Supporting information for

Temperature-controlled Morphology Evolution of Porphyrin Nanostructures from Oil-aqueous Interface

Jinhua Cai,[À,ÿ] Ting Wang,[À] Jingxia Wang,[*,À] Yanlin Song,[§] and Lei Jiang[À*,§]

[À]Laboratory of Bio-Inspired Smart Interface Sciences, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

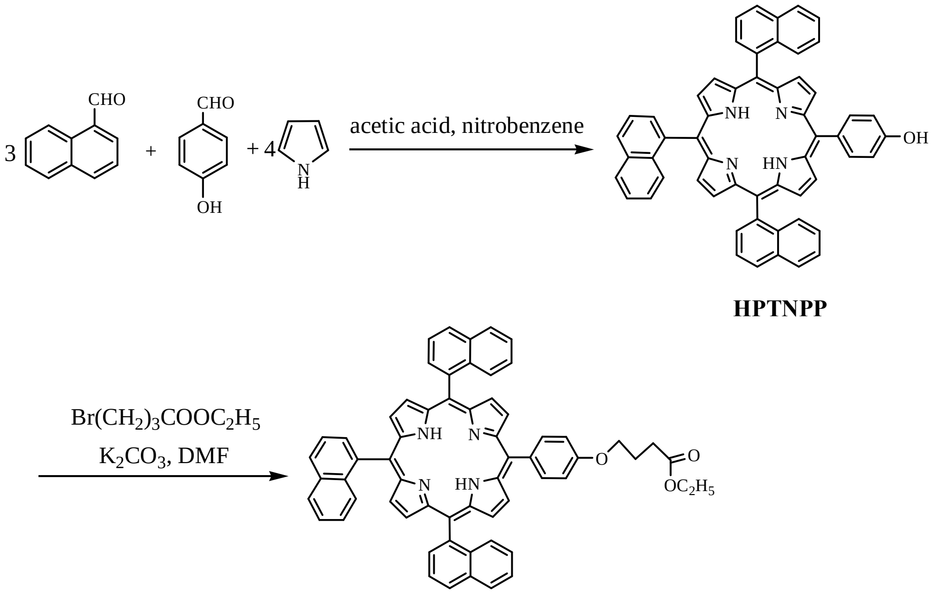
[§]Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Organic Solids, Key Laboratory of Green Printing, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

[ÿ] College of Chemistry & Chemical Engineering, Jinggangshan University, Jian, Jiangxi Province 340039, P. R. China

1. Materials

1.1 Synthesis of 5-(4-(ethylcarboxypropoxy)phenyl)-10,15,20-tri(naphthyl) porphyrin (CPTNPP)

CPTNPP was prepared by the scheme S1.



CPTNPP

Scheme S1. Synthetic procedure of CPTNPP

Firstly, HPTNPP was synthesized by the method similar to the literatures.[1] In detailed, 4.7 g naphthalaldehyde (30 mmol) and 1.2 g 4-hydroxybenzaldehyde (10 mmol) were dissolved in a mixture of acetic acid (120 ml) and nitrobenzene (60 ml). 2.7 g pyrrole (40 mmol) was added into the system followed by the temperature of system was raised to 120°C, and the system was kept at 120 ℃ for 1.5 h. Finally, the solution was then allowed to cool to room temperature and purple residues were obtained by filter. The crude material was purified on a silica gel chromatograph using $CHCl_3$ as an eluent. The second band was collected and the solvent was evaporated. Purple solid HPTNPP was obtained in 2.6% yield.

ESMS [$CHCl_3$, *m*/*z*]: 781 ([HPTNPP]$^{+}$).

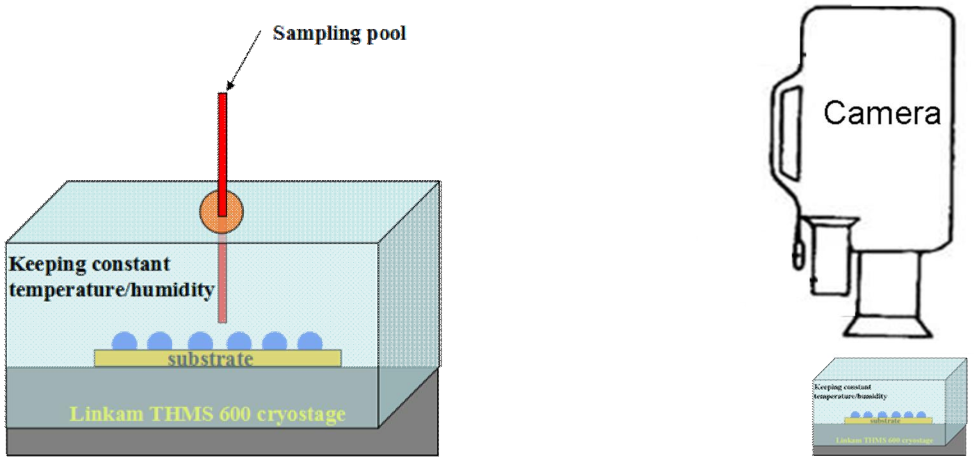
1H NMR (300MHz, $CDCl_3$): 8.56-8.58 (d, 8H, б-pyrroles),8.04-8.07 (d, 2H, 2,6-phenyl), 8.43-8.47(d, 6H, 2,8- naphthyl), 8.12 (s, 3H, 4- naphthyl), 7.53-7.57(d, 6H, 3,5- naphthyl), 7.45-7.49(d, 6H, 6,7- naphthyl), 7.11 (d, 2H, 3,5-phenyl), ī 2.36 (s, 2H, NH, pyrrole).

CPTNPP was synthesized by esterification reaction of HPTNPP. A mixture of 0.3902 g HPTNPP, 1.8 g K_2CO_3 and 50 mL N,N-Dimethylformamide(DMF) was stirred at 90 ℃. 2mL ethyl 4-bromobutyrate dissolved in 5ml DMF was added dropwise. After 10 h, the mixture was washed with H_2O several times to neutrality, drying over anhydrous Na_2SO_4 and concentrating via rotary evaporation, the residue was chromatographed on a silica gel column using $CHCl_3$ as eluent. The first band was collected and the solvent was evaporated. Purple solid CPTNPP was obtained in 85% yield.

