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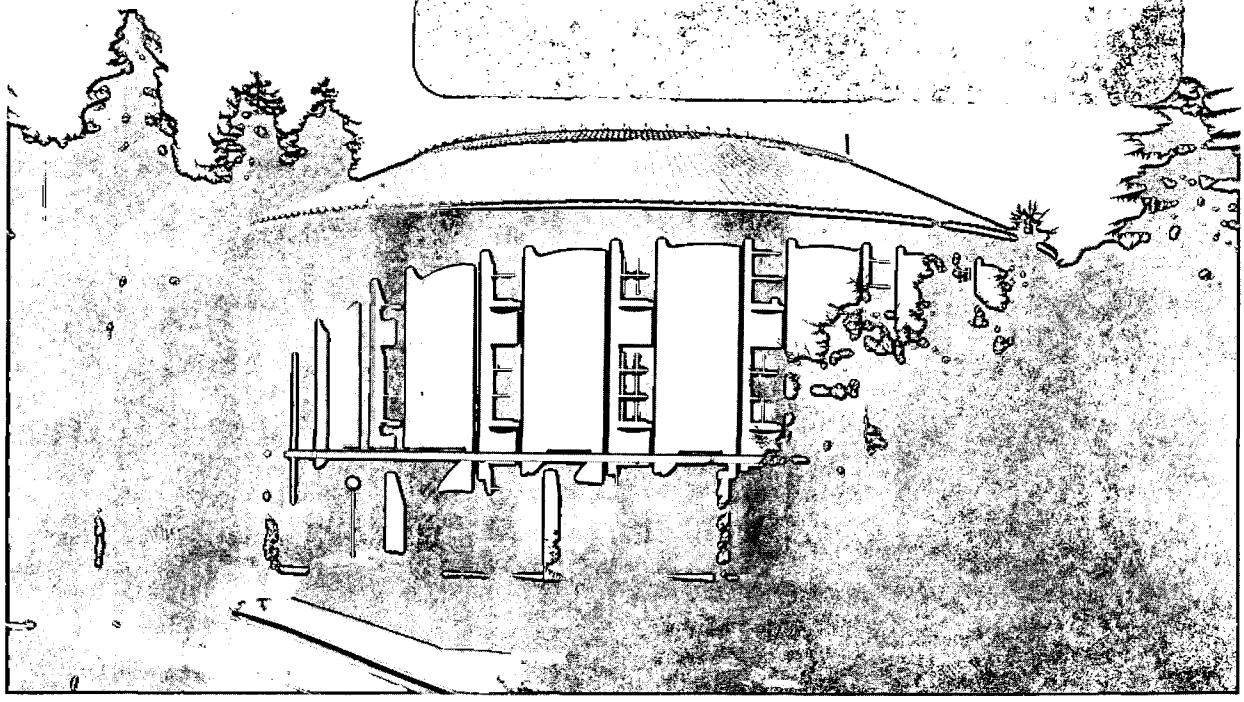

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PHOTOINDUCED ELECTRON TRANSFER REACTIONS OF MEMBRANE ANCHORED ZINC AND MANGANESE PORPHYRINS

Rafael Rafaeloff, Anthony C. Maliyackel, Janice L. Grant,
John W. Otvos and Melvin Calvin
Department of Chemistry and Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720

ABSTRACT

Photosensitized electron transport across the vesicle walls of DHP or PtdGly membranes in which ZnTpyP-C_{16} was anchored on both sides and MnTpyP-C_{16} anchored outside of the membrane has been achieved. The electron transport is mediated by PVS, entrapped between the vesicle walls. Upon illumination, the overall reaction is oxidation of the vesicle, Mn(II) and $PVS^{\cdot -}$ formation.

Abbreviations: DHP: dihexadecylphosphate. PtdGly: L-α-phosphatidyl-DL-glycerol, egg sodium salt. PVS: N,N-bis-sulfonato-n-propyl-4,4'-bipyridyl (propyl viologen). MV: 1,1'-dimethyl-4,4'-bipyridinium dichloride (methyl viologen). $Ru(bpy)_3^{2+}$: tris(2-2'-bipyridine) ruthenium(II) chloride hexahydrate. ZnTpyP-C_{16}: 5-(1'-hexadecylpyridinium-4'-yl)-10,15,20-tris-(4'-pyridyl)-21H,23H-porphine zinc perchlorate semihydrate. MnTpyP-C_{16}: bromo[5-(1'-hexadecylpyridinium-4'-yl)-10,15,20-tris(4'-pyridyl)-21H,23H-porphine manganese(III) perchlorate trihydrate.

INTRODUCTION

Considerable efforts have been made toward the goal of artificial photosynthesis, to lay the foundation for efficient and economically viable conversion of sunlight to storable high energy compounds.[1-3] One general approach has involved separate studies of hydrogen production and oxygen production using a sacrificial donor or a sacrificial acceptor, respectively, in separate cells.

