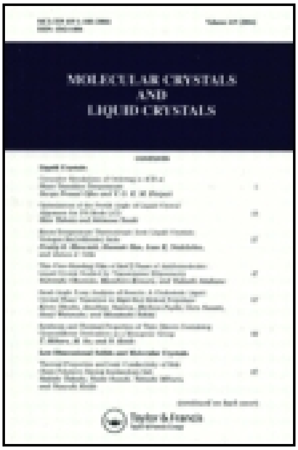

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Influence of External Stimuli on the Nano-ordered Rows and Honeycombs in Mercaptomethyloligothiophene Monolayers on Au (111)

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Nano-ordered structures, *i.e.* one-dimensional molecular rows and two-dimensional honeycombs consisting of mercaptomethylthiophene derivatives were observed on Au (111) by scanning tunneling microscopy at room temperature. It was suggested that mercaptomethylthienyl group plays a key role for the formation of the specific structures. When the samples were immersed in ethanol solution of transition metal chlorides, the nanostructures remained intact although the deposition of nanoclusters was observed in some cases. The effect of applying electric field on the nanostructures in the ethanol solution was also investigated.

Keywords: Mercaptomethyloligothiophenes; thiol/gold system; self-assembled monolayers; scanning tunneling microscopy

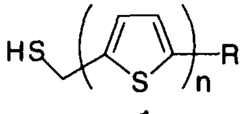
INTRODUCTION

In this decade, alkanethiol/gold systems have received increasing attention in an effort to apply the systems toward new functional materials as well as to understand fundamentally the self-assembling mechanism of the thiols.[1,2] The alkanemonothiols, which have been most widely studied, are believed to be bound to gold surfaces at thiol groups with end-on configuration, leading to the formation of self-assembled monolayers (SAMs). Among them we have recently found that mercaptomethylthiophenes form one-dimensional molecular rows with an interrow spacing of 14.0 Å and two-dimensional honeycomb structures with an interhole spacing of 11.6 Å on Au (111).[3] In this study we will report on the structural changes of the nanostructures when they are immersed in ethanol solution of transition metal chlorides, and further when the electric field is applied to the nanostructures.

EXPERIMENTAL

Single crystal Au (111) surfaces were prepared by vacuum deposition of gold on mica at 623 K with a thickness of 1000 Å followed by annealing in H_2 flame. Thiol derivatives **1** were synthesized and carefully purified by recrystallization and/or column chromatography using hexane as eluent. The SAMs were prepared by exposing the Au (111) surfaces to the vapor of thiol **1** under ambient conditions. The coverages were controlled by changing the exposing time. Next the nanostructures consisting of thiol **1** were immersed in ethanol solutions of metal ions such as dehydrated ferrous, ferric, nickel(II), and hydrated chromium(III) chloride. Electric field was applied to the sample by using a Potentiostat/Galvanostat HA-201S (Hokuto Denko, Ltd.). Scanning tunneling microscopy (STM) measurements (bias voltage 0.7 - 2.0 V, tunneling current 0.09 - 1.5 nA) were performed at room temperature under ultrahigh-vacuum condition by using a JEOL 4500 XT. Elemental analyses were made by Auger electron spectroscopy (AES) with a VG Scientific AX

100 analyzer, irradiating electron beam in the accelerating voltage 4 KeV from a VG Scientific LEG 63 electronic gun.



1

1	n	R
a	2	H
b	3	H
c	3	CH_2SH

FIGURE 1 Chemical structures of the thiols **1** used in this study.

RESULTS AND DISCUSSION

Formation of Nanostructures Consisting of Mercaptomethyl-oligothiophene Derivatives 1

The formation of nanostructures of **1** on Au (111) was investigated using STM. When the coverage was small, no ordered structures were seen for **1a**, **b** or **c**. However, on increasing the coverage an ordered phase was observed for **1a** and **b**, and two ordered phases were detected for **1c**.

