Supporting information

# **Temperature-controlled Morphology Evolution of Porphyrin Nanostructures on Hydrophobic Substrate**

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## **1. Experimental Section**

**1.1** The synthesis procedure and basic characterization of porphyrin derivative used in the experiment



Fig. S1. Synthetic procedure for the compound 5 (porphyrin derivative).

# 1.1.1 Synthesis of 5-(4-(carboxypropoxy)phenyl)-10,15,20-tri(naphthyl) porphyrin (compound 3)

Firstly, **compound 1** was synthesized by the method similar to the literature.<sup>[1]</sup> 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 °C 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<sub>3</sub> as an eluent. The

second band was collected and the solvent was evaporated. Purple solid 1 was obtained in 2.6% yield. **compound 2** was synthesized by esterification reaction of **compound 1**. A mixture of 0.3902 g **compound 1**, 1.8 g K<sub>2</sub>CO<sub>3</sub> and 50 mL N,N-Dimethylformamide (DMF) was stirred at 90 °C. 2 mL ethyl 4-bromobutyrate dissolved in 5ml DMF was added dropwise. After 10 h, the mixture was washed with H<sub>2</sub>O several times to neutrality, drying over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrating via rotary evaporation, the residue was chromatographed on a silica gel column using CHCl<sub>3</sub> as eluent. The first band was collected and the solvent was evaporated. Purple solid **compound 2** was obtained in 85% yield. The mixed solvents of chloroform and methanol (20 mL) of **compound 2** (420.0 mg, 1.0 mmol) was mixed with NaOH aqueous solution (1 mL, 2.0 M) and stirred at room temperature. After 3 h, purple solid was precipitated in the mixture. The precipitated was purified on a silica gel chromatograph using ethylic acid/chloroform (1:10) to obtain **compound 3** as a purple powder.

#### 1.1.2 Synthesis of 4-(1,2,2-triphenylvinyl) phenol (compound 4)

**Compound 4** was prepared according to the reported procedures,<sup>[2]</sup> into a 100 mL roundbottom flask with condenser, a mixture of 4-hydroxylbenzophenone (0.496 g, 2.5 mmol) , benzophenone (0.456 g, 2.5 mmol) and zinc dust (0.4053 g, 6.2 mmol) in freshly distilled THF (60 mL) was cooled to -78 °C under N<sub>2</sub>. TiCl<sub>4</sub> (6.2 mL, 6.2 mmol) was added dropwise to the cold mixture. The suspension was warmed to room temperature and then refluxed overnight. After warming to room temperature, the excess zinc residue was removed by flash chromatography using THF as solvent and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography using chloroform to obtain TPE-OH compound 4 as a yellow powder (0.283 g, yield 32%).

#### 1.1.3 Synthesis of compound 5 (TPPTPB)

**Compound 3** was coupled with **compound 4** by using dicyclohexylcarbodiimide (DCC) (1 equiv) in the presence of a catalytic amount of 4-dimethylaminopyridine (DMAP) in dry dichloromethane on an ice-bath for 1 h and then allowed to come to room temperature with vigorous stirring for 36 h. The crude compound 5 was purified by

column chromatography using petroleum ether/chloroform (1:4) to obtain TPE-OH **compound 5** as a purple powder.

[1] X. B. Du, J. Qi, Z. Q. Zhang, D. G. Ma and Z. Y. Wang, Chem. Mater. 2012, 24, 2178-2185.

[2] J. H. Cai, S. R. Chen, L. Y. Cui, C. C. Chen, B. Su, X. Dong, P. L. Chen, J. X. Wang, D. J. Wang, Y. L. Song and L. Jiang, *Adv. Mater. Interf.*, 2014, 2, 1400365.



Fig. S2. FTIR spectrum of TPPTPB.

Fig. S2 shows the FTIR spectra of TPPTPB. The appearance of a sharp band at 1757 cm<sup>-1</sup> confirms the synthesis of TPPTPB because of the characteristic absorption band for the carbonyl ester stretching vibration. The stretching vibration of =C–N and –C=N bands (pyrrole) appeared at 1386 cm<sup>-1</sup>. The stretching asymmetric and symmetric vibration bands attributed to the C–H (CH<sub>2</sub>) bands are discernible at 2939 cm<sup>-1</sup>. The peaks appearance at 1504 cm<sup>-1</sup> and 1110 cm<sup>-1</sup> could be attributed to C-O-C and C=C band.



Fig. S3. The mass spectrum of compound 1.





<sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  9.97 (s, 1H), 8.79 (d, *J* = 23.5 Hz, 2H), 8.53 (s, 2H), 8.41 (d, *J* = 7.0 Hz, 4H), 8.36 – 8.17 (m, 8H), 8.08 – 7.80 (m, 5H), 7.53 (d, *J* = 6.9 Hz, 4H), 7.25 – 6.87 (m, 8H), -2.46 (s, 2H). MS (MALDI-TOF): m/z = 781.4 [M + H] + (calcd. for C <sub>56</sub> H <sub>36</sub> N <sub>4</sub> O m/z = 780).



Fig. S5. The mass spectrum of compound 2.



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.80 – 8.45 (m, 8H), 8.30 – 8.24 (m, 5H), 8.12 (t, *J* = 9.9 Hz, 5H), 7.87 – 7.79 (m, 3H), 7.50 – 7.45 (m, 3H), 7.25 – 7.21 (m, 3H), 7.19 – 7.07 (m, 5H), 4.29 – 4.20 (m, 4H), 2.68 (t, *J* = 7.3 Hz, 2H), 2.29 (t, *J* = 6.7 Hz, 2H), 1.31 (d, *J* = 7.1 Hz, 3H), -2.36 (s, 2H). MS (MALDI-TOF): m/z = 895.3 [M + H] + (calcd. for C <sub>62</sub> H <sub>45</sub> N <sub>3</sub> O<sub>3</sub> m/z = 894).



Fig. S7. The mass spectrum of compound 3.



Fig. S8. The H-NMR spectrum of compound 3.

<sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  8.79 (s, 2H), 8.52 (s, 2H), 8.42 (s, 4H), 8.25 (d, *J* = 9.5 Hz, 7H), 8.14 – 7.88 (m, 6H), 7.56 – 6.89 (m, 13H), 4.25 (s, 2H), 2.11 (s, 2H), 1.36 (s, 2H), -2.47 (s, 2H). MS (MALDI-TOF): m/z = 867.3 [M + H] + (calcd. for C <sub>60</sub> H <sub>42</sub> N <sub>4</sub> O<sub>3</sub> m/z = 866).



Fig. S9. The mass spectrum of TPPTPB.





<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.55 (d, *J* = 41.8 Hz, 8H), 8.28 (d, *J* = 13.6 Hz, 6H), 8.18 – 8.08 (m, 5H), 7.86 (d, *J* = 15.1 Hz, 3H), 7.53 – 7.46 (m, 3H), 7.28 – 6.90 (m, 27H), 4.35 (t, *J* = 6.0 Hz, 2H), 2.92 (t, *J* = 7.2 Hz, 2H), 2.44 – 2.35 (m, 2H), -2.35 (s, 2H). MS (MALDI-TOF): m/z = 1197.7 [M + H] + (calcd. for C <sub>86</sub> H <sub>60</sub> N <sub>4</sub> O<sub>3</sub> m/z = 1196).





**Fig. S11**. (A) UV-vis absorption spectra of the dichloromethane solution of TPPTPB and the TPPTPB dispersion obtained by mixing its dichloromethane solution and hexane at the volume ratio of 1:1. (B) Magnified spectra of (A).

UV-vis absorption spectra (Fig. S11(A, B)) of dichloromethane solution of TPPTPB and the TPPTPB dispersion. Comparing the spectra of monomeric TPPTPB in dichloromethane solution, new peak centered at 915 nm emerges for the spectra of TPPTPB dispersion. These phenomena suggest the formation of vesicles in the TPPTPB dispersion<sup>[2-5]</sup>.

[3] J. H. Cai, T. Wang, J. X. Wang, Y. L. Song and L. Jiang, *J. Mater. Chem. C*, 2015, 3, 2445-2449.
[4] T. Wang, S. R. Chen, F. Jin, J. H. Cai, Y. M. Zheng, J. X. Wang, Y. L. Song and L. Jiang, *Chem. Commun.*, 2015, 51, 1367-1370.
[5] T. Wang, M. X. Kuang, F. Jin, J. H. Cai, L. Shi, Y. M. Zheng, J. X. Wang and L. Jiang, *Chem.*

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# 1.3 Experimental set-up for porphyrin assembly



Fig. S12. (A) Set-up for the porphyrin assembly and (B) the integration with the camera.

