

Redox Photochromism Involving Near Infrared
Absorption Maximum

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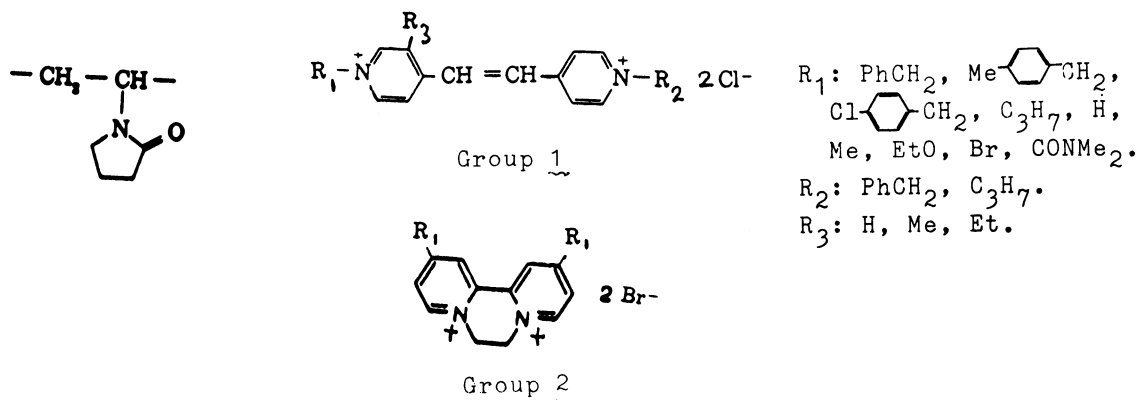
trans-4,4'-Vinylenebis(1-benzylpyridinium) dichlorides and 1,1'-ethylene-2,2'-bipyridinium dibromides in a poly(N-vinyl-2-pyrrolidone) matrix film exhibited reversible absorption maxima in the near IR (ca. 800 nm) upon UV irradiation. The thermal stability of the absorption maximum thus developed was influenced by the surroundings as well as the kind of compound.

There are many compounds or compound systems indicating the reversible spectral change by light, photochromism.¹⁾ However, this reversible change has so far been limited to the UV-UV, UV-Visible, or Visible-Visible region as regards absorption maximum.

Arakawa, Kondo, and Seto reported that, for spirothiopyrans containing the thioether structure, the absorption spectra after irradiation extended up to the near IR, but their maxima were mostly at the visible region.²⁾

We reported the reversible UV-near IR change by light in the case of 3,3'-dimethyl-4,4'-bipyridinium dibromide embedded in a poly(N-vinyl-2-pyrrolidone) (PVP) matrix film.³⁾ This might be the first case in which an absorption maximum appeared in the 800 nm region upon UV irradiation. Photochromism involving the near IR absorption maximum may be useful, considering the present state of semiconductor laser technology.

In this letter, we wish to report the appearance of a new absorption maximum in the near IR for the two groups of compounds when embedded in PVP matrix film and subjected to UV irradiation. These two groups are shown below.



Compounds 1 and 2 were prepared from the corresponding trans-1,2-bis(4-pyridyl)ethylenes⁴⁾ and 2,2'-bipyridines⁵⁻⁷⁾ using the Menschutkin reaction. Analytical data (CHN, IR, ¹H NMR) were all satisfactory.

Compounds 1 and 2 were dissolved in water with PVP (\overline{MW} = 40000) so as to afford a 5% concentration/PVP, and the resulting solutions were spread over glass plates to make films 0.01 mm in thickness when air dried. A film on a glass plate was covered with another glass plate while the film was still sticky to afford an air tight glass sandwiched film. The film thus prepared was left to stand in a dark place at least for a week, and several irradiations and the ensuing bleachings were made before each measurement to obtain reproducible results. By this procedure, the air oxygen, initially present in the film, appears to be used up for the oxidation of the viologen radical-cation produced by irradiation back to the original dication.⁸⁾ The moisture, also present in the film and when in a proper amount, makes the smooth progress of of this kind of photochromism possible.⁸⁾

The film sample was irradiated at a distance of 5 or 10 cm from a 75 W high pressure mercury lamp (Toshiba SHL100UV).

