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Supporting Information

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Controlled Self-assembly Behaviour of an Amphiphilic Bis-porphyrin-Bipyridinium-Palladium Complex: from Multi-bilayer Vesicles to Hollow Capsules

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General. The chemical reagents were purchased reagent-grade from Acros or Aldrich Corporation and were used without further purification unless otherwise stated. All solvents were purified using standard procedures. Evaporation and concentration *in vacuo* were carried out at water aspirator pressure and compounds were dried at 10^{-2} Torr. Column chromatography: SiO_2 (160-200meshes). TLC glass plates coated with SiO_2 F_{254} were visualized by UV light. UV/Vis spectra were measured on a Hitachi U-3010 spectrometer. FT-IR spectra were recorded as KBr pellets on a Perkin-Elmer System 2000 spectrometer. ^1H NMR spectra were recorded on Bruker ARX400 or DMX300 spectrometer; 100MHz ^{13}C NMR spectra were recorded on Bruker DPX400 spectrometer. The solvent signal was used as an internal reference for both ^1H and ^{13}C NMR spectra. MALDI-TOF mass spectrometric measurements were performed on Bruker Biflex Ⅲ MALDI-TOF spectrometer. Elemental analysis was performed on Carlo-Erba-1106 instrument.

BPY-H_2P: 0.5mmol 2, 2'-bipyridine-4, 4'-dicarbonyl chloride[1]was dissolved in anhydrous toluene (30mL), and 5, 10, 15-tri (3, 4, 5-trimethoxyl) phenyl-20-(p-amino) phenyl) porphyrin (2.5 equiv.) and 1 mL anhydrous pyridine were added. The suspension was stirred at room temperature for 2 h under an anhydrous atmosphere. After the removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, CH_2Cl_2) to give BPY-H_2P (600 mg, yield, 60%). ^{1}HNMR(300 MHz, $CDCl_3$, 25 °C [ppm]), δ 9.10 (s, 2 H), 9.06 (s, 2 H, J = 4.8 Hz), 8.98 (m, 12 H), 8.91 (d, J = 4.5 Hz), 8.53 (s, 2 H), 8.26 (d, 4 H, J = 8.1 Hz), 8.12 (m, 6 H), 7.48 (m, 12 H), 4.19 (s, 18 H), 3.98 (s, 36 H), -2.75 (s, 4 H). ^{13}CNMR (100 MHz, $CDCl_3$, 25 °C [ppm]) δ 164.5, 156.2, 151.5, 150.4, 143.5, 138.8, 137.9, 137.7, 137.5, 135.1, 129.1, 128.2, 125.3, 122.5, 12.2, 120.1, 119.6, 118.9, 118.4, 112.9,

61.4, 56.4. MS (MALDI-TOF): $C_{118}H_{102}N_{12}O_{20}$ Cald 2008.1, found 2008.2. IR (KBr, [cm^{-1}]): 3315, 2933, 2830, 1682, 1580, 1501, 1465, 1406, 1356, 1318, 1234, 1126, 1004, 974, 924, 800, 724.

