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Bi-directional Inclusion Complexation of Methylalkyl Viologens with β-Cyclodextrin and Naphthyl Group-Tethered β-Cyclodextrins

JOON WOO PARK* and SOO YEON LEE
Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea

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Abstract

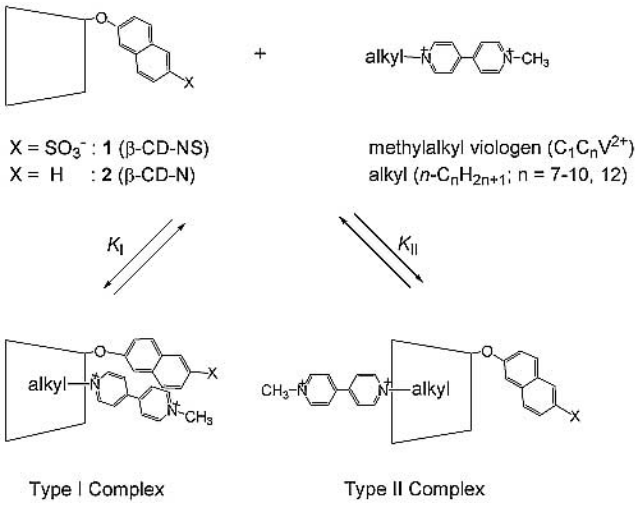
Inclusion complexation of methylalkyl viologens ($C_1C_nV^{2+}$; n = 7–10, 12) with mono-6-O-(2-sulfonato-6-naphthyl)-β-CD (**1**) and mono-6-O-(2-naphthyl)-β-CD (**2**) were studied by steady-state and time-resolved fluorescence spectroscopies and compared with the binding of the viologens with native β-CD investigated by induced circular dichroism. The viologens form bimodal complexes with **1** and **2**, in which the bipyridinium group of the viologens is placed on the primary side (type I complex) and secondary side (type II complex) of β-CD cavity, while the group is predominantly on the secondary side in complexes with native β-CD. The microscopic binding constants K_I and K_{II} were calculated from the analysis of fluorescence data. The formation of the type I complexes with **1** and **2** appears to be largely due to the charge–transfer interaction between the bipyridinium and naphthyl groups in the complexes. This work shows that the location of the bipyridinium group in β-CD complexes and in the type II complexes of the viologens with **1** and **2** depends little on the length of alkyl chain of the viologens.

Introduction

Cyclodextrins (CDs) are torus-shaped cyclic oligosaccharides with hydrophobic cavities and are widely used as host moieties in supramolecular chemistry and building units for supramolecular structures in basic researches as well as in various fields of industries [1–3]. Guest molecules can be included from both ends of CD cavities, which differ in the size of opening and acidity of hydroxyl groups. The directional inclusion of guests into CD cavities, and thus the orientation of guests in CD complexes are believed to be very important in molecular recognition and chemical reactions mediated by CDs [4].

A long alkyl chain is a typical part of guest molecules for CDs. Alkyl viologens, 1,1′-dialkyl-4,4′-bipyridinium salts, are prototypical electron acceptors [4–9]. Inclusion complexation of alkyl viologens with CDs has been a subject of numerous studies [9–15] as viologens are widely used as electron acceptor or relay in CD-based supramolecular donor-acceptor systems and CDs affect the redox chemistry of viologens.

In a previous report [4], we have shown that the bipyridinium moiety of methyloctyl viologen ($C_1C_8V^{2+}$) is preferentially placed above the wider secondary side of native β-CD, while the moiety favors the primary side in complexation with 6-O-(2-sulfonato-6-naphthyl)-β-CD (β-CD-NS: **1**) mainly due to the charge–transfer interaction between the bipyridinium and naphthylsulfonate groups.



Scheme 1. Bimodal inclusion complexation of methylalkyl viologens with naphthyl group-tethered β-CDs (the dimerization equilibria of **1** and **2** [16] are omitted for clarity).

This differs from reports by Kodaka who concluded that the bipyridinium group is placed on the primary side of CDs from induced circular dichroism of diheptyl viologen/CD complexes [9–11]. In this work, we extend the previous finding and report the dependence of the bi-directional inclusion complexation of methylalkyl viologens with **1** and 6-O-(2-naphthyl)-β-CD (β-CD-N: **2**) on the length of alkyl chains of viologens (Scheme 1).

