Electronic Supplementary Information

Boron Subphthalocyanine Axial Groups: A Comprehensive Set for Studying the Tuning of Photophysical and Electrochemical Properties

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Array of Axially Substituted BsubPcs

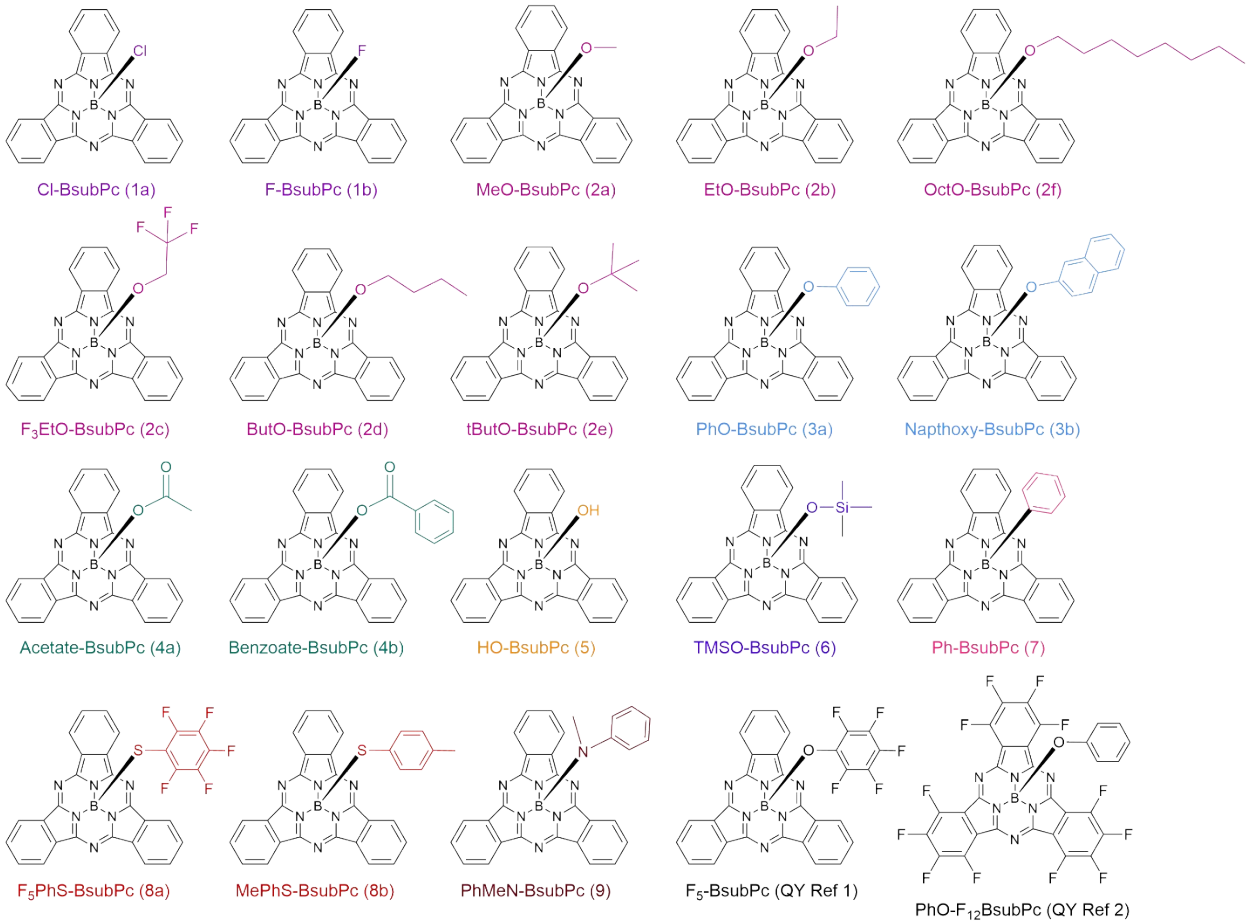


Figure S1. Structures of axially substituted BsubPcs and reference compounds used in relative QY calculations.

Synthetic Methods

Bromo-boron subphthalocyanine (Br-BsubPc). Br-BsubPc was prepared according to a modified literature procedure from Potz et al.[1] Phthalonitrile (42.3 g, 0.330 mol, 3.1 equiv), bromobenzene (136 mL), and toluene (362 mL) were added to an oven-dried 1 L three-neck round-bottom flask equipped with a glass stopper, an addition funnel, and a gas inlet under an inert atmosphere of argon gas. The addition funnel was charged with boron tribromide (10.0 mL, 0.106 mol, 1 equiv.), which was subsequently added to the reaction mixture dropwise. An immediate colour change to dark brown was observed. The reaction was allowed to stir at room temperature overnight. The following morning, the stirring was turned off, and the reaction left undisturbed for 1 hour. The reaction was gravity filtered, and the solid immediately washed with methanol (250 mL) and dried in a vacuum oven, resulting in a brown solid (23.1 g, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.91-8.93 (6H, dd), 7.96-7.98 (6H, dd). HRMS DART [$M+H^+$] exact mass calculated for $C_{24}H_{12}BN_6Br$ + H: m/z 475.0464 found 475.0473.

Chloro-boron subphthalocyanine (Cl-BsubPc, 1a). Cl-BsubPc was synthesized according to a method adapted from Zyskowski et al.[2] 44 mL of 1,2-dichlorobenzene was added to 1.067 g of phthalonitrile (8.33 mmol, 1 equiv.) in an argon-purged 250 mL three-neck round bottom flask. 20 mL (2.4 equiv.) of BCl_3 (1.0M in heptane) was then added and the mixture heated to 165°C for 1 hour to remove the heptane through distillation using a short-path condenser. After distillation, the short-path condenser was removed, and the reaction was heated at reflux (180 °C) for 1.5 hours. A positive pressure of argon was maintained throughout the reaction. The mixture was then cooled, and the solvent removed by rotary evaporation. The dry solid was placed in a cellulose thimble and washed with methanol in a Soxhlet extraction apparatus overnight. The solid was then dried in a vacuum oven at 50 °C overnight (0.393 g, 33% crude yield). The product was further purified

by train sublimation at 405 °C (113 mTorr) to yield 0.238 g of gold crystals (99.4% HPLC purity, 63% sublimation recovery). ^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.86-8.91 (6H, m), 7.91-7.95 (6H, m). ^{11}B NMR (128 MHz, $CDCl_3$): δ -13.54 (1B, s). HRMS DART [M+H$^+$] exact mass calculated for $C_{24}H_{12}BN_6Cl$ + H: m/z 431.0975 found 431.0978.

Fluoro-boron subphthalocyanine (F-BsubPc, 1b). F-BsubPc was synthesized as previously reported[3] and sublimed twice at 420 °C (99.6% HPLC purity, 25% recovery from first sublimation, 94% recovery from second sublimation). ^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.90-8.92 (6H, dd), 7.95-7.97 (6H, dd). ^{11}B NMR (128 MHz, $CDCl_3$): δ -14.13 (1B, d). HRMS DART [M+H$^+$] exact mass calculated for $C_{24}H_{12}BN_6F$ + H: m/z 415.1269 found 415.1273.

Synthesis of Axially Substituted Boron Subphthalocyanines. A temperature calibration of the hot plate used for all reactions was performed so that the external temperature could be correlated to the internal reaction temperature. Unless otherwise stated, an internal temperature of 75 °C was desired, which corresponds to an external temperature of 92 °C based on the conducted calibration (**Figure S135**). When possible, train sublimation was used for purification using the previously described apparatus.[4, 5] Sublimation temperature profiles are provided below (**Table S1 - S13**). Reaction progress was monitored by HPLC with a mobile phase of 80:20 (v:v) ACN/DMF, unless otherwise stated. All HPLC purities are reported for samples run with a mobile phase of 80:20 (v:v) ACN/DMF.

Methoxy-boron subphthalocyanine (MeO-BsubPc, 2a). Br-BsubPc (0.500 g, 1.05 mmol, 1 equiv.) and anhydrous chlorobenzene (11 mL) were stirred in an argon-purged 100 mL three-neck round-bottom flask. Methanol (0.43 mL, 10.52 mmol, 10 equiv.) was added and the mixture heated to 92 °C and stirred under a positive pressure of argon. HPLC reaction monitoring was conducted using a mobile phase of 95:5 ACN/DMF. The reaction reached ~95% conversion of Br-BsubPc in

the first 4 hours but did not react further overnight. An additional 0.22 mL (5 equiv.) of methanol was added 22 hours into the reaction, but no further conversion of Br-BsubPc was observed 3 hours after the second addition. An additional 1.0 mL (23.5 equiv.) of methanol was added and the reaction was stirred for another 2 hours, reaching 99% conversion of Br-BsubPc. The total reaction time was 28 hours. After cooling to room temperature, the solvent was removed by rotary evaporation to obtain the crude product (0.327 g, 73% crude yield, 95.5% HPLC purity). The crude product was purified by train sublimation at 300 °C (114 mTorr), resulting in 0.145 g of gold crystals (>99.9% HPLC purity, 46% sublimation recovery).^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.83-8.88 (6H, m), 7.88-7.93 (6H, m), 1.50 (3H, s). ^{11}B NMR (128 MHz, $CDCl_3$): δ -14.52 (1B, s). HRMS DART [M+H$^+$] exact mass calculated for $C_{25}H_{15}BN_6O$ + H: m/z 427.1480 found 427.1473.

Ethoxy-boron subphthalocyanine (EtO-BsubPc, 2b). Br-BsubPc (1.00 g, 2.10 mmol, 1 equiv.) and anhydrous chlorobenzene (22 mL) were stirred in an argon-purged 100 mL three-neck round-bottom flask. Absolute ethanol (1.23 mL, 21.05 mmol, 10 equiv.) was added and the mixture heated to 92 °C. The reaction was stirred under a positive pressure of argon for 4.5 hours until all of the Br-BsubPc was consumed. The solvent and excess ethanol were removed by short-path distillation and the crude product collected (0.664 g, 72% crude yield, 98.4% HPLC purity). The crude product was purified by train sublimation at 295 °C (112 mTorr), resulting in 0.210 g of gold crystals (99.4% HPLC purity, 33% sublimation recovery). ^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.83-8.87 (6H, m), 7.87-7.92 (6H, m), 1.49-1.55 (2H, q), 0.15-0.19 (3H, t). ^{11}B NMR (128 MHz, $CDCl_3$): δ -14.80 (1B, s). HRMS DART [M+H$^+$] exact mass calculated for $C_{26}H_{17}BN_6O$ + H: m/z 441.1629 found 441.1630.

Trifluoroethoxy-boron subphthalocyanine (F_3EtO-BsubPc, 2c). Br-BsubPc (1.00 g, 2.10 mmol, 1 equiv.) and anhydrous chlorobenzene (22 mL) were stirred in an argon-purged 100 mL three-neck round-bottom flask. 2,2,2-trifluoroethanol (1.51 mL, 21.05 mmol, 10 equiv.) was added and the mixture heated to 92 °C. The reaction was stirred under a positive pressure of argon for 22 hours until all of the Br-BsubPc was consumed. HPLC reaction monitoring was conducted using a mobile phase of 95:5 ACN/DMF. After cooling to room temperature, the solvent and excess trifluoroethanol were removed by rotary evaporation and the crude product collected (0.658 g, 63% crude yield, 94.4% HPLC purity). The crude product was purified by train sublimation at 305 °C (118 mTorr), resulting in 0.357 g of gold crystals (99.9% HPLC purity, 58% sublimation recovery). ^{1}H NMR (400 MHz, $CDCl_3$, Me4 Si): δ 8.85-8.89 (6H, m), 7.92-7.94 (6H, m), 1.82-1.89 (2H, q). ^{11}B NMR (128 MHz, $CDCl_3$): δ -14.65 (1B, s). HRMS DART [M+H$^+$] exact mass calculated for $C_{26}H_{14}BN_6OF_3$ + H: m/z 495.1346 found 495.1347.

Butoxy-boron subphthalocyanine (ButO-BsubPc, 2d). Br-BsubPc (1.00 g, 2.10 mmol, 1 equiv.) and anhydrous chlorobenzene (22 mL) were stirred in an argon-purged 100 mL three-neck round-bottom flask. 1-Butanol (0.96 mL, 10.52 mmol, 5 equiv.) was added and the mixture heated to 92 °C. The reaction was stirred under a positive pressure of argon for 22 hours until all of the Br-BsubPc was consumed. After cooling to room temperature, the solvent was removed by rotary evaporation and the crude product collected (1.070 g, 109% crude yield, 96.7% HPLC purity). The crude product was purified by train sublimation at 265 °C (108 mTorr), resulting in 0.325 g of gold crystals (99.7% HPLC purity, 31% sublimation recovery). ^{1}H NMR (400 MHz, $CDCl_3$, Me4 Si): δ 8.83-8.87 (6H, m), 7.87-7.92 (6H, m), 1.42-1.45 (2H, t), 0.45-0.56 (4H, m), 0.40-0.43 (3H, t). ^{11}B NMR (128 MHz, $CDCl_3$): δ -14.78 (1B, s). HRMS DART [M+H$^+$] exact mass calculated for $C_{28}H_{21}BN_6O$ + H: m/z 469.1935 found 469.1943.

Tertbutoxy-boron subphthalocyanine (tButO-BsubPc, 2e). Br-BsubPc (0.500 g, 1.05 mmol, 1 equiv.) and anhydrous chlorobenzene (11 mL) were stirred in an argon-purged 50 mL three-neck round-bottom flask. Tert-butanol (1.01 mL, 10.52 mmol, 10 equiv.) was added and the mixture heated to 92 °C. After stirring for 24 hours, ~98% of the Br-BsubPc had been consumed. Another 1.01 mL of tert-butanol (10 equiv.) was added at this point, but no further conversion was observed after 2 hours, so the reaction was cooled to room temperature. The total reaction time was 26 hours. The solvent was removed by rotary evaporation and the crude dried in a vacuum oven for 3 hours to yield 0.493 g of gold solids (100% crude yield, 63.0% HPLC purity). The crude product was purified by column chromatography on standard basic alumina with an eluent of 5:1 DCM/Hexanes, yielding 49 mg of gold powder with 99.5% HPLC purity (10% column recovery) and 98 mg of gold powder with 98.8% HPLC purity (20% column recovery). ^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.81-8.86 (6H, m), 7.86-7.90 (6H, m), 0.04 (9H, s). ^{11}B NMR (128 MHz, $CDCl_3$): δ -15.51 (1B, s). HRMS DART [M+H$^+$] exact mass calculated for $C_{28}H_{21}BN_6O$ + H: m/z 469.1940 found 469.1943.

Octoxy-boron subphthalocyanine (OctO-BsubPc, 2f). Br-BsubPc (1.00 g, 2.10 mmol, 1 equiv.) and anhydrous chlorobenzene (22 mL) were stirred in an argon-purged 100 mL three-neck round-bottom flask. 1-Octanol (1.7 mL, 10.52 mmol, 5 equiv.) was added and the mixture heated to 92 °C. The reaction was stirred under a positive pressure of argon for 23 hours until all of the Br-BsubPc was consumed. After cooling to room temperature, the solvent was removed by rotary evaporation, but excess octanol remained. A minimal amount of hexanes was added to the residue, which dissolved most of the product but not the impurities. The solids were separated by gravity filtration and the hexanes removed from the filtrate by rotary evaporation, once again leaving the crude slightly wet with octanol. The crude was washed with methanol and gravity filtered to collect

0.502 g of crude material (45% crude yield, 97.9% HPLC purity). The crude product was purified by train sublimation at 275 °C (112 mTorr). The sublimed product deposited as a thick pink film on the sublimation insert, which broke up into gold chunks when scraped with a spatula. 0.090 g of sublimed material was collected (98.6% HPLC purity, 20% sublimation recovery).^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.83-8.87 (6H, m), 7.87-7.92 (6H, m), 1.41-1.45 (2H, t), 1.06-1.13 (2H, p), 0.87-1.01 (4H, m), 0.75-0.79 (5H, t), 0.46-0.49 (4H, p). ^{11}B NMR (400 MHz, $CDCl_3$): δ -14.77 (1B, s). HRMS DART [M+H$^+$] exact mass calculated for $C_{32}H_{29}BN_6O$ + H: m/z 525.2561 found 525.2569.

Phenoxy-boron subphthalocyanine (PhO-BsubPc, 3a). Br-BsubPc (0.500 g, 1.05 mmol, 1 equiv.) and anhydrous chlorobenzene (11 mL) were stirred in an argon-purged 50 mL three-neck round-bottom flask. Phenol (0.495 g, 5.26 mmol, 5 equiv.) was added and the mixture heated to 92 °C. The reaction was stirred under a positive pressure of argon for 1 hour until all of the Br-BsubPc was consumed. After cooling to room temperature, the solvent was removed by rotary evaporation and the resulting crude was washed with 50 mL of a 4:1 methanol/water mixture to remove the excess phenol. 0.270 g of crude material was collected by vacuum filtration (53% crude yield, 97.5% HPLC purity). The crude product was further purified by train sublimation at 330 °C (112 mTorr), resulting in 0.165 g of gold crystals (99.7% HPLC purity, 67% sublimation recovery). ^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.83-8.87 (6H, m), 7.89-7.93 (6H, m), 6.73-6.77 (2H, m), 6.60-6.63 (1H, t), 5.38-5.40 (2H, m). ^{11}B NMR (128 MHz, $CDCl_3$): δ -14.79 (1B, s). HRMS DART [M+H$^+$] exact mass calculated for $C_{30}H_{17}BN_6O$ + H: m/z 489.1622 found 489.1630.

β-Naphthoxy-boron subphthalocyanine (Naphthoxy-BsubPc, 3b). Br-BsubPc (0.500 g, 1.05 mmol, 1 equiv.) and anhydrous chlorobenzene (11 mL) were stirred in an argon-purged 50 mL three-neck round-bottom flask. 2-naphthol (0.300 g, 2.63 mmol, 2.5 equiv.) was added and the

mixture heated to 92 °C. The reaction was stirred under a positive pressure of argon for 2 hours until all of the Br-BsubPc was consumed. After cooling to room temperature, the solvent was removed by rotary evaporation and the resulting crude was washed with 100 mL of a 4:1 methanol/water mixture to remove the excess naphthol. 0.372 g of crude material was collected by vacuum filtration (66% crude yield, 98.2% HPLC purity). The crude product was further purified by train sublimation at 315 °C (115 mTorr), resulting in 0.107 g of gold crystals (>99.9% HPLC purity, 40% sublimation recovery). ^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.84-8.88 (6H, m), 7.89-7.93 (6H, m), 7.49-7.51 (1H, d), 7.35-7.37 (1H, d), 7.23-7.24 (1H, d), 7.22 (1H, s), 7.15-7.19 (1H, m), 5.70-5.71 (1H, d), 5.65-5.68 (1H, dd). ^{11}B NMR (128 MHz, $CDCl_3$): δ -14.69 (1B, s). HRMS DART [M+H$^+$] exact mass calculated for $C_{34}H_{19}BN_6O$ + H: m/z 539.1791 found 539.1786.

Acetate-boron subphthalocyanine (Acetate-BsubPc, 4a). Br-BsubPc (1.00 g, 2.10 mmol, 1 equiv.) and anhydrous chlorobenzene (22 mL) were stirred in an argon-purged 100 mL three-neck round-bottom flask. Glacial acetic acid (0.60 mL, 10.52 mmol, 5 equiv.) was added and the mixture heated to 92 °C. The reaction was stirred under a positive pressure of argon for 24 hours until all of the Br-BsubPc was consumed. HPLC reaction monitoring was conducted using a mobile phase of 95:5 ACN/DMF. After cooling to room temperature, the reaction mixture was added to 250 mL of stirring hexanes to precipitate the product, which was collected by vacuum filtration (0.863 g, 90% crude yield, 97.7% HPLC purity). The crude product was purified by train sublimation at 290 °C (111 mTorr), resulting in 0.448 g of gold crystals (99.3% HPLC purity, 58% sublimation recovery). ^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.86-8.90 (6H, m), 7.88-7.93 (6H, m), 1.05 (3H, s). ^{11}B NMR (128 MHz, $CDCl_3$): δ -15.24 (1B, s). HRMS DART [M+H$^+$] exact mass calculated for $C_{26}H_{15}BN_6O_2$ + H: m/z 455.1417 found 455.1422.

Benzoate-boron subphthalocyanine (Benzoate-BsubPc, 4b). Br-BsubPc (1.00 g, 2.10 mmol, 1 equiv.) and anhydrous chlorobenzene (22 mL) were stirred in an argon-purged 100 mL three-neck round-bottom flask. Benzoic acid (1.285 g, 10.52 mmol, 5 equiv.) was added and the mixture heated to 92 °C. The reaction was stirred under a positive pressure of argon for 27 hours until all of the Br-BsubPc was consumed. HPLC reaction monitoring was conducted using a mobile phase of 95:5 ACN/DMF. After cooling to room temperature, the reaction mixture was added to 250 mL of stirring hexanes to precipitate the product, which was collected by vacuum filtration and dried under vacuum (1.215 g, 112% crude yield, 93.9% HPLC purity). The crude product was purified by train sublimation at 355 °C (112 mTorr), resulting in 0.448 g of gold crystals (99.1% HPLC purity, 45% sublimation recovery). ^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.88-8.93 (6H, m), 7.90-7.95 (6H, m), 7.17-7.22 (1H, m), 7.14-7.18 (2H, m), 6.98-7.01 (2H, m). ^{11}B NMR (400 MHz, $CDCl_3$): δ -14.65 (1B, s). HRMS DART [M+H$^+$] exact mass calculated for $C_{31}H_{17}BN_6O_2$ + H: m/z 517.1586 found 517.1579.

Hydroxy-boron subphthalocyanine (HO-BsubPc, 5). HO-BsubPc was synthesized according to a method adapted from Paton and Bender.[6] Br-BsubPc (1.00 g, 2.10 mmol, 1 equiv.) was added to a 3:1 (v:v) mixture of acetone (93 mL) and water (31 mL) in a 250 mL one-neck round-bottom flask. The mixture was stirred and heated at 60°C for 20 hours until all of the Br-BsubPc was consumed. After cooling to room temperature, the volatiles were removed by rotary evaporation to yield 0.903 g of crude material (104% crude yield, 95.7% HPLC purity) The crude product was purified by train sublimation at 420 °C (112 mTorr), resulting in 31 mg of gold powder (99.9% HPLC purity, 4% sublimation recovery). ^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.79-8.84 (6H, m), 7.86-7.91 (6H, m). ^{11}B NMR (128 MHz, $CDCl_3$): δ -15.07 (1B, s). HRMS DART [M+H$^+$] exact mass calculated for $C_{24}H_{13}BN_6O$ + H: m/z 413.1322 found 413.1317.

Trimethylsiloxy-boron subphthalocyanine (TMSO-BsubPc, 6). Br-BsubPc (1.00 g, 2.10 mmol, 1 equiv.) and anhydrous chlorobenzene (44 mL) were stirred in an argon-purged 100 mL three-neck round-bottom flask. Trimethylsilanol (1.2 mL, 10.52 mmol, 5 equiv.) was added and the mixture heated to 50 °C. The reaction was stirred at 50 °C under a positive pressure of argon for 23 hours, then 92 °C for an additional 27 hours. The reaction stalled at ~70% conversion of Br-BsubPc. After cooling to room temperature, the solvent was removed by rotary evaporation and the crude product collected (0.920 g, 90% crude yield, 65.8% HPLC purity). A portion of the crude product was purified by column chromatography on standard basic alumina with an eluent of 1:1 DCM/Hexanes, yielding 37 mg of gold powder with >99.9% HPLC purity (7% column recovery). The remaining crude was purified by train sublimation at 350 °C (113 mTorr), resulting in 15 mg of gold powder (94.7% HPLC purity, 4% sublimation recovery). ^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.83-8.86 (6H, dd), 7.88-7.90 (6H, dd), -0.83 (9H, s). ^{11}B NMR (128 MHz, $CDCl_3$): δ -16.20 (1B, s). HRMS DART [M+H$^+$] exact mass calculated for $C_{27}H_{21}Bn_6Osi$ + H: m/z 485.1718 found 485.1712.

Phenyl-boron subphthalocyanine (Ph-BsubPc, 7). Ph-BsubPc was synthesized according to a method adapted from Bonnier et al.[7] Br-BsubPc (0.500 g, 1.05 mmol, 1 equiv.) and anhydrous tetrahydrofuran (82.5 mL) were stirred in an argon-purged 250 mL three-neck round-bottom flask. Phenylmagnesium bromide (1.0M in THF) (2.63 mL, 2.63 mmol, 2.5 equiv.) was added dropwise and the mixture heated to reflux for 45 h. After cooling to room temperature, the excess phenylmagnesium bromide was quenched with 2 mL of methanol and stirred for 10 – 15 minutes. The reaction mixture was gravity filtered to remove insoluble salts from the quenched Grignard reagent. Volatiles were removed by rotary evaporation and the crude product collected (0.552 g, 111% crude yield, 16.3% HPLC purity). The crude product was purified by column

chromatography on standard basic alumina with an eluent of 2:1 DCM/Hexanes, yielding 31 mg of product (6% column recovery, 89.0% HPLC purity). ^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.84-8.87 (6H, m), 7.88-7.92 (6H, m), 6.70-6.73 (1H, t), 6.56-6.60 (2H, m), 5.43-5.45 (2H, d). HRMS DART [M+H$^+$] exact mass calculated for $C_{30}H_{17}BN_6$ + H: m/z 473.1680 found 473.1681.

Pentafluorothiophenoxy-boron subphthalocyanine (F_5PhS-BsubPc, 8a). Br-BsubPc (0.500 g, 1.05 mmol, 1 equiv.) and anhydrous chlorobenzene (11 mL) were stirred in an argon-purged 100 mL three-neck round-bottom flask. Pentafluorothiophenol (0.7 mL, 5.26 mmol, 5 equiv.) was added and the mixture heated to 92 °C. The reaction was stirred under a positive pressure of argon for 96 hours until no additional conversion of Br-BsubPc was observed. Chlorobenzene and excess pentafluorothiophenol were removed by short-path distillation, and the resulting crude was collected (0.431 g, 69% crude yield, 45.6% HPLC purity). The crude product was purified by column chromatography on standard basic alumina with an eluent of 1:1 DCM/Hexanes, yielding 18 mg of product with 98.1% HPLC purity (4% column recovery). ^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.85-8.87 (6H, dd), 7.94-7.96 (6H, dd). ^{11}B NMR (128 MHz, $CDCl_3$): δ -13.55 (1B, s). HRMS DART [M+H$^+$] exact mass calculated for $C_{30}H_{12}BN_6SF_5$ + H: m/z 595.0932 found 595.0930.

4-Methylthiophenoxy-boron subphthalocyanine (MePhS-BsubPc, 8b). Br-BsubPc (0.500 g, 1.05 mmol, 1 equiv.) and anhydrous chlorobenzene (11 mL) were stirred in an argon-purged 50 mL three-neck round-bottom flask. 1.307 g of p-toluenthiol (10.52 mmol, 10 equiv.) was added and the mixture heated to 92 °C. The reaction was stirred under a positive pressure of argon for 44 hours until all of the Br-BsubPc was consumed. HPLC reaction monitoring was conducted using a mobile phase of 95:5 ACN/DMF. After cooling to room temperature, the reaction mixture was added to 130 mL of stirring hexanes to precipitate the product and remove excess p-toluenethiol.

0.454 g of crude product was collected by vacuum filtration (83% crude yield, 71.9% HPLC purity). The crude product was purified by chromatography though a plug of standard basic alumina with DCM as the eluent. DCM was removed by rotary evaporation, and the resulting product recrystallized from THF/pentane. The final recrystallized product was collected by vacuum filtration (7 mg, 98.5% HPLC purity, 2% plug yield). ^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.81-8.83 (6H, dd), 7.89-7.92 (6H, dd), 6.67-6.69 (2H, d), 6.06-6.08 (2H, d), 2.24 (3H, s). ^{11}B NMR (128 MHz, $CDCl_3$): δ -13.36 (1B, s). HRMS DART [$M+H^+$] exact mass calculated for $C_{31}H_{19}BN_6S$ + H: m/z 519.1568 found 519.1558.

N-Phenyl-N-methyl-amino-boron subphthalocyanine (PhMeN-BsubPc, 9). Br-BsubPc (1.00 g, 2.10 mmol, 1 equiv.) and anhydrous chlorobenzene (22 mL) were stirred in an argon-purged 100 mL three-neck round-bottom flask. N-methylaniline (2.28 mL, 21.05 mmol, 10 equiv.) was added and the mixture heated to 92 °C. The reaction was stirred under a positive pressure of argon for 26 hours until all of the Br-BsubPc was consumed. After cooling to room temperature, the reaction mixture was added to 300 mL of stirring hexanes to precipitate the product, which was collected by vacuum filtration (0.610 g, 58% crude yield, 49.0% HPLC purity). The crude product was purified by column chromatography on standard basic alumina with an eluent of 5:1 DCM/Hexanes. The solvent was removed by rotary evaporation, yielding a pink oil. The oil was recrystallized from THF/pentane, yielding gold crystals that were collected by filtration (15 mg, >99.9% HPLC purity, 3% column recovery). Additional pentane was added to the filtrate and left in a fridge overnight to yield a second crop of gold crystals (62 mg, 99.2% HPLC purity, 10% column recovery). ^{1}H NMR (400 MHz, $CDCl_3$, Me4Si): δ 8.80-8.84 (6H, dd), 7.86-7.91 (6H, m), 6.71-6.75 (2H, t), 6.51-6.55 (1H, t), 5.45-5.47 (2H, d), 1.07 (3H, s). ^{11}B NMR (128 MHz, $CDCl_3$):

δ -15.20 (1B, s). HRMS DART [M+H$^+$] exact mass calculated for $C_{31}H_{20}BN_7$ + H: m/z 502.1953 found 502.1946.

Pentafluorophenoxy-boron subphthalocyanine (F_5-BsubPc). F_5-BsubPc was synthesized as previously reported.[4]

Phenoxy-dodecafluoro boron subphthalocyanine (PhO-F_{12}BsubPc). PhO-F_{12}BsubPc was synthesized as previously reported.[4]

Sublimation Temperature Profiles

Our in-house train sublimation apparatus has been previously described in detail.[4, 5] A "ramp and soak" heating method was used whereby the ramp time indicates the time to heat up from the previous temperature to the set temperature and the soak time indicates the amount of time spent at the set temperature. The temperature profiles used for the BsubPcs that were purified by train sublimation are provided below. In general, the first set temperature of (150 – 165 °C) is used to remove any small organics or volatiles, and the second set temperature is the sublimation temperature of the BsubPc. The temperature profile for HO-BsubPc (**5**) (**Table S12**) followed a previously reported method.[8]

Table S1. Train Sublimation Temperature Profile used for Cl-BsubPc (**1a**)

Temperature (°C)	Ramp Time (hours)	Soak Time (hours)
150	1	1
405	1	18
25	2	50

Table S2. Train Sublimation Temperature Profile used for F-BsubPc (**1b**)

Temperature (°C)	Ramp Time (hours)	Soak Time (hours)
150	1	1
420	1	20
25	1	50

Table S3. Train Sublimation Temperature Profile used for MeO-BsubPc (**2a**)

Temperature (°C)	Ramp Time (hours)	Soak Time (hours)
150	1	1
300	1	18
25	2	50

Table S4. Train Sublimation Temperature Profile used for EtO-BsubPc (**2b**)

Temperature (°C)	Ramp Time (hours)	Soak Time (hours)
150	1	1
295	1	18
25	2	50

Table S5. Train Sublimation Temperature Profile used for F_3EtO-BsubPc (**2c**)

Temperature (°C)	Ramp Time (hours)	Soak Time (hours)
165	1	1
305	1	18
25	2	50

Table S6. Train Sublimation Temperature Profile used for ButO-BsubPc (**2d**)

Temperature (°C)	Ramp Time (hours)	Soak Time (hours)
150	1	1
265	1	18
25	2	50

Table S7. Train Sublimation Temperature Profile used for OctO-BsubPc (**2f**)

Temperature (°C)	Ramp Time (hours)	Soak Time (hours)
150	1	1
275	1	18
25	2	50

Table S8. Train Sublimation Temperature Profile used for PhO-BsubPc (**3a**)

Temperature (°C)	Ramp Time (hours)	Soak Time (hours)
150	1	1
330	1	18
25	2	50

Table S9. Train Sublimation Temperature Profile used for Naphthoxy-BsubPc (**3b**)

Temperature (°C)	Ramp Time (hours)	Soak Time (hours)
150	1	1
315	1	18
25	2	50

Table S10. Train Sublimation Temperature Profile used for Acetate-BsubPc (**4a**)

Temperature (°C)	Ramp Time (hours)	Soak Time (hours)
150	1	1
290	1	18
25	2	50

Table S11. Train Sublimation Temperature Profile used for Benzoate-BsubPc (**4b**)

Temperature (°C)	Ramp Time (hours)	Soak Time (hours)
150	1	1
250	1	1
355	1	18
25	2	50

Table S12. Train Sublimation Temperature Profile used for HO-BsubPc (**5**)[8]

Temperature (°C)	Ramp Time	Soak Time
120	10 min	30 min
180	10 min	30 min
220	10 min	1 h
320	1h 40 min	1 h
420	5.5 h	8 h
25	2 h	50 h

Table S13. Train Sublimation Temperature Profile used for TMSO-BsubPc (**6**)

Temperature (°C)	Ramp Time (hours)	Soak Time (hours)
150	1	1
250	1	1
350	1	18
25	1	50

HPLC Maxplots, NMR Spectroscopy, and Mass Spectrometry

Characterization by HPLC, NMR, and mass spectrometry of the purified axially substituted BsubPcs is provided below.

Cl-BsubPc (1a)

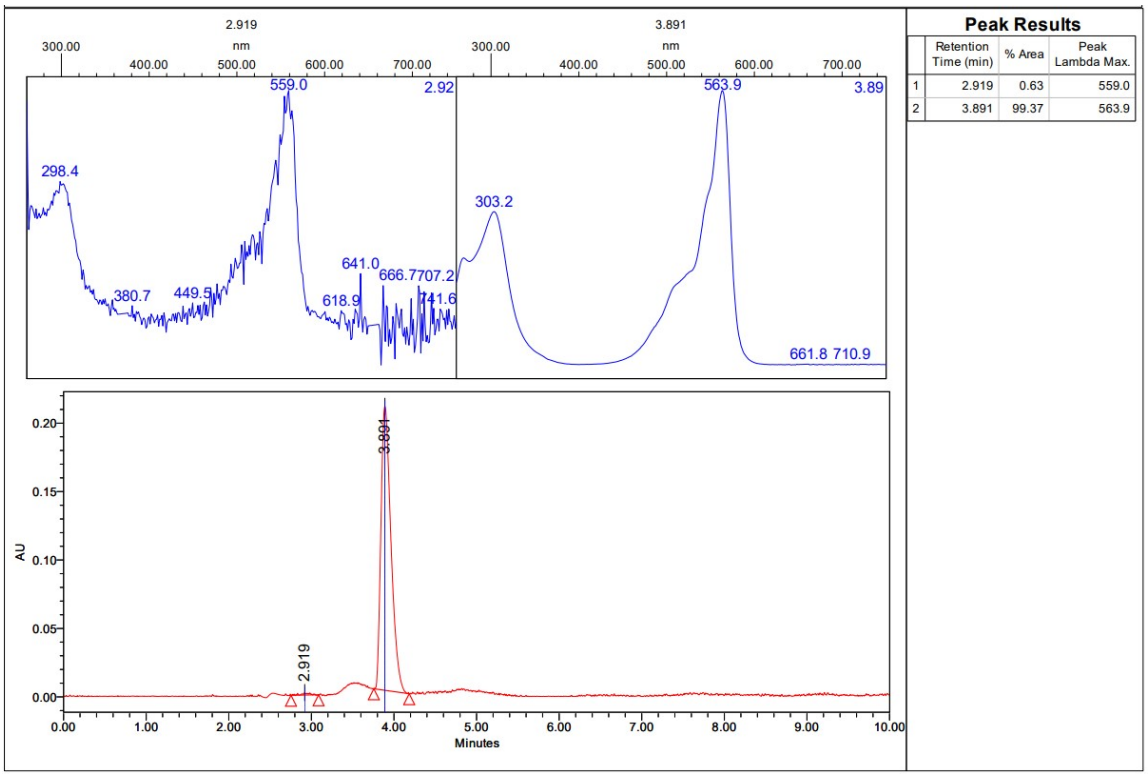


Figure S2. HPLC maxplot of sublimed Cl-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. Cl-BsubPc has a retention time of 3.891 minutes. The unintegrated peak around 3.6 minutes was confirmed to be an impurity in the HPLC solvent system.

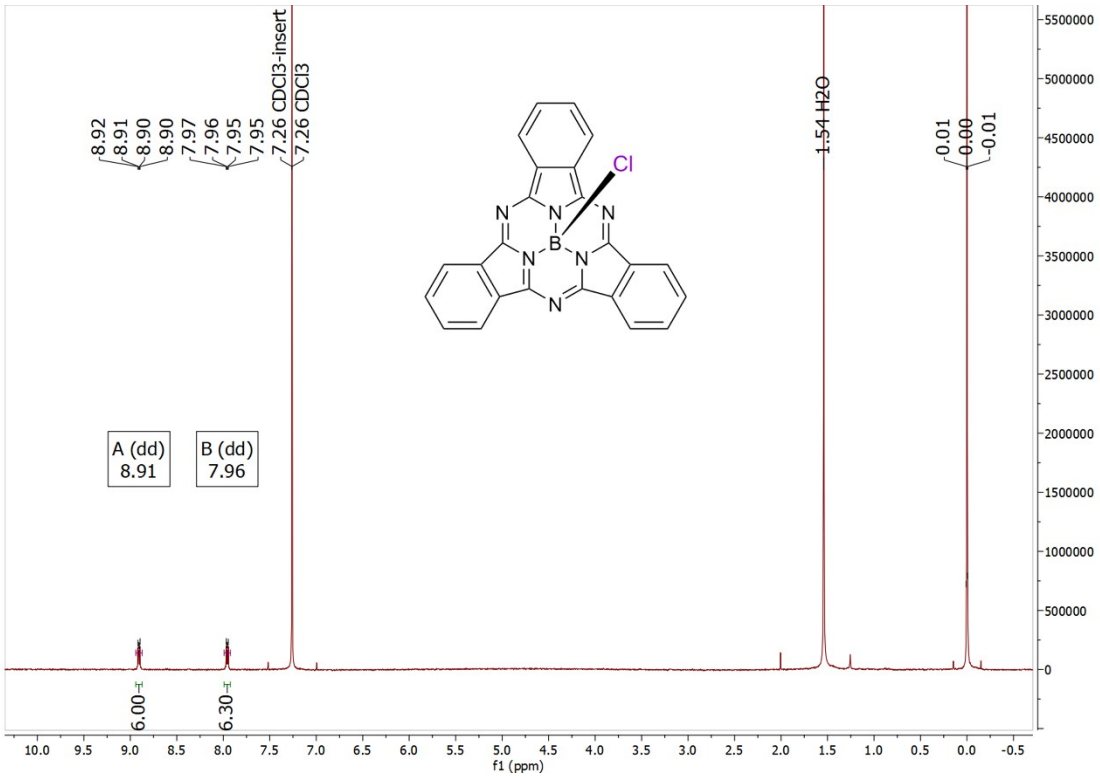


Figure S3. ^{1}H NMR spectrum of sublimed Cl-BsubPc (400 MHz, $CDCl_3$).

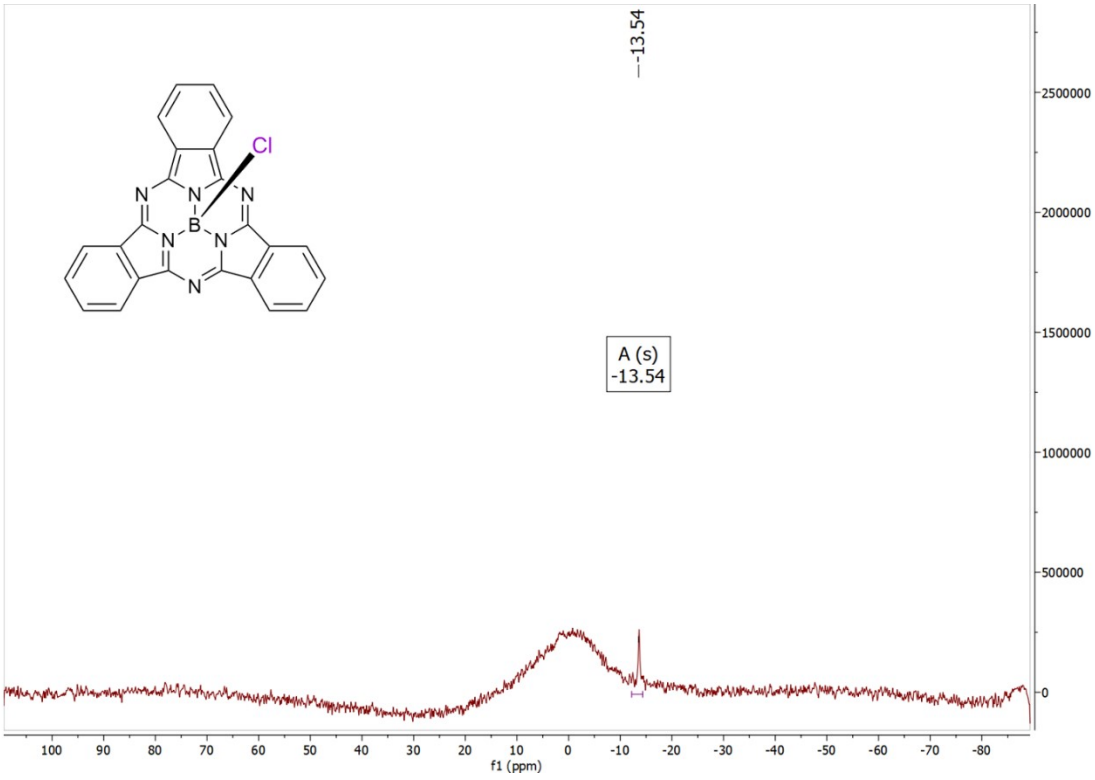


Figure S4. ^{11}B NMR spectrum of sublimed Cl-BsubPc (128 MHz, $CDCl_3$).

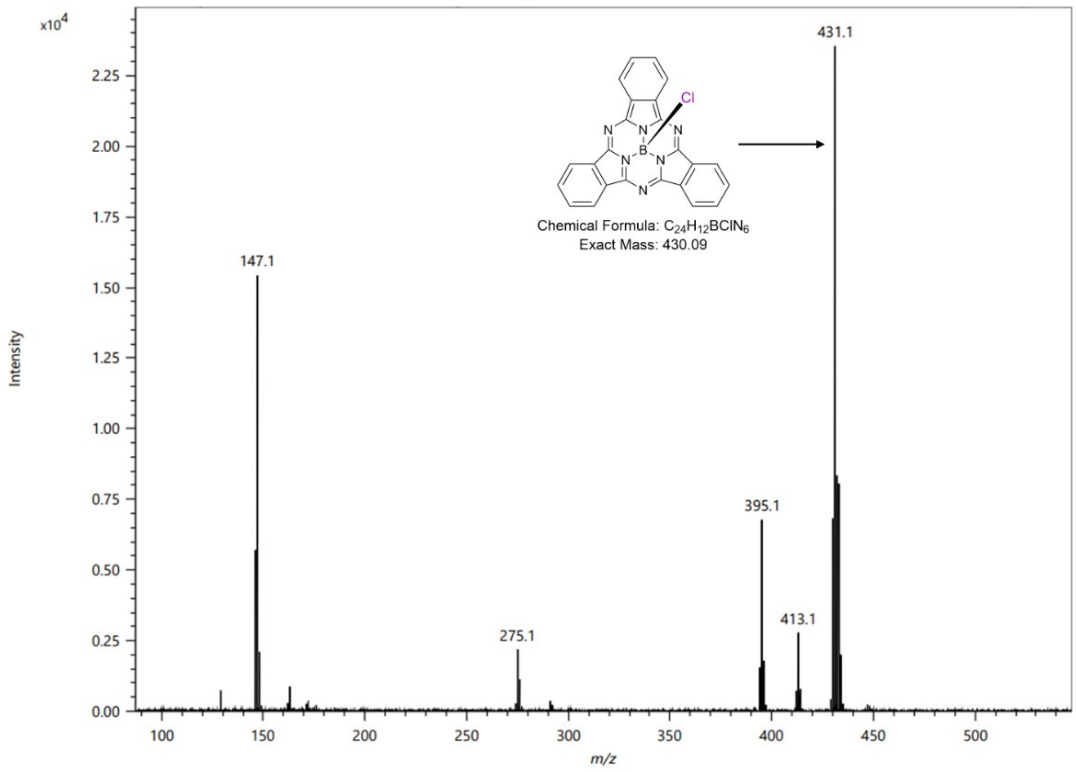
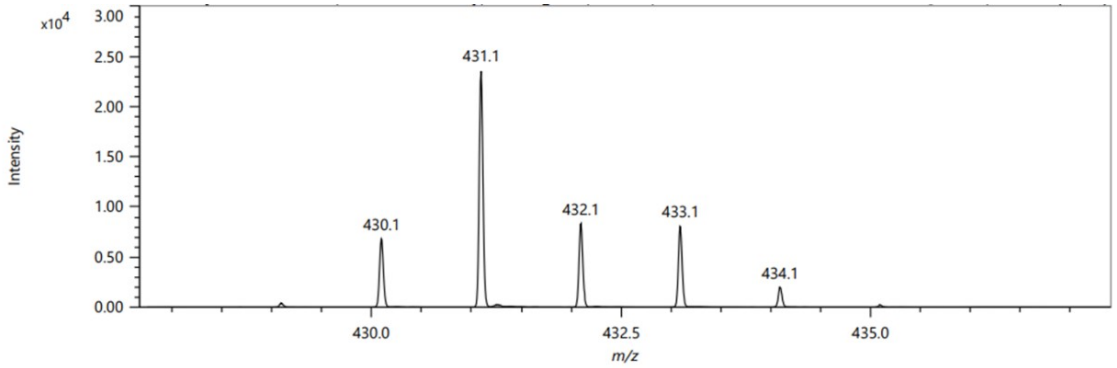


Figure S5. DART-MS [M+H] of sublimed Cl-BsubPc.



Elemental Composition

Parameters		Elements Set 1:						
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	Cl	B
Electron:	Even	Min	0	0	0	0	1	1
Charge:	+1	Max	100	200	20	10	1	1
DBE:	-1.5 - 100.0							

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
431.09753	23545.77	C24 H13 B N6 Cl ←	431.09778	-0.25	-0.59	21.5
		C10 H25 B O15 Cl	431.09695	0.57	1.33	-1.5
		C11 H21 B N4 O11 Cl	431.09829	-0.77	-1.78	3.5
		C23 H17 B N2 O4 Cl	431.09644	1.08	2.52	16.5
		C7 H17 B N10 O9 Cl	431.09561	1.92	4.45	4.5
		C12 H17 B N8 O7 Cl	431.09963	-2.10	-4.88	8.5

Figure S6. Zoomed-in DART-HRMS [M+H] of sublimed Cl-BsubPc.

