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STM Observations of the Self-Assembled Monolayers of α-Aryl-α-′-Mercaptomethylthiophenes on Au(111)

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STM Observations of the Self-Assembled Monolayers of α-Aryl-α′-Mercaptomethylthiophenes on Au(111)

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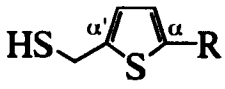
A series of α′-mercaptomethylthiophenes with substituents at the α position were synthesized. The STM images of the SAMs of the thiophene derivatives showed domain structures with constant row-to-row spacings of 14 and 15 Å for methyl and mesityl derivatives, respectively. However, the anthracenyl derivative gave different structures. These results suggest that the substitution at the α position does not have strong effect on the row-to-row spacing unless the substituent is bulkier than a mesityl group.

Keywords: self-assembled monolayers; thiophene; thiol; STM

INTRODUCTION

Self-assembled monolayers (SAMs) of alkanethiols on Au(111) have been attracting considerable interest. We have prepared the SAMs of mercaptomethylthiophenes (MTs) on Au, and observed ordered stripe patterns with an interrow spacing of 14 Å[1,2]. These results suggest that

the adsorbed MTs are arranged on Au(111) surface with an end-on configuration because the introduction of *n*-alkyl and thienyl groups at the α position did not change the period of the ordered structures. In this paper, bulkier substituents are introduced at the α position of MT. The SAMs of these derivatives have been observed using STM to investigate the effect of bulkiness at the α position on the structures of SAMs.



1 [R = Methyl (**1a**), Mesityl(**1b**), 9-Anthracenyl(**1c**)]

EXPERIMENTAL

Au(111) surfaces and the SAMs were prepared as described in the previous papers[1,2]. MT derivatives **1a** - **c** were synthesized by mercaptomethylation of the corresponding methyl- and aryl-thiophene[3]. STM images were taken using a Pt/Ir tip in constant current mode (V_b = 100~200 mV, I_t = 100~200 pA) under atmospheric conditions. The distance in the STM images was calibrated using HOPG and the error was ± 1 Å.

RESULTS AND DISCUSSION

Figure 1(a) shows the STM image of the SAM of **1a** on Au(111) with an adsorption time of 5 s, followed by a ripening time of 5 days. The ripening process was often needed before nano-ordered structures were

observed. This means that diffusion and/or relaxation of the molecules **1** on Au(111) is necessary for the formation of nano-ordered structures. The film of **1a** consists of domains having ordered structures with a row-to-row spacing of 14 ± 1 Å. This structure is essentially the same with those of other α-alkyl derivatives reported in the previous papers[1,2]. The longer adsorption times did not give ordered structures. Two molecular rows were sometimes observed in each of the 14-Å-spacing rows.

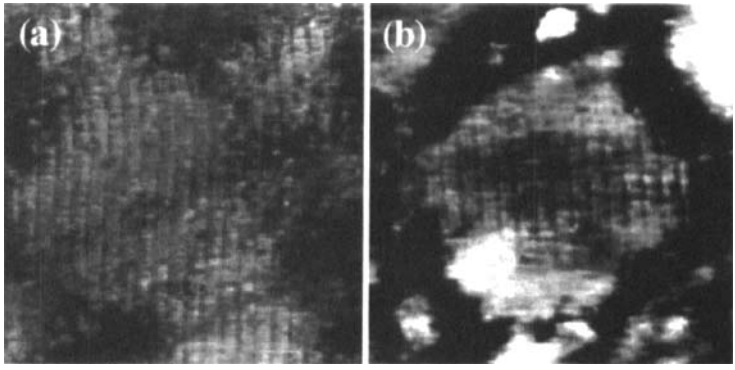


FIGURE 1. STM topographs (300 Å × 300 Å) on Au(111) of the SAMs of (a) **1a**; (b) **1b**.

Figure 1(b) shows the STM image of the SAM of **1b** on Au(111) with an adsorption time of 5 s and a ripening time of 7 days. This image is similar to the one in Figure 1(a) except that the row-to-row spacing is 15 ± 1 Å. Two molecular rows were sometimes observed in each of the 15-Å-spacing rows. It is surprising that the introduction of a mesityl group, much bulkier than a methyl group, does not change the spacing to a large extent. This suggests that the bulkiness of mesitylene

at the α position will not have strong effect on the row-to-row spacing.

No ordered structures were found for the SAMs of **1c** with an adsorption time of 5 s to 20 min except for the one with an adsorption time of 10 min and a ripening time of 2 days. In this case, we observed a stripe pattern with a row-to-row spacing of 35 ± 1 Å, which disappeared during the STM observations. Instability of the stripe structure suggests that the intermolecular interaction between molecules **1c**, *e.g.* the interaction between adjacent anthracenyl groups and/or thiophene rings is not strong. The fact that the obtained SAMs of **1c** are different from those of **1a** and **1b** suggests that the bulky anthracenyl groups do not allow the adjacent thiophene moieties to maintain the intermolecular distance appropriate for the 14-Å-spacing rows. These results show that the interrow spacing of nano-striped structures is determined by the mercaptomethylthienyl moiety unless the substituent at the α position is bulkier than a mesityl group. However, detailed molecular arrangement in the rows is not clear at present.

In summary, we have investigated the effect of bulky substituents at the α position of MT on the structures of the SAMs. The results indicate that the structures of the SAMs can be changed by the chemical modification of MT molecule.

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