Supporting Information

BODIPY-based Ratiometric Fluorescent Probe for Sensitive and Selective Sensing of Cyanide Ion

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Supporting information

Instrumentation

^{1}H NMR and ^{13}C NMR spectra were taken on a 400 MHz Varian Unity Inova spectrophotometer instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, chemical shifts (δ) are given in ppm relative to solvent peaks (^{1}H: δ 7.26; ^{13}C: δ 77.3) as internal standard. Absorption spectra were taken on a Perkin Elmer Lambda 35 UV-Vis spectrometer. Fluorescence spectra were recorded on a Jobin Yvon Fluoromax-4 spectrofluorometer.

Optical Measurements

All the absorption and emission spectra were recorded by using standard 1 cm path length quartz fluorescence cuvette at room temperature. The slit width of excitation and emission were set to 3 nm and excitation wavelength is set at 470 nm for fluorescence spectroscopy. 100 mM and 10 mM stock solution of sodium cyanide in water and 2.0 mM stock solution of probe **1-3** in acetonitrile were prepared for spectra titration studies. Quantitative amount of stock solution of probe (**1-3**) was transferred into small vials by pipettor. After drying of acetonitrile in vials, probe **1-3** was then diluted to the corresponding concentration (20 μM) with mix solution of CH_3CN-Tris (10 mM, pH = 9.3, 9:1, v/v) or Tris buffer (10 mM, pH = 9.3). Various sodium salts were used for anions selectivity measurements except for HSO_4^- for which its potassium salt was used. Each absorption and fluorescence spectrum was recorded after stirring the solution for 30 min at room temperature.

Non-linear fitting of absorption titration data of probe 1

This reaction is almost irreversible and has thermodynamic equilibrium. We assume 1:1 reaction of probe **1** and CN^- which can be expressed by the equation:

$$\mathbf{1} + \mathrm{CN}^- \xrightarrow{K_{ass}} \mathbf{1}\text{–}\mathrm{CN}$$

This reaction will give:

$$K_{ass} = \frac{[\mathbf{1}\text{–}\mathrm{CN}]}{[\mathbf{1}][\mathrm{CN}^-]} \qquad (1)$$

Where $[\mathbf{1}\text{–CN}]$, $[\mathbf{1}]$ and $[\mathrm{CN}^-]$ is the equilibrium concentration of addition product **1**-CN, probe **1** and cyanide ion in buffer solution, respectively. Considering that $[\mathbf{1}] = [\mathbf{1}]_0 - [\mathbf{1}\text{–CN}]$ and $[\mathrm{CN}^-] = [\mathrm{CN}^-]_0 - [\mathbf{1}\text{–CN}]$ ($[\mathbf{1}]_0$ and $[\mathrm{CN}^-]_0$ is the initial concentration of probe **1** and cyanide ion respectively), the following equation can be obtained:

$$[\mathbf{1}\text{–CN}] = K_{ass} \times ([\mathbf{1}]_0 - [\mathbf{1}\text{–CN}])([\mathrm{CN}^-]_0 - [\mathbf{1}\text{–CN}]) \qquad (2)$$

Solve equation 2 will give:

$$[\mathbf{1}\text{–CN}] = \frac{1}{2}\left[\frac{1}{K_{ass}} + [\mathbf{1}]_0 + [\mathrm{CN}^-]_0 - \sqrt{\left(\frac{1}{K_{ass}} + [\mathbf{1}]_0 + [\mathrm{CN}^-]_0\right)^2 - 4[\mathbf{1}]_0[\mathrm{CN}^-]_0}\right] \qquad (3)$$
$$= \mathcal{F}([\mathbf{1}]_0, [\mathrm{CN}^-]_0)$$

From Beer's law, the absorbance at 546 nm is given by follow:

$$A = \varepsilon_1 l[\mathbf{1}] + \varepsilon_2 l[\mathbf{1}\text{–CN}]$$
$$A_0 = \varepsilon_1 l[\mathbf{1}]_0$$
$$A_{min} = \varepsilon_2 l[\mathbf{1}\text{–CN}]_0$$

A_0 is the absorbance of probe **1** without addition of cyanide ion. A_{min} is the absorbance of probe **1** with addition of excess amount of cyanide ion. ε_1 and ε_2 is the extinction coefficient of **1** and **1**-CN, respectively. The equation 2 can be replaced as follows:

$$\frac{A - A_0}{(A - A_{min})K_{ass}} + [\mathrm{CN}^-]_0 = [\mathbf{1}\text{–CN}] \qquad (4)$$

From equation (3) and (4), the following equation can be obtained:

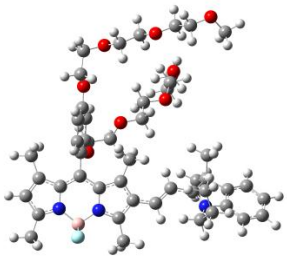
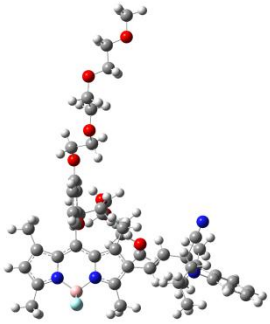
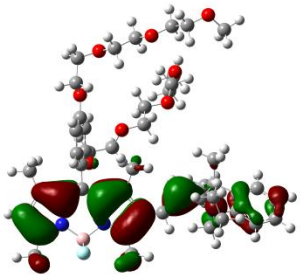
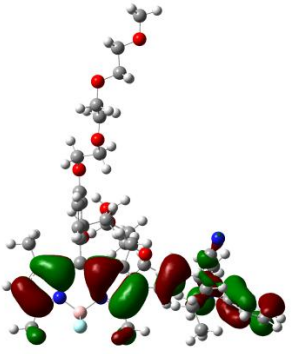
$$A = \frac{A_{min}K_{ass}\{\mathcal{F}([\mathbf{1}]_0, [\mathrm{CN}^-]_0) - [\mathrm{CN}^-]_0\} - A_0}{K_{ass}\{\mathcal{F}([\mathbf{1}]_0, [\mathrm{CN}^-]_0) - [\mathrm{CN}^-]_0\} - 1} \qquad (5)$$

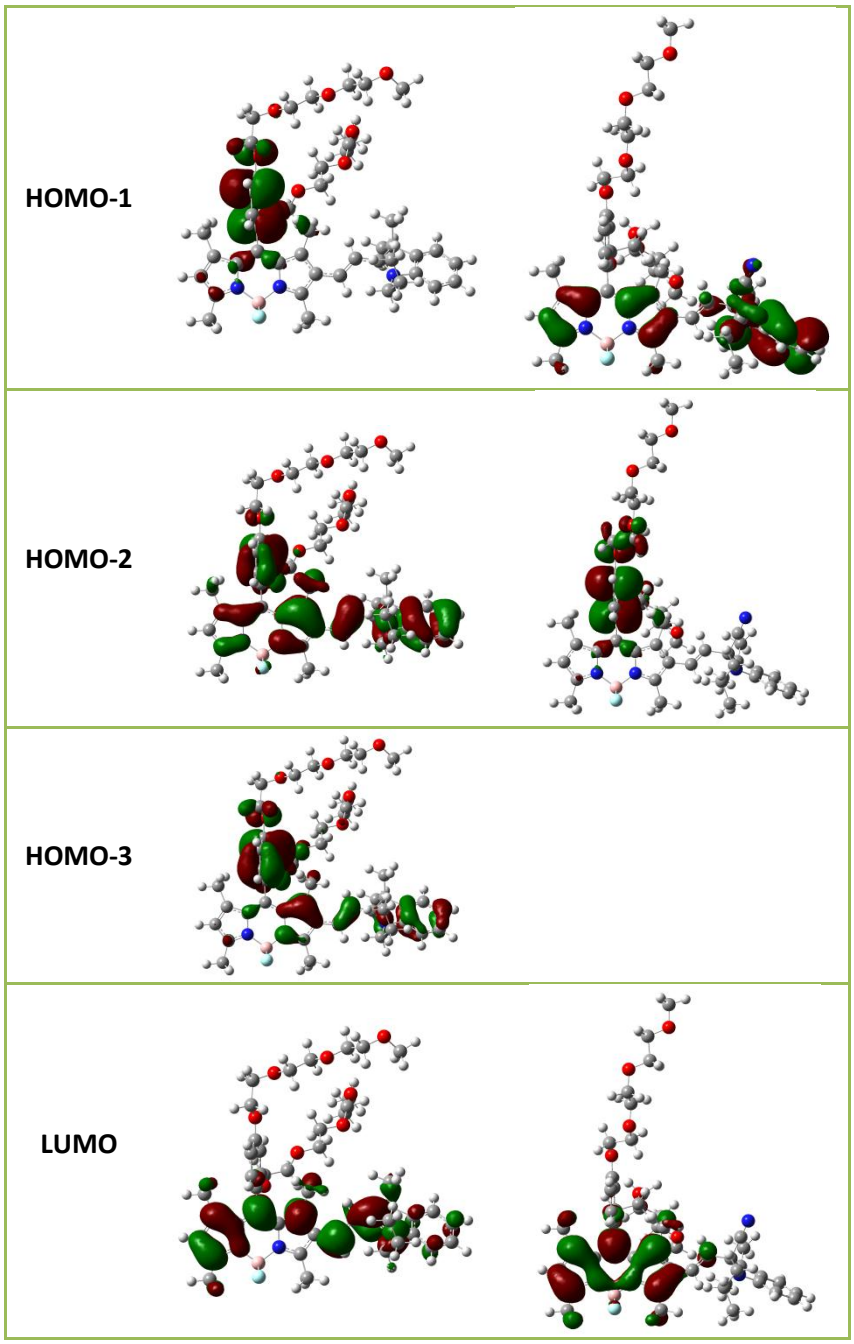
The equation 5 was used for non-linear fitting of absorption titration data of probe **1** with $[CN^-]_0$. The parameter K_{ass} was determined to be $K_{ass} = (3.3 \pm 0.6) \times 10^5\ M^{-1}$

Computational Methods

Results for the optimized structures and the relative electronic properties were obtained at B3LYP and 6-311G(d,p) level of theory as implemented in Gaussian09. The Continuum Polarizable Conductor Model (CPCM) was employed to consider the effect of acetonitrile as the solvent used to experimentally determine the optical properties of probe 1 and 1-CN. For both the structures, TD-DFT calculations were performed to investigate excitations to the first singlet excited state on the geometries as previously optimized at DFT level. Table S1 report the HOMO-i/LUMO distributions for probe 1 (i = 0, 1, 2, 3) and probe 1-CN (i = 0, 1, 2) for those levels involved in the excitations.

Table S1. Optimized structures and HOMO-i/LUMO electronic distribution of probe **1** and **1**-CN

	Probe 1	adduct 1-CN
Structure		
HOMO		



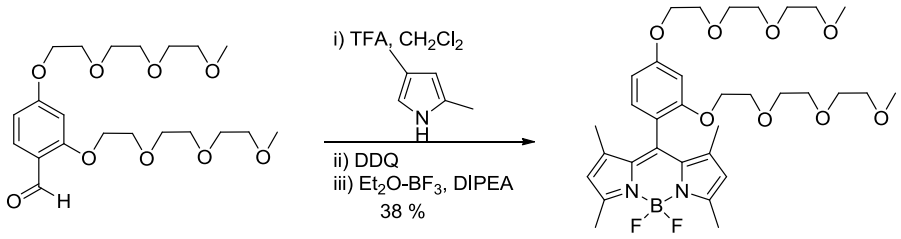
Transition probability (calculated from TD-DFT):

Probe **1**: HOMO to LUMO 90%

1-CN: HOMO to LUMO 96%

Synthesis of Fluorescent Probes.

Materials. Unless otherwise indicated, all reagents and solvents were obtained from commercial suppliers (Aldrich, Sigma, Fluka, Acros Organics, Fisher Scientific, Lancaster) and used without further purification. Air- and moisture-sensitive reactions were conducted in oven-dried glassware using a standard Schlenk line or drybox techniques under an inert atmosphere of dry nitrogen.



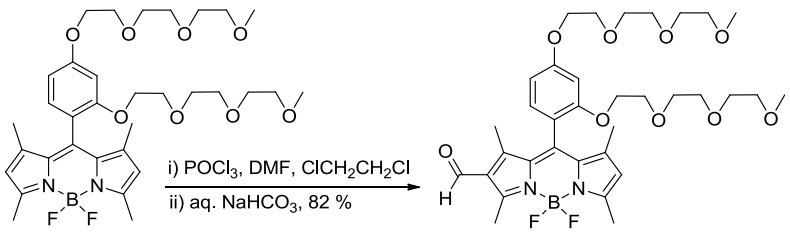
2a **3a**

Compound **2a** was prepared according to our reported procedure (*Org. Lett.*, **2011**, 438-441).

4,4-Difluoro-8-[2,4-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}phenyl]-1,3,5,7-tetramethyl-4-bora-3a,4adiaza-s-indacene (3a).

Compound **2a** was prepared according general procedure. The aldehyde compound **2a** (5.0 g, 11.6 mmol) and 2,4-dimethylpyrrole (2.75 g, 29 mmol) were dissolved in dry CH_2Cl_2 (800 mL). Five drops of trifluoroacetic acid (TFA) were added to the reaction mixture, and the resulting mixture was stirred in the dark overnight under nitrogen atmosphere at room temperature. Then DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) (3.2 g) was added to the reaction mixture. When the mixture was stirred for 40 min, 16 mL of diisopropylethylamine (DIPEA) and 16 mL of $BF_3 \cdot OEt_2$ were added to the mixture. After the mixture was further stirred for 40 min, it was concentrated, and then was washed twice with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography to obtain orange red oil **3a** (2.9 g, 38%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (d, J = 7.6 Hz, 1H), 6.59-6.57 (m, 2H), 5.92 (s, 2H), 4.14 (t, J = 4.0 Hz, 2H), 4.03 (t, J = 4.8 Hz, 2H), 3.87 (t, J = 5.2 Hz, 2H), 3.76-3.64 (m, 8H), 3.55-3.39 (m, 8H), 3.38-3.36 (m, 5H), 3.33 (s, 3H), 2.51 (s, 6H), 1.47 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 156.9, 154.9, 142.9, 139.2, 132.2, 130.1, 120.9, 116.8, 106.4, 100.6, 72.1, 72.0, 71.2, 71.1, 70.9, 70.8, 70.7, 70.4, 69.9, 69.2, 67.8, 59.3,

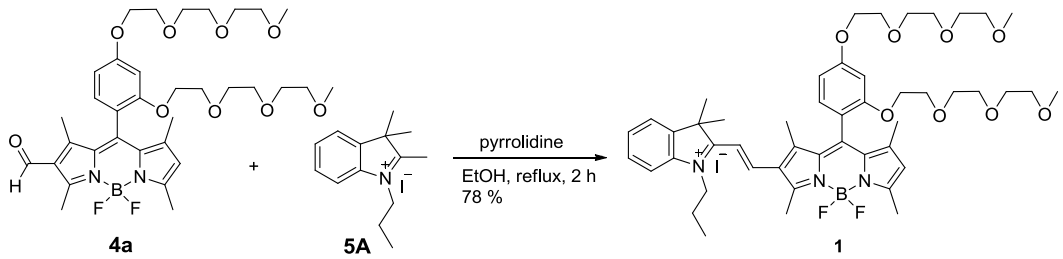
59.1, 14.7, 14.2. IR (cm^{-1}): 2872, 1609, 1577, 1542, 1507, 1468, 1409, 1363, 1303, 1269, 1189, 1155, 1105, 1083, 1043, 971, 835, 766, 705. HRMS (FAB) calcd for $C_{33}H_{47}BF_2N_2O_8$ $[M]^+$, 648.3394; found, 648.3396.



3a **4a**

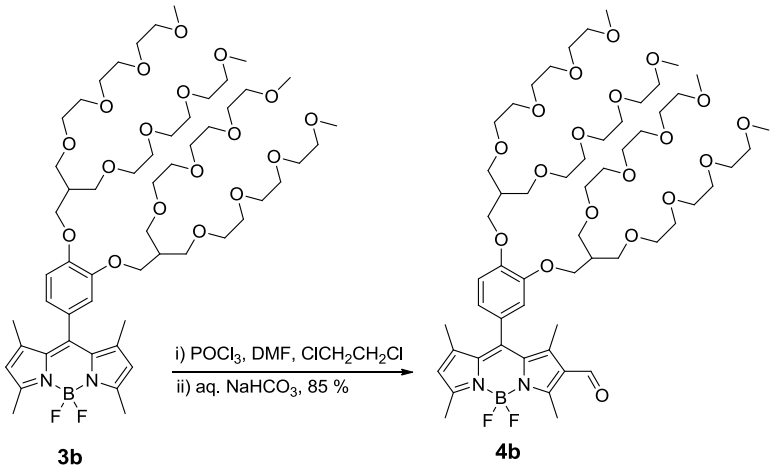
4,4-Difluoro-8-[2,4-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}phenyl]-1,3,5,7-tetramethyl-2-formyl-4-bora-3a,4adiaza-s-indacene (4a).

