Multi-mode Chemical Transducers. Part 2.[1] Electrochromic and Photochromic Properties of Azoquinone Compounds

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Several molecules having multiple regions independently responsive to stimulations have been investigated. A 2-(4-methoxyphenylazo)anthraquinone (**1**) having both an electrochromic quinone group and a photochromic azo group has been synthesized and its electrochromic and photochromic properties investigated. It shows 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. Moreover the *syn–anti* thermal isomerization rate of the azo region of the molecule is dependent on the state of the electrochromic quinone region. The rate for the quinone form is more than 30 times faster than that of the hydroquinone form. Additionally three other azoquinone compounds have been synthesized and investigated in the same way. The results show that these molecules have functions of multiple responsibilities for distinguishable stimulations as multi-mode chemical signal transducers.

The direction electronic technology is pursuing is towards making more miniaturized and more accumulated electronic devices. Carter proposed the concept of 'molecular electronic devices'[2] that will pass over the minimal limit of micro photolithography. Since then there have been significant advances, both theoretical and experimental, such that it may be possible to develop devices of the size of individual molecules. Owing to the increasing interest in molecular electronic devices, the responsive functions of molecules which can be switched from one configuration to another by external stimulations have been receiving attention as basic actions of future devices. There have been many investigations of configuration change in molecules, *e.g.* photochromic,[3–5] electrochromic,[6] thermochromic,[7] piezochromic,[8,9] *etc.* by external stimulation, *e.g.* light, electron transfer, thermal energy, physical force, *etc.* In other words, these molecules work as chemical transducers which transform the input signal into the output signal by configuration changes. In particular, molecules whose configuration is changeable by light or electronic stimulation have been investigated as basic functions of molecular electronic devices.

However, such conventional chemical transducers have been considered to work in single transformation mode, responding to a respective stimulation. For the purpose of realizing a more accumulated device, it is important that the molecule has multiple transformation modes. A molecule with multiple integrated transformation functions will give the device a higher information processing ability than that of a single function one; moreover a new logic function should be expected to appear. Fig. 1 shows a typical case of the interconversion of a molecule with two integrated transformable functions. A functional group 1, whose conformation responds to an external stimulation 1 from A to A′, and functional group 2, which responds to another external stimulation 2 from B to B′, are combined through a spacer. Because each of the functional groups has two configurations responsive to independent external stimulations, the molecule has four distinct configurations, AB, A′B, AB′ and A′B′. Although the functional groups each respond to independent external stimulations, there would be some perturbation between their interconversion processes.

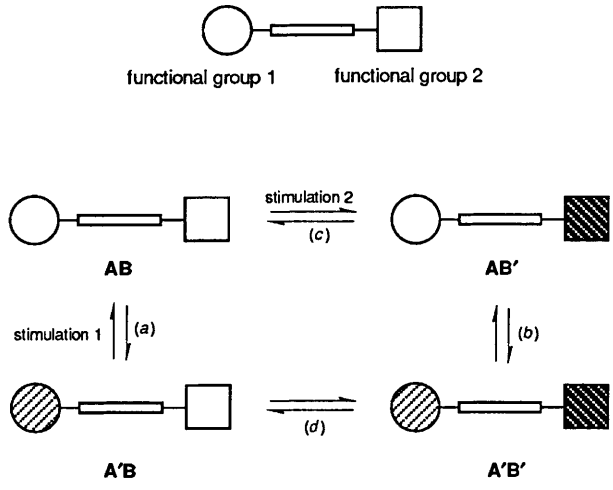

Fig. 1 Interconversion of a molecule containing two transformable functions

For example, path *a* shows different nature from path *b*, because the two conformations of functional group 2, B and B′, have different interactions with functional group 1. Paths *c* and *d* show different natures, in the same way as paths *a* and *b*. Consequently, it can be said that a molecule with *n* responsive groups has 2^n conformations corresponding to *n* transformation modes for each independent external stimulation. In addition, the transformation natures are qualitatively independent and quantitatively dependent. The molecule can be named a multi-mode chemical transducer.

For the purpose of synthesizing a model molecule to materialize our concept of a multi-mode chemical transducer, we chose anthraquinone as an electrochromic group and azobenzene as a photochromic group, because a quinone form and a hydroquinone form in the redox system are stable enough to be isolated[10] and *trans–cis* photoisomerization of the azobenzene shows a large stereochemical change.[11] In a preliminary communication, we have reported the electrochromic and the photochromic properties of an azoquinone compound, 2-(4-methoxyphenylazo)anthraquinone.[1] The present paper contains a more detailed investigation on the remarkable properties of the azoquinone compound as a

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chemical transducer operating in dual modes, both electrochromism and photochromism, and, in addition, those of other three azoquinone compounds.

