Supporting Information for

Highly Selective Ratiometric Fluorescent Sensing for Hg^{2+} and Au^{3+} Respectively in Aqueous Media

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1. General methods.

All solutions were prepared in deionised water. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Flash chromatography was carried out on silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on the Bruker 400 MHz instruments, and spectral data were reported in *ppm* relative to tetramethylsilane (TMS) as internal standard. Mass spectra were obtained using Bruker Daltonics esquire 6000 mass spectrometer. UV-vis absorption spectra were determined on a Varian UV-Cary100 spectrophotometer. Fluorescence emission spectra were recorded on a Hitachi F-4500 fluorescence spectrofluorometer. The pH value was measured using a Sartorius PB-10 pH meter equipped with a PY-ASI combination glass pH electrode.

Stock solutions (10 mM) of the perchlorate salts of Hg^{2+}, Li^{+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Pb^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Ag^{+}, Zn^{2+}, Al^{3+}, Sr^{2+} and Cd^{2+} in deionized water and the chloride salt of Au^{+} ion in DMSO were prepared. Stock solution (10 mM) of chloride salt of Au^{3+} and Pd^{2+} in methanol was prepared. Stock solution of **1** (10 mM) was also prepared in DMSO. Test solutions were prepared by placing 1 μL of the probe stock solution into a test tube, diluting the solution to 2 mL with HEPES (0.01 M, pH = 7.40), and adding an appropriate aliquot of each ions stock. For all measurements, the fluorescence spectra were obtained by excitation at 420 nm. Both the excitation and emission slit widths were 5 nm, respectively. Fluorescence spectra were measured after addition of Hg^{2+} (Au^{3+}) for 5min (20min). Stock solutions of HEPES (0.01 M) at different pH values were adjusted with $HClO_4$ (1M in water) or Bu_4NOH (1 M in water) in HEPES (0.01 M, pH= 7.04). Stock solutions of **1** (10 mM) were prepared in these stock solutions of HEPES (0.01 M) to keep the same ionic strength. Test solutions were prepared by placing 1 μL of the probe stock solution into a test tube, diluting the solution to 2 mL with HEPES (0.01 M) at corresponding pH value, and adding 0.1 μL of Hg^{2+} stock solution (10 mM in deionized water). The fluorescence spectra were obtained after addition of Hg^{2+} for 5min by excitation at 420 nm. Both the excitation and emission slit widths were 5 nm, respectively.

2. Synthesis and characterization.

4-nitro-1,8-naphthalic anhydride

To a stirred solution of sodium bichromate (2.24 g, 7.5 mmol) in acetic acid (5 mL) was added 5-nitroacenaphthene (0.60 g, 3 mmol) in acetic acid (5 mL). After 5 h at refluxing, the reaction mixture was mixed with water (50 mL) at 0 °C, then filtered and washed with water until the filtrate was neutral. The residue was dried in *vacuo* to afford the product (90 % yield). ^{1}H NMR (d_6-DMSO, 400 MHz): δ 8.75 (d, J = 8.8 Hz, 1H), 8.66 (d, J = 7.2 Hz, 1H), 8.63 (d, J = 8.4 Hz, 1H), 8.56 (d, J = 8.0 Hz, 1H), 8.12 (t, J = 8.0 Hz, 1H), ppm; ^{13}C NMR (d_6-DMSO, 100 MHz): δ 160.0, 159.4, 149.5, 133.2, 131.1, 130.6, 130.3, 129.8, 124.3, 124.0, 122.8, 120.0 ppm; ESI–MS: (*m/z*) 243.9 $[M+H]^+$, calcd. for $C_{12}H_5NO_5$ = 244.0.

N-Propargyl-4-nitro-1,8-naphthalimide

2-Propyn-1-amine (0.1 mL, 1.54 mmol) was quickly added to a cloudy solution of 4-nitro-1,8-naphthalic anhydride (340 mg, 1.4 mmol) in ethanol (7 mL). After 6 h at refluxing under N_2, the reaction was allowed to cool to room temperature and filtered off, washed with cool ethanol (2 mL). The residue was dried in *vacuo* to afford the product (92 % yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.85 (d, J = 8.8 Hz, 1H), 8.78 (d, J = 7.2 Hz, 1H), 8.74 (d, J = 8.0 Hz, 1H), 8.41 (d, J = 8.0 Hz, 1H), 8.01 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 4.97 (d, J = 2.4 Hz, 2H), 2.23 (t, J = 2.4 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.4, 161.7, 149.9, 132.8, 130.2, 130.0, 129.7, 129.1, 126.6, 123.8, 123.7, 122.7, 77.8, 71.1, 29.8 ppm; ESI–MS: (*m/z*) 281.1 $[M+H]^+$, calcd. for $C_{15}H_9N_2O_4$ = 281.1.

N-Propargyl-4-amido-1,8-naphthalimide (1)

To a stirred cloudy solution of *N*-Propargyl-4-nitro-1,8-naphthalimide (140 mg, 0.5 mmol) in ethanol (5 mL) was added dropwise the solution of $SnCl_2{\cdot}2H_2O$ (677 mg, 3 mmol) in concentrated hydrochloric acid (1 mL) at room temperature. The reaction was quenched with aqueous 10 % Na_2CO_3 and filtered off. After washed with water (3 × 10 mL) the residue was dried in *vacuo* to afford compound **1** (89 % yield). ^{1}H NMR (d_6-DMSO, 400

MHz): δ 8.62 (d, J = 8.0 Hz, 1H), 8.43 (d, J = 7.2 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 8.0 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 4.72 (d, J = 2.4 Hz, 2H), 3.05 (t, J = 2.4 Hz, 1H) ppm; ^{13}C NMR (d_6-DMSO, 100 MHz): δ 163.0, 162.0, 153.0, 134.2, 131.2, 129.7 (2C), 124.0, 121.4, 119.3, 108.2, 107.0, 80.0, 72.3, 28.6 ppm; ESI–MS: (*m/z*) 250.8 $[M+H]^+$, calcd. for $C_{15}H_{11}N_2O_2$ = 251.1. IR (film): ν_{max} = 3472, 3359, 3246, 2118, 1677, 1643, 1578, 1526, 1478, 1374, 1331, 1244, 1177, 1144, 988, 949, 774 cm^{-1}.

_N_-acetylmethyl-4-amido-1,8-naphthalimide (3)

A solution of **1** (25 mg, 0.1 mmol) in DMSO (3 mL) was treated with $Hg(ClO_4)_2$ (40 mg, 0.1 mmol) at room temperature. Methyl ketone **3** was observed immediately by TLC and complete conversion of **1** need 6 h. Then reaction mixture was diluted with ether. The precipitates were collected as an orange solid (71% yield). ^{1}H NMR (d_6-DMSO, 400 MHz): δ 8.64 (d, J = 8.0 Hz, 1H), 8.42 (d, J = 7.2 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 6.86 (d, J = 8.8 Hz, 1H), 4.87 (s, 2H), 2.24 (s, 3H) ppm; ^{13}C NMR (d_6-DMSO, 100 MHz): δ 202.2, 163.5, 162.5, 152.9, 134.2, 131.3, 129.9, 129.7, 124.1, 121.4, 119.4, 108.2, 107.6, 49.0, 27.2 ppm; ESI–MS: (*m/z*) 269.1 $[M+H]^+$, calcd. for $C_{15}H_{13}N_2O_3$ = 269.1. IR (film): ν_{max} = 3446, 3357, 3256, 1727, 1681, 1644, 1579, 1526, 1477, 1374, 1324, 1248, 1178, 1146, 1105, 1031, 773, 754 cm^{-1}.

