

Contribution from the Fuel Sciences Division, Sandia National Laboratories, Albuquerque, New Mexico 87185, and Institut de Chimie Physique, Ecole Polytechnique Federale de Lausanne, 1015 Lausanne, Switzerland

## Sensitization and Photoredox Reactions of Zinc(II) and Antimony(V) Uroporphyrins in Aqueous Media

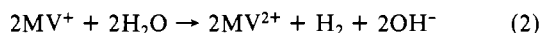
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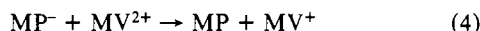
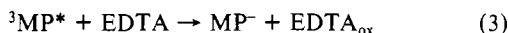
The utility of Zn(II) and Sb(V) uroporphyrins ( $\text{Zn}^{\text{II}}\text{UroP}^{8-}$ ,  $\text{Sb}^{\text{V}}(\text{O})(\text{Cl})\text{UroP}^{8-}$ ) as photosensitizers for redox processes in solution and in photoelectrochemical systems involving large band gap semiconductor has been investigated by steady-state and flash photolysis techniques. The reductive quenching of these porphyrins by EDTA is an efficient process,  $\text{SbUroP}$  yielding stable porphyrin anions in aqueous solution. In three-component systems (involving sensitizer-viologen-EDTA), extensive ground-state complexation of  $\text{ZnUroP}$  with  $\text{MV}^{2+}$  drastically reduces the efficiency of the sensitization process. The corresponding system based on  $\text{Sb}(\text{O})\text{UroP}$  however gives reasonable net yields of reduced viologen upon photolysis. Flash photolysis studies using colloidal  $\text{TiO}_2$  indicate that charge injection occurs from both the singlet and triplet excited states of  $\text{ZnUroP}$ .

### Introduction

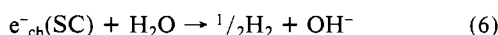
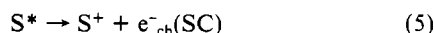
Photoredox reactions and sensitization processes involving metalloporphyrins are of much interest for the understanding of charge separation mechanisms of plant photosynthesis<sup>1</sup> and in connection with the utilization of solar energy.<sup>2</sup> One of the most popular schemes for the visible light induced photoreduction of water to molecular hydrogen has been the one that involves sensitized photoreduction of relay molecules such as methyl viologen ( $\text{MV}^{2+}$ ) using electron donors such as EDTA and suitable redox catalysts:



Due to their long-lived excited states, excellent visible light absorption, and redox properties, water-soluble porphyrins have been widely studied as photosensitizers for these processes. Indeed, cationic porphyrin derivatives such as  $\text{ZnTMPyP}(4)^{4+}$  [(tetrakis(*N*-methyl-4-pyridiniumyl)porphinato)zinc(II)] have been found to be most effective.<sup>2</sup> Studies with anionic porphyrin derivatives such as  $\text{ZnTPPS}(4)^{4-}$  [(tetrakis(4-sulfonatophenyl)porphinato)zincate(II)] or  $\text{ZnUroP}^{8-}$  have yielded less impressive results due to extensive ground-state complexation of the electron-acceptor relay  $\text{MV}^{2+}$  with the metalloporphyrins. Preliminary studies have shown that axial ligation of the metal center (as in  $\text{Sn}^{\text{IV}}(\text{OH})_2$ - or  $\text{Sb}^{\text{V}}(\text{O})(\text{Cl})\text{UroP}$ ) was found to inhibit the formation of such ground-state complexation and enhance the utility of metallouroporphyrins to serve as true photosensitizers. In an earlier communication,<sup>3</sup> it was shown that  $\text{MV}^{2+}$  can be photoreduced in high quantum yield by using  $\text{Sn}(\text{IV})$  and  $\text{Sb}(\text{V})$  uroporphyrins as photosensitizers, presumably via reactions 3 and 4.



An alternative approach to sensitized photoreduction of water that is currently being examined involves charge injection from an excited state of a dye to the conduction band of an appropriate semiconductor such as  $\text{TiO}_2$ , according to reactions 5 and 6.<sup>2,4-10</sup>



Recently, in our studies of sensitization of large band gap semiconductors such as  $\text{TiO}_2$ , it was found that dyes with carboxyl groups ( $-\text{COOH}$ ) as peripheral substituents have been found to be very efficient, e.g., (tetrakis(4-carboxyphenyl)porphinato)zincate(II) ( $\text{ZnTPPC}(4)^{4-}$ ),<sup>6b</sup> tris(dicarboxybipyridyl)ruthenium(II) ( $[\text{Ru}\{\text{bpy}(\text{COOH})_2\}_3]^{2+}$ ),<sup>5b</sup> and eosin.<sup>4</sup>

In continuation of our studies on the photochemistry and redox chemistry of water-soluble porphyrins,<sup>5</sup> an assay on the per-

formance of naturally occurring anionic porphyrin derivatives in some of the above photoprocesses was made. Herein we present a detailed examination of the sensitized photoreduction of methyl viologen and sensitization of  $\text{TiO}_2$  by two metallouroporphyrins using steady-state and flash photolysis techniques. It was found that Sb and Zn uroporphyrins perform with distinctly contrasting behaviors as photosensitizers. It is shown that photoreduction of triplet-state  $\text{SbUroP}$  yields stable anions and photoreduction of Zn- and  $\text{SbUroP}$  is efficient. Sensitized photoreduction of  $\text{MV}^{2+}$  involves largely reductive redox quenching cycles. As regards sensitization of  $\text{TiO}_2$ , it is shown that for  $\text{ZnUroP}$  both singlet and triplet excited states inject charges into the conduction band of  $\text{TiO}_2$ .

