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Monomolecular Leaflets of 2,8,12,18-Tetraethyl-3,7,13,17-tetrapyridin-4-ylporphyrin in Bulk Aqueous Media

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Several amphiphilic porphyrins with a hydrophobic "northern" and a hydrophilic "southern" edge have been assembled into long-lived micellar fibers in aqueous media.[1−3] The tendency to form fibers of high curvature also leads to low solubilities of monomers and to a very low tendency to crystallize.[4] Porphyrins with a symmetrical arrangement of water-soluble groups around the macrocycle, on the other hand, are much more soluble in water,[5] and some of them have been crystallized.[6] We report here for the first time on a porphyrin bolaamphiphile **1** (in Figure 1) which produces planar monolayer leaflets in colloidal aqueous solutions.

2,8,12,18-Tetraethyl-3,7,13,17-tetrapyridin-4-ylporphyrin (**1**, type II isomer) was synthesized together with type I, III, and IV isomers and separated by silica gel chromatography. The overall yield of **1** from 4-ethyl-3-pyridin-4-yl-1*H*-pyrrole-2-carboxylic acid ethyl ester was 2%; 200 mg of **1** has been made routinely within 10 days. Only type II isomer **1** produced defined molecular assemblies in bulk water; type I, III, and IV isomers did not. The ^{1}H-NMR spectrum of **1** produced the expected signal patterns containing two well-separated methine bridge proton signals ($\delta = 10.2$ and 11.3 ppm). The electronic spectrum in chloroform showed a Soret band at 413 nm with an extinction coefficient of $\epsilon = 2.1 \times 10^5$, a half-bandwidth of 30 nm, and an etio-type visible spectrum. **1** was insoluble in water and formed stable surface monolayers with a molecular area of 87 Å^2, indicating slightly tilted lateral assemblies with interdigitated pyridine rings. The minimum surface area of a totally flat arrangement corresponds to 96 Å^2/molecule. LB films on glass showed no measurable fluorescence. The surface pressure before collapse was very high (75 mN/m) at pH 3,7, and 11, and a single Soret band at 431 nm with a half-width of 30 nm was measured in the pressure range from 0 to 55 mN/m. The long-wavelength shift of 18 nm of the Soret band indicates weak, lateral interactions, which have not been observed in *meso*-tetrapyridylporphyrin assemblies.[7] At pH 2 and below, the molecular surface area decreased to 50−70 Å^2/molecule. A 422 nm Soret band with small side bands at 360 and 470 nm was found, but the monolayer dissolved slowly in the subphase (creep test, $t_{1/2} = 60$ min).

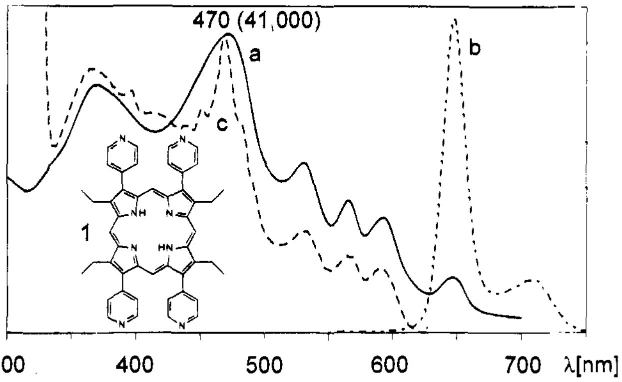

Figure 1. (a) Electronic spectrum of the porphyrin assemblies at pH 2.6, showing a split Soret band. (b) A strong fluorescence spectrum is found. (c) The excitation spectrum closely resembles the assembly spectrum (a).

1 dissolved in 25% hydrochloric acid with a blue color and produced a stable red solution when diluted with water and adjusted to pH 1. The visible spectrum still showed four bands of the free base porphyrin.[8]

Titration with sodium hydroxide did not lead to immediate precipitation of **1** from water, but at pH 2.5, the spectrum of the solution changed: the Soret band became very broad, with a long-wavelength maximum at 470 nm and a smaller band at 350 nm which slowly shifted to 370 nm. The visible bands had also slightly shifted (Figure 1a). The fluorescence spectrum of the solution decreased by 30% and shifted from 640 and 698 nm to 651 and 710 nm (Figure 1b). The fluorescence excitation spectrum ($\lambda_{\text{exc}} = 651$ nm) corresponds to the aggregate's absorption spectrum (Figure 1c). This clearly shows that indeed the polymeric assembly is the major fluorescing entity and not the trace amounts of monomers or smaller aggregates.

