



# Two polymorphic forms of 10,12-pentacosadiyn-1-ol molecular layers on graphite transferred from an aqueous surface



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## ABSTRACT

Molecular layers of the diacetylene (DA) 10,12-pentacosadiyn-1-ol (PCDYol) were transferred from an aqueous surface onto a highly oriented pyrolytic graphite (HOPG) substrate. Two polymorphic forms, having herringbone and parallel molecular arrangements, were observed by scanning tunneling microscopy (STM) in air. In contrast to DA molecules having the COOH end group, where only the parallel arrangement is realized, the herringbone and parallel polymorphic forms arise from the flexibility of hydrogen bonds between the OH end groups of PCDYol, as observed for alkanols. The area ratio for these arrangements on the HOPG surface depended on the density of the molecules on the water surface and the sample preparation temperature. By one-dimensional (1D) contrast modulation (moiré pattern), the point-on-line coincidence between the lattice points of the PCDYol layers and the HOPG surface was determined for the herringbone and parallel arrangements. Because it promotes stability of the alkane, the epitaxy is primarily controlled by the coincidence of the molecular zigzag skeleton in the parallel arrangement with the benzenoid rings of graphite. In contrast, the herringbone arrangement was lacking in this coincidence with the graphite structure. Therefore, as is evident from the fluctuation of the orientation of molecular arrays (lamella axes), the herringbone arrangement is relatively unstable on the HOPG substrate. Consequently, we conclude that the herringbone arrangement is quasi-stable while the parallel arrangement is stable.

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## 1. Introduction

Hydrogen bonding has been widely exploited for surface patterning because of its high degree of directionality [1,2]. In particular, the COOH group forms a robust hydrogen bond with other COOH groups where the hydroxyl group acts as a donor and the carbonyl oxygen acts as an acceptor [3–8]. Some research groups have reported that the COOH-terminated chain of diacetylene (DA) molecules ( $C_nH_{2n+1}-C\equiv C-C\equiv C-C_mH_{2m}COOH$ ) is oriented perpendicular to the lamella direction on highly oriented pyrolytic graphite (HOPG) substrates. This satisfies the optimal bond angle of  $180^\circ$  for the hydrogen bond formed by the COOH groups, while no other polymorphs are observed [9–15]. For alkanol layers on an HOPG substrate, the molecules sometimes exhibit multiple polymorphic arrangements because the directionality of hydrogen bonds between OH groups is more flexible than that between COOH groups. In particular, their molecular axes form obtuse angles with each other across the O···HO hydrogen bond formed at the edge of the chains [16–19]. However, alkanols sometimes exhibit different molecular orientations and their molecular axes form an angle of  $180^\circ$  with each other [20–22]. Therefore, we hypothesize that multiple polymorphic forms of DA chains come from the replacement of COOH groups with OH groups at chain edges.

In this work, 10,12-pentacosadiyn-1-ol (PCDYol,  $C_{12}H_{25}-C\equiv C-C\equiv C-C_9H_{18}OH$ , Fig. 1) molecules were transferred from a water surface to an HOPG surface to prepare self-assembled layers. The advantage of this technique is that the density of molecules per unit area of water surface can be controlled by the volume of the solution droplets containing the target molecules. Furthermore, the uniform self-assembled layers were formed on the substrate (3D fine crystals were not observed on the substrate). The solution-casting technique where the solution drops are placed directly onto a substrate surface is one of the most common and convenient means to obtain self-assembled layers [4,12,23–25]. However, this technique was not used here because regional inhomogeneity may result because of the concentration gradient that is formed by the gradual evaporation of solvent. This leads to either 3D fine crystals or no ordering of the PCDYol molecules on the substrate surface. Using scanning tunneling microscopy (STM), we show that two polymorphic arrangements, herringbone (i.e., where molecular axes form a  $130^\circ$  angle) and parallel (i.e., where molecular axes are oriented parallel to each other), are observed in the PCDYol molecular layers.

## 2. Materials and methods

STM images were acquired with a Nanoscope IIIa SPM (Digital Instruments, Santa Barbara, CA, USA), and mechanically cut Pt/Ir tips (90/10). PCDYol (Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used without further purification. To prepare self-assembled

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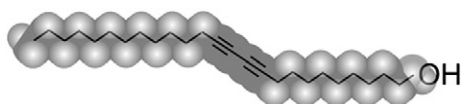


Fig. 1. Molecular structure of PCDYol.

PCDYol layers, the molecules were dissolved in chloroform at a concentration of 0.1 mg/mL and drops (5 or 50  $\mu\text{L}$ ) were placed onto a purified water surface in a Petri dish about 27 mm within the inner diameter. After the chloroform evaporated, the thin film of molecules was transferred from the water surface to a freshly cleaved (0001) surface of HOPG (Advanced Ceramics Co., grade ZYH) by “nearly” horizontal dipping (detaching a part of the thin film from water interface by bringing the horizontally oriented substrate in contact with the film from the air side). The temperature was maintained at 20 or 30  $^{\circ}\text{C}$ . All the STM images were recorded in constant-current mode in air at 25  $^{\circ}\text{C}$ . Specific tunneling conditions are given in the figure captions. To determine the deposition condition of the PCDYol on the graphite, a surface pressure–area isotherm of the PCDYol on the water surface was obtained by using a commercial Langmuir–Blodgett deposition trough (KSV 2000, KSV, Finland) at 21  $^{\circ}\text{C}$ .

