

Supporting Information

Polyfluoroalkyl substituted phthalocyanine based supramolecular light switch for photothermal and photodynamic antibacterial activity against *Escherichia coli*

2. Experiments

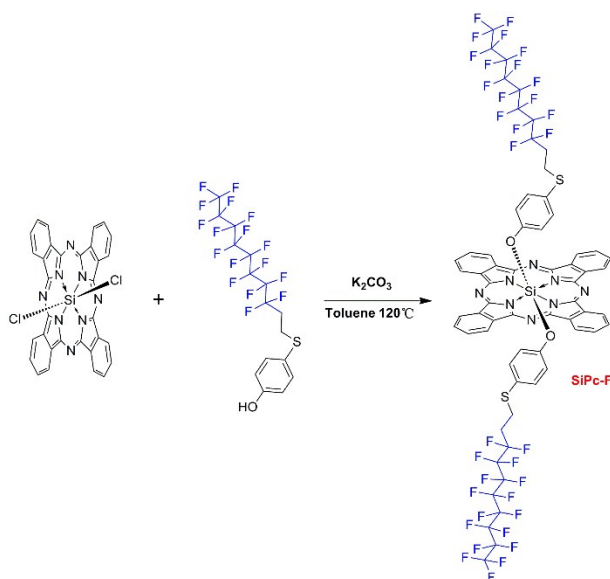
2.1 Materials and Equipment

All solvents for organic synthesis were reagent grade quality. β -Cyclodextrin (β -CD), 1-pyrenebutyric acid, 4-dimethylaminopyridine (DMAP), dicyclohexylcarbodiimide (DCC) and 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylthio) phenol were all purchased from Energy Chemical of China. SWNTs-COOH was purchased from Times Nano of China with 1-2 nm in length and purity more than 90%. The Infrared spectra (KBr pellets) were recorded on a PE-983G spectrometer. ^1H NMR spectra were recorded on a Bruker 400 MHz FT-NMR spectrometer using tetramethyl silane (TMS) as an internal standard. Mass spectra (MS) were measured on a matrix assisted laser desorption/ionization time-of-flight spectrometry (MALDI-TOF MS) or a LCQ Deca XP Max mass spectrometer. UV/Vis spectra were performed on Cary50 UV/Vis spectrophotometer. Fluorescence emission spectra were carried out on FL900/FS920 fluorescence spectrophotometers. Thermo gravimetric analyses curves (TGA) were recorded on a TGA/SDTA851e (Mettler-Toledo) thermal analyzer. The products were heated from 30 °C to 800 °C under nitrogen with a heating rate of 10 °C/min. The X-ray photoelectron spectroscopy (XPS) measurements were performed by an Omicron Sphera II hemisphere energy analyzer. Transmission electron microscopy (TEM) images were obtained using a JEM 1400 transmission electron microscope at an accelerating voltage of 100 kV.

Raman scattering spectra was performed with an excitation light at 532 nm by a Xplora Plus system. The laser beam was tightly focused on a sample surface with the use of a 50× long working distance (LWD) microscope objective. The Raman spectra was recorded in the spectral range 200-1900 cm^{-1} with a spectral resolution $\pm 1 \text{ cm}^{-1}$ and a spatial resolution of about 1 μm .

2.2.1 Synthesis of polyfluoroalkyl substituted silicon phthalocyanine (SiPc-F)

A mixture of dichloro-phthalocyanine silicon (SiPcCl₂) (0.061g, 0.1 mmol), potassium carbonate (0.24 g, 1.0 mmol), and 4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecylthio) phenol (0.17 g, 0.3 mmol) in toluene (20 mL) was heated at 120 °C for 24 h. The mixture was cooled to room temperature. The solvent was removed by filtration and evaporated under reduced pressure. The crude product was purified with silica gel column chromatography using dichloromethane and hexane (v:v=1:2) as eluent. A blue solid SiPc-F was obtained. Yield: 32%. IR ν/cm^{-1} : 734 (Ar-H), 1079 (Si-O), 1150 (C-F), 2929 (-CH₂); ¹H NMR (400 MHz, CDCl₃) δ/ppm : 9.64 (m, 8H, H^e), 8.39 (m, 8H, H^f), 5.70 (d, $J=8\text{Hz}$, 4H, H^d), 2.43 (d, $J=8\text{Hz}$, 4H, H^c), 2.33 (m, 4H, H^b), 1.79 (m, 4H, H^a); ESI-MS $[M]^+$: 1682.1 m/z (100%).



