conclusion being supported by studies with [5-^{13}C]Glu-bR. Possible changes of the four Asp residues are proposed in Table I. It is interesting to note that the currently favored models[12] for the folding of bR show that of the nine Asp residues, four reside within the interior of the membrane. Groups which change protonation state concomitantly with the proton-pumping process might be involved as a conducting wire.[13] In addition to Asp, we have observed protonation/deprotonation steps in the following changes: DA (Tyr-OH) → LA (Tyr-O$^-$) → (Tyr-OH) → L (Tyr-OH) → M (Tyr-O$^-$),[4f,g] while Rothschild and co-workers have also shown[2f] that a tyrosinate protonates in LA → K. Clearly the technique of difference FTIR provides a powerful method which will contribute to the understanding of subtle dynamic processes exemplified by proton translocation.

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Supplementary Material Available: The DA/LA, K/LA, L/LA, and M/LA difference spectra of the entire region and of the expanded carboxylate region for native and [4-^{13}C]Asp-bR; the DA/LA, K/LA, L/LA, and M/LA difference spectra for native and [5-^{13}C]Glu-bR (12 pages). Ordering information is given on any current masthead page.

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TiO$_2$ and CdS Colloids Stabilized by β-Cyclodextrins: Tailored Semiconductor–Receptor Systems as a Means to Control Interfacial Electron-Transfer Processes

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The photocatalytic activity of semiconductor particles is of substantial interest in synthesis[1] as well as a means of solar energy conversion and storage.[2,3] Electron-transfer reactions such as charge ejection or charge injection at semiconductor–solution interfaces are important factors that control the photocatalytic activity of the semiconductors.[4,5] Electrostatic attraction of solute to the semiconductor surface has improved charge ejection from the excited semiconductor to solute relays.[6] Adsorption of dyes to the semiconductor surface, i.e., by hydrophobic interactions, resulted in effective charge injection to the semiconductor and consequently the photocatalytic activity of semiconductors operative in the UV region could be shifted to the visible absorption spectrum.[5,7] Substantial efforts have also been directed in recent years toward the preparation of semiconductor particles in colloidal forms to improve their light harvesting and interfacial electron-transfer properties.[8-10] Stabilization of semiconductor colloids by polymers, microemulsions, and vesicle encapsulation[10] has been reported. Here we report on a novel method for stabilizing semiconductor colloids by β-cyclodextrin (β-CD).

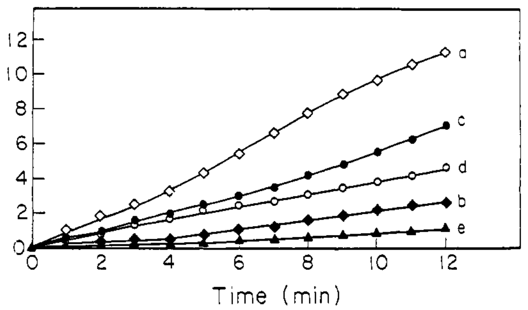

Figure 1. Rate of $C_8V^{\cdot+}$ and $MV^{\cdot+}$ formation at time intervals of illumination in the presence of TiO_2–β-CD colloid. All experiments include $[C_8V^{2+}]$ or $[MV^{2+}] = 5 \times 10^{-5}$ M, 2 mL of TiO_2, 2 g·L^{-1}, stabilized by 1% β-CD: (a) $C_8V^{\cdot+}$ formation, (b) $MV^{\cdot+}$ formation, (c) rate of $C_8V^{\cdot+}$ formation, with [phenol] = 0.018 M, (d) $C_8V^{\cdot+}$ formation with [phenol] = 0.024 M, (e) $C_8V^{\cdot+}$ formation, with [phenol] = 0.05 M.

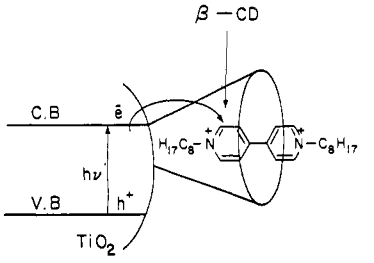

Figure 2. Schematic function of the receptor–semiconductor colloid in improving interfacial electron transfer.

Cyclodextrins have been extensively examined as molecular receptors that bind solutes to their hydrophobic cavities[11-12] Thus, the tailored semiconductor-receptor configuration allows the association of solutes to the β-CD cavity and consequently improves the interfacial electron transfer process at the semiconductor-solution interface.

