Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Constructing a Four-Input Molecular Keypad Lock with a Multi-Stimuli-Responsive Phthalocyanine

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Contents

Fig. S9 (a-e) Changes in electronic absorption spectra of mixtures of **2** (2 μM) and DPBF (initial concentration = 30 μM) in PBS (pH 7.4) in response to 2 mM of GSH and/or red-light irradiation (λ > 610 nm) for 10 min in different sequence upon further irradiation (λ > 610 nm) for 270 s. (f) Comparison of the corresponding rates of decay of DPBF as monitored spectroscopically at its absorbance at 417 nm.

Fig. S10 Changes in electronic absorption spectra of mixtures of **3** (2 μM) and DPBF (initial concentration = 30 μM) in PBS (pH 7.4) in response to 2 mM of GSH and/or acid (pH 6.0) in different sequence upon irradiation (λ > 610 nm) for 270 s.

Fig. S11 Electronic absorption spectra of **3** (2 μM) in PBS (pH 7.4) in response to two 2 mM of GSH and/or acid (pH 6.0) in different sequence.

Fig. S12 (a) Change in fluorescence spectrum (λ_{ex} = 345 nm) of **1** (2 μM) in PBS (pH 7.4) upon sequential treatment with GSH (2 mM), acid (pH 6.0) and red-light irradiation (λ > 610 nm) over a period of 10 min. (b) Plot of the fluorescence intensity at 375 nm *vs.* the irradiation time.

Fig. S13 Fluorescence spectra (λ_{ex} = 610 nm) of **1** (2 μM) in PBS (pH 7.4) in response to 2 mM of GSH, acid (pH 6.0) and/or red-light irradiation (λ > 610 nm) for 10 min under (a) one-input, (b) two-input and (c) three-input conditions.

Fig. S14 Electronic absorption spectra of **1** (2 μM) in PBS (pH 7.4) in response to 2 mM of GSH, acid (pH 6.0) and/or red-light irradiation (λ > 610 nm) for 10 min under (a) one-input, (b) two-input and (c) three-input conditions.

Fig. S15 (a-d) Changes in electronic absorption spectra of mixtures of **1** (2 μM) and DPBF (initial concentration = 30 μM) in PBS (pH 7.4) in response to 2 mM of GSH, acid (pH 6.0) or red-light irradiation (λ > 610 nm) for 10 min upon further

irradiation (λ > 610 nm) for 270 s. (e) Comparison of the corresponding rates of decay of DPBF as monitored spectroscopically at its absorbance at 417 nm.

Fig. S16 (a-g) Changes in electronic absorption spectra of mixtures of **1** (2 μM) and DPBF (initial concentration = 30 μM) in PBS (pH 7.4) in response to 2 mM of GSH, acid (pH 6.0) and/or red-light irradiation (λ > 610 nm) for 10 min under two-input conditions upon further irradiation (λ > 610 nm) for 270 s. (h) Comparison of the corresponding rates of decay of DPBF as monitored spectroscopically at its absorbance at 417 nm.

Fig. S17 (a-g) Changes in electronic absorption spectra of mixtures of **1** (2 μM) and DPBF (initial concentration = 30 μM) in PBS (pH 7.4) in response to 2 mM of GSH, acid (pH 6.0) and red-light irradiation (λ > 610 nm) for 10 min under three-input conditions upon further irradiation (λ > 610 nm) for 270 s. (h) Comparison of the corresponding rates of decay of DPBF as monitored spectroscopically at its absorbance at 417 nm.

Fig. S18 Molecular keypad lock constructed with **1** with three inputs and two intermediate outputs ($I_{720\ nm}$ and $^1O_2$ generation). Only when the correct password "**GA6**" [**G** = GSH, **A** = acid and **6** = red-light irradiation (λ > 610 nm) for 10 min] is entered, the two outputs are switched on and the Output 3 is also in an ON (or "1") stage.

Fig. S19 Truth table for the combinatorial logic operations with three inputs (GSH, Acid and L610) based on compound **1**.

Fig. S20 Molecular keypad lock was constructed with **1** with two intermediate outputs (fluorescence at 720 nm and singlet oxygen generation) and final output (fluorescence at 375 nm). Only when the correct password "**GA63**" [**G** = GSH, A = acid, **6** = red-light irradiation (λ > 610 nm) for 10 min and **3** = blue-light

excitation (λ = 345 nm)] is entered, the fluorescence at 375 is turned on and it can unlock the molecular keypad lock. The table shows the results of all outputs in response to the different input sequences.

Molecular Design

The multi-stimuli-responsive compound (compound **1**, Fig. 1) contains several interrelated functional units. The first part involves a zinc(II) phthalocyanine core substituted with three 2,4-dinitrobenzenesulfonate (DNBS) moieties. These strongly electron-withdrawing substituents can effectively quench the fluorescence emission and singlet oxygen generation of the phthalocyanine through photoinduced electron transfer (PET). Upon interaction with glutathione (GSH), these groups can be removed to restore the photoactivities of the phthalocyanine.[1] Being the most abundant intracellular thiol, GSH is often upregulated in tumour cells and can therefore be regarded as a tumour biomarker.[2] As a result, there has been considerable interest in development of selective fluoresent probes for this species[3] and using it to trigger drug release in cancer cells.[4] This phthalocyanine unit is also connected to a bis(ferrocenylethenyl) boron dipyrromethene (BODIPY) moiety through an acid-cleavable ketal linker. We have reported earlier that ferrocenyl BODIPYs can serve as broad-spectrum dark quenchers for Förster resonance energy transfer (FRET)-based activatable probes.[5] With an extended π system, this BODIPY unit absorbs in the near-infrared region that can overlap with the fluorescence band of the phthalocyanine to enable an efficient FRET process. The presence of two redox-active ferreocenyl units can effectively quench the indirectly excited BODIPY through intramolecular charge transfer (ICT). Hence, this ferrocenyl BODIPY moiety can provide another quenching pathway for the phthalocyanine unit that can be relaxed upon

the treatment with acid. On the basis that tumour cells generally have a lower extracellular pH than normal cells, a slightly acidic environment can also be regarded as a tumour-associated stimulus.[6] Furthermore, the phthalocyanine is further connected to a pyrene unit acted as an energy donor[7] through a singlet oxygen-responsive thioketal linker.[8] Hence, the FRET process from the excited pyrene to the phthalocyanine will be disrupted if singlet oxygen is generated from the phthalocyanine core. With this specially designed molecule, it was expected that it would be responsive towards several stimuli, including GSH, acid and the two light sources for excitation of the phthalocyanine ($\lambda_1 > 610$ nm) and pyrene ($\lambda_2 = 345$ nm) units, and the signals generated could be manipulated to construct a molecular keypad lock.

References

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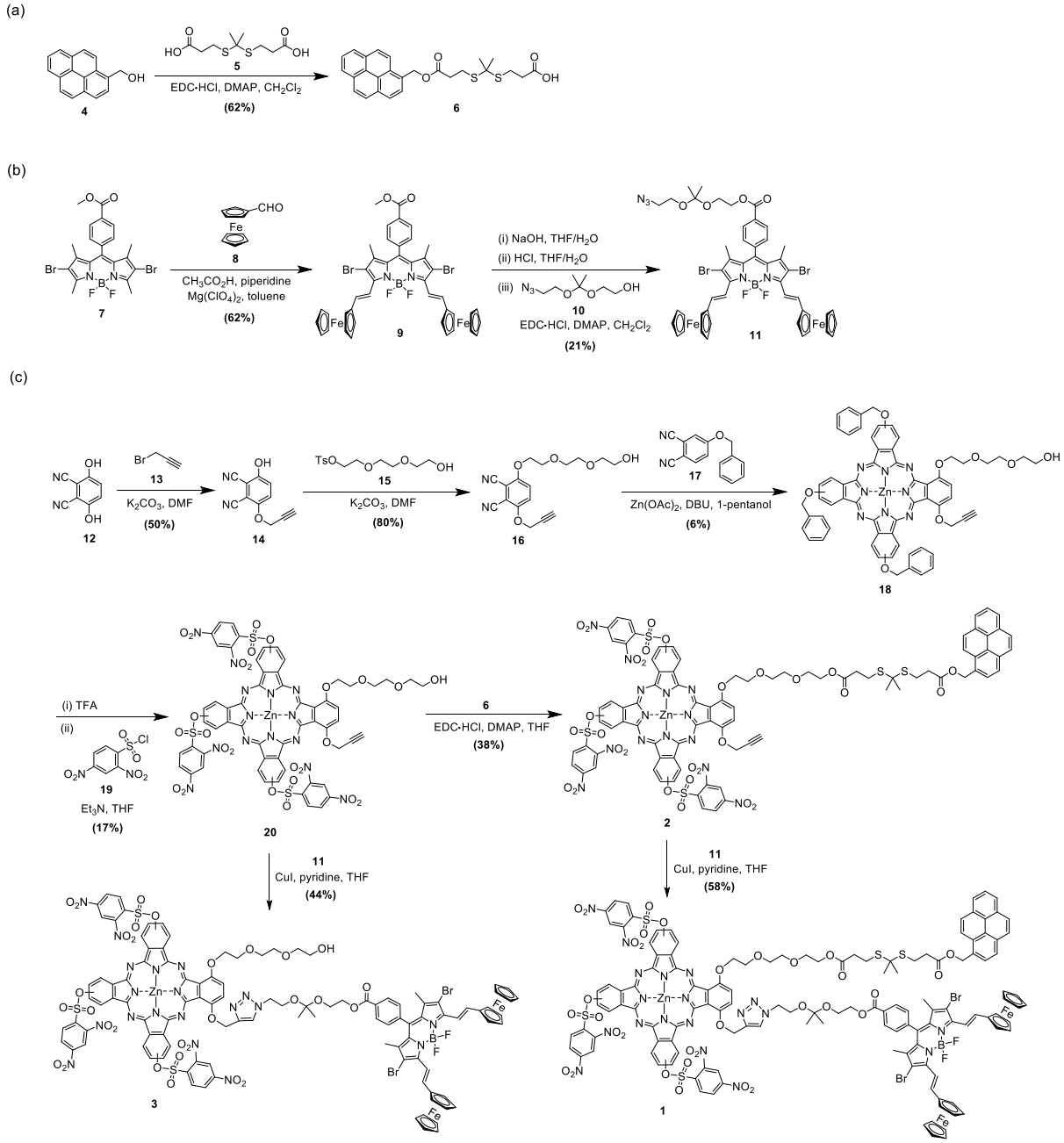
Synthesis and Characterisation

The synthetic route used to prepare compound **1** is shown in Scheme S1. The thioketal-linked pyrene **6** was first prepared by the condensation reaction of pyren-1-ylmethanol (**4**) and one equiv. of thioketal-linked dicarboxylic acid **5** in the presence of *N*-ethyl-*N*'-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) and 4-dimethylaminopyridine (DMAP) (Scheme S1a). For the ferrocenyl BODIPY component **11**, it was prepared according to Scheme S1b. Knovenagel condensation of BODIPY **7** with excess ferrocenecarboxaldehyde (**8**) in the presence of acetic acid, piperidine and a catalytic amount of $Mg(ClO_4)_2$ gave the bis(ferrocenylethenyl) BODIPY **9**. After alkaline hydrolysis followed by acidic workup, the carboxy intermediate product formed was coupled with the ketal-linked azido alcohol **10** using EDC·HCl and DMAP as the activating agents to afford **11**. To construct the phthalocyanine core, 3,6-dihydroxyphthalonitrile (**12**) was used as a starting material. As shown in Scheme S1c, treatment of this compound with propargyl bromide (**13**) and K_2CO_3 gave the mono-substituted product **14**, which underwent further alkylation with mono-tosylated triethylene glycol **15** to afford phthalonitrile **16**. Mixed cyclisation of this compound with an excess amount of 4-(benzyloxy)phthalonitrile (**17**) in the presence of $Zn(OAc)_2$ and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 1-pentanol gave the unsymmetrical phthalocyanine **18** as a mixture of structural isomers arising from the positions of the benzyloxy groups. The benzyloxy groups of this compound were then removed in refluxing trifluoroacetic acid (TFA).

The hydroxy intermediate product formed was treated with 2,4-dinitrobenzenesulfonyl chloride (**19**) and Et_3N in tetrahydrofuran (THF) to give the tris-DNBS-substituted phthalocyanine **20**. This compound was then condensed with the thioketal-linked pyrene **6** to give the phthalocyanine-pyrene conjugate **2**. With a free alkynyl group, this compound underwent copper-promoted alkyne-azide Huisgen cycloaddition with the azido BODIPY **11** to give the target phthalocyanine-pyrene-BODIPY conjugate **1**, which was purified by size-exclusion chromatography followed by recrystallisation from a mixture of THF, CH_3OH and hexane. By using **20** instead of **2** as the starting material, the reaction afforded the phthalocyanine-BODIPY conjugate **3**, which together with the phthalocyanine-pyrene conjugate **2** were used as the control compounds. All the new compounds were fully characterised with various spectroscopic methods, including ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy and high-resolution mass spectrometry. The experimental details and the characterisation data are given below.



Scheme S1. Synthetic pathways for conjugate **1** and the control compounds **2** and **3**.

Spectroscopic and Photophysical Properties

The electronic absorption spectra of conjugates **1**-**3** were recorded in *N*,*N*-dimethylformamide (DMF). All the compounds showed typical spectral features of zinc(II) phthalocyanines with a B-band at *ca.* 340 nm, a vibronic band at *ca.* 620 nm and an intense Q-band at *ca.* 695 nm (Fig. S1). For **1** and **2,** two additional bands at *ca.* 330 and 345 nm assignable to the pyrene chromophore were also observed. The Q-bands of **1** and **3** were slightly broadened compared with that of **2**, which could be attributed to the overlapped absorption of the bis(ferrocenylethenyl) BODIPY moiety. The fluorescence spectra of these three compounds were also recorded in DMF upon excitation at two different wavelengths (345 and 610 nm). As shown in Fig. S2, upon excitation at 345 nm where pyrene absorbs, several extremely weak emission bands at *ca.* 360-430 nm were observed for **1** and **2**, which could be due to the residual fluorescence of the pyrene unit in the compounds. The intensity was much weaker than that of free pyrene, suggesting the presence of an efficient FRET process from the excited pyrene moiety to the phthalocyanine and BODIPY units in these conjugates. In fact, the fluorescence bands of free pyrene were partially overlapped with the B-band absorptions of phthalocyanine **18** and bis(ferrocenylethenyl) BODIPY **9** (Fig. S3), showing that these two FRET pathways were thermodynamically favourable. Upon excitation at 610 nm, while a strong fluorescence band at *ca.* 720 nm was observed for **18**, no fluorescence could be detected for **1**-**3** (Fig. S4). As the fluorescence emission band of **18** was also overlapped well with the longest-wavelength

absorption of **9** (Fig. S3), FRET from the excited phthalocyanine unit to the BODIPY moiety was also a favourable process. Nevertheless, the above results suggested that the excited phthalocyanine and BODIPY moieties in **1** formed either through FRET or direct excitation were relaxed effectively *via* PET due to the three DNBS units and the two ferrocenylethenyl moieties respectively.

Apart from fluorescence emission, the singlet oxygen generation was also completely quenched for all the three phthalocyanines. By contrast, without the pyrene and BODIPY moieties, phthalocyanine **18** served as an efficient singlet oxygen generator as shown by the rapid decay of the singlet oxygen scavenger 1,3-diphenylisobenzofuran (DPBF) (Fig. S5). The quenching mechanisms for singlet oxygen generation were expected to be the same as those for fluorescence emission. Hence, the photoactivities, including fluorescence emission and singlet oxygen generation, of the three conjugates were completely quenched in their intact state.

Experimental Section

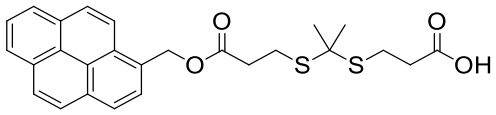
General

DMF and 1-pentanol were distilled under reduced pressure from barium oxide and sodium respectively. THF, CH_2Cl_2 and toluene were purified using an INERT solvent purification system. All other solvents and reagents were of reagent grade and used as received. All the reactions were performed under an atmosphere of nitrogen and monitored by thin-layer chromatography (TLC; Merck precoated silica gel 60_{F254} plates). Chromatographic purification was performed with column chromatography on silica gel (Macherey-Nagel, 2300-400 mesh). Size-exclusion chromatography was carried out on Bio-Beads S-X1 beads (200-400 mesh). Compounds **4**,[1] **5**,[2] **7**,[3] **8**,[4] **10**,[5] **15**[6] and **17**[7] were prepared according to the literature procedure.

NMR spectra were recorded on a Bruker Avance III 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100.6 MHz) in deuterated solvents. Spectra were referenced internally by using the residual solvent (^{1}H: δ = 7.26 for $CDCl_3$, δ = 2.05 for acetone-d_6, δ = 1.72 and 3.58 for THF-d_8) or solvent (^{13}C: δ = 77.2 for $CDCl_3$, δ = 206.3 for acetone-d_6) resonances relative to $SiMe_4$. High-resolution electrospray ionisation (ESI) mass spectra were recorded on a Thermo Finnigan MAT 95 XL or a Bruker SolariX 9.4T Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. Matrix-assisted laser desorption/ionisation time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Daltonics autoflex III spectrometer with α-cyano-4-hydroxycinnamic acid or 2, 5-dihydroxybenzoic acid as the matrix. Electronic absorption and

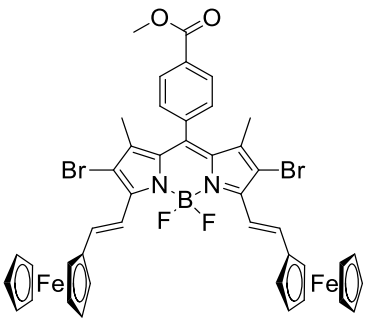
steady-state fluorescence spectra were taken on a Cary 5G UV-Vis-NIR spectrophotometer and a HORIBA FluoroMax-4 spectrofluorometer respectively. pH Values of the solutions were measured with an ORION STAR AIII pH meter.

Synthesis of 6



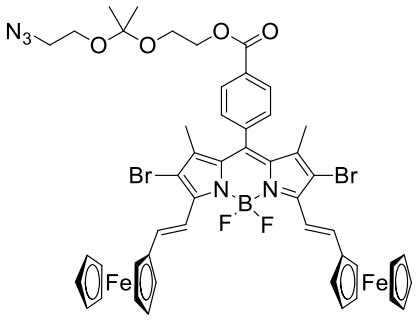
EDC·HCl (82 mg, 0.43 mmol) and DMAP (6.0 mg, 0.050 mmol) were added to a mixture of **4** (0.10 g, 0.43 mmol) and **5** (0.11 g, 0.43 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 16 h, and then the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using CH_2Cl_2/MeOH (100:1, v/v) as the eluent to give a yellow oil (0.13 g, 62%). ^{1}H NMR ($CDCl_3$): δ 9.95 (br s, 1 H, COOH), 8.09-8.24 (m, 5 H, ArH), 7.98-8.05 (m, 4 H, ArH), 5.83 (s, 2 H, $ArCH_2$), 2.90 (t, J = 7.2 Hz, 2 H, CH_2), 2.81 (t, J = 7.2 Hz, 2 H, CH_2), 2.69 (t, J = 7.2 Hz, 2 H, CH_2), 2.62 (t, J = 7.2 Hz, 2 H, CH_2), 1.56 (s, 6 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 178.0, 172.1, 131.8, 131.2, 130.7, 129.5, 128.6, 128.2, 127.9, 127.8, 127.4, 126.1, 125.6, 125.5, 124.8, 124.6 (two overlapping signals), 122.9, 65.1, 56.4, 34.5, 34.3, 30.8, 25.3, 24.5. HRMS (ESI): m/z calcd for $C_{26}H_{25}O_4S_2$ $[M-H]^-$ 465.1200, found 465.1201.