Scheme 1 The synthesis of *polyfluoroalkyl substituted silicon phthalocyanine* (SiPc-F)

2.2.2 *Preparation of singlet-walled carbon nanotube-pyrene-labelled β -Cyclodextrin-polyfluoroalkyl substituted silicon phthalocyanine (SWNTs-p- β -CD-SiPc-F)*

2.2.2.1 *Preparation of pyrene-labelled β -Cyclodextrin (p- β -CD)*

A solution of β -CD (1.14 g, 1.00 mmol) and 1-pyrenebutyric acid (0.32g, 1.10 mol) and 4-dimethylaminopyridine (0.06 g, 0.5 mmol) in dry DMF solution (10 mL) was added at 0 °C, and the mixture was stirred at 0°C for 30 min under nitrogen atmosphere. Then dicyclohexylcarbodiimide (0.21g, 1.0 mmol) was added, and the mixture was continuous stirred at 0 °C for 2 h. Next the reaction mixture temperature was raised to room temperature and the mixture was stirred overnight. After the removal of insoluble salts by filtration, the participates were re-crystallized in acetone. The participates were washed several times with distilled water to remove unreacted β -CD. After being dried in a vacuum, p- β -CD was obtained as a yellow solid with yield of 15%. ^1H NMR (400 MHz, DMSO-d₆) δ /ppm: 8.41 ~ 7.78 (m, 9H; H^m), 5.82 ~ 5.69 (m, 14H; H^{g, h}), 4.87 ~ 4.84 (m, 7H; H^a), 4.62 ~ 4.36 (m, 6H; Hⁱ), 3.65 ~ 3.58 (m, 28H; H^{c, e, f}), 3.41 ~ 3.34 (m, 16H; H^{b, d, l}), 2.50 (t, 2H; H^j), 2.00 (m, 2H; H^k). MALDL-TOF Mass: [M+Na]⁺: 1699 *m/z*.

2.2.2.2 *Preparation of singlet-walled carbon nanotube-pyrene-labelled β -Cyclodextrin (SWNTs-p- β -CD)*

The p- β -CD (80.0 mg, 0.056 μmol) was soluble in DMF (20.0 mL). SWNTs (20.0 mg) was added into the p- β -CD solution. The mixture was sonicated for 30 min at room temperature. Then the solution was filtrated by a poly tetra fluoroethylene micro-porous membrane (0.22 μm). SWNTs-p- β -CD was collected and washed by DMF several times. The product was dried under

a vacuum at room temperature for 48 h.

2.2.2.3 Preparation of singlet-walled carbon nanotube-pyrene-labelled β -Cyclodextrin-prefluoreine silicon phthalocyanine (SWNTs-p- β -CD-SiPc-F)

SiPc-F (40.0 mg) was added into a DMF solution (20.0 mL) containing SWNTs-p- β -CD (20.0 mg). The mixture was sonicated for 30 min at room temperature then centrifuged at 10000 rpm for 10 min and finally filtered with 0.22 μ m membrane. SWNTs-p- β -CD-SiPc-F was collected and washed with DMF. The product was dried in a vacuum at room temperature for 48 h.

2.2.2.4 The photo-induced control release of SiPc-F from SWNTs-p- β -CD-SiPc-F

SWNTs-p- β -CD-SiPc-F (0.3 mg) was dispersed in a vial containing DMSO (10 mL). The vial was irradiated with infrared light (680 nm, 400 mW/cm²). The temperature was recorded every 2 minutes using a thermocouple thermometer. The control groups were SWNTs alone and DMSO. Meantime, SiPc-F released from SWNTs-p- β -CD-SiPc-F by the laser irradiation was collected by centrifugation and redissolved in DMSO. The fluorescence intensity of the released SiPc-F from SWNTs-p- β -CD-SiPc-F by a photoinduced process was measured in DMSO, and the concentration of the SiPc-F was calculated.

