which relates the absolute MCD signs of the four lowest energy electronic transitions of systems derivable from a $(4N + 2)$-electron [*n*]annulene perimeter with their molecular structure. According to this model the signs of the A[11a] or B[11b] terms of such systems are directly related to the relative size of the orbital-energy differences between the two highest occupied (ΔHOMO) and the two lowest unoccupied (ΔLUMO) molecular orbitals. In the event that ΔHOMO – ΔLUMO > 0 a normal (–+–+) sign pattern is predicted, whereas if ΔHOMO – ΔLUMO < 0, then an inverted (+–+–) sign pattern should result.[11d] Michl has applied his model to porphyrins and reduced porphyrins. However, it is evident (Figure 1 and 2) that the MCD sign pattern of chlorins is far more sensitive to substituent effects than had earlier been supposed. Therefore, it is important to examine the model in greater detail.

The representations (Figure 3A) of the porphin four-orbital MO's given by Gouterman,[12] which agree qualitatively with the electron density maps computed for magnesium porphine by Spangler et al.,[13] provide a visual basis for estimating the relative magnitudes of the effects of substituents on the energy levels of the HOMO and LUMO orbitals. The work of Meot-Ner and Adler[14] indicates that meso phenyl groups behave as conjugative electron donating ($-E$) substituents with respect to the porphyrin ring. They are effective in splitting the HOMO's, since the ratio $\epsilon_{max}(Q_{0-0})/\epsilon_{max}(Q_{0-1})$[15] changes from 0.06 to about 1 on going from porphine dianion to tetraphenylporphyrin dianion. Alkyl groups donate electrons to the porphyrin ring[12] but their $-E$ effect[16] is relatively weak, since the visible band ratio for octaethylporphyrin dianion is only 0.5. In addition, an alkyl group is considered to raise the HOMO orbital more than the LUMO's since, although the porphine orbital coefficients at the pyrrole positions (Figure 3A) are larger in the LUMO's than in the HOMO's, the latter are closer in energy to those of the alkyl donor orbitals. Finally, the electron-withdrawing effect of zinc[12] is not strong since the band ratio for zinc porphine is again about 0.5.

With these caveats in mind we summarize the qualitative effects of substituents and ring reduction on the energy levels of the HOMO's and LUMO's of porphine in Figure 3B. Porphine dication (or, equivalently porphine dianion), for which the LUMO's are degenerate by symmetry and the HOMO's accidentally so, is taken as the reference compound. Replacement of the four central protons of porphine dication by zinc lowers the energy of the a_{2u} orbital. ΔHOMO – ΔLUMO > 0 and a normal MCD sign pattern is predicted for ZnP as is observed.[17] Saturation of the pyrrole double bond of ring IV (Figure 3A) reduces the size of the conjugation path, thereby raising the energies of the e_g1 and a_{1u} orbitals but has little effect on the e_g2 and a_{2u} orbitals, since for them the electron density in ring IV is small. The energy shift is greater for e_g1 than for a_{1u} because of the relative difference in the electron densities in the two orbitals at the site of reduction. For ZnC ΔHOMO – ΔLUMO < 0 and an inverted MCD sign pattern is predicted (in agreement with Michl's conclusion[11b] for chlorin dianion) and observed at least for the Q_0^y and Q_0^x bands (Figure 2).[11d]