BPY-ZnP: A saturated methanol solution of $Zn(OAc)_2$ (5 ml) was added to a solution of BPY-H_2P (200 mg) in $CHCl_3$ (50 ml) and refluxed for 3 h. After cooling, the reaction mixture was washed with water for two times and dried over anhydrous Na_2SO_4, and then the solvent was removed. Flash column chromatography on silica gel with $CHCl_3$ /CH_3OH (100/1) as the eluent gave BPY-ZnP as a dark solid (98% yield, 209 mg). The solid is redissolved in presence of polar solvent. BPY-ZnP-pyridine: ^{1}HNMR (300 MHz, $CDCl_3$, 25 °C [ppm]), δ 9.08 (s, 2 H), 9.02 (m, 14 H), 8.93 (d, 4 H, J = 4.7 Hz), 8.58 (s, 2 H), 8.21 (d, 4 H, J = 8.0 Hz), 8.05 (m, 6 H), 7.47 (s, 12 H), 6.68 (m, 2 H_{py}), 5.95 (m, 4 H, H_{py}), 4.17 (s, 18 H), 3.96 (s, 36 H), 2.71 (m, 2 H, H_{py}). BPY-ZnP: ^{1}HNMR (400 MHz, $CDCl_3$/CD_3OD (10/1), 25 °C [ppm]), δ 8.92 (m, 20 H), 8.22~8.06 (m, 10 H), 7.43 (s, 12 H), 4.10 (s, 18 H), 3.90 (s, 36 H). MS (MALDI-TOF): Cald. 2134.8, found 2131.0. Anal for $C_{118}H_{98}N_{12}O_{20}Zn_2$, C 66.39, H 4.63, N 7.87; found: C 66.30, H 4.55, N 7.75. IR (KBr, [cm^{-1}]): 2933, 2831, 1680, 1649, 1581, 1497, 1460, 1406, 1348, 1235, 1126, 1000, 941, 798, 722.

Compound 1 was synthesized according to literature [2]. ^{1}HNMR (400 MHz, $C_2D_2Cl_4$, 25 °C, [ppm]), δ 10.10 (m, 2 H), 9.28 (m, 2 H), 9.00 - 8.93 (m, 16 H), 8.50 - 8.15 (m, 10 H), 7.41 - 7.25 (m, 12 H), 4.02 (s, 6 H), 3.90 (s, 12 H), 3.85 (s, 12 H), 3.74 (s, 24 H). MS (MALDI-TOF): $C_{118}H_{98}Cl_2N_{12}O_{20}PdZn_2$, Cald. 2312.22, found 2240.2(M-2Cl, $C_{118}H_{98}N_{12}O_{20}PdZn_2$, 2241.31). IR (KBr, [$cm^{-1}$]): 3280, 2927, 2851, 1681, 1581, 1525, 1450, 1458, 1406, 1348, 1236, 1126, 1001, 941, 800, 721.

Crystallographic data for (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-257749. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code + (1223) 336-033; email: teched@chemcrys.cam.ac.uk).

[1] F. M. N. Hubertus, C. F. Martinus, J. M. N. Roeland, *J. Org. Chem.* **2002**, *67*, 5901.
[2] Y. Tomohiro, A. Satake, Y. Kobuke, *J. Org. Chem.* **2001**, *66*, 8442.

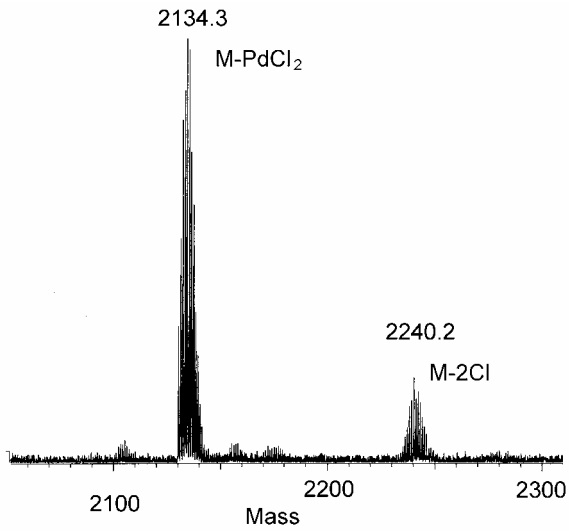
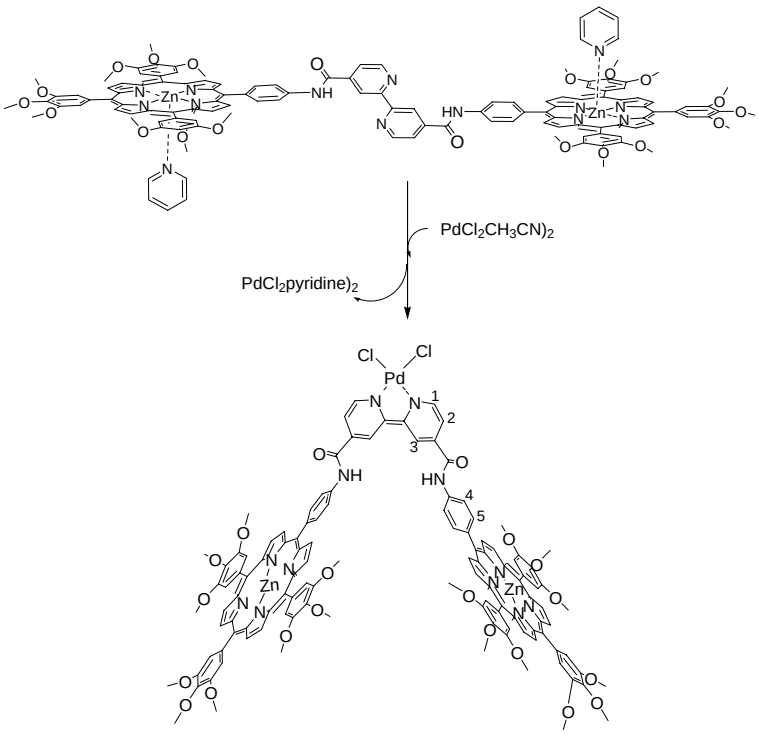


