

Supporting Information

Pyrene-Fused Poly-Aromatic Regioisomers: Synthesis, Columnar Mesomorphism and Physical Properties

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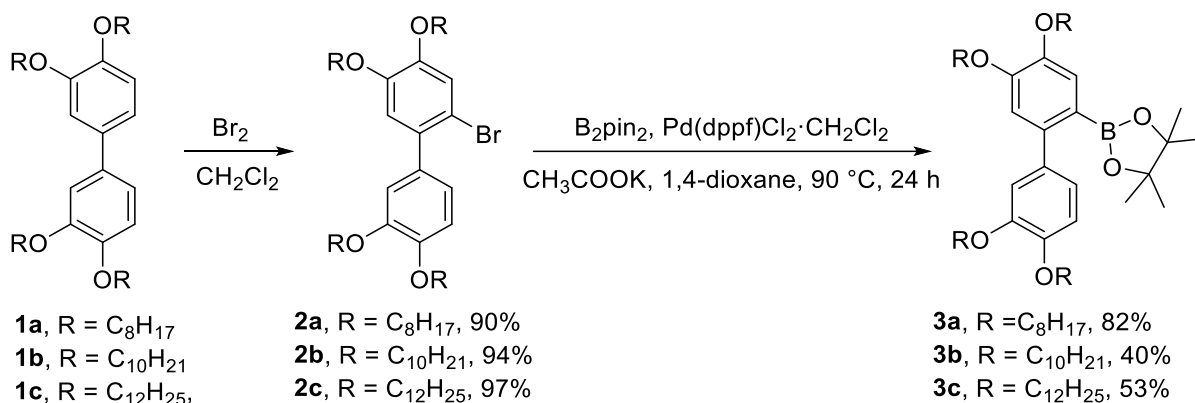
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1. Synthesis and Characterization

1.1. Synthesis and characterization of the biphenylboronic ester derivatives (3a/3b/3c)



Scheme S1. Preparation of the biphenylboronic ester derivatives.

1.1.1. 2-Bromo-3',4,4',5-tetrakis(alkoxy)-1,1'-biphenyl (2a/2b/2c)

Compound **1a/1b/1c** (1.0 equiv.) was dissolved in dry chloroform (0.015 M), bromine (1.0 equiv.) was diluted with chloroform (0.1 M) and added slowly by a constant-pressure dropping funnel. The resulting solution was stirred at room temperature until completion of the reaction. The reaction mixture was quenched with aqueous sodium hydrogen sulfite and extracted with dichloromethane. The combined organic layers were dried over anhydrous MgSO₄ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel with dichloromethane/petroleum ether (1/2) mixture as eluent. Finally, recrystallized from ethyl acetate and ethanol gave compounds **2a/2b/2c** in yield of 90-97%.

2a: According to the general synthesis procedure, **1a** (1.50 g, 2.25 mmol) was converted to the white solid **2a** (1.68 g, 90%). ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.10 (s, 1H, ArH), 6.95 (s, 1H, ArH), 6.89 (s, 2H, ArH), 6.84 (s, 1H, ArH), 4.05 - 3.95 (m, 8H, OCH₂), 1.87 - 1.76 (m, 8H, CH₂), 1.48 - 1.43 (m, 8H, CH₂), 1.33 - 1.29 (m, 32H, CH₂), 0.91 - 0.86 (m, 12H, CH₃).

2b: According to the general synthesis procedure, **1b** (0.63 g, 0.81 mmol) was converted to the white solid **2b** (0.65 g, 94%). ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.11 (s, 1H, ArH), 6.95 (s, 1H, ArH), 6.90 (s, 2H, ArH), 6.84 (s, 1H, ArH), 4.05 - 3.95 (m, 8H, OCH₂), 1.86 - 1.78 (m, 8H, CH₂), 1.48 - 1.27 (m, 56H, CH₂), 0.90 - 0.86 (m, 12H, CH₃).

2c: According to the general synthesis procedure, **1c** (3.29 g, 3.70 mmol) was converted to the white solid **2c** (3.50 g, 97%). ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.10 (s, 1H, ArH), 6.94 (s, 1H, ArH), 6.89 (s, 2H, ArH), 6.84 (s, 1H, ArH), 4.04 - 3.95 (m, 8H, OCH₂), 1.87 - 1.75 (m, 8H, CH₂), 1.50 - 1.42 (m, 8H, CH₂), 1.36 - 1.26 (m, 64H, CH₂), 0.89 - 0.86 (m, 12H, CH₃).

1.1.2. 4,4,5,5-Tetramethyl-2-(3',4,4',5-tetrakis(alkoxy)-[1,1'-biphenyl]-2-yl)-1,3,2-dioxaborolane (3a/3b/3c)

Compound **2a/2b/2c** (1.0 equiv.), bis(pinacolato)diboron (1.5 equiv.), CH₃COOK (3.0 equiv.), Pd(dppf)Cl₂·CH₂Cl₂ (5 mol%), 1,4-dioxane (0.06 M) were added in a round bottom flask. The resulting solution was stirred under nitrogen at 90 °C for 24 h. The reaction mixture was cooled to room temperature and extracted with dichloromethane. The combined organic layers were

dried over anhydrous MgSO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel with dichloromethane/petroleum ether (1/3) mixture as eluent. Finally, recrystallized from ethyl acetate and methanol gave **3a/3b/3c** in yield of 40-82%.

3a: According to the general synthesis procedure, **2a** (4.00 g, 5.37 mmol) was converted to the white solid **3a** (3.51 g, 82%). ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.20 (s, 1H, ArH), 6.92 (s, 1H, ArH), 6.85 (s, 3H, ArH), 4.06 - 3.99 (m, 8H, OCH_2), 1.83 - 1.80 (m, 8H, CH_2), 1.47 - 1.46 (m, 8H, CH_2), 1.38 - 1.28 (m, 32H, CH_2), 1.19 (s, 12H, CH_3), 0.92 - 0.88 (m, 12H, CH_3).

3b: According to the general synthesis procedure, **2b** (1.20 g, 1.40 mmol) was converted to the white solid **3b** (1.27 g, 40%). ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.21 (s, 1H, ArH), 6.92 (s, 1H, ArH), 6.85 (s, 3H, ArH), 4.06 - 4.00 (m, 8H, OCH_2), 1.85 - 1.78 (m, 8H, CH_2), 1.52 - 1.27 (m, 56H, CH_2), 1.20 (s, 12H, CH_3), 0.90 - 0.86 (m, 12H, CH_3).

3c: According to the general synthesis procedure, **2c** (2.60 g, 2.70 mmol) was converted to the white solid **3c** (1.44 g, 53%). ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.21 (s, 1H, ArH), 6.92 (s, 1H, ArH), 6.85 (s, 3H, ArH), 4.05 - 4.00 (m, 8H, OCH_2), 1.85 - 1.80 (m, 8H, CH_2), 1.50 - 1.26 (m, 72H, CH_2), 1.20 (s, 12H, CH_3), 0.90 - 0.87 (m, 12H, CH_3).

1.2. Synthesis and characterization of the DBP n and BBP n

D8: HRMS (ESI) calcd for $\text{C}_{104}\text{H}_{154}\text{O}_8$ $[\text{M}]^{+}$ m/z : 1532.1677 (100.0%), 1531.1644 (88.9%), 1533.1711 (55.7%), 1534.1744 (20.5%), 1535.1778 (5.6%), 1536.1811 (1.2%); found: 1532.1667 (100%), 1531.1635 (87.8%), 1533.1700 (59.1%), 1534.1734 (23.9%), 1535.1770 (6.5%), 1536.1808 (1.5%).

D10: HRMS (ESI) calcd for $\text{C}_{120}\text{H}_{186}\text{O}_8$ $[\text{M}]^{+}$ m/z : 1756.4181 (100.0%), 1755.4148 (77.0%), 1757.4215 (64.4%), 1758.4248 (27.4%), 1759.4282 (8.7%), 1760.4315 (2.2%); found: 1756.4185 (100%), 1755.4150 (76.6%), 1757.4217 (69.0%), 1758.4252 (30.6%), 1759.4286 (8.3%), 1760.4320 (2.8%).

D12: HRMS (ESI) calcd for $\text{C}_{136}\text{H}_{218}\text{O}_8$ $[\text{M}]^{+}$ m/z : 1980.6685 (100.0%), 1981.6719 (73.0%), 1979.6652 (68.0%), 1982.6752 (35.3%), 1983.6786 (12.7%), 1984.6819 (3.6%); found: 1980.6688 (100%), 1981.6715 (79.4%), 1979.6658 (67.5%), 1982.6746 (40.9%), 1983.6782 (16.7%), 1984.6821 (5.0%).

B8: HRMS (ESI) calcd for $\text{C}_{104}\text{H}_{154}\text{O}_8$ $[\text{M}]^{+}$ m/z : 1532.1677 (100.0%), 1531.1644 (88.9%), 1533.1711 (55.7%), 1534.1744 (20.5%), 1535.1778 (5.6%), 1536.1811 (1.2%); found: 1532.1660 (100%), 1531.1629 (86.4%), 1533.1692 (58.6%), 1534.1727 (23.6%), 1535.1762 (6.8%), 1536.1801 (1.8%).

B10: HRMS (ESI) calcd for $\text{C}_{120}\text{H}_{186}\text{O}_8$ $[\text{M}]^{+}$ m/z : 1756.4181 (100.0%), 1755.4148 (77.0%), 1757.4215 (64.4%), 1758.4248 (27.4%), 1759.4282 (8.7%), 1760.4315 (2.2%); found: 1756.4177 (100%), 1755.4145 (77.2%), 1757.4211 (66.7%), 1758.4247 (30.2%), 1759.4280 (9.8%), 1760.4315 (2.7%).

B12: HRMS (ESI) calcd for $\text{C}_{136}\text{H}_{218}\text{O}_8$ $[\text{M}]^{+}$ m/z : 1980.6685 (100.0%), 1981.6719 (73.0%), 1979.6652 (68.0%), 1982.6752 (35.3%), 1983.6786 (12.7%), 1984.6819 (3.6%); found: 1980.6695 (100%), 1981.6731 (77.3%), 1979.6666 (67.2%), 1982.6764 (36.7%), 1983.6806 (14.4%), 1984.6826 (4.8%).

DBP8: According to the general synthesis procedure, the substrate 1,6-dibromopyrene (28.5 mg, 0.079 mmol) was converted into a yellow solid **DBP8** (72.2 mg, 60%). **¹H NMR** (400 MHz, CDCl₃, TMS) δ 9.18 (d, *J* = 9.2 Hz, 2H, ArH), 9.14 (s, 2H, ArH), 8.44 (s, 2H, ArH), 8.37 (d, *J* = 9.4 Hz, 2H, ArH), 8.28 (s, 2H, ArH), 7.95 (s, 2H, ArH), 7.93 (s, 2H, ArH), 4.36 - 4.29 (m, 12H, OCH₂), 4.23 (t, *J* = 6.5 Hz, 4H, OCH₂), 2.02 - 1.92 (m, 16H, CH₂), 1.61 - 1.55 (m, 16H, CH₂), 1.45 - 1.25 (m, 64H, CH₂), 0.93 - 0.86 (m, 24H, CH₃). **¹³C NMR** (100 MHz, CDCl₃, TMS) δ 149.78, 149.34, 149.15, 147.77, 128.84, 127.52, 127.13, 127.08, 126.86, 125.50, 124.97, 124.68, 124.52, 123.83, 123.78, 117.89, 114.66, 107.94, 107.45, 107.08, 69.72, 69.54, 69.45, 31.89, 29.53, 29.48, 29.38, 29.35, 26.22, 26.19, 22.73, 22.70, 14.16. **Elemental Analysis** (C₁₀₄H₁₅₀O₈, MW 1528.34, %): calc. C 81.73, H 9.89; found C 81.85, H 9.55. **HRMS** (ESI) calcd for C₁₀₄H₁₅₀O₈ [M]⁺⁺ *m/z*: 1528.1364 (100.0%), 1527.1331 (88.9%), 1529.1398 (57.4%), 1530.1431 (20.5%); found: 1528.1332 (100.0%), 1527.1301 (81.0%), 1529.1354 (59.5%), 1530.1372 (24.0%).

DBP10: According to the general synthesis procedure, the substrate 1,6-dibromopyrene (26.8 mg, 0.074 mmol) was converted into a yellow solid **DBP10** (74.7 mg, 57%). **¹H NMR** (600 MHz, CDCl₃, TMS) δ 9.18 (d, *J* = 9.2 Hz, 2H, ArH), 9.15 (s, 2H, ArH), 8.44 (s, 2H, ArH), 8.38 (d, *J* = 9.3 Hz, 2H, ArH), 8.28 (s, 2H, ArH), 7.95 (s, 2H, ArH), 7.93 (s, 2H, ArH), 4.36 - 4.30 (m, 12H, OCH₂), 4.23 (t, *J* = 6.5 Hz, 4H, OCH₂), 2.04 - 1.93 (m, 16H, CH₂), 1.65 - 1.54 (m, 16H, CH₂), 1.47 - 1.25 (m, 96H, CH₂), 0.91-0.84 (m, 24H, CH₃). **¹³C NMR** (100 MHz, CDCl₃, TMS) δ 149.79, 149.36, 149.17, 147.80, 128.86, 127.54, 127.16, 127.10, 126.89, 125.52, 124.99, 124.70, 124.54, 123.85, 123.80, 117.91, 114.69, 107.98, 107.48, 107.12, 69.74, 69.57, 69.46, 31.97, 31.93, 29.75, 29.68, 29.64, 29.60, 29.58, 29.55, 29.50, 29.44, 29.39, 26.25, 26.20, 22.74, 22.71, 14.17, 14.14. **Elemental Analysis** (C₁₂₀H₁₈₂O₈, MW 1752.77, %): calc. C 82.23, H 10.47; found C 82.01, H 10.34. **HRMS** (ESI) calcd for C₁₂₀H₁₈₂O₈ [M]⁺⁺ *m/z*: 1752.3868 (100.0%), 1751.3835 (77.0%), 1753.3902 (64.3%), 1754.3935 (27.4%), 1755.3969 (7.6%); found: 1752.3857 (100.0%), 1751.3825 (72.9%), 1753.3905 (68.7%), 1754.3948 (35.4%), 1755.3996 (12.5%).

DBP12: According to the general synthesis procedure, the substrate 1,6-dibromopyrene (35.1 mg, 0.097 mmol) was converted into a yellow solid **DBP12** (101.5 mg, 53%). **¹H NMR** (400 MHz, CDCl₃, TMS) δ 9.18 (d, *J* = 9.2 Hz, 2H, ArH), 9.14 (s, 2H, ArH), 8.45 (s, 2H, ArH), 8.37 (d, *J* = 9.3 Hz, 2H, ArH), 8.28 (s, 2H, ArH), 7.95 (s, 2H, ArH), 7.92 (s, 2H, ArH), 4.36 - 4.29 (m, 12H, OCH₂), 4.24 (t, *J* = 6.4 Hz, 4H, OCH₂), 2.01 - 1.92 (m, 16H, CH₂), 1.62 - 1.54 (m, 16H, CH₂), 1.46 - 1.24 (m, 128H, CH₂), 0.91 - 0.84 (m, 24H, CH₃). **¹³C NMR** (100 MHz, CDCl₃, TMS) δ 149.78, 149.35, 149.15, 147.79, 128.85, 127.53, 127.14, 127.09, 126.88, 125.51, 124.98, 124.69, 124.52, 123.84, 123.79, 117.89, 114.66, 107.96, 107.47, 107.09, 69.76, 69.73, 69.55, 69.45, 31.96, 31.92, 29.78, 29.72, 29.68, 29.60, 29.58, 29.55, 29.48, 29.42, 29.39, 26.24, 26.20, 22.73, 22.69, 14.16, 14.13. **Elemental Analysis** (C₁₃₆H₂₁₄O₈, MW 1977.20, %): calc. C 82.62, H 10.91; found C 82.69, H 10.72. **HRMS** (ESI) calcd for C₁₃₆H₂₁₄O₈ [M]⁺⁺ *m/z*: 1976.6372 (100.0%), 1977.6406 (73.0%), 1975.6339 (68.0%), 1978.6439 (35.8%); found: 1976.6398 (100.0%), 1977.6444 (88.0%), 1975.6359 (63.0%), 1978.6502 (51.0%).

BBP8: According to the general synthesis procedure, the substrate 1,8-dibromopyrene (27.2 mg, 0.076 mmol) was converted into a yellow solid **BBP8** (74.1 mg, 64%). **¹H NMR** (400 MHz, CDCl₃, TMS) δ 9.12 (s, 2H, ArH), 9.05 (s, 2H, ArH), 8.64 (s, 2H, ArH), 8.26 (s, 2H, ArH), 8.17 (s, 2H, ArH), 7.93 (d, *J* = 11.5 Hz, 4H, ArH), 4.38 - 4.27 (m, 16H, OCH₂), 2.04-1.94 (m, 16H,

CH₂), 1.68 - 1.61 (m, 16H, CH₂), 1.50 - 1.27 (m, 64H, CH₂), 0.95 - 0.85 (m, 24H, CH₃). **¹³C NMR** (100 MHz, CDCl₃, TMS) δ 149.60, 149.22, 149.12, 147.68, 129.48, 127.86, 127.02, 126.60, 125.87, 125.43, 124.78, 124.51, 124.29, 123.80, 123.63, 118.87, 114.12, 107.53, 106.93, 106.79, 69.65, 69.54, 69.46, 69.15, 31.94, 31.92, 29.80, 29.73, 29.61, 29.60, 29.54, 29.47, 29.45, 29.43, 26.59, 26.30, 26.28, 22.76, 22.72, 14.19, 14.18, 14.13. **Elemental Analysis** (C₁₀₄H₁₅₀O₈, MW 1528.34, %): calc. C 81.73, H 9.89; found C 81.79, H 9.75. **HRMS** (ESI) calcd for C₁₀₄H₁₅₀O₈ [M]⁺ m/z: 1528.1364 (100.0%), 1527.1331 (88.9%), 1529.1398 (57.4%), 1530.1431 (20.5%), 1531.1465 (4.6%); found: 1528.1332 (100.0%), 1527.1330 (83.0%), 1529.1361 (57.0%), 1530.1389 (23.9%), 1531.1449 (7.0%).

