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Supporting Information

Redox-responsive Supramolecular Amphiphilies Based on Pillar[5]arene for Enhanced Photodynamic Therapy

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1. Synthesis of PEG-P[5]A

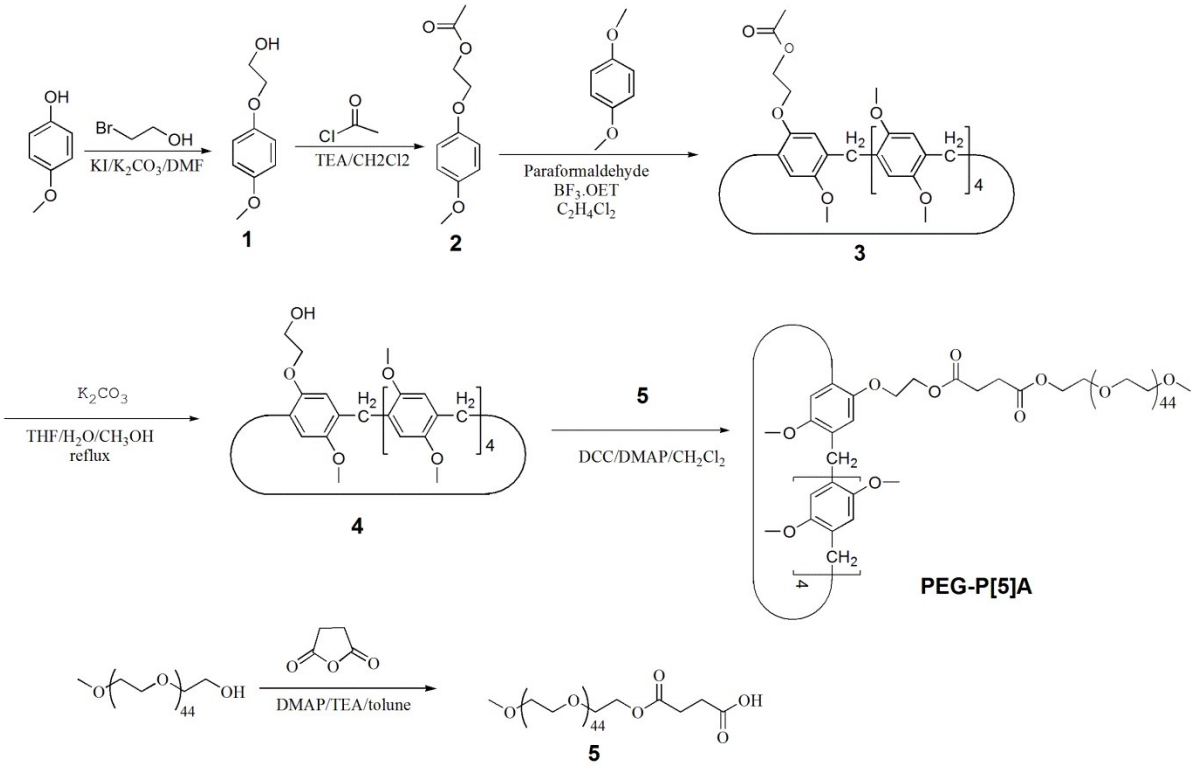
Poly(ethylene glycol)-functionalized pillar[5]arene (PEG-P[5]A) was prepared according to our previous work[1] and the synthetic procedure was shown in **Scheme. S1**.

2. Synthesis of TPPC6-SS-COOH

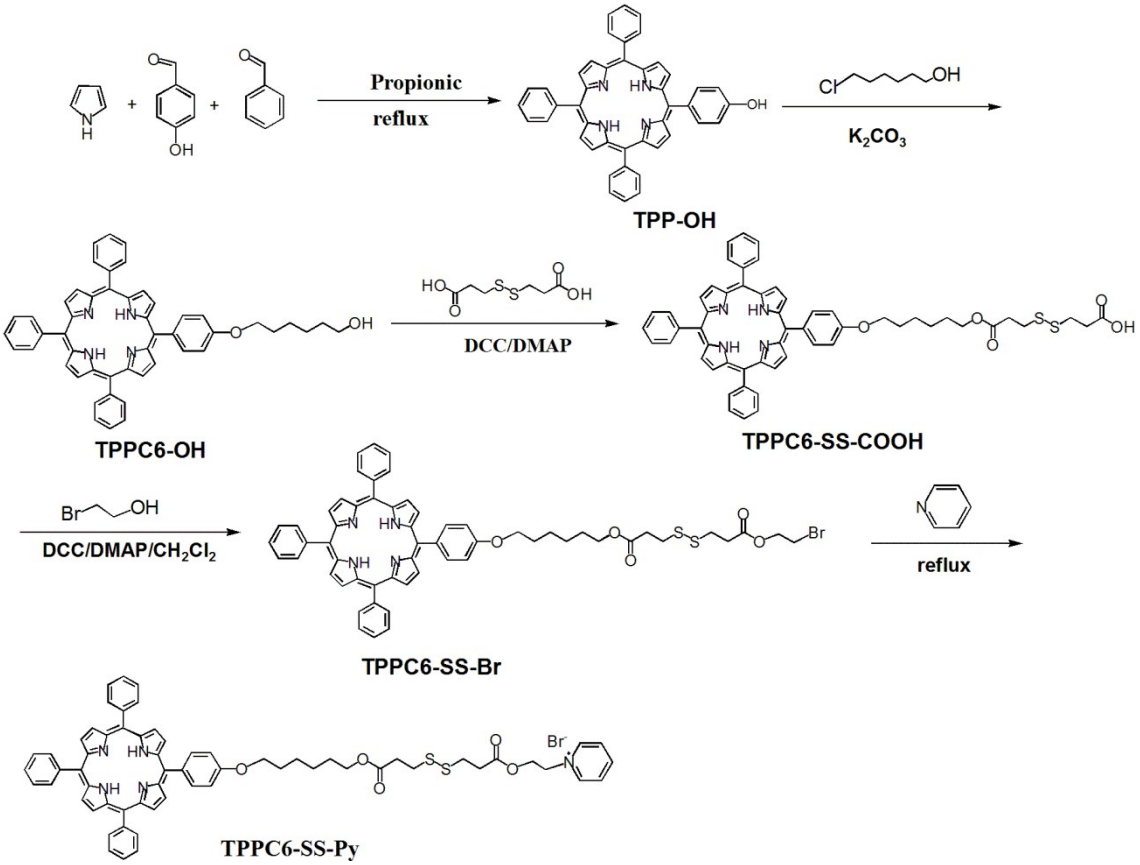
The carboxyl-termined porphyrin (TPPC6-SS-COOH) was prepared according to our previous work[2] and TPPC6-SS-COOH was further used to synthesize pyridinium-terminated porphyrin derivative bearing a disulfide bond (TPPC6-SS-Py), as shown in **Scheme. S2**.

