Supporting Information

One-pot Efficient Synthesis of Dimeric, Trimeric, and Tetrameric BODIPY Dyes for Panchromatic Absorption

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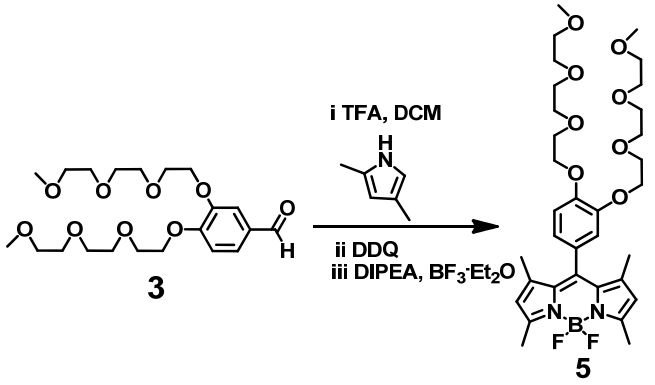
Instrumentation. ^{1}H NMR, ^{13}C NMR and ^{11}B NMR spectra were taken on a 400 MHz Varian Unity Inova spectrophotometer instrument. UV spectra were taken on a Hewlett-Packard 8452A Diode Array UV-visible spectrophotometer. Fluorescence spectra were recorded on a Spex Fluorolog 1681 0.22m steady-state fluorometer. Fluorescence quantum yields of BODIPY dyes were measured in dichloromethane, which were calculated by using fluorescein excited at 490 nm in 0.1 N NaOH as the reference quantum efficiency (ϕ_n = 85%).[1-4] Concentrations of BODIPY dyes ranging from 1.0 x 10^{-7} mol/L to 5.0 x 10^{-8} mol/L (in which the quantum yields do not change with varying concentration) were used to measure fluorescence quantum yields, absorption and fluorescent spectra.

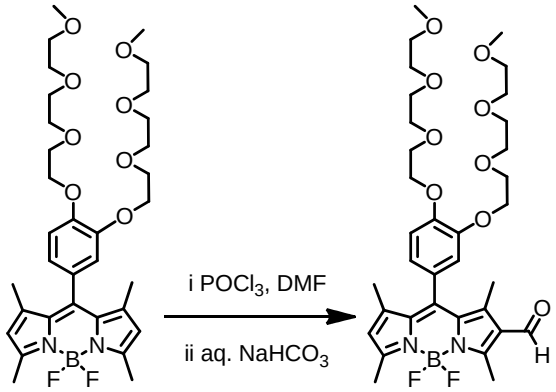
Materials. Unless otherwise indicated, all reagents and solvents were obtained from commercial suppliers (Aldrich, Sigma, Fluka, Acros Organics, Fisher Scientific, Lancaster) and were used without further purification. Air- and moisture-sensitive reactions were conducted in oven-dried glassware using a standard Schlenk line or drybox techniques under an inert atmosphere of dry nitrogen. Compound **3** was prepared according to the reported procedure.[5]

General Remarks for the Synthesis



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

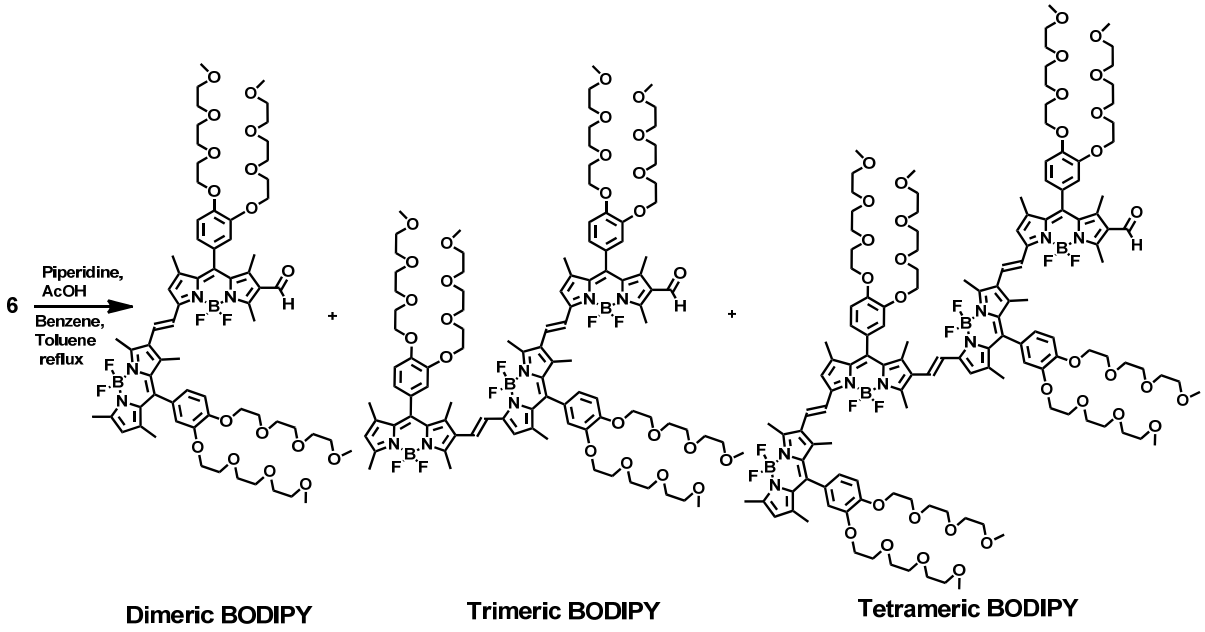
The aldehyde derivative (**3)** (3.2 g, 7.44 mmol) and 2,4-dimethylpyrrole **2** (1.77 g, 18.6 mmol) were dissolved in dry CH_2Cl_2 (500 mL). Five drops of trifluoroacetic acid (TFA) were added to the reaction mixture, and the resulting mixture was stirred in the dark for 12 h under nitrogen atmosphere at room temperature. After the complete consumption of the aldehyde derivative (**3)**, DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) (2.0 g, 8.77 mmol) was added to the reaction mixture. When the mixture was stirred for 40 min, 12 mL of diisopropylethylamine (DIPEA) and 12 mL of $BF_3{\cdot}OEt_2$ were added to the mixture. After the mixture was further stirred for 40 min, it was concentrated, washed twice with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using hexane/Acetone/CH_2Cl_2 (4/2/2, v/v) to obtain BODIPY dye (**5**) as a dark brown oil (1.54 g, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 1.6 Hz, 1H), 6.76 (dd, *J* = 8.4, 1.6 Hz, 1H), 5.94 (s, 2H), 4.19 (t, *J* = 4.8 Hz, 2H), 4.10 (t, *J* = 5.2 Hz, 2H), 3.88 (t, *J* = 4.8 Hz, 2H), 3.82 (t, *J* = 5.2 Hz, 2H), 3.75-3.47 (m, 16H), 3.34 (s, 3H), 3.32 (s, 3H), 2.51 (s, 6H), 1.43 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 149.9, 149.7, 143.3, 141.7, 131.9, 127.9, 121.2, 114.7, 114.4, 72.2, 72.1, 71.1, 70.9, 70.8, 70.7, 70.0, 69.9, 69.3, 68.9, 59.2, 59.1, 14.7, 14.6. IR (cm^{-1}): 2922, 2872, 1542, 1506, 1468, 1409, 1371, 1363, 1304, 1276, 1262, 1191, 1155, 1104, 1083, 1051, 973, 835, 811, 759, 750, 726, 700. HRMS (FAB) calcd for $C_{33}H_{47}N_2F_2BO_8$ $[M]^+$, 648.3394; found, 648.3396.