3. The detection limit of the sensor 1 with Hg^{2+}.

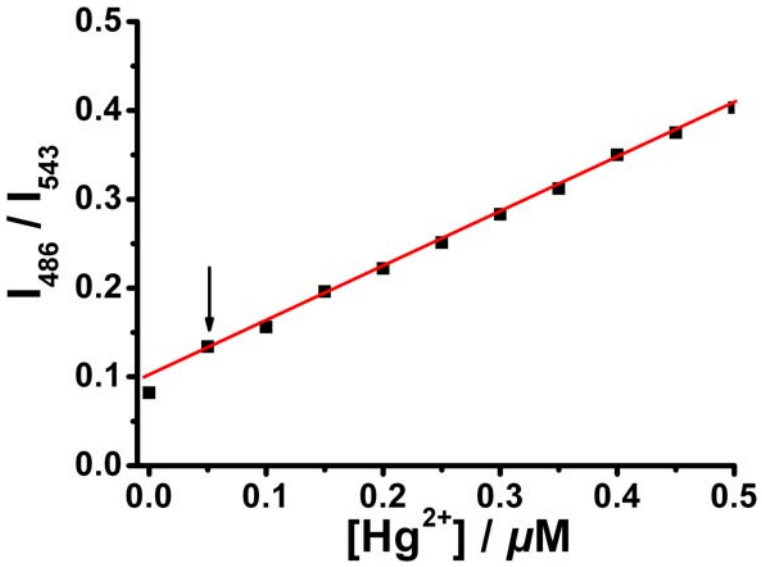

Figure S1. Plot of the ratio of intensity at 473 nm to 509 nm for a mixture of probe **1** (5 μM) and Hg^{2+} in HEPES buffer (0.01 M, pH = 7.40) (0.05% DMSO, v/v) in the range 0.05–0.5 μM, taken after 5 min of mixing. λ_{ex} = 420 nm.

4. The pH dependence of the fluorescence intensity change.

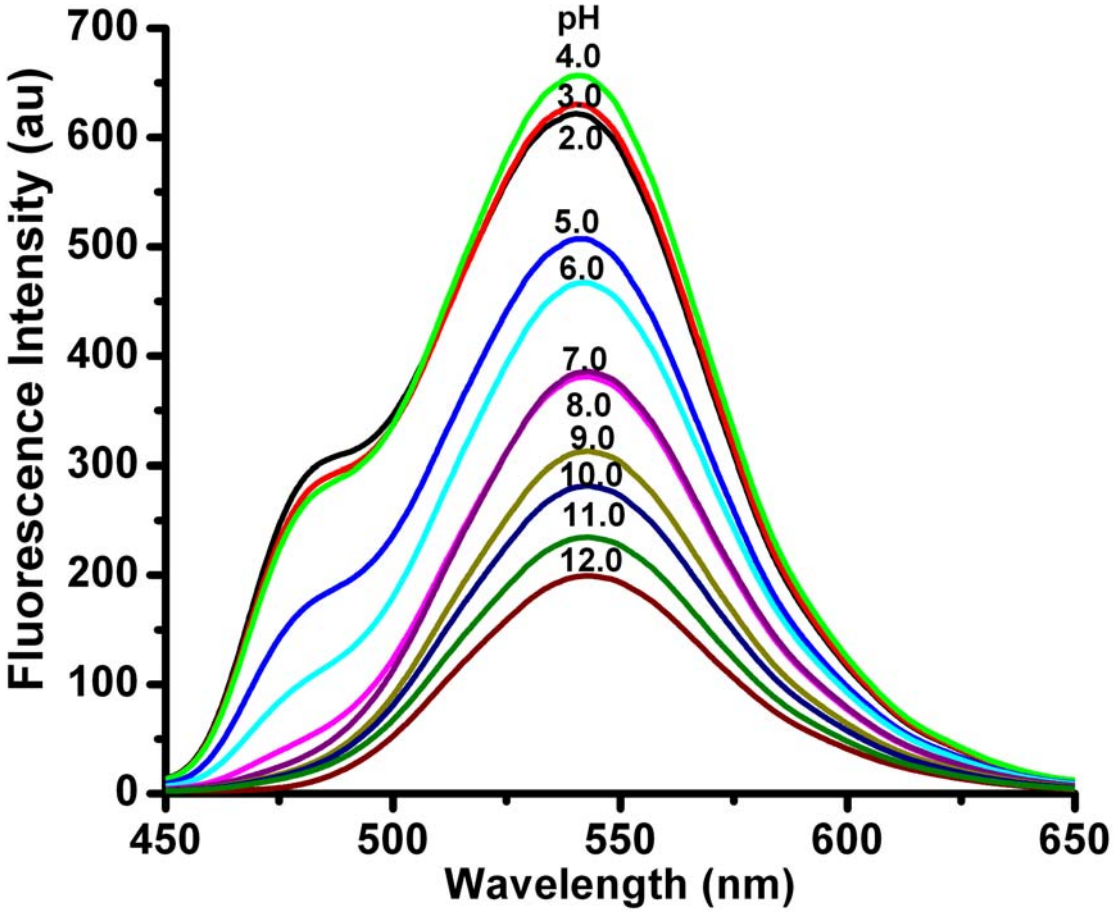

Figure S2. Fluorescence intensity of **1** (5 μM) in HEPES (0.01 M) (0.05% DMSO, v/v) of different pH in the presence of 0.5 μM Hg^{2+}. (λ_{ex} = 420 nm).

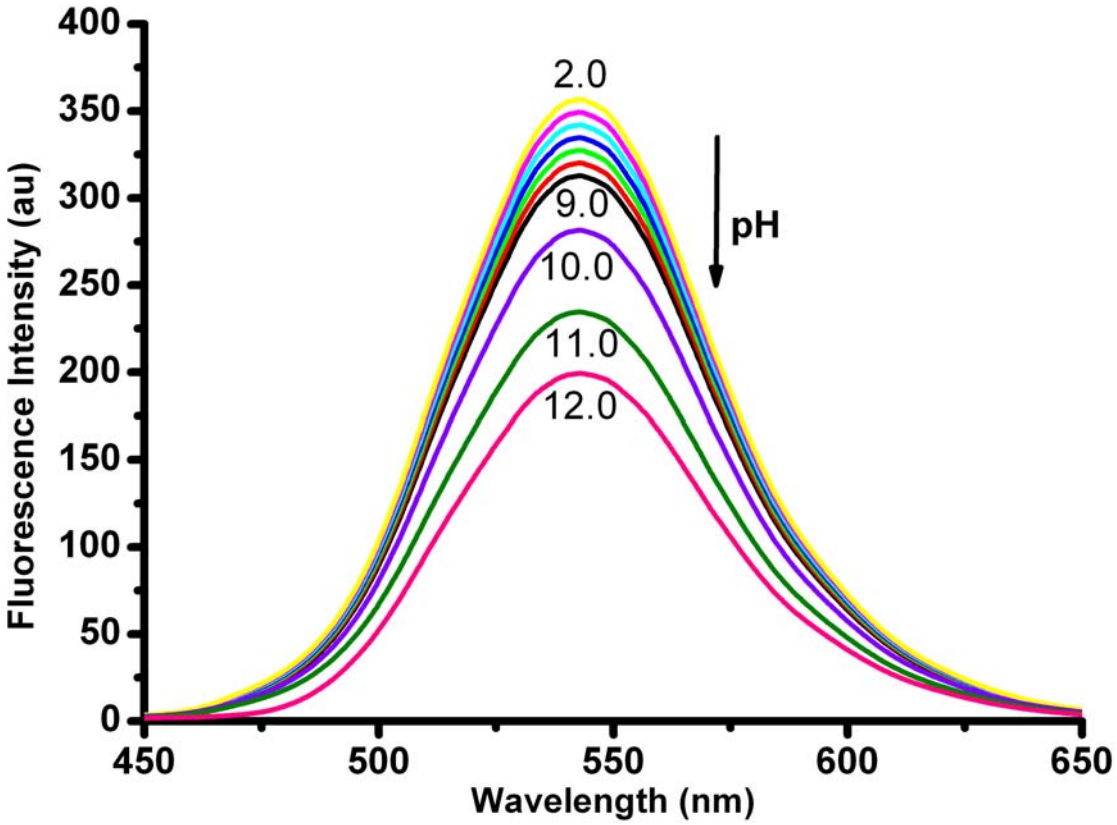

Figure S3. Fluorescence intensity of free **1** (5 μM) in HEPES (0.01 M) (0.05% DMSO, v/v) of different pH. (λ_{ex} = 420 nm).