The colloidal porphyrin solution was then examined by transmission electron microscopy. Uranyl acetate stained probes appeared as rolled-up black leaflets ("positive staining", Figure 2a). We assume that the uranyl ions are complexed by the pyridyl units on the leaflet surface. Unstained cryomicroscopy[9] showed folded leaflets, whose thickness can be measured at foldings. Here, one detects 4 nm edges with a white streak in the center (Figure 2b). A single leaflet is therefore about 2 nm thick, which agrees with the molecular length of the amphiphilic porphyrin **1**. The 2 nm measurement can also be found directly. Amphiphile tilting and stacking at the edges of folded leaflets result in a density increase, which causes stronger contrast in a fringe of monolayer thickness (Figure 2c and inset therein). The same phenomenon also allowed, for example, determination of the thickness of vesicle membranes and rippled phases in cryo preparations.[10] A porphyrin−porphyrin distance also became measurable, because regular 7.3 Å striations appeared on some of the electron micrographs (Figure 2d). This distance correlates well with the assumed distance between the porphyrin planes in our leaflet model (Figure 3).

The structures of the surface and bulk monolayers are not the same, as is shown by the 431 and 370/470 nm Soret bands. The protonation of the pyridine rings obviously leads to water solubility of monolayers and to a stacking with large porphyrin−porphyrin distances (7.3 Å; Figure 3) and therefore to fluorescing assemblies. The 470 nm Soret band, on the other hand,

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(1) Fuhrhop, J.-H.; Demoulin, C.; Böttcher, C.; Köning, J.; Siggel, U. *J. Am. Chem. Soc.* **1992**, *114*, 4165.

(2) Fuhrhop, J.-H.; Bindig, U.; Siggel, U. *J. Am. Chem. Soc.* **1993**, *115*, 11036.

(3) Fuhrhop, J.-H.; Bindig, U.; Siggel, U. *Chem. Commun.* **1994**, 1583.

(4) Little, R. G.; Dymock, K. R.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 4532.

(5) Fülling, G.; Schröder, D.; Franck, B. *Angew. Chem.* **1989**, *101*, 1550.

(6) (a) Ford, K. G.; Pearl, L. H.; Nadle, S. *Nucleic Acids Res.* **1987**, *15*, 6553. (b) Körber, F. C. F.; Smith, J. R. L.; Prince, S.; Rizkallah, P.; Reynolds, C. D.; Schawcross, D. R. *J. Chem. Soc., Dalton Trans.* **1991**, 3291.

(7) Porteu, F.; Palacin, S.; Ruandel-Teixier, A.; Barraud, A. *J. Phys. Chem.* **1991**, *95*, 7438.

(8) The pK_a of *meso*-tetrapyridylporphyrin is about 1.1, see: Fleischer, E. B.; Webb, L. E. *J. Phys. Chem.* **1963**, *67*, 1131.

(9) Adrian, M.; Dubochet, J.; Lepault, J.; McDowall, A. W. *Nature* **1984**, *308*, 32. The specified *d*-spacings from optical diffraction patterns were obtained with a 632.8 nm laser.

(10) Vinson, P. K.; Bellare, J. R.; Davis, H. T.; Miller, W. G.; Scriven, L. E. *J. Colloid Interface Sci.* **1991**, *142*, 74.

