Micellar Fibres of Tin(IV) Porphyrins with Axial Hydrogen Chloride Ligands as Facial Head Groups

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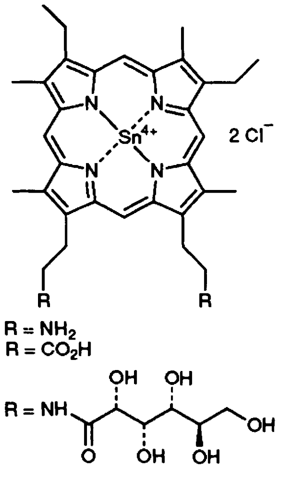
Amphiphilic tin(IV) porphyrinate dichlorides form micellar fibres with an average diameter of 5 nm and a length of several µm at pH 0; electronic and circular dichroism spectra indicate a lateral arrangement of facially protonated monomers.

Amphiphilic porphyrins have recently been assembled to micellar fibres and vesicular tubules[1,2] in bulk water. The nonfluorescing molecular assemblies produced anion radicals upon flash irradiation[2] and they gave strong CD-signals, if their water-soluble side-chains were chiral. It is known that monomeric porphyrin anion radicals or their protonation products, the phlorins, produce molecular hydrogen in the presence of platinum colloids.[3] They are most easily accessible and stabilized, when diamagnetic, high-valent, central ions, *e.g.* tin(IV), are present.[4,5] Here we report for the first time on the formation of ultrathin tin(IV) porphyrin fibres, which are only stable at low pH. They behave in a completely different manner from the known tin(IV)-µ-oxy polymers.[6]

The tin(IV) dichloride porphyrins **1a–c** were prepared by standard procedures.[2,7] All three compounds, the mesoporphyrin IX carboxylate **1b**, the ammonium salt **1a**, and the gluconamide **1c** were soluble in water at pH 5–7. The Soret band of **1a–c** appears at 381 nm, indicating face-to-face aggregates possibly of the µ-oxy type. No extended molecular assemblies were, however, detectable under the electron microscope. Base addition led to a replacement of the 381 by a 400 nm Soret band probably indicating the dissociation of small µ-oxy assemblies (...–O–Sn–O–Sn–O...) and formation of a monomeric dihydroxy complex. Addition of HCl, on the other hand, first produced some tin(IV) dichloride monomers, indicated by a 396 nm Soret band as well as by a rise in fluorescence (pH $\geqslant$ 2). At pH values lower than 1, the 396 nm monomer band disappeared within two hours and was replaced by two bands at 450 and 381 nm indicating a lateral assembly[1] (Fig. 1). A few percent of monomers remained in solution and were responsible for most of the fluorescence of the fibre suspension. The diammonium salt **1a** and the gluconamide **1c** formed this assembly at concentrations above 8×10^{-6} mol dm^{-3}, the carboxylic acid **1b** already in 3×10^{-6} mol dm^{-3} solutions. The observed spectral changes were similar in all these cases. Addition of 0.5 mol dm^{-3} sodium chloride allowed fibre formation already at pH 3. Hydrochloric acid could be replaced by HBr, but not by HF nor by H_2SO_4.



1a R = NH_2
b R = CO_2H
c R =

CD-spectra of the gluconamide **1c** were taken of the same solution at about the same time intervals. The CD-band at 465 nm rises parallel to the 450 nm band in the visible spectrum (Fig. 2). The molar ellipticity is close to the free base porphyrin value. The build-up of the CD-spectra was slowed down at higher temperature. Porphyrin assemblies of the achiral monomers **1a**, **b** gave no CD-spectra.

The same solution which produces the visible and CD-spectra in Fig. 1 and 2 was also blotted on electron microscopic grids and dried *without addition of stain*. Contrast for the electron beam was provided by the tin ions. Uniform micellar fibres of 4–5 nm width were observed (Fig. 3).

The observed pH-dependent, reversible assembly of tin(IV) porphyrins was unexpected. Originally we had anticipated the formation of µ-oxy polymers at neutral or slightly acidic pH. Dimers or short oligomers are indeed formed, as indicated by

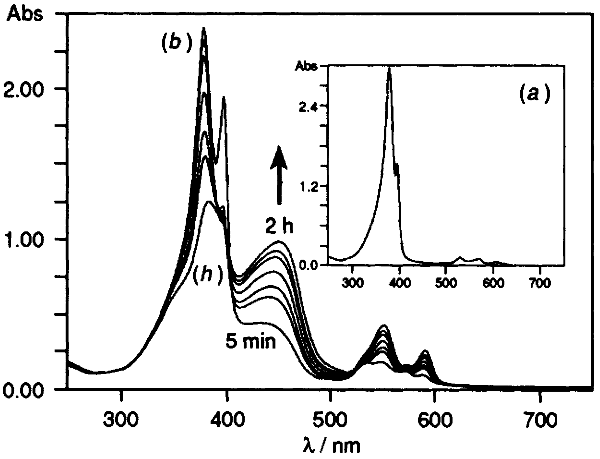


Fig. 1 Time-dependent absorption spectra of an aqueous solution of tin(IV) porphyrinate **1c**: (*a*) 2.5×10^{-5} mol dm^3, pH 5.8; after addition of HCl (*b*)–(*h*), 2.5×10^{-5} mol dm^{-3} pH 0 over 2 h

