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Journal of Photochemistry and Photobiology A: Chemistry 92 (1995) 91-97

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

Photoelectrochromic properties of a spirobenzopyran derivative

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Abstract

In order to study the possible use of spiro compounds as optically–electrically controllable molecular switches, the electrochemical behavior of the photochromic spiropyran derivative 1,3,3-trimethyl-6-nitrospiro(2H-1-benzopyran-2,2'-indoline) (SP-1) in dimethylformamide (DMF) solution was investigated. The electrochromic behavior, which is associated with a redox process of the nitro group occurring in the potential range of −1.8 V to +0.8 V (vs. Ag quasi- reference electrode (QRE)), was observed at −42 °C by monitoring the absorption spectral changes and potential dependence of the colored species produced on switching the applied potential. Spectroelectrochemical and low-temperature proton nuclear magnetic resonance (^{1}H NMR) measurements revealed that the electrochromism of SP-1 can be attributed to the production of the radical anion of the closed-ring isomer via reduction and the open-ring merocyanine (MC) isomer via oxidation from either the photoinduced open-ring (MC) or closed-ring (SP, spiropyran) isomers. On the basis of these observations, a photoelectrochromic three-state conjugated system was obtained. A number of possible unique applications in photoelectrochemical molecular switching are described.

Keywords: Photoelectrochromism; Spirobenzopyran; Merocyanine

1. Introduction

In order to facilitate further development towards the practical realization of molecular switching devices [1], many studies have recently been devoted to the build-up of highly integrated transformation modes into single molecular units which can be regulated in response to external stimuli such as electrical bias, light irradiation and temperature changes. A molecule which can undergo different types of transformation depending on the type of external stimulus may be utilized as a material in molecular devices for multiple-mode information processing. Recently, much work has focused on the fabrication of an optical memory system which responds to electrical inputs [2–5]. For example, the selective reduction of the photogenerated cis isomer of an azobenzene derivative to the hydrazobenzene form has been studied in our laboratory [3]. Another example involves the combination of the photochromic and electrochromic properties of azoquinone derivatives: a dual-mode chemical signal transducer model has been proposed by Saika et al. [4]. Both of these proposed information storage systems are based on the combination of two types of reversible process, namely photochemical cis–trans isomerization and electrochemical oxidation and reduction, thus offering the possibility of readout and writing in either optical or electrical modes. However, the photoisomerization of the azo group has been shown to have the disadvantages of relatively low photosensitivity and a limited wavelength region for the colored form [6]. These difficulties hinder the development of azo compounds for practical molecular switching devices.

In contrast, a feature which makes spiropyrans one of the most widely studied classes of photochromic compounds is the intense absorption of the colored form in the visible region, which is of great importance for practical applications of spiropyrans in display and photochromic memory systems [7]. Although the main emphasis of the work reported thus far has been on the photochemically induced open/closed-ring isomerization process, much less attention has been paid to the electrochemical behavior. To our knowledge, the only published report which involves the redox reactions of nitrospironaphthopyrans focused on the structure of the radicals produced by electrolysis or chemical reduction, as examined by in situ electron paramagnetic resonance (EPR) [8], and did not provide detailed information on the electrochemical behavior.

Recently, we have reported the photoelectrochromic behavior associated with the photochromic open-ring merocyanine (MC) $\rightleftharpoons$ closed-ring spiropyran (SP) isomerization

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SSDI 1010-6030(95)04167-2

and the electrochromic closed-ring radical anion ⇌ open-ring (MC) isomerization of 1,3,3-trimethyl-6-nitrospiro(2H-1-benzopyran-2,2′-indoline) (SP-1) in dimethylformamide (DMF) solution [9,10]. In an effort to clarify further the electrochemically induced color formation processes of SP-1, we have carried out spectroelectrochemical and low-temperature (− 40 °C) proton nuclear magnetic resonance (^{1}H NMR) measurements on SP-1 in DMF. In addition, the spectral changes accompanying the redox reaction have been re-examined, and the influence of the applied potential and the quantity of charge on the electrochromic properties of SP-1 has been evaluated using spectroelectrochemical methods. In agreement with previous assignments [9,10], an electrochemically induced closed/open-ring isomerization process was successfully observed by monitoring changes in the ^{1}H NMR spectra of the redox species obtained by holding the potential at − 1.3 V and + 0.8 V (vs. Ag quasi- reference electrode (QRE)).

