PHOTOCHEMISTRY OF ORGANIC CHROMOPHORES INCORPORATED INTO FATTY ACID MONOLAYERS

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Abstract - The photochemical behavior of several different chromophores in-corporated as surfactant molecules in organized monolayer assemblies is reported. For several systems rather pronounced differences are observed between reactivity in solution and in the assemblies. Many of the differences can be ascribed to packing phenomena and to restrictions on diffusion and molecu-lar motion in the condensed assemblies. Among the reactions studied which are subject to strong environmental influences in the assemblies are cis-trans photoisomerization, ligand photoejection, excimer and photodimer formation and electron transfer reactions. Photoreactions occurring at an assembly-solution interface have also been observed including the cleavage of water mediated by a layer-bound excited state of a surfactant ruthenium complex.

INTRODUCTION

It has long been known that amphipathic molecules such as fatty acids, which contain both water soluble (hydrophilic) and water insoluble (hydrophobic) groups, form monolayers when spread on water or other polar surfaces. Techniques for the study of such monolayer films were developed by Pockels (1) and Langmuir and Blodgett (2) and in many cases the films were used to investigate molecular properties such as shape and size. It was found by Langmuir as early as 1917 that monolayer films spread on water could be transferred to solid supports (ref. 3). Although the techniques for handling these films have been widely used, it has been only recently that the techniques have been refined and applied to the construction of highly organized molecular systems. Simplification and elaboration of the techniques for preparation and study of monolayer assemblies has been due largely to the investigations of Kuhn and coworkers (4-6). These investigators have also used organized monolayer assemblies to study a variety of phenomena ranging from electronic energy transfer and photographic sensitization to interference and electrooptical effects (ref. 4). To a large extent the rapid progress in the use and study of monolayer assemblies has been made possible by the application of modern spectroscopic techniques. The facility with which absorption and luminescence spectra can be obtained for monolayer assemblies on optically transparent supports suggested that these techniques might also be applied to investigate reactions and photoprocesses.

One of our chief reasons for investigating reactions in organized monolayer assemblies is that the controlled regular structure of the assembly provides a bridge between the extremes of crystalline solid and fluid solution. The intermediacy of a monolayer assembly between liquid and solid is suggested by several observations. It is generally found that chromo-phores of component surfactant molecules maintain specific orientation with respect to the layer plane (ref. 4). Studies of the distance dependence of singlet-singlet energy transfer also indicate a regular structure with the spacing anticipated on the basis of closely-packed extended chains of the hydrophobic polymethylene side chains (of component fatty acids or similar molecules (ref. 7-9). In addition, the areas/molecule measured for long chain alcohols or acids in condensed molecules are nearly the same as the cross sectional areas of hydrocarbon chains determined by x-ray analysis in crystals (ref. 10). The individual layers in a monolayer assembly are generally stable and no appreciable rearrange-ment is normally observed. On the other hand, there is considerable evidence that small to moderate size molecules can diffuse through several layers of a monolayer assembly with-out destroying the organization. It was found, for example, by Kuhn and coworkers that a surfactant diazonium salt contained as a component in a monolayer assembly could react with coupling agents as large as α-naphthol which were placed in contact with the assembly via a water solution (ref. 4, 11). Nonetheless, diffusional processes in the monolayer assembly are certainly slower than in solution; therefore the assemblies offer the possibi-lity of rendering slower but not totally inhibiting processes that depend upon diffusion or

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*Photochemical Reactions in Organized Monolayer Assemblies. VI.

large conformational changes. Unlike a crystal where the order is usually obtained by a repeating pattern with a single component, it is possible with the monolayer assembling technique to build organized assemblies containing two or more components in regular arrays. The very high local concentrations attainable within a single film-layer or between adjacent layers can often greatly exceed concentrations obtainable in solution. Not surprisingly we have found several instances of bimolecular reactions and photoprocesses occurring in monolayer assemblies which are not observable in solution.

The self-organizing properties of surfactant molecules are the basis for construction of other structurally related systems such as micelles and the lipid-bilayer portions of biological membranes and it might be expected that organized monolayer assemblies should be reasonable models for the latter systems. Although our own investigations have not yet progressed to the point of modelling closely biological or photobiological processes, it is reasonable to anticipate that some of the phenomena we have observed may have reasonable analogies in biological systems. It is the purpose of this paper to outline and summarize some of the patterns of reactivity we have observed in recent investigations of the photoreaction of several different types of surfactant molecules in condensed monolayers. In these studies we have found that both unimolecular processes such as isomerization and bimolecular reactions such as photodimerization, excimer formation and electron transfer reactions are strongly modified in the assemblies. In addition we have found that novel reactions can occur at a monolayer-solution interface between chromophores incorporated in monolayer assemblies and reactive species in solution.

