Supporting Information

Near-infrared fluorescent and columnar liquid crystal: Synthesis, mesomorphic and photophysical properties of triphenylene-Bodipy-triphenylene triad

Xiaoting Fang[a], Hongyu Guo[a*], Fafu Yang [a,b*], and Jianrong Lin[a]

†College of Chemistry and Chemical Engineering, Fujian Normal University, Fuzhou 350007, P. R. China
‡Fujian Key Laboratory of Polymer Materials, Fuzhou 350007, P. R. China

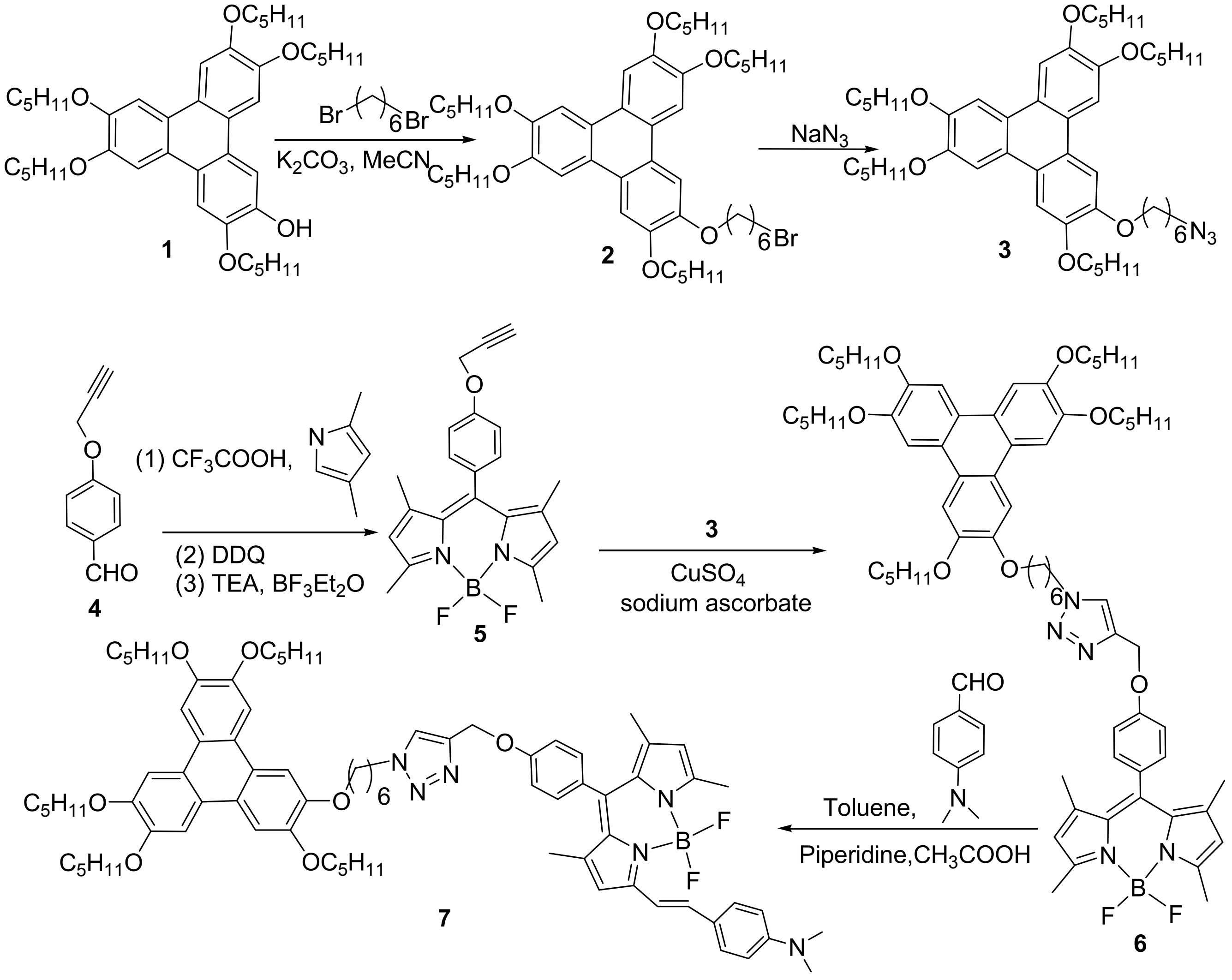
E-mail: yangfafu@fjnu.edu.cn

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 600 instrument at 25°C. Chemical shifts are reported in ppm, using tetramethylsilane (TMS) as internal standard. MS spectra were obtained from Bruck mass spectrometer. 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 quantum yields were determined by the equation: $\Phi_{F(sample)} = (F_{sample}/F_{ref})(A_{ref}/A_{sample})(n_{sample}^2/n_{ref}^2)\Phi_{F(ref)}$, where F, A, and n are the measured fluorescence (area under the emission peak), the absorbance at the excitation position, and the refractive index of the solvent, respectively. OH-Bodipy was used as the reference (Φ_F=0.94) (Liu, J. Y.; Yeung, H. S.; Xu, W.; Li, X. Ng, D. K. P. *Org. Lett.* **2008**, *10*, 5421-5424). The fluorescence absolute Φ_F values of solid films were measured using an Edinburgh Instruments FLS920 Fluorescence Spectrometer with a 6-inch integrating sphere. 4-(prop-2-ynyloxy)benzaldehyde **4** and 3, 4-bis-(prop-2-ynyloxy)benzaldehyde **8** were prepare by the published procedure (Hongyu Guo, Xiaoting Fang, Fafu Yang, Yingmei Zhang, J. Incl Phenom. Macrocycl. Chem, 2016, 84(1), 79-86). Compounds **1**, **2** and **3** were syhthesized according to the reference (Biqiong Hong, Fafu Yang, Hongyu Guo, and Ziyu Jiao, Tetrahedron Letters, 2014, 55, 252-255).

---

* Corresponding author. Tel.: +0086-591-83465225; fax: +0086-591-83465225; e-mail: yangfafu@fjnu.edu.cn



Scheme S1. The synthetic route for triphenylene-Bodipy dyad derivative **7**

2.1. Synthesis of BODIPY derivative 5

Under N_2 atmosphere, four drops of trifluoroacetic acid were added in the CH_2Cl_2 solution(120 mL) of compound **4** (0.1 g, 0.6 mmol) and 2,4-dimethyl-1*H*-pyrrole (0.14g, 1.5 mmol). The solution was stirred at room temperature for 12 h. Subsequently, 2,3-dichloro-5,6-dicyano-p-benzoquinone (0.16 g, 0.7 mmol) was added in reaction system. The mixtural solution was reacted continuously for another 4 h. Furthermore, triethylamine (6 mL, 0.043 mol) and $BF_3 \cdot Et_2O$ (6 mL, 0.05 mol) was added into reaction system. The obtained mixture was further stirred at room temperature overnight. After reaction, 90 mL of water was added in the mixture and the orgainc layer was separated. The organic portion was further washed with 100 mL of 5% aqueous $NaHCO_3$ solution and then dried over anhydrous $MgSO_4$. After filteration, the solution was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (eluent: CH_2Cl_2/ petroleum ether =1:1). Compound **5** was obtained as an red solid in yield of 22%. Compound **5**: ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 1.40 (s, 6H, CH_3), 2.54 (s, 1H, CH), 2.57 (s, 6H, CH_3), 4.74 (s, 2H, OCH_2), 5.97 (s, 2H, ArH), 7.02 (d, 2H, J = 8.0Hz, ArH), 7.18 (d, 2H, J = 8.0Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 14.55, 18.51, 29.71, 53.20, 55.76, 75.73, 77.80, 115.63, 120.99, 127.99, 129.24, 131.77, 141.61, 143.15, 155.37, 158.04. HR-MS(ESI) ($C_{22}H_{22}BF_2N_2O$) $[M]^+$: Calcd.: 379.1791. found: 379.1789.