2. Experimental details

2.1. Reagents

SP-1 was purchased from Nippon Kankoh-shikiso Kenkyusho Co., Ltd. and was used without further purification. Spectroscopic grade DMF (Tokyo Kasei) was dried over calcium hydride and then freshly distilled under reduced pressure. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (Tokyo Kasei) was used as received as the supporting electrolyte.

2.2. Spectroelectrochemical measurements

A thin-layer cell was used for the spectroelectrochemical measurements. The optically transparent electrode was obtained by sandwiching a Pt mesh between glass plates with a 0.2 mm thick Teflon spacer. All applied potentials were measured and are reported vs. Ag QRE. A given volume of purified DMF was distilled via a vacuum line into an air-tight glass thin-layer cell containing supporting electrolyte (0.1 M) and SP-1 (10^{-3} M). All of the measurements were conducted under anaerobic conditions. The potentials of the electrochemical system were controlled by a potentiostat (Fusou Seisakujyo Co., Ltd.). In situ spectroelectrochemical measurements were performed with a UV–visible absorption spectrophotometer (JASCO, UVIDEC-650).

Low-temperature measurements were conducted by suspending the thin-layer cell in a transparent Dewar containing a mixture of ethanol and liquid nitrogen; the temperature was maintained at − 42 °C by adjusting the concentration of liquid nitrogen.

UV light from a 150 W Hg–Xe lamp (Hayashi Watch-Works Co., Ltd.) was selected by using a glass bandpass filter centered at 356 nm with a bandwidth of 60 nm. Visible light from a 100 W tungsten lamp equipped with a glass filter (wavelength, greater than 440 nm) was used to induce the photobleaching of the merocyanine.

^{1}H NMR spectra were recorded with a JNM-GX400 spectrophotometer, using the solvent as internal standard. Controlled potential electrolysis was carried out in dimethylformamide-d_6, and the product-containing solution from the transparent electrode was transferred into NMR tubes under a nitrogen atmosphere. Chemical shifts are reported in δ.

3. Results and discussion

3.1. Photochromic behavior

The photochromic behavior of spirobenzopyran derivatives has been investigated by many researchers [11–17]. From absorption studies of SP-1, it is well established that SP-1 exhibits photochromism, as shown in Fig. 1. The compound is stable in its closed-ring (SP) isomeric form with a colorless or pale yellow solution, while UV irradiation produces a metastable open-ring isomer (MC), which has an optical absorption peak at 550–600 nm. The original colorless form of SP can be restored either via visible light irradiation or thermally. The remarkable photoinduced color change can be explained by the extension of the conjugated system in the open-ring MC form compared with the orthogonal structure of the SP form. Under our experimental conditions, the absorption spectra (from 350 to 600 nm) of the colorless SP form and photocolored MC form of SP-1 in DMF are illustrated in Fig. 2. In addition, curve (c) in Fig. 2 shows the effect of cooling on the spectrum of a DMF solution of MC. At − 42 °C, the absorbance peak of the open-ring (MC) form increases in intensity and a slight blue shift in the band position is observed (560 nm → 556 nm). The spectral properties of SP-1 in the SP and MC forms were used to monitor the presence of the open- and closed-ring isomers respectively.

