

**A MULTI-MODE CHEMICAL TRANSDUCER 1
NEW CONJUGATED FUNCTION OF PHOTOCHROMISM AND
ELECTROCHROMISM OF AZO-QUINONE COMPOUND**

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Abstract : A new class of chemical transducer, azo-quinone (1) shows both electrochromism and photochromism. Moreover, the rate of thermal decay of cis-form was dependent on quinone region.

Since F. L. Carter proposed the concept of a "molecular electronic device",¹ various advanced, both theoretical and experimental, approaches to the promising device have been beginning to take shape with wide interests in science and technology. Regarding a responsive function of a molecule as a basic action of the device, numerous molecules showing appropriate structure changes responsive to an external stimulation, e.g., light, electron transfer, electric and magnetic field, etc., have been investigated.² These molecules can be recognized as a chemical transducer from the input signal of one stimulation to the output signal of another due to its molecular structural changes. However, such conventional chemical transducers show single transformation mode responded by a respective stimulation. In order to design a molecule for the coming chemical transducer, one will be forced not only to improve the intrinsic functions by synthesizing its derivatives but also to gift highly-integrated transformation modes to one molecule. As to one of the latter approaches, we are demonstrating a new class of chemical transducer, which has multiple transformation modes by independent stimulations, and consequently, whose response by one stimulation can be regulated by another stimulation. The basic requirements are as follows. (1) The molecule has multiple regions, i.e., functional groups, responsive independently to stimulations. (2) These regions have some interactions through conjugated system between them. Consequently, a molecule with n responsive regions would have 2^n states corresponding to n transformation processes for every independent stimulation. Also, all the transformation mode would be dependent each other. The independent signal transformation is termed as conjugated functions.

Based on the above concept, we have investigated the conjugated transformation of multi-mode chemical transducer, 2-(4'-methoxyphenylazo)-anthraquinone (**1**),³ having an electrochromic quinone region and a photochromic azo region in conjugated system. (**1**) was obtained from 2-aminoanthraquinone by azo-coupling with phenol, followed by methylation of phenolic hydroxyl group. In this paper, all the states are abbreviated by **Q-A**, **Q-S**, **HQ-A**, and **HQ-S**, where **Q**, **HQ**, **A**, and **S** denote quinone-, hydroquinone-, anti-, and syn-forms, respectively. (Fig. 1)

Firstly, the cyclic voltammogram of (**1**) had two reversible redox waves at $E_{1/2} = -0.69$ V and -1.21 v.s. SCE in DMF containing 0.1 mol/l tetrabutylammonium fluoroborate, characteristic of a usual quinone compound. In thin layer electrolysis of the anti-type (**1**), clear electrochromism between quinone- and hydroquinone-forms (**Q-A** \rightleftharpoons **HQ-A**) through its semiquinone radical intermediate was observed.⁴ When **Q-A** in CHCl_3 (3.15×10^{-5} mol/l) was irradiated at 380 nm (incident photon flux $= 10^{-10}$ einstein/sec), the characteristic absorption bands at 340 nm and 390 nm decreased accompanied with distinct isosbestic points at 316 nm and 416 nm and the absorbance around 500 nm increased slightly (Fig. 2(a)). This spectrum change implied that the converted compound was to be **Q-S**. The **Q-S** was completely converted back to the **Q-A** under irradiation at 500 nm. The reversible photochromism was due to photoisomerization of azo group between anti- and syn-forms in quinone-type (**1**). The **HQ-A**, obtained by reductive electrolysis or by chemical reduction with NaBH_4 ,⁵ also showed another photochromism, different from that of quinone-type (**1**). Under irradiation at 350 nm in CHCl_3 (1.61×10^{-5} mol/l), the absorbance at 354 nm decreased with isosbestic points at 308 nm and 415 nm and a new broad absorption band around 445 nm appeared (Fig. 2(b)). This spectrum change suggested that the converted compound was to be **HQ-S**. It was reversibly converted back to **HQ-A** under irradiation at 500 nm. These observations confirmed that (**1**) had 4 ($= 2^2$) distinguishable states corresponding to redox states of the quinone-hydroquinone region and geometric isomers of the azo regions. Consequently, (**1**) has been shown to have remarkable properties of chemical transducer operating in dual modes, electrochromism and photochromism (Fig. 1).

Secondly, both electrochromism and photochromism were expected to affect one another since the quinone-region was linked to the azo-region through conjugated system. All the photochromism from **Q-S** to **Q-A** was apparently 30 times faster than that from **HQ-S** to **HQ-A**. In the thermal isomerization from syn- to anti-forms, a distinct interdependent transformation was observed. The syn-anti thermal isomerization of quinone-type (**1**) proceeded with rate constant $4.3 \times 10^{-4} \text{ sec}^{-1}$, while that of hydroquinone type (**1**) did $1.2 \times 10^{-5} \text{ sec}^{-1}$ at 25°C . The quite difference of

