Supporting Information

Boron-, Carbon-, and Silicon-Bridged 1,12-Dihydroxy-Perylene Bisimides with Tuned Structural and Optical Properties

Oliver Nagler,[a] *Kazutaka Shoyama,*[a,b] *Olga Anhalt,*[a] *Matthias Stolte,*[a,b] *Rajeev K. Dubey,*[b] *Zengqi Xie*[c] *and Frank Würthner**[,a,b]

[a] Center for Nanosystems Chemistry (CNC), Universität Würzburg, Theodor-Boveri-Weg, 97074 Würzburg, Germany

[b] Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

[c] State Key Laboratory of Luminescent Materials and Devices, South China University of Technology (SCUT), 510640 Guangzhou, China

*E-mail: wuerthner@uni-wuerzburg.de

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1. Materials and Methods

Chemicals: All reagents were purchased from commercial suppliers (TCI, Sigma Aldrich, BLDPharm, Merck) and used as received, unless otherwise stated. Reagent grade solvents were distilled prior to use. Column chromatography was performed on silica (silica gel, particle size 40-63 μm).

Characterization: ^{1}H-, ^{13}C-NMR spectra were recorded on a Bruker Avance III HD 400 or Bruker Avance III HD 600 spectrometer and were calibrated to the residual solvent signals. Coupling constant (J) values are given in Hz. Abbreviations which were used to designate multiplicities are: s = singlet, br s = broad singlet, d = doublet, t = triplet, sept = septet, m = multiplet.

High resolution mass spectra were obtained by matrix-assisted laser desorption/ionization (MALDI) on a Bruker Daltonics UltrafleXtreme spectrometer. *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) was used as matrix.

Melting points were measured with an Olympus BX41 polarization microscope connected to a TP84 Linkam scientific temperature regulator.

Spectroscopy: UV-vis spectra were recorded on a Jasco V-770 UV-vis spectrometer equipped with a PAC-743R Peltier for temperature control. Fluorescence measurements were carried out on a FLS980-D2D2-ST0 spectrometer from Edinburgh Instruments. Spectra were corrected against the photomultiplier sensitivity and the lamp intensity. Fluorescence quantum yields in solution were calculated by the optical dilution method ($A \leq 0.05$) relative to *N,N'*-bis(2,6-diisopropylphenyl)-perylene-3,4:9,10-bis(dicarboximide) (Φ_{fl} = 100% in chloroform) or *N,N*-bis(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-bis(dicarboximide) (Φ_{fl} = 96% in chloroform).[S1,S2] Absolute quantum yields of the materials were measured using a Hamamatsu Ulbricht sphere A9924-01 with Xe lamp and Hamamatsu photonic multi-channel analyser C10027. Fluorescence lifetimes were determined with EPL picosecond pulsed diode lasers (λ_{ex} = 505.8 and 479.7 nm) for time correlated single photon counting. All spectroscopic measurements were performed with spectroscopic grade solvents from ACROS Organics or Merck. Conventional quartz cells (light path 10 mm) were used.

Single-crystal X-ray analysis: The single crystal of **Naphtho-PBI-(O-C-O)** was obtained by slow evaporation of its dichloromethane solution. The single crystal of **Spiro-PBI-Borate** was obtained by layering *n*-hexane over a solution of the compound in dichloromethane. The single crystals of remaining compounds were obtained by slow diffusion of methanol vapours into their dichloromethane solutions.

X-ray crystallographic analysis for **Octyne-PBI-(O-C-O)** (CCDC-No.: 2284409), **Naphtho-PBI-(O-C-O)** (CCDC-No.: 2284414), **Ph-PBI-(O-Si-O)** (CCDC-No.: 2284413) and **Octyne-PBI-(O-Si-O)**

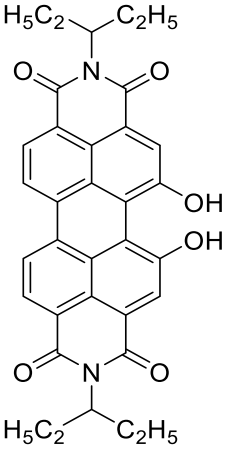
(CCDC-No.: 2284411) was done on a Bruker D8 Quest Kappa diffractometer with a Photon II CPAD area detector using Cu$_K$α radiation.

Single crystal X-ray diffraction data for **Br-PBI-(O-C-O)** (CCDC-No.: 2284408), **Ph-PBI-(O-C-O)** (CCDC-No.: 2284416), **PhO-PBI-(O-C-O)** (CCDC-No.: 2284415), **Br-PBI-(O-Si-O)** (CCDC-No.: 2284410) and **Spiro-PBI-Borate** (CCDC-No.: 2284412) were collected at the P11 beamline at DESY. The diffraction data were indexed, integrated, and scaled using the XDS program package.[S3] The structures were solved using SHELXT,[S4] expanded with Fourier techniques and refined using the SHELX software package.[S5] Hydrogen atoms were assigned idealized positions and were included in the calculation of structure factors. All non-hydrogen atoms in the major disorder part of main residues were refined anisotropically. Disorders in the side-chains and solvent molecules were modelled with constraints and restraints using standard SHELX commands such as EADP, DFIX, FLAT, SAME, SADI, DELU, SIMU, CHIV, ISOR, and RIGU. Verification of crystal structures with the checkcif routine implemented in PLATON[S6] generated two level A alerts for **Ph-PBI-(O-C-O)**, which were caused by weak reflections originating from large unit cell. No level A alerts were found by the same routine for other structures.

2. Synthesis and Characterization

The preparation of literature known **PBI a**, **PBI b**, **PBI c** was adopted from reported reaction conditions with 3-pentylamine (**a**), 4-heptylamine (**b**) and cyclohexylamine (**c**) in imidazole at 120 °C in yields between 67-91%.[S7,S8,S9] Synthesis of compounds **PBA-(OH)$_2$**, **PBI-(OH)$_2$ c**, **PBI-(O-C-O)**, **Br-PBI-(O-C-O)**, **PBI-(O-C-O)-Br**, **PBI-(O-C-O)-Br$_2$**, and **PBI-(O-Si-O) a** was previously described.[S10,S11]

***N,N'*-Di(pentan-3-yl)-1,12-dihydroxyperylene-3,4:9,10-bis(dicarboxNimide) [PBI-(OH)$_2$ a]**



Route A: PBI a (500 mg, 0.94 mmol) was dissolved in concentrated H_2SO_4 (7.5 mL) in a round-bottom flask and boric acid (250 mg, 4.05 mmol) was added. The mixture was diluted with water (1.5 ml) and cooled to 0 °C. Subsequently, manganese dioxide (550 mg, 6.31 mmol) was slowly added, and the reaction mixture was stirred for 24 h at room temperature. Afterwards water (40 mL) and Na_2SO_3 (500 mg, 3.97 mmol) were added, and the reaction mixture refluxed for 1 h on a heating block. The precipitate was filtered after cooling to room temperature, washed with water and dried. The product was purified by column chromatography (silica, DCM/MeOH 5 %)

Yield: 502 mg (0.89 mmol, 95%) of a dark purple solid.

Route B: This procedure was previously described.[S10]

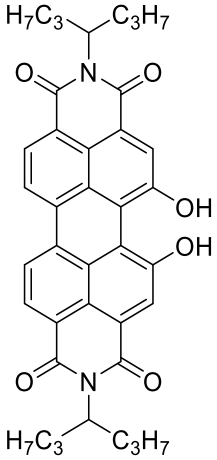
^{1}H-NMR (400 MHz, $CDCl_3/CD_3OD$, 295 K): δ = 8.52-8.46 (m, 4H), 8.25 (s, 2H), 4.99-4.91 (m, 2H), 2.21-2.09 (m, 4H), 1.88-1.77 (m, 4H), 0.81 ppm (t, J = 7.47 Hz, 12H).

^{13}C-NMR (151 MHz, $CDCl_3/CD_3OD$, 295 K): δ = 165.1, 164.1, 153.0, 133.7, 129.0, 128.7, 124.9, 124.5, 123.6, 122.8, 122.3, 119.2, 57.7, 24.9, 11.1 ppm.

HRMS: (MALDI-TOF, negative mode, DCTB): m/z calcd for $C_{34}H_{29}N_2O_6$ $[M–H]^-$: 561.2031; found: 561.2024.

m.p.: >400 °C.

N,N'-Di(heptan-4-yl)-1,12-dihydroxyperylene-3,4:9,10-bis(dicarboximide) [PBI-(OH)$_2$ b]



Route A: PBI b (553 mg, 0.94 mmol) was dissolved in concentrated H_2SO_4 (7.5 mL) in a round-bottom flask and boric acid (250 mg, 4.05 mmol) was added. The mixture was diluted with water (1.5 ml) and cooled to 0 °C. Subsequently, manganese dioxide (550 mg, 6.31 mmol) was slowly added, and the reaction mixture was stirred for 25 h at room temperature. Afterwards, water (40 mL) and Na_2SO_3 (500 mg, 3.97 mmol) were added, and the mixture was refluxed for 1 h on a heating block. The precipitate was filtered after cooling to room temperature, washed with water and dried. The product was purified by column chromatography (silica, DCM/MeOH 5 %).

Yield: 489 mg (0.81 mmol, 84%) of a purple solid.

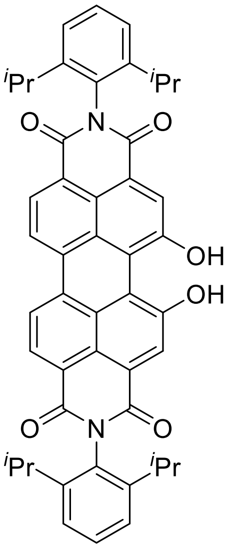
^{1}H-NMR (400 MHz, $CDCl_3/CD_3OD$, 295 K): δ = 8.50 (br s, 4H), 8.26 (s, 2H), 5.19-5.11 (m, 2H), 2.23-2.14 (m, 4H), 1.79-1.70 (m, 4H), 1.34-1.23 (m, 8H), 0.85 ppm (t, J = 7.35 Hz, 12H).

^{13}C-NMR (151 MHz, $CDCl_3/CD_3OD$, 295 K): δ = 165.3, 165.0, 164.3, 164.0, 153.1, 133.8, 129.1, 128.9, 128.3, 125.4, 124.5, 124.0, 123.3, 122.8, 122.0, 119.3, 54.2, 34.5, 20.1, 13.9 ppm.

HRMS: (MALDI-TOF, negative mode, DCTB): m/z calcd for $C_{38}H_{37}N_2O_6$ $[M-H]^-$: 617.2657; found: 617.2665.

m.p.: >400 °C.

N,N'-Di(2,6-diisopropylphenyl)-1,12-dihydroxyperylene-3,4:9,10-bis(dicarboximide) [PBI-(OH)$_2$ d]



Route B: PBA-(OH)$_2$[S10] (500 mg, 1.18 mmol) was suspended in molten imidazole (5 g) in a round-bottom flask and 2,6-diisopropylphenylamine (2.22 mL, 11.8 mmol) was added dropwise. The reaction mixture was stirred for 22 h at 130 °C on a heating block. The mixture was acidified with hydrochloric acid and extracted with DCM until the water phase was colorless. The solvent was dried over Na_2SO_4 and removed under reduced pressure. The crude product was purified by column chromatography (silica, DCM/MeOH 5%). Finally, it was precipitated with *n*-hexane from DCM/MeOH solution and washed with *n*-hexane.

Yield: 602 mg (0.81 mmol, 69%) of a purple solid.

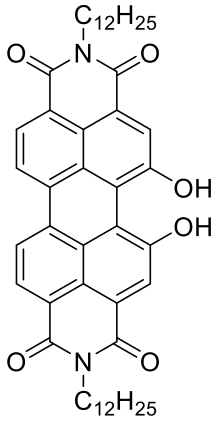
^{1}H-NMR (400 MHz, CD_2Cl_2/MeOD, 295 K): δ = 8.73-8.65 (m, 4H), 8.42 (s, 2H), 7.51 (t, J = 7.81 Hz, 2H), 7.36 (d, J = 7.72 Hz, 4H), 2.75 (sept, J = 6.85 Hz, 4H), 1.14 ppm (d, J = 6.92 Hz, 24H).

^{13}C-NMR (101 MHz, CD_2Cl_2/MeOD, 295 K): δ = 164.6, 164.4, 154.3, 146.4, 134.7, 131.4, 129.94, 129.86, 129.3, 125.9, 125.4, 124.5, 123.7, 123.5, 122.5, 120.3, 29.5, 24.0 ppm.

HRMS: (MALDI-TOF, negative mode, DCTB): m/z calcd for $C_{48}H_{42}N_2O_6$ $[M-H]^-$: 741.2970; found: 741.2937.

m.p.: >400 °C.

N,N'-Di(*n*-dodecyl)-1,12-dihydroxyperylene-3,4:9,10-bis(dicarboximide) [PBI-(OH)$_2$ e]



Route B: PBA-(OH)$_2$[S10] (1.00 g, 2.36 mmol) was suspended in molten imidazole (20 g) in a round-bottom flask and *n*-dodecylamine (2.22 mL, 11.8 mmol) was added dropwise. The reaction mixture was stirred for 19 h at 130 °C on a heating block. Thereafter, the mixture was acidified with hydrochloric acid, filtered, and washed with water until neutral. The crude product was purified by column chromatography (silica, DCM/MeOH 10%). Finally, the product was precipitated with *n*-hexane from a DCM/MeOH solution and washed with *n*-hexane.

Yield: 982 mg (1.29 mmol, 55%) of a purple solid.

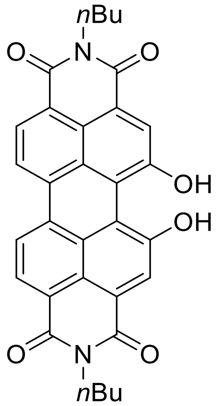
^{1}H-NMR (400 MHz, $CDCl_3$/MeOD, 295 K): δ = 8.39-8.34 (m, 4H), 8.17 (s, 2H), 4.04 (t, J = 7.55 Hz, 4H), 1.65-1.58 (m, 4H), 1.34-1.12 (m, 36H), 0.73 ppm (t, J = 6.80 Hz, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$/MeOD, 295 K): δ = 163.9, 163.5, 152.9, 133.6, 128.8, 128.4, 124.7, 124.0, 123.2, 122.7, 121.9, 119.1, 40.6, 31.8, 29.53, 29.51, 29.50, 29.45, 29.3, 29.2, 28.0, 27.0, 22.5, 13.9 ppm.

HRMS: (MALDI-TOF, negative mode, DCTB): m/z calcd for $C_{48}H_{57}N_2O_6$ $[M-H]^-$: 757.4222; found: 757.4199.

m.p.: >400 °C.

N,N'-Di(*n*-butyl)-1,12-dihydroxyperylene-3,4:9,10-bis(dicarboximide) [PBI-$(OH)_2$ f]



Route B: PBA-$(OH)_2$[S10] (1.00 g, 2.36 mmol) was suspended in water (20 mL) in a round-bottom flask and *n*-butylamine (932 µL, 9.43 mmol) was added dropwise. The reaction mixture was stirred for 18 h at 80 °C on a heating block. The mixture was made acidic with hydrochloric acid, filtered, and washed with water until neutral. The dry solid was purified by column chromatography (silica, DCM/MeOH 10%). Finally, the product was suspended in DCM and filtered.

Yield: 841 mg (1.57 mmol, 67%) of a purple solid.

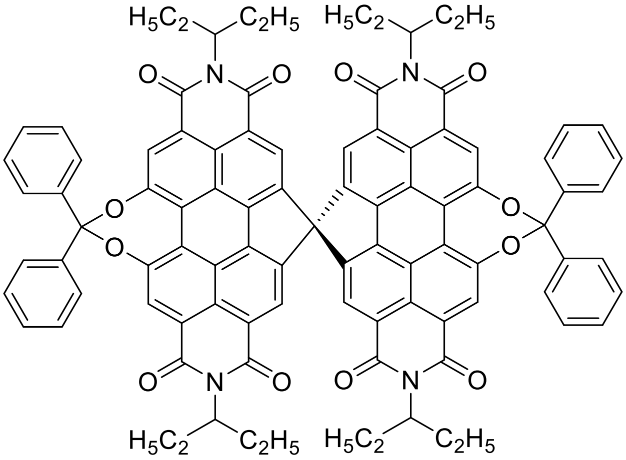
^{1}H-NMR (400 MHz, $CDCl_3$/MeOD, 295 K): δ = 8.35-8.27 (m, 4H), 8.11 (s, 2H), 4.05 (t, J = 7.63 Hz, 4H), 1.66-1.58 (m, 4H), 1.41-1.32 (m, 4H), 0.90 ppm (t, J = 7.37 Hz, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$/MeOD, 295 K): δ = 163.8, 163.4, 153.2, 133.2, 128.5, 128.0, 124.8, 123.7, 122.8, 122.4, 121.6, 119.0, 40.3, 30.0, 20.3, 13.7 ppm.

HRMS: (MALDI-TOF, negative mode, DCTB): m/z calcd for $C_{32}H_{25}N_2O_6$ $[M-H]^-$: 533.1718; found: 533.1710.

m.p.: >400 °C.

Spiro-PBI-(O-C-O)



Br-PBI-(O-C-O)[S10] (150 mg, 186 µmol), Pd(OAc)$_2$ (4.2 mg, 18.6 µmol), $KHCO_3$ (149 mg, 1.49 mmol), KOAc (164 mg, 1.68 mmol) were set under nitrogen in a Schlenk tube followed by the addition of CH_2Br_2 (91.0 µL, 1.30 mmol), *i*PrOH (28.7 µL, 372 µmol) and 1,4-dioxane (5 mL). The mixture was stirred for 19 h at 75 °C on a heating block. Thereafter, water was added, and the precipitate was filtered, washed with water until neutral, and dried. The crude product was purified by column chromatography (silica, DCM/cyclohexane, 7:3).

Yield: 21 mg (14.4 µmol, 15%) of red solid.

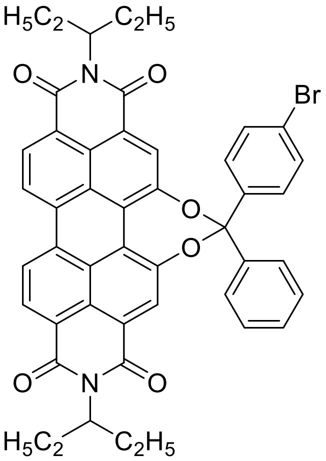
^{1}H-NMR (400 MHz, CD_2Cl_2, 295 K): δ = 8.75 (s, 4H), 7.92 (s, 4H), 7.74-7.72 (m, 8H), 7.37-7.28 (m, 12H), 4.97 (br s, 4H), 2.14 (br s, 8H), 1.83-1.80 (m, 8H), 0.83 ppm (t, J = 7.44 Hz, 24H).

^{13}C-NMR (101 MHz, CD_2Cl_2, 295 K): δ = 165.7, 164.4, 163.2, 155.9, 141.5, 140.6, 139.8, 129.3, 129.1, 127.9, 127.2, 126.3, 125.3, 125.0, 124.0, 121.9, 106.6, 74,5 58.0, 25.3, 11.4 ppm.

HRMS: (MALDI-TOF, negative mode, DCTB): m/z calcd for $C_{95}H_{72}N_4O_{12}$ $[M]^-$: 1460.5152; found: 1460.5147.

m.p.: >400 °C.

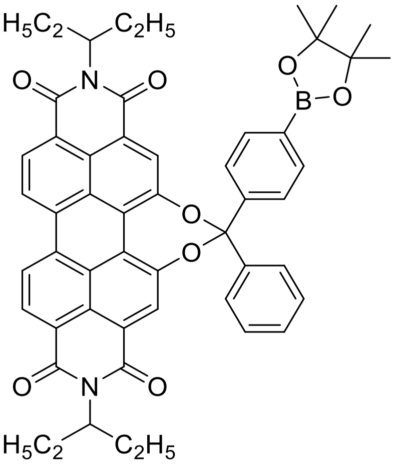
PBI-(O-C-O)-Br



The synthetic procedure was previously described.[S10]

Optical Properties: (Absorption, Chloroform, c = 20 µM): $\lambda_{\mathrm{max,s}}$ = 540 nm, $\varepsilon_{\mathrm{max,s}}$ = 66000 $\mathrm{M^{-1}\,cm^{-1}}$ (Emission, Chloroform, $A \leq 0.05$): $\lambda_{\mathrm{em,s}}$ = 552 nm, $\Delta\tilde{\nu}_{\mathrm{Stokes}}$ = 400 $\mathrm{cm^{-1}}$, $\Phi_{\mathrm{fl,s}}$ = 100±3%, $\tau_{\mathrm{fl,s}}$ = 5.06 ns

PBI-(O-C-O)-Bpin



PBI-(O-C-O)-Br[S10] (100 mg, 124 µmol), bis(pinacolato)diboron (47.3 mg, 186 µmol), Pd(dppf)Cl_2 (4.5 mg, 6.2 µmol) and KOAc (41.7 mg, 424 µmol) were set under nitrogen in a Schlenk tube and dissolved in degassed anhydrous 1,4-dioxane (20 mL). The mixture was stirred for 45 h at 100 °C. After cooling, the solvent was removed under reduced pressure and the resultant crude product was purified by column chromatography (silica, DCM).

Yield: 45 mg (52.8 µmol, 43%) of a red solid.

^{1}H-NMR (400 MHz, CD_2Cl_2, 295 K): δ = 8.70 (s, 2H), 8.64 (d, J = 8.21 Hz, 2H), 8.57 (d, J = 8.07 Hz, 2H), 7.67-7.64 (m, 2H), 7.61-7.57 (m, 4H), 7.32-7.23 (m, 3H), 5.08-5.00 (m, 2H), 2.30-2.19 (m, 4H), 1.99-1.89 (m, 4H), 1.22 (s, 12H), 0.93 ppm (t, J = 7.45 Hz, 12H).

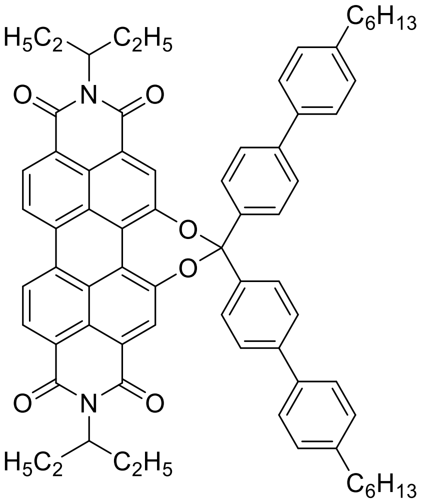
^{13}C-NMR (101 MHz, CD_2Cl_2, 295 K): δ = 164.0, 154.5, 142.9, 140.8, 135.1, 134.1, 129.6, 129.1, 128.9, 128.4, 128.2, 126.7, 126.3, 126.1, 124.5, 123.5, 123.2, 122.0, 106.4, 84.3, 58.1, 25.3, 24.9, 11.6 ppm.

HRMS: (MALDI-TOF, negative mode, DCTB): m/z calcd for $C_{53}H_{49}BN_2O_8$ $[M]^-$: 852.3587; found: 852.3592.

m.p.: 273-274 °C.

Optical Properties: (Absorption, Chloroform, c = 20 µM): $\lambda_{\mathrm{max,s}}$ = 542 nm, $\varepsilon_{\mathrm{max,s}}$ = 64000 $\mathrm{M^{-1}\,cm^{-1}}$ (Emission, Chloroform, $A \leq 0.05$): $\lambda_{\mathrm{em,s}}$ = 555 nm, $\Delta\tilde{\nu}_{\mathrm{Stokes}}$ = 400 $\mathrm{cm^{-1}}$, $\Phi_{\mathrm{fl,s}}$ = 99±2%, $\tau_{\mathrm{fl,s}}$ = 5.18 ns

PBI-(O-C-O)-Ar$_2$



PBI-(O-C-O)-Br$_2$[S10] (30.0 mg, 33.9 µmol), *p*-hexylphenylbronic acid pinacol ester (22.5 mg, 78.0 µmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos) (2.8 mg, 6.8 µmol), [$Pd_2(dba)_3$]*$CHCl_3$ (1.8 mg, 1.7 µmol) and Cs_2CO_3 (33.2 mg, 102 µmol) were taken in a Schlenk tube and set under nitrogen. Subsequently, degassed toluene (2 mL) and water (1 mL) were added, and the mixture was stirred for 22 h at 100 °C on a heating block. Thereafter, more water was added, and the product was extracted with DCM. The organic layers were collected, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product was purified by column chromatography (silica, DCM).

Yield: 34 mg (32.4 µmol, 96%) of red crystalline solid.

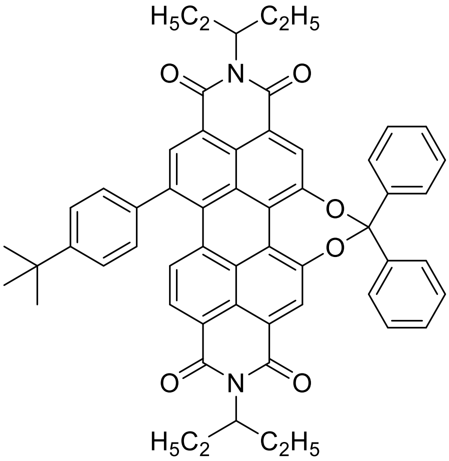
^{1}H-NMR (400 MHz, CD_2Cl_2, 295 K): δ = 8.59 (s, 2H), 8.43 (d, *J* = 8.08 Hz, 2H), 8.35 (d, *J* = 8.24 Hz, 2H), 7.61 (d, *J* = 8.45 Hz , 4H), 7.46 (d, *J* = 8.49 Hz, 4H), 7.38 (d, *J* = 8.12 Hz 4H), 7.17 (d, *J* = 8.16 Hz 4H), 5.09-5.01 (m, 2H), 2.58 (t, *J* = 7.62 Hz, 4H), 2.33-2.21 (m, 4H), 2.05-1.95 (m, 4H), 1.61-1.54 (m, 4H), 1.35-1.26 (m, 12H), 0.98 (t, *J* = 7.44 Hz, 12H), 0.88-0.85 ppm (m, 6H).

^{13}C-NMR (101 MHz, CD_2Cl_2, 295 K): δ = 164.4, 163.7, 154.4, 143.2, 141.7, 139.3, 137.4, 133.9, 129.5, 129.2, 128.4, 128.2 127.24, 127.20, 127.1, 126.2, 124.5, 123.5, 123.0, 121.9, 106.0, 58.1, 35.9, 32.1, 31.8, 29.4, 25.4, 23.0, 14.2, 11.7 ppm.

HRMS: (MALDI-TOF, negative mode, DCTB): m/z calcd for $C_{71}H_{70}N_2O_6$ $[M]^-$: 1046.5239; found: 1046.5278.

m.p.: 168-170 °C.

N,N'-Di(pent-3-yl)-6-(4-*tert*-butylphenyl)-1,12-(14,14-di-phenyl-dioxepin)perylene-3,4:9,10-bis(dicarboximide) [Ph-PBI-(O-C-O)]



Br-PBI-(O-C-O)[S10] (30.0 mg, 37.2 µmol), 4-*tert*-butylphenylbronic acid (9.9 mg, 55.9 µmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos) (3.1 mg, 7.4 µmol), $[Pd_2(dba)_3]*CHCl_3$ (1.9 mg, 1.9 µmol) and Cs_2CO_3 (36.4 mg, 111 µmol) were taken in a Schlenk tube. The mixture was set under nitrogen, dissolved in degassed toluene (1 mL) and water (0.5 mL), and stirred for 17 h at 100 °C on a heating block. Subsequently, water was added and the product extracted with DCM. The organic layers were collected, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The resultant crude product was purified by column chromatography (silica, DCM) and, finally, crystallized with MeOH from a DCM solution.

Yield: 32 mg (37.2 µmol, 100%) of red crystalline solid.

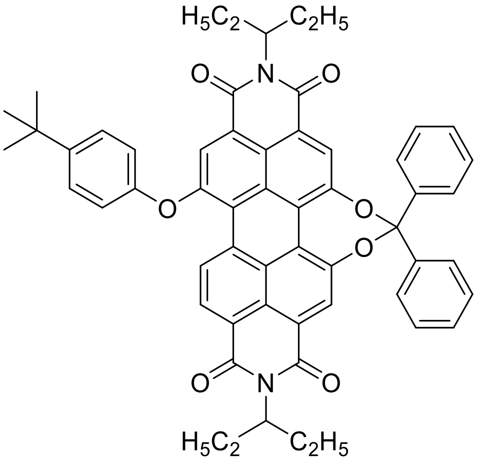
^{1}H-NMR (400 MHz, CD_2Cl_2, 295 K): δ = 8.48 (s, 1H), 8.43 (s, 1H), 8.42 (s, 1H), 7.98 (d, J = 8.24 Hz, 1H), 7.89 (d, J = 8.29 Hz, 1H), 7.69-7.66 (m, 4H), 7.51-7.48 (m, 2H), 7.38-7.29 (m, 8H), 5.04-4.93 (m, 2H), 2.27-2.13 (m, 4H), 1.87-1.83 (m, 4H), 1.39 (s, 9H), 0.92-0.86 ppm (m, 12H).

^{13}C-NMR (101 MHz, CD_2Cl_2, 295 K): δ = 164.3, 154.3, 154.1, 152.2, 141.7, 140.9, 140.2, 134.7, 134.1, 132.2, 130.4, 130.0, 129.6, 129.3, 128.9, 128.7, 128.3, 127.7, 127.4, 126.9, 125.7, 125.3, 125.2, 124.4, 123.9, 123.4, 122.4, 114.9, 58.0, 57.9, 35.0, 31.5, 25.3, 11.53, 11.51 ppm.

HRMS: (MALDI-TOF, negative, DCTB): m/z calcd for $C_{57}H_{50}N_2O_6$ $[M]^-$: 858.3674; found: 858.3669.

m.p.: 251-252 °C.

N,N'-Di(pent-3-yl)-6-(4-*tert*-butylphenoxy)-1,12-(14,14-di-phenyl-dioxepin)perylene-3,4:9,10-bis(dicarboximide) [PhO-PBI-(O-C-O)]



4-*tert*-Butylphenol (10.6 mg, 37.2 µmol), 18-Crown-6 (76.8 mg, 290 µmol) and K_2CO_3 (20.1 mg, 145 µmol) were set under nitrogen in a Schlenk tube, dissolved in dry toluene (4 mL), and stirred for 20 min at room temperature. Thereafter, **Br-PBI-(O-C-O)**[S10] (30.0 mg, 37.2 µmol) was added and the mixture was stirred for 4 h at 90 °C on a heating block. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, DCM). Finally, the product was crystallized with MeOH from a DCM solution.

Yield: 29 mg (33.1 µmol, 89%) of red crystalline solid.

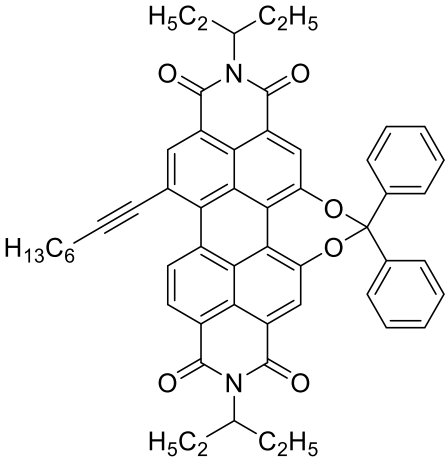
^{1}H-NMR (400 MHz, CD_2Cl_2, 295 K): δ = 9.51 (d, *J* =8.37 Hz, 1H), 8.50 (d, *J* = 8.36 Hz, 1H) 8.39 (s, 1H), 8.30 (s, 1H), 8.15 (s, 1H), 7.70-7.68 (m, 4H), 7.50-7.46 (m, 2H), 7.38-7.32 (m, 6H), 7.11-7.07 (m, 2H), 5.03-4.89 (m, 2H), 2.25-2.09 (m, 4H), 1.94-1.81 (m, 4H), 1.35 (s, 9H), 0.90-0.84 ppm (m, 12H).

^{13}C-NMR (101 MHz, CD_2Cl_2, 295 K): δ = 164.1, 156.5, 154.5, 153.6, 153.0, 148.6, 140.8, 133.1, 130.7, 130.3, 129.3, 129.0, 128.9, 128.5, 127.8, 127.6, 127.0, 126.0, 125.5, 125.3, 124.1, 123.3, 122.6, 122.4, 119.6, 117.9, 58.1, 57.9, 34.8, 31.6, 25.34, 25.31, 11.52, 11.50 ppm.

HRMS: (MALDI-TOF, negative mode, DCTB): m/z calcd for $C_{57}H_{50}N_2O_7$ $[M]^-$: 874.3624; found: 874.3651.

m.p.: 215-216 °C.

N,N'-Di(pent-3-yl)-6-(1-octynyl)-1,12-(14,14-di-phenyl-dioxepin)perylene-3,4:9,10-bis(dicarboximide) [Octyne-PBI-(O-C-O)]



Br-PBI-(O-C-O)[S10] (50.0 mg, 62.1 µmol), [$PdCl_2(PPh_3)_2$] (1.74 mg, 2.5 µmol), CuI (236 µg, 1.3 µmol) were set under nitrogen in a Schlenk tube followed by the addition of degassed THF (2.5 mL), (i-Pr)$_2$NH (1.3 mL) and 1-octyne (11.0 µL, 74.5 µmol). Thereafter, the Schlenk tube was sealed by a rubber septum and the mixture was stirred for 17 h at 80 °C on a heating block. The solvent was removed under reduced pressure and the crude product purified by column chromatography (silica, DCM/cyclohexane, 6:4). Finally, the product was crystallized with MeOH from a DCM solution.

Yield: 48 mg (58.0 µmol, 93%) of dark red crystalline solid.

