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Spontaneous Color Development Encountered for Diquaternary Salts of 1,10-Phenanthrolines in Various Media

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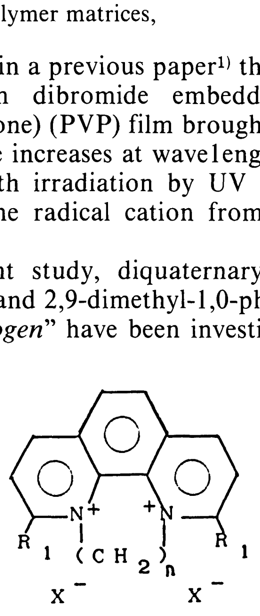
Synopsis. Diquaternary salts of 1,10-phenanthroline or, 2,9-dimethyl-1,10-phenanthroline (viologen), prepared according to the Menshutkin reaction, developed intense colors spontaneously, presumably due to high reduction potentials. The extent and $\lambda_{\max}$ of the colors developed were dependent upon both the kind of viologen and the media such as solvents and polymer matrices,

It was shown in a previous paper[1] that 1,1′-ethylene-2,2′-bipyridinium dibromide embedded in poly(*N*-vinyl-2-pyrrolidone) (PVP) film brought about remarkable absorbance increases at wavelengths between 400 and 500 nm with irradiation by UV light, indicating generation of the radical cation from the 2,2′-bipyridinium portion.

In the present study, diquaternary salts of 1,10-phenanthroline and 2,9-dimethyl-1,0-phenanthroline as shown as "*Viologen*" have been investigated expecting higher photosensitivities because of their dark reduction potentials higher than that of 1,1′-ethylene-2,2′-bipyridinium.[2]



Viologen

Viologen	R_1	X	*n*
I	H	Br	2
II	H	Br	3
III	H	BF_4	2
IV	H	PF_6	2
V	CH_3	Br	2

In the present case, however, spontaneous color developments have been observed for both the solutions and polymer films bearing viologen even in the presence of air, the $\lambda_{\max}$ and $\varepsilon_{\max}$ of the color developed depending on both the kind of viologen and the media.

Experimental

Materials. Viologen **I**, **II**, and **V** were synthesized from the respective phenanthrolines with the corresponding α,ω-dibromoalkanes according to the Menshutkin reactions.[3] Viologen **III** and **IV** were prepared by the anion exchange reactions of **I** with HBF_4 and HPF_6, respectively. Polymers used for matrix films were PVP ($\overline{M}_w$, 40000), poly(vinyl alcohol) (PVA; $\overline{DP}$, 2000), poly(*N*,*N*-dimethylacrylamide) (PDAM; $[\eta]$, 0.3 dl g^{-1} in H_2O at 25 °C), and poly(acrylamide) (PAM; $[\eta]$, 1.0 dl g^{-1} in H_2O at 25 °C).

Film Preparation. A solution of a matrix polymer and viologen (1% on the basis of polymer) in either H_2O or H_2O–EtOH (1 : 1 v/v) was spread over a glass plate so as to afford a film ca. 0.01 mm in thickness upon drying at 20 °C for a week.

Storage Conditions and Operations for Films. Films were stored in a dark brown disiccator regulated to RH 58% and kept at 20 °C, except for such operations as exposure to a light at a distance of 10 cm from a 75 W high pressure Hg lamp(Toshiba) for 2 min, heating at 80 °C, and the measurements of visible absorption spectra using a Hitachi 215 spectrophotometer. The values of absorbance thus obtained were reduced to those for 0.01 mm film thickness.

Results and Discussion

Table 1 indicates typical examples of the spontaneous yellowish orange color ($\lambda_{\max}$, 441—465 nm) developments

Table 1. Spontaneous Color Development for Viologen in I—IV in Various Media

Exp. No.	Viologen	Medium	Absorbance at $\lambda_{\max}$[a)] At 20 °C[b)] In dark	 At 20 °C[b)] Irradiated	 At 80 °C[b)] In dark
1-1	**I**	H_2O	0.00 (none)	0.00 (none)	0.00 (none)
1-2	**I**	EtOH	0.23 (445)	0.23 (445)	0.24 (445)
1-3	**I**	PVP film	0.10 (441)	0.11 (441)	0.20 (442)
1-4	**I**	PVA film	0.13 (441)	0.14 (441)	0.22 (449)
1-5	**I**	PAM film	0.10 (448)	0.11 (448)	—
2-1	**II**	PVP film	0.09 (452)	0.10 (451)	0.19 (452)
2-2	**III**	PVA film	0.11 (456)	0.11 (456)	—
2-3	**II**	PAM film	0.15 (465)	0.15 (465)	—
3	**III**	PVP film	0.08 (448)	0.08 (449)	0.16 (449)
4-1	**IV**	PVP film	0.05 (456)	0.06 (456)	0.10 (456)
4-2	**IV**	PVA film	0.03 (456)	0.04 (456)	—

