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

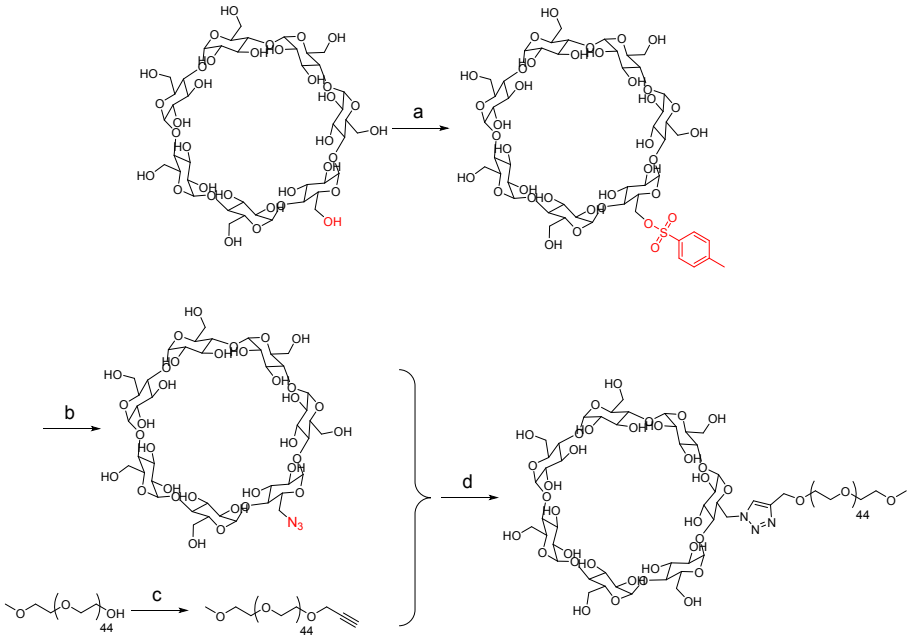

**Supporting Information**

# Photo Controllable Release and Enhancement of Photodynamic Therapy Based on Host-Guest Supramolecular Amphiphiles

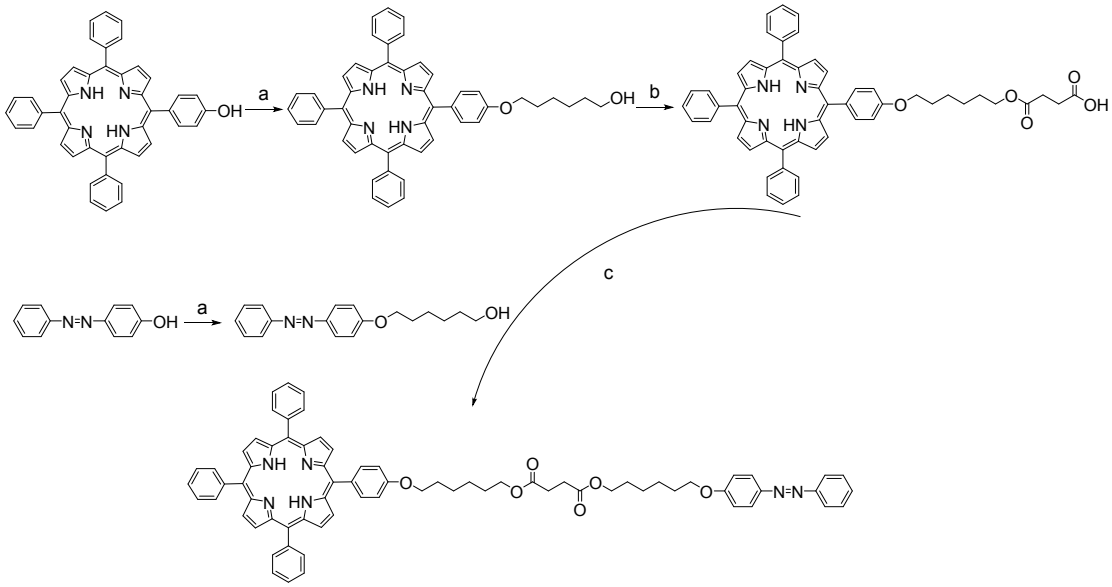
Lei Xu[1], Wenyan Zhang[1], Haibo Cai[1], Feng Liu[1]*, Yong Wang[2], Yun Gao[1], Weian Zhang[1]*

[1]Shanghai Key Laboratory of Functional Materials Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P. R. China.