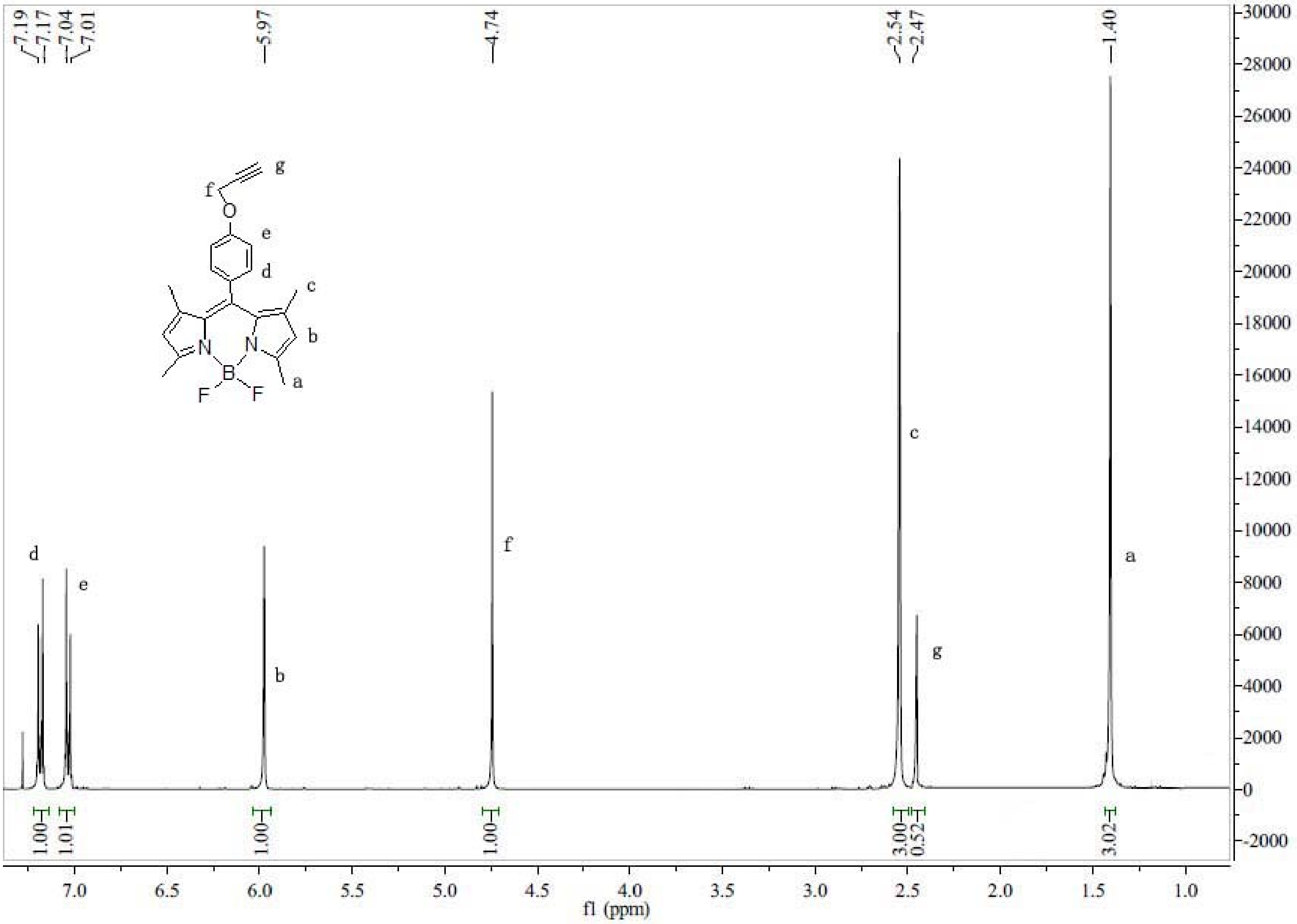


Figure S1. ^{1}H NMR spectrum of **5**

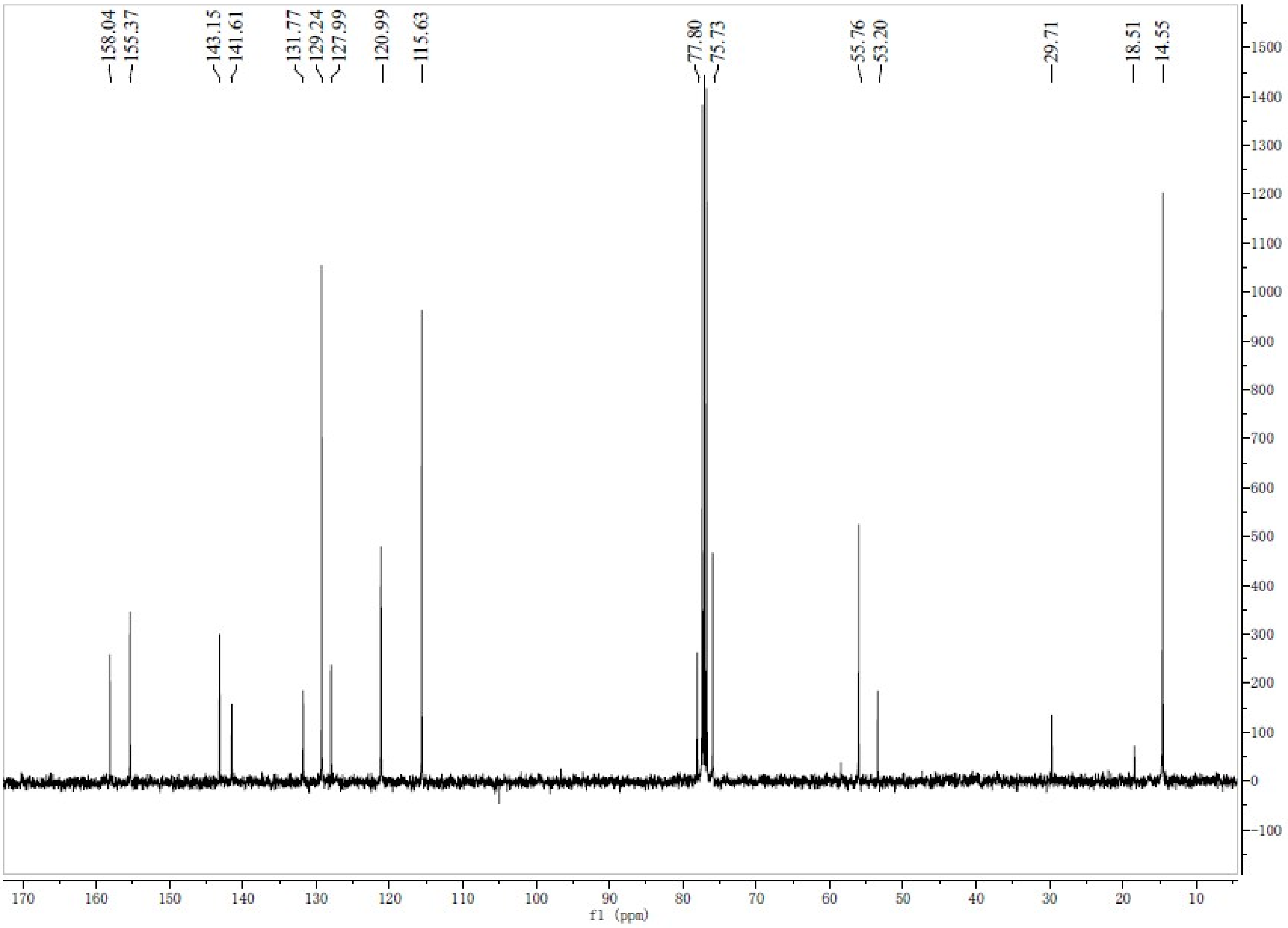


Figure S2. ^{13}C NMR spectrum of **5**

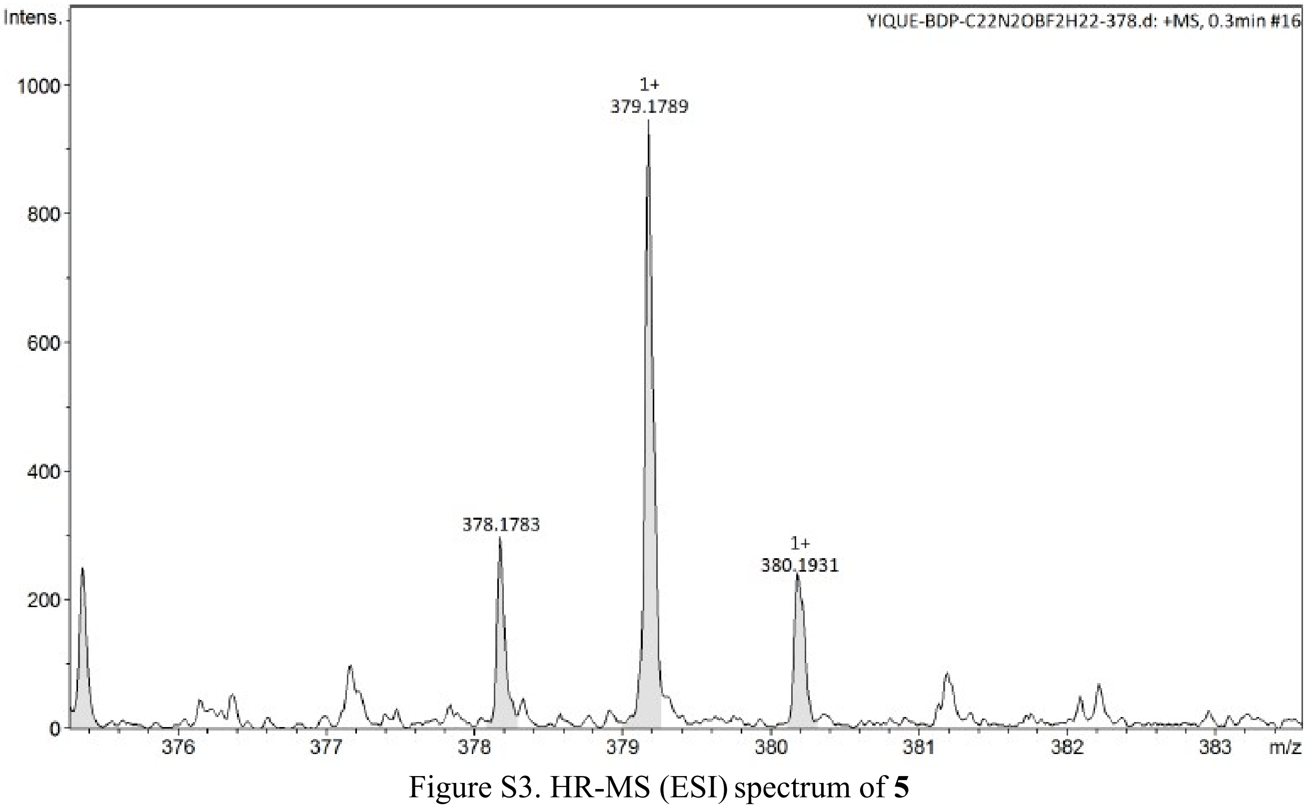


Figure S3. HR-MS (ESI) spectrum of **5**

2.2. Synthesis of compound 6

$CuSO_4 \cdot 5H_2O$ (62 mg, 0.25 mmol) and sodium ascorbate (100 mg, 0.5 mmol) were added into the DMF solution (20 mL) of compound **5** (75 mg, 0.2 mmol) and compound **3** (72 mg, 0.1 mmol). The mixture was stirred at 100°C for 15 h. After cooling, the solution was partitioned by $CHCl_3$ (50 mL) and water (50 mL). The organic phase was separated, washed by water (3×30mL) and then dried over $MgSO_4$. After filtration, the solvent removed under reduced pressure. The residue was purified by silica gel column chromatography with the eluent of CH_2Cl_2/ petroleum ether (1:1). Compound **6** was collected as an red solid in yield of 66%.

Compound **6**: ^1H NMR (400 MHz, $CDCl_3$) δppm: 0.97 (t, 15H, $CH_2\underline{CH_3}$), 1.35~2.03 (m, 44H, CH_2 and CH_3), 2.54 (s, 6H, CH_3), 4.22(bs, 12H, OCH_2), 4.43 (t, 2H, *J*=8.0Hz, NH_2), 5.19 (bs, 2H, OCH_2-trazole), 5.96 (s, 2H, ArH), 7.04 (d, 2H, *J* = 8.0Hz, ArH), 7.11-7.15 (m, 3H, ArH and H-trazole), 7.83 (bs, 6H, TpH); ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 13.97, 14.41, 22.42, 25.38, 26.10, 28.39, 29.15, 29.54, 29.85, 50.44, 61.67, 69.01, 69.48, 107.01, 115.21, 115.69, 120.60, 122.55, 123.68, 127.74, 129.02, 131.77, 141.35, 142.88, 143.65, 146.73, 148.93, 155.16, 158.80; MALDI-TOF-MS Calcd.for *m*/*z* = 1177.7, found: *m*/*z* = 1179.3$(M+H)^+$. HR-MS(ESI) ($C_{71}H_{94}BF_2N_5O_7$) $[M]^+$: Calcd.: 1177.7220. found:1077.7260. Elemental Analysis Calcd.: C 72.37, H 8.04, N 5.94%. Found: C 72.33, H 8.09, N 5.86%.

