Electronic Supplementary Information (ESI)

Novel biocompatible fluorescent polymeric micelles based on 1,8-naphthalimide derivatives for cell imaging

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Contents

1. Materials and Measurement

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N-(2-hydroxyethyl) piperazine (98%), CuBr (99%), and *N, N′, N′, N″, N″*-pentamethyldietylenetriamine (PMDETA, 99%) were purchased from Aladdin reagent (Shanghai, China), 4-piperidineethanol (96%) was purchased from J & K Scientific respectively, and used as received. Dichloromethane (DCM) and Dimethylformamide (DMF), tetrahydrofuran (THF) were dried and distilled first with purification. Ultra-pure water was used in the experiments. All other agents and solvents were purchased from commercial sources and used directly without further purification. Methoxy-poly(ethylene glycol)-azide (**mPEG$_{2000}$-N$_3$**)[1] and 6-nitro-2-(prop-2-yn-1-yl)-1*H*-benzo[de]-isoquinoline-1,3(2*H*)-dione (**1**)[2] were synthesized according to literature reported so as the preparation of stearoyl chloride[3].

^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker DMX400 Spectrometer in $CDCl_3$ and given in relative to internals reference TMS standard. HRMS spectral data were measured on a Bruker Daltonics Bio TOF mass spectrometer. Gel permeation chromatography (GPC) to comfirm the polymer molecular weights and their distributions was carried out on a Waters HPLC system equipped with a model 1515 isocratic pump, a 717 plus autosampler, and a 2424 refractive index (RI) detector with Waters Styragel® HT3 and HT4 columns in series. The eluting solvent was THF at a flow rate of 1.0mL/min at 45℃. The retention times were calibrated against poly (ethylene glycol) standard with the molecular weight range 600 – 80000 Da. Transmission electrom microscopy (TEM, Hitachi H-600) at an acceleration voltage of 100kV was performed to investigate the micelle morphology. The samples were prepared by dropping 2 mg/mL and 1.25 mg/mL of micellar solution of **P1** and **P2** onto a copper grid followed by negatively staining with a 1 wt% aqueous solution of phosphotungstic acid, respectively. The size of the micelles was determined using dynamic light scattering (DLS) with the micellar solutions (1.25 mg mL^{-1}) filtered through a 0.45 μm syringe filter prior to measurement. The measurements were carried out at 25 ℃ using a Zetasizer Nano-ZS90 system from Malvern Instruments equipped with a 633 nm He-Ne laser using backscattering detection with a fixed detector angle of 90°. The critical micelle concentration (CMC) was determined *via* fluorescence spectrometer. Fluorescence emission spectra were recorded on a FluoroMax-4 Spectrofluorophotometer (HORIBA Jobin Yvon) at 298 K. Absorption spectra were recorded on a Hitachi PharmaSpec UV-1900UV-Visible Spectrophotometer. MTT method was used for testing the cell viability and described in the experimental section (Cell culture and imaging, S6). HeLa cells were obtained from Shanghai Institute of Biochemistry and Cell Biochemistry and Cell Biology, Chinese Academy of Science. To confirm that the micelles did not hydrolyze in water, **P1** in PBS buffer solution (pH 7.40 or 4.00) were placed in incubator

shaker under 37 °C for 30 minutes or 6 hours and then lyophilized respectively. These samples were tested by NMR and GPC measurement as shown in Fig. S23 and Fig. S22. **P1** also dissolved in NaOH aqueous solution, after refluxing under 80 °C for 1h, the GPC profiles in Fig. S22 obtained the trace of the 1,8-naphthalimide derivatives fragments (f-alkaline degradation). The synthesis of **P1** and **P2** were also confirmed by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) as shown in Fig. S24 and Fig. S25. α-Cyano-4-hydroxycinnamic acid was used as the matrix for MALDI-TOF MS measurements. The matrix was prepared at a concentration of 10 mg mL^{-1}.

2. Synthesis of various compound

2.1 Synthesis of the fluorophore

2.1.1:6-(4-(hydroxyenthl)piperazin-1-yl)-2(prop-2-yn-1-yl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione (C1)

1 (1 mmol) was dissolved in dry DMF (3 mL), then the solution of N-(2-hydroxyethyl) piperazine (1.2 mmol, 1 mL DMF) was poured into above solution while stirring at room tempearature. After 24 h, DMF was removed by rotary evaporators. The crude product was then puried on silica gel column using methanol / dichloromethane (v / v = 20 : 1) as eluent. The raw product was yellow powder and about 255 mg in 70% yield with a loss in the process of purification.

^{1}H NMR (400MHz, $CDCl_3$, δ): 8.62 (dd, J_1 = 6.4 Hz, J_2=1 Hz, 1H, Ar-H), 8.56 (d, J = 8 Hz, 1H, Ar-H), 8.43 (dd, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H, Ar-H), 7.70 (m, 1H, Ar-H), 7.23 (d, J = 8 Hz, 1H, Ar-H), 4.95 (d, J = 2.4 Hz, 2H, NCH_2), 3.72 (t, J = 5.4 Hz, 2H, CH_2OH), 3.33 (m, 4H, piperazin), 2.88 (m, 4H, piperazin), 2.72 (t, J = 5.4 Hz, 2H, piperazin-CH_2), 2.17 (t, J = 2.6 Hz, 1H, C≡CH).

^{13}C NMR (100MHz, $CDCl_3$, δ): 163.7, 163.2, 156.2, 133.0, 131.5, 130.6, 130.0, 126.2, 125.7, 123.0, 116.4, 115.0, 78.8, 70.3, 59.3, 57.8, 53.1, 53.0, 29.3.

HRMS (ESI): Calcd for $[M+H]^+$, 364.1661; Found, 364.1662.

2.1.2:2-(4-(1,3-dioxo-2-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-benzo[de]isoquinolin-6-yl)piperazin-1-yl)ethyl stearate (C3)：

C1 (prepared above) was dissolved in dry DCM, and triethylamine (Et_3N, 1.4 mmol) was added. Then stearoyl chloride (1.05 mmol) dissolved in dry DCM was added dropwise with an ice bath. After the reaction

stirred at room temperature overnight, the mixture extracted by DCM and washed with saturated brine solution. The organic phase was dried over Na_2SO_4 and concentrated by evaporation. The resultant product was puried by column chromatography on silica gel using petroleum ether / ethyl acetate (v / v=1 : 10). The product was yellow powder and about 370mg in 84% yield with a loss in the process of purification.

^{1}H NMR (400MHz, CDCl3, δ): 8.62 (dd, J_1 = 6.8 Hz, J_2 = 0.8 Hz, 1H, Ar-H), 8.56 (d, J = 8 Hz, 1H, Ar-H), 8.43 (dd, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H, Ar-H), 7.70 (m, 1H, Ar-H), 7.22 (d, J = 8 Hz, 1H, Ar-H), 4.95 (d, J = 2.4 Hz, 2H, NCH2), 4.29 (t, J = 5.8 Hz, 2H, piperazin-CH_2CH_2), 3.31 (m, 4H, piperazin), 2.85 (m, 4H, piperazin), 2.79 (t, J = 5.8 Hz, 2H, piperazin-CH_2), 2.35 (t, J = 7.6 Hz, 2H, $COCH_2$), 2.18 (t, J = 2.4 Hz, 1H, C≡CH), 1.64 (m, 2H, $COCH_2CH_2$), 1.24 (m, 28H, C_{18}-$(CH_2)_{14}$), 0.88 (t, J = 6.8 Hz, 3H, C_{18}-$(CH_2)_{14}$-CH_3).

^{13}C NMR (100MHz, $CDCl_3$, δ): 173.8, 163.7, 163.2, 156.3, 133.0, 131.5, 130.7, 130.0, 126.2, 125.7, 122.9, 116.2, 115.0, 78.8, 70.3, 61.4, 56.7, 53.4, 53.0, 34.3, 31.9, 29.7-29.2, 25.0, 22.7, 14.1.

HRMS (ESI): Calcd for $[M+H]^+$, 630.4271; Found, 630.4269.

2.2 Preparation of fluorescent polymeric micelles P1.

2-(4-(2-((1-(2-monomethoxy poly(ethylene glycol)-1H-1,2,3-triazol-4-yl) methyl)-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)piperazin-1-yl)ethyl stearate (mPEG-F_{PAZ}-C18, P1):

C3 (0.2 mmol) and **$mPEG_{2000}$-N_3** (0.2 mmol) added in the flask. After replacing the air with argon, 3 mL dry THF was added *via* injection. Subsquently, CuBr (0.08 mmol) and PMDETA (0.08 mmol) put into the reaction mixture. The reaction was carried out at room temperature for 24 h under argon. The final product (bright yellow solid) was obtained after puring by column chromatography on silica gel using DCM / MeOH (v / v = 20 : 1). Yield : 0.52g, 98%. Micelles of **P1** was prepared by dialysis method.[5]

^{1}H NMR (400MHz, $CDCl_3$, δ): 8.59(dd, J_1 = 6.4 Hz, J_2 = 0.8 Hz, 1H, Ar-H), 8.52 (d, J = 8 Hz, 1H, Ar-H), 8.40 (dd, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H, Ar-H), 7.78 (bs, 1H,CH=C- N=N-), 7.68 (m, 1H, Ar-H), 7.20 (d, J = 8 Hz, 1H, Ar-H), 5.49 (s, 2H, NCH_2), 4.47 (t, J = 5.2 Hz, 2H, NCH_2 in mPEG unit),4.28 (t, J = 5.8 Hz,2H, piperazin-CH_2CH_2), 3.83, 3.65 (m, 174H, methylene in mPEG unit), 3.38 (s, 3H, mPEG-terminal methyl), 3.29 (m, 4H, piperazin), 2.84 (m, 4H, piperazin), 2.78 (t, J = 5.8 Hz, 2H, piperazin-CH_2), 2.34 (t, J = 5.6 Hz, 2H, $COCH_2$), 1.64 (m, 2H, $COCH_2CH_2$), 1.25 (m, C_{18}-$(CH_2)_{14}$), 0.88 (t, J = 6.8 Hz, 3H, C_{18}-$(CH_2)_{14}$-CH_3).