In order to achieve the goal of water decomposition to hydrogen and oxygen by visible light, two processes must be achieved. Charge separation is achieved by electron transfer across a phase boundary. This must be followed by two different catalytic reactions to transform the separated charge into stable separated products. One of the first systems examined for this purpose was the charge separation that can be induced at the surface of a semiconductor, depending upon the internal field of the semiconductor surface to maintain the charge separation.[4-7] Another phase boundary system involves the use of highly charged microparticles such as silica[8] or micelles.[9] If the initial acceptor is neutral and becomes negative upon receiving an electron, a highly negatively charged silica colloid will help to maintain separation of the positively charged donor from the negatively charged acceptor.

Most of the work has been done on the hydrogen generating side of the system, and the irreversible donors for this purpose have in general been ethylenediaminetetraacetic acid or triethanolamine, which, upon removal of an electron, decompose, thus becoming unavailable for the recombination reaction.[10-13]

Little progress has been made on the goal of oxygen formation, which is significantly more difficult to accomplish homogeneously because four electrons are involved in the oxidation reactions.[14-16] For efficient energy conversion, the reactants must be brought sufficiently close to each other to allow the interactions that may result in reactions and, on the other hand, back reactions must be avoided.

A high degree of organization, which provides compartments of potentially controllable microenvironments for the sensitizer, relay and electron donor and which allows vectorial charge separations, can be achieved by using organized assemblies, such as synthetic or natural vesicular systems which mimic the functions of the thylakoid membrane in photosynthesis.[17]

Manganese in its oxidation state of four, or higher, has been used as an oxidation catalyst in organic chemistry.[18] In photosynthesis as well, nature seems to make use of manganese compounds when oxygen is evolved from chloroplasts under illumination.[19] In fact, we have succeeded in photooxidizing Mn(III) porphyrin using an irreversible acceptor.[20]

In connection with our longtime interest in mimicking natural photosynthesis[21-26] we have studied vesicular systems containing manganese(III) porphyrins. As a model for this study we used vesicles made from DHP and PtdGly which had ZnTpyP-C_{16} as a sensitizer, Mn(III)TpyP-C_{16} as a donor and PVS as an electron acceptor.

EXPERIMENTAL

Materials. The preparation, purification and characterization of 5-(1'-hexadecylpyridinium-4'-yl)-10,15,20-tris(4'-pyridyl)-21H,23H-porphine zinc perchlorate semihydrate (ZnTpyP-C_{16}),

bromo[5-(1'-hexadecylpyridinium-4'-yl)-10,15,20-tris(4'-pyridyl)21H-23H porphine]manganese(III) perchlorate trihydrate (MnTpyP-C_{16}) have been described previously.[27]

N,N'-bis-sulfonato-n-propyl-4-4'-bipyridyl (propyl viologen sulfonate, PVS) has been prepared by heating a mixture of three times recrystallized 4-4'-dipyridyl (1 g) and 1,3-propane sulton (3 g), both from Aldrich Chemical Co., in a sealed vial for 20 hrs at 120°C. The gray compound obtained was dissolved in water and precipitated three times by adding an excess of acetone. The precipitate was washed with hot methanol. The crude compound was recrystallized three times from water-methanol and three additional times from water-ethanol. Finally, the white crystals obtained were washed with hot ethanol and dried overnight in a vacuum desiccator. Elemental analysis: Calcd for $C_{16}H_{20}N_2S_2O_6 \cdot 3H_2O$: C, 42.27; N, 6.16; H, 5.77; S, 14.10. Found: C, 42.41; N, 6.13; H, 5.90; S, 14.16.

The three molecules of water were removed by heating the compound overnight at 67°C in a vacuum oven. The IR spectrum of this compound did not show the specific absorption band for water molecules. Elemental analysis: Calcd. for $C_{16}H_{20}N_2S_2O_6$: C, 47.98; N, 6.99; H, 5.04; S, 15.99. Found: C, 47.85; N, 6.95; H, 5.05; S, 15.91.

The purity was also confirmed by the ^1H NMR spectra in D_2O as solvent.[28]

δ ppm: 8.98, 8.39, 4.73, 2.85 and 2.36.

Dihexadecylphosphate (DHP), Sigma Chemical Co., L-α-phosphatidyl-DL-glycerol, egg sodium salt (PtdGly) from CalBiochem, were used without further purification.

The organic solvents CH_3OH and $CHCl_3$ were Mallinckrodt spectra pure reagents. Unless otherwise noted, all other chemicals were obtained from commercial suppliers at the highest available purity and used without further purification.

Aqueous solutions were prepared from doubly deionized water, passed through a Millipore system (Millipore Milli-Q water purification system) and then distilled twice in a glass apparatus.

The pH of the solutions was adjusted by addition of carbonate-free NaOH. Argon gas for sample deaeration was passed through a heated column of a copper catalyst to remove oxygen.

Apparatus. Absorption spectra were measured with a Hewlett-Packard 8450A diode array spectrophotometer. The light source for steady-state illumination was a 450W Xenon arc lamp (Oriel). The light was first passed through a quartz condensing lens in the lamp housing, then through a water filter which absorbed infrared light, then through a 350 nm cut-off filter and spotted on the illuminated cuvette with a fiber optical device. pH measurements were made with a Corning 125 pH meter. Sonication was performed with a Braun 2000 sonicator equipped with a 3/8" intermediate probe. Constant temperature was maintained by using a Haake FE2 constant temperature circulation bath. All measurements were performed at 25±0.5°C.

