Electrochemical Properties of TTF Derivative Self-Assembled Monolayers: Influence of Alkyl Chain Legs and Contacting Medium

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Crystalline form organic charge transfer complexes such as TTF-TCNQ 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 molecular devices, transferring their properties to thin films on solid substrates has attracted a great deal of attention. In this perspective, we attempt to construct a TTF-based conducting thin film by using self-assembled monolayers (SAMs) technique. To separate gold substrate and conducting part in the film, we employ long-alkyl-chain(s)-substituted TTF derivatives **1** and **2**, where alkyl-chain(s) work as resistance (Figure 1).

Surface plasmon resonance (SPR) measurement was carried out to investigate adsorption kinetics and film thickness and to characterize molecular packing in various contact media. Cyclic voltammetry (CV) in dichloromethane and water was measured to confirm electrochemical oxidation processes and their relations to film structures. Gold substrates for SPR measurements (~50 nm) and CV measurements (~300 nm) were prepared by evaporation of gold on glass plates. Acetone solution of 0.1 mM TTF derivative **1** or **2** was used for monolayer preparation. Refractive index and thickness of the film were evaluated from the SPR results by changing the contacting solvent (contrast variation technique). CV was performed in 0.1 M tetrabuthylammonium perchlorate / dichloromethane and 0.5 M $HClO_4$ aq.

The SPR results are summarized in Table 1. Film thickness of SAM of **1** and **2** becomes about 65 % and 80 % of their molecular length (~27 Å), respectively. This discrepancy is discussed below. Solvent permeability to the film evaluated by contrast variation technique strongly depends on the molecular structure and the solubility of the molecule; SAM of **1** is more permeable than **2**, and the higher the solubility of the molecule to the solvent, the more permeable the SAM. With respect to the former trend, molecular model analysis suggests that molecule **2** can form the film structure with less clearance than molecule **1**, which leads to larger film thickness of SAM of **2**. The immersion time of monolayer preparation for CV measurements is decided to 16 ± 4 h in consideration of saturation time of **1** and **2**.

Voltammograms in highly soluble solvent (dichloromethane) show well defined two redox peaks (**1**: $E_1^0 = 0.27$ V, $E_2^0 = 0.51$ V, **2**: $E_1^0 = 0.30$ V, $E_2^0 = 0.52$ V) whose potentials are close to the peak potentials of solution **1** and **2** (same: $E_1^0 = 0.26$ V, $E_2^0 = 0.56$ V) (Figure 2). However, the peak shapes depend on the molecular structure. The full width of half maximum (FWHM) of the second redox peak is less than 90 mV (no intermolecular interaction case) in both cases (Table 2), which indicates attractive interaction working between redox species. The magnitude of the peak width is correlated with the solvent permeability. That is, the more permeable the solvent into the film, the narrower FWHM.

Voltammograms in low soluble solvent (water) indeed reflect this trend. Taking into account the fact that FWHM of the first redox peak is broader than that of the second redox peak, which indicates the conformational change of the film after the TTF donors acquire charges, the counter anions are considered to participate in producing the attractive interaction. The efficiencies of the counter anions depend on the degree of freedom of the molecule on the film. These intermolecular correlation phenomena and correlation length should be taken into account to design molecular based systems. The studies on the interaction correlation length with various sizes of TTF islands in the alkanethiol SAM will be discussed in presentation.
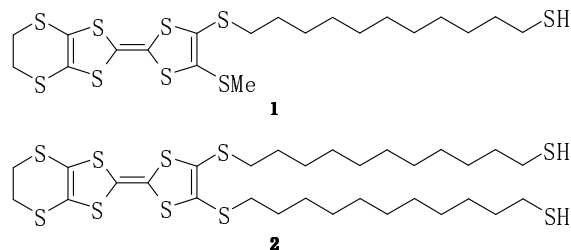

Figure 1: Molecular structure of TTF derivative.

Table 1: Film formation time and film properties evaluated from SPR measurements.

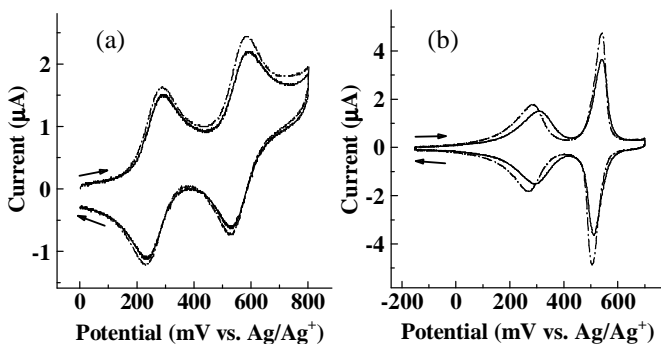| Molecule	1	2
Saturation time (h)	~12	~16
Film thickness (Å)	17.1 ± 0.5	21.7 ± 0.5
Refractive index	1.61 ± 0.01	1.63 ± 0.01

Figure 2: (a) Cyclic voltammograms of 0.1 mM **1** (dashed line) and **2** (solid line) in 0.1 M TBAP / dichloromethane; scan rate: 20 mV/s, working electrode: grassy carbon, counter electrode: Pt wire. (b) Cyclic voltammograms of SAMs of **1** (dashed line) and **2** (solid line) in 0.1 M TBAP / dichloromethane; scan rate: 20 mV/s, counter electrode: Pt wire.

Table 2: FWHM of the second redox peak.

Solvent / Molecule	1	2
Dichloromethane	47 ± 2 mV	56 ± 2 mV
Water	~60 mV	~70 mV