Supporting Information

Photodynamic Therapy of Oligoethylene Glycol Dendronized Reduction-Sensitive Porphyrin

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Synthesis of G1-Et coupled Disulfide Porphyrin (TPP-S-S-G1)

The synthesis of TPP-S-S-G1 was similar to that of TPP-S-S-G2. Yield: 0.97 g (67.9 %). ^{1}H NMR (400 MHz, $CDCl_3$), δ ppm: 8.89 (m, 8H, β-H), 8.24 (m, 6H, 10,15,20-Ar-*o*-H), 8.14 (m, 2H, 5-Ar-*o*-H), 7.78 (m, 9H, 10,15,20-Ar-*m*- and *p*-H), 7.30 (m, 2H, 5-Ar-*m*-H), 6.60 (s, 2H, C*H*), 5.04 (s, 2H, -O-CH_2-CH-), 4.28 (t, 2H, -O-CH_2-CH_2-CH_2-), 4.21 (-CH_2-CH_2-O-), 4.16 (m, 6H, CH-O-CH_2-CH_2-O-), 3.87-3.49 (m, 36H, -O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_3), 2.98 (t, 4H, -CH_2-CH_2-S- and -S-CH_2-CH_2-), 2.81 (q, 4H, -CO-CH_2-CH_2- and -CH_2-CH_2-CO-), 2.02 (m, 2H, -O-CH_2-CH_2-CH_2-), 1.84-1.64 (m, 6H, -O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-O-), 1.22 (t, 9H, -CH_2-CH_3), -2.75 (s, 2H, -N*H*-). MALDI-TOF-MS spectrum for TPP-S-S-G1, calcd for $C_{174}H_{254}N_4O_{53}S_2$, 1 541.92; found 1 541.56.

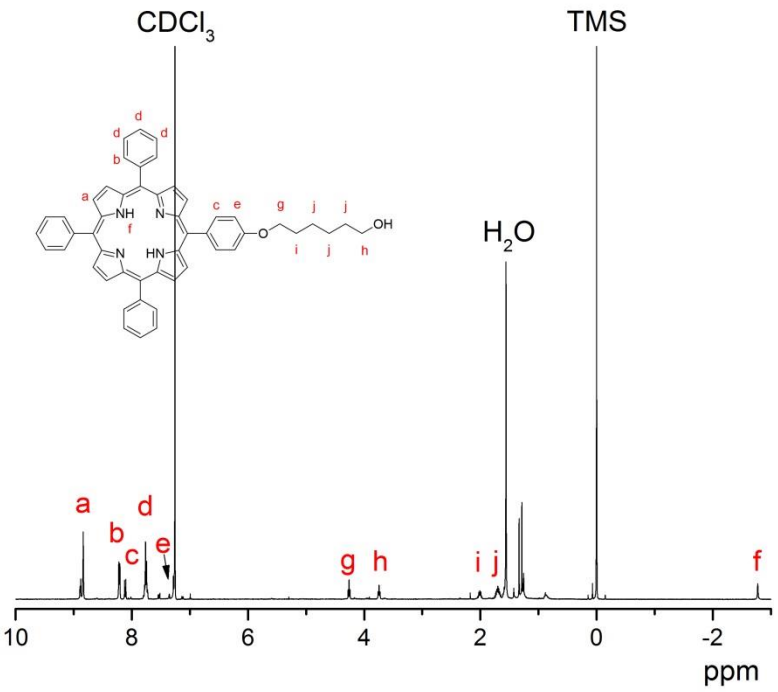

Fig. S1. ^{1}H-NMR spectrum of TPPC6-OH in $CDCl_3$.

