Table I. Turnover Numbers for Components[a] Involved in the Photosensitized Reduction of NO_3^- and NO_2^- to Ammonia

	$Ru(bpy)_3^{2+}$	MV^{2+}	nitrate[e] reductase	nitrite[e] reductase
NO_3^- reduction[b]	80	18.5	6.2×10^4	
NO_2^- reduction[c]	38.5	7		2.4×10^4
combined system[d]	32	6	9×10^4	2.1×10^4

[a] Turnover number (TN) is defined as TN = mol of product formed/mol of component. [b] 60% conversion of NO_3^- to NO_2^-. [c] 28.5% conversion of NO_2^- to NH_4^+. [d] 23.8% conversion of NO_3^- to NH_4^+. [e] Molecular weight of nitrate reductase and nitrite reductase was estimated as 200 000 cf. ref 2b.

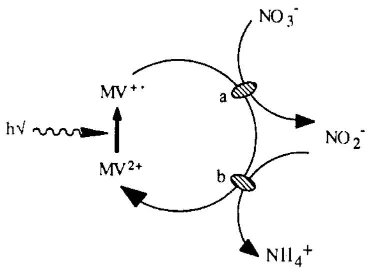

Figure 3. Scheme for biocatalyzed sequential reduction of NO_3^- to NH_4^+. a = nitrate reductase, b = nitrite reductase.

sacrificial electron donor, NO_2^-, 0.01 M, and the enzyme nitrite reductase (E.C. 1.6.6.4), 0.06 units, isolated from spinach leaves,[15] results in the formation of ammonia. The rate of ammonia formation[16] at time intervals of illumination is displayed in Figure 1b. The quantum yield of ammonia formation is $\phi = 0.06$. Control experiments reveal that all components in the two systems are required to effect the reduction of NO_3^- or NO_2^-, respectively. Also, no reduction of NO_3^- or NO_2^- takes place in the two systems in the dark. Exclusion of the enzymes nitrate reductase or nitrite reductase from the respective systems results in the formation of $MV^{\bullet+}$. Addition of the enzymes to the respective systems that include NO_3^- or NO_2^- and photogenerated $MV^{\bullet+}$ results in the depletion of $MV^{\bullet+}$ and reduction of NO_3^- to nitrite or of NO_2^- to ammonia, respectively.

Illumination ($\lambda > 420$ nm) of a photosystem that includes $Ru(bpy)_3^{2+}$, 7.4×10^{-5} M, as photosensitizer, $MV^{\bullet+}$, 4.2×10^{-4} M, as electron relay, EDTA, 0.02 M, the substrate nitrate, and the two enzymes nitrate reductase, 1.0 units, and nitrite reductase, 0.35 units, results in the reduction of NO_3^- to ammonia (eq 3) through the intermediate formation of nitrite. The rate of ammonia formation in this system is shown in Figure 2a, and curve 2b shows the amount of NO_2^- that is present in the system at time intervals of illumination. It is evident that only after a concentration of NO_2^- that corresponds to 3×10^{-3} M is formed, ammonia is effectively produced. During the illumination, no $MV^{\bullet+}$ is accumulated in the system. This suggests that the route of NO_2^- and ammonia formation is limited by the photochemical process that generates $MV^{\bullet+}$. The quantum yield of ammonia formation in the system that includes the two enzymes corresponds to $\phi = 0.08$. Table I summarizes the turnover numbers of the various components in the different systems. It is evident that the components are recycled during the reduction of NO_3^- and NO_2^- and that the enzymes exhibit stability in the artificial media. Figure 3 represents the schematic sequential cycle that leads to the reduction of NO_3^- to ammonia through nitrite as an intermediate. The photoinduced electron-transfer process generates $MV^{\bullet+}$ that acts as electron carrier for the two enzymes.

The primary step involves the reduction of NO_3^- to nitrite in the presence of nitrate reductase. The latter photoproduct acts as substrate for the enzyme nitrite reductase that mediates the reduction of NO_2^- to ammonia. The relatively high quantum yields for NO_2^- or ammonia formation are noteworthy. These originate from effective charge separation of $MV^{\bullet+}$ in the photosensitized electron-transfer process and the subsequent complementary dark reduction[17] of MV^{2+} by the oxidation product of the sacrificial electron donor, EDTA.

We thus describe the light driven reduction of NO_3^- to ammonia using an artificial photosystem and two biocatalysts. Further experiments to immobilize the enzymes and design of organized assemblies for this process are under way in our laboratory.

