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Photoreactions and Photoelectrochemical Effects in Supported Multilayer Assemblies. Mechanisms of Interfacial Reactions Involving Reactive Supports, Metalloporphyrin Surface Films, and Solutions[1]

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Abstract: An investigation of photoprocesses occurring in molecular assemblies consisting of monolayers and multilayers of water-insoluble surfactant tin porphyrins supported on tin oxide optically transparent electrodes and other potentially reactive surfaces in contact with aqueous solutions containing potentially reducing solutes is reported. In each case the light-absorbing species is the surface-bound tin porphyrin. While irradiation of glass- or quartz-supported monolayers and multilayers of the tin porphyrins in contact with aqueous reductants such as amines, hydroquinone, or *p*-dimethoxybenzene leads to net photoreduction and photoaddition processes for the porphyrin to yield chlorin- and isobacteriochlorin-type products, the net reactivity of the porphyrin is totally quenched or sharply reduced when it is contained in assemblies in contact with n-type SnO_2, PtO_2, or platinum films. Several experiments were carried out which demonstrate that excited states of the porphyrin are not strongly quenched by the various supports; thus in this case the major effect of the surface is to intercept reduced species formed in the interfacial photoreaction of the porphyrins with the reducing solute. The SnO_2-supported porphyrin assemblies can serve as photoanodes for the oxidation of solution reductants; in typical experiments slides having areas ca. 3 cm^2 give photocurrents in the $\sim$300-nA range with a quantum efficiency of 0.3%. The low quantum efficiency observed is comparable to that measured for interfacial or homogeneous-solution reduction of the tin porphyrin by the same solutes; thus the net reactivity of the porphyrin in solution and at interfaces appears relatively comparable in these cases and is probably limited by net physical quenching of the porphyrin and triplet by the solute reductant.

Introduction

The interfacial reactivity of excited states or other reactive reagents chemically or physically bound to surfaces in contact with solutions has developed into an area of intense and diverse activity in recent years.[4-14] Several studies have focused on the improved properties of chemically derivatized electrodes in a number of electrochemical and photoelectrochemical processes.[15-19] Other investigations have demonstrated that the effectiveness and perhaps selectivity of a number of heterogeneous catalysts can be improved by chemical or physical modification with a variety of reagents.[5,6,20] A number of investigations have dealt with photochemical or photoelectrochemical reactions originating from direct activation of surface-bound molecules in single crystals, amorphous solids, or powders in contact with solutions containing potential reactants not excited by the irradiating light.[4-22] Although in certain cases the mechanism and efficiencies of these interfacial reactions appear to be reasonably well understood, in many others the overall events occurring are rather ill-defined.

One area of surface modification which has been the focus of some photochemical studies involves the formation of supported multilayer assemblies from water-insoluble monolayer films generated at an air–water interface.[4,8-12] A number of studies have shown that chromophores exhibiting photochemical reactivity in solution retain at least some of their reactivity upon incorporation into supported multilayers in contact with solutions containg potentially reactive reagents.[4,12,23,24] Other investigations have shown that such multilayers, when deposited on potentially reactive supports such as semiconductor electrode surfaces, can produce electrochemical effects upon illumination of the multilayer-bound chromophore in what are clearly multilayer–solid interfacial processes.[8-11] Our investigations in this area have focused to a large extent on multilayer–solution interfacial reactions; in particular we have investigated a number of reactions involving multilayer-incorporated porphyrins, metalloporphyrins, and other transition metal complexes.[12,24] We recently reported a study of reductive photoaddition reactions occurring between assembly-bound palladium, tin, and zinc porphyrins and solution reductants such as tertiary amines, ascorbic acid, and stannous chloride.[12] In these studies, in which the metalloporphyrins bound to inert supports such as glass or quartz were selectively excited with visible or near-UV light, we observed reactivity formally similar to that occurring with both porphyrin and reductant contained in homogeneous solutions. However, in these studies we were able to observe a number of effects on relative reactivity which emphasize the influence of the organized multilayer en-

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vironment on both reactivity and the access of solutes to the excited chromophore.

In the present study we have investigated further the photoactivity of a water-insoluble surfactant tin(IV) porphyrin incorporated into multilayer assemblies deposited on a variety of supports including n-type tin oxide semiconductor electrodes, platinum foil, and platinum oxide coated glass. These studies indicate clearly that interfacial photoprocesses involving interaction between the electron-accepting support, reducing solutes present in the solution, and the photoexcited chromophore can occur with moderate efficiency. In several cases it has been found that the multilayer-bound metalloporphyrin can serve as a catalyst to mediate net reactions involving the solution and support. For the particular systems investigated in these studies, we have obtained sufficient evidence to outline the dominant excited-state quenching and ground-state reaction paths involved in the overall reactions. In addition, by taking advantage of the precision and versatility of the monolayer assembling technique, it has been possible to gain some idea of the range and extent of the different interfacial processes involved in these reactions.

Experimental Section

Materials. The $\alpha,\alpha,\alpha,\alpha$-tetraaminophenylporphyrin was prepared as described by Collman and co-workers.[25] The (4,0) atropisomer was isolated chromatographically and converted to the corresponding hexadecyltetramide (H_2PF,THA) as described previously.[25,26] The purity of the (4,0) atropisomer was checked by high-pressure liquid chromatography.[26] The tin(IV) complex was prepared as described earlier by a slight modification of the procedure of O'Rourke and Curran;[12,27] its purity was routinely checked by thin layer chromatography (one spot R_f 0.75) on silica gel with *N*,*N*-dimethylformamide as eluent. Triethylamine, *N*,*N*-dimethylaniline, and diisopropylethylamine were purified by vacuum distillation prior to use. Photopurified hydroquinone (Mallinckrodt) and *p*-dimethoxybenzene (Aldrich) were used as received. The aqueous solutions used in the photochemical and photoelectrochemical experiments were prepared within 24 h of their use. All other chemicals were reagent grade and were used as received.

