Photosensitized Electron-Transfer Reactions in β-Cyclodextrin Aqueous Media: Effects on Dissociation of Ground-State Complexes, Charge Separation, and H_2 Evolution

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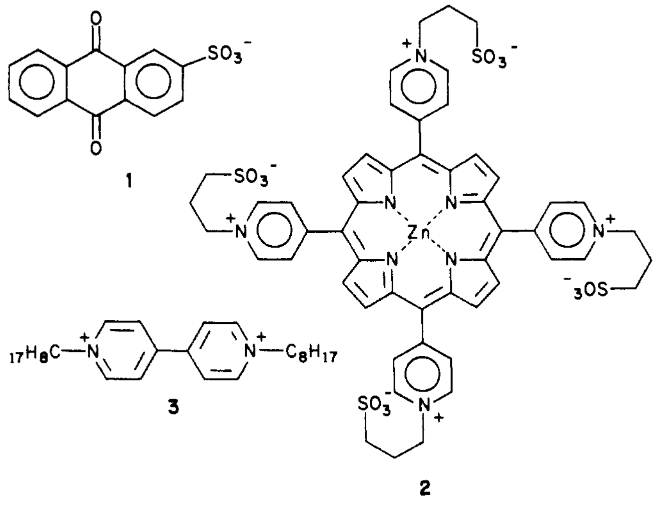
Abstract: Zinc(II) *meso*-tetrakis[1-(3-sulfonatopropyl)-4-pyridino]porphyrin, ZnTPSPyP (**2**), forms a ground state complex with anthraquinone-2-sulfonate, AQS^- (**1**). The formation of the complex results in internal static quenching of the excited S state of the sensitizer and recombination of the photoproducts in the cage structure. In the presence of β-cyclodextrin (β-CD), the complex is separated due to selective association of AQS^- to the receptor cavity. This process leads to the effective decay of excited ZnTPSPyP to the T state that undergoes diffusional quenching by β-CD-bound AQS^-. The electron-transfer photoproducts are stabilized against back-electron-transfer reaction and $AQHS^{-\bullet}$ can be accumulated under continuous illumination in the presence of cysteine as the electron donor. Photoreduction of *N,N'*-dioctyl-4,4'-bipyridinium, C_8V^{2+}, with $Ru(bpy)_3^{2+}$ as the sensitizer and Na_2EDTA as the donor leads to the formation of a dimer aggregate $(C_8V^{+\bullet})_2$. The aggregate is inactive in H_2 evolution. In the presence of β-CD, the aggregate formation is prevented due to the selective association of $C_8V^{+\bullet}$ monomer to the cyclodextrin cavity. High quantum yields for H_2 evolution in the presence of a Pt-colloid are observed with β-CD, $\phi = 4 \times 10^{-2}$. Flash photolysis studies reveal that the association of $C_8V^{+\bullet}$ to the β-CD stabilizes the intermediate photoproducts against back-electron-transfer reactions.

Photosensitized electron-transfer reactions are of substantial interest as a means of solar energy conversion and storage.[1–4] Serious efforts have been devoted in studying photoinduced electron-transfer reactions in organized microenvironments such as micelles,[5–7] charged colloids,[8,9] microemulsions,[10,11] and vesicles.[12] With these organized systems, control of the photosensitized electron-transfer processes has been accomplished. Namely, the quenching process could be improved, charge separation has been facilitated, and the stabilization of photoproducts against back-electron-transfer reactions has been accomplished. Cyclodextrins (CD) are cyclic polysugars composed of glucose units linked by 1–4α-glycoside bonds.[11,13] The cyclic structure forms a hydrophobic cavity capable of associating organic substrates.[14] Application of cyclodextrins as an organizing microenvironment in photochemical reactions has been initiated recently and revealed selectivity in products distribution.[15,16] In principle, one could apply the association properties of cyclodextrins for controlling the recombination process between photoproducts by the selective binding of one of the electron-transfer products.

Here we wish to report on the effects of β-CD on photosensitized electron-transfer reactions in aqueous media. We find that in the presence of β-CD, the photosensitized reduction of anthraquinone-2-sulfonate, AQS^- (**1**) using the neutral zinc porphyrin, zinc(II) *meso*-tetrakis[1-(3-sulfonatopropyl)-4-pyridino]porphyrin, ZnTPSPyP (**2**), and cysteine as the electron donor is possible. Without CD the process is prevented due to the formation of a ground-state complex between the sensitizer and the anthraquinone acceptor. This complex avoids the separation of electron-transfer photoproducts. Also, we report on the photosensitized reduction of *N,N'*-dioctyl-4,4'-bipyridinium (octylviologen), C_8V^{2+} (**3**), using ruthenium(II) tris(bipyridine), $Ru(bpy)_3^{2+}$, as the sensitizer in the presence and absence of β-CD. Without cyclodextrin, photoreduction of C_8V^{2+} yields a dimer aggregate of the reduced



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(1) (a) *Energy Resources Through Photochemistry and Catalysis*; Gratzel, M., Ed.; Academic: New York, 1983. (b) Bard, A. J. *Science (Washington, D.C.)* **1980**, *207*, 138.

(2) (a) Gratzel, M. *Acc. Chem. Res.* **1981**, *14*, 376–384. (b) Maverick, A. W.; Gray, B. H. *Pure Appl. Chem.* **1980**, *52*, 2339–2348.

(3) Whitten, D. G.; Russel, J. C.; Schmell, R. H. *Tetrahedron* **1982**, *38*, 2455–2487.

