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Redox photochromism of viologen in organized solid state

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Abstract

N,N′-Diphenylbipyridinium(viologen) having alkylbenzene sulfonate with long alkyl chains (C_6–C_{15}) was synthesized by three reaction sequences. The viologens with alkyl chains of C_{10}–C_{15} exhibit a liquid crystal phase and display smectic-A type. Upon irradiation with near-UV light, viologen films change from pale yellow to blue–green, whose absorption maxima shift remarkably to red and the shapes differ with the length of the alkyl chain of the counter anions. The colour induced by light is maintained above 95% at 30 °C and can be bleached at higher temperature. This has made possible, for the first time, the colour development by light and bleaching by heat of transparent anisotropic thin films. © 1997 Elsevier Science S.A.

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1. Introduction

It is well known that colourless viologens composed of diquaternary salts of 4,4′-bipyridine, 2,2′-bipyridine and 1,10-phenanthroline turn to intensively coloured radical cations with reducing agents [1] or by electrochemical reactions [2], and change to neutral quinonoids by two-electron reduction. The first one-electron reduction also proceeds by photoreaction in the presence of appropriate reductants such as 2-propanol [3]. However, the colour species are generally observed within the flash-photolytic scale or under anaerobic conditions, because the radical cation produced one-electron reduction is highly oxidation sensitive. When viologens are embedded in a polar aprotic matrix such as poly-(*N*-vinyl-2-pyrrolidone) (PVP), the viologen cation radicals are stabilized by the surrounding solid matrix through restriction of both air oxidation and the thermal reverse electron transfer. The resulting photogenerated colour species can be observed with visible life-time in ordinary sunlight [4].

Recently a reversible colour change (photochromism) has received much attention for application to EDRAW (erasable and directly reading and writing) in high-speed and high-density optical devices; a number of photochromic compounds have been synthesized and their reversible colour change induced by heterocyclic cleavages [5] or by pericyclic reactions [6] have been examined. As for the photochromism of viologens by a redox mechanism, there have been reported viologen layered films [7] and vapor coated films of polymerized viologen [8]; we also reported the effect of air oxygen on coloured species in polymer matrices [9] and synthesized viologens possessing an absorption in near-IR region [10]. In order to evaluate the photochromic behavior of viologen, the present paper describes the syntheses of *N,N′*-diarylviologens with alkylbenzene sulfonate anions and their peculiar behavior concerning reversible photoreduction in the organized solid state. This has made possible for the first time the colour development by light and bleaching by heat of transparent anisotropic thin films practically.

2. Experimental

2.1. Materials

All reagents employed were of the highest purity, unless otherwise noted. IR, ^{1}H-NMR and visible absorption spectra were recorded on a Hitachi 215 spectrometer, a JMN-PMX60 spectrometer, and a Shimazu UV-169 spectrophotometer, respectively. The X-ray diffraction pattern was measured with a Rigaku X-ray Rad 2B system using Ni-filtered Cu K2 radiation, and elemental analyses were conducted with a Carbo Erba EA1108.

2.1.1. *N,N′-Diphenyl-4,4′-bipyridinium chloride (Ar-Vio)*

The solution of 4,4′-bipyridine (3.2 g, 20 mmol) and 2,4-dinitrochlorobenzene (14.0 g, 70 mmol) in anhydrous acetonitrile (MeCN, 60 ml) was heated to reflux for 72 h with

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stirring, the resulting turbid solution was diluted with MeCN (60 ml) to give a yellow precipitate of *N,N'*-bis(2,4-dinitrophenyl)-4,4'-bipyridinium dichloride in 97% yield. To the solution of dinitrophenyl pyridinium compound (3.3 g, 6 mmol) in 50% aq. EtOH (100 ml), aniline (2.7 ml, 27 mmol) in EtOH (150 ml) was added dropwise with stirring, the resulting red solution stirred for 25 h at room temperature, and then concentrated in vacuo. The residue was washed with ether and dissolved in water (50 ml). The reaction mixture was heated at 100 °C for 24 h, an insoluble by-product filtered off, and then the filtrate freeze dried. The residue was recrystallized from EtOH–AcOEt to give a yellow powder of Ar-Vio in 87% yield, m.p. 290 °C (decomp. ^{1}H-NMR(D_2O): δ 7.9 (s, 10 H, phenyl), 8.9 (d, 2 H, 2,6-Py-H), 9.5 (d, 2 H, 3,5-Py-H) ppm.