A mixture of DMF (7.5 mL) and $POCl_3$ (7.5 mL) was stirred in an ice bath for 5 min under argon. After being warmed to room temperature, it was stirred for additional 30 min. To this reaction mixture was added compound **3a** (400 mg, 0.617 mmol) in dichloroethane (70 mL), the temperature was raised to 50 ^oC, and the mixture was stirred for an additional 2 h. The reaction mixture was cooled to room temperature and slowly poured into saturated aqueous $NaHCO_3$ under ice-cold conditions till no gas formed. After being warmed to room temperature, the reaction mixture was further stirred for 30 min and washed with water. The organic layers were combined, dried over anhydrous Na_2SO_4, and evaporated in vacuum. The crude product was further purified using column chromatography to give BODIPY **4a** (340 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.61-6.58 (m, 2H), 6.08 (s, 1H), 4.14 (t, *J* = 4.4Hz, 2H), 4.03 (t, *J* = 4.8Hz, 2H), 3.87 (t, *J* = 4.8 Hz, 2H), 3.74-3.62 (m, 8H), 3.54-3.35 (m, 13 H), 3.30 (s, 3H), 2.76 (s, 3H), 2.56 (s, 3H), 1.75 (s, 3H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 185.9, 161.4, 160.8, 156.5, 155.7, 147.1, 142.2, 141.0, 134.7, 130.2, 129.6, 125.9, 123.4, 115.6, 106.4, 100.6, 71.9, 71.7, 70.9, 70.8, 70.6, 70.5, 70.4, 70.2, 69.6, 69.0, 68.7, 67.6, 59.0, 58.9, 14.9, 14.5, 12.9, 11.0. HRMS (ESI) calcd for $C_{34}H_{47}BF_2N_2O_9Na$ $[M+Na]^+$, 699.3240; found, 699.3252.



4,4-Difluoro-8-[2,4-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}phenyl]-1,3,5,7-tetramethyl-2-[(*E*)-(1,3,3-trimethyl-3*H*-indol-1-ium-2-yl)vinyl]-4-bora-3a,4adiaza-s-indacene (1).

BODIPY dye **4a** (800 mg, 1.18 mmol) and indolium derivative **5A** (0.96 g, 4 eq.) were dissolved in 30 mL of EtOH, then pyrrolidine (0.1 mL) was added to the solution. The reaction mixture was stirring at 86 ^{o}C for 40-60 min till starting materials was consumed by TLC monitoring and then evaporated in vacuum. The resulting solid was dissolved in CH_2Cl_2, and the organic layer was washed three times with water, dried over anhydrous Na_2SO_4, and evaporated in vacuum. The residue was purified by column chromatography on silica (DCM / MeOH, 90:0.5 v/v) and then was further purified by TLC plate (Hexanes/DCM/EtoAc/EtOH, 5/3/1/0.5) to attain compound **1** (882 mg, 78 %) as dark purple oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 16.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.49-7.40 (m, 2H), 6.94 (d, *J* = 4.4 Hz, 1H), 6.90 (d, *J* = 16.0 Hz, 1H), 6.18 (s, 1H), 4.55 (t, *J* = 6.8 Hz, 2H), 4.16 (t, *J* = 4.4 Hz, 2H), 4.06 (q, *J* = 4.4 Hz, 2H), 3.86 (t, *J* = 4.4 Hz, 2H), 3.73-3.59 (m, 8H), 3.52-3.31 (m, 13H), 3.25 (s, 3H), 2.78 (s, 3H), 2.56 (s, 3H), 1.95 (m, 2H), 1.76 (s, 3H), 1.75 (s, 3H), 1.74 (s, 3H), 1.53 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.7, 163.8, 162.0, 156.8, 155.6, 149.2, 146.1, 142.4, 141.1, 140.5, 139.2, 136.2, 132.1, 130.0, 129.8, 129.1, 125.0, 122.9, 115.1, 114.8, 108.4, 107.2, 101.0, 72.1, 72.0, 71.0, 70.9, 70.8, 70.7, 70.6, 70.5, 69.8, 69.3, 69.0, 68.0, 59.2, 59.1, 51.8, 49.5, 28.1, 21.8, 15.5, 15.0, 14.5, 13.4, 11.9. HRMS (FAB) calcd for $C_{48}H_{65}O_8N_3F_2B$ $[M\text{-}I]^+$, 860.4833; found, 860.4830.

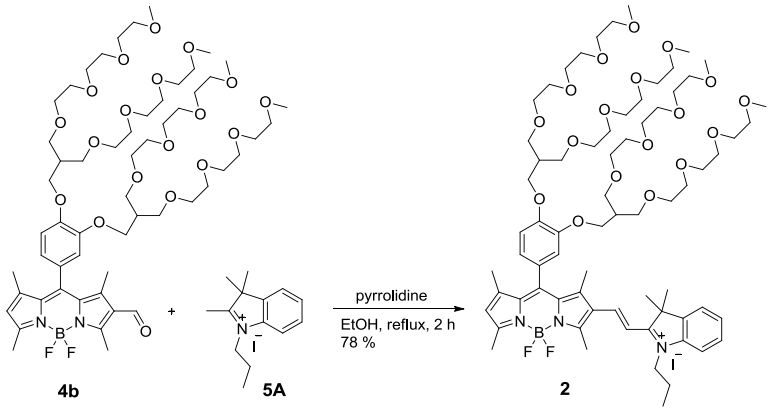


3b **4b**

Compound **3b** was prepared according to our reported procedure (*Org. Lett.*, **2011**, 438-441).

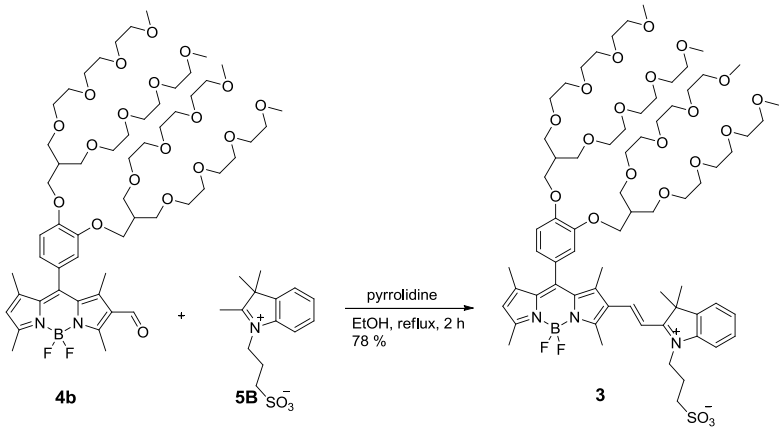
4,4-Difluoro-8-[3,4-bis(3-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}-2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxymethyl}propoxy)phenyl]-1,3,5,7-tetramethyl-2-formyl-4-bora-3a,4adiaza-s-indacene (4b).

Compound **4b** was prepared by the same procedure of synthesis of compound **4a**. DMF (8 mL) and $POCl_3$ (8 mL) compound **3b** (750 mg, 0.67 mmol) in dichloroethane (40 mL), give BODIPY **4b** (620 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (s, 1H), 6.92 (d, *J* = 8 Hz, 1H), 6.65-6.70 (m, 2H), 6.05 (s, 1H), 4.00 (d, *J* = 5.6Hz, 2H), 4.89 (d, *J* = 5.6Hz, 2H), 3.55-3.39 (m, 56H), 3.39-3.23 (m, 12H), 2.69 (s, 3H), 2.48 (s, 3H), 1.65 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 185.4, 161.0, 155.9, 149.7, 147.0, 143.4, 142.5, 134.0, 129.7, 125.9, 125.8, 123.5, 120.0, 113.5, 112.6, 71.6, 71.5, 70.3, 70.3, 70.2, 70.2, 70.1, 70.1, 69.5, 69.0, 67.2, 66.8, 58.7, 58.6, 39.7, 14.8, 12.7, 11.4. HRMS (ESI) calcd for $C_{56}H_{91}BF_2N_2O_{19}Na$ $[M+Na]^+$, 1167.6175; found, 1167.6182.



4,4-Difluoro-8-[3,4-bis(3-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}-2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxymethyl}propoxy)phenyl]-1,3,5,7-tetramethyl-6-[(*E*)-(2,3,3-trimethyl-3*H*-indol-1-ium-2-yl)vinyl]-4-bora-3a,4adiaza-s-indacene (2).

Probe **2** was prepared by BODIPY dye **4b** and indolium derivative **5A** with the same synthesis procedure of probe **1**.BODIPY dye **4b** (240 mg, 0.21 mmol), indolium derivative **5A** (170 mg, 4 eq.), 6 mL of EtOH, pyrrolidine (18 μL), give compound **2** (230 mg, 75 %) as dark purple oil. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.10 (d, J = 15.6 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.62-7.55 (m, 2H), 7.20 (d, J = 8.4 Hz), 7.19 (s, 1H), 7.00-6.92 (m, 2H), 6.50 (s, 1H), 4.50 (t, J = 6.4 Hz, 2H), 4.07 (d, J = 5.2 Hz, 2H), 4.00 (s, 2H), 3.57-3.33 (m, 56H), 3.21-3.18 (m, 12H), 2.82 (s, 3H), 2.57 (s, 3H), 1.86 (sex, 2H), 1.75 (s, 6H), 1.72 (s, 3H), 1.54 (s, 3H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 181.0, 173.3, 162.2, 155.2, 153.0, 149.6, 149.5, 147.7, 145.2, 143.2, 142.8, 140.9, 139.9, 134.1, 130.7, 129.1, 128.9, 125.5, 125.2, 124.7, 123.0, 120.6, 114.8, 114.1, 113.3, 110.6, 71.3, 71.2, 70.0, 69.8, 69.8, 69.7, 69.6, 68.4, 67.1, 66.7, 58.0, 51.6, 47.4, 26.4, 21.3, 14.8, 14.6, 13.8, 12.9, 10.9. HRMS (ESI) calcd for $C_{70}H_{109}O_{18}N_3F_2B$ $[M-I]^+$, 1328.7767; found, 1328.7756.



4,4-Difluoro-8-[3,4-bis(3-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}-2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxymethyl}propoxy)phenyl]-1,3,5,7-tetramethyl-6-[(*E*)-(3,3-trimethyl-1-(3-sulfonatepropyl)-3*H*-indol-1-ium-2-yl)vinyl]-4-bora-3a,4adiaza-s-indacene (3).

Probe **3** was prepared by BODIPY dye **4b** and indolium derivative **5B** with the same synthesis procedure of probe **1**.BODIPY dye **4b** (160 mg, 0.14 mmol), indolium derivative **5B** (120 mg, 4 eq.), 5 mL of EtOH, pyrrolidine (12 μL), give compound **3** (100 mg, 50 %) as dark purple oil. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.08(d, J = 16 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H). 7.81 (d, J = 7.6 Hz, 1H), 7.57 (m, 2H), 7.18 (d, J = 8.4 Hz, 1H) 7.11-7.05 (m, 2H), 6.93 (d, J = 8 Hz, 1H), 6.47 (s, 1H), 4.71 (t, 2H), 4.07 (d, J = 5.6 Hz, 1H), 3.99 (d, J = 4.8 Hz, 1H), 3.57-3.27 (m, 56H), 3.23-3.15 (m, 12H), 2.86 (s, 3H), 2.60-2.56 (m, 5H), 2.11 (quin, 2H), 1.72 (s, 6H), 1.70 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 180.9, 161.8, 155.5, 149.6, 149.5, 142.8, 140.7, 133.9, 130.6, 129.1, 125.5, 124.5, 122.9, 120.5, 114.8, 113.3, 110.4, 99.8, 71.3, 71.2, 70.0, 69.9, 69.8, 69.7, 69.6, 68.4, 67.1, 66.7, 58.0, 57.9, 51.6, 47.4, 26.4, 15.2, 14.6, 12.6. HRMS (ESI) calcd for $C_{70}H_{108}BF_2N_3O_{21}SNa$ $[M+Na]^+$, 1430.7155; found, 1430.7163.

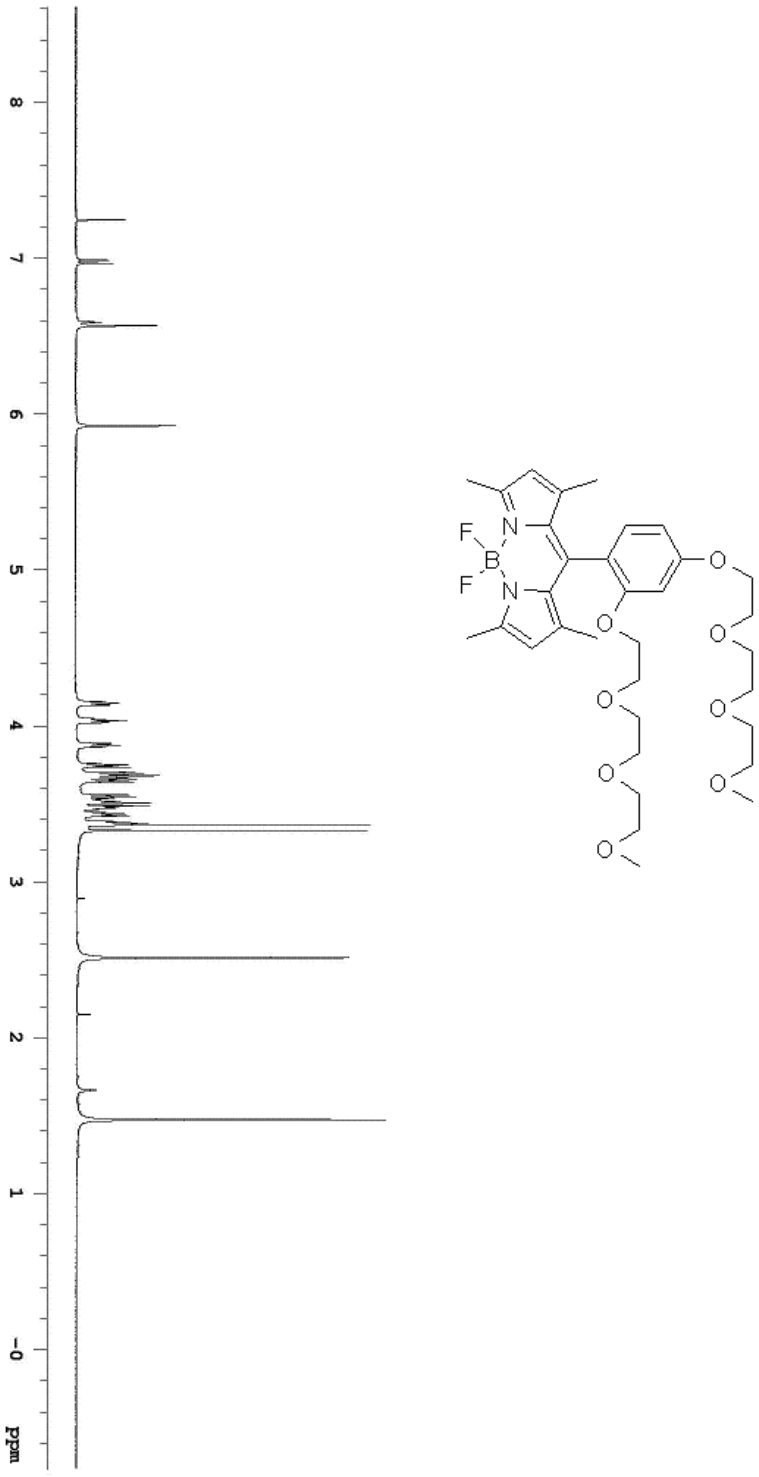


Figure S1. ^{1}H NMR spectrum of BODIPY dye **3a** in $CDCl_3$ solution.

