Supporting Information

Redox-responsive Supramolecular Amphiphilies Constructed via Host-guest Interaction for Photodynamic Therapy

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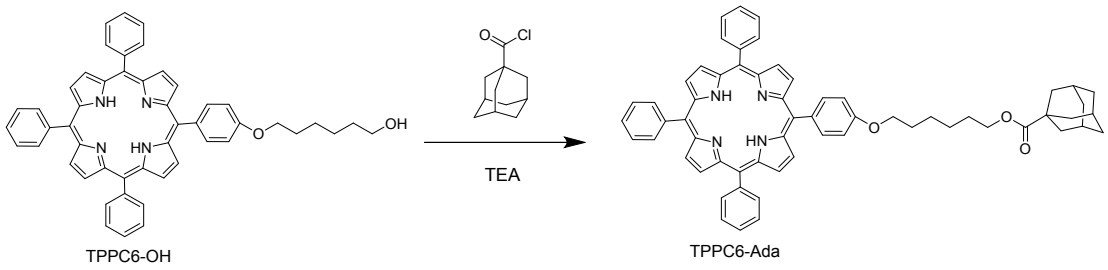

Scheme S1. The synthesis process of TPPC6-Ada.

Synthesis of Adamantane Terminal Porphyrin (TPPC6-Ada)

TPPC6-Ada was prepared by reaction between TPPC6-OH and 1-adamantanecarboxylic acid chloride. TPPC6-OH (0.1 g, 0.137 mmol) was dissolved in 15 mL dry THF, and TEA was added dropwise into the solution. 1-Adamantanecarboxylic acid chloride (0.272 g, 1.37 mmol) was dissolved in 10 mL dry THF, and added dropwise under ice-bath. Then the reaction was performed at room temperature for 4 h. The solution was washed with deionized water three times, extracted with dichloromethane, and dried with anhydrous $MgSO_4$. Then the solvent was removed by evaporation. The crude product was purified by column chromatography on silica, eluting with petroleum ether/ethyl acetate（5:1, v/v） as the eluent. Yield: 0.097 g (79.1%). ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 8.87 (m, 8H, *β-H*), 8.21 (m, 6H, 10, 15, 20-Ar-*o-H*), 8.11 (m, 2H, 5-Ar-*o-H*), 7.76 (m, 9H, 10, 15, 20-Ar-*m*- and *p-H*), 7.28 (m, 2H, 5-Ar-*m-H*), 4.26 (t, 2H, -O-CH_2-CH_2-), 3.75 (t, 2H, -CH_2-O-), 2.10 (s, 3H, -CH_2-C*H*(CH_2)-CH_2-), 1.98 (d, 6H, -C(CH_2)$_3$-CH(CH_2)$_2$-), 1.78 (q, 6H, -CH(CH_2)$_2$-CH_2-CH(CH_2)$_2$-), 1.66-1.49 (m, 6H, -CH_2-(CH_2)$_3$-CH_2-OH), -2.77 (s, 2H, -N*H*-). The ^{1}H NMR spectrum of TPPC6-Ada is shown in **Fig. S12.**

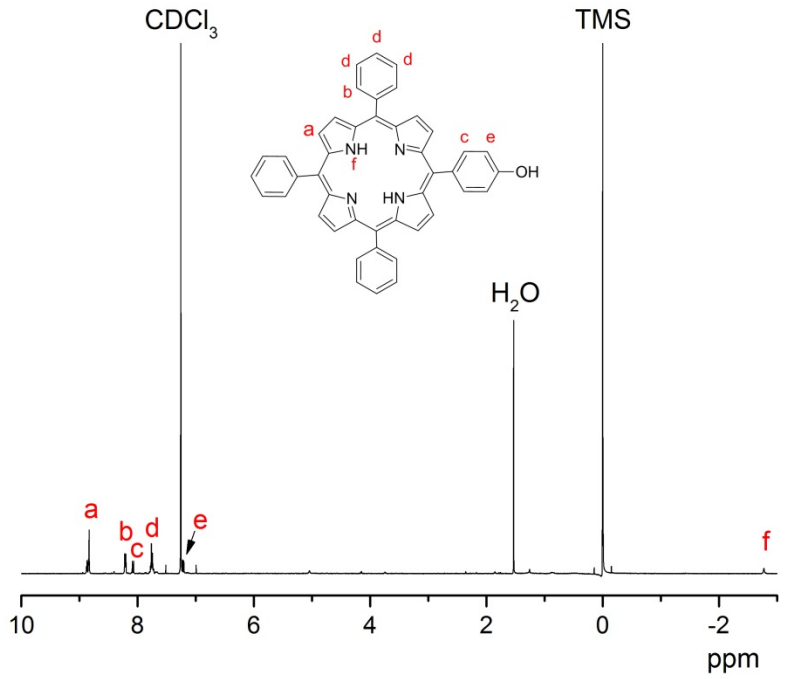

Fig. S1. ^{1}H NMR spectrum of TPP-OH in $CDCl_3$.