(4) (a) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717–2738. (b) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159–244.

(5) Turro, N. J.; Gratzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 675–696.

(6) (a) Brugger, P. A.; Infelta, P. P.; Braun, A. M.; Gratzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 320–326. (b) Evans, C. A.; Bolton, J. R. *Photochem. Photobiol.* **1979**, *30*, 697–707.

(7) (a) Matsuo, T.; Takuma, K.; Tsusui, Y.; Nishigima, T. *Coord. Chem. Rev.* **1980**, *10*, 195–216. (b) Moroi, Y.; Infelta, P. P.; Gratzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 573–579. (c) Moroi, Y.; Braun, M. A.; Gratzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 567–572.

(8) (a) Willner, I.; Otvos, J. W.; Calvin, M. *J. Am. Chem. Soc.* **1981**, *103*, 3203–3205. (b) Willner, I.; Yang, J. M.; Otvos, J. W.; Calvin, M. *J. Phys. Chem.* **1981**, *85*, 3277–3282. (c) Degani, Y.; Willner, I. *J. Am. Chem. Soc.* **1983**, *105*, 6228–6233.

(9) Willner, I.; Laane, C.; Otvos, J. W.; Calvin, M. In *Inorganic Reactions in Organized Media*; Holt, S. L., Ed.; ACS Symposium Series 177; American Chemical Society: Washington, DC, 1982; pp 71–95.

(10) Mandler, D.; Degani, Y.; Willner, I. *J. Phys. Chem.* **1984**, *88*, 4366–4370.

(11) Jones, C. A.; Weaner, L. E.; Mackay, R. A. *J. Phys. Chem.* **1980**, *84*, 1495–1500.

(12) (a) Sudo, Y.; Toda, F. *Nature (London)* **1979**, *279*, 808. (b) Matsuo, T.; Itoh, K.; Takuma, K.; Hashimoto, K.; Nagamura, T. *Chem. Lett.* **1980**, 1009–1012. (c) Fendler, J. H. *J. Phys. Chem.* **1980**, *84*, 1485–1491. (d) Infelta, P. P.; Gratzel, M.; Fendler, J. H. *J. Am. Chem. Soc.* **1980**, *102*, 1497.

(13) (a) Saenger, A. Q. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 344. (b) Cramer, F.; Hettler, H. *Naturwissenschaften* **1967**, *54*, 625. (c) Bender, M. L.; Kamiyama, M. *Cyclodextrin Chemistry*; Springer: Berlin, 1978.

(14) (a) Tabushi, I. *Acc. Chem. Res.* **1982**, *15*, 66. (b) Breslow, R. *Science (Washington, D.C.)* **1982**, *218*, 532. (c) Tabushi, I.; Yamamura, K. *Topp. Curr. Chem.* **1983**, *113*, 145. (d) Willner, I.; Goren, Z. *J. Chem. Soc., Chem. Commun.* **1983**, 1469–1470.

(15) (a) Okuno, Y.; Chiba, Y.; Yonemitsu, O. *J. Chem. Soc., Chem. Commun.* **1984**, 1638–1639. (b) Sidney, G. C.; Hauptman, P. J.; Turro, N. J. *Photochem. Photobiol.* **1984**, *39*, 597–601.

(16) Kano, K.; Takenoshita, I.; Ogawa, T. *Abstr. Pap.—Am. Chem. Soc.* **1982**, *186*, 1833–1838.

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photoproduct $C_8V^{+\bullet}$. This aggregate is inactive in subsequent H_2 evolution. In the presence of β-CD, the formation of the aggregate is prevented due to the association of $C_8V^{+\bullet}$ monomer to the CD cavity. Consequently, subsequent effective H_2 evolution in the presence of a Pt catalyst is possible. The studies reveal that the cyclodextrins stabilize effectively the intermediate photoproducts, formed in the different reactions, against back-electron-transfer reactions.

Experimental Section

Absorption spectra were recorded with a Uvikon-820 (Kontron) spectrophotometer equipped with a ψ-80 computer (Kontron) for spectra accumulation and manipulation. Fluorescence spectra were recorded with a SEM-25 spectrophotometer (Kontron). Flash photolysis experiments were performed with a DL200 (Molectron) dye laser pumped by a UV-IU (Molectron) nitrogen laser. Flashes were recorded on Biomation 8100, and pulse collection was performed with a Nicolet-1170. Steady-state illuminations were performed with a 1000-W halogen quartz lamp. Light was filtered through a 400-nm cut-off filter. Photon flux was determined by Reinecke salt actinometry[17] to be 2×10^{-2} einsteins·L^{-1}·min^{-1}. Hydrogen analysis was performed with a Hewlett-Packard 427 gas chromatograph, 5-Å molecular sieve column.

Zinc(II) *meso*-tetrakis[1-(3-sulfonatopropyl)-4-pyridino]porphyrin (**2**) was prepared as described previously.[18] *N,N'*-Dioctyl-4,4'-bipyridinium dibromide (**3**) was prepared by refluxing 4,4'-bipyridine with a 6-fold excess of octyl bromide in dimethylformamide. To the cool solution, acetone was added and the precipitate was washed several times with acetone. All compounds gave satisfactory elementary analysis.