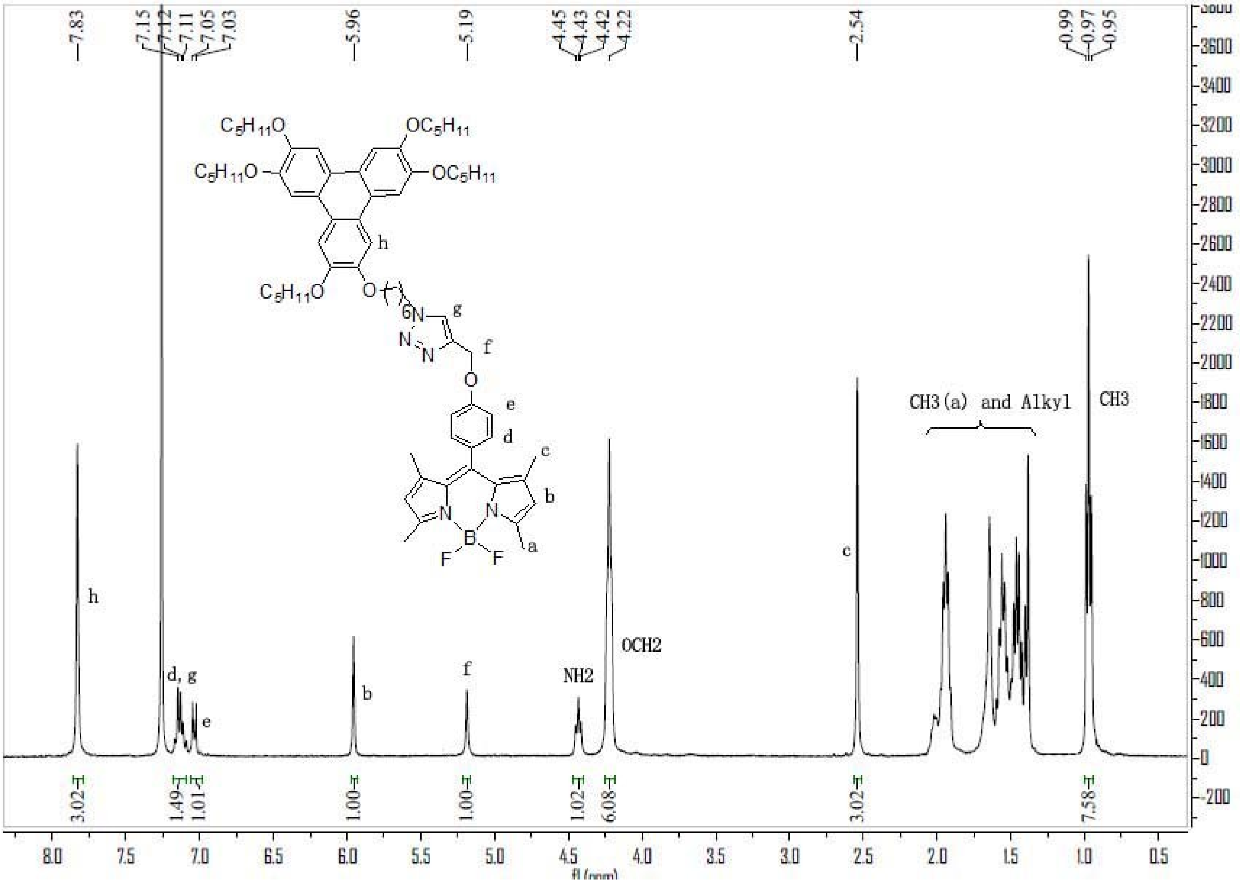


Figure S4. ^1H NMR spectrum of **6**

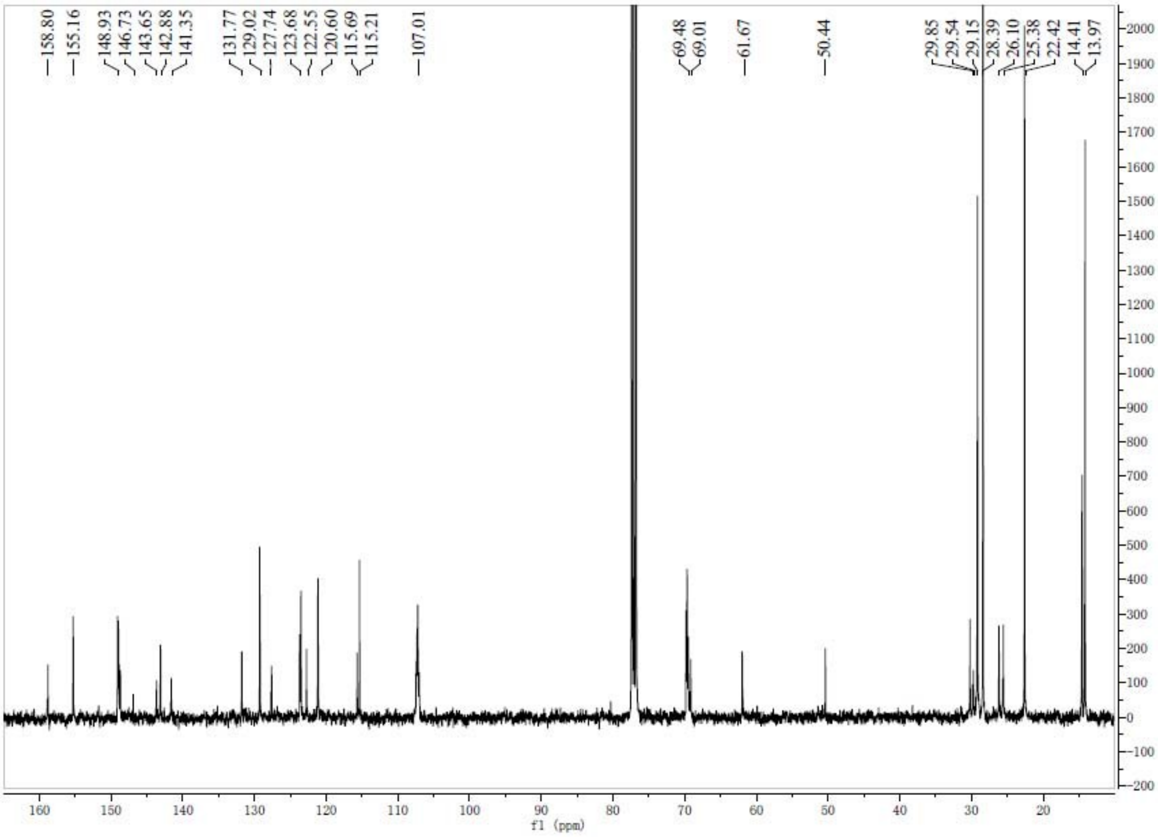


Figure S5. ^{13}C NMR spectrum of **6**

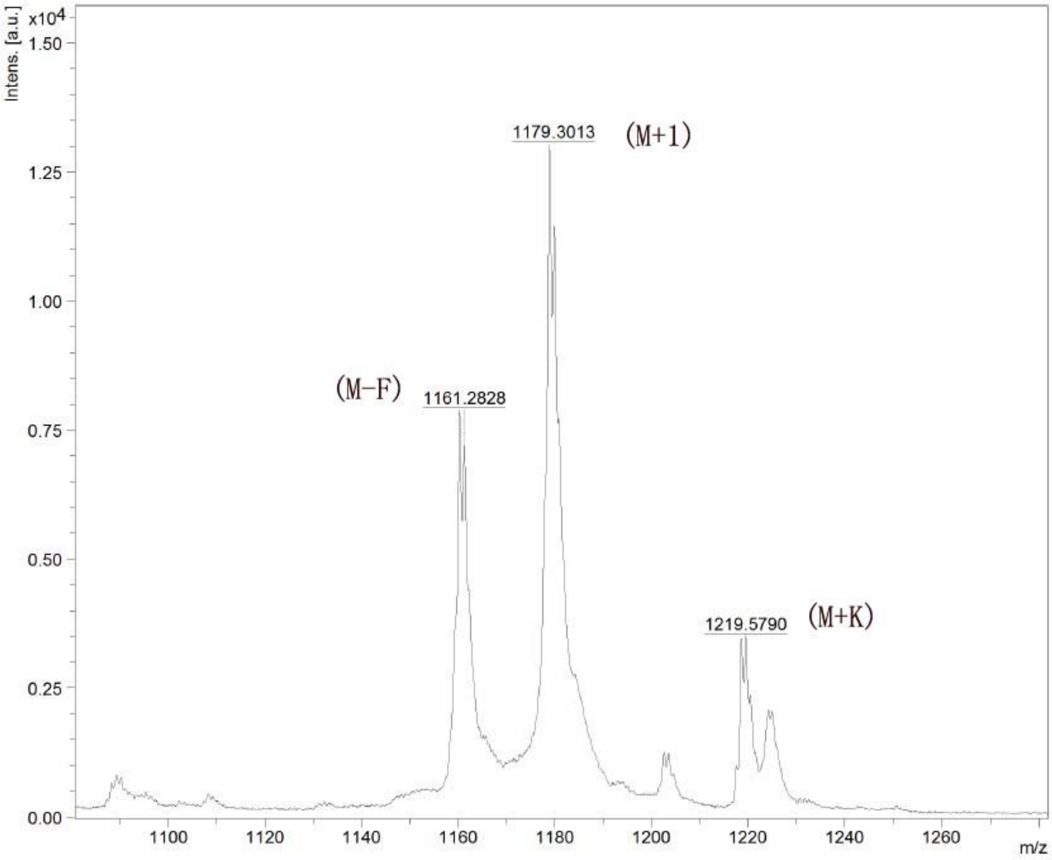


Figure S6. MALDI-TOF-MS spectrum of compound **6**

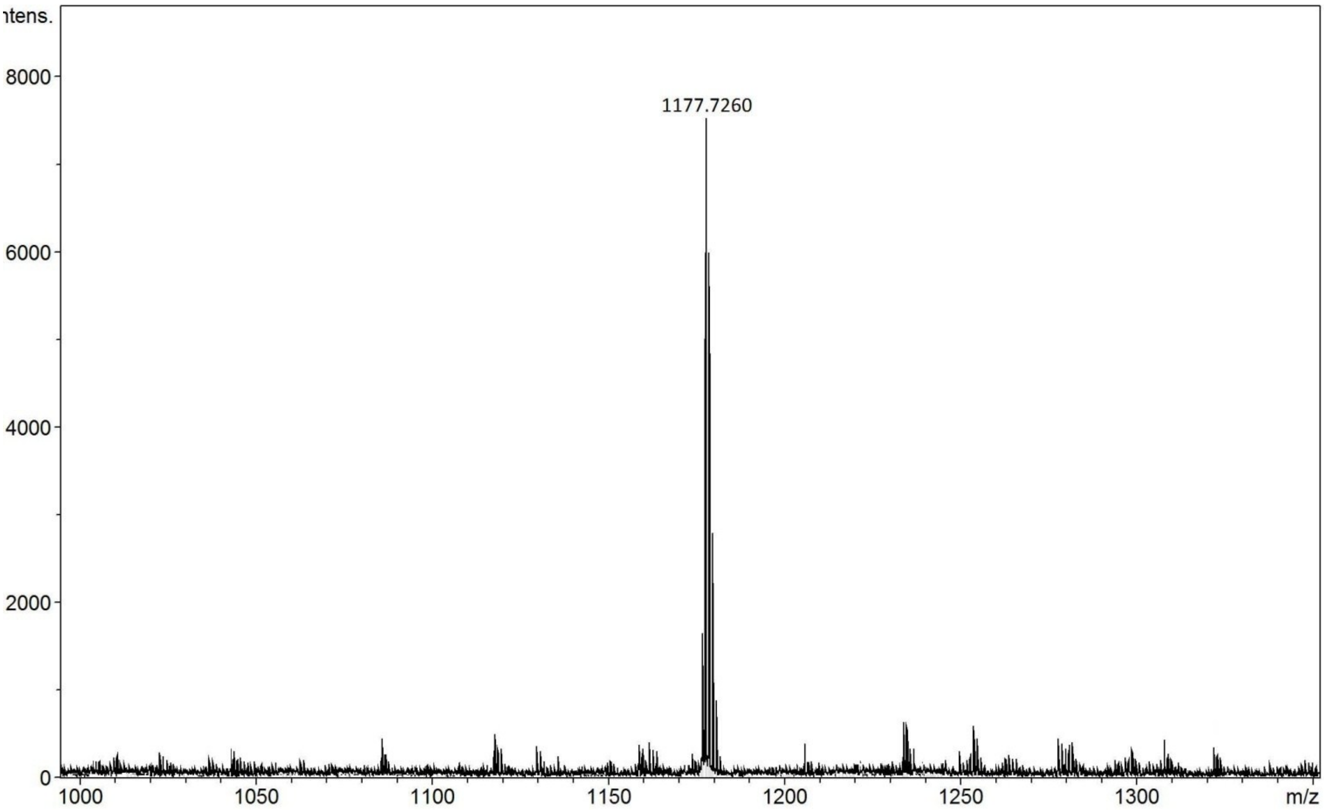


Figure S7. HR-MS (ESI) spectrum of **6**

2.3. Synthesis of compound 7

Under N_2 atmosphere, compound **6** (200 mg, 0.17 mmol) and *p*-dimethylaminobenzaldehyde (45 mg, 0.30 mmol) were add in a round-bottomed flask with 30 mL of dry toluene. 2 mL of piperidine, 2 mL of glacial acetic acid and a small amount of 3 Å molecular sieves were added in the flask. The mixture was stirred and refluxed for 5 h. After cooling, the solvent was evaporated under reduced pressure. The residue was partitioned by $CHCl_3$ and the solution of NH_4Cl (10%). The organic layer was dried with NaCl (satd.) and anhydrous $MgSO_4$. After concentration, the product was purified by silica gel column chromatography using CH_2Cl_2/ petroleum ether (2:1) as eluent. A purple solid was obtained in the yield of 20%. Compound **7**: ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 0.99 (t, 15H, *J* = 8.0Hz, CH_3), 1.40~2.10 (m, 44H, CH_2 and CH_3), 2.59 (s, 3H, CH_3), 3.04 (s, 6H, NCH_3), 4.24 (bs, 12H, OCH_2), 4.45 (t, 2H, *J* = 8.0Hz, NCH_2), 5.19 (s, 2H, OCH_2), 5.96 (s, 1H, ArH), 6.59 (s, 1H, ArH), 6.68 (d, 2H, *J* = 8.0Hz, ArH), 7.00 (s, 1H, ArH), 7.02 (d, 2H, *J* = 8.0Hz, ArH), 7.05 (s, 1H, ArH), 7.17 (d, 2H, *J* = 8.0Hz, ArH), 7.51 (d, 2H, *J* = 8.0Hz, ArH), 7.66 (s, 1H, ArH), 7.85 (bs, 6H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 14.15, 22.72, 28.38, 29.39, 29.72, 29.94, 30.32, 31.86, 33.69, 40.26, 50.34, 61.98, 69.13, 69.52, 69.71, 69.94, 106.94, 107.25, 107.41, 112.01, 113.97, 115.14, 117.64, 120.37, 122.68, 123.59, 124.42, 124.74, 124.93, 127.91, 129.11, 129.55, 129.93, 130.85, 131.75, 133.48, 136.08, 137.58, 139.30, 148.60, 151.03, 152.78, 154.63, 158.57; MALDI-TOF-MS Calcd.for *m/z* = 1308.8, found: *m/z* = 1309.7 ($M+H^+$). HR-MS(ESI) ($C_{80}H_{103}BF_2N_6O_7$) $[M+H]^+$: Calcd.: 1309.8035. found:1309.8004. Elemental Analysis Calcd.: C 73.37, H 7.93, N 6.42%. Found: C 73.31, H 7.98, N 6.34%.