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Tailored Semiconductor-Receptor Colloids: Improved Photosensitized H_2 Evolution from Water with TiO_2-β-Cyclodextrin Colloids

Itamar Willner* and Yoav Eichen

Department of Organic Chemistry
The Hebrew University of Jerusalem
Jerusalem 91904, Israel

Arthur J. Frank*

Solar Energy Research Institute
1617 Cole Boulevard, Golden, Colorado 80401

Received October 11, 1988

Redox reactions in microheterogeneous semiconductor systems are of much interest as a means of converting light to chemical energy.[1,2] Either direct excitation of a semiconductor or a photosensitizing dye, adsorbed on the particle surface, can activate electron (or hole) transfer to solution species at the semiconductor-liquid interface. Surface recombination and back electron (or hole) transfer from solution species to either the semiconductor or the adsorbed dye molecule can lower the overall yield of the desired product(s) and thus the conversion efficiency of light to chemical energy. Electrostatic interactions in colloidal semiconductor dispersions have been utilized to control interfacial electron transfer and to improve the quantum yield for H_2 evolution from water.[3] Surface adsorption of β-cyclodextrin (β-CD) to semiconductor colloids has been found[4] to improve the kinetics for charge transfer from the photoexcited semiconductor to electron acceptors retained in the β-CD cavity. β-Cyclodextrin also served to stabilize the colloids against aggregation.

Dye sensitization of a semiconductor affords the possibility of using sub-bandgap light and the electronic transport properties of the semiconductor to effect charge separation. Both organic dyes, such as Rhodamine B, and transition-metal complexes have been utilized as photosensitizers of wide bandgap semiconductor materials.[5,6] Diffusion-limited charge transfer from the pho-

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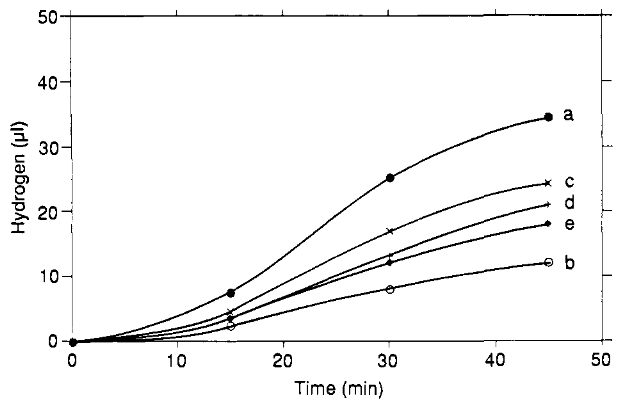

Figure 1. Production of H_2 with irradiation time ($\lambda_{ex} > 400$ nm) for aqueous solutions (pH 1.8) of Pt–TiO_2 colloids [5% Pt on TiO_2 (w/w)] with 5.1×10^{-5} M proflavin dihydrogen chloride and 0.1 M cysteine. In a 3-mL sample, 2-mL headspace: curves a, Pt–TiO_2–β-CD; b, Pt–TiO_2–PVA; c–e, Pt–TiO_2–β-CD with *N*-octylpyridinium bromide, C_8PyBr, c, 2.2×10^{-4} M C_8PyBr; d, 4.4×10^{-4} C_8PyBr; and e, 8.8×10^{-2} M C_8PyBr.

toexcited dye molecule is generally inefficient, because of the short lifetime of the excited state of the dye and competing reactions. Physical adsorption of dye molecules to the semiconductor surface by means of hydrophobic or electrostatic interactions facilitates charge injection.[7] Molecular interactions in dye aggregates can, however, substantially quench electron transfer.[8] An effective approach to disperse dye aggregates is to use cyclodextrins (CD) to complex the dye monomer in the CD cavity.[9] Formation of inclusion complexes between cyclodextrin and other molecules is mainly based on size selectivity and hydrophobic interactions.[10]

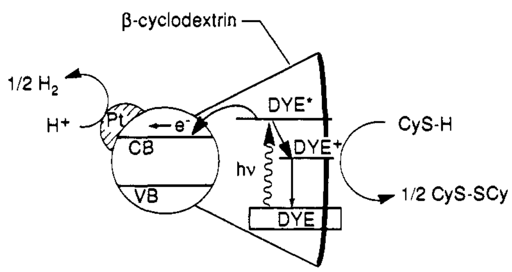

Figure 2. Representation of mechanism: Photoinitiated electron transfer from monomeric dye sensitizer, in cavity of β-cyclodextrin (β-CD), through conduction band of semiconductor (CB) to catalytic Pt surface sites, where H_2 is evolved. The oxidized dye sensitizer is recycled by oxidation of electron donor cysteine, Cys-H.

