Photoinduced Electron Transfer from (Alkoxyphenyl)triphenylporphyrins to Interface Water of Dihexadecyl Phosphate, Dipalmitoylphosphatidylcholine, and Dioctadecyldimethylammonium Chloride Vesicles

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Photoionization of (alkoxyphenyl)triphenylporphyrins (C_nOPTPP) in dihexadecyl phosphate (DHP), dipalmitoylphosphatidylcholine (DPPC), and dioctadecyldimethylammonium chloride (DODAC) frozen vesicle solutions at 77 K occurs via electron transfer from C_nOPTPP to bulk water at the interface of the vesicles. This process results in C_nOPTPP$^+$ formation which is characterized and quantitated by electron spin resonance. The cation yield decreases with increasing C_n alkyl chain length of C_nOPTPP due to an increasing interaction distance between the porphyrin headgroup and interface water. This change in interaction distance is directly measured with electron spin echo modulation by measuring the deuterium modulation depth associated with C_nOPTPP$^+$ interactions with deuterated water at the interface. The cation yield also decreases from cationic DODAC to neutral DPPC to anionic DHP vesicles because of a charge effect on electron transfer through the interface.

Introduction

Photoinduced electron transfer from photoactive molecules in molecular assemblies such as micelles, vesicles, and reverse micelles has been studied to optimize conversion of light energy into chemical energy.[1-6] Optimization of the photoionization efficiency has been achieved by varying the interface charge and the location of electron donor molecules relative to the surfactant assembly interface. The interface charge has been varied by using surfactant molecules with different headgroup charges or by mixing surfactants with different charges.[7-10] Location control has been achieved by adding slightly water soluble surface-active additives like alcohols,[11] cholesterol,[12-15] and ureas,[16,17] and by varying the alkyl chain length of the photoionizable molecule like alkylphenothiazines.[18-24] Here we demonstrate that location control may also be achieved for bulkier alkylporphyrin systems.

Porphyrin derivatives have been used as photosensitive electron donor molecules due to their structural and functional similarities to chlorophylls and their absorption of visible light.[25,26] The net photoionization efficiency is enhanced over homogeneous solutions by localization of the porphyrins within surfactant assemblies. Naturally occurring porphyrins interact with biological membranes.[27,28] The porphyrin charge and substituents exert significant effects on the localization of porphyrins in membrane assemblies.[9] The yields of photoproduced porphyrin cation radical or converted paramangetic products can be measured in the frozen state with electron state resonance (ESR). The location of the porphyrin moiety relative to a surfactant assembly interface can be determined by the deuterium modulation depth of electron spin echo modulation (ESEM) of the photoproduced cation in surfactant assemblies in deuterated water.[4,5]

Such electron magnetic resonance studies have been carried out in the frozen state because the lifetimes of photoproduced radical cations are short at room temperature and the exploitation of ESEM to measure weak dipolar interactions requires solid-state systems.[5,29,30] Hence the molecular assemblies are frozen rapidly in order to make such analyses possible. Numerous studies have demonstrated that micellar and vesicular structure is retained in rapidly frozen aqueous solutions.[5]

In a previous study with alkylporphyrin derivatives, the localization and photoionization of a limited series of (alkylpyridyl)triphenylporphyrins in vesicular systems are investigated.[9] The photoproduced cation radical yield of (alkylpyridyl)-porphyrins decreased with increasing alkyl chain length which was attributed to an increasing hydrophobic interaction of the longer chain (alkylpyridyl)porphyrin molecules with the surfactants. However, with these (alkylpyridyl)porphyrins no electron spin echo signals could be detected in the vesicle systems which did not allow verification of the purported location changes. One possible disadvantage in using (alkylpyridyl)triphenylporphyrins in vesicle surfactant aggregates is that the ionic characteristics of the quaternary nitrogen act to impede much penetration associated with the alkyl chain. Thus in the present study a series of less polar (alkoxyphenyl)triphenylporphyrins were synthesized and investigated in cationic dioctadecyldimethylammonium chloride (DODAC), neutral dipalmitoylphosphatidylcholine (DPPC), and anionic dihexadecylphosphate (DHP) vesicles. The photoproduced cation, C_nOPTPP$^+$, could be detected by both ESR and ESEM so that photoyields and changes in interaction distance of the porphyrin moiety from the vesicle interface water could be determined.