3.2. Electrochemical and electrochromic behavior

A cyclic voltammogram of SP-1 in 0.1 M $TBAPF_6$–DMF solution was obtained on visible irradiation. When the potential scan was reversed at a more negative potential (− 1.8 V vs. Ag QRE) than that of the potential of reduction wave R_1, two oxidation waves (O_2, O_3) were observed at + 0.4 V and + 0.7 V respectively as shown in Fig. 3. This indicates that the species responsible for the O_2 and O_3 waves is formed as

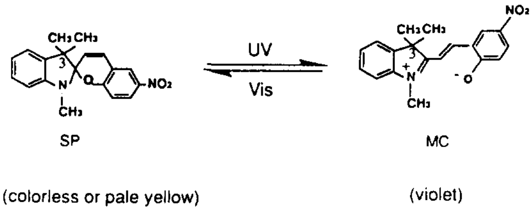

Fig. 1. Scheme for the photochromism of SP-1.

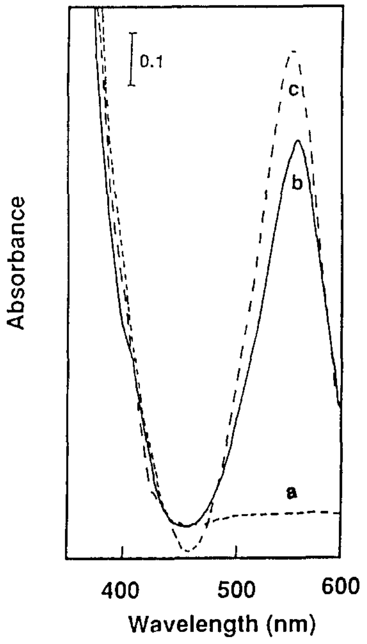

Fig. 2. Absorption spectra of SP-1 in DMF at room temperature and at −42 °C: (a) after irradiation by visible light for 15 min at room temperature; (b) after irradiation by UV light for 15 min at room temperature; (c) after irradiation by UV light for 15 min at −42 °C.

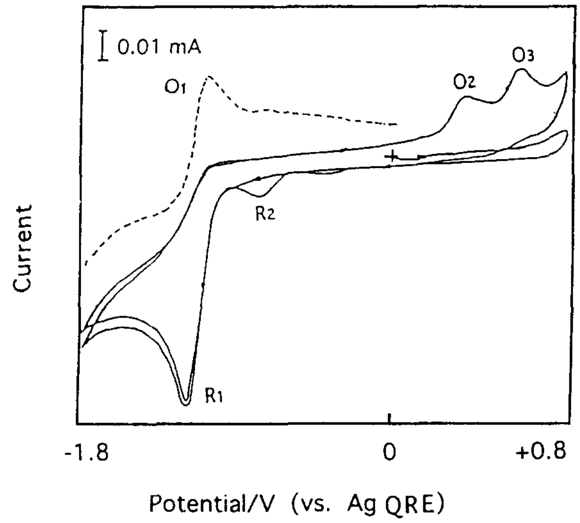

Fig. 3. Cyclic voltammograms for the closed-ring isomer of SP-1 (obtained after visible irradiation for 15 min) in DMF at room temperature. Scan rate: full line, 60 mV s^{-1}; broken line, 800 mV s^{-1}; supporting electrolyte, $TBAPF_6$.

a result of reduction wave R_1. Reduction wave R_1 forms a quasi-reversible couple (O_1) at sweep rates of 800 mV s^{-1} or greater (Fig. 3, broken line). Comparison with literature data suggests that the R_1/O_1 pair corresponds to the redox behavior of the nitro group [18–21], i.e. $NO_2 \rightleftharpoons NO_2^{\bullet -}$. However, no reduction waves coupled reversibly to the oxidation waves (O_2 and O_3) were observed under the present experimental conditions.

It is interesting to note that, in parallel with the cathodic (R_1) and anodic (O_2, O_3) processes, the color cycles between bright yellow during reduction (R_1) and violet during oxidation (O_2, O_3) of the SP-1 solution at the working electrode on irradiation by visible light. Furthermore, the color changes between bright yellow and violet associated with the changes in the cyclic voltammogram are highly reproducible even after repeated potential sweeps when the experiment is carried out at −42 °C. In situ spectroelectrochemical measurements were performed at −42 °C using a thin-layer cell.

