

Catenane and inclusion complex as photochromic compounds involving viologen units



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ABSTRACT

Catenane (**1**) consisting of a tetracationic cyclophane (**2**) and *p*-benzocrown ether (**5**) has been prepared to investigate its photochromic behavior in a poly(*N*-vinyl-2-pyrrolidone) (PVP) film by comparing with that of **2** in the absence and the presence of π -electron donating guests such as indole (**6**) and *p*-dimethoxybenzene (**7**). The PVP film containing **1** showed a red color due to the π -donor/ π -acceptor charge transfer interaction between the viologen and the dialkoxybenzene units in **1**. Upon photoirradiation the film changed the color to blue with the absorption maximum ($\lambda_{\max}$) at 620 nm, associated with the photoreduction of the viologen unit from the dication to the radical cation, and reverted to the original dication with the half-life ($\tau_{1/2}$) of 15 min. The pale yellow film containing **2** showed the similar photochromic behavior to that of **1** with $\lambda_{\max}$ at 610 nm and $\tau_{1/2}$ at 24 min, which are shifted to blue side by 10 nm and to longer time by 9 min as compared with those of **1**. The difference in the photochromic behavior between **1** and **2** is resulted from the existence of the π -electron donating unit, **5**, which is interlocked with the ring of **2** in the compound **1**. The effect of the π -electron donating unit on the photochromic behavior of viologen was confirmed by the addition of **6** and **7** to the film containing **2** or its acyclic analog, **3**. The $\lambda_{\max}$ and $\tau_{1/2}$ for the photoreduced **2** were observed at 620 nm and 14 min, and at 615 nm and 20 min in the presence of **6** and **7**, respectively. The larger effect of **6** rather than **7** on the photochromic properties of **2** was interpreted in terms of the larger binding constant of **6** with **2** than that of **7** in dimethylacetamide (DMAc) (3.0 and 2.3 M⁻¹ for **6** and **7**, respectively). The addition of **6** and **7** to the film containing **3** caused no change in the photochromic properties of **3** ($\lambda_{\max}$ = 611 nm and $\tau_{1/2}$ = 22 min). When the simple benzylviologen (**4**) was used as the photochromic compound, the reversion rate of the photoreduced **4** was accelerated by the addition of **5** but it was not accelerated by **7**. All these results demonstrate that the cyclic structure as well as the catenane promote the strong interaction between viologen and π -electron donating units. The interaction leads the change not only in color of the film before photoirradiation but also in the photochromic behaviors of viologen derivatives.

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1. Introduction

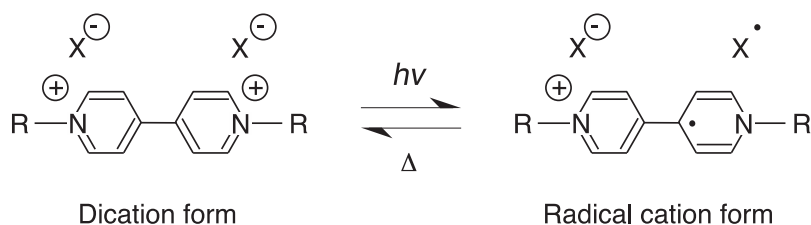
Interlocked molecules such as catenane and rotaxane are of great interest due to their unique properties as a result of the cooperative or synergistic effect of each component molecule. In past two decades, various types of catenane and rotaxane have been prepared and their structural and dynamic properties have been investigated in both solid and solution states [1]. One of the excellent works has been done by Stoddart and coworkers. They have prepared a variety of self-assembled catenane and rotaxane involving the intermolecular charge transfer interaction between viologen and dialkoxybenzene derivatives [2]. These are based

on the ability of the tetracationic cyclic viologen derivative or *p*-benzocrown ether to form inclusion complexes with π -electron donating compounds or linear viologen units, respectively. These catenane and rotaxane showed excellent performances as the molecular machines that are driven by the chemical or electrochemical stimulus [3]. Although light has been also used as the external stimulus to induce the mechanical movements, there are few reports on the photoinduced spectroscopic properties of these molecules, or photochromism [4].