Experimental

Materials.—2-(4-*Methoxyphenylazo*)*anthraquinone* (**1**, Q–A). Sodium nitrite (568 mg, 8.32 mmol) was added portionwise to a mixture of 2-aminoanthraquinone (1.784 g, 8 mmol) in 10 cm^3 of concentrated sulfuric acid and 0.5 cm^3 of water and stirred at room temperature for 30 min. The reaction mixture was then poured into 200 cm^3 ice-water. The precipitated diazonium sulfate was washed with cold saturated aqueous sodium sulfate. The filtered cake was added to a solution of phenol (752 mg, 8 mmol) in 100 cm^3 of 0.1 mol dm^{-3} sodium hydroxide solution containing 50 g of sodium acetate. After standing for 1 h, the precipitate was collected by filtration. The precipitate was washed with water and dried *in vacuo* (2.20 g, 83%).

Dimethylsulfate (0.5 cm^3) was added to a suspension of 2-(4-hydroxyphenylazo)anthraquinone (2.02 g, 6.71 mmol) in 200 cm^3 of 1 mol dm^{-3} sodium hydroxide at 40 °C and stirred for 1 h. The precipitate was collected by filtration and washed with water. The filtrate was purified by column chromatography on silica gel and recrystallization from chloroform. **1**, Q–A was obtained as orange needles (1.48 g, 64%, m.p. > 300 °C) (Found: C, 73.6; H, 4.1; N, 8.15. Calc. for $C_{21}H_{14}N_2O_3$: C, 73.68; H, 4.12; N, 8.16%.) $\delta_H(CDCl_3)$ 3.97 (3 H, s), 7.06 (2 H, d, *J* 9.9), 7.82 (1 H, dd, *J* 8.0 and 4.0), 7.84 (1 H, dd, *J* 8.0 and 4.0), 8.02 (2 H, d, *J* 9.9), 8.23 (1 H, dd, *J* 9.8 and 2.0), 8.33–8.38 (2 H, m), 8.46 (1 H, d, *J* 8.0) and 8.75 (1 H, d, *J* 2.0); $\delta_C(CDCl_3)$ 182.82 (C=O); ν_{max}(KBr)/cm^{-1} 1680 (C=O).

2-(4-*Methoxyphenylazo*)*anthracene-9,10-diol* (HQ–A). Sodium borohydride (55 mg, 1.46 mmol) was added to a solution of Q–A, (500 mg, 1.462 mmol), in 200 cm^3 tetrahydrofuran and 50 cm^3 propan-2-ol and stirred for 1 h. The residue after concentration of the reaction mixture was diluted with water and extracted with chloroform. The organic phase was dried (sodium sulfate) and evaporated *in vacuo*. Usual work-up followed by silica gel column chromatography gave HQ–A as light orange crystals (320 mg, 63%, m.p. > 300 °C) (Found: C, 73.6; H, 4.1; N, 8.15. Calc. for $C_{21}H_{16}N_2O_3$: C, 73.68; H, 4.12; N, 8.16%.) $\delta_H(CDCl_3)$ 3.95 (3 H, s), 7.02 (2 H, d, *J* 9.9), 7.40 (1 H, dd, *J* 8.0 and 4.0), 7.42 (1 H, dd, *J* 8.0 and 4.0), 7.65–7.72 (2 H, m), 7.79 (1 H, d, *J* 8.9), 7.89 (1 H, dd, *J* 8.9 and 2.0), 7.94 (2 H, d, *J* 9.9) and 8.16 (1 H, d, *J* 1.0); ν_{max}(KBr)/cm^{-1} 3400 (br, OH).

2-(4-*Acetoxynaphthylazo*)*anthraquinone* (**2**). **2** was synthesized by a diazo-coupling of the anthraquinone-2-diazonium salt with 1-naphthol according to the same procedure as **1** followed by acetylation with acetyl chloride in pyridine. Usual work-up followed by silica gel column chromatography gave **2** as red needles (m.p. > 300 °C) (Found: C, 74.5; H, 3.6; N, 6.65. Calc. for $C_{26}H_{16}N_2O_4$: C, 74.46; H, 3.85; N, 6.68%.) δ_H ($CDCl_3$) 4.13 (3 H, s), 6.96 (1 H, d, *J* 8.3), 7.61 (1 H, ddd, *J* 8.4, 4.0 and 1.0), 7.73 (1 H, ddd, *J* 8.4, 4.0 and 1.0), 7.79–7.86 (2 H, m), 8.06 (1 H, d, *J* 8.4), 8.28–8.39 (3 H, m), 8.49 (1 H, d, *J* 8.3), 8.85 (1 H, d, *J* 2.0) and 9.04 (1 H, d, *J* 8.4).

2-(4-*Dimethylaminophenylazo*)*anthraquinone* (**3**). **3** was synthesized by a diazo-coupling of the anthraquinone-2-diazonium salt with dimethylaniline according to same procedure as **1**. Usual work-up followed by silica gel column chromatography gave **3** as red needles, m.p. 264–269 °C (Found: C, 74.2; H, 4.85; N, 11.75. Calc. for $C_{22}H_{17}N_3O_2$: C, 74.35; H, 4.82; N, 11.82%.) $\delta_H(CDCl_3)$ 3.14 (6 H, s), 6.78 (2 H, d, *J* 9.2), 7.81 (1 H, dd, *J* 7.8 and 3.9), 7.83 (1 H, dd, *J* 7.8 and 3.9), 7.96 (2 H, d, *J* 9.2), 8.19 (1 H, dd, *J* 8.4 and 2.0), 8.32–8.38 (2 H, m), 8.42 (1 H, d, *J* 8.4) and 8.71 (1 H, d, *J* 2.0).

