Supporting Information

Diphenylacrylonitrile-connected BODIPY dyes: The fluorescence enhancement based on dark and AIE resonance energy transfer

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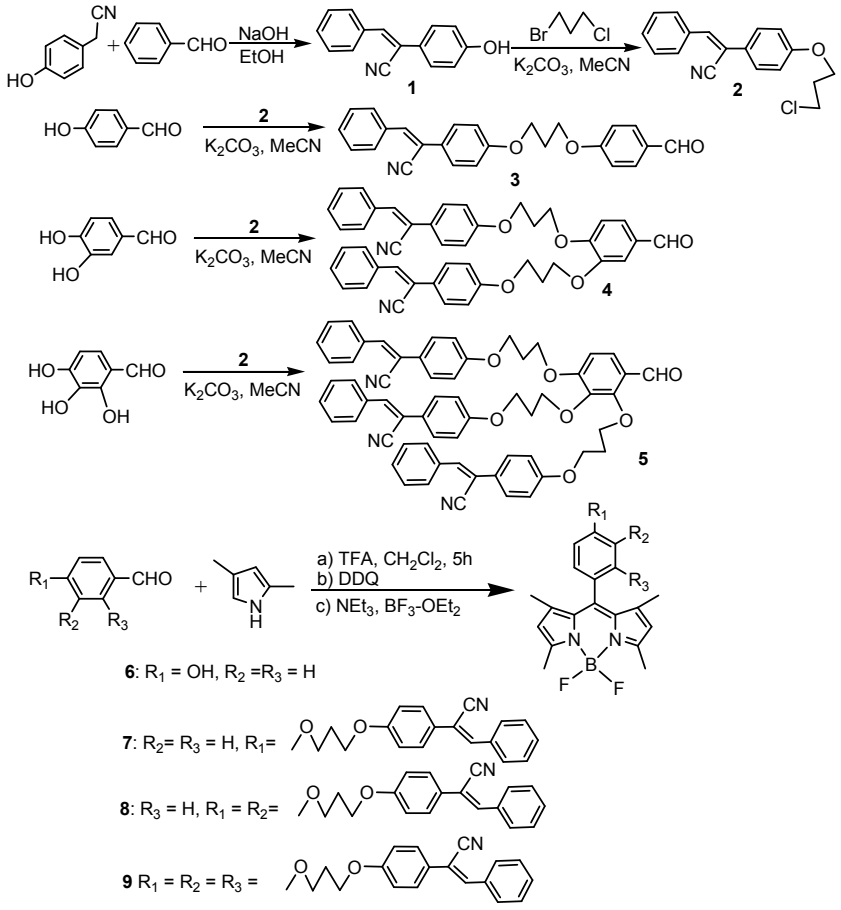
1. General

All chemical reagents were obtained from commercial suppliers and used without further purification. The other organic solvents and inorganic reagents were purified according to standard anhydrous methods before use. TLC analysis was performed byusing pre-coated glass plates. Column chromatography was carried out by using silic a gel (200-300 mesh). NMR spectra were recorded in $CDCl_3$ on a Bruker-ARX 400 instrument at 25°C. Chemical shifts are reported in ppm, using tetramethylsilane (TMS) as internal standard. MS spectra were obtained from Bruker mass spectrometer. OH-Bodipy **6** was synthesized according to published procedure (Liu, J. Y.; Yeung, H. S.; Xu, W.; Li, X. Ng, D. K. P. *Org. Lett*. **2008**, *10*, 5421-5424).

UV-Vis were recorded on Varian UV-Vis spectrometer. Fluorescence spectra were measured in a conventional quartz cell (10×10×45 nm) at 25 °C on a Hitachi F-4500 spectrometer equipped with a constant-temperature water bath, with excitation and emission slits 10nm wide. The fluorescence absolute Φ_F values were measured using an Edinburgh Instruments FLS920 Fluorescence Spectrometer with a 6-inch integrating sphere.

2. The synthetic process and characteristic spectra.



Scheme S1. Synthetic routes of compounds **7**, **8** and **9**

2.1 Synthesis of compound 1.

A mixture of 4-hydroxyphenylacetonitrile (0.51 g, 3.8 mmol), benzaldehyde (0.40 g, 3.8 mmol) and NaOH (0.30g, 7.5mmol) in 40 mL of EtOH solution was stirred for 10 h at room temperature. The reaction were detected by TLC technique, which suggested the dissapearance of the materials. After reaction, 20 mL of HCl solution (1M) was poured into the reaction mixture. The precipitate was formed and filtered. The obtained precipitate was purified by recrystallization in MeOH/water (1:1, *V*/*V*). After dryness, compound **1** was collected as a pale yellow solid in yield of 80%. ^{1}H NMR (400 MHz, DMSO) δ: 8.32(s, 1H, OH), 7.88(d, J = 8.0 Hz, 2H, ArH), 7.84(s, 1H, CH), 7.59 (d, J = 8.0 Hz, 2H, ArH), 7.46-7.54 (m, 3H, ArH), 6.89 (d, J = 8.0 Hz, 2H, ArH).

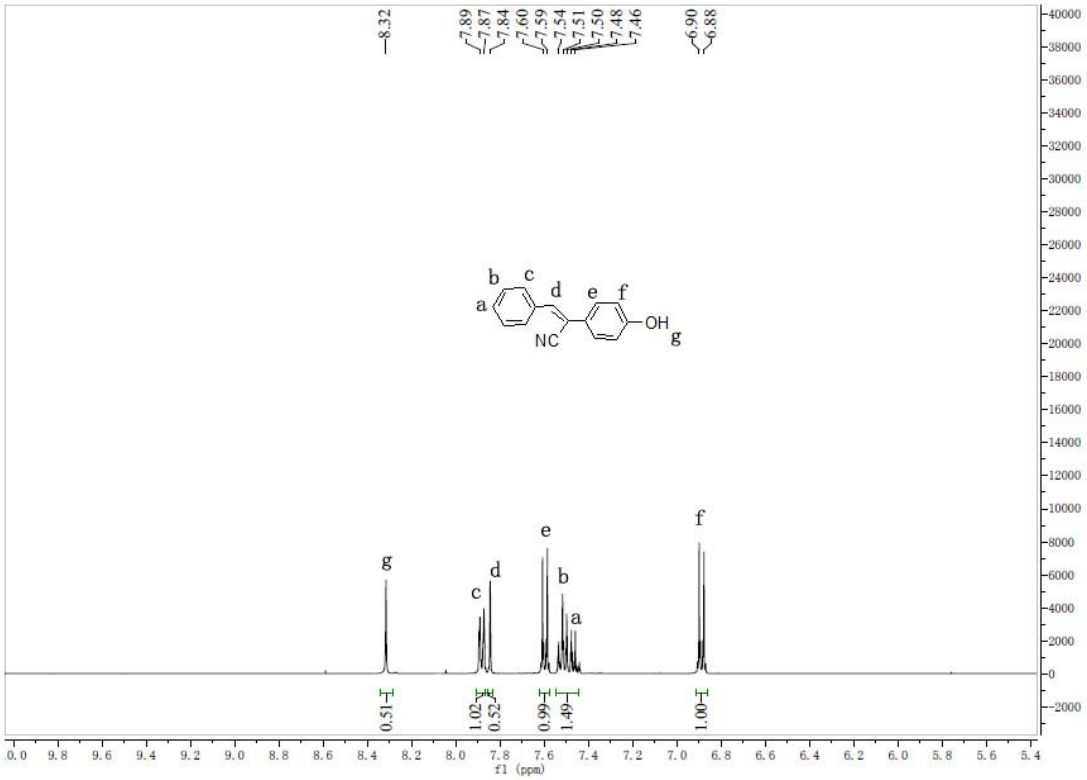


Figure S1. The ^{1}H NMR spectrum of compound **1**

2.2 Synthesis of compound 2.

Under N_2 atmosphere, a mixture of compound **1** (0.33g, 1.5mmol), 1-bromo-3-chloropropane (0.44g, 2.8mmol), and K_2CO_3 (0.36g, 2.6 mmol) was stirred and refluxed in 30 mL of dry MeCN for 24 h at 88°C. The reaction was monitored by TLC technique implying the disappearance of reactants. After reaction, the mixture was treated with 50 mL of HCl (1 M) and extracted with 40 mL of $CHCl_3$. The $CHCl_3$ layer was partitioned, washed by 20 mL of distilled water, dried over anhydrous $MgSO_4$, and then concentrated. The residue was treated by 20 mL of MeOH and the precipitate was obtained. The crude product was further purified by recrystallization in MeOH/CH_2Cl_2 (2:1, *V*/*V*). After dryness, compound **2** was collected as a pale yellow solid in yield of 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84(s, 1H, CH), 7.63(d, J = 8.0 Hz, 2H, ArH), 7.43-7.48 (m, 3H, ArH), 7.04 (d, J = 8.0 Hz, 2H, ArH), 6.99 (d, J = 8.0 Hz, 2H, ArH), 4.29 (t, J = 8.0 Hz, 2H, $ClCH_2$), 4.24 (t, J = 8.0 Hz, 2H, OCH_2), 2.35 (m, 2H, CH_2).

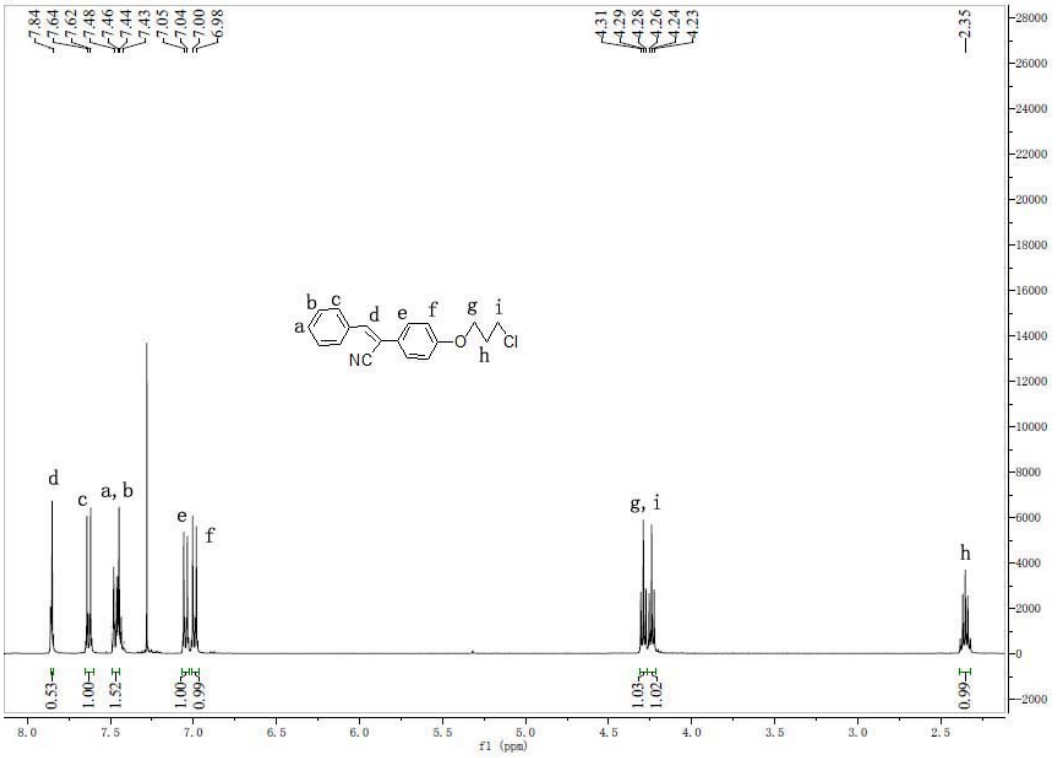


Figure S2. The ^{1}H NMR spectrum of compound **2**

2.3 Synthesis of compound 3.

Under N_2 atmosphere, a mixture of compound **2** (0.30g, 1.0mmol), 4-hydroxybenzaldehyde (0.20g, 1.6mmol), K_2CO_3 (0.28g, 2.0 mmol) and KI (0.1g, 0.6 mmol) was stirred and refluxed in 20 mL of dry MeCN for 20 h at 90 °C. The reaction was monitored by TLC technique implying the disappearance of reactants. After reaction, the mixture was treated with 40 mL HCl (1 M) and extracted with 30 mL $CHCl_3$. The $CHCl_3$ layer was partitioned, washed by 20 mL of distilled water, dried over anhydrous $MgSO_4$, and then concentrated. The residue was treated by 15 mL of MeOH and the precipitate was obtained. The crude product was further purified by column chromatography using CH_2Cl_2/hexane (1:1, *V*/*V*) as eluant. After dryness, compound **3** was collected as a pale yellow solid in yield of 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.89 (s, 1H, CHO), 7.83-7.87 (m, 4H, ArH and CH), 7.61(d, J = 8.0 Hz, 2H, ArH), 7.40-7.48 (m, 4H, ArH), 7.01 (d, J = 8.0 Hz, 2H, ArH), 6.97 (d, J = 8.0 Hz, 2H, ArH), 4.27 (t, J = 8.0 Hz, 2H, OCH_2), 4.22 (t, J = 8.0 Hz, 2H, OCH_2), 2.30-2.36 (m, 2H, CH_2). MALDI-TOF-MS ($C_{25}H_{21}NO_3$) Calcd.for m/z = 383.5, found: m/z = 385.9 (MH^+).