Synthesis of 9



A mixture of compound **7** (0.10 g, 0.19 mmol), **8** (0.25 g, 1.2 mmol), piperidine (0.4 mL), acetic acid (0.3 mL) and a small amount of $Mg(ClO_4)_2$ in toluene (50 mL) was heated under reflux for 18 h. The water formed during the reaction was removed azeotropically with a Dean-Stark apparatus. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using CH_2Cl_2/hexane (1:1, v/v) as the eluent to give a dark purple solid (0.11 g, 62%). ^{1}H NMR ($CDCl_3$): δ 8.21 (d, *J* = 8.0 Hz, 2 H, ArH), 7.94 (d, *J* = 16.0 Hz, 2 H, C=CH), 7.41 (d, *J* = 8.0 Hz, 2 H, ArH), 7.29 (d, *J* = 16.0 Hz, 2 H, C=CH), 4.68 (virtual s, 4 H, Fc-H), 4.49 (virtual s, 4 H, Fc-H), 4.24 (s, 10 H, Fc-H), 4.00 (s, 3 H, CH_3), 1.37 (s, 6 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.5, 148.4, 140.9, 140.3, 140.0, 135.8, 131.7, 131.3, 130.6, 128.9, 115.4, 110.6, 82.5, 71.2, 70.2, 68.5, 52.6, 14.0. HRMS (ESI): *m*/*z* calcd for $C_{43}H_{35}BBr_2F_2Fe_2N_2NaO_2$ $[M+Na]^+$ 954.9712, found 954.9712.

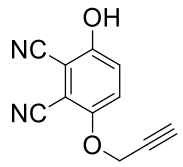
Synthesis of 11



An aqueous NaOH solution (4 M, 5.0 mL) was added dropwise to a solution of **9** (70 mg, 75 μmol) in THF (5 mL). The mixture was stirred at room temperature for 24 h. The volatiles were then removed *in vacuo*, and the residue was mixed with CH_2Cl_2 (30 mL) and water (30 mL). The mixture was acidified to pH 4 with 1 M HCl solution. The aqueous layer was extracted with CH_2Cl_2 (50 mL × 3). The combined organic portions were dried over anhydrous Na_2SO_4 and evaporated *in vacuo*. The crude hydrolysed product was mixed with **10** (30 mg, 0.16 mmol), EDC·HCl (29 mg, 0.15 mmol) and DMAP (18 mg, 0.15 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at room temperature for 16 h, and then the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using CH_2Cl_2/hexane (1:1, v/v) as the eluent to give a dark purple solid (17 mg, 21%). ^{1}H NMR ($CDCl_3$): δ 8.22 (d, *J* = 8.4 Hz, 2 H, ArH), 7.94 (d, *J* = 16.4 Hz, 2 H, C=CH), 7.42 (d, *J* = 8.4 Hz, 2 H, ArH), 7.29 (d, *J* = 16.4 Hz, 2 H, C=CH), 4.68 (t, *J* = 1.6 Hz, 4 H, Fc-H), 4.54 (t, *J* = 4.8 Hz, 4 H, CH_2), 4.49 (t, *J* = 1.6 Hz, 4 H, Fc-H), 4.24 (s, 10 H, Fc-H), 3.87 (t, *J* = 4.8 Hz, 2 H, CH_2), 3.67 (t, *J* = 5.2 Hz, 2 H, CH_2), 3.35 (t, *J* = 5.2 Hz, 2 H, CH_2), 1.44 (s, 6 H, CH_3), 1.37 (s, 6 H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.0, 148.4, 140.9, 140.3, 139.9, 135.7, 131.6, 131.3,

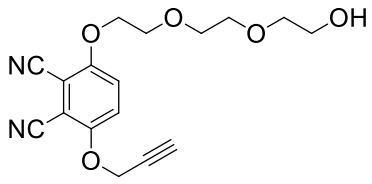
130.6, 128.9, 115.3, 110.6, 100.6, 82.4, 71.2, 70.2, 68.5, 64.9, 60.2, 59.2, 51.1, 24.9, 14.0. HRMS (ESI): *m*/*z* calcd for $C_{49}H_{46}BBr_2F_2Fe_2N_5O_4$ $[M]^+$ 1089.0668, found 1089.0686.

Synthesis of 14



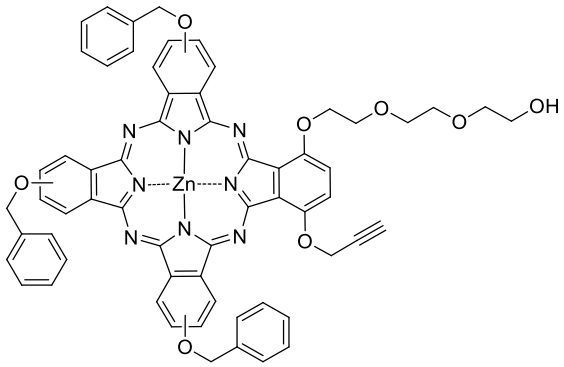
A mixture of 3,6-dihydroxyphthalonitrile (**12**) (5.0 g, 31 mmol), propargyl bromide (**13**) (3.7 g, 31 mmol) and K_2CO_3 (4.3 g, 31 mmol) in DMF (20 mL) was stirred at 60 °C for 24 h. The volatiles were removed under reduced pressure. The residue was mixed with water (50 mL) and the mixture was neutralised with 1 M HCl. It was then extracted with ethyl acetate (100 mL × 3). The combined organic portions were collected and dried over anhydrous Na_2SO_4. After evaporation, the residue was purified by column chromatography on silica gel using CH_2Cl_2/ethyl acetate (5:1, v/v) as the eluent to give a white solid (3.1 g, 50%). ^{1}H NMR (acetone-d_6): δ 7.57 (d, *J* = 9.6 Hz, 2 H, ArH), 7.43 (d, *J* = 9.6 Hz, 2 H, ArH), 4.99 (d, *J* = 2.4 Hz, 2 H, CH_2), 3.22 (t, *J* = 2.4 Hz, 1 H, C≡CH). ^{13}C{^{1}H} NMR (acetone-d_6): δ 156.3, 154.1, 123.6, 121.8, 114.3, 114.0, 105.1, 102.8, 78.6, 78.3, 58.3. HRMS (ESI): *m*/*z* calcd for $C_{11}H_6N_2NaO_2$ $[M+Na]^+$ 221.0322, found 221.0321.

Synthesis of 16



A mixture of phthalonitrile **14** (0.50 g, 2.5 mmol), **15** (1.2 g, 3.9 mmol) and K_2CO_3 (1.0 g, 7.2 mmol) in DMF (10 mL) was stirred at 60 °C for 24 h. The volatiles were removed under reduced pressure. Water (50 mL) was then added and the mixture was neutralised with 1 M HCl. The mixture was extracted with ethyl acetate (50 mL × 3). The combined organic portions were dried over anhydrous Na_2SO_4, and then evaporated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using $CHCl_3/CH_3OH$ (50:1, v/v) as the eluent to give a white solid (0.66 g, 80%). ^{1}H NMR ($CDCl_3$): δ 7.36 (d, *J* = 9.6 Hz, 2 H, ArH), 7.27 (d, *J* = 9.6 Hz, 2 H, ArH), 4.82 (d, *J* = 2.4 Hz, 2 H, CH_2) 4.25 (t, *J* = 4.4 Hz, 2 H, CH_2), 3.91 (t, *J* = 4.4 Hz, 2 H, CH_2), 3.75-3.77 (m, 2 H, CH_2), 3.71-3.73 (m, 2 H, CH_2), 3.67-3.69 (m, 2 H, CH_2), 3.60 (t, *J* = 4.4 Hz, 2 H, CH_2), 2.60 (t, *J* = 2.4 Hz, 1 H, C≡CH), 2.41 (br s, 1 H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.9, 153.7, 119.7, 119.0, 113.0, 112.8, 106.2, 105.9, 77.8, 76.8, 72.6, 71.3, 70.5, 70.2, 69.5, 61.9, 57.6. HRMS (ESI): *m*/*z* calcd for $C_{17}H_{18}N_2NaO_5$ $[M+Na]^+$ 353.1108, found 353.1104.

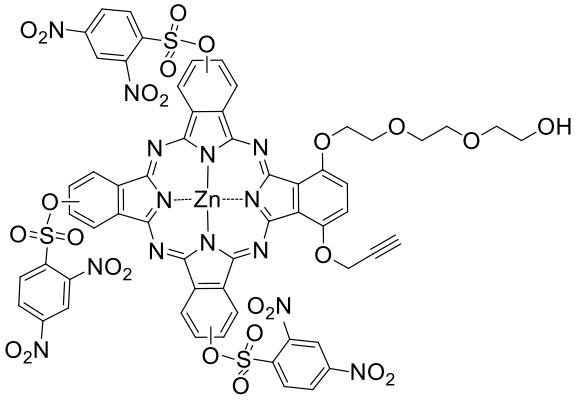
Synthesis of 18



A mixture of **16** (0.45 g, 1.4 mmol), **17** (3.3 g, 14 mmol) and anhydrous $Zn(OAc)_2$ (1.0 g, 5.5 mmol) in 1-pentanol (60 mL) was heated to 90 °C with stirring, and then DBU (0.5 mL, 3.3 mmol) was added. The mixture was kept stirring at 140 °C for 19 h. After brief cooling, the volatiles were removed under reduced pressure. The residue was dissolved in $CHCl_3$ (100 mL) and the solution was filtered. The filtrate was collected and evaporated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel using $CHCl_3/CH_3OH$ (50:1, v/v) as the eluent. The crude product was recrystallised from a mixture of $CHCl_3$ and hexane to give a dark green solid (90 mg, 6%). ^{1}H NMR ($CDCl_3$ with a trace amount of pyridine-d_5): δ 8.78-9.05 (m, 3 H, Pc-H_α), 8.43-8.72 (m, 3 H, Pc-H_α), 7.72-7.82 (m, 6 H, Pc-H_β and/or ArH), 7.61-7.68 (m, 2 H, Pc-H_β and/or ArH), 7.51-7.59 (m, 6 H, Pc-H_β and/or ArH), 7.42-7.49 (m, 4 H, Pc-H_β and/or ArH), 7.31-7.41 (m, 1 H, Pc-H_β and/or ArH), 7.16-7.23 (m, 1 H, Pc-H_β and/or ArH), 5.77-5.87 (m, 2 H, CH_2), 5.49-5.60 (m, 6 H, CH_2), 4.78-4.87 (m, 2 H, CH_2), 4.45-4.52 (m, 2 H, CH_2), 4.12-4.14 (m, 1 H, CH_2), 3.97-3.99 (m, 1 H, CH_2), 3.86-3.88 (m, 1 H, CH_2), 3.68-3.70 (m, 1 H, CH_2), 3.62-3.66 (m, 2 H, CH_2), 3.56-3.59 (m, 1 H, CH_2),

3.52-3.53 (m, 1 H, CH_2), 3.11 (br s, 1 H, OH), 2.78-2.91 (m, 1 H, C≡CH). HRMS (ESI): *m*/*z* calcd for $C_{62}H_{48}N_8NaO_8Zn$ $[M+Na]^+$ 1119.2779, found 1119.2783.

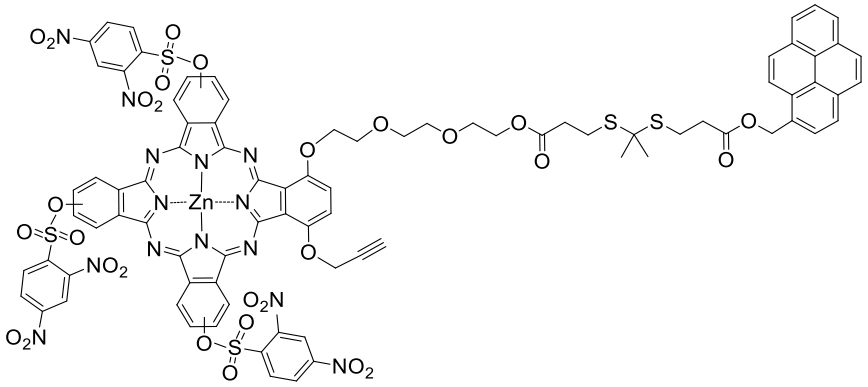
Synthesis of 20



A solution of **18** (0.10 g, 91 μmol) in TFA (10 mL) was heated under reflux for 24 h. After brief cooling, the volatiles were removed under reduced pressure. The residue was dissolved in $CHCl_3$ (10 mL) and precipitated by adding a large amount of hexane. The precipitate was filtered off and washed with hexane. The crude intermediate product was mixed with 2,4-dinitrobenzenesulfonyl chloride (0.10 g, 0.38 mmol) and Et_3N (0.10 mL, 0.72 mmol) in THF (10 mL). The mixture was stirred at room temperature for 6 h, and then the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using $CHCl_3$/CH_3OH (50:1, v/v) as the eluent. The purified product was recrystallised from a mixture of THF, CH_3OH and hexane to give a dark green solid (23 mg, 17%). ^{1}H NMR (THF-d_8): δ 9.10- 9.13 (m, 3 H, Pc-H$_\alpha$ and ArH), 8.77-8.95 (m, 5 H, Pc-H$_\alpha$ and ArH), 8.50-8.72 (m, 7 H, Pc-H$_\alpha$ and ArH), 7.72-7.92 (m, 3 H, Pc-H$_\beta$), 7.30-7.66 (m, 2 H, Pc-H$_\beta$), 5.79 (virtual t, *J*

= 12.0 Hz, 2 H, CH_2), 4.76-4.89 (m, 2 H, CH_2), 4.38-4.51 (m, 2 H, CH_2), 4.15-4.18 (m, 1 H, CH_2), 4.04-4.06 (m, 1 H, CH_2), 3.86-3.88 (m, 1 H, CH_2), 3.76-3.78 (m, 1 H, CH_2), 3.49-3.53 (m, 2 H, CH_2), 3.43-3.46 (m, 2 H, CH_2), 3.29-3.34 (m, 1 H, C≡CH). HRMS (ESI): *m*/*z* calcd for $C_{59}H_{36}N_{14}NaO_{26}S_3Zn$ $[M+Na]^+$ 1539.0271, found 1539.0276.

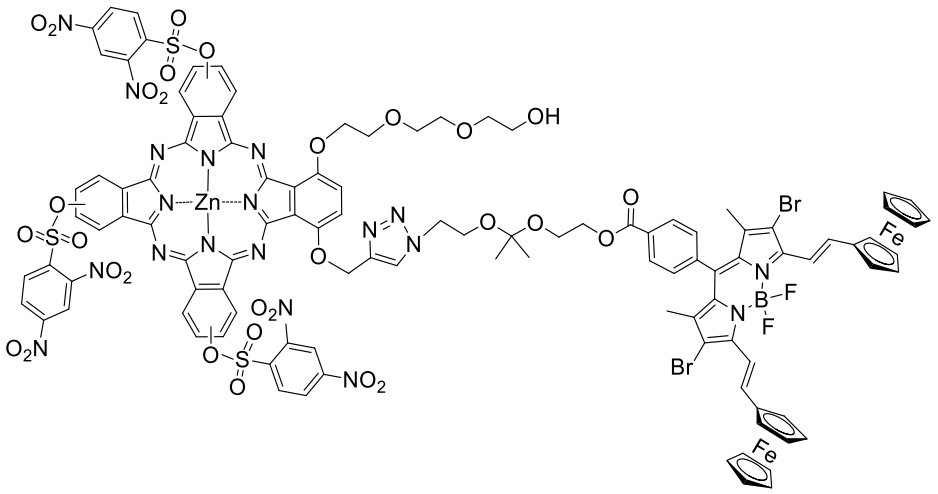
Synthesis of 2



EDC·HCl (15 mg, 78 μmol) and DMAP (5.0 mg, 41 μmol) were added to a mixture of **20** (60 mg, 40 μmol) and **6** (40 mg, 86 μmol) in THF (2 mL). The mixture was stirred at room temperature for 18 h, and then the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using $CHCl_3$/MeOH (100:1, v/v) as the eluent. The purified product was recrystallised from a mixture of THF and hexane to give a dark green solid (30 mg, 38%). ^{1}H NMR (THF-d_8): δ 8.81-9.12 (m, 9 H, Pc-H$_\alpha$ and ArH), 8.47-8.68 (m, 6 H, Pc-H$_\alpha$ and ArH), 7.43-7.91 (m, 14 H, Pc-H$_\beta$ and ArH), 5.79-5.82 (m, 2 H, CH_2), 5.56-5.61 (m, 2 H, CH_2), 4.82-4.88 (m, 2 H, CH_2), 4.46-4.51 (m, 2 H, CH_2), 4.03-4.16 (m, 4 H, CH_2), 3.83-3.88 (m, 1 H, CH_2), 3.77-3.79 (m, 1 H, CH_2), 3.66-3.75 (m, 2 H, CH_2), 3.29-3.34

(m, 1 H, C≡CH), 2.70-2.76 (m, 4 H, CH_2), 2.44-2.55 (m, 4 H, CH_2), 1.41-1.44 (m, 6 H, CH_3). HRMS (ESI): *m*/*z* calcd for $C_{85}H_{60}N_{14}NaO_{29}S_5Zn$ $[M+Na]^+$ 1989.1442, found 1989.1432.

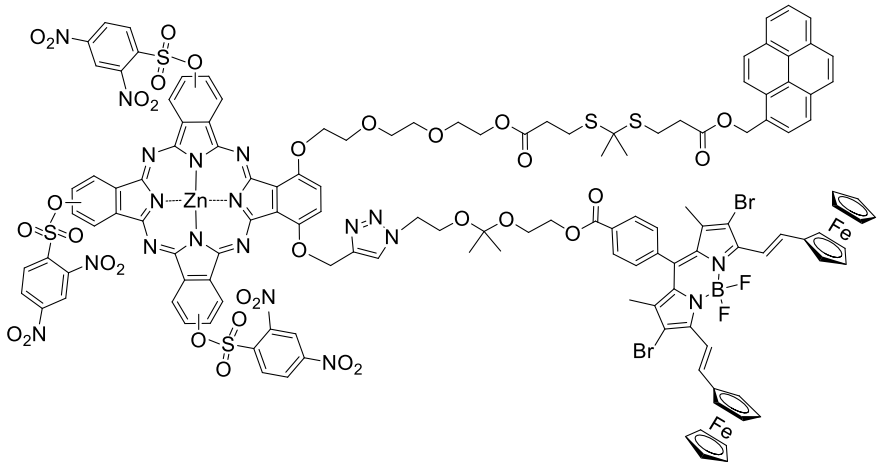
Synthesis of 3



Compounds **20** (20 mg, 13 μmol) and **11** (15 mg, 14 μmol) were added to a solution of CuI (0.50 mg, 2.6 μmol) and pyridine (0.10 mL, 1.2 mmol) in THF (1 mL). The mixture was stirred at room temperature for 18 h. After filtration, the filtrate was evaporated and then the residue was purified by size-exclusion chromatography using THF as the eluent followed by recrystallisation from a mixture of THF, CH_3OH and hexane to give a dark blue solid (15 mg, 44%). ^{1}H NMR (THF-d_8): δ 9.08-9.13 (m, 3 H, Pc-H$_\alpha$ and ArH), 8.85-8.92 (m, 5 H, Pc-H$_\alpha$ and ArH), 8.47-8.75 (m, 9 H, Pc-H$_\alpha$ and ArH), 8.16-8.20 (m, 2 H, C=CH), 7.76-7.89 (m, 5 H, Pc-H$_\beta$ and ArH), 7.52-7.54 (m, 3 H, Pc-H$_\beta$ and H$_{triazole}$), 7.16-7.20 (m, 2 H, ArH), 6.02-6.13 (m, 2 H, CH_2), 4.78-4.83 (m, 4 H, CH_2), 4.61 (virtual s, 4 H, Fc-H), 4.48 (virtual s, 4 H, Fc-H), 4.34-4.40 (m, 4 H, CH_2), 4.18 (s, 10 H, Fc-H), 4.01-4.16 (m, 4 H, CH_2), 3.75-3.84 (m, 4 H, CH_2),

3.47-3.57 (m, 4 H, CH_2), 1.29-1.31 (m, 12 H, CH_3). HRMS (MALDI-TOF): *m*/*z* calcd for $C_{108}H_{82}BBr_2F_2Fe_2N_{19}O_{30}S_3Zn$ $[M]^+$ 2607.1071, found 2607.1090.