2-(4-*Dimethylaminonaphthylazo*)*anthraquinone* (**4**). **4** was synthesized by a diazo-coupling of the anthraquinone-2-diazonium salt with 4-dimethylaminonaphthalene according to the same procedure as **1**. Usual work-up followed by silica gel column chromatography gave **4** as red-violet needles, m.p. 238 °C (Found: C, 77.3; H, 4.65; N, 10.1. Calc. for $C_{26}H_{19}N_3O_2$: C, 77.02; H, 4.72; N, 10.37%.) $\delta_H(CDCl_3)$ 3.08 (6 H, s), 7.10 (1 H, d, *J* 9.0), 7.58 (1 H, ddd, *J* 7.8, 6.8 and 1.0), 7.68 (1 H, ddd, *J* 7.7, 6.8 and 1.0), 7.55 (1 H, dd, *J* 7.0 and 3.5), 7.81 (1 H, dd, *J* 7.0 and 3.5), 8.01 (1 H, d, *J* 8.4), 8.22 (1 H, dd, *J* 7.7 and 1.0), 8.32–8.40 (3 H, m), 8.48 (1 H, d, *J* 8.0), 8.85 (1 H, d, *J* 2.0) and 9.08 (1 H, dd, *J* 7.7 and 1.0).

Spin-coating of **1** *+ Polymer Solution to Prepare Immobilized Films.*—*Q–A/PAN film.* A Q–A (171 mg) was dissolved in a solution of polyacrylonitrile (PAN, 2 g) on dimethylformamide (DMF, 100 cm^3). The mixture was spin-coated on quartz glass (2.5 cm × 5 cm) at 2000 rpm.

HQ–A/PAN film. A HQ–A/PAN coated quartz glass was prepared in same way as Q–A/PAN film from HQ–A (516 mg).

Q–A/PMMA film. Q–A (300 mg) was dissolved in a solution of polymethyl methacrylate (PMMA 3 g) in dichloroethane (100 cm^3). The mixture was spin-coated on a quartz glass (2.5 cm × 5 cm) at 2000 rpm.

HQ–A/PMMA film. A HQ–A/PMMA coated quartz glass was prepared in same way as Q–A/PMMA film from HQ–A (400 mg).

Other chemicals were reagent grade samples and were used as received without further purification.

General Procedure.—Absorption spectra were recorded on a Shimadzu MPS-2000 spectrophotometer. Proton and carbon NMR spectra were recorded in [^{2}H]chloroform on a JEOL FX-270 spectrometer. All chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane (TMS) and coupling constants in Hz. EPR spectra were recorded on a JEOL JES-3X spectrometer operating with 100 kHz magnetic field modulation.

Cyclic voltammograms were recorded on a Nikko Keisoku potentio-galvanostat DPGS-1 and a function generator NFG-3. A three-electrode system, consisting of platinum wire working and counter electrodes and a saturated calomel electrode (SCE) as reference, was adopted. The electrolytic solvent was DMF containing 0.1 mol dm^{-3} tetrabutylammonium fluoroborate ($TBABF_4$) as supporting electrolyte. A transparent indium–tin oxide coated glass (ITO glass) was used as a working electrode in spectroscopic measurements. Photoisomerization was performed by a 500 W Xenon lamp (Ushio 500D) associated with a monochromator (Nihon Bunko CT25N) as a light source.

Results and Discussion

Synthesis.—The azoquinone compounds **1**–**4** were prepared by diazo coupling from 2-aminoanthraquinone. These compounds have a conjugated system of anthraquinone region and azobenzene region sharing a benzene-ring. According to the present concept, they should have four distinct forms responding to electrochromism and photochromism. First, we describe the case of **1**, because it showed the most typical behaviour as a multi-mode chemical signal transducer. Its four distinct forms are expressed as Q–A, Q–S, HQ–A and HQ–S, where Q, HQ, A and S denote quinone-, hydroquinone-, *anti*- and *syn*-form (Fig. 2). The reduced form of **1**, HQ–A, 2-(4-methoxyphenylazo)anthracene-9,10-diol, was obtained from Q–A by chemical reduction with sodium borohydride.

Electrochromism of **1**.—Anthraquinone undergoes a reversible two-step redox reaction from quinone to hydroquinone dianion with two electrons, *via* a semiquinone radical in aprotic solvents such as DMF.[10] Q–A showed similar electrochemical

