Supporting Information

Synthesis and fluorescence property of a Boron-dipyrrin Functionalized Perylenediimide Derivative

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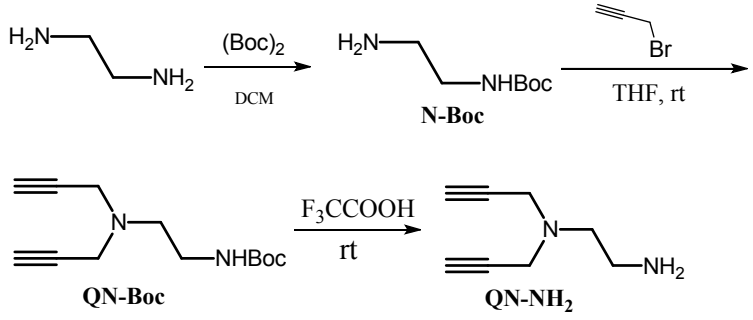
Materials and Methods

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DMX 300 NMR spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Chemical shifts are given in parts per million (ppm). HRMS were recorded on an Ultraflex II MALDI-TOF mass spectrometer, which was used only for the target compound **PDI-BODIPY-SS** duo to its high cost. Mass spectra of other compounds were recorded on Agilent 1100 LC-MSD. UV-visible absorption spectra were determined on a Shimadu UV-3600 spectrophotometer. Fluorescence spectra were measured on a HORIBA FL-4 Max spectrometer. FT-IR spectra were recorded on a Nicolet 750 series in the region of 4000-400 cm^{-1} using KBr pellets. All reagents used were purchased from Aldrich, Fluka or Alfa Aesar. Anhydrous dichloromethane were used in the synthesis of compound **BODIPY-1**. All solvents used in spectroscopic measurements were analytical grade. Reactions were monitored by thin layer chromatography using Merck TLC Silica gel 60 F254. Silica gel column chromatography was performed over Merck Silica gel 60.

Scheme-1

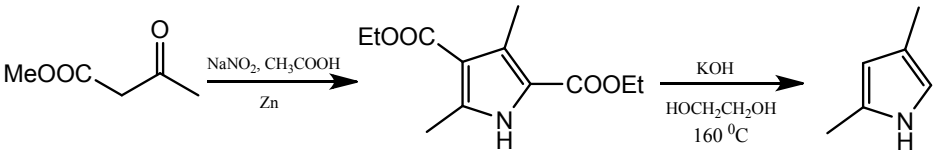


*Compound **N-Boc*** [1]: A dichloromethane solution (500 mL) of di-tertbutyl dicarbonate (8 g, 36.7 mmol) was added dropwise over 6 h to vigorously stirred dichloromethane (50 mL) solution of ethylenediamine (13.2 g, 220 mmol) at 0 ℃. The reaction mixture was then left stirring overnight. The solvent was removed under a reduced pressure to give an oily liquid which was then dissolved in water (100 mL), filtered, and then extracted with dichloromethane (2×300 mL). The final product obtained was a viscous, colourless oily liquid (5.22 g). Yield: 88%. ^{1}H NMR ($CDCl_3$, ppm): δ 5.35 (s, 1H, Boc-N<u>H</u>-), 3.01-2.99 (m, 2H, -N<u>H</u>$_2$), 2.64-2.60 (m, 2H, Boc-NH-C<u>H</u>$_2$-), 1.55(s, 2H, -C<u>H</u>$_2$-NH$_2$) 1.28 (s, 9H, (C<u>H</u>$_3$)$_3$-). TOF-MS-ES: m/z. Calculated: $([M + H])^+$ =161.1, found: 161.2.

*Compound **QN-Boc***: To a mixture of compound **N-Boc** (1g, 6.25 mmol) and 3-bromoprop-1-yne (2.2 g, 18.6 mmol) in dry THF (50 mL), K_2CO_3 (2.0g, 14.5 mmol) was added, stirred at room temperature for 3 days, water (50 mL) was added, and then extracted with dichloromethane (2×100 mL), the organic was dried with Na_2SO_4, the excess solvent was removed under reduced pressure, A more rigorous purification was then carried out via column chromatography (eluting with DCM/methanol = 30:1). A yellow oily compound **QN-Boc** got 0.95 g. Yield: 65 %. ^{1}H NMR ($CDCl_3$, ppm): δ 4.95 (s, 1H, Boc-N<u>H</u>-), 3.42-3.41 (d, 4H, J = 6Hz, -N<u>H</u>$_2$), 3.22-3.17 (m, 2H, -N<u>H</u>$_2$), 2.67-2.63 (t, 2H, J = 6Hz, Boc-NH-C<u>H</u>$_2$-), 2.23-2.21(t, 2H, J = 3Hz, -C<u>H</u>$_2$-NH$_2$) 1.42 (s, 9H, (C<u>H</u>$_3$)$_3$-). TOF-MS-ES: m/z. Calculated: $([M + Na])^+$ = 259.2, found: 259.2.

Compound ***QN-NH$_2$***: Compound **QN-Boc** (1.2 g, 1.3 mmol) was placed into a round bottom flask to which dichloromethane (25 mL) and trifluoroacetic acid (6 mL) was added. The mixture was stirred vigorously and the reaction was followed by TLC (DCM:methanol = 10:1). On completion of the reaction the excess trifluoroacetic acid and dichloromethane were removed under reduced pressure. A yellow oily liquid (**QN-NH$_2$**) got 1.34 g. Yield: 98%. Compound **QN-NH$_2$** was used for the next reaction without further purification.

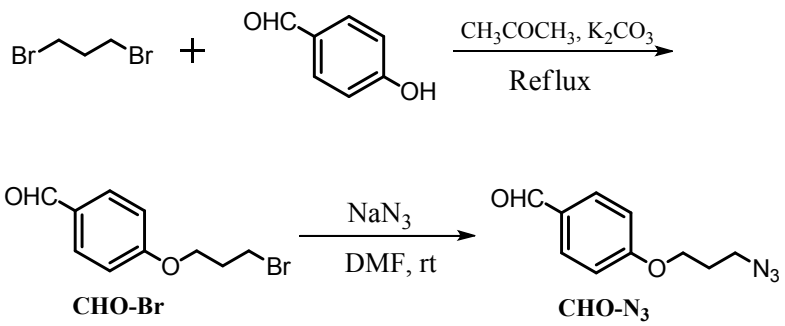
Scheme-2



Diethyl 3,5-dimethyl-1H-pyrrole-2,4-dicarboxylate this compound was prepared according to the literature [2].

2,4-dimethylpyrrole A mixture of diethyl 3,5-dimethyl-1H-pyrrole-2,4-dicarboxylate (3.00g, 14 mmol) and patassium hydroxide (4.06 g, 72mmol) in ethylene glycol (10 ml) was heated for 4 h at 160 ℃. The result solution was extracted with chloroform, dried with anhydrous sodium sulfate and then concentrated to give the crude product. The crude product was distilled in vacuum to give the pure product 0.96 g. Yield: 81%. The ^{1}H NMR data are identical to the data in the literature [3].

Scheme-3



CHO-Br **CHO-N$_3$**

Compound ***CHO-Br***: A mixture of 4-(2-bromoethyloxy) benzaldehyde (26.3 mmol, 3.2 g) and 1,3-dibromopropane (0.078 mol, 15.6 g) in acetone (10 mL) was heated for 8 h at 62 ℃. After completion of the reaction, water (80 mL) and dichloromethane (100 mL) was added, the organic phase was washed with water and dried over Na_2SO_4. The crude product was purified by silica gel column chromatography using dichloromethane as eluent to give an oily compound **CHO-Br** 4.09 g. Yield: 76 %. ^{1}H NMR ($CDCl_3$, ppm): δ 9.86 (s, 1H, PhC<u>H</u>O), 7.82-7.80 (d, 2H, J = 6Hz, Ph), 6.99-6.97 (d, 2H, J = 6Hz, Ph), 4.13-4.09 (t, 2H, J = 6Hz, Ph-C<u>H</u>$_2$-CH$_2$-), 3.54-3.49(t, 2H, J = 9Hz, -C<u>H</u>$_2$-N$_3$), 2.11-2.02 (m, 2H, CH$_2$C<u>H</u>$_2$CH$_2$). ^{13}C NMR ($CDCl_3$, ppm): δ 190.3, 163.3, 131.6, 129.8, 114.4, 68.3, 64.6, 47.7, 36.0, 28.2. TOF-MS-ES: m/z. Calculated: ([M + Na])$^+$ = 243.0, found: 243.0.

Compound ***CHO-N$_3$***: A mixture of 4-(2-bromoethyloxy) benzaldehyde **CHO-Br** (10.3 mmol, 2.5 g) and sodium azide (15 mmol, 2.01 g) in DMF (10 mL) was stirred at room temperature for 24 h. After completion of the reaction, dichloromethane (100 mL) and water (100 mL) was added and the organic phase was washed with water and dried over Na_2SO_4. Removing of the excess solvent a colorless oily compound got 2.06 g. Yield: 98%. ^{1}H NMR ($CDCl_3$, ppm): δ 9.86 (s, 1H, PhC<u>H</u>O), 7.82-7.80 (d, 2H, J = 6Hz, Ph), 6.99-6.97 (d, 2H, J = 6Hz, Ph), 4.13-4.09 (t, 2H, J = 6Hz, Ph-C<u>H</u>$_2$-CH$_2$-), 3.54-3.49(t, 2H, J = 9Hz, -C<u>H</u>$_2$-N$_3$), 2.11-2.02 (m, 2H, CH2C<u>H</u>$_2$CH$_2$). ^{13}C NMR (CDCl3, ppm): δ 190.4, 163.4, 131.7, 129.9, 114.6, 68.83, 65.5, 34.7, 31.9, 29.5. TOF-MS-ES: m/z. Calculated: ([M + Na])$^+$ = 228.0, found: 228.0.