a) ε ($\times 10^4$ dm^3 mol^{-1} cm^{-1}) for solutions (Exp. Nos. 1-1 and 1-2). Values for 0.01 mm thickness as to films (Nos. 1-3—4-2). b) Figures in parentheses indicate $\lambda_{\max}$ in nm.

observed for the viologen **I**—**IV** in various media in the presence of air.

Thus, while a solution of **I** in H_2O (very soluble) does not develop appreciable colors by any operations including standing in dark, irradiating light, and heating to 80 °C (Exp. No. 1-1), its solution in ethanol, in which **I** is hardly soluble and therefore considered to exist in the form of an ion pair to a large extent, spontaneously develops a color (λ_{max}, 445 nm) (No. 1-2). As for **II**—**IV**, the same behaviors as that of **I** are also observed with λ_{max} ranging from 440 to 460 nm.

It was also recognized that the colorless aqueous solutions of **I**—**IV** and matrix polymers gave highly colored films upon drying at 20 °C (Nos. 1-3—4-2). In Table 1, the values of the absorbance at λ_{max} reduced for the films of 0.01 mm thickness were given to make accurate comparisons possible. These values increase slightly upon irradiating at 20 °C but significantly upon heating to 80 °C. These absorbance increases with heating are almost reversible, thereby suggesting that the colot development of the present study is of the heat mode nature (thermochromism).

Values of λ_{max} for the colors spontaneously developed do not essentially differ among viologen **I**—**IV** in various media but the stability of the viologen counter anion in the medium appears to affect the extent of the color development significantly, as observed in previous studies on related viologens.[4] Thus, PF_6^-, a stabilized anion, provided much smaller values of absorbance at λ_{max} (Exp. Nos. 4-1 and 4-2) than Br^- did (Nos. 1-3 and 1-4).

The visible absorption spectra developed spontaneously for viologen in various media are exemplified in Fig. 1.

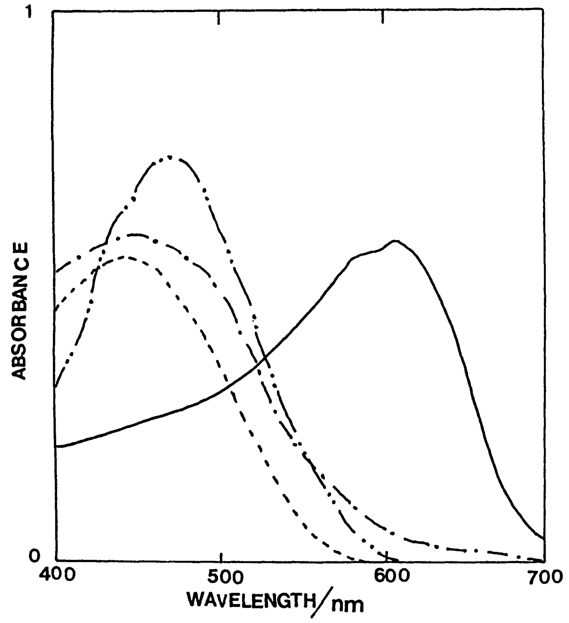
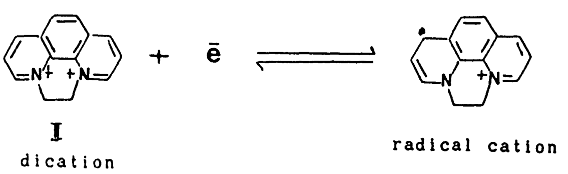


Fig. 1. Visible absorption spectra developed spontaneously for the viologen in various media at 20 °C in the presence of air.
—·— **I** in EtOH-H_2O (1 : 1 v/v); —··— **I** in H_2O in the presence of excess $Na_2S_2O_4$; ---- **I** embedded in PVA film; —— **V** embedded in PVA film.
Absorption spectra are given qualitatively as for absorbance in order to make comparisons easier.