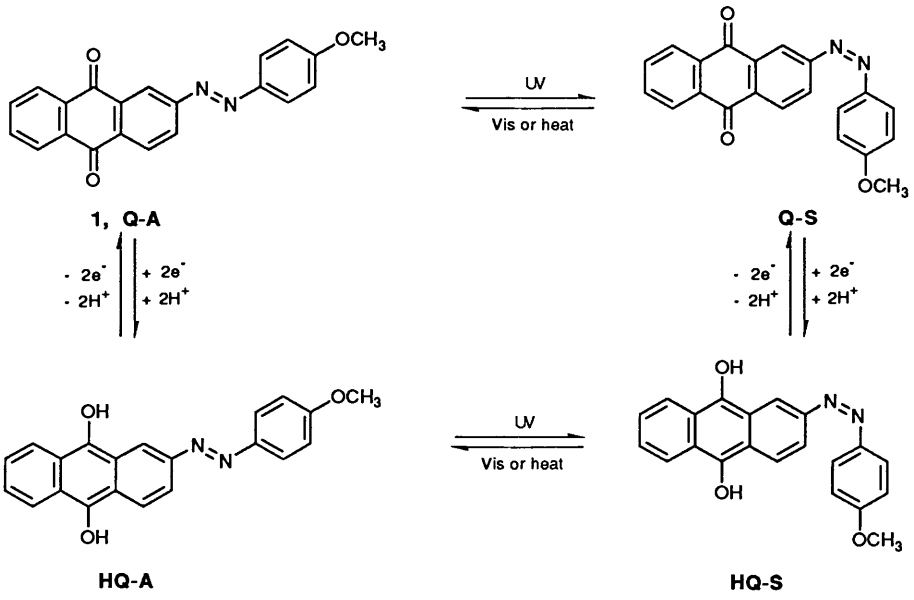
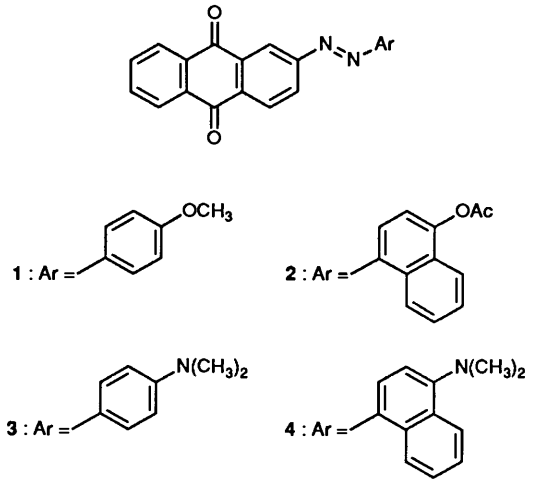


Fig. 2 Interconversion of the four forms of **1**



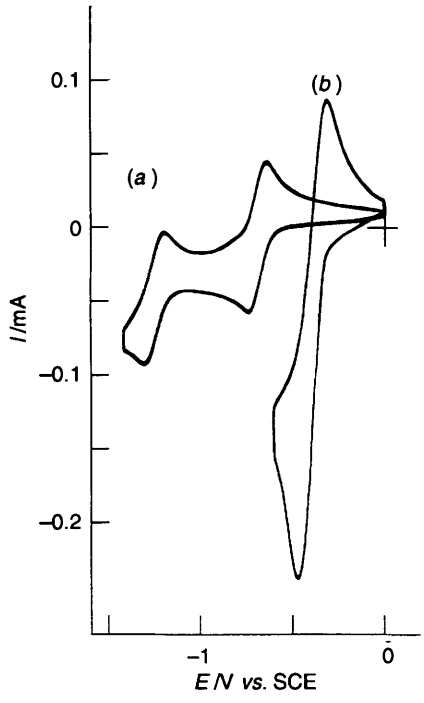


Fig. 3 Cyclic voltammograms of Q–A in DMF containing (*a*) 0.1 mol dm^{-3} $TBABF_4$ and (*b*) 0.01 mol dm^{-3} H_2SO_4

behaviour. Fig. 3(*a*) shows the cyclic voltammogram of Q–A obtained in a saturated solution of DMF containing $TBABF_4$ (0.1 mol dm^{-3}) by using platinum wires as working and counter electrodes and SCE as reference. This cyclic voltammogram shows two reversible redox waves at $E^1_{\frac{1}{2}} = -0.69$ V and $E^2_{\frac{1}{2}} = -1.21$ V *vs.* SCE. These two redox waves indicated that the quinone regions of the azoquinone compounds were reduced to hydroquinone dianion, $HQ\text{–}A^{2-}$, *via* the semiquinone radical.[12,13] The semiquinone radical of Q–A was confirmed by EPR spectroscopy ($g = 2.004$, line width = 4.3 G) electrolysing at −0.8 V *vs.* SCE in the same DMF solution as used for the cyclic voltammogram. On the addition of sulfuric acid to the electrolytic solution, the above two redox waves disappeared and a new redox wave appeared in the more anodic region.[14,15] Fig. 3(*b*) shows the cyclic voltammogram of Q–A in DMF containing 0.01 mol dm^{-3} sulfuric acid. It shows only one redox wave at $E_{\frac{1}{2}} = -0.36$ V due to a two-electron and two-proton reduction from Q–A to hydroquinone, HQ–A. Additionally, chemically synthesized HQ–A showed the same cyclic voltammograms as those of Q–A.