### Experimental Section

**Materials and Methods.** The metal derivatives of uroporphyrin I were obtained from Porphyrin Products (Logan, UT) and in some cases further purified by column chromatography on Sephadex G-50-40. Methyl viologen ( $\text{MV}^{2+}$ ) and EDTA disodium salt were p.a. grade chemicals from Fluka and were used as supplied. Colloidal  $\text{TiO}_2$  dispersions were

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**Table I.** Absorption, Photophysical, and Redox Properties of Zn(II) and Sb<sup>V</sup>(O)(Cl) Uroporphyrins in Aqueous Solution

property	ZnUroP in water	ZnOEP/ ZnEtioP in toluene/ DMF	Sb <sup>V</sup> (O)- (Cl)UroP in water	Sb(OEP)- (OH) <sub>2</sub> in EPA
Absorption ( $\lambda_{\max}$ , nm ( $\epsilon$ , mM <sup>-1</sup> cm <sup>-1</sup> ))				
B(0,0)	408 (340)	408 (328)	399 (292)	397
Q(1,0)	538 (18.0)		532 (18)	532
Q(0,0)	574 (14.0)	573 (16.9)	572 (13.8)	570
Fluorescence				
Q(0,0), nm	574	575	574	569
Q(0,1), nm	632	625	631	624
$\tau_f$ , ns		2.2	<1	
$\phi_f$		0.043 (RT) <sup>f</sup>		0.020 (RT)
Triplet State				
T(0,0), nm	706	702	708	702
$\tau_{trip}$ , ms	3.3 (RT)	57 (77 K), 5 (RT)	2.0 (RT)	26 (77 K)
$\phi_{trip}$		0.86		
$\phi_{phos}$		0.065 (77 K)		0.026 (77 K)
T-T, abs		411 (45.3)		
$\lambda_{\max}$ , nm	440 (100)	440 (99)	427 (40) ( $\Delta\epsilon$ )	
( $\epsilon$ , mM <sup>-1</sup> cm <sup>-1</sup> )	770 (10)		555 (4.0) ( $\Delta\epsilon$ )	
Redox Potentials (V vs SCE) <sup>g</sup>				
$E_{1/2}^{ox}(1)$	0.83	0.63	>1.8	>1.6
$E_{1/2}^{red}(1)$	-1.41	-1.61	-0.35	-0.55
Ref	a, b	c	a	d

<sup>a</sup>This work. <sup>b</sup>Reference 9. <sup>c</sup>Gradyushko, A. T.; Tsvirko, M. P. *Opt. Spectrosc. (Engl. Transl.)* **1971**, *31*, 291, 548. Gradyushko, A. T.; Sevchenko, A. N.; Solov'ev, K. N.; Tsvirko, M. P. *Izv. Akad. Nauk SSSR, Ser. Fiz.* **1970**, *34*, 557. <sup>d</sup>Reference 6. <sup>e</sup>MUroP values are estimates as described in the text. For MEtioP, see ref 11. <sup>f</sup>RT = room temperature.

prepared by controlled hydrolysis of titanium isopropoxide, according to the procedures outlined earlier.<sup>4</sup> Concentrations in the range of 0.2–0.5 g/L were employed.

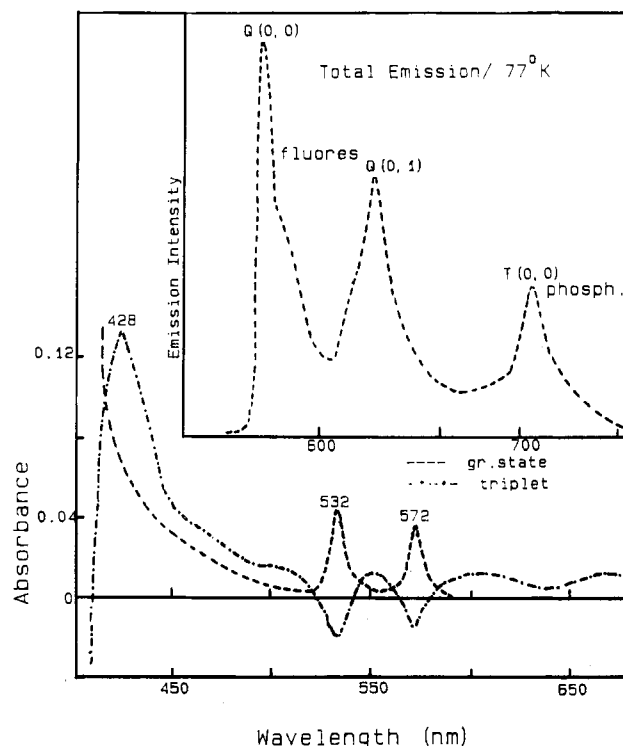
Flash photolysis studies were made on a frequency-doubled ruby laser system (347-nm laser pulses, duration 15 ns) using Ar-purged aqueous solutions. Steady-state photolysis experiments employed a 150-W tungsten-halogen lamp filtered to remove IR and UV radiation ( $\lambda \leq 400$  nm). Fluorescence spectra were recorded on a Perkin-Elmer MPF 4F spectrofluorometer equipped with a red-sensitive R948 PM tube. Details on these and quantum yield measurements have been described in earlier publications.<sup>5</sup>

## Results and Discussion

### I. Photophysical Properties of Zn(II) and Sb<sup>V</sup>(O)(Cl) Uroporphyrins in Aqueous Solution and Their Energetics.

In order to obtain a comprehensive picture on the performance of the Zn and Sb Uroporphyrins as photosensitizers, their photophysical properties in aqueous solution were first determined. Table I presents data measured on the two porphyrins' properties in the ground and excited states in aqueous solution. For comparison, the table also includes corresponding data on the neutral octaethylporphyrin (M(OEP)) analogues. Sb<sup>V</sup>(O)(Cl)UroP, in particular, belongs to the class of "metalloid" porphyrins not widely studied. In aerated solutions, the resting state of antimony porphyrins is Sb(V). (Sb(III) porphyrins are rather unstable in air and readily oxidized to the Sb(V) state. Showing a hyper-type absorption spectrum, Sb(III) porphyrins do not fluoresce and show short-lived phosphorescence<sup>6</sup>). Sb(V) porphyrins show a "normal" metalloporphyrin absorption spectrum with mirror-image fluorescence and phosphorescence intensity, comparable to Sn<sup>IV</sup>(P (P = porphyrin)).

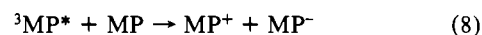
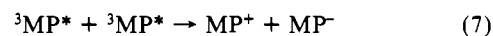
Figure 1 presents the triplet-triplet absorption spectrum of Sb<sup>V</sup>(O)(Cl)UroP in aqueous solution and also the total emission spectrum at 77 K in ethanol-water glass. In aqueous solution, both the Zn(II) and Sb(V) uroporphyrins show moderate fluorescence, triplet absorption intensity, and lifetimes that permit quantitative analysis of the excited-state reactions with other molecules. In the absence of potential quencher molecules such as EDTA and MV<sup>2+</sup>, the triplet excited states of Zn- and Sb<sup>V</sup>(O)(Cl)UroP are long-lived ( $k_0 = 300$  and  $500$  s<sup>-1</sup> for <sup>3</sup>ZnP\* and



**Figure 1.** Absorption spectra of the ground state and of the triplet excited state (difference spectrum) of Sb<sup>V</sup>(O)(Cl)UroP in aqueous (pH 9.0 buffer) solutions. Insert: Total emission spectrum of Sb<sup>V</sup>(O)(Cl)UroP in ethanol-water (1:1 v/v) glass at 77 K.

