

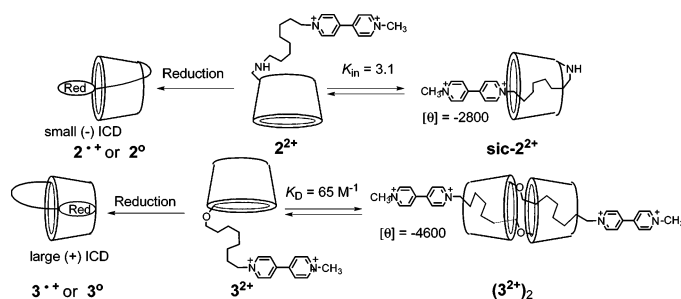
Self-Inclusion Behavior and Circular Dichroism of Aliphatic Chain-Linked β -Cyclodextrin–Viologen Compounds and Their Reduced Forms Depending on the Side of Modification

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The self-inclusion behavior and induced circular dichroism (ICD) characteristics of two β -cyclodextrin (β -CD) derivatives, in which a 1-methyl-4,4'-bipyridinium (viologen) group is connected by an octamethylene chain to either the primary (2^{2+}) or secondary (3^{2+}) side of β -CD, and of their reduced forms, are investigated. ^1H NMR studies showed that 2^{2+} forms an intramolecular self-inclusion complex with $K_{\text{in}} = 3.1 \pm 0.4$, whereas 3^{2+} forms a head-to-head type of dimer with $K_{\text{D}} = 65 \pm 10 \text{ M}^{-1}$ at 25°C . 2^{2+} and 3^{2+} form [2]pseudorotaxanes with α -CD, with the secondary side of the α -CD facing the viologen moiety. The ICD characteristics of mono-6-[4-(1-methyl-4-pyridinio)-1-pyridinio]- β -CD (1^{2+}), 2^{2+} , 3^{2+} , and methyloctyl viologen- β -CD complexes were obtained for the oxidized and reduced states of the viologen units. The results indicated dimer formation for 1° , and intramolecular complexation for 2° and 2^{+} in which the reduced viologen units are outside the β -CD cavity. The results also indicated intramolecular complexation for 3° and 3^{+} , but with reduced viologen units inside the cavity. This work provides unequivocal evidence of the preference of the secondary side of cyclodextrins for viologen groups, regardless of their oxidation states, and the dependence of ICD of the viologen chromophores on their location with respect to the CD cavity.

Introduction

Cyclodextrins (CDs) are important hosts in supramolecular chemistry, and have been widely used in various fields of basic research and industries.¹ CDs can be modified at either the narrower primary hydroxyl side or the wider secondary hydroxyl side of the cavities.² The

CD derivatives with a suitable pendant group can form self-included complexes intramolecularly^{3–8} or intermolecularly.^{9–13} It was shown that CD derivatives with the same pendant group but on different sides sometimes exhibit quite contrasting self-inclusion,⁷ guest-binding

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behaviors,^{7,8,14} or enzyme-like activity.¹⁴ It has also been well-recognized that the orientation of guest molecules in CD complexes, and thus the selectivity for the side of the CD cavity in the inclusion of guest molecules, is important to the physicochemical properties of CD complexes and in designing CD-based supramolecular structures.^{15–17} A potentially powerful method for determining the structures of CD complexes is induced circular dichroism (ICD), which theoretically relates the sign and magnitude of the ICD spectrum of a chromophore to the location and orientation of the chromophore with respect to the CD cavity.^{16–21} However, there is a paucity of reports showing an ICD spectral change of the same chromophore, depending on its location in CD complexes.^{16,17}

Viologens (*N,N'*-disubstituted 4,4'-bipyridinium salts) have been widely used as electron acceptors or mediators in many photochemical and electrochemical reactions,

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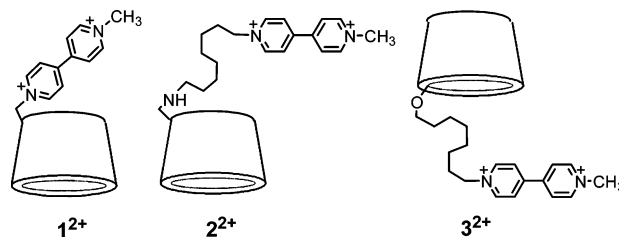
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and inclusion complexation of viologens with CDs has been a subject of numerous studies.^{15,17,19–23} β -CD derivatives with covalently linked viologen units exhibit many interesting inclusion behaviors, depending on the oxidation states of the viologen unit.^{9,10,24–28} For the β -CD–viologen compounds in which the bipyridinium group is directly attached to the primary side of β -CD (**1**²⁺ and the analogues having various *N*-alkyl groups), facile dimerization of the β -CD–viologens was observed upon one-electron⁹ or two-electron¹⁰ reduction of the viologen moiety. In contrast to this, the β -CD–viologens in which the viologen unit is linked to the secondary face of the β -CD via polymethylene chains (**3**²⁺ and the analogue with a tetramethylene linkage instead of an octamethylene chain) exhibit little tendency to dimerize upon one-electron reduction of their viologen moiety,²⁶ but the two-electron reduction product of **3**²⁺ exhibits a much higher stability against reaction with water than does the two-electron reduction product of **1**²⁺ or dimethyl viologen (MV²⁺).^{26,27} Facile photoinduced electron-transfer reactions from excited guest photosensitizers to **1**²⁺ or **3**²⁺ via inclusion complexation were also reported.^{24,28}



In this work, we studied self-inclusion behavior and circular dichroism characteristics of β -CD–viologens **2**²⁺ and **3**²⁺ and their one- and two-electron-reduced compounds by ¹H NMR and circular dichroism spectroscopic methods. The compounds **2**²⁺ and **3**²⁺ were chosen because they have similar linkage lengths between the β -CD skeleton and bipyridinium groups, but the side of attachment is different. The major points to be addressed are as follows: (1) difference in the self-inclusion behavior of **2**²⁺ and **3**²⁺, and their reduced forms; (2) generalization of the previously observed face selectivity of the oxidized form of viologens in their intermolecular complexation with CDs^{15,17} to the reduced forms of viologen as well as to intramolecular complexation; (3) ICD characteristics of the oxidized and reduced viologen chromophores located in the different positions with respect to the CD cavity.

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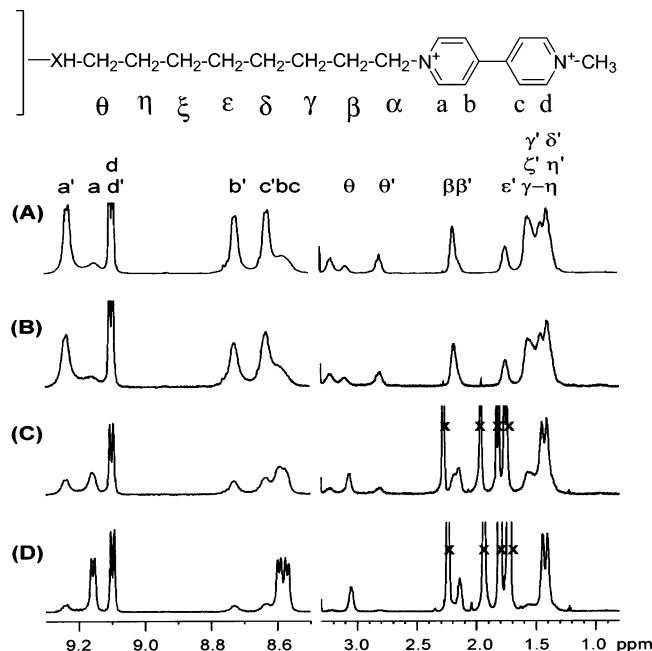


FIGURE 1. ^1H NMR (D_2O) spectra of $\beta\text{-CD-6-N-C}_8\text{V}^{2+}$ (2^{2+}): (A) 4.0×10^{-3} M 2^{2+} , (B) 0.8×10^{-3} M 2^{2+} , (C) 0.8×10^{-3} M $2^{2+} + 1.0 \times 10^{-3}$ M AdaCl, (D) 0.8×10^{-3} M $2^{2+} + 3.6 \times 10^{-3}$ M AdaCl. Peaks from the Ada^+ ion are marked as 'x'. Primed (') peaks are those from the included complex.

