Location and Aggregation Behaviour of Tetra-aryl-porphyrins in Dioctadecyldimethylammonium Chloride Vesicles

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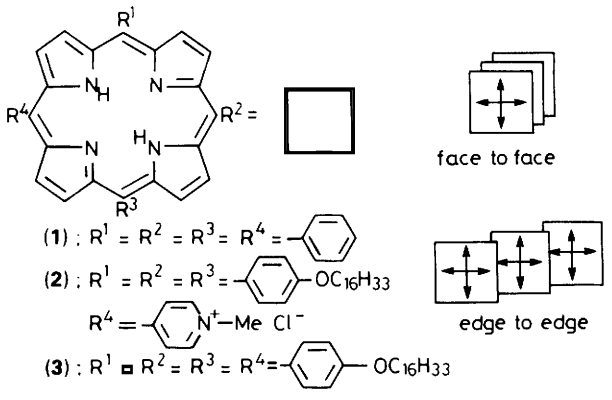
5,10,15,20-Tetrakis(4-hexadecyloxyphenyl)porphyrin forms unusual edge to edge type of aggregates in bilayers of dioctadecyldimethylammonium chloride vesicles.

The catalytic[1] and photophysical[2] properties of porphyrins anchored to synthetic vesicles are currently receiving much interest. Such systems are supposed to mimic certain biological functions, *e.g.*, substrate oxidations by membrane-bound enzymes (Cytochrome P450)[3] and light-energy conversion by membrane-bound proteins.[4] For a proper evaluation of these systems a knowledge of the location and state of aggregation of the porphyrin in the bilayer-membrane is essential. Here we report on the incorporation characteristics of tetra-aryl-porphyrins (**1**)—(**3**)[1a,5] into bilayers of dioctadecyldimethylammonium chloride (DODAC) vesicles. Evidence is presented that porphyrin (**3**) which bears four long aliphatic substituents forms unusual 'edge to edge' aggregates. In contrast, amphiphilic porphyrin (**2**) forms 'face to face' aggregates (Scheme 1).

Vesicle solutions were prepared either by sonication of a mixed film of DODAC and the porphyrin in water[6] or by a modified ethanol injection method.[7] Both methods resulted in the formation of small unilamellar vesicles in which the porphyrins were incorporated. At low porphyrin concentrations, *e.g.*, porphyrin to DODAC ratios (R) $< 5 \times 10^{-4}$, the porphyrins showed strong fluorescence behaviour. Quenching of this fluorescence was studied with various hydrophilic and hydrophobic quenchers (Table 1), which provides information on the location of the fluorophore within the bilayers.[8] Linear Stern–Volmer plots were obtained up to a quencher concentration of at least 0.2 mM (10% of the DODAC concentration). The data in Table 1 show that (**2**) is easily quenched by I^- but not by the hydrophobic brominated fatty acids. In contrast, the fluorescence of (**3**) is hardly affected by I^-, whereas it is effectively quenched by 16-bromopalmitic acid. Most likely, (**2**) is bound near the surface of the bilayer, whereas (**3**) is located close to the centre. The less efficient quenching of (**1**) by I^- suggests that this porphyrin is situated in the hydrophobic part of the bilayer. Its position, however, is not well defined as the two brominated fatty acids quench the fluorescence equally well. This conclusion is in line with the observation that (**1**) can act as an electron carrier across bilayer membranes.[9]



Scheme 1

Increasing the porphyrin to DODAC ratio causes changes in the absorption spectra (Table 1, Figure 1A) as well as a decrease of the fluorescence intensity (Figure 1B). These changes are due to exciton coupling between the porphyrin molecules.[10] Apparently, at higher concentrations the porphyrins aggregate within the bilayer.[11—13] However, we observed remarkable differences in the changes of the absorption spectra of the three porphyrins. For (**2**) a small blue-shift of the B-(Soret) band was observed, which according to exciton theory suggests that 'face to face' aggregates are formed (Scheme 1). The fluorescence self-quenching curve could very well be fitted by assuming that these aggregates are dimers.[14] Porphyrin (**3**) displayed a remarkable splitting of the B-band at 421 nm into a band of lower intensity at 402 nm and one with higher intensity at 436 nm (Table 1, Figure 1A). This spectroscopic behaviour of (**3**) is in line with the formation of 'edge to edge' type of aggregates.[10] The Q-band spectral

Table 1. Spectroscopic data of porphyrins in DODAC vesicles.