For steady-state illumination, photoreduction of AQS^- was performed in a system composed of an aqueous 0.02 M phosphate buffer, pH 6, that included the sensitizer ZnTPSPyP, 7×10^{-6} M, the electron acceptor, AQS^-, 3.0×10^{-4} M, and the electron donor L-cysteine, 2.0×10^{-3} M. Photoreduction of C_8V^{2+} was performed in an aqueous system composed of a phosphate buffer, pH 5.5, that included ruthenium(II) tris(bipyridine), $Ru(bpy)_3^{2+}$, 5.5×10^{-5} M, as the sensitizer, octylviologen C_8V^{2+}, 5×10^{-3} M, as the electron acceptor, and disodioethylenediaminetetraacetic acid, Na_2EDTA, 1.0×10^{-1} M, as the electron donor. β-Cyclodextrin (Aldrich) was dissolved in the different systems at the specified concentrations. For H_2 evolution a Pt colloid (12 mg·L^{-1}) was introduced into the system. The Pt colloid was prepared by the citrate reduction method (particle size ~10 Å).[19,20] The Pt colloids were dialyzed before use. Samples (3 mL) of the aqueous solutions of the systems were transferred into 1 × 1 cm Pyrex glass cuvettes equipped with a valve and serum stopper. Samples were deaerated by repeated evacuation followed by flushing with oxygen-free argon. The samples were illuminated with a 1000-W halogen quartz lamp, and the formation of products was followed spectroscopically. $AQSH^{-\bullet}$ formation was followed[21] at $\lambda = 384$ (ϵ 12000 M^{-1} cm^{-1}). $C_8V^{+\bullet}$ was followed at $\lambda = 602$ nm (ϵ 13800 M^{-1} cm^{-1}), and the dimer $(C_8V^{+\bullet})_2$ was followed at $\lambda = 569$ nm (ϵ 6200 M^{-1} cm^{-1}). Fluorescence measurements were performed in aqueous 0.02 M phosphate buffer samples (3 mL) that included the sensitizer, ZnTPSPyP, 5×10^{-6} M, and the decay of fluorescence upon addition of AQS^- was measured at $\lambda = 622$ nm. Quenching of the triplet *ZnTPSPyP by AQS^- was followed by its decay at $\lambda = 790$ nm (excitation at $\lambda = 448$ nm). Charge separation and recombination of $ZnTPSPyP^+$ was followed at $\lambda = 680$ nm. Quenching of $^*Ru(bpy)_3^{2+}$ by C_8V^{2+} was followed by steady-state fluorescence quenching ($\lambda = 602$ nm). Charge separation of $C_8V^{+\bullet}$ and its recombination with $Ru(bpy)_3^{3+}$ was measured by following the formation and decay of $C_8V^{+\bullet}$ at $\lambda = 602$-nm excitation at $\lambda = 455$ nm. H_2 evolution was followed by injection of 300 μL of the gaseous atmosphere of the flask into the gas chromatograph at time intervals of illumination.

Results and Discussion

Photosensitized Reduction of Anthraquinone-2-sulfonate in the Presence of β-CD. Zinc(II) *meso*-tetrakis[1-(3-sulfonatopropyl)-4-pyridino]porphyrin, ZnTPSPyP (**1**), is an aqueous soluble neutral metalloporphyrin. Its photophysical properties have been previously characterized.[22,23] It exhibits a fluorescence emission at $\lambda = 622$ nm and a short-lived singlet state ($\tau \sim 10 \times 10^{-9}$ s) that undergoes effective crossing to a long-lived triplet state ($\tau = 0.5$ ms, $\phi = 0.9$). Addition of anthraquinone-2-sulfonate, AQS^- (**1**), to an aqueous solution of ZnTPSPyP, 5×10^{-6} M, results in substantial changes in the absorption spectrum and emission properties of the metalloporphyrin. In the absorption spectrum (Figure 1), the Soret absorption band of **2** is shifted from $\lambda = 439$ to 444 nm in the presence of AQS^-. The effects of added AQS^- on the emission of ZnTPSPyP are shown in Figure 2. It can be seen that the fluorescence emission is totally quenched at $[AQS^-] = 5.0 \times 10^{-5}$ M. Laser flash studies reveal that under these conditions the singlet excited state is totally quenched and no formation of the T state is observed.

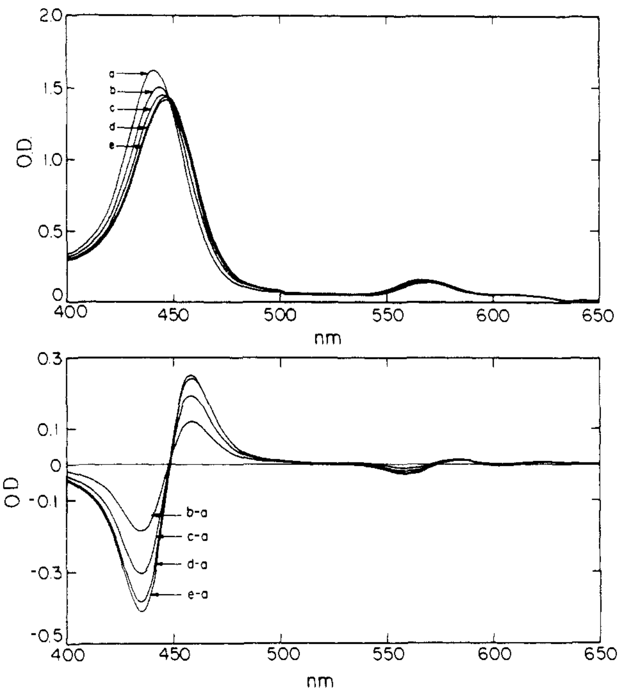

Figure 1. Absorption spectra (top) and differential absorption spectra (bottom) of ZnTPSPyP (7×10^{-6} M) obtained after addition of AQS^-: (a) no added AQS^-; (b) $[AQS^-] = 2 \times 10^{-6}$ M; (c) $[AQS^-] = 4 \times 10^{-6}$ M; (d) $[AQS^-] = 6 \times 10^{-6}$ M.