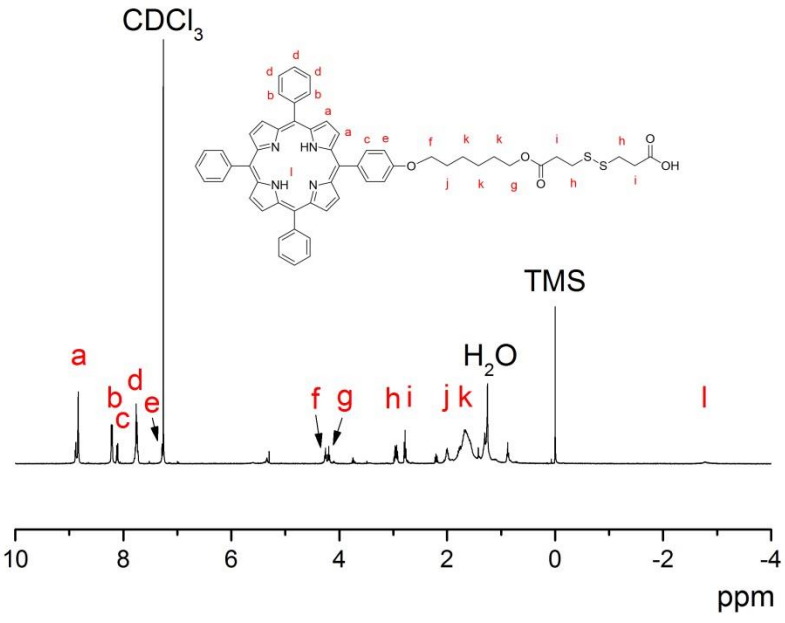

Fig. S2. ^{1}H-NMR spectrum of TPP-S-S-COOH in $CDCl_3$.

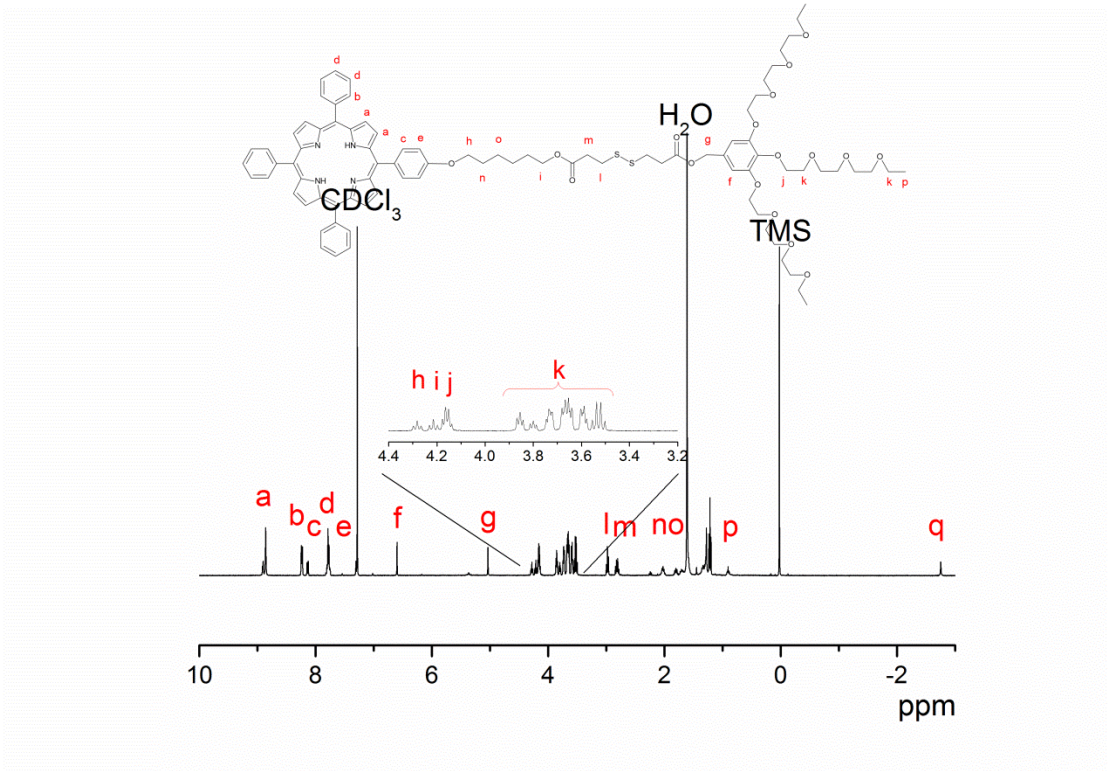

Fig. S3. ^{1}H-NMR spectrum of TPP-S-S-G1 in $CDCl_3$.

