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Redox Photochromism of Arylviologen Crystals

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Synopsis. Reversible color development induced by near UV light (photochromism) was observed for some crystalline powder of 1,1′-diaryl-4,4′-bipyridinium bis(*p*-toluenesulfonate). Redox mechanism by the electron transfer from the sulfonate anion to viologen dication is claimed.

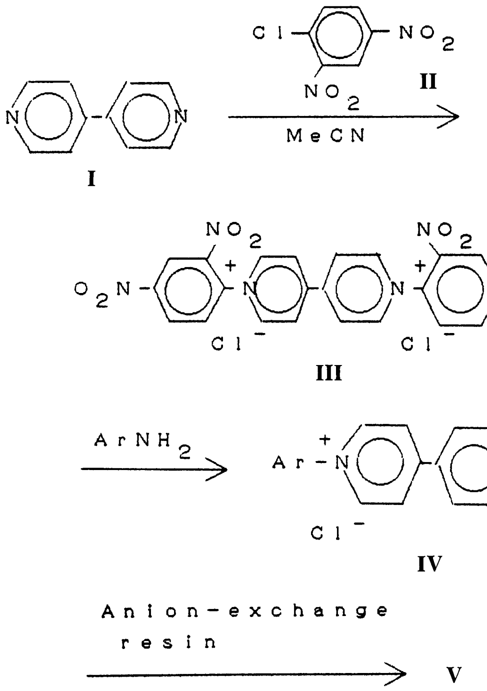
In previous papers,[1,2] we have reported for the first time that some 1,1′-disubstituted 4,4′-bipyridinium salts (4,4′-viologens), in the crystalline solid state without any additives, exhibit reversible intense *blue or pink* color development with irradiation of near-UV light (photochromism).

In the present study, we wish to report another class of 4,4′-viologens, some members of which are also susceptible to near-UV light in the crystalline state to exhibit reversible *green* color development.

The viologens synthesized and investigated for photochromic behavior in this study were 1,1′-diaryl-4,4′-bipyridinium bis(*p*-toluenesulfonate) (to be abbreviated below as "arylviologen"), as shown in Table 1.

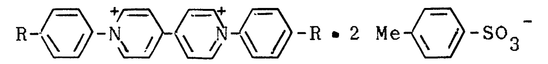
Results and Discussion

Arylviologens (**V**) were prepared by the anion-exchange reaction of the corresponding viologens having the chloride counter ion (**IV**) with *p*-toluenesulfonate anion (PTS$^-$), using an anion-exchange resin loaded with PTS$^-$. Compounds **IV** were synthesized, in its turn, starting with 4,4′-bipyridine (**I**) via its diquaternary pyridinium salt (**III**) with 2,4-dinitrochlorobenzene (**II**), followed by the amine-exchange reaction of **III**, as is indicated in Eq. 1.[3]



(1)

Table 1. Arylviologens Employed in the Present Study



Viologen	R	Viologen	R
IV-1	H[a]	**V-3**	MeO
V-1	H	**V-4**	F
V-2	Me	**V-5**	Cl

a) 1,1′-Diphenyl-4,4′-bipyridinium dichloride.

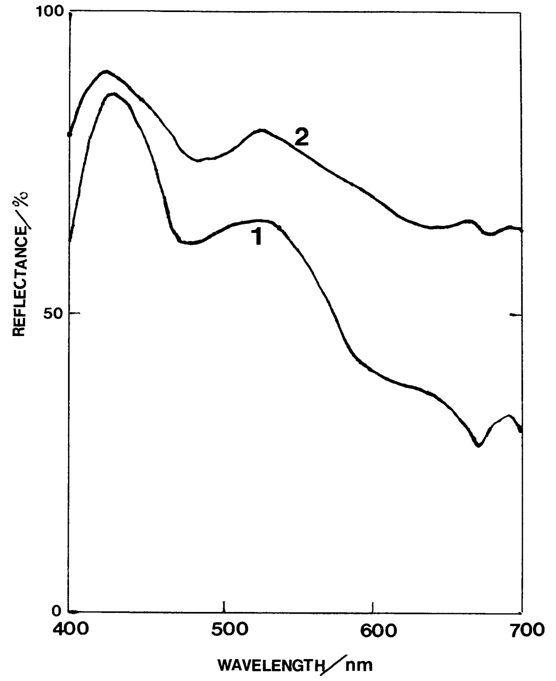


Fig. 1. Typical visible reflection spectra of the colors developed on viologen crystals with irradiation of near-UV light. Ordinate indicates values against those for the unirradiated sample. Curve 1: immediately after 10 s irradiation in air; curve 2: 10 min standing in the dark after irrad., each for 1,1′-bis(*p*-methylphenyl)-4,4′-bipyridinium bis(*p*-toluenesulfonate)(viologen No. **V-2**).