ESMS [$CHCl_3$, *m*/*z*]: 895.3([CEPTNP]$^{+}$).

1H NMR (300MHz, $CDCl_3$): 8.53-8.57 (d, 8H, б-pyrroles), 8.05-8.07 (d, 2H, 2,6-phenyl), 8.41-8.46(d, 6H, 2,8- naphthyl), 8.10 (s, 3H, 4- naphthyl), 7.76-7.78(d, 6H, 3,5- naphthyl), (7.41-7.47(d, 6H, 6,7-naphthyl), 7.18 (d, 2H, 3,5-phenyl), 4.16-4.26 (s, 4H, Cï CH_2ï O), 2.26(s, 2H, C-CH_2-C=O), (1.51 (s, 2H,C- CH_2-C), 1.29 （d, 3H, CH_3-C-）ī 2.39 (s, 2H, NH, pyrrole).

1.2 Experimental set-up for porphyrin assembly



Scheme S2. (left) Set-up for the porphyrin assembly and (Right) the integration with the camera.

Scheme S2 presents the experimental apparature for porphyrin assembly. The experimental is carried out at a closed box keeping constant temperature and humidity. And the temperature of the substrate is controlled by the linkam THMS 600 cryostage. And the water droplet is formed from the condensation of the water vapor onto the substrate. The porphyrin dispersion is charged onto the droplet template by the sampling pool. The whole experimental apparatus can be connected with the high-speed camera as shown in right part in Scheme S2.

2. Assembly and characterization of porphyrin nanostructures

Substrate preparation: The used substrate includes ITO glass, cover glass and pristine silicon wafers. The substrates were treated by sequentially cleaning the silicon wafers by sonication in ethanol, acetone, and ultrapure water. Ultrapure water was provided by a Milli-Q reference system. The water CA of the pristine silicon wafer is 53.6±0.8°, the θ_R is 44.1°.

Formation of water droplet template. The water droplet template was formed by a Linkam THMS 600 cryostage according to the literature method as follows: the cleaned and treated substrate was placed into the linkam THMS, and a 0.5 εL water macrodroplet (MilliQ, 18.2 MΩ cm) was placed at the edges of the solid substrates. After raising the temperature and subsequently lowering the temperature, the water droplet evaporated and condensed around the surface of substrates，forming the water droplet template.

Preparation of Porphyrin dispersion. Porphyrin dispersion is obtained by the following process: firstly, the CPTNPP is dissolved into chloroform in 10^{-5}~10^{-6} mol/L, and then the CPTNPP chloroform solution was dispersed into IPA in a changing volume ratio of IPA of 50%. And the mixture was ultrasonicated 0.5 h at room temperature to form porphyrin dispersion.

Porphyrin assembly. The porphyrin dispersion was casted onto the previously-formed water droplet template adsorbed on the substrate at a certain temperature, the temperature can be alternated from -20^{o}C to 30^{o}C. After the solvent evaporated, the designed porphyrin assemblies were obtained.

Characterization of porphyrin assembly

The porphyrin assemblies were characterized by SEM (S-4800, Japan Hitachi) operating at 5.0 kV. UV-vis spectra were collected using a Hitachi U-4100. Optic microscopy images and Fluorescent image of the sample were collected from the Olympus.

3. Results and properties

3.1 The confirmation of CPTNPP vesicles in the dispersion

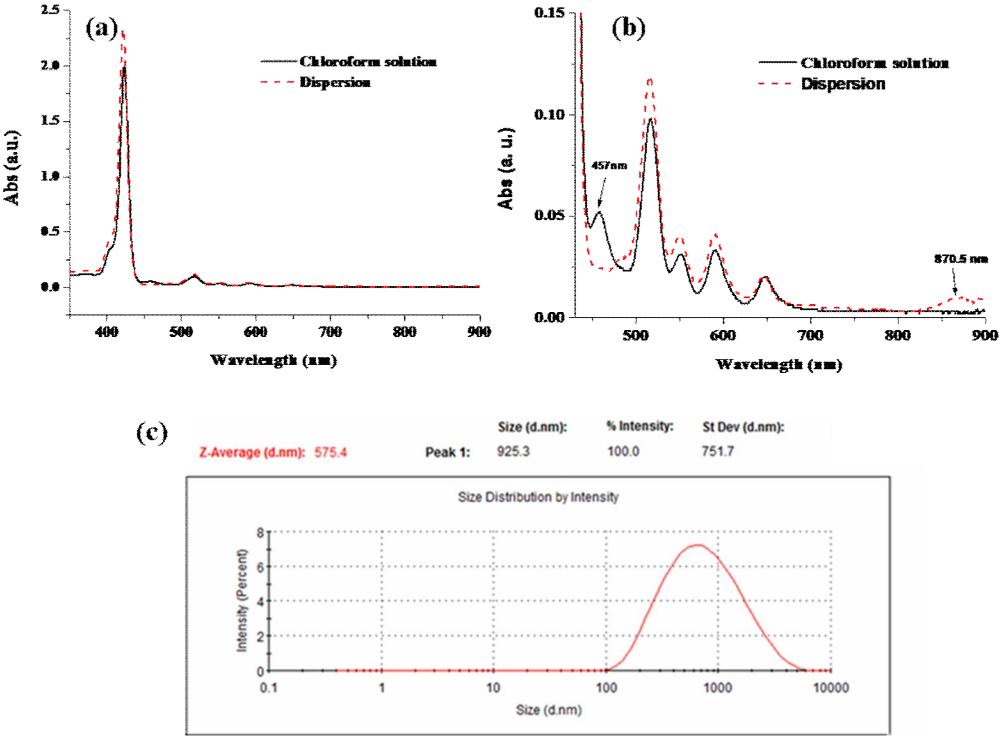


Figure S1. (a, b) UV-vis absorption spectra of the chloroform solution of CPTNPP and the CPTNPP dispersion obtained by mixing its chloroform solution and IPA at the volume ratio of 1:1. (c) Dynamic light scattering data of the CPTNPP dispersion from Malvern Lazer Particle Analyzer.