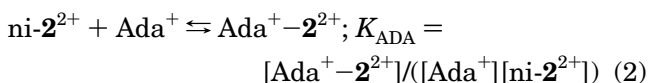
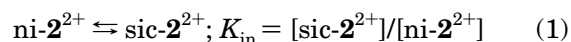
Results and Discussion

The synthesis of the dichloride salt of 3^{2+} has been described in a previous paper.²⁶ The compound $2^{2+} \cdot 2\text{Cl}^-$ is synthesized and fully characterized in this work. First, we present ^1H NMR spectra of 2^{2+} and 3^{2+} , and discuss the self-inclusion behavior of the $\beta\text{-CD}$ -viologen compounds. Next, we show the ICD characteristics of 1^{2+} - 3^{2+} and their reduced forms, and relate them to the structures of the self-included complexes and ICD rules of CD complexes derived theoretically.

^1H NMR Study of Mono-6-deoxy-6-N-[4-(1-methyl-4-pyridinio)-1-pyridinio]octylamino- $\beta\text{-CD}$ ($\beta\text{-CD-6-N-C}_8\text{V}^{2+}$; 2^{2+}). Figure 1 shows the partial ^1H NMR spectra of 2^{2+} in the absence and presence of 1-adamantylammonium chloride (AdaCl). The spectra taken in the absence of AdaCl (spectra A and B) show more than four resonance signals in the bipyridinium proton resonance region. This suggests the presence of more than one chemical species with a slow exchange rate on the ^1H NMR time scale. No significant variation of the ^1H NMR spectra of 2^{2+} with its concentration was found, indicating little tendency of intermolecular association of 2^{2+} . The presence of AdaCl changes the ^1H NMR spectrum of 2^{2+} in the resonance region of bipyridinium protons as well as in the aliphatic linkage proton regions. As the Ada^+ ion has a large binding affinity for the $\beta\text{-CD}$ cavity and replaces the self-included appended groups from the cavity,²⁹ these results indicate the self-inclusion complexation of 2^{2+} and disruption of the complexation by Ada^+ ion. As intermolecular self-inclusion is ruled out because of the lack of dependence of the ^1H NMR

spectrum on concentration, the self-inclusion complexation of 2^{2+} should be intramolecular.

The assignments of the NMR signals to the nonincluded species and the self-inclusion complex are easily made from the effect of AdaCl on the spectra. The resonance signals that decrease upon the addition of AdaCl are assigned to those from the complexed species, whereas signals increased by the presence of AdaCl are assigned to those from the nonincluded species. No appreciable difference was observed between chemical shifts of the bipyridinium and aliphatic-linkage protons of the nonincluded species and those of its Ada^+ complex. Microscopically, the intramolecular self-included complex of 2^{2+} (sic- 2^{2+}) is in equilibrium with the nonincluded open form (ni- 2^{2+}), and only the ni- 2^{2+} is in direct equilibrium with Ada, as expressed in eqs 1 and 2, however Ada^+ binding shifts the self-inclusion complexation equilibrium of eq 1 to the left.



From the integration ratios of the resonance signals of the spectra taken in the absence of AdaCl, the intramolecular complexation constant (K_{in}) of 2^{2+} was determined to be 3.1 ± 0.4 : the average values of the integration ratios of a to a', b to b', and θ to θ' protons were used for the calculation. From the NMR integration data, the apparent intramolecular complexation constants ($K_{\text{in,app}}$) of 2^{2+} in the presence of AdaCl were found to be 0.66 ± 0.06 when the initial concentration of AdaCl ($[\text{Ada}^+]_0$) is 1.0×10^{-3} M, and 0.17 ± 0.01 at $[\text{Ada}^+]_0 = 3.6 \times 10^{-3}$ M. This gave the binding constant of Ada^+ with ni- 2^{2+} (K_{ADA}) as $6500 \pm 700 \text{ M}^{-1}$.³⁰ The K_{ADA} value of 2^{2+} is smaller than the reported binding constant of Ada^+ with native $\beta\text{-CD}$, $8900 \pm 1000 \text{ M}^{-1}$,²⁹ presumably due to electrostatic interaction in the Ada^+-2^{2+} complex.

The bipyridinium dication is too hydrophilic to be included inside the $\beta\text{-CD}$ cavity.²¹ The aliphatic spacer between the $\beta\text{-CD}$ skeleton and the bipyridinium unit of 2^{2+} as well as 3^{2+} is long enough to traverse the CD cavity. This was shown as cross-peaks between $\beta\text{-CD}$ protons and aliphatic-linkage protons in a two-dimensional ROESY spectrum (see Supporting Information). Thus it would be safe to conclude that the bipyridinium group of 2^{2+} is outside the secondary side of the $\beta\text{-CD}$ cavity in the intramolecular self-inclusion complex.

^1H NMR Study of Mono-2-O-[4-(1-methyl-4-pyridinio)-1-pyridinio]octyl- $\beta\text{-CD}$ ($\beta\text{-CD-2-O-C}_8\text{V}^{2+}$; 3^{2+}). Figure 2 shows the ^1H NMR spectra of 3^{2+} . At high concentration, the spectra also show more than four peaks in the bipyridinium region as in the case of 2^{2+} . However, in contrast to 2^{2+} , the spectrum of 3^{2+} exhibits a large concentration dependence. The spectrum of 3^{2+} taken at 0.85 mM (spectrum C) is almost identical to that of 2^{2+} in the presence of a high concentration of AdaCl

(30) As ni- 2^{2+} and the Ada^+-2^{2+} complex cannot be differentiated from the NMR spectra, $K_{\text{in,app}}$ is expressed as $K_{\text{in,app}} = [\text{sic-}2^{2+}]/([\text{ni-}2^{2+}] + [\text{Ada}^+-2^{2+}])$ and is related to K_{in} and the concentration of uncomplexed Ada^+ ($[\text{Ada}^+]$) by $K_{\text{in,app}} = K_{\text{in}}/(1 + K_{\text{ADA}}[\text{Ada}^+])$. Combination of the mass balance for 2^{2+} and the definition of equilibrium constants gives $[\text{Ada}^+] = [\text{Ada}^+]_0 - [2^{2+}]_0(K_{\text{in}} - K_{\text{in,app}})/(K_{\text{in}}(1 + K_{\text{in,app}}))$.

