

Supporting Information

Complementary Semiconducting Polymer Blends: the Influence of Conjugation-Break Spacer Length in Matrix Polymers

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Materials and Synthesis

All reagents and starting materials were purchased from Sigma Aldrich and used without further purification unless specified.

1,2-di(thiophen-2-yl)ethane (ThC₂Th): 1.00 g of 2,2'-thenil (4.50 mmol), 1.68 mL of 65% hydrazine hydrate, 1.77 g of KOH (31.49 mmol, 7 equiv.) were dissolved in 10 mL of ethylene glycol and placed in a 100 mL Schlenk tube with a Dean-Stark trap. The solution was refluxed at 110 °C for 2 hours, before the temperature was raised to 195 °C and kept overnight. White crystals formed on the neck of the tube due to sublimation, which is purified over a silica gel column with hexanes as eluent. The produce was obtained as a colorless crystal. (0.71 g, 81%). ¹H NMR (300 MHz, CDCl₃): 7.07 (dd, 2H, *J*₁ = 4.8 Hz, *J*₂ = 0.9 Hz), 6.87 (dd, 2H, *J*₁ = 5.1 Hz, *J*₂ = 3.3 Hz), 6.76 (d, 2H, *J* = 3.3 Hz), 3.15 (s, 4H)

1,2-bis((5-trimethylstannyl)thiophen-2-yl)ethane (Me₃SnThC₂ThSnMe₃): 0.71 g of 1,2-bis(thiophen-2-yl)ethane (3.65 mmol) was dissolved in 25 mL of anhydrous tetrahydrofuran. The solution was cooled to -40 °C in a dry-ice-isopropanol bath and 3.7 mL of 2.5 M n-butyl lithium in hexanes (9.1 mmol, 2.5 equiv.) was added drop wise. The solution was kept in the bath for 20 minutes, followed by being heated at 60 °C for 2 hours for complete lithiation. The suspension was then cooled back to -40 °C, after which 9.1 mL of 1.0 M trimethyltin chloride in hexanes (9.1 mmol, 2.5 equiv.) was added slowly. The solution was allowed to warm back to room temperature slowly and stirred overnight. The mixture was diluted with ethyl acetate and washed with saturated ammonium chloride (3 × 50 mL) and dried over anhydrous MgSO₄. Active charcoal was applied for decoloration and the product was precipitated from methanol at -18 °C (209 mg, 11.0%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.02 (d, 2H, *J* = 2.7 Hz), 6.95 (d, 2H, *J* = 2.7 Hz), 3.24 (s, 4H), 0.35 (s, 18H). ¹³C NMR (400 MHz, CDCl₃), δ (ppm): 149.83, 135.30, 135.01, 125.79, 32.14, -8.38. MS (EI, M⁺) for C₁₆H₂₆S₂Sn₂: *calc'd* 521.9520 *found* 521.9531.

1,3-bis((5-trimethylstannyl)thiophen-2-yl)propane (Me₃SnThC₃ThSnMe₃): The synthesis has been previously reported (*Macromolecules* **2015**, 48, 2048-2053). MS (EI, M⁺) for C₁₇H₂₈S₂Sn₂: *calc'd* 535.9677 *found* 535.9675.

General method for monomer synthesis (m = 3 to 12)

Thiophene (97 mmol, 4 equiv.) was dissolved in 50 mL of anhydrous tetrahydrofuran in an oven dried flask. The solution was cooled to -40 °C with a dry-ice-isopropanol bath, followed by the addition of n-butyl lithium solution in hexanes (72.5 mmol, 3 equiv.) drop wise with a syringe. The solution was kept in the bath for 30 minutes before warmed back to room temperature and stirred for an additional 30 minutes. The solution was cooled back to -40 °C and the dibromoalkane (24 mmol) was added drop wise through a syringe. The mixture was slowly warmed up to room temperature by the removal of cooling bath and the mixture of left stirred overnight. Water was added and the mixture was extracted with hexanes (3 × 50 mL). The combined organic layers were dried over MgSO₄ and concentrated *in vacuo*. The crude product was purified by silica gel chromatography with hexane as the eluent. The obtained colorless oil was dissolved in anhydrous tetrahydrofuran and cooled to -40 °C. n-butyl lithium in hexanes (2.5 equiv.) was added drop wise with a syringe. The mixture was kept at -40 °C for 30 minutes, before warmed back to room temperature and stirred for an additional 30 minutes. The solution was then cooled back to -40 °C, followed by addition of

trimethyltin chloride in hexanes (2.5 equiv.). The mixture was slowly warmed up to room temperature by the removal of cooling bath and stirred overnight. Water was added and the mixture was extracted with ethyl acetate (3 × 50 mL). The organic phases were combined washed with brine and dried over anhydrous MgSO₄. Activated charcoal was applied for decoloration. After the solvent was removed in vacuo, the products were obtained as white solids or colorless liquids from cold ethanol with overall yields in the range of 9% to 51%.

1,4-bis((5-trimethylstannyl)thiophen-2-yl)butane (Me₃SnThC₄ThSnMe₃): Product obtained as a white crystal. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.03 (d, 2H, *J* = 3.2 Hz), 6.92 (d, 2H, *J* = 2.9 Hz), 2.92 (t, 4H), 1.80 (t, 4H), 0.36 (s, 18H). ¹³C NMR (400 MHz, CDCl₃), δ (ppm): 151.16, 134.96, 134.79, 125.49, 31.22, 29.56, -8.38. MS (EI, M⁺) for C₁₈H₃₀S₂Sn₂: *calc'd* 549.9833 *found* 549.9834.

1,5-bis((5-trimethylstannyl)thiophen-2-yl)pentane (Me₃SnThC₅ThSnMe₃): Product obtained as a colorless liquid. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.03 (d, 2H, *J* = 3.0 Hz), 6.91 (d, 2H, *J* = 3.0 Hz), 2.88 (t, 4H, *J* = 7.6 Hz), 1.74 (m, 4H), 1.51 (m, 2H), 0.21 (s, 18H). ¹³C NMR (400 MHz, CDCl₃), δ (ppm): 151.47, 134.94, 134.70, 125.39, 31.52, 29.73, 28.69, -8.38. MS (EI, M⁺) for C₁₉H₃₂S₂Sn₂: *calc'd* 563.9990 *found* 563.9968.