5 **6**

4,4-Difluoro-8-[3,4-bis{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}phenyl]-1,3,5,7-tetramethyl-6-formyl-4-bora-3a,4adiaza-s-indacene (6).

A mixture of DMF (7.5 mL) and $POCl_3$ (7.5 mL) was stirred in an ice bath for 5 min under argon atmosphere. After the reaction mixture was warmed to room temperature, it was stirred for additional 30 min. To the reaction mixture was added compound **5** (300 mg, 0.31 mmol) in 1, 2-dichloroethane (75 mL). After the mixture was stirred for 2 h at 50 ^{o}C, it was cooled to room temperature and slowly poured into saturated aqueous $NaHCO_3$ (200 mL) under an ice-cold condition. After the reaction mixture was warmed to room temperature, it was further stirred for 30 min and washed with water. The organic layers were combined, dried over anhydrous Na_2SO_4, and evaporated in vacuo. The crude product was further purified using column chromatography (silica gel, hexane/Acetone/CH_2Cl_2, 5/2/2, v/v) to give BODIPY dye (**6)** (302 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 2.0 Hz, 1H), 6.78 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.13 (s, 1H), 4.21 (t, *J* = 4.8 Hz, 2H), 4.12 (t, *J* = 5.2 Hz, 2H), 3.90 (t, *J* = 4.8 Hz, 2H), 3.84 (t, *J* = 5.2 Hz, 2H), 3.77-3.48 (m, 16H), 3.36 (s, 3H), 3.33 (s, 3H), 2.79 (s, 3H), 2.56 (s, 3H), 1.72 (s, 3H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.1, 161.7, 156.6, 150.1, 147.5, 143.6, 143.0, 134.6, 130.2, 126.9, 126.5, 124.1, 121.1, 114.7, 114.1, 72.2, 72.1, 71.1, 70.9, 70.8, 70.8, 70.7, 69.9, 69.8, 69.4, 68.9, 59.2, 59.2, 15.3, 15.2, 13.2, 11.9. IR (cm^{-1}): 2958, 2925, 2857, 1725, 1676, 1600, 1580, 1541, 1515, 1462, 1380, 1266, 1200, 1187, 1120, 1071, 1039, 981, 958, 768, 739, 704. HRMS (FAB) calcd for $C_{34}H_{47}N_2F_2BO_9$ $[M]^+$, 676.3343; found, 676.3336.



Dimeric, trimeric and tetrameric BODIPY dyes.

BODIPY dye **6** (200 mg, 0.30 mmol) was dissolved in a mixed solution of benzene (30 mL), toluene (10 mL), piperidine (0.5 mL) and AcOH (0.4 mL). The mixture was heated under reflux under a nitrogen atmosphere for 3 hours and any water formed during the reaction, was removed azeotropically by heating the mixture in a Dean-Stark apparatus. The mixture was concentrated in vacuo, diluted with EtOAc and washed with water and brine, respectively. The organic phase was collected, dried over Na_2SO_4 and concentrated under a reduced pressure. The crude product was simply purified by silica gel column chromatography (hexane/EtOAc/CH_2Cl_2/MeOH, 4/1/3/0.5 to hexane/acetone/CH_2Cl_2/MeOH, 4/2/2/0.5), and then further purified using silica gel plate to obtain dimeric BODIPY dye (82 mg, 41%) as light blue oil compound, trimeric BODIPY dye (28 mg, 14%) as purple blue oil compound and tetrameric BODIPY dye (9 mg, 5%) as dark blue oil compound. Dimeric BODIPY, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.33 (d, *J* = 16.4 Hz, 1H), 7.24 (d, *J* = 16.4 Hz, 1H), 7.02-6.98 (m, 2H), 6.83-6.77 (m, 4H), 6.67 (s, 1H), 6.05 (s, 1H), 4.23-4.19 (m, 4H), 4.14-4.10 (m, 4H), 3.92-3.88 (m, 4H), 3.85-3.82 (m, 4H), 3.77-3.47 (m, 32H), 3.35 (s, 6H), 3.32 (s, 6H), 2.78 (s, 3H), 2.73 (s, 3H), 1.71 (s, 3H), 1.63 (s, 3H), 1.52 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 158.6, 158.3, 155.8, 155.2, 150.0, 146.2, 145.6, 142.2, 141.2, 140.7, 139.5, 135.9, 133.3, 131.8, 131.6, 130.5, 127.4, 127.3, 126.9, 126.2, 122.8, 121.5, 121.3, 119.4, 118.9, 114.7, 114.6, 114.4, 72.1, 72.0, 71.1, 71.0,

70.9, 70.8, 70.7, 70.0, 69.9, 69.4, 69.3, 68.9, 59.2, 59.2, 15.4, 15.1, 14.0, 13.5, 13.3, 11.9. IR (cm^{-1}): 2921, 2973, 1665, 1608, 1536, 1501, 1472, 1429, 1360, 1307, 1264, 1195, 1100, 1064, 989, 853, 814, 762, 726. HRMS (FAB) calcd for $C_{68}H_{92}N_4F_4B_2O_{17}$ $[M]^+$, 1334.6580; found, 1334.6578. Trimeric BODIPY, ^1H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.36-7.14 (m, 4H), 7.02-6.98 (m, 3H), 6.85-6.78 (m, 6H), 6.68 (s, 1H), 6.62 (s, 1H), 6.03 (s, 1H), 4.24-4.19 (m, 6H), 4.15-4.10 (m, 6H), 3.93-3.89 (m, 6H), 3.86-3.82 (m, 6H), 3.78-3.47 (m, 48H), 3.36 (s, 3H), 3.35 (s, 6H), 3.32 (s, 6H), 3.31 (s, 3H), 2.78 (s, 3H), 2.74 (s, 6H), 2.56 (s, 3H), 1.71 (s, 3H), 1.64 (s, 3H), 1.63 (s, 3H), 1.53 (s, 3H), 1.51 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 158.5, 157.9, 156.0, 155.6, 154.7, 150.0, 149.9, 146.2, 145.0, 144.7, 142.0, 140.9, 140.4, 139.8, 139.4, 138.2, 136.0, 134.8, 133.1, 132.2, 131.9, 131.6, 129.8, 127.7, 127.3, 126.8, 126.1, 122.5, 121.5, 121.4, 119.5, 118.5, 114.7, 114.4, 72.2, 72.1, 71.1, 70.9, 70.8, 70.8, 70.7, 70.0, 69.9, 69.4, 68.9, 59.2, 59.1, 15.4, 15.3, 15.0, 14.1, 13.5, 11.9. IR (cm^{-1}): 2871, 1664, 1605, 1580, 1533, 1493, 1473, 1419, 1355, 1302, 1263, 1193, 1163, 1139, 1057, 987, 852, 821, 760, 727. HRMS (FAB) calcd for $C_{102}H_{137}N_6F_6B_3O_{28}$ $[M]^+$, 1992.9817; found, 1992.9843. Tetrameric BODIPY, ^1H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.35-7.13 (m, 6H), 7.03-6.99 (m, 4H), 6.86-6.79 (m, 8H), 6.69 (s, 1H), 6.64 (s, 1H), 6.61 (s, 1H), 6.03 (s, 1H), 4.24-4.20 (m, 8H), 4.15-4.11 (m, 8H), 3.93-3.89 (m, 8H), 3.87-3.83 (m, 8H), 3.70-3.46 (m, 64H), 3.37-3.36 (s x 4, 12H), 3.33-3.32 (s x 4, 12H), 2.79 (s, 3H), 2.75 (s, 6H), 2.74 (s, 3H), 2.56 (s, 3H), 1.71 (s, 3H), 1.65 (s, 6H), 1.63 (s, 3H), 1.53 (s, 3H), 1.52 (s, 6H), 1.47 (s, 3H). IR (cm^{-1}): 2921, 2873, 1665, 1606, 1580, 1533, 1492, 1421, 1355, 1302, 1264, 1248, 1194, 1164, 1141, 1060, 1014, 990, 853, 822, 782, 761, 727. HRMS (MALDI) calcd for $C_{136}H_{183}N_8F_8B_4O_{36}$ $[M+H]^+$, 2652.3132; found, 2652.3159.

