Two-dimensional ordering of benzenethiol self-assembled monolayers guided by displacement of cyclohexanethiols on Au(111)†

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Although the adsorption of benzenethiols (BT) on Au(111) usually leads to the formation of disordered phases, we demonstrate here that the displacement of preadsorbed cyclohexanethiol self-assembled monolayers (SAMs) on Au(111) by BT molecules can be a successful approach to obtain two-dimensional BT SAMs with long-range ordered domains.

Tailoring the surface properties of organic ultrathin films on solid surfaces is one of the major issues that impact their practical incorporation into nanotechnology and biotechnology applications. The most promising of these systems is self-assembled monolayers (SAMs) formed by the spontaneous adsorption of organic thiols on gold, because the properties of their outer surface can be easily tuned by changing the end group of organic thiols.[1–3] Recently, SAMs of aromatic thiols have drawn much attention due to their interesting electrical and optical properties that may be applicable in molecular electronics.[4] It has been demonstrated that the electrical properties of SAM-based molecular devices are markedly influenced by changes in both functionality[5] and orientation[6] of adsorbed molecules. However, to improve device performance and obtain reliable data, the ability to reliably fabricate two-dimensional (2D) ordered SAMs of aromatic thiols is necessary. The structural ordering of aromatic thiol SAMs can be improved when a flexible alkyl spacer is introduced between the sulfur headgroups and the aromatic backbone[7–9] or when the number of aromatic rings in the molecular backbone is increased.[9,10]

To understand the adsorption structure and self-assembly of aromatic thiols on gold, SAMs of benzenethiol (BT), the simplest aromatic thiol, have been extensively characterized by means of various surface analysis techniques.[7–13] Yet, despite a number of BT studies, controversy remains regarding the 2D structural ordering[7–14] and orientation[15,16] of BT molecules on Au(111) surfaces. Scanning tunnelling microscopy (STM) imaging reveals that BT SAMs formed in ethanolic solutions are composed mainly of disordered phases with bright Au adatom islands,[7–10] whereas Silien *et al.* reported that BT can form SAMs with small ordered domains exhibiting lateral dimensions of less than 15 nm.[16] However, there have been no reports to date regarding the formation of BT SAMs with long-range, well-ordered domains. We report herein the first STM result showing well-ordered BT SAMs on Au(111) and a new methodology to fabricate 2D-ordered BT SAMs.

We assume that the large discrepancy in structural order and orientation of BT SAMs may be due to a minimal difference in the energy gained by the interactions between the phenyl group and the gold surface and by the interactions between phenyl groups. Therefore, we considered the possibility that 2D ordered BT SAMs can be formed *via* direct adsorption of BT molecules onto gold surfaces without the formation of a striped phase where the phenyl ring lies flat on the surface. Such direct adsorption can be obtained by displacing preadsorbed SAMs with target thiols in solution.[17] To obtain long-range ordered BT SAMs, complete displacement should occur in a short time such that it can be accomplished using 2D ordered SAMs with a weak lateral interaction and a lower adsorption density instead of alkanethiolate SAMs as a transient adlayer. Among potential transient layers, cyclohexanethiol (CHT) SAMs are one of the most promising because they have a 2D ordered structure with a molecular density 4 times less than that of alkanethiolate SAMs.[18] The lower molecular density of CHT SAMs is ascribed to the molecular backbone of the flexible aliphatic ring, which has both axial and equatorial conformers, the result of which gives CHT molecules a much larger molecular volume in CHT SAMs. From a preliminary STM study, we clearly demonstrated that CHT molecules on Au(111) can be fully replaced by octanethiols (OTs) within 20 min, resulting in the formation of OT SAMs. Therefore it is expected that CHT on Au(111) can also be fully replaced by BT in a short time. Scheme 1 shows the strategy for obtaining 2D ordered BT SAMs *via* the displacement of preadsorbed CHT SAMs on Au(111) by BT molecules.

CHT and BT were purchased from Tokyo Chemical Industry (Tokyo, Japan) and used without further purification. The Au(111) substrates on mica were fabricated by vacuum deposition as previously described.[18] Fully covered CHT SAMs were prepared by dipping the gold substrates in a 1 mM ethanol solution of CHT for 1 day at room temperature; the detailed molecular packing structure of CHT SAMs under such conditions has been reported previously by our group.[18] Displacement experiments were performed by immersing the preadsorbed CHT molecules into a 1 mM ethanol solution of BT for periods ranging from a few minutes to 90 min at room