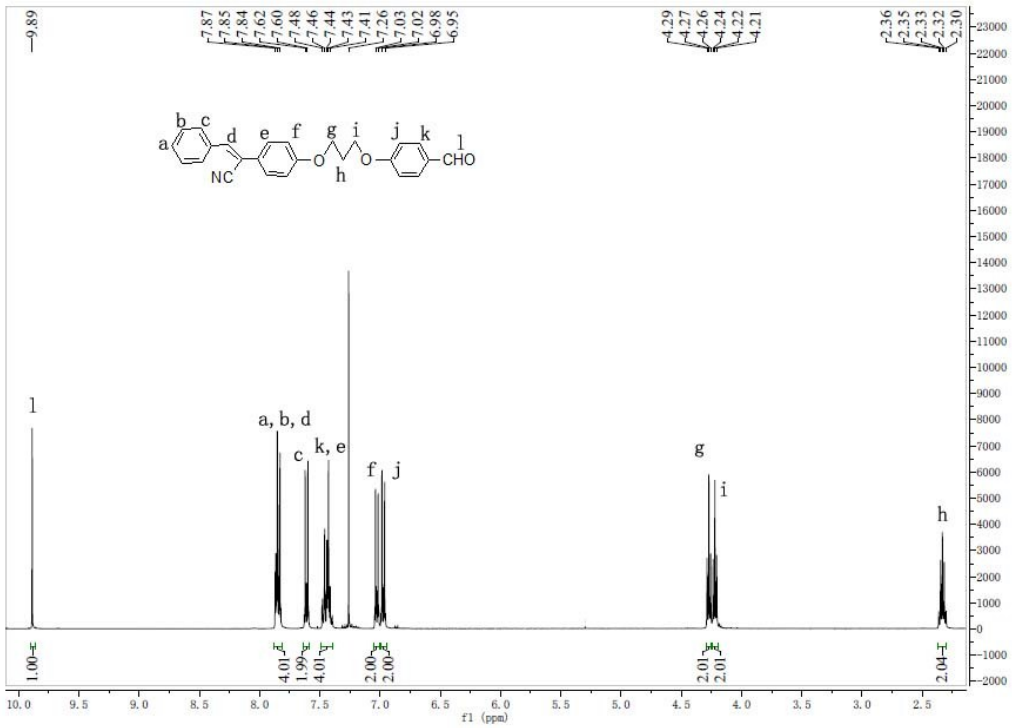


Figure S3. The ^{1}H NMR spectrum of compound **3**

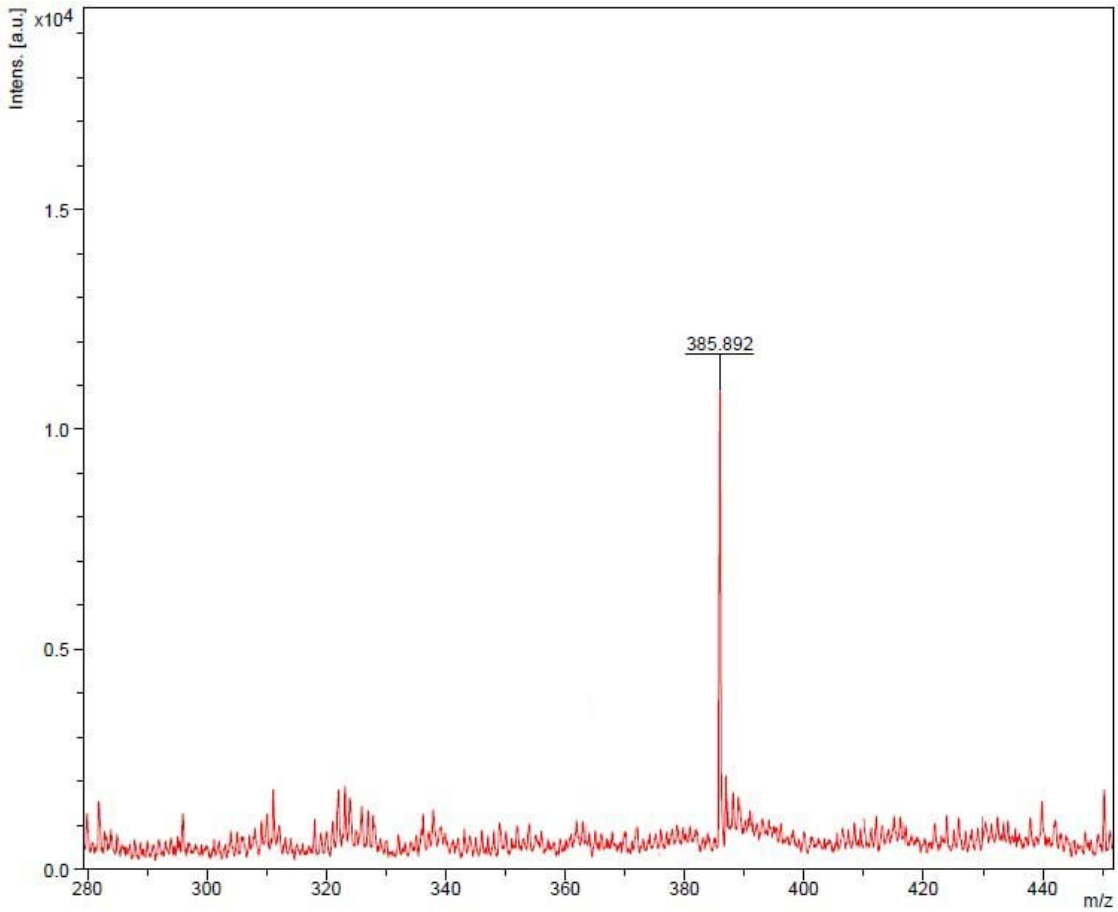


Figure S4. The MALDI-TOF-MS spectrum of compound **3**

2.4 Synthesis of compound 4.

Under N_2 atmosphere, a mixture of compound **2** (0.30g, 1.0mmol), 3,4-dihydroxybenzaldehyde (0.07g, 0.5mmol), K_2CO_3 (0.42g, 3.0 mmol) and KI (0.1g, 0.6 mmol) was stirred and refluxed in 20 mL of dry MeCN for 36 h at 90 °C. The reaction was monitored by TLC technique implying the disappearance of reactants. After reaction, the mixture was treated with 40 mL of HCl (1 M) and extracted with 30 mL of $CHCl_3$. The $CHCl_3$ layer was partitioned, washed by 20 mL of distilled water, dried over anhydrous $MgSO_4$, and then concentrated. The residue was treated by 15 mL of MeOH and the precipitate was obtained. The crude product was further purified by column chromatography using CH_2Cl_2/hexane (2:1, *V*/*V*) as eluant. After dryness, compound **4** was collected as a pale yellow solid in yield of 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.85 (s, 1H, CHO), 7.83 (d, J = 8.0 Hz, 4H, ArH), 7.57(d, J = 8.0 Hz, 4H, ArH), 7.37-7.46 (m, 10H, ArH and CH), 7.02 (d, J = 8.0 Hz, 1H, ArH), 6.94 (d, J = 8.0 Hz, 2H, ArH), 6.95 (d, J = 8.0 Hz, 2H, ArH), 4.28-4.31 (m, 4H, OCH_2), 4.22 (t, J = 8.0 Hz, 4H, OCH_2), 2.31-2.36 (m, 4H, CH_2). MALDI-TOF-MS ($C_{43}H_{36}N_2O_5$) Calcd.for m/z = 660.7, found: m/z = 683.8 (MNa^+).