The absorption spectral changes of a DMF solution of the SP isomer, recorded at various applied potentials (after 30 s delay at each potential) at −42 °C, are depicted in Figs. 4 and 5. The solution of the SP isomer was obtained after

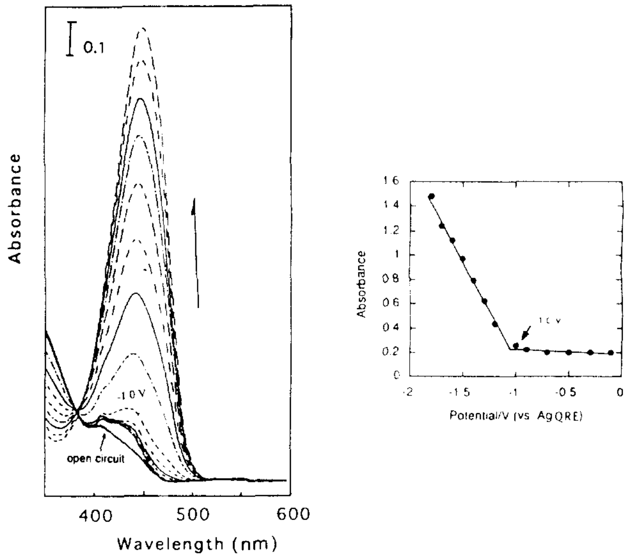

Fig. 4. Absorption spectral response of SP isomer in DMF–$TBAPF_6$ at −42 °C recorded when the applied potentials were changed from 0 V to −1.8 V (after 30 s delay at each potential) vs. Ag QRE.

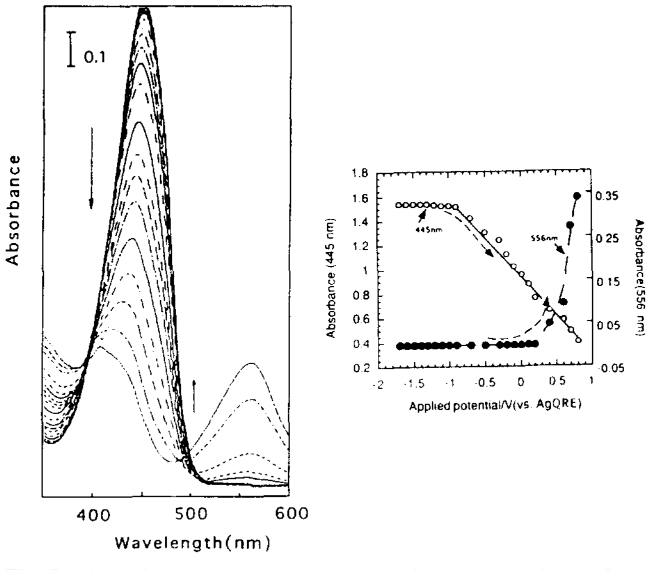

Fig. 5. Absorption spectral response of the absorption band at 445 nm (obtained in Fig. 4) in DMF–$TBAPF_6$ at −42 °C recorded when the applied potential was changed from −1.8 V to +0.8 V (after 30 s delay at each potential) vs. Ag QRE.

irradiating an SP-1 solution with visible light for 15 min. Little absorbance change was observed when the potentials were changed from 0 V to −0.9 V, but a new absorption band centered at about 445 nm (corresponding to bright yellow) began to increase rapidly in intensity at more negative potentials (Fig. 4). In parallel with the results of the cyclic voltammogram, shown in Fig. 3, the potential value at which the absorbance at 445 nm increases corresponds to the beginning of reduction wave R_1, i.e. reduction of the nitro group. According to the spectral results obtained by Kemula and Sioda [21] on nitrobenzene reduction in DMF solution, the absorption band at 445 nm can be assigned to an analog of the radical anion of nitrobenzene.