Synthesis of 1



Compounds **2** (10 mg, 5.1 μmol) and **11** (6.0 mg, 5.5 μmol) were added to a solution of CuI (0.50 mg, 2.6 μmol) and pyridine (0.10 mL, 1.2 mmol) in THF (1 mL). The mixture was stirred at room temperature for 18 h. After filtration, the filtrate was evaporated and then the residue was purified by size-exclusion chromatography using THF as the eluent followed by recrystallisation from a mixture of THF, CH_3OH and hexane to give a dark blue solid (9.0 mg, 58%). ^{1}H NMR (THF-d_8): δ 8.89-9.10 (m, 9 H, Pc-H$_\alpha$ and ArH), 8.44-8.66 (m, 6 H, Pc-H$_\alpha$ and ArH), 8.16-8.21 (m, 2 H, C=CH), 6.99-7.90 (m, 21 H, Pc-H$_\beta$, H$_{triazole}$, C=CH, and ArH), 6.07-6.21 (m, 2 H, CH_2), 5.52-5.59 (m, 2 H, CH_2), 4.73-4.88 (m, 4 H, CH_2), 4.54-4.62 (m, 4 H, Fc-H), 4.36-4.47 (m, 8 H, Fc-H and CH_2), 4.03-4.18 (m, 16 H, Fc-H and CH_2), 3.84-3.86 (m, 1 H, CH_2), 3.76-3.78 (m, 1 H, CH_2), 3.71-3.74 (m, 2 H, CH_2), 3.57-3.71 (m, 2 H, CH_2), 2.70-2.78

(m, 4 H, CH_2), 2.47-2.51 (m, 4 H, CH_2), 1.42-1.44 (m, 6 H, CH_3), 1.26-1.35 (m, 12 H, CH_3). HRMS (MALDI-TOF): *m*/*z* calcd for $C_{134}H_{106}BBr_2F_2Fe_2N_{19}O_{33}S_5Zn$ $[M]^+$ 3056.2233, found 3056.2291.

UV-Vis and fluorescence spectroscopic studies

Compounds **1**-**3** were dissolved in DMF to give 1 mM stock solutions, which were diluted to 2 μM with PBS (pH = 7.4) with 1% Tween 80 (v/v). An aliquot of these solutions (3 mL) was mixed with different solutions. For studying the effect of GSH, it was mixed with an aqueous solution of GSH (2 mM) for 12 h. For studying the effect of acid, it was kept in an aqueous solution at pH 6.0 for 12 h. For examining the effect of irradiation (λ > 610 nm), the solutions were illuminated with red light coming from a 100 W halogen lamp after passing through a water tank for cooling and a colour glass filter (Newport) cut-on at 610 nm for 10 min. The UV-Vis and fluorescence spectra (λ_{ex} = 610 nm, λ_{em} = 630-800 nm) of these solutions were recorded at room temperature. For studying the effect of irradiation (λ = 345 nm), the solutions were excited with the spectrofluorometer directly. The UV-Vis and fluorescence spectra (λ_{ex} = 345 nm, λ_{em} = 360-660 nm) of these solutions were recorded.

Singlet oxygen generation studies

Solutions of **1**-**3** were prepared and treated under different conditions as described above. The

resulting solutions were mixed with a solution of DPBF in DMF (9 mM, 10 μL) and illuminated with red light coming from a 100 W halogen lamp after passing through a water tank for cooling and a colour glass filter (Newport) cut-on at 610 nm for 270 s. The decay of DPBF at 417 nm was monitored with a spectrophotometer during the irradiation period.

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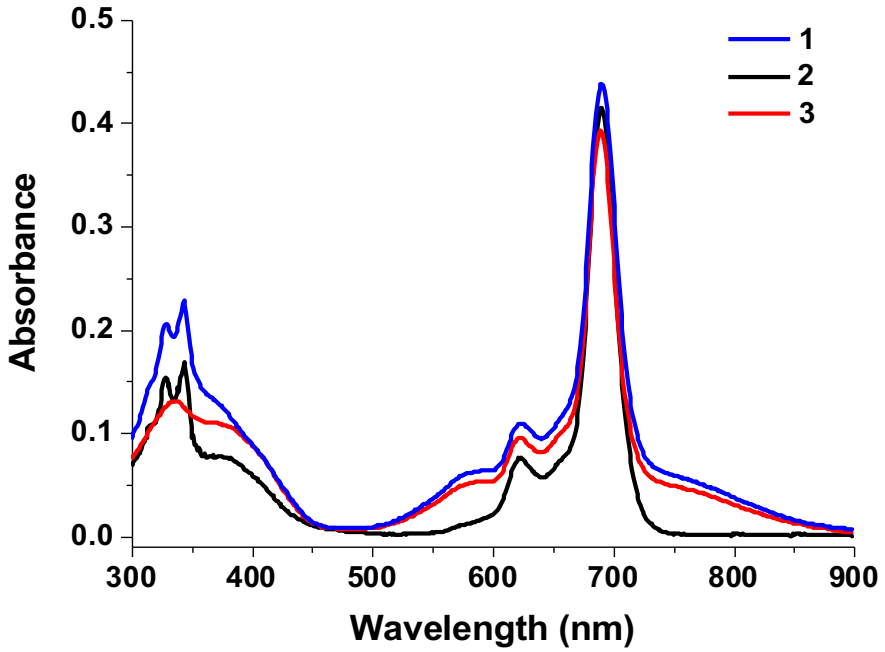


Fig. S1 Electronic absorption spectra of **1**-**3** (all in 2 μM) in DMF.

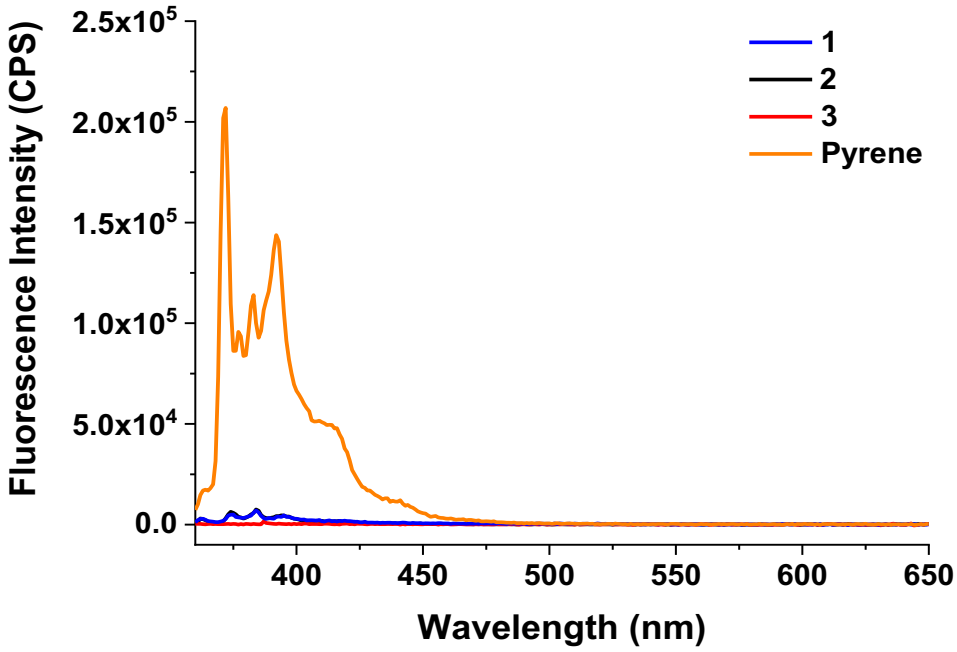


Fig. S2 Fluorescence spectra (λ_{ex} = 345 nm) of **1**-**3** and free pyrene (all in 2 μM) in DMF.

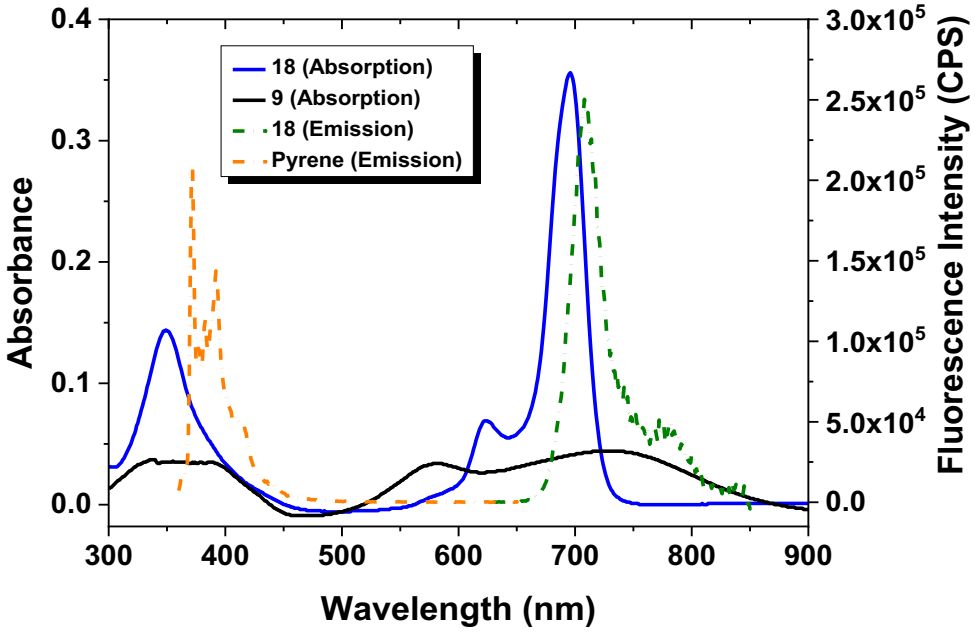


Fig. S3 Spectral overlap between the fluorescence bands of free pyrene (λ_{ex} = 345 nm) and the B-band absorptions of phthalocyanine **18** and bis(ferrocenylethenyl) BODIPY **9**, as well as between the fluorescence band of **18** (λ_{ex} = 610 nm) and the longest-wavelength absorption of **9** (all in 2 μM) in DMF.

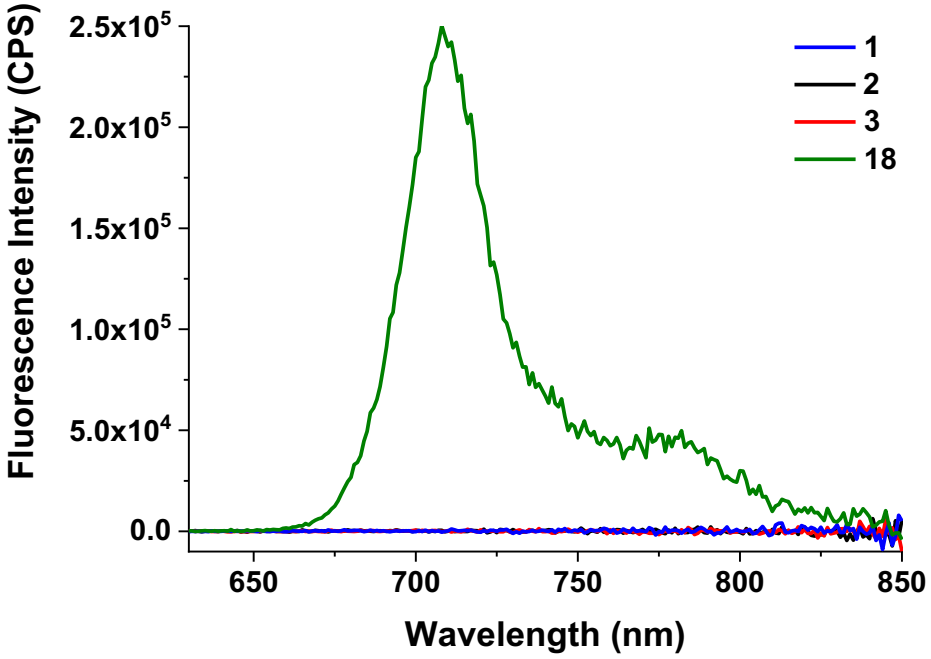


Fig. S4 Fluorescence spectra (λ_{ex} = 610 nm) of **1**-**3** and **18** (all in 2 μM) in DMF.

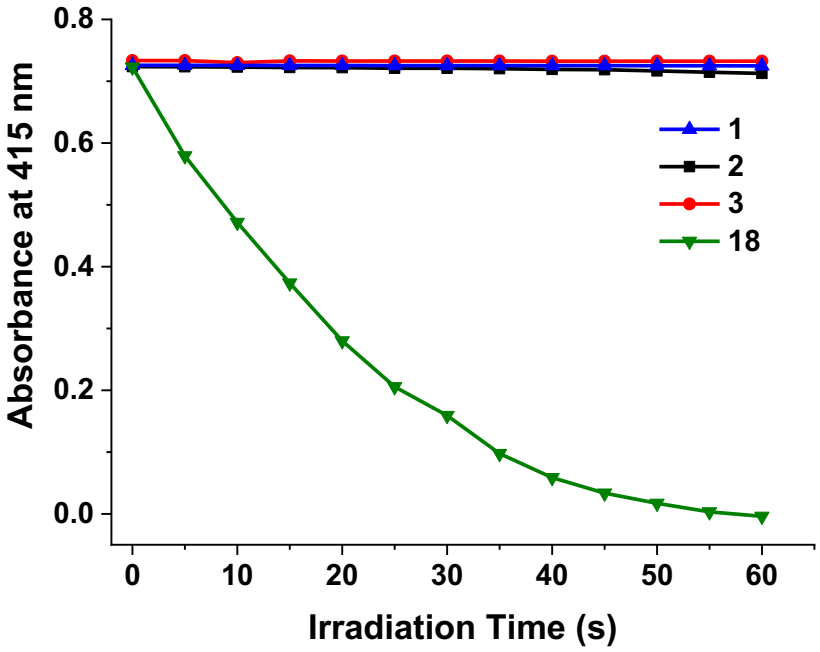
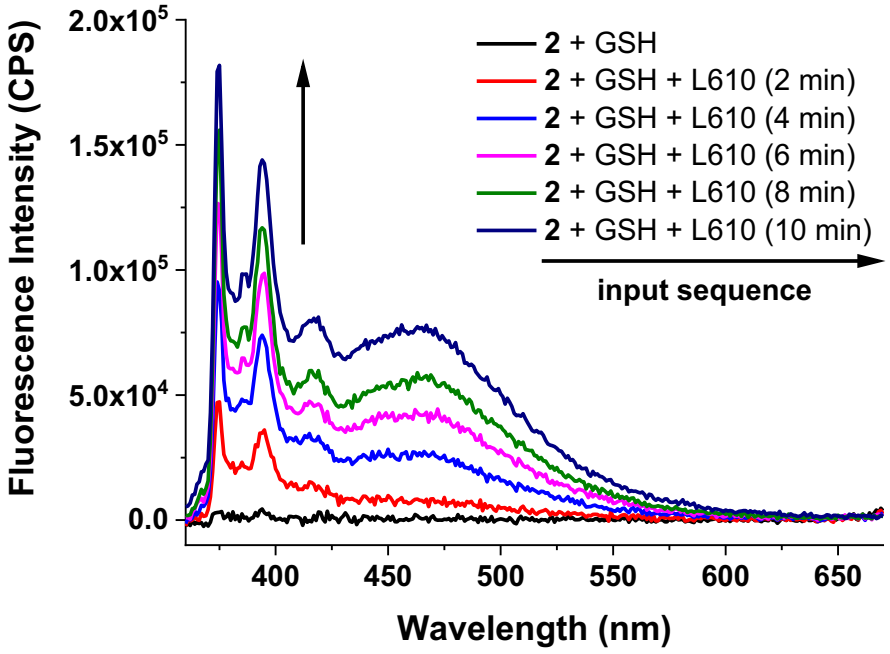


Fig. S5 Comparison of the rates of decay of DPBF (initial concentration = 30 μM) as monitored spectroscopically at its absorbance at 415 nm using **1**-**3** and **18** (all in 2 μM) as the photosensitisers in DMF.

(a)



(b)

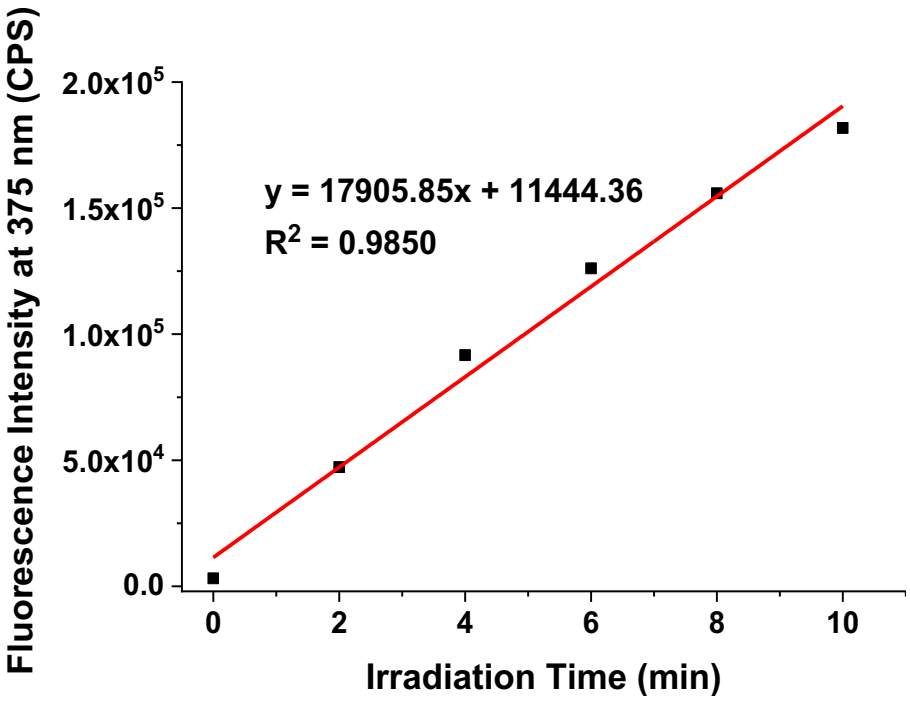


Fig. S6 (a) Change in fluorescence spectrum (λ_{ex} = 345 nm) of **2** (2 μM) in PBS (pH 7.4) upon treatment with GSH (2 mM) followed by red-light irradiation (λ > 610 nm) over a period of 10 min. (b) Plot of the fluorescence intensity at 375 nm *vs.* the irradiation time.

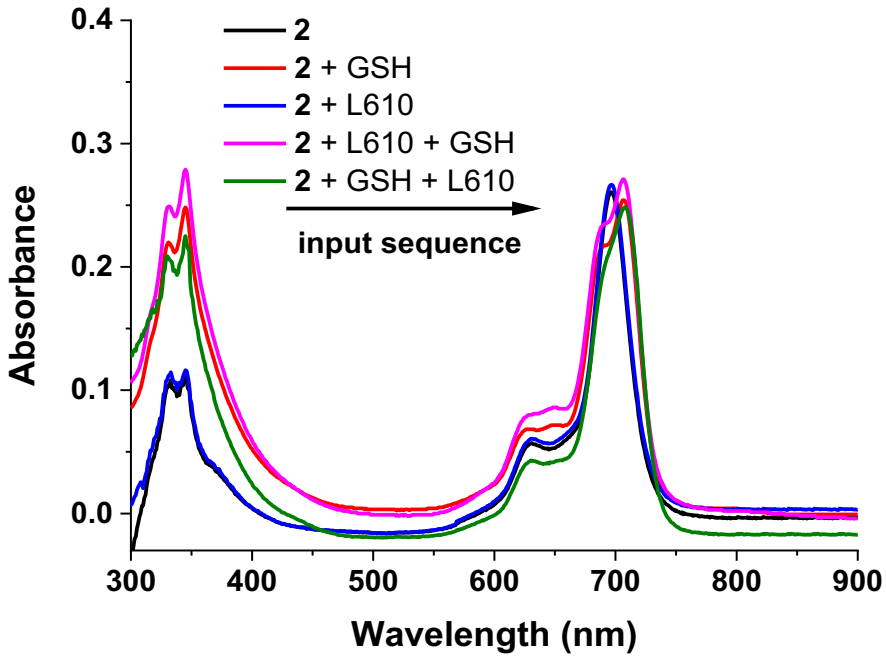


Fig. S7 Electronic absorption spectra of **2** (2 μM) in PBS (pH 7.4) in response to 2 mM of GSH and/or red-light irradiation (λ > 610 nm) for 10 min in different sequence.

