

Role of Lateral Alkyl Chains in Modulation of Molecular Structures on Metal Surfaces

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We use low energy electron diffraction, scanning tunneling microscopy, first-principles density-functional theory, and molecular mechanics calculations to analyze the adsorption and growth of quinacridone derivatives (QA) with alkyl chains of 4 and 16 carbon atoms on a Ag(110) substrate. Surprisingly, we find that the alkyl chains determine the orientation of the molecular overlayers. While the interaction of QA and the Ag substrate is primarily due to chemical bonding of oxygen to the silver substrate, determining the molecular orientation and preferred adsorption site, the intermolecular arrangement can be adjusted via the length of alkyl chains. We are thus able to fabricate uniform QA films with very well controlled physical properties.

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In recent years, the structure and growth of functional molecular thin films have been widely investigated due to their potential application for molecular devices [1–4]. However, understanding the interactions between organic molecules and noble metal substrates is not straightforward and has proven to be rather challenging [1–5]. In this respect, the ability to control the structure of molecular thin films provides a method of tuning the functional properties in a discrete manner. Previous work demonstrated that linear aromatic hydrocarbons attach to a silver substrate via interactions of the lowest unoccupied molecular orbital (LUMO) and silver $4d$ orbitals [6]. The match of the LUMO and the silver $4d$ orbitals also dominates the structural properties of the ensuing molecular film. Subsequent work concerned the lateral functional groups interacting with silver substrates, such as CN and CO groups in DMe-DCNQI and PTCDA [7]. The work suggested that the adsorbate-substrate geometry of large aromatic molecules on noble metal surfaces can be precisely controlled by functional groups of the molecule. However, the intermolecular geometry is less well researched due to lack of experimental data. Correspondingly, the understanding of intermolecular interaction is still somewhat shallow.

For example, quinacridone and its derivatives (QA) are well-known chemically stable pigments. They display excellent photovoltaic and photoconductive properties [8–10]. The performance of organic light emitting devices based on QA have been widely investigated [11–14]. The QA molecular structure can be varied by the substitution of C atoms by N and O. QA can also be modified by attaching lateral alkyl chains to N heteroatoms and by the formation of QAnC, as shown in Fig. 1(a), where n denotes the number of carbon atoms in each alkyl chain. Accordingly, the photoelectric or electrical property can be adjusted by structural alterations of the molecule. It is quite

possible that the lateral alkyl chains act as spacers and modulate the intermolecular distance. In this case the energy transfer between QAnC functional units is modified by noncovalent interactions between molecules, which are tuned by the length of their alkyl chains. Then light and electron transmission can be chemically controlled [15].

Previous work showed the assembly of long-chain molecules including QAnC on solid-liquid interfaces and a highly oriented pyrolytic graphite surface [12,13,15,16], in which the molecule-substrate interaction is normally the non-site-specific pi-pi interactions and the structures were arranged by relative weak intermolecular interactions at solid-liquid interface. However, from the viewpoint of modeling the growth, noble metal substrates are much more attractive and versatile. On these substrates the role of relatively short lateral alkyl chains is still not properly understood. In particular, the suitability of lateral alkyl

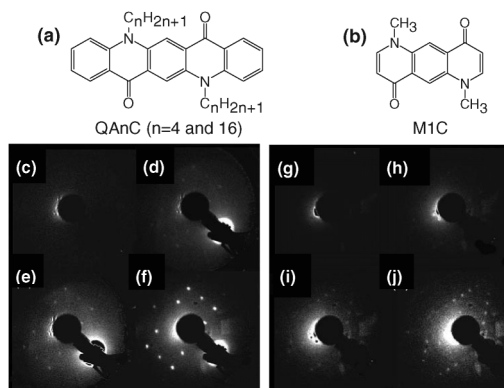


FIG. 1. General formula of alkyl substituted Quinacridone (a) and their functional core (MIC) is shown in (b). LEED images of QA4C (c), (d), (e), (f) and QA16C (g), (h), (i), (j) on Ag(110) with coverage of 0.2 ML (c) and (g), 0.5 ML (d) and (h), 0.8 ML (e) and (i), and 1 ML (f) and (j).

chains as spacers for the arrangement of the molecule's functional core is still untested.