F-BsubPc (1b)

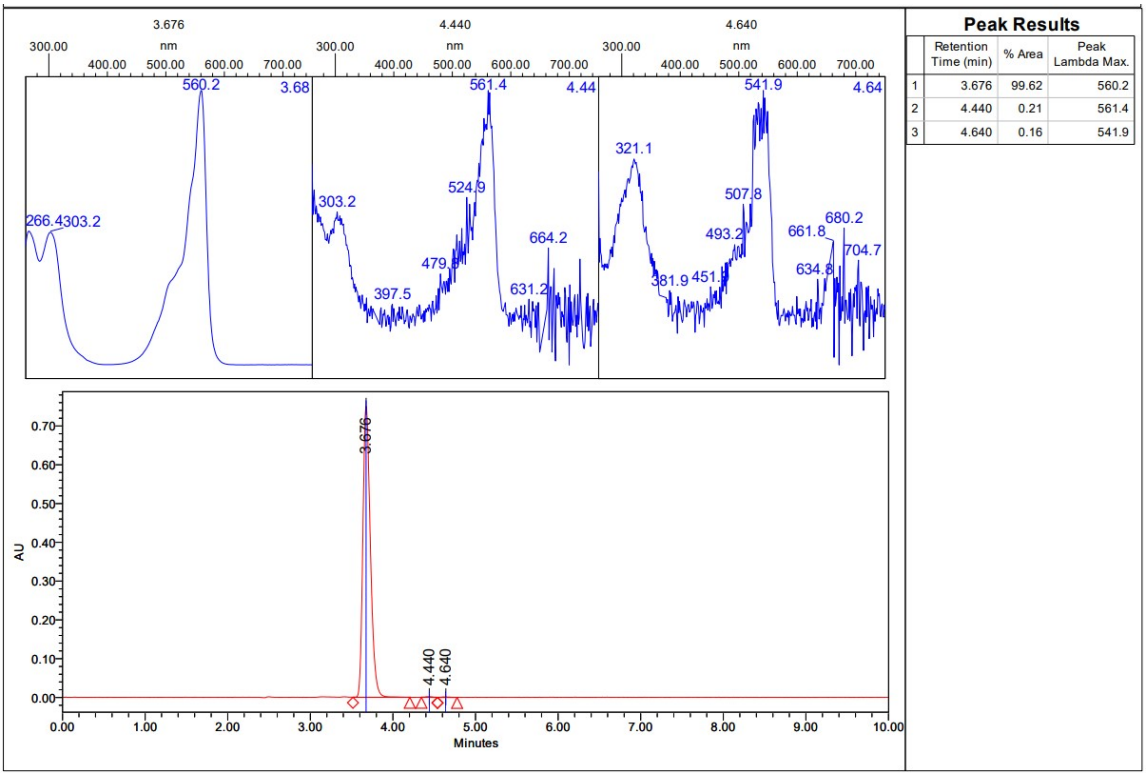


Figure S7. HPLC maxplot of sublimed F-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. F-BsubPc has a retention time of 3.676 minutes.

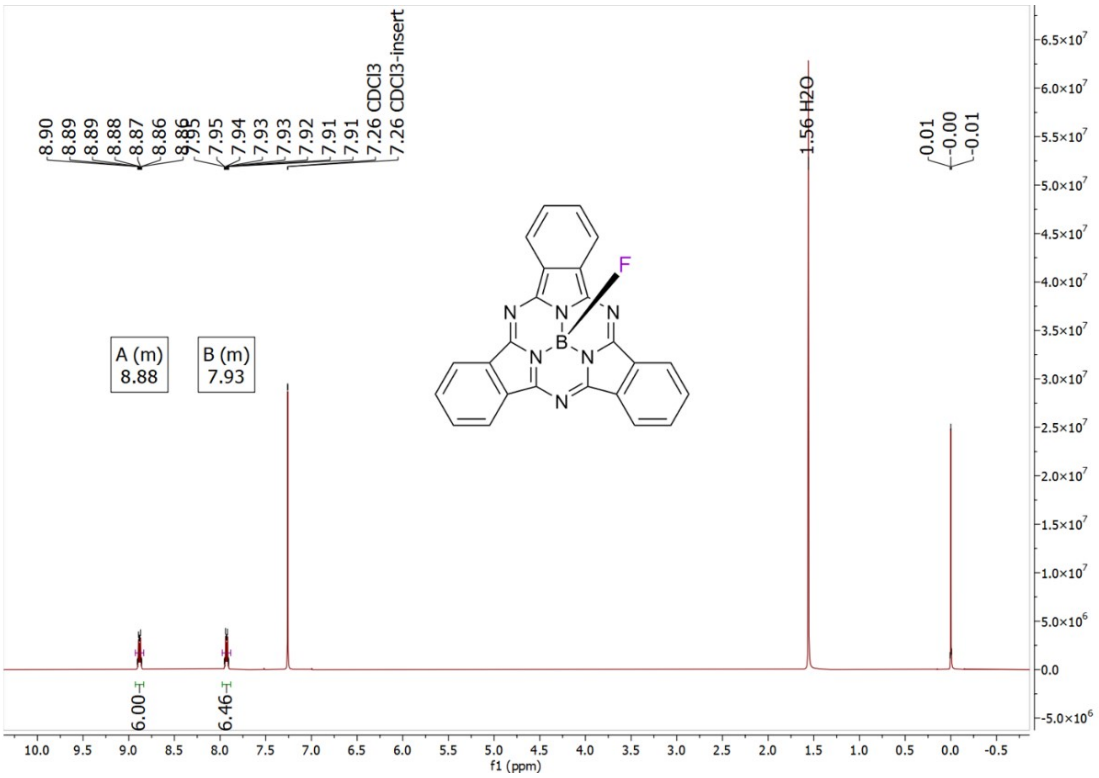


Figure S8. ^{1}H NMR spectrum of sublimed F-BsubPc (400 MHz, $CDCl_3$).

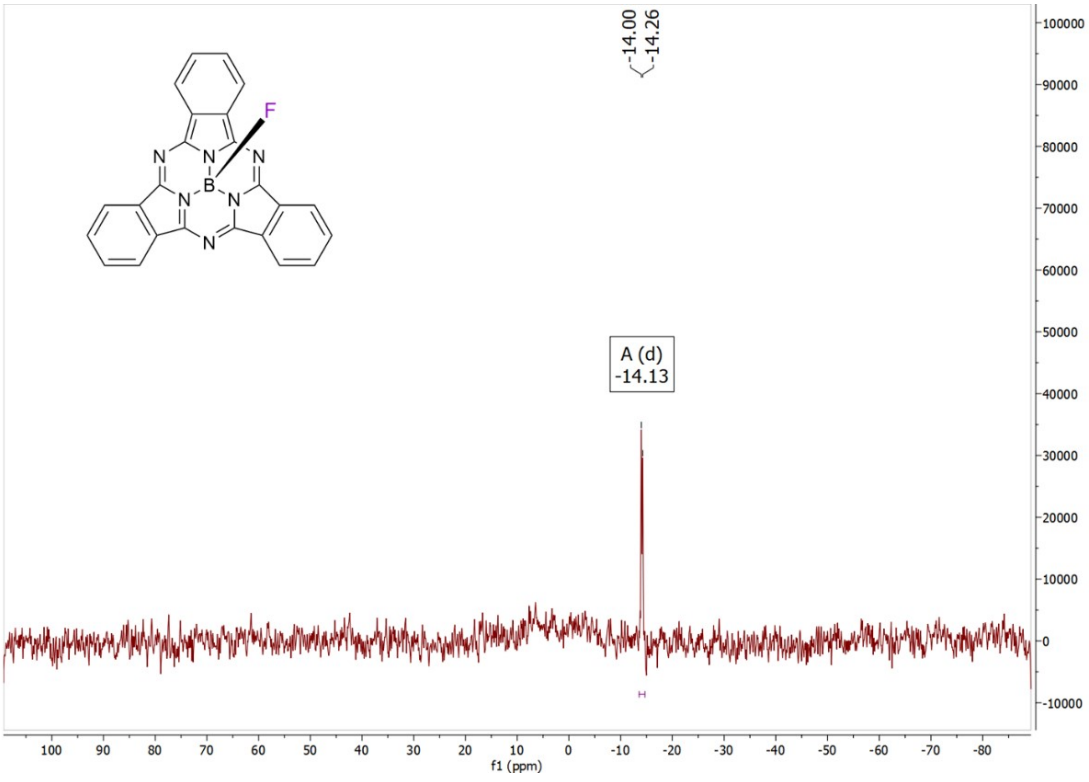


Figure S9. ^{11}B NMR spectrum of sublimed F-BsubPc (128 MHz, $CDCl_3$).

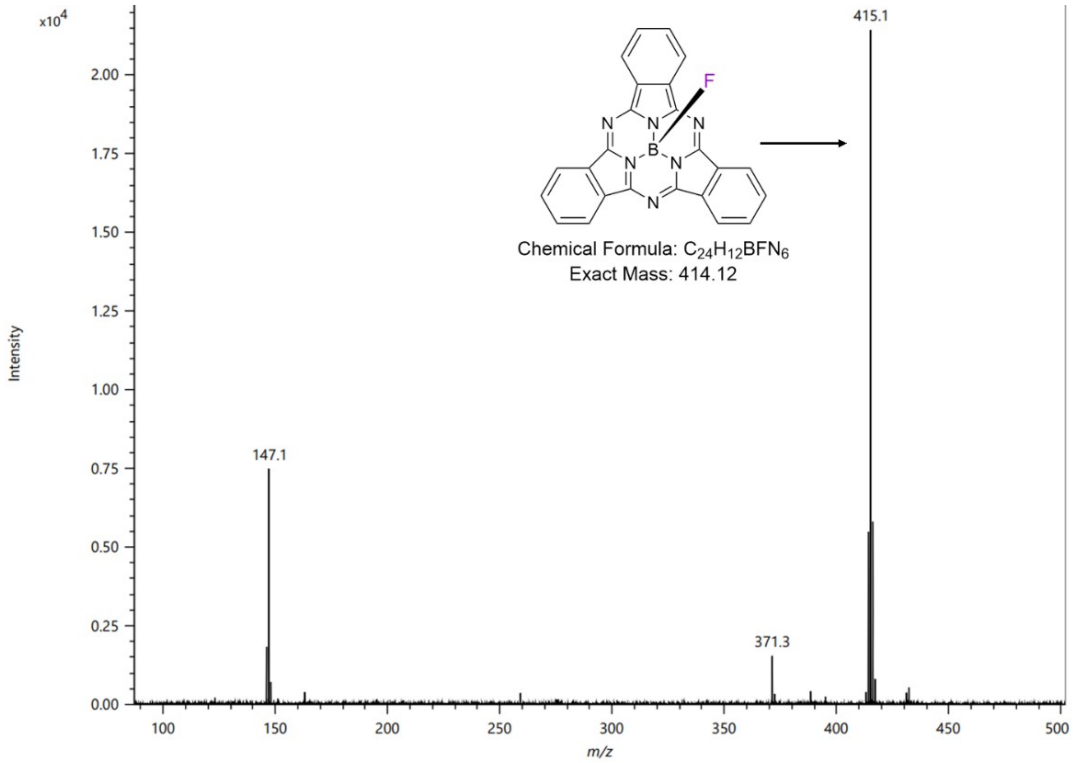
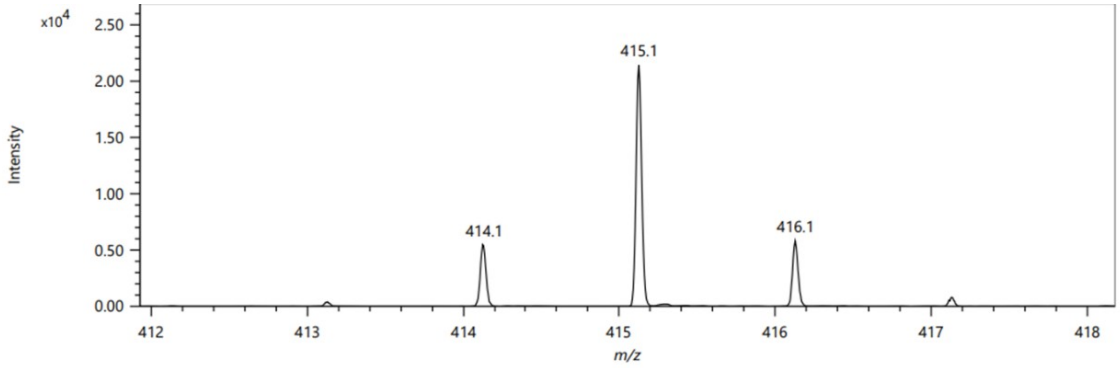


Figure S10. DART-MS [M+H] of sublimed F-BsubPc.



Elemental Composition

Parameters		Elements Set 1:						
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	F	B
Electron:	Even	Min	0	0	0	0	1	1
Charge:	+1	Max	100	200	20	10	1	1
DBE:	-1.5 - 100.0							

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
415.12690	21434.64	C10 H25 B O15 F	415.12651	0.40	0.95	-1.5
		C24 H13 B N6 F ←	415.12733	-0.43	-1.03	21.5
		C23 H17 B N2 O4 F	415.12599	0.91	2.19	16.5
		C11 H21 B N4 O11 F	415.12784	-0.94	-2.27	3.5
		C7 H17 B N10 O9 F	415.12516	1.74	4.20	4.5
		C12 H17 B N8 O7 F	415.12918	-2.28	-5.49	8.5

Figure S11. Zoomed-in DART-HRMS [M+H] of sublimed F-BsubPc.

MeO-BsubPc (2a)

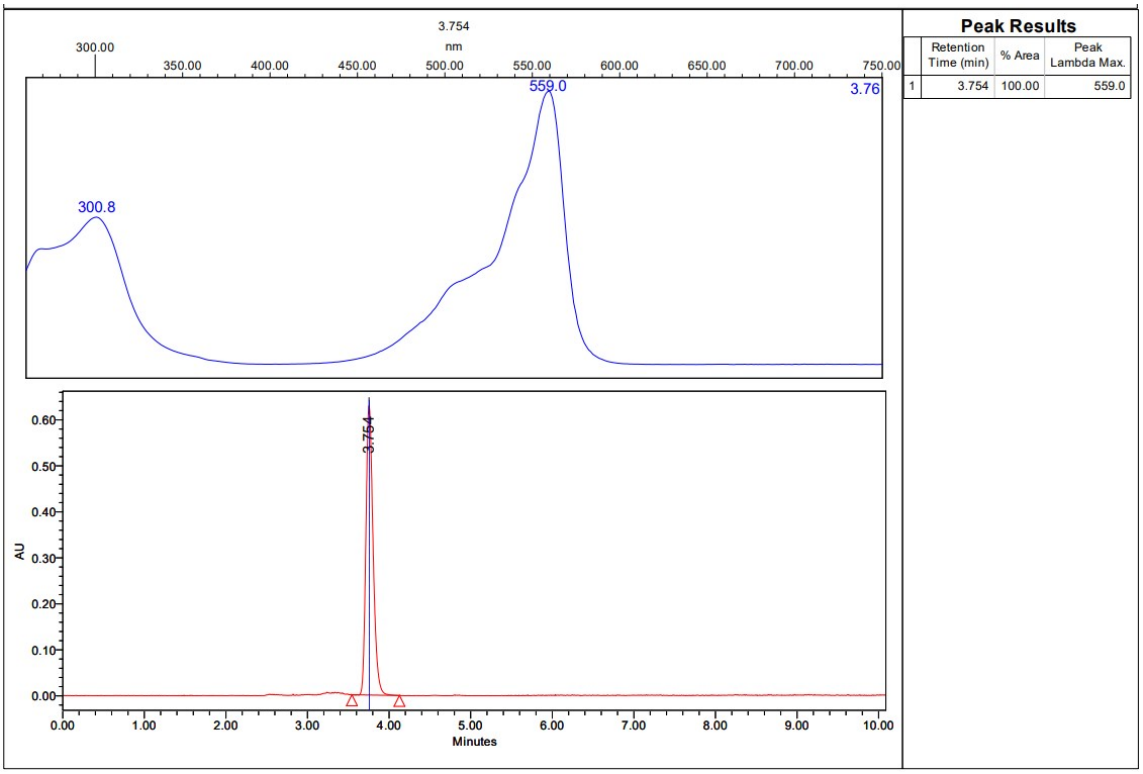


Figure S12. HPLC maxplot of sublimed MeO-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. MeO-BsubPc has a retention time of 3.754 minutes.

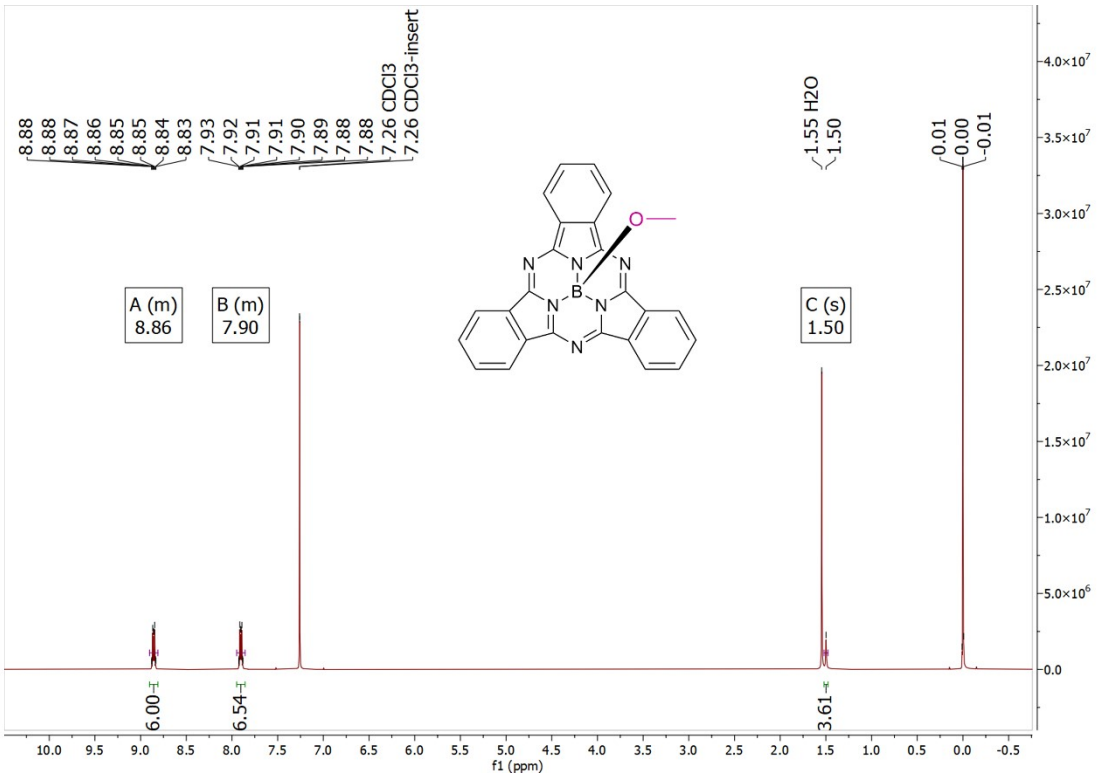


Figure S13. ^{1}H NMR spectrum of sublimed MeO-BsubPc (400 MHz, $CDCl_3$).

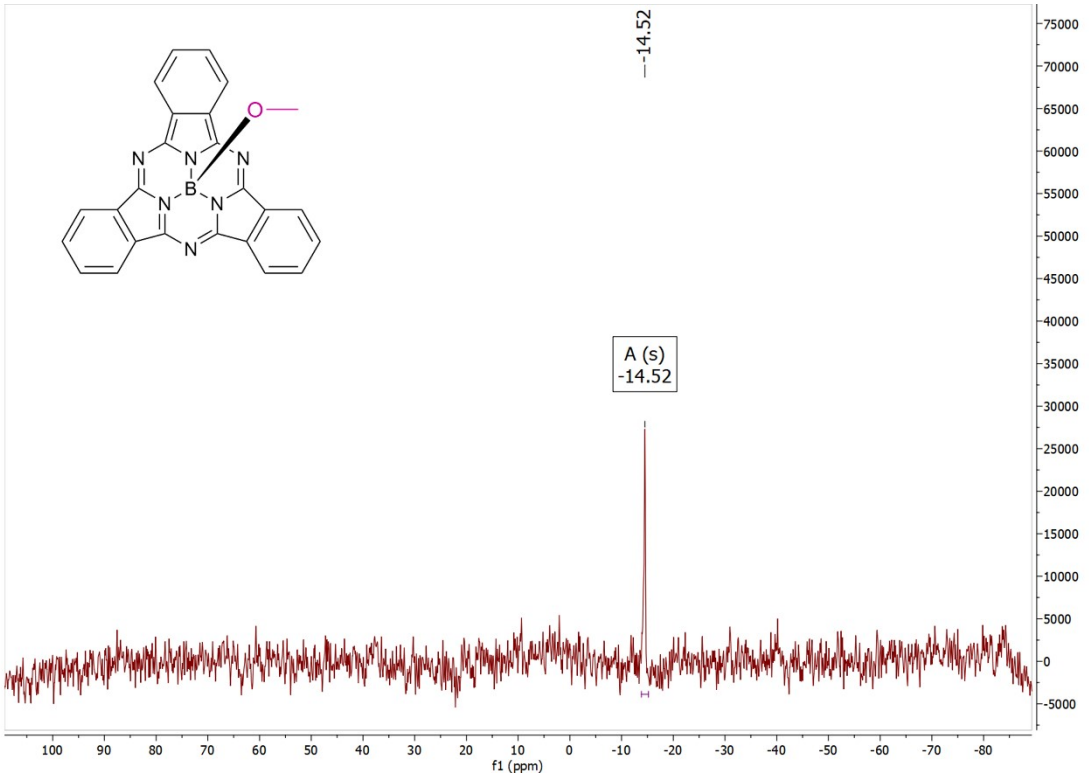


Figure S14. ^{11}B NMR spectrum of sublimed MeO-BsubPc (128 MHz, $CDCl_3$).

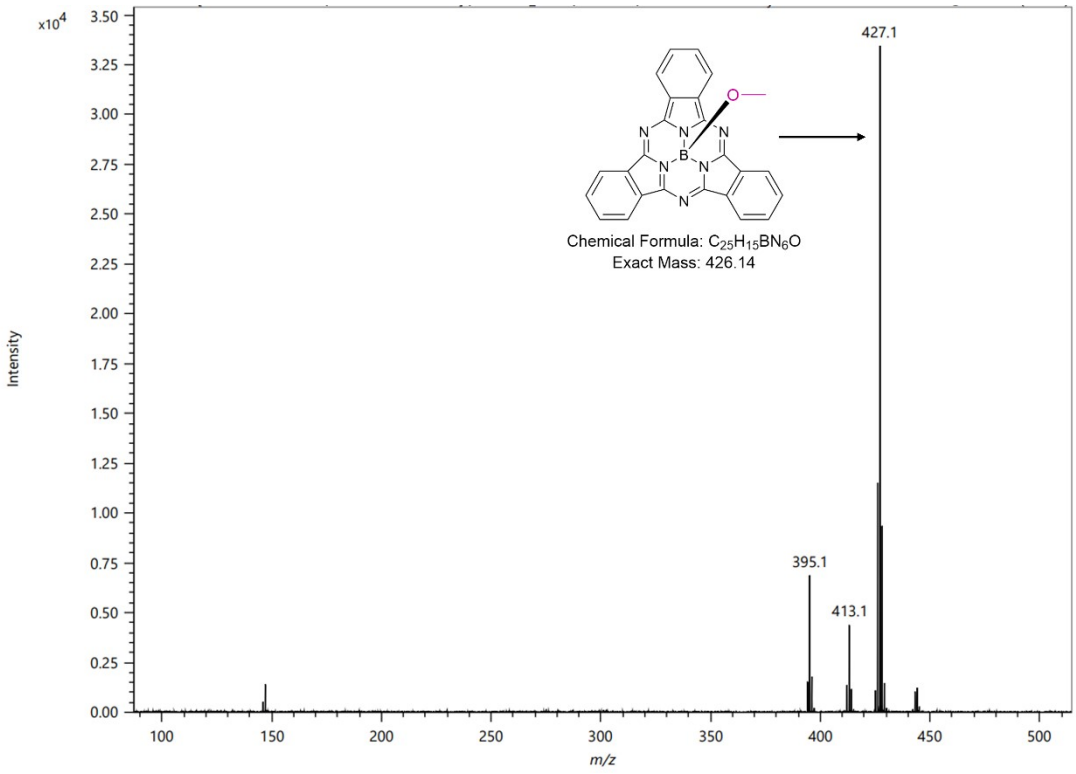
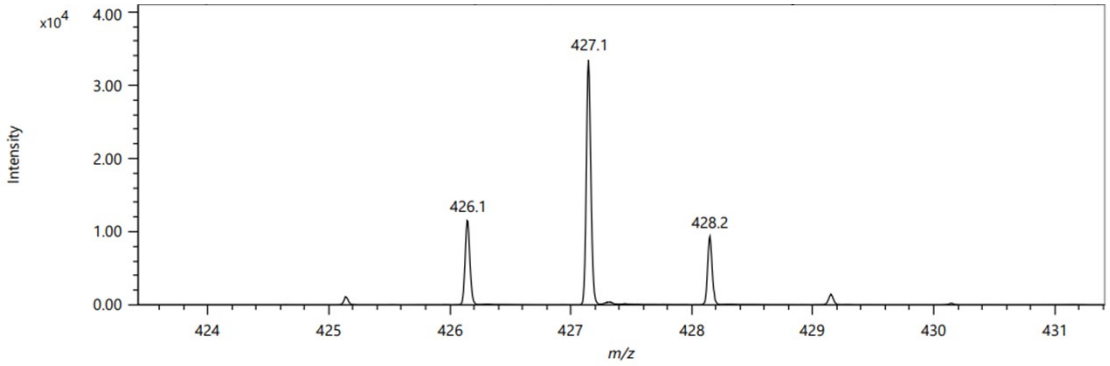


Figure S15. DART-MS [M+H] of sublimed MeO-BsubPc.



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Even	Min	0	0	0	0	1
Charge:	+1	Max	100	200	20	10	1
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
427.14797	33458.71	C12 H24 B N4 O12	427.14783	0.14	0.32	3.5
		C25 H16 B N6 O ←	427.14732	0.65	1.52	21.5
		C13 H20 B N8 O8	427.14917	-1.20	-2.81	8.5
		C11 H28 B O16	427.14649	1.47	3.45	-1.5
		C24 H20 B N2 O5	427.14598	1.99	4.65	16.5
		C29 H20 B O3	427.15000	-2.04	-4.77	20.5

Figure S16. Zoomed-in DART-HRMS [M+H] of sublimed MeO-BsubPc.

EtO-BsubPc (2b)

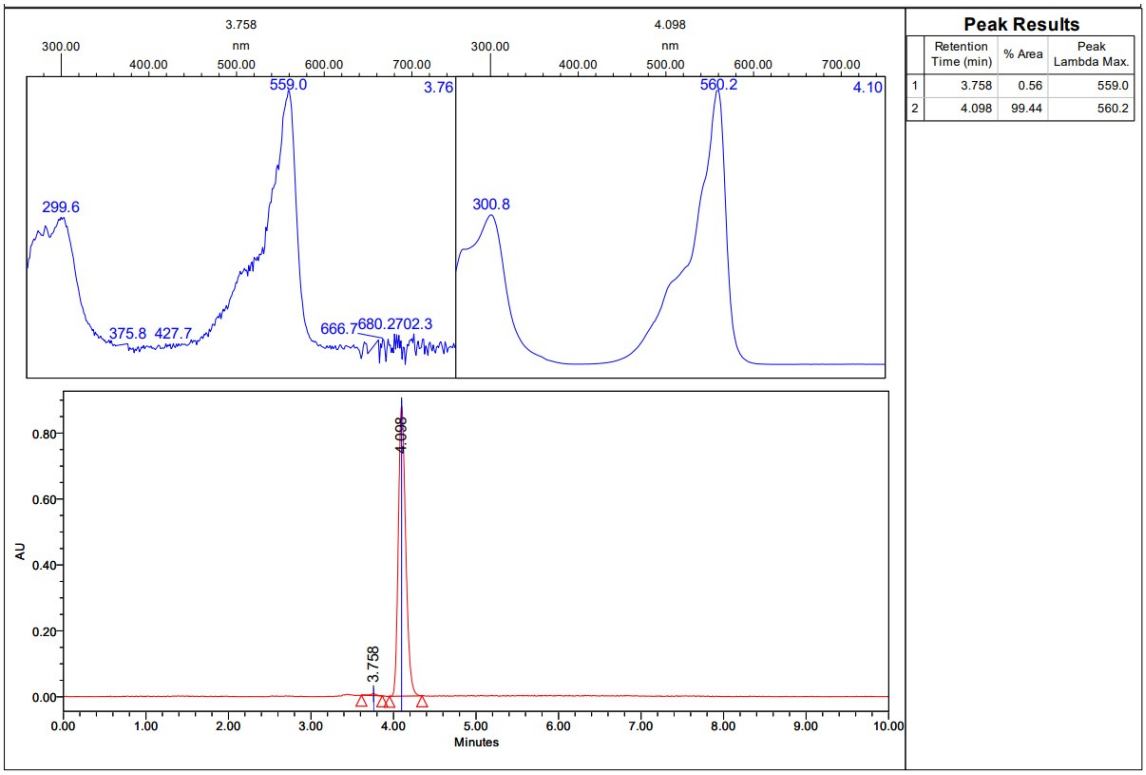


Figure S17. HPLC maxplot of sublimed EtO-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. EtO-BsubPc has a retention time of 4.098 minutes.

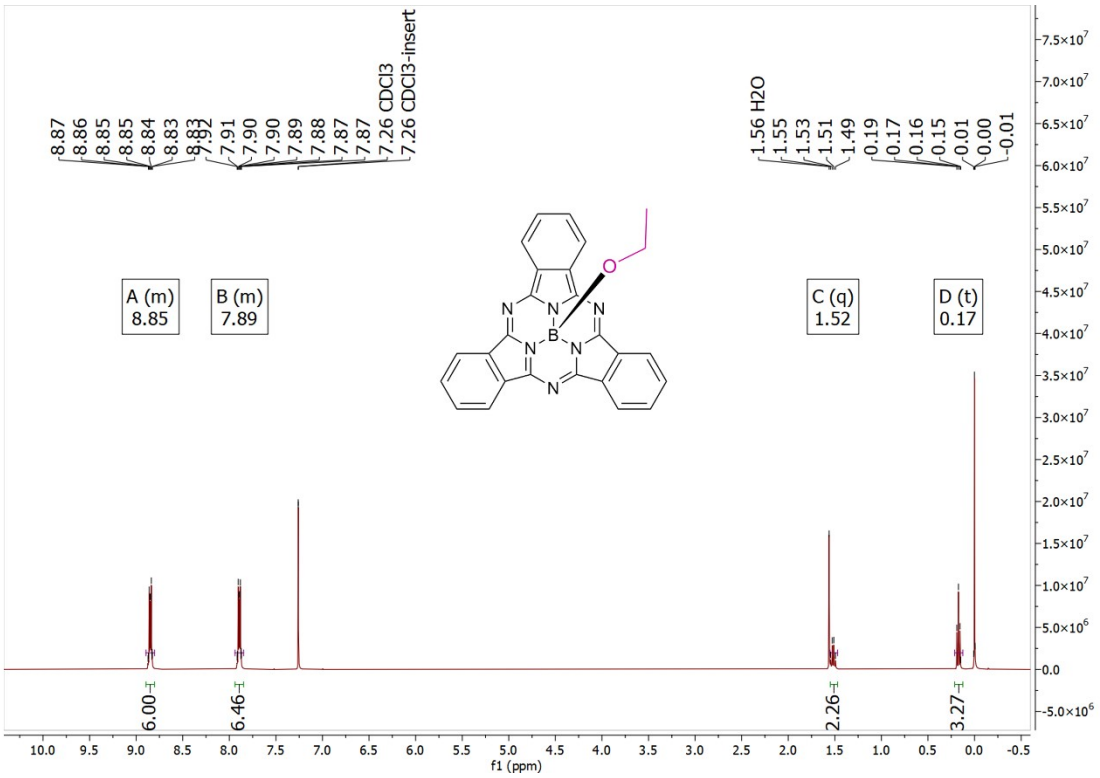


Figure S18. ^{1}H NMR spectrum of sublimed EtO-BsubPc (400 MHz, $CDCl_3$).

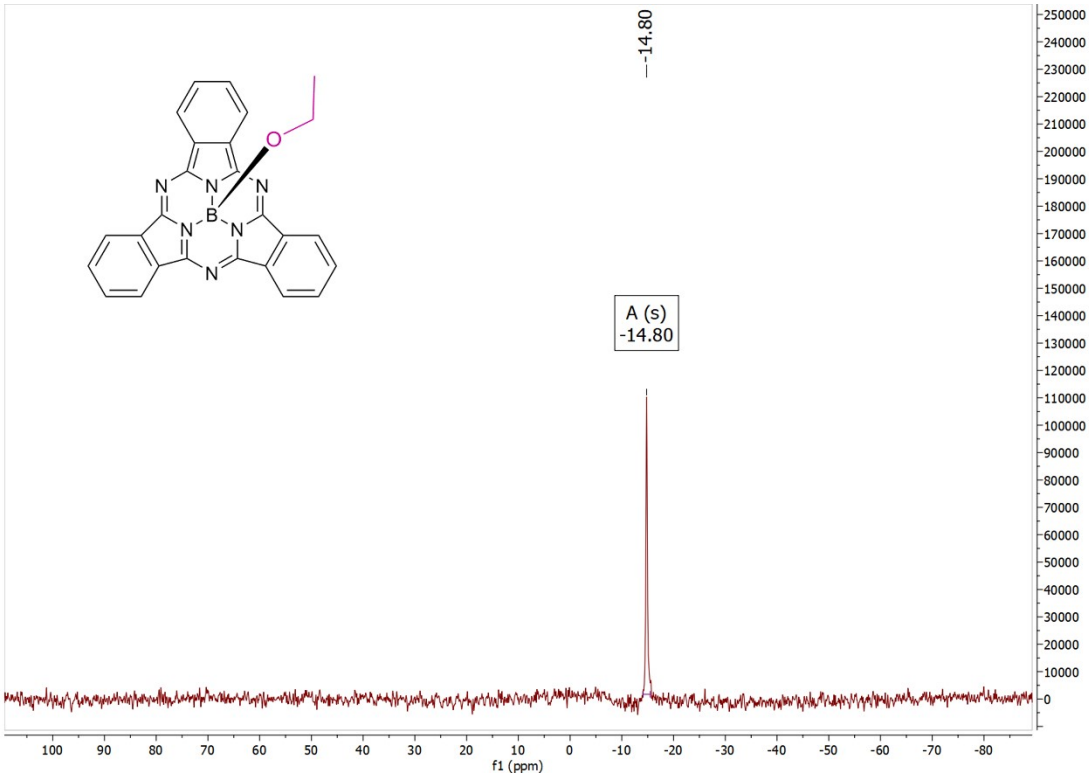


Figure S19. ^{11}B NMR spectrum of sublimed EtO-BsubPc (128 MHz, $CDCl_3$).

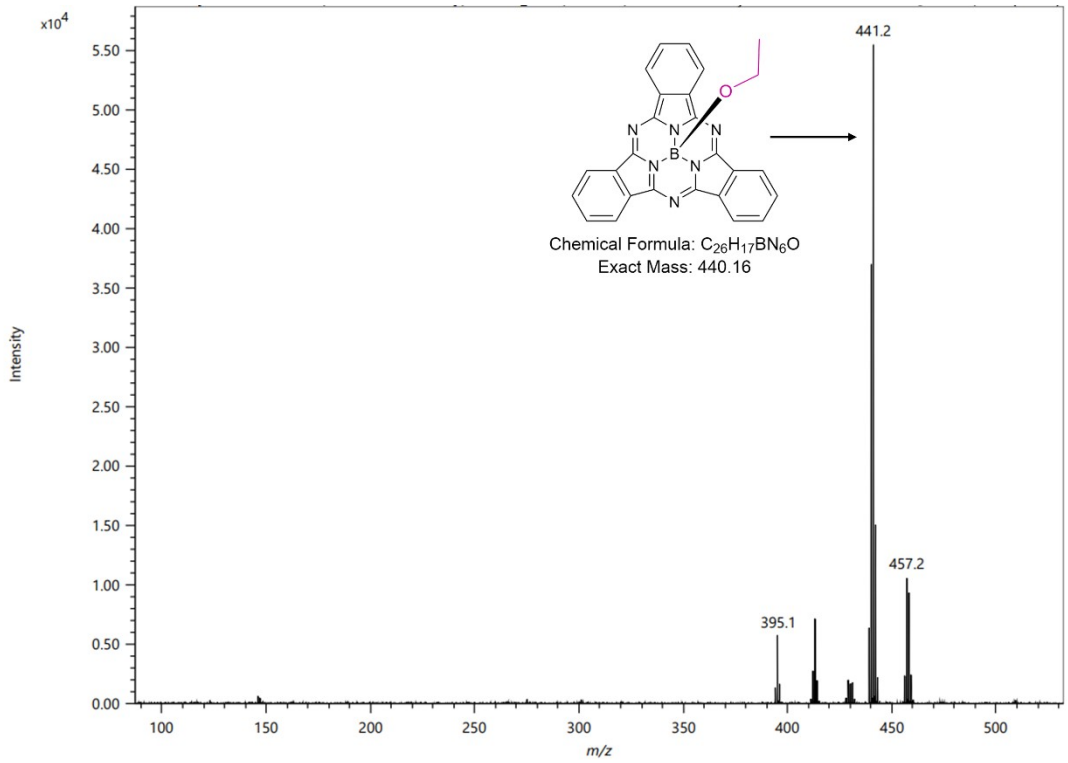
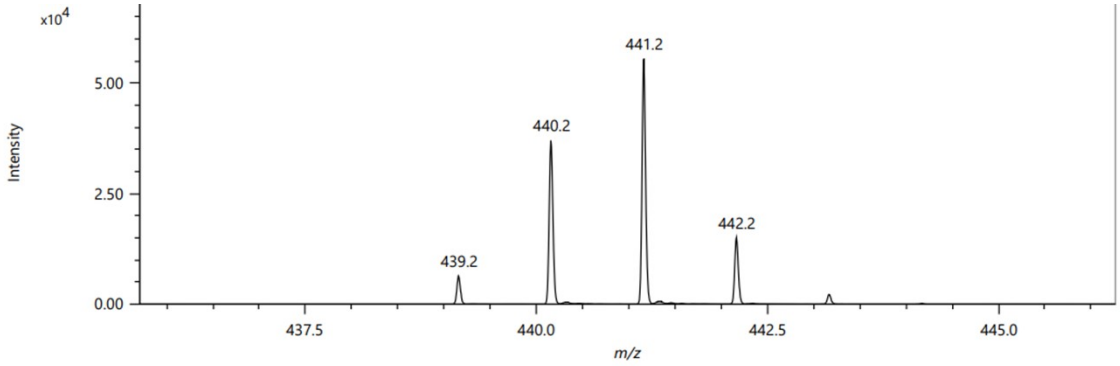


Figure S20. DART-MS [M+H] of sublimed EtO-BsubPc.



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Even	Min	0	0	0	0	1
Charge:	+1	Max	100	200	20	10	1
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
441.16291	55536.46	C26 H18 B N6 O ←	441.16297	-0.06	-0.12	21.5
		C13 H26 B N4 O12	441.16348	-0.57	-1.29	3.5
		C12 H30 B O16	441.16214	0.77	1.74	-1.5
		C25 H22 B N2 O5	441.16163	1.28	2.91	16.5
		C14 H22 B N8 O8	441.16482	-1.91	-4.32	8.5
		C9 H22 B N10 O10	441.16079	2.12	4.80	4.5

Figure S21. Zoomed-in DART-HRMS [M+H] of sublimed EtO-BsubPc.

F_3EtO-BsubPc (2c)

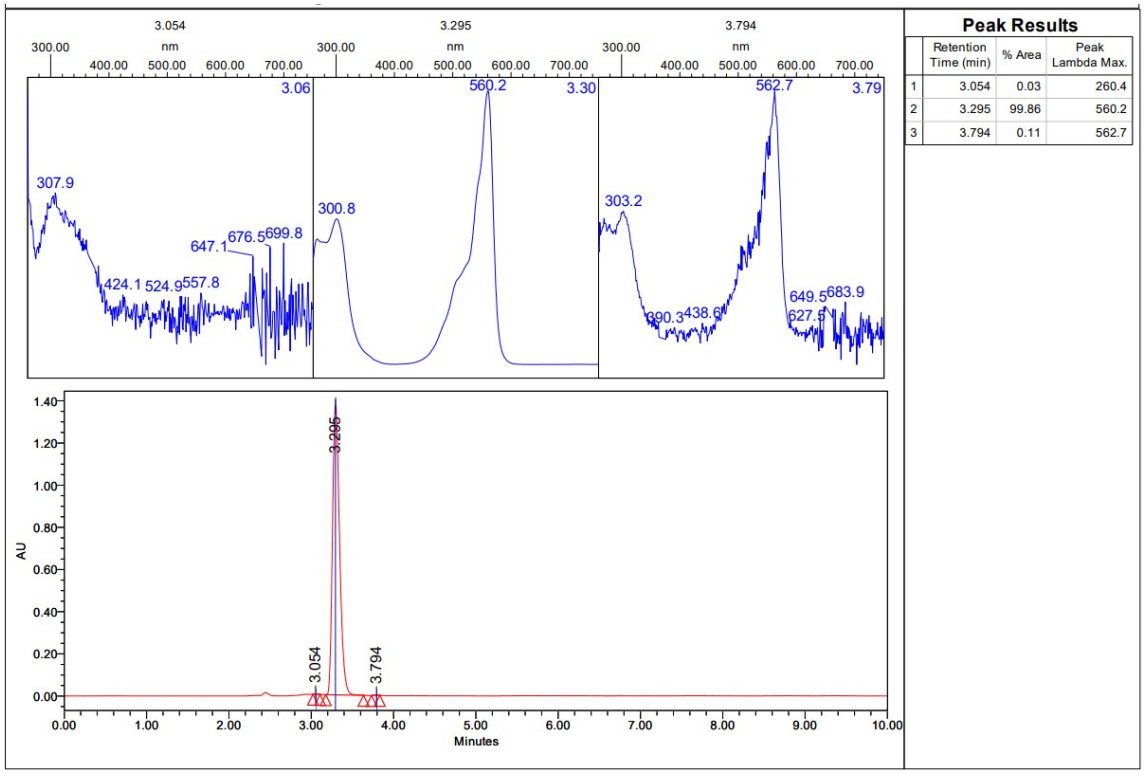


Figure S22. HPLC maxplot of sublimed F_3EtO-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. F_3EtO-BsubPc has a retention time of 3.295 minutes. The unintegrated peak around 2.4 minutes was confirmed to be an impurity in the HPLC solvent system.

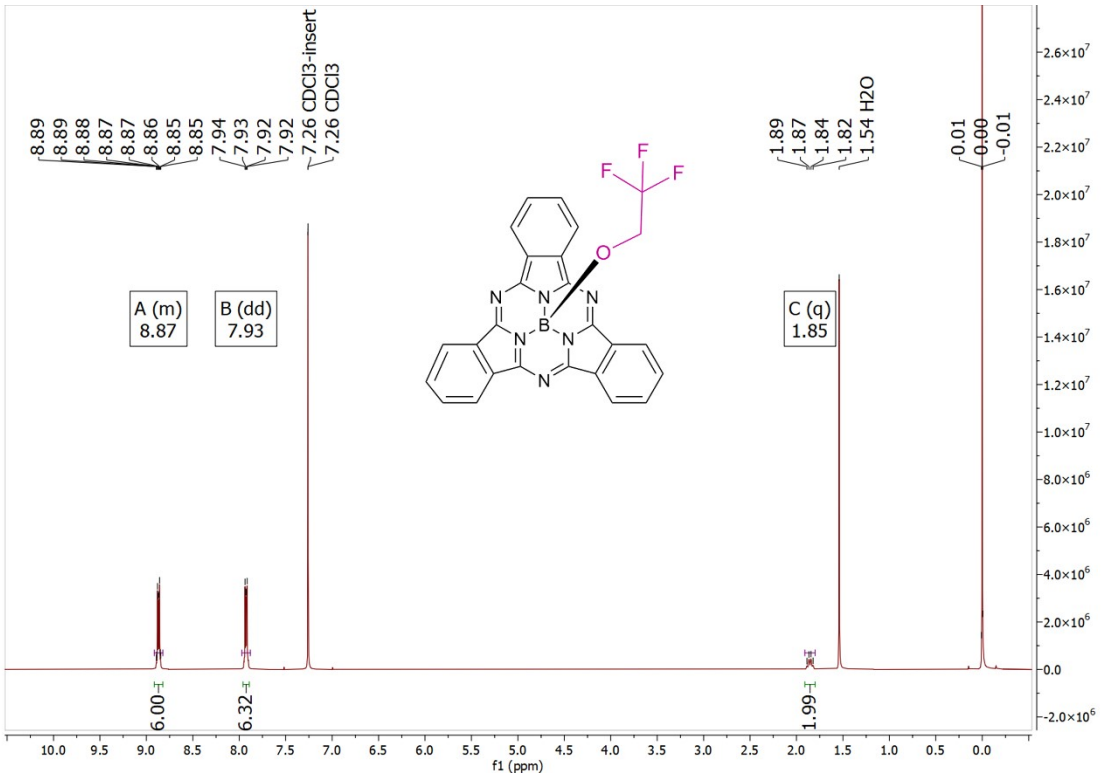


Figure S23. ^{1}H NMR spectrum of sublimed F_3EtO-BsubPc (400 MHz, $CDCl_3$).

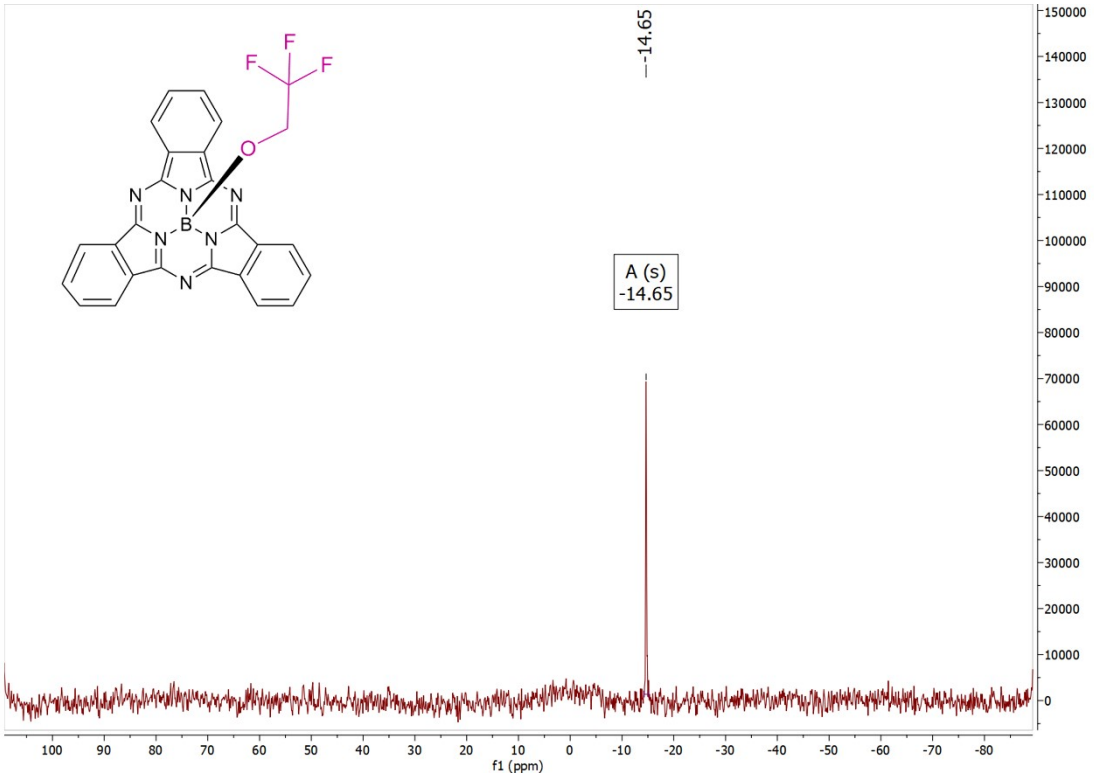


Figure S24. ^{11}B NMR spectrum of sublimed F_3EtO-BsubPc (128 MHz, $CDCl_3$).