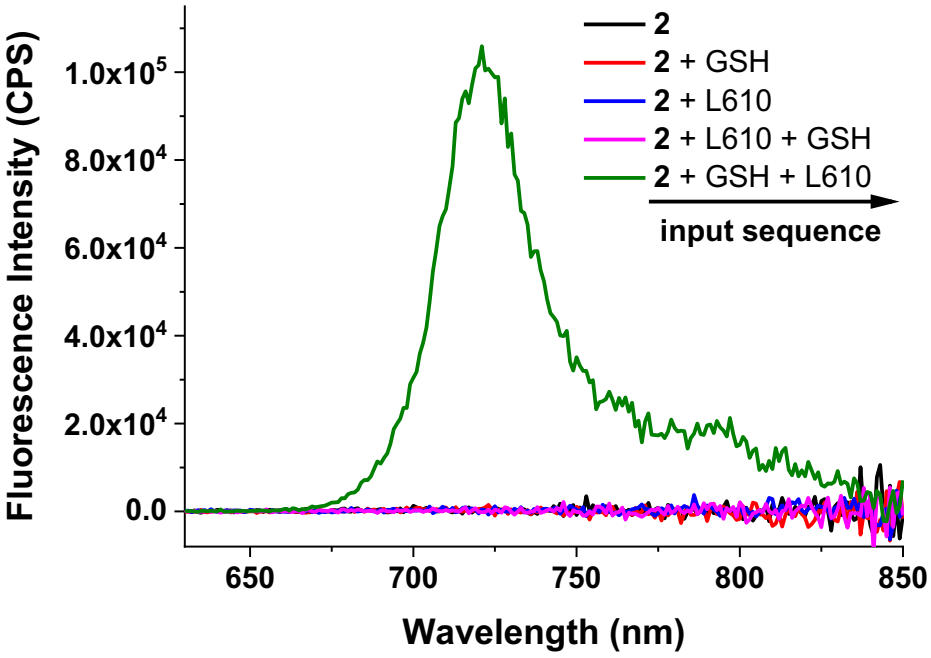
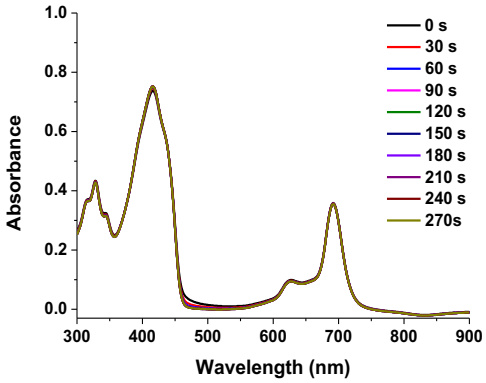
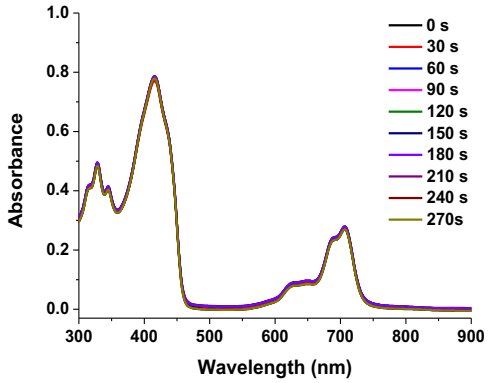


Fig. S8 (a) Fluorescence spectra (λ_{ex} = 610 nm) of **2** (2 μM) in PBS (pH 7.4) in response to 2 mM of GSH and/or red-light irradiation (λ > 610 nm) for 10 min in different sequence.

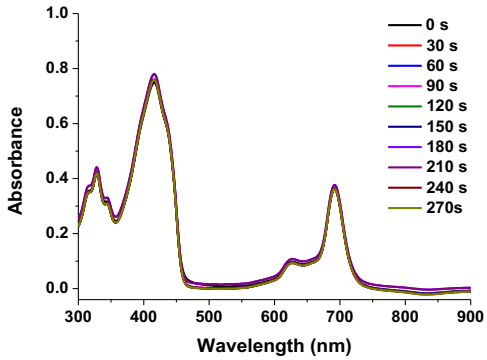
(a) 2 + DPBF



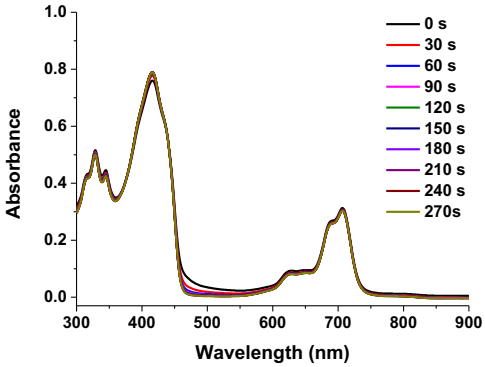
(b) 2 + DPBF + GSH



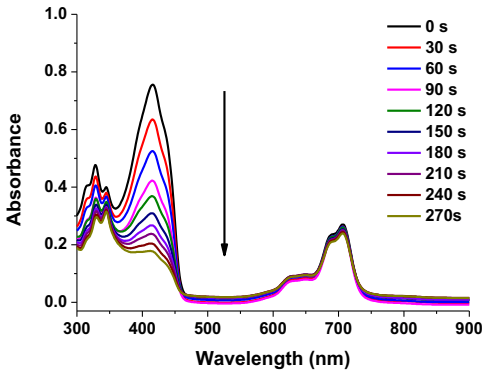
(c) 2 + DPBF + L610



(d) 2 + DPBF + L610 + GSH



(e) 2 + DPBF + GSH + L610



(f)

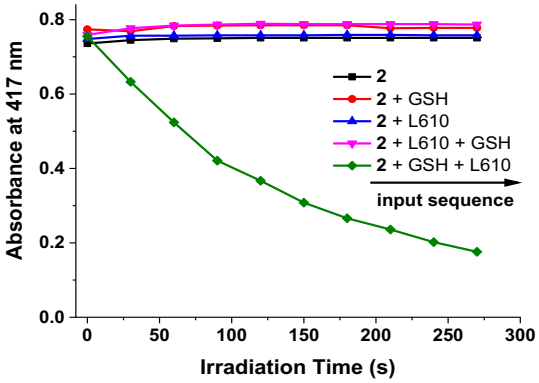
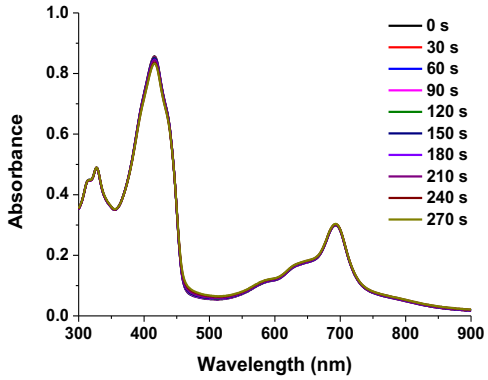
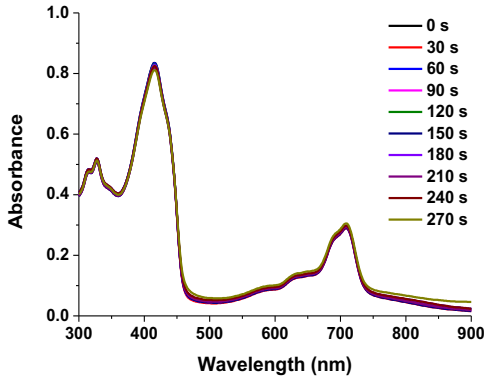


Fig. S9 (a-e) Changes in electronic absorption spectra of mixtures of **2** (2 μM) and DPBF (initial concentration = 30 μM) in PBS (pH 7.4) in response to 2 mM of GSH and/or red-light irradiation (λ > 610 nm) for 10 min in different sequence upon further irradiation (λ > 610 nm) for 270 s. (f) Comparison of the corresponding rates of decay of DPBF as monitored spectroscopically at its absorbance at 417 nm.

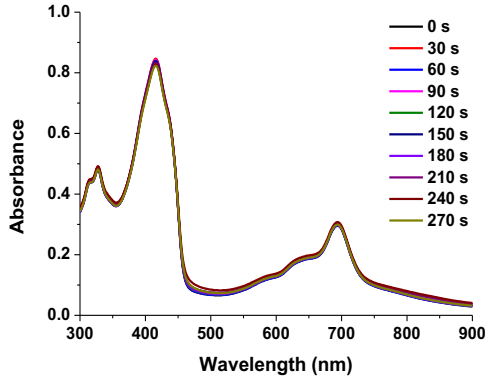
(a) 3 + DPBF



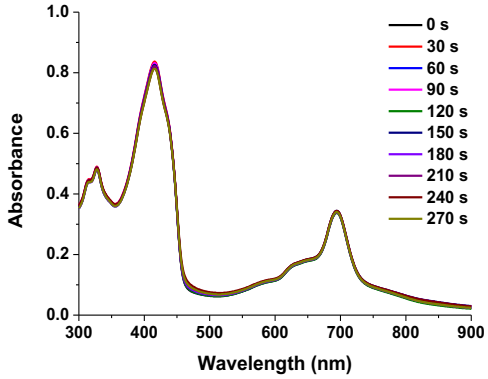
(b) 3 + DPBF + GSH



(c) 3 + DPBF + Acid



(d) 3 + DPBF + Acid + GSH



(e) 3 + DPBF + GSH + Acid

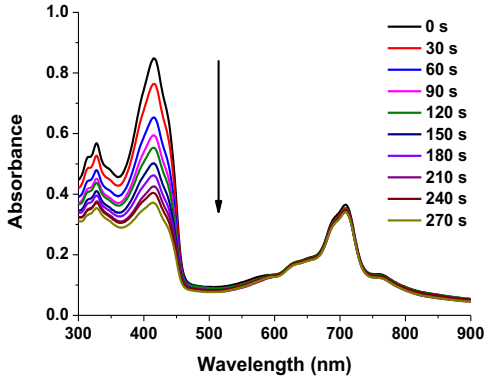


Fig. S10 Changes in electronic absorption spectra of mixtures of **3** (2 μM) and DPBF (initial concentration = 30 μM) in PBS (pH 7.4) in response to 2 mM of GSH and/or acid (pH 6.0) in different sequence upon irradiation (λ > 610 nm) for 270 s.

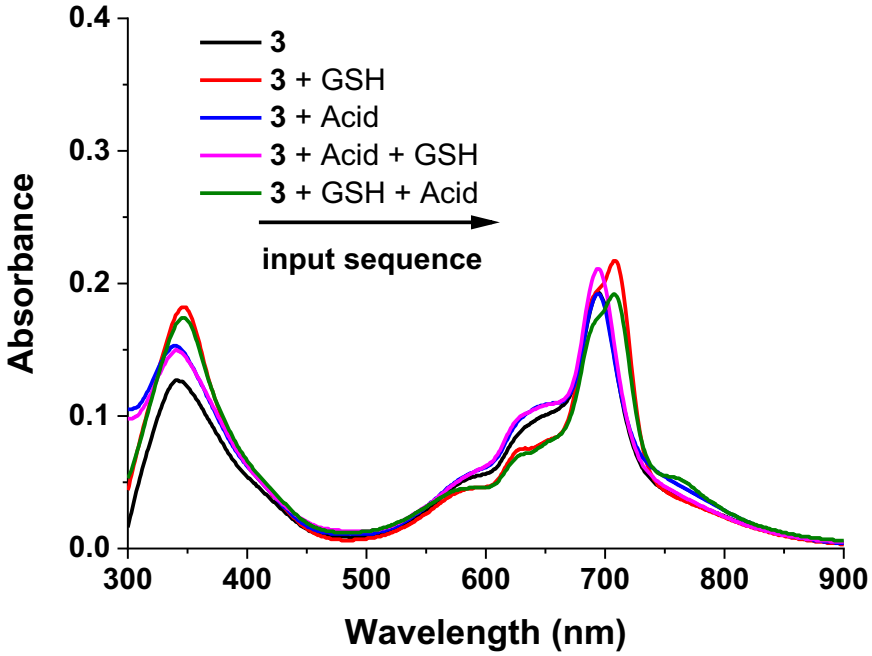
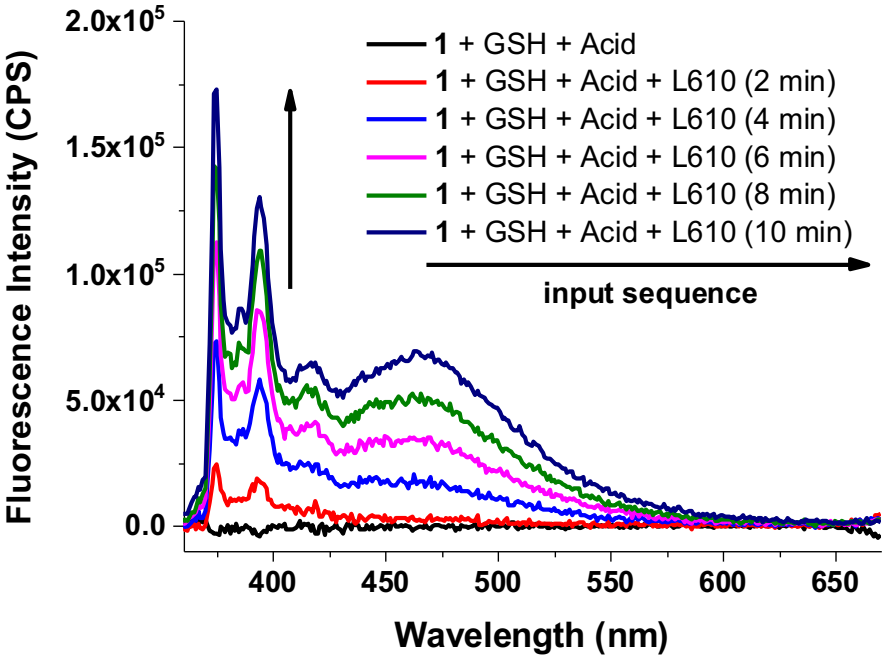


Fig. S11 Electronic absorption spectra of **3** (2 μM) in PBS (pH 7.4) in response to two 2 mM of GSH and/or acid (pH 6.0) in different sequence.

(a)



(b)

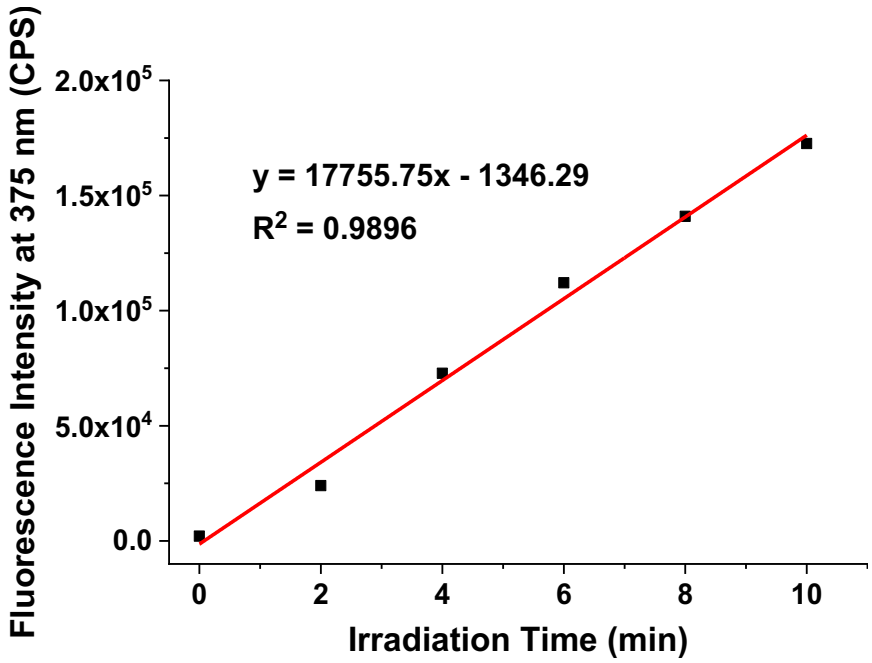


Fig. S12 (a) Change in fluorescence spectrum (λ_{ex} = 345 nm) of **1** (2 μM) in PBS (pH 7.4) upon sequential treatment with GSH (2 mM), acid (pH 6.0) and red-light irradiation (λ > 610 nm) over a period of 10 min. (b) Plot of the fluorescence intensity at 375 nm *vs.* the irradiation time.

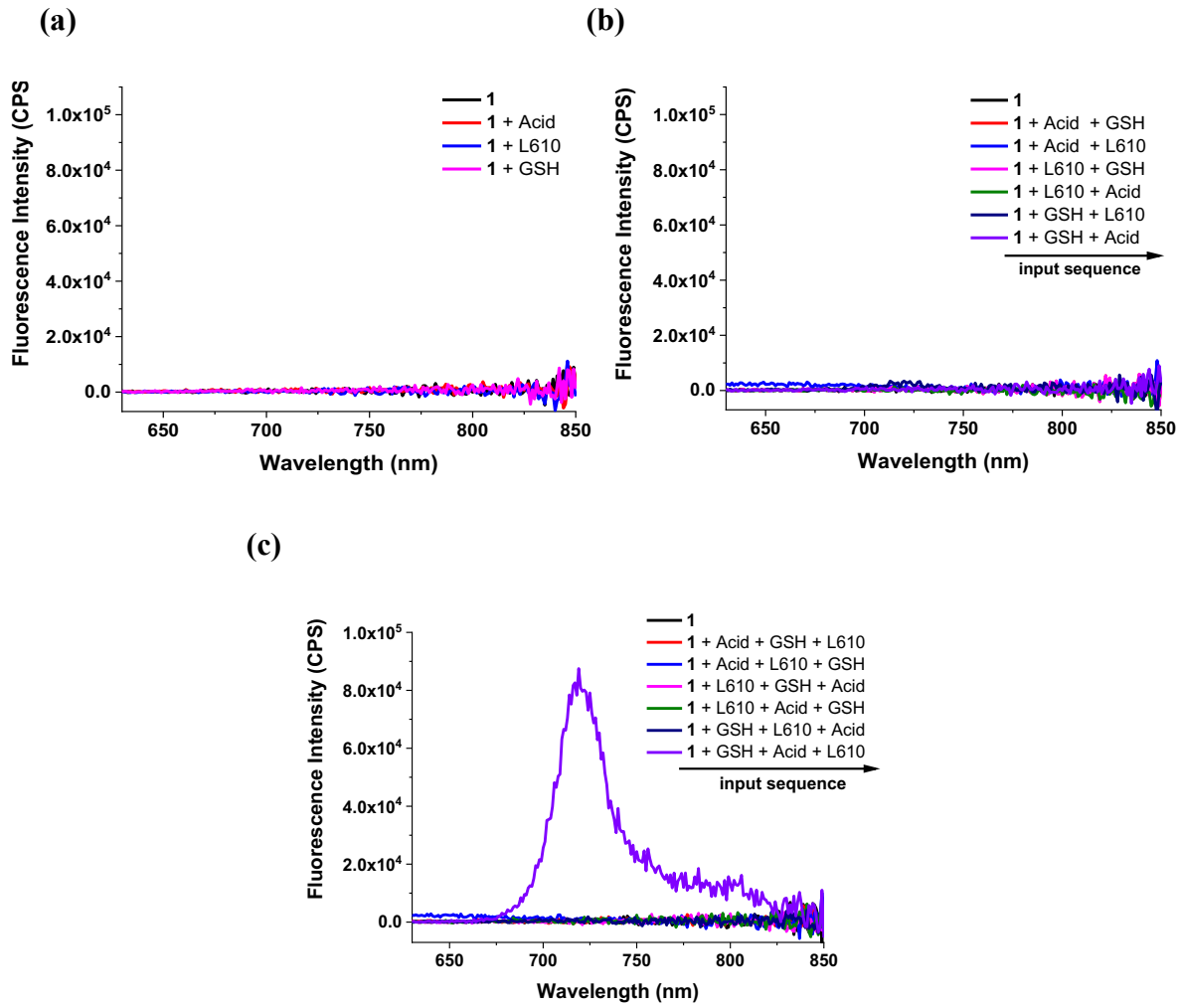


Fig. S13 Fluorescence spectra (λ_{ex} = 610 nm) of **1** (2 μM) in PBS (pH 7.4) in response to 2 mM of GSH, acid (pH 6.0) and/or red-light irradiation (λ > 610 nm) for 10 min under (a) one-input, (b) two-input and (c) three-input conditions.