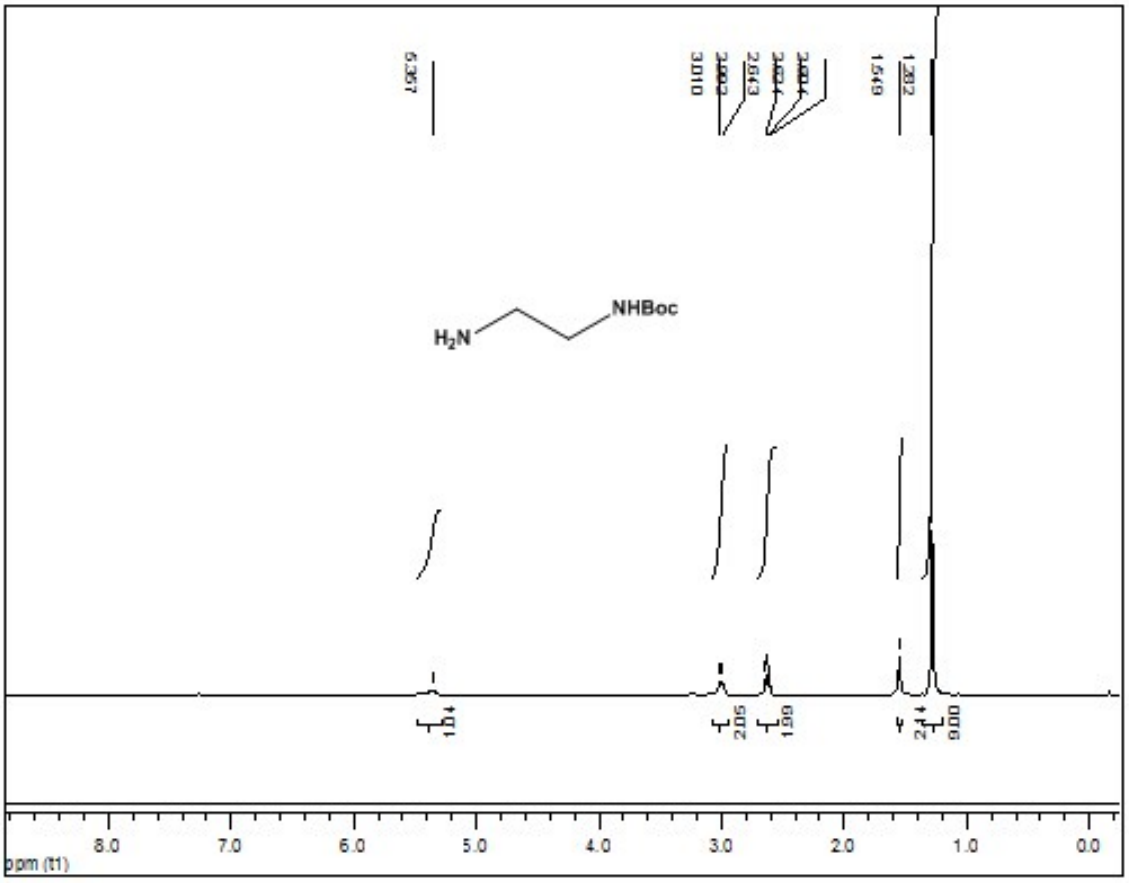


Fig. S1 ^{1}H NMR spectrum of compound **N-Boc** in $CDCl_3$

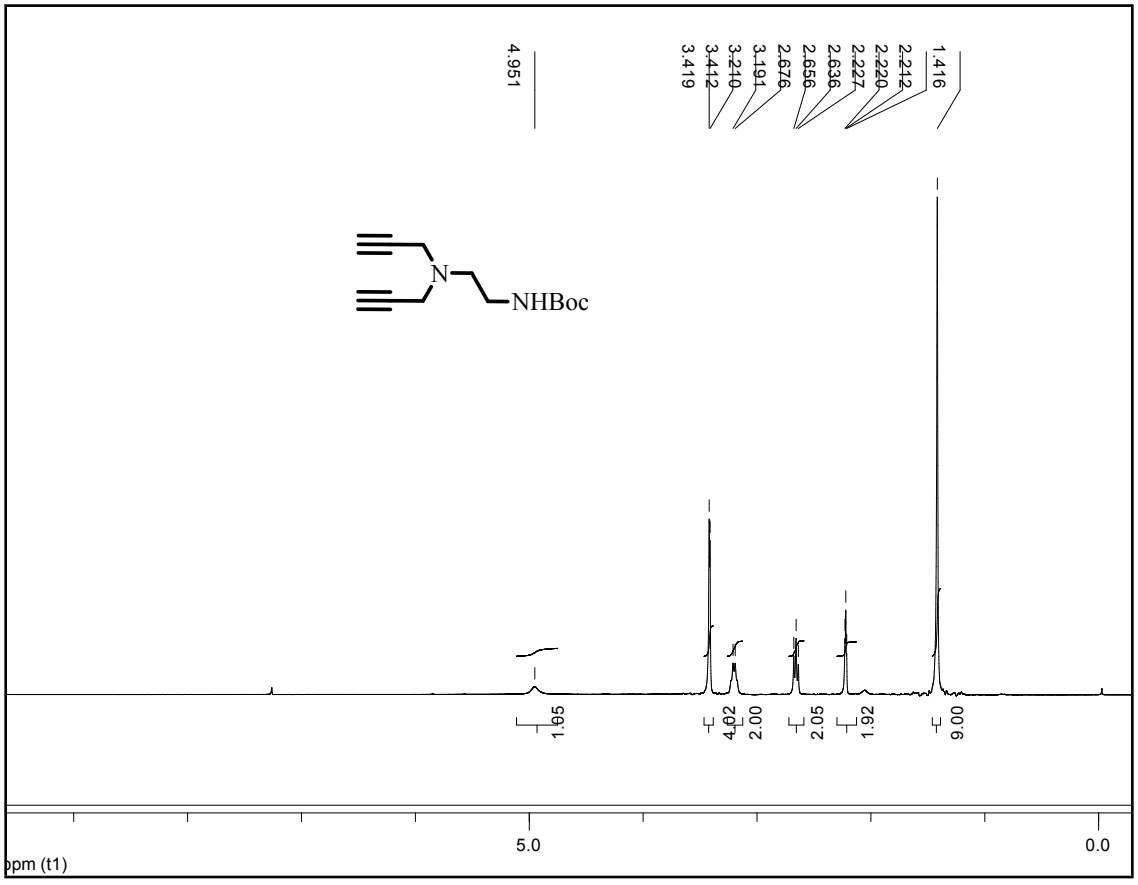


Fig. S2 ^{1}H NMR spectrum of compound **QN-Boc** in $CDCl_3$

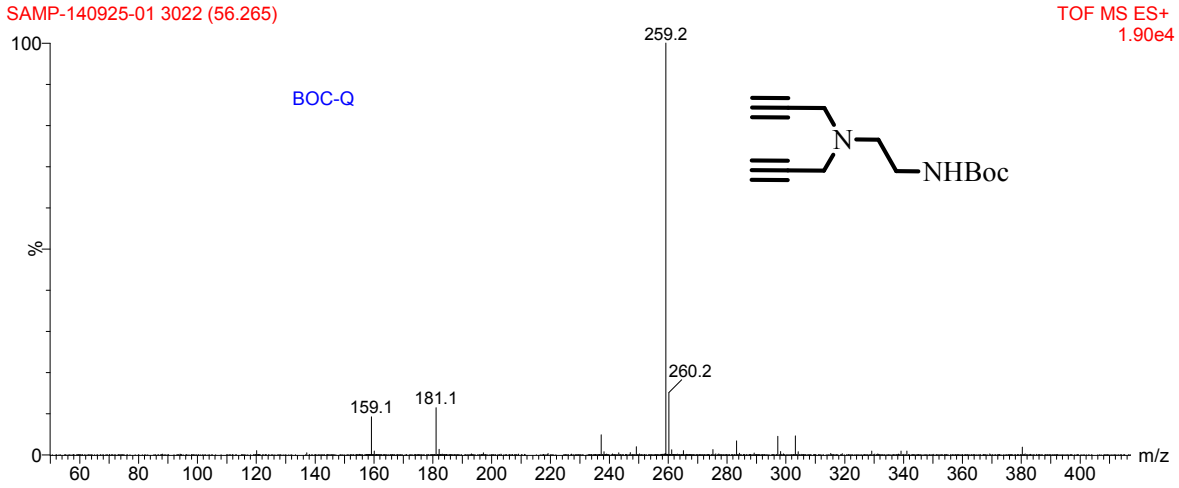


Fig. S3 TOF-MS-ES spectrum of compound **QN-Boc**

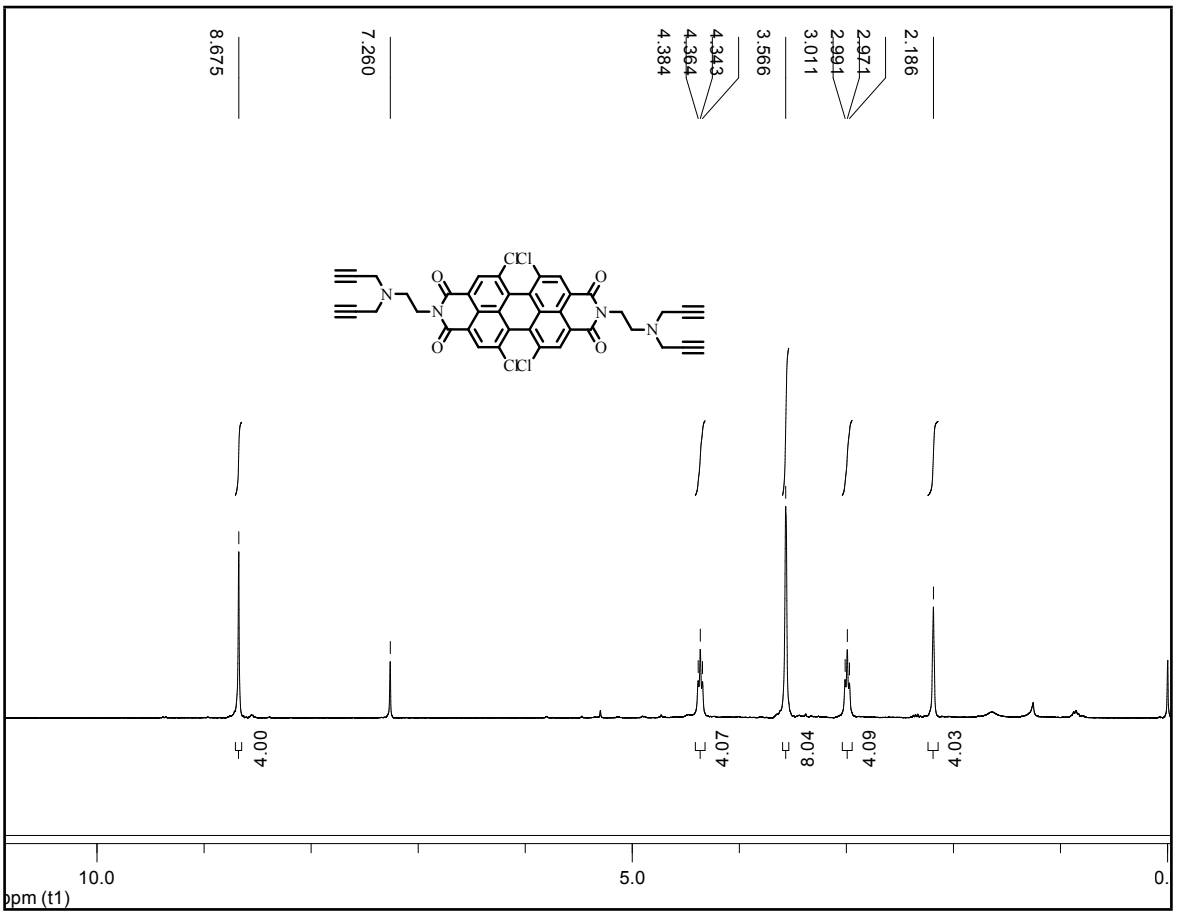


Fig. S4 ^{1}H NMR spectrum of compound **PDI-2** in $CDCl_3$

