Supporting Information

Novel AIE columnar liquid crystals: The influences of the number of diphenylacrylonitrile groups on mesomorphic and fluorescent properties

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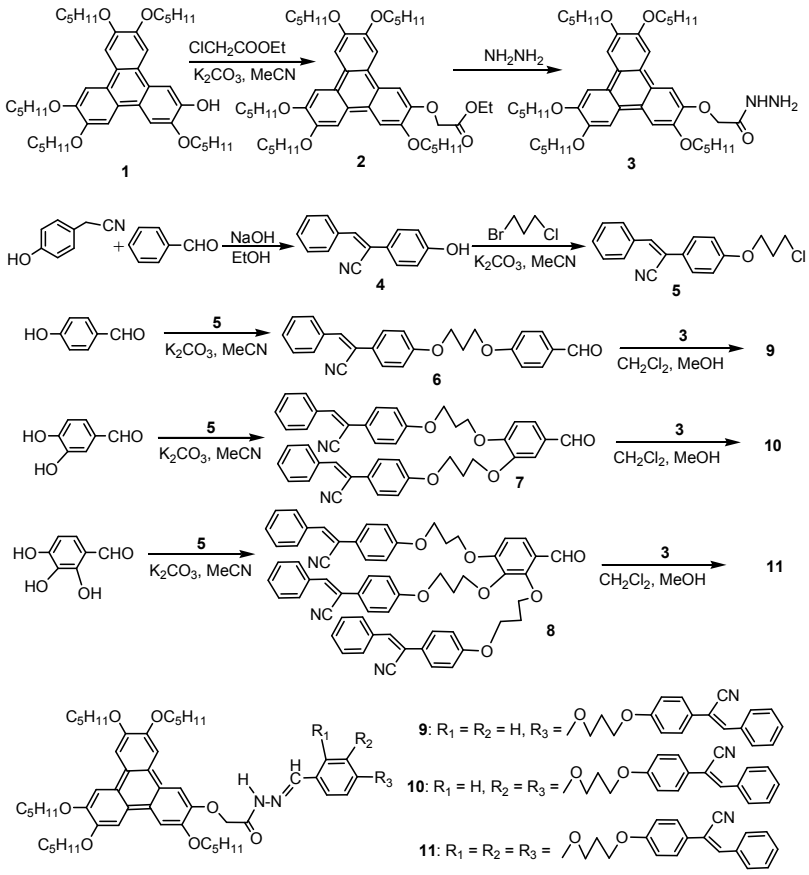
1. General

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 using pre-coated glass plates. Column chromatography was performed using silica 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. Compounds **1**, **2** and **3** were synthesized according to the published literature (Liquid Crystals, 2014, 41, 137-143.)

UV-Vis and fluorescence spectra 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. A polarized optical microscopy (Leica DMRX) was used along with a hot stage (Linkam THMSE 600) to examine phase transitions. Thermal analysis of the materials was carried out using a differential scanning calorimeter (DSC) (Thermal Analysis Q100) at a scanning rate of 10°C/min under N_2 atmosphere. XRD experiments were performed on SEIFERT-FPM (XRD7), using Cu Kα 1.5406Å as the radiation source with 40 kV, 30 mA power.

2. The synthetic process of target compounds and their characteristic spectra.



Scheme S1. Synthetic routes of compounds **9**, **10** and **11**

2.1 Synthesis of compound 4.

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 **4** 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).

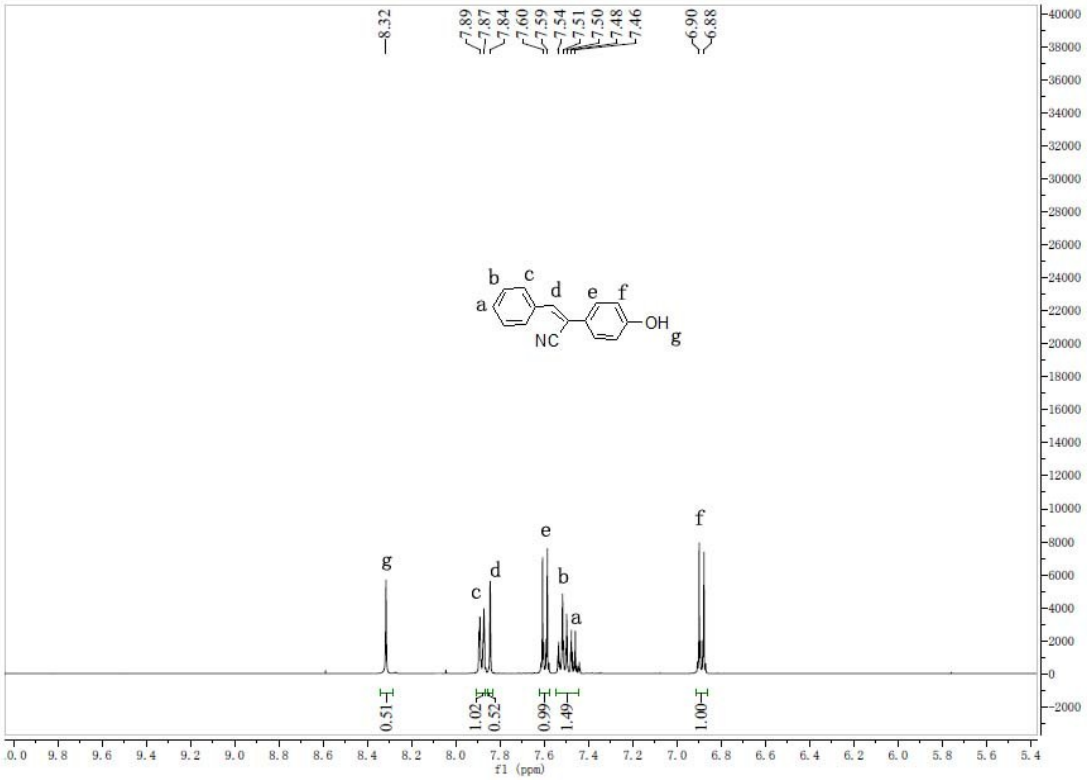


Figure S1. The ^{1}H NMR spectrum of compound **4**

2.2 Synthesis of compound 5.

Under N_2 atmosphere, a mixture of compound **4** (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 **5** 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).

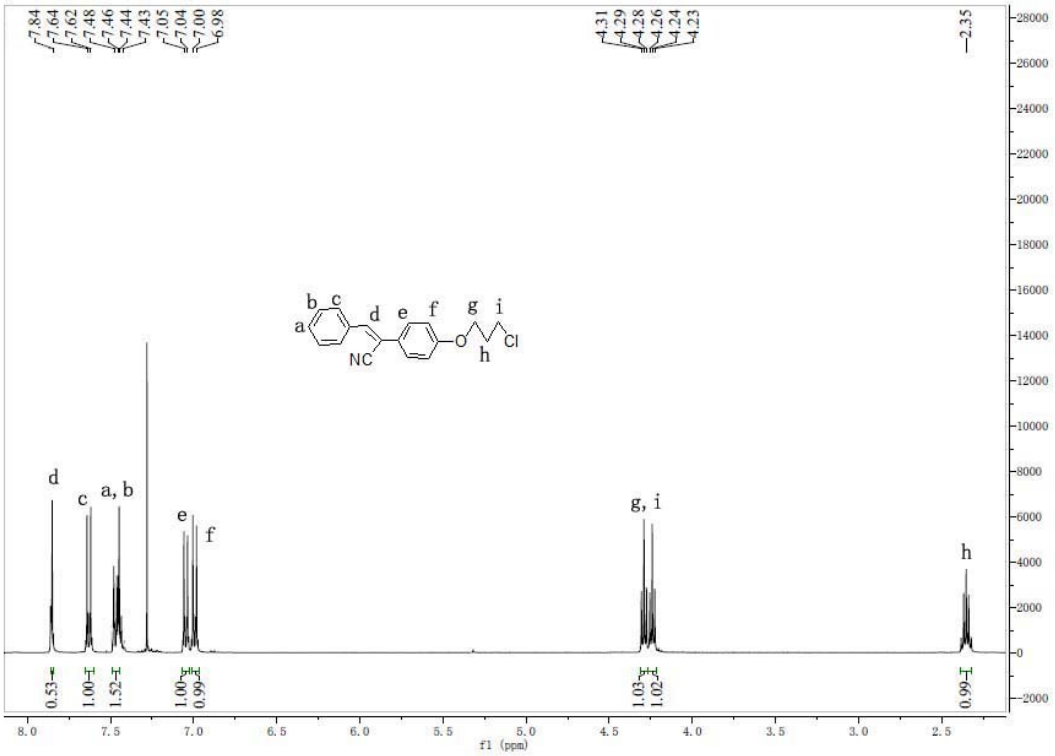


Figure S2. The ^{1}H NMR spectrum of compound **5**

2.3 Synthesis of compound 6.

Under N_2 atmosphere, a mixture of compound **5** (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 **6** 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^+).