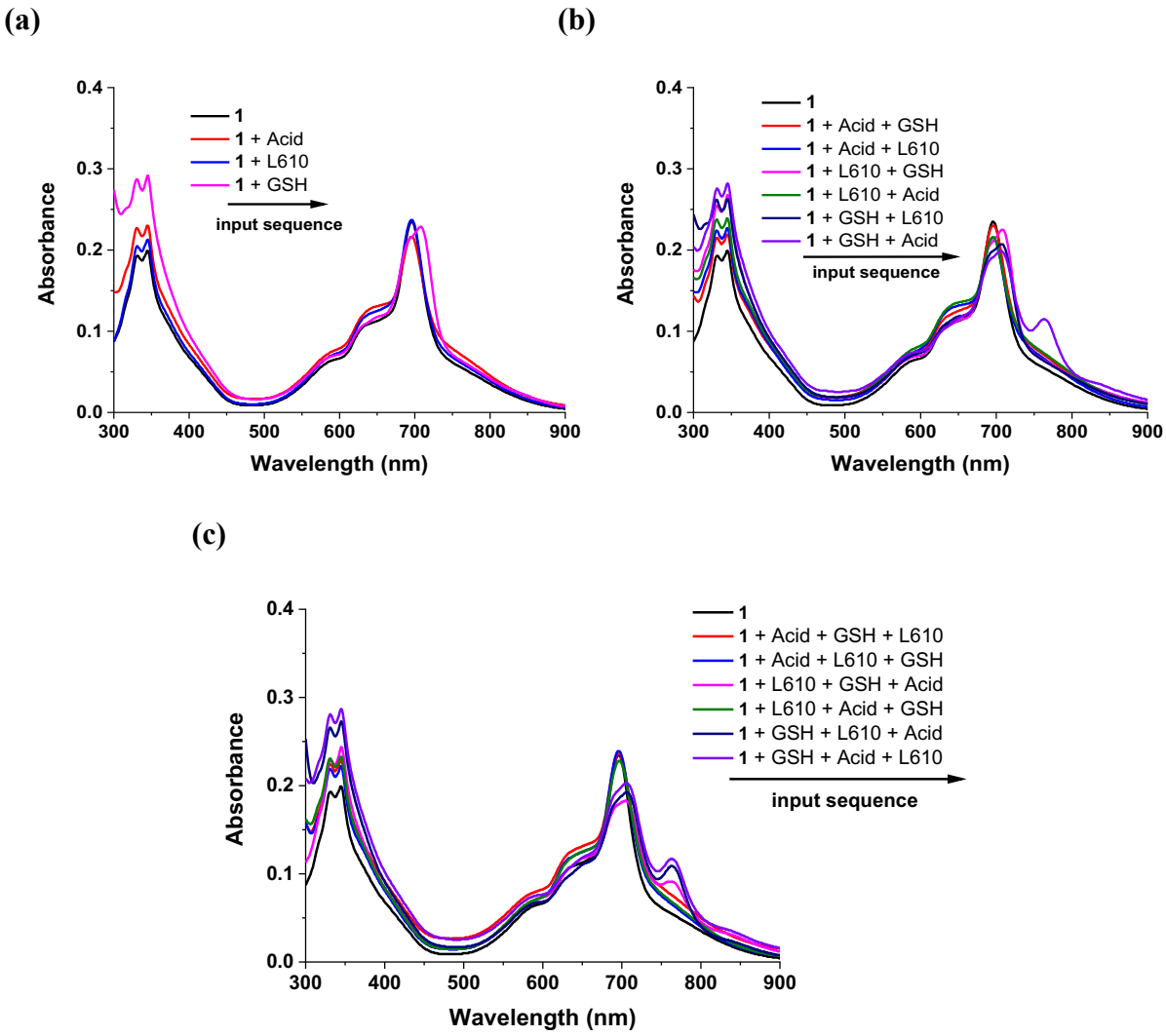
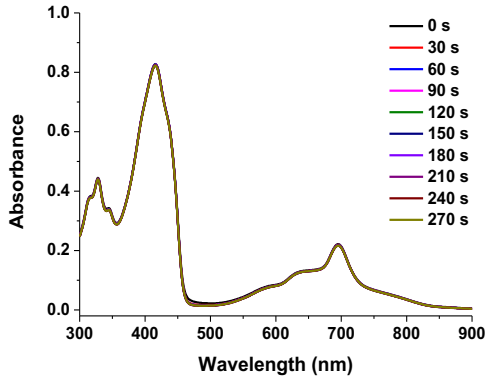
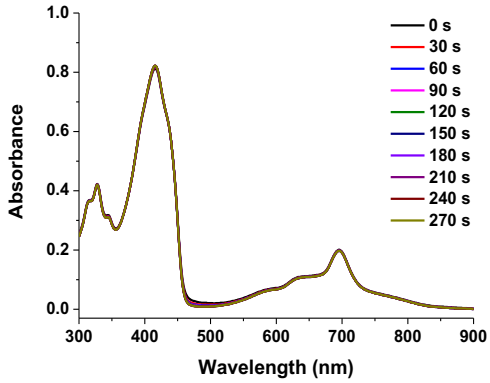


Fig. S14 Electronic absorption spectra of **1** (2 μM) in PBS (pH 7.4) in response to 2 mM of GSH, acid (pH 6.0) and/or red-light irradiation (λ > 610 nm) for 10 min under (a) one-input, (b) two-input and (c) three-input conditions.

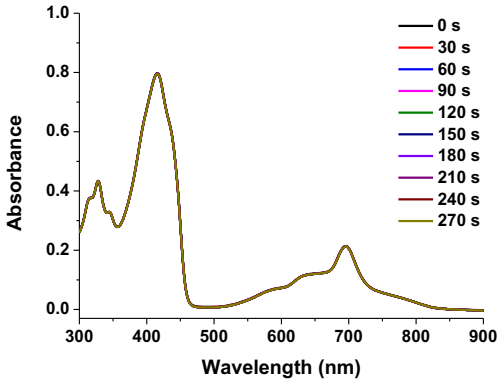
(a) 1 + DPBF



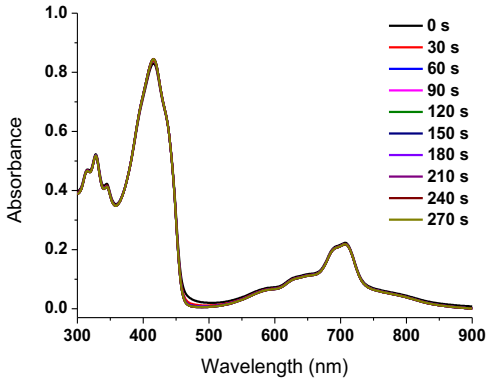
(b) 1 + DPBF + Acid



(c) 1 + DPBF + L610



(d) 1 + DPBF + GSH



(e)

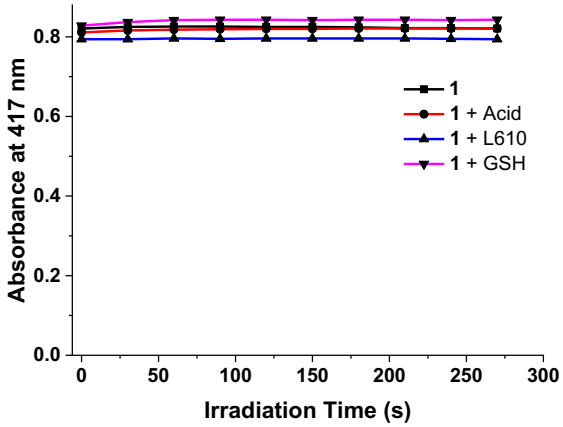


Fig. S15 (a-d) Changes in electronic absorption spectra of mixtures of **1** (2 μM) and DPBF (initial concentration = 30 μM) in PBS (pH 7.4) in response to 2 mM of GSH, acid (pH 6.0) or red-light irradiation (λ > 610 nm) for 10 min upon further irradiation (λ > 610 nm) for 270 s. (e) Comparison of the corresponding rates of decay of DPBF as monitored spectroscopically at its absorbance at 417 nm.

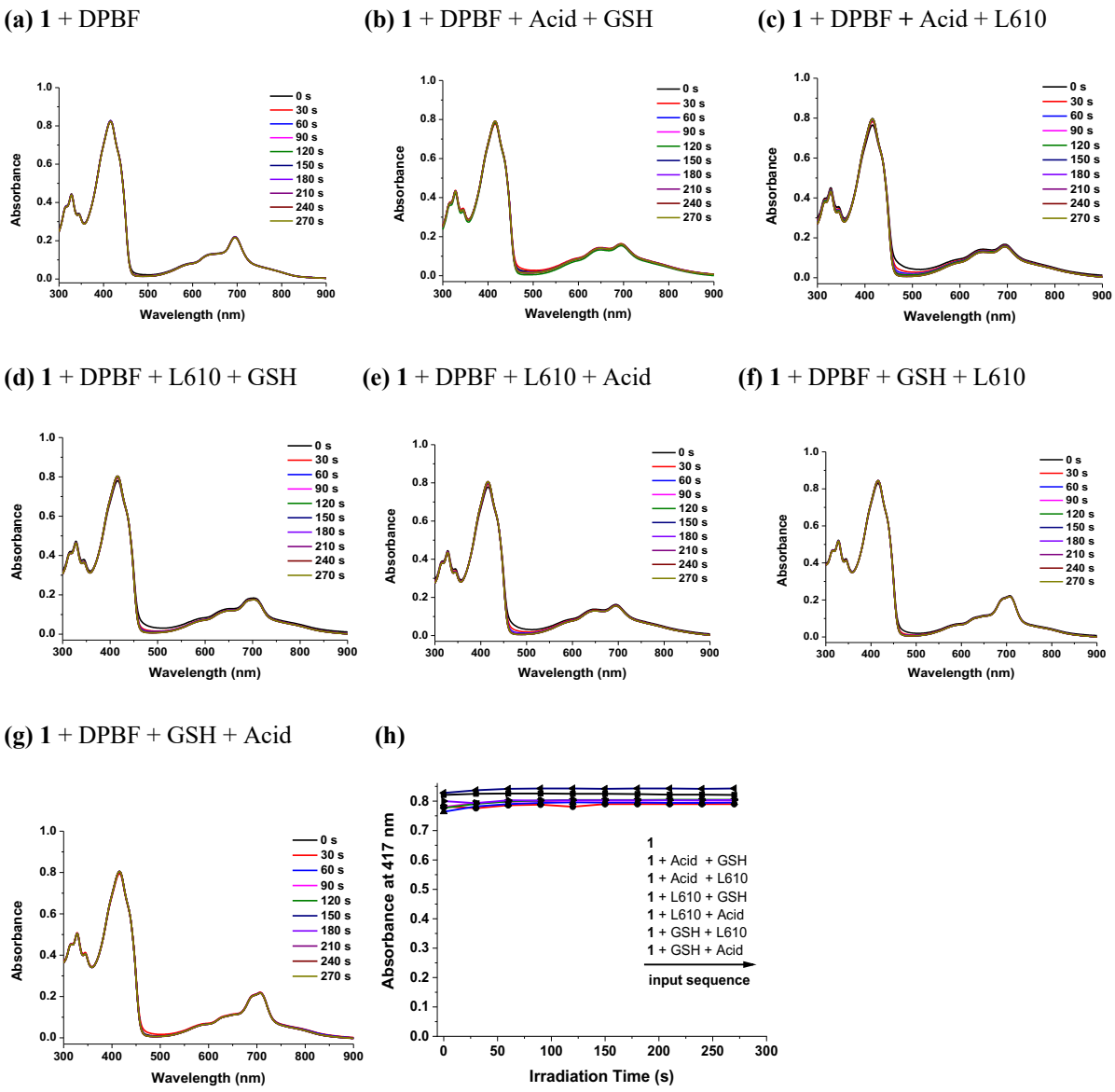


Fig. S16 (a-g) Changes in electronic absorption spectra of mixtures of **1** (2 μM) and DPBF (initial concentration = 30 μM) in PBS (pH 7.4) in response to 2 mM of GSH, acid (pH 6.0) and/or red-light irradiation (λ > 610 nm) for 10 min under two-input conditions upon further irradiation (λ > 610 nm) for 270 s. (h) Comparison of the corresponding rates of decay of DPBF as monitored spectroscopically at its absorbance at 417 nm.

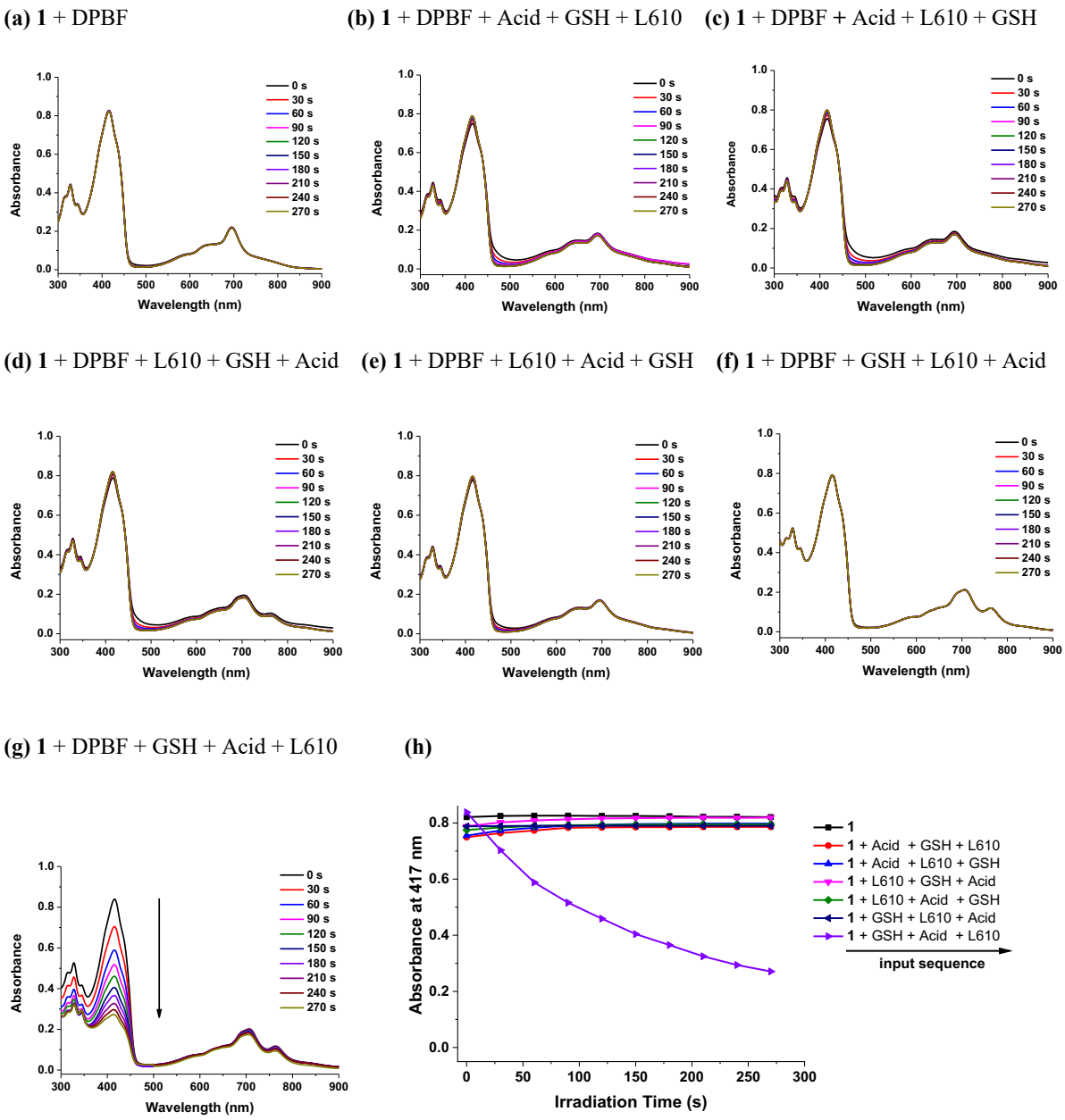
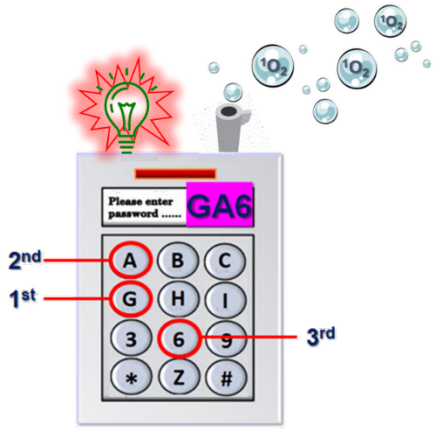


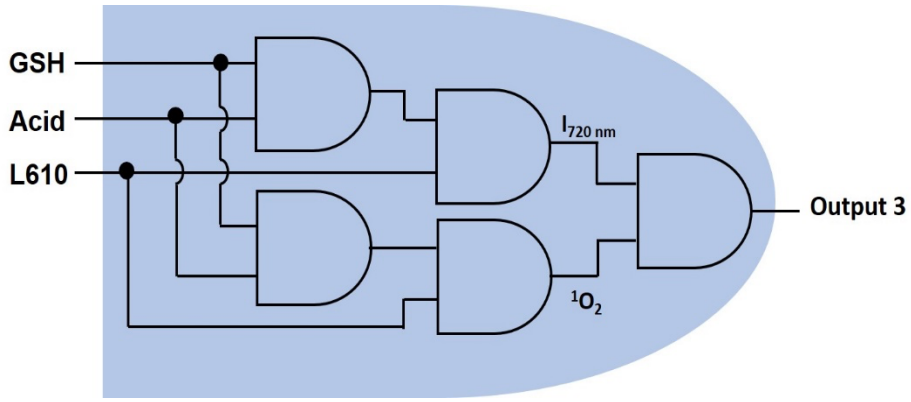
Fig. S17 (a-g) Changes in electronic absorption spectra of mixtures of **1** (2 μM) and DPBF (initial concentration = 30 μM) in PBS (pH 7.4) in response to 2 mM of GSH, acid (pH 6.0) and red-light irradiation (λ > 610 nm) for 10 min under three-input conditions upon further irradiation (λ > 610 nm) for 270 s. (h) Comparison of the corresponding rates of decay of DPBF as monitored spectroscopically at its absorbance at 417 nm.



G = GSH, A = acid, 6 = red light > 610 nm

Entry	Output 1 ($I_{720\ nm}$)	Output 2 ($^1O_2$)	Output 3
6AG	0	0	0
6GA	0	0	0
A6G	0	0	0
AG6	0	0	0
G6A	0	0	0
GA6	1	1	1

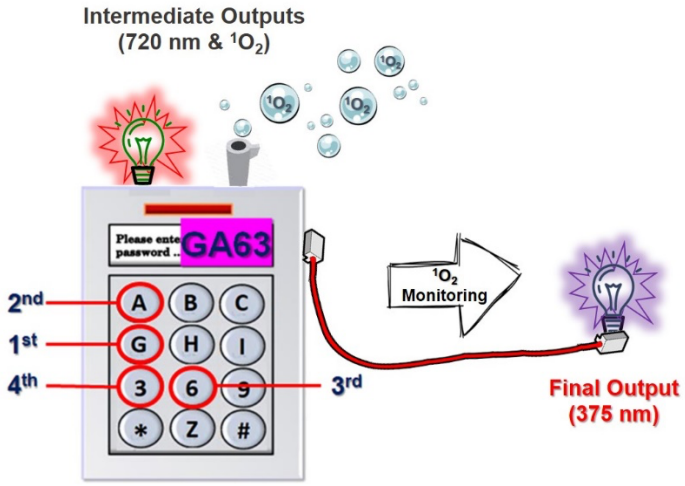
Fig. S18 Molecular keypad lock constructed with **1** with three inputs and two intermediate outputs ($I_{720\ nm}$ and $^1O_2$ generation). Only when the correct password "**GA6**" [**G** = GSH, **A** = acid and **6** = red-light irradiation (λ > 610 nm) for 10 min] is entered, the two outputs are switched on and the Output 3 is also in an ON (or "1") stage.



Entry	Input 1[a] (GSH)[b]	Input 2[a] (Acid)[c]	Input 3[a] (L610)[d]	Output 1 ($I_{720\ nm}$)	Output 2 ($^1O_2$)	Output 3
1	0	0	0	0	0	0
2	1	0	0	0	0	0
3	0	1	0	0	0	0
4	0	0	1	0	0	0
5	1	1	0	0	0	0
6	1	0	1	0	0	0
7	0	1	1	0	0	0
8	1	1	1	1	1	1

[a] Input *i* as the *i*th input. [b] 2 mM of GSH. [c] pH 6.0. [d] Irradiation (λ > 610 nm) for 10 min.