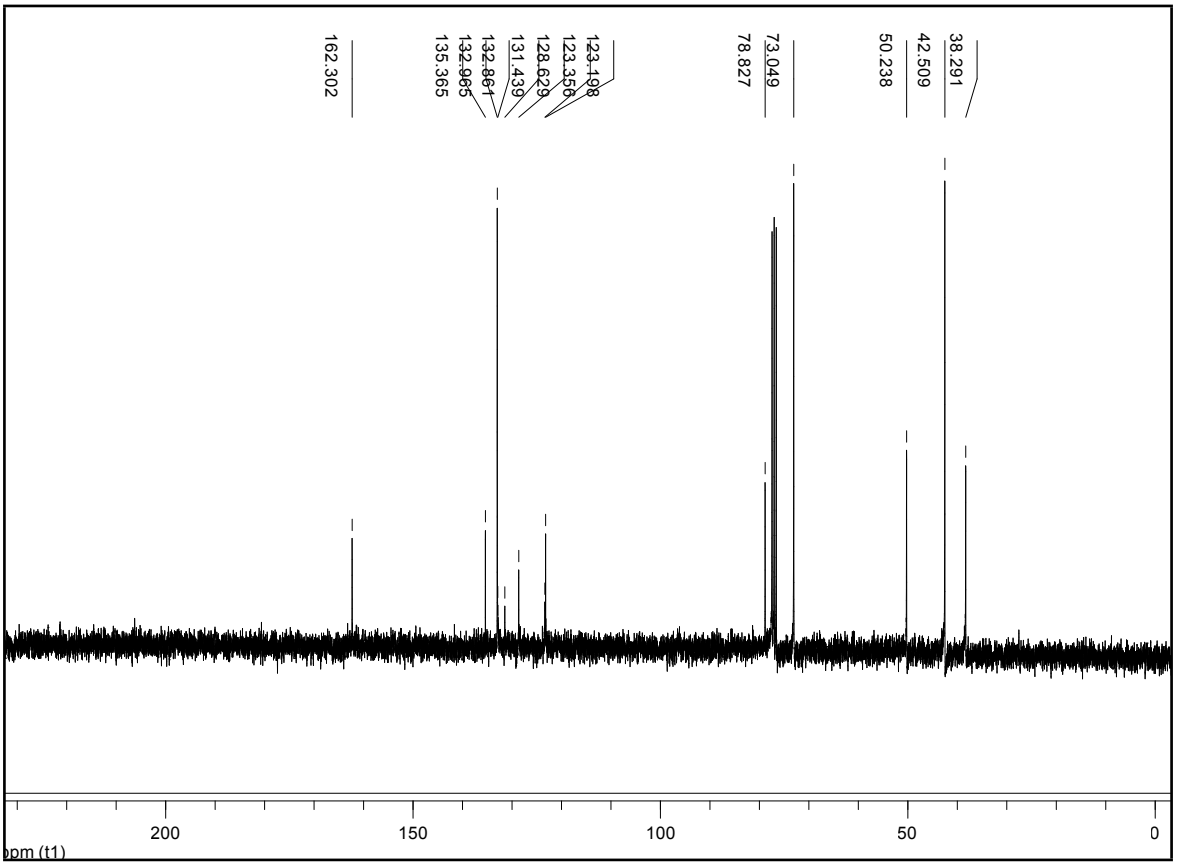


Fig. S5 ^{13}C NMR spectrum of compound **PDI-2** in $CDCl_3$

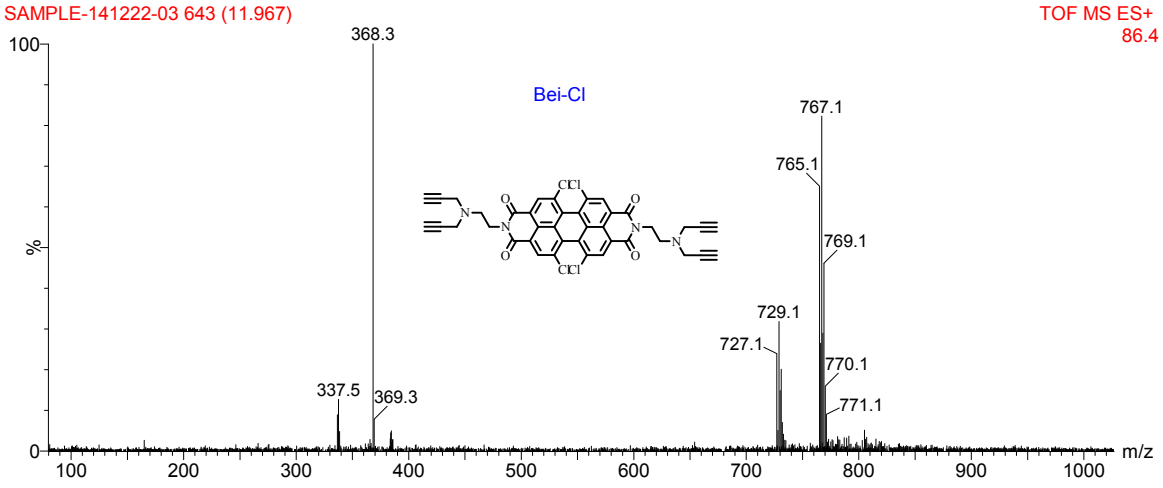


Fig. S6 TOF-MS-ES spectrum of compound **PDI-2**

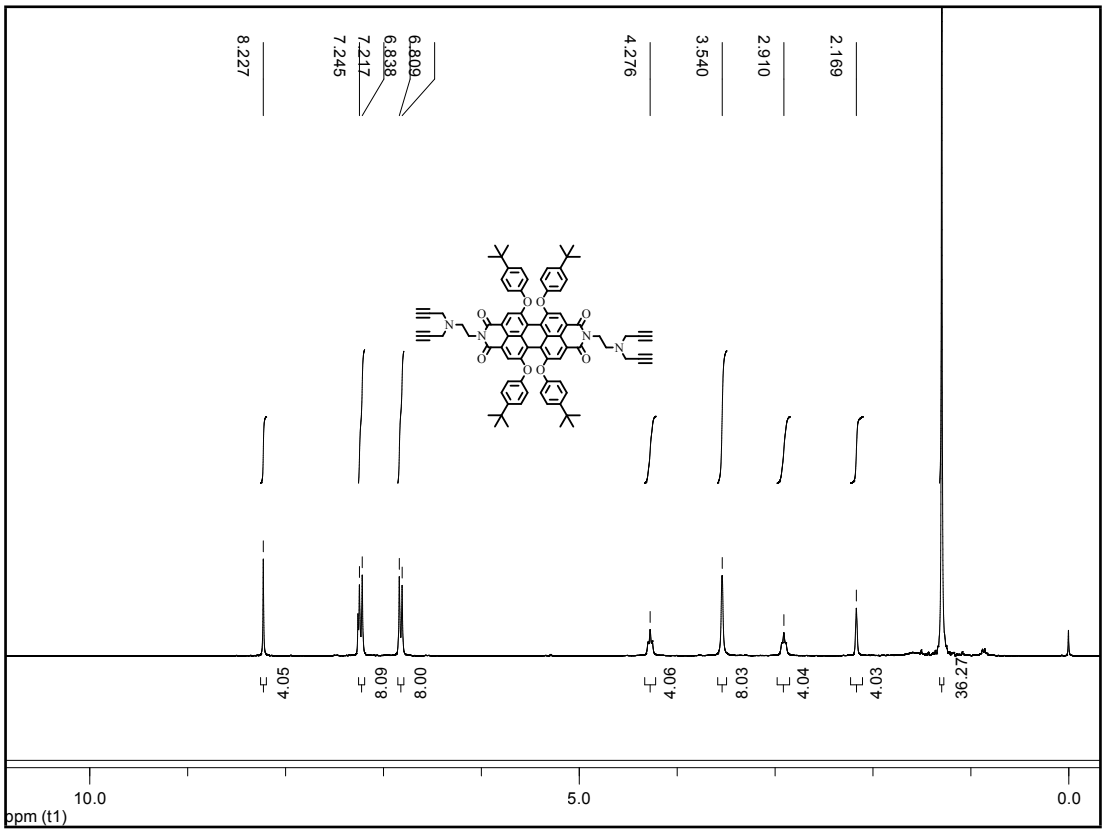


Fig. S7 ^{1}H NMR spectrum of compound **PDI-3** in $CDCl_3$

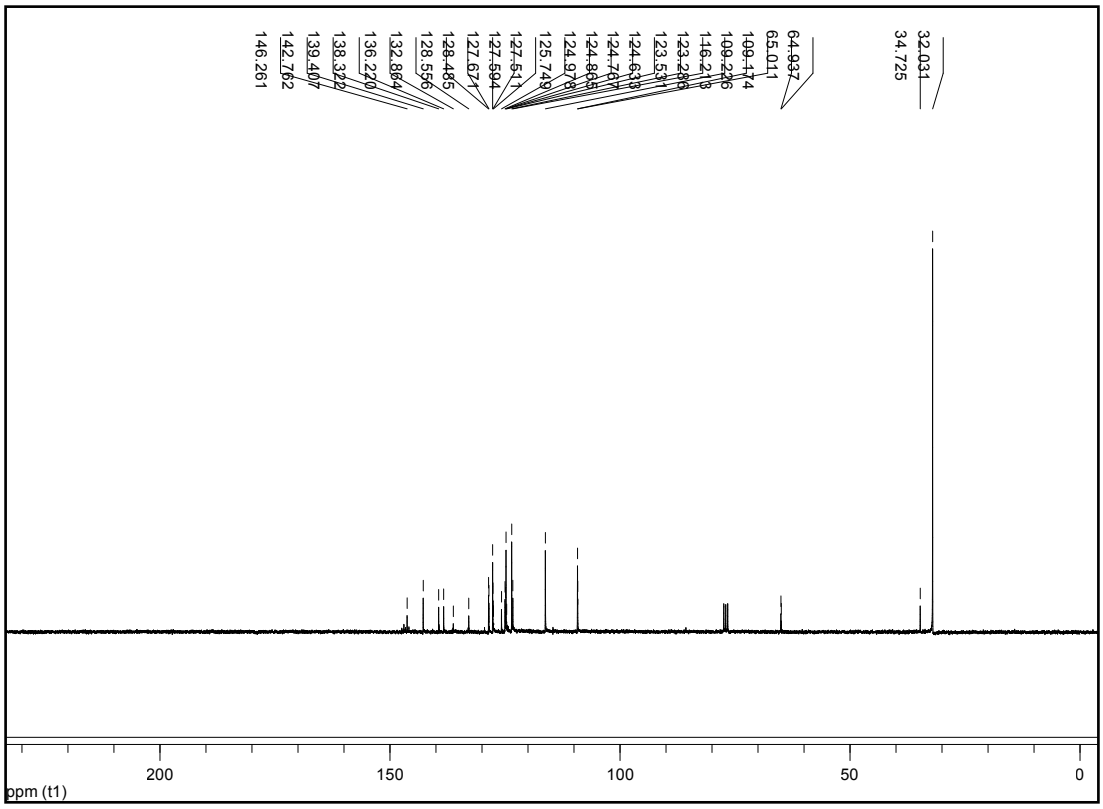