* Author for correspondence. E-mail: jwpark@mm.ewha.ac.kr

Experimental

Materials

β-CD (Aldrich) was recrystallized from water and vacuum-dried. 2-Naphthol was purified by sublimation at reduced pressure. C-6-Mono-tosylated β-CD (β-CD-OTs) was prepared according to a literature procedure [17]. Synthesis and characterization of 6-O-(2-sulfonato-6-naphthyl)-β-CD **1** and 6-methoxy-2-naphthalenesulfonate (MNSS) are reported elsewhere [16]. The synthetic procedure of mono-6-O-(2-naphthyl)-β-CD **2** is described below. Dimethyl viologen dichloride ($C_1C_1V^{2+}\cdot 2Cl^-$) was obtained from Aldrich and used without further purification. The chloride salts of other viologens ($C_1C_nV^{2+}\cdot 2Cl^-$: n = 7–10, 12) were prepared by reacting 1-methyl-4,4′-bipyridinium iodide with the corresponding alkyl halides in acetonitrile, followed by anion exchange to Cl^- by stirring with AgCl in aqueous solutions.

Synthesis of mono-6-O-(2-naphthyl)-β-CD (β-CD-N) **2**

β-CD-OTs (4.6 g, 3.6 mmol) and 2-naphthol (1.0 g, 7.2 mmol) were reacted in 15 mL dry DMF containing 0.29 g of NaOH for 4 days at 70 °C under N_2 atmosphere. After precipitation with acetone, the product was purified by silica-gel chromatography (eluent : EtOAc : *i*-PrOH : H_2O = 7 : 7 : 4 (v/v)). The UV active and β-CD-active fractions were concentrated and precipitation with diethyl ether afforded the title compound (0.90 g, 20%): UV(H_2O) λ_{max}/nm, 272, 312, 326; mp 215–216 °C (dec.); ^{1}H NMR in D_2O : DMSO-d_6 = 3 : 1 at 25 °, δ 7.3–7.4 (m, 2H), 7.4–7.5 (m, 2H), 7.8 (m, 1H), 7.95 (d, 2H) (peaks from CD protons appear at δ 5.1 and δ 3.5–4.1); MS (FAB): 1260.4167 (Calcd. for $C_{52}H_{76}O_{35}$, 1260.4163).

Spectral measurements

Absorption spectra were recorded with a Cintra 20 UV-vis spectrophotometer. Difference spectra for charge-transfer complexation were taken from mixing tandem double cells recording the spectra of the mixtures against unmixed solutions. Steady-state fluorescence spectra (λ_{ex} = 326 nm) were obtained with a Hitachi F-3010 spectrofluorimeter. Fluorescence decay measurements were performed using time-correlated single photon counting setup assembled at Korea Basic Science Research Institute. FAB MS data were collected at the Korea Basic Science Research Institute. Concentrations of **1** and MNSS were calculated from the reported UV absorption data [16]: due to the low solubility of **2** in water ($\sim 10^{-4}$ M), we could not determine its molar absorptivity with reasonable accuracy, but assumed that it is the same as that of 3-(2-naphthoxyl)-1-aminopropane, $\varepsilon_{272} = 4460\ M^{-1}\ cm^{-1}$ [6]. The viologen concentration was calculated by using $\varepsilon_{262} = 21000\ M^{-1}\ cm^{-1}$ [18]. Circular dichroism spectra for viologen/β-CD complexation were taken with a JASCO J-810 spectropolarimeter as described in a previous paper [4]. All measurements were carried out at 25 °C using appropriate temperature controller. Unless otherwise specified, ionic strength of solutions was maintained as 0.10 M with NaCl.

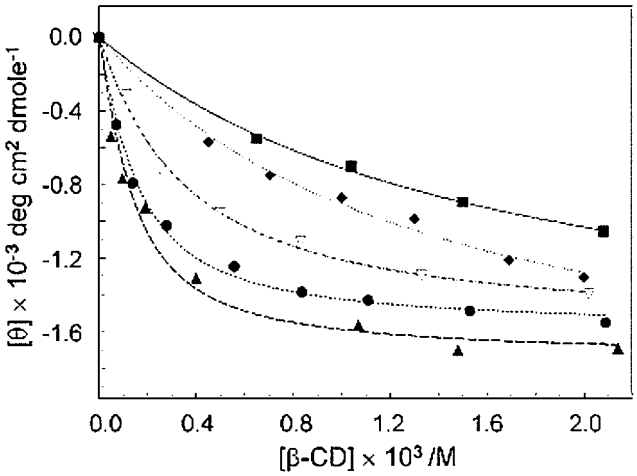


Figure 1. Dependence of the apparent molar ellipticity of 1.0×10^{-4} M of methylalkyl viologen/β-CD systems at 255 nm on the concentration of β-CD. Viologens are $C_1C_7V^{2+}$ (■), $C_1C_8V^{2+}$ (♦), $C_1C_9V^{2+}$ (▽), $C_1C_{10}V^{2+}$ (●), and $C_1C_{12}V^{2+}$ (▲).