1,6-bis((5-trimethylstannyl)thiophen-2-yl)hexane (Me₃SnThC₆ThSnMe₃): Product obtained as a white crystal. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.02 (d, 2H, *J* = 3.0 Hz), 6.91 (d, 2H, *J* = 2.8 Hz), 2.87 (t, 4H, *J* = 7.6 Hz), 1.71 (m, 4H), 1.43 (m, 4H), 0.35 (s, 18H). ¹³C NMR (400 MHz, CDCl₃), δ (ppm): 151.60, 134.9, 134.65, 125.35, 31.64, 29.80, 28.84, -8.39. MS (EI, M⁺) for C₂₀H₃₄S₂Sn₂: *calc'd* 578.0146 *found* 578.0127.

1,7-bis((5-trimethylstannyl)thiophen-2-yl)heptane (Me₃SnThC₇ThSnMe₃): Product obtained as a colorless liquid. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.03 (d, 2H, *J* = 3.1 Hz), 6.91 (d, 2H, *J* = 3.0 Hz), 2.87 (t, 4H, *J* = 7.6 Hz), 1.70 (m, 4H), 1.39 (br, 6H), 0.355 (s, 18H). ¹³C NMR (400 MHz, CDCl₃), δ (ppm): 151.68, 134.93, 134.61, 125.33, 31.74, 29.82, 29.02, -8.39. MS (EI, M⁺) for C₂₁H₃₆S₂Sn₂: *calc'd* 592.0303 *found* 592.0279.

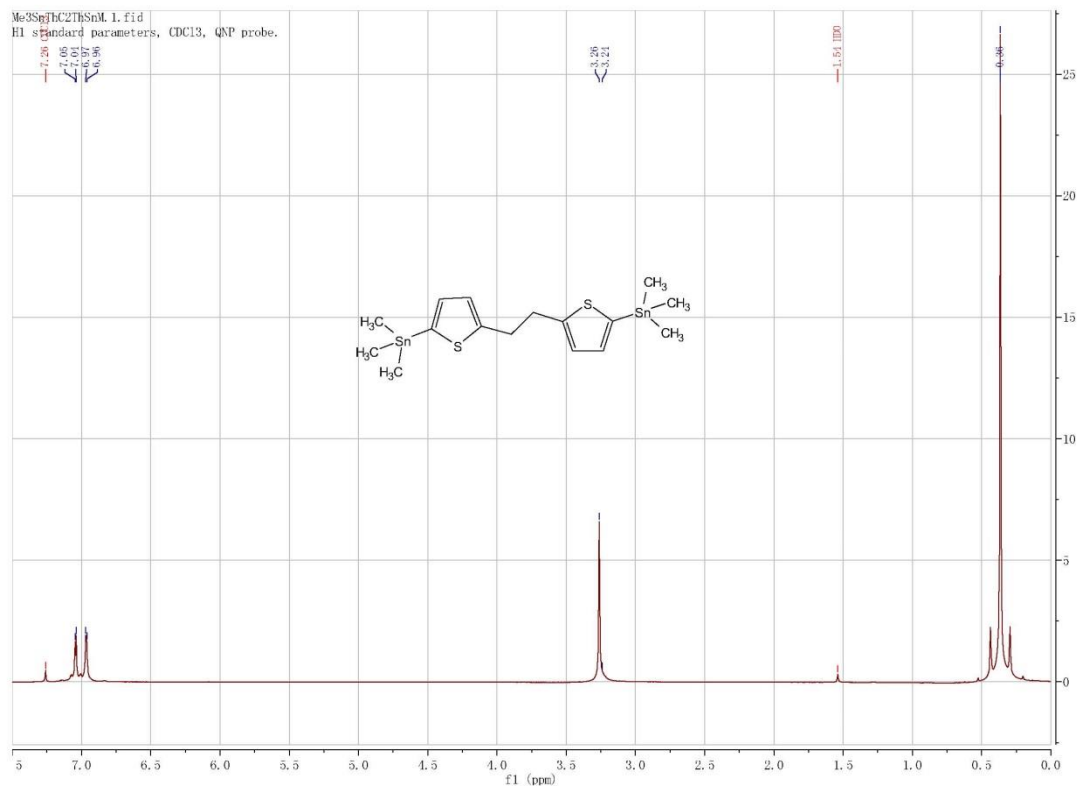
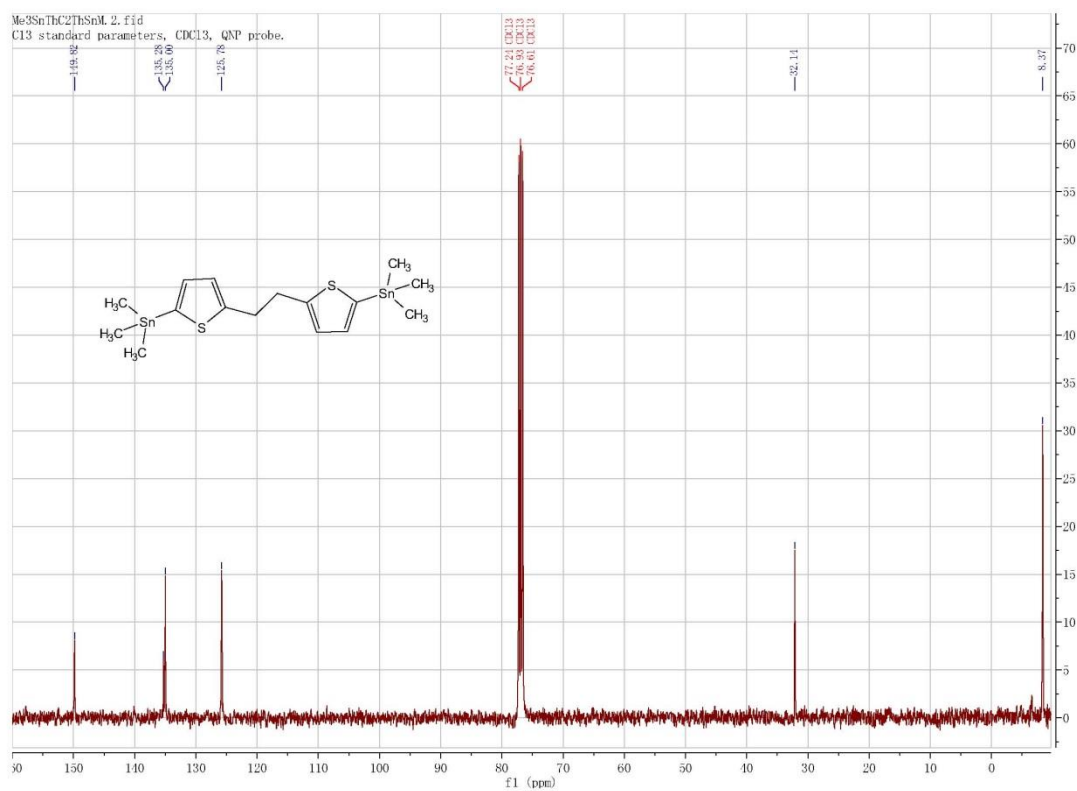
1,8-bis((5-trimethylstannyl)thiophen-2-yl)octane (Me₃SnThC₈ThSnMe₃): Product obtained as a white crystal. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.02 (d, 2H, *J* = 3.2 Hz), 6.90 (d, 2H, *J* = 3.1 Hz), 2.86 (t, 4H, *J* = 7.6 Hz), 1.68 (m, 4H), 1.34 (br, 8H), 0.35 (s, 18H). ¹³C NMR (400 MHz, CDCl₃), δ (ppm): 151.73, 134.92, 134.59, 125.30, 31.74, 29.83, 29.17, 29.10, -8.41. MS (EI, M⁺) for C₂₂H₃₈S₂Sn₂: *calc'd* 606.0459 *found* 606.0461.

