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Synthesis and Characterization of an Alkanethiol Thin Film Containing a Hemicyanine Dye

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ABSTRACT: Two kinds of thiol compounds with hemicyanine dyes of dimethyl and dibutyl end groups were synthesized. These formed self-assembled monolayers (SAM's) on gold surfaces. The SAM's were characterized by UV-VIS reflection spectroscopy, surface plasmon resonance, and second order harmonic generation measurements. It was found that the structures of the SAM's were largely affected by the end groups.

Keywords: Self-Assembled Monolayers; Hemicyanine Dye; Thiol; Reflection Spectrum; Surface Plasmon Resonance; Second Order Nonlinear Susceptibility

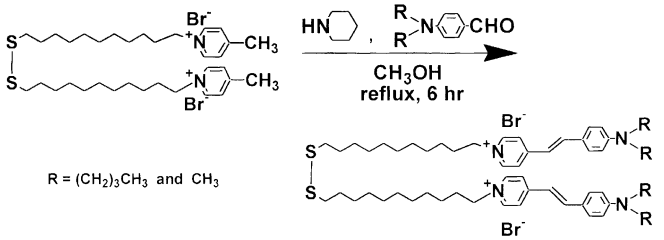
INTRODUCTION

Long alkanethiols form self-assembled monolayers (SAM's) on a metallic surface.[1] In these SAM's, thiol molecules are packed densely. There have been many studies on their structures and the mechanism of their formation using X-ray photoelectron spectroscopy (XPS),[2-4] infrared reflection and absorption spectroscopy (IR-RAS),[5,6] ellipsometry,[3] surface plasmon spectroscopy (SPS),[7,8] and scanning probe microscopy (SPM).[9,10] The SAM's are expected to exhibit the novel optical and electrical properties by introducing functional chromophores, such as dyes, into the unique structure. Owens et al. fabricated a merocyamine SAM on a SAM of alkanethiol with carboxyl groups and observed J-aggregates of dyes.[11] In the previous work, we synthesized an alkanethiol precursor, 11,11'-dithio-di[1-undecyl-4'- (4"-dibutyaminostyryl)pyridinium bromide], including hemicyanine dye groups and fabricated its SAM on a gold surface. In this study, we synthesized another alkanethiol precursor with hemicyanine groups and investigated the structure of the SAM.

EXPERIMENTAL

A precursor, 11,11'-dithio-di[1-undecyl-4'-(4"-dibutylaminostyryl)pyridinium bro-

mide] was obtained by the following method. 4-dibutylaminobenzaldehyde (4.71 g, 20 mmol) and 11,11'-dithio-di(1- undecyl-4-picolinium bromide) (5.59 g, 7.8 mmol), piperidine (1 mL) were dissolved in methanol (100 mL). The mixture was refluxed for 6 hr and was poured into ethyl acetate (500 mL). The crude product was filtered and was purified by reverse phase chromatography (elution; methanol : dichloromethane = 3 : 1). By recrystallization from benzene, reddish crystal was obtained (6.60 g, yield 73.4 %). The structure of compound was characterized by ^{1}H-NMR measurement. A dimethyl derivative, 11,11'-dithio-di[1-undecyl-4'-(4''-dimethylamino- styryl)pyridinium bromide] was also obtained by a similar procedure (Scheme).



SCHEME. Syntheses of the dye alkanethiol precursors.

MEASUREMENT

Polycrystalline thin films of gold were prepared by thermal evaporation of gold on slide glasses. The SAM of the dye was fabricated on the gold surface by dipping the gold substrate into the dye ethanol solution (concentration; 1 mmol/L) for 1 hr and by rinsing ethanol several times. Cast films for UV-VIS absorption measurement were also prepared from the solution.

UV-VIS absorption spectra of the dye solutions in methanol (concentration; 10^{-3} mmol/L) were measured by using a SHIMADZU UV-1600 spectrophotometer. Surface plasmon resonance in Kretschmann configuration was measured by utilizing a He-Ne laser (638 nm). Second harmonic generation measurement of the SAM was carried out by monitoring p-polarized reflected second harmonics using p-polarized Nd:YAG laser as light source (λ = 1064 nm).