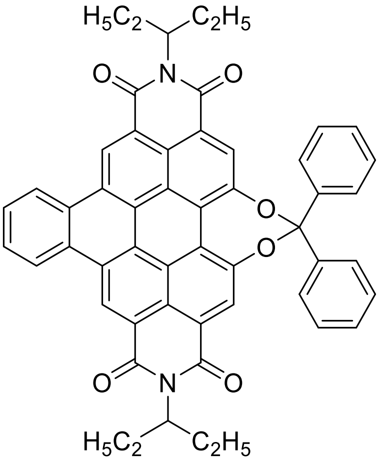
^{1}H-NMR (400 MHz, CD_2Cl_2, 295 K): δ = 10.11 (d, J = 8.22 Hz, 1H), 8.62 (s, 1H), 8.55 (d, J = 8.22 Hz, 1H), 8.45 (s, 1H), 8.40 (s, 1H), 7.65-7.63 (m, 4H), 7.33-7.27 (m, 6H), 5.05-4.96 (m, 2H), 2.64 (t, J = 7.14 Hz, 2H), 2.27-2.17 (m, 4H), 1.97-1.89 (m, 4H), 1.77-1.72 (m, 2H), 1.57-1.52 (m, 2H), 1.41-1.34 (m, 4H), 0.93-0.89 ppm (m, 15H).

^{13}C-NMR (101 MHz, CD_2Cl_2, 295 K): δ = 163.9, 154.4, 154.2, 140.7, 137.2, 133.9, 133.8, 129.3, 129.1, 128.83, 128.76, 127.7, 127.1, 126.9, 125.6, 124.92, 124.85, 124.5, 123.8, 123.4, 122.2, 121.2, 114.8, 101.3, 82.6, 58.1, 58.0, 31.8, 29.3, 28.7, 25.34, 25.30, 23.0, 20.5, 14.3, 11.5 ppm.

HRMS: (MALDI-TOF, negative mode, DCTB): m/z calcd for $C_{55}H_{50}N_2O_6$ $[M]^-$: 834.3674; found: 834.3688.

m.p.: 230-232 °C.

N,N'-Di(pent-3-yl)-6,7-naphtho-1,12-(14,14-di-phenyl-dioxepin)perylene-3,4:9,10-bis(dicarboximide) [Naphtho-PBI-(O-C-O)]



Br-PBI-(O-C-O)[S10] (10.0 mg, 12.4 µmol), Pd(dba)$_2$ (1.8 mg, 3.1 µmol), tri(*o*-tolyl)-phosphine (1.3 mg, 4.3 µmol) and CsF (5.7 mg, 37.2 µmol) were set under nitrogen in a Schlenk tube, and dissolved in dry toluene (2 mL) and acetonitrile (0.2 mL). 2-(Trimethylsilyl)phenyl trifluoromethanesulfonate (6.20 µL, 24.8 µmol) was added and the mixture stirred for 18 h at 100 °C on a heating block. The solvent was removed under reduced pressure and the resultant crude product was purified by column chromatography (silica, DCM). Finally, the product was crystallized from a DCM solution.

Yield: 8 mg (9.99 µmol, 80%) of orange crystalline solid.

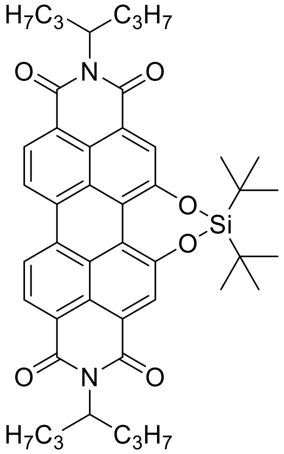
^{1}H-NMR (400 MHz, CD_2Cl_2, 295 K): δ = 9.72 (s, 2H), 9.02-9.00 (m, 2H) 8.83 (s, 2H), 8.05-8.01 (m, 2H), 7.61-7.58 (m, 4H), 7.22-7.12 (m, 6H), 5.20-5.12 (m, 2H), 2.42-2.31 (m, 4H), 2.16-2.06 (m, 4H), 1.06 ppm (t, *J* = 7.45 Hz, 12H).

^{13}C-NMR (101 MHz, CD_2Cl_2, 295 K): δ = 164.1, 154.3, 140.7, 129.2, 129.04, 128.98, 128.7, 127.9, 127.0, 126.5, 126.0, 125.8, 124.6, 124.3, 123.5, 123.0, 122.6, 122.2, 106.3, 58.3, 25.4, 11.8 ppm.

HRMS: (MALDI-TOF, negative mode, DCTB): m/z calcd for $C_{53}H_{40}N_2O_6$ $[M]^-$: 800.2892; found: 800.2869.

m.p.: >400 °C.

N,N'-Di(hept-4-yl)-1,12-(14,14-di-*tert*-butyl-dioxosilan)perylene-3,4:9,10-bis(dicarboximide) [PBI-(O-Si-O) b]



PBI-(OH)$_2$ b (50.0 mg, 80.8 µmol) was dissolved in dry DMF (40 mL) and di-*tert*-butylsilyl-bis(trifluoromethanesulfonate) (79.0 µL, 242 µmol) was added dropwise. Afterwards, Et_3N (33.6 µL, 242 µmol) was added and the reaction mixture was stirred for 6 h at room temperature. The solvent was removed under reduced pressure and the resulted crude product was purified by column chromatography (silica, DCM). Finally, the product was crystalized with MeOH from a DCM solution.

Yield: 46 mg (60.6 µmol, 75%) of orange crystals.

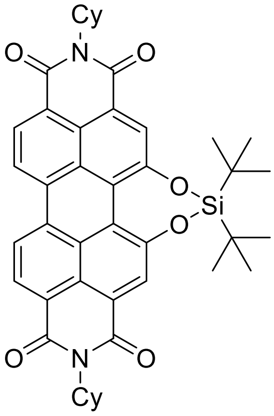
^{1}H-NMR (400 MHz, $CDCl_3$, 295 K): δ = 8.60-8.56 (m, 4H), 8.39 (s, 2H), 5.25-5.19 (m, 2H), 2.31-2.22 (m, 4H), 1.87-1.79 (m, 4H), 1.41-1.27 (m, 8H), 1.23 (s, 18H), 0.93 ppm (t, *J* = 7.32 Hz, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$, 295 K): δ = 165.1, 164.4, 164.1, 163.4, 154.6, 134.0, 129.7, 129.4, 129.1, 128.5, 125.4, 124.5, 123.8, 123.3, 123.0, 122.6, 122.2, 54.3, 34.6, 28.0, 22.0, 20.3, 14.2 ppm.

HRMS: (MALDI-TOF, positive mode, DCTB): m/z calcd for $C_{46}H_{54}N_2O_6Si$ $[M]^+$: 758.3746; found: 758.3746.

m.p.: 283-285 °C

N,N'-Di(cyclohexyl)-1,12-(14,14-di-*tert*-butyl-dioxosilan)perylene-3,4:9,10-bis(dicarboximide) [PBI-(O-Si-O) c]



PBI-(OH)$_2$ c[S10] (50.0 mg, 85.2 µmol) was dissolved in dry DMF (40 mL) and di-*tert*-butylsilyl-bis(trifluoromethanesulfonate) (41.7 µL, 128 µmol) was added dropwise. Afterwards Et$_3$N (17.7 µL, 128 µmol) was added and the reaction mixture was stirred for 4 h at room temperature. The solvent was removed under reduced pressure, and the resulted crude product was purified by column chromatography (silica, DCM). Finally, the product was crystalized with MeOH from a DCM solution.

Yield: 46 mg (63.3 µmol, 74%) of red crystals.

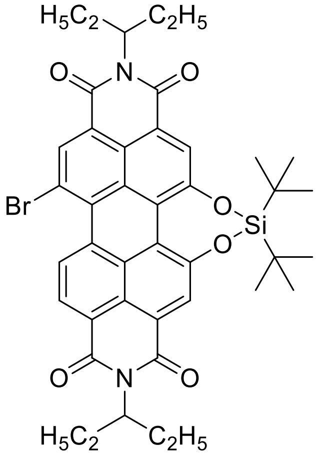
^{1}H-NMR (400 MHz, CDCl$_3$, 295 K): δ = 8.61-8.53 (m, 4H), 8.36 (s, 2H), 5.09-5.01 (m, 2H), 2.63-2.52 (m, 4H), 1.94-1.90 (m, 4H), 1.80-1.73 (m, 6H), 1.52-1.32 (m, 6H), 1.22 ppm (s, 18H).

^{13}C-NMR (101 MHz, CDCl$_3$, 295 K): δ = 164.3, 163.7, 154.6, 133.9, 129.35, 129.26, 128.5, 125.2, 124.5, 123.2, 123.0, 122.2, 54.2, 29.3, 28.0, 26.7, 25.6, 22.0 ppm.

HRMS: (MALDI-TOF, negative mode, DCTB): m/z calcd for $C_{44}H_{46}N_2O_6Si$ $[M]^-$: 726.3130; found: 726.3122.

m.p.: >400 °C

N,N’-Di(pent-3-yl)-6-bromo-1,12-(14,14-di-*tert*-butyl-dioxosilan)perylene-3,4:9,10-bis(dicarboximide) [Br-PBI-(O-Si-O)]



PBI-(O-Si-O) a[S11] (270 mg, 384 µmol) was dissolved in DCM (100 mL) in a round-bottom flask and Br_2 (1.97 mL, 38.4 mmol) was added. The reaction was refluxed for 19 h on a heating block. Thereafter, the excess bromine was quenched with aqueous Na_2SO_3 solution. The organic layer was separated, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The obtained crude product was purified by column chromatography (silica, DCM). Finally, the product was crystallized with MeOH from a DCM solution.

Yield: 279 mg (357 µmol, 93%) of orange crystals.

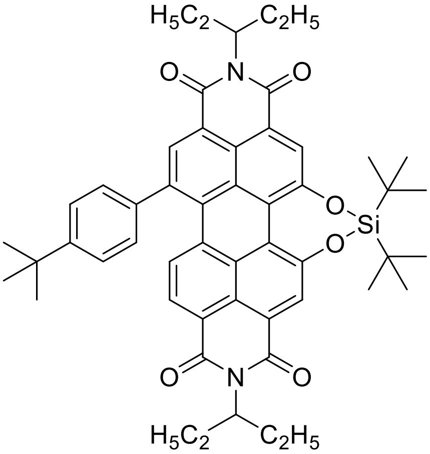
^{1}H-NMR (400 MHz, $CDCl_3$, 295 K): δ = 9.38 (d, J = 8.16 Hz, 1H), 8.84 (s, 1H), 8.60 (d, J = 8.17 Hz, 1H), 8.39 (s, 1H) 8.38 (s, 1H), 5.10-5.00 (m, 2H), 2.32-2.19 (m, 4H), 2.00-1.89 (m, 4H), 1.20 (s, 18H), 0.95-0.90 ppm (m, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$, 295 K): δ = 163.7, 154.7, 154.6, 136.3, 133.1, 132.4, 131.7, 130.4, 128.1, 124.4, 124.0, 123.7, 123.5, 122.9, 122.3, 121.7, 121.1, 120.6, 58.1, 57.9, 28.0, 25.2, 25.1, 22.0, 11.51, 11.48 ppm.

HRMS: (MALDI-TOF, negative mode, DCTB): m/z calcd for $C_{42}H_{45}BrN_2O_6Si$ $[M]^-$: 780.2236; found: 780.2236.

m.p.: 291-292 °C.

N,N'-Di(pent-3-yl)-6-(4-*tert*-butylphenyl)-1,12-(14,14-di-*tert*-butyl-dioxosilan)perylene-3,4:9,10-bis(dicarboximide) [Ph-PBI-(O-Si-O)]



Br-PBI-(O-Si-O) (30.0 mg, 38.4 µmol), 4-*tert*-butylphenylbronic acid (10.3 mg, 57.6 µmol), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos) (3.2 mg, 7.7 µmol), $[Pd_2(dba)_3]$*$CHCl_3$ (2.0 mg, 1.9 µmol) and Cs_2CO_3 (37.5 mg, 115 µmol) were taken in a Schlenk tube and set under nitrogen. Subsequently, degassed toluene (1 mL) and water (0.5 mL) were added. The mixture was stirred for 17 h at 100 °C on a heating block. After cooling, more water was added, and the product was extracted with DCM. The organic layers were collected, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The resultant crude product was purified by column chromatography (silica, DCM) and, finally, the product was crystallized with MeOH from a DCM solution.

Yield: 32 mg (37.8 µmol, 99%) of orange/red crystals.

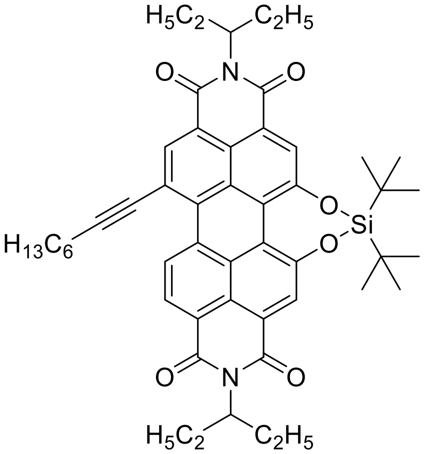
^{1}H-NMR (400 MHz, CD_2Cl_2, 295 K): δ = 8.50 (s, 1H), 8.36 (s, 1H), 8.35 (s, 1H), 7.97 (d, J = 8.17 Hz, 1H), 7.82 (d, J = 8.16 Hz, 1H), 7.49-746 (m, 2H), 7.39-7.37 (m, 2H), 5.06-4.95 (m, 2H), 2.29-2.14 (m, 4H), 1.97-1.83 (m, 4H), 1.38 (s, 9H), 1.23 (s, 18H), 0.93-0.87 ppm (m, 12H).

^{13}C-NMR (101 MHz, CD_2Cl_2, 295 K): δ = 164.6, 154.8, 154.5, 152.0, 141.5, 140.2, 133.9, 133.8, 132.1, 131.5, 131.0, 130.0, 129.1, 128.1, 127.6, 127.2, 125.0, 124.4, 124.2, 122.7, 122.3, 122.2, 57.9, 57.8, 35.0, 31.5, 28.0, 25.4, 22.1, 11.5 ppm.

HRMS: (MALDI-TOF, negative mode, DCTB): m/z calcd for $C_{52}H_{58}N_2O_6Si$ $[M]^-$: 834.4070; found: 834.4065.

m.p.: 325-326 °C.

N,N'-Di(pent-3-yl)-6-(1-octynyl)-1,12-(14,14-di-*tert*-butyl-dioxosilan)perylene-3,4:9,10-bis(dicarboximide) [Octyne-PBI-(O-Si-O)]



Br-PBI-(O-Si-O) (50.0 mg, 64.0 µmol), $[PdCl_2(PPh_3)_2]$ (2.6 mg, 1.8 µmol), CuI (244 µg, 1.3 µmol) were set under nitrogen in a Schlenk tube followed by the addition of degassed THF (2.5 mL), $(i\text{-Pr})_2$ NH (1.25 mL) and 1-octyne (11.3 µL, 76.7 µmol). The mixture was stirred for 17 h at 80 °C on a heating block. The solvent was removed under reduced pressure and the crude product purified by column chromatography (silica, DCM/cyclohexane, 6:4). Finally, the product was crystallized with MeOH from a DCM solution.

Yield: 45 mg (55.5 µmol, 87%) of red crystals.

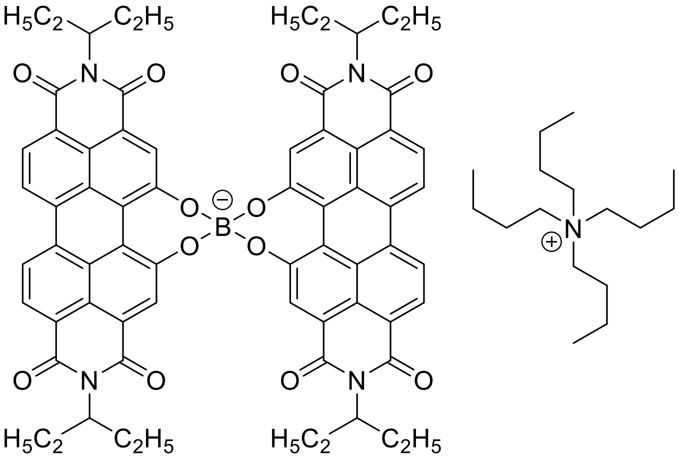
^{1}H-NMR (400 MHz, $CDCl_3$, 295 K): δ = 9.85 (d, J = 8.17 Hz, 1H), 8.68 (s, 1H), 8.58 (d, J = 8.20 Hz, 1H), 8.39 (s, 1H) 8.35 (s, 1H), 5.11-5.01 (m, 2H), 2.59 (t, J = 7.09 Hz, 2H), 2.33-2.20 (m, 4H), 2.00-1.89 (m, 4H), 1.76-1.68 (m, 2H), 1.56-1.49 (m, 2H), 1.39-1.34 (m, 4H), 1.21 (s, 18H), 0.95-0.89 ppm (m, 15H).

^{13}C-NMR (101 MHz, $CDCl_3$, 295 K): δ = 163.9, 154.6, 154.5, 136.3, 134.0, 133.4, 130.3, 130.1, 128.4, 127.7, 126.8, 124.6, 123.9, 123.5, 122.8, 122.2, 121.7, 121.1, 99.1, 82.1, 57.9, 57.8, 31.5, 29.0, 28.4, 28.0, 25.2, 25.1, 22.7, 22.0, 20.3, 14.2, 11.49, 11.48 ppm.

HRMS: (MALDI-TOF, neg, DCTB): m/z calcd for $C_{50}H_{58}N_2O_6Si$ $[M]^-$: 810.4070; found: 810.4080.

m.p.: 252-253 °C.

Tetrabutylammonium bis[[*N,N'*-di(pentan-3-yl)perylene-3,4:9,10-bis(dicarboximide)]-1,12-diolato-*O,O'*] borate [Spiro-PBI-Borate]



PBI-(OH)$_2$ a (235 mg, 418 µmol) was dissolved in anhydrous DMF (20 mL) in a round-bottom flask. Boronic acid (12.5 mg, 202 µmol) and 55 % w/w aqueous tetrabutylammonium hydroxide (108 µL, 105 mg, 222 µmol) were added, and the reaction mixture was refluxed for 23 h. After cooling to room temperature, the solvent was removed under reduced pressure and the product was purified by column chromatography (silica, 0-2% MeOH/DCM).

Yield: 145 mg (105 µmol, 52%) of a dark purple crystalline solid.

^{1}H-NMR (400 MHz, CDCl$_3$, 295 K): δ = 8.58-8.52 (m, 8H), 8.13 (s, 4H), 5.05-4.98 (m, 4H), 3.13-3.09 (m, 8H), 2.26-2.19 (m, 8H), 1.93-1.83 (m, 8H), 1.53-1.45 (m, 8H), 1.22-1.13 (m, 8H), 0.88 (t, J = 7.45 Hz, 24H), 0.73 ppm (t, J = 7.33 Hz, 12H).

^{13}C-NMR (101 MHz, CDCl$_3$, 295 K): δ = 165.2, 164.6, 134.2, 129.8, 129.5, 129.3, 128.3, 125.0, 123.5, 122.7, 122.2, 122.0, 59.0, 57.4, 25.1, 24.0, 13.5, 11.5 ppm.

HRMS: (MALDI-TOF, negative mode, DCTB): m/z calcd for $C_{68}H_{56}BN_4O_{12}$ [M]$^-$: 1131.3993; found: 1131.4034.

m.p.: 353-355 °C.

3. Crystallographic Data

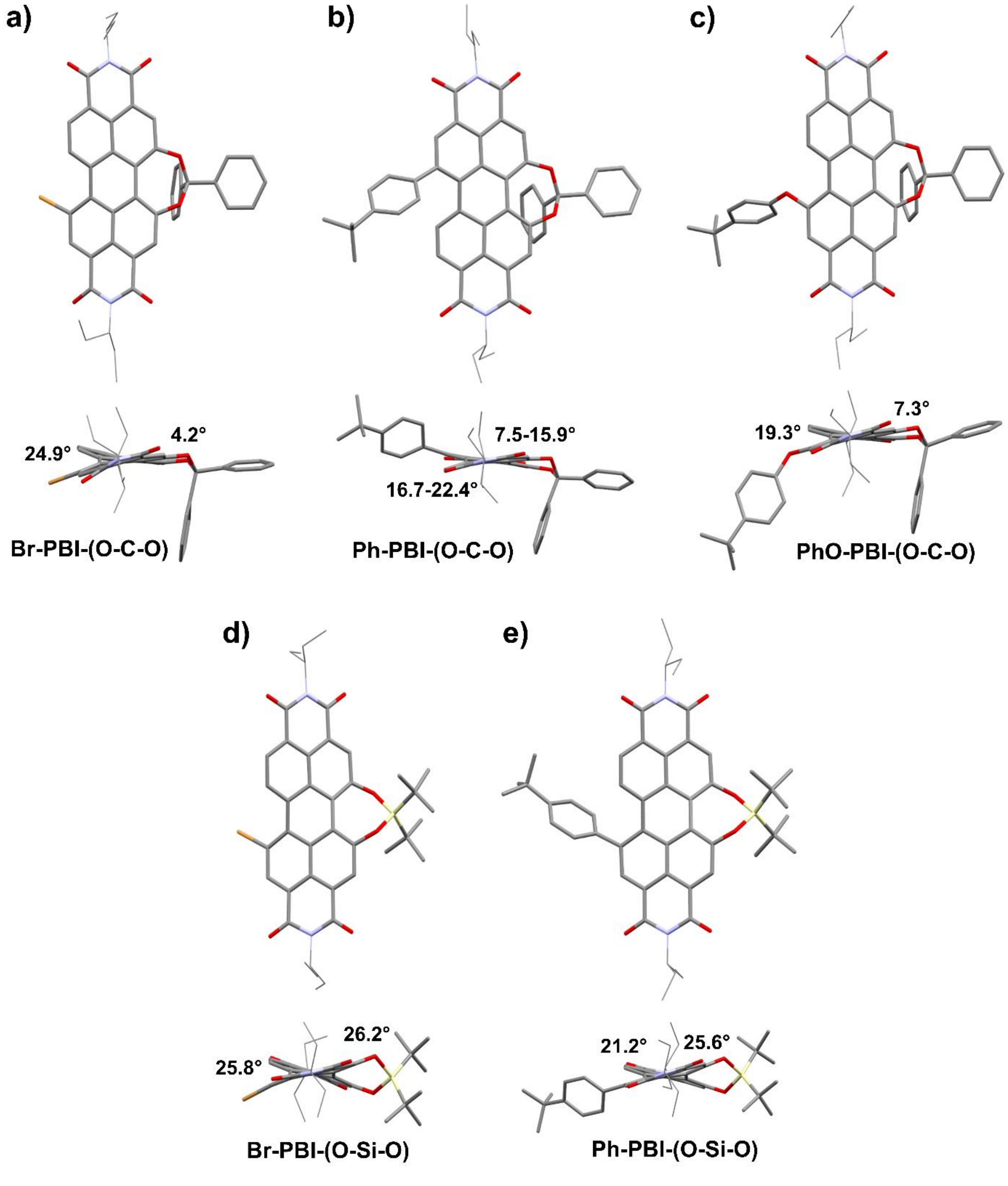


Figure S1. Top view (top) and view along the *N,N'* axis with twist angles of the perylene bay region (bottom) determined by single-crystal X-ray analysis: Solid-state molecular structure of a) **Br-PBI-(O-C-O)**, b) **Ph-PBI-(O-C-O)**, c) **PhO-PBI-(O-C-O)**, d) **Br-PBI-(O-Si-O)** and e) **Ph-PBI-(O-Si-O)**. Hydrogen atoms, disorder and solvent molecules are omitted for clarity.

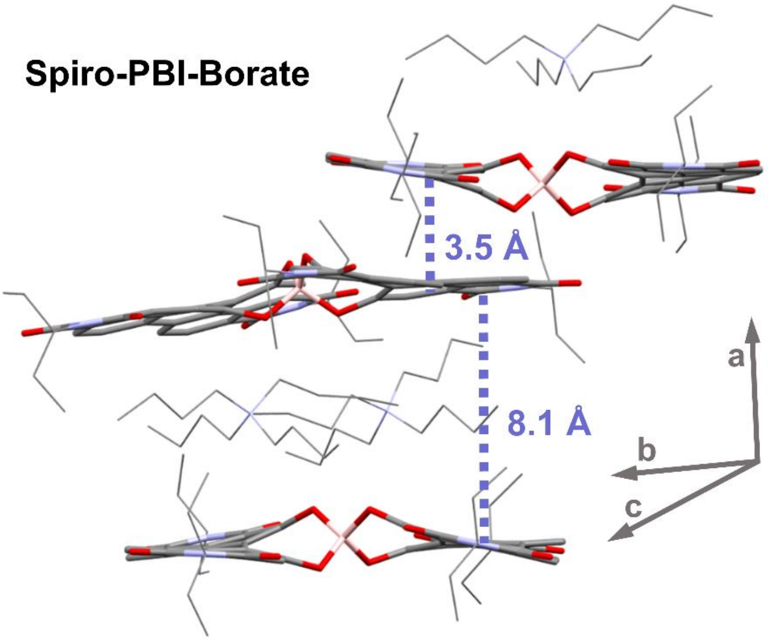


Figure S2. Single-crystal structure of **Spiro-PBI-Borate** with center-to-plane distances to the two closest neighboring perylene molecules. Hydrogen atoms, disorder and solvent molecules are omitted for clarity. The imide substituents as well as the counter anion are displayed in wireframe

Table S1. Crystallographic data of compounds **Ph-PBI-(O-C-O)**, **Octyne-PBI-(O-C-O)** and **Naphtho-PBI-(O-C-O).**

	Ph-PBI-(O-C-O)	**Octyne-PBI-(O-C-O)**	**Naphtho-PBI-(O-C-O)**
CCDC number	2284416	2284409	2284414
Formula	$C_{59.47}H_{52.94}Cl_{1.50}N_2O_{7.72}$	$C_{55.85}H_{53.38}N_2O_{6.85}$	$C_{54.50}H_{43}Cl_3N_2O_6$
Formula weight / g mol^{-1}	972.31	862.07	928.26
Crystal size	0.100 × 0.030 × 0.030 mm	0.239 × 0.052 × 0.012	0.134 × 0.077 × 0.040 mm
Temperature / K	100	100	100
Wavelength / Å	0.61992	1.54178	1.54178
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1$	$P\bar{1}$	$P\bar{1}$
a / Å	12.357(16)	10.6796(18)	11.041(2)
b / Å	35.92(4)	13.079(3)	13.644(2)
c / Å	22.557(17)	17.512(4)	14.896(3)
α / °	90	94.295(7)	77.583(10)
β / °	90.90(2)	104.201(9)	81.405(16)
γ / °	90	109.667(13)	78.256(13)
V / Å^3	10011(19)	2198.0(8)	2132.5(7)
Z value	8	2	2
ρ_{cal} / g cm^{-3}	1.290	1.303	1.446
F(000)	4088.2	914.4	966
Number of reflections measured	186667	49686	50137
Number of unique reflections	48016	8637	8384
Measured range of θ / °	0.787 to 28.147	3.646 to 72.565	3.056 to 72.187
Completeness	0.927	0.999	0.999
R_{int}	0.1926	0.0571	0.0340
T_{min}, T_{max}	0.996, 0.997	0.958, 0.992	0.800. 0.908
Goodness of fit for F^2	0.913	1.086	1.046
Final R_1 indices [$I > 2\sigma(I)$] (R_{obs}, wR_{all})	0.0971, 0.2529	0.0719, 0.1796	0.0464, 0.1259
R indices [all data] (R_{obs}, wR_{all})	0.2672, 0.3595	0.0851, 0.1888	0.0530, 0.1333
Largest diff peak and hole / e Å^{-3}	0.411 and –0.242	0.499 and –0.310	0.740 and –0.539

Table S2. Crystallographic data of compounds **Ph-PBI-(O-Si-O)**, **Octyne-PBI-(O-Si-O)** and **Spiro-PBI-Borate.**

	Ph-PBI-(O-Si-O)	**Octyne-PBI-(O-Si-O)**	**Spiro-PBI-Borate**
CCDC number	2284413	2284411	2284412
Formula	$C_{52}H_{58}N_2O_6Si$	$C_{50}H_{58}N_2O_6Si$	$C_{177}H_{203}B_2N_{10}O_{24}$
Formula weight / g mol^{-1}	835.09	811.07	2876.12
Crystal size	0.196 × 0.170 × 0.112 mm	0.375 × 0.055 × 0.010	0.200 × 0.050 × 0.050 mm
Temperature / K	100	100	100
Wavelength / Å	1.54178	1.54178	0.61991
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a / Å	11.9749(11)	8.5675(11)	22.679(6)
b / Å	13.6186(14)	19.478(2)	17.614(7)
c / Å	15.4930(17)	25.774(4)	38.697(6)
α / °	70.251(5)	90	90
β / °	84.855(6)	94.281(8)	97.286(3)
γ / °	66.898(7)	90	90
V / Å^3	2184.6(4)	4289.1(10)	15333(8)
Z value	2	4	4
ρ_{cal} / g cm^{-3}	1.270	1.256	1.246
F(000)	892	1736	6148
Number of reflections measured	51470	71179	276732
Number of unique reflections	8608	8453	44240
Measured range of θ / °	3.034 to 72.302	2.846 to 72.214	0.863 to 28.034
Completeness	1.000	1.000	0.99
R_{int}	0.0256	0.0588	0.0311
T_{min}, T_{max}	0.838, 0.904	0.942, 0.991	0.996. 0.997
Goodness of fit for F^2	1.046	1.017	1.035
Final R_1 indices [$I > 2\sigma(I)$] (R_{obs}, wR_{all})	0.0442, 0.1245	0.0416, 0.1034	0.0663, 0.1910
R indices [all data] (R_{obs}, wR_{all})	0.0477, 0.1286	0.0529, 0.1103	0.0839, 0.2096
Largest diff peak and hole / e Å^{-3}	0.733 and −0.273	0.330 and −0.269	0.762 and −0.607

Table S3. Crystallographic data of compounds **Br-PBI-(O-C-O)**, **PhO-PBI-(O-C-O)** and **Br-PBI-(O-Si-O).**

	Br-PBI-(O-C-O)	**PhO-PBI-(O-C-O)**	**Br-PBI-(O-Si-O)**
CCDC number	2284408	2284415	2284410
Formula	$C_{47}H_{37}BrN_2O_6$	$C_{115}H_{104}N_4O_{15}$	$C_{42}H_{45}BrN_2O_6Si$
Formula weight / g mol^{-1}	805.69	1782.02	781.82
Crystal size	0.100 × 0.010 × 0.010 mm	0.050 × 0.050 × 0.010	0.100 × 0.100 × 0.020 mm
Temperature / K	100	100	100
Wavelength / Å	0.61992	0.61991	0.61991
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2/c$	$P2_1/c$
a / Å	10.362(2)	16.611(12)	24.199(8)
b / Å	13.619(2)	11.948(10)	8.476(5)
c / Å	14.5990(18)	24.039(14)	19.773(6)
α / °	99.833(3)	90	90
β / °	107.846(5)	99.361(5)	112.407(8)
γ / °	107.722(9)	90	90
V / Å^3	1787.0(5)	4707(6)	3749(3)
Z value	2	2	4
ρ_{cal} / g cm^{-3}	1.497	1.257	1.385
F(000)	832	1884	1632.1
Number of reflections measured	9464	85730	67790
Number of unique reflections	9464	13166	10691
Measured range of θ / °	1.336 to 27.916	1.084 to 28.015	0.794 to 27.848
Completeness	0.960	0.989	0.990
R_{int}	0.0744	0.0722	0.0535
T_{min}, T_{max}	0.990, 0.992	0.997, 0.999	0.921. 0.984
Goodness of fit for F^2	1.086	0.987	1.054
Final R_1 indices $[I > 2\sigma(I)]$ (R_{obs}, wR_{all})	0.0768, 0.2605	0.0854, 0.2754	0.0767, 0.2481
R indices [all data] (R_{obs}, wR_{all})	0.0803, 0.2651	0.1916, 0.3687	0.1048, 0.2749
Largest diff peak and hole / e Å^{-3}	1.387 and –0.824	0.172 and –0.255	0.325 and –0.810

4. Optical Properties

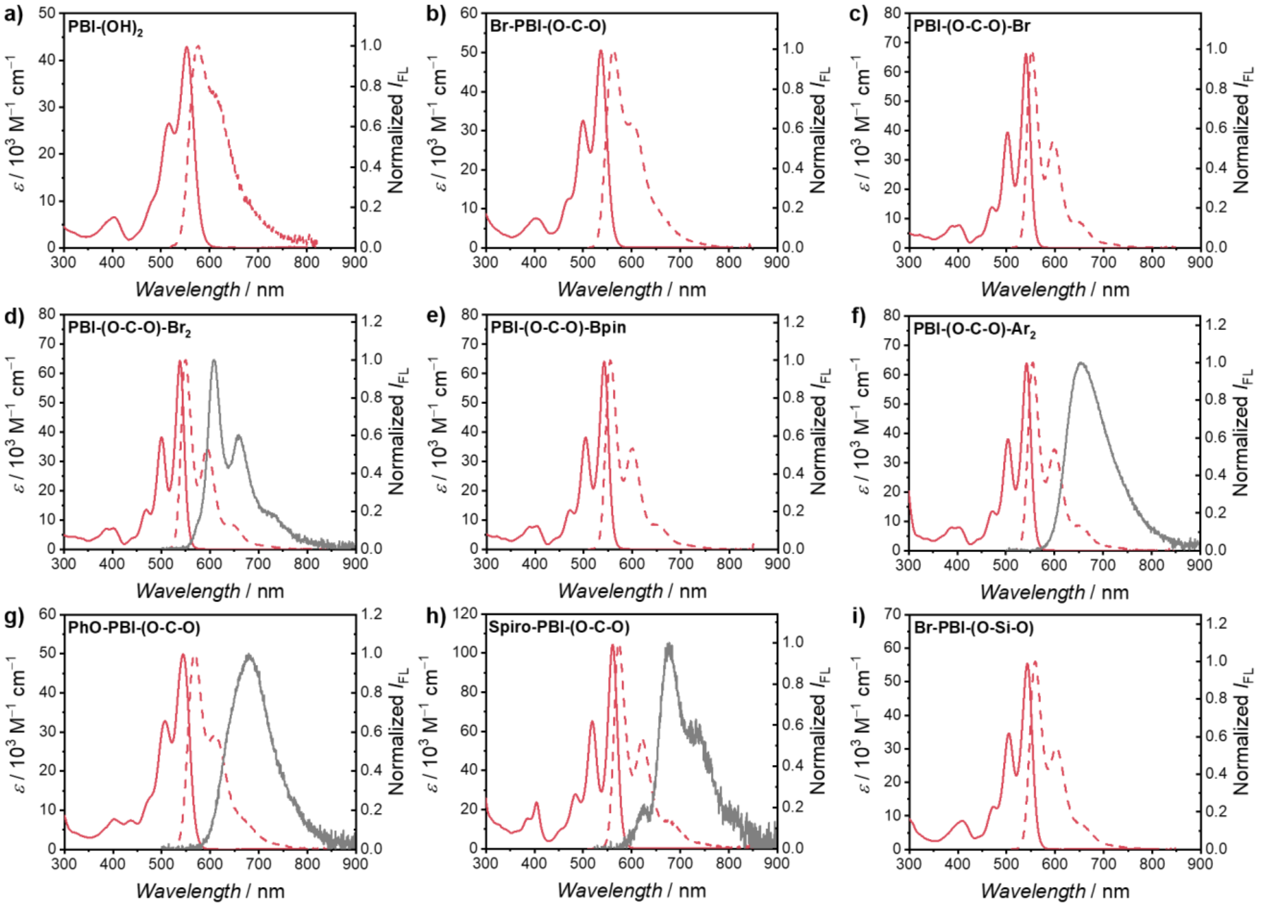


Figure S3. UV-vis absorption spectra (red, solid line, c = 20 μM) and normalized fluorescence spectra (red, dashed line) of oxygen–carbon–oxygen- and oxygen–silicon–oxygen-bridged PBI derivatives in chloroform at 295 K. Normalized powder emission spectra (grey, solid line) of selected compounds are displayed as well.