Recently supramolecular regulation of the photochromism by the additives, which is capable of interacting with the photochromic molecule intermolecularly, has been investigated. Takeshita et al. have reported the increase in the quantum yield for the photochromic reaction of diarylethenes by the complexation with the cyclodextrin [5]. The addition of metal ions switched on the trans-cis isomerization of azobenzene derivatives [6]. The thermal stability of colored merocyanine form of spirobenzopyrane derivatives has been also enhanced upon addition of metal ions [7].

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Scheme 1. Photoreduction of viologen.

Viologen is also known to show the photoinduced color change from colorless to blue in solutions [8]. This involves the photoinduced electron transfer from counter anion to bipyridinium dication to form the colored radical cation species (Scheme 1). Because of the rapid back reaction or quenching by dissolved oxygen in solutions, the colored radical cation can be observed only within the flash-photolytic scale under anaerobic conditions [9]. When dispersed in isotropic thin polymer films, however, the radical cation photogenerated is stabilized relatively owing to surrounding solid matrix through restriction of oxidation and the decrease in rate of the reverse electron transfer [8,10].

In the previous communication we have firstly reported on supramolecular photochromism of viologen derivatives in the polymer film. The photochromic properties of viologen derivatives are regulated by the addition of π -electron donating chemical substrates, which interact with the viologen derivatives to form supramolecular complexes in the polymer film like in the solution. The intermolecular interactions cause modulation of color and regulation of the recovery rate in the photochromism of viologen derivatives in the polymer film [11,12].

In the extension of our investigation, we wish to report here the photochromism of catenane (**1**) consisting of the tetracationic cyclic viologen derivative (**2**) and *p*-benzocrown ether (**5**) in the polymer film. The photochromic behavior of catenane **1** may be different from that of its component, **2**, as well as the acyclic viologen analogs, **3** and **4**. However, the addition of the guest into the film of **2** may cause the change in the photochromic property of **2**, especially, when the π -electron donating molecule is used as the guest. This is a first report on the photochromism of catenane and inclusion complexes containing the viologen unit in the polymer film.

2. Experiment

2.1. Materials

Chemical structures of the compounds used in this study are shown in Fig. 1. Compounds, **1**, **2**, and **5**, were prepared by according to a literature method [13]. The precursor of **3** was prepared by Menshtkin reaction of 4,4'-bipyridine with 1,4-bis(bromomethyl)-benzene, followed by the reaction with benzylbromide. The compound **3** was obtained as the hexafluorophosphate salts by the anion-exchange reaction with ammonium hexafluorophosphate. While **4** was prepared by the reaction with 4,4'-bipyridine and benzylbromide, followed by the anion-exchange reaction. All bipyridinium derivatives were obtained as hexafluorophosphate salts. These products were identified by ^1H NMR and elemental analysis. Indole (**6**) was used as the π -electron donating guest for host **2**. *p*-Dimethoxybenzene (**7**) was also used as the guest and as the acyclic analog of **5**. Benzenonitrile (**8**) was used as the π -electron deficient guest. Poly(*N*-vinyl-2-pyrrolidone) (PVP), whose Mw is 40,000, was purchased from Tokyo Kasei. Dimethylacetamide (DMAc) and acetone were used for studying complexation phenomenon. DMAc and dimethylformamide (DMF) were used for preparing the polymer films.

2.2. Measurements

^1H NMR was run on a Varian UNITY plus-400 and a Bruker AVANCE 400. The elemental analysis was performed with a Carlo Erba EA1108. Absorption spectra were measured on a Shimadzu UV-160 and UV-2500 spectrophotometer at 25 °C.