We have stabilized CdS and TiO$_2$ colloids in aqueous solutions with β-CD. The CdS colloid has been prepared by slow addition of Cd(NO$_3$)$_2$ into the solution of 1% β-CD + Na$_2$S. The TiO$_2$ colloid was prepared by the slow addition of TiCl$_4$ to the β-CD solution at 0 °C. The mean diameter of the CdS and TiO$_2$ particles was determined by TEM to be 80 and 100 Å, respectively. In the absence of β-cyclodextrin the semiconductors precipitate out of solution.

N,*N*′-Dioctyl-4,4′-bipyridinium (octyl viologen, C_8V^{2+}) associates with the β-CD cavity[13] (eq 1), $K_{ass} = 5.6 \times 10^3$ M^{-1}. Illumination of the TiO_2–β-CD colloid ($\lambda > 335$ nm), pH 2.5, in the presence of C_8V^{2+}, 5×10^{-5} M, and 2-propanol, 5×10^{-3} M, as electron donor results in the formation of $C_8V^{\cdot+}$ in its monomer form. Figure 1a shows the rate of $C_8V^{\cdot+}$ formation at time intervals of illumination that corresponds to a quantum yield of $\phi = 1.1 \times 10^{-3}$.[14] Similarly, illumination of the CdS–β-CD colloid

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in the presence of C_8V^{2+}, pH 6, and Na_2S, 5×10^{-2} M, as donor, results in the monomer photoproduct, $C_8V^{\bullet+}$, $\phi = 0.2$.[14] When

$$C_8V^{2+} + \beta\text{-CD} \rightleftarrows C_8V^{2+}\cdots\beta\text{-CD} \qquad (1)$$

methyl viologen, MV^{2+}, is used as charge relay instead of C_8V^{2+}, substantially lower quantum yields of $MV^{\bullet+}$ are observed. Figure 1b shows the rate of $MV^{\bullet+}$ formation at time intervals of illumination with the TiO_2–β-CD colloid. The quantum yield corresponds to $\phi = 2.6 \times 10^{-4}$ and is 4.4 times lower than that for $C_8V^{\bullet+}$ formation in the analogous system. Similary, the quantum yield for $MV^{\bullet+}$ formation with CdS–β-CD is 3.6 times lower as compared to $C_8V^{\bullet+}$ production. It should be noted that methyl viologen (MV^{2+}) is not associated with β-cyclodextrin.[15] Thus, the high quantum yields for $C_8V^{\bullet+}$ formation in the presence of the β-CD semiconductor stabilized colloids, as compared to that of MV^{2+} photoreduction, is attributed to improved interfacial electron transfer from the excited semiconductor to the relay substrate, C_8V^{2+} (Figure 2). Association of C_8V^{2+} to the β-CD hydrophobic cavity increases the local concentration of the relay in proximity with the semiconductor interface. Consequently, the interfacial electron-transfer rates and reduction of the relay C_8V^{2+} by conduction band electrons are improved. Indeed, the photoreduction process of C_8V^{2+} using the semiconductor–β-CD stabilized colloids is strongly inhibited in the presence of phenol, which associates with the β-CD hydrophobic cavity. Figure 1 (c–e) shows the rate of $C_8V^{\bullet+}$ formation at time intervals of illumination and different concentrations of added phenol. It is evident that the quantum yield for $C_8V^{\bullet+}$ production decreases as the concentration of phenol increases. Thus, phenol that associates to β-CD expels the charge relay C_8V^{2+} from the receptor and consequently the superior configuration for electron transfer is destroyed. Similarly, TiO_2 colloids were stabilized with α-cyclodextrins. The association properties of C_8V^{2+} to α-CD are weaker than those to β-CD (K_a = 4500 M^{-1}). Accordingly, the specificity toward C_8V^{2+} photoreduction as compared to MV^{2+} reduction decreases, $\phi(C_8V^{\bullet+})/\phi(MV^{\bullet+}) = 4.0$.

We have compared the photoreduction reactions of C_8V^{2+} and MV^{2+} using TiO_2–β-CD colloids to the similar reactions induced by TiO_2 colloids stabilized by poly(vinyl alcohol), PVA. With TiO_2–PVA colloids the quatnum yield ratio $\phi(C_8V^{\bullet+}){:}\phi(MV^{\bullet+})$ is 1:1, implying similar efficiencies. With the TiO_2–β-CD colloids the ratio is 4.4:1 and it demonstrates selectivity in the reduction of the C_8V^{2+} relay system.