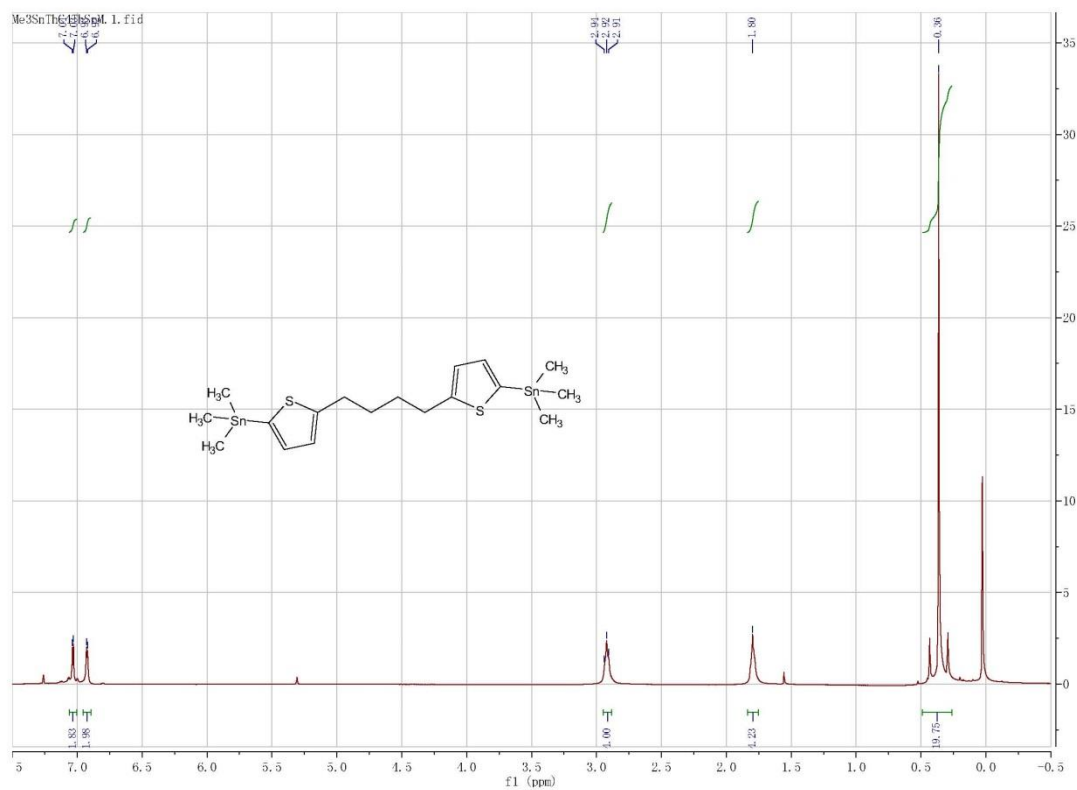
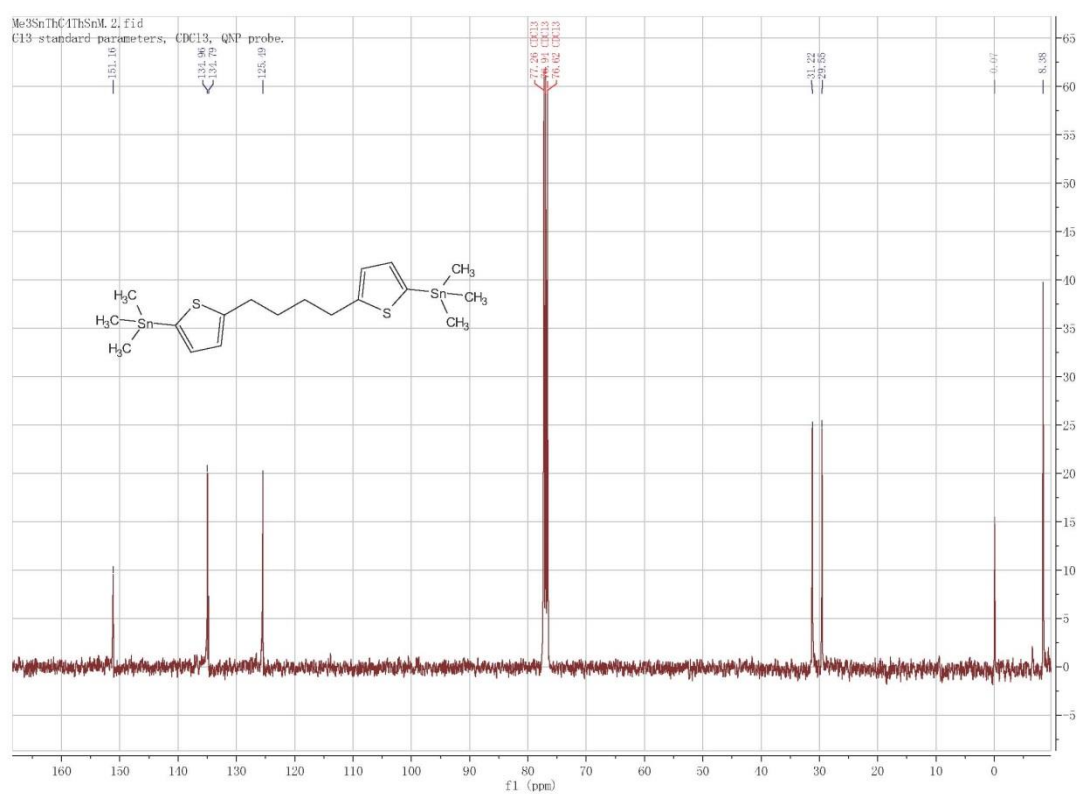
1,9-bis((5-trimethylstannyl)thiophen-2-yl)nonane (Me₃SnThC₉ThSnMe₃): Product obtained as a white wax, which easily melts when being handled. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.02 (d, 2H, *J* = 3.0 Hz), 6.90 (d, 2H, *J* = 3.1 Hz), 2.86 (t, 4H, *J* = 7.6 Hz), 1.68 (m, 4H), 1.31 (br, 10H), 0.34 (s, 18H). ¹³C NMR (400 MHz, CDCl₃), δ (ppm): 151.75, 134.91, 134.58, 125.29, 31.76, 29.83, 29.26, 29.12, -8.41. MS (EI, M⁺) for C₂₃H₄₀S₂Sn₂: *calc'd* 620.0616 *found* 606.0615.

