Supporting Information

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

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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$_3$), $\delta$ ppm: 8.87 (m, 8H, $\beta$-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, -C$_2$H$_4$-O-), 2.10 (s, 3H, -CH$_2$-CH(CH$_3$)$_2$-CH$_2$-), 1.98 (d, 6H, -C(CH$_3$)$_3$-CH(CH$_2$)$_2$-), 1.78 (q, 6H, -CH(CH$_2$)$_2$-CH$_2$-CH(CH$_3$)$_2$-), 1.66-1.49 (m, 6H, -CH$_2$-(CH$_2$)$_3$-CH$_2$-OH), -2.77 (s, 2H, -NH-). 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$_4$O$_2$: 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$_{5}$O$_{5}$S$_{2}$: 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$_{5}$O$_{4}$S$_{2}$: 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\textsubscript{3} (b) and β-CD-OTs (c).

Fig. S14. ¹H NMR spectrum of PEG-β-CD in DMSO-\textit{d}_6.
**Fig. S15.** Plot of the $I_{383}/I_{372}$ ratio vs different concentrations of TPPC6-SS-Ada/PEG-$\beta$-CD micelles.

**Fig. S16.** Plot of the $I_{383}/I_{372}$ ratio vs different concentrations of TPPC6-Ada/PEG-$\beta$-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 CHCl₃.