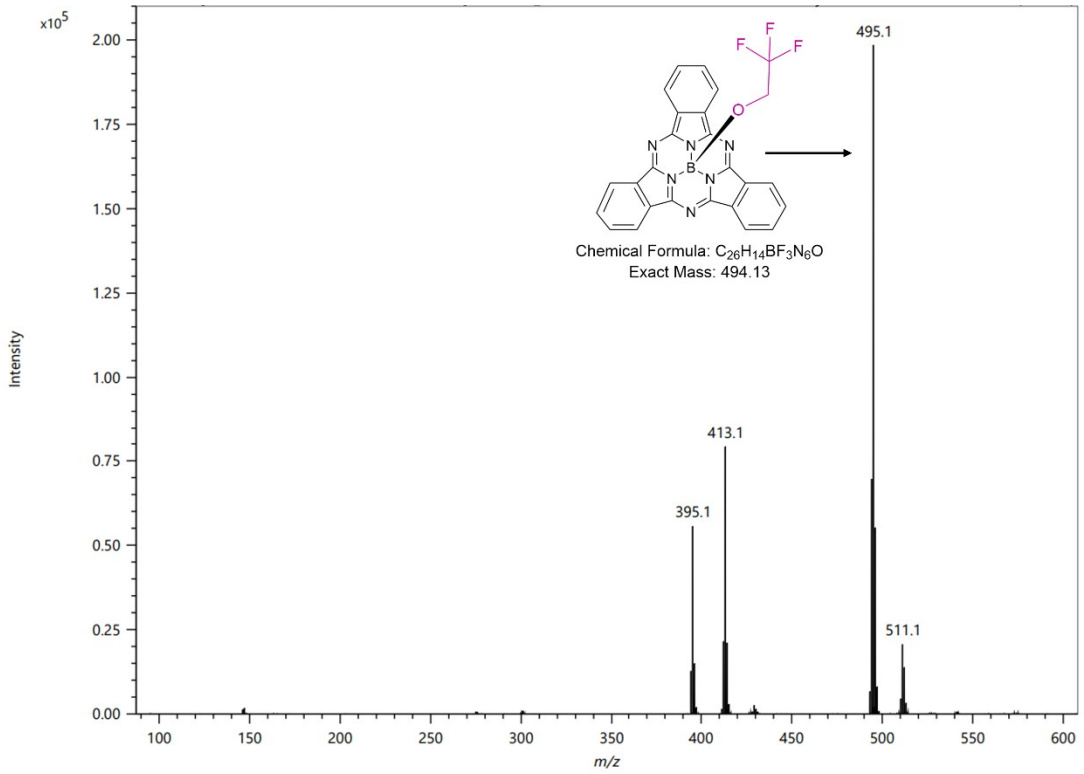
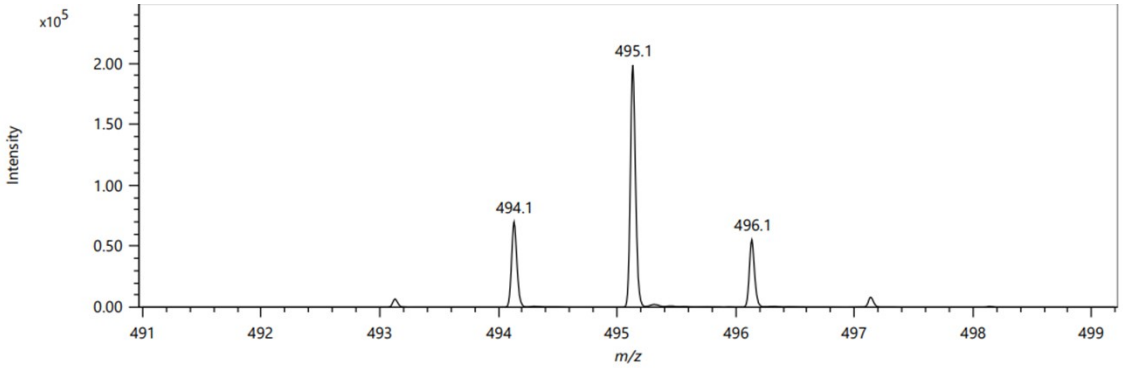


Figure S25. DART-MS [M+H] of sublimed F_3EtO-BsubPc.



Elemental Composition

Parameters		Elements Set 1:						
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B	F
Electron:	Even	Min	0	0	0	0	1	3
Charge:	+1	Max	100	200	20	10	1	3
DBE:	-1.5 - 100.0							

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
495.13459	198603.81	C26 H15 B N6 O F3 ←	495.13470	-0.11	-0.23	21.5
		C13 H23 B N4 O12 F3	495.13521	-0.63	-1.27	3.5
		C12 H27 B O16 F3	495.13388	0.71	1.43	-1.5
		C25 H19 B N2 O5 F3	495.13336	1.22	2.47	16.5
		C14 H19 B N8 O8 F3	495.13655	-1.96	-3.97	8.5
		C9 H19 B N10 O10 F3	495.13253	2.06	4.16	4.5

Figure S26. Zoomed-in DART-HRMS [M+H] of sublimed F_3EtO-BsubPc.

ButO-BsubPc (2d)

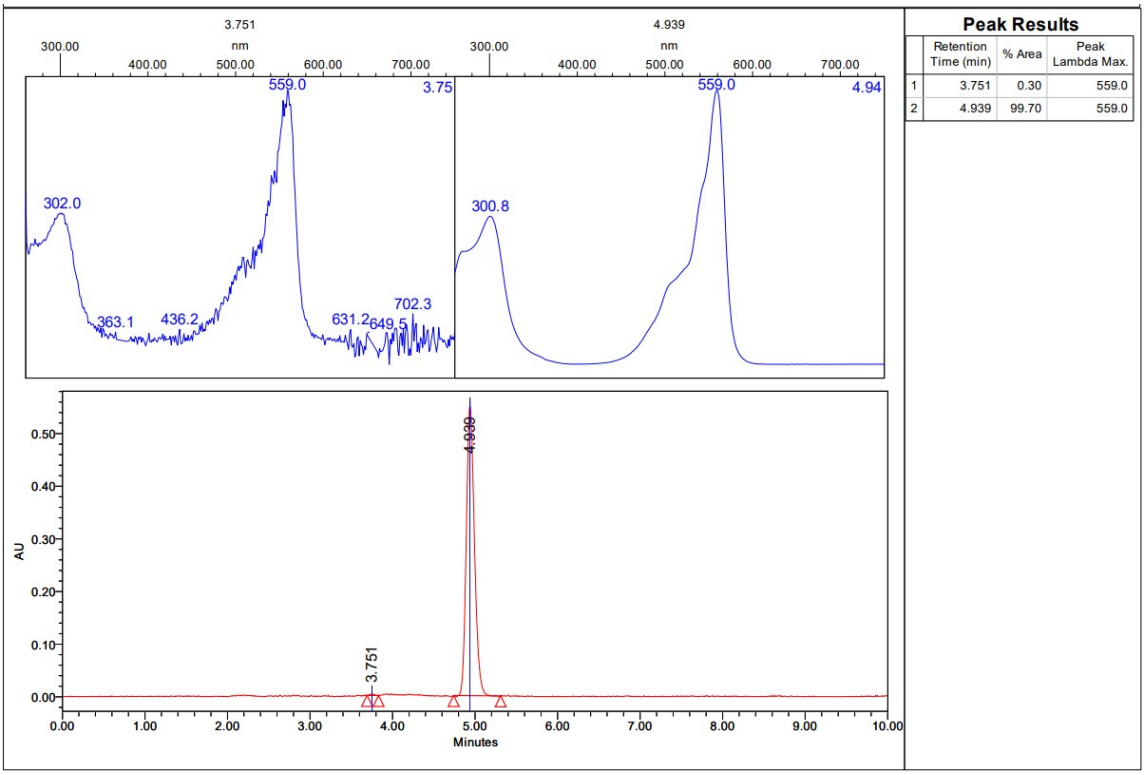


Figure S27. HPLC maxplot of sublimed ButO-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. ButO-BsubPc has a retention time of 4.939 minutes.

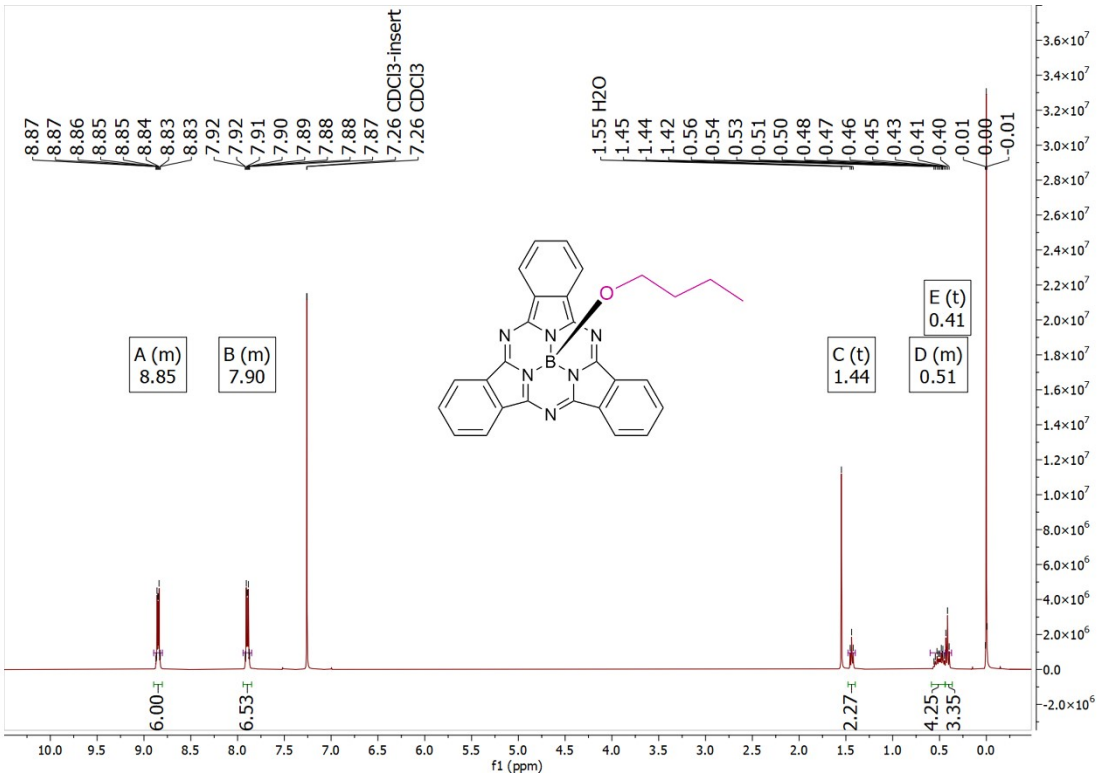


Figure S28. ^{1}H NMR spectrum of sublimed ButO-BsubPc (400 MHz, $CDCl_3$).

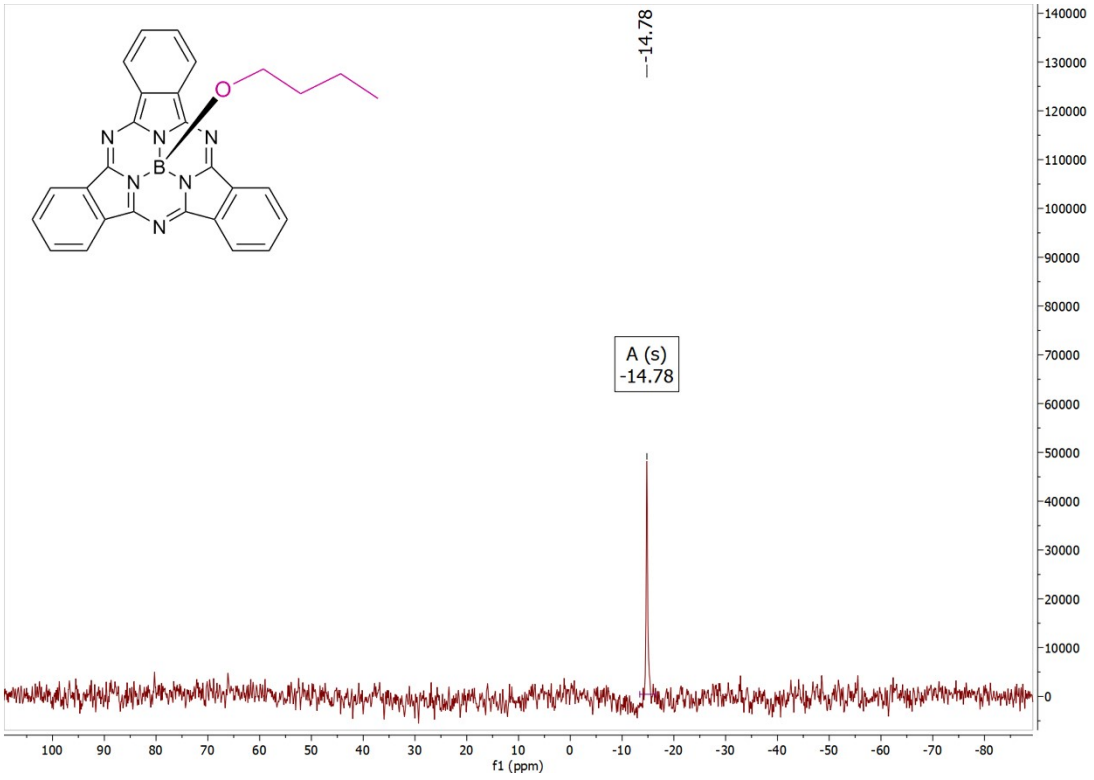


Figure S29. ^{11}B NMR spectrum of sublimed ButO-BsubPc (128 MHz, $CDCl_3$).

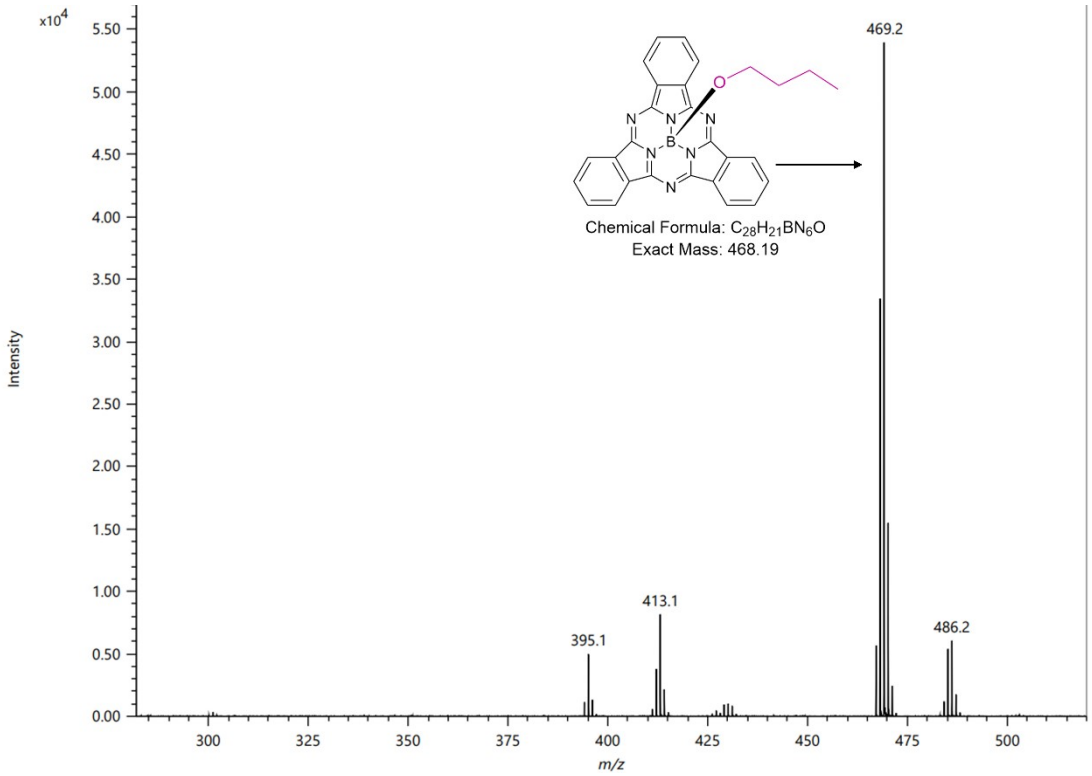
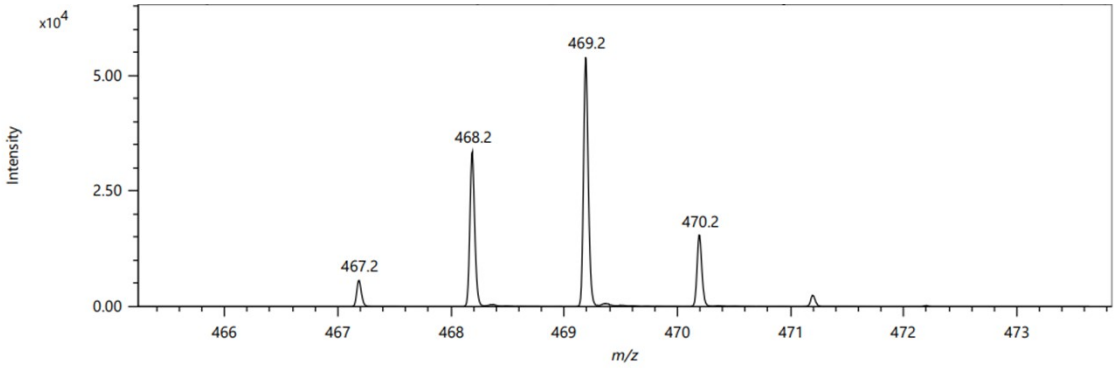


Figure S30. DART-MS [M+H] of sublimed ButO-BsubPc.



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Even	Min	0	0	0	0	1
Charge:	+1	Max	100	200	20	10	1
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
469.19345	53962.03	C14 H34 B O16	469.19344	0.00	0.01	-1.5
		C27 H26 B N2 O5	469.19293	0.52	1.10	16.5
		C28 H22 B N6 O ←	469.19427	-0.82	-1.75	21.5
		C15 H30 B N4 O12	469.19478	-1.33	-2.84	3.5
		C11 H26 B N10 O10	469.19209	1.35	2.88	4.5
		C16 H26 B N8 O8	469.19612	-2.67	-5.69	8.5

Figure S31. Zoomed-in DART-HRMS [M+H] of sublimed ButO-BsubPc.

tButO-BsubPc (2e)

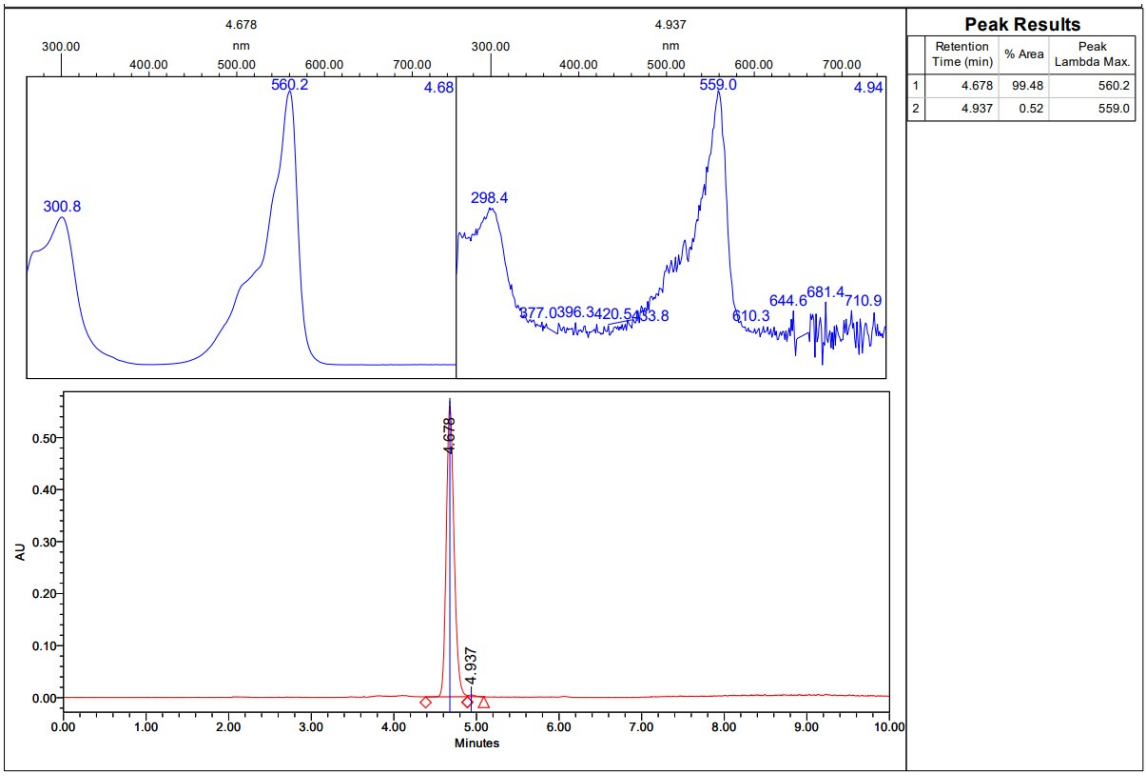


Figure S32. HPLC maxplot of column-purified tButO-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. tButO-BsubPc has a retention time of 4.937 minutes.

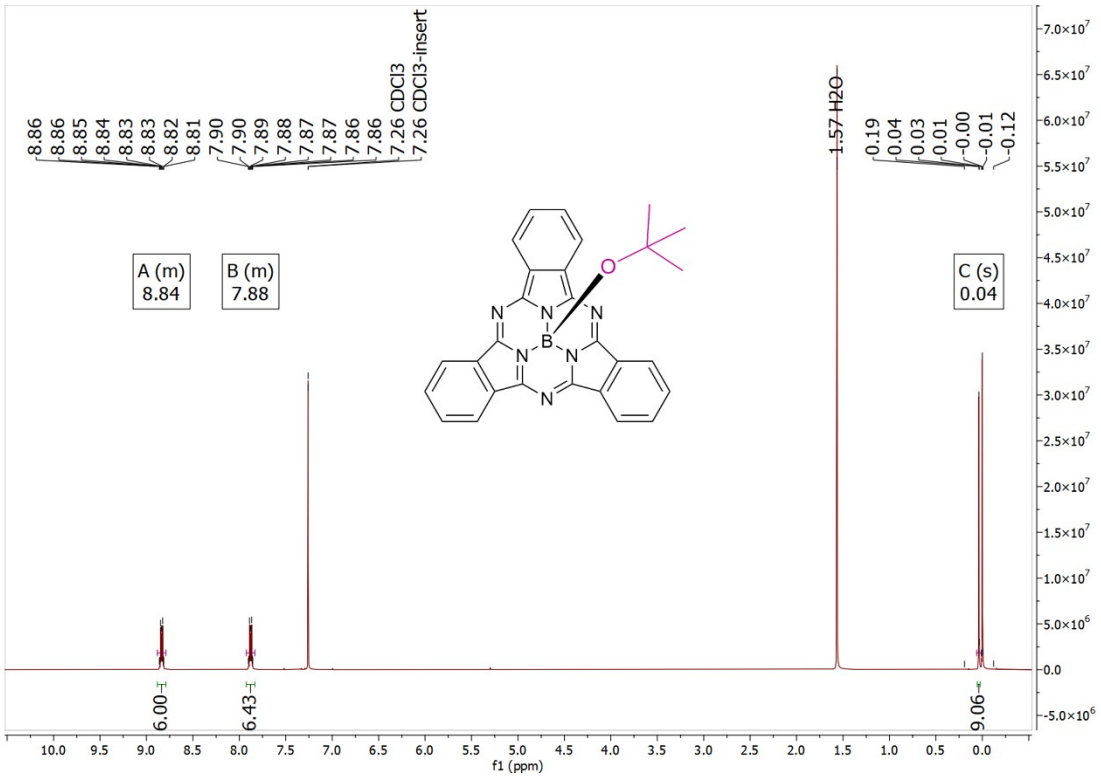


Figure S33. ^{1}H NMR spectrum of column-purified tButO-BsubPc (400 MHz, $CDCl_3$).

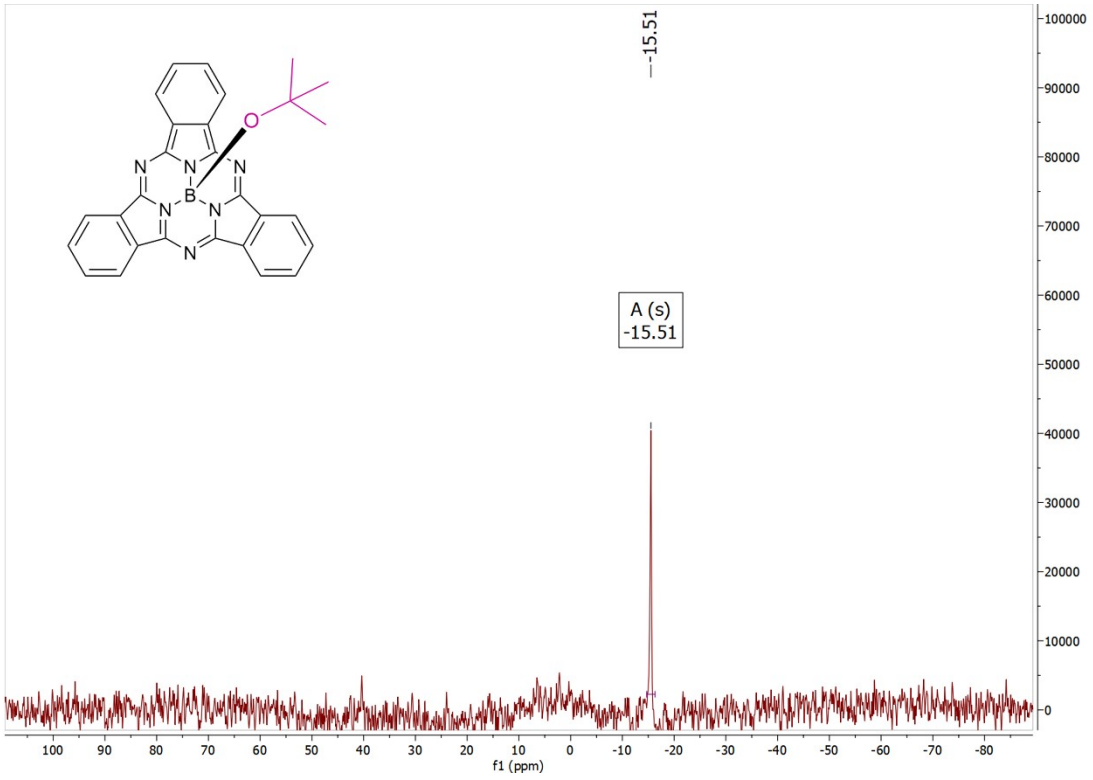


Figure S34. ^{11}B NMR spectrum of column-purified tButO-BsubPc (128 MHz, $CDCl_3$).

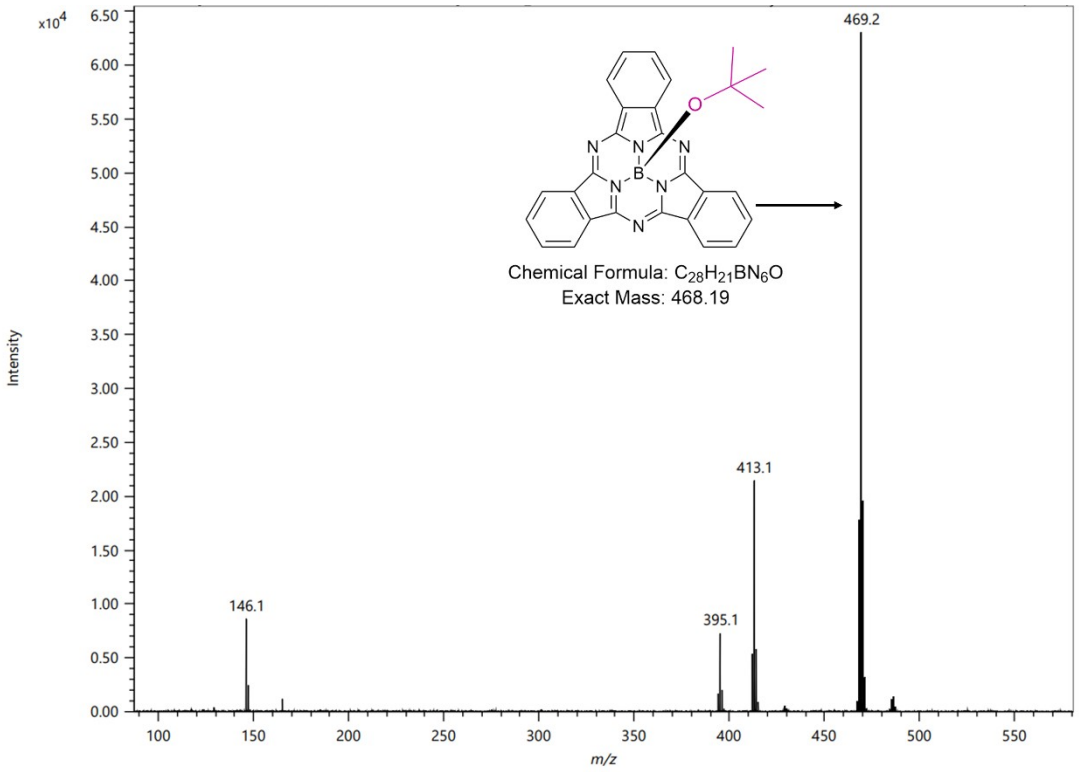
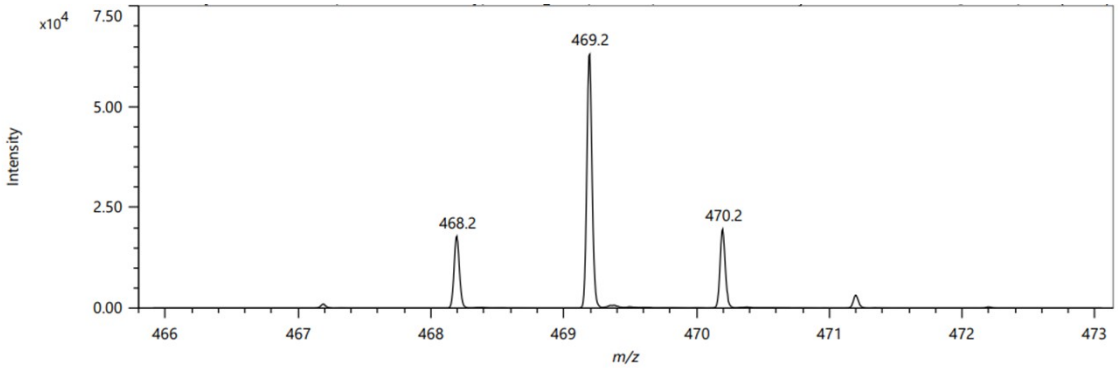


Figure S35. DART-MS [M+H] of column-purified tButO-BsubPc.



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Even	Min	0	0	0	0	1
Charge:	+1	Max	100	200	20	10	1
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
469.19397	63047.34	C28 H22 B N6 O ←	469.19427	-0.30	-0.63	21.5
		C14 H34 B O16	469.19344	0.53	1.12	-1.5
		C15 H30 B N4 O12	469.19478	-0.81	-1.73	3.5
		C27 H26 B N2 O5	469.19293	1.04	2.22	16.5
		C11 H26 B N10 O10	469.19209	1.87	3.99	4.5
		C16 H26 B N8 O8	469.19612	-2.15	-4.58	8.5

Figure S36. Zoomed-in DART-HRMS [M+H] of column-purified tButO-BsubPc.

OctO-BsubPc (2f)

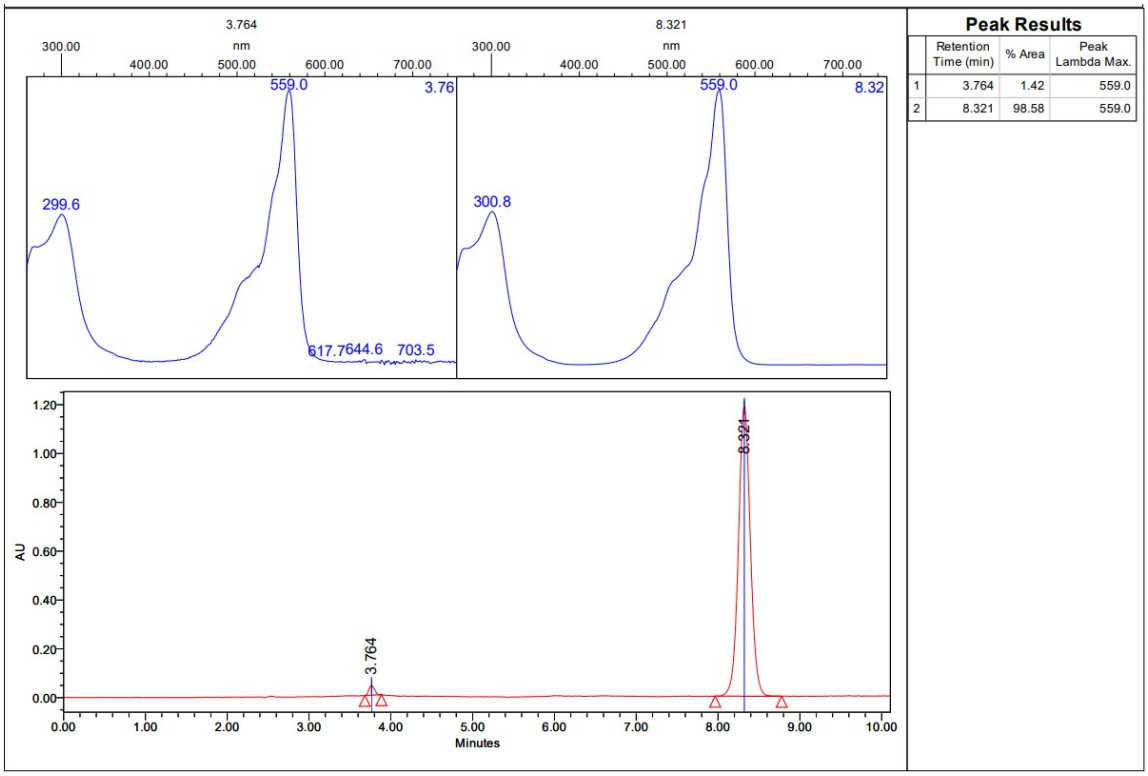


Figure S37. HPLC maxplot of sublimed OctO-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. OctO-BsubPc has a retention time of 8.321 minutes.

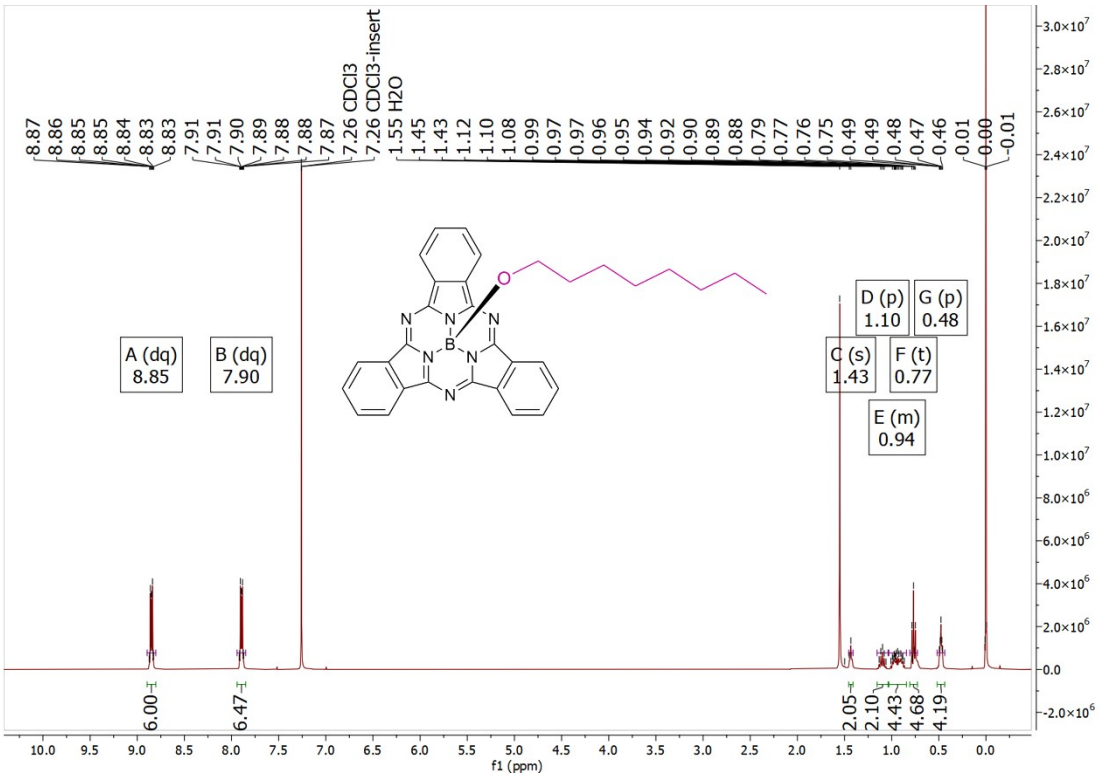


Figure S38. ^{1}H NMR spectrum of sublimed OctO-BsubPc (400 MHz, $CDCl_3$).

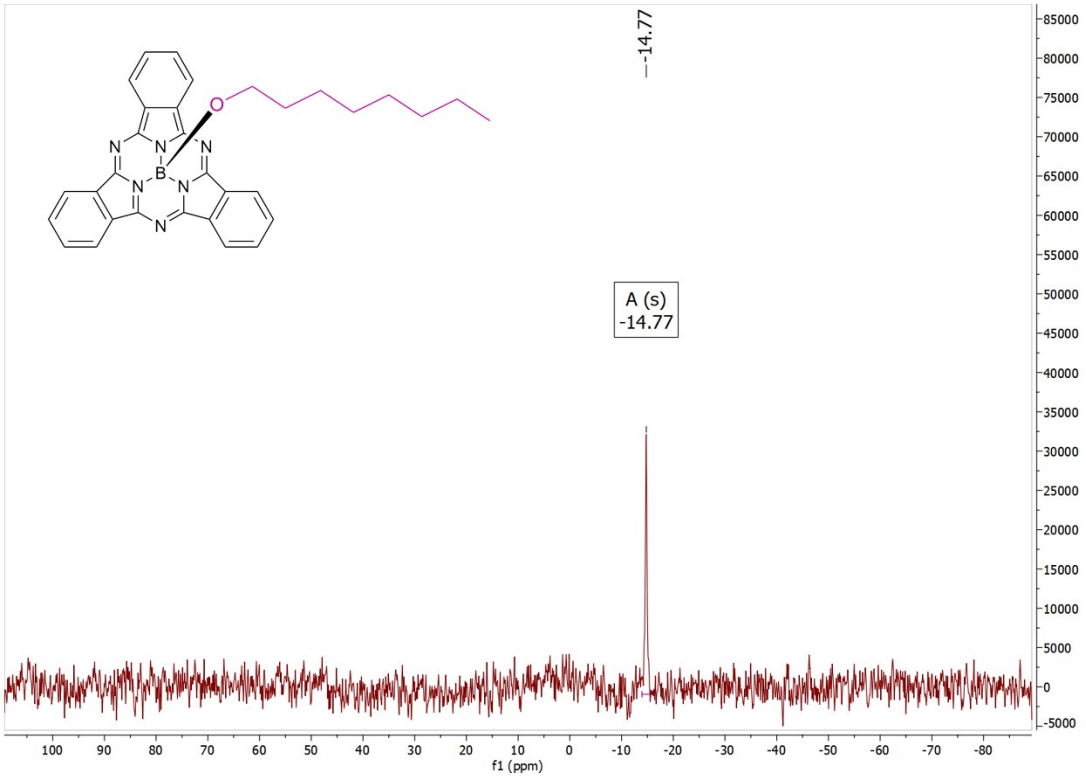


Figure S39. ^{11}B NMR spectrum of sublimed OctO-BsubPc (128 MHz, $CDCl_3$).

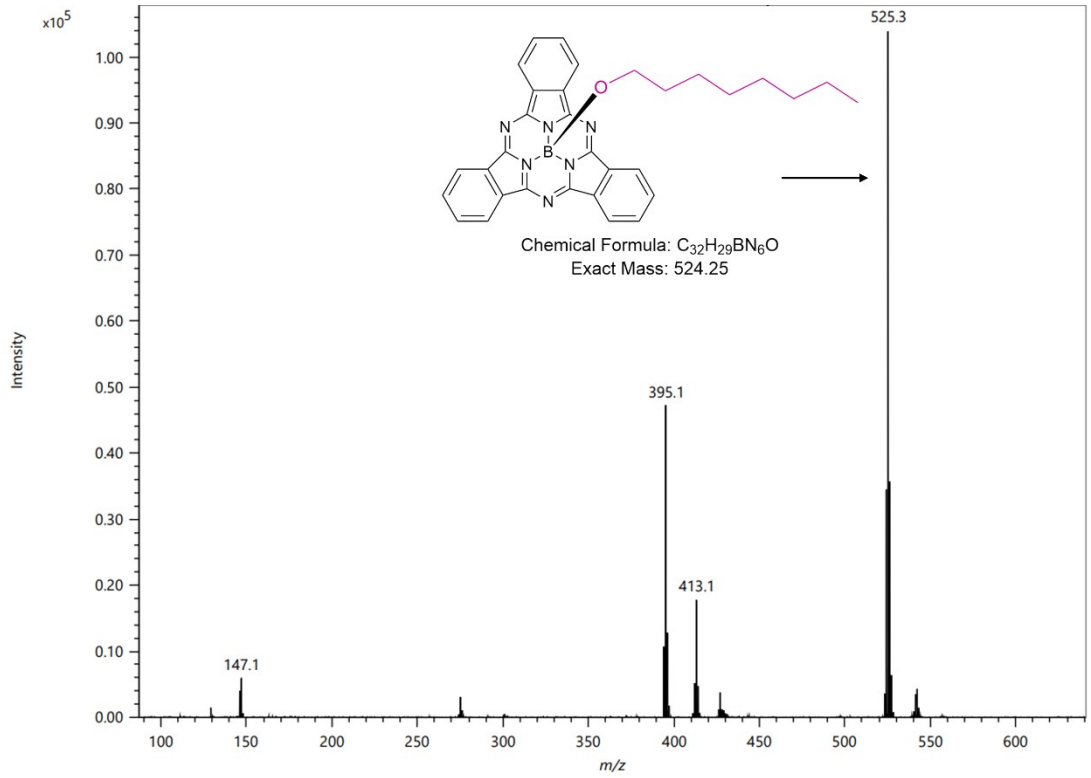
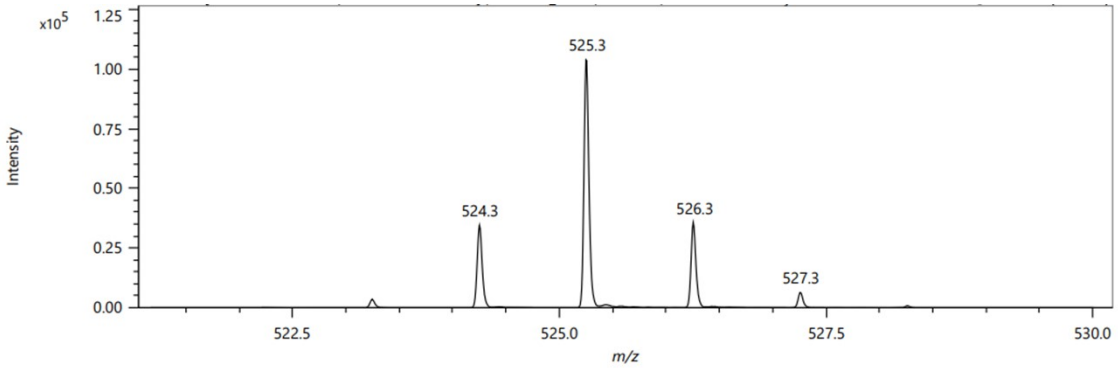


Figure S40. DART-MS [M+H] of sublimed OctO-BsubPc.



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Even	Min	0	0	0	0	1
Charge:	+1	Max	100	200	20	10	1
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
525.25614	103879.45	C18 H42 B O16	525.25604	0.10	0.19	-1.5
		C31 H34 B N2 O5	525.25553	0.62	1.17	16.5
		C32 H30 B N6 O ←	525.25687	-0.72	-1.38	21.5
		C19 H38 B N4 O12	525.25738	-1.24	-2.35	3.5
		C15 H34 B N10 O10	525.25469	1.45	2.76	4.5
		C20 H34 B N8 O8	525.25872	-2.57	-4.90	8.5

Figure S41. Zoomed-in DART-HRMS [M+H] of sublimed OctO-BsubPc.