2.3. Absorption spectra and binding constants in solution

The absorption spectrum of **1** was measured by using a 1 cm cell in DMAc solution. While 1 mm width cell was used for investigating the complexation of **2** with **6** and **7** (**6@2** and **7@2**), which was monitored by measuring the charge transfer band that developed upon mixing two components in DMAc. The concentration of **2** was fixed at 1.25 mM and that of the guest was varied from 0 to 1.25 mM. The binding constant was obtained by non-linear least-square curve fitting of the experimental guest-induced absorption intensity at 450 nm to the following equation, which is derived based on 1:1 host-guest equilibrium,

$$\Delta I = \frac{\Delta I_{\max} \left[(V_0 + D_0 + 1/K) - \left\{ (V_0 + D_0 + 1/K)^2 - 4 \cdot V_0 \cdot D_0 \right\}^{1/2} \right]}{2 \cdot V_0}$$

where K is the binding constant between **6@2** and **7@2**. V_0 and D_0 represent the initial concentration of **2** and guest, respectively. ΔI denotes the guest-induced absorption intensity at 450 nm for inclusion complexes of **6@2** and **7@2**. If all host molecule binds to the guest, ΔI is equal to $\Delta I_{\max}$. On the other hand, the similar method was applied for studying the complexation behavior of **4@5** in acetone. The absorption spectra were measured by using the 1 cm cell at the fixed concentration of **4** (0.3 mM) with varying the concentration of **5** from 0 to 3 mM. The binding constant K for **4@5** was estimated by the similar fitting method employed above equation. In this equation, V_0 and D_0 represent the initial concentration of **4** and **5**, respectively. ΔI indicates the absorption intensity at 450 nm, which is developed by mixing **4** and **5** in acetone. When all of **4** is bound to **5**, ΔI is equal to $\Delta I_{\max}$.

2.4. Photoirradiation

Photoirradiation experiments were carried out in poly(*N*-vinyl-2-pyrrolidone) (PVP) films. The films were prepared by solvent cast method from DMAc solution on the glass plate with $8 \times 38 \text{ mm}^2$ size. 0.14 ml of DMAc solution contained 0.014 g of PVP and 25 μmol polymer g^{-1} of **1**, **2**, or **3** was dropped to spread onto this glass plate and the solvent was removed gradually under the reduced pressure. The obtained films were kept under the 58% RH atmosphere in dark before irradiation. The films of **2** and **3** were also prepared in the presence of 1000 equivalent of **6**, **7** or **8**. For preparing the film containing **4**, the DMF solution containing 50 μmol polymer g^{-1} of **4** in the absence and the presence of **5** equivalent of **5** was used. Further addition of **5** caused the heterogeneous films. The film of **4** containing 100 equivalent of **7** in place of **5** was also prepared. These film thicknesses were ca. 0.06 mm. Photoirradiation of the films was performed with a 75-W Hg lamp

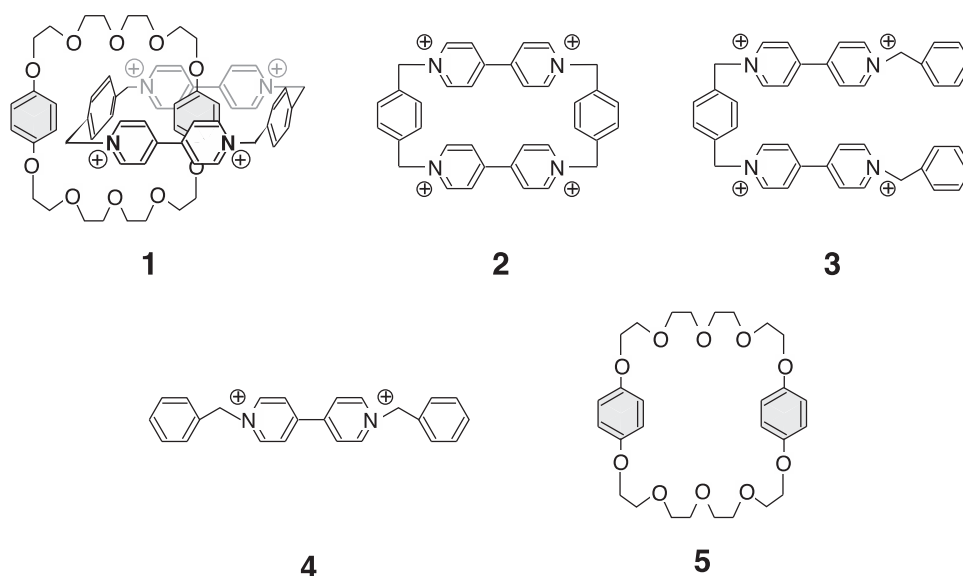


Fig. 1. Structures of some compounds used in this study.