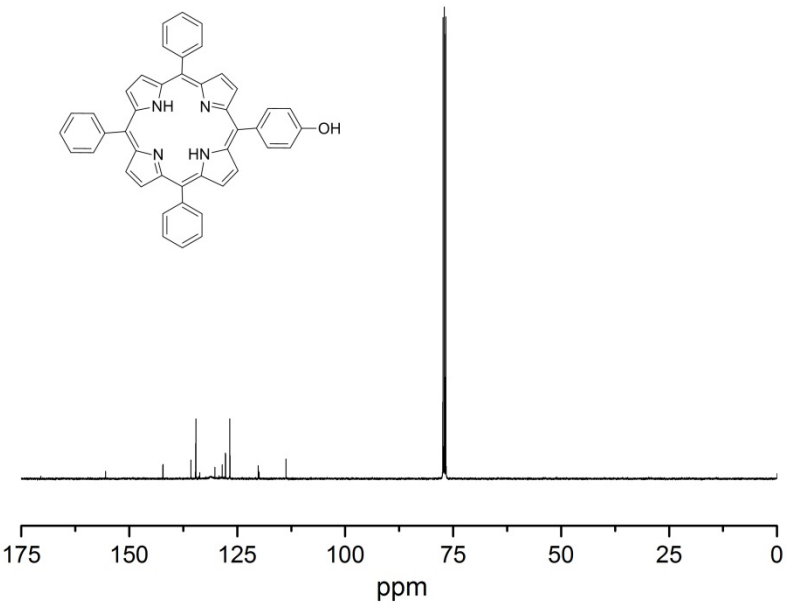

Fig. S2. ^{13}C NMR spectrum of TPP-OH in $CDCl_3$.

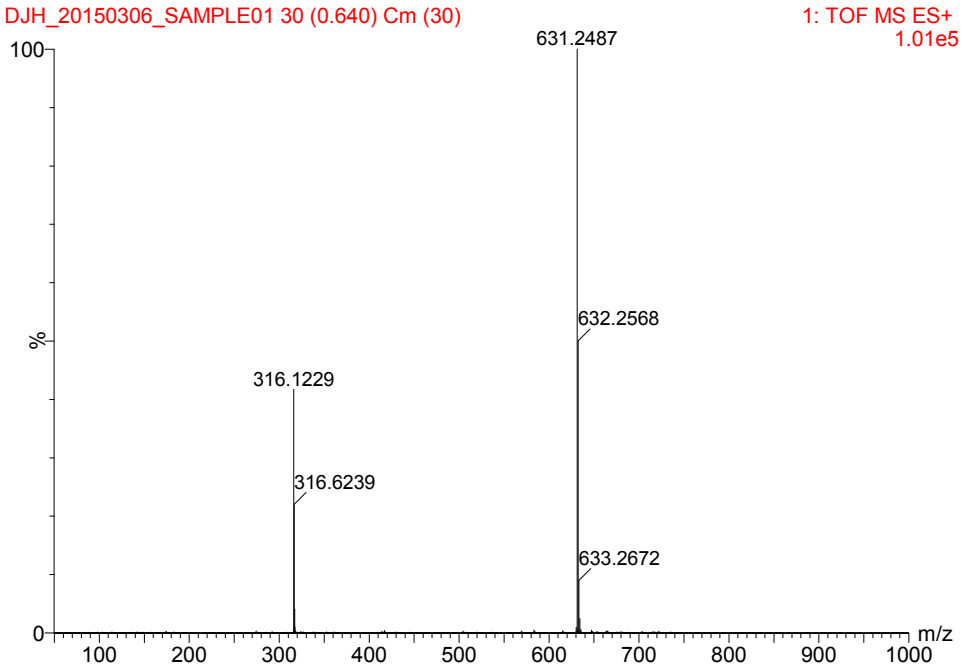

Fig. S3. TOF-MS spectrum of TPP-OH, calcd for $C_{44}H_{30}N_4O$: 630.20; found: 630.2487.