BBP10: According to the general synthesis procedure, the substrate 1,8-dibromopyrene (41.8 mg, 0.116 mmol) was converted into a yellow solid **BBP10** (114.1 mg, 56%). **¹H NMR** (400 MHz, CDCl₃, TMS) δ 9.14 (s, 2H, ArH), 9.07 (s, 2H, ArH), 8.65 (s, 2H, ArH), 8.27 (s, 2H, ArH), 8.19 (s, 2H, ArH), 7.94 (d, *J* = 12.4 Hz, 4H, ArH), 4.33 (m, 16H, OCH₂), 2.01 - 1.96 (m, 16H, CH₂), 1.63 - 1.57 (m, 16H, CH₂), 1.45 - 1.25 (m, 96H, CH₂), 0.90 - 0.85 (m, 24H, CH₃). **¹³C NMR** (100 MHz, CDCl₃, TMS) δ 149.64, 149.23, 149.14, 147.73, 129.52, 127.86, 127.04, 126.64, 125.90, 125.45, 124.79, 124.55, 124.32, 123.80, 123.67, 118.87, 114.17, 107.56, 107.01, 106.83, 69.66, 69.56, 69.48, 69.17, 31.99, 31.95, 29.82, 29.81, 29.78, 29.74, 29.72, 29.70, 29.66, 29.64, 29.57, 29.53, 29.45, 26.57, 26.31, 26.28, 22.75, 22.72, 14.17, 14.13. **Elemental Analysis** (C₁₂₀H₁₈₂O₈, MW 1752.77, %): calc. C 82.23, H 10.47; found C 81.93, H 10.30. **HRMS** (ESI) calcd for C₁₂₀H₁₈₂O₈ [M]⁺ m/z: 1752.3868 (100.0%), 1751.3835 (77.0%), 1753.3902 (64.3%), 1754.3935 (27.4%), 1755.3969 (7.6%); found: 1752.3867 (100.0%), 1753.3909 (75.0%), 1751.3826 (67.0%), 1754.3951 (35.4%), 1755.3991 (12.5%).

BBP12: According to the general synthesis procedure, the substrate 1,8-dibromopyrene (37.6 mg, 0.105 mmol) was converted into a yellow solid **BBP12** (111.8 mg, 54%). **¹H NMR** (400 MHz, CDCl₃, TMS) δ 9.14 (s, 2H, ArH), 9.07 (s, 2H, ArH), 8.66 (s, 2H, ArH), 8.27 (s, 2H, ArH), 8.18 (s, 2H, ArH), 7.94 (d, *J* = 12.3 Hz, 4H, ArH), 4.37 - 4.29 (m, 16H, OCH₂), 2.05 - 1.92 (m, 16H, CH₂), 1.67 - 1.58 (m, 16H, CH₂), 1.47 - 1.23 (m, 128H, CH₂), 0.91 - 0.84 (m, 24H, CH₃). **¹³C NMR** (100 MHz, CDCl₃, TMS) δ 149.64, 149.23, 149.14, 147.73, 129.53, 127.87, 127.06, 126.65, 125.91, 125.45, 124.80, 124.56, 124.33, 123.81, 123.67, 118.87, 114.17, 107.56, 107.00, 106.81, 69.65, 69.56, 69.46, 69.17, 31.97, 29.80, 29.78, 29.75, 29.67, 29.64, 29.57, 29.52, 29.44, 26.57, 26.31, 26.28, 22.73, 22.72, 14.16, 14.14. **Elemental Analysis** (C₁₃₆H₂₁₄O₈, MW 1977.20, %): calc. C 82.62, H 10.91; found C 82.90, H 10.78. **HRMS** (ESI) calcd for C₁₃₆H₂₁₄O₈ [M]⁺ m/z: 1976.6372 (100.0%), 1977.6406 (73.0%), 1975.6339 (68.0%); found: 1976.6375 (100.0%), 1977.6385 (74.0%), 1975.6348 (60.0%).

2. ^1H NMR

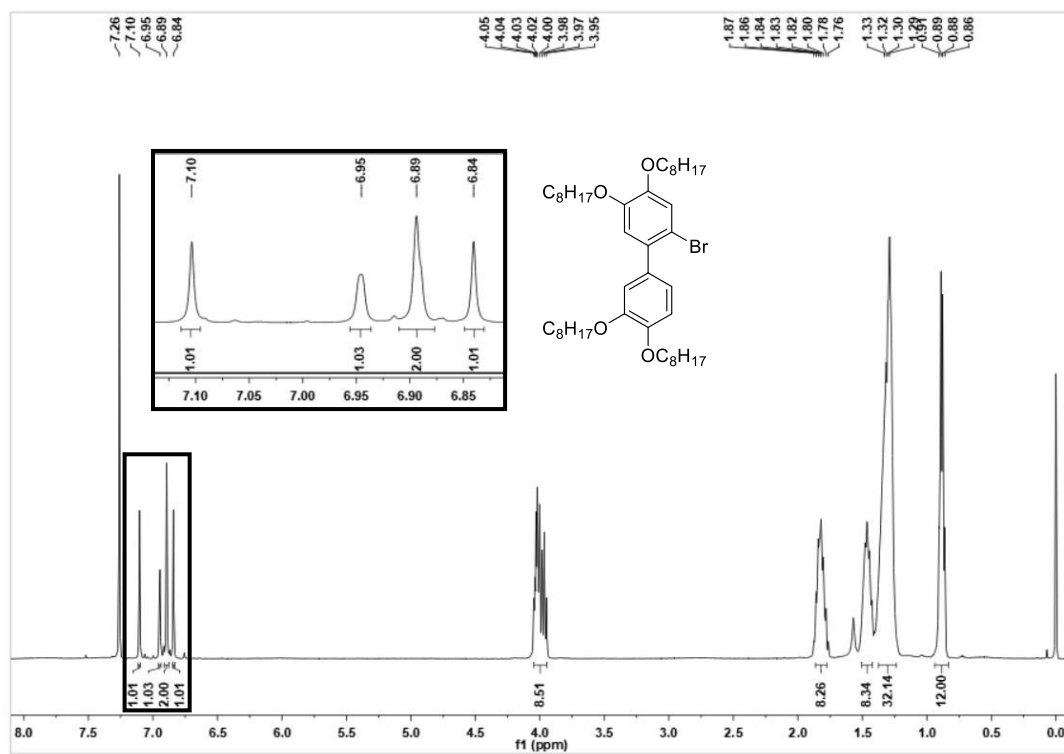


Figure S1. ^1H NMR spectrum of **2a**.

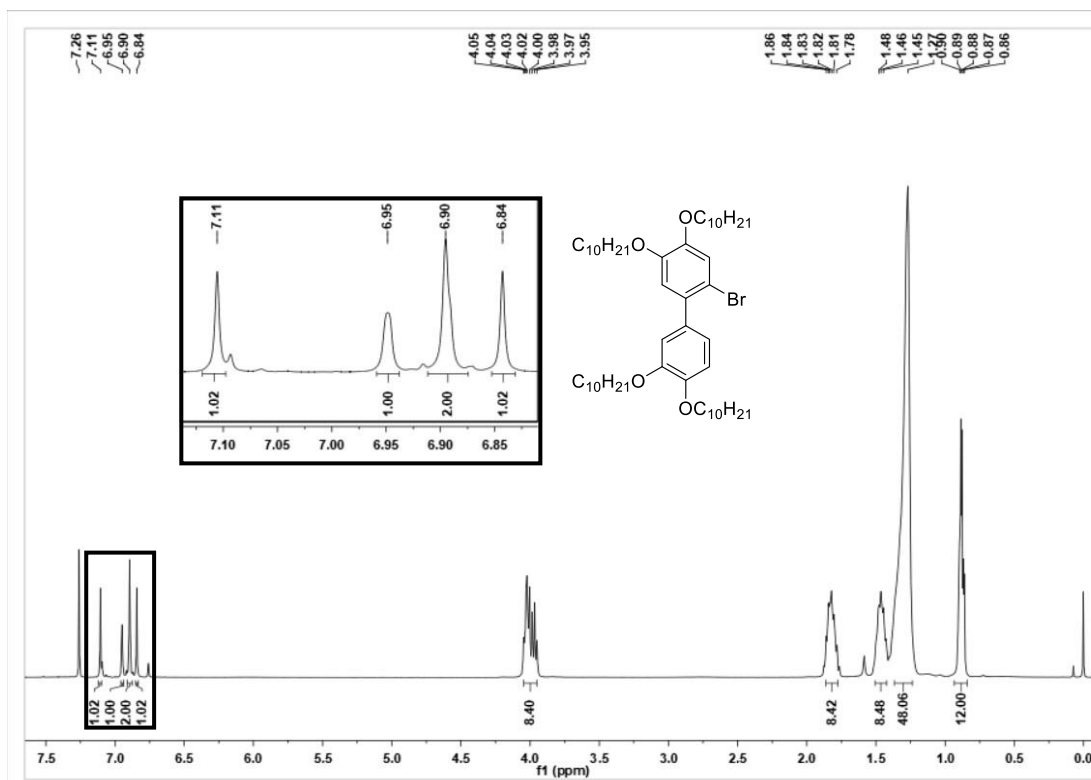


Figure S2. ^1H NMR spectrum of **2b**.

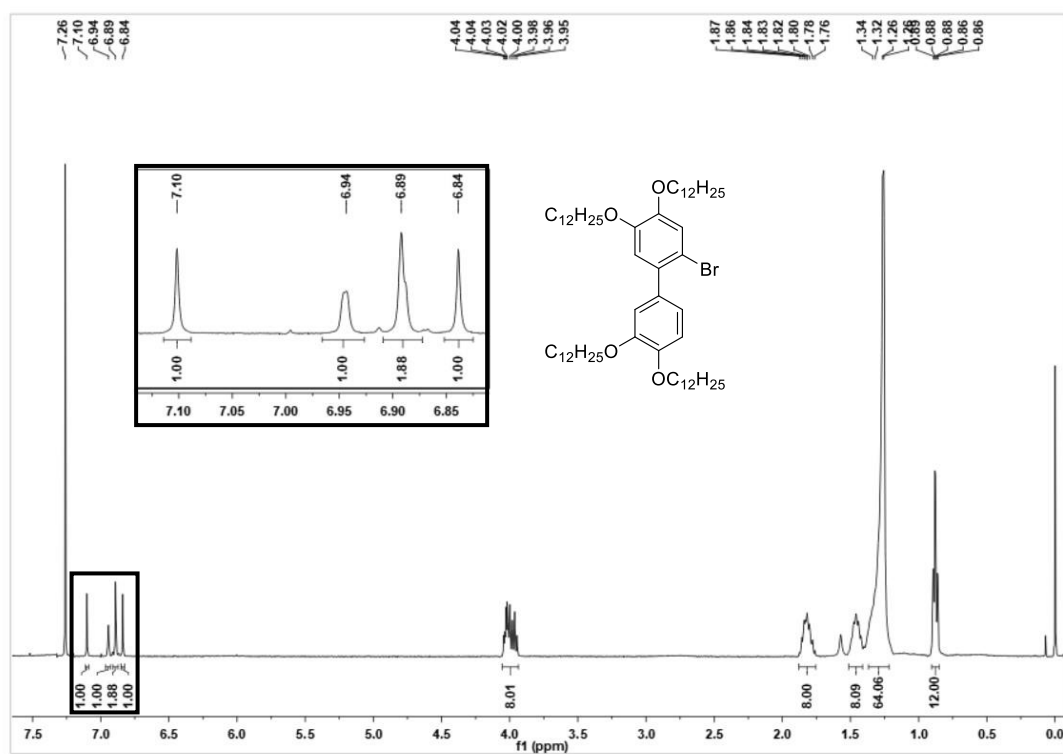


Figure S3. ¹H NMR spectrum of **2c**.

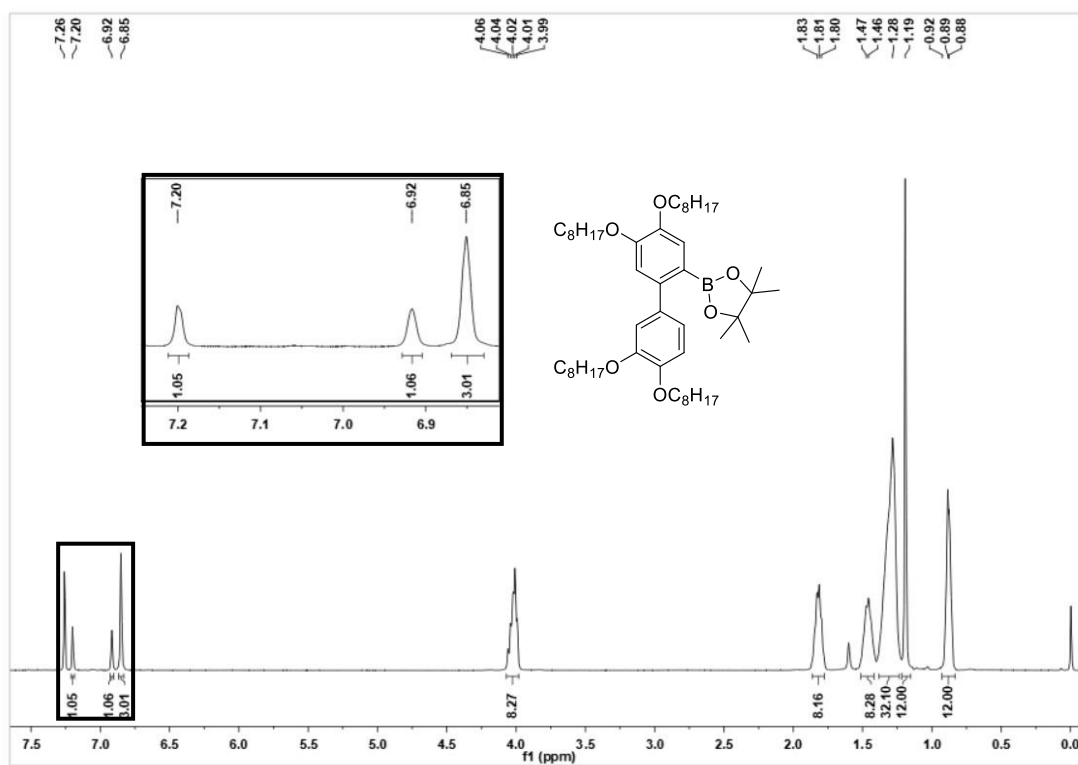


Figure S4. ¹H NMR spectrum of **3a**.

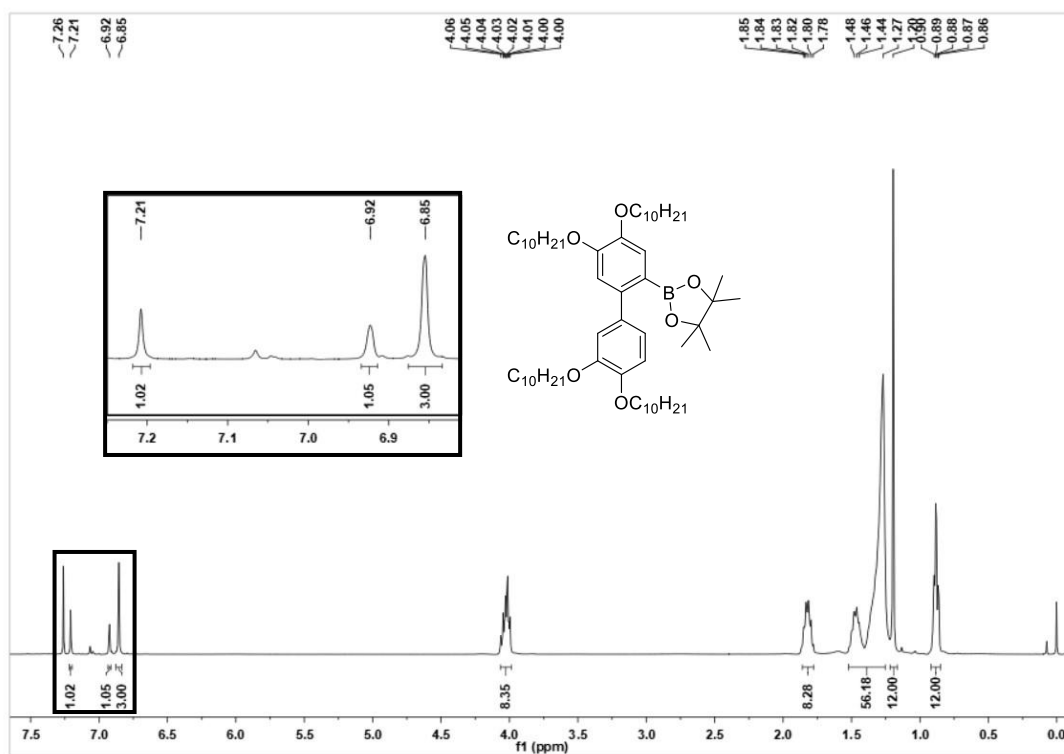


Figure S5. ¹H NMR spectrum of **3b**.