Low-doped n-type SnO_2 optically transparent electrodes (OTE)[21] were received as a gift from Professor R. W. Murray. These were treated with refluxing heptane for several hours to remove grease or other organic substances. They were then etched with dilute (<0.1 M) nitric acid, rinsed several times with triply distilled water, and air-dried. Platinum oxide (PtO_2) coated slides were prepared by spraying aqueous hexachloroplatinic acid (10^{-3} M) on red-hot quartz slides. The coated slides were subsequently etched with dilute nitric acid, washed with water, and air-dried. The glass and quartz slides were cleaned by procedures previously reported.[28]

Monolayer Film and Multilayer Deposition Studies. The general methods used for preparing films and assemblies have been described elsewhere.[28] Most studies employed a double-barrier round trough of the type designed and described by Fromherz.[29] The tin porphyrin, SnPF,THA·X_2, was introduced to a clean water solution as the chloride salt (X = Cl) by spreading a 4×10^{-4} M solution in chloroform. In most studies layers of pure tin porphyrin were prepared; however, mixed layers with arachidic acid also show good behavior and could be used to form supported multilayers. In typical experiments, 20 μL of the solution were added in small portions from a microliter syringe. The layer was allowed to sit for at least 2 min to permit the chloroform to evaporate, and then the barriers were compressed. The molecular area for the pure tin complex at 20 dyn/cm is 129 Å^2. The layers were transferred at this pressure to various supports at a speed of 1 cm/min; transfer ratios of 1 ± 0.05) were obtained in each case. For each of the supports employed in these studies the layers were deposited by first withdrawing the immersed support through the film and by a subsequent procedure of consecutive immersion and withdrawal until the desired number of layers was obtained.[28]

Photochemical Studies. Photochemical experiments were carried out by immersing slides coated with multilayers of SnPF,THA·X_2 in 2- or 5-mm pathlength spectrophotometer cells provided with a ground-glass joint and stopper to facilitate bubble deaeration with nitrogen or argon. In general the reductant was present as 2×10^{-3} M aqueous solution in contact with the multilayer-coated slide. The light source was a "super-pressure" 200-W mercury lamp filtered through a grating monochromator (Bausch and Lomb 33-86-02) and an 0-51 Corning glass filter. For most experiments 430-nm light was used. Conversion of the tin porphyrin to reductive addition products (chlorin and isobacteriochlorin) was followed by monitoring absorbance changes in the visible on a Perkin-Elmer spectrometer. In the experiments where singlet oxygen was generated, *N*,*N*-dimethylnitrosoaniline and imidazole were added to the aqueous solutions as a singlet oxygen detector trap.

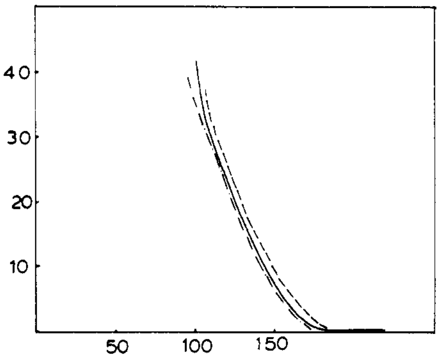

Figure 1. Pressure–area isotherms for SnPF,THA·Cl_2 spread over different subphases: (—) $CdCl_2$ (curve for ClO_4^- is superimposable); (---) HCO_3^-; (–·–) pure pyridine. Ordinate is dyn/cm; abscissa is area/molecule in square angstroms.

ESR Experiments. The photochemical ESR experiments were carried out using a cell containing an ESR flat cell fused to a reservoir in which the slide containing the supported multilayer assembly was immersed. The solution was magnetically stirred so that an exchange of the aqueous solution between the ESR flat cell and reservoir occurred. The deaerated aqueous solution contained the spin traps 5,5-dimethyl-1-pyrroline 1-oxide (DMPO). The apparatus was positioned with the flat cell in the ESR cavity and with an appropriately filtered light beam directed toward the supported multilayer assembly in the reservoir. The spectrometer was a Bruker ER-20 with an ER-400X-RL cavity.

Laser Flash Photolysis. Slides containing one or multiple layers of SnPF,THA·X_2 were exposed to the 347-nm beam of a ruby laser equipped with a steady transient monitoring lamp. Experiments were carried out with dry slides, contained in an argon-purged tube or with slides immersed in aqueous solutions with or without reductants present.

Photoelectrochemical Experiments. Photocurrents were measured in a single-compartment Pyrex cell. A 1-cm^2 polished platinum foil was used as the counter electrode and was mounted permanently in the cell. A SnO_2 optically transparent electrode (OTE) coated with one or more layers of SnPF,THA·X_2 was used as the working electrode. Electrical contact was established by clipping the electrode directly to a lead connected with alligator clips or with a copper foil between the electrode and clips. The electrodes were covered with a 0.2 M aqueous potassium chloride solution containing the reductant. The aqueous solution was deaerated by purging with nitrogen for about 40 min, and the atmosphere above the solution was continuously flushed with nitrogen throughout the experiment. The irradiations employed the lamp described above; 0-51 Corning glass filters were used in conjunction with the monochromator for experiments with light above 500 nm to ensure no leakage of UV light onto the multilayer. Photocurrents were measured with a Keithley microvolt ammeter (Model 150B). When the lamp shutter is closed there is a small dark current (ca. 10 nA). When the shutter is opened the maximum steady-state photocurrent is reached in 1.2 s. The steady-state current is generally stable for several minutes; upon closing the shutter the current decays within a few seconds. Action spectra were obtained by measuring the difference between current measured with the shutter opened and closed.