<sup>3</sup>SbUroP\*, respectively). Molecular oxygen efficiently quenches the triplet excited state with a quenching rate constant of  $k_q = 8.8 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>. Intensity saturation experiments carried out by varying the Sb porphyrin concentration and laser intensity yielded the following molar  $\Delta\epsilon$  values for the triplet excited states:  $4.0 \times 10^4$  and  $4.0 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup> at 428 and 555 nm, respectively.

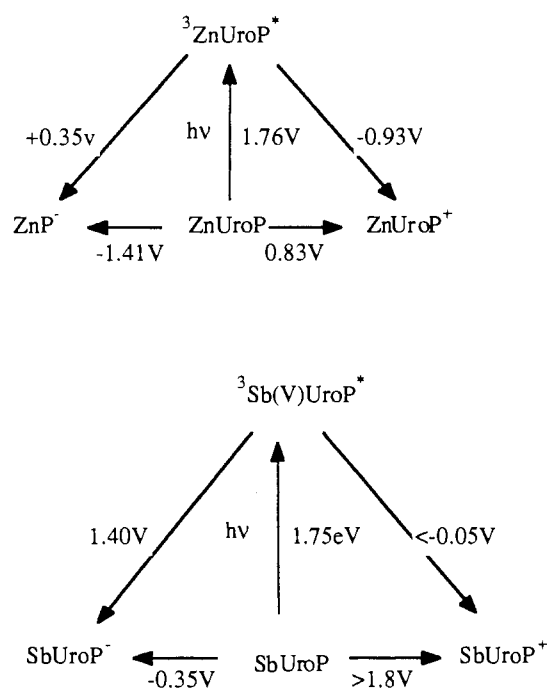
For both uroporphyrins, the triplet lifetime decreases with increasing ionic strength of the solvent medium and laser intensity. One possible cause can be the efficient occurrence of T-T and T-G annihilation reactions, as has been shown earlier for <sup>3</sup>Zn-OEP.<sup>7</sup> These lead to the formation of porphyrin anion and cations (MP<sup>+</sup> and MP<sup>-</sup>):



It has been shown earlier<sup>8</sup> that metallouroporphyrins undergo aggregation at high porphyrin concentration or at high ionic strength or upon acidification. The aggregation is an efficient process for several metal derivatives (including Zn) except for those metal derivatives having strongly bound axial ligands (e.g., Sb(O)(Cl)UroP and Sn<sup>IV</sup>(OH)<sub>2</sub>UroP. Salt-induced aggregates are smaller (perhaps dimers—no precipitation), and acid aggregates are larger (polymers of stacked dimers?). Triplet quenching observed at high ionic strength can arise from such salt-induced aggregation effects. Significant ionic strength effects on the triplet-state decay have also been observed earlier<sup>5f</sup> for highly charged water-soluble porphyrins—porphyrins that show inefficient aggregation, such as ZnTMPyP(4)<sup>4+</sup> and ZnTPPS(4)<sup>4-</sup>. Triplet lifetimes decrease by 1 order of magnitude upon small increase of ionic strength,  $\mu = 0.1$ . The enhanced quenching efficiency can be readily understood as due to kinetic salt effects—rate constants for reactions 7 and 8 increases rapidly for cases where the product of reactant charges  $Z_A Z_B$  is very high (64 for uroporphyrins!).

There have been a few photochemical studies on ZnUroP<sup>8-</sup> in water, mostly by Mauzerall et al.<sup>9</sup> The oxidative and reductive quenching of the triplet excited state of ZnUroP has been studied earlier by Carapellucci and Mauzerall.<sup>9</sup> The reported absorption spectral features of the triplet excited state of ZnUroP has been

Scheme 1

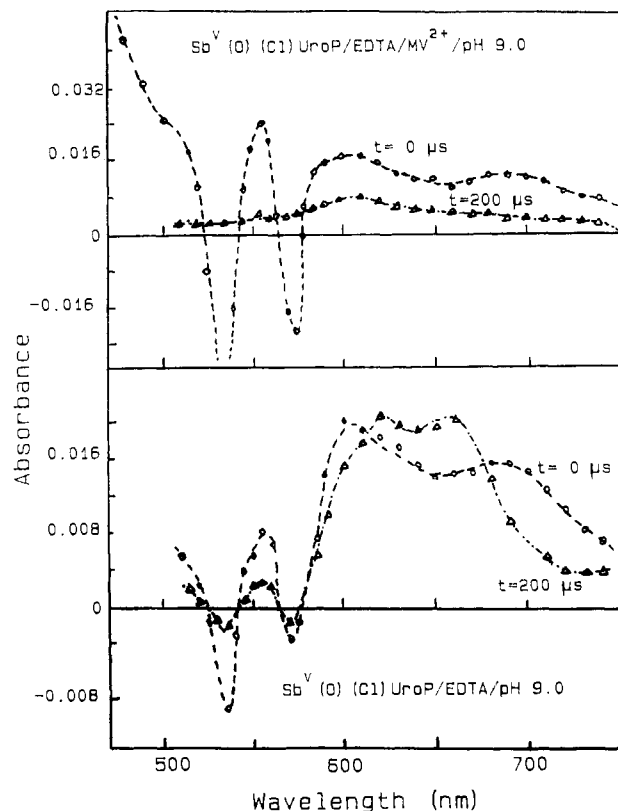


confirmed in this work (absorption maxima at 440 and 770 nm with nearly null absorptions in the 600–680-nm region). The spectral features of the triplet state of SbUroP are quite different from those of ZnUroP. Sb(V) porphyrin triplets have their absorption maxima located at 428, 600, and 690 nm. The reductive quenching of  $^3\text{ZnUroP}^*$  by  $\text{NADH}_2$  was found to be efficient.