2.1.2. *N,N'-Diphenyl-4,4'-bipyridinium bis(alkylbenzenesulfonate) (1)*

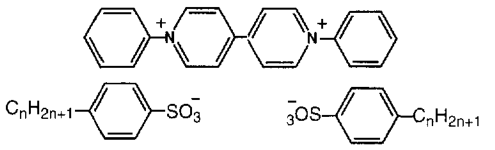
p-Alkylbenzenesulfonic acid (10-molar equivalent to Ar-Vio), which had been prepared by sulfonation of p-alkylbenzene with 30% fuming sulfuric acid, was added to the solution of Ar-Vio (0.9 g) in hot EtOH (200 ml). The reaction mixture was stirred at 80 °C overnight, and then cooled to room temperature. The resulting white precipitate was filtered, and washed with ether. When the product did not precipitate in the reaction mixture, the solution was concentrated in vacuo, the residue was washed thoroughly with ether, and then dissolved in hot water. The crude product thus precipitated was recrystallized from EtOH–ether to give a yellow powder of **1** in 45–65% yield (Scheme 1).

1a (C_6H_{13}, carbon chain in alkylbenzene sulfonate): m.p., 215 °C. IR (KBr), 1200, 1120 (S=O), 1040, 1020 (SO) cm^{-1}, ^{1}H-NMR (DMSO *d*-6), δ 0.9 (t, 6 H, CH_3), 1.3 (s, 16 H, CH_2), 2.5 (t, 4 H, Ar–CH_2), 7.1 (d, 4 H, Bz), 7.5 (d, 4 H, Bz), 7.8 (m, 10 H, Aryl), 9.0 (d, 4 H, 2,6-Py-H), 9.6 (d, 2 H, 3,5-Py-H) ppm. Anal. Found: C, 69.55; N, 3.58; H, 7.74%. Calcd for $C_{46}H_{52}N_2S_2O_6$: C, 69.67; N, 3.53; H, 6.61%.

1b (C_8H_{17}): m.p., 210 °C. Anal. Found: C, 70.37; N, 3.25; H, 7.95%. Calcd for $C_{50}H_{60}N_2S_2O_6$: C, 70.72; N, 3.30; H, 7.12%.

1c ($C_{10}H_{21}$): m.p., Crystal (Cr) 205 °C $\rightleftarrows$ Smectic A (SA) $\rightleftarrows$ 285 °C Decomposed (Dec) Anal. Found: C, 71.44; N, 3.06; H, 8.25%. Calcd for $C_{54}H_{68}N_2S_2O_6$: C, 71.65; N, 3.10; H, 7.57%.

1d ($C_{13}H_{27}$); m.p., Cr 190 °C $\rightleftarrows$ SA $\rightleftarrows$ 280 °C Dec. Anal. Found: C, 72.62; N, 2.79; H, 9.11%. Calcd for $C_{60}H_{80}N_2S_2O_6$: C, 72.84; N, 2.83; H, 8.15%.



Scheme 1. **1a**, **1b**, **1c**, **1d**, and **1e** for *n* = 6, 8, 10, 13, and 15, respectively.

1e ($C_{15}H_{31}$): m.p., Cr 168 °C $\rightleftarrows$ SA $\rightleftarrows$ 290 °C Dec. Anal. Found: C, 73.48; N, 2.69; H, 9.75%. Calcd for $C_{64}H_{88}N_2S_2O_6$: C, 73.52; N, 2.68; H, 8.48%.

2.2. *Measurements*

2.2.1. *Preparation of the glass sandwiched films*

Fine powder of **1** (0.1 g) was spread on a glass plate and melted quickly above 220 °C, followed by covering tightly with another glass plate and cooled to room temperature to afford an almost air-tight glass-sandwiched film ranging in thickness from 8 to 12 μm. All these operations were carried out in a glove box filled with nitrogen in order to exclude the effect of atmospheric oxygen.

2.2.2. *Photochromic measurements*

Irradiation of sandwiched films was carried out at 25 °C using a 75 W high-pressure Hg lamp. The resulting colour development was determined by transmission.

3. Result and discussion

N,N'-Aryl viologens possessing alkylbenzenesulfonate anions were synthesized by *N,N'*-quaternization of 4,4'-bipyridine with chlorobenzene activated by 2,4-dinitro groups, the amine exchange reaction of *N*-dinitrophenyl groups with aniline [11], and then anion exchange reaction of chloride counter ion with alkylbenzene sulfonic acid (alkylchain: C_6–C_{15}) [12]. *N,N'*-Diphenylbipyridinium benzenesulfonate (**1**) thus synthesized melts below 220 °C without decomposition. From the observation by micro-melting apparatus equipped with a polarizer, the viologens with carbon number $C_{10} \sim C_{15}$ (**1c** ~ **1e**) exhibit a liquid crystal phase and display a smectic A-type by the comparison of texture phases. Fig. 1 indicates the possible molecular arrangement by means of an X-ray diffraction study. In this model, cationic pyridinium ions and anionic sulfonate ions stabilize each other, and long alkyl chains orient to form the smectic phase.