Vesicle Preparation. In a typical preparation a CH_3OH-$CHCl_3$ (1:1) solution of DHP and ZnTPyP-C_{16} was evaporated to dryness under nitrogen. The material was then dried overnight at room temperature in a vacuum desiccator. To the dry residue a water solution of PVS and NaOH was added and the suspension was sonicated at 80°C for 30 min at 70W. The PtdGly vesicles were prepared in the same solvents but sonicated at

20°C for 5 min at 30W. After sonication traces of titanium released by the microtip of the sonicator were removed by centrifugation. A solution of MnTpyP-C_{16} was slowly injected into the stirred vesicle suspension. By this procedure the unsymmetrical vesicular system shown in Figure 1 was prepared. The required volume was adjusted with water to give a final concentration of DHP or PtdGly (2×10^{-3} M), ZnTpyP-C_{16} (1×10^{-5} M) anchored on both sides of the membrane;MnTpyP-C_{16}(2×10^{-5}M) anchored outside the membrane; PVS (1×10^{-2} M) and NaOH (2×10^{-3} M) both located inside the vesicle and outside in the continuous aqueous phase.

The uniformity of the vesicle and the capture of the porphyrins by the vesicle were tested by gel filtration of the vesicle suspension through a Sephadex G-25 column, once soon after the vesicle was prepared and the second time after a few days. The porphyrins anchored to the vesicle and any PVS inside the vesicle remained with the vesicle during the gel filtration and the gel bed remained colorless. When necessary, externally adsorbed or nonadsorbed PVS (or other compounds) were removed by passing the vesicle suspension through a chromatograph column filled with Sephadex G-25 or by ultrafiltration in an Amicon ultrafiltration stirred cell of 65 ml capacity, equipped with a Diaflo membrane of 100,000 nominal molecular cut-off (type YM100).

Illumination. The illumination was performed after the vesicle suspension was transferred into an optical glass air tight cuvette with 1 cm light path, equipped with a glass stopcock, a teflon stirring bar and a septum. Prior to illumination the vesicle system was deaerated by repeated evacuation and flushing with oxygen-free argon. The solution was stirred magnetically throughout the experiment. The collimated light

emerging from the optical glass fiber was spotted on the cuvette. During illumination absorbance spectra were measured at predetermined times.

RESULTS AND DISCUSSION

Organization of compounds incorporated in a vesicular system in a non-random position was achieved by using synthetic surfactant DHP or natural egg PtdGly. Water-insoluble compounds bearing C_{16} aliphatic chains were anchored onto the vesicle walls on both sides of the membrane, or only on the outside. Water-soluble compounds were positioned inside, or outside, or on both sides of the membrane in the continuous aqueous phase. The experimental results are summarized in Tables 1-3. In Table 1 are given the spectral changes during illumination of homogeneous solutions of ZnTpyP-C_{16}, MnTpyP-C_{16} and a mixture of both and also when they are anchored to DHP membranes. In Table 2 are given the spectral changes during illumination of DHP vesicular systems in which ZnTpyP-C_{16} and MnTpyP-C_{16} are anchored to the membrane and PVS is located in different positions in the aqueous phase of the membrane. In Table 3 are given the spectral changes during illumination of PtdGly vesicular systems in which ZnTpyP-C_{16} or $Ru(bpy)_3^{2+}$ are used as photosensitizers. Unless otherwise noted, the illumination experiments were performed with a 350-800 nm cut-off filter. On illumination, a strong bleaching was observed with both DHP (Table 2) and PtdGly (Table 3) vesicles when the photosensitizer ZnTpyP-C_{16} alone was anchored on both sides of the membrane with no new absorption appearing at wavelengths longer than 350 nm. Similar bleaching was observed when the

Table 1

Spectral changes during illumination of DHP vesicular systems in which ZnTpyP-C_{16} is anchored on both sides of the membrane, MnTpyP-C_{16} is anchored on the outside of the membrane, and also of homogeneous solutions of ZnTpyP-C_{16} and MnTpyP-C_{16} dissolved in 1:1 methanol-chloroform and methanol respectively. Concentrations: DHP $2x10^{-3}$ M; ZnTpyP-C_{16} $1x10^{-5}$ M; MnTpyP-C_{16} $2x10^{-5}$M.