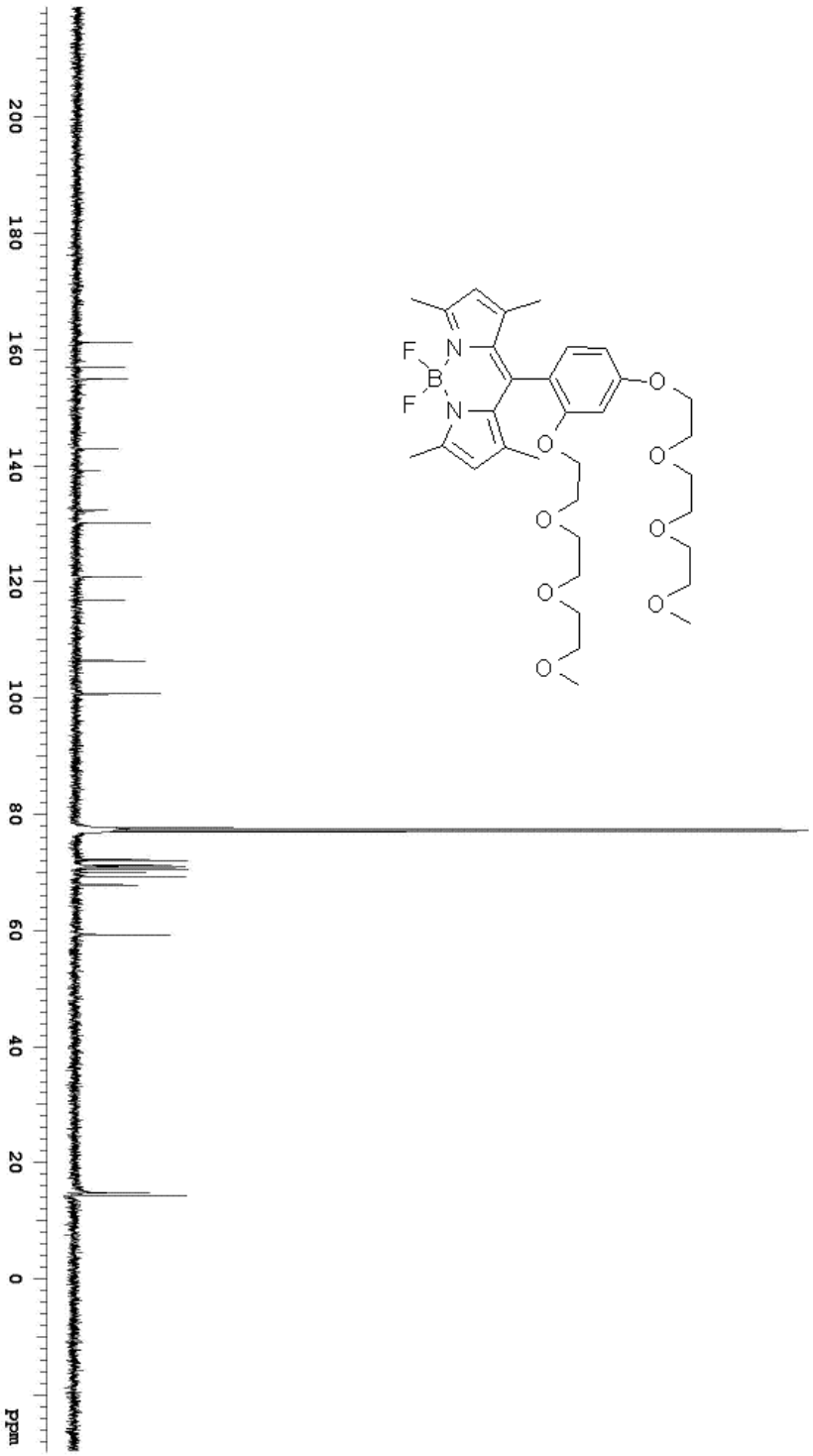


Figure S2. ^{13}C NMR spectrum of BODIPY dye **3a** in $CDCl_3$ solution.

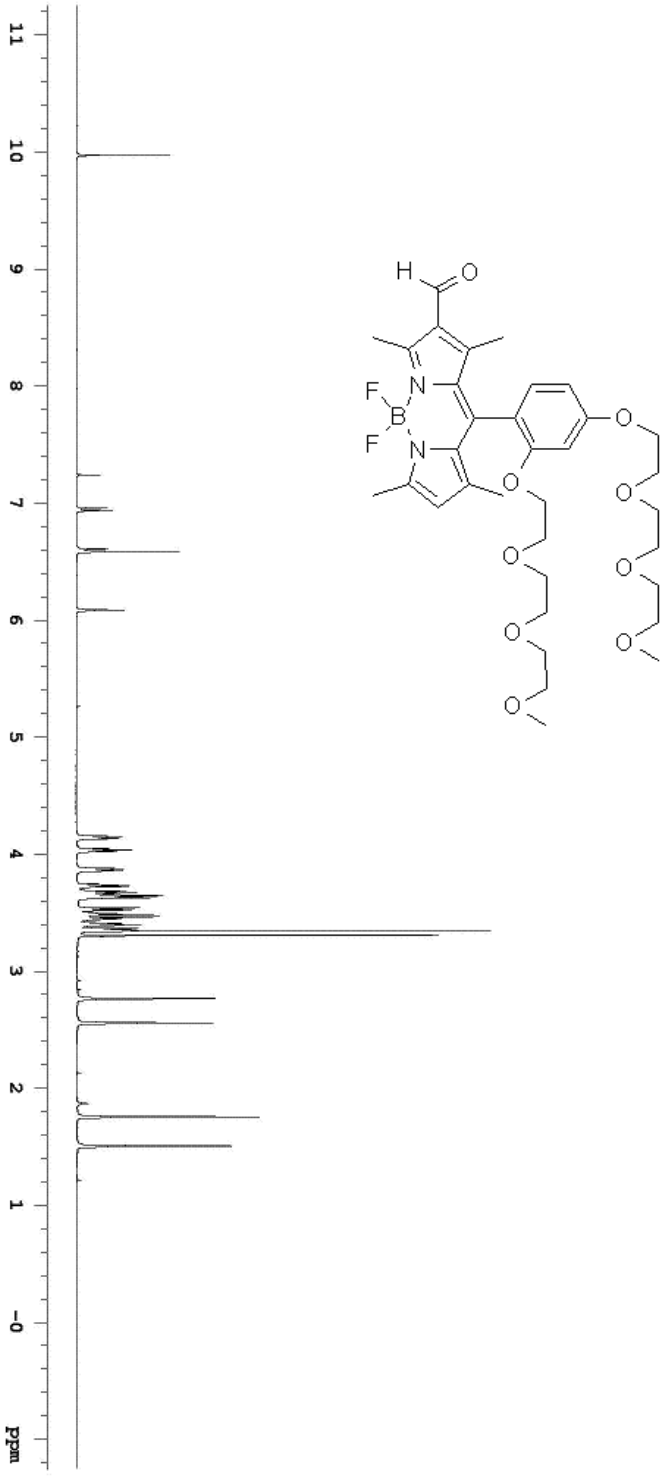


Figure S3. ^{1}H NMR spectrum of BODIPY dye **4a** in $CDCl_3$ solution.

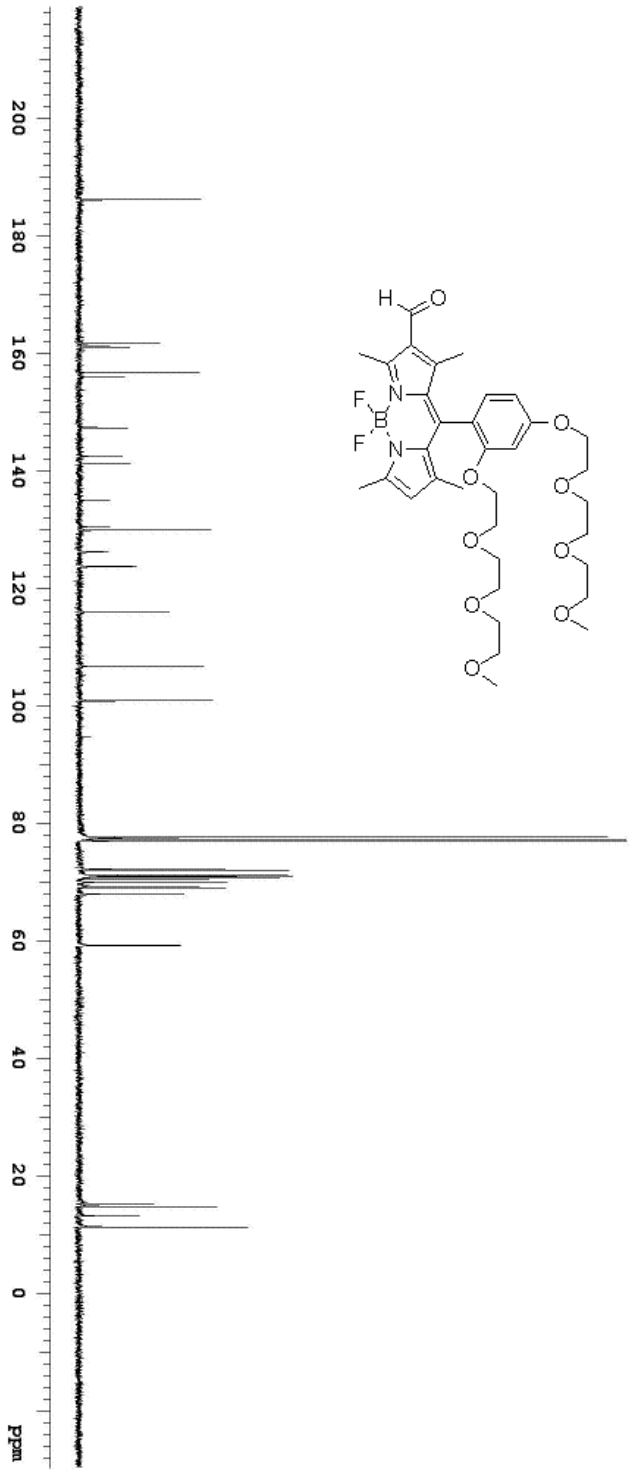


Figure S4. ^{13}C NMR spectrum of BODIPY dye **4a** in $CDCl_3$ solution.

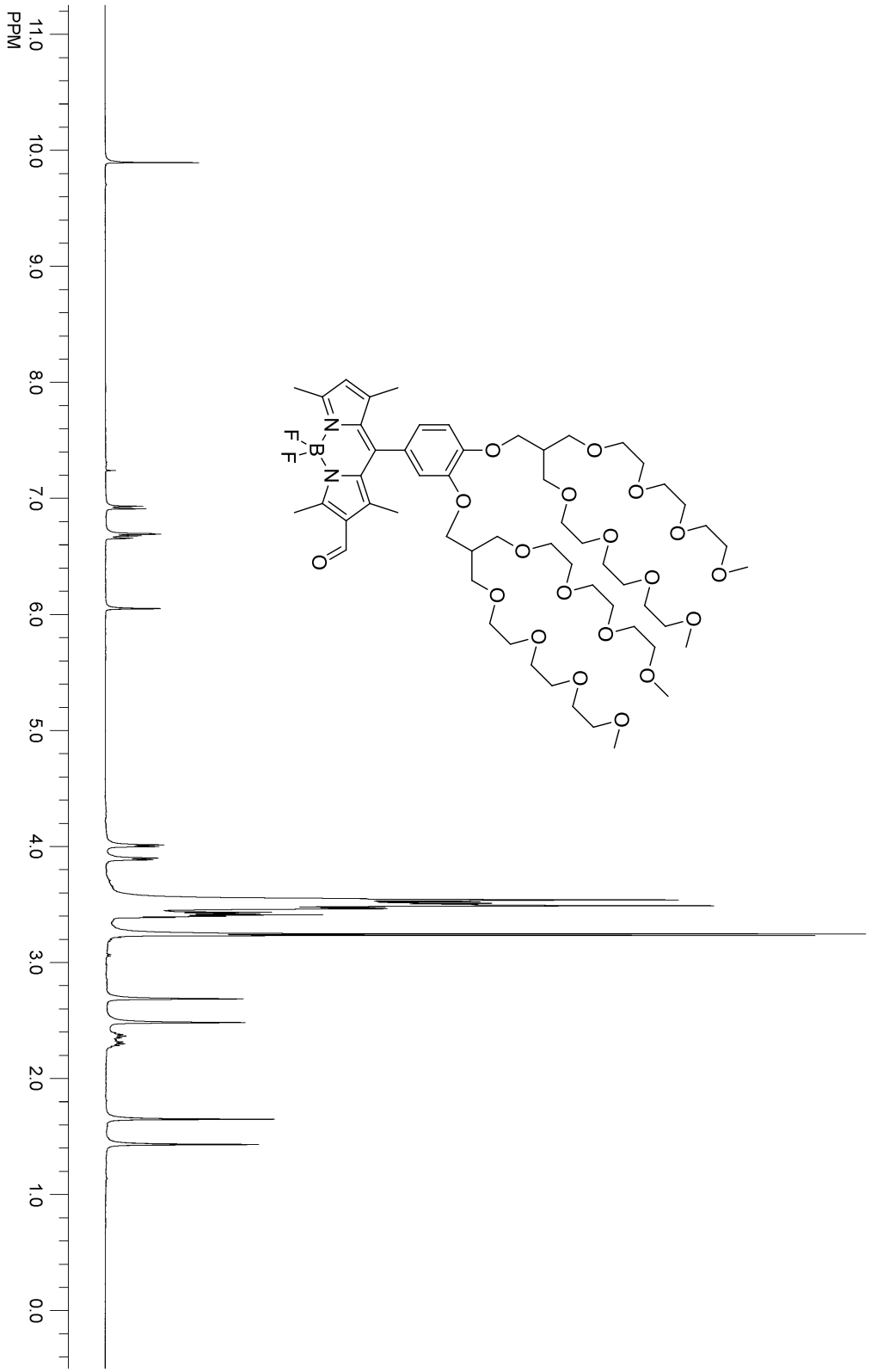


Figure S5. ^{1}H NMR spectrum of BODIPY dye **4b** in $CDCl_3$ solution.

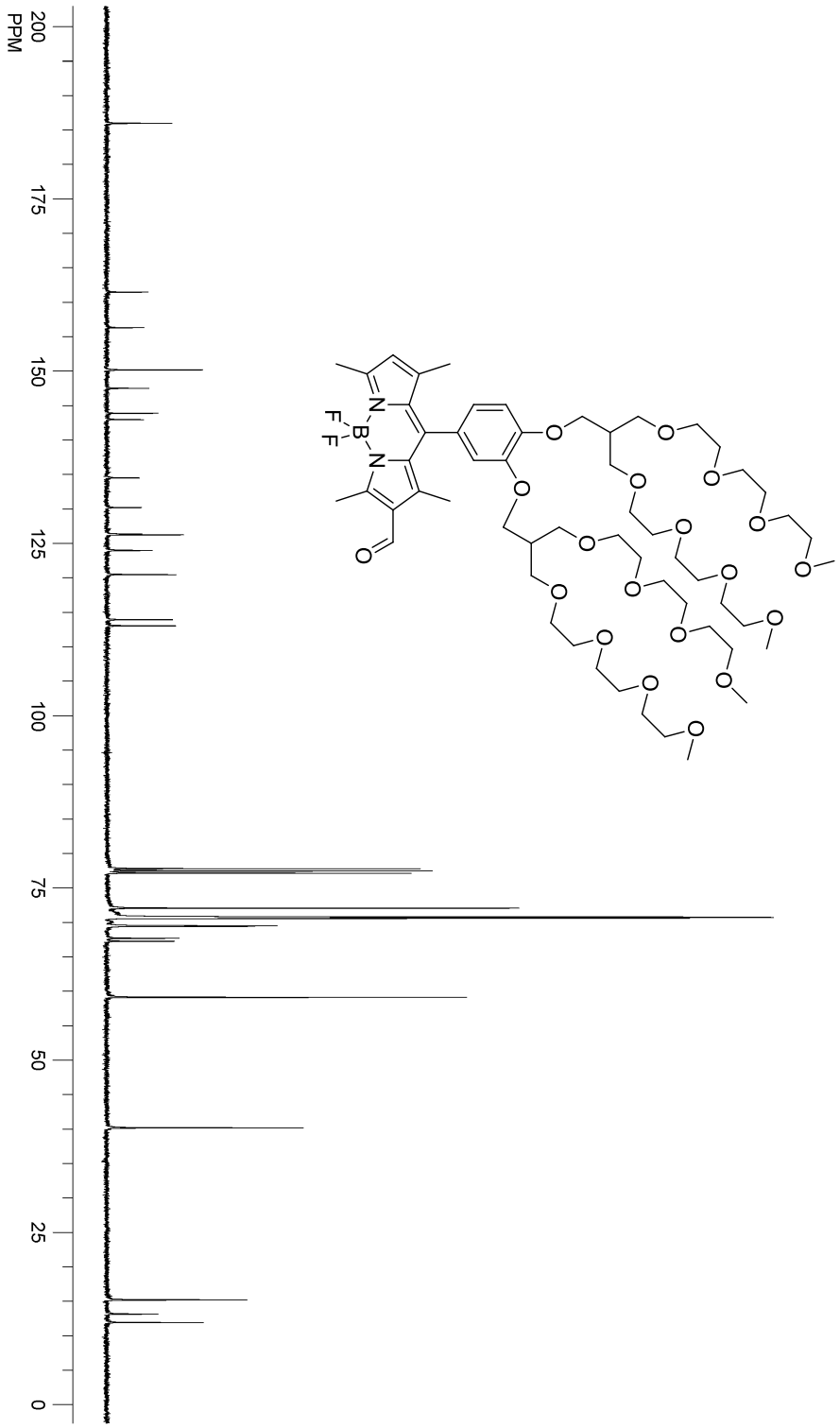


Figure S6. ^{13}C NMR spectrum of BODIPY dye **4b** in $CDCl_3$ solution.