RESULTS AND DISCUSSION

Unimolecular Processes
Our investigations of unimolecular photoreactions in condensed monolayer assemblies and films have centered on two processes, cis-trans isomerization of olefins and ligand photoejection in metalloporphyrin complexes. Both of these processes have been investigated in solution for the reactive chromophores used in our studies; although the same initial photoprocesses apparently occur in both solutions and condensed monolayers, the net chemical changes observed are quite different due to environmental factors.
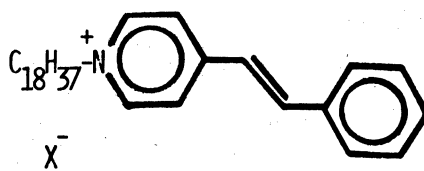
Photoisomerization phenomena have been investigated with two types of molecules containing an isomerizable olefinic link: the alkyl-substituted thioindigo dyes (1 - 3) and the surfactant N-(1-octadecyl)-4-stilbazole salts (4) (ref. 12, 13).
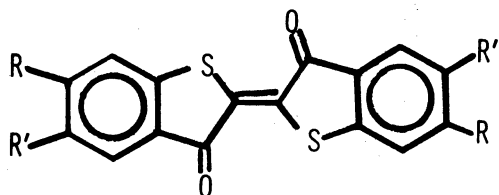
trans-1   R = n-$C_6H_{13}O^-$

trans-2:   R = H-, R' = n-C_4H_9-, R' = H-

trans-3:   R = H-, R' = tert-amyl-

trans-4

For both systems the isomerizable olefinic bond is part of a chromophore incorporated into the hydrophilic portion of the surfactant molecule. Studies with polarized light indicate that trans isomers of 1 and 4 form assemblies with the chromophore lying planar in the layer plane. The thioindigo dyes 1-3 were found to form films in mixtures with the fatty acid ester tripalmitine (TP) that were stable over a surface pressure range 5-30 dyn/cm; the films could be transferred to glass supports and assemblies consisting of several layers were readily constructed. It was possible to prepare assemblies containing nearly isomerically pure trans or cis isomers by irradiating chloroform solutions of thioindigo-TP mixtures at selected wavelengths (For 1, irradiation at 453 nm gives predominantly trans-1 while irradiation at 539 nm gives solutions containing almost exclusively cis isomer.) and by preparing the films and assemblies in the dark. Although the thermal cis→trans isomerization which is frequently observed for thioindigo dyes was not observed in the assemblies - the assemblies containing 1-3 were found to be indefinitely stable in the dark - it was found that irradiation of assemblies containing cis 1-3 led to rapid, complete and irreversible conversion to the corresponding trans isomer (fig. 1). Assemblies containing trans 1-3 prepared either from films of trans 1-3 or by irradiation of assemblies initially containing cis olefin were found to be photostable; no conversion to the cis was observed even upon prolonged irradiation. Fluorescence was observed from trans isomers for thioindigo
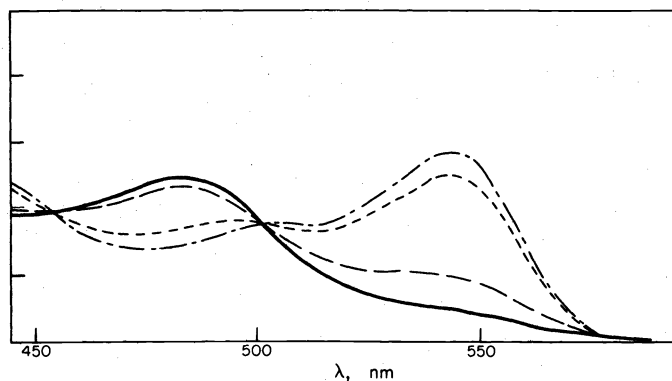
Figure 1: Absorption spectra of trans (–––) and cis (———) isomers of
1 in monolayer assemblies. (— —) and (– – –) indicate intermediate
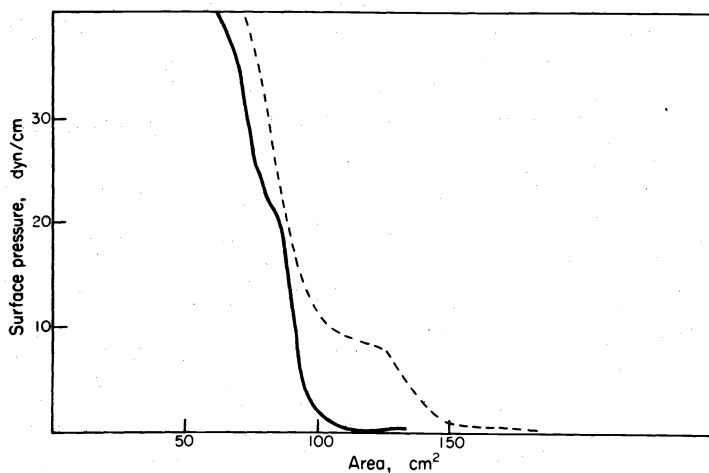points in the conversion of cis 1 to trans.