These results are attributed to the formation of a ground-state complex between ZnTPSPyP and AQS^- (eq 1), where the S state is being quenched in the complex structure. From the changes in the absorption spectrum of ZnTPSPyP upon addition of AQS^-, the association constant of the complex [ZnTPSPyP···AQS^-], eq 2, is estimated to be $K_1 = 4.35 \pm 0.5 \times 10^5$ M^{-1}. Furthermore,

$$\text{ZnTPSPyP} + \text{AQS}^- \overset{K_1}{\rightleftharpoons} [\text{ZnTPSPyP}\cdots\text{AQS}^-] \qquad (1)$$

$$K_1 = [\text{ZnTPSPyP}\cdots\text{AQS}^-]/[\text{ZnTPSPyP}][\text{AQS}^-] \qquad (2)$$

assuming that the metalloporphyrin does not emit, then the fluorescence intensity is proportional to the concentration of free porphyrin. This allows us to determine the concentration of free and bound metalloporphyrin at each concentration of AOS^-. When this method is used, the association constant of the complex is estimated to be $K_1 = 4.5 \pm 1 \times 10^5$ M^{-1}, a value that is in good agreement to the value obtained by the changes in the absorption spectrum.

It is well established[14] that cyclodextrins bind aromatic compounds into the hydrophobic cavity of the CD. Indeed, addition of β-CD to an aqueous solution ZnTPSPyP and AQS^-, under conditions where the metalloporphyrin is in the complex structure, restores the emission properties of ZnTPSPyP (Figure 2). This

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(17) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.

(18) (a) Willner, I.; Degani, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 1249-1251. (b) Degani, Y.; Willner, I. *J. Phys. Chem.* **1985**, *89*, 56859

(19) Furlong, D. A.; Launikonis, A.; Sasse, H. F.; Walfgang, H. F. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 571-588.

(20) Aika, K.; Ban, L. L.; Okura, I.; Namba, S.; Turkevich, J. *J. Res. Inst. Catal., Hokkaido Univ.* **1976**, *24*, 55.

(21) Rao, P. S.; Hayon, E. *J. Phys. Chem.* **1973**, *77*, 2274-2276.

(22) Harriman, A.; Porter, G.; Richoux, M. C. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1955-1970.

(23) Houlding, V. H.; Kalyanasundaram, K.; Gratzel, M.; Milgrom, L. R. *J. Phys. Chem.* **1983**, *87*, 3175-3179.

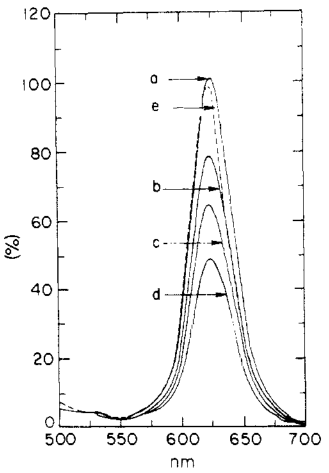

Figure 2. Fluorescence spectra of ZnTPSPyP (5×10^{-6} M) upon addition of AQS^-: (a) no added AQS^-; (b) $[AQS^-] = 2 \times 10^{-6}$ M; (c) $[AQS^-] = 4 \times 10^{-6}$ M; (d) $[AQS^-] = 8 \times 10^{-6}$ M; (e) $[AQS^-] = 8 \times 10^{-6}$ M and $[\beta\text{-CD}] = 1 \times 10^{-2}$ M.

implies that upon addition of β-CD the complex of the two components is separated by the selective association of AQS^- to the CD cavity (eq 3). The restoration of the emission properties of the zinc porphyrin in the presence of β-CD allows one to determine the association constant of AQS^- to β-CD (eq 3 and 4). Since

$$AQS^- + \beta\text{-CD} \overset{K_2}{\rightleftharpoons} AQS^- \cdots \beta\text{-CD} \quad (3)$$

$$K_2 = [AQS^- \cdots \beta\text{-CD}]/[AQS^-][\beta\text{-CD}] \quad (4)$$

the fluorescence intensity is only due to free porphyrin ZnTPSPyP, the concentration of free quinone and β-CD-bound AQS^- can be derived from eq 2a and 5, where $[AQS^-]_f$ and $[AQS^-]_0$ correspond to the free and total concentration of the quinone. When this analysis is used, the derived association constant of AQS^- to β-CD is $K_2 = 3 \pm 0.5 \times 10^3\ M^{-1}$.

$$[AQS^-]_f = K_1[\text{ZnTPSPyP}]/[\text{ZnTPSPyP} \cdots AQS^-] \quad (2a)$$

$$[AQS^- \cdots \beta\text{-CD}] = [AQS^-]_0 - [AQS^-]_f - [\text{ZnTPSPyP} \cdots AQS^-] \quad (5)$$

The separation of the complex structure between the metalloporphyrin and AQS^- by β-CD allows the accumulation of electron-transfer products upon illumination. Irradiation of an aqueous solution (λ > 400 nm) that includes ZnTPSPyP (7.0×10^{-6} M), AQS^- (3.0×10^{-4} M), and cysteine (2.0×10^{-3} M) as the electron donor does not yield any photoproducts in the absence of β-CD. In turn, in the presence of β-CD, 1×10^{-2} M, the reduced hydroquinone radical, $AQHS^{-\bullet}$ is formed upon illumination, $\phi = 1.35 \times 10^{-3}$. Exclusion of cysteine from the composition that includes β-CD prohibits the formation of $AQHS^{-\bullet}$ upon illumination. This implies that cysteine acts as the electron donor in the photosensitized reduction of AQS^-.