Figure S1. MALDI-TOF spectra of **1**.



Scheme S1. Preparation of **1** from pyridine coordinated BPY-ZnP.

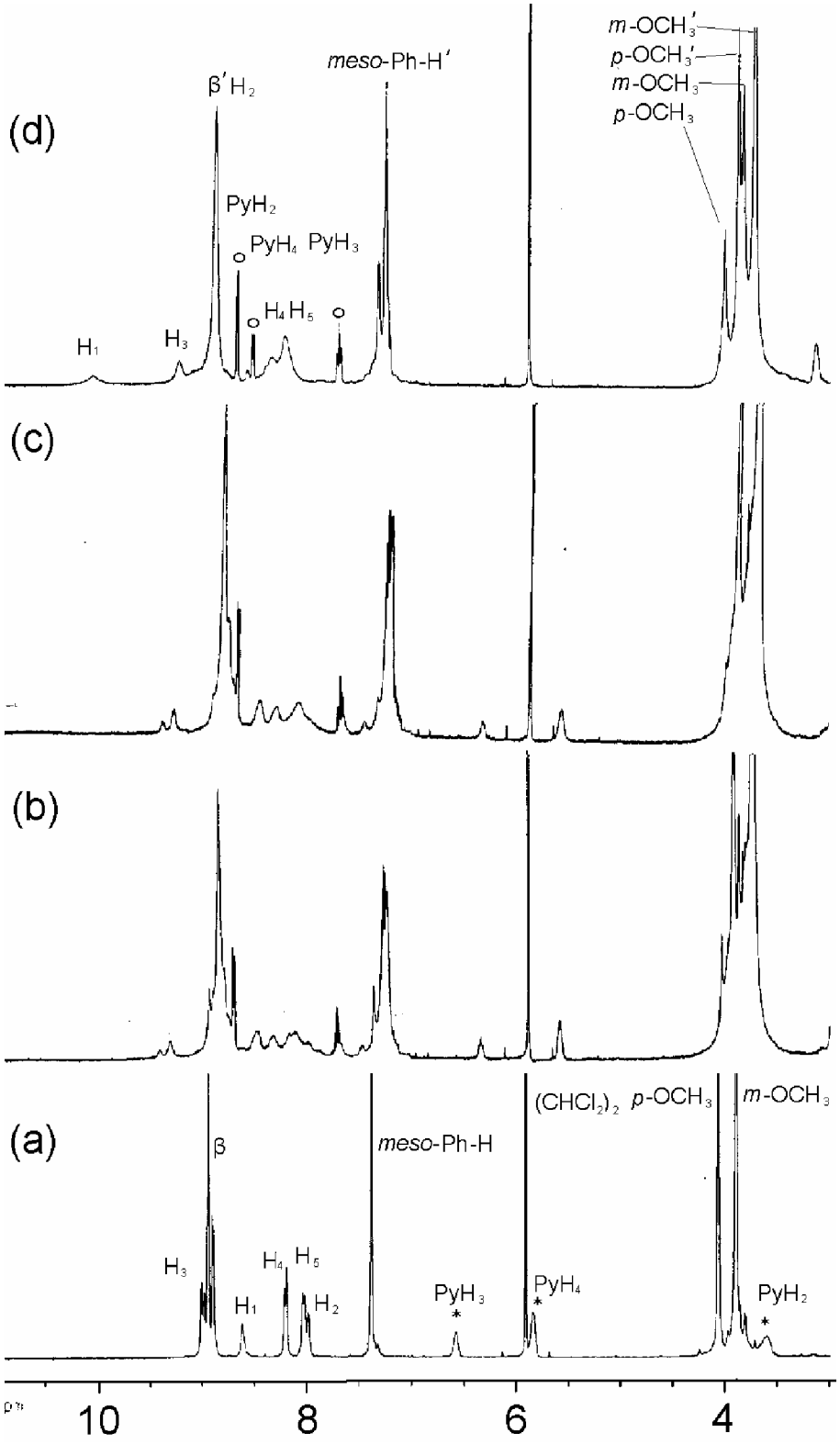


Figure S2. ^{1}H NMR titration of **BPY-ZnP-pyridine** with $PdCl_2$ (400MHz, $C_2D_2Cl_4$). (a) **BPY-ZnP**. (b) **BPY-ZnP** +0.5equiv $PdCl_2(CH_3CN)_2$. (c) **BPY-ZnP** +1.1equiv $PdCl_2(CH_3CN)_2$. (d) **BPY-ZnP** +2.2equiv $PdCl_2(CH_3CN)_2$. **(✶)** Coordinated pyridine, (O) $PdCl_2$(pyridine)$_2$.

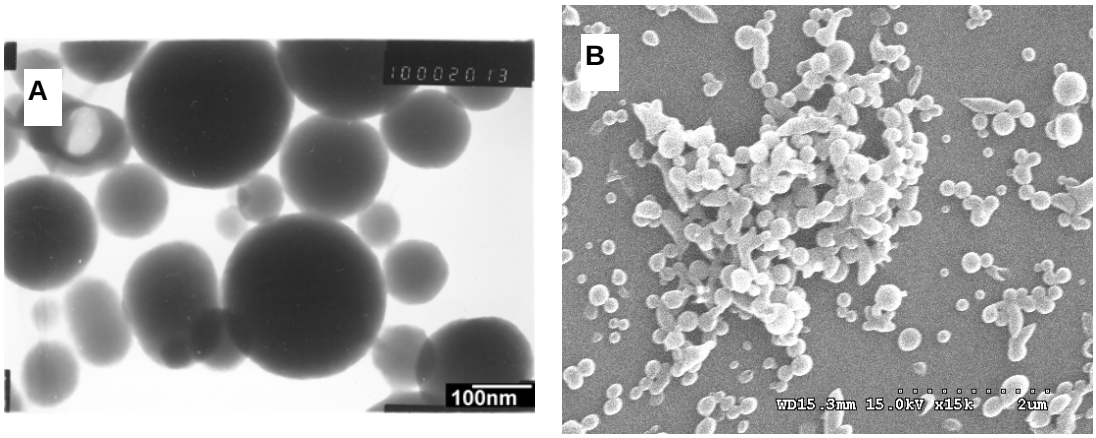


Figure S3. A) TEM of **1** derived vesicles prepared in $CHCl_3/CH_3OH$ (1/1) at room temperature; B) SEM of samples prepared as a) kept at room temperature for 12 days.