Fig. S8 ^{13}C NMR spectrum of compound **PDI-3** in $CDCl_3$

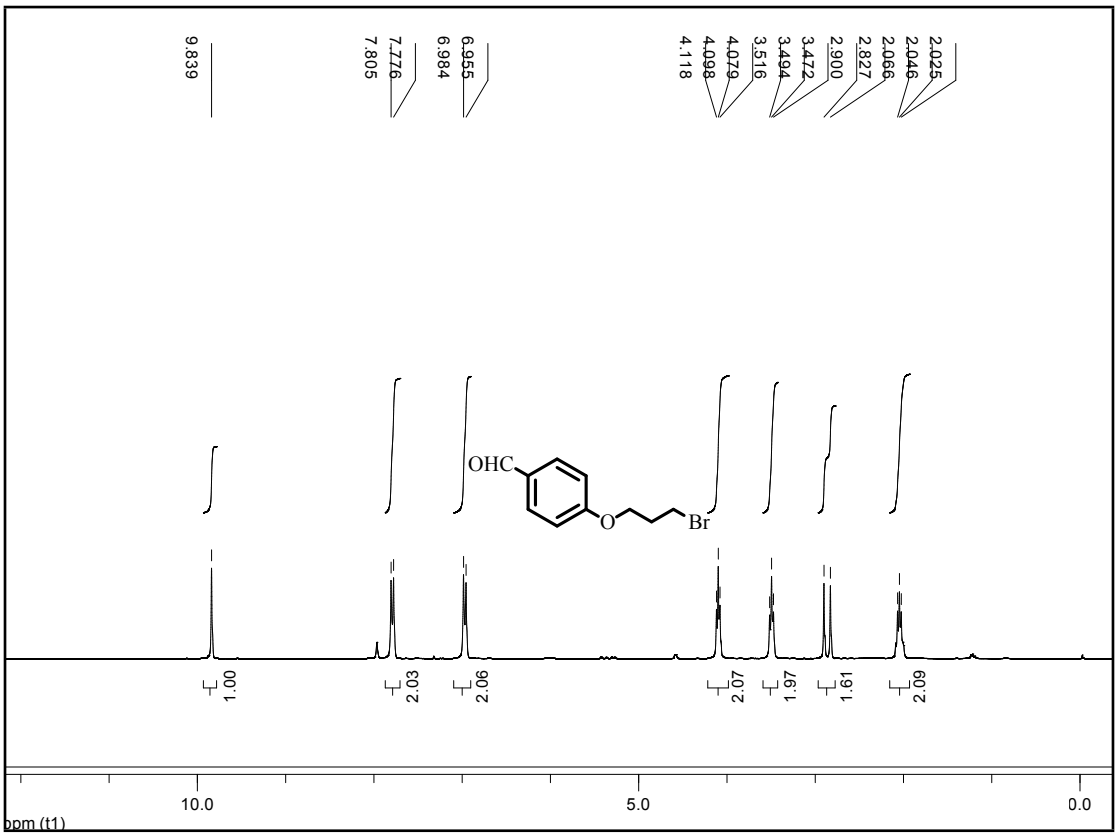


Fig. S9 ^{1}H NMR spectrum of compound **CHO-Br** in $CDCl_3$

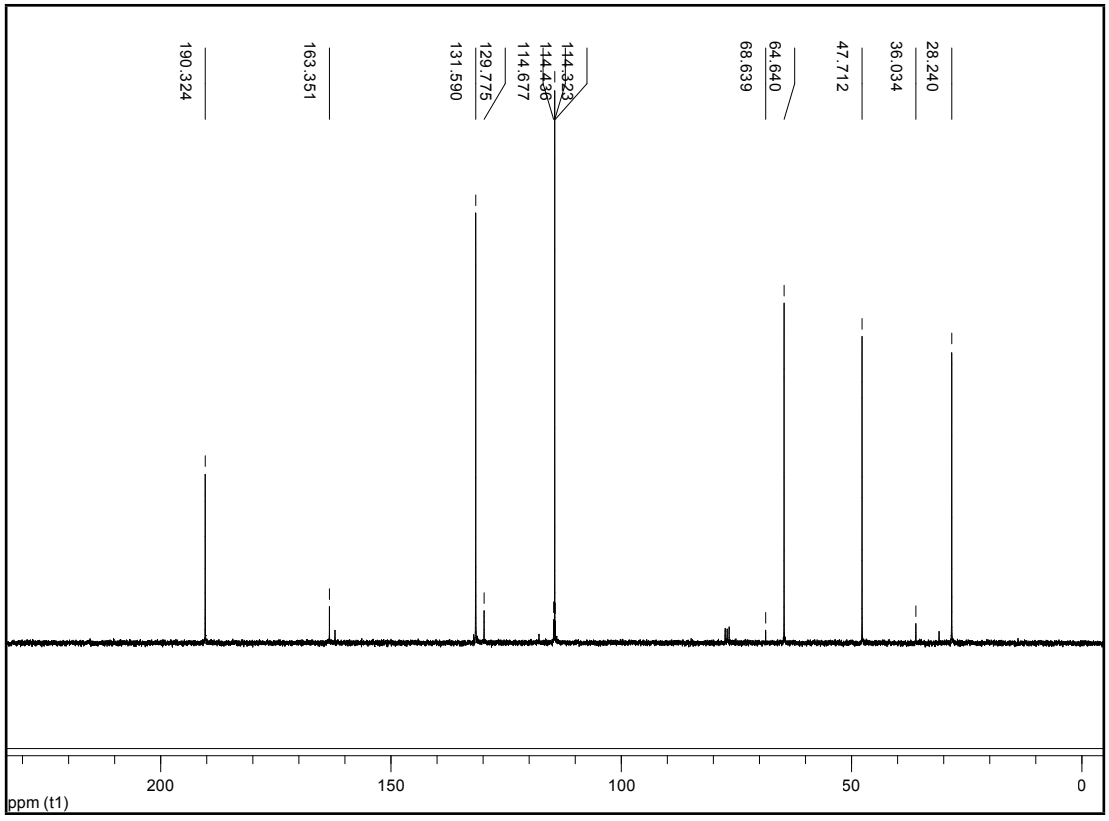


Fig. S10 ^{13}C NMR spectrum of compound **CHO-Br** in $CDCl_3$

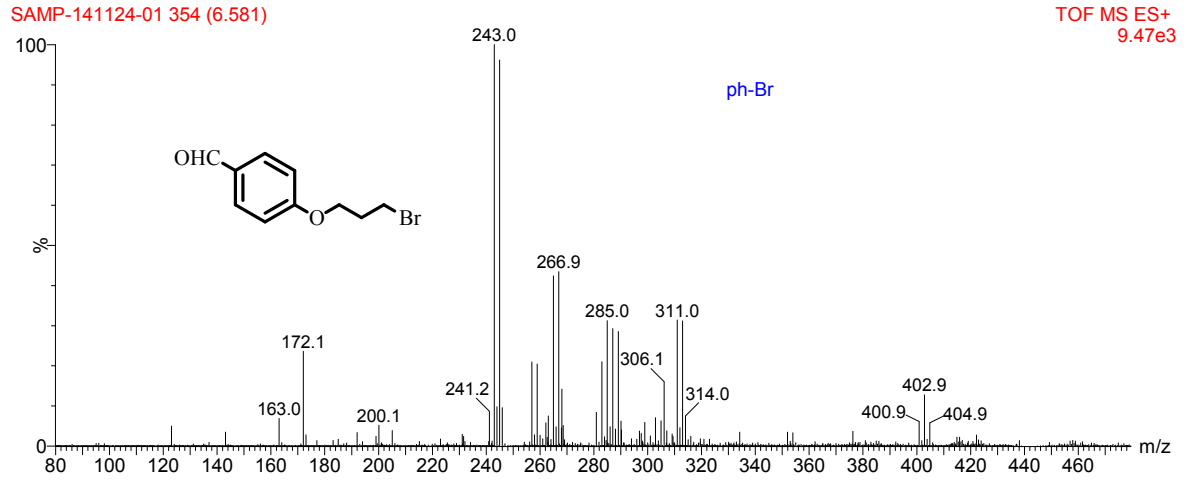


Fig. S11 TOF-MS-ES spectrum of compound **CHO-Br**

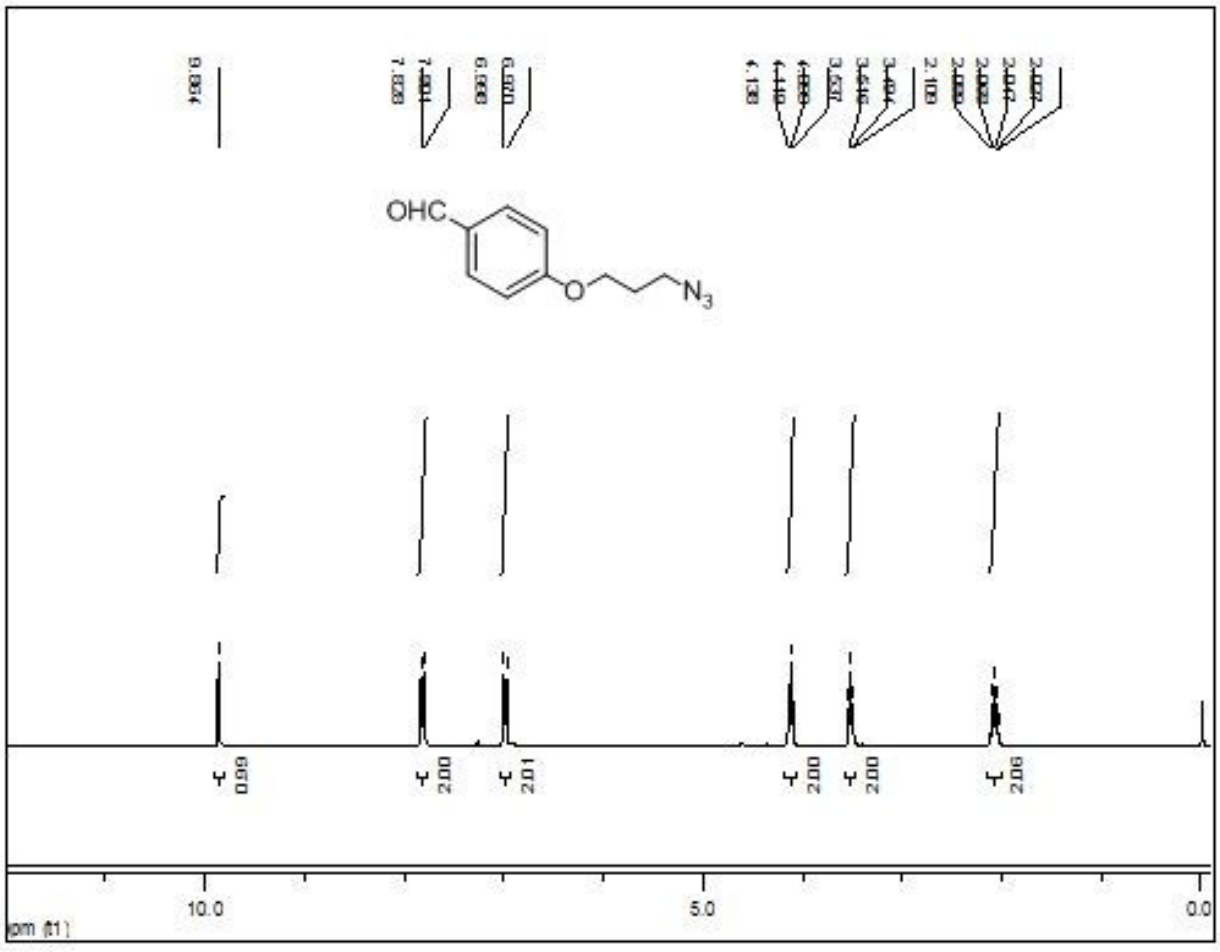