2.3. Photophysical and Photochemical properties

2.3.1 Photophysical properties of SiPc-F

Fluorescence quantum yields (Φ_F) of SiPc-F were determined in DMF by the comparative method using Eq. 1[1].

$$\Phi_F = \Phi_{F(std)} \cdot F \cdot A_{Std} \cdot n^2 / (F_{Std} \cdot A \cdot n_{std}^2) \quad (\text{Eq. 1})$$

Where F and F_{Std} are the integral areas of emission curves of SiPc-F and the unsubstituted ZnPc (n-ZnPc), respectively. A and A_{Std} are the absorbance's of the SiPc-F and the standard n-ZnPc

at the excitation wavelengths, respectively. n^2 and n^2_{Std} are the refractive indexes of solvents of SiPc-F and standard, respectively. n-ZnPc in DMF ($\Phi_{F(std)}=0.28$) was employed as the standard [2].

2.3.2 Singlet oxygen quantum yields of SiPc-F and SWNTs-p-β-CD-SiPc-F

The determinations of singlet oxygen quantum yield (Φ_{Δ}) were carried out using the chemical trapping method [3]. For singlet oxygen measurements, DPBF was used as chemical quencher ($\Phi_{\Delta}= 0.57$ for n-ZnPc in DMF [4]). The mixture of SiPc-F or SWNTs-p-β-CD-SiPc-F (3 mL, 1×10^{-6} mol/L) and diphenylisobenzofuran (DPBF $\sim 3 \times 10^{-5}$ M) in oxygen saturated DMF was irradiated at 680 nm. DPBF degradation at 417 nm was monitored. The light intensity used for Φ_{Δ} determinations was 400mW/cm². Φ_{Δ} value was calculated by the relative method using n-ZnPc as the reference (Eq. 2):

$$\Phi_{\Delta} = \Phi_{\Delta} Std \cdot \frac{R}{R^{Std}} \cdot \frac{I_{Abs}^{Std}}{I_{Abs}} \quad (\text{Eq. 2})$$

2.3.3 The loading rate of SiPc-F in the SWNTs-p-β-CD

The amount of SiPc-F loaded on SWNTs-p-β-CD-SiPc-F was determined as follow. The concentration of SiPc-F in the supernatant liquor was determined according to standard concentration curve of SiPc-F obtained by UV-vis spectroscopic method. The loading rate of SiPc-F on SWNTs-p-β-CD-SiPc was determined using eq 3

$$\phi = \frac{M_{SiPc-F} - M_{SiPc-F}'}{M_{SWNTs-p-\beta-CD-SiPc-F}} \quad \text{eq3}$$

Where ϕ is the *loading rate* of SiPc-F loaded on SWNTs-p-β-CD-SiPc-F, M_{SiPc-F} is the initial amount of SiPc-F, M_{SiPc-F}' is the amount of SiPc-F in the supernatant liquor, and $M_{SWNTs-p-\beta-CD-Pc}$ is the amount of SWNTs-p-β-CD added.

2.4 Antibacterial activity of SWNTs-p-β-CD-SiPc-F

A single colony of *Escherichia coli* (*E. coli*, DH5α) was selected using a sterile pipette. The tip was dropped into a falcon tube containing 3 mL of the liquid medium (Luria-Bertani). The bacteria were incubated at 37°C for 12 h. After incubation, the optical density (OD) of the culture was measured at 600nm. The bacteria at a concentration of approximately 10^7 bacteria/mL (OD_{600 nm}=0.6) were diluted 1:10 in LB medium. 40 μL SWNTs-p-β-CD-SiPc-F (4 mg/mL) was dissolved in sterile distilled water and in 10% DMSO was added into 20 μL of the bacterial dilutions, respectively. The suspensions of *E. coli* with SWNTs-p-β-CD-SiPc-F were illuminated by 660nm laser light for 15 min with light dosage of 120 mW/cm². Cell survival was measured by LB agar plates. After illumination, the bacteria were diluted in a series of 10 folds with LB medium, 2 μL of each dilution was dropped on LB agar plate and incubated at 37 °C for 12-16 h. For bacteria counting, an aliquot of 200 μL was plated on 10 cm LB agar plates. Each experiment was performed by triplicate. The control groups without laser illumination were also carried out accordingly.