Figure 1 indicates a typical absorption spectrum for group 1 subjected to UV irradiation, compared with that for a conventional viologen, 1,1'-dibenzyl-4,4'-bipyridinium dichloride. It can be seen from this figure that the vinylene bridge (CH=CH) between two 4-pyridinium rings brings about the extension of π -electron delocalization due to conjugation, as compared with that of 4,4'-bipyridinium rings, so that the absorption maximum of the colored form of the latter

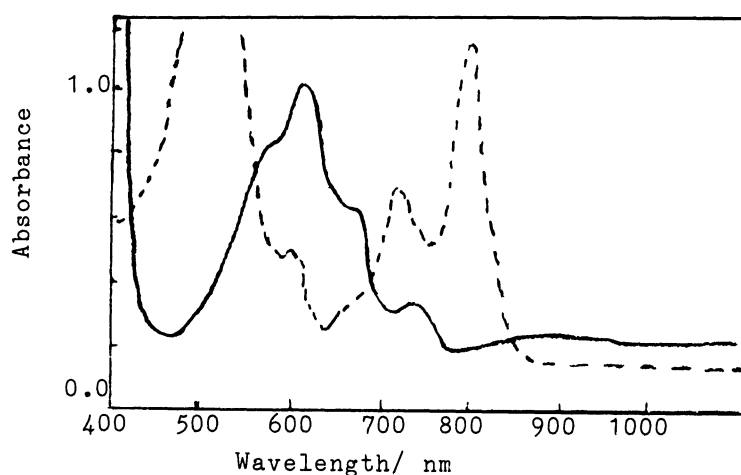


Fig. 1. Absorption spectra upon irradiation
 — 1,1'-dibenzyl-4,4'-bipyridinium dichloride,
 ---- trans-4,4'-vinylenebis(1-benzylpyridinium)
 dichloride, both in PVP matrix films.

around 730 nm appears to be red shifted up to the 800 nm region in the case of group 1 with an enhanced intensity, although the visible color was red due to a strong absorption maximum around 530 nm.

Figure 2 shows a typical absorption spectrum for the group 2 after development by light. In this case, a broad absorption centered on 800 nm and extending up to 1100 nm appeared and was maintained for a long time when the sandwiched film was treated as above and free from oxygen.

When the film was irradiated in the presence of air, however, the broad absorption attributable to the radical-cation produced bleached within a couple of hours, presumably due to air oxidation as in the case of the conventional viologens.⁸⁾ This kind of photochromism could be repeated at least 50 times. The photosensitivity, however, was inferior to group 1, as shown later in Table 1.

On the other hand, PVP containing group 1, even though sandwiched between

Fig. 2. Typical absorption spectrum upon irradiation for group 2, 1,1'-ethylene-2,2'-bipyridinium dibromide, in PVP matrix film. — After irradiation, ----- Before irradiation.