Filter Used nm	DHP Vesicles or Homogeneous Solutions	ZnTpyP-C_{16}	MnTpyP-C_{16}	Spectral Changes
350-800	homog.	+	0	Bleaching
400-800	homog.	+	0	Bleaching
350-800	homog.	+	+	Very weak absorption at 434 nm
400-800	homog.	+	+	" " "
350-800	DHP	+	0	Strong bleaching
400-800	DHP	+	0	Weak bleaching
440	DHP	+	0	Very weak bleaching
350-800	DHP	+	+	None

Table 2

Photochemical reactions during illumination with visible light (350-800 nm) of DHP vesicular systems

Arrangement of reactants and concentrations: DHP $2x10^{-3}$ M; ZnTpyP-C_{16} $1x10^{-5}$ M; MnTpyP-C_{16} $2x10^{-5}$ M: PVS $1x10^{-2}$ M; MV $5x10^{-4}$ M. pH at illumination 10.7-11.2

Location in the Vesicle		Location in the Vesicle		Spectral Changes
Anchored		Aqueous Phase		
ZnTpyP-C_{16}	MnTpyP-C_{16}	PVS	MV	
bs	0	0	0	Bleaching
bs	0	in	0	Bleaching
bs	0	ou	0	Bleaching
bs	0	bs	0	Bleaching
0	ou	0	0	None
0	ou	bs	0	None
bs	ou	0	0	None
bs	ou	in	0	Mn(II)
bs	ou	ou	0	None
bs	ou	bs	0	$PVS^{\bullet -}$, Mn(II)
bs	ou	in	ou	$PVS^{\bullet -}$, Mn(II)
bs	ou	ou	in	None
bs	ou	0	bs	None
bs	bs	bs	0	None
ou	ou	ou	0	None

ou = outside; in = inside; bs = both sides

Table 3

Photochemical reactions during illuminaton with visible light (350-800 nm) of PtdGly vesicular systems

Arrangement of reactants and concentrations: PtdGly $2x10^{-3}$ M; ZnTpyP-C_{16} $1x10^{-5}$ M; $Ru(bpy)_3^{2+}$ $7x10^{-5}$ M; MnTpyP-C_{16} $2x10^{-5}$ M; PVS $1x10^{-2}$M.

pH at illumination 10.5-11.2

Location in the vesicle Anchored		Location in the vesicle Aqueous Phase		Spectral changes
ZnTpyP-C_{16}	MnTpyP-C_{16}	$Ru(bpy)_3^{2+}$	PVS	
bs	0	0	0	Bleaching
bs	ou	0	ou	None
bs	ou	0	bs	$PVS\cdot^-$, Mn(II)
bs	ou*	0	bs	None
0	ou	bs	in	None
0	ou	bs	bs	$PVS\cdot^-$, Mn(II)

* MnTpyP-C_{16} $2x10^{-6}$M

ou = outside; in = inside; bs = both sides

acceptor PVS was added either on the inside or the outside or on both sides of the membrane (Table 2). In order to investigate whether the bleaching is due to illumination with wavelengths lower than 400 nm, illumination experiments were performed with homogeneous ZnTpyP-C_{16} solutions in 1:1 methanol-chloroform and of DHP vesicular systems in which ZnTpyP-C_{16} is anchored on both sides of the membrane(Table 1). For the illumination three different optical filters were used: a 350 or 400 nm cut-off filter or a narrow band filter with peak wavelength of 440 nm and bandwidth at 0.5 peak of 10 nm.

Upon illumination of $1x10^{-5}$ M ZnTpyP-C_{16} homogeneous solutions in 1:1 methanol-chloroform similar bleaching was observed when using a 350 nm or 400 nm cut-off filter (Table 1). On the other hand, the observed bleaching of the ZnTpyP-C_{16} absorption in DHP vesicular systems depends strongly on the illumination wavelength (Table 1). When using a 40 nm cut-off filter the bleaching intensity decreased. When using a 440 nm narrow band filter a very weak bleaching was found even after 18 hrs of illumination. The results observed indicate that upon illumination with wavelengths between 350-400 nm some interaction exists between the surfactant molecule and ZnTpyP-C_{16} anchored on both sides of the membrane. When MnTpyP-C_{16} is anchored onto the outside of the vesicular system, the bleaching of the ZnTpyP-C_{16} absorption is totally inhibited and no other spectral changes appeared (Table 1). This is due to the quenching of the ZnTpyP-C_{16} triplet state.[29] Upon illumination of a homogeneous solution of ZnTpyP-C_{16} and MnTpyP-C_{16} in 1:1 methanol-chloroform using a 350 or a 400 nm cut-off filter, a change in the absorption spectra which indicates a new weak absorption at 434 nm was observed (Table 1).

Figure 1 shows a highly organized unsymmetrical vesicular system. It shows that the photosensitizer ZnTpyP-C_{16} is anchored on both sides of the membrane; the MnTpyP-C_{16} is anchored only on the outside of the membrane, and the acceptor PVS is located in the aqueous phase on both sides of the membrane. Illumination of this system with visible light resulted in spectral changes shown in Figure 2.

A new absorption band at 398 nm due to the $PVS^{\cdot -}$ appeared. The intensity of the Mn(III) absorption band at 460 nm decreases and a new absorption band at 436 nm appears. This change in the absorption spectra of Mn(III) during illumination is attributed to the reduction of Mn(III) to Mn(II). Admission of air into the vesicle suspension resulted in the conversion of the absorption spectra to the original form in a few minutes.[30]

Plots of these absorptions in this vesicular system are given in Figure 3 which shows the build-up of $PVS^{\cdot -}$ radicals and Mn(II) as a function of illumination time. The concentration of $PVS^{\cdot -}$ is 5×10^{-6} M, formed after one hour illumination (.05% of the total PVS); the Mn(II) concentration at the same time is 2×10^{-6} M (10% of the total manganese present). Solutions illuminated for 25.5 hrs and kept in the dark for 5 days showed no changes in the $PVS^{\cdot -}$ (4.01×10^{-5} moles dm^{-3}) and Mn(II) (3.92×10^{-6} moles dm^{-3}) concentrations, indicating that free oxygen was not present in the solution.