Results

Monolayers and Supported Multilayers of SnPF,THA·X_2. Although a number of the porphyrins and metalloporphyrins previously studied in monolayer films and assemblies give structurally unstable films collapsing at low surface pressures or forming stable films only in mixtures,[12,30,31] the tin porphyrin was

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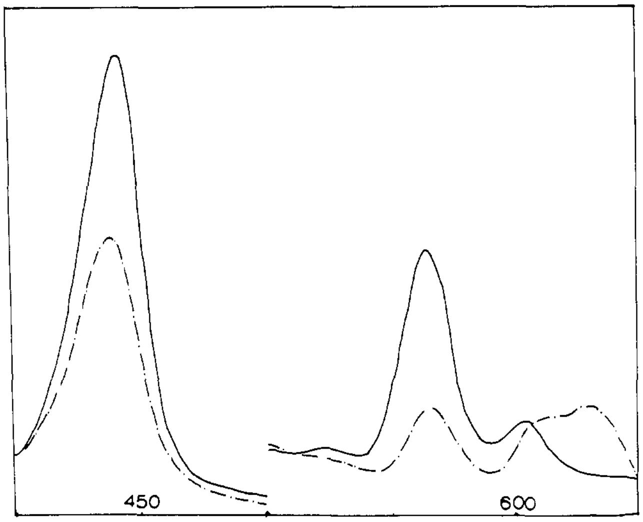


Figure 2. Absorption spectra of multilayer assemblies of SnPF,THA·X_2 on glass: (—) spectrum of a nine-layer assembly prior to irradiation; (-·-) spectrum obtained after irradiation of the assembly at 436 nm for 240 min (filtered 1000-W Hg–Xe lamp) in the presence of aqueous *N*,*N*-dimethylaniline (2.5 mM) with argon purging.

found to form highly stable films giving good isotherms (Figure 1) which can readily be transferred to a variety of supports. Assemblies containing several multilayers are readily obtainable from these films by the usual techniques; the transfer ratios are close to unity, suggesting little or no rearrangement as the layers are transferred. The isotherms of films of the tin porphyrin (Figure 1) show virtually no sensitivity to anions added to the aqueous subphase such as ClO_4^- or HCO_3^-. Films spread over pure pyridine gave very similar isotherms; while these films appeared stable, no attempt was made to transfer layers from a pyridine–air interface. The area/molecule at 20 dyn/cm is 129 Å^2 which is larger than the cross-sectional areas of four paraffin chains;[28] this area is in reasonable agreement with that anticipated for a porphine derivative with no β-alkyl substituents on the pyrrole rings.[32] Absorbance measurements at various incident angles suggest that the porphyrin chromophore is oriented randomly in the plane of the support (layer plane).[28] The absorption spectrum in the multilayer assemblies (Figure 2) is very similar to that obtained for the same or other tin porphyrins in solution. That the porphyrin is not substantially altered during the layering process[31] is confirmed by the finding that solutions of the tin porphyrin rinsed off of the rigid supports give identical spectra to unlayered analytical samples.

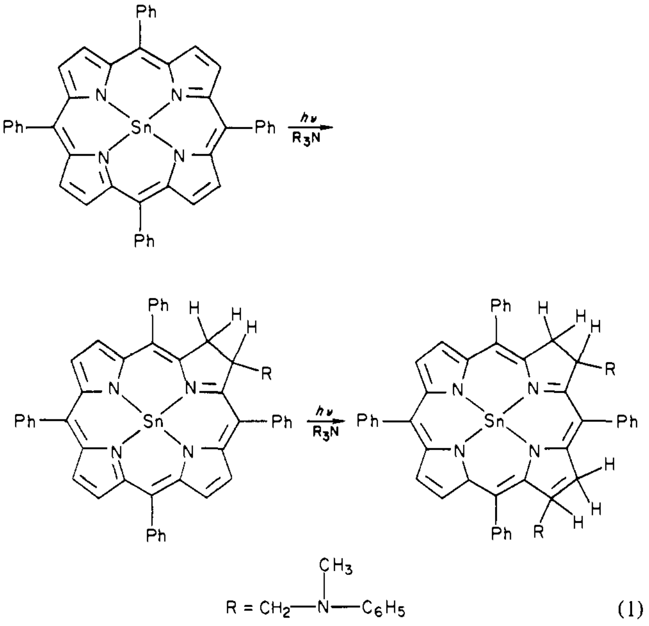
The tin porphyrin multilayers were examined by ESCA on glass supports. The ESCA spectra obtained confirmed the regular or homogeneous character of the supported multilayers (five-layer samples were used); silicon was not detected but good signals were obtained for tin (497.9, 489.2 eV), oxygen (533.1, 535.3 eV), nitrogen (422.2 eV), and carbon (293 eV). The fact that chlorine was not detectable in the anticipated region (ca. 200 eV) indicates that the chloride anion present in the analytical sample, SnPF,THA·Cl_2, must be exchanged during the layering process. The ESCA results are thus consistent with the porphyrin being either a dihydroxy or oxo compound (X = OH or $^1/_2O$); this would not be surprising in view of other studies with tin(IV) porphyrins which indicate an affinity for oxygen ligands.[33,34] The supported multilayers of the tin porphyrin show good stability on standing in the dark and do not rapidly degrade upon immersion in water.