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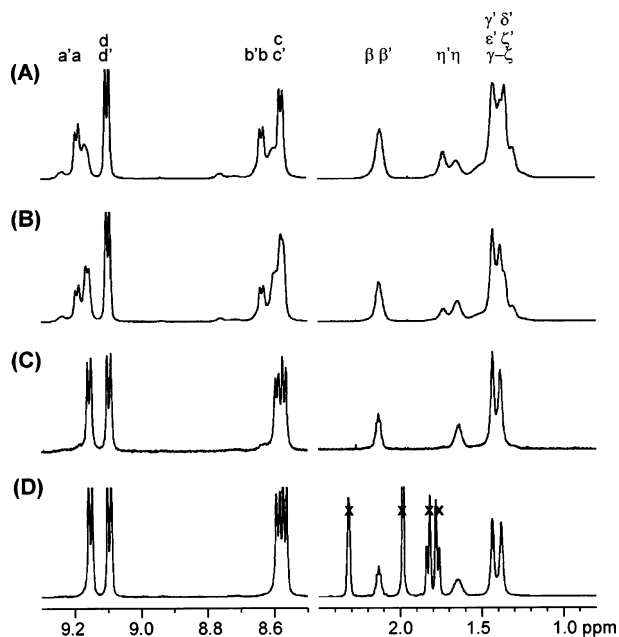


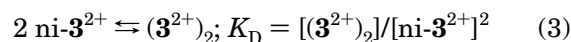
FIGURE 2. ^1H NMR (D_2O) spectra of $\beta\text{-CD-2-O-C}_8\text{V}^{2+}$ ($\mathbf{3}^{2+}$): (A) $14 \times 10^{-3} \text{ M } \mathbf{3}^{2+}$, (B) $3.4 \times 10^{-3} \text{ M } \mathbf{3}^{2+}$, (C) $0.85 \times 10^{-3} \text{ M } \mathbf{3}^{2+}$, (D) $0.85 \times 10^{-3} \text{ M } \mathbf{3}^{2+} + 4.9 \times 10^{-3} \text{ M AdaCl}$. Notations of protons and marks are the same as those in Figure 1.

(Figure 1D), and the spectrum changes little with the presence of AdaCl (Figure 2D). These results clearly suggest that $\mathbf{3}^{2+}$ forms the intermolecular self-inclusion complex. The peaks that increase in intensity by lowering the concentration of $\mathbf{3}^{2+}$ are assigned to those from the nonincluded form ($\text{ni-}\mathbf{3}^{2+}$), and those that decrease in intensity by lowering the concentration are from the intermolecularly self-included complex of $\mathbf{3}^{2+}$.

For intermolecular association of $\mathbf{3}^{2+}$, dimerization is the first step. Both head-to-tail (HT) and head-to-head (HH) arrangements of the $\beta\text{-CD}$ moiety are possible in the dimer. In the HT dimer, the aliphatic linkage of a molecule traverses the CD cavity of its counter molecule, placing its own bipyridinium group in proximity to the bipyridinium group of the counter molecule. A stronger association beyond dimerization is not feasible, as the protruding group would interfere with the inclusion of the nonincluded pendant group of the dimer into the CD cavity of another molecule to form a trimer. The bipyridinium moiety of the nonincluded pendant in the HT dimer would be far from the CD cavity, and is expected to show a resonance similar to that of the $\text{ni-}\mathbf{3}^{2+}$. Thus, if the intermolecularly self-included complex is mostly the HT dimer, the peak intensities of protons of the included pendant group cannot be larger than those of the corresponding protons of the nonincluded pendant group. Spectrum A in Figure 2 clearly indicates that this is not the case for $\mathbf{3}^{2+}$, and suggests that the major dimeric species of $\mathbf{3}^{2+}$ is not the HT type.³¹ In case of the HH dimer of $\mathbf{3}^{2+}$, the pendant groups of both molecules are included, placing the bipyridinium groups on the primary side of the counter molecules and showing the

(31) At high concentrations of $\mathbf{3}^{2+}$, weak peaks are observed at 9.23 and 8.76 ppm. Absence of the peaks at low concentration and the similarity of the position of these peaks to those of the $\text{sic-}\mathbf{2}^{2+}$ suggest that these might be from the HT dimer existing as a minor species.

NMR signals of the included species. Thus we can conclude that $\mathbf{3}^{2+}$ mostly forms the HH dimer. Such HH dimers are stabilized by mutual inclusion of the pendant groups into the CD cavities of counter molecules.^{9–13} The dimerization equilibrium of $\mathbf{3}^{2+}$ is expressed in eq 3, where $(\mathbf{3}^{2+})_2$ represents the HH dimer. The ratios of monomer to dimer of $\mathbf{3}^{2+}$ were calculated from the average value of NMR integration ratios of a to a', b to b', and η to η' protons for each concentration of $\mathbf{3}^{2+}$. The dimerization constant (K_D) of $\mathbf{3}^{2+}$ was obtained from the concentration dependence of the ratio, and was found to be $65 \pm 10 \text{ M}^{-1}$.



General Aspects of Induced Circular Dichroism of CD Complexes and CD Derivatives. Induced circular dichroism (ICD) has been widely used for studies of inclusion complexation of guest molecules with CDs and structures of the CD complexes or CD derivatives.^{6,7,12,15–21} The structural features are usually deduced from ICD spectra using the rules derived for ICD of chiral supramolecular systems, which were initially derived for CD complexes^{18,19} and then generalized for complexes of chiral macrocycles.^{20,21} The rules predict the following: (1) the sign of ICD is positive for a transition polarized parallel to the axis of macrocyclic host, and negative for that polarized perpendicular to the axis; (2) the sign of ICD is reversed when a chromophore moves from the inside of the host cavity to the outside, and the direction of the transition moment is not changed; (3) the absolute value of ICD is greater when a chromophore exists on the outside of the narrower rim than when it exists on the outside of the wider rim; (4) the ICD value of a transition polarized perpendicularly to the axis of a macrocycle is $-1/2$ of that of a parallelly polarized one, and the sign of the ICD changes at 54.7°C . The rules were also found to be useful for conformational analysis of CD derivatives with covalently bonded chromophores.^{6,7,15,21} The major transition of viologens is a $\pi\text{-}\pi^*$ transition³² that is polarized along the long axis of the viologen.^{15,19,20}

Circular Dichroism of Oxidized Forms of $\beta\text{-CD}$ -Viologens. Figure 3 shows ICD spectra of $\beta\text{-CD}$ -viologens $\mathbf{1}^{2+}$ – $\mathbf{3}^{2+}$ in aqueous solution. In all cases, negative Cotton effects are observed around 255 nm, corresponding to the absorption band of the viologen moiety. This indicates that the bipyridinium chromophores are present outside the $\beta\text{-CD}$ cavity, and that the angle between the axes of CD and viologen is less than 54.7° . No appreciable concentration dependence of the apparent molar ellipticities $[\theta]_{\text{app}}$ was found for $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$, whereas the magnitude of $[\theta]_{\text{app}}$ of $\mathbf{3}^{2+}$ became greater as the concentration was increased. The $[\theta]_{\text{app}}$ versus concentration profiles of $\mathbf{2}^{2+}$, $\mathbf{3}^{2+}$, and the one-electron reduction product of $\mathbf{3}^{2+}$, $\mathbf{3}^{+}$, are shown in Figure 4.