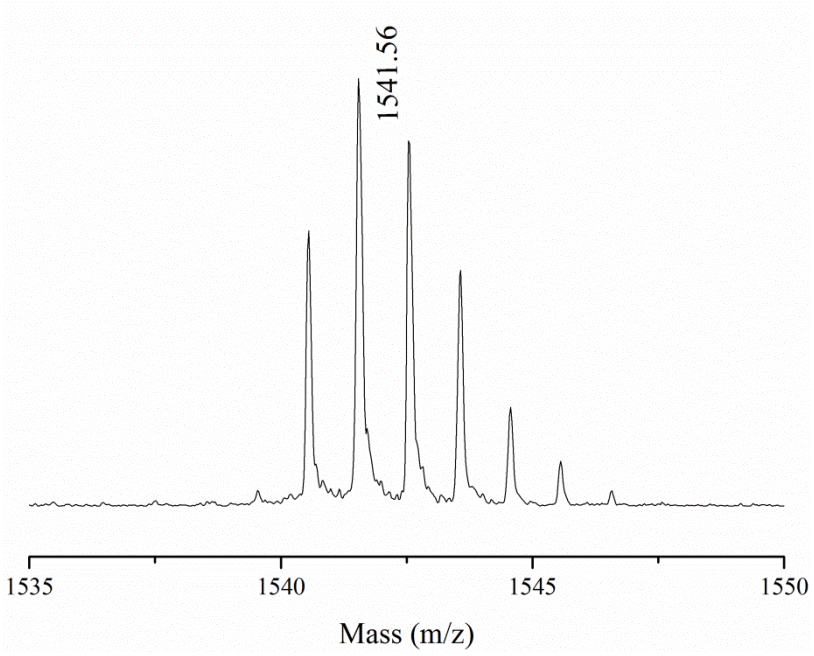

Fig. S4. MALDI-TOF-MS spectrum for TPP-S-S-G1, calcd for $C_{174}H_{254}N_4O_{53}S_2$,1541.92; found 1541.56.

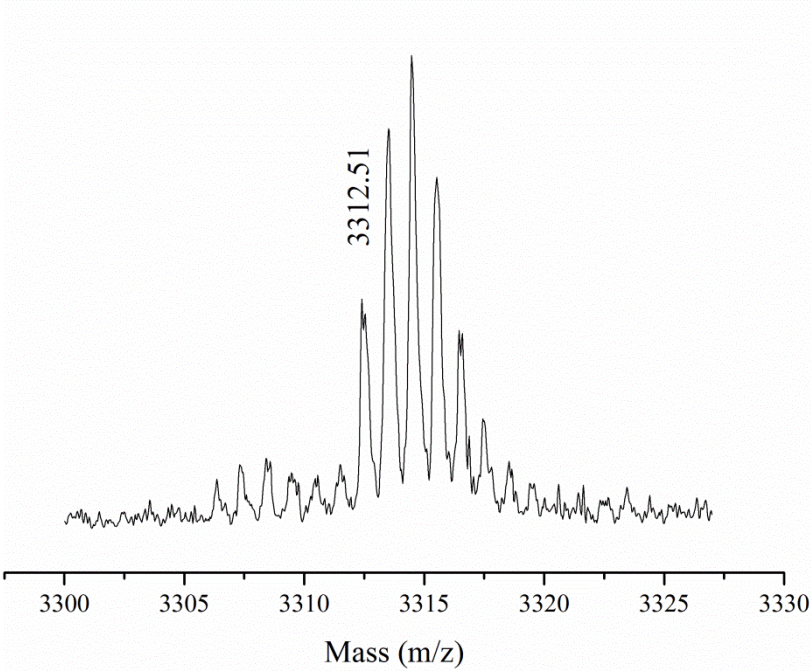

Fig. S5. MALDI-TOF-MS spectrum for TPP-S-S-G2, calcd for $C_{174}H_{254}N_4O_{53}S_2$,3314.04; found 3312.51.

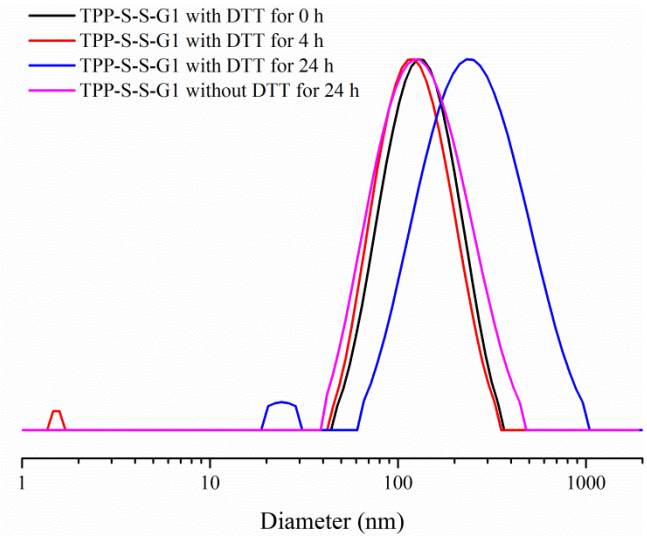

Fig. S6. Size distribution of TPP-S-S-G1 micelles determined by DLS. Blank line: DTT for 0 h, red line: DTT for 4 h, green line: DTT for 24 h, pink line: without DTT for 24 h.