Figures 2A and B show the domains of nano-ordered one-dimensional rows of **1a** and **b** on Au(111), respectively, at room temperature. The spacing between two adjacent rows was 14.0 ± 0.5 Å for both of the samples. This value coincides with those of other mercaptomethylthiophenes with different molecular lengths,[3] though the row-structures with larger spacings were reported for thiols without mercaptomethylthienyl moieties.[3-5] These results strongly suggest that mercaptomethyloligothiophenes **1** are arranged on the surface with upright configuration in the row-structures and support that the mercaptomethylthienyl moiety in the vicinity of the Au surface is a building unit for the formation of rows with the specific interrow spacing.

Two ordered phases are observed in the case of thiol **1c** / Au system. One is the one-dimensional molecular rows with the same interrow spacing for **1a**, **b** and the other is a two-dimensional honeycomb structure having holes arranged periodically with a center-to-center spacing of 11.6 ± 0.5 Å (Figure 2C). This periodicity is in agreement with those of other mercaptomethylthiophene analogs.[3] These two phases exist as domains and these domains coexist in a wide range of coverage in the **1 c** / Au system. The results show that molecules **1 c** are also aligned with end-on configuration in two phases and that mercaptomethylthienyl group plays a key role to form these structures. These nanostructures obtained were stable under ambient conditions, but decomposed over *ca.* 80℃.

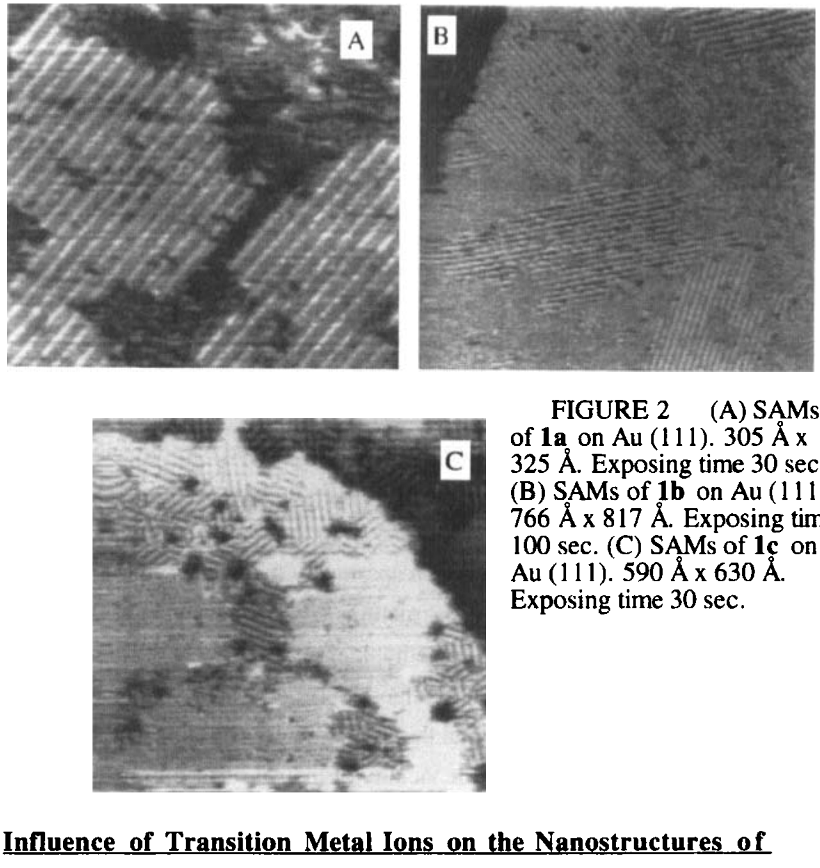


FIGURE 2 (A) SAMs of **1a** on Au (111). 305 Å x 325 Å. Exposing time 30 sec. (B) SAMs of **1b** on Au (111). 766 Å x 817 Å. Exposing time 100 sec. (C) SAMs of **1c** on Au (111). 590 Å x 630 Å. Exposing time 30 sec.

