Porphyrins

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Controlled Self-Assembly Behavior of an Amphiphilic Bisporphyrin–Bipyridinium– Palladium Complex: From Multibilayer Vesicles to Hollow Capsules**

Yongjun Li, Xiaofang Li, Yuliang Li,* Huibiao Liu, Shu Wang, Haiyang Gan, Junbo Li, Ning Wang, Xiaorong He, and Daoben Zhu*

The construction of supramolecular assemblies with welldefined nano-structures is of great interest owing to their potential applications in diverse fields such as molecular electronics, light-energy conversion, and catalysis.^[1,2] The ability to control the specific shapes, dimensions, and pattern formation of supramolecular organization by nonconvalent interactions is still a challenging task in the materials field.^[3] Nanoscale hollow capsules represent an important class of materials because their unique structural, optical, and surface properties may lead to a wide range of applications, such as capsule agents for drug delivery, filters, coatings, chemical catalysis, or templates for functional architectural composite materials.^[4] Various efforts have been made to prepare inorganic^[5] and organic^[6] hollow capsules. Hollow polymer spheres were produced by McDonald et al. through the encapsulation of hydrocarbon solvents within polymer particles during an emulsion polymerization.^[7] C₆₀-derived amphiphiles have a tendency to form closed submicrospheres with a bilayer shell below the critical aggregation concentration and multibilayer vesicles above the critical aggregation concentration.^[8] Meanwhile, 1D nanotubes and nanowires have attracted much attention because of their unique optical, electronic, and mechanical properties, which result in promising applications in electrical and optoelectronic nanodevices.[9]

Porphyrins have remarkable photo-, catalytic-, electro-, and biochemical properties, and so the self-assembly of porphyrin derivatives has attracted considerable attention in

[*] Y. J. Li, Dr. X. F. Li, Prof. Y. L. Li, Dr. H. B. Liu, Prof. S. Wang,	
H. Y. Gan, J. Li, N. Wang, X. R. He, Prof. D. B. Zhu	
CAS Key Laboratory of Organic Solids	
Institute of Chemistry	
Chinese Academy of Sciences	
Beijing 100080 (P.R. China)	
Fax: (+86) 10-8261-6576	
E-mail: ylli@iccas.ac.cn	
zhudb@iccas.ac.cn	

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author. recent years.^[10,11] The introduction of molecular recognition motifs into the porphyrin building blocks, such as hydrogen bonding, π - π stacking, electrostatic interactions, and metalligand bonds offers an easy way to access well-defined arrays such as fibers, sheets, grids, cubes, wheels, and rings.^[12–14] Amphiphilic porphyrins have been exploited in the preparation of simple micelles,^[15] fibers,^[16] and vesicles.^[17] Their optoelectronic features are strictly related to their aggregation states and strongly depend on the microstructural environment.^[18]

Herein, we describe the aggregation behavior of a new zinc porphyrin derivative 1 (Scheme 1) in which two zinc



Scheme 1. Synthesis of bpy–ZnP and 1. a) toluene/pyridine, RT, 60%; b) Zn(OAc)₂/CH₃OH, CHCl₃, 98%; c) PdCl₂(CH₃CN)₂, CHCl₃/CH₃CN.

porphyrins were attached to the 4,4'-position of the 2,2'bipyridyl group, and the 2,2'-bipyridine (bpy) was complexed with palladium (II) dichloride. The precursor of **1**, bpy–ZnP, has one structural feature: the two porphyrin units can rotate freely around the central bipyridine bond and as such, the relative position of two porphyrins can be controlled by the addition/elimination equilibrium of metal ions.^[19] Bipyridyl groups are strong ligands for various transition metal ions, **1** is an amphiphile because the bipyridine–PdCl₂ units exhibit hydrophilic properties and the porphyrin units show hydrophobic interactions under specific solvent environments.^[20,21]

Compound 1 was synthesized according to Scheme 1. Characterization was performed through NMR spectroscopy and MALDI-TOF MS. The MALDI-TOF mass spectra of 1 exhibited two signals that could be assigned as [M-2Cl] and $[M-PdCl_2]$.