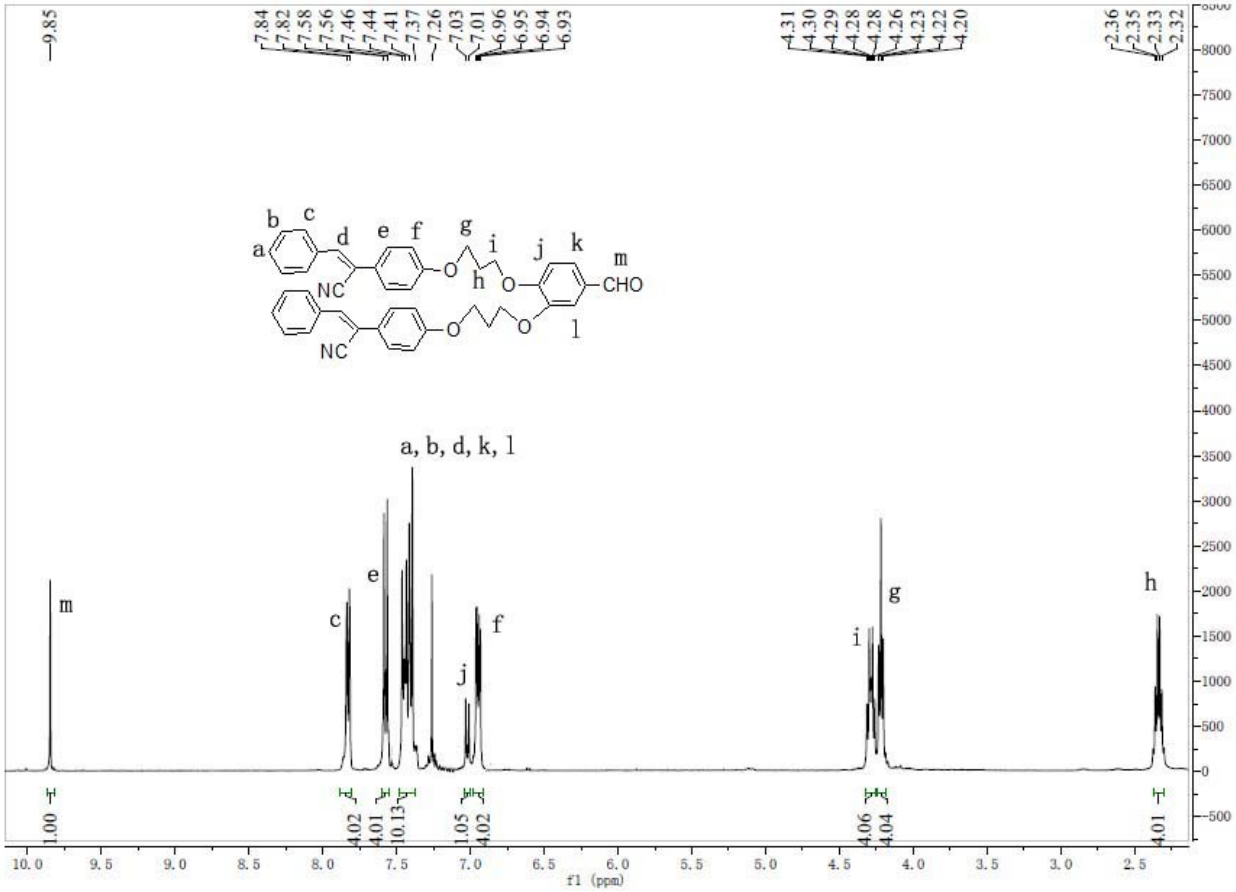


Figure S5. The ^{1}H NMR spectrum of compound **4**

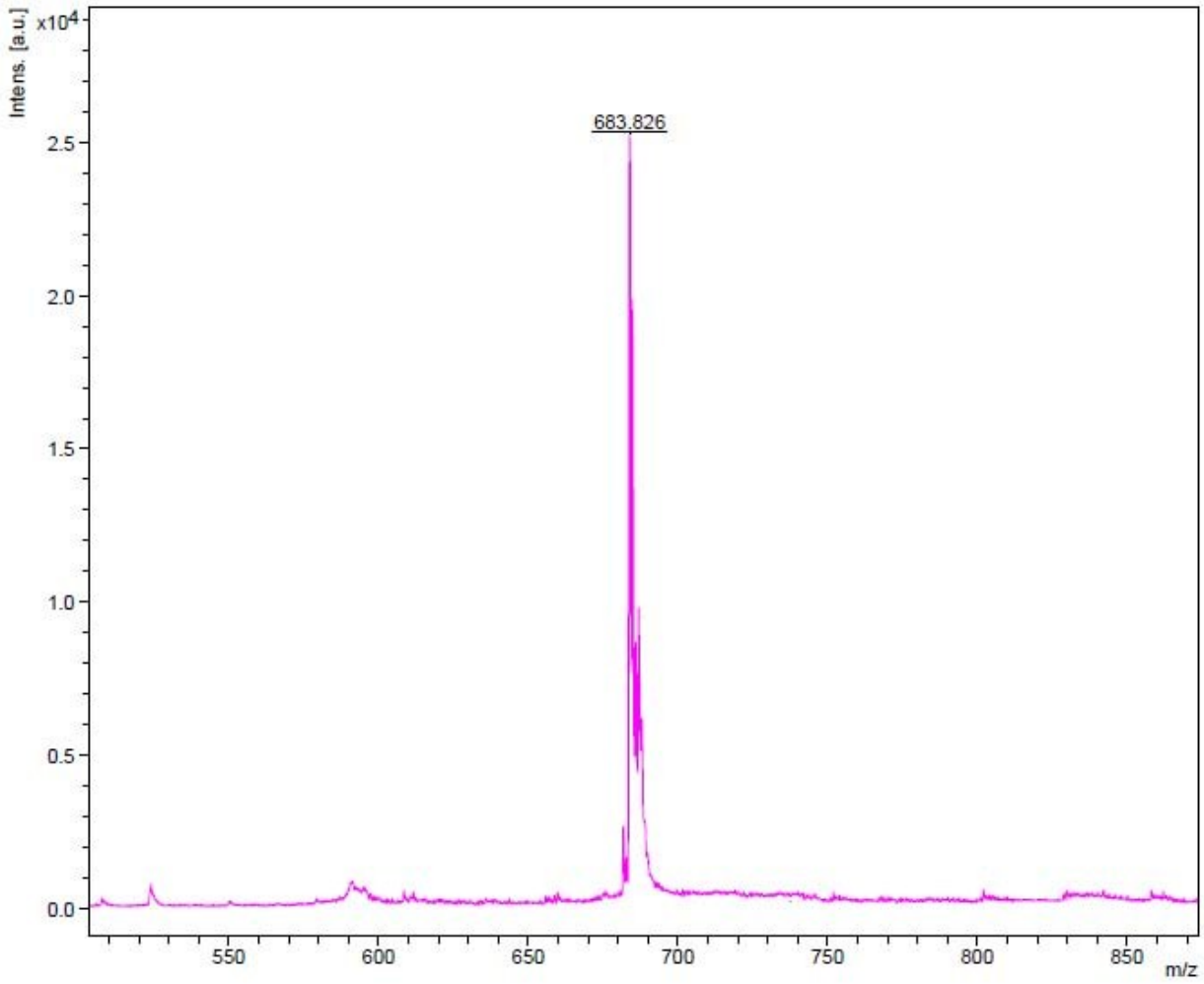


Figure S6. The MALDI-TOF-MS spectrum of compound **4**

2.5 Synthesis of compound 5.

Under N_2 atmosphere, a mixture of compound **2** (0.50g, 1.7mmol), 2,3,4-trihydroxybenzaldehyde (0.07g, 0.5mmol), K_2CO_3 (0.66g, 4.8 mmol) and KI (0.1g, 0.6 mmol) was stirred and refluxed in 20 mL of dry MeCN for 48 h at 90 °C. The reaction was monitored by TLC technique implying the disappearance of reactants. After reaction, the mixture was treated with 40 mL of HCl (1 M) and extracted with 30 mL of $CHCl_3$. The $CHCl_3$ layer was partitioned, washed by 20 mL of distilled water, dried over anhydrous $MgSO_4$, and then concentrated. The residue was treated by 15 mL of MeOH and the precipitate was obtained. The crude product was further purified by column chromatography using CH_2Cl_2/hexane (4:1, *V*/*V*) as eluant. After dryness, compound **5** was collected as a pale yellow solid in yield of 66%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.24 (s, 1H, CHO), 6.89-7.86 (m, 31H, ArH), 6.81 (d, J = 8.0 Hz, 1H, ArH), 4.37 (t, J = 8.0 Hz, 2H, OCH_2), 4.27 (t, J = 8.0 Hz, 2H, OCH_2), 4.12-4.28 (m, 8H, OCH_2), 2.12-2.31 (m, 6H, CH_2). MALDI-TOF-MS ($C_{61}H_{51}N_3O_7$) Calcd.for m/z = 938.1, found: m/z = 976.7 (MK^+).

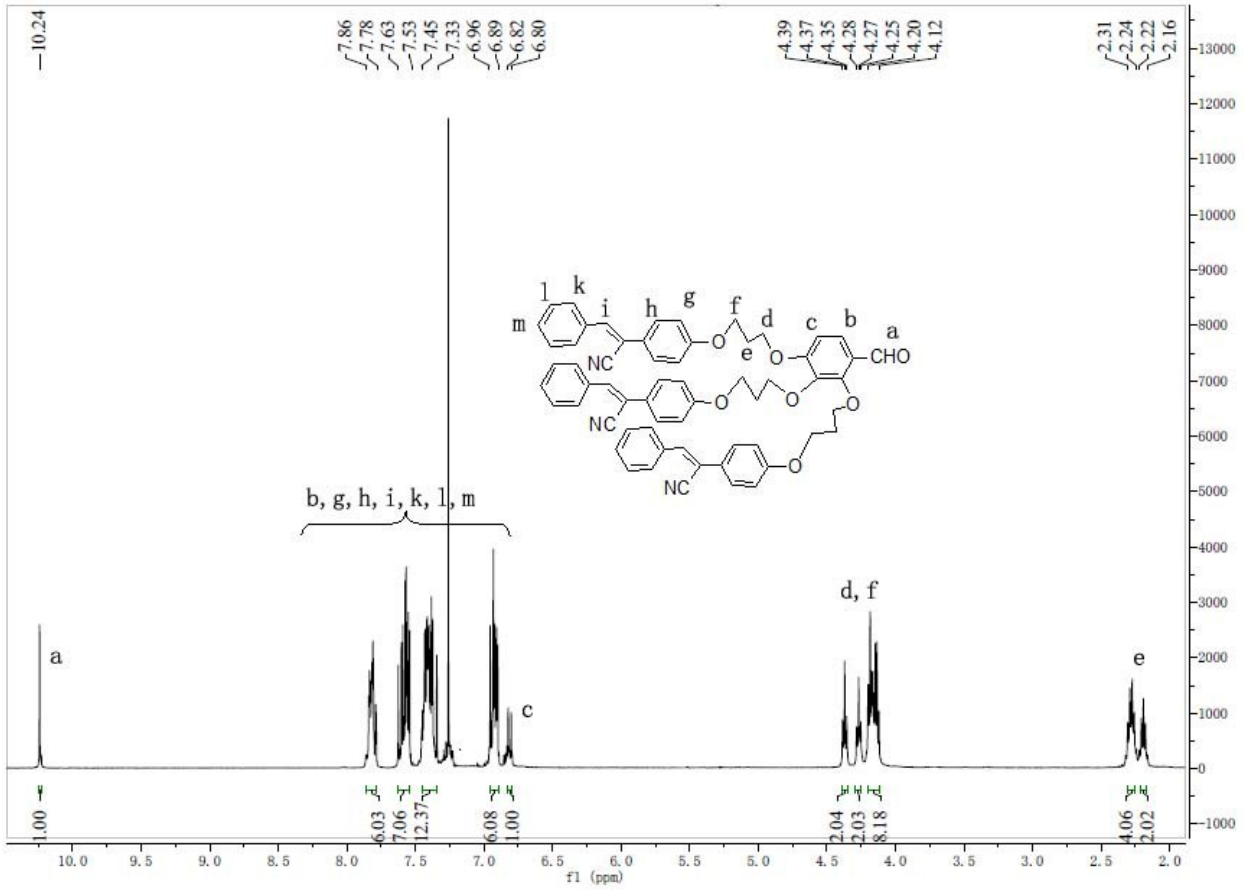


Figure S7. The ^{1}H NMR of compound **5**

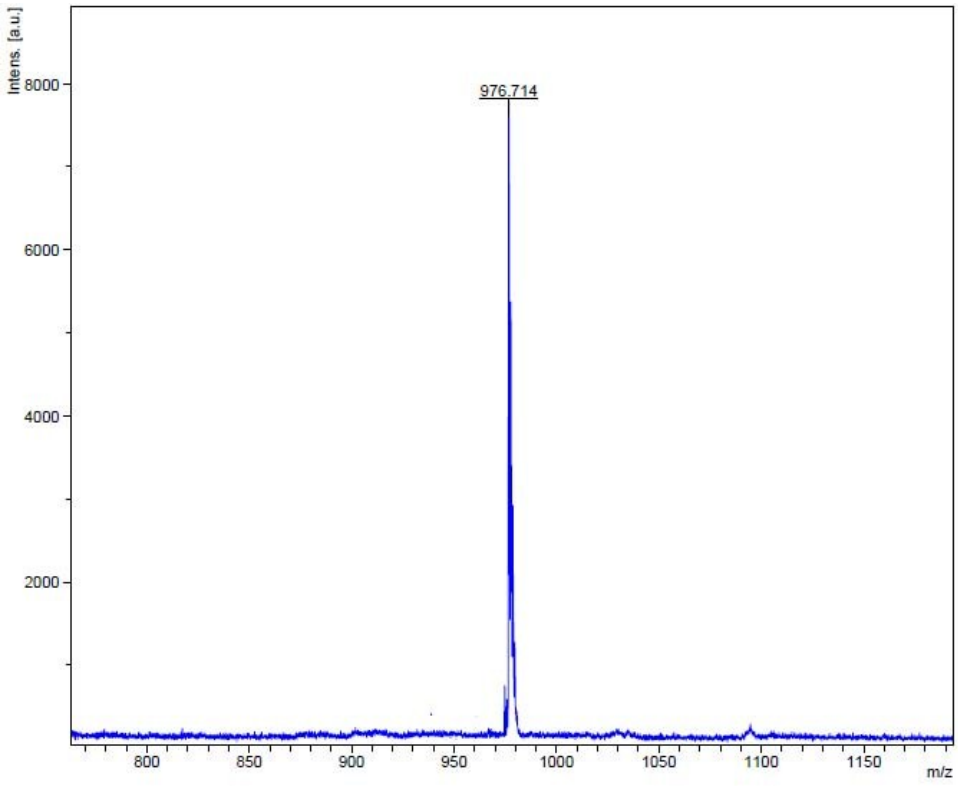


Figure S8. The MALDI-TOF-MS spectrum of compound **5**

2.6 Syntheses of compounds 7, 8, 9.

Under the protection of N_2 atmosphere, three drops of trifluoroacetic acid was added in the CH_2Cl_2 (90 mL) solution containing formyl derivative **3** (**4** or **5**, 1 mmol) and 2,4-dimethyl-1*H*-pyrrole (0.21g, 2.3 mmol). The mixture was stirred at room temperature for 8 h. 2,3-dichloro-5,6-dicyano-p-benzoquinone (0.25 g, 1.1 mmol) was added in the reaction mixture. The mixture was reacted under room temperature for another 4 h. Furthermore, triethylamine (9.7 mL, 0.07 mol) and $BF_3{\cdot}Et_2O$ (9.7 mL, 0.08 mol) was successively added into the mixture. The mixture was stirred unceasingly overnight at room temperature. After reaction, the obtained mixture was partitioned by water (ca. 100 mL). The organic layer was separated, washed with $NaHCO_3$ solution (5%, 100 mL) and distilled water (100 mL × 2). The organic portion was dried over anhydrous $MgSO_4$ and then was concentrated under reduced pressure. The crude product was purified by column chromatography (eluent: CH_2Cl_2). Compounds **7**, **8** and **9** were collected as red solids in yields of 28%, 24% and 21%, respectively.

Compound **7**: ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 1.43 (s, 6H, CH_3), 2.34 (s, 2H, J = 7.2Hz, CH_2), 2.55 (s, 6H, CH_3), 4.21~4.26 (m, 4H, OCH_2), 5.97 (s, 2H, ArH), 7.00 (d, 2H, J = 8.0Hz, ArH), 7.02 (d, 2H, J = 8.0Hz, ArH), 7.16 (d, 2H, J = 8.0Hz, ArH), 7.42-7.46 (m, 4H, ArH), 7.62 (d, 2H, J = 8.0Hz, ArH), 7.86 (d, 2H, J = 8.0Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 14.65, 29.27, 53.47, 64.40, 64.59, 111.13, 114.97, 118.05, 121.14, 127.39, 128.95, 129.09, 129.26, 130.23, 140.28, 141.72, 143.16, 155.28, 159.38, 159.70; MALDI-TOF-MS Calcd.for m/z = 601.1, found: m/z = 602.1(MH^+). HR-MS(ESI) ($C_{37}H_{34}BF_2N_3O_2$) $[M+K]^+$: Calcd.: 640.2350. found: 640.2361(MK^+), 624.2610 (MNa^+).

