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An Amphiphilic Porphyrin with Unexpected Aggregation Behaviour

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Abstract. *The amphiphilic porphyrin 5,10,15-tris(1-methylpyridinium-4-yl)-20-[4-(hexadecyloxy)phenyl]-21H,-23H-porphine tritosylate forms vesicles on dispersal in water.*

As a part of our studies on synthetic models of cytochrome P450 enzymes,¹ we have synthesised porphyrin **1**, (Figure 1) which contains three positively charged methylpyridinium groups and one hexadecyloxyphenyl chain. We report here that **1** unexpectedly forms vesicles when it is dispersed in water.

Compound **1** was synthesised from *p*-(hexadecyloxy)benzaldehyde, pyridine-4-carboxaldehyde and pyrrole following a procedure described in the literature.² *N*-Methylation of the pyridinium groups was carried out with methyl tosylate and the compound was purified (column chromatography, silica 60H, eluent chloroform to remove the impurities then methanol to obtain the product) and characterised with ¹H-NMR, FAB-MS and UV-vis spectroscopy.³

Electron micrographs of a dispersion of **1** in water (0.1mM) are shown in Figure 1. Large spherical particles with diameters varying from 2,000 to 10,000 Å are visible. UV-vis spectroscopy was used to determine the critical aggregate concentration (cac) of **1**. The absorbance at 522 nm (Q band of porphyrin) was followed as a function of the amphiphile concentration. The curve followed Beer's law up to 10⁻⁵ M at which point an inflection was visible.

