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Photochromism of Viologen Crystals

Hiroyoshi KAMOGAWA* and Tsuyoshi SUZUKI
Department of Applied Chemistry, Yamanashi University, Takeda 4, Kofu 400

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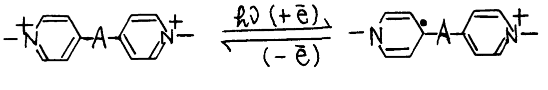
Synopsis. Some viologen crystals bearing a *p*-toluenesulfonate anion as a counter ion were shown to exhibit reversible photoreductions (photochromism) either in air or under vacuum, whereas in a poly(*N*-vinyl-2-pyrrolidone) matrix all investigated viologens indicated reversible photocolor developments. Amphoteric ions such as 1,1′-bis(3-sulfonatopropyl)-4,4′-bipyridinium also developed colors with high stabilities.

It was known that viologens undergo reversible photoreductions in either poly(*N*-vinyl-2-pyrrolidone) (PVP) matrix[1] or in films of the copolymers of *N*-vinyl-2-pyrrolidone (VP) containing viologen units as pendants.[2] Some viologen crystals, on the other hand, have been found to undergo reversible photoreductions accompanied by intense blue or pink color developments.[3]

In this study, various viologen crystals were synthesized and subjected to irradiations of UV light either in air or under vacuum. The resulting color developments were measured to provide preliminary data in order to utilize this phenomenon in the fields of photomemory or control of light quantity.

Results and Discussion

Viologens were synthesized as bromides in acetonitrile as described before.[1] The bromides were converted to *p*-toluenesulfonate (PTS)s either by adding a large excess of *p*-toluenesulfonic acid to precipitate the latters or by passing through an anion-exchange resin (Diaion SA 10) loaded with *p*-toluenesulfonic acid. Amphoteric ions like 1,1′-bis(3-sulfonatopropyl)-4,4′-bipyridinium were synthesized by treating 4,4′-bipyridine with sultones. Analytical data indicated that all viologens were satisfactorily pure. All viologens were soluble in water but amphoteric types provided turbid films when incoporated in a PVP matrix from aqueous solutions. Some viologen crystals afforded (more or less) intense color developments when they were irradiated by near-UV light.[3] Their reflection spectra are shown in Fig. 1 as either absorbance (on a spectrophotometer) or reflectance (on a color sensor). The shapes and positions of the absorption maximum and reflectance minima correspond exactly with those of single radical cations of viologens.[4] The appearance of ESR signals also corresponds to color development, thereby indicating the following generation of radical cation by ilumination:



(1)

Here, A denotes -CH=CH- or none.

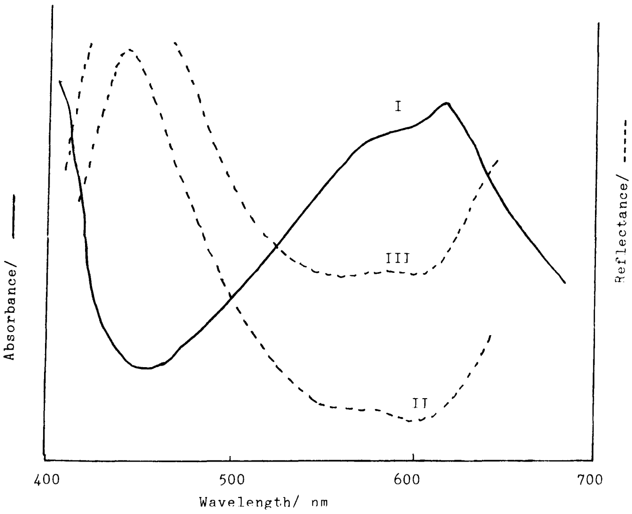
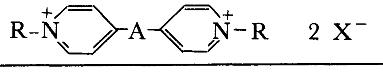


Fig. 1. Reflection curves of the colors developed on viologen crystals with irradiation of near UV light(>350 nm). Curve I: Absorbances for 1,1'-bis-(3-sulfonatopropyl)-4,4'-bipyridinium (**6**). Curves II and III: Reflectances for 1,1'-dibenzyl-4,4'-bipyridinium bis(*p*-toluenesulfonate) (**1a**) under vacuum immediately after 90s irradiation and 10 min after, respectively (color sensor).

In Table 1 can be found the results of an investigation of UV irradiation for viologen crystals synthesized in this experiment. It can be recognized in this table that only viologens having PTS as counter anion afford color development in crystals (**1a** and **5a**). In PVP matrix, however, all investigated viologens provided blue (absorption maximum, 610 nm) color developments. Viologen crystals in the form of amphoteric ions also develop colors on UV irradiation (**6**, **7**, and **9**).

