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Ryota Yuge [a], Akira Miyazaki [a], Toshiaki Enoki [a], Eisuke Ito [b], Fumio Nakamura [b] & Masahiko Hara [b]

[a] Department of Chemistry, Tokyo Institute of Technology, Ookayama 2-12-1, Meguro-ku, Tokyo, 152-8551, Japan

[b] Frontier Research System, RIKEN (The Institute of Physical and Chemical Research), 2-1, Hirosawa, Wako-shi, Saitama, 351-0198, Japan

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Characterization and Electronic Properties of TTF SAMs on Au (111)

RYOTA YUGE[1], AKIRA MIYAZAKI[1], TOSHIAKI ENOKI[1], EISUKE ITO[2], FUMIO NAKAMURA[2] and MASAHIKO HARA[2]

[1]*Department of Chemistry, Tokyo Institute of Technology, Ookayama 2-12-1, Meguro-ku Tokyo 152-8551, Japan and* [2]*Frontier Research System, RIKEN (The Institute of Physical and Chemical Research), 2-1, Hirosawa, Wako-shi, Saitama, 351-0198, Japan*

Self-assembled monolayer of mesoscopic size with Tetrathiafuluvalene (TTF) skeleton has attracted because it is expected to have quantum size effect for perpendicular to the substrate as well as two-dimensional π -electron interaction. Surface plasmon resonance (SPR) revealed that TTF-CH_2SH monolayer is formed on Au (111) only at proper concentration. The presence of etch pits which is characteristic to chemisorbed SAMs was confirmed by scanning tunneling microscopy (STM). From those SPR and STM results, it has been suggested that the molecular long axis of TTF-CH_2SH was aligned nearly perpendicular to the substrate. In addition, cyclic voltammogram (CV) result indicates that TTF-thiolate SAMs on gold electrode are stable in repeated scans.

Keywords: Self-assembled monolayer; TTF derivative; Surface plasmon resonance; Scanning tunneling microscopy

INTRODUCTION

Recently, self-assembled monolayers (SAMs) of alkanethiol molecules and their derivatives have attracted considerable attention as methods easily constructed on closely packed two-dimensional structure on metal surface. The structures of alkanethiol SAMs have been widely studied using several analytical methods such as STM [1-3]. In contrast to a large amount of reports on alkanethiol SAMs, π -electron system such

as TTF thiolate is not well investigated yet. In this study, we investigate the characterization and electronic properties of SAM whose molecules structure is shown in FIGURE 1.

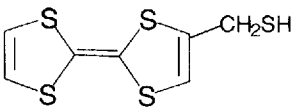

FIGURE 1. The molecular structure of TTF-CH_2SH

EXPERIMENTS

We prepared the gold substrate with the surface of (111) orientation by vacuum evaporation on mica. Immediately after preparation of Au substrates, they were immersed in various solutions of TTF-CH_2SH. After 24 h immersion, the samples were removed from the solution, rinsed with pure solvent, and dried by N_2 gas. In order to investigate dependence of film thickness and adsorption kinetics on concentrations and solvents, SPR was introduced at room temperature. Topology of the SAMs was observed in detail by STM. CV was carried out for TTF thiolate SAMs on gold electrode.

RESULTS AND DISCUSSION

STM image of TTF-SAMs on Au (111)

FIGURE 2 shows an STM image after adsorption of TTF-CH_2SH on Au (111). The image was recorded in the constant current mode, using a bias voltage of +500 mV positive and a tunneling current of 300pA. Gold vacancy islands (i.e., "etch pits") are clearly visible on the surface. Since the depth of etch pits is about 2.5 Å, It is characteristic to chemisorbed SAMs on reconstructed gold (111) [4]. However unlike the etch pit of the general alkanethiol SAMs, their shapes are not uniform.

In this case, it is thought that two-dimensional arrangements of TTF molecules are not well ordered on Au substrate probably due to the methyl pairs that provides freedom for the molecular direction.

2. Adsorption process by SPR

Formation process of TTF-SAM structure was confirmed by *in-situ* SPR measurements in various organic solvents and concentrations. FIGURE 3 shows kinetics curves for adsorption of TTF-SAMs in different conditions using ethanol solvent. In this case we obtained different dependence on the several concentrations. It was proven that 0.1 mM solution of TTF-CH_2SH was optimum also in the case of ethanol, chloroform and acetonitrile in SPR measurements. In such SPR studies, it is revealed that the TTF molecule is perpendicularly aligned to the substrate from the film thickness calculation. In addition, the increase in the film thickness was confirmed by SPR experiment in 1 mM ethanol solution. The intermolecular interaction through four sulfur atoms become dominant when SAMs are formed in poor solvent. It is considered that the aggregation is easily preceded for TTF-CH_2SH. On the other hand, kinetic curve showed low saturation of film

FIGURE 2. STM image of a 300 nm × 300 nm section of Au substrate.

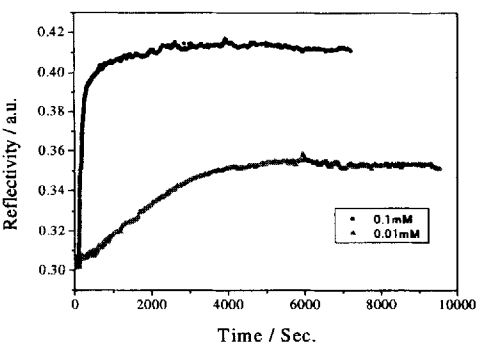

FIGURE 3. Adsorption kinetics of SPR

thickness. This indicates that it is not sufficiently self-assembled on the substrate. Therefore, It is expected that solvent dependence and the concentrations are important factor for such π-electron SAMs.

3. Electronic properties on CV measurement

CV measurements were carried out for studying the electronic properties in detail. It was revealed that TTF-SAMs were electrochemically very stable on Au (111) electrode because redox response didn't change in repeated scans over the 0 to +1.0 V range. Further we observed that redox peaks are broad. In this case, it is thought that the overlap of the wave function in the lateral direction of TTF SAM has been disturbed.

CONCLUSION

We succeeded in the preparation of the new monolayer by the TTF molecules with the functionality arranged to two-dimensional. It is expected to have strong interaction for the metal substrate since the methyl chain between functional molecule and substrate is short. From these studies, Wide application for a molecule device of such π-electron SAMs will be considered with the mesoscopic effect.

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