Electronic Supplementary Information

A specific environment-sensitive near-infrared fluorescent turn-on probe for synergistic enhancement of anticancer activity of chemo-drug

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Figures

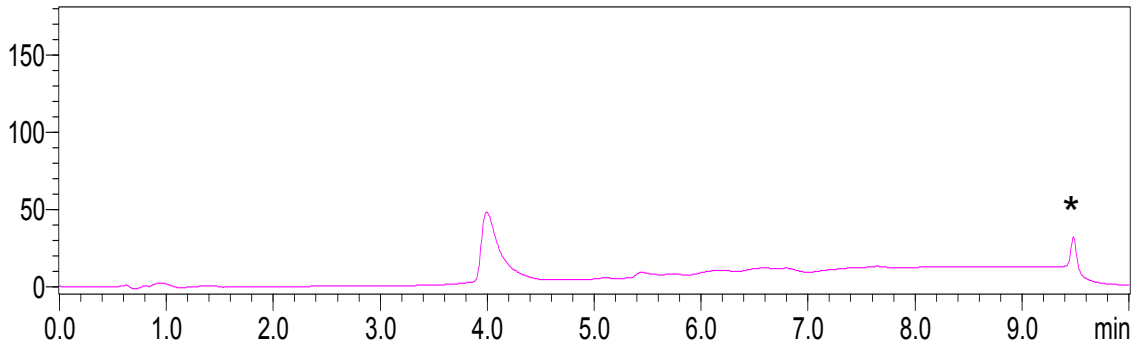

Fig. S1 LC spectrum of N_3-EEGYLFFVFER (the stars represent systemic peaks).

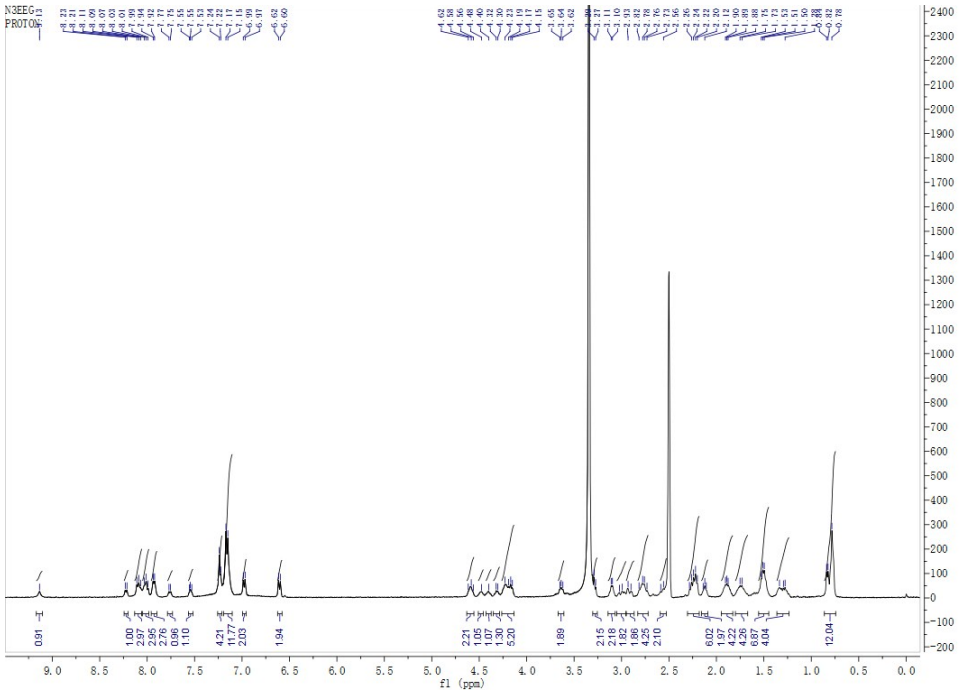

Fig. S2 ^{1}H NMR spectrum of N_3-EEGYLFFVFER in DMSO-d_6.