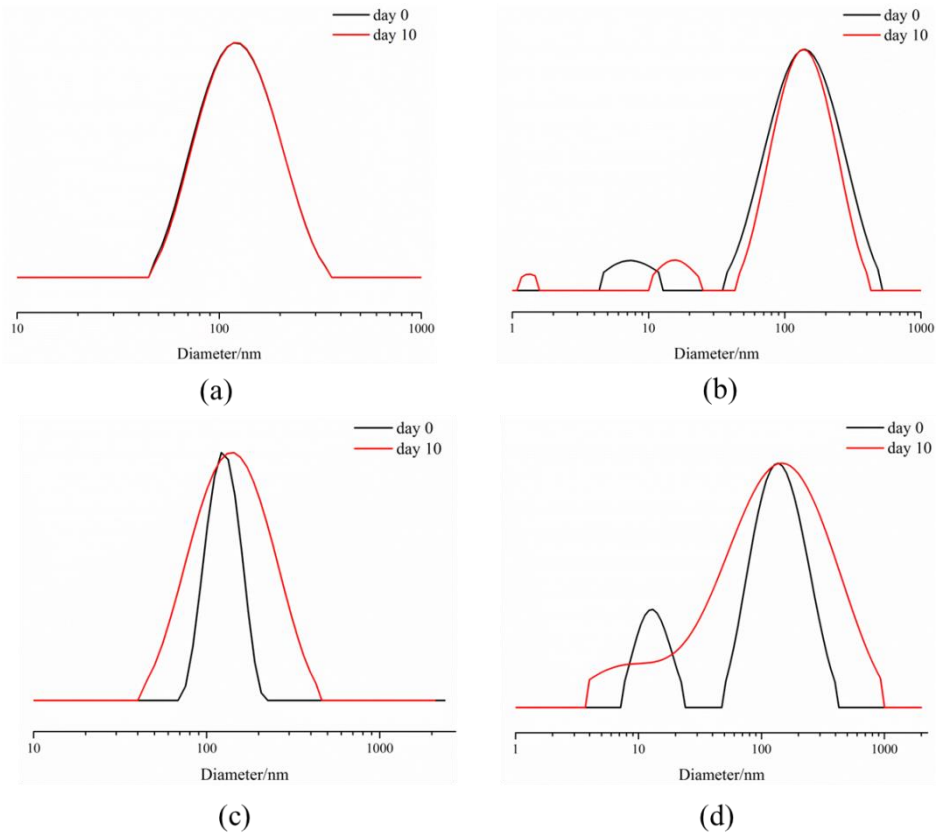

Fig.S7. Size distribution of TPP-S-S-Gn micelles in PBS and DMEM at 37 ℃ with different days. (a) TPP-S-S-G1 in PBS, (b) TPP-S-S-G1 in DMEM, (c) TPP-S-S-G2 in PBS, (d) TPP-S-S-G2 in DMEM.

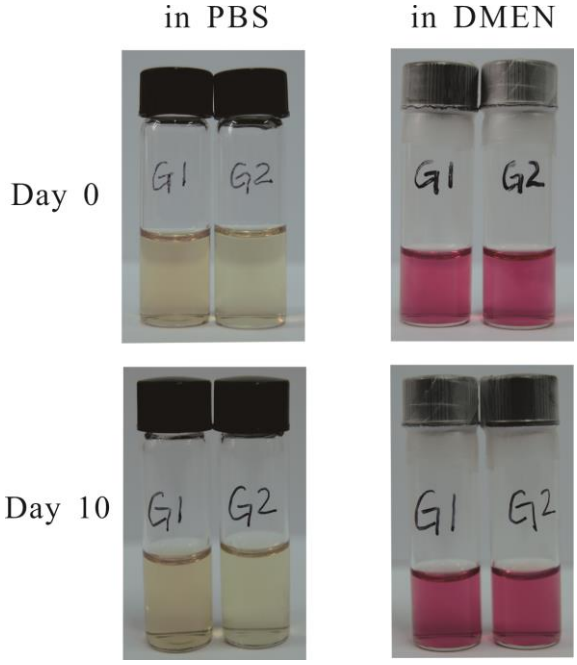

Fig. S8. Photographs of TPP-S-S-Gn micelles in PBS and DMEM at 37 ℃ with different days.