Figure S1a, b show UV-vis absorption spectra of chloroform solution of CPTNPP and the CPTNPP dispersion. Comparing the spectra of monomeric CPTNPP in chloroform solution, the peak centered at 457.0 nm disappears, and new peak centered at 871 nm emerges for the spectra of CPTNPP dispersion. These phenomena suggest the formation of vesicles in the CPTNPP dispersion.

The data in **Figure** S1c is obtained from dynamic light scattering of Malvern Lazer Particle analyzer for the CPTNPP dispersion. It was found that the as-formed vesicle has average size of 575.4 nm, indicating the presence of the CPTNPP vesicle in the dispersion.

3.1 Droplet template obtained at different temperature

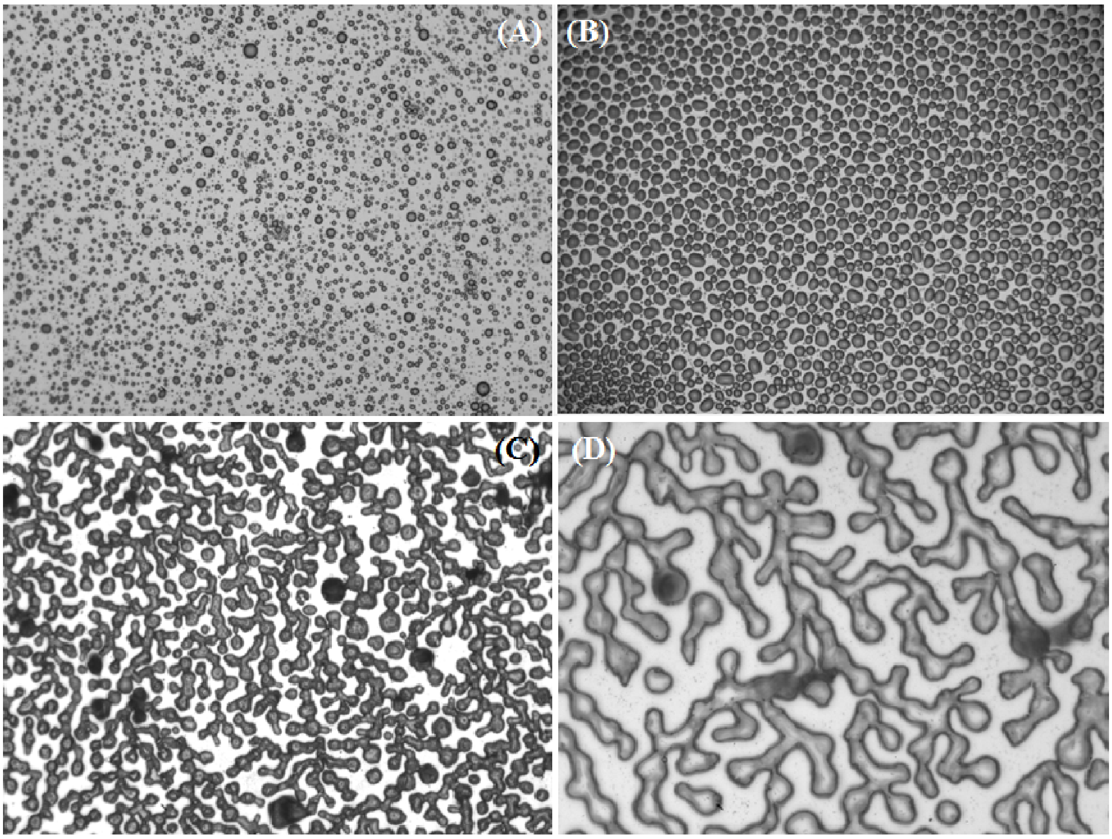


Figure S2. Optic microscopy images of the droplet template obtained at different temperature. (A) 0^{o}C (B) -5^{o}C, (C,D) -10^{o}C

3.2 Morphology characterization of the porphyrin nanostructures.

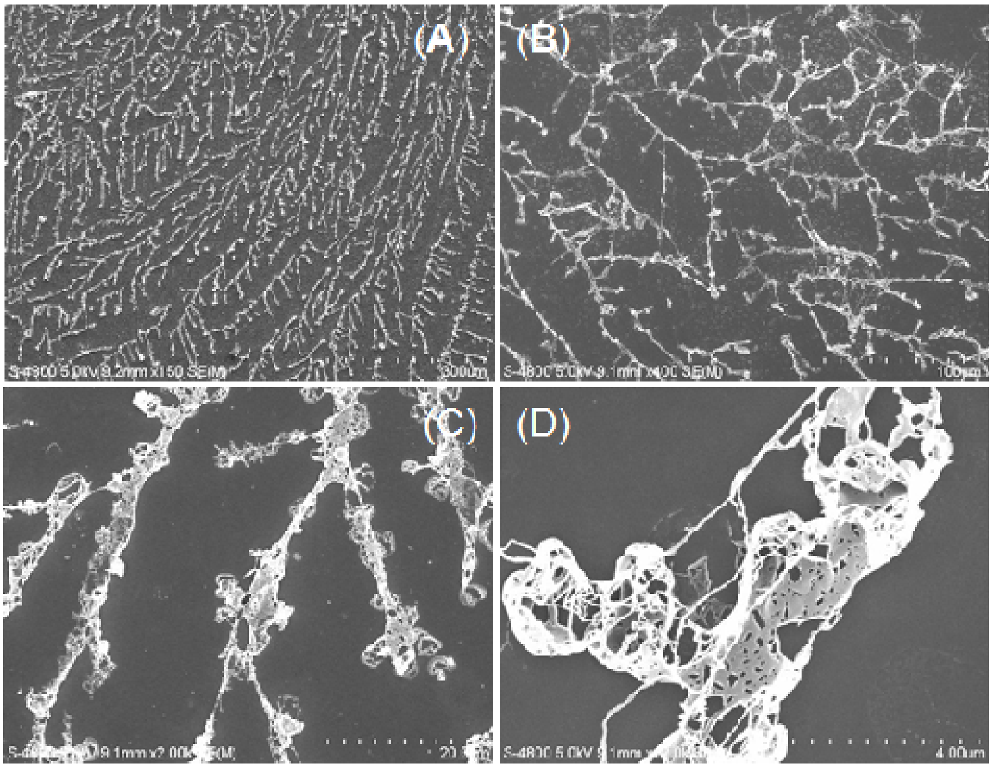


Figure S3. SEM-images of the tree-like porphyrin nanostructure assembled at -20°C