Laser flash experiments confirm that improved electron transfer occurs to C_8V^{2+} in the presence of TiO_2–β-CD. Flashing the systems that include TiO_2–β-CD and MV^{2+} on C_8V^{2+} at λ = 337.1 nm results in the formation of $MV^{\bullet+}$ or $C_8V^{\bullet+}$. With MV^{2+} as charge relay, instantaneous accumulation of $MV^{\bullet+}$ is observed that results from electrostatically associated MV^{2+} to the TiO_2–colloid.[5c] With C_8V^{2+} as relay, the instantaneous formation of $C_8V^{\bullet+}$ is followed by a diffusional charge ejection to C_8V^{2+} associated with the β-CD, and the total amount of accumulated $C_8V^{\bullet}$ is ca. 4 times larger than that of $MV^{\bullet+}$.

In conclusion we have stabilized TiO_2 and CdS semiconductor colloids with β-cyclodextrins. The tailored semiconductor–receptor configuration and proper design of the charge relay provide means to control interfacial electron transfer and introduce selectivity in the reduction of relay substrates. The association of the relay to the receptor sites increases the local concentration of the relay at the colloid interface and consequently improves the interfacial electron-transfer process. Further applications of semiconductor–receptor colloids could be envisaged. These include effective and selective charge injection via the selective association of chromophores to β-CD or selective synthesis through immobilization of catalysts on the semiconductor sites. These aspects are now being examined in our laboratory.

Acknowledgment. The support of the Singer Foundation is gratefully acknowledged.

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Spectroscopic and Structural Evidence of Temperature Dependent Charge Localization and Structural Differentiation of the Fe Sites within the $[Fe_6S_6X_6]^{2-}$ Clusters (X = Cl, Br)

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The recently reported $[Fe_6S_6L_6]^{3-}$ clusters[2] are new members in the general series of the synthetic Fe/S clusters that contain the $[Fe_2S_2]_n^{n+}$ cores. They are metastable species and thermally or catalytically can be converted quantitatively to the $[Fe_4S_4X_4]^{2-}$ "cubanes" (eq 1).

$$2[Fe_6S_6X_6]^{3-} \rightarrow 3[Fe_4S_4X_4]^{2-} \qquad (1)$$

The oxidized, $[Fe_6S_6X_6]^{2-}$, prismane clusters can be obtained in nearly quantitative yields by chemical oxidation of the $[Fe_4S_4X_4]^{2-}$ clusters[2c] (eq 2) (X = Cl, Br) with $[(C_5H_5)_2Fe]^+$-$[PF_6^-]$.

$$3[Fe_4S_4X_4]^{2-} + 2[Fe(C_5H_5)_2]^+ \rightarrow 2[Fe_6S_6X_6]^{2-} + 2Fe(C_5H_5)_2 \qquad (2)$$

The Mossbauer spectra of the $[Fe_6S_6X_6]^{2-}$ clusters for X = Cl, I [or Br, II], were examined at various temperatures in the range from 1.6 K to ambient temperature (AT). The spectra (Figure 1) generally show two broad lines of unequal intensities at temperatures above 100 K. The average values of the isomer shift (IS) and quadrupole splitting (Δ_{Eq}) for these doublets above 100 K are 0.44 (1), 0.62 (1) and 0.44 (1), 0.70 (1) mm/s, respectively, for I and II. These values, which represent iron atoms in a formal +2.66 oxidation state, as expected, are somewhat smaller than corresponding values for the $[Fe_6S_6X_6]^{3-}$ clusters, which contain iron atoms in a +2.5 formal oxidation state.[2b] For the latter, IS and Δ_{Eq} values of 0.52 (1) and 0.95 (1) mm/s for X = Cl and 0.54 (1) and 1.00 (1) mm/s for X = Br have been observed at 125 K. At 1.6 K the high velocity line clearly shows partially resolved structure that suggests at least three peaks. The structure persists to about 50 K and gradually becomes obscure at higher temperatures. The spectra for both I and II at 4.2 K were fitted by the superposition of three symmetric quadrupole doublets constrained to equal intensities and line widths. This model implies the grouping of the iron ions into three pairs characterized by different IS and Δ_{Eq} values with the irons within each pair being equivalent. Two realistic combinations of six peaks into quadrupole doublets can be chosen.[3] For combination (a) in the low tem-

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