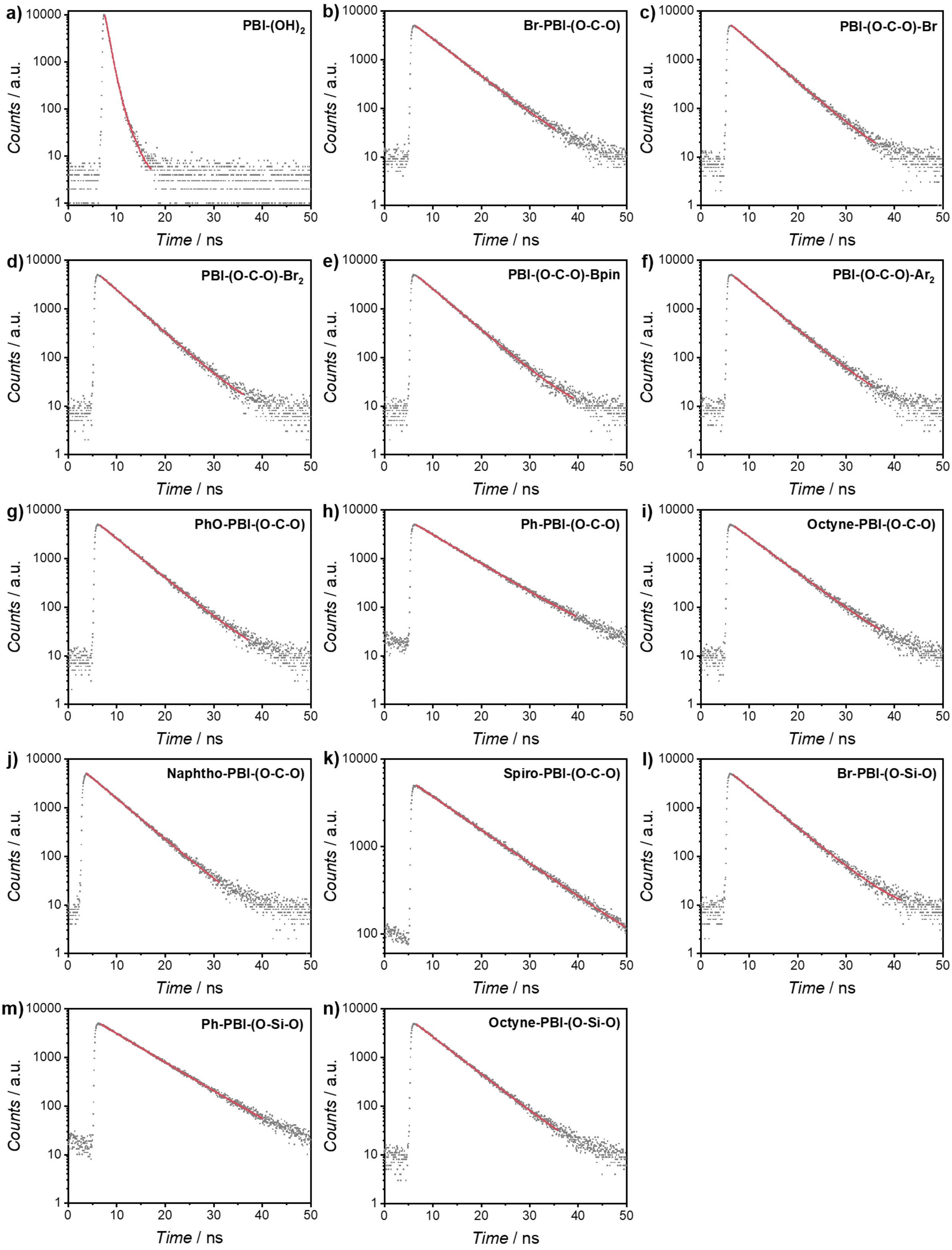


Figure S4. Fluorescence decay (grey symbols) and their respective mono-/bi-exponential fit (red line) of oxygen–carbon–oxygen- and oxygen–silicon–oxygen-bridged PBI derivatives in chloroform at 295 K.

5. Electrochemical Properties

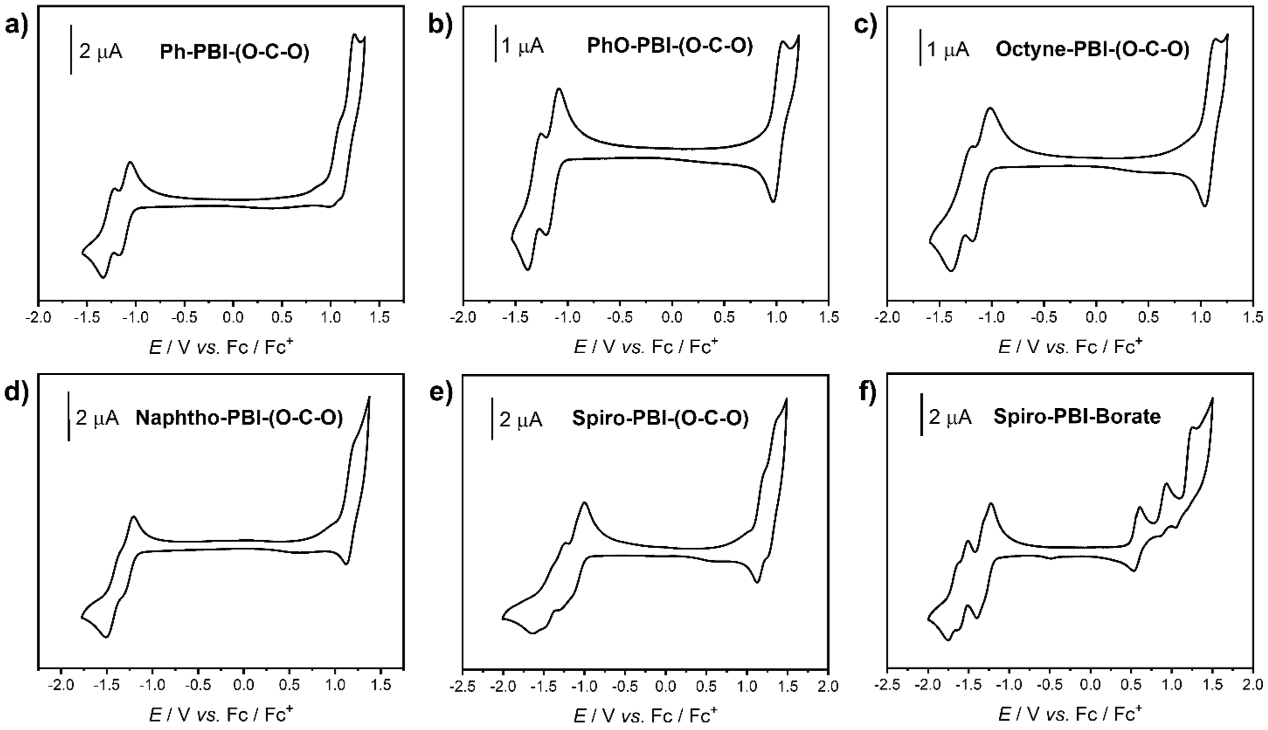


Figure S5. Cyclic voltammograms of a) **Ph-PBI-(O-C-O)**, b) **PhO-PBI-(O-C-O)**, c) **Octyne-PBI-(O-C-O)**, d) **Naphtho-PBI-(O-C-O)**, e) **Spiro-PBI-(O-C-O)** and f) **Spiro-PBI-Borate** in CH_2Cl_2 solution ($c = 3 \times 10^{-4}$ M). The measurements were performed under argon atmosphere at room temperature using TBAHFP as electrolyte (scan rate: 100 mVs^{-1}) and calibrated with the internal standard Fc/Fc$^+$.

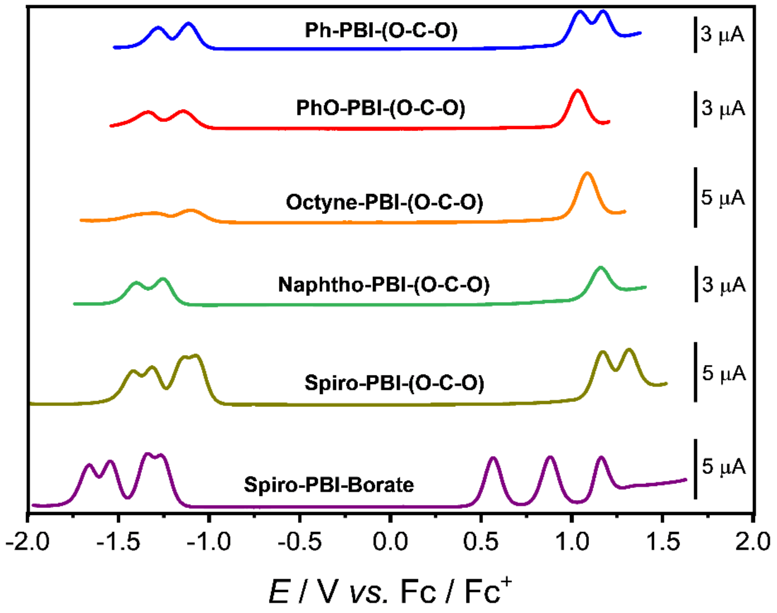


Figure S6. DPV curves of **Ph-PBI-(O-C-O)** (blue), **PhO-PBI-(O-C-O)** (red), **Octyne-PBI-(O-C-O)** (orange), **Naphtho-PBI-(O-C-O)** (green), **Spiro-PBI-(O-C-O)** (dark yellow) and **Spiro-PBI-Borate** (purple) in CH_2Cl_2 solution ($c = 3 \times 10^{-4}$ M). The measurements were performed under argon atmosphere at room temperature using TBAHFP as electrolyte and calibrated with the internal standard Fc/Fc$^+$.

Table S4. Electrochemical Properties of oxygen–carbon–oxygen derivatives and **Spiro-PBI-Borate**.[a]

Compound	E_{1red}	E_{2red}	E_{3red}	E_{4red}	E_{1ox}	E_{2ox}	E_{3ox}	E_{LUMO} [eV][b]	E_{HOMO} [eV][c]	$E_{g\,(CV)}$ [eV][d]
PBI-(O-C-O)[S10]	–1.16	–1.28	-	-	+1.11	-	-	–3.99	–6.26	2.27
PBI-(O-Si-O)[S11]	–1.23	–1.41	-	-	+1.06	-	-	–3.92	–6.21	2.29
Ph-PBI-(O-C-O)	–1.11	–1.28	-	-	+1.02	+1.13	-	–4.04	–6.17	2.13
PhO-PBI-(O-C-O)	–1.14	–1.34	-	-	+1.03	-	-	–4.01	–6.18	2.17
Octyne-PBI-(O-C-O)	–1.10	–1.29	-	-	+1.09	-	-	–4.05	–6.24	2.19
Naphtho-PBI-(O-C-O)	–1.26	–1.40	-	-	+1.15	-	-	–3.89	–6.30	2.41
Spiro-PBI-(O-C-O)	–1.08	–1.13	–1.30	–1.40	+1.15	+1.28	-	–4.07	–6.30	2.23
Spiro-PBI-Borate	–1.26	–1.33	–1.54	–1.65	+0.57	+0.87	+1.14	–3.89	–5.72	1.83

[a] The redox potentials (V vs Fc/Fc^+) obtained by DPV in DCM (c = 0.3 mM) using TBAHFP as electrolyte. [b] The LUMO levels were estimated from $E_{LUMO} = -(E_{1red} + 5.15\text{eV})$.[S12] [c] Estimated from $E_{HOMO} = -(E_{1ox} + 5.15\text{eV})$. [d] Electrochemical band gap $E_g = E_{LUMO} - E_{HOMO}$.

6. NMR Spectra

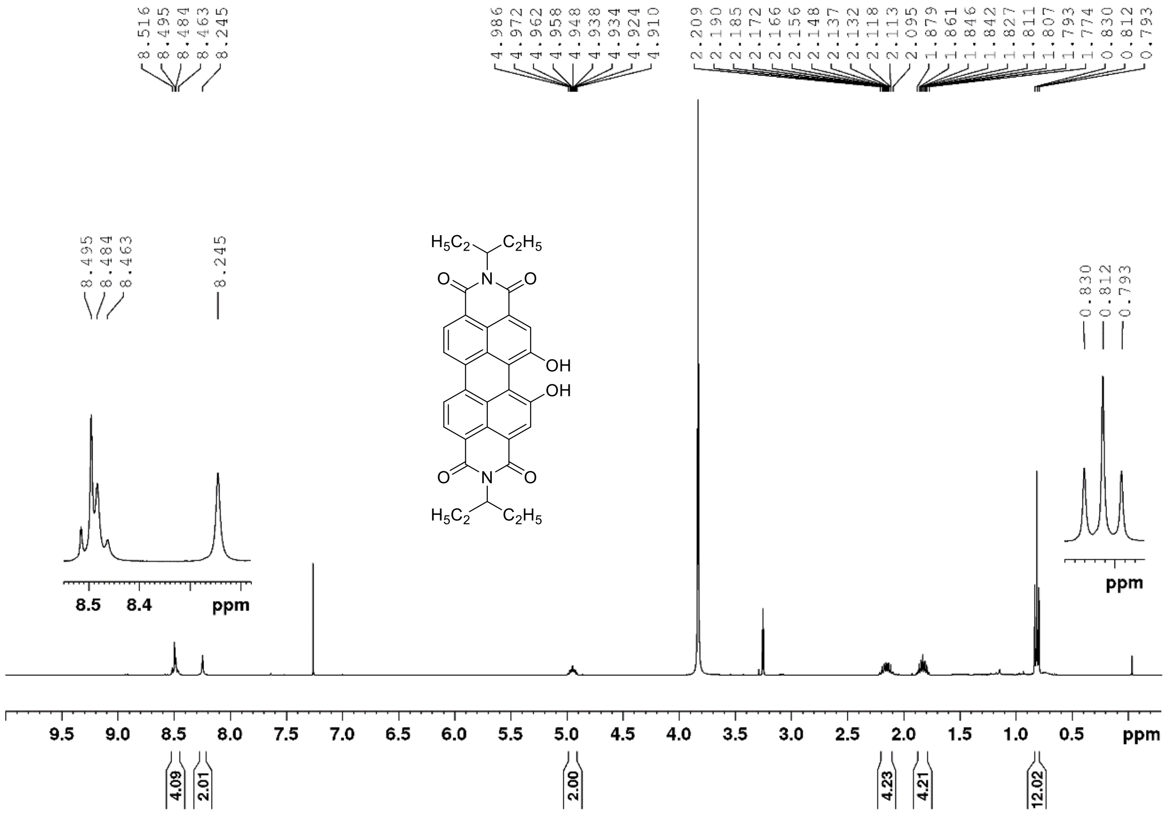


Figure S7. ^{1}H-NMR (400 MHz) of compound **PBI-(OH)$_2$ a** in CDCl$_3$/CD$_3$OD at 295 K.

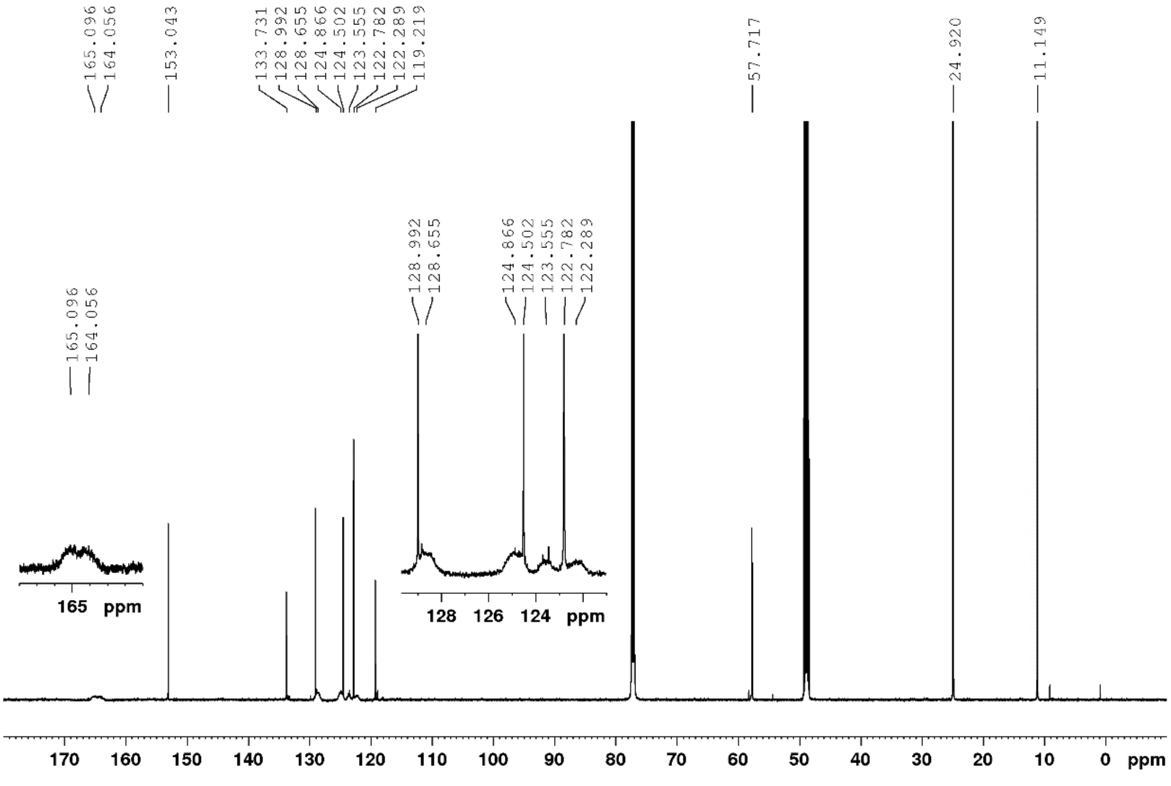


Figure S8. ^{13}C-NMR (151 MHz) of compound **PBI-(OH)$_2$ a** in CDCl$_3$/CD$_3$OD at 295 K.

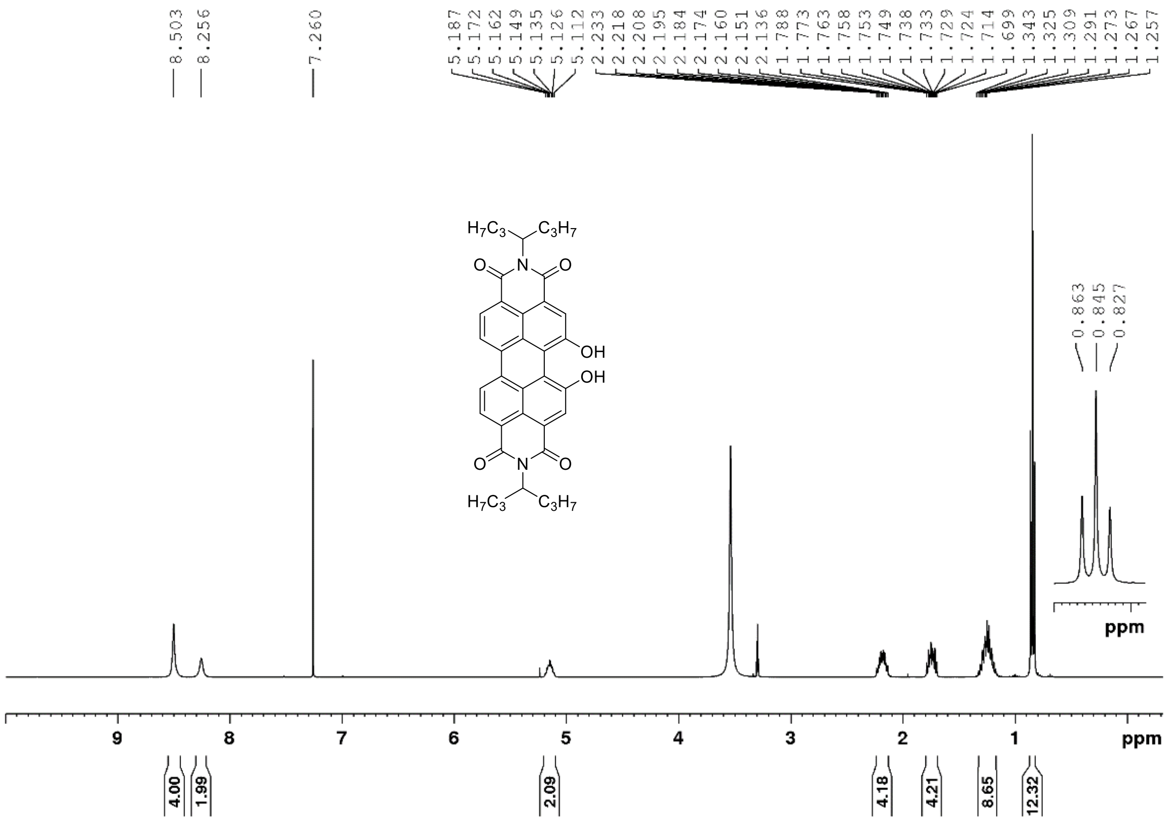


Figure S9. ^{1}H-NMR (400 MHz) of compound **PBI-(OH)$_2$ b** in $CDCl_3/CD_3OD$ at 295 K.

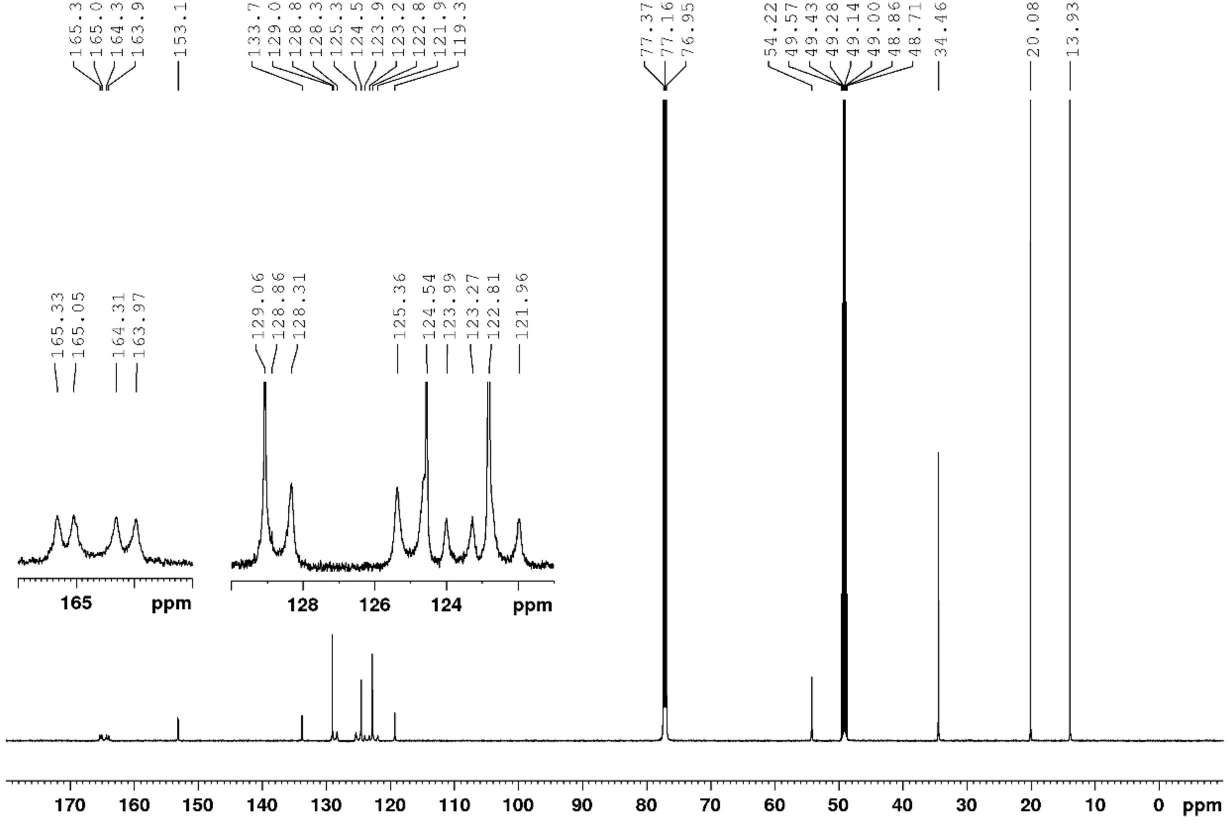


Figure S10. ^{13}C-NMR (151 MHz) of compound **PBI-(OH)$_2$ b** in $CDCl_3/CD_3OD$ at 295 K.

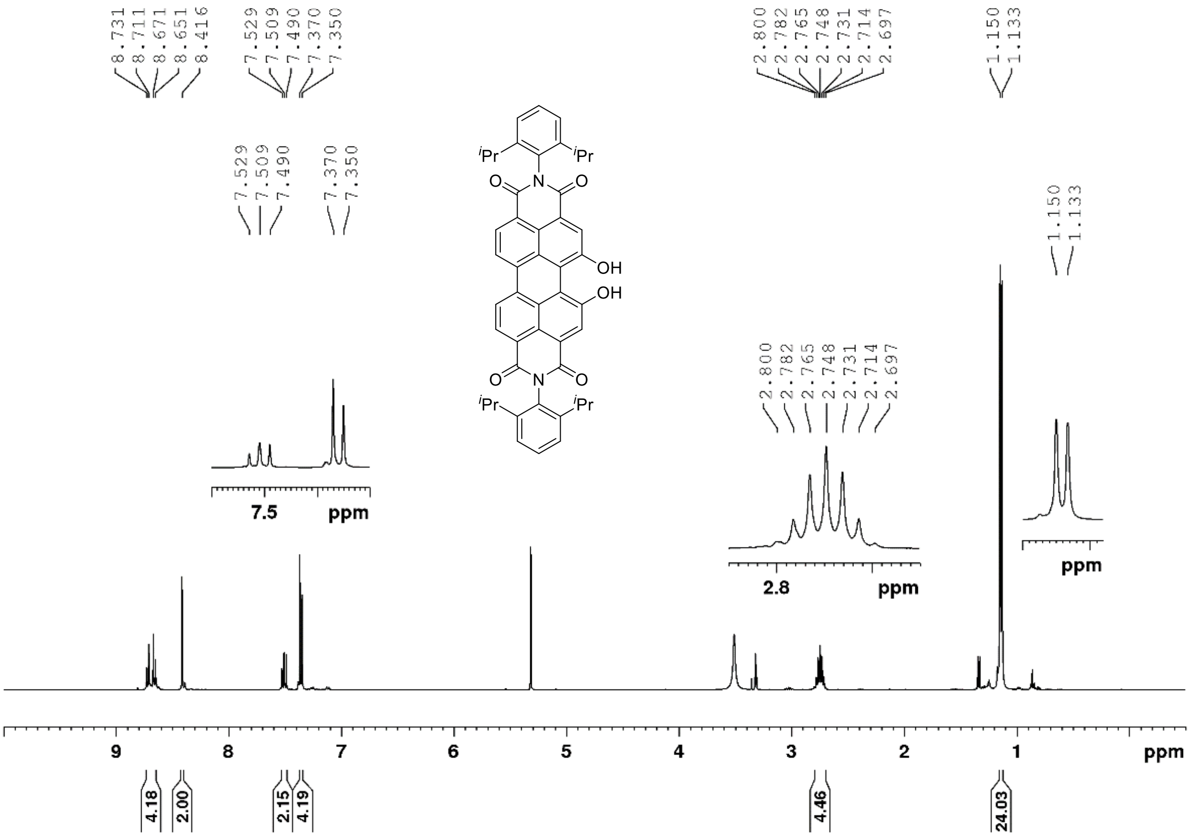


Figure S11. ^{1}H-NMR (400 MHz) of compound **PBI-(OH)$_2$ d** in CD_2Cl_2/CD_3OD at 295 K.

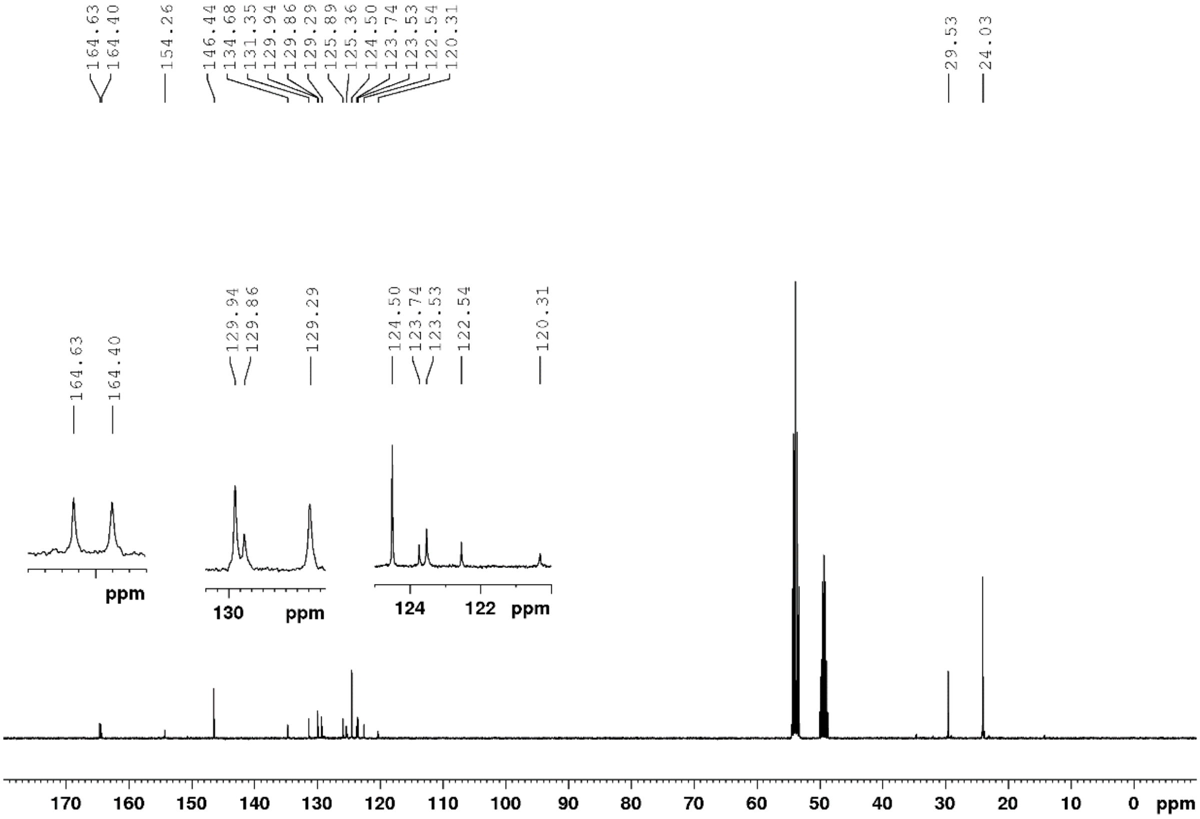


Figure S12. ^{13}C-NMR (101 MHz) of compound **PBI-(OH)$_2$ d** in CD_2Cl_2/CD_3OD at 295 K.