Experimental Section

Materials. The (alkoxyphenyl)triphenylporphyrins (C_nOPTPP) with n = 3, 6, 10, 12 were synthesized as described earlier.[31] C_nOPTPP stock solutions of 1×10^{-2} M were prepared in chloroform. Deuterium oxide (D_2O) was purchased from Aldrich Chemical Co. (99.8 atom % D) and was deoxygenated by purging with nitrogen gas for 20 min before use. DHP and DPPC were obtained from Sigma Chemical Co. and used without further purification. Dioctadecyldimethylammonium bromide (DODAB) was purchased from Eastman Kodak and purified by recrystallization from acetone. A methanol/chloroform (70:30, v/v) solution of DODAB was passed through a chloride ion exchange resin type AG 2 × 8, 20–50 mesh, from Biorad Laboratories to make DODAC. The eluent containing DODAC was evaporated, and the solid residue was recrystallized two times from acetone/water (99:5, v/v). Tris(hydroxymethyl)aminomethane (Tris, Gold Label, 99.9+%) and 2 N hydrochloric acid were purchased from Aldrich and Sigma Chemical Co., respectively. Stock 30 mM solutions of the vesicle monomers (DHP, DPPC, and DODAC) were prepared in chloroform.

Sample Preparation. A 70-μL quantity of each C_nOPTPP stock solution in chloroform and 0.6 mL of DHP, DPPC, and DODAC

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stock solution were transferred into a 16- × 125-mm Fisher test tube. The solvent was evaporated by nitrogen gas flowing over the surface of the solution, which resulted in the formation of a thin film on the test tube wall. After the film had formed, 1 mL of D_2O was added to the DODAC and DPPC films. The resulting solutions were sonicated for 30 min at 55 ± 3 °C under nitrogen gas to form completely solubilized clear solutions.

For the preparation of DHP solutions, 1 mL of a 20 mM Tris buffered (D_2O) solution, adjusted to pH = 7.8 with hydrochloric acid, was added to a DHP thin film. The solution was then sonicated for 30 min at 70 ± 3 °C under nitrogen gas. The concentration of each C_nOPTPP in the vesicle solution was determined to be 1.4 × 10^{-4} M by using optical absorption spectroscopy (λ_{max} = 565 nm in chloroform; log ϵ = 5.02).[32]

Photolysis. The samples for photoirradiation were prepared by transferring 100 μL of each sample solution into a 2-mm-i.d. × 3-mm-o.d. Suprasil quartz tube which was flame sealed at one end. The tubes were shaken to equilibrate the solution, and then the samples were frozen by rapid plunging into liquid nitrogen.

Photoirradiation for ESR measurements was carried out for 12 min at 77 K. Samples for ESEM experiments were irradiated for 7 min to minimize secondary radical formation. The irradiation source used was a 300-W Cermax xenon lamp (LX 300 UV) with a power supply from ILC Technology. The light passed through a 10-cm water filter and a Corning No. 0-56 glass filter which passes light of wavelengths longer than 300 nm. The samples were irradiated in liquid nitrogen in a quartz dewar that was rotated at 4 rpm to ensure even irradiation of the sample. The light intensity at the sample position was measured with a YSI-Kettering Model 65 radiometer as 1.0 × 10^{-3} W·m².

Magnetic Resonance Experiments. ESR spectra were recorded at 77 K at the X-band using a Bruker ESP 300 spectrometer with 100-kHz field modulation. The irradiated sample cell was placed in a quartz ESR dewar (Wilmad Glass Co.) which was filled with liquid nitrogen and secured in a TE_{102} rectangular cavity. The loaded Q factor of this cavity was measured as about 1700. The microwave power was 1.97 mW. The microwave frequency was measured with a Hewlett-Packard 5350B frequency counter, and the magnetic field was monitored with a Bruker ER 032M Hall effect field controller. The photoinduced radical yield was determined by double integration of the ESR spectra using the ESP 300 software. Each relative photoyield value is an average of triple determinations and was normalized by dividing by the photoyield of the $C_3OPTPP/DODAC/D_2O$ sample.