3. Synthesis of the Model Guest Compound (G_M)

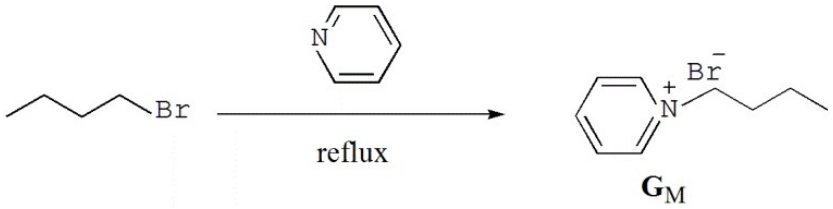
1-Bromobutane (0.685 g, 5 mmol) and excessive amount of pyridine (0.5 mL, 6 mmol) were refluxed in acetone at 70 ℃ for 1 day. After the solvent was removed under vacuum, the product $\mathbf{G_M}$, *N*-butyl pyridinium bromide was obtained as a yellow solid (0.98 g, 90%). ^{1}H NMR (400 MHz, D_2O) δ (ppm): 9.47 (d, 2H, pyridinium-H), 8.69 (t, 1H, pyridinium-H), 8.18 (m, 2H, pyridinium-H), 5.03 (t, 2H, N-CH_2-), 2.02 (m, 2H, N-CH_2-CH_2-), 1.51 (m, 2H, N-$(CH_2)_2$-CH_2-), 1.01 (t, 3H, -CH_3) (**Fig. S15**).