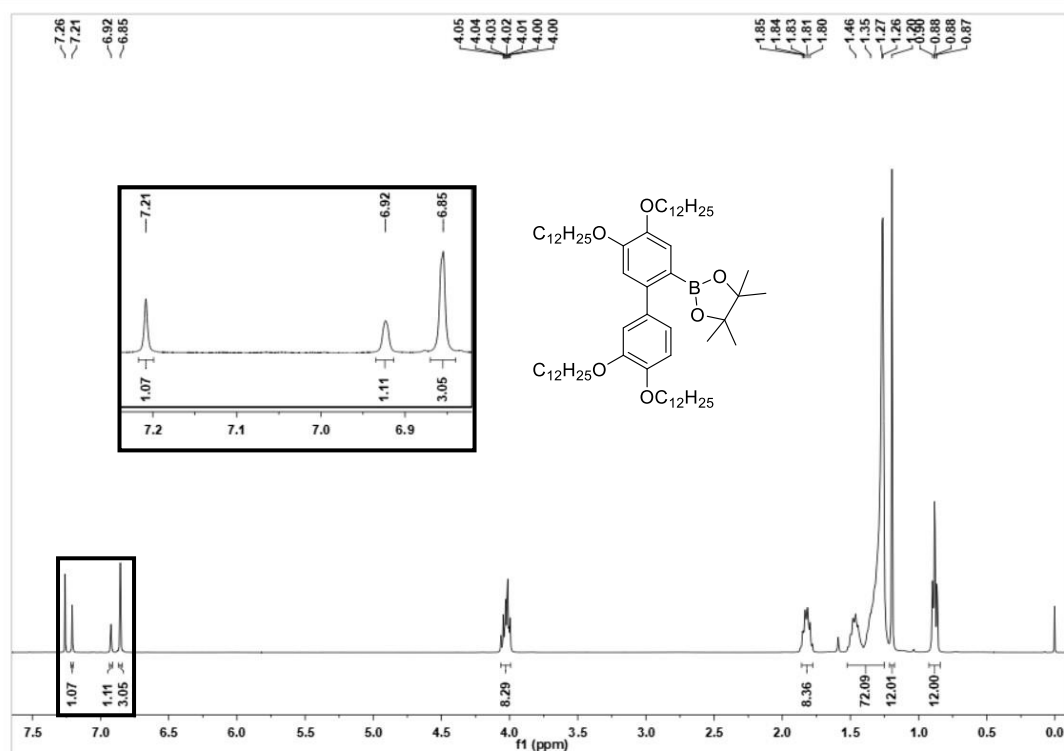


Figure S6. ¹H NMR spectrum of **3c**.

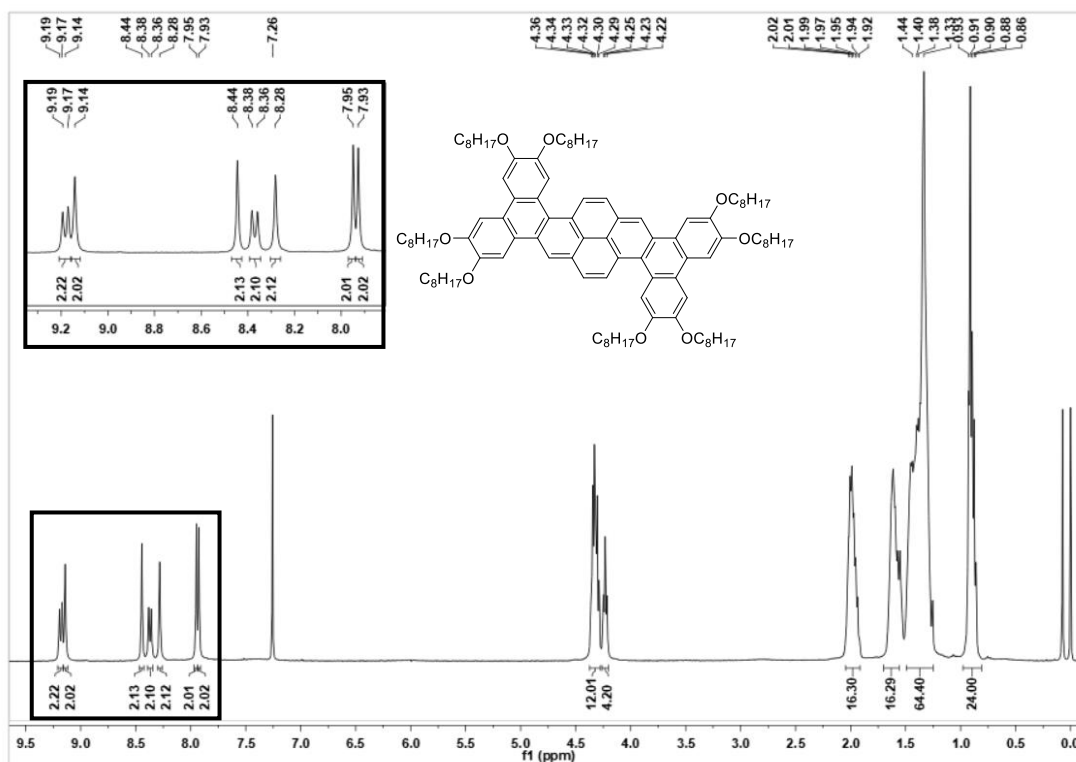


Figure S7. ^1H NMR spectrum of DBP8.

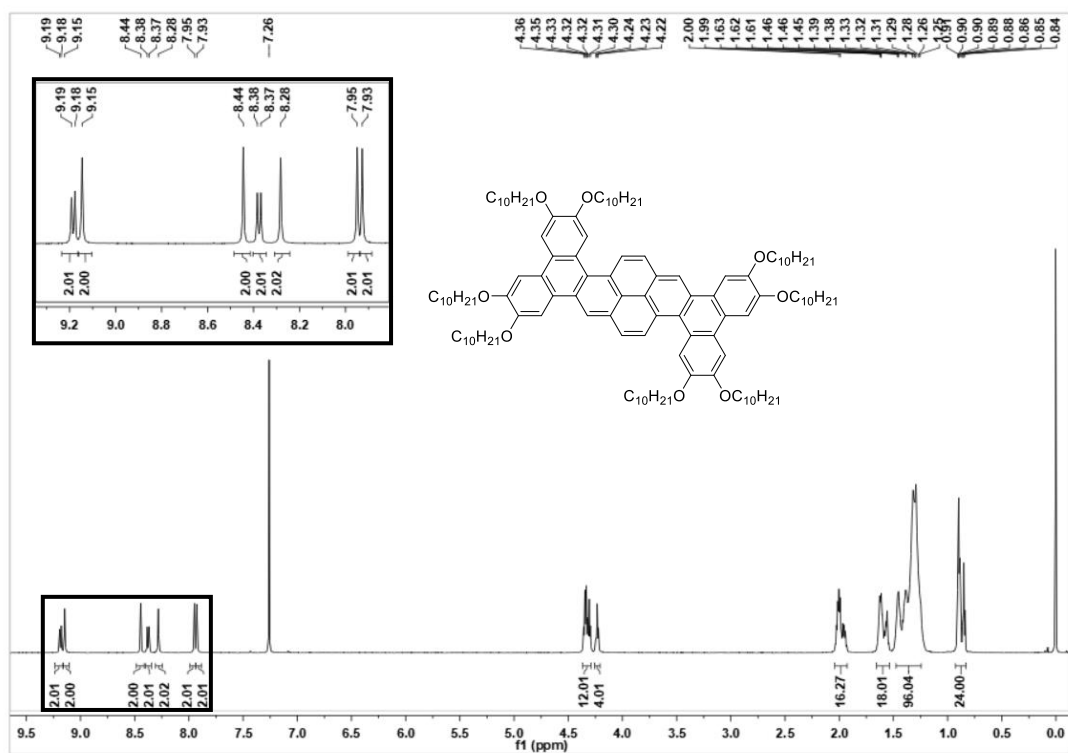


Figure S8. ^1H NMR spectrum of DBP10.

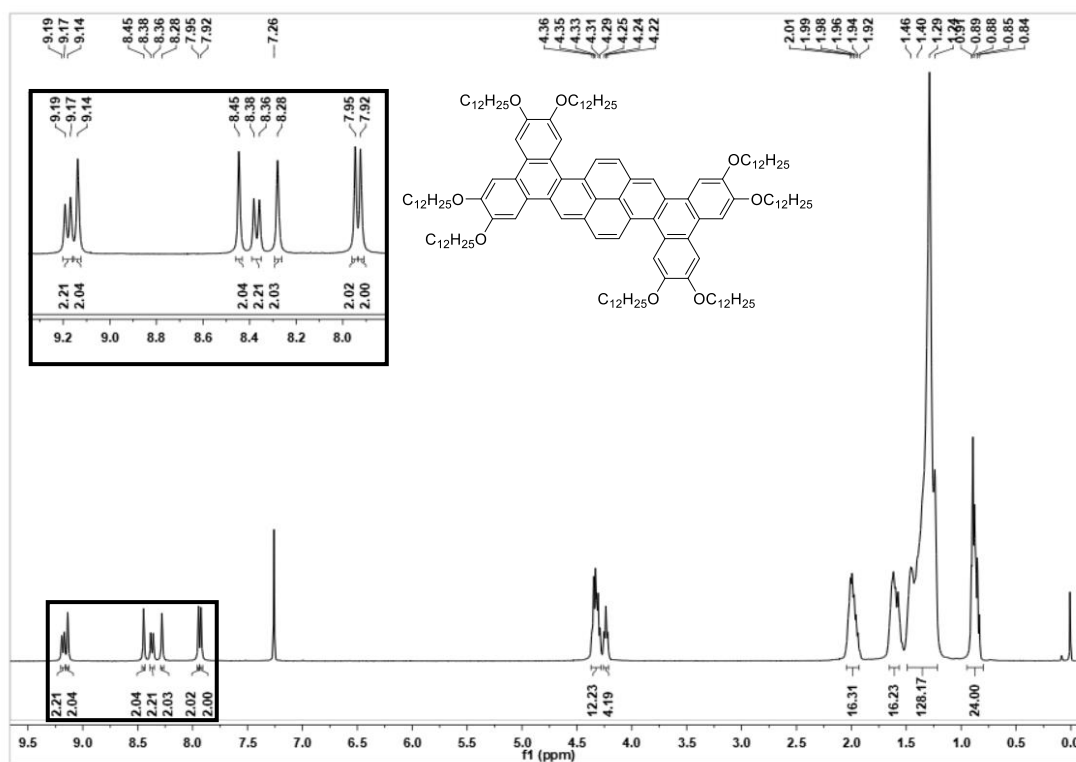


Figure S9. ^1H NMR spectrum of DBP12.

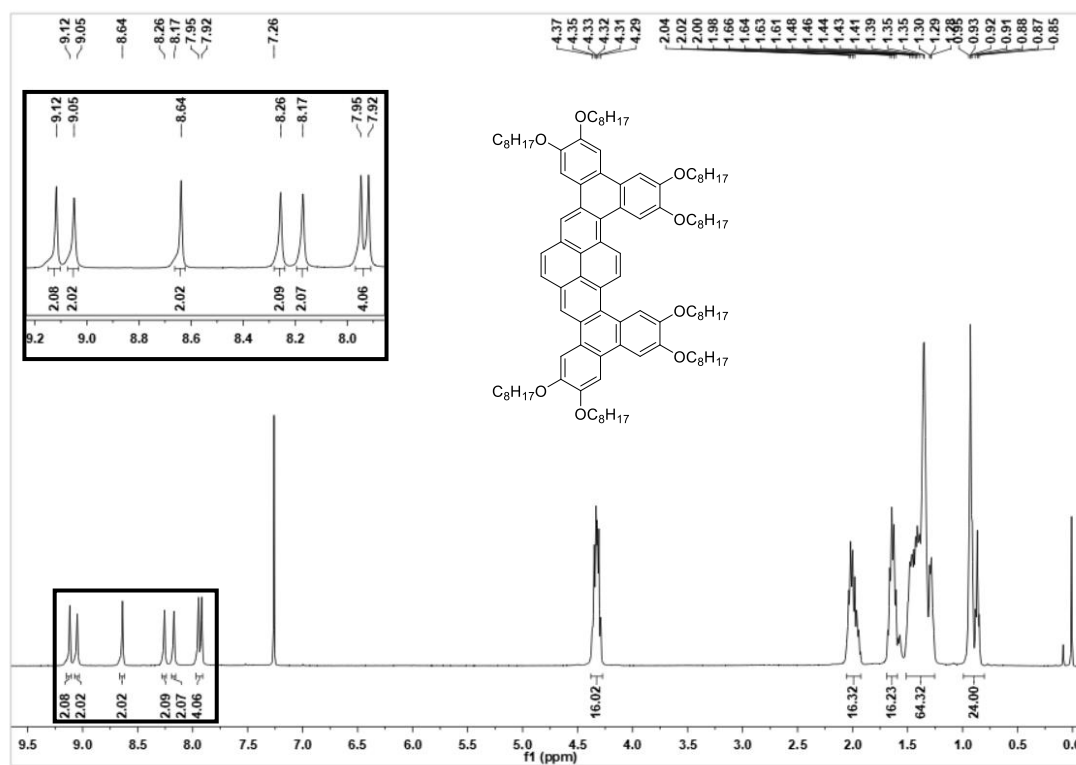


Figure S10. ^1H NMR spectrum of BBP8.

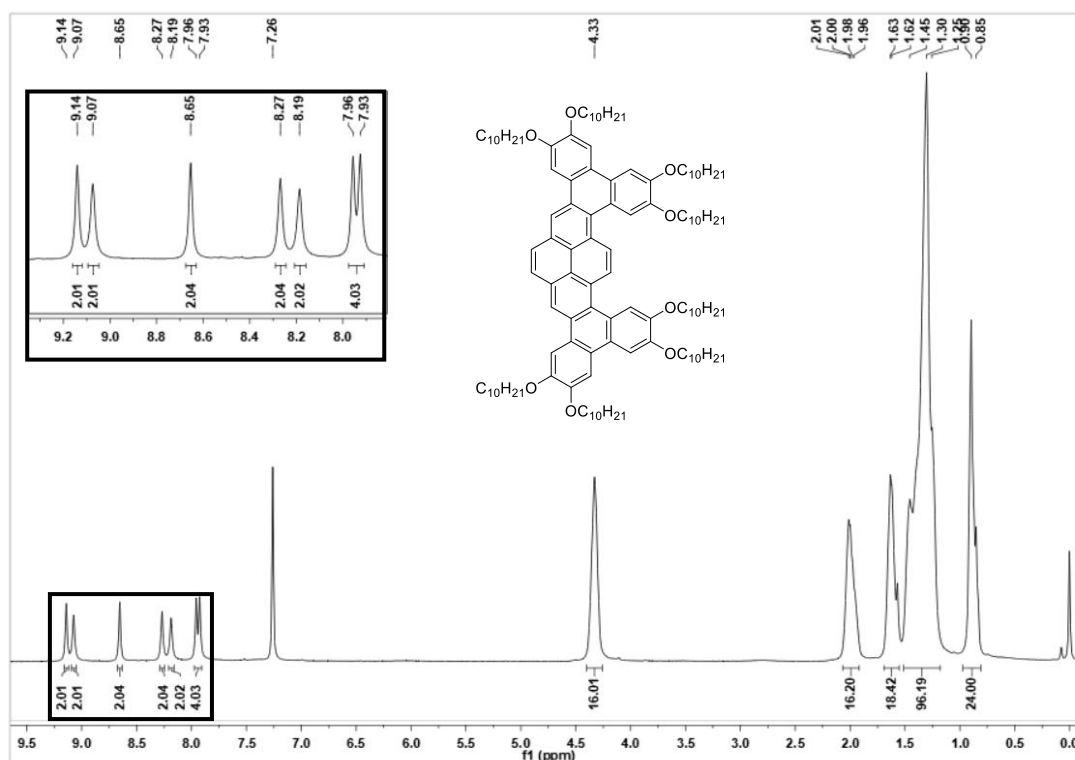


Figure S11. ^1H NMR spectrum of BBP10.

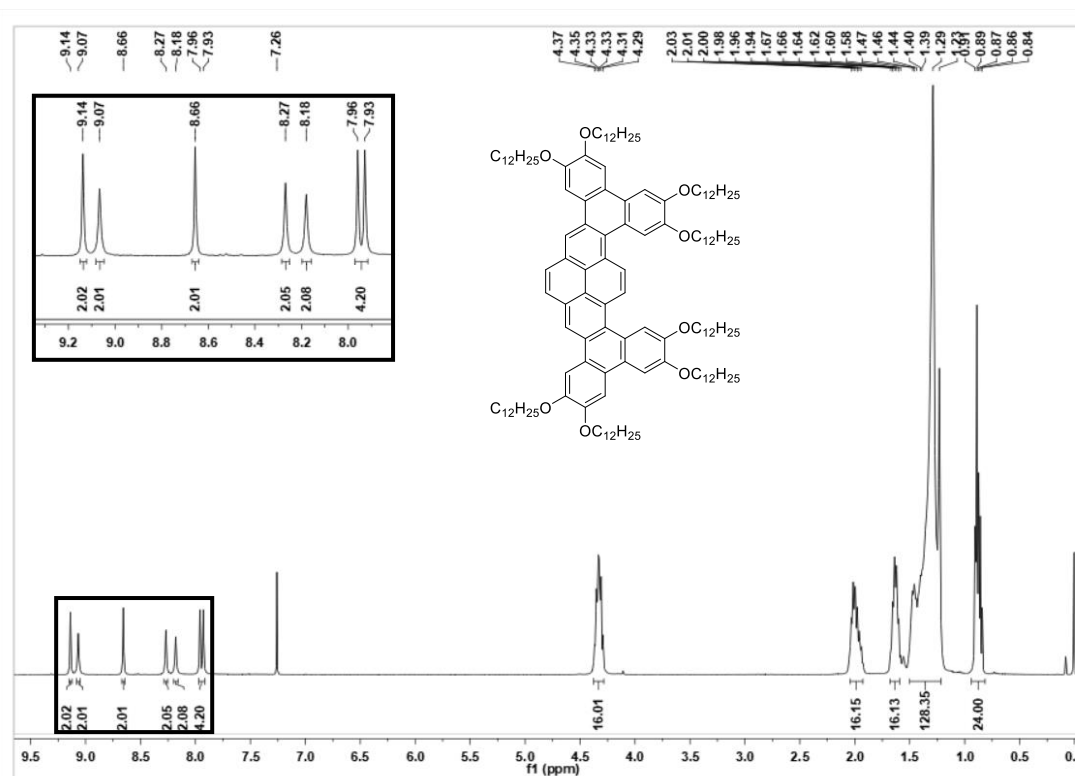


Figure S12. ^1H NMR spectrum of BBP12.