by using a glass filter to obtain the light of the wavelengths longer than 300 nm. Photoirradiation of the films of **1**, **2**, **3**, **4**, and **4@5** was performed for 3 min, while the films of **6@2** and **6@3** were irradiated for 20 min and those of **7@2** and **8@2** were irradiated for 5 min. The absorption spectra of the film were measured on the glass plate fixed in a 1 cm cell from 350 to 900 nm before and after photoirradiation.

3. Results and discussion

3.1. Absorption and complexation behavior in solution

Anelli and coworkers have reported that **1** showed a broad absorption band around 480 nm in acetonitrile, associated with the charge transfer band between the viologen and the dialkoxybenzene unit in a molecule of **1** [13]. The alternating π -donor/ π -acceptor stacking structure of **1** was also confirmed by X-ray crystallography measurement in the solid state [13]. Fig. 2 shows the absorption spectra of **1** in DMAc. A red color with the absorption maximum at 480 nm in DMAc indicates that **1** adopts the similar stacking structure in DMAc to that in acetonitrile or the solid state.

The charge transfer band of the DMAc solution containing **2** and the π -electron donating guests is also shown in Fig. 2. When **6** and **7** were added as the guest to the DMAc solution containing **2**, the charge transfer band developed with increasing the guest concentration. The maximum wavelengths of the charge transfer bands were observed at 447 and 456 nm for **6@2** and **7@2**, respectively (Table 1). Since it is known that the maximum wavelength of the charge transfer band increases along with the decreasing

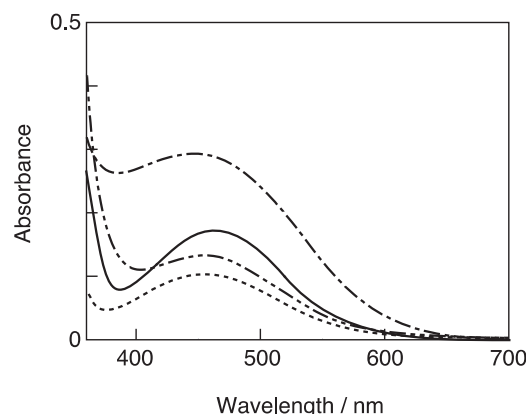


Fig. 2. Visible absorption spectra of the DMAc solutions of 0.02 mM of **1** (—), the solution of 2.6 mM of **2** in the presence of 0.3 mM **6** (---) or **7** (····), and the acetone solution containing 2.6 mM **4** and 0.3 mM **5** (····).

the ionization potential of the donor component [14], the result obtained may be due to the lower ionic potential of **7** than that of **6** [15]. A similar trend was observed in acetonitrile [13,15], although both the charge transfer bands of **6@2** and **7@2** in acetonitrile were shifted to the longer side as compared with those in DMAc (Table 1). The plot of the guest-induced charge transfer intensity at 450 nm in DMAc as a function of the guest concentration was well fitted to the theoretical fitting curves derived from the 1:1 stoichiometry, as shown in Fig. 3. This indicates the formation of the 1:1 inclusion complexes of **6@2** and **7@2** in DMAc, whose binding constants were estimated to be 3.0 and 2.3 M⁻¹, respectively

Table 1
Binding constants and spectroscopic data for the complexes of **6@2**, **7@2** and **5@4** in solutions.