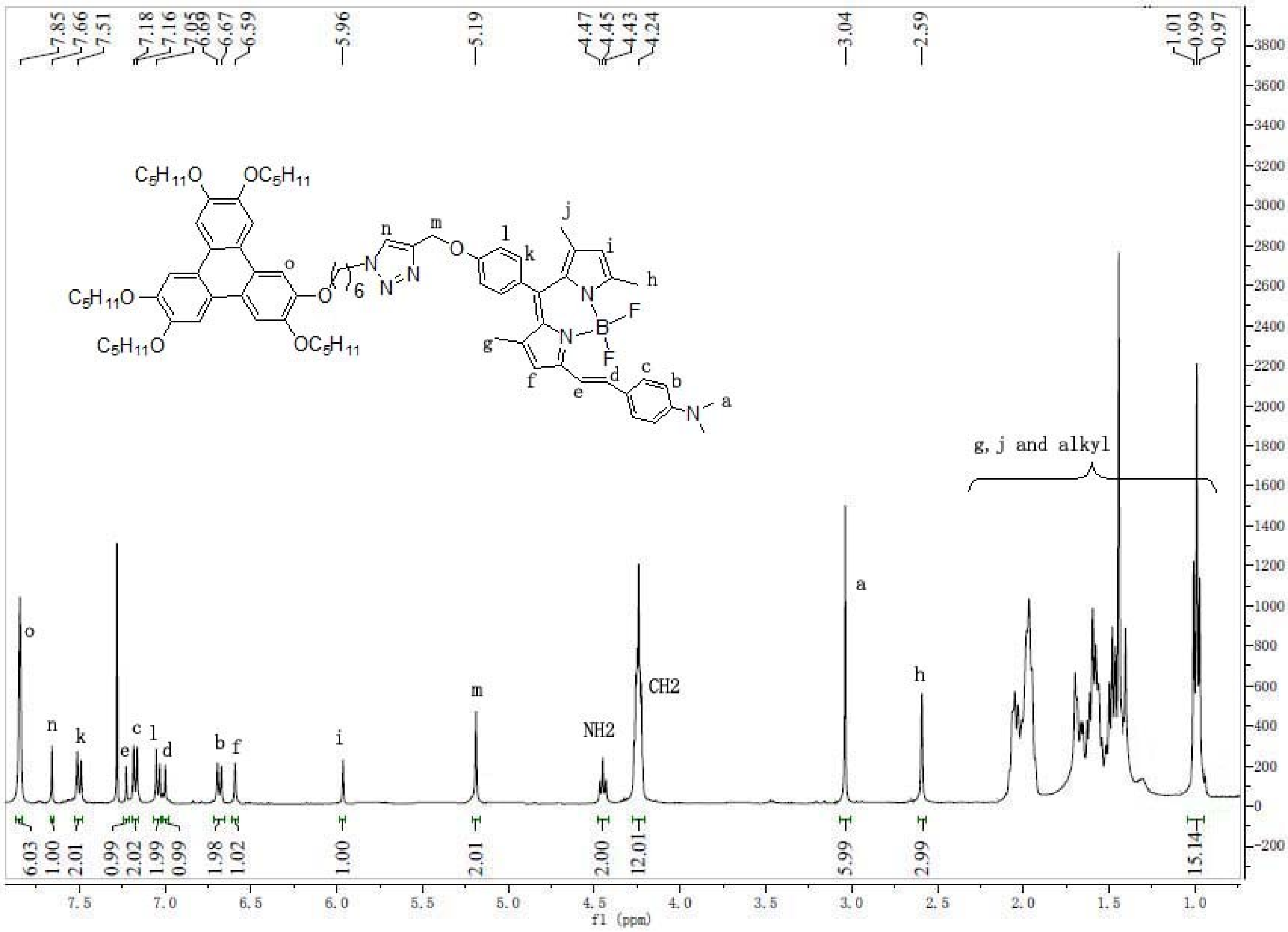


Figure S8. ^{1}H NMR spectrum of **7**

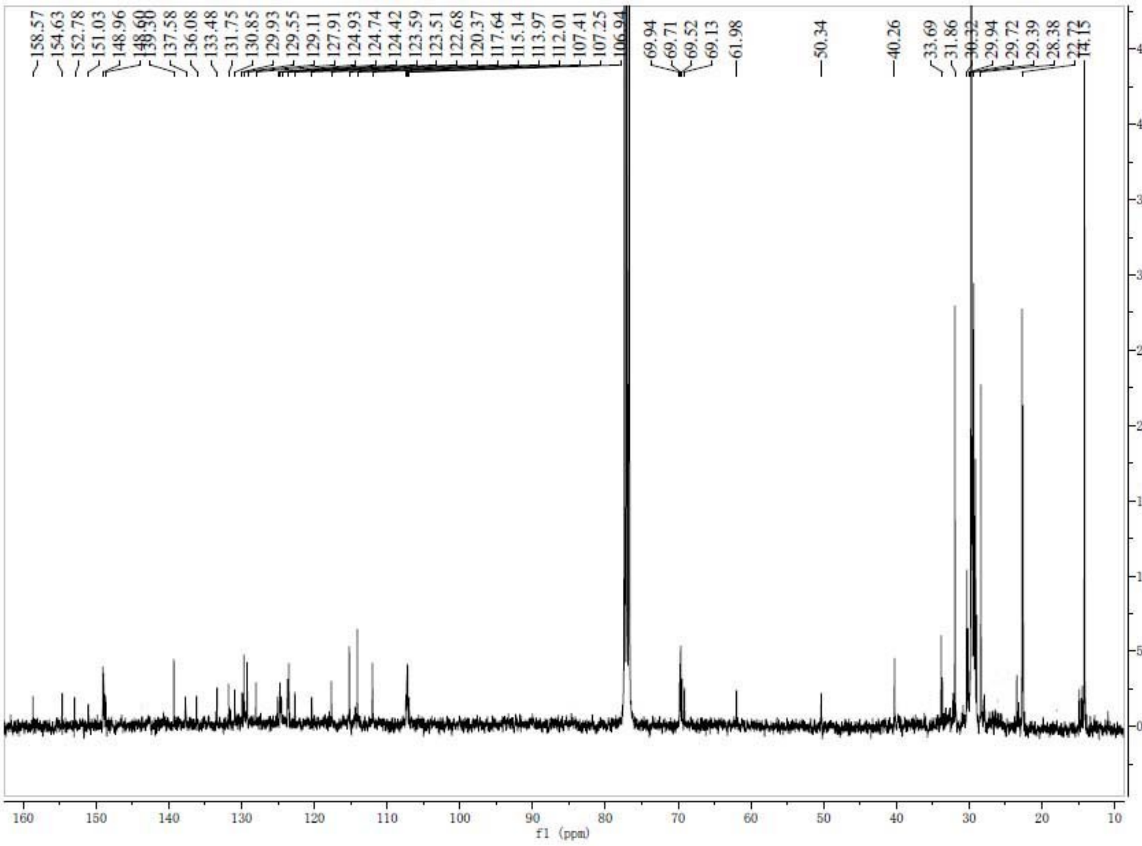


Figure S9. ^{13}C NMR spectrum of **7**

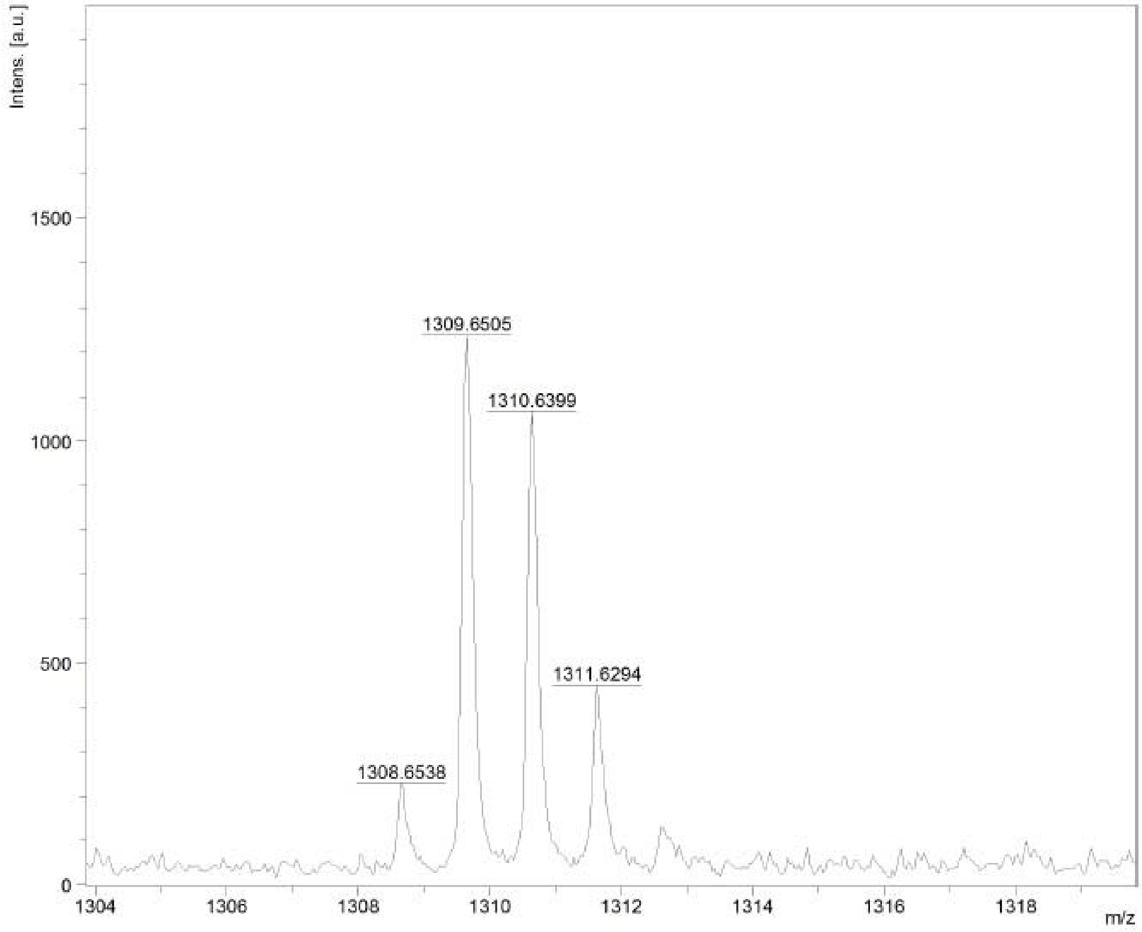


Figure S10. MALDI-TOF-MS spectrum of **7**

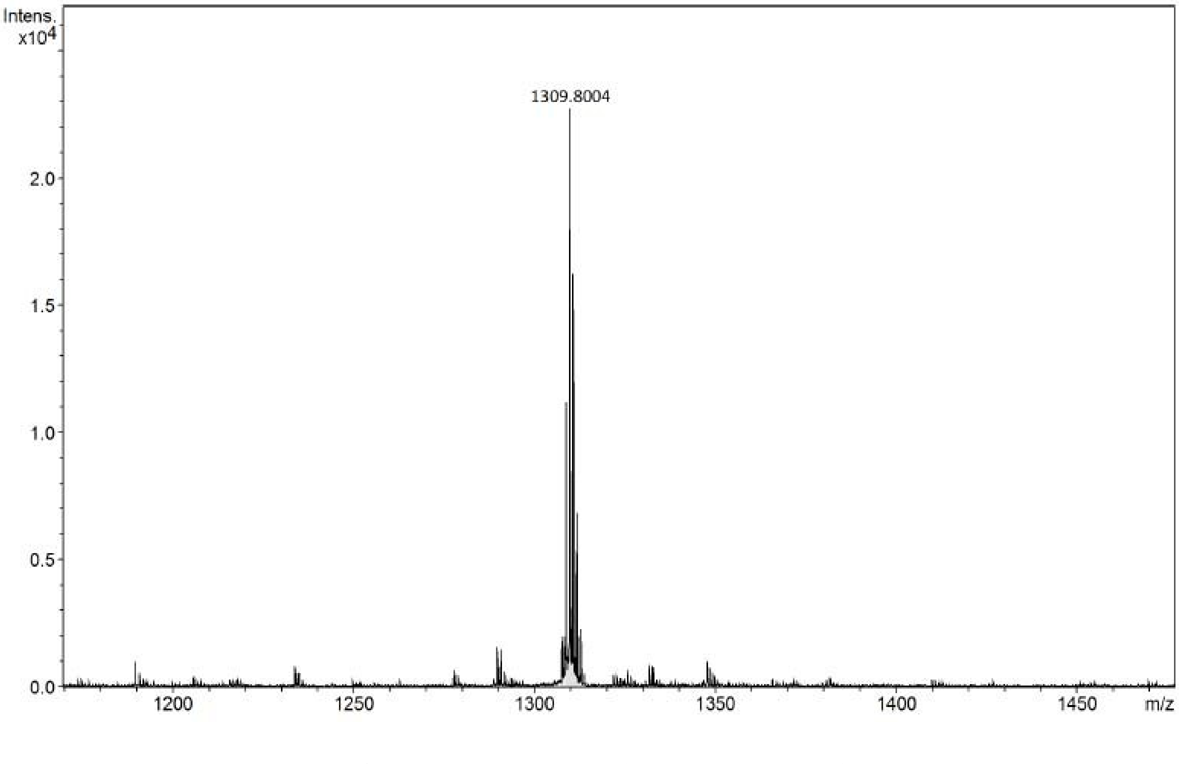
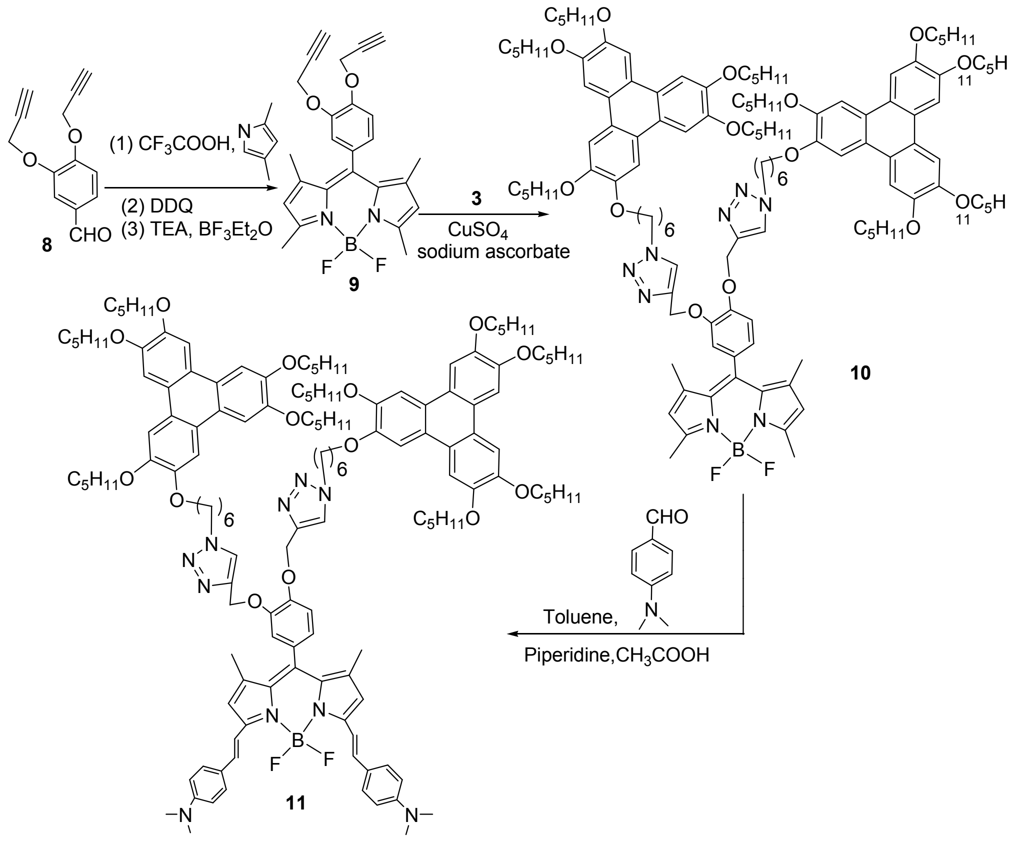


Figure S11. HR-MS (ESI) spectrum of **7**



Scheme S2. The synthetic route for triphenylene-Bodipy-triphenylene triad derivative **11**

2.4. Synthesis of compound 9

Under N_2 atmosphere, four drops of trifluoroacetic acid were added in the CH_2Cl_2 solution(120 mL) of compound **8** (0.13 g, 0.6 mmol) and 2,4-dimethyl-1*H*-pyrrole (0.14g, 1.5 mmol). The solution was stirred at room temperature for 12 h. Subsequently, 2,3-dichloro-5,6-dicyano-p-benzoquinone (0.16 g, 0.7 mmol) was added in reaction system. The mixtural solution was reacted continuously for another 4 h. Furthermore, triethylamine (6 mL, 0.043 mol) and $BF_3 \cdot Et_2O$ (6 mL, 0.05 mol) was added into reaction system. The obtained