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Modified Cyclodextrin System for Controlling Photosensitized Reduction of Viologen by Guests

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The invesitigation of photosensitized reduction of viologen-appended β-cyclodextrin ($CDxEV^{2+}$) using Rose Bengal as a sentizer has revealed that the reduction of the viologen moiety of $CDxEV^{2+}$ is remarkably affected by the presence of guests. The spatial position of the viologen moiety in $CDxEV^{2+}$, which can be changed by guest binding, is suggested to be the factor that governs the reduction.

Photosensitized reduction of viologens (RV^{2+}) has been studied as a model system for conversion of solar energy.[1] In order to assist charge separation and retard the back reaction between the reduced species of acceptor and the sensitizer, many organized assemblies such as micelles[2] and liposomes[3] have been used. When Rose Bengal (RB^{2-}) is used as the sensitizer, the reduction includes the following processes

$$RB^{2-} + \text{light} \longrightarrow {}^1RB^{2-}\ (\text{singlet state}) \longrightarrow {}^3RB^{2-}\ (\text{triplet state}) \quad (1)$$

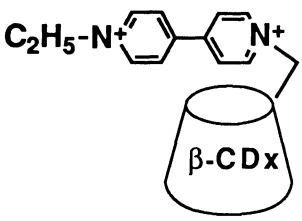
$${}^1RB^{2-} + RV^{2+} \longrightarrow [{}^1RB^{2-}...RV^{2+}] \quad \text{no reaction} \quad (2)$$

$${}^3RB^{2-} + RV^{2+} \longrightarrow RB^{-\cdot} + RV^{+\cdot} \quad (3)$$

$$RB^{-\cdot} + RV^{+\cdot} \longrightarrow RB^{2-} + RV^{2+} \quad (4)$$

$$RB^{-\cdot} + EDTA \longrightarrow RB^{2-} + EDTA^{+} \quad (5)$$

The photosensitized reduction is retarded by back reaction of electron transfer (Eq.4) and formation of non-productive complex[4] between the sensitizer and viologen (Eq.2). Much effort has been invested to remove these unfavorable reactions. For example, Willner et al. used β-cyclodextrin (β-CDx) in the reduction of benzyl and octyl viologens, employing Zn(II)-meso-tetraphenylsulfonato porphyrin as the sensitizer and improved the reaction yield as the result of inclusion complex formation between the viologen derivatives and β-CDx.[5] Similar results were also reported by Okuno et al.[6] However, in these studies, β-CDx was shown to have no ability to modify the reaction of methyl viologen (MV^{2+}) or ethyl viologen (EV^{2+}) due to the fact that β-CDx does not form any inclusion complex with such dications. In the present study, photosensitized reduction of ethyl viologen-modified β-CDx ($CDxEV^{2+}$)[7] in aqueous solution containing RB^{2-} (5.0×10^{-6} mol dm^{-3}) as the sensitizer and EDTA (1.0×10^{-2} mol dm^{-3}) as the electron donor has been undertaken, and we wish to report here the unique reaction behavior of viologen in $CDxEV^{2+}$ where the viologen reaction can be controlled by organic compounds acting as the guests.



$CDxEV^{2+}$

Table 1 shows induced circular dichroism (ICD) spectral data of $CDxEV^{2+}$ at 255 nm in the absence and presence of guests such as 1-adamantanol (ADN), 1-adamantanecarboxylic acid (ACA) or sodium cholate (SC). It has been previously shown that $CDxEV^{2+}$ form inclusion complexes with these guests, the association

constants being in the range $4x10^3$ - $5x10^4$ mol^{-1} dm^3.[8] The negative CD band observed around 255 nm suggests that the viologen moiety was included into the cavity of $CDxEV^{2+}$, taking the orientation perpendicular to the axis of CDx.[7] The absolute intensity of the band increased upon addition of ACA whereas decreased upon addition of SC. On the other hand, the intensity was hardly affected by ADN. These ICD data indicate that the position of the viologen moiety changes depending on the guest species. The increase induced by ACA may be caused by the insertion of the viologen moiety into the deeper interior of the cavity of $CDxEV^{2+}$. This is the result of the hydrophobic interaction between the viologen moiety and ACA which is inserted into the cavity from the opposite wider secondary hydroxyl side. This argument is consistent with the report that ACA sits on the wider face of β-CDx.[9] The fact that ICD band intensity was enhanced by ACA and not ADN implies that coulombic interaction also plays an important role in this conformational change. On the contrary, the decrease in the ICD intensity caused by SC may be due to the exclusion of the viologen moiety from the cavity by deeper involvement of SC into the cavity.

