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Porphyrin Wheels

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Abstract: A simple method to prepare porphyrin "wheels" on a micrometer scale is described. It is possible to arrange several types of porphyrin derivatives, including Protoporphyrin IX and Chlorophyll-*a*, in the form of rings using this method. A mechanism for the formation of these types of assemblies is proposed that is based on the generation of "2D-gas bubbles" which induces aggregation of the porphyrin molecules.

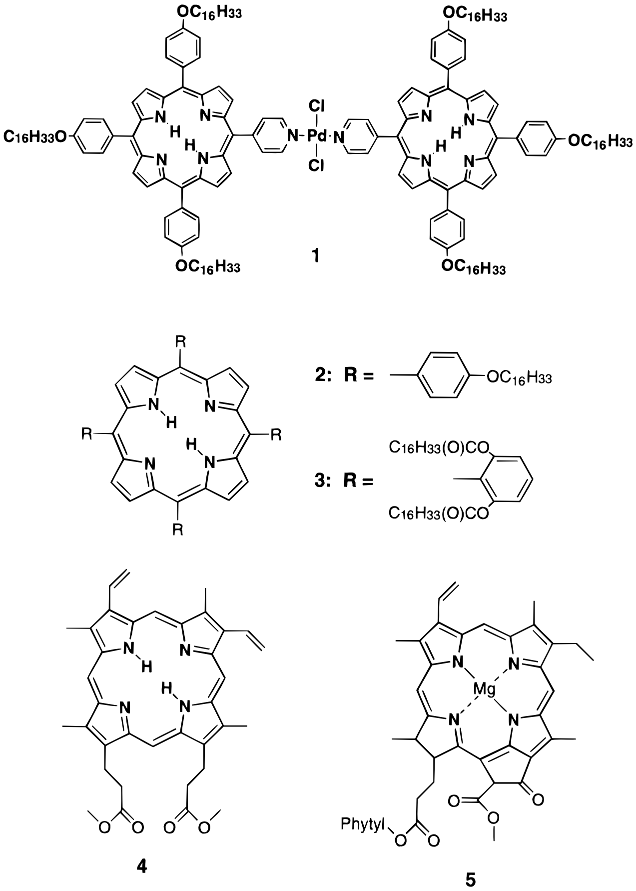
Introduction

The construction of molecular assemblies having well-defined shapes, dimensions (molecular objects), and pattern formation by self-assembly of molecules is a topic of great current interest.[1,2] Applications of these supramolecular structures can be foreseen in fields such as electronics, information storage, light energy conversion, and catalysis. Porphyrins are attractive building blocks to form such molecular materials since they are (photo)catalytically active and have interesting electronic properties.[3,4]

As part of our program aimed at the development of energy and electron storing and transporting systems from phthalocyanine and porphyrin molecules,[5,6] we describe here a simple method to prepare porphyrin "wheels" on a micrometer scale. It is possible to arrange several types of porphyrin derivatives, including Protoporphyrin IX and Chlorophyll-*a* in the form of rings, by this method. The diameter of these rings can be altered by varying the temperature. Ring-shaped assemblies of porphyrins are known to occur in nature, *viz.* in the bacterial light-harvesting complex LH2,[7] which is responsible for the absorption of light and the storage and transportation of light energy to the reaction center, where it is converted into chemical energy. In the LH2 complex the porphyrin molecules are arranged as in the wheels of a turbine.

Results and Discussion

Chart 1



We discovered the formation of ring-shaped objects from porphyrins while studying the properties of compound **1** (Chart 1). A droplet of a 1 × 10^{-4} M solution of **1** in chloroform was placed on a carbon-coated copper grid and the solution was allowed to evaporate for 10 s at 20 °C and then drained with a filter paper. Transmission electron micrographs of these grids, taken without staining, revealed the presence of rings (Figure 1a). The possibility of globular structures, such as droplets or vesicles, was ruled out because the inner compartments of the rings were colorless. The staining in the present case originates from the strong electron scattering by the palladium metal centers in the molecules of **1**. Scanning electron micrographs of the samples showed that dimer **1** forms large wheels with diameters varying between 1 and 5 μm (Figure 1b). Electron diffraction studies indicate that the wheels had an amorphic structure. The rings were also visible by confocal laser scanning microscopy in the fluorescence mode. The observed diameters were in the same range as those observed by the electron microscopy. The average width and height of the bands of the rings could be determined using near-field scanning optical