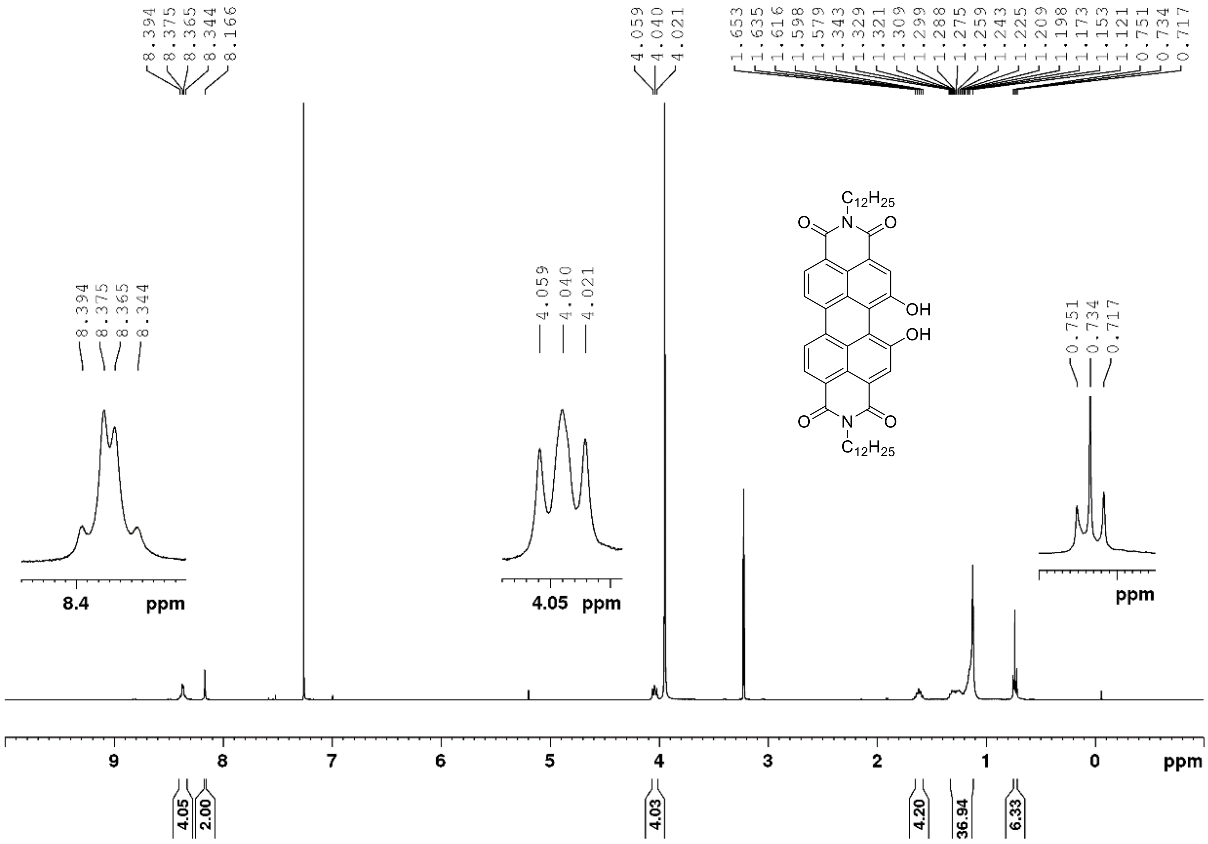


Figure S13. ^{1}H-NMR (400 MHz) of compound **PBI-(OH)$_2$ e** CDCl$_3$/CD$_3$OD at 295 K.

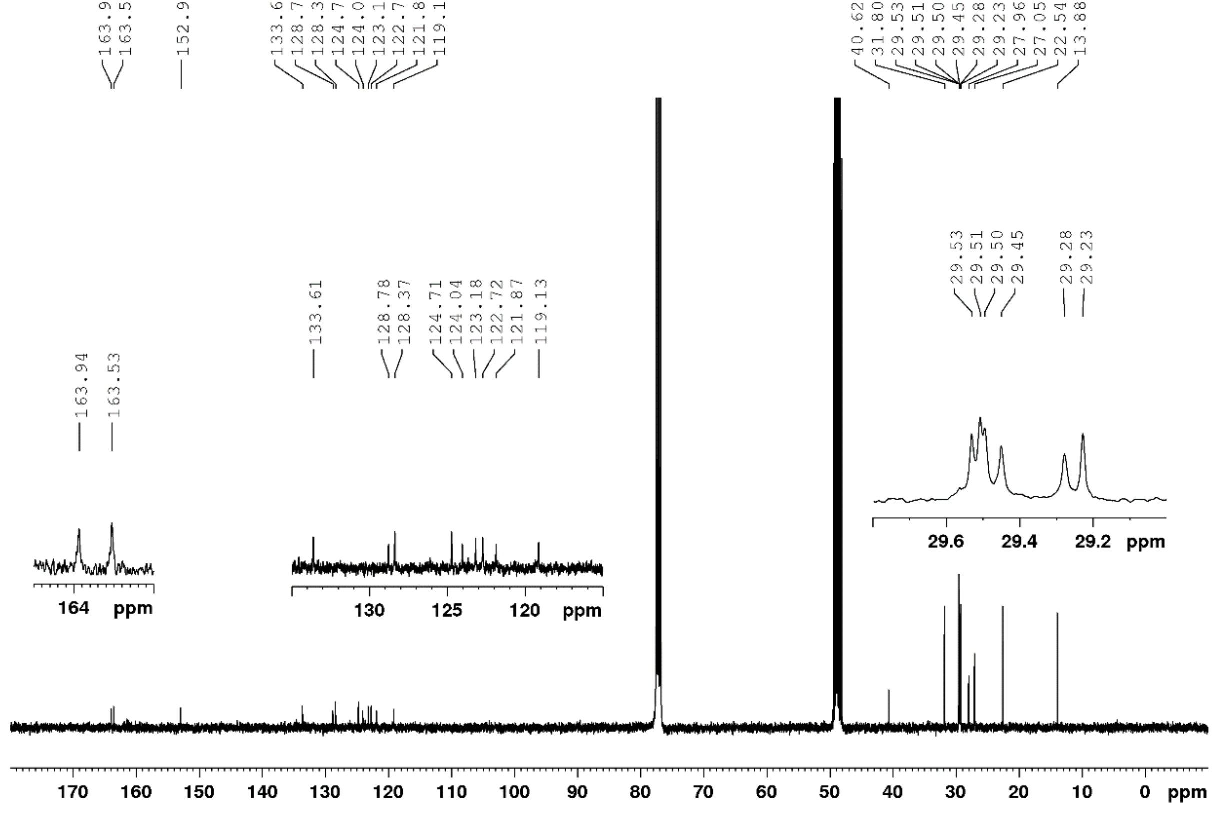


Figure S14. ^{13}C-NMR (101 MHz) of compound **PBI-(OH)$_2$ e** in CDCl$_3$/CD$_3$OD at 295 K.

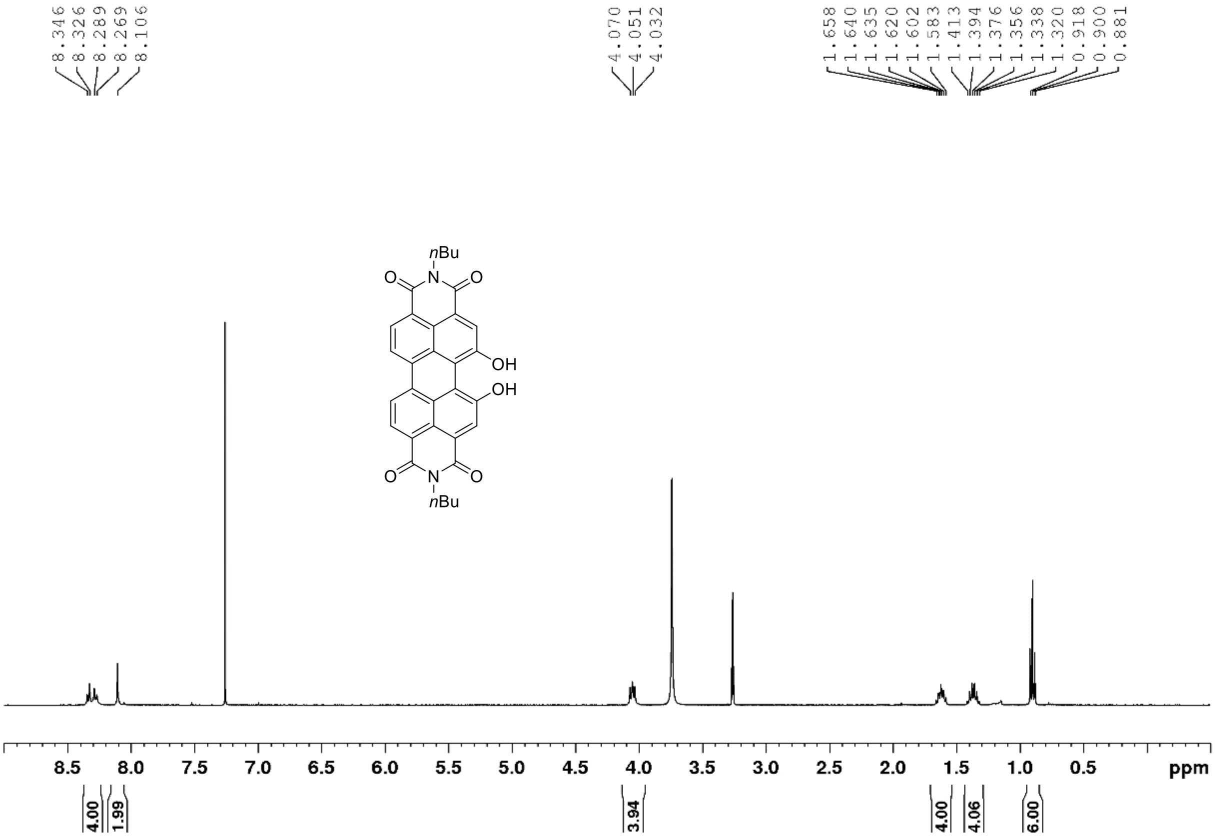


Figure S15. ^{1}H-NMR (400 MHz) of compound **PBI-(OH)$_2$ f** in $CDCl_3/CD_3OD$ at 295 K.

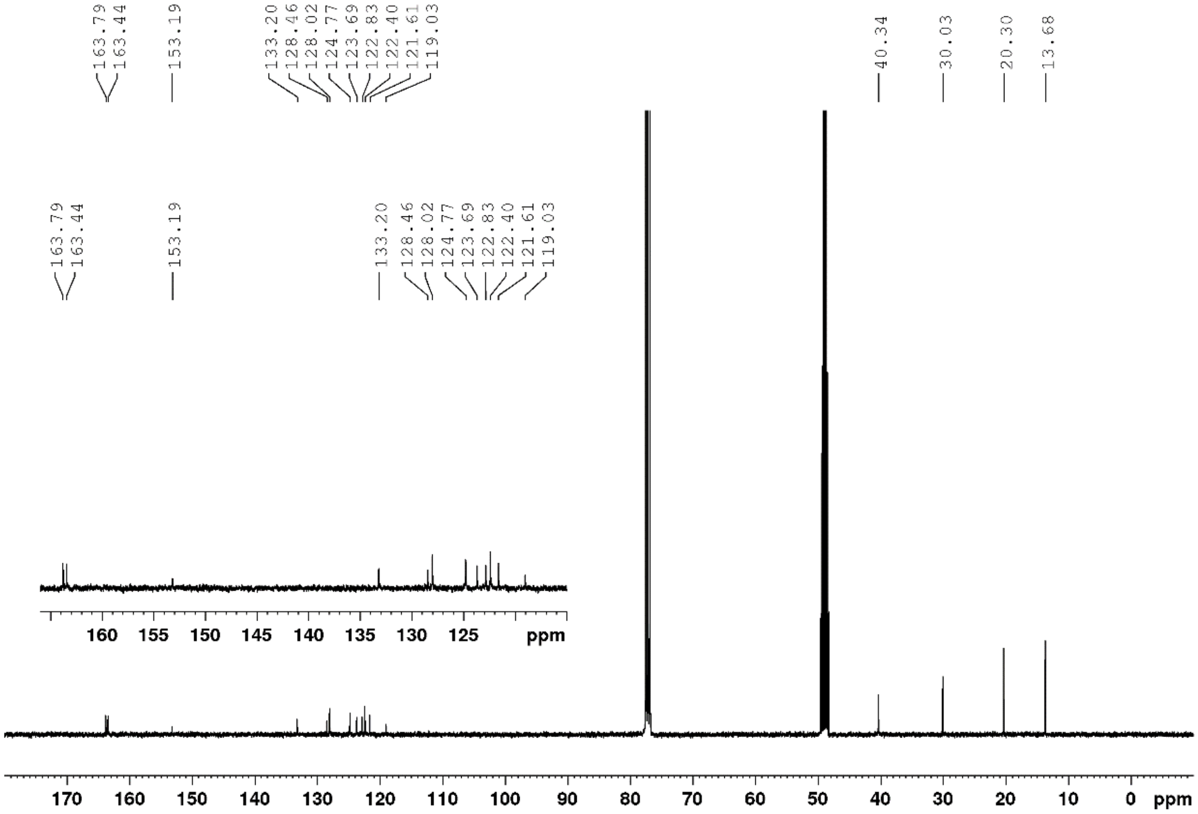


Figure S16. ^{13}C-NMR (101 MHz) of compound **PBI-(OH)$_2$ f** in $CDCl_3/CD_3OD$ at 295 K.

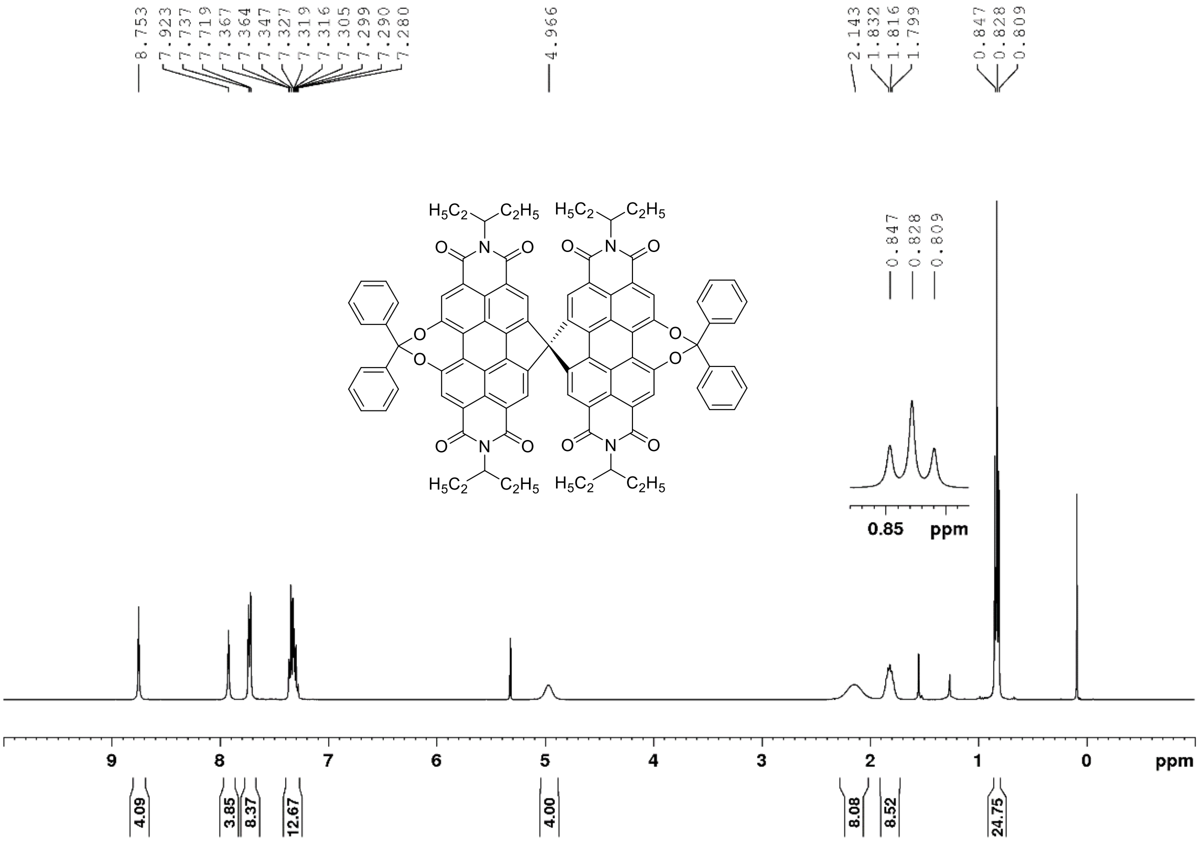


Figure 17. ^{1}H-NMR (400 MHz) of compound **Spiro-PBI-(O-C-O)** in CD_2Cl_2 at 295 K.

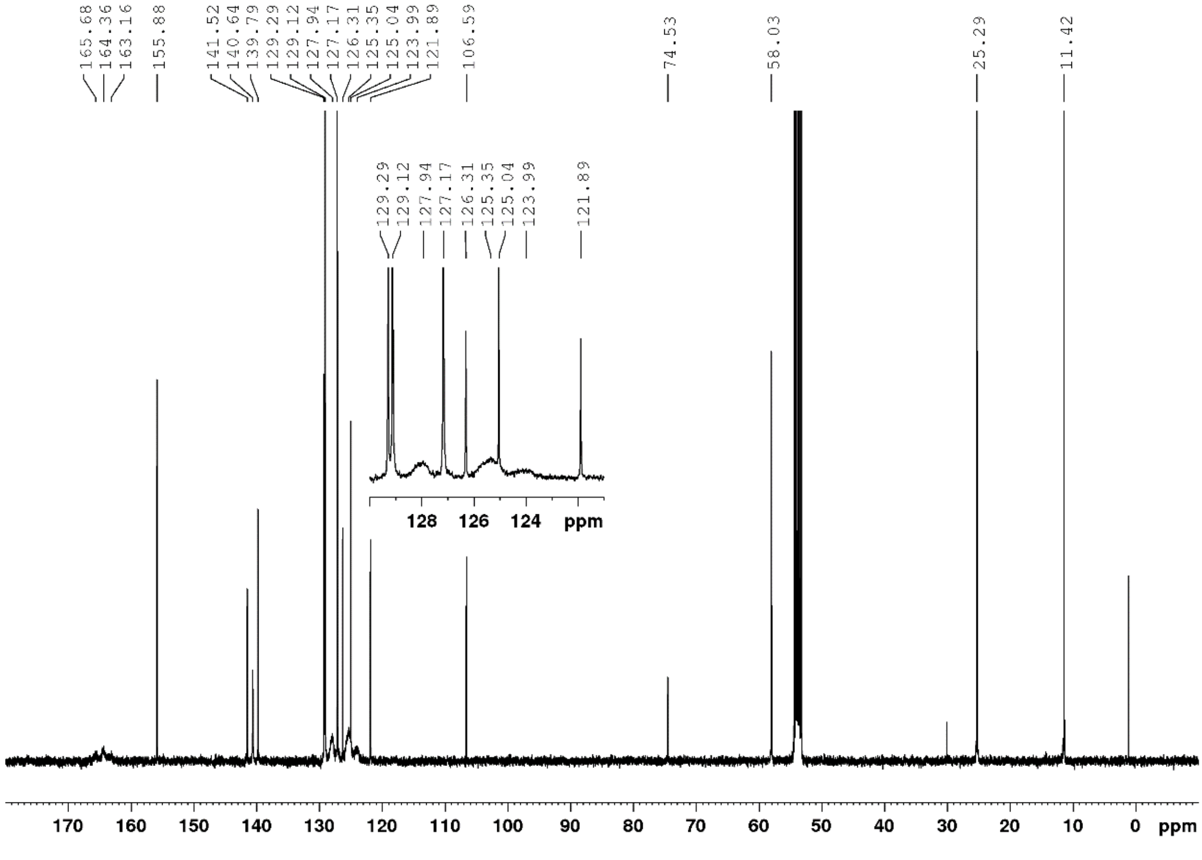


Figure S18. ^{13}C-NMR (101 MHz) of compound **Spiro-PBI-(O-C-O)** in CD_2Cl_2 at 295 K.

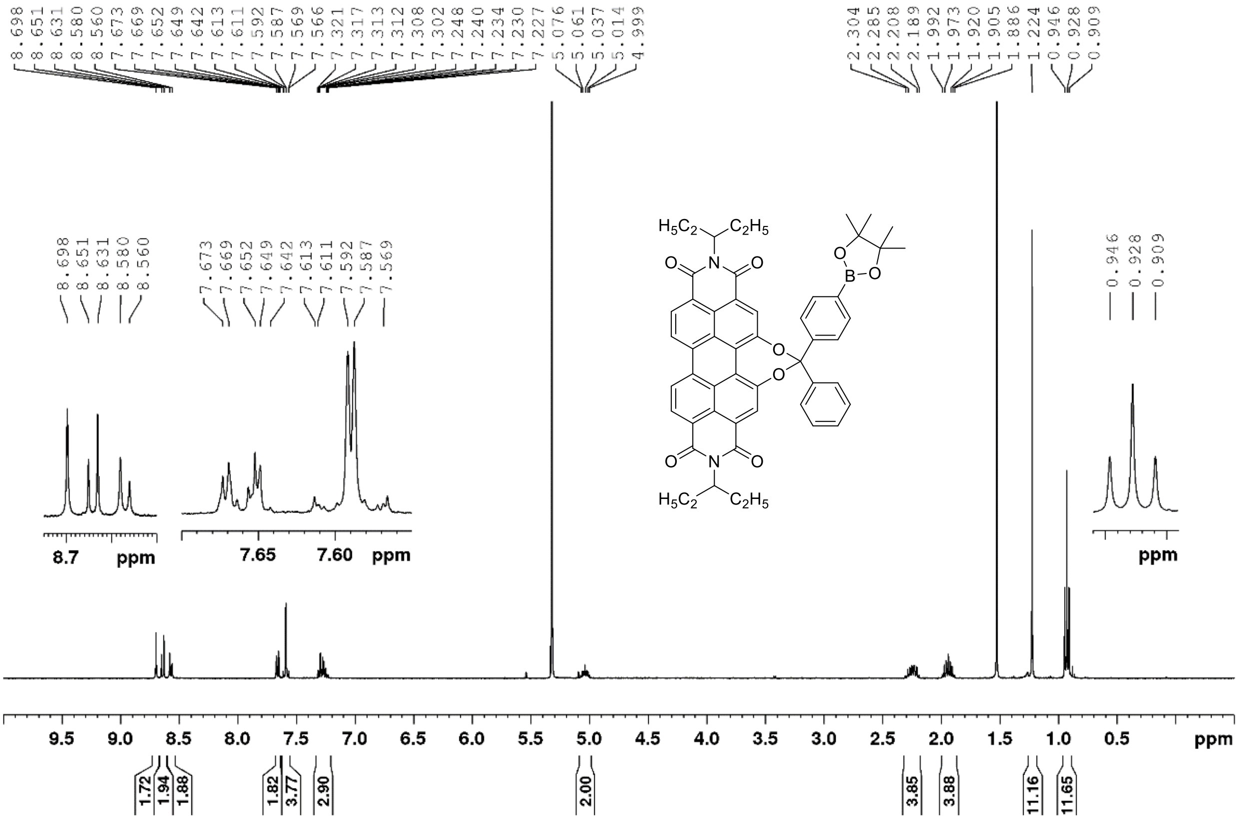


Figure S19. ^{1}H-NMR (400 MHz) of compound **PBI-(O-C-O)-Bpin** in CD_2Cl_2 at 295 K.

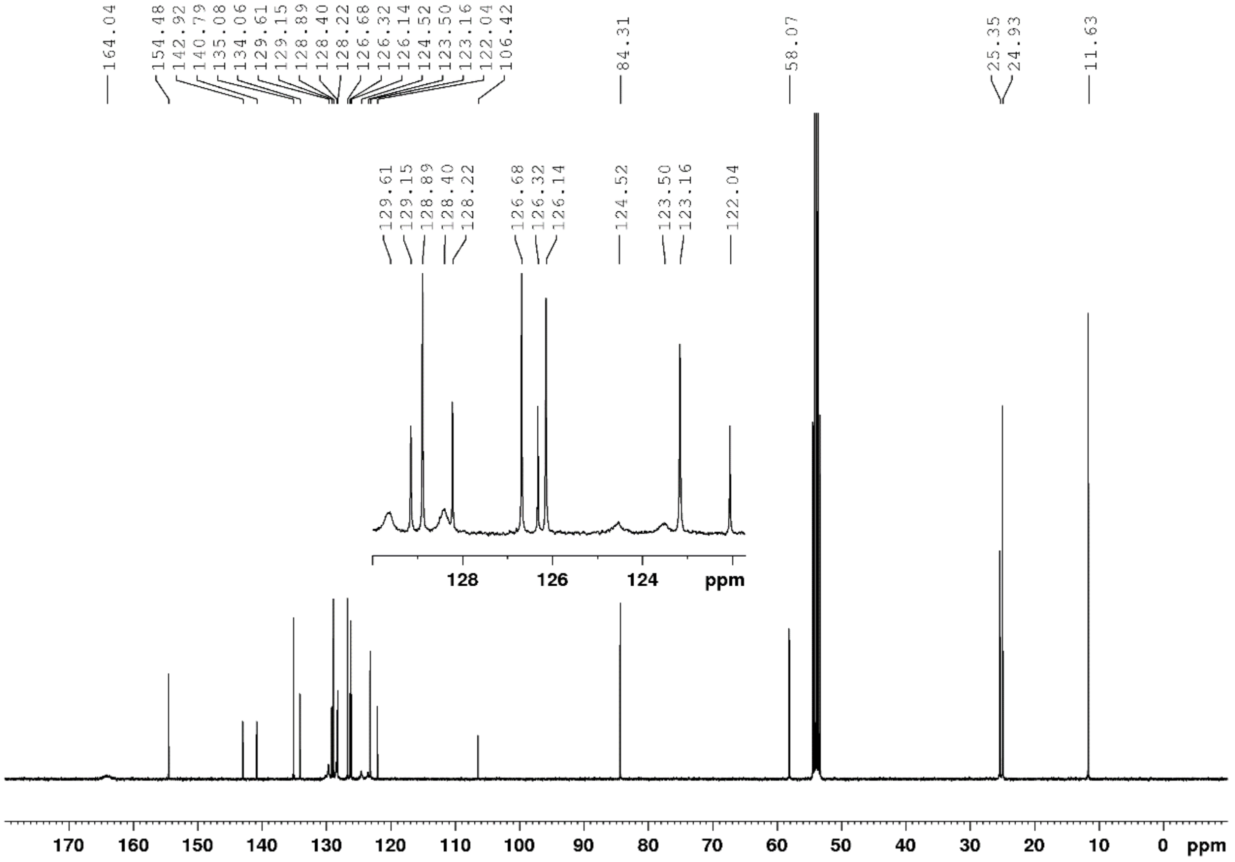


Figure S20. ^{13}C-NMR (101 MHz) of compound **PBI-(O-C-O)-Bpin** in CD_2Cl_2 at 295 K.

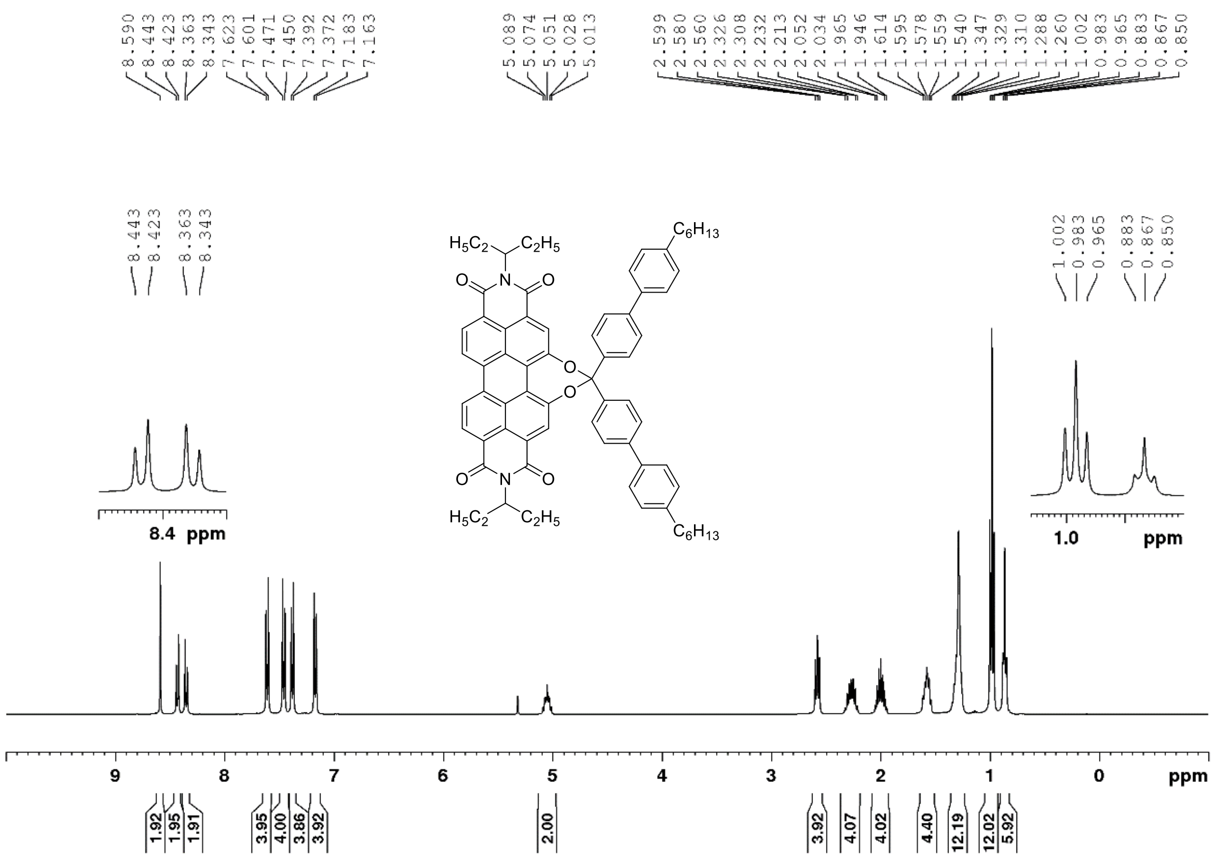


Figure S21. ^{1}H-NMR (400 MHz) of compound **PBI-(O-C-O)-Ar$_2$** in CD_2Cl_2 at 295 K.

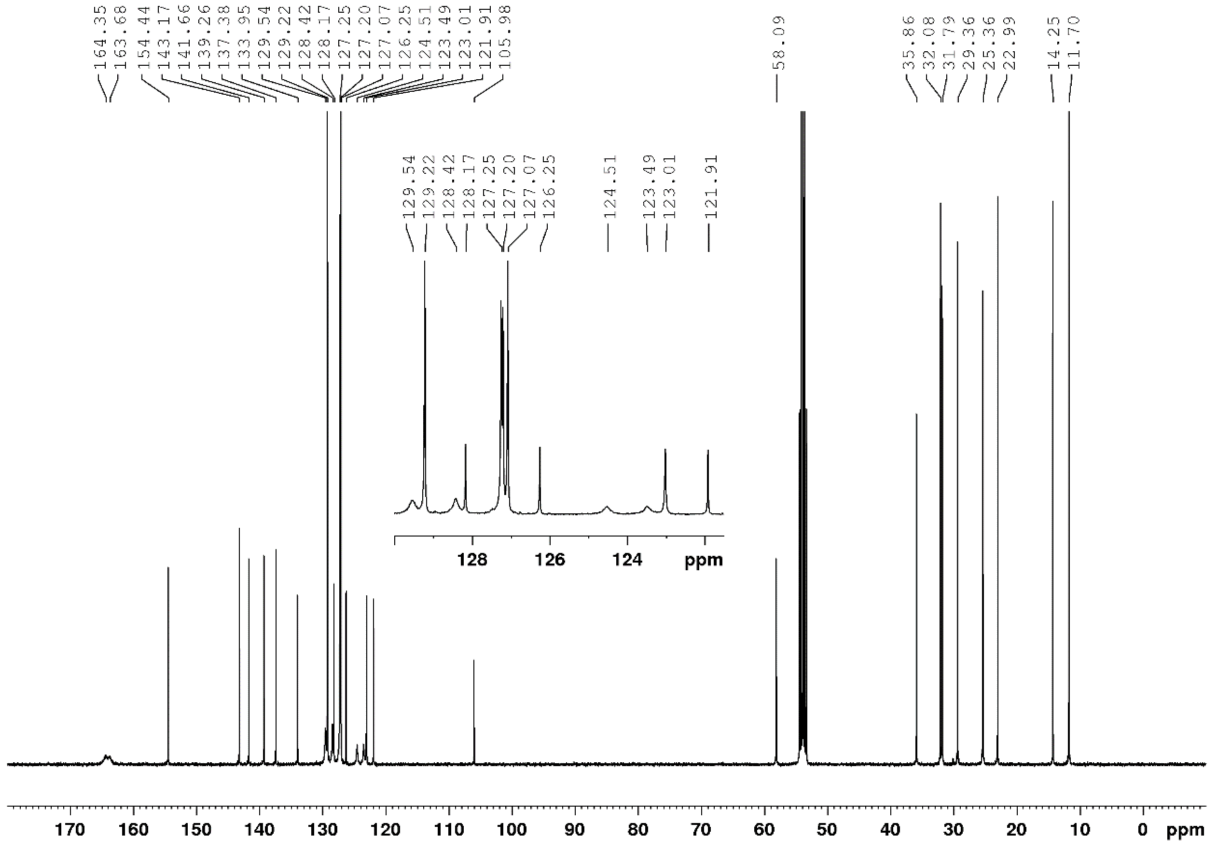


Figure S22. ^{13}C-NMR (101 MHz) of compound **PBI-(O-C-O)-Ar$_2$** in CD_2Cl_2 at 295 K.