Scheme. S1 Synthetic route of **PEG-P[5]A**



Scheme. S2 Synthetic route of **TPPC6-SS-Py**



Scheme. S3 Synthetic route of $\mathbf{G_M}$

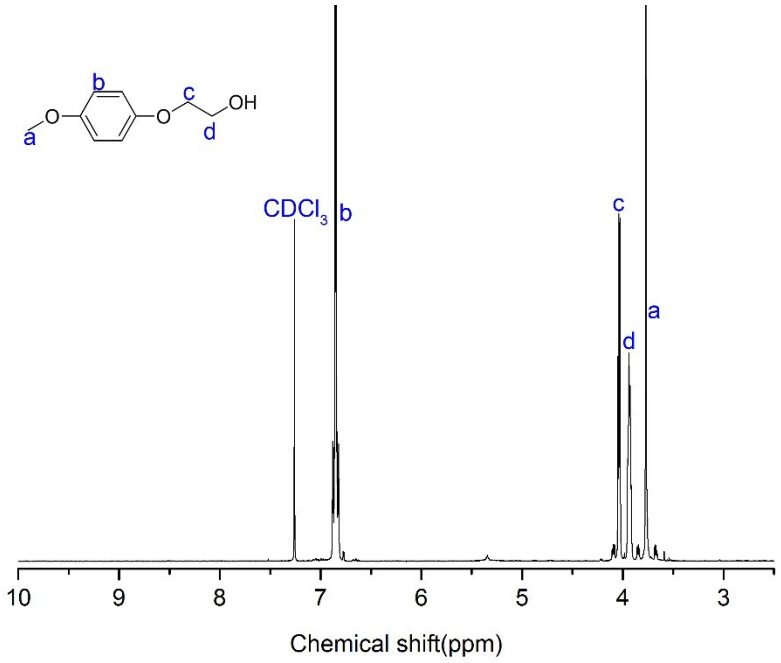


Fig. S1 ^{1}H NMR spectrum of **1**

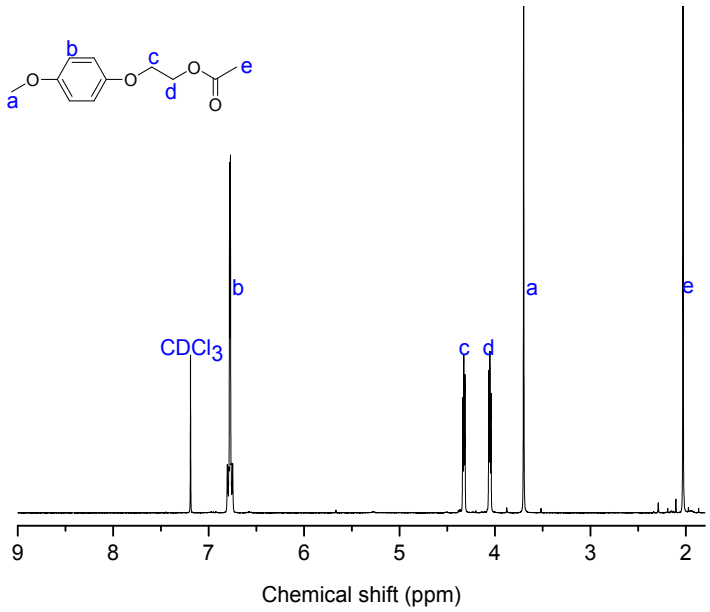


Fig. S2 ^{1}H NMR spectrum of **2**

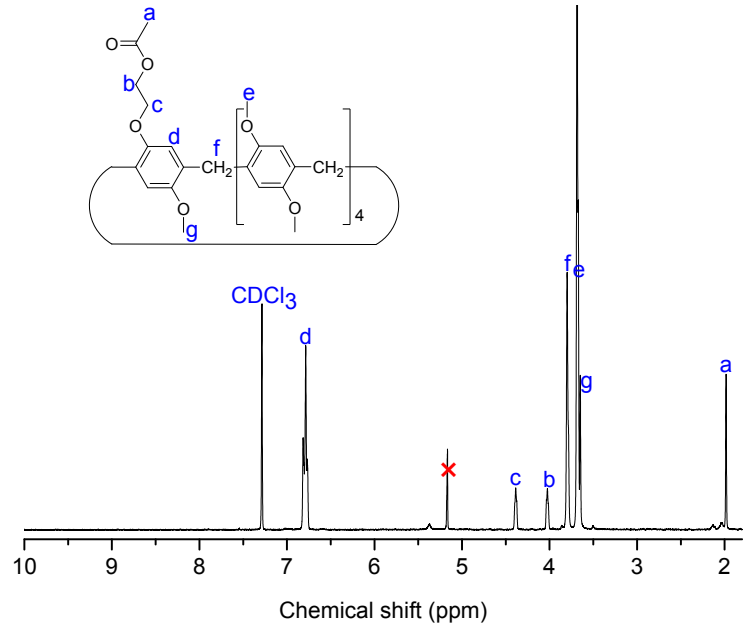


Fig. S3 ^{1}H NMR spectrum of **3**

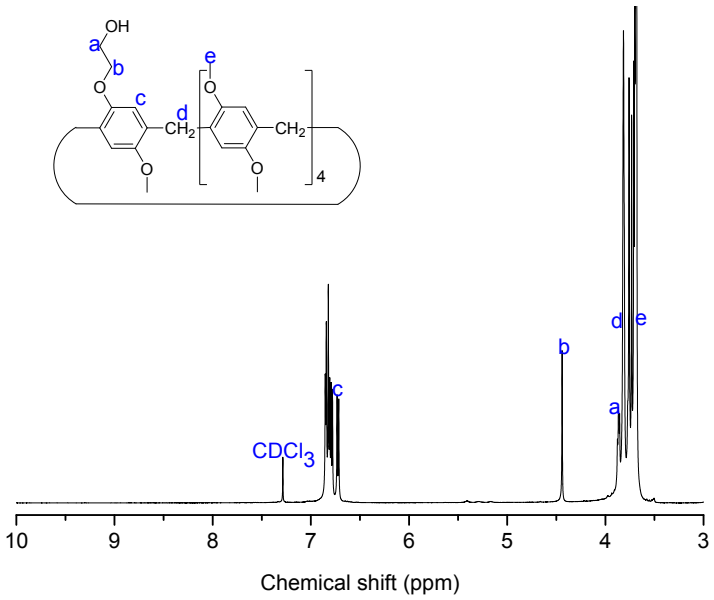


Fig. S4 ^{1}H NMR spectrum of **4**

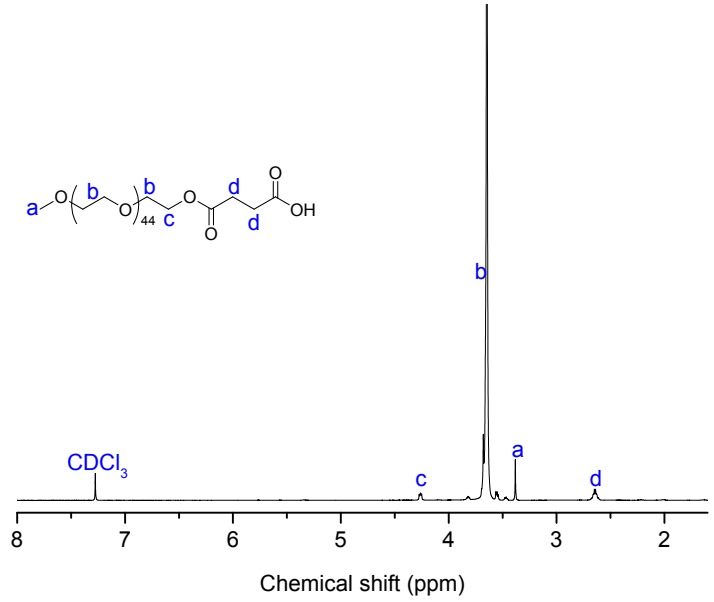


