Supporting Information

Cis-Silicon Phthalocyanine Conformation Induces *J*-Aggregated Nanosphere with Unique Near-Infrared Absorbance and Fluorescence Enhancement: A Tumor Sensitive Phototheranostic Agent with Deep Tissue Penetrating

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Materials and Methods. All the reactions were performed under an atmosphere of nitrogen. *N*,*N*-Dimethylformamide (DMF), pyridine and toluene were distilled from barium oxide,

calcium hydride and sodium respectively. All other reagents are in the purity of analytical grade and were used without further purification.

Synthesis of SiPc-NH_2.[1] Silicon phthalocyanine dichloride ($SiPcCl_2$) (0.33 mmol), 2-(2-Aminoethoxy)ethanol (2.64 mmol), K_2CO_3 (2.64 mmol) and pyridine (2 mL) were dissolved in 30 mL toluene. The reaction mixture was heated and refluxed at 130 ° C for 12 h under nitrogen atmosphere. After evaporation the volatiles, the residue was dissolved in chloroform (100 mL) and filtered. The filtrate was washed three times with deionized water and then concentrated under reduced pressure. The crud product was recrystallized from chloroform / n-hexane to give SiPc-NH_2 as a green solid (56.2%).^{1}H NMR (CD_3OD, 300 MHz): δ -1.87 (4H, t, J = 3.4 Hz, CH_2), 0.54 (4H, t, J =3.6 Hz, CH_2), 1.72 (4H, t, J = 3.6 Hz, CH_2), 1.81 (4H, t, J = 3.8 Hz, CH_2), 8.43–8.46 (8H, m, Pc-H_β), 9.68–9.70 (8H, m, Pc-H_α).^{13}C NMR (CD_3OD, 75 MHz): δ 150.9, 137.1, 132.8, 124.8, 73.6, 73.4, 73.2, 62.2. MS (MALDI-TOF): m/z 749.004 calcd. for $[M+H]^+$ 749.269; Φ_f=0.12.

Synthesis of SiPc-NH_2-S. Silicon phthalocyanine dichloride ($SiPcCl_2$) (0.33 mmol), 2-Aminoethanol (2.64 mmol), K_2CO_3 (2.64 mmol) and pyridine (2 mL) were dissolved in 30 mL toluene. The reaction mixture was heated and refluxed at 130 ° C for 12 h under nitrogen atmosphere. After evaporation the volatiles, the residue was dissolved in chloroform (100 mL) and filtered. The filtrate was washed three times with deionized water and then concentrated under reduced pressure. The crud product was recrystallized from chloroform / n-hexane to give SiPc-NH_2 as a green solid (65.3%).。 ^{1}H NMR ($CDCl_3$, 300 MHz): δ = -2.12 (4H, t, J = 5.1 Hz, CH_2), -0.31 (4H, t, J = 5.1 Hz, CH_2), 8.29–8.35 (8H, m, Pc-H_β), 9.47–9.64 (8H, m, Pc-H_α); ^{13}C NMR (75 MHz, CDCl3): δ = 149.0, 135.6, 130.7, 123.4, 57.3, 29.7; MS (MALDI-TOF): m/z 660.724, calcd. for $[M]^+$660.217. Φ_f=0.11.