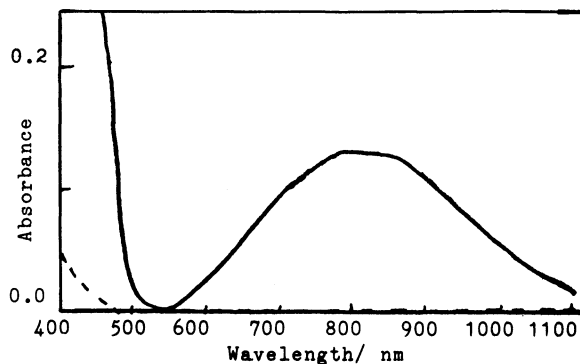
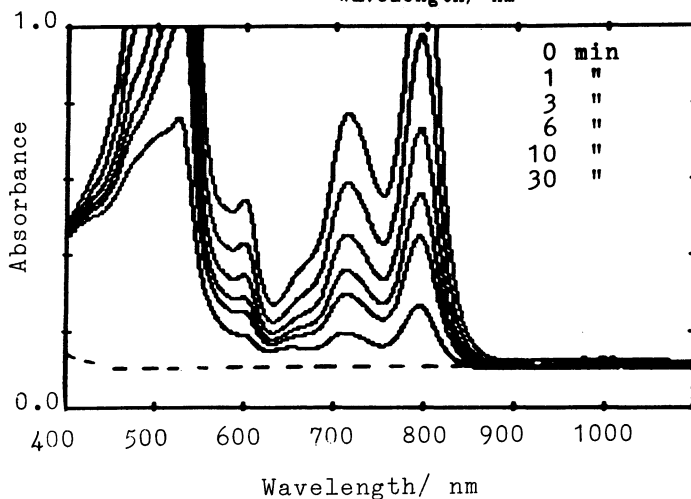
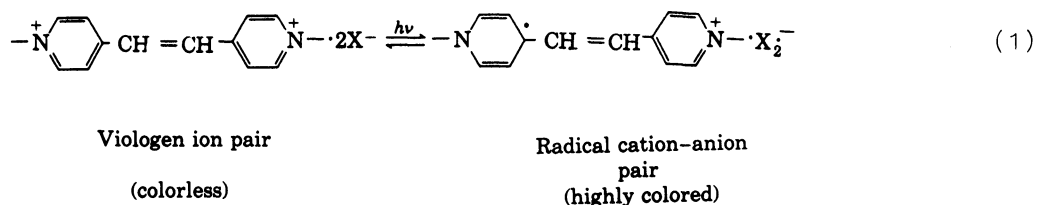


Fig. 3. Spontaneous bleaching of the absorption spectrum developed by light for PVP film containing group 1, trans-4,4'-vinylenebis(1-benzylpyridinium) dichloride. Figures in the diagram denote bleaching time at 25 °C.



two glass plates and free from oxygen, indicated a rapid bleaching of the color, as shown in Fig. 3. This kind of photochromism could be reiterated also at least 50 times. This may indicate that the appearance of strong absorption above 400 nm by light in this system occurs mainly by the redox electron transfer between the counter ions within an ion pair in PVP matrix (Eq. 1), as already shown in the cases of other types of viologen.⁸⁾





Thus, the highly colored radical ion pair produced by light would return spontaneously to the original colorless viologen dication-anion pair by the reverse reaction of its formation, when air is excluded from the redox system. This reversible color development, i. e., photochromism, is brought about by the electron transfer within the starting ion pair and the resulting radical cation-anion pair.

The thermal stability of the absorption thus developed above 400 nm is considered to be dependent upon the stability of the radical ion pair in PVP matrix film.⁸⁾

At any rate, as shown in Table 1, the compounds of groups 1 and 2, with excep-

tion of sample Nos. 6, 14, and 15, have absorption maxima at 700-900 nm (near IR) when embedded in a PVP matrix film and irradiated by the light from a high pressure mercury lamp, which is unusual in conventional photochromic compounds or compound systems.

Table 1. Near IR Absorption Peak Developed For Compounds 1 and 2 In PVP Matrix With Irradiation By Light^{a)}

Sample No.	Compound	R ₁	R ₂	R ₃	Abs. Peak Developed by Light	
					Visible nm	Near IR nm
1	1 ^{b)}	PhCH ₂	PhCH ₂	H	530	790
2	"	"	"	Me	540	790
3	"	"	"	Et	530	790
4	"	Me-  -CH ₂	"	H	530	790
5	"	Cl-  -CH ₂	"	"	530	790
6	"	n-C ₃ H ₇	n-C ₃ H ₇	"	None	None
11	2 ^{c)}	H	-	-	-	800
12	"	Me	-	-	-	730
13	"	CONMe ₂	-	-	-	870
14	"	OEt	-	-	-	680
15	"	Br	-	-	-	None

a) For glass-sandwiched film with irradiation from a 75 W mercury lamp.

b) Irradiation: 10 cm x 10 s from the lamp.

c) Irradiation: 5 cm x 120 s from the lamp.

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