References

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(5) Nielsen, C. B., Johnsen, M., Arnbjerg, J., Pittelkow, M., McIlroy, S. P., Ogilby, P. R., Jorgensen, M., *J. Org. Chem.* **2005**, *70*, 7065.

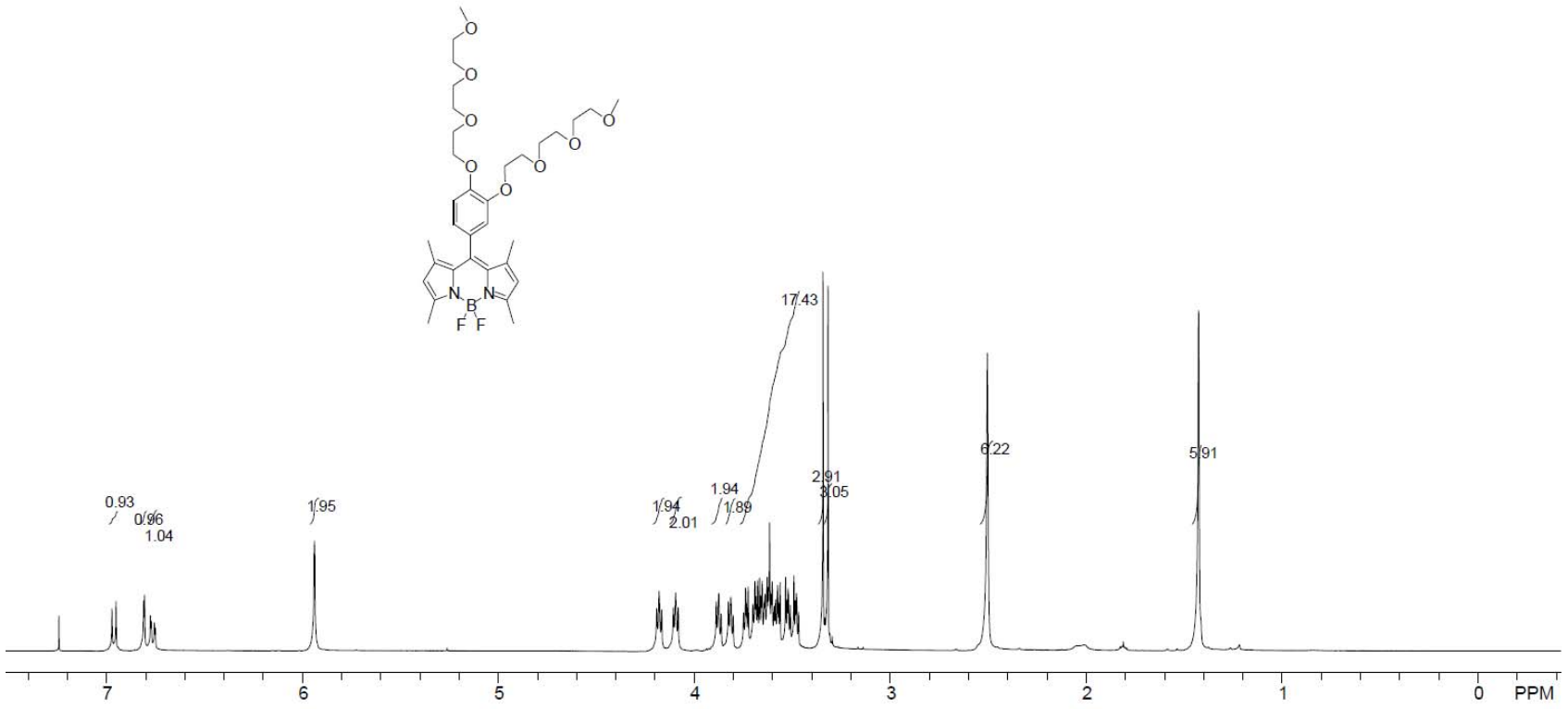


Figure 1. ^{1}H NMR spectrum of BODIPY dye **5** in $CDCl_3$ solution.