### 3. Results

Fig. 2(a) shows an STM image of two adjacent domains in a PCDYol self-assembled layer on the HOPG (0001) surface; individual molecules are well resolved within each domain. This was obtained by dropping 50  $\mu\text{L}$  of chloroform solution onto a water surface (0.069  $\text{nm}^2$  per molecule; a denser condition) at 20  $^{\circ}\text{C}$ . The molecules exhibited the herringbone arrangement in the domain that covers the left and bottom sides of the image. In contrast, a parallel arrangement appears in the domain at the upper right of Fig. 2(a). The area ratio of the herringbone was 0.5 against the total area of the molecular layers (parallel 0.5). By increasing the molecular mean area on the water surface to 0.69  $\text{nm}^2$  (less dense condition) at 20 or 30  $^{\circ}\text{C}$ , only the parallel arrangement was observed. By keeping the molecular mean area at 0.069  $\text{nm}^2$  and increasing the preparation temperature to 30  $^{\circ}\text{C}$ , the ratio of the herringbone arrangement decreased to 0.3 (parallel 0.7), as summarized in Table 1.

A high-resolution image of the herringbone arrangement is shown in Fig. 3(a). By increasing the tunneling current, we observed atomic images of the HOPG surface underneath the PCDYol layers. The PCDYol images were corrected for distortion due to drift by using the underlying HOPG images as a reference. On the basis of the relationship between the PCDYol lattice parameters and those of HOPG obtained from a pair of STM images, we derived the herringbone adsorption model shown in Fig. 3(b). The highly ordered lamellae of the PCDYol molecules on the surface are clearly shown. The DA moieties are brighter in the STM image than the alkyl chains because triple bonds contribute substantially to the HOMO or LUMO near the Fermi level. The black arrows in Fig. 3(a) indicate this effect. Alkyl sidechains are observed as fine linear contrasts on both sides of the triple bonds. Each overall fine contrast has a substantial overlap with the shape of the extended single molecule, suggesting that the PCDYol chains are lying flat on the HOPG surface along with the other DA chains [9–15]. In particular, the chains exhibited a feather-like pattern along the lamella and their molecular axes form a 130 $^{\circ}$  angle between the adjacent molecules across the OH groups. In a few cases, stacking defects of the lamellae were observed in the reverse direction as indicated by the black arrows in Fig. 2(a). Fig. 2(b) shows an STM height image centered on the domain of the herringbone arrangement from Fig. 2(a). The brightness oscillation is observed along a lamella, and white circles indicate the brightness peaks. As suggested by the white lines (each white line connects the brightness peaks of the adjacent lamellae), a one-dimensional (1D) moiré pattern emerges from the point-on-line coincidence between the lattice points of PCDYol and HOPG. This means that every point of the PCDYol is on a lattice line parallel to the  $a_g$  axis (or  $b_g$  axis) of the HOPG, decreasing the interfacial energy between PCDYol and the HOPG [26]. Two similar orientations of the 1D contrast modulation were captured in the domain.

The high-resolution image and the derived model of the parallel arrangement are shown in Fig. 3(c) and (d), respectively. The PCDYol molecules were oriented in the same direction (i.e., parallel to each other). The DA moieties are still brighter than the alkyl chains as indicated by the black and gray arrows in Fig. 3(c). Again, the overall fine contrast is almost consistent with the shape of the extended molecule lying on the HOPG surface. The brightness of particular groups in an STM image depends subtly on the interaction of the electron wave functions of both the adsorbate and the substrate. Indeed, the image of the adsorbed layer can change with the relative position along the

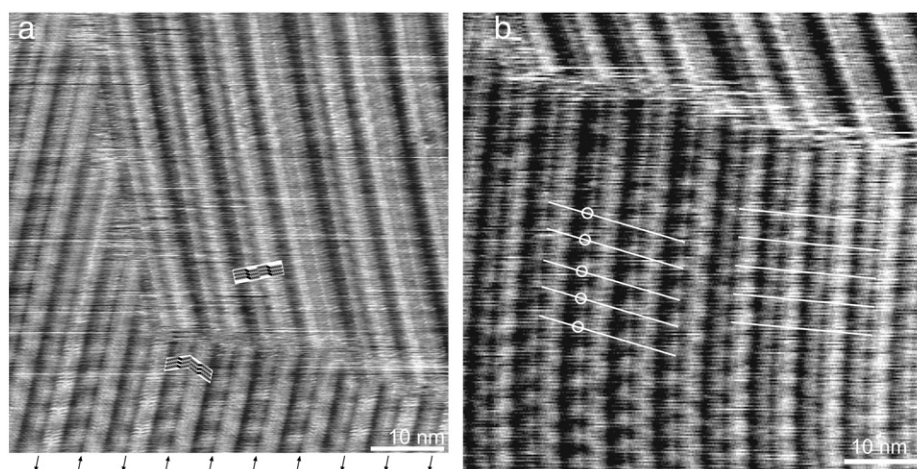


Fig. 2. (a) STM height image of the PCDYol layers on HOPG [sample bias voltage (tip grounded)  $V_s = -100$  mV and tunneling current  $I_t = 10$  pA]. When models are superimposed, the molecules exhibit a herringbone arrangement in the domain that covers the left and bottom sides of the image. The reversal of the lamella direction in the herringbone arrangement is observed as a stacking defect, as indicated by black arrows. A parallel arrangement appears in the domain at the upper right of the image. (b) STM height image centering on the domain of the herringbone arrangement from (a) [sample bias voltage (tip grounded)  $V_s = -100$  mV and tunneling current  $I_t = 10$  pA]. The brightness oscillates along a lamella due to the moiré effect between the PCDYol layers and HOPG (the brightness peaks are indicated by white circles). Each white line connecting the peaks of the brightness in the adjacent lamellae indicates the 1D moiré pattern. Two similar orientations of the 1D contrast modulation are seen in the domain.

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