	$\lambda_{max.}$[a]/nm		K_{SV}[b]/mol^{-1} dm^3			
Porphyrin	$R = 5 \times 10^{-4}$	$R = 4 \times 10^{-3}$	I^-	9(10)-bromo-stearic acid	16-bromo-palmitic acid	N[c]
(1)	418	420	430	156	388	3.5 ± 0.4
(2)	426	424	1170	60	156	2[d]
(3)	421	402, 436	117	78	492	4.2 ± 0.26

[a] $\lambda_{max.}$ of B-bands in DODAC vesicles, [porphyrin] = 10^{-6} M. [b] K_{SV} is the Stern–Volmer quenching constant, [porphyrin] = 10^{-6} M, [DODAC] = 1.5×10^{-3} M, T = 50 °C. [c] Aggregation numbers were determined by using mixtures of Cu and Zn porphyrins according to a procedure described in ref. 15, [porphyrin] = 10^{-6} M, [DODAC] = 1.5×10^{-3} M, T = 50 °C. [d] This value was estimated by fitting the fluorescence self-quenching curve to a model in which only dimers are involved (correlation coefficient is 0.99).[15]

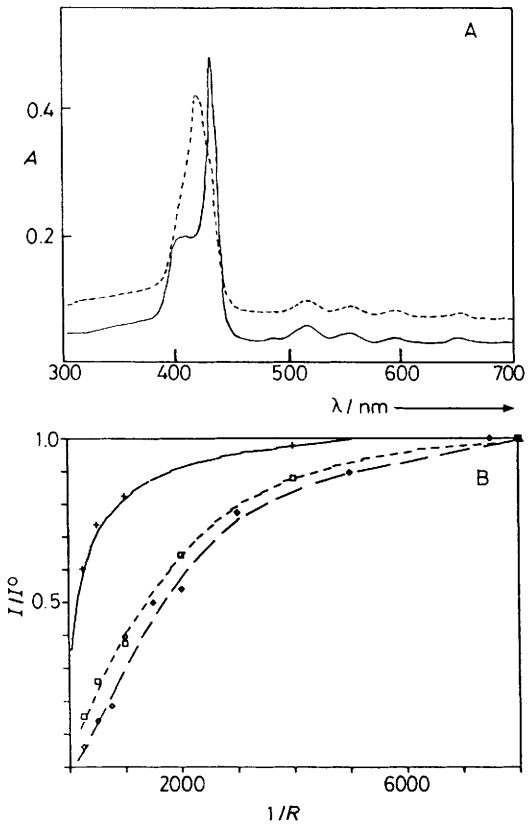


Figure 1. A: UV-VIS absorption spectra of (3) in DODAC vesicles, [porphyrin] = 10^{-6} M, (- - -) $R = 5 \times 10^{-4}$, (——) $R = 4 \times 10^{-3}$. B: Self-quenching of the fluorescence, (1) (□), (2) (+), (3) (◇), I° is the fluorescence intensity at $R = 10^{-4}$, [porphyrin] = 10^{-6} M, T = 50 °C.

features of (3) did not change, indicating that the observed B-state splitting is not due to the presence of different species within the bilayer. According to exciton theory the red-shifted B-band would originate from an in line arrangement of one of the transition moments of the porphyrin molecules and the blue-shifted band from a parallel arrangement of the other transition moment (Scheme 1). Other orientations of the molecules, however, cannot be excluded. Recently, Schick *et al.* also observed a splitting of the B-band for monolayer assemblies of 5,10,15,20-tetrakis [4-(octyloxy)phenyl]porphyrin (OOP).[15] Apparently, aggregates of (3) in DODAC vesicles have a similar molecular arrangement of porphyrin molecules as OOP has in monolayers. For (1) a broad absorption spectrum was observed at high porphyrin concentrations with shoulders on the red side as well as on the blue side. This suggests that the B-band of this compound undergoes a similar but less well resolved splitting as the B-band of (3). A possible explanation for the different behaviour of (1) is that it forms aggregates with a higher positional freedom. This will lead to different exciton coupling energies resulting in a broadening of the spectrum.[13]

From the fluorescence self-quenching curves in Figure 1 it can be concluded that the formation constants of the aggregates are larger for (1) and (3) than for (2). Also the aggregation number is higher for (1) and (3) than for (2) (Table 1). This different behaviour may be related to the presence or absence of charges on the porphyrin molecules.

It can be foreseen that the observed difference in aggregation behaviour and location of (1)—(3) in bilayer assemblies will lead to a difference in chemical reactivity. We are currently investigating how this feature can be exploited.

Received, 5th December 1989; Com. 9/05183J

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