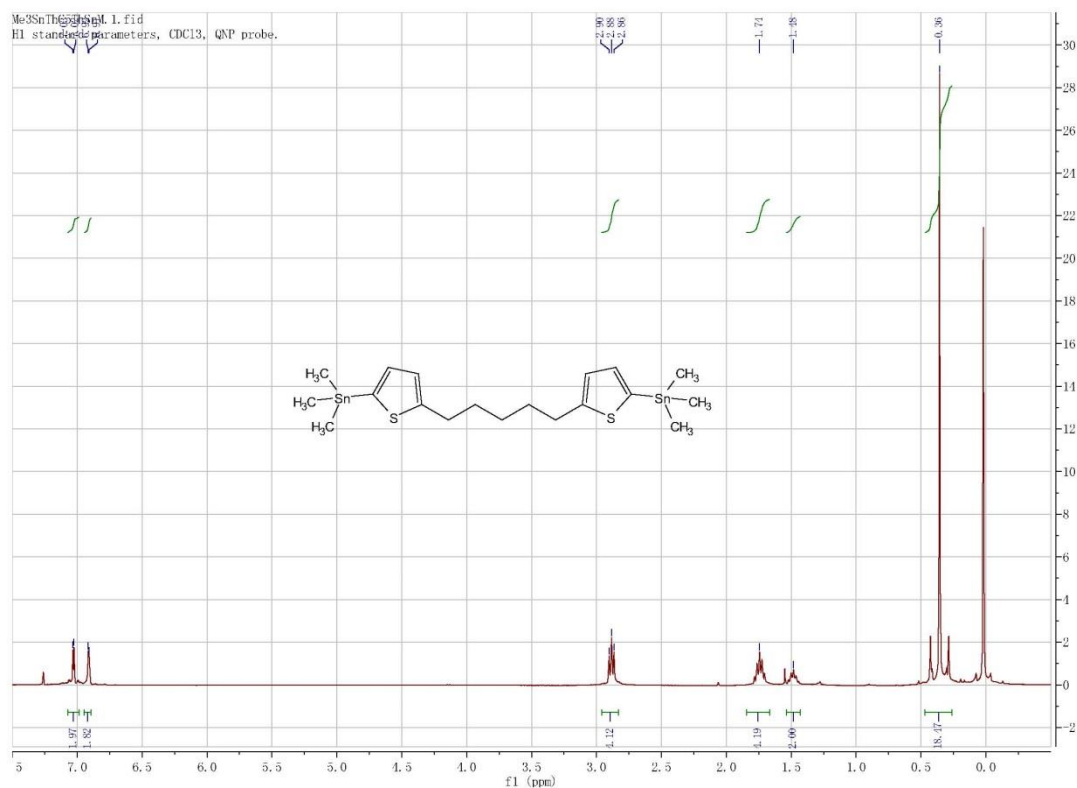
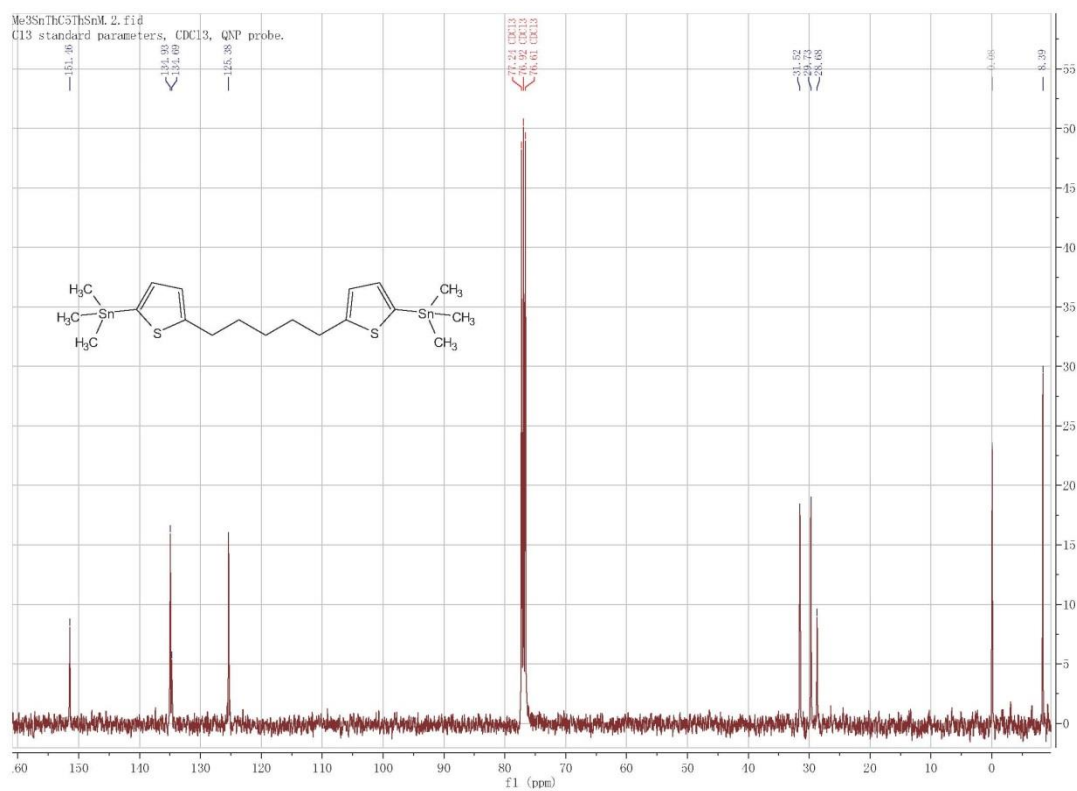
1,10-bis((5-trimethylstannyl)thiophen-2-yl)decane (Me₃SnThC₁₀ThSnMe₃): Product obtained as a white crystal. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.016 (d, 2H, *J* = 3.2 Hz), 6.901 (d, 2H, *J* = 3.1 Hz), 2.856 (t, 4H, *J* = 7.6 Hz), 1.682 (m, 4H), 1.288 (br, 12H), 0.342 (s, 18H). ¹³C NMR (400 MHz, CDCl₃), δ (ppm): 151.75, 134.91, 134.58, 125.29, 31.76, 29.83, 29.42, 29.27, 29.14, -8.42. MS (EI, M⁺) for C₂₄H₄₂S₂Sn₂: *calc'd* 634.0772 *found* 634.0766.

