SUPPORTING INFORMATION

A Switchable Peptide Sensor for Real-time Lysosomal Tracking

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Contents

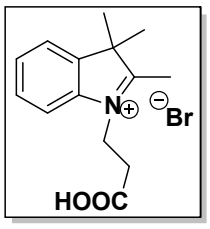
1. General information:

All solvents were dried and distilled before use. Anhydrous dichloromethane (DCM) and dimethyl formamide (DMF) were distilled over $CaCl_2$ and CaH_2 respectively, and kept anhydrous with 4Å molecular sieves. 5-nitrosalicylaldehyde, 2,3,3-trimethyl-3H-indole, 3-bromo-propionic acid were purchased from Aladdin Chemistry Co., Ltd. (shanghai); N,N-Diisopropylethylamine (DIEA), Benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP) were purchased from Suzhou Highfine Biotech Co., Ltd.; Fmoc-protected amino acid were purchased from GL Biochem (shanghai) Ltd..

All melting points were measured with a Bruker Melting-Point B-450 apparatus with open end glass capillary tube. The melting points were not corrected. The ^{1}H and ^{13}C NMR spectra were recorded at room temperature with Bruker AV 400 spectrometer. The analytical "High Performance Liquid Chromatography" (HPLC) was performed with the following parameters: reversed phase, RP-C18 HPLC column (10 μm particle size) and UV detector. The mobile phase was a gradient of 10-90% of methanol aqueous solution containing 0.5‰ TFA at a total flow rate of 0.8 mL/min. The UV absorption peaked at 410 nm of the elution was recorded for analysis. FT-IR spectra were taken on NICOLET 380 FT-IR, Thermo Electron Corp. The UV/Vis spectra and fluorescence spectra were recorded with a Varian Cary 100 Conc UV-Visible Spectrometer and a Varian Cary Eclipse Fluorescence Spectrometer, respectively. pH was measured by a Mettler Toledo FE 20K pH meter.

2. General procedure of indolinobenzospiropyran：

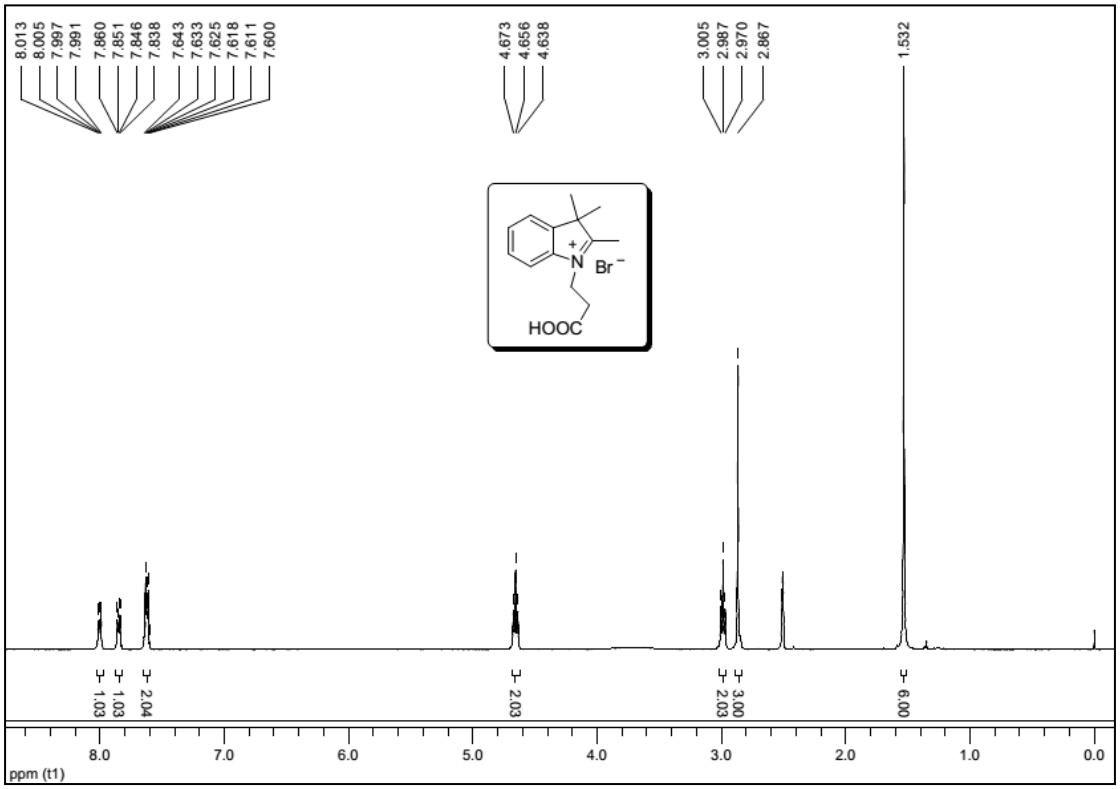
1-(2-carboxyethyl)-2,3,3-trimetyl-3H-indolium bromide: [1]



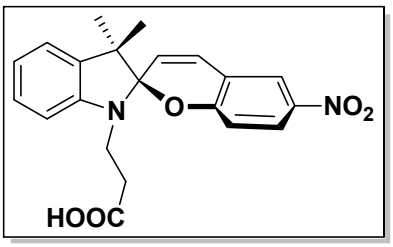
1-(2-carboxyethyl)-2,3,3-trimetyl-3H-indolium bromide was prepared by a slight modification of previous reported procedure. A mixture of 2,3,3-trimethyl-3H-indole (10.0 g, 62.8 mmol) and 3-bromo-propionic acid (19.2 g, 125.6 mmol) in dry CH_3CN (60 mL) was refluxed for 12 h. CH_3CN was removed under reduced pressure to obtain a dark purple residue. Then, the residue was washed three times with Et_2O (60 mL) to remove unreacted starting material. The crude product was recrystallized with dichloromethane/acetone (1/5,v/v) to get a pale purple solid (8.4 g, 42.9%). ^{1}H

NMR (400 MHz, DMSO-d_6): δ 1.53 (s, 6H), 2.87 (s, 3H), 2.99 (t, J = 7.2 Hz, 2H), 4.66 (t, J = 7.2 Hz, 2H), 7.60-7.65 (m, 2H), 7.83-7.86 (m, 1H), 7.99-8.02 (m, 1H).

^{1}H NMR:

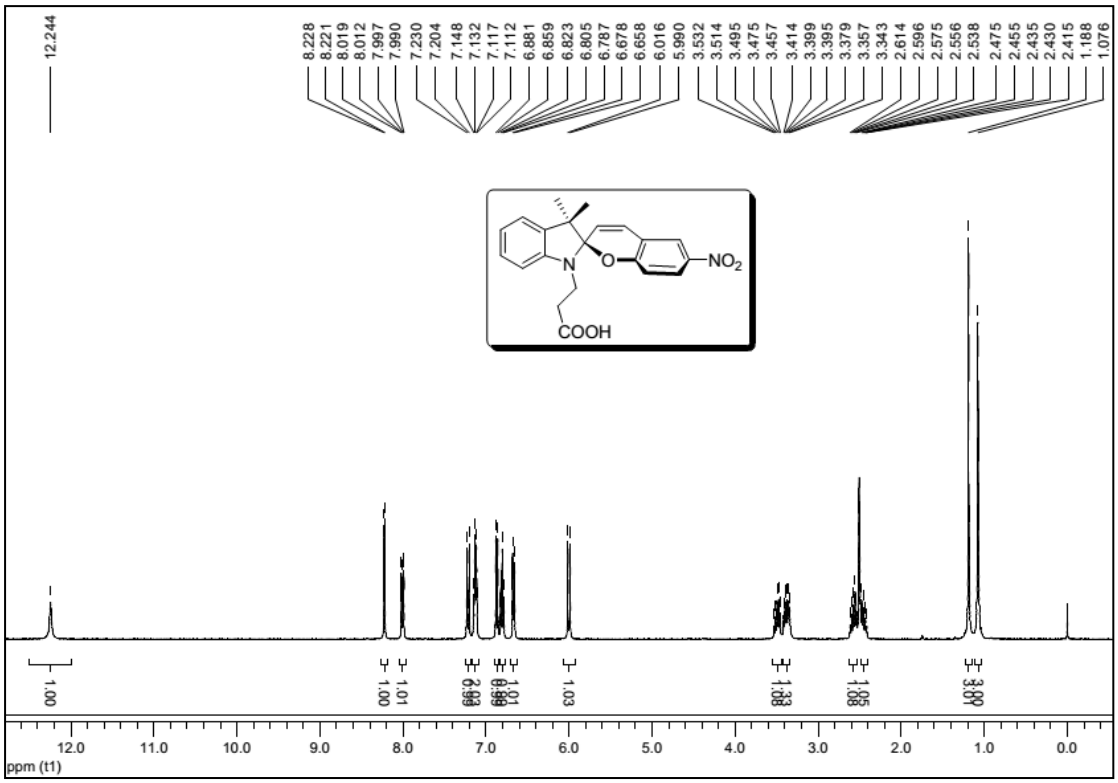


Synthesis of 3, 3-bimethyl-6-nitrospiro-[(2H)-1-benzopyran-2, 2-indoline] derivative: [2]