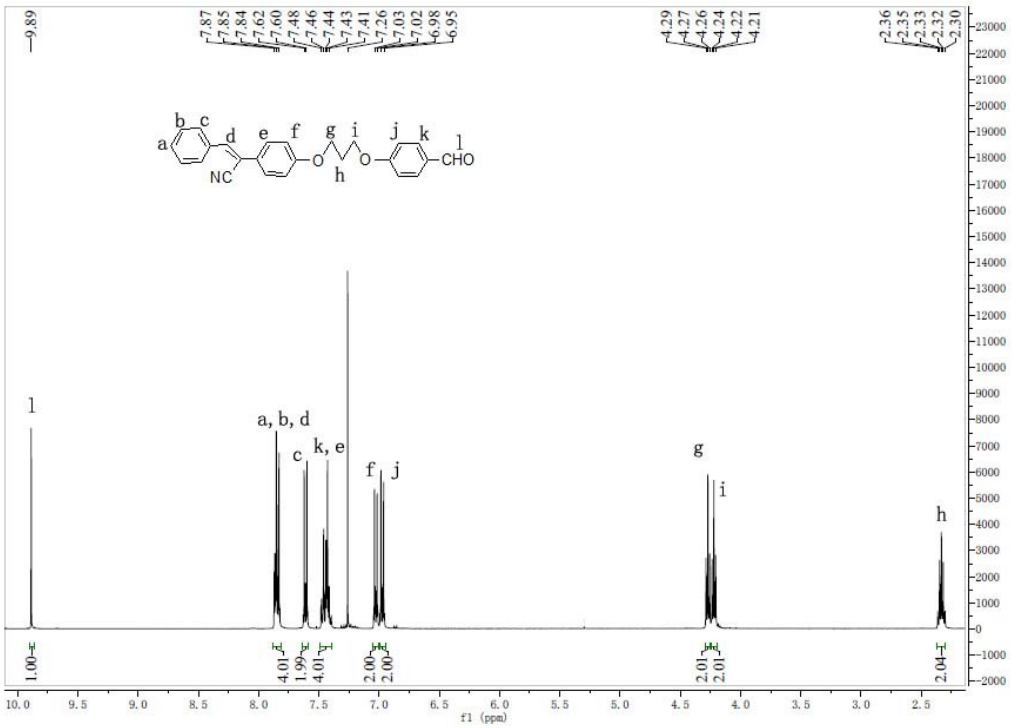


Figure S3. The ^{1}H NMR spectrum of compound **6**

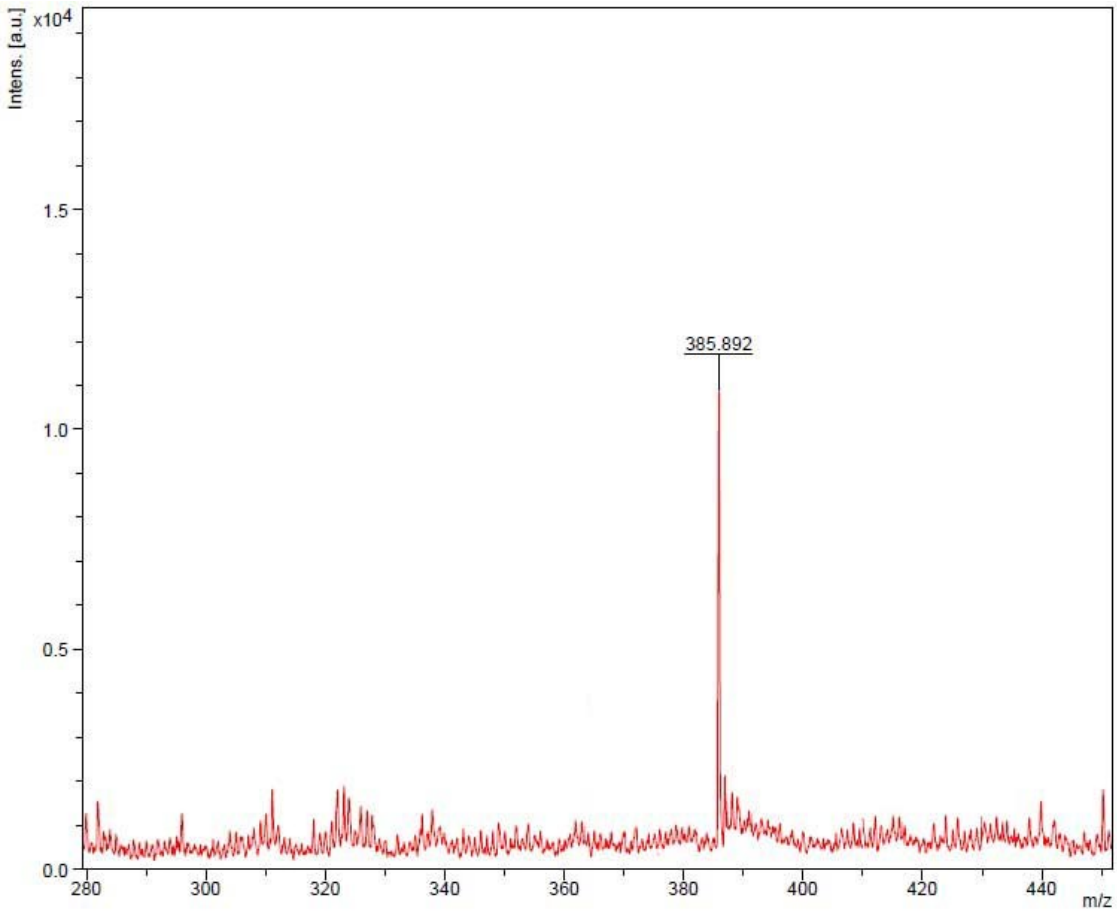


Figure S4. The MALDI-TOF-MS spectrum of compound **6**

2.4 Synthesis of compound 7.

Under N_2 atmosphere, a mixture of compound **5** (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 **7** 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^+).

