Solid Vesicle Membrane Made of
meso-Tetrakis[(bixinylamino)-*o*-phenyl]porphyrins

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Abstract: Tetrakis(aminophenyl)porphyrin with four bixin side chains in statistical orientation with respect to the porphyrin plane and its zinc(II) complex produced stable colloidal solutions in water at pH 9. Cryoelectron microscopy showed spherical unilamellar vesicles with diameters ranging from 30 to 120 nm and a membrane thickness of 4.7 ± 0.5 nm, corresponding to a monomolecular layer with the bixin side chains tilted by 30°. The stiff vesicle membranes were not sensitive to the addition of sodium chloride and survived adsorption to dry solid surfaces. Furthermore, the vesicles were totally polymerized by visible light. These polymer vesicles remained intact in 95% ethanol, and scanning force microscopy (SFM) images showed perfectly spherical shapes on graphite. A slow collapse is only observed on hydrated mica. The tetrabixinporphyrin also produced stable monolayers on water surface which polymerized upon irradiation. Combination of the polyene vesicle with an electron-accepting porphyrin, namely a synthetic guanidinium porphyrin or 2-anthraquinone sulfonate, led to light-induced long-lived charge separations.

Introduction

In nature, β-carotene protects chlorophyll from photooxidation,[1] and in model systems, covalently bound carotenes are thought to donate electrons to the cation radicals of quinone-containing porphyrin triads.[2] The natural bolaamphiphilic carotenoid *bixin* (**2**), on the other hand, is an electron-poor polyene and its aqueous solutions are relatively light and oxygen stable. It has been used as a dyestuff ("Annatto or Orlean") for centuries. In concentrated solution or in the solid state, however, one observes decolorization;[3] similar photochemical reactions of crystalline materials have been observed in hexatriene-1,6-dicarboxylate, leading to cyclobutane dimers as well as polymers.[4] We report here for the first time rigid polyene membranes made of *meso*-tetrakis[(bixinylamino)-*o*-phenyl]-porphyrins which polymerize to form a single vesicular molecule with unique properties. A preliminary report on photochemical properties is also given.

Experimental Section

Methods and Materials. Bixin was purchased from Fa. Roth (Germany) and purified by recrystallization before use. 5,10,15,20-Tetrakis(*o*-aminophenyl)porphyrin and 2,18-bis(2-aminoethyl)-7,12-diethyl-3,8,13,17-tetramethyl-21*H*,23*H*-porphyrin and its cycloguanidinium derivative were prepared according to the previously reported procedure.[5−8] Other chemicals were commercial high-purity grades and not further purified. The water used was deionized using a Millipore-Q system. Infrared spectra were recorded with a Perkin-Elmer 580B IR or Nicolet 800 FT/IR spectrometer. ^{1}H NMR spectra were measured with samples dissolved in CDCl₃, CD₃OD, or DMSO-*d₆* at room temperature using a Bruker AM 270 SY spectrometer. Chemical shifts are expressed in parts per million downfield from Me₄Si as an internal standard. Mass spectra were obtained from a Varian-MAT 7U spectrometer using EI and FAB methods. Elemental analysis was performed by the Mikrolabor der Freien Universität Berlin. UV−vis absorption spectra were obtained on a Perkin-Elmer Lambda 16 spectrophotometer. Thin-layer chromatography (TLC) was carried out on 0.2 mm precoated plates of silica gel 60 F₂₅₄ (Merck) or RP-18 F₂₅₄S (Merck). Purification was performed by silica gel 60 (Merck) or octadecyl-functionalized silica gel (Aldrich) column chromatography. The buffer (pH 1.2) used for RP-18 TLC was water/trifluoroacetic acid/28% aqueous ammonia (478/12/10 mL). The buffer (pH 1.2) used for octadecyl-functionalized silica gel columns was prepared by adjusting 0.1 M hydrochloric acid and 2 M aqueous ammonia. Fluorescence emission spectra were recorded on a Perkin-Elmer MPF-44B.

Experimental details of the syntheses, spectra (^{1}H and ^{13}C NMR, IR, MS), and elemental analyses are supplied as Supporting Information.