Influence of Transition Metal Ions on the Nanostructures of Mercaptomethyloligothiophenes 1b and c

The influence of transition metal ions such as ferrous, ferric, nickel(II), and chromium(III) on the nanostructures was investigated by immersing the films of **1 b** and **c** into the ethanol solutions of the above metal ions, followed by

STM measurements. The concentration of the solutions was in the range of 0.1 μM to 1 mM.

The nanostructures of **1b** did not change significantly when the films were immersed in 0.1 μM $NiCl_2$ ethanol solution as is shown in Figure 3A where the one-dimensional rows remain intact. This is consistent with the results of AES: the signals of carbon and sulfur atoms were clearly seen while that of nickel species was absent. This means that nickel ions do not have strong influence on the nano-ordered structures under these conditions.

The influence of transition metals on the nanostructures was further investigated using **1c**. When the nanostructures of **1c** were immersed into 10 μM $CrCl_3$ ethanol solution, a number of nano-clusters were observed over the surface (Figure 3B). However, the nanostructures of **1c** are clearly seen and have the same periodicity as before. Similar results were obtained for $FeCl_2$ and $FeCl_3$ although the concentration of Fe ions (1 mM) was higher compared with the other ions. From these results, we conclude that the nanostructures are stable in the ethanol solution of transition metal ions (MCl_n; M = Ni, Cr, Fe, n = 2, 3) under ambient conditions.

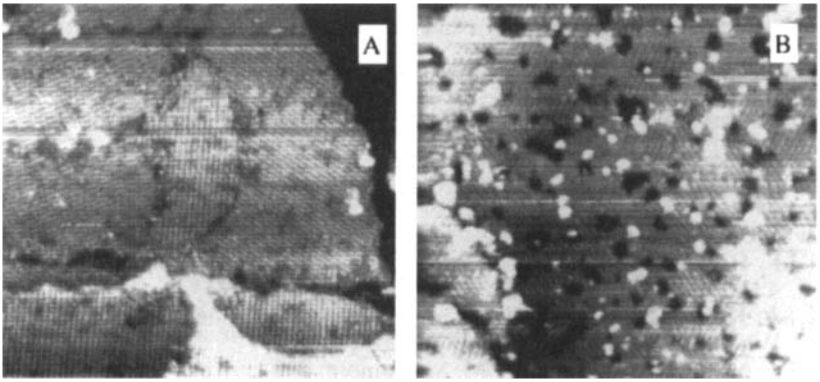


FIGURE 3 (A) SAMs of **1b** on Au (111) after immersed in $NiCl_2$ ethanol solution (0.1 μM). 861 Å x 919 Å. Immersing time 2 sec. (B) SAMs of **1c** on Au (111) after immersed in $CrCl_3$ ethanol solution (10 μM). 789 Å x 842 Å. Immersing time 3 min.

Furthermore the effect of the electric field on the nanostructures in the ethanol solution of nickel(II) chloride was investigated. Weak negative voltage of *ca.* -30 mV was applied to the nanostructures of **1b** for 15 sec in 0.1 μM ethanol solution of nickel chloride. This procedure changed the structure significantly. The nanostructures were not well-defined anymore and few rows, though blurred, were barely seen. Additionally, a large number of clusters were observed on the surface. These clusters are most probably related to nickel oxide since the signals due to nickel and oxygen atoms were observed by AES.

CONCLUSIONS

We have observed that mercaptomethyloligothiophenes **1a** and **b** form monolayers consisting of one-dimensional rows with an interrow spacing of 14.0 ± 0.5 Å on Au surfaces and bis(mercaptomethyl)terthiophene **1c** forms monolayers of two-dimensional honeycomb structures with an interhole spacing of 11.6 ± 0.5 Å as well as the row structures. We have also found that these nanostructures are stable in the ethanol solution of transition metal ions such as ferrous, ferric, nickel(II), and chromium(III) chloride. However, significant changes were observed when the films were heated over *ca.* 80℃ or weak negative voltage was applied to the films in the ethanol solution of nickel chloride.

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