On illumination of a DHP vesicular system in which ZnTpyP-C_{16} was anchored on both sides of the membrane, the MnTpyP-C_{16} was anchored only into the outside of the membrane, and two different electron acceptors located in two different positions were used, viologen radicals and Mn(II) were also formed (Table 2). The PVS was located only inside and

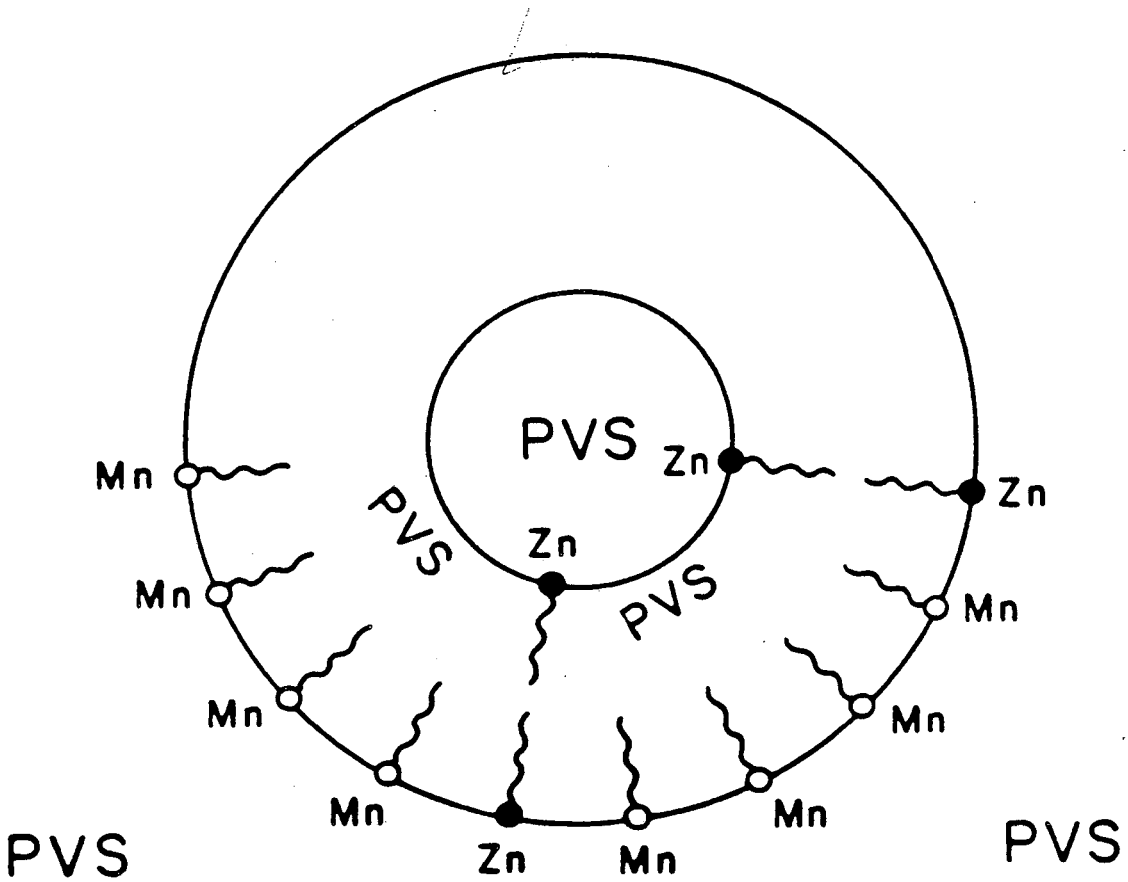

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Fig. 1. A diagram of a highly organized unsymmetrical negatively charged vesicular system. The photosensitizer ZnTpyP-C_{16} is anchored on both sides of the membrane; the MnTpyP-C_{16} is anchored only outside on the membrane; and the electron acceptor PVS is located in the continuous phase on both sides of the membrane and between the vesicle walls.

