Micellar Rods and Vesicular Tubules Made of 14‴,16‴-Diaminoporphyrins

Jürgen-Hinrich Fuhrhop,*,† Uwe Bindig,† and Ulrich Siggel‡

Institut für Organische Chemie
Freien Universität Berlin, Takustrasse 3
14195 Berlin, Germany
Max Volmer Institut für Physikalische Chemie
Technischen Universität, Strasse des 17, Juni 135
10623 Berlin 12, Germany

Received July 28, 1993

The most important natural porphyrin, namely protoporphyrin IX, is an amphiphilic molecule which is prone to form molecular bilayer assemblies in aqueous media.[1,2] Very long lived micellar fibers have recently been obtained from the corresponding glyconamides and identified by electron microscopy.[2] They showed a characteristic UV/vis spectrum with a split Soret band (360, 460 nm) indicating strong lateral as well as stacking exciton interactions within the porphyrin assemblies. They did not fluoresce; their photochemistry has not been reported.

Here we report on aminoporphyrin **1** and its pH-dependent molecular assemblies in water and their photochemistry. The porphyrin was obtained[3] from protoporphyrin IX dimethyl ester by treatment with hydrazine in pyridine, which reduced the vinyl groups and hydrazinolyzed the ester, and by subsequent treatment with nitrous acid, rearrangement to the isolable urethane, and HCl-catalyzed hydrolysis. The overall yield was 50%. The electroneutral diamine **1** was insoluble in water (pH = 11) and formed stable monolayers on water surfaces. At zero surface pressure, the Soret band occurred at 460 nm (Figure 1), presumably indicating lateral interactions within porphyrin domains.[4-6] At 40 mN/m surface pressure, this long-wavelength band had disappeared and was replaced by a 420-nm band. The collapse pressure of the monolayer was 58 mN/m; the corresponding molecular area 55 Å^2, indicating stable layers and an upright orientation of the porphyrin chromophores. At low surface pressure we assume an angle close to 45°, such as that found in fluid black lipid membranes.[5] Higher surface pressures[6-8] probably enforce an angle close to 90°, which is indicated by the molecular surface area corresponding to the product of porphyrin thickness (4.0 Å) times width including two methyl groups (12 Å).

The dihydrochloride of the aminoporphyin **1** dissolved in aqueous acid showed a blue-shifted Soret band at 370 nm in the pH range from 4 to 6. At higher pH values, the Soret band appears split at 445 and at 360 nm. At pH 7.4, the conversion is halfway; at pH 8.9, it is complete (Figure 2). The titration curve is somewhat asymmetric and steeper than that of a single deprotonation reaction. The apparent pK_a of the amino groups

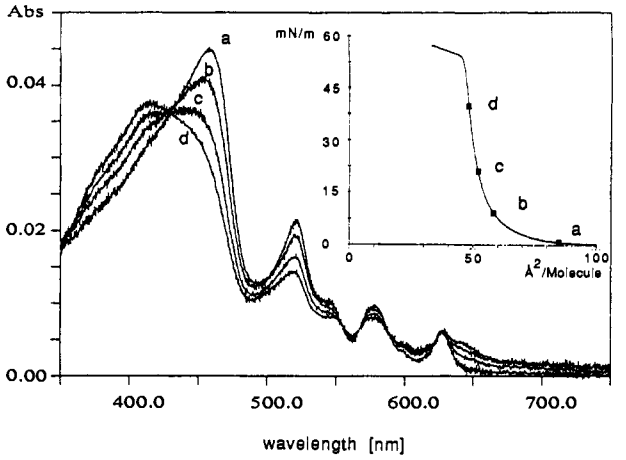

Figure 1. Dependence of absorption spectra of molecular monolayers of aminoporphyrin **1** on surface pressure.

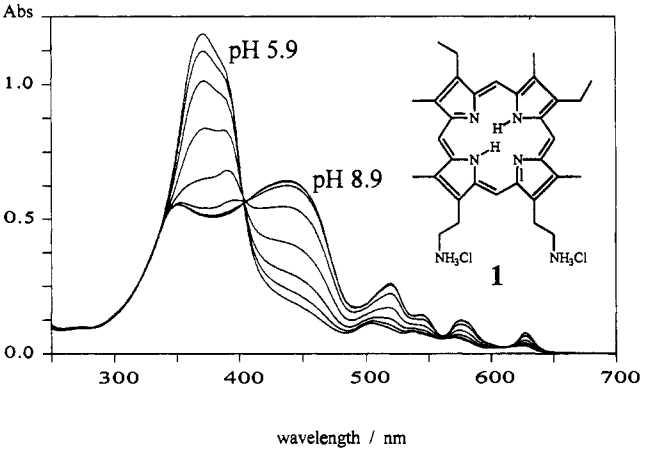

Figure 2. Absorption spectrum of an aqueous colloidal solution of the aminoporphyrin **1** fibers at various pH values (5.9, 6.5, 7, 7.4, 7.6, 8.05, 8.55, and 8.9).

is obviously lowered by the electric potential of the protonated amino groups[9] on the bilayers surface.