Relative to ZnC the energy of the a_{1u} orbital of ZnOEC is raised owing to the substitution of the six effective (for this orbital) alkyl perturbers. The energies of both LUMO's are also raised; however, only two alkyl groups perturb the e_g1 orbital, whereas four are effective in raising the energy of the e_g2 orbital. Thus, relative to ZnC ΔLUMO is decreased but ΔHOMO is increased. ΔHOMO – ΔLUMO > 0 and the predicted normal sign pattern is consonant with the experimental spectrum (Figure 2). In ZnTPC the a_{2u} orbital is strongly raised (vide supra) so that now ΔHOMO ~ 0 which is consistent with the inverted sign pattern (Figure 1). In addition, from a comparison of |ΔHOMO – ΔLUMO| for ZnC and ZnTPC one can readily understand the basic cause of the large difference between the values of $[\theta]_M$ for the two chlorins (>8x for the Q_0^y bands). Finally, note that in ZnRhC (Figure 1) a vinyl and a methoxycarbonyl group are situated on rings I and III, respectively. The methoxycarbonyl group, in particular, is strongly electron withdrawing, and substitution of this group for an alkyl in ZnOEC should lower the energies of the e_g2 and a_{1u} orbitals while leaving the e_g1 and a_{2u} orbitals largely unaffected. As a result ΔHOMO – ΔLUMO < 0, thus rationalizing the inverted sign pattern.

We believe that the data and analyses reported here on the effects of substituents on the MCD of reduced porphyrins strongly support the utility and applicability of Michl's model[11] for these systems. In a detailed report[18] we will show that a similar perturbation treatment is required to explain other instances of substituent-induced sign and intensity variations in the MCD of other chlorins, bacteriochlorins, and isobacteriochlorins.

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Photosensitized Electron-Transfer Reactions in Colloidal SiO_2 Systems: Charge Separation at a Solid–Aqueous Interface

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Separation of products formed in photoinduced electron-transfer processes is essential for efficient energy storage.[1,2] Several approaches involving systems such as functionalized micelles,[3,4] liposomes,[5,6] microemulsions,[7] and polyelectrolytes[8,9] have been used as means to assist charge separation. In these processes the thermodynamically favored back reactions of the photoproducts can be retarded, and further utilization of the photochemical energy so stored can make feasible the decomposition of water. Particular attention has been devoted to the photosensitized re-

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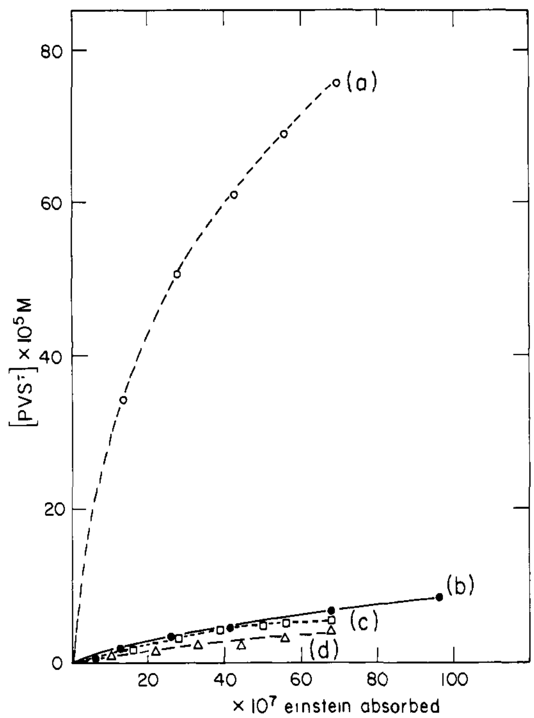
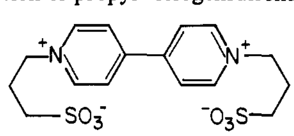


Figure 1. Propyl viologen radical (PVS$^{-}\cdot$) formation as a function of light absorbed. All experiments at pH 10.2, [PVS^0] = 2×10^{-3} M, [TEA] = 1×10^{-2} M. (a) 0.1% SiO_2 colloidal system, sensitizer Zn(TMPyP)$^{4+}$ (3.5×10^{-6} M). (b) Homogeneous aqueous solution, sensitizer Zn(TMPyP)$^{4+}$ (3.5×10^{-6} M). (c) 0.1% SiO_2 colloidal system, sensitizer Zn(TPPS)$^{4-}$ (9.2×10^{-6} M). (d) Homogeneous aqueous solution, sensitizer Zn(TPPS)$^{4-}$ (9.2×10^{-6} M).

