Supplementary Material (ESI) for Chemical Communications

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

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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 $CHCl_3$ and CH_3OH (v:v = 4:1) were prepared at room temperature, $c_{Mn(III)\text{-}TPP(\text{-}COOH)}$ = 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) CH_3OH 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 Γ. 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 $CHCl_3$ and CH_3OH 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.

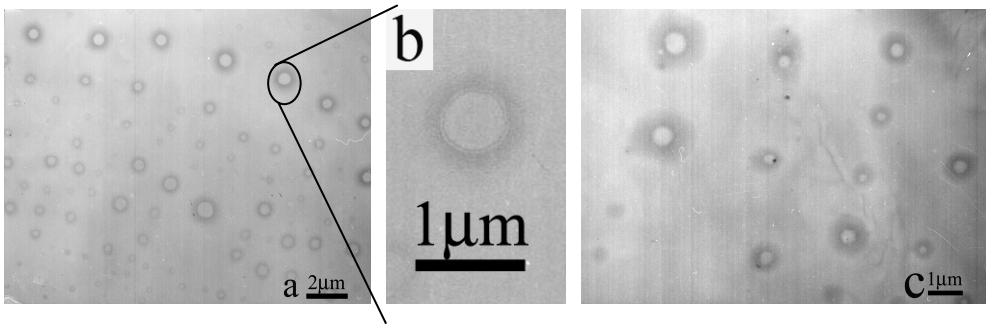

Fig. 1. TEM images of Mn(III)-TPP(-COOH) vesicles formed in $CHCl_3$ and CH_3OH (volume ratio = 4:1) for two samples with two concentrations of 0.26 (a) and 0.52 mg mL^{-1} (c). Magnification of a vesicle to identify the interlamellar spacing between two adjacent layers (b).

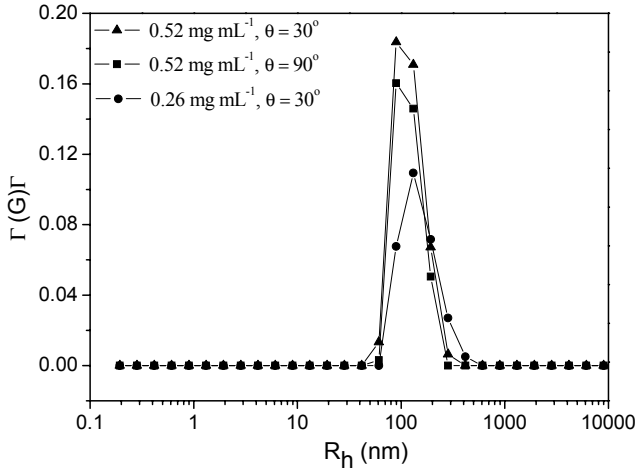

Fig. 2. Apparent hydrodynamic radius distributions of spherical vesicles in $CHCl_3$ and CH_3OH. c = 0.26 mg mL^{-1} at θ = 30° (●) and c= 0.52 mg mL^{-1} at θ = 30° (▲) and 90° (■).

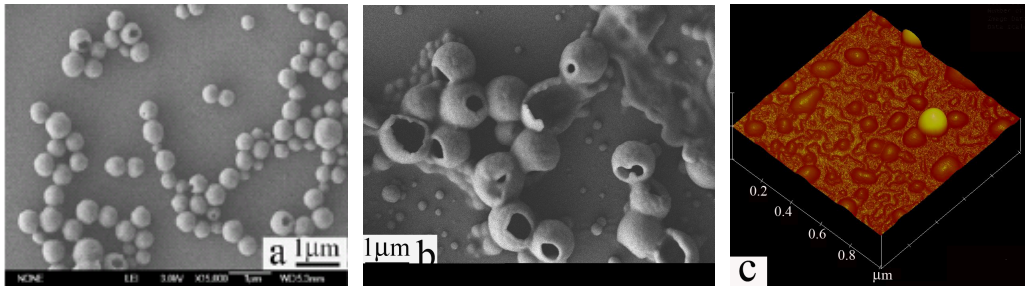

Fig. 3. SEM (a and b) and AFM (c) images of hollow shells survived from vesicles of Mn(III)-TPP(-COOH) in $CHCl_3$ and CH_3OH. $c_{Mn\text{-}TPP(\text{-}COOH)}$ = 0.52 (a) and 0.26 mg mL^{-1} (b and c).

References

1. J. Liu, Master's Degree Thesis, Shandong University, 1990.

2. a) Provencher, S. W. *Biophys. J.* **1976**, *16*, 27; b) Provencher, S. W. *J. Chem. Phys.* **1976**, *64*, 2772.