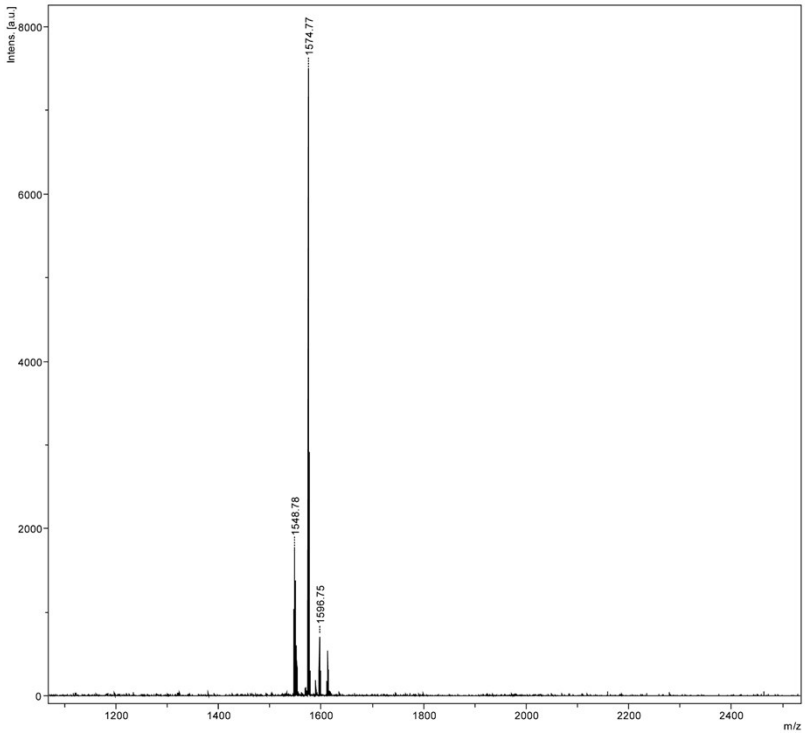

Fig. S3 MALDI-TOF-MS profile of N_3-EEGYLFFVFER.

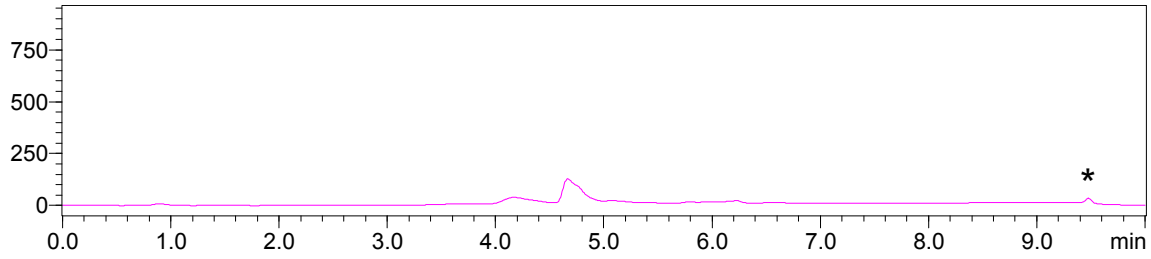

Fig. S4 LC spectrum of DBT-2EEGYLFFVFER (the stars represent systemic peaks).

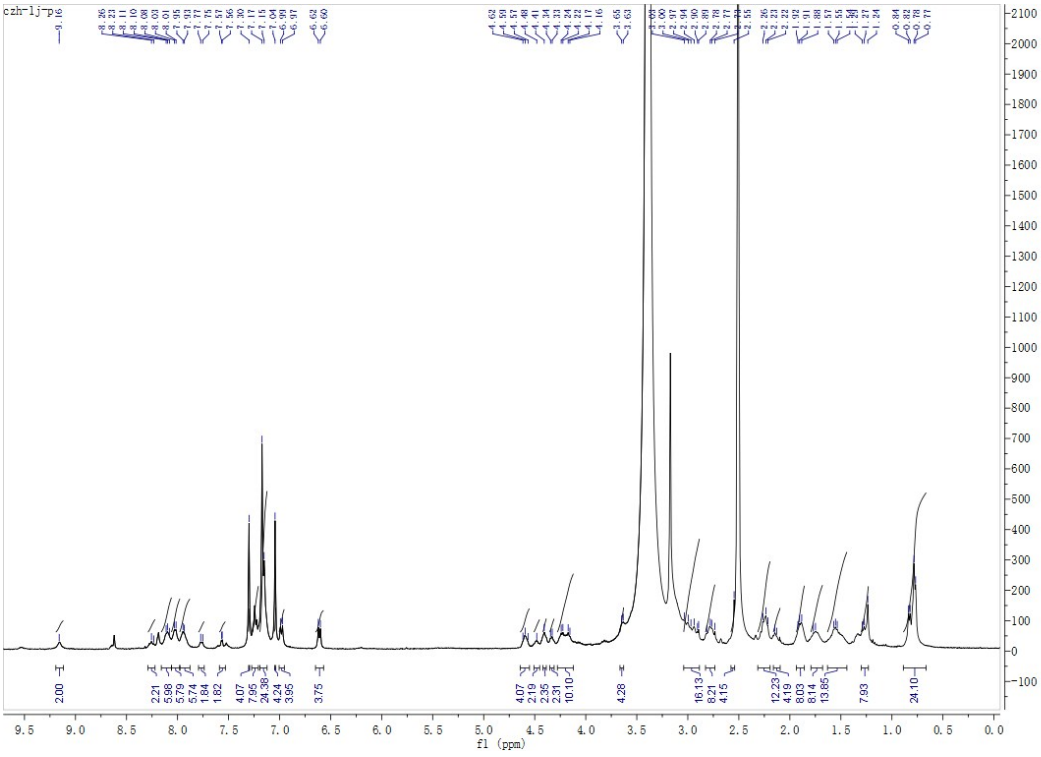

Fig. S5 ^{1}H NMR spectrum of DBT-2EEGYLFFVFER in DMSO-d_6.