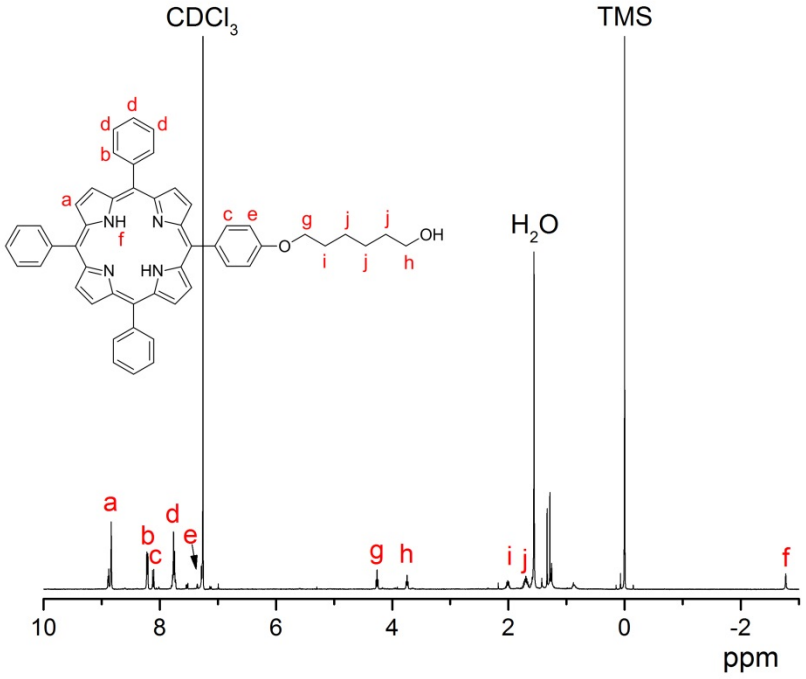

Fig. S4. ^{1}H NMR spectrum of TPPC6-OH in $CDCl_3$.

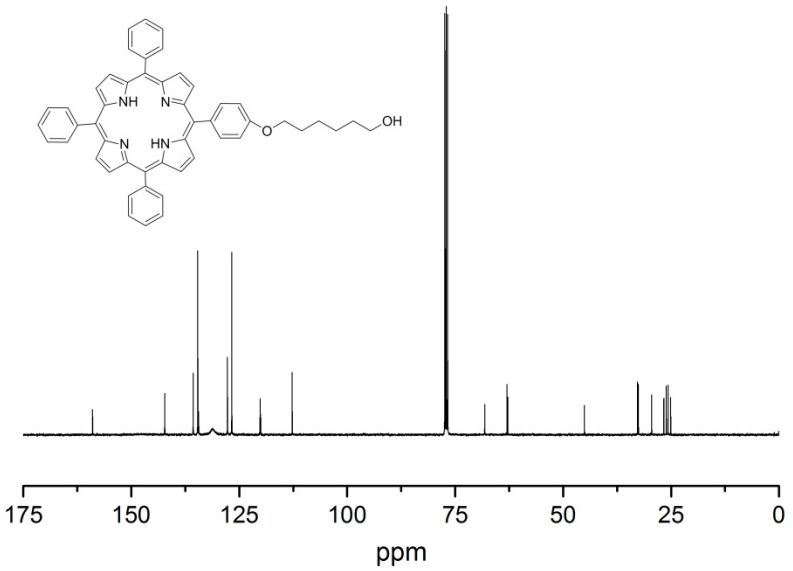

Fig. S5. ^{13}C NMR spectrum of TPPC6-OH in $CDCl_3$.

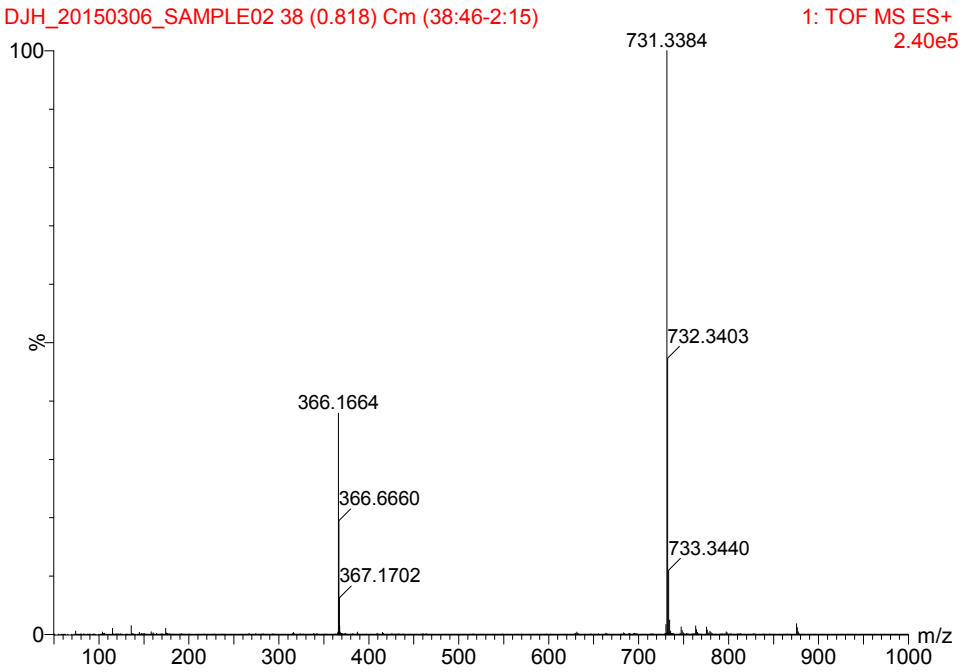

Fig. S6. TOF-MS spectrum of TPPC6-OH, calcd for $C_{50}H_{42}N_4O_2$: 730.35; found: 730.3384.