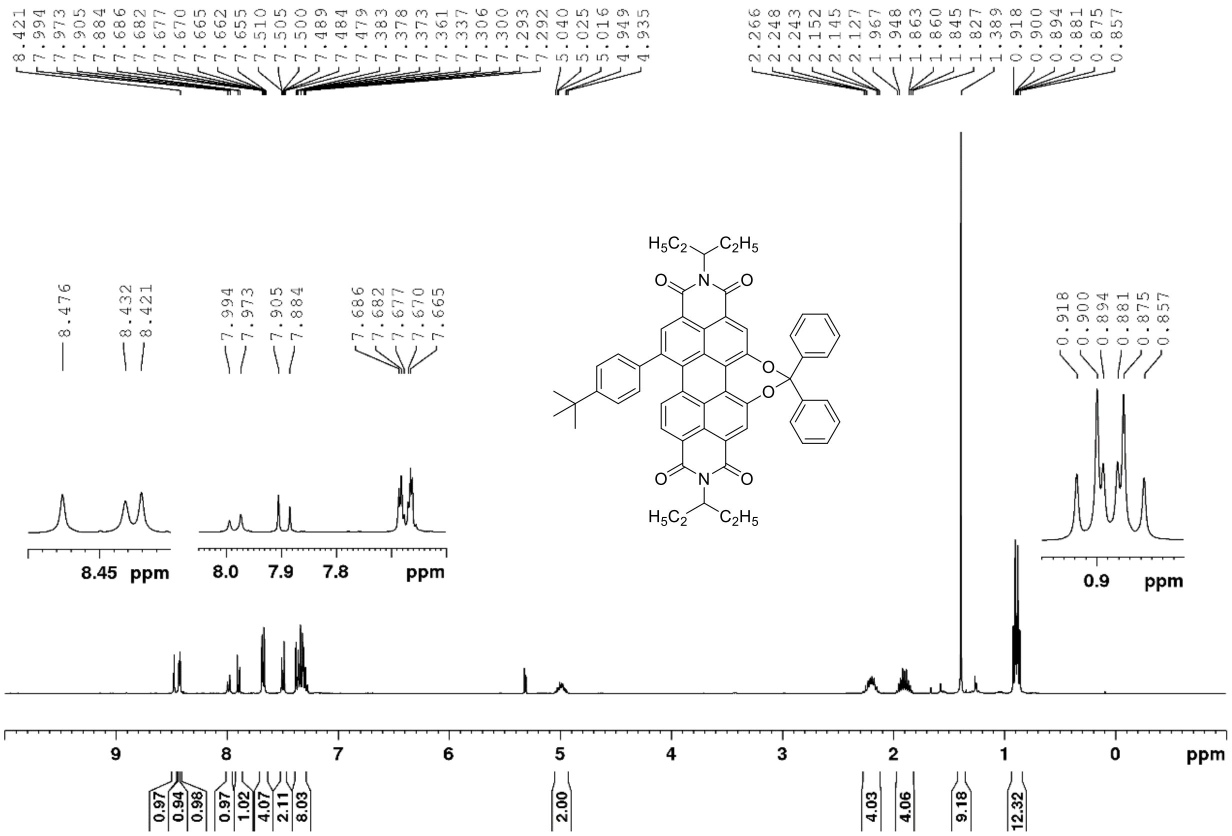


Figure S23. ^{1}H-NMR (400 MHz) of compound **Ph-PBI-(O-C-O)** in CD_2Cl_2 at 295 K.

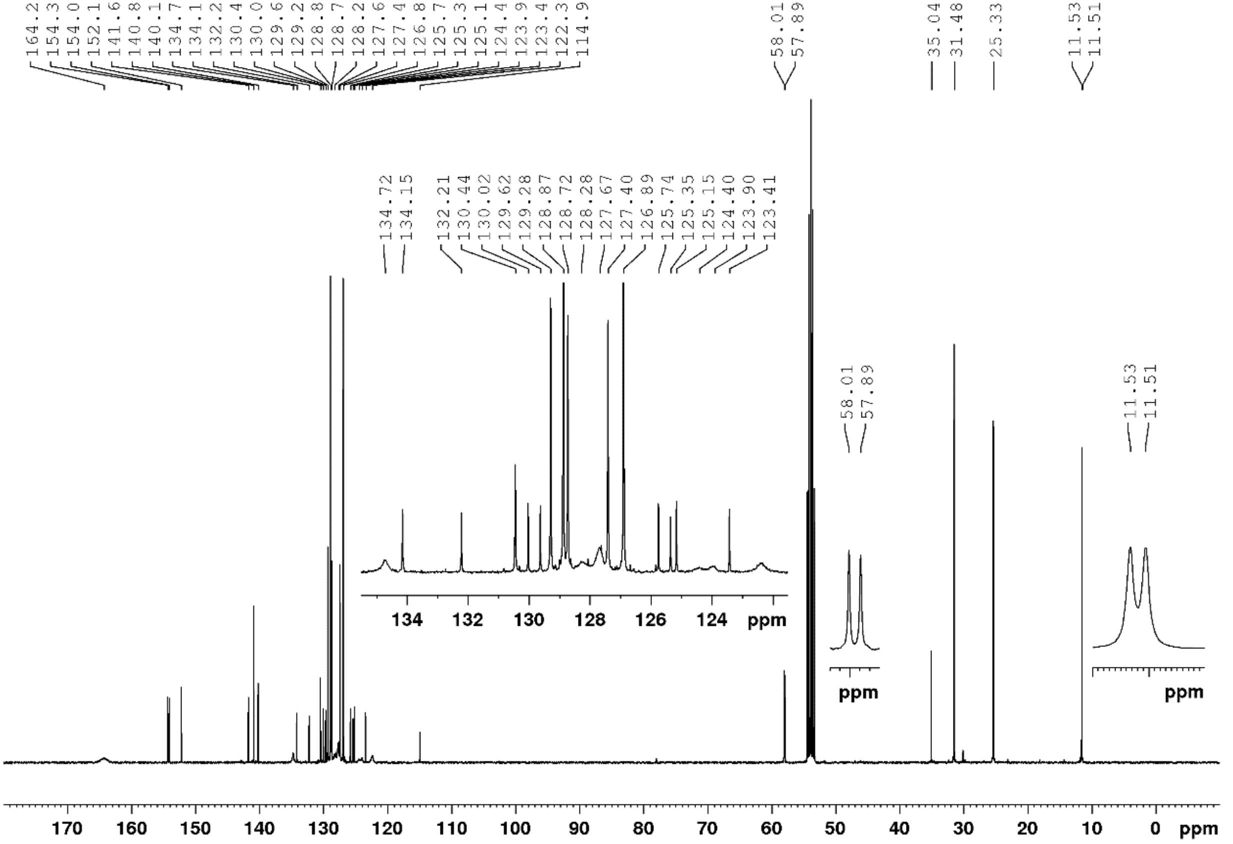


Figure S24. ^{13}C-NMR (101 MHz) of compound **Ph-PBI-(O-C-O)** in CD_2Cl_2 at 295 K.

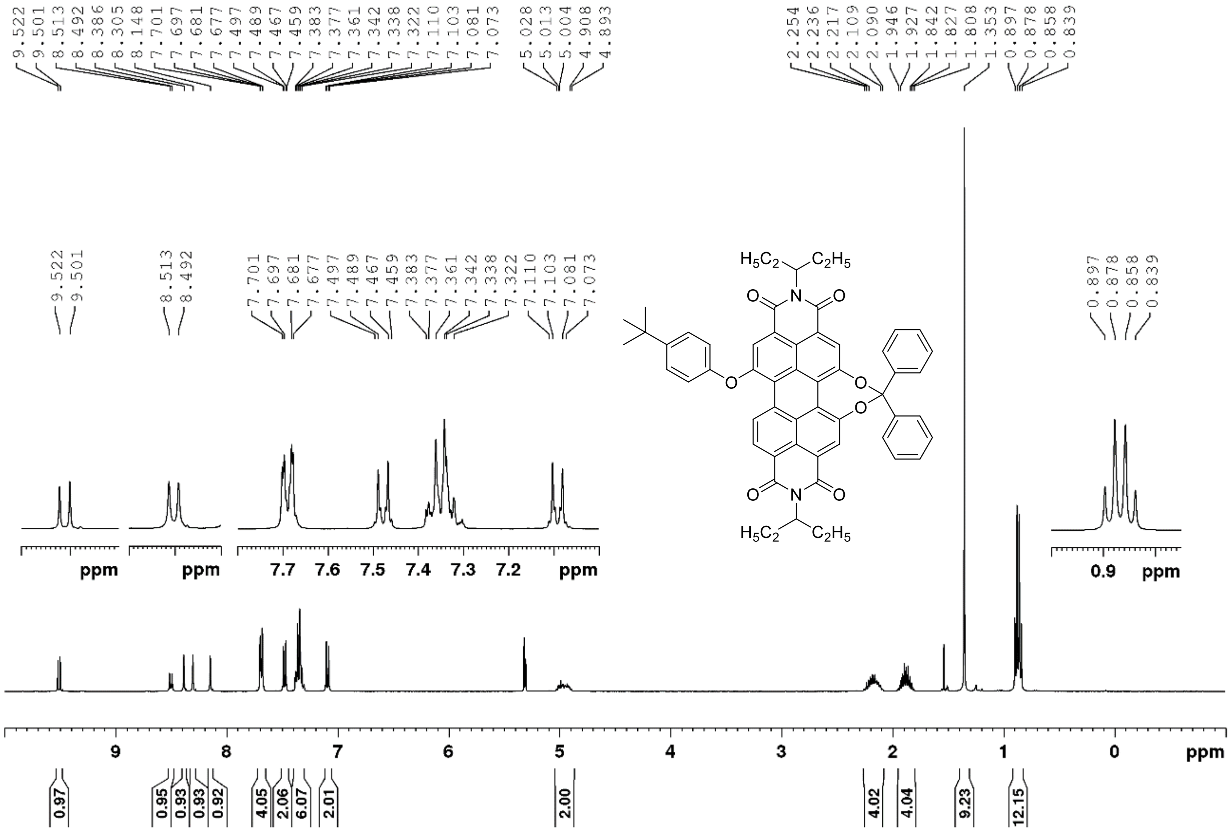


Figure S25. ^{1}H-NMR (400 MHz) of compound **PhO-PBI-(O-C-O)** in CD_2Cl_2 at 295 K.

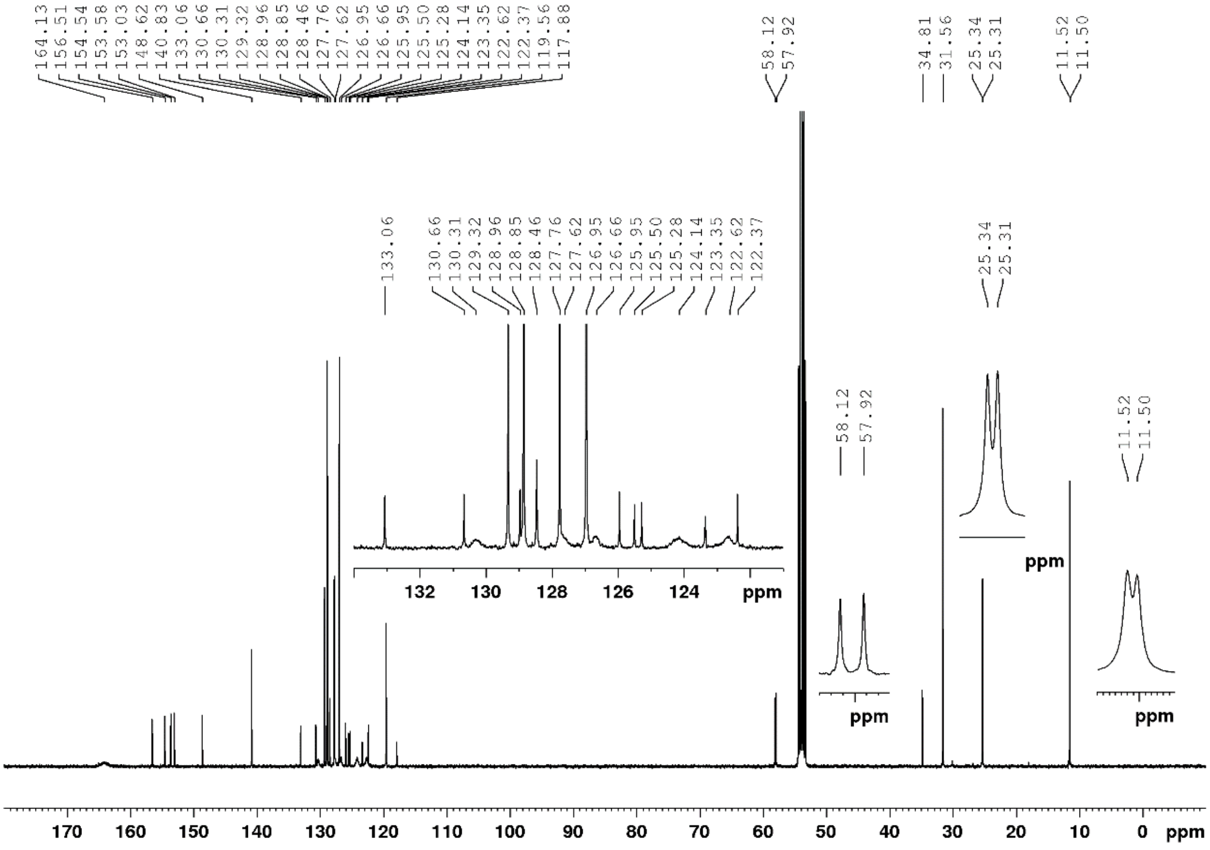


Figure S26. ^{13}C-NMR (101 MHz) of compound **PhO-PBI-(O-C-O)** in CD_2Cl_2 at 295 K.

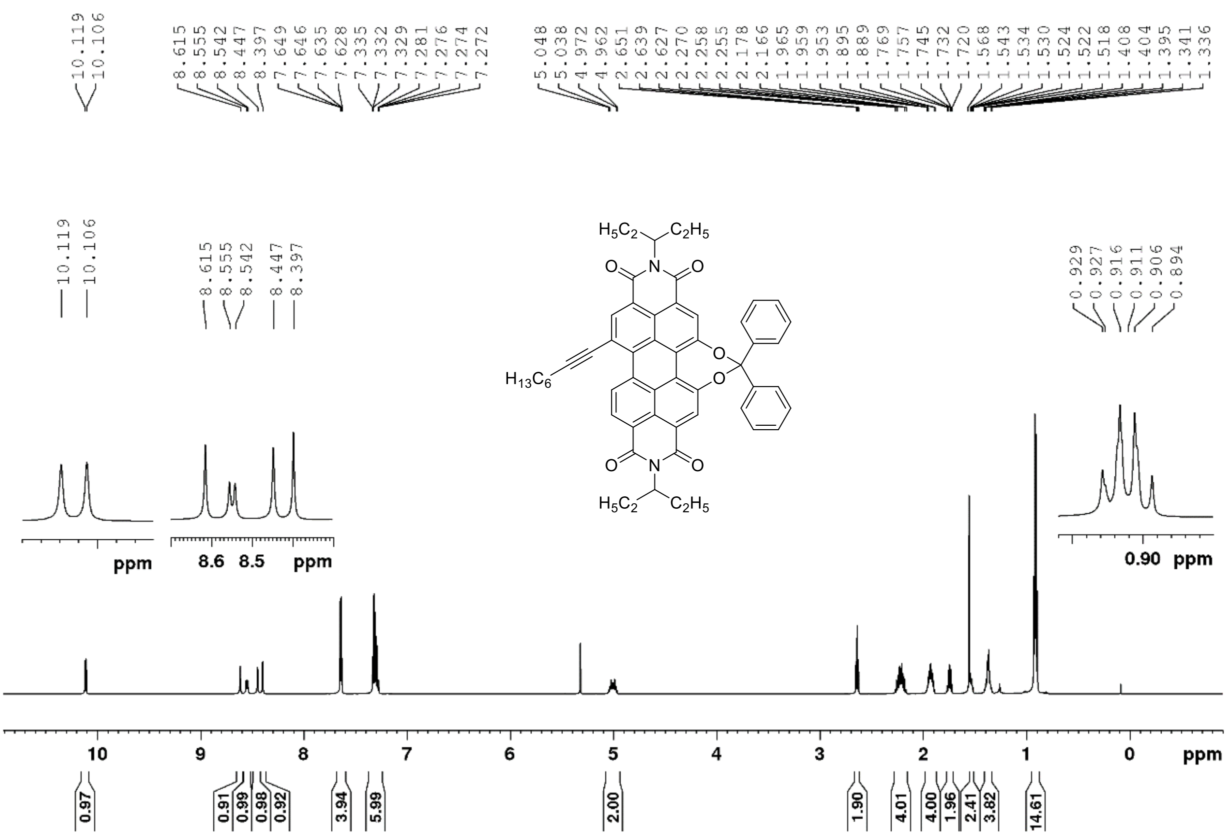


Figure S27. ^{1}H-NMR (400 MHz) of compound **Octyne-PBI-(O-C-O)** in CD_2Cl_2 at 295 K.

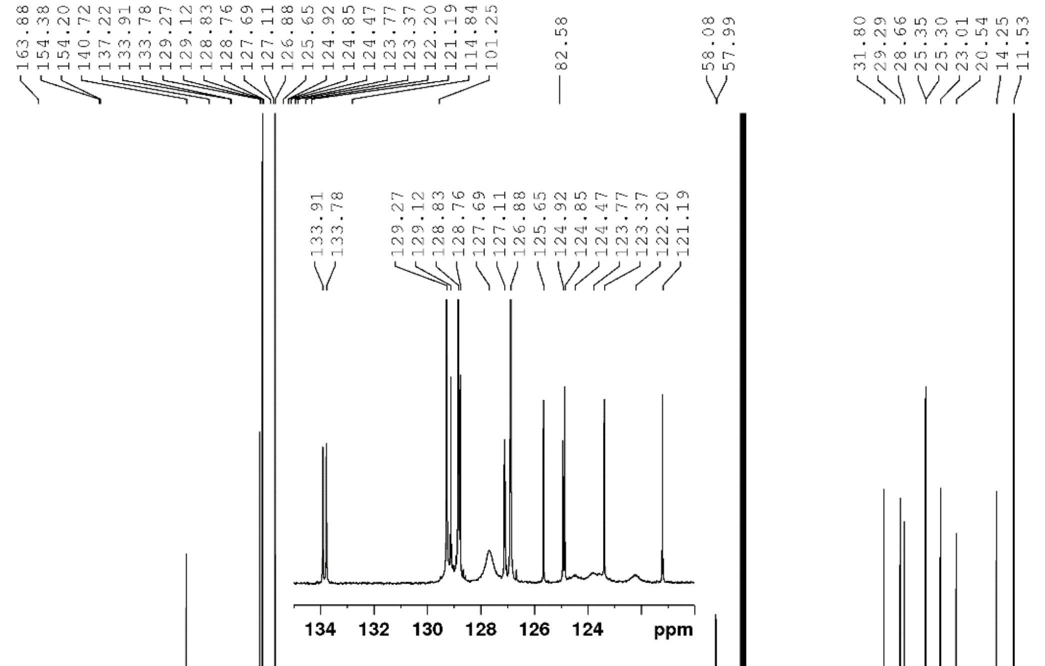


Figure S28. ^{13}C-NMR (101 MHz) of compound **Octyne-PBI-(O-C-O)** in CD_2Cl_2 at 295 K.

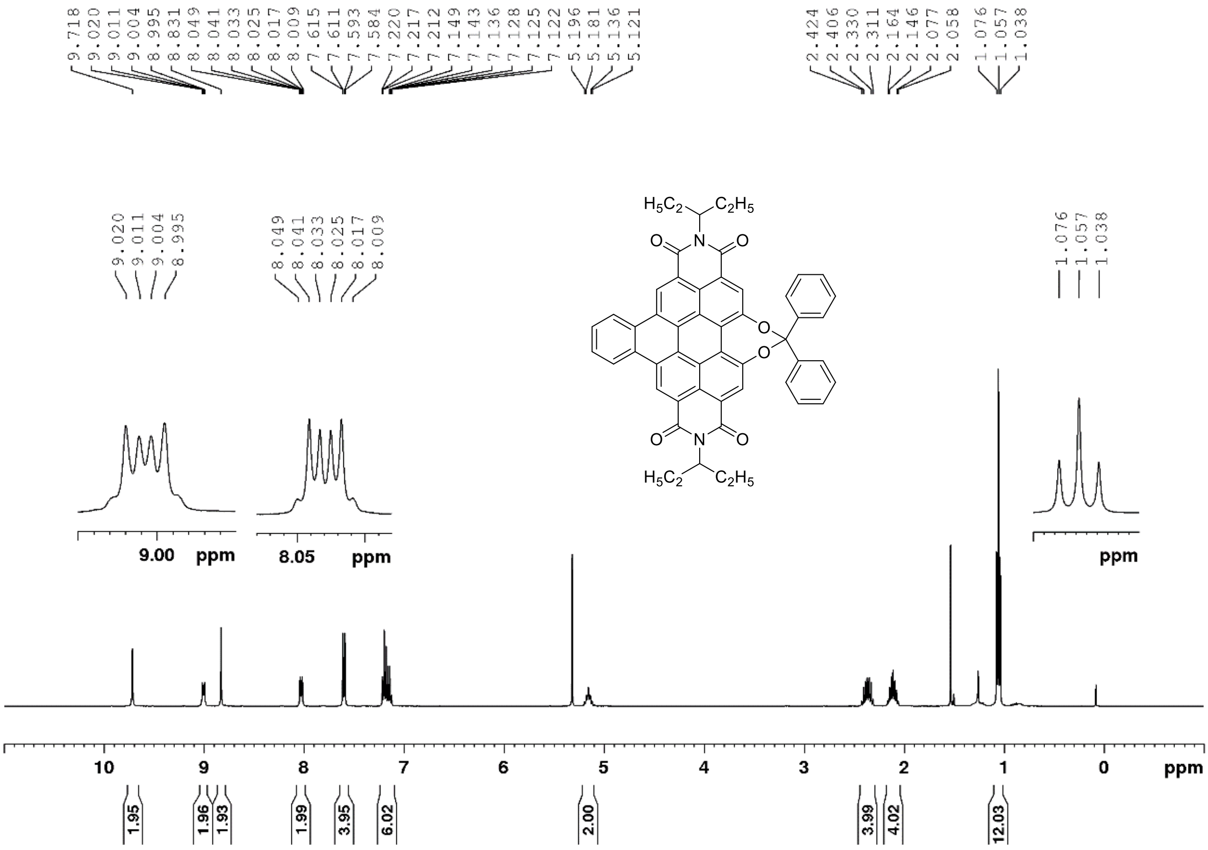


Figure S29. ^{1}H-NMR (400 MHz) of compound **Naphtho-PBI-(O-C-O)** in CD_2Cl_2 at 295 K.

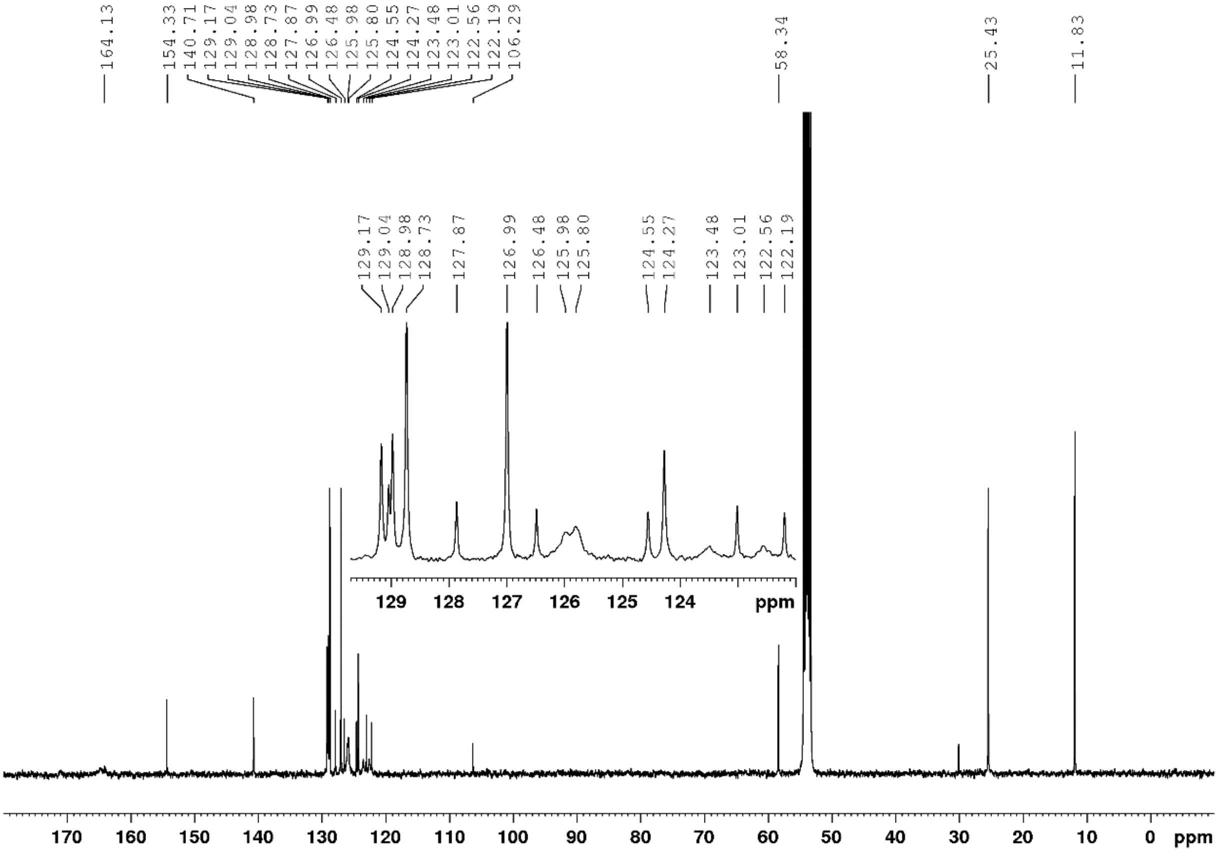


Figure S30. ^{13}C-NMR (101 MHz) of compound **Naphtho-PBI-(O-C-O)** in CD_2Cl_2 at 295 K.

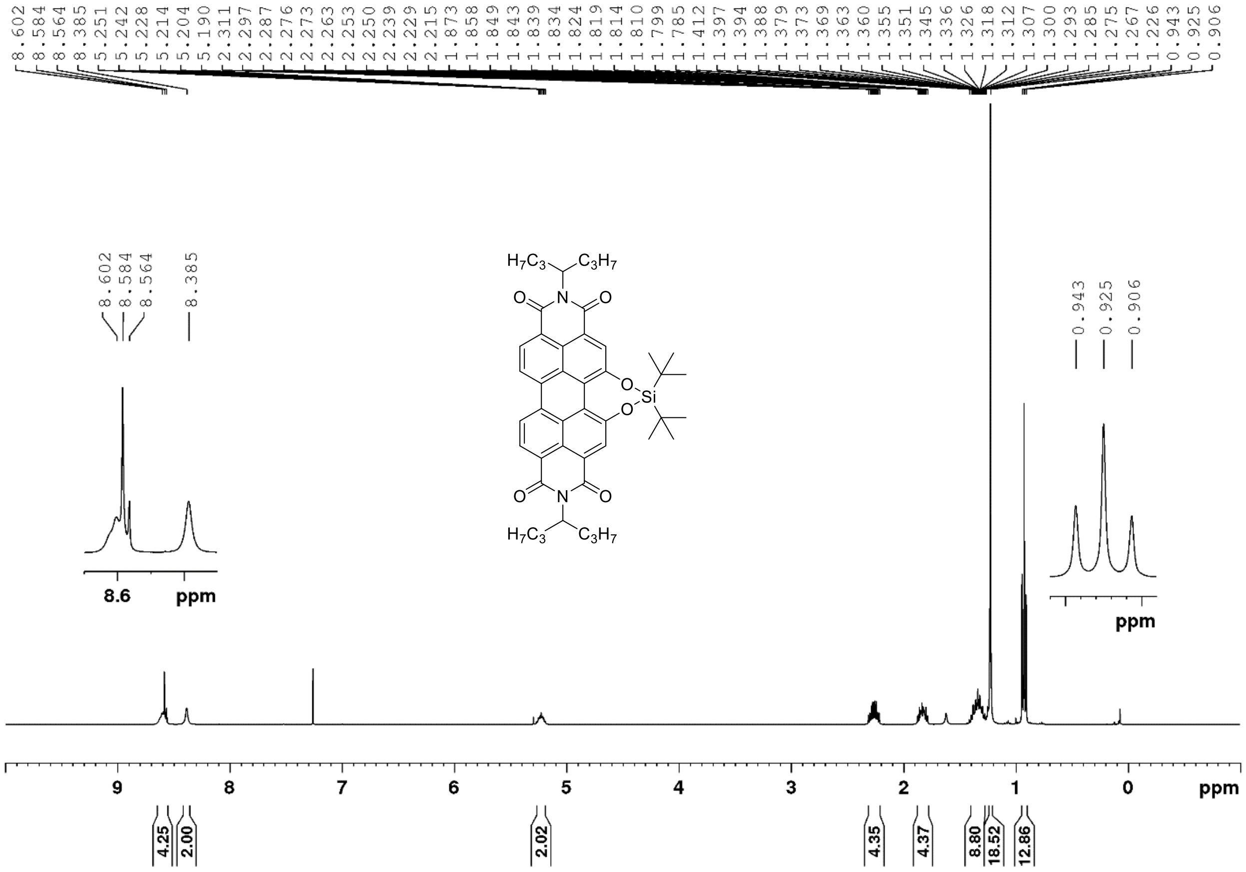


Figure 31. ^{1}H-NMR (400 MHz) of compound **PBI-(O-Si-O) b** in $CDCl_3$ at 295 K.

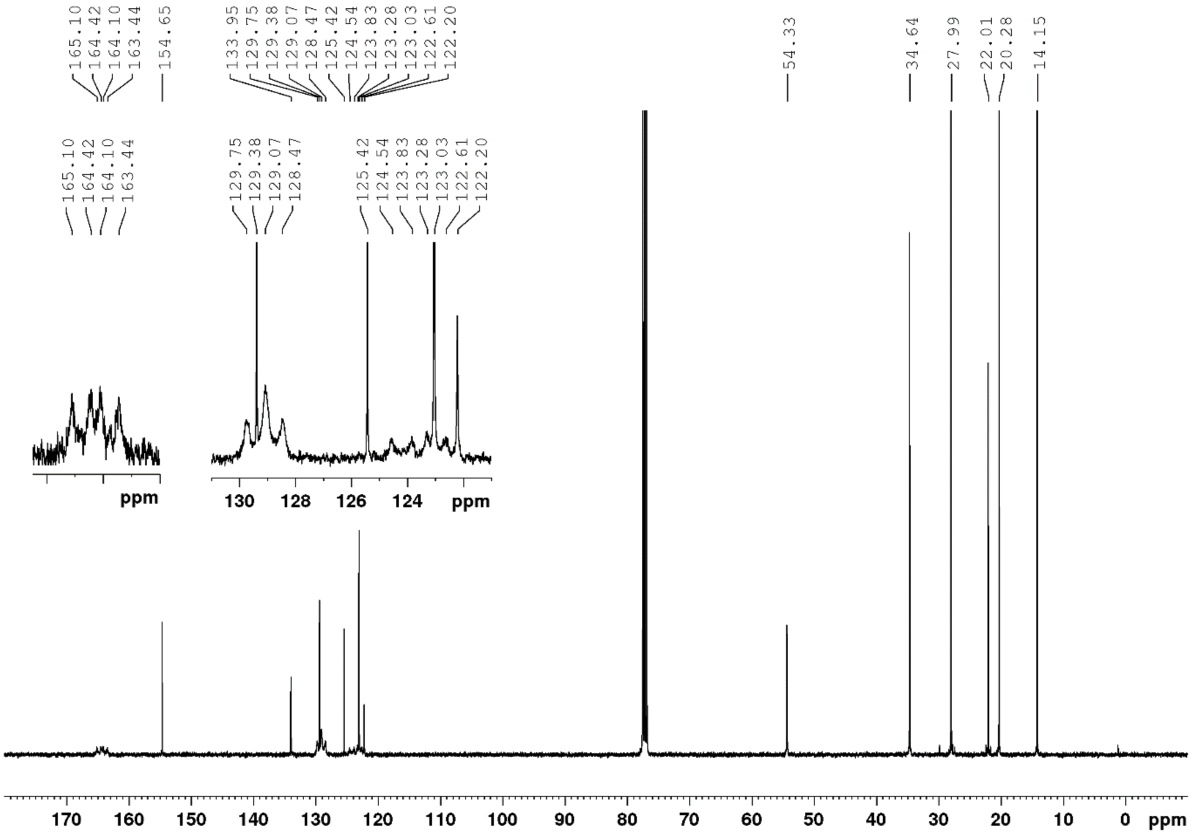


Figure 32. ^{13}C-NMR (101 MHz) of compound **PBI-(O-Si-O) b** in $CDCl_3$ at 295 K.

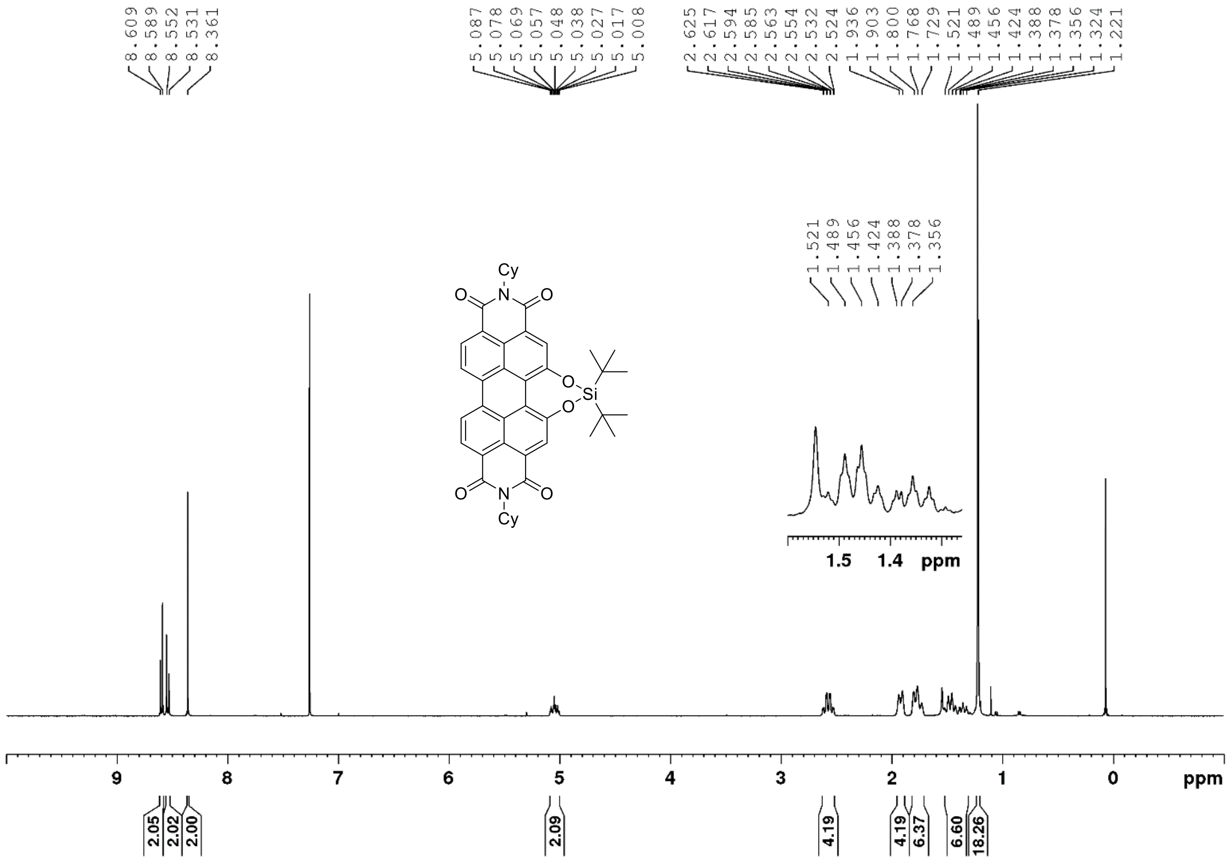


Figure 33. ^{1}H-NMR (400 MHz) of compound **PBI-(O-Si-O) c** in CDCl$_3$ at 295 K.