mixture was further stirred at room temperature overnight. After reaction, 90 mL of water was added in the mixture and the orgainc layer was separated. The organic portion was further washed with 100 mL of 5% aqueous $NaHCO_3$ solution and then dried over anhydrous $MgSO_4$. After filteration, the solution was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (eluent: CH_2Cl_2/ petroleum ether =1:1). Compound **9** was obtained as an red solid in yield of 24%. Compound **9**: ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 1.50 (s, 6H, CH_3), 2.47 (s, 1H, CH), 2.56 (s, 1H, CH), 2.57 (s, 6H, CH_3), 4.79 (s, 2H, OCH_2), 4.85 (s, 2H, OCH_2), 6.00 (s, 2H, ArH), 6.91 (d, 1H, *J* = 8.0Hz, ArH), 7.00 (s, 1H, ArH), 7.18 (d, 1H, *J* = 8.0Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) δppm:14.44, 14.60, 29.71, 53.48, 56.71, 57.06, 76.28, 76.33, 77.88, 78.11, 114.58, 115.49, 121.20, 121.58, 128.46, 131.63, 141.07, 143.07, 148.05, 155.39. HR-MS(ESI) ($C_{25}H_{24}BF_2N_2O_2$) $[M]^+$: Calcd.: 433.1897. found:433.1869.