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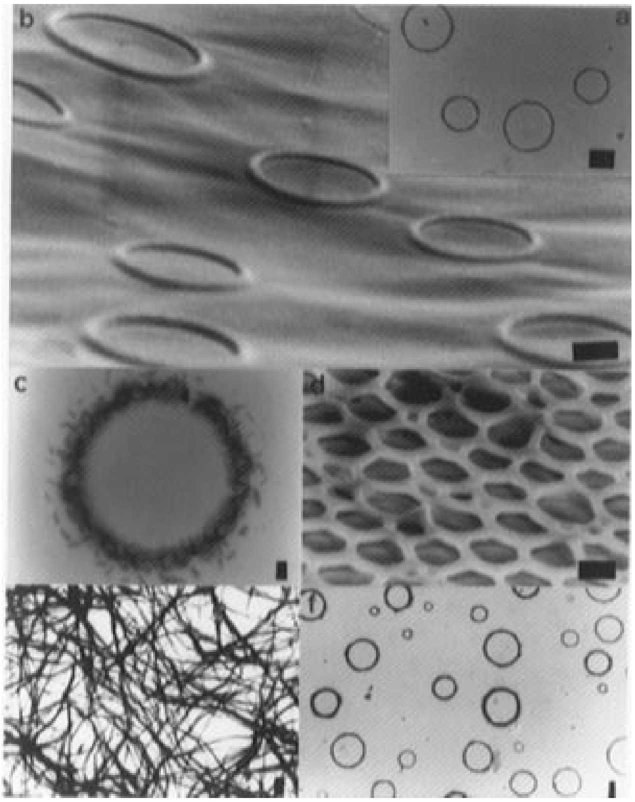

Figure 1. (a) Transmission electron micrograph of a 1 × 10^{-4} M dispersion of **1** in chloroform without staining. Draining was applied after 10 s at 20 °C. The bar represents 1 μm. (b) Scanning electron micrograph of a 1 × 10^{-4} M dispersion of **1** in chloroform drained after 10 s at 20 °C. The bar represents 1 μm. (c) Transmission electron micrograph of a 1 × 10^{-4} M dispersion of **1** in chloroform drained after 10 s at −40 °C. The bar represents 30 nm. (d) Scanning electron micrograph of a 1 × 10^{-2} M dispersion of **1** in chloroform drained after 10 s at 20 °C. The bar represents 1 μm. (e) Transmission electron micrograph of a 1 × 10^{-4} M dispersion of **1** in methanol/chloroform (1:9, v/v) without staining. The bar represents 0.1 μm. (f) Transmission electron micrograph of a 1 × 10^{-4} M dispersion of chlorophyll-*a* (**5**) in chloroform drained after 10 s at 20 °C. The bar represents 0.1 μm. Sample shaded with Pt.

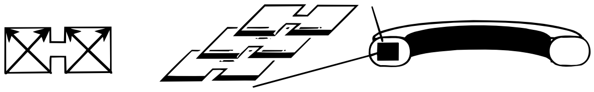

Figure 2. Schematic representation of the porphyrin wheels constructed from porphyrin **1**. The arrows indicate the transition dipole moments of the porphyrin molecules in the dimers. The two sets of dipole moments in a dimer make an angle of $\alpha = \pi/4$ with neighboring sets of dipole moments, which results in a red shift of the porphyrin B-band.[9]

microscopy (NSOM) and atomic force microscopy (AFM). These two values were very similar and varied between 10 and 100 nm, depending on the size of the ring, which corresponds to 1 to 10 molecules of **1**. UV−vis spectroscopy on the porphyrin rings showed that the porphyrin B-band was red shifted (22 nm) while the Q-bands were unaffected, suggesting, according to exciton theory, that head-to-tail type aggregates had been formed.[9] The B-band was narrow which illustrates that the porphyrin molecules have a well-defined arrangement in the supramolecular structure. Based on the data above, we propose that the rings have a molecular architecture as illustrated in Figure 2.