We initiated the research described in this report to determine whether modification of the semiconductor particle surface with β-cyclodextrin (β-CD) would provide an effective microenvironment for both increasing the number of surface sites for dye–semiconductor interaction and promoting photosensitized H_2 evolution from water. The basic semiconductor system consisted of Pt-charged TiO_2–β-CD colloids that were exposed to the photoactive dye proflavin (3,6-diaminoacridine).[11]

Optically transparent TiO_2–β-CD colloids were prepared by slow hydrolysis of $TiCl_4$ in an aqueous 1% (w/w) β-CD solution at 0 °C. The resulting colloidal solution (2 g L^{-1} TiO_2; pH 1.8) was stable for 9 months, the period of observation. The TiO_2 colloid was loaded with 5% Pt by weight by photoreduction of H_2PtCl_4. Hydrogen was analyzed on a gas chromatograph equipped with a thermal conductivity detector, a 5 Å molecular sieve column, and argon carrier gas. Illumination ($\lambda_{ex} > 400$ nm) of the aqueous colloidal Pt–TiO_2–β-CD solution (pH 1.8) containing proflavin dihydrogen chloride[11] (5.1×10^{-5} M) and the sacrificial electron donor cysteine (0.1 M) generated H_2, as shown in Figure 1a. The quantum yield for H_2 production in this system was 1.1×10^{-3}. Omission of either the dye or the electron donor eliminated H_2 production. Emission studies revealed that the excited state of the dye was not quenched by either β-CD or cysteine. Absorption and emission spectra indicated no dye aggregation at the concentration of proflavin used. The emission intensity of proflavin showed only a small increase (~10%) in the presence of β-cyclodextrin, implying that the photophysical properties of the dye were not altered appreciably by the β-CD receptor. In the absence of TiO_2, illumination of β-CD-covered Pt colloids with proflavin and cysteine produced only trace quantities of H_2. These studies suggest that H_2 evolution involves electron transfer from the photoexcited dye through the conduction band of TiO_2 to catalytic Pt surface sites, as portrayed in Figure 2.

To determine the role of the β-CD molecule on photosensitized H_2 production, a comparative study was made of Pt–TiO_2–β-CD and Pt–TiO_2 colloids; the latter was stabilized against aggregation with poly(vinyl alcohol) PVA (14 000 MW). Figure 1b shows the photoproduction of H_2 in the Pt–TiO_2–PVA system (5% Pt/TiO_2, w/w) with proflavin (5.1×10^{-5} M) and cysteine (0.1 M). The quantum yield for H_2 production in this system was 4×10^{-4}, which is a factor of three less than that of the Pt–TiO_2–β-CD system. The relatively large quantum yield of the Pt–TiO_2–β-CD system for H_2 production correlates, in part, with an enhanced dye concentration on the semiconductor surface. By a flow dialysis technique,[12] 2.5 times more proflavin was found to be associated with TiO_2–β-CD colloids than with TiO_2–PVA colloids. The photolysis and flow dialysis experiments suggest that the presence of the β-CD receptor effects an increase in the number of dye-semiconductor interactive sites, leading to an im-

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provement in the quantum conversion efficiency for electron transfer from proflavin to TiO_2. The association of the dye with β-CD involves the uptake of the dye monomer into the CD cavity. The association constant K_a of proflavin with β-CD at pH 1.8 was determined spectrophotometrically to be 550 ± 60 M^{-1}, corresponding to the reaction

$$\text{dye} + \beta\text{-CD} \overset{K_a}{\rightleftharpoons} [\text{dye}\cdots\beta\text{-CD}] \qquad (1)$$

Further evidence that the association of proflavin with β-CD improves the efficiency of electron injection from the dye molecule to TiO_2 came from studies involving *N*-octylpyridinium bromide, C_8PyBr. The *N*-octylpyridinium cation (C_8Py^+) has a high association constant ($K_a = 870 \pm 120\ M^{-1}$) for β-CD and is expected to impede the diffusion of proflavin into the CD cavity. Curves c-e of Figure 1 show that as the concentration of C_8Py^+ increases, the yield and rate of H_2 production decrease, indicating a decline in the quantum conversion efficiency for charge transfer from the excited state of proflavin to TiO_2. At the highest concentration of C_8Py^+ (8.8×10^{-2} M), the rate of H_2 production was comparable to that of the $Pt-TiO_2-PVA$ system. Addition of C_8Py^+ to the $Pt-TiO_2-PVA$ system had no effect on the rate of H_2 evolution, suggesting that C_8Py^+ blocked the inclusion of the dye molecule into the cavity of β-CD. These studies clearly imply that the photosensitization efficiency for charge injection from proflavin to TiO_2 is improved by the association of the dye monomer with the β-CD receptor on the surface of the semiconductor particles.