1. Characterisation analysis:

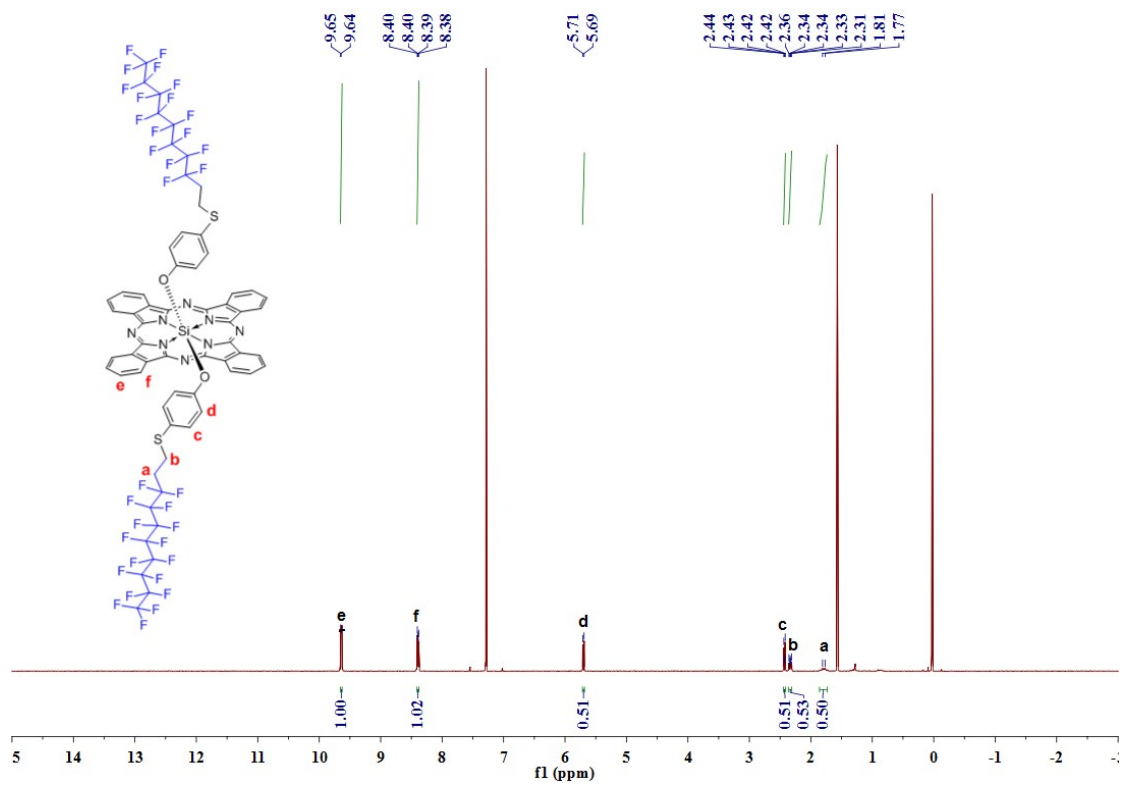


Fig.S1 The ¹H NMR spectrum of SiPc-F (400M Hz, CDCl₃)