In addition, the spectral changes at 445 nm are further modified at various applied potentials (after 30 s delay at each potential) on going from negative to positive. As shown in Fig. 5, very little change was noted when the applied potential was changed from −1.8 V to −0.9 V; however, a gradual decrease in the band intensity at 445 nm was observed at more positive potentials than −0.9 V, and a characteristic absorption band centered at about 556 nm (corresponding to violet) began to increase in intensity when the applied potentials were raised from +0.2 V to +0.8 V (Fig. 5). In parallel with the anodic processes observed in the cyclic voltammogram for SP (Fig. 3), the potential value at which the absorbance at 556 nm increases rapidly corresponds to the beginning of oxidation waves O_2 and O_3. Therefore it can be deduced that the reversible color response found in SP-1 is associated with the redox behavior of the nitro group occurring in the potential range of −1.8 V to +0.8 V.

The reproducibility of the electrochromic response is one of the most important factors for practical utilization. SP-1 shows exceptional promise for electrochromic switching; in order to confirm the reversibility of the color response, the absorbance changes at the transparent electrode on application of a triangular-wave bias were monitored at either 445 nm or 556 nm in DMF–TBAPF$_6$ (Fig. 6). Consistent with the spectroelectrochemical results presented above, the response profile at each of these two wavelengths is essentially opposite to that seen at the other for a given input waveform (curves (b) and (c) respectively), and the changes reversibly reflect the change in the electrode potential.

3.3. Photoelectrochromic behavior

In order to develop a better understanding of the relationship between the photochromism and electrochromism of SP-1, as described in the previous section, the spectroelectrochemical behavior of the closed-ring (SP) and open-ring (MC) isomers was investigated by stepping the potential at −1.3 V and +0.8 V at −42 °C. The SP and MC forms of SP-1 were prepared beforehand in a thin-layer cell by irradiating the sample solution with visible (greater than 440 nm) and UV light respectively for 15 min.

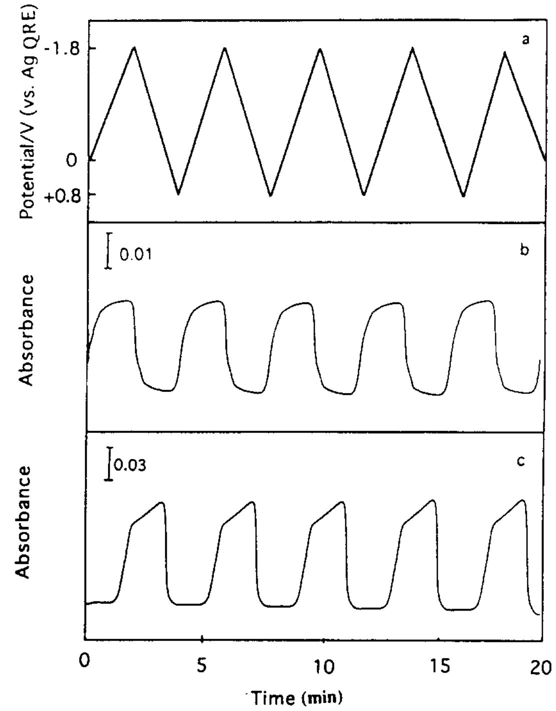

Fig. 6. Reversibility of the color response of SP-1 in DMF solution at −42 °C as a function of the potential sweep recorded in the range −1.8 V to +0.8 V vs. Ag QRE. The absorption changes were monitored at 556 nm (b) and 445 nm (c).