In this Letter, we investigate the role of the alkyl chain in the modulation of the QAnC molecular structure on Ag(110) substrates. *In situ* molecular-beam epitaxy and low-energy-electron diffraction (MBE LEED) are used to examine the adsorption of QAnC molecules with alkyl chains of 4 and 16 carbon atoms, respectively. First-principles density-functional theory (DFT) and molecular mechanics (MM) calculations are employed to evaluate the preferred adsorption sites of QAnC molecules on Ag(110) and their behavior due to different alkyl chains. The simulations reveal the details of molecule-substrate interaction and elucidate the role the length of the alkyl chains plays in the molecular assembly. Subsequently, the theoretical results are validated by scanning tunneling microscopy (STM) observations of QAnC on Ag(110), where we obtain excellent agreement between theory and experiment.

The LEED experiments of both molecules and the STM scans of QA4C molecules on Ag(110) were performed in a combined UHV MBE-STM system [17], while the experiments on QA16C molecule were conducted in an Omicron low temperature STM-MBE (LTSTM-MBE) system. The sample was prepared by standard UHV techniques [18–21].

Figures 1(c)–1(f) shows a series of LEED patterns of QA4C molecules on Ag(110). All LEED measurements were taken with electron beam energy of 13 eV. Increasing the molecular coverage, we observe a change of the LEED pattern. As shown in Fig. 1(c) the LEED pattern initially resembles a diffuse halo with a rough coverage of 0.2 monolayer (ML). At higher coverage of 0.5 ML, the pattern changes to diffused spots [Fig. 1(d)]. Increasing the coverage up to 0.8 ML drastically increases the sharpness of individual spots, as shown in Fig. 1(e). The sharpness indicates a well-ordered structure of the molecular interface. A complete monolayer and its corresponding diffraction pattern are shown in Fig. 1(f). The diffraction patterns indicate that the molecules on the substrate act like a two dimensional gas (diffuse halo), a fluid (diffuse spots), and a periodic crystal (sharp spots). Similar three-state transitions were also observed in the adsorption of organic π -conjugated molecules on a Ag(110) substrate [20,21]. The final ordered QA4C superstructure on Ag(110) in Fig. 1(f) can be described in matrix notation by [22]

$$\text{QA4C} = \begin{pmatrix} 6 & 0 \\ 0 & 4 \end{pmatrix} \text{Ag}(110);$$

i.e., the vector of QA4C adsorbate is $a_1 = 6a = 17.337 \text{ \AA}$, $b_1 = 4b = 16.345 \text{ \AA}$, and the angle of rotation $\gamma_1 = 90^\circ$.

Similar to the LEED patterns of QA4C, four LEED patterns of QA16C on the same substrate with coverages of 0.2, 0.5, 0.8, and 1 ML are shown in Figs. 1(g)–1(j). They also reveal successive changes of the LEED pattern with increasing molecular coverage. From the geometrical analysis of the LEED pattern in Fig. 1(h) we find that the

QA16C structure on Ag(110) is described by the matrix

$$\begin{pmatrix} 3 & -1 \\ 5 & 6 \end{pmatrix};$$

i.e., the vector is $a_2 = 3a - b = 9.583 \text{ \AA}$, $b_2 = 5a + 6b = 28.458 \text{ \AA}$, and the angle of rotation $\gamma_2 = 84.7^\circ$.

The LEED analysis of the ordered molecular structures of QA4C and QA16C proves that the symmetry of QA16C molecules in an ordered structure differs from that of QA4C. It provides the first indication that the alkyl chains themselves influence the arrangement of QAnC on the substrate. However, the effect of the alkyl chains is somewhat more complex than simply changing the distance between neighboring QAnC molecules. In order to determine the changes due to the change of the alkyl chain length and to understand interactions and bond formation between molecules and the substrate, we simulated the adsorption by DFT calculations [23] combined with MM simulations [20] for larger molecular arrays.