^{13}C NMR (100MHz, $CDCl_3$, δ): 173.8, 164.1, 163.6, 156.1, 132.8, 131.3, 130.4, 130.0, 126.6, 125.6, 124.2,

123.1, 116.5, 114.9, 71.9, 70.5, 69.5, 61.4, 59.0, 56.7, 53.4, 53.0, 50.1, 35.1, 34.3, 31.9, 29.6-29.1, 25.0, 22.7, 14.1.

2.3 C2, C4 and P2 were synthesized followed the same way as C1, C3 and P1, respectively.

2.3.1:6-(4-(2-hydroxyethyl)piperidin-1-yl)2-(prop-2-yn-1-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (C2)

^{1}H NMR (400MHz, $CDCl_3$, δ): 8.61 (dd, J_1 = 6.8 Hz, J_2=0.4 Hz, 1H, Ar-H), 8.53 (d, J = 8.4 Hz, 1H, Ar-H), 8.39 (dd, J_1 = 7.6 Hz, J_2 = 0.4 Hz, 1H, Ar-H), 7.68 (m, 1H, Ar-H), 7.19 (d, J = 8 Hz, 1H, Ar-H), 4.95 (d, J = 2.4 Hz, 2H, NCH_2), 3.81 (t, J = 6.4 Hz, 2H, CH_2OH), 3.62 (d, J = 1.2 Hz, 2H, piperidin), 2.93 (t, J = 11.4 Hz, 2H, piperidin), 2.17 (t, J = 2.2 Hz, 1H, C≡CH), 1.95 (d, J = 12.8 Hz, 2H, piperidin), 1.69 (t, J = 6.4 Hz, piperidin-CH_2), 1.64 (m, 2H, piperidin), 1.39 (bs, J = 5.4 Hz, 1H, piperidin).

^{13}C NMR (100MHz, $CDCl_3$, δ): 163.8, 163.2, 157.3, 133.1, 131.4, 131.0, 130.0, 126.3, 125.4, 122.8, 115.6, 114.8, 78.9, 70.2, 60.4, 53.8, 39.3, 32.6, 32.5, 29.3.

HRMS (ESI): Calcd for $[M+H]^+$, 363.1709; Found, 363.1705.

2.3.2:2-(1-(1.3-dioxo-2-(prop-2-yn-1-yl)-2,3-dihydro-1*H*-benzo[*de*]isoquinolin-6-yl)piperidin-4-yl)-ethyl stearate (C4):

^{1}H NMR (400MHz, $CDCl_3$, δ): 8.58 (d, J = 6.8 Hz, 1H, Ar-H), 8.50 (d, J = 8 Hz, 1H, Ar-H), 8.36(d, J = 8.4 Hz, 1H, Ar-H), 7.67 (m, 1H, Ar-H), 7.17 (d, J = 8 Hz, 1H, Ar-H), 4.94 (bs, 2H, NCH_2), 4.21 (t, J = 6.2 Hz, 2H, piperadin-CH_2CH_2), 3.61 (d, J = 11.2 Hz, 2H, piperadin), 2.91 (t, J = 11.2 Hz, 2H, piperadin), 2.33 (d, J = 7.4 Hz, 2H, $COCH_2$), 2.18 (bs, 1H, C≡CH), 1.95 (d, J = 10.4 Hz, 2H, piperadin), 1.74 (t, J = 5.2 Hz, 2H, piperadin-CH_2), 1.65(m, 2H, $COCH_2CH_2$, 3H, piperadin), 1.25 (m, 28H, C_{18}-$(CH_2)_{14}$), 0.87 (t, J = 6 Hz, 3H, C_{18}-$(CH_2)_{14}$-CH_3).

^{13}C NMR (100MHz, $CDCl_3$, δ): 174.0, 163.7, 163.1, 157.1, 133.0, 131.4, 130.9, 129.9, 126.2, 125.4, 122.7, 115.6, 114.8, 78.9, 70.2, 61.9, 53.7, 35.2, 53.0, 34.4, 32.9, 32.4, 31.9, 29.7-29.2, 25.0, 22.7, 14.1.

HRMS (ESI): Calcd for $[M+H]^+$, 629.4318; Found, 629.4315.

2.3.3: 2-(1-(2-((1-(2-monomethoxy poly(ethylene glycol)-1H-1,2,3-triazol-4-yl) methyl)-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6- yl)piperidin-1-yl)ethyl stearate (mPEG-F_{PID}-C18, P2):

^{1}H NMR (400MHz, $CDCl_3$, δ): 8.58(d, J_1 = 6.4 Hz, 1H, Ar-H), 8.51 (d, J = 8.4 Hz, 1H, Ar-H), 8.37 (d, J_1 = 8.4 Hz, 1H, Ar-H), 7.78 (bs, 1H,CH=C- N=N-), 7.67 (m, 1H, Ar-H), 7.18 (d, J = 8 Hz, 1H, Ar-H), 5.49 (s, 2H, NCH_2), 4.47 (t, J = 7.0 Hz, 2H, NCH_2 in mPEG unit), 4.20 (t, J = 6.2 Hz,2H, piperidin-CH_2CH_2), 3.83, 3.65 (m,176, methylene in mPEG unit, piperidin), 3.38 (s, 3H, mPEG-terminal methyl), 2.91 (t, J = 11.2 Hz, 2H, piperidin), 2.33 (t, J = 7.6 Hz, 2H, $COCH_2$), 1.95 (d, J = 10.0 Hz, 2H, piperidin), 1.73 (t, J = 5.2 Hz, 2H, piperidin-CH_2),), 1.64 (m, 5H, $COCH_2CH_2$, piperidin), 1.25 (m, 28H, C_{18}-$(CH_2)_{14}$), 0.88 (t, J = 12.8 Hz, 3H, C_{18}-$(CH_2)_{14}$-CH_3).

^{13}C NMR (100MHz, $CDCl_3$, δ): 173.9, 164.2, 163.7, 156.9, 132.9, 131.3, 130.6, 130.0, 126.3, 125.4, 124.2, 123.0, 116.0, 114.8, 71.9, 70.5, 69.5, 61.9, 59.0, 53.7, 50.1, 35.2, 35.1, 34.4, 32.9, 32.4, 31.9, 29.7-29.2, 25.00, 22.7, 14.1.

2.4 Cell culture and imaging

2.4.1 Cell culture HeLa cells were grown in Dulbecco's modification of Eagle's medium (DMEM) supplemented with 10% (v/v) foetal bovine serum (FBS) and 1% antibiotics (penicillin-streptomycin, 10000 U mL^{-1}). Cells were incubated in a 5% CO_2 humidified incubator at 37 °C, and the medium was replenished every other day.[4]

2.4.2 Cell imaging HeLa cells were pre-washed twice and then incubated with 25 μg mL^{-1} **P1** and **P2** in PBS at 37 °C for 30 minutes. Then the cells were washed to remove unbounded probes before in situ imaging by inverted fluorescence microscope (Nikon TS100) and LEICA TCS SP8 confocal laser scanning microscopy respectively. As for confocal laser scanning microscopy (CLSM) analysis of HeLa cells upon various pH buffers, HeLa cells were then immersed with 20 mM PBS buffers for about 5 min at different pH values. Finally, images at different pH values were recorded *via* CLSM analysis.

2.4.3 Cytotoxicity assay Toxicity toward HeLa cells was determined by MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-di-phenyltetrazolium bromide) reduction assay following literature procedures.[4] About 7000 cells per well were seeded in 96-well plates and cultured overnight for 70-80% cell confluence. The medium was replaced with 100 μL of fresh medium without FBS, to which 100 μL complexes at 200 μL. 24 or 48 hours later, 20 μL of 5 mg mL^{-1} MTT solution in PBS was added to each well for additional 4h incubation. Blue formazan crystals were seen at well when checked under microscope. The medium was replaced by 150 μL of DMSO to dissolve the formazan crystal. The absorbance was measured in an ELISA plate reader (model

550, BioRad) at a wavelength of 570 nm. The metabolic activity of the probes treated cells was expressed as a relative to untreated cell controls taken as 100% metabolic activity.

3. **Results**

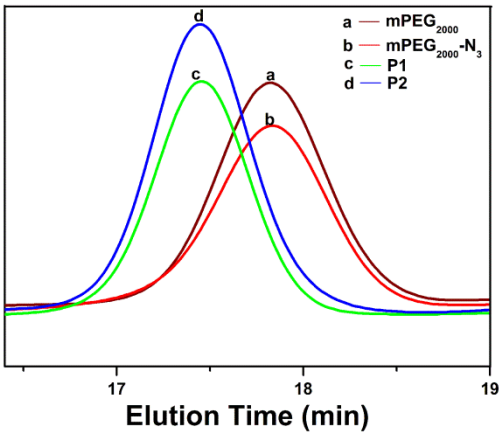

Fig. S1 GPC profiles of (a) **mPEG$_{2000}$** (Mn = 1980, PDI = 1.04), (b) **mPEG$_{2000}$-N$_3$** (Mn = 2010, PDI = 1.05), (c) **P1** and (d) **P2**.

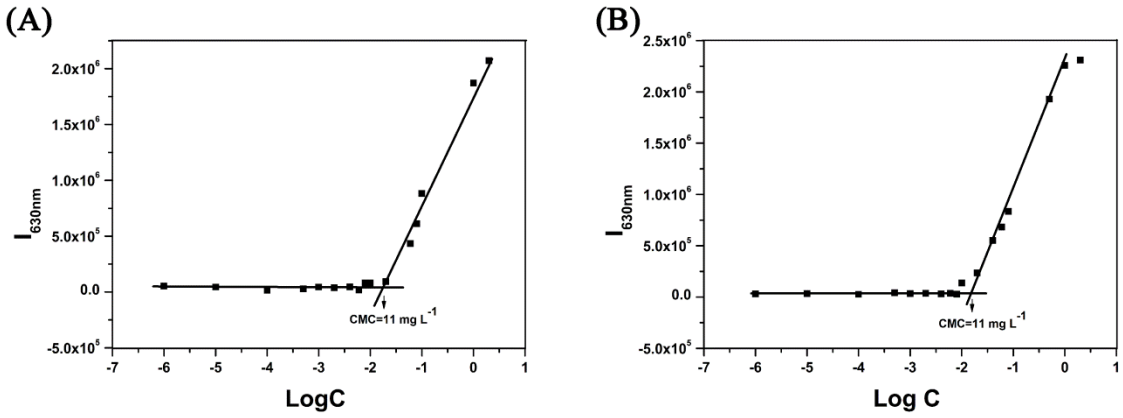

Fig. S2 Critical micelle concentration determination: (A) **P1** (B) **P2**. Fluorescence intensity at λ_{em} = 630 nm of Nile red as function of logarithm of the polymer concentrations in PBS buffer solution (10 mM, pH = 7.40).