Table 1. The circular dichroism spectra data of $CDxEV^{2+}$ in the presence and absence of the various guests [a]

	$CDxEV^{2+}$	$CDxEV^{2+}$ + ACA	$CDxEV^{2+}$ + AND	$CDxEV^{2+}$ + SC
$\Delta\varepsilon$ / mol^{-1} dm^3cm^{-1}	(-) 2.73	(-) 3.5	(-) 2.8	(-) 2.2
$\Delta\varepsilon/\Delta\varepsilon CDxEV^{2+}$	1.00	1.30	1.03	0.81

$[CDxEV^{2+}] = 1x10^{-4}$mol dm^{-3}; [each guest] = $1.5x10^{-3}$mol dm^{-3} at 25 °C in pH 9.6 borate buffer. Wavelength = 255 nm.

Figure 1 shows Stern-Volmer plots for the quenching of the fluorescence of RB^{2-} (570 nm) by MV^{2+} or $CDxEV^{2+}$ in the absence or presence of guest species. Since the fluorescence lifetime of RB^{2-} is only 0.1-0.2 ns and the concentration of MV^{2+} or $CDxEV^{2+}$ is below a few millimolar, the quenching may occur within the complex between RB^{2-} and MV^{2+} or the viologen moiety of $CDxEV^{2+}$ (static quenching). The slope of the Stern-Volmer plots can be equated with the association constants under the conditions and the values are shown in Table 2. Since no change in the fluorescence intensity was induced by introducing β-CDx into the solution of RB^{2-} and MV^{2+}, β-CDx itself is inert in this reaction. When $CDxEV^{2+}$ was used in place of MV^{2+}, higher quenching efficiency was observed reflecting the fact that the complex between RB^{2-} and the viologen moiety of $CDxEV^{2+}$ is stabilized. Although the reason for this stabilization is not yet clear, this stabilization became more remarkable upon addition of SC as the guest of $CDxEV^{2+}$, 1.64-fold larger association constant than that of $CDxEV^{2+}$, alone. In contrast to the case of SC, the complex is slightly destabilized by the presence of ACA. These results indicate that the complex between RB^{2-} and the viologen moiety of $CDxEV^{2+}$ can be controlled by guest species.

Figure 2 shows the absorption spectra of the aqueous solution containing RB^{2-}, EDTA, and $CDxEV^{2+}$, measured at different times under light irradiation (>540 nm). The increases in the absorption intensities around 400 and 600 nm indicate the occurrence of photoinduced reduction of $CDxEV^{2+}$. Table 2 shows the yields of $MV^{+\cdot}$ or $CDxEV^{+\cdot}$ in the absence or presence of guest species after 5 min of irradiation. The presence of β-CDx did not affect the photoreduction of MV^{2+}. It is interesting that $CDxEV^{2+}$ gives 2.6-fold higher yield than

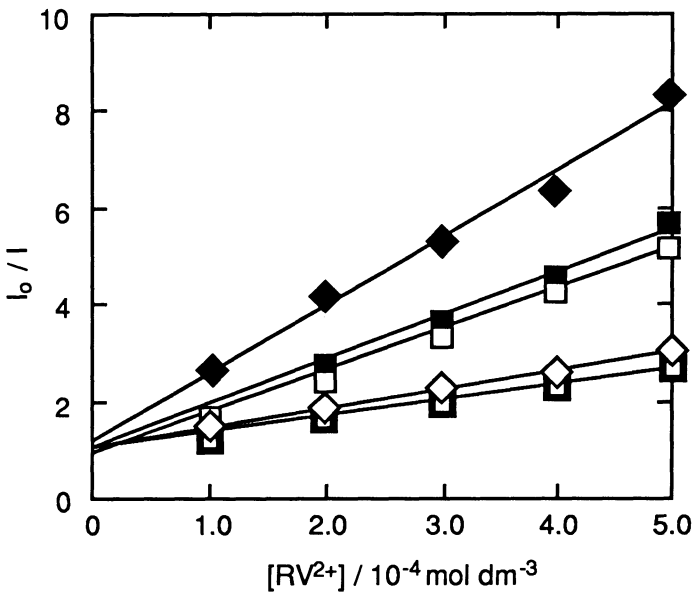


Fig.1. Stern-Volmer plots for quenching of luminescence of $1x10^{-6}$ mol dm^{-3} Rose Bengal by methyl viologen (◇), $CDxEV^{2+}$(□), $CDxEV^{2+}$ in the presense of the guest (◆ ■ ◘), respectively. (◆) [SC] =$5x10^{-3}$mol dm^{-3}, (■) [ADN] =$2x10^{-3}$mol dm^{-3}, (◘) [ACA]=$2x10^{-3}$mol dm^{-3}