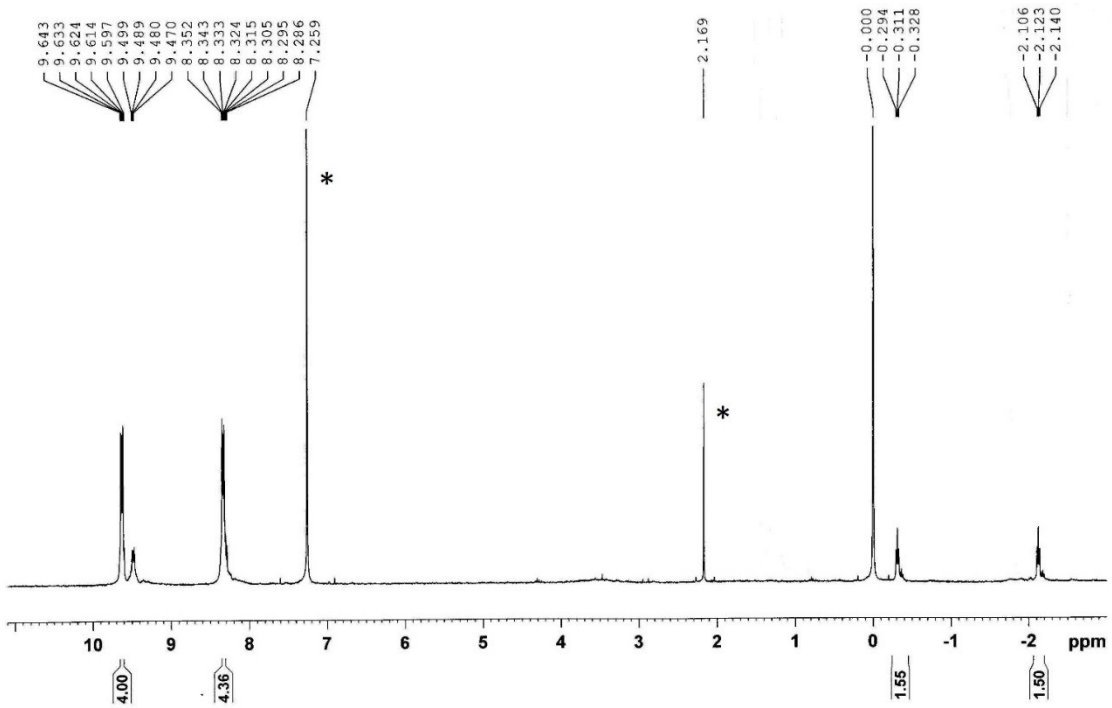

Figure S1. ^{1}H NMR spectrum of SiPc-NH_2-S in $CDCl_3$.

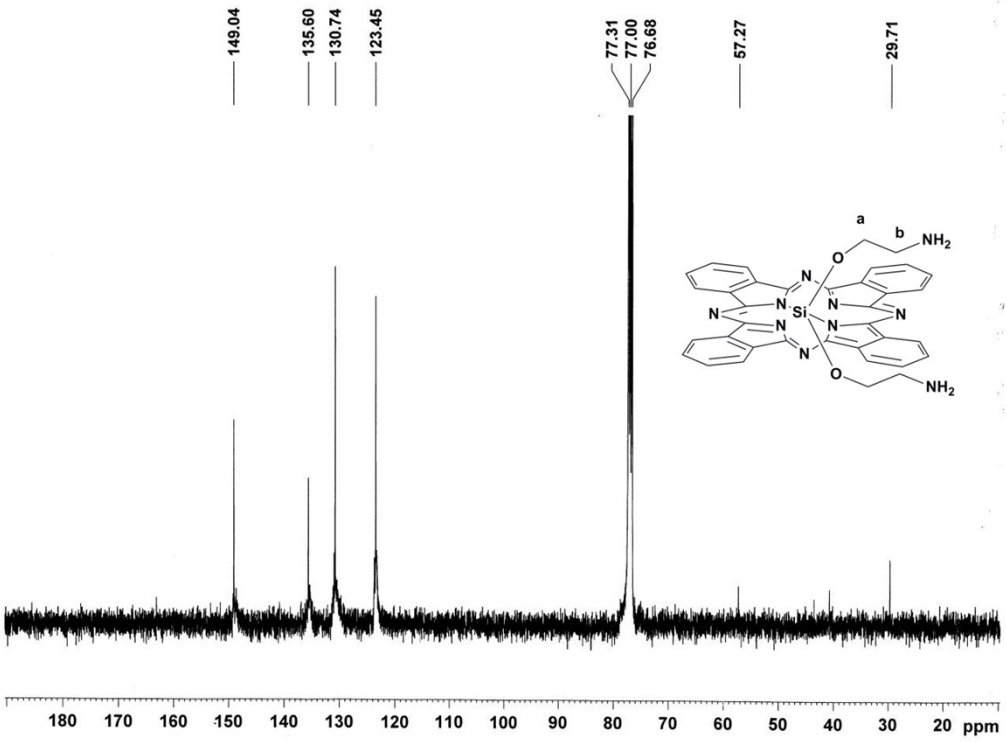

Figure S2. ^{13}C NMR spectrum of SiPc-NH_2-S in $CDCl_3$.