The functions of β-CD in the photosensitized reduction of AQS^- have been elucidated by means of laser flash photolysis.

The sensitizer, ZnTPSPyP^0, decays upon excitation to the long-lived T state ($\tau = 0.5$ ms, $\phi = 0.9$). Addition of AQS^- (**1**) results in a decrease in the T state yield, and at a $[AQS^-] = 4 \times 10^{-6}$, the T-state yield corresponds to 0.5 of the value obtained in the absence of AQS^-. This is in accordance with our previous results that indicated the formation of the complex $\text{ZnTPSPyP} \cdots AQS^-$, where the excited sensitizer is quenched in the S state. This intramolecular quenching prohibits the formation of the long-lived triplet state. Addition of β-CD to the solution of ZnTPSPyP and AQS^- restores the effective formation of the T state and shortening of the T state lifetime. This result implies that a different quenching mechanism occurs where the ZnTPSPyP T state is quenched by AQS^- (eq 6). The quenching rate constant corresponds to $k_q = 3.3 \times 10^6\ M^{-1}\ s^{-1}$. This quenching process leads to separated electron-transfer products

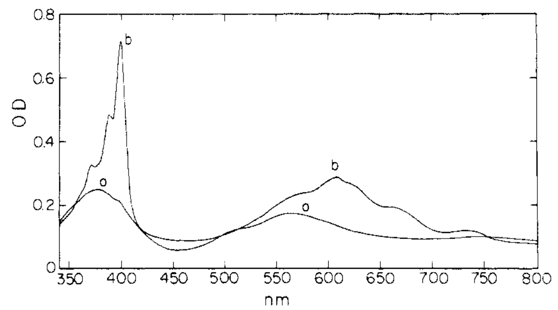

Figure 3. Absorption spectra of the photoreduced product of C_8V^{2+} (5.0×10^{-3} M) in the presence of $Ru(bpy)_3^{2+}$, 1.0×10^{-5} M, and Na_2EDTA, 1.0×10^{-1} M: (a) in the absence of β-CD; (b) in the presence of β-CD, 1.0×10^{-2} M.

(eq 6) that recombine (eq 7) with a bimolecular recombination rate constant of $k_b = 2.5 \times 10^7\ M^{-1}\ s^{-1}$. Comparison of the

$$^*\text{ZnTPSPyP (T)} + AQS^- \cdots \beta\text{-CD} + H^+ \xrightarrow{k_q} \text{ZnTPSPyP}^+ + AQHS^{-\bullet} \cdots \beta\text{-CD} \quad (6)$$

$$\text{ZnTPSPyP}^+ + AQHS^{-\bullet} \cdots \beta\text{-CD} \xrightarrow{k_b} \text{ZnTPSPyP} + AQS^- \cdots \beta\text{-CD} + H^+ \quad (7)$$

recombination rate of the electron-transfer products in the presence of β-CD to the value obtained in the absence of β-CD[24] indicates that the back-electron-transfer process is 10-fold retarded in the presence of β-CD.

Thus, in view of the flash photolysis results, we can conclude that the added β-CD participates in the electron-transfer process in two routes: (i) it separates the complex structure $\text{ZnTPSPyP} \cdots AQS^-$ and allows the formation of the T state of the excited sensitizer, and (ii) it stabilizes the electron-transfer products against back-electron-transfer reactions, by the selective association of $AQHS^{-\bullet}$ within the cyclodextrin cavity. These two functions of β-CD allow the effective accumulation of $AQHS^{-\bullet}$ under continuous illumination.

Photoreduction of Octylviologen and H_2 Evolution in the Presence of β-CD. Photoreduction of alkylviologens in the visible spectrum has been extensively examined using various sensitizers[25-27] and organized microenvironments.[28,29] Emphasis has been directed to the utilization of the photoproducts, viologen radicals, in H_2 evolution in the presence of metal colloids such as Pt catalysts.[30-32] Interestingly, illumination of an aqueous solution, pH 5.5, that includes the sensitizer, ruthenium(II) tris(bipyridine), $Ru(bpy)_3^{2+}$, *N,N'*-dioctyl-4,4'-bipyridinium, octylviologen, C_8V^{2+}, as the electron acceptor and disodioethylenediaminetetraacetic acid, Na_2EDTA, as the electron donor, results in the formation

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(24) At low AQS^- concentration electron-transfer products are formed inefficiently via quenching of uncomplexed sensitizer in the T state. The recombination rate is estimated to be $K_b = 2.9 \times 10^7$.

(25) Okura, I.; Takeuchi, M.; Kim-Thuan, N. *J. Mol. Catal.* **1979**, *6*, 227.

(26) Kalyanasundaram, K.; Gratzel, M. *Helv. Chim. Acta* **1980**, *63*, 478.