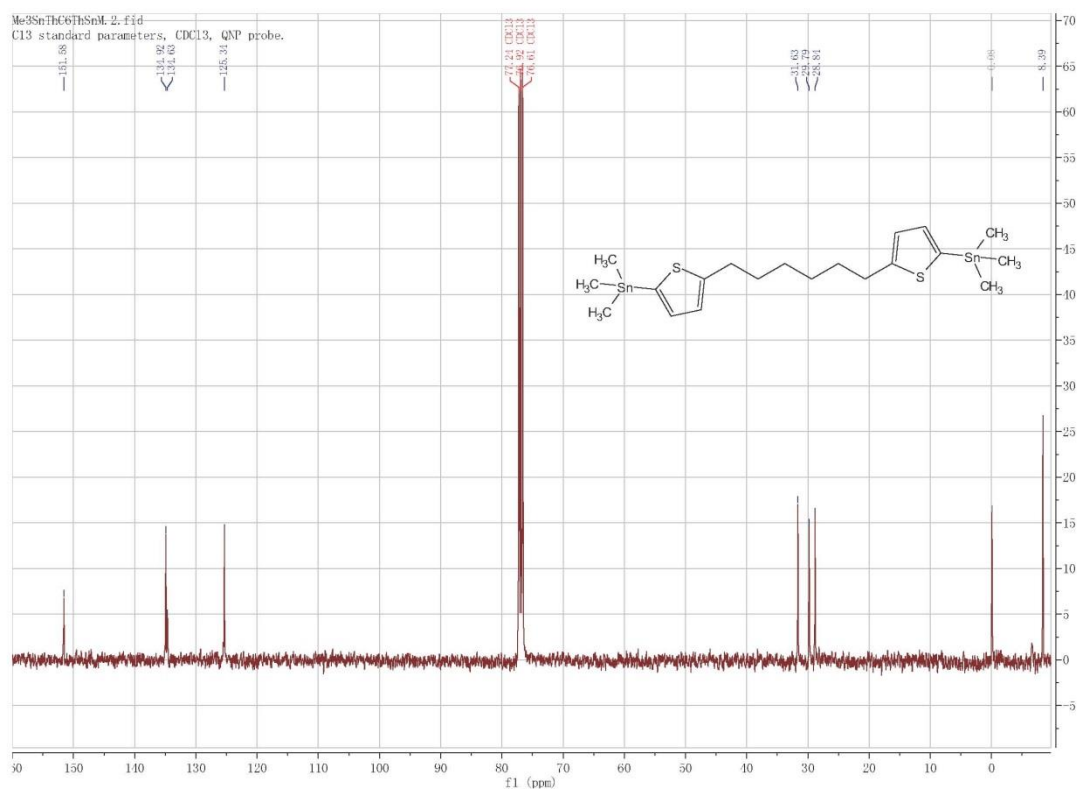
1,11- bis((5-trimethylstannyl)thiophen-2-yl)undecane (Me₃SnThC₁₁ThSnMe₃): Product obtained as a white crystal. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.01 (d, 2H, J = 3.0 Hz), 6.90(d, 2H, J = 3.1 Hz), 2.86 (t, 4H, J = 7.5 Hz), 1.68 (m, 4H), 1.28 (br, 14H), 0.34 (s, 18H). ¹³C NMR (400 MHz, CDCl₃), δ (ppm): 151.79, 134.92, 134.56, 125.28, 31.78, 29.84, 29.44, 29.29, 29.15, -8.42. MS (EI, M⁺) for C₂₅H₄₄S₂Sn₂: *calc* 'd 648.0929 *found* 648.0942.

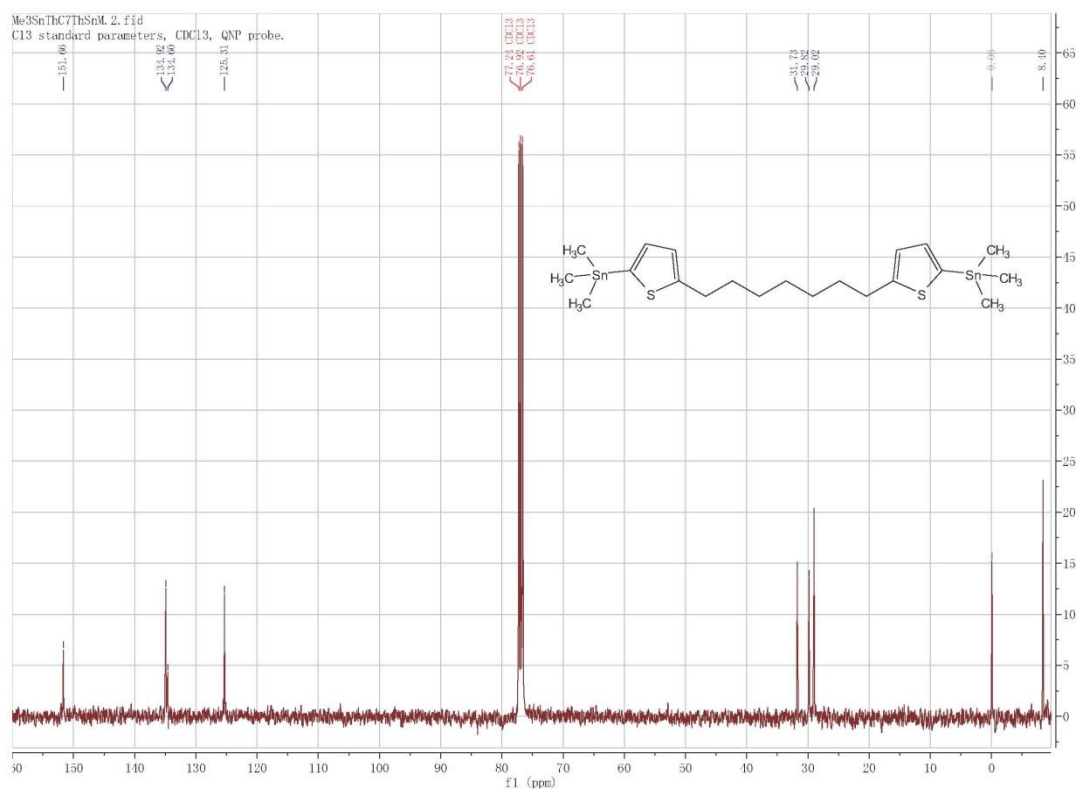
1,12- bis((5-trimethylstannyl)thiophen-2-yl)dodecane (Me₃SnThC₁₂ThSnMe₃): Product obtained as a white crystal. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 7.02 (d, 2H, J = 3.0 Hz), 6.90 (d, 2H, J = 3.3 Hz), 2.86 (t, 4H, J = 7.7 Hz), 1.68 (m, 4H), 1.26 (br, 16H), 0.34 (s, 18H). ¹³C NMR (400 MHz, CDCl₃), δ (ppm): 151.79, 134.91, 134.56, 125.27, 31.78, 29.85, 29.54, 29.46, 29.30, 29.16, -8.42. MS (EI, M⁺) for C₂₆H₄₆S₂Sn₂: *calc* 'd 662.1085 *found* 662.1085.