[2] State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing Tech University, Nanjing 210009, China.



**Scheme S1.** Synthesis of PEG-*β*-CD, a: NaOH, p-toluenesulfonyl chloride and water; b: $NaN_3$, KI and DMF; c: NaH, propargyl bromide and toluene; d: PMDETA, CuBr and DMF.



**Scheme S2.** Synthesis of TPP-Azo. (a) 6-chloro-1-hexanol, $K_2CO_3$ and DMF; (b) succinic anhydride, DMAP and THF; (c) DCC, DMAP and THF.

**Synthesis of Mono-6-Deoxy-6-(p-tolylsulfonyl)-*β*-Cyclodextrin (*β*-CD-OTs)**

*β*-Cyclodextrin (*β*-CD) (30 g, 26.95 mmol) was suspended in 200 mL of water and NaOH (3.29 g, 82 mmol) in 10 mL of water was added dropwise in a short time at an ice-water bath. *p*-Toluenesulfonyl chloride (5.04 g, 26.45 mmol) in 15 mL of acetonitrile was added dropwise, causing formation of white precipitation immediately. After stirring for 2 h, the white precipitate was removed by suction filtration, and the pH of the filtrate was adjusted to 8 by dropping HCl aqueous solution, and the product was obtained. The product was further purified by recrystallization in water at least three times to remove unreacted *p*-toluenesulfonyl chloride and *β*-CD. The final product was dried at 50 °C under vacuum. Yield: 5.2 g, (17 %).

**Synthesis of Mono-6-Deoxy-6-Azido-*β*-Cyclodextrin (*β*-CD-$N_3$)**

*β*-CD-OTs (1.03 g, 0.8 mmol), $NaN_3$ (0.26 g, 4 mmol) and KI (0.032 g, 0.194 mmol) were dissolved in 10 mL DMF at 70 °C for 24 h. The mixed solution was cooled to room temperature and precipitated in 200 mL acetone. The precipitation was then dissolved in 7 mL water and precipitated in 200 mL acetone for 2 times. The solid was then dried under vacuum at 60 °C. Yield: 0.94 g (91 %).

**Synthesis of Monoalkynyl-Terminated PEG (*Alkynyl*-PEG)**

PEG-OH (10.0 g, 5 mmol) was dissolved in anhydrous toluene (80 mL) and refluxed overnight at 90 °C. After the traces of water were removed by azeotropic distillation of toluene at reduced pressure, the mixture was cooled down to 0 °C and NaH (0.96 g, 40 mmol) was added under nitrogen. After stirring for about 1 h at room temperature, propargyl bromide (1.52 mL, 20 mmol) in 30 mL of anhydrous toluene was added dropwise. The mixed solution was then stirred at room temperature for 24 h. After the insoluble salts were removed, the filtrate was evaporated. The obtained solid was dissolved in 100 mL DCM and washed with brine. DCM was then dried by anhydrous $MgSO_4$. After filtration, the solution was precipitated in cold diethyl ether. The solid was dried under vacuum at room temperature. Yield 7.6 g (75.4 %).

**Synthesis of Poly(ethylene glycol)-*β*-Cyclodextrin (PEG-*β*-CD)**

The PEG-*β*-CD was synthesized by click reaction between *Alkynyl*-PEG and *β*-CD-$N_3$. Typically, *β*-CD-$N_3$ (2.61 g, 2.25 mmol), *alkynyl*-PEG (3.1 g, 1.5 mmol), and PMDETA (0.313 mL, 1.5 mmol) dissolved in 10 mL DMF. The solution was degassed by three freeze-pump-thaw cycles and CuBr (216 mg, 1.5 mmol) was added under protection of nitrogen. The reaction flask was sealed under nitrogen and conducted at 45 °C for 2 days. Then the mixture was exposed to air, and evaporated, and then the residue was dissolved in water and extracted with $CHCl_3$ to remove unreacted *β*-CD-$N_3$. The organic phase was dried over anhydrous $MgSO_4$. The final product was obtained by precipitation in cold diethyl ether and dried under vacuum. Yield: 3.5 g (73 %).