Figure 2: Surface pressure-area diagrams for films on water containing
equal amounts of: (a) cis-1:TP, 1:2 (dashed line) and (b) trans-
1:TP, 1:2 (solid line). In each case the films were prepared
from 50 μl of a CHCl₃ solution with [1] = 0.18 x 10⁻³ M and
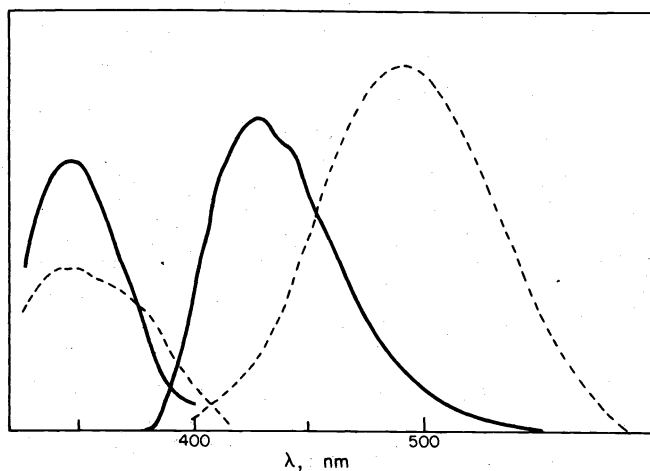[TP] = 0.36 x 10⁻³M.

Figure 3: Absorption and emission spectra of trans-4 in acetonitrile solution
(solid line) and in condensed monolayer assemblies (dashed line).

dye-olefins 1-3; for trans-1 the estimated ϕ_f is 0.1 compared to a value of 0.03 in solution. The quantum yield of cis→trans isomerization for 1 in the assemblies was estimated as 0.01-0.02, considerably lower than that obtained for similar thioindigo dyes in solution (ref. 14-16). Rapid photoisomerization of cis-1 to trans but not the reverse was also observed for spread films of pure cis-1 or cis-1:TP mixtures on a water surface. Irradiation of spread films with visible light for only a few seconds resulted in quantitative conversion.

Similar behavior has also been observed with the stilbazole derivative 4 (ref. 13) although its photoisomerization behavior has been less fully investigated due to the occurrence of other photoprocesses in assemblies containing trans-4 (vide infra). As with the thioindigo dyes, the trans isomer of 4 fluoresces but does not convert to cis-4 on irradiation in the assemblies. Irradiation of solutions containing 4 rapidly leads to attainment of a photostationary cis/trans ratio; at 366 nm this mixture is less than 30% trans. Films could be prepared from trans-4 or from the photostationary mixtures and from these films assemblies could be prepared. In general assemblies were constructed from mixtures of 4 with arachidic acid or TP. Both the solutions and assemblies prepared from photostationary mixtures showed only fluorescence from the trans isomer; however, the fluorescence from assemblies prepared from isomerically pure trans-4 is much more intense than that from assemblies prepared from the photostationary mixture. Irradiation of assemblies prepared from the photostationary mixture leads to a very rapid increase in the long wavelength absorption concurrent with an increase in the fluorescence intensity. Prolonged irradiation leads to subsequent photoreactions discussed in a later section. The changes are consistent with selective cis→trans isomerization; although the quantum yield has not been precisely determined it is in the range 0.1 - 0.5.

