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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-pyrroridone) (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 dialkoxybenezene units in **1**. Upon photoirradiation the film changed the color to blue with the absorption maximum (λ_{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 λ_{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 λ_{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** (λ_{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.

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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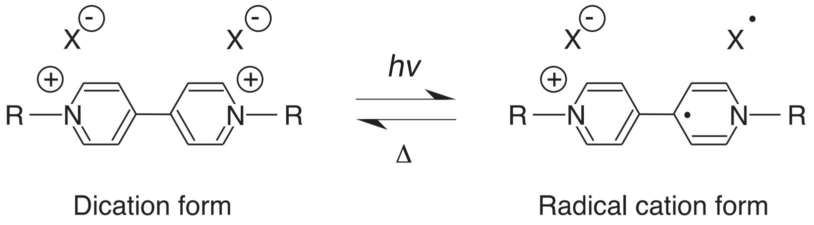

Scheme 1. Photoreduction of violognen.

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 Menschtkin reaction of 4,4′-bipiyridine 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′-bipiyridine and benzylbromide, followed by the anion-exchange reaction. All bipyridinum derivatives were obtained as hexafluorophosphate salts. These products were identified by ^{1}H 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-pyrroridone) (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

^{1}H 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_0represent 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_0represent 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-pyrroridone) (PVP) films. The films were prepared by solvent cast method from DMAc solution on the glass plate with 8 × 38 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