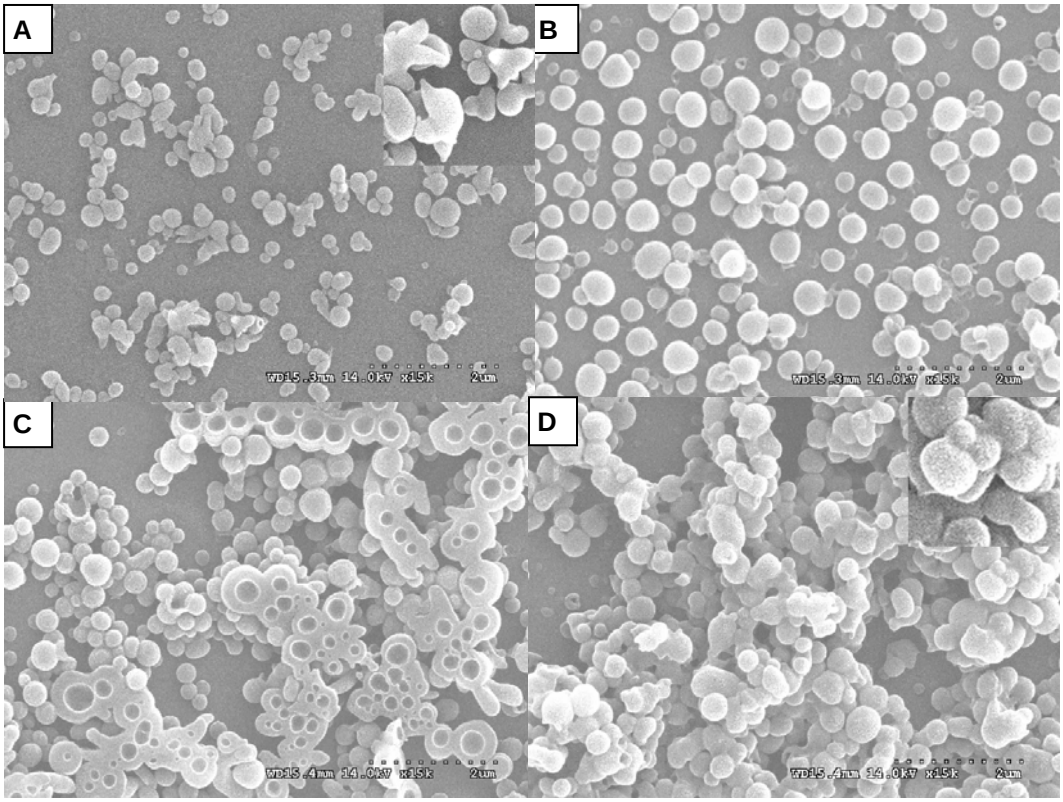


Figure S4. SEM of the vesicle heated at 40°C for 0.5h (A), at 50°C for 0.5h (B), at 70°C for 0.5h (C) and at 90°C for 0.5h (D).