5. Fluorescence responses of 1 with various cations in water (pH = 1.0).

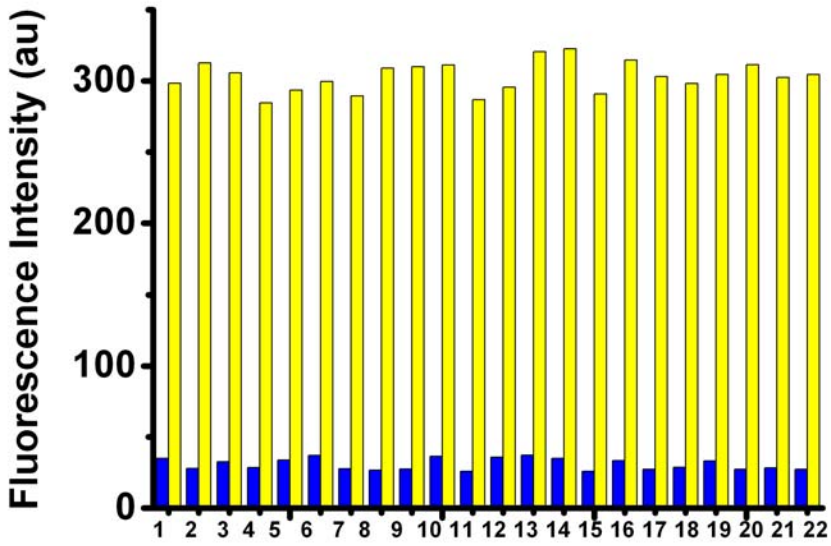

Figure S4. Fluorescence responses of **1** (5 μM) with various cations in water (pH = 1.0) (0.05% DMSO, v/v). The blue bars represent the emission intensity of **1** in the presence of other cations (10 μM). The yellow bars represent the emission intensity that occurs upon the subsequent addition of 10 μM of Hg^{2+} to the above solution. From 1 to 21: none, Ag^{+}, Au^{3+}, Au^{+}, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Li^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Sr^{2+}, Zn^{2+} and Pd^{2+}. The emission intensities were recorded at 486 nm, and the excitation wavelength was 420 nm.

6. Fluorescence spectra of 1 in the presence of different concentrations of Hg^{2+} in water (pH = 1.0).

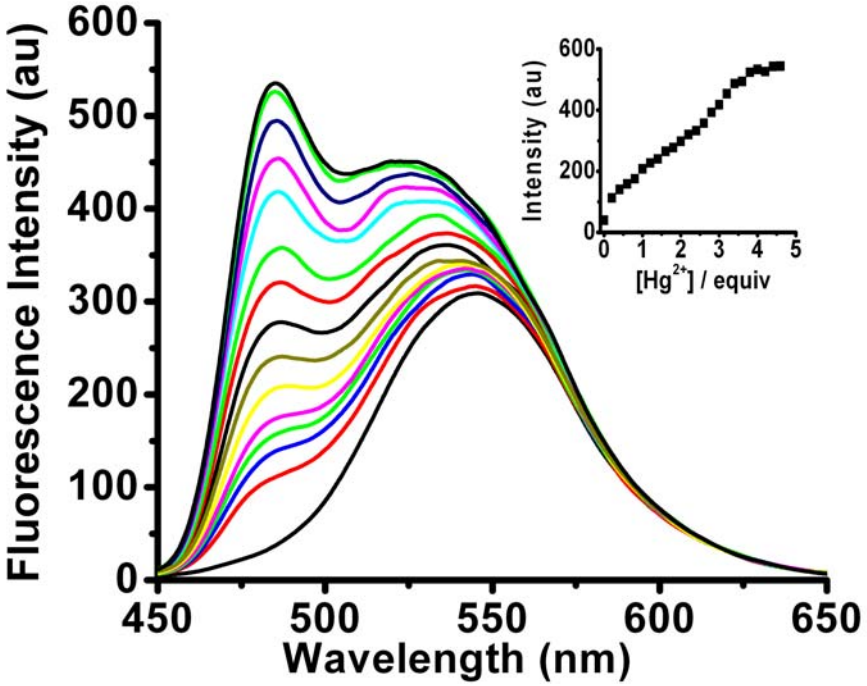

Figure S5. Fluorescent spectra of **1** (5 μM) in the presence of different concentrations of Hg^{2+} in water (pH = 1.0) (0.05% DMSO, v/v). Excitation wavelength was 420 nm. Inset: the ratio of intensity at 486 nm as a function of Hg^{2+} concentration.

7. The fluorescent spectra of 2 in different media.

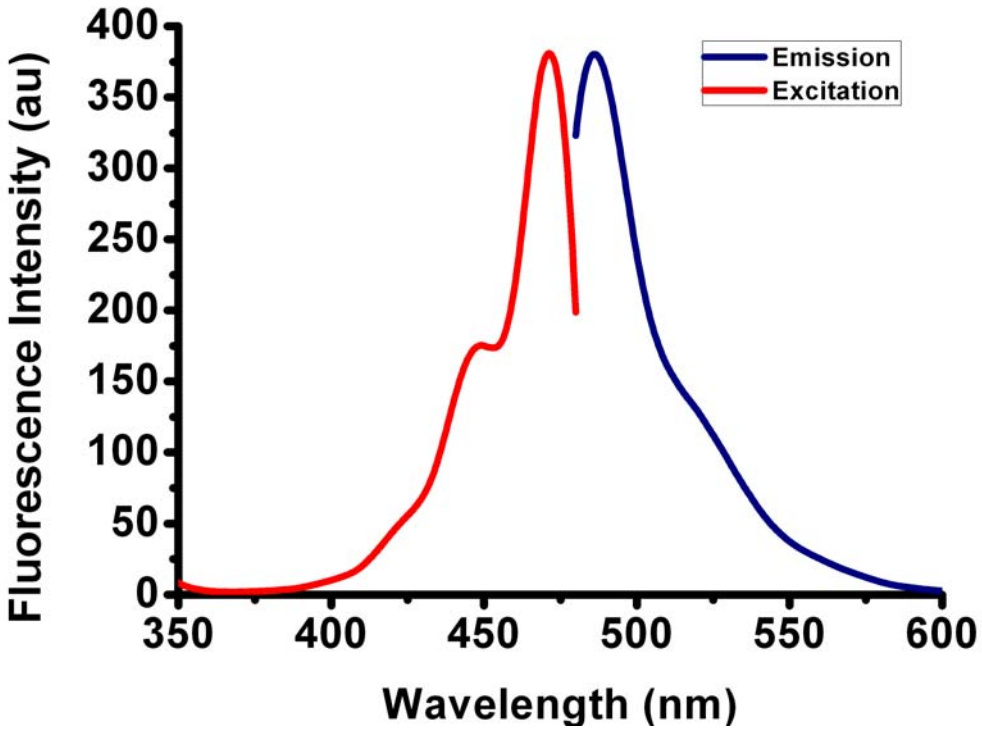

Figure S6. Fluorescent spectra of **2** (5 μM) in H_2O (0.05% DMSO v/v). Excitation wavelength was 471 nm, and emission wavelength was 486 nm.