Table S1. DLS results and zeta potential of TPP-S-S-Gn micelles in PBS and DMEM

	Day 0			Day 10		
	D_h (nm)	PDI	Zeta (mV)	D_h (nm)	PDI	Zeta (mV)
TPP-S-S-G1+PBS	112.8	0.144	-34.42	112.3	0.133	-13.26
TPP-S-S-G1+DMEM	101.8	0.307	-12.76	103.3	0.280	-2.19
TPP-S-S-G2+PBS	128.9	0.141	-29.34	132.7	0.197	-16.81
TPP-S-S-G2+DMEM	82.0	0.333	-12.25	87.4	0.371	-3.97

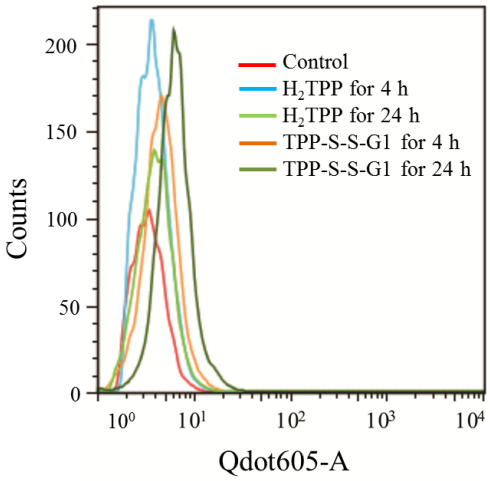

Fig. S9. The cellular uptake of free poprhyrin and TPP-S-S-G1 micelles at different time, red line: control, blue line: free porphyrin for 4h, aqua line: free porphyrin for 24 h, orange line: TPP-S-S-G1 for 4 h, black green line: TPP-S-S-G1 for 24 h.

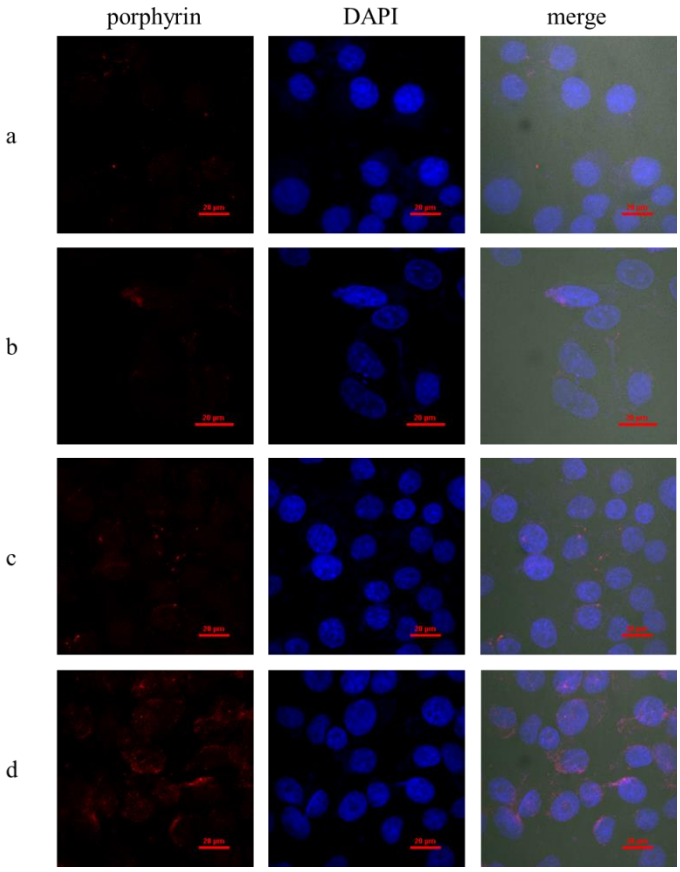

Fig. S10. Confocal laser scanning microscopy images of cellular internalization of free porphyrin and TPP-S-S-G1 micelles with MCF-7 cells (a) free porphyrin for 4 h, (b) free porphyrin for 24 h, (c) TPP-S-S-G1 for 4 h, (d) TPP-S-S-G1 for 24 h. The images from left to right were porphyrin fluorescence, nuclear staining with DAPI and overlays of images. Scale bar: 20 μm.