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Color-modulation by Additives for Photochromism of Cyclic Viologen Derivatives

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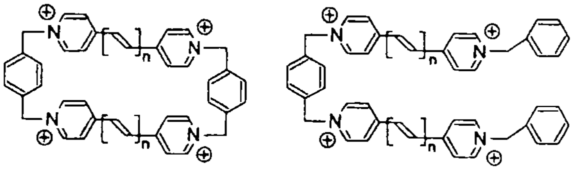
Two cyclic viologen derivatives were prepared in order to investigate their photochromic properties in a thin polymer film. The absorption peaks of photoreduced cyclic viologen units were shifted to the red side by the inclusion of indole or 1,4-dimethoxybenzene, although those of photoreduced acyclic analogues were not shifted in the presence of the guests.

Keywords: Cyclic viologen, photochromism, color-modulation, inclusion, supramolecule

Great interest is currently devoted to develop the molecular or supramolecular systems capable of performing various functions under photoirradiation [1]. Various types of photochromic compounds based on spiropyrans and diarylethenes have been synthesized and their photochromic properties have been investigated [2–3]. Viologens, 1,1′-disubstituted bipyridinium salts, exhibit the reversible photoreduction accompanied by color development without any additives in thin isotropic films [4]. Nagamura *et al.*, has reported the photochromism of the ion-pair charge-transfer complexes of viologens with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate as a counter anion [5]. On the other hand, a variety of self-assembled rotaxanes and catenanes involving cyclobis(paraquat-*p*-phenylene), 1^{4+}, was synthesized by Stoddart and coworkers [6]. Although 1^{4+} contains two viologen units in its structure, there is few report for 1^{4+} as a photochromic compound [7].

Here we wish to report the photochromism of 1^{4+} and a related cyclophane which has an extended macrocycle, 2^{4+}, in the absence and the presence of guest molecules, compared to those of the acyclic analogues, 3^{4+} and 4^{4+}, respectively. The photochromic behaviors of 1^{4+} and 2^{4+} may be influenced by the presence of the guest which is included in the cavities.



1^{4+}: n=0
2^{4+}: n=1

3^{4+}: n=0
4^{4+}: n=1

CHART 1

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The compound 1^{4+} and 2^{4+} were prepared according to a literature methods [6]. The preparations of 3^{4+} and 4^{4+} involve two steps of Menschtkin reactions. The reactions of 1,4-bis(bromomethyl)benzene with 2.5 equivalent of 4,4′-bipiyridine or *trans*-1,2-bis(4-pyridyl)ethylene, followed by benzylbromide gave precursors of 3^{4+} and 4^{4+}. 3^{4+} and 4^{4+} were obtained as PF_6^- salts by the anion-exchange reaction with NH_4PF_6. These products were identified by ^1H-NMR and elemental analysis [8].

Kaifer *et al.*, has reported that 1^{4+} forms a 1:1 inclusion complex with π-electron donating guests in solution driven by charge transfer (CT) interactions [9]. We have also confirmed the complex formation of 1^{4+} with guests in *N,N*-dimethylacetamide (DMAc) solution. Upon addition of the indole (IND) as a guest to the DMAc solution of 1^{4+}, an absorption band around 450 nm developed, which corresponds to the CT complex between 1^{4+} and IND. Similar results were obtained when 1,4-dimethoxybenzene (DMB) was used as the guest in place of IND. The curve-fitting analysis of guest-induced absorption variations at 450 nm performed by using a Benedi-Hildebrand type equation gave the binding constants (Tab. I). The binding constant for 1^{4+} with IND was larger than that with DMB, which is parallel to the result obtained in acetonitrile (MeCN) [9]. These values in DMAc are much smaller than those in MeCN. It is clear, however, that 1^{4+} can form the inclusion complex by CT interaction with these guests in DMAc. Similar trends were observed for 2^{4+} with smaller binding constant even in MeCN (Tab. I). This is interpreted in terms of the larger cavity of 2^{4+} compared to 1^{4+}.

TABLE I Binding constants of 1^{4+} and 2^{4+} with IND and DMB

		K(M^{-1})	
Host	Solvent	IND	DMB
1^{4+}	DMAc	3.0	2.3
	MeCN[a]	150	18
2^{4+}	MeCN	17	3.4

[a] Ref. [9] for IND and Ref. [6] for DMB.

Photoirradiation experiments were carried out in poly(*N*-vinyl-2-pyroridone) (PVP) films, which were prepared by solvent cast method from DMAc solution of viologen derivatives (25 μmol·g^{-1}) so as to afford ca. 0.06 mm thickness. The films containing the guest were prepared in the similar manner from the DMAc solution containing 1000 equivalent of IND or DMB. Photoirradiation of the films was performed with a 75 W Hg lamp by using a glass filter to obtain the light > 300 nm for 3 minutes in the absence of the guest and for 5 and 20 minutes in the presence of DMB and IND, respectively. The spectral changes were recorded at 25°C.