The blue-shifted Soret band at around pH 5 points to stacked assemblies of face-to-face oligomers.[2] The visible spectra contain four bands. Therefore, the porphyrin chromophore occurs as the free base. Only the peripheral amino groups should be protonated. Electron micrographs of such solutions show tubules with an outer diameter around 30 nm and an average length of 800 nm (Figure 3 top). At high concentration (≥2 × 10^{-2} M), a long-lived, thixotropic gel is formed, and no change of the Soret band absorption occurs. Electron micrographs now show very long micellar rods with diameters between 6 and 20 nm (no figure). Similar fibers have been obtained from DMSO/water (1:1) solutions (Figure 3 bottom). Such solutions were long-lived and showed the Soret band at 370 nm. The 445-nm band at high pH, on the other hand, is consistent with a lateral ribbon stabilized by ammonium–amine hydrogen bonds. Electron micrographs show short 30-Å ribbons (not shown). At pH 8.6, about 50% of the amino groups should be deprotonated. Up to this pH, the aminoporphyrin solutions are colloidal, with a tendency toward further aggregation. At higher pH values, all of the amino groups become electroneutral and immediate precipitation occurs. As in the case of the 370-nm stacks, long-lived solutions can be obtained in DMSO/water (1:1) at pH 8.6.

On excitation of the deaereated solutions in 1:2 DMSO/water mixtures of pH 8.6 with 10-μs flashes, a photoreaction occurred.

† Freien Universität Berlin.
‡ Technischen Universität.

(1) Inamura, I.; Uchida, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2005–2007.
(2) Fuhrhop, J.-H.; Demoulin, C.; Boettcher, C.; Köning, J.; Siggel, U. *J. Am. Chem. Soc.* **1992**, *114*, 4159–4165.
(3) (a) Fischer, H.; Haarer, E.; Stadler, F. *Hoppe-Seyler's Z. Physiol. Chem.* **1936**, *241*, 209–221. (b) Baker, E. W.; Ruccia, M.; Corwin, A. H. *Anal. Biochem.* **1964**, *8*, 512–518.
(4) Bergeron, J. A.; Gaines, G. L.; Bellamy, W. D. *J. Colloid Interface Sci.* **1967**, *25*, 97–106.
(5) Steinemann, A.; Stark, G.; Läuger, P. *J. Membr. Biol.* **1972**, *9*, 177–194.
(6) Möhwald, H.; Miller, A.; Stich, W.; Knoll, W.; Ruandel-Teixier, A.; Lehmann, T.; Fuhrhop, J.-H. *Thin Solid Films* **1986**, *141*, 261–275.
(7) Désormeaux, A.; Ringuet, M.; Leblanc, R. M. *J. Colloid Interface Sci.* **1991**, *147*, 57–66.
(8) Barber, C.; Freitag-Beeston, R. A.; Whitten, D. G. *J. Phys. Chem.* **1991**, *95*, 4074.
(9) Fuhrhop, J.-H.; Penzlin, G.; Tank, H. *Chem. Phys. Lipids* **1987**, *43*, 147–158.

0002-7863/93/1515-11036$04.00/0

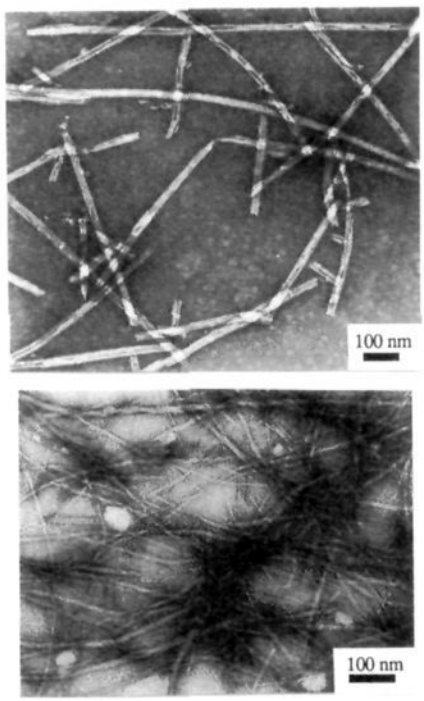

Figure 3. Transmission electron micrographs of porphyrin fibers (top) in water, pH 6.5, $c = 1.0 \times 10^{-5}$ M; vesicular tubules o.d. = 25–33 nm, i.d. = 5 nm; Soret band, 370 nm; and (bottom) in water/DMSO (1:1), pH 5.0, $c = 1.0 \times 10^{-2}$ M, micellar rods $d = 3$ nm.

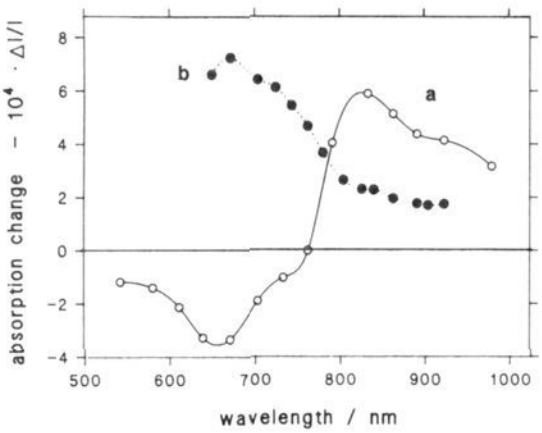

Figure 4. Difference spectra induced by 10-μs flashes of blue light under nitrogen. Curve a: DMSO/H_2O (1:2), pH 8.6, $c = 2.5 \times 10^{-5}$ M; colloidal solution of short micellar fibers (electron transfer). Curve b: H_2O, pH 0, $c = 5 \times 10^{-6}$ M; monomeric porphyrin tetracation (triplet state).