Fig. 4 shows the electrochromism between Q–A and HQ–A. The spectral changes were observed in thin layer electrolysis by using an ITO glass working electrode. Q–A has two absorption maxima at 340 nm and 388 nm. On stepping the electrode potential from −0.5 V to −1.2 V, these absorption maxima were decreased and a new absorption band appeared at 360 nm showing a distinct isosbestic point at 375 nm. The new absorption maximum at 360 nm was in agreement with the absorption maximum of chemically synthesized HQ–A. The broad absorption band in the long wavelength region was attributed to its semiquinone radical. After the electrode potential was returned to −0.5 V, the absorption spectrum was replaced by Q–A.

Photochromism of **1**.—Azobenzene shows an absorption spectrum change in *trans–cis* photoisomerization.[8] Fig. 5 shows the photochromic properties of Q–A and HQ–A, originating in the azobenzene regions. On irradiation at 380 nm, the characteristic absorption maxima of Q–A in chloroform (3.15×10^{-5} mol dm^{-3}) at 340 nm ($\varepsilon = 16\,500$) and 390 nm ($\varepsilon = 17\,700$) decreased, accompanied by distinct isosbestic

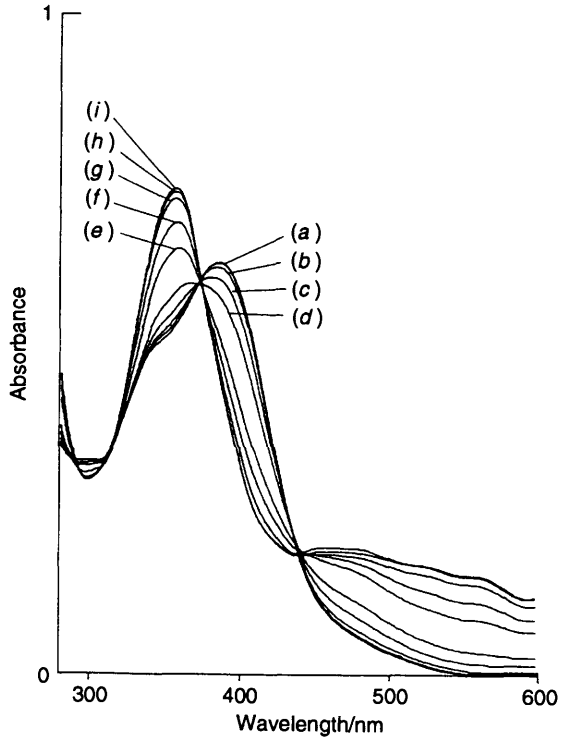


Fig. 4 Absorbance spectra showing the change from Q–A to HQ–A on stepping the electrode potential from −0.5 (*a*) to −1.2 V (*i*)

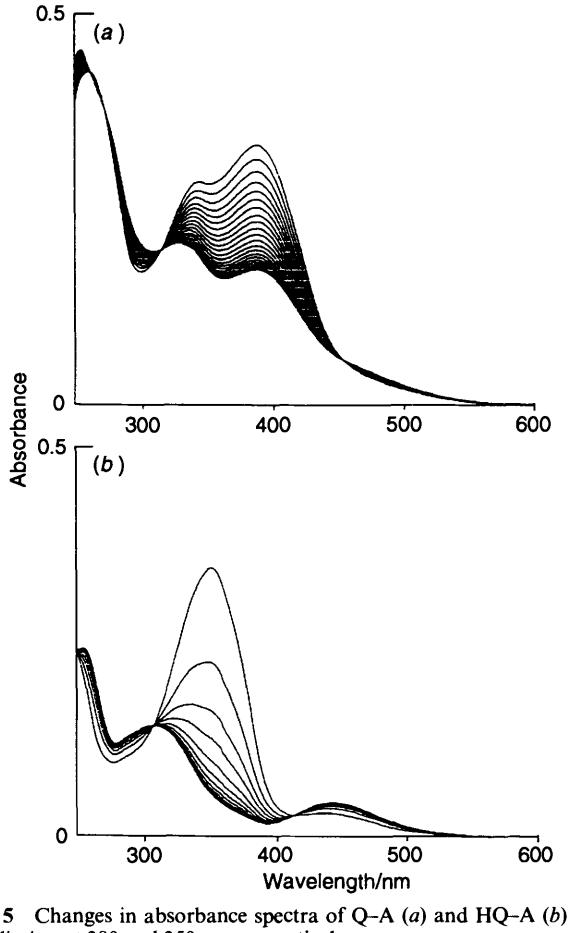


Fig. 5 Changes in absorbance spectra of Q–A (*a*) and HQ–A (*b*) on irradiation at 380 and 350 nm, respectively

points at 316 nm and 416 nm and the absorbance around 500 nm increased slightly [Fig. 5(*a*)]. This spectrum change implied that the converted compound was the *syn* form, Q–S. It was