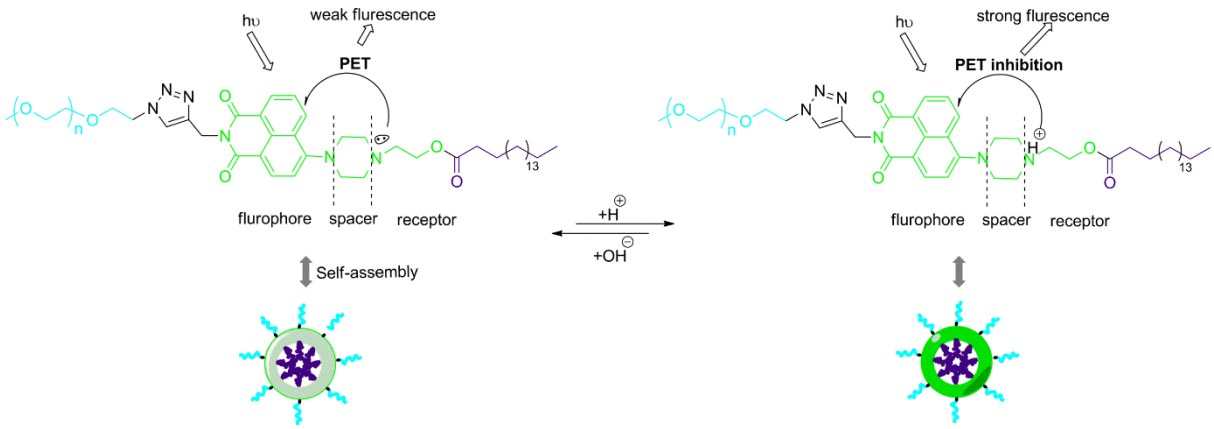

Fig. S3 The pH response of **P1** based on PET mechanism.

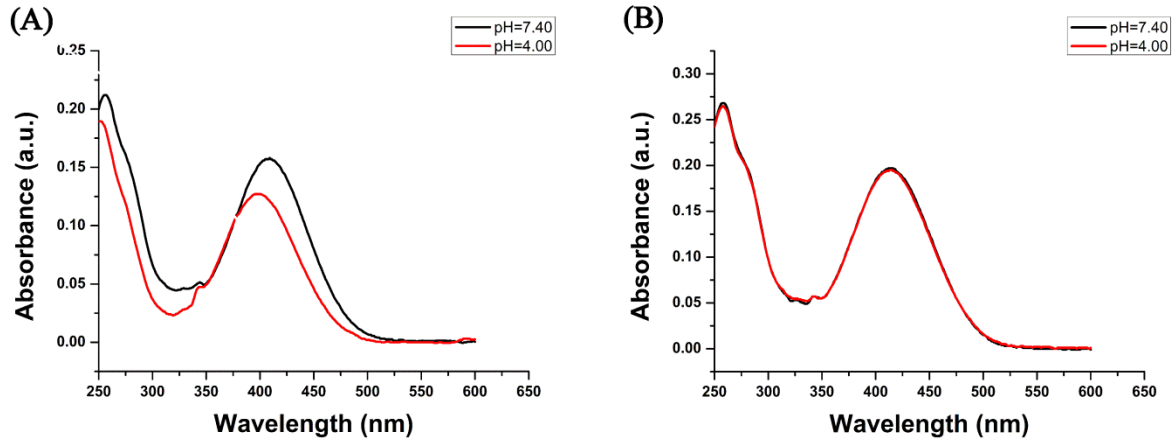

Fig. S4 UV-vis absorption spectra of **P1** (A) and **P2** (B) in B-R buffer solution.

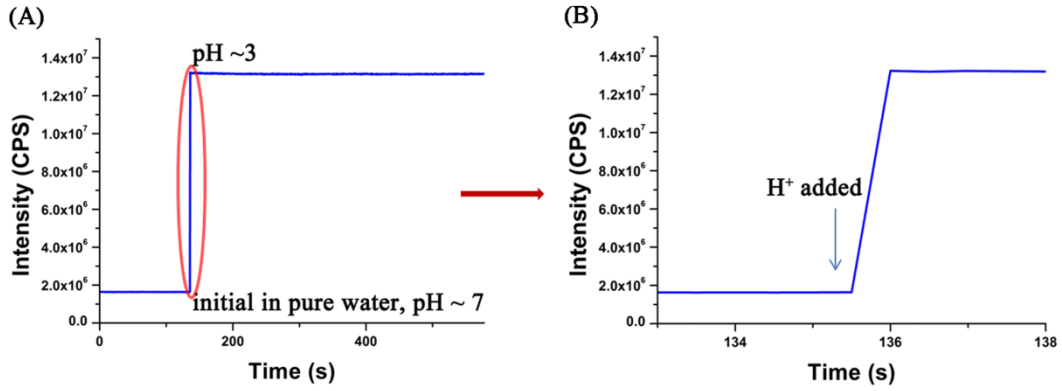

Fig. S5 Temporal profile of fluorescence intensity of **P1** at maximum λ_{em} after adding 3μL HCl solution (1 N) to water, data was recorded every 0.5 s. (B) partial enlarged image.

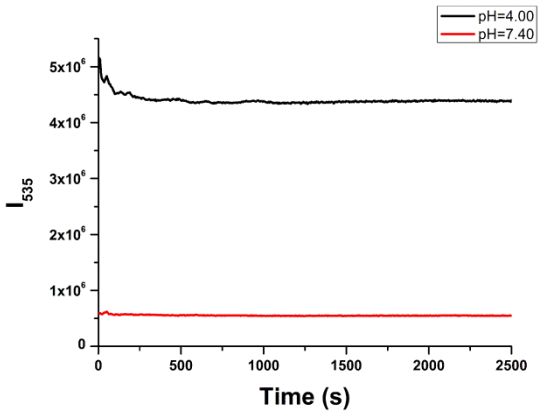

Fig. S6 Temporal profile of **P1** at λ_{535nm} upon pH 7.40 (red) and 4.00 (black) in B-R buffer solution, the fluorescence investigated immediately after adding stock solution of **P1** in ultra-pure water, data were recorded every 5 s.

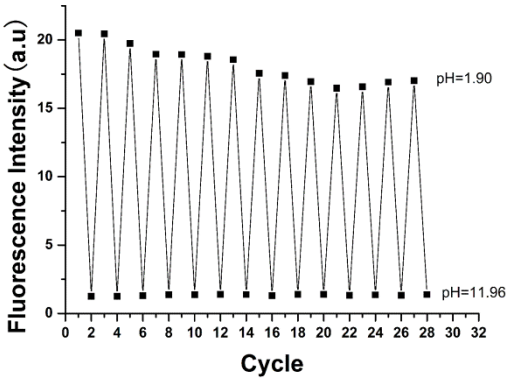

Fig. S7 Fluorescence intensity of **P1** upon alternating pH changing between 1.90 and 11.96 at room temperature in water.

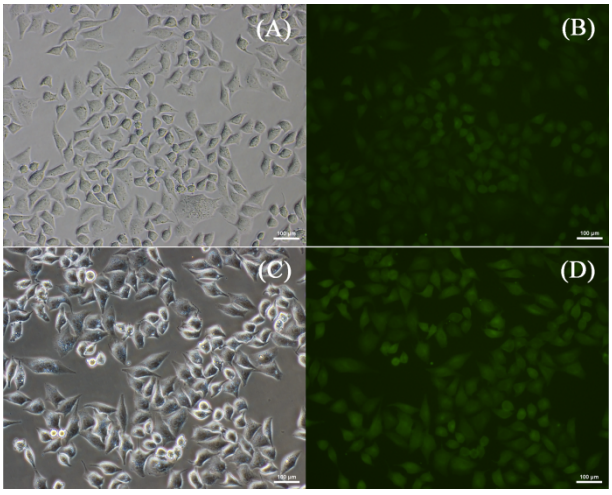

Fig. S8 Cell images of HeLa cells recorded on inverted fluorescence microscope of **P1** (A, B) and **P2** (B, D) (pH = 7.40). (A), (C) bright field; (B), (D) excited with 405 nm laser.

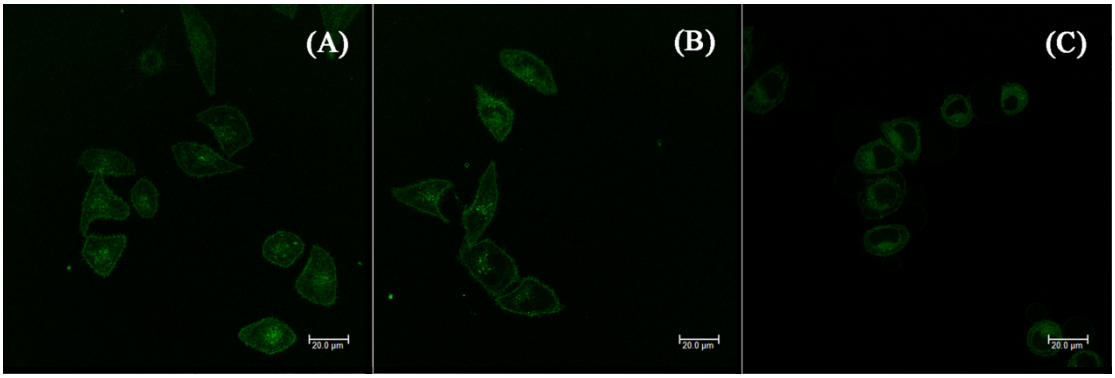

Fig. S9 Confocal fluorescence images of **P2** in HeLa cells at (A) pH = 7.40, (B) pH = 4.00 and (c) pH = 2.00, respectively (the scale bar represents 20μm).

Table S1 Quantum Yied was calculated *via* fluorescein in 0.1 N NaOH as reference.

