Electronic Supplementary Information

Bio-inspired AIE pillar[5]arene probe with multiple binding sites to discriminate alkanediamines

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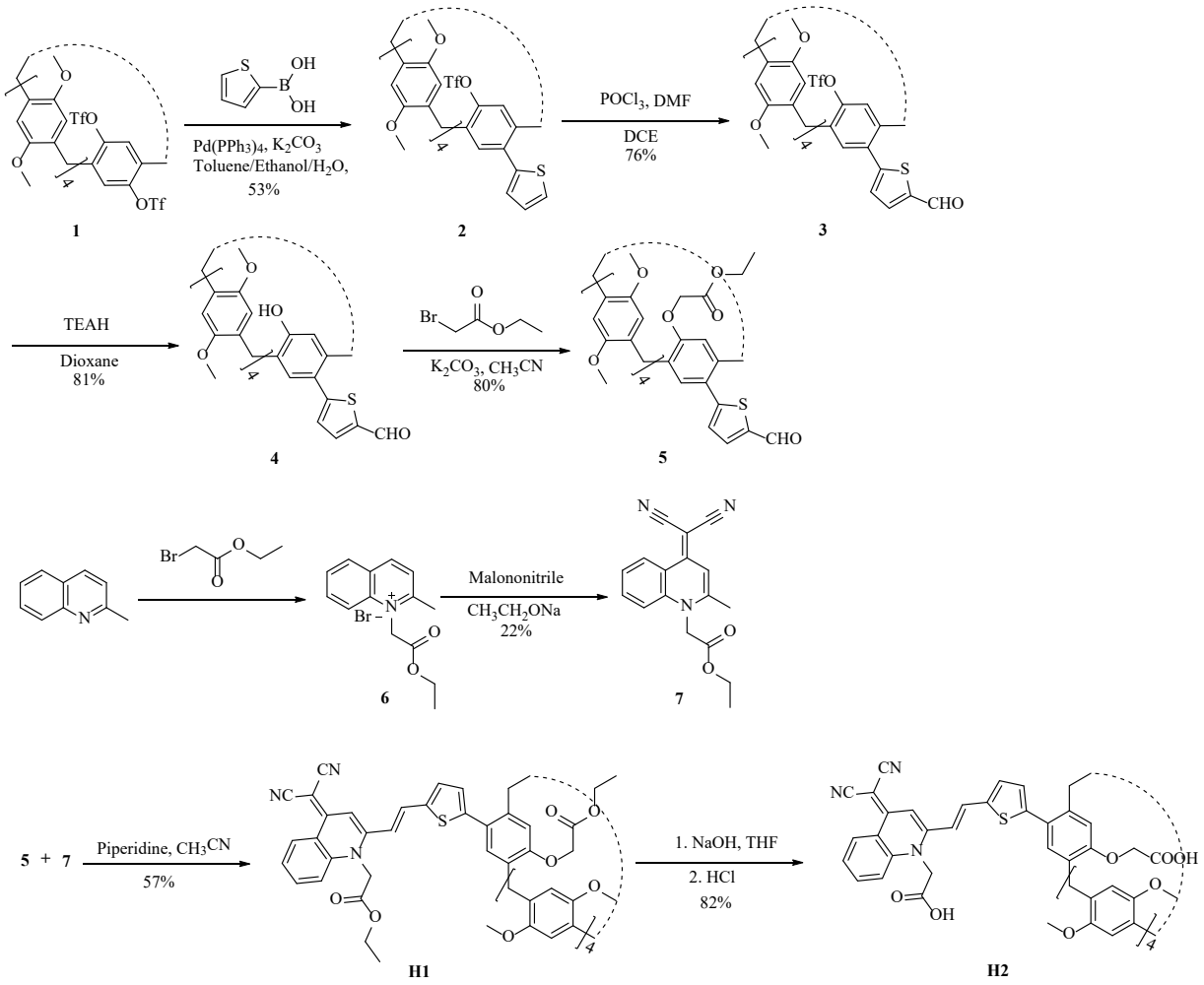
1. Experimental

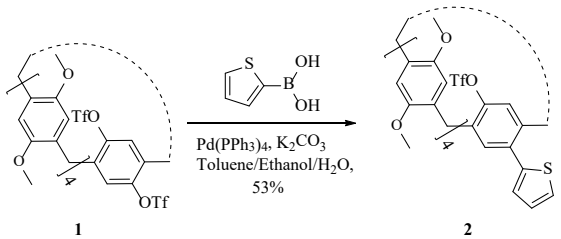
Measurements and Materials

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on Bruker DRX 400 NMR or Bruker DRX 500 NMR spectrometer using $CDCl_3$ as a solvent and trimethylsilane as a reference. High resolution mass spectrometry (HRMS) was determined using a Bruker maXis impact instrument. Fluorescence spectra were mesured on a Hitachi F-4500 fluorescence spectrophotometer. UV–Vis absorption were recorded on a Helios Alpha UV-vis scanning spectraphotometer. Single-crystal X-ray diffraction experiments were conducted using a Bruker SMART II CCD area detector. The binding constants (*K*) and relative fluorescence quantum yield (Φ) were calculated by non-linear fitting of the binding isotherm with a 1:1 binding model using software *Scientist 3* (Micromath, USA) according to the procedure we reported before[1]. Geometry optimizations of five complexes (H2⊃G6, H2⊃G8, H2⊃G10, H2⊃G12, and H1⊃G8) were performed using B3LYP/6–31G(d, p) method[2-3]. Compound 1 was prepared according to the reported procedures[4]. All solvents were obtained from commercial resources or dried according to the standard procedure. Other materials were purchased from Aladdin, J&K and were used for synthesis without further purification.

Syntheses and Characterization

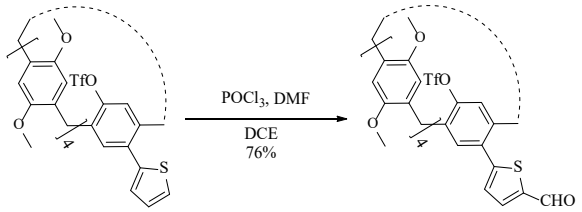


Scheme S1. Synthetic routes of **H1** and **H2.**



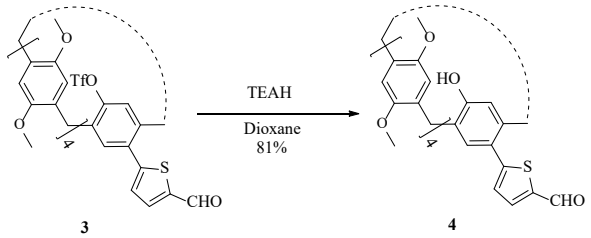
Compound 1 (986 mg, 1 mmol), 2-thiopheneboronic acid (167 mg, 1,3 mmol), K_2CO_3 (483 mg, 3.5 mmol) and $Pd(PPh_3)_4$ (50 mg, 0.32 mmol) were dissolved in toluene/ethanol/H_2O (25 mL/5 mL/2 mL) mixture. The mixture was stirred at 90 °C under N_2 atmosphere for 24 h. After cooling, the mixture was extracted with dichloromethane for three times. The combined organic layers were concentrated under reduced pressure and purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1, v/v) as the eluent to afford pure compound 2 as a white solid (53% yield, 488 mg). M.p. 183–185 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.32–7.30 (m, 2H), 7.22

(s, 1H), 7.07–7.05 (m, 1H), 6.91–6.90 (m, 1H), 6.78 (s, 1H), 6.76 (s, 1H), 6.76 (s, 1H), 6.74 (s, 1H), 6.73 (s, 1H), 6.68 (s, 1H), 6.67 (s, 1H), 6.03 (s, 1H), 3.95 (s, 2H), 3.85 (s, 2H), 3.82 (s, 2H), 3.81 (s, 2H), 3.74 (s, 2H), 3.72 (s, 3H), 3.67 (s, 3H), 3.66 (s, 3H), 3.63 (s, 3H), 3.62 (s, 3H), 3.56 (s, 3H), 3.53 (s, 3H), 3.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 150.99, 150.95, 150.85, 150.73, 150.70, 150.65, 150.25, 147.91, 141.84, 140.64, 134.99, 133.05, 130.58, 129.48, 128.81, 128.48, 128.31, 128.27, 127.86, 127.10, 126.91, 126.70, 125.61, 124.91, 122.70, 118.62 (d, J_{CF} = 318.8 Hz), 114.48, 114.18, 114.08, 114.02, 114.00, 113.75, 113.49, 113.21, 55.94, 55.83, 55.75, 55.72, 55.69, 55.49, 55.22, 55.19, 32.59, 31.36, 29.98, 29.46, 29.38. HRMS (m/z): calcd. for $[M+Na]^+$ $C_{48}H_{47}F_3NaO_{11}S_2$: 943.2410; found 943.2404.



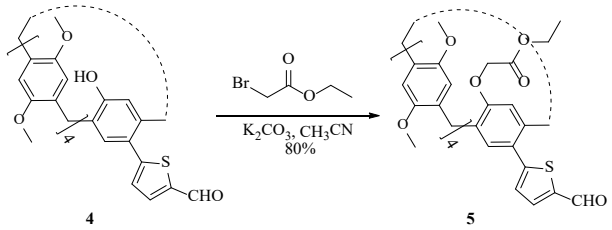
2 3

Compound 2 (461 mg, 0.5 mmol) and 1 mL *N,N*-dimethylformamide were dissolved in 10 mL dichloroethane. 1 mL $POCl_3$ was added under ice bath conditions and stirred for 40 min, then the mixture was stirred at 85 °C under N_2 atmosphere for 48 h. After the reaction was completed, saturated K_2CO_3 solution was added until no bubbles were formed. The mixture was extracted with dichloromethane for three times. The combined organic layers were concentrated under reduced pressure and purified by silica gel chromatography using petroleum ether/ethyl acetate/ dichloromethane (25:4:1, v/v) as the eluent to afford pure compound 3 as a white solid (76% yield, 360 mg). M.p. 144–146 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.87 (s, 1H), 7.64 (d, J = 3.8 Hz, 1H), 7.21 (s, 1H), 7.21 (s, 1H), 6.90 (d, J = 3.8 Hz, 1H), 6.75 (s, 1H), 6.74 (s, 1H), 6.71 (s, 1H), 6.71 (s, 1H), 6.70 (s, 1H), 6.66 (s, 1H), 6.61 (s, 1H), 5.98 (s, 1H), 3.87 (s, 2H), 3.81 (s, 2H), 3.78 (s, 2H), 3.77 (s, 2H), 3.69 (s, 5H), 3.65 (s, 3H), 3.63 (s, 3H), 3.62 (s, 3H), 3.58 (s, 3H), 3.54 (s, 3H), 3.45 (s, 3H), 3.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 182.77, 152.23, 150.88, 150.84, 150.79, 150.66, 150.64, 150.60, 150.19, 148.55, 143.58, 140.55, 136.64, 134.51, 131.71, 131.05, 129.60, 129.18, 128.50, 128.42, 128.28, 128.06, 127.61, 126.00, 124.38, 123.08, 118.56 (d, J_{CF} = 318.3 Hz), 114.27, 113.99, 113.94, 113.85, 113.65, 113.38, 112.98, 55.89, 55.79, 55.68, 55.64, 55.48, 55.17, 55.08, 32.76, 31.34, 29.87, 29.30, 29.24. HRMS (m/z): calcd. for $[M+Na]^+$ $C_{49}H_{47}F_3NaO_{12}S_2$: 971.2359; found 971.2353.

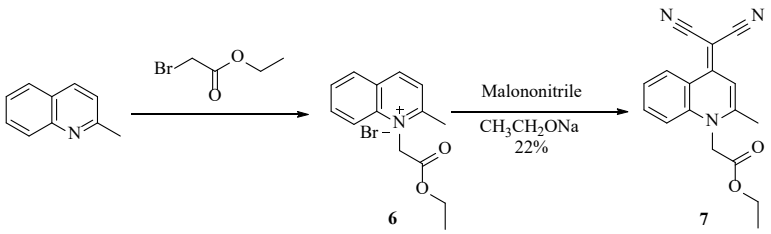


3 4

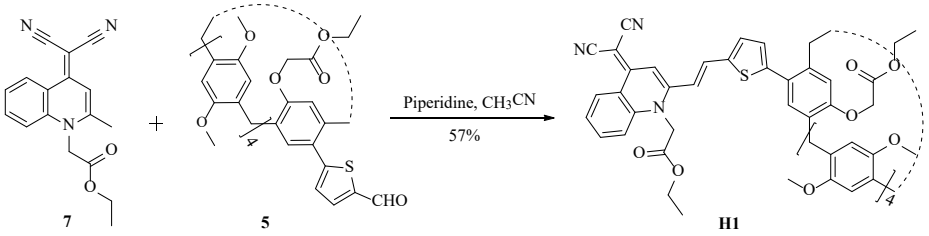
Compound 3 (100 mg, 0.11 mmol) and tetraethyl ammonium hydroxide (124 mg, 0.22 mmol) were dissolved in 3 mL 1,4-dioxane. The mixture was reacted at 60 °C for half an hour and then transferred to room temperature for 3 hours. After the reaction was completed, the mixture was extracted with dichloromethane for three times. The combined organic layers were concentrated under reduced pressure and purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1, v/v) as the eluent to afford pure compound 4 as a pale yellow solid (81% yield, 70 mg). M.p. 119–121 °C. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.90 (s, 1H), 7.74 (d, *J* = 3.8 Hz, 1H), 7.40 (s, 1H), 7.13 (s, 1H), 7.11 (d, *J* = 3.8 Hz, 1H), 6.99 (s, 1H), 6.81 (s, 1H), 6.79 (s, 1H), 6.76 (s, 1H), 6.68 (s, 1H), 6.66 (s, 1H), 6.57 (s, 1H), 6.44 (s, 1H), 6.43 (s, 1H), 3.88–3.88 (m, 5H), 3.80 (s, 2H), 3.78 (s, 2H), 3.77 (s, 4H), 3.75 (s, 3H), 3.68 (s, 3H), 3.67 (s, 3H), 3.66 (s, 3H), 3.65 (s, 3H), 3.59 (s, 3H), 3.16 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 182.84, 155.18, 155.12, 151.91, 151.09, 150.91, 150.74, 150.68, 150.64, 150.60, 147.97, 142.32, 139.94, 136.81, 131.94, 129.74, 128.98, 128.12, 128.10, 127.97, 127.82, 127.64, 127.58, 125.36, 125.18, 124.65, 118.40, 114.57, 114.39, 114.29, 113.94, 113.86, 113.60, 113.34, 112.87, 56.38, 56.03, 55.93, 55.77, 55.76, 55.70, 55.56, 55.17, 32.59, 30.34, 30.22, 29.69, 28.97. HRMS (m/z): calcd. for $[M+Na]^+$ $C_{48}H_{48}NaO_{10}S$: 839.2866; found 839.2860.



Compound 4 (600 mg, 0.74 mmol), ethyl bromoacetate (247 mg, 1.48 mmol) and K_2CO_3 (413 mg, 3 mmol) were dissolved in 15 mL acetonitrile. The mixture was stirred at 80 °C for 24 h. After cooling, the mixture was extracted with dichloromethane for three times. The combined organic layers were concentrated under reduced pressure and purified by silica gel chromatography using petroleum ether/ethyl acetate (3:1 v/v) as the eluent to afford pure compound 5 as a pale yellow solid (80% yield, 530 mg). M.p. 185–187 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.92 (s, 1H), 7.78 (d, *J* = 3.8 Hz, 1H), 7.34 (s, 1H), 7.11 (d, *J* = 3.8 Hz, 1H), 6.92 (s, 1H), 6.87 (s, 1H), 6.86 (s, 1H), 6.82–6.81 (m, 3H), 6.77 (s, 1H), 6.66 (s, 1H), 6.06 (s, 1H), 4.53 (s, 2H), 3.86 (s, 2H), 3.80–3.78 (m, 10H), 3.73–3.70 (m, 18H), 3.62 (s, 3H), 3.50 (s, 3H), -1.70 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 182.91, 168.23, 156.59, 154.83, 151.52, 150.69, 150.61, 150.40, 150.32, 149.99, 149.75, 149.30, 142.84, 139.90, 137.13, 133.48, 128.94, 128.57, 128.43, 128.29, 128.04, 128.02, 127.31, 126.84, 126.22, 123.20, 115.31, 113.99, 113.94, 113.77, 113.19, 112.99, 112.55, 112.46, 111.73, 64.14, 60.68, 55.92, 55.82, 55.70, 55.55, 55.23, 55.08, 32.06, 31.03, 30.19, 28.85, 28.58, 10.39. HRMS (m/z): calcd. for $[M+Na]^+$ $C_{52}H_{54}NaO_{12}S$: 925.3234; found 925.3228.