Data presented in Table I show that, as with the water-soluble derivatives of the meso-substituted porphyrins (TPP and TPyP derivatives, for example),<sup>5,10</sup> the photophysical properties of the neutral (OEP) and octaanionic uroporphyrin derivatives are nearly identical. The peripheral ionic groups do not influence the excited-state photophysics (spectra, lifetimes, and energies) of the porphyrin, but the *can* affect the ground-state redox potentials (and hence indirectly the excited-state redox potentials). The variations in the  $\text{p}K_a$  values of the corresponding free-base porphyrins are often a good guide to deduce shifts in the redox potentials upon introduction of charged groups (the  $E_{1/2}$  values shift anodically by ca. 100 mV per unit increase in the  $\text{p}K_a$  value).<sup>5,10</sup>

Table I also includes estimates on the ground-state redox potentials of the two porphyrins. (The estimates are based principally on the observation that the redox potentials of the metallo-OEPs are shifted cathodically by ca. 200 mV with respect to those of metallo-UroPs.<sup>11,12</sup> Such estimates are consistent with the  $\text{p}K_a$  of the corresponding free-base porphyrins.  $\text{p}K_a$  values: OEP = EtioP, 5.8; UroP, 4.5; TPP, 4.6; TPyP(4)<sup>4+</sup>, 1.50.) Together with the excited-state energies, these values can be used to deduce the excited-state redox potentials. Scheme I illustrates such values in the form of a Latimer diagram. (Since the  $\text{p}K_a$  measurement is for the protonated carboxylate form of UroP and protonated carboxylates in general are more electron withdrawing than the ionized groups, the redox potentials of the uroporphyrins can be almost identical with those of OEP or EtioP.)

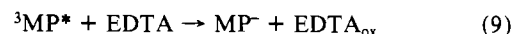
It can be noted that, with respect to ZnUroP, the redox potentials of  $\text{Sb}^{\text{V}}\text{P}$  are shifted anodically by nearly 1 eV. The implications are that the triplet state of ZnUroP acts as a moderate oxidant and reductant, while that of SbP can act only as a strong oxidant. In the subsequent section, we present experimental studies



**Figure 2.** Bottom: Transient absorption spectra recorded during laser flash photolysis of  $\text{Sb}^{\text{V}}\text{UroP}(10^{-5} \text{ M})\text{-EDTA}(0.02 \text{ M})$  solutions (degassed) at pH 9.0 ((—○—) spectrum at  $t = 0$  ( $^3\text{MP}^*$ ); (—△—) spectrum at  $t = 200 \mu\text{s}$  ( $\text{MP}^*$ )). Top: Transient absorption spectra recorded during laser flash photolysis of  $\text{Sb}(\text{O})\text{UroP}(1.2 \times 10^{-5} \text{ M})\text{-EDTA}(0.02 \text{ M})\text{-MV}^{2+}(4 \times 10^{-3} \text{ M})$  solutions (degassed) at pH 9.0 ((—○—) spectrum at  $t = 0$  ( $^3\text{MP}^*$ ); (—△—) spectrum at  $t = 200 \mu\text{s}$  ( $\text{MV}^+$ )).

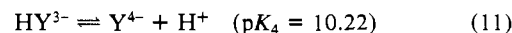
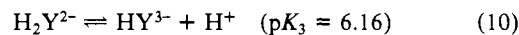
designed to check some of these deductions concerning the excited-state reactivity of the metallourtoporphyrins in water.

**II. Sensitized Photoreduction of Methyl Viologen. A. Reductive Quenching of the Triplet Excited State of  $\text{Sb}^{\text{V}}(\text{O})(\text{Cl})$  and  $\text{Zn}(\text{II})$  Uroporphyrins by Electron Donors.** Figure 2 (bottom) presents the time evolution of the transient absorption difference spectra in  $\text{Sb}(\text{O})\text{UroP}$  solution containing EDTA alone in pH 9 buffer solutions. The transient spectrum recorded at the end of a laser pulse is characterized by absorption maxima located at 600 and 680 nm with isobestic points at 523, 542, 565, and 578 nm and is readily identified as the triplet excited state. The disodium salt of EDTA quenches the triplet state of  $\text{Sb}(\text{O})\text{UroP}$  with a quenching rate constant of  $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  (reaction 9). The



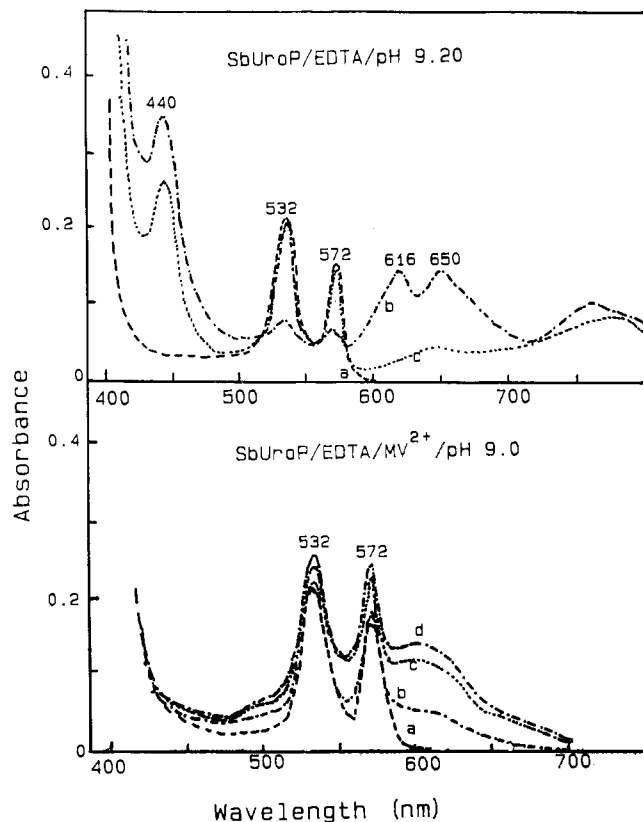
quenching is accompanied by the formation of radical-ion products (Figure 2): porphyrin anion  $\text{MP}^-$  (absorption maxima at 615 and 650 nm) and oxidized EDTA radical. The product porphyrin anion appears to be a stable product, as evidence by the absence of any significant decay during several milliseconds. Given the large driving force for reaction 9, the  $k_q$  values measured are significantly below the diffusion-controlled limit. Huge electrostatic repulsion between the octaanionic porphyrin and the anionic quencher probably is responsible.