PhO-BsubPc (3a)

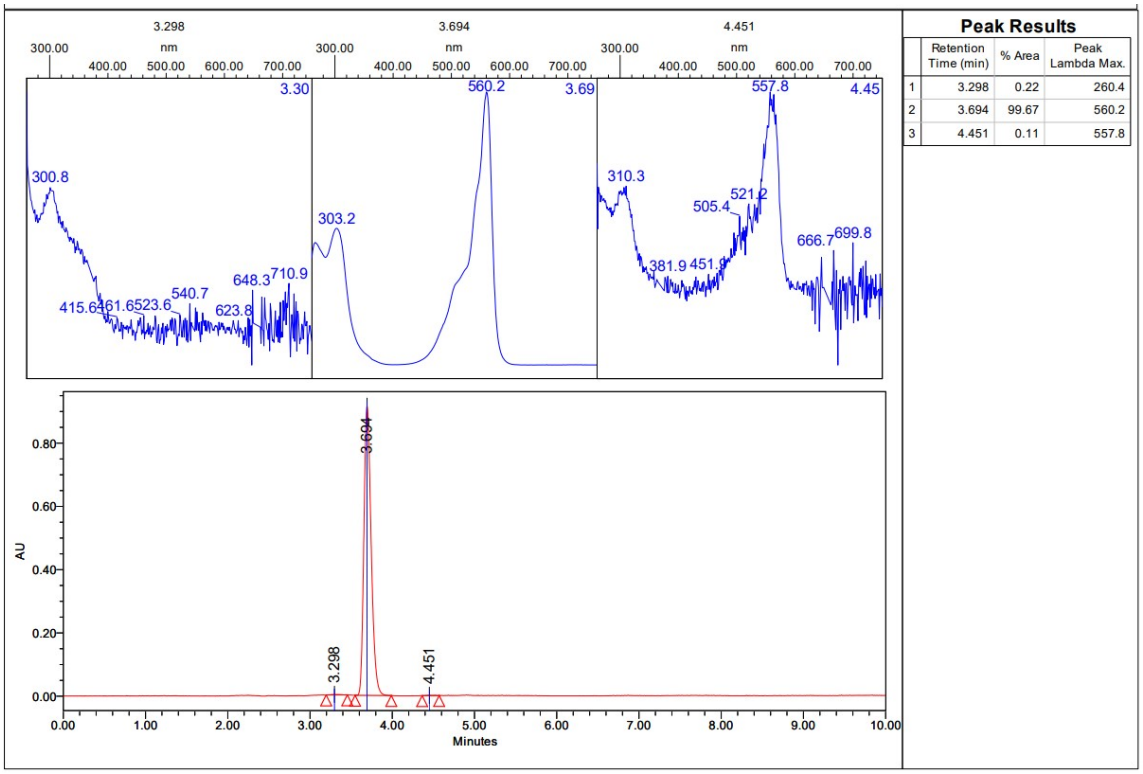


Figure S42. HPLC maxplot of sublimed PhO-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. PhO-BsubPc has a retention time of 3.694 minutes.

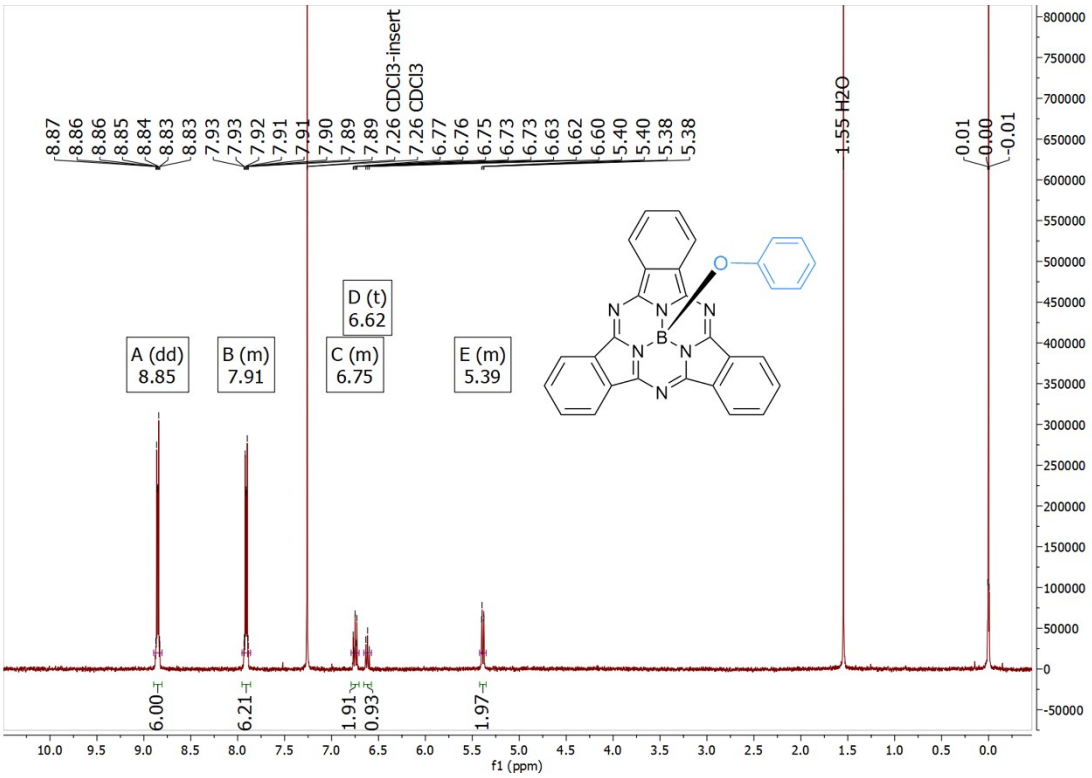


Figure S43. ^{1}H NMR spectrum of sublimed PhO-BsubPc (400 MHz, $CDCl_3$).

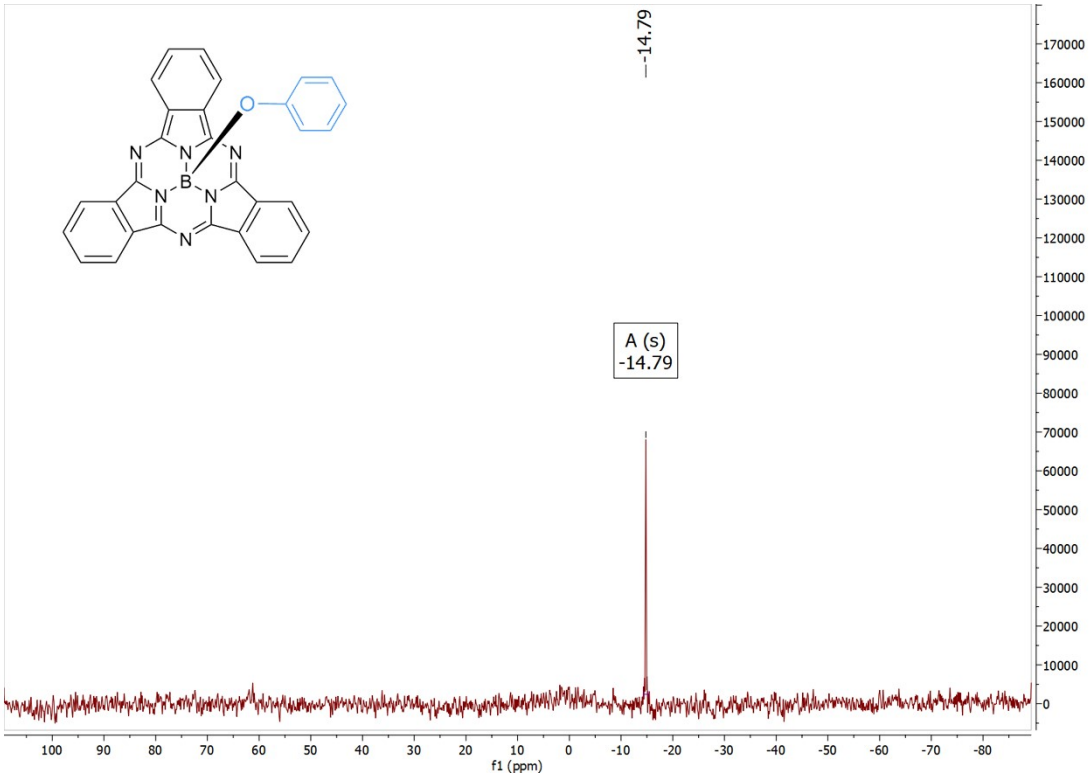


Figure S44. ^{11}B NMR spectrum of sublimed PhO-BsubPc (128 MHz, $CDCl_3$).

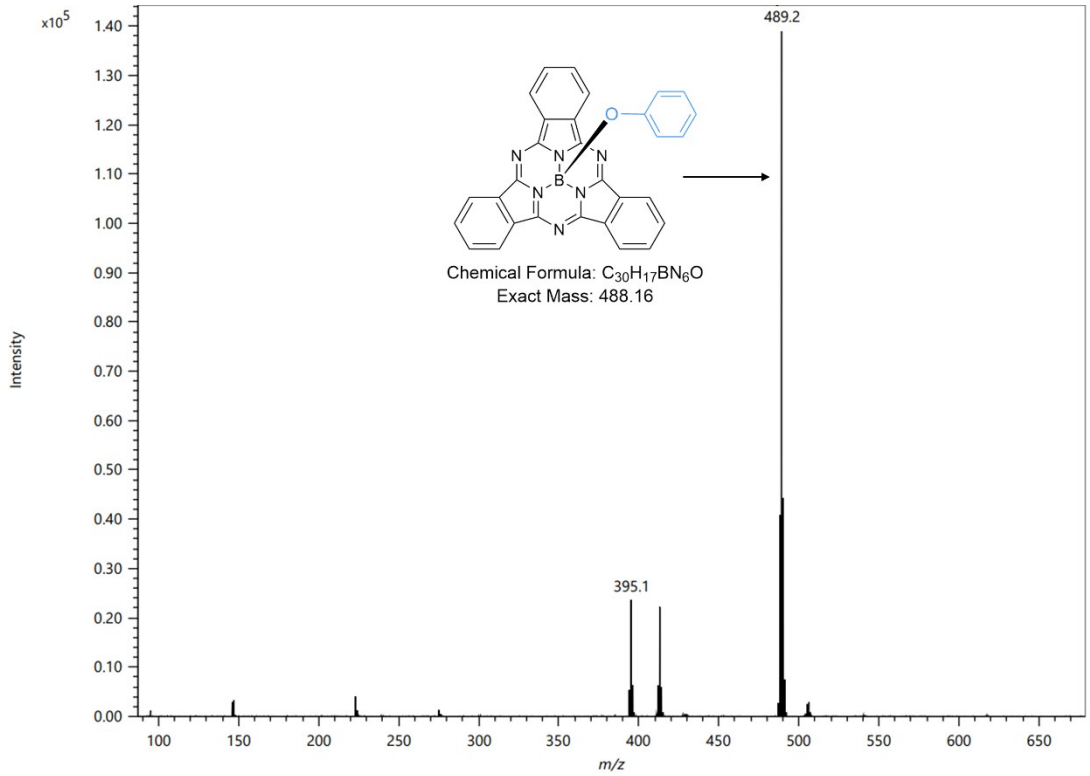
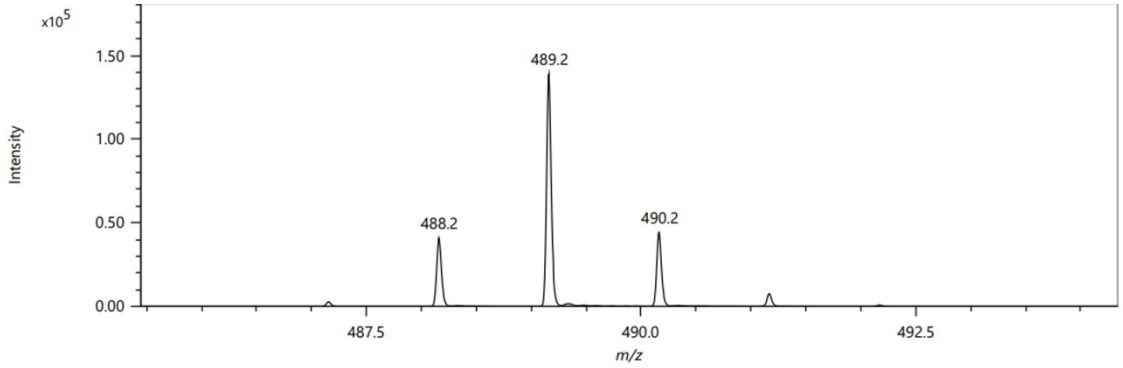


Figure S45. DART-MS [M+H] of sublimed PhO-BsubPc.



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Even	Min	0	0	0	0	1
Charge:	+1	Max	100	200	20	10	1
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
489.16220	138946.82	C16 H30 B O16	489.16214	0.05	0.11	2.5
		C29 H22 B N2 O5	489.16163	0.57	1.16	20.5
		C30 H18 B N6 O ←	489.16297	-0.77	-1.57	25.5
		C17 H26 B N4 O12	489.16348	-1.28	-2.62	7.5
		C13 H22 B N10 O10	489.16079	1.40	2.87	8.5
		C18 H22 B N8 O8	489.16482	-2.62	-5.36	12.5

Figure S46. Zoomed-in DART-HRMS [M+H] of sublimed PhO-BsubPc.

Naphthoxy-BsubPc (3b)

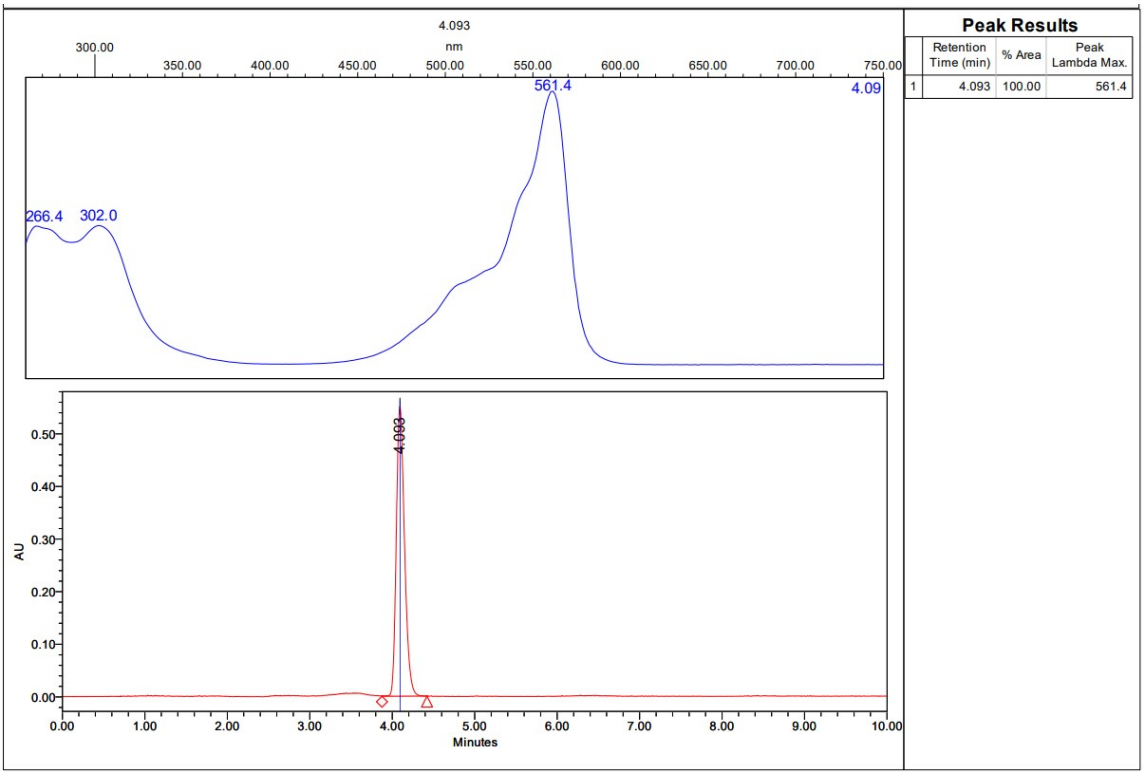


Figure S47. HPLC maxplot of sublimed naphthoxy-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. Naphthoxy-BsubPc has a retention time of 4.093 minutes.

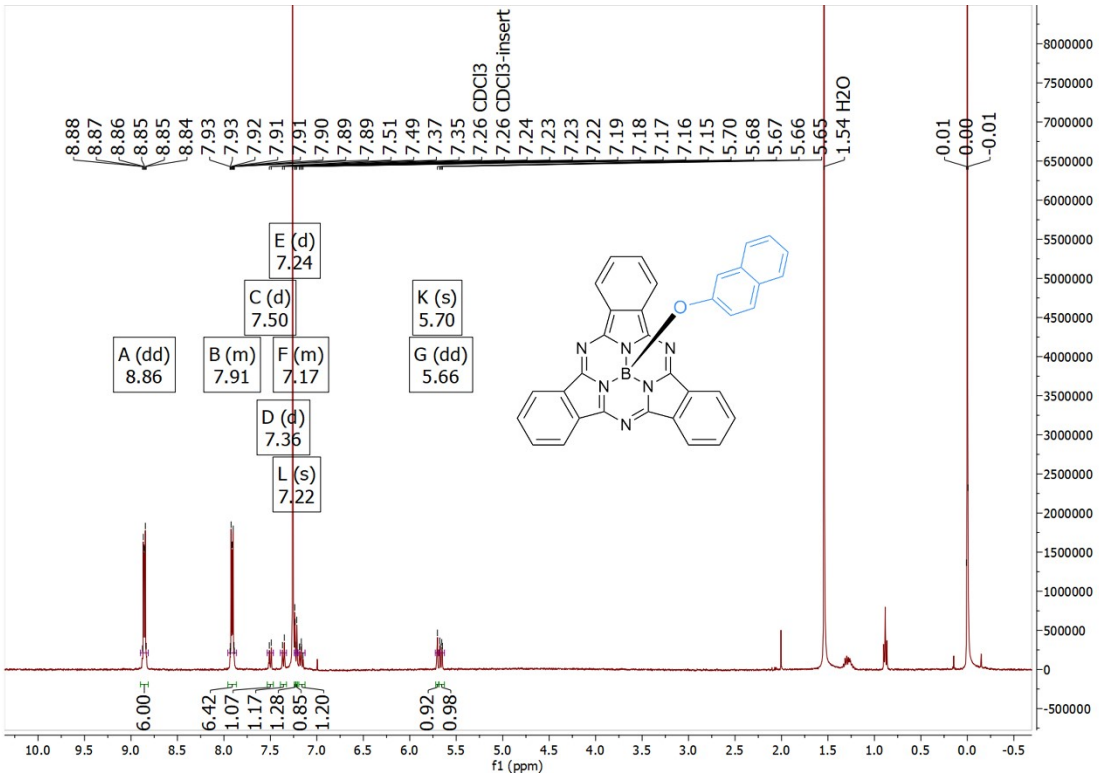


Figure S48. Full ^{1}H NMR spectrum of sublimed naphthoxy-BsubPc (400 MHz, $CDCl_3$).

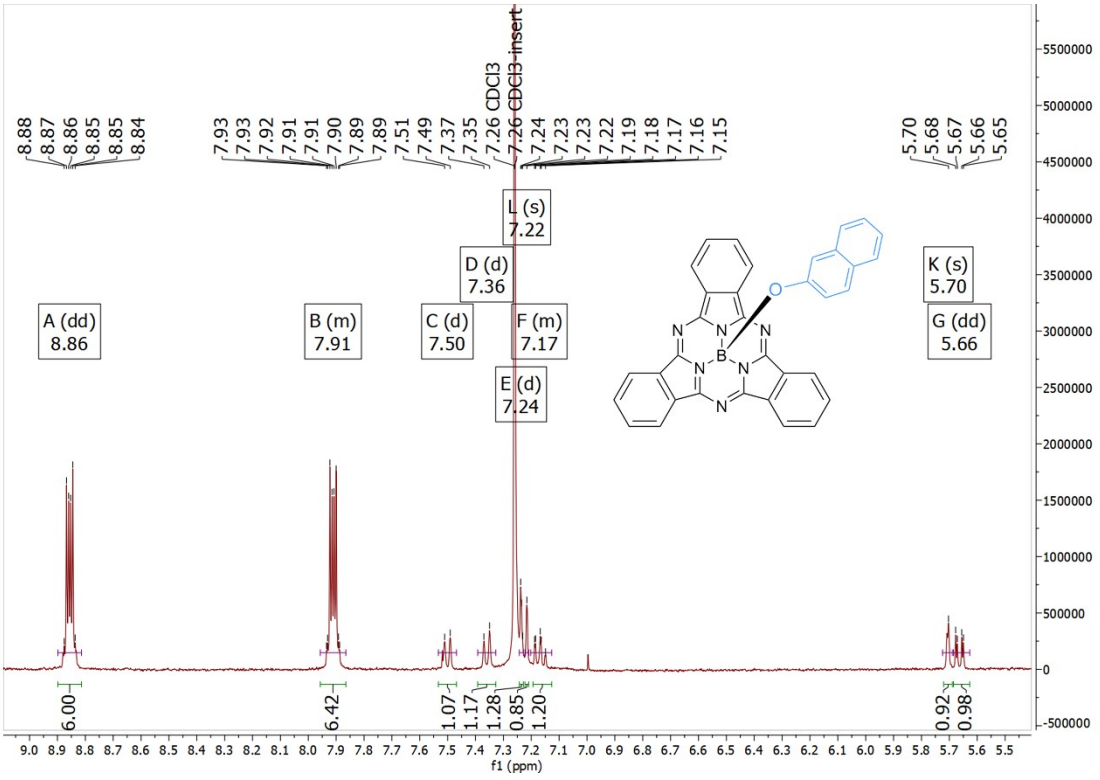


Figure S49. Zoomed-in ^{1}H NMR spectrum of sublimed naphthoxy-BsubPc (400 MHz, $CDCl_3$).

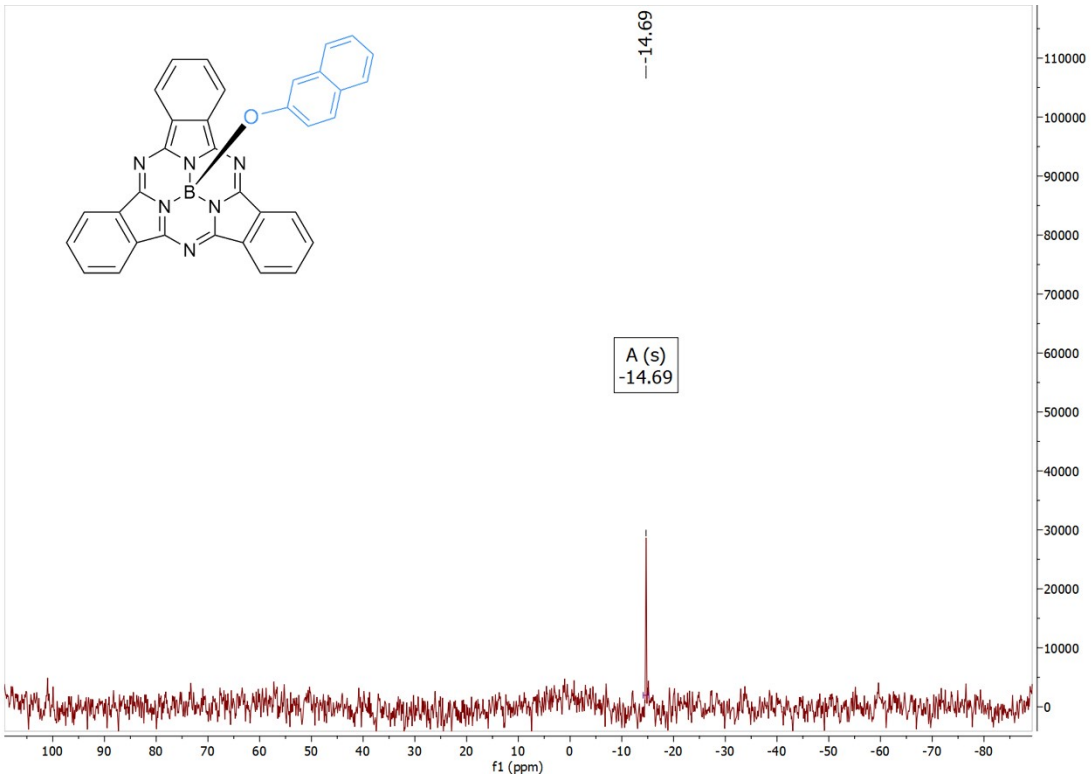


Figure S50. ^{11}B NMR spectrum of sublimed naphthoxy-BsubPc (128 MHz, $CDCl_3$).

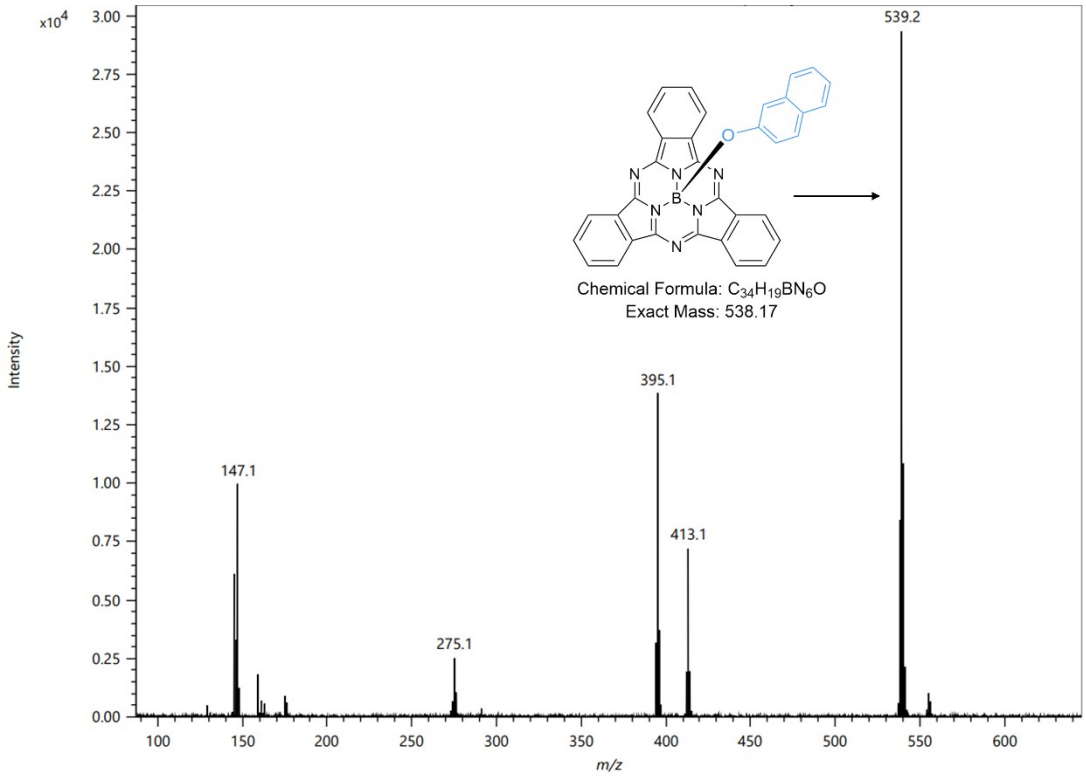
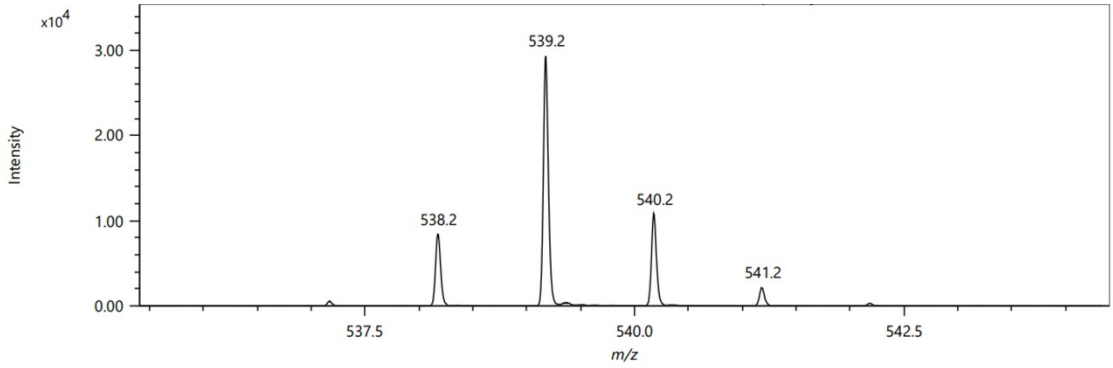


Figure S51. DART-MS [M+H] of sublimed naphthoxy-BsubPc.



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Even	Min	0	0	0	0	1
Charge:	+1	Max	100	200	20	10	1
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
539.17909	29338.43	C21 H28 B N4 O12	539.17913	-0.04	-0.07	10.5
		C34 H20 B N6 O ←	539.17862	0.47	0.88	28.5
		C20 H32 B O16	539.17779	1.30	2.41	5.5
		C22 H24 B N8 O8	539.18047	-1.38	-2.55	15.5
		C33 H24 B N2 O5	539.17728	1.81	3.36	23.5
		C38 H24 B O3	539.18130	-2.21	-4.10	27.5

Figure S52. Zoomed-in DART-HRMS [M+H] of sublimed naphthoxy-BsubPc.

Acetate-BsubPc (4a)

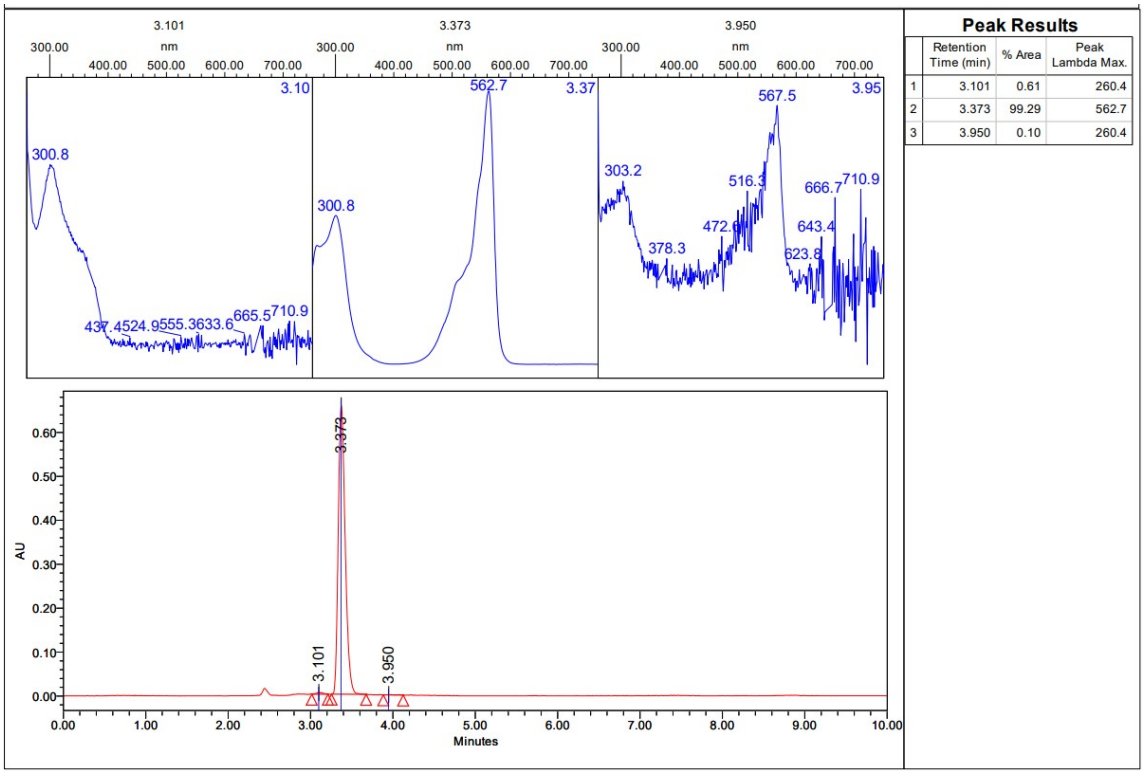


Figure S53. HPLC maxplot of sublimed acetate-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. Acetate-BsubPc has a retention time of 3.373 minutes. The unintegrated peak around 2.4 minutes was confirmed to be an impurity in the HPLC solvent system.

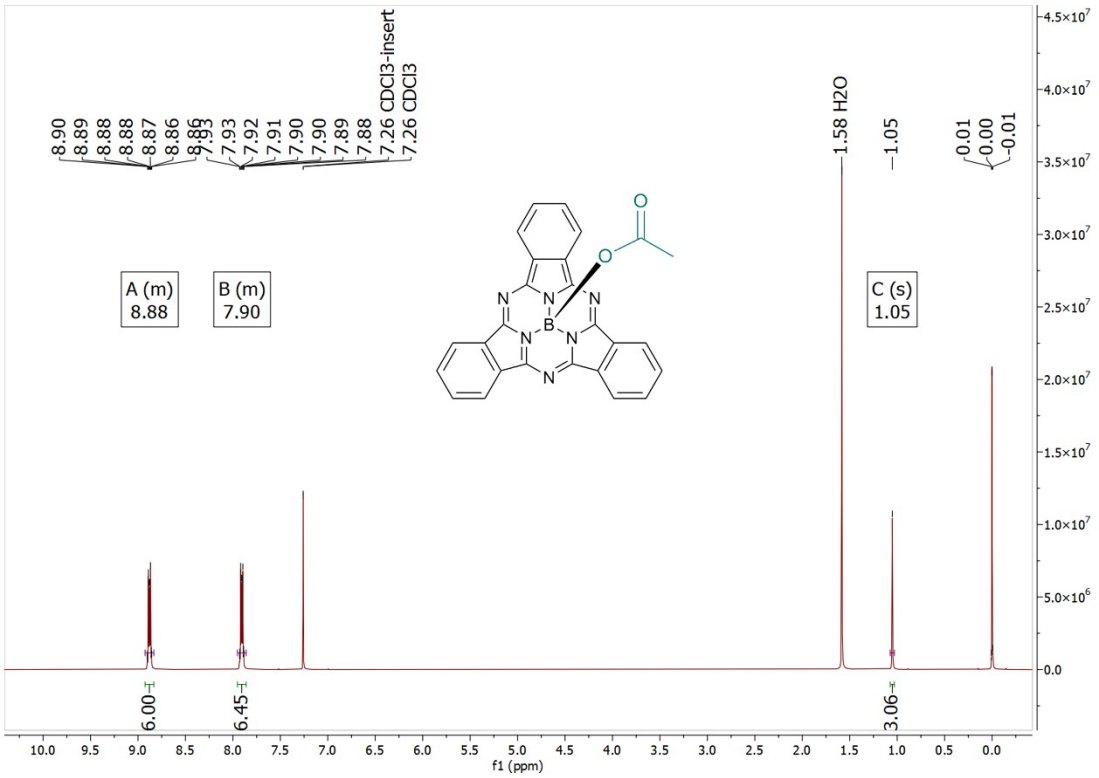


Figure S54. ^{1}H NMR spectrum of sublimed acetate-BsubPc (400 MHz, $CDCl_3$).

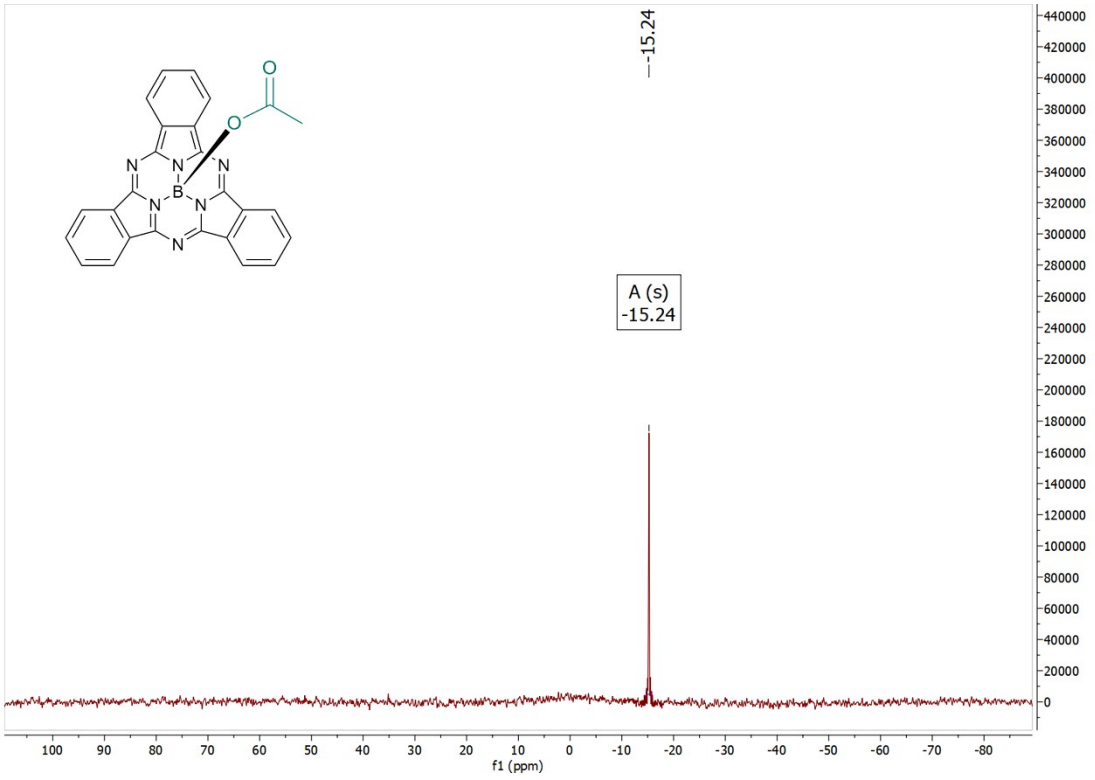


Figure S55. ^{11}B NMR spectrum of sublimed acetate-BsubPc (128 MHz, $CDCl_3$).

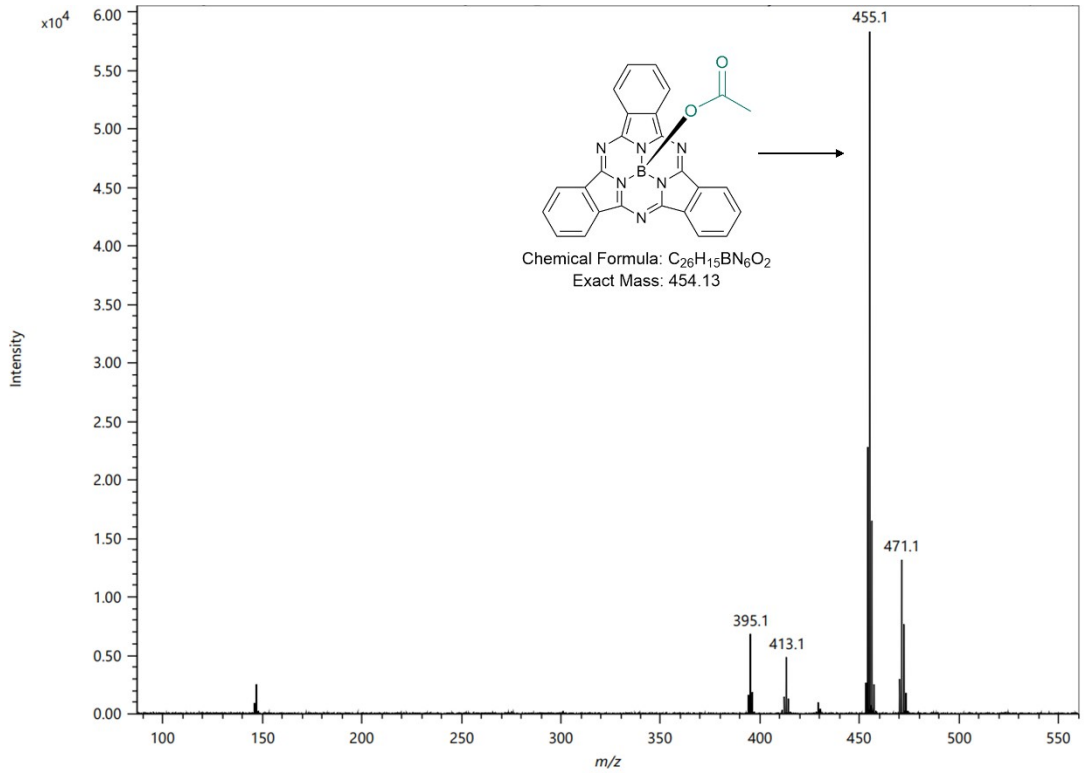
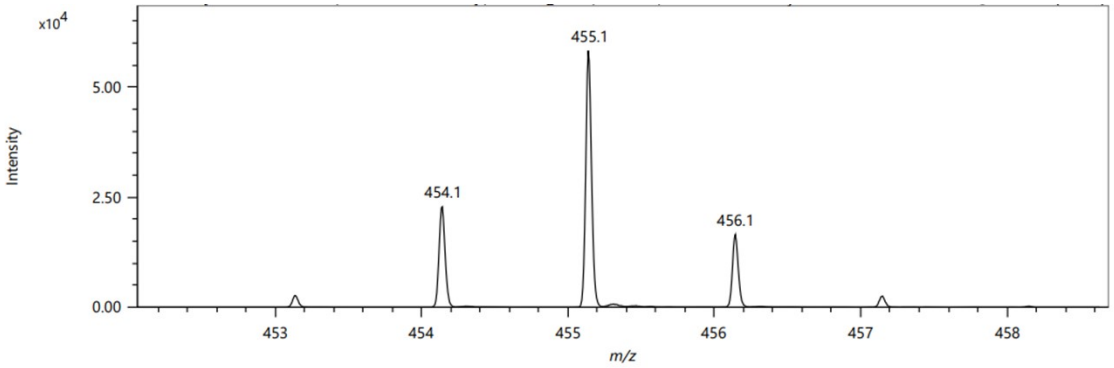


Figure S56. DART-MS [M+H] of sublimed acetate-BsubPc.



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Even	Min	0	0	0	0	1
Charge:	+1	Max	100	200	20	10	1
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
455.14167	58312.83	C12 H28 B O17	455.14141	0.26	0.58	-0.5
		C26 H16 B N6 O2 ←	455.14223	-0.56	-1.23	22.5
		C25 H20 B N2 O6	455.14089	0.78	1.70	17.5
		C13 H24 B N4 O13	455.14274	-1.07	-2.36	4.5
		C9 H20 B N10 O11	455.14006	1.61	3.54	5.5
		C14 H20 B N8 O9	455.14408	-2.41	-5.30	9.5

Figure S57. Zoomed-in DART-HRMS [M+H] of sublimed acetate-BsubPc.

Benzoate-BsubPc (4b)

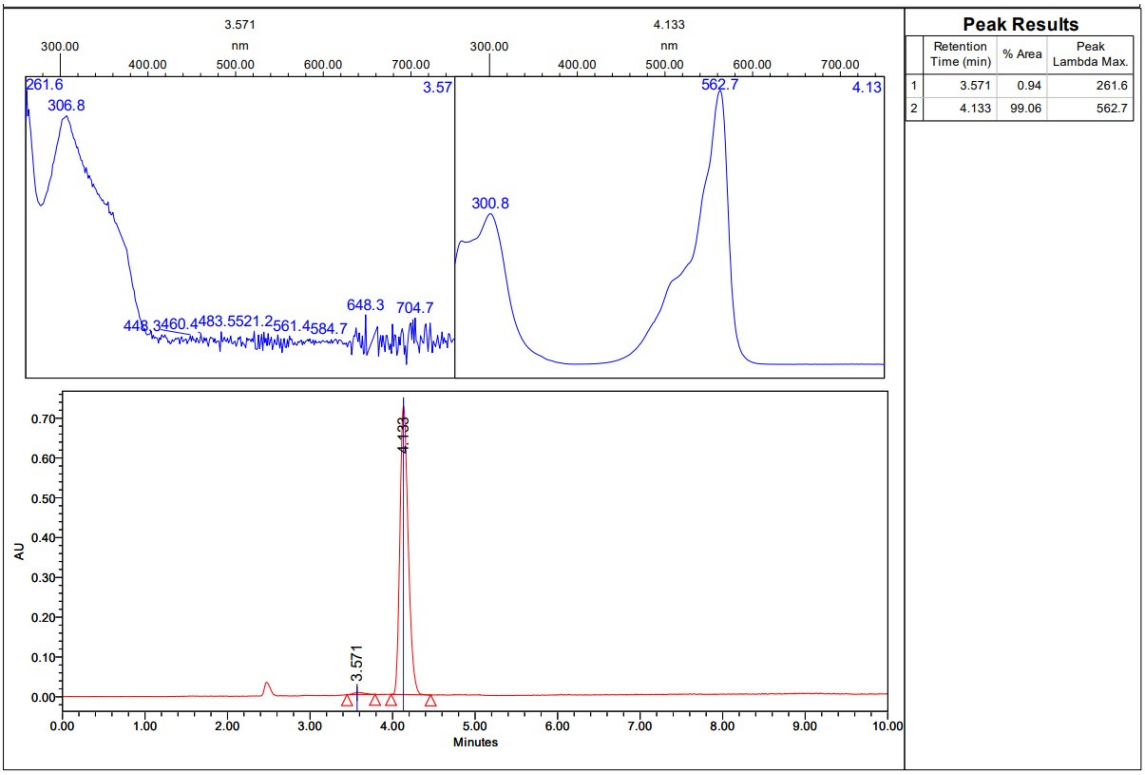


Figure S58. HPLC maxplot of sublimed benzoate-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. Benzoate-BsubPc has a retention time of 4.133 minutes. The unintegrated peak around 2.4 minutes was confirmed to be an impurity in the HPLC solvent system.

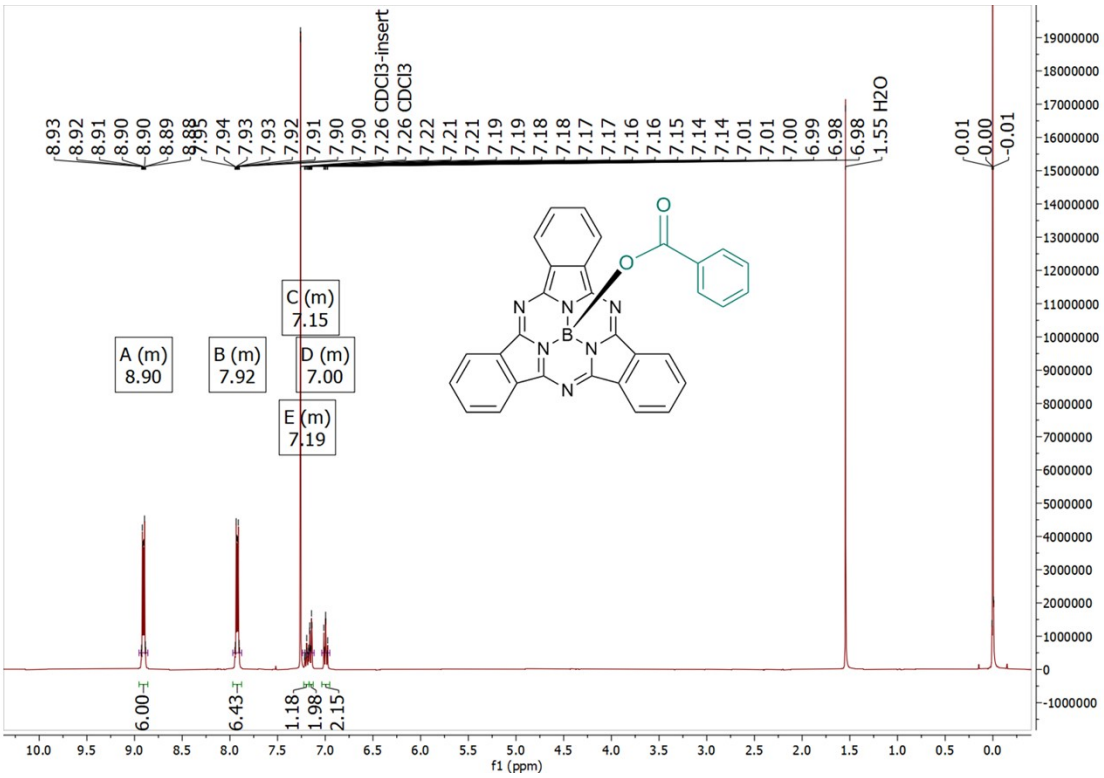


Figure S59. ^{1}H NMR spectrum of sublimed benzoate-BsubPc (400 MHz, $CDCl_3$).