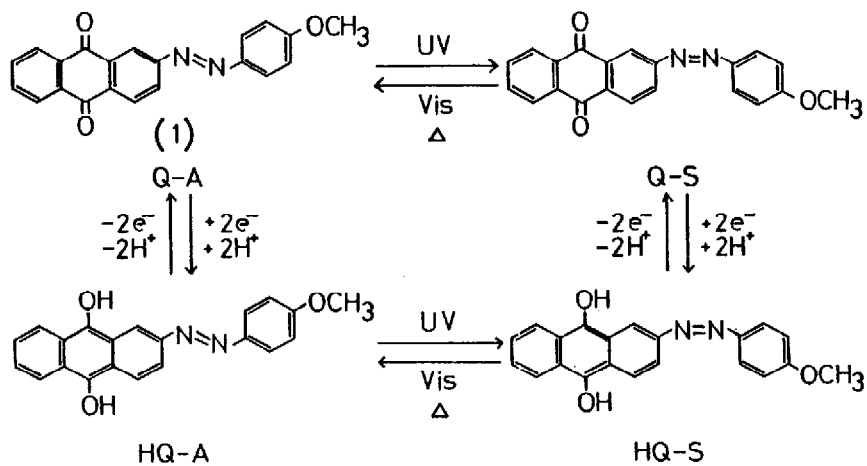


Fig. 1 Interconversion of (1).

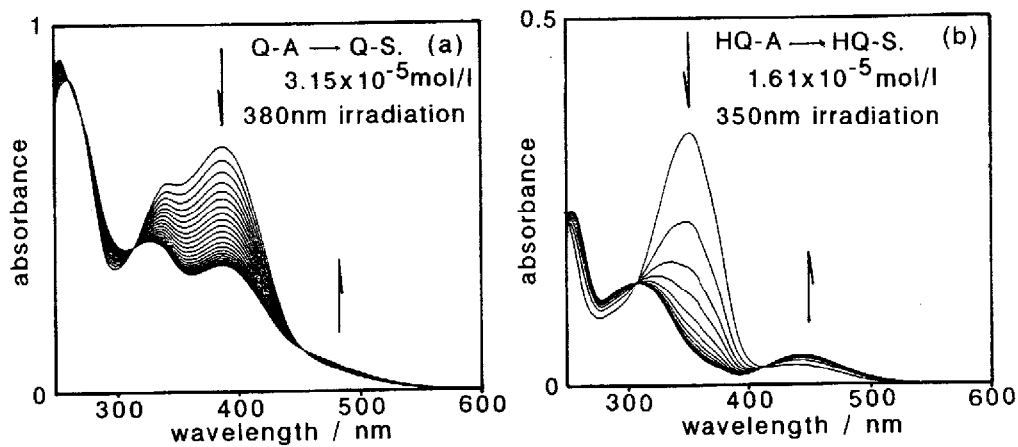


Fig. 2 Photochromism of (1) in CHCl₃.
Measurements were done in every 1 min.

the rates indicated that thermal isomerization of the azo region was affected electronically by redox states of the quinone region.

These characteristics of the present multi-mode chemical transducer afford two memory modes. Electrochromic mode is applied thermally irreversible memory. On the other hand photochromic mode is applied thermally unstable memory. Thus the former can be compared to "deep" memory and the latter to "shallow" one. Moreover, photochromic mode may be applicable to another dual-mode memory; one is "shallow" memory mode for quinone-type photochromism and the other is "deep" memory mode in hydroquinone-type one by their stabilities. The present concept will have potential extensions to other responsive functions and provides one of the basic strategies to lead to molecular device. The design of the multiple and interdependent chemical transducer is taking a step forward to gift some logic functions to a molecule.

Acknowledgment

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References and Notes

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2. (a) G. H. Brown ed., "Techniques of Chemistry, Vol III, Photochromism", Wiley-Interscience (1971). (b) Y. Hirschberg, *J. Am. Chem. Soc.*, **78**, 2303(1956). (c) C. J. Schoot, *Appl. Phys. Lett.*, **23**, 2(1973). (d) J. R. Platt, *J. Chem. Phys.*, **34**, 862(1961).
3. (1) was obtained as orange needle crystals. : m.p. 232°C. Anal. Calcd for $C_{21}H_{14}N_2O_3$: C, 73.68; H, 4.12; N, 8.16. Found: C, 73.46; H, 3.87; N, 8.15%. 1H -NMR($CDCl_3$) δ ppm: 3.95(3H,s), 7.05(2H,d), 7.83(2H,d,t), 8.02(2H,d), 8.23(1H,d,d), 8.36(2H,d,d). IR(KBr) $1/\lambda$ cm^{-1} : 2940, 1680, 1590, 1500, 1410, 1330, 1295, 1258, 1145, 1020, 935, 842, 715.
4. The semiquinone radical of anti-type (1) was confirmed by ESR spectroscopy ($g=2.004$, line width=4.3G) at -0.8 V v.s. SCE in same DMF solution as the cyclic voltammogram. Preliminary experiments showed that the cyclic voltammogram of (1) under irradiation at 350 nm was slightly different from that of the anti-type (1). A precise cyclic voltammogram of the syn-type (1) is now being obtained.
5. HQ-A : 1H -NMR($CDCl_3$) δ ppm: 3.95(3H,s), 7.41(2H,d,t), 7.02(2H,d), 7.70(2H,d,d), 7.79(1H,d), 7.88(1H,d,d), 7.94(2H,d), 8.16(1H,d). IR(KBr) $1/\lambda$ cm^{-1} : 3200, 2950, 2860, 1600, 1505, 1420, 1300, 1260, 1150, 1105, 840, 760.

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