Molecular Mass of Polymer. The polymerization was carried out by irradiation of aqueous or methanolic solution with incandescent light until the carotene bands had disappeared completely. Typically 100−300 W tungsten lamps were used, and irradiation times were between 5 and 240 min. The solvent was then removed and the residue refluxed in various solvents (DMSO, CHCl₃, DMF, ethanol). No porphyrin fluorescence was detectable. We then tried to dissolve 3 mg of the lyophilized vesicle polymer in 3 mL of 1-chloronaphthalene at 250 °C. After filtration at 250 °C, 500 μL of the solution was injected onto a 240GPC-3506 column (Senshu Kagaku Model VHT SSC-700

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equipped with a 6L-Scieno GPC-350b column and UV−vis detector) again at 250 °C. The column oven temperature was 210 °C (flow rate 1 mL/min). Polystyrenes labeled with pyrene were used as molecular weight standards. The eluent was monitored at 420 nm (Soret band), but no absorption could be detected. The solubility in 1-chloronaphthalene at 250 °C was therefore $<10^{-6}$ M, in all other solvents tried $<10^{-8}$ M.

Preparation of Aqueous Porphyrin Solutions. A tetrabixinylporphyrin vesicle solution was prepared under an argon atmosphere in the dark. **1c** (or **1d**) in THF (40 mL, 12.6 mM) was, for example, rapidly injected to pH 9.0 water (5 mL), and the obtained orange-red solution was sonicated for several minutes by a Ultrasonics Sonicator W-220F under water bath. Guanidinium porphyrin **3e** (645 mg, 1 mmol) was first dissolved in 0.1 mL of DMSO and diluted by 0.9 mL of water, giving a 1 mM stock solution. For spectral measurements, this solution was injected into 3 mL of water in a cuvette by microsyringe.

Transmission Electron Microscopy (TEM). The negatively stained and cryospecimens for TEM were prepared as described elsewhere.[8] For stained samples, a 2% aqueous solution of phosphotungstate (pH 8.7) was used. The obtained grids were observed in a Philips CM12 electron microscope at an accelerating voltage of 100 kV and primary magnification of 60 000×. Platinum/carbon shadowed specimen were prepared as follows. A droplet of the aqueous tetrabixinylporphyrin solution was placed onto a carbon-coated copper grid (400 mesh), and after 1 min, excess fluid was blotted off. The remaining thin film of the sample was air-dried for 12 h. The specimen was then shadowed by Pt/C evaporation under angle of 66° using a BALTEC MED-020 coating system. In the case of mica surface, the obtained Pt/C replica was floated off in ethanol solution and loaded onto a carbon-coated copper grid.

Scanning Force Microscopy (SFM). Five milliliters of the tetrabixinylporphyrin vesicle solution (30−60 mM) was placed onto freshly cleaved highly oriented pyrolytic graphite (HOPG) or mica. After 1 min, excess fluid was carefully blotted off by filter paper and air-dried. SFM measurements were carried out using a Nanoscope III (Digital Instruments, Inc., Santa Barbara, CA) in the tapping mode under ambient conditions. Silicon cantilevers (length 125 mm, width 30 mm, thickness 3−5 mm) with a spring constant between 17 and 64 N/m and a resonance frequency in the range 240−400 kHz were used. Resonance peaks in the frequency response of the cantilever were selected in the range between 280 and 320 kHz for the tapping mode oscillation. Scanning rate was usually 0.5−1.0 Hz. Imaging was performed displaying the amplitude signal and the height signal, simultaneously.

Langmuir−Blodgett Monolayers. Monolayers were prepared at the air−water interface in a LAUDA Langmuir Filmwaage. The tetrabixinylporphyrins were spread from a 50−70 mM solution in DMSO/CH$_3$OH/CH$_2$Cl$_2$ (1/10/39 v/v/v). The subphase was 10^{-3} M HCl. The obtained monolayers were polymerized by exposure to a 300 W incandescent lamp which was kept at a distance of 30 cm from the water surface. The light irradiation was performed for 1 h at a constant surface pressure of 30 mN/m. Absorption spectra were taken as the reflectivity differences between the water−air interface covered by a monolayer and a clean reference surface, using light guides (Perkin-Elmer) and a silver-mirror (Schindler and Hoyer) on the bottom of the trough.