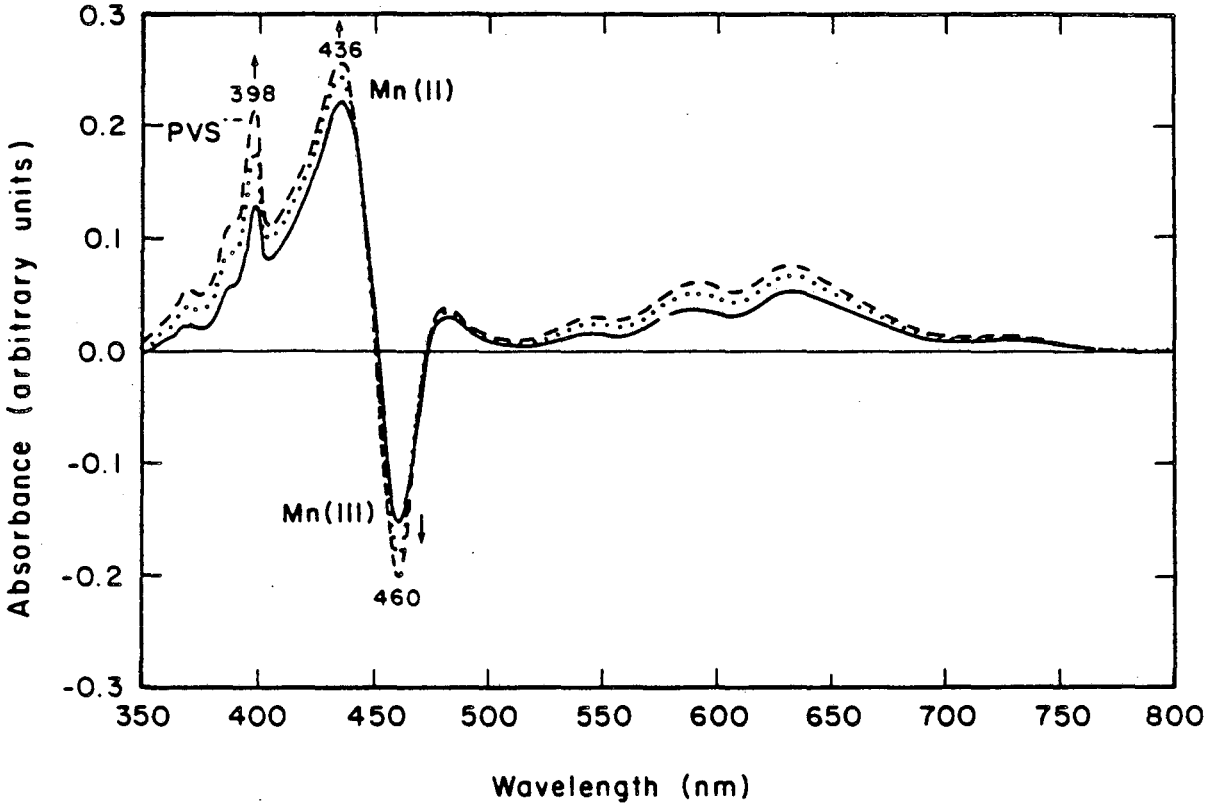

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Fig. 2. Optical difference spectra showing the 0,20,40 and 60 minutes formation of $PVS^{\cdot -}$ and Mn(II) as well as the decrease of Mn(III) upon illumination (350-800 nm) of a DHP ($2x10^{-3}$M) vesicular system. The ZnTpyP-C_{16} ($1x10^{-5}$ M) was anchored on both sides of the membrane; the MnTpyP-C_{16} ($2x10^{-5}$ M) was anchored only outside on the membrane; and the PVS ($1x10^{-2}$ M) was located on both sides of the membrane in the aqueous phase.