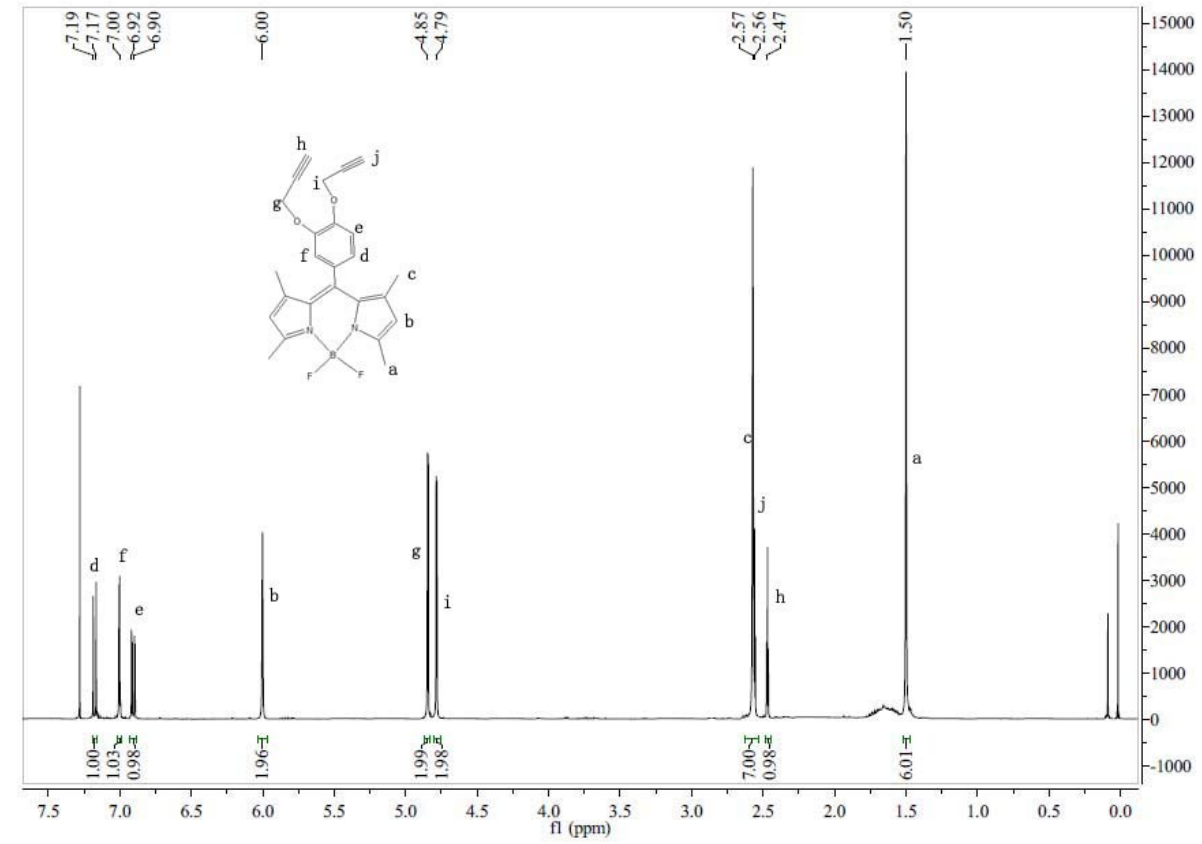


Figure S12. ^{1}H NMR spectrum of **9**

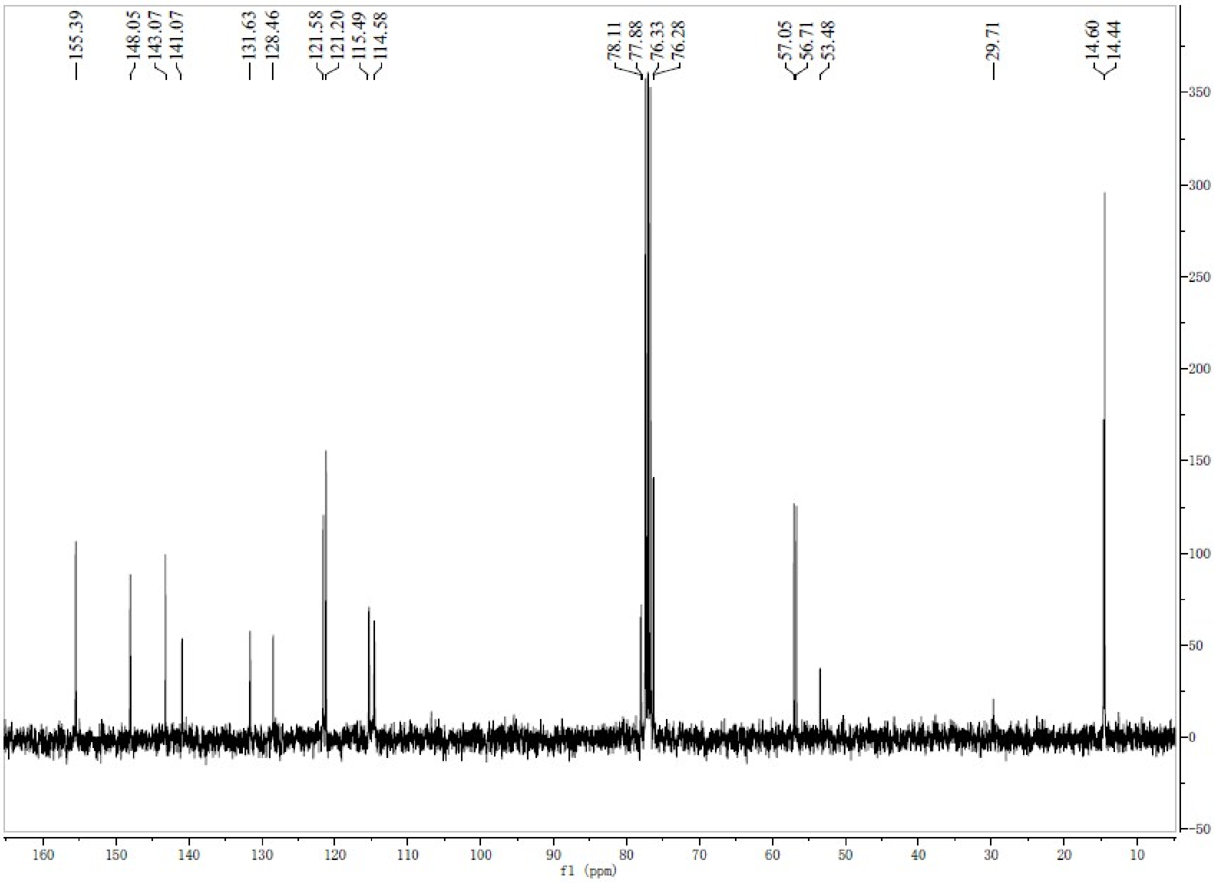


Figure S13. ^{13}C NMR spectrum of **9**

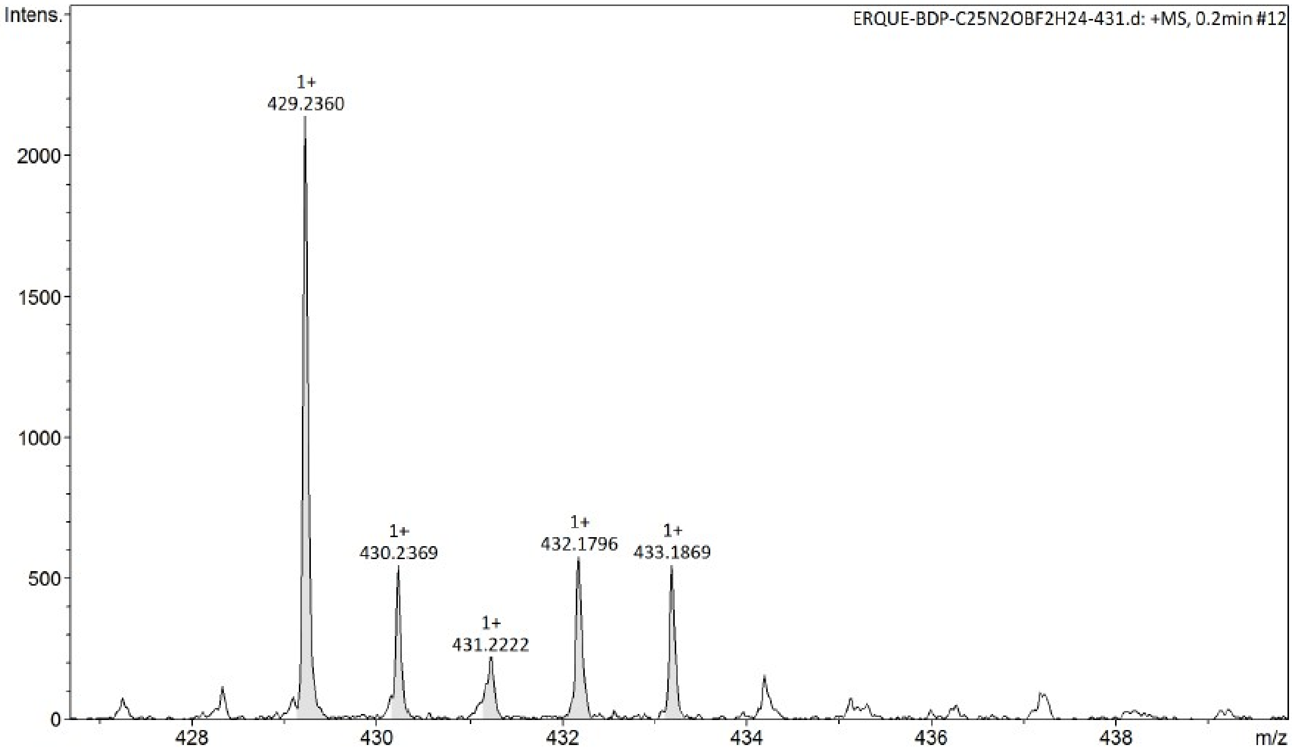


Figure S14. HR-MS (ESI) spectrum of **9**

2.5. Synthesis of compound 10

$CuSO_4{\cdot}5H_2O$ (62 mg, 0.25 mmol) and sodium ascorbate (100 mg, 0.5 mmol) were added into the DMF solution (20 mL) of compound **9** (90 mg, 0.21 mmol) and compound **3** (72 mg, 0.1 mmol). The mixture was stirred at 100°C for 15 h. After cooling, the solution was partitioned by $CHCl_3$ (50 mL) and water (50 mL). The organic phase was separated, washed by water (3×30mL) and then dried over $MgSO_4$. After filtration, the solvent removed under reduced pressure. The residue was was purified by silica gel column chromatography with the eluent of CH_2Cl_2/ petroleum ether (1:1). Compound **10** was collected as an red solid in yield of 64%.

Compound **10**: ^1H NMR (400 MHz, $CDCl_3$) δppm: 0.99 (t, 30H, $CH_2\underline{CH_3}$), 1.33~2.02 (m, 82H, CH_2 and CH_3), 2.54 (s, 6H, CH_3), 4.23(m, 24H, OCH_2), 4.38 (m, 4H, NH_2), 5.22 (bs, 4H, OCH_2-trazole), 5.96 (s, 2H, ArH), 6.79 (d, 1H, *J* = 8.0Hz, ArH), 6.94 (s, 1H, ArH), 7.05 (d, 1H, *J* = 8.0Hz, ArH), 7.70--7.73 (m, 2H, H-trazole), 7.84 (bs, 12H, TpH); ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 14.11, 14.35, 20.46, 22.57, 25.50, 25.63, 26.09, 26.38, 28.38, 29.70, 30.13, 31.32, 33.16, 50.27, 65.57, 69.17, 69.52, 69.69, 80.17, 107.02, 107.34, 107.41, 107.51, 115.59, 115.69, 121.16, 123.45, 123.68, 128.33, 128.81, 130.89, 131.58, 140.95, 142.99, 148.76, 148.89, 149.02, 155.38; MALDI-TOF-MS Calcd.for *m*/*z* = 2033.5, found: *m*/*z* = 2035.2 ($M+H^+$). HR-MS(ESI) ($C_{123}H_{169}BF_2N_8O_{14}$) $[M+Na]^+$: Calcd.: 2055.2754. found:2055.2663. Elemental Analysis Calcd.: C 72.68, H 8.38, N 5.51%. Found: C 72.63, H 8.44, N 5.42%.

