Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

SUPPORTING INFORMATION

Specific Modification and Self-Transport of Porphyrins and Their Multi-Mechanism Cooperative Antitumor Studies

Shuxin Jia[a], Shaochen Wang[a], Shanshan Li[a], Peng Hu[a], Shuling Yu[a]*, Jiahua Shi[a]*, Jintao Yuan[b]*

a. Key Laboratory of Natural Medicine and Immune-Engineering of Henan Province, Henan University, Kaifeng, Henan, 475004, People's Republic of China.

b. College of Public Health, Zhengzhou University, Zhengzhou, 450001, People's Republic of China.

*Address correspondence to: yushuling@henu.edu.cn, sjiahua@henu.edu.cn, jtyuan@zzu.edu.cn.

Materials

Pyrrole was purchased from Bailing wei Technology Co., Ltd., p-nitrobenzaldehyde, benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (pyBOP), 1,3-diphenylisobenzofuran (DPBF) and 2,7-dichlorodihydrofluorescein (DCFH-DA) were provided by damas-beta, acetic anhydride and triethylamine (TEA) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd., mPEG$_{2K}$ was obtained from TCI, D-a-tocopheryl polyethylene glycol 1000 succinate (TPGS) and dimethylaminopyridine (DMAP) were purchased from Aladdin, succinic anhydride was obtained from Sinopharm Group Co., Ltd, taxol (PTX) was purchased from Chongqing Taihao Pharmaceutical Co., Ltd., 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) was obtained from VWR, fetal bovine serum (FBS) was purchased from Hangzhou Sijiqing Biological Engineering Materials Co., Ltd., DMEM was purchased from Solarbio.

The cell lines HL-7702, HepG2, 4T1, MCF-7 were respectively cultured in a DMEM culture medium supplemented with 10% FBS, at 37 °C in a 5% humidified CO_2 incubator.

Synthesis of 5,10,15,20-Tetrakis(4-Aminophenyl)-21H,23H-Porphine (TAPP) P-nitrobenzaldehyde (50 mmol, 7.561 g), acetic anhydride (86 mmol, 8.2 mL), and propionic acid (200 mL) were added to a two-necked flask. The reaction system was heated to 80 ºC in an oil bath, and then the mixture solution of freshly distilled pyrrole (50 mmol, 3.5 mL) and propionic acid (10 mL) were slowly added dropwise into the two-necked flask by a constant pressure dropping funnel with condensation. After ending the dropwise addition, the temperature was raised to 135 ºC and refluxed for 30 min. The reaction solution was cooled to room temperature and stayed overnight at 4 ºC, then a precipitate appeared, filtered, and the filter cake was washed with distilled water (3 × 80 mL) and dried under vacuum. The crude product was dissolved in 80 mL of pyridine, and the solution was refluxed for 1 h, cooled to room temperature and then stood at 0 ºC for 24 h. The solid was collected and washed with acetone until the rinse became colorless. Finally, the solid was dried under vacuum and collected again, the purple solid (1.093 g) was obtained and the yield is about 11%.

The product prepared above (1.3 mmol, 1.0069 g) was dissolved in 50 mL of concentrated hydrochloric acid and the solution was bubbled with nitrogen for 20 min. At the same time, $SnCl_2 \cdot 2H_2O$ (19.1 mmol, 4.3127 g) was dissolved in 70 mL of concentrated hydrochloric acid and the solution was also bubbled with nitrogen for 20 min. Then, the above two solutions were mixed, and reacted at 80 ºC for 30 min, and then the reaction system was stopped heating and cooled to room temperature. Then the reaction continued in the ice bath, then 62.5 mL of $NH_2 \cdot H_2O$ was added to the reaction system for neutralizing the concentrated hydrochloric acid. Simultaneously, the solid appeared and was filtered with a sand core funnel, finally the filtrate was collected. 100 mL of 5% NaOH solution was added the filtrate, then the solution was vigorously stirred and some solid appeared, then the solid was collected by filtering, and the filter cake was washed three times with distilled water, and dried under vacuum. The crude product was further purified in acetone by Soxhlet extractor, a purple solid (TAPP) was obtained with a yield of 15.1% and was analyzed using ^1H NMR and MS.