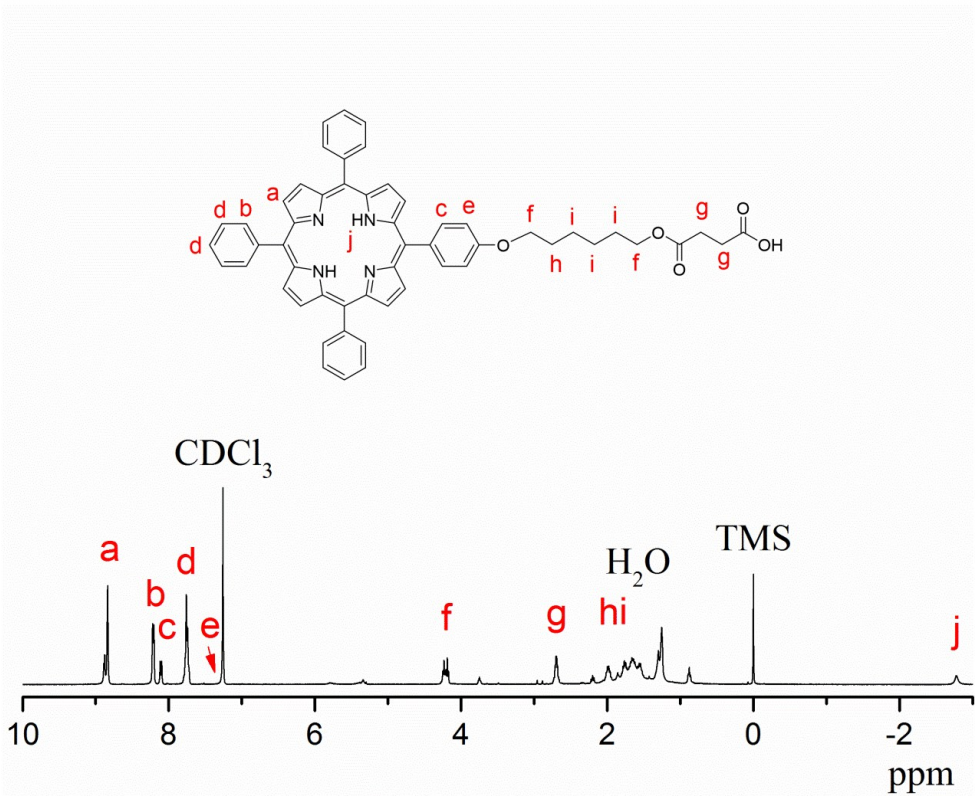



**Figure S1.** $^1$H-NMR of TPPC6-COOH in $CDCl_3$.

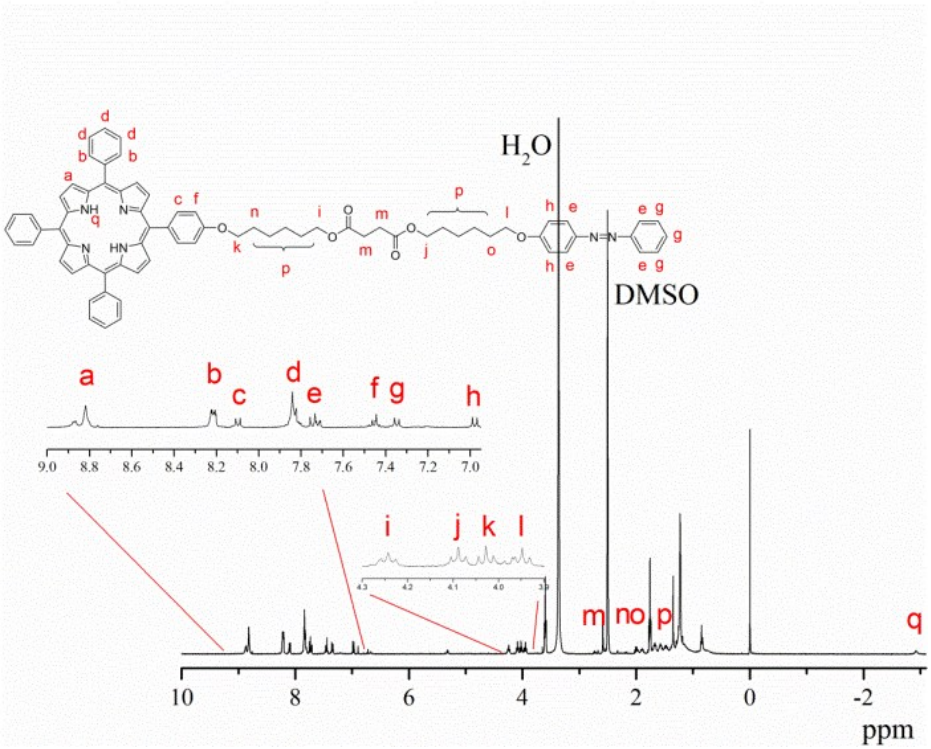



**Figure S2.** $^{1}$H NMR spectrum of TPP-Azo in $d_6$-DMSO.

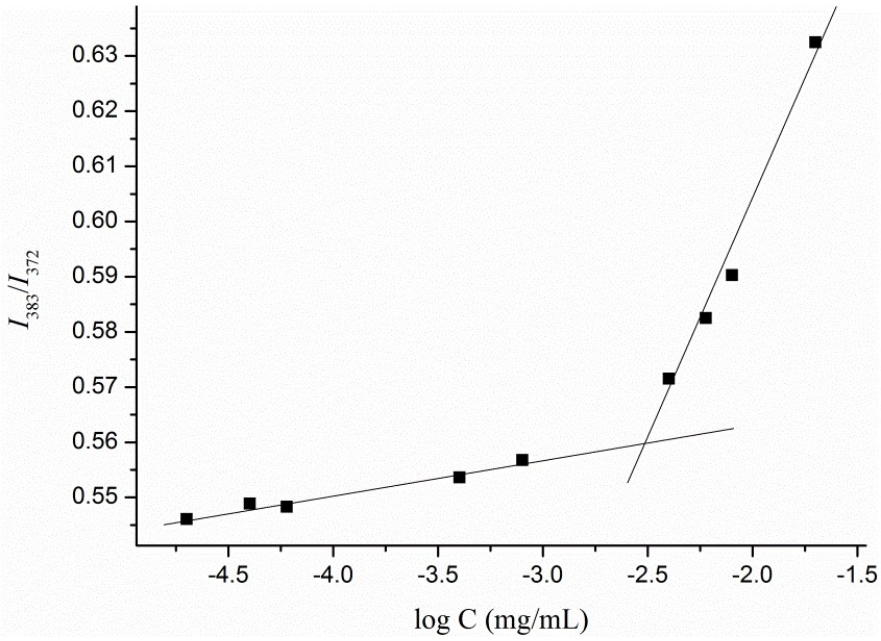