Polymer	pH=10.94	pH=7.40	pH=4.00	pH=1.91
P1	0.008	0.01	0.2	0.4
P2	0.01	0.01	0.01	0.01

NMR of various compounds

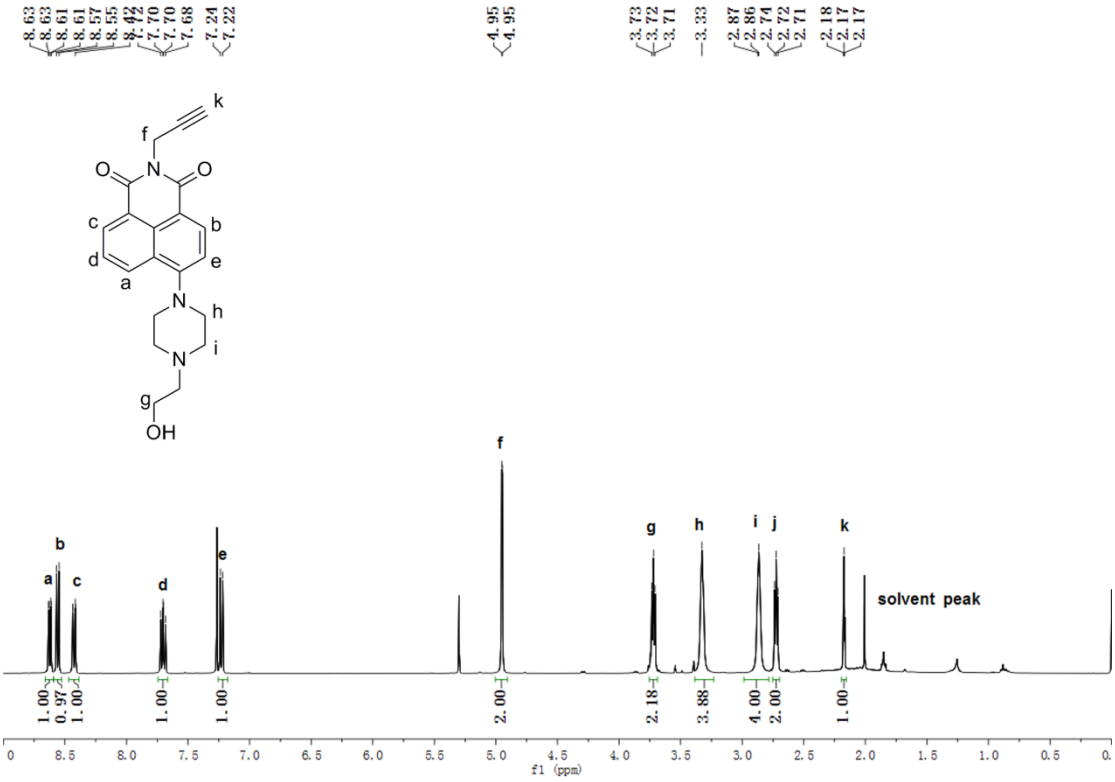

Fig. S10 ^{1}H NMR spectrum of **C1** in $CDCl_3$

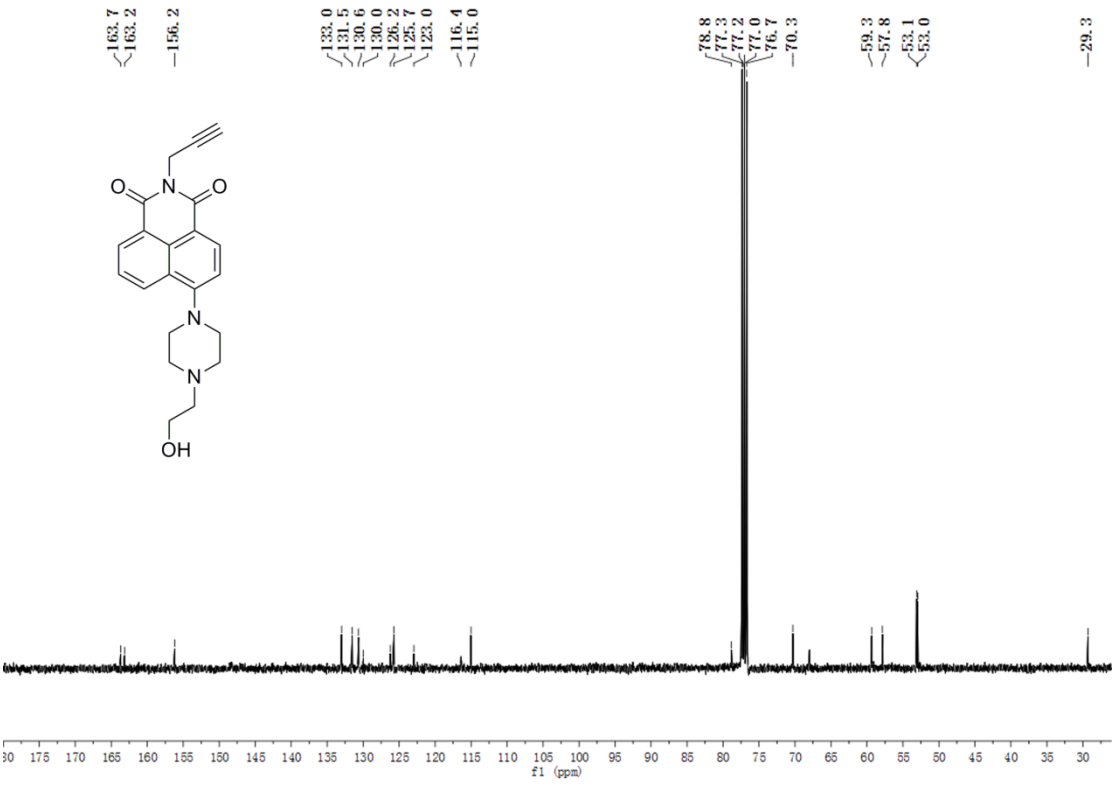

Fig. S11 ^{13}C NMR spectrum of **C1** in $CDCl_3$

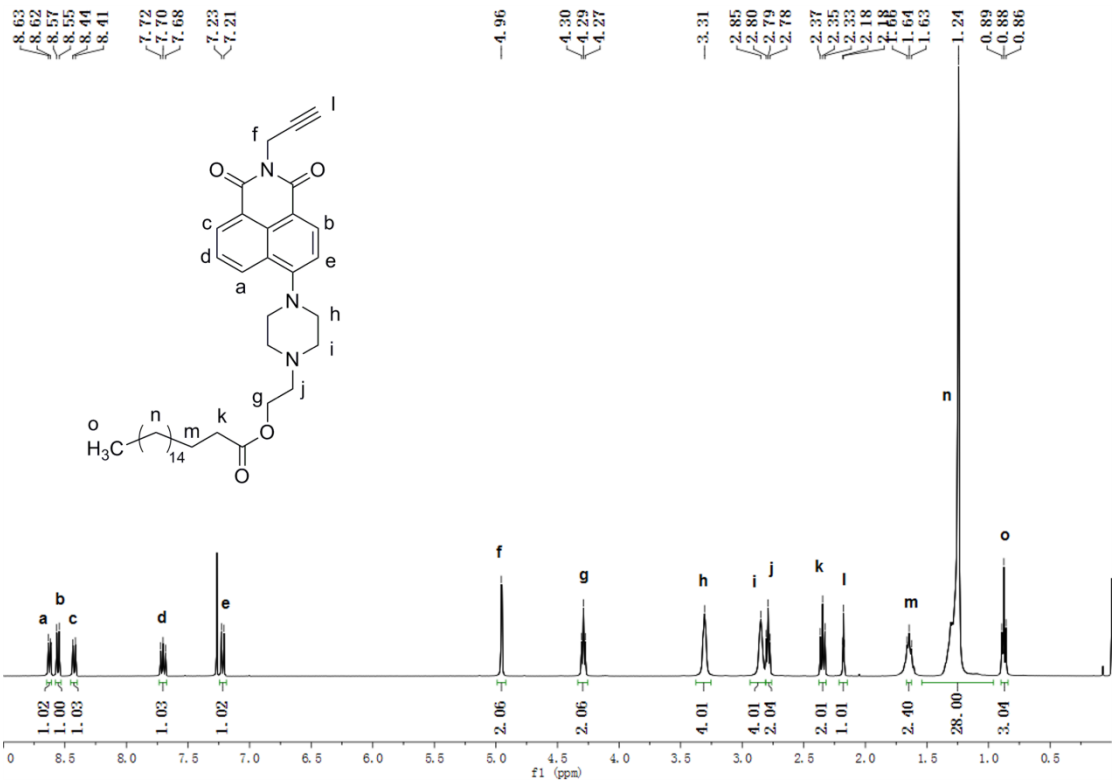

Fig. S12 ^{1}H NMR spectrum of **C3** in $CDCl_3$

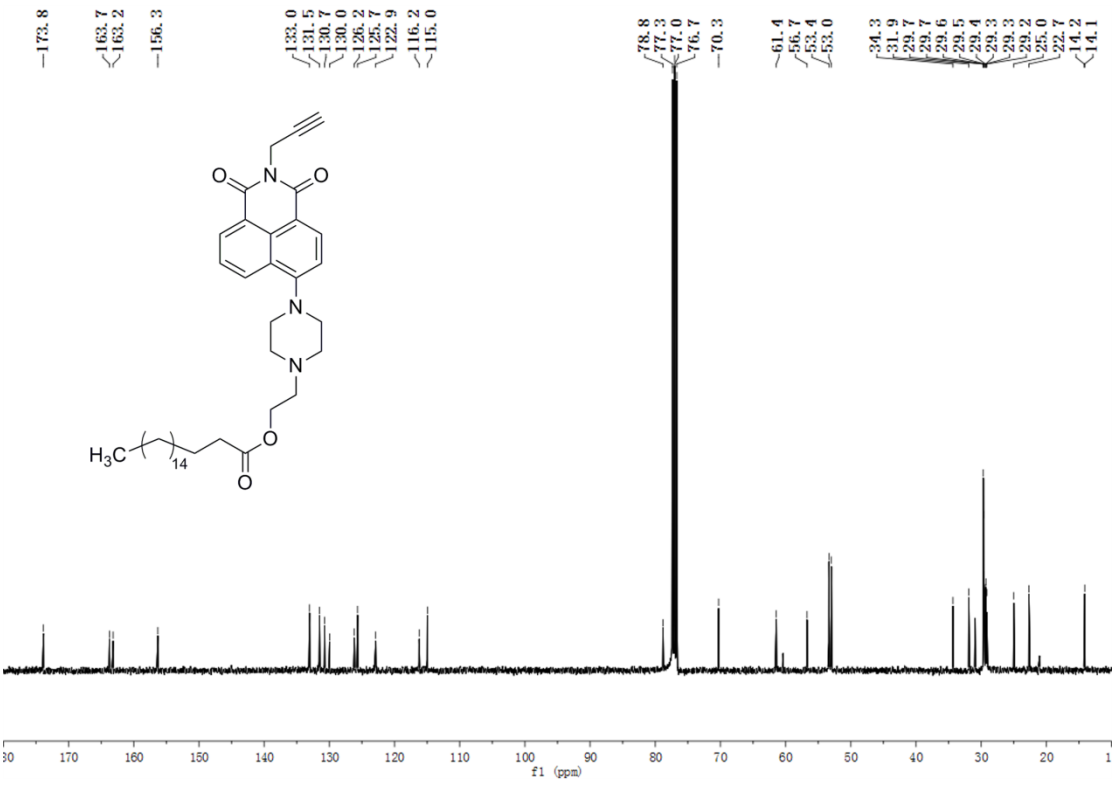

Fig. S13 ^{13}C NMR spectrum of **C3** in $CDCl_3$