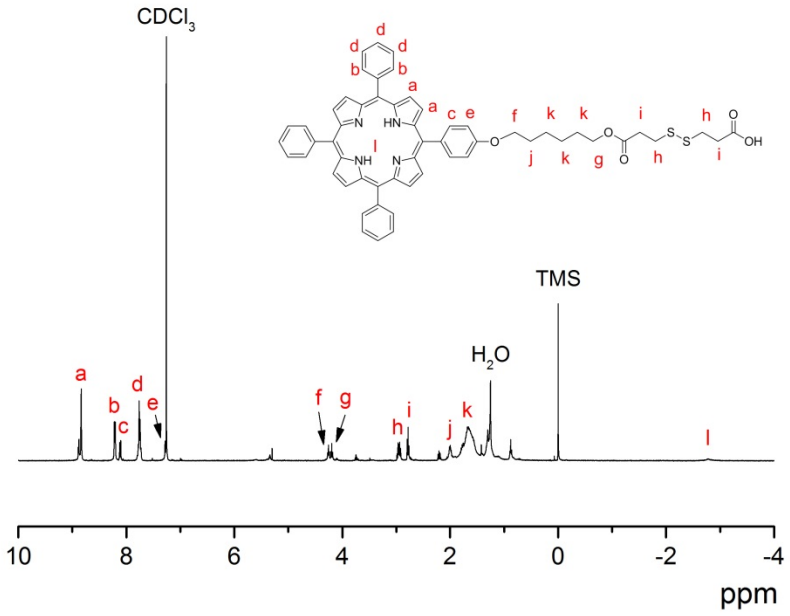

Fig. S7. ^{1}H NMR spectrum of TPPC6-SS-COOH in $CDCl_3$.

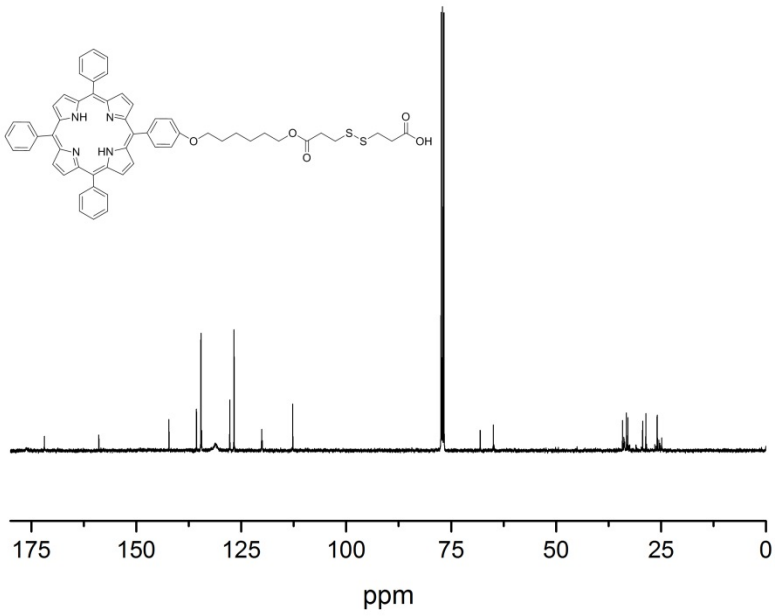

Fig. S8. ^{13}C NMR spectrum of TPPC6-SS-COOH in $CDCl_3$.

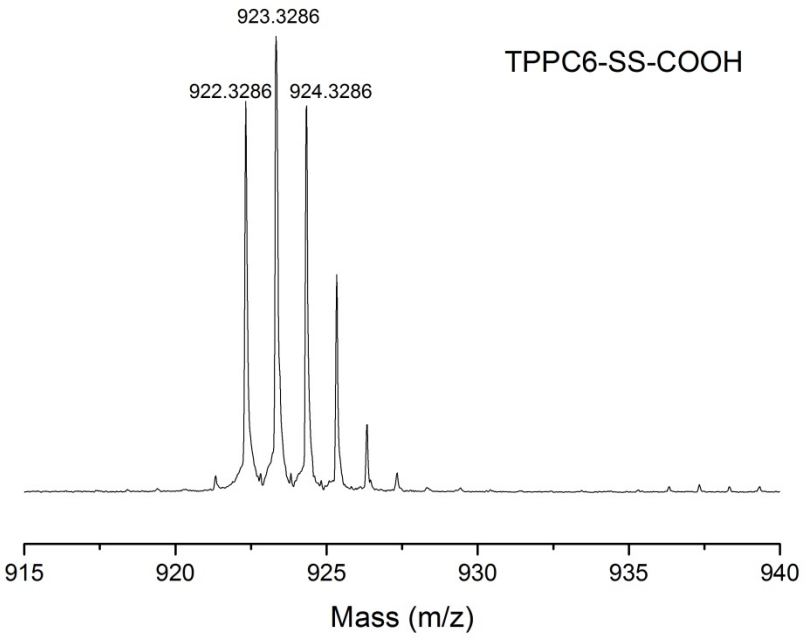

Fig. S9. MALDI-TOF-MS spectrum for TPPC6-SS-COOH, calcd for $C_{56}H_{50}N_5O_5S_2$: 923.32; found: 923.3286.