(27) Okura, I.; Aono, S.; Takeuchi, M.; Kusunoki, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3637–3638.

(28) (a) Brugger, P. A.; Gratzel, M. *J. Am. Chem. Soc.* **1980**, *102*, 2461–2463. (b) Kamogawa, H.; Masui, T.; Nanasawa, M. *Chem. Lett.* **1980**, 1145–1148.

(29) (a) Brugger, P. A.; Infelta, P. P.; Braun, A. M.; Gratzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 320–326. (b) Wheeler, J.; Thomas, K. J. *J. Phys. Chem.* **1982**, *86*, 4540–4544. (c) Maidan, R.; Goren, Z.; Becker, J. Y.; Willner, I. *J. Am. Chem. Soc.* **1984**, *106*, 6217–6222.

(30) (a) Kiwi, J.; Gratzel, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 624–626. (b) Okura, I.; Nakamura, S.; Nakamura, K. I. *J. Mol. Catal.* **1979**, *6*, 71–73. (c) Koriakin, B. V.; Dzhabiev, T. S.; Shilon, A. *Dokl. Akad. Nauk. SSSR* **1977**, *233*, 620.

(31) (a) Keller, P.; Moradpour, A.; Amouyal, E.; Kagan, H. B. *Nouv. J. Chim.* **1980**, *4*, 377–384; *J. Am. Chem. Soc.* **1980**, *102*, 7193–7196. (b) Harriman, A.; Porter, G.; Richoux, M. C. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1939–1948. (c) Harriman, A.; Porter, G.; Richoux, M. C. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 833–844.

(32) (a) Krasna, A. I. *Photochem. Photobiol.* **1980**, *31*, 75–81. (b) Frank, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 593–594. (c) Okura, I.; Kim-Thuan, N. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 1411–1415. (d) Keller, P.; Moradpour, A.; Amouyal, E. *Ibid.* **1982**, *78*, 3331–3340.

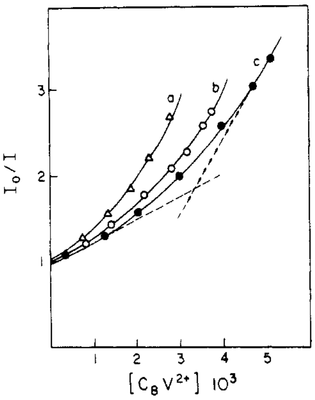

Figure 4. Fluorescence quenching of $Ru(bpy)_3^{2+}$, 4×10^{-5} M, by C_8V^{2+} in the presence of β-CD: (a) [β-CD] = 1×10^{-3} M; (b) [β-CD] = 5×10^{-3} M; [β-CD] = 7.5×10^{-3} M.

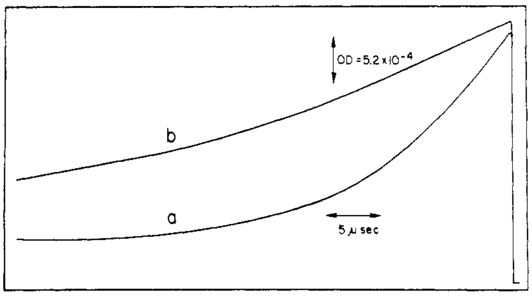

Figure 5. Transient decay of the photoreduced product of C_8V^{2+} followed at λ = 600 nm. Excitation of $Ru(bpy)_3^{2+}$, 4×10^{-5} M, at λ = 455 nm, $[C_8V^{2+}] = 2.0 \times 10^{-3}$ M: (a) without β-CD; (b) in the presence of β-CD = 1×10^{-2} M.

of a violet solution of the octylviologen radical in its dimer form $(C_8V^{+\bullet})_2$ (Figure 3).[33] The quantum yield for the octylviologen radical dimer formation corresponds to $\phi = 10.6 \times 10^{-2}$. It is well established[33] that viologen radicals tend to aggregate at high concentrations of the radicals. With octylviologen, the dimer aggregate is the predominating species, even at very low concentrations of the reduced photoproduct. Further illumination of the system results in the precipitation of a deep violet product from the aqueous solution that is presumably a higher aggregate form of the single electron-transfer product $C_8V^{+\bullet}$. We believe that due to the hydrophobic character of $C_8V^{+\bullet}$, the aggregation process is favored as a result of intermolecular hydrophobic interactions. Similar hydrophobic interactions have been previously discussed[28] in the photoreduction of *N*-methyl-*N'*-dodecadecyl-4,4'-bipyridinium, $MeC_{14}V^{2+}$. With this charge relay, the reduced photoproduct, $MeC_{14}V^{+\bullet}$ forms micellar aggregates as a result of hydrophobic interactions. The absorption pattern of the micellar aggregate of $MeC_{14}V^{+\bullet}$ resembles that of the $C_8V^{+\bullet}$ dimer complex.

Previous studies have indicated that cyclodextrins induce deaggregation of dyes such as thionine[34] or rhodamine B[35] by the selective association of the monomer dye form to the CD cavity. We have examined the possibility to prevent the aggregation of $C_8V^{+\bullet}$ in the presence of β-CD. Illumination of the previously described system, λ > 400 nm, in the presence of β-CD, 1×10^{-2} M, results in the formation of the monomer photoproduct, $C_8V^{+\bullet}$ (Figure 3). The quantum yield of $C_8V^{+\bullet}$ formation in the presence of β-CD is $\phi = 8.8 \times 10^{-2}$. The formation of the monomer $C_8V^{+\bullet}$ in the presence of β-CD is attributed to the binding of the reduced photoproduct to the hydrophobic cavity of the cyclodextrin (vide infra). The size of the CD cavity (6.2-Å diameter, 7-Å height)[13c] limits the accommodation of the monomer form only, and consequently aggregation is prevented.