The diameter of the wheels can be tuned by varying the temperature. When the temperature was increased during the evaporation of the chloroform, the diameter of the rings also increased. Rings with an average diameter of 50 μm were formed at a temperature of 60 °C. At a temperature of −40 °C the ring structures were imperfect and small arrays of aggregated porphyrin molecules were mainly visible (Figure 1c). This result is of interest for the mechanism of the ring formation, which is discussed below. When the concentration of porphyrin **1** was increased to 1 × 10^{-2} M, honeycomb-like structures were generated (Figure 1d), while a 1 × 10^{-6} M solution gave relatively small rings with a very narrow ring band corresponding to the length of approximately one porphyrin molecule. Blocks of porphyrin molecules were observed when the chloroform solution was immediately drained and vulcano-like structures were obtained when the solution was evaporated completely.

Carbon tetrachloride was found to be the best solvent for the formation of the porphyrin rings. On going from carbon tetrachloride to chloroform and then to dichloromethane, the structures became progressively less perfect. The boiling points of these solvents also decrease in this order, which could indicate that slow evaporation stimulates the formation of well-defined rings (see also below). No rings were observed when THF or toluene was employed. The addition of a small amount of methanol to a chloroform solution of **1** caused the structures to change from rings into fibers (Figure 1e). UV−vis spectroscopy revealed that the molecules of **1** are aggregated in this solvent mixture. In general, it was found that no rings are formed when the porphyrin is aggregated in a particular solvent.[6] This suggests that it is important for them to be present as monomers in solution otherwise the structure, after slow evaporation and draining, is determined by the aggregate structure in solution.

Two mechanisms may be envisaged for the formation of rings from **1**. The first possibility is that two-dimensional phase separation takes place between a porphyrin-rich and a porphyrin-poor solution. This process may occur at nucleation sites where solid domains of porphyrins are formed. Domain formation is a known process in, for exmaple, two-dimensional assemblies of lipids or block copolymers.[10,11,12] In the latter case solid domains can be formed during the compression of the molecules at the air−water interface. The shape of the domains is determined by competition between repulsive electrostatic forces (favoring elongation of the domains) and interfacial line tension (favoring the formation of circular domains).[11] In our case solid circular domains of porphyrin could be formed initially during the evaporation of the chloroform. These could then undergo transition from a circular to a torus-shaped structure, when they then increase in size. This phenomenon has been shown to be concentration dependent and to occur in only a very narrow concentration range.[13] In the concentration range used by us (1 × 10^{-2} to 1 × 10^{-6} M) ring structures were always obtained making this mechanism less likely.

The second possibility, and preferred mechanism, is that the presence of gas bubbles in the solution causes the formation of rings.[14] Bubble-induced aggregation is a well-documented phenomenon and is the result of a complex process determined by hydrodynamic and surface effects.[15−17] In our case the

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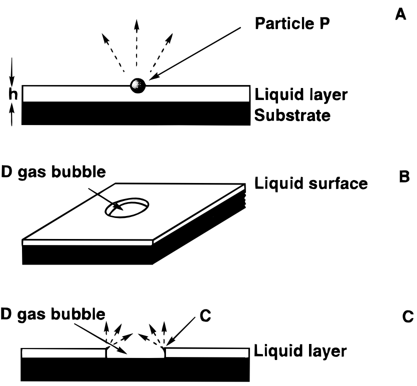

Figure 3. Schematic representation of the formation of porphyrin wheels. Dashed arrows indicate the direction of the stream of evaporating molecules. For further explanation see text.

development of rings can be interpreted in principle within the framework of what we would like to term "2D gas bubble" formation and the nucleation and growth of a porphyrin amorphous phase around the gas bubbles. We have observed that although the possibility of formation of 3D chloroform gas bubbles in the bulk liquid below the boiling point of the solution can be excluded, the formation of 2D gas bubbles at the free surface of a rapidly evaporating solution is very possible, since the vapor pressure of chloroform in the air is much lower than the saturation pressure of chloroform itself. Referring to Figure 3, the nucleation free energy barrier for the saturation pressure formation of 2D gas bubbles with radius R is given by