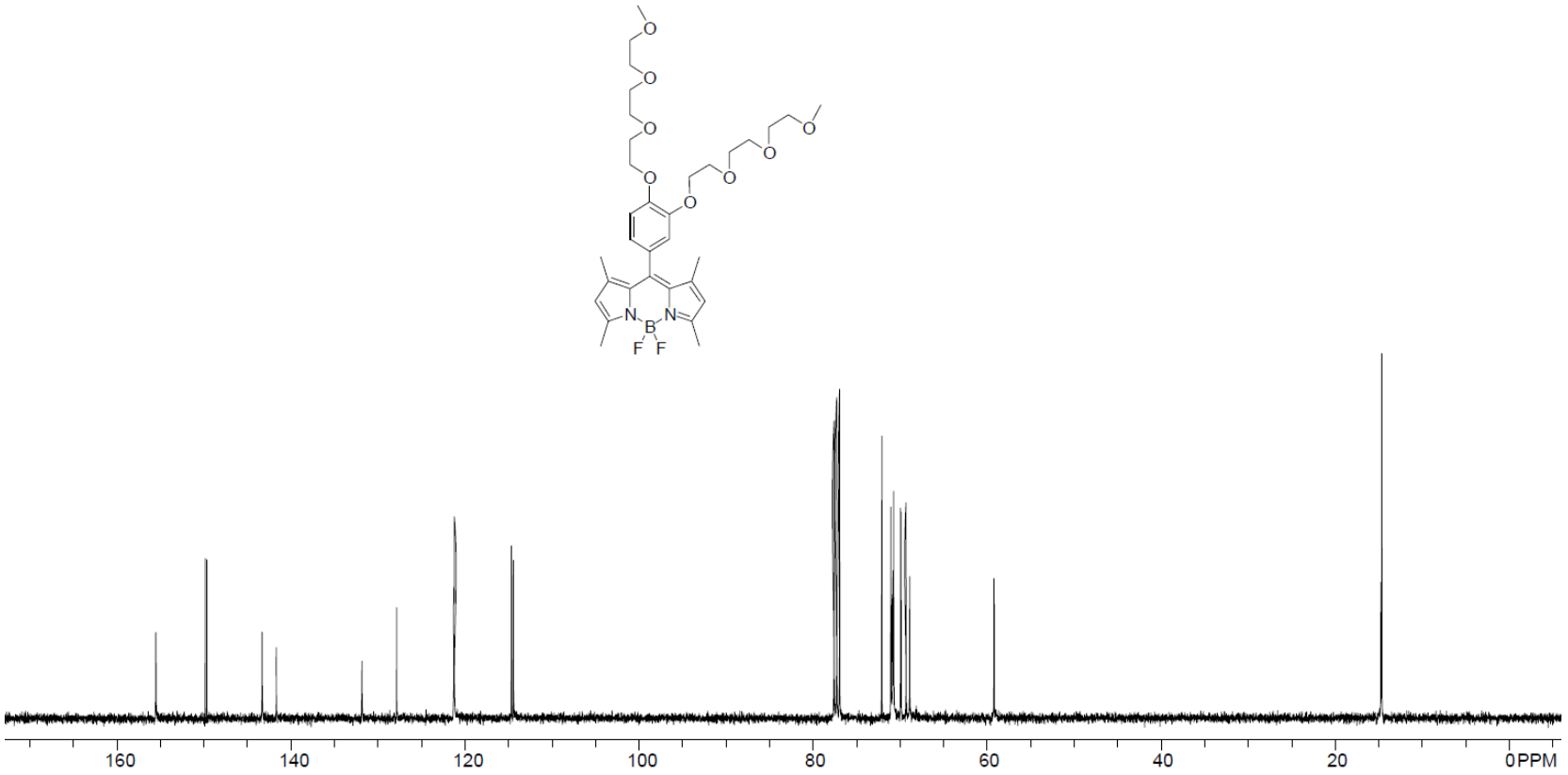


Figure 2. ^{13}C NMR spectrum of BODIPY dye **5** in $CDCl_3$ solution.

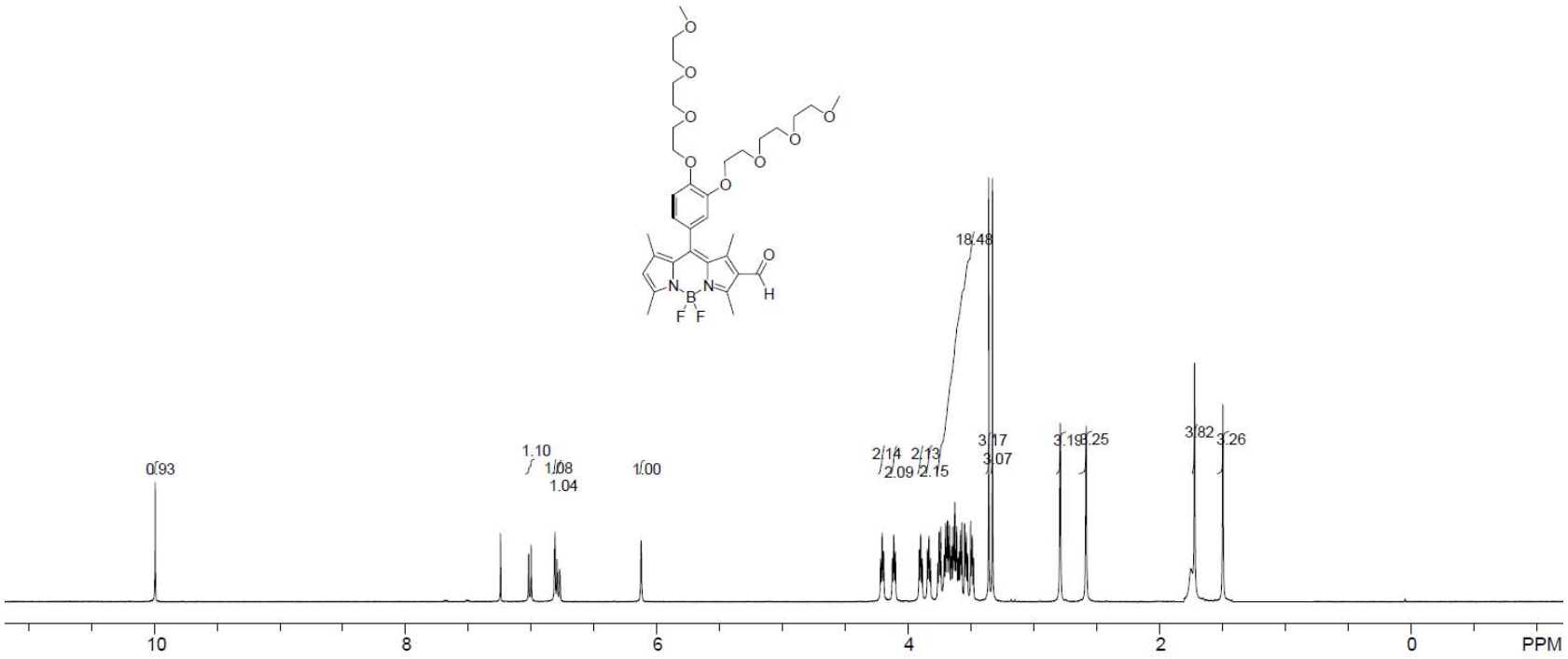


Figure 3. ^{1}H NMR spectrum of BODIPY dye **6** in $CDCl_3$ solution.