Previously we have shown that oxygen atoms, rather than hydrocarbons, provide the functional centers for the adsorption of organic compounds on a Ag substrate [7]. In our present simulations we have therefore simplified the QA4C and QA16C molecules to their active backbone denoted as MIC [27] [see Figs. 1(a) and 1(b)]. The following first-principles simulations are thus primarily concerned with the interaction of MIC with Ag(110). A large 6×4 supercell of Ag(110) is used to reduce intermolecular interaction. MIC is adsorbed on one side of the slab. We found six stable molecular orientations in the calculations, denoted as Ori-1 to Ori-6, which are shown in Fig. 2(a). In these configurations two oxygen atoms of the molecule are on top of two silver atoms. The details of the simulation method are described in Ref. [28].

Figure 2(a) also indicates the adsorption energy for each possible orientation. The adsorption energy of about 1.5 eV strongly suggests chemical bonding between the oxygen and substrate Ag atoms. By comparing these adsorption energies we found the most possible adsorption structure; it

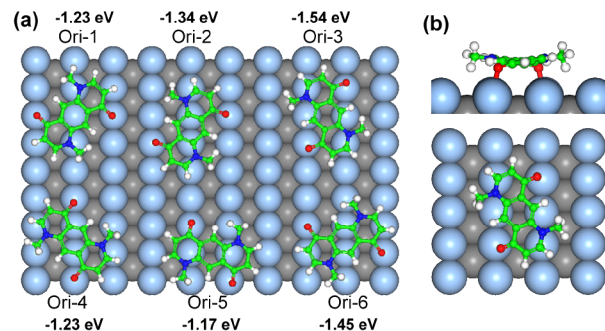


FIG. 2 (color online). First-principles calculations of the possible orientations of the functional core on Ag(110) substrate. (a) Initial configurations of the functional core on Ag(110), in which two oxygen atoms of the molecule are at the top Ag surface atoms. These orientations are denoted as Ori-1 to Ori-6. (b) Fully relaxed structure originates from orientation Ori-3.

is the optimized structure from Ori-3 [29]. The fully relaxed structure of Ori-3 is shown in Fig. 2(b). As expected, oxygen atoms are chemically bound to the substrate Ag atoms, resulting in a slight distortion of the molecular backbones. But while DFT calculations and LEED analysis allow us to determine the geometry of the molecular backbone on Ag(110), they do not contain information about the lateral alkyl chains. In addition, the underlying mechanism, how the lateral alkyl chains actually influence the structure of self-assembled molecular thin films, remains ambiguous. Therefore, MM calculations were employed to identify the structure of alkyl chains and to understand their influence on the structure of the adsorbed molecule.

The MM+ force field was used to calculate the impact of the molecular chain length on the structure of the molecular monolayer and its orientation on the substrate [20]. The initial geometry of the molecular backbone was determined by DFT simulations (Ori-3, as shown in Fig. 2). As a first step, we simulated an isolated QAnC molecule in the vacuum. The length of the alkyl chain was varied from 4, to 8, to 12, and finally to 16. The optimized structures reveal that short alkyl chains are tilted with respect to the molecular plane, while longer chains remain parallel to the molecular plane. The black line in Fig. 3(a) describes the evolution of the angle between two alkyl chains with increasing chain length. The angle increases from about 0° ($n = 4$) to 108° ($n = 16$). Adding two, four, and six layers of the Ag(110) substrate, the evolution of the tilt angles converges, as shown in Fig. 3(a). To find a transition between $n = 4$ and $n = 8$, we simulated an additional system of $n = 6$. Including six layers of the substrate, we found an angle of 36° ($n = 4$), 150° ($n = 6$), and 180° ($n = 8$). An increase of n beyond eight does not change the angle. The critical number ($n = 8$) to obtain an angle of 180° is consistent with other experimental observations [30].