Fig. S19 Truth table for the combinatorial logic operations with three inputs (GSH, Acid and L610) based on compound **1**.



Key	Fluorescence at 720 nm	ROS generation	Output (375 nm)
36AG	0	0	0
36GA	0	0	0
3A6G	0	0	0
3AG6	0	0	0
3G6A	0	0	0
3GA6	1	1	0
63AG	0	0	0
63GA	0	0	0
A36G	0	0	0
A3G6	0	0	0
G36A	0	0	0
G3A6	1	1	0

Key	Fluorescence at 720 nm	ROS generation	Output (375 nm)
6A3G	0	0	0
6G3A	0	0	0
A63G	0	0	0
AG36	0	0	0
G63A	0	0	0
GA36	1	1	0
6AG3	0	0	0
6GA3	0	0	0
A6G3	0	0	0
AG63	0	0	0
G6A3	0	0	0
GA63	1	1	1

Fig. S20 Molecular keypad lock was constructed with **1** with two intermediate outputs (fluorescence at 720 nm and singlet oxygen generation) and final output (fluorescence at 375 nm). Only when the correct password "**GA63**" [**G** = GSH, A = acid, **6** = red-light irradiation (λ > 610 nm) for 10 min and **3** = blue-light excitation (λ = 345 nm)] is entered, the fluorescence at 375 is turned on and it can unlock the molecular keypad lock. The table shows the results of all outputs in response to the different input sequences.

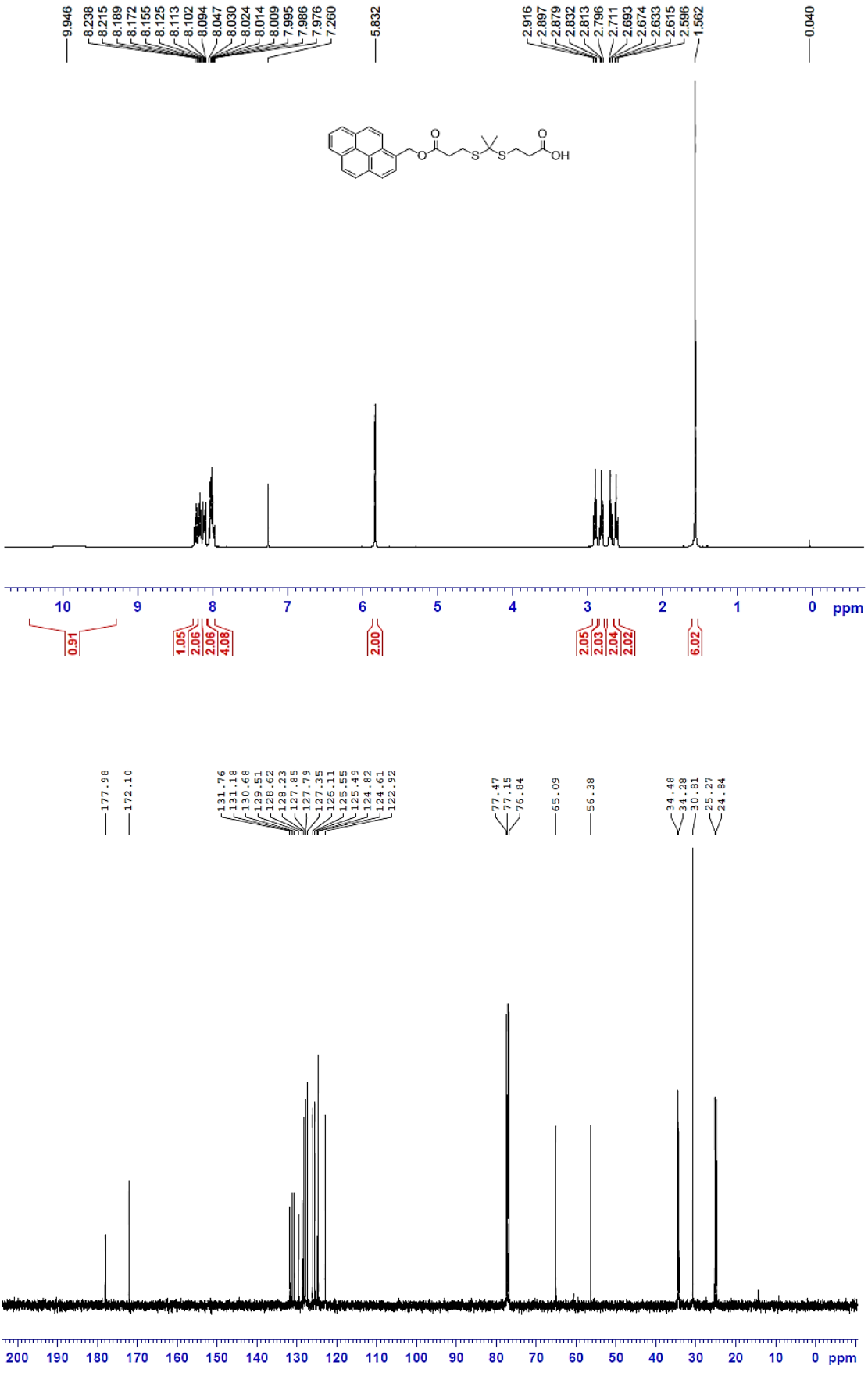


Fig. S21 ^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of **6** in $CDCl_3$

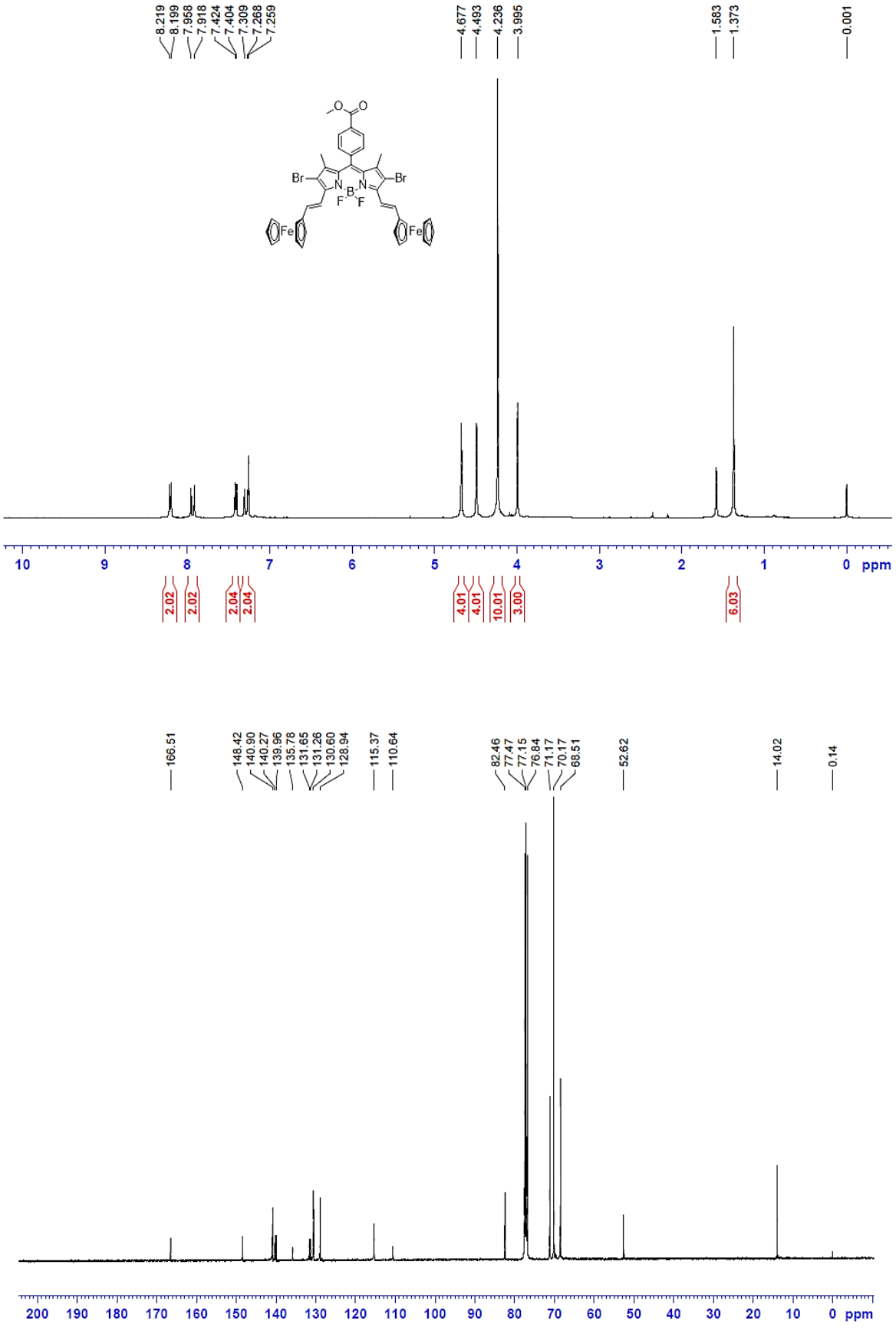


Fig. S22 ^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of **9** in $CDCl_3$

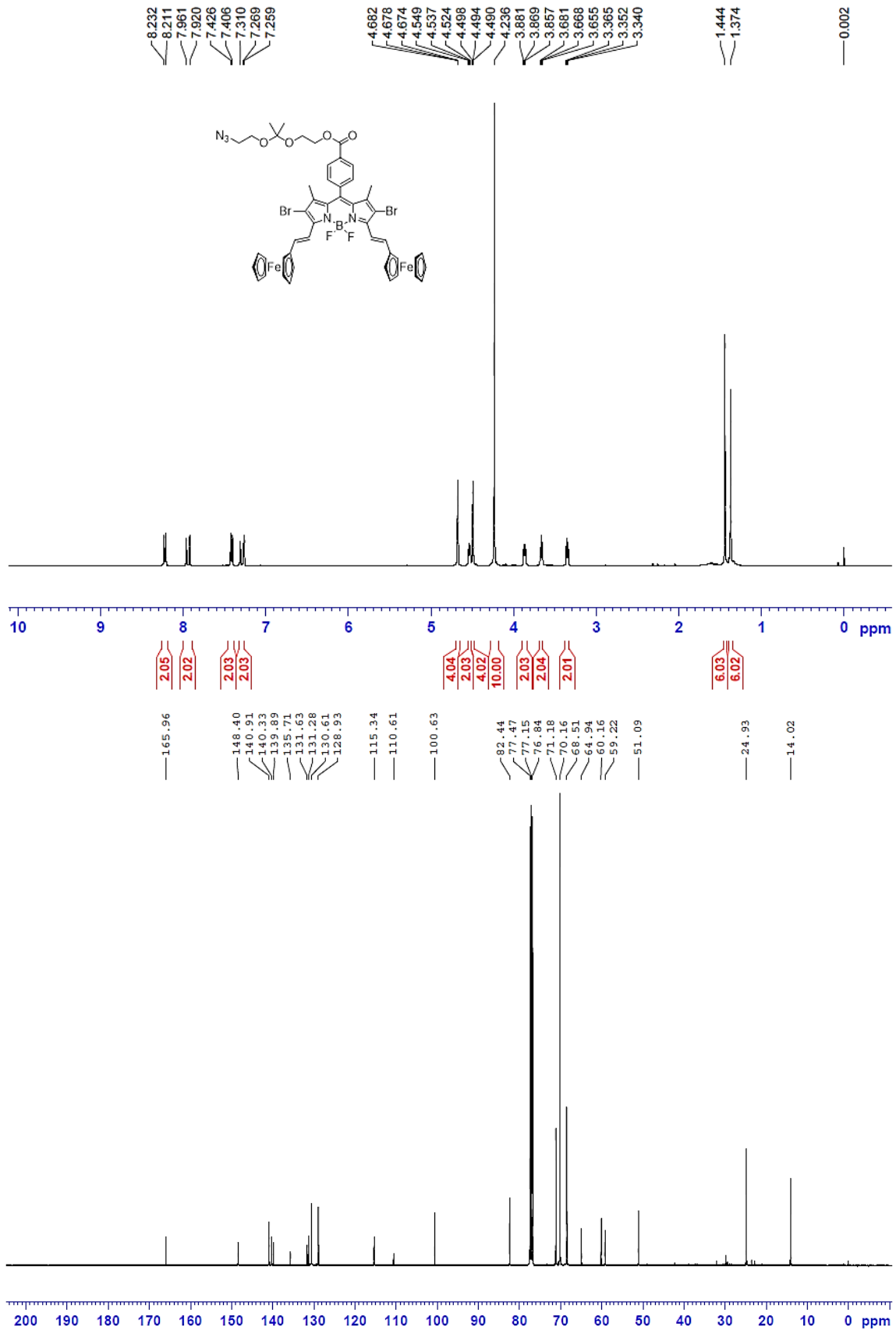


Fig. S23 ^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of **11** in $CDCl_3$

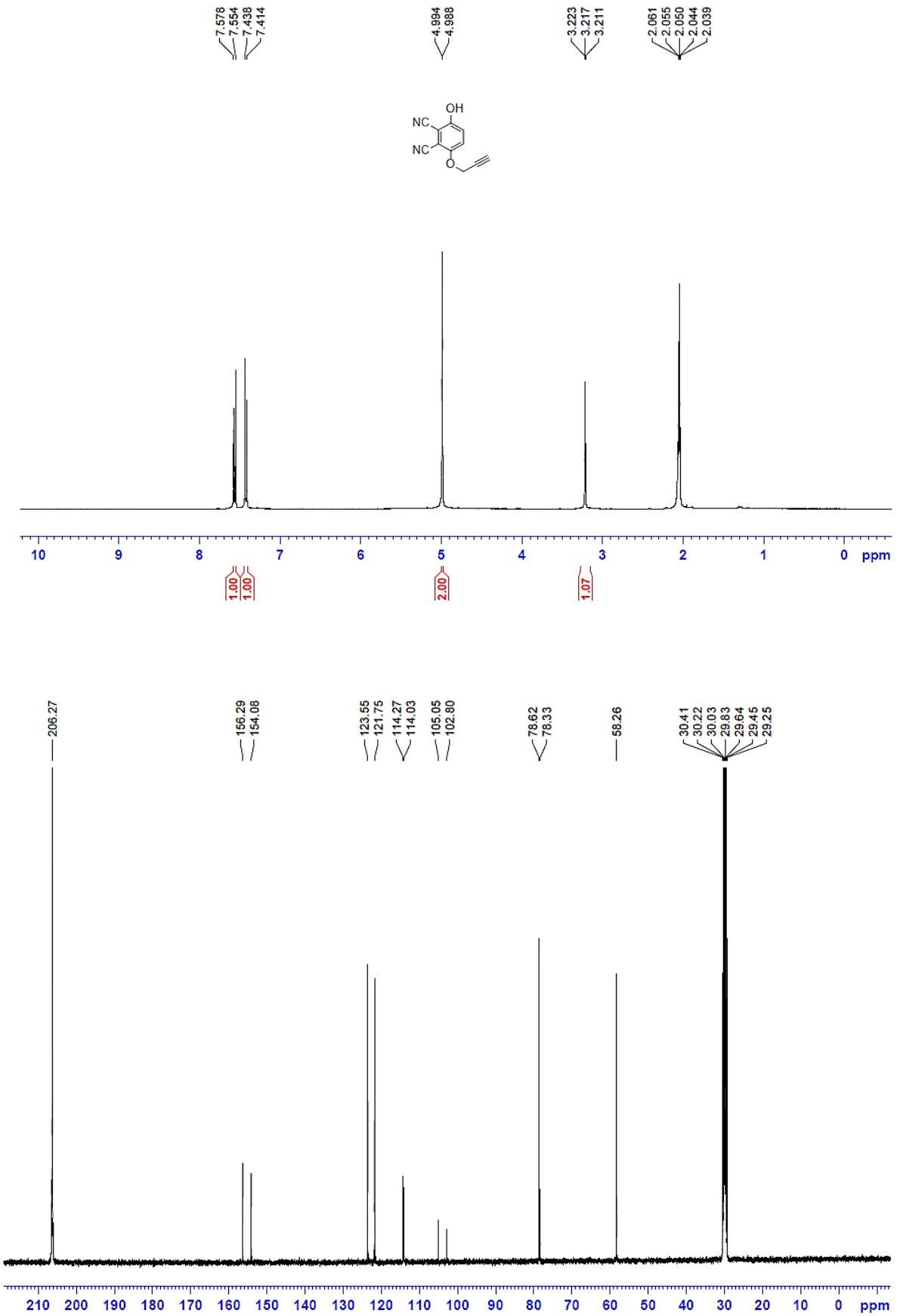


Fig. S24 ^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of **14** in acetone-d_6

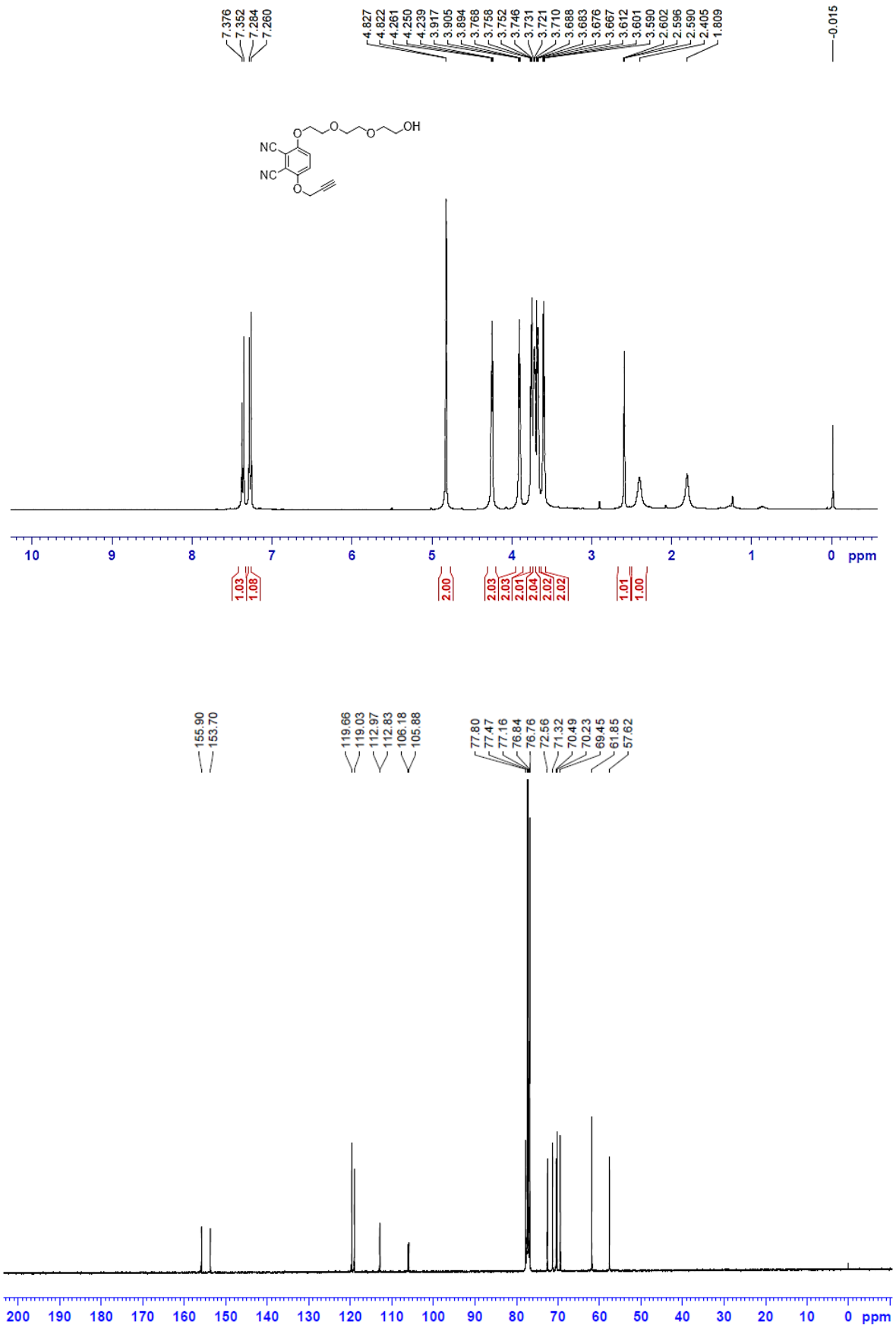


Fig. S25 ^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of **16** in $CDCl_3$