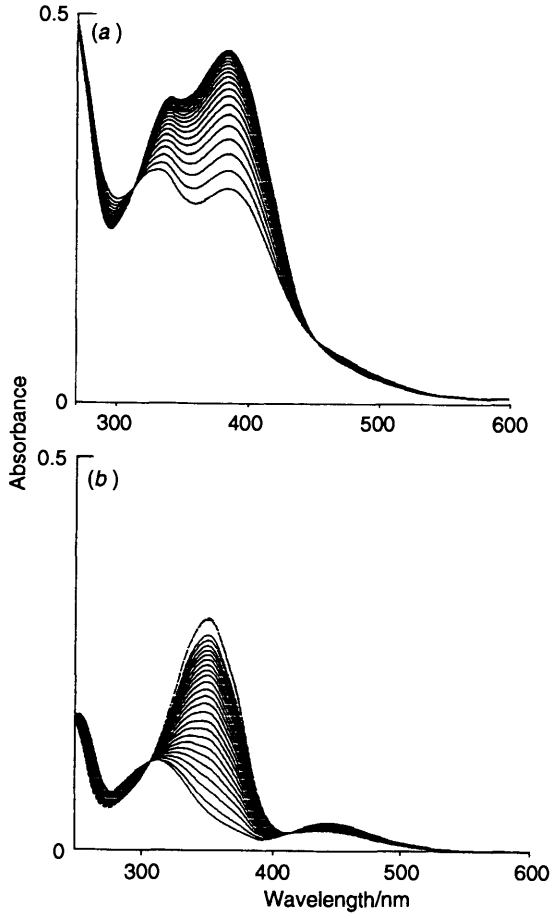


Fig. 6 Changes in absorbance spectra of Q–S (*a*) and HQ–S (*b*) in chloroform at 30 °C

completely converted back to Q–A under irradiation at 500 nm. In contrast, HQ–A showed another photochromism. The absorption maximum of HQ–A in chloroform (1.61×10^{-5} mol dm^{-3}) at 354 nm decreased, with isosbestic points at 308 nm and 415 nm, and a new broad absorption band around 445 nm appeared under irradiation at 350 nm [Fig. 5(*b*)]. This spectrum change suggested that the converted compound was the *syn* form, HQ–S. It was reversibly converted back to HQ–A under irradiation at 500 nm. Both Q–A and HQ–A showed photochromism in methanol and in acetone similar to those in chloroform.

Interdependence of Functions.—These electrochromic and photochromic observations confirmed that the azoquinone compound had 4 ($=2^2$) distinct states corresponding to redox states of the quinone-hydroquinone regions and geometrical isomers of the azo regions (Fig. 2). Consequently, the compound has been shown to have remarkable properties of chemical transducer operating in dual modes, electrochromism and photochromism, according to the present concept.

Both electrochromism and photochromism were expected to be affected by one another, since the quinone group was linked to the azo group *via* a conjugated system. In the thermal isomerization from *syn* forms to *anti* forms, a distinct interdependence was observed. Fig. 6 shows the thermal isomerization behaviour from *syn* to *anti* conformation in chloroform at 30 °C. Fig. 6(*a*) shows thermal isomerization from Q–S to Q–A recorded every 5 min; it was finished within 100 min. On the other hand, Fig. 6(*b*) shows that from HQ–S to HQ–A recorded every 100 min; it needed more than 3000 min to finish. Table 1 shows $k(\equiv k_{syn\rightarrow anti})$ values and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values calculated by

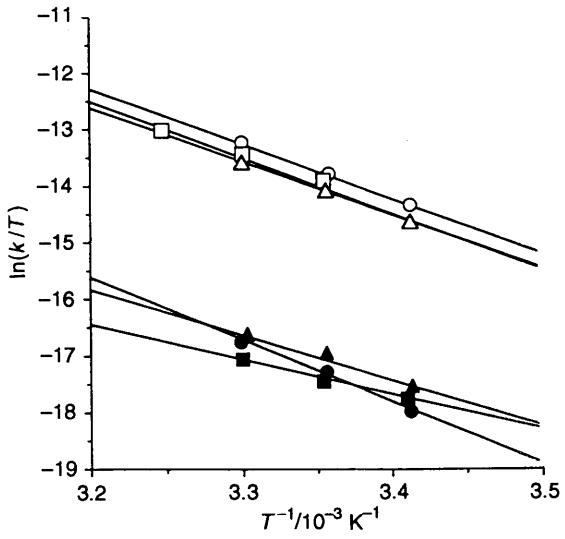


Fig. 7 Eyring plots for thermal isomerization of Q–S (empty symbols) and HQ–S (filled symbols)

Table 1 Solvent effect on the thermal isomerization

	Solvent	k/s^{-1}	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J mol^{-1} K^{-1}
Q–S → Q–A	$CHCl_3$	4.33×10^{-4}	78.9	−49.2
	Me_2CO	3.90×10^{-4}	78.0	−52.9
	MeOH	5.44×10^{-4}	90.4	−42.5
HQ–S → HQ–A	$CHCl_3$	1.19×10^{-5}	51.2	−170.2
	Me_2CO	1.69×10^{-5}	67.2	−113.6
	MeOH	1.62×10^{-5}	91.1	−36.0

Table 2 Thermal isomerization rate of *syn* to *anti* form

	$k_{23\,°C}$/s^{-1}	
	Q–S → Q–A	HQ–S → HQ–A
$CHCl_3$	2.06×10^{-4}	7.36×10^{-6}
PMMA	4.47×10^{-4}	1.01×10^{-5}
PAN	8.83×10^{-4}	1.78×10^{-5}

Eyring plots (Fig. 7) of thermal isomerization of Q–S and HQ–S measured at several temperatures in chloroform, methanol and acetone. These rate constants showed that the thermal isomerization from Q–S to Q–A was apparently more than 30 times faster than that from HQ–S to HQ–A in each solvent.