Micelles stability test

TAPP-mPEG and TAPP-TPGS micelle solutions were separately placed at room temperature, and the UV absorption intensity was measured by UV spectrophotometer on 1th and 7th days, respectively. The ultraviolet absorption intensity of two nanomicelles did not change significantly, when two micelles were irradiated by the UV lamp, the fluorescent color and the brightness of nanomicelles did not change obviously, too, and their Tyndall phenomenon could be detected by laser pointer.

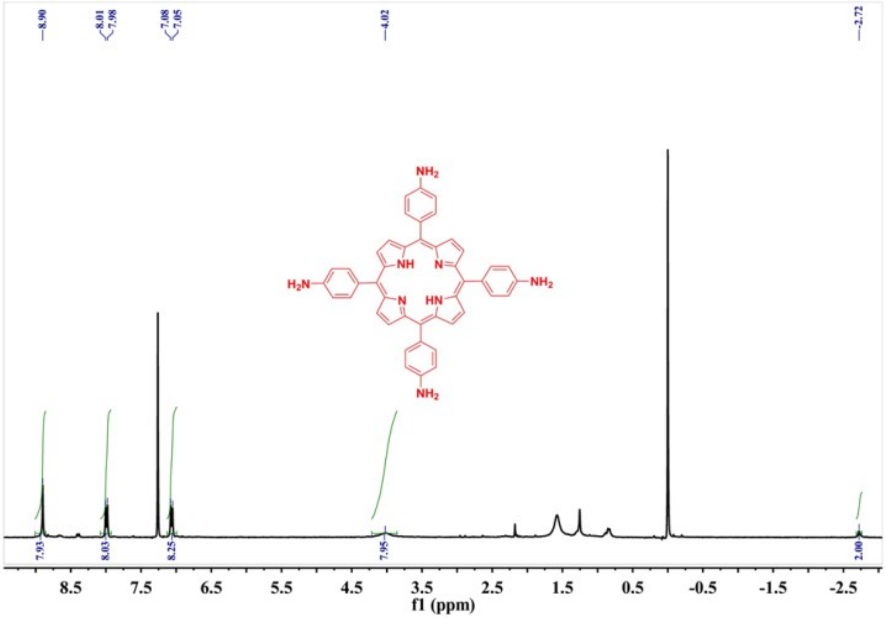

Figure S1. ^{1}H NMR spectrum of TAPP in chloroform-d.

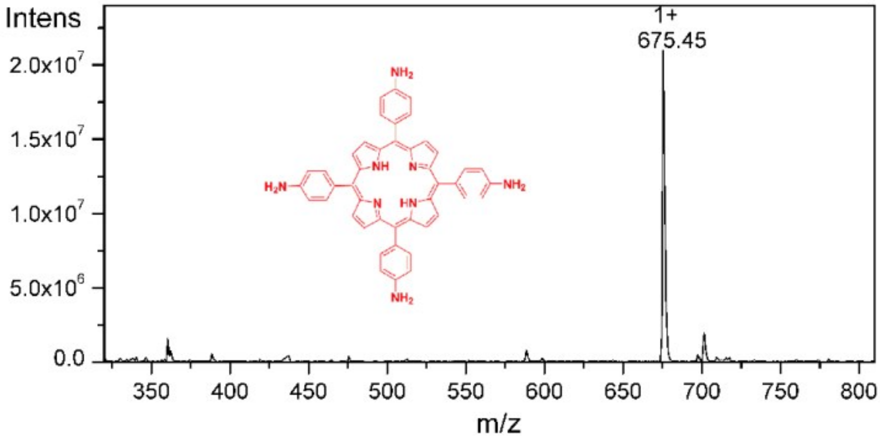

Figure S2. Mass spectrometric of TAPP.