**Figure S3.** Plot of the $I_{383}/I_{372}$ ratio against log C of host-guest supramolecular amphiphiles in deionized water.

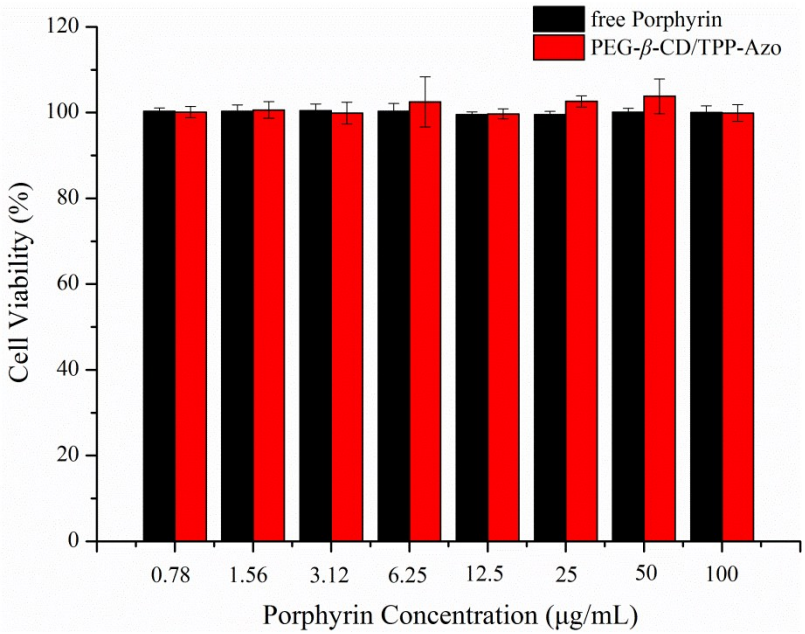



Figure S4**.** The dark cytotoxicity of MCF-7 cells treated with free porphyrin and PEG-*β*-CD/TPP-Azo micelles which determined by using MTT assay