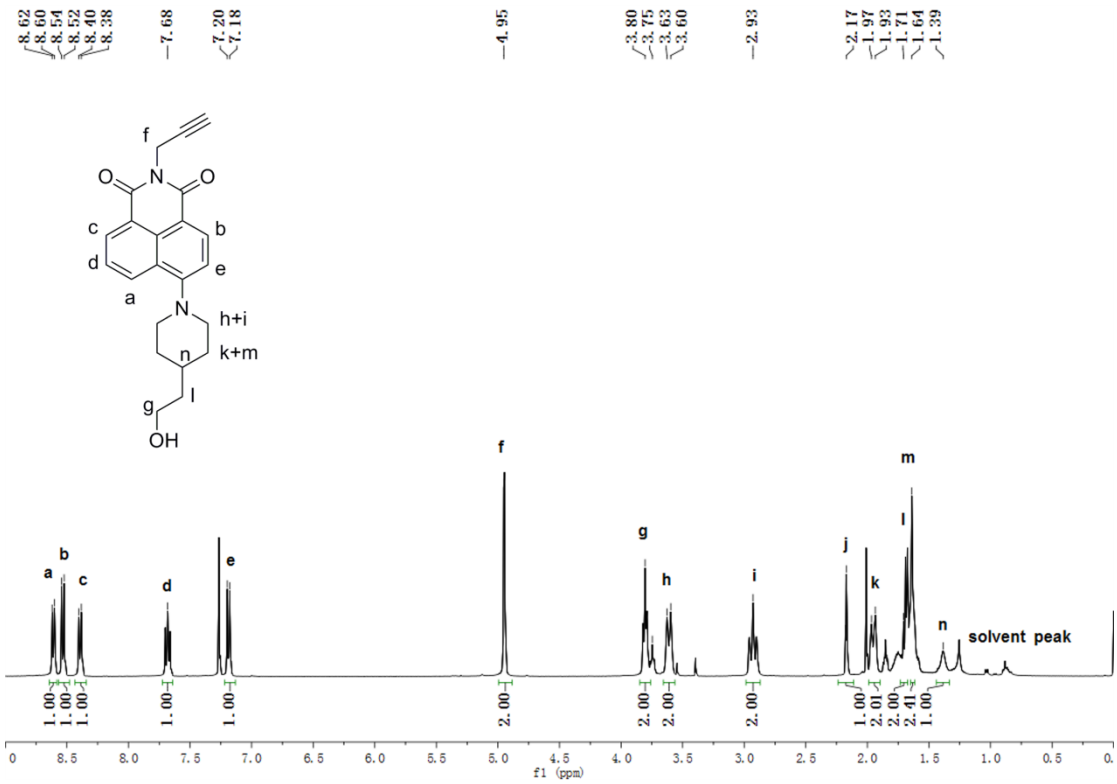

Fig. S14 ^{1}H NMR spectrum of **C2** in $CDCl_3$

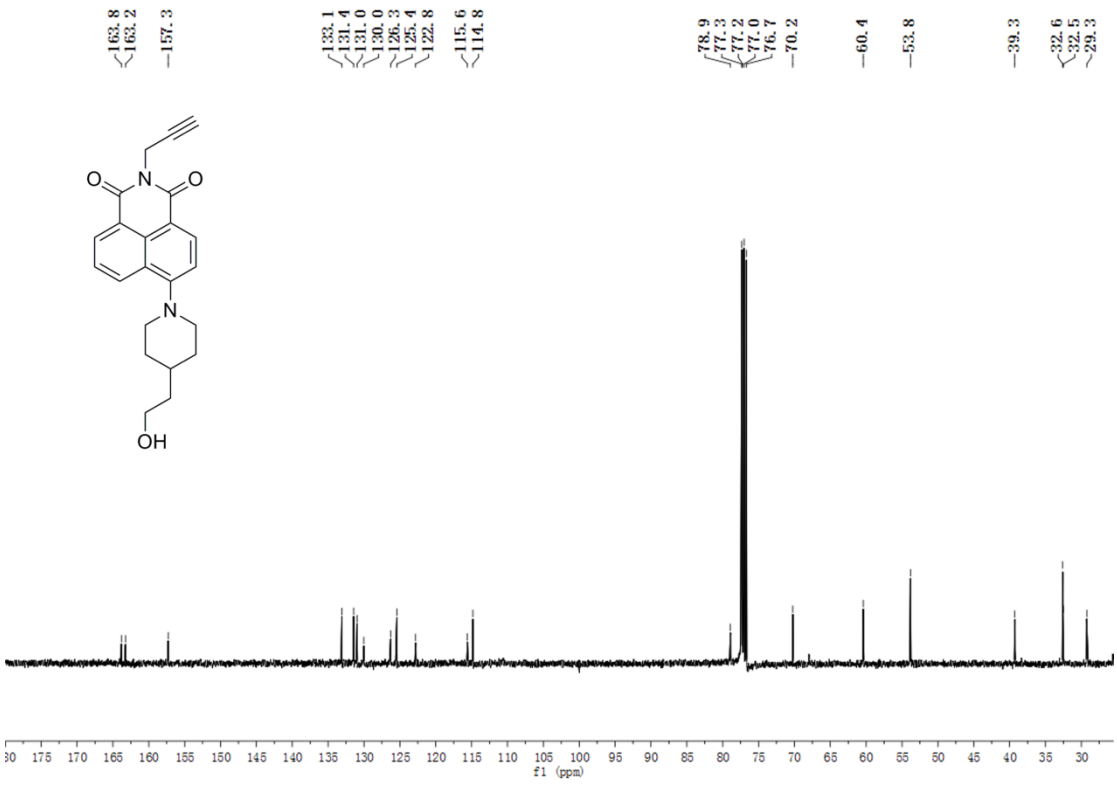

Fig. S15 ^{13}C NMR spectrum of **C2** in $CDCl_3$

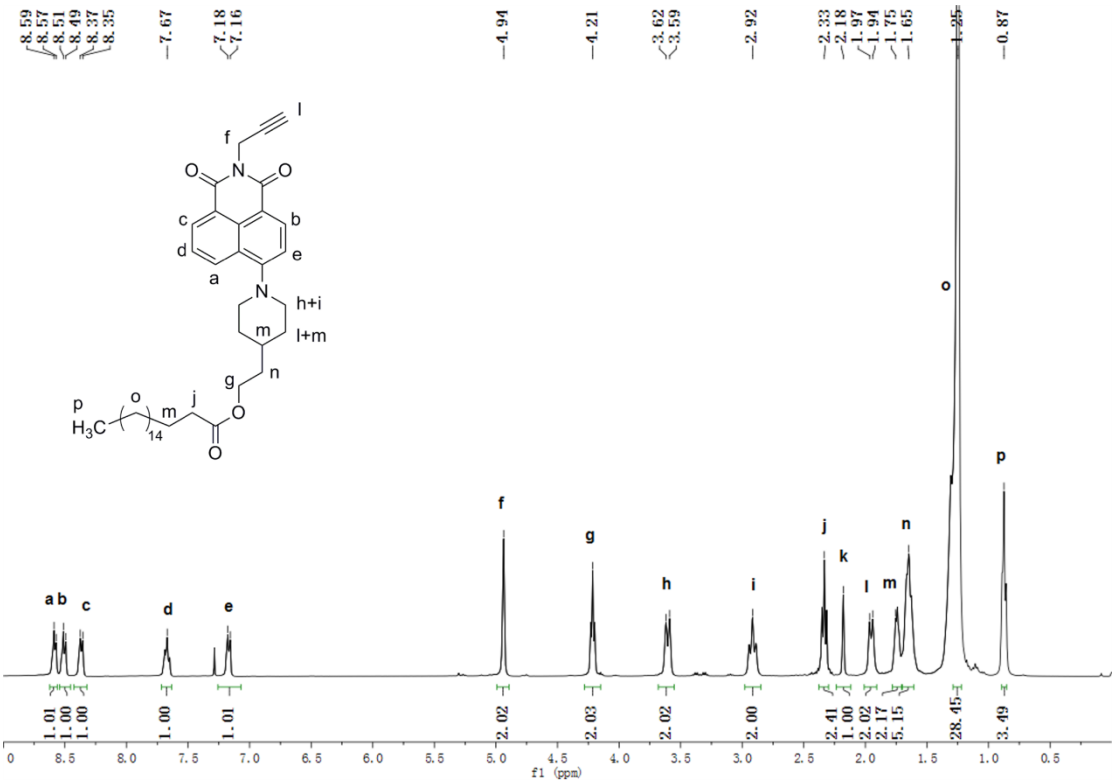

Fig. S16 ^{1}H NMR spectrum of **C4** in $CDCl_3$

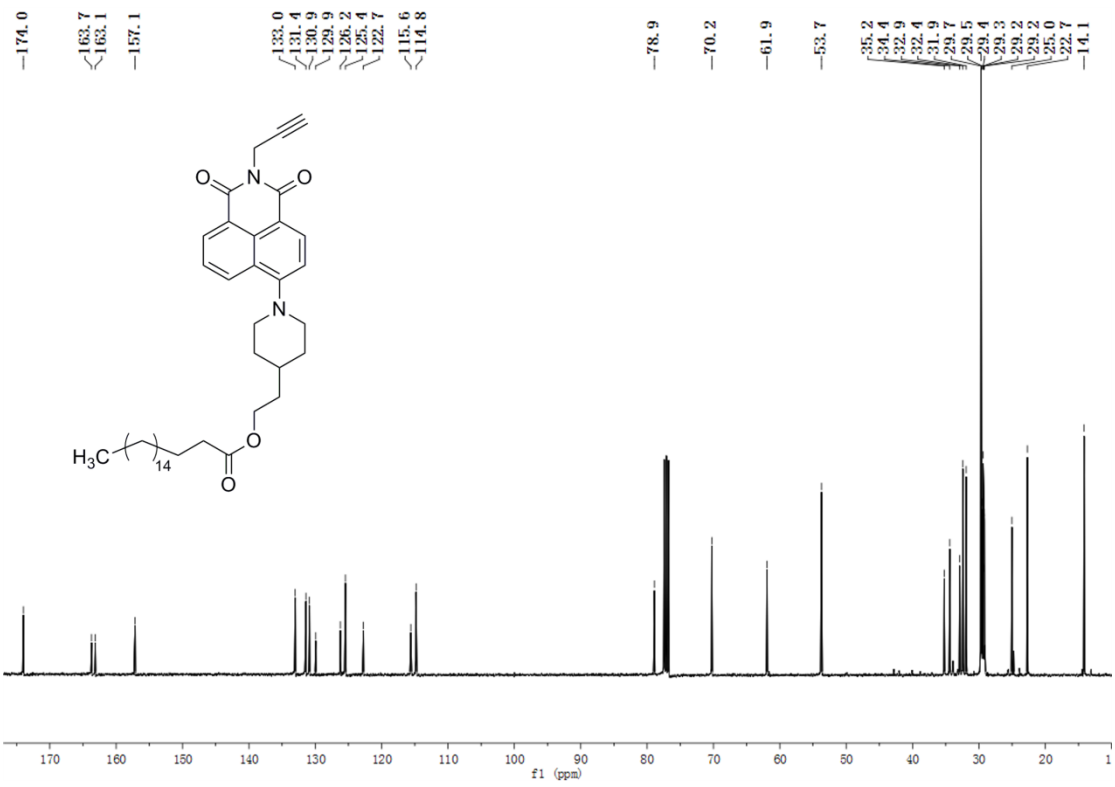

Fig. S17 ^{13}C NMR spectrum of **C4** in $CDCl_3$

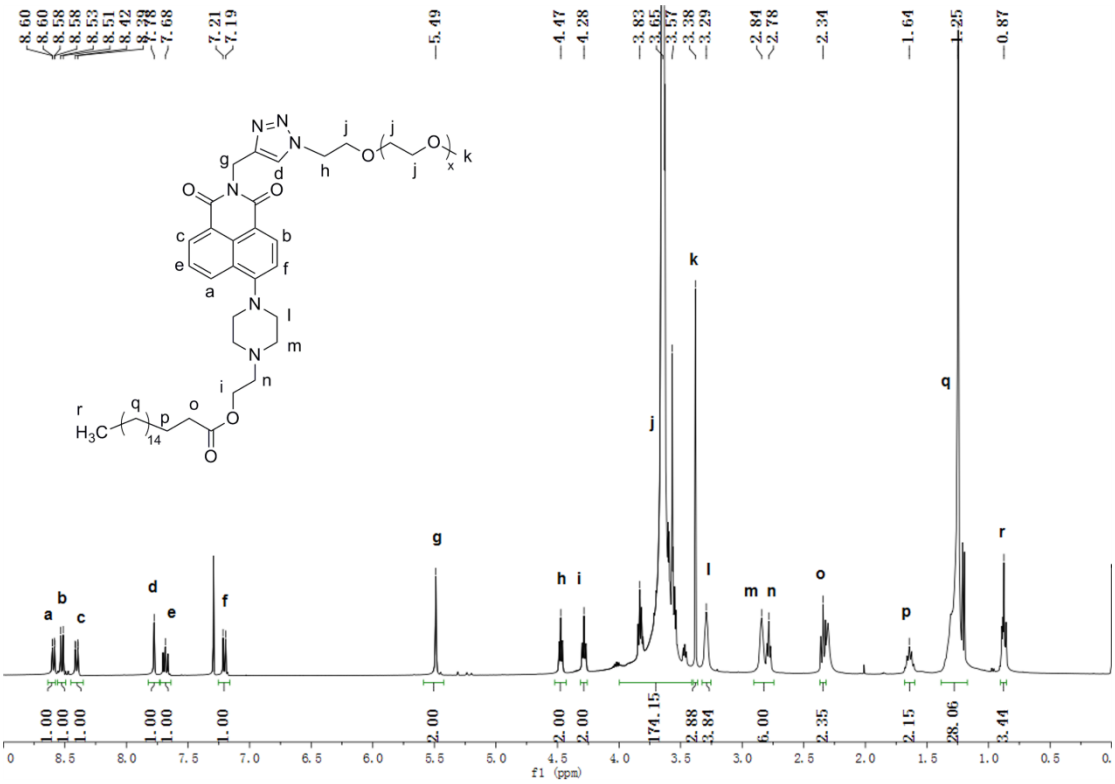

Fig. S18 ^{1}H NMR spectrum of **P1** in $CDCl_3$