In conclusion, the utility of β-cyclodextrin for enhancing dye sensitization of semiconductors has been demonstrated. The β-cyclodextrin molecule offers a unique microenvironment for augmenting the number of surface sites for dye-semiconductor interaction and for promoting charge injection from photoexcited dye molecules to the semiconductor. Further characterization of cyclodextrin complexes with other dye systems is in progress.

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Cyclizations of Ene Radicals. Imidoyl Radicals as Intermediates in the Synthesis of Heterocyclic Compounds

Mario D. Bachi* and Daniella Denenmark

Department of Organic Chemistry
The Weizmann Institute of Science
Rehovot 76100, Israel

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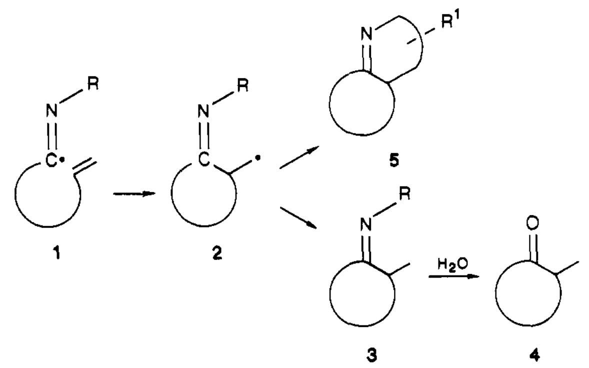
The construction of cyclic systems through the intramolecular addition of carbon centered free radicals to carbon-carbon multiple bonds is well documented.[1] A convenient method for the site-specific generation of carbon-centered free radicals involves the chemospecific homolysis of a C-halogen, C-S, or C-Se bond by trialkyltin radicals generated from the corresponding tin hydrides.[2] The tin hydride induced free radical cyclizations are not restricted to alkyl radical intermediates. Stork has introduced[3] the use of vinyl radicals in synthesis and we have shown[4] that alkoxycarbonyl radicals are excellent intermediates in a general synthesis of α-alkylidene-γ-lactones. These results[5] prompted us to investigate the potential that other carbon-centered ene radicals, isoelectronic with vinyl and carbonyl radicals, may have as intermediates in the synthesis of functionalized cyclic compounds. Herein we report on preliminary results that illustrate the employment of imidoyl radicals, as intermediates in the synthesis of cyclic ketones and polyheterocyclic compounds.

Scheme I



This new method for ring formation is based on the tri-*n*-butyltin hydride (TBTH) induced generation of the imidoyl radical, followed by its intramolecular addition to a suitably positioned double bond as outlined in Scheme I.[6] We reasoned that imidoyl radicals of type **1** may cyclize to radicals **2**, which carry an exocyclic imine group. Direct hydrogen transfer to **2** would give an imine **3** that could be hydrolized to a cyclic ketone **4**. In this transformation the imidoyl radical performs as a synthetic equivalent to the carbonyl radical. However, if the R moiety in **2** would bear a radical trapping functionality a second cyclization, to a compound of type **5**, may occur. The following preliminary results (Schemes II-IV) prove the validity of these hypotheses. As starting materials we used the selenoimidates **6**, **11**, and **12** and the thioamides **18** and **20**.[7] Under standard conditions starting material (1 mmol), TBTH (1.15 mmol), and AIBN (0.15 mmol) were heated (110 °C) in dry degased toluene for 3-6 h (t.l.c.).

Treatment of selenoimidate **6** with TBTH under standard conditions followed by aqueous workup afforded nitrile **8** (50%) and chromanone **10** (50%) (Scheme II). Although the generation of imidoyl radical **7** is quantitative cyclization to imine **9** is accompanied by fragmentation into nitrile **8** and benzyl radical. When the benzyl group of the starting material was substituted by a lower alkyl group only chromanone **10** was obtained. A different reaction course was observed when *N*-aryl selenoimidates were used. Thus, *N*-tolyl derivative **11** afforded a polycyclic compound **15** (R = Ph).[8] Oxidation by DDQ resulted in the loss of two hydrogen atoms and the formation of chromanoquinoline **16** (84% from **11**). Similarly compound **12** was converted into

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