The quenching rate constant  $k_q$  and the yield of the porphyrin anions ( $\text{MP}^-$ ) formed both increase with increasing pH. (Between pH 7.0 and 12.0, for example, the  $k_q$  increases by a factor of 12.) The pH dependence of the quenching rate constant can be readily understood in terms of the well-known stepwise ionization of the carboxylic groups of EDTA and different quenching efficiencies of various ionized forms:



(11) (a) Gouterman, M.; et al., unpublished work. Quoted in: Felton, R. H. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. V, Part C, Chapter 2. (b) Fuhrhop, J. H.; Kadish, K. M.; Davis, D. G. *J. Am. Chem. Soc.* 1973, 95, 5140.

(12) Felton, R. H. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. V, Part C.



**Figure 3.** Top: Evolution of the absorption spectrum during the steady-state photolysis of Sb(O)UroP ( $1.2 \times 10^{-5}$  M)-EDTA (0.01 M) solutions (degassed) at pH 9.0. Bottom: Evolution of the absorption spectrum during the steady-state photolysis of degassed solutions of Sb<sup>V</sup>UroP ( $1.2 \times 10^{-5}$  M)-EDTA (0.01 M)-MV<sup>2+</sup> ( $4 \times 10^{-3}$  M) (in pH 9.0 buffer).

Only the HY<sup>3-</sup> and Y<sup>4-</sup> species have a lone electron pair on the N atom and can serve as electron donors. It is interesting to note that the efficiency of the ionized form HY<sup>3-</sup> exceeds the electrostatic repulsive forces between the two anionic reactants (M-(UroP)<sup>8-</sup> and HY<sup>3-</sup>) to be active as a donor in alkaline solutions.

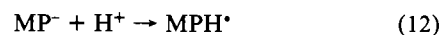
The higher yield of the porphyrin anion radical (MP<sup>-</sup>) with increasing pH is largely due to more efficient quenching, rather than due to a real increase in the cage escape yield of products of reaction 9. Such enhanced quenching efficiency of higher ionized forms of EDTA has been documented earlier in the quenching studies of triplet-state thionine<sup>13</sup> and recently with Zn and Pd tetrakis(*N*-methylpyridiniumyl)porphyrins.<sup>5b</sup> The consequences of more efficient quenching in alkaline solutions can also be seen in the higher quantum yield of reduced methyl viologen (MV<sup>+</sup>) obtained during steady-state photolysis of Sb<sup>V</sup>-(O)(Cl)UroP-EDTA-MV<sup>2+</sup> solutions.

Photolysis of degassed alkaline solutions of Sb<sup>V</sup>UroP-EDTA with visible light (or sunlight!) causes rapid color changes from pink to greenish yellow. Examination of the absorption spectra during steady-state photolysis (Figure 3, (top)) shows that the same porphyrin anion (with characteristic absorption maxima at 616 and 650 nm) builds up as the major product along with some additional product(s) (maxima at 442 and 758 nm). Aeration of the photolyzed solutions leads to a rapid disappearance of the absorptions corresponding to the porphyrin anion (with concomitant formation of the porphyrin MP), leaving product(s) with absorption maxima at 442 and 760 nm.

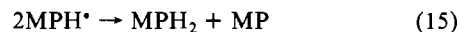
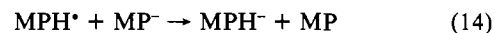
The product with absorption maxima at 616 and 650 nm can be identified as the porphyrin anion (MP<sup>-</sup>) by (i) its extreme air sensitivity and (ii) similarity of its spectra with those of MP<sup>-</sup>

species measured by flash photolysis.

In aqueous solution, two principal dismutation pathways for the porphyrin anions are protonation (reaction 12) and disproportionation (reaction 13). Extensive irradiation leads to for-



mation of either phlorin anion (MPH<sup>-</sup>) or chlorin (MPH<sub>2</sub>) as products. The former is formed largely in alkaline solutions, and the latter, in neutral or acidic solutions, via the sequence of reactions



The formation of porphyrin  $\pi$ -anions as stable anions in aqueous solutions with uroporphyrins is a rare phenomenon in porphyrin redox chemistry. Recently, in their extensive radiolysis studies (pulsed as well as steady state), Neta and co-workers<sup>14</sup> have characterized some of the important features that control the stability of porphyrin anions in aqueous solutions. It was found that SbTPyP was one of the very few porphyrin complexes that formed stable anions in aqueous solution (stable without undergoing protonation up to pH 1.0). The stability of  $\pi$ -anions of Sb(V) porphyrin is attributed to the large difference (>200 mV) in the successive reduction potentials [ $E_{1/2}(1) - E_{1/2}(2)$ ] and the consequent inefficient occurrence of the disproportionation pathways involving porphyrin anions (reaction 13). [The reported<sup>10,11</sup> reduction potential values ( $E_{1/2}(1)$ ,  $E_{1/2}(2)$  values) for Sb<sup>VOEP</sup> and Sb<sup>VTPyP</sup> are -0.55, -1.05 and -0.2, -0.4 V, respectively].

In contrast to the behavior of Sb<sup>V</sup>P but in full agreement with earlier reported results,<sup>9</sup> reductive quenching of triplet-state ZnUroP yields the porphyrin anion as a short-lived transient ( $t_{1/2} < 1$  ms). The ZnP anions are characterized by absorption spectra with split Soret bands and moderately intense absorptions in the red, near-IR region (absorption maxima at 418, 432, 625, and 820 nm). The structures of various reduction products obtained during steady-state photolysis and pulse radiolysis of Zn uro- and hematoporphyrins have been subject to detailed scrutiny.<sup>15</sup> In alkaline solutions, initially formed porphyrin anions rapidly dismutate and yield phlorin anions (MPH<sup>-</sup>) (reactions 13 and 14). On longer time scales these species protonate to yield dihydro-porphyrins as stable products. Since the spectral and kinetic features of these processes have been described earlier, we will not repeat them here.