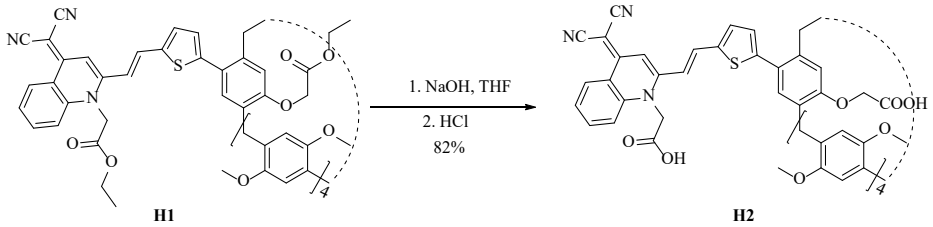


2-Methylquinoline (2.86g, 20 mmol) and ethyl bromoacetate (5 g, 30 mmol) were added in 25 mL round-bottomed flask, and stirred at 110 °C under N_2 atmosphere for 3 h. A large amount of solid precipitated after the reaction was over. Methanol was poured to dissolve the solid and recrystallized in ethyl acetate to obtain the crude product 6. The crude product 6 was put into the next step without further purification. Compound 6 (6 g, 30 mmol), malononitrile (4 g, 60 mmol), sodium ethoxide (4 g, 60 mmol) were dissolved in 35 mL ethanol. The mixture was stirred at room temperature for 16 h. After the reaction was completed, the mixture was extracted with dichloromethane for three times. The combined organic layers were concentrated under reduced pressure and purified by silica gel chromatography using petroleum ether/ethyl acetate (1:1, v/v) as the eluent to afford pure compound 7 as a yellowish green solid (22% yield, 1.3 g). M.p. 151–153 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ) 9.03 (d, J = 8.4 Hz, 1H), 7.73–7.69 (m, 1H), 7.44–7.40 (m, 1H), 7.33 (d, J = 8.8 Hz, 1H), 6.80 (s, 1H), 4.94 (s, 2H), 4.30 (q, J = 7.1 Hz, 2H), 2.52 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.64, 153.86, 147.75, 138.86, 133.45, 126.84, 124.82, 120.99, 119.50, 118.28, 115.29, 109.58, 62.83, 52.78, 49.24, 21.73, 14.07. HRMS (m/z): calcd. for $[M+H]^+$ $C_{17}H_{16}N_2O_2$: 294.1243; found 294.1237.



Compound 5 (300 mg, 0.26 mmol), compound 7 (70 mg, 0.24 mmol) and piperidine 0.3 mL were dissolved in 7 mL acetonitrile. The mixture was stirred at 80 °C under N_2 atmosphere for 24 h. After cooling, 50 mL methanol was added and large amounts of solids were precipitated. The crude product was obtained after reduced pressure filtration. Then, the crude product washed with methanol for three times (3 × 30 mL) to give pure H1 as a red solid (57% yield, 161 mg). M.p. 255–257 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.14–9.12 (m, 1H), 7.76–7.72 (m, 1H), 7.50–7.46 (m, 2H), 7.33–7.32 (m, 2H), 7.30 (d, J = 3.6 Hz, 1H), 7.17 (s, 1H), 6.96 (d, J = 3.6 Hz, 1H), 6.92 (s, 1H), 6.89 (s, 1H), 6.87 (s, 1H), 6.82 (s, 3H), 6.76 (s, 1H), 6.69 (d, J = 15.4 Hz, 1H), 6.62 (s, 1H), 6.17 (s, 1H), 4.96 (s, 2H), 4.51 (s, 2H), 4.36 (q, J = 7.1 Hz, 2H), 3.92 (s, 2H), 3.81–3.78 (m, 10H), 3.73–3.70 (m, 18H), 3.61 (s, 3H), 3.55 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H), -1.67 (t, J = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 168.24, 167.03, 156.17, 153.58, 151.47, 150.69, 150.62, 150.34, 150.33, 149.93, 149.80, 149.38, 148.08, 147.55, 139.94, 139.09, 138.86, 133.57, 133.51, 133.45,

131.01, 128.93, 128.85, 128.51, 128.38, 128.27, 128.18, 127.91, 127.28, 126.69, 126.63, 126.43, 124.82, 123.47, 121.05, 119.53, 118.53, 116.84, 115.58, 115.30, 114.05, 113.96, 113.88, 113.40, 112.91, 112.72, 112.42, 111.58, 107.27, 64.01, 62.76, 60.60, 55.97, 55.79, 55.75, 55.71, 55.62, 55.47, 55.26, 55.04, 53.33, 50.68, 32.17, 31.08, 30.21, 28.83, 28.52, 14.10, 10.46. HRMS (m/z): calcd. for $[M+Na]^+$ $C_{69}H_{67}N_3NaO_{13}S$: 1200.4292; found 1200.4287.



H1 **H2**

H1 (190 mg, 0.16 mmol) and NaOH (66 mg, 1.64 mmol) were dissolved in THF/H_2O (25 mL/5 mL) mixture. The mixture was stirred at 73 ºC for 12 h. After cooling, the mixture was concentrated under reduced pressure to remove THF and then 2 M HCl was added until no more solids precipitated. The crude product was obtained after reduced pressure filtration and purified by silica gel chromatography using ethyl acetate/ methanol (2:1, v/v) as the eluent to afford pure H2 as a red solid (82% yield, 148 mg). M.p. 176–178 ºC. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.07 (d, *J* = 8.3 Hz, 1H), 7.75–7.72 (m, 1H), 7.52–7.39 (m, 4H), 7.27 (s, 1H), 7.15 (s, 1H), 6.99–6.99 (m, 1H), 6.84 (s, 1H), 6.78 (s, 1H), 6.76 (s, 1H), 6.69–6.59 (m, 5H), 6.55 (s, 1H), 6.15 (s, 1H), 4.95 (s, 2H), 4.43 (s, 2H), 3.93 (s, 2H), 3.84 (s, 2H), 3.77 (s, 2H), 3.76 (s, 2H), 3.74–3.73 (m, 5H), 3.68 (s, 3H), 3.67 (s, 3H), 3.63 (s, 3H), 3.58 (s, 3H), 3.48–3.45 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 170.38, 169.04, 154.84, 153.61, 151.40, 150.99, 150.85, 150.84, 150.78, 150.64, 150.46, 150.19, 148.14, 147.02, 139.52, 139.39, 138.86, 133.53, 133.12, 131.56, 128.85, 128.78, 128.32, 128.23, 128.11, 127.78, 127.72, 127.52, 127.18, 126.44, 125.75, 124.92, 120.99, 119.75, 118.74, 116.86, 115.94, 115.44, 114.99, 114.58, 114.40, 114.30, 114.09, 113.91, 113.61, 113.52, 106.96, 64.87, 57.02, 56.52, 56.24, 56.17, 55.97, 55.81, 55.48, 52.02, 50.64, 32.72, 30.14, 29.88, 29.64, 29.45. HRMS (m/z): calcd. for $[M+Na]^+$ $C_{65}H_{59}N_3NaO_{13}S$: 1144.3666; found 1144.3661.

2. NMR and HRMS Spectra of Compounds

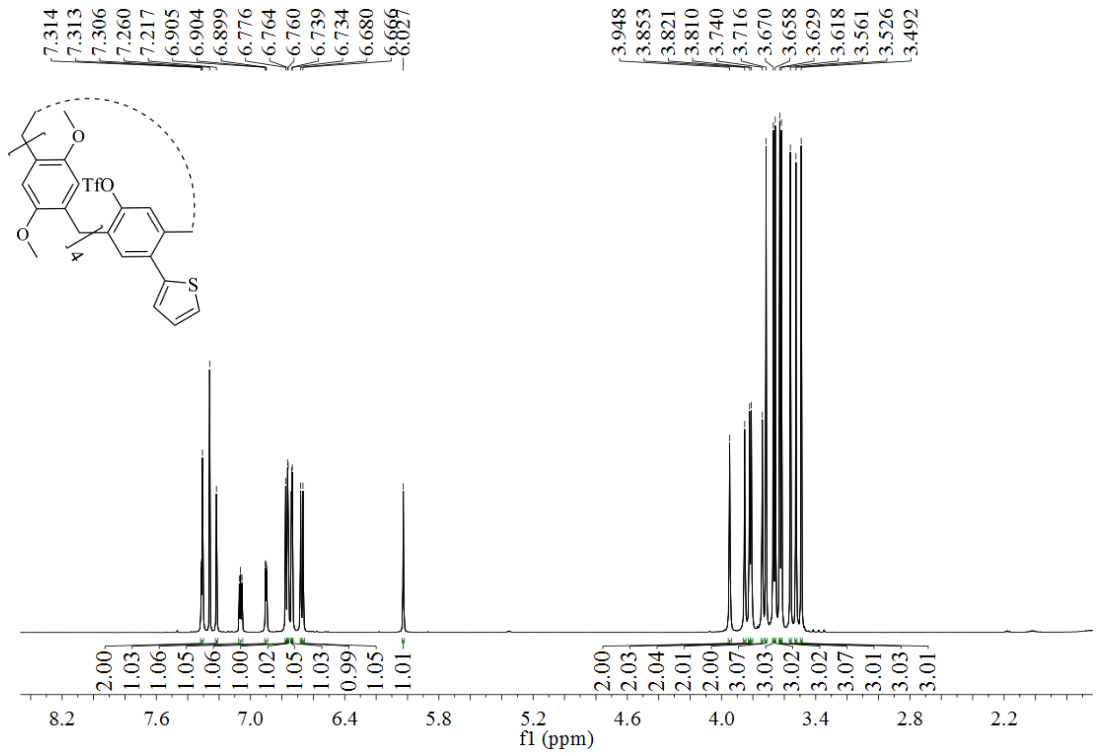


Figure S1. ^{1}H NMR spectrum of compound **2** (500 MHz, $CDCl_3$).

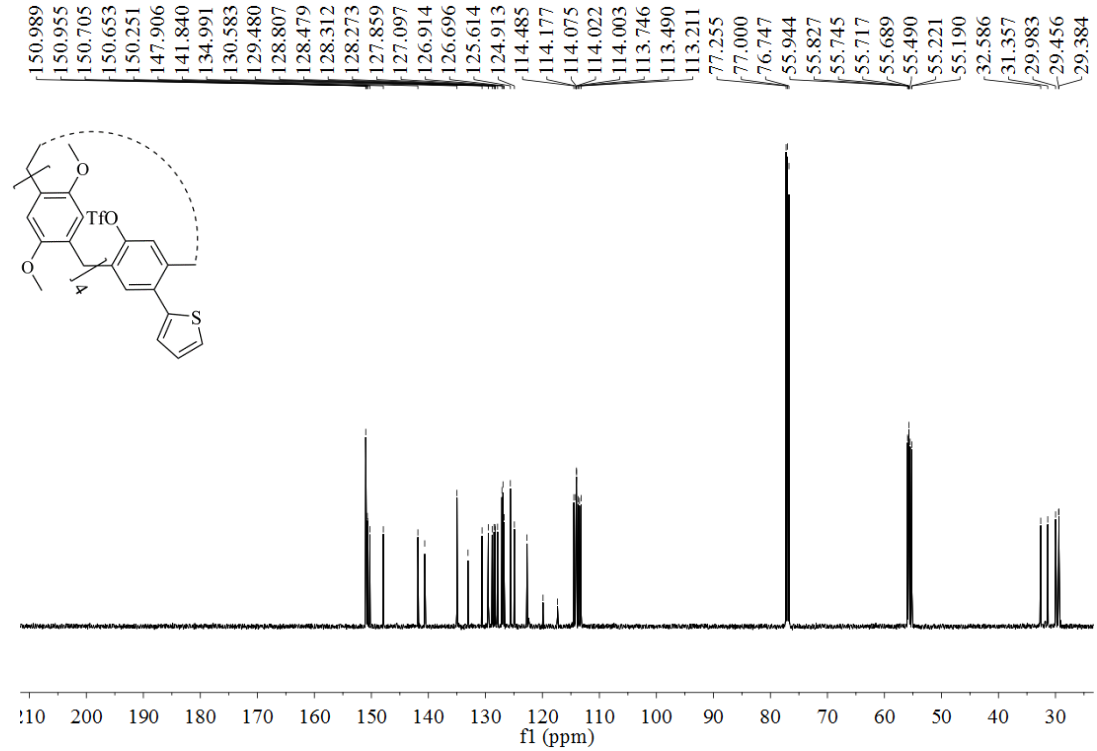


Figure S2. ^{13}C NMR spectrum of compound **2** (125 MHz, $CDCl_3$).

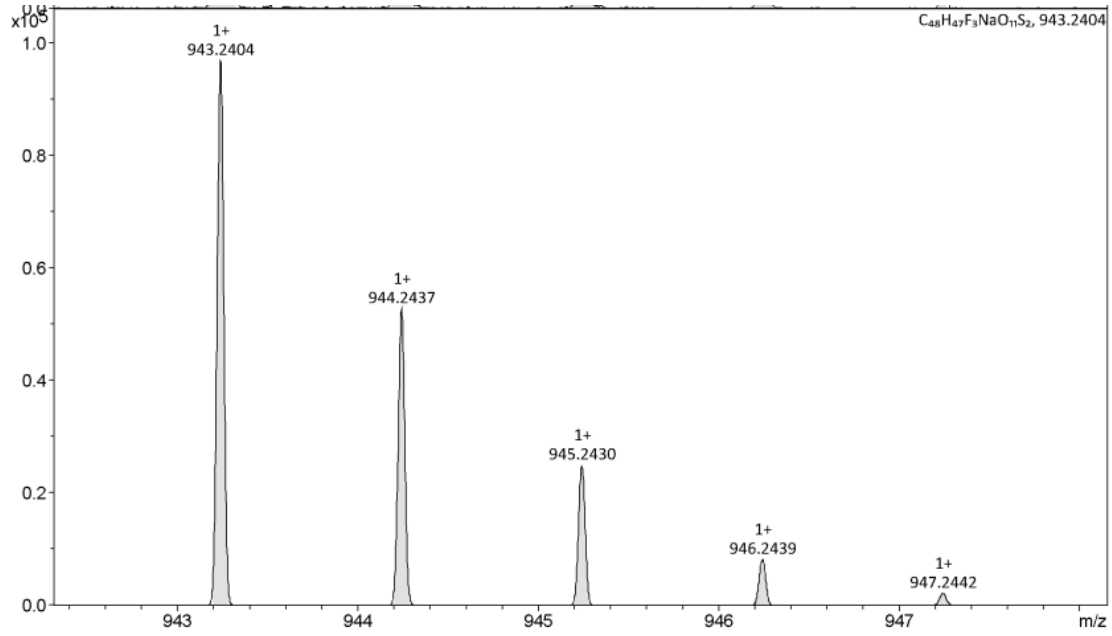


Figure S3. HRMS spectrum of compound **2**.