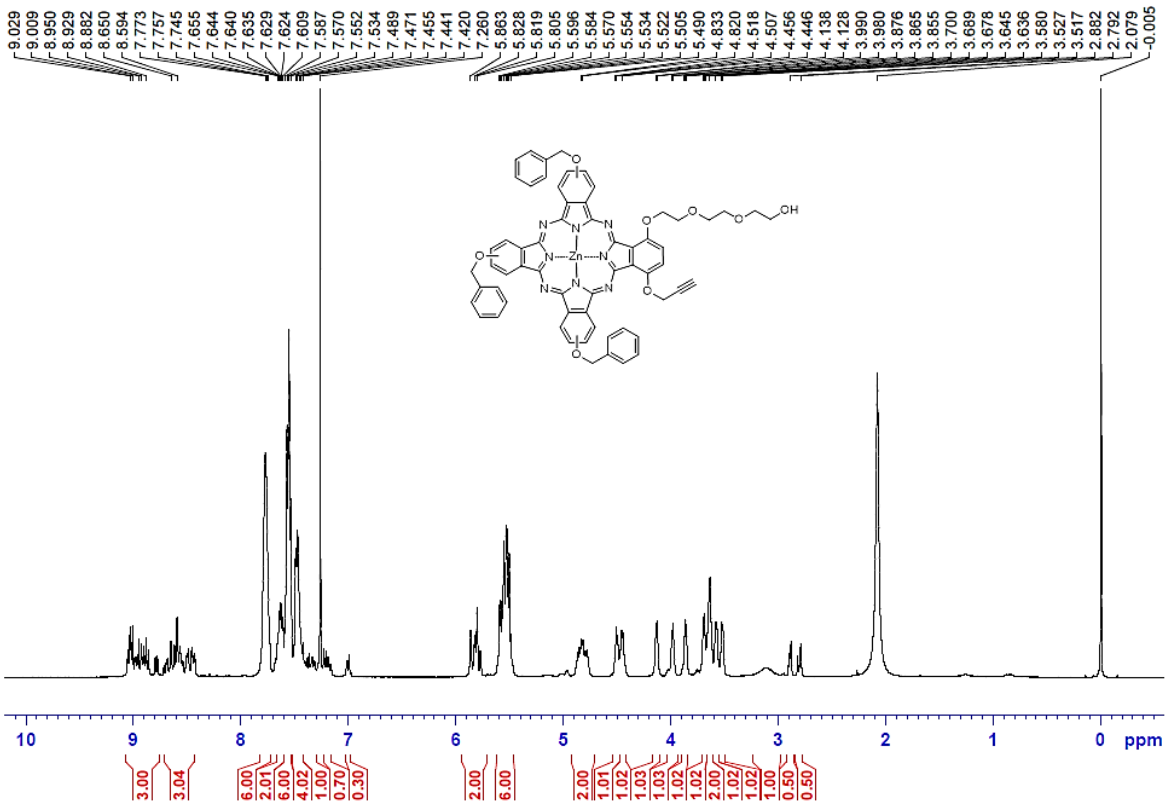


Fig. S26 ^{1}H NMR spectrum of **18** in $CDCl_3$ with a trace amount of pyridine-d_5