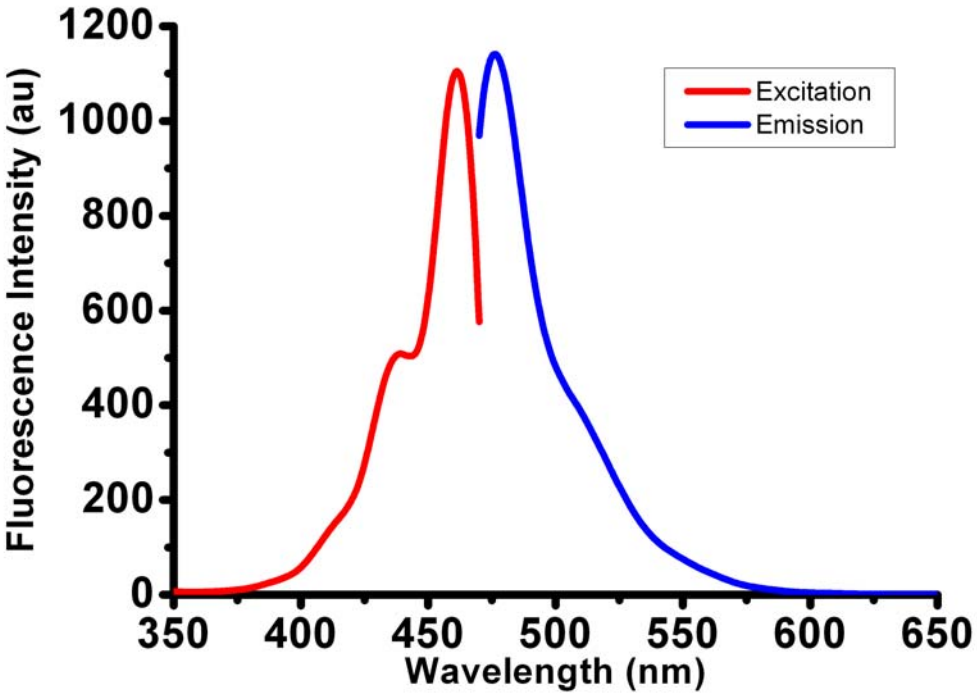

Figure S7. Fluorescent spectra of **2** (5 μM) in CH_3OH (5% H_2O v/v). Excitation wavelength was 461 nm, and emission wavelength was 473 nm.

8. The UV-vis spectrum of 2.

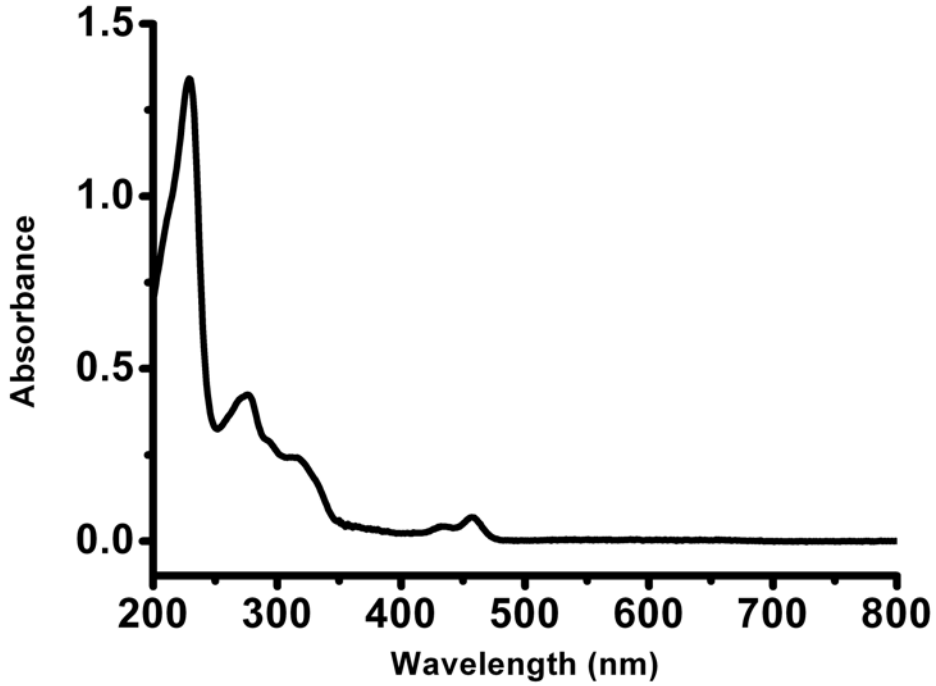

Figure S8. UV-vis spectrum of **2** (5 μM) in CH_3OH/H_2O (95:5 v/v).

9. The fluorescent spectra of 3 in different media.

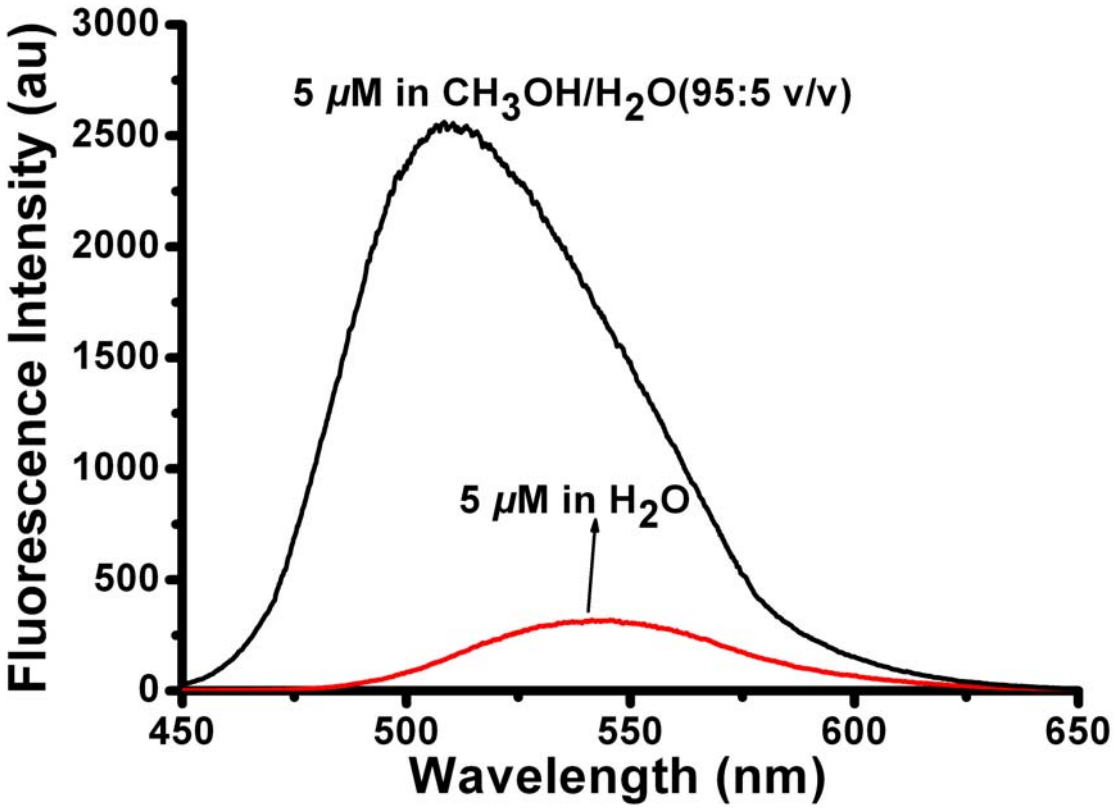

Figure S9. Fluorescent spectra of **3** (5 μM) in different media.

10. ^{1}H NMR spectrum of 2.

