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# PROPERTY OF SELF-ASSEMBLED MONOLAYERS OF LONG-ALKYL-CHAIN-SUBSTITUTED TTF DIRIVATIVE

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*Self-assembled monolayers (SAMs) of an electron donor TTF derivative with long alkyl chains (-$C_{11}H_{22}$-) are formed on Au (111). STM, surface plasmon resonance, and FTIR reflection absorption spectroscopy measurements suggest that TTF backbone is isolated from the gold substrate by long alkyl chains. Cyclic voltammograms reveal two redox peaks ($E_1^{1/2} = 263\,mV$, $E_2^{1/2} = 508\,mV$ vs. $Ag/Ag^+$) corresponding to $TTF/TTF^+$ and $TTF^+/TTF^{2+}$. These peak currents are proportional to the scan rates, indicating that the TTF backbone maintains its electrochemical activity in the SAMs. In addition, the peak-to-peak separations between oxidation and reduction are roughly proportional to the scan rates, which indicates that a potential drop takes place at the long alkyl chains, which work as resistance in the electron transport.*

*Keywords*: cyclic voltammetry; long alkyl chain; self-assembled monolayer; surface plasmon resonance; scanning tunneling microscopy; tetrathiafulvalene

## INTRODUCTION

Organic charge transfer complexes such as TTF-TCNQ (TTF; tetrathiafulvalene, TCNQ; 7,7,8,8-tetracyano-quinodimethane) in the single crystal form have been extensively studied for the three decades, because a variety of low dimensional conducting properties (from semiconducting to superconducting) can be obtained. For the purpose of producing new devices, transferring their properties to two dimensional (2D) thin films on substrates have been attempted by using Langmuir-Blodgett (LB) method and self-assembled monolayers (SAMs) method [1]. SAMs have attracted

a great deal of attention, because of its possibility that we could control nano-scale well-defined 2D-structures only by immersing metal substrates to the solutions. Although many functional SAMs have been constructed and characterized for a decade, there are only a few reports concerning their lateral conducting properties in comparison with LB films [2]. This may come from the fact that evaluation of conducting properties of SAMs is more difficult, because substrates are more conducting than the conducting parts of SAMs. In order to evaluate lateral conducting properties in SAMs, we attempt to separate conducting TTF moieties from gold substrate by long alkyl chains (-$C_{11}H_{22}$-). Following this purpose, we designed and synthesized TTF derivatives with long alkyl chains as shown in Figure 1. In this study we investigate the structure and electronic properties of SAMs of EDT-TTF($SC_{11}H_{22}SH)_2$ on gold substrates.



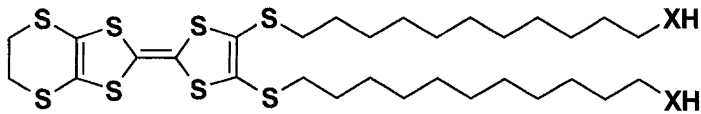
## EXPERIMENTS

Au (111) substrates were prepared by vacuum evaporation on freshly cleaved mica sheets. After annealed at 400°C for 3 h, the substrates were immersed in 1,2-dichloroethane solutions of EDT-TTF($SC_{11}H_{22}SH)_2$ for 24 h. Then the substrates were taken out from the solutions and rinsed with pure 1,2-dichloroethane. Surface plasmon resonance (SPR) was measured to investigate adsorption kinetics and film thickness. STM imaging was carried out to confirm microscopic surface topography in air. The conformational ordering was evaluated by FTIR reflection absorption spectroscopy (FTIR-RAS). Then electrochemical characteristics of SAMs and solutions were obtained by cyclic voltammetry (CV) technique.

## RESULTS AND DISCUSSION

### 1. Adsorption Study by SPR

SPR measurements were carried out to study the adsorption process for 0.1 mM 1,2-dichloroethane solutions of EDT-TTF($SC_{11}H_{22}SH)_2$ and EDT-TTF($SC_{11}H_{22}OH)_2$. Figure 1 shows the kinetics curves for the two species.