Fig. S5 ^{1}H NMR spectrum of **5**

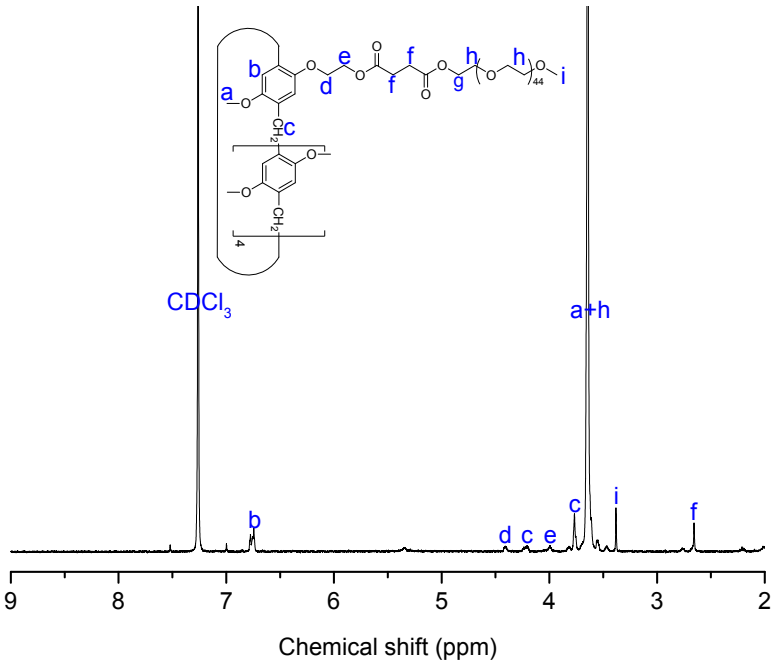


Fig. S6 ^{1}H NMR spectrum of **PEG-P[5]A**

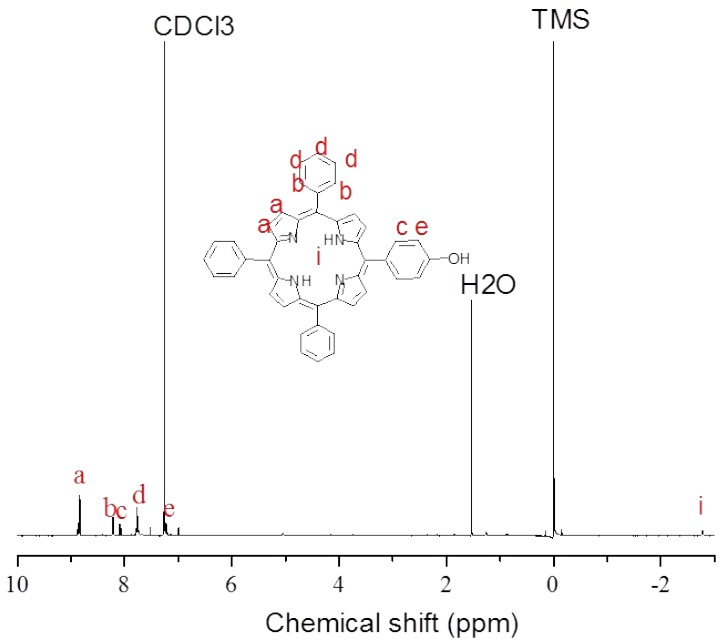


Fig. S7 ^{1}H NMR spectrum of **TPP-OH**

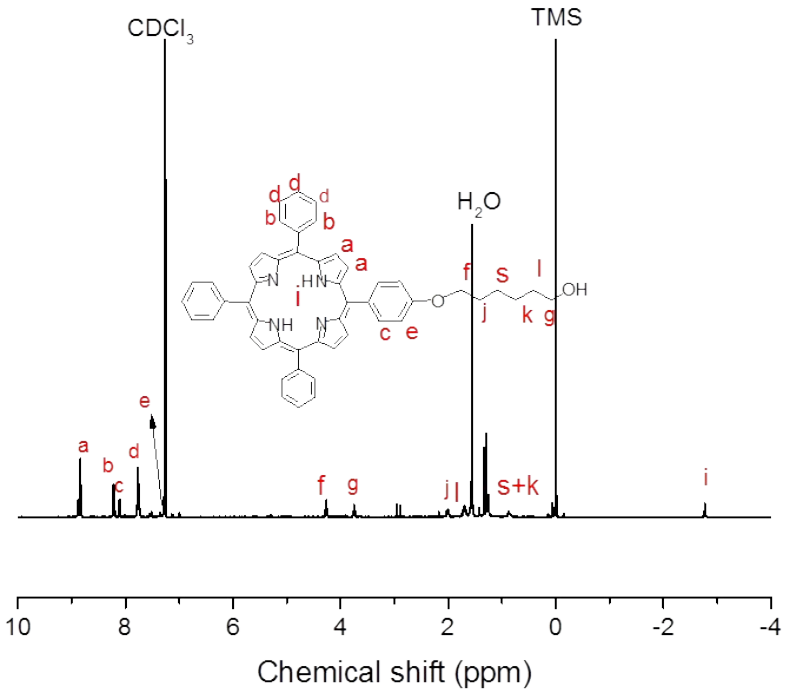


Fig. S8 ^{1}H NMR spectrum of **TPPC6-OH**

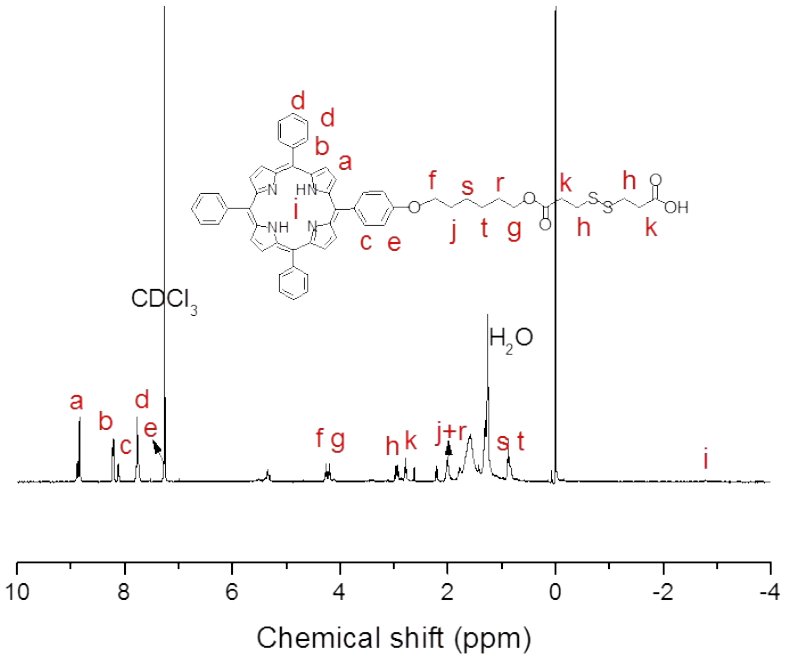


Fig. S9 ^{1}H NMR spectrum of **TPPC6-SS-COOH**

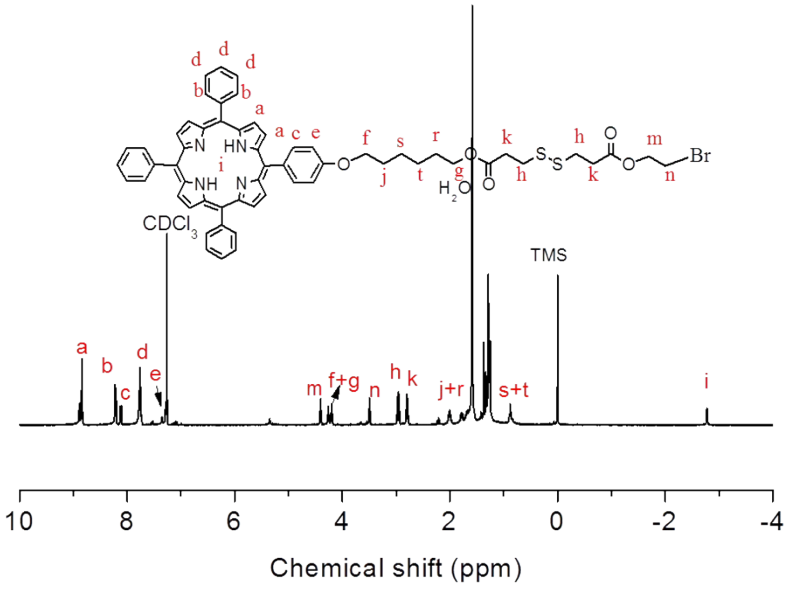


Fig. S10 ^{1}H NMR spectrum of **TPPC6-SS-Br**

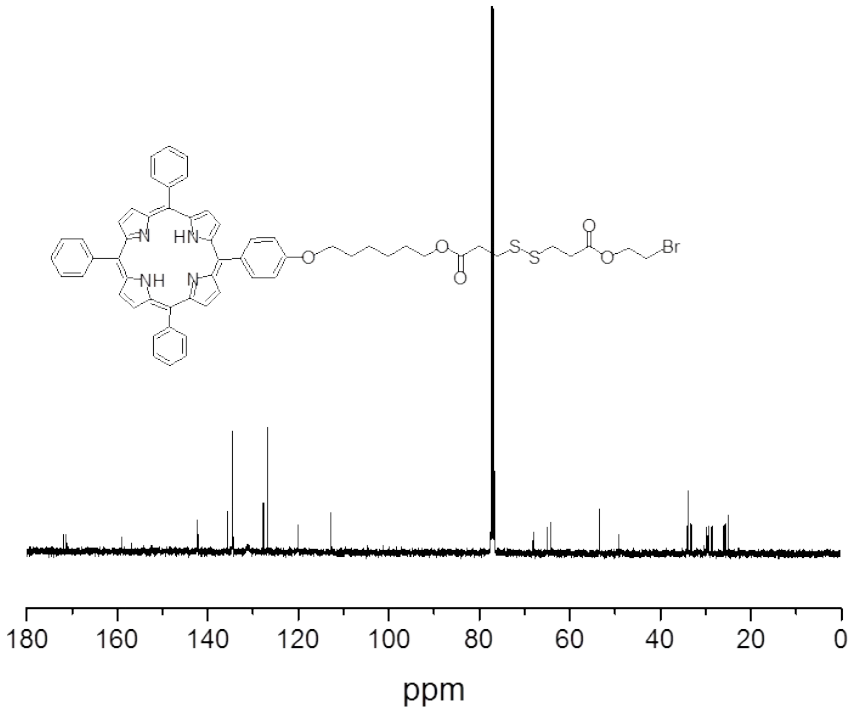