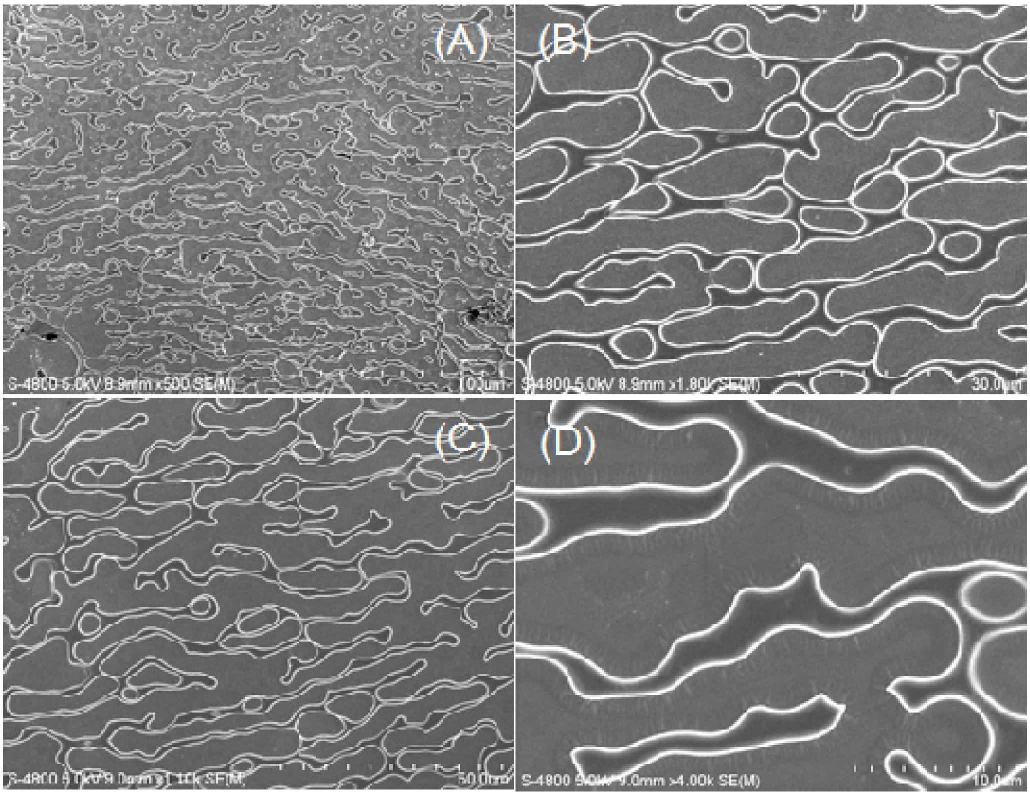


Figure S4. SEM-images of the wavy-like porphyrin nanostructures assembled at -10°C

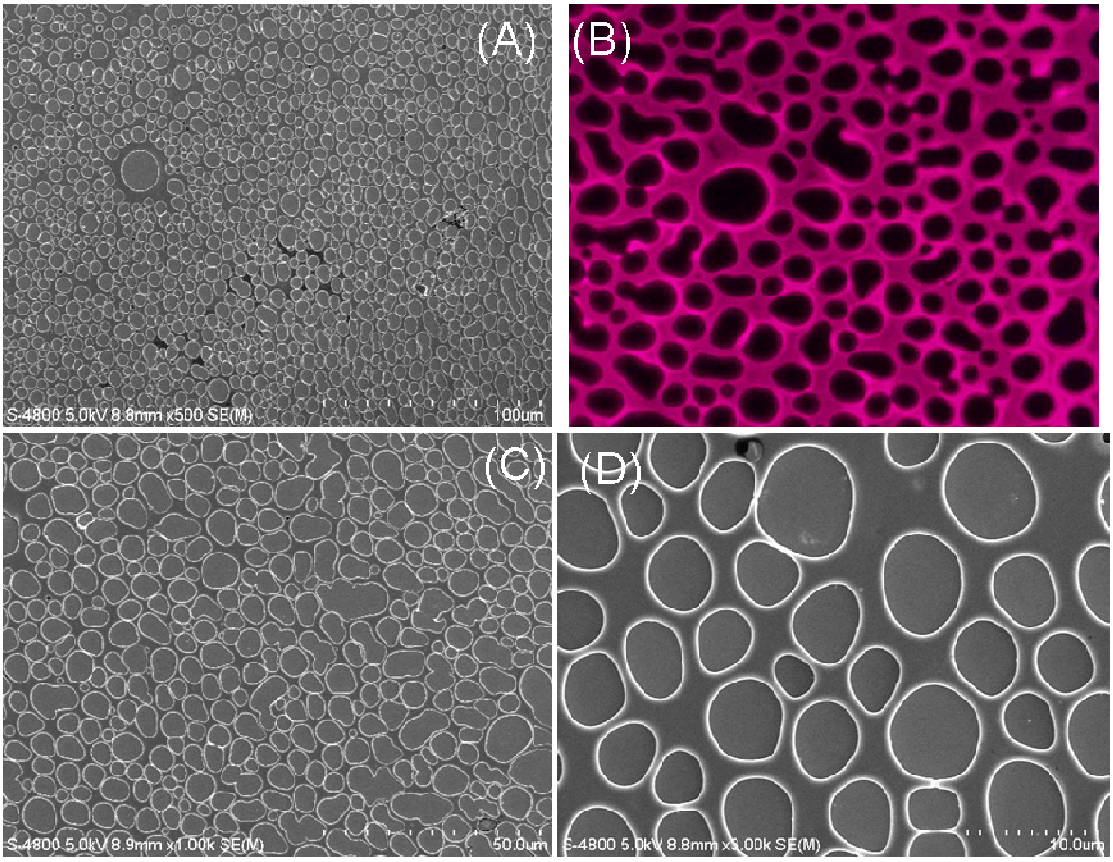


Figure S5. SEM-images (A, C and D) and fluorescent image(B) of the honey-comb porphyrin nanostructures assembled at -10^{o}C