**SCHEME 1** The molecular structure of EDT-TTF($SC_{11}H_{22}XH)_2$. EDT; ethylenedithio, X = S, O.

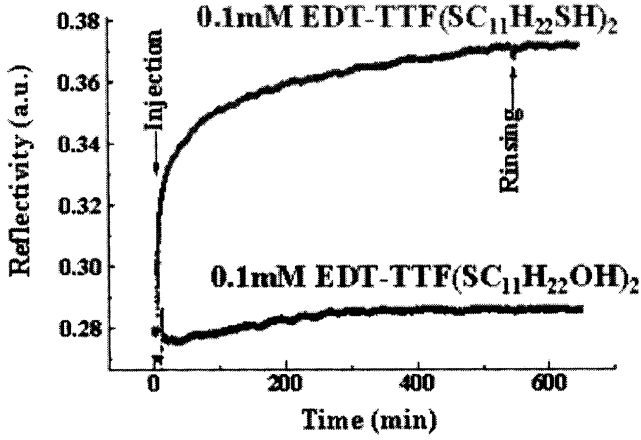



**FIGURE 1** Adsorption kinetics for 0.1 mN 1,2-dichloroethane solutions of EDT-TTF$(SC_{11}H_{22}XH)_2$ (X = S, O).

It appeared that the kinetics of EDT-TTF$(SC_{11}H_{22}SH)_2$ is similar to those of ordinary *n*-alkanethiol SAMs [3], suggesting the formation of a SAMs. However there is no significant reflectivity change in the case of EDT-TTF$(SC_{11}H_{22}OH)_2$, although it has eight sulfur atoms expected to strongly interact with gold substrate. Hence we conclude that the presence of –SH functional groups is crucial for the formation of TTF-type SAMs. The film thickness is evaluated from the plasmon resonance curve fitting. Assuming the refractive index of EDT-TTF$(SC_{11}H_{22}SH)_2$ to 1.56 [4], the film thickness is $26 \pm 3$ Å. This result is in good agreement with the calculated molecular length (27 Å), suggesting that the EDT-TTF$(SC_{11}H_{22}SH)_2$ are aligned perpendicular to the substrate.

## 2. STM Image of EDT-TTF$(SC_{11}H_{22}SH)_2$ on Au (111)

Figure 2 shows an STM image of EDT-TTF$(SC_{11}H_{22}SH)_2$ SAMs on Au (111). The image was recorded in the constant current mode, using a bias voltage of 700 mV (tip positive) and a tunneling current of 700 pA. Gold vacancy islands (so called "etch pits") are clearly observed on the surface, which evidences chemisorptions between gold and sulfur atoms [5]. Their depths are about 2.4 Å which is usually observed value in normal alkanethiol SAMs. In addition, the presence of etch-pits reveals that EDT-TTF$(SC_{11}H_{22}SH)_2$ SAMs are in standing-up phase, which means that the molecular axes of the adsorbents are standing up from the surface. That is in good agreement with the SPR measurement. However any lattice images have not been successfully observed, the shapes and sizes of etch pits are

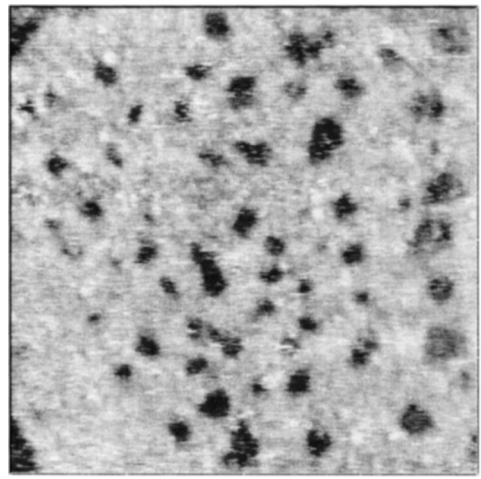


**FIGURE 2** An STM image of the EDT-TTF$(SC_{11}H_{22}SH)_2$ SAMs on Au (111). Scan size (80 nm × 80 nm).

not uniform, and some disorder parts are visible around the etch pits. The origin of them may come from the following reasons; (1) the van der Waals radii of long alkyl chains and those of TTF moieties are mismatched, so structural disorder and defects are induced especially around the etch pits, (2) the bridging sulfur atoms between alkyl chains and TTF moieties induce the disorder of molecular packing by increasing the degree of freedom to bond angle compared to carbon atoms.