The indolinobenzospiropyran derivative was synthesized by a similar procedure reported previously. The light was avoided during the preparation. A solution of 1-(2-carboxyethyl)-2,3,3-trimetyl-3H-indolium bromide (8.4 g, 26.9 mmol), 5-nitrosalicylaldehyde (4.5 g, 26.9 mmol) and triethylamine (4.5 mL, 32.0 mmol) was refluxed in EtOH (70 mL) under argon for 6 h. The precipitate was filtered and washed with cool EtOH to obtain the green powder (7.3 g, 71.6%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.08 (s, 3H), 1.19 (s, 3H), 2.41-2.48 (m, 1H), 2.53-2.62 (m, 1H), 3.34-3.42 (m, 1H), 3.46-3.54 (m, 1H), 6.00 (d, J = 10.4 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 6.81 (t, J = 7.2 Hz, 1H), 6.87 (d, J = 8.8 Hz, 1H), 7.11-7.15 (m, 2H), 7.22 (d, J = 10.4 Hz, 1H), 7.99-8.02 (dd, J = 2.8 Hz, 8.8 Hz, 1H), 8.23 (d, J = 2.8 Hz, 1H), 12.24 (s, 1H).

^{1}H NMR:



3. General procedure for the synthesis of peptide 1:

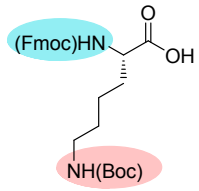
Fmoc Removal: The Fmoc protecting group was cleavage by treatment with 20% piperidine in DMF (2×20 mL, 5 min each) under microwave radio condition (35 W, 60±5 °C, 5 min). Then, the resin was washed 7×20 mL with DMF (*ca*. 1 min each) to remove the last traces of piperidine. A positive Kaiser test confirmed the cleavage of the Fmoc group and the presence of free amino function.

Standard Fmoc solid phase peptide synthesis techniques (SPPS): Each amino acid was attached using 0.81 mmol/g loading Fmoc Rink amide resin under microwave radio (35 W, 60±5 °C, 20 min). Then, the resin was washed 7×8 mL with DMF (*ca*.1 min each) to remove the last traces of the amino acid. A negative Kaiser test confirmed the attachment of the corresponding amino acid.

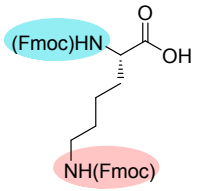
Cleavage from the Resin: Cleavage of the product from the resin was achieved by treatment with a mixture of TFA/H_2O/triisopropylsilane (95:2.5:2.5) for 2.5 h. The yellow cleavage mixture was collected by filtration and the resin was washed twice with pure TFA (10 mL). The filtrates were

combined and concentrated under vacuum to obtain an oily residue. The peptide was precipitated by adding dry diethyl ether to the oil, followed by centrifugation of the mixture. To obtain the yellow hydrochloride salt, the solid was dissolved in water (10 mL), acidified with hydrochloric acid (10%, 1 mL) and lyophilized. This step was repeated three times. Purity of the peptides was checked by HPLC on a RP-C18 column using water/MeOH as eluent.

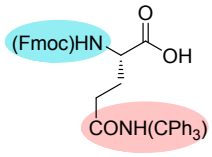
As starting Fmoc-based amino acids were used as followed:



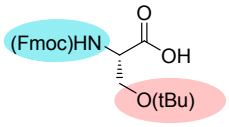
Fmoc-Lys(Boc)-OH(K)



Fmoc-Lys(Fmoc)-OH(K)



Fmoc-Gln(CPh_3)-OH (Q)

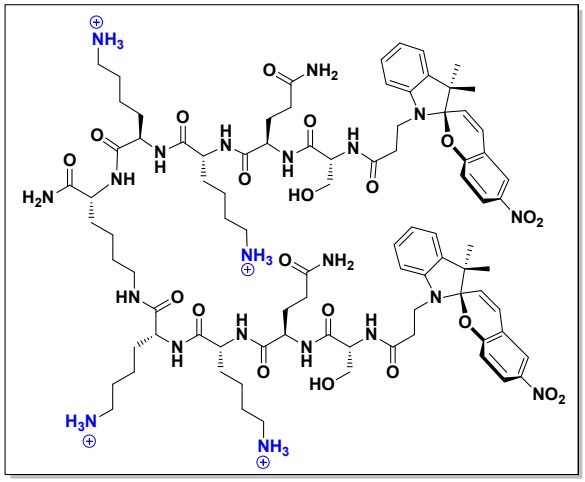


Fmoc-Ser(tBu)-OH (S)

Synthesis of Lys-(Lys-Lys-Gln-Ser-SP)2 (Peptide 1):

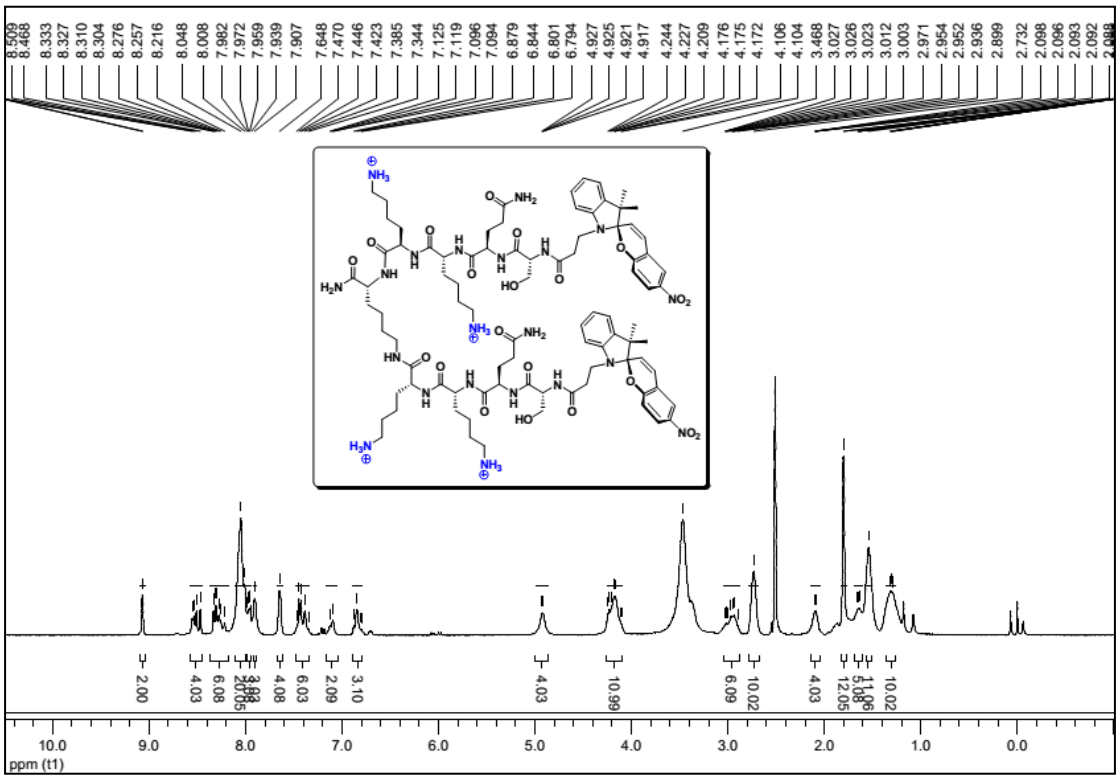
Rink amide resin (617 mg, 810 μmol/g, 500 μmol, 1 equiv.) was weighed out into plastic peptide synthesis vessel and allowed to swell in DMF (15 mL) for 2 h. Then, the Fmoc protection group was removed by treatment with piperidine (20%) in DMF (15 mL) under microwave radio condition. After an intensive washing cycle with DMF, the following four amino acid were attached under microwave condition for SPPS: Fmoc-Lys(Fmoc)-OH (1.5 mmol, 3 equiv), PyBOP (1.5 mmol, 3 equiv) and N-methyl-morpholine (4.0 mmol, 8 equiv); Fmoc-protected amino acid (3.0 mmol, 6.0 equiv), PyBOP (3.0 mmol, 6.0 equiv) and N-methyl-morpholine (8.0 mmol, 16.0 equiv) in DMF (25.0 mL). Then, the resin was transferred into a glass peptide synthesis vessel, and the reaction of peptide and indolinobenzospiropyran derivative (3.0 mmol, 6.0 equiv) was conducted in the presence of PyBOP (3.0 mmol, 6.0 equiv), DIEA (8.0 mmol, 16.0 equiv); The mixture was shaken for 6 h to ensure quantitative coupling. The final product was cleaved from the solid support according to the general procedure for the Rink amide resin.