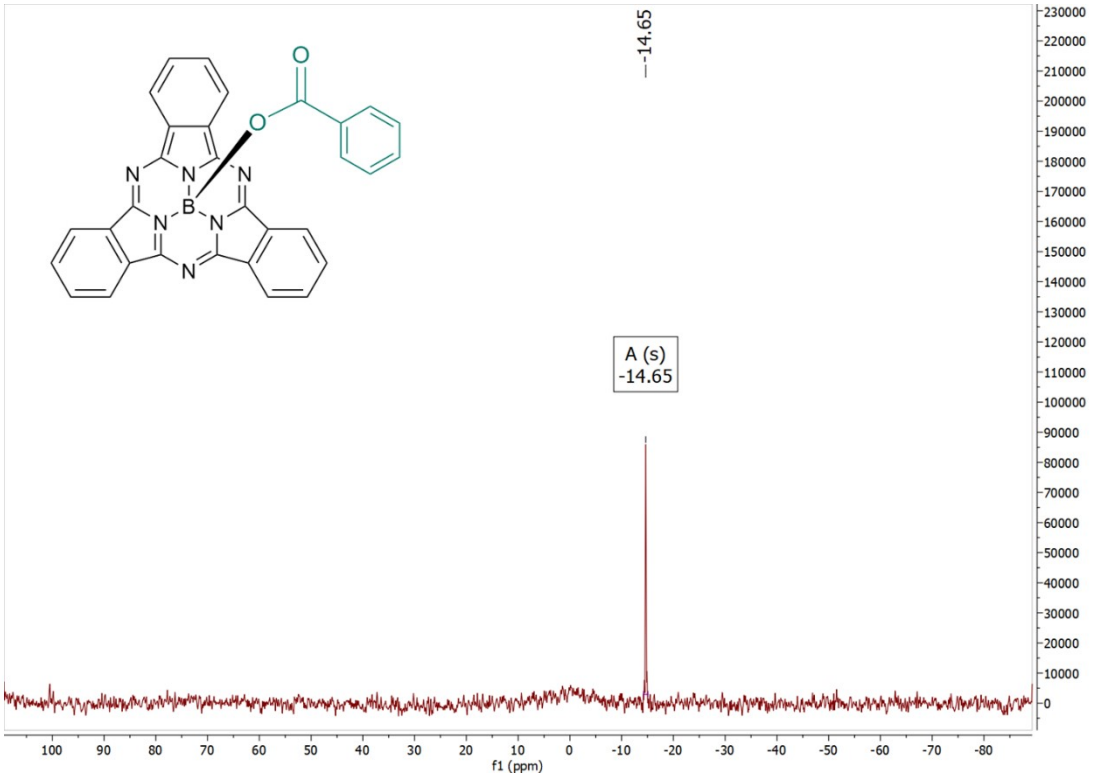


Figure S60. ^{11}B NMR spectrum of sublimed benzoate-BsubPc (128 MHz, $CDCl_3$).

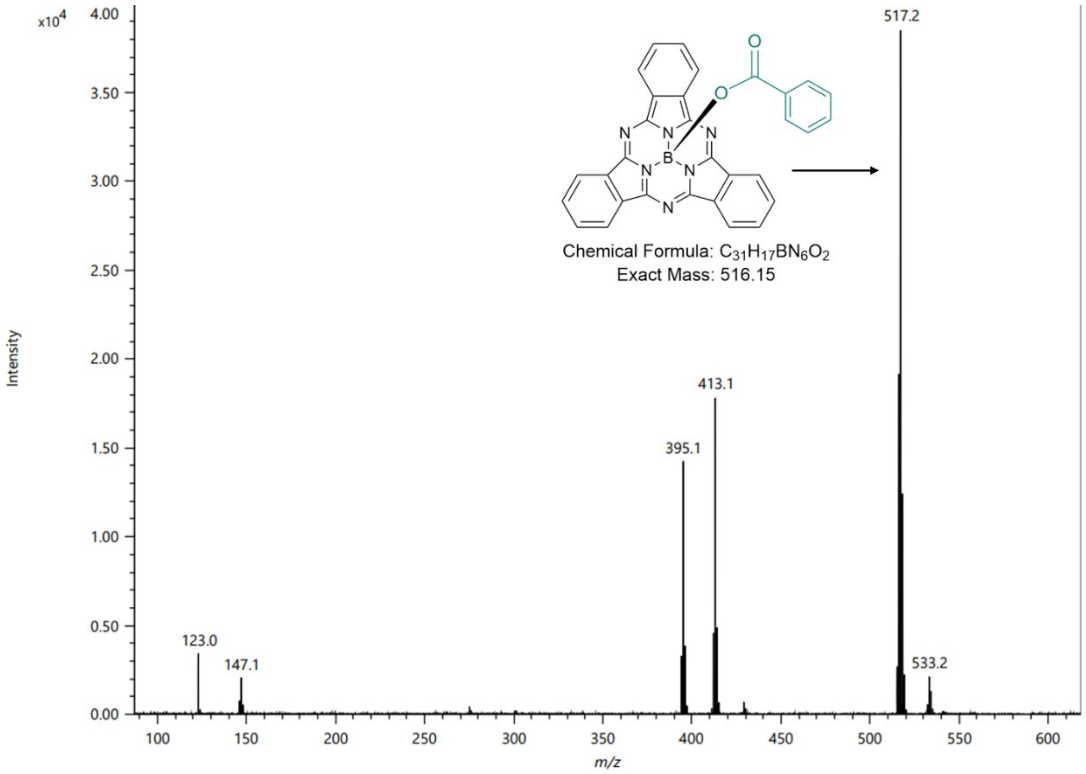
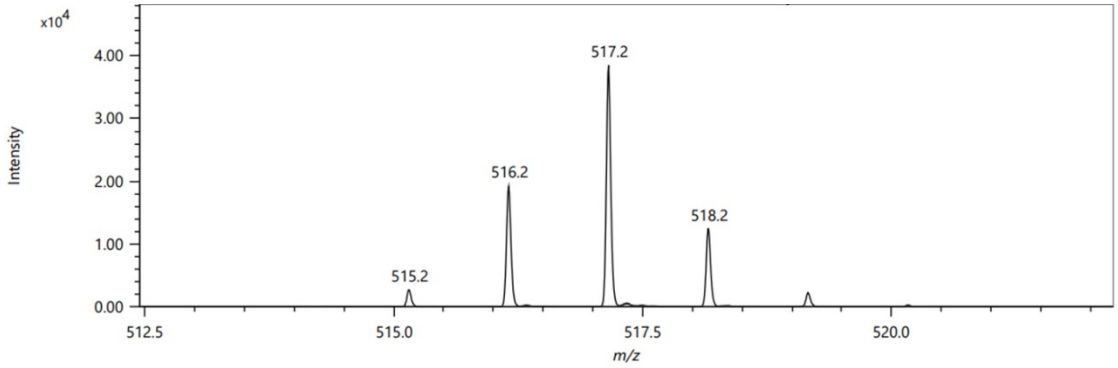


Figure S61. DART-MS [M+H] of sublimed benzoate-BsubPc.



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Even	Min	0	0	0	0	1
Charge:	+1	Max	100	200	20	10	1
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
517.15863	38509.54	C18 H26 B N4 O13	517.15839	0.24	0.46	8.5
		C31 H18 B N6 O2 ←	517.15788	0.75	1.45	26.5
		C19 H22 B N8 O9	517.15973	-1.10	-2.12	13.5
		C17 H30 B O17	517.15706	1.58	3.05	3.5
		C35 H22 B O4	517.16057	-1.93	-3.74	25.5
		C30 H22 B N2 O6	517.15654	2.09	4.04	21.5

Figure S62. Zoomed-in DART-HRMS [M+H] of sublimed benzoate-BsubPc.

HO-BsubPc (5)

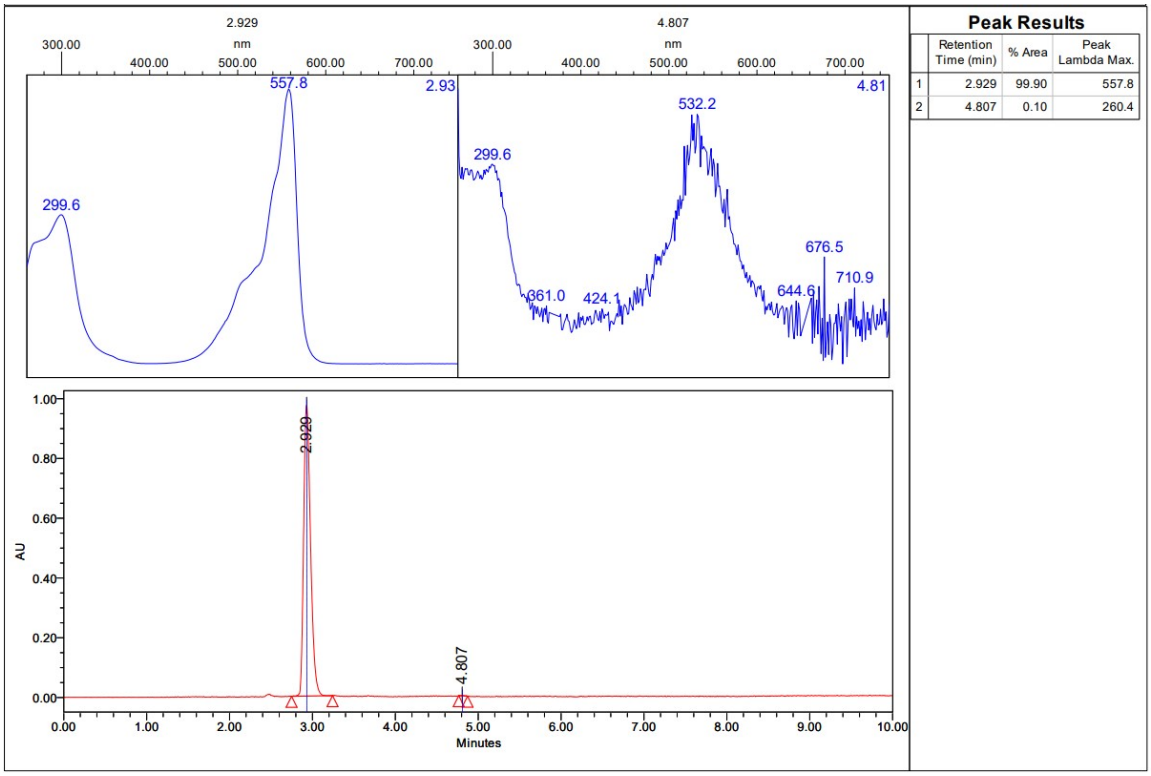


Figure S63. HPLC maxplot of sublimed HO-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. HO-BsubPc has a retention time of 2.929 minutes. The unintegrated peak around 2.4 minutes was confirmed to be an impurity in the HPLC solvent system.

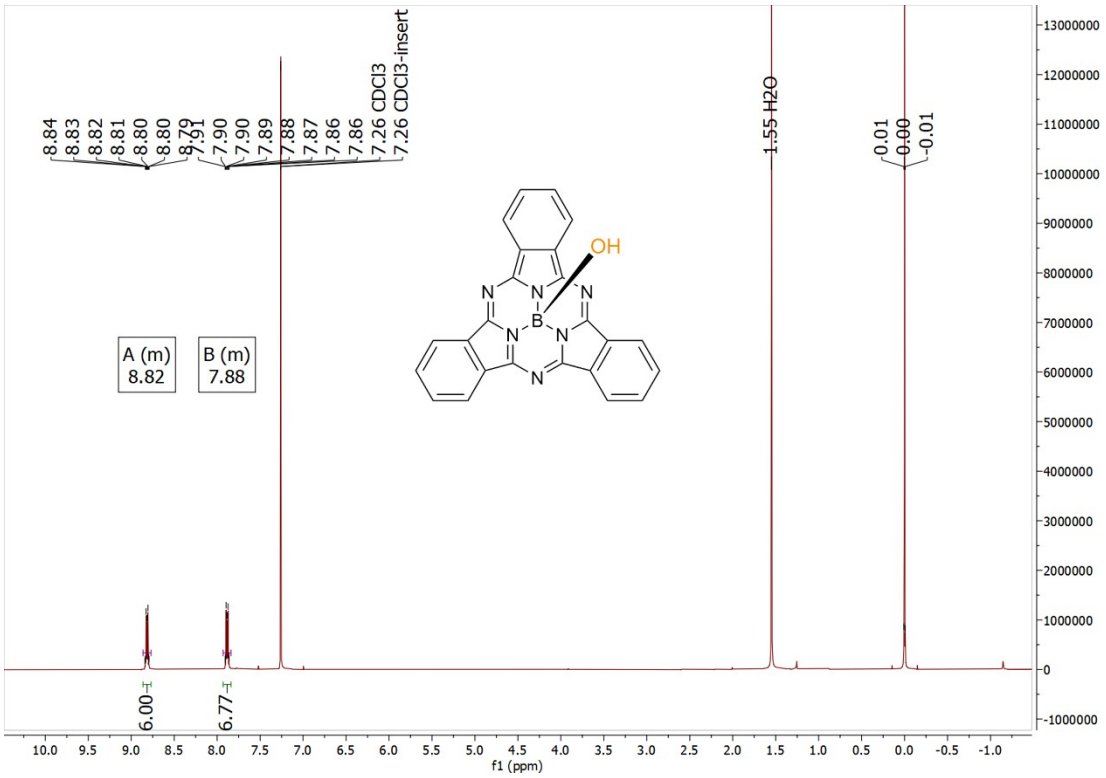


Figure S64. ^{1}H NMR spectrum of sublimed HO-BsubPc (400 MHz, $CDCl_3$).

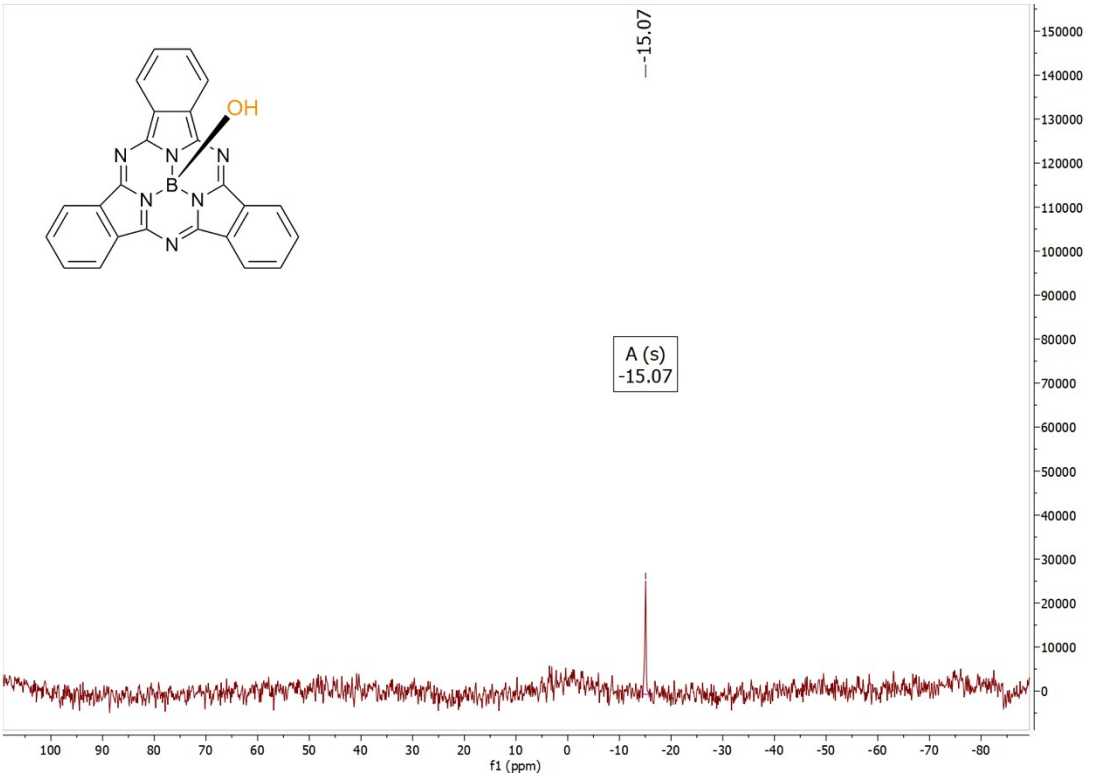


Figure S65. ^{11}B NMR spectrum of sublimed HO-BsubPc (128 MHz, $CDCl_3$).

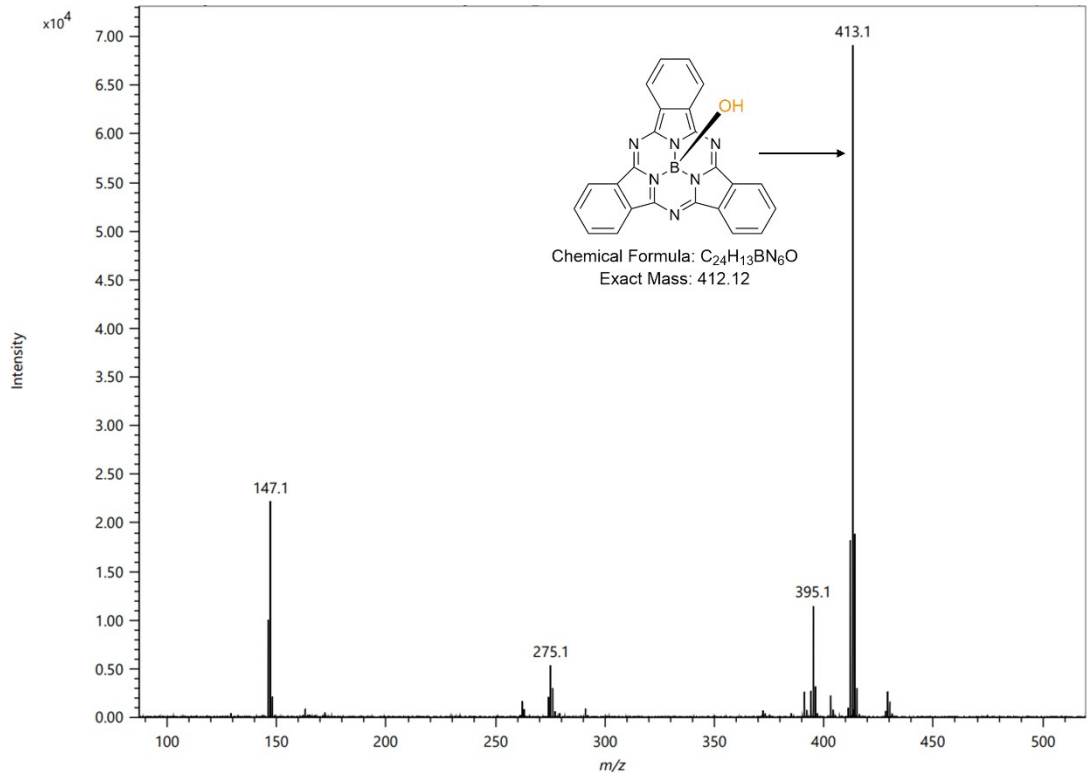
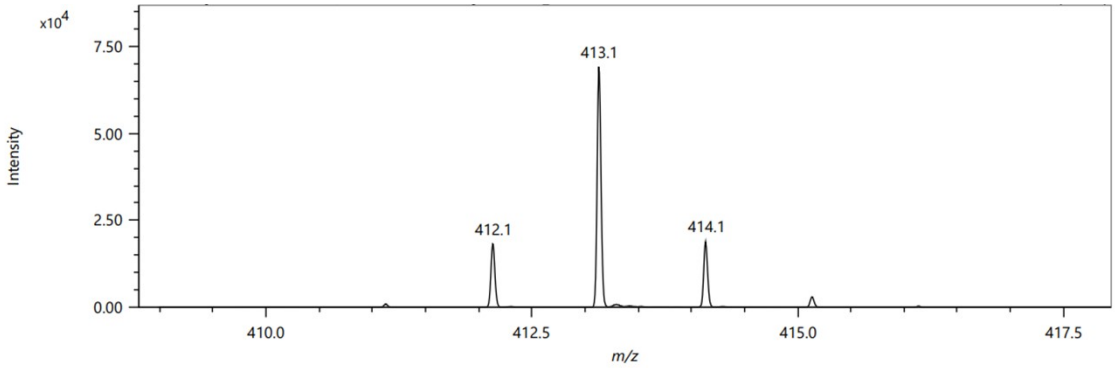


Figure S66. DART-MS [M+H] of sublimed HO-BsubPc.



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Even	Min	0	0	0	0	1
Charge:	+1	Max	100	200	20	10	1
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
413.13224	69134.81	C11 H22 B N4 O12	413.13218	0.06	0.14	3.5
		C24 H14 B N6 O ←	413.13167	0.57	1.38	21.5
		C12 H18 B N8 O8	413.13352	-1.28	-3.10	8.5
		C10 H26 B O16	413.13084	1.40	3.38	-1.5
		C23 H18 B N2 O5	413.13033	1.91	4.62	16.5
		C28 H18 B O3	413.13435	-2.11	-5.12	20.5

Figure S67. Zoomed-in DART-HRMS [M+H] of sublimed HO-BsubPc.

TMSO-BsubPc (6)

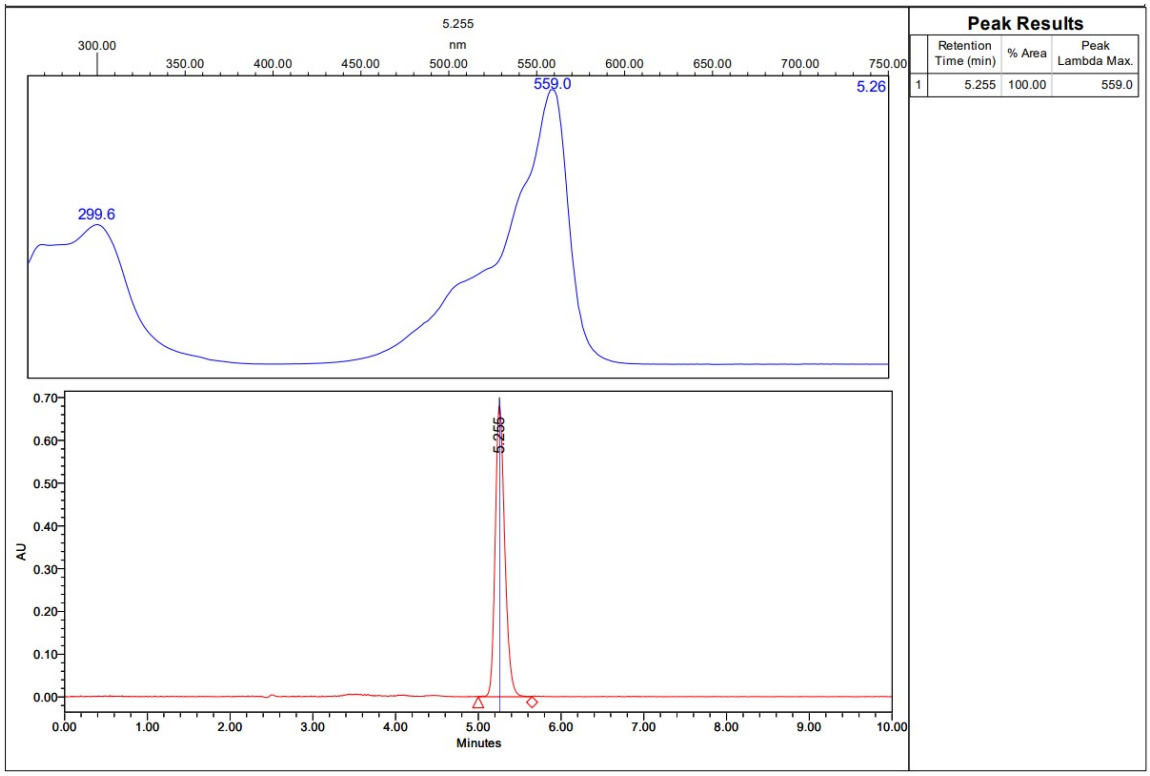


Figure S68. HPLC maxplot of column-purified TMSO-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. TMSO-BsubPc has a retention time of 5.255 minutes.

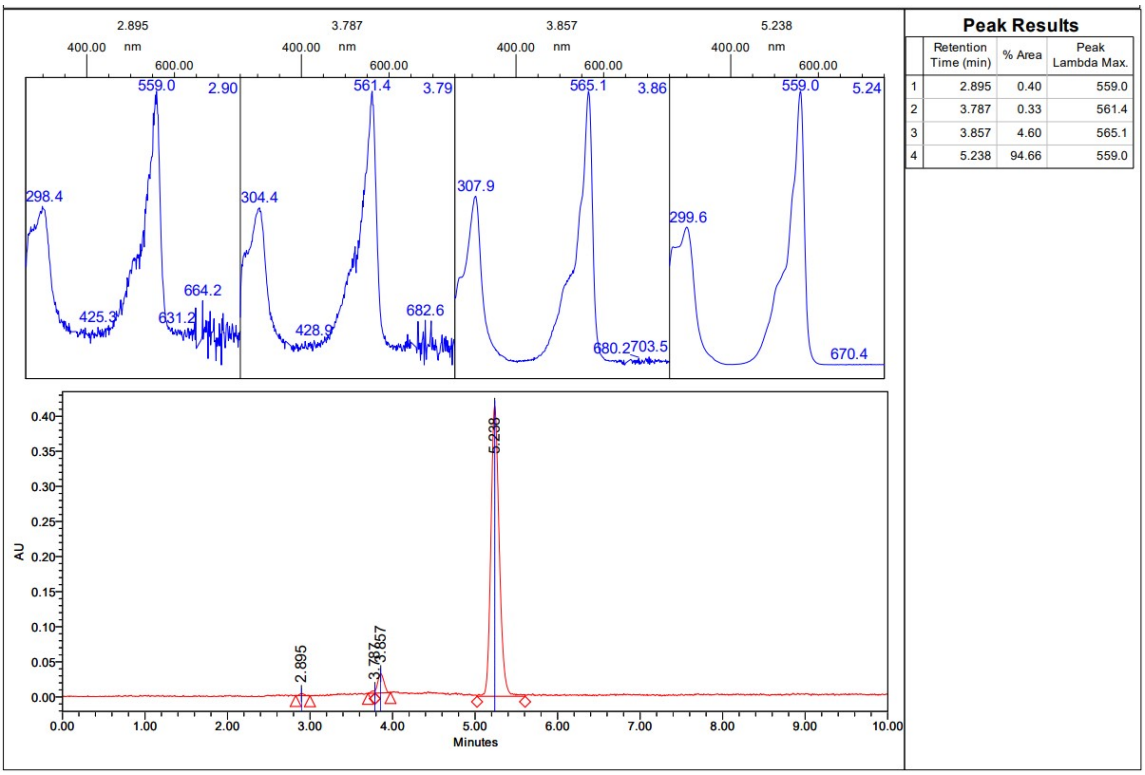


Figure S69. HPLC maxplot of sublimed TMSO-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. TMSO-BsubPc has a retention time of 5.238 minutes.

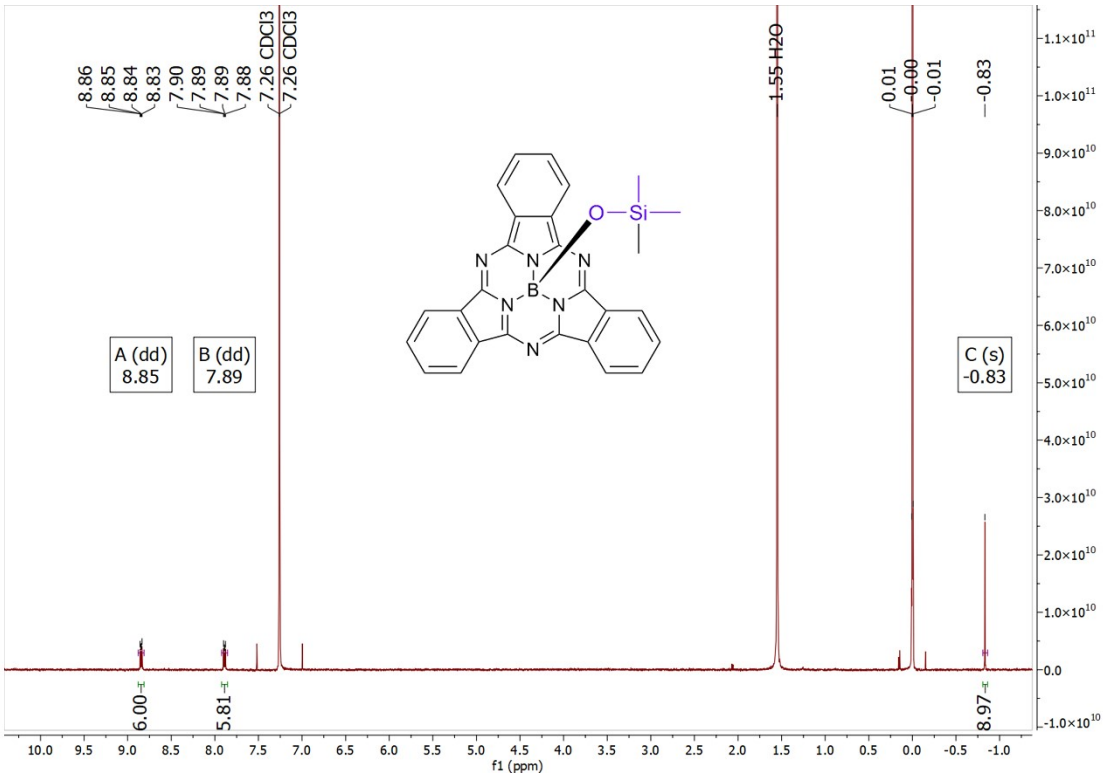


Figure S70. ^{1}H NMR spectrum of column-purified TMSO-BsubPc (400 MHz, $CDCl_3$).

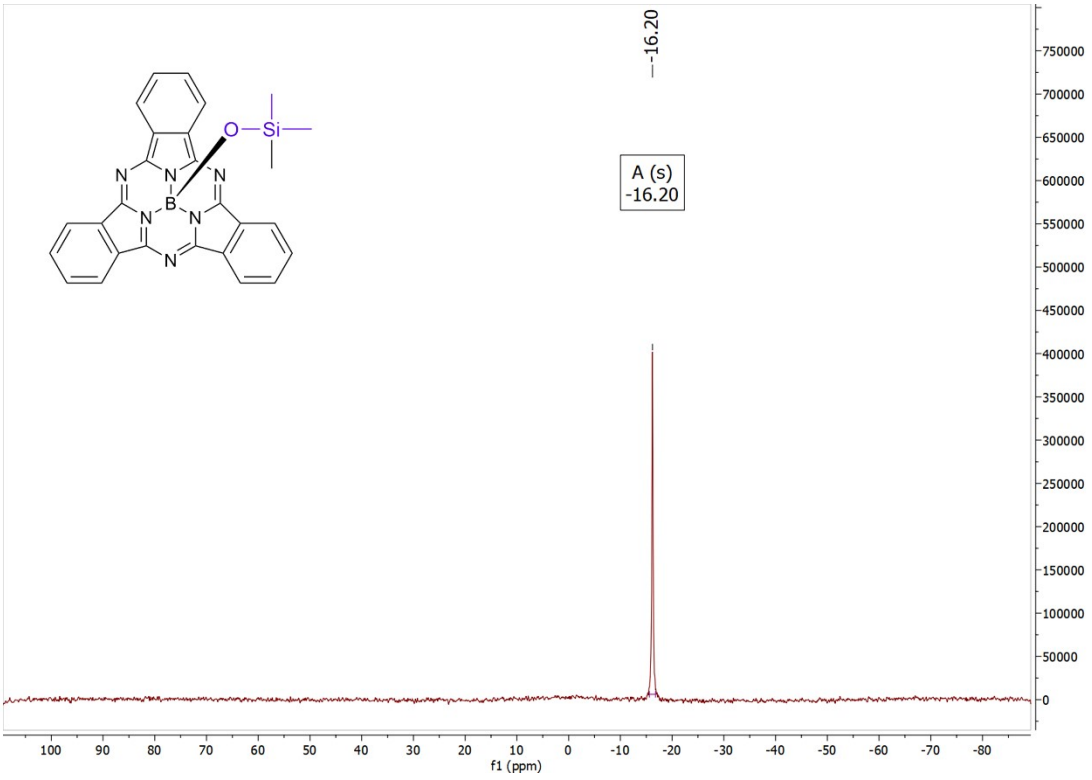


Figure S71. ^{11}B NMR spectrum of column-purified TMSO-BsubPc (128 MHz, $CDCl_3$).

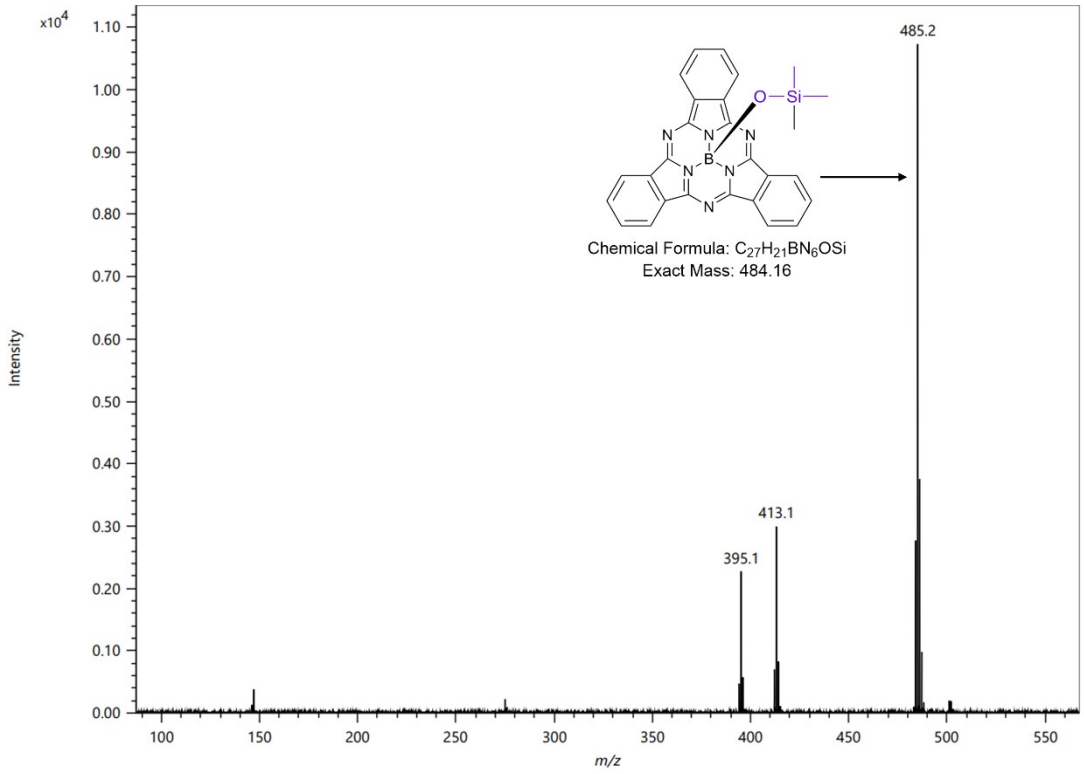
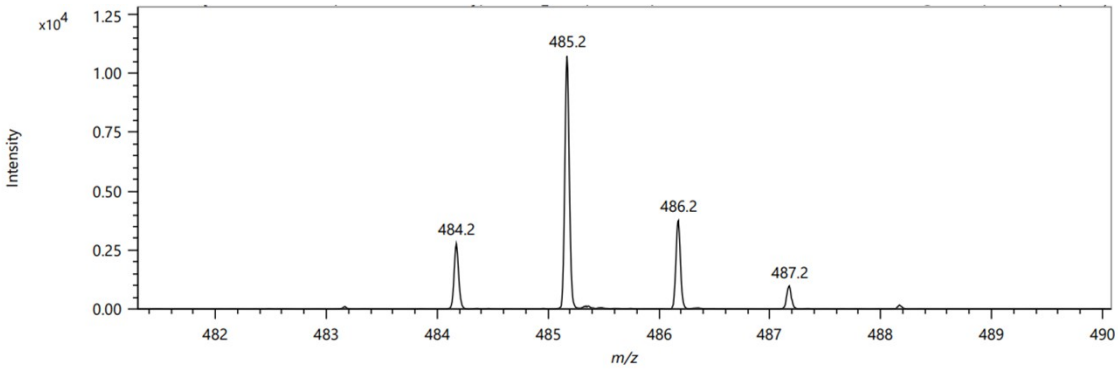


Figure S72. DART-MS [M+H] of column-purified TMSO-BsubPc.



Elemental Composition

Parameters		Elements Set 1:						
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B	Si
Electron:	Even	Min	0	0	0	0	1	1
Charge:	+1	Max	100	200	20	10	1	1
DBE:	-1.5 - 100.0							

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
485.17185	10733.20	C14 H30 B N4 O12 Si	485.17171	0.15	0.30	3.5
		C27 H22 B N6 O Si ←	485.17119	0.66	1.36	21.5
		C15 H26 B N8 O8 Si	485.17304	-1.19	-2.46	8.5
		C13 H34 B O16 Si	485.17037	1.48	3.06	-1.5
		C26 H26 B N2 O5 Si	485.16986	2.00	4.11	16.5
		C31 H26 B O3 Si	485.17388	-2.03	-4.18	20.5

Figure S73. Zoomed-in DART-HRMS [M+H] of column-purified TMSO-BsubPc.

Ph-BsubPc (7)

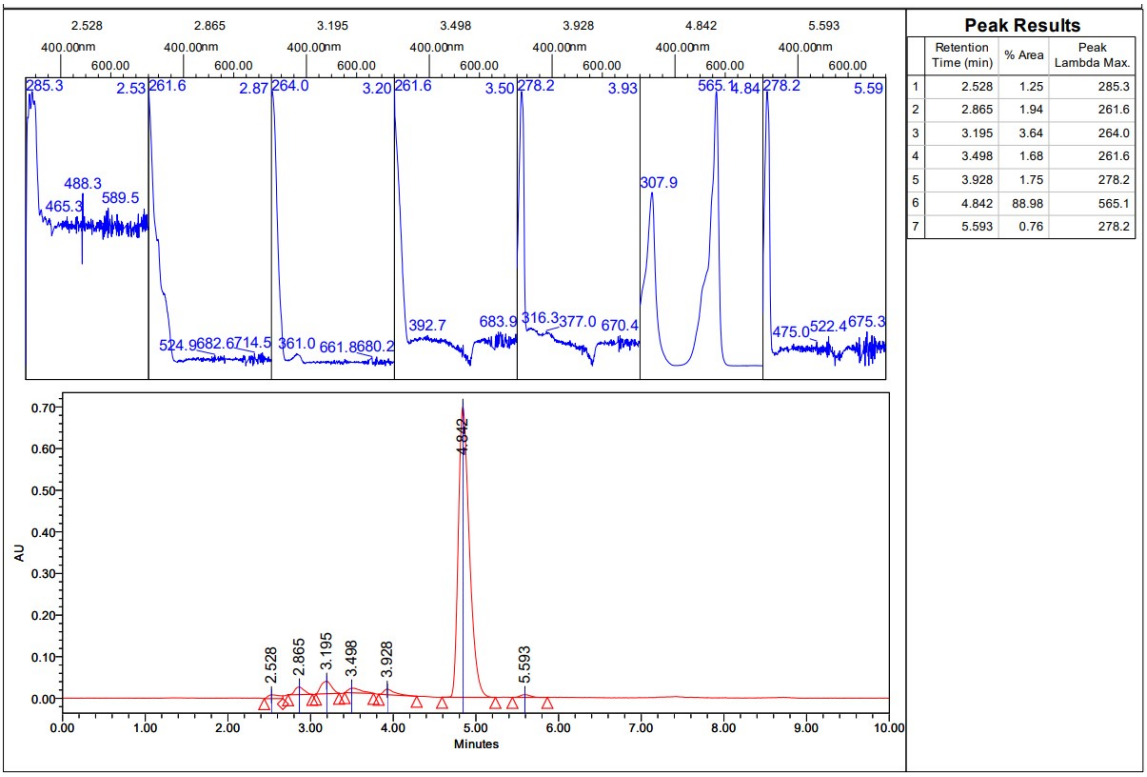


Figure S74. HPLC maxplot of column-purified Ph-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. Ph-BsubPc has a retention time of 4.842 minutes.

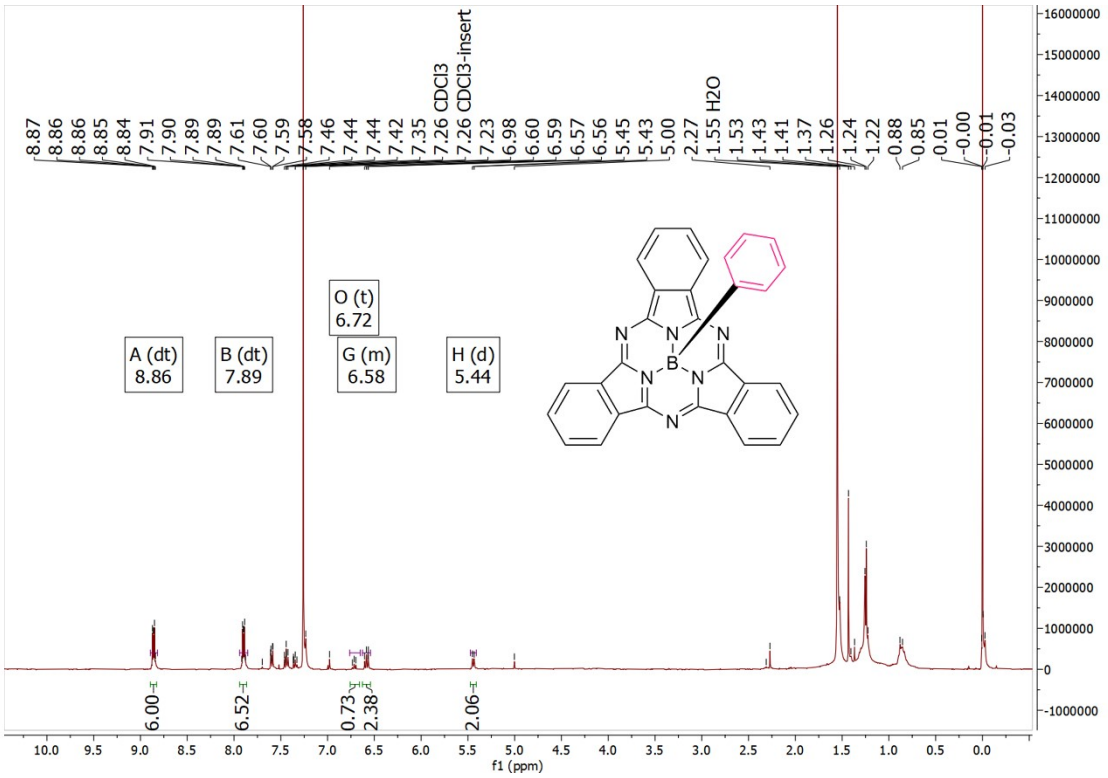


Figure S75. Full ^{1}H NMR spectrum of column-purified Ph-BsubPc (400 MHz, $CDCl_3$).

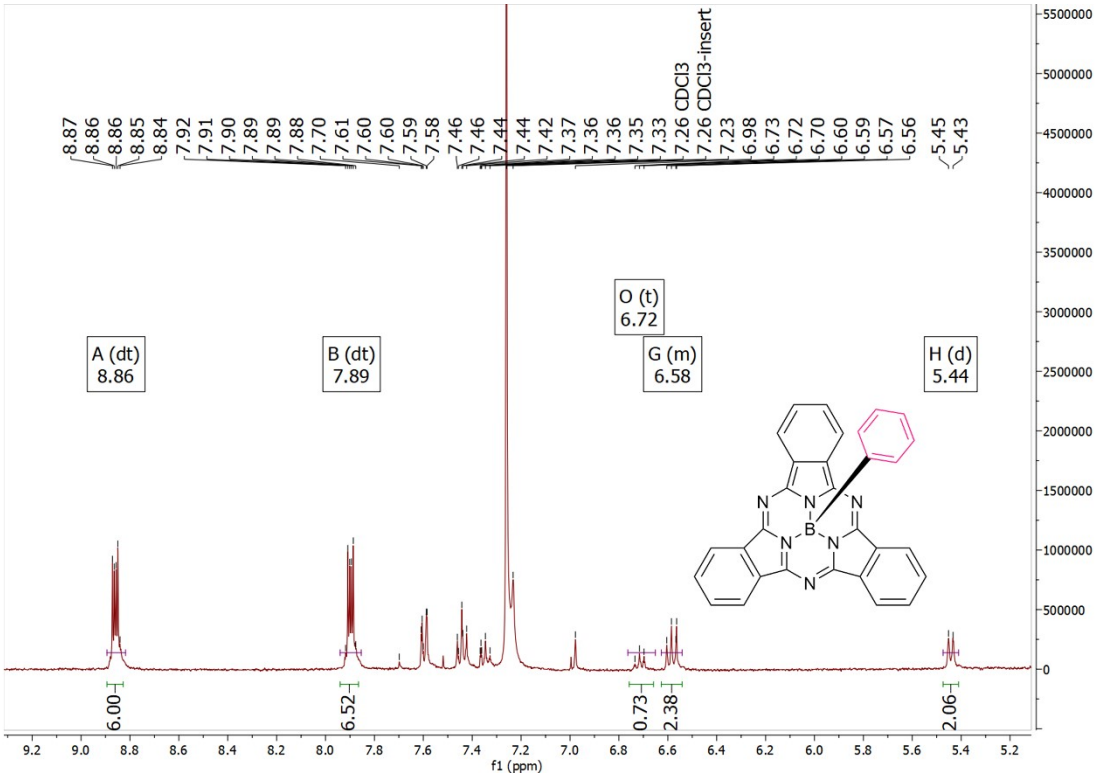


Figure S76. Zoomed-in ^{1}H NMR spectrum of column-purified Ph-BsubPc (400 MHz, $CDCl_3$).