Films of **1** prepared by heating fine powders are transparent and considered to be an anisotropic phase from the observation of crossed polarizers. Upon irradiation with near-UV, initially pale yellow films gradually develop visible colours with an almost linear increase in the absorbance and the photoreduction reaches a stationary phase within 30 min. Fig. 2 shows typical absorption spectra of viologens after near-UV irradiation. The photosensitivity for crystalline viologens is apparently small compared with those incorporated in PVP matrix, presumably due to the restriction of electron transfer from counter anions to pyridinium cations within crystal lattice [4,13]. The red shift of the absorption maximum compared with radical cations of *N,N'*-dialkyl viologens can be interpreted as the dication parts of aryl-viologen molecules which are wholly conjugated, so that the whole

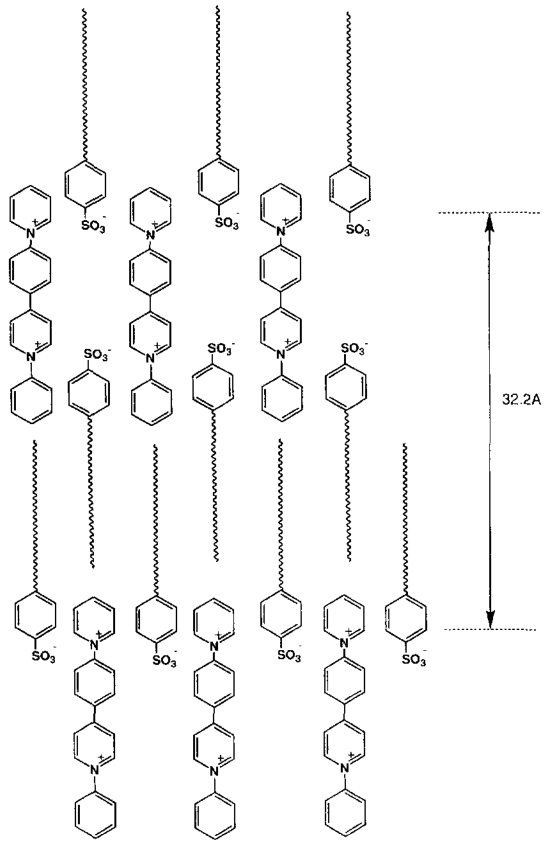
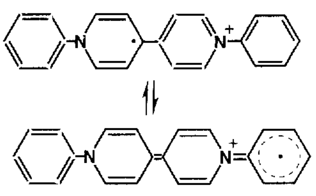


Fig. 1. Possible molecular arrangement of **1c**–**1e**.

part of it might participate in radical cation formation, as exemplified in Eq. (1).



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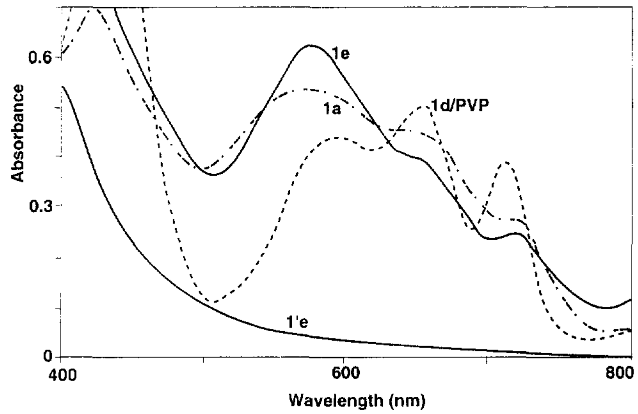

Fig. 2. Typical visible absorption spectra of **1** subjected to near UV irradiation. Curves **1a** and **1e** indicate the spectra immediately after irradiation, and **1'e** that before irradiation or completely recovered. Curves **1d**, films in a PVP matrix (4×10^{-10} mol g^{-1}) after 1 min irradiation. Film thickness, 10 μm.