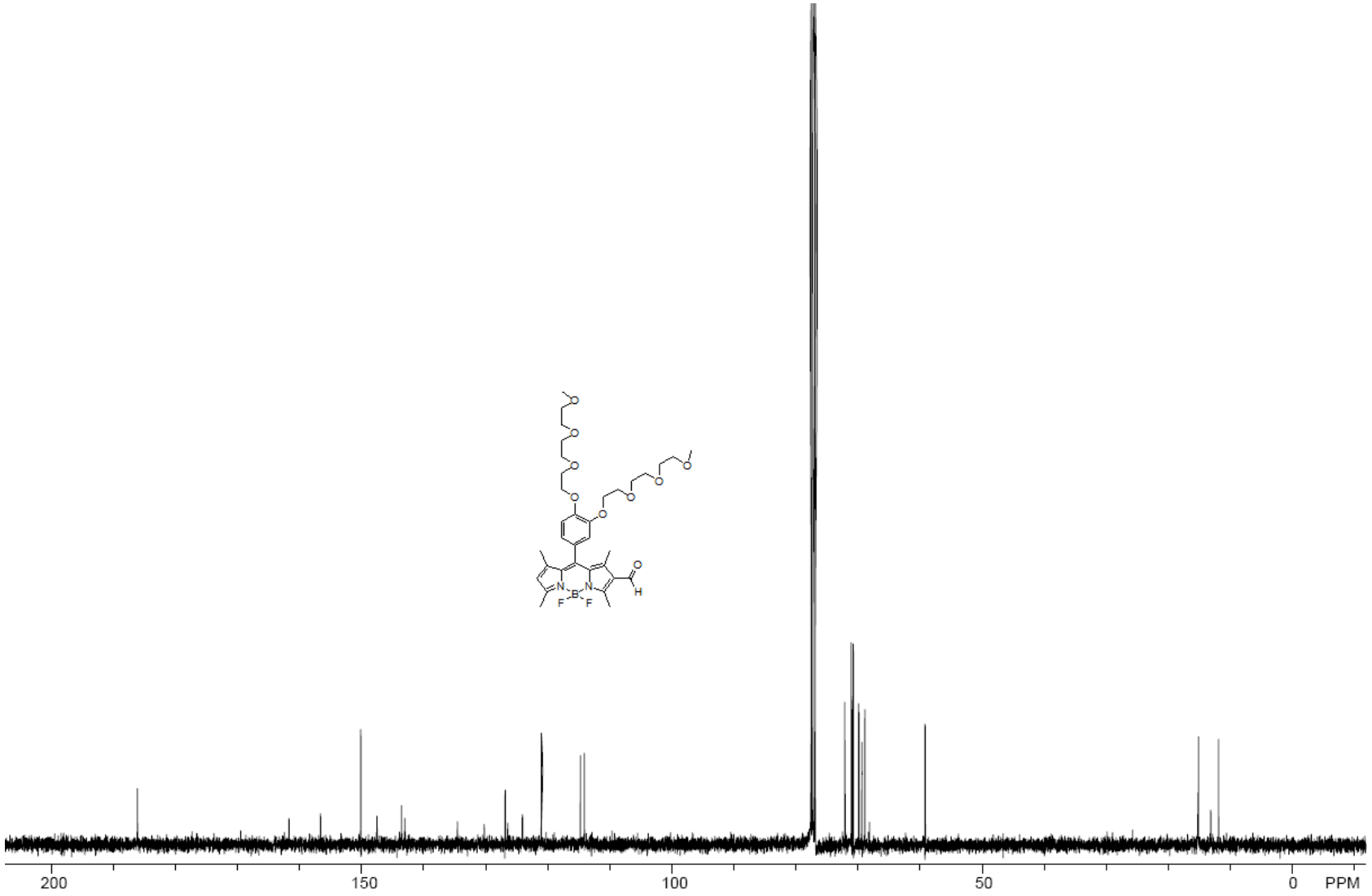
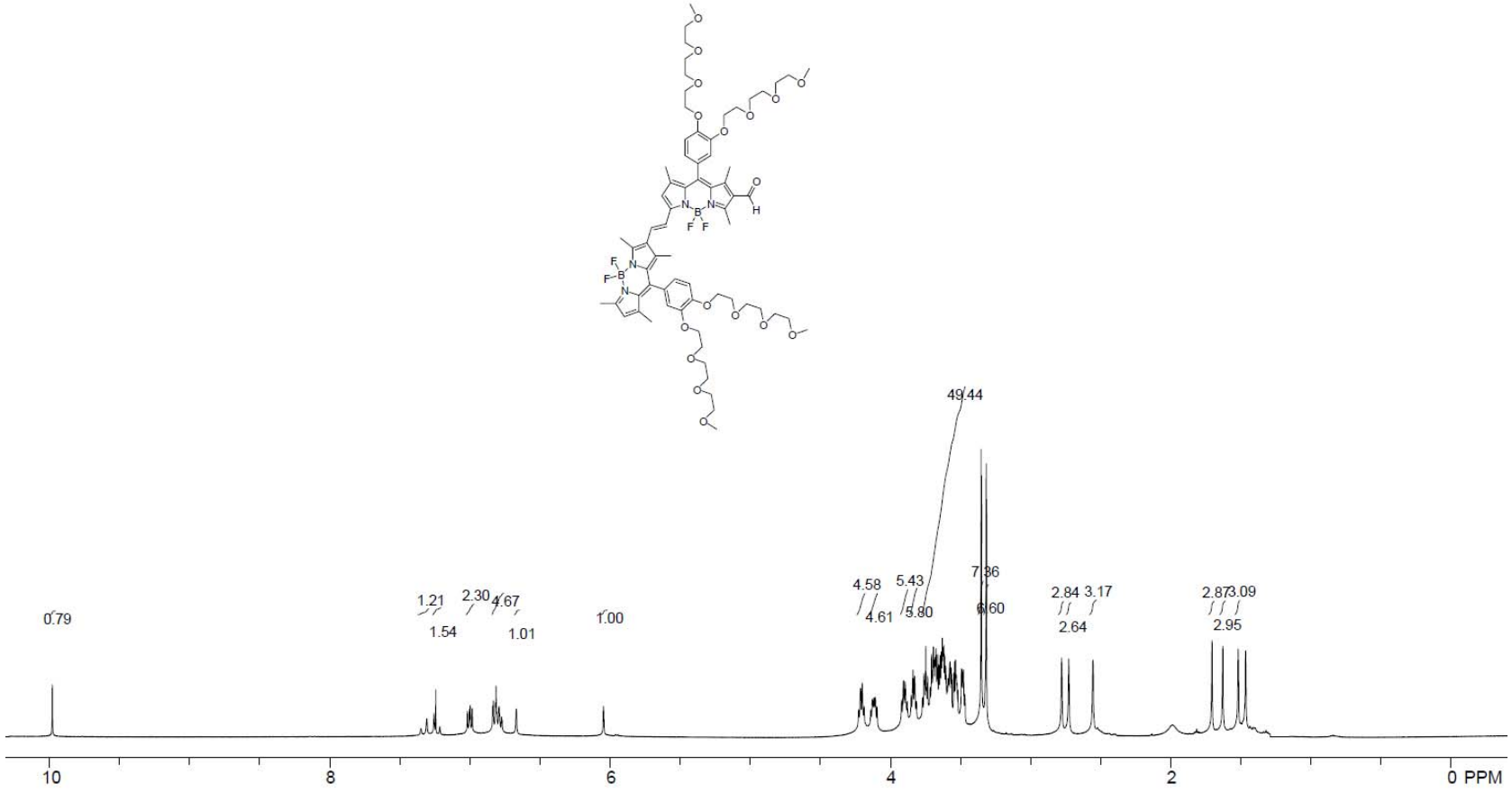


Figure 4. ^{13}C NMR spectrum of BODIPY dye **6** in $CDCl_3$ solution.



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igure 5. ^{1}H NMR spectrum of dimeric BODIPY dye in $CDCl_3$ solution.