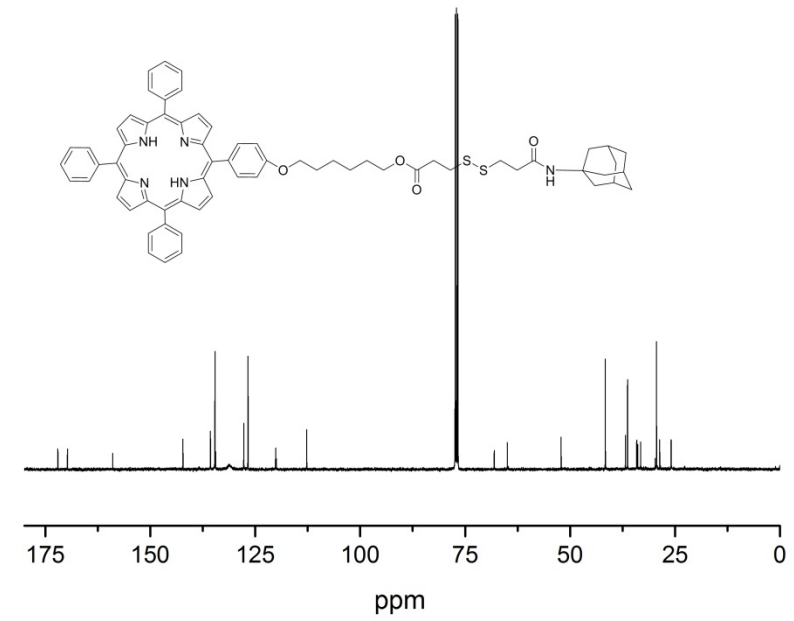

Fig. S10. ^{13}C NMR spectrum of TPPC6-SS-Ada in $CDCl_3$.

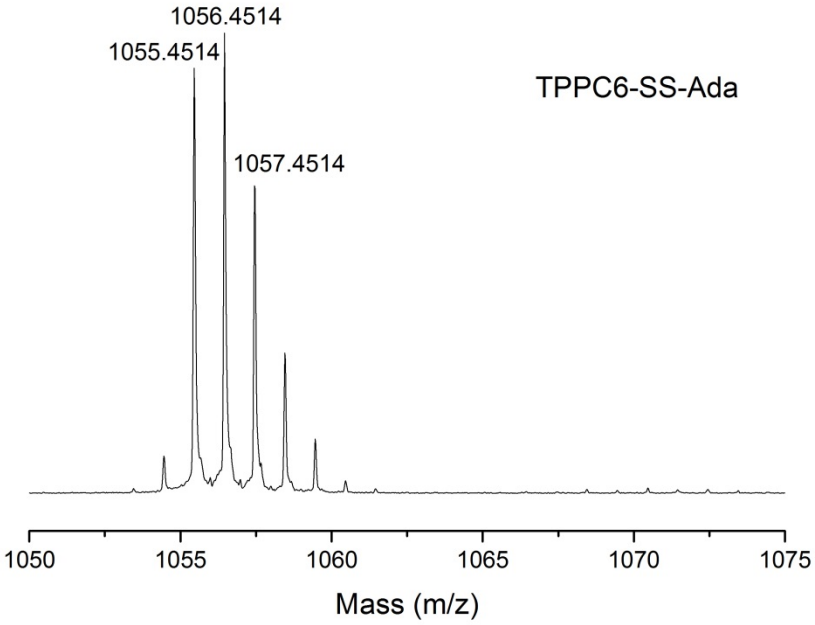

Fig. S11. MALDI-TOF-MS spectrum for TPPC6-SS-Ada, calcd for $C_{66}H_{65}N_5O_4S_2$: 1056.44; found: 1056.4514.

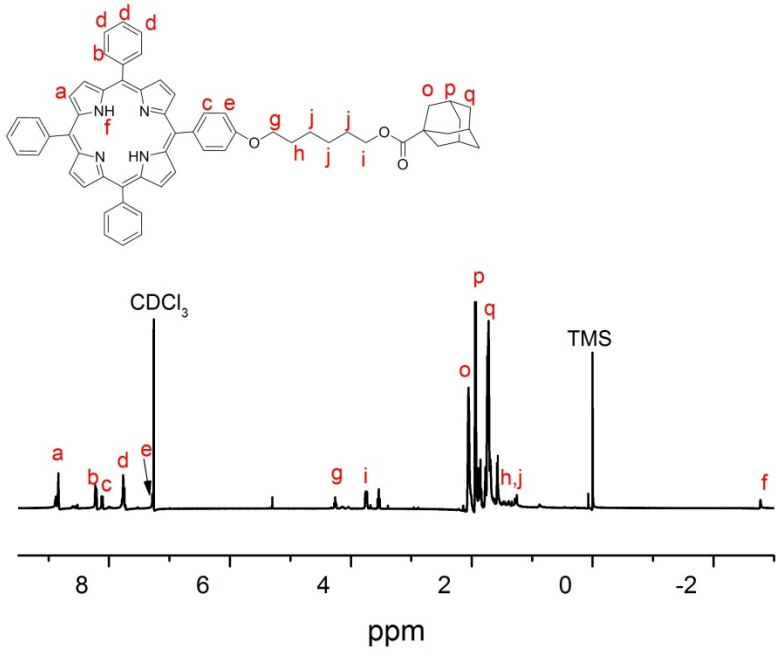

Fig. S12. ^{1}H NMR spectrum of TPPC6-Ada in $CDCl_3$.