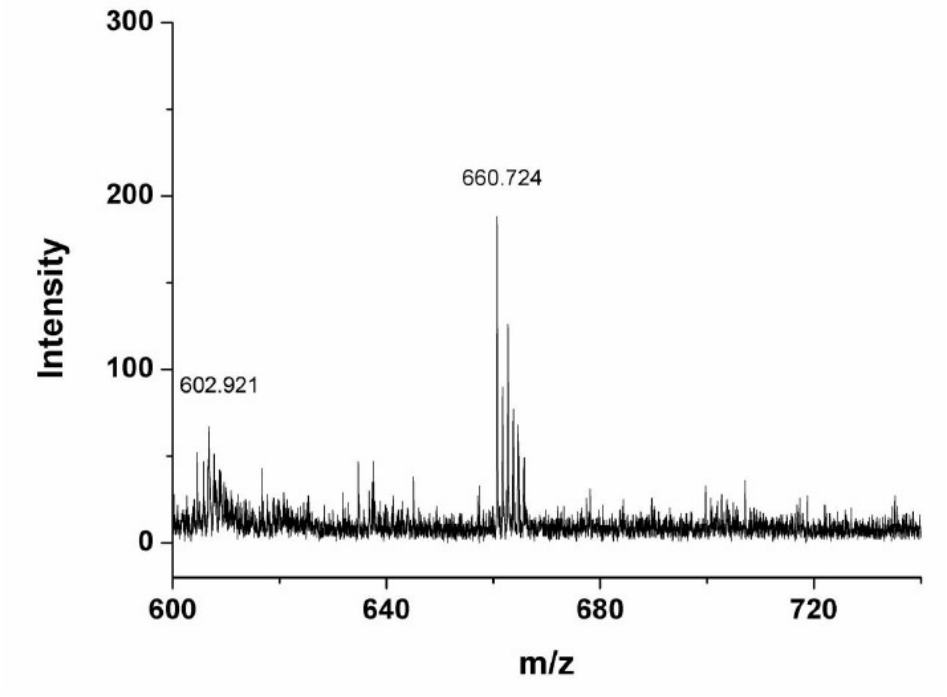

Figure S3. MALDI-TOF spectrum of SiPc-NH2-S.