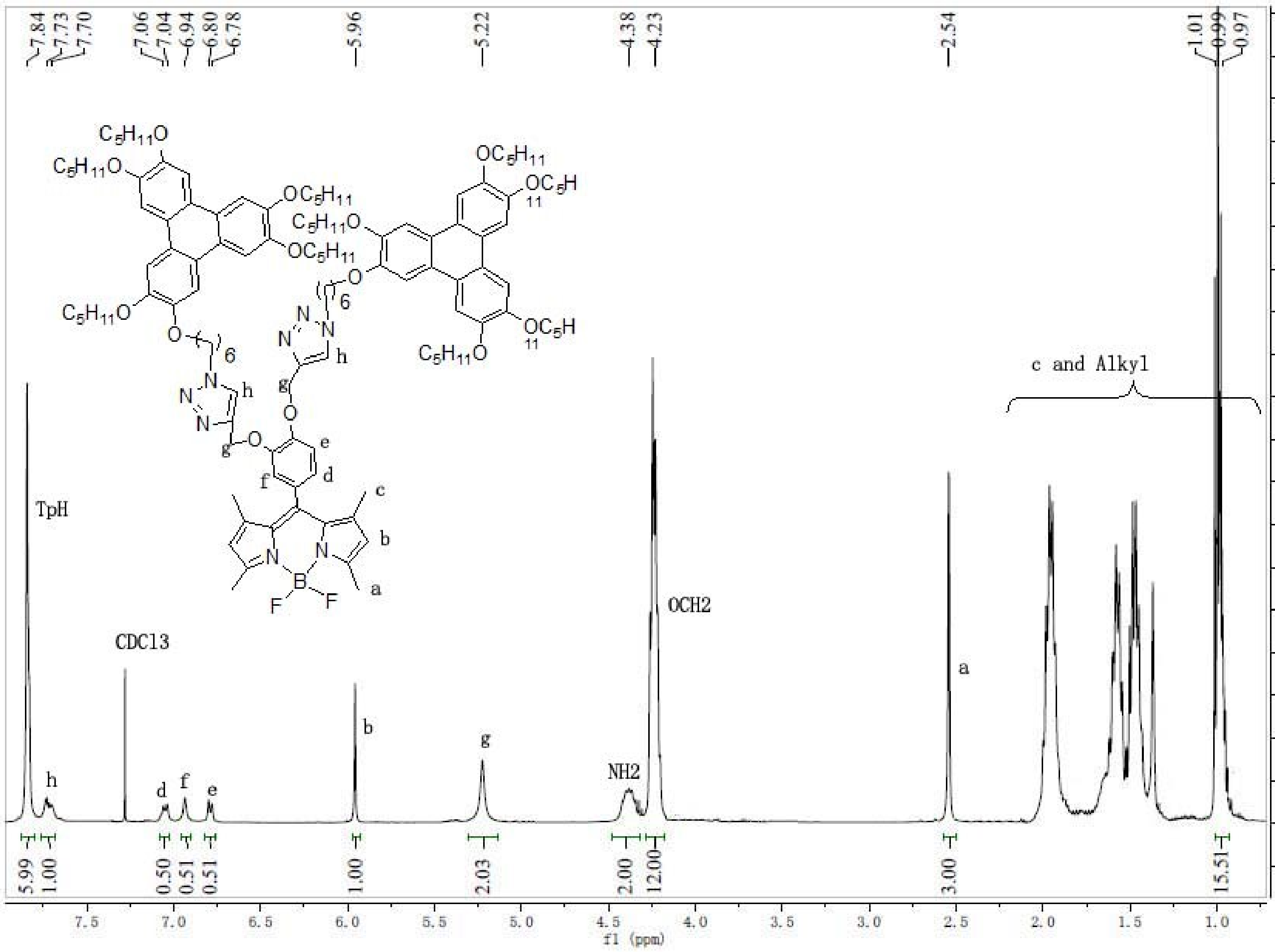


Figure S15. ^{1}H NMR spectrum of **10**

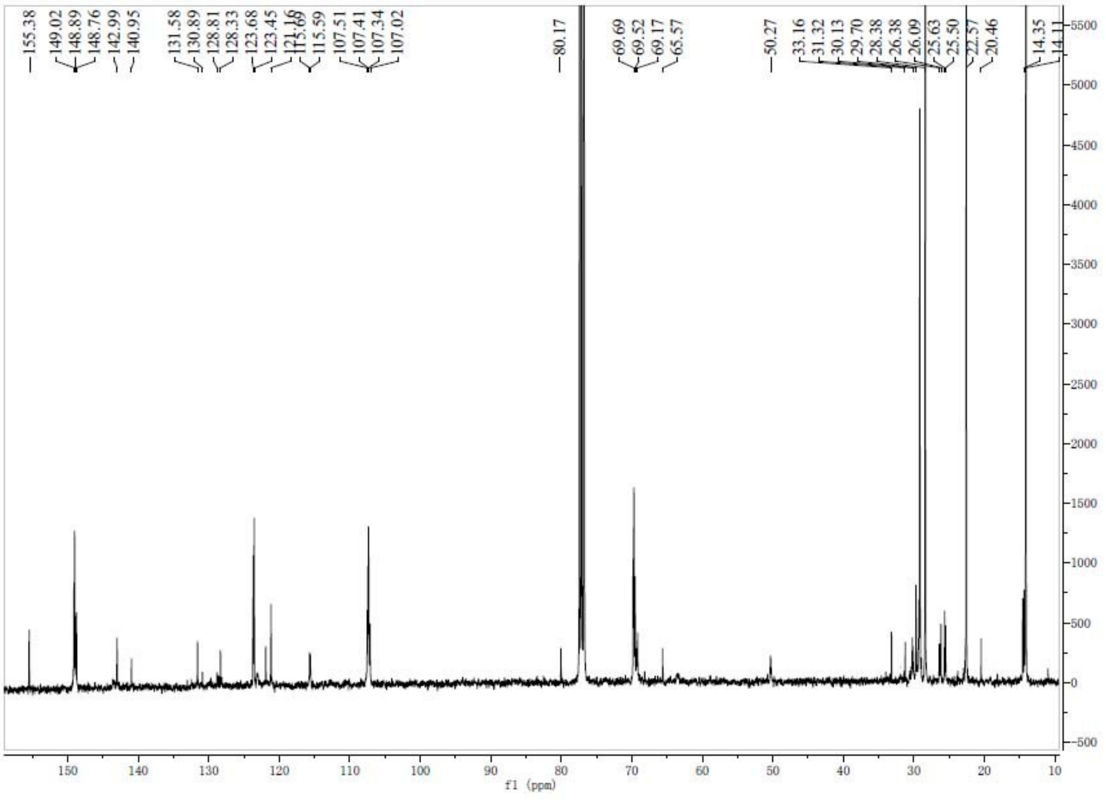


Figure S16. ^{13}C NMR spectrum of **10**

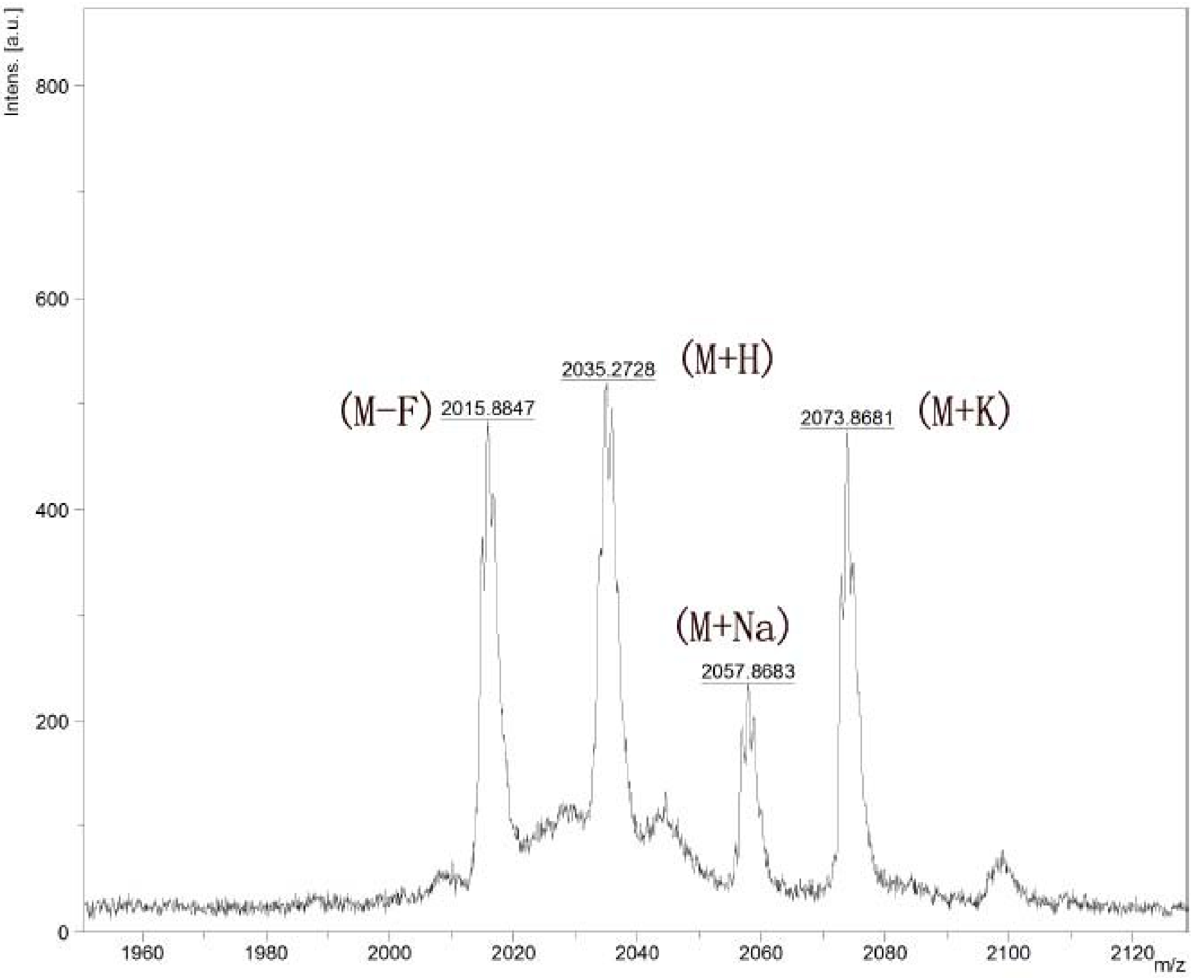


Figure S17. MALDI-TOF-MS spectrum of **10**

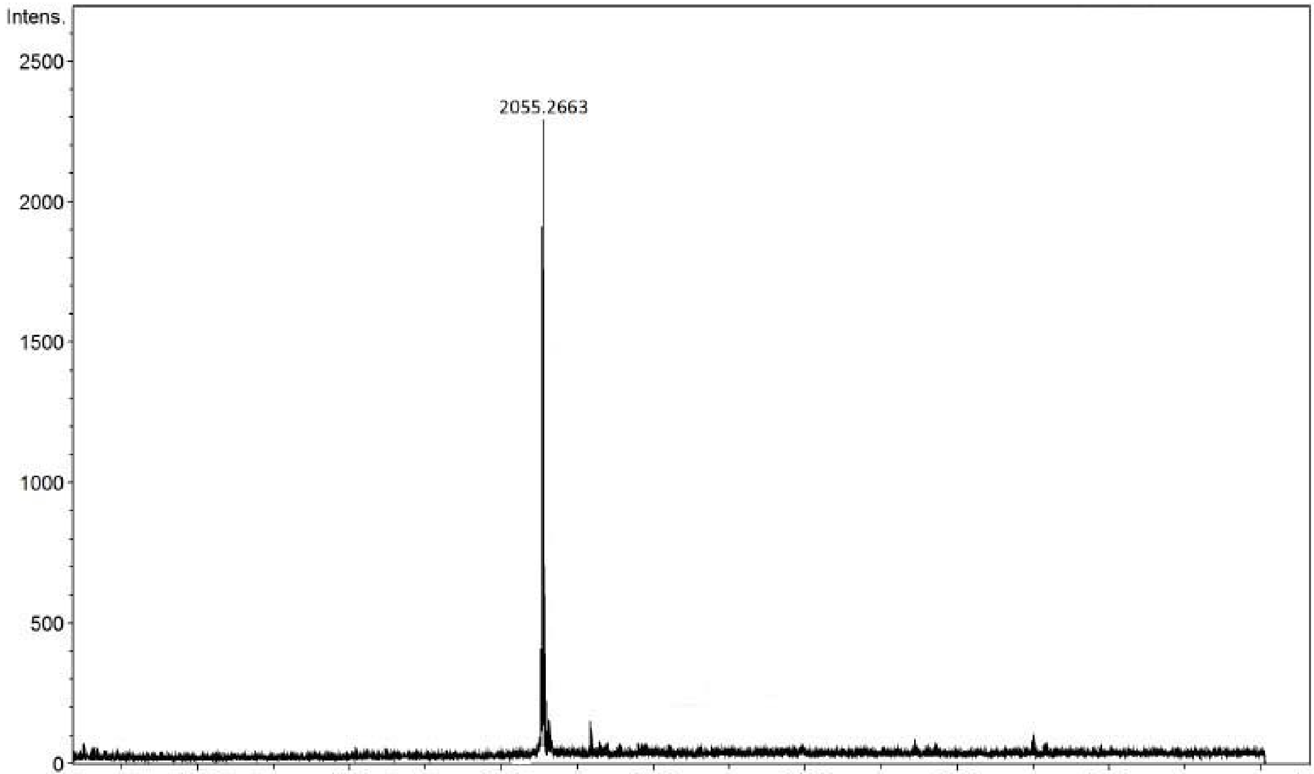


Figure S18. HR-MS (ESI) spectrum of **10**

2.6. Synthesis of compound 11

Under N_2 atmosphere, compound **10** (200 mg, 0.98 mmol) and *p*-dimethylaminobenzaldehyde (36 mg, 2.5 mmol) were add in a round-bottomed flask with 30 mL of dry toluene. 2 mL of piperidine, 2 mL of glacial acetic acid and a small amount of 3 Å molecular sieves were added in the flask. The mixture was stirred and refluxed for 5 h. After cooling, the solvent was evaporated under reduced pressure. The residue was partitioned by $CHCl_3$ and the solution of NH_4Cl (10%). The organic layer was dried with NaCl (satd.) and anhydrous $MgSO_4$. After concentration, the product was purified by silica gel column chromatography using CH_2Cl_2/ petroleum ether (2:1) as eluent. A green solid was obtained in the yield of 21%.

Compound **11**: ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 0.98 (t, 30H, $CH_2\underline{CH_3}$), 1.35~2.03 (m, 82H, CH_2 and CH_3), 3.00 (s, 12H, NCH_3), 4.23(m, 24H, OCH_2), 4.39 (m, 4H, NH_2), 5.24 (s, 2H, OCH_2-trazole), 5.27 (s, 2H, OCH_2-trazole), 6.59 (s, 2H, ArH), 6.66 (d, 4H, *J* = 8.0Hz, ArH), 6.84 (d, 1H, *J* = 8.0Hz, ArH), 6.96 (s, 1H, ArH), 7.05 (d, 1H, *J* = 8.0Hz, ArH), 7.16 (d, 2H, *J* = 12.0Hz, CH=), 7.49 (d, 4H, *J* = 8.0Hz, ArH), 7.53 (d, 2H, *J* = 12.0Hz, CH=), 7.69 (s, 1H, H-trazole), 7.76 (s, 1H, H-trazole), 7.83 (bs, 12H, TpH); ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 14.13, 15.77, 22.71, 23.75, 25.54, 26.75, 27.30, 28.49, 288.88, 29.53, 30.05, 31.94, 32.63, 33.07, 33.84, 38.78, 50.13, 63.39, 68.17, 69.18, 69.33, 69.85, 107.07, 107.31, 114.08, 116.45, 116.99, 119.92, 122.93, 123.54, 124.51, 126.40, 128.22, 128.85, 129.10, 129.46, 130.79, 131.60, 132.24, 132.42, 133.30, 133.94, 135.45, 138.11, 139.16, 140.41, 145.24, 148.91, 149.70, 151.53, 157.15, 157.95; MALDI-TOF-MS Calcd.for *m*/*z* = 2294.5, found: *m*/*z* = 2296.6 (M+H$^+$). HR-MS(ESI) ($C_{141}H_{187}BF_2N_{10}O_{14}$) [M]$^+$: Calcd.: 2294.4327. found:2294.4277. Elemental Analysis Calcd.: C 73.80, H 8.21, N 6.10%. Found: C 73.73, H 8.28, N 6.01%.