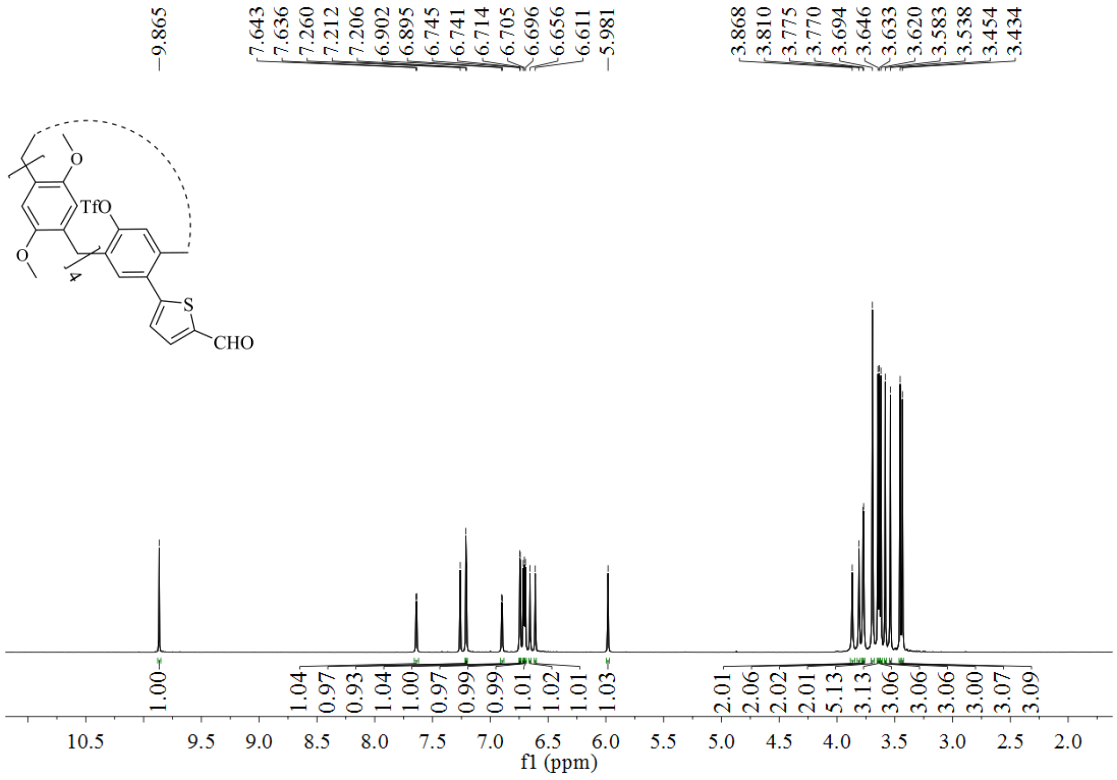


Figure S4. ^{1}H NMR spectrum of compound **3** (500 MHz, $CDCl_3$).

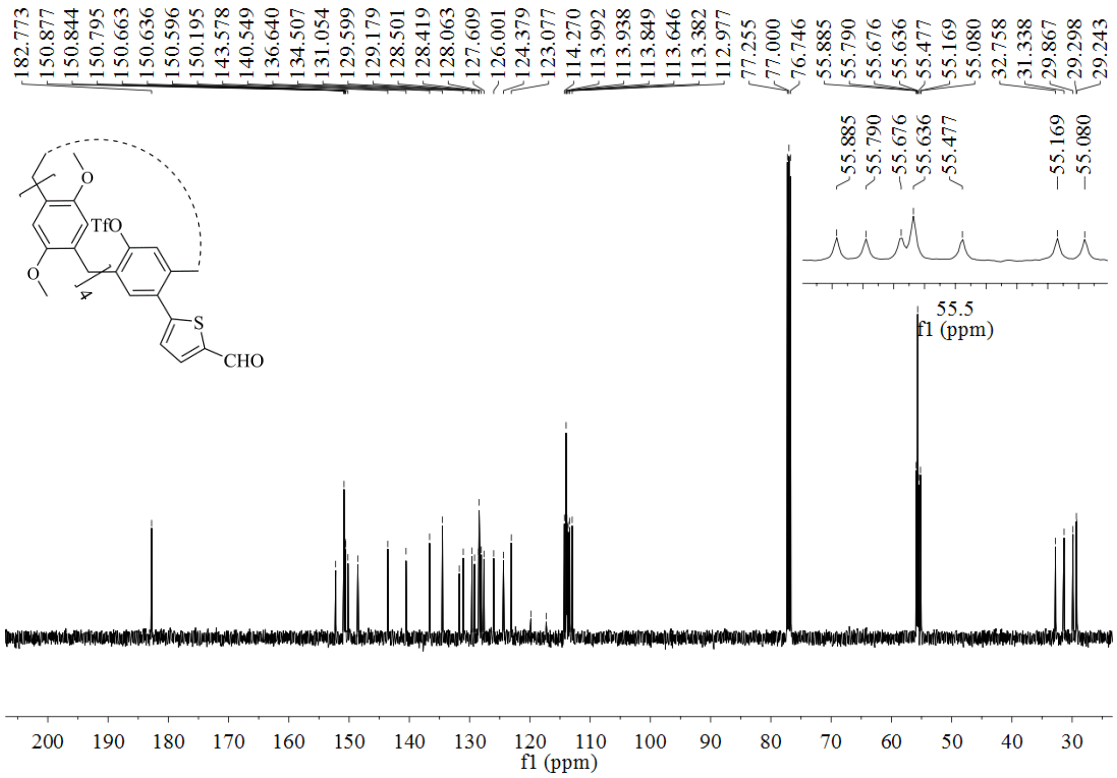


Figure S5. ^{13}C NMR spectrum of compound **3** (125 MHz, $CDCl_3$).

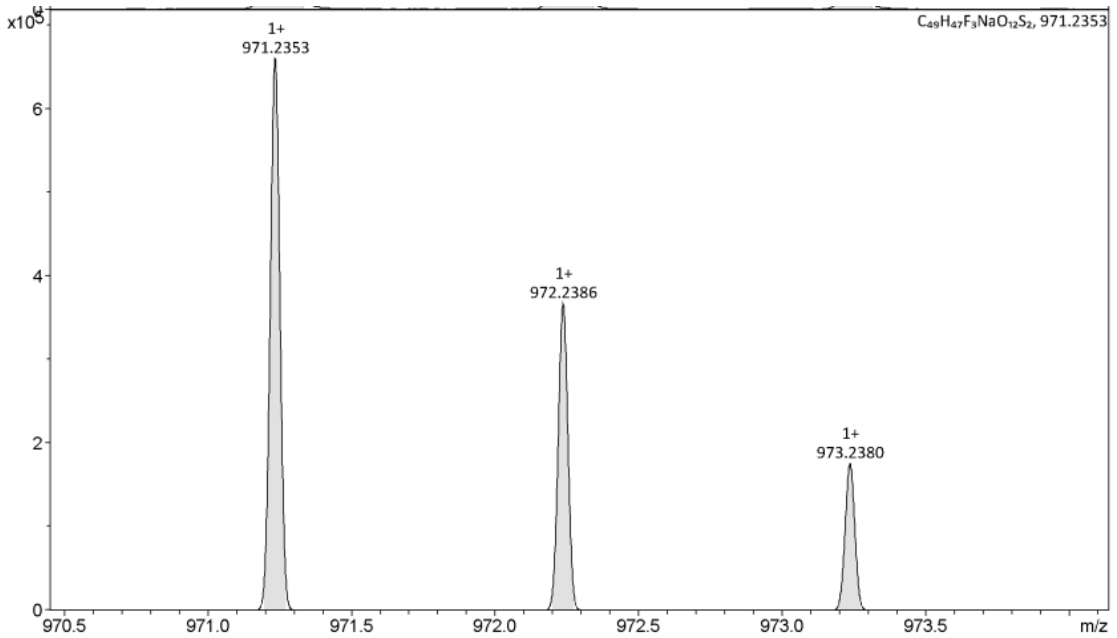


Figure S6. HRMS spectrum of compound **3**.

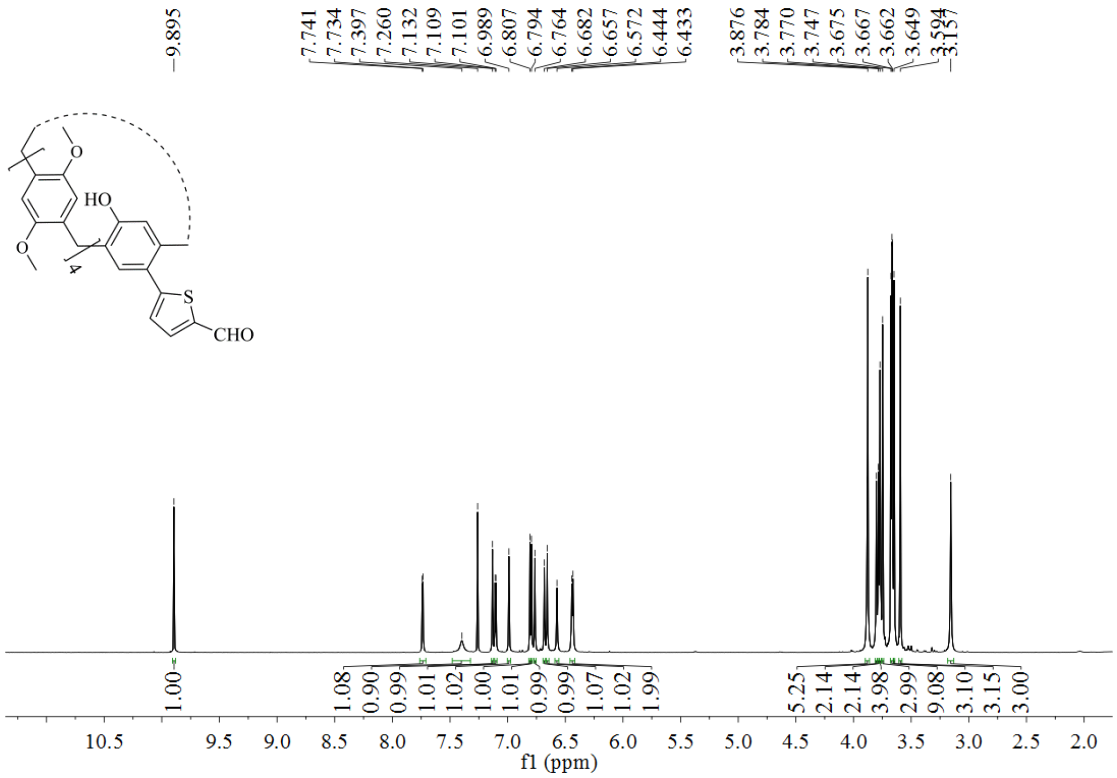


Figure S7. ^{1}H NMR spectrum of compound **4** (500 MHz, $CDCl_3$).

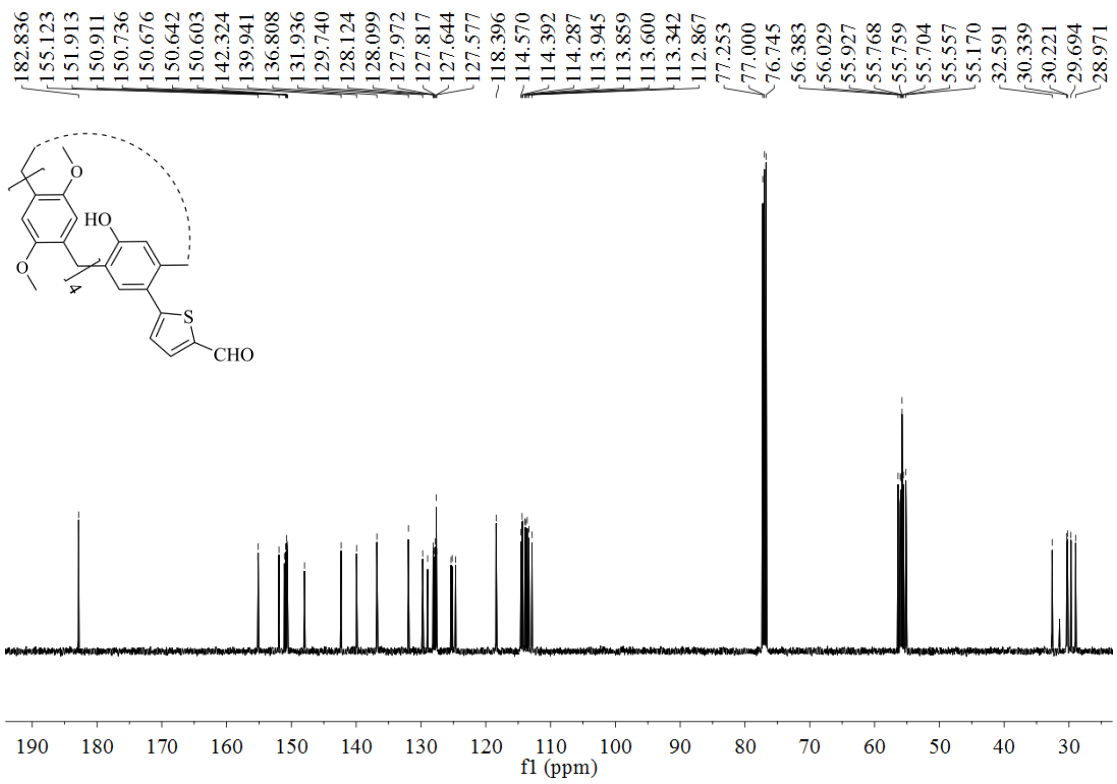


Figure S8. ^{13}C NMR spectrum of compound **4** (125 MHz, $CDCl_3$).

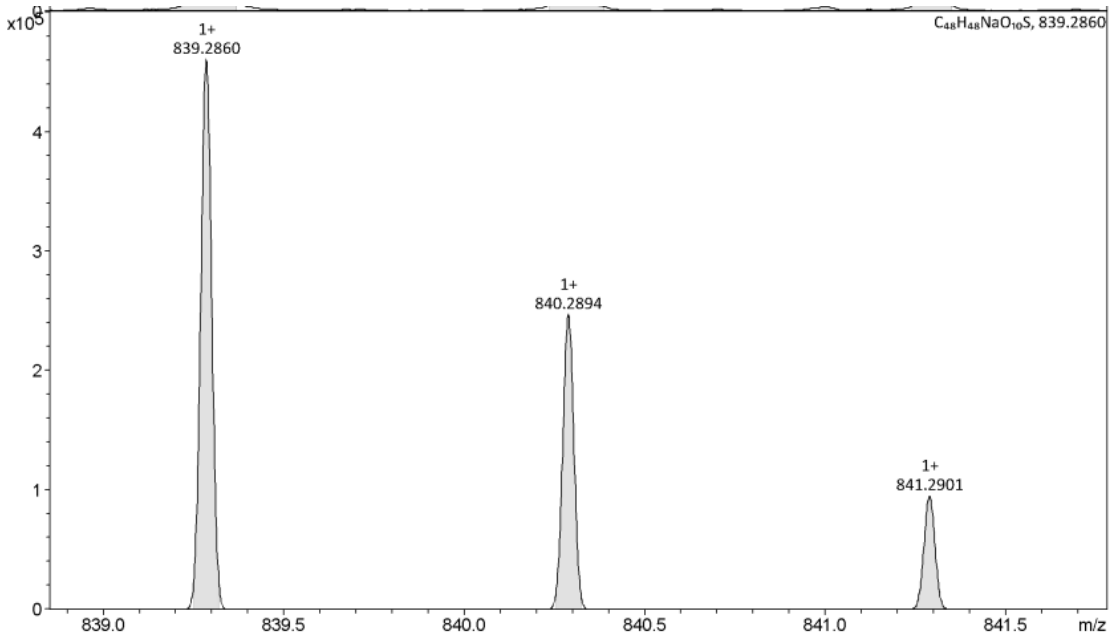


Figure S9. HRMS spectrum of compound **4**.