Laser Flash Photolysis. Laser flash photolysis studies were carried out according to the previously reported procedure by using a Q-switched Nd:YAG laser (Spectrum Co.) which generated a second-harmonic (532 nm) pulse of 2 ns duration.[8] The porphyrin solutions for flash photolysis were held in a 1 cm cuvette under argon. Porphyrin concentrations used were normally 5−10 mM. For quenching experiments, several milliliters of **3e** and 2-anthraquinone sulfonate (2-AQS) aqueous solutions were injected to 3 mL of the porphyrin solutions. Most experiments were carried out at 20 °C.
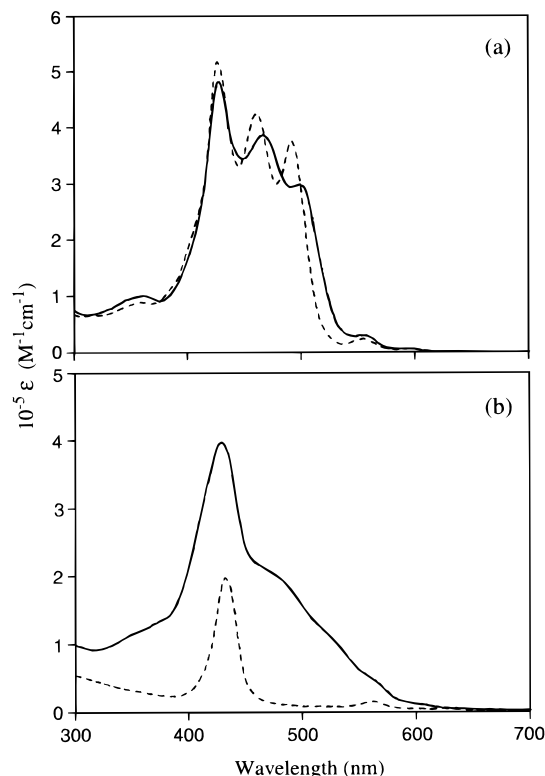
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Figure 1. Visible absorption spectra of tetrabixinporphyrin: (a) **1d** in THF (solid line) and zinc tetrakis(aminophenyl)porphyrinate with bixin **2** (molar ratio = 1:4, dotted line), (b) aqueous vesicular solution (pH 9.0) (solid line) and its polymer (dotted line).
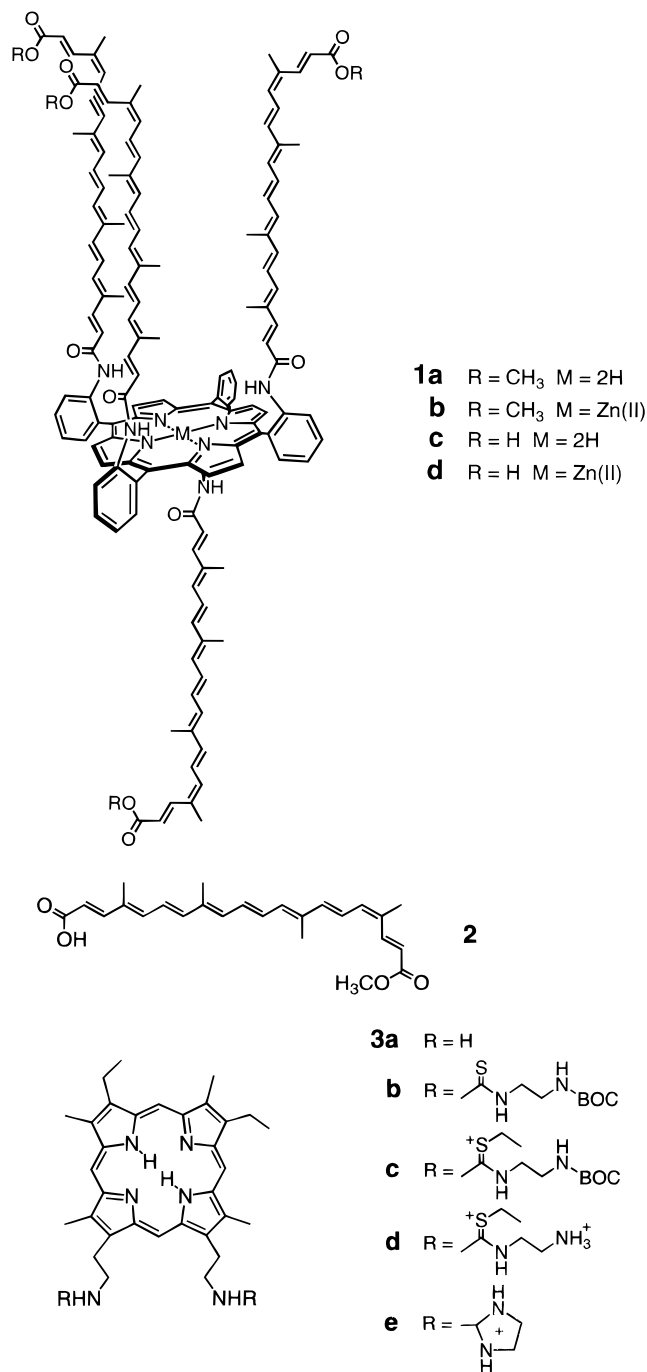
Results and Discussion