3. ^{13}C NMR

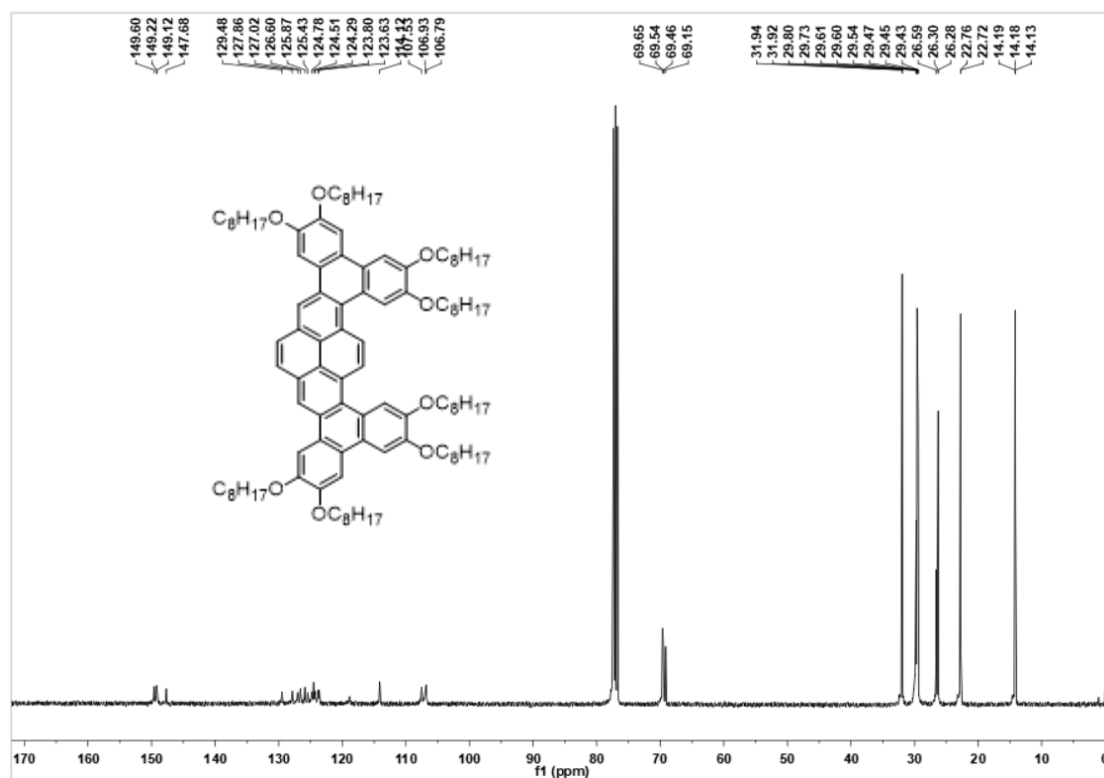


Figure S13. ^{13}C NMR spectrum of BBP8.

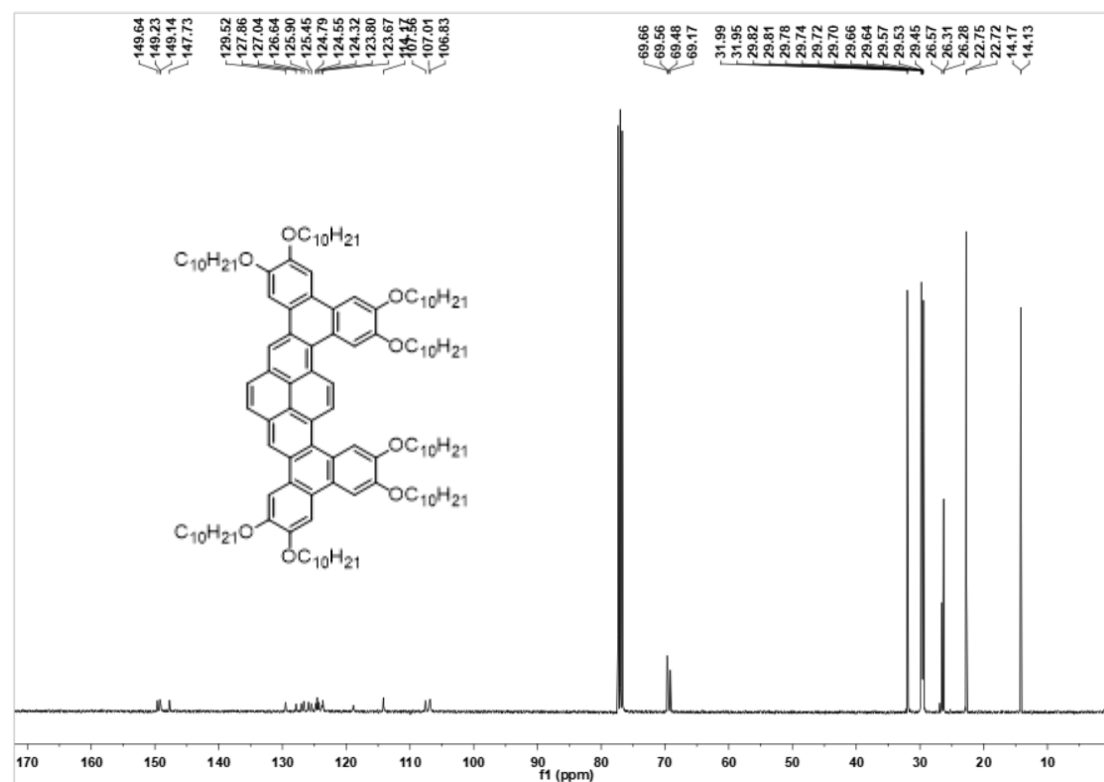


Figure S14. ^{13}C NMR spectrum of BBP10.

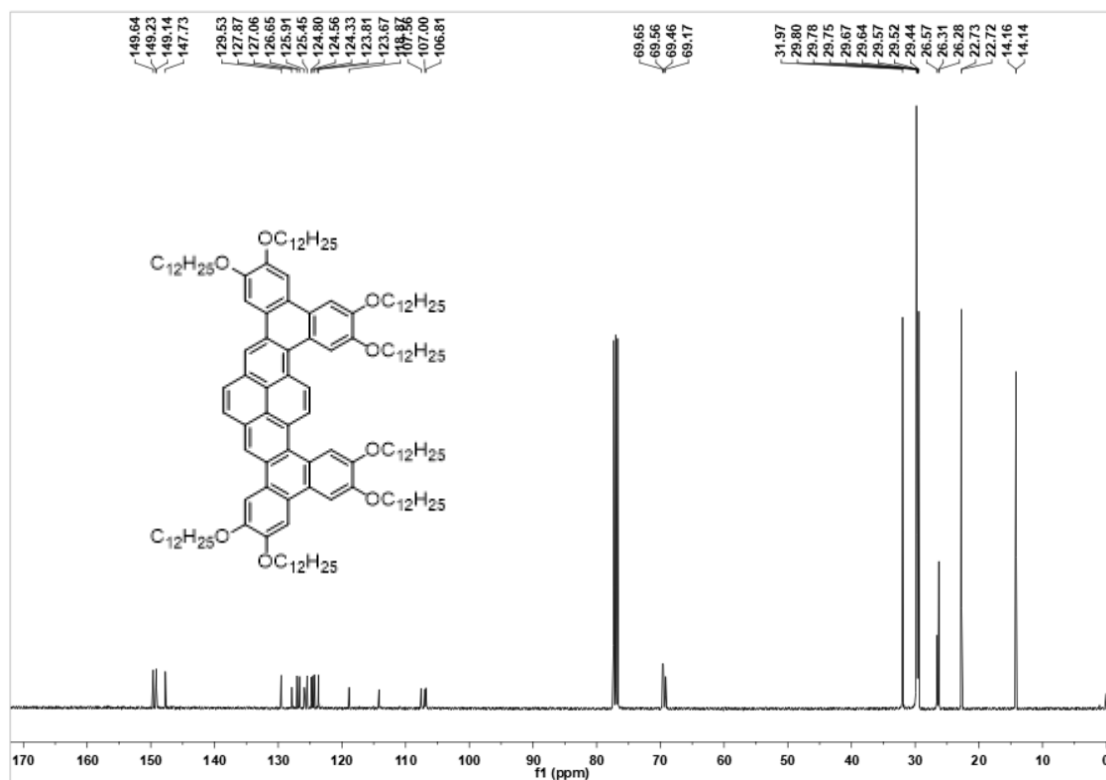


Figure S15. ¹³C NMR spectrum of **BBP12**.

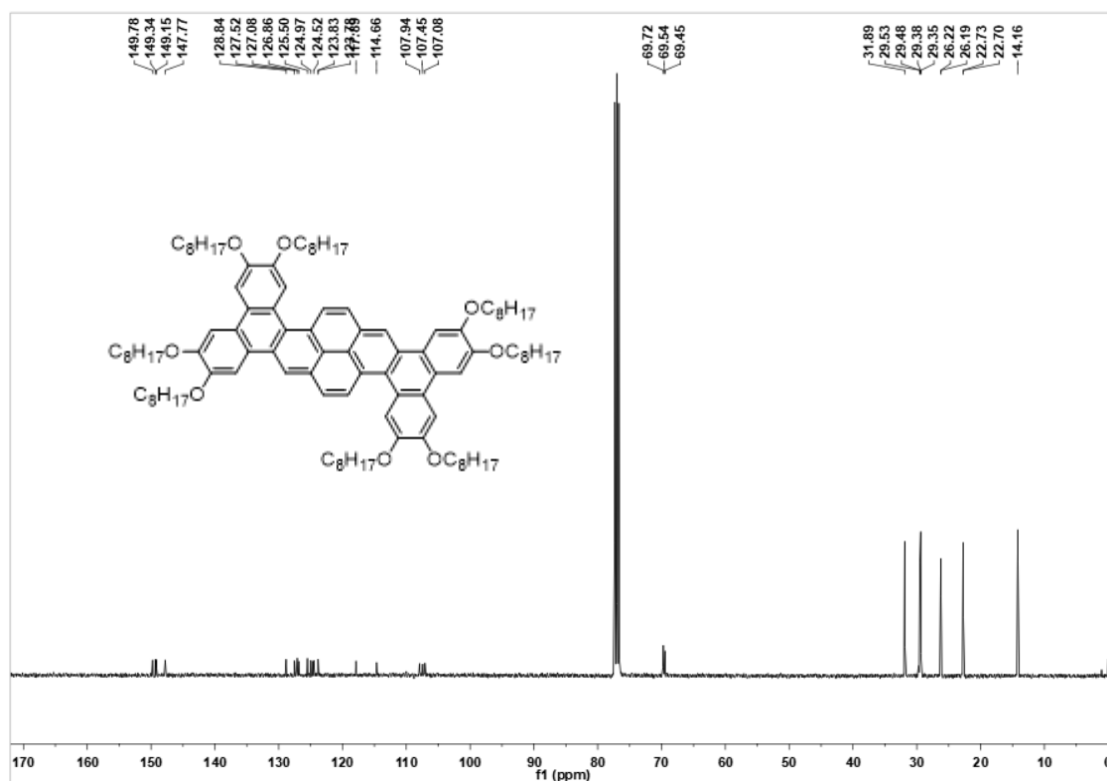


Figure S16. ¹³C NMR spectrum of **DBP8**.

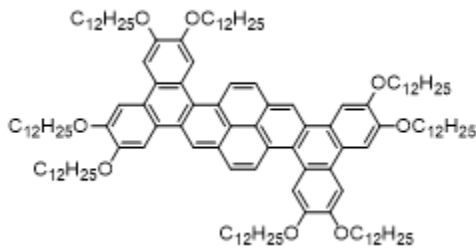
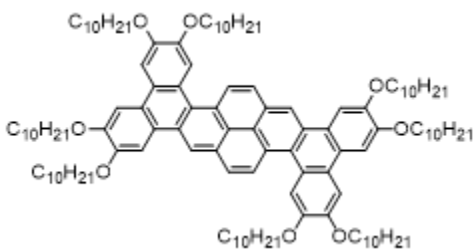


Figure S18. ^{13}C NMR spectrum of **DBP12**.

4. HRMS

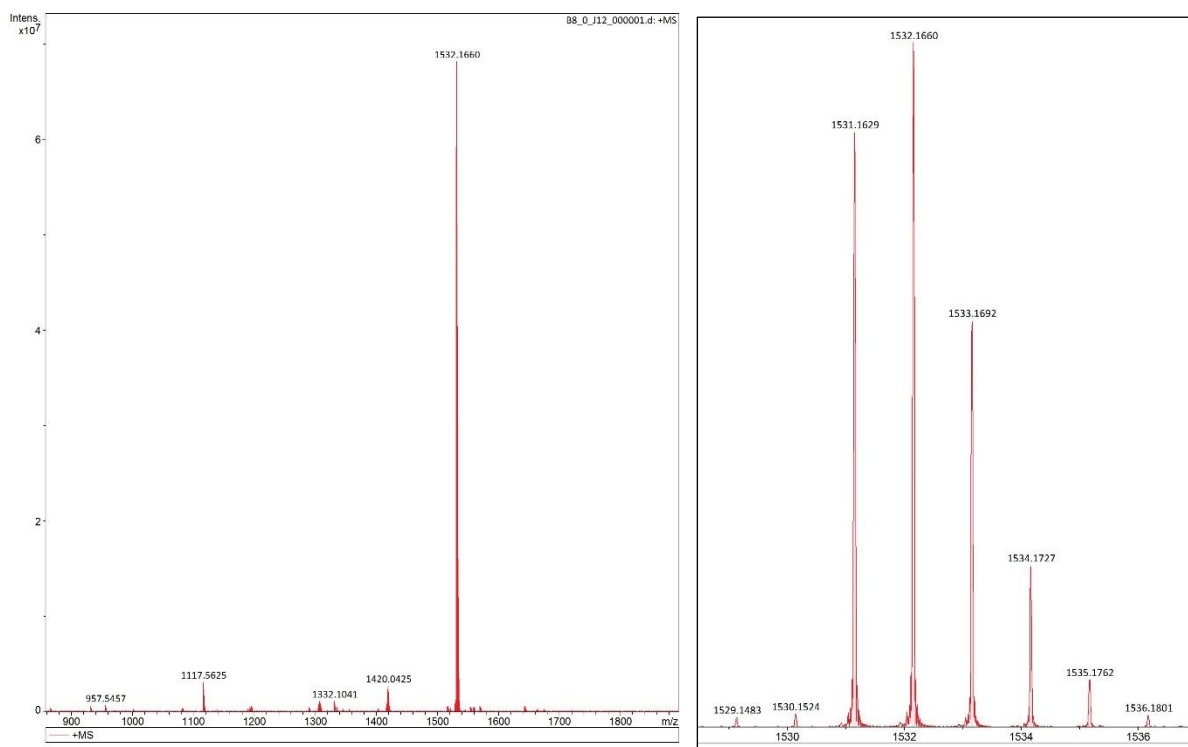


Figure S19. HRMS of B8.

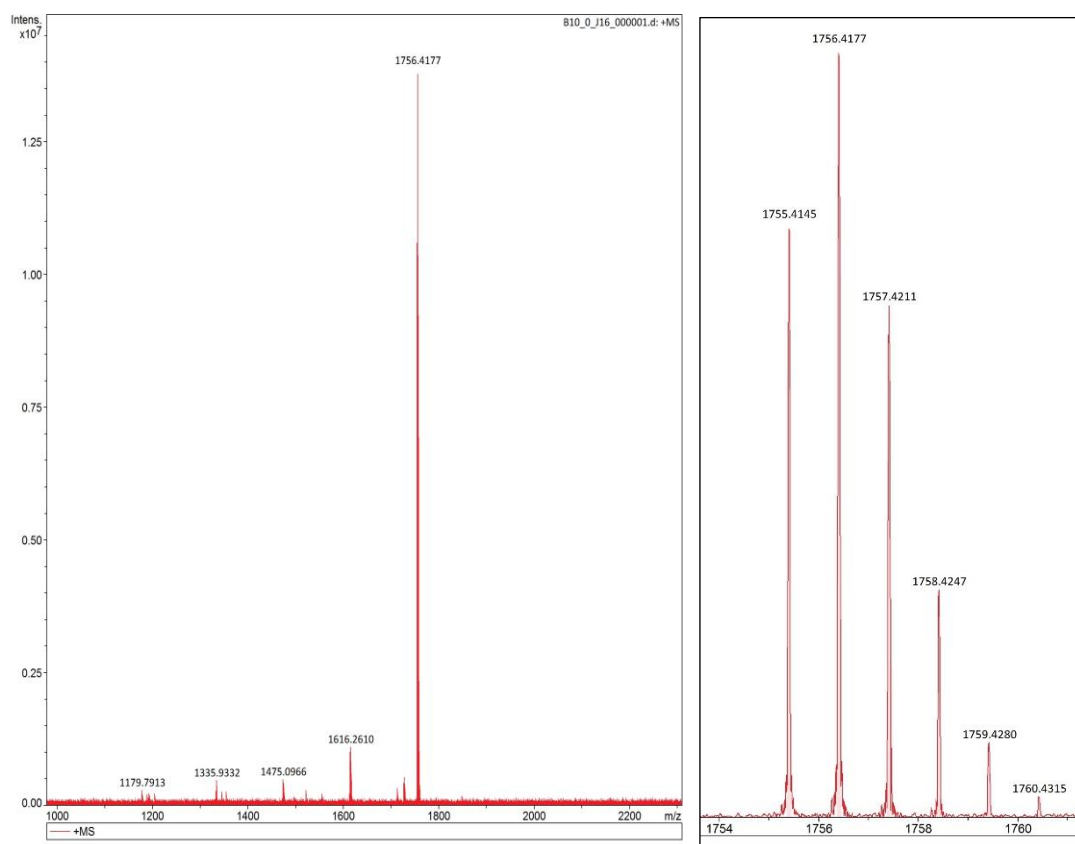


Figure S20. HRMS of B10.