In Fig. 7, at open circuit, SP-1 in the SP form shows no peaks between 350 and 600 nm (curve (a)). When the potential was held at −1.3 V, a new absorption band centered at about 445 nm (curve (b)) increased in intensity with increasing charge passed. This band is characteristic of the radical anion of nitrobenzene [18–21]; subsequently, the applied

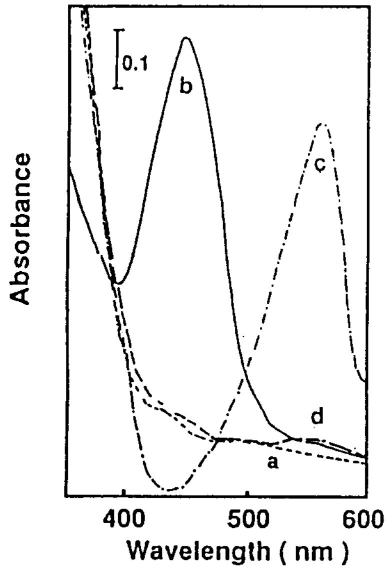

Fig. 7. Absorption spectral changes of SP-1 in DMF at −42 °C: (a) measured after visible light irradiation of SP-1 for 15 min; (b) after reduction of solution in (a) at −1.3 V with a total charge of 1.2 C; (c) after oxidation of reduced species in (b) at +0.8 V with a total charge of 1.0 C; (d) after solution in (c) was irradiated with visible light for 25 min.

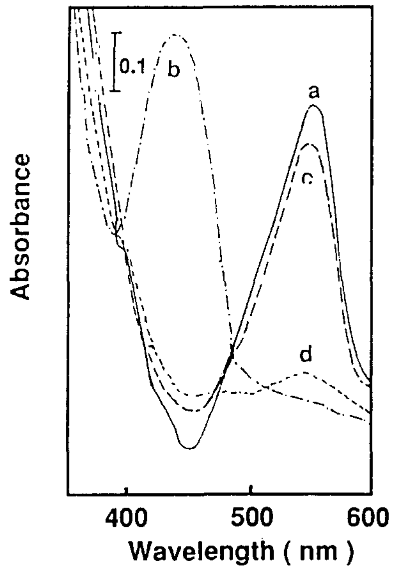

Fig. 8. Absorption spectral changes of SP-1 in DMF at −42 °C: (a) measured after UV light irradiation of SP-1 for 15 min; (b) after reduction of solution in (a) at −1.3 V with a total charge of 1.2 C; (c) after oxidation of reduced species in (b) at +0.8 V with a total charge of 1.0 C; (d) after solution in (c) was irradiated with visible light for 25 min.

potential was set at +0.8 V, and a gradual decrease in the peak intensity at 445 nm and the appearance of a distinct peak at about 556 nm, which appears to be identical to that of the open-ring isomer (MC) obtained on UV irradiation of SP-1 (curve (b) in Fig. 2), were clearly observed with increasing charge passed (curve (c)). Therefore this spectral result indicates that the absorption band at 556 nm, obtained by holding the electrode potential at +0.8 V, is due to the open-ring form, i.e. MC (molecular species). As shown in Fig. 7, the 556 nm absorption band (curve (c)) can be bleached by visible light irradiation (curve (d)). Furthermore, the absorbance at 445 nm (curve (b)) reappears when the bleached species is again reduced by holding the electrode potential at −1.3 V. Hence it is suggested that the bleached species is the closed-ring isomer (SP), which can be electrochemically reduced to form the nitrobenzopyran radical anion; this exhibits absorbance at 445 nm, as described above.

Fig. 8 shows the spectral changes of MC associated with the same applied potentials as in Fig. 7 (−1.3 V and +0.8 V vs. Ag QRE). MC shows an absorption maximum at 556 nm (curve (a)) at open circuit at −42 °C; when the electrode potential is held at −1.3 V in the dark, a new absorption peak at 445 nm (curve (b)) increases and, at the same time, the peak at 556 nm disappears with increasing charge passed. This spectral change at 445 nm on electrochemical reduction is identical to that described for SP. Furthermore, the 445 nm absorbance can be bleached and the 556 nm peak reappears on changing the applied potential from −1.3 V to +0.8 V (curve (c)). This absorbance at 556 nm can be bleached (curve (d)) by visible light irradiation and, subsequently, the 445 nm band is observed again on reduction of this bleached species by holding the electrode potential at −1.3 V.