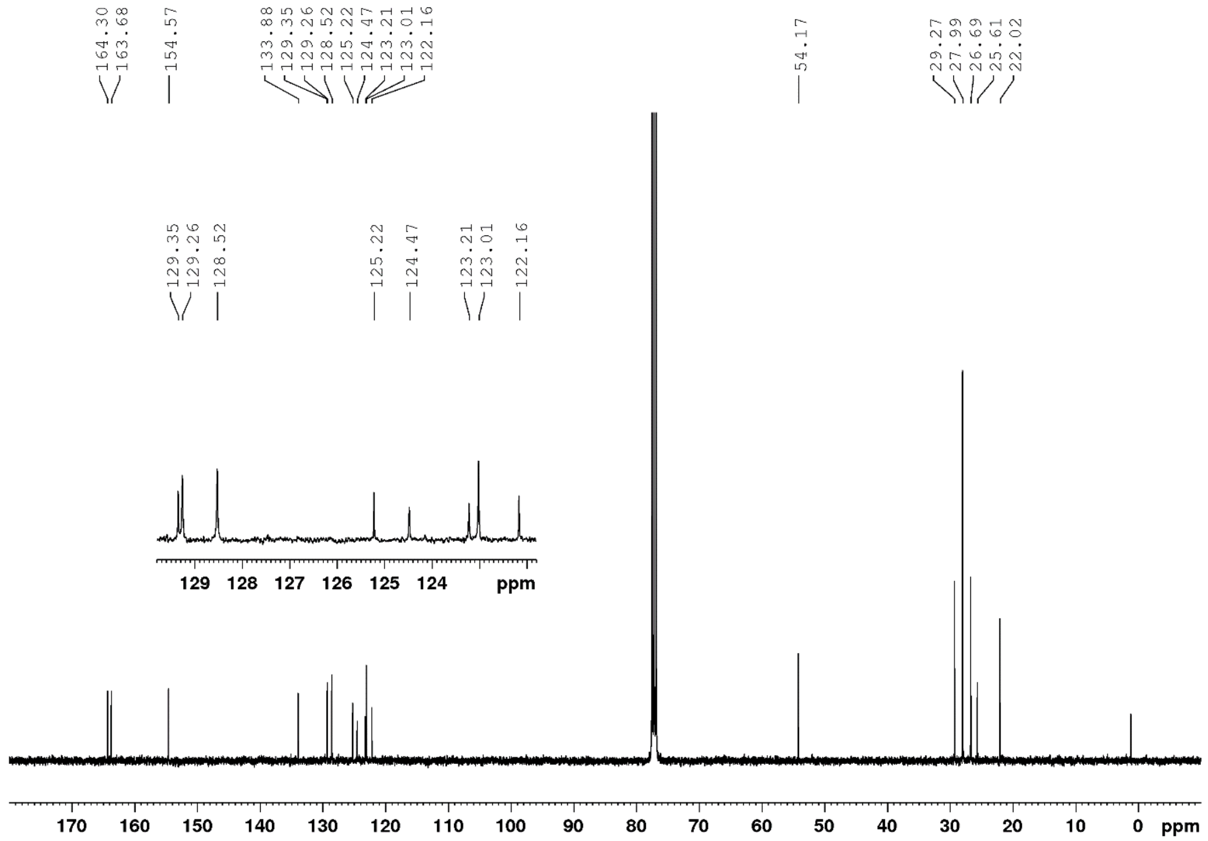


Figure 34. ^{13}C-NMR (101 MHz) of compound **PBI-(O-Si-O) c** in CDCl$_3$ at 295 K.

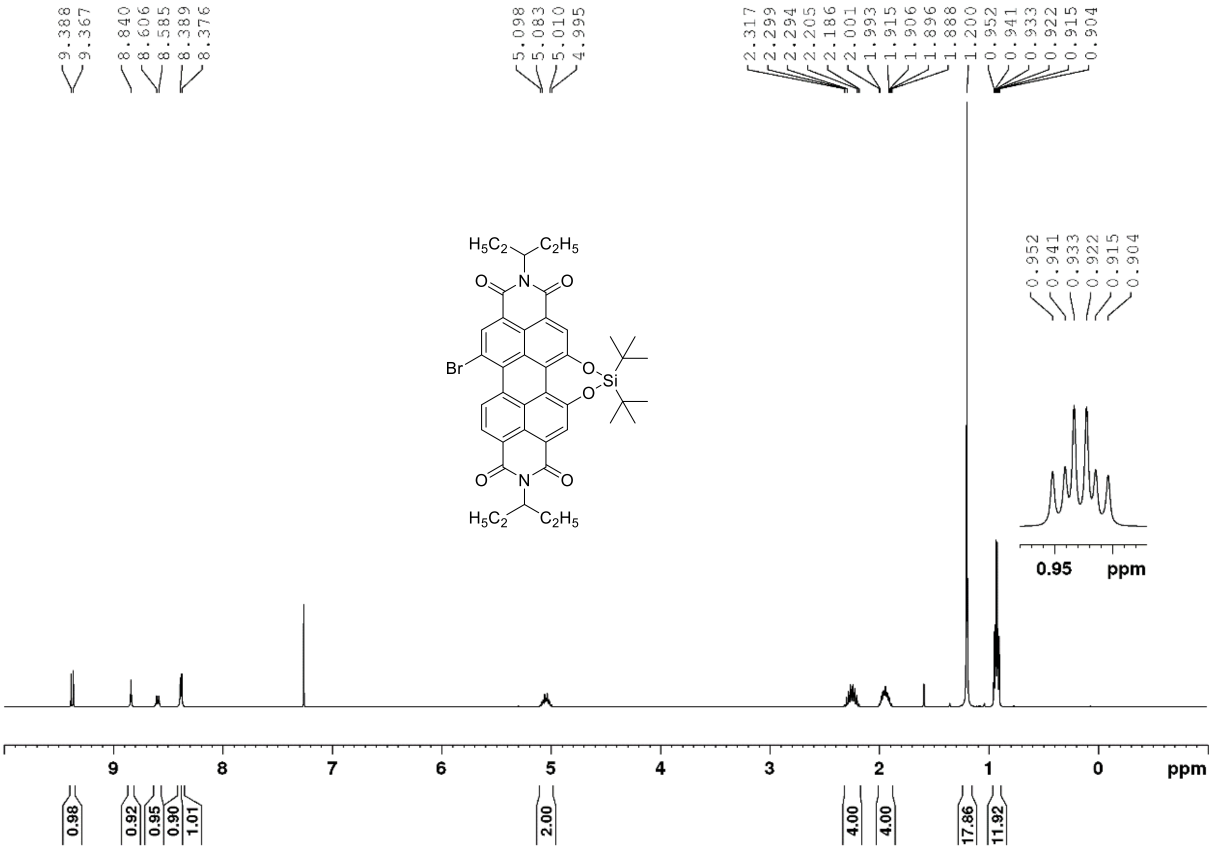


Figure S35. ^{1}H-NMR (400 MHz) of compound **Br-PBI-(O-Si-O)** in CDCl$_3$ at 295 K.

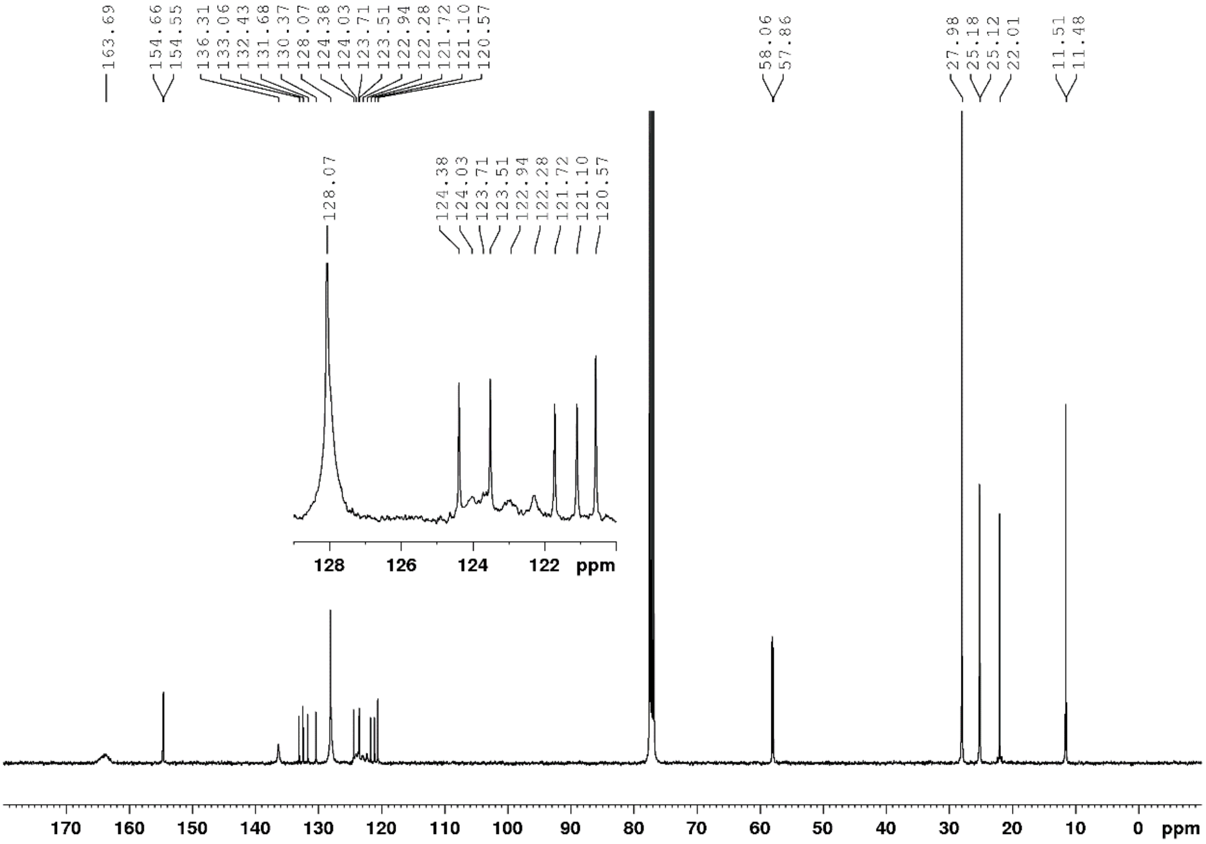


Figure S36. ^{13}C-NMR (101 MHz) of compound **Br-PBI-(O-Si-O)** in CDCl$_3$ at 295 K.

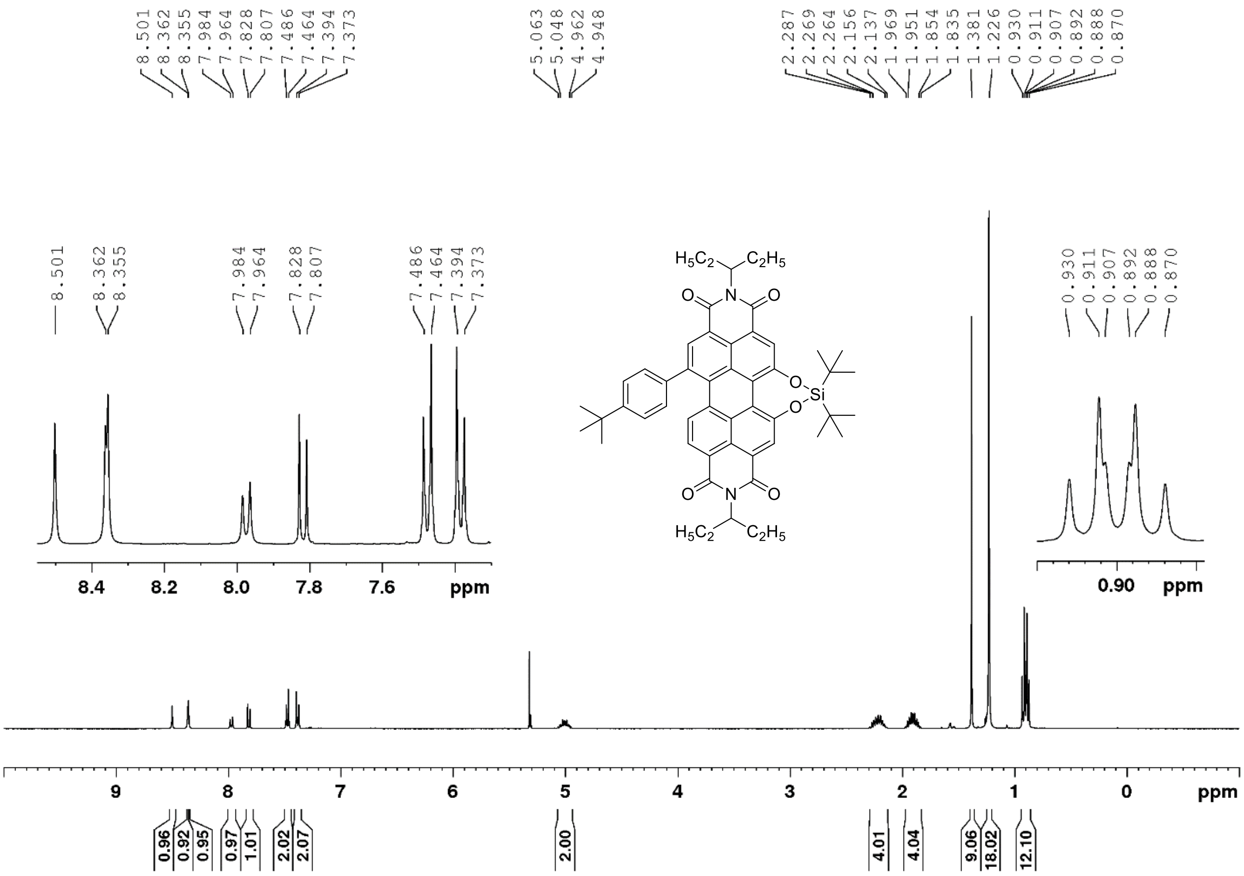


Figure S37. ^{1}H-NMR (400 MHz) of compound **Ph-PBI-(O-Si-O)** in CD_2Cl_2 at 295 K.

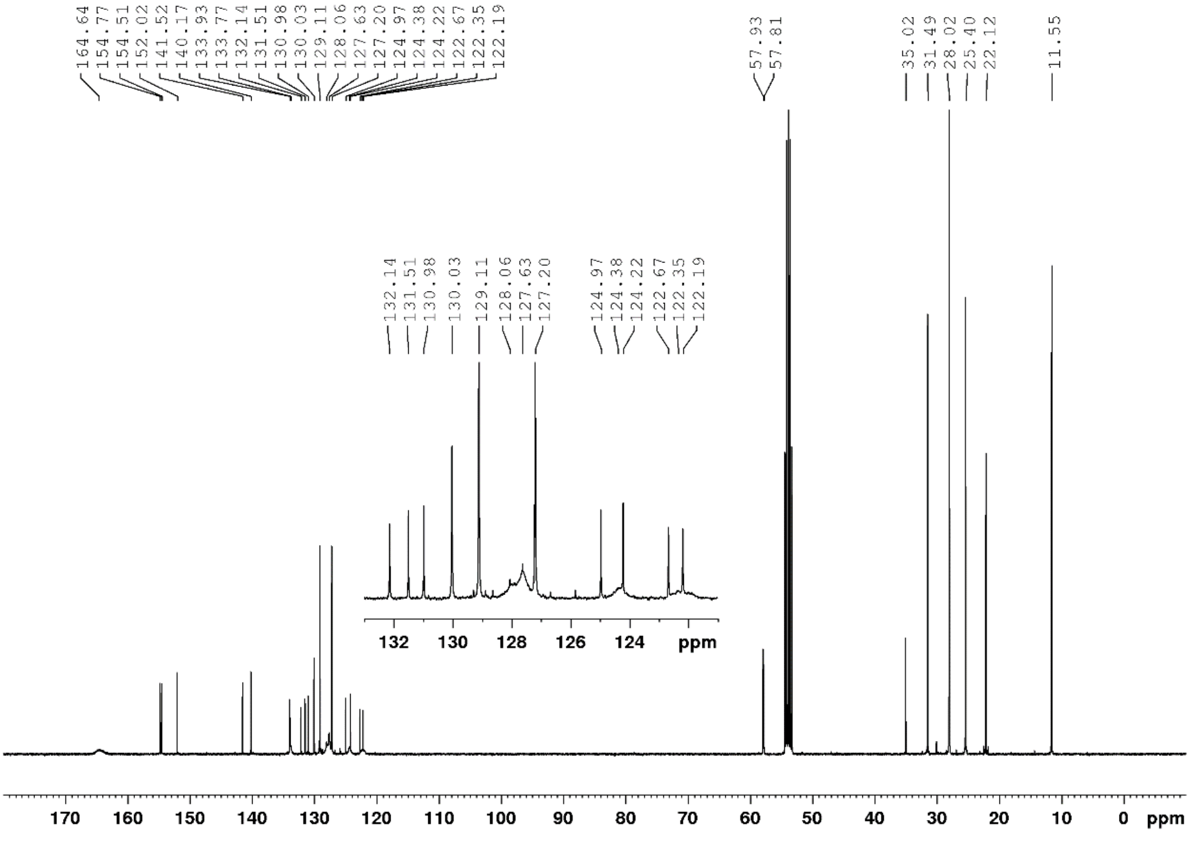


Figure S38. ^{13}C-NMR (101 MHz) of compound **Ph-PBI-(O-Si-O)** in CD_2Cl_2 at 295 K.

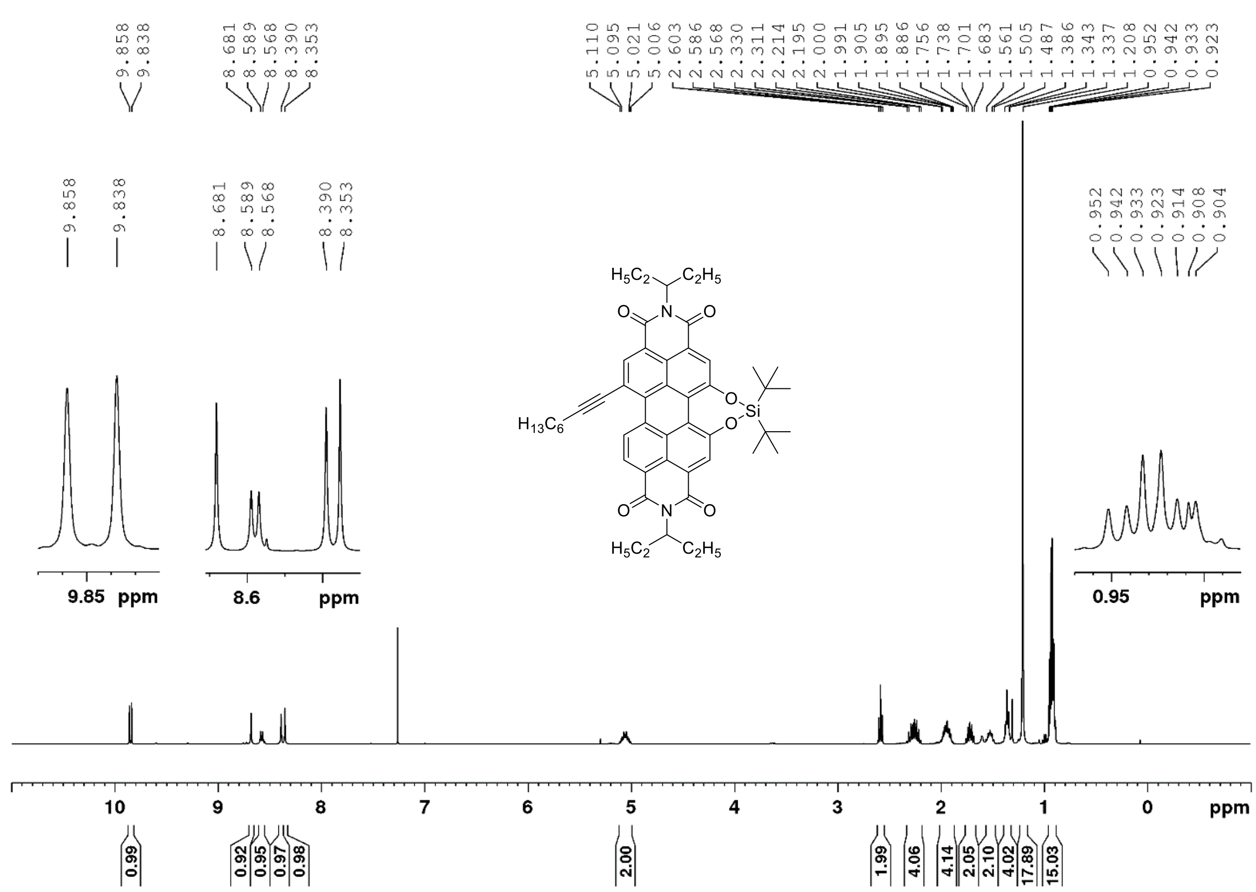


Figure S39. ^{1}H-NMR (400 MHz) of compound **Octyne-PBI-(O-Si-O)** in $CDCl_3$ at 295 K.

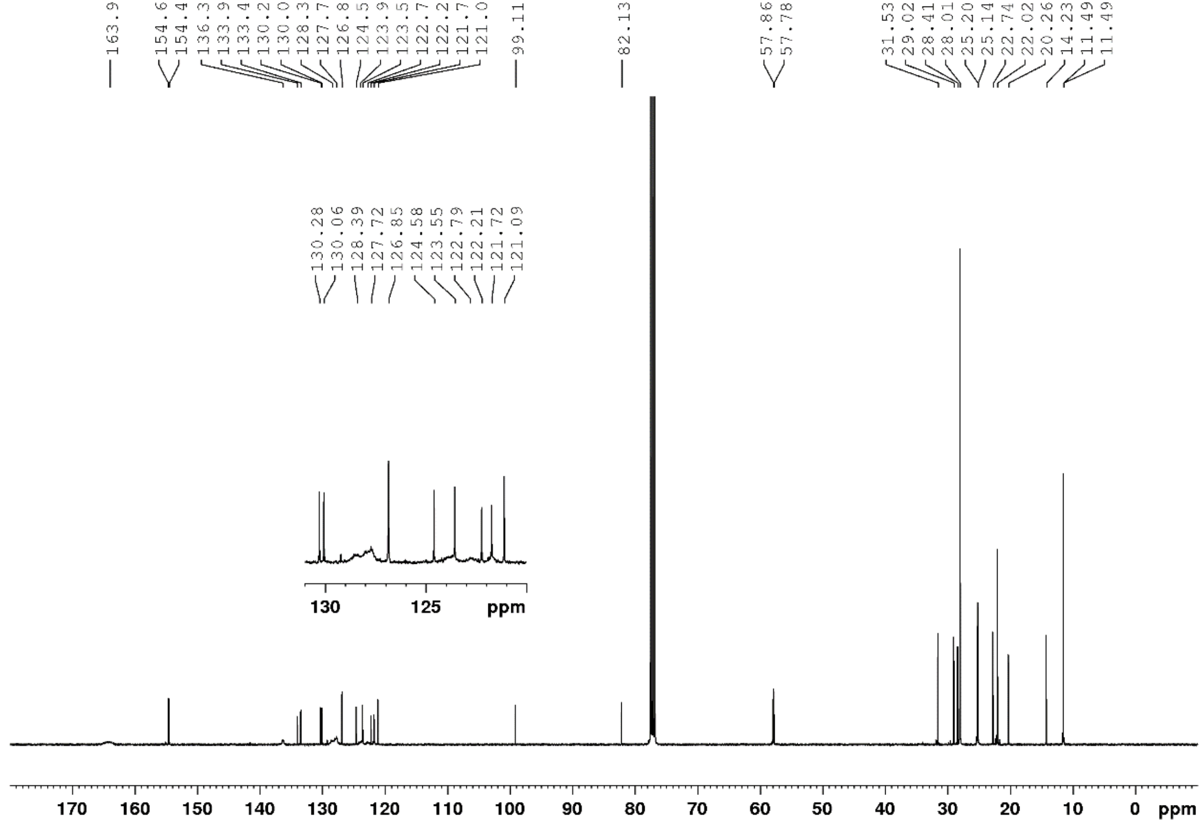


Figure S40. ^{13}C-NMR (101 MHz) of compound **Octyne-PBI-(O-Si-O)** in $CDCl_3$ at 295 K.

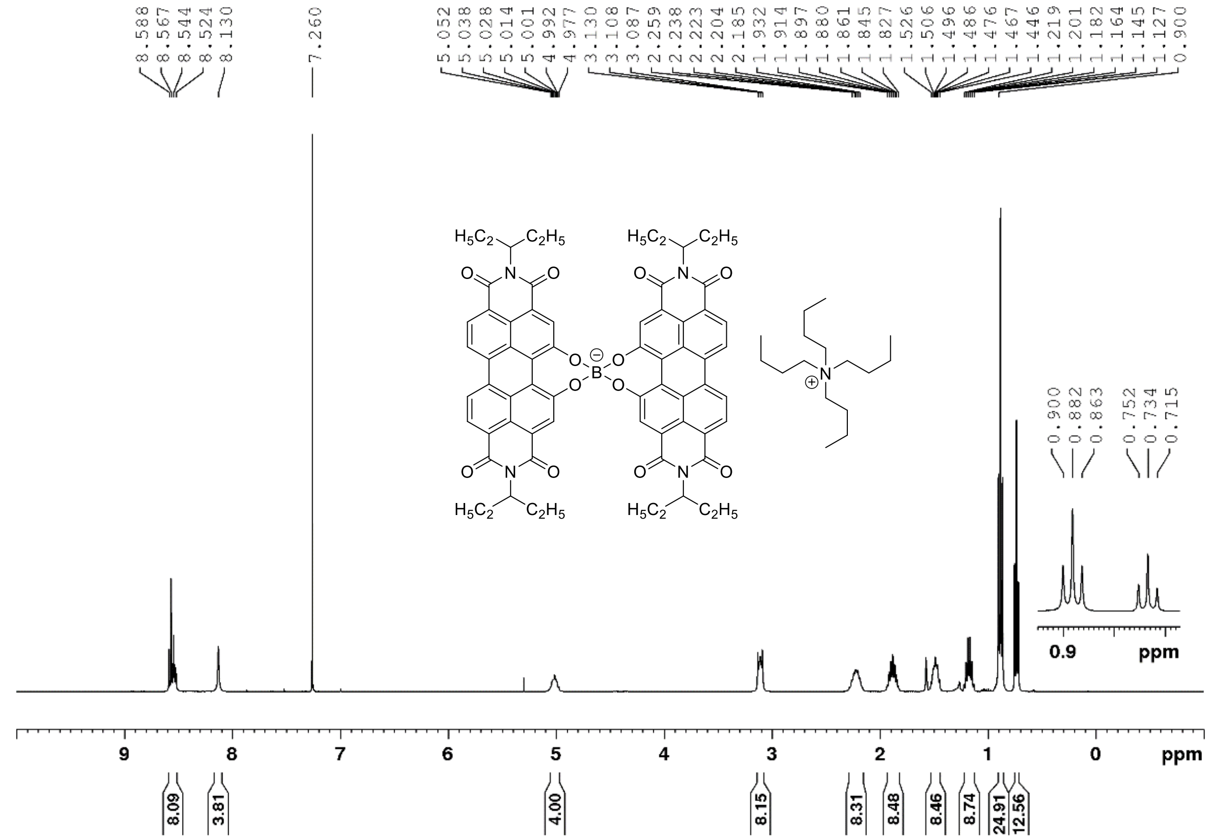


Figure S41. ^{1}H-NMR (400 MHz) of compound **Spiro-PBI-Borate** in $CDCl_3$ at 295 K.

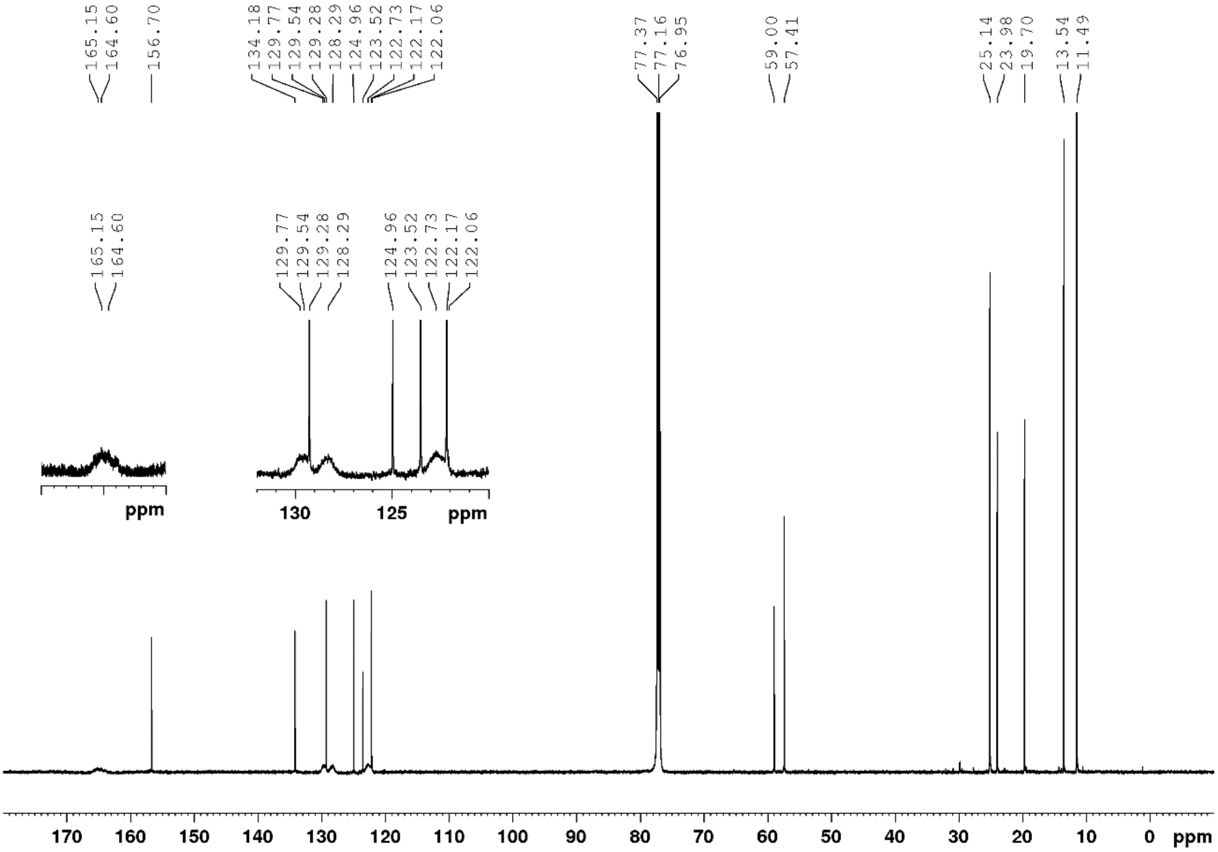


Figure S42. ^{13}C-NMR (101 MHz) of compound **Spiro-PBI-Borate** in $CDCl_3$ at 295 K.

7. HR-MS Spectra

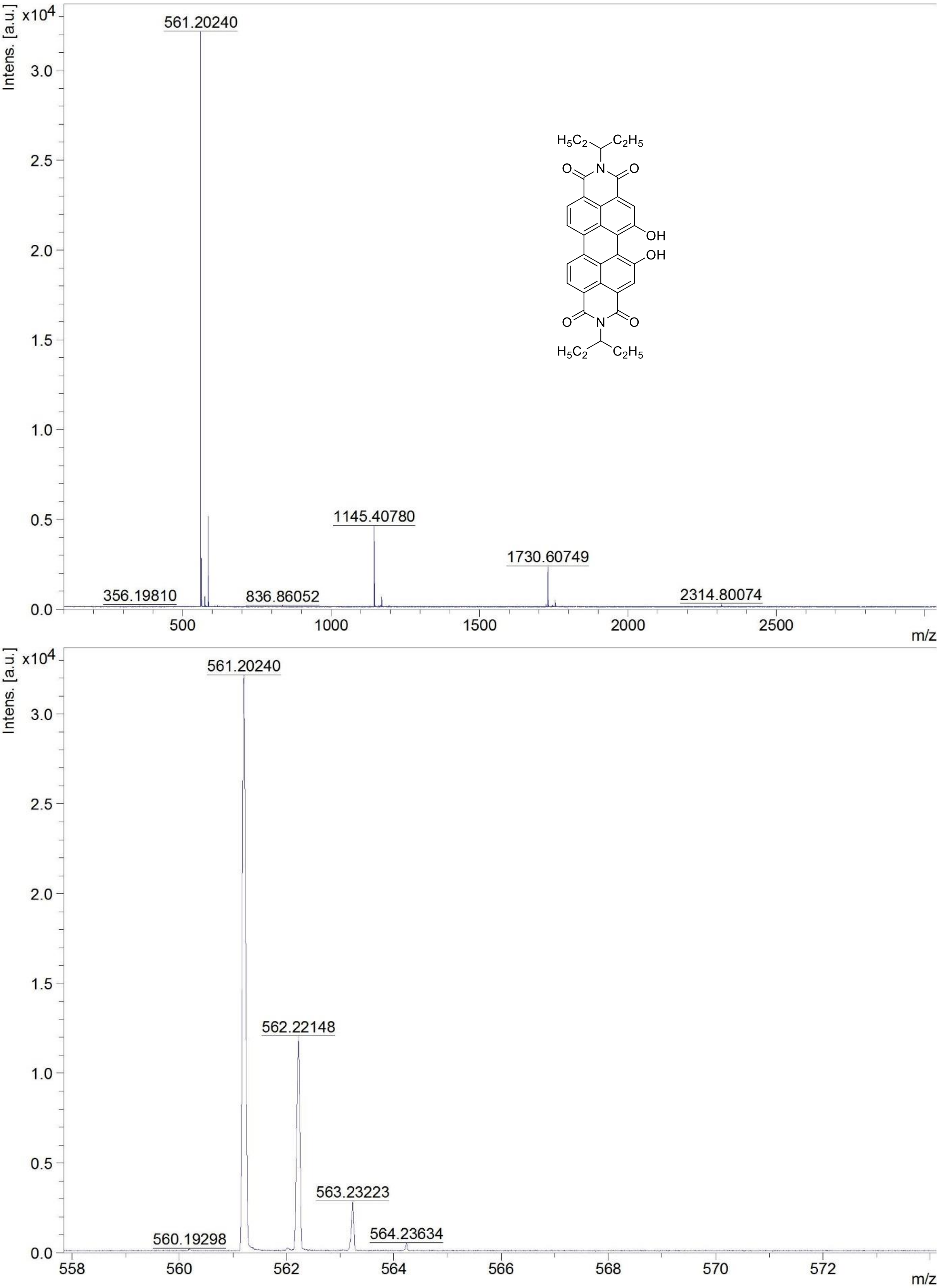


Figure S43. HRMS of compound **PBI-(OH)$_2$ a** (MALDI-TOF, negative mode, DCTB).