Two-pulse ESEM signals were recorded at 4.2 K on a home-built spectrometer using 40- and 80-ns excitation pulses.[33,34] The deuterium modulation appeared with about 0.5-μs periodicity. The modulation depths were normalized by dividing the depth at the first deuterium modulation minimum by the depth to the baseline at the same interpulse time.[35,36] The deuterium modulation experiments were performed in triplicate.

Results

The structures of the molecules used in this study are shown in Figure 1. The samples which do not contain C_nOPTPP did not show any ESR signals. Also, the sample before photoirradiation does not show any ESR signal. This indicates that C_nOPTPP is the only photoionizable molecule in the system.

Figure 2 shows representative ESR spectrum of $C_{12}OPTPP$ in vesicles. The ESR signal of photoirradiated samples shows a singlet at g = 2.0023, which is assigned to the photoproduced cation radical C_nOPTPP^+, and a background multiplet which is assigned to a secondary alkyl radical by photoinduced radical conversion[10] from the (alkoxyphenyl)triphenylporphyrin cation radical to the alkyl chain of the surfactants. Radical conversion was enhanced by prolonged irradiation of the samples. The signal intensity of the (alkoxyphenyl)triphenylporphyrin cation radical

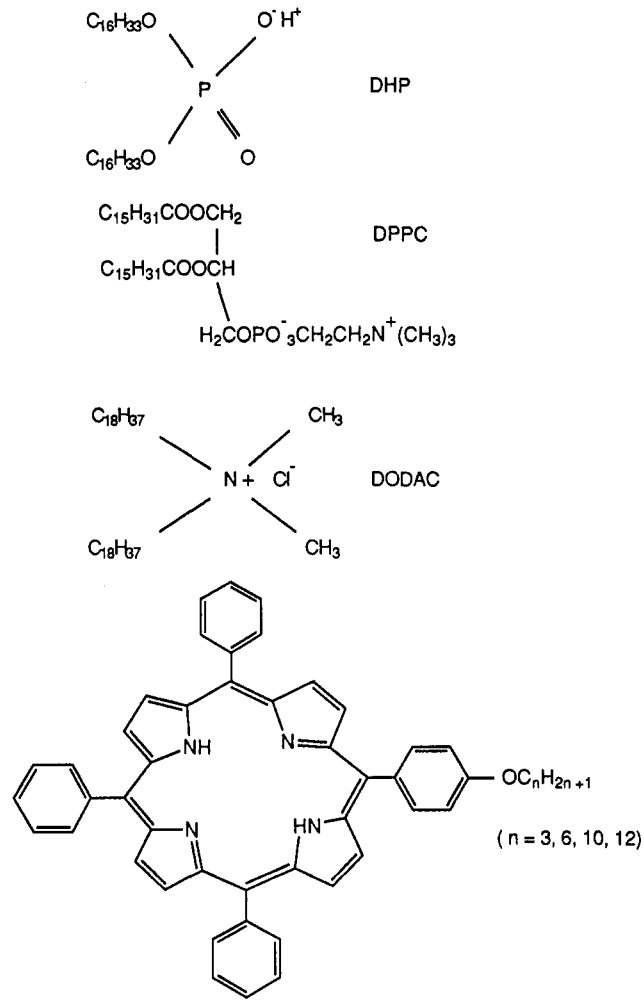

Figure 1. Structures of vesicles and (alkoxyphenyl)triphenylporphyrins (C_nOPTPP) used in this study.