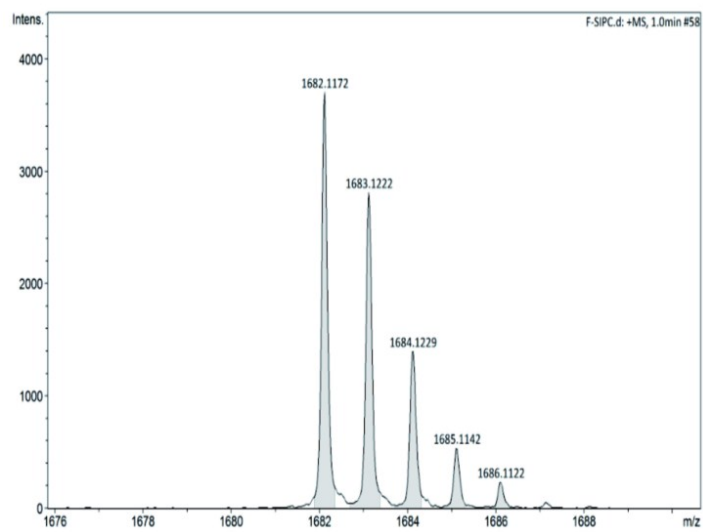


Fig.S2 The ESI-MS spectrum of SiPc-F

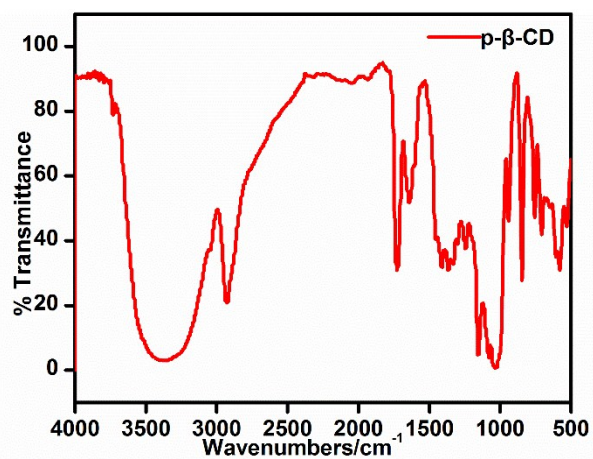


Fig.S3 The FT-IR spectrum of p- β -CD

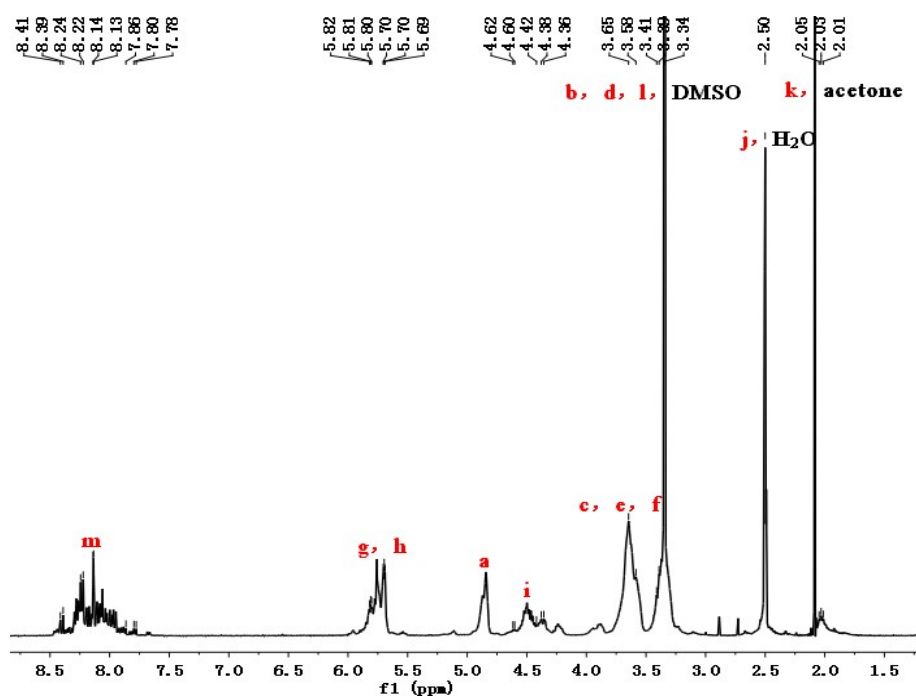
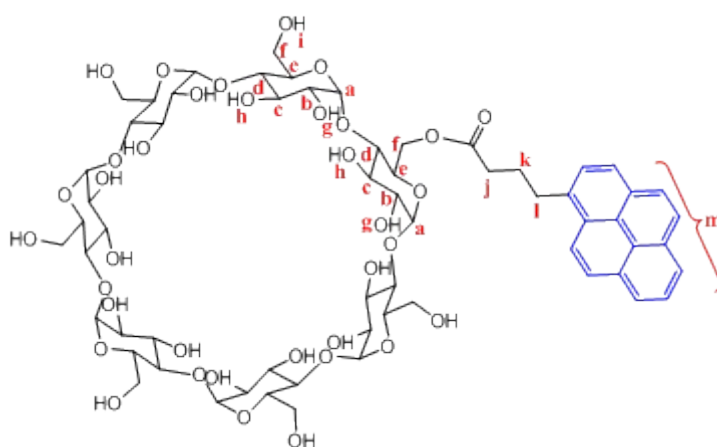