The results observed with the two olefinic systems are attributed to the cooperation of two factors, the molecular environmental restraints imposed by the condensed monolayer assembly and the difference in size between cis and trans isomers of the olefinic chromophores. As outlined in the Introduction, the assemblies are effectively quite viscous and rather tightly packed such that diffusion and molecular motion are considerably slower and more difficult in the assemblies than in solution. Thus a process such as isomerization which requires relatively large molecular motion should be slower and less efficient in the assemblies in any case. Molecular motion requiring a large volume expansion should be even more restricted if not prohibited during the lifetime of an excited state. For several olefins, especially stilbene derivatives, it has been shown that the planar trans isomer is smaller than the non-planar cis isomer (ref. 17, 18). For stilbene itself it has been found that during the increase in viscosity that accompanies the change from fluid media to the glassy state the cis→trans photoisomerization persists much longer than the reverse (ref. 17). It has even been suggested that the order of size is cis>twisted isomerization transition state>trans; in any case the non-planarity of the cis isomer should minimize the distortion required to reach the transition state (ref. 17, 19). Thus it is reasonable that in the assemblies the isomerization transition state is relatively easy to reach from the cis side where little volume expansion and a minimum of molecular motion are required. In contrast expansion from trans to the transition state and subsequently to cis should be a highly disfavored process. Evidence that this picture is reasonable for the thioindigo isomers comes from an investigation of surface pressure-area relationships for the two isomers in spread monolayer films with TP. Fig. 2 compares the surface pressure-area diagrams contained for the two isomers; the area for the films of trans-1 is always smaller than that for those containing the same amount of cis-1. The differences can be rather dramatically illustrated by preparing films of cis-1 in the dark and monitoring the change in surface pressure (at constant area) upon illumination. Changes of ten-fold within less than 10 sec occur on irradiation of these films (for example at an initial surface pressure of 8 dyn/cm) with even a weak (15 W) desk lamp. As mentioned previously the stilbazole isomerization in films and assemblies is not so readily investigated in detail due to the difficulty in isolating isomerically pure cis-4 and the photoreactions that ensue following the cis to trans conversion. A surface pressure-area study of trans-4 in mixtures with arachidic acid gives an area/molecule of ca. 22 $Å^2$ at 30 dyn/cm where stable films are formed. This corresponds roughly to the cross sectional area of the hydrocarbon chain (ref. 10) and suggests that the chromophore is packed in "beneath" fatty acid molecules in the film. It would thus be anticipated that the differences in surface pressure-area relationships would be smaller for the isomers of 4 even though the same general relationships probably apply.

A second type of unimolecular photoreaction which has been investigated in condensed monolayer assemblies is ligand photoejection from transition metal complexes of the porphyrins. Our work to date has focused on the ruthenium (II) porphyrins. As mentioned above the same initial photoreaction-ejection of a CO ligand-occurs in solution and condensed monolayers. The differences in overall chemistry in this case are due to the restricted diffusion in the assemblies which permits the isolation and selective reaction of intermediates which cannot generally be isolated or trapped in solution.

We have studied extensively the various photochemical, redox and thermal reactions of ruthenium (II) porphyrins in solution (ref. 20-22). A prominent reaction is the photo-

ejection of CO from the ruthenium (II) CO porphyrin; in solution the resulting CO-free intermediate rapidly reacts with solute or solvent molecules containing unshared pairs of electrons or recaptures CO. Although the CO-free intermediate can be detected in flash photolysis experiments, it is too reactive to be isolated in any experiments attempted to date. The ruthenium (II) CO complexes of the dioctadecyl ester of mesoporphyrin IX (5)and the tetradehydrocholesteryl ester of α,β,γ,δ-tetra(4-carboxyphenyl)porphine (6) have recently been prepared and found to form good films and condensed monolayer assemblies when mixed with an arachidic acid host. The complexes can be incorporated into the assemblies with either pyridine or water as the sixth ligand. Irradiation of the dry assemblies from 5 in a vacuum leads to the loss of CO; this can readily be followed by changes in the electronic spectrum of the complex. The decarbonylated species from 5 readily and completely regenerates the starting complex on admission of CO but it is stable indefinitely in the evacuated cell. If the decarbonylated species (7)is treated with nitrogen gas a new species (8) is obtained whose uv-visible spectrum is only slightly different from that of 7; this product does not change under prolonged pumping in vacuo. In sharp contrast to the results with 7, exposure of 8 to a CO atmosphere results in no instantaneous conversion to 5 but on standing a slow recapture of CO can be observed. Irradiation of the product from nitrogen treatment, 8, in the presence of CO results in an accelerated conversion to starting 5. Treatment of 7 with pyridine vapor leads to rapid formation of a species with the typical ruthenium (II) porphyrin dipyridinate structure. In contrast only slow conversion to this species occurs when 8 is exposed to pyridine vapor.

Reaction of the decarbonylated species 7 with oxygen also occurs; the resulting product (9) has a spectrum similar to that of 7 and its behavior on treatment with CO is quite so,o;ar/ The oxygen product is stable under prolonged pumping; it slowly recaptures CO.