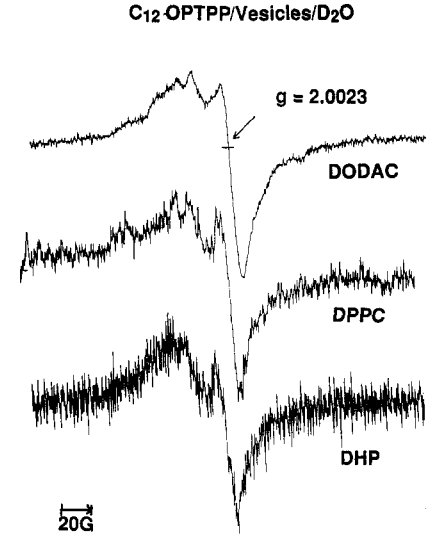

Figure 2. X-band ESR signals at 77 K of $C_{12}OPTPP$ in DODAC, DPPC, and DHP vesicles after 12 min of photoirradiation at 77 K.

decreased as a function of the irradiation time, whereas the intensity of the secondary radical signal increased.

Figure 3 shows the normalized photoyield of C_nOPTPP in DODAC, DPPC, and DHP vesicles after 12 min of photoirradiation at 77 K. The photoyield decreases in the order DODAC

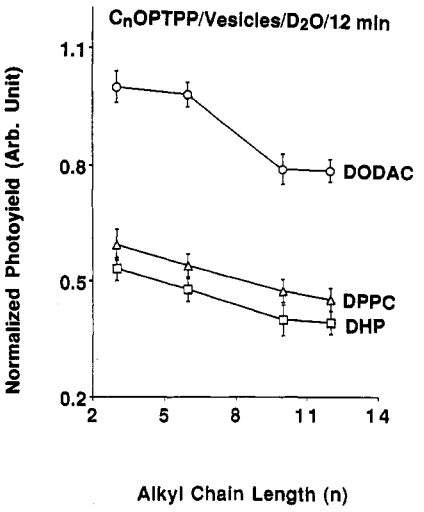

Figure 3. Normalized photoyields at 77 K of C_nOPTPP in DODAC (○), DPPC (△), and DHP (□) vesicles versus the C_n alkyl chain length after 12 min of photoirradiation at 77 K.

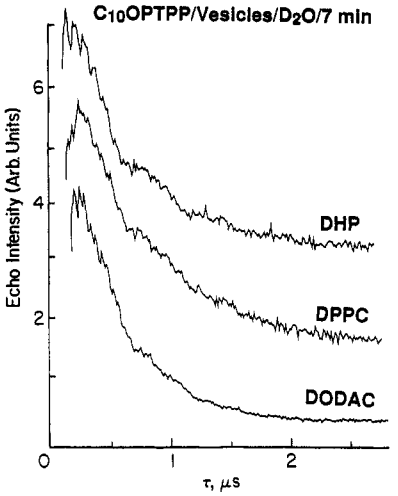

Figure 4. Representative ESEM signals at 4.2 K of $C_{10}OPTPP$ in DODAC, DPPC, and DHP vesicles after 7 min of photoirradiation at 77 K.

> DPPC > DHP vesicles. The photoyield also decreases with the increasing alkyl chain length of C_nOPTPP.

Figure 4 shows representative ESEM signals at 4.2 K of C_nOPTPP^+ in vesicles. They show approximately 0.5-μs periodicity, characteristic of deuterium modulation. The normalized deuterium modulation depths of C_nOPTPP^+ in the three vesicle systems are shown in Figure 5. The deuterium modulation depth decreases in the order DHP > DPPC > DODAC and decreases with the increasing C_n alkyl chain length of C_nOPTPP.

Discussion

In previous studies the (alkylpyridyl)triphenylporphyrin cation radical and *meso*-tetraphenylporphyrin cation radical were characterized by g values of 2.0026 and 2.0028.[9,37] The singlet ESR signal of photoionized (alkoxyphenyl)triphenylporphyrin in the vesicle systems at $g = 2.0023$ is consistent with these previous reports.

Effect of Alkyl Chain Length of C_nOPTPP. The distance from the porphyrin moiety to the bulk interface water (D_2O) which acts as an electron acceptor is a critical factor for the efficiency of photoinduced electron transfer from C_nOPTPP. A shorter distance from the porphyrin moiety to the interface water provides more efficient electron transfer and gives a higher cation radical yield.