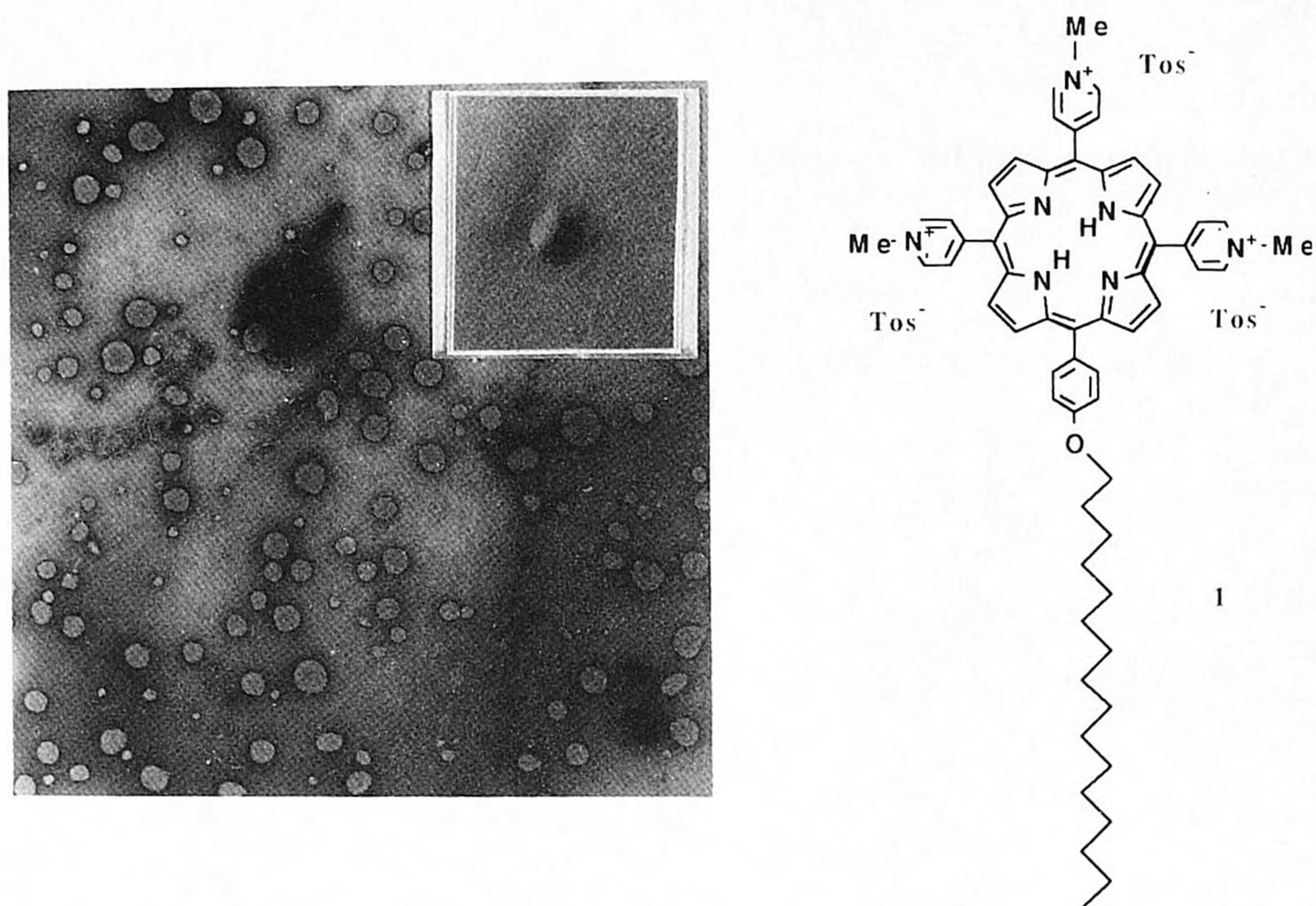


Figure 1 Electron micrograph of 0.1 mM dispersion of **1** in water. Negative staining with 1% uranylacetate, magn. 20,000 X (inset: freeze fracture micrograph).

Further increase in concentration caused a deviation from linearity due to the formation of aggregates. This result suggests that the cmc value of **1** is approximately 10^{-5} M. In the concentration range above cmc no decrease of absorbance was observed during several hours at room temperature, indicating that the vesicle dispersions are stable.⁴ The half-width of the Soret band in aqueous solution of **1** (426 nm for all concentrations above cac), which is a parameter for aggregation, was found to be 41 nm. When an 1:1 DMF:H₂O mixture was used as the solvent, this half-width decreased to 26 nm. This suggests that in this solvent mixture the amphiphile is in the monomeric form.

Considering its shape (calculated packing parameter from cpk space filling models $p \approx 0.1$) we would have expected that **1** would form micelles rather than vesicles in water.⁵ The unusual and unexpected formation of vesicles may be tentatively ascribed to the presence of strong stacking interactions between the porphyrin rings themselves and between these rings and the tosylate counter ions (see Figure 2).