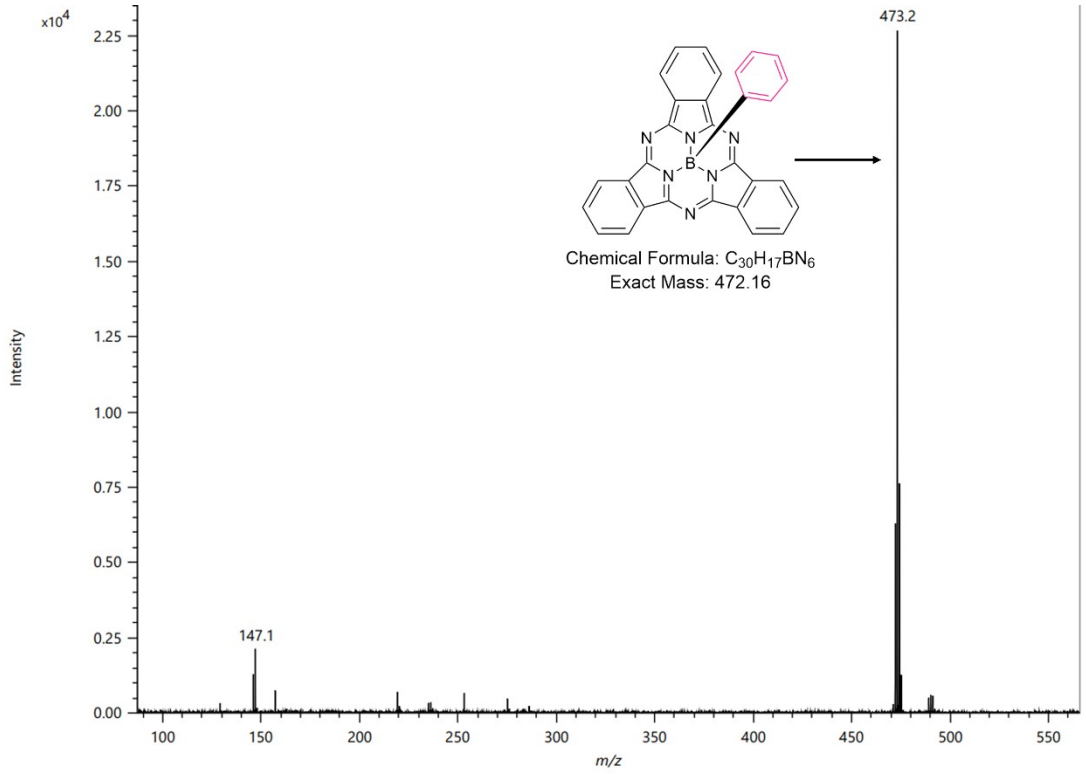
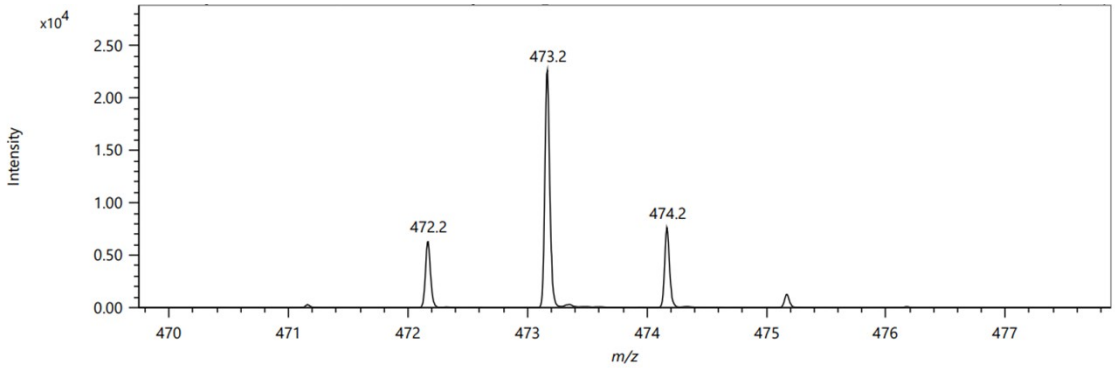


Figure S77. DART-MS [M+H] of column-purified Ph-BsubPc.



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Even	Min	0	0	0	0	1
Charge:	+1	Max	100	200	20	10	1
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
473.16728	22669.74	C16 H30 B O15	473.16723	0.05	0.11	2.5
		C29 H22 B N2 O4	473.16671	0.56	1.19	20.5
		C30 H18 B N6 ←	473.16805	-0.77	-1.63	25.5
		C17 H26 B N4 O11	473.16856	-1.29	-2.72	7.5
		C13 H22 B N10 O9	473.16588	1.40	2.96	8.5
		C18 H22 B N8 O7	473.16990	-2.62	-5.54	12.5

Figure S78. Zoomed-in DART-HRMS [M+H] of column-purified Ph-BsubPc.

F_5PhS-BsubPc (8a)

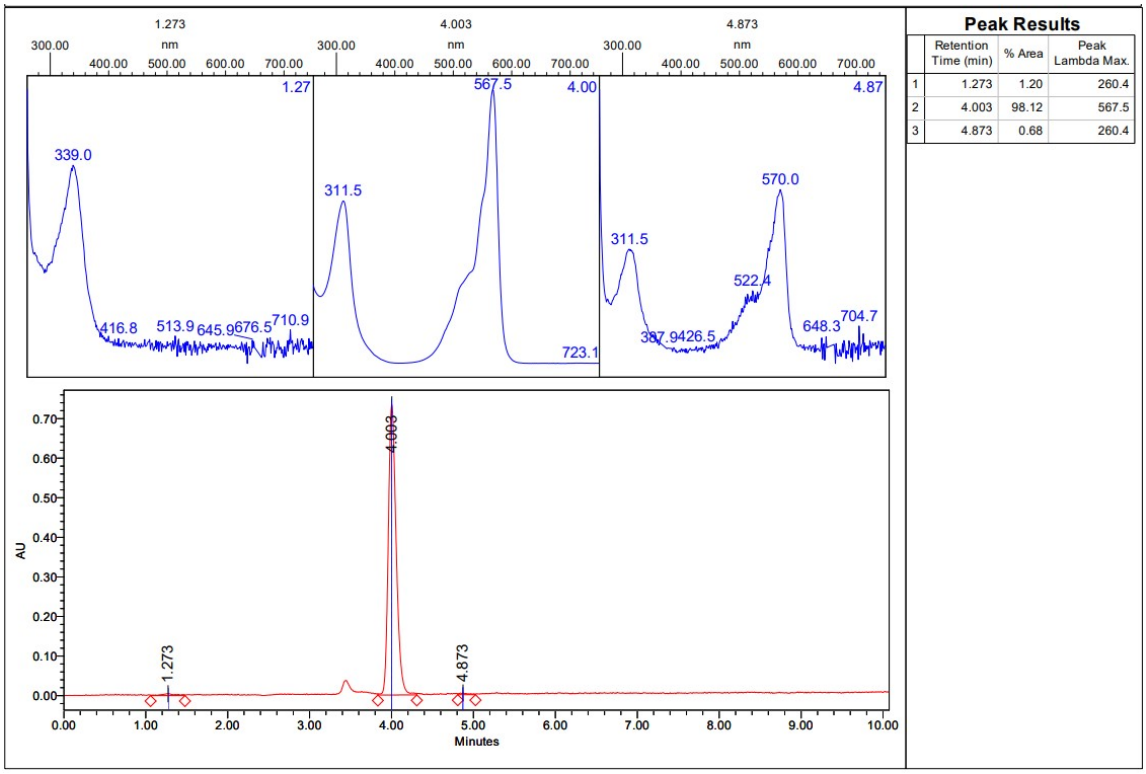


Figure S79. HPLC maxplot of column-purified F_5PhS-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. F_5PhS-BsubPc has a retention time of 4.003 minutes.

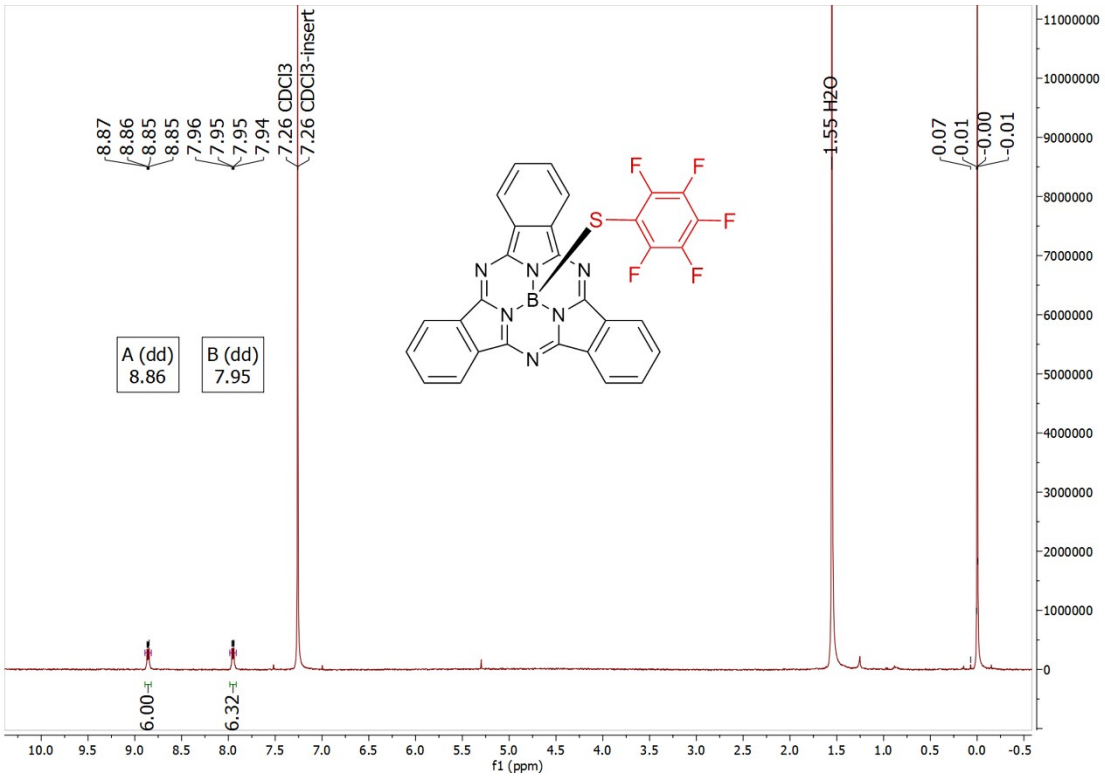


Figure S80. ^{1}H NMR spectrum of column-purified F_5PhS-BsubPc (400 MHz, $CDCl_3$).

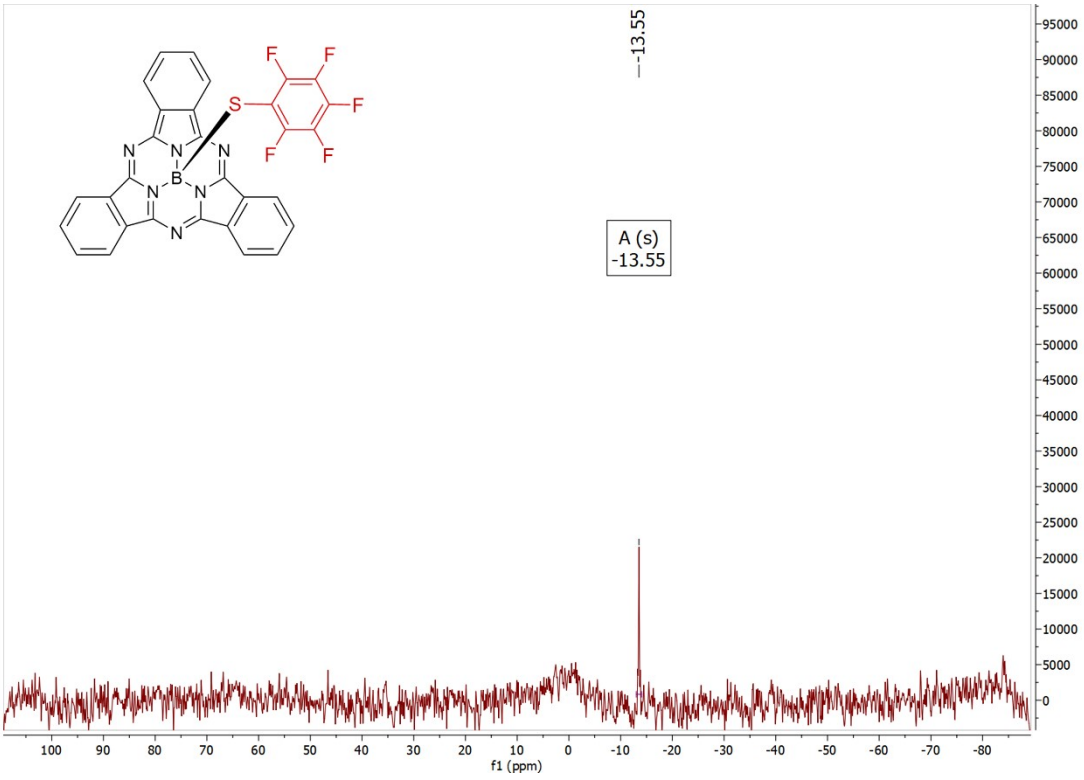


Figure S81. ^{11}B NMR spectrum of column-purified F_5PhS-BsubPc (128 MHz, $CDCl_3$).

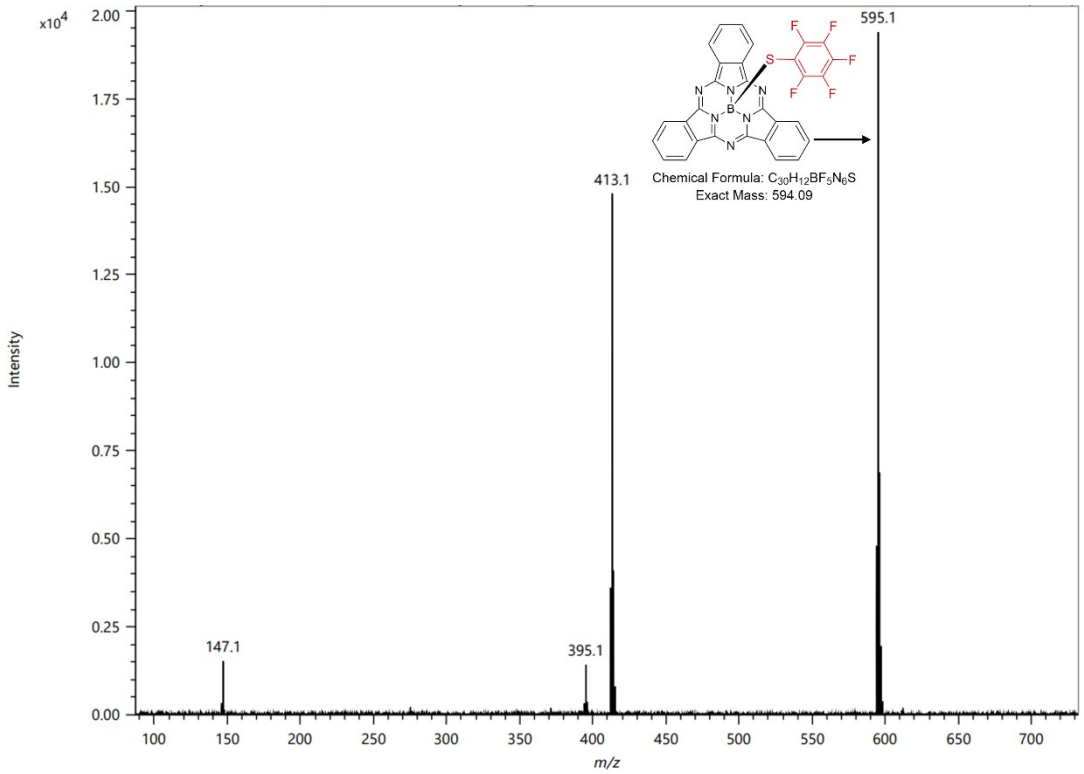
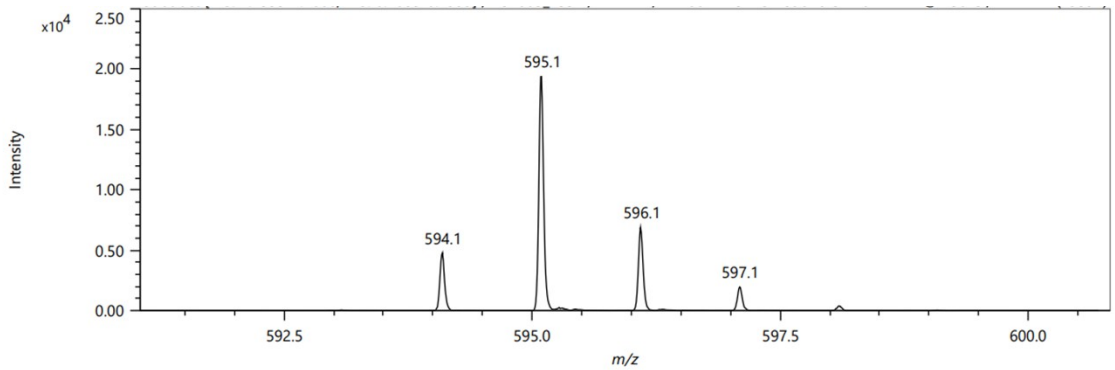


Figure S82. DART-MS [M+H] of column-purified F_5PhS-BsubPc.



Elemental Composition

Parameters		Elements Set 1:							
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	S	B	F
Electron:	Even	Min	0	0	0	0	1	1	5
Charge:	+1	Max	100	200	20	10	1	1	5
DBE:	-1.5 - 100.0								

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
595.09317	19392.39	C30 H13 B N6 F5 S ←	595.09301	0.16	0.27	25.5
		C17 H21 B N4 O11 F5 S	595.09353	-0.35	-0.59	7.5
		C16 H25 B O15 F5 S	595.09219	0.99	1.66	2.5
		C29 H17 B N2 O4 F5 S	595.09168	1.50	2.52	20.5
		C18 H17 B N8 O7 F5 S	595.09486	-1.69	-2.84	12.5
		C13 H17 B N10 O9 F5 S	595.09084	2.33	3.92	8.5

Figure S83. Zoomed-in DART-HRMS [M+H] of column-purified F_5PhS-BsubPc.

MePhS-BsubPc (8b)

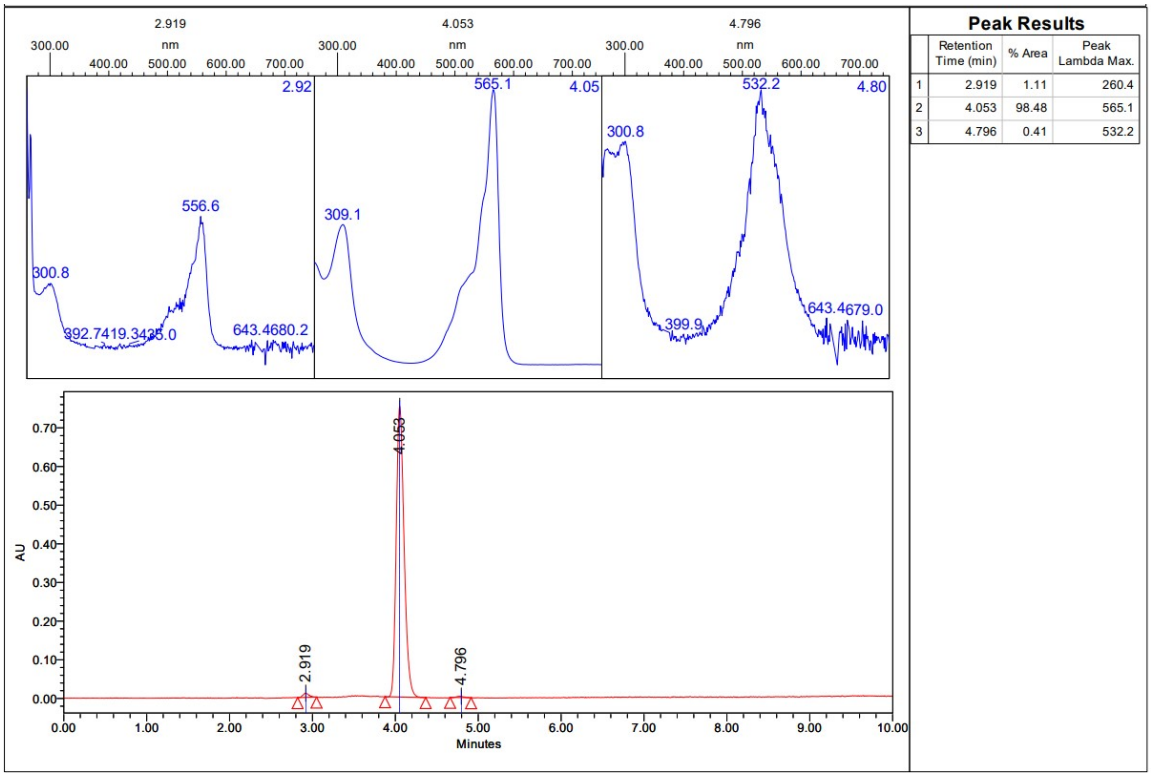


Figure S84. HPLC maxplot of column-purified MePhS-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. MePhS-BsubPc has a retention time of 4.053 minutes.

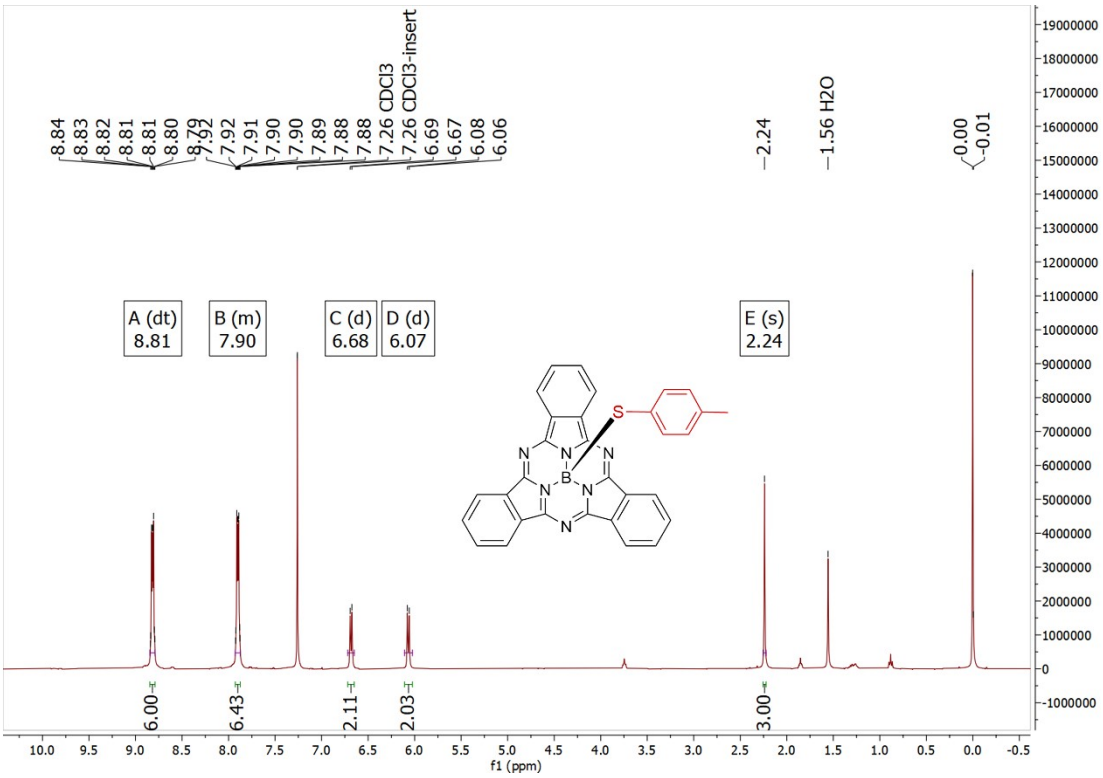


Figure S85. ^{1}H NMR spectrum of column-purified MePhS-BsubPc (400 MHz, $CDCl_3$).

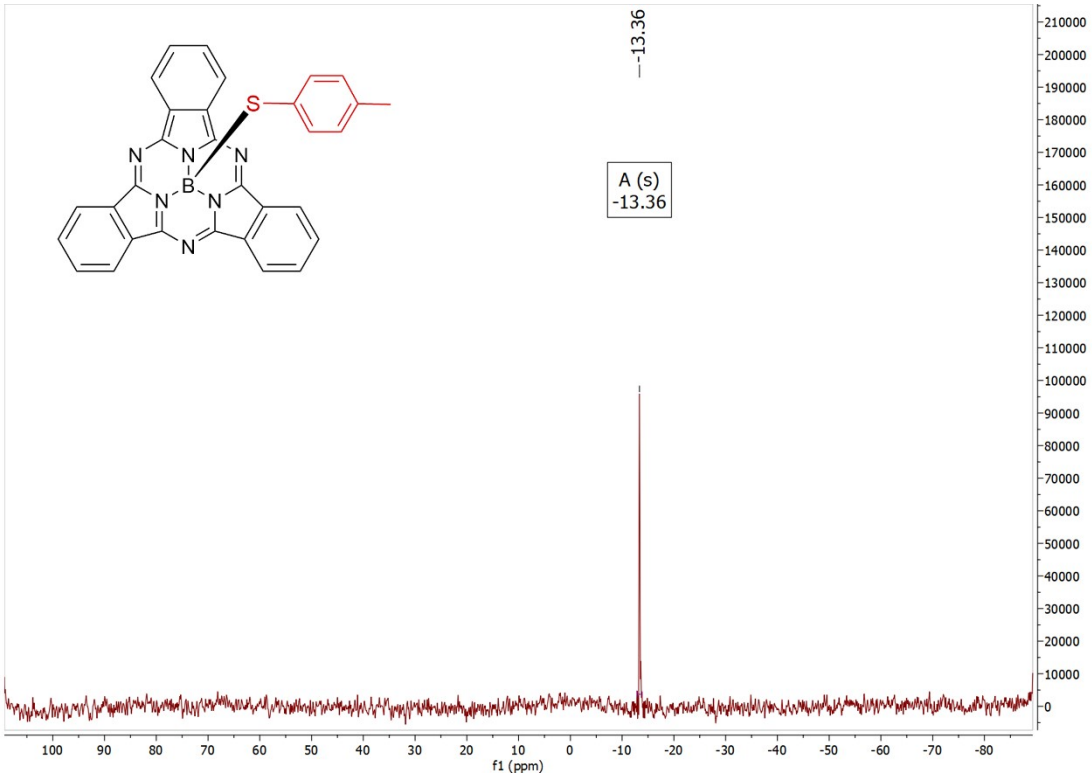


Figure S86. ^{11}B NMR spectrum of column-purified MePhS-BsubPc (128 MHz, $CDCl_3$).

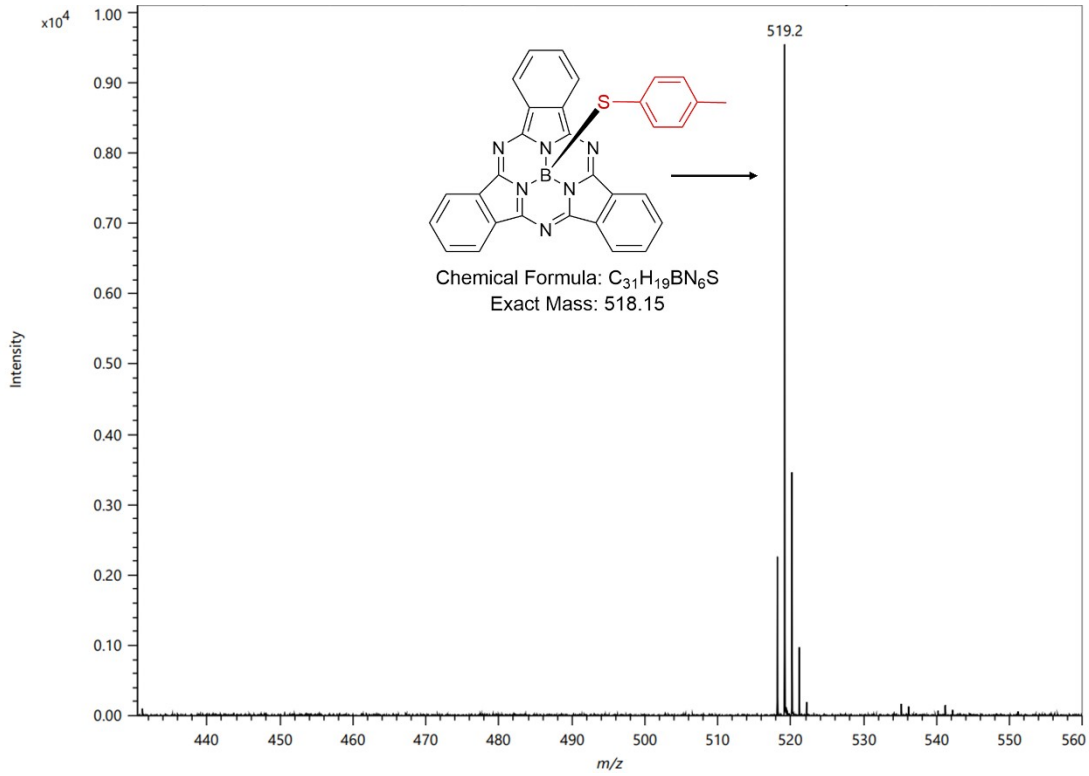
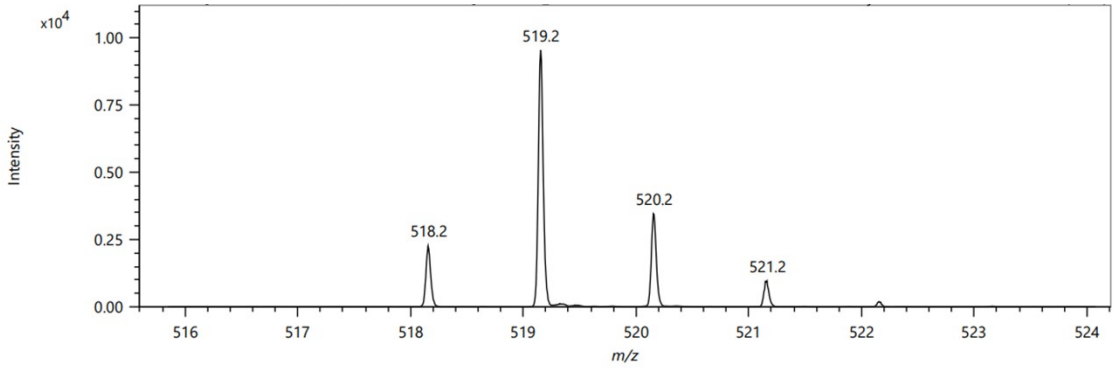


Figure S87. DART-MS [M+H] of column-purified MePhS-BsubPc.



Elemental Composition

Parameters		Elements Set 1:						
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B	S
Electron:	Even	Min	0	0	0	0	1	1
Charge:	+1	Max	100	200	20	10	1	1
DBE:	-1.5 - 100.0							

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
519.15676	9548.75	C18 H28 B N4 O11 S	519.15629	0.47	0.91	7.5
		C19 H24 B N8 O7 S	519.15762	-0.86	-1.66	12.5
		C31 H20 B N6 S ←	519.15577	0.99	1.90	25.5
		C35 H24 B O2 S	519.15846	-1.70	-3.27	24.5
		C17 H32 B O15 S	519.15495	1.81	3.49	2.5
		C30 H24 B N2 O4 S	519.15443	2.32	4.48	20.5

Figure S88. Zoomed-in DART-HRMS [M+H] of column-purified MePhS-BsubPc.

PhMeN-BsubPc (9)

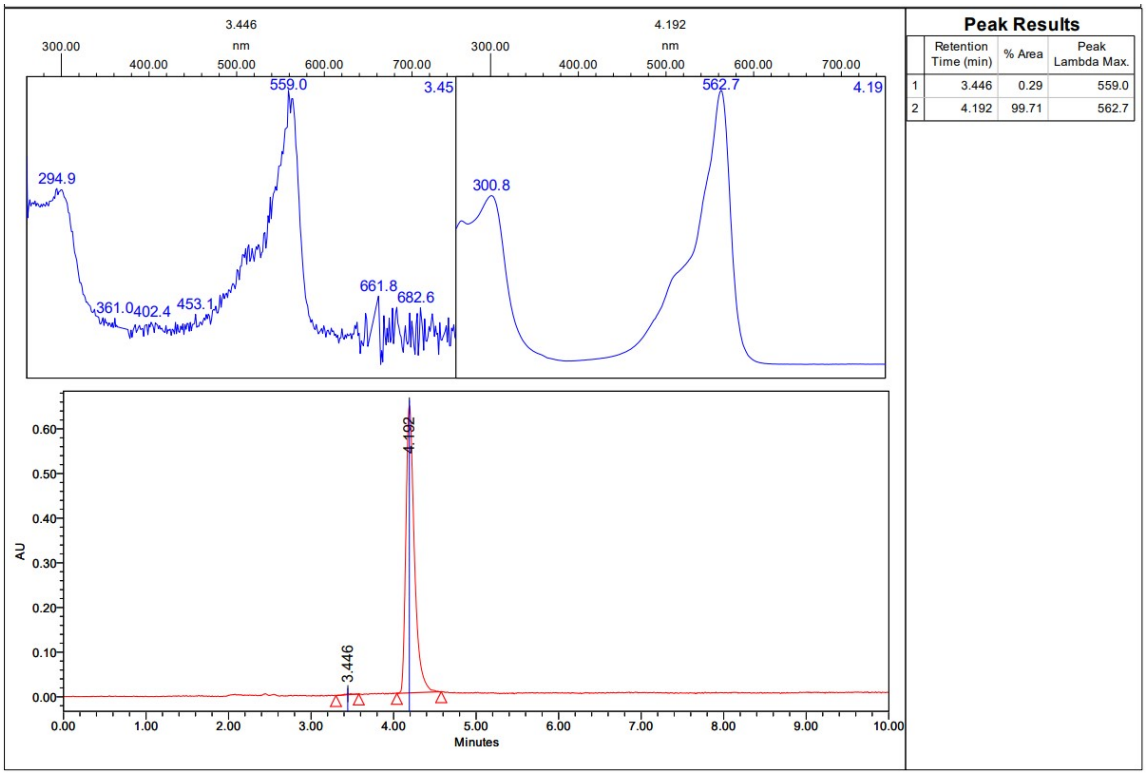


Figure S89. HPLC maxplot of column-purified PhMeN-BsubPc with a mobile phase of 80:20 (v:v) ACN/DMF. PhMeN-BsubPc has a retention time of 4.192 minutes.

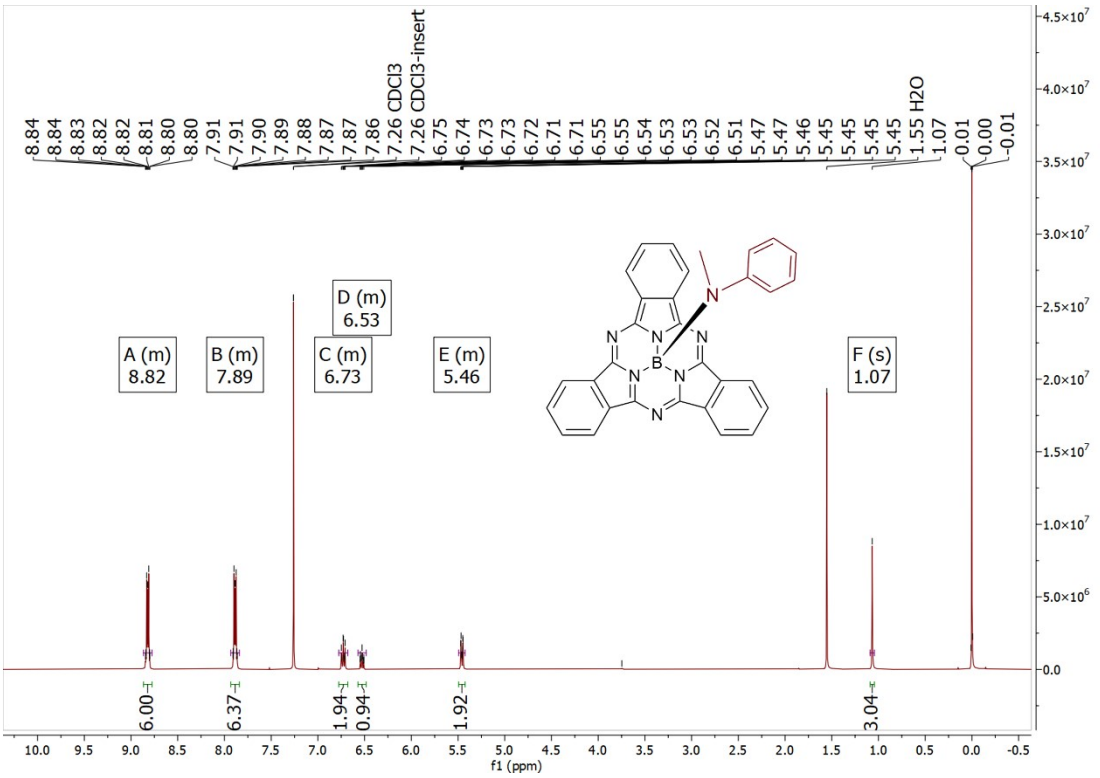


Figure S90. ^{1}H NMR spectrum of column-purified PhMeN-BsubPc (400 MHz, $CDCl_3$).

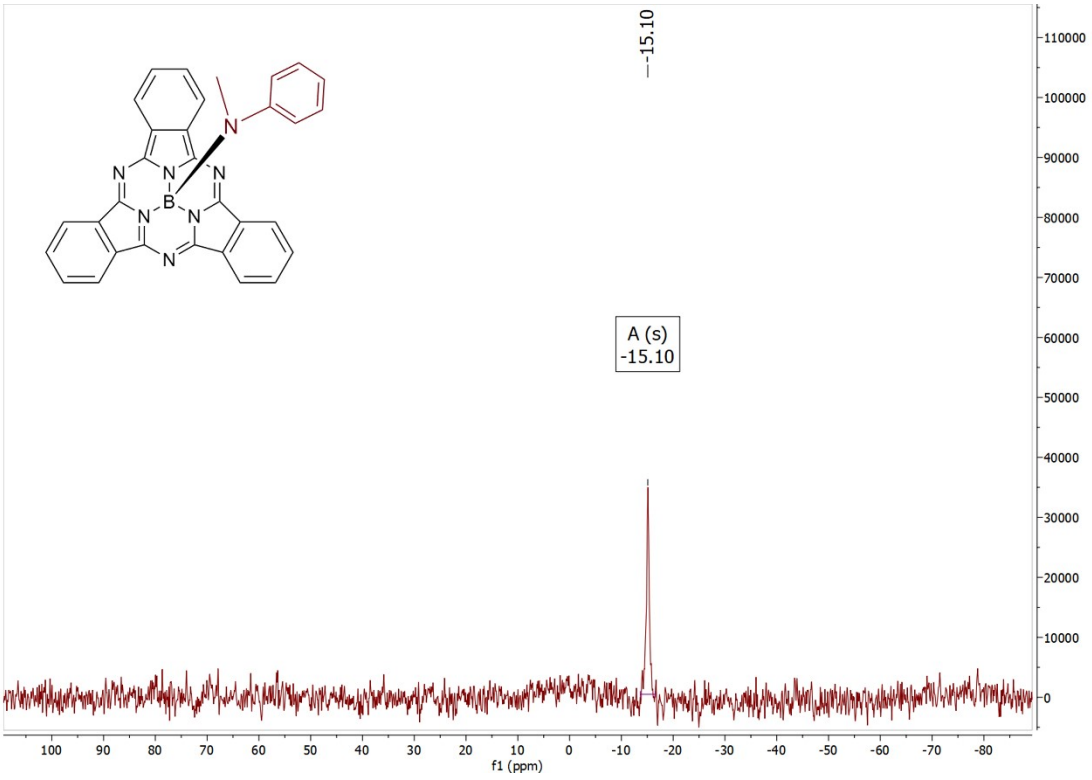


Figure S91. ^{11}B NMR spectrum of column-purified PhMeN-BsubPc (128 MHz, $CDCl_3$).

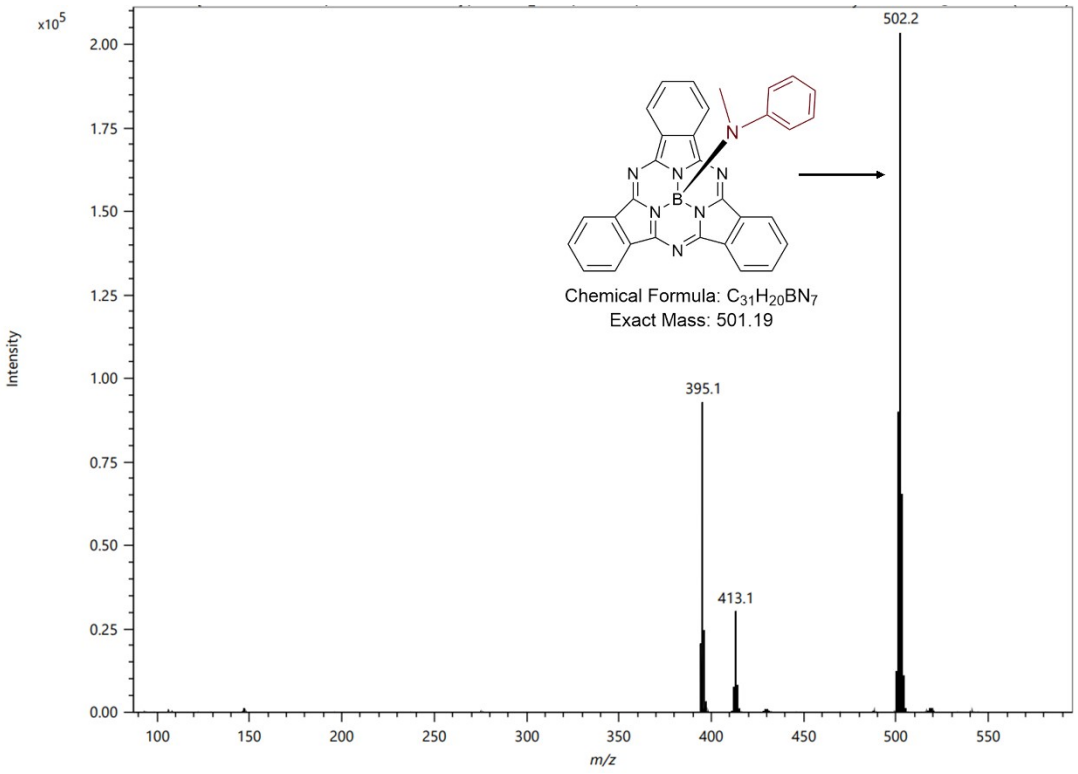
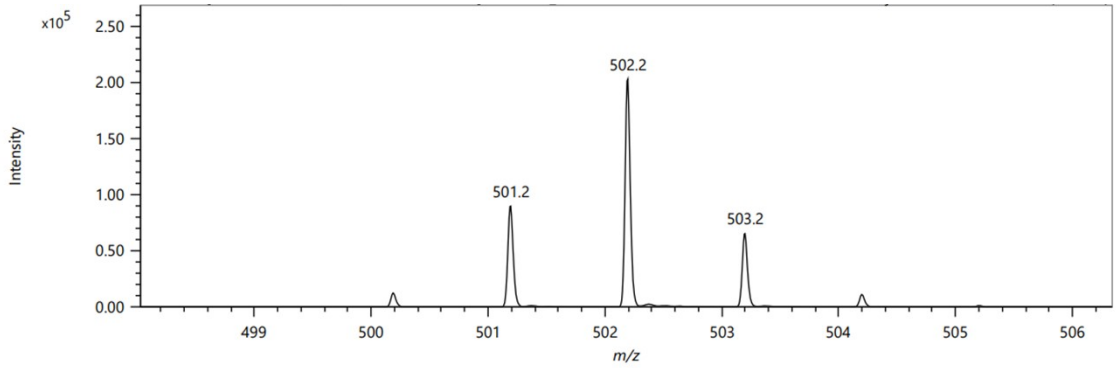


Figure S92. DART-MS [M+H] of column-purified PhMeN-BsubPc.



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±10.00 mDa	Symbol	C	H	O	N	B
Electron:	Even	Min	0	0	0	0	1
Charge:	+1	Max	100	200	20	10	1
DBE:	-1.5 - 100.0						

Results

Mass	Intensity	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
502.19532	203473.68	C18 H29 B N5 O11	502.19511	0.21	0.42	7.5
		C31 H21 B N7 ←	502.19460	0.72	1.44	25.5
		C19 H25 B N9 O7	502.19645	-1.13	-2.25	12.5
		C17 H33 B N O15	502.19378	1.55	3.08	2.5
		C35 H25 B N O2	502.19729	-1.96	-3.91	24.5
		C30 H25 B N3 O4	502.19326	2.06	4.10	20.5

Figure S93. Zoomed-in DART-HRMS [M+H] of column-purified PhMeN-BsubPc.