Bixin (**2**) was converted to the mono acid chloride mono methyl ester using thionyl chloride in THF. Further reaction with *meso*-tetrakis(*o*-aminophenyl)porphyrin produced the tetrabixinamide **1a** in 58% yield after column chromatography. No attempt was made to separate the atropisomers ($\alpha\alpha\alpha\alpha$:$\alpha\beta\alpha\beta$:$\alpha\alpha\beta\beta$:$\alpha\alpha\alpha\beta$ = 1:2:1:4). Zinc ions were introduced to give the complexes **1b,d**. The cycloguanidinium porphyrin **3e** was made from 2,18-bis(aminoethyl)mesoporphyrin and [2-[(*tert*-butoxycarbonyl)amino]ethyl]isothiocyanate according to a modified procedure for cycloguanidinium derivatives by Kneeland et al.[7]

The UV−vis spectrum of zinc tetrabixinylporphyrinate **1d** in THF is dominated by a porphyrin Soret band at 427 nm (e = 4.8×10^5) and two broad polyene absorptions at 467 and 499 nm in **2** (Figure 1a). This spectroscopic pattern was similar to the spectrum of a 1:4 molecular mixture of zinc tetrakis-(aminophenyl)porphyrinate and **2**, but a 6−7 nm wavelength shift of the bixin chromophore indicated interaction between the porphyrin and the carotenoid (Figure 1a). The porphyrin **1d** showed 8% of the fluorescence of bixin-free porphyrin. Upon injection of the tetrabixinylporphyrins **1c** or **1d** into water at pH 9 (sodium hydroxide), a transparent orange-red solution ($\leq 2 \times 10^{-4}$ M) was obtained, which produced broader absorption bands (Figure 1b) and showed *no* fluorescence at all.

Cryoelectron micrographs displayed the vesicles as ideal spheres with diameters between 30 and 120 nm. The membrane thickness was found to be 4.7 ± 0.5 nm, corresponding to a monomolecular layer of **1d** with a tilt of about 30° of the bixin side chains. The dense packing of the rigid polyene chains produced highly contrasted images of the membrane without any staining. Addition of a 4-fold molar excess of bixin to the vesicular solution at pH 9 led to the expected increase of the broad absorption bands at 480 nm, indicating that the free bixin had been incorporated into the vesicle. The cryo-TEM image

1a R = CH₃ M = 2H
b R = CH₃ M = Zn(II)
c R = H M = 2H
d R = H M = Zn(II)

2

3a R = H
b R = thiourea-BOC
c R = S-ethyl isothiouronium-BOC
d R = S-ethyl isothiouronium-NH₃⁺
e R = imidazolidine

Figure 2. (a) Cryoelectron micrograph of tetrabixinylporphyrin vesicles in vitreous ice without staining (**1d**/bixin, molar ratio = 1:4, pH 9.0). (b) SFM image (tapping mode) of **1d** vesicles on HOPG and its cursor profile (vertical distances: a−a 42 nm, c−c 27 nm; lateral distance: b−b 62 nm).

was as same as before (Figure 2a). The membrane did not become significantly thicker. Furthermore, the tetrabixinylporphyrin **1c** or **1d** vesicles were not sensitive to the addition of electrolytes. Sodium chloride (0.15 M), for example, did not cause precipitation or shrinking. The perfectly circular shape of single vesicles also showed no flattening upon contacting with other vesicles. These observations point to extreme rigidity and porosity of the vesicle membranes.