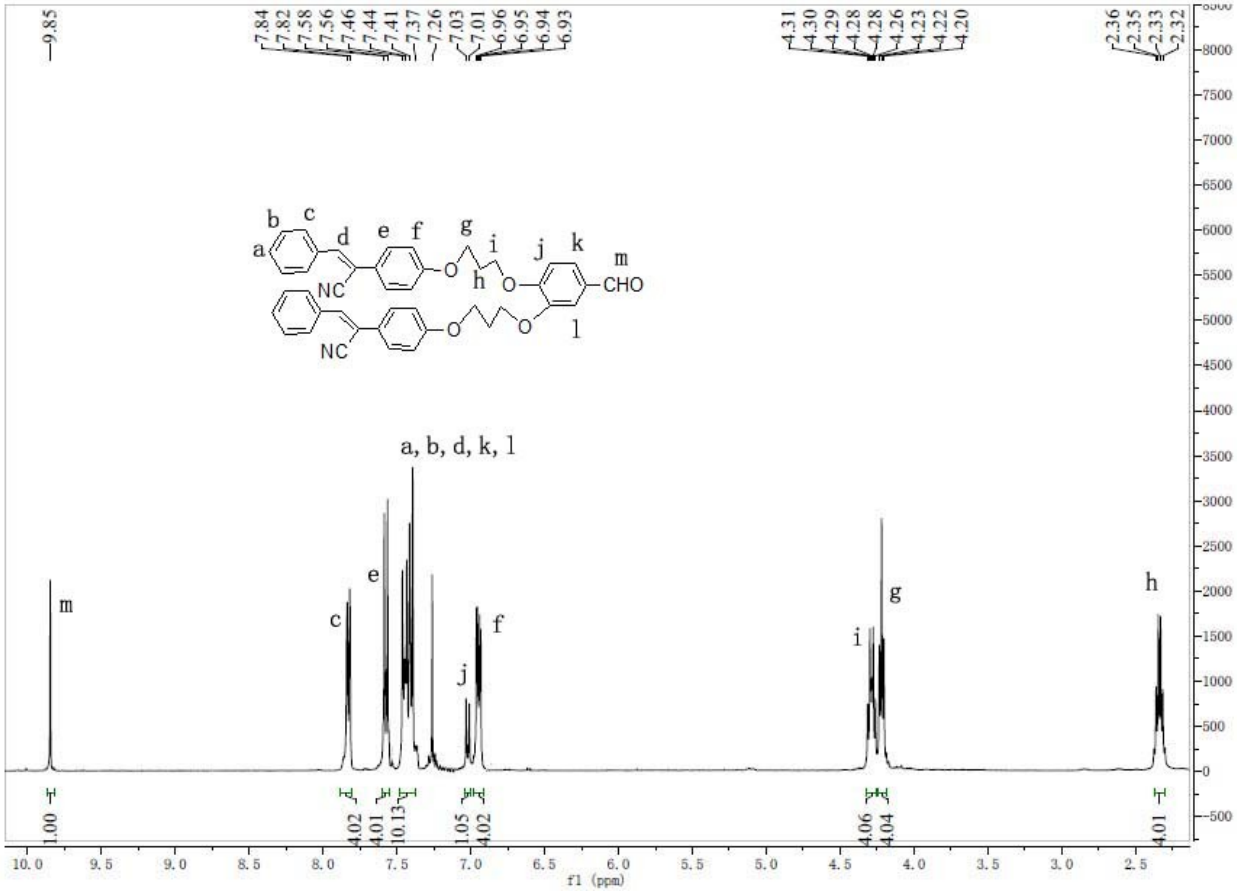


Figure S5. The ^{1}H NMR spectrum of compound **7**

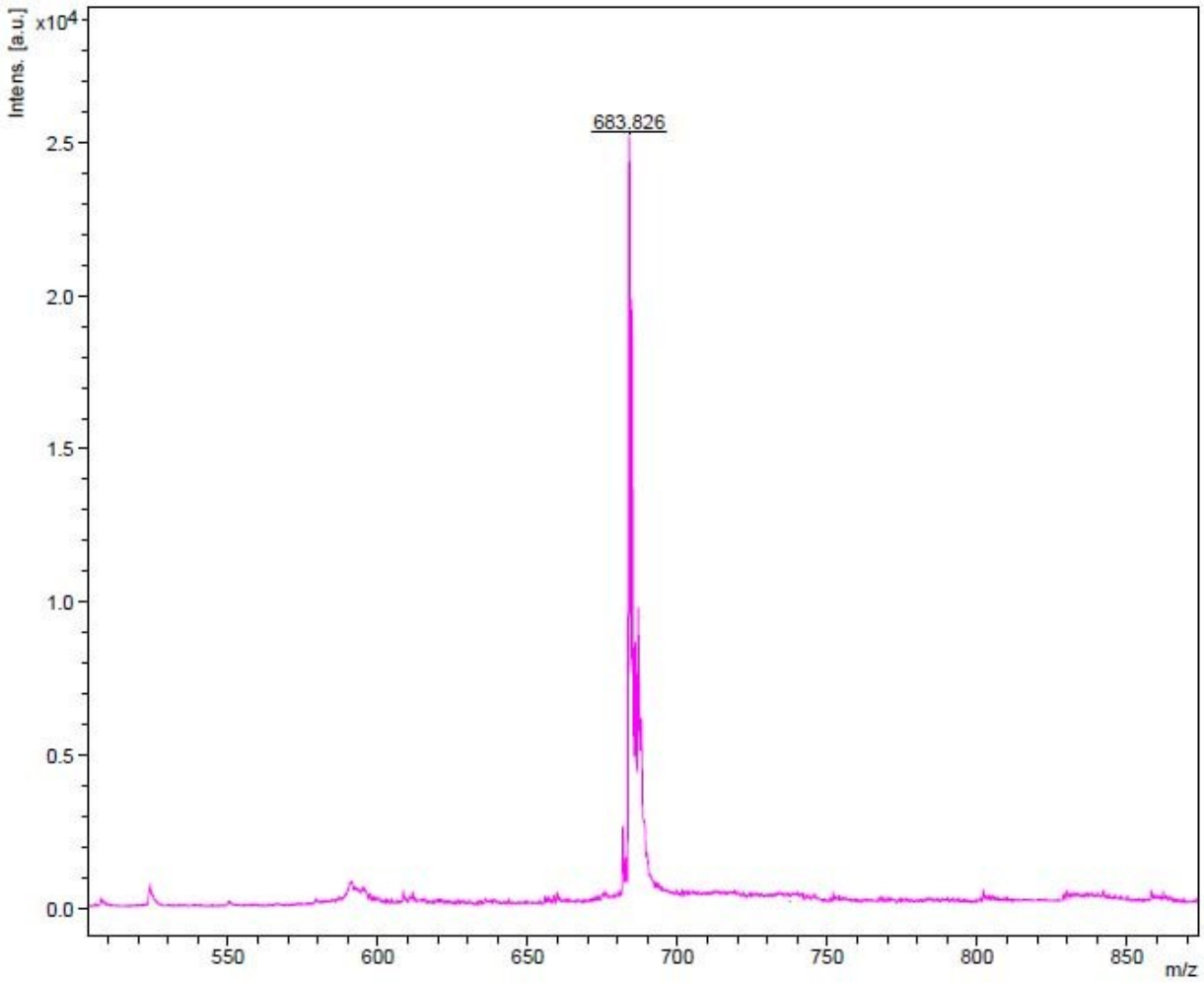


Figure S6. The MALDI-TOF-MS spectrum of compound **7**

2.5 Synthesis of compound 8.

Under N_2 atmosphere, a mixture of compound **5** (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 **8** 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^+).