Fig. 1 indicates typical reflectance changes for crystalline powder of arylviologens upon irradiation and subsequent standing in dark.

Thus, with irradiation of light including the near-UV region, reflectances particularly at 600—700 nm decreased rapidly with simultaneous decrease of those at 400—500 nm. Since the viologen crystalline powder before irradiation showed some absorptions at 400—500 nm, the visual color was deep green for the sample during and immediately after the irradiation (curve 1).

It can be also recognized from this Figure that

Table 2. Photochromic Behavior of Viologen Crystals

Viologen No.	Reflectance[a] in air			Abs.[b] peak/ nm	Color[c]	Reflectance[a] under vacuum			Abs.[b] peak/ nm	Color[c]
	0	10	30			0	10	30		
IV-1	100	100	100	d)	Pale Yellow	100	100	100	d)	Pale Yellow
V-1	76	88	89	660	Green	60	60	61	660	Green
V-2	28	64	66	670	Green	22	24	26	670	Green
V-3	79	81	87	660	Green	60	62	63	660	Green
V-4	63	81	84	630	Green	56	58	63	630	Green
V-5	90	94	100	660	Greenish Yellow	75	80	83	660	Green

a) % Values (based on those for unirradiated viologens) in 0, 10, and 30 min after 10 s irradiation. b) Absorption peak newly developed above 600 nm as a result of irradiation. Reflectance was measured at this wavelength. c) Visual color developed upon irradiation. d) No new peak. The reflectances indicated are those throughout the whole visible range.

reflectance for the irradiated sample was recovered significantly on standing for 10 min in dark (curve 2) [Photochromism].

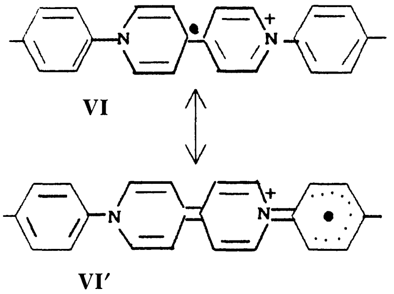
Table 2 also summarizes the results obtained for the crystalline powder of various arylviologens irradiated and let stand in air or under vacuum.

It can be known from this Table that, in the case of arylviologen, all samples investigated are susceptible to near-UV light, except viologen No. IV-1 bearing the chloride counter anion. This behavior differs notably from that in the previous study,[2] in which only limited numbers of viologens with sulfonate anions showed photochromism in crystals.

The fact that the arylviologens bearing the PTS^- counter anion in the present study exhibit photochromic behavior generally might indicate that the electron transfer to viologen dication from the counter anion induced by light and vice versa in dark (redox photochromism) are allowed in the crystal lattice.

The generation of the radical cation from the viologen dication as a result of photoreduction was demonstrated by the EPR change corresponding to reflectance change. This electron transfer to viologen dication from the sulfonate counter anion has also been observed on the transparent and isotropic films made singly of viologens bearing a long alkyl group in the counter anion part.[4]

In the present case, however, the dication part of the arylviologen molecule is wholly conjugated, so that the whole part of it might participate in radical cation formation, as exemplified in Eq. 2.



VI

VI′ (2)

This whole conjugation may be the cause of a remarkable red shift of a reflectance peak around 600 nm for the radical cations derived from the conventional viologens[1,2] to that at 660 nm or so in this case, with simultaneous shift of that around 400 nm to a yellow region (blue→green color).

High photosensitivities observed in the present type of viologen crystals might also be caused, to some extents, by this extension of conjugation, which might lower the potential barrier of this photoinduced redox reaction.

Table 2 also indicates that the presence of air oxygen promotes the bleaching of the color developed by light considerably due to oxidation of the radical cation (**VI**-VI′) back to original dication. Bleachings become very slow mostly at intermediate stages even in air, presumably because some or the major part of the radical cations (VI–VI′) within crystal lattices are untouchable with air oxygen.