It is characterized by a difference spectrum with a maximum at 835 nm and a minimum at 660 nm (Figure 4). This does *not* correspond to the triplet-state spectrum, which is found on excitation of nonaggregated solutions. Such a spectrum with a maximum at 670 nm could only be obtained for the aminoporphyrin **1** at pH = 0. The 835-nm band is very likely related to a charge separation within the fiber leading to an anion radical and a cation radical. This reaction cannot occur from the triplet state because it would be endergonic. It should, however, be possible from the singlet state. The porphyrin–porphyrin distances within the fibrous assembly should be short enough for very fast electron transfer which has to compete with fast internal conversion. The porphyrin fluorescence is nearly totally quenched at pH 8.6 and becomes measurable at pH 5. The excitation spectrum shows that this emission (maxima at 611 and 671 nm) is due to some monomer being present. Thus both aggregates, characterized by absorptions at 370 and 445 nm, respectively, are essentially nonfluorescing.

The following experimental results are in favor of a charge separation from the singlet state.

(i) The absorption changes occur nearly unchanged in the presence of oxygen, which would strongly accelerate triplet relaxation. In our preparation, the triplet state does not seem to be populated.

(ii) The absorption changes are fully reversible. The absorption spectrum is unchanged after prolonged flashing. This also explains the extreme longevity of the solutions, which are light- and oxygen-stable for several months. An irreversible photoreaction of the porphyrin with impurities in solution is thus excluded.

(iii) The reversibility of the photoreaction is lost after addition of the electron acceptor benzylviologen (1,1′-dibenzyl-4,4′-bipyridinium dichloride). The viologen radical (λ_{max} 395 and 620 nm) appears, and the solution turns blue. The porphyrin aggregate is now slowly destroyed. Its spectrum is not restored after reoxidation of the viologen radical with oxygen. The longevity of the viologen radical also indicates that the porphyrin cation radical, which must be formed in a charge-separation process, is short-lived. The photolability of the porphyrin assembly–viologen mixture prevented measurements of meaningful action spectra.

(iv) Triplet-state relaxation to the ground state would be exponential if triplet-triplet annihilation can be excluded. Exponential kinetics is observed for electron back transfer in a radical pair, formed by excitation of a dimer.[10] The relaxation kinetics of the absorption changes of aminoporphyrin assembly at pH 8.6 is, however, more complex. An exponential fast phase of 20 μs half-time can be separated, which amounts to some 40% of the signal in the far red region. The fast phase exhibits the same difference spectrum was the end-of-flash signal. The slower phases (not relaxed after 4 ms) show similar but not identical difference spectra. At 734 nm, for example, there is only the fast phase. Even on nanosecond laser excitation, the relaxation kinetics remains complex. A fast phase and slower phases on a different time scale are again observed.

We thus assume light-induced charge separation between two identical molecules. These are controversially discussed in the literature. No electron transfer has, for example, been observed in covalently connected symmetric diporphyrins.[10] Charge separation from the excited singlet state has, however, been considered for a positively charged zinc (tetramethylpyridinium)-porphyrin, localized on the surface of negatively charged DHP vesicles.[11] Photocurrents in a photovoltaic cell containing zinc octaalkyl ether porphyrin organized in cofacial stacks in discotic mesophases[12] have also been related to charge separation. Finally, even zinc octaethylporphyrin monomers in organic solution have been shown to yield ion radicals by quenching of the triplet state by ground-state porphyrin.[13] This may be an example of nonequilibrium electron transfer. The electron transfer from the excited singlet state of a porphyrin to the ground state of a neighboring molecule of the same porphyrin is favored by the fact that the LUMOS of both molecules have the same symmetry. The structural and energetic requirements for optimal charge separation in all of these systems need, however, to be established.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (SFB 312 "Vectorial Membrane Processes"), the Fonds der Chemischen Industrie, and the Förderungskommission für Forschung der Freien Universität Berlin. We thank Prof. G. Renger for useful discussions and permission to use his flash photometer.

(10) Netzel, T. L.; Bergkamp, M. A.; Chang, C.-K. *J. Am. Chem. Soc.* **1982**, *104*, 1952.
(11) Hurst, J. K.; Lee, L. Y. C.; Grätzel, M. *J. Am. Chem. Soc.* **1983**, *105*, 7048.
(12) Gregg, B. A.; Fox, M. A.; Bard, A. J. *J. Phys. Chem.* **1990**, *94*, 1586.
(13) Ballard, S. G.; Mauzerall, D. C. *J. Phys. Chem.* **1980**, *72*, 933.