Photoreduction Studies. As reported previously,[12] irradiation of glass-supported multilayers of SnPF,THA·X_2 in contact with aqueous $SnCl_2$ leads to spectral changes consistent with consecutive reduction of the metalloporphyrin first to the chlorin and subsequently to the dihydrochlorin or isobacteriochlorin (eq 1) as had been earlier observed in solution.[35-39] When glass-supported assemblies containing variable numbers of layers are immersed in aqueous solutions containing organic reductants such as *N*,*N*-dimethylaniline, tertiary alkylamines, hydroquinone, or 1,4-di-

Table I. Reductive Photoaddition to Multilayer-Incorporated Tin Porphyrins on Various Supports

no. of layers	support	irradiation time, min[a]	reductant (mM)	% reaction[b]
1	glass	100	DMA[c] (2.5)	12
1	glass	60	DIPEA[d] (2)	5
1	glass	100	DIPEA (2)	9
1	glass	200	HQ[e] (6)	10
1	SnO_2	100	DIPEA (2)	0
1	SnO_2	150	DIPEA (2)	0
1	SnO_2	100	TEA[f] (3)	0
1	SnO_2	90	DMA (3)	0
1	SnO_2	200	HQ (6)	0
1	PtO_2	150	HQ (6)	0
1	PtO_2	150	DIPEA (2)	0
3	glass	90	DMA (2.5)	9
3	glass	400	HQ (6)	14
3	SnO_2	180	DMA (2.5)	3
3[g]	PtO_2	90	DMA (2.5)	<2
7[g]	SnO_2	120	DMA (2.5)	12
7[g]	glass	120	DMA (2.5)	22
9	glass	90	TEA (3)	7
9	glass	90	*p*-dimethoxybenzene (2)	22
15	glass	60	HQ (6)	<2
15	glass	100	HQ (6)	2
15	glass	60	DIPEA (2)	4
15	glass	90	DMA (2.5)	20

[a] Filtered 436-nm line of a 1000-W Hg–Xe lamp used as a light source; solutions were bubble-deaerated with argon. [b] Reaction followed spectrophotometrically by monitoring decrease of the Soret band intensity. [c] *N*,*N*-Dimethylaniline. [d] Diisopropylethylamine. [e] Hydroquinone. [f] Triethylamine. [g] The palladium complex PdPF,THA used in these studies.



$$R = CH_2-N(CH_3)-C_6H_5 \qquad (1)$$

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methoxybenzene and irradiated with 436-nm light, similar spectroscopic changes are observed (Figure 2, Table I). In each case the Soret band at 440 nm decreases concurrently with an increase in absorbance at 630 nm where chlorin-type products absorb. The quantum yield for reduction of a glass-supported 15-layer assembly with 0.0025 M *N,N*-dimethylaniline at 436 nm is 0.0015; this is very nearly the same as that measured in homogeneous (acetonitrile) solution containing the same concentration of amine. As with the palladium and tin porphyrin investigated earlier,[12,40] the products from these reactions could be determined chromatographically to be mostly reductive adducts rather than unsubstituted chlorins or isobacteriochlorins. In general it was observed that reaction proceeds equally well for multilayers as for single layers with the tin porphyrins and amines or 1,4-dimethoxybenzene. However, for *p*-hydroquinone the reaction was extremely slow even for assemblies consisting of only five layers; presumably this can be attributed to the hydrophilicity of this solute which should hinder to some extent its penetration of multilayer assemblies.[30]

In contrast with the glass or quartz-supported assemblies it was found that assemblies deposited on the SnO_2 OTE surfaces are relatively inert to photoreduction of the porphyrin (Table I). Thus, it was found that iradiation of a slide containing a single layer of SnPF,THA·X_2 on the tin oxide immersed in aqueous 0.0025 M dimethylaniline with 436-nm light led to no changes in the absorption spectrum even after several hours of irradiation; under comparable conditions with a single layer on glass the disappearance of the porphyrin to chlorin and subsequent products is nearly complete.

Similar results were observed in experiments with triethylamine and hydroquinone as reductants; under conditions where appreciable reaction is observed for a glass-supported monolayer there is no reaction for a monolayer on SnO_2 OTE slides containing 3, 5, 7, and 15 layers of the tin porphyrin. While the reaction of the three-layer assemblies with dimethylaniline was strongly suppressed at long times (2 h), some reduction product could be detected. For the assemblies containing 5, 7, and 15 layers, photoreaction of the tin porphyrin with dimethylaniline was readily detectable, but the rate of reaction (Table II) was always slower than for a glass slide containing the same number of layers and irradiated under identical conditions.

Cyclic voltammetry on the layers of tin porphyrin supported on SnO_2 OTE and immersed in water showed reversible reduction waves at −0.94 V, very close to those observed for similarly substituted tin tetraphenylporphyrins in organic solvents. The waves can be observed for a single layer on the SnO_2 or for multiple layers; in the latter case they become somewhat broader as the number of layers is increased past 10. Addition of dimethylaniline to an aqueous solution into which an electrode containing a single monolayer of the tin porphyrin was immersed resulted in appearance of a new reduction peak having $E_{1/2} = -1.1$ V.

The suppression of the reductive photoaddition reaction of supported metalloporphyrins is not restricted to tin porphyrins or SnO_2 surfaces. It was found, for example, that photoreaction of a single layer of PdPF,THA by aqueous triethylamine (0.003 M) was totally suppressed on SnO_2 OTE under conditions where more than 10% reaction on glass is observed. Single layers of the tin porphyrin deposited on PtO_2 sputtered on quartz slides immersed in aqueous triethylamine (0.003 M) were also found to be relatively unreactive compared to assemblies on glass (Table I).

Table II. Comparison of Interfacial Photoreaction of Tin Porphyrins in Multilayers Supported on Glass and SnO_2 Optically Transparent Electrodes with Tertiary Amines in Aqueous Solution[a]

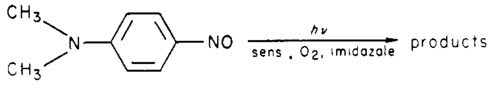
no. of layers of porphyrin	support		reductant (mM)	time of irradiation, min
	glass % reaction	SnO_2 % reaction		
1	9	0	DIPEA (2)	100
3	9	3[b]	DMA (2.5)	90
5	20	5	DMA (2.5)	120
7	12	5	DMA (2.5)	120

[a] For conditions, see Table 1. [b] 180-min irradiation time.