Additional UV-Vis Absorbance and Fluorescence Spectra

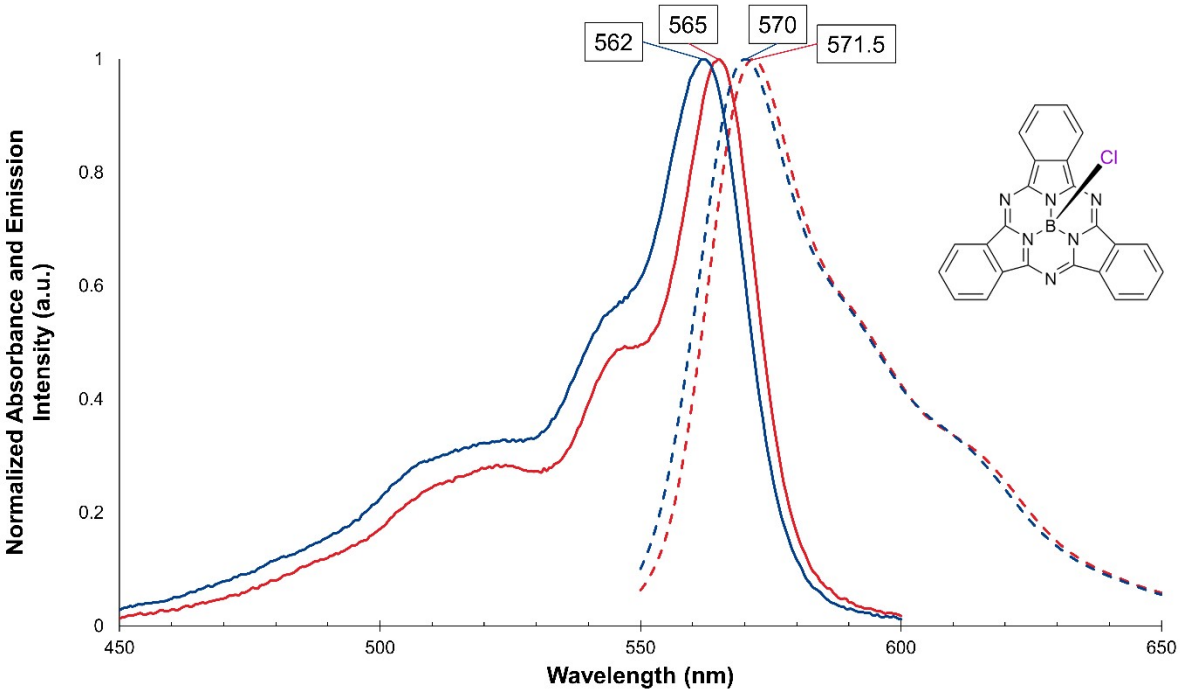


Figure S94. Normalized absorbance (solid lines) and emission (dashed lines) spectra of sublimed Cl-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

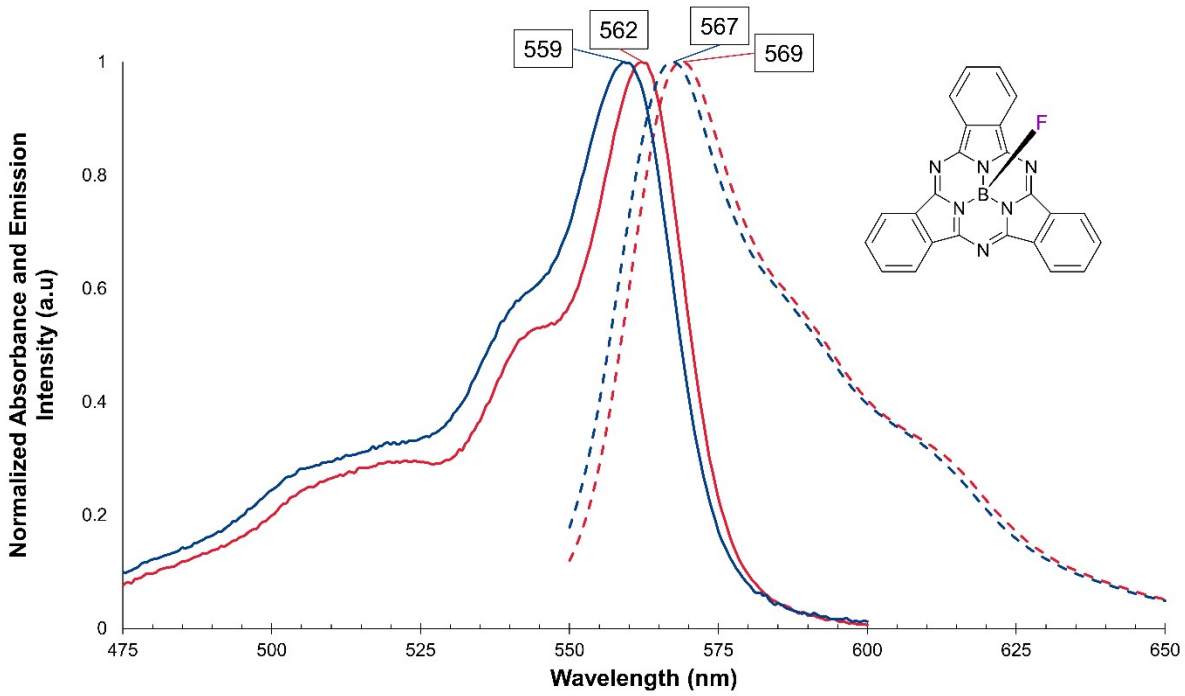


Figure S95. Normalized absorbance (solid lines) and emission (dashed lines) spectra of sublimed F-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

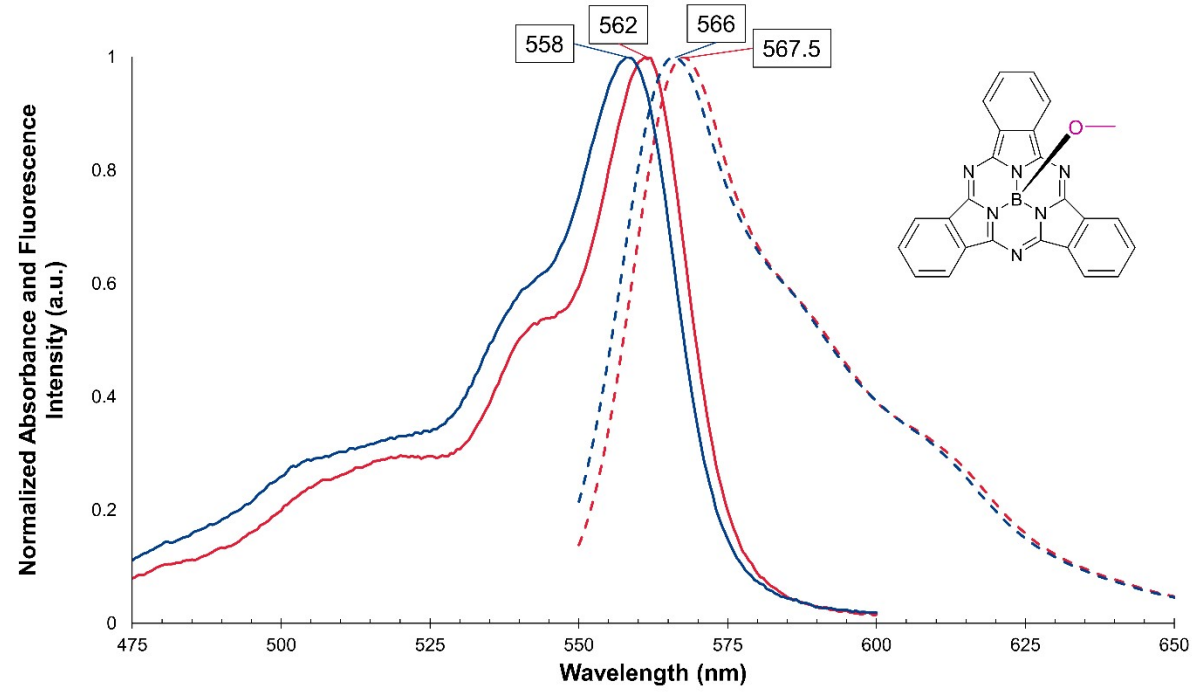


Figure S96. Normalized absorbance (solid lines) and emission (dashed lines) spectra of sublimed MeO-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

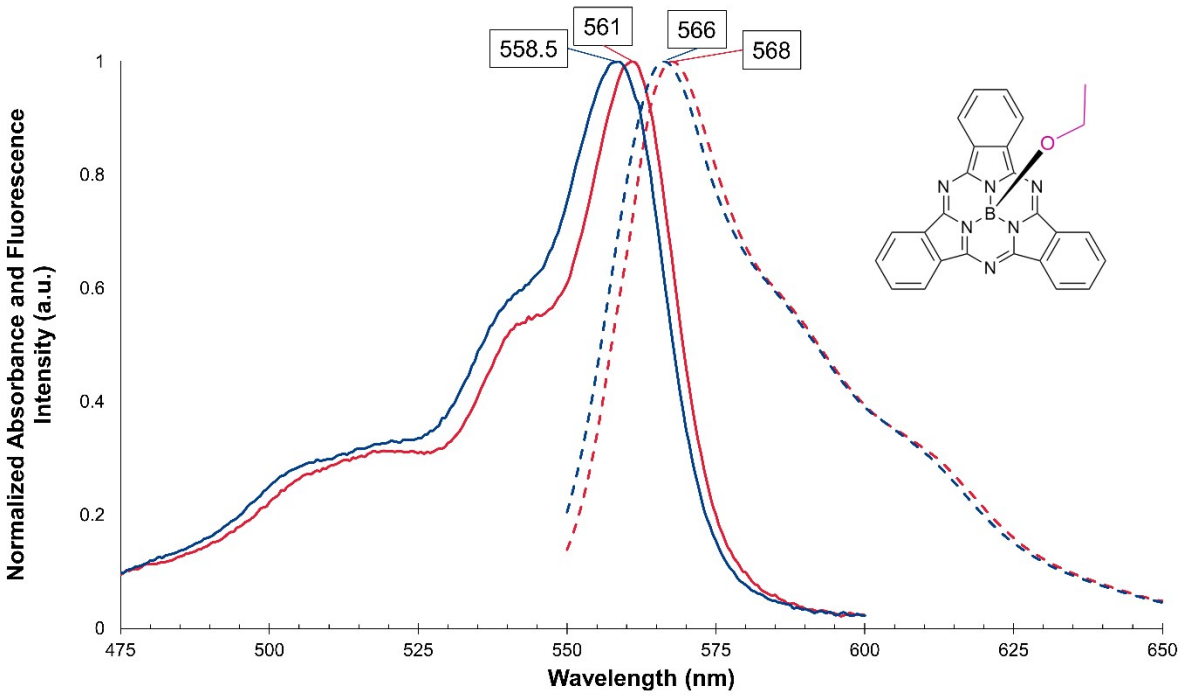


Figure S97. Normalized absorbance (solid lines) and emission (dashed lines) spectra of sublimed EtO-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

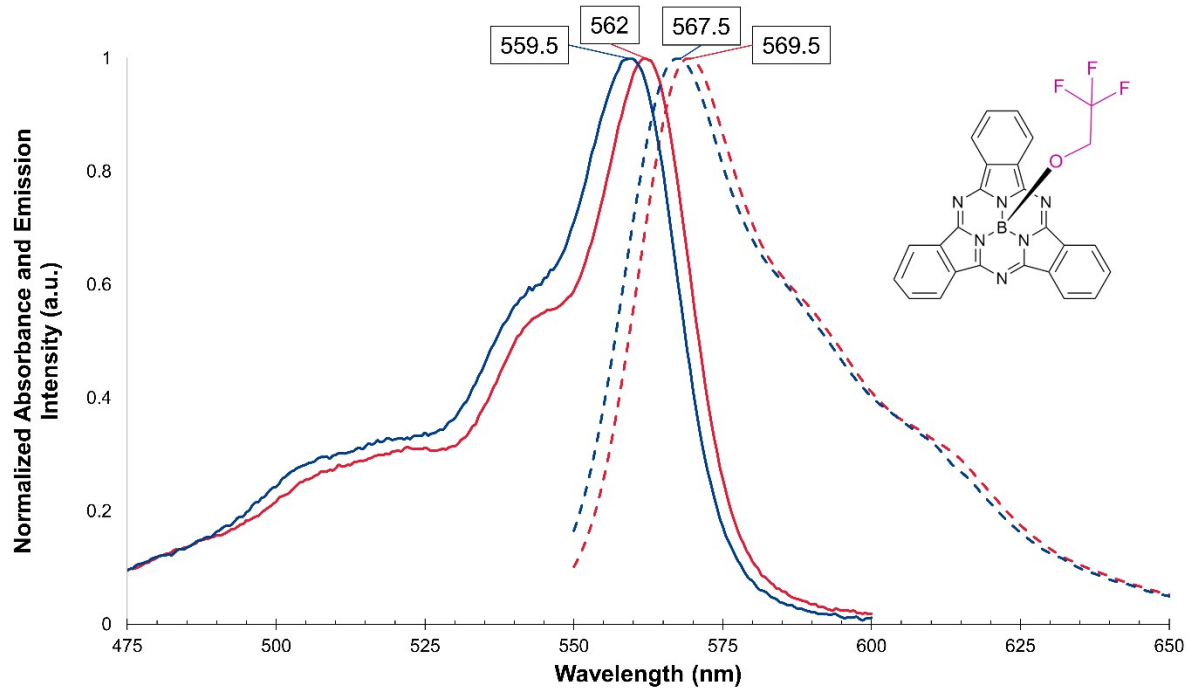


Figure S98. Normalized absorbance (solid lines) and emission (dashed lines) spectra of sublimed F_3EtO-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

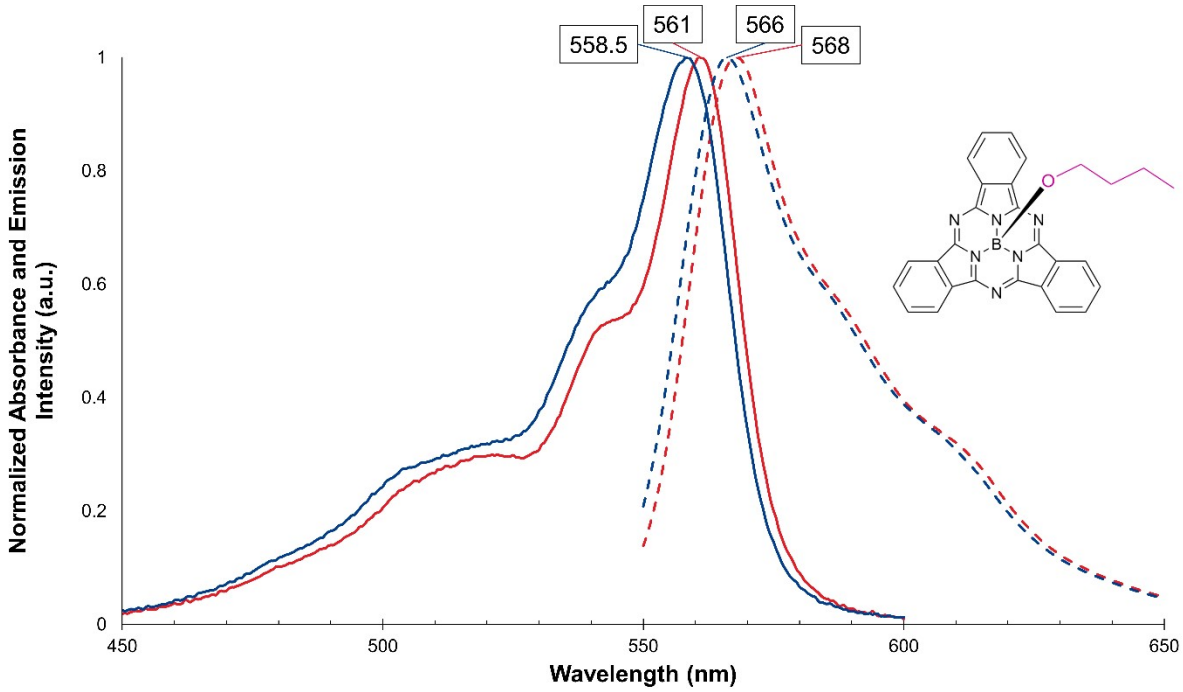


Figure S99. Normalized absorbance (solid lines) and emission (dashed lines) spectra of sublimed ButO-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

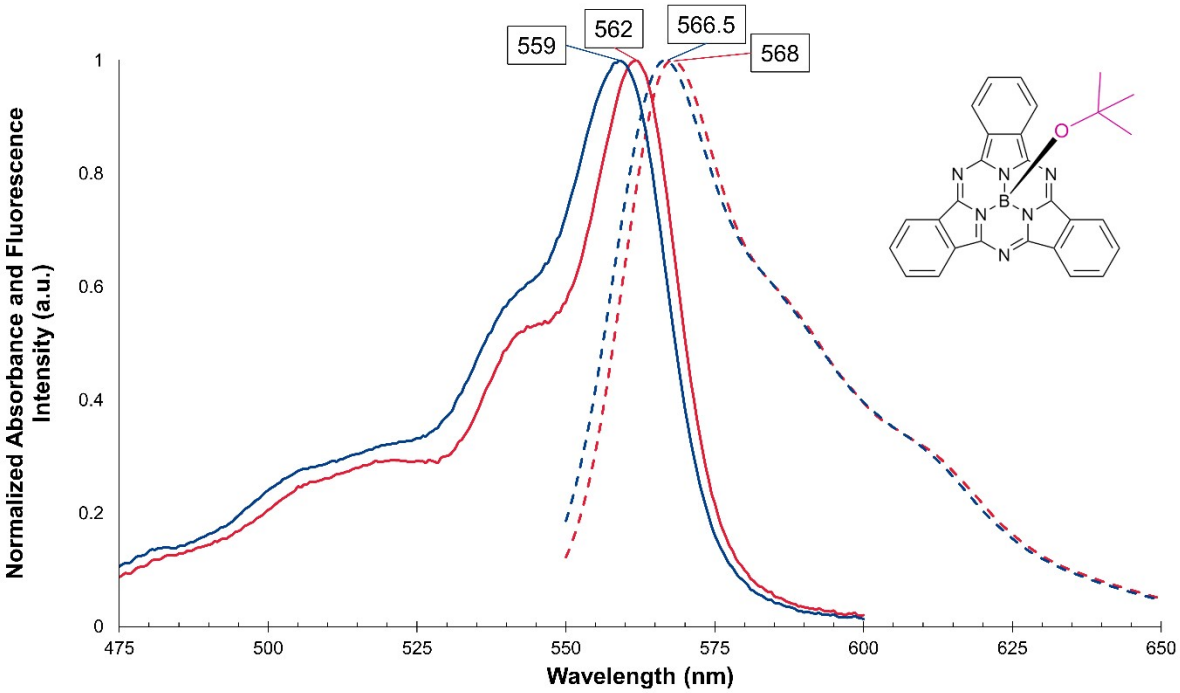


Figure S100. Normalized absorbance (solid lines) and emission (dashed lines) spectra of column-purified tButO-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

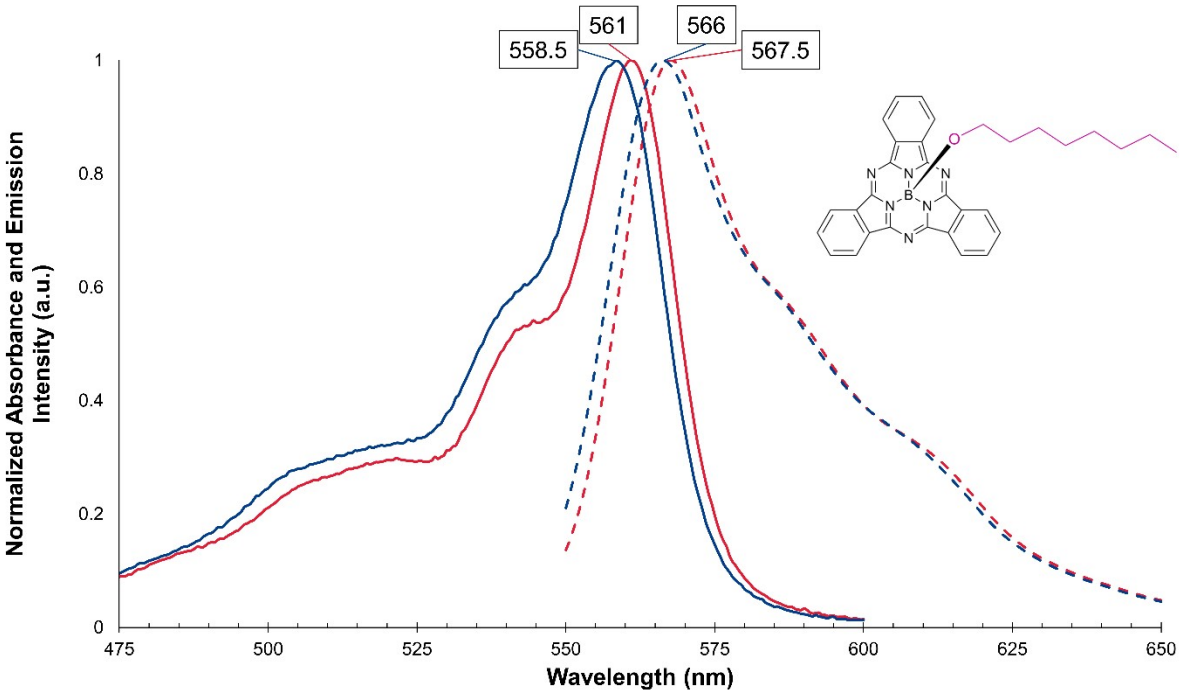


Figure S101. Normalized absorbance (solid lines) and emission (dashed lines) spectra of sublimed OctO-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

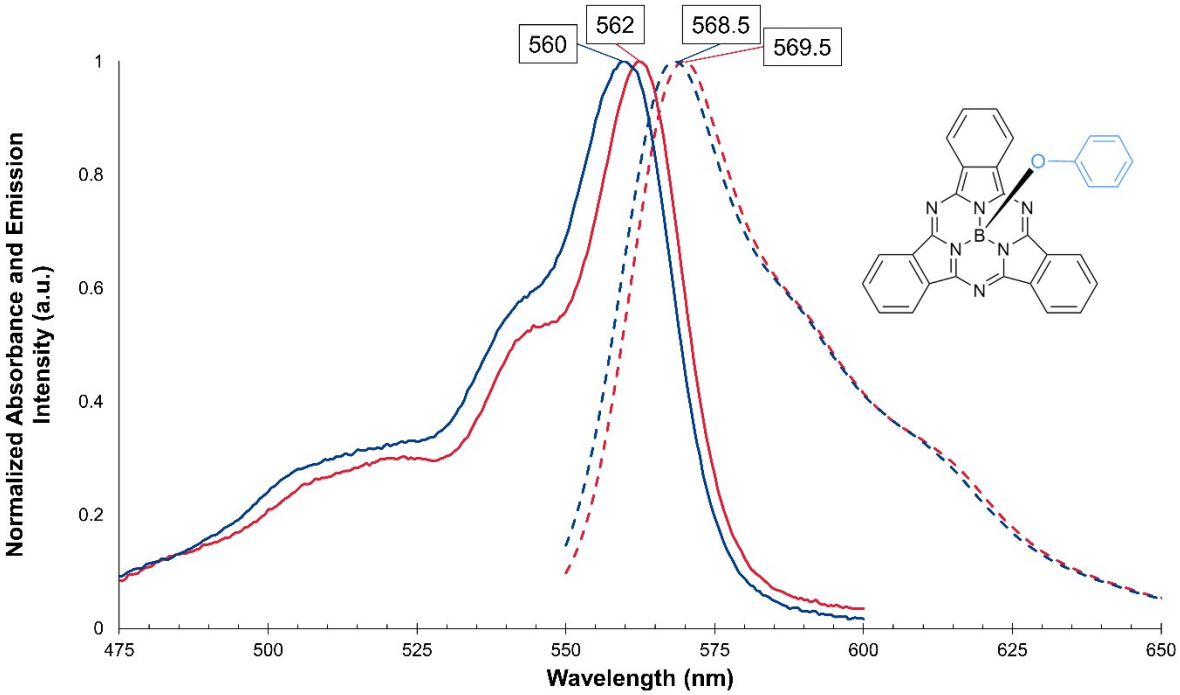


Figure S102. Normalized absorbance (solid lines) and emission (dashed lines) spectra of sublimed PhO-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

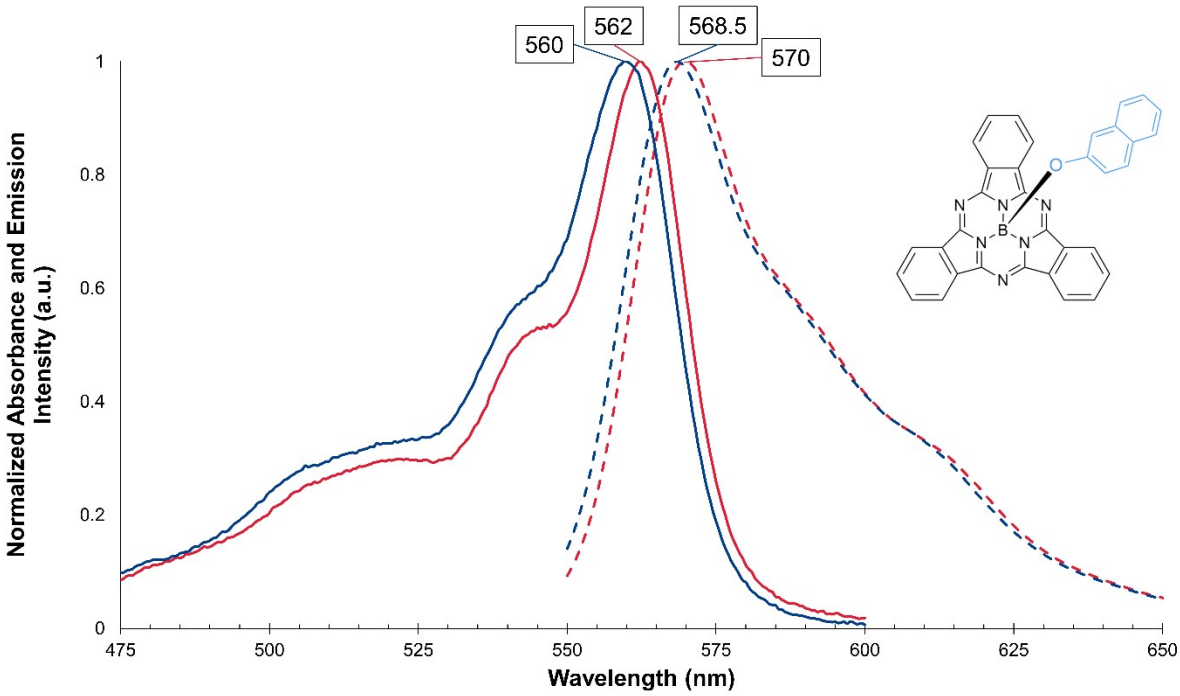


Figure S103. Normalized absorbance (solid lines) and emission (dashed lines) spectra of sublimed naphthoxy-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

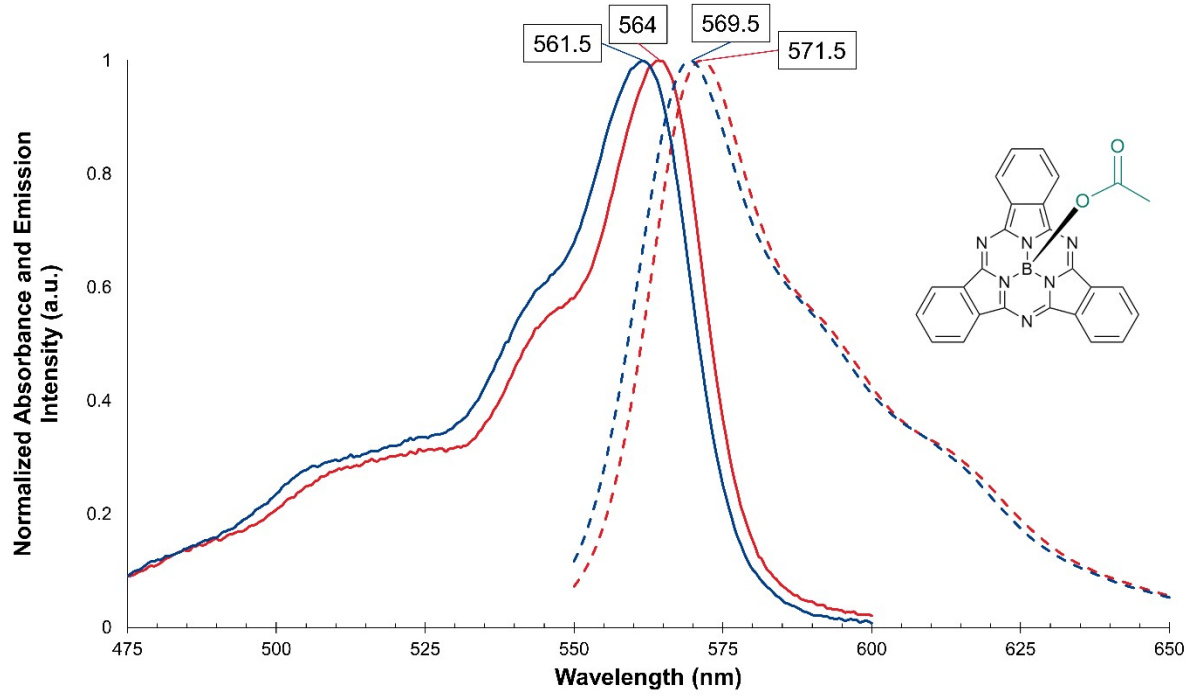


Figure S104. Normalized absorbance (solid lines) and emission (dashed lines) spectra of sublimed acetate-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

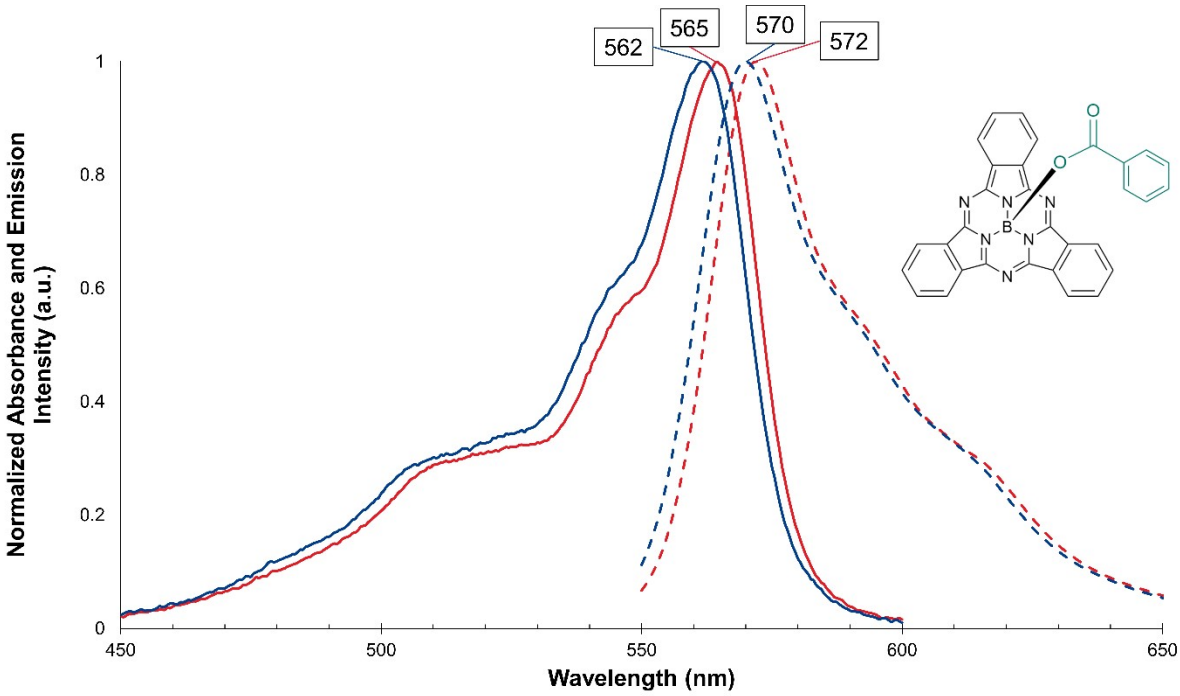


Figure S105. Normalized absorbance (solid lines) and emission (dashed lines) spectra of sublimed benzoate-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

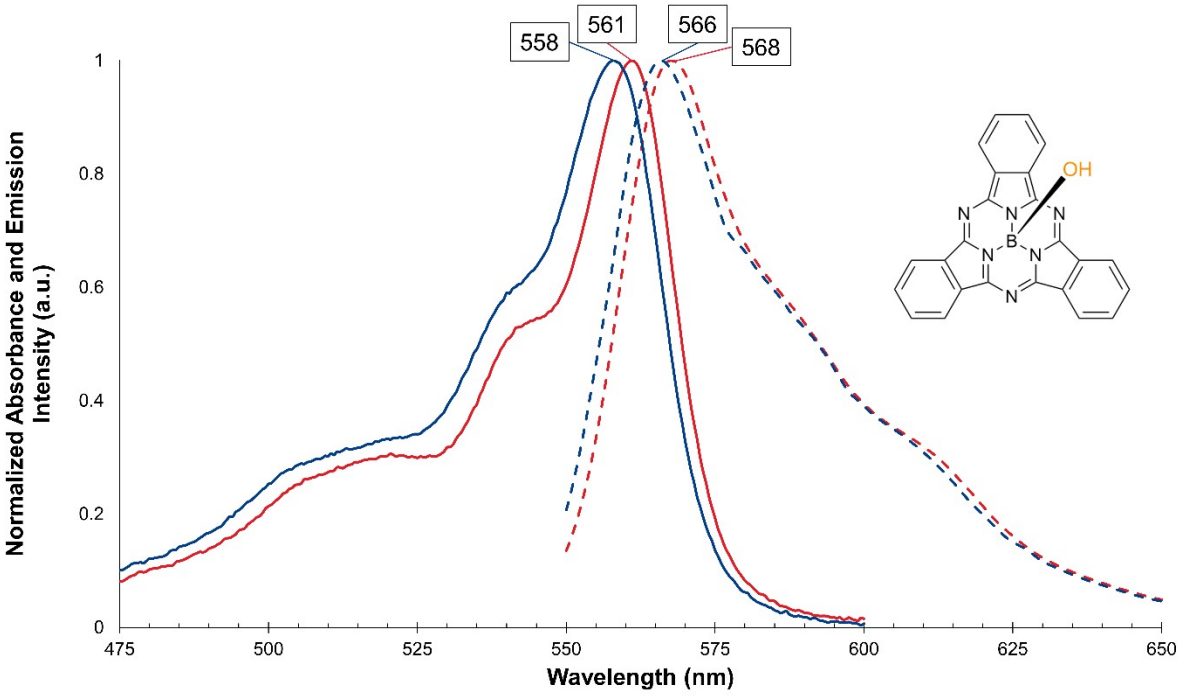


Figure S106. Normalized absorbance (solid lines) and emission (dashed lines) spectra of sublimed HO-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

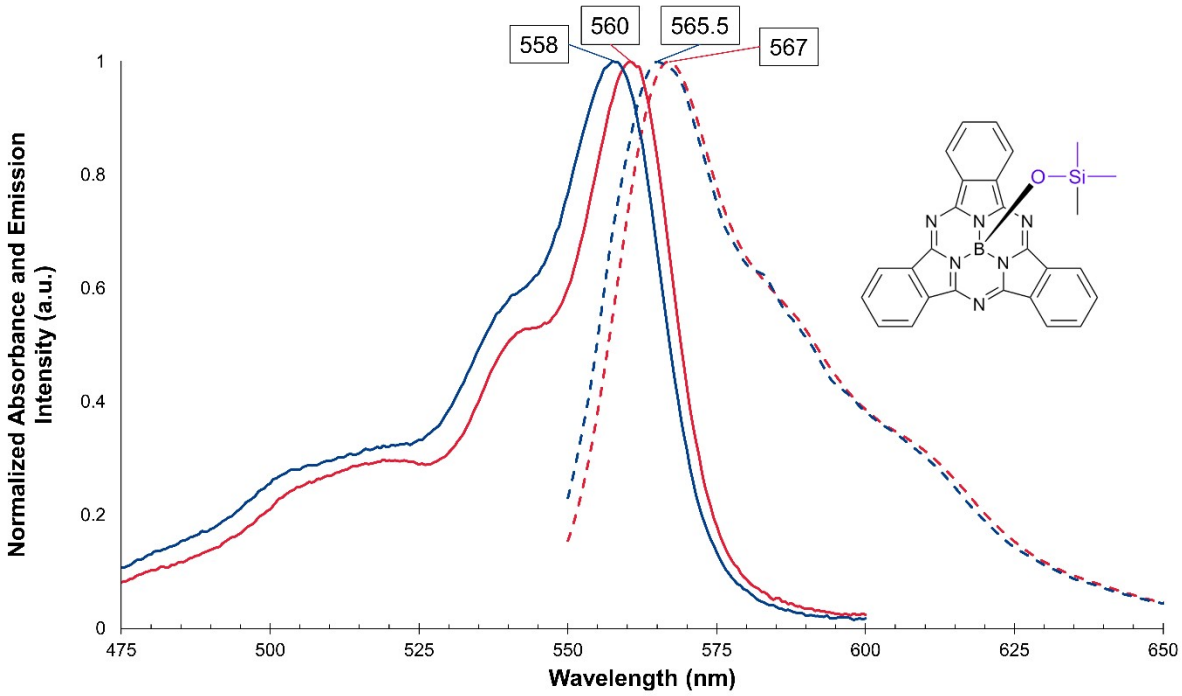


Figure S107. Normalized absorbance (solid lines) and emission (dashed lines) spectra of column-purified TMSO-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

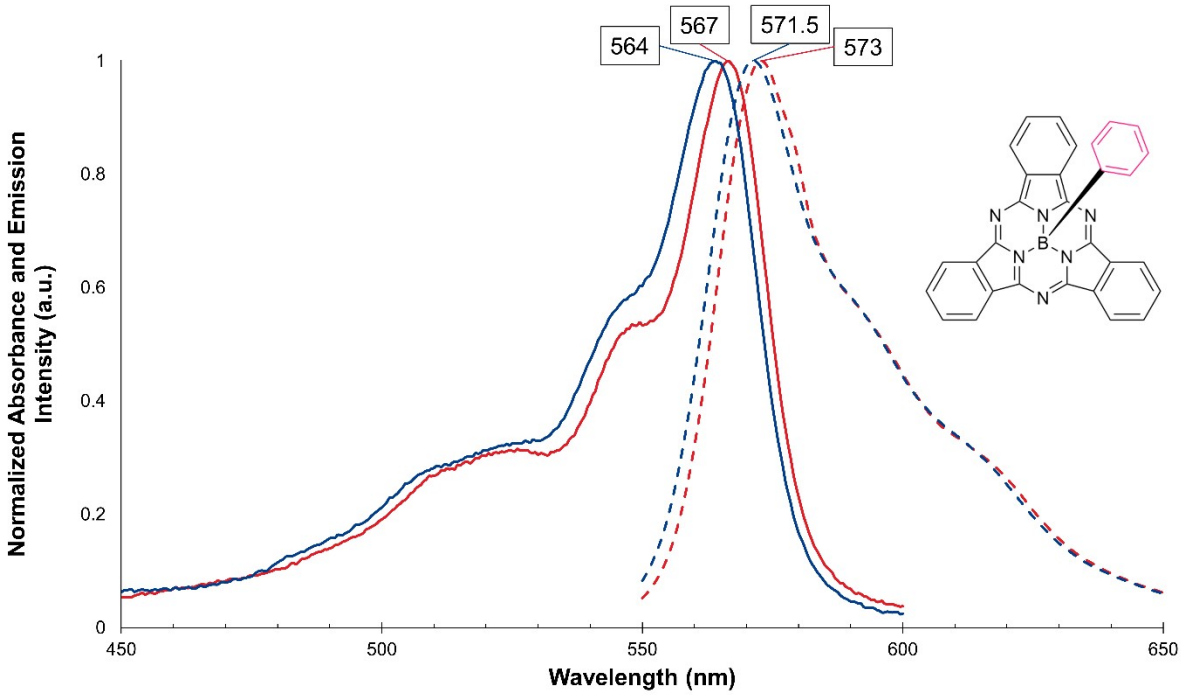


Figure S108. Normalized absorbance (solid lines) and emission (dashed lines) spectra of column-purified Ph-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

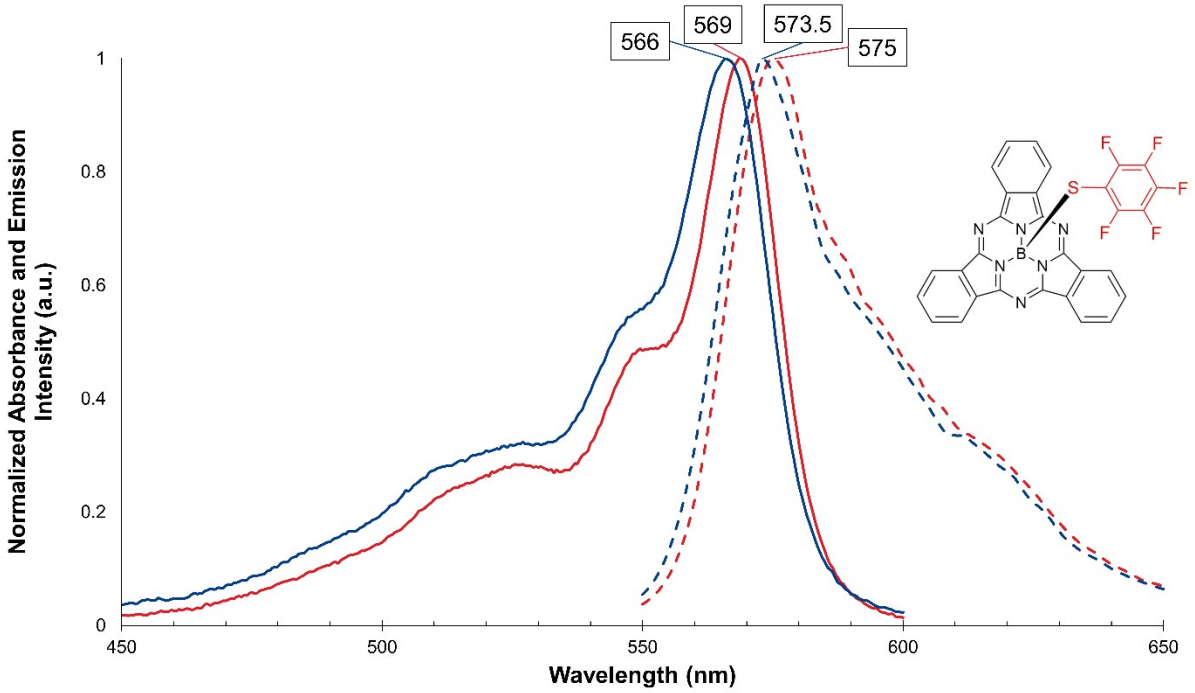


Figure S109. Normalized absorbance (solid lines) and emission (dashed lines) spectra of column-purified F_5PhS-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

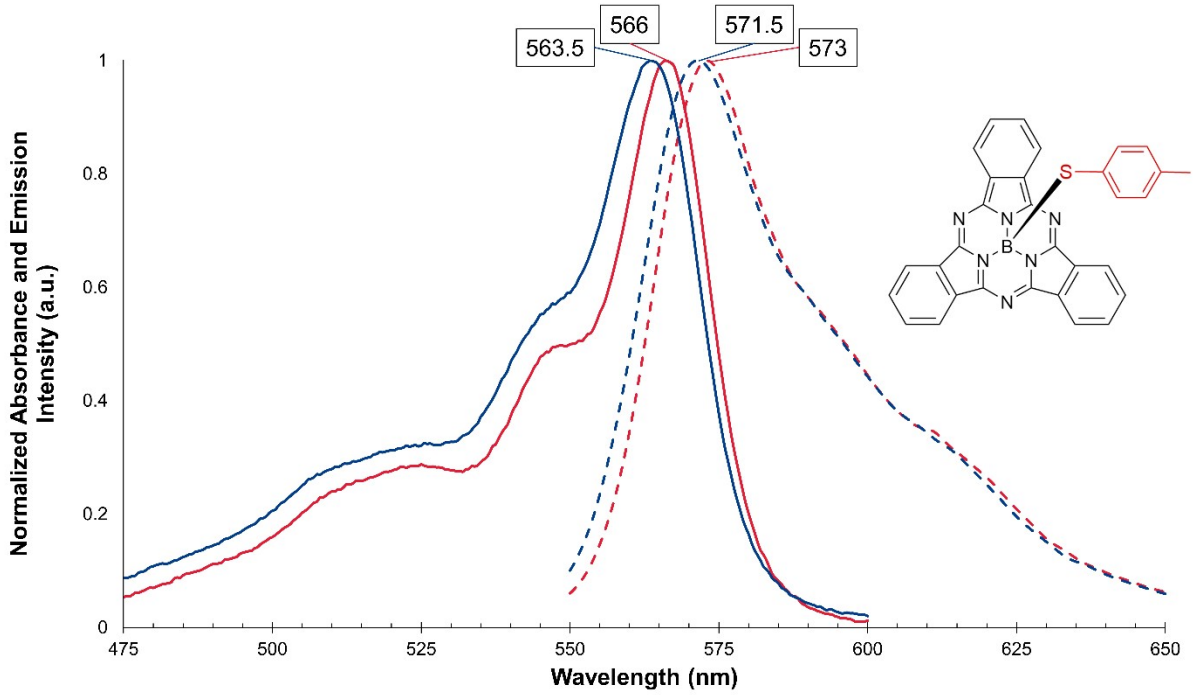


Figure S110. Normalized absorbance (solid lines) and emission (dashed lines) spectra of column-purified MePhS-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

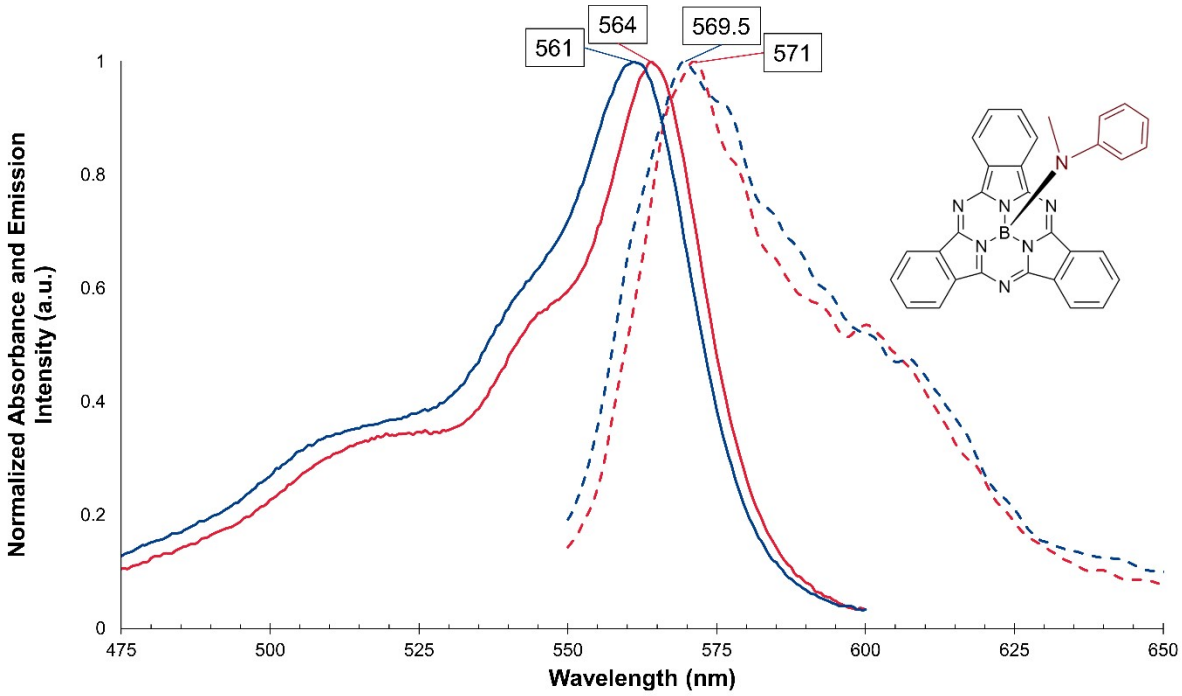


Figure S111. Normalized absorbance (solid lines) and emission (dashed lines) spectra of column-purified PhMeN-BsubPc in toluene (red) and α,α,α-trifluorotoluene (blue).

Additional CV and DPV Voltammograms

The experimental conditions used for all compounds area as follows: 0.1 M tetrabutylammonium perchlorate as the electrolyte solution in nitrogen-degassed dichloromethane at room temperature with a scan rate of 100 mV s^{-1} *vs* Ag/AgCl and ferrocene as the internal reference (dashed yellow line). CV potentials were corrected tot the half-wave potential of ferrocene (0.546 V *vs* Ag/AgCl) and DPV potentials were corrected tot eh maximum potential of ferrocene (0.522 *vs* Ag/AgCl).

