Stable Porphyrin Bilayer Vesicles Formed in Nonaqueous Media and Dried to Produce Hollow Shells†

Lili Wang, Hongguo Liu and Jingcheng Hao*

Key Laboratory of Colloid and Interface Chemistry (Shandong University), Ministry of Education, Jinan 250100, P. R. China.
Fax: +86-531-88564750; Tel: +86-531-88366074; E-mail: jhao@sdu.edu.cn

Experimental Section

Materials: amphiphilic manganese tetraphenylporphyrin [Mn(III)-TPP(-COOH)] was synthesized according to the literature,[1] the temperatures of melting of the tetraphenylporphyrin metallo-complexes measured by the DSC method is 197°C. Two sample solutions of Mn(III)-TPP(-COOH) in the mixed solvents of CHCl₃ and CH₃OH (v:v = 4:1) were prepared at room temperature, \( c_{\text{Mn(III)-TPP(-COOH)}} = 0.52 \) and 0.26 mg mL⁻¹.

Method: Negative stained specimen for the TEM images were prepared as described below. A droplet of nonaqueous vesicular solution was dropped onto a TEM grid (copper grid, 3.02 mm, 200 mesh, coated with carbon film), immediately the nonaqueous vesicular solution was stained with 2% uranyl acetate (~4 μL) CH₃OH solution. The grid was allowed to air-dry and TEM images were taken on a JEOL JEM100cx III electron microscope operating at an accelerating voltage of 100 kV.

The transparent green solution samples were free of dust by filtering with Millipore MILLEX-VV 0.65 μm filters (Low Protein Binding Durapore membrane). A standard Brookhaven Commercial laser light scattering spectrometer equipped with a Coherent Radiation 200 mW diode pumped solid-state (DPPS) 488 laser, and a Brookhaven Instruments Corporation (BI-9000AT) correlator operating at 488 nm were used for the DLS measurements. The spectrometer is capable of making measurements of both the angular dependence of absolute integrated scattered...
intensity over a scattering angular range of 20° to 140° and of intensity-intensity
digital photon correlation over a similar angular range (DLS and Dynamic
depolarisation light scattering). About 2~3 mL of the sample solutions were
transferred into scattering cells for light scattering measurements. The scattering cells
were held in a brass thermostat block filled with refractive index-matching silicone
oil. The temperature was controlled to within ±0.05°C. The CONTIN method[2] was
used to analyze the first-order field correlation function $g^{(1)}(\tau)$ as determined by DLS.
Then, the hydrodynamic radius ($R_h$) of the particles can be calculated from the
characteristic line width $\Gamma$. DLS measurements also provide information on the
particle-size distribution in solution from a plot of $\Gamma G(\Gamma)$ versus $R_h$.

SEM images were obtained after evaporating the mixed solvent of CHCl₃ and
CH₃OH at T = 25.0 ± 0.1°C for two days with a JEOL JSM6700F field-emission
scanning electron microscope.

The Solid hollow shells were observed using a Nanoscope IIIa Multimode AFM
(Digital Instruments Inc., USA) at 25.0 ± 0.5°C. The samples were prepared by
placing a drop of bilayer vesicle solution (~1.0 μL) on a freshly cleaved mica surface
and drying it in air. Silicon cantilevers with a resonance frequency about 200 kHz
were utilized for tapping mode at a scan rate of 0.5 Hz.

![TEM images of Mn(III)-TPP(-COOH) vesicles formed in CHCl₃ and CH₃OH (volume ratio = 4:1) for two samples with two concentrations of 0.26 (a) and 0.52 mg mL⁻¹ (c). Magnification of a vesicle to identify the interlamellar spacing between two adjacent layers (b).](image)

Fig. 1. TEM images of Mn(III)-TPP(-COOH) vesicles formed in CHCl₃ and CH₃OH (volume ratio = 4:1) for two samples with two concentrations of 0.26 (a) and 0.52 mg mL⁻¹ (c). Magnification of a vesicle to identify the interlamellar spacing between two adjacent layers (b).
Fig. 2. Apparent hydrodynamic radius distributions of spherical vesicles in CHCl₃ and CH₃OH. c = 0.26 mg mL⁻¹ at θ = 30° (●) and c = 0.52 mg mL⁻¹ at θ = 30° (▲) and 90° (■).

Fig. 3. SEM (a and b) and AFM (c) images of hollow shells survived from vesicles of Mn(III)-TPP(-COOH) in CHCl₃ and CH₃OH. c_{Mn-TPP(-COOH)} = 0.52 (a) and 0.26 mg mL⁻¹ (b and c).

References