0002-7863/95/1517-8273$09.00/0

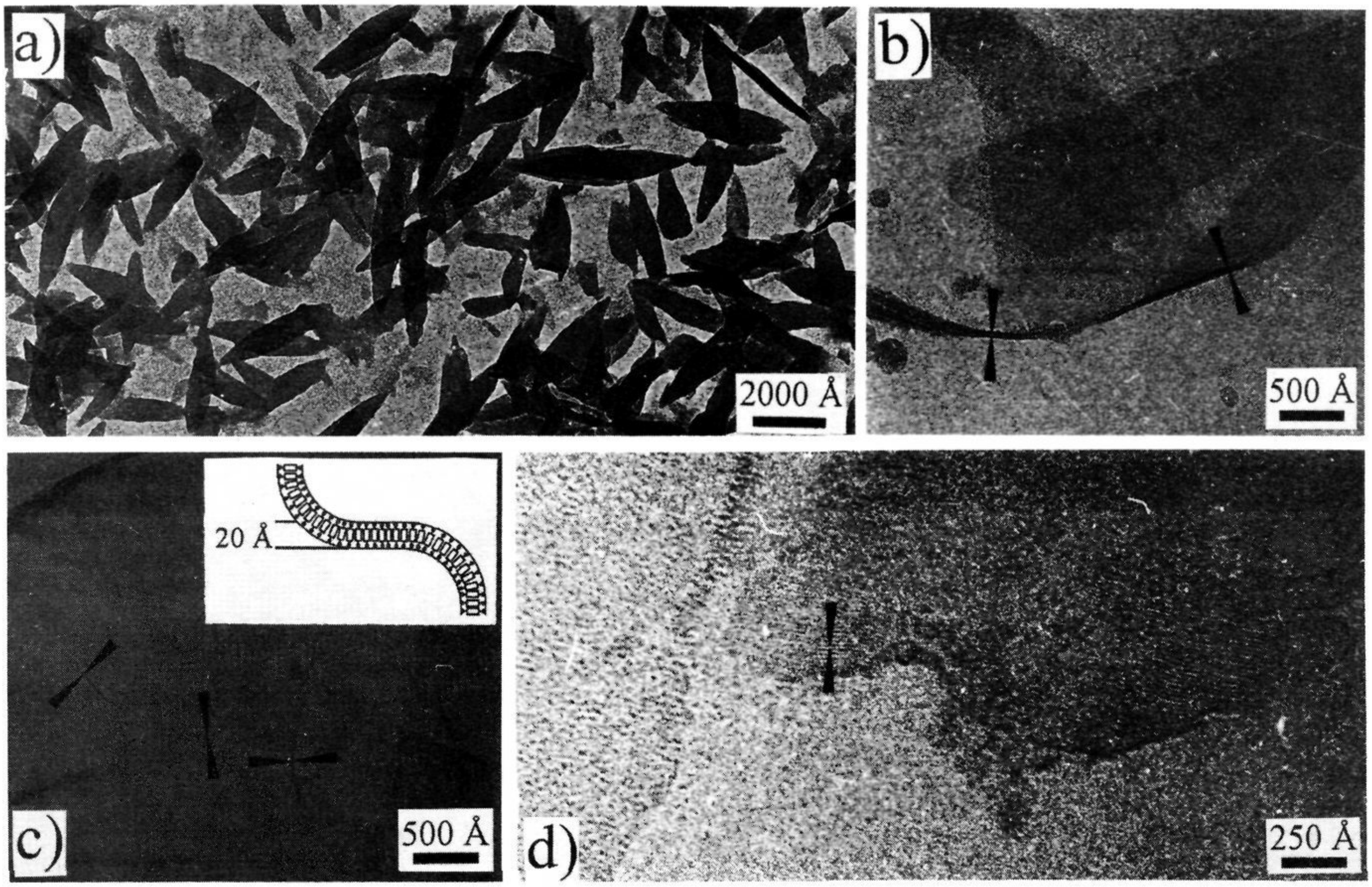

Figure 2. Transmission electron micrographs of the porphyrin **1** assemblies obtained in water at pH 2.6 (a) dried and negatively stained with uranyl acetate (1% w/w). (b–d) Cryo preparations in vitreous ice without stain. The arrows indicate (b) a double layer, (c) a monolayer, and (d) 7.3 Å porphyrin–porphyrin spacings (see text and Figure 3).

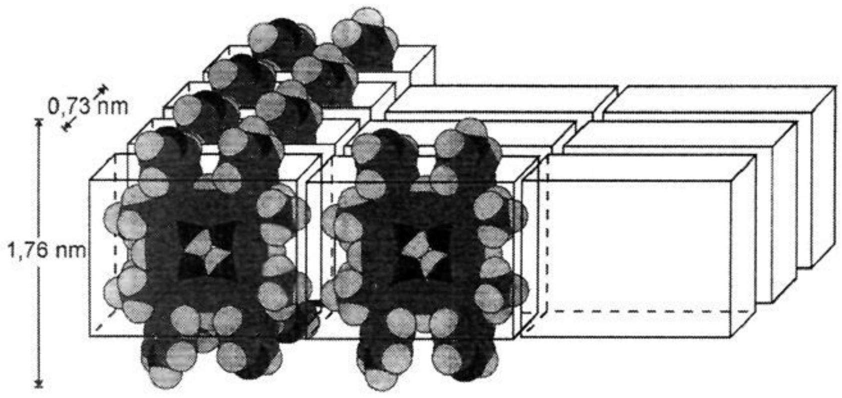

Figure 3. Model of the porphyrin **1** leaflets with the electron microscopic distances.

points to a strong lateral interaction of the porphyrins.[1] The cryo TEM pictures (Figure 2) show that molecular monolayers prevail (Figure 3); the partly protonated pyridine hinder the formation of 3D crystals. The weak interaction between the hydrophobic edges should allow undulations of the monolayer, which provides additional stabilization of the colloidal solutions. The solutions remain stable for several hours and can probably be further stabilized by the addition of various metal ions, which bind to the neighboring pyridyl units. The photochemistry of such assemblies and the adsorption of the monolayer leaflets on solid surfaces are currently under investigation.

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