The aqueous vesicular solution was then transferred to a graphite surface and subjected to scanning force microscopy (SFM). As anticipated, the stiff vesicle membranes survived the drying and adsorption processes. Deformed balloon-like vesicles became detectable (Figure 2b, horizontal distance 62 nm, vertical distance 27 nm). To the best of our knowledge, this is the first picture of a three-dimensional vesicle in the dry state. Experiments with other vesicles showed an immediate collapse on solid surfaces.[9] Dried samples of egg yolk lecithin vesicles, for example, showed only planar circles under the same
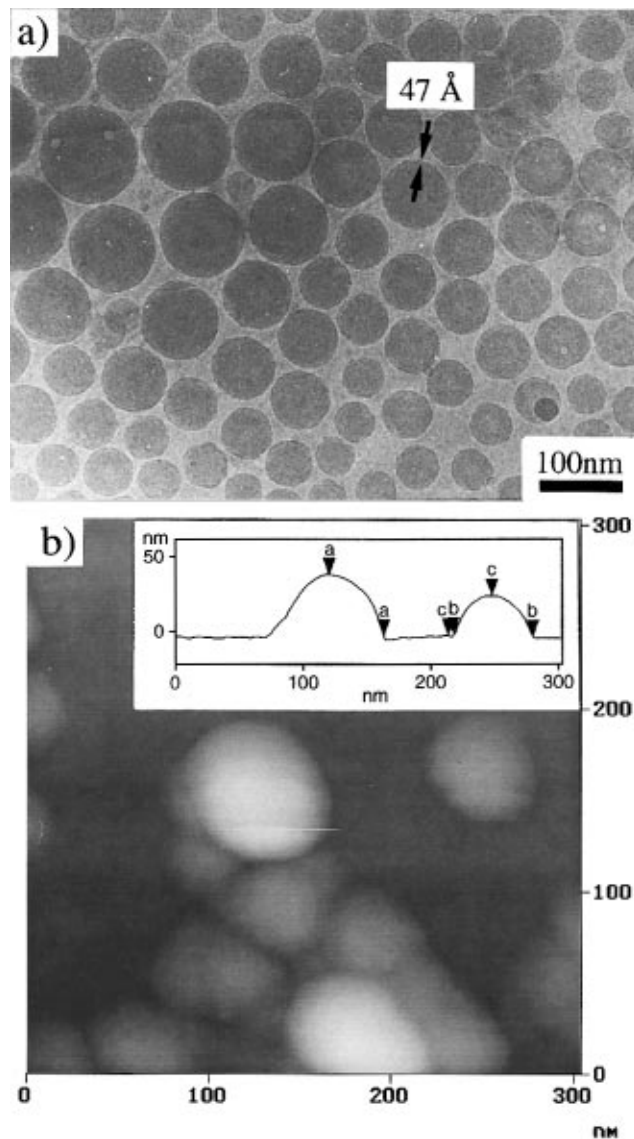
conditions and bolaamphiphile vesicles made of disodium 2,5,20,23-tetraoxo-1,6,19,24-tetraoxacyclohexatriacontan-3,21(22)-diylbis(thio)bis(acetate)[10] crystallized quickly upon drying to form circular platelets of double layer thickness (3.2 nm).

The orange-red vesicles made of **1c** or **1d** bleached rapidly in air and light. The bixin absorption disappeared completely within 1 day in daylight and within 1 h or so under a 300 W incandescent lamp (Figure 1b). The porphyrin Soret band only diminished by less than 10% under the same conditions, and a strong fluorescence at 650 nm was observed after the carotene bleaching was complete. The process of bixin-bleaching could consist either of a porphyrin-sensitized oxidation, a polymerization reaction, or a combination of both. The lyophilized polymer powder was insoluble in organic solvents and showed no C=C stretching bands around 1600 cm⁻¹ or C−H deformation vibration bands of alkenes at 900−1000 cm⁻¹ in the infrared spectra. These bands were, however, also weak in the original bixinporphyrin. ¹H NMR spectra of the polymers showed only