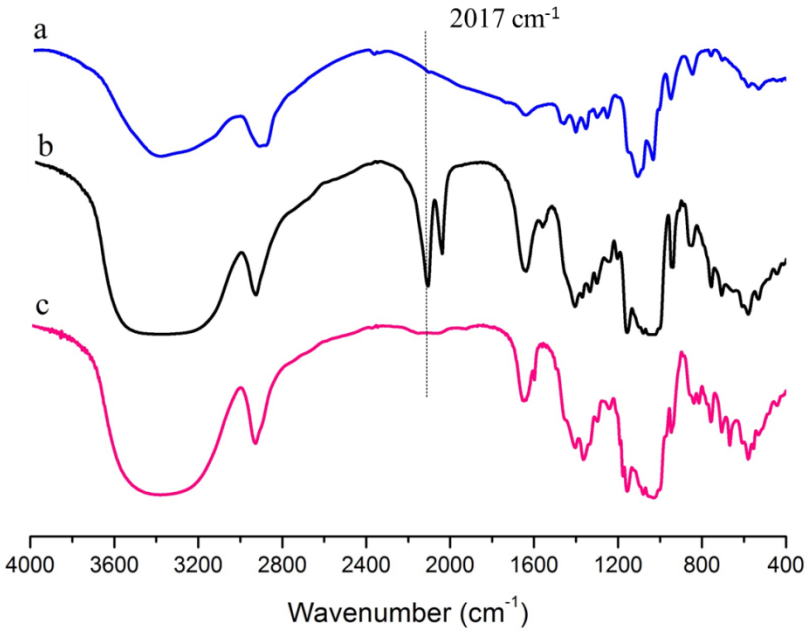

Fig. S13. FT-IR spectra of PEG-*β*-CD (a), *β*-CD-N_3 (b) and *β*-CD-OTs (c).

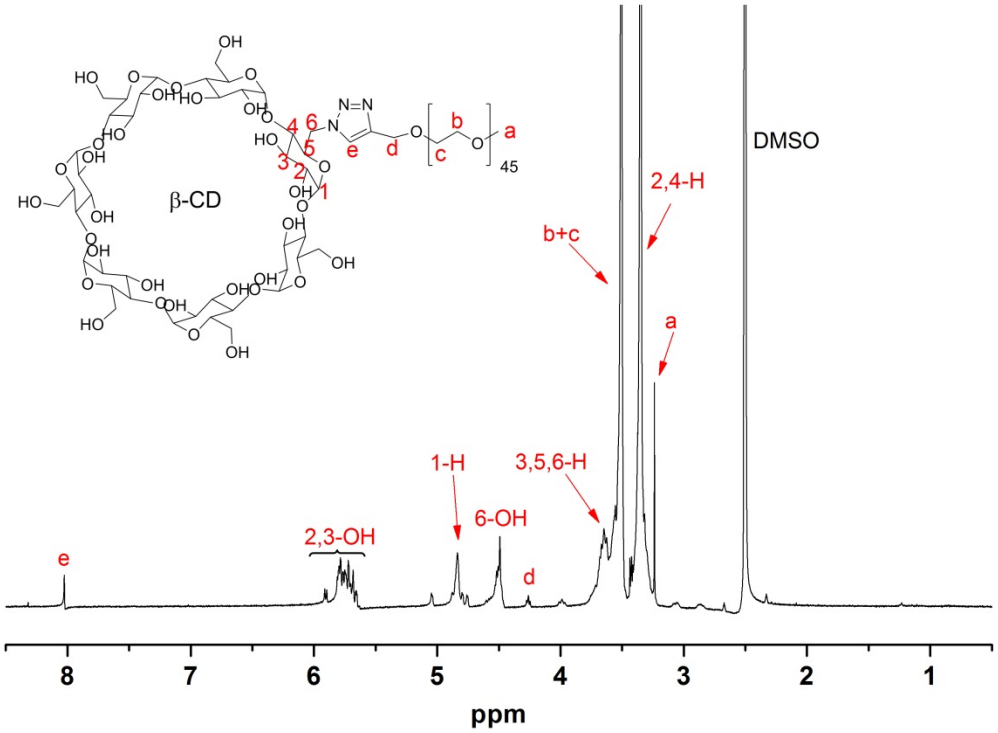

Fig. S14. ^{1}H NMR spectrum of PEG-*β*-CD in DMSO-d_6.