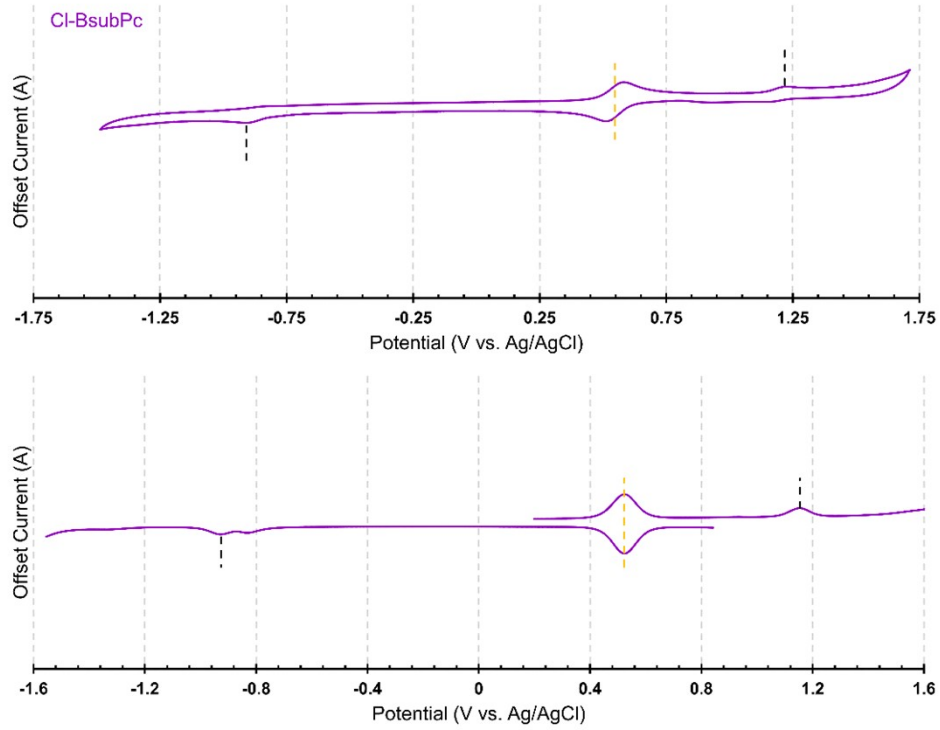


Figure S112. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of sublimed Cl-BsubPc.

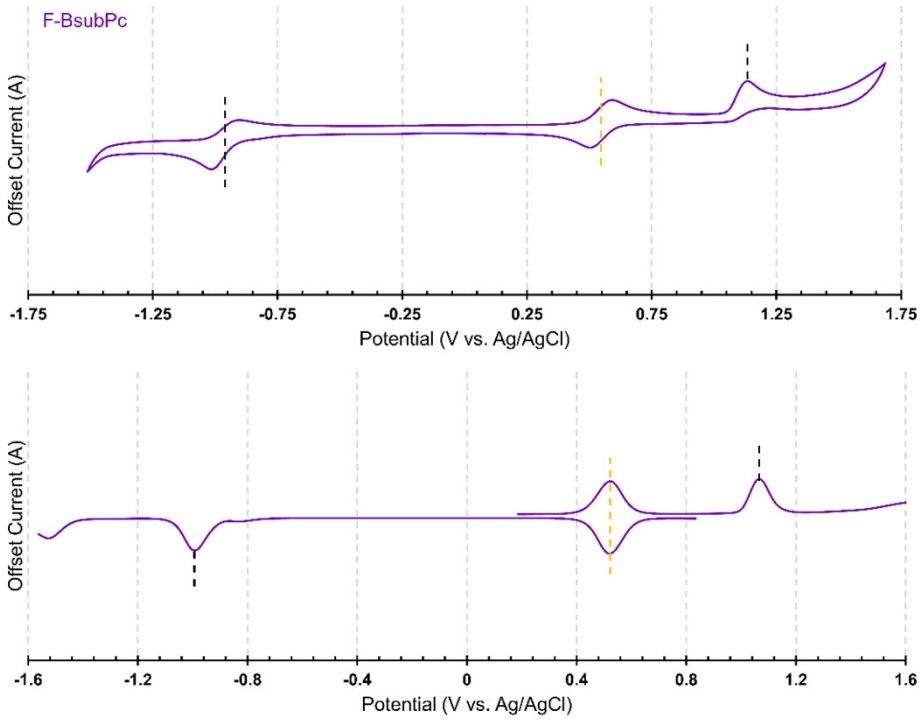


Figure S113. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of sublimed F-BsubPc.

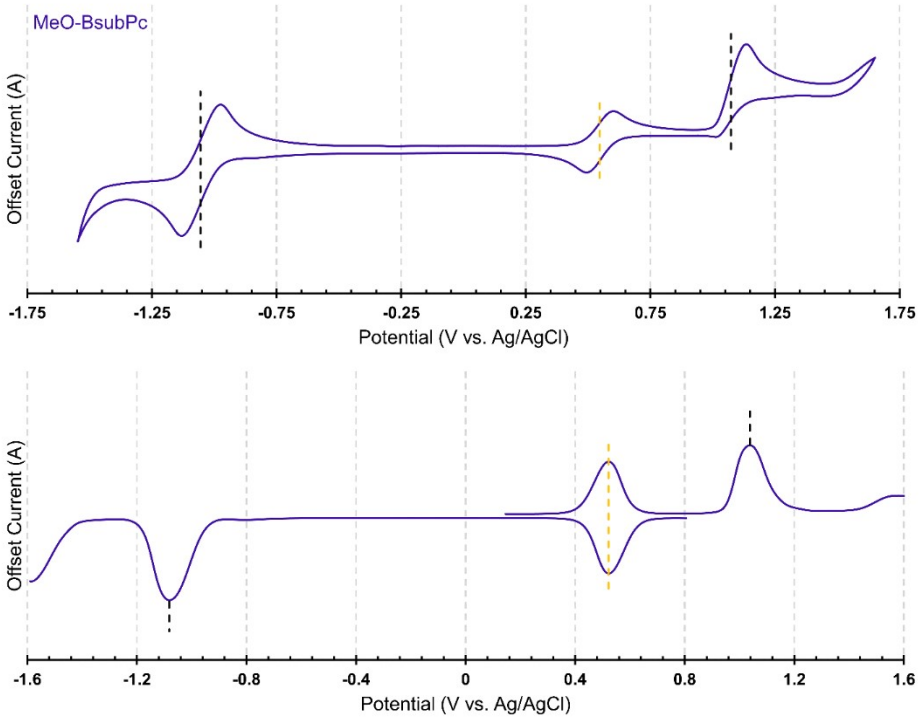


Figure S114. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of sublimed MeO-BsubPc.

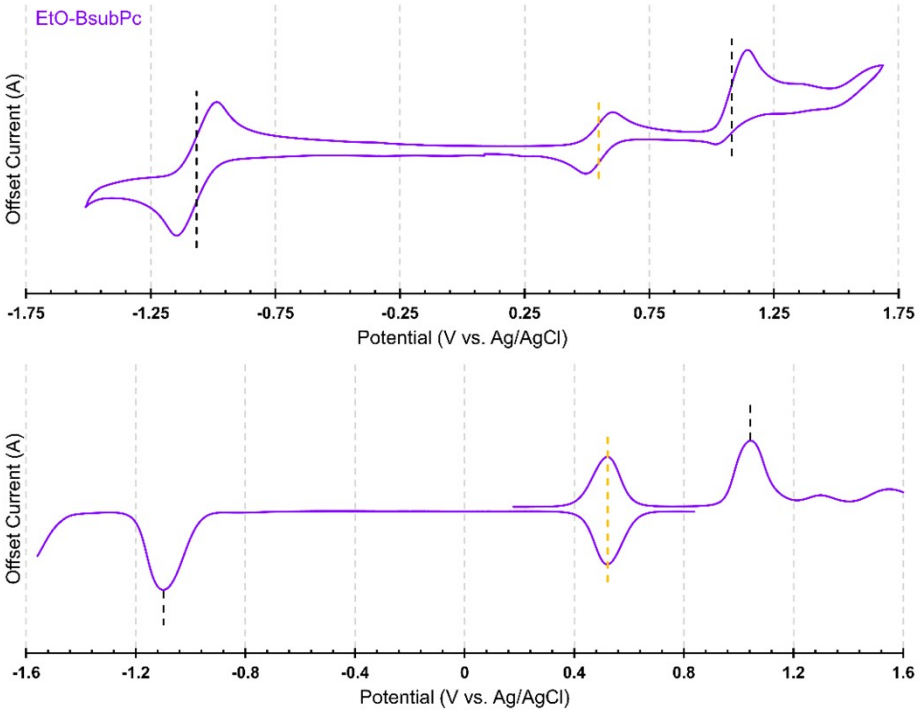


Figure S115. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of sublimed EtO-BsubPc.

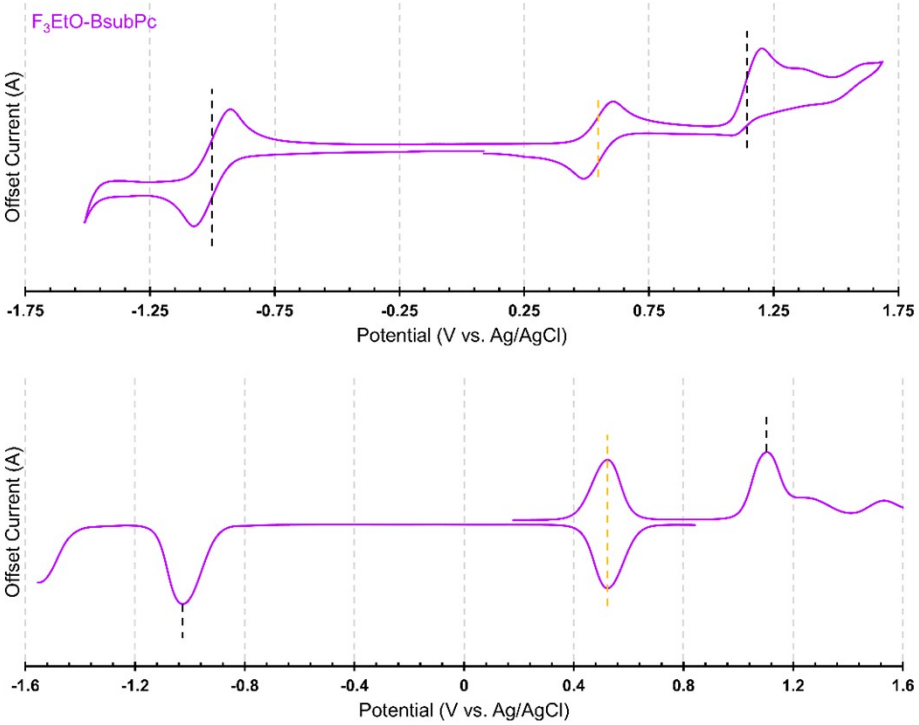


Figure S116. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of sublimed F_3EtO-BsubPc.

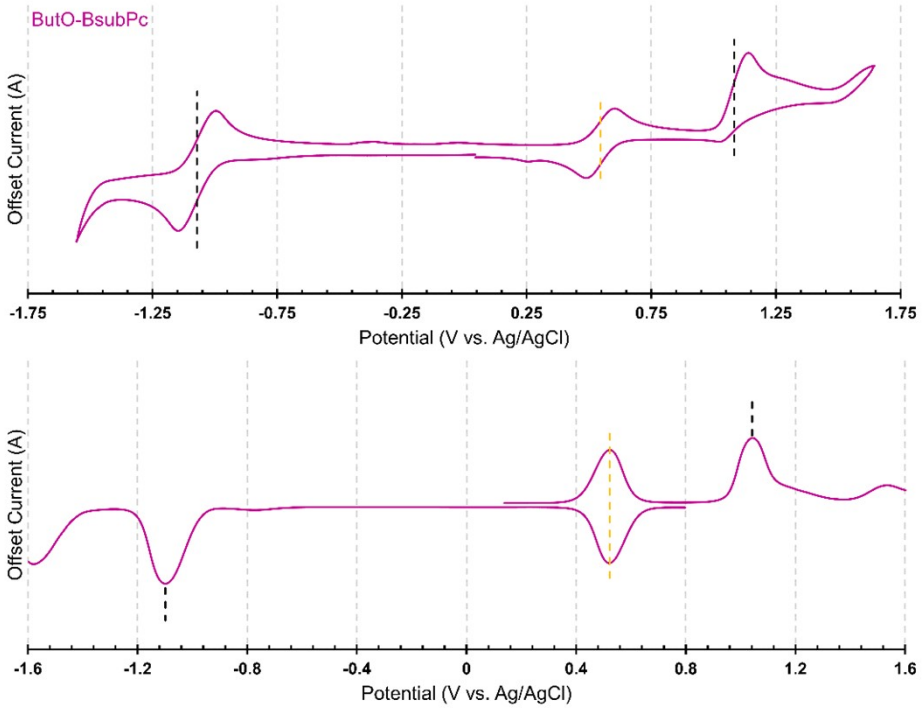


Figure S117. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of sublimed ButO-BsubPc.

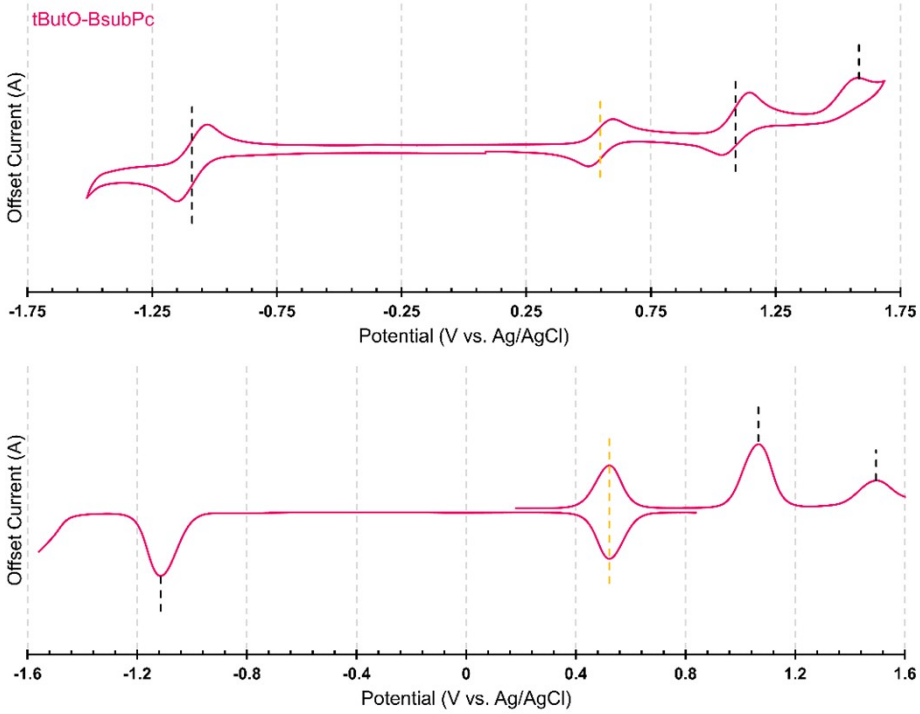


Figure S118. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of column-purified tButO-BsubPc.

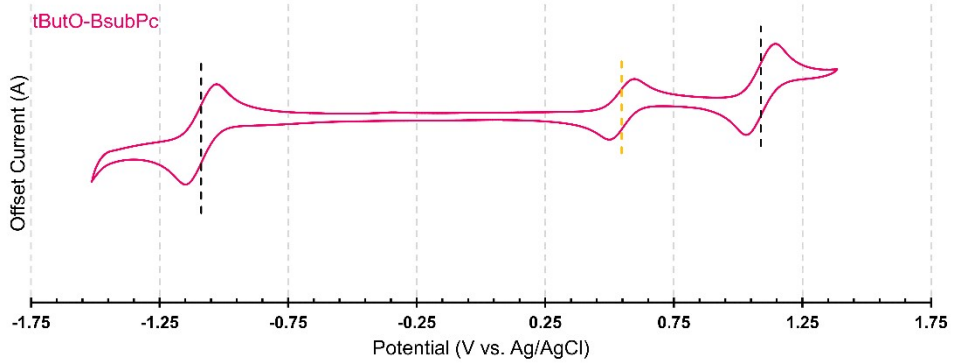


Figure S119. Smaller range (- 1.6 V to + 1.3 V) CV trace of column-purified tButO-BsubPc to assess the reversibility of the first oxidation.

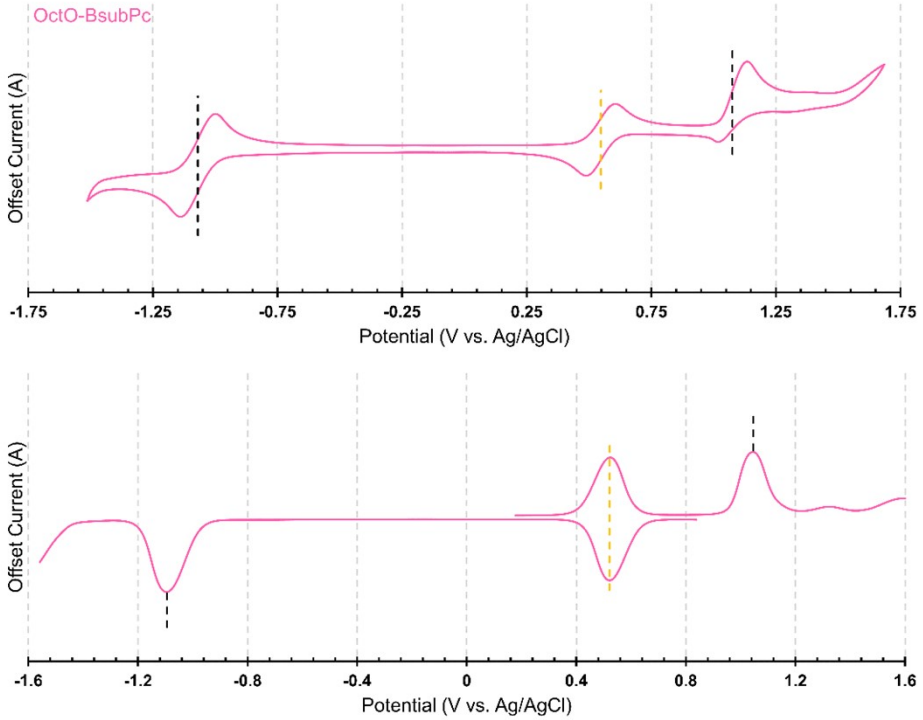


Figure S120. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of sublimed OctO-BsubPc.

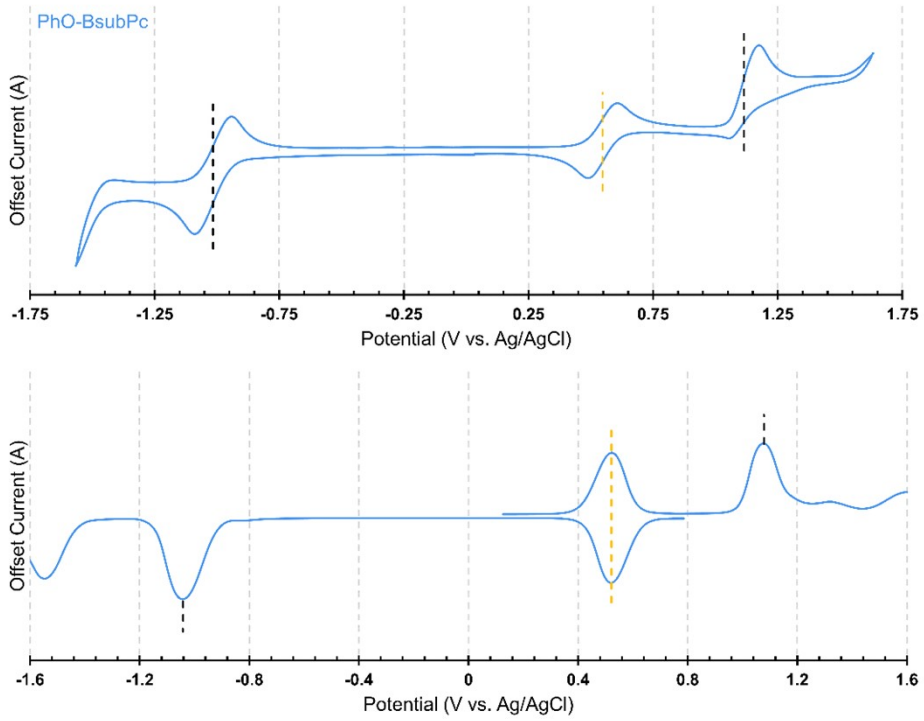


Figure S121. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of sublimed PhO-BsubPc.

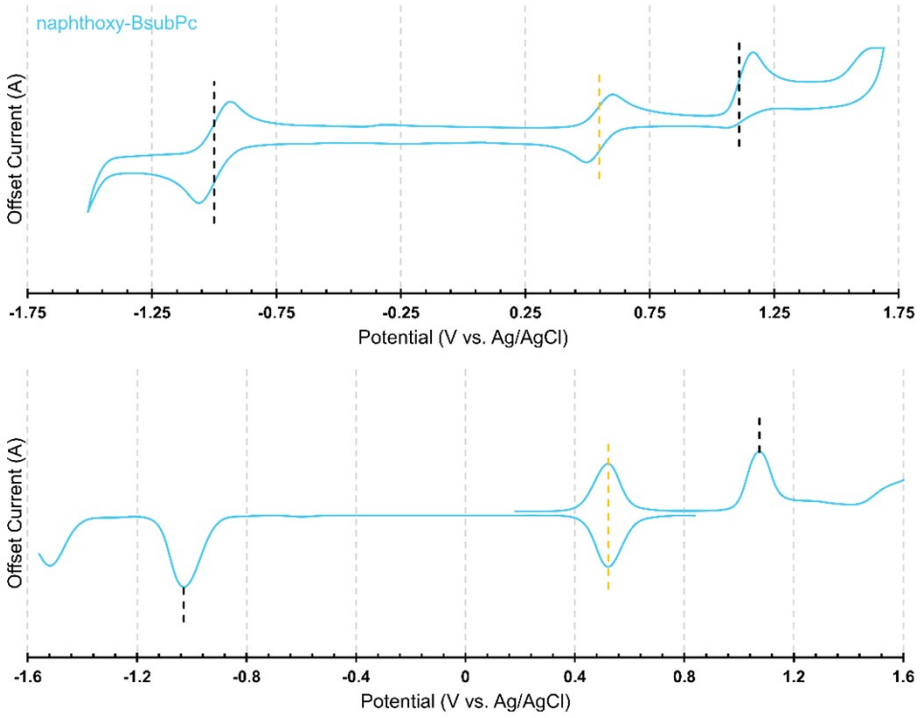


Figure S122. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of sublimed naphthoxy-BsubPc.

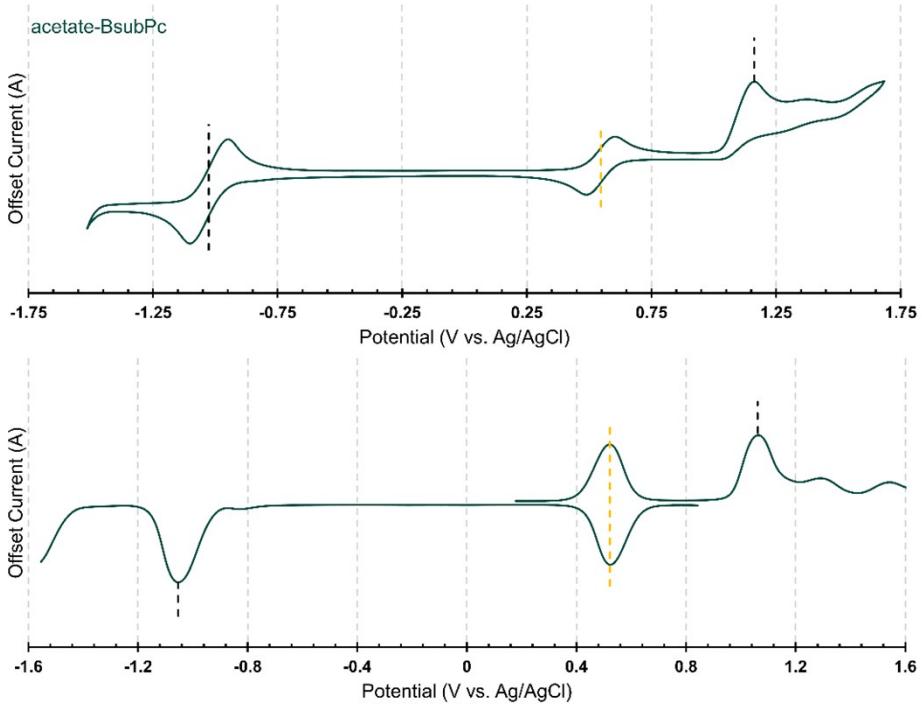


Figure S123. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of sublimed acetate-BsubPc.

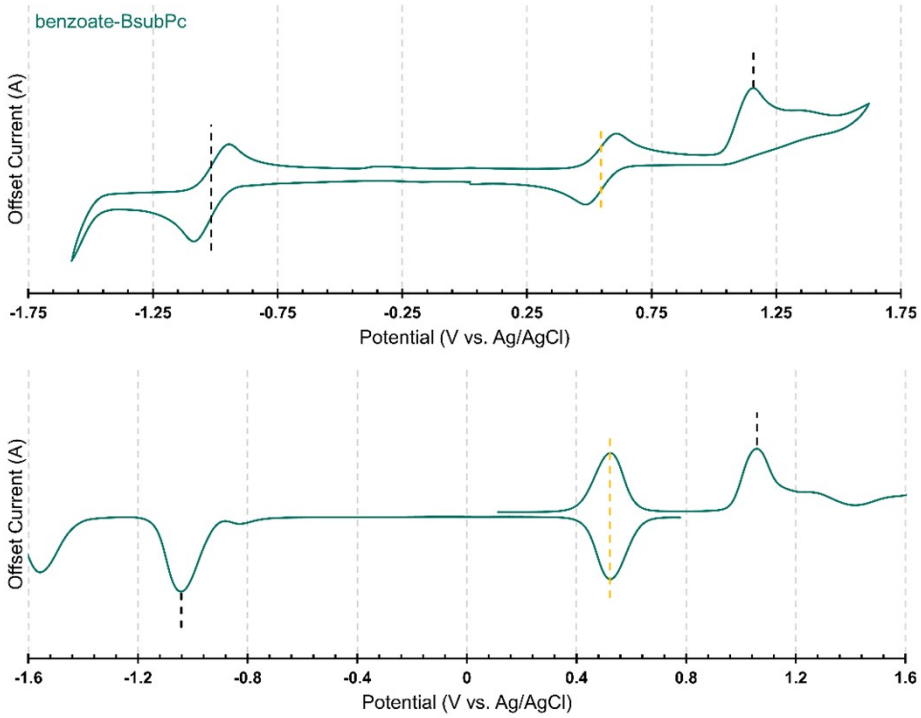


Figure S124. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of sublimed benzoate-BsubPc.

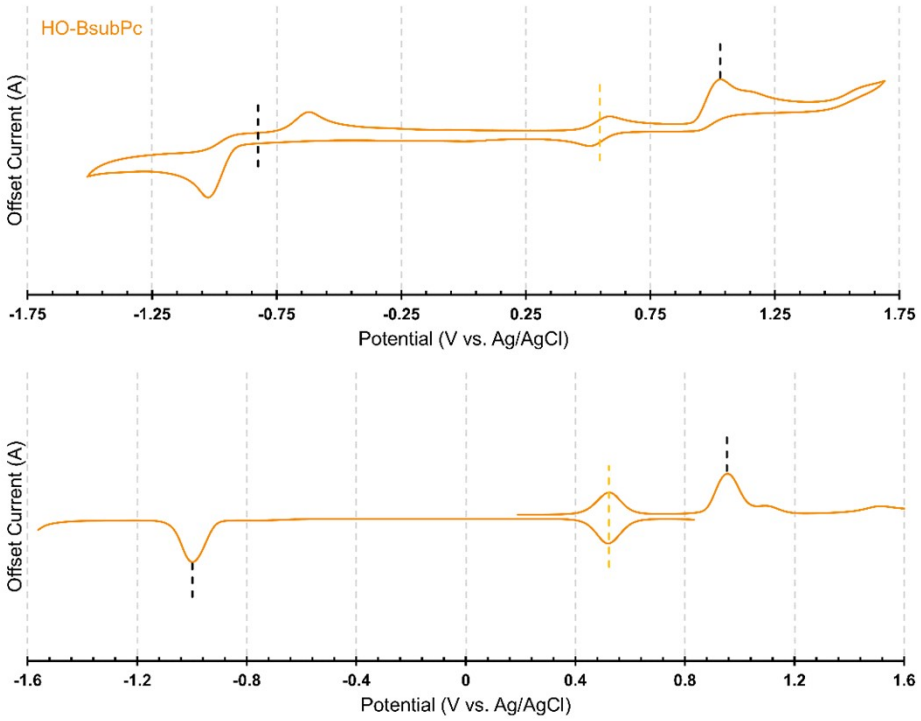


Figure S125. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of sublimed HO-BsubPc.

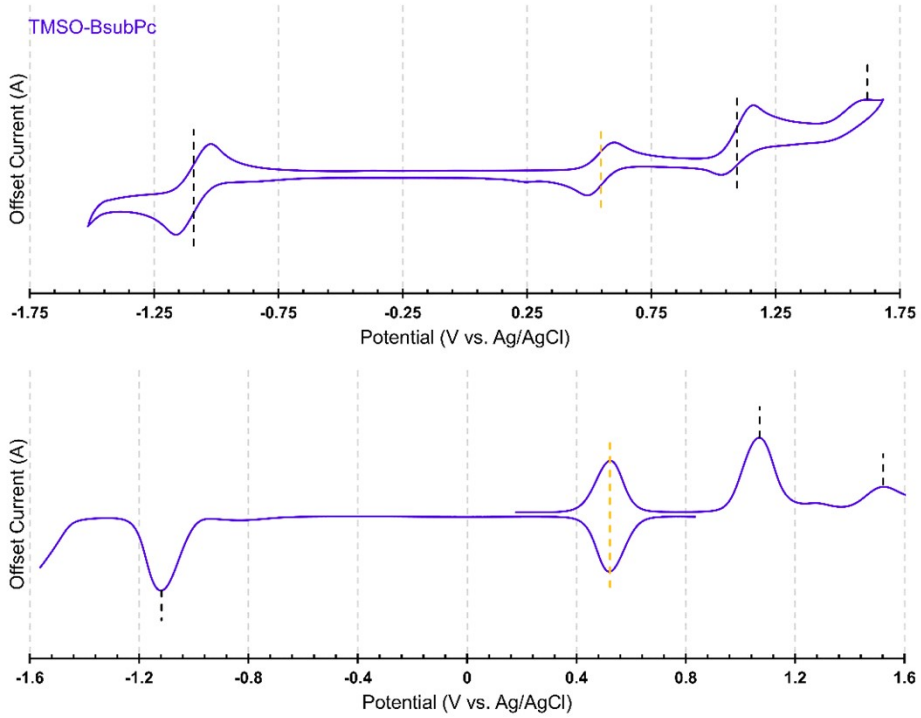


Figure S126. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of column-purified TMSO-BsubPc.

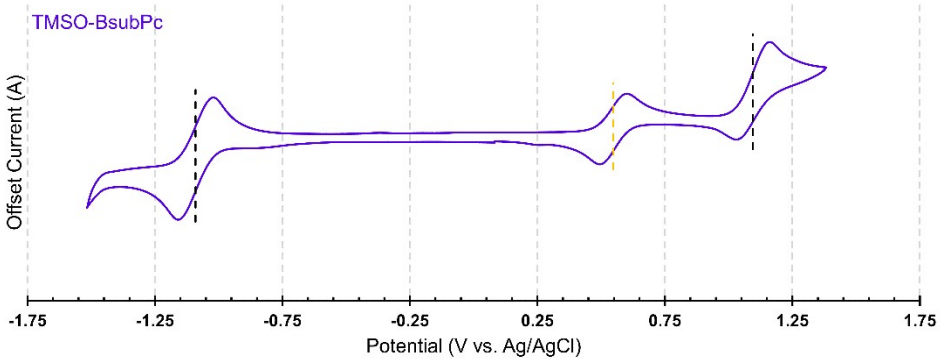


Figure S127. Smaller range (- 1.6 V to + 1.3 V) CV trace of column-purified TMSO-BsubPc to assess the reversibility of the first oxidation.

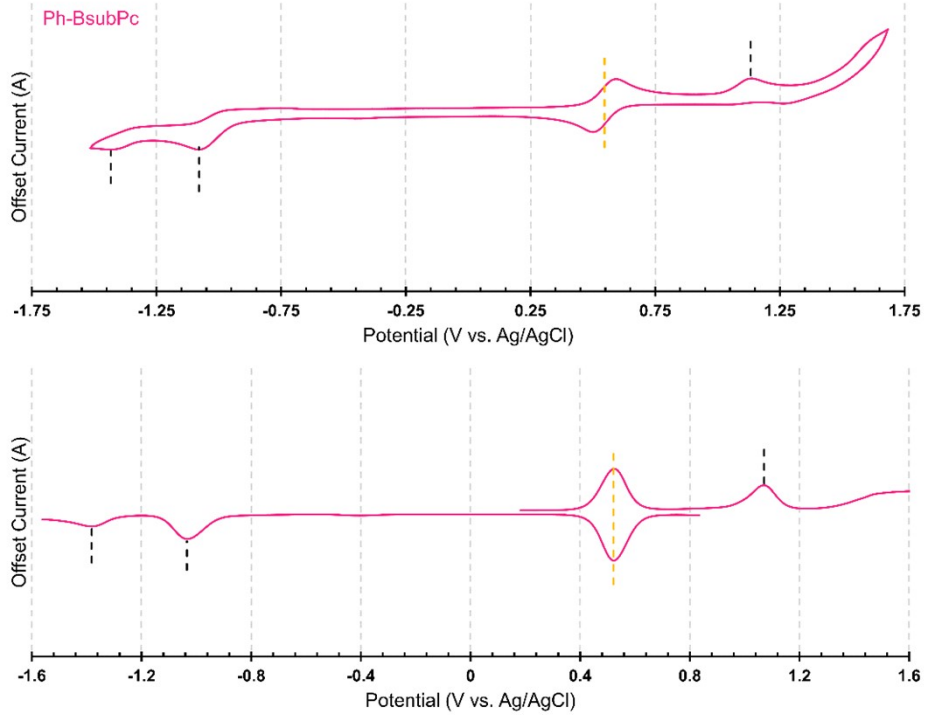


Figure S128. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of column-purified Ph-BsubPc.

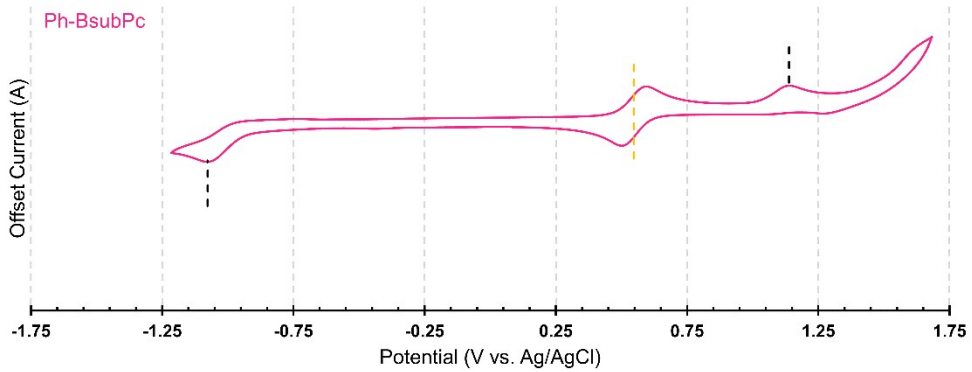


Figure S129. Smaller range (- 1.3 V to + 1.6 V) CV trace of column-purified Ph-BsubPc to assess the reversibility of the first reduction.

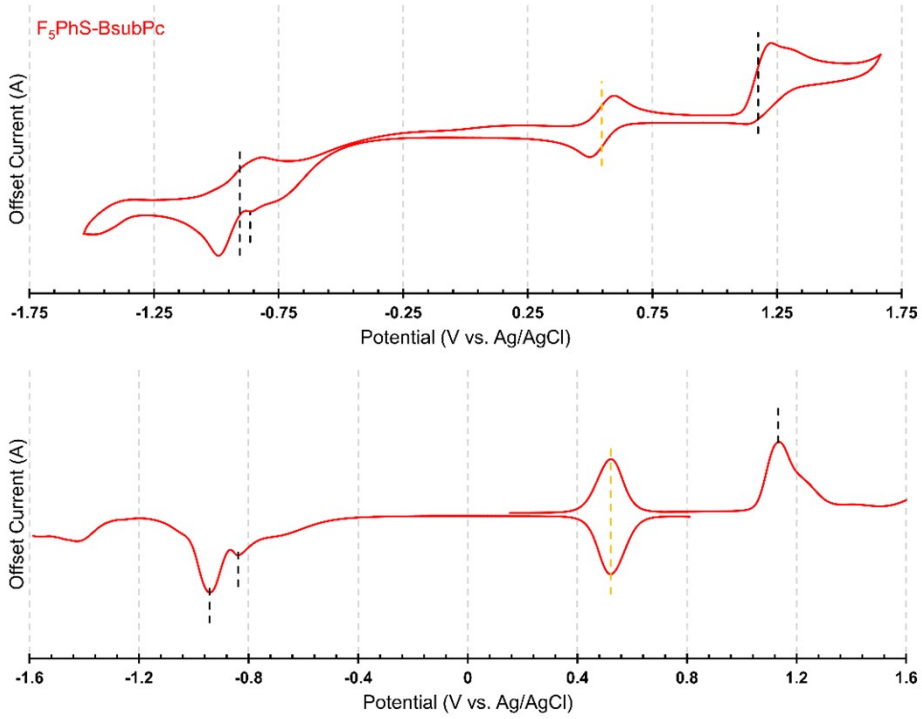


Figure S130. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of column-purified F_5PhS-BsubPc.

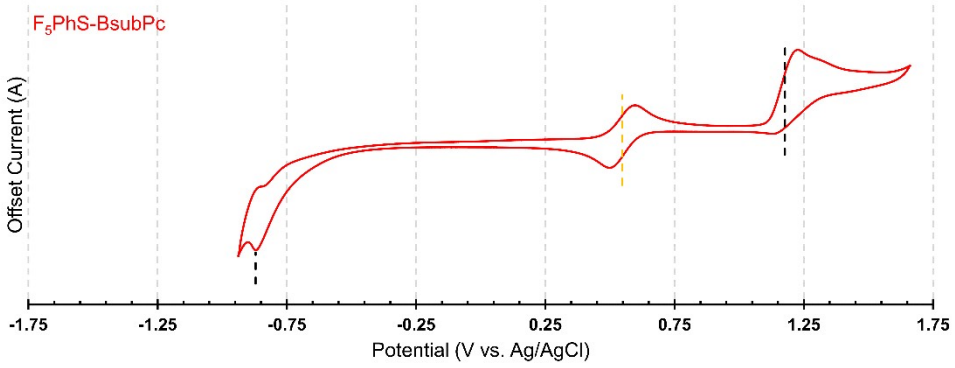


Figure S131. Smaller range (- 1.0 V to + 1.6 V) CV trace of column-purified F_5PhS-BsubPc to assess the reversibility of the first reduction.

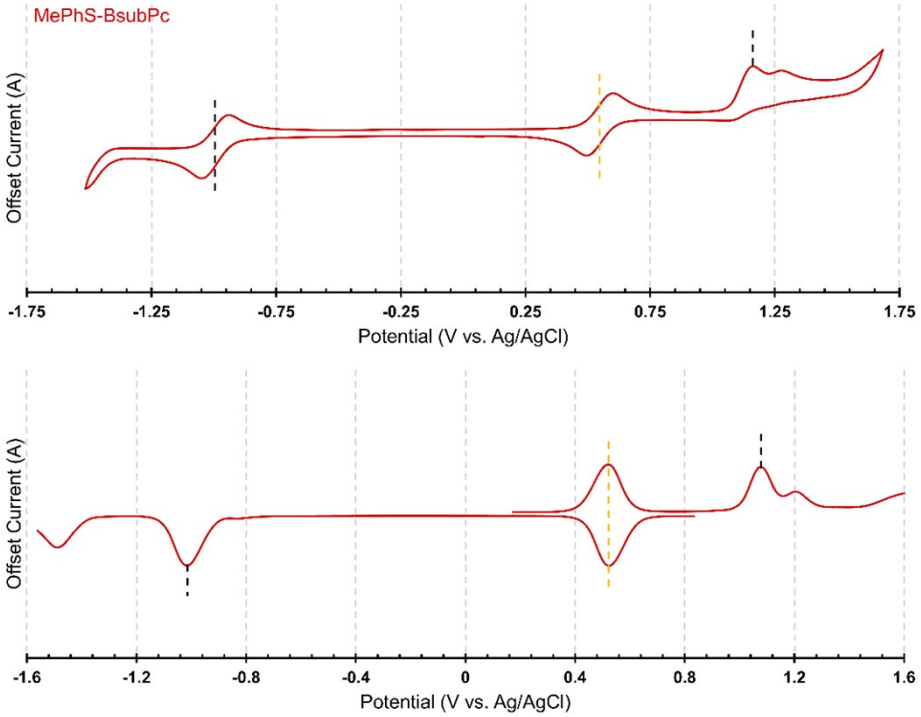


Figure S132. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of column-purified MePhS-BsubPc.

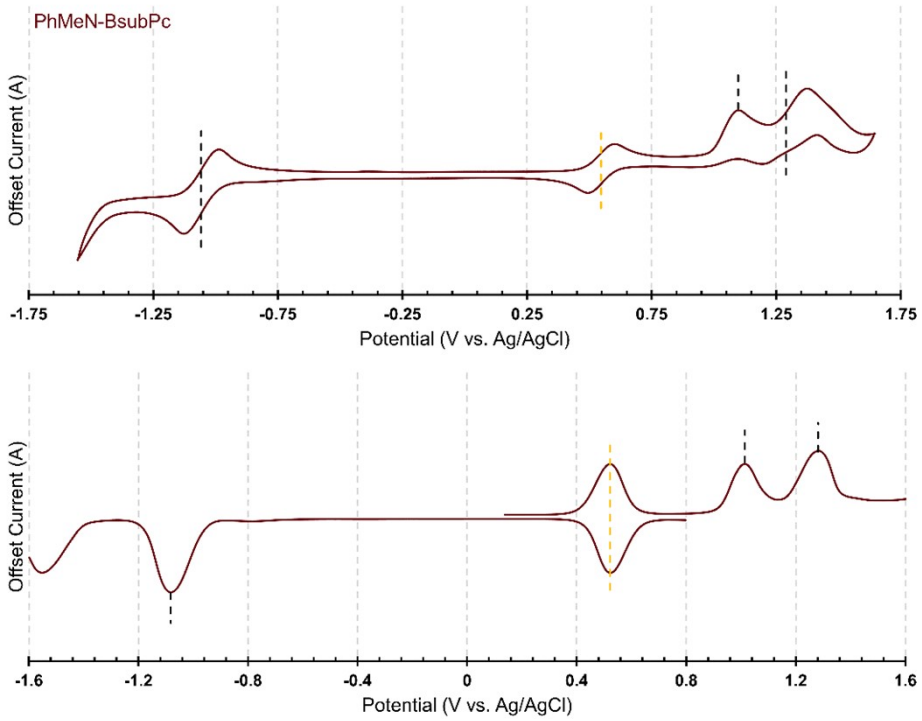


Figure S133. Full range (- 1.6 V to + 1.6 V) CV (top) and DPV (bottom) traces of column-purified PhMeN-BsubPc.

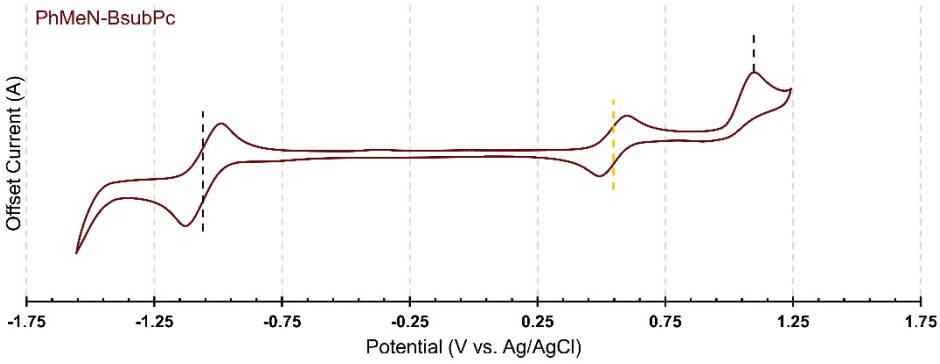


Figure S134. Smaller range (- 1.6 V to + 1.2 V) CV trace of column-purified PhMeN-BsubPc to assess the reversibility of the first oxidation.

Hot Plate Temperature Calibration

A temperature calibration was conducted on the hot plate used for all reactions to correlate the external temperature of the hot plate to the internal reaction temperature. The calibration was conducted using 125 mL of water in a 250 mL round-bottom flask.

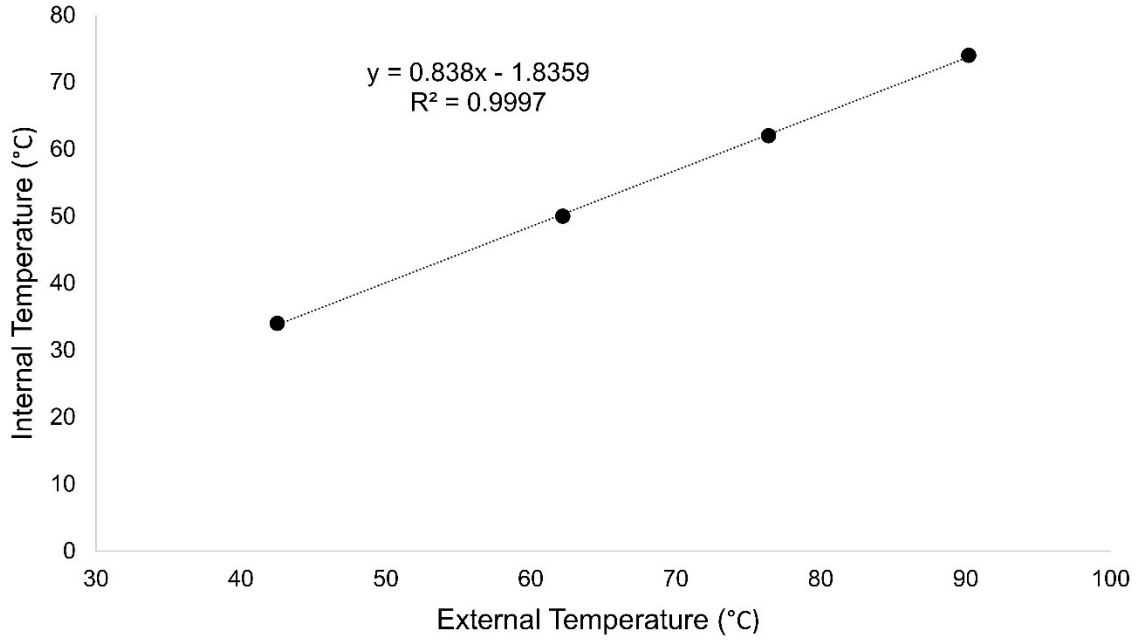


Figure S135. Hot plate temperature calibration curve.

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