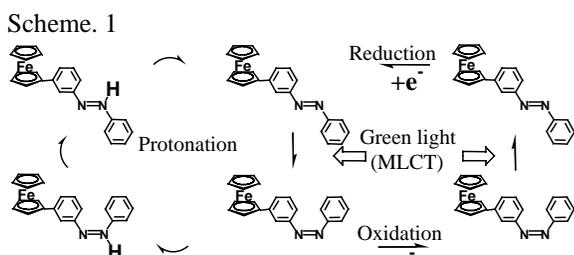


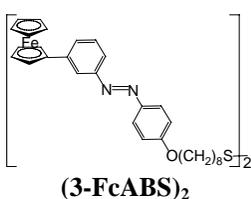
Photo- and electrochemical behaviors of 3-Ferrocenylazobenzene SAMs on two varieties of electrodes.

Aiko Sakamoto, Katsuhiko Kanaizuka, Masaki Murata, Tetsu Yonezawa, Hiroshi Nishihara
 Department of Chemistry, School of Science, The University of Tokyo
 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

3-Ferrocenylazobenzene (3-FcAB) derivatives have unique physical properties different from azobenzene [1]. Trans-cis isomerization of these molecules occurs with irradiation by not only UV light but also by green light



and cis molar ratios are controlled with redox of ferrocene moieties in solution. Moreover, addition of catalytic amount of photon source changes cis isomers to trans isomers immediately. On the other hand, Self-assembled monolayers (SAMs) have attracted much attention because their preparation is very convenient and has various possible applications, such as sensors, storage media, and electronic devices. Based on these backgrounds, we aim



preparation of 3-ferrocenylazobenzene SAMs in order to construct interesting interface that is responsive to light, redox, and proton in this study.

We synthesized a 3-FcAB derivative with disulfide terminated alcohyl chain (3-FcABS)₂ for preparation of SAM on gold. This derivative was synthesized from 3-ferrocenylaniline and nitrosophenol p-toluenesulfonate. After the synthesis of the azo group, deprotection was performed by KOH and the following Williamson's ether synthesis with 1,8-dibromooctane. Then, bromo group terminated alcohyl chains were converted into dialcohyl disulfide of the product. After photo- and electrochemical behavior of (3-FcABS)₂ was confirmed, sel-assembled monolayers were prepared. Photoisomerization behavior of (3-FcABS)₂ solution in dichloromethane with irradiation at 365 nm was observed but irradiation at 546 nm could produce little amount of cis molar ratio. However, this derivative rapidly returned form cis to trans isomer by oxidation of ferrocene moieties with dichloroferrocenium salt as the oxidizing agents. It is considered that properties of 3-FcAB were changed when the electron donating alkoxy group was introduced.

For preparation of SAMs, two types of substrate were used. One is Au (111)/mica because of its flatness, and the other is Au/ITO/quartz for transparency of light. First, cyclic voltammetry of SAMs on Au(111)was conducted. As scan rate was changed, peak current was linearly increased up to the rate of 100 mV/s, showing the behavior of surface-attached redox species. But over 100 mV/s, plot bent over, indicating the contribution of electron transfer kinetics in the redox behavior.

Photo-electrochemistry was carried out using a thin-

layer electrochemical cell. Differences in the spectra of SAM on Au/ITO/quartz substrate from the spectrum of Au/ITO/quartz substrate upon photo-irradiation were displayed in Fig. 1. Production of SAMs was confirmed by the fact that all the peak wavelengths of SAMs were consistent with those of the samples in solution. We could observe photoisomerization behavior of SAMs on Au/ITO/quartz substrates under dry condition with irradiation at 365 nm (π - π^* band) although cis molar ratio was decreased and photoisomerization behavior was not detected in case of using green light (this behavior was similar to the results of solution of (3-FcOC8SAB)₂ in dichloromethane). The cis molar ratio at the irradiation of the MLCT band in solution was very small compared to that at the irradiation of the π - π^* band, probably because the steric effect generated by closed packing structure on the flat solid surface. The study on the interaction between redox and photoisomerization behavior will be also presented.

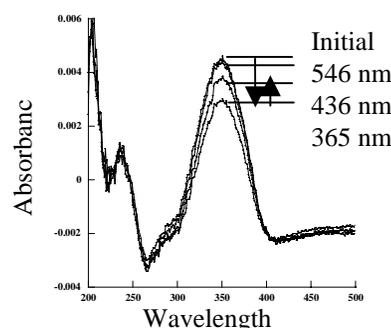
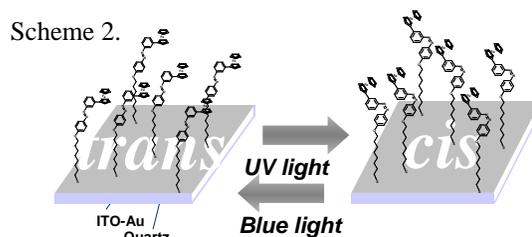


Fig. 1. UV-vis spectra of (3-FcABS)₂ SAM on aITO/Au/quartz electrode after irradiation.



[1]M. Kurihara et al. *J. Am. Chem. Soc.* **2002**, 124, 8800.

This study was supported by a Grant-in-aid for The 21st Century COE Program for Frontiers in Fundamental Chemistry from the Ministry of Education, Culture, Sports, Science and Technology.