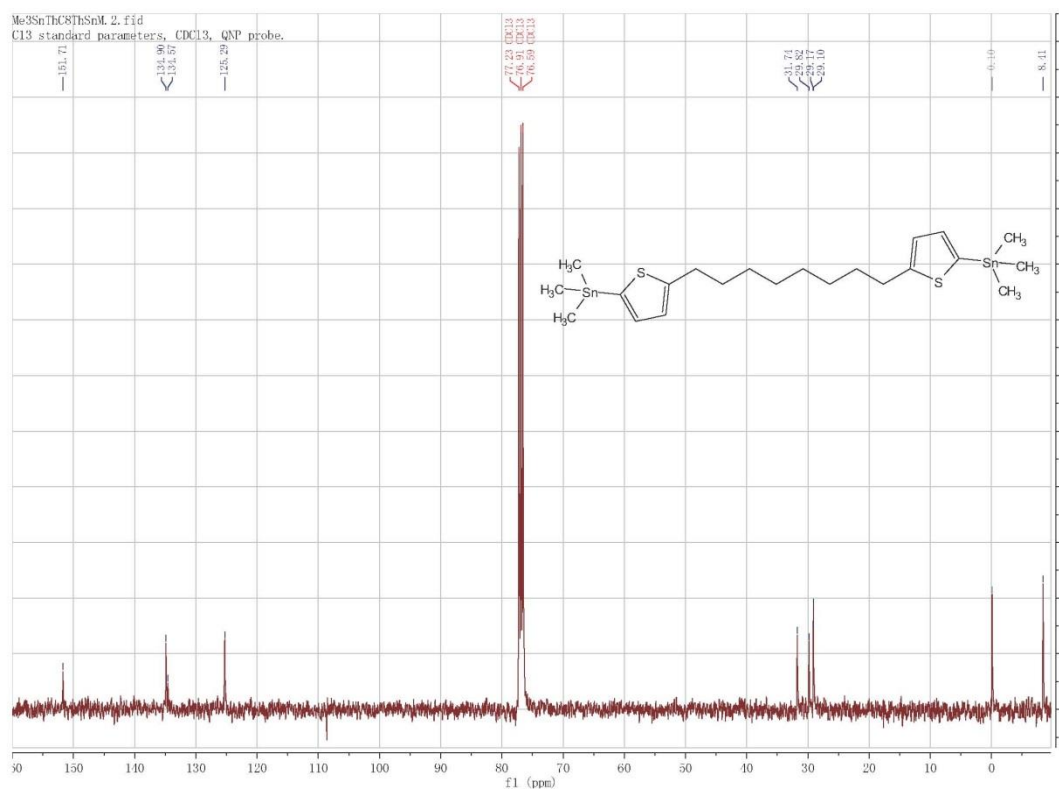


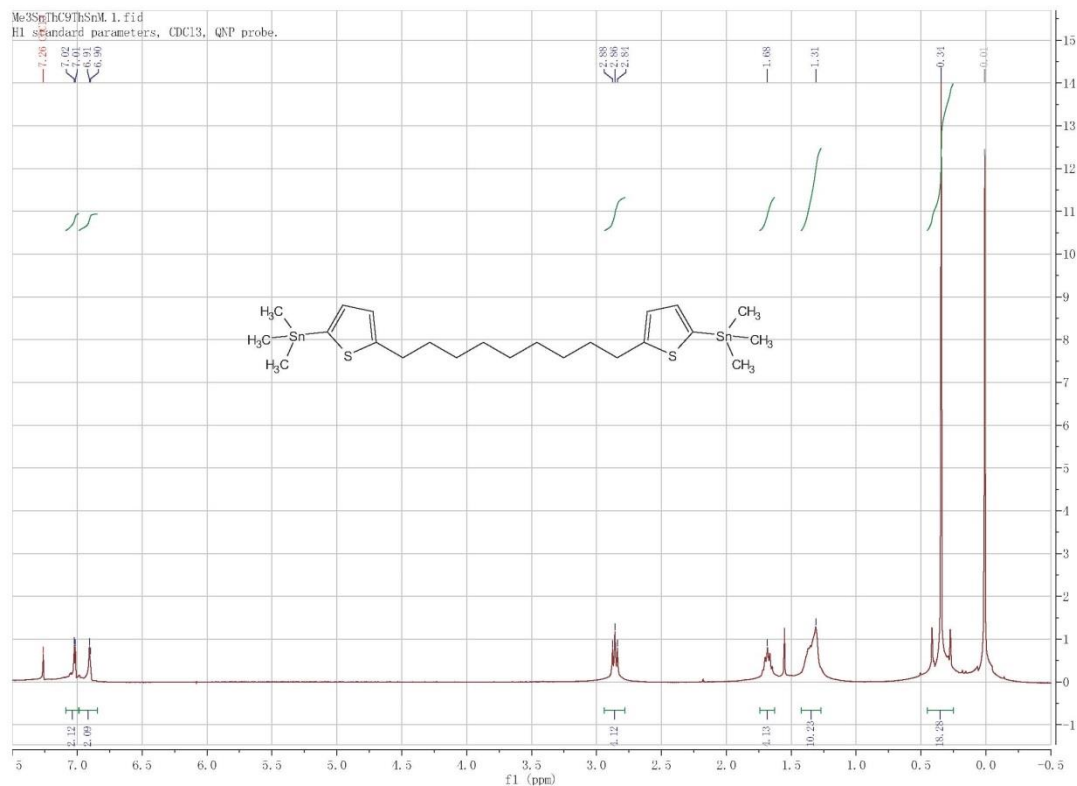
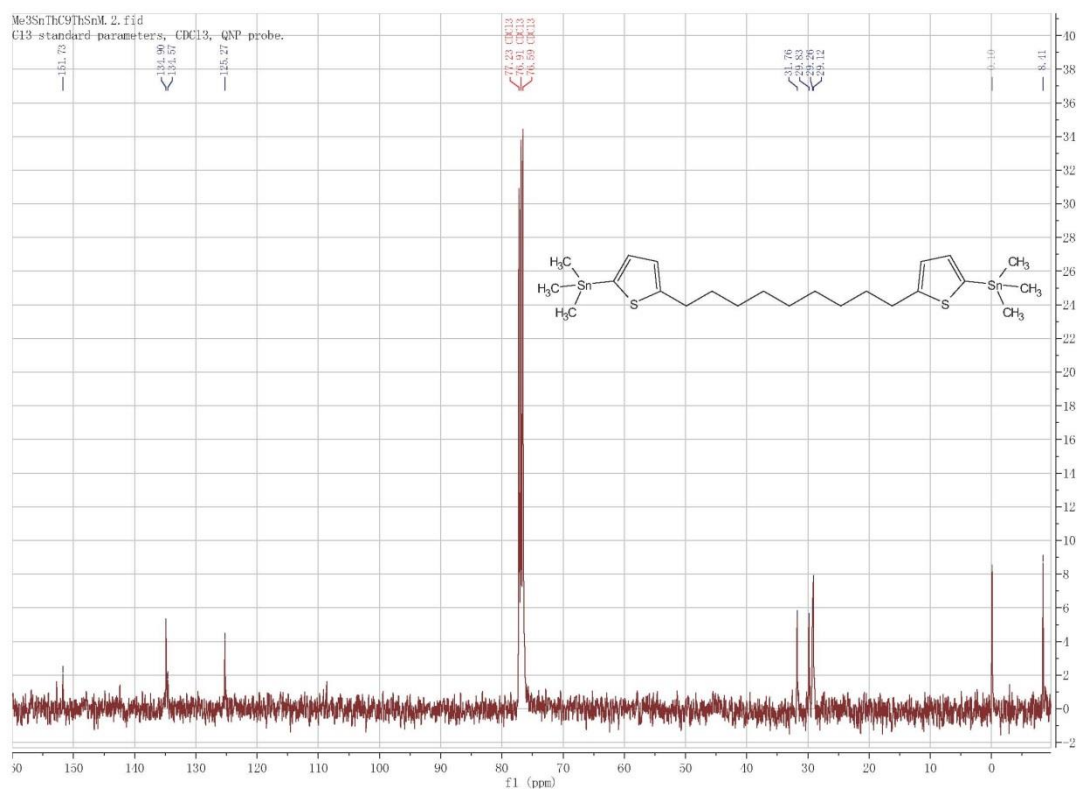