**B. Studies on M(UroP)-Methyl Viologen Solutions.** The formation of an electrostatically bound  $\pi$ - $\pi$  complex between methyl viologen and various metallouroporphyrins has been demonstrated earlier.<sup>3</sup> Four-coordinated metalloporphyrins with metals such as Zn(II), Pd(II), Cu(II), Ni(II), Ag(I), and Pt(I) all form 2:1 complexes with log *K* values in the range of 5.6-5.9. Strong axial ligation was found to disrupt the normal  $\pi$ - $\pi$  interactions, resulting in 1:1 complexes for 5-coordinated metalloporphyrins (e.g., V(O)P, log *K* = 4.3) and total disruption of  $\pi$ - $\pi$  complexes with 6-coordinated metals (e.g., Sn<sup>IV</sup>(OH)<sub>2</sub>P, log *K* = 2.2). Such ground-state complexations drastically reduce the feasibility of the porphyrin excited state to take part in normal photoredox reactions (e.g., reaction 11). Monitoring of the triplet state of ZnUroP in the presence of varying concentrations of MV<sup>2+</sup>

(13) (a) Bonneau, R.; Jousset-Dubien J.; Faure, J. *Photochem. Photobiol.* **1973**, *17*, 313. (b) Bonneau, R.; Pereyre, J. *Photochem. Photobiol.* **1975**, *21*, 173. (c) Fife, D. J.; Moore, W. M. *Photochem. Photobiol.* **1979**, *29*, 43.

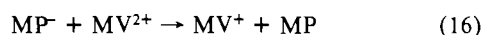
(14) (a) Neta, P. *J. Phys. Chem.* **1981**, *85*, 3678. (b) Baral, S.; Hambright, P.; Neta, P. *J. Phys. Chem.* **1984**, *88*, 1595. (c) Baral, S.; Neta, P.; Hambright, P. *Radiat. Phys. Chem.* **1984**, *24*, 245. (d) Richoux, M.-C.; Neta, P.; Baral, S.; Harriman, A.; Hambright, P. *J. Phys. Chem.* **1986**, *90*, 2462. (e) Abou-Gamra, Z.; Harriman, A.; Neta, P. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2337.

(15) (a) Mauzerall, D. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. V, Part C, p 29. (b) Mauzerall, D. *J. Am. Chem. Soc.* **1962**, *84*, 2437, 2531; **1960**, *82*, 1832, 2601. (c) Seely, G. R.; Talmage, K. *Photochem. Photobiol.* **1980**, *31*, 451. (d) Harel, Y.; Meyerstein, D. *J. Am. Chem. Soc.* **1974**, *96*, 2720. (e) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1963**, *85*, 818.

showed drastic reductions in the triplet-state yields in the presence of  $MV^{2+}$  with concentrations as low as  $10^{-4}$  M, in good agreement with the expected behavior. The quenching process is of the static quenching and not of the redox type.

With  $Sb(O)(Cl)UroP$ , however, one can observe some dynamic quenching of the triplet excited state, though very inefficient ( $k_q = 1.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for  $MV^{2+}$  in the concentration range 0.5–5.0 mM). Long-lived triplets in the presence of  $MV^{2+}$  do confirm the absence of extensive ground-state complexation of the porphyrin. The yield of the redox product  $MV^+$  however was found to be quite low. Comparative studies using the  $ZnTMPyP-MV^{2+}$  system indicate the cage escape yield of  $MV^+$  to be less than 1%.

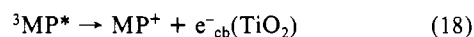
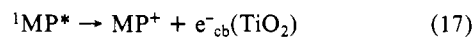
**C. Photolysis of Three-Component ( $M(UroP)-EDTA-MV^{2+}$ ) Systems.** In the  $Sb(O)UroP-EDTA$  system, the presence of  $MV^{2+}$  at very low concentrations ( $<10^{-3}$  M) readily scavenges the  $MP^-$  anions radicals (without quenching of the triplet excited state), yielding the reduced  $MV^+$  radical as a stable, permanent product (Figure 2 (top) spectrum at  $t > 200 \mu\text{s}$  and Figure 3 (bottom)).



Analysis of  $MV^+$  growth at the isobestic points of the triplet/ground states and anion/ground states (e.g., 578 nm) yielded the rate constant for reaction 16 as  $K_{16} = 4.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . Using the initial transient absorbance values (end of laser pulse) and, at long times (stable  $MV^+$  radical), the  $\epsilon$  values of the triplet state and  $MV^+$ , we have estimated the overall yield of the  $MV^+$  radical to be 0.32. This value is somewhat lower than 0.45, measured for sensitized reduction using the  $Sn(OH)_2UroP-EDTA$  system (steady-state measurements).<sup>3</sup>

Ground-state complexing of  $ZnUroP$  with  $MV^{2+}$  leads to static quenching of the excited state, and hardly any overall formation of  $MV^+$  is observed during the steady-state photolysis of  $ZnUroP-EDTA-MV^{2+}$  solutions. It should be pointed out that the main reduction product (at least in the case of  $SnUroP$ ) is just as photochemically active in producing  $MV^+$  as is the porphyrin itself. This is, of course, important because the strong red shift and increased extinction coefficient of the reduced species (such as chlorin) make them better solar absorbers. Photosensitivity of chlorins to undergo secondary photolysis has been established earlier.<sup>16</sup> Chlorophyll is a typical chlorin with excellent sensitivity to undergo photoredox processes using red light.

**III. Visible Light Sensitization of  $TiO_2$  Using Metallouroporphyrins.** As was pointed out in the introductory paragraphs, one of the most exciting potential application of metallouroporphyrins is for their use as sensitizing dyes for charge injection processes on large band gap semiconductors such as  $TiO_2$ :



A variety of structurally very different dyes have been examined<sup>4,17</sup> (e.g., metallouroporphyrins, metallophthalocyanines, erythrosin, eosin, hydroxyquinoline, and polypyridyl complexes of Ru). Among the few dyes that have been found to be efficient, a unifying feature was the presence of peripheral carboxylic groups.<sup>4</sup> Hence, it was