To confirm the intramolecular self-inclusion of $\mathbf{2}^{2+}$ and obtain ICD characteristics of the $\text{sic-}\mathbf{2}^{2+}$ and $\text{ni-}\mathbf{2}^{2+}$ species, we recorded the ICD spectra of $\mathbf{2}^{2+}$ in the presence of various concentrations of AdaCl (Figure 5). As the concentration of AdaCl becomes greater, the

(32) Braterman, P. S.; Song, J.-I. *J. Org. Chem.* **1991**, *56*, 4678.

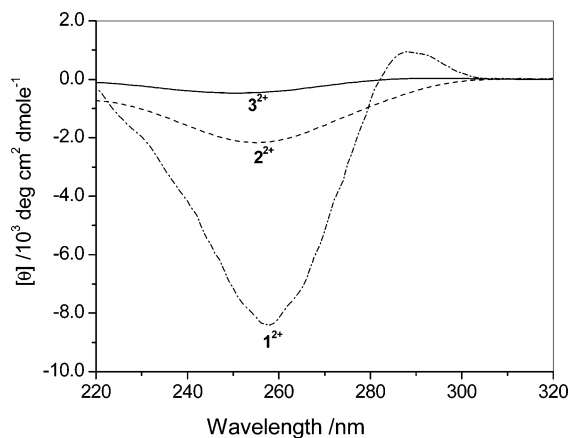


FIGURE 3. Circular dichroism spectra of 1.0×10^{-4} M β -CD-viologens 1^{2+} – 3^{2+} .

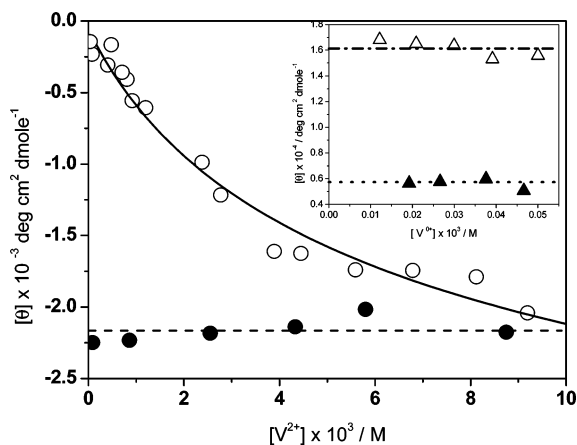


FIGURE 4. Concentration dependences of apparent molar ellipticity of 2^{2+} (●) and 3^{2+} (○) at 255 nm. Inset shows the concentration dependence of molar ellipticity of 3^{2+} at 398 nm in the absence (Δ) and presence (\blacktriangle) of 1.0×10^{-3} M AdaCl.

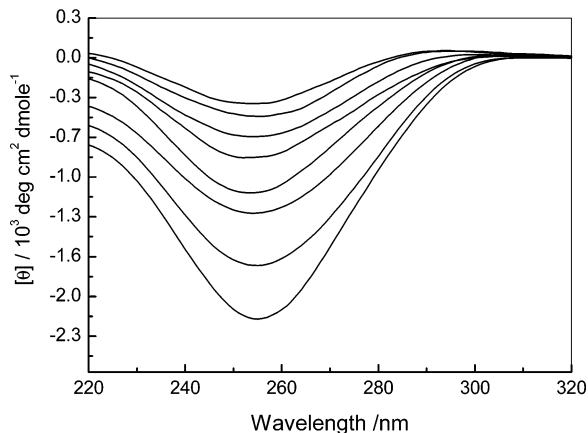


FIGURE 5. Dependence of the circular dichroic spectrum of 1.0×10^{-4} M 2^{2+} on the concentration of AdaCl. Concentrations of AdaCl are 0.00, 0.20×10^{-3} , 0.50×10^{-3} , 1.0×10^{-3} , 2.0×10^{-3} , and 5.0×10^{-3} M (from bottom to top).

magnitude of the ICD band of 2^{2+} becomes smaller. This suggests that the ICD band of 2^{2+} is mainly due to self-inclusion complexation. As $[\theta]_{\text{app}}$ is the weight average of the contributions from the existing species, the $[\theta]_{\text{app}}$ is related to $[\text{Ada}^+]$ and the apparent binding constant

($K_{\text{ADA,app}}$) of Ada^+ with the β -CD-viologen by eq 4.

$$[\theta]_{\text{app}} = ([\theta]_0 + [\theta]_c K_{\text{ADA,app}} [\text{Ada}^+]) / (1 + K_{\text{ADA,app}} [\text{Ada}^+]) \quad (4)$$

where $[\theta]_0$ is the apparent molar ellipticity of 2^{2+} in the absence of AdaCl, -2200 ± 100 deg cm^2 dmol^{-1} ; $[\theta]_c$ is the molar ellipticity of the Ada^+ – 2^{2+} complex. The $K_{\text{ADA,app}}$ is related to K_{in} and K_{ADA} , defined in eqs 1 and 2, by eq 5; $[2^{2+}]$ denotes the concentration of Ada^+ -unbound 2^{2+} , which is $[\text{sic-}2^{2+}] + [\text{ni-}2^{2+}]$.

$$K_{\text{ADA,app}} = [\text{Ada}^+ - 2^{2+}] / ([\text{Ada}^+] [2^{2+}]) = K_{\text{ADA}} / (1 + K_{\text{in}}) \quad (5)$$

The nonlinear least-squares fitting of the ICD titration data of 2^{2+} with AdaCl shown in Figure 5 gave a $K_{\text{ADA,app}}$ value of 1600 ± 200 M^{-1} and a $[\theta]_c$ value of -300 ± 100 deg cm^2 dmol^{-1} .³³ Using the K_{in} value of 3.1 ± 0.4 obtained from NMR measurements, the K_{ADA} value for 2^{2+} is estimated to be 6600 ± 1500 M^{-1} . This agrees with the value of 6500 ± 700 M^{-1} obtained from NMR data.

The $[\theta]_0$ value of 2^{2+} can be given as the sum of the contributions from $\text{sic-}2^{2+}$ ($[\theta]_{\text{sic}}$) and $\text{ni-}2^{2+}$ ($[\theta]_{\text{ni}}$) by eq 6; f_{sic} denotes the fraction of the self-included complex and is calculated to be 0.75 ± 0.03 from $K_{\text{in}} = 3.1 \pm 0.4$.

$$[\theta]_0 = [\theta]_{\text{sic}} f_{\text{sic}} + (1 - f_{\text{sic}}) [\theta]_{\text{ni}} \quad (6)$$

Because the relative orientation and position of the bipyridinium group with respect to the β -CD unit would be similar in $\text{ni-}2^{2+}$ and the Ada^+ – 2^{2+} complex, the ICD characteristics of both species might also be similar. Using $[\theta]_c = -300 \pm 100$ deg cm^2 dmol^{-1} for $[\theta]_{\text{ni}}$, the $[\theta]_{\text{sic}}$ value of 2^{2+} is calculated to be -2800 ± 300 deg cm^2 dmol^{-1} from eq 6, using the observed value of $[\theta]_0 = -2200 \pm 100$ deg cm^2 dmol^{-1} and $f_{\text{sic}} = 0.75 \pm 0.03$. The $[\theta]_{\text{sic}}$ value is similar to that for the β -CD complex of methyl-octyl viologen ($\text{C}_1\text{C}_8\text{V}^{2+}$), -2000 ± 100 deg cm^2 dmol^{-1} .¹⁵ However, it is much smaller than the molar ellipticity of 1^{2+} , -8500 ± 200 deg cm^2 dmol^{-1} , in which the bipyridinium moiety is present above the primary face of the β -CD. As the bipyridinium moiety of 2^{2+} in the self-included complex should be above the secondary face of β -CD, the present result supports the conclusion that the bipyridinium unit of the $\text{C}_1\text{C}_8\text{V}^{2+}$ – β -CD complex is mostly above the secondary side of CDs,¹⁵ rather than above the primary side as claimed by Kodata.^{19,20}