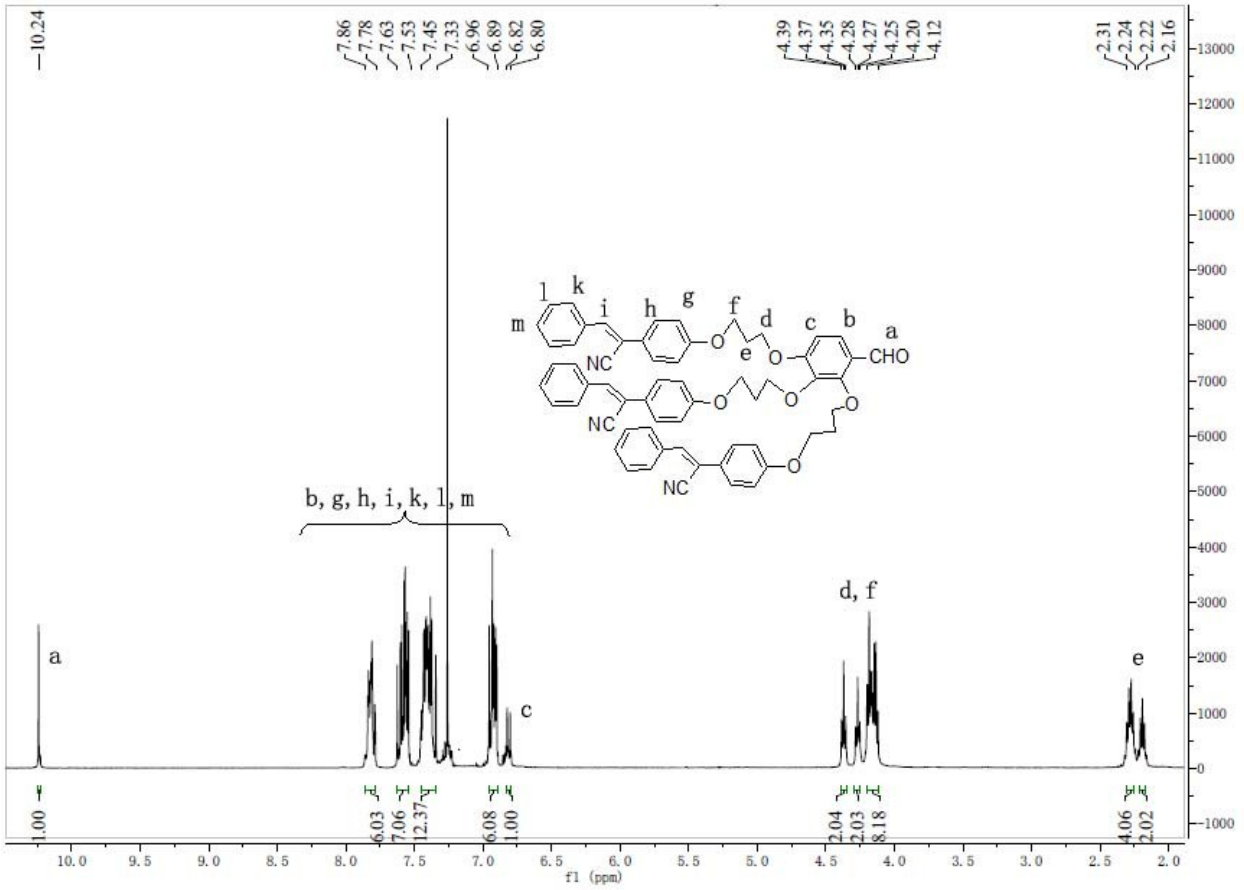


Figure S7. The ^{1}H NMR of compound **8**

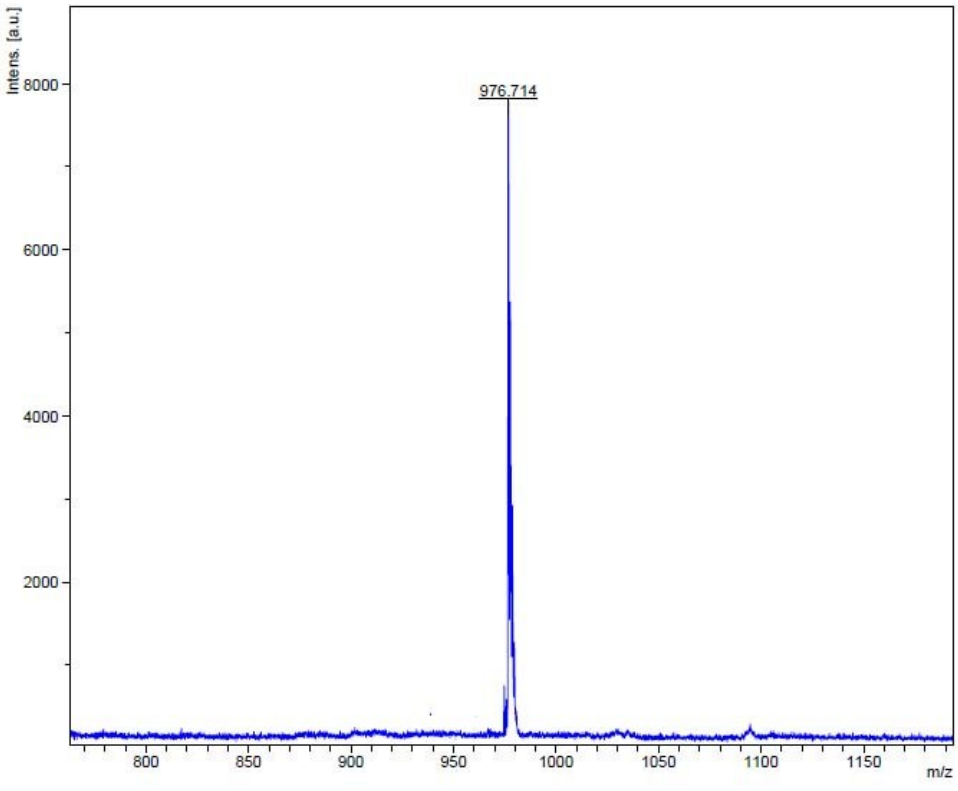


Figure S8. The MALDI-TOF-MS spectrum of compound **8**

2.6 Syntheses of compounds 9, 10 and 11.

Under N_2 atmosphere, a mixture of compound **3** (0.20g, 0.26mmol) and compound **6** (or **7** and **8**) (0.26 mmol) was stirred and refluxed in 30 mL of CH_2Cl_2-MeOH solution (3:1, *V*/*V*). Several drops of glacial acetic acid were added as catalyst. The reaction was monitored by TLC technique implying the disappearance of reactants. After reaction, most of solvents were distilled under reduced pressure at room temperature. The residue was further purified by column chromatography using CH_2Cl_2 as eluant. compounds **9, 10** and **11** were collected as a pale yellow solid in yields of 83%, 78% and 75%, respectively.

Compound **9:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.05 (s, 1H, NH), 8.14 (s, 1H, CH), 7.80-7.86 (m, 6H, TpH), 7.71-7.75 (m, 3H, ArH and CH), 7.60 (d, *J* = 8.0 Hz, 2H, ArH), 7.40-7.47 (m, 3H, ArH), 7.29 (d, *J* = 8.0 Hz, 2H, ArH), 6.95 (d, *J* = 8.0 Hz, 2H, ArH), 6.86 (d, *J* = 8.0 Hz, 2H, ArH), 4.88 (s, 2H, OCH_2O), 4.16-4.28 (m, 14H, OCH_2), 2.26-2.33 (m, 2H, CH_2), 1.40-2.00(m, 30H, CH_2), 0.96-0.99(m, 15H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 164.64, 161.02, 159.65, 159.50, 149.59, 149.34, 148.88, 148.45, 142.91, 140.20, 133.87, 130.30, 129.54, 129.06, 128.55, 126.08, 125.24, 125.02, 124.26, 123.43, 123.25, 123.00, 120.30, 114.93, 109.45, 107.62, 107.48, 107.10, 106.38, 69.94, 69.86, 69.69, 69.58, 69.44, 69.24, 64.48, 53.12, 29.18, 28.38, 22.56, 14.09.

MALDI-TOF-MS Calcd.for *m*/*z* = 1111.6, found: *m*/*z* = 1112.9 (MH^+).

HR-MS(ESI) ($C_{70}H_{85}N_3O_9$) $[MNa]^+$: Calcd.: 1134.6178. found:1134.6177.