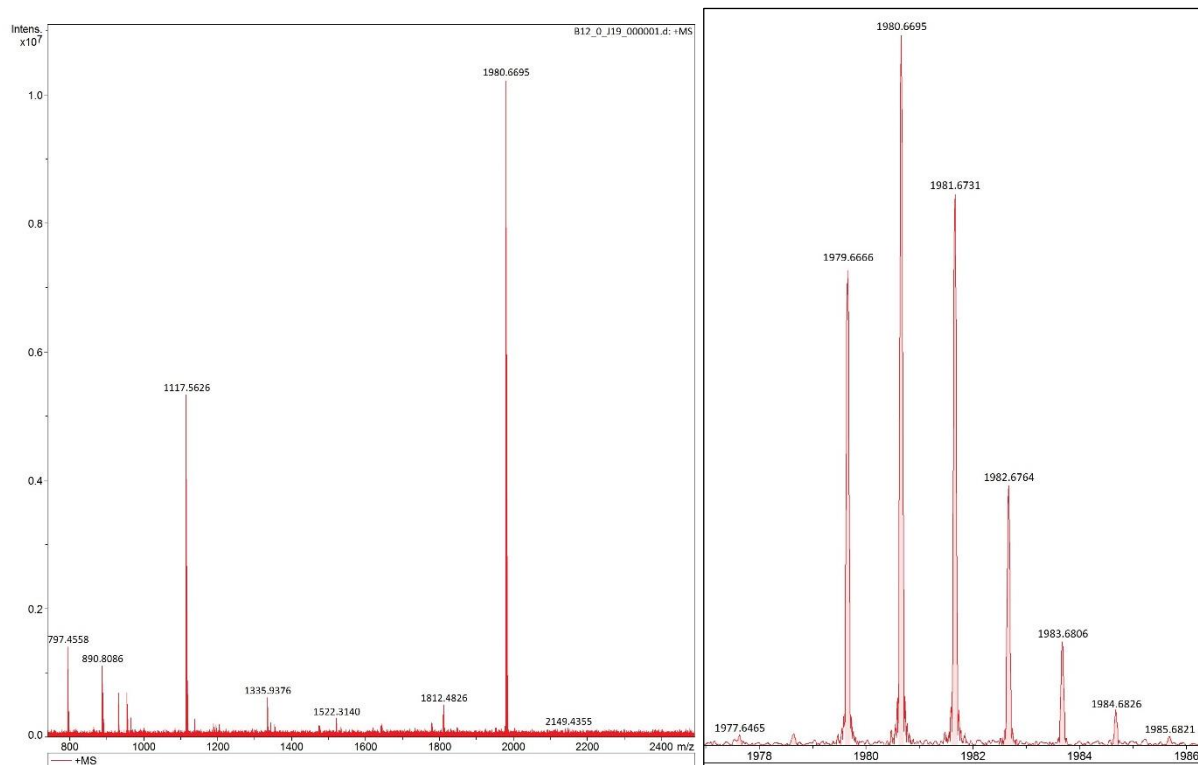


Figure S21. HRMS of B12.

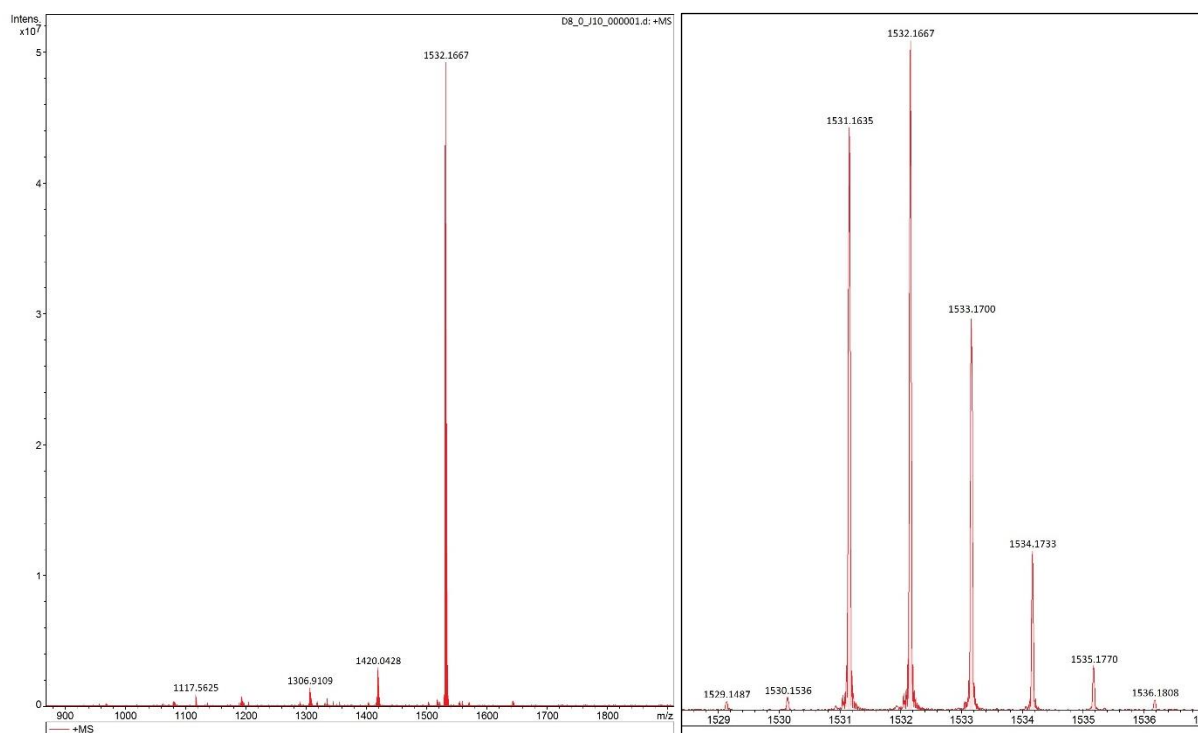


Figure S22. HRMS of D8.

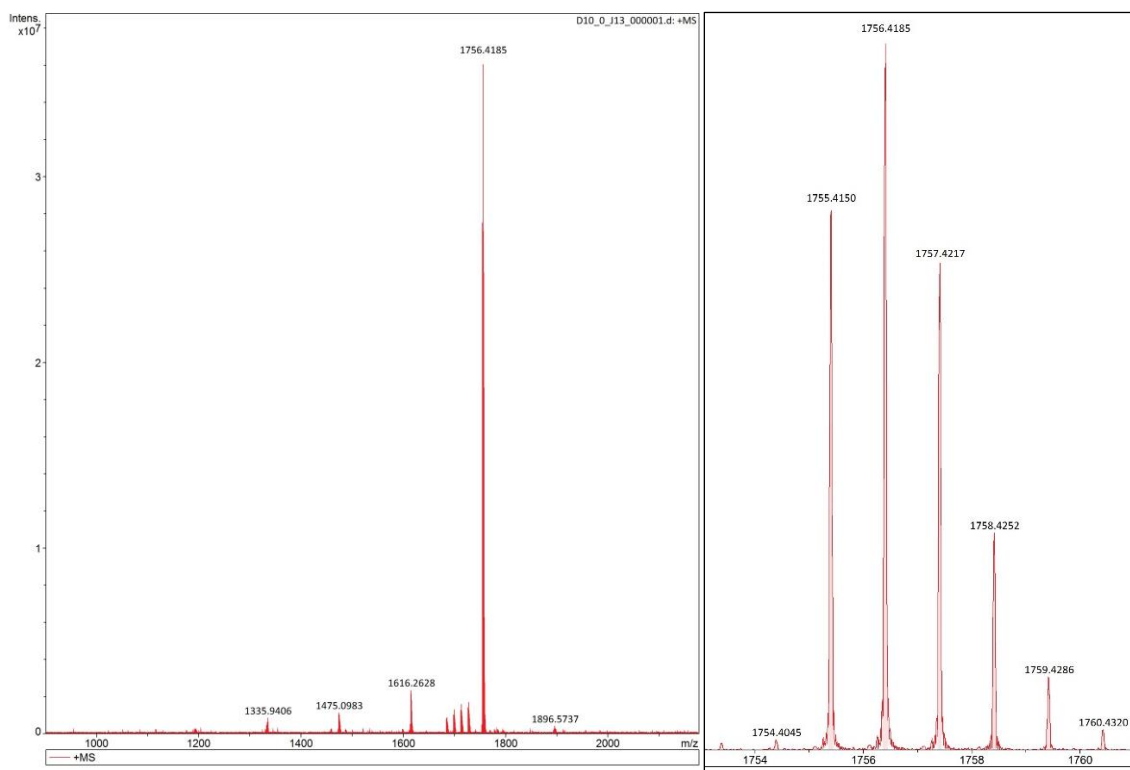


Figure S23. HRMS of D10.

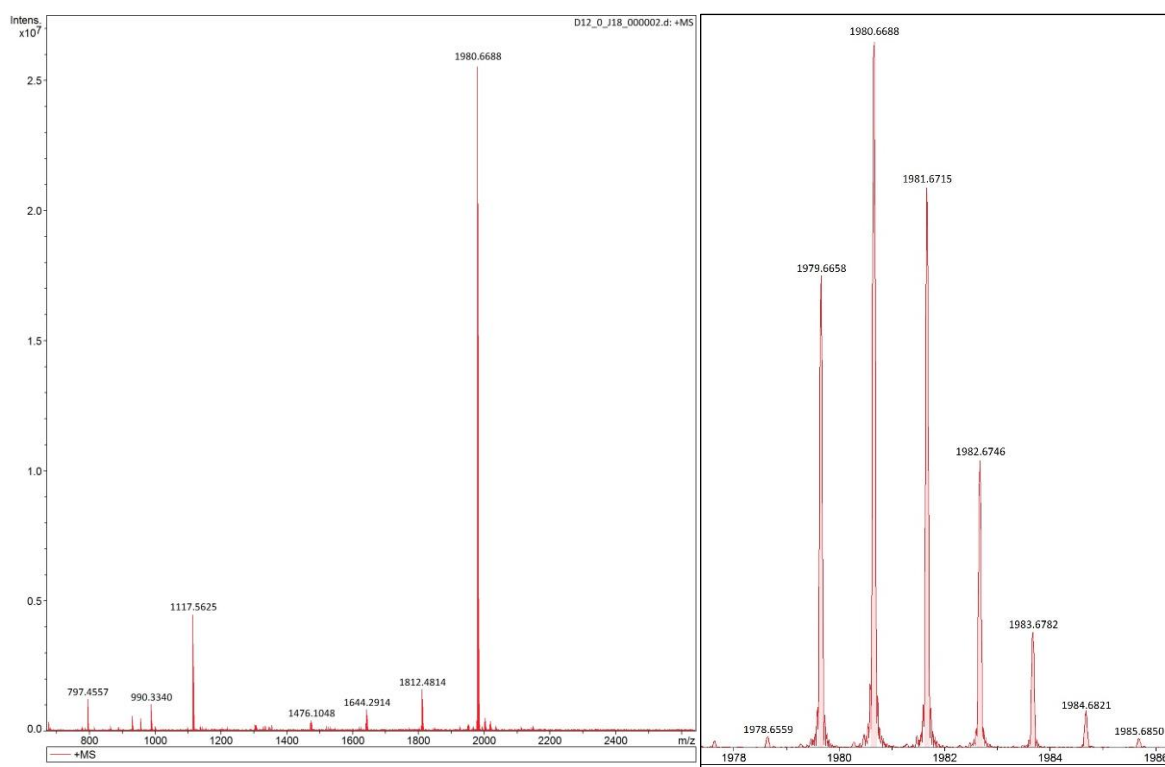


Figure S24. HRMS of D12.

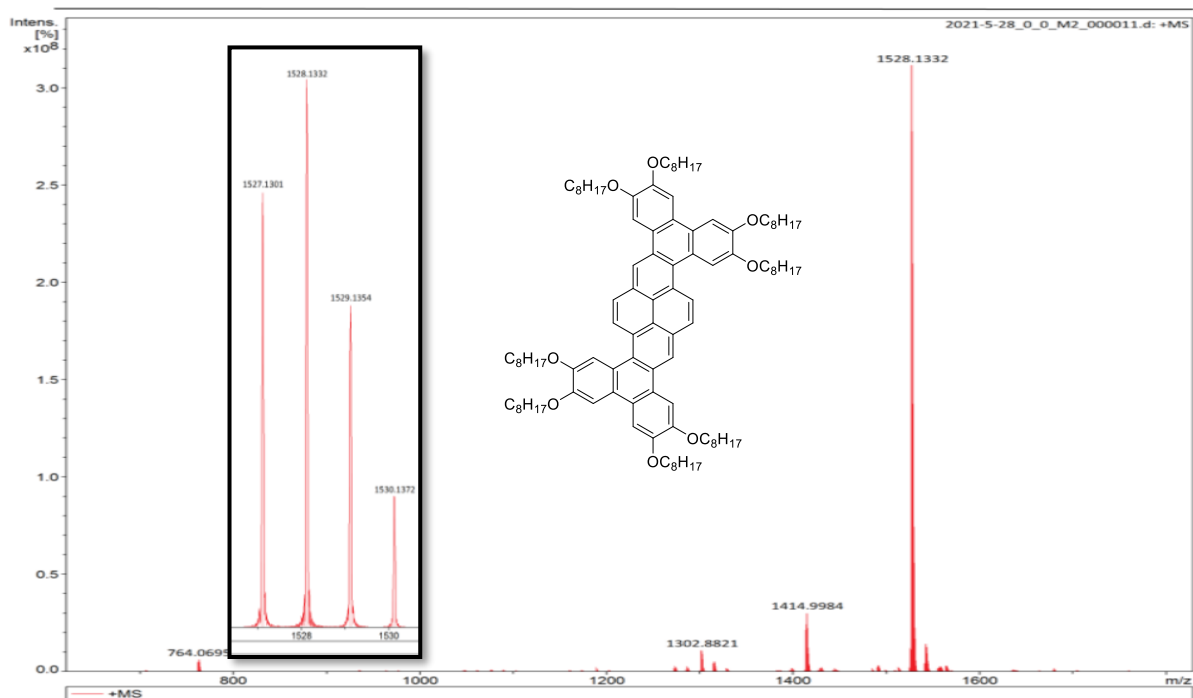


Figure S25. HRMS of DBP8.

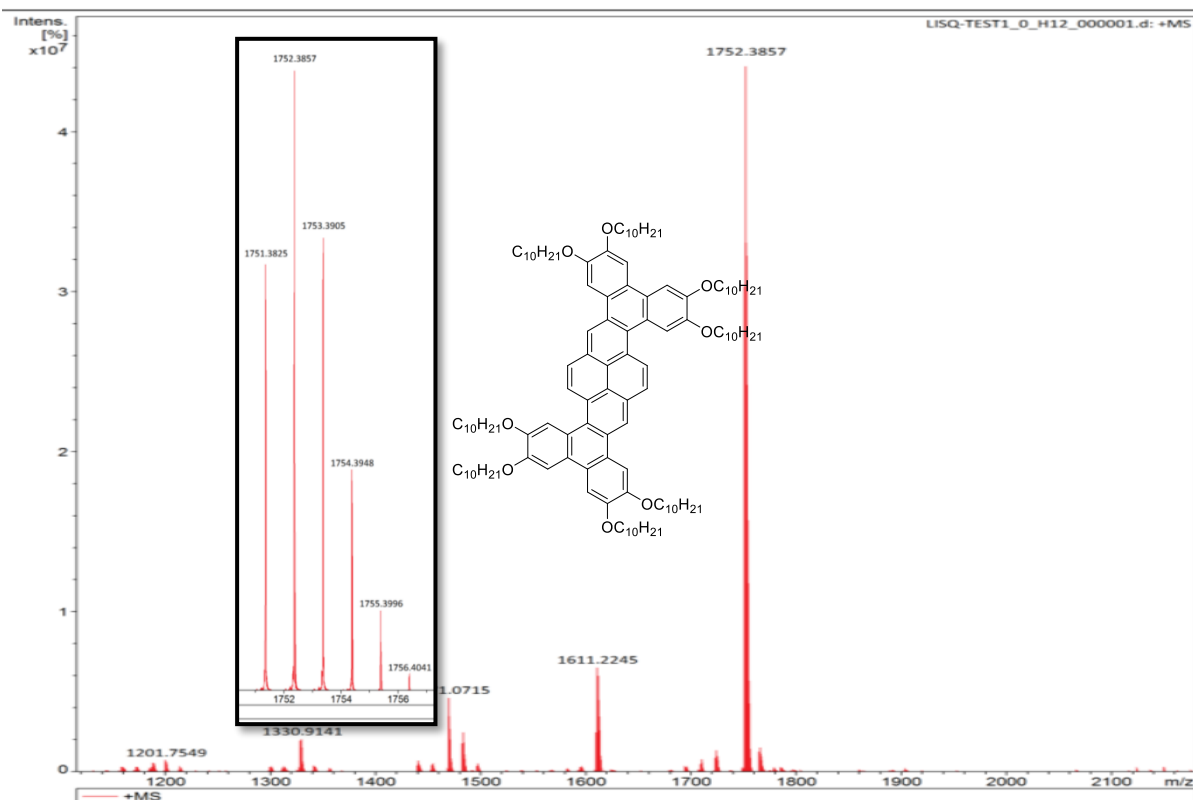


Figure S26. HRMS of DBP10.

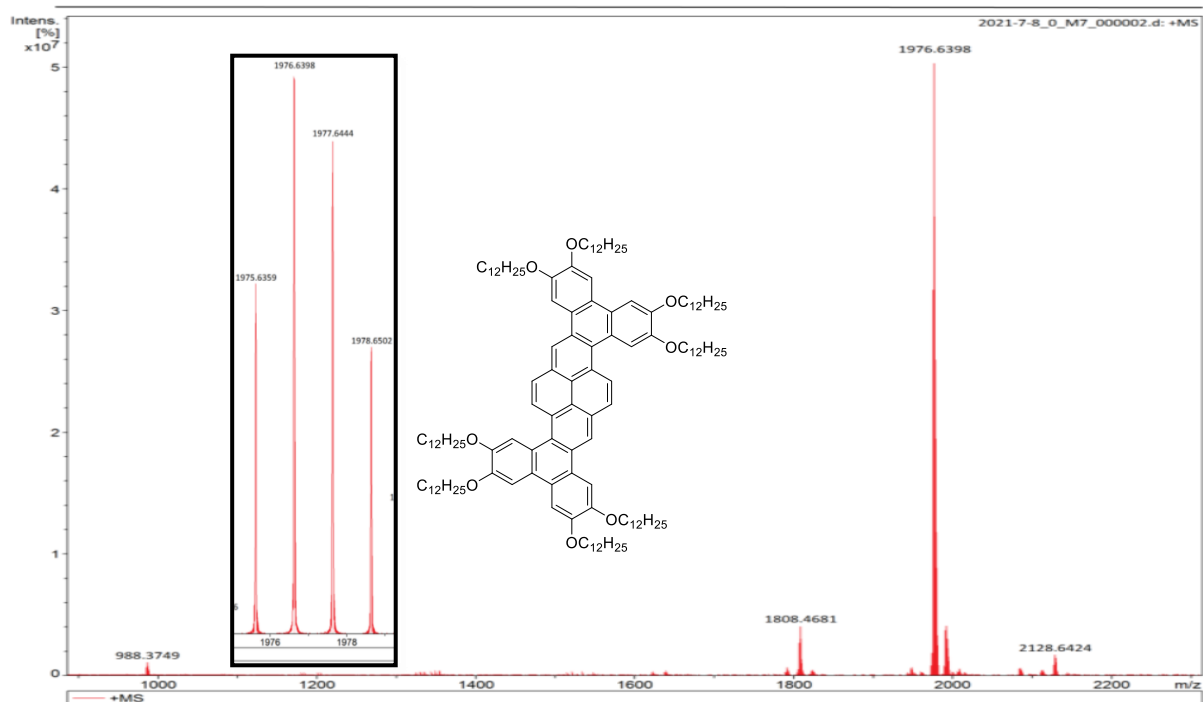


Figure S27. HRMS of DBP12.