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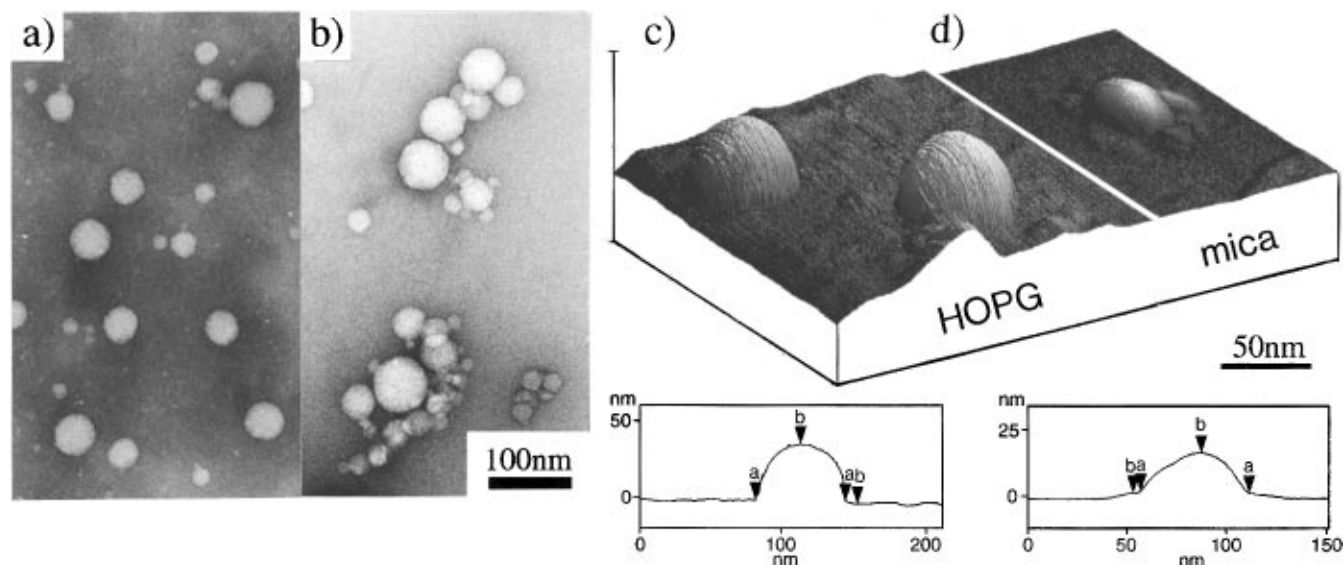
Figure 3. Electron micrographs of negatively stained samples of polymerized tetrabixinylporphyrin (**1d**) vesicles with phosphotungstate (a) in water (pH 9) and (b) after resuspension in 50% ethanol. SFM images (tapping mode) and its cursor profiles (c) on HOPG (lateral distance a−a: 60 nm; vertical distance b−b: 41 nm) and (d) on mica (lateral distance a−a: 55 nm; vertical distance b−b: 15 nm).

signals for saturated hydrocarbons and no methine protons neighboring oxygen atoms or at carbon−carbon double bonds. We conclude that massive intra- and intermolecular cross-linking of the polyene chains and not oxidation was responsible for bleaching. Intermolecular polymerization was also confirmed by the finding that the vesicles not only survived water evaporation and resuspension (Figure 3a) but also could be dissolved in 50% or 95% ethanol without losing their perfectly spherical shape as was shown by TEM (Figure 3b) or SFM on freshly cleaved graphite (Figure 3c). The calculated lateral diameter of the polymerized vesicle (40 nm) in the SFM image is in good agreement with the measured height (41 nm, vertical distance between b−b in Figure 3c), if one considers the lateral broadening effect by the tip's shape.[11,12] Shadowing experiments for TEM also confirmed their perfectly round shape. The diameters of the Pt/C shadowed vesicles on carbon-coated grids were always constant independent of the observation angle (0− 45°). Only on mica did the polymer vesicles show flattening (Figure 3d) and eventually collapse. When the graphite preparation had aged, flattening also occurred. We assume that one-sided hydration is responsible for the strong adsorption of the vesicle membranes on mica. The collapsed vesicles finally have a height of about 7 nm, indicating a disordered double layer.

These tetrabixinporphyrin vesicles constitute the first spherical membrane structure of molecular thickness which is an isolable entity. Attempts to measure the molecular mass of the vesicular polymer failed because it was insoluble in organic solvents. Refluxing of lyophilized vesicles in chloroform−methanol or dimethyl sulfoxide or dimethylformamide gave, after filtration, no fluorescing solutions. Heating in 1-chloronaphthalene to 250 °C and gel chromatography at 210 °C resulted in no porphyrin absorption at 420 nm. We conclude that the molecular mass is $\gg 10^6$ Da; the expected molecular mass of the vesicle polymer would be in the order of 10^7 Da. It may be considered as a single, balloon-shaped polymer molecule. In the case of other polymerized lipid vesicular membranes, vesicle curvature generally prevents formation of extended polymers originated from ene or diyne monomers.[13−20] Only central vinyl groups