Results and discussion

Binding of methylalkyl viologens with β-CD

Complexation of viologens with β-CD induces negative circular dichroism corresponding to the absorption band of the bipyridinium moiety around 255 nm [4, 9–11]. For a given viologen solution, the induced circular dichroic (ICD) spectra grow and level off to a constant value as the concentration of β-CD increases as shown in the Figure 1. For 1 : 1 complexation between a viologen and β-CD (Equation (1)), the dependence of the ellipticity [θ] of a given viologen solution on the concentration of β-CD is given by Equation (2) [4].

$$V^{2+} + \beta\text{-CD} \rightleftarrows V^{2+}\text{-}\beta\text{-CD};$$
$$K = [V^{2+}\text{-}\beta\text{-CD}]/\{[V^{2+}][\beta\text{-CD}]\}, \quad (1)$$

$$[\theta] = ([\theta]_{complex}/2[V^{2+}]_0\{([V^{2+}]_0 + [\beta\text{-CD}]_0 + 1/K)^2) - \sqrt{([V^{2+}]_0 + [\beta\text{-CD}]_0 + 1/K)^2 - 4[V^{2+}]_0[\beta\text{-CD}]_0}\}, \quad (2)$$

where $[\theta]_{complex}$ is the molar ellipticity of the complex at the measured wavelength and the subscripts '0' denote the initial concentrations. The [θ] vs [β-CD] data presented in Figure 1 fitted well to Equation (2): we cannot rule out the possibility of the formation of 1 : 2 viologen/β-CD complexes for $C_1C_{12}V^{2+}$, but the consideration of the formation of 1 : 2 complexes resulted in little improvement in fitting, presumably due to the small 1 : 2 complexation constant [19, 20]. The determined binding constants of viologens with β-CD are listed in Table 1.

The binding constants of the viologens with β-CD increase with the length of alkyl chains and the values are similar to those of alkylsulfonate with the corresponding alkyl chain [19]. This is an usual trend observed with surfactants having long alkyl chains [19, 20] and indicates that the binding is mainly driven by inclusion of the alkyl chain into β-CD cavity *via* apolar hydrophobic effect.

Table 1. Formation constants (K, K_C) of methylalkyl viologens with β-CD and naphthyl group-tethered β-CDs and the fraction (γ) of residual fluorescence intensities of the viologen/**1** or **2** complexes at 25.0 °C in 0.1 M aqueous NaCl solutions.[a]

Viologen	β-CD	β-CD-NS: **1**		β-CD-N: **2**	
	K/M^{-1}	γ	K_C/M^{-1}	γ	K_C/M^{-1}
$C_1C_7V^{2+}$	440	0.11	1700	0.19	1200
$C_1C_8V^{2+}$	890	0.090	4700	0.18	2500
$C_1C_9V^{2+}$	2400	0.081	15500	0.19	7000
$C_1C_{10}V^{2+}$	7800	0.085	33000	0.17	19700
$C_1C_{12}V^{2+}$	12000	–[b]	–[b]	0.17	53000

[a] The K_C values are the apparent binding constants of viologens with **1** or **2** and correspond to $(K_I + K_{II})$ in Scheme 1.
[b] Too large to be determined with reasonable accuracy.

Contrast to the binding constants, the $[\theta]_{complex}$ values did not show a systematic dependence on the length of alkyl chains of viologens and the averaged value was $-1900(\pm 0.15)$ deg cm^2 dmole^{-1}. As the sign and magnitude of ICD of a chromophore/β-CD complex depend highly on the position and orientation of the chromophore with respect to β-CD cavity [9–11], this result indicates that the bipyridinium moieties of the viologens in their β-CD complexes take similar position with respect to β-CD cavity, predominantly on the secondary side of β-CD as concluded for $C_1C_8V^{2+}$/β-CD complex [4].

Fluorescence quenching studies on the binding of methylalkyl viologens with naphthyl group-tethered β-CDs

The fluorescence of naphthyl compounds is quenched by viologens due to the electron transfer from the excited fluorophore to bipyridinium moiety of viologens [4, 7]. We investigated the fluorescence quenching of **1** and **2** by $C_1C_nV^{2+}$ (n = 7–10, 12). As shown in our previous work for **1** by $C_1C_8V^{2+}$ [4], the quenching by $C_1C_nV^{2+}$ was much more efficient than that by dimethyl viologen ($C_1C_1V^{2+}$). For an example for this, the fluorescence quenching of **1** by $C_1C_1V^{2+}$ and $C_1C_9V^{2+}$ are compared in the Figure 2. The efficiency of the quenching becomes greater as the alkyl chain of the viologen quenchers is longer (see below). Compared to this, the fluorescence quenching of MNSS was much less efficient and the viologens showed similar quenching efficiency. These results clearly indicate that the fluorescence quenching of the naphthyl group-tethered β-CDs is facilitated by inclusion of the alkyl group of the quenchers into the β-CD cavity. Such an efficient quenching mediated by the inclusion complexation has been reported with other β-CD-tethered donors and acceptors [4, 6, 21–25].