Peptide 1

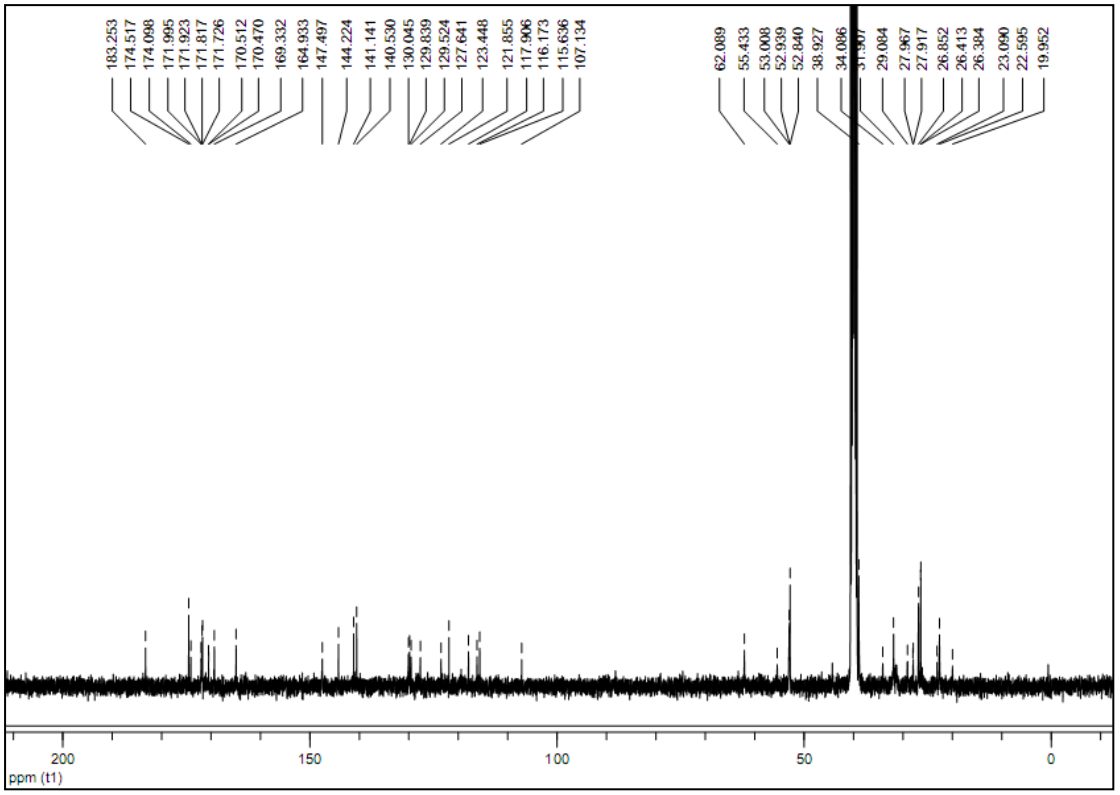


A bright orange solid (250 mg, 123 mmol, Yield: 24.6%, purity HPLC: 99.8%), Mp: 175.3-178.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.29-1.33 (m, 10H), 1.54 (s, 11H), 1.64-1.66 (m, 5H), 1.80 (d, J = 2.4 Hz, 12H), 2.08-2.10 (m, 4H), 2.73 (s, 10H), 2.89-3.03 (m, 6H), 4.10-4.25 (m, 11H), 4.91-4.93 (m, 4H), 6.79-6.88 (m, 3H), 7.09-7.13 (m, 2H), 7.34-7.47 (m, 6H), 7.65 (s, 4H), 7.91 (s, 3H), 7.94-7.99 (m, 3H), 8.00-8.05 (m, 20H), 8.21-8.34 (m, 6H), 8.46-8.56 (m, 4H), 9.07 (d, J = 2.0 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 183.3, 174.5, 174.1, 172.0, 171.9, 171.8, 171.7, 170.5, 170.4, 169.3, 164.9, 147.5, 144.2, 141.1, 140.5, 130.1, 129.8, 129.5, 127.6, 123.5, 121.9, 117.9, 116.2, 115.6, 107.1, 62.1, 55.4, 53.0, 52.9, 52.8, 38.9, 34.1, 31.9, 29.1, 28.0, 27.9, 26.9, 26.5, 26.4, 23.1, 22.6, 20.0. FT-IR (pure): ν [cm^{-1}] 3423, 2360, 1654, 1608, 1534, 1458, 1384, 1341, 1144, 1090, 993, 628. MALDI-TOF(m/z): calcd for $C_{88}H_{125}N_{21}O_{21}$ 1811.9359, found $[M+H]^+$ 1812.9272.

^{1}H NMR



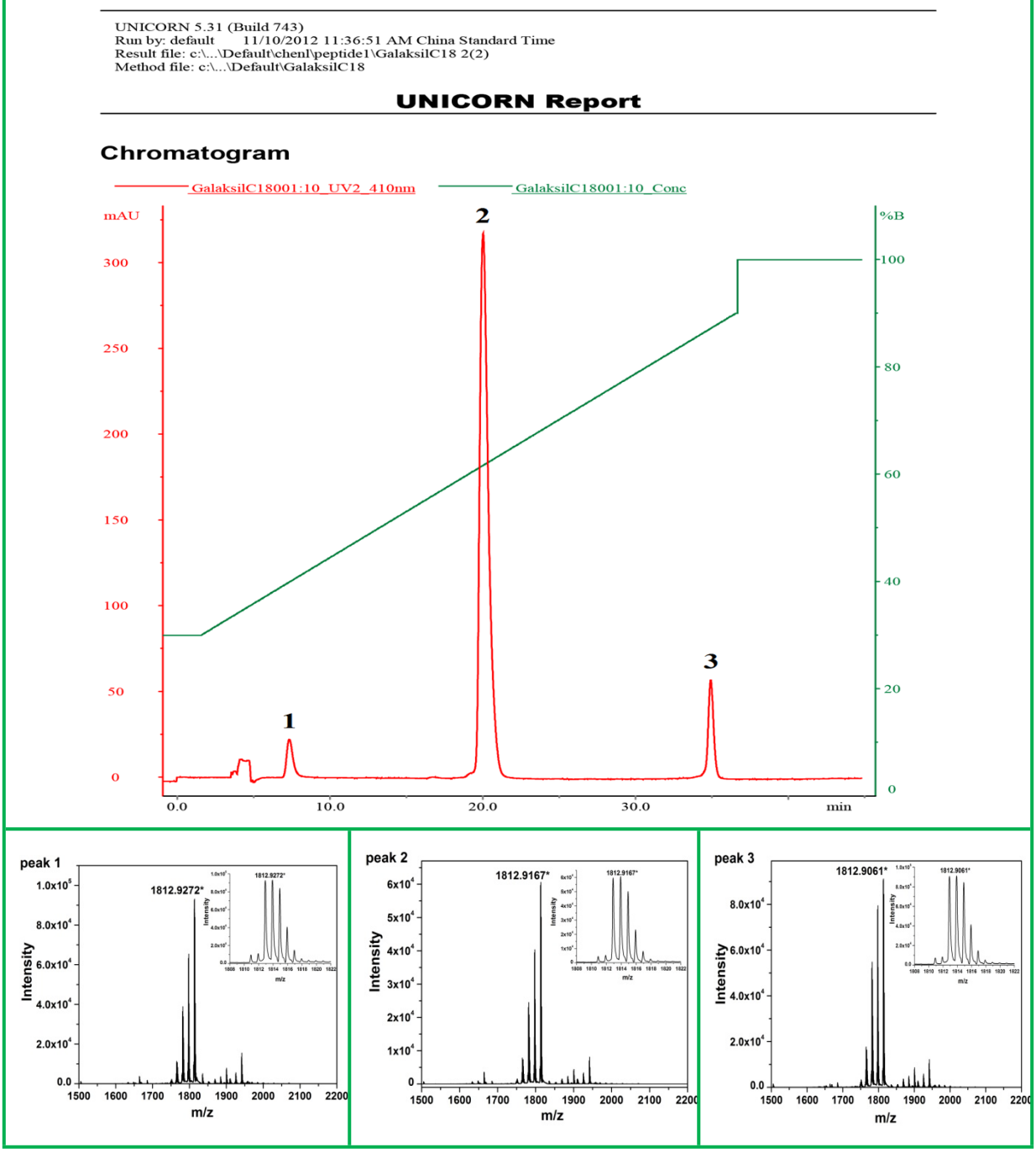
^{13}C NMR



4. HPLC analysis report and MALDI-TOF MS characterization of peptide 1

Table S1 HPLC analysis report and MALDI-TOF MS characterization of peptide **1**

Peak 1	Peak 2	Peak 3



Note: According to the MALDI-TOF MS reports, we can confirm that these three peaks mainly represent three different formats of peptide **1**, which were attributed to the effect of TFA in mobile phase. Through relevant literatures and the analysis of polarity of the peaks, we suppose that peak

1, **2** and **3** represents the "Mc-form", "McH$^+$-form" and "Sp-form", respectively (see Figure S0).[3]