connecting both ends of a bilayer membrane lead to very high molecular weights.[16a,c,20b] Such cross-linked bilayers do, however, not survive 95% ethanol. In our case, there are so many polymerizable double bonds almost over the whole width of the monolayered membrane that the vesicle curvature can be retained if covalent bonds are formed at very different membrane sites. In tetraphenylporphyrin crystalline sheets, one finds a parallel stacking of nearest-neighbor phenyl groups[21] and photoreactions between polyene substituents[22] should be very favorable within the vesicle membranes (Figure 4). We propose that upon porphyrin- and bixin-sensitized triplet formation, the unpaired electrons dissipate over the chromophore and react to cyclic dimers (Figure 4). Since essentially all bixin chromophores disappear and the intramolecular distance between the four side chains is large, we also assume that they rotate slowly from one porphyrin side to the other. The slowness of the process may explain, why the 50% bleaching occurs within a few minutes, whereas total bleaching takes hours. The vesicle membranes may be taken as fluid−crystalline sheets rigidified by the stiff acid side chains.

At pH 3, the tetrabixinylporphyrin formed stable monolayers on water surfaces. The surface pressure was an unprecedented

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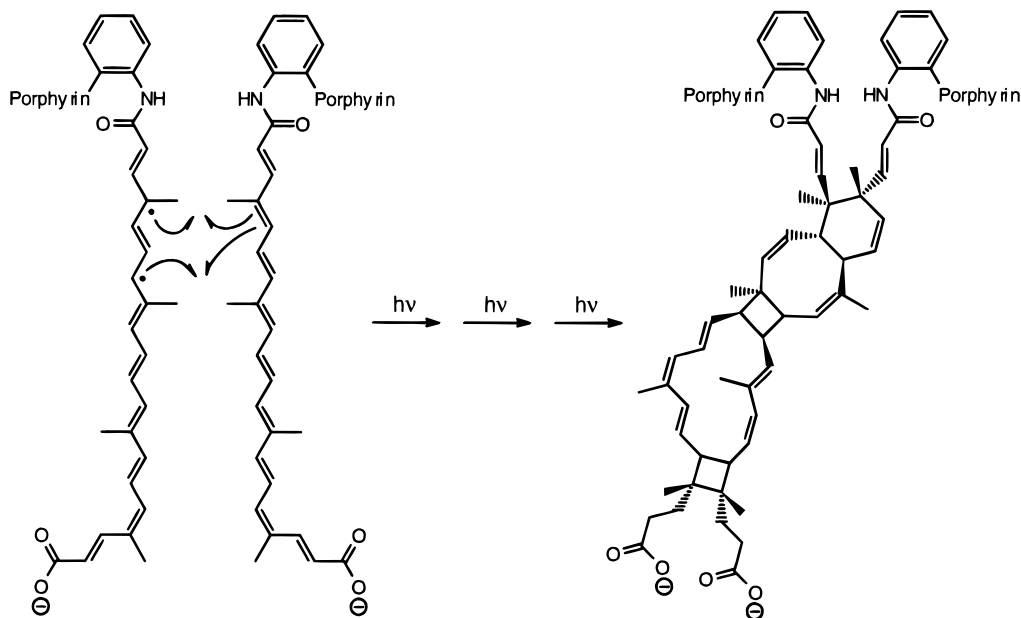
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Figure 4. Model of the bixin polymer connected to the porphyrin.

70 mN/m for a porphyrin monolayer and the molecular area was 2.75 nm². This area corresponds to the value usually found for tetraphenylporphyrin with four hydrophobic side chains,[23,24] and we assume that the porphyrin plane lies about 2.5 nm above the water surface, corresponding to the length of the bixin chains. This assumption is qualitatively supported by the finding that the porphyrin chromophores are *not* protonated on an aqueous substrate of pH 3. Upon light irradiation at a constant surface pressure of 30 mN/m, the bixin chromophore was quantitatively bleached, whereas the porphyrin absorption essentially remained and increased. The $p-A$ isotherm of the obtained polymer showed again a high collapse pressure (70 mN/m), but the molecular area decreased to 2.00 nm². Covalent binding between the side chains to form presumably a single polymer molecule leads to 30% decreasing of the molecular surface. The increased absorption of the porphyrin moieties is most likely due to the enhanced concentration of the chromophores in the surface layer as indicated by the molecular surface areas, which is smaller in the polymer by a factor of 1.4. Preliminary experiments to remove this molecule as a "*monolayer cloth*" from the water surface failed, however.

