [11]. The shift for the *n*-alkanes appears due to a strong intermolecular interaction, which is responsible for the formation of a tilted lamella-like structure on Au(111) (Fig. 3b). According to the proposed model and the measured distances, the positions of the ends of terminal groups of alkyl chains of neighboring molecules (marked by doted circles) are not equivalent on the Au(111) surface. This is supported by the observation of various STM contrasts of terminal groups of alkyl chains (Fig. 3c) under the same STM parameters and related to the different channels of electron tunnelling [12]. The reason for such behavior is not clear so far, but could be deal with a tendency of molecules to form as much as possible densely packed self-assembled monolayers, since the equivalent positions of terminal groups require more space for the alignment making a monolayer less dense.

Thus, we conclude that the alkyl chains of 10CB have inclination toward <110> crystallographic direction, and the nature of the 10CB alignment on Au(111) is mainly encouraged by the substrate-alkyl chain and chain-chain interactions. The similar conclusions have been previously formulated for HOPG and $MoS_2$ [4,6]. However, the most crucial

difference between the packings of 10CB molecules on Au(111) and those substrates consists in the coexistence of two types of molecular packing on Au(111), namely 4-to-4 and 5-to-5. To the best of our knowledge, the self-assembled monolayers of 10CB on HOPG and $MoS_2$ contain exclusively the 5-to-5 packing. Such difference in the packing on different substrates might be explained by a more weak intermolecular interaction on Au(111). However, in the case of Au(111), the molecules are more densely packed than those on $MoS_2$ appealing to the existence of a specific repulsion force between the biphenyl rings of molecules on Au(111). But this argument does not make sense taking into account that, on a HOPG surface with 5-to-5 packing, the distances between molecules smaller than those on Au(111). Another reason can be related to a mismatch of the required local energy minima position for biphenyl rings for the fifth molecule on the surface of Au(111) with the potential relief. As a result, the attraction between neighboring alkyl chains and the surface is insufficient to keep the molecule in the position of the fifth molecule on a gold surface in contrast to HOPG and $MoS_2$ surfaces. Finally, this pushes the molecule to slide down the alkyl chain direction (<110>) and to start the formation of 4-to-4 molecular packing. Obviously, these arguments partially explain the formation of a self-assembled monolayer on Au(111), since the 5-to-5 molecular packing rarely but also present.

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