Although the growth of a single crystal from bpy–ZnP in different solvents was not successful, we succeeded in growing the single crystal of the bpy–ZnP–pyridine complex in *n*-hexane (the crystal data are shown in the Supporting Information). The single-crystal X-ray structure analysis showed that the porphyrin rings are distorted. Each zinc



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porphyrin coordinates with one pyridine molecule that alternates above and below the plane (Figure 1). The distance between the nitrogen atom with the coordinated pyridine and the zinc atom is 2.113 Å. The two nitrogen atoms of bipyridine



Figure 1. Crystal structure of the bpy–ZnP–pyridine complex. Hydrogen atoms, 3,4,5-trimethoxyphenyl, and solvent molecules are omitted for clarity.

face in the opposite direction, whereas the bipyridine and two amides are nearly planar (the mean deviation from the plane is 0.0321). The two benzene rings connecting the porphyrin and the amide are parallel (the dihedral angel is 0°). The dihedral angel between these benzene rings and the bipyridine plane is 30.1°. From the crystal-packing mode of the bpy–ZnP–pyridine complex, we can see that the bipyridine of one molecule overlaps with the porphyrin part of another molecule.

The growth of a single crystal of 1 in a variety of different solvents was not successful. Computer simulations were used to gain insight into the structure.^[6a] The simulation results indicated that bpy-ZnP showed linear conformers similar to the X-ray crystal structure, which indicated that this simulation method was fit for our porphyrin dimer system. The simulation results showed that 1 was a V-shaped structure (Figure 2), which was confirmed by NMR spectroscopictitration experiments. After the addition of 2.2 equivalents of $[PdCl_2(CH_3CN)_2]$, palladium complex 1 was completely formed along with the [PdCl₂(pyridine)₂] complex.^[19] The large downfield shift of 1-H (+1.5 ppm) reflected the development of a δ + charge upon complexation with PdCl₂. The most-sensitive shielding effect of the porphyrinring current appeared at the meso phenyl groups. According to symmetry, there were two sets of meso phenyl groups in bpy-ZnP, namely, four 3,4,5-trimethoxyphenyl groups adjacent to, and two opposite to the bipyridyl groups. Before complexation, these groups were not distinguishable from one another in the ¹H NMR spectrum because of free and rapid rotation around the bond connecting the two pyridyl units. Thus, the protons of the meso phenyl groups (meso-Ph-H) appeared as a single peak near $\delta = 7.4$ ppm; the *para*-methoxy and meta-methoxy groups in these meso phenyl groups appeared as a single peak near $\delta = 4.06$ and 3.89 ppm, respectively. When palladium complex 1 was formed, each of the single peaks split into a doublet. Peak separations between the meso-Ph-H as well as between the methoxy groups in the two sets of meso phenyl groups became detectable owing to differences in the distances from the facing porphyrin plane. These results showed that the addition of 2.2 equivalents of Pd^{II} completely converted the



Figure 2. Space-filling models of bpy–ZnP from a top view (a), and a top view (b) and side view (c) of complex **1**. The MM2 force field was used to calculate the minimium-energy conformation.

bpy–ZnP from a freely rotating conformation to a cofacial V-shaped one.