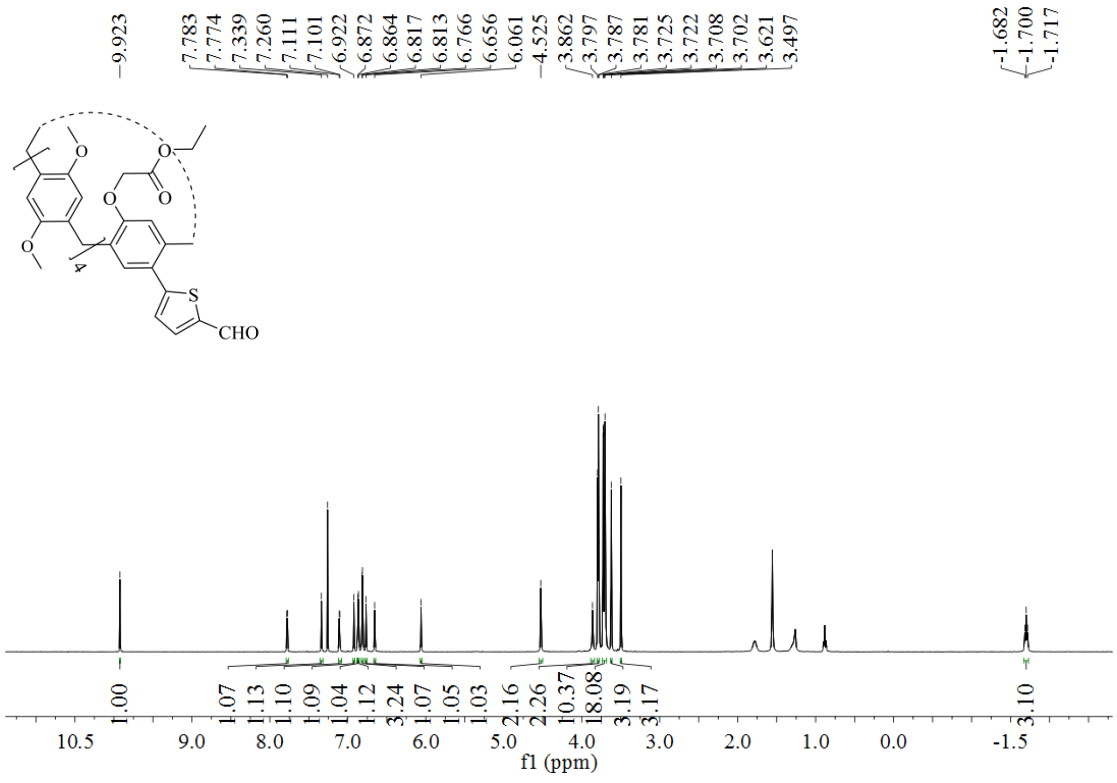


Figure S10. ^{1}H NMR spectrum of compound **5** (400 MHz, $CDCl_3$).

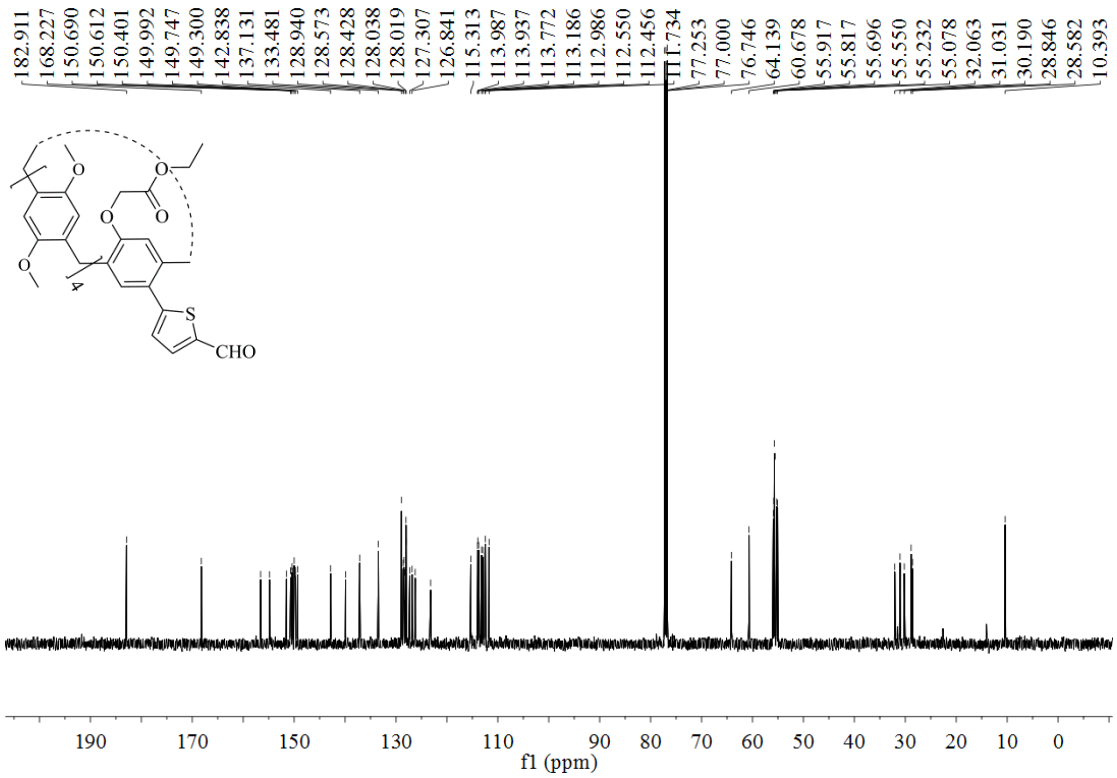


Figure S11. ^{13}C NMR spectrum of compound **5** (125 MHz, $CDCl_3$).

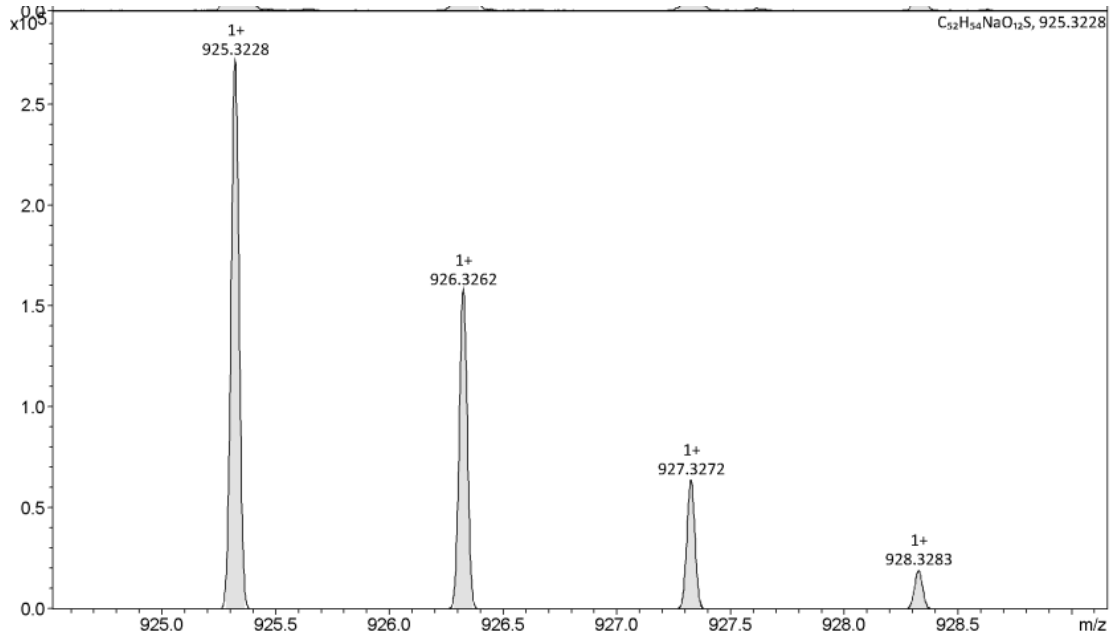


Figure S12. HRMS spectrum of compound **5**.

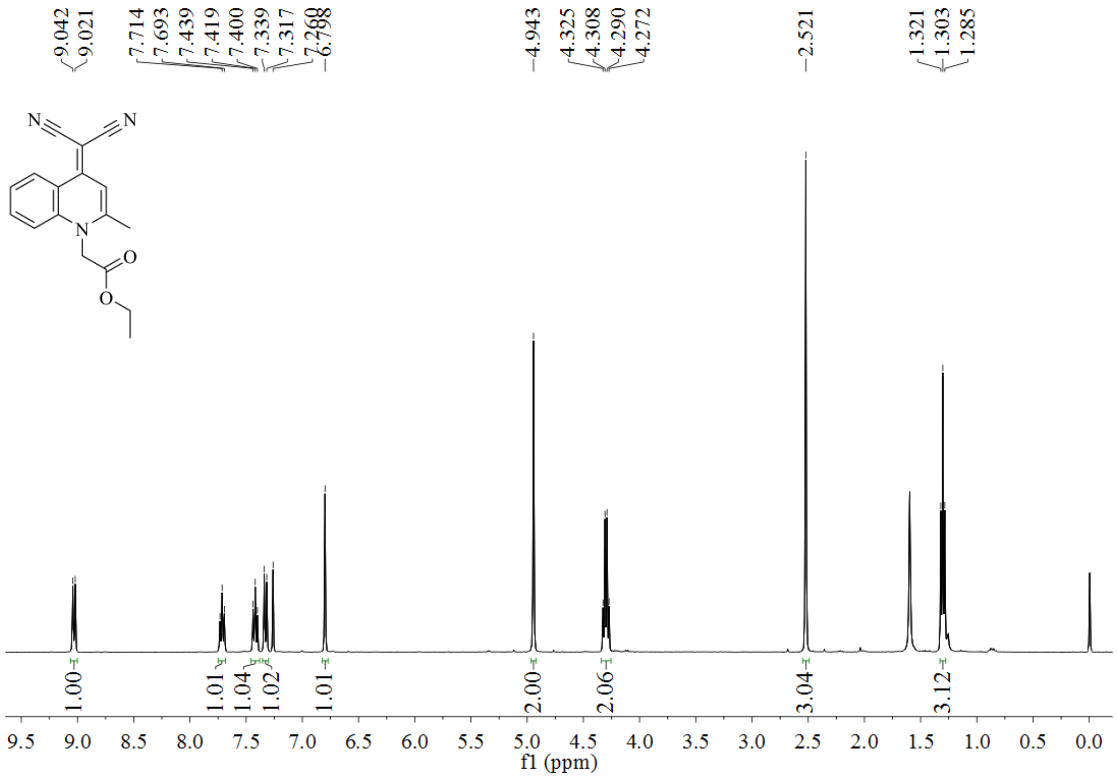


Figure S13. ^{1}H NMR spectrum of compound **7** (400 MHz, $CDCl_3$).

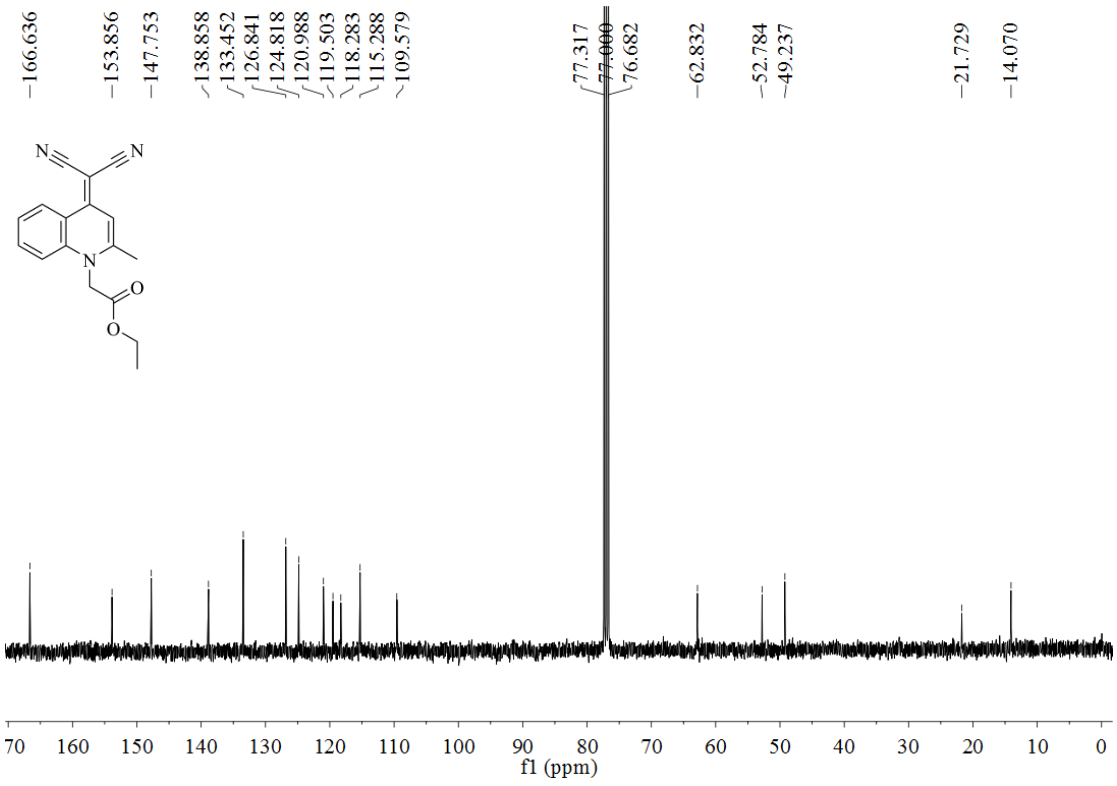


Figure S14. ^{13}C NMR spectrum of compound **7** (100 MHz, $CDCl_3$).

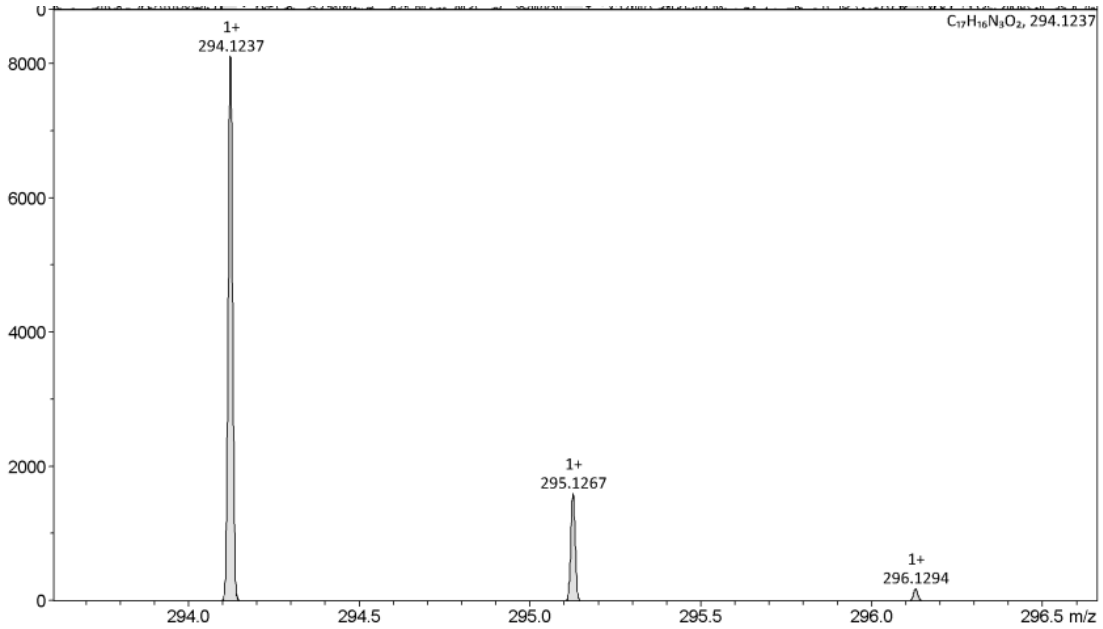


Figure S15. HRMS spectrum of compound **7**.

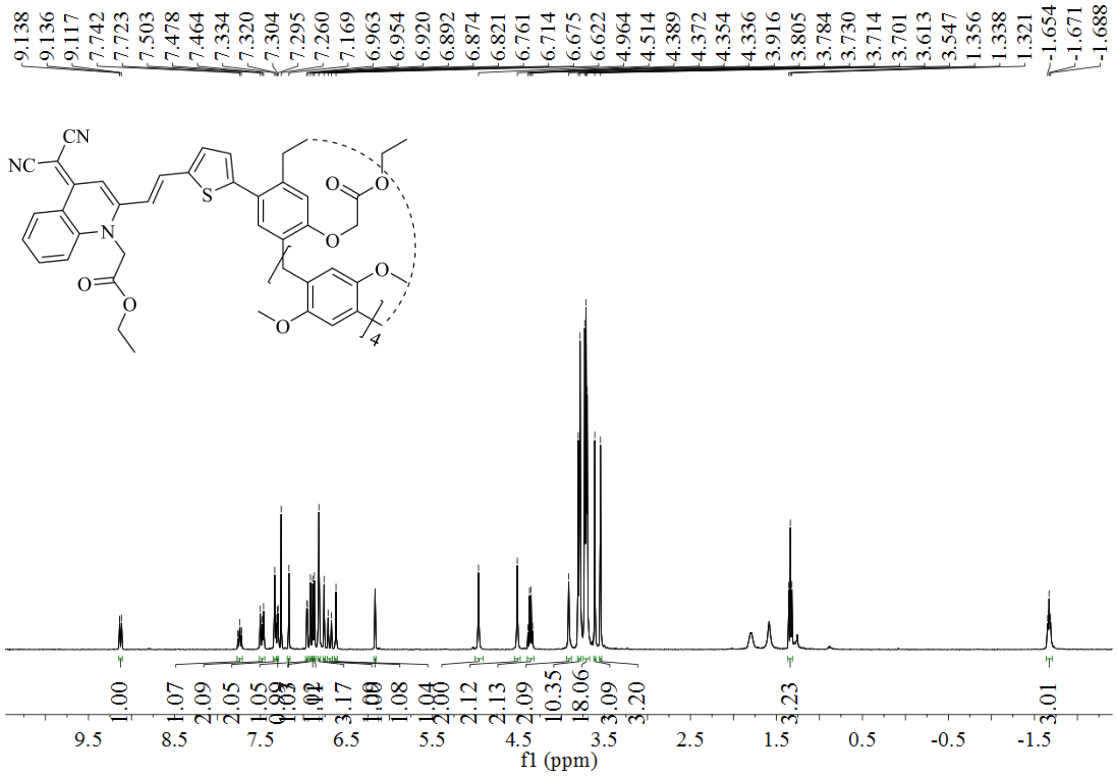


Figure S16. ^{1}H NMR spectrum of compound **H1** (400 MHz, $CDCl_3$).