## 3. Spectroscopic Analysis by FTIR-RAS

Figure 3 shows the IR spectrum of bulk EDT-TTF$(SC_{11}H_{22}SH)_2$ dispersed in KBr in the C–H stretching mode in the high frequency region (2800–3000 $cm^{-1}$). Each peak is deconvoluted by Lorentzian curve fitting. Peaks at 2923, 2851, and 2892 $cm^{-1}$ are assigned to the methylene asymmetric ($\nu_{as}(CH_2)$) and symmetric ($\nu_s(CH_2)$) stretches and Fermi resonance of $\nu_s(CH_2)$, respectively. A shoulder peak of $\nu(CH_2)$ at the EDT-bridge is also observed at 2958 $cm^{-1}$ [6]. The RAS spectrum of EDT-TTF$(SC_{11}H_{22}SH)_2$ monolayers is shown in Figure 4. All peaks are easily assigned by comparing to those of KBr method. The difference between the bulk and SAM spectra reflects the arrangement of molecules in the SAMs. $\nu(CH_2)$ from the EDT-bridge whose transition dipole is nearly parallel to the TTF backbone plane is enhanced in the RAS spectra. According to the surface selection rule, the TTF backbone plane is standing up from the surface. In addition, Yamamoto et al. reported that long alkane whose molecular

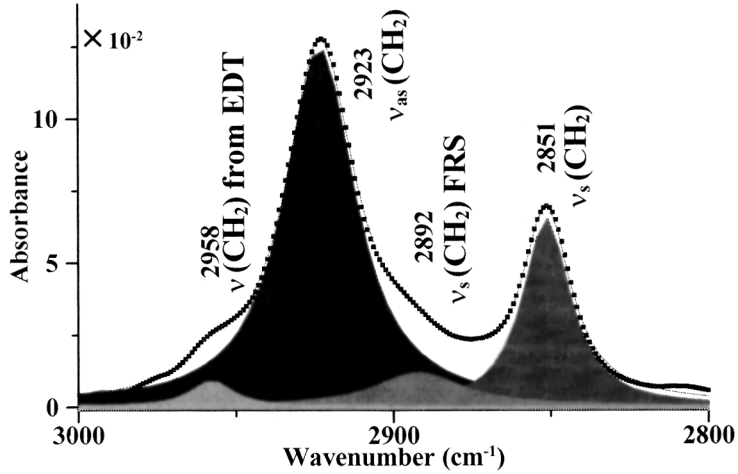



**FIGURE 3** IR spectrum of the Bulk EDT-TTF$(SC_{11}H_{22}SH)_2$.

axis is parallel to the Au (111) induces a band at 2910 $cm^{-1}$ due to the dipole-image dipole interactions [7]. Because no peaks are observed around 2910 $cm^{-1}$, the long alkyl chains of EDT-TTF$(SC_{11}H_{22}SH)_2$ do not lie on the surface but stand up. Taking account of these points, we conclude that EDT-TTF$(SC_{11}H_{22}SH)_2$ molecules are almost standing up from the substrate, and the TTF backbone is located above the long alkyl chains.