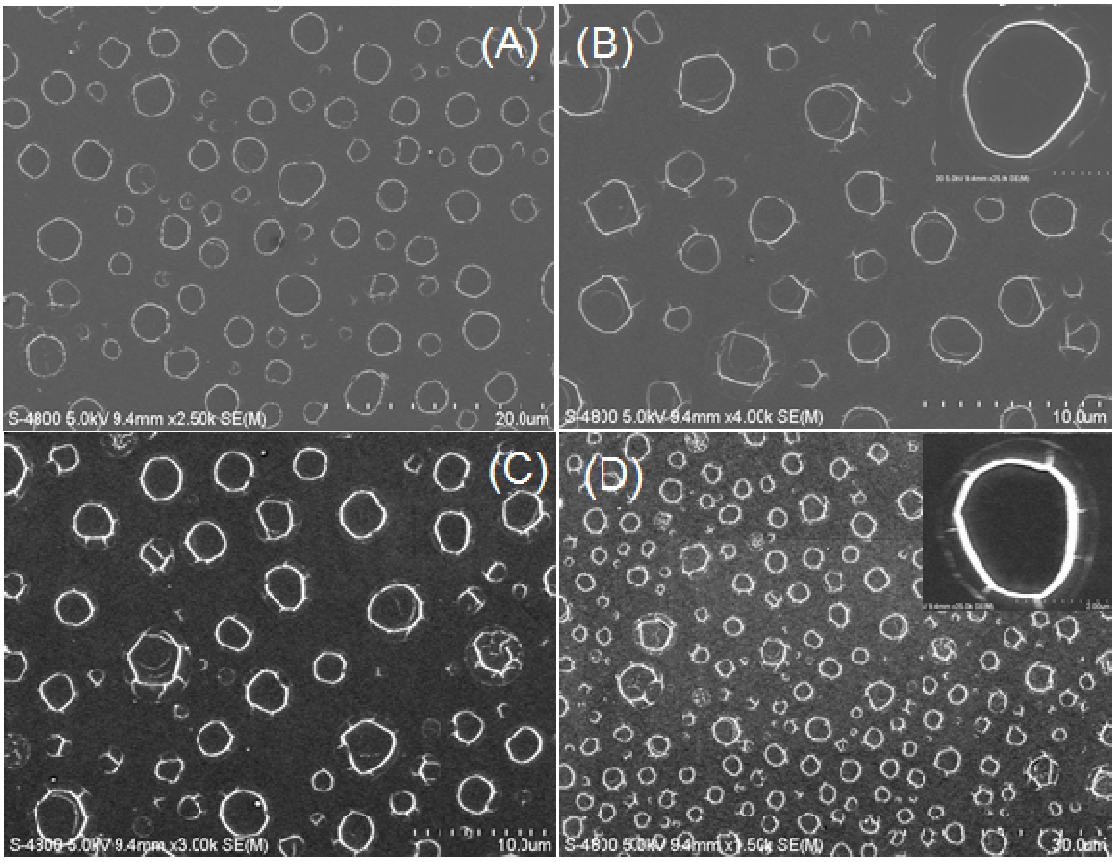


Figure S6. SEM-images of the ring-like porphyrin nanostructures assembled at -5°C

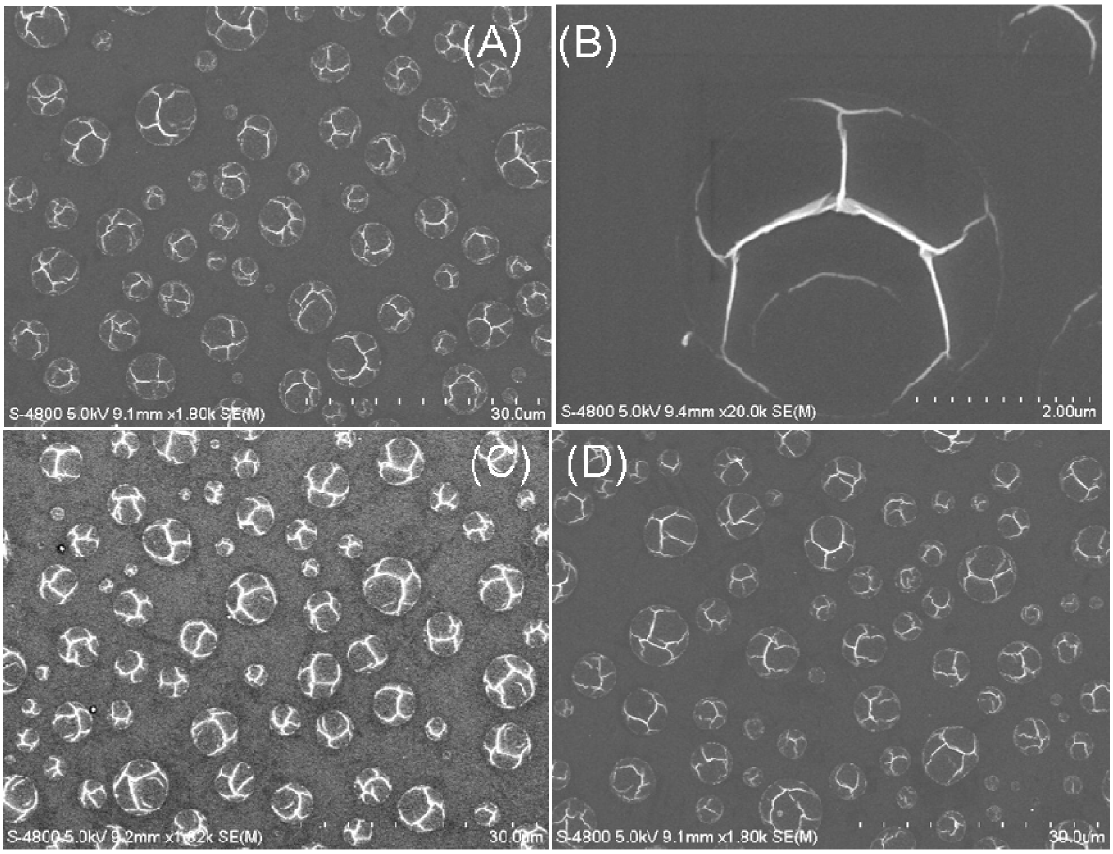


Figure S7. SEM-images of the skeleton-like porphyrin nanostructures assembled at 0°C