duction of 4,4′-bipyridinium salts (viologens) by Ru(bpy)$_3^{2+}$ and zinc porphyrins.[10,11] With these systems the photoreduction of water to hydrogen as well as photooxidation of water have been accomplished.[12,13]

Here, we wish to report that an aqueous SiO_2 colloid provides an especially effective solid–liquid interface. It has a very high, negative surface charge density that can retard the back reactions while allowing the forward reaction with a neutral electron acceptor to proceed.

The colloidal SiO_2 suspension employed is composed of particles with a mean diameter of 40 Å. At pH >6 the particles are negatively charged and characterized by a high surface potential.[14] As a result, the interfacial system is capable of producing electrostatic attractions and repulsions with charged species formed in the photosensitized electron transfer. We have investigated the effect of the negatively charged solid interface on the photosensitized reduction of propyl viologensulfonate, PVS^0 (**1**), by



each of two positively charged sensitizers, zinc *meso*-tetramethylpyridinium porphyrin, Zn(TMPyP)$^{4+}$, and Ru(bpy)$_3^{2+}$. Triethanolamine (TEA) was used as the electron donor in each case. This electron donor (E^0 = 0.82 V) is irreversibly decomposed during its oxidation.[12a,b]

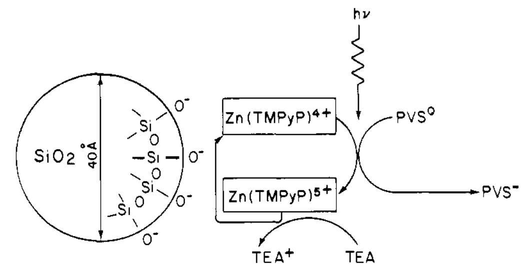


Figure 2. Schematic function of SiO_2 particles in the photosensitized electron-transfer process.

A typical reaction mixture was composed of an aqueous SiO_2 colloidal suspension, including PVS^0, Zn(TMPyP)$^{4+}$, and TEA. The solution was deaerated with argon and illuminated at intervals of 15 s with a Xe 1000-W lamp (light filtered through a $CuSO_4$ solution and Corning 3-72 and Corning 5-57 filters, λ = 430–550 nm, incident photon flux 5.0×10^{-7} einstein s^{-1}). A rapid formation of the blue viologen radical (PVS$^{-}\cdot$) was observed, and its rate of production was followed spectroscopically at λ 735 nm (ϵ 2500 M^{-1} cm^{-1}) (Figure 1a). The initial quantum yield was ϕ_{max} = 0.37. Exclusion of the SiO_2 particles resulted in a significantly reduced rate of PVS$^{-}\cdot$ production, ϕ_{max} = 0.038 (Figure 1b). The dramatic enhancement of the electron-transfer process quantum yield in the colloidal system (10-fold) is attributed to the presence of negatively charged particles, which assist the separation of the photoproducts and retard their recombination (Figure 2). The positively charged sensitizer [Zn(TMPyP)$^{4+}$] is adsorbed to the surface of the particle by Coulombic attractions.[15] Electron transfer to the neutral, zwitterionic acceptor **1** results in formation of the oxidized sensitizer Zn(TMPyP)$^{5+}$ and the negatively charged acceptor PVS$^{-}\cdot$ (eq 1). The negatively

$$\mathrm{Zn(TMPyP)^{4+} + PVS^0 \underset{k_b}{\overset{h\nu}{\rightleftharpoons}} Zn(TMPyP)^{5+} + PVS^{-}\cdot} \quad (1)$$

charged silica particles (surface potential ca. −170 mV)[15] eject the reduced acceptor into the bulk aqueous phase, thus retarding its recombination with Zn(TMPyP)$^{5+}$. The oxidized sensitizer is then available for the necessary oxidation of TEA.