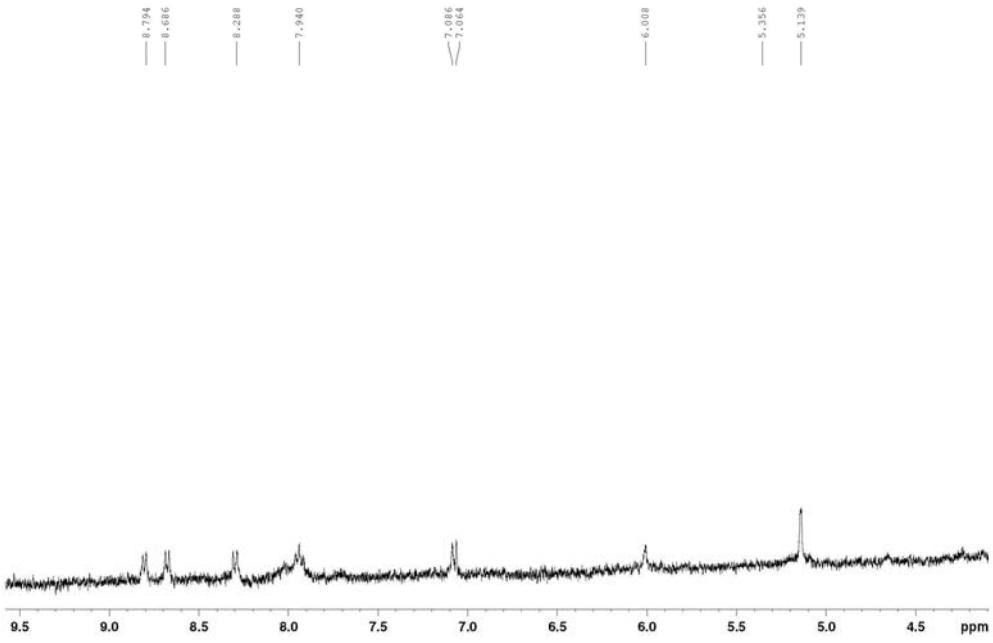

Figure S10. Partial ^{1}H NMR (d_6–DMSO, 400 MHz) spectrum of **1** with Hg^{2+}.

11. ESI-MS spectrum of 2.

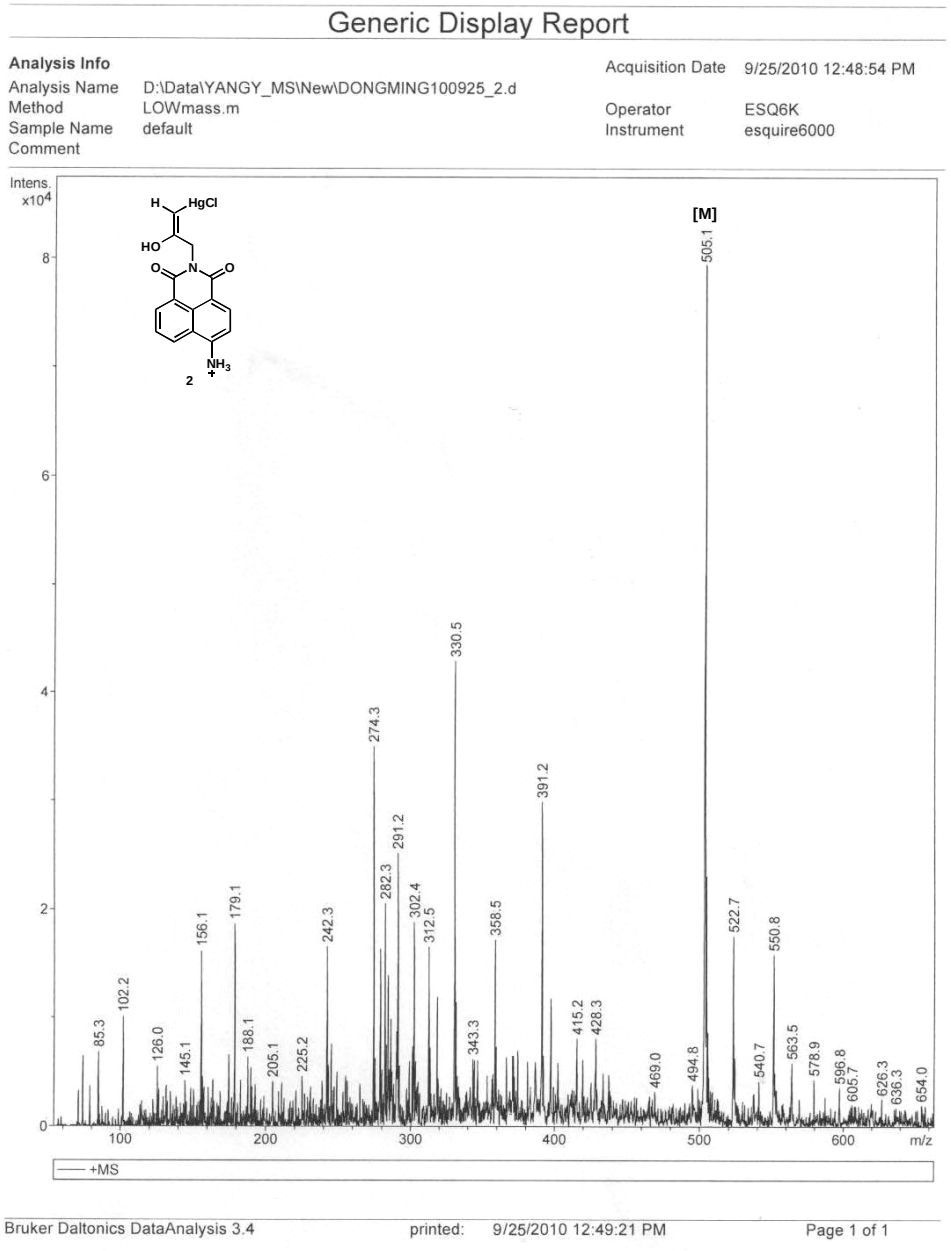

Figure S11. ESI mass spectrum of **2**. ESI–MS: (*m/z*) 505.1 $[M]^+$, calcd. for $C_{15}H_{12}ClN_2O_3Hg$ = 505.02.