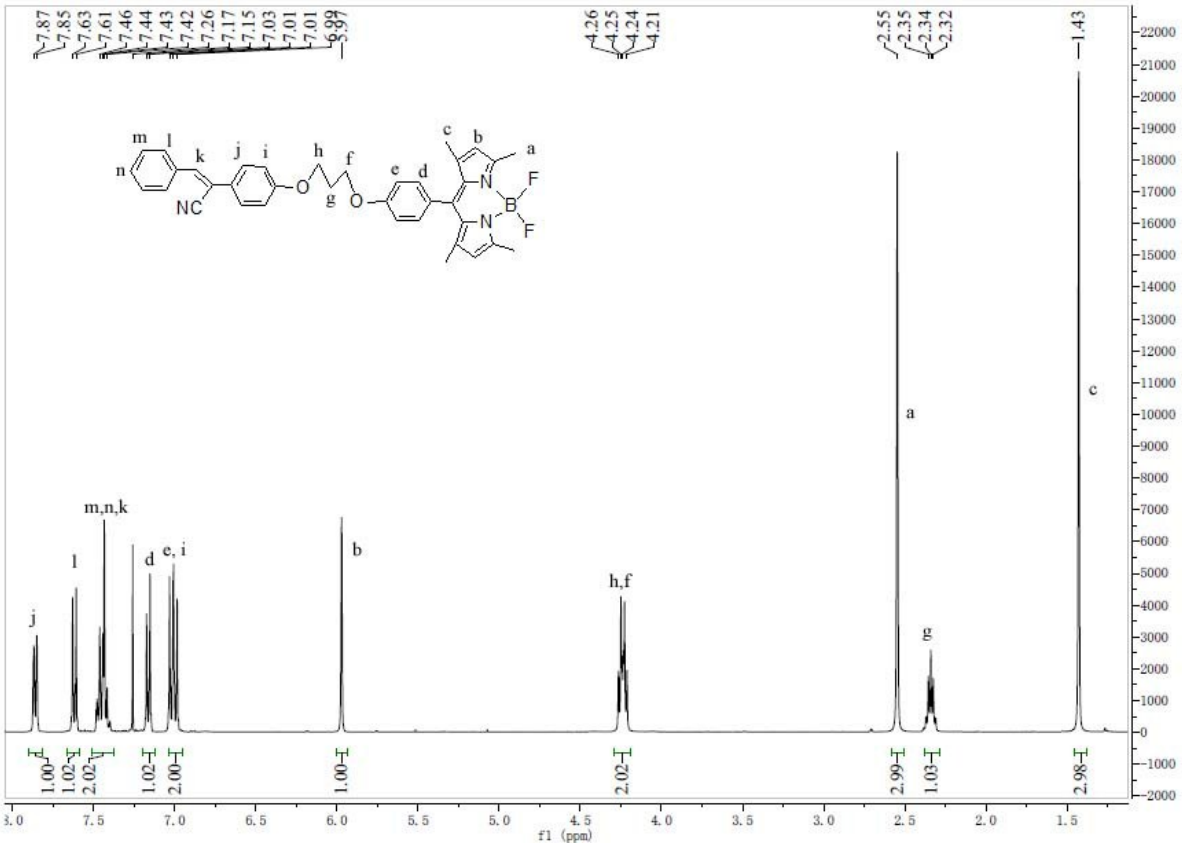


Figure S9. The ^{1}H NMR of compound **7**

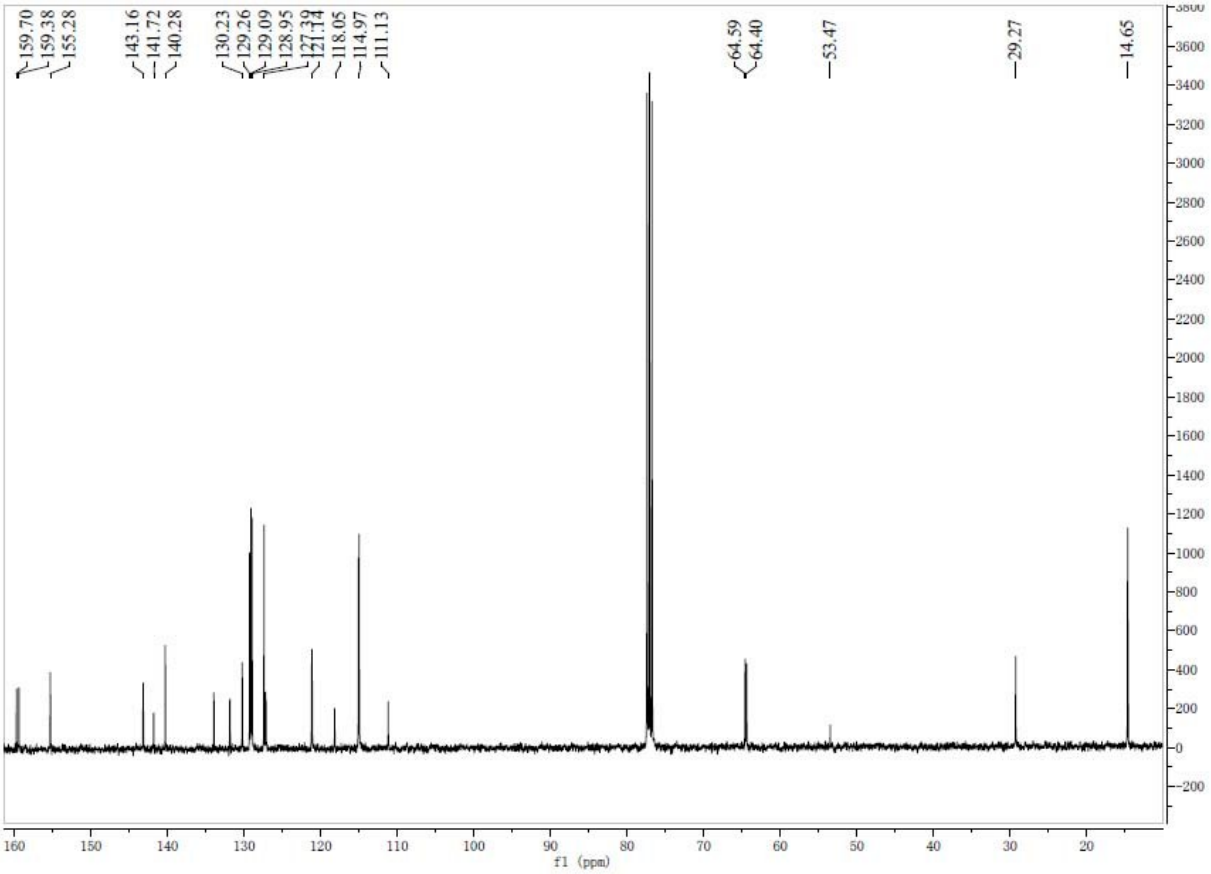


Figure S10. The ^{13}C NMR of compound **7**

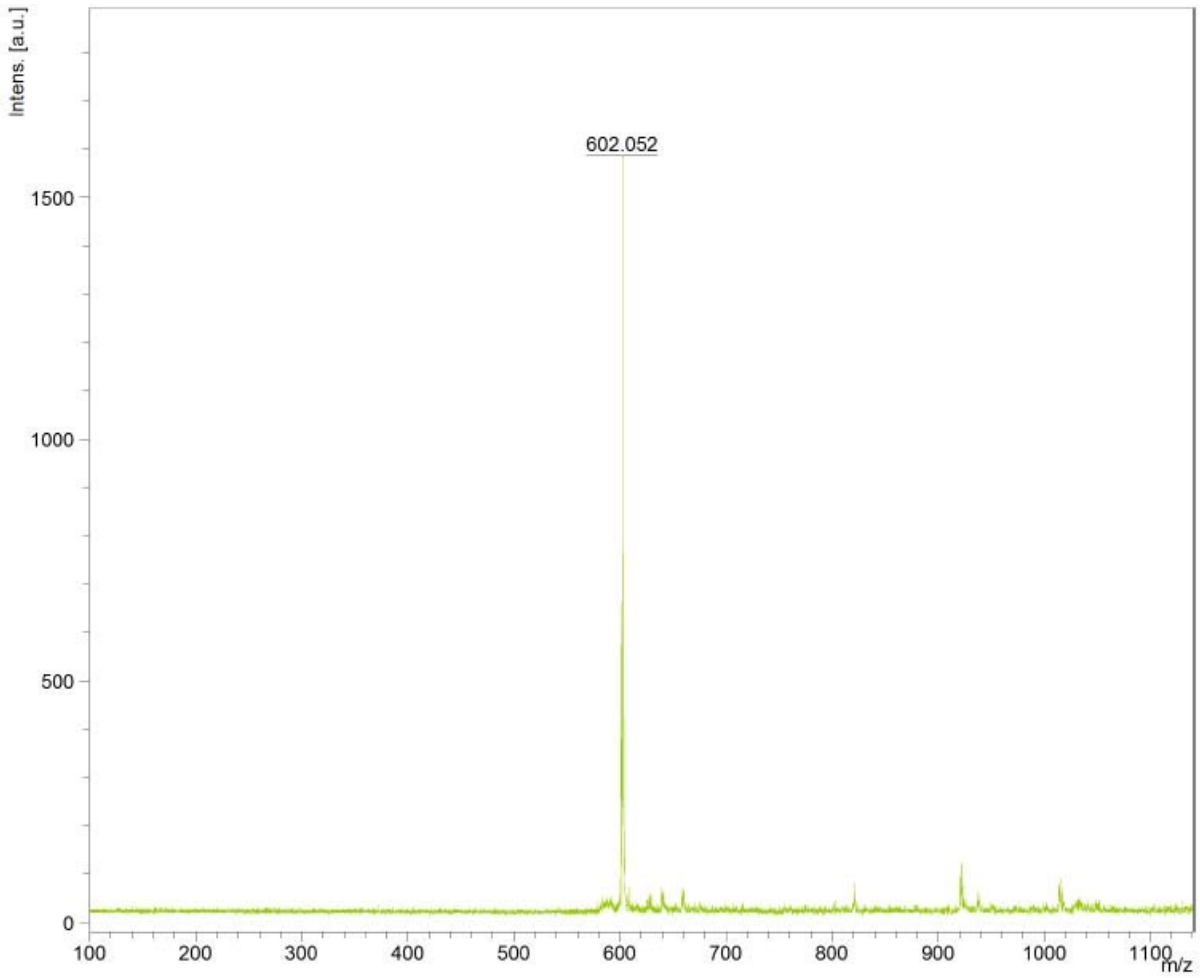


Figure S11. The MALDI-TOF-MS spectrum of compound **7**

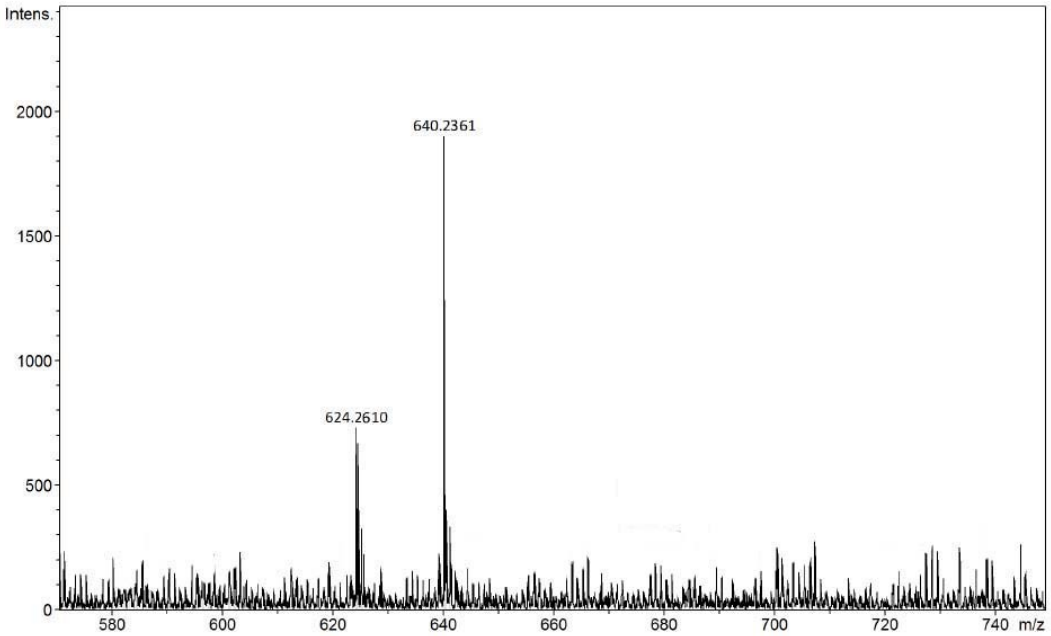


Figure S12. The HR-MS spectrum of compound **7**

Compound **8:** ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 1.46 (s, 6H, CH_3), 2.24-2.35 (m, 4H, CH_2), 2.54 (s, 6H, CH_3), 4.13~4.26 (m, 8H, OCH_2), 5.97 (s, 2H, ArH), 6.80-7.86 (m, 23H, CH and ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 14.59, 29.37, 29.71, 31.94, 64.45, 64.53, 65.56, 65.94, 111.15, 113.62, 113.99, 114.90, 118.14, 120.33, 121.02, 121.16, 128.56, 128.92, 129.63, 140.27, 142.92, 143.08, 149.34, 155.44, 159.49, 159.69; MALDI-TOF-MS Calcd.for *m*/*z* = 878.4, found: *m*/*z* = 860.7(M-F)$^{+}$. HR-MS(ESI) ($C_{55}H_{49}BF_2N_4O_4$) [M-F]$^{+}$: Calcd.: 859.3835. found:859.3852.