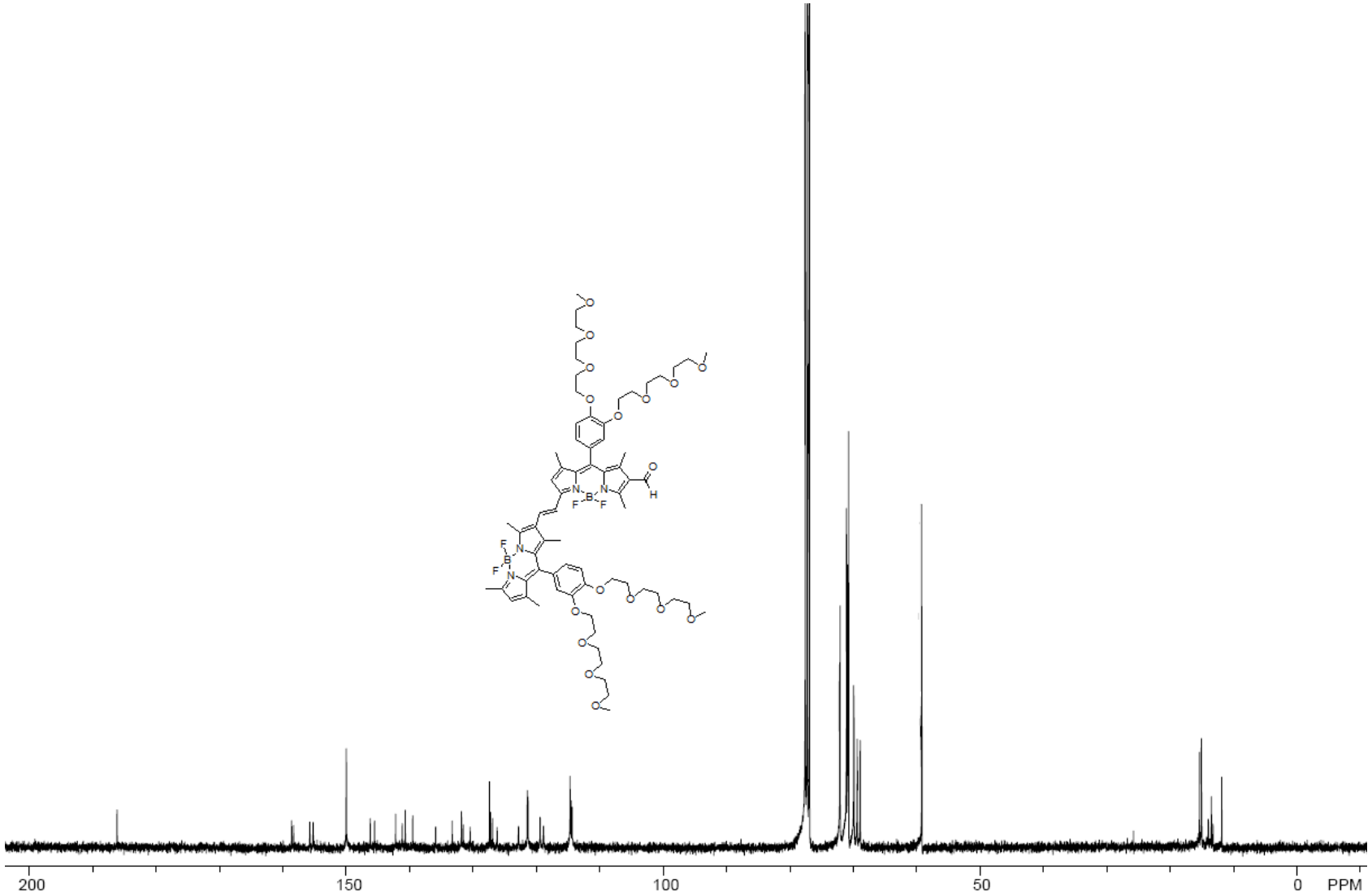

Figure 6. ^{13}C NMR spectrum of dimeric BODIPY dye in $CDCl_3$ solution.

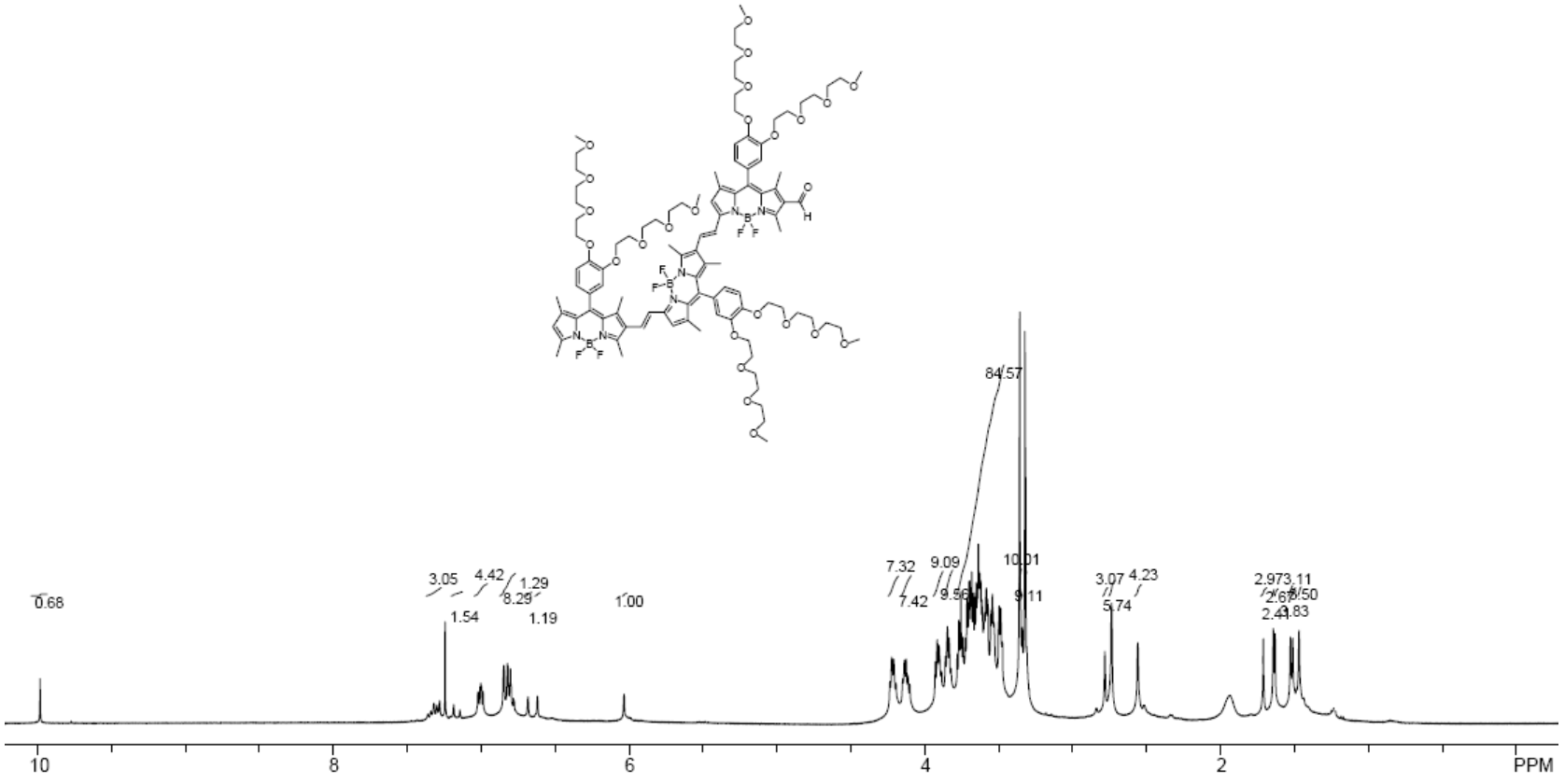

Figure 7. ^{1}H NMR spectrum of trimeric BODIPY dye in $CDCl_3$ solution.