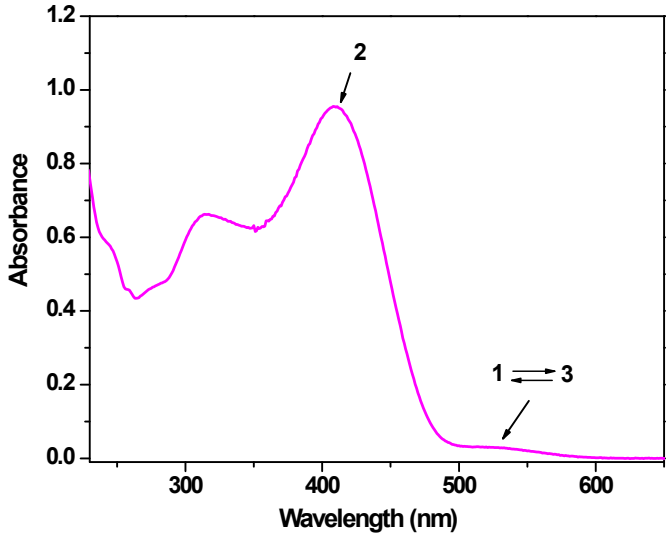


Figure S0. Absorbance of peptide dissolved in mobile phase containing 0.5 ‰ TFA. McH$^+$-form (**2**) is characterized by a sharp absorbance at 410nm, while a relative mild absorbance near 515nm suggests equilibrium between Mc-form (**1**) and Sp-form (**3**).

5. UV-Vis and Fluorescence experiments:

All fluorescence and absorption spectra were recorded using a VARIAN Fluorescence and UV-visible spectrometer at 20 °C. The samples were each excited at the wavelength appropriate for the fluorescent peptide. The slit widths were set to 10 nm for excitation and emission. The data points were collected at 1 nm increments with a 0.1 s integration period. All spectra were corrected for intensity using the manufacturer-supplied correction factors and corrected for background fluorescence and absorption by subtracting a blank scan of the buffer system.

UV-Vis absorption and fluorescence spectroscopies were studied in Tris-HCl buffer solutions (TBS) at a pH range from 2.0 to 10.0. Each sample was treated with visible-light for 10 min before test in order to make sure the SP fluorophores were in the closed-form, and corresponding absorption and fluorescence emission were then recorded as a function of time for 12 h in darkness without UV light.

(1) pH = 2.0

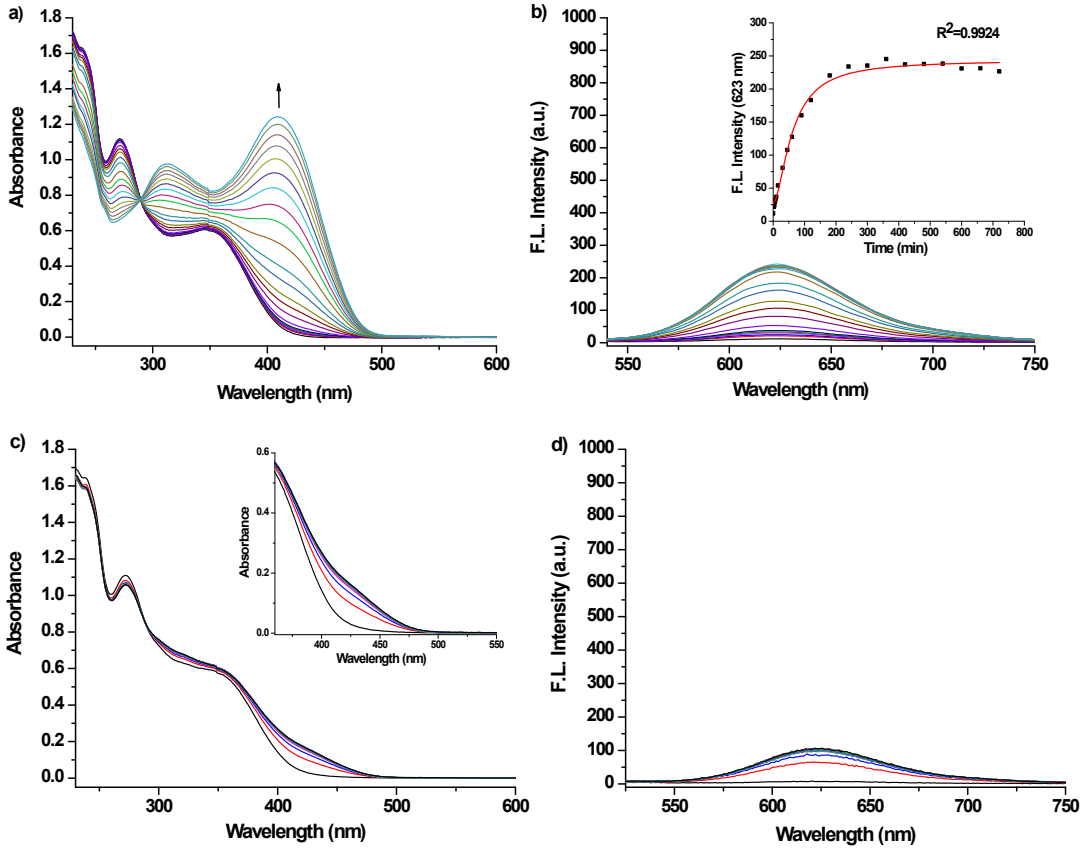


Figure S1 Time dependent on (**a**) Absorbance and (**b**) Emission (λ_{ex} = 411 nm, inset: time course of fluorescence intensity enhancement at λ_{max} = 623 nm) spectra of peptide **1** (50 μM) in TBS (pH 2.0, 50 mM Tris., 50 mM NaCl, 20°C) in darkness for 0~12 h, respectively; (**c**) Absorbance (inset: partial enlarged view from 360 nm to 550 nm) and (**d**) Emission spectra of peptide **1** (50 μM) as a function of irradiation time with UV-light (365 nm, *ca.* 0.2 W/cm^2 for 0~2 h) in TBS (pH 2.0, 50 mM Tris., 50 mM NaCl, 20°C), respectively.

(2) pH = 4.0

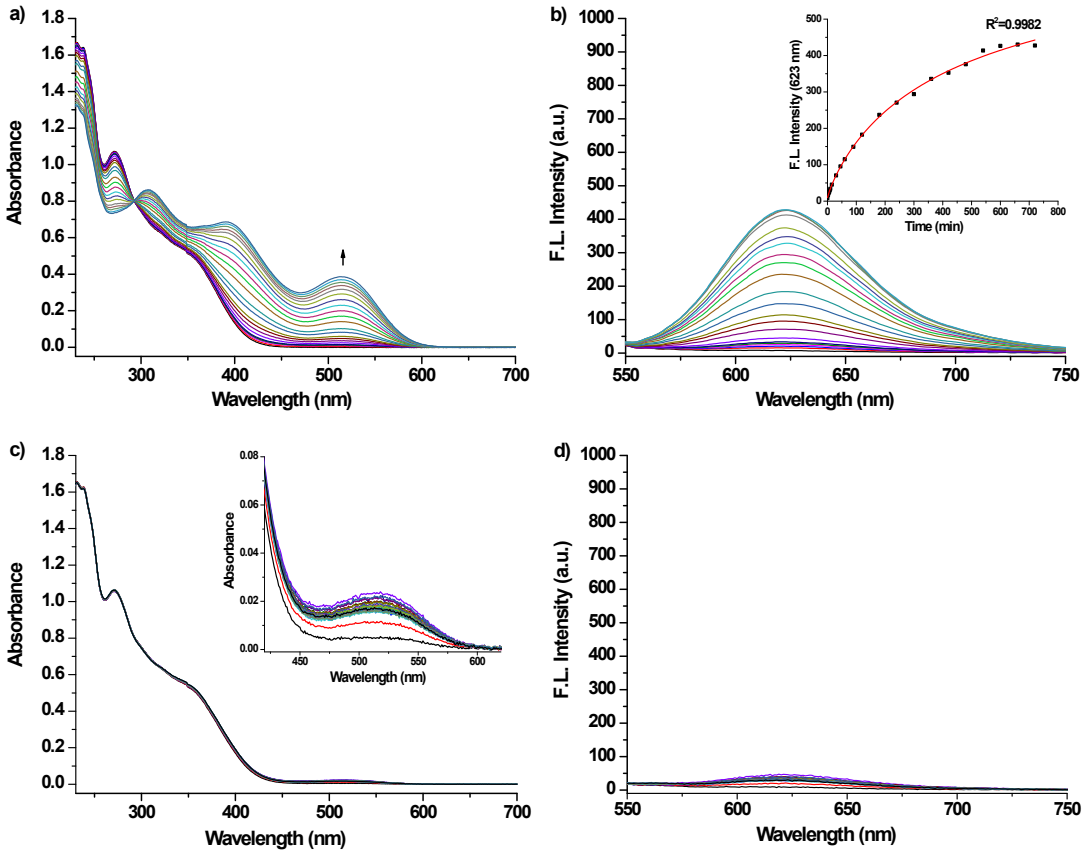
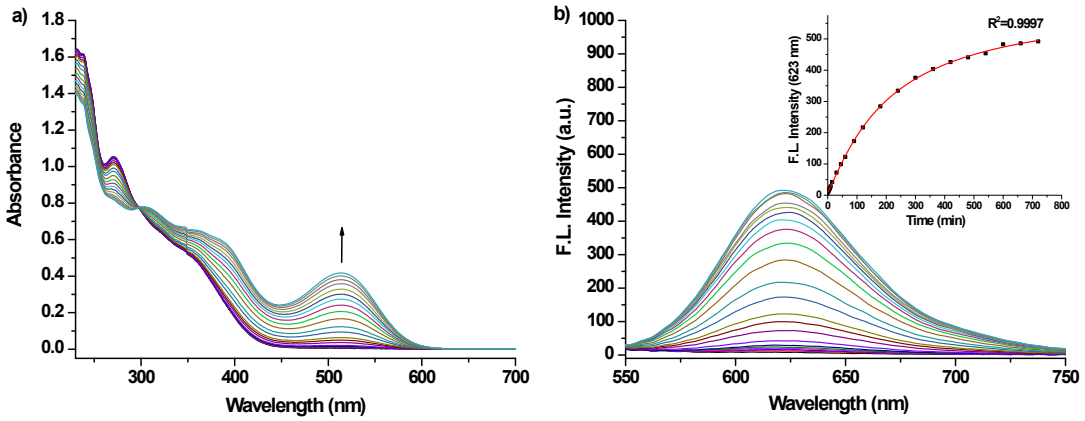