Fig. S12 ^{1}H NMR spectrum of compound **CHO-N_3** in $CDCl_3$

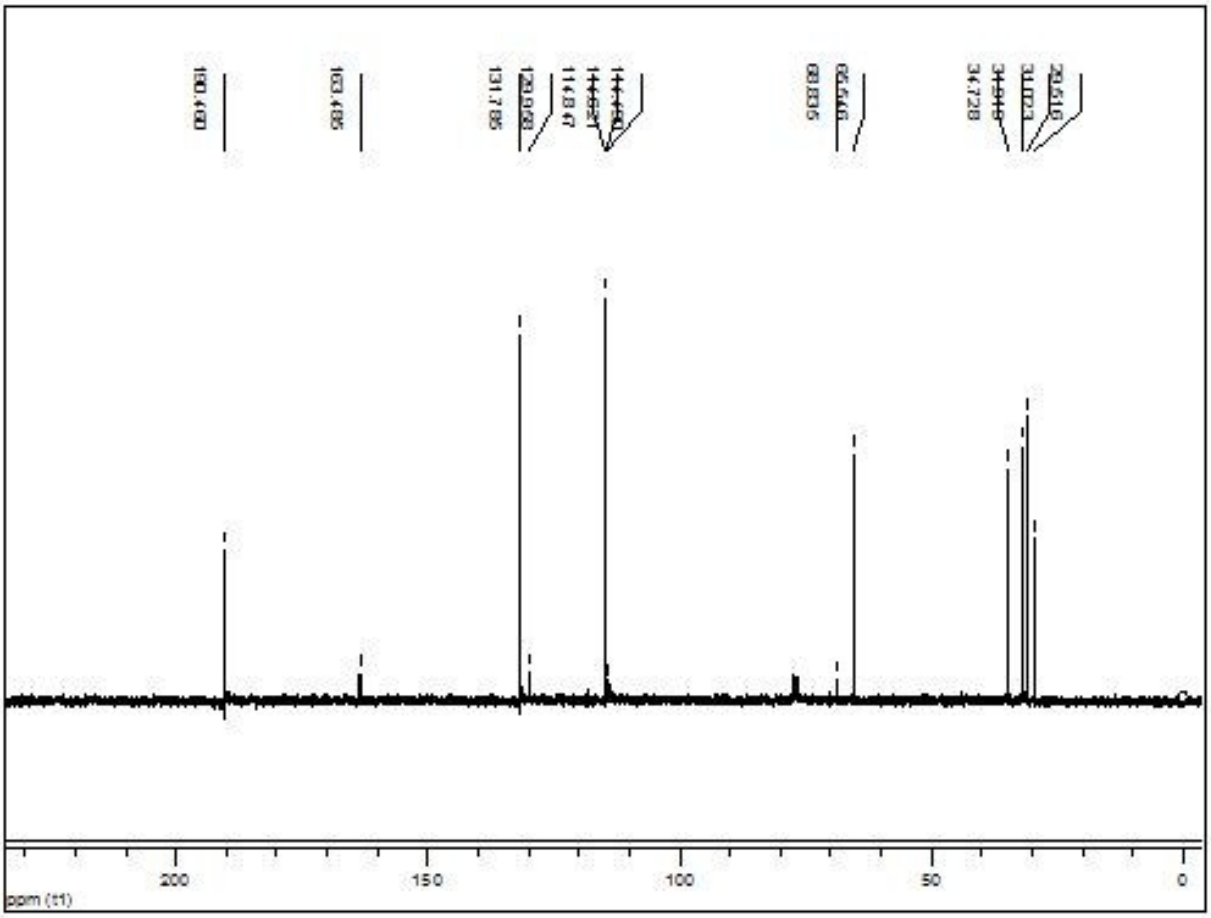


Fig. S13 ^{13}C NMR spectrum of compound **CHO-N_3** in $CDCl_3$

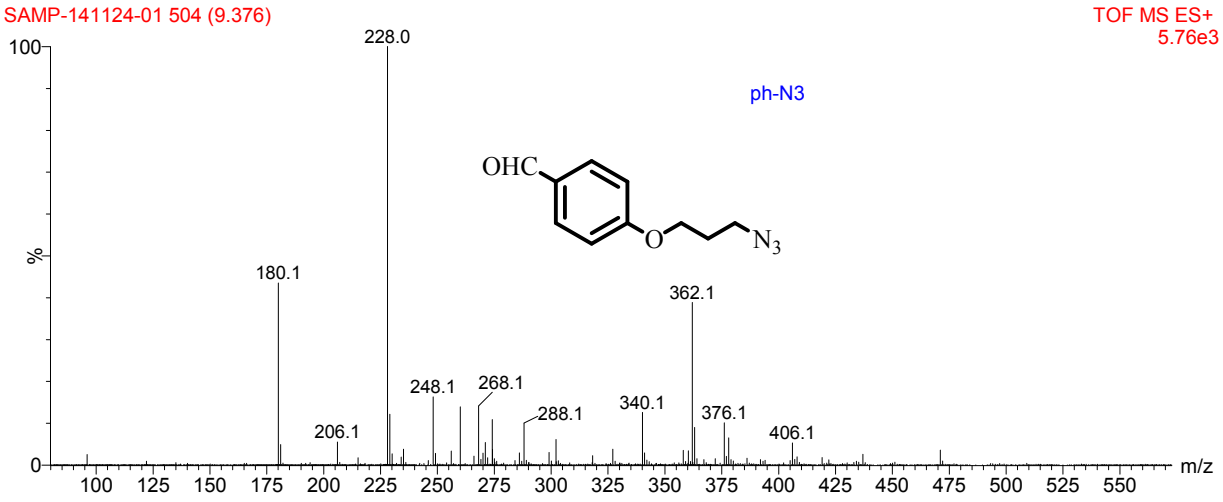


Fig. S14 TOF-MS-ES spectrum of compound **CHO-N_3**

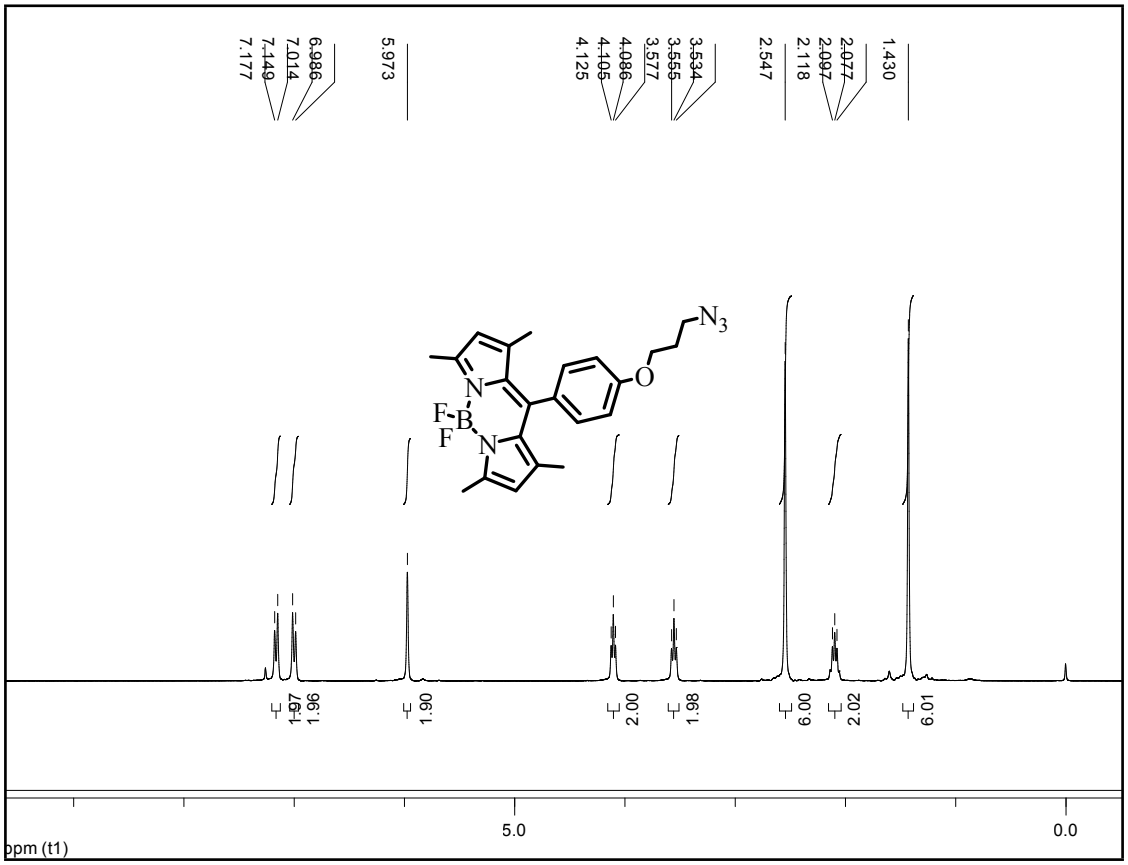


Fig. S15 ^{1}H NMR spectrum of compound **BODIPY-1** in $CDCl_3$