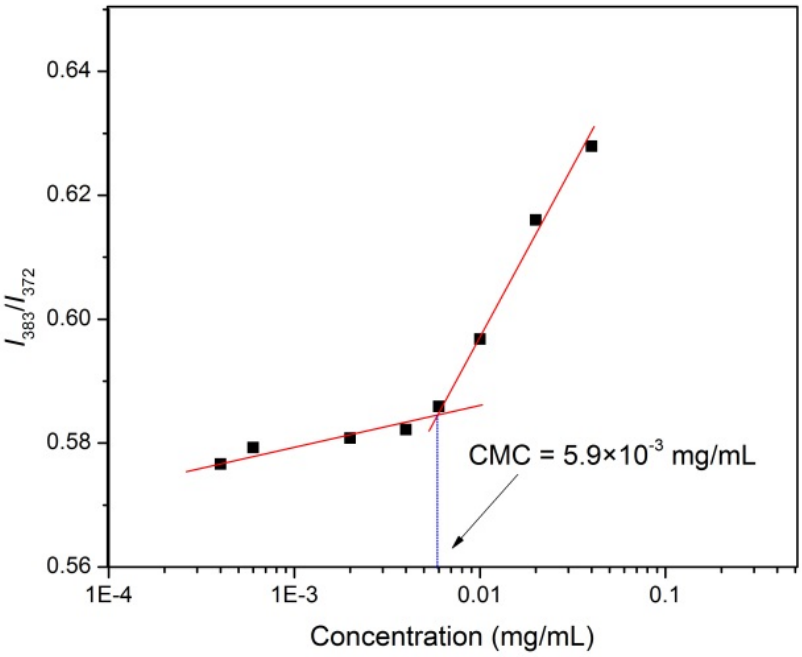

Fig. S15. Plot of the I_{383}/I_{372} ratio vs different concentrations of TPPC6-SS-Ada/PEG-β-CD micelles.

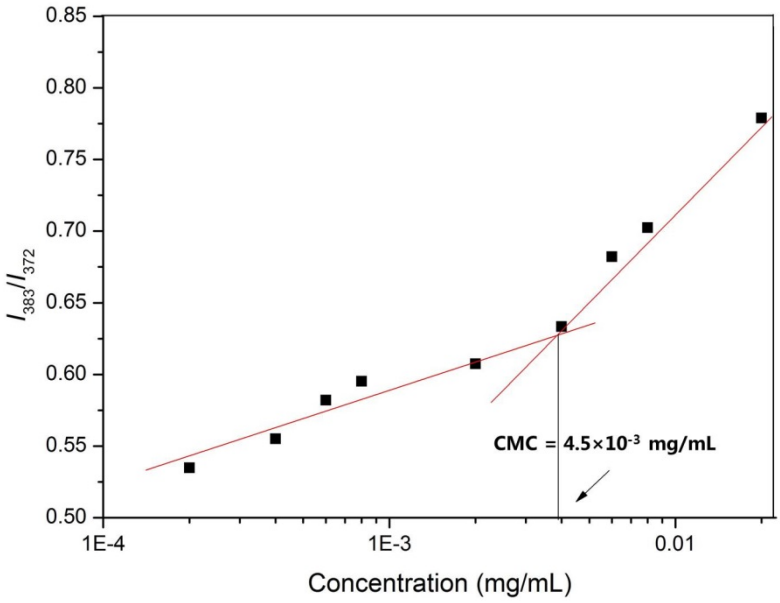

Fig. S16. Plot of the I_{383}/I_{372} ratio vs different concentrations of TPPC6-Ada/PEG-β-CD micelles.

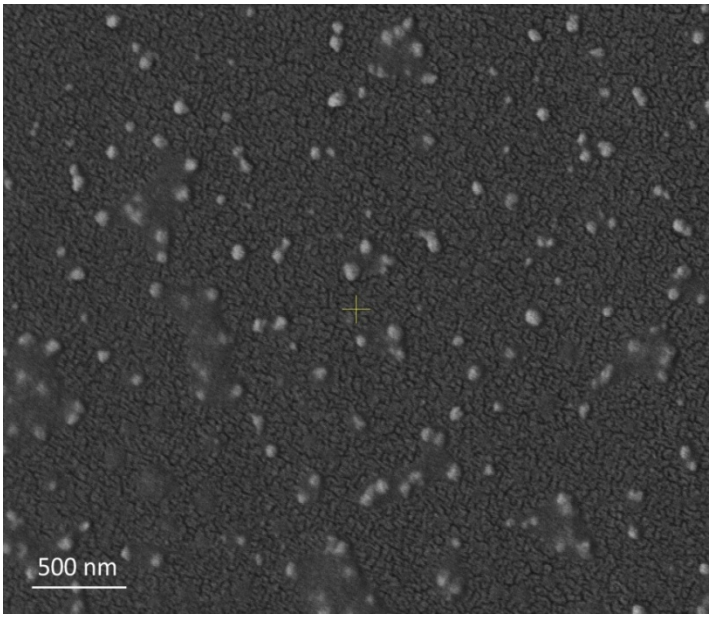

Fig. S17. SEM images of TPPC6-SS-Ada/PEG-*β*-CD.