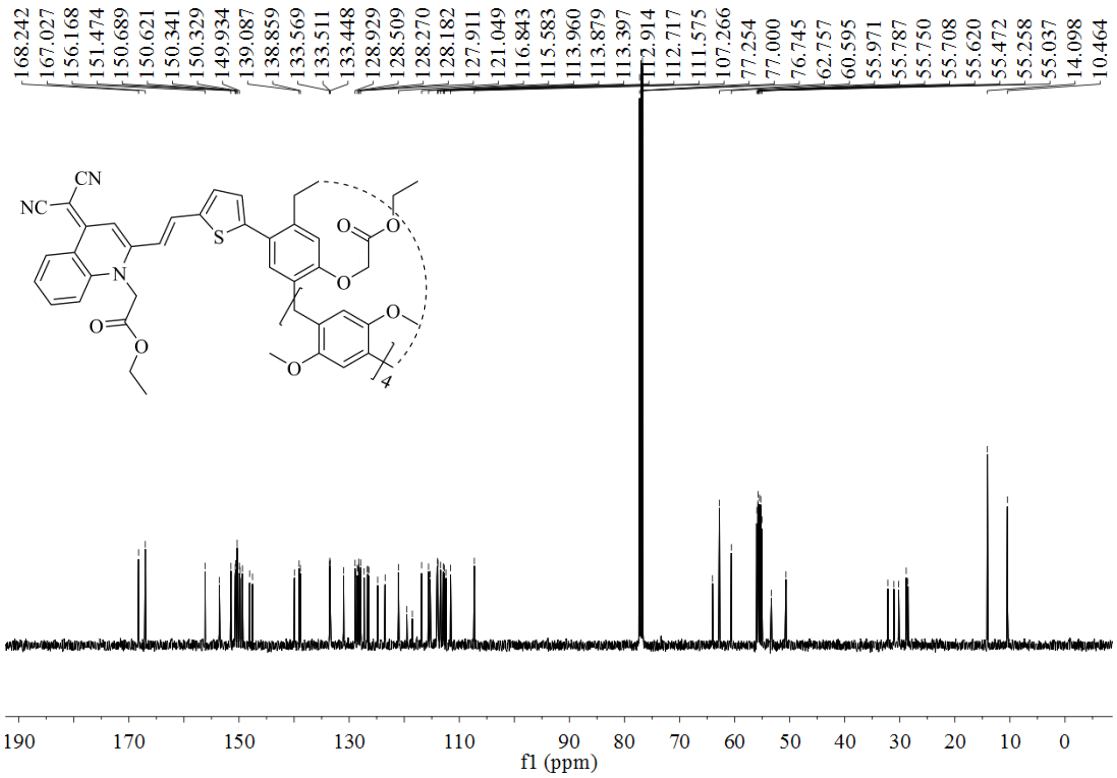


Figure S17. ^{13}C NMR spectrum of compound **H1** (125 MHz, $CDCl_3$).

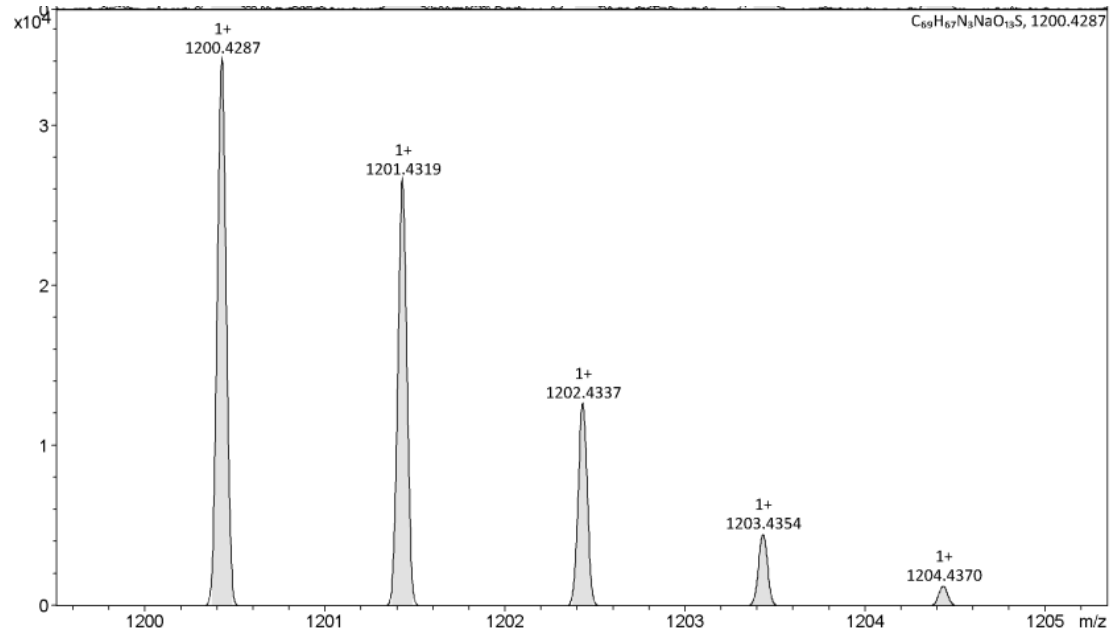


Figure S18. HRMS spectrum of compound **H1**.

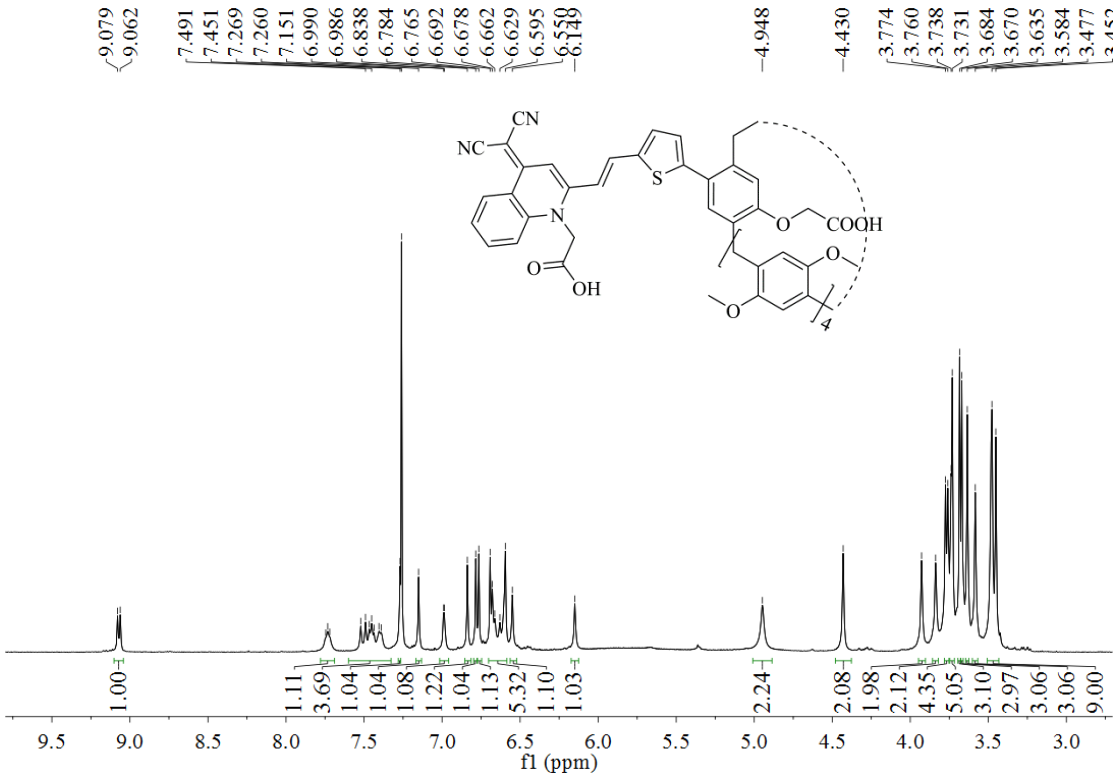


Figure S19. ^{1}H NMR spectrum of compound **H2** (500 MHz, $CDCl_3$).

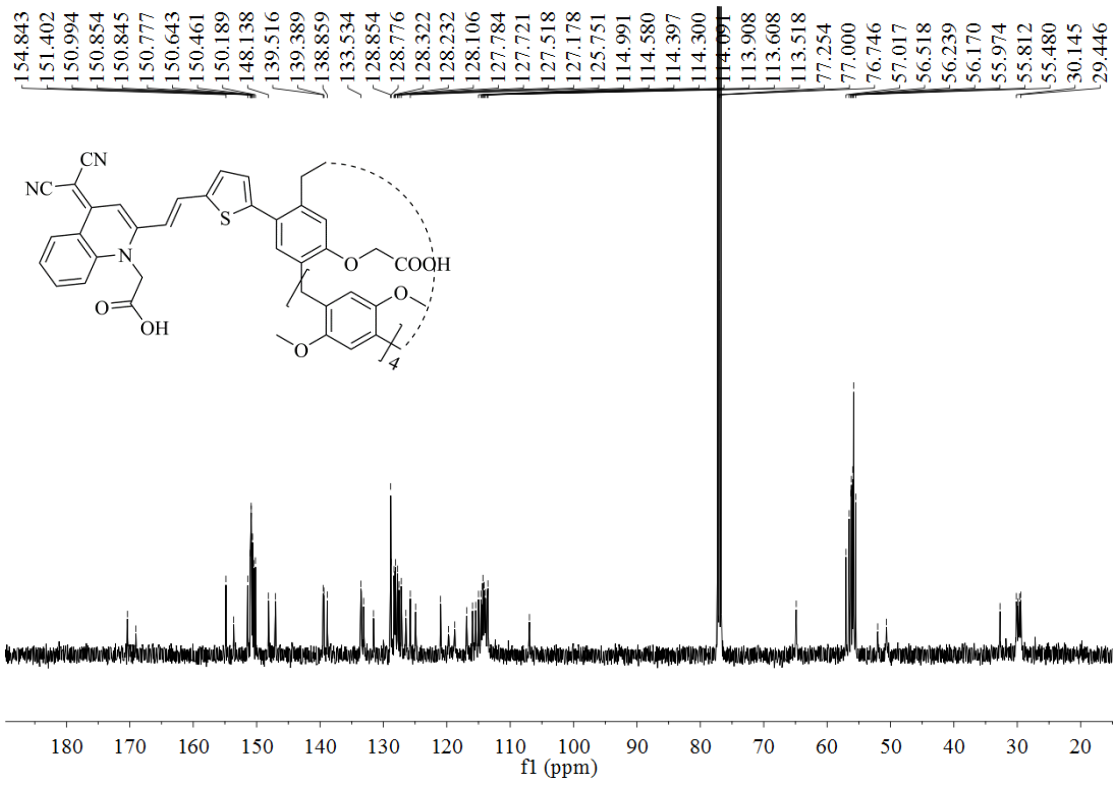


Figure S20. ^{13}C NMR spectrum of compound **H2** (125 MHz, $CDCl_3$).

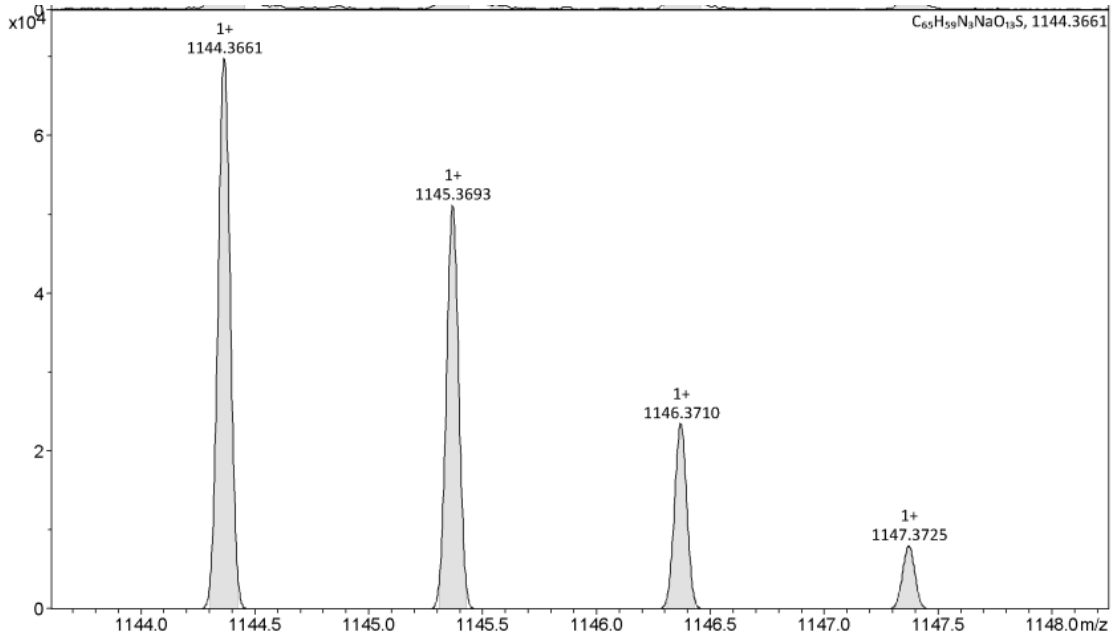


Figure S21. HRMS spectrum of compound **H2**.

3. Supplementary Figures and Table

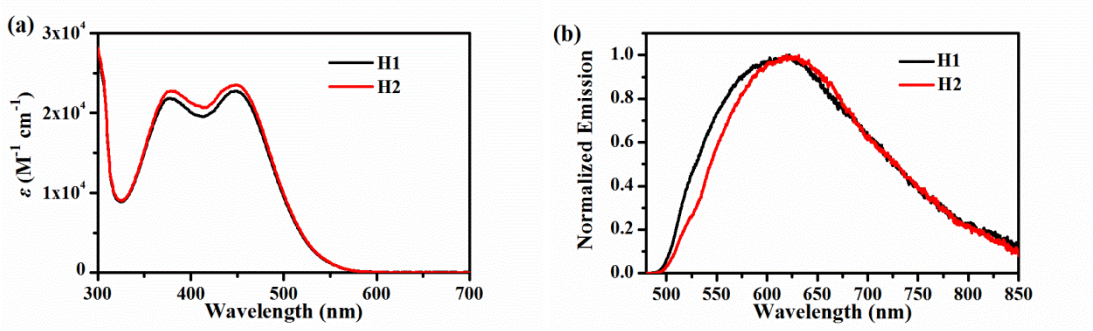


Figure S22. (a) UV-visible absorption spectra of **H1** and **H2. (b)** fluorescence spectra of **H1** and **H2** in ethyl acetate solution (25 μM).