The concentration dependence of the ICD of 3^{2+} (Figure 4) agrees well with the finding from the NMR study that 3^{2+} forms an intermolecular self-inclusion complex. The $[\theta]_{\text{app}}$ of 3^{2+} is the sum of contributions from monomeric (M) and dimeric (D) species, and is given in eq 7.

$$[\theta]_{\text{app}} = [\theta]_{\text{D}} f_{\text{D}} + [\theta]_{\text{M}} (1 - f_{\text{D}}); f_{\text{D}} = \{ (8K_{\text{D}} [3^{2+}]_0 + 1)^{1/2} - 1 \} / 4K_{\text{D}} [3^{2+}]_0 \quad (7)$$

where f_{D} is the fraction of 3^{2+} in dimeric form; $[\theta]_{\text{M}}$ and

(33) For the fitting, we first assumed $[\text{Ada}^+]_0 = [\text{Ada}^+]$, and calculated the trial parameters, $K_{\text{ADA,app}}$ and $[\theta]_c$. $[\text{Ada}^+]$'s were then corrected by $[\text{Ada}^+] = [\text{Ada}^+]_0 - [2^{2+}]_0 \{ ([\theta]_0 - [\theta]_{\text{app}}) / ([\theta]_0 - [\theta]_c) \}$ for each piece of data, and we again calculated the parameters. This process was repeated until we obtained consistent fitted parameters.

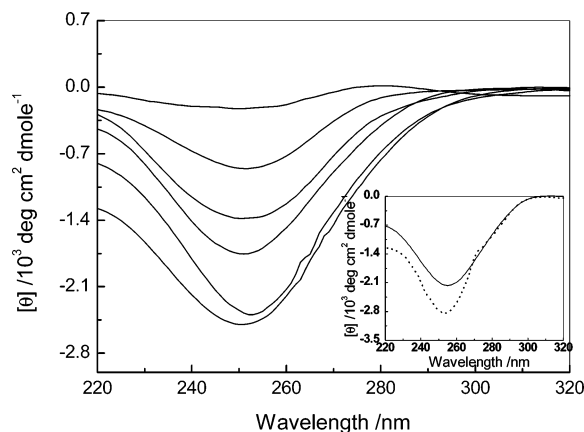


FIGURE 6. Effect of α -CD on the circular dichroism spectrum of 1.0×10^{-4} M 3^{2+} . Concentrations of α -CD are 0.00, 2.0×10^{-3} , 5.0×10^{-3} , 10×10^{-3} , 20×10^{-3} , and 50×10^{-3} M (from top to bottom). Inset shows the spectra of 1.0×10^{-4} M 2^{2+} in the absence (solid line) and presence (dashed line) of 50×10^{-3} M α -CD.

$[\theta]_D$ are the molar ellipticities (per viologen unit) of the monomeric and dimeric forms, respectively. The nonlinear least-squares fitting of the $[\theta]_{app}$ versus $[3^{2+}]_0$ profile to eq 7 gave $K_D = 80 \pm 30$ M $^{-1}$, $[\theta]_D = -4600 \pm 700$ deg cm 2 dmol $^{-1}$, and $[\theta]_M = -40 \pm 30$ deg cm 2 dmol $^{-1}$. Though there is a relatively large uncertainty in the fitted K_D value, it is in fair agreement with that obtained from the NMR results, 65 ± 10 M $^{-1}$.

It is noted that the monomeric form of 3^{2+} shows a negligibly small ellipticity. This can be taken as evidence that the 3^{2+} monomer has little tendency toward intramolecular self-inclusion complexation, as suggested from the ^1H NMR results. Also, the small ICD ellipticity values of ni- 2^{2+} and ni- 3^{2+} suggest that the bipyridinium chromophores of these species are too far from the β -CD skeleton to feel the chiral environment significantly. The bipyridinium moieties of $(3^{2+})_2$ are above the primary face of the β -CD, and exhibit much larger ellipticity values than that of sic- 2^{2+} , in which the bipyridinium moiety is placed above the secondary face. This is also in good agreement with the theoretical prediction^{19,20} that the CD complex having a chromophore above the primary face exhibits a much larger ellipticity than that having the chromophore above the secondary face of the CD cavity.³³

Formation of [2]Pseudorotaxanes of 2^{2+} and 3^{2+} with α -CD. The β -CD–viologens 2^{2+} and 3^{2+} can form [2]pseudorotaxanes with α -CD, in which the α -CD ring is stationed on the octamethylene linkages. To further confirm the different self-inclusion behaviors of 2^{2+} and 3^{2+} and examine the orientation of α -CD in the [2]pseudorotaxanes, we studied the complexation behaviors of 2^{2+} and 3^{2+} with α -CD. Figure 6 shows the circular dichroism titration results. The ICD signals of β -CD–viologens become more intense as the concentration of α -CD increases. This reflects inclusion of the aliphatic spacers of the β -CD–viologens into the α -CD cavity, forming [2]pseudorotaxanes.

The titration data of 3^{2+} were fitted to eq 4 after substituting $[\alpha\text{-CD}]$ for $[\text{Ada}^+]$, and gave the apparent binding constant of α -CD with 3^{2+} and the $[\theta]_c$ value of the [2]pseudorotaxane as 160 ± 30 M $^{-1}$ and -2800 ± 200 deg cm 2 dmol $^{-1}$, respectively. Interestingly, the molar

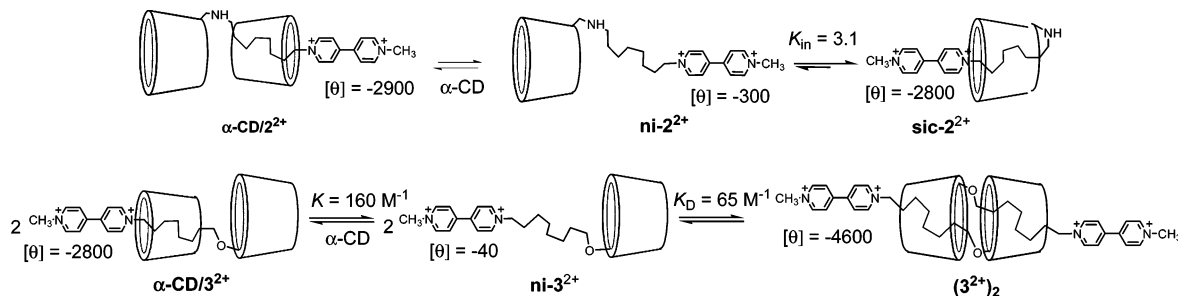
ellipticity of the 3^{2+} – α -CD [2]pseudorotaxane is very close to that of the self-included complex of 2^{2+} . This might be due to combination of two factors. One is that the parent β -CD moiety is too far from the bipyridinium chromophore in the [2]pseudorotaxane to contribute to the ICD signals significantly. This is well supported by the small ellipticity of the nonincluded forms and the Ada^+ complex (vide supra). The other is that the bipyridinium group in the 3^{2+} – α -CD [2]pseudorotaxane is adjacent to the secondary face of the α -CD, and α -CD and β -CD would induce similar circular dichroism in the viologen chromophore. To check the latter, we performed an ICD titration of 1.00×10^{-4} M $\text{C}_{12}\text{V}^{2+}$ with α -CD and found the binding constant of $\text{C}_{12}\text{V}^{2+}$ with α -CD and the molar ellipticity of the complex to be 3300 ± 300 M $^{-1}$ and -1920 ± 40 deg cm 2 dmol $^{-1}$, respectively. The corresponding values for the β -CD complex were reported as 890 ± 60 M $^{-1}$ and -2000 ± 100 deg cm 2 dmol $^{-1}$.¹⁵ This indicates that α -CD and β -CD complexes of the viologen show essentially the same ICD, though the stability of the α -CD complex is greater.