The theoretically predicted structures of QAnC with 4, 6, 8, 12, and 16 carbon alkyl chains on the Ag(110) substrate are shown in Fig. 3(b). These results indicate that the interaction between alkyl chains and the Ag substrate is attractive and tends to orient the chains parallel to the substrate surface. Identical calculations of QAnC molecules on six substrate layers were also performed for other orientations of the molecule. They show that the role of different alkyl chains is independent of the orientation. In addition, the result was tested by calculating the adsorption of a larger fragment of the molecule, including two four-carbon alkyl chains [M4C, see Fig. 3(c)], with DFT. Its backbone is oriented in the Ori-3 configuration; the adsorption geometry is shown in Fig. 3(d).

Comparing the geometries obtained by DFT (M4C) and MM (QA4C), we obtain the consistent result that the four-carbon alkyl chains are tilted. The combination of DFT and MM calculations allows us to determine the geometries of QA4C and QA16C molecular overlayers on Ag(110), as shown in Figs. 4(a) and 4(b). Large scale and high resolution experimental STM images of the QA4C on Ag(110)

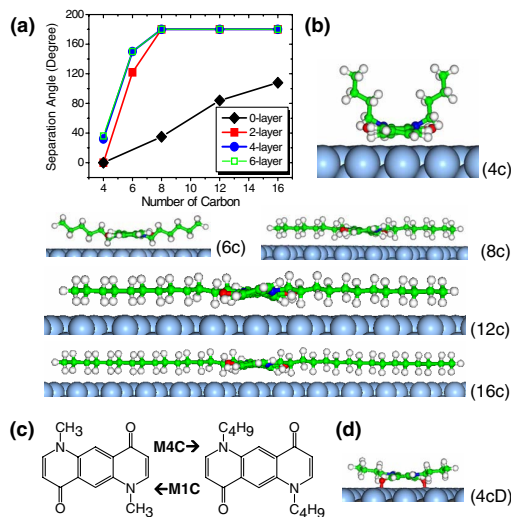


FIG. 3 (color online). Arrangement of QAnC with varying length of alkyl chains. (a) MM calculations of the angle between two alkyl chains with increasing number of carbon atoms. The graphs denote isolated QAnC molecules, with two, four, and six substrate layers of Ag(110). (b) Predicted MM structures of QAnC with different alkyl chains on six layers of Ag(110). The chain length is varied from $n = 4$ to $n = 6, 8, 12,$ and 16 , as labeled. (c) Structure comparison of M1C and M4C. (d) Relaxed structure of M4C with the backbone in orientation of Ori-3 obtained by DFT simulations.

are shown in Fig. 4(c) right inset. STM images were simulated by constant density contours with a sample bias voltage of 1.3 V, shown in Fig. 4(c) left inset, which is in excellent agreement with our experimental result [31]. The STM image of the molecule is mainly due to the density of the LUMO of, e.g., the QA4C molecule. We have inserted a constant density contour of the LUMO in Fig. 4(c) right inset and find that it fits experimental STM results very well. The agreement strongly supports our calculation method and justifies the simplification of the QAnC to its M1C functional core. It also indicates that the present treatment, e.g., simplification, of QAnC should be useful in a wide variety of large aromatic molecules. The STM image and an inserted structure model of QA16C are shown in Fig. 4(d). The alkyl chains can be observed and overall features of the image are consistent with the prediction as shown in Fig. 4(b). The lattice parameters of calculated values are $a_2 = 9.77 \text{ \AA}$, $b_2 = 29.03 \text{ \AA}$, $\gamma = 84.7^\circ$, and the STM observed values are $a_2 = 10.1 \text{ \AA}$, $b_2 = 29.9 \text{ \AA}$, $\gamma = 82.3^\circ$. All sets of lattice parameters are in an error less than 5%.