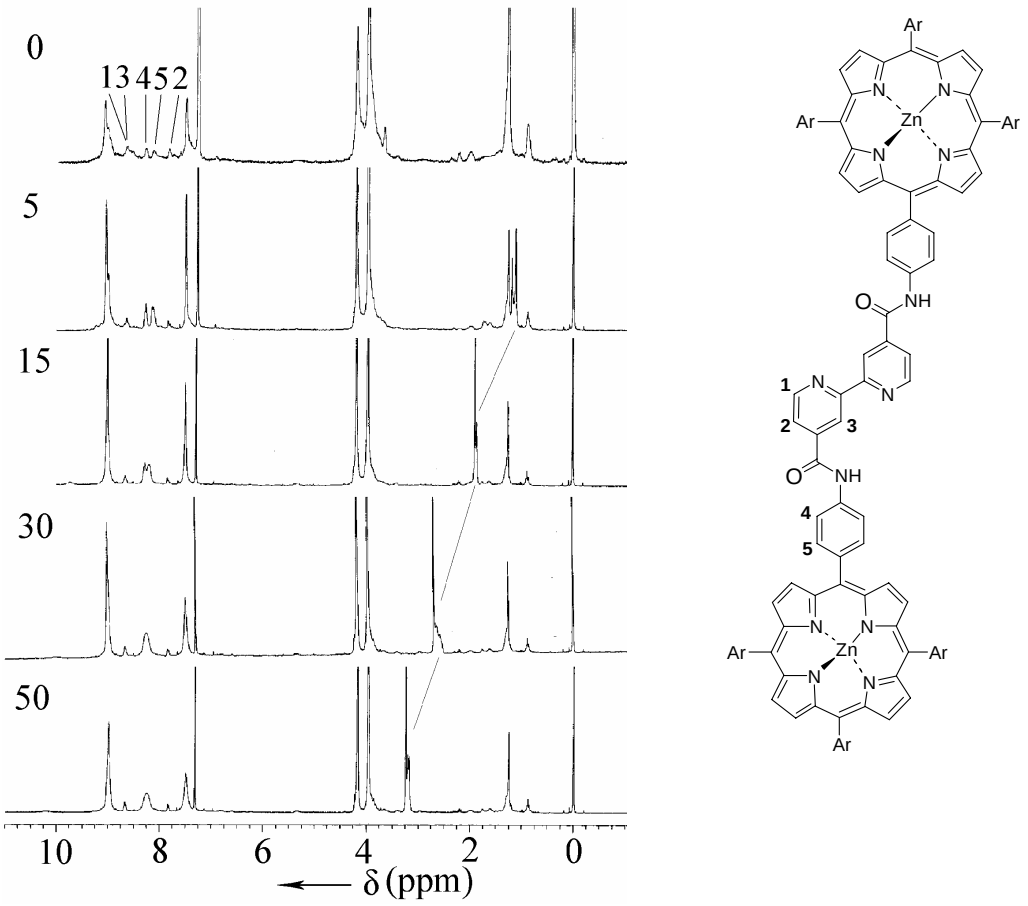


Figure S5. ^{1}H NMR spectra (300MHz) of a solution of BPY-ZnP in $CDCl_3$ at room temperature. The numbers stand for the addition of methanol-d4 (μL). Ar=3,4,5-trimethocylphenyl. And this result indicates methanol can coordinate with the zinc-porphyrin.

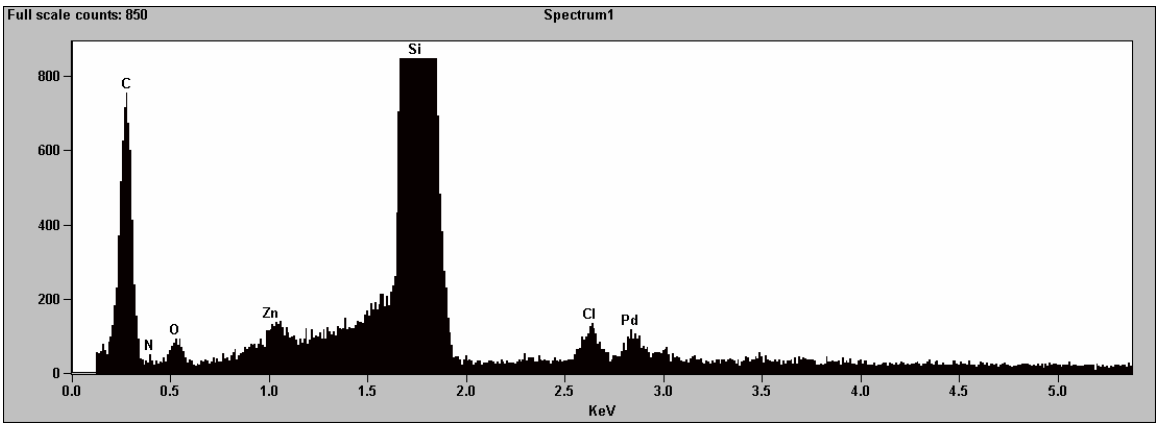


Figure S6. EDX spectra of vesicles prepared in $CHCl_3/CH_3OH$ (1/1) at room temperature