The $\Delta H^{\ddagger}$ and the $\Delta S^{\ddagger}$ values of Q–S in each solvent were typical for azobenzene compounds.[16-18] On the other hand those of HQ–S showed strong solvent effect. The k value (1.19×10^{-5} s^{-1}) of HQ–S in $CHCl_3$ was smaller than the k value of Q–S (4.33×10^{-4} s^{-1}), in spite of the $\Delta H^{\ddagger}$ value (51.2 kJ mol^{-1}) of HQ–S being smaller than that of Q–S (78.9 kJ mol^{-1}). This big difference in thermal isomerization implied that the thermal stability of the azo region might be affected electronically by the redox state of the quinone region.

This multi-mode functional property of **1** appeared in the same manner in some polymer matrices as in solution. The cyclic voltammogram of **1** immobilized in PAN on platinum wire showed a two-step reversible redox wave caused by the redox of the anthraquinone region with half-wave potentials at $E^1_{\frac{1}{2}} = -0.78$ V and $E^2_{\frac{1}{2}} = -1.02$ V *vs.* SCE in propylene-carbonate containing 0.1 mol dm^{-3} $TBABF_4$. Fig. 8 shows the photochromic properties of Q–A/PAN and HQ–A/PAN film

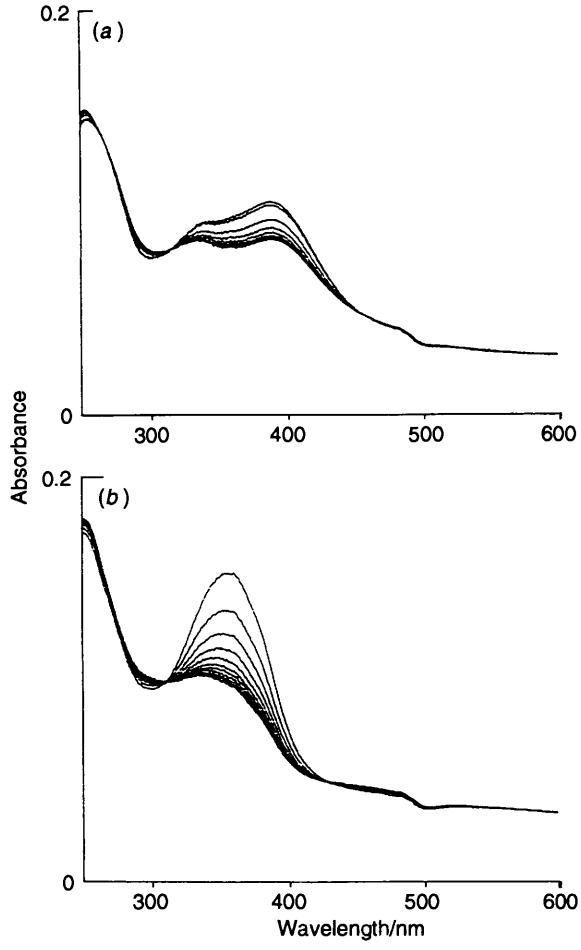


Fig. 8 Changes in absorbance spectra of Q–A/PAN (*a*) and HQ–A/PAN (*b*) on irradiation

spin-coated on quartz glass and Table 2 shows the thermal isomerization rates of Q–S and HQ–S in PAN and PMMA matrixes. These rate constants showed that the thermal isomerization from Q–S to Q–A was also 30 times faster than that from HQ–S to HQ–A in each polymer matrix, as in solution.

Recently, Newell and Utley reported another interdependence in the electrochromism and photochromism of 2-(2-arylvinyl)-9,10-anthraquinones, whose *trans–cis* isomers had different reduction potentials.[19] In this azoquinone compound, a dependence of the redox properties on the photochromic isomer was not observed in DMF electrolyte.

Electrochromic and Photochromic Properties of Other Compounds.—When considering using semiconductor laser light in reading and writing of optical memory, a material having an absorbance in the near-infrared region is favourable. Unfortunately the absorbances of **1** were in the ultraviolet–visible region. Therefore, compounds **2**, **3** and **4** were synthesized in the expectation that they should have absorbances in longer wavelength region than **1**, because of the long conjugated system of the naphthyl group and/or the strong acceptor ability of dimethylamino groups. Cyclic voltammograms of **2**, **3** and **4**, showed reversible two-step redox processes assigned to the anthraquinone group. Table 3 shows the half-wave potentials of these in DMF containing 0.1 mol dm^{-3} $TBABF_4$ and the absorption maxima of their electrochromic isomers in thin layer electrolysis by using an ITO glass working electrode. Figs. 9, 10 and 11 show photochromic absorption spectra change of **2**, **3** and **4** in $CHCl_3$. In the case of **2**, absorption maxima at 331 nm (ε = 16 200) and 408 nm (ε = 19 300) were decreased by

