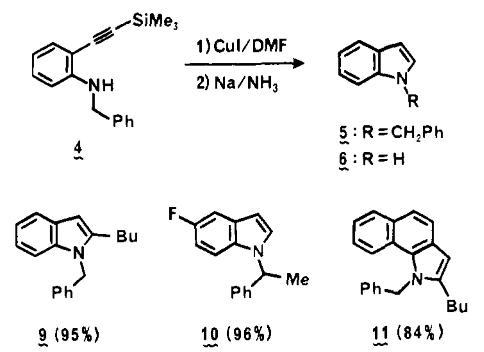

produced functionalized indoles **9**, **10**, and **11**, respectively, in excellent yields.

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Registry No. 1, 87587-23-3; **2** (R = Me), 5405-13-0; **2** (R = C≡CBu), 87587-24-4; **2** (R = C≡CSiMe$_3$), 87587-25-5; **2** (R = C≡CPh), 87587-26-6; **3** (R = Me), 5405-15-2; **3** (R = C≡CBu), 87587-27-7; **3** (R = C≡CSiMe$_3$), 87587-28-8; **3** (R = C≡CPh), 87587-29-9; **5**, 3377-71-7; **6**, 120-72-9; **7** (R = Me; R′ = CH$_2$Ph), 87587-30-2; **7** (R = C≡CBu; R′ = CH$_2$Ph), 87587-31-3; **7** (R = C≡CBu; R′ = CHMePh), 87587-32-4; **7** (R = C≡CSiMe$_3$; R′ = CHMePh), 87587-33-5; **8** (R = Me), 87587-34-6; **8** (R = C≡CBu), 87587-35-7; **8** (R = C≡CSiMe$_3$), 87587-36-8; **9**, 87587-40-4; **10**, 87587-41-5; **11**, 87587-42-6; Me$_3$Al, 75-24-1; (BuC≡C)$_3$Al, 45234-85-3; (Me$_3$SiC≡C)$_3$Al, 87587-48-2; (PhC≡C)$_3$Al, 47461-44-9; *N*-benzyl-4-methyl-1-naphthalenamine, 87587-37-9; *N*-benzyl-4-(1-hexynyl)-1-naphthalenamine, 87587-38-0; *N*-benzyl-4-(trimethylsilylethynyl)-1-naphthalenamine, 87587-39-1; *N*-benzyl-*N*-(trimethylsilyloxy)-1-naphthalenamine, 87587-43-7; *N*-benzyl-4-fluoro-*N*-(trimethylsilyloxy)aniline, 87587-44-8; 4-fluoro-*N*-(1-phenethyl)-*N*-(trimethylsilyloxy)aniline, 87587-45-9; *N*-(benzyl)-4-ethyl-*N*-(trimethylsilyloxy)aniline, 87587-46-0; 4-ethyl-*N*-(1-phenethyl)-*N*-(trimethylsilyloxy)aniline, 87587-47-1.

Photoreduction of Methylviologen Sensitized by Dihydroxytin(IV) Uroporphyrin

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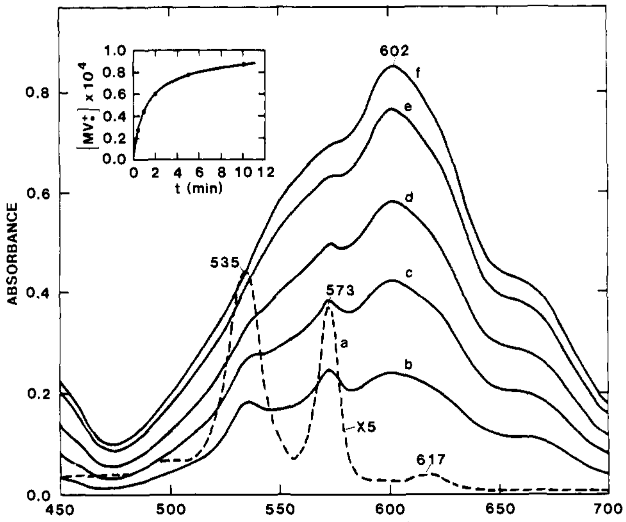

Figure 1. Absorption spectral changes upon irradiation of an aqueous solution of Sn(OH)$_2$UroP I (1.5×10^{-5} M), MV^{2+} (5.1×10^{-3} M), and EDTA (0.27 M) (a) before irradiation (×5), (b) 30 s, (c) 1 min, (d) 2 min, (e) 5 min, and (f) 10 min total irradiation time. The weak band at 617 nm is from a small amount of the chlorin (see ref 11) formed when the sample was previously deaerated, irradiated to generate over 5 times as much $MV^{+\cdot}$ as porphyrin in the system, aerated to remove the $MV^{+\cdot}$ generated, and then deaerated again. Inset: Plot of [$MV^{+\cdot}$] vs. irradiation time. Total power on sample is about 0.4 W (see text).