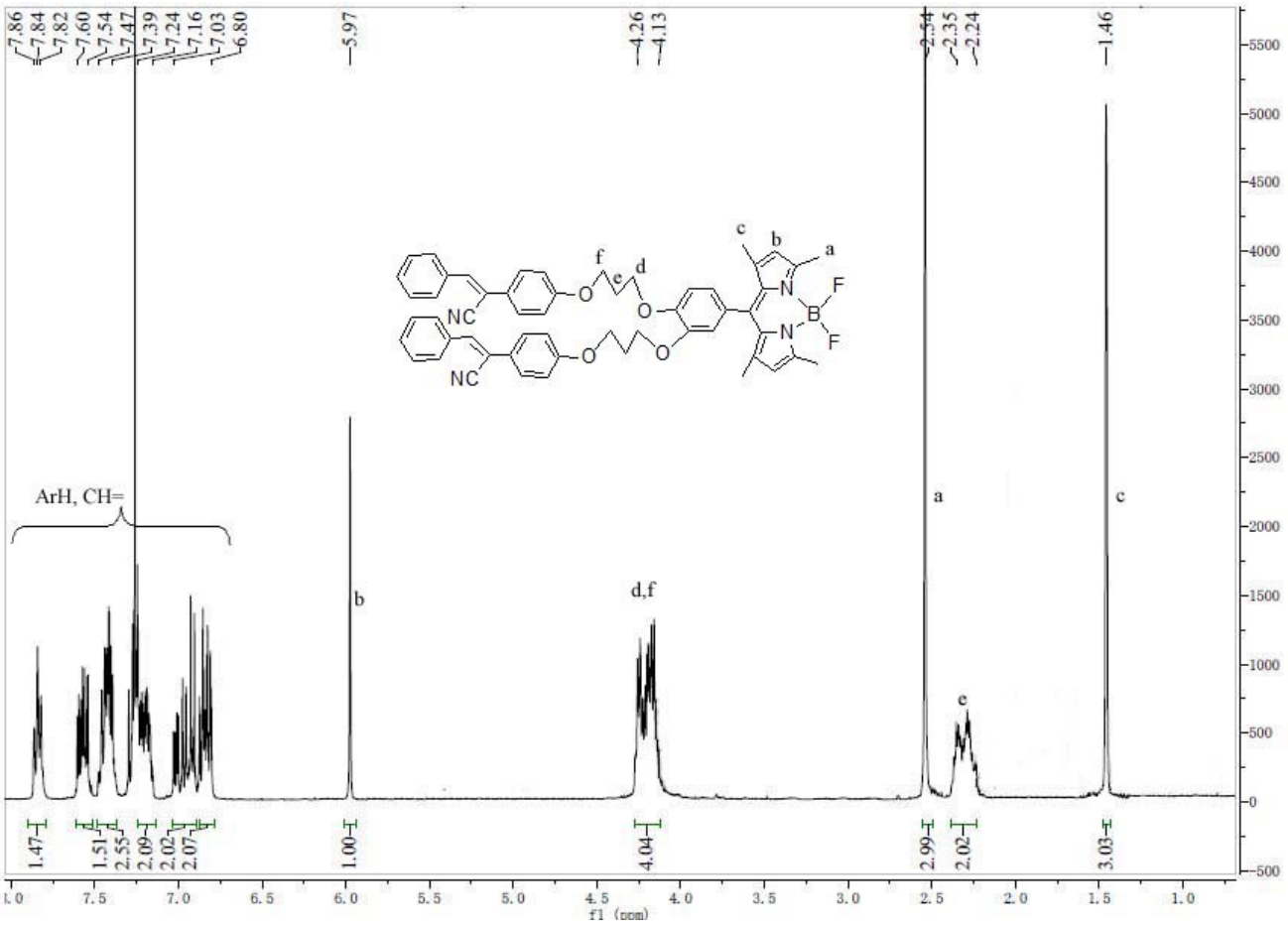


Figure S13. The ^{1}H NMR of compound **8**

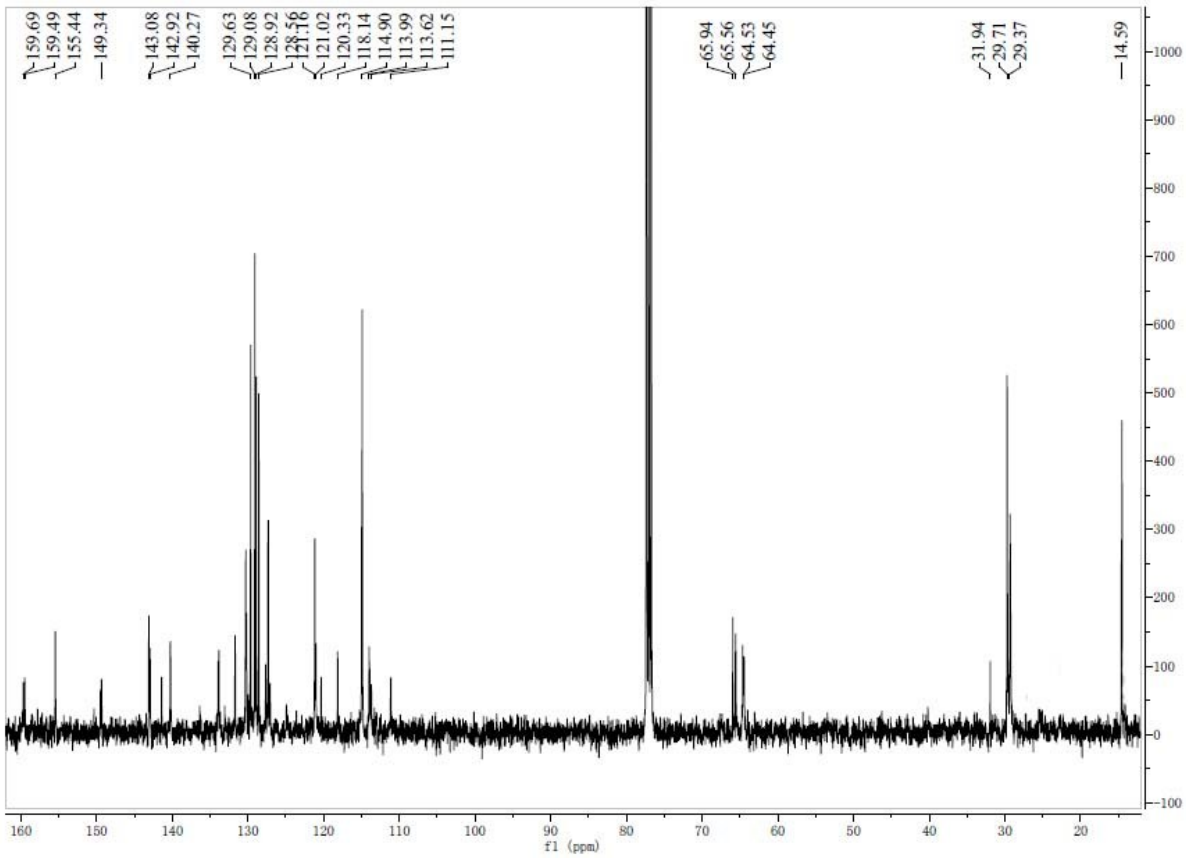


Figure S14. The ^{13}C NMR of compound **8**

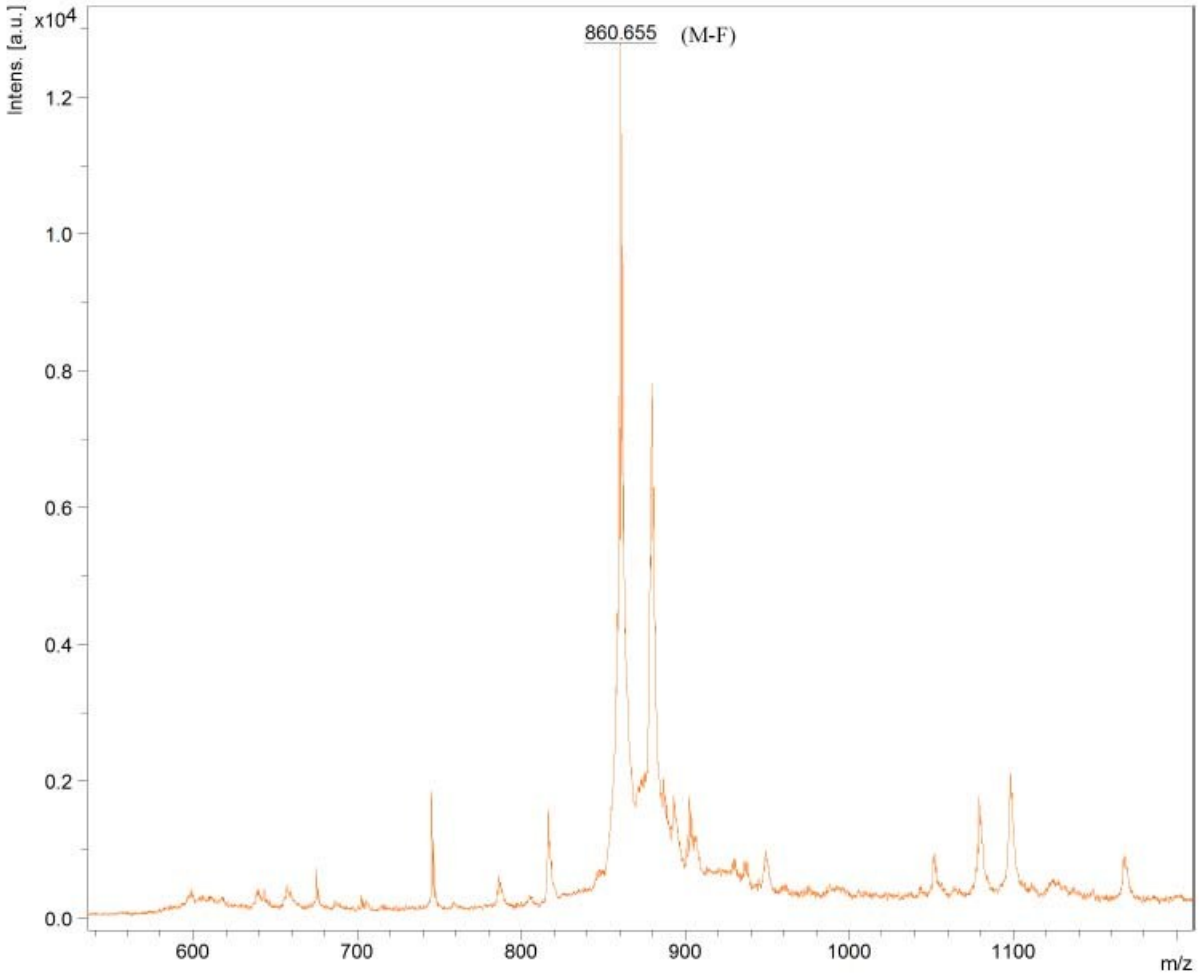


Figure S15. The MALDI-TOF-MS spectrum of compound **8**

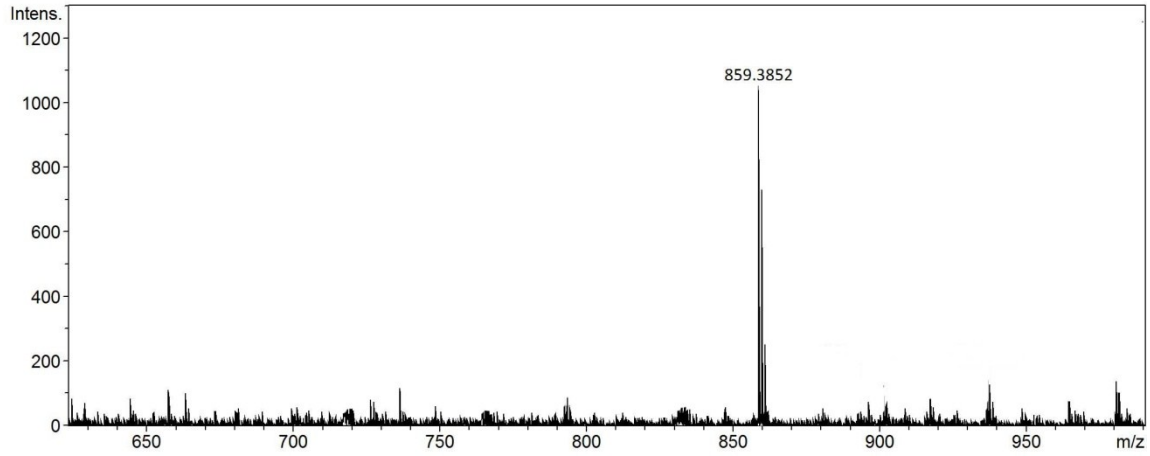


Figure S16. The HR-MS spectrumof compound **8**

Compound **9:** ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 1.46 (s, 6H, CH_3), 1.92-2.33 (m, 6H, CH_2), 2.54 (s, 6H, CH_3), 3.79 (t, 2H, J=7.2 Hz, OCH_2), 4.16~4.26 (m, 10H, OCH_2), 5.91 (s, 2H, ArH), 6.79-7.85 (m, 32H, CH and ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 14.30, 29.30, 29.74, 30.15, 31.97, 64.29, 64.53, 65.35, 65.62, 69.49, 69.77, 108.92, 110.97, 111.17, 114.90, 118.22, 121.21, 121.69, 124.06,

126.55, 126.91, 127.17, 127.37, 128.91, 129.09, 130.09, 130.24, 131.86, 133.87, 134.01, 139.35, 139.86, 140.01, 14028, 141.96, 142.50, 150.04, 154.13, 155.26, 159.67; MALDI-TOF-MS Calcd.for *m*/*z* = 1136.5, found: 1138.1(M-F)$^+$. HR-MS(ESI) ($C_{73}H_{64}BF_2N_5O_6$) [M-F]$^+$: Calcd.: 1136.4939. found: 1136.4933(M-F)$^+$.