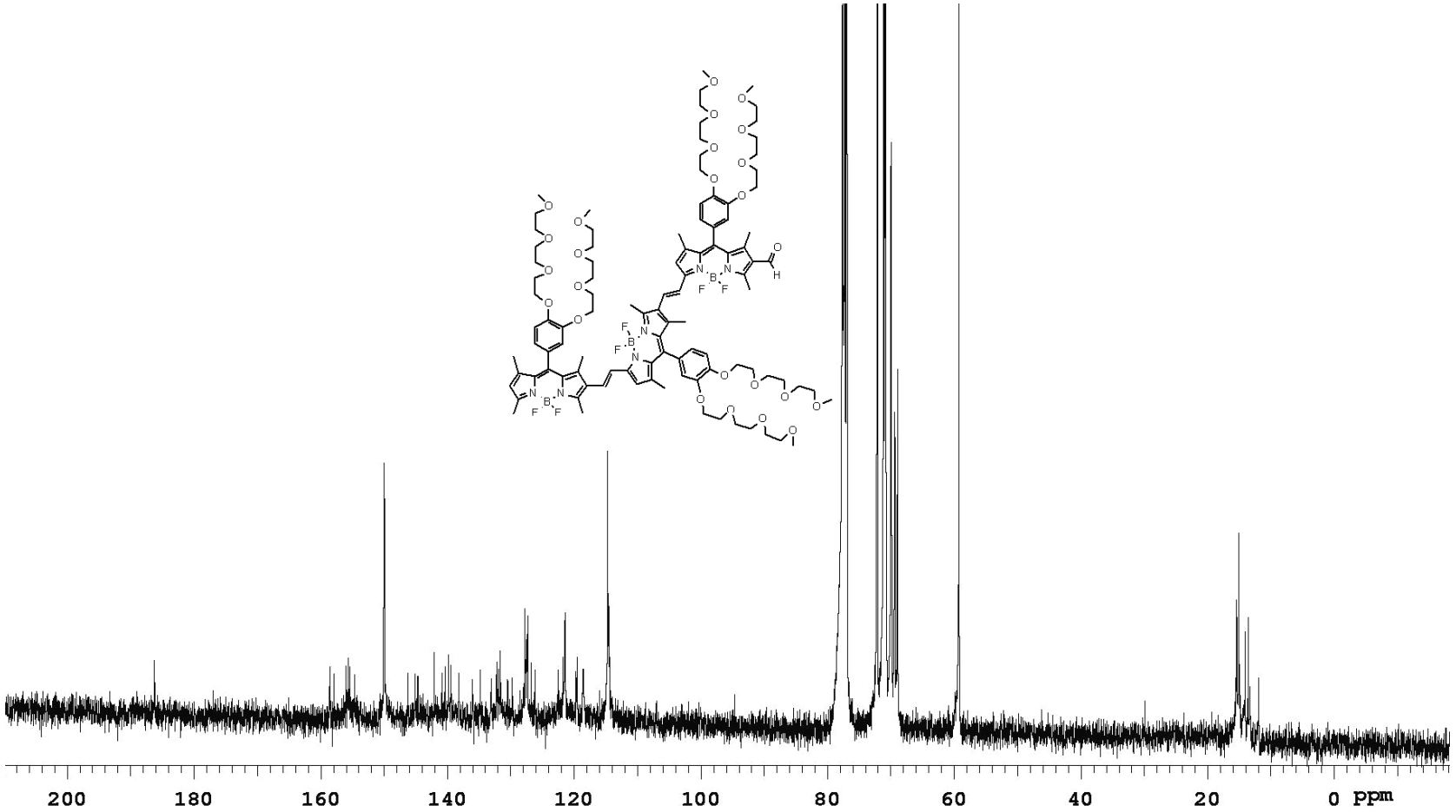

Figure 8. ^{13}C NMR spectrum of trimeric BODIPY dye in $CDCl_3$ solution.