Figure S2. Time dependent on (**a**) Absorbance and (**b**) Emission (λ_{ex} = 514 nm, inset: time course of fluorescence intensity enhancement at λ_{max} = 623 nm) spectra of peptide **1** (50 μM) in TBS (pH 4.0, 50 mM Tris., 50 mM NaCl, 20 °C) in darkness for 0~12 h, respectively; (**c**) Absorbance (inset: partial enlarged view from 420 nm to 620 nm) and (**d**) Emission spectra of peptide **1** (50 μM) as a function of irradiation time with UV-light (365 nm, *ca.* 0.2 W/cm^2 for 0~2 h) in TBS (pH 4.0, 50 mM Tris., 50 mM NaCl, 20°C), respectively.

(3) pH = 4.6



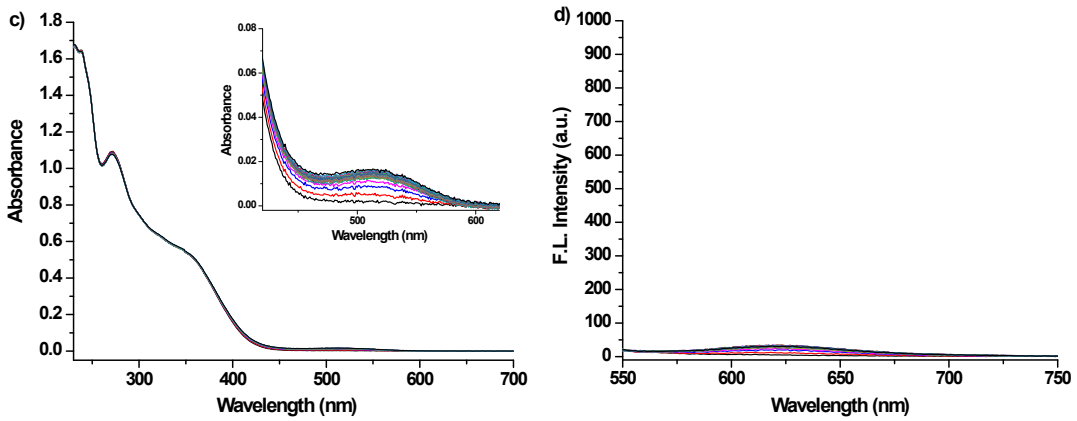


Figure S3. Time dependent on (**a**) Absorbance and (**b**) Emission (λ_{ex} = 514 nm, inset: time course of fluorescence intensity enhancement at λ_{max} = 623 nm) spectra of peptide **1** (50 μM) in TBS (pH 4.6, 50 mM Tris., 50 mM NaCl, 20°C) in darkness for 0~12 h, respectively; (**c**) Absorbance (inset: partial enlarged view from 420 nm to 620 nm) and (**d**) Emission spectra of peptide **1** (50 μM) as a function of irradiation time with UV-light (365 nm, *ca.* 0.2 W/cm^2 for 0~2 h) in TBS (pH 4.6, 50 mM Tris., 50 mM NaCl, 20°C), respectively.

(4) pH = 5.2

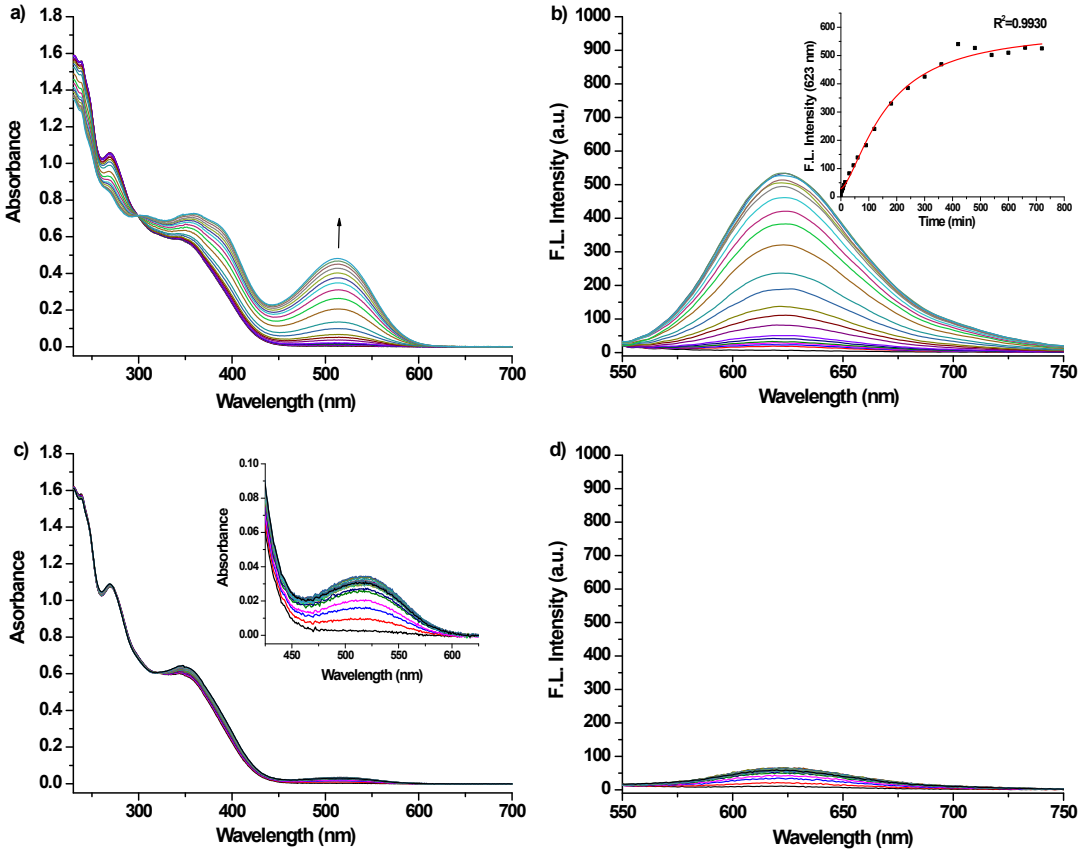


Figure S4. Time dependent on (**a**) Absorbance and (**b**) Emission (λ_{ex} = 514 nm, inset: time course of fluorescence intensity enhancement at λ_{max} = 623 nm) spectra of peptide **1** (50 μM) in TBS (pH 5.2, 50 mM Tris., 50 mM NaCl,

20°C) in darkness for 0~12 h, respectively; (**c**) Absorbance (inset: partial enlarged view from 425 nm to 625 nm) and (**d**) Emission spectra of peptide **1** (50 μM) as a function of irradiation time with UV-light (365 nm, *ca.* 0.2 W/cm^2 for 0~2 h) in TBS (pH 5.2, 50 mM Tris., 50 mM NaCl, 20°C), respectively.