Photocatalytic reduction of methylviologen (MV^{2+}) using porphyrins[1-13] or phthalocyanines[14-16] as sensitizers has been reported by several workers. In the presence of suitable catalyst[1-3] $MV^{+\cdot}$ reduces water to H_2 at the expense of a sacrificial electron donor. Central to efficient electron transfer and charge separation is the nature of the MV^{2+}–metalloporphyrin complex.

With metalloporphyrins that have their water solubility conferred by positively charged substituents on the macrocycle, electrostatic repulsion of MV^{2+} prevents close approach and π–π complex formation; electron transfer is slow, but the repulsive interaction in the encounter complex allows reduced acceptor ($MV^{+\cdot}$) to diffuse away before the back reaction can occur. The result is quantum yields for $MV^{+\cdot}$ production ($\phi = 2\phi_{H_2}$) as high as 0.75.[1,2,17,18]

On the other hand for negatively charged substituents, strong electrostatic attraction of the viologen dication results in a tight ground-state complex with the metalloporphyrin. Efficient electron transfer occurs in the complex, but rapid back reaction prevents charge separation and significant production of reduced viologen.[2,8]

The uroporphyrins in alkaline aqueous solutions are an extreme example of the latter category.[19] With eight negatively charged carboxylate groups on the porphyrin ring, MV^{2+} forms a very tight ($\log K \geq 6$) ground-state complex.[19-23] The complex most likely has the pyridinium rings of MV^{2+} flat against and in π–π interaction with the porphyrin π system. Unfortunately, as for the negatively charged meso-substituted porphyrins that have been previously investigated, the π–π complex is photochemically much less active than the repulsive encounter complexes.[1,2,8,17,18]

In contrast with the H_2, Cu, Zn, Pd, Ag, V(IV)O, and other metallouroporphyrins for which we have observed tight π–π complexes and no reduction of MV^{2+}, dihydroxytin(IV) uroporphyrin I (Sn(OH)$_2$UroP) is an efficient photosensitizer of viologen reduction. Figure 1 shows the result of irradiation of a solution containing ethylenediaminetetraacetic acid as an electron

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donor, MV^{2+}, and Sn(OH)$_2$UroP. Dichlorotin(IV) uroporphyrin I was purchased from Porphyrin Products and further purified and converted to the dihydroxy complex by chromatography on a G-50-40 Sephadex column. [We have been able to make the halogen complexes (SnCl$_2$UroP and SnBr$_2$UroP) in water only in 5 M acid (HCl or HBr).][24]

Upon irradiation of this system a rapid buildup of MV$^{+\cdot}$ is detected by its broad absorption with maximum near 602 nm (ϵ_{602} = 1.0×10^4 M^{-1} cm^{-1}) as illustrated in Figure 1. The sample was irradiated with white light from a 25-W tungsten (Tensor) lamp using an ultraviolet sharp-cut filter (Corning, CS3-75) to eliminate UV light below 380 nm. Under similar conditions Cu-, Ag-, Zn-, Pd-, and V(IV)OUroP and the free base[13] give no reduced viologen.

The quantum yield ϕ for production of MV$^{+\cdot}$ was measured with a band-pass filter (Oriel S-60) (524–565 nm) and a 200-W quartz-iodide lamp source and power meter (Spectra Physics, Model 404). A solution containing EDTA (0.2 M), Sn(OH)$_2$UroP (2.4×10^{-5} M), and MV^{2+} (0.011 M) at pH 9 gave a quantum yield of 0.42 ± 0.1. This value is at least an order of magnitude higher than for other anionic porphyrins[18] and is similar to high quantum yields found for cationic porphyrins such as zinc tetrakis(*N*-methylpyridyl)porphyrin (ZnTMPyP) for which ϕ = 0.75.[18]

As shown in the inset in Figure 1, MV$^{+\cdot}$ reaches a steady-state concentration of about 0.9×10^{-4} M. This is close to the steady-state concentration of 1×10^{-4} M measured by McLendon and Miller[1] for ZnTMPyP under similar conditions. The saturation effect is partly due to screening by the strong absorption of MV$^{+\cdot}$ in the region of the metalloporphyrin absorption bands.[8] The quantum yields quoted are calculated from the maximum rate of MV$^{+\cdot}$ generation at early times before screening is significant.