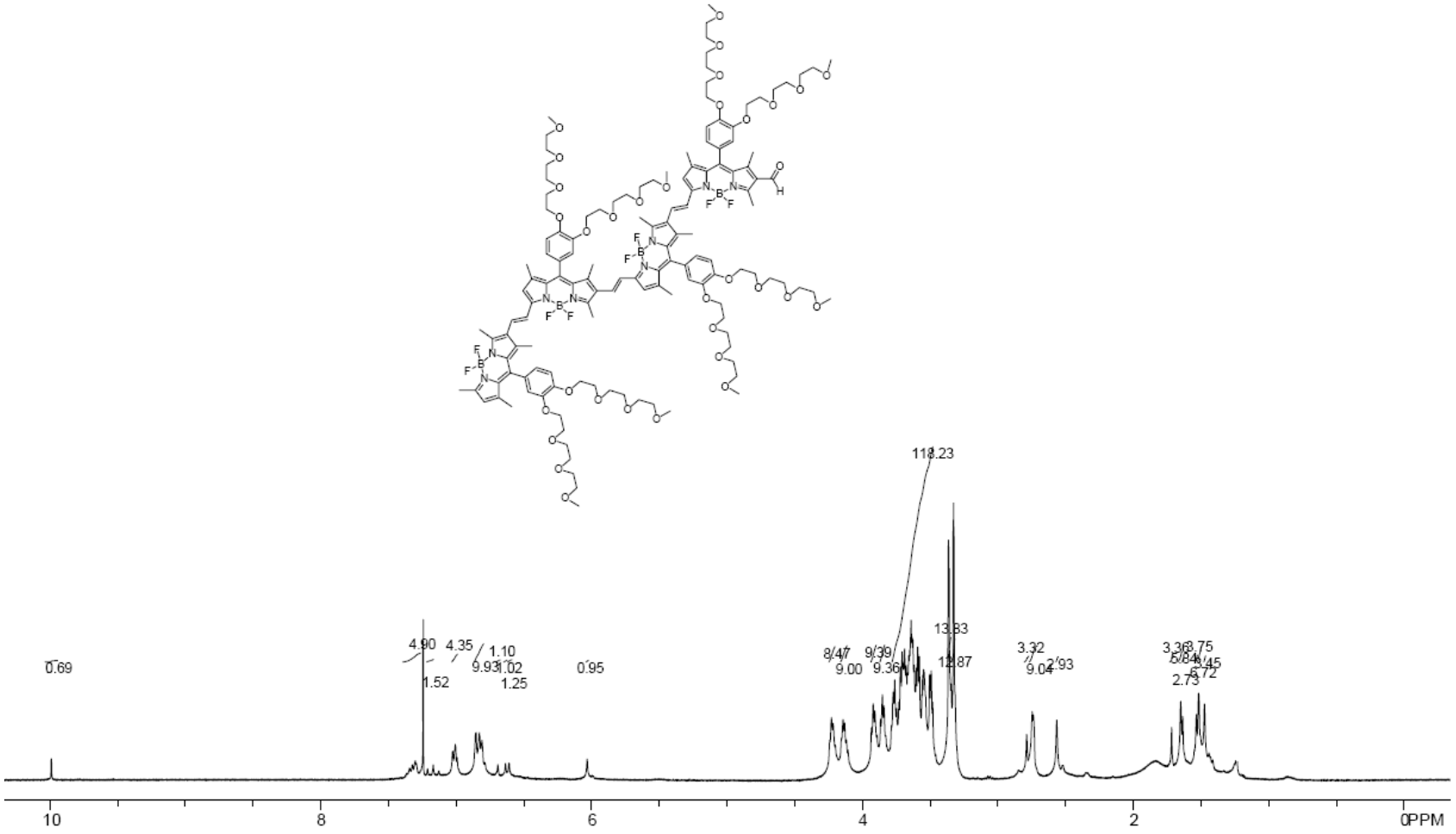

Figure 9. ^{1}H NMR spectrum of tetrameric BODIPY dye in $CDCl_3$ solution.

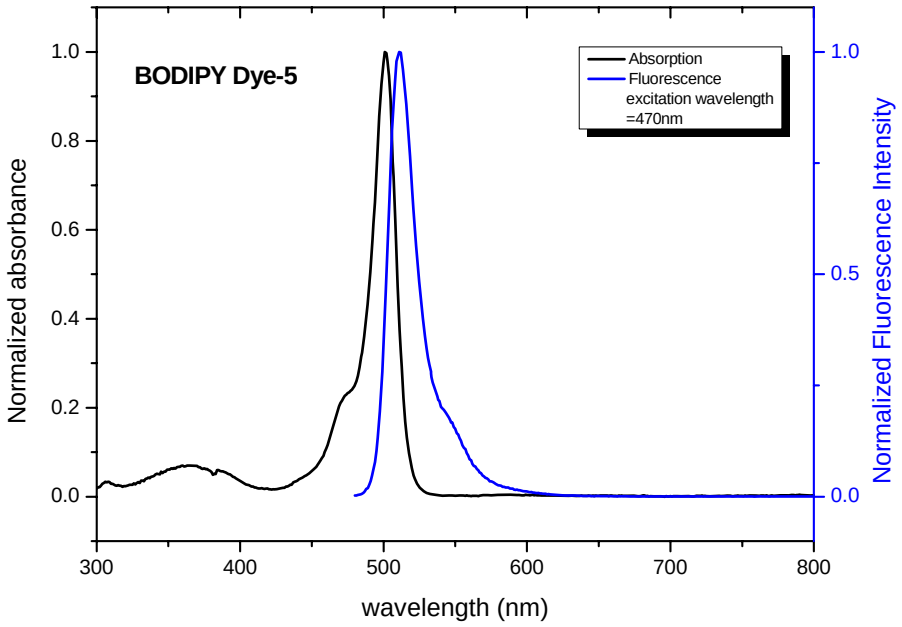

Figure 10. Absorption and fluorescence spectra of BODIPY dye **5** in dichloromethane.

Quantum Yield =92%

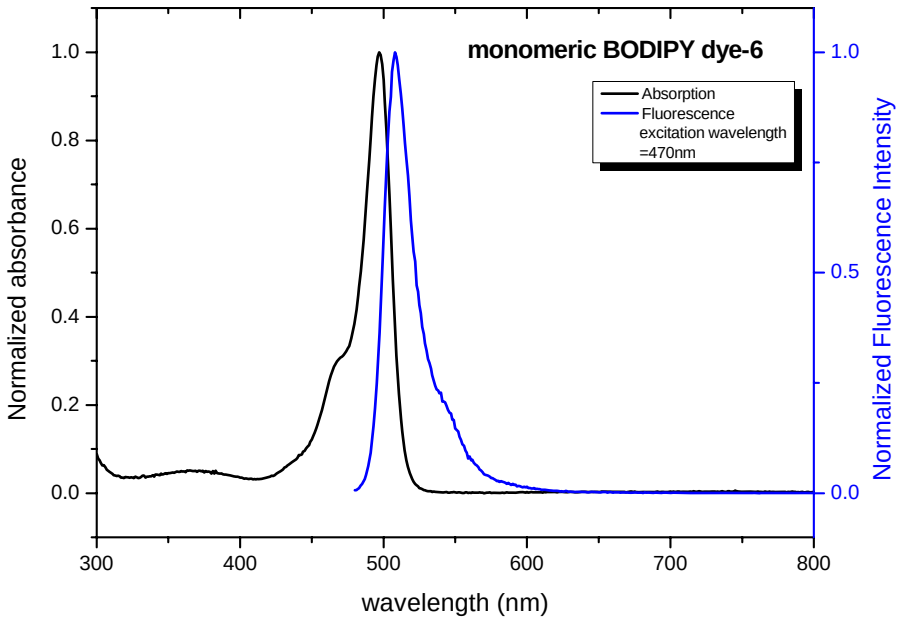

Figure 11. Absorption and fluorescence spectra of monomeric BODIPY dye in dichloromethane.

Quantum Yield = 35.5%

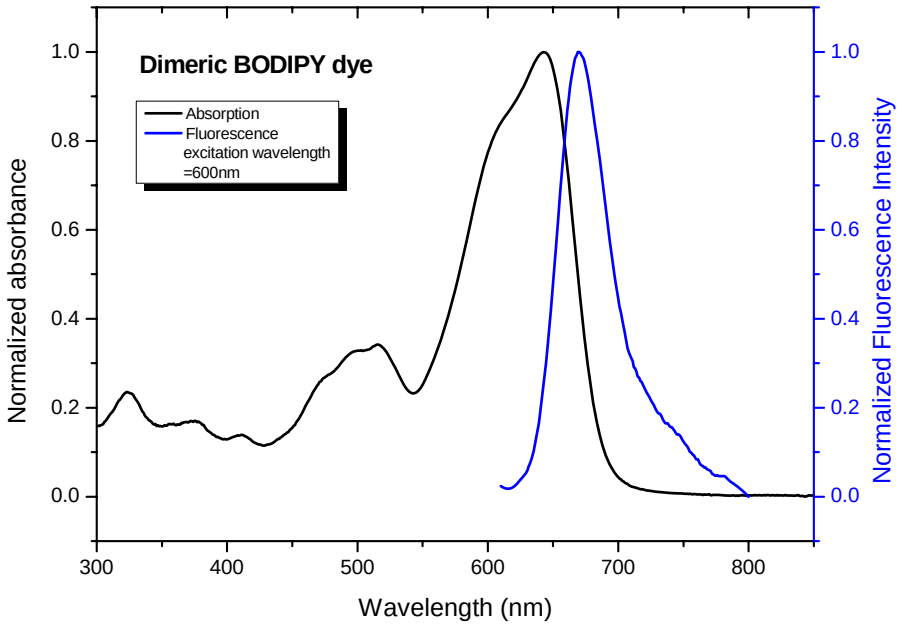

Figure 12. Absorption and fluorescence spectra of dimeric BODIPY dye in dichloromethane.