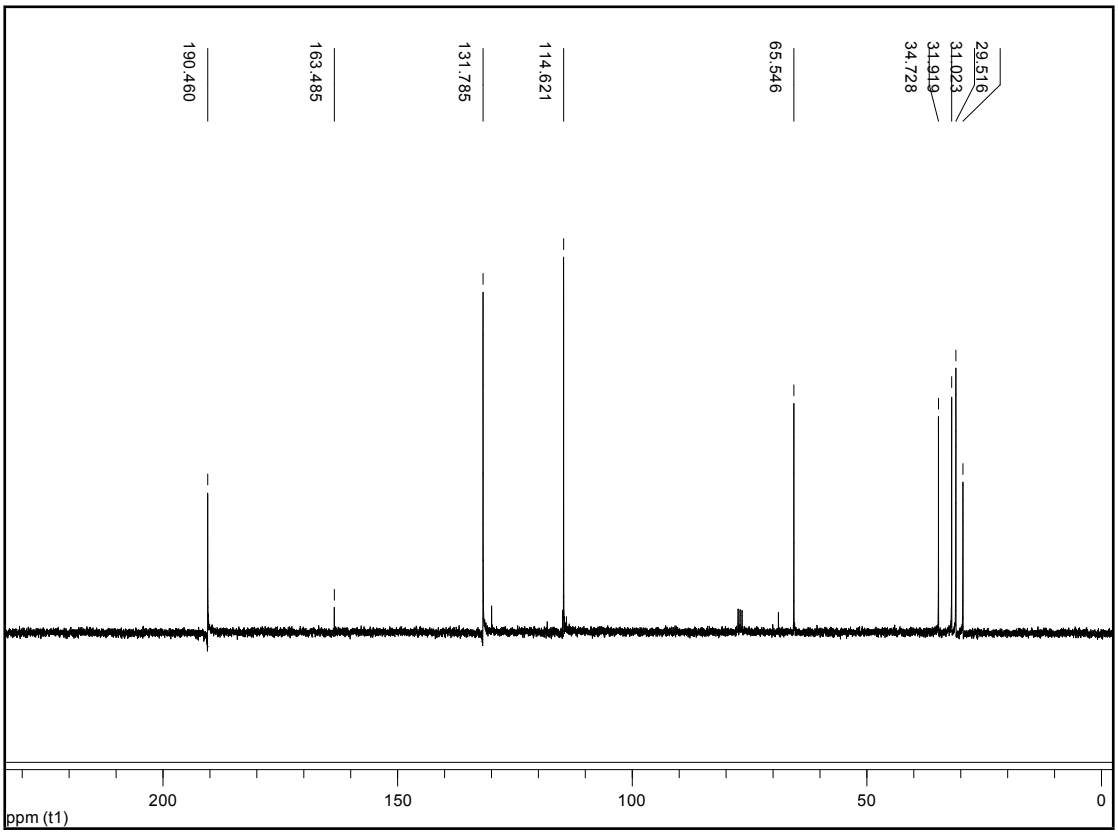


Fig. S16 ^{13}C NMR spectrum of compound **BODIPY-1** in $CDCl_3$

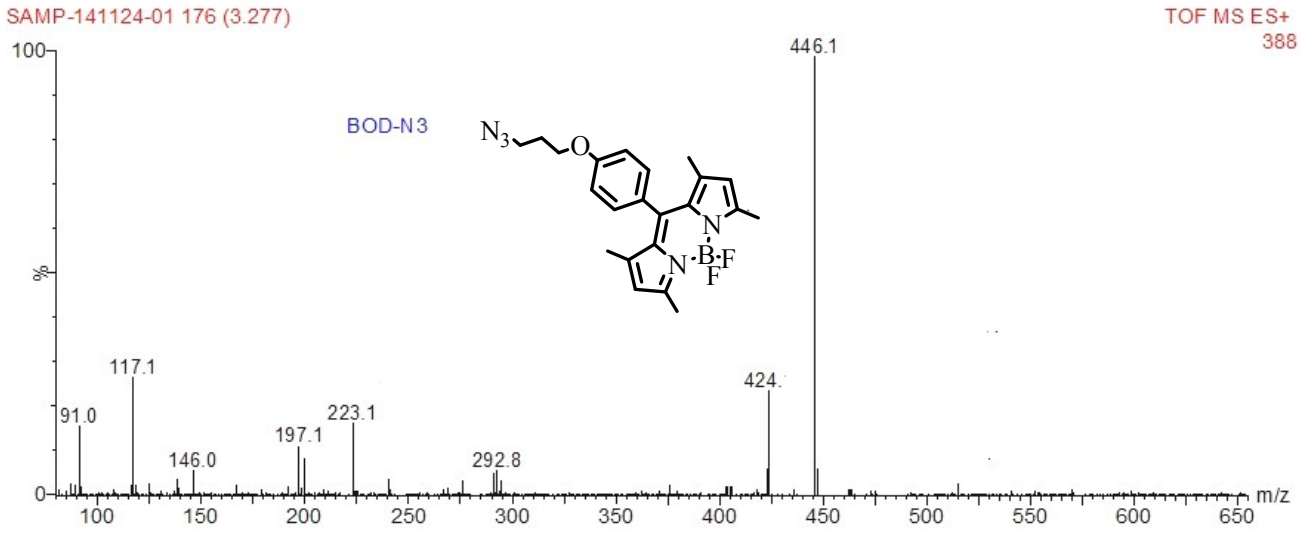


Fig. S17 TOF-MS-ES spectrum of compound **BODIPY-1**

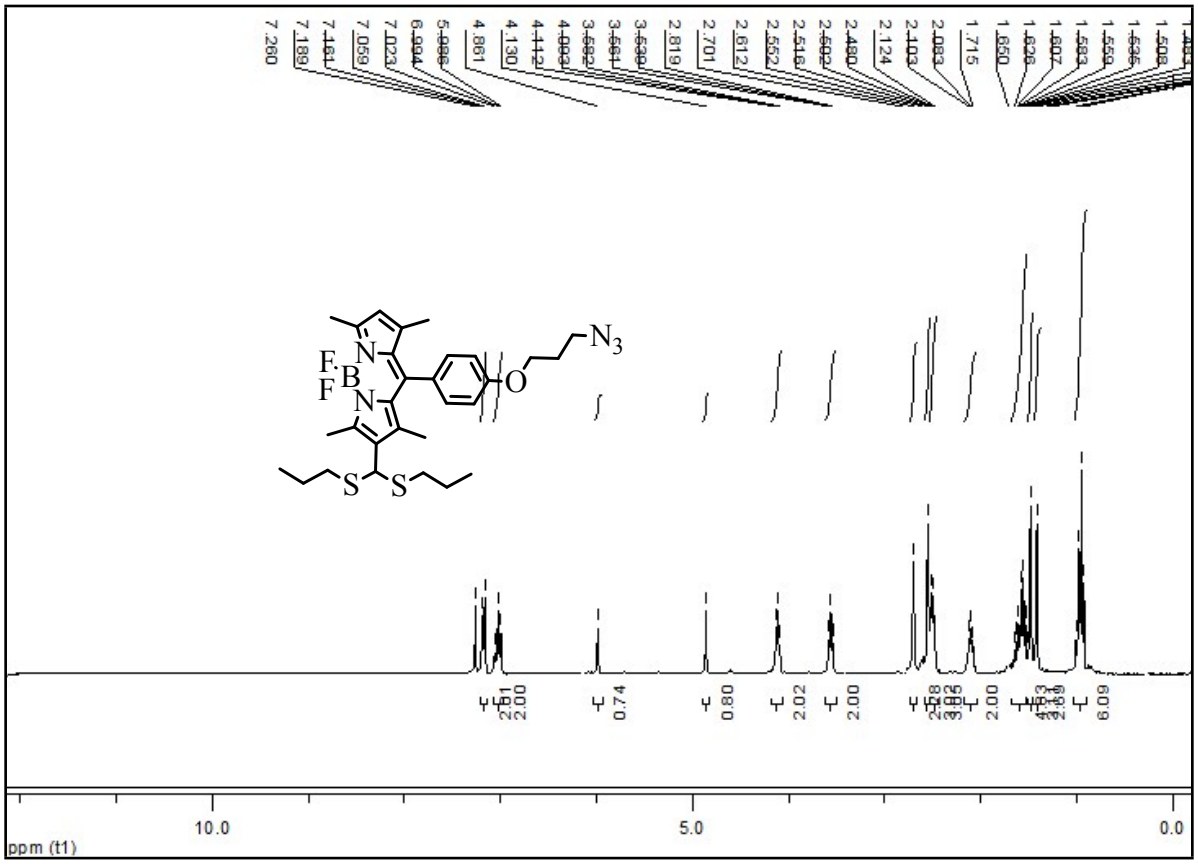


Fig. S18 ^{1}H NMR spectrum of compound **BODIPY-SS** in $CDCl_3$

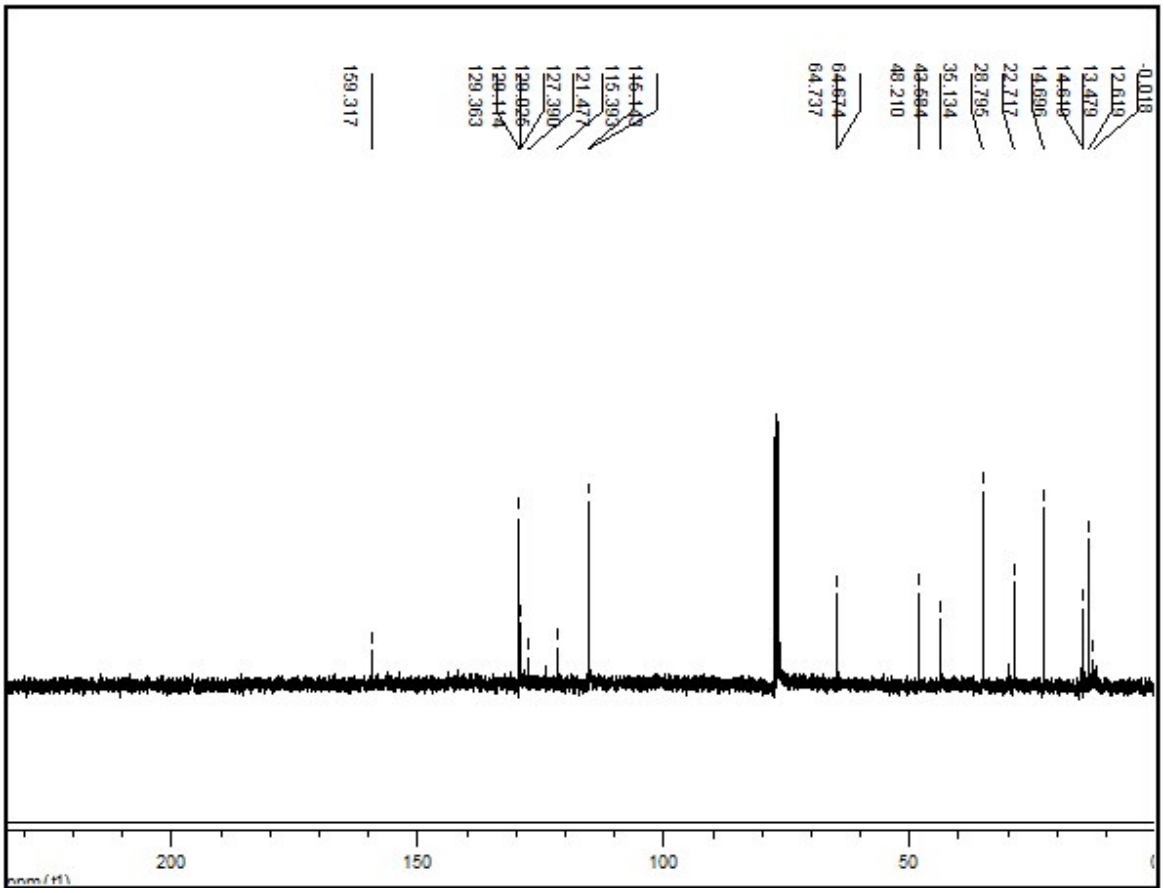


