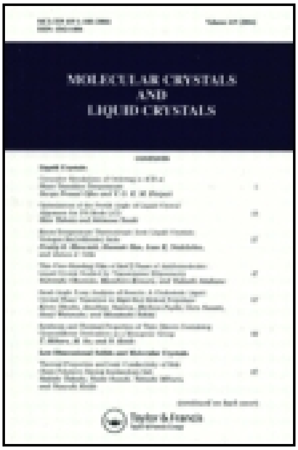

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Multi-Mode Chemical Transducer 3: Redox Control by Photoisomerization of 2-Arylazo-9,10-Anthraquinone

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MULTI-MODE CHEMICAL TRANSDUCER 3: REDOX CONTROL BY PHOTOISOMERIZATION OF 2-ARYLAZO-9,10-ANTHRAQUINONE

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Abstract Reduction potentials of the 2-arylazo-9,10-anthraquinone are switched by the photoisomerization. It shows two-step reversible reductions and the reduction potentials of the *syn*-isomer are in a more anodic region than those of the *anti*-isomer. It is cleared that its photochemical and electrochemical properties are dependent on each other.

INTRODUCTION

Electronic technology is pursuing the direction of making more miniature and more accumulated electronic devices. Since Carter proposed the concept of 'molecular electronic devices'[1] that will pass over the minimal limit of micro-photolithography, molecules whose configuration is changeable by light or electronic stimulation have been investigated as basic functions of the future devices.

For the purpose of realizing a more accumulated device, it is important that the molecule has multiple transformation modes. A molecule integrated with multiple transformation functions will give the device a higher information processing ability than that of a single function one. Also, all the transformation modes would be dependent on each other. We have investigated 2-arylazo-9,10-anthraquinones which showed interconversion of four distinct states caused by multiplication of two electrochromic redox states, quinone and hydroquinone, and two photochromic geometrical isomers, *anti* and *syn* forms (FIGURE 1).[2,3] We recently reported that the *syn-anti* thermal isomerization rate of the azo group was dependent on the state of the electrochromic quinone group. In a typical case, the rate of the quinone state was more than 30 times faster than that of the hydroquinone state.

We herein report another interdependence that reduction potentials of the 2-arylazo-9,10-anthraquinone are switched by the photoisomerization.

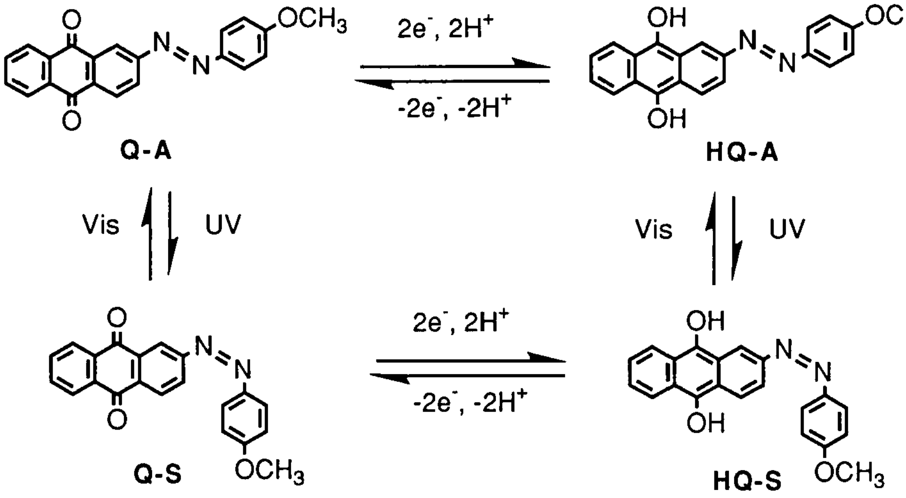

FIGURE 1 Interconversion of 2-arylazo-9,10-anthraquinone.

EXPERIMENTAL

Cyclic voltammograms were recorded on a Hokutodenko potentio-galvanostat HA-501G and a function generator HB-105. A three-electrode system, consisting of platinum wire working and counter electrodes and a $Ag/AgClO_4$ as a reference, was adopted. The potential of the $Ag/AgClO_4$ reference electrode is 490 mV *vs.* NHE. Photoisomerization was performed by a 500 w Xenon lamp (Ushio 500D) associated narrow band filter.