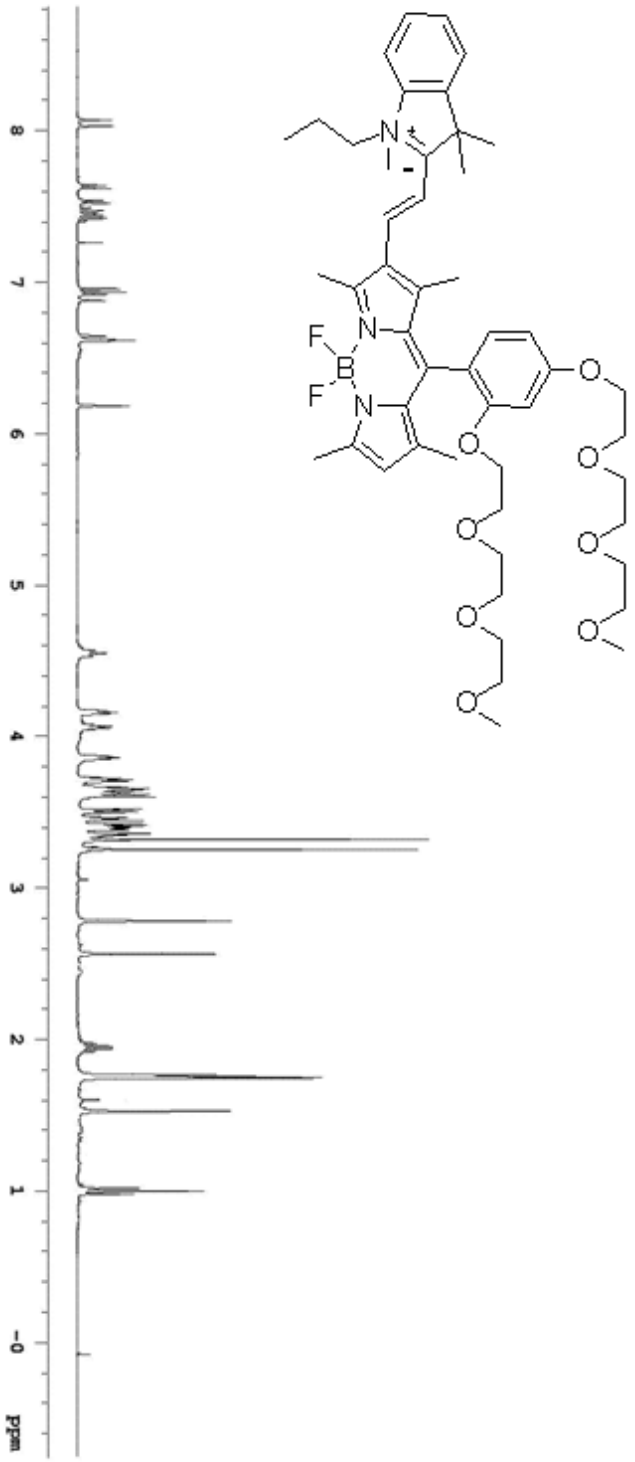


Figure S7. ^{1}H NMR spectrum of probe **1** in $CDCl_3$ solution.

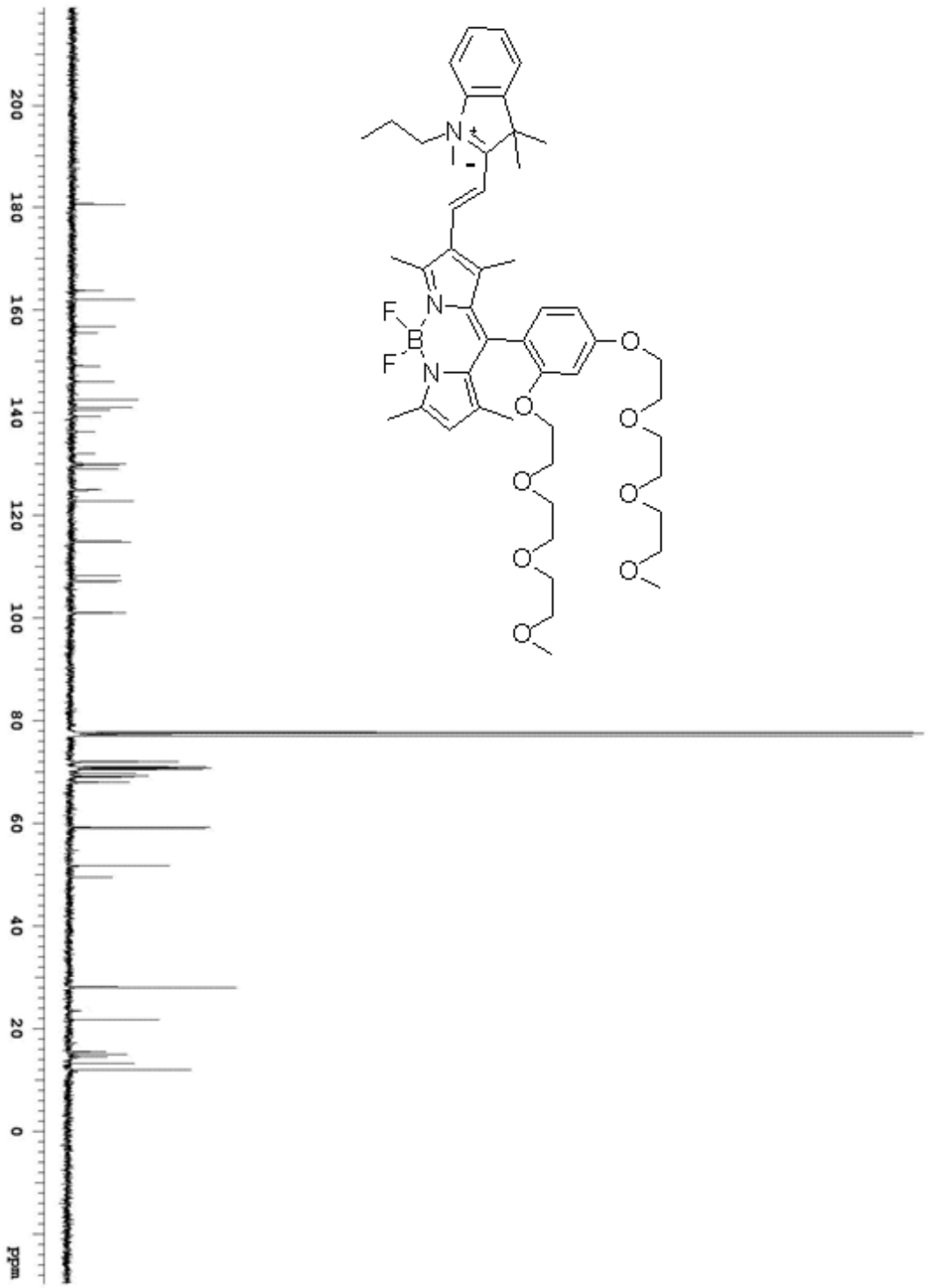


Figure S8. ^{13}C NMR spectrum of probe **1** in $CDCl_3$ solution.

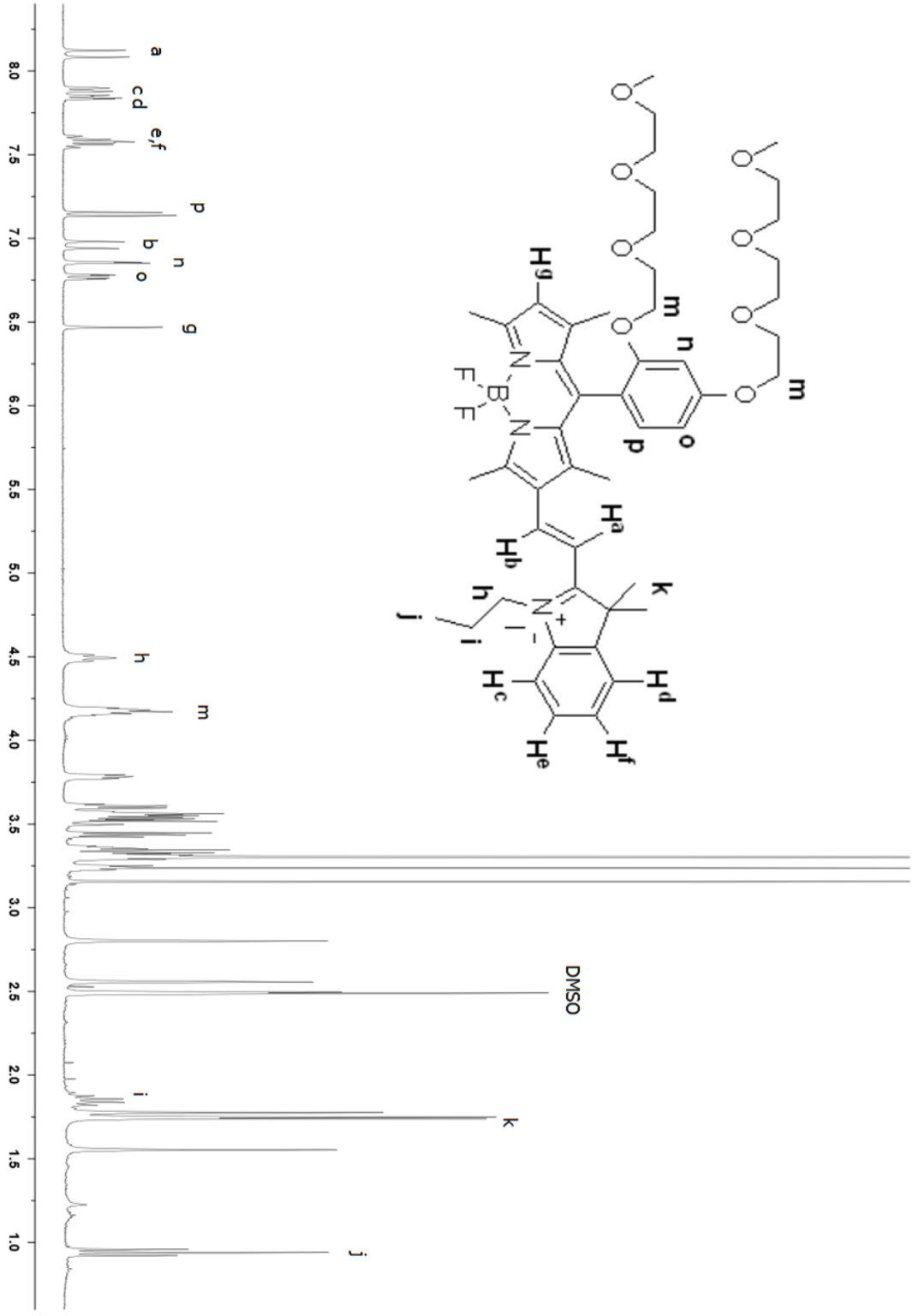


Figure S9. ^{1}H NMR spectrum of probe **1** in DMSO-d_6 solution.

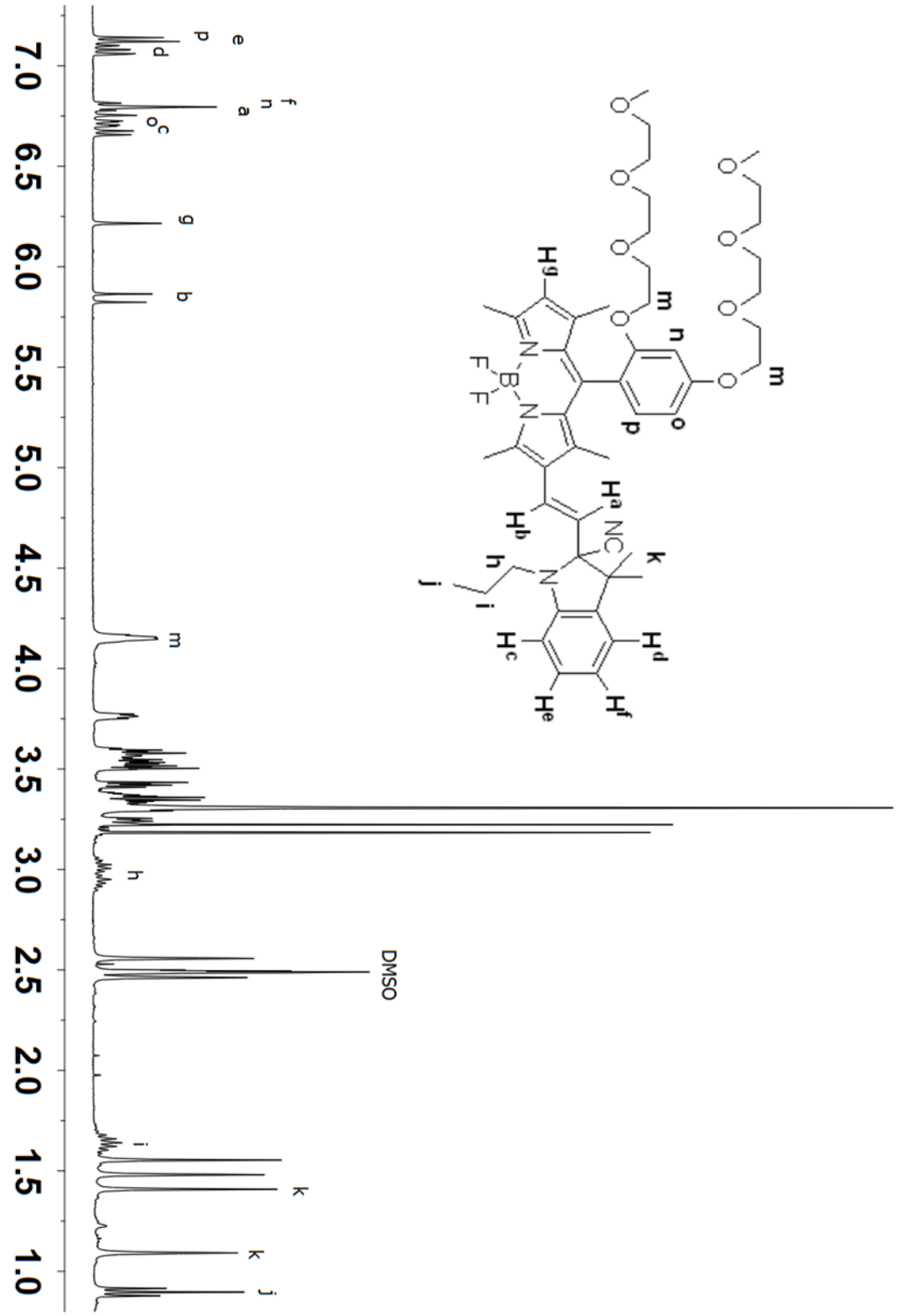


Figure S10. ^{1}H NMR spectrum of **1-CN** adduct in DMSO-d_6 solution.

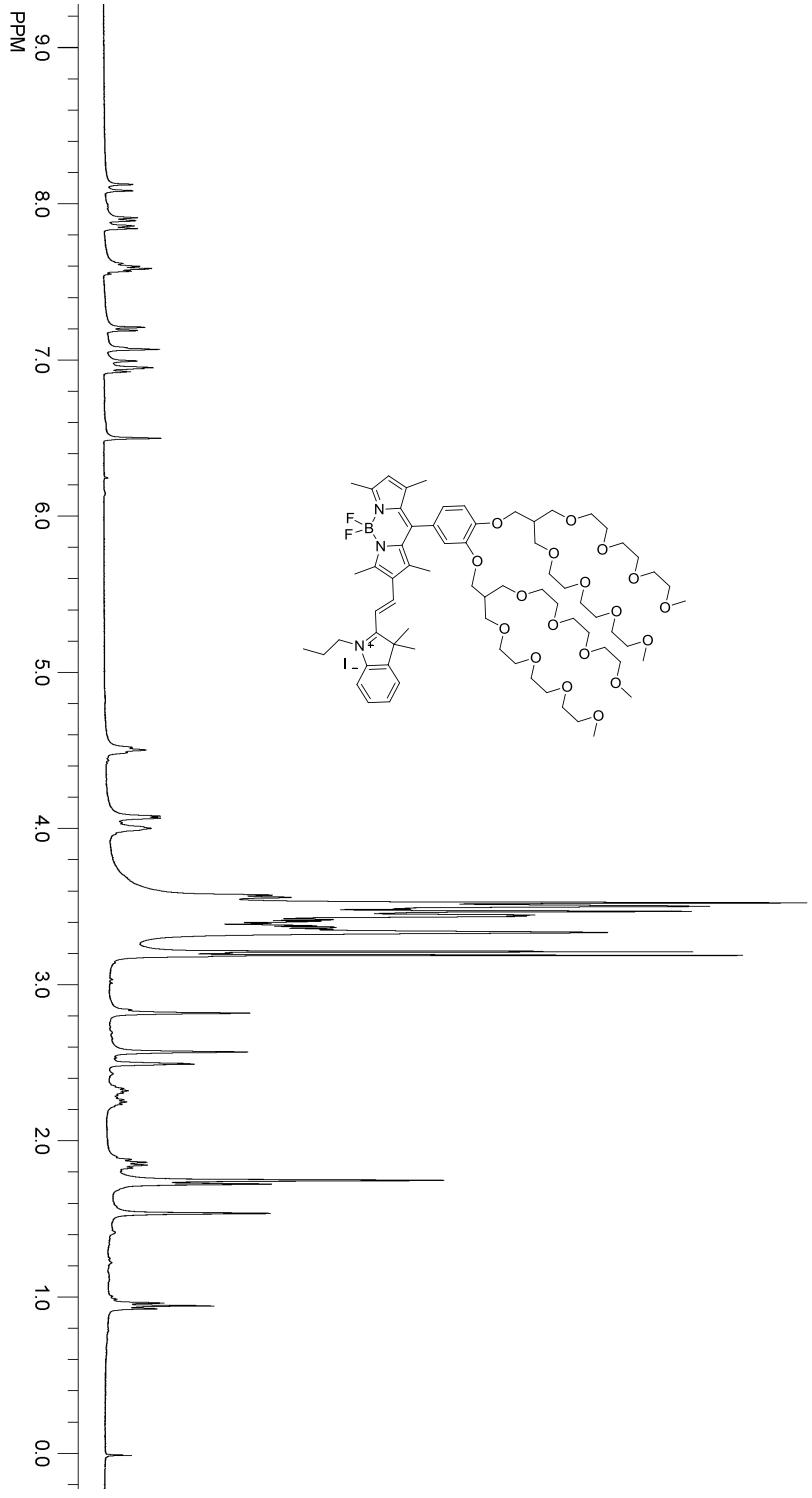


Figure S11. ^{1}H NMR spectrum of probe **2** in DMSO-d_6 solution.