The quantum yield is a strong function of solution conditions. For example, the MV$^{+\cdot}$ concentration at saturation ranges from 2.5×10^{-6} M at pH 3.2 to 3.5×10^{-4} M at pH 13.1. Therefore, the quantum yield of 0.42 at pH 9 is clearly not obtained at optimum pH. For the donor triethanolamine (0.01 M) at pH 10.2, the concentration of MV$^{+\cdot}$ reached under steady-state conditions is about 50% higher than with EDTA at the same pH and 0.3 M. No photodecomposition of the porphyrin is observed with TEA, whereas some porphyrin decomposition is noted at EDTA concentrations below 0.2 M and at acid pH.

The high activity of the tin uroporphyrin system when compared with other anionic metalloporphyrins can be understood in terms of the electrostatic and steric interactions of the porphyrin and acceptor. Strong axial ligation of hydroxides blocks formation of the tight π–π complex usually favored by the electrostatic, hydrophobic, and charge-transfer forces. Addition of MV^{2+} to a solution of Sn(OH)$_2$UroP produces only subtle changes in the absorption spectrum of the porphyrin. These changes are not typical of the π–π complex for which the Soret band shifts and large absorbance changes in the Soret and visible bands are noted.[8,19–23] Shifts in Raman lines are observed also, and they indicate the porphyrin ring acts as an acceptor in the ground-state complex.[20–23]

That the axial ligands block π–π complex formation is further supported by the failure of Sn(OH)$_2$UroP to aggregate under solution conditions for which other uroporphyrins aggregate as evidenced by characteristic changes in their absorption spectra. At room temperature in 0.1 M NaOH (pH 14) uroporphyrins are monomeric up to about 0.01 M.[19–23,25–27] Upon addition of salt (5 M) most metallouroporphyrins dimerize resulting is large spectral changes, especially in the Soret.[19–23,25–27] In contrast, the absorption spectrum of Sn(OH)$_2$UroP is unchanged by addition of NaCl. Neutralization of the carboxylates by protonation at acid pH normally also results in spectral changes characteristic of π–π aggregation, but not in the case of Sn(OH)$_2$UroP.[27]

Another indication that the axial ligands block π–π aggregation is that dihydroxytin coproporphyrin, which has uroporphyrin's four acetates replaced by methyl groups and, hence, has a lower charge (−4), does not show a change in its absorption spectrum upon extreme dilution (8×10^{-8} M). Other metallocoproporphyrins, e.g., Cu, are normally aggregated down to 10^{-6} M and below this concentration show a characteristic shift in the Soret band upon formation of monomer.[27]

The high activity of anionic Sn(OH)$_2$UroP in photoreduction of MV^{2+} results from (1) prevention of unreactive complexes by the steric constraints provided by the strongly bound axial ligands of tin(IV) and (2) electrostatic interactions of MV^{2+} and charged donor species with the negatively charged porphyrin. At present we cannot distinguish between reductive and oxidative quenching mechanisms for photosensitization, but redox potentials deduced from the dihydroxytin octaethylporphyrin analogue suggest a reductive cycle is operative.[11,12,28–30] Even in the case of a reductive quenching mechanism π–π complexation with MV^{2+} would render the system photochemically inactive. Ag and VO porphyrins also have redox potentials that indicate the possibility of a reductive cycle, but they form strong MV^{2+} complexes and are found to be inactive.[27] Neutral or positively charged electron donors (e.g., TEA) show some advantage over EDTA. The pH dependence of the steady-state concentration probably results from varying the charge at the ring periphery and from successive deprotonations of EDTA. Weak attraction of donors and acceptors coupled with steric blocking of tight, inactive complexes by strongly bound axial ligands may enhance Sn(OH)$_2$UroP activity.

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Photocatalytic Conversion of Primary Amines to Secondary Amines and Cyclization of Polymethylene-α,ω-diamines by an Aqueous Suspension of TiO$_2$/Pt

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A number of studies concerning the photocatalytic action of semiconductor materials, particularly n-type TiO$_2$ and related composites, have focused on the utilization of solar energy to produce hydrogen from water.[1] More recently several attempts have been made to extend heterogeneous photocatalysis with dispersed semiconductors to synthetic chemistry.[2–7] We report

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