RESULTS AND DISCUSSIONS

The UV-VIS absorption spectra of the cast films and solutions of the precursors are shown in FIGURE 1. The both spectra of the cast films have broad peaks largely blue-shifted compared to the corresponding peaks in the spectra of the solutions. This strong blue-shift may be attributed to the aggregates of the dyes in the cast film. The shift in the spectrum of the dimethyl precursor is lager than that in the spectrum of the dibutyl precursor. This implies that the interaction between dimethyl hemicyanine dye molecules is stronger than that between the dibutyl molecules. The UV-VIS reflection spectra of the SAM's are shown in FIGURE 2. Only one peak is observed at 530 nm and is attributed to the monomeric dye species. The intensity of the peak for the dimethyl precursor is larger than that for the dibutyl precursor. The surface plasmon resonance curves for the both SAM's also indicate that the coverage of the dibutyl SAM is less than that of the dimethyl SAM (FIGURE 3). Thus, the result of the reflection spectra suggests that the dye molecules in the SAM of the dibutyl dye are packed more loosely that that of the dimethyl dye because of the steric hindrance of dibutyl substitutes.

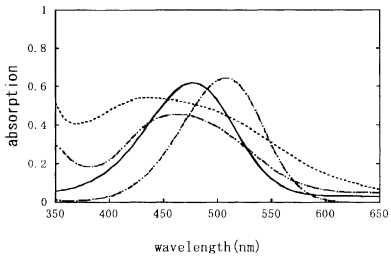


FIGURE 1. UV-VIS absorption spectra of the cast film and the solutions of the precursors. The dimethyl precursor: the cast film (▪▪▪▪▪▪▪), and the chloroform solution (———) and the dibutyl precursor: the cast film (— ▪ ▪), and the chloroform solution (— ▪ ▪)

By the second order nonlinear optical measurement, second order nonlinear susceptibilities, χ_{pp}'s were obtained. The values of $|\chi_{pp}|$ were estimated to be 5.13×10^{-8} esu for the dibutyl SAM and 3.48×10^{-8} esu for the dimethyl SAM. The value of the dibutyl SAM is ca. 1.5 times larger than that of the dimethyl SAM in spite of the lower density of the dye in the dibutyl SAM. Differently from simple alkanethiols, there are two kinds of interaction between the dye molecules. One is a dipole-dipole interaction between hemicyanine groups and the other is a van der Waals interaction between the methylene groups. The former causes the anti-parallel orientation of the dye molecules. The latter causes the formation of the SAM and the parallel orientation of dye molecules. Bulky dibutyl groups reduce the dipole-dipole interaction and the density of packing but enhance the orientation of the dye. This can explain the results of the SHG measurement.

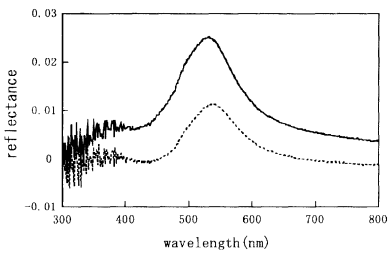


FIGURE 2. VIS reflection spectra of the SAM's of the dimethyl and the dibutyl precursors. The dimethyl precursor (———) and the dibutyl precursor (▪▪▪▪▪▪▪).

CONCLUSION

We synthesized two kinds of the precursors including dimethyl and dibutyl groups. The precursors formed SAM's on gold surfaces. Optical measurement showed that the alkyl end groups affect on the structures of the SAM's.

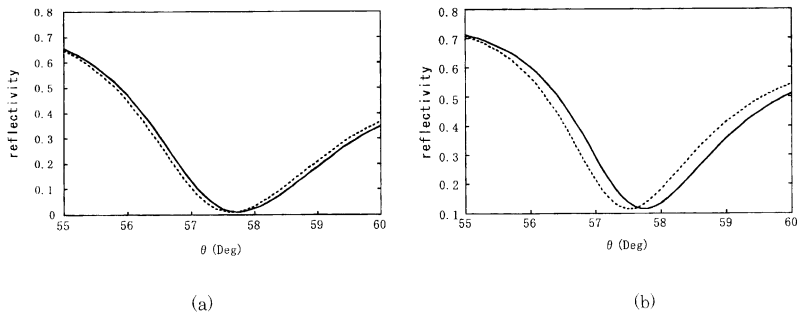


FIGURE 3. Surface plasmon resonance of the dibutyl (a) and the dimethyl (b) SAM's on gold surface. The SAM's (▬▬) and gold surfaces (▪▪▪▪▪).

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