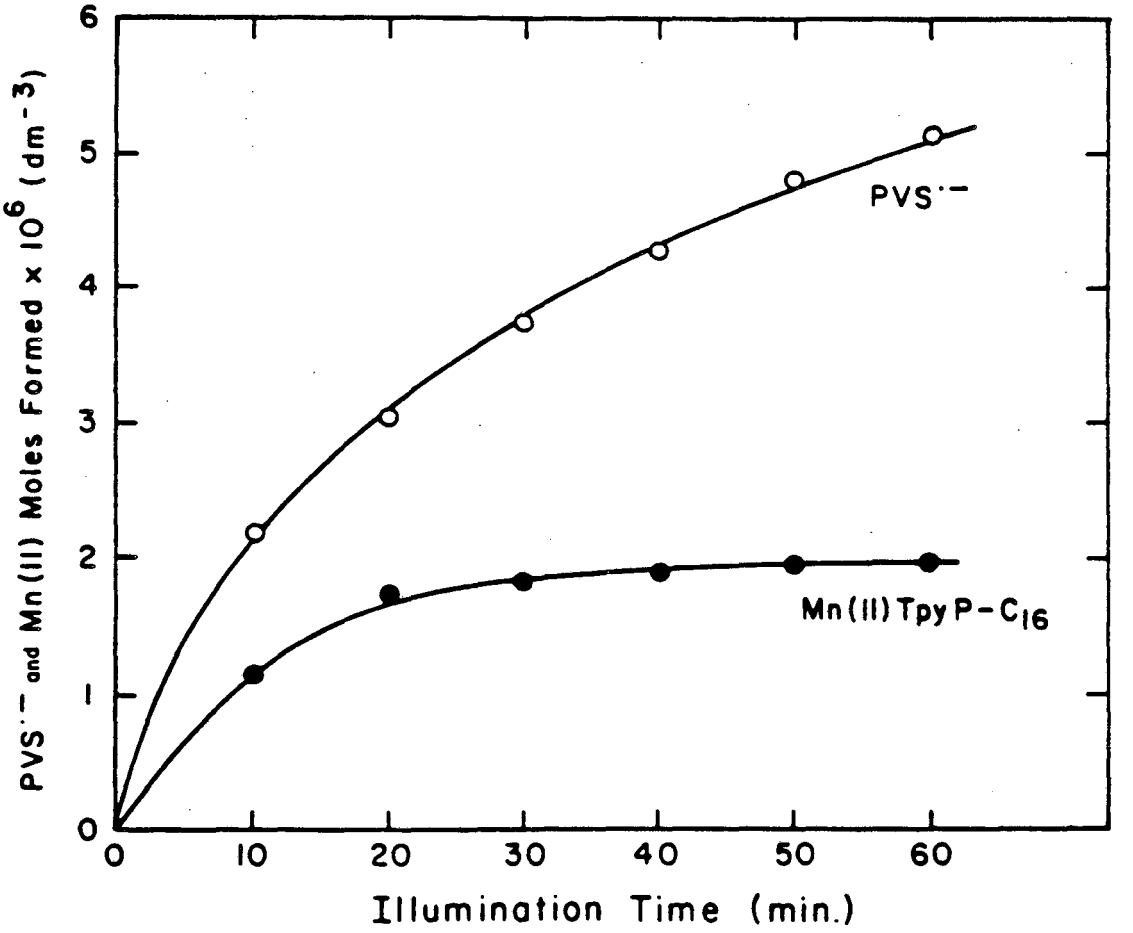

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Fig. 3. Plots of $PVS^{\cdot -}$ and Mn(II) formations during 1 hour illumination of DHP ($2x10^{-3}$ M) vesicular system. The $ZnTpyP-C_{16}$ ($1x10^{-5}$ M) was anchored on both sides, $MnTpyP-C_{16}$ ($2x10^{-5}$ M) anchored only outside the membrane and PVS($1x10^{-2}$ M) located on both sides in the continuous aqueous phase of the membrane.

the MV was located only outside, both in the aqueous phases. In the same vesicular systems when MV was located inside the membrane and PVS was located outside in the aqueous phase or only MV was located on both sides of the aqueous phase of the membrane no photochemical reactions were observed.

Reactions were not observed on illumination of symmetrical vesicles in which ZnTpyP-C_{16} and MnTpyP-C_{16} were anchored on both sides of the membrane and PVS was located in the aqueous phase on both sides of the membrane. Reactions also were not observed in vesicular systems in which ZnTpyP-C_{16} was anchored on both sides of the membrane, MnTpyP-C_{16} anchored only outside on the membrane, and PVS located on the outside in the continuous aqueous phase. In the same vesicular system when PVS is located only inside the membrane Mn(II) was formed but no net $PVS^{\cdot -}$ is observed (Table 2). Presumably the competitive back reaction is faster than if there is an electron acceptor on the outside.

Attempts to use the membrane as a negatively charged surface on which ZnTpyP-C_{16} and MnTpyP-C_{16} were anchored on the outside and PVS was located only outside in the continuous aqueous phase gave no observable photochemical reactions. The photochemical reactions observed with PtdGly vesicles are similar to those observed with DHP vesicular systems (Table 3). $PVS^{\cdot -}$ and Mn(II) are formed upon illumination of PtdGly vesicles in which ZnTpyP-C_{16} is anchored on both sides of the membrane, MnTpyP-C_{16} is anchored on the outside of the membrane and PVS is located on both sides. When the MnTpyP-C_{16} concentration was decreased by a factor of ten to 2×10^{-6} M, $PVS^{\cdot -}$ and Mn(II) formation was not observed.

In some experiments $Ru(bpy)_3^{2+}$ was used as a photosensitizer (Table 3). Only <u>highly organized unsymmetrical systems</u> containing $Ru(bpy)_3^{2+}$

and PVS, located in the aqueous phase on both sides of the membrane, and MnTpyP-C_{16} anchored on the outside of the membrane gave $PVS^{\cdot -}$ and Mn(II) upon illumination.

The general conclusion drawn so far from the experimental results makes it clear that the oxidation-reduction mechanism of these highly organized unsymmetrical vesicular systems (Figure 1) in which $PVS^{\cdot -}$ and Mn(II) were formed upon illumination are very complex (Tables 2 and 3). Several reports of electron transfer across vesicle bilayers have recently appeared.[31-33] Although the spatial organization and chemical composition of the vesicular systems vary, in each case the photosensitizer is usually bound to the vesicle. The thickness of the vesicle wall is 40-50 Å.[34] Ten Å of this thickness are due to and occupied by the vesicle polar head groups. Because of the 40 Å distance that the electron must travel across the membrane, electron transport becomes possible in the presence of appropriate electron mediators incorporated into the vesicle wall. The general claim is that the electron transfer rates decrease exponentially with increasing distance between the donor and acceptor, and an electron tunneling through the lipid wall of more than 20 Å has been suggested.[35]

Charged or zwitterionic viologens are widely used as electron acceptors. Upon illumination, dimerization of the viologen radicals has been reported.[36-37] The dimerized viologen radicals can penetrate the surface of organized molecular assemblies and associate with the hydrocarbon core via hydrophobic interactions.[40]

PVS molecules are also located in the membrane between the vesicle walls, which is due to the molecule penetration of the vesicle walls

during sonication in the vesicle preparation and the PVS leaking through the membrane.