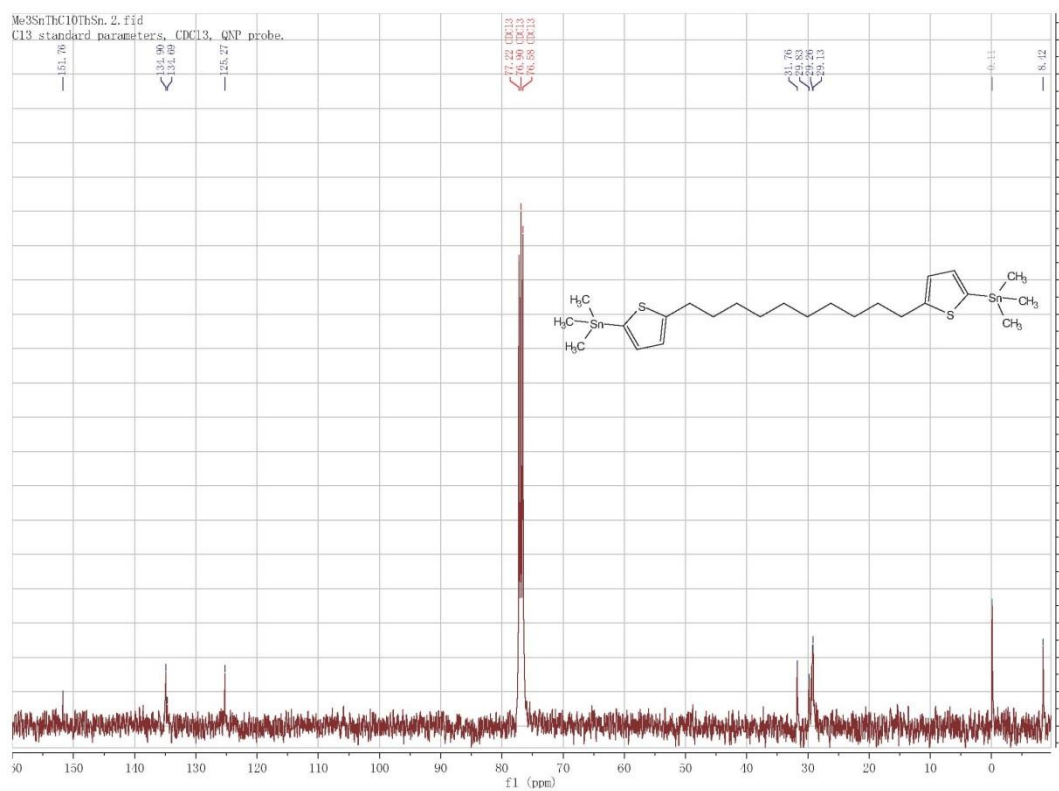


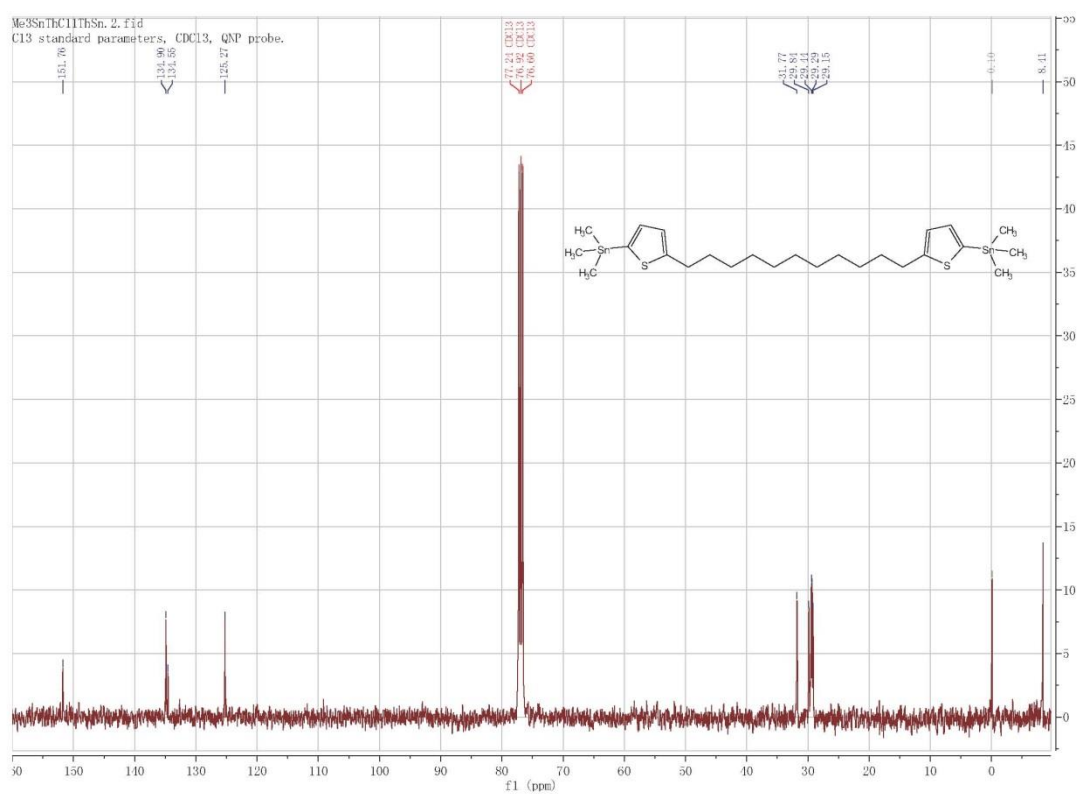