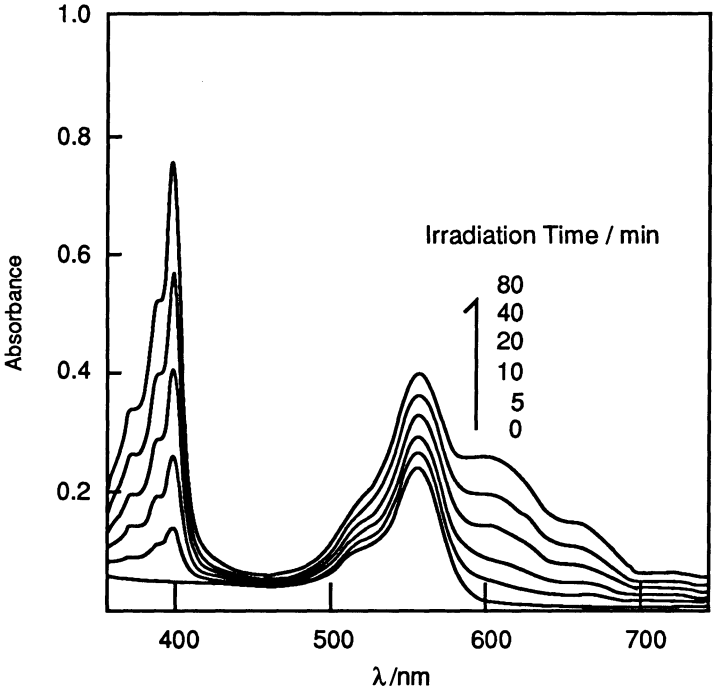


Fig.2. Absorption spectral changes on photolysis of $5x10^{-6}$mol dm^{-3} Rose Bengal in pH7.0 phosphate buffer solution containing $1x10^{-2}$ mol dm^{-3} EDTA and $1x10^{-3}$ mol dm^{-3} $CDxEV^{2+}$.

MV^{2+} in spite of the fact that the viologen moiety of $CDxEV^{2+}$ forms the ground-state complex with RB^{2-} with higher association constant. This reduction yield became much higher (3.7-fold) in the presence of ACA. Since this yield is too high to be explained only by the decreased value of K of the $CDxEV^{2+}$-ACA system (Table 2), back electron transfer (Eq.4) is likely to be suppressed in this case. This phenomenon may be related with the locational change of the viologen moiety from the position proximal to the open mouth of $CDxEV^{2+}$ to the deeper cavity of $CDxEV^{+\cdot}$ associated with the decrease in the positive charge of the viologen unit. The yield of $CDxEV^{2+}$ in the presence of SC or ADN is the intermediate between MV^{2+} and the above system, and the effect of the suppression of the back reaction may be partly cancelled by the remarkable increases in the K value. In conclusion, the photoreduction of viologen could be modified by guests when $CDxEV^{2+}$ was used and the high yield of the reaction was attained by the presence of ACA. Therefore we have shown that both back electron transfer and formation of non-productive complex between sensitizer and viologen can be controlled in the system where viologen is combined with CDx.

Table 2. Association constants (K) and the formation yield of viologen cation radical in RB^{2-}-MV^{2+} or RB^{2-}-$CDxEV^{2+}$ systems in the absence and presence of β-CDx or the various guests [a]

	MV^{2+}	MV^{2+} +β-CDx	$CDxEV^{2+}$	$CDxEV^{2+}$ +ACA	$CDxEV^{2+}$ +SC	$CDxEV^{2+}$ +ADN
$K / mol^{-1}dm^3$	3980	3980	8420	3290	13800	9090
	(1.0)	(1.0)	(2.1)	(0.82)	(3.5)	(2.3)
$[RV^{+\cdot}] / moldm^{-3}$ [b]	$4.6x10^{-6}$	$4.6x10^{-6}$	$1.2x10^{-5}$	$1.7x10^{-5}$	$7.5x10^{-6}$	$1x10^{-5}$
	(1.0)	(1.0)	(2.6)	(3.7)	(1.6)	(2.1)

a) In pH 9.6 borate buffer at 15 °C. Relative values to the data of MV^{2+} shown in the first column (K/KMV^{2+} or $[RV^{+\cdot}]/[MV^{+\cdot}]$) are indicated in parentheses. b) After 5 minute under illumination.

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