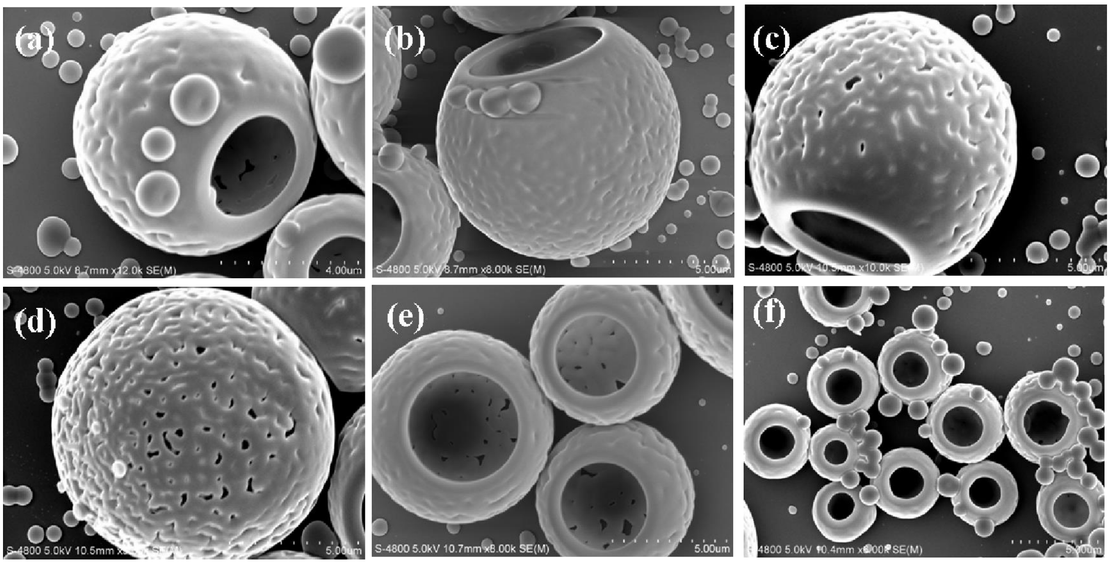


Figure S8. SEM-images of the jar-like porphyrin nanostructures assembled at 10°C

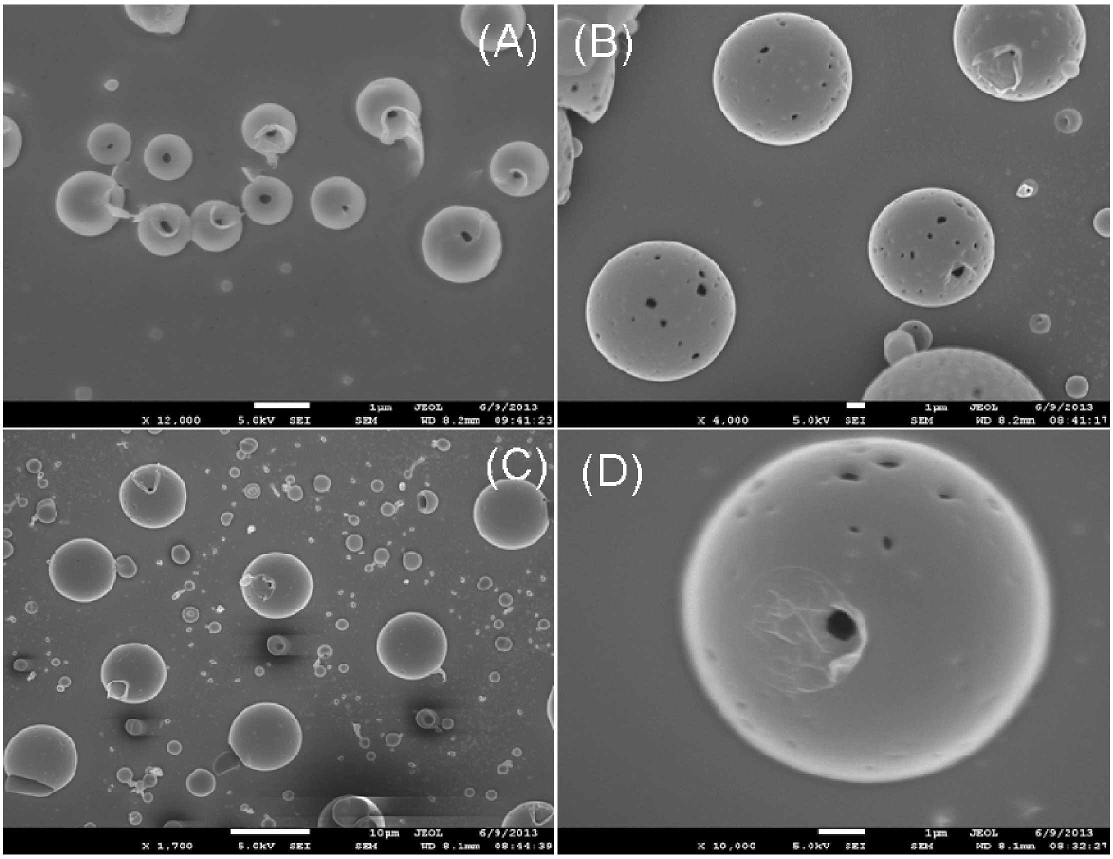


Figure S9. SEM-images of the hollow spheric porphyrin nanostructures assembled at 20^{o}C