The aggregation behavior of 1 was subsequently studied by injecting a solution of 1 in $CHCl_3$ (at a concentration of 1 × 10^{-4} M) into CH₃OH to give a final chloroform/methanol ratio of 1:1 (v/v). After the solution was allowed to equilibrate over one day, one drop of the solution was evaporated on silicon slides to observe the aggregate behavior in the solid state. The morphology of molecule 1 on the substrate was examined by scanning electron microscopy (SEM; Figure 3). In SEM images, spherical particles with a uniform diameter of about 200 nm were observed. Energy-dispersive X-ray spectroscopy (EDX) indicated the presence of C, N, O, Cl, Pd, and Zn, and the atom ratio of Cl/Pd/Zn was about 2:1:2. The majority of the spherical particles were larger than the typical micelle size of 20-30 nm in diameter as they were derived from small molecular amphiphiles.^[22] A few of the particles started to form opening holes on their surfaces, which showed that they had a hollow interior. To confirm this possibility and substantiate whether these vesicles are hollow in nature, the perfect spherical vesicles (Figure 3a) prepared at a $5.0 \times$ 10^{-5} M were subjected to heat treatment for one hour (heating pattern I). This then allowed us to see that the holes were formed on the particles surface (Figure 3b); one example of the typical open vesicles is shown in the inset of Figure 3b. TEM images also showed that some capsulelike structures with holes were formed (Figure 3c). According to the irregularity of the size and shape of the hole and the location of defective sites at the surface, we suggested that these holes are not a result of the density-gradient image of the spherical



Figure 3. a) SEM of 1 derived vesicles prepared in CHCl₃/CH₃OH (1:1) at room temperature. b) SEM and c) TEM of compound 1 vesicles derived from the heat treatment (pattern I at 70 °C) of the vesicles prepared as in a). The inset of b) shows a close up of a vesicle, and the inset of c) shows the membrane thickness, indicated by arrows. d) Schematic representation of compound 1. e) Schematic representation of a compound 1 vesicle formed in methanol with a close up of the vesicle membrane showing the proposed multibilayer structure. The blue dots represent the ligated CH₃OH. f) Schematic representation of an interdigitated bilayer structure.

vesicles.^[22] The edge of these holes should be measurable to reveal the thickness of the vesicle shell. As shown in the inset of Figure 3c, we found that the morphology of the slightly "tilted" shell membrane on the top was surrounded by a dark ring area with an irregular wall width and shape. Measuring the membrane-wall thickness at the tilted-membrane site (perpendicular to the view as marked by the arrow) gave an edge width of about 15-20 nm. These distances across the membrane wall fit approximately with 2-3 bilayers with a molecular dimension of 12-18 nm, estimated by the 3D molecular structural modeling of 1. These results indicate that the most likely membrane structure of the hollow spherical vesicles in methanol was a shell-like complex multilayer structure resembling that of a liposome at the vesicle surface (Figure 3c). Our vesicles were very stable on the solid surface, even when heated at 50-60°C (Figure 4a) or stored for 12 days (see the Supporting Information). Furthermore, they were unlike other vesicles that showed an immediate collapse on solid surfaces;^[23] dried samples of egg-yolk lecithin vesicles showed only planar circles and bolaamphiphile vesicles crystallized quickly upon drying to form circular platelets of double-layer thickness.[24]

Figure 4 and the Supporting Information show SEM images of the vesicles on a silica slide after heating at different temperatures for 0.5 h and then cooling to room temperature. The volume of encapsulated methanol expanded when the vesicles were heated at 40 °C (lower than the boiling point of methanol) and as such, the methanol that flowed from the aperture of the membrane couldn't evaporate quickly. The nearby molecules then flowed with the methanol and formed the "tail" morphology. "Tails" located



Figure 4. Morphology transition of the vesicle heated a) at 60 °C for 0.5 h (inset $2.6 \times$ enlargement), b) at 80 °C for 0.5 h (inset $2.6 \times$ enlargement), and wormlike aggregates of 1 derived from the heat treatment (heating pattern II) of the vesicles prepared as Figure 3 a, c) SEM and d) TEM.