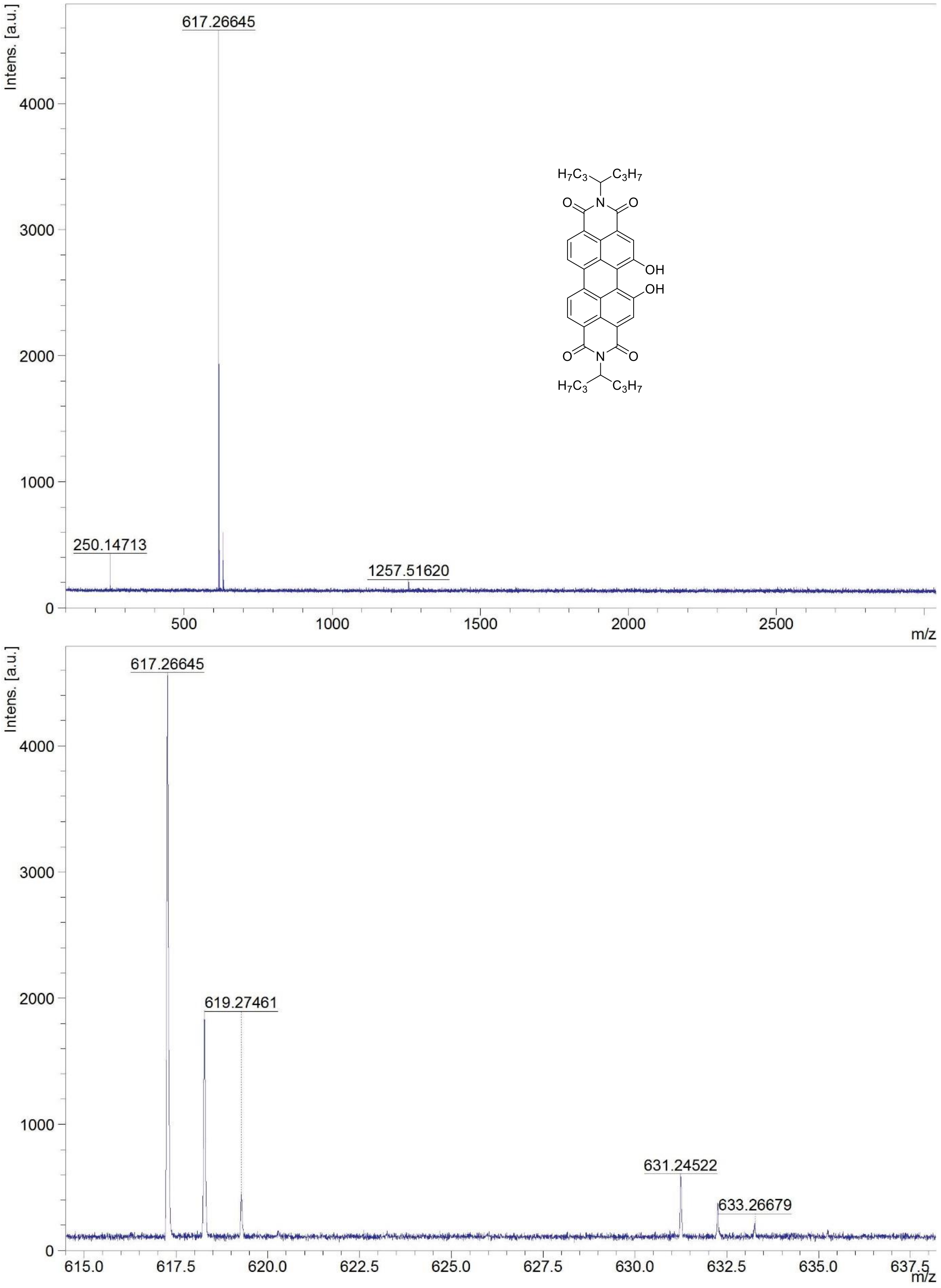


Figure S44. HRMS of compound **PBI-(OH)$_2$ b** (MALDI-TOF, negative mode, DCTB).

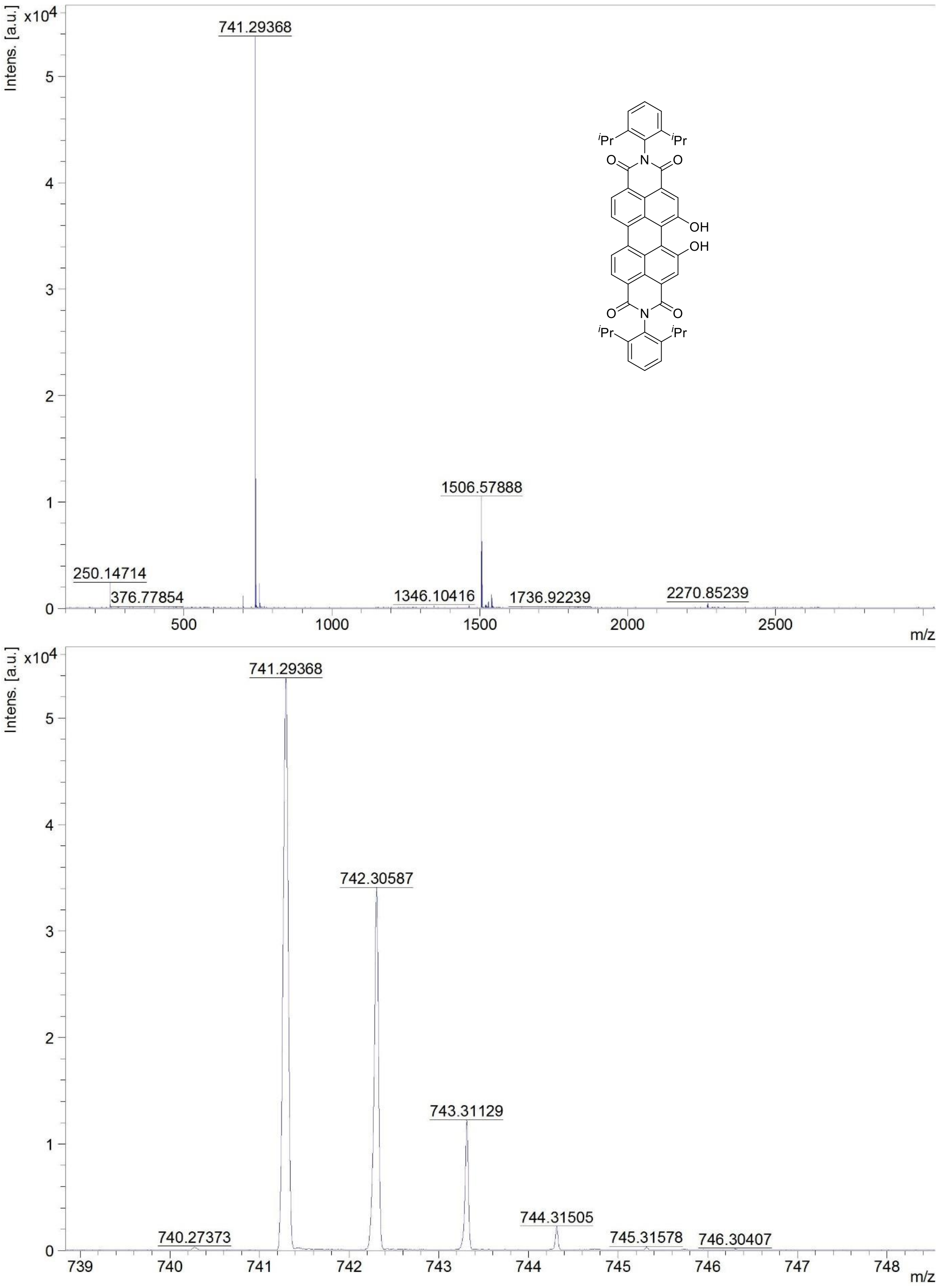


Figure S45. HRMS of compound **PBI-$(OH)_2$ d** (MALDI-TOF, negative mode, DCTB).

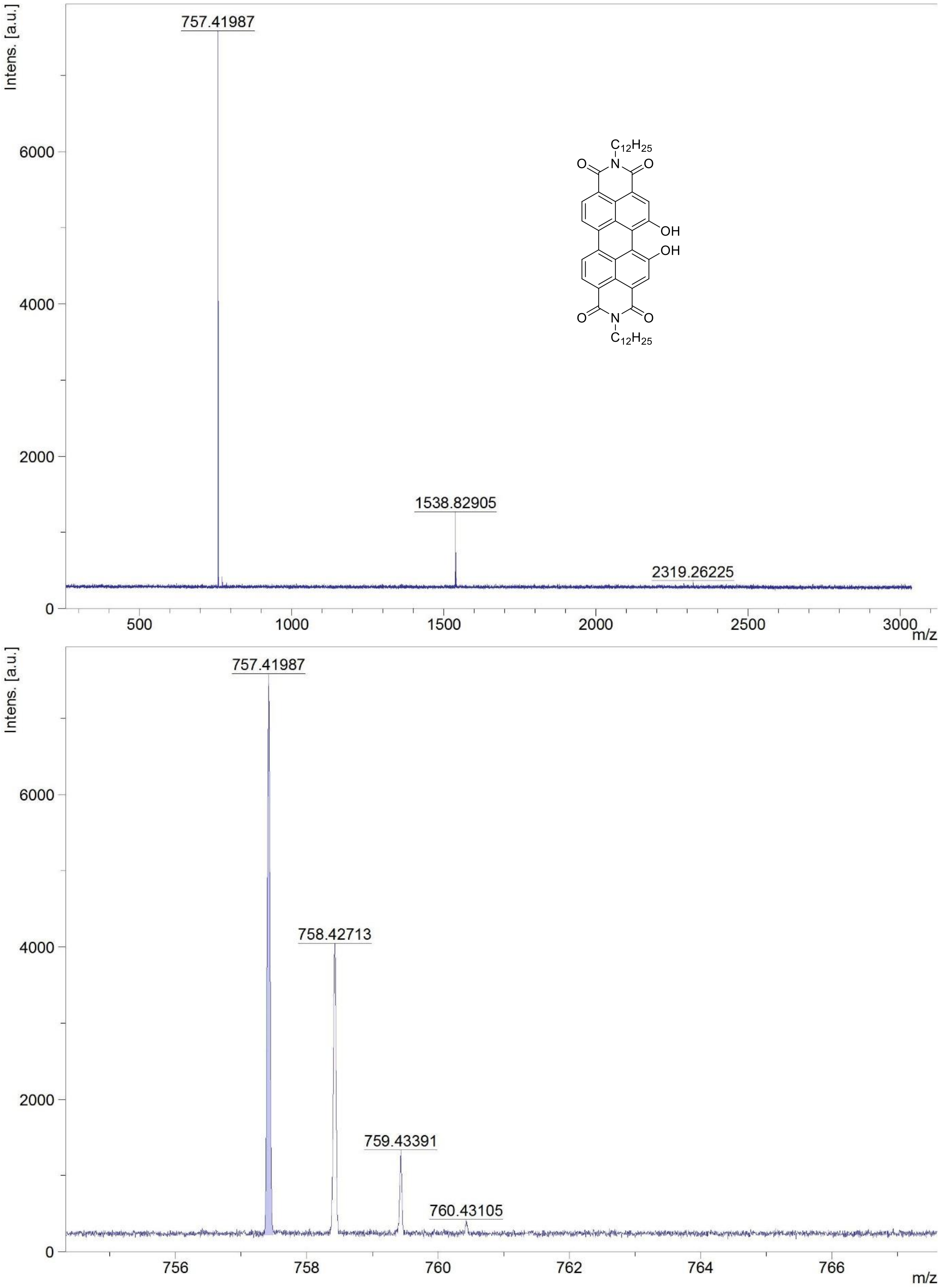


Figure S46. HRMS of compound **PBI-(OH)$_2$ e** (MALDI-TOF, negative mode, DCTB).

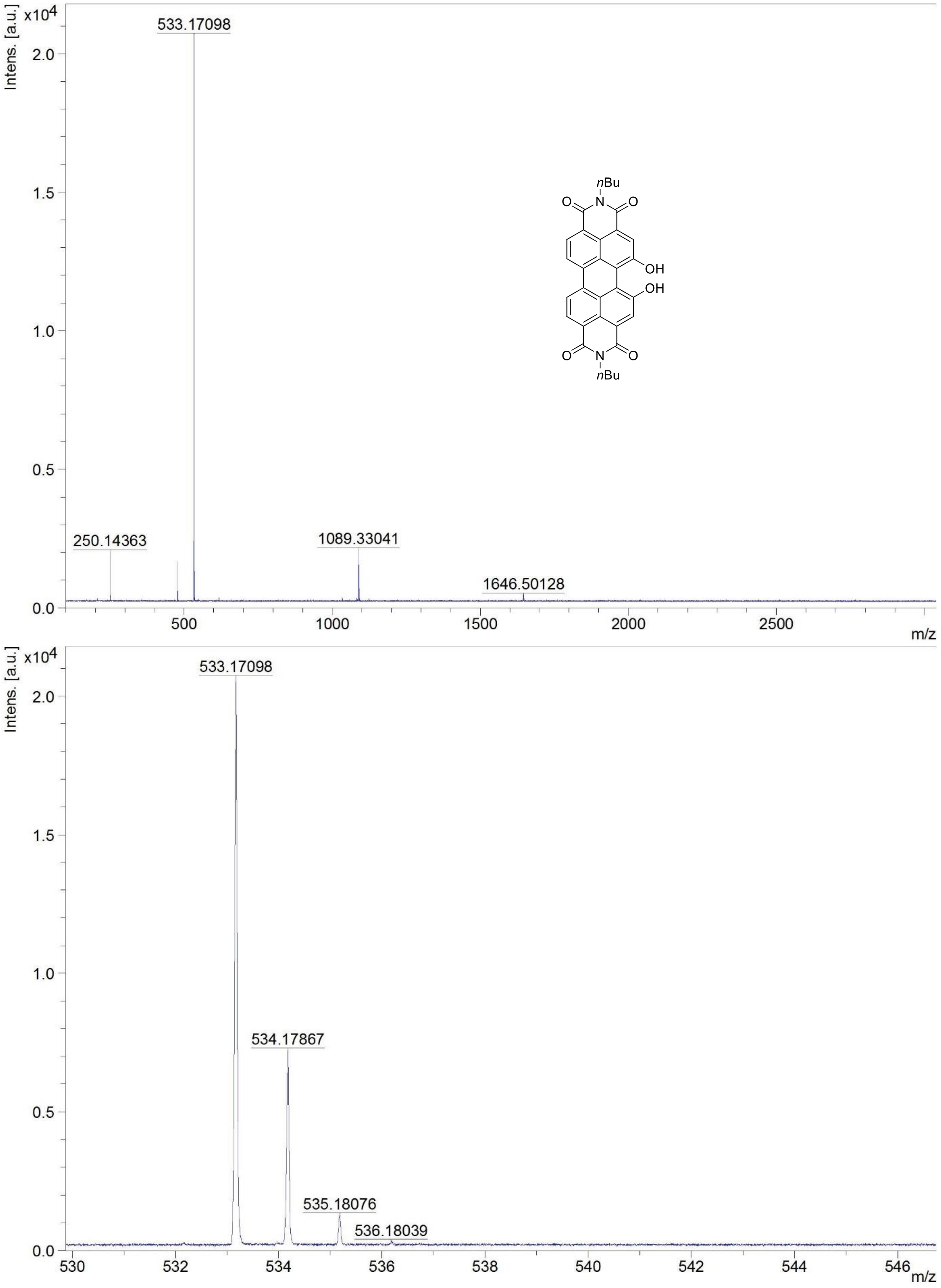


Figure S47. HRMS of compound **PBI-(OH)$_2$ f** (MALDI-TOF, negative mode, DCTB).

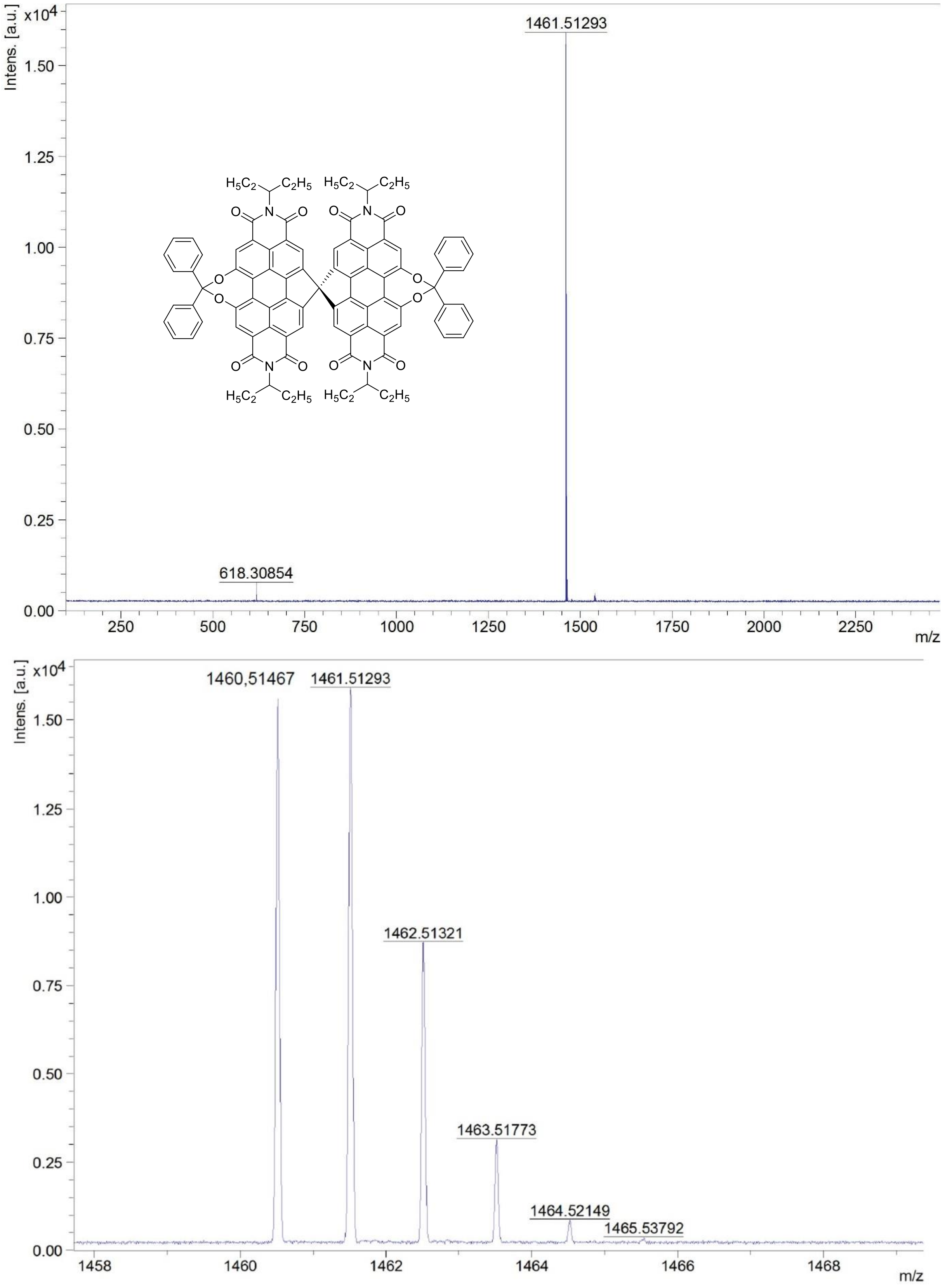


Figure S48. HRMS of compound **Spiro-PBI-(O-C-O)** (MALDI-TOF, negative mode, DCTB).

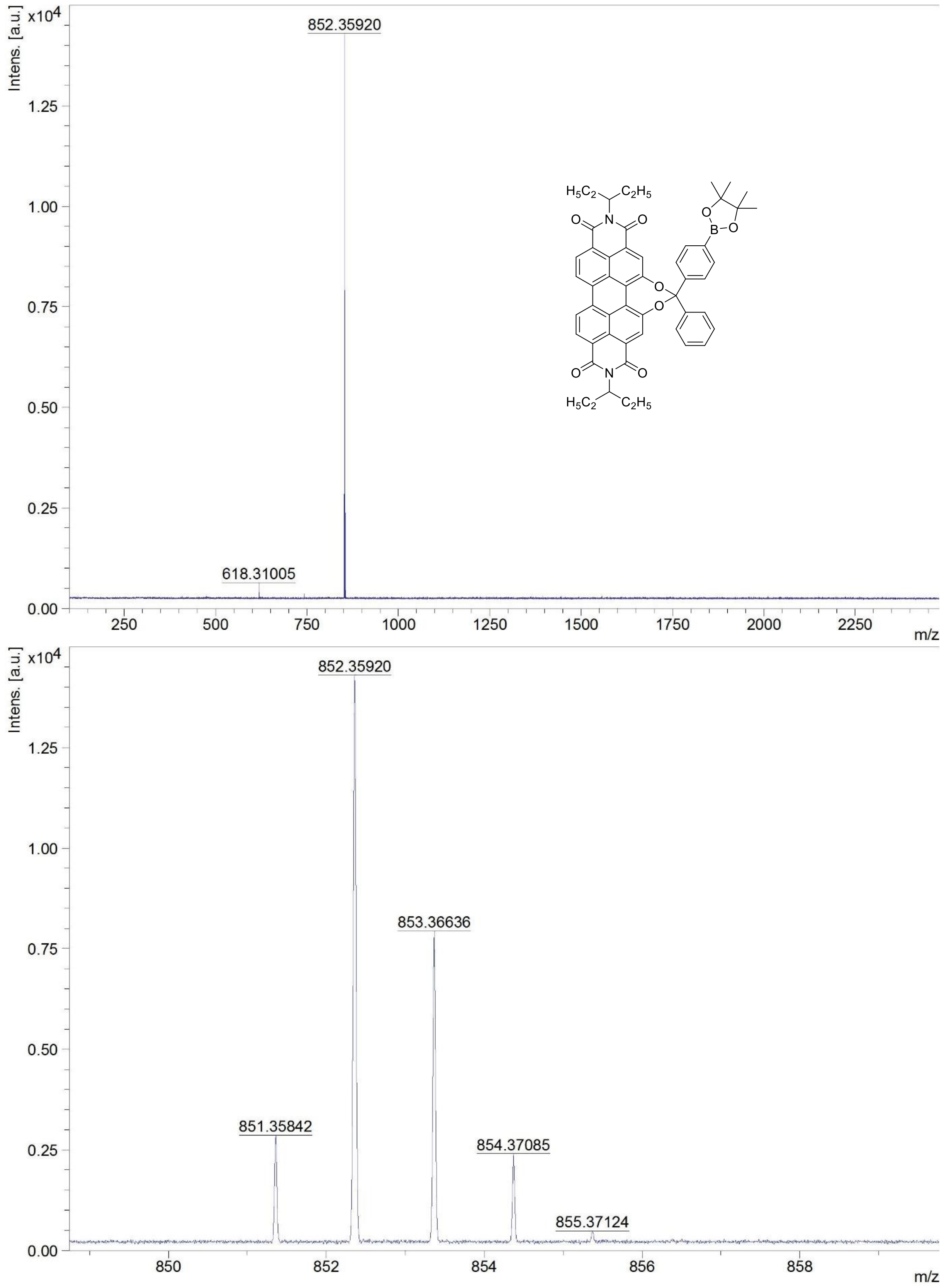


Figure S49. HRMS of compound **PBI-(O-C-O)-Bpin** (MALDI-TOF, negative mode, DCTB).

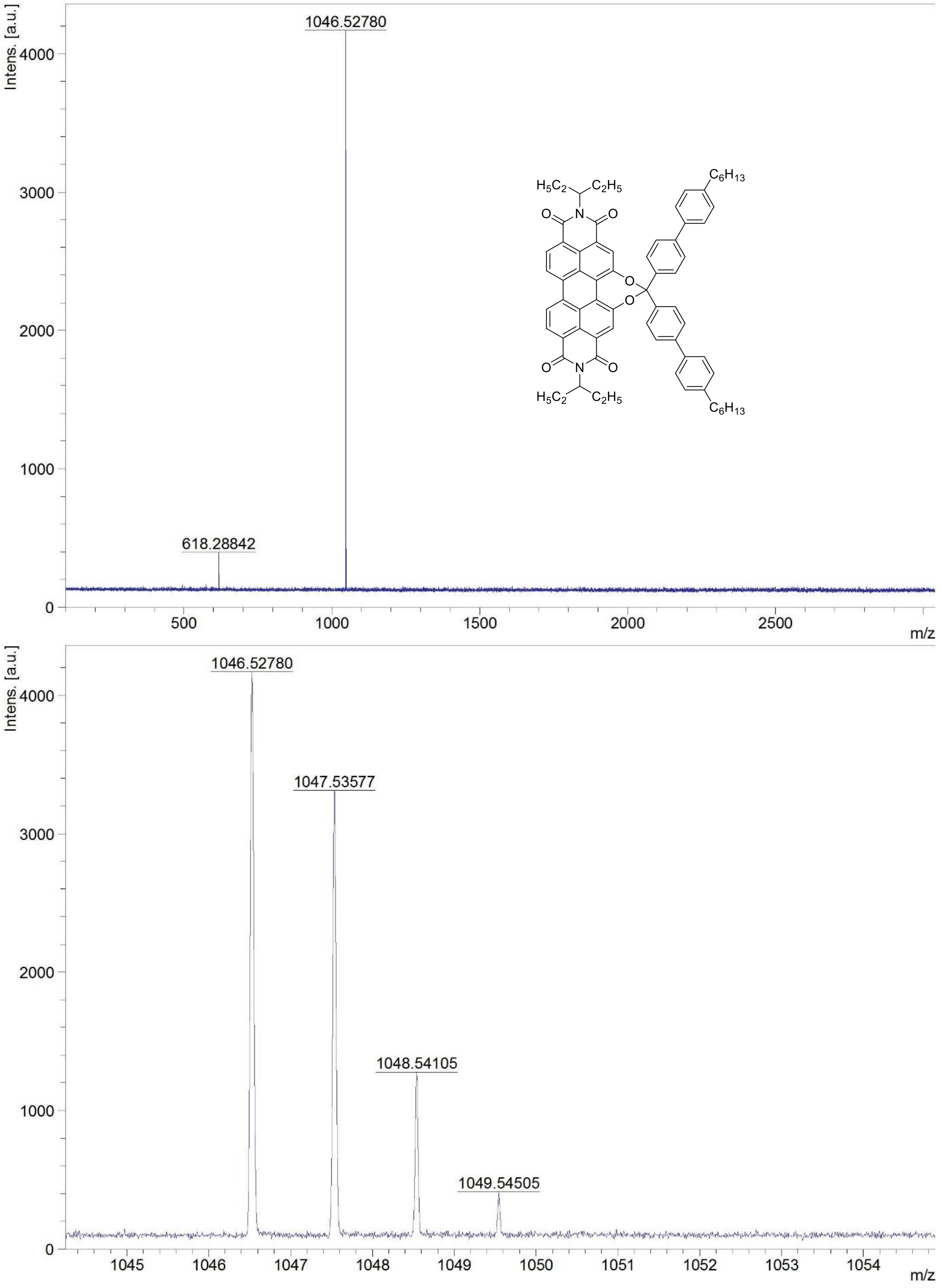


Figure S50. HRMS of compound **PBI-(O-C-O)-Ar$_2$** (MALDI-TOF, negative mode, DCTB).

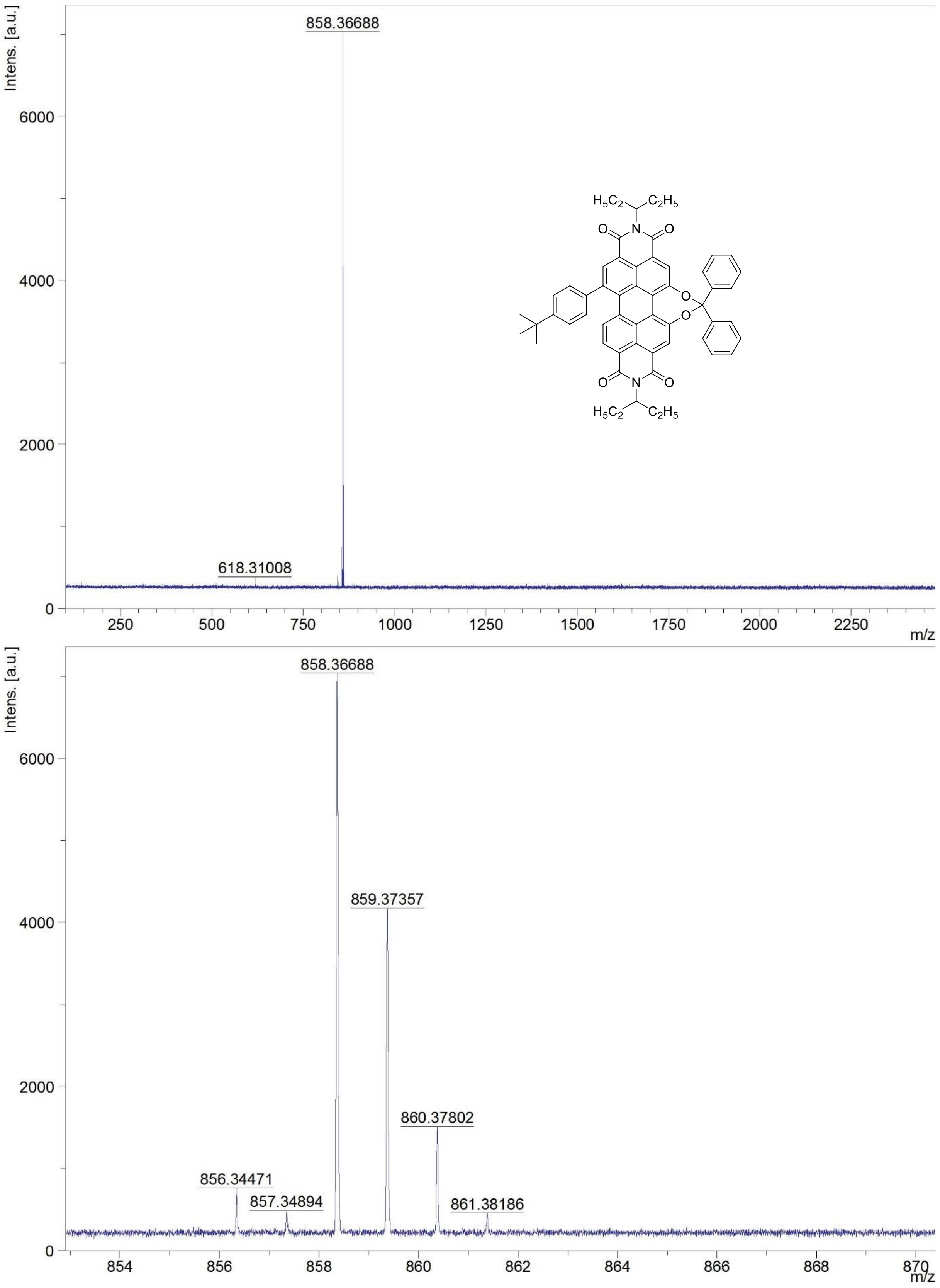


Figure S51. HRMS of compound **Ph-PBI-(O-C-O)** (MALDI-TOF, negative mode, DCTB).