The effect of α -CD on the ICD spectrum of 2^{2+} is much less pronounced than that of 3^{2+} . The spectrum of 2^{2+} continues to grow even above 20 mM α -CD, whereas it virtually levels off in the case of 3^{2+} . The sluggish dependence of $[\theta]$ of 2^{2+} on the concentration of α -CD reflects the smaller apparent binding constant of α -CD with 2^{2+} due to the intramolecular self-inclusion of the pendant group. The $[\theta]_c$ value of 2^{2+} was -2900 deg cm 2 dmol $^{-1}$ in the presence of 50 mM α -CD, which is similar to that of sic- 2^{2+} . This strongly implies that sic- 2^{2+} and 2^{2+} – α -CD [2]pseudorotaxane have very similar ICD characteristics, and that the secondary face of the ring α -CD is oriented toward the viologen unit in the 2^{2+} – α -CD [2]pseudorotaxane as it is in the 3^{2+} – α -CD [2]pseudorotaxane.

The equilibria of the self-inclusion complexation of 2^{2+} and 3^{2+} and their [2]pseudorotaxane formation with α -CD, together with the molar ellipticity data, are summarized in Scheme 1.

Circular Dichroism of One-Electron-Reduced β -CD–Viologens. Irradiation of a deaerated aqueous solution of viologen in the presence of $\text{Ru}(\text{bpy})_3^{2+}$ and EDTA at pH 10 reduces the viologen dication to the viologen radical cation, which is stable in the absence of oxygen.⁹ The photosensitized reduction of 3.2×10^{-5} M β -CD–viologens 1^{2+} – 3^{2+} to radical cations $1^{+\cdot}$ – $3^{+\cdot}$ was achieved, and UV–vis and ICD spectra were taken at various irradiation times. In all cases, no significant dependence of the shape and the molar ellipticities of the ICD spectra on the concentration of the viologen radical cations (see inset of Figure 4 for $3^{+\cdot}$) was observed; the concentrations of the viologen radical cations were calculated from absorption data using $\epsilon_{602} = 13\,700$ M $^{-1}$ cm $^{-1}$.⁹ Figure 7 shows the ICD spectra of $1^{+\cdot}$ – $3^{+\cdot}$.

It is known that the viologen radical cations form a dimer by stacking interaction, for which the absorption spectrum is distinctly different from that of the monomer.^{9,23b,c} The shape of the ICD spectra of the radical cations $1^{+\cdot}$ – $3^{+\cdot}$ in Figure 7 is virtually the same as that of the absorption spectrum of the monomeric form. This can be explained by the relatively small dimerization constants: the dimerization constants of $1^{+\cdot}$ and $3^{+\cdot}$ via the stacking interaction were reported as 500 and 750

SCHEME 1. Self-Inclusion Complexation, [2]Pseudorotaxane Formation with α -CD, and Molar Ellipticities, $[\theta]$, of 2^{2+} and 3^{2+} ^a


^a $[\theta]$'s are taken at 255 nm and given in deg cm² dmol⁻¹ units. 1^{2+} , for which $[\theta]$ is -8500 deg cm² dmol⁻¹, does not form either a self-inclusion complex or [2]pseudorotaxane with α -CD.

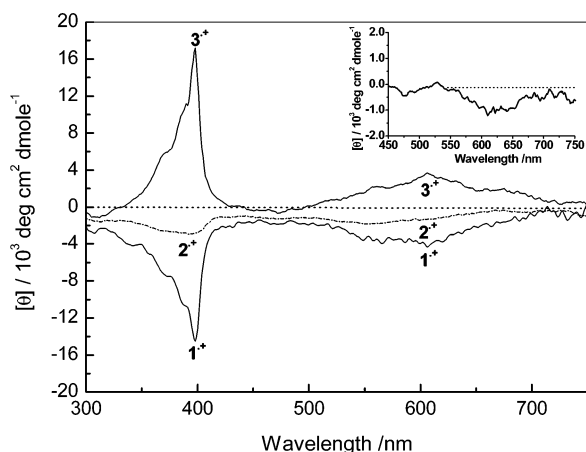


FIGURE 7. Circular dichroism spectra of 3.0×10^{-5} M $1e^{-}$ -reduced β -CD-viologens 1^{+} – 3^{+} . Inset shows the spectrum of 3^{+} in the presence of 50×10^{-3} M α -CD.

M^{-1} , respectively,^{9,26} which predicts that the fraction of monomeric forms would be greater than 0.97 under the present experimental conditions. The presence of AdaCl resulted in a decrease in the intensity of the ICD bands of 2^{+} and 3^{+} (see inset of Figure 4 for 3^{+}), and no appreciable ICD band was seen at $[Ada^{+}]_0 > 15 \times 10^{-3}$ M, although the absorption spectra indicated the formation of viologen radical cations. This and the lack of dependence of the ICD characteristics of 2^{+} and 3^{+} on their concentrations suggest that the ICD bands of 2^{+} and 3^{+} are mainly due to intramolecular self-inclusion of the pendant groups into the β -CD cavity.

Figure 7 shows that the sign of the ICD bands of 1^{+} and 2^{+} is opposite to that of 3^{+} . One possible explanation for this is that the V^{+} moieties of 1^{+} – 3^{+} are outside the β -CD cavity, but there is a parallel/perpendicular orientation difference between the V^{+} units of 1^{+} and 2^{+} and that of 3^{+} , with respect to the β -CD axis. However, CPK modelings indicated that the aliphatic linkages are not long enough to allow the perpendicular orientation of the V^{+} moiety in the intramolecularly self-included complexes of 2^{+} and 3^{+} . Thus the opposite sign of the ICD bands can be taken as an indication of the inside/outside difference in the location of the V^{+} units with respect to the β -CD cavity. It was reported that, unlike the V^{2+} group, the V^{+} moiety has an appreciable binding affinity for the β -CD cavity, with binding constants of 30 – 100 M^{-1} .²² As the transitions responsible for the ICD bands of V^{+} are also π – π^{*} , they are polarized

along the long axis of viologen. Thus it appears that the V^{+} unit of 3^{+} is inside the β -CD cavity, whereas that of 2^{+} is outside the cavity. For 1^{+} , the inclusion of the V^{+} group into its β -CD cavity is not feasible sterically, and thus the V^{+} group should be outside of the primary face of the β -CD cavity. The large negative Cotton effect of 1^{+} suggests that the long axis of V^{+} of 1^{+} is almost parallel to the β -CD axis.