It is known from this Figure that, for viologen **I**, the shape of the absorption spectrum in an ethanolic solution (—·—) is essentially identical with that in PVA film (- - -) and these spectra are also similar to that obtained by reducing **I** with $Na_2S_2O_4$(—··—) as well as those of the radical cations generated from the corresponding 2,2′-bipyridiniums.[1] The spectrum for **V** having the 2,9-dimethyl substituents neighboring to the N atoms and embedded in PVA (—), on the other hand, much differs from those and is very similar to the spectra for the radical cations generated from conventional 4,4′-bipyridinium by the one-electron reduction.[4]

The peculiar facts so far described may suggest that the color development encountered in the present study is brought about by the spontaneous one-electron reduction[5] of the dication parts of the viologen **I**—**V**, which possess high dark reduction potentials,[2] with the counter anions activated within the ion pairs to produce highly-colored radical ion pairs,[5] as exemplified for the dication part of **I** in Eq. 1.



(1)

The effects of the kind of the medium on the spontaneous color development of **V** are summarized in Table 2.

A remarkable fact in this Table is that, as regards the viologen **V** bearing two methyl substituents at the 2,9-positions neighboring to the quaternary N atoms, both λ_{max} and absorbance at λ_{max} are affected strikingly by the kind of matrix polymer as well as the kind of solvent, a typical shape of absorption spectrum being given already in Fig. 1. Thus, it is considered that, in the case of **V** in matrix polymer films, the two methyl substitu-

Table 2. Effect of Medium Upon Color Development of **V**

Exp. No.	Medium	Absorbance at λ_{max}[a]		
		At 20 °C[b]		At 80 °C[b]
		In dark	Irradiated	In dark
5-1	H_2O	0.00 (580)	—	—
5-2	EtOH	1.02 (558)	—	—
5-3	DMF[c]	0.36 (392)	—	—
		0.27 (540[e])		
5-4	NMP[d]	0.16 (552[e])	—	—
		0.23 (582)		
5-5	PVP film	0.69 (418)	0.70 (418)	1.46 (419)
		0.18 (560[e])	0.18 (560[e])	0.44 (560[e])
5-6	PVA film	0.80 (608)	0.80 (608)	1.63 (608)
5-7	PDAM film	0.80 (561)	0.81 (561)	1.59 (559)
5-8	PAM film	0.13 (452)	0.14 (452)	0.21 (450)

a) ε ($\times 10^4$ $dm^3\,mol^{-1}\,cm^{-1}$) for solutions (Exp. Nos. 5-1—5-4). Values for 0.01 mm thickness as to films (Nos. 5-5—5-8). b) Figures in parentheses indicate λ_{max} in nm. c) *N*,*N*-Dimethylacrylamide. d) *N*-Methyl-2-pyrrolidone. e) Shoulder.

ents exert characteristic steric hindrances to the delocalization state of electrons in the radical cation generated as in Eq. 1. The effect of the steric hindrance on the delocalization state might depend on the kind of matrix and the visual colors, which are inert to air, hardly affected by light, but sensitive to heat, are surprisingly yellowish orange, brown, pink, and blue for PAM, PVP, PDAM, and PVA, respectively (Exp. No. 5-5—5-8). This phenomenon is quite novel and may well be referred to as "Matrichromism".

Judging from the values of λ_{max} and absorbance at λ_{max}, the colored species of viologen **I**—**IV** (Table 1) and **V** embedded in PAM (Table 2; Exp. No. 5-8) do not appear to undergo the steric hindrances appreciably characteristic to the delocalization states of electrons, since they indicate λ_{max} around 450 nm, which are nearly identical with that of the radical cation from the 1,1′-ethylene-2,2′-bipyridinium,[1] together with the values of the absobance comparable to each other.

In the case of **V** embedded in the polymers other than PAM, however, the steric hindrance to the delocalization state of electrons appears to be much more characteristic, since these matrices afford varied λ_{max} together with larger values of absorbance at λ_{max} than PAM (Nos. 5-5— 5-7). The larger values suggest that **V** may exist in the ion-pair form to larger extents. The steric structure, therefore the delocalization state of electrons, of the radical ion pair generated may be subjected to the effect of the binding to matrix, as a result of which the visible absorption spectra with varied shapes and λ_{max} were obtained dependent upon the kind of matrix polymer and, in the case of PVA matrix, the spectrum is very similar to that of the radical cation generated from the 4,4′-bipyridinium (Fig. 1).[4]

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