A flash photolysis study has confirmed the role of the interface in retarding recombination of photoproducts. The bimolecular rate constant for disappearance of PVS$^{-}\cdot$ and Zn(TMPyP)$^{5+}$ was close to that for a diffusion-controlled reaction in the homogeneous solution but slower by a factor of at least 100 in the presence of SiO_2 colloid. Replacement of the positively charged sensitizer with a negatively charged one would be expected to diminish the enhancing effect of the charged interface. Indeed, substitution of zinc *meso*-tetraphenylporphyrinsulfonate [Zn(TPPS)$^{4-}$] for Zn(TMPyP)$^{4+}$ gives in the colloidal system a quantum yield (ϕ_{max} = 0.016) very similar to that obtained in the corresponding homogeneous solution (ϕ_{max} = 0.012) (Figure 1c,d). Thus, repulsion of the two negatively charged photoproducts by the SiO_2 particles allows a recombination rate similar to that observed in a homogeneous solution.

The role of the surface potential in enhancing the quantum yield of the electron-transfer process was confirmed by varying the ionic

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(15) By using a positively charged spin label it has been confirmed independently that the positive species interacts with the negative SiO_2 interface. The sharp ESR signal of the spin label in a homogeneous aqueous solution becomes very broad upon addition of SiO_2 particles. Increasing the ionic strength of the colloidal system results in the reappearance of the sharp signal characteristic of homogeneous solution. On the basis of the number of ionized sites on the particle a value of ca. −170 mV for the surface potential has been calculated. A comprehensive correlation of surface potential with the observed photosensitized electron-transfer process as well as the binding constant measurements of Ru(bpy)$_3^{2+}$ to the SiO_2 particles will be published elsewhere.

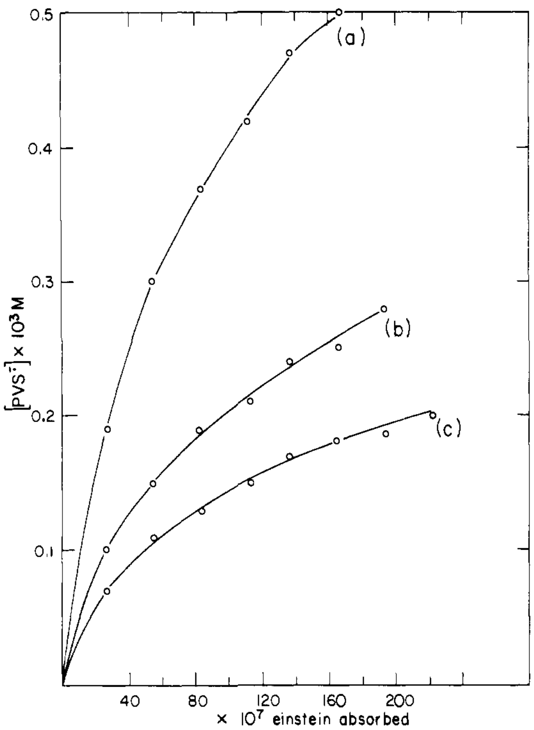

Figure 3. Propyl viologen radical ($PVS^{-}\cdot$) formation as a function of ionic strength of the system. Experiments at pH 9.8, $[PVS^0] = 1 \times 10^{-3}$ M, [TEA] = 1×10^{-3} M; sensitizer $Zn(TMPyP)^{4+}$ (4×10^{-6} M). (a) [NaCl] = 0.002 M; (b) [NaCl] = 0.1 M; (c) [NaCl] = 0.5 M.

strength of the reaction medium. Increasing the ionic strength is expected to decrease the surface potential of the particles[15,16] and shorten the range of effective electrostatic repulsions. Indeed, at an ionic strength of 0.5 M NaCl the quantum yield of $PVS^{-}\cdot$ production dropped to $\phi_{max} = 0.07$ (Figure 3).