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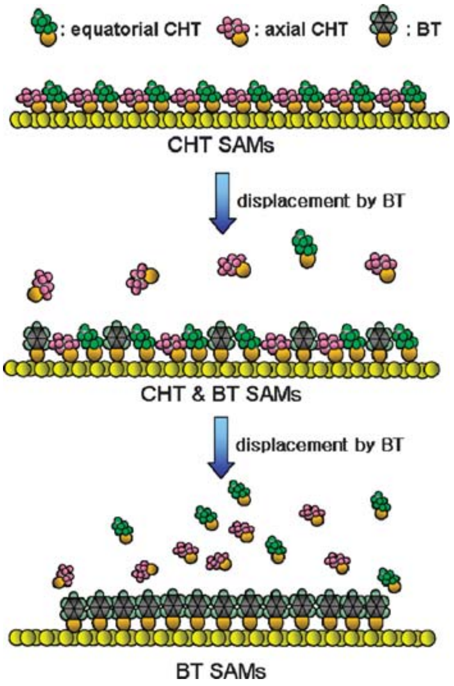

Scheme 1 Schematic view showing the formation of 2D ordered BT SAMs *via* the displacement of preadsorbed CHT SAMs on Au(111) by BT molecules.

temperature. The resulting SAM samples were then carefully rinsed with pure ethanol to remove any physisorbed molecules on the surface. STM measurements were performed with a NanoScope E (Veeco, Santa Barbara, CA, USA) using a commercially available Pt/Ir tip, and all STM images were taken under ambient conditions at room temperature using the constant current mode. The imaging conditions were as follows: bias voltage between 400 and 600 mV and tunneling current between 0.30 and 0.50 nA.

The STM images in Fig. 1 show typical structures of BT and CHT SAMs on Au(111) formed after immersion of gold substrates in 1 mM ethanol solutions of BT and CHT for 1 day at room temperature. The STM image in Fig. 1a shows the surface structures of BT SAMs containing disordered phases and Au adatom islands (bright domains), which have been revealed by numerous STM studies.[7–10] In comparison with BT SAMs, CHT SAMs have long-range ordered domains, which can be described as a $(5 \times 2\sqrt{10})R48^\circ$ structure (Fig. 1b).[18] Based on these STM results, we considered that the formation of the disordered phase of BT SAMs is markedly influenced by the relatively strong interactions between the phenyl group and gold substrate during SAM growth.

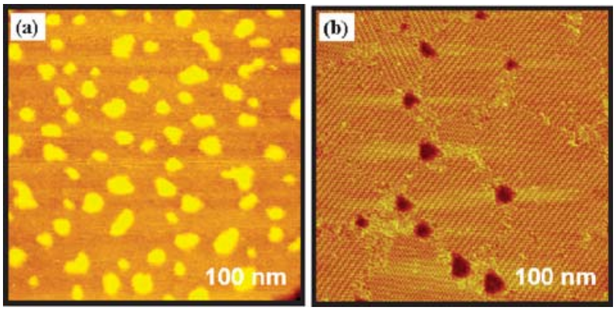

Fig. 1 STM images of (a) BT and (b) CHT SAMs on Au(111) formed after immersion of the gold substrates in a 1 mM ethanolic solution of BT and CHT for 24 h at room temperature.

To obtain BT SAMs with a high structural order, preadsorbed CHT SAMs on Au(111) were displaced by BT molecules in a 1 mM ethanolic solution of BT as a function of displacement time, according to the strategy described in Scheme 1. The STM image in Fig. 2a shows a significant structural change of CHT SAMs on Au(111), even after a displacement of only 3 min. Indeed, the well-ordered phases of CHT SAMs, as shown in Fig. 1b, were changed to significantly mixed phases containing both ordered (region A) and disordered phases (region B); the domain structure of ordered phases was the same as that of CHT SAMs. Therefore, we hypothesized that the formation of disordered phases was caused by the structural instability of SAMs due to the displacement of BT, which often appeared prior to the formation of 2D-ordered SAMs. Interestingly, after a longer displacement time of 20 min, we observed new ordered domains with a molecular row structure that was totally different from the structure observed for CHT SAMs, as shown in Fig. 2b. This result strongly suggests that the advent of ordered domains results from an increase in surface coverage of BT molecules derived from the longer displacement. We also found that the ordered BT SAMs grew directionally, not randomly, and that the distance between the molecular rows was 12.9 Å; further structural details will be discussed later. In addition, STM imaging clearly showed that there were two domains with different imaging contrasts in the ordered molecular row domains. The height difference between the two different domains was measured as 0.5 Å, which may have originated from a change in the tunneling current derived from

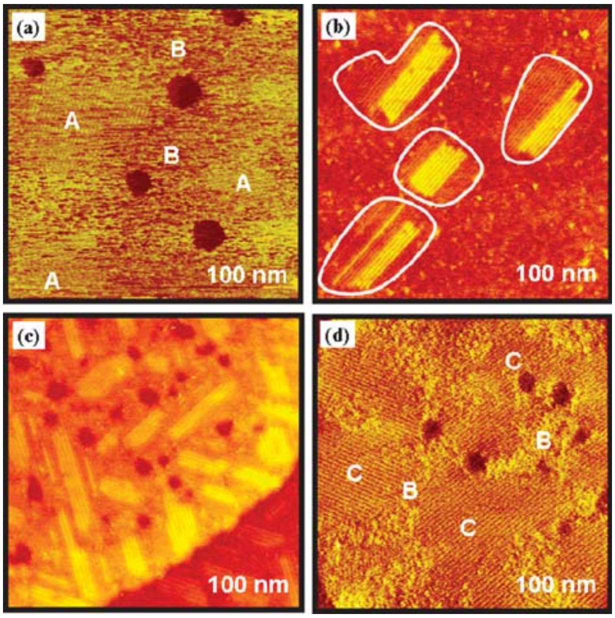

Fig. 2 STM images showing the phase transition from CHT to BT SAMs *via* the displacement of preadsorbed CHT on Au(111) by BT for (a) 3 min, (b) 20 min, (c) 60 min, and (d) 90 min.