The relative photoproduced radical yield is obtained by doubly integrating the first derivative ESR signal. This photoyield

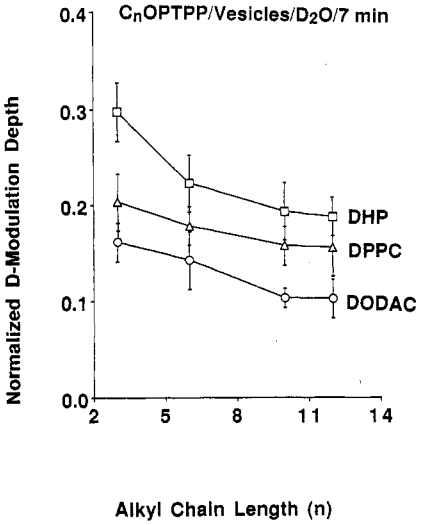

Figure 5. Normalized deuterium modulation depths at 4.2 K of C_nOPTPP in DODAC (○), DPPC (△), and DHP (□) vesicles versus the C_n alkyl chain length after 7 min of photoirradiation at 77 K.

indicates the efficiency of electron transfer. A decreasing photoyield with increasing alkyl chain length, as shown in Figure 3, is interpreted as an increasing distance for electron transfer from the porphyrin to interface water of the vesicle systems as C_n increases.

The relative distance changes of the porphyrin moiety from the vesicle interface are directly measured from the deuterium modulation depths of C_nOPTPP^+. An increasing interaction distance of the porphyrin moiety from the interface water for increasing C_n alkyl chain length is shown in Figure 5. This can be explained by an increase in the hydrophobic interaction of C_nOPTPP with the surfactant molecules as the C_n alkyl chain length increases. This greater hydrophobic interaction locates the porphyrin moiety deeper into the hydrocarbon region of the vesicle for greater C_n. The longer distance for electron travel from the porphyrin to interface water decreases the yield of the charge separated state by electron transfer. The decreasing photoyield of C_nOPTPP with increasing alkyl chain length is well supported by this distance change data. These results are analogous to those for alkylphenothiazines in vesicles.[20-24]

Effects of Interface Charge and Interface Order. The photoyield is also affected by the strength and kind of interface charge of the vesicles which varies the barrier for electron penetration through the vesicle interface. An anionic interface charge constitutes a higher energy barrier for electron transfer across the interface than a cationic charge. Consequently, electron transfer through a cationic vesicle interface results in the best photoyield.

The less ordered interface region of DODAC vesicles due to their bulky dimethylammonium headgroup allows greater penetration of porphyrin molecules into the hydrocarbon region of the vesicle compared to that of the DHP and DPPC vesicles which have a more oriented interface. This accounts for the increasing order of deuterium modulation depth for DODAC < DPPC < DHP vesicles, as shown in Figure 5. This indicates that the interaction distance between porphyrin and interface water (D_2O) increases as DODAC > DPPC > DHP. Even with a shorter interaction distance in anionic DHP vesicles the photoyield of C_nOPTPP is lower than that in neutral DPPC and cationic DODAC vesicles. This indicates that the interface charge affects the electron transfer efficiency more critically than the distance of the porphyrin moiety from interface water. A cationic interface allows more efficient electron transfer and results in a higher photoyield, as shown in Figure 3. A higher photoyield in cationic micelles, reverse micelles, and vesicles has been consistently found in previous studies.[9,10,16-24]

Conclusions

Photoinduced electron transfer from C_nOPTPP alkoxyporphyrins to interface water in vesicles results in a charge separated state whose yield decreases with increasing C_n. This yield change with C_n reflects a changing electron transfer distance between the porphyrin moiety and interface water as measured by ESEM. The increasing hydrophobic interaction of C_nOPTPP with vesicle surfactants for increasing C_n locates the porphyrin moiety deeper into the hydrocarbon region of the vesicles. The decreasing order of photoproduced cation radical yield from cationic DODAC to neutral DPPC to anionic DHP vesicles shows that the vesicle interface charge critically affects the electron transfer efficiency through the vesicle interface. A cationic interface charge gives a lower energy barrier for electron transfer through the vesicle interface and hence the highest yield.

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