The Stern–Volmer plots [26] for the quenching of β-CD-appended naphthalenes (**1** and **2**) showed downward curvature, whereas the plots of quenching data of MNSS exhibited good linearity (Figure 3). The downward curvature in the Stern–Volmer plots is an indication that the naphthalene fluorescence is not completely quenched in the complexes with viologens. To visualize the residual fluorescence of the complexes and dependence of the quenching on the alkyl

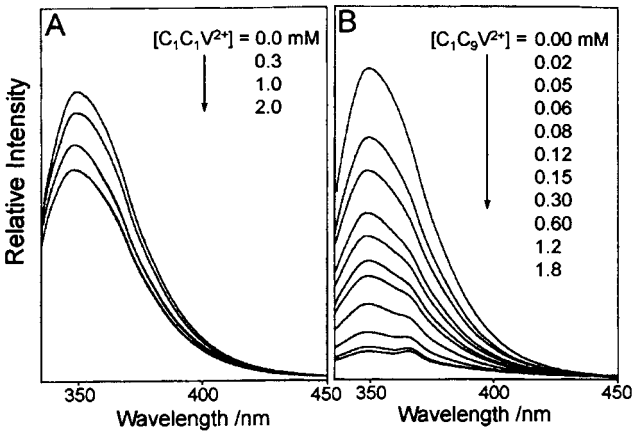


Figure 2. Quenching of the fluorescence of 1.0×10^{-5} M of **1** by $C_1C_1V^{2+}$ (A) and $C_1C_9V^{2+}$ (B). The concentrations of viologens are given in the figure.

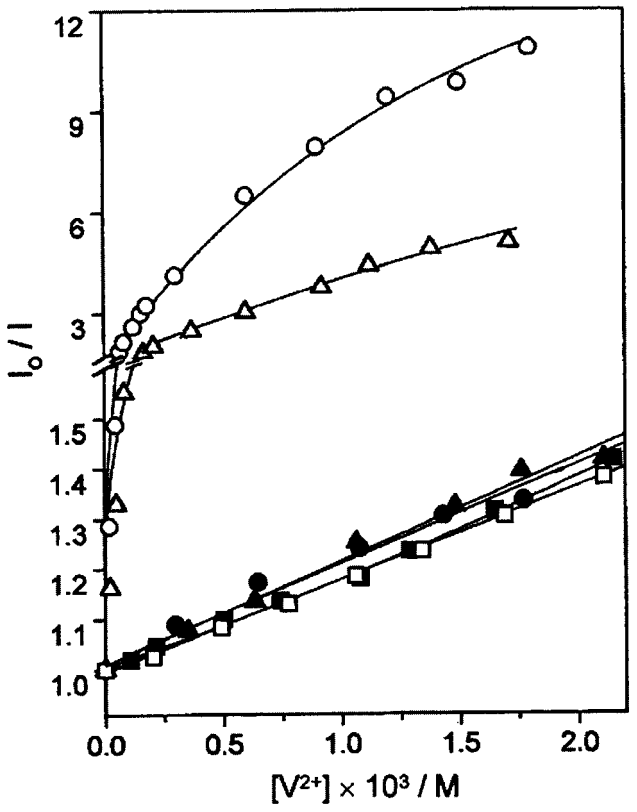


Figure 3. Stern–Volmer plots for quenching of **1** (○, ●), **2** (△, ▲) and **3** (□, ■) by $C_1C_1V^{2+}$ (filled symbols) and $C_1C_9V^{2+}$ (open symbols).

chain length of viologens, we plotted the fluorescence intensity as a function of quencher concentration in Figure 4. Figure 4 clearly shows that the intensity of the residual fluorescence of complexes of **2** is larger than that of **1**.

It was shown that the compound **1** forms a head-to-head dimer by mutual inclusion of the appended sulfonatonaphthyl groups inside the β-CD cavities of counter molecules. The dimerization constant (K_D) was found to be 9700 M^{-1} from concentration dependence of circular dichroism and NMR spectra, and the fluorescence intensity of the naphthyl group in the dimer is 2.2 times greater than that in the monomer [16]. We could not determine the K_D value