The stability of VI-VI′ confined in crystal lattices may be dependent on temperature and other factors including the kind of the counter anion. Bleaching was complete when crystals were heated above 100 °C for 10 min or so, indicating that the back reaction took place by the application of heat energy.

Judging from the results so far obtained, including those in previous studies,[1,2] it can be said safely that the 4,4′-viologens bearing the sulfonate counter anion should exhibit redox photochromism in the solid crystalline state, in case various requisites, especially as the occurrence of the electron transfer within the crystal lattice, are satisfied.

Experimental

Infrared (IR), ^{1}H NMR, and elemental analyses were conducted using a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, and a Perkin-Elmer 240 instrument, respectively. Visible reflectance and EPR were taken with a Hitachi C-1020 color sensor and a JES-FE1XG spectrometer, respectively.

1,1′-Bis(2,4-dinitrophenyl)-4,4′-bipyridinium Dichloride (III). A solution of 4,4′-bipyridine (1.6 g, 10 mmol) and 2,4-dinitrochlorobenzene (7.0 g, 35 mmol) in anhydrous acetonitrile (30 mL) was refluxed for 72 h with exclusion of moisture. The reaction mixture was diluted with acetonitrile (30 mL) to afford yellowish precipitate in 95% yield.

Found: C, 47.17; H, 2.71; N, 14.67%. Calcd for

$C_{22}H_{14}N_6O_8C_{12}$: C, 46.91; H, 2.50; N, 14.92%. IR (KBr) 1510, 1330 (NO_2) cm^{-1}.

1,1′-Diphenyl-4,4′-bipyridinium Dichloride (IV-1). Compound **III** (1.1 g, 2 mmol) was dissolved in 50% ethanol (40 mL) by the application of heat. To the stirred resulting solution was then added dropwise a solution of aniline (0.9 mL, 9 mmol) in ethanol (50 mL), followed by stirring at 20 °C for 24 h. The red solution was evaporated to dryness on a rotary evaporator, followed by stirring the residue in ether (100 mL) for 30 min. The resulting residue was stirred in water (50 mL) at 100 °C for 24 h. Upon cooling, the mixture was filtered and the filtrate was freeze dried to provide crude product, which was recrystallized from ethanol–ethyl acetate (yield, 86%).

Found: C, 69.08; H, 4.82; N, 7.05%. Calcd for $C_{22}H_{18}N_2Cl_2$: C, 68.94; H, 4.73; N, 7.31%. NMR (D_2O) δ=7.9 (s, 10H, 2 phenyl), 8.8 (d, 4H, pyridinium), 9.5 (d, 4H, pyridinium).

1,1′-Diphenyl-4,4′-bipyrdinium Bis(*p*-toluenesulfonate) (V-1). An anion-exchange resin (Diaion SA 10A; 20 g) loaded with *p*-toluenesulfonate anion in the conventional manner was added to a solution of **V** (1.0 g) in water (50 mL). The mixture was stirred gently overnight, filtered, and the filtrate was freeze dried to provide crude product, which was recrystallized from methanol–ether (yield, 60%).

IR (KBr) 1190 (SO_3^-) cm^{-1}. NMR (D_2O) δ=2.3 (s, 6H, 2Me), 7.1—8.0 (18H, Aryl), 8.8 (d, 4H, Pyridinium), 9.1 (d, 4H, Pyridinium).

V-2, **V-3**, and **V-5** were prepared in the same manner as that for **V-1**, except that, in the **III—IV** step, *p*-toluidine, *p*-anisidine, and *p*-chloroaniline were employed instead of aniline, respectively. In the case of **V-4**, stirring with *p*-fluoroaniline at 80 °C for 24 h was effected at the first stage of the **III—IV** step, instead of stirring with aniline at 20 °C for 24 h, other procedures being equal to those for **V-1**. Analytical results for these viologens synthesized were also satisfactory.

Measurement of Reflection Spectra. Viologen crystals finely powdered (0.2 g) were packed tightly in a glass tube for 5 mL use, which, if necessary, was evacuated carefully under 0.1 mmHg for 30 min and sealed off. The tube was then subjected to the light reflectance measurement using a color sensor covering 400 to 700 nm in approximately one second. Light irradiation to the tube was carried out at a distance of 10 cm from a 75W high-pressure Hg lamp (Toshiba SHLUV-2) for 10 s.

References

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