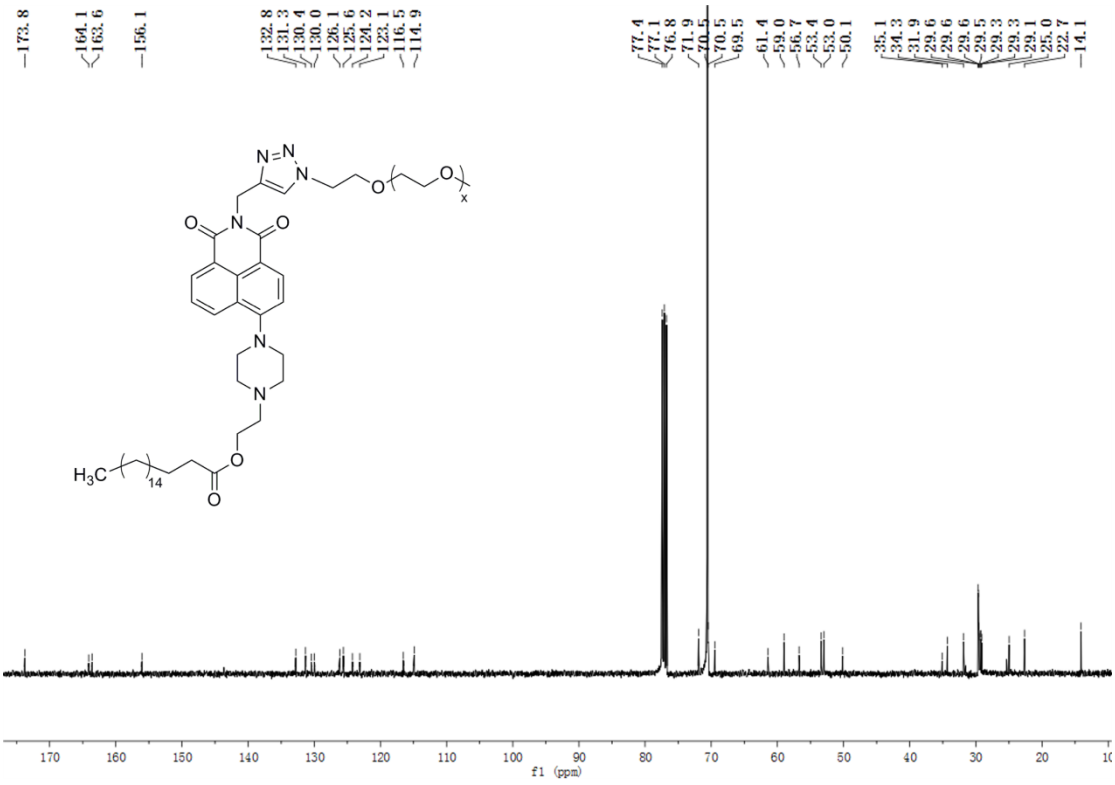

Fig. S19 ^{13}C NMR spectrum of **P1** in $CDCl_3$

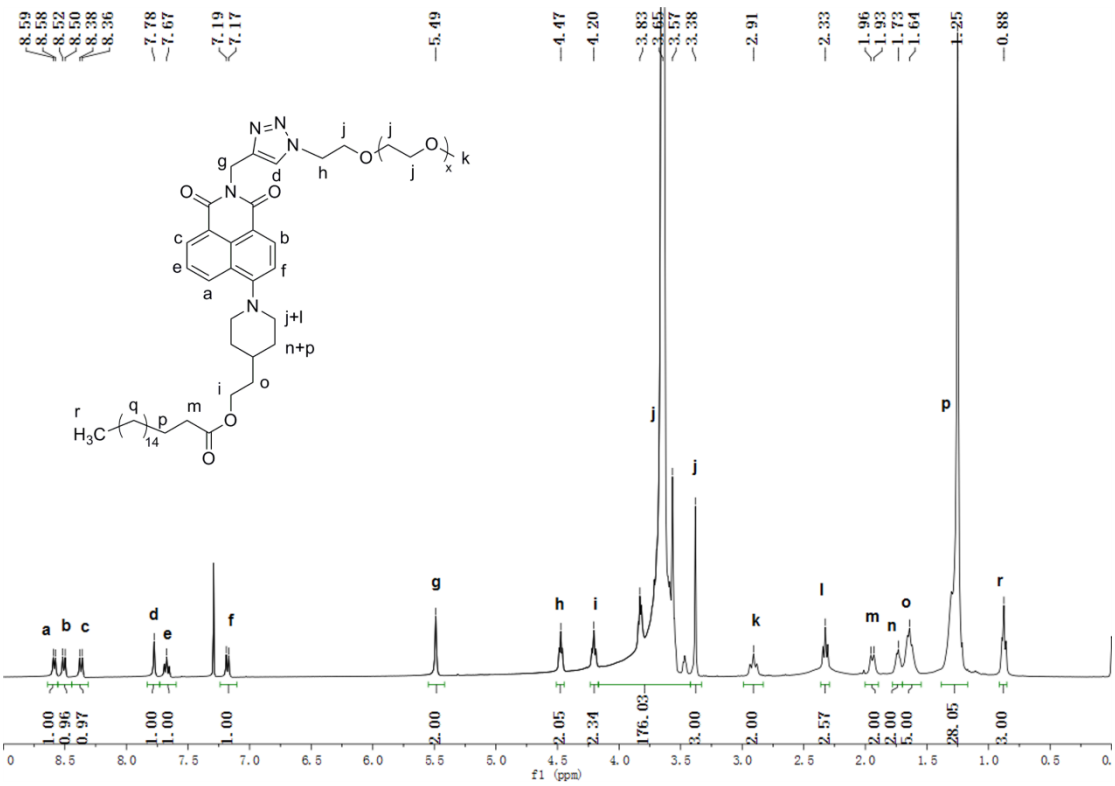

Fig. S20 ^{1}H NMR spectrum of **P2** in $CDCl_3$

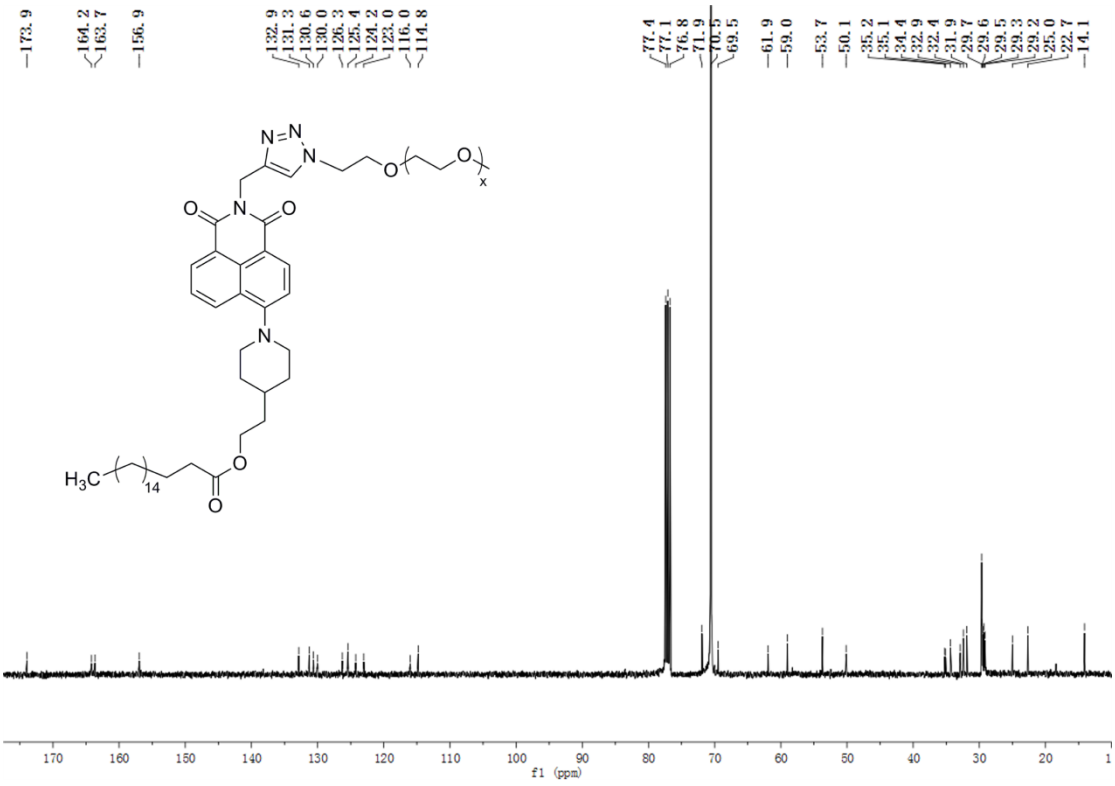

Fig. S21 ^{13}C NMR spectrum of **P2** in $CDCl_3$

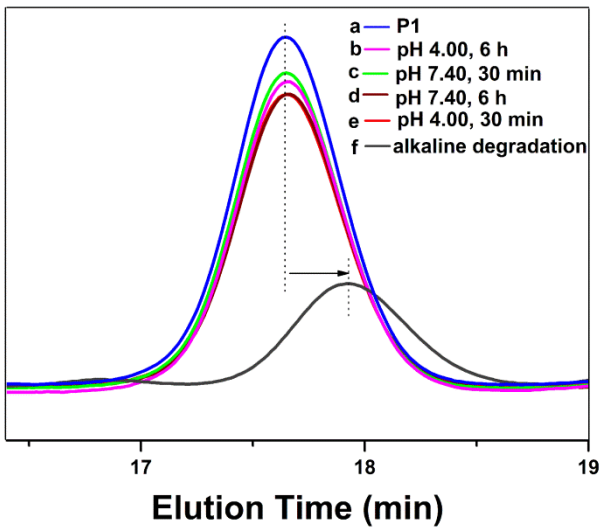

Fig. S22 GPC profiles of (a) **P1** original. (b) **P1** at pH 4.00 for 6 h. (c) **P1** at pH 7.40 for 30 min. (d) **P1** at