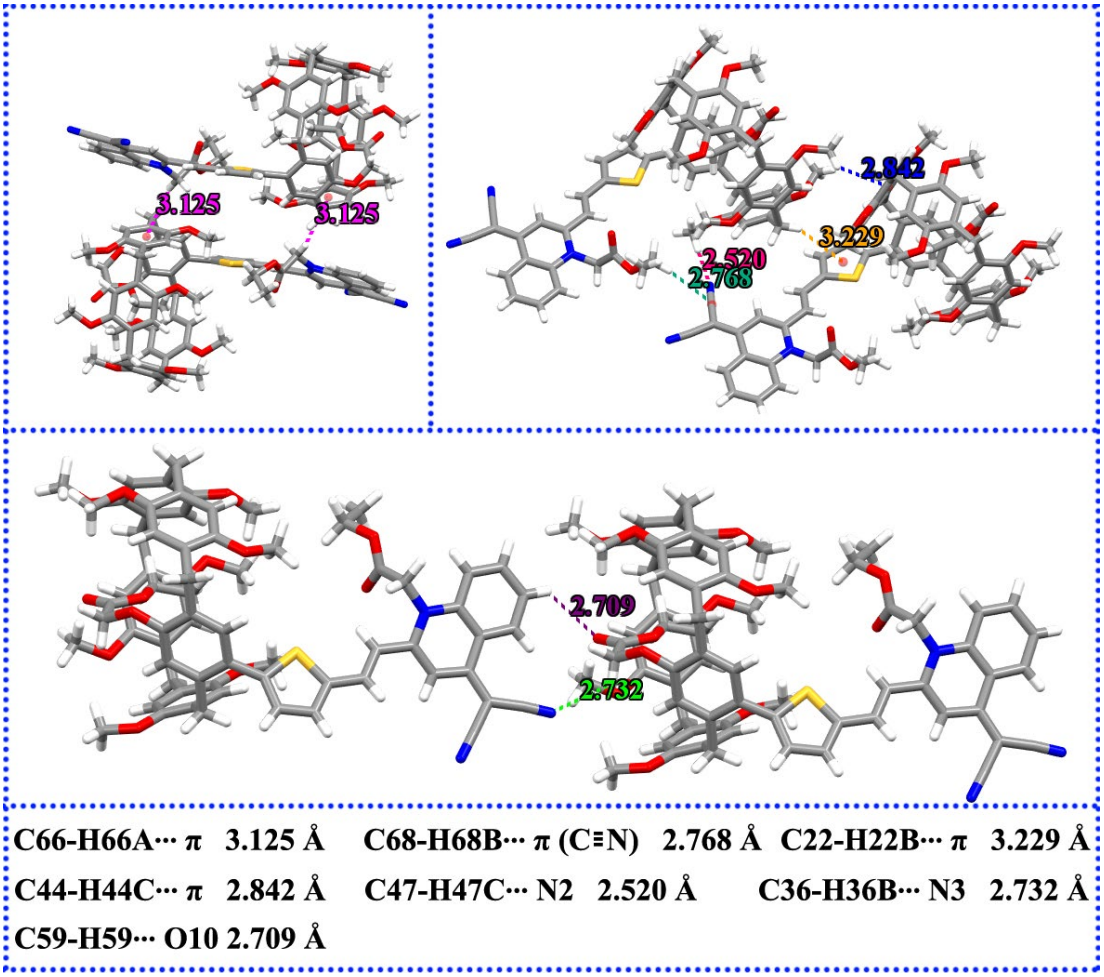


Figure S23. The intermolecular interactions in the crystal of **H1.**

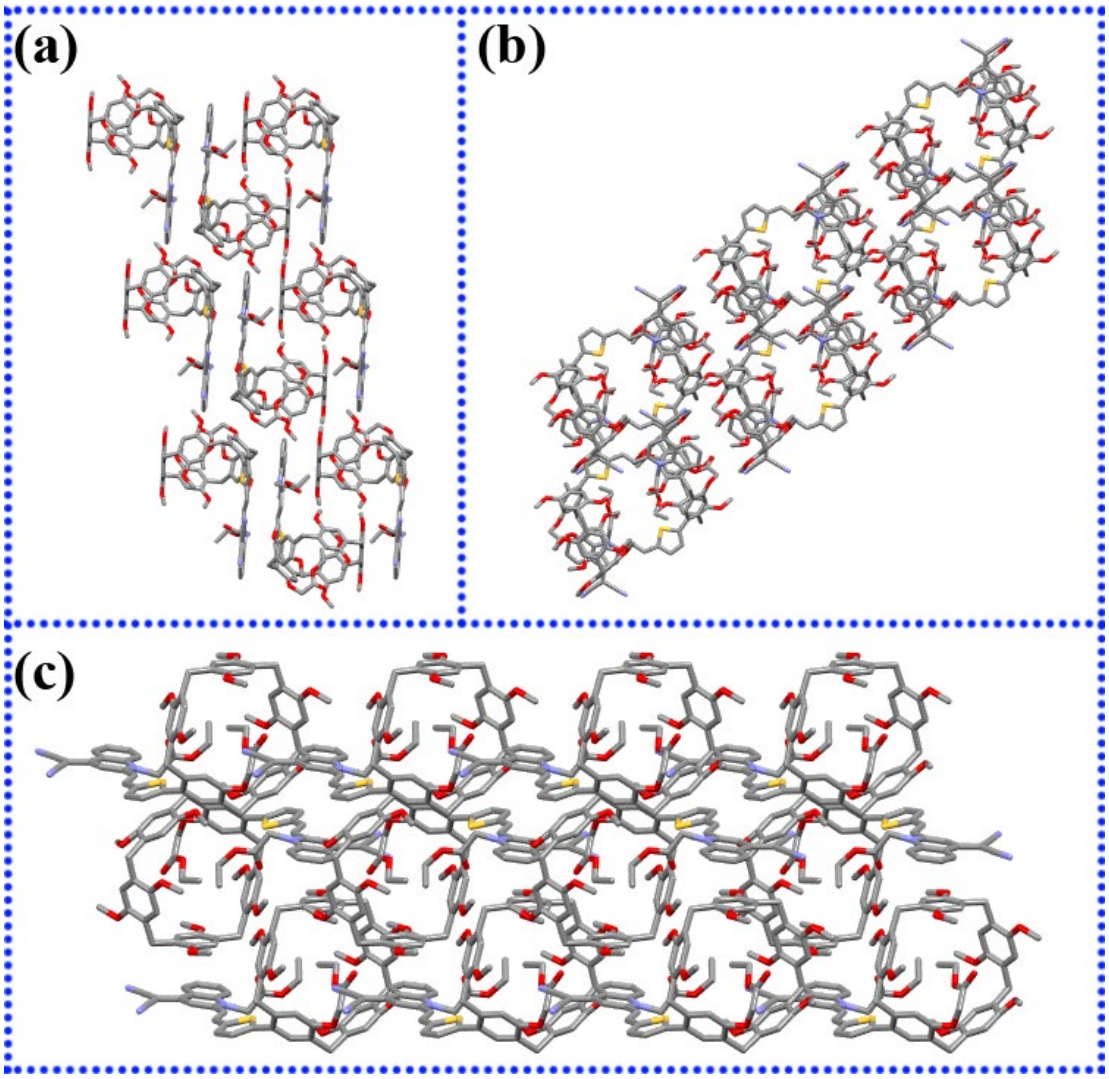


Figure S24. The molecular stacks in the crystal of **H1**: viewed along the a-axis (a), b-axis (b), and c-axis (c), respectively. Hydrogen atoms are omitted for clarity.

Table S1. Crystal data and details of collection and refinement for **H1**.

	H1
CCDC	2106589
Empirical formula	$C_{69}H_{67}N_3O_{13}S$
Formula weight	1178.31
Temperature (K)	193
Crystal system	Triclinic
Space group	P -1
Z	2
D_{calcd} [Mg/m^3]	1.286
F (000)	1244
θ range [°]	2.085 - 25.000
R_1 [I>2σ(I)]	0.0932
wR_2 [I>2σ(I)]	0.1741
a [Å]	12.7652(9)
b [Å]	16.0114(13)
c [Å]	16.5435(12)
α [deg]	75.891(2)
β [deg]	82.879(2)
γ [deg]	68.192(2)
V [Å^3]	3042.5(4)
GOF	1.030
R(int)	0.1088
No. of reflcns collected	56680
No. of unique reflcns	10699
R_1 (all data)	0.1954
wR_2 (all data)	0.2271

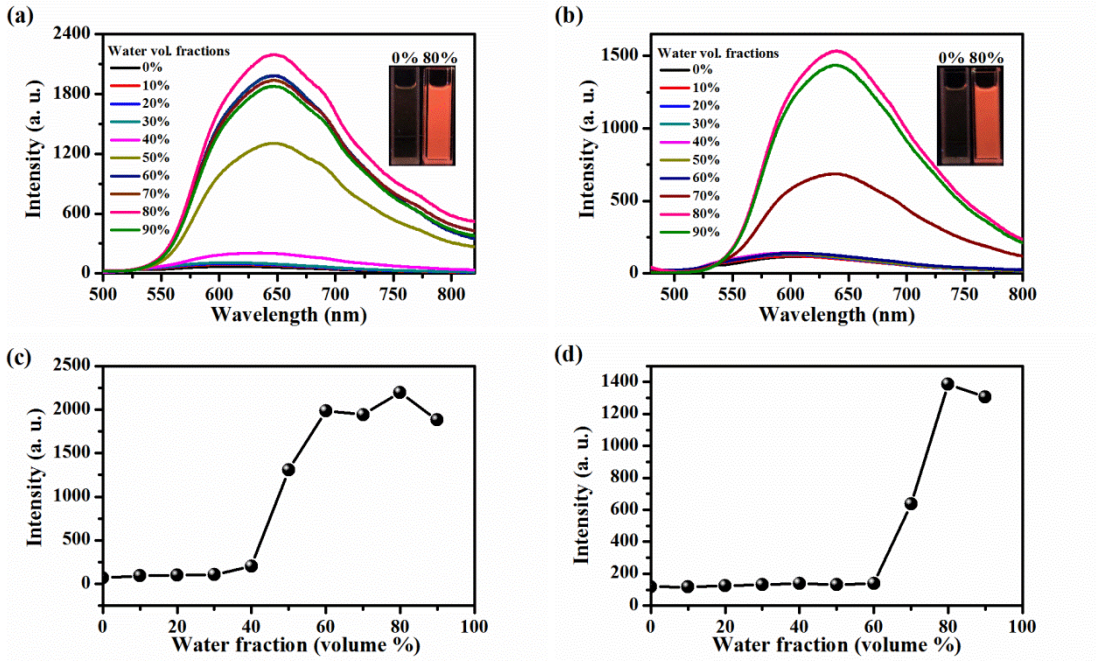


Figure S25. Fluorescence spectra of **H1** (a) and **H2** (b) in ethanol/H_2O mixtures (10 μM) with f_w values from 0 to 90%. Insets: photographs of **H1** and **H2** at f_w = 0% and 80% under 365 nm UV illumination. The changes in the fluorescence intensity of **H1** (c) and **H2** (d) with different f_w values.

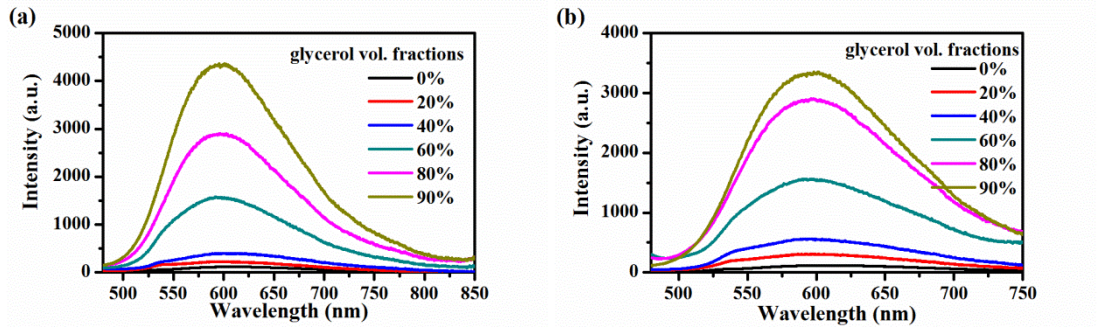


Figure S26. Fluorescence spectra of **H1** (a) and **H2** (b) in dimthyl sulfoxide/glycerol mixture (10 μM) with different glycerol volume fractions.

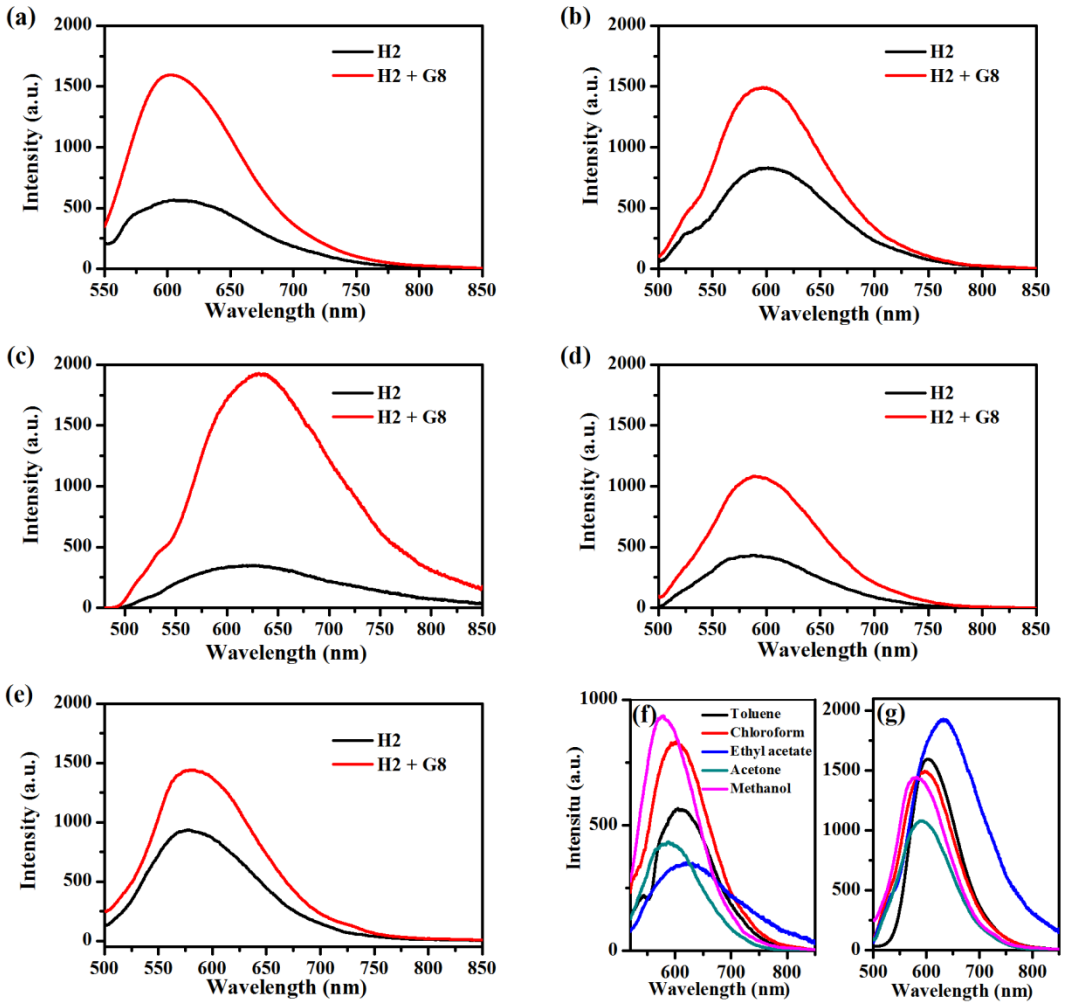


Figure S27. Fluorescence spectra of **H2** (25 μM) before and after adding G8 (15 μM) in toluene (a), chloroform (b), ethyl acetate (c), acetone (d), and methanol (e); the combined fluorescence spectra of **H2** (f) and **H2**⊃G8 complex (g) in different solvents.