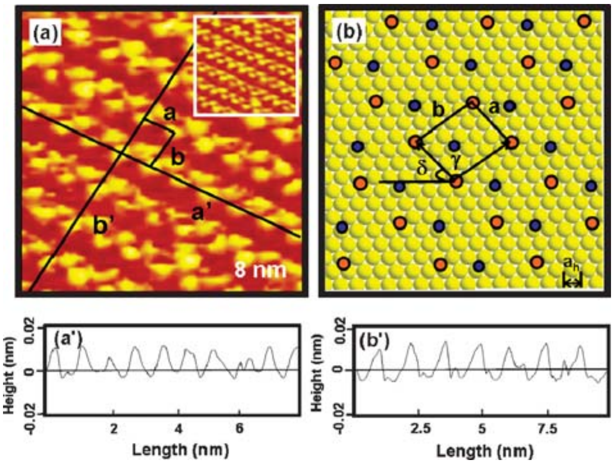

Fig. 3 (a) Molecularly resolved STM image of BT SAMs on Au(111) formed after complete displacement of CHT for 90 min. The inset shows a 2D filtered STM image. (a′ and b′) Height profiles along lines a′ and b′ on the image show the superperiodicities of the adsorbed molecules. (b) Schematic structural model of the proposed structure for BT SAMs on Au(111).

a difference in adsorption configuration of the BT molecules. After a longer displacement for 60 min, the domains with the dark rows were completely disappeared, as shown in Fig. 2c. Although we tried to observe a change in the size of domains containing the dark rows as a function of displacement time, we couldn't observe any change. Therefore we suggested that the domains with the dark rows can be considered as a metastable intermediate phase appearing prior to the formation of ordered domains with the bright rows. In addition, the ordered domains with three domain orientations increased with increasing displacement time, as shown in Fig. 2c. Finally, although disordered phases (region B) were still present near domain boundaries or vacancy islands (VIs), as with alkanethiol SAMs, long-range ordered BT SAMs (region C) with domain sizes larger than 30 nm were formed after displacement for 90 min (Fig. 2d). These results clearly demonstrate that 2D ordered BT SAMs can be successfully fabricated *via* the displacement of preadsorbed CHT SAMs on Au(111) by BT molecules.

The molecularly resolved STM image in Fig. 3a shows well-ordered 2D packing arrangements (8 nm × 8 nm) of BT SAMs on Au(111) formed after complete displacement of CHT for 90 min. The cross-sectional profiles in Fig. 3(a′) and (b′) along lines a′ and b′ corresponding to the oblique unit cell in Fig. 3(a) show the periodic molecular arrangements of BT molecules on Au(111). Based on this high-resolution STM image, we extracted the lattice constants of an oblique unit cell: a = 10.4 Å = $\sqrt{13}a_h$, b = 12.9 Å = $2\sqrt{5}a_h$, δ = 46° and γ = 81° (see Fig. 3b), where a_h = 2.89 Å denotes the interatomic distance of the Au(111) lattice. On the basis of this STM result, we proposed a schematic structural model for BT SAMs on Au(111), as shown in Fig. 3b. The molecular packing structure can be described as a $(\sqrt{13} \times 2\sqrt{5})R46^\circ$ structure, which is comparable to a $(\sqrt{13} \times \sqrt{13})R13.9^\circ$ structure containing many structural defects for BT SAMs formed in a 0.1 M $HClO_4$ solution.[11] From the model of Fig. 3b, it was assumed that all the sulfur atoms in the BT SAMs occupied bridge sites of the Au(111) lattice. After displacement of CHT (88.3 Å^2 per molecule) by BT (67.08 Å^2 per molecule), the molecular adsorption density increased, resulting that the interactions between the sulfur and gold surface can be largely increased. This can be a main driving force for the facile displacement of CHT by BT.

In conclusion, we have demonstrated that 2D-ordered BT SAMs can be successfully fabricated *via* the displacement of preadsorbed CHT SAMs on Au(111) by BT molecules. STM imaging clearly revealed that the BT SAMs contained long-range ordered domains, which could be described as having a $(\sqrt{13} \times 2\sqrt{5})R46^\circ$ structure. We also found that CHT SAMs on Au(111) can be used as an effective transient monolayer for guiding 2D SAM growth of organic molecules that can be potentially used in various technical applications.

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