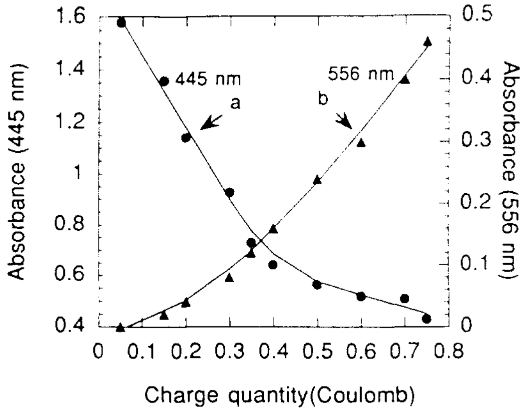

Fig. 9. Changes in the absorbance of the SP-1 isomer in DMF solution at −42 °C with increasing anodic charge, starting with the electrochemically reduced MC form (curve (b) in Fig. 2). Each point was recorded after the application of a potential step at +0.8 V vs. Ag QRE for the indicated amount of charge given on the *x* axis. The wavelengths monitored are 445 nm (a) and 556 nm (b).

Thus the present spectroelectrochemical results suggest that a reversible open/closed-ring process is involved in the redox reaction of the SP and MC forms of SP-1 in DMF [9,10], namely a nitrobenzopyran radical anion via reduction and an open-ring MC isomer via oxidation.

In addition, the variation of the absorbance of the SP-1 isomer in DMF solution at 445 and 556 nm as a function of the anodic charge was measured (after electrochemical reduction of the UV-generated MC form), and the results are shown in Fig. 9. A decrease in absorbance at 445 nm (curve (a)) and an increase in absorbance at 556 nm (curve (b)) were observed with increasing anodic charge.

3.4. Identification of the redox species by NMR

It is well established that the photochromic SP → MC isomerization is the result of the rehybridization of the spiro carbon from sp^3 to sp^2 to form coplanar rings (MC), in contrast with the non-planarity of the rings in the closed-ring isomer (SP). The NMR spectra, in particular the resonances of the methyl protons at the 3 position of the indoline ring, can provide information concerning the opening and closing of the benzopyran ring. Specifically, the presence of two methyl resonances suggests a non-planar ring structure for SP, while a single methyl resonance confirms the equivalence of the two methyl groups at the 3 position and thus the planarity of the open-ring MC species [22,23].

Fig. 10 shows the low-temperature (−40 °C) 400 MHz NMR spectra of the methyl protons at the 3 position in DMF-d_6 after controlled potential electrolysis at −1.3 V and +0.8 V. As shown in Fig. 10(a), after reduction of SP at −1.3 V, two signals are observed at $\delta = 1.10$ and $\delta = 1.20$, which can be assigned to the methyl protons at the 3 position [22]. This indicates the existence of magnetically non-equivalent methyl groups, i.e. a closed-ring SP-type form for the radical anion. Moreover, a single resonance at approximately $\delta = 1.23$ is observed for the oxidized species, therefore con-

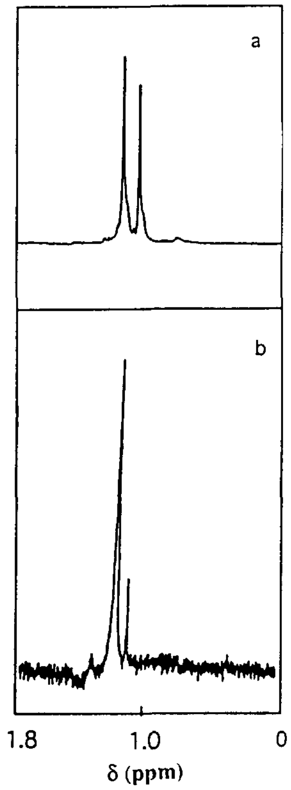

Fig. 10. NMR spectra (400 MHz) of the methyl groups at the 3 position of the indoline ring in DMF-d_6: (a) after reduction at − 1.3 V of the SP isomer obtained by visible irradiation for 15 min; (b) after oxidation of reduced species in (a) at + 0.8 V. The total charge was 2.0 C in each case.