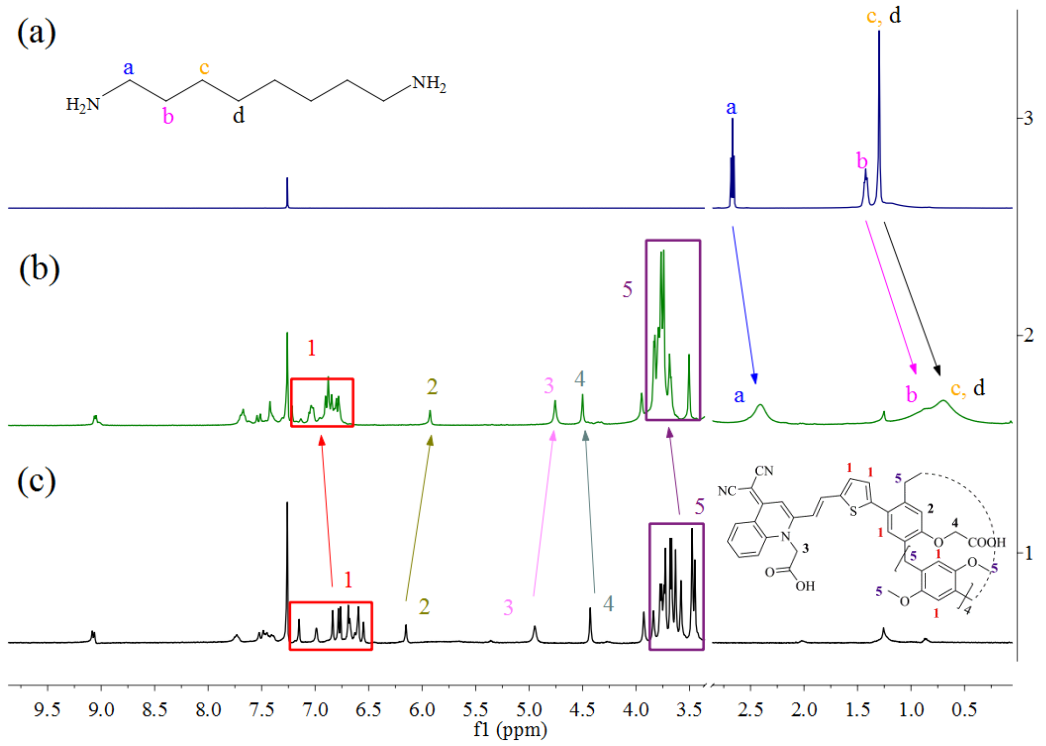


Figure S28. ^{1}H NMR spectra for the binding of **H2** with guest **G8** (500 MHz, $CDCl_3$). (**a**) **G8** (15 mM); (b) **H2** (10 mM) and **G8** (15 mM); (c) **H2** (10 mM).

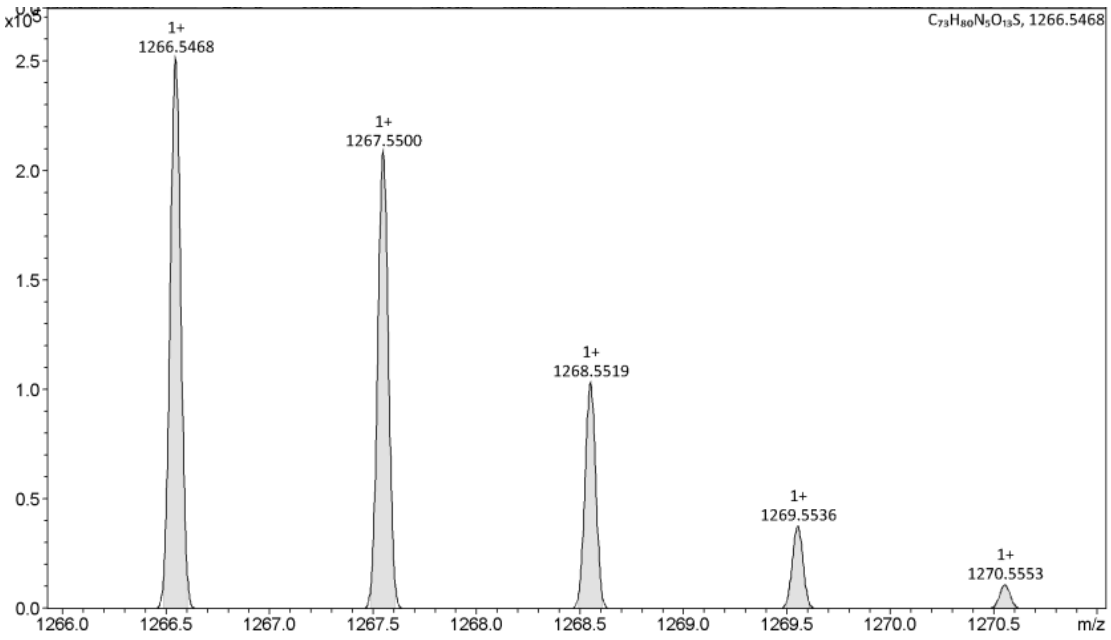


Figure S29. ESI-MS spectrum of **H2⊃G8** complex (m/z: calcd. for [**H2⊃G8**+H]$^{+}$ $C_{73}H_{80}N_5O_{13}S$: 1266.5473; found 1266.5468).

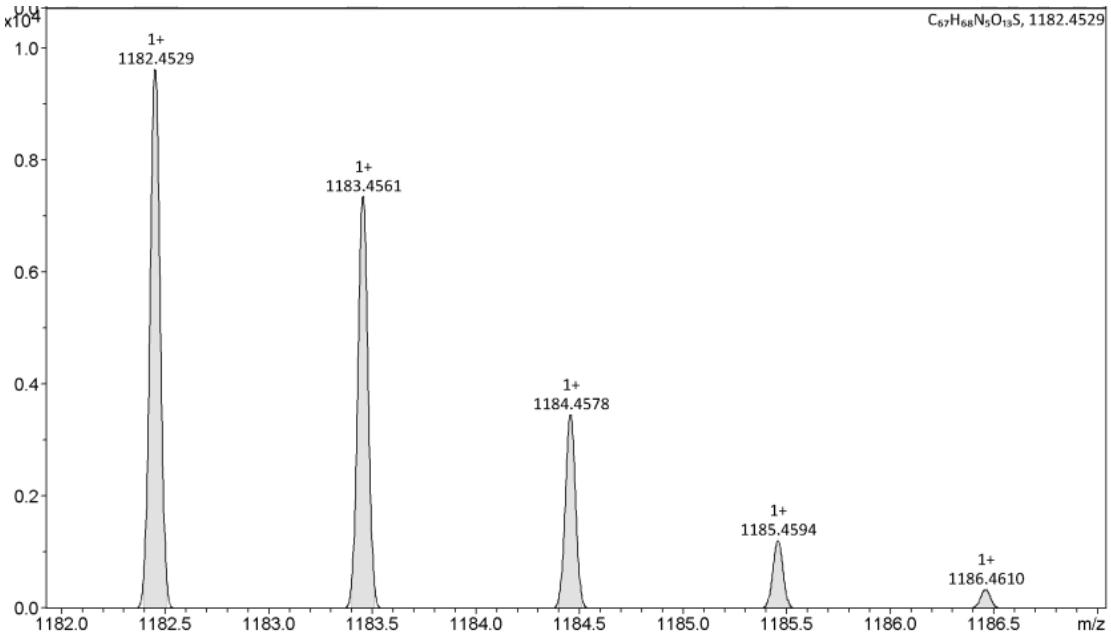


Figure S30. ESI-MS spectrum of **H2⊃G2** complex (m/z: calcd. for [**H2⊃G2**+H]$^+$ $C_{67}H_{68}N_5O_{13}S$: 1182.4534; found 1182.4529).

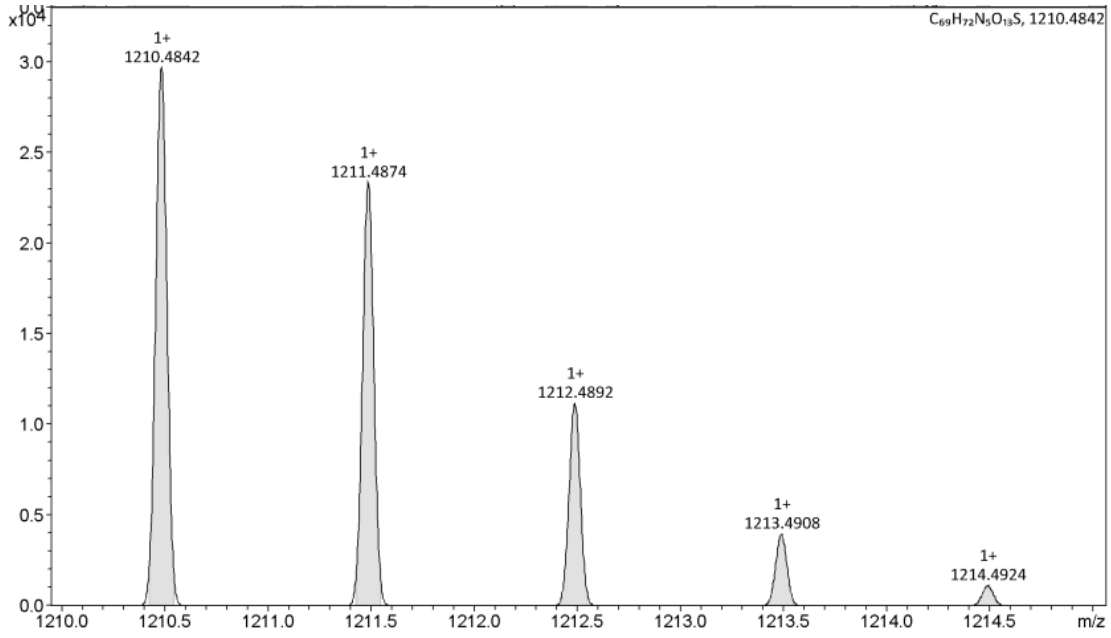


Figure S31. ESI-MS spectrum of **H2⊃G4** complex (m/z: calcd. for [**H2⊃G4**+H]$^+$ $C_{69}H_{72}N_5O_{13}S$: 1210.4847; found 1210.4842).

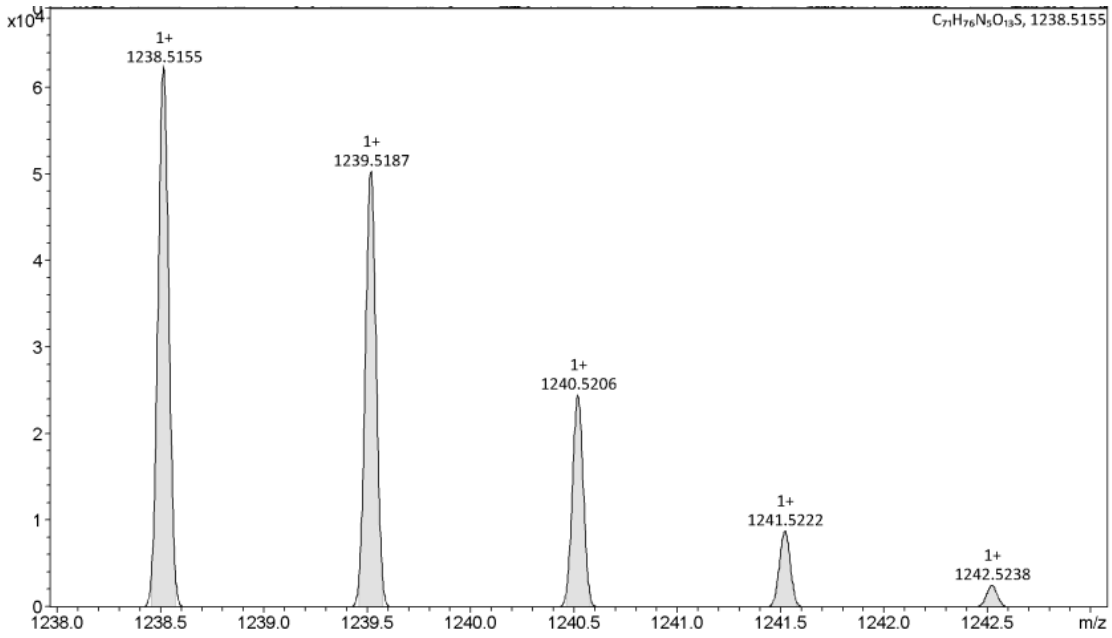


Figure S32. ESI-MS spectrum of **H2⊃G6** complex (m/z: calcd. for [**H2⊃G6**+H]$^+$ $C_{71}H_{76}N_5O_{13}S$: 1238.5160; found 1238.5155).

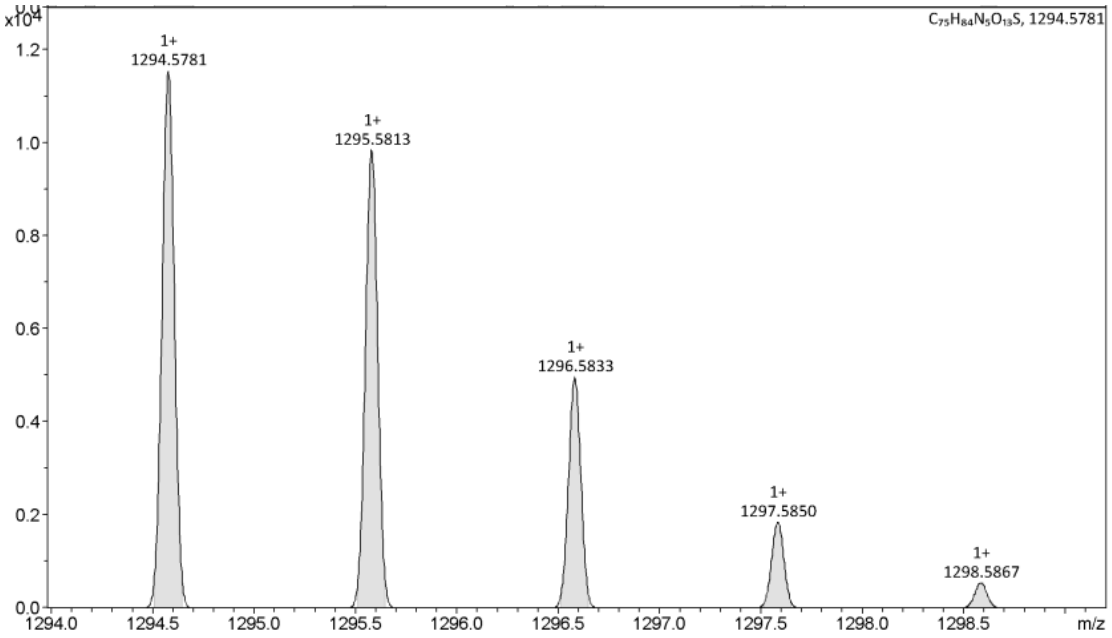


Figure S33. ESI-MS spectrum of **H2⊃G10** complex (m/z: calcd. for [**H2⊃G10**+H]$^+$ $C_{75}H_{84}N_5O_{13}S$: 1294.5786; found 1294.5781).

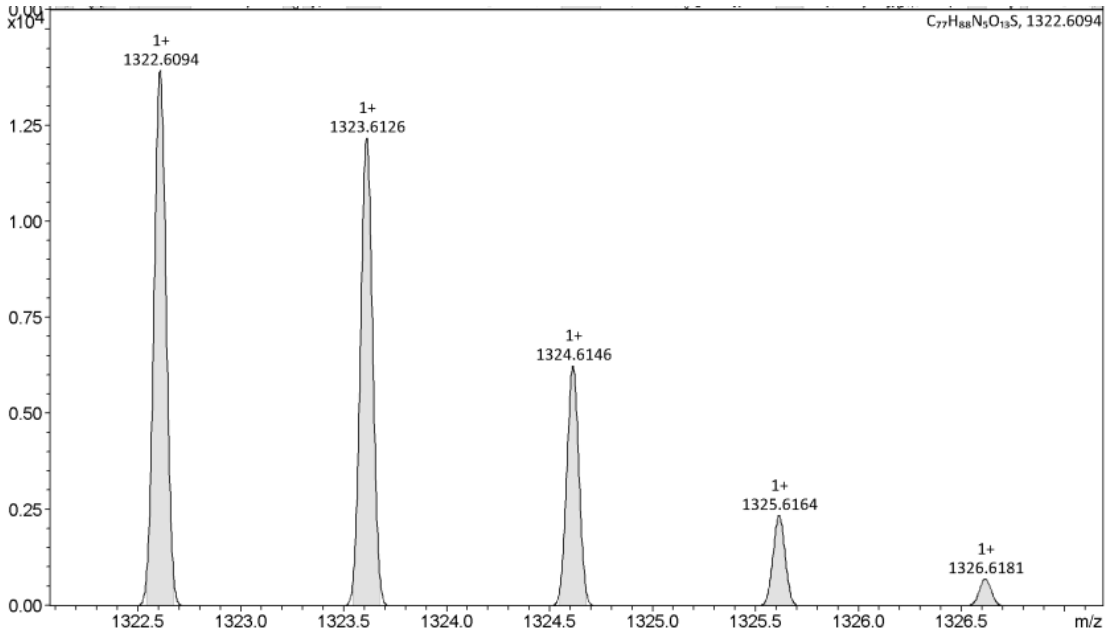


Figure S34. ESI-MS spectrum of **H2⊃G12** complex (m/z: calcd. for [**H2⊃G12**+H]$^+$ $C_{77}H_{88}N_5O_{13}S$: 1322.6099; found 1322.6094).