The chemistry of the ruthenium (II) porphyrins in monolayer assemblies is summarized below:
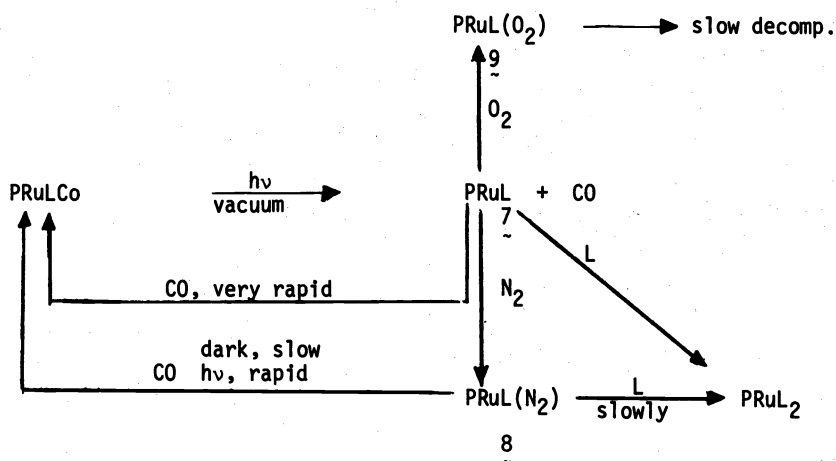
Although other aspects of the reactivity of 5 and 6 in the assemblies remain to be explored, it is clear that there are significant differences from the solution behavior. The isolation of 7 which exists only as a short-lived intermediate in solution enables the selective preparation of nitrogen and oxygen adducts 8 and 9 which are not observed in solution. Although the normal solution product can be formed in the assemblies, the control of diffusion permits isolation of intermediate 7 and its diversion to novel products.

Bimolecular Processes: Excimer Formation and Photodimerization.
As discussed in the previous section the surfactant olefin N-(1-octadecyl)-trans-4-stilbazole (4) forms good monolayer assemblies in mixtures with arachidic acid or TP. Absorption spectra from assemblies are nearly identical to those obtained for 4 in solution. However, as mentioned previously, trans→cis isomerization does not occur in the assemblies; irradiation of 4 in assemblies instead leads to two photoprocesses not observed in solution. The fluorescence from 4 in assemblies shows a pronounced red-shift from that observed in solution (fig. 3); in addition rapid disappearance of the long wavelength absorption occurs on irradiation. Since the bleaching is almost identical to that observed in crystals where dimers are the exclusive isolated product and where the same red-shifted fluorescence is observed, (ref. 24) it appears reasonable that dimer formation is also occurring in the layers and that the red-shifted fluorescence is due to an excimer intermediate in the photo-dimerization process. This is reinforced by the finding that the extent and rate of "bleaching" is dependent upon the "concentration" and configuration of assemblies containing 4 (ref. 24). The observation that the insertion of inert spacer layers between layers

containing 4 reduces the rate and extent of reaction indicates that both intralayer and interlayer reactions are occurring. Since migration of the chromophore within the assembly is expected to be very slow or non-existent the observed behavior can be attributed to the presence of dimeric sites containing two of the stilbazole chromophores in close proximity. That both dimeric and monomeric sites are present in the assemblies is also indicated by the finding of some residual long-wavelength absorption and monomer fluorescence that persists after the bleaching process ceases. As mentioned above crystals of 4 show similar behavior in cases where the anion, X⁻, is p-chlorobenzene sulfonate or p-bromobenzene sulfonate; the crystals having fluoroborate or bromide as the counterion for the stilbazole salt show only monomer fluorescence and no photodimerization (ref. 13-24). In contrast to the similarities between the photochemistry of 4 in monolayer assemblies and crystals, irradiation of 4 in micelles with cetyltrimethylammonium bromide leads to only monomer fluorescence and facile cis-trans isomerization with efficiencies comparable to those observed in solution (ref. 13).

The contrast between the behavior of 4 in micelles and in monolayer assemblies is significant. The fact that dimerization and excimer formation do not occur in micelles indicates that simply orienting the chromophores of 4 at a hydrophilic-hydrophobic interface with high local concentrations (the local concentrations of 4 are comparable in the assemblies and micelles) is insufficient to force bimolecular interactions. Micelles are generally indicated to be relatively disordered with the hydrophobic core effectively having a "liquid hydrocarbon" structure (ref. 25). In contrast condensed monolayers usually have a nearly crystalline hydrocarbon zone in which the chains are packed in a mostly "straight-up" configuration (ref. 10). As mentioned earlier the measured area/molecule of 4 is 22 $Å^2$ which is close to that indicated for hydrocarbons in the crystalline state. The interchain spacing of ordered hydrocarbons is typically ca. 4.2 Å which is within the range determined by Schmidt et al. for dimerization and excimer formation in the crystal state (ref. 26). Thus it appears reasonable that for both crystals and assemblies of 4 packing of the hydrocarbon chains leads to a structure in which the 4-stilbazole chromophores are packed favorably for excimer formation and dimerization.