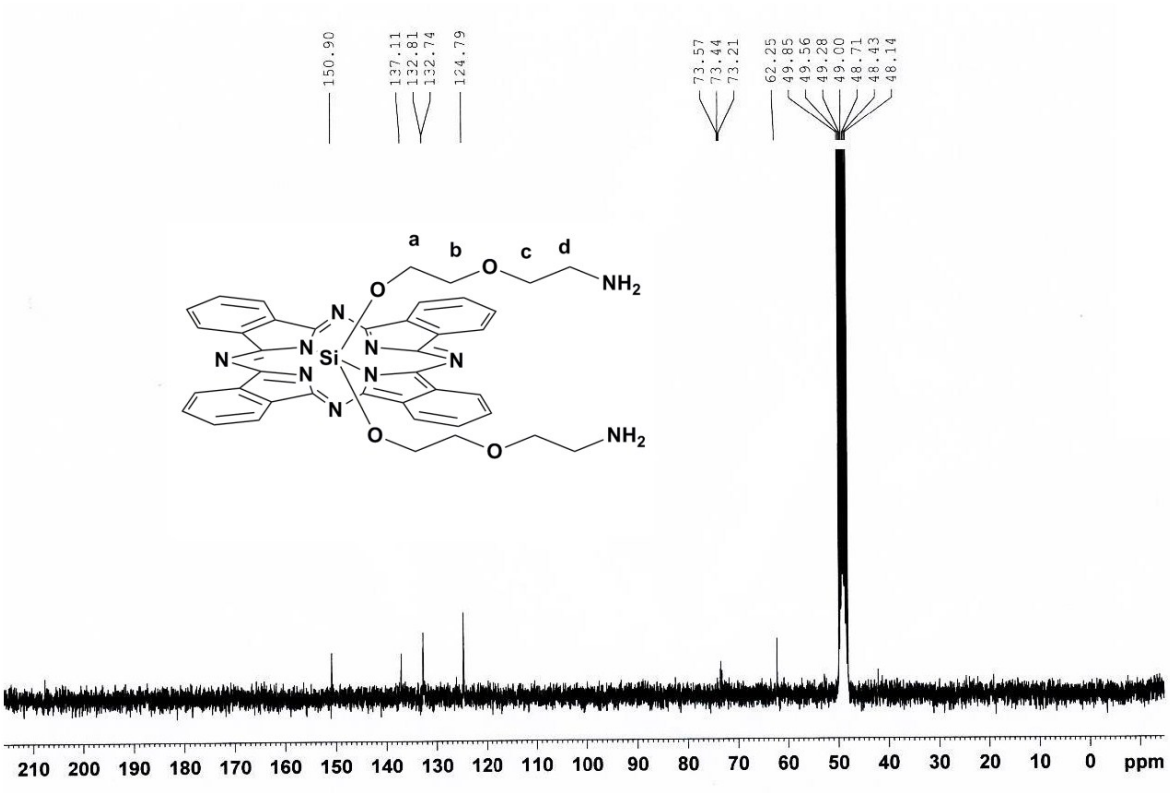

Figure S4. ^{13}C NMR spectrum of SiPc-NH_2 in CD_3OD.[1]

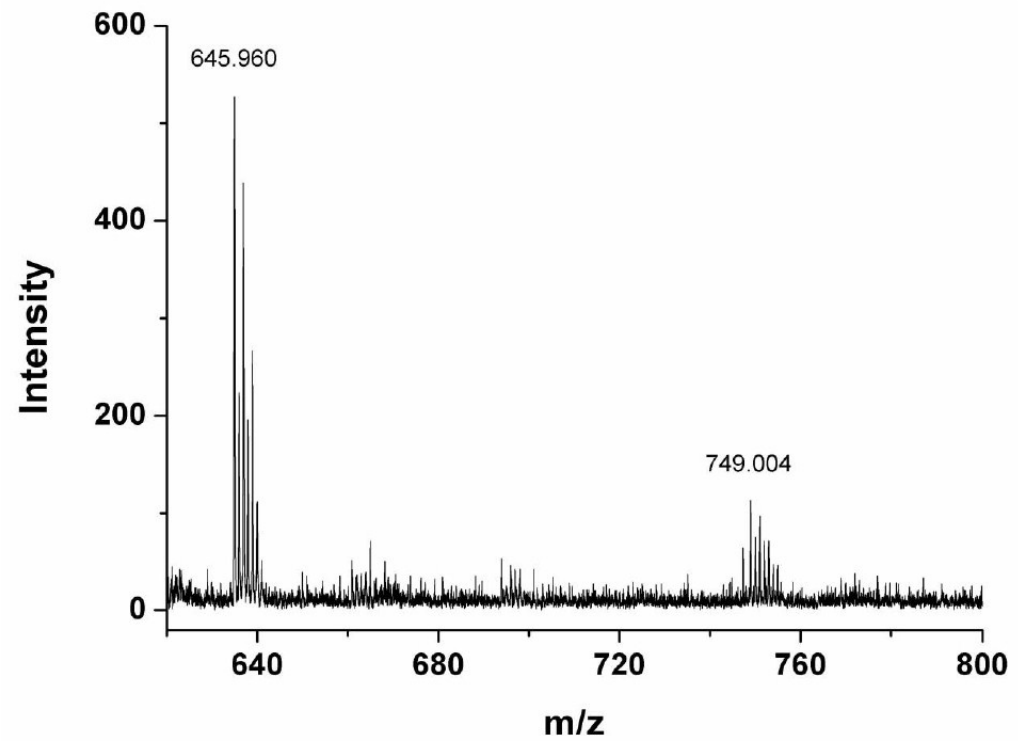

Figure S5. MALDI-TOF spectrum of SiPc-NH_2.