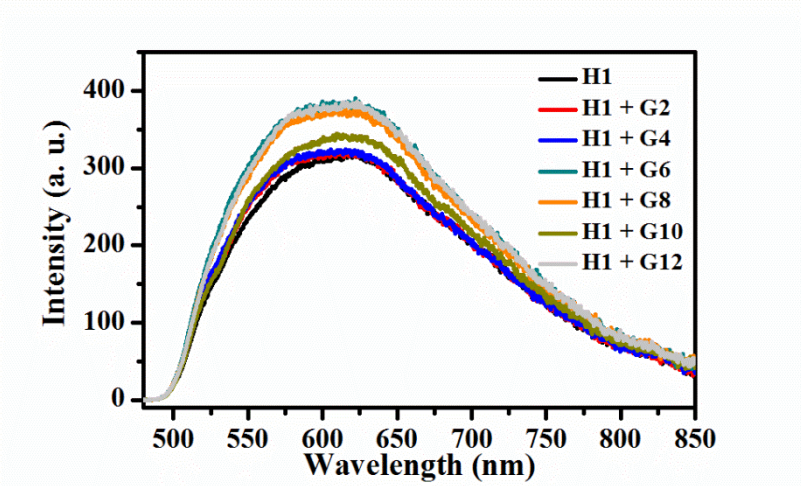


Figure S35. The fluorescence spectra of **H1** (25 μM) with different alkyldiamines (50 μM) in ethyl acetate solution.

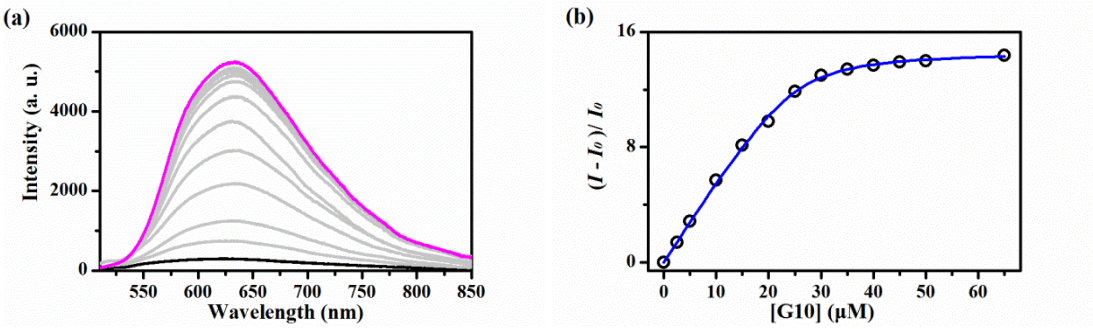


Figure S36. (a) Dependence of fluorescence of **H2** on the concentration of **G10** in ethyl acetate solution (from 0 – 65 μM). (b) Binding isotherm of **H2⊂G10** complex fitted with 1:1 binding model. [**H2**] = 25 μM for all samples.

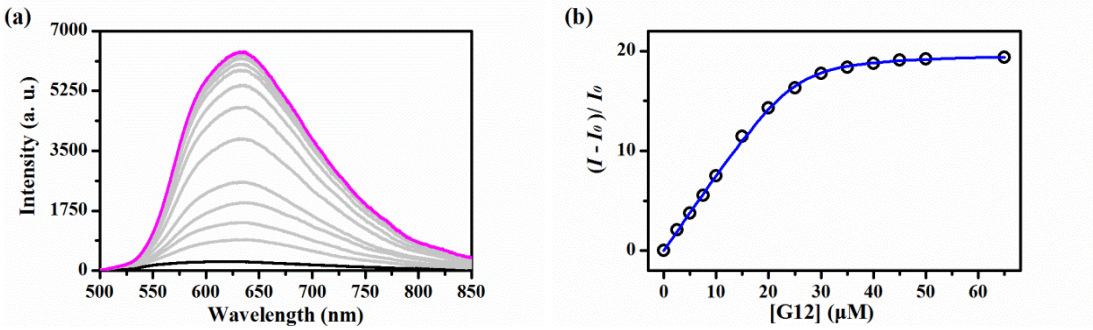


Figure S37. (a) Dependence of fluorescence of **H2** on the concentration of **G12** in ethyl acetate solution (from 0 – 65 μM). (b) Binding isotherm of **H2⊂G12** complex fitted with 1:1 binding model. [**H2**] = 25 μM for all samples.

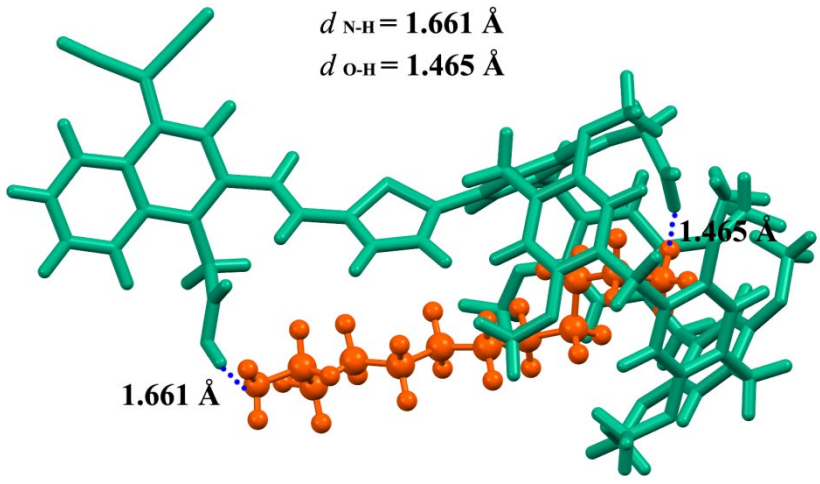


Figure S38. The complex structure of **H2⊂G10** predicted by DFT calculation.

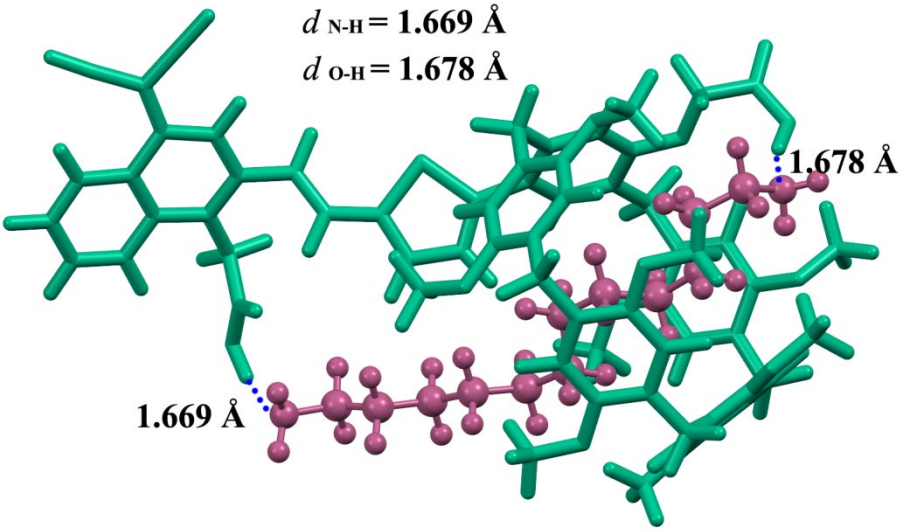


Figure S39. The complex structure of **H2⊂G12** predicted by DFT calculation.

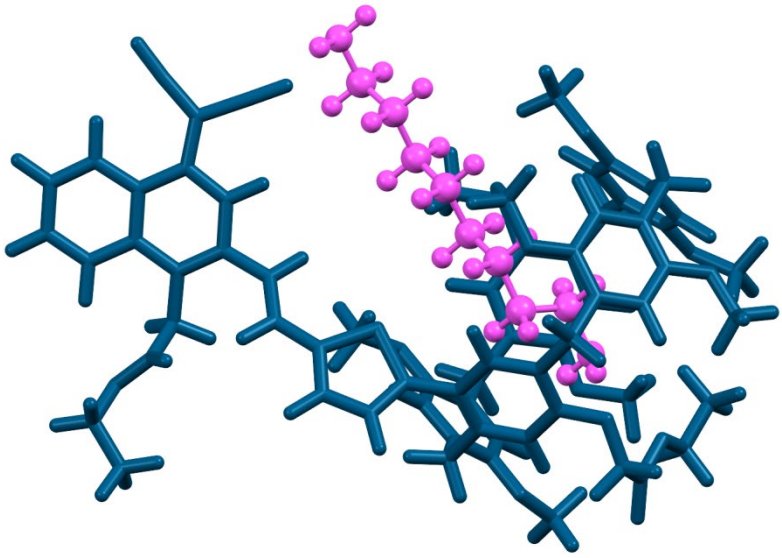


Figure S40. The complex structure of **H1⊂G8** predicted by DFT calculation.

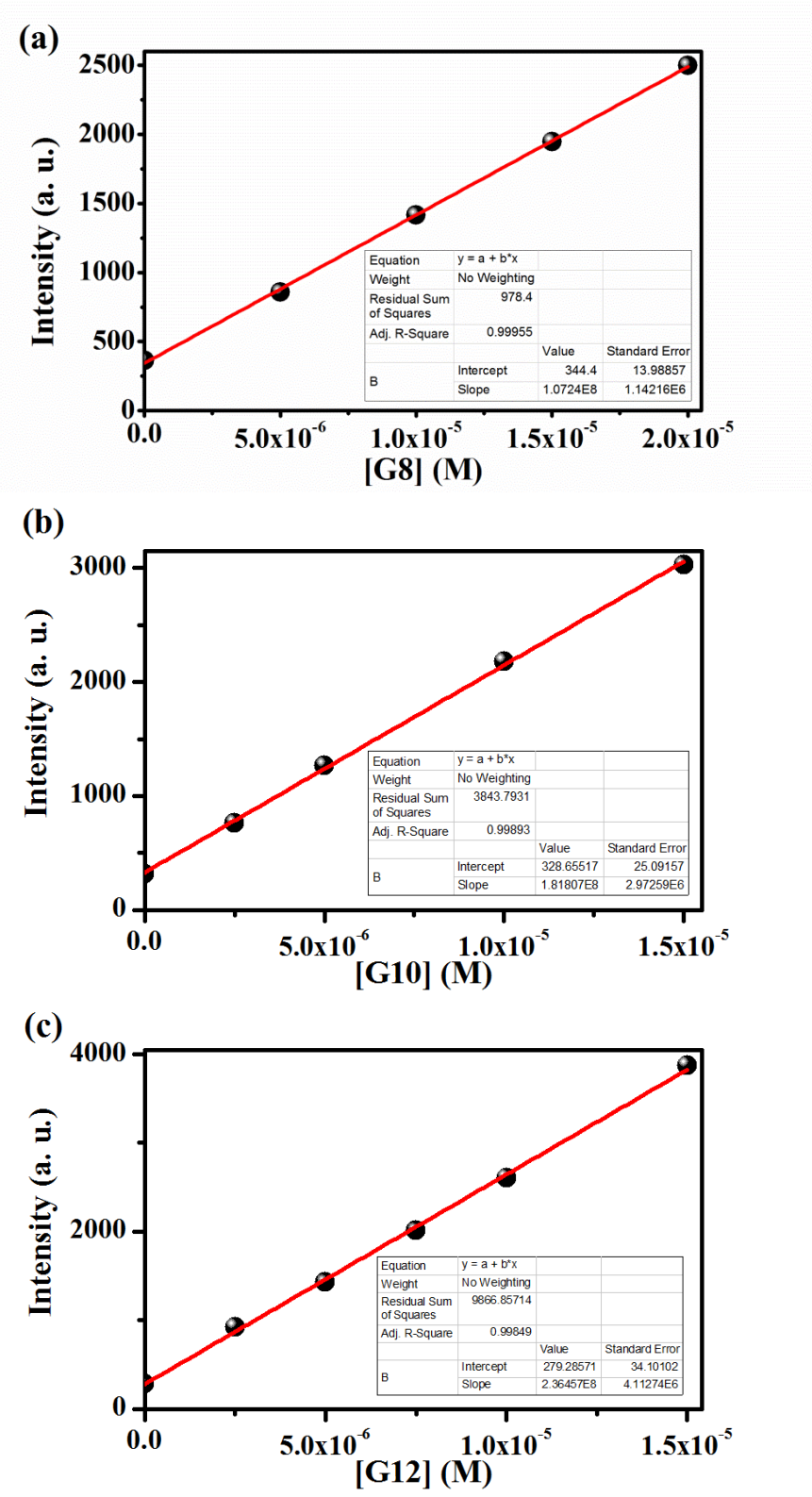
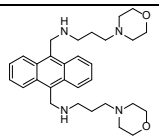
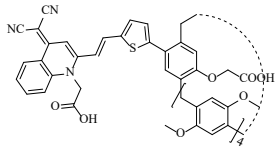


Figure S41. The linear relationship value of **H2** with **G8** (a), **G10** (b), and **G12** (c). The limit of detection (LOD) was calculated with the following equation: LOD = 3σ/S. Here, σ was the standard deviation of the blank and *S* was the slope of the intensity of fluorescence against the guest's concentration.

Table S2. The comparison of the AIE pillar[5]arene probe with others.

Probes	LOD	Remark	Reference
Phenolphthalein with two crown loops	No data	Host-Guest interaction, On-Off type	Org. Biomol. Chem., 2009, **7**, 4689–4694
pyrrolopyrrole aza-BODIPY	Putrescine: 36 nM Cadaverine: 32 nM 1,3-propanediamine: 33 nM	Colorimetric and fluorescent, rapid (30 s), high sensitivity, high selectivity	Sensors & Actuators: B. Chemical, 2020, **312**, 127953
Water-soluble pillar[5]arene modified silver nanoparticles	No data	Host–guest recognition, surface-enhanced Raman spectroscopy (SERS)-based selective assays	Chem.Commun., 2014, **50**, 869-871
Pyrene modified pillar[5]arene	No data	Host–guest recognition, fluorescence turn off	J. Am. Chem. Soc. 2011, **133**, 5668–5671
peptide-Pillar[5]arene conjugate	No data	Host–guest recognition, fluorescence turn off	*Nat. Commun.*, 2019, **10**, 3546
Polymer–Surfactant Complexation	Spermine: 330 nM	Electrostatic interactions	Anal. Chem. 2016, **88**, 7358-7364
	Putrescine: 780 nM	fluorescence turn-off	Sensors & Actuators: B. Chemical, 2018, **254**, 842-854
	1,8-diaminooctane: 16.8 nM 1,10-diaminodecane: 9.9 nM 1,12diaminododecane: 7.6 nM	fluorescence turn-on, rapid, high sensitivity, high selectivity	This work

4. Reference

1. L. X. Xu, R. R. Wang, W. Cui, L. Y. Wang, H. Meier, H. Tang and D. R. Cao, *Chem. Commun.*, 2018, **54**, 9274-9277.
2. M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys*, 1982, **77**, 3654-3665.
3. A. D. Becke, *J. Chem. Phys*, 1993, **98**, 5648-5652.
4. W. Cui, L. Wang, L. Xu, G. Zhang, H. Meier, H. Tang and D. Cao, *J. Phys. Chem. Lett.*, 2018, **9**, 1047-1052.