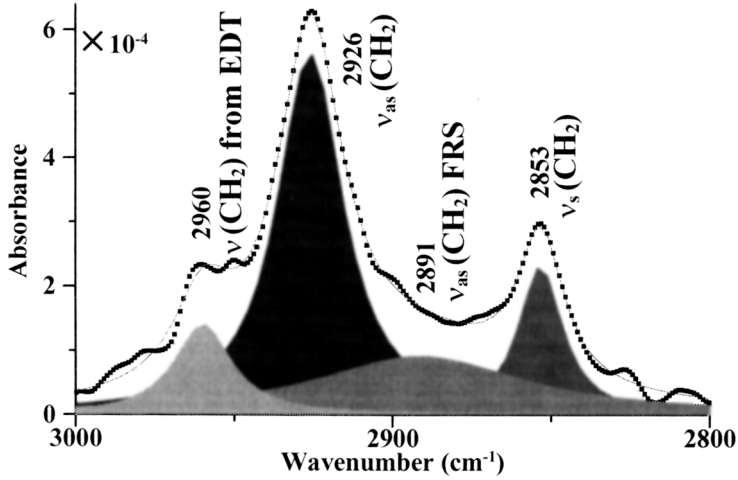



**FIGURE 4** Reflection spectrum of the SAMs of EDT-TTF$(SC_{11}H_{22}SH)_2$.

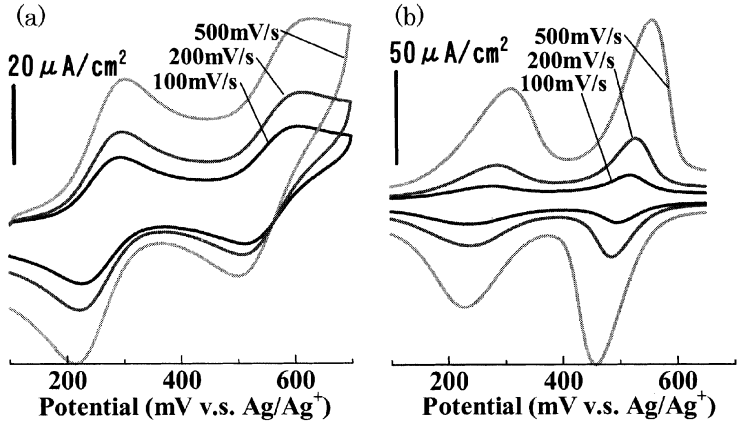



**FIGURE 5** Cyclicvoltammograms for (a) dichloromethane solutions of 0.1 mM EDT-TTF$(SC_{11}H_{22}SH)_2$, and (b) SAMs of EDT-TTF$(SC_{11}H_{22}SH)_2$ at different scan rates.

However the peak positions for the $v_{as}(CH_2)$ and $V_s(CH_2)$ are shifted to the higher wavenumber compared to the bulk spectra, suggesting a liquid-like packing state, which supports the STM results showing the presence of disorder [8].

## 4. Electrochemical Characteristics

CV measurements were carried out for studying the feature of electron transfer between TTF backbone and metal electrode. Figure 5 (a) shows an cyclic voltammogram of about 0.1 mM EDT-TTF$(SC_{11}H_{22}SH)_2$ dichloromethane solutions including 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as a supporting electrolyte. Two reversible one-electron redox couples corresponding to $TTF/TTF^+$ and $TTF^+/TTF^{2+}$ appeared at ${E_1}^{1/2} = 257$ mV and ${E_2}^{1/2} = 574$ mV, respectively. The peak currents are proportional to the square of scan rates, indicating a "diffusion wave". For SAMs of EDT-TTF$(SC_{11}H_{22}SH)_2$, as shown in FIGURE-5 (b), the peak currents are observed to be proportional to the scan rates, indicating a "surface wave". Two peak potentials are ${E_1}^{1/2} = 263$ mV and ${E_2}^{1/2} = 508$ mV, roughly similar to diffusion wave. It is revealed that EDT-TTF$(SC_{11}H_{22}SH)_2$ molecules maintain their redox activity in the SAMs. The redox responses of previously reported TTF-type SAMs with short alkyl chains have shown peak potentials independent of the scan rates [4]. However the peak to peak separations in the present study were nearly proportional to the scan rates, indicating that a potential drop takes place at long alkyl chains, which work as resistance in the electron transport. Further studies are

progressing to reveal the details of resistance and peak shape difference between the first and second peaks.

## CONCLUSION

We succeeded to prepare a monolayer of EDT-TTF$(SC_{11}H_{22}SH)_2$ and put alkyl chains between TTF backbone and gold substrate as resistance. SAMs of EDT-TTF$(SC_{11}H_{22}SH)_2$ are confirmed to take a charge transfer reaction between $TTF^+$ and $TTF^{2+}$ states without direct interaction of gold substrate, where the presence of the long alkyl chains makes the TTF moiety apart from the substrate. These studies suggest a wide variety of application for 2D TTF-type conducting SAMs such as a quantum device.

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