To determine the origin of the resistance of the tin porphyrins layers on SnO_2 OTE surfaces to interfacial photoreduction, several experiments were carried out. It has been well established that several porphyrins and metalloporphyrins can sensitize production of singlet oxygen from their excited triplets (eq 2).[41-43] If this

$$P^{3*} + O_2 \rightarrow P + O^{1*}_2 \qquad (2)$$

process occurs interfacially, excitation of the porphyrin found in supported monolayers or multilayers should produce reaction of singlet-oxygen-sensitive substrates in solution. Recently a new method for determining singlet oxygen in aqueous solution has been developed.[44,45] This makes use of a primary acceptor, imidazole, which subsequently, after oxidation, induces reaction of the substrate *p*-nitrosodimethylaniline (NDMA). The bleaching of NDMA can be easily followed spectroscopically. Irradiation



(3)

of a single monolayer of tin porphyrin supported on a quartz slide was found to promote reaction of the NDMA, presumably through a sequence of eq 2 and 3. Comparison studies were carried out in which quartz and SnO_2 OTE slides, each containing a single monolayer of SnPF,THA·X_2 in contact with aerated aqueous solutions of NDMA and imidazole, were irradiated (436 nm) under identical conditions. In each case the yield of NDMA photooxidation for the quartz- and SnO_2-OTE-supported layers was the same within experimental error. No reaction occurred on irradiation of the solution themselves or blank slides immersed in them.

In previous studies we have demonstrated that photoreactions involving oxidation of amines via an electron-transfer mechanism can be monitored by trapping of the neutral radicals formed via eq 4 and 5.[46,47] A good trap for the radicals derived from oxidation

$$Ox^* + RCH_2NR'_2 \rightarrow Ox^{-}\cdot + RCH_2\overset{+}{N}R'_2 \qquad (4)$$

$$R\text{-}CH_2\text{-}\overset{+}{N}R'_2 + B \rightarrow BH^+ + R\text{-}CH\text{-}NR'_2 \qquad (5)$$

of triethylamine and *N,N*-dimethylaniline is 5,5-dimethyl-1-pyroline 1-oxide (DMPO). To determine whether amine radicals are generated in the various interfacial systems, slides containing one and five layers of tin porphyrin on glass were immersed in aqueous triethylamine (0.003 M) containing ca. 0.01 M DMPO and irradiated in a stirred two-part cell consisting of a reservoir containing the slide (irradiated) and an ESR flat cell placed in the ESR cavity. Upon irradiation of the porphyrin-containing assemblies, both samples gave rise to readily detectable ESR spectra with the characteristic hyperfine for the DMPO adduct of the triethylamine-derived radical $CH_3\dot{C}HNEt_2$.[46] This indicates that these radicals are generated in the interfacial photoprocesses and that some of the radicals survive sufficiently long to be trapped by the DMPO. Similar experiments were performed using layers of the tin porphyrin supported on SnO_2 OTE. For these samples, for which essentially no net reaction of the porphyrin is observed, the same ESR spectrum obtained from the glass-supported layers was observed. However, the ESR signal from DMPO-trapped radicals was nearly 10 times more intense for the SnO_2-OTE-

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Table III. Photocurrents Generated by Irradiation of Monolayers of Tin Porphyrins Supported on SnO_2 Optically Transparent Electrodes and Contacted with Aqueous Solutions of Potential Reductants

reductant[a]	photocurrent ±15% (nA)	% reaction[b] ± 15%
TEA	75	7
DMA	300	20
DIPEA	65	6
HQ	200	2
p-dimethoxybenzene	125	22

[a] 2 mM dissolved in water containing 0.2 M potassium chloride. [b] Amount of chlorin-type product observed by irradiating 10-layer assemblies on glass slides at 436 nm in 90 min.

supported layers than for the glass-supported assemblies in which net photoreaction of the tin porphyrin occurs.

Laser flash photolysis studies were performed using glass and SnO_2-OTE-supported assemblies of SnPF,THA·X_2, both dry (deaerated) and immersed in aqueous (0.003 M) triethylamine solutions. With the 347-nm excitation provided by the ruby laser, it was found that both glass- and SnO_2-OTE-supported assemblies undergo a reversible bleaching of the intense porphyrin transition at 440 nm; in addition transients absorbing at 397, 425, 500, and 600 nm were observed following laser flash excitation. The duration of transients and bleaching was ca. 8 ms for both samples, and the transient changes were generally similar to those observed upon flash photolysis of tin(IV) tetraphenylporphyrin dichloride in acetonitrile.[48] Flash excitation of supported assemblies (five layers) in aqueous triethylamine also leads to transient bleaching at 440 nm; for the glass-supported assemblies the bleaching is partially irreversible while for the SnO_2-OTE-supported assemblies complete recovery on the first few flashes is observed. While it is not possible to establish with certainty the nature of the transients detected in these studies, the lifetimes obtained and the similarity of the transient spectra obtained for the "dry" films to that obtained for the tin porphyrin in acetonitrile suggests that the transients detected are triplet states of the assembly-incorporated tin porphyrin.

Photoelectrochemical Experiments. Since the above-described studies indicated that irradiation of SnO_2-OTE-supported layers of SnPF,THA·X_2 immersed in aqueous reductants did result in oxidation of the solution-phase reductants, it appeared reasonable that the net unreactivity of the porphyrin might be attributable to electron-transfer processes involving the reactive support. Consequently studies were undertaken to investigate the possibility that irradiation of the SnO_2-OTE-supported porphyrin was found to give appreciable photocurrents for several reductants as indicated in Table III. The action spectrum for the photocurrent obtained with aqueous *N*,*N*-dimethylaniline as a reductant is shown in Figure 3; the spectrum shows a clear maximum corresponding to the porphyrin Soret band which is not present for a blank slide and a smaller net photocurrent in the region where the porphyrin absorbs in the visible. The maximum photocurrent obtained for monolayer-coated slide of SnO_2 OTE corresponds fairly closely to the extent of photoreaction obtained on glass slides for monolayers for each reductant except hydroquinone.