pH 7.40 for 6h. (e) **P1** at pH 4.00 for 30 min. (f) **P1** after alkaline degradation (NaOH, 80 °C).

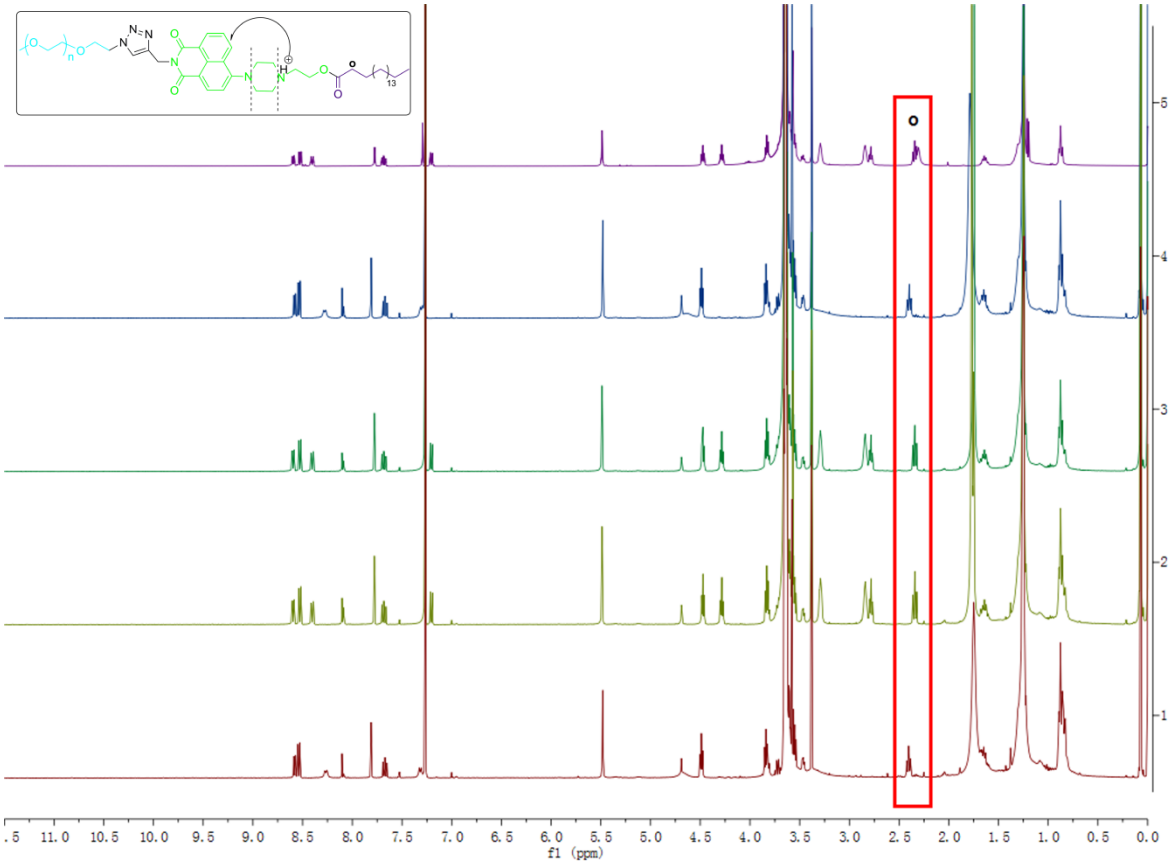

Fig. S23 ^{1}H NMR overlaps of **P1** after different treatment: (1) at pH 4.00 for 30 min; (2) at pH 7.40 for 6 h; (3) at pH 7.40 for 30 min; (4) at pH 4.00 for 6 h; (5) original.

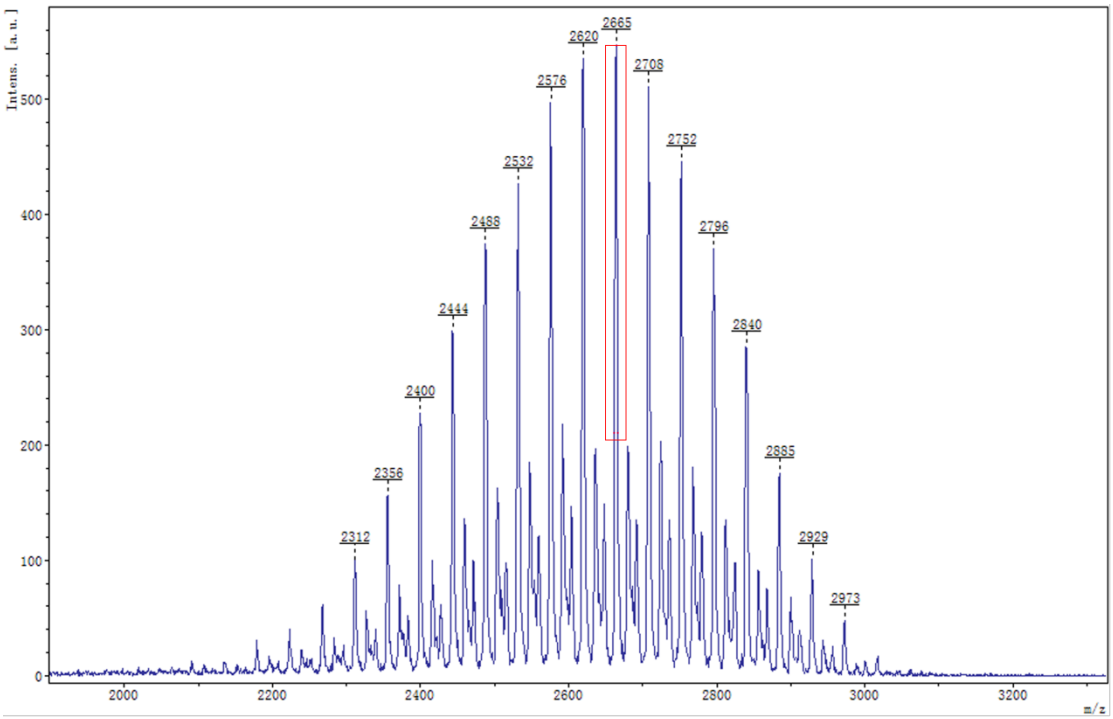

Fig. S24 MALDI mass spectra of **P1** (a peak with m/z of 2665 (Na adduct, n=45) was observed).