Scheme II

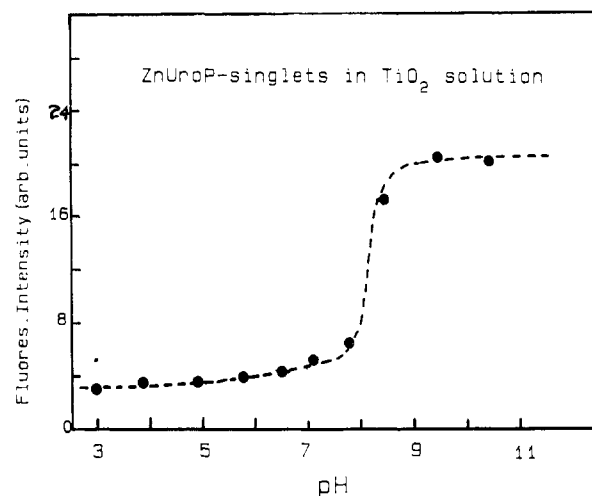
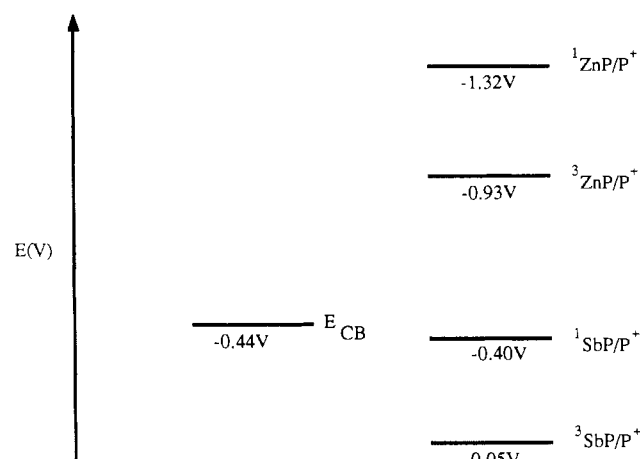
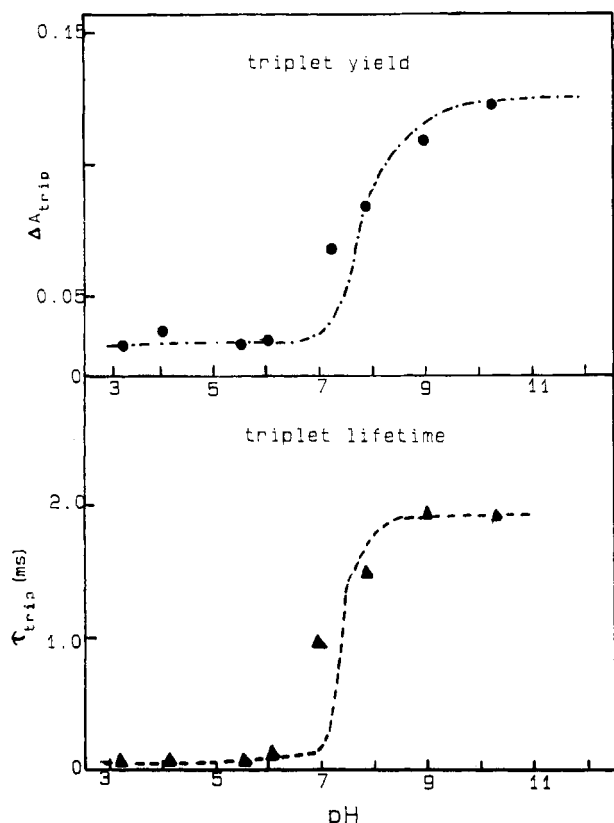


Figure 4. pH dependence of  $ZnUroP$  fluorescence in  $ZnUroP$  ( $10^{-5}$  M)-colloidal  $TiO_2$  solutions. (Fluorescence intensity monitored at 574 nm.)

considered worthwhile to examine the performance of some metallouroporphyrins (especially  $ZnUroP^{8-}$ ), due to the presence of eight peripheral carboxylic groups. Examination of the porphyrin photophysical properties in the presence of colloidal dispersions of semiconductors provides a simple yet elegant way of examining excited-state interactions of the porphyrin with the semiconductor. Scheme II provides the relative location of the energy levels of the conduction band of  $TiO_2$  with respect to the porphyrin excited-state processes of interest. (The  $E_{cb}$  value shown is for solutions at pH 7.0 and for amphoteric oxides such as  $TiO_2$  the flat-band potentials are pH dependent.)

$ZnUroP$  fluoresces weakly in aqueous solution (emission maxima at 574 and 627 nm). The presence of colloidal  $TiO_2$  in the solution has a very pronounced effect on the fluorescence of  $ZnUroP$ , especially in the acidic and neutral pH regions. As shown in Figure 4, the fluorescence intensity decreases sharply between pH 9 and 7 (nearly 6-fold). The quenching of fluorescence of  $ZnUroP$  by  $TiO_2$ , reminiscent of similar behavior in the  $ZnTP-PC-TiO_2$  system reported earlier,<sup>8b</sup> is caused possibly by the transformation of the porphyrin from the free to surface-bound state. The  $TiO_2$  surface consisting of surface hydroxyl groups is known to be amphoteric, carrying net positive charge in the acidic region and net negative charge at alkaline pH values. Sharp increase in the fluorescence quenching efficiency of colloidal  $TiO_2$  occurs in a region closer to the isoelectric point for colloidal  $TiO_2$  preparations of the present type than the region of acid-induced aggregation. The  $pK_a$  for the acid-induced aggregation—i.e., pH at which the initial metallouroporphyrin concentration is reduced to half—is ca. 6.6 for metallouroporphyrins with  $Fe(III)$  and  $Cu(II)$ , ca. 6.0 for those with  $Pt(II)$ ,  $Ni(II)$ ,  $Ag(I)$ , and  $Pd(II)$ ,

- (16) See for example: (i) Suboch, V. P.; Losev, A. P. Gurinovich, G. P. *Photochem. Photobiol.* **1974**, *20*, 183. (ii) Sidorov, A. N. In *Elementary Photoprocesses in Molecules*; Neporent, B. S., Ed.; Plenum: New York, 1968; p 201.
- (17) (a) Phthalocyanines: Fan, F. R. F.; Bard, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 6139. Giraudeau, A.; Fan, F. R. F.; Bard, A. J. *J. Am. Chem. Soc.* **1981**, *102*, 5137. (b) Ru(polypyridyls): Dare-Edwards, M. P.; Goodenough, J. B.; Hammett, A.; Seddon, K. R.; Wright, D. *Faraday Discuss. Chem. Soc.* **1980**, *70*, 285 and references cited therein. Hashimoto, K.; Kawai, T.; Sakata, T. *Nouv. J. Chim.* **1983**, *7*, 249. Takemura, K.; Saji, T.; Fujihara, M.; Aoyagui, S.; Hashimoto, K.; Sakata, T. *Chem. Phys. Lett.* **1985**, *122*, 496. Furlong, D. N.; Wells, D.; Sasse, W. H. F. *J. Phys. Chem.* **1986**, *90*, 1107. (c) Porphyrins: Kamat, P. V.; Chauvet, J.-P.; Fessenden, R. W. *J. Phys. Chem.* **1986**, *90*, 1389. (d) Prussian blue: Itaya, K.; Uchida, I.; Toshima, S.; De la Rue, R. M. *J. Electrochem. Soc.* **1984**, *131*, 2086. (e) Erythrosin: Kamat, P. V.; Fox, M. A. *Chem. Phys. Lett.* **1983**, *102*, 379. (f) Hydroxyquinoline: Houlding, V.; Grätzel, M. *J. Am. Chem. Soc.* **1983**, *105*, 6595.