Fig. S11 ^{13}C NMR spectrum of **TPPC6-SS-Br** in $CDCl_3$

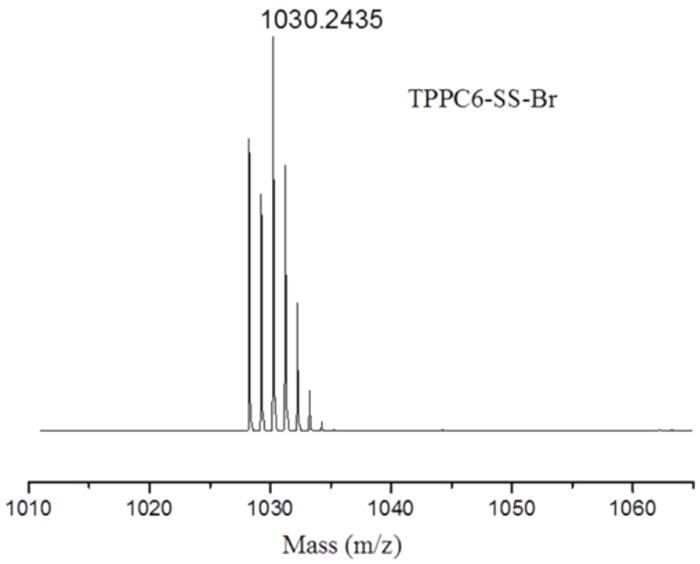


Fig. S12 MALDI-TOF-MS spectrum for **TPPC6-SS-Br**, calcd for $C_{58}H_{53}BrN_4O_5S_2$, 1030.10; found: 1030.2435.

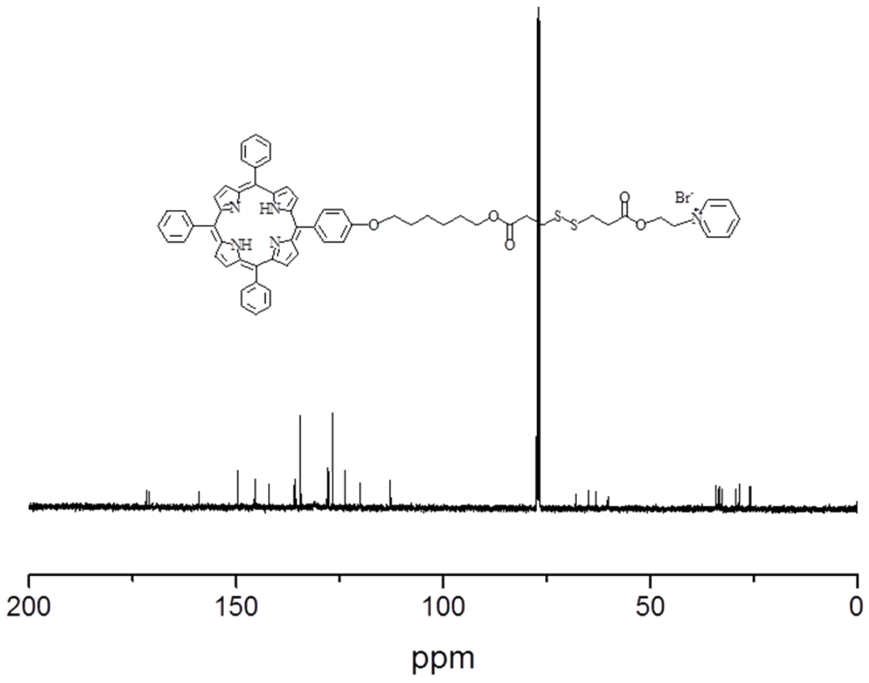


Fig. S13 ^{13}C NMR spectrum of **TPPC6-SS-Py** in $CDCl_3$

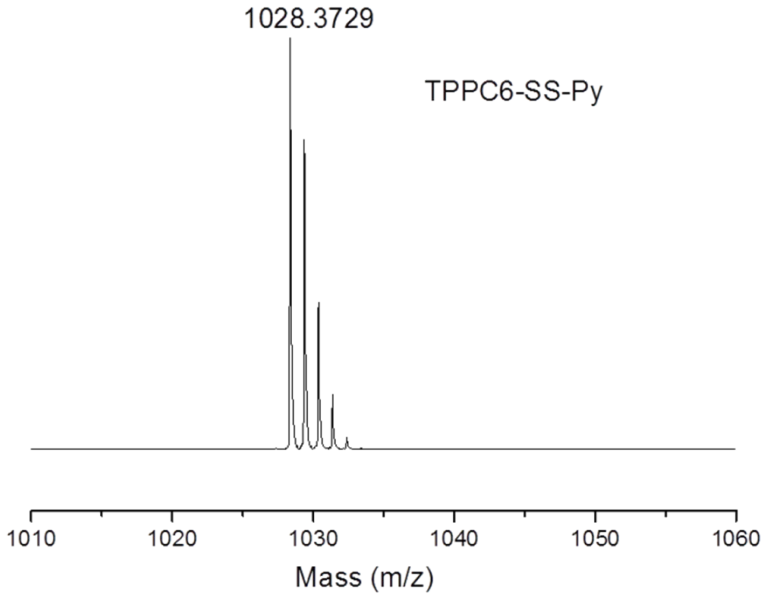


Fig. S14 MALDI-TOF-MS spectrum of TPPC6-SS-Py, calcd for $[M-Br]^+$: $C_{63}H_{58}N_5O_5S_2$, 1028.39; found: 1028.3729.