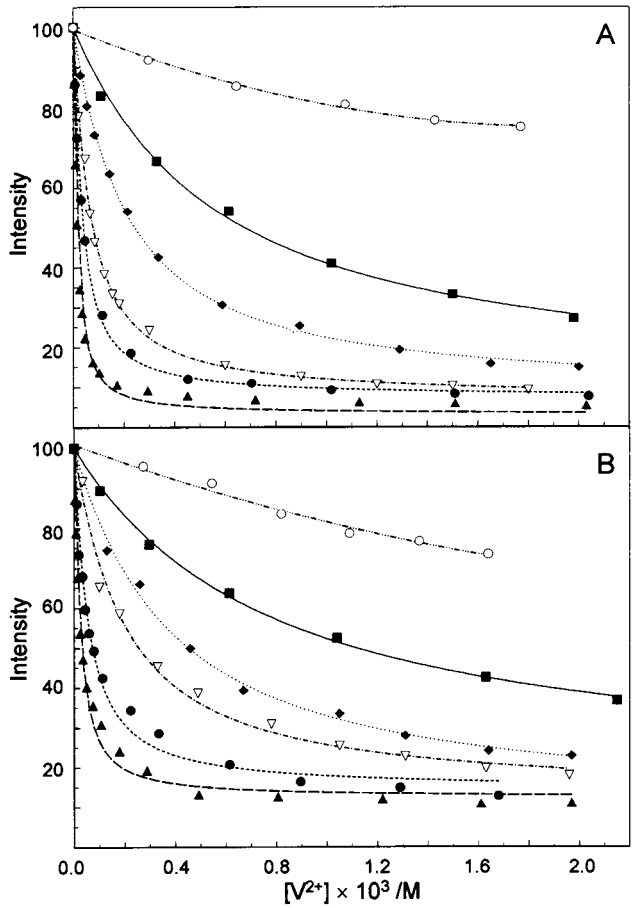


Figure 4. Variation of fluorescence intensities of **1** (A) and **2** (B) with the concentration of viologen quenchers. [**1**] = [**2**] = 1.0×10^{-5} M; viologens are $C_1C_1V^{2+}$ (○), $C_1C_7V^{2+}$ (■), $C_1C_8V^{2+}$ (♦), $C_1C_9V^{2+}$ (▽), $C_1C_{10}V^{2+}$ (●), and $C_1C_{12}V^{2+}$ (▲).

of **2** with reasonable accuracy due to the low solubility ($\sim 10^{-4}$ M). The distance between the sulfonate groups in the dimer of **1** was estimated to be about 17 Å from CPK model. This suggests that the electrostatic repulsion between the sulfonate groups in the dimer of **1** would be negligible, especially in the medium of ionic strength of 0.1 M employed here. Thus we can assume that K_D and the ratio of fluorescence intensities of the dimeric and monomeric forms of **2** are the same as those of **1**.

The observed fluorescence intensity (I_{obs}) is the sum of contributions from existing species in solutions, i.e., the monomer and dimer of the fluorescent hosts and viologen type I and II complexes shown in Scheme 1. In the concentration of 1.0×10^{-5} M for **1** or **2** used for the fluorescence measurements, the fraction of monomeric form is 0.85 and thus the dimerization equilibria of the naphthyl-group-tethered β-CDs can be ignored in the analysis of the fluorescence titration data. For a given viologen, the ratio of concentrations of type I and type II complexes is the same as the ratio of the equilibrium constants of the complexation reactions and is independent of the concentration of the viologen. Thus, the dependence of I_{obs} on the concentration of viologens [V^{2+}] is expressed as Equation (3).

$$I_{obs}/I_o = (1 + \gamma K_C[V^{2+}])/(1 + K_C[V^{2+}]), \qquad (3)$$

where I_o is the fluorescence intensity in the absence of a viologen; K_C is the apparent binding constant of the viologen with the fluorescent hosts; γ is the ratio of fluorescence intensities of the viologen complex and the monomeric forms of the fluorescent hosts and corresponds to the fraction of residual fluorescence at high viologen concentration [4]. The equilibrium concentration of free viologen [V^{2+}] is related to the total concentrations of the β-CD-naphthalene $[F]_o$ and viologen $[V^{2+}]_o$ by Equation (4) from mass balance.

$$[V^{2+}] = \{([V^{2+}]_o - [F]_o - 1/K_C) + (([V^{2+}]_o + [F]_o + 1/K_C)^2 - 4[V^{2+}]_o[F]_o)\}^{1/2}\}/2. \qquad (4)$$

Nonlinear least-squares fitting of fluorescence intensity *vs* [viologen] profiles (Figure 4) to Equation (3) under the restriction of Equation (4) gave K_C and γ values. The results are included in Table 1: the variation of K_D value gives small difference in K_C and γ values, e.g., from 2500 M^{-1} and 0.14, respectively, when $K_D = 0$ M^{-1} to 2700 M^{-1} and 0.20 when $K_D = 20000$ M^{-1} for the quenching of **2** by $C_1C_8V^{2+}$.

The K_C value increases as the alkyl chain length of the viologen is longer and the value was much greater than the binding constants of the corresponding viologen with native β-CD. For a corresponding viologen, it is also seen that the K_C value with **1** is considerably larger than that with **2**. However, for a given naphthyl group-tethered β-CD, no systematic variation of γ values on the alkyl chain length of viologens was found and the averaged γ values were 0.092 ($\pm$0.013) for **1** and 0.18($\pm$0.01) for **2**. This is reminiscent of independence of the molar ellipticity of viologen/β-CD complexes on the length of alkyl chains of viologens described in the preceding section.