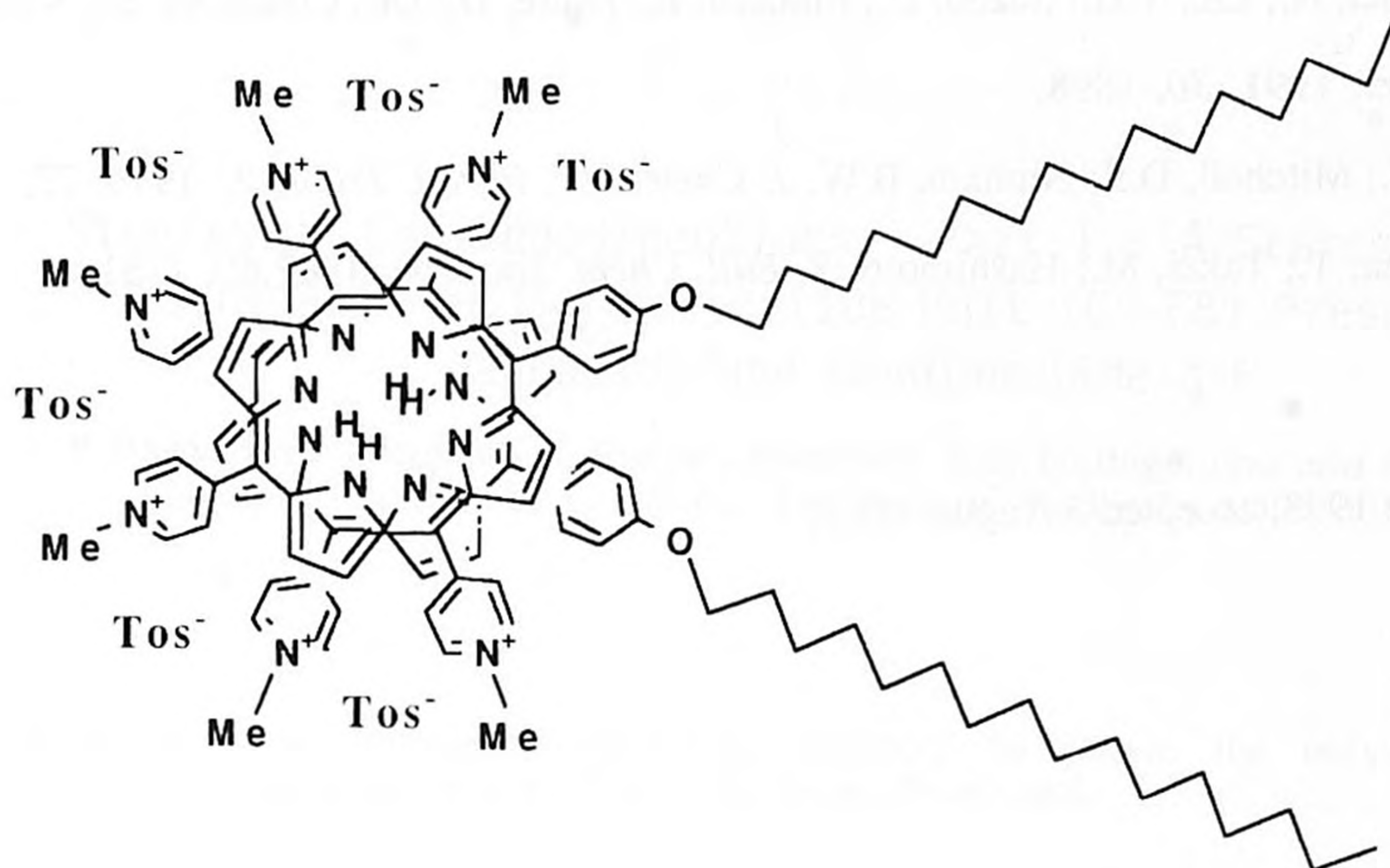


Figure 2 Proposed stacking arrangement of porphyrin rings in a bilayer of **1**

As a result of these interactions, the effective headgroup area in the aggregate will be smaller than that of a single hydrated porphyrin molecule **1**. Thus, p will be larger and may reach a value normally observed for vesicle forming amphiphiles ($0.5 < p < 1$). We are currently studying the physical properties of **1** and related amphiphilic porphyrins in more detail. Results will be published elsewhere.

References

1. van Esch, J.H.; Roks, M.F.M.; Nolte, R.J.M. *J. Am. Chem. Soc.*, **1986**, *108*, 6093.
2. Takagi, S.; Yamamura, T.; Nakajima, M.; Ishiguro, K.; Kawanishi, Y.; Nihojima, S.; Tsuchiya, H.; Saito, T.; Sasaki, Y. *Bull. Chem. Soc. Jpn.*, **1981**, *54*, 3879
3. **1**: ¹H-NMR (CD₃OD) δ : 9.5 (d, 2H, pyridyl), 9.2 (d, 6H, pyridyl), 8.9 (s, 8H, β -pyrrole), 8.3 (d, 2H, phenyl), 7.6 (d, 2H, phenyl), 7.3 (d, 6H, tosylate), 7.1 (d, 6H, tosylate), 4.9 (s, 9H, NCH₃), 4.3 (t, 2H, OCH₂), 2.2 (s, 9H, tosylate-CH₃), 1.3-1.5 (b, 28H, CH₂), 0.8 (t, 3H, CH₃), -2.5 (b, 2H, NH). FAB MS (matrix: nitrobenzyl alcohol): $m/z = 1246$ (M-Tos). UV/vis (DMF) λ/nm , ($\log(\epsilon/M^1 \cdot cm^{-1})$): 418(5.01), 522(3.89), 552(3.68), 587(3.47), 645(3.25).

4. Guillard, R.; Senglet, N.; Liu, Y.H.; Sazou, D.; Findsen, E.; Faure, D.; Des Courieres, D.; Kadish, K.M. *Inorg. Chem.* **1991**, *30*, 1898.
5. Israelachvili, J.N.; Mitchell, D.J.; Ninham, B.W. *J. Chem. Soc. Farad. Trans. 2*, **1976**, *72*, 1525.
6. Kano, K.; Nakjima, T.; Takei, M.; Hashimoto, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1281.

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