We also took the ICD spectrum of the $C_{12}C_8V^{+}$ – β -CD complex, which was obtained from the photosensitized reduction of $C_{12}C_8V^{2+}$ in the presence of 1.0×10^{-2} M β -CD. The spectral shape and molar ellipticity of the $C_{12}C_8V^{+}$ – β -CD complex were almost indistinguishable from those of 2^{+} . This suggests that the V^{+} moiety in the β -CD– $C_{12}C_8V^{+}$ complex is also located above the secondary rim of β -CD. The order of magnitude of the ICD ellipticities is $3^{+} > 1^{+} \gg 2^{+}$. This agrees with the prediction from theoretical calculations that the order of magnitude of the ICD ellipticities for a given transition is (inside CD cavity) $>$ (above the primary face) $>$ (above the secondary face).^{19,20}

We also investigated the effect of α -CD on the ICD spectrum of 3^{+} . The positive ICD signal of 3^{+} was decreased by the presence of α -CD, and became negative and similar to that of 2^{+} at a high concentration of α -CD (see the inset of Figure 7). This reflects the formation of [2]pseudorotaxane between α -CD and 3^{+} , and indicates that the V^{+} moiety is outside the CD cavity in the [2]pseudorotaxane. In contrast to 3^{+} , the addition of α -CD to the 2^{+} solution gave no appreciable change in the ICD spectrum. This implies that the self-inclusion complexation of 2^{+} is nearly quantitative, and that the position of V^{+} in the 2^{+} – α -CD [2]pseudorotaxane complex is almost the same as in the self-inclusion complex of 2^{+} ; i.e., the V^{+} moiety is adjacent to the secondary face of α -CD in the [2]pseudorotaxane.

Circular Dichroism of Two-Electron-Reduced β -CD-Viologens. Two-electron reductions of viologen units of β -CD-viologens 1^{2+} – 3^{2+} to 1^{0} – 3^{0} were achieved by continuous electrolysis,²⁶ and ICD spectra of 1^{0} – 3^{0} were recorded in situ. The spectra are shown in Figure 8. In all cases, no appreciable ICD signal was observed above 450 nm, indicating that the reduction products are free from the contamination of $1e^{-}$ -reduced species.

The spectrum of 2^{0} shows a negative band, whereas that of 3^{0} exhibits a positive one. This is analogous to the observation made with $1e^{-}$ -reduced forms of the corresponding compounds (Figure 7), and indicates that

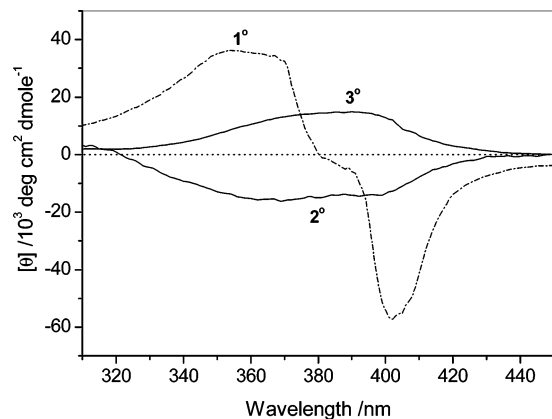


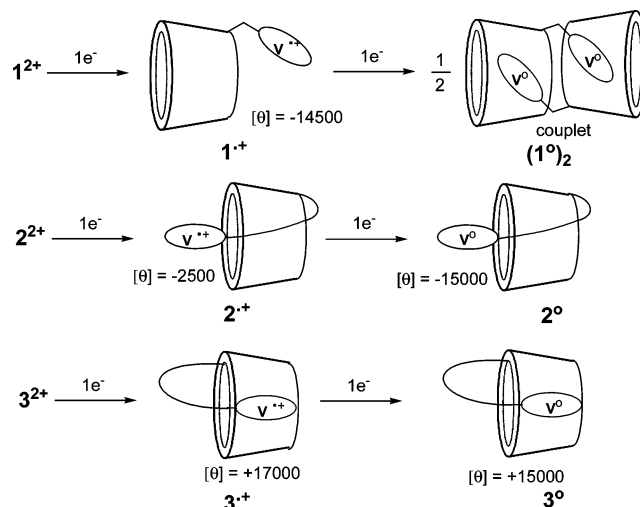
FIGURE 8. Circular dichroism spectra of $2e^-$ -reduced β -CD-viologens 1° – 3° .

the V° moiety of 2° is present mostly outside of the β -CD cavity, whereas that of 3° is inside the cavity. The compound 1° shows a split-type ICD, but the shape of the spectrum is slightly different from a typical exciton-split band; the magnitude of ellipticity of the positive band is smaller than that of the negative band, and the spectrum has a shoulder in the crossover region.

The shape of the ICD spectrum of 1° can be interpreted in terms of the monomer–dimer equilibrium of the compounds. Mirzoian and Kaifer suggested that 1° forms a cyclic dimer by mutual inclusion of the V° unit into the β -CD cavity of the counter molecule.¹⁰ The dimerization constant was estimated to be in the range 10^3 – 10^4 M^{-1} , which gives the fraction of monomeric 1° in the 0.16–0.4 range under the experimental condition $[1^\circ]_{\text{total}} \approx 1.5 \times 10^{-3}$ M. The dimer is expected to show a typical exciton-split curve as reported for the similar-type dimer of 6-*O*-(2-sulfonato-6-naphthyl)- β -CD.¹¹ The monomeric 1° would give a negative ICD band similar to that of 2° , but with higher molar ellipticity. The sum of contributions from both the dimeric and monomeric 1° appears to result in the observed unusual ICD pattern of 1° . The scheme for self-inclusion complexation of 1° – 3° and the molar ellipticity data of the complexes are summarized in Scheme 2.

Finally, we discuss briefly the reactivity of the two-electron-reduced β -CD-viologens. It is known that the two-electron-reduced viologen (V°) reacts with water and is transformed into redox inert species, which does not absorb light above 300 nm.^{26,27,34} Previously, we reported that the pseudo-first-order rate constants for the reactions of 1° and 3° are about 1/5 and 1/100, respectively, of that of neutral dimethyl viologen (MV°).²⁶ The difference in the reactivity among 1° – 3° was also revealed in the present work. Though we used the same concentration of 1^{2+} – 3^{2+} and the same electrolysis time, we always observed that the average concentration of V° during circular dichroism measurements is on the order of $2^\circ < 1^\circ < 3^\circ$. This implies that the order of reactivity of the viologen neutrals is $2^\circ > 1^\circ > 3^\circ$. The high stability of 3° against the reaction with water can be attributed to the extensive encapsulation of its neutral viologen moiety inside the β -CD cavity via self-inclusion complexation.

SCHEME 2. Self-Inclusion Behaviors and Molar Ellipticities of Reduced Forms of 1^{2+} – 3^{2+}



^a $[\theta]$'s are taken at 398 nm for $V^{\bullet+}$ and 380 nm for V° , and are in $\text{deg cm}^2 \text{ dmol}^{-1}$ units.

The presence of the monomeric form of 1° could account for the higher reactivity of 1° than of 3° . The higher reactivity of 2° than of 1° and 3° can be attributed to the presence of the V° unit of 2° outside the β -CD cavity, and thus its exposure to the bulk aqueous phase.