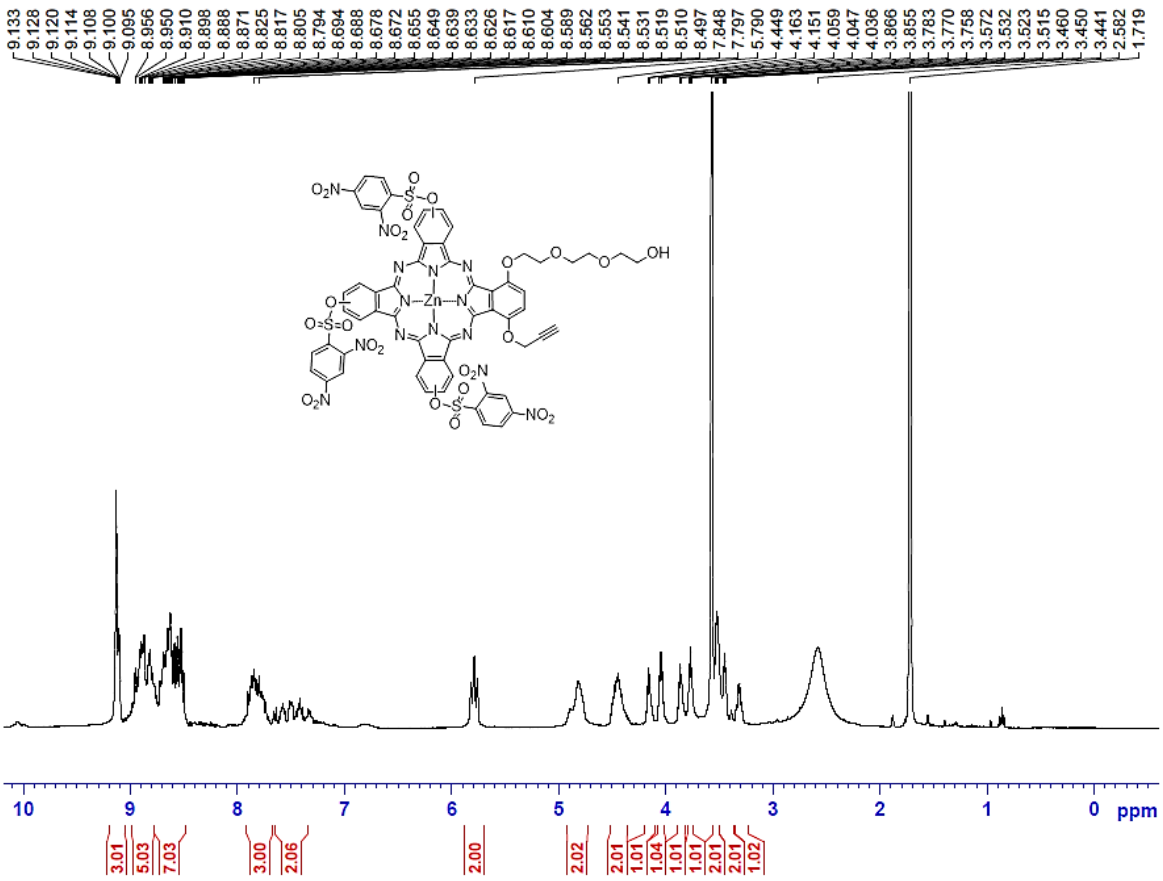


Fig. S27 ^{1}H NMR spectrum of **20** in THF-d_8

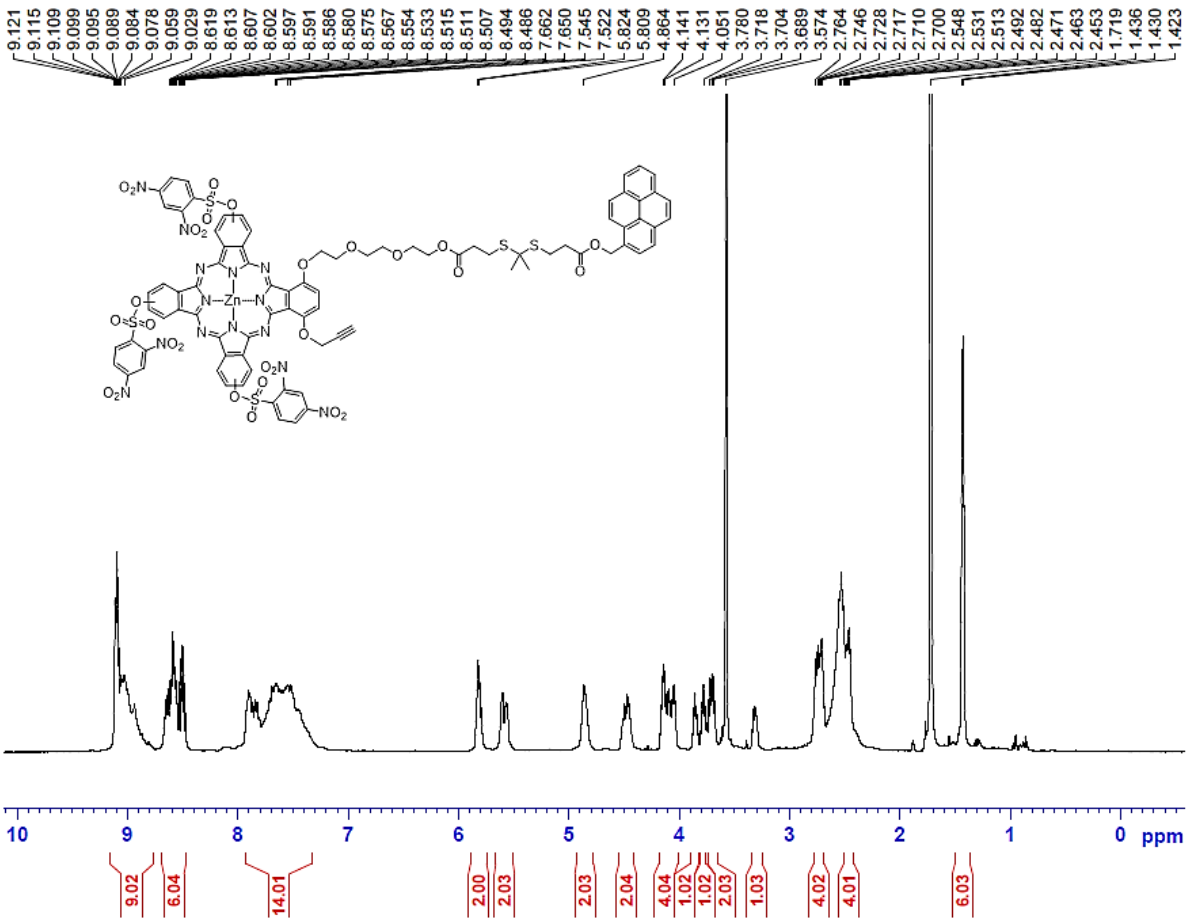


Fig. S28 ^{1}H NMR spectrum of **2** in THF-d_8

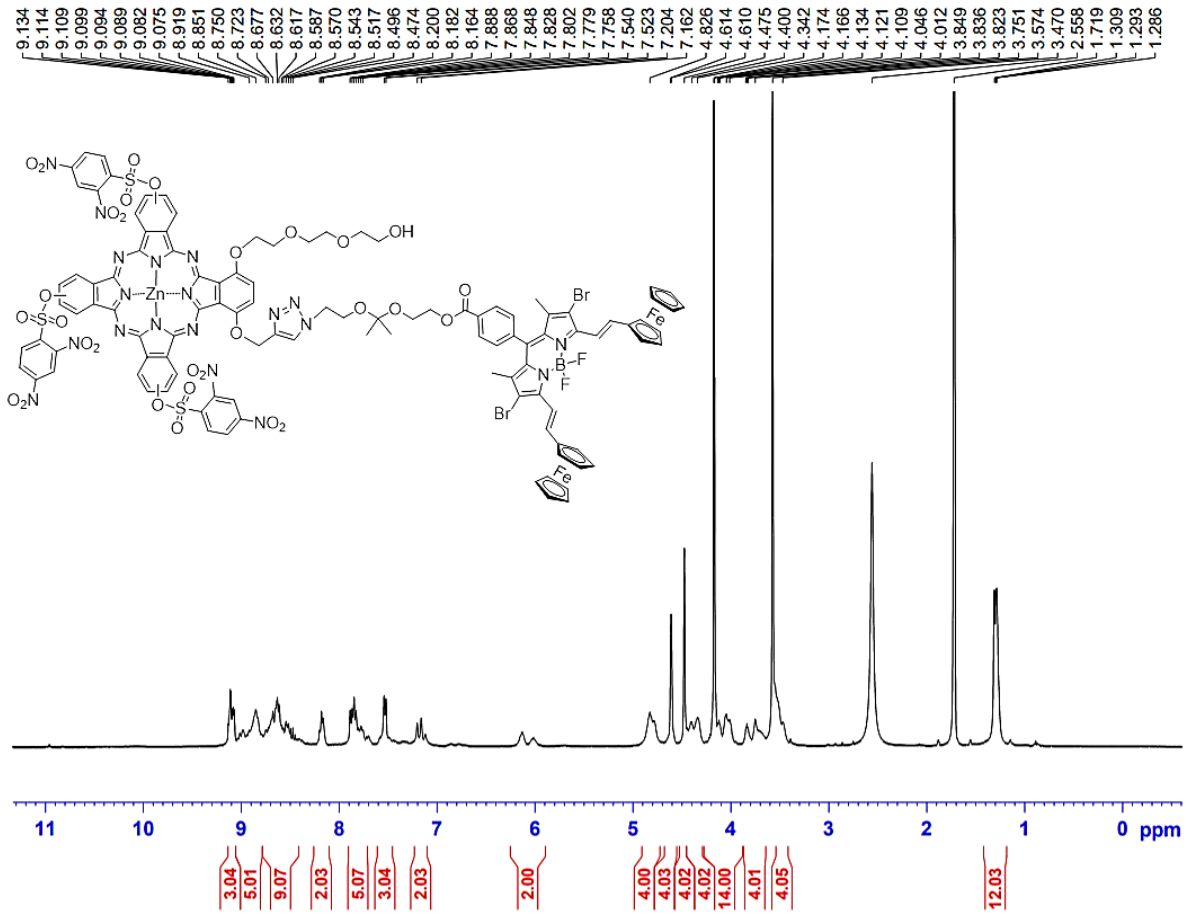


Fig. S29 ^{1}H NMR spectrum of **3** in THF-d_8

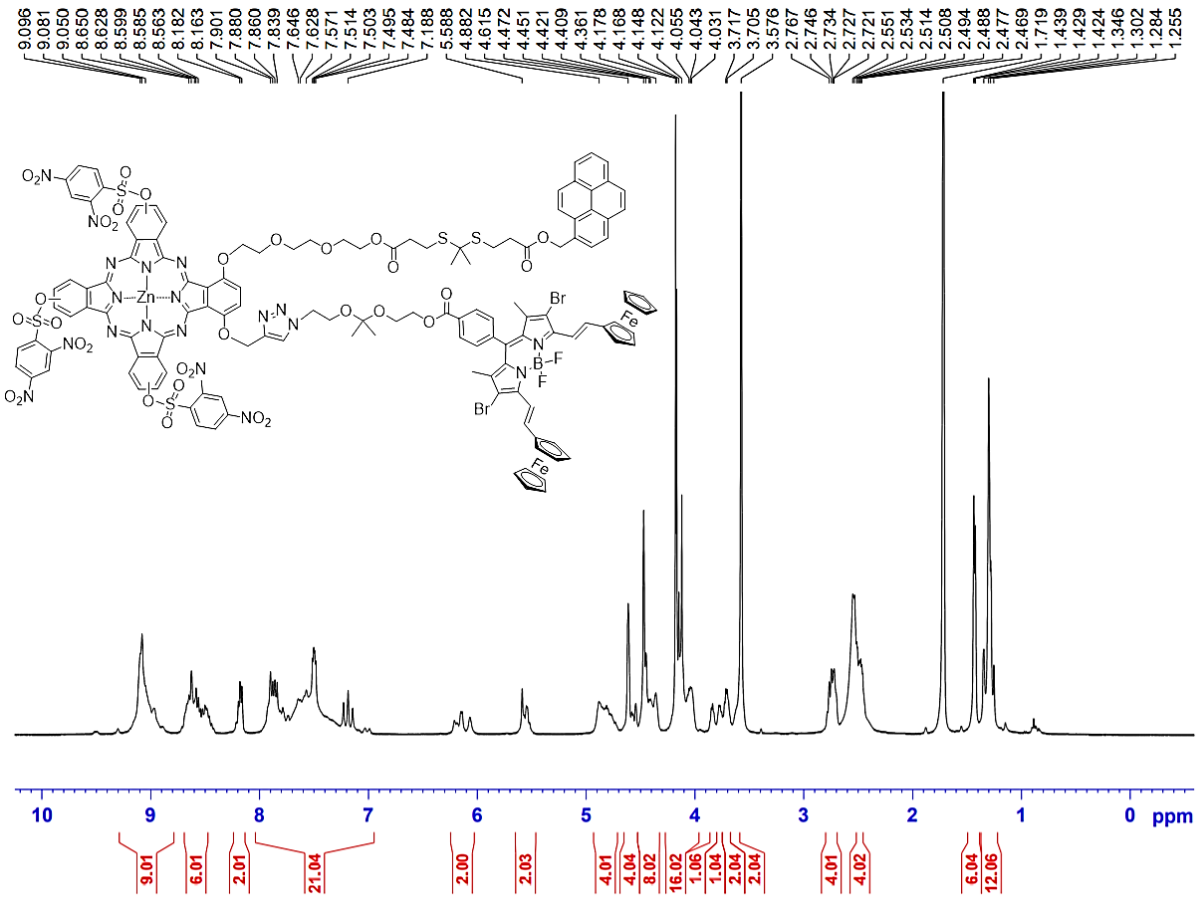


Fig. S30 ^{1}H NMR spectrum of **1** in THF-d_8

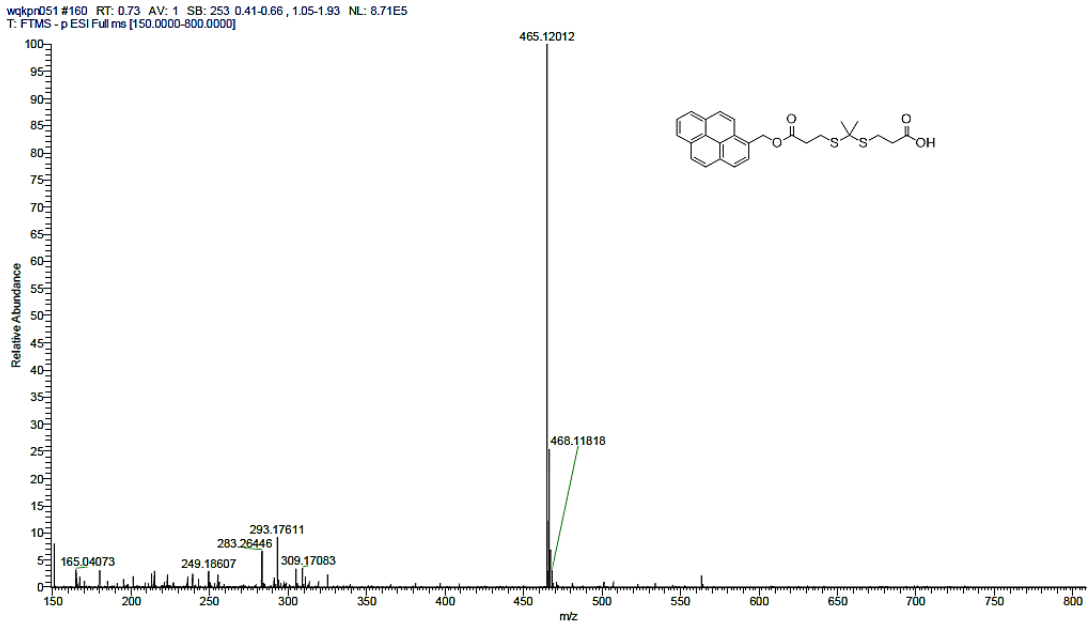


Fig. S31 ESI mass spectrum of **6**

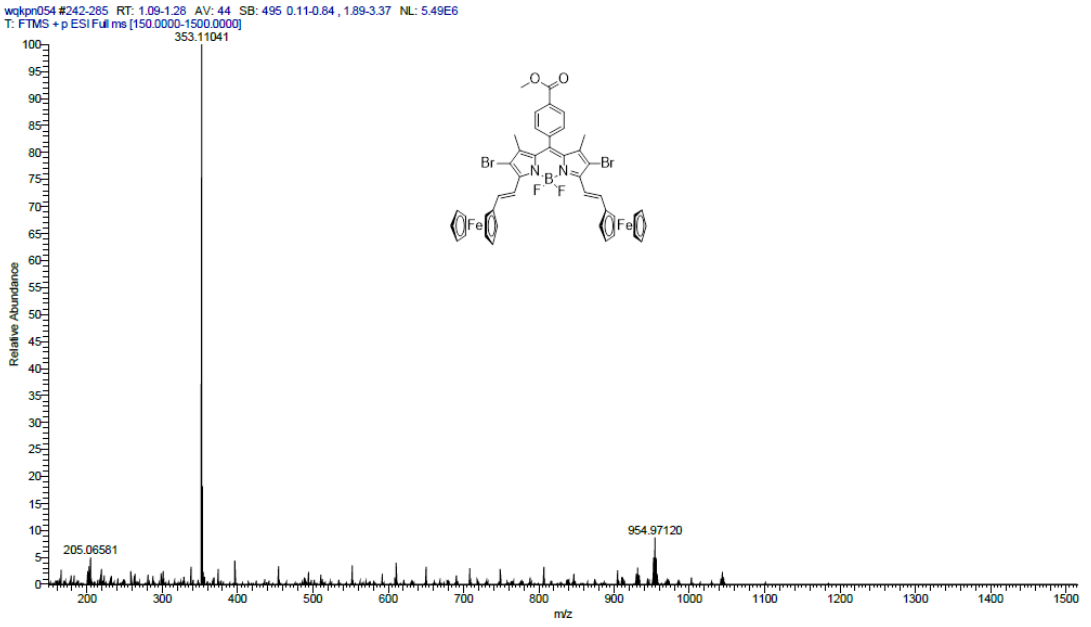


Fig. S32 ESI mass spectrum of **9**

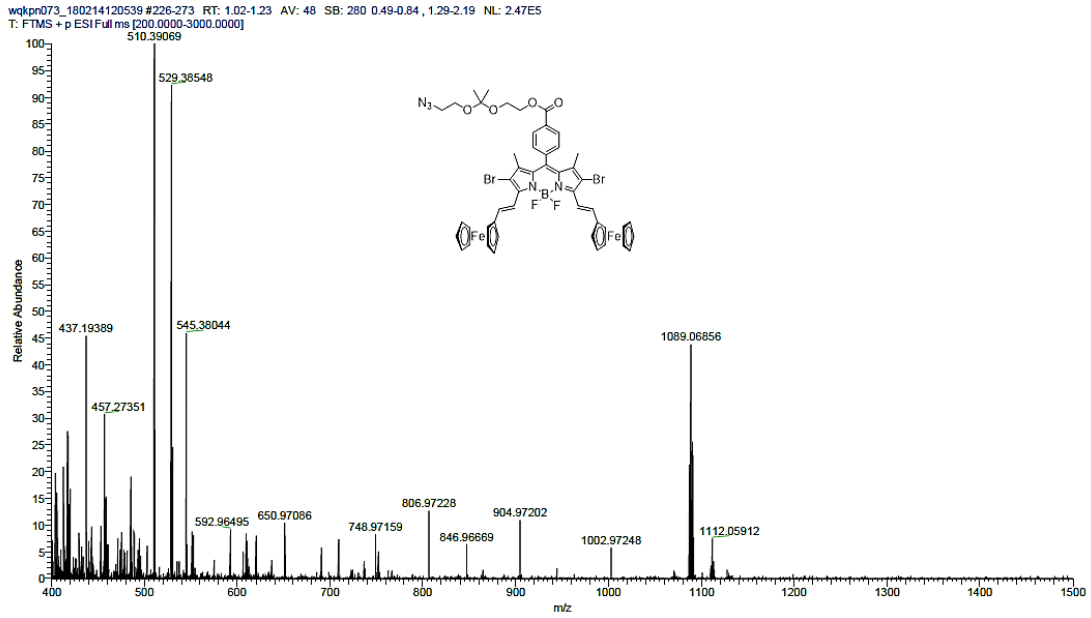


Fig. S33 ESI mass spectrum of **11**

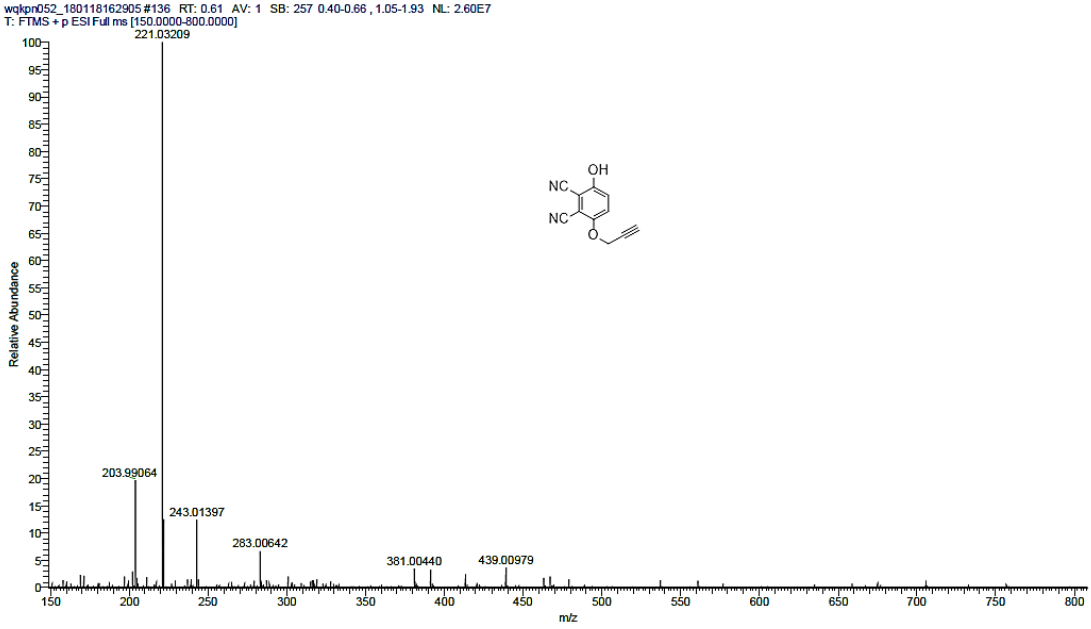


Fig. S34 ESI mass spectrum of **14**

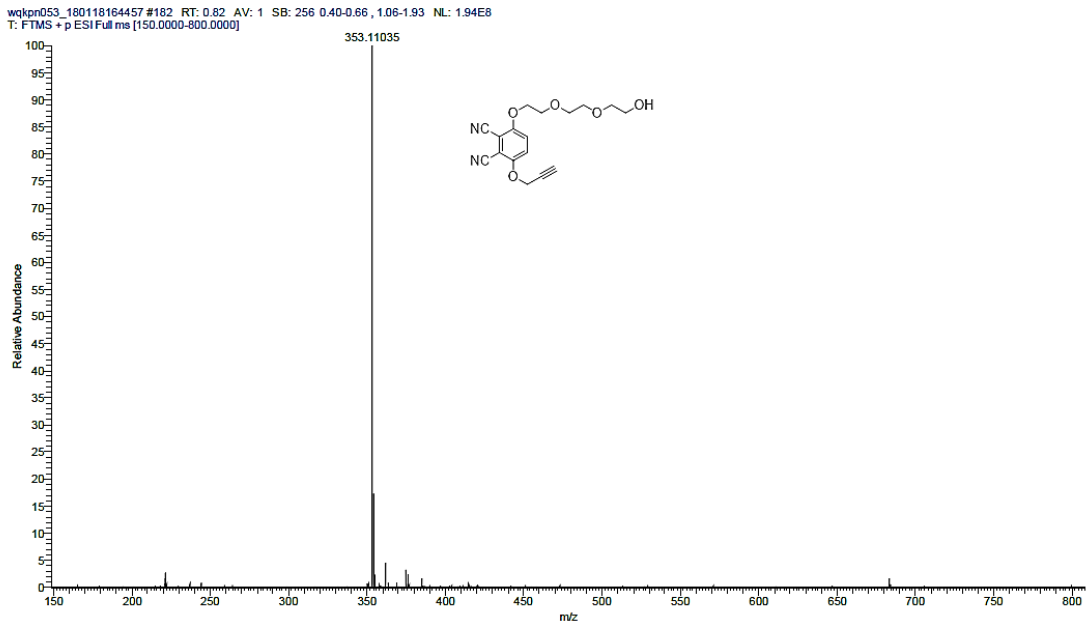


Fig. S35 ESI mass spectrum of **16**

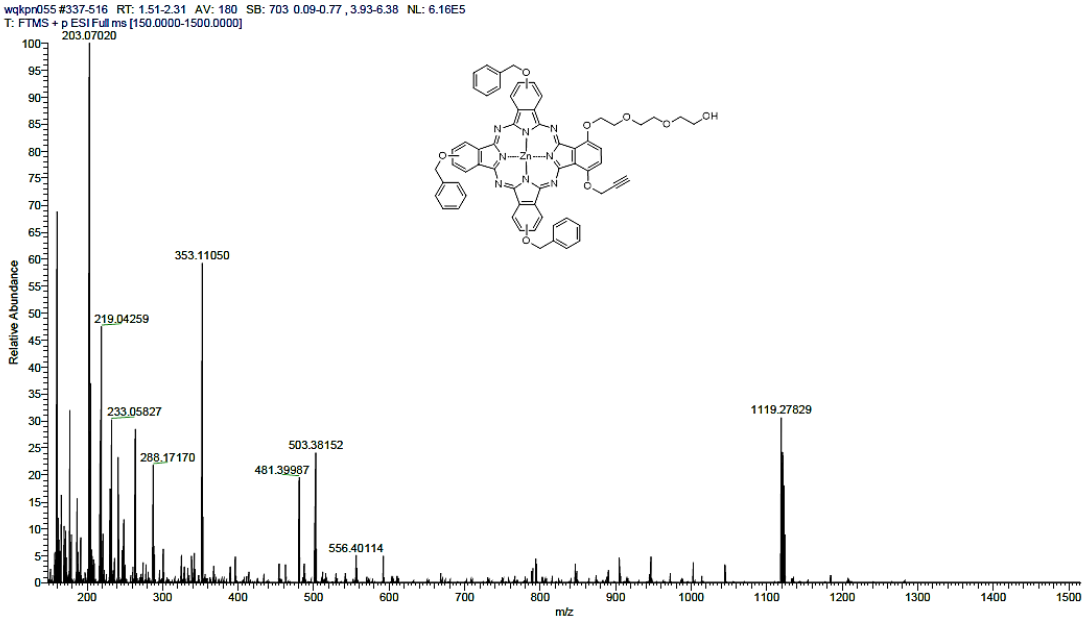


Fig. S36 ESI mass spectrum of **18**

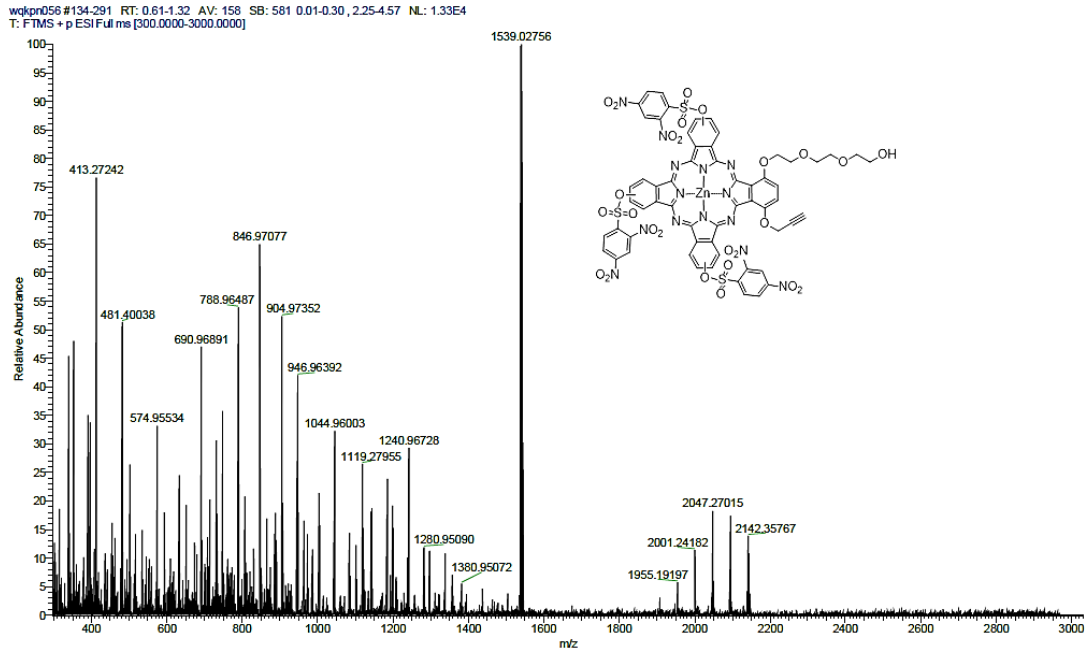


Fig. S37 ESI mass spectrum of **20**

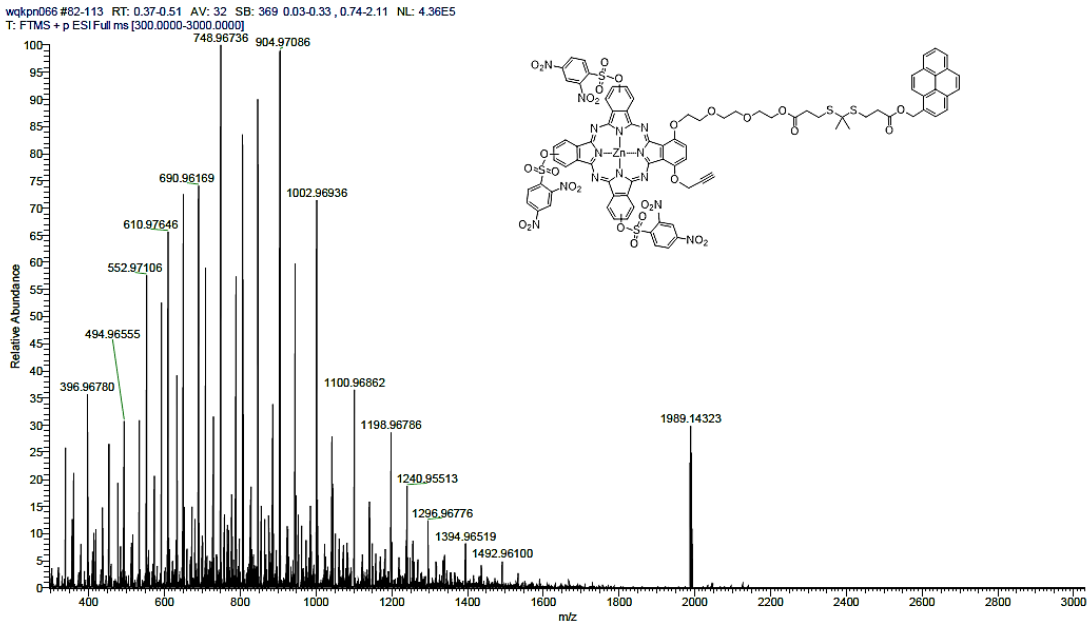


Fig. S38 ESI mass spectrum of **2**

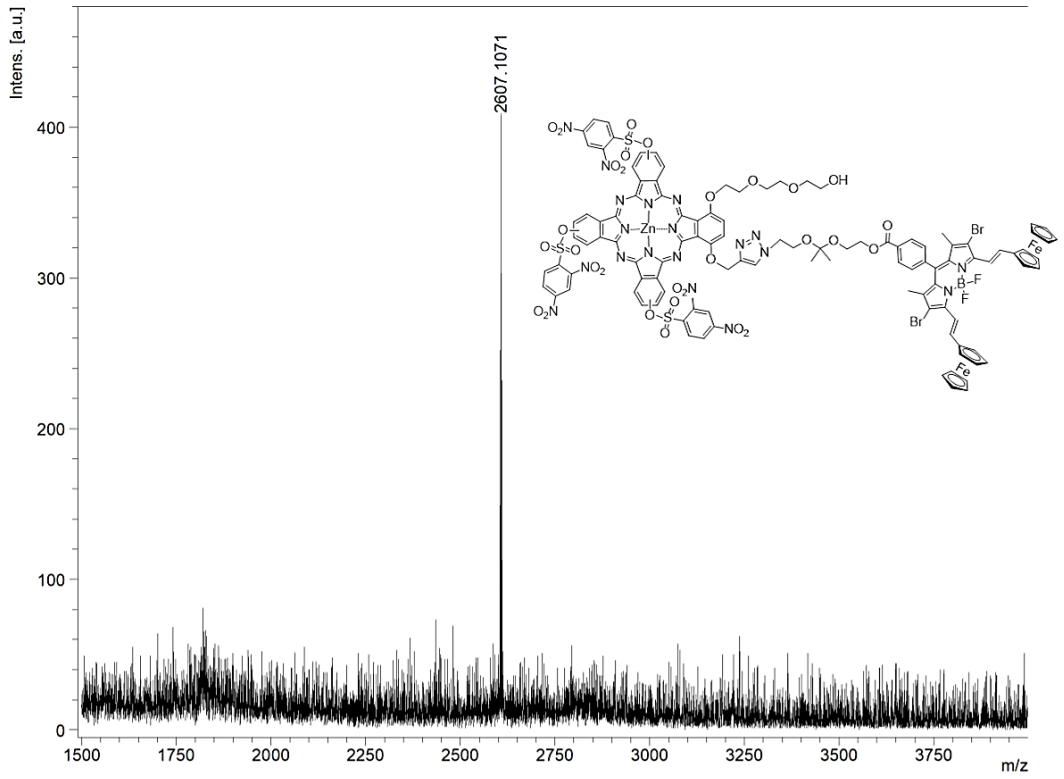


Fig. S39 MALDI-TOF mass spectrum of **3**

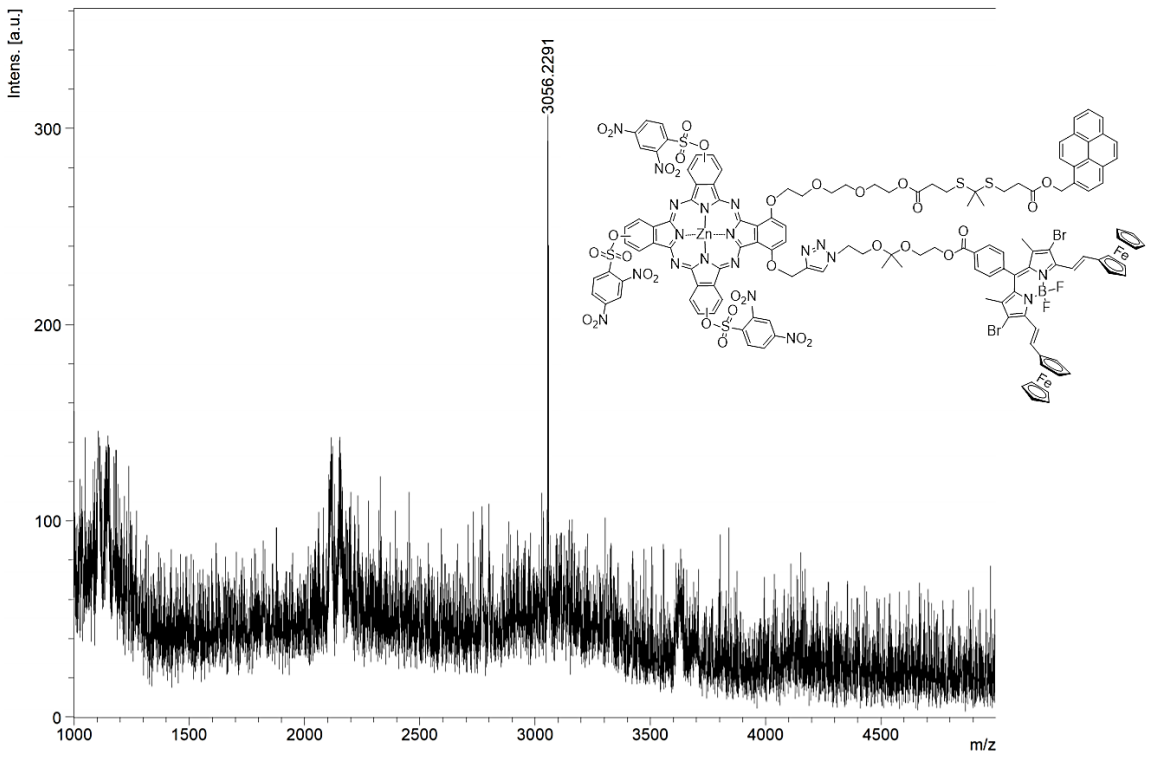


Fig. S40 MALDI-TOF mass spectrum of **1**