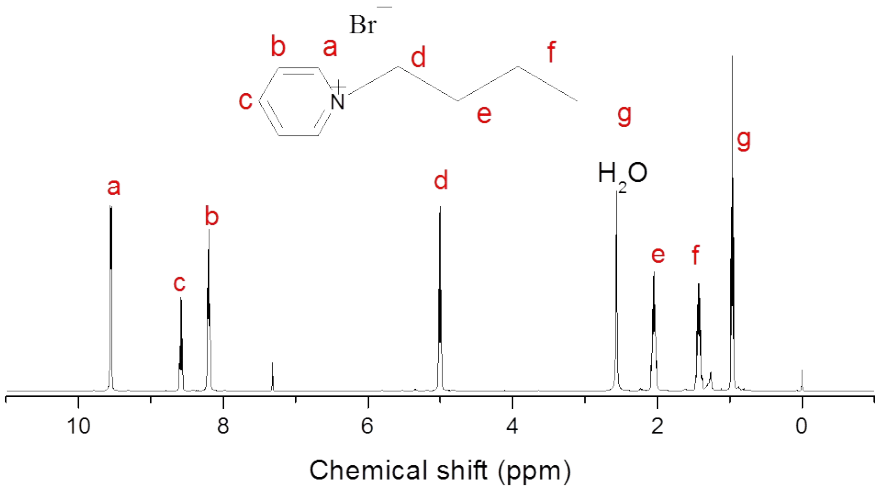


Fig. S15 ^{1}H NMR spectrum of $\mathbf{G_M}$

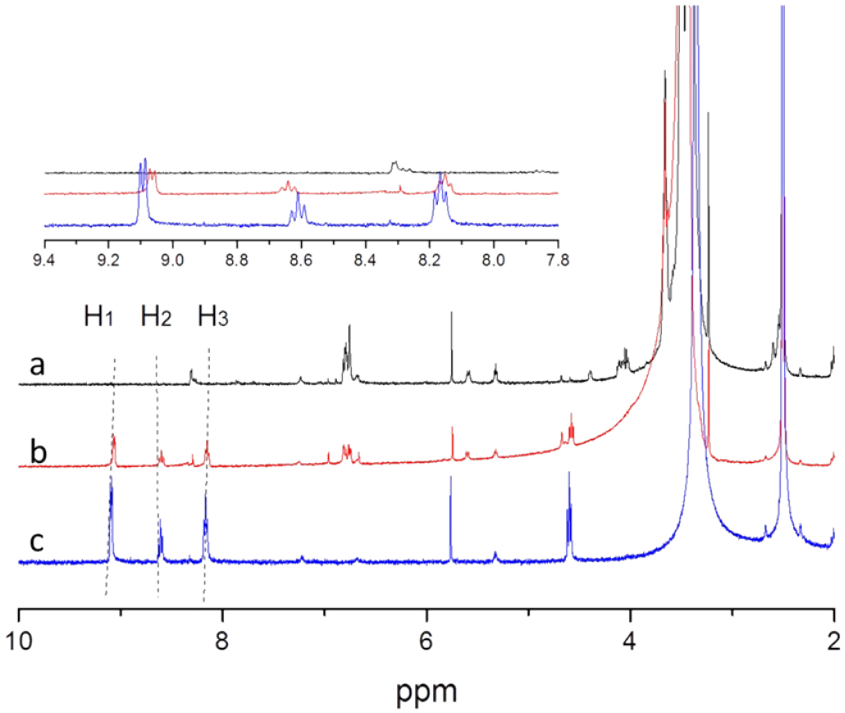


Fig. S16 Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6) of a) PEG-P[5]A (2 mM), b) a 1:1 mixture of PEG-P[5]A and G_M and c) G_M (2 mM).

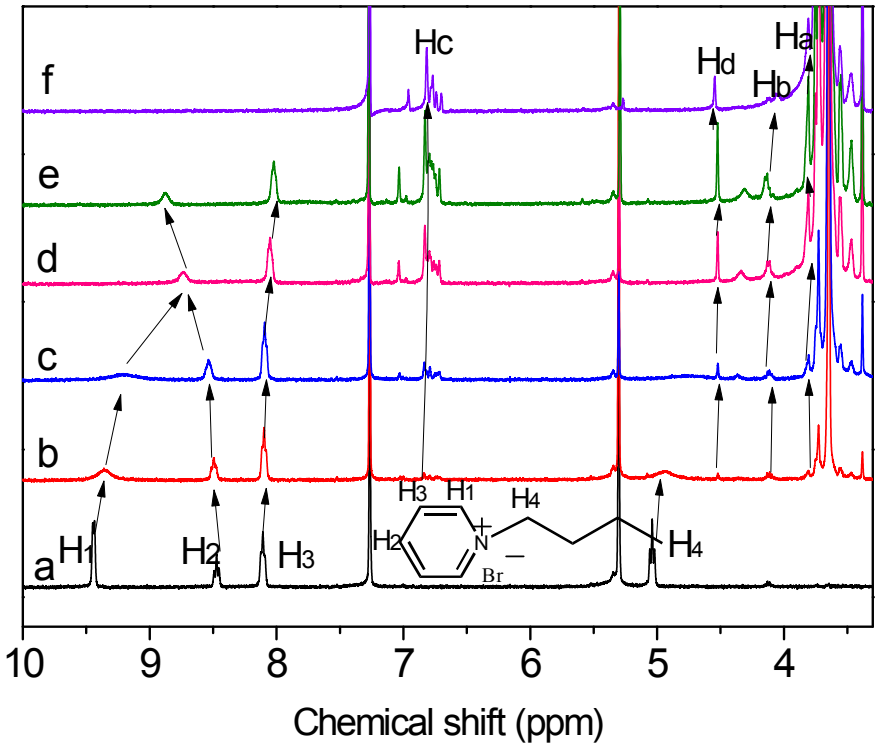


Fig. S17 Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$) of G_M at a constant concentration of 2 mM with different concentrations of PEG-P[5]A: (a) 0.00 mM, (b) 0.5 mM, (c) 1.00 mM, (d) 2.00 mM, (e) 4.00 mM, and (f) only PEG-P[5]A at 2 mM.

Investigation of the Interactions between PEG-P[5]A and G_M

To determine the association constant for the complexation between PEG-P[5]A and G_M, fluorescence titration experiments were carried out in solutions which had a constant concentration of PEG-P[5]A (2.5×10^{-5} M) and varying concentrations of G_M. By a non-linear curve-fitting method, the association constant (K_a) of PEG-P[5]A⊃G_M was estimated.[3]

The non-linear curve-fittings were based on the equation:

$$\Delta F = (\Delta F_\infty/[H]_0)\ (0.5[G]_0 + 0.5([H]_0 + 1/K_a) - (0.5\ ([G]_0^2 + (2[G]_0(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5})) \quad \text{(eq. 1)}$$

Where ΔF is the fluorescence intensity changes at 330 nm at $[H]_0$, ΔF_∞ is the fluorescence intensity changes at 330 nm when PEG-P[5]A is completely complexed, $[G]_0$ is the initial concentration of G_M, and $[H]_0$ is the fixed initial concentration of PEG-P[5]A.