As depicted in Scheme 1, viologens can form complexes with the naphthyl group-tethered β-CDs by inclusion from either side of the CD cavity. The type I complex is non-fluorescent and exhibits charge-transfer absorption band, whereas the fluorescence of naphthyl group is not completely quenched in the type II complex giving the residual fluorescence [4]. Thus, the apparent binding constant K_C is related to the microscopic binding constants defined in Scheme 1 by $K_C = (K_I + K_{II})$, and γ value is related to the ratio fluorescence intensities of the type II complex and the corresponding monomeric form of the fluorescent hosts ($I_{complex,II}/I_o$) and the microscopic binding constants becomes $\gamma = (I_{complex,II}/I_o) \cdot K_{II}/(K_I + K_{II})$ [4]. The difference in γ values between **1** and **2** complexes can arise from difference in the ratios of type I and type II complexes and/or in intracomplex quenching efficiency. To delineate this, we measured fluorescence lifetimes of **1** and **2** in the presence and in the absence of viologens.

Fluorescence lifetimes and directional binding constants

We previously reported that the fluorescence of **1** decays bi-exponentially with lifetimes of 8.5 ($\pm$1.0) ns and 14.5

Table 2. Formation constants of the type I and type II complexes between naphthyl group-tethered β-CDs and viologens at 25.0 °C in 0.1 M aqueous NaCl solutions (see Scheme 1)[a,b]

Viologen	β-CD-NS: **1**		β-CD-N: **2**	
	K_I/M^{-1}	K_{II}/M^{-1}	K_I/M^{-1}	K_{II}/M^{-1}
$C_1C_7V^{2+}$	1300	400	610	590
$C_1C_8V^{2+}$	3600	1100	1300	1200
$C_1C_9V^{2+}$	11800	3700	3600	3400
$C_1C_{10}V^{2+}$	25100	7900	10000	9700
$C_1C_{12}V^{2+}$	–	–	27000	26000

[a] K_I and K_{II} values were calculated from the relationships $K_C = (K_I + K_{II})$, and $K_I/K_{II} = 3.2$ and 1.0 for **1** and **2**, respectively (see text for details).
[b] The estimated uncertainty of the absolute ratio of K_I and K_{II} values is about 25%, 15% from γ values and 10% from lifetimes.

(±2.0) ns, which correspond to those of monomer and dimer of the compound, respectively [4]. The fluorescence decay profile of **2** was virtually the same as that of **1**, indicating that the presence of the sulfonate group on naphthalene ring does not make significant change in lifetimes of the naphthyl group-tethered β-CD. The decay profiles of **1** and **2** in the presence of viologens also showed the bi-exponential behaviors with the longer component (τ_1) of 9.0(±1.0) ns and the short component (τ_2) of 3.3 (±0.2) ns for both compounds, independently on the alkyl chain length of viologens. The components are attributed to the lifetimes of the free monomeric fluorescent host and type II complex, respectively: it seems that the decay of dimer is not clearly resolved from monomer due to the shift of the monomer-dimer equilibrium upon the binding of viologen. The absence of another short component in the decay profiles supports our earlier assumption that the type I complex is non-fluorescent. The same fluorescence lifetime of the type II complexes of various viologens with **1** and **2** can be taken as an evidence that the distance between and the bipyridinium and naphthyl groups in the complexes and thus the position of bipyridinium group do not vary significantly with the length of alkyl chain. This is consistent with the conclusion from the observation of independence in the molar ellipticity value of β-CD/viologen complexes described in an earlier section.

As the type I complex is non-fluorescent, the ratio of fluorescence intensity of the complex to that of the monomer, γ, is related to the lifetimes by Equation (5) [4].

$$\gamma = \frac{K_{II}}{K_I + K_{II}} \times \frac{\tau_2}{\tau_1}. \quad (5)$$

From the averaged γ values obtained from the steady-state fluorescence experiments and the lifetime data, we obtained K_I/K_{II} values as 3.2 for **1** and 1.0 for **2**. From these ratios and K_C ($= K_I + K_{II}$) values (Table 1), we evaluated K_I and K_{II} values. They are listed in Table 2.

Except $C_1C_{12}V^{2+}$, the binding constants of viologens with **1** and **2** forming type II complexes are similar to each other. This implies that the presence of the sulfonate group in **1** little affects the binding of viologen from the secondary side of β-CD, presumably due to large separation of the sulfonate group of **1** from the bipyridinium moiety in the complex to give significant electrostatic interaction energy in the binding. The K_{II} value of a given viologen with the naphthalene-tethered β-CDs is also similar to the binding constant of the corresponding viologen with native β-CD (Table 1). This supports our previous conclusion that the bipyridinium group of viologen is preferentially placed on the secondary side of β-CD cavity in the complexation with native β-CD [4]. The alkyl chain of $C_1C_{12}V^{2+}$ is long enough to protrude from the primary side of β-CD cavity [19, 20] and can interact with the appended naphthyl group. This seems to be the reason why K_{II} value of the viologen with **2** is much greater than the binding constant of the viologen with native β-CD.