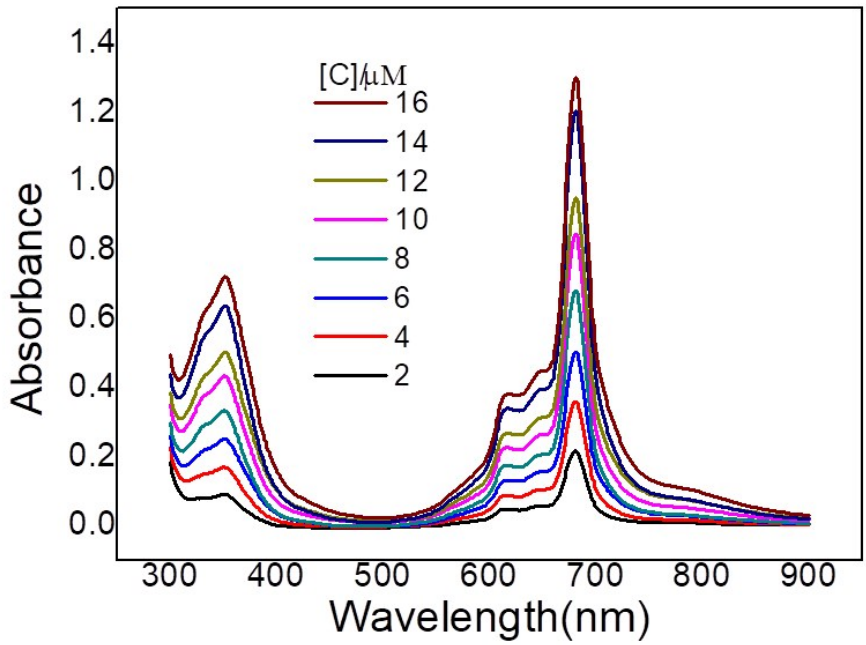

Figure S6. UV-Vis absorption of SiPc-NH_2-S at different concentration in water.

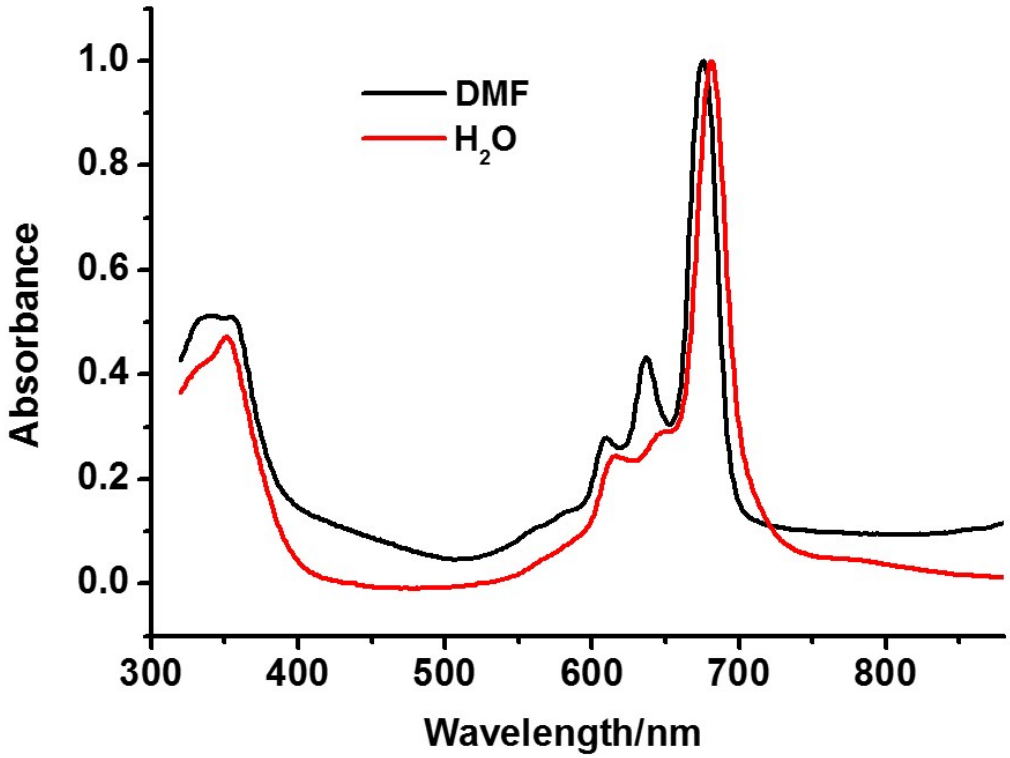

Figure S7. Absorption comparison of SiPc-NH_2-S in DMF (black) and H_2O (red).