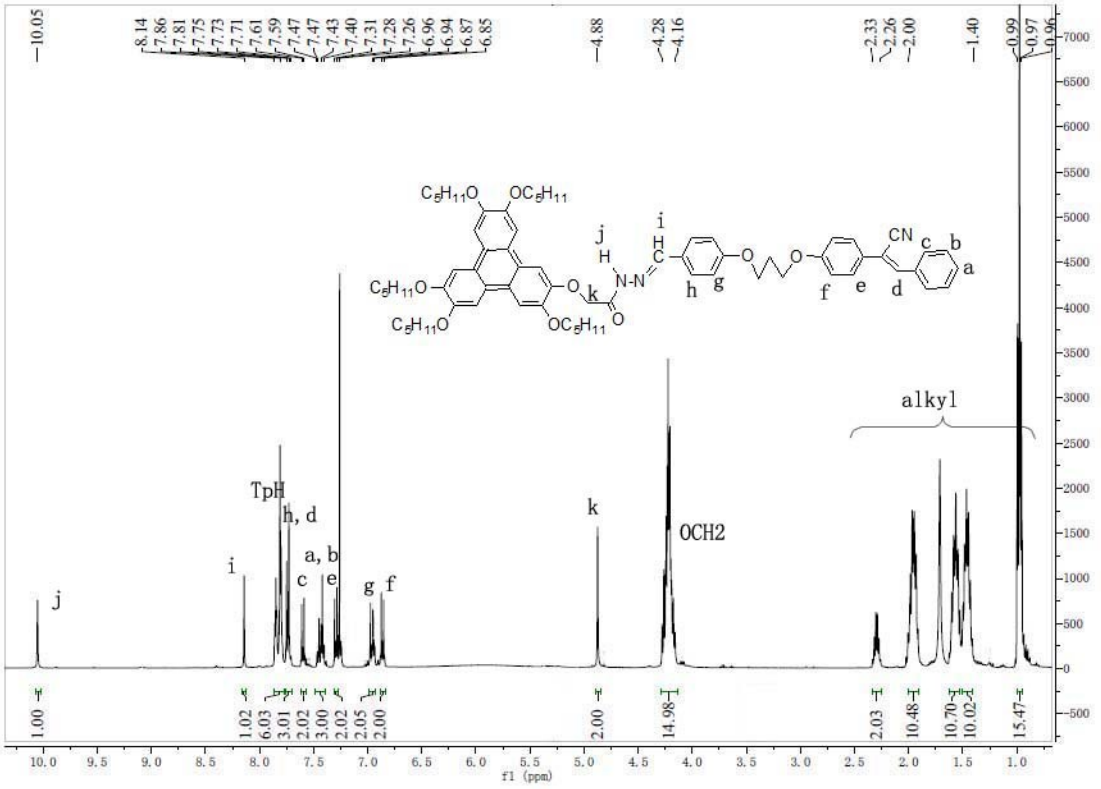


Figure S9. The ^{1}H NMR of compound **9**

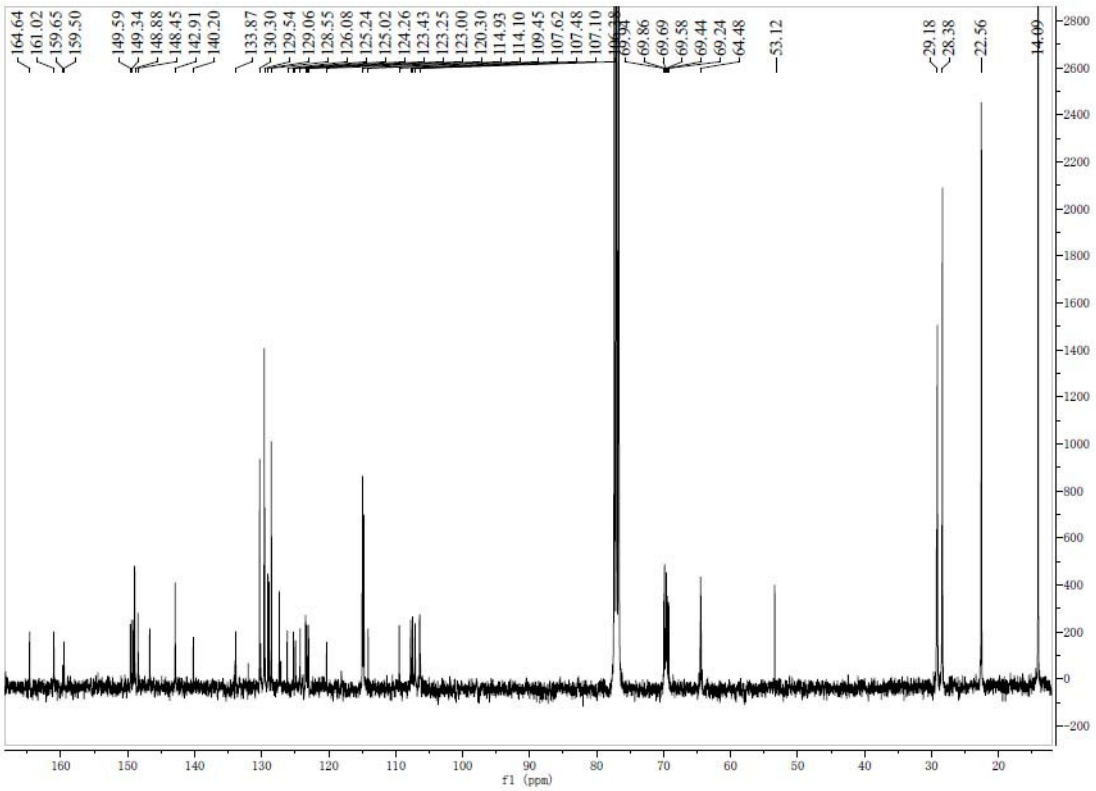


Figure S10. The ^{13}C NMR of compound **9**

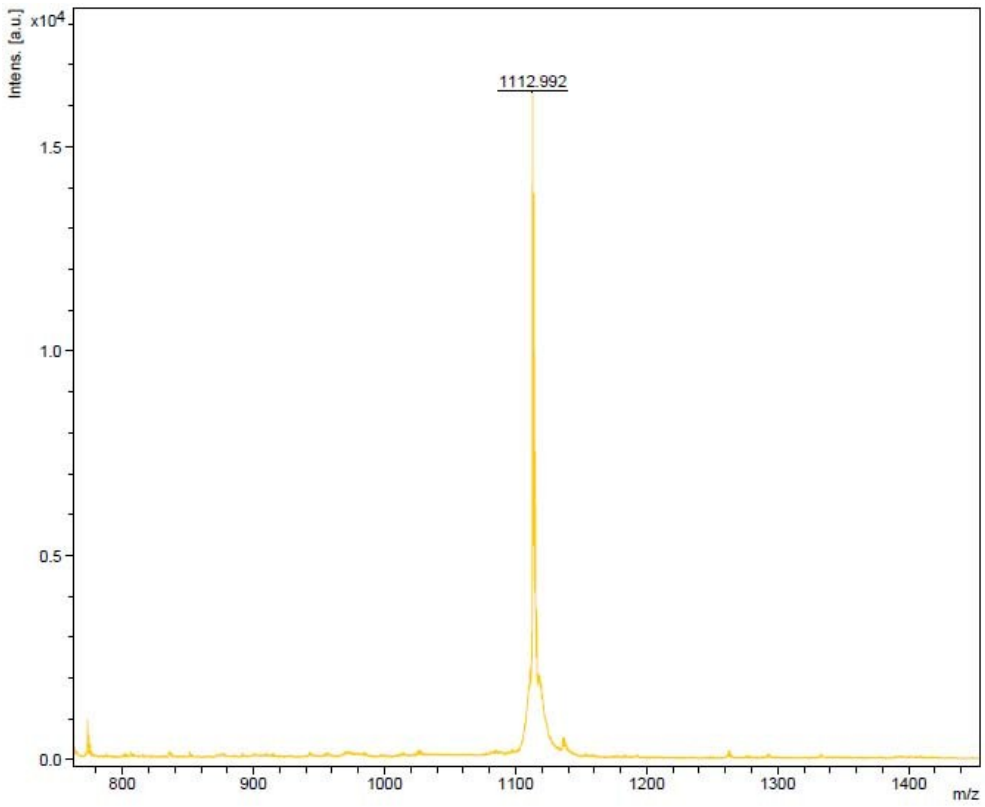


Figure S11. The MALDI-TOF-MS spectrum of compound **9**

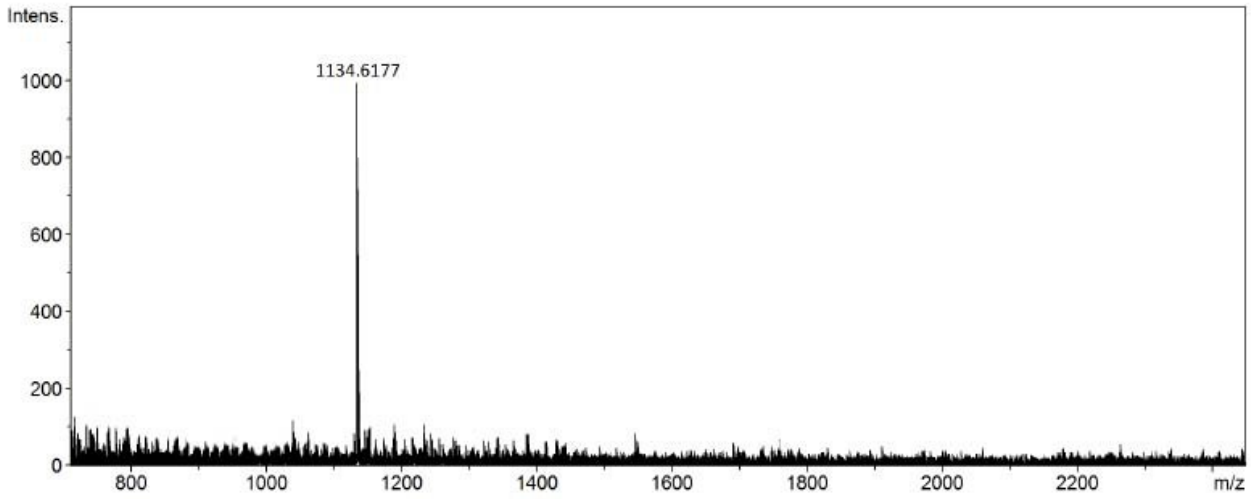


Figure S12. The HR-MS spectrum of compound **9**

Compound **10:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.02 (s, 1H, NH), 8.14 (s, 1H, CH), 7.76-7.89 (m, 10H, TpH, ArH and CH), 6.89-7.58 (m, 19H, ArH), 4.89 (s, 2H, OCH_2O), 4.17-4.29 (m, 18H, OCH_2), 2.31-2.34 (m, 4H, CH_2), 1.44-2.03(m, 30H, CH_2), 0.98(t, J = 8.0 Hz, 15H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 164.65, 159.78, 159.70, 149.61, 149.43, 149.21, 148.47, 142.83, 140.07, 130.30,130.13, 129.61, 129.07, 128.87, 128.54, 127.34, 126.73, 124.28, 123.47, 123.24, 123.00, 114.91, 109.52, 107.79, 107.49, 107.12, 106.44, 69.95, 69.76, 69.59, 69.46, 69.23, 65.69, 65.46, 64.66, 64.46, 29.65, 29.14, 28.38, 22.56, 14.09.

MALDI-TOF-MS Calcd.for m/z = 1388.7, found: m/z = 1390.0 (MH^+).

HR-MS(ESI) ($C_{88}H_{100}N_4O_{11}$) $[MNa]^+$: Calcd.: 1411.7281. found:1411.7230.