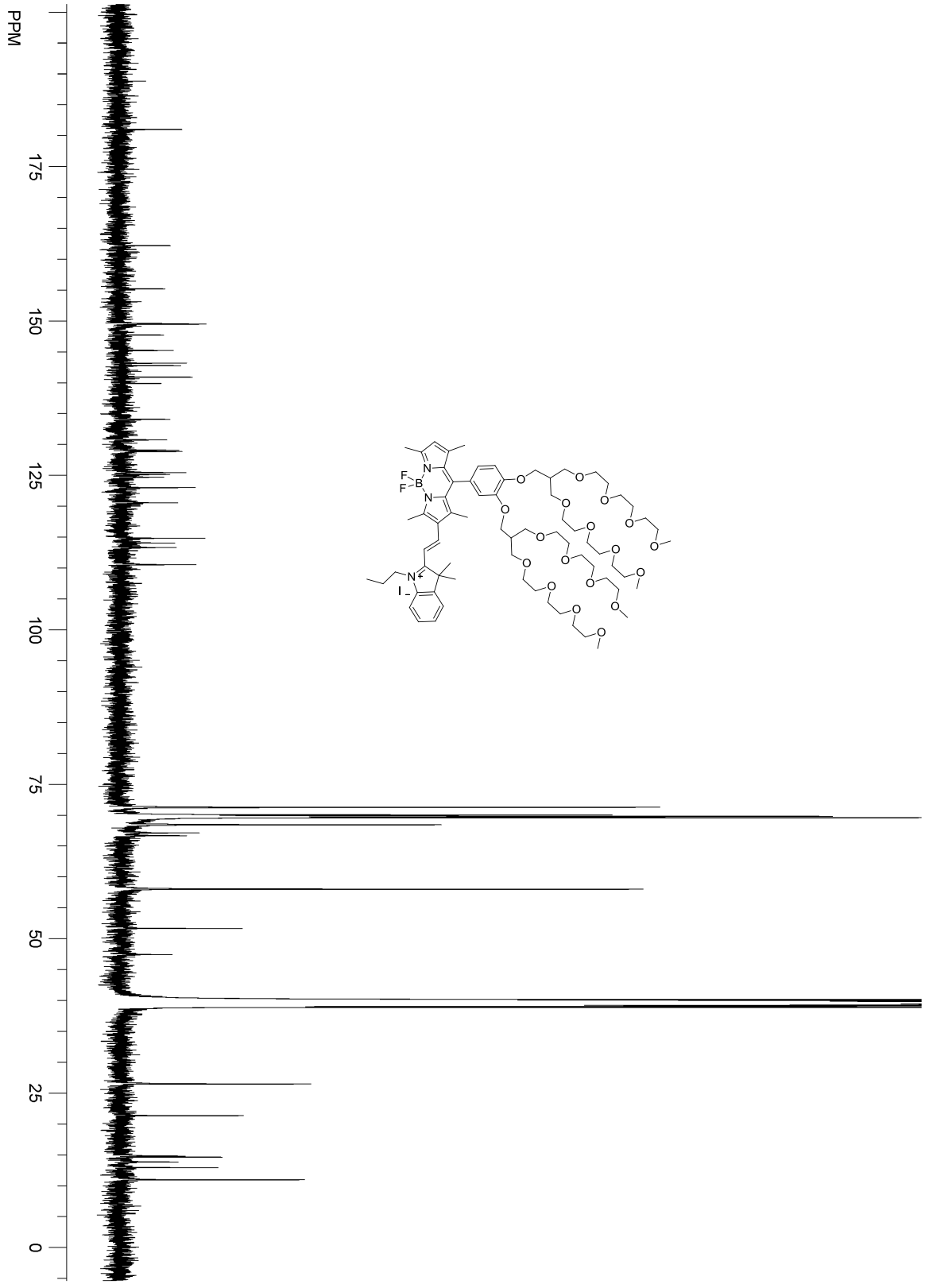


Figure S12. ^{13}C NMR spectrum of probe **2** in DMSO-d_6 solution.

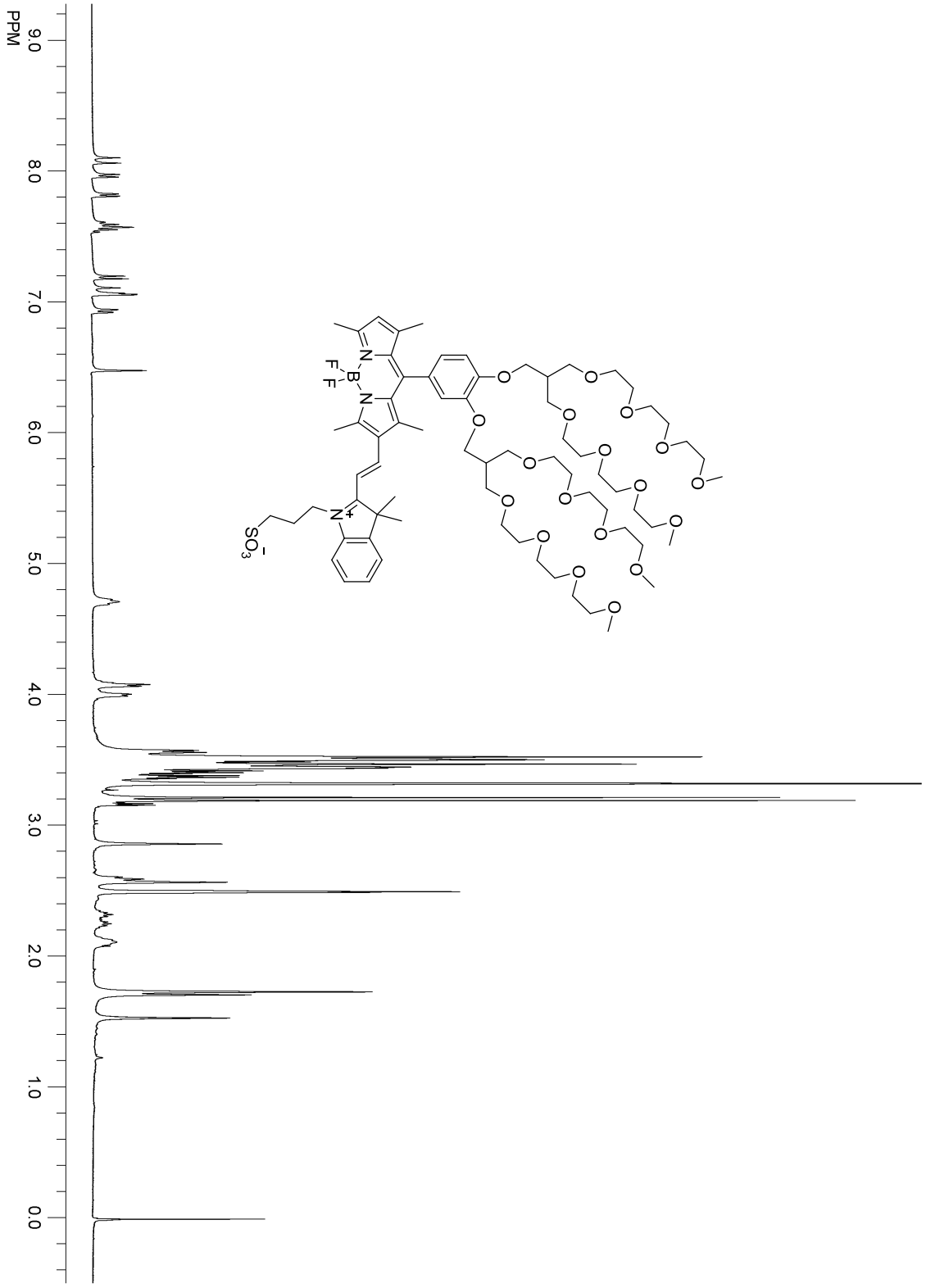


Figure S13. ^{1}H NMR spectrum of probe **3** in DMSO-d_6 solution.

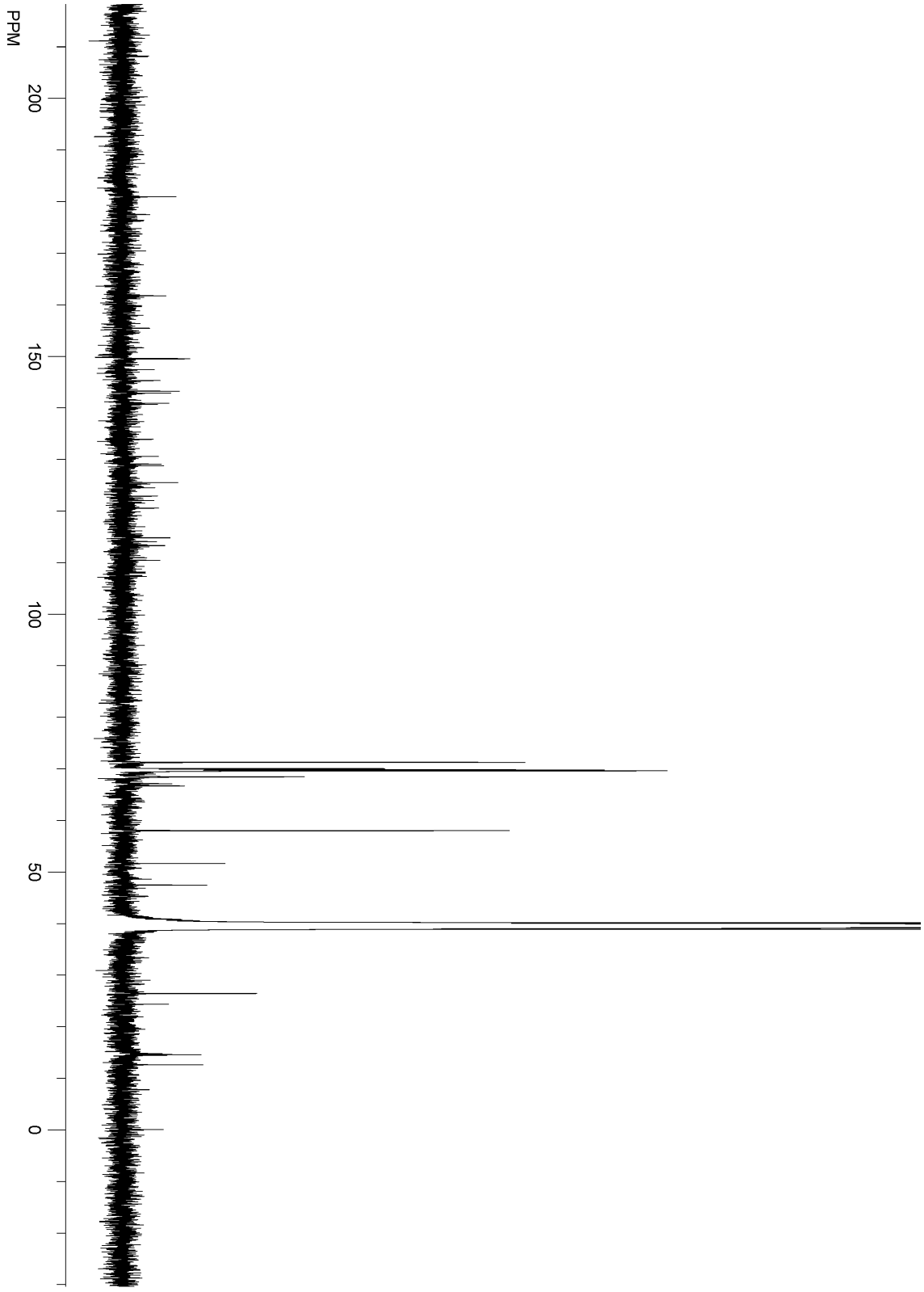


Figure S14. ^{13}C NMR spectrum of probe **3** in DMSO-d_6 solution.

g

[Elemental Composition] Page: 1

Data : 12May10_14-001 Date : 10-May-2012 16:43
Sample: g
Note : NBA
Inlet : Direct Ion Mode : FAB+
RT : 0.07 min Scan#: (1,4)
Elements : C 400/0, H 800/0, O 8/8, N 3/3, F 2/2, B 1/1
Mass Tolerance : 20mmu
Unsaturation (U.S.) : -0.5 - 1000.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
860.4830	100.0	-0.3 / -0.2	17.5	C 48 H 65 O 8 N 3 F 2 B = 860.4833

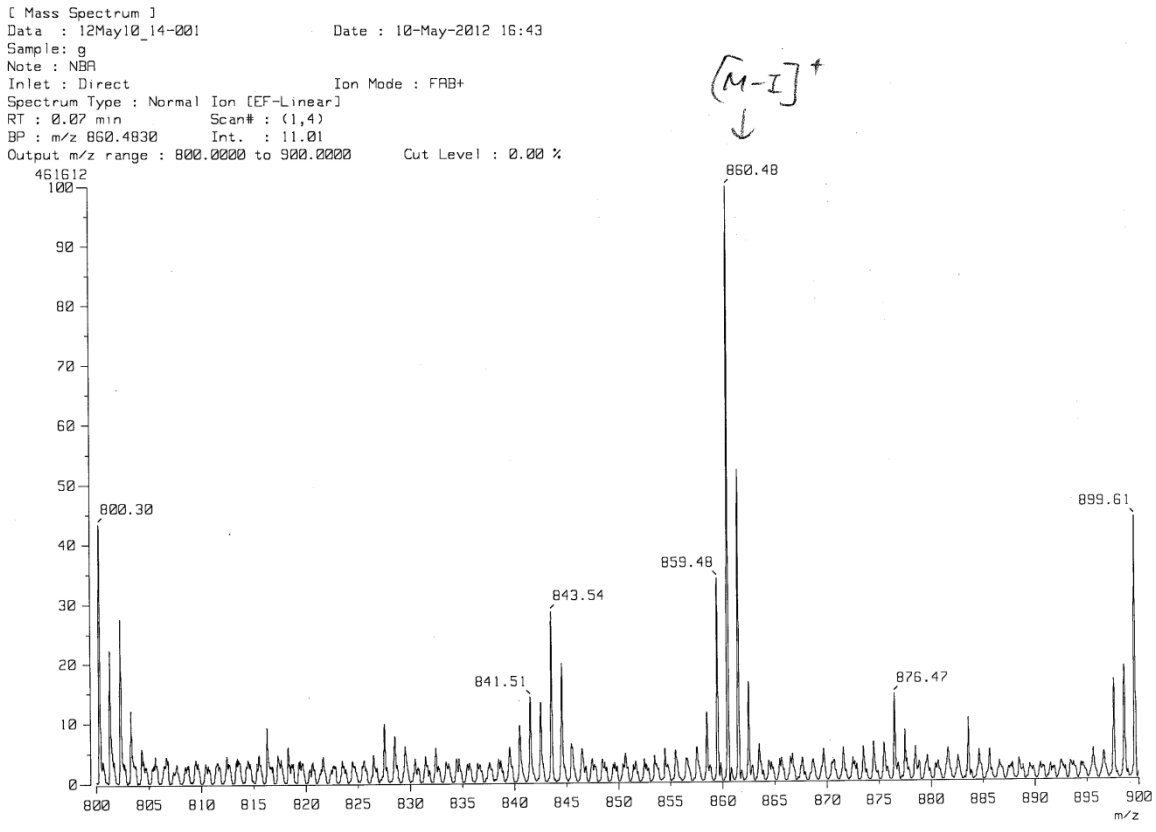


Figure S15. The HRMS (FAB) of probe **1**.

h

[Elemental Composition] Page: 1

Data : 12May10_10-001 Date : 10-May-2012 15:56
Sample: h
Note : NBA
Inlet : Direct Ion Mode : FAB+
RT : 0.06 min Scan#: (1,4)
Elements : C 400/0, H 800/0, O 8/8, N 4/4, F 2/2, B 1/1
Mass Tolerance : 20mmu
Unsaturation (U.S.) : -0.5 - 1000.0

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
886.4857	56.4	-0.7 / -0.6	19.0	C 49 H 65 O 8 N 4 F 2 B = 866.4864