In the excitation energy or electron donor–acceptor complexes or dyad compounds, the lifetime of donor fluorescence (τ) is shorter than that of free donor (τ_0) by the excitation transfer reactions following $\tau_o/\tau = 1 + \tau_o k_{et}$, which can be written as Equation (6) for type II viologen/β-CD-appended naphthalenes [26].

$$k_{et} = \frac{1}{\tau_{\text{complex}}} - \frac{1}{\tau_{\text{monomer}}}. \quad (6)$$

The intracomplex electron transfer rate constant in the type II complex is estimated from the lifetime data using Equation (6) to be 1.9 (±0.2) × 10^8 s^{-1}: k_{et} corresponds to the electron transfer rate constants from the excited naphthyl group to a viologen through β-CD cavity at center to center distance of about 15 Å, which is estimated from the CPK model. This is two orders of magnitude less than the through-polymethylene bond transfer rate: the distance from naphthyl to viologen in the type II complexes is similar to that of pentamethylene chain-linked naphthyl/viologen dyad extended by permethylated β-CD, in which k_{et} was observed as 1.8 × 10^{10} s^{-1} [7].

Driving forces for the formation of type II complexes

As discussed in a previous paper [4], two factors contribute to the stability of the type I complexes. One is the inclusion of alkyl chain of viologen into β-CD cavity by hydrophobic interaction. The other is the charge–transfer interaction between naphthyl and bipyridinium groups. Thus K_I can be represented as $K_I = K_{\text{alkyl}} \times K_{CT}$. It is expected that the K_{CT} value of 2-sulfonatonaphthyl moiety of **1** with viologens would not be significantly different from the formation constants of the charge–transfer complexes between MNSS and viologens, which are 28 (±5) M^{-1} for $C_1C_1V^{2+}$ and 48 (±6) M^{-1} for $C_1C_{10}V^{2+}$ [4]. These values are close to the charge–transfer complexation constant, 26 (±1) M^{-1}, between $C_1C_8V^{2+}$ and **1** disaggregated by the presence of 50 mM 1-adamantanammonium [4]. Thus, the contribution of the charge–transfer interaction to K_I of **1**/viologen complexes, i.e., K_{CT} value, can be approximated as about 30 M^{-1}, for all viologens used. This gives K_{alkyl} values as 1/30 of the K_I values, which are about one-tenth of K_{II} values for the corresponding viologen with **1**. This generalizes our earlier conclusion [4] that, without the charge–transfer interaction, alkyl viologens would prefer the

secondary side of β-CD about 10 times more favorably to the primary face.

In the complexation of viologens with **1** to form the type I complexes and with MNSS, both the donor–acceptor and electrostatic interactions contribute to the stability of the complexes. However, only the donor–acceptor interaction contributes to the stability of the type I complexes of **2**. It was reported that the formation constants of $C_1C_1V^{2+}$/3-(2-naphthyl)propylammonium (NPA) complex is 3.6 ($\pm$0.5) M^{-1} [7]. If we assume that the intrinsic donor ability of the 2-naphthyl group of NPA is not significantly different from that of 2-methoxynaphthalene group of MNSS, the electrostatic interaction would enhance the K_{CT} value for MNSS, but reduce the value for NPA by the same factor from that expected in the absence of the interaction. The factor is the square-root of the ratio of K_{CT} values of the two donors and is 2.8. This matches well with the about 3 times greater K_I values for **1** than **2** with corresponding viologen.