Upon illumination, the generated electrons can flow across the vesicle walls through the PVS, which behaves as an electron mediator. Evidence for this postulate is that $PVS^{\cdot -}$ and Mn(II) are formed upon illumination when the PVS is located on both sides of the membrane, or when the PVS located outside in the aqueous phase was replaced with methyl viologen (Table 2).

For the explanation of these complex photochemical reactions we should take into consideration also the fact that the MnTpyP-C_{16} is a quencher of the ZnTpyP-C_{16} triplet excited state, and that the rate of $PVS^{\cdot -}$ formation is higher than that of the Mn(II) formation (Figure 3). The outside part of the membrane, to which ZnTpyP-C_{16} and MnTpyP-C_{16} in a molar ratio of 1 to 4 are anchored on the outside wall of the vesicle, is photochemically inactive. The photochemical reactions occurred only on the inner part of the membrane. During illumination the excited ZnTpyP-C_{16} which is anchored on the inner wall of the membrane transfers an electron to the PVS relay which is located in the aqueous phase inside the membrane, and $PVS^{\cdot -}$ radicals are formed. The electron from the formed $PVS^{\cdot -}$ can flow across the membrane through the conducting PVS which is located inside the membrane between the opposite walls of the vesicle and reduce the Mn(III) to Mn(II). The PVS located outside in the aqueous phase of the membrane can also be reduced to $PVS^{\cdot -}$ from the electron flow across the membrane. Since the formed ZnTpyP-$C_{16}{}^{\cdot +}$ radical is a strong oxidizing agent [41,42] it can oxidize the vesicle and return to its ground state. The postulated events for the $PVS^{\cdot -}$ and Mn(II) formation are summarized in Scheme 1.

Scheme 1

$$ZnTpyP\text{-}C_{16_{in}} \xrightarrow{h\nu} {}^{3}ZnTpyP\text{-}C^{*}_{16_{in}}$$ excitation

$${}^{3}ZnTpyP\text{-}C^{*}_{16_{in}} \longrightarrow ZnTpyP\text{-}C_{16_{in}}$$ radiationless decay

$${}^{3}ZnTpyP\text{-}C^{*}_{16_{in}} + PVS^{o}_{in} \longrightarrow ZnTpyP\text{-}C^{\cdot +}_{16_{in}} + PVS^{\cdot -}$$ electron transfer quenching

$${}^{3}ZnTpyP\text{-}C^{*}_{16_{in}} + PVS^{o}_{in} \longrightarrow ZnTpyP\text{-}C_{16_{in}} + PVS^{o}_{in}$$ collisional quenching

$$ZnTpyP\text{-}C^{\cdot +}_{16_{in}} + PVS^{\cdot -}_{in} \longrightarrow ZnTpyP\text{-}C^{\cdot}_{16_{in}} + PVS^{o\cdot}_{in}$$ back reaction

$$ZnTpyP\text{-}C^{\cdot +}_{16_{in}} + \text{vesicle} \longrightarrow$$

$$ZnTpyP\text{-}C_{16_{in}} + \text{oxidation of the vesicle}$$ oxidation reaction

$$PVS^{\cdot -}_{in} + Mn(III)TpyP\text{-}C_{16_{ou}} \longrightarrow PVS^{o}_{in} + Mn(II)TpyP\text{-}C_{16_{ou}}$$ electron transfer across the membrane

$$PVS^{\cdot -}_{in} + PVS_{ou} \longrightarrow PVS^{o}_{in} + PVS^{\cdot -}_{ou}$$ electron transfer across the membrane

CONCLUSION

On steady-state illumination only highly organized unsymmetrical DHP or PtdGly vesicular systems in which the photosensitizer ZnTpyP-C_{16} is anchored on both sides of the membrane, the Mn(III)TpyP-C_{16} is anchored on the outside of the membrane, and PVS is located in the aqueous phases on both sides of the membrane resulted in formation of $PVS^{\cdot -}$ and Mn(II). There was no evidence for intermediate formation of Mn(IV). The photochemical reactions occurred only on the inner part of the membrane. During illumination the excited ^{3}ZnTpyP-C_{16}^{*} which is anchored to the inner wall of the membrane transfers an electron to the PVS relay located inside in the aqueous phase of the membrane, and $PVS^{\cdot -}$ radical is formed. The Mn(III) is reduced directly to Mn(II) by the electron flow across the membrane. Also, the PVS located outside in the aqueous phase is reduced to $PVS^{\cdot -}$ by this transmembrane electron flow. The ZnTpyP-$C^{\cdot +}_{16}$ cation radical oxidizes the vesicle and returns to its ground state. The use of microheterogeneous organic media does not seem promising for the oxidation of Mn(III) to Mn(IV).

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