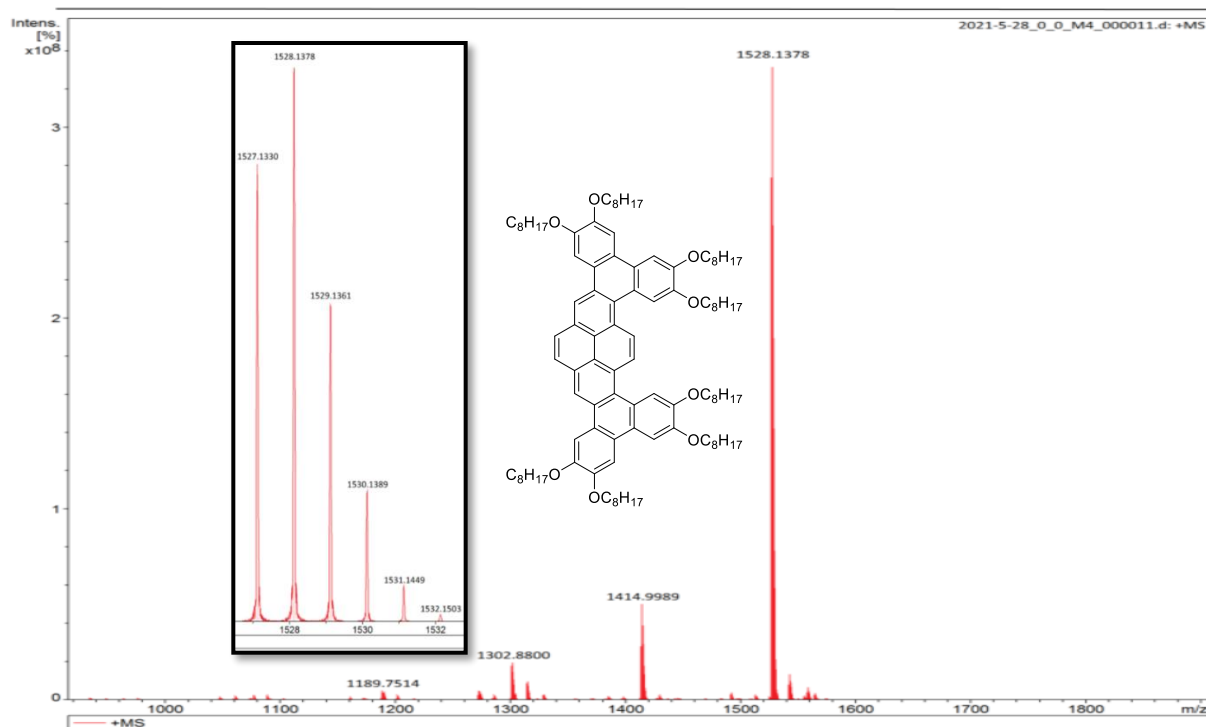


Figure S28. HRMS of BBP8.

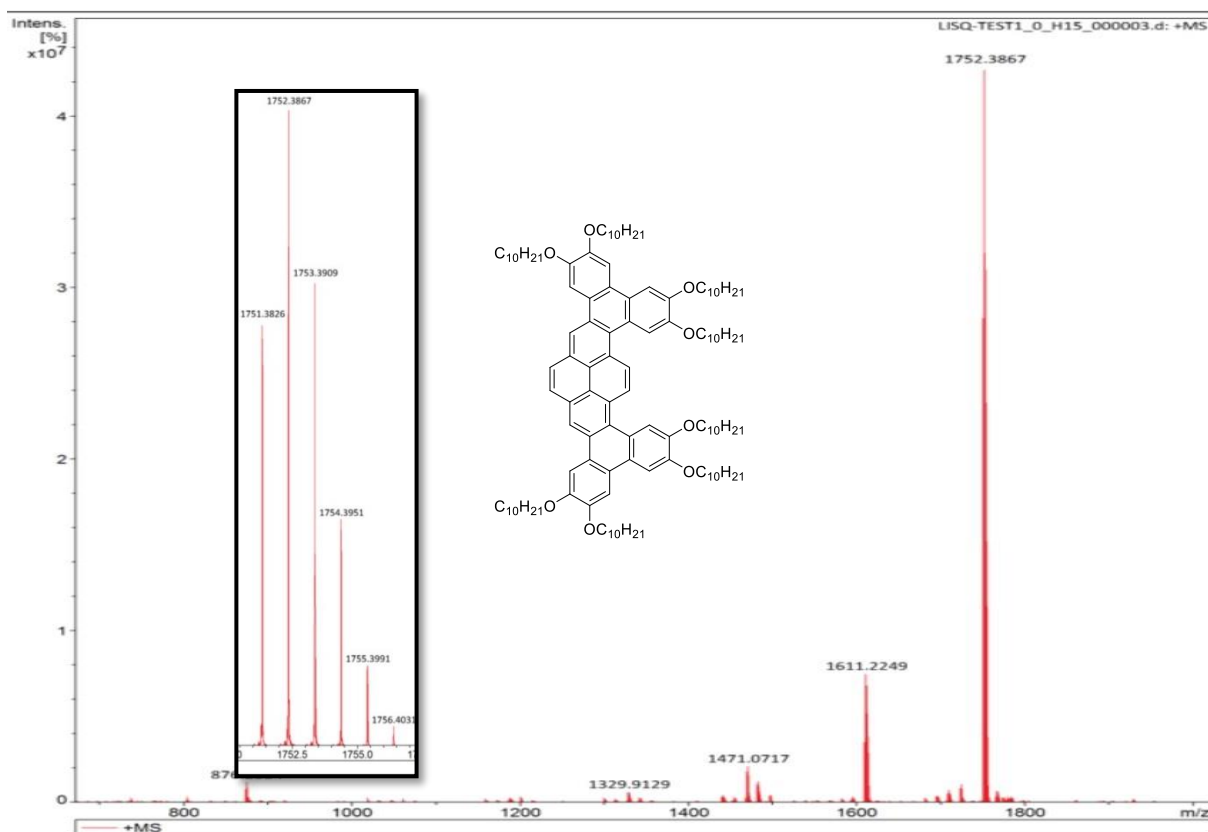


Figure S29. HRMS of BBP10.

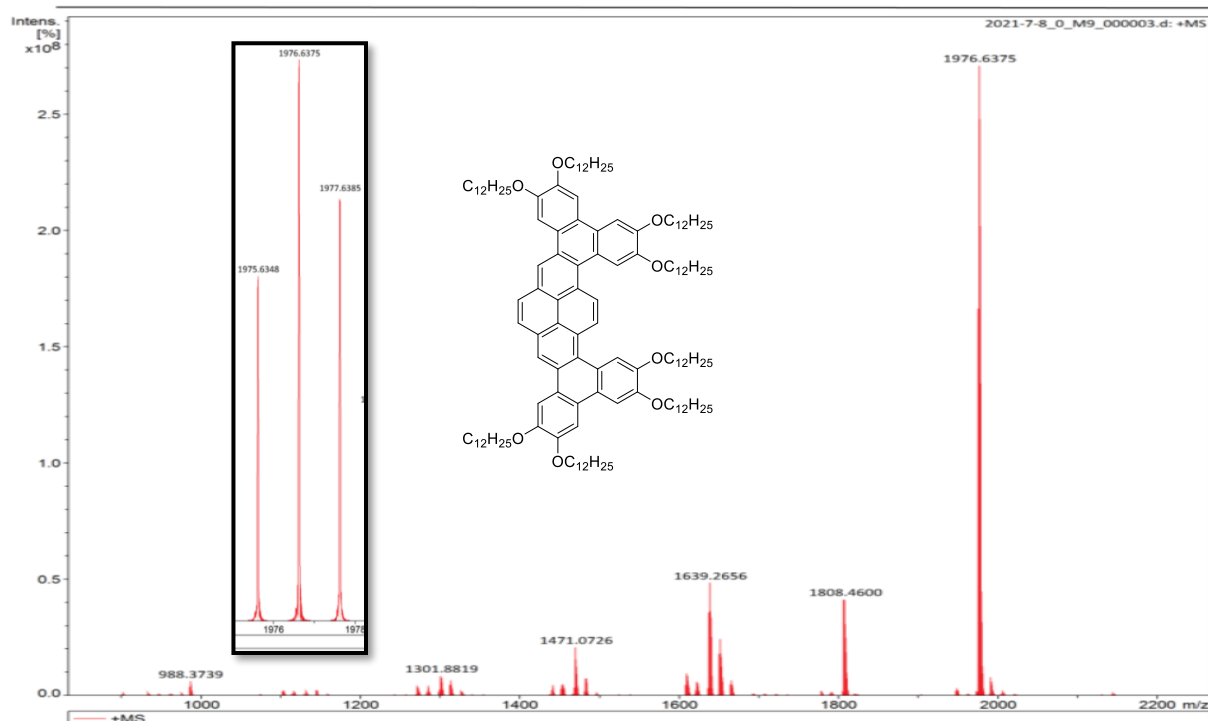


Figure S30. HRMS of BBP12.

5. TGA

Table S1. Temperatures of decomposition at 1%, 2% and 5% weight-loss for **BBP_n** and **DBP_n**.

Compd.	T _{dec} /°C(1% loss)	T _{dec} /°C(2% loss)	T _{dec} /°C(5% loss)
BBP8	363	377	394
BBP10	363	377	393
BBP12	363	378	395
DBP8	366	380	396
DBP10	364	378	394
DBP12	362	376	393

6. DSC

Table S2. Mesophases, transition temperatures and enthalpy changes for **DBP8/10/12** and **BBP8/10/12** (DSC heating/cooling rate is 10 °C/min).

Cpds	Mesophases, transition temperature and enthalpy changes	
	2nd heating / °C (ΔH, kJ·mol ⁻¹)	1st cooling / °C (ΔH, kJ·mol ⁻¹)
DBP8	Cr -15 (3.3) Cr' 123 (-6.0) Cr'' 130 (43.4) Col _{hex} 185 (2.0) I	I 181 (-1.7) Col _{hex} 104 (-25.9) Cr' 70 (-2.1) Cr
DBP10	Cr 12 (6.7) Cr' 97 (-7.5) Cr'' 127 (129.5) Col _{hex} 168 (5.3) I	I 167 (-4.2) Col _{hex} 100 (-28.6) Cr'' 66 (-2.1) Cr' 8 (-5.0) Cr
DBP12	Cr 31 (4.5) Cr' 98 (-7.6) Cr'' 119 (127.3) Col _{hex} 153 (3.9) I	I 150 (-3.0) Col _{hex} 99 (-26.6) Cr' 27 (-2.9) Cr
BBP8	Cr 60 (2.5) Cr' 67 (-4.1) Cr'' 82 (42.1) Col _{rec} 95 (1.5) Col _{hex} 275 (5.8) I	I 272 (-5.9) Col _{hex} 93 (-1.7) Col _{rec} 26 (-51.2) Cr
BBP10	Cr 61 (52.3) Col _{hex} 248 (5.1) I	I 246 (-6.1) Col _{hex} 35 (-56.7) Cr
BBP12	Cr 66 (92.8) Col _{hex} 235 (6.5) I	I 231 (-9.9) Col _{hex} 45 (-100.8) Cr

Abbreviations: Cr/Cr'/Cr''/Cr''': crystalline phases; Col_{hex}: columnar hexagonal phase; Col_{rec}: columnar rectangular phase; I: isotropic liquid.

