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Synthesis of Viologens with Extended π−Conjugation and Their Photochromic Behavior on Near-IR Absorption

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Colorless viologens composed of diquaternary salts of 4,4′-bipyridine turn to colored radical cations with reducing agents[1] or by electrochemical reaction,[2] whose colored species spontaneously disappear in the liquid phase, because the rate of back electron transfer is rapid and accelerated by the existence of oxygen in the system. When viologens were dispersed in appropriate aprotic matrixes such as poly(*N*-vinylpyrrolidone) (PVP) or layered as organized solid films, photogenerated radical cations were stabilized by the surrounding solid matrix through restriction of both thermal reverse electron transfer and air oxidation. The resulting colored species exist with visible lifetime (redox photochromism).[3,4] The absorption of viologen radical cation, its photosensitivity, and the bleaching rate depend on the kind of viologens, the polymer matrixes employed, and film preparations. Photochromism involving an IR absorption maximum is required for some purpose, e.g., IR reading technology.[5,6] Described herein is the synthesis of two groups of viologens with extended π-conjugation (Scheme 1) and their peculiar photocolor development in the near-IR region.

N-Aryl viologens (**1**−**3**) were synthesized by the method adopted for *N*-phenylpyridinium chloride:[7] *N*,*N*′-quaternization of 4,4′-bipyridine with 2,4-dinitrochlorobenzene and subsequent amine-exchange reaction with arylamines. Although unstable polydienylideniminium intermediates might be formed during amine-exchange reaction, compounds **1**−**3** could be obtained in relatively high yield. Compound **5** was synthesized by the Wittig reaction with 4-bromomethylpyridine and glycosal, followed by the Menschutkin reaction with benzyl bromide. The vinylene protons in 4,4′-di(4-pyridyl)butadiene present an AA′BB′ system in the ^{1}H NMR spectrum, and the compound exists as the *E*,*E*-form. The proton signals of conjugated double bonds shift markedly to lower field by the quaternization of both pyridine rings (0.7 ppm for compound **4**; 1.11 and 0.45 ppm for Hα and Hβ in **5**), indicating positive charge on nitrogen atoms to be delocalized throughout π-conjugated system.

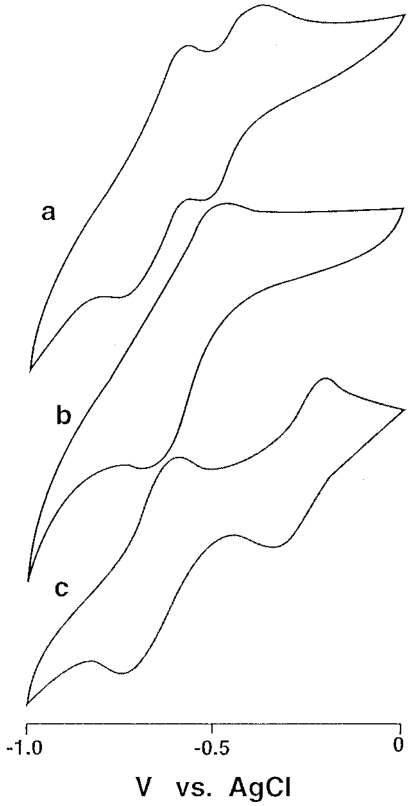
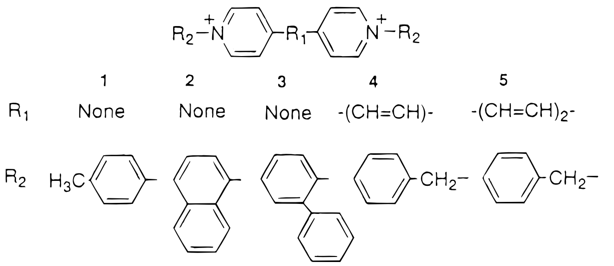


Figure 1. Cyclic voltammetry of (a) **4**, (b) **5**, and (c) **6** in DMF (electrolyte Bu$_4$NCl (0.1 M), glassy carbon electrode, scan rate 500 mV s^{-1}, versus Ag/AgCl, at 25 °C).

Scheme 1



The shape of the cyclic voltammogram of **4** is quite similar to that of *N*,*N*′-dibenzyl-4,4′-bipyridinium dibromide (**6**); however, the first redox potential shifts cathodically by 170 mV relative to that of **6**, and **5** exhibits the single reduction potential ($E_{1/2} = -0.57$ V, Figure 1). The radical cation in **6** is stabilized by delocalization within the π-conjugated system of vicinal pyridinium rings, while the ethylene bond between two rings might reduce the electron-withdrawing character against another ring, and the stability of the radical cation throughout two pyridinium rings resulted in the shift of the first reduction potential to the negative direction.[8]

The absorption maxima of **1**−**3** shift to longer wavelength compared with that of **6** (Table 1); however, the shift decreased with *N*-substitutions with large molecular size despite an increase in the contribution of the resonance structures. The bulky aryl group reduces the planarity with the pyridinium ring, which hinders the

