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Syntheses and Photochromic Behavior of Biquinolinium Salts

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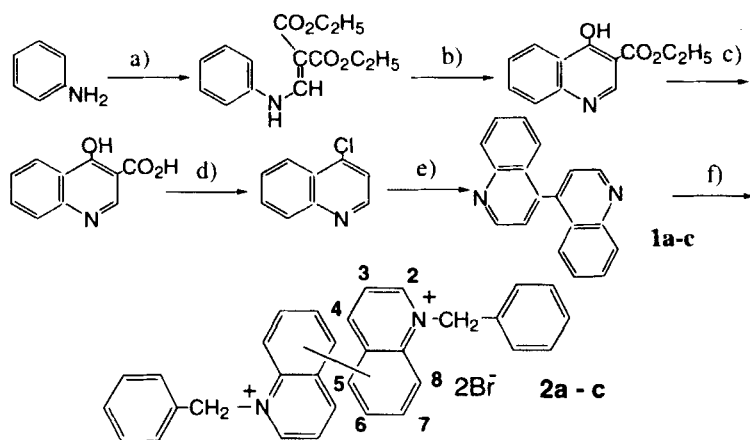
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Three isomers of N,N'-dibenzy-biquinolinium dibromide were synthesized and their photoinduced coloration properties were investigated in the thin poly(N-vinylpyrrolidone) films. Upon photo-irradiation, the colorless film of 4,4'-biquinolinium salt became intense purple and had a near IR-absorption at 970 nm, whose color gradually bleached, reaching original ones. While photo-induced absorption maxima of 6,6'-biquinolinium salt does not shift to longer wavelength and 5,5'-one exhibits thermochromism.

Keywords: Synthesis of bisquinolinium salt; photo-induced near IR-absorption

The viologens, bis-diquaternary salts of bipyridine undergo one-electron transfer to give highly colored radical cation by electrochemical reaction¹ or by radiation in the presence of reductants.² The photo-induced electron transfer also takes place when viologens are dispersed in appropriate aprotic matrices such as poly(N-vinylpyrrolidone) (PVP) or layered as organized solid films.^{3,4} The resulting color species exist with visible life time through restriction of air-oxidation by the surrounding solid matrix ,

and thermal back electron transfer proceeds predominantly when air is absent in the system. The absorption of viologen radical cation, its photosensitivity and the bleaching rate depend on the kind of viologen, polymer matrix employed, and film preparation. Previously we reported the reversible UV-near IR change by light in the case of 4,4'-viologens, having N-aryl groups or conjugated double bonds between pyridinium rings. We present here the synthesis of following new type of viologen analogues expanded pyridinium rings (biquinolinium salt: Scheme 1) and their photo-color development in the near IR region.



a) $\text{C}_2\text{H}_5\text{OCH}=\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$, 93%, mp, 43–45 °C b) $\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$, 25%, 257–258 °C
 c) 10% NaOH, 99% d) $\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$, POCl_3 , 62%, 26–27 °C e) Et_3NI , Zn, $(\text{Ph}_3\text{P})_2\text{NiBr}_2$, THF, **1a**: 72 %, 171–172 °C; **1b**, 69 %, 167–169 °C; **1c**, 50 %, 179–180 °C. f) $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ / CH_3CN : **2a**, 53 %, **2b**, 89 %, **2c**, 84 %.

SCHEME 1

EXPERIMENTAL

Materials. 4-Chloroquinoline was synthesized by Skraup reaction adopted for 4,7-dichloroquinoline.⁵ 5-Chloroquinoline was prepared by Sandmyer reaction of 5-aminoquinolin.⁶ 4,4', 5,5', 6,6'-biquinoline (**1a**, **1b**, **1c**) were synthesized by homocoupling reaction with chloroquinoline using an active nickel complex,⁷ followed by Menschtkin reaction with benzyl bromide to afford biquinolinium salts, **2a-c** (Scheme 1).

Preparation of polymer thin films and photochromic measurements:

A solution of biquinolinium salts, **2a-c** (1.5×10^{-5} mol) and PVP (Mn: 20,000, 0.3 g) in water (0.3 ml) was spread homogeneously on a glass plate (1.3 X 3.8 cm²), followed by dried in a dark place. In the case of the preparation of glass-sandwiched film, a thin-layered film dried to a tacky appearance was covered tightly with another glass plate and then dried for 1 week to afford a transparent film ranging in thickness from 0.05 to 0.1 mm. The film was irradiated at a distance of 10 cm with a 75 W mercury lamp for 3 min through UV cut-filter, and the resulting color development was determined by transmission.