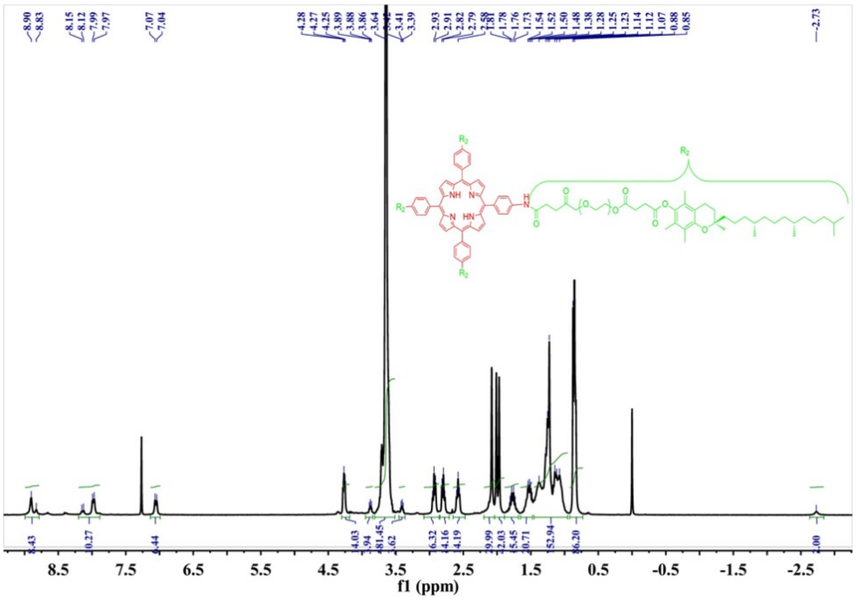

Figure S3. ^{1}H NMR spectrum of TAPP-TPGS in chloroform-d.

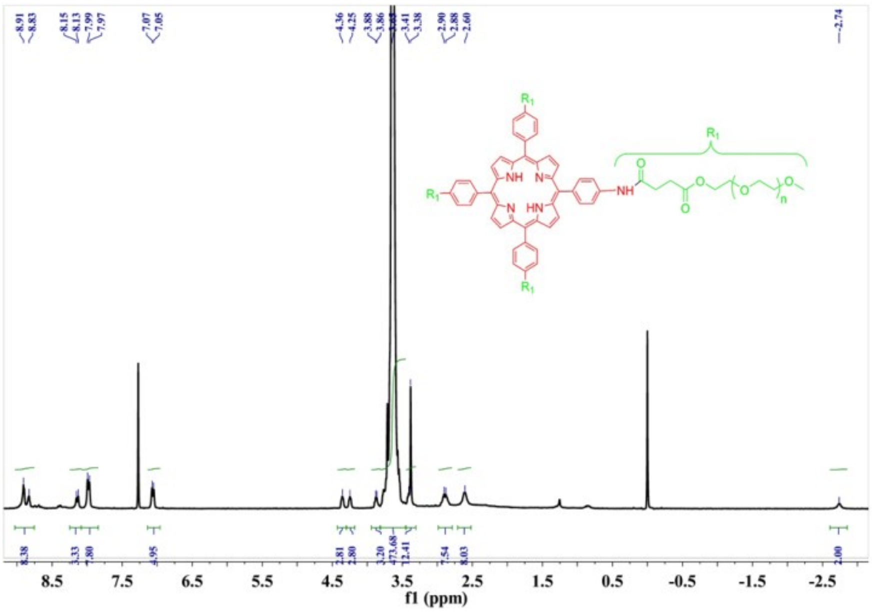

Figure S4. ^{1}H NMR spectrum of TAPP-mPEG in chloroform-d.

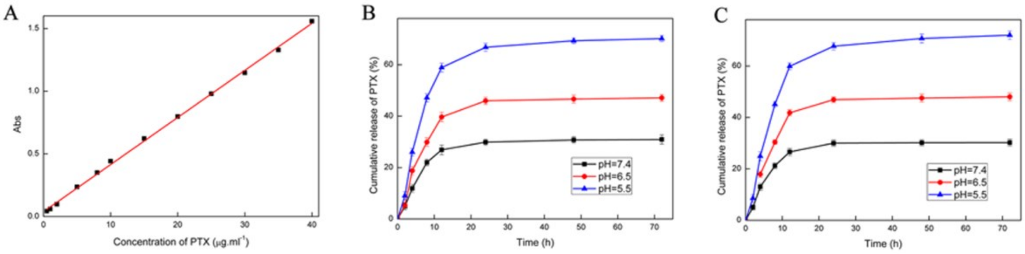

Figure S5. PTX standard curve (A), Release profile of TAPP-mPEG (B) and TAPP-TPGS (C) nanomicelles loaded with PTX at different pH.