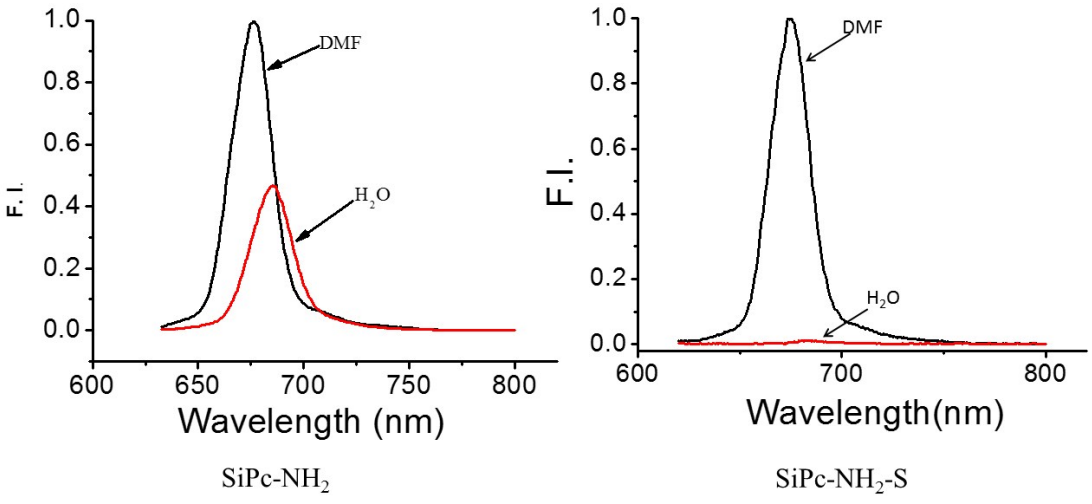

Figure S8. Comparison of fluorescence emission of SiPc-NH2 (left) and SiPc-NH_2-S (right) in DMF and Water.

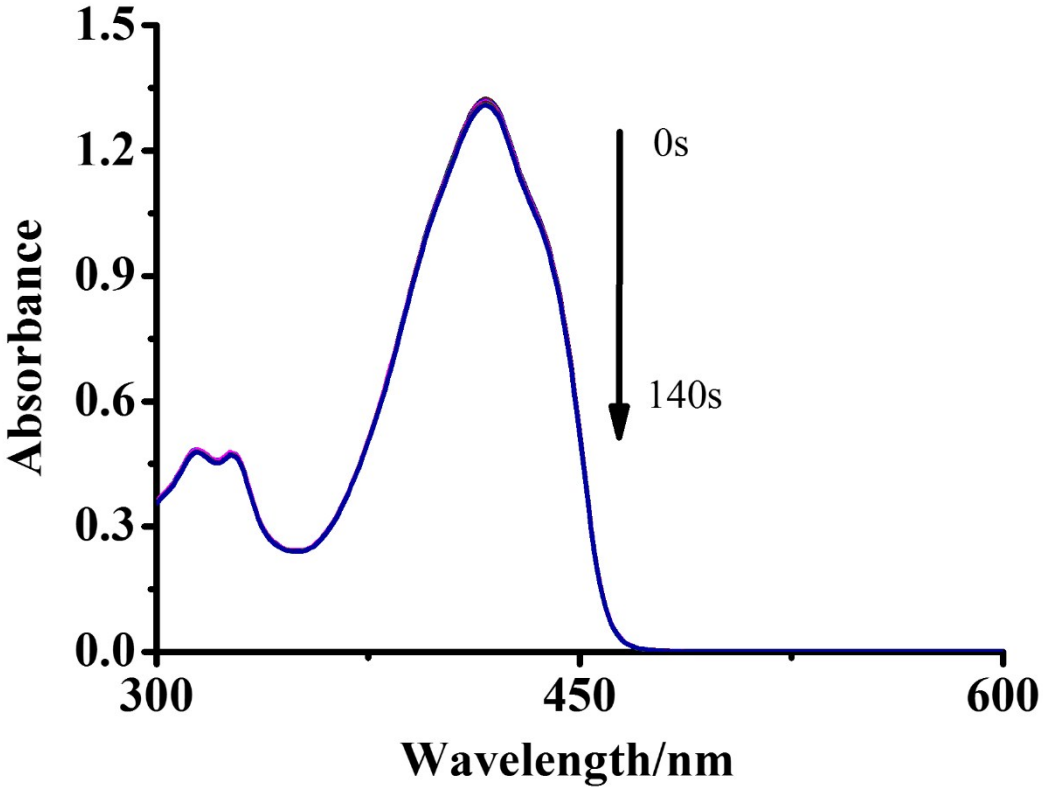

Figure S9. Absorption changes of DPBF only in water exposed to light λ > 610 nm.