In summary, the adsorption of Quinacridone derivatives with 4 and 16 alkyl chains on a Ag(110) substrate was investigated by *in situ* MBE LEED, STM, first-principles calculations, and molecular mechanics simulations. The interaction of QAnC and the Ag substrate is primarily due to the chemical bonds between oxygen and silver. The spatial match or mismatch of the O atoms of the molecules with the underlying Ag substrate may determine

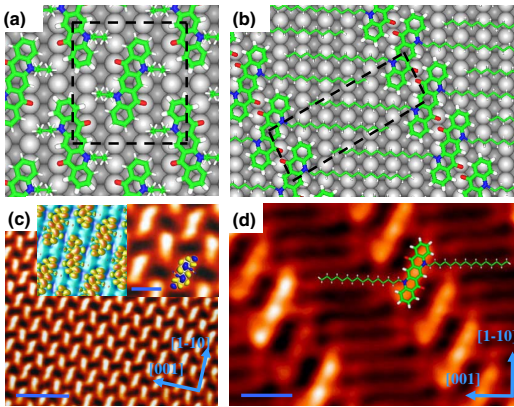


FIG. 4 (color online). Comparison of simulated and experimental STM images. (a) and (b) Predicted geometry of QA4C and QA16C monolayers on Ag(110). (c) Large scale STM image of QA4C. High resolution experimental scans [right inset in (c)] in good agreement with simulations [left inset in (c)]. Tunneling current in (c): 0.25 nA, bias voltage on sample: 1.3 V and scale bar: 1 nm for (c) left inset and 5 nm for (c). The inset in the right inset of (c) is the LUMO of the QA4C molecule. (d) STM image of QA16C at 77 K which precisely fits the predictions in (b). The tunneling current is 0.04 nA and 0.8 V for sample bias. The scale bar is 1 nm.

the orientation and adsorption sites of the molecular backbones. It is therefore, in essence, determined by geometrical constraints. The lateral alkyl chains are perpendicular to the substrate plane when the number of carbon atoms is less than six. In this case, the ordered structure of the self-assembled molecular monolayer is unaffected by the alkyl chains. However, longer lateral chains tend to be parallel to the molecular plane due to the interaction between QAnC molecules and the substrate. This feature then determines the actual distance between and the orientation of the molecules. It means that QAnC molecules can be arranged in a wide variety of distances and arrangements, depending only on the length of the alkyl chains. Taking into account the role of lateral alkyl chains found in the work, the distance between the large aromatic molecules on metal surfaces could be controlled in a discrete manner, which is helpful for designing molecular nanostructures and their applications in molecular devices. Fully controlling the molecular nanostructures on metals can be realized by further understanding of the interaction between the metal substrate and bare hydrocarbons [6] or oxygen/nitrogen of their derivatives [7].

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- [23] Our first-principles calculations were carried out using DFT, the Perdew-Wang generalized gradient approximation for the exchange-correlation energy [24], projector augmented waves [25], and a plane wave basis set as implemented in the Vienna *ab initio* simulation package (VASP) [26].
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- [27] According to our calculations, the oxygen atoms in both QA1C and MIC prefer to interact with substrate Ag atoms and the backbone of each molecule in a fully relaxed structure is quite similar. The molecular orientation and favorable adsorption site of QA4C and QA16C are primarily determined by the interaction of molecular oxygen atoms and substrate Ag atoms. This simplification is further supported by corresponding STM experiments and simulations.
- [28] See EPAPS Document No. E-PRLTAO-96-014625 for the details of the simulations. For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.
- [29] We have also tried other initial structures, for example, the two O atoms in a bridge site or hollow site of the substrate. These initial configurations lead to states with higher total energy than the relaxed structures presented.
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- [31] The lattice parameters of calculated values are $a_1 = 14.68 \text{ \AA}$, $b_1 = 16.67 \text{ \AA}$, $\gamma = 90^\circ$, and the STM observed values are $a_2 = 18.0 \text{ \AA}$, $b_2 = 16.5 \text{ \AA}$, $\gamma = 91.9^\circ$. All sets of lattice parameters are in an error less than 4%.