12. ESI-MS spectrum of probe 1 with Au^{3+}.

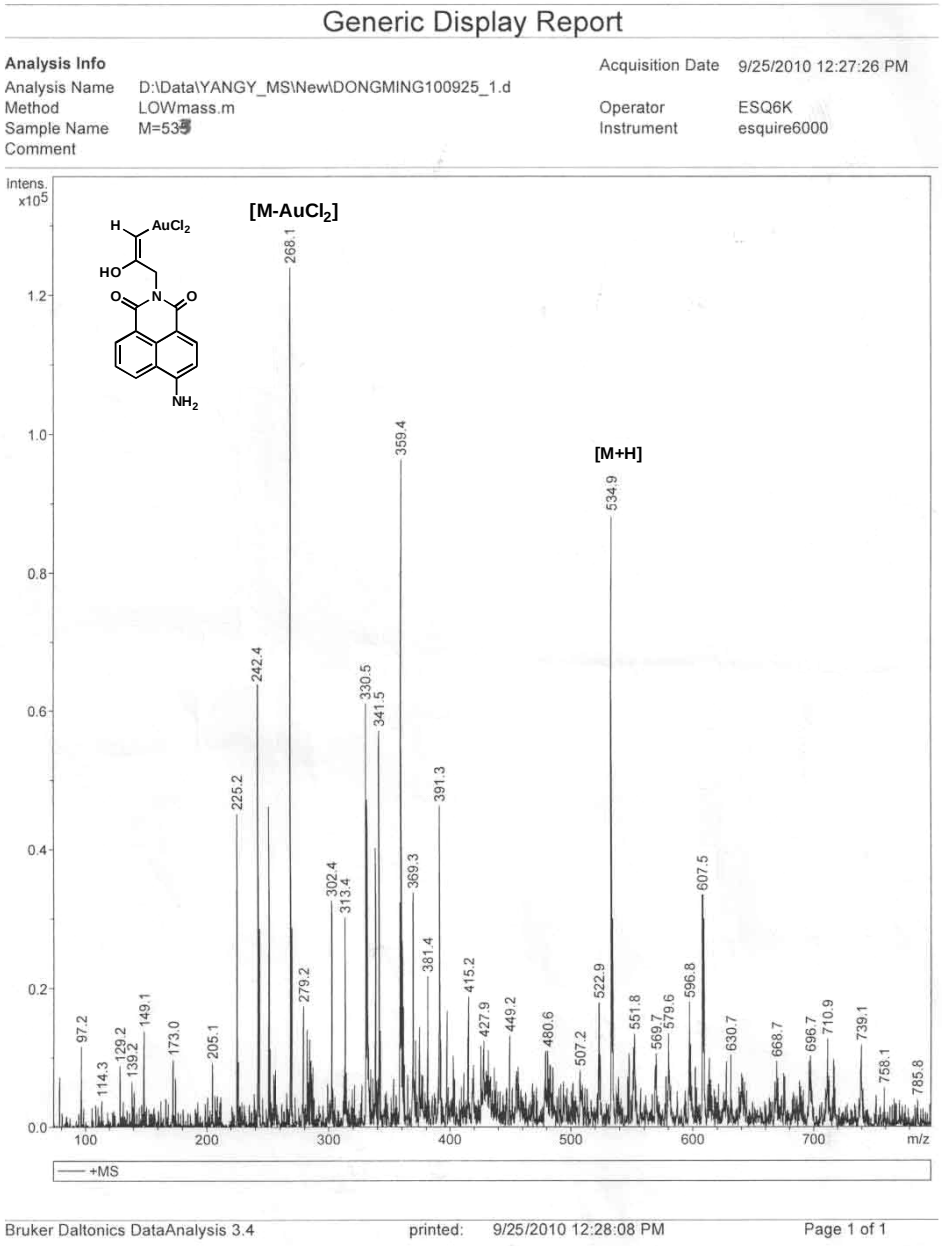

Figure S12. ESI mass spectrum of **1** in the presence of Au^{3+}. ESI–MS: (*m/z*) 534.9 $[M+H]^+$, calcd. for $C_{15}H_{11}Cl_2N_2O_3Au$ = 533.98.

13. NMR and ESI-MS copies.

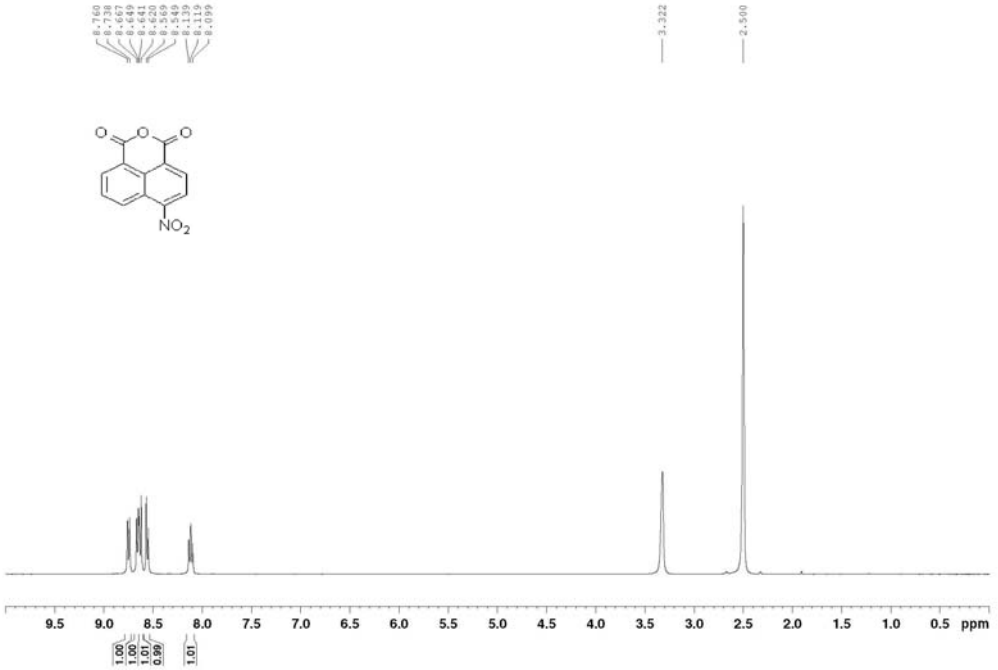

Figure S13. ^{1}H NMR (d_6–DMSO, 400 MHz) spectrum of **4-nitro-1,8-naphthalic anhydride**.

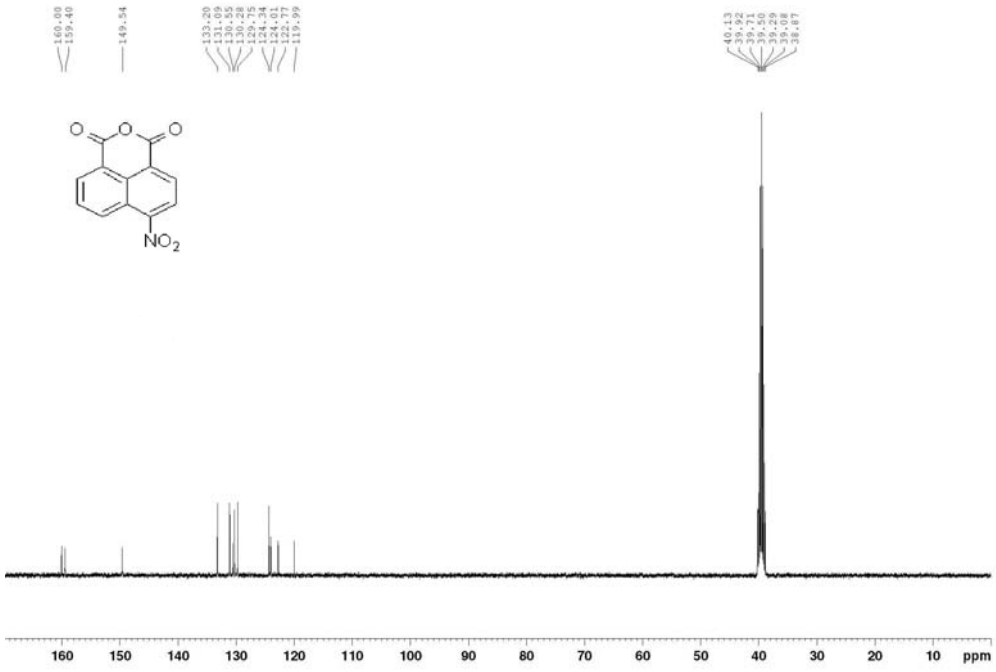

Figure S14. ^{13}C NMR (d_6–DMSO, 400 MHz) spectrum of **4-nitro-1,8-naphthalic anhydride**.

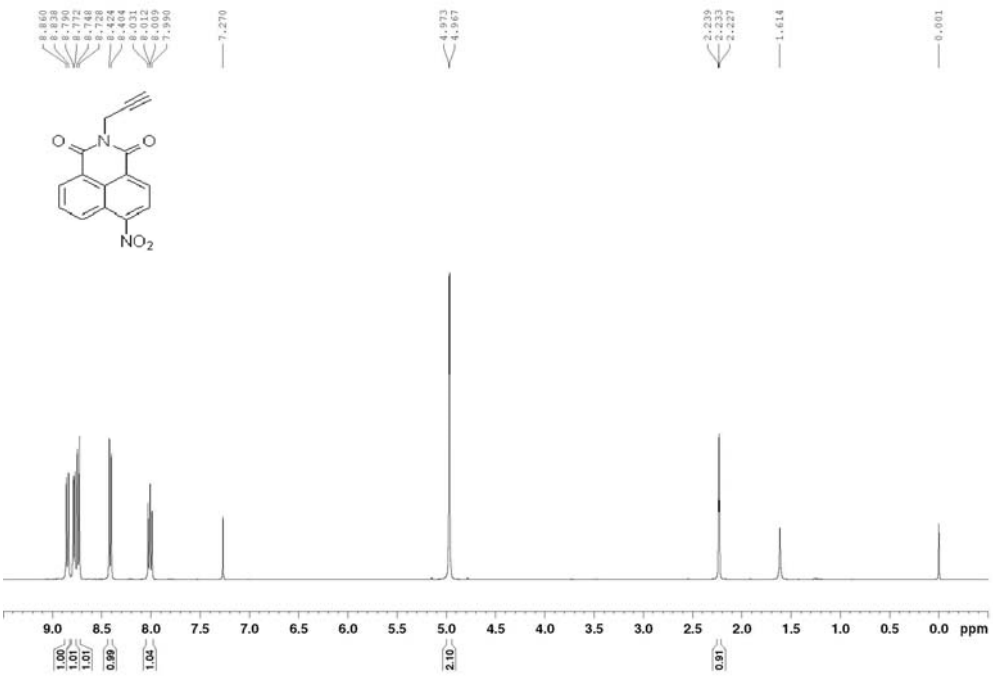

Figure S15. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of ***N*-Propargyl-4-nitro-1,8-naphthalimide**