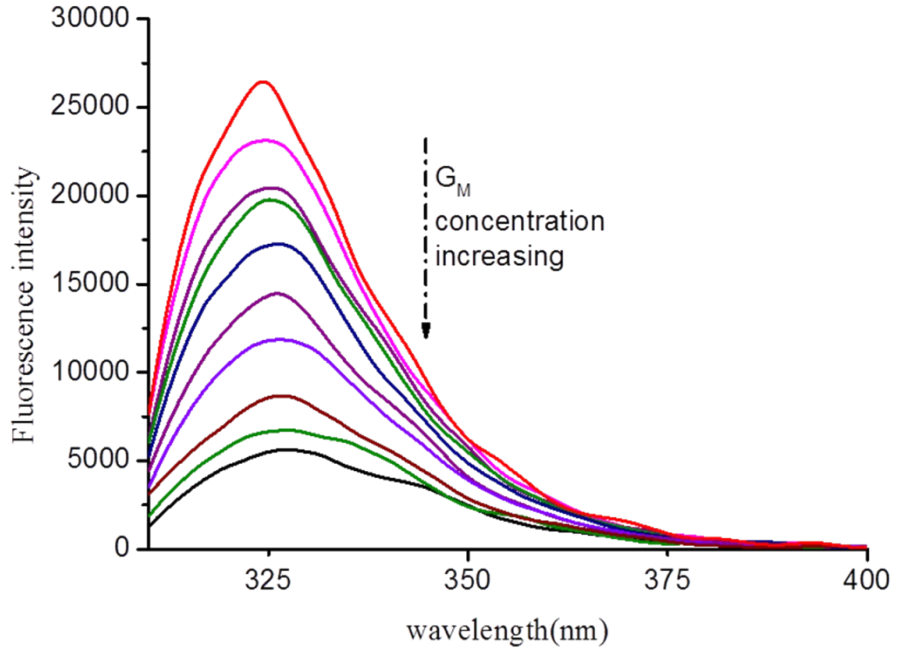


Fig. S18 Fluorescence spectra of PEG-P[5]A (2.5×10^{-5} M) upon addition of G_M (0 - 14. 5×10^{-5} M) in DMF at room temperature. Upon addition of G_M, emission from PEG-P[5]A was quenched, indicating the formation of the PEG-P[5]A-G_M complex.

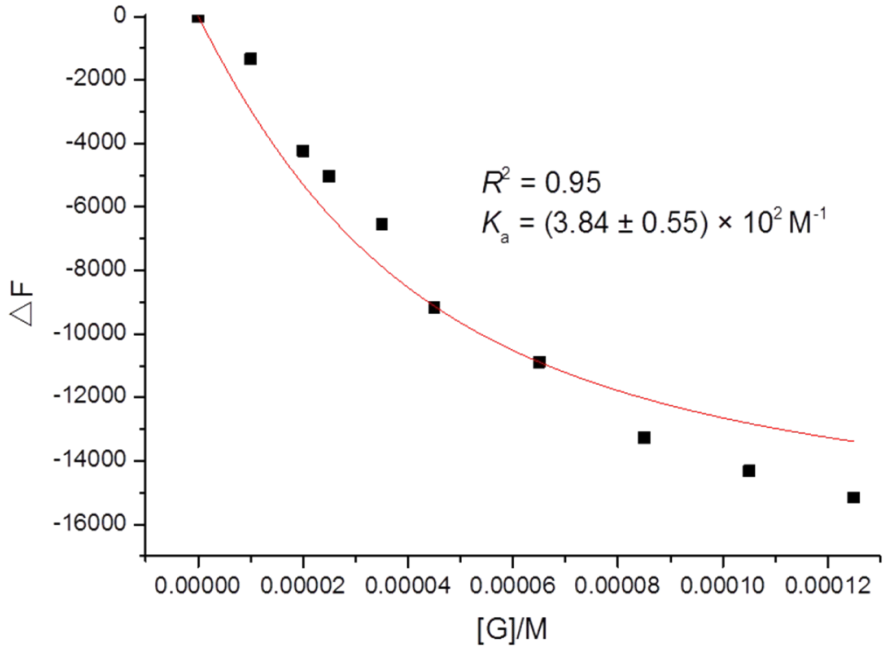


Fig. S19 The fluorescence changes of PEG-P[5]A upon addition of G_M. The red solid line was obtained from the non-linear curve-fitting using eq. 1.

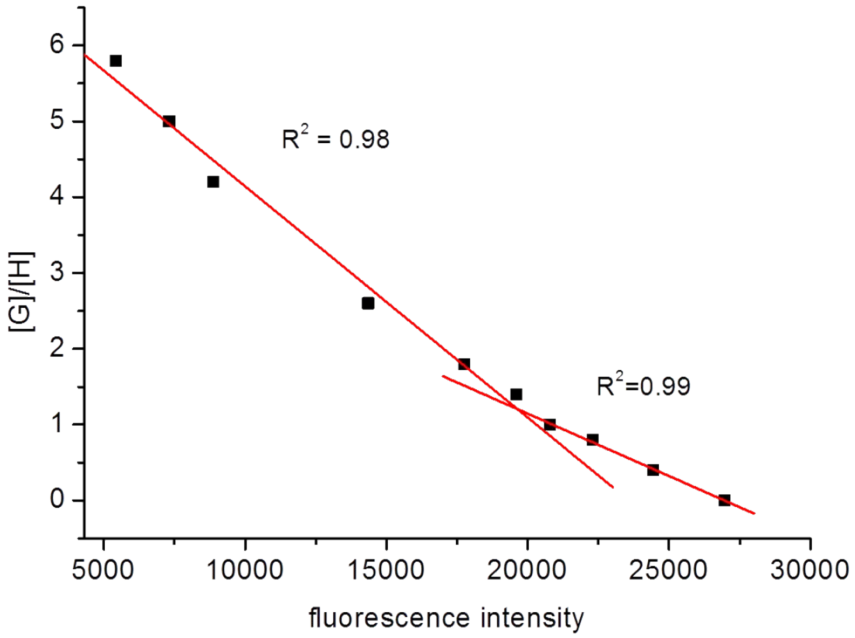


Fig. S20 Mole ratio plot for PEG-P[5]A and G_M, indicating a 1:1 stoichiometry.