Conclusions

Two β -CD-viologens in which 1-methyl-4,4'-bipyridinium units are linked to the primary and the secondary side of the β -CD via an octamethylene linkage show quite contrasting self-inclusion behavior and induced circular dichroism (ICD). The compound having the pendant group on the primary side (2^{2+}) forms an intramolecular self-inclusion complex having the viologen moiety outside the secondary face of the β -CD cavity, with $K_{\text{in}} \approx 3.1$, whereas that modified at the secondary side (3^{2+}) forms the head-to-head-type dimer in which the viologen moieties are placed outside the primary face of the β -CD cavity, with $K_{\text{D}} \approx 65$ M^{-1} . One- or two-electron-reduced forms of the β -CD-viologens form intramolecular self-inclusion complexes. The reduced viologen units of $2^{\bullet+}$ and 2° are outside the β -CD cavity, whereas those of $3^{\bullet+}$ and 3° are inside the cavity. The β -CD-viologens, in both oxidized and reduced states of the viologen moiety, form [2]pseudorotaxanes with α -CD in which the secondary face of the ring α -CD is oriented toward the viologen unit. This work shows that the viologen unit, regardless of its oxidation state, prefers to reside above the secondary face rather than above the primary face of CDs; the reduced viologen units prefer the inside of the CD cavity more than the outside of the primary face but less than the outside of the secondary face. The ICD characteristics of β -CD-viologens 2^{2+} and 3^{2+} , mono-6-deoxy-6-[4-(1-methyl-4-pyridinio)-1-pyridinio]- β -CD (1^{2+}), and methyl-4-viologen ($C_{12}H_{16}N_2V^{2+}$)- β -CD complex in both oxidized and reduced states of the viologen unit are obtained. The dependence of the ICD of viologen chromophores on their locations with respect to the CD cavity, which was predicted theoretically, is demonstrated unequivocally. This work also confirms the dimerization of 1° from ICD,

(34) Kim, J. Y.; Lee, C.; Park, J. W. *J. Electroanal. Chem.* **2001**, *504*, 104.

and explains the order of reactivity of the viologen neutrals with water, $2^{\circ} > 1^{\circ} > 3^{\circ}$, on the basis of the structures of self-included complexes. We believe that the results provided here would be very useful in the structural elucidation and design of the CD-based supramolecular structures. Also, the change in the self-inclusion behaviors of 3^{2+} upon the reduction of the viologen unit could be utilized to modulate the assembling behaviors of the β -CD–viologens by light and electrical stimuli.

Experimental Section

Materials and Concentration Calculations. Dichloride salts of mono-6-deoxy-6-[4-(1-methyl-4-pyridinio)-1-pyridinio]- β -CD (1^{2+}),⁹ methyloctyl viologen ($C_{18}V^{2+}$),⁹ and mono-2-*O*-[4-(1-methyl-4-pyridinio)-1-pyridinio]octyl- β -CD (3^{2+})²⁶ were described in previous reports. All spectral measurements were carried out at 25 °C. The ionic strength of the solutions was fixed at 0.1 M with NaCl. The concentrations of viologens and viologen radical cations were assayed from UV–vis absorption data using $\epsilon_{262} = 21\,000\text{ M}^{-1}\text{ cm}^{-1}$ and $\epsilon_{602} = 13\,700\text{ M}^{-1}\text{ cm}^{-1}$, respectively.⁹ The concentrations of CDs were calculated from optical rotation data using reported specific rotations.³⁵

Mono-6-deoxy-6-*N*-[4-(1-methyl-4-pyridinio)-1-pyridinio]amino- β -CD Dichloride ($2^{2+}\cdot 2Cl^{-}$). Mono-6-deoxy-6-amino- β -CD (β -CD-6-NH₂) was prepared from mono-6-*O*-(*p*-toluenesulfonyl)- β -CD via a β -CD-6-azide intermediate.³⁶ To a solution of β -CD-6-NH₂ (4.12 g, 3.64 mmol) in dry DMF (40 mL) under a nitrogen atmosphere at 25 °C was added 1,8-diiodooctane (1.47 g, 4.00 mmol) dropwise, and the solution was stirred for 8 h at the same temperature. After evaporation of the solvent under reduced pressure, acetone (250 mL) was added to obtain 4.53 g of precipitate. The crude product was purified by reverse-phase column chromatography on C18 silica column using a linear gradient of aqueous CH₃CN (0–30 v/v %) to afford 3.0 g (60% yield) of mono-6-deoxy-6-(8-iodooctyl)amino- β -CD **4**. To the solution of **4** (0.43 g, 0.31 mmol) in dry DMF (5 mL) was added a solution of 1-methyl-4,4'-bipyridinium iodide (0.93 g, 3.1 mmol) in dry DMF (5 mL), and the reaction mixture was heated at 50 °C for a day under a nitrogen atmosphere. After evaporation of the solvent, acetone (100 mL) was added to obtain the yellow crude

product. The product was washed with hot ethanol (20 mL) and then purified by cation-exchange chromatography on a CM-25 column using a linear gradient of aqueous NaCl solution (0.0–0.5 M). The fractions showing UV absorption and optical rotation were combined, desalted by ultrafiltration through MW cutoff 500 cellulose membrane, and finally freeze-dried to obtain 0.11 g (23% yield based on **4**) of analytically pure $2^{2+}\cdot 2Cl^{-}$: mp 222 °C dec; ¹H NMR (D₂O, $\delta_{HDO} = 4.800$) δ 1.25–1.85 (m, 10H), 2.1–2.3 (br s, 2H), 2.7–4.1 (m, 44H), 4.54 (s, 3H), 4.91 (br s, 2H), 5.1–5.3 (m, 7H), 8.53–8.67 (br s, 2.5H), 8.69–8.77 (br s, 1.5H), 9.09 (d, 2H), 9.12–9.18 (br s, 0.5H), 9.23 (br d, 1.5H); MALDI TOF MS 1415.76, calcd for [C₆₁H₉₇N₃O₃₄]²⁺ 1415.59. Anal. Calcd for C₆₁H₉₇N₃O₃₄Cl₂·9H₂O: C, 44.42; H, 7.03; N, 2.55. Found: C, 44.24; H, 6.95; N, 2.43.

Photochemical Reduction of Viologens to Viologen Radical Cations. The reduction of viologen dication to viologen radical cation was carried out by irradiating the deaerated 3.2×10^{-5} M viologen solution containing 5×10^{-5} M Ru(bpy)₃²⁺ as a photosensitizer and 0.1 M EDTA as a sacrificial electron donor in 0.1 M aqueous NaCl at pH 10 with a tungsten lamp.⁹ The reduction was monitored by the characteristic UV–vis absorption of the viologen radical cation.⁹

Electrochemical Reduction of Viologen to Viologen Neutrals and Circular Dichroism Spectra of Viologen Neutrals. A spectroelectrochemical cell was assembled with a demountable 100 μm path length rectangular cuvette and an ITO coated glass cover as described.²⁶ The cell was filled with 6.7×10^{-3} M viologen solution in 0.10 M KCl at pH 8.9, adjusted with 0.01 M borate buffer, and mounted in the cell compartment of a spectropolarimeter. The CD spectra of viologen neutral were recorded in situ while applying -1.2 V versus Ag wire potentiostatically. The high-tension voltage (HV) data from the spectropolarimeter were converted to absorbance data, and the concentration of viologen neutral was calculated from the absorbance data using $\epsilon_{394} = 41\,500\text{ M}^{-1}\text{ cm}^{-1}$.²⁷ The calibration of HV data was made with viologen radical cation solutions.

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Supporting Information Available: General procedure for spectral measurements, ¹H NMR and two-dimensional ROESY spectra of 2^{2+} and 3^{2+} . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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