firming that an open-ring isomer is produced during oxidation of the reduced species at + 0.8 V. Hence the ^{1}H NMR spectral results provide strong evidence in support of the involvement of a reversible open/closed-ring process in the redox reaction of SP-1 in DMF-d_6.

3.5. A unique optical–electrical conjugated system and its possible applications

According to the results presented above, the photoelectrochemical behavior of SP-1 in DMF at low temperature can be summarized as illustrated in Fig. 11. Because of the combined photochemical and electrochemical properties of SP-1, a unique photoisomerization–electroisomerization three-state conjugated system can be operated with SP-1. This new class of conjugated system offers a number of possible applications.

Spirobenzopyrans as photochromic compounds exhibit vivid coloration in the visible region, which is an important feature for industrial applications in various fields (photochromic glasses, non-linear optics, biological probes, etc.) [24]. Our experimental results provide another possibility, i.e. electrical display devices making use of SP-1. Several advantages are found in the present system, e.g. a vivid color contrast between redox states (yellow to violet) which is not obtained in the azobenzene photoelectrochemical system [3,4], low switching voltage and no viewing angular dependence; all are important characteristics for electrochromic display devices. In addition, the conjugated system found in SP-1 leads to possible electrical–optical switching applications, making use of the combined photochromism and electrochromism in a single molecular unit, and this system can be recognized as an example of a new class of dual-mode chemical signal transducers with distinctive color changes.

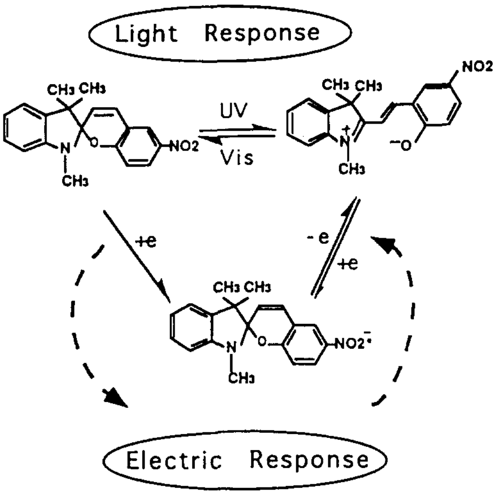

Fig. 11. Scheme for the photoelectrochemical operation of the conjugated SP-1 system.

4. Conclusions

As outlined in this paper, considerable experimental progress has been made in understanding the earlier results on the electrochromism of SP-1 reported by this laboratory. The results of cyclic voltammetry and the potential dependence of the absorption at 445 and 556 nm suggest that the electrochromic behavior of SP-1 is associated with a redox process of the nitro group occurring in the potential range of − 1.8 V to + 0.8 V. Furthermore, the spectroelectrochemical and low-temperature ^{1}H NMR measurements have provided strong evidence that a reversible electroisomerization process, involving a nitrobenzopyran radical anion of the closed-ring isomer and an open-ring MC isomer, can be obtained by switching the electrode potential.

Finally, we believe that the present results demonstrate the potential use of nitrospirobenzopyran in dual-mode optically–electrically controllable molecular switching devices.

Acknowledgements

The authors thank Dr. Donald A. Tryk for helpful discussions and suggestions. This work was supported in part by a Grant-in-Aid for Scientific Research on New Programs from the Ministry of Education, Science and Culture of Japan.

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