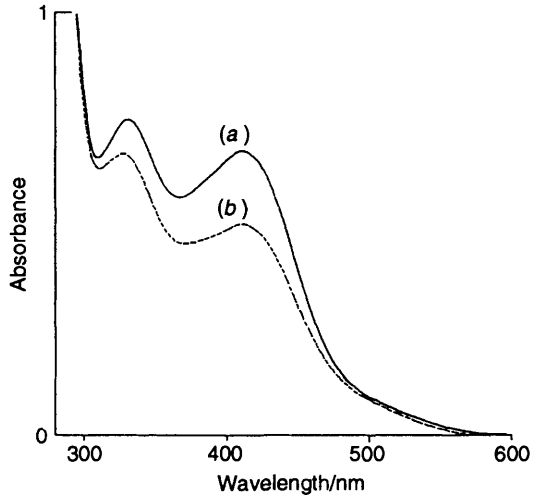


Fig. 9 Absorbance spectra of **2** before (*a*) and after (*b*) irradiation at 410 nm

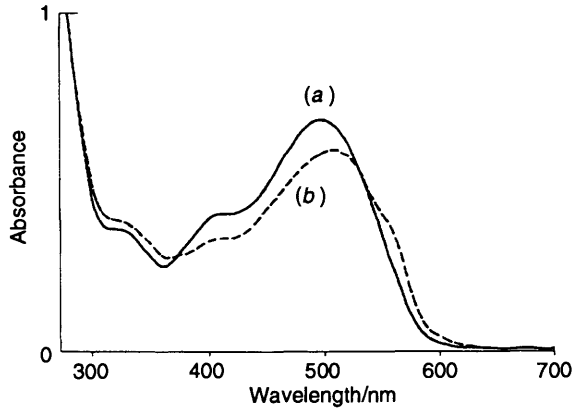


Fig. 10 Absorbance spectra of **3** before (*a*) and after (*b*) irradiation at 500 nm

Table 3 Half-wave potentials and absorption maxima of quinone and hydroquinone forms of azoquinone compounds in 0.1 mol dm^{-3} $TBABF_4$/DMF

Compound	$E^1_{\frac{1}{2}}$/V	$E^2_{\frac{1}{2}}$/V	λ_{max}Q/nm	λ_{max}HQ/nm
1	−0.690	−1.210	388, 340	360
2	−0.615	−1.121	410	< 330
3	−0.601	−1.201	510	417
4	−0.675	−1.170	500	420

irradiation at 410 nm and then converted back thermally (Fig. 9). In the case of **3**, an absorption maximum at 498 nm (ε = 20 700) was decreased by irradiation at 500 nm and a new shoulder appeared at 560 nm (Fig. 10), implying a thermal back conversion. In the case of **4**, an absorption maximum at 486 nm (ε = 19 300) was decreased slightly by irradiation at 480 nm and absorbance around 600 nm was increased a little (Fig. 11). These absorption changes were due to *anti–syn* isomerization of the azo groups. Compounds **2**, **3** and **4** had absorption bands in longer wavelength regions than that of **1**, so to get an azoquinone compound having absorptions in the infrared region may be possible.

Conclusions

The azoquinone compounds showed the distinctive natures for a multi-mode chemical transducer caused by dual mode, electrochromic and photochromic, conformational changes. In

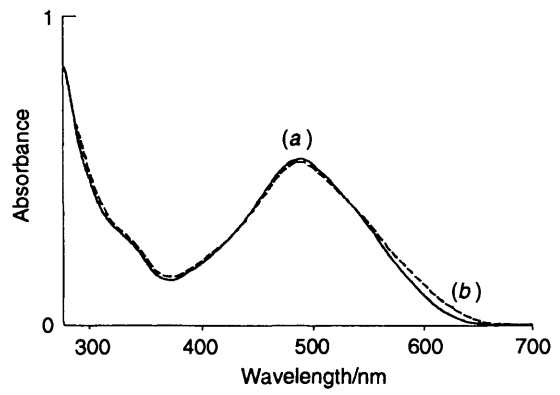


Fig. 11 Absorbance spectra of **4** before (*a*) and after (*b*) irradiation at 480 nm

particular the photochromic mode showed the interdependence, in that the electrochemical state decided the thermal stability of the photochromic metastable species. Therefore the photochromic mode may be applicable to the dual-mode memory; one is a 'shallow' memory mode in the quinone form, and the other is a 'deep' memory mode in the hydroquinone form using the difference of their stabilities. In addition, the photochromic mode has a thermal back reaction and the electrochromic mode has no spontaneous back reaction; accordingly the former can be compared to a shallow memory and the latter to a deep memory. These characteristics of the present multi-mode chemical transducer integrating electrochromism and photochromism may also imply conversion of an electric signal to a light signal and/or a light signal to an electric signal. The present concept will have potential extensions to other responsive functions and provides one of the basic strategies to lead to the molecular device. The design of the multiple and interdependent chemical transducer is taking a step forward to give some logic functions to a molecule.

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