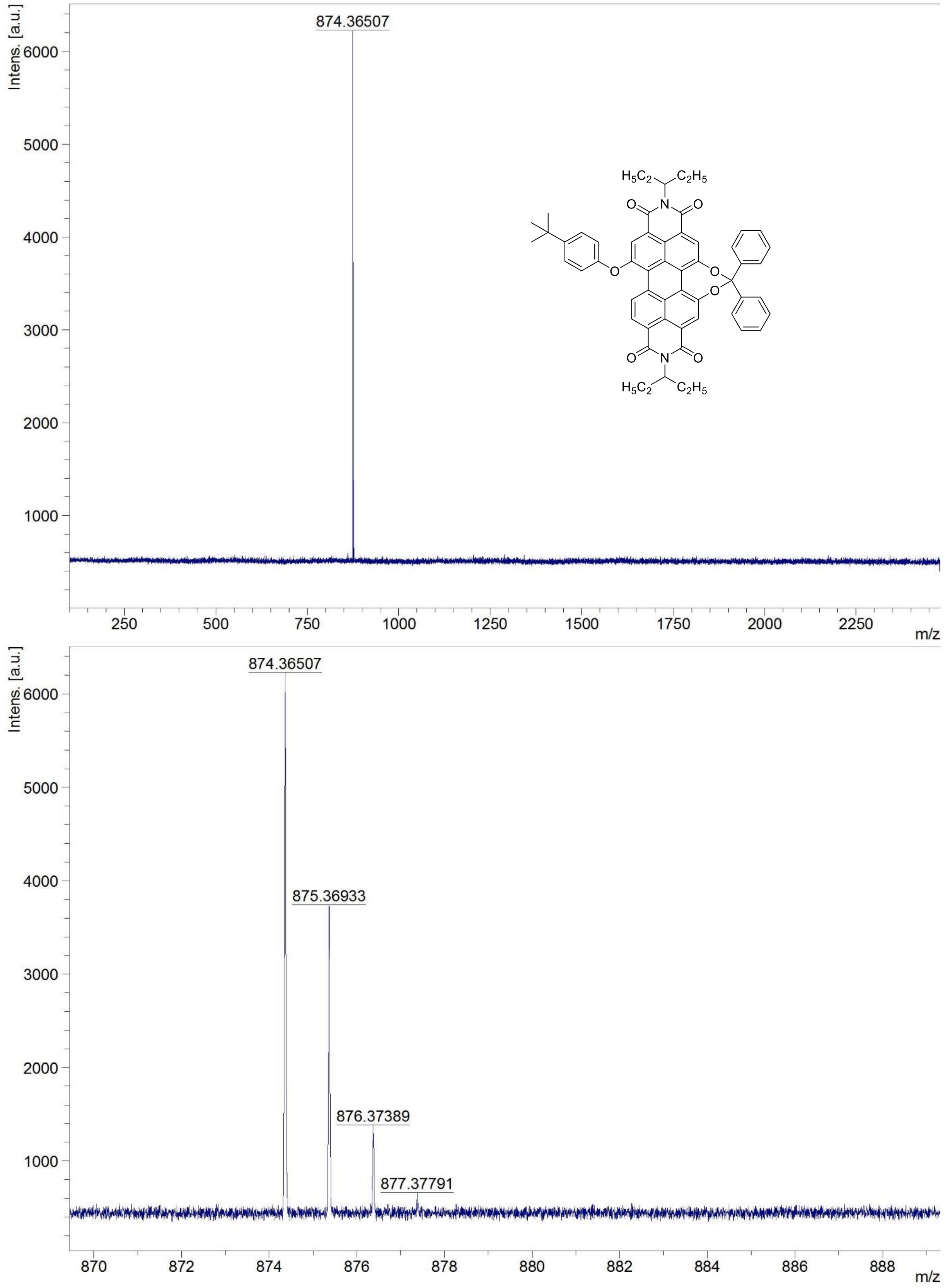


Figure S52. HRMS of compound **PhO-PBI-(O-C-O)** (MALDI-TOF, negative mode, DCTB).

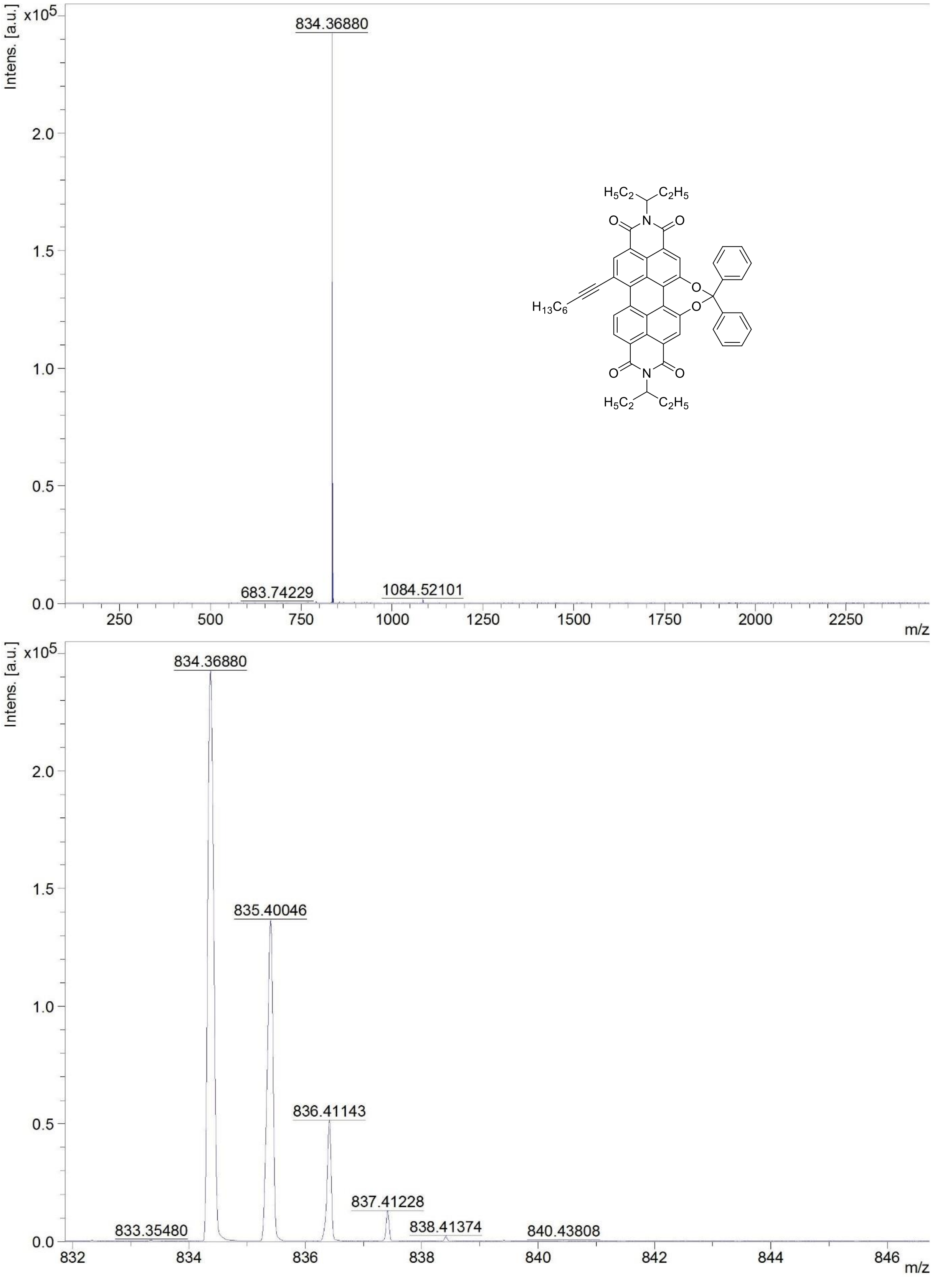


Figure S53. HRMS of compound **Octyne-PBI-(O-C-O)** (MALDI-TOF, negative mode, DCTB).

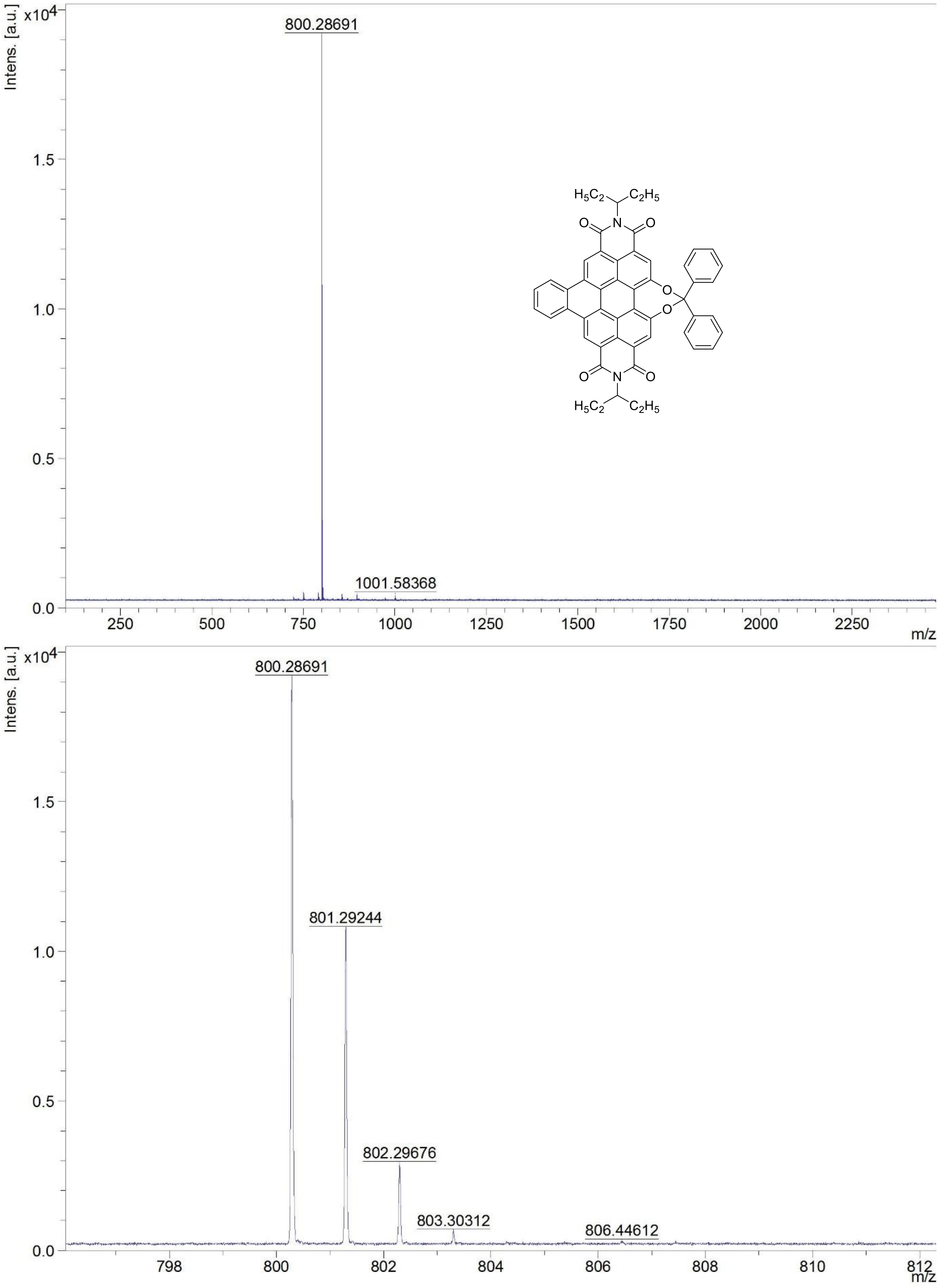


Figure S54. HRMS of compound **Naphtho-PBI-(O-C-O)** (MALDI-TOF, negative mode, DCTB).

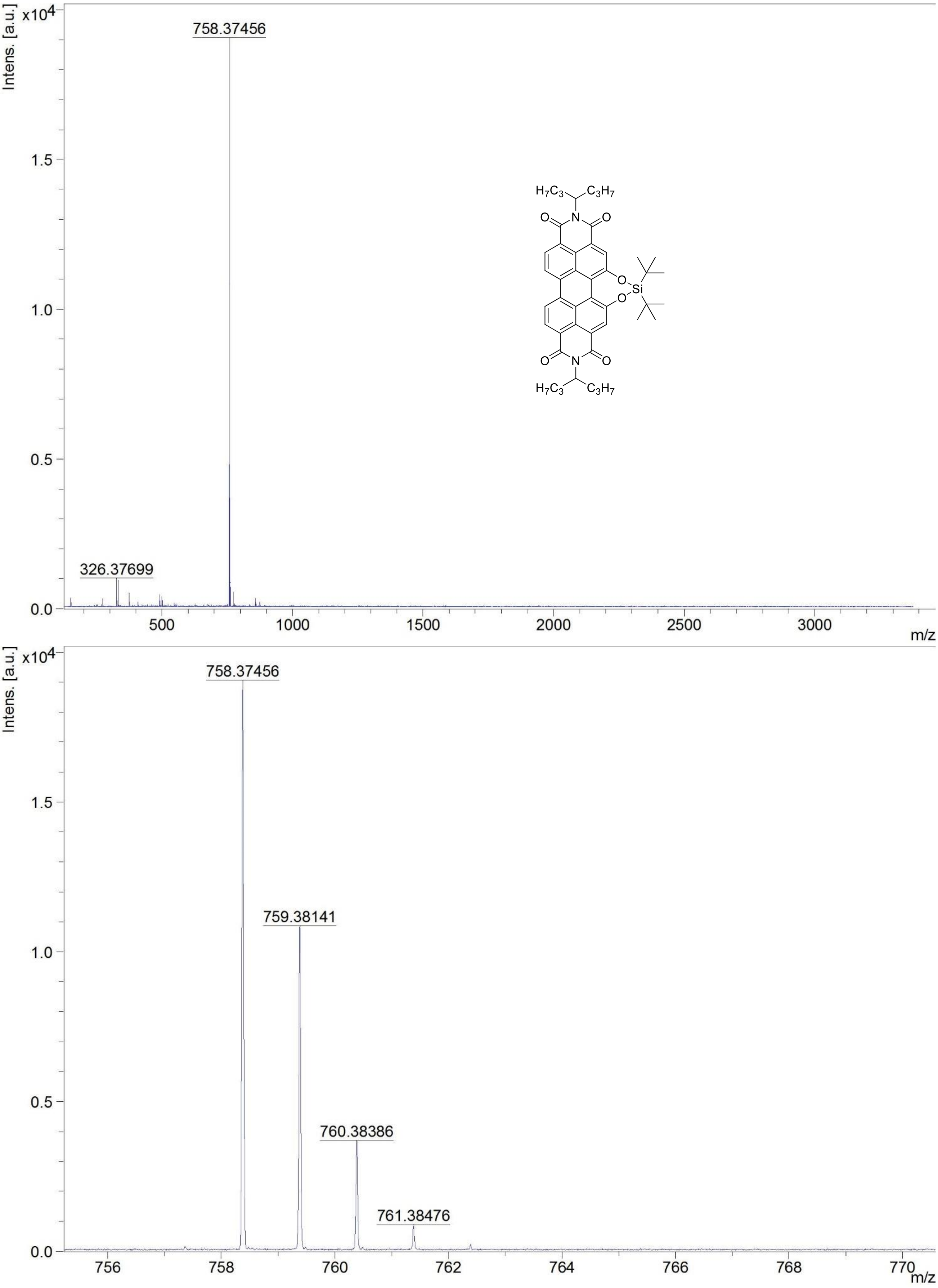


Figure S55. HRMS of compound **PBI-(O-Si-O) b** (MALDI-TOF, positive mode, DCTB).

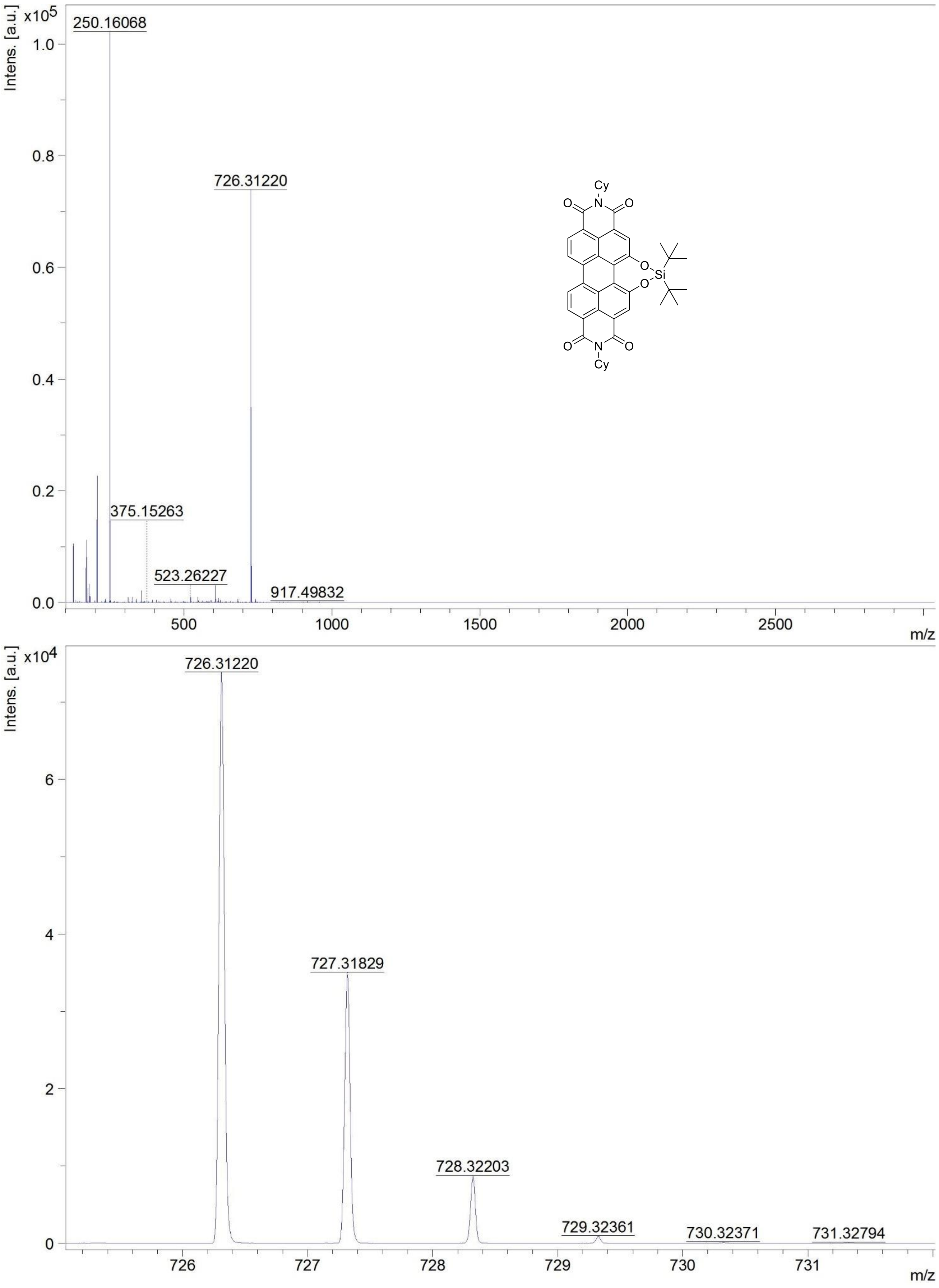


Figure S56. HRMS of compound **PBI-(O-Si-O) c** (MALDI-TOF, negative mode, DCTB).

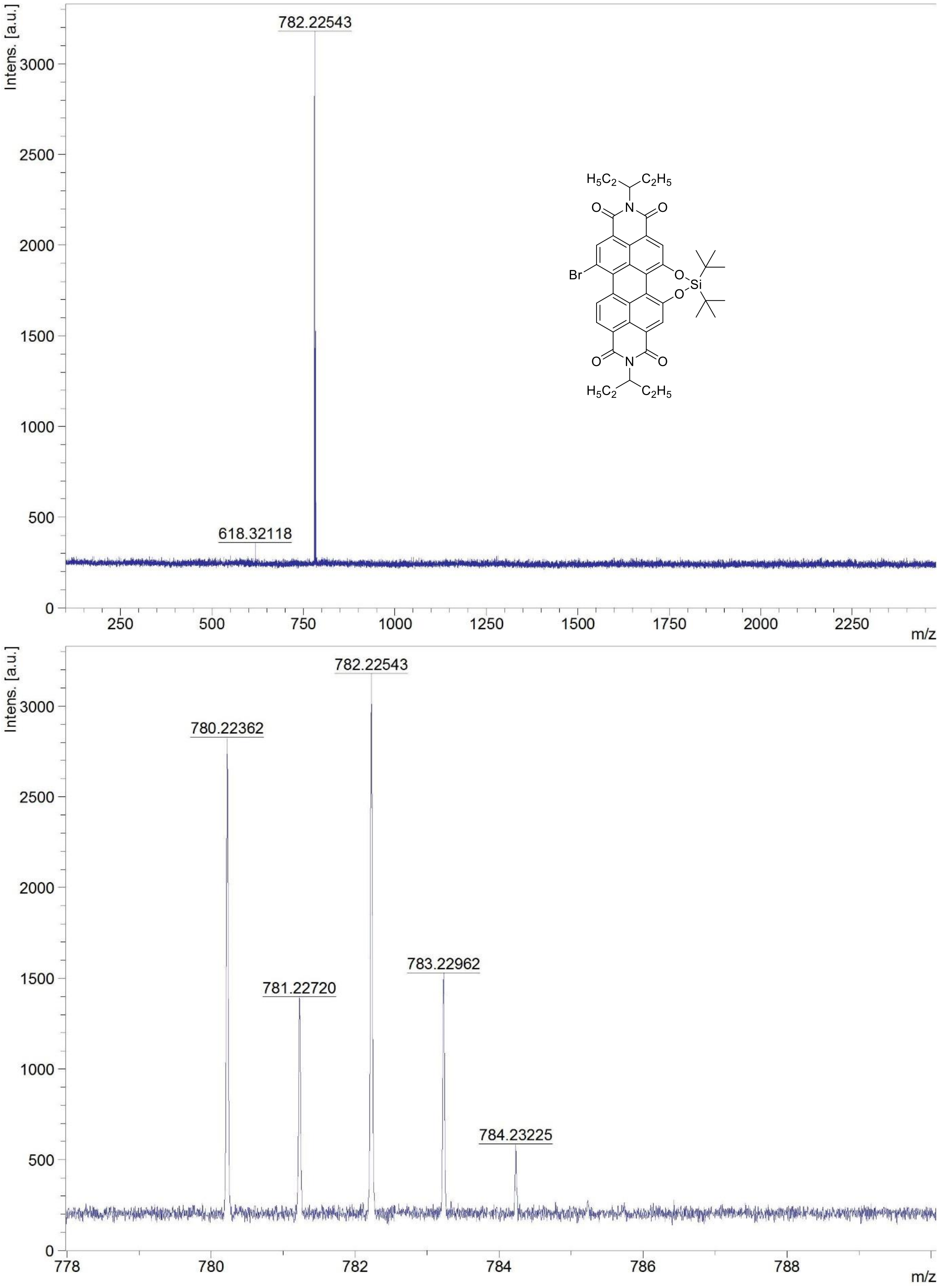


Figure S57. HRMS of compound **Br-PBI-(O-Si-O)** (MALDI-TOF, negative mode, DCTB).

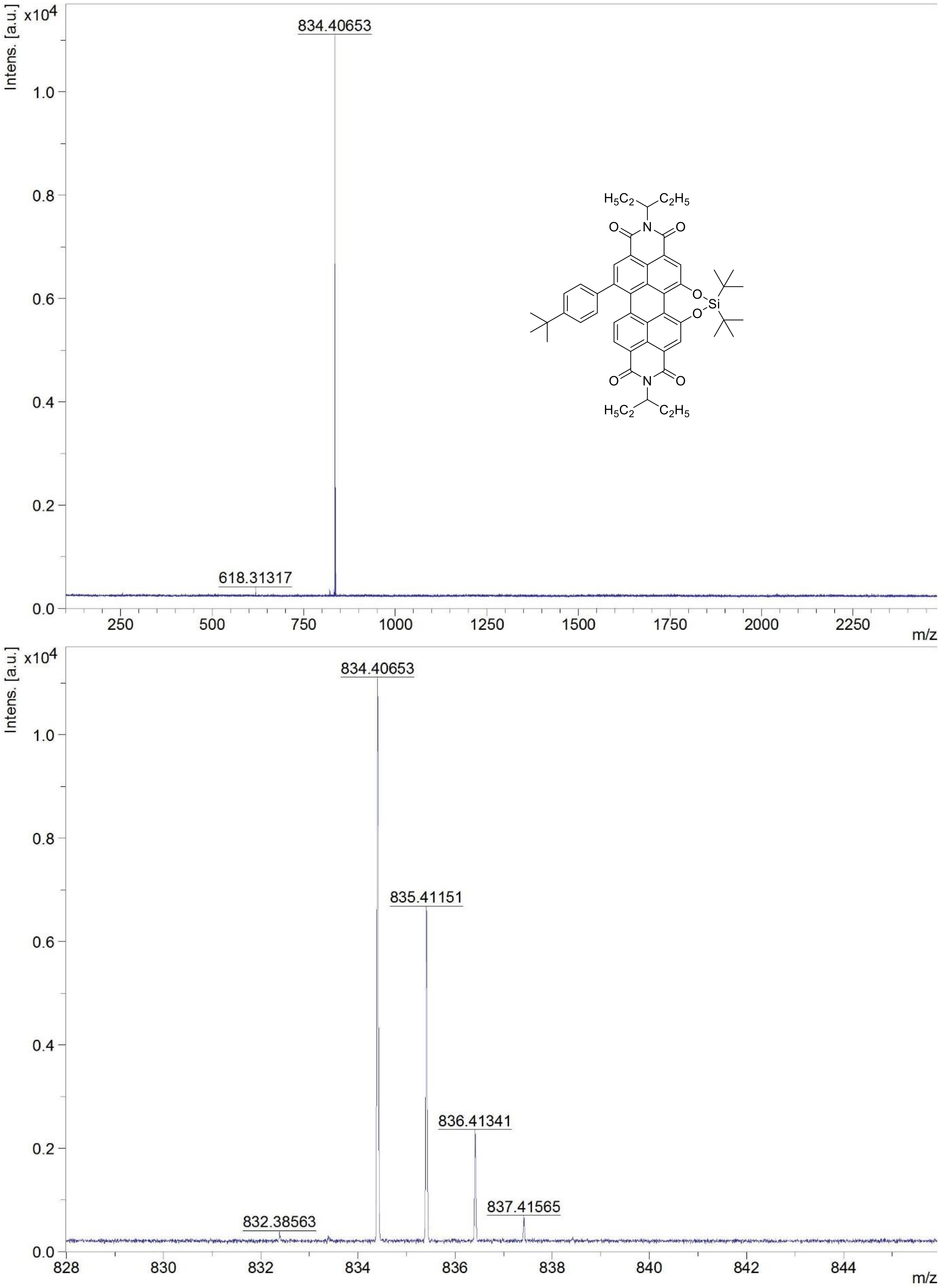


Figure S58. HRMS of compound **Ph-PBI-(O-Si-O)** (MALDI-TOF, negative mode, DCTB).

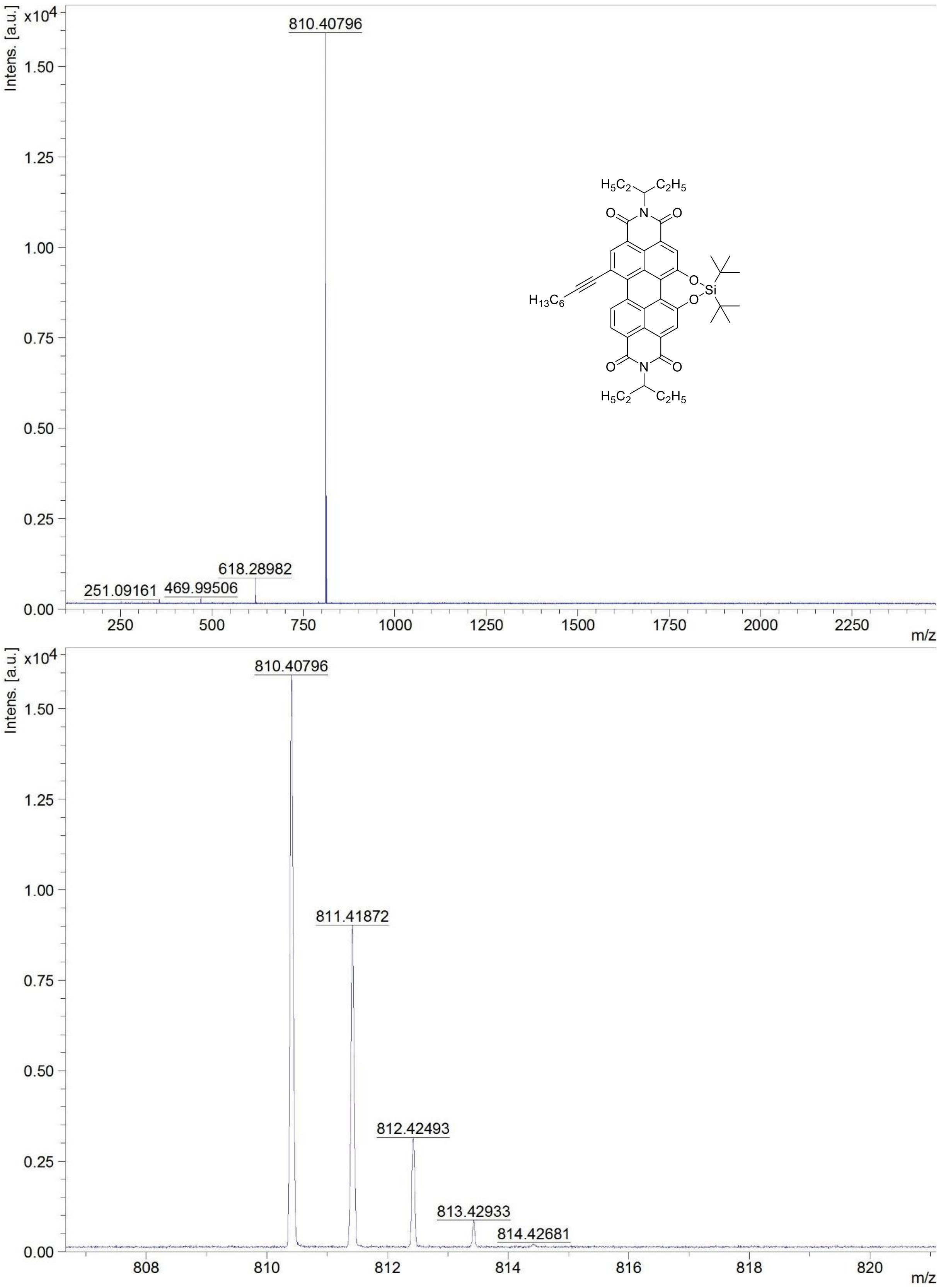


Figure S59. HRMS of compound **Octyne-PBI-(O-Si-O)** (MALDI-TOF, negative mode, DCTB).

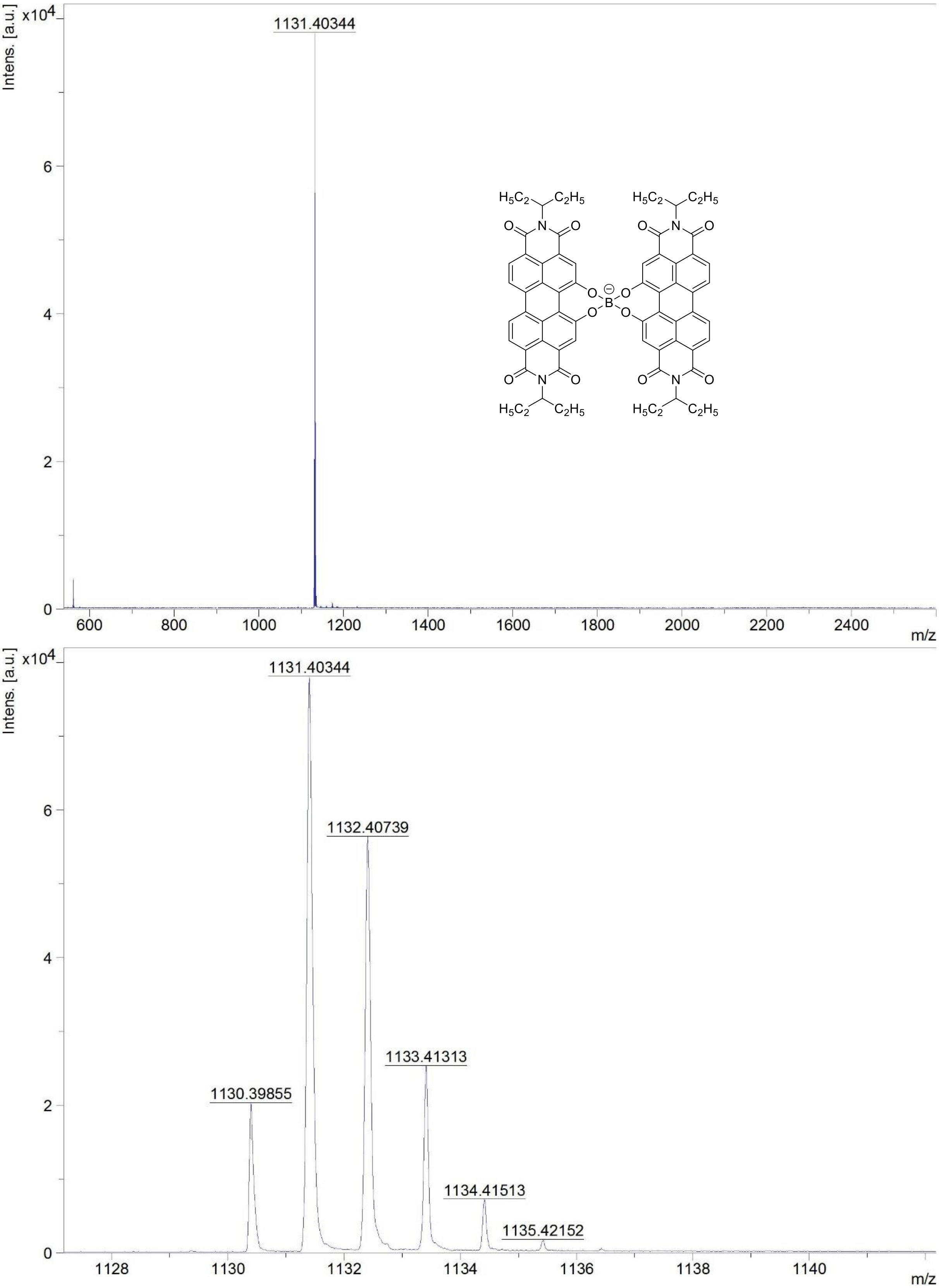


Figure S60. HRMS of compound **Spiro-PBI-Borate** (MALDI-TOF, negative mode, DCTB).

8. Supporting References

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