Fig.S4 The ^1H NMR spectrum of p- β -CD (400 MHz, DMSO- d_6)

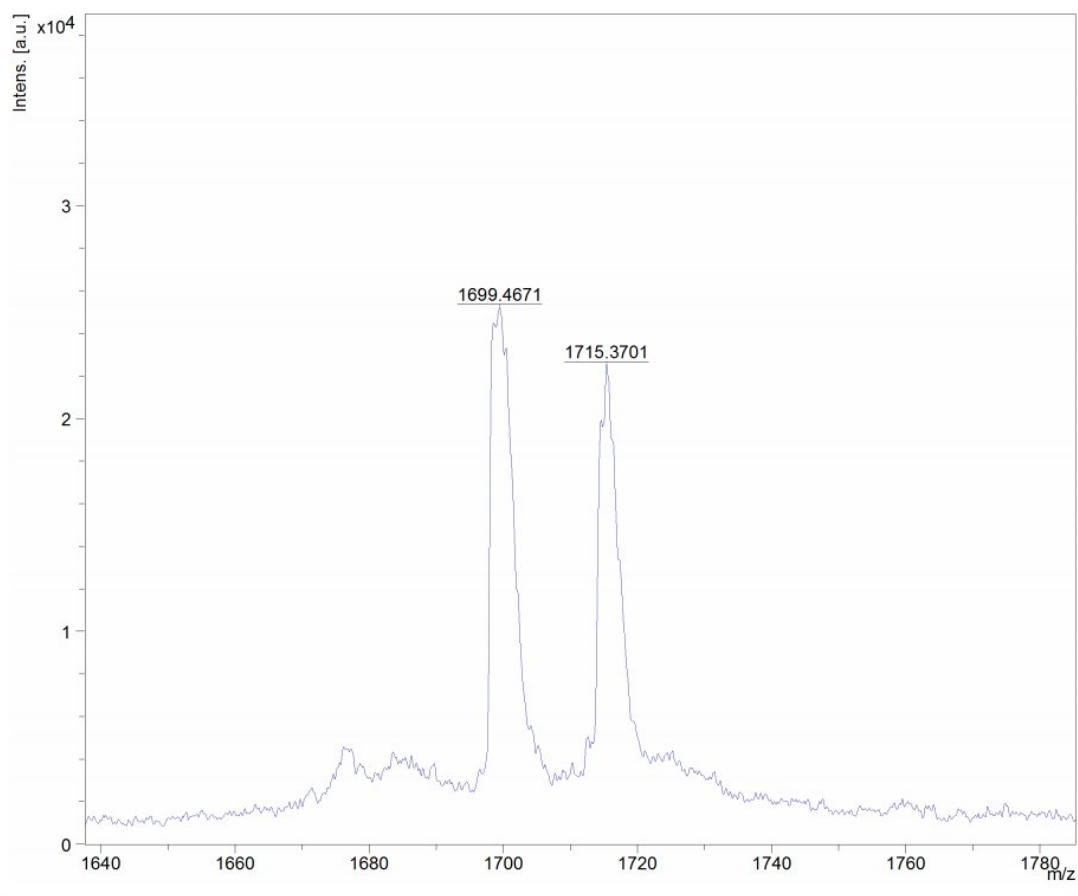


Fig.S5 The MALDL-TOF-MS spectrum of p-β-CD

2. Photophysical properties of SWNTs-p-β-CD-SiPc-F

Table S1 Photophysical and photochemical properties of SiPc-F and SWNTs-p-CD-SiPc-F

Complexes	Absorption	Emission	Φ_F^*	τ_s /ns	Φ_Δ
	λ_{Qmax} /nm	λ_{Qmax} /nm			
SiPc-F	683	673	0.0399	1.10	0.494
SWNTs-p-β-CD-SiPc-F	679	--	--	--	0.0754