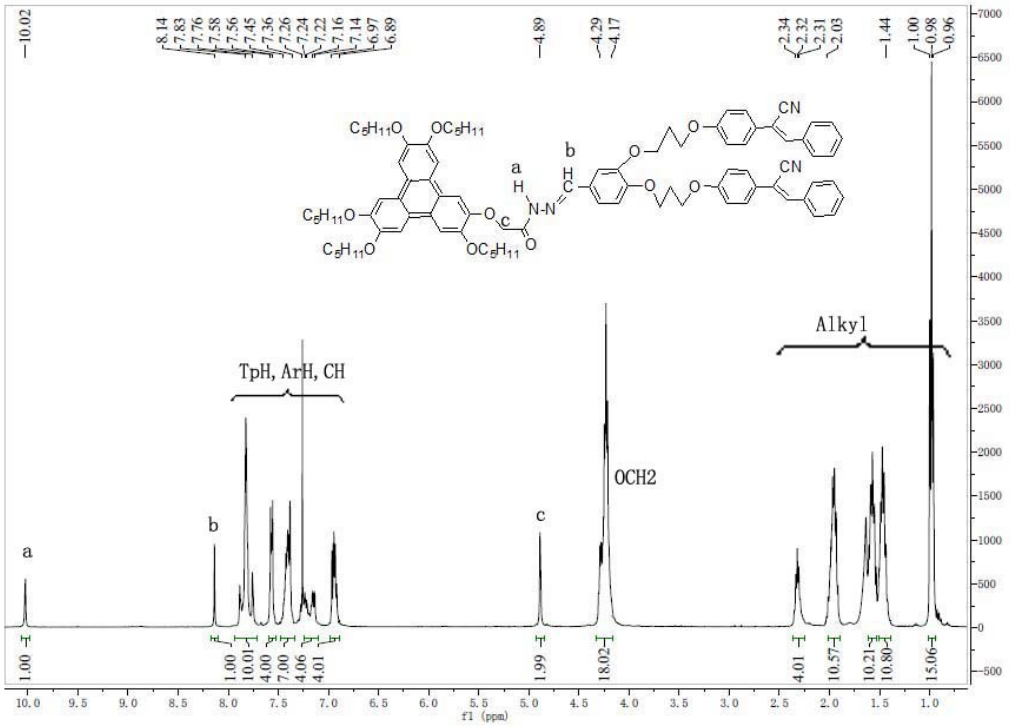


Figure S13. The ^{1}H NMR of compound **10**

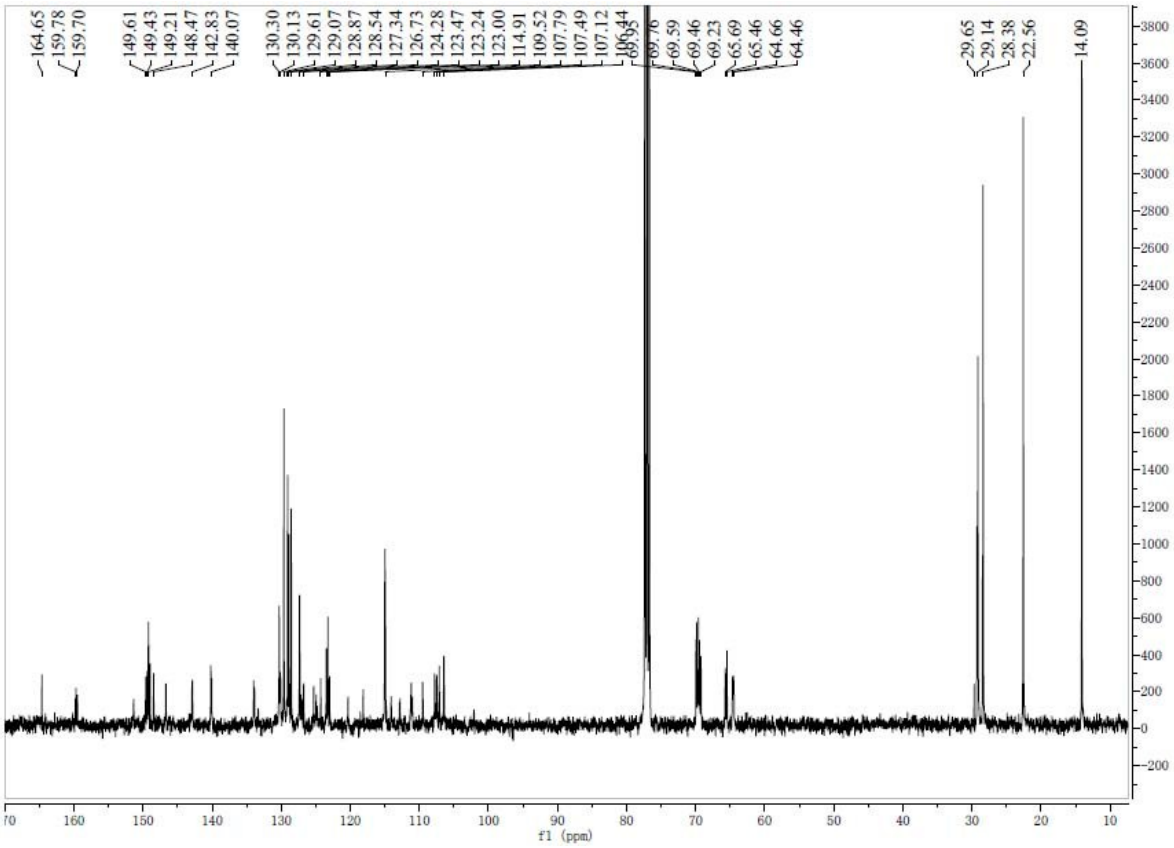


Figure S14. The ^{13}C NMR of compound **10**

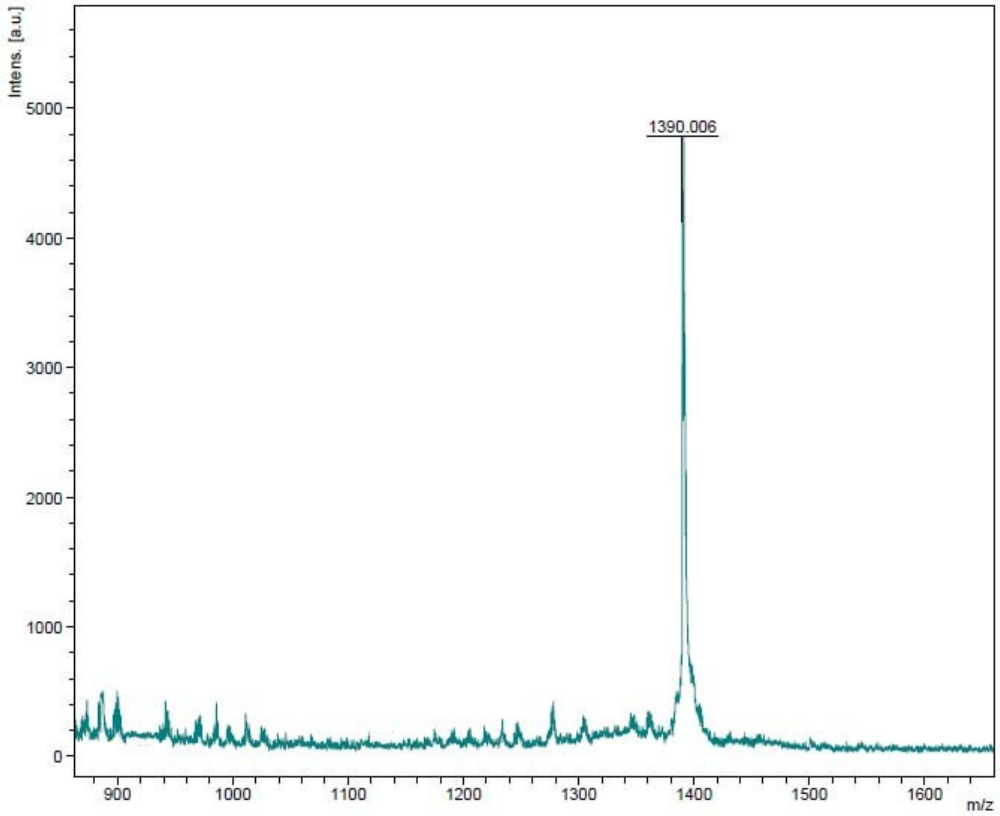


Figure S15. The MALDI-TOF-MS spectrum of compound **10**

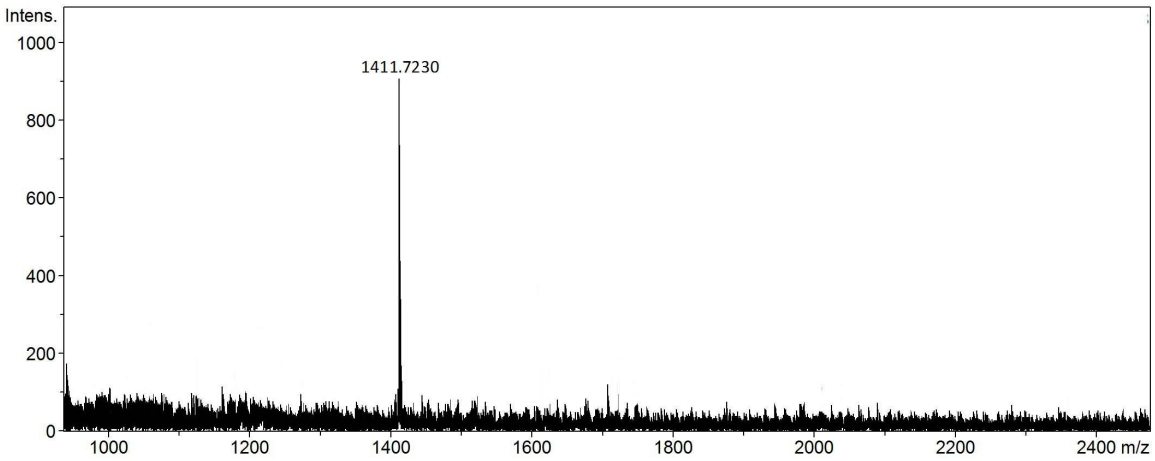


Figure S16. The HR-MS spectrumof compound **10**

Compound **11:** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.98 (s, 1H, NH), 8.47 (s, 1H, CH), 6.88-7.92 (m, 38H, TpH, ArH and CH), 4.86 (s, 2H, OCH_2O), 4.10-4.30 (m, 22H, OCH_2), 2.15-2.32 (m, 6H, CH_2), 1.40-2.02(m, 30H, CH_2), 0.89-0.98(t, J = 8.0 Hz, 15H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 164.51, 159.75, 159.60, 155.30, 152.50, 149.51, 149.35, 149.07, 148.90, 148.45, 145.16, 140.92, 140.12, 133.87, 133.60, 130.17, 129.91, 129.16, 128.74, 128.64, 127.21, 125.32, 123.43, 123.19, 122.80, 122.65, 120.37, 118.14, 114.90, 114.67, 11.06, 110.97, 110.58, 109.75, 109.18, 107.64,

107.35, 106.98, 106.41, 70.92, 69.93, 69.79, 69.53, 69.36, 69.17, 65.33, 64.57, 64.43, 30.11, 29.91, 29.18, 28.40, 22.54, 14.13.

MALDI-TOF-MS Calcd.for *m*/*z* = 1667.8, found: *m*/*z* = 1669.0 (MH^+).

HR-MS(ESI) ($C_{106}H_{115}N_5O_{13}$) $[M]^+$: Calcd.: 1666.8518. found:1666.8539.