It appears that the combination of packing phenomena and imbalance in the cross sectional areas of hydrophobic and hydrophilic portions of surfactant molecules can lead to the formation of dimeric or aggregated sites in assemblies as a fairly general phenomenon. The diene 10 which is structurally similar to 4 shows very similar photobehavior in both crystals and condensed monolayers. A difference in the latter phase is the finding that the photodimerization of 10 is apparently entirely an intralayer process since the insertion of inert spacer layers in assemblies between layers containing 10 produces no effect on the rate or extent of dimerization. Several surfactant porphyrins and their metal complexes


10
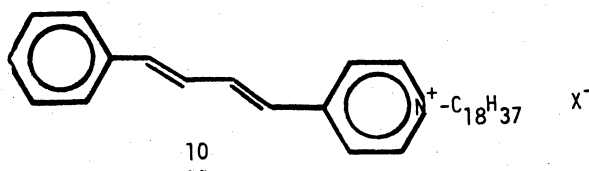
such as 11 and 12 have been found to form assemblies in which dimeric sites predominate. Here ground state effects of dimerization are observable both in films and monolayer assemblies (ref. 23, 27). Assemblies constructed from 11 have absorption and fluorescence spectra very similar to those obtained from dimers formed in hydrocarbon solution at low


11   12 $C_{18}H_{37}$
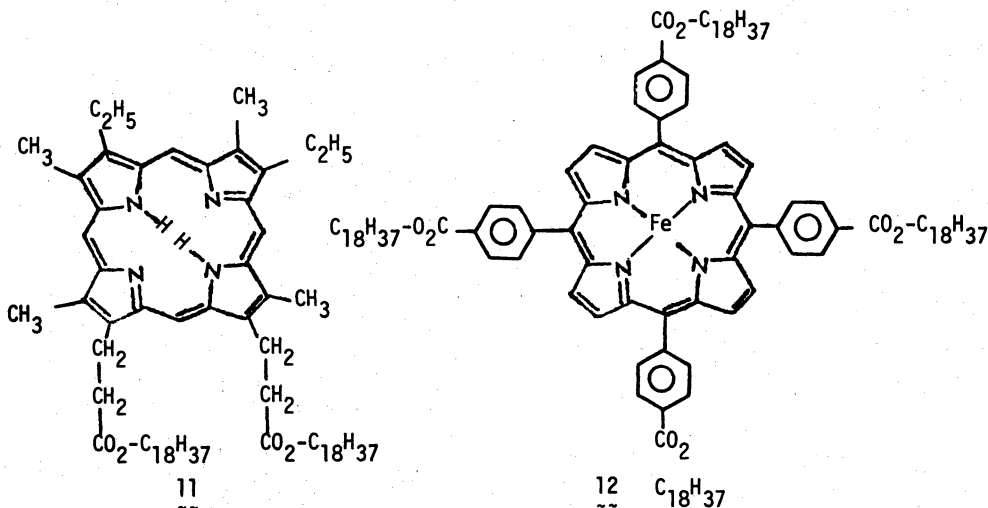
temperature (ref. 27). The area/molecule for 11 obtained from a surface pressure-area study is 57 Å² at 23 dyne/cm which is only about half the area of 120 Å² calculated using molecular models. That dimeric sites are generated during the formation of spread films is indicated by the finding that only the μ-oxo dimer of 12 (PFe-O-FeP) can be isolated as solutions of monomeric 12 are spread on water (ref. 23). In contrast, it is found that μ-oxo dimers are formed in solution only slowly and at relatively high pH. Studies of the rate and pH dependence of μ-oxo dimer formation in solution and in films indicate that the generation of dimeric sites favorably affects both the rate and equilibrium for dimer formation (ref. 23).

Excimer formation has also been observed in monolayer assemblies for surfactant molecules having the reactive chromophore in the hydrophobic region (ref. 28) although this region has been much less extensively investigated. The pyrene derivative 13 has been found to form good assemblies in mixtures with arachidic acid. Absorption spectra of 13 in the assemblies are non-identical to those obtained in hydrocarbon solution; fluorescence from 13 in the assemblies consists of monomer and excimer similar to that observed in solution. In concentrated layers the excimer fluorescence is much more intense than the monomer; the most striking finding is that excimer fluorescence persists to 13: arachidic acid ratios as low as 1:300 (ref. 28).


$(CH_2)_{15}$—COOH

13
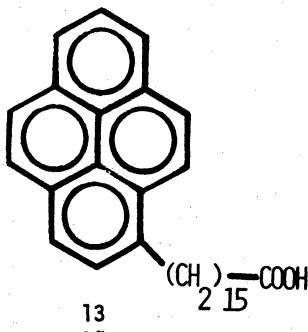
Photoinduced Electron Transfer Processes and Monolayer Assembly-Solution Reactions.