3. Singlet oxygen quantum yield (Φ_Δ) of SiPc-F and SWNTs-p-β-CD-SiPc-F

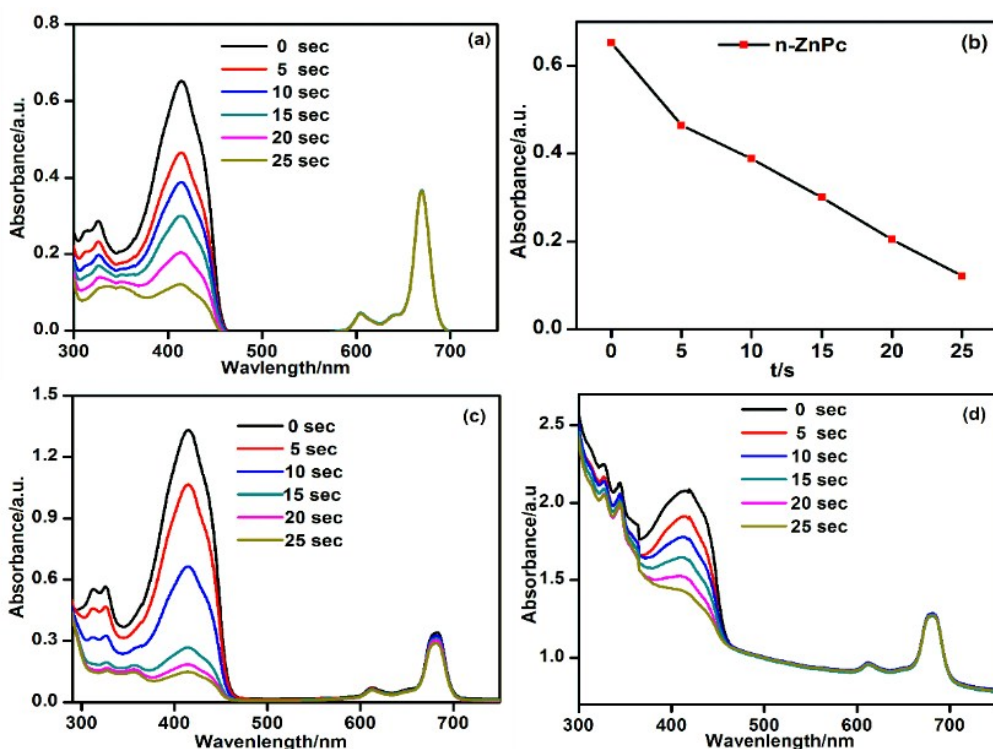


Fig. S6 A typical spectra for the determination of singlet oxygen quantum yield of unsubstituted ZnPc (a), plots of DPBF absorbance versus time of n-ZnPc (b), SiPc-F (c), SWNTs-p-β-CD-SiPc-F (d) in DMF using DPBF as a singlet oxygen quencher. Concentration= 1×10^{-6} mol/L of n-ZnPc and SiPc-F.