(5) pH = 6.0

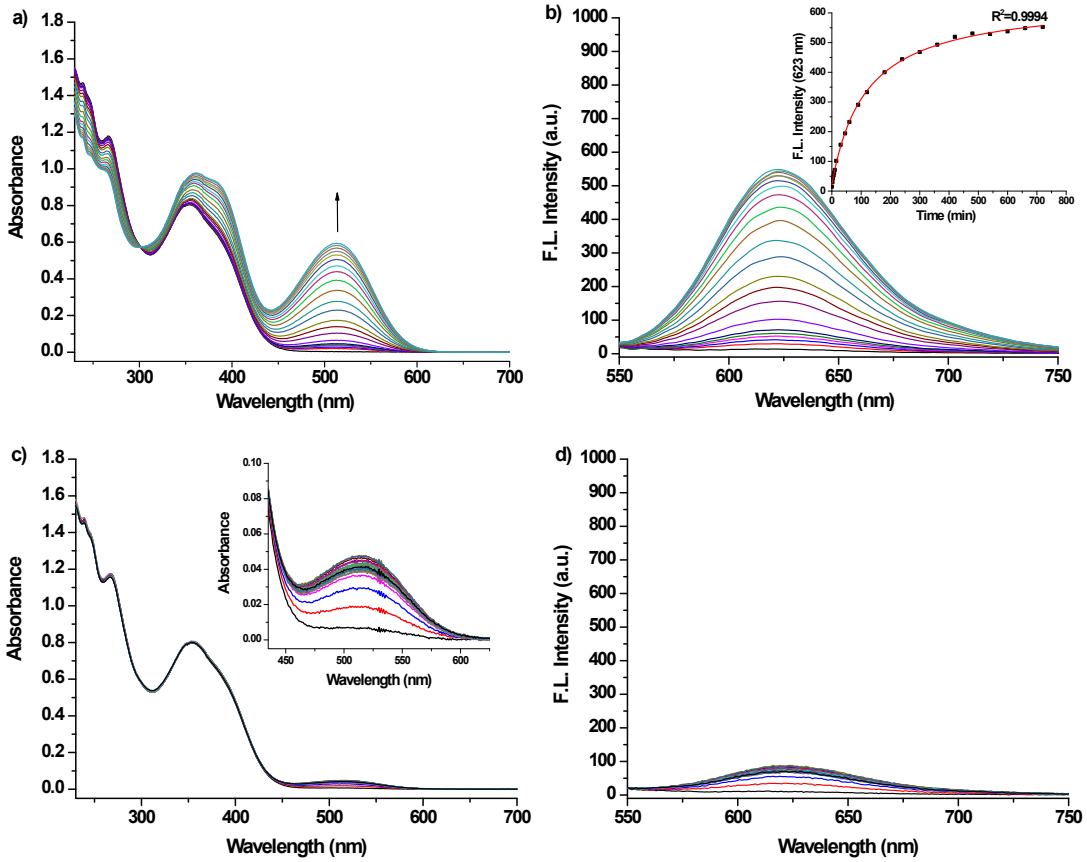


Figure S5. Time dependent on (**a**) Absorbance and (**b**) Emission (λ_{ex} = 514 nm, inset: time course of fluorescence intensity enhancement at λ_{max} = 623 nm) spectra of peptide **1** (50 μM) in TBS (pH 6.0, 50 mM Tris., 50 mM NaCl, 20°C) in darkness for 0~12 h, respectively; (**c**) Absorbance (inset: partial enlarged view from 435 nm to 625 nm) and (**d**) Emission spectra of peptide **1** (50 μM) as a function of irradiation time with UV-light (365 nm, *ca.* 0.2 W/cm^2 for 0~2 h) in TBS (pH 6.0, 50 mM Tris., 50 mM NaCl, 20°C), respectively.

(6) pH = 7.4

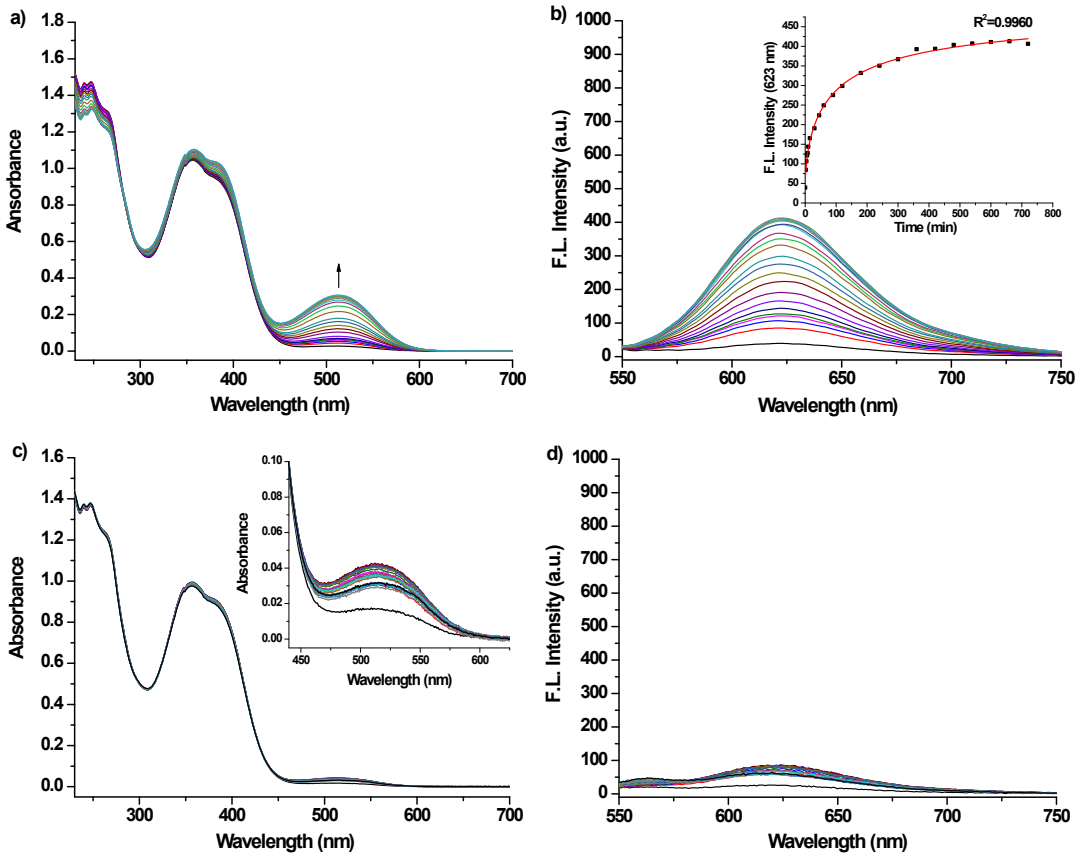
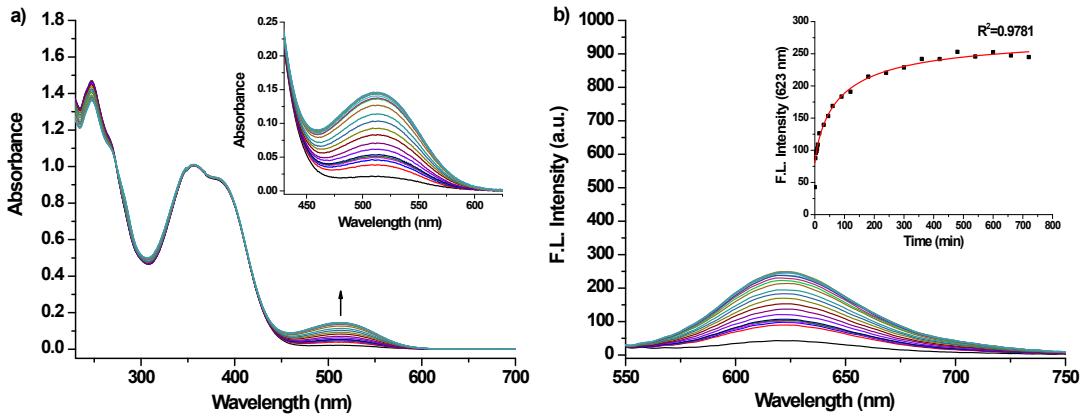


Figure S6. Time dependent on (**a**) Absorbance and (**b**) Emission (λ_{ex} = 514 nm, inset: time course of fluorescence intensity enhancement at λ_{max} = 623 nm) spectra of peptide **1** (50 μM) in TBS (pH 7.4, 50 mM Tris., 50 mM NaCl, 20°C) in darkness for 0~12 h, respectively; (**c**) Absorbance (inset: partial enlarged view from 440 nm to 625 nm) and (**d**) Emission spectra of peptide **1** (50 μM) as a function of irradiation time with UV-light (365 nm, *ca.* 0.2 W/cm^2 for 0~2 h) in TBS (pH 7.4, 50 mM Tris., 50 mM NaCl, 20°C), respectively.