Fig. S19 ^{13}C NMR spectrum of compound **BODIPY-SS** in $CDCl_3$

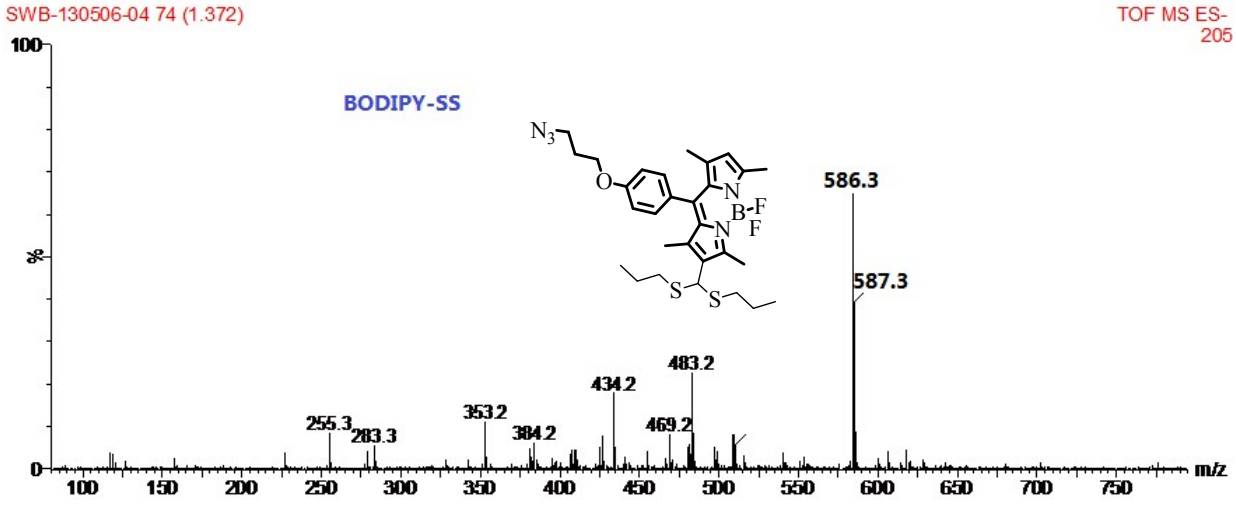


Fig. S20 TOF-MS-ES spectrum of compound **BODIPY-SS**

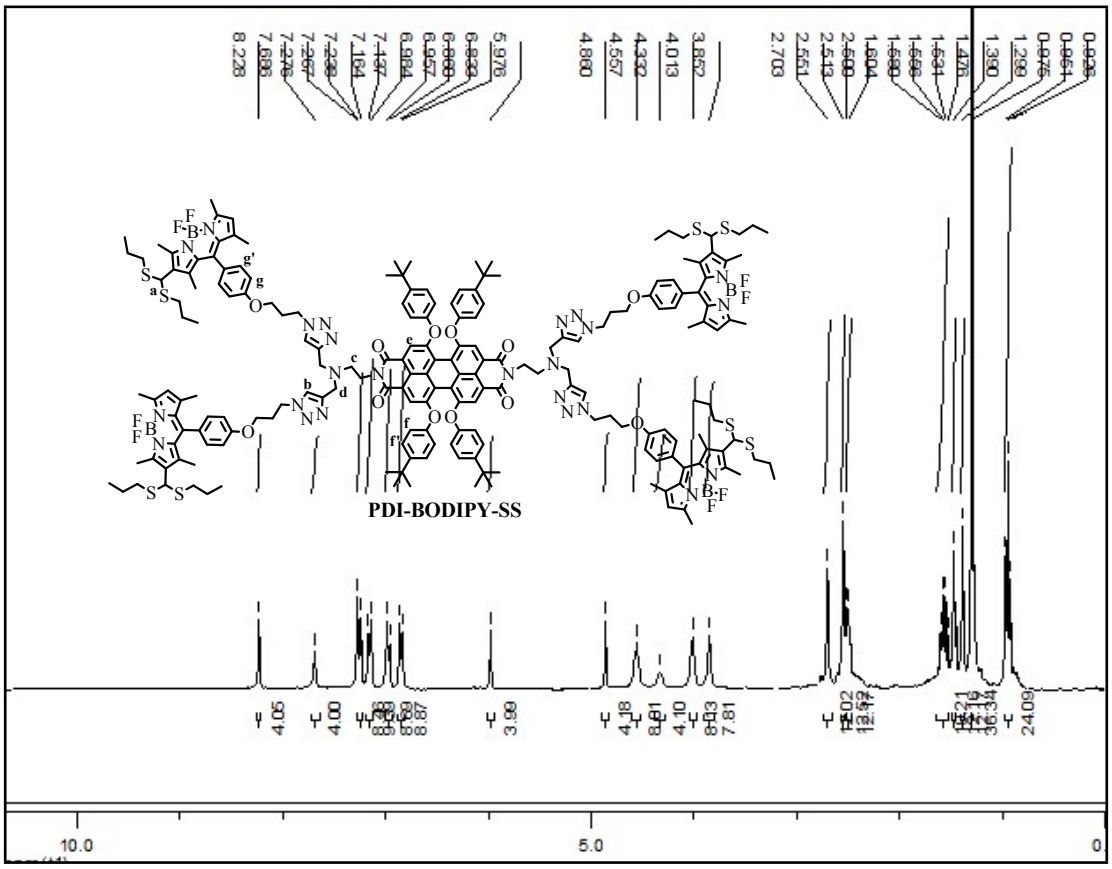


Fig. S21 ^{1}H NMR spectrum of compound **PDI-BODIPY-SS** in $CDCl_3$

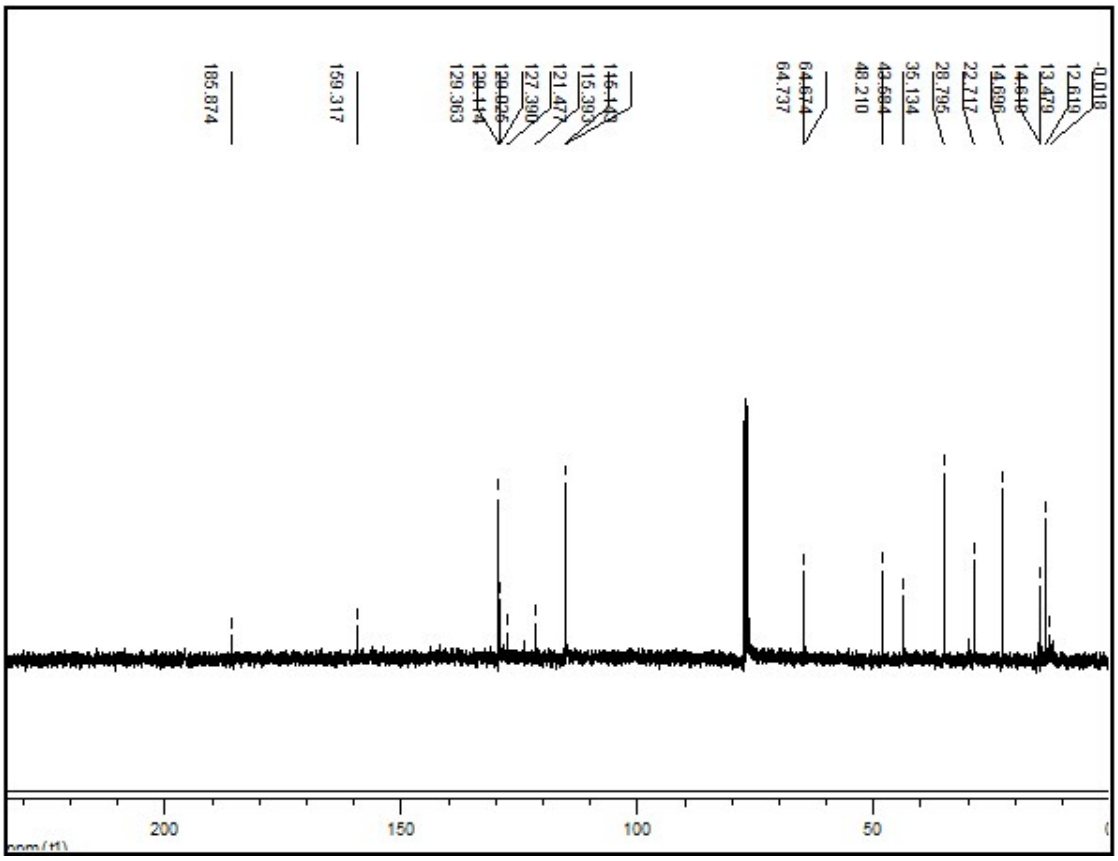


Fig. S22 ^{13}C NMR spectrum of compound **PDI-BODIPY-SS** in $CDCl_3$