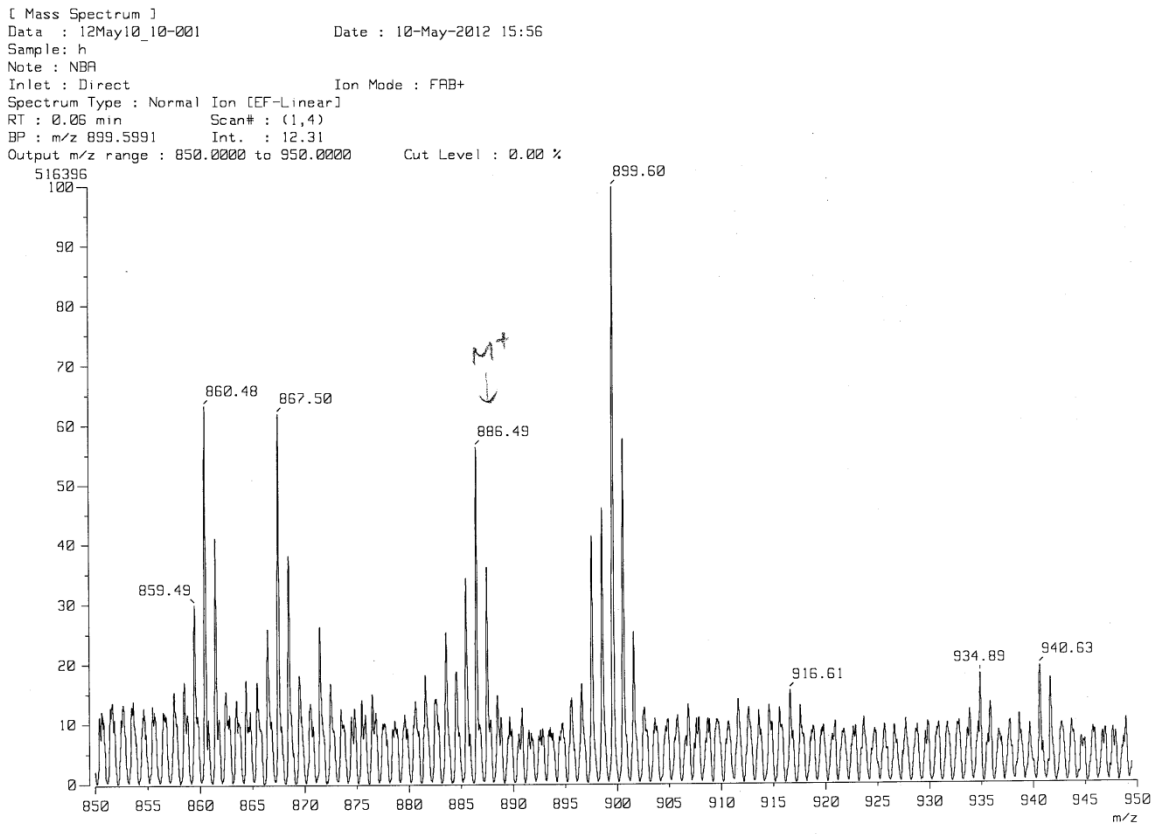
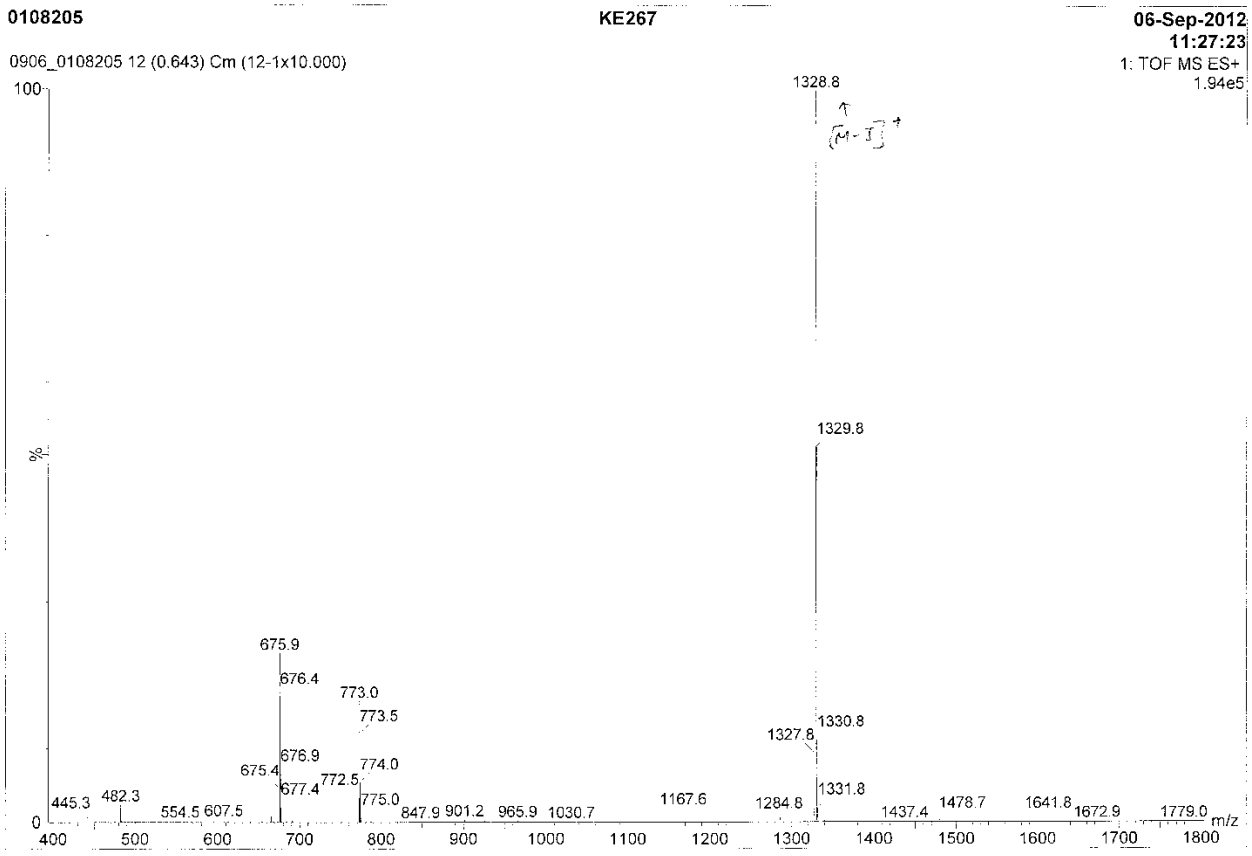


Figure S16. The HRMS (FAB) of 1-CN adduct.

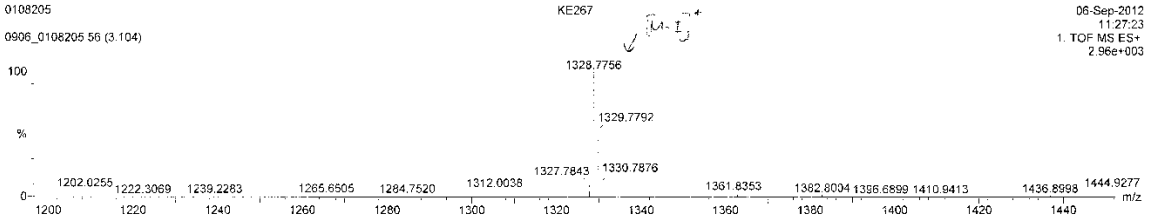


0108205 (HR ESI)

Elemental Composition Report **Page 1**

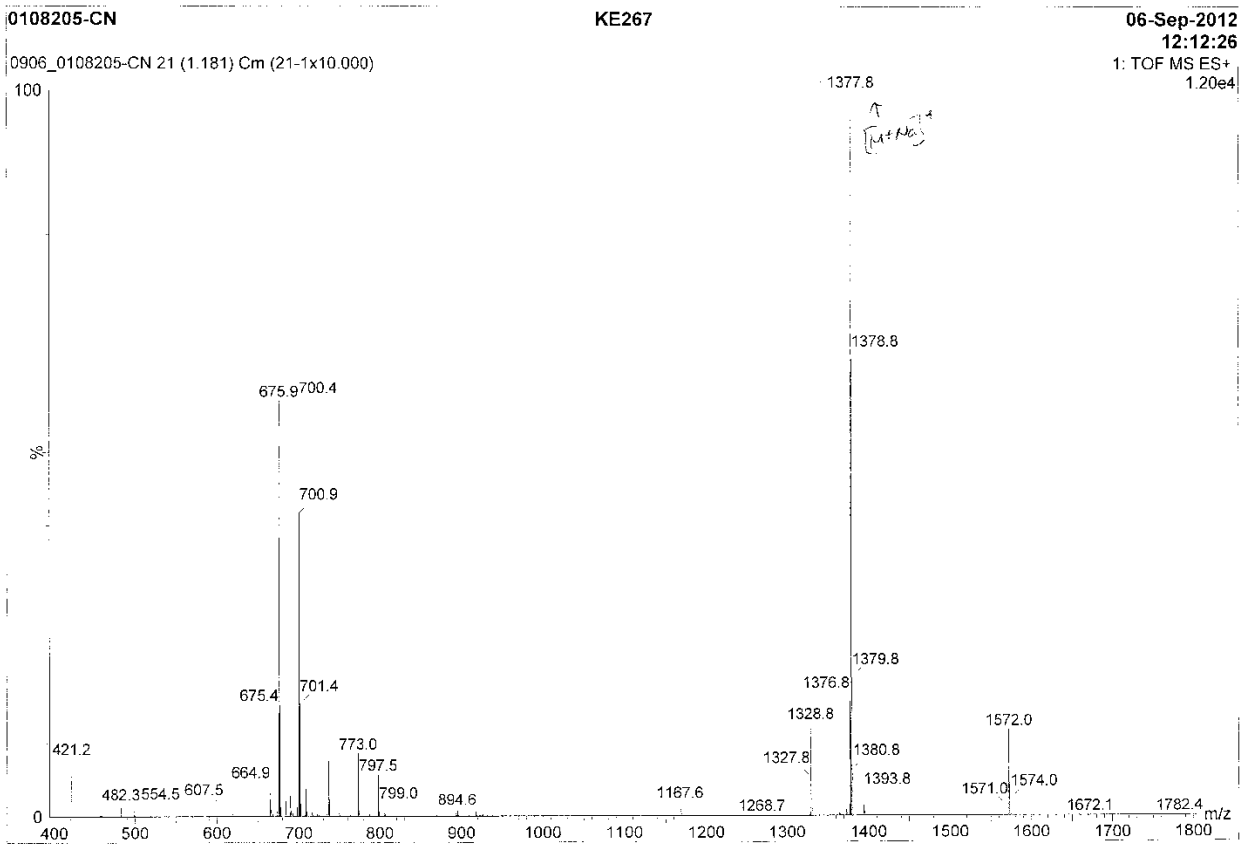
Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -100.0, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
27 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-400 H: 0-1000 B: 1-1 N: 3-3 O: 18-18 F: 2-2



Minimum:				-100.0			
Maximum:		5.0	20.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1328.7756	1328.7767	1.1	0.8	17.5	30.5	0.0	C70 H109 B N3 O18 F2

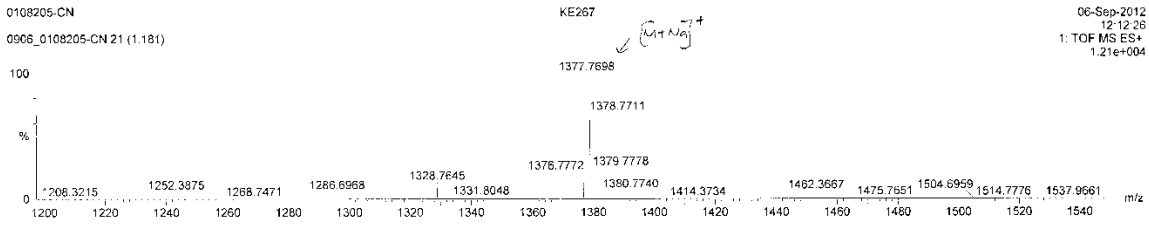
Figure S17. The LRMS(top) and HRMS(bottom) (ESI) of probe **2**.



Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -100.0, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
27 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-400 H: 0-1000 N: 4-4 O: 18-18 F: 2-2 B: 1-1 Na: 1-1



Minimum:				-100.0			
Maximum:		5.0	50.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1377.7698	1377.7696	0.2	0.1	18.5	47.0	0.0	C71 H109 N4 O18 F2 B Na

Figure S18. The LRMS(top) and HRMS(bottom) (ESI) of **2-CN**.

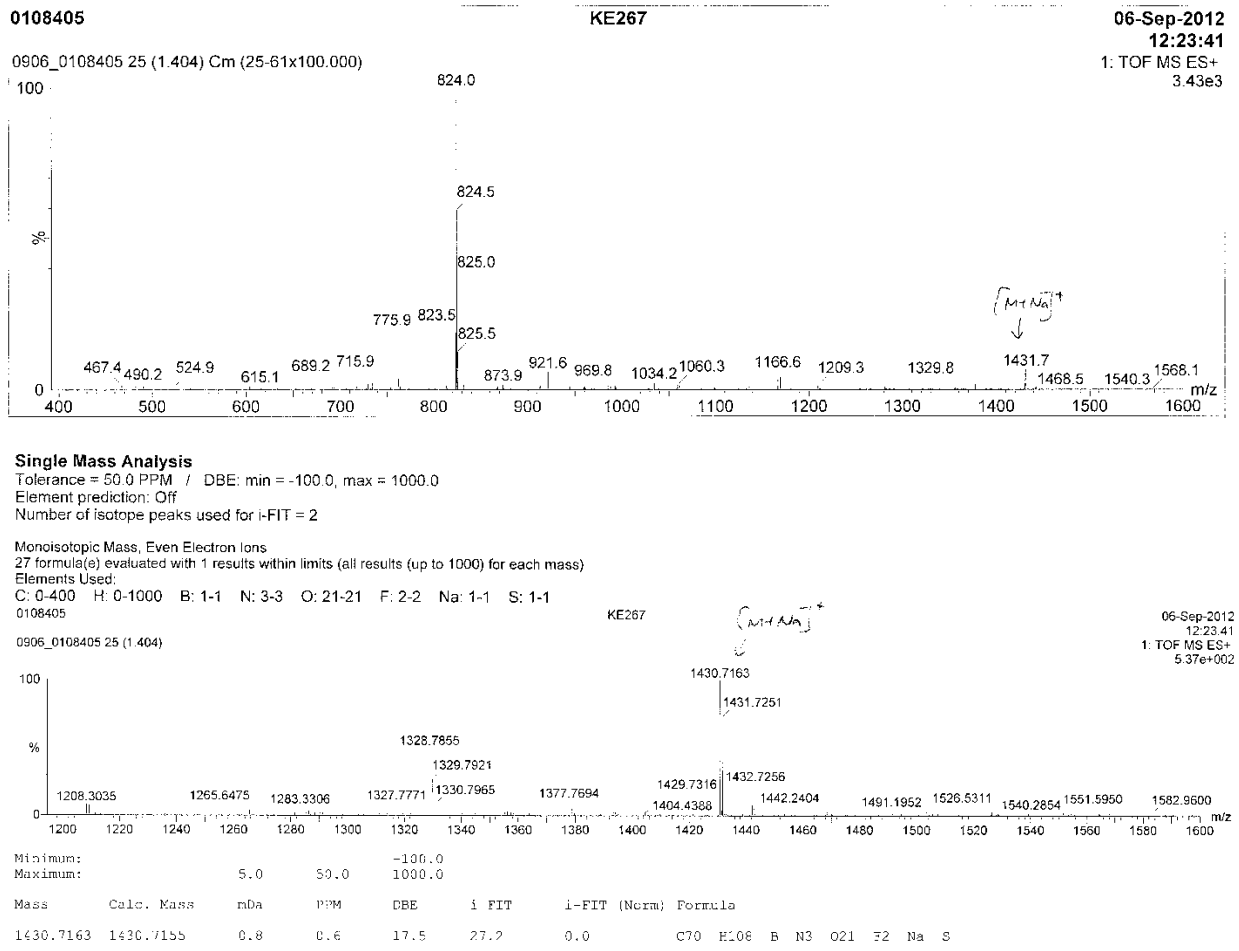
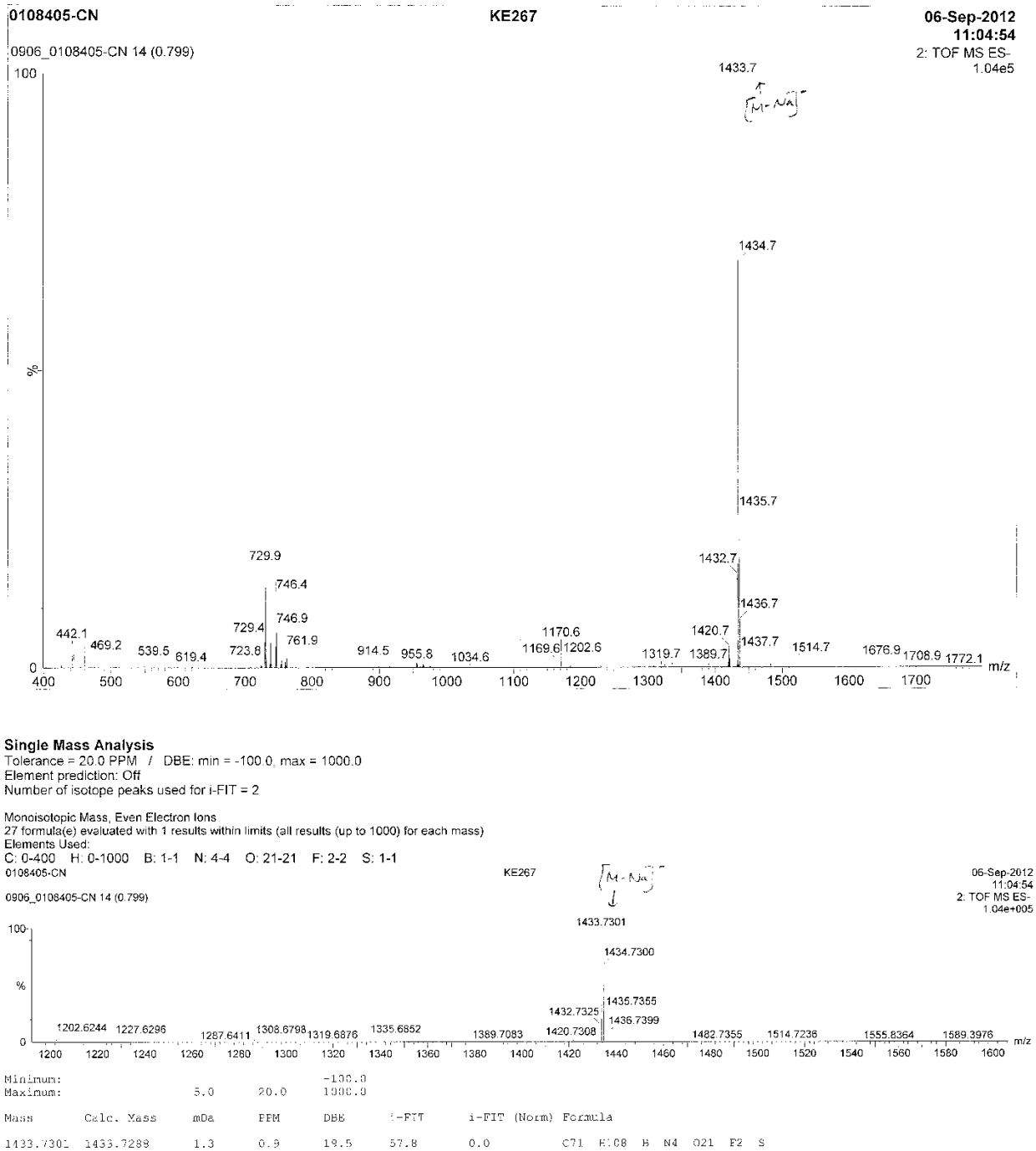


Figure S19. The LRMS(top) and HRMS(bottom) (ESI) of probe **3**.



Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -100.0, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
27 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-400 H: 0-1000 B: 1-1 N: 4-4 O: 21-21 F: 2-2 S: 1-1

Minimum:				-100.0			
Maximum:		5.0	20.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1433.7301	1433.7288	1.3	0.9	19.5	57.8	0.0	C71 H108 B N4 O21 F2 S

Figure S20. The LRMS(top) and HRMS(bottom) (ESI) of **3**-CN

Table S2. maximum absorption peaks, emission peaks and extinction coefficients of probe **1-3 and** their CN adducts

	Maximum Absorption (nm)	Maximum Emission (nm)	Extinction Coefficient ($\times 10^4$ M^{-1} cm^{-1})	Solvent
Probe 1	564	605	6.8	ACN-Tris buffer mix
1-CN	521	555	5.8	ACN-Tris buffer mix
Probe 2	558	596	3.7	Tris buffer
2-CN	522	559	2.3	Tris buffer
Probe 3	560	600	5.2	Tris buffer
3-CN	520	550	3.7	Tris buffer

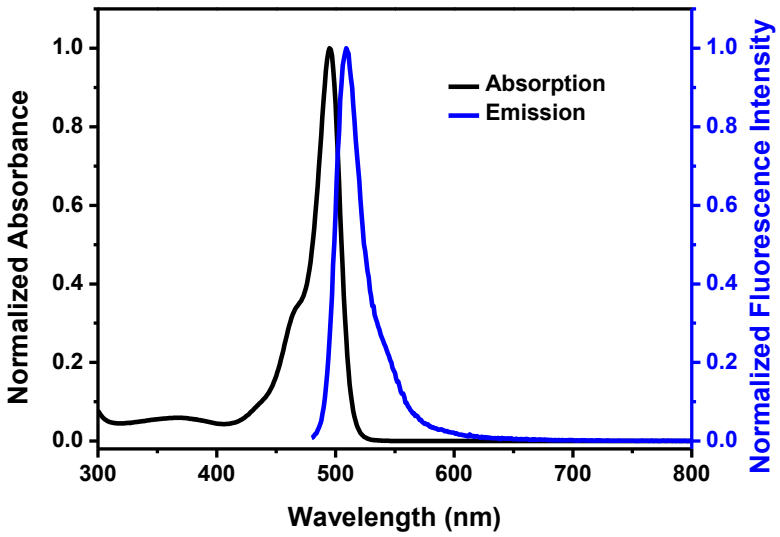


Figure S21. Normalized absorption and emission spectra of BODIPY dye **4a** in acetonitrile solution. (excitation wavelength = 470 nm)

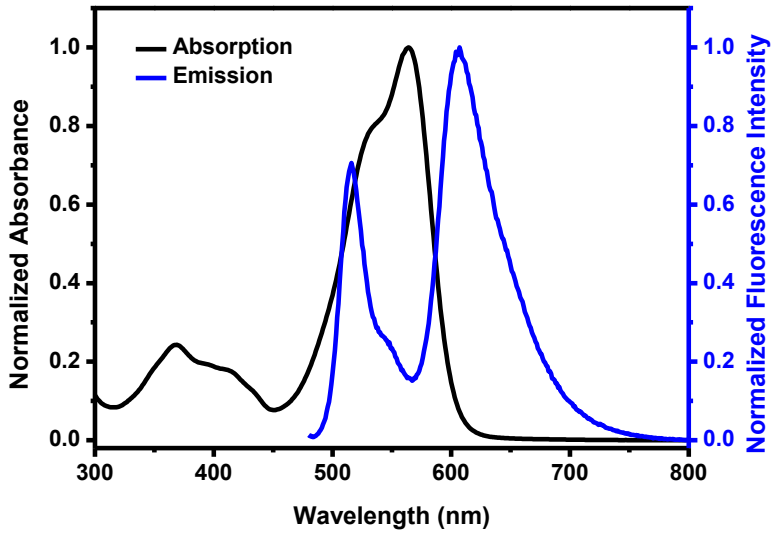


Figure S22. Normalized absorption and emission spectra of fluorescent probe **1** in acetonitrile solution.

(excitation wavelength = 470 nm)

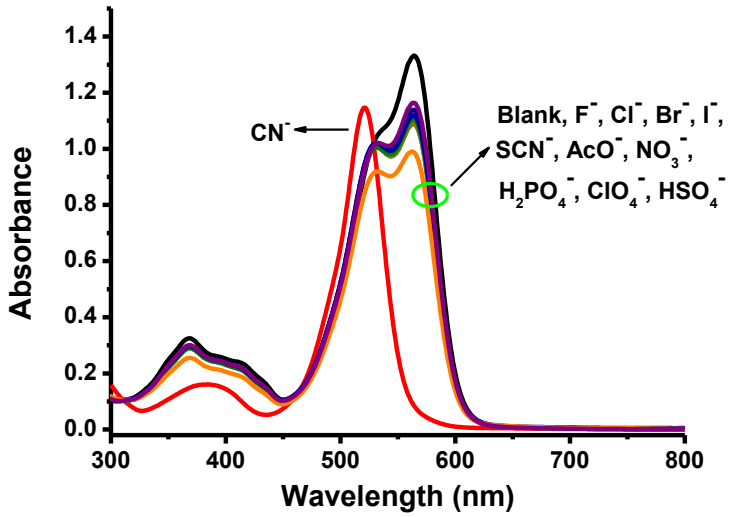


Figure S23. Absorption spectra of probe **1** in the presence of different anions (100 μM) in a mixed solution of CH_3CN and Tris • HCl buffer (10 mM, pH = 9.3) (9:1, v/v).

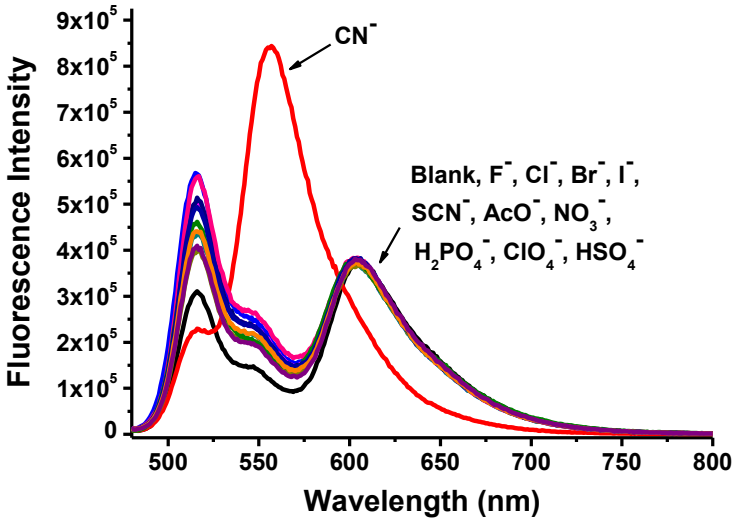


Figure S24. The fluorescent spectra of probe **1** to different anions (100 μM) in mixed solution of CH_3CN and Tris buffer (10 mM, pH = 9.3) (9:1, v/v).

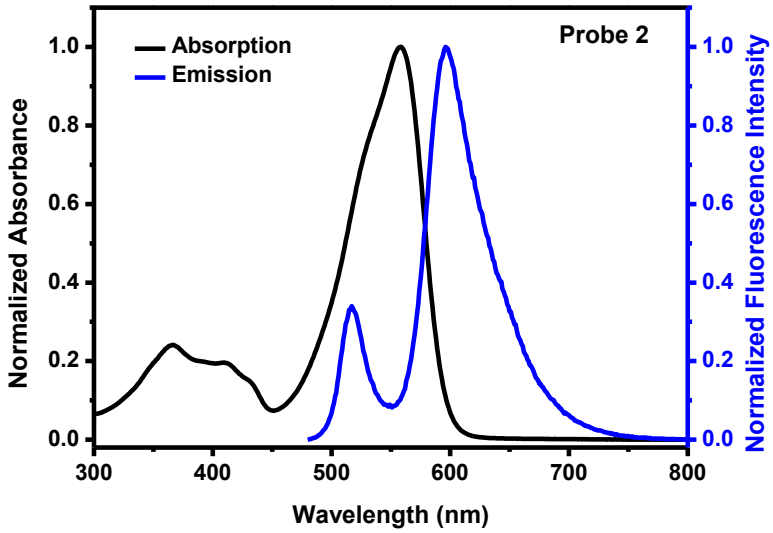


Figure S25. Normalized absorption and emission spectra of fluorescent probe **2** in Tris buffer solution (10 mM, pH 9.3)

(excitation wavelength = 470 nm)

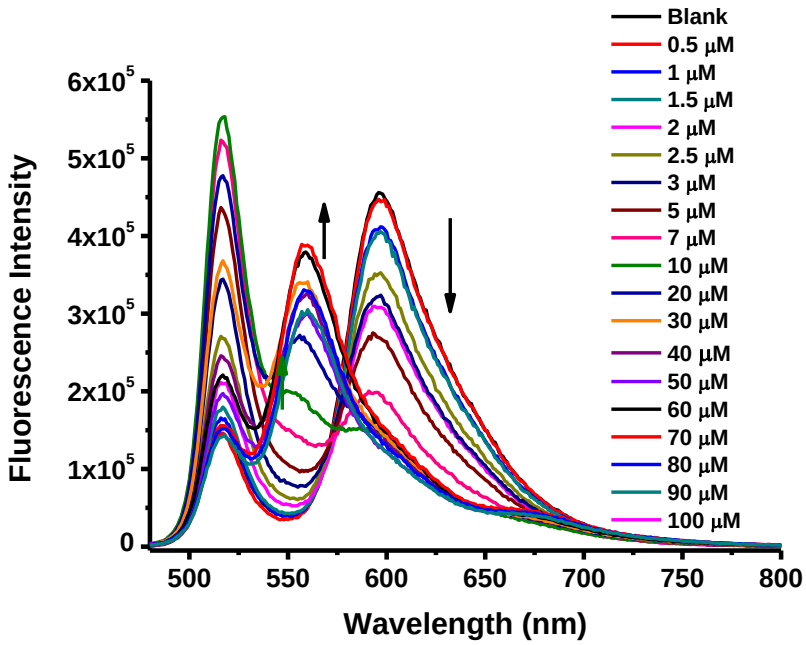


Figure S26. Fluorescence spectra of the fluorescent probe **2** (20 μM) in the absence and presence of different amounts of cyanide ion in Tris buffer (10 mM, pH 9.3) solution.

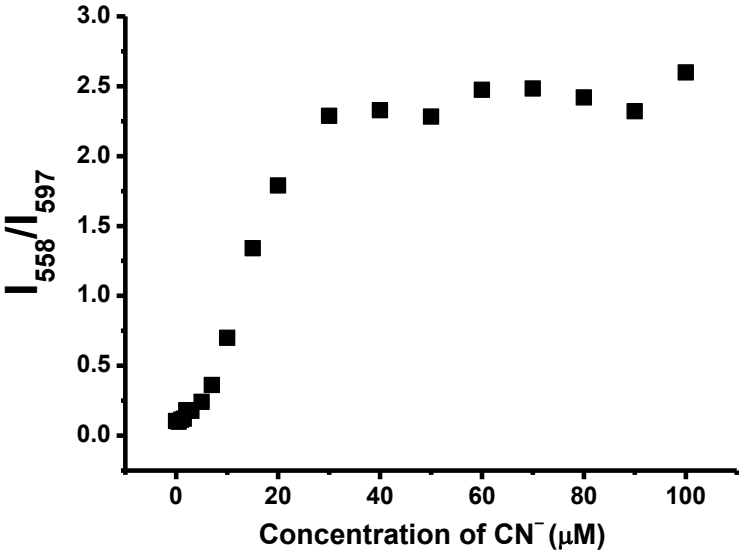


Figure S27. Fluorescent intensity ratio change at 558 nm and 597 nm (I_{558}/I_{597}) of the fluorescent probe **2** (20 μM) upon titration of cyanide ion (range 0-100 μM)in Tris buffer (10 mM, pH 9.3) solution.

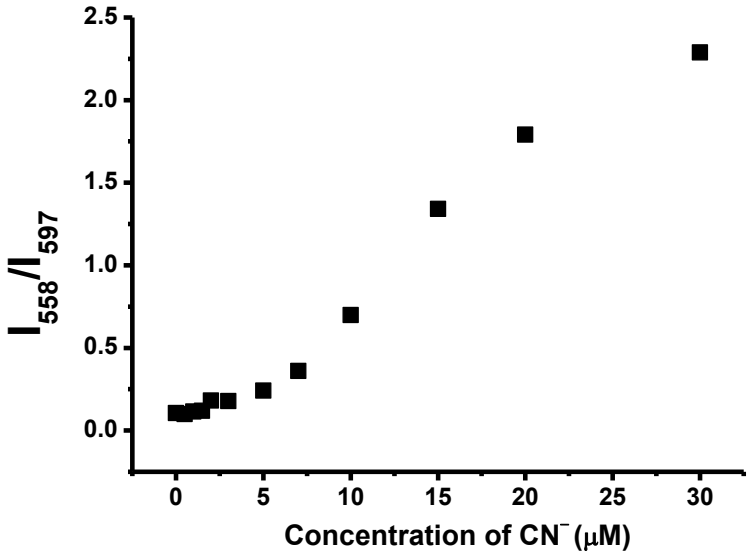


Figure S28. Fluorescent intensity ratio change at 558 nm and 597 nm (I_{558}/I_{597}) of the fluorescent probe **2** (20 μM) upon titration of cyanide ion (range 0-30 μM)in Tris buffer (10 mM, pH 9.3) solution.

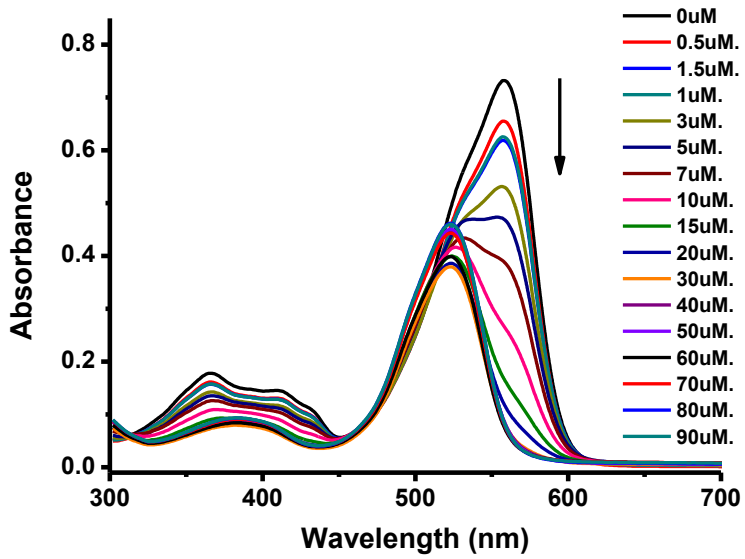


Figure S29. Absorption spectra of the probe **2** (20 μM) in the absence and presence of different amount of cyanide ion in Tris buffer (10 mM, pH 9.3) solution.