Conclusions

We have determined the binding constants of methylalkyl viologens ($C_1C_nV^{2+}$; n = 7–10, 12) with native β-CD by induced circular dichroic titrations of the viologens with β-CD. We also have investigated the fluorescence quenching of 6-O-(2-sulfonato-6-naphthyl)-β-CD (**1**) and 6-O-naphthyl-β-CD (**2**) by the viologens using steady state and time-resolved fluorescence methods and analyzed the quenching data in terms of bi-directional inclusion complexation of the viologens with the naphthyl group tethered-β-CDs. From these studies, we obtained the following conclusions. (1) For all viologens, the bipyridinium group in their complexes with native β-CD is preferentially placed on the secondary side of β-CD. (2) For the same viologen, the binding constant of the viologen with native β-CD and those (K_{II}'s) with **1** and **2** placing the bipyridinium group on the secondary side of β-CD cavity (type II complexes) are approximately the same. (3) The location of the bipyridinium group in the type II complexes does not depend appreciably on the length of alkyl chain of viologens. (4) The intracomplex photoinduced electron transfer rates in the type II complexes of the viologens with **1** and **2** are 1.9 ($\pm$0.2) $\times$ 10^7 s^{-1} and about two orders of magnitude smaller than the rate through-polymethylene bond at similar distance. (5) The binding constants (K_I) of viologens placing the bipyridinium group on the primary side of β-CD of the naphthyl tethered β-CDs (type I complexes) are greater than K_{II} values by about 3 times for **1**, but similar for **2**. The difference in K_I values between **1** and **2** is mainly due to the electrostatic interaction in complexes of **1**. (6) The type I complexes are mainly stabilized by charge–transfer and electrostatic interactions between the appended naphthyl and bipyridinium groups. Without the interactions, the bipyridinium group of the viologens would favor the secondary side to the primary side of β-CD by about 10 times.

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References

1. (a) J. Szejtli and T. Osa, eds.: *Comprehensive Supramolecular Chemistry*, Vol. 3, Pergamon Press (1996); (b) V.T. D'Souza and K. B. Lipkowicz, eds.: *Cyclodextrins, Chem. Rev.* **98** (1998).
2. A.R. Kahn, P. Forgo, K.J. Stine, and V.T. D'Souza: *Chem. Rev.* **98**, 1977 (1998).
3. S.T. Tian, H.H. Zhu, P. Forgo, and V.T. D'Souza: *J. Org. Chem.* **65**, 2624 (2000).
4. J.W. Park, H.E. Song, and S.Y. Lee: *J. Phys. Chem. B.* **106**, 7186 (2002) and references cited therein.
5. S. Sankararaman, K.B. Yoon, T. Yabe, and J.K. Kochi: *J. Am. Chem. Soc.* **113**, 1419 (1991).
6. J.W. Park, S.H. Park, B.A. Lee, and S.-Y. Lee: *Chem. Lett.*, 1043 (1997).
7. J.W. Park, B.A. Lee, and S.Y. Lee: *J. Phys. Chem.* **102**, 8209 (1998).
8. K. Tsukahara, J. Kaneko, T. Miyaji, and K. Abe: *Tetrahedron Lett.* **37**, 3149 (1996).
9. M. Kodaka and T. Fukaya: *Bull. Chem. Soc. Jpn.* **59**, 2032 (1986)
10. M. Kodaka and T. Fukaya: *Bull. Chem. Soc. Jpn.* **62**, 1154 (1989).
11. M. Kodaka: *J. Am. Chem. Soc.* **115**, 3702 (1993).
12. J.W. Park, N.H. Choi, and J.H. Kim: *J. Phys. Chem.* **100**, 769 (1996).
13. C. Lee, C. Kim, and J.W. Park: *J. Electroanal. Chem.* **374**, 115 (1994).
14. A. Mirzoian and A. E. Kaifer: *Chem. Eur. J.* **3**, 1052 (1997).
15. S.A. John, T. Okajima, and T. Osaka: *J. Electroanal. Chem.* **466**, 67 (1999).
16. J.W. Park, H.E. Song, and S.Y. Lee: *J. Phys. Chem. B.* **106**, 5177 (2002).
17. R. Petter, J.S. Salek, C.T. Sikorski, G. Kumaravel, and F. -T. Lin: *J. Am. Chem. Soc.* **112**, 3860 (1990).
18. T. Watanabe and K. Honda: *J. Phys. Chem.* **86**, 2617 (1982).
19. J.W. Park and H.J. Song: *J. Phys. Chem.* **93**, 6454 (1989).
20. J.W. Park and K.H. Park: *J. Incl. Phenom. Mol. Recognit.* **17**, 277 (1994).
21. Y. Kuroda, M. Ito, T. Sera, and H. Ogoshi: *J. Am. Chem. Soc.* **115**, 7003 (1993).
22. M.F. Acquavella, M.E. Evans, S.W. Farraher, C.J. Nevoret, and C.J. Abelt: *J. Chem. Soc., Perkin Trans. 2*, 385 (1995).
23. B.K. Hubbard, L.A. Beilstein, C.E. Heath, and C.J. Abelt: *J. Chem. Soc., Perkin Trans. 2*, 10 (1996).
24. K. Sasaki, M. Nagasaka, and Y. Kuroda: *Chem. Commun.*, 2630 (2001).
25. Y.H. Wang, H.M. Zhang, L. Liu, Z.X. Liang, Q.X. Guo, C.H. Tung, Y. Inoue, and Y.C. Liu: *J. Org. Chem.* **67**, 2429 (2002).
26. J.R. Lakowicz: *Principles of Fluorescence Spectroscopy*, 2nd ed. Kluwer Academic, New York (1999).