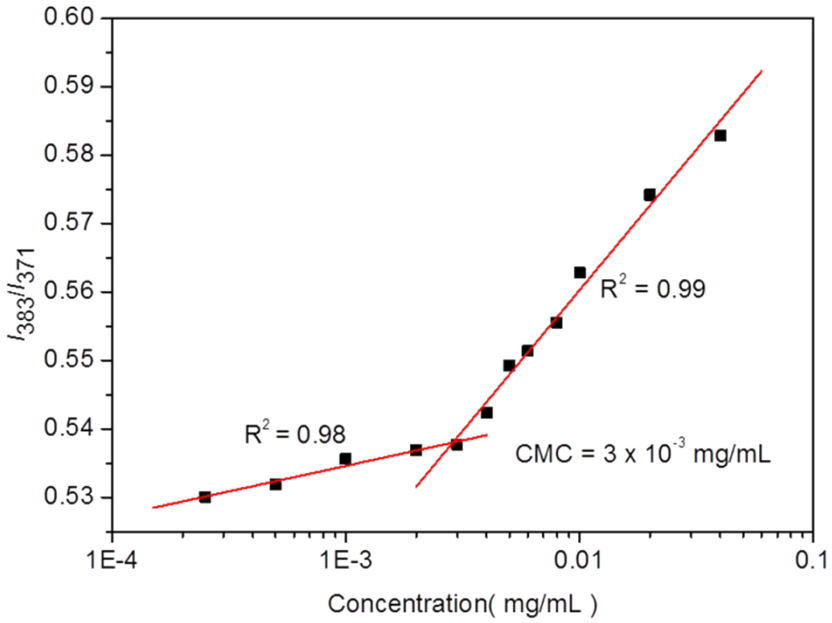


Fig. S21 Plot of the I_{382}/I_{372} ratio with different concentrations of PEG-P[5]A /TPPC6-SS-Py micelles.

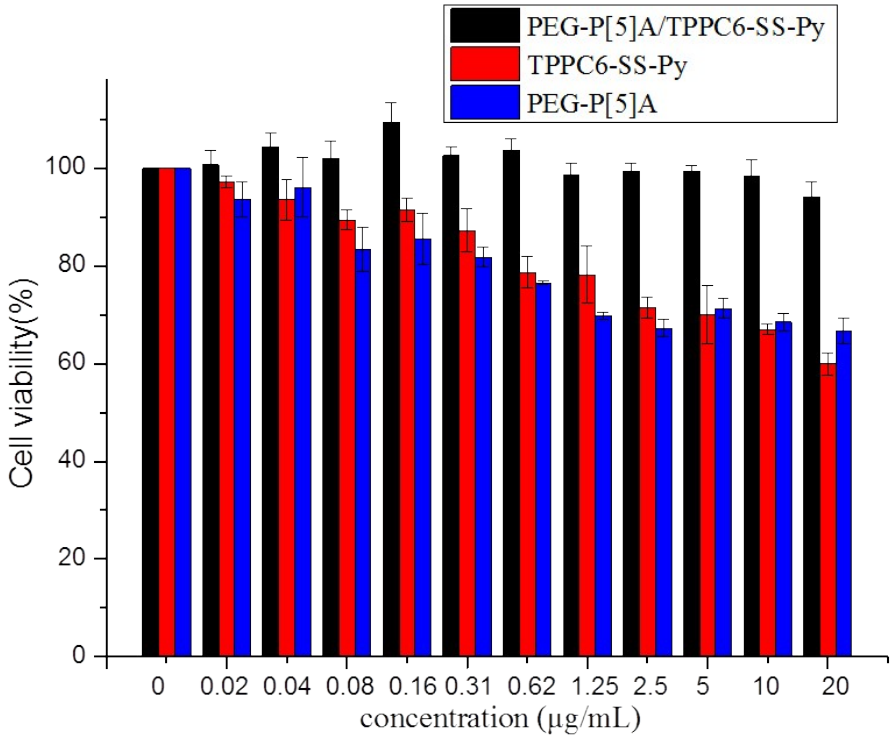


Fig. S22 Viability of A549 cells measured by the MTT assay after treating with different concentration of PEG-P[5]A/TPPC6-SS-Py, TPPC6-SS-Py and PEG-P[5]A without light irradiation.

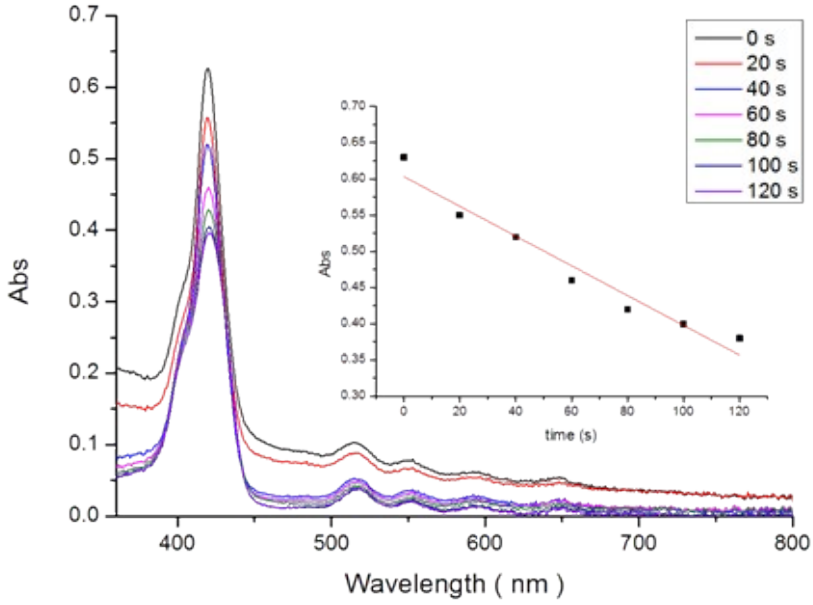


Fig. S23 UV-Vis absorption spectra of DPBF with supremolecular micelles after irradiation for different times (inset: plot of absorbance versus concentration).

References

1. L. Rui, L. Liu, Y. Wang, Y. Gao and W. Zhang, *ACS Macro Lett.*, 2016, **5**, 112-117.
2. F. Liu, Y. Ma, L. Xu, L. Liu and W. Zhang, *Biomater. Sci.*, 2015, **3**, 1218-1227.
3. Q. Duan, Y. Cao, Y. Li, X. Hu, T. Xiao, C. Lin, Y. Pan and L. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 10542-10549.