RESULT AND DISCUSSION

¹H-NMR spectra indicate H5 proton in **1a** (7.39 ppm) shift to higher field compared with that in **1c** (8.11) and 4-methylquinoline (8.01), indicating H5 proton in **1a** being shielded by another ring. This is

interpreted by the spectrum of its benzylation compounds (Figure 1): two methylene protons in **2b** or **2c** appeared as singlet (equivalent), while those in **2a** appeared as quartet (unequivalent), indicating that **2a** exists as prochiral compound,⁸ so that electron withdrawing positive nitrogens at para-position is much influenced on atropisomerism of two quinolinium rings. UV spectra of **2a-c** also shows π -conjugation system of two rings: molar absorption coefficient (ϵ) of longer absorption peak in **2a** is smaller than that of **2b** (Table 1), so that the coplanarity of two rings is reduced by steric hindrance.

Transparent PVP film of **2a** was colored violet upon near-UV irradiation, whose color gradually bleached, reaching the original one within a couple of hours (Figure 2). A photo-induced coloration in polymer matrix is considered to proceed in a similar way to that in solution⁹: the viologen

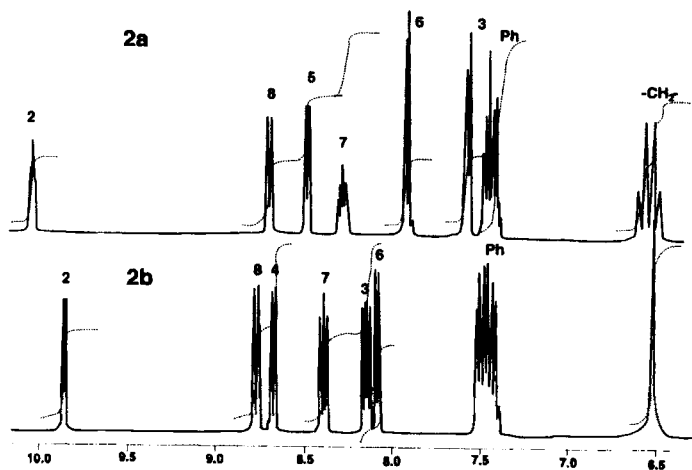


FIGURE 1 ^1H -NMR spectra of **2a** and **2b** (400 MHz, $\text{DMSO}-d_6$)

radical cation might be mainly formed by intramolecular electron transfer from counter anion.^{3,10} The reverse electron transfer with counter anion radical is largely restricted in solid state, because reductive anion radicals might be oxidized by a surrounding polymer functions in some extent,^{11,12} and the oxidation proceeds as a diffusion control in solid state, thus the color species exist for long time.

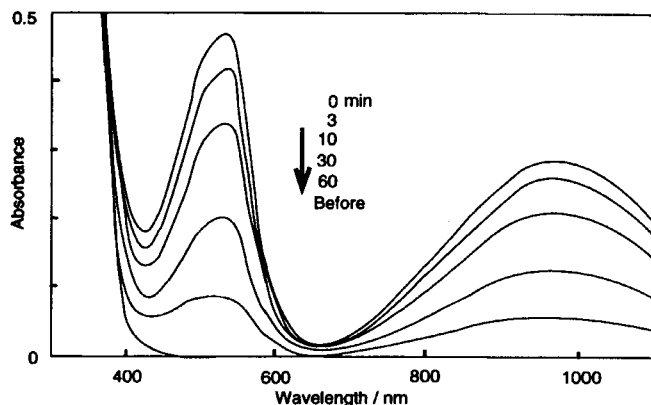


FIGURE 2 Absorption spectra of 2a in PVP after irradiation and recovery
Figures in the diagram denote bleaching time at 25 °C.

TABLE 1

Absorption maxima and photo-induced color development of
Biquinolinium salt

	$\alpha_{\max} (\epsilon \times 10^5)$ nm / H ₂ O	$\alpha_{\max}(\text{abs.})$ developed by UV-light ¹⁾ nm / PVP	Remark
2a	237 (3.45)	533 (0.47)	Reversible
	326 (0.90)	970 (0.28)	
2b	236 (7.08)	533 (0.18)	Irreversible Thermochromism
	321 (2.20)		
2c	273 (2.56)	483 (0.23)	Thermal bleaching
	327 (0.75)		

1) 3 min-irradiation. Absorbances normalized to 0.05-mm thickness.

The absorption peaks of radical cations largely shift to longer wavelength compared with that of a conventional viologens (600nm), because quinolinium rings participate for delocalization of radical cation. Similarly, compound **2c** indicates photochromism, while there is no absorption peak at longer wavelength due to two positive charges not to conjugate through two rings. Photo-coloration of **2b** is much different from that of two compounds: a photo-induced absorption peak does not disappeared at dark, even by heating. However its PVP-film and aprotic solution such as DMF exhibit thermochromism (yellow). The thermal coloration might be took part in the participation of quinonoide structure of biquinolinium rings similar way to that of bianthrone.¹³

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