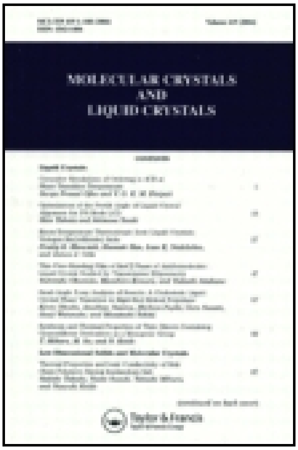

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Kenichi Morigaki [a] , Tadashi Enomoto [a] , Kazuhito Hashimoto [a] & Akira Fujishima [a]

[a] Department of Synthetic Chemistry, University of Tokyo, Hongo 113, Tokyo, Japan

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PHOTOELECTROCHROMIC AND POTENTIOCHROMIC BEHAVIOURS OF AZOBENZENE LB FILM

KENICHI MORIGAKI, TADASHI ENOMOTO, KAZUHITO HASHIMOTO, AKIRA FUJISHIMA
Department of Synthetic Chemistry, University of Tokyo, Hongo, 113, Tokyo, Japan

Abstract Two novel cis-trans conversion pathways have been studied using the assembled monolayer films of azobenzene derivative on solid electrodes. The first one is electrostatic isomerization induced by strong electric field at the interface of electrode and electrolyte. The second one is inverted redox reactions which leads to the simultaneous conversion of cis-ABD to the trans isomer at UV light irradiation. These reactions may provide new strategies to the chromic applications of azobenzene.

INTRODUCTION

Azobenzene has been studied extensively as a photochromic material [1]. It has a wide range of potential applications based on its photochemical trans-cis isomerization. For example, the isomerization was used to control capacitance, structures of supermolecular systems, and binding abilities of enzymes to other compounds. Although photochemical isomerization seems to be the only pathway for the trans-cis conversion of azobenzene, it is not the case in the reverse cis-trans conversion (ex. thermal isomerization). We reported previously a distinct difference of the electrochemical reduction potentials between trans and cis isomers in an assembled monolayer film of azobenzene derivative (ABD) [2]. Selective electrochemical reduction of cis-ABD provides a new pathway to its trans isomer via hydrazobenzene derivative (HBD).

In this report, we would like to report on two novel cis-trans conversion pathways which we found using the assembled monolayer films of ABD. The first one is electrostatic isomerization induced by strong electric field at the interface of electrode and electrolyte. The second one is inverted redox reactions which leads to the simultaneous conversion of cis-ABD to the trans isomer at UV light irradiation.

EXPERIMENTAL SECTION

Reagents. The azobenzene derivative, 4-octyl-4'-(5-carboxyl-trimethylene-oxy)-azobenzene (ABD) is commercially available from Dojindo Laboratory (Kumamoto, Japan). All chemicals were of reagent grade and used without further purification.

Fabrication of ABD Films The ABD monolayer film was deposited onto the thiol monolayer modified gold substrate (Thiol/Au) or SnO_2 conductive glass substrates in the trans form by the Langmuir-Blodgett method using a commercial instrument (Kyowa, HBM-AP; Tokyo). A 0.2mM $CdCl_2$ aqueous solution was used as the subphase. All samples were prepared at a constant surface pressure, 25mN m^{-1}.

Photoelectrochemical Measurements. The photoelectrochemical measurements were conducted using the three-electrode cell set-up, where the ABD monolayer film was used as the working electrode, and Pt wire as the counter electrode. The potential of the working electrode was controlled versus a Ag/AgCl(saturated KCl) reference electrode by a potentiostat (Toho, PS-07; Tokyo). A 0.1M aqueous sodium perchlorate solution whose pH was controlled with the citrate/Na_2HPO_4 buffer was employed as the electrolyte. Before each experiment, the electrolyte was deaerated with high purity Ar for 15 min.

RESULTS AND DISCUSSION

The electrostatic cis-trans isomerization of ABD monolayers

Figure 1 shows the cyclic voltammograms of the ABD monolayer deposited on SnO_2 glass. Cis-ABD was created by UV light irradiation at 0.0V (vs. Ag/AgCl). Cis-ABD showed large redox peaks at -0.3V and at +0.1V (b), although trans-ABD did not show any faradaic reaction within the same potential scan range (-0.5V - +0.4V) (a). It indicates the difference in the electrochemical properties between trans and cis-ABD. This difference arises from the relative instability of cis isomer.