One of the most interesting possibilities for using monolayer assemblies in photochemistry involves reactions between an excited chromophore immobilized in an assembly or at a surface and a mobile solute in a solution in contact with the assembly. Some studies of this sort using chromophores immobilized in bilayer membranes, monolayer assemblies, or chromophore-impregnated metal foils or polymer membranes have already yielded some very important and exciting results (ref. 29-33). Our investigations in this area have centered around photo-induced electron transfer processes. In solution studies we have found the complex salt tris(2,2'-bipyridine)ruthenium(II)²⁺ (14)to be an excellent electron donor from its long-lived excited state (ref. 34-36). In other investigations it has been found that 14* can also serve as an oxidant (ref. 37). The reactions of 14* with electron acceptors proceed with high efficiency of energy conversion; in a series of experiments with aromatic nitro-compounds it was found that essentially all the excitation energy of 14 could be used to drive energetically uphill electron transfer processes (ref. 35). In an effort to investigate these processes at a monolayer assembly-solution interface a complex, 15, a surfactant derivative of 14 was prepared.

14

15
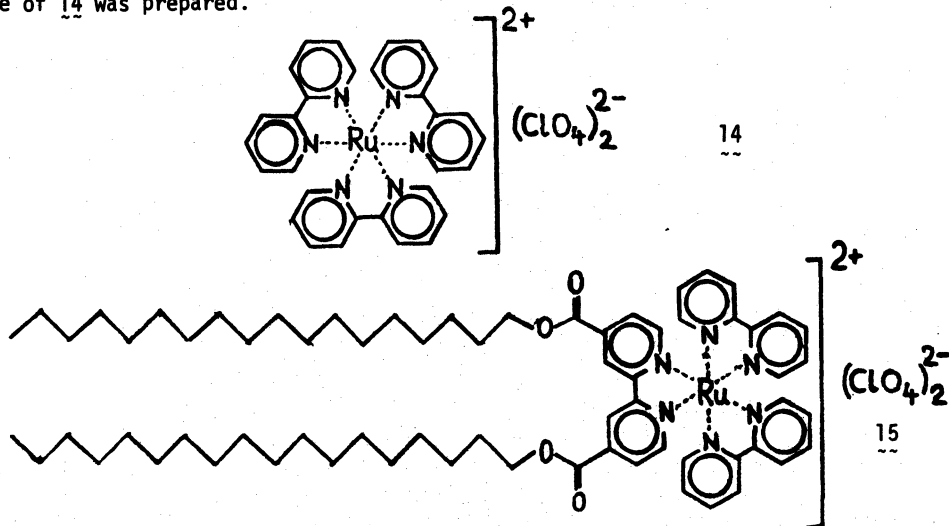
In contrast to 14 which is water soluble and luminesces strongly in water, 15 is water in-
soluble and forms films when spread on water which can be incorporated into monolayer assem-
blies. Assemblies containing an outermost hydrophobic layer of 15 show absorption and
luminescence spectra similar to those obtained for 14 and 15 in solution. 15 luminesces
strongly in the assemblies; an estimated quantum efficiency of ca. 0.3 is obtained for 15
in the assemblies. One of the efficient solution quenchers of the luminescence of 14 is
paraquat (N,N'-dimethyl-4,4'-bipyridine^{2+}) (16); flash photolysis studies clearly indicate
that quenching of the luminescence of 14 by 16 involves electron transfer to yield oxidized
14 and reduced 16 (ref. 34). The electron-transfer products rapidly react with each other
to regenerate unexcited starting materials. A surfactant analog of 16, 17 was prepared
by replacing the N-methyl groups with octadecyl groups. 17 was found to form films and
assemblies in mixtures with arachidic acid. Not surprisingly it was found that assemblies
containing 15 and 17, either within the same layer or in adjacent layers with contact through
the hydrophilic-hydrophilic interface, the luminescence of 15 was sharply reduced, presumably
through electron-transfer quenching. In typical experiments it was found that hydrophilic
contact of layers containing pure 15 with those containing pure 17 led to ca. 78% quenching
of the luminescence of 15. For mixed layers (1:1 ratio 15:17) the quenching was on the order
of 88-90%. In both these cases only transient bleaching is observed; evidently the electron
transfer quenching processes occurring within the layers are followed by rapid reverse
electron transfer similar to that observed in solution.