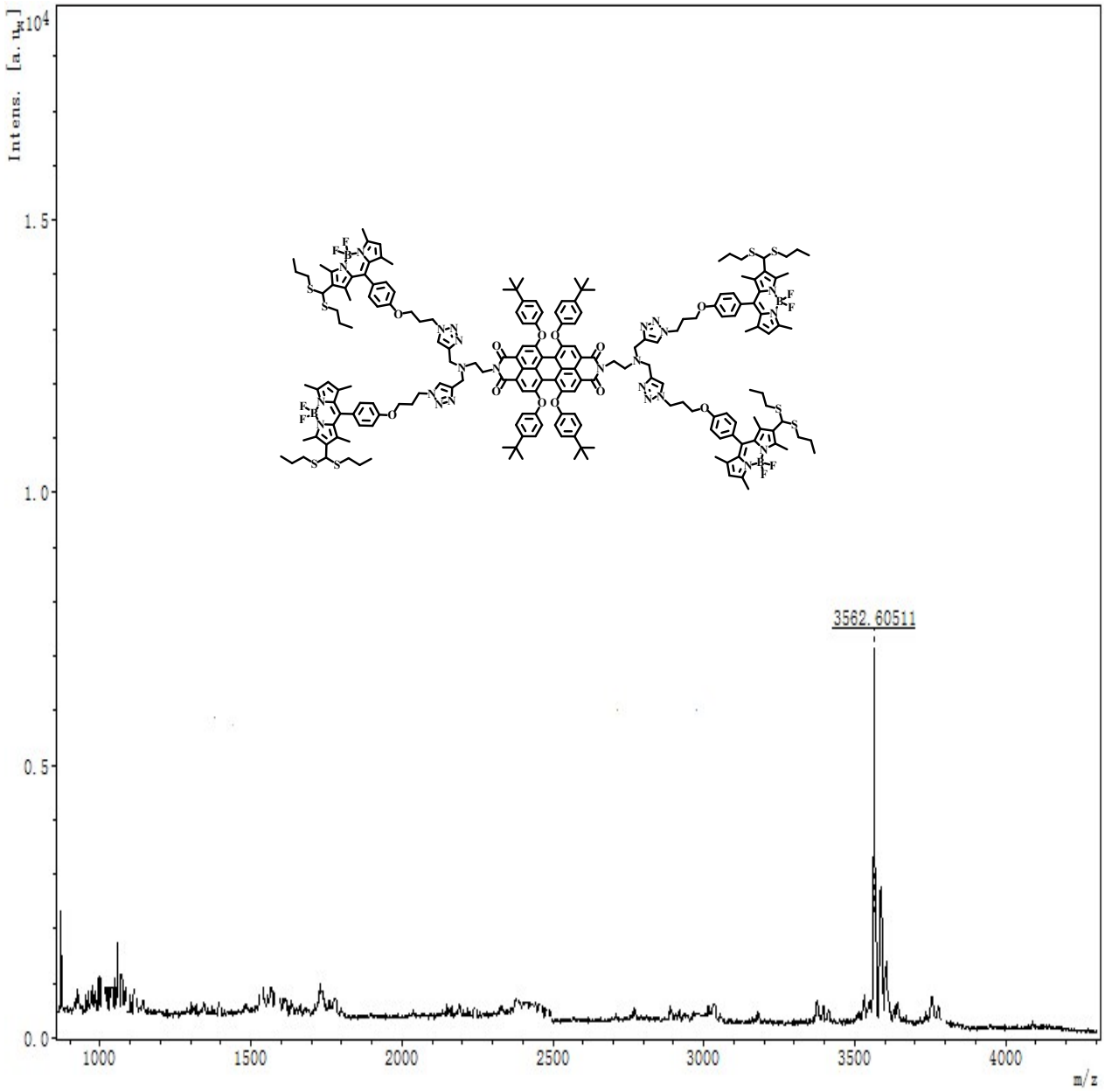


Fig. S23 MALDI-TOF-MS spectrum of compound **PDI-BODIPY-SS**

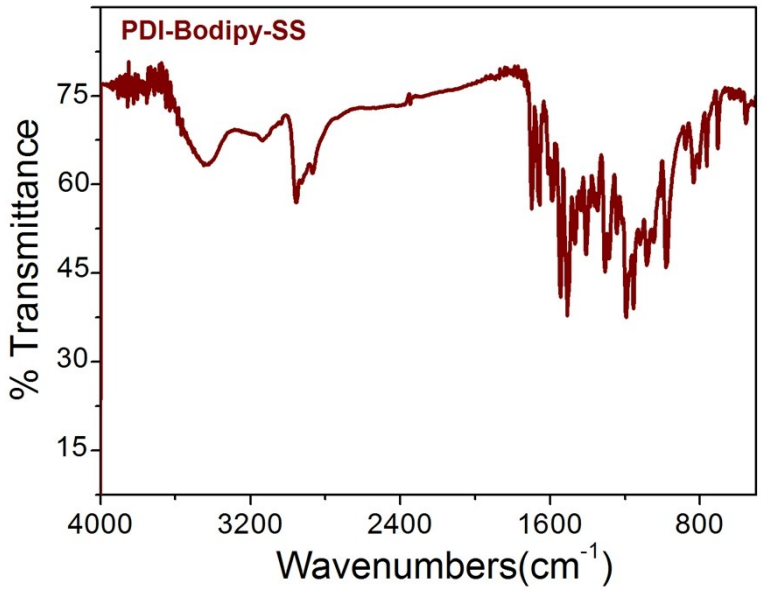


Fig. S24 FTIR spectra of compound **PDI-BODIPY-SS**

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(2) V. B. John, N. H. Robert. Org. Prep. Proced. Int. 1983, 15, 292.

(3) H. J. Wollweber, C. Wentrup. J. Org. Chem. 1985, 50, 2041.