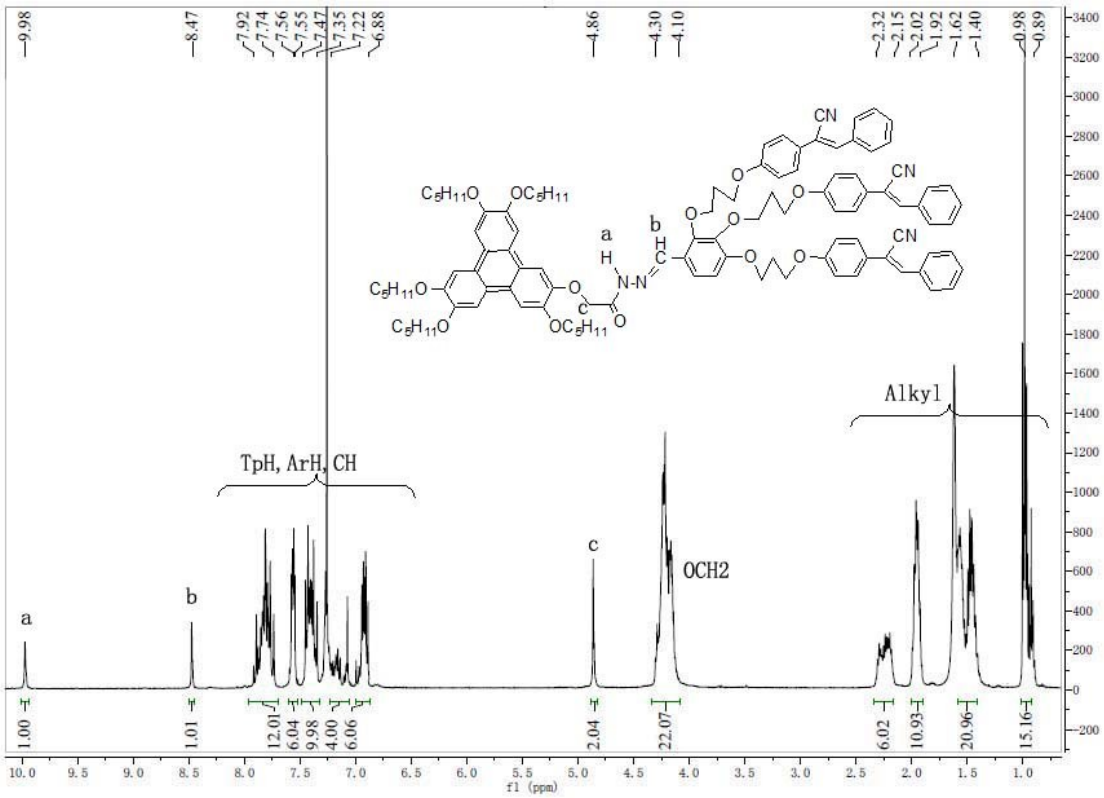


Figure S17. The ^{1}H NMR of compound **11**

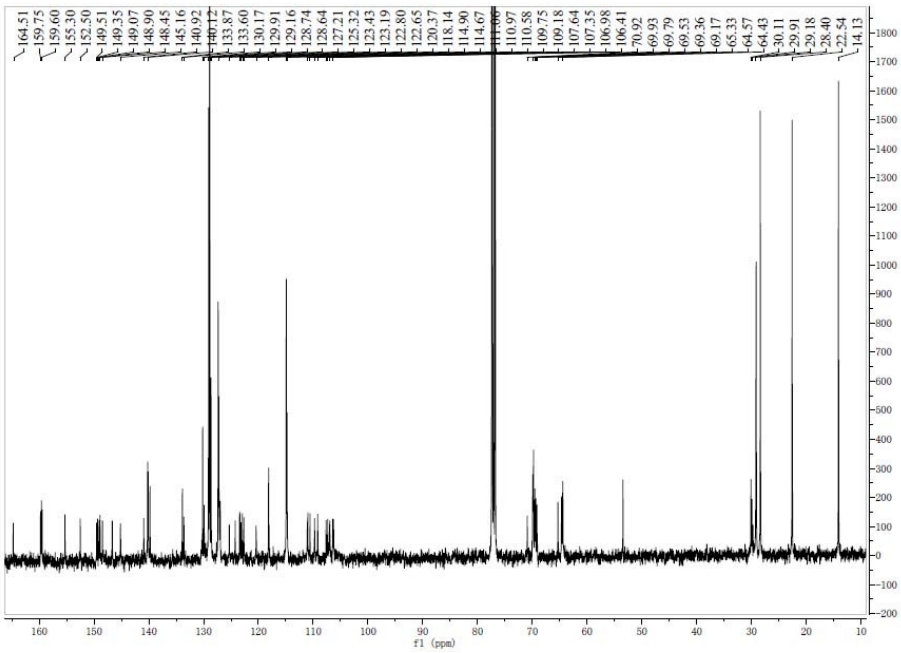


Figure S18. The ^{13}C NMR of compound **11**

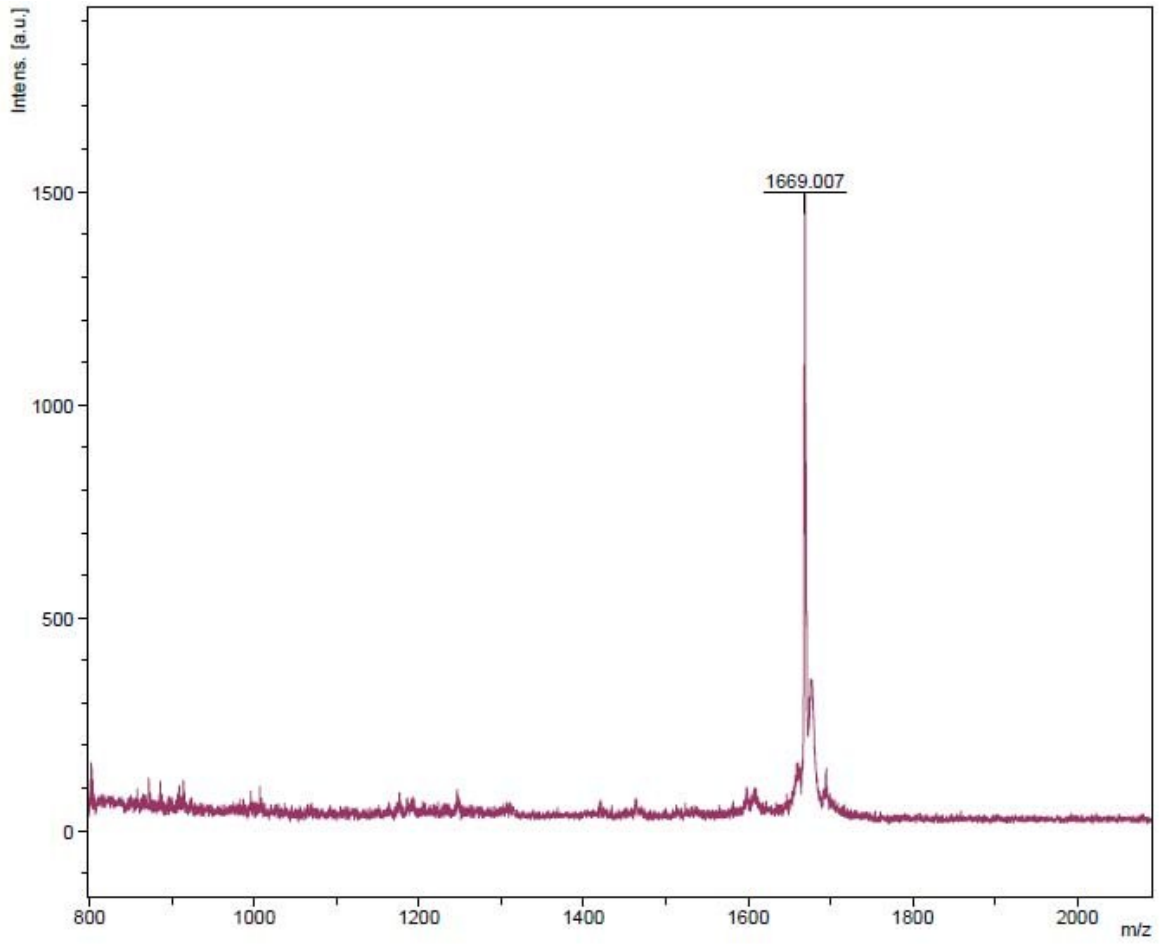


Figure S19. The MALDI-TOF-MS spectrum of compound **11**

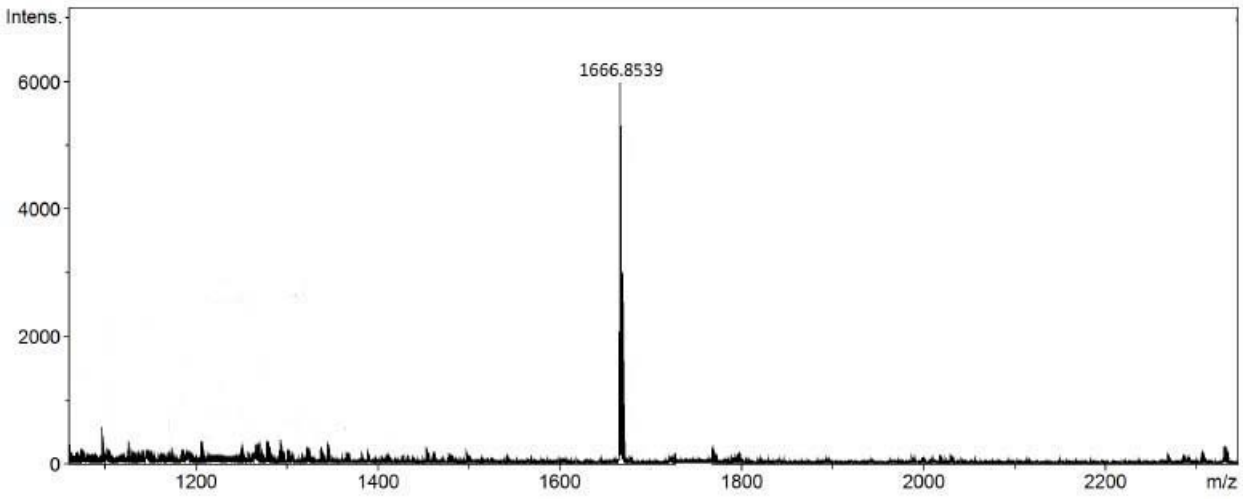


Figure S20. The HR-MS spectrum of compound **11**

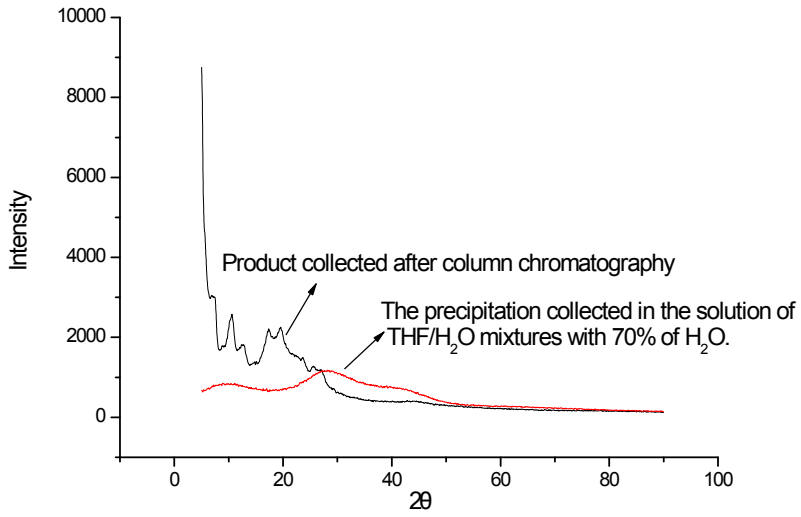