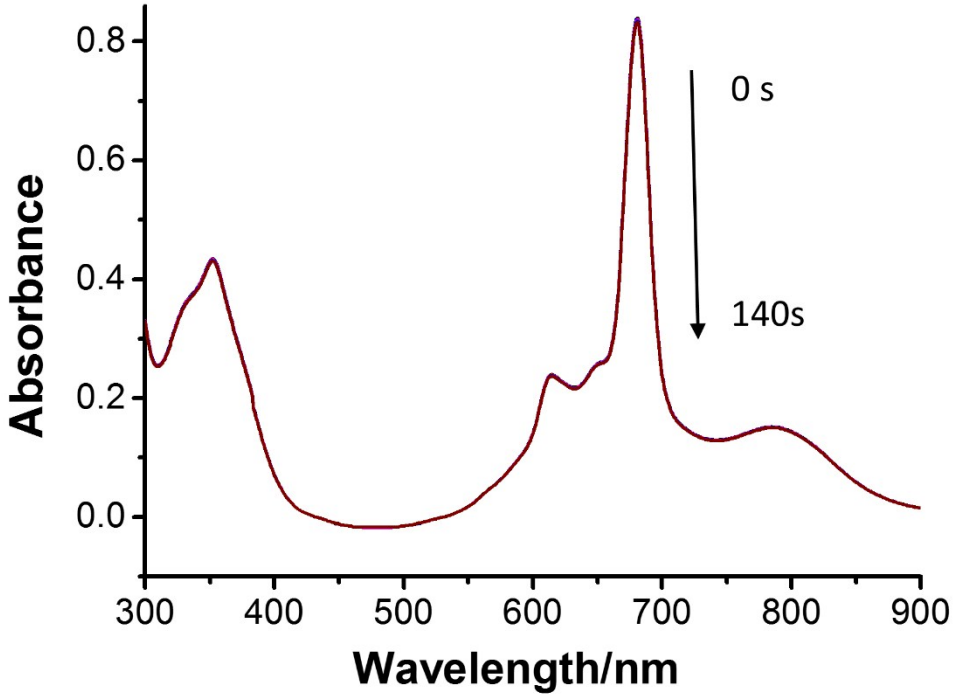

Figure S10. Absorption changes spectra of SiPcNano only in water exposed to light λ > 610 nm.

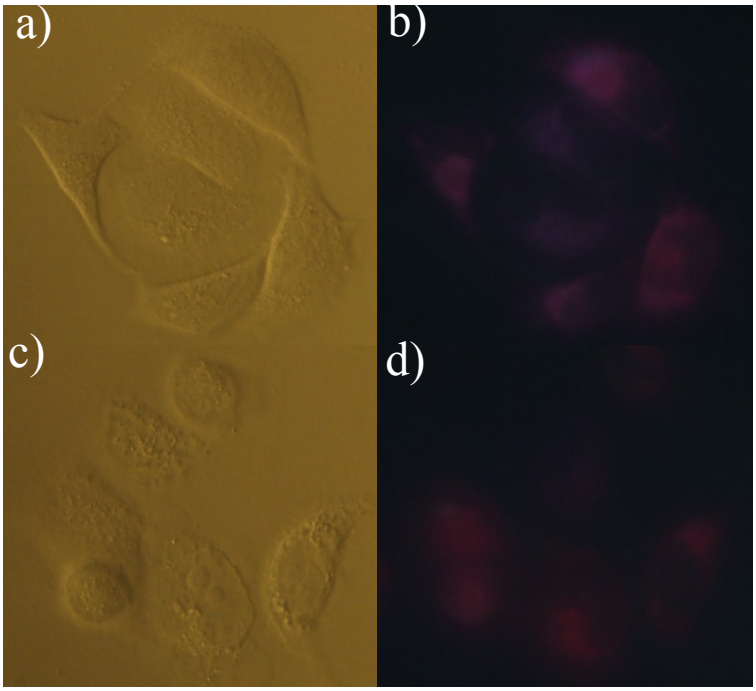

Figure S11. Intracellular fluorescence images of Hela cells after being incubated with SiPc-NH_2 (a, b) and SiPc-NH_2-S (c, d) both at 10 μM formulated with Cremophor EL for 4h.