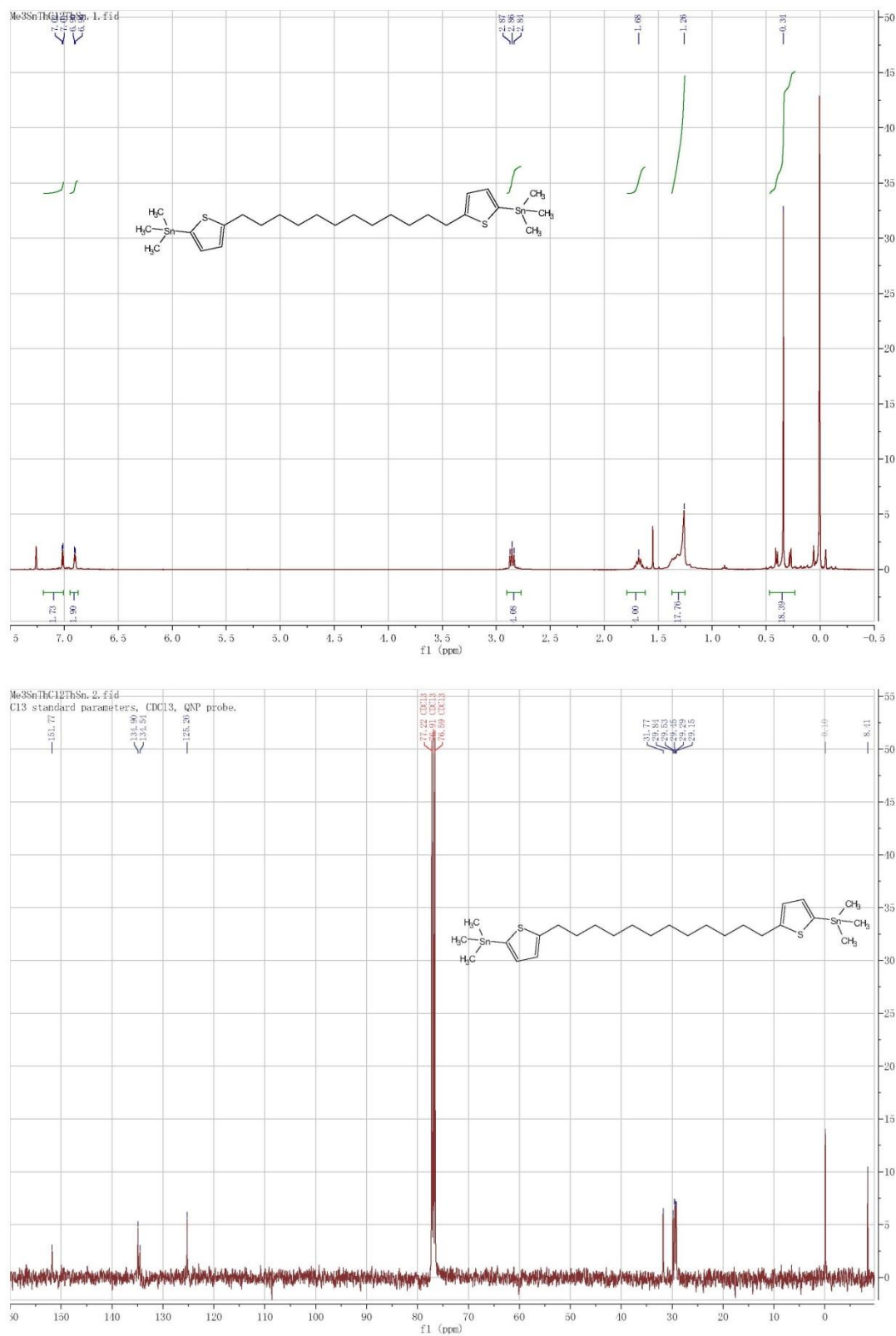