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Table 1. Absorption Maxima and Photoinduced Color Development of Conjugated Viologens

viologen	λ_{max}, nm (ϵ) (H_2O)	λ_{max} nm, (abs), immediately after irradiation[a] (PVP matrix)	$\zeta_{1/2}$,[b] min
1	337 (1.84), 296 (1.20), 250 (1.48)	445 (1.84), 600 (0.89), 650 (1.02)	42
2	277^{sh} (3.80), 271 (3.87)	390 (1.79), 441 (1.51), 646 (1.36)	31
3	291 (1.0), 246 (2.08)	418^{sh} (3.11), 585 (1.71), 642 (1.60)	39
4	324 (3.85), 339^{sh} (2.50)	524 (1.54), 716 (0.59), 796 (0.97)	18
5	382 (4.49), 365 (5.41)	631 (1.96), 944 (0.99	41
6	259 (2.96)	400 (1.95), 569^{sh} (0.90), 605 (1.07)	34

[a] 3 min of irradiation. Numbers in parentheses are the absorbance normalized to 0.01 mm thickness. [b] Half-life of the highest near-IR absorption peak at 25 °C.

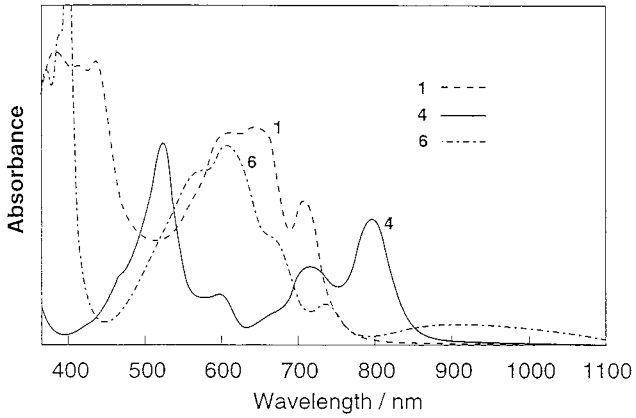

Figure 2. Typical visible absorption spectra developed by light for PVP films. The measure of absorbance is arbitrary only to show the shapes of the absorption spectra.

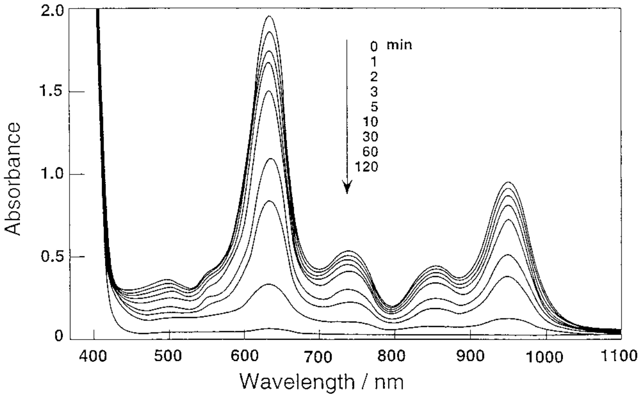

Figure 3. Bleaching of the absorption spectrum developed by light for a PVP film containing compound **5**. Numbers in the diagram denote the bleaching time at 25 °C.

π-conjugation into *N*-aryl groups.[9] While the red shift of vinylene viologens (**4**, **5**) increased with increasing number of ethylene bonds, the shift per ethylene bond is estimated to be an intermediate value between neutral α,ω-diphenylpolyenes and ionic cyanine dyes.[10]

Transparent PVP films of **1**−**6** colored varying from blue to green upon near-UV irradiation (Figure 2, Table 1), whose color gradually bleached, reached the original one within a couple of hours (Figure 3). A photoinduced coloration in the polymer matrix is considered to proceed in a way similar to that in solution:[11] the viologen radical cation might be mainly formed by intramolecular electron transfer from the counteranion.[3,12] The reverse electron transfer with the counteranion radical and air oxidation is largely restricted in the solid state, because the reductive anion radical might be oxidized by surrounding polymer functions to some extent,[12,13] and the later air oxidation proceeds with diffusion control in the solid state; thus, the colored species exist for a long time. The absorption peaks of radical cations of *N*-aryl viologens shift about 40 nm to longer wavelength compared with that of **6**, presumably due to participation of the *N*-aryl group in delocalization of the radical cation. The red shift decreases upon increasing *N*-aryl conjugation from tolyl to naphthyl and biphenyl as mentioned above, whereas the absorption peaks of **4** and **5** radical cations appear in the near-IR region, and the shifts of **5** amount to 230 nm for the absorption peak at 400 nm and up to 340 nm for the 605 nm peak of a conventional viologen radical cation. The shift value per ethylene bond is much greater than those of ionic polyeneazomethines (100 nm),[10] indicating that the delocalization of the radical is extremely large in the ionic π-conjugated system. Although a bleaching process proceeds by the reverse electron transfer to the counteranion radical or by air oxidation, there is no relationship between $E_{1/2}$ and the half-life ($\zeta_{1/2}$), suggesting that the bleaching proceeds predominantly by air oxidation, with diffusion control in the polymer matrix.