Table 2 shows the half recovery times of the color developments in crystals as compared with those in a PVP matrix. It can be seen from this table that the effect of air oxygen is very great for viologens **1a** and **5a**, whereas **6** and **7** are almost insensitive to air oxygen. This fact, together with the very long half recovery times, tells us that amphoteric-type viologens, particularly **6**, afford stable color developments for long times under dry conditions. The developed color disappears quickly upon strong heating. Quantitative data have not yet been taken. The reason why only PTS gives cation radicals discernible even in air is unknown at the present stage. One reason may be that radical anion produced on the part of PTS by a photoelectron transfer from the tosylate anion to viologen dication is relatively stable due to a delocalization of both odd electron and negative charge. The crystal structure, i.e., relative position of an anion against a viologen dication in the crystal lattice, may also make the electron transfer impossible, since the benzenesulfonate (**1b**) does not afford any color development as indicated in Table 1. The effect of air oxygen on both

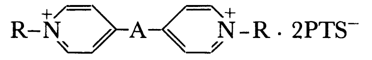
Table 1. Color Developments of Viologen Crystals with Illumination



Viologen No.	A	R	X	Color development	
				In air	Under vacuum
1	None	$PhCH_2$	Br	None	None
1a			PTS	Blue (610 nm)[b]	Blue (610 nm)[b]
1b			Benzenesulfonate	None	None
1c			$MeSO_3$	None	None
1d			1-Naphthalenesulfonate	None	None
2	None	*p*-TolylCH_2	Br	None	None
2a			PTS	None	None
3	None	*m*-TolylCH_2	Br	None	None
3a			PTS	None	None
4	None	C_3H_7	Br	None	None
4a			PTS	None	None
5	None	$PhCH_2CH_2$	Br	None	None
5a			PTS	Blue (610 nm)[b]	Blue (610 nm)[b]
6	None	$-(CH_2)_3SO_3^-$	—	Blue (610 nm)[b]	Blue (610 nm)[b]
7	None	$-(CH_2)_4SO_3^-$	—	Blue (610 nm)[b]	Blue (610 nm)[b]
8	-CH=CH-	$PhCH_2$	Br	None	None
8a			PTS	None	Pink (530 nm)[b]
9	-CH=CH-	$-(CH_2)_3SO_3^-$	—	Pink (530 nm)[b]	Pink (530 nm)[b]

a) Irradiation time, 90 s. b) Figures in parentheses indicate absorption maxima or reflection minima.

Table 2. Half Recovery of the Color Developed on Viologen Crystal with Irradiation by UV Light[a]



Viologen No.	A	R	Half Recovery/min[b]		
			In air	Under vacuum	In PVP matrix
1a	None	$PhCH_2$	1.1	39.1	2.7
5a	None	$PhCH_2CH_2$	26.1	2136	8.1
6	None	$-(CH_2)_3SO_3^-$[c]	509	542	3698[e]
7	None	$-(CH_2)_4SO_3^-$[c]	364	383	142[e]
9	-CH=CH-	$-(CH_2)_3SO_3^-$[c]	238[d]	380[d]	80.6[d,e]

a) Irradiation time, 90 s. b) At 610 nm except for d (530 nm). c) No PTS. e) Turbid films.

color development and its recovery is significant for some viologen crystals, e.g., viologens **1a** and **5a** in Table 2. Generally, the oxygen accelerates the back oxidations of viologen radical cations to dications. The color developed in the crystal lattice, however, may be more stable to air oxidation than that on a crystal surface. It appears that the rate and extent of the back reaction depend upon the stability of radical ion pair generated in crystal, as shown in pendant copolymers,[5] when the effect of air oxygen, i.e., environmental conditions, is the same.

Experimental

Infrared (IR), ^1H NMR, and elemental analyses were conducted using a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, and a Perkin-Elmer 240 instrument, respectively. The esr was taken with a JES-FE1XG spectrometer.

1,1′-Dibenzyl-4,4′-Bipyridinium Dibromide(1). This compound was prepared according to a previous report[1] starting with 4,4′-bipyridine (2.00 g, 12.8 mmol) and benzyl bromide (3.91 g, 25.6 mmol) in anhydrous acetonitrile (50 ml) under 6 h refluxing (yield, 93%). Found: C, 57.96; H, 4.33; N, 5.52%. Calcd for $C_{24}H_{22}N_2Br_2$: C, 57.80; H, 4.45; N, 5.62%. IR (KBr) 1630 cm^{-1}; ^1H NMR (D_2O) δ=6.0 (s, 4H, $2CH_2$), 7.7 (s, 10H, ArH), 8.6 (d, 4H, bipyridinium H), 9.3 (d, 4H, bipyridinium H).

All other viologen bromides were prepared in the same manner. Analytical data were all satisfactory.

1,1′-Dibenzyl-4,4′-Bipyridinium Bis(*p*-toluenesulfonate) (1a). To a solution of *p*-toluenesulfonic acid (6.88 g, 40 mmol) in absolute ethanol (50 ml) was added 1,1′-dibenzyl-4,4′-bipyridinium dibromide (**1**; 2.00 g, 4 mmol). To the resulting solution was added anhydrous ether (70 ml) and the mixture was allowed to stand overnight in order to precipitate a crude product, which was recrystallized from methanol-ether to provide white crystalline powder in 56% yield. Found: C, 66.84; H, 5.23; N, 4.12%. Calcd for $C_{38}H_{38}N_2S_2O_6$: C, 67.04; H, 5.33; N, 4.11%. IR (KBr) 1630 cm^{-1}; ^1H NMR (D_2O+DMSO-d_6) δ=2.4 (s, 6H, $2CH_3$), 7.2—7.8 (m, 18H, PTS+ArH), 8.6 (d, 4H, bipyridinium H), 9.3 (d, 4H, bipyridinium H).