On the other hand, a film which underwent anodic polarization up to +0.9V after the creation of cis-ABD did not show the reduction of cis isomer (c). From spectroscopic studies, we confirmed that cis-ABD was converted into trans-ABD during the anodic polarization. This cis-trans isomerization proceeded through a non-faradaic process, since no discernible faradaic current was observed in the anodic potential scan (d). Considering the strong electric field near the electrode, we came to a conclusion that the cis-trans isomerization was induced by the effect of the strong electric field. This electrostatic reaction provides a new pathway to the cis-trans conversion of ABD monolayers. It indicates the possibility that two isomers of ABD can be switched by the electric field.

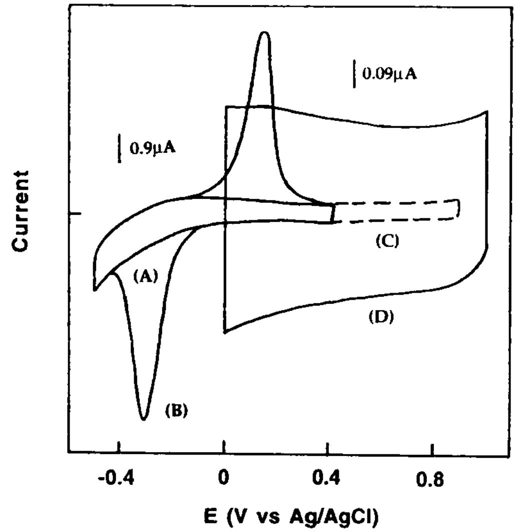

FIGURE 1 Cyclic voltammograms of ABD monolayer on a SnO_2 glass electrode. (A) Trans-ABD. (B) After 1min. UV irradiation: cis-ABD. (C) Cis-ABD which underwent anodic polarization. (D) Enlargement of (C).

Inversion of the redox potentials

As mentioned above, electrochemical reactions provide a pathway to convert cis-ABD to trans-ABD via HBD. The photoelectrochemical properties of ABD monolayers have been studied on gold substrates covered by thiol monolayers. Thiol monolayer was introduced to control the distance between the electrode and azo molecules (i.e. the barrier for the electron-transfer) by changing the length of the molecule. When ABD monolayers are separated from the gold substrate by a monolayer of relatively short thiol molecules (ethanethiol or 2-mercaptoethanol), the redox reaction of cis-ABD was not observed by voltammetric measurements. However, UV light irradiation to these films at cathodic potentials revealed that electrochemical reactions were occurring. Figure 2 shows the results. Figure 2(A) is the UV irradiation at -0.1V. No electrical response was observed indicating that the photochemically created cis isomer is electrochemically inactive at this potential bias. On the other hand, the UV irradiation at -0.2V caused a pair of electrical spike signals shown in figure 2(B). When the irradiation started, a sharp cathodic current spike was observed, and when the UV light extinguished, an anodic current spike was observed. Both spikes decayed quickly to the original current level. This behaviour indicates that both the reduction of cis-ABD and the oxidation of HBD are occuring simultaneously at this potential. Figure 2(C) is the UV irradiation at -0.35V. It caused cathodic current response, indicating that only the reduction of cis-ABD took place.

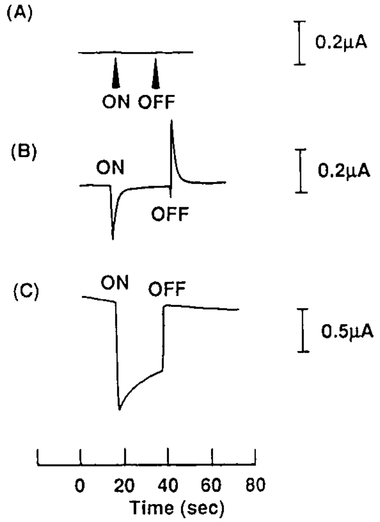

FIGURE 2 Electrochemical response of the ABD monolayer deposited on ethanethiol monolayer to UV light at cathodic potential bias: (A) -0.1V; (B) -0.2V; (C) -0.35V.

The spike responses indicate that both the reduction of cis-ABD and oxidation of HBD are occurring at -0.2V. To explain these observations, we propose a hypothesis that, for this system, the reduction of cis azobenzene occurs at a more anodic potential than the oxidation of hydrazobenzene to *trans*-ABD. For this "inverted redox reactions", the reduction of cis isomer was not observed in voltammetric measurements because it is cancelled out by the simultaneous oxidation of hydrazobenzene.

These hypothesis and experimental observations may be able to give a new insight on the electrochemical behaviours of cis and trans azobenzene. On the other hand, the spike like responses indicate that the film has a differential response to the light intensity, which is analogous to the biological system of vision. It is an interesting property for the construction of molecular devices.

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