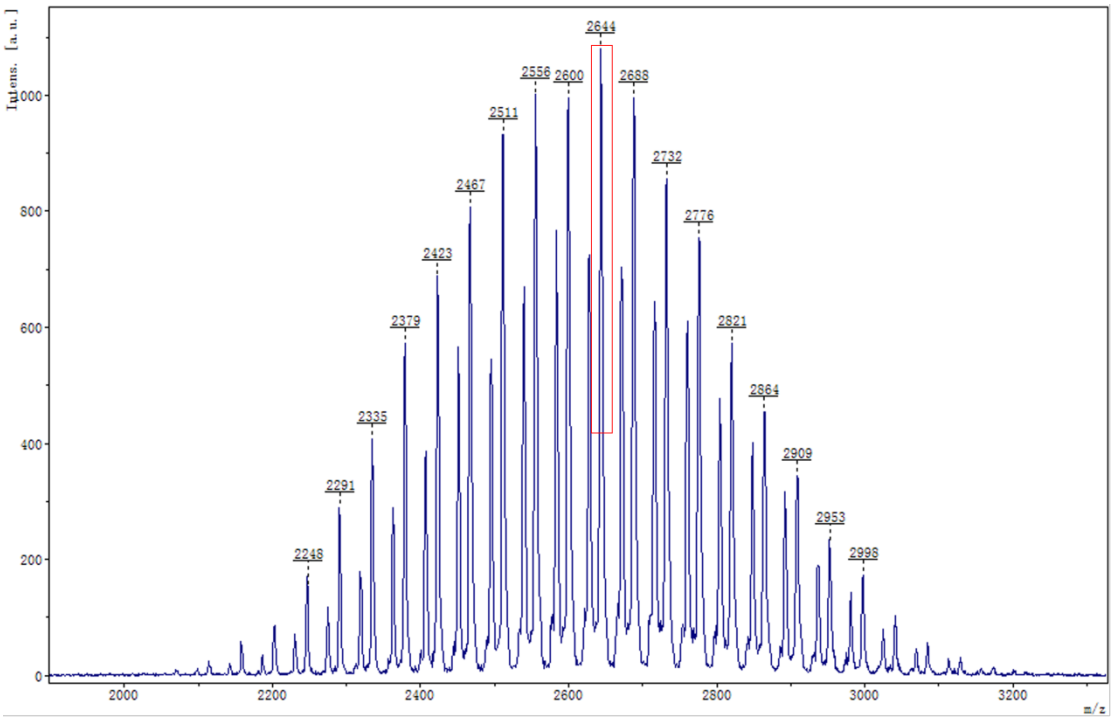

Fig. S25 MALDI mass spectra of **P2** (a peak with m/z of 2644 (K adduct, n=44) was observed).

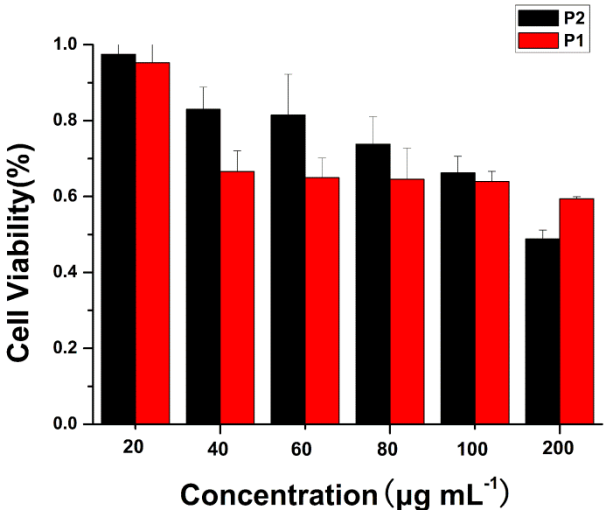

Fig. S26 Celll viability in the presence of the two probes at different concentrations (20 ~ 200 μg mL^{-1}) for 48h. The results were obtained using the MTT assay.

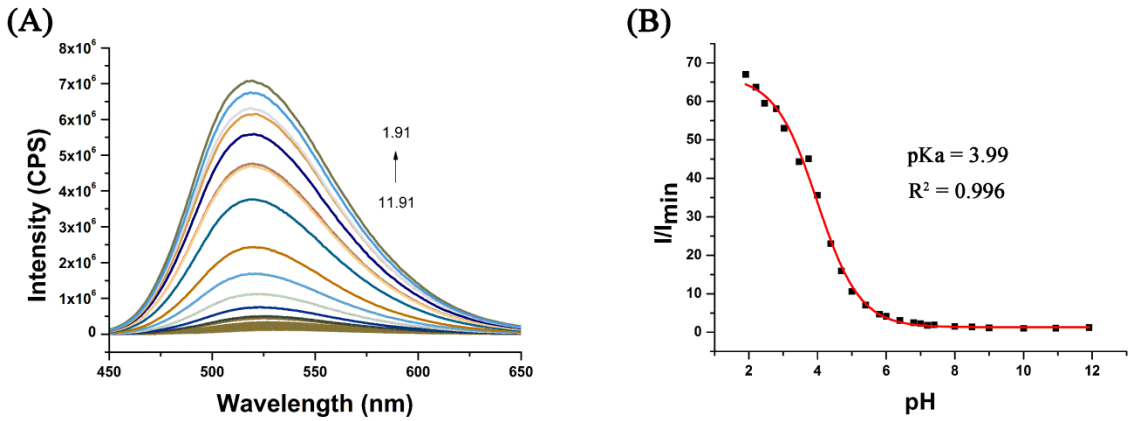

Fig. S27 Fluorescence spectra of **P1** (0.01 mg mL-1) in B-R buffer solution at various pH values (pH=11.91, 10.94, 10.00, 9.00, 8.50, 8.00, 7.40, 7.20, 7.00, 6.80, 6.40, 6.00, 5.80, 5.40, 5.00, 4.70, 4.39, 4.00, 3.74, 3.46, 3.03, 2.80, 2.46, 2.21, 1.91).

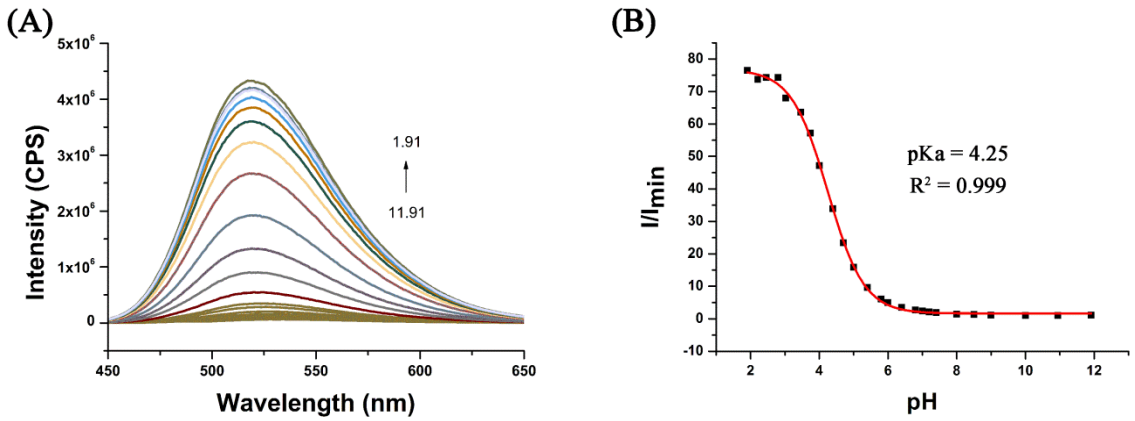

Fig. S28 Fluorescence spectra of **P1** (0.005 mg mL-1) in B-R buffer solution at various pH values (pH=11.91, 10.94, 10.00, 9.00, 8.50, 8.00, 7.40, 7.20, 7.00, 6.80, 6.40, 6.00, 5.80, 5.40, 5.00, 4.70, 4.39, 4.00, 3.74, 3.46, 3.03, 2.80, 2.46, 2.21, 1.91).

Reference:

1. C. von der Ehe, K. Kempe, M. Bauer, A. Baumgaertel, M. D. Hager, D. Fischer, and U. S. Schubert, *Macromol. Chem. Phys.,* 2012, **213**, 2146-2156.

2. M. Dong, Y.-W. Wang, and Y. Peng, *Org. Lett.,* 2010, **12**, 5310-5313.

3. A. Sarı, C. Alkan, A. Biçer, A. Karaipekli, *Sol. Energy Mater. Sol. Cells,* 2011, **95**, 3195-3201.

4. Q.-F. Zhang, W.-J. Yi, B. Wang, J. Zhang, L. Ren, Q.-M. Chen, L. Guo, and X.-Q. Yu, *Biomaterials,* 2013, **34**, 5391-5401.

5. W.-X. Wu, N. Wang, B.-Y. Liu, Q.-F. Deng, and X.-Q. Yu, *Soft Matter,* 2014, **10**, 1199-1213.