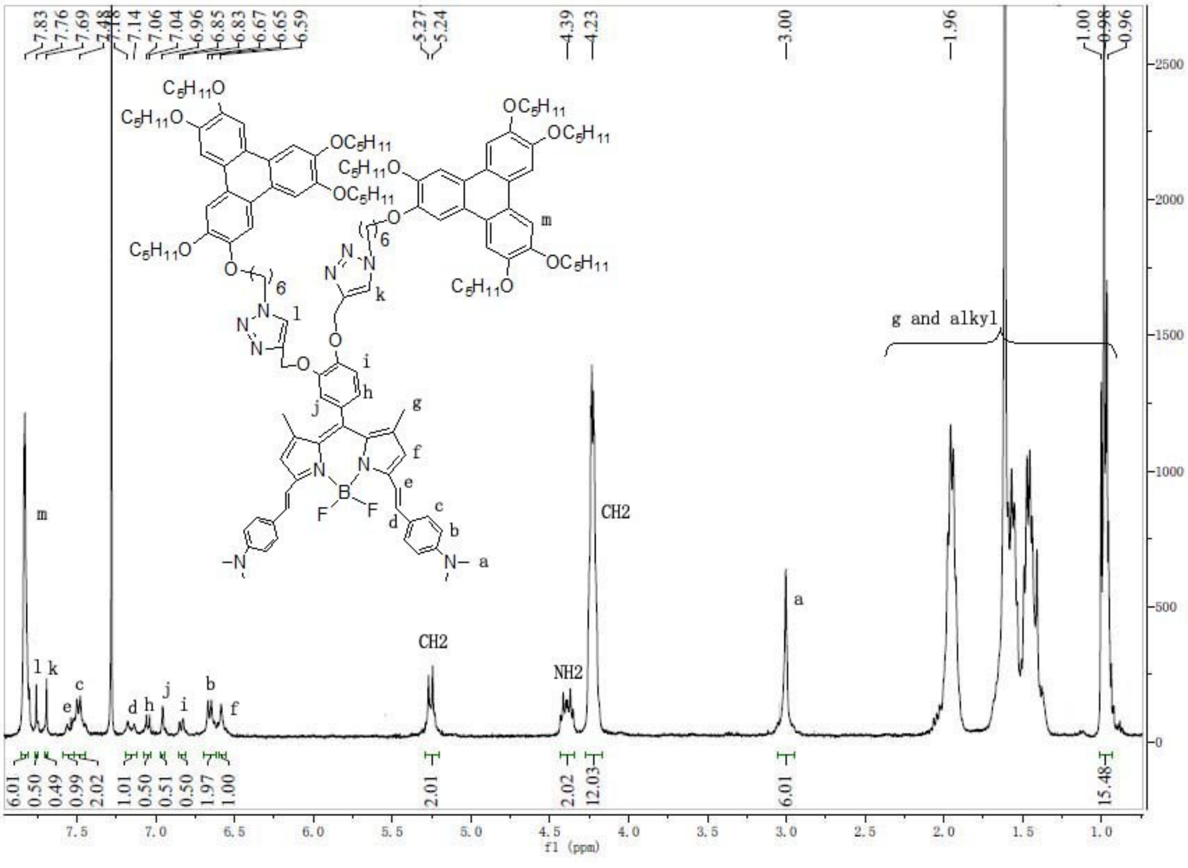


Figure S19. ^{1}H NMR spectrum of **11**

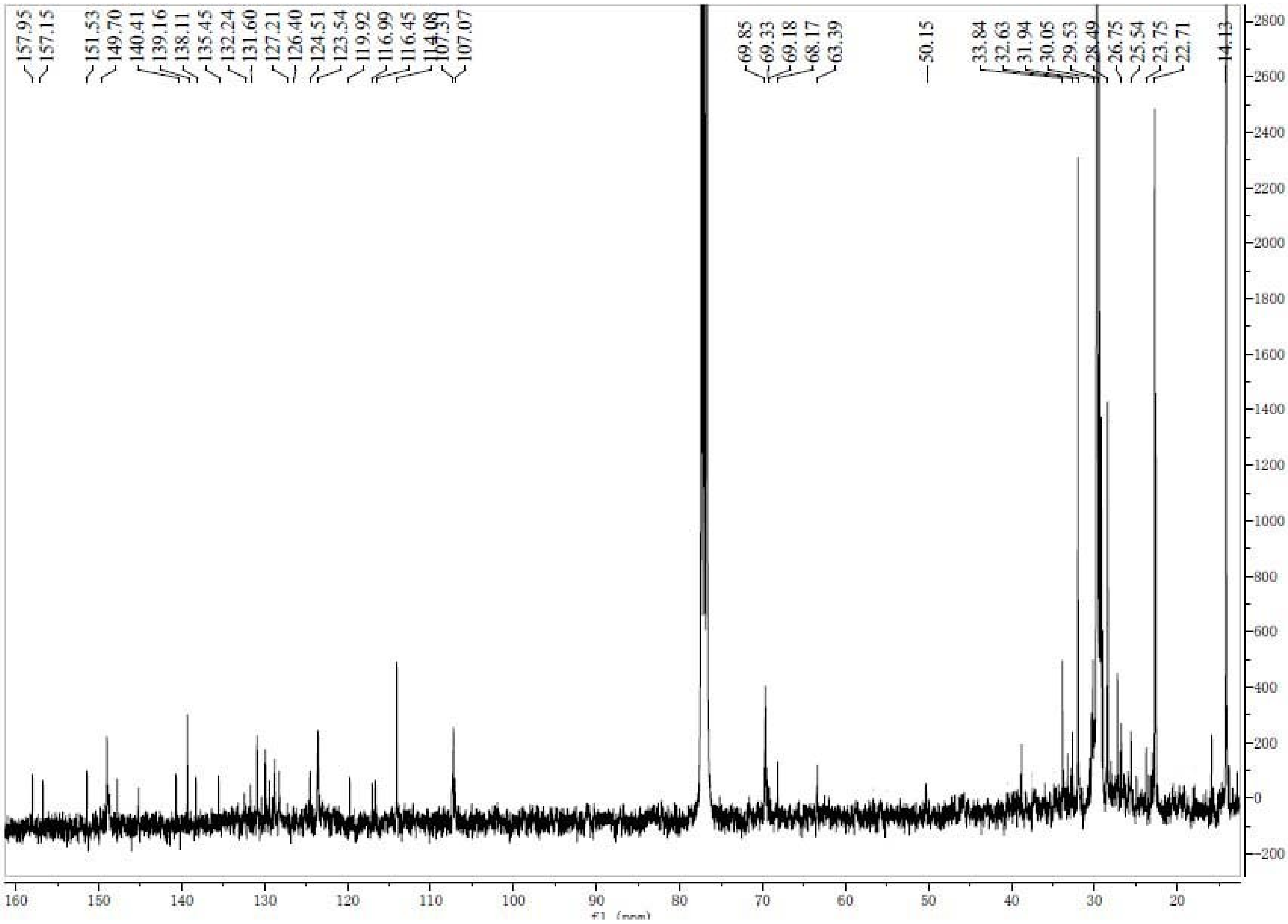


Figure S20. ^{13}C NMR spectrum of **11**

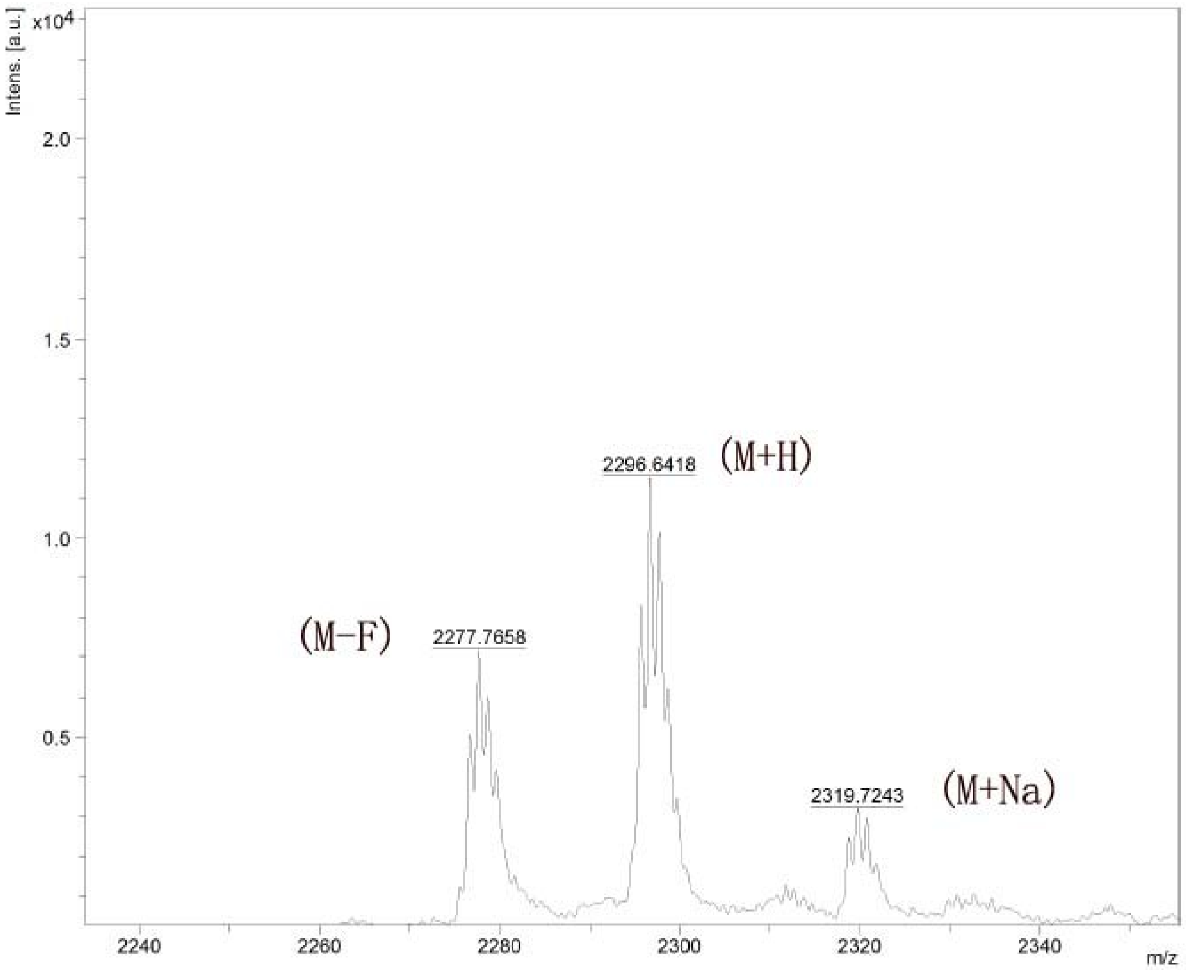


Figure S21. MALDI-TOF-MS spectrum of **11**

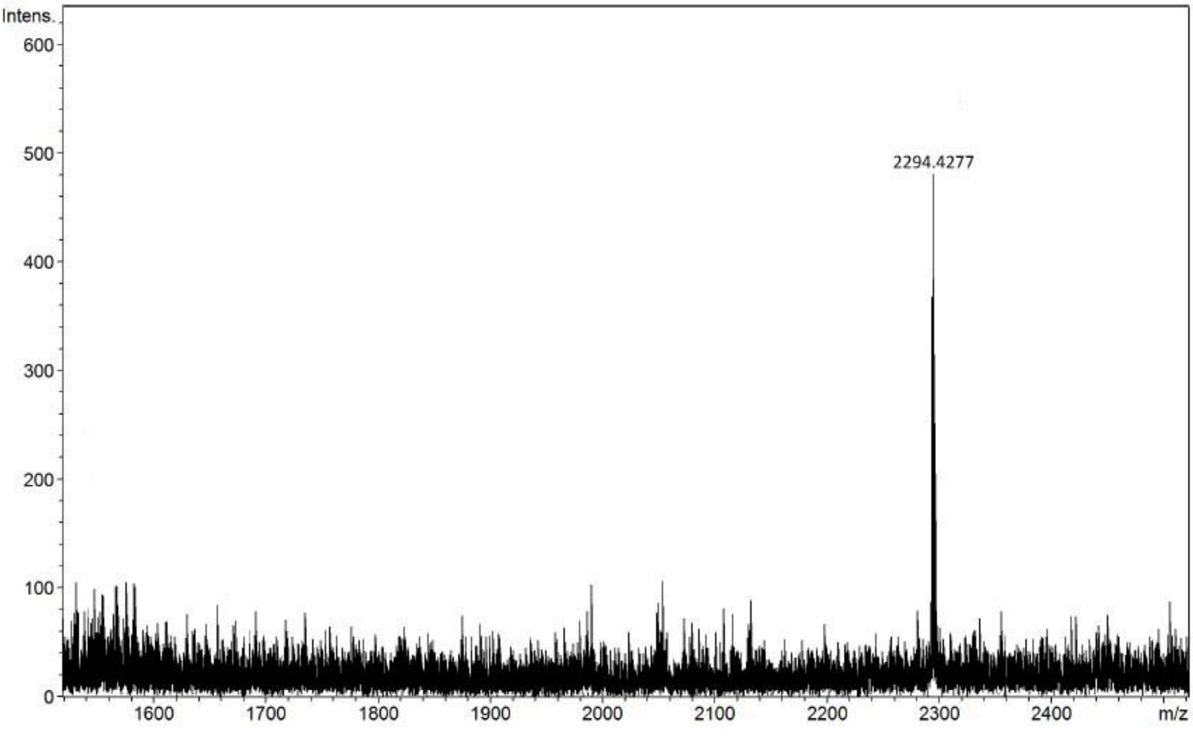


Figure S22. HR-MS (ESI) spectrum of **11**

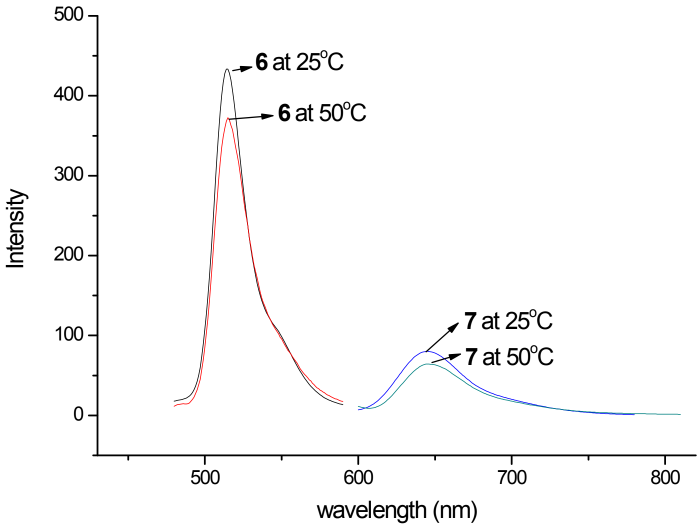


Figure S23. Fluorescence emission spectra of compounds **6** and **7** in toluene at different temperature.

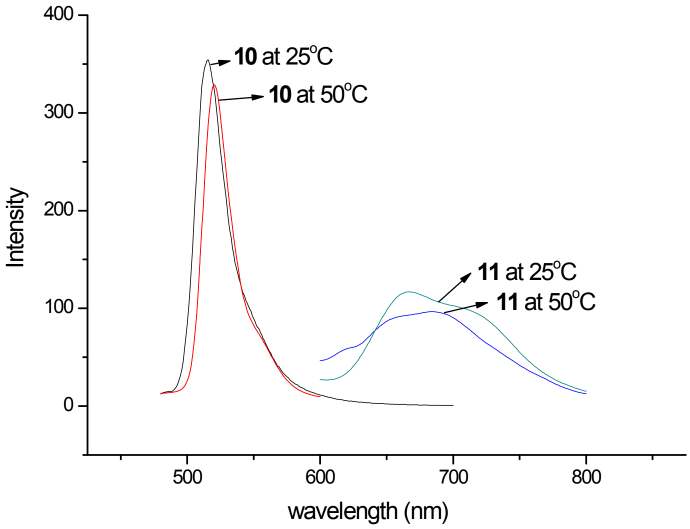


Figure S24. Fluorescence emission spectra of compounds **10** and **11** in toluene at different temperature.