$$CH_3-^+N \bigcirc\!\!\!\!\bigcirc N^+- CH_3$$

16

$$C_{18}H_{37}-^+N \bigcirc\!\!\!\!\bigcirc N^+- C_{18}H_{37}$$

17
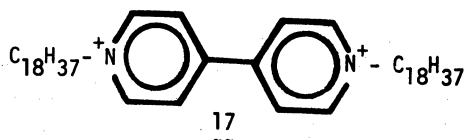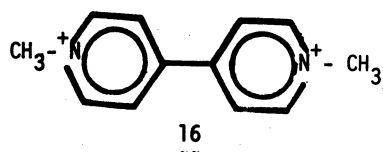
The strong luminescence of 15 in assemblies is almost completely quenched when the
assemblies are immersed into liquid water (ref. 38). Interestingly we find this
quenching peculiar to the monolayer assembly since no quenching of the luminescence is
observed when water, acid or base are added to dioxane solutions of 15. The luminescence
quenching is reversible; drying of quenched assemblies in vacuo regenerates the original
luminescence. No changes in the absorption spectrum of 15 are observed upon treatment or
immersion in water. The quenching occurs independently of whether or not the water is
degassed. Although water should not be able to quench excited states of 15 by energy trans-
fer, electron transfer quenching by reduction of water should be energetically favored if
one considers simple redox half cell potentials (ref. 39, 40). It has been pointed out by
several investigators that photoinduced electron transfer from metal complexes such as 14
should represent a feasible process for cleavage of water to hydrogen and oxygen. In fact
Sutin and coworkers have shown that oxidized 14 reacts with water (or -OH) to yield molecular
oxygen and 14 (ref. 39). Thus all that would be needed for a cyclic process for energy
conversion would be a reaction whereby excited 14 reduces water by electron transfer. Such
a reaction evidently occurs when monolayer incorporated 15 is irradiated in assemblies in
contact with liquid water (ref. 38). Irradiation of a set of several slides containing a
hydrophobic outer layer of 15 immersed in water with a 100 W mercury lamp (through Pyrex)
leads to a steady production of gas. The gas was shown by V.P.C. and mass spectral analysis
to contain hydrogen and oxygen as the principal components. In typical experiments a set
of 10 slides (ca. 1 x 3 cm) led to production of an average 0.5 cc/24 hrs; the reaction is
evidently catalytic with respect to 15 since turnovers greater than 10^3 molecules of gas/
molecule of 15 have been obtained. The reasonable conclusion from these results is that the
net reaction occurring is a photoinduced cleavage of water in which 15 functions as a light
absorbing catalyst:

$$2 (15^*) + H_2O \longrightarrow H_2 + \tfrac{1}{2} O_2 + 2 (15)$$

The net process represents a rather efficient energy-storing process since from the 45-50
kcal/mole excited state of 15, 28 kcal/mole of electrons is used in the cleavage of water to
hydrogen and oxygen. Several factors make it difficult to measure precise quantum efficien-
cies for the process but preliminary measurements suggest it is at least 0.1, thus
indicating the process to be a promising system for useful energy conversion.

Several aspects of this process are currently under investigation including details as to
the scope and mechanism. The reaction has been found to proceed smoothly with sunlight
as the energy source. As mentioned above the monolayer assembly environment is important
to the process since up until now we have not observed quenching of 15* by water in solution.
Although it would be premature to suggest a mechanism at this time, it would appear likely
that the hydrophobic environment assists either in lowering the activation barrier to the
electron transfer process or in providing a barrier to geminate recombination of products

with the ruthenium site. There have been reports of plant-algal systems and photosystems from chloroplasts which can produce hydrogen by light induced reduction of water (ref. 41,42). It is possible that a membrane or hydrophobic environment in these systems may permit the operation of a similar or related mechanism. We have made preliminary investigations with a few other surfactant molecules including several metalloporphyrins. To date irradiation of these molecules in assemblies has not led to sustained production of gas. It will be of importance to determine initial products of the excited-state quenching; the preliminary indication that the hydrogen/oxygen ratio may be slightly lower than predicted by the net equation suggests the possibility that stabilization of a hydrogen atom by forming a bound intermediate may be an important step in the hydrogen production. It has been suggested that the stepwise production of oxygen by oxidized 15 and water may involve such a species (ref. 39).

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NOTE ADDED IN PROOF: Subsequent investigations with more highly purified
samples of 15 do not lead to the production of hydrogen and oxygen upon
irradiation.   In fact it is found that purified samples of 15 are rapidly
removed from assemblies on irradiation under water in what appears to be
at least partially a photohydrolysis of the ester linkage. Evidently the
initial results were due to impurities contained in the original sample;
liquid chromatographic analysis of this sample indicates the presence of
other surfactant ruthenium (II) complexes as well as some of the free
dicarboxylic acid.