Table 1
Effect of chain length of R on photoreduction and thermal bleaching behavior of viologen

Film no.	R [a]	Absorbance increase induced by light		Half lives [b]
		570 nm	660 nm	min at 70 °C
1	n-C_6H_{13}	0.487	0.429	6.5
2	n-C_8H_{17}	0.503	0.430	5.6
3	n-$C_{10}H_{21}$	0.543	0.411	5.1
4	n-$C_{13}H_{27}$	0.569 0.560 [c]	0.381 0.376 [c]	4.0
5	n-$C_{15}H_{31}$	0.553	0.360	4.1

[a] R, carbon chain in alkylnenzene sulfonate anion.
[b] At 570 nm.
[c] Values after 10 cycles of irradiation and subsequent thermally bleaching.

It can be also recognized from Fig. 2 that the shapes of the absorption peak are different with the length of the alkyl chain in alkylbenzene sulfonate anions: an increase in carbon number, that is, increase in anisotropic character, decreases the characteristic absorption of the monomeric radical cation at 660 nm and increases the absorption of associated dimeric radical cations at 570 nm (Table 1) [14]. Generally, an equilibrium between monomeric and dimeric forms in the liquid phase is favorable to the latter and the equilibrium constant (ln K) of exothermic dimerization for methylviologen is calculated as 5.5 in methanol [15]. Whereas, the association of the viologen radical cation in polymer matrices or in the crystalline state might be difficult, because the molecular motion is highly restricted in the solid state, therefore the monomeric absorption peak appears in an amorphous solid state (PVP matrix in Fig. 2). In the case of an anisotropically organized state, two bipyridinium rings are aligned next to each other induced by the orientation of the long alkyl chains (Fig. 1), so that the dimerization between dication and radical cation proceeds even in the solid state. This feature is specified on absorption spectra of anisotropic viologen films.

The thermal back electron transfer from radical cations to counter ions (bleaching process) is dependent on temperature and affected by the nature of anisotropy of the film. The typical absorption change on bleaching is illustrated in Fig. 3. The values of the absorbance are reduced to those of the 10 μm thickness. It should be noted that the absorbances of radical cations immediately after irradiation are maintained above 95% at 30 °C, which values persist for a long time (live of months to years) at that temperature. While the bleaching increases with an increase in temperature: in this case, the bleaching is almost complete at 120 °C within 5 min. Fig. 3 also indicates the difference between the bleaching of the dimeric and momomeric radical cation (at the present time, it is difficult to determine the bleaching rate spectrophotometrically, because dimeric radical cation **1** cannot be separated in a pure form). The absorption peak at 570 nm corresponds to the dimeric radical cation decreases more rapidly than that of the monomeric ones at higher tempera-

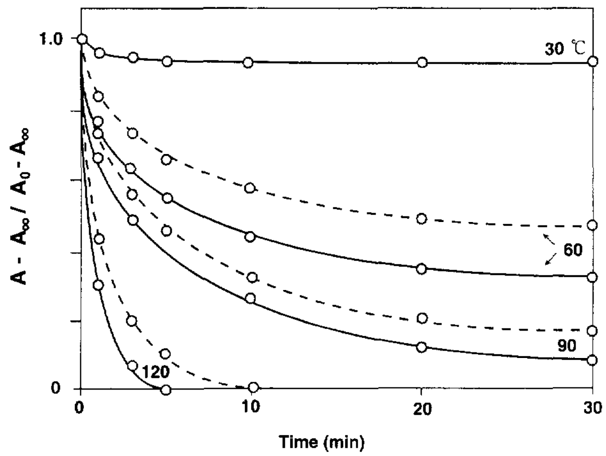

Fig. 3. Temperature dependence on bleaching of color developed by **1c**. A, absorbance at a certain time; A_0, after irradiation; A_∞, before irradiation and completely recovered. Numbers indicate bleaching temperature. ———, the absorption changes at 570 nm; - - -, the absorption changes at 660 nm.

ture. The reason why the dimeric radical cation formed in an anisotropic phase is unstable may be due to the dication and counter anion parts of the viologen molecules being situated next to each other by the orientation of the long alkyl chains in solid phase, so that the dimerization of radical cations produced by photo-reduction might present a metastable state. Thus the reverse electron transfer of the dimeric radical cation in the anisotropic phase is faster than that of the monomeric one (a stereoscopic view of the dimeric form was elucidated by X-ray crystallography [16]).

The colour species developed with near-UV light is hardly affected by irradiation with visible light, indicating that the back electron transfer is of the heat mode nature. The films of the present study could be subjected to at least 10-photochromic redox cycles (Table 1, film no. 4), one of which was composed of the irradiation and subsequent 15 min standing at 70 °C (the bleaching at 120 °C induces the formation of inactive species for photo-reduction after several cycles of repetitions). The result suggests that data written optically can be stored in solid thin films, where data can be read with a diode laser and can be erased thermally.

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