The bixin chromophore in vesicle membranes and the surface monolayer is thus destroyed within hours in light and oxygen. Nevertheless, the anionic bixin membrane with the porphyrin center also shows interesting short-term photochemistry especially in connection with the guanidinium porphyrin **3e** counterion. Laser flash photolysis (Nd:YAG laser, 532 nm) of the vesicular solution of the zinc complex **1d** under argon gave a product with a halflife of 1.5 μs (Figure 5), characterized by a difference spectrum with a maximum at 834 nm assigned presumably to bixin radical cations.[25] It is in the picosecond time range formed by reductive quenching of the excited porphyrin, which is beyond the resolution of our apparatus. The back-reaction with the porphyrin radical anion, which we resolve, is much slower than expected and should correspond to a intermolecular back reaction. This reaction is further
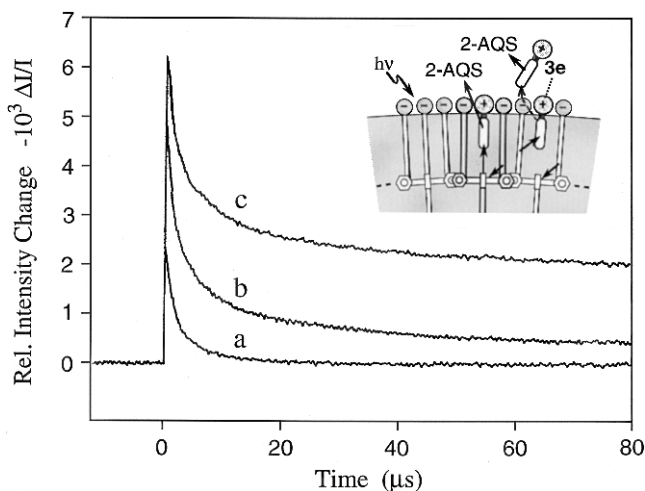
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Figure 5. Transient absorption decays (834 nm) of aqueous zinc tetrabixinylporphyrinate (**1d**) vesicle solution (pH 9) following laser excitation with 2 ns pulses of 532 nm light: (a) **1d** vesicles (6.5 mM), (b) with **3e** (molar ratio = 1:1), (c) with **3e** and 2-AQS (1 mM). Arrows in the inserted picture are conceivable courses of electron transfer.

slowed and becoming biphasic by the addition of secondary electron acceptors. The electron-accepting diguanidinium porphyrin **3e** occurs as a diprotonated dication at pH 9 and was incorporated into the surface region of the bixin vesicle. This was evident by a broadening of its Soret band, reduction of the Soret band of **1d** (isosbestic points), precipitation of the vesicle after addition of 3-fold excess of **3e,** and the fact that **3e** alone forms molecular fibers in water with a very broad and split Soret band. The same difference spectrum was measured as without **3e**. But, relaxation of the absorption change was now slower and biphasic with 70% decaying with $t_{1/2} = 2.6$ ms and 30% decaying with $t_{1/2} = 1$ ms (Figure 5). After reduction, the guanidinium porphyrin macrocycle becomes more hydrophilic and can leave into the bulk aqueous phase. The back-reaction with bixin cations within the vesicle is a slow second-order reaction. In the presence of a second electron acceptor, 2-anthraquinonesulfonate (2-AQS), the amount of slower phase increased to 50% of the signal. The synkinetic system combining a carotenoid vesicle with membrane-trapped porphyrin cations and quinone anions therefore leads to long-lived

carotenoid radicals. Details of the photochemical reactions are currently being investigated.

Conclusion

The bolaamphiphilic **1d** with a central porphyrin sensitizer and four rigid carotenoic acid side chains shows a unique polymerization behavior. The polyene chains provide so many polymerization sites that vesicles or macroscopic monolayers are connected to totally coherent nets to which apparently each molecule of the monolayer becomes covalently linked. The multi- and monomolecular vesicles remain spherical in the dry state, and their slow collapse on polar surfaces may be caused by surface water layer. The anionic polyene vesicle membranes with a central porphyrin core can presumably also be used in light-induced charge separation processes with external electron acceptors.

Supporting Information Available: Experimental details of the syntheses, spectra (^{1}H and ^{13}C NMR, IR, MS), and elemental analyses (5 pages). See any current masthead page for ordering and Internet access instructions.

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