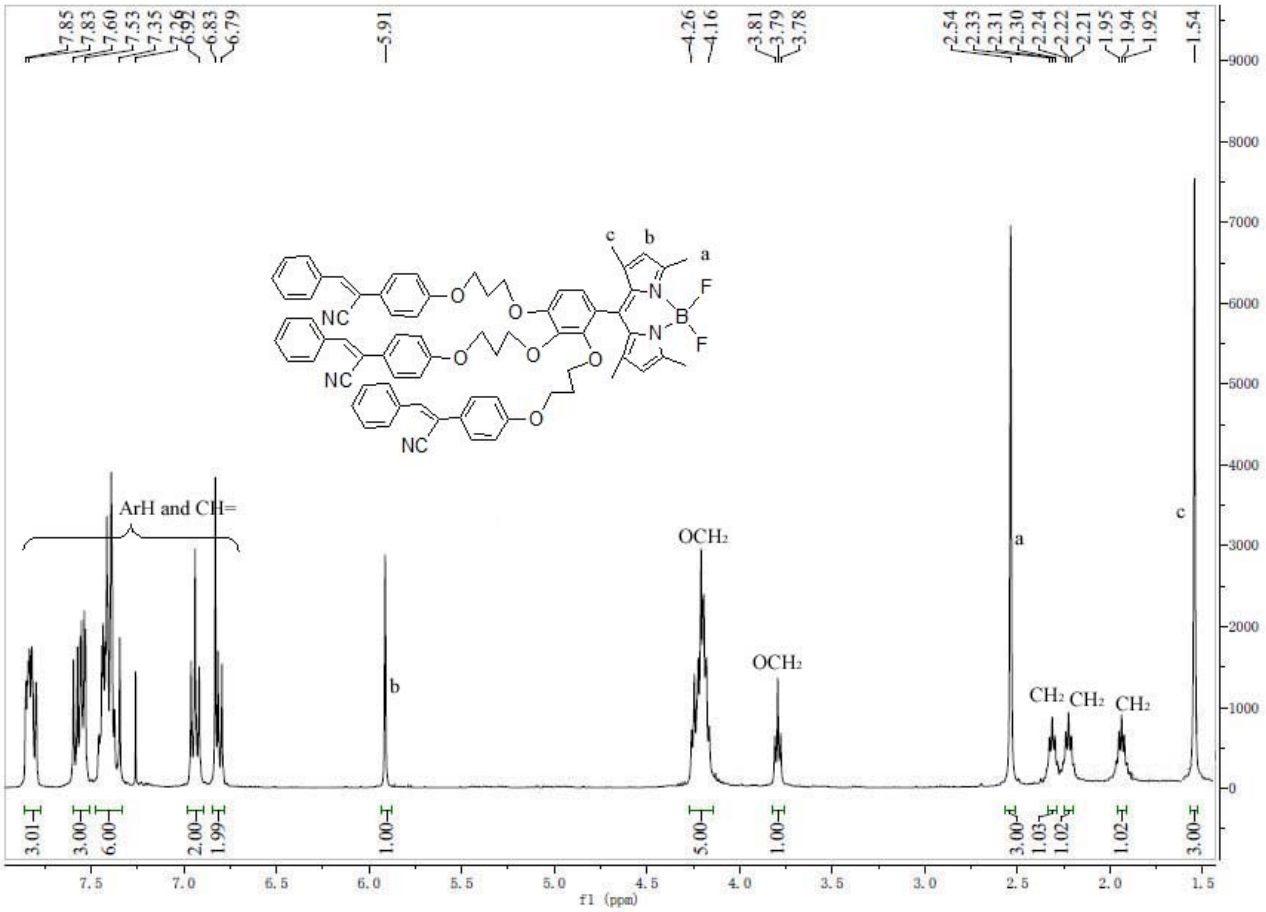


Figure S17. The ^{1}H NMR of compound **9**

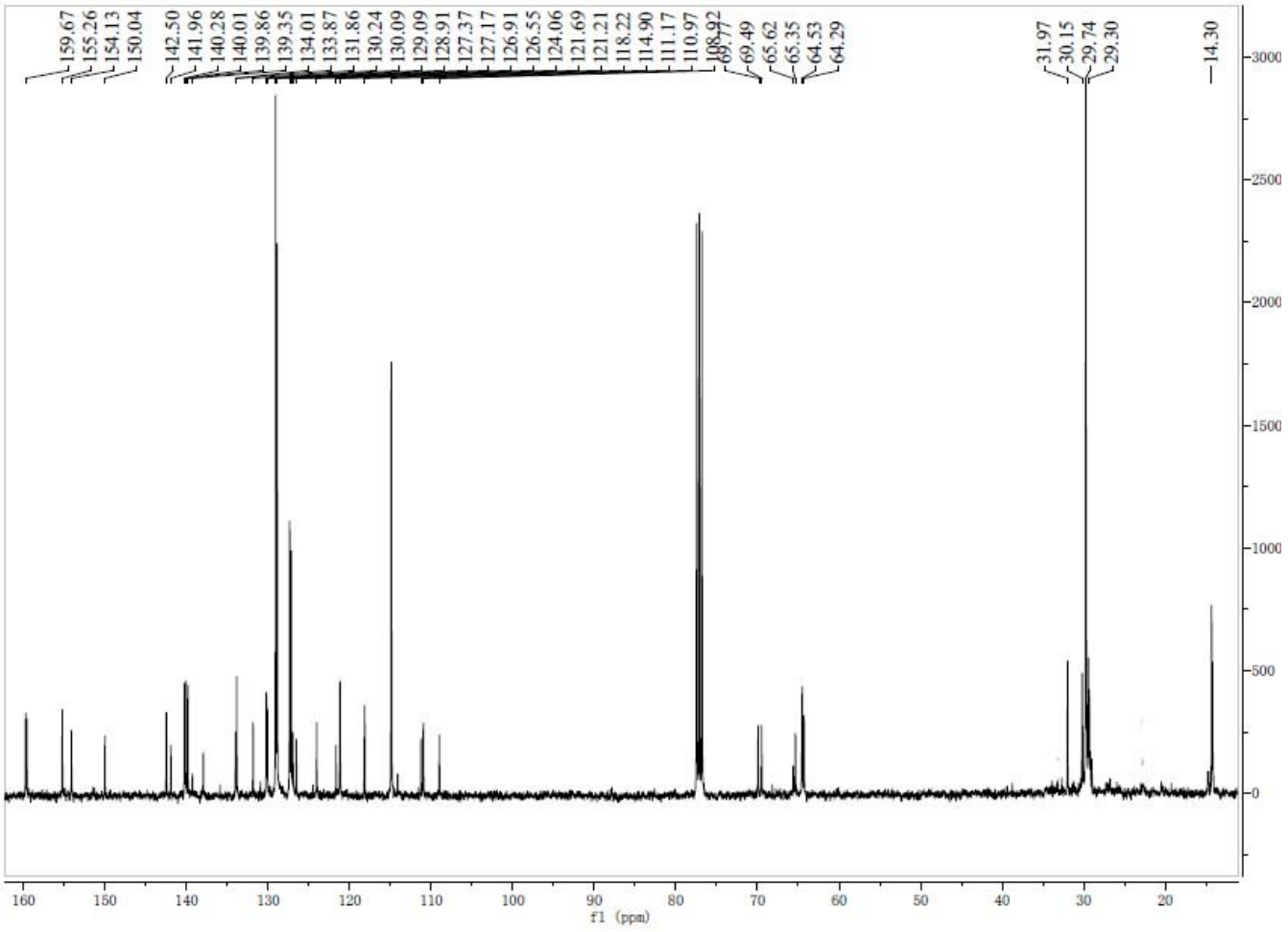


Figure S18. The ^{13}C NMR of compound **9**

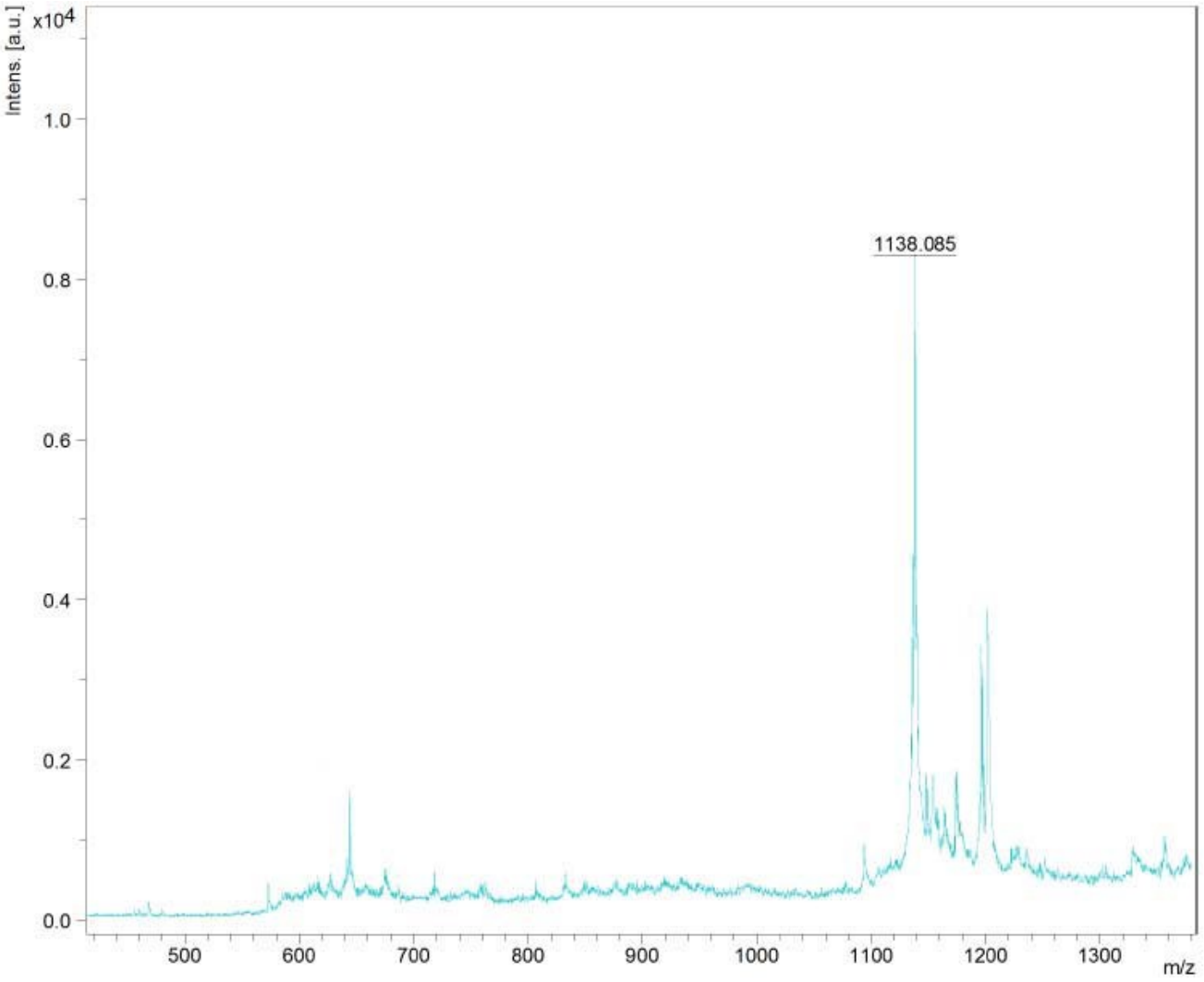


Figure S19. The MALDI-TOF-MS spectrum of compound **9**

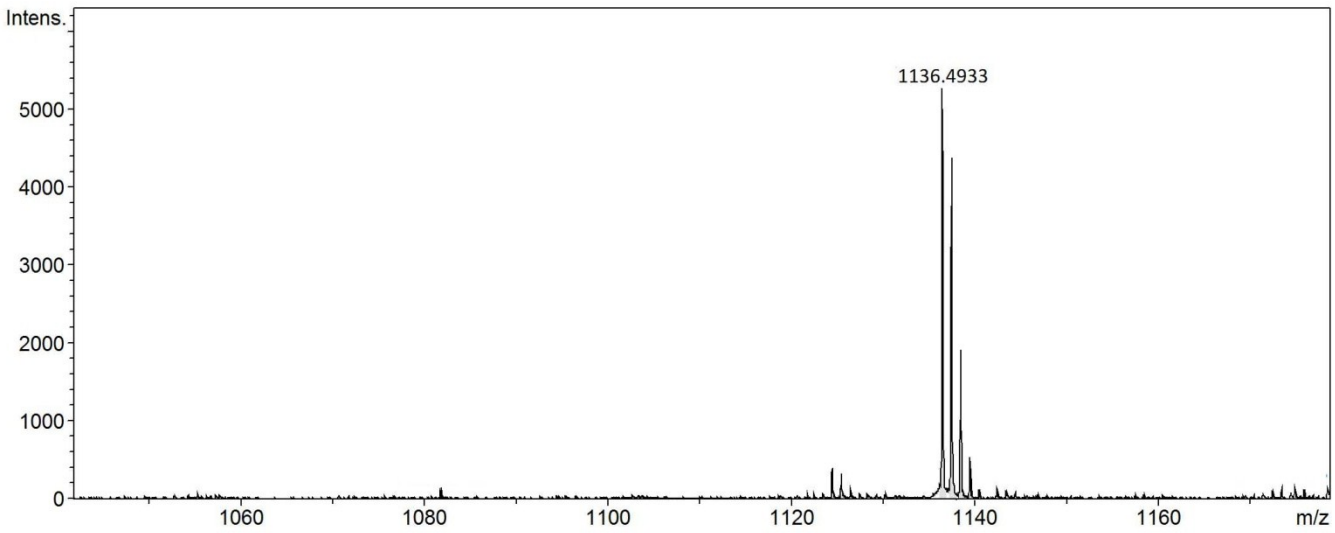


Figure S20. The HR-MS spectrum of compound **9**

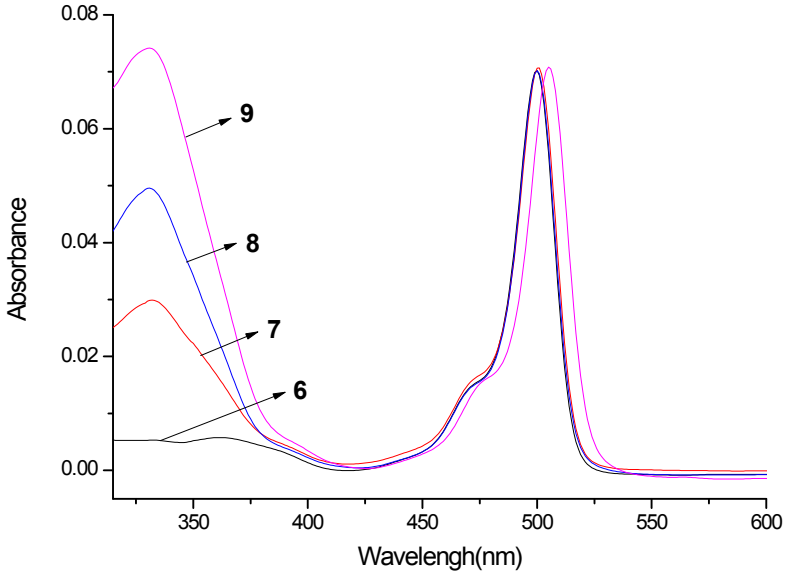


Figure S21 The UV-Vis absorption spectra of compounds **6**, **7**, **8** and **9** in THF solution (1×10^{-6} M).

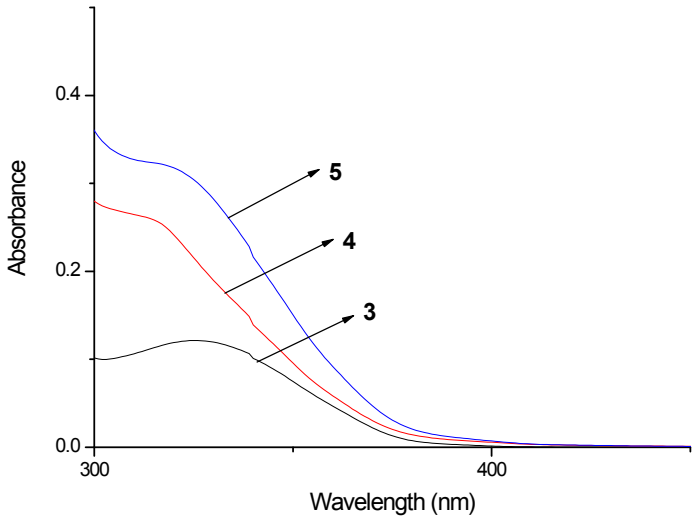


Figure S22 The UV-Vis absorption spectra of compounds **3**, **4** and **5** in THF solution (1×10^{-5} M).

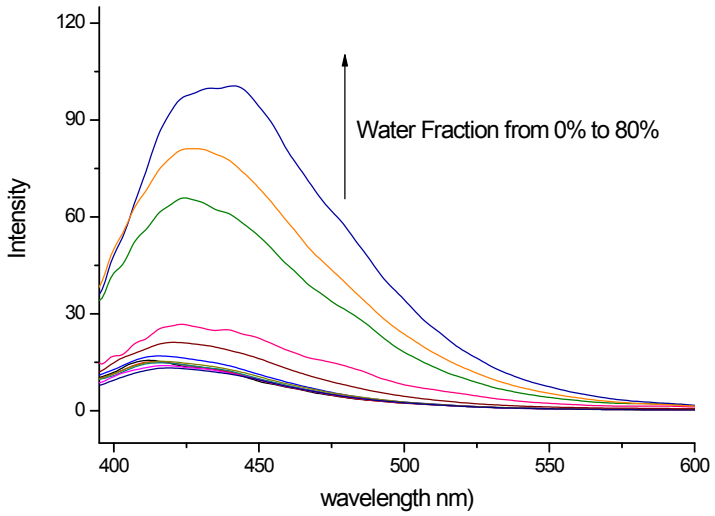