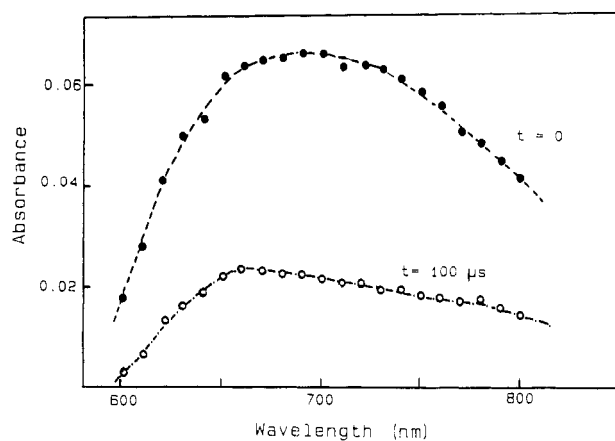


**Figure 5.** pH dependence of triplet yields (indicated as transient absorbance values at 440 nm) and triplet lifetimes of ZnUroP in ZnUroP-colloidal  $\text{TiO}_2$  solutions.

ca. 5.5 for those with Pt(II), and ca. 4.4 for ZnUroP. Hence, it is very likely that ZnUroP species are adsorbed onto  $\text{TiO}_2$  as monomers before the neutralization of the surface carboxyl groups occurs.

The concomitant quenching, if any, of the triplet excited state of the porphyrin in  $\text{TiO}_2$ -containing solutions was examined by laser flash photolysis techniques. Figure 5 presents the variation in the triplet excited state yields (shown are triplet absorbances at 440 nm) and lifetimes as a function of pH in ZnUroP- $\text{TiO}_2$  solutions. As in the fluorescence, both the triplet excited state yield and lifetime decrease sharply in the pH region 7–9, remaining constant at further lower pH values. The fluorescence and triplet quenching clearly indicate that both the singlet and triplet excited states of the ZnUroP are involved in the charge-injection process (reactions 17 and 18). The triplet quenching of ZnUroP in the presence of colloidal  $\text{TiO}_2$  contrasts the behavior of ZnTPPC.<sup>4b</sup> Obviously 0.5-eV excess energy available on the ZnUroP triplet is responsible for the observed triplet reactivity.

Support for the occurrence of charge injection can be obtained from transient absorption spectral studies on ZnUroP- $\text{TiO}_2$  solutions. Figure 6 presents the evolution of transient absorption spectra recorded during laser photolysis of ZnUroP- $\text{TiO}_2$  solutions at pH 3.0. The transient spectrum recorded at the end of the laser pulse has a broad absorption maximum at 680 nm being composed of the ZnP triplets and the  $\text{ZnP}^+$  cation. At longer times, the



**Figure 6.** Transient absorption spectra recorded during laser photolysis of ZnUroP ( $10^{-5}$  M)-colloidal  $\text{TiO}_2$  (0.2 g/L) solutions at pH 3.0: (—●—) spectrum at  $t = 0$ ; (---○---) spectrum at  $t = 100 \mu\text{s}$ .

triplet decay is accompanied by the formation of  $\text{ZnP}^+$  (reaction 18). The decay of  $\text{ZnP}^+$  occurs so rapidly, on time scales comparable to those of the triplet decay, that we could observe only the decay of  $\text{ZnP}^+$  at 640 nm and a growth. (It may be noted that in the region of 600–650 nm only the  $\text{ZnP}^+$  absorbs.) Further support for the involvement of the charge-injection process with colloidal  $\text{TiO}_2$  has been obtained by the absence of any quenching of singlet and triplet states in the presence of an insulator colloid  $\text{SiO}_2$  (Ludox Silica SM).

**Note Added in Proof.** Experimental confirmation of charge injection from the excited state of ZnUroP to the conduction band of  $\text{TiO}_2$  has been obtained in photoelectrochemical studies on dye-coated polycrystalline  $\text{TiO}_2$  electrodes. [Conditions:  $\text{TiO}_2$ , anatase, fractal type electrodes, 0.28- $\text{cm}^2$  area; dye deposition using 0.2 mg/mL aqueous solution at pH 4.0, 1-h dipping; photocurrent measurements using 0.1 M hydroquinone and 0.1 M  $\text{LiClO}_4$ , pH 3.0, at 0.2 V vs SCE.] Stable photocurrents with action spectrum corresponding to the absorption spectral features of ZnUroP are obtained, with incident monochromatic photon to current efficiency (IPCE) of 4.5% at 540 nm [ $Q(1,0)$  band of ZnUroP].

## Conclusions

The present study establishes some of the basic photophysical properties and redox photoreactivity of metallouroporphyrin derivatives of Zn(II) and Sb(V). In addition, it allows putting on a firm basis some of the earlier conjectures on the possible mechanism for the sensitized photoreduction of methyl viologen using this class of water-soluble porphyrins and on the potential applications of the porphyrin derivatives with peripheral carboxylic groups in dye sensitization processes involving semiconductors.

**Acknowledgment.** It is a pleasure to acknowledge financial support of this work by the Swiss National Funds for Scientific Research (K.K. and M.G.), U.S. Department of Energy Contract DE-AC04-76D00789, and Gas Research Institute Contract 5082-260-0767 (J.A.S.). Assistance in some of the experimental work by Patrick Sturzenegger is greatly appreciated.

**Registry No.** ZnUroP, 55972-25-3;  $\text{MV}^{2+}$ , 4685-14-7;  $\text{Sb}^{\text{V}}\text{UroP}$ , 115162-52-2;  $\text{Sb}^{\text{V}}(\text{O})(\text{Cl})\text{UroP}$ , 115162-54-4;  $\text{Sb}(\text{O})\text{UroP}$ , 115162-53-3; EDTA, 60-00-4;  $\text{TiO}_2$ , 13463-67-7;  $\text{H}_2\text{O}$ , 7732-18-5;  $\text{H}_2$ , 1333-74-0.