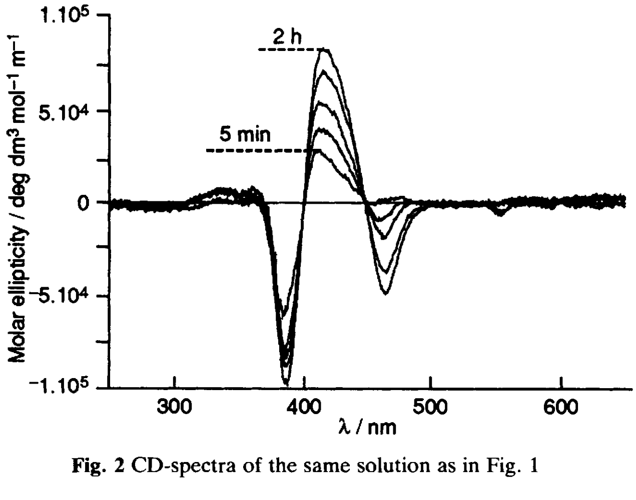


Fig. 2 CD-spectra of the same solution as in Fig. 1

the blue-shifted broad Soret band, but they are too small to be detectable by electron microscopy and neither was a CD-effect observed. At low pH two axial ligands on the central tin ions prevent the metalloporphyrin from stacking but a surprisingly efficient lateral assembly now becomes favourable. We find the fully reproducible formation of defined micellar fibres producing similar split Soret bands as the metal-free analogues.[1] We assume that Cl^- $H\cdots Cl^-$ hydrogen bonds,[8,9] which cover about the same distance of 0.35 nm as half a porphyrin macrocycle, are responsible for their assemblage. The cationic HCl-pairs on both sides of the porphyrins would then act as kind of 'facial' head groups[10] and make the hydration of the porphyrin plane possible (Fig. 4). The only remaining hydrophobic effect then consists of strong lateral porphyrin–porphyrin interactions between the three apolar porphyrin edges, which are indicated by the intense exciton coupling effects.[1] The measured exciton bands at 450 and 381 nm were in reasonable agreement with results from simple exciton theory and two centre-to-centre distances of 0.69 and 0.93 nm (Fig. 4). Fluoride and sulfate counterions inhibited stacking, but did not support lateral self-assembly.

The aggregate appears to be photochemically inactive. On excitation with laser flashes of 532 nm only absorption changes corresponding to the triplet state of the monomer were observed. Continuous irradiation in the presence of ascorbate produced a small amount of chlorin probably originating from monomers. The photochemistry of the porphyrin is thus totally quenched in the fibres as a combined effect of aggregation and the heavy metal ion tin(IV). Photoactive fibres[1,2] with a few percent of co-crystallized tin(IV) porphyrin as electron traps are currently being investigated as 'charge harvesting' molecular assemblies.

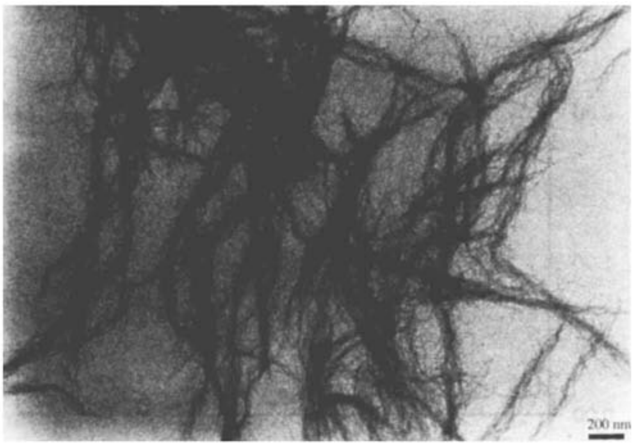


Fig. 3 Electron micrograph of micellar fibres made of **1c** without staining

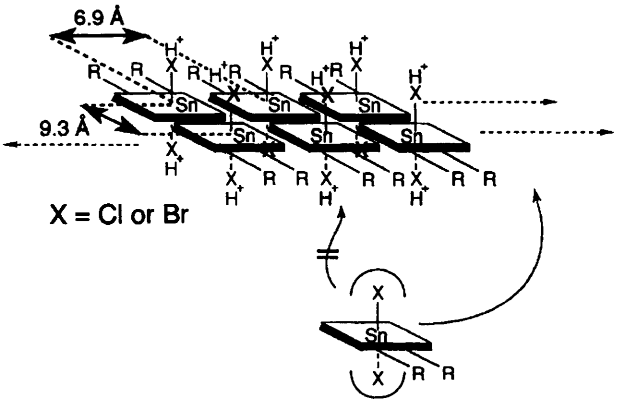


Fig. 4 Molecular model of the tin(IV) dihalide porphyrinate fibres

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