(7) pH = 8.0



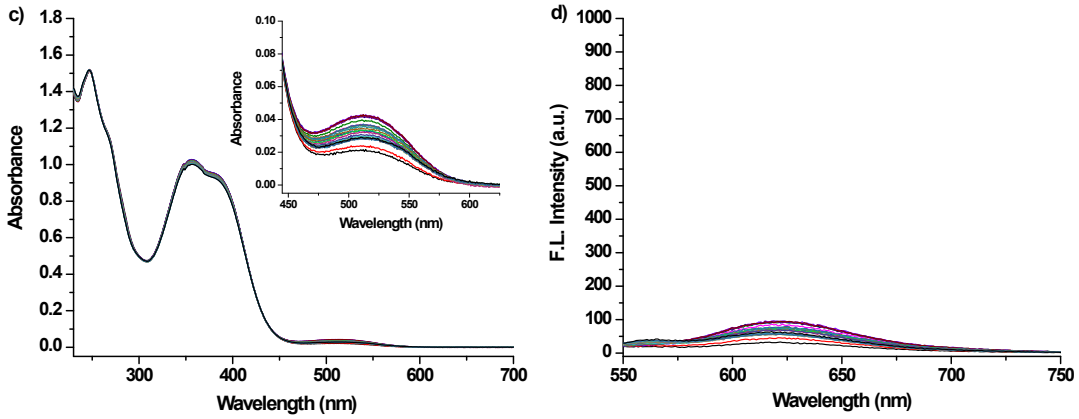


Figure S7. Time dependent on (**a**) Absorbance (inset: partial enlarged view from 430 nm to 625 nm) and (**b**) Emission (λ_{ex} = 514 nm, inset: time course of fluorescence intensity enhancement at λ_{max} = 623 nm) spectra of peptide **1** (50 μM) in TBS (pH 8.0, 50 mM Tris., 50 mM NaCl, 20°C) in darkness for 0~12 h, respectively; (**c**) Absorbance (inset: partial enlarged view from 445 nm to 625 nm) and (**d**) Emission spectra of peptide **1** (50 μM) as a function of irradiation time with UV-light (365 nm, *ca.* 0.2 W/cm^2 for 0~2 h) in TBS (pH 8.0, 50 mM Tris., 50 mM NaCl, 20°C), respectively.

(8) pH=10.0

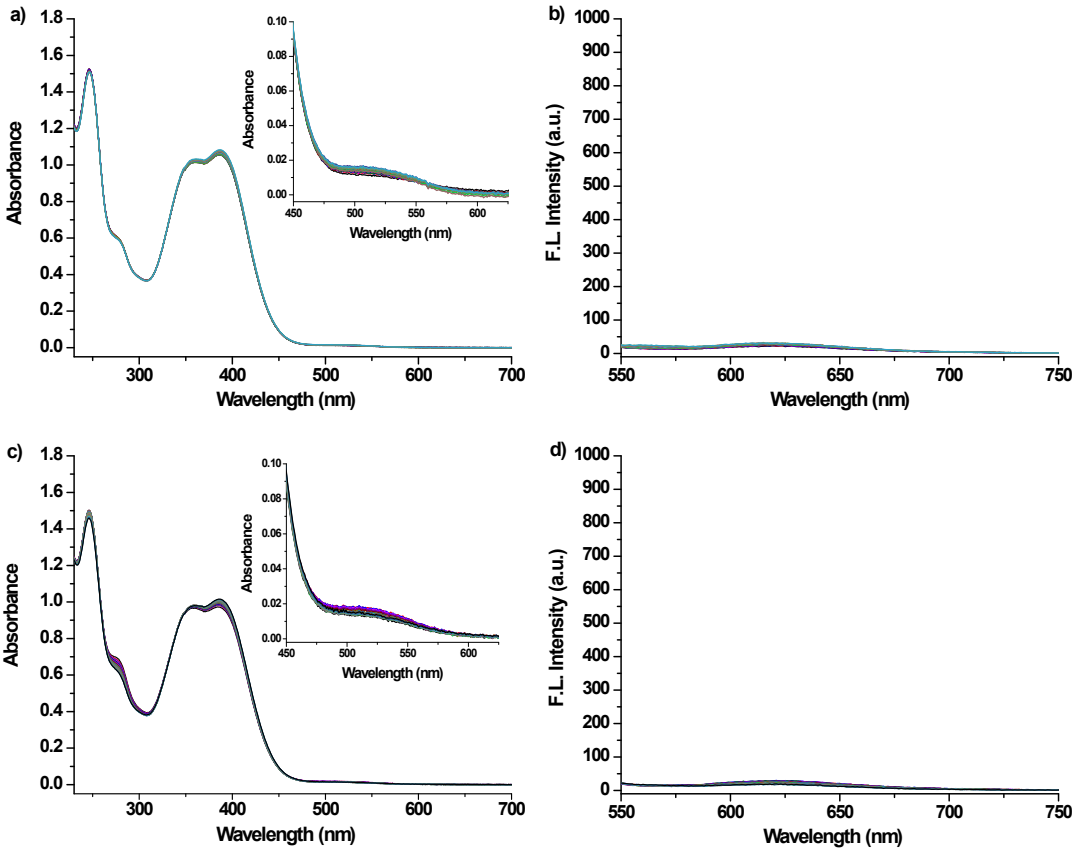


Figure S8. Time dependent on (**a**) Absorbance (inset: partial enlarged view from 450 nm to 625 nm) and (**b**)

Emission spectra of peptide **1** (50 μM) in TBS (pH 10.0, 50 mM Tris., 50 mM NaCl, 20°C) in darkness for 0~12 h, respectively; (**c**) Absorbance (inset: partial enlarged view from 450 nm to 625 nm) and (**d**) Emission spectra of peptide **1** (50 μM) as a function of irradiation time with UV-light (365 nm, *ca.* 0.2 W/cm^2 for 0~2 h) in TBS (pH 10.0, 50 mM Tris., 50 mM NaCl, 20°C), respectively.

6. Fluorescence quantum yield and Lifetime measurements

Absolute fluorescence quantum yield and Lifetime were measured with Fluoromax-4 Spectrofluorometer (HORIBA Scientific) and Life Spec-ps (EDINBURGH INSTRUMENTS), respectively. Samples are dissolved in TBS (50 mM Tris, 50 mM NaCl, 20°C, pH 2.0~10.0) and placed in darkness for 12 h before test.

Table S2. Absolute quantum yield and Lifetime of peptide **1** at different range of pHs in TBS (50 mM Tris, 50 mM NaCl, 20°C).

pH	Absolute quantum yield	Lifetime	
	Φ (%) ± SD[a]	τ (ns)	χ^2 (%)
2.0 ± 0.1	1.52±0.08	0.36	1.067
4.0 ± 0.1	2.79±0.17	0.37	1.059
4.6 ± 0.1	2.83±0.19	0.37	1.020
5.2 ± 0.1	2.87±0.15	0.38	1.004
6.0 ± 0.1	3.10±0.28	0.38	1.072
7.4 ± 0.1	2.53±0.19	0.37	1.012
8.0 ± 0.1	1.54±0.21	0.37	1.098
10.0 ± 0.1	-	-	-

[a] Results were presented as mean ± SD (n = 3).

7. Cell experiments:

7.1 Cell imaging:

A549 cells were seeded in a 35 mm petri dish with a glass cover slide and allowed to adhere for 24 h. The cells were washed and incubated with peptide **1** (10 μM) in RPMI-1640 medium for 1 h at either 4 or 37 °C. Cell imaging was then carried out after washing the cells with PBS (pH = 7.4) with confocal laser scanning microscope (Olympus FluoView FV1000, 60× oil-immersion objective).Channel: excitation: 515 nm, emission collected: 600-650 nm.

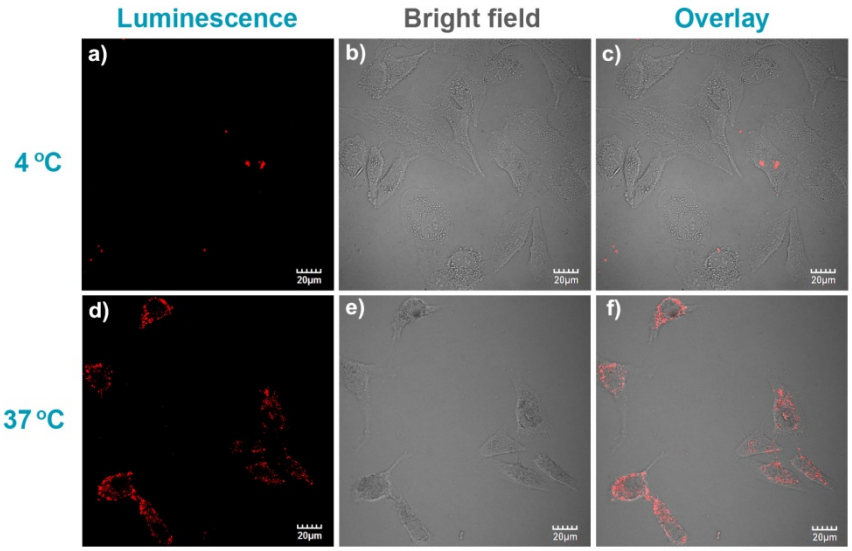


Figure S9. Confocal luminescence image (xy-scan) and bright-field images of A549 cells incubated with peptide **1** (10 μM) for **1** h at 4 °C (**a**, **b** and **c**) and 37 °C (**d**, **e** and **f**) in RPMI-1640 medium.