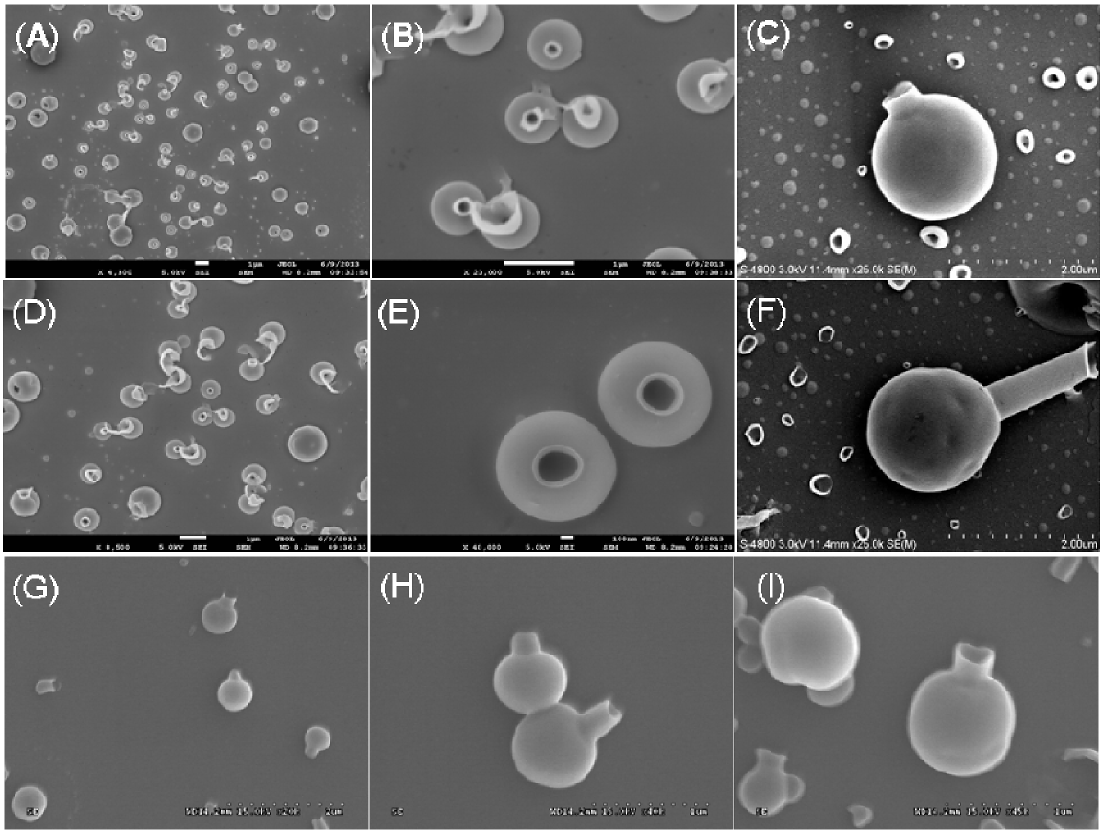


Figure S10. SEM-images of the flask-like porphyrin nanostructures assembled at 30^{o}C

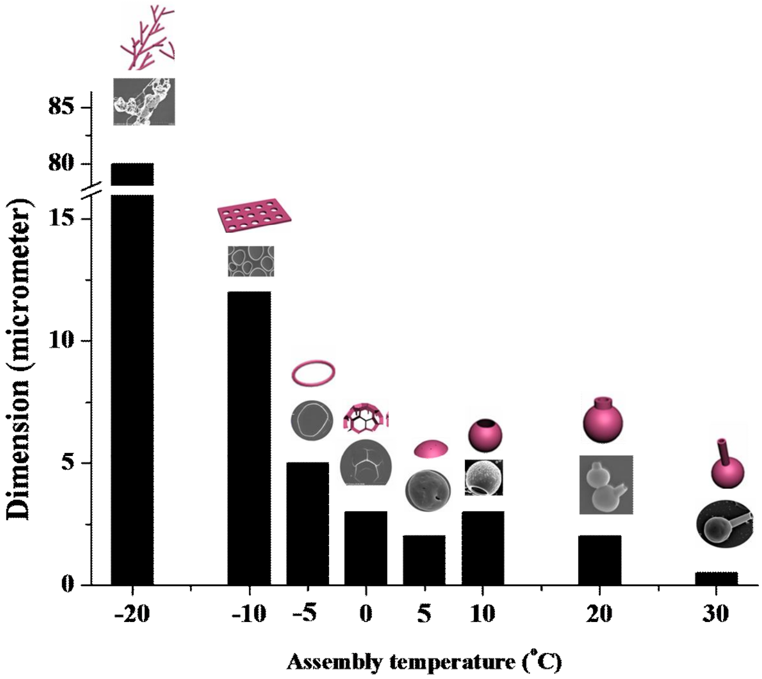


Figure S11. The relationship between assembly temperature and sample dimension.

The tree-like structure dimension is *ca.* 80 εm. The dimension of wavy-like or honey-comb structure is *ca.* 10 εm. The dimension of ring-, skeleton- and cap-like nanostructures is *ca.* 2-3 εm. The dimension of the jar- and the hollow-sphere structure is *ca.* 3-5 εm, and the flask-shaped structure is *ca.* 500 nm.