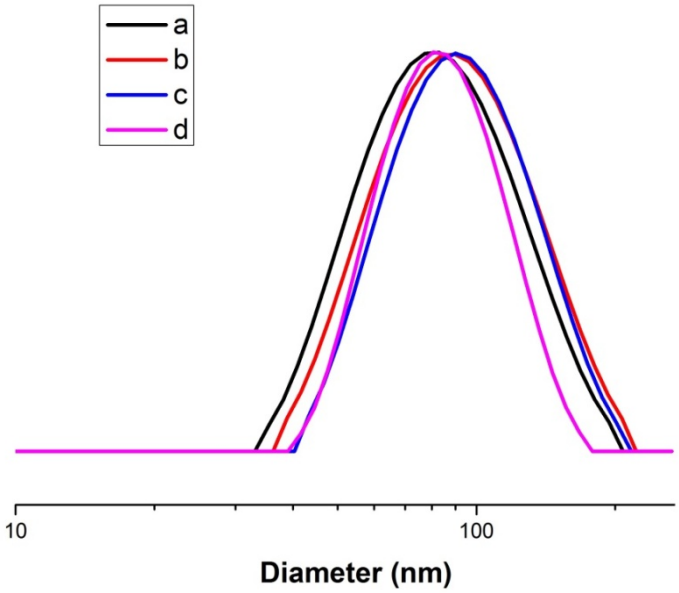

Fig. S18. Hydrodynamic diameter distribution of TPPC6-Ada/PEG-*β*-CD micelles (a, D_h = 86.4 nm, PDI = 0.112), TPPC6-Ada/PEG-*β*-CD micelles treated without GSH for 24 h (b, D_h = 92.5 nm, PDI = 0.140), and with 10 mM of GSH for 4 h (c, D_h = 94.0 nm, PDI = 0.162) and 24 h (d, D_h = 87.7 nm, PDI = 0.132).

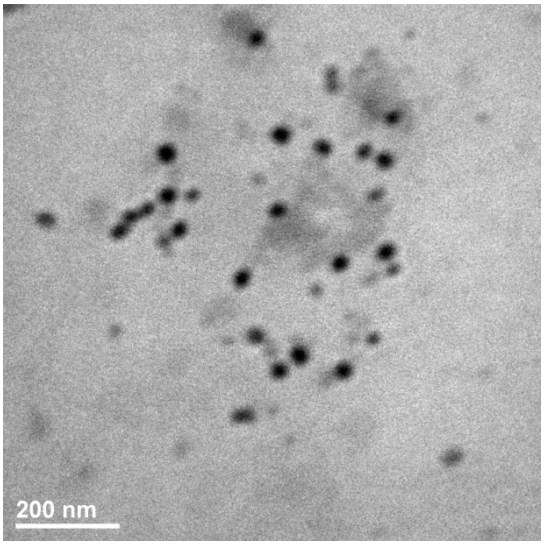

Fig. S19. TEM images of TPPC6-Ada/PEG-β-CD micelles treated with 10 mM of GSH for 24 h.

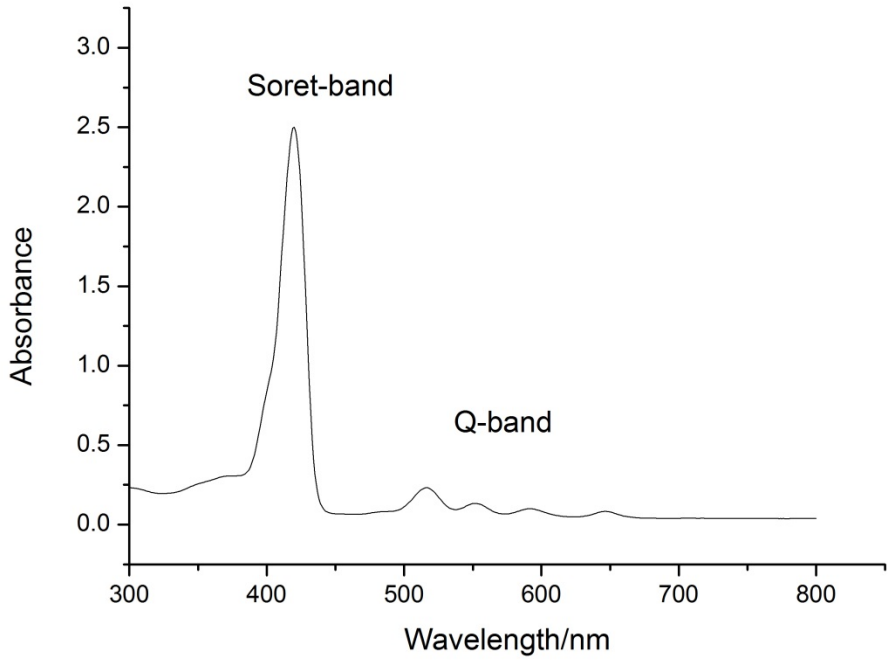

Fig. S20. The UV-Vis absorption spectrum of TPPC6-SS-Ada in $CHCl_3$.