7.2 Co-localization imaging of Cell:[4]

A549 cells were seeded in a 35 mm petri dish with a glass cover slide. After overnight culture, cells were incubated with peptide **1** (10 μM) in RPMI-1640 medium at 37 °C under 5% CO_2 for 1 h and the medium was replaced with fresh medium. Then, cells were stained with LTG (0.1 μM) and Hoechst 33258 (10 μg/mL) for another 5 min. Before imaging, the cells were washed with PBS (pH = 7.4) solution for three times. Then, the images were taken with confocal laser scanning microscope .

For confocal image: Channel 1: excitation: 515 nm, emission collected: 600-650 nm; Channel 2: excitation: 488 nm, emission collected: 500-550 nm; Channel 3: excitation: 405 nm, emission collected: 420-470 nm.

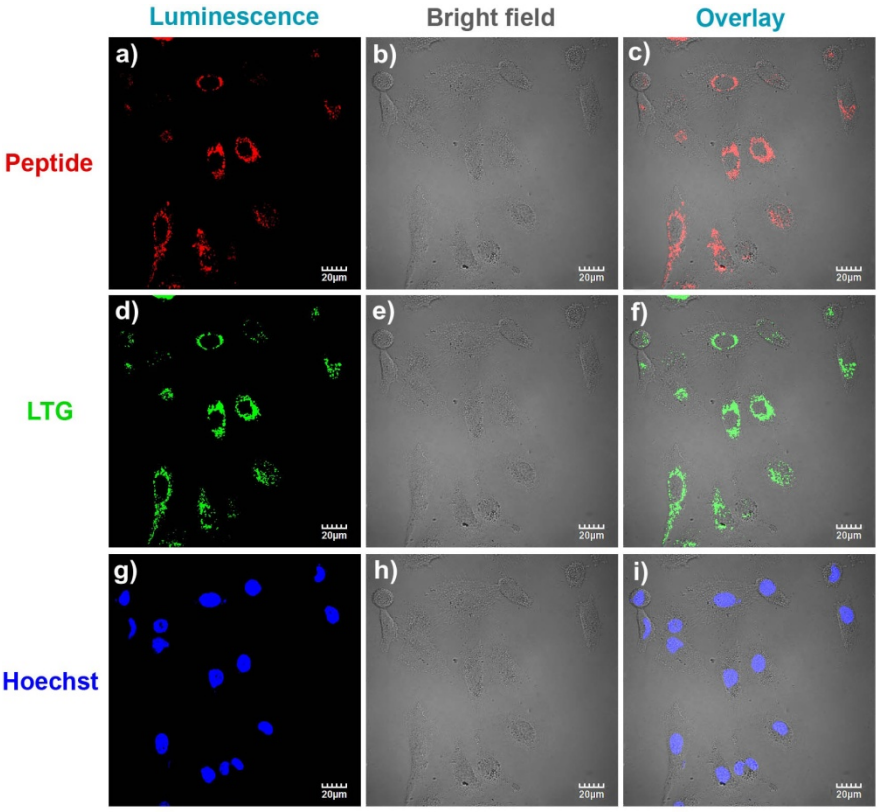


Figure S10. Cellular uptake of peptide **1**, Lyso Tracker Green DND-26 (LTG) and Hoechst 33258 observed by confocal laser scanning microscopy in A549 cells. First row: (**a**) 10 μM peptide **1** (Channel 1: excitation: 515 nm, emission collected: 600-650 nm), (**b**) bright field, (**c**) overlay of (**a**) and (**b**); Second row: (**d**) 0.1 μM LTG (Channel 2: excitation: 488 nm, emission collected: 500-550 nm); (**e**) bright field, (**f**) overlay of (**d**) and (**e**); Third row: (**g**) 10 μg/mL Hoechst 33258 (Channel 3: excitation: 405nm, emission collected: 420-470 nm), (**h**) bright field, (**i**) overlay of (**g**) and (**h**).

7.3 Photoswitchable lysosomal imaging in cells

A 549 cells were incubated with peptide **1** (10 μM) in RPMI-1640 medium for 1 h. Then, the switch-off process was performed by irradiation of visible light for *ca.* 5 min, the images were recorded immediately. After placed in darkness for *ca.* 15 min, the fluorescence images were taken again. These processes were repeated for eight times.

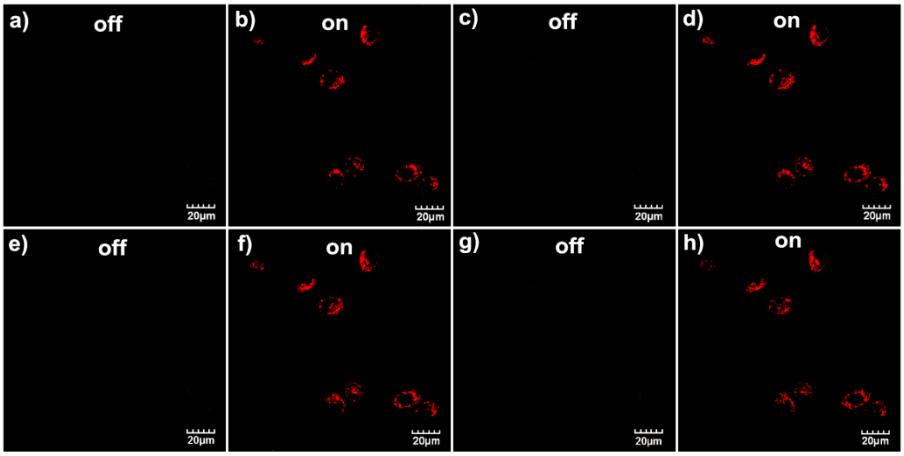


Figure S11. Images of switching process of **1** within lysosomes in A549 cell lines. (**a**) switch-off state: irradiation of Vis-light for ca. 5min erases the red fluorescence; (**b**) switch-on state: placed in darkness for ca. 15 min makes the red fluorescence revive; (**c**), (**e**) and (**g**) repeat of (**a**); (**d**), (**f**) and (**h**) repeats of (**b**).

7.4 Cytotoxicity assay:

The cytotoxicity was measured using the 3-(4,5-dimethylthiazol-2-yl)-2, 5-diphenyltetrazolium bromide (MTT) assay with HeLa and A549 cell lines. Cells growing in log phase were seeded into 96-well cell-culture plate at 1×10^5/well. The cells were incubated for 24 h at 37 ^oC under 5% CO_2. A solution of peptide **1** (100.0 μL/well) at concentrations of 5, 10, 20, 40 μM in RPMI-1640 medium was added to the wells of the treatment group, whereas for final negative control group 100.0 μL of RPMI-1640 was added, respectively. The cells were incubated for 12 h at 37 °C under 5% CO_2. After removal of the medium, a solution of 0.5 mg/mL MTT (100 μL/well) was then added to the plates for an additional 4 h incubation, allowing viable cells to reduce the yellow tetrazolium salt (MTT) into dark blue formazan crystals. After removal of the medium, formazan extraction was performed with 100 μL DMSO and its quantity determined colorimetrically using a Mutil reader (BioTek, Synergy H4), which was used to measure the OD 490 nm (Absorbance value). The following formula was used to calculate the viability of cell growth: Viability (%) = (mean of Absorbance value of treatment group/mean Absorbance value of control) × 100.

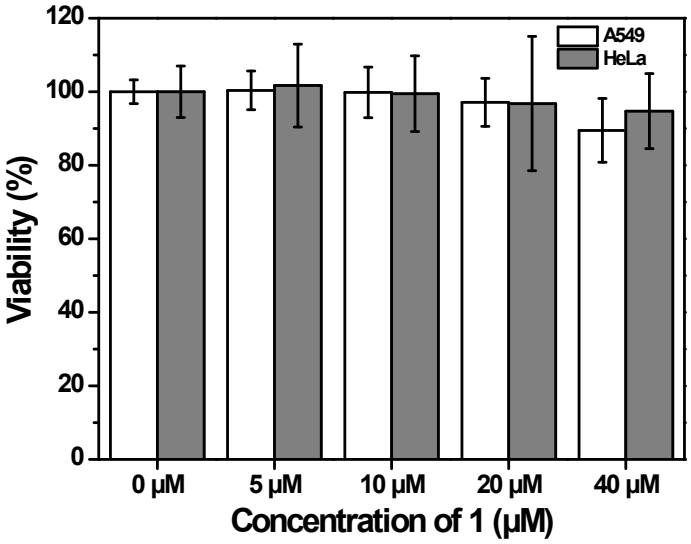


Figure S12. Cell viability values (%) estimated by MTT proliferation test at different concentrations of **1**. A549 and HeLa cells were cultured in the presence of 1 at 37 °C for 12 h.

8. Zeta Potential measurement

The zeta potential were measured with Nano-ZS(zata sizer, Malvern) instrument. Samples were dissolved in TBS (50 mM Tris, 50 mM NaCl, 20°C) at specific pH 2.0, 5.2, 10.0 and placed in darkness for 12 h before test. All data were corrected by subtracting a blank scan of the buffer system. Results were presented as mean ± SD (n=3).

Reference:

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