Photocurrents were also investigated for SnO_2-OTE-supported assemblies containing several multilayers as a function of reductant and the number of layers of porphyrin. For a relatively hydrophobic reductant[12] such as triethylamine, the photocurrent increases as the number of layers increases (Figure 4) until a maximum value is obtained at ca. seven layers of porphyrin. In contast, for the more hydrophilic reductant hydroquinone the photocurrent reaches a maximum at four layers and then decreases sharply as additional layers are added. Much smaller photocurrents were observed when layers of tin porphyrin deposited on platinum oxide or foil were irradiated in the presence of aqueous reductants; since these currents were close to the limit of reliable detection, no detailed studies were done on the effect of layer geometry or reductant.

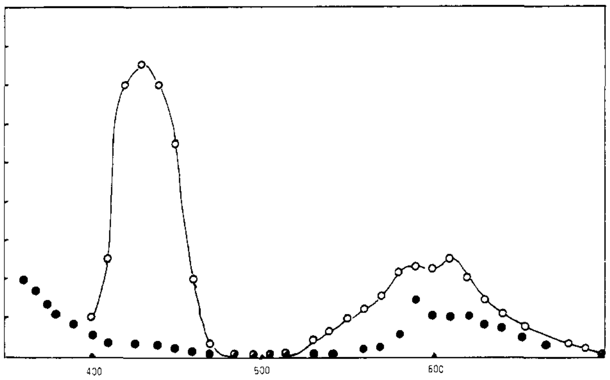

Figure 3. Spectral response for photocurrent obtained upon irradiation of a single monolayer of SnPF,THA·X_2 on SnO_2 OTE immersed in aqueous triethylamine (3 mM): (○) responses for the porphyrin-coated slide; (●) responses for a SnO_2 OTE slide not coated with porphyrin. The spectral response is not corrected for light intensity variations with wavelength or for the fraction of light absorbed. The ordinate is the light-induced current in nanoamperes and the abscissa is the wavelength in nanometers.

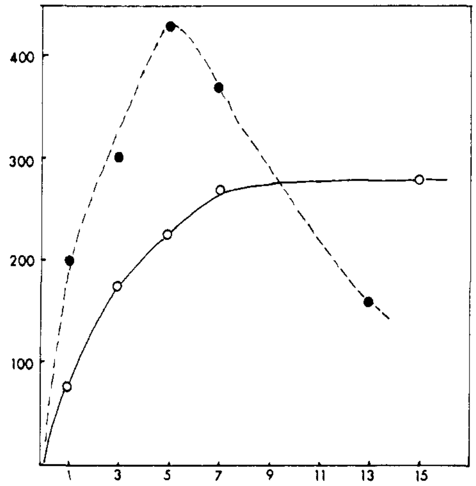

Figure 4. Effect of the number of layers of SnPF,THA·X_2 on the photocurrent obtained on irradiation at 436 nm with different aqueous solutes present: (—) (open circles) shows the current for different layers in the presence of 3 mM triethylamine; (- - -) (dark circles) shows the current obtained for 6 mM *p*-hydroquinone. The ordinate is the light-induced current in nanoamperes. The abscissa is the number of layers of tin porphyrin coating the SnO_2 OTE slide.

The quantum efficiency for electron flow initiated by irradiation of a monolayer assembly of SnPF,THA·X_2 on SnO_2 OTE contacted with 0.002 M *N*,*N*-dimethylaniline is estimated as 2.4×10^{-3}. This is very close to the photoreduction quantum efficiency observed for tin(IV) tetraphenylporphyrin dichloride for the same reductant in acetonitrile solution. The photocurrents obtained for the SnO_2-OTE-supported porphyrins are stable for several minutes and decay only slowly thereafter. From the light intensity used in these experiments (4×10^{-8} einstein/s) and the quantum yield, it can be estimated that approximately $^1/_{85}$th of the assembly-bound porphyrin reacts every second. Thus, modest turnover numbers for the photocurrent can be estimated indicating the tin porphyrin functions as a photocatalyst in the net photoelectrochemical reaction.

Discussion

Present and previous[12] studies have shown that glass-supported multilayers of SnPF,THA·X_2 are photoreactive toward amines and other reductants at interfaces in reactions similar to those occurring with the same reagents in homogeneous solution. The reaction occurring with tertiary amines such as *N*,*N*-dimethyl-

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(48) Chandrasekaran, K., unpublished results.

aniline, triethylamine, or diisopropylethylamine as the reductant is summarized in eq 6–9 where SnPF is an abbreviated symbol

$$\mathrm{SnPF} \xrightarrow{h\nu} \mathrm{SnPF}^{1*} \xrightarrow{\mathrm{isc}} \mathrm{SnPF}^{3*} \qquad (6)$$

$$\mathrm{SnPF}^{3*} + \mathrm{RCH_2NR'_2} \rightarrow \mathrm{SnPF}^{-} + \mathrm{RCH_2}\overset{+}{\mathrm{N}}\mathrm{R'_2} \qquad (7)$$

$$\mathrm{SnPF}^{-} + \mathrm{RCH_2}\overset{+}{\mathrm{N}}\mathrm{R'_2} \rightarrow \mathrm{SnPFH}\cdot + \mathrm{R\dot{C}HNR'_2} \qquad (8)$$

$$\mathrm{SnPFH}\cdot + \mathrm{R\dot{C}HNR'_2} \rightarrow \text{products} \qquad (9)$$

for the multilayer-incorporated surfactant tin porphyrin, SnPF,THA·X_2. This mechanism is clearly interpreted when the porphyrin is supported on the potentially reactive supports SnO_2 OTE, PtO_2, or platinum foil; the results shown in Tables I and II demonstrate that the "normal" reaction is essentially stopped for monolayer coverage and attenuated for multilayers up to several. There are a number of potential sources for quenching the interfacial photoreaction by the support. For example, Memming,[7,11] Bolton,[10] and Honda[9] have all observed photocurrents which evidently arise via quenching of excited states coated as surfactant monolayers or otherwise physically attached to semiconductor (SnO_2) or metal electrodes. Thus, it would not be unreasonable to expect that quenching of either excited state formed in eq 6 could be responsible both for the observed photocurrent as well as the inhibition of net photoreaction of the porphyrin. However, a number of the results presented above indicate that direct quenching of excited states produced in the multilayer assemblies is not an extremely important process and further that it plays a relatively small role both in inhibiting the photoreduction or in generating the current in the photoelectrochemical experiments.