The enhancing effect of the SiO_2 particles on the quantum yield is similar in a system that includes the positively charged $Ru(bpy)_3^{2+}$ instead of $Zn(TMPyP)^{4+}$ as sensitizer. A colloidal suspension of 0.1% SiO_2 particles containing $Ru(bpy)_3^{2+}$ (7.6×10^{-5} M), PVS^0 (1×10^{-3} M) and TEA (10^{-3} M) at pH 9.6 was deaerated and illuminated under the conditions previously described. The quantum yield for the photosensitized production of $PVS^{-}\cdot$ in the interfacial system ($\phi_{max} = 0.04$) was 13-fold that in the corresponding homogeneous system ($\phi_{max} = 0.003$). Again, as with the zinc sensitizer, flash photolysis experiments showed a large reduction in back-reaction rate (eq 2) in the presence of

$$Ru(bpy)_3^{2+} + PVS^0 \underset{k_b}{\overset{h\nu}{\rightleftharpoons}} Ru(bpy)_3^{3+} + PVS^{-}\cdot \qquad (2)$$

SiO_2: $k_b = 5.7 \times 10^7$ M^{-1} s^{-1} compared with $k_b = 7.9 \times 10^9$ M^{-1} s^{-1} in the homogeneous solution.

In conclusion, we have demonstrated that the introduction of the solid SiO_2 interface can affect strongly the efficiency of the photosensitized electron-transfer process. By proper charge functionalization of the electron acceptor and donor, electrostatic repulsive or attractive interactions can be established. The high charge density of the colloidal silica particles provides a driving force for charge separation and diminishes back reactions. The stabilized intermediary photoproducts might then be further coupled with efficient reactions that result in the decomposition of water. These aspects are currently being investigated.

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(16) Reference 14, Chapter 5, p 108.

3-Acyltetramic Acid Antibiotics. 1. Synthesis of Tirandamycic Acid[1]

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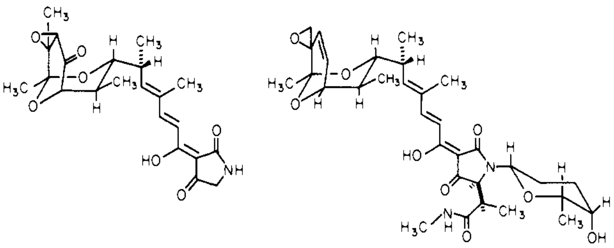
Tirandimycin (**1**)[2] is a member of a small group of 3-acyltetramic acid antibiotics[3] that have occasioned considerable interest[4] due to their potent inhibition of bacterial DNA-directed RNA polymerase[5] and the selective inhibition of terminal deoxynucleotidyltransferase from leukemic cells.[6] Together with the



1 **2**

structurally similar streptolydigin[3a] (**2**), these antibiotics seem to exhibit contrasting activity to the simpler 3-acyltetramic acids known;[7] it is possible[4] that the differing activities is a result of the complex, 2,9-dioxabicyclo[3.3.1]nonane system common to both antibiotics. This very complexity as well as the opportunity to develop synthetic strategy for the construction of more diverse analogues of these interesting antibiotics prompted an investigation of their total synthesis. The successful conclusion of the first phase of this program—namely, the synthesis of tirandamycic acid (**23**)[2] in its optically active, natural form from D-glucose—is recorded here.[8]

The basic plan for this synthesis was the construction of a suitably substituted 2,9-dioxabicyclo[3.3.1]nonane system from the pyran form of the sugar and then modification of the rudimentary substitution to fit the complex pattern of the antibiotic. The first problem was the conversion of the sugar to an appropriate *C*-glycoside. This was efficiently accomplished through application of the ester enolate Claisen rearrangement[9] to the propionate **4** derived from the commercially available glycal **3**[10] (Scheme I),

† Postdoctoral Fellow of the National Institute of General Medical Sciences, 1978–1979.

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