Upon photoirradiation to the PVP film containing 1^{4+}, the film turned to blue with an absorption peak at 610 nm (Fig. 1). This result indicates the structural change of the viologen units in 1^{4+}; the colorless dication form is converted into a blue radical cation species, which is generated by photoinduced reduction. The absorbance around 610 nm was decreased with time proceeding and the film was reverted to the original color after 120 minutes. This cycle can be repeated more than several times. 3^{4+} and *N,N*′-dibenzylviologen show similar spectral change upon photoirradiation. The absorption peaks were observed at 611 and 610 nm for 3^{4+} and *N,N*′-dibenzylviologen, respectively. These results indicate that there is no interaction between two viologen units in a molecule of 1^{4+}. In the presence of IND as the guest, however, the absorption peak was observed at longer wavelength by 10 nm (at 620 nm) as compared to that of 1^{4+} alone (Fig. 1). When irradiated to the film of 3^{4+}-IND, no shift in absorption peak was observed as compared to that of 3^{4+} alone. A red shift of the peak of the photoirradiated 1^{4+} by the presence of IND may be the result of one of following reasons; (i) the change of the environment around the viologen unit of 1^{4+} due to the replacement of solvent

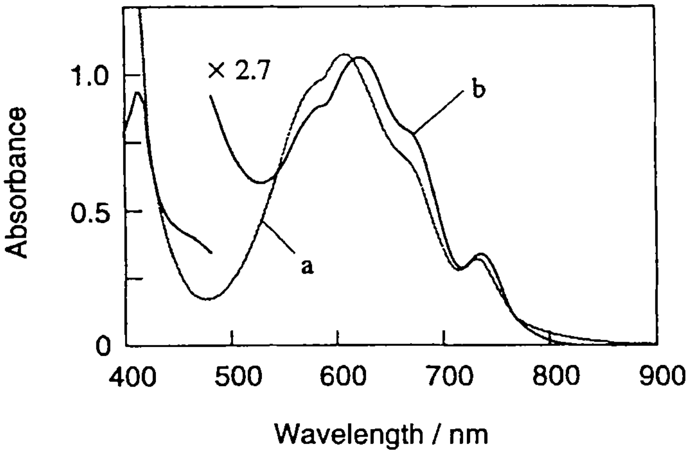

FIGURE 1 Absorption spectra of 1^{4+} alone (a) and in the presence of IND (b) after photoirradiation immediately.

molecules in the 1^{4+} cavity by the guest molecule, (ii) the decrease in the transition energy due to the interaction of the transition dipole moment between viologen unit and IND, or (iii) the change in the interaction between viologen units by the insertion of the guest molecule between the units. Furthermore, the spectrum after photoirradiation was reverted to original one after ca. 60 minutes. The rate of reversion was two times faster than that for 1^{4+} in the absence of IND. Such faster reversion suggests the faster back reaction in the presence of IND. A guest-induced red shift in the absorption peaks of the photoreduced viologen unit was also observed in the system of 1^{4+}-DMB, which exhibits the absorption peak at 615 nm. The smaller red shift for 1^{4+}-DMB system may reflect the weaker interaction between the host and DMB, which was implied by the smaller binding constant of 1^{4+} and DMB as compared to that of 1^{4+} and IND.

Such guest-induced red shift in the absorption peaks of the photoreduced viologen unit was also observed for 2^{4+} (Fig. 2). The photoreduced peaks for 2^{4+} were observed at 530, 717 and 799 nm in the absence of the guest, while those were observed at 535, 730 and 812 nm in the presence of IND, and 530, 719 and 806 nm in the

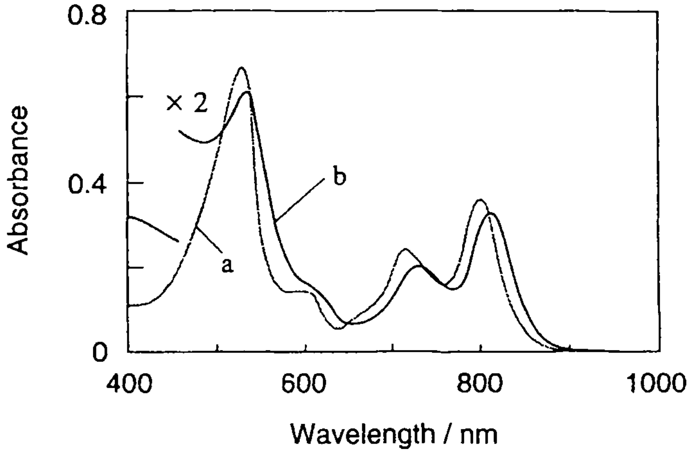

FIGURE 2 Absorption spectra of 2^{4+} alone (a) and in the presence of IND (b) after photoirradiation immediately.

presence of DMB, respectively. The peaks of photoreduced 4^{4+} at 527, 714 and 796 nm was not shifted by the addition of the guest.

In conclusion, we have shown guest-induced color-modulation for photochromism of the cyclic viologens. In this system, it is possible that the guest molecules act as the electron donor for photoreduction of the viologen units. Further work to clarify this point and the photochromic behavior of cyclic viologens is being investigated.

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[8] Data for 3^{4+}: ^{1}H-NMR (500 MHz, DMSO-d_6) δ 6.03 (s, 4H), 6.05 (s, 4H), 7.55–7.62 (6H), 7.69–7.73 (4H), 7.79 (s, 4H), 8.81 (d, J = 7.0 Hz, 4H), 8.84 (d, J = 7.0 Hz, 4H), 9.58 (d, J = 7.0 Hz, 4H), 9.61 (d, J = 7.0 Hz, 4H); Anal. Found: C, 42.42; H, 3.17; N, 4.78%. Calcd for $C_{42}H_{38}N_4F_{24}P_4$: C, 42.80; H, 3.25; N, 4.75%. Data for 4^{4+}: ^{1}H-NMR (500 MHz, DMSO-d_6) δ 5.95 (s, 4H), 5.96 (s, 4H), 7.54–7.62 (6H), 7.63–7.68 (4H), 7.74 (s, 4H), 8.20 (s, 4H), 8.46 (d, J = 7.0 Hz, 4H), 8.47 (d, J = 7.0 Hz, 4H), 9.32 (d, J = 7.0 Hz, 4H), 9.34 (d, J = 7.0 Hz, 4H); Anal. Found: C, 44.29; H, 3.41; N, 4.54%. Calcd for $C_{46}H_{42}N_4F_{24}P_4$: C, 44.89; H, 3.44; N, 4.55%.

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