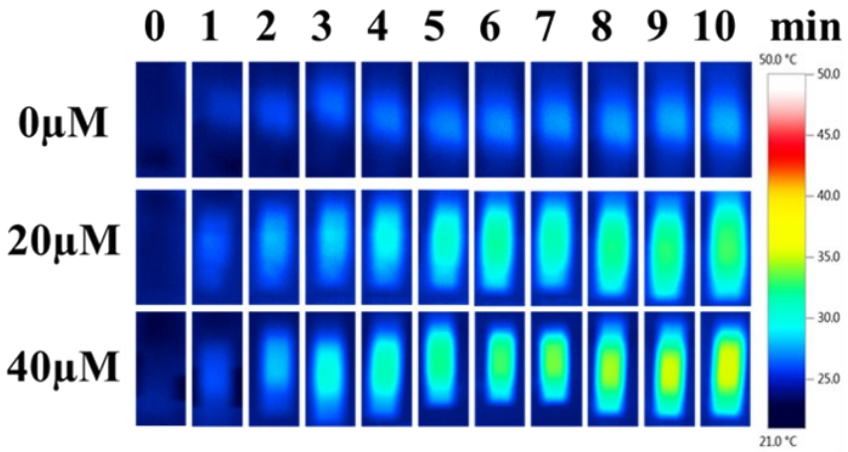

Figure S12. Thermal images of SiPcNano under 671 nm laser irradiation (0.5 W/cm^2) at different concentrations in water

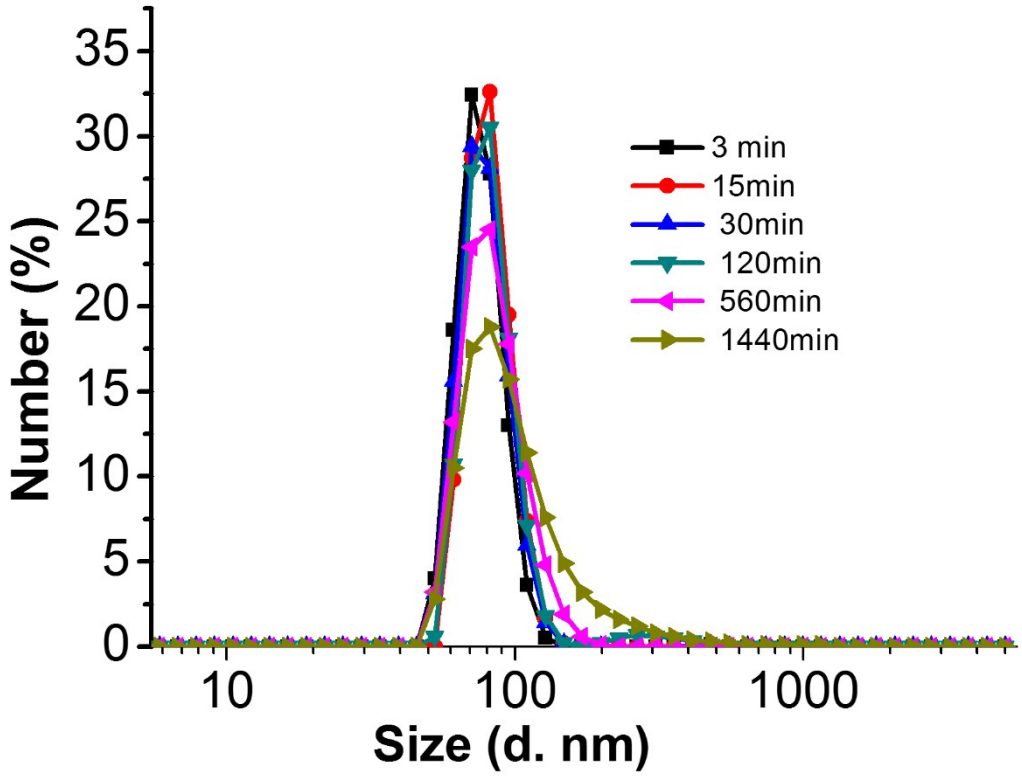

Figure S13. The stability of SiPcNano in PBS solution via DLS method.

1. Pan, J.; Yang, Y.; Fang, W.; Liu, W.; Le, K.; Xu, D.; Li, X., Fluorescent Phthalocyanine-graphene Conjugate with Enhanced NIR Absorbance for Imaging and Multi-Modality Therapy. *ACS Applied Nano Materials* **2018,** *1* (6), 2785-2795.