4. X-ray photoelectron spectroscopy (XPS)

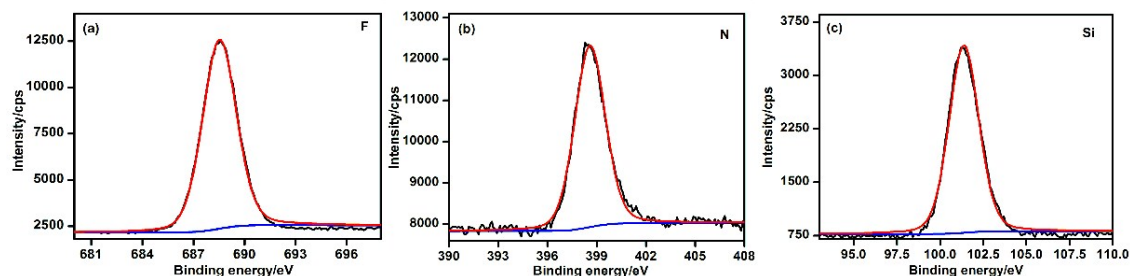


Fig. S7 X-ray photoelectron spectroscopy of SWNTs-p-β-CD-SiPc-F

5. Confocal laser scanning microscopy (CLSM) analysis for the fluorescence recovery of SWNTs-p-β-CD-SiPc-F.

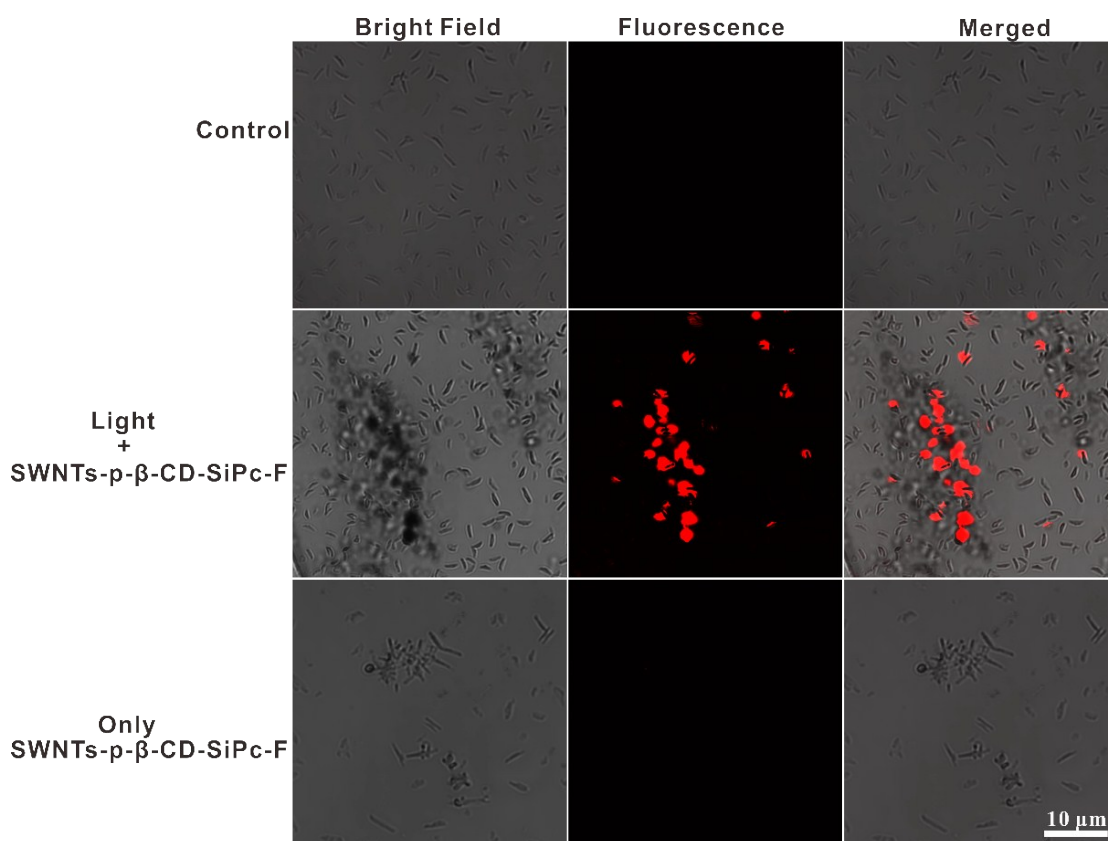


Fig S8. CLSM analysis for the fluorescence recovery of SWNTs-p-β-CD-SiPc-F. The *E. coli* was incubated with SWNTs-p-β-CD-SiPc-F dissolved in 10% DMSO-water solution, and then was irradiated with laser (680 nm) for 10 min. The *E. coli* without laser irradiation and treated with SWNTs-p-β-CD-SiPc-F were used as controls.

References

- [S1] X. H. Peng, S. F. Chen, B. Y. Zheng, B. D. Zheng, Q. F. Zheng, X. S. Li, M. R. Ke and J. D. Huang, *Tetrahedron*, 2017, **73**, 378-384.
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- [S3] N. Nwahara, J. Britton, T. Nyokong, *J. Coord. Chem.*, 2017, **70**, 1601-1616.
- [S4] I. Seotsanyana-Mokhosi, N. Kuznetsova, T. Nyokong, *J. Photochem. Photobiol. C: Chem.*, 2001, **140**, 215-222.