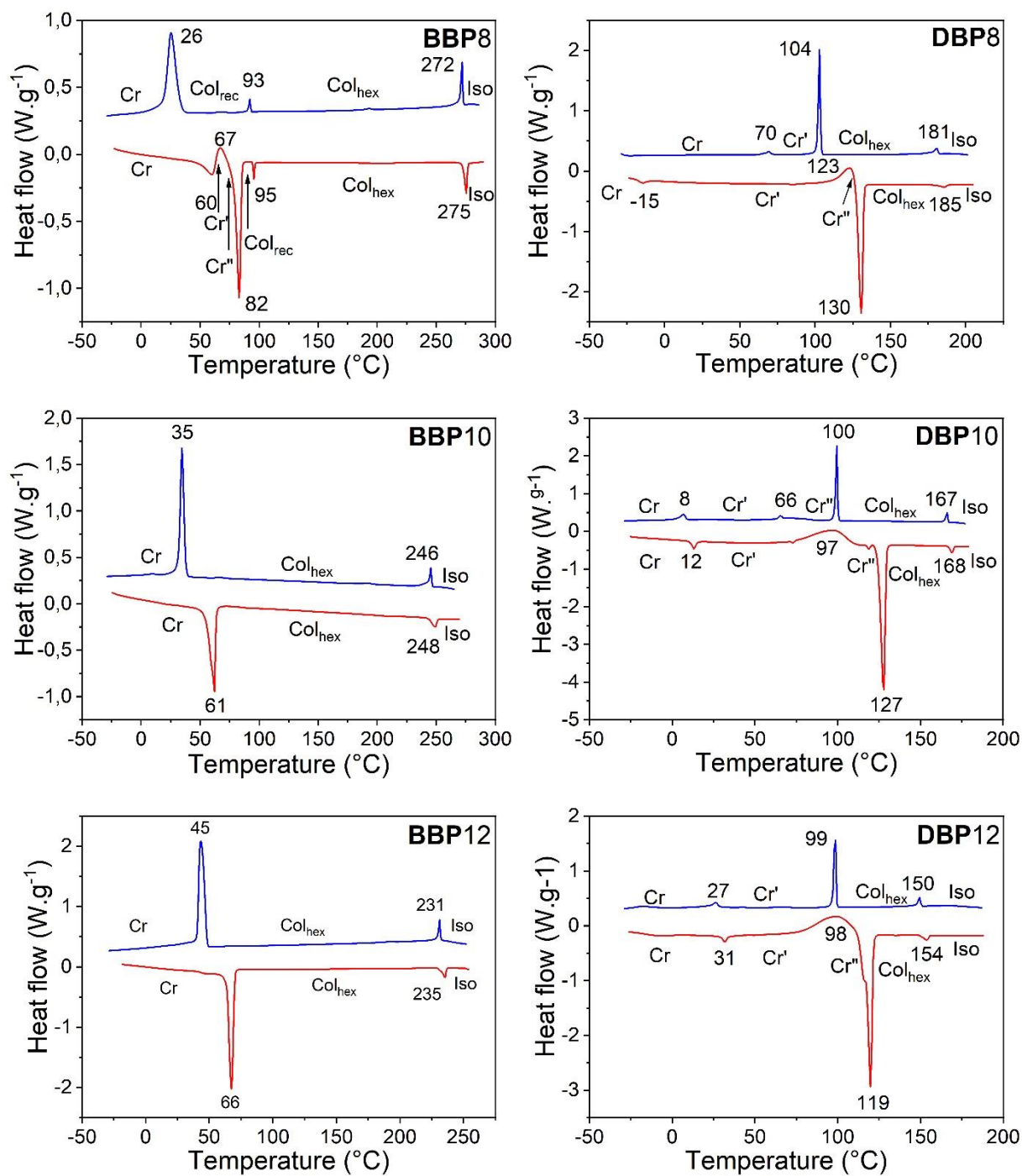
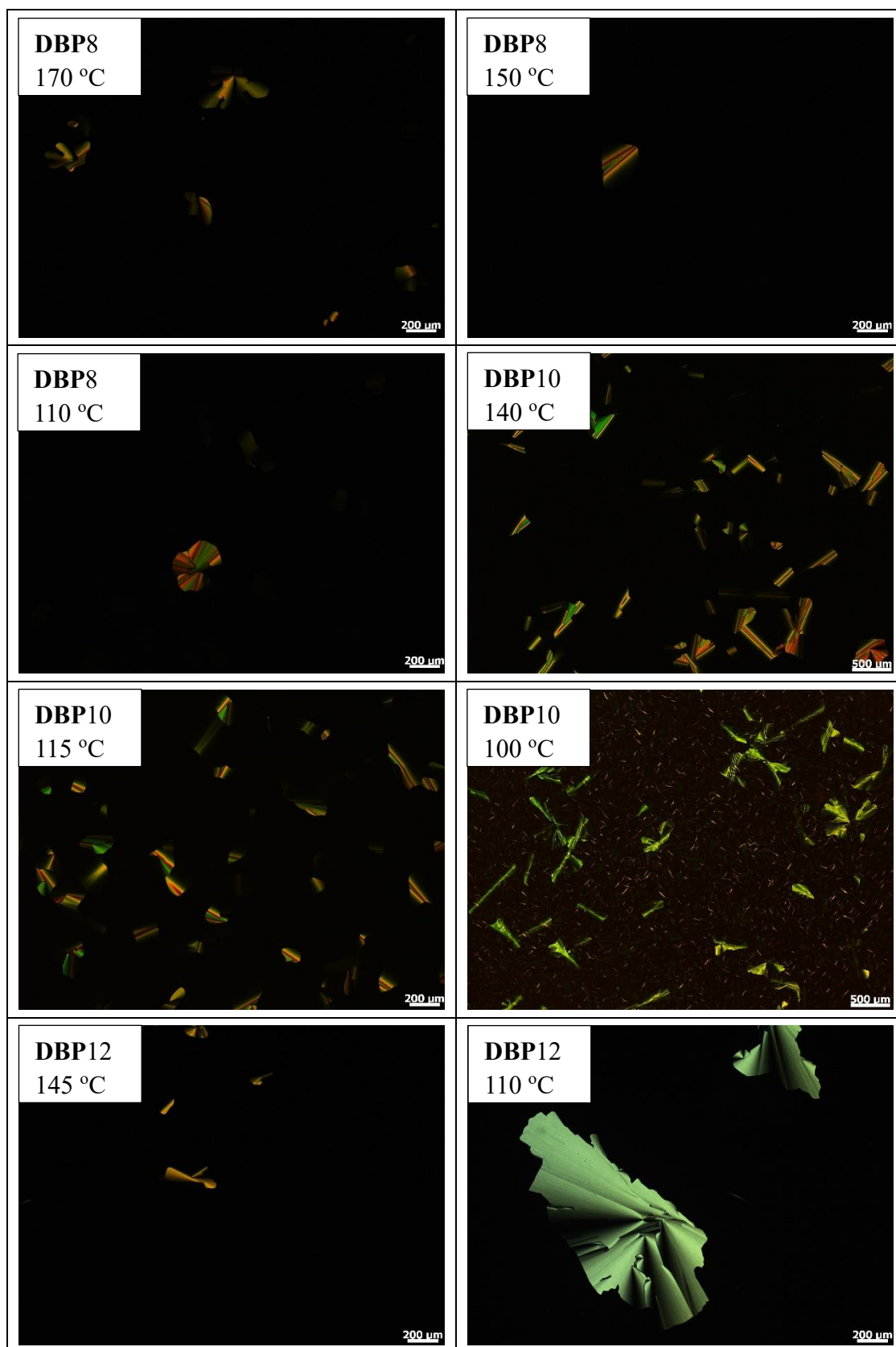
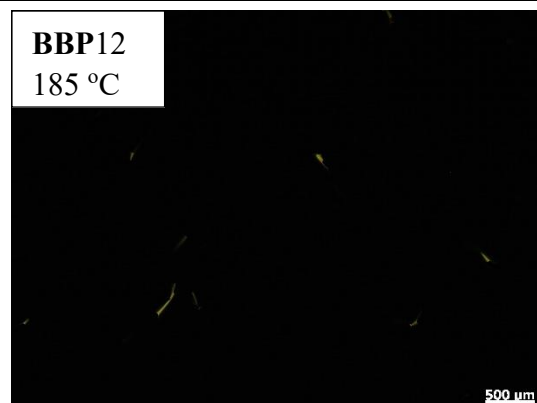
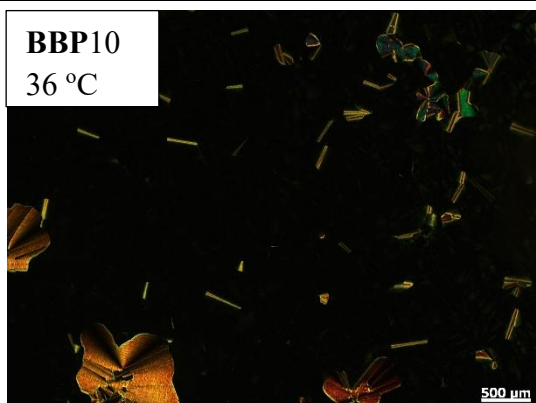
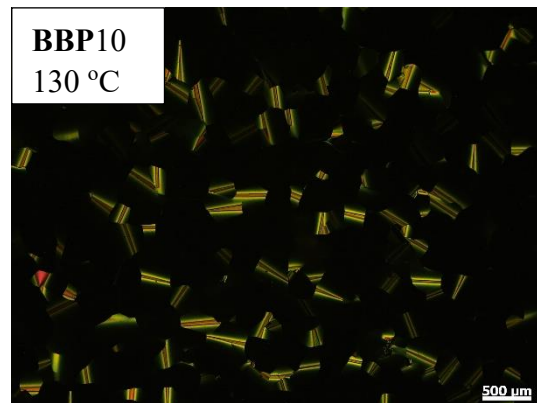
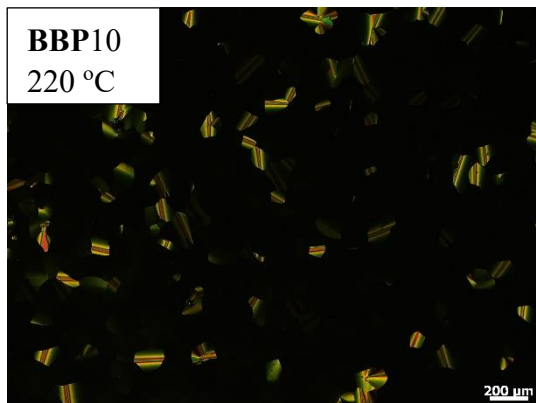
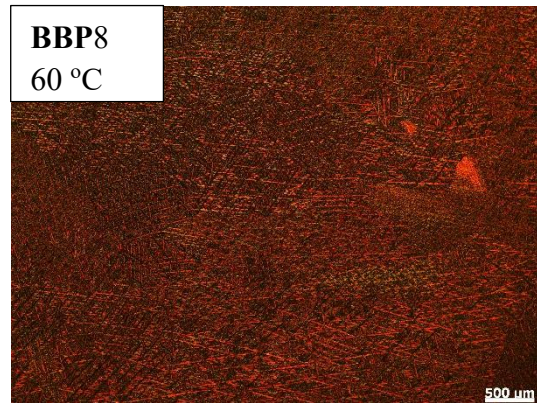
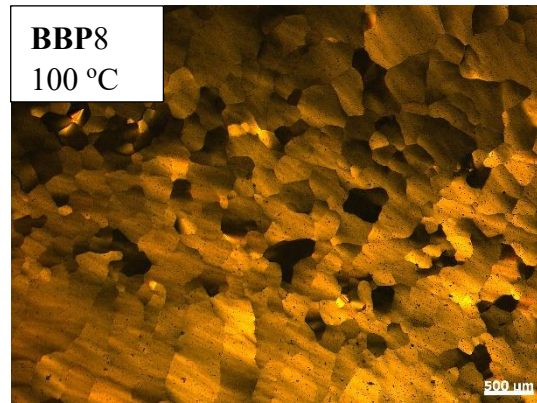
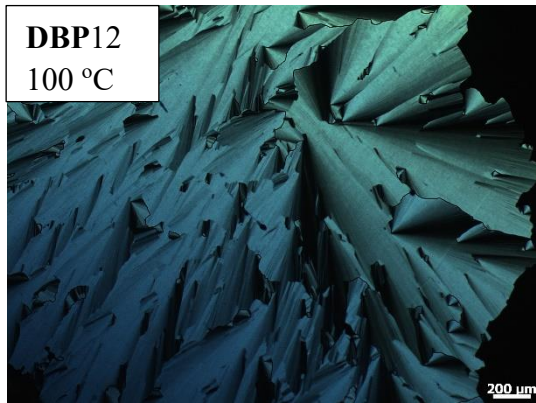


Figure S31. DSC traces of **BBP_n** and **DBP_n** at scanning rate of 10 °C/min (heating red, cooling in blue).

7. POM





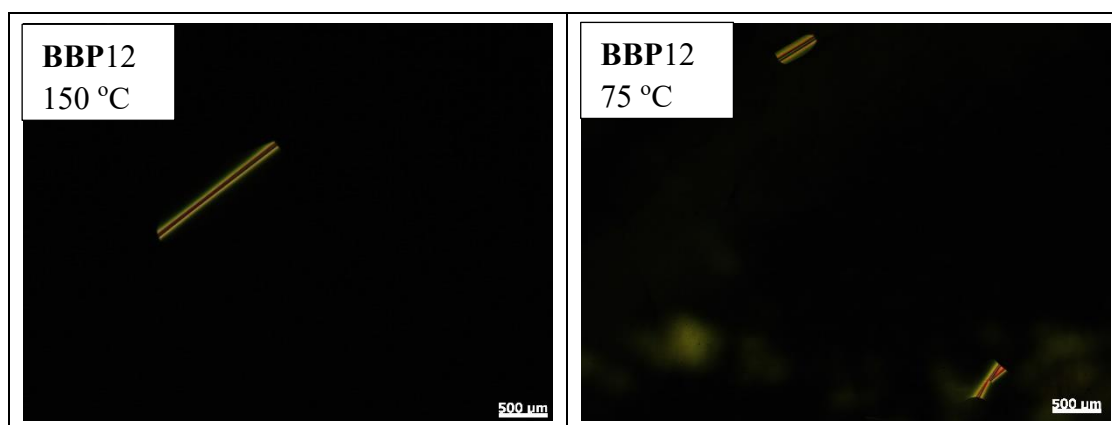


Figure S32. POM textures of **DBP n** and **BBP n** on cooling from the isotropic liquid.

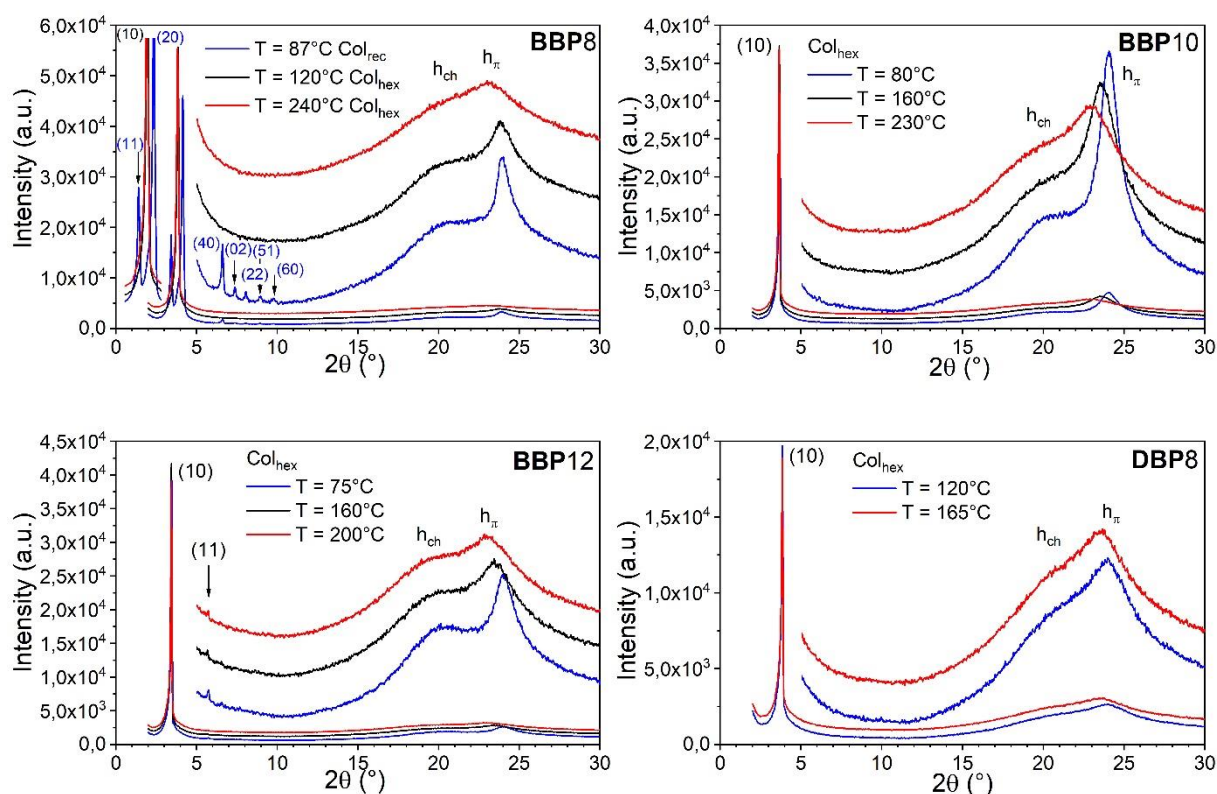
8. SWAXS

Table S3. Indexation and geometrical parameters of the columnar mesophases of **DBP n** and **BBP n** .

Compd.	$2\theta_{\text{exp}} (^{\circ})$	$d_{\text{exp}} (\text{\AA})$	$d_{\text{cal}} (\text{\AA})$	I (%)	hk	Lattice parameters
BBP8 (87°C)	3.282	26.90	-	S	11	$a = 53.80 \text{ \AA}$ $b = 24.05 \text{ \AA}$ $A = 1293.89 \text{ \AA}^2$
	4.020	21.96	-	VS	20	
	6.566	13.45	13.45	W	40	
	7.373	11.98	12.02	VW	02	
	8.045	10.98	10.98	VW	22	
	8.934	9.89	9.82	VW	51	
	9.776	9.04	8.97	VW	60	
	20.70	4.29	-	S	h_{ch}	
	23.94	3.71	-	VS	h_{π}	
BBP8 (120°C)	3.771	23.41	-	VS	10	$a = 27.03 \text{ \AA}$ $A = 632.82 \text{ \AA}^2$
	20.53	4.32	-	VW	h_{ch}	
	23.80	3.74	-	VS	h_{π}	
BBP8 (240°C)	3.744	23.58	-	VS	10	$a = 27.23 \text{ \AA}$ $A = 641.98 \text{ \AA}^2$
	20.42	4.34	-	VW	h_{ch}	
	23.15	3.84	-	VS	h_{π}	
BBP10 (80°C)	3.615	24.42	-	VS	10	$a = 28.20 \text{ \AA}$ $A = 688.60 \text{ \AA}^2$
	20.54	4.32	-	VW	h_{ch}	
	24.04	3.70	-	VS	h_{π}	
BBP10 (160°C)	3.590	24.59	-	VS	10	$a = 28.39 \text{ \AA}$ $A = 698.22 \text{ \AA}^2$
	20.19	4.39	-	VW	h_{ch}	
	23.59	3.77	-	VS	h_{π}	
BBP10 (230°C)	3.585	24.62	-	VS	10	$a = 28.43 \text{ \AA}$ $A = 700.17 \text{ \AA}^2$
	19.69	4.51	-	VW	h_{ch}	
	22.98	3.87	-	VS	h_{π}	
BBP12 (75°C)	3.335	26.47	26.48	VS	10	$a = 30.56 \text{ \AA}$ $A = 809.04 \text{ \AA}^2$
	5.770	15.30	15.29	VW	11	
	20.11	4.41	-	VS	h_{ch}	
	23.94	3.71	-	VS	h_{π}	
BBP12 (160°C)	3.323	26.56	26.56	VS	10	$a = 30.67 \text{ \AA}$ $A = 814.56 \text{ \AA}^2$
	5.756	15.34	15.34	VW	11	
	20.29	4.37	-	VS	h_{ch}	
	23.48	3.78	-	VS	h_{π}	
BBP12 (200°C)	3.310	26.67	26.67	VS	10	$a = 30.79 \text{ \AA}$ $A = 821.32 \text{ \AA}^2$
	5.733	15.40	15.40	VW	11	
	19.57	4.53	-	VS	h_{ch}	
	22.91	3.88	-	VS	h_{π}	

DBP8 (120°C)	3.857	22.89	-	VS	10	a = 26.43 Å A = 604.93 Å ²
	20.72	4.28	-	VW	h _{ch}	
	23.98	3.71	-	VS	h _π	
DBP8 (165°C)	3.851	22.92	-	VS	10	a = 26.47 Å A = 606.81 Å ²
	20.77	4.27	-	VW	h _{ch}	
	23.61	3.76	-	VS	h _π	
DBP10 (110°C)	3.604	24.49	-	VS	10	a = 28.28 Å A = 692.81 Å ²
	20.35	4.36	-	VW	h _{ch}	
	24.02	3.70	-	VS	h _π	
DBP10 (150°C)	3.570	24.06	-	VS	10	a = 28.55 Å A = 706.06 Å ²
	20.17	4.39	-	VW	h _{ch}	
	23.89	3.72	-	VS	h _π	
DBP12 (125°C)	3.354	26.31	26.31	VS	10	a = 30.38 Å A = 799.30 Å ²
	5.812	15.19	15.19	VW	11	
	20.56	4.32	-	VS	h _{ch}	
DBP12 (140°C)	23.87	3.72	-	VS	h _π	a = 30.67 Å A = 814.56 Å ²
	3.327	26.53	26.56	VS	10	
	5.754	15.35	15.33	VW	11	
	20.64	4.30	-	VS	h _{ch}	
	23.61	3.76	-	VS	h _π	

Annotation: $2\theta_{\text{exp}}$: measured diffraction angles corresponding to each peak; d_{exp} and d_{cal} : measured and calculated distance corresponding to each peak; hk : Miller indices of columnar lattice reflection; h_{ch} : average distance between alkyl chains; h_{π} : average distance of π - π stacking of molecules; a , b : columnar lattice parameters; A : lattice area.



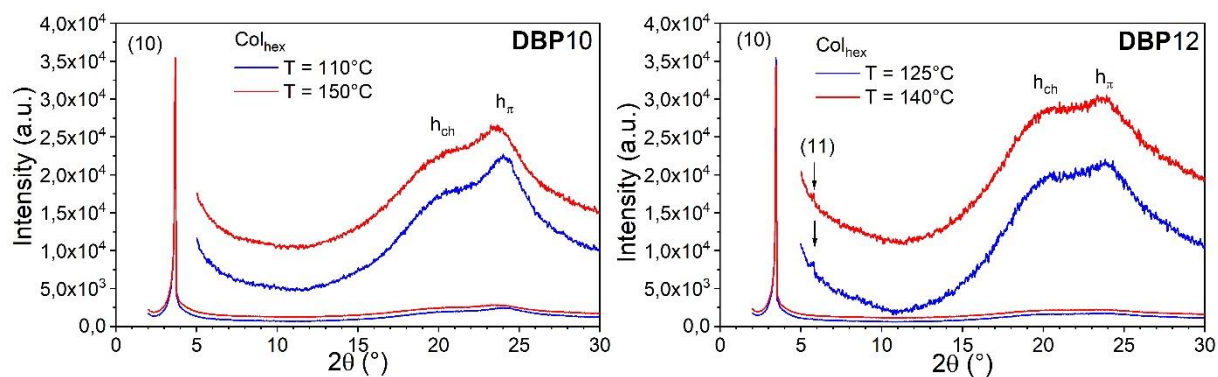


Figure S33. SAXS patterns of the mesophases of compounds **DBP_n** and **BBP_n** (recorded on cooling).