Compound	DMAc		Acetonitrile		Acetone	
	$\lambda_{\max}$ (nm)	K (M ⁻¹)	$\lambda_{\max}$ (nm)	K (M ⁻¹)	$\lambda_{\max}$ (nm)	K (M ⁻¹)
1	461	—	—	—	—	—
6@2	447	3.0	460 ^a	150 ^a	460 ^a	100 ^a
7@2	456	2.3	475 ^b	18 ^b	—	—
4@5	^c	^c	—	—	450	230

^a Ref. [15].

^b JACS, 1993, 115, 5296.

^c The data could not be obtained.

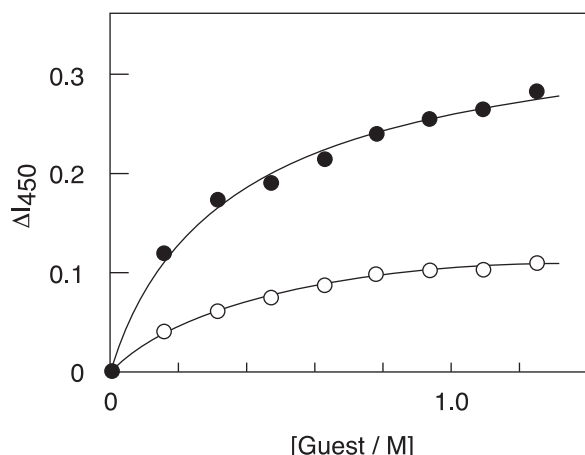


Fig. 3. Plots of the intensity of the guest-induced charge transfer band for **2** as a function of the concentration of **6** (●) and **7** (○).

(Table 1). The larger binding constant for **6@2** than that of **7@2** indicates the higher binding ability of **6** than that of **7**, which is coincident with the observation in other solutions such as acetonitrile [13,15]. However, the binding constants estimated in DMAc are much smaller than those in the other solutions. This may be due to different experimental condition, in which the concentrations of **2** and guest in this study are much higher than those reported [13,15]. When **8** was added to the DMAc solution containing **2**, no charge transfer band was observed, indicating no intermolecular interaction between **8** and **2** because of the π -electron deficient character of **8**.

On the other hand, the solution containing **3** did not exhibit the charge transfer band in the presence of the guest **6** and **7** in DMAc. This fact indicates no interaction between **3** and these guests intermolecularly because of the acyclic structure of **3** as well as the guest molecules. The cyclic structure of **2** may promote the strong intermolecular interaction between the viologen and the π -electron donating guest.

The visible absorption spectrum of the acetone solution containing **4** and **5** is also shown in Fig. 2. The charge transfer band around 450 nm indicates the intermolecular interaction between **4** and the dialkoxybenzene unit in **5** [13,16,17]. The analysis by nonlinear least square curve fitting of the experimental absorption intensity at 450 nm gave the binding constant of **4@5** with the value of 230 M^{-1} (Table 1). This value is the similar order of the binding ability to that for **6@2** in acetone [15]. In DMAc the binding constant of **4@5** could not be obtained because of the unstable absorption spectrum of **4** in the presence of **5**.

3.2. Photochromism of **1** in the polymer matrix

The PVP film containing **1** showed a red color with a broad absorption band around 480 nm, suggesting the charge transfer interaction between the viologen and the dialkoxybenzene units in **1**. As mentioned above, **1** adopted the structure with alternating π -donor/ π -acceptor stacking interaction in a molecule in both solution and solid states [13]. The charge transfer band of **1** observed in the polymer matrix indicates that **1** adopts the similar structure to that in those states.