The mechanistic steps leading to the photoreduction of C_8V^{2+} in the absence and presence of β-CD have been studied in detail using laser flash photolysis. The primary process involves the electron-transfer quenching of the excited sensitizer by C_8V^{2+} (eq 8). In the absence of β-CD, the Stern-Volmer plot following

$$^*Ru(bpy)_3^{2+} + C_8V^{2+} \xrightarrow{k_q} [Ru(bpy)_3^{3+}\cdots C_8V^{+\bullet}] \qquad (8)$$

the quenching process is linear and the quenching rate constant corresponds to $k_q = 2.5 \times 10^9$ M^{-1} s^{-1}, a value very similar to that reported for other viologen charge relays.[4b,36] The Stern-Volmer plots following the quenching process in the presence of β-CD show a nonlinear behavior and depend on the β-CD concentration (Figure 4). It can be seen that the quenching curves exhibit a hyperbolic shape and that the curvatures rises at a lower C_8V^{2+} concentration when the β-CD concentration decreases. Furthermore, it is evident that for each β-CD concentration the quenching plots rise with an asymptotic slope similar to the value observed in the absence of β-CD. These results suggest that the quenching plots can be interpreted by two complementary quenching processes: at low C_8V^{2+} concentrations, the charge relay is mainly associated with the β-CD, and the quenching of the excited species occurs by CD-bound C_8V^{2+}, $(C_8V^{2+})_{CD}$ (eq 9). From the different curves the calculated quenching rate

$$^*Ru(bpy)_3^{2+} + (C_8V^{2+})_{CD} \xrightarrow{k_q^{CD}} [Ru(bpy)_3^{2+}\cdots(C_8V^{+\bullet})_{CD}] \qquad (9)$$

constant for β-CD-bound C_8V^{2+} corresponds to $k_q^{CD} = 8.5 \times 10^8$ M^{-1} s^{-1}. At high C_8V^{2+} concentration, the binding sites of β-CD are saturated, and consequently the quenching process occurs by free C_8V^{2+} with a rate constant similar to that observed in the absence of β-CD. Certainly, the amount of free C_8V^{2+} needed to saturate the cyclodextrin cavities will depend on the β-CD concentration and will be controlled by the association constant of C_8V^{2+} to β-CD. This is consistent with the result that the quenching plots are curved at lower C_8V^{2+} concentrations, when the β-CD concentration decreases. The curved parts of the quenching plots are thus representing stages where the excited sensitizer is quenched by the free and bound quencher concomitantly. The studies reveal that the effectiveness of the quenching process of the excited sensitizer by β-CD-bound C_8V^{2+} is ca. 3-fold decreased as compared to the similar process by the free quencher.

Nevertheless, the quantum yields of the reduced photoproducts, $(C_8V^{+\bullet})_2$ and $(C_8V^{+\bullet})_{CD}$, under continuous illumination are very similar ($\phi \sim 10\%$), despite the inefficient primary process involved in the electron transfer in the presence of β-CD. This phenomenon suggests that an additional reaction participating in the overall process is improved in the presence of β-CD and compensates for the inefficient quenching process. We have thus examined the recombination process of the separated photoproducts. These reactions were characterized by following the decay of the photogenerated products $(C_8V^{+\bullet})_2$ or $(C_8V^{+\bullet})_{CD}$, eq 10 and 11 (Figure 5). The recombination rate constant of the photoproducts in the

$$Ru(bpy)_3^{3+} + {}^1/_2(C_8V^{+\bullet})_2 \xrightarrow{k_b} Ru(bpy)_3^{2+} + C_8V^{2+} \qquad (10)$$

$$Ru(bpy)_3^{3+} + (C_8V^{+\bullet})_{CD} \xrightarrow{k_b^{CD}} Ru(bpy)_3^{2+} + (C_8V^{2+})_{CD} \qquad (11)$$

absence of β-CD is $k_b = 3.2 \times 10^8$ M^{-1} s^{-1}. It should be noted that the value of the back-electron-transfer rate constant using C_8V^{2+} as the charge relay is ca. 1 order of magnitude lower than the recombination rates of the alkylviologen radical and $Ru(bpy)_3^{3+}$ that are almost diffusion controlled. This might be attributed to electrostatic repulsion of the oxidized product by the positively charged octylviologen radical aggregate.[28,29] Yet, in the presence of β-CD, the back-electron-transfer rate constant of the photoproducts is $k_b^{CD} = 3.2 \times 10^7$ M^{-1} s^{-1}. These results imply that the back-electron-transfer process is 10-fold retarded as compared to the system without cyclodextrin and ca. 2 orders of magnitude slower than a diffusion-controlled process. Thus, we conclude that the separated photoproducts are stabilized against

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(33) Kosower, E. M.; Cotter, J. L. *J. Amer. Chem. Soc.* **1964**, *86*, 5524.

(34) Dan, P.; Willner, I. *J. Chem. Soc., Perkin Trans. 2* **1984**, 455-459.

(35) Degani, Y.; Willner, I.; Haas, Y. *Chem. Phys. Lett.* **1984**, *104*, 496-499.