9. DFT Calculation

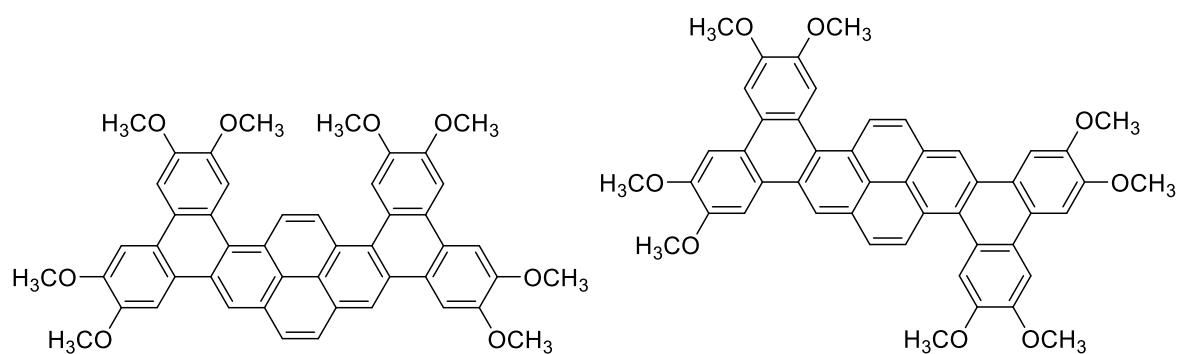


Figure S34. Molecular structures of model compounds **BBP1** and **DBP1**.

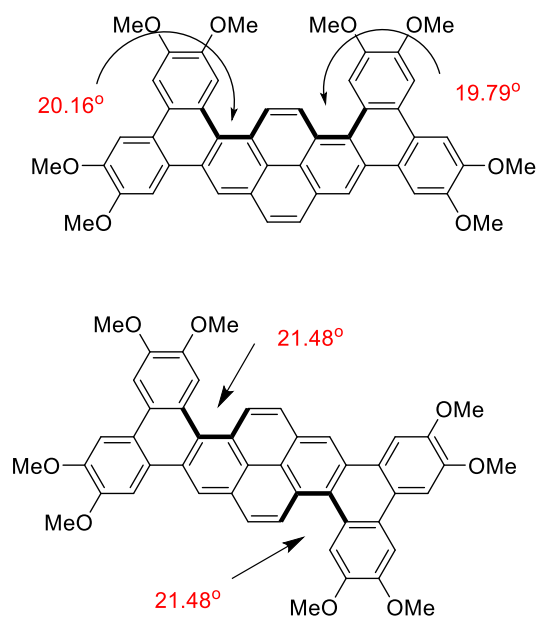


Figure S35. Dihedral angles of compounds **BBP1** and **DBP1**.

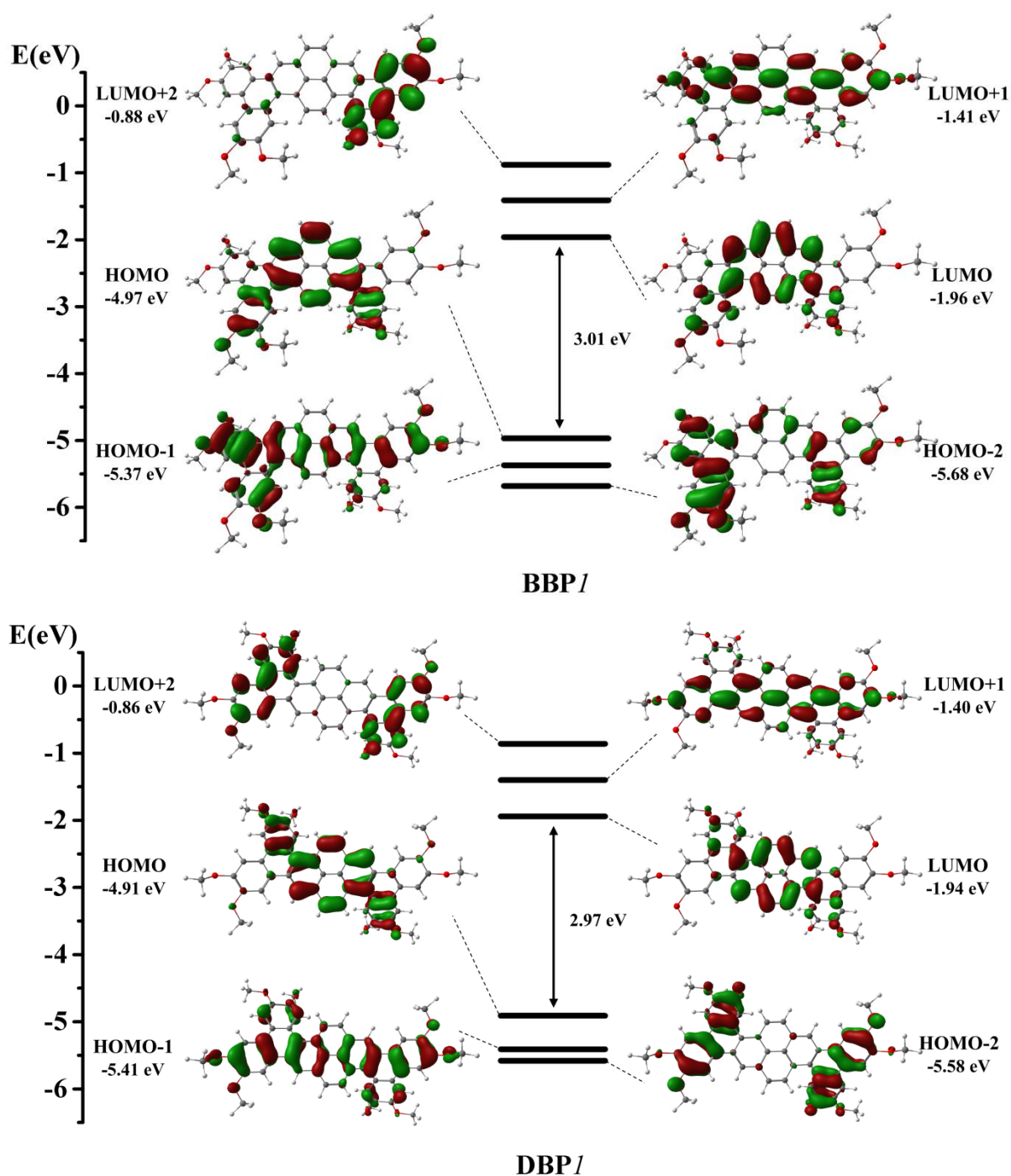


Figure S36. Partial molecular orbital diagram for **BBP1** and **DBP1** with some selected isodensity (Isovalues = 0.02) frontier molecular orbital mainly involved in the electronic transitions. All the DFT energy values are given in electronvolts (eV). The arrows are intended to highlight the HOMO-LUMO energy gaps.

Table S4. List of selected molecular orbital energies for **BBP1** and **DBP1** and their HOMO-LUMO energy gaps (ΔE).

Compd.	HOMO-2 (eV)	HOMO-1 (eV)	HOMO (eV)	ΔE (eV)	LUMO (eV)	LUMO+1 (eV)	LUMO+2 (eV)
BBP1	-5.68	-5.37	-4.97	3.01	-1.96	-1.41	-0.88

DBP1 -5.58 -5.41 -4.91 2.97 -1.94 -1.40 -0.86

Table S5. Selected calculated excitation energies (ΔE), oscillator strengths (f), main orbital components, and assignment for the **BBP1** and **DBP1** in the gas phase.^a

Compd.	$\lambda_{\text{exc}}/\text{nm}$	$\Delta E/\text{eV}$	f	Transitions (Percentage Contribution)
BBP1	455.2	2.72	0.6581	H→L(+69%)
	441.0	2.81	0.0039	H-1→L(+55%), H→L+1(+43%)
	390.8	3.17	0.0196	H-2→L(+46%), H-1→L(+45%)
	379.2	3.27	0.0087	H-3→L(+67%)
	367.7	3.37	0.1645	H-2→L(+50%), H→L+1(+39%)
	349.2	3.55	0.9634	H-1→L+1(+63%), H→L+3(+15%), H→L+2(+14%)
	343.3	3.61	0.0377	H→L+2(+63%)
	337.5	3.67	0.0757	H-4→L(+46%), H-2→L+1(+29%), H-1→L+3(+11%)
	336.7	3.68	0.2251	H→L+3(+62%), H→L+2(+13%)
	325.2	3.81	0.2052	H-2→L+1(+50%), H→L+4(+26%), H-1→L+3(+11%)
	325.0	3.82	0.0249	H→L+4(+52%), H-4→L+0(+28%), H-3→L+1(+19%)
	323.1	3.84	0.0063	H-3→L+1(+54%), H-1→L+3(+17%), H→L+2(+16%)
	319.1	3.89	0.0035	H→L+5(+50%), H→L+6(+22%), H-5→L(+15%)
	308.0	4.03	0.0299	H-5→L(+48%), H-1→L+3(+40%), H-1→L+2(+18%)
	304.6	4.07	0.0940	H→L+6(+52%), H-1→L+2(+29%), H-2→L+1(+24%)
	297.7	4.16	0.1027	H-1→L+2(+39%), H→L+5(+18%), H-2→L+1(+16%)
	295.9	4.19	0.1444	H-1→L+4(+36%), H→L+4(+19%), H-4→L+1(+15%)
	293.5	4.22	0.0490	H-1→L+4(+46%), H-1→L+5(+27%), H-5→L(+19%)
	289.2	4.29	0.0696	H-4→L+1(+40%), H-5→L(+14%)
	287.6	4.31	0.0044	H-9→L(+42%), H-8→L(+32%), H-7→L(+13%)
	285.7	4.34	0.0019	H-6→L(+49%), H-9→L(+30%), H-8→L(+19%)
	284.2	4.36	0.0660	H-2→L+2(+41%), H-4→L+1(+30%), H-2→L+3(+22%)
	280.6	4.42	0.1374	H-2→L+2(+37%), H-7→L(+36%)
	279.2	4.44	0.1009	H-7→L(+40%), H-1→L+5(+21%), H-1→L+6(+17%)
	278.2	4.46	0.1852	H-2→L+3(+32%), H-7→L(+30%), H-3→L+2(+27%)
	275.1	4.51	0.0273	H-3→L+3(+39%), H-2→L+4(+30%), H-3→L+2(+23%)
	274.6	4.52	0.1989	H-8→L(+36%), H-2→L+3(+18%), H-2→L+4(+13%)
	271.8	4.56	0.0927	H-1→L+6(+50%), H-3→L+2(+22%), H-4→L+1(+18%)
	271.4	4.57	0.0107	H-1→L+6(+28%), H-3→L+3(+25%), H-2→L+2(+21%)
	269.2	4.61	0.1048	H-5→L+1(+34%), H-2→L+3(+25%), H-3→L+3(+21%)
	267.5	4.63	0.0378	H-2→L+4(+37%), H→L+7(+29%), H-5→L+1(+21%)
	265.3	4.67	0.1153	H-3→L+4(+43%), H-2→L+3(+21%), H-1→L+6(+17%)
	264.6	4.69	0.2382	H-2→L+5(+44%), H-3→L+4(+28%), H-2→L+3(+19%)
	263.0	4.71	0.2071	H-3→L+5(+51%), H-5→L+1(+28%), H-2→L+2(+14%)
	262.2	4.73	0.0699	H-10→L(+57%), H-2→L+5(+19%), H-6→L+1(+19%)
	258.7	4.79	0.0986	H→L+7(+50%), H-4→L+2(+16%), H-3→L+3(+14%)
	254.1	4.88	0.0261	H-4→L+2(+44%), H-6→L+1(+35%), H-1→L+5(+12%)

	252.9	4.90	0.0762	H-4→L+3(+39%), H-4→L+2(+22%)
	251.9	4.92	0.0381	H-2→L+6(+40%), H→L+8(+29%), H-10→L(+14%)
	250.8	4.94	0.0582	H-4→L+3(+40%), H-2→L+6(+29%), H-6→L+1(+27%)
	250.1	4.96	0.0107	H→L+8(+44%), H-11→L(+31%), H-6→L+1(+11%)
	249.2	4.97	0.0606	H-3→L+6(+49%), H-4→L+2(+17%), H-8→L+1(+11%)
	247.7	5.01	0.0117	H-9→L+1(+48%), H-7→L+1(+21%), H-8→L+1(+18%)
	246.6	5.03	0.0260	H-8→L+1(+34%), H-3→L+6(+13%), H-6→L+2(+13%)
	245.0	5.06	0.0227	H-8→L+1(+39%), H-4→L+4(+28%), H-7→L+1(+24%)
	243.8	5.09	0.0192	H-4→L+4(+50%), H-5→L+3(+16%), H→L+8(+14%)
	243.1	5.10	0.0025	H-11→L(+35%), H-4→L+5(+12%)
	242.1	5.12	0.0453	H-1→L+7(+43%), H-11→L(+32%), H-5→L+3(+18%)
	241.1	5.14	0.0340	H-5→L+2(+45%), H-4→L+5(+21%), H-8→L+1(+17%)
	238.3	5.20	0.0549	H-4→L+5(+53%), H-13→L+0(+27%), H-5→L+3(+11%)
DBP1	462.1	2.68	0.5798	H→L(+69%), H-1→L+1(+12%)
	439.5	2.82	0.0014	H-1→L(+50%)
	393.2	3.15	0.0004	H-2→L(+70%)
	378.2	3.28	0.6872	H-1→L(+48%), H→L+1(+47%), H-3→L(+16%)
	357.1	3.47	0.0000	H-4→L(+54%), H→L+4(+31%)
	351.9	3.52	0.2981	H-3→L(+52%), H-1→L+1(+27%)
	346.5	3.58	0.0083	H→L+2(+65%)
	341.8	3.63	0.4925	H-1→L+1(+50%)
	336.9	3.68	0.4815	H→L+3(+56%), H-1→L+1(+37%), H-3→L(+18%)
	332.9	3.72	0.0004	H-2→L+1(+55%), H→L+4(+24%), H→L+2(+19%)
	328.6	3.77	0.0114	H→L+4(+51%), H-1→L+2(+22%), H→L+6(+15%)
	316.4	3.92	0.0029	H→L+5(+62%), H-1→L+2(+11%)
	314.0	3.95	0.1723	H-3→L+1(+51%), H-2→L+4(+16%), H-4→L+2(+15%)
	305.9	4.05	0.0007	H→L+6(+59%), H-4→L+1(+21%)
	301.8	4.11	0.0016	H-5→L(+45%), H→L+6(+23%), H-2→L+3(+13%)
	299.5	4.14	0.0163	H-4→L+1(+47%), H-1→L+2(+32%), H-5→L(+30%)
	295.6	4.19	0.1113	H-1→L+3(+46%), H-3→L+1(+36%)
	293.5	4.22	0.0288	H-1→L+4(+38%), H-5→L(+22%), H-2→L+3(+18%)
	290.4	4.27	0.0154	H-8→L(+37%)
	287.3	4.32	0.0281	H-6→L(+42%), H-3→L+1(+21%), H-7→L(+18%)
	286.7	4.33	0.0097	H-8→L(+40%), H-1→L+4(+26%), H-1→L+5(+16%)
	281.9	4.40	0.5011	H-2→L+2(+51%), H-6→L(+26%), H-3→L+1(+17%)
	280.3	4.42	0.0030	H-1→L+5(+38%), H-2→L+3(+29%)
	278.6	4.45	0.0310	H-2→L+4(+38%), H-1→L+3(+24%), H-6→L(+22%)
	277.4	4.47	0.0761	H-9→L(+38%), H-2→L+3(+36%), H-8→L(+22%)
	276.8	4.48	0.1209	H-7→L(+48%), H-2→L+4(+33%), H-2→L+2(+21%)
	274.4	4.52	0.0532	H-9→L(+42%), H-8→L(+31%), H-1→L+5(+24%)
	269.1	4.61	0.0022	H-2→L+5(+62%), H→L+7(+17%)
	266.2	4.66	0.0001	H-1→L+6(+43%), H-8→L+1(+21%)
	265.9	4.66	0.0025	H-3→L+2(+36%)
	265.5	4.67	0.0805	H→L+7(+41%), H-4→L+2(+38%), H-10→L(+23%)

	264.0	4.70	0.0659	H-3→L+3(+44%), H-4→L+2(+12%)
	262.0	4.73	0.0561	H-3→L+2(+46%), H-1→L+6(+32%), H-4→L+3(+22%)
	259.6	4.78	0.0848	H-3→L+3(+38%), H-10→L(+34%), H-6→L+1(+34%)
	257.7	4.81	0.0246	H-6→L+1(+34%), H-4→L+2(+34%), H-4→L+4(+28%)
	257.1	4.82	0.0883	H-5→L+1(+53%), H-3→L+2(+32%), H-1→L+5(+18%)
	255.2	4.86	0.2925	H-10→L(+37%), H-4→L+5(+17%), H-4→L+2(+14%)
	254.8	4.87	0.0143	H-3→L+4(+48%), H-3→L+5(+11%)
	253.1	4.90	0.3586	H-4→L+4(+47%), H-3→L+3(+16%), H-4→L+5(+15%)
	251.1	4.94	0.0466	H-2→L+6(+59%), H-7→L+1(+18%), H-4→L+2(+15%)
	250.4	4.95	0.0382	H-3→L+5(+51%), H-8→L+1(+23%), H→L+9(+15%)
	249.2	4.98	0.0068	H-8→L+1(+49%), H-11→L(+30%), H-3→L+4(+22%)
	249.0	4.98	0.0608	H-7→L+1(+51%)
	247.5	5.01	0.3177	H→L+8(+50%), H-10→L(+29%), H-4→L+4(+18%)
	246.3	5.03	0.0017	H-9→L+1(+37%), H-8→L+1(+27%), H→L+9(+27%)
	246.0	5.04	0.0004	H-9→L+1(+50%), H-11→L(+28%), H-3→L+5(+20%)
	244.8	5.06	0.0725	H-4→L+5(+47%), H-7→L+1(+33%), H-6→L+1(+14%)
	239.5	5.18	0.0139	H-1→L+7(+55%), H-5→L+2(+28%), H-4→L+6(+10%)
	238.5	5.20	0.0003	H-12→L(+58%), H-2→L+7(+12%)
	238.1	5.21	0.0006	H-12→L(+35%), H→L+9(+31%), H-11→L(+27%)
^a H = HOMO, L = LUMO, H-n = HOMO-n and L+n = LUMO+n.				