Photoirradiation of the film containing **1** caused the development of the blue color with an absorption peak at 620 nm, as shown in Fig. 4. This indicates the structural change of the viologen unit in **1** from a dication to a radical cation, which is generated by the photoinduced reduction. The photoinduced absorption band decreased with time, and completely disappeared after

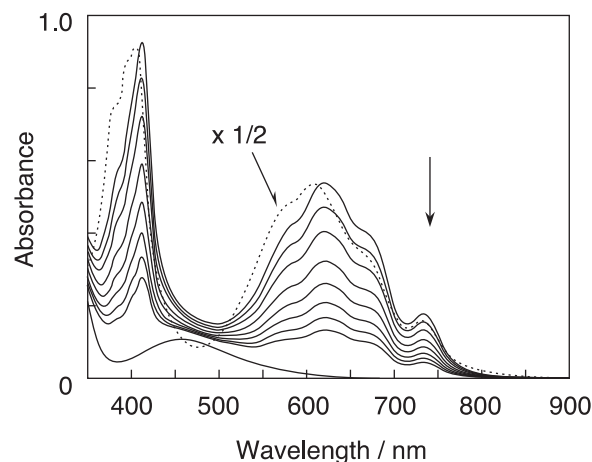


Fig. 4. Change in the absorption spectra of **1** (—) and **2** (---) in dark and immediately after photoirradiation. 0, 2, 5, 10, 15, 20, 25, 30 min, and dark.

80 min to regenerate to the original red film. This suggests that the photogenerated radical cation reverted to the dication form. The bleaching reaction may proceed in the following mechanism; (i) the recombination of the photogenerated radicals and/or, (ii) the oxidation by oxygen dissolved in the polymer matrix [8,10]. However, such longer lifetime of the radical cation as compared to that in solution would be associated with stabilization by polymer matrix through restriction of both back electron transfer and air-oxidation [8,10]. The freedom and the mobility of **1** might be extremely restricted in the polymer [18]. Since the photochromic reaction can be repeated more than several times, the former bleaching process may be dominant rather than the later one. The decay curve of the photoreduced **1** is shown in Fig. 5a, and the half-life of the photogenerated viologen radical estimated is summarized in Table 2. The half-life of the photoreduced **1** in the polymer matrix was much longer than that of the photoreduced viologen in the solution [19]. This might be due to the restriction of the back reaction in the polymer matrix. The photogenerated products would be not only fixed and stabilized in the polymer matrix but also shielded from air oxidation.

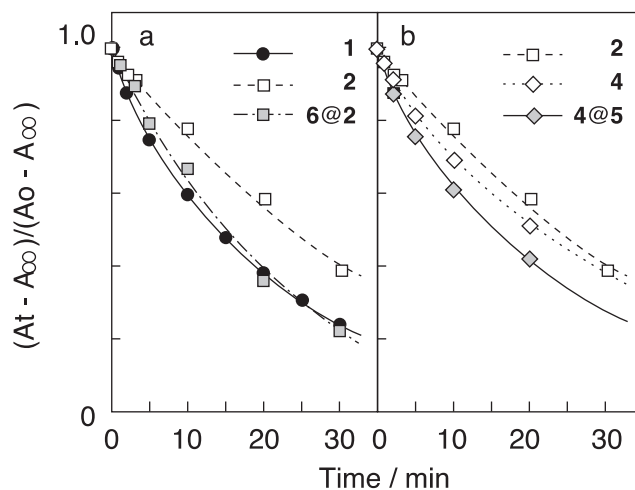


Fig. 5. Time profile of the decay of the photogenerated reduced viologen of **1** (●), **2** alone (□) and in the presence of **6** (■), **4** alone (◇) and in the presence of **5** (◆), respectively. Here, we define A_{∞} as the absorbance before photoirradiation at 620 nm for **1** and **6@2**, at 615 nm for **7@2** and at 610 nm for **2**, **4**, **4@5**, respectively, A_0 as the absorbance immediately after irradiation, and A_t , as the absorbance at the time t .

Table 2The $\lambda_{\max}$ and $\tau_{1/2}$ for the photoreduced viologen radical cations.