3.4 In-situ evaporation process for the droplet on the low-temperature substrate

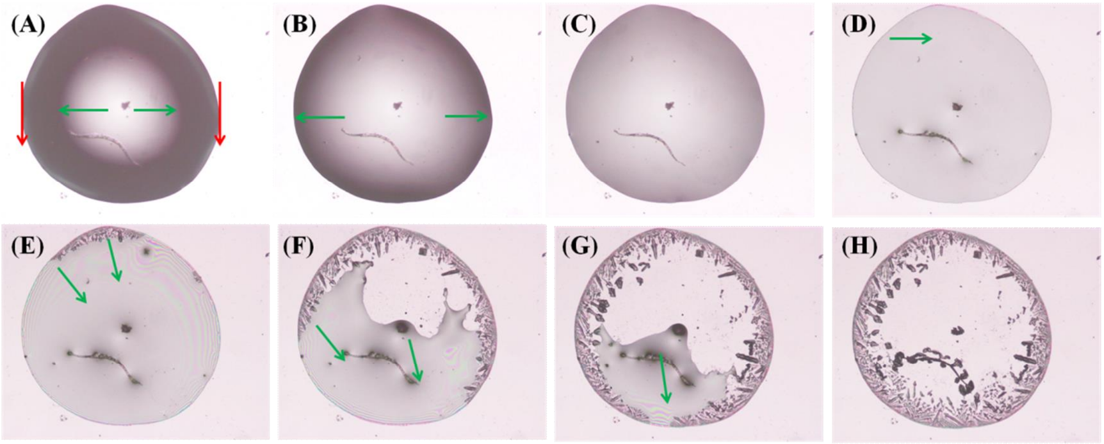


Figure S12. *In-situ* optic microscopy images of the droplet during evaporation process at 0 °C, the red arrow indicates the pinning three phase contact line (TCL), while the green arrow indicates the sliding direction of evaporation front during evaporation process.

At low temperature, TCL pins firstly, the solvent flow move from the center toward the brim of the droplet (A, B, C), when approaching a single-layer liquid film in D, the evaporation front move from brim toward the other part of the droplet (E, F, G, and H) with part pinning of TCL.

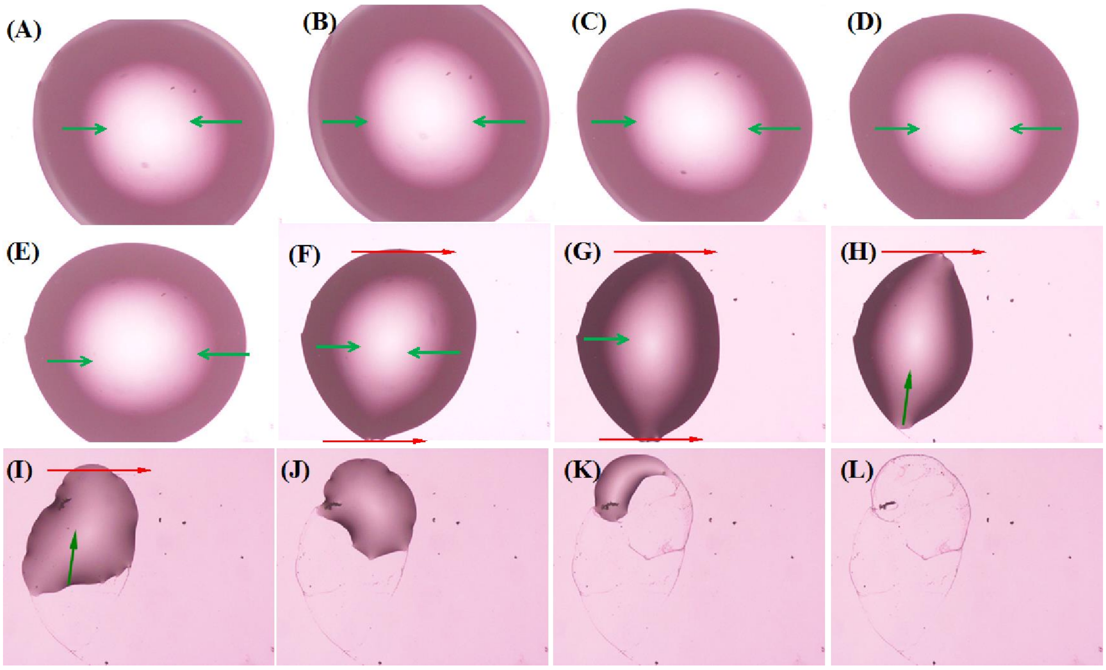


Figure S13. In-situ optic microscopy images of the droplet during evaporation process on substrate at 5^{O}C. (red arrow indicates the pinning TCL, while the green arrow indicates the sliding direction for the evaporation flow).

At high temperature, the droplet firstly evaporation from the brim to the center with TCL sliding from the brim toward the center in (A, B, C, D, E, and F). Subsequently, keep part pinning of TCL, evaporate flow sliding from part brim toward the other part (from F to L), leaving a shrinkable stain.

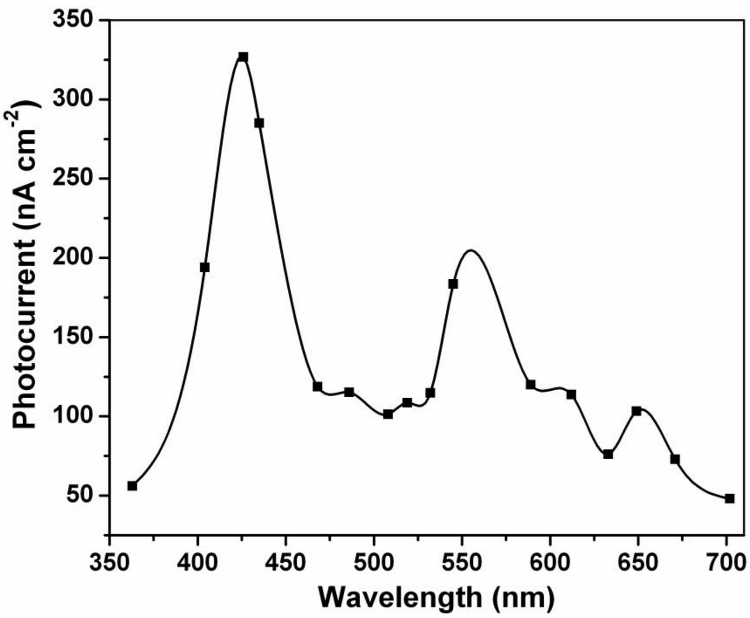


Figure S13. The relationship between the photocurrent and the irradiation wavelength of light. Action spectrum of ITO/Porphyrin/TEA/Pt system; input power, 500 mW cm^{-2}; applied potential, +0.10 V versus Ag/AgCl (sat. KCl); an argon-saturated 0.1 M Na_2SO_4 aqueous solution containing 50 mM TEA.

The Figure 13 indicates the photoactive materials of the porphyrin nanostructure, it photoelectrochemical properties depends on its absorbance spectra.