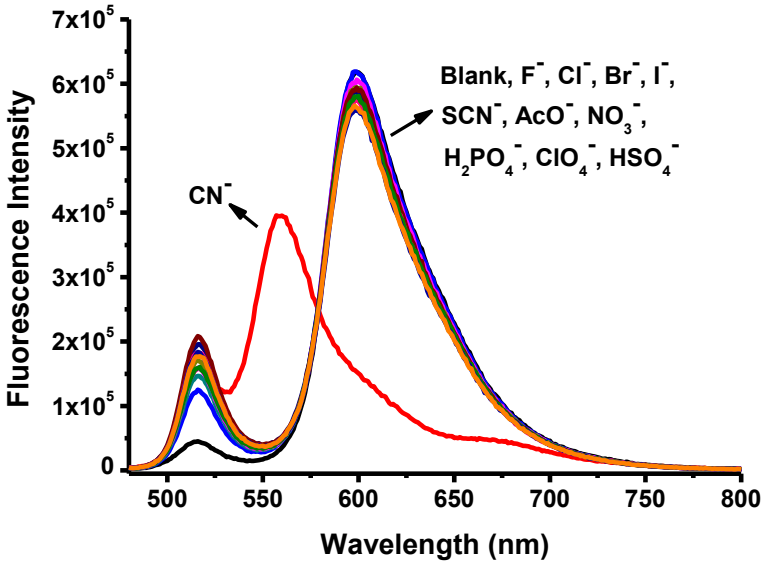


Figure S30. Emission spectra of probe **2** in the presence of different anions (100 μM) in Tris buffer (10 mM, pH 9.3) solution.

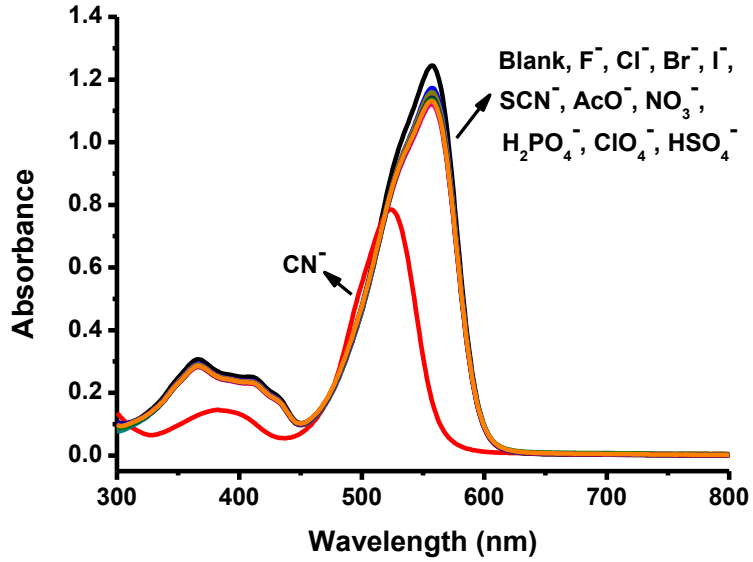


Figure S31. Absorption spectra of probe **2** in the presence of different anions (100 μM) in Tris buffer (10 mM, pH 9.3) solution.

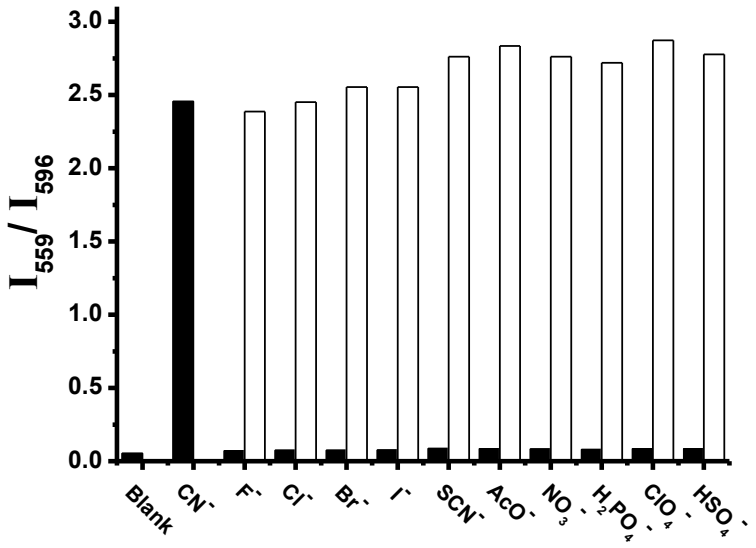


Figure S32. The fluorescent ratiometric responses of probe **2** to different anions (100 μM) in Tris buffer solution (10 mM, pH 9.3) in the presence and presence of 70 μM cyanide ion. Black bars show the fluorescent responses of the probe **2** to different anions while white bars display the fluorescent responses of the probe to different anions in the presence of cyanide ion.

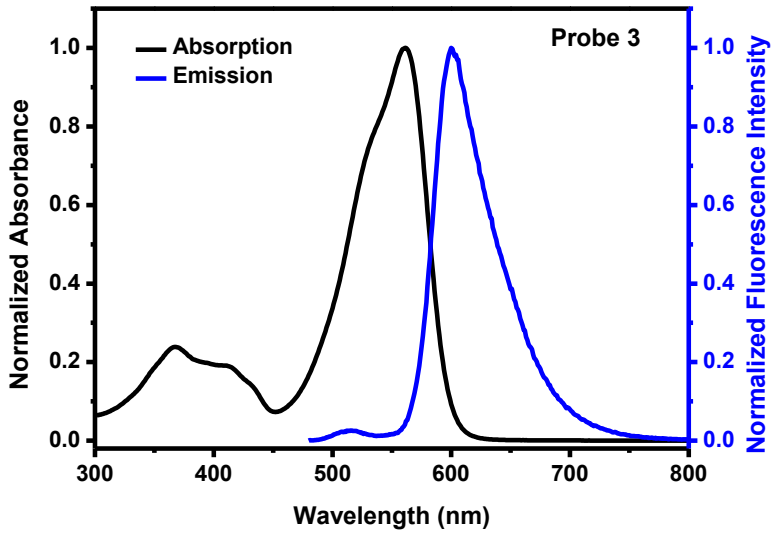


Figure S33. Normalized absorption and emission spectra of fluorescent probe **3** in Tris buffer solution (10 mM, pH 9.3)

(excitation wavelength = 470 nm)

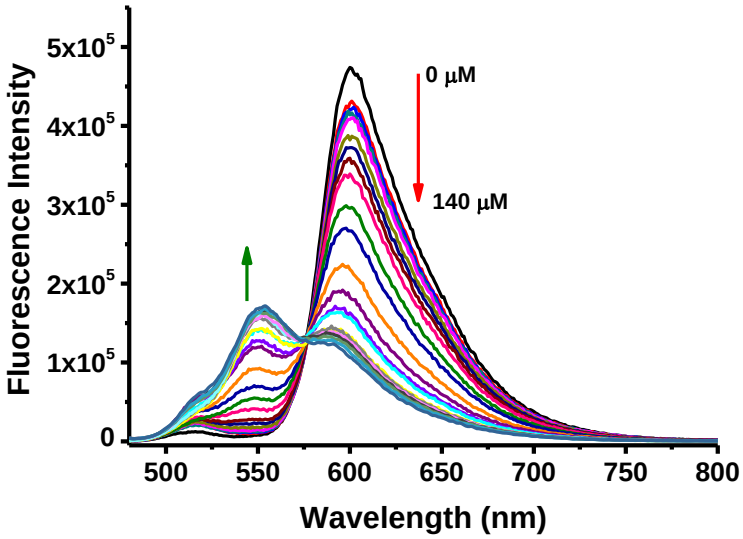


Figure S34. Fluorescence spectra of the fluorescent probe **3** (20 μM) in the absence and presence of different amounts of cyanide ion in Tris buffer (10 mM, pH 9.3) solution.

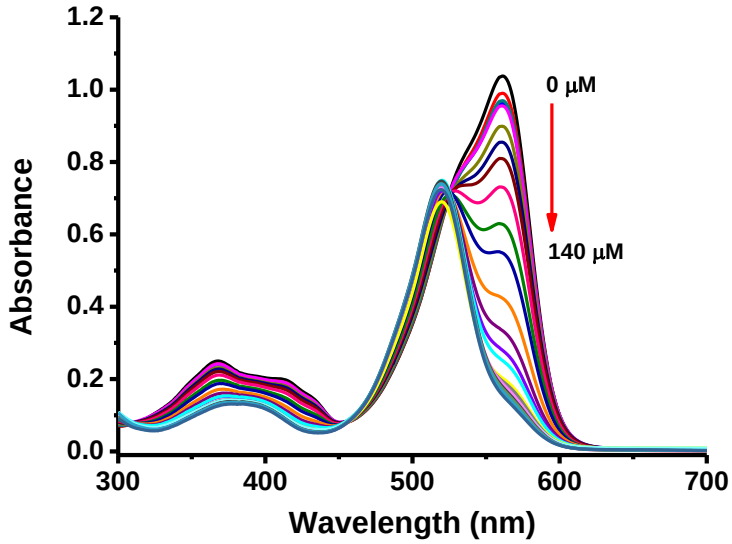


Figure S35. Absorption spectra of the probe **3** (20 μM) in the absence and presence of different amount of cyanide ion Tris buffer (10 mM, pH 9.3) solution.

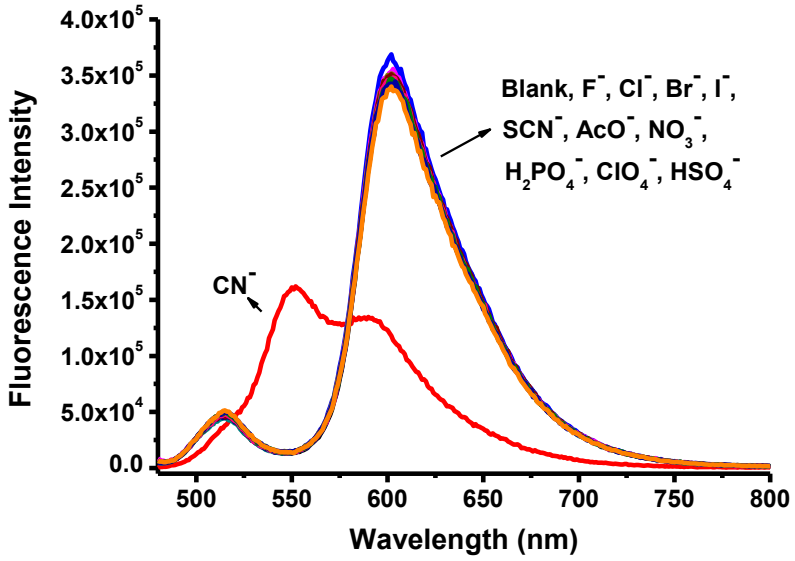


Figure S36. Emission spectra of probe **3** in the presence of different anions (100 μM) in Tris buffer (10 mM, pH 9.3) solution.

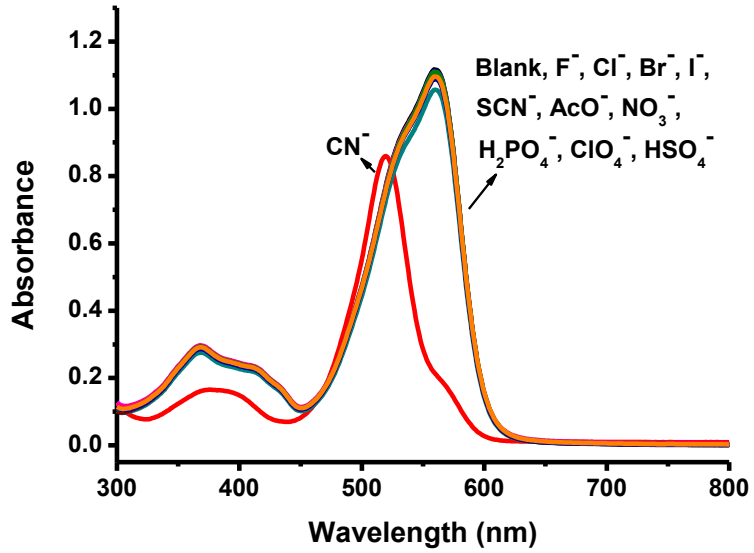


Figure S37. Absorption spectra of probe **3** in the presence of different anions (100 μM) in Tris buffer (10 mM, pH 9.3) solution.

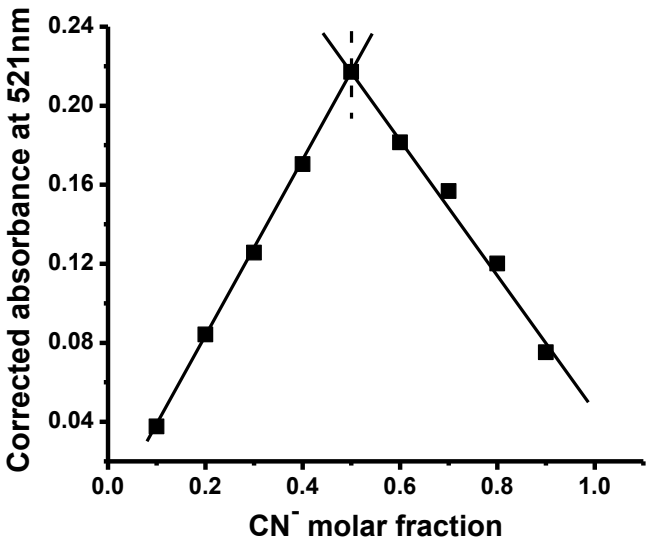


Figure S38 Job's plot of probe **1** with cyanide ion in mixed solution of CH_3CN and Tris buffer (10 mM pH = 9.3, 9 : 1, v/v). Total concentration of probe **1** and cyanide ion is 50 μM.

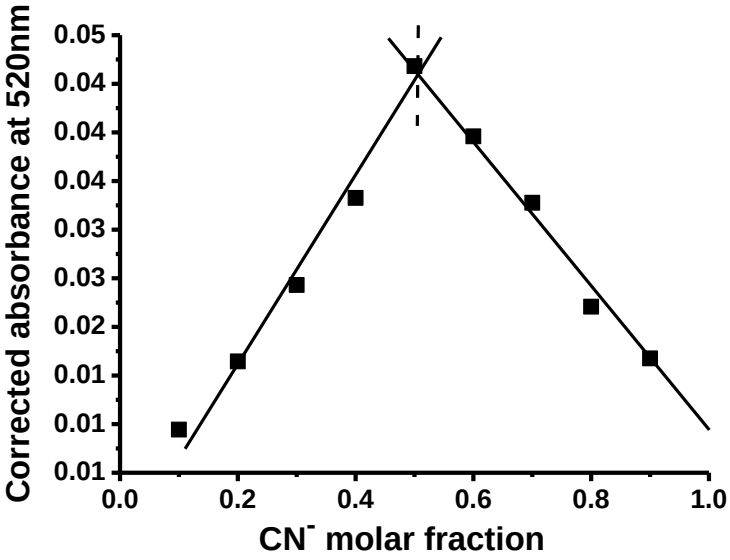


Figure S39 Job's plot of probe **3** with cyanide ion Tris buffer (10 mM pH = 9.3). Total concentration of probe **3** and cyanide ion is 50 μM.

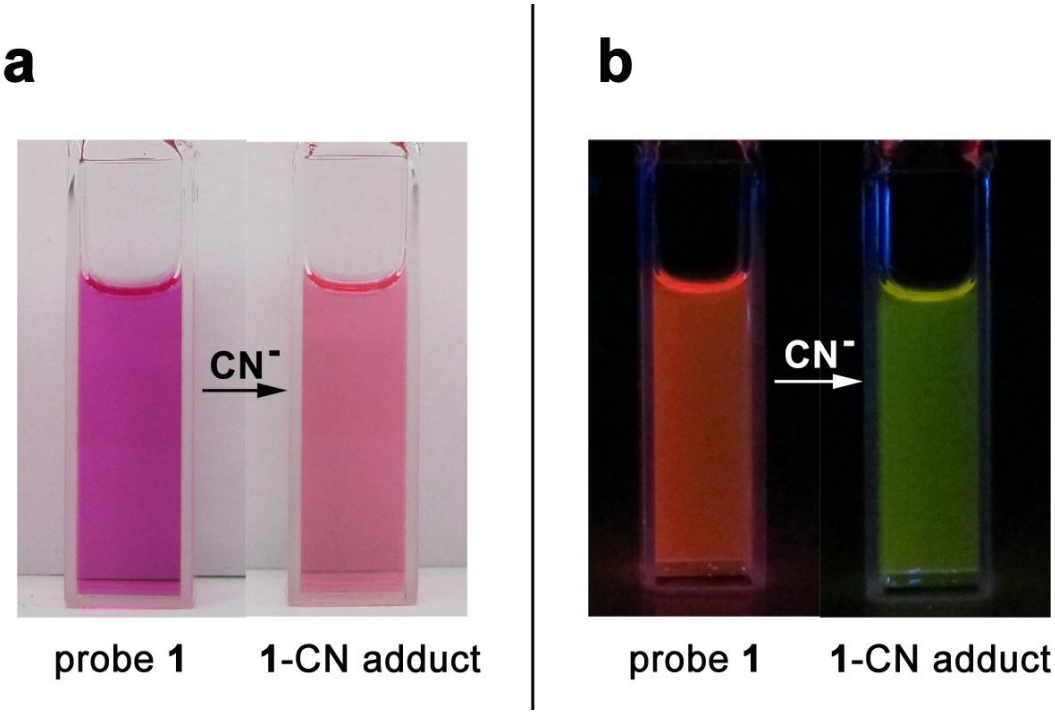


Figure S40. Comparison of visible color (**a**) and luminescence color (**b**) of probe **1** in absence and presence of cyanide ion.