Viologen derivatives	Added π -electron donating component	Photoreduced viologen radical cation	
		$\lambda_{\max}$ (nm)	$\tau_{1/2}$ (min)
1		620	15
2		610	24
	6	620	14
	7	615	20
3		611	22
	6	611	22
4		610	22
	5	610	15

3.3. Photochromism of **2** as compared with **1**

When irradiated to the pale yellow film containing **2**, the film showed the similar spectral change to that of **1** (Fig. 4). This indicates that photogeneration of the viologen radical cation and the reversion to the dication with time proceeding. However, the photogenerated $\lambda_{\max}$ of **2** was observed at 610 nm, which is shifted to shorter wavelength by 10 nm as compared with that of **1** (620 nm), while the film containing **3** and **4** exhibited the photogenerated absorption peak at 611 and 610 nm, respectively. Since the radical cation dimer is known to show the peak at 360 and 520 nm [20], the obtained results suggest that there is no interaction between two viologen units in a molecule of **2** and that the red shift of the photogenerated absorption peak for **1** is unusual. The following reasons can be considered for interpreting the red shift of the photoreduced viologen peak of **1**; (i) the difference of the environment around the viologen unit between **1** and **2** due to the different species included in the cavity of the tetracationic cyclophane; the dialkoxybenzene unit for **1** and solvent molecules for **2**, (ii) the decrease in the transition energy due to the interaction of the transition dipole moment between viologen and dialkoxybenzene unit, or (iii) the change in the interaction between viologen units by the insertion of the dialkoxybenzene molecule between the units.

Furthermore, the difference in the photochromic property between **1** and **2** was observed in the bleaching rate of the photoreduced viologen. The bleaching rate of the photoreduced **2** was slower than that of **1** but was similar to those of **3** and **4**, as shown in Fig. 5. (The data of **3** was not shown.) The faster reversion of the photogenerated viologen radical of **1** suggests the faster back reaction as compared with that of **2** as well as **3** and **4**. Among two quenching processes mentioned above, the recombination reaction of the photogenerated radicals might be affected by making the catenane structure. The existence of π -electron donating dialkoxybenzene unit around the photochromic viologen unit may promote the recombination reaction of the photogenerated radicals. This may be resulted from the stability of the viologen under the condition of the π -electron donating environment. The viologen included in the π -electron donating cavity may prefer to exist as the dication rather than the reduced radical cation due to the donor–acceptor electrostatic interaction. Therefore the photoreduced viologen radical cation of **1** reverts to the dication with the faster rate than that of **2**.

3.4. Photochromism of **2** in the presence of the guest

To confirm the effect of the π -electron donating species on the absorption peak and the bleaching rate of the photoreduced viologen radical, the photoirradiation of the film containing **2** has been carried out in the presence of the π -electron donating guest such as **6** and **7**.

When **6** was used as the π -electron donating guest, the film containing **6@2** exhibited the orange color before photoirradiation,

which correspond to the charge transfer band between **6** and the viologen unit of **2**. This indicates that **6** is included in the cavity of **2** to form the inclusion complex, **6@2**. In other words, the π -electron deficient cavity of **2** is occupied by the π -electron donating molecule, **6**.

Upon photoirradiation of the film containing **6@2**, the photogenerated absorption peak was observed at 620 nm, which is shifted to longer wavelength by 10 nm as compared with that of the guest free film of **2**. This result suggests that the addition of the guest caused the red shift of the photoreduced absorption peak of **2**. When irradiated to the film of the acyclic analog, **3**, in the presence of **6**, the photoinduced absorption peak was observed at 611 nm, which was the same wavelength to that of the **6** free film of **3**. This suggests that there is no interaction between **3** and **6**, which was supported by no observation of the charge transfer absorption band between **3** and **6** in the solution. The supramolecular structure, in which the π -electron donating guest is included in the cavity of **2**, is important to cause the red shift of the photoreduced viologen radical. The guest-induced red shift of the photoreduced **2** may be resulted from the same reason as the case of **1**.