Experimental Section

All reagents were of commercial quality. ^{1}H NMR spectra were recorded at 60 and 400 MHz. Cyclic voltammetry was conducted with a glassy carbon working electrode, Ag/AgCl reference electrode, and Pt-wire auxiliary electrode in DMF containing 0.1 M tetrabutylammonium chloride.

General Procedure for *N,N′*-Diaryl-4,4′-bipyridinium Dichloride (1−3). 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 stirring, and then diluted with MeCN (60 mL). The resulting yellow precipitate was filtered, and washed with ethyl ether to afford *N,N′*-bis(2,4-dinitrophenyl)-4,4′-bipyridinium dichloride in 97% yield. To the solution of the dinitrophenylbipyridinium dichloride (3.3 g, 6 mmol) in 50% aqueous ethanol (EtOH,100 mL) was added arylamine (27 mmol) in EtOH (150 mL) dropwise with stirring, the reaction mixture being stirred at room temperature for 25 h, and then concentrated in vacuo. The residue was washed with ethyl ether and dissolved in water (50 mL). The reaction mixture was heated at 100 °C for 24 h, an insoluble byproduct was filtered off, and then the filtrate was lyophilized. The residue was recrystallized from EtOH−ethyl acetate (1:2) to give a pale yellow powder.

1: yield 83%; mp 290 °C dec; IR (KBr) 1620 (C=C), 1430 (C=N) cm^{-1}. Anal. Calcd for $C_{24}H_{22}N_2Cl_2$: C, 70.41; H, 5.42; N, 6.84%. Found: C, 70.27; H, 5.57; N, 6.67%.

2: yield 60%; mp 285 °C dec. Anal. Calcd for $C_{30}H_{22}N_2Cl_2$: C, 74.85; H, 4.61; N, 5.82. Found: C, 74.87; H, 4.73; N, 5.78.

3: yield 74%; mp 273 °C dec. Anal. Calcd for $C_{34}H_{26}N_2Cl_2$: C, 76.55; H, 4.88; N, 5.25. Found: C, 76.40; H, 5.11; N, 5.14.

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1,2-Bis(*N*-benzyl-4-pyridinium)ethylene Dibromide (4). 1,2-Di(4-pyridyl)ethylene was prepared according to the literature,[15] and the *E*-form was isolated by recrystallization from hexane−benzene. *N*-benzylation of 1,2-di(4-pyridyl)ethylene was conducted by refluxing with benzyl bromide in MeCN, and the product **4** was recrystallized from methanol (MeOH)−ethyl ether (1:3): yield 80%; mp 245 °C dec. Anal. Calcd for $C_{26}H_{24}N_2Br_2$: C, 59.56; H, 4.61; N, 5.34. Found: C, 59.34; H, 4.74; N, 5.19.

1,4-Bis(*N*-benzyl-4-pyridinium)butadiene Dibromide (5). 1,4-Di(4-pyridyl)butadiene was prepared by the method adapted from Carsky:[16] To the suspension of 4-pyridylmethyltriphenylphosphonium bromide (4.34 g, 10 mmol) in CH_2Cl_2 (15 mL), prepared from triphenylphosphine and 4-pyridylmethyl bromide, were added a 40% aqueous solution of glyoxal (0.32 mL, 5.5 mmol) and then 50% NaOH solution (5 mL) under nitrogen atmosphere. The reaction mixture was stirred for 1 h at room temperature, and then diluted with CH_2Cl_2 (25 mL) and H_2O (25 mL). The organic layer was concentrated in vacuo, and the residue was dissolved in anhydrous EtOH (50 mL). Passing HCl gas through the EtOH solution gave a yellow precipitate, which was collected and then dissolved in H_2O. The solution was basified with Na_2CO_3 (pH > 10) and CH_2Cl_2 extraction followed by solvent evaporation gave 1,4-di(4-pyridyl)butadiene. The product was recrystallized from MeOH−H_2O (1:1) to give colorless needles: yield 18%; mp 160−161 °C (lit. mp 158−161 °C). *N*-benzylation was conducted in a manner similar to that of **4**, and the product **5** was recrystallized from H_2O: yield 30%; mp 185 °C dec; IR (KBr) 1645 (C=C) cm^{-1}. Anal. Calcd for $C_{28}H_{26}N_2Br_2$: C, 61.10; H, 4.76; N, 5.09. Found: C, 61.04; H, 4.80; N, 5.19.

Preparation of Polymer Thin Films and Photochromic Measurements. The solution of viologens **1**−**6** (3.0×10^{-6} mol) and PVP (M_n 20 000, 0.2 g) in water (0.2 mL) was spread homogeneously on a glass plate (1.3×3.8 cm^2), followed by drying in a dark place to afford a transparent film ranging in thickness from 6 to 9 μm, measured by a digital micrometer. The film thus prepared was stored in a dark desiccator held at 58% relative humidity (saturated NaBr solution) at least overnight before use, and then irradiated at a distance of 10 cm with a 75 W mercury lamp for 3 min through a UV cutoff filter. The resulting color development was determined by transmission.

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