Figure S21. The XRD curves of compound **9** collected after column chromatography and the precipitation of compound **9** collected in the solution of THF/H_2O mixtures with 90% of H_2O.

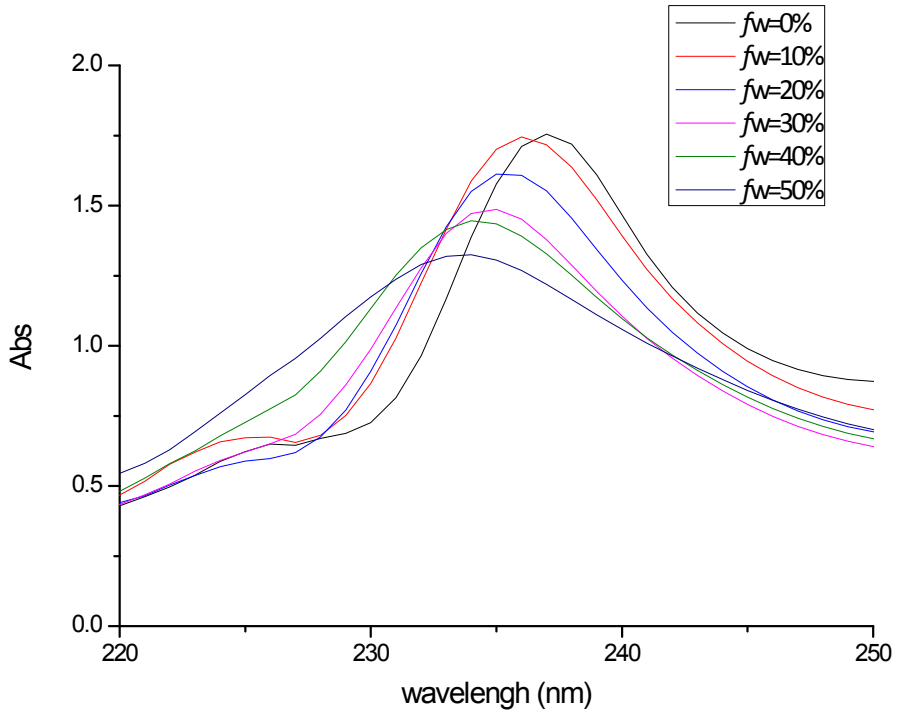


Figure S22. The UV absorption spectra of compound **10** in the solution of THF/H_2O mixtures with 0%, 10%, 20%, 30%, 40%, 50% of H_2O, respectively.