close to each other could fuse together during this process. When the vesicles were heated at 50-60 °C, the methanol escaped and evaporated quickly from the aperture of the membrane without resulting in obvious changes in morphology. However, when heated at 70-80 °C (higher than the boiling point of methanol), the evaporating methanol bumped and the gas broke quickly through the membrane. This resulted in deformation and the hollow spherical vesicles were formed. When heated at 90 °C for 0.5 h, in addition to the escape of methanol (some hollow capsules were visible), the molecular motion of 1 was excited and rearrangement was achieved during the cooling process. Some fused vesicles were found in which the hollow capsules were empty. Although heated with pattern II, a wormlike morphology was observed by using SEM as shown in Figure 4c, and TEM images (Figure 4d) also confirmed the wormlike structure. These results indicated that heating temperature and pattern are able to control the rate of methanol release and lead to a controllable process for producing hollow capsules and wormlike structures from these vesicles.

The UV/Vis spectra of the aggregated species were significantly different from that of the corresponding porphyrin solutions. The absorption spectra of the films resulting from a chloroform/methanol mixture (ν/ν , 1:1) are shown in Figure 5. Together with the expected bands at 440 nm and the Q bands in the range from 500–700 nm, there was one additional band at 680 nm. Both the Soret and Q absorption bands of the films were broadened and red shifted when compared with the organic solution phase. These vesicular supramolecular structures suggest "J-type" (edge-to-edge) interaction in the vesicles.^[21,25]

In selective solvents, block copolymer systems or amphiphilic molecules like liposomes form micellar or vesicular supramolecular structures that would normally belong to the superstrong segregation limit (SSSL). This is mainly owing to

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Figure 5. UV/Vis spectra of solutions of **1** in chloroform (dotted line), chloroform/methanol (1:1; solid line), and the film cast from the chloroform/methanol (1:1) solution (dashed line).

the different solubility of the blocks or the hydrophilic and hydrophobic units.^[26] For 1, methanol was a good solvent for the bipyridine-Pd complex unit, but was a poor solvent for the porphyrin moiety. On the contrary, chloroform was a good solvent for porphyrin but not for the bipyridine-Pd complex unit. In this solvent system, 1 became an amphiphilic molecule and could assemble into layered structures that could then close to form vesicles. These two parts should completely segregate in the membrane. Because methanol can coordinate with zinc porphyrin (see the Supporting Information), the amphiphiles self-organize into a bilayer structure (Figure 3e) and the resulting membrane has many little holes owing to the loose packing of porphyrin. With the removal of methanol by heating with pattern II, 1 rearranged into the dense packing and low interfacial free energy interdigitated layer (Figure 3 f), which resulted in the wormlike aggregates shown in Figure 4 c,d.

In summary, a novel amphiphilic porphyrin derivative composed of two porphyrins connected with 2,2'-bipyridyl group, in which 2,2'-bipyridine was complexed with palladium(II) dichloride, has been synthesized. The crystal structure of the Pd-free porphyrin–bipyridine derivative was obtained. Computer simulations and NMR spectroscopic-titration experiments indicated that the Pd complex showed a V-shaped conformer. A simple and controllable process for producing the hollow capsules from vesicles was described. SEM and TEM imagines confirmed that this molecule is able to self-assemble into vesicles with a diameter of 200 nm in CHCl₃/CH₃OH. These vesicles could assemble into hollow capsules and wormlike structure on demand.

Experimental Section

Heat treatment of the samples: Pattern I, the silicon slides containing the samples were placed in a petri dish and the petri dish was heated with water at 40, 50, 60, 70, 80, and 90 °C, for 0.5 h each. Pattern II, the silicon slides containing the samples were placed in a petri dish, which was then set on water at 90 °C and the water was then allowed to cool to room temperature.

SEM images were taken by using a field emission scanning electron microscope (JEOL JSM 6700F and Hitachi S4300) operated at an acceleration voltage of 5–15 kV. TEM images were taken by using a JEOL-100 microscope operated at 50 kV. The samples were prepared by transferring them from the silicon slides by carbon-copper grids dampened with methanol.

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