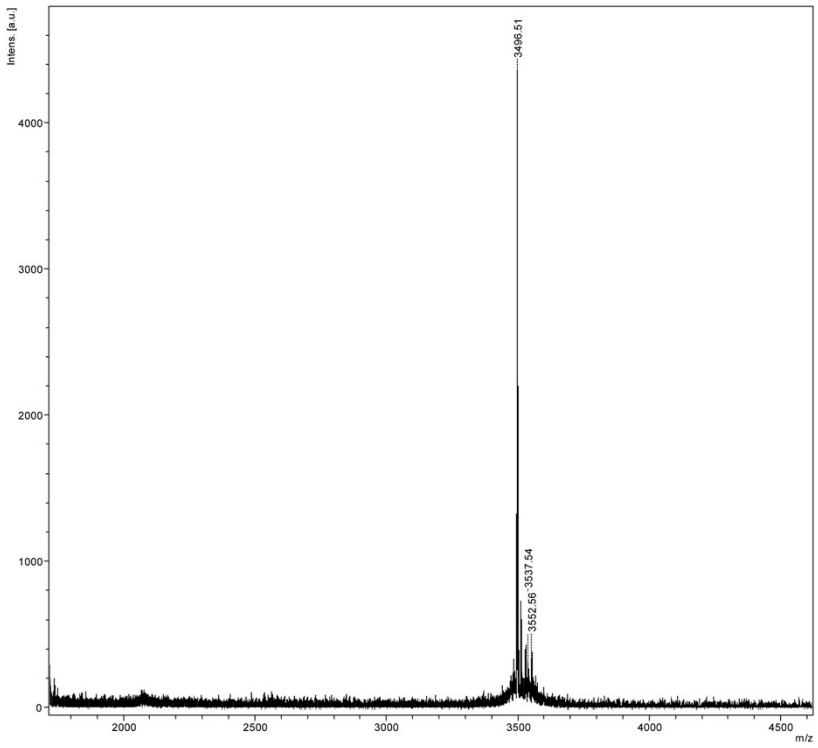

Fig. S6 MALDI-TOF-MS profile of DBT-2EEGYLFFVFER.

Materials and methods

1. Materials

Fmoc-OSu and other Fmoc-amino acids were purchased from GL Biochem (Shanghai, China). 2-Cl-trityl chloride resin (1.0-1.2 mmol g^{-1}) was purchased from Nankai University Resin Co. Ltd. Trypsin, chymotrypsin, pancreatin, proteinase K, ribonuclease A (RNase A), glutathione (GSH), 2′,7′-dichlorodihydrofluorescein diacetate (DCF-DA) and 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT) were purchased from Sigma-Aldrich and used as received without further purification. HER2 protein was obtained from ACROBiosystems. Dulbecco's modified Eagle medium (DMEM), McCoy's 5A Medium, penicillin-streptomycin solution and fetal bovine serum (FBS) were obtained from Gibco (Invitrogen, BioSciences, Ltd., Dublin, Ireland). All the other starting materials were obtained from Alfa. Chemical reagents and solvents were used as received from commercial sources. Bisethynyl-functionalized DBT (BE-DBT) was synthesis according to our previous report.[1]

2. Characterization

^{1}H NMR spectra were measured on a Bruker ARX 400 NMR spectrometer using DMSO-d_6 as a solvent and tetramethylsilane (TMS; δ = 0) was chosen as an internal reference. Matrix-Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) were received on a Bruker Daltonics Autoflex III LRF200-CID (Germany). High-pressure liquid chromatography (HPLC) was carried out at a LUMTECH HPLC (Germany) system using a C_{18}RP column with MeOH (0.1% of TFA) and water (0.1% of TFA) as the eluents. LC-MS was conducted at the LCMS-20AD (Shimadzu) system. UV-vis absorption and photoluminescence (PL) spectra were recorded on a Shimadzu UV-1700 spectrometer and a

Perkin-Elmer LS 55 spectrofluorometer, respectively. Cell imaging studies were performed by confocal laser scanning microscopy (CLSM, Zeiss LSM 410, Jena, Germany).

3. Intracellular detection of ROS

The ROS production of DBT-2EEGYLFFVFER in SKBR-3 cancer cells upon exposure to light was assessed using DCF-DA as the indicator. After incubation with 10 μM of DBT-2EEGYLFFVFER at 37 ^{o}C for 90 min in the dark, SKBR-3 cancer cells were incubated with 1 μM of DCF-DA for 5 min. Subsequently, the cells were washed with 1 × PBS and exposed to white light irradiation (0.1 W cm^{-2}) for 2 min, followed by imaging with CLSM. For DCF detection: excitation at 488 nm and signal collection at 530 ± 10 nm.

References

1 H. Wang, J. Liu, A. Han, N. Xiao, Z. Xue, G. Wang, J. Long, D. Kong, B. Liu, Z. Yang and D. Ding, *ACS Nano*, 2014, **8**, 1475.