(36) Bock, O. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 4710.

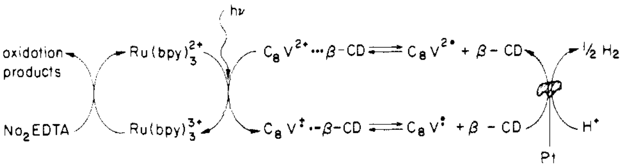

Figure 6. Schematic function of β-CD in photogeneration of $C_8V^{+\bullet}$ monomer and subsequent H_2 evolution.

the back-electron-transfer reaction in the presence of β-CD. This stabilization is attributed to the selective binding of the photoproduct $C_8V^{+\bullet}$ to the hydrophobic cavity of the cyclodextrin. This stabilization allows the effective subsequent regeneration of the sensitizer by the electron donor, Na_2EDTA (Figure 6). Therefore, the high quantum yields observed in the photoreduction of C_8V^{2+} in the presence of β-CD are mainly attributed to the stabilization of the photoproducts against destructive back-electron-transfer processes. Previous studies have shown that organized microenvironments such as micelles,[5-7] colloids,[8,9] polyelectrolytes,[37] vesicles,[12] and microemulsions[10,11] can control electron-transfer reactions and stabilize the photoproducts against back reactions. The present study reveals a novel approach for retardation of the recombination rate that uses cyclodextrins for controlling the process. These host receptors associate selectively with one of the photoproducts, and consequently, the photoproduct is being stabilized toward the back-electron-transfer process.

It is well established that *N,N'*-dialkyl-4,4'-bipyridinium radicals act as charge relays that mediate H_2 evolution in the presence of metal colloids such as Pt.[30-32] Introduction of a Pt colloid to an aqueous solution that includes the sensitizer, Ru(bpy)$_3^{2+}$, the electron acceptor, C_8V^{2+}, and Na_2EDTA does not yield any hydrogen upon illumination although the reduced photoproduct $(C_8V^{+\bullet})_2$ is formed efficiently. This implies that the aggregate, $(C_8V^{+\bullet})_2$, is not active as a charge relay for H_2 evolution. Yet, in the presence of β-CD, where the reduced product is in the monomer form, $C_8V^{+\bullet}$, effective H_2 evolution is accomplished, $\phi = 4 \times 10^{-2}$ (eq 12).

$$2C_8V^{+\bullet} + 2H^+ \xrightarrow{Pt} H_2 + 2C_8V^{2+} \qquad (12)$$

The reason for the inertness of the dimer aggregate $(C_8V^{+\bullet})_2$ is still questionable. The redox properties of C_8V^{2+} have been examined in aqueous solutions in the presence and absence of β-CD using cyclic voltammetry. In the presence of β-CD, the reduction potential of C_8V^{2+} corresponds to $E° = -0.36$ V (vs. NHE). In the absence of β-CD the reduction potential is more positive by ca. 0.05 V.[38] For H_2 formation at pH 5.5, the charge relay must exhibit a limiting redox potential of $E° = -0.33$ V, excluding over potential needs. Thus, the relatively positive redox potential of the dimer aggregate $(C_8V^{+\bullet})_2$, together with its low solubility in water, might eliminate H_2 evolution.

Conclusions

We have studied different photosensitized electron-transfer reactions in aqueous media containing β-cyclodextrins. We find several functions of the CD receptor in the photoinduced process. β-Cyclodextrin could destroy a ground-state complex between a neutral zwitterionic zinc porphyrin and anthraquinone-2-sulfonate. Similarly β-CD separates the dimer photoproduct $(C_8V^{+\bullet})_2$. This separation ability of β-CD toward aggregated forms is a result of the binding properties of the cyclodextrin receptor. The different separation processes that were studied have significant consequences on the photosensitized electron-transfer reactions in the β-CD microenvironments. In the former system, the restoration of the photophysical properties of the zinc porphyrin has been accomplished. In the latter system the formation of an active charge relay, $C_8V^{+\bullet}$, that mediates H_2 evolution was established. Further effects of β-CD are apparent in controlling the photosensitized electron-transfer process. Substantial stabilization of the intermediate photoproducts against back-electron-transfer reactions is achieved, by selective binding of one of the photoproducts to the CD cavity.

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Registry No. 1, 5776-56-7; **2**, 84431-54-9; **3**, 36437-30-6; β-CD, 7585-39-9; Ru(bpy)$_3^{2+}$, 15158-62-0.

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(37) (a) Meisel, D.; Matheson, M. *J. Am. Chem. Soc.* **1977**, *99*, 6577. (b) Meisel, D.; Matheson, M.; Rabani, J. *J. Am. Chem. Soc.* **1978**, *100*, 117.

(38) The reduction potentials of C_8V^{2+} in water and in the presence of β-CD should be related by $E_w{}^0 = E_{CD}{}^0 + 0.029 \log K_{dim}$ where $E_w{}^0$ and $E_{CD}{}^0$ are the standard reduction potentials of C_8V^{2+} in water and in the presence of β-CD, respectively, and K_{dim} is the equilibrium constant of the dimerization process $2C_8V^{+\bullet} \rightleftharpoons (C_8V^{+\bullet})$. The observed difference in the reduction potential in water and β-CD media allows us to estimate the equilibrium constant of the dimerization process to be $K_{dim} = 52.98 \pm 4.8$ M^{-1}. We thank one of the referees for pointing out the possibility to estimate the dimerization constant by this approach.