Figure S22 The fluorescence spectra of compound **3** with different fractions of H_2O in THF/H_2O mixtures (1×10^{-5} M, λ_{ex} = 330 nm).

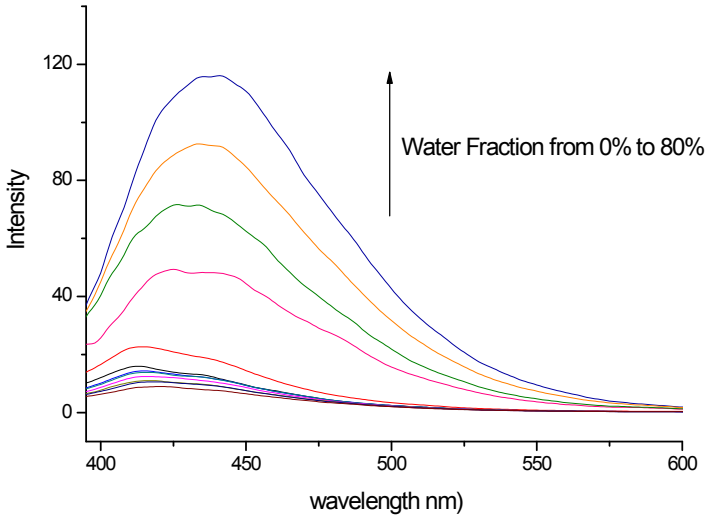


Figure S23 The fluorescence spectra of compound **4** with different fractions of H_2O in THF/H_2O mixtures (1×10^{-5} M, λ_{ex} = 330 nm).

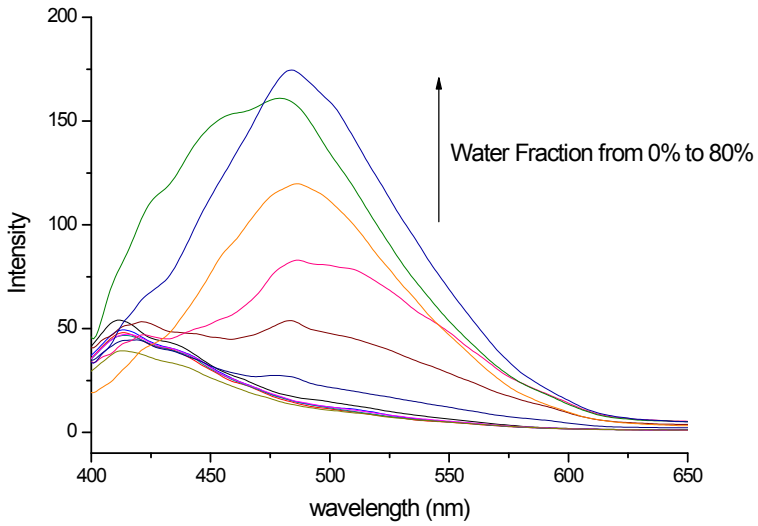


Figure S24 The fluorescence spectra of compound **5** with different fractions of H_2O in THF/H_2O mixtures (1×10^{-5} M, λ_{ex} = 330 nm).

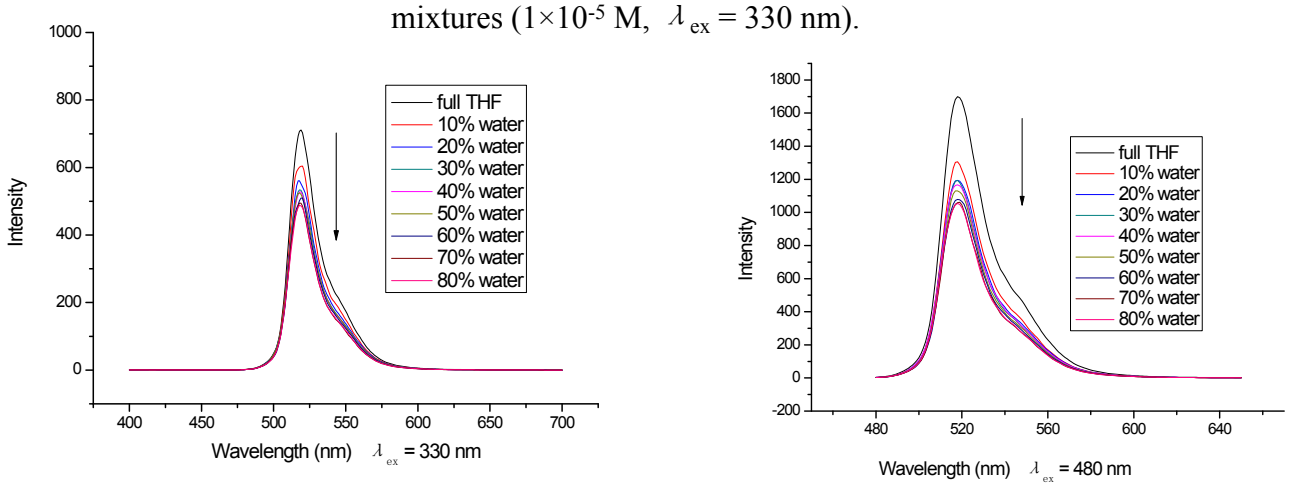


Figure S25 The fluorescence spectra of compound **6** with different fractions of H_2O in THF/H_2O mixtures (1×10^{-5} M).

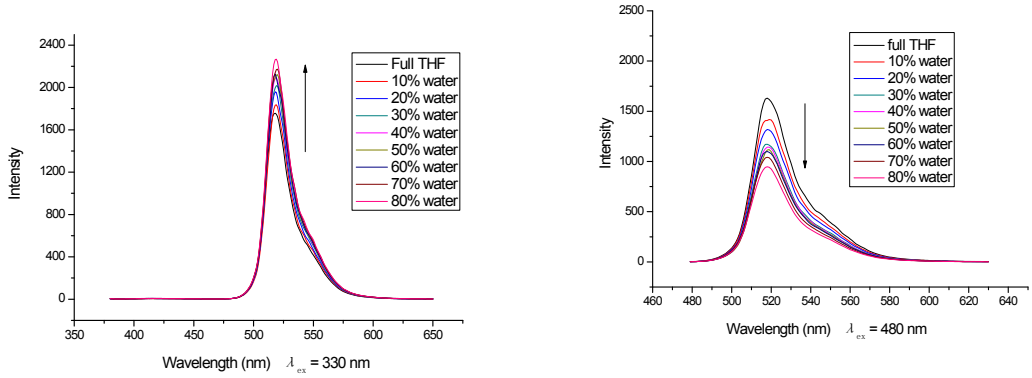


Figure S26 The fluorescence spectra of compound **7** with different fractions of H_2O in THF/H_2O mixtures (1×10^{-5} M).