$$\Delta G = -\frac{\pi R^2 h}{\Omega}\Delta\mu + 2R\pi h\gamma_{\mathrm{gl}} + R^2\pi(m-1)\gamma_{\mathrm{gl}} \qquad (1)$$

with

$$m = \cos\alpha = (\gamma_{\mathrm{gs}} - \gamma_{\mathrm{ls}})/\gamma_{\mathrm{gl}} \qquad (-1 \le m \le 1) \qquad (2)$$

with h being the thickness of the liquid layer, Ω the molecular volume per structural unit, α the wetting angle between the liquid and the substrate, and γ_{gs}, γ_{ls}, and γ_{gl} the surface free energy between gas and substrate, between liquid and substrate, and between gas and liquid, respectively. $\Delta\mu$ denotes the difference in chemical potential between the liquid and the gas phase. According to the basic principles of thermodynamics, $\Delta\mu$ can be expressed as

$$\Delta\mu = kT\ln(p/p') \qquad (3)$$

where p is the equilibrium vapor pressure of the liquid phase and p' the actual vapor pressure in the surrounding gas phase. Setting the first derivative of ΔG to zero, one obtains for the critical size (R^{c}) of the gas nuclei the follwing expression:

$$R^{\mathrm{c}} = \frac{\gamma_{\mathrm{gl}}\Omega}{\Delta\mu - \dfrac{\Omega}{h}(m-1)\gamma_{\mathrm{gl}}} \qquad (4)$$

or

$$R^{\mathrm{c}} = \frac{\gamma_{\mathrm{gl}}\Omega}{kT\ln(p/p') - \dfrac{\Omega}{h}(m-1)\gamma_{\mathrm{gl}}} \qquad (5)$$

The smaller the value of R^{c} is, the lower the nucleation barrier will be, thereby facilitating gas bubble formation. Equations 4 and 5 have the following implications. First, the critical radius of 2D gas bubbles for $m \approx -1$ will be much smaller than that for $m \approx 1$ (in the latter case, the expression of R^{c} is identical to that for 3D spherical gas bubble formation). In other words, 2D gas bubbles can be formed more easily if the substrate cannot be "wetted" by the liquid, and less readily when the substrate is very well "wetted" by the liquid. Secondly, R^{c} decreases with h suggesting that the thinner the liquid layer is, the more easily 2D bubbles will be formed. This explains the common observation that 2D bubbles are always generated in a later stage of the evaporation process.

In our case, the liquid will not wet the substrate particularly well because of the poor interaction between the liquid and the substrate, and hence m must be approaching -1. The liquid layer applied to the substrate will become increasingly thinner due to the rapid evaporation of the chloroform, making it more likely that 2D gas bubbles will be formed gradually. At a site P, where foreign particles or bubbles occur at the free surface of the liquid (Figure 3a), the local vapor pressure p will be particularly high if the radii of these particles is much smaller than that of the flat liquid layer. The driving force for the formation of 2D bubbles is much higher, therefore, at this site than in the surrounding solution (cf. eq 5). Foreign particles will also lower the free energy barrier for 2D bubble formation.[18] 2D gas bubbles will therefore be formed preferentially around the floating foreign particles providing the liquid layer is not too thick resulting in a shape as shown in Figure 3b. Once a 2D gas bubble is formed, the upper corner of the circumference C will maintain a very high evaporation rate (indicated by the dashed arrows in Figure 3c) due to the very large radius of curvature, and the bubbles will continue to grow.

The concentration of porphyrin molecules at the circumference of the bubbles will be built up rapidly due to the rapid evaporation, and this local concentration can easily reach a value higher than the equilibrium concentration of the porphyrin amorphous phase. Nucleations and growth of the porphyrin amorphous phase will then occur at the circumference of the gas bubbles. The porphyrin rings are then obtained by draining the rest of the solution.

In the case of highly concentrated solutions, amorphous particles of porphyrins can be formed easily at a very early stage. These particles are transported by convection into the liquid bulk where, at that moment, the concentration of porphyrins is already higher than the equilibrium concentration of the porphyrin amorphous phase. These particles are distributed homogeneously in the solution and will serve as nucleation centers for the formation of the next generation of 2D gas bubbles, which lead subsequently to the observed honeycomb-like structures (Figure 1d).