A closed box (Fig. S12(A)) with constant temperature and humidity can be used as an apparatus to conduct for porphyrin assembly. And the temperature of the substrate is controlled by the linkam THMS 600 cryostage. The water droplet is formed owing to the condensation of the water vapor onto the substrate. The porphyrin dispersion is charged onto the droplet template through the sampling pool. The whole experimental apparatus can be recorded with the high-speed camera as shown in Fig. S12(B).





Fig. S13. (A-D) SEM images of the jar-like porphyrin nanostructures assembled at -20°C.



Fig. S14. (A-D) SEM images of the flask-like porphyrin nanostructures assembled at -15°C.



Fig. S15. (A-D) SEM images of the cup-like porphyrin nanostructures assembled at -10°C.



Fig. S16. (A-D) SEM images of the open smile-like porphyrin nanostructures assembled at -5°C.



Fig. S17. (A-D) SEM images of the tulip-like porphyrin nanostructures assembled at -5°C.



Fig. S18. (A-D) SEM images of the chain-like porphyrin nanostructures assembled at 0°C.



Fig. S19. The relationship between assembly temperature and sample dimension.

The jar-like structures dimension is ca.  $0.95\pm0.1$  um. The dimension of flask-like structures is ca.  $2.3\pm0.2$  um. The dimension of cap-like nanostructures is ca.  $2.4\pm0.2$  um. The dimension of the open smile-/tulip-like structures is ca. 1.4-1.6 um, and the dimension of chain-like structures is ca.  $0.75\pm0.2$  um.



**Fig. S20.**  $(A_1-A_3)$  SEM images of porphyrin nanostructures assembled from different solvent ratios of hexane: dichloromethane.  $(A_1)$  1:1,  $(A_2)$  1:2,  $(A_3)$  1:3.

In details, when the sample was fabricated from the volume ratio of hexane and dichloromethane of 1:1, the resultant nanostructures (Fig.  $S20(A_1)$ ) showed good and separate assembly structures. However, the edge of assembly structures (Fig.  $S20(A_2, A_2)$ ) A<sub>3</sub>)) was not clear and became a continuous phase when changing the solvent ratio of hexane: dichloromethane to 1:2 or 1:3. In details, little favourable assembly structures (Fig.  $S20(A_2)$ ) were obtained when the solvent ratio of hexane: dichloromethane was 1:2, but almost complete continuous structures (Fig.  $S20(A_3)$ ) occurred on the condition that the solvent ratio of hexane: dichloromethane was 1:3. The reason was closely related to the preparation process of TPPTPB suspension. Briefly, the TPPTPB suspension was prepared by dissolving TPPTPB into the dichloromethane with a concentration of 10<sup>-</sup>  $^{5}\sim10^{-6}$  mol/L and subsequently adding the formed solution into hexane in different volume ratios. In this process, the poor solubility of TPPTPB in hexane resulted in the formation of TPPTPB vesicles in the suspension, with hydrophobic porphyrin core toward the dichloromethane phase, and the hydrophilic ether group toward the hexane phase. When the volume ratio of dichloromethane was too large, TPPTPB vesicles contacted with each other during the assembly process around the water droplet and formed a poor and continuous assembly structures owing to the redundant TPPTPB vesicles and close distance between water droplets.

# 3. Optic properties of the sample



## 3.1 Luminescence decay for different forms of TPPTPB

**Fig. S**21. (A, B, C) Luminescence decays (375 nm excitation) of (A) TPPTPB solution (dissolved in dichloromethane with concentration of 10<sup>-5</sup>-10<sup>-6</sup> mol/L), (B) TPPTPB smooth film and (C) cup-like nanostructures. (D) Total spectra.

### 3.2 UV-vis absorption spectra of sample



**Fig. S22** (A) UV-vis absorption spectra of the dichloromethane solution of TPPTPB and asprepared film. (B) Magnified spectra of (A).

The possible aggregate mode of TPPTPB molecules could be confirmed from the UV-vis absorption spectra of the dichloromethane solution of TPPTPB and as-prepared film. The most of TPPTPB could be possibly organized as J-like aggregates owing to the as-prepared film displayed a spitted blue-shifted Soret-band at *ca*. 388 nm and part red-shifted Soret-band at 446 nm compared to the the original Soret-band (422 nm) of the monomeric TPPTPB in dichloromethane solution.<sup>[6-8]</sup> Notably, a relatively sharper adsorbent band located at 650 nm appeared while the corresponding band of monomeric TPPTPB in dichloromethane solution was broad, suggesting the formation of well-orientated aggregation: the hydrophobic porphyrin core toward the interior while the hydrophilic group toward the outside.

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