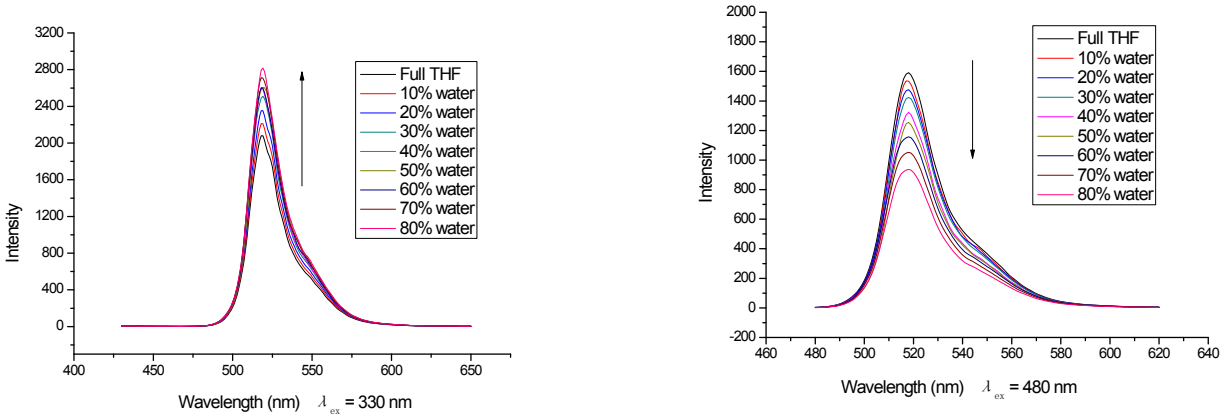


Figure S27 The fluorescence spectra of compound **8** with different fractions of H_2O in THF/H_2O mixtures (1×10^{-5} M).

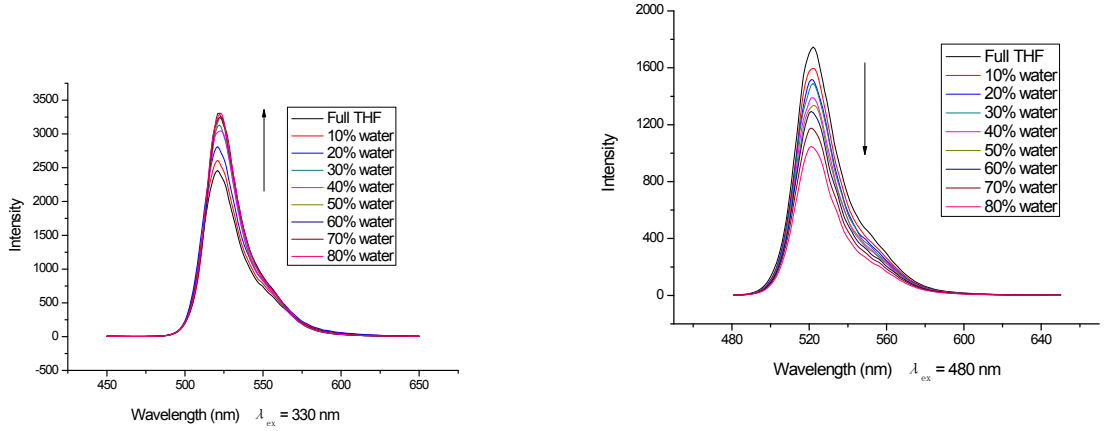


Figure S28 The fluorescence spectra of compound **9** with different fractions of H_2O in THF/H_2O mixtures (1×10^{-5} M).

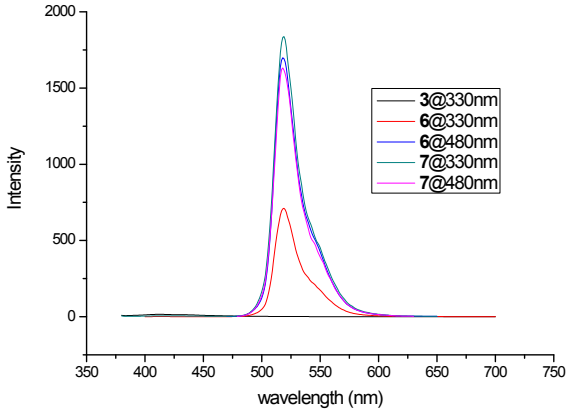


Figure S29 The fluorescence spectra of compound **3**, **6** and **7** (1×10^{-5} M in THF solution) excited at λ = 330 and 480 nm, respectively.

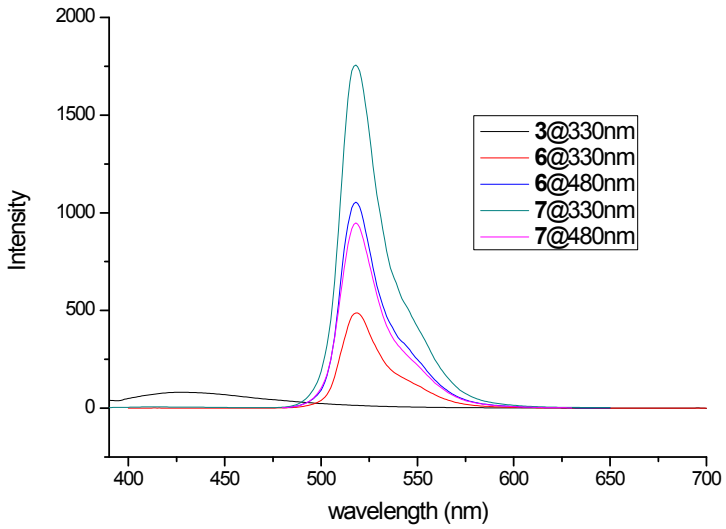


Figure S30 The fluorescence spectra of compound **3**, **6** and **7** (1×10^{-5} M in THF/water(V:V=2:8)) excited at λ = 330 and 480 nm, respectively.

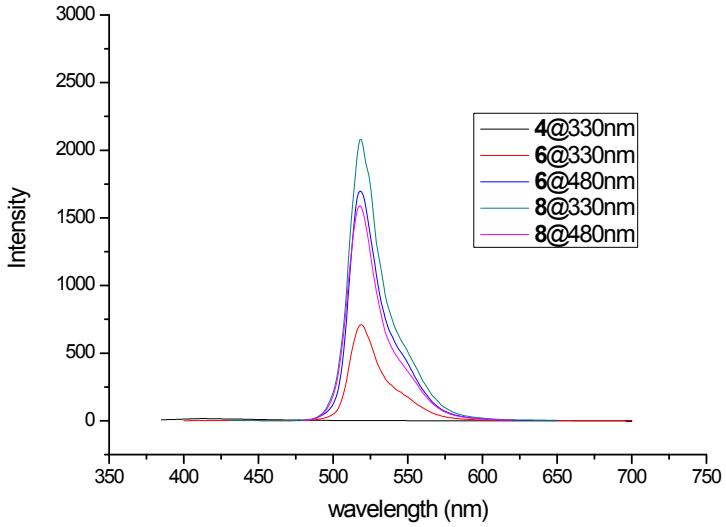


Figure S31 The fluorescence spectra of compound **3**, **6** and **8** (1×10^{-5} M in THF solution) excited at λ = 330 and 480 nm, respectively.

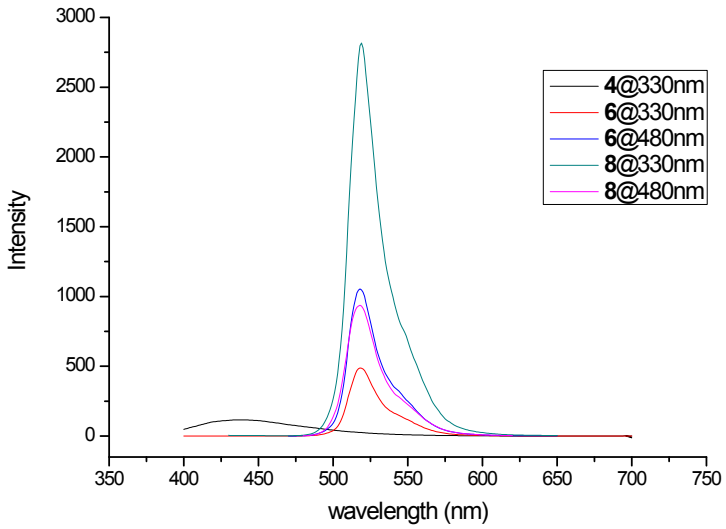


Figure S32 The fluorescence spectra of compound **3**, **6** and **8** (1×10^{-5} M in THF/water(V:V=2:8)) excited at λ = 330 and 480 nm, respectively.

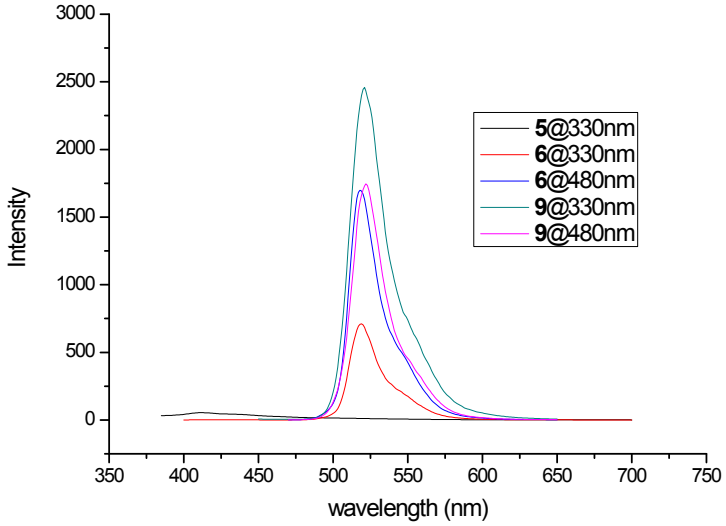


Figure S33 The fluorescence spectra of compound **3**, **6** and **9** (1×10^{-5} M in THF solution) excited at λ = 330 and 480 nm, respectively.

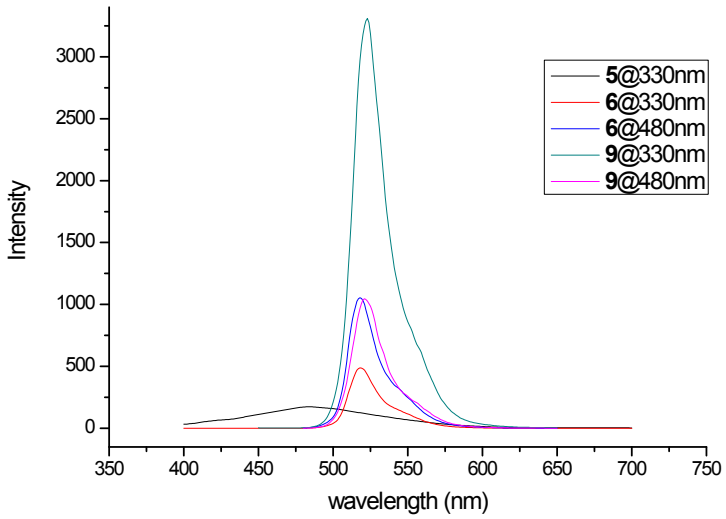


Figure S34 The fluorescence spectra of compound **3**, **6** and **9** (1×10^{-5} M in THF/water(*V*:*V*=2:8)) excited at λ = 330 and 480 nm, respectively.

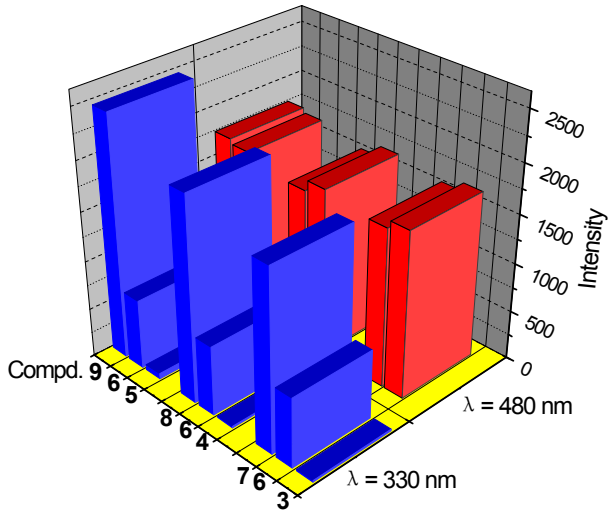


Figure S35 Comparative emission maxima (1×10^{-5} M in THF) of compounds **3**, **4**, **5**, **6**, **7**, **8** and **9** excited at λ = 330 and 480 nm, respectively.

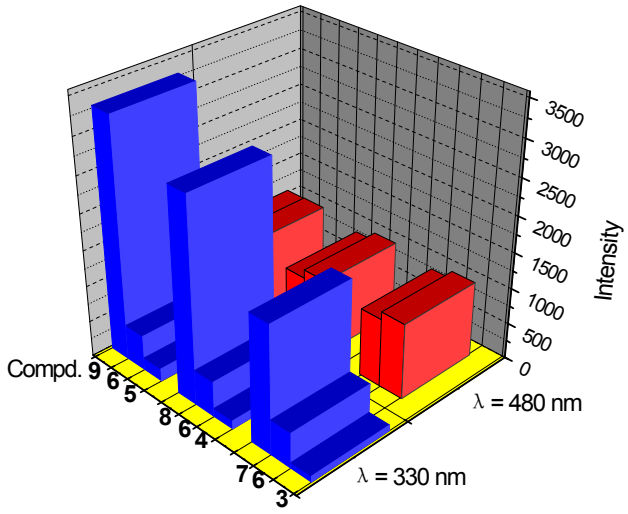


Figure S36 Comparative emission maxima (1×10^{-5} M in THF/water(*V*:*V*=2:8)) of compounds **3**, **4**, **5**, **6**, **7**, **8** and **9** excited at λ = 330 and 480 nm, respectively.