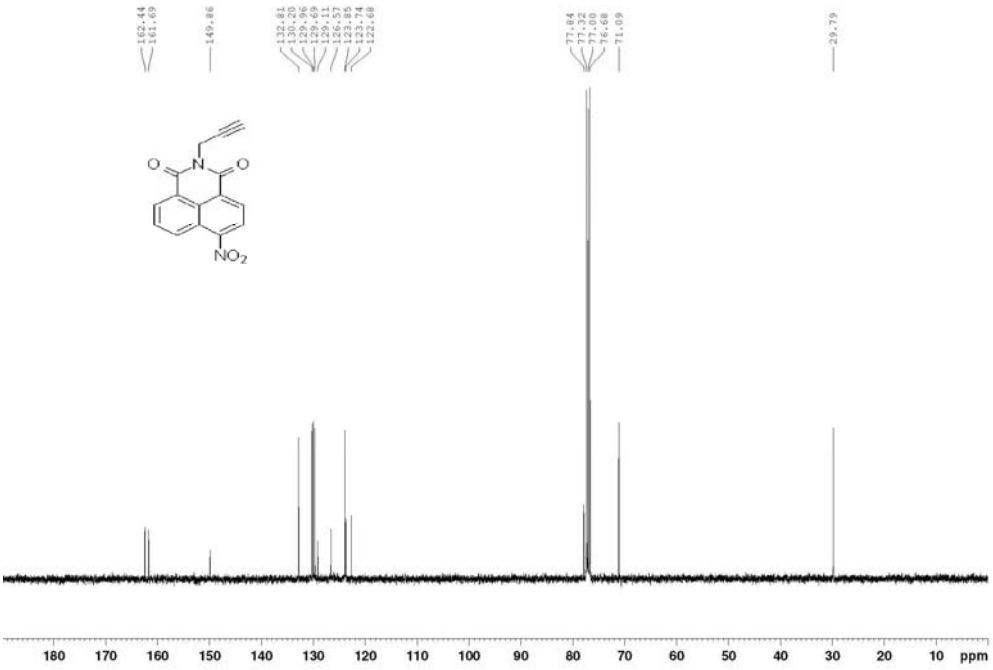

Figure S16. ^{13}C NMR ($CDCl_3$, 400 MHz) spectrum of ***N*-Propargyl-4-nitro-1,8-naphthalimide**.

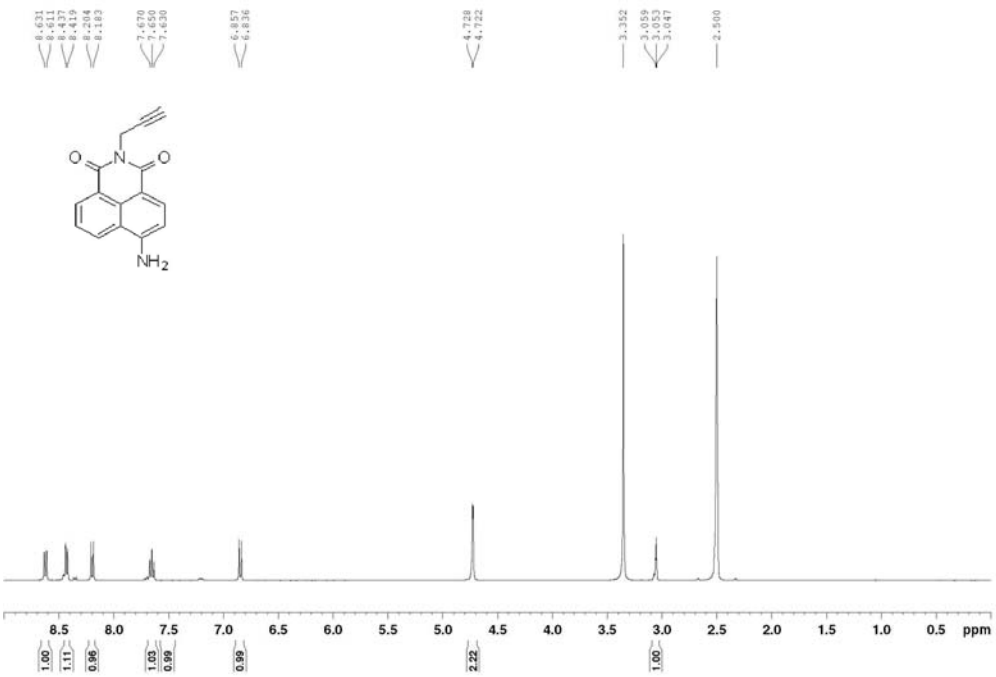

Figure S17. ^{1}H NMR (d_6–DMSO, 400 MHz) spectrum of **1**.

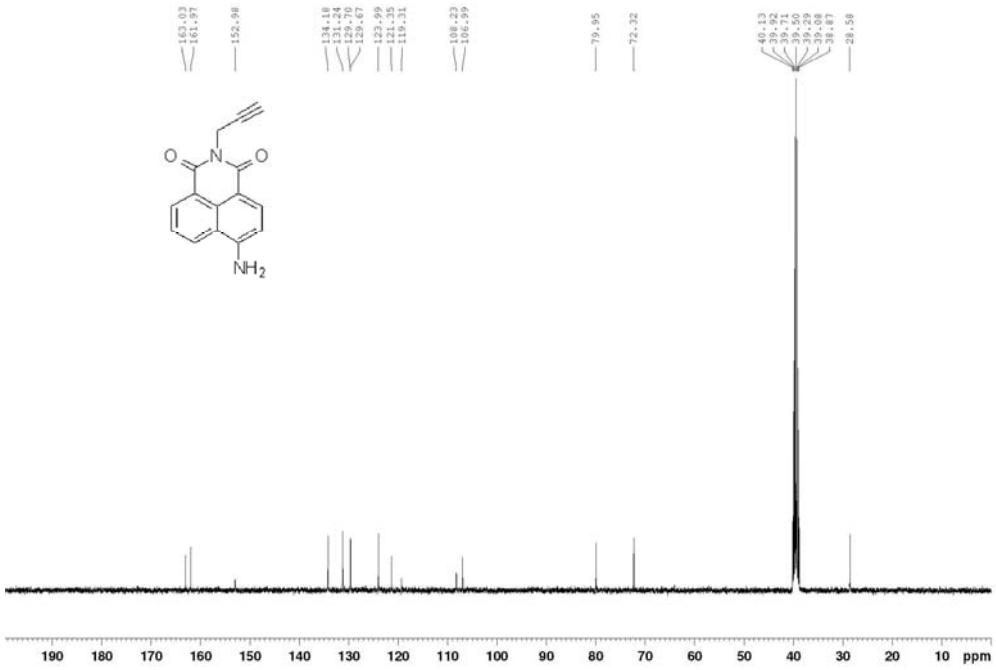

Figure S18. ^{13}C NMR (d_6–DMSO, 400 MHz) spectrum of **1**.