The above conclusion can be reached from several pieces of evidence. The laser flash photolysis studies show relatively long-lived transients occurring for both glass- and SnO_2-OTE-supported multilayers having lifetimes, intensities, and spectra similar to each other and to those for structurally similar tin porphyrins in solution. Furthermore, the interfacial studies on singlet oxygen sensitization by irradiation of supported tin porphyrin assemblies give essentially the same yield of net oxygenation product for both "inert" (glass) and "active" (SnO_2) supports. This implies that the yield of interceptable tin porphyrin triplet states is the same for both assemblies. A third piece of evidence suggesting that direct quenching of porphyrin excited states by the support is not of major importance is the observation that the photocurrents obtained in the photoelectrochemical experiments are strongly dependent upon the nature of the reductant and the number of layers of porphyrins (Figure 4, Table III); indeed, there is no photocurrent produced unless a reductant is present. Finally the ESR studies indicate that radicals produced by the oxidation of amine are trapped when multilayers of porphyrin on either glass or SnO_2 are irradiated; the fact that yields are substantially higher for the latter support suggests that reaction 9 may be inhibited to some extent with the SnO_2 support, perhaps by depletion of the porphyrin radical.

Thus, while the above discussion suggests that quenching of porphyrin excited singlet and/or triplet states is relatively unimportant in explaining the photoelectrochemical effects and the lack of net porphyrin photoreduction on the SnO_2 and platinum supports, it is clear that one of the intermediates produced subsequent to the triplet in eq 7–9 must be "quenched" in such a way as to produce an anodic photocurrent and regenerate ground-state porphyrin. The reported potentials for the first one-electrode oxidation and reduction of octoethylporphyrin tin(IV) dihydride are +1.4 and −0.90 V, respectively;[49–51] we have confirmed values close to this for tin(IV) tetraphenylporphyrin dichloride (+1.475 and −0.91 V, respectively) and for SnPF,THA·Cl_2 in methylene chloride.[48] Considering the reported conduction band level for SnO_2 of ca. 0.2 V,[9] we would anticipate that both direct oxidation of the neutral excited states (SnPF,THA·X_2^*) or the reduced form (SnPF,THA·X_2^-) should be energetically favorable, the latter being the more favorable process by ca. 0.3 V. The potential for the reduced, protonated species, radical SnPFH (or SnPFH,THA·X_2·), should probably also be favorable for reduction of the SnO_2 conduction band but certainly less favorable than that for SnPF,THA·X_2^-. The regeneration of the porphyrin starting material probably involves either or both reactions 10 or 11. Since

$$\mathrm{SnPF}^{-} + \mathrm{SnO_2} \rightarrow \mathrm{SnPF} + \mathrm{SnO_2}^{\mathrm{red}} \qquad (10)$$

$$\mathrm{SnPFH}\cdot + \mathrm{SnO_2} \rightarrow \mathrm{SnPF} + \mathrm{H}^{+} + \mathrm{SnO_2}^{\mathrm{red}} \qquad (11)$$

relatively low light intensities were used in all of the steady-state experiments, it is not likely that excessive "charging" of the SnO_2 should occur. Any products such as hydrogen or other reduced products resulting from discharge of the trapped electrons would be difficult, if not impossible, to detect at the levels produced under the conditions employed. At present it is impossible to distinguish between the two possibilities; the presence of relatively basic solution such as the amines should certainly facilitate reaction 11. However, the observation that surface-multilayer interactions can extend over several layers suggests that there is some migration of the reduced species from noncontacting layers of the tin porphyrin to the reactive support. This could suggest that the predominant reductant is $SnPF^-$ and that simple electron-hopping is the mode of interaction by which porphyrin in separated layers gives rise to photocurrents. This could also account for the increased yield of trappable amine radicals $R'\text{-}\dot{C}H\text{-}NR'_2$ when the irradiated porphyrin is supported on SnO_2 compared to glass. Other studies from our laboratories suggest that while this radical is a reasonably good reducing agent, its potential may not be sufficient to directly reduce the tin porphyrin;[52,53] hence its survival could be enhanced by rapid interception of reduced porphyrin by reaction 10. Formation of the amine radical could readily occur, as demonstrated previously, by amine-induced deprotonation (eq 12).[47] The enhanced yield of trappable amine radicals suggests

$$\mathrm{RCH_2}\overset{+}{\mathrm{N}}\mathrm{R'_2} + \mathrm{R'_3N}\!: \rightarrow \mathrm{R_3NH^+} + \mathrm{R\dot{C}HNR'_2} \qquad (12)$$

that this radical is not appreciably oxidized by the SnO_2 support; since its potential should be sufficient to reduce the semiconductor, the enhanced yields of trapped radicals probably reflect favorable competition between escape of the radical to the solution (from the multilayer) vs. migration to the support–multilayer boundary.