Furthermore, the addition of **6** to the film of **2** caused the faster bleaching of the photoreduced viologen of **2** as compared with that of the film of **2** alone, as shown in Fig. 5a. In the presence of **6**, the bleaching rate of the photoreduced **2** is similar to that of **1**, indicating that the bleaching rate is affected by the presence of the π -electron donating guest. The guest-induced faster reversion of the photoreduced **2** may be resulted from the same reason as the case of **1**. The half-life of **6@2** is almost same as that of **1** (Table 2). So it can be concluded that the photochromic behavior in not only the photoreduced absorption peak but also the bleaching rate of the photoreduced **6@2** is similar to that of **1**. Furthermore, the ability of complex formation is the polymer matrix seems to be similar to that in the solution, although the mobility of the compounds is restricted as mentioned above [18].

When **7** was used as the guest in place of **6**, the photogenerated absorption peak of **2** was observed at 615 nm. Furthermore, the half-life of the film of **7@2** was observed at 20 min (Table 2). As compared with **2**, the red shift and the faster bleaching of the photoreduced viologen of **7@2** were observed. The smaller effects of **7** on the red shift in absorption peak and the reversion rate as compared with those of **6** may be resulted from the weaker interaction of **7** with **2** than that of **6**. This is coincident with the fact that the binding constant of **7@2** is smaller than that of **6@2**.

Upon addition of benzonitrile, **8**, which was used as the π -electron deficient guest in place of the π -electron donating one, into the film containing **2**, the absorption peak and the bleaching rate of the photoreduced viologen of **2** was not affected. This result indicates that there is no change in the photochromic properties of **2** when the π -electron deficient guest was used. It can be concluded that the red shift and the faster reversion of the photogenerated viologen radical of **2** are induced by the addition of the π -electron donating guest, which is included in the cavity of the tetracationic cyclophane, **2**, by means of the π -donor/ π -acceptor interaction.

3.5. Photochromism of **4** in the presence of **5**

The effect of the π -electron donating cyclic molecule on the photochromic behavior of the acyclic viologen was also investigated in the polymer matrix [14]. **4** and **5** were used as the acyclic viologen and the π -electron donating cyclic molecule, respectively.

As mentioned above, the film containing **4** exhibited the photoinduced color development of the maximum at 610 nm and bleached with the half-life time of 22 min. This photoinduced spectral variation was similar to that of the guest free film of **2**.

The film containing **4** in the presence of **5** exhibited the charge transfer band around 450 nm before photoirradiation, indicating

the formation of the inclusion complex of **4** with **5** (**4@5**) even in the polymer matrix as like in the solution or the solid state [13].

When irradiated to the film containing **4@5**, the similar spectral change was observed to the case of **5** free film of **4**. Although no shift in the photogenerated absorption peak was observed, the acceleration of the reversion rate was observed upon addition of **5** into the film of **4** (Fig. 5b). The half-life for the film of **4@5** was almost same as that of **1** and **7@2** (Table 2). These results indicate that the reversion of the photoreduced **4** became faster by being included in the π -electron donating cavity of **5**. This is coincident with the result obtained in the case of **1**. The reason for no shift of the photoreduced absorption peak of **4** is interpreted in terms of the small amount of **5** added into the film of **4**. This was due to the experimental limit because further addition of **5** caused the heterogeneous film of **4**. When **7** was used as the acyclic analog in place of **5**, no change in the photochromic properties of the film containing **4** and **7** was observed, indicating no interaction between **4** and **7**.

These results demonstrate that the photoreduced viologen reverts to the dication with the faster bleaching rate by being included in the cavity of π -electron donating macrocyclic molecule of **5**.

4. Conclusion

The redox-type photochromic property of catenane consisting of the tetracationic cyclic viologen and *p*-benzocrown ether is different from that of the tetracationic cyclic viologen, which is the component molecule of catenane. However, the cyclic viologen showed the similar photochromic behavior to that of catenane when the π -electron donating guest was present, which is included in the cavity of the cyclic viologen. The difference in photochromic behavior between catenane and the no complexed viologen derivatives is attributed to the intermolecular charge transfer interaction between the viologen and the dialkoxybenzene units. There is a possibility that the electron transfer pathway change by the presence of the π -electron donating macrocycle. Further study to clarify in this point is now under way.

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