RESULTS AND DISCUSSION

2-(4-Methoxyphenylazo)-9,10-anthraquinone was synthesized according to Ref.3 and all the states are abbreviated by **Q-A**, **Q-S**, **HQ-A**, and **HQ-S** in this paper (FIGURE 1). Electrochemical and spectroscopic measurement was carried out in a saturate acetonitrile solution of **Q-A** containing 0.1 mol dm^{-3} tetrabuthylammonium tetrafluoroborate. On irradiation at 380 nm, the characteristic absorption maxima of **Q-A** at 380 nm decreased, accompanied by distinct isosbestic points at 295 nm and 460 nm and the absorbance around 500 nm increased slightly. This spectrum change implied that the converted compound was the *syn*-isomer, **Q-S**. It was completely converted back to **Q-A** under irradiation at 500 nm or thermal isomerization within 90 min. Isolation of pure *syn*-isomer has not been successful, due to rapid thermal isomerization.

Reduction potentials were determined by cyclic voltammetry. **Q-A** undergo a reversible two-step reduction from quinone to hydroquinone dianion, **HQ-A**$^{2-}$, with two electrons, *via* a semiquinone radical in aprotic solvent. Both first and second reduction waves were reversible and diffusion controlled. **Q-A** showed two redox waves at $E^1_{1/2}$= -1.10 V and $E^2_{1/2}$=-1.56 V (*vs.* Ag/AgClO$_4$) [FIGURE 2(a)]. After UV irradiation for 30 min, the photoisomerization was equilibrated. The *syn*-composition of the mixture was almost 40% determined by the UV spectrum, if the syn-isomer had no absorbance at 380 nm. The cyclic voltammetry of the mixture of *syn*- and *anti*-isomer was closely similar to that of **Q-A**. The mixture showed $E^1_{1/2}$=-1.09 V and $E^2_{1/2}$=-1.51 V [FIGURE 2(b)]. It showed that the reduction potentials of the *syn*-isomer were in a more anodic region than those of the *anti*-isomer.

Recently, Newell and Utley reported similar interdependence in the electrochromism and photochromism of 2-(2-arylvinyl)-9,10-anthraquinones, whose *anti- and syn*-isomers had different reduction potentials.[4] Magnitudes of those differences in reduction potential are on a similar order to the results of 2-arylazo-9,10-anthraquinone.

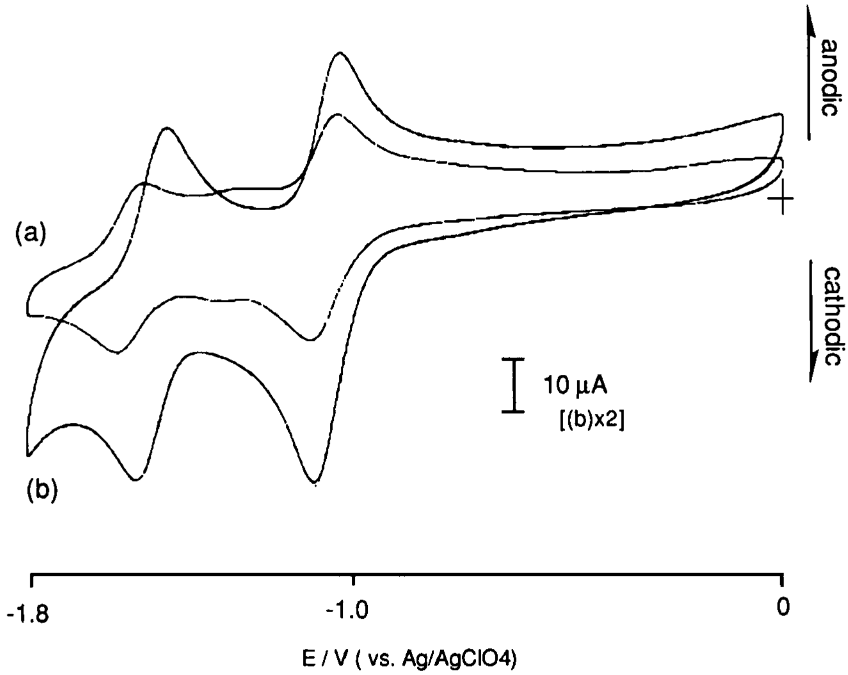

FIGURE 2 Cyclic voltammograms before (a) and after (b) irradiation at 380 nm.

The above results showed that the reduction potentials were switched by the photoisomerization. Considering thermal stabilities of the photoisomers are changed by the electrochemical states,[1] it is clear that photochromic and electrochromic properties are mutually controllable in this multi-mode chemical transducer.

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