The apparent failure of the SnO_2 to efficiently oxidize excited triplet states of the porphyrin in even the first monolayer is rather remarkable. Since it appears reasonable that there should be good contact between the porphyrin chromophore and the support in these assemblies,[54] excited-state electron transfer would be expected to occur readily. Furthermore, the long lifetime of the assembly-bound triplet suggests that even relatively slow quenching should be able to occur with reasonable efficiency. It is perhaps possible that the excited-state energies or redox potentials are altered in the assemblies from those measured in dilute solution; however, the fact that "normal" photoreduction reactions occur for glass-supported assemblies suggests these alterations must not be too severe.

The overall sequence of reactions occurring for the SnO_2- (and Pt- and PtO_2-) supported assemblies is interesting for several reasons. First of all, the overall reactions occur by a three-way cooperation involving the support, the irradiated monolayer or multilayer, and the solute dissolved in the aqueous solution. The controlled structure of the monolayer assembly–support solution system allows the photoexcited porphyrin to serve as a catalyst for a redox reaction involving the solution species and support which would otherwise not occur, and at the same time the

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(54) Even if the perpendicular phenyl rings hold the porphyrin from direct contact, the distance between porphyrin and support shold be only a few (<3) Å.

"normal" photoreaction of the porphyrin is suppressed. We have previously shown that tin(IV) tetraphenylporphyrin dichloride can function in a solution-phase photoelectrochemical process with the same amines as reductants; here, however, rapid conversion of the porphyrin to a partially reduced species occurs, severely limiting the stability and steady-state current of the cell.[55] The most significant aspects of this study is the clear delineation of the effect of thickness of the multilayer and solute penetration on the three-way cooperative process. Thus, we find that for relatively hydrophobic solutes such as triethylamine or *N*,*N*-dimethylaniline, which readily penetrate the multilayers, there is an increase in the photocurrent up to ca. nine layers; at the same time there is considerable retardation of the "normal" photoreaction for these solutes with up to at least seven layers of porphyrin. Since the layer thickness should be on the order of 30 Å, the fact that quenching is observed suggests that the reactive porphyrin intermediate intercepted in eq 10 or 11 can migrate over distances in the range 210–270 Å. Experiments are currently underway to determine if this distance can be adjusted by the addition of cosurfactants including ones with extensive unsaturation or other redox active groups.

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Registry No. SnO_2, 18282-10-5; PtO_2, 1314-15-4; SnPF,THA·Cl_2, 83152-03-8; O_2, 7782-44-7; PMA, 121-69-7; DIPEA, 7087-68-5; HQ, 123-31-9; TEA, 121-44-8; PdPF,THA, 83152-04-9; platinum, 7440-06-4; *N*,*N*-dimethyl-*p*-nitrosoaniline, 138-89-6; imidazole, 288-32-4; *p*-dimethoxybenzene, 150-78-7.

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Direct Measurement of the Chemical Shift Anisotropy of Thallium-205 Using the Matrix Isolation Technique. The $Tl/K/NO_3$ System

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Abstract: Solid-state NMR spectra of ^{203}Tl and ^{205}Tl in pure $TlNO_3$ and mixtures of $TlNO_3$ with various monovalent metal nitrates have been determined in order to evaluate the magnitude of the thallium shielding anisotropy in ionic environments. The room-temperature line width of pure $TlNO_3$ arises mainly from indirect scalar exchange interactions and chemical shielding anisotropy at 2.114 T. Samples prepared from mixed melts of $TlNO_3$ with $LiNO_3$, $NaNO_3$, or $AgNO_3$ show ^{205}Tl spectra identical with those of pure $TlNO_3$ from 25 to 160 °C, suggesting ion segregation in the solid. Dramatic narrowing of the resonance line in $Tl/K/NO_3$ mixtures allows observation of NMR powder patterns which strongly reflect the microscopic structure of KNO_3. At room temperature, the shift is about −300 ppm, suggesting high ionic character, and $\sigma_\perp - \sigma_\parallel$ is about 50 ppm. Above the KNO_3 II → I phase transition at 128 °C, the shielding is nonaxially symmetric with $\sigma_{33} - \sigma_{11}$ of about 90 ppm. The large $\Delta\delta$ values exhibited by thallium in this ionic system suggest the potential for enormous shielding anisotropies in covalent thallium compounds.

Among the areas of vigorous current research in NMR spectroscopy is the study of nuclei undergoing restricted motion. Although the practical difficulties associated with these studies can be formidable, the efforts of a growing number of laboratories have produced a significant body of knowledge concerning the NMR properties of spins in rigid or semirigid systems. This is especially true of some of the "classical" nuclides (e.g., ^1H and ^{13}C) but is much less true of many of the other observable elements in the periodic table.

One of the most interesting among this latter group is thallium. Two common isotopes exist, both with spin $^1/_2$. The most abundant (70.5%) is ^{205}Tl with a magnetogyric ratio of 15.44×10^7 rad s^{-1} T^{-1}, while ^{203}Tl makes up the remaining 29.5% and possesses a magnetogyric ratio of 15.29×10^7 rad s^{-1} T^{-1}. ^{205}Tl has an excellent NMR receptivity (0.1355 relative to ^1H) and a chemical shift range approaching 7500 ppm, making it an attractive probe for NMR investigations of chemical systems.

It is clear that a better understanding of the NMR shielding tensor properties of thallium will enhance its value as a probe, even in solution. This has been demonstrated, for example, by the recent finding[1] that the ^{205}Tl shielding anisotropy of the solid Tl(I)–valinomycin complex is actually much smaller than predicted[2] from spin–lattice relaxation times in solution. The shift of this ionic complex nevertheless exhibits a surprisingly large anisotropy of 150 ppm. Few other thallium chemical shift anisotropies have been reported,[3-6] and highly ionic systems such as the one investigated here have been particularly neglected.

Several methods may be used to characterize the NMR shielding tensor. One approach involves measurement of the orientation dependence of the chemical shift of a single crystal, and all nine shielding tensor elements may be determined by this technique. If only a powder is available, the NMR spectrum may exhibit singularities at chemical shifts corresponding to values of

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