The scope of the method was tested with other porphyrin derivatives (**2**−**5**). The so-called picket-fence porphyrin **3** gave no rings in chloroform, while compound **2** formed rings. It is known that picket-fence porphyrins hardly stack due to the ortho substituents on their phenyl rings.[19,20b] It can be concluded, therefore, that $\pi-\pi$ stacking interactions between the molecules

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are important in generating the circular solid domains. It was also possible to construct rings from protoporphyrin IX (**4**) and chlorophyll-*a* (**5**) (Figure 1f) using the procedure described. This may open a route to construct synthetic wheels of bacteriochlorophyll.

In summary, we have developed a facile technique for the construction of ring-shaped assemblies of porphyrins on the micrometer scale. Futher studies are in progress to determine whether the rings can function as molecular synchrotrons and store energy or electrons.

Experimental Section

Transmission and scanning electron microscopy experiments were carried out on a Philips EM 201 and a JEOL 100 CX II instrument, respectively. Atomic force microscopy was performed on a Nanoscope IIIA MMAFM instrument. Near-field scanning optical microscopy (NSOM) was performed on a TopoMetrix Aurora instrument by Dr. M. Rucker in the group of Prof. F. de Schrijver (Katholieke Universiteit Leuven, Belgium). The setup for these measurements is described elsewhere.[8] UV−vis spectra were obtained with a thermostatted Perkin-Elmer Lambda 5 spectrophotometer. Protoporphyrin IX and Chlorophyll-*a* were commercial products (Aldrich) and were used as received. 21*H*,23*H*-5-(4-Pyridyl)-10,15,20-tris(4-hexadecyloxyphenyl)porphyrin and compounds **2** and **3** were prepared according to literature procedures.[20] The synthesis of compound **1** is given below.

Compound 1. *trans*-Bis(benzonitrile)palladium(II) dichloride (7.2 mg, 18 mmol) was added with stirring to a solution of 21*H*,23*H*-5-(4-pyridyl)-10,15,20-tris(4-hexdecycloxyphenyl)porphyrin (50 mg, 37 mmol) in 50 mL of dichloromethane. After 2 h the solvent was evaporated, and the resulting solid was adsorbed on silica. Compound **1** was isolated by column chromatography (eluent $CHCl_3$/MeOH, 95/5 v/v). Yield: 34 mg (64%). TLC (silica, MeOH/$CHCl_3$, (5/95, v/v)) $R_f = 0.95$. Mp: 225 °C (decomposition to starting materials). ^{1}H-NMR (200 MHz, $CDCl_3$): δ 9.58 (d, 4H, pyridyl, $J = 6.4$ Hz), 8.99 (d, 4H, β-pyrrole, $J = 4.9$ Hz), 8.89 (d, 8H, β-pyrrole, $J = 4.6$ Hz), 8.82 (d, 4H, β-pyrrole, $J = 4.9$ Hz), 8.37 (d, 8H, pyridyl, $J = 6.6$ Hz), 8.18 (d, 12H, phenyl, $J = 8.4$ Hz), 7.45 (d, 12H, phenyl, $J = 8.4$ Hz), 4.40 (t, 12H, OCH_2, $J = 2.6$ Hz), 2.0−1.3 (b, 168H, CH_2), 1.00 (t, 18H, CH_3), −2.75 (b, 4H, NH). FD MS: Found for $C_{182}H_{250}N_{10}O_6Pd$ $m/z = 2776.86576$, Calcd 2776.86156. UV−vis ($CHCl_3$) λ/nm (log(ϵ/M^{-1}·cm^{-1})): 426 (5.9), 521, (4.6), 558 (4.5), 592 (4.2), 651 (4.2). Anal. Calcd for $C_{182}H_{248}N_{10}O_6PdCl_2$: C, 76.72; H, 8.77; N, 4.92. Found: C, 76.59; H, 8.96; N, 4.85. IR (KBr, cm^{-1}): 3433, 2923, 2852. CV: $E_{1/2} = -1.67$ V (*vs* F_c/F_{c^+}), $\Delta E_p = 69$ mV, $E_{1/2} = -1.98$ V, $I_b/I_f = 1$.

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