The formation of small unilamellar vesicles in which the amphiphilic porphyrin (3) which bears four long aliphatic chains forms unusual edge to edge type of aggregates in bilayers of dioctadecyldimethylammonium chloride vesicles. Evidence is presented that porphyrin (3) which bears four long aliphatic chains forms unusual edge to edge type of aggregates in bilayers of dioctadecyldimethylammonium chloride vesicles. Evidence is presented that porphyrin (3) which bears four long aliphatic chains forms unusual edge to edge type of aggregates in bilayers of dioctadecyldimethylammonium chloride vesicles.

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References


We have found that a characteristic C-13 quaternary carbon signal is observed in the 13C NMR spectra of all 13,14-anhydroamphotericin B derivatives at around δ 153. Compounds (6), (7), and (8) show absorptions at δ 152.8, 153.5, and 153.3 respectively.

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

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

The catalytic and photophysical 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) and light-energy conversion by membrane-bound proteins. 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-arylporphyrins (1)—(3) 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 or by a modified ethanol injection method. 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 × 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. 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.

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. Apparently, at higher concentrations the porphyrins aggregate within the bilayer. 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. 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. The Q-band spectral...
Table 1. Spectroscopic data of porphyrins in DODAC vesicles.

<table>
<thead>
<tr>
<th>Porphyrin</th>
<th>( \lambda_{\text{max},b}^{a}/\text{nm} )</th>
<th>( K_{\text{SV}}^{b}/\text{mol}^{-1}\text{dm}^{3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>418, 421</td>
<td>430, 117</td>
</tr>
<tr>
<td>(2)</td>
<td>426, 424</td>
<td>1170, 78</td>
</tr>
<tr>
<td>(3)</td>
<td>402, 436</td>
<td>156, 492</td>
</tr>
</tbody>
</table>

\( \lambda_{\text{max}}^{a} \) of B-hands in DODAC vesicles, [porphyrin] = 10^{-6} M.

\( K_{\text{SV}}^{b} \) is the Stern-Volmer quenching constant, [porphyrin] = 10^{-6} M, [DODAC] = 1.5 \times 10^{-3} M, \( T = 50^\circ C \).

References