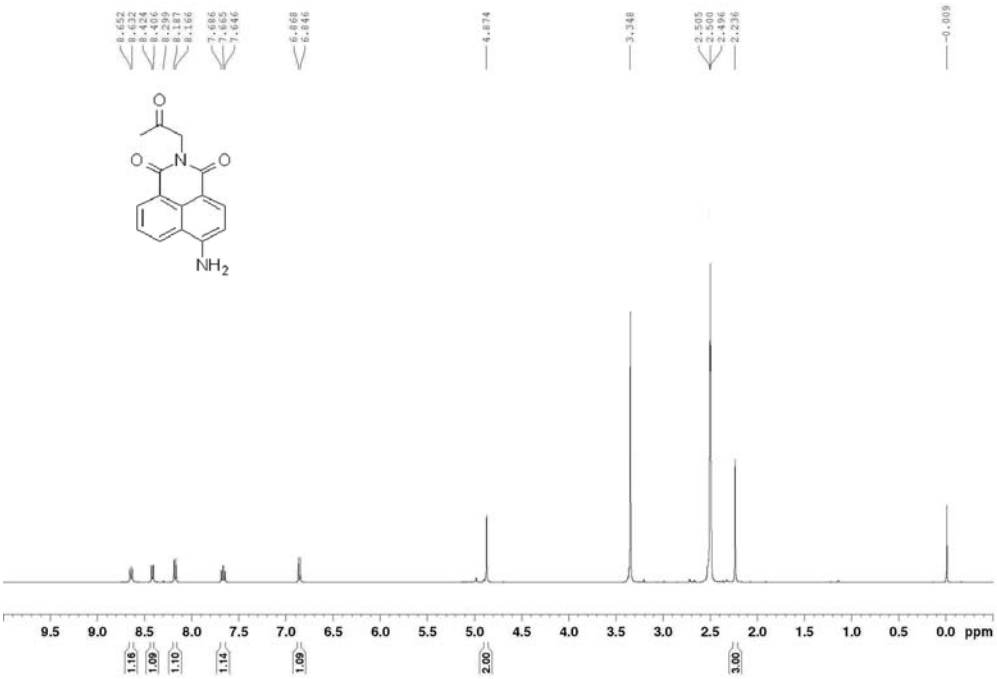

Figure S19. [1]H NMR (d_6–DMSO, 400 MHz) spectrum of **3**.

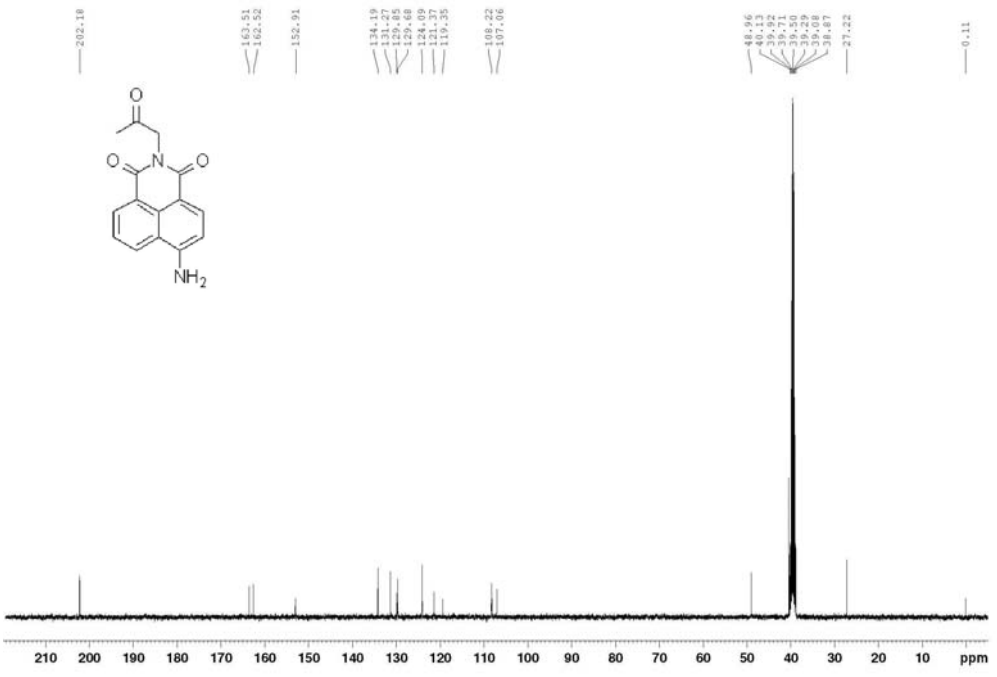

Figure S20. [13]CNMR (d_6–DMSO, 400 MHz) spectrum of **3**.

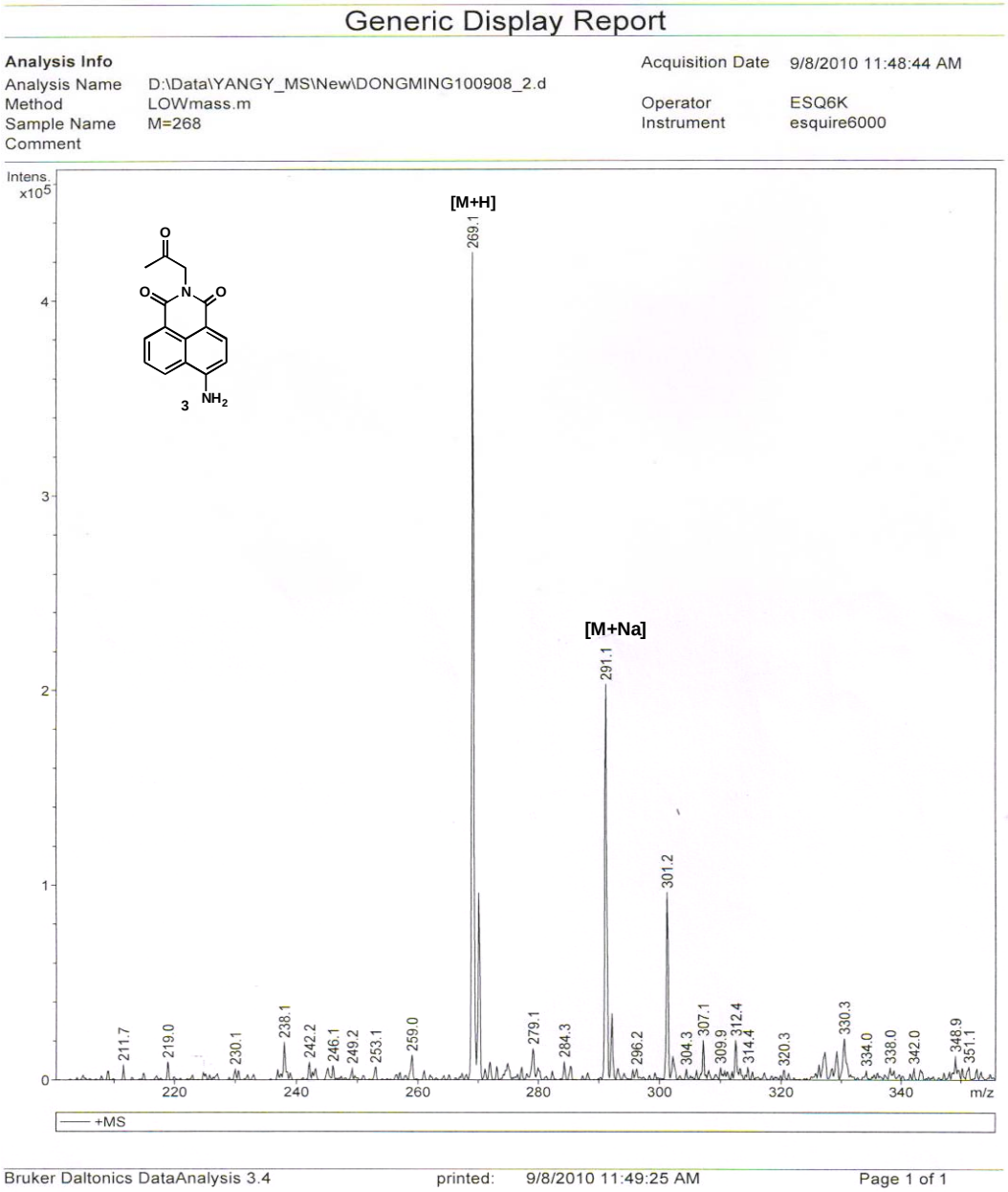

Figure S21. ESI mass spectrum of **3**.