1,1′-Dibenzyl-4,4′-bipyridinium bis(benzenesulfonate) (**1b**; yield, 52%), 1,1′-dibenzyl-4,4′-bipyridinium bis(1-naphthalenesulfonate) (**1d**; 79%), and trans-4,4′-vinylenebis[1-benzylpyridinium] bis(*p*-toluenesulfonate) (**8a**; 45%) were prepared in the same manner using benzene- and 1-naphthalenesulfonic acids(water as solovent) and *p*-toluenesulfonic acid from respective bromides.

The results of elemental analyses, IR, and NMR were all satisfactory.

1,1′-Diphenethyl-4,4′-bipyridinium Bis(*p*-toluenesulfonate) (5a). A solution of *p*-toluenesulfonic acid (20 g) in water (50 ml) was stirred with an anion-exchange resin (Diaion SA 10A, OH-type, 16 g) overnight. The mixture was then filtered, and the resin was washed thoroughly with distilled water until a neutral to litmus. A solution of 1,1′diphenethyl-4,4′-bipyridinium dibromide (5; 2.00 g) in water (70 ml) was added and the mixture was gently stirred overnight. The ion-exchange resin was filtered off and the filtrate was freeze dried to afford a crude product, which was recrystallized from methanol–ether to give white crystalline powder in 59% yield. Found: C, 67.45; H, 5.79; N, 3.76%. Calcd for $C_{40}H_{40}N_2S_2O_6$: C, 67.70; H, 5.69; N, 3.95%. IR (KBr) 1620 cm^{-1}; ^{1}H NMR (D_2O) δ=2.3 (s, 6H, $2CH_3$), 3.3 (t, 4H, $2CH_2$), 5.0 (t, 4H, $2CH_2\text{-}\overset{+}{N}\leqq$), 7.0—7.7 (m, 18H, PTS+ArH), 8.3 (d, 4H, bipyridinium H), 8.7 (d, 4H, bipyridinium H).

1,1′-Dibenzyl-4,4′-bipyridinium bis(methanesulfonate) (**1c**; 53%), 1.1′-bis(*p*- and *m*-methylbenzyl)-4,4′-bipyridinium bis(*p*-toluenesulfonate) (**2a**, **3a**; 76, 71%), and 1,1′-dipropyl-4,4′-bipyridinium bis(*p*-toluenesulfonate) (**4a**; 45%) were prepared in the same manner using methane- and *p*-toluenesulfonic acids from respective bromides. All analytical data were satisfactory.

1,1′-Bis(3-sulfonatopropyl)-4,4′-bipyridinium (6). A solution of 4.4′-bipyridine (2.00 g, 12.8 mmol) and 1,3-propanesultone (7.8 g, 64 mmol) in anhydrous acetonitrile(50 ml) was heated under reflux for 48 h. The resulting mixture was filtered, washed with acetonitrile, and recrystallized from water to give a white crystalline powder in 77% yield. Found: C, 48.22; H, 5.17; N, 6.89%. Calcd for $C_{16}H_{20}N_2S_2O_6$: C, 48.01; H, 5.00; N, 7.00%. IR (KBr) 1640 cm^{-1}; ^{1}H NMR (D_2O) δ=2.0—3.6 (m, 8H, $2CH_2CH_2$), 5.2 (t, 4H, $2CH_2\text{-}\overset{+}{N}\leqq$), 8.8 (d, 4H, bipyridinium H), 9.3 (d, 4H, bipyridinium H).

1,1′-Bis(4-sulfonatobutyl)-4,4′-bipyridinium (**7**; DMF, 90—100 °C, yield 78%) and trans-4,4′-vinylenebis[1-(3-sulfonatopropyl)pyridinium] (**9**; 61%) were prepared in similar manners using 1,4-butane- and 1,3-propanesultones, respectively.

Measurements of Photoreductions. Crystals (in air). A Hitachi 200-10 spectrophotometer fitted with a reflection attachment was employed for measurements of reflection spectra in air (20 °C).

Crystals (under vacuum). When measurements in the absence of air oxygen were required, a sample of viologen crystals was sealed in a 5-ml Pyrex glass tube under vacuum (0.1 mmHg) as usual. The sealed tubes were subjected to measurements of reflection spectra on a Hitachi C-120 Color Sensor and spectra ranging from 400 to 700 nm were taken within one second.

In Matrices. Measurements were performed using a Hitachi 200-10 spectrophotometer, as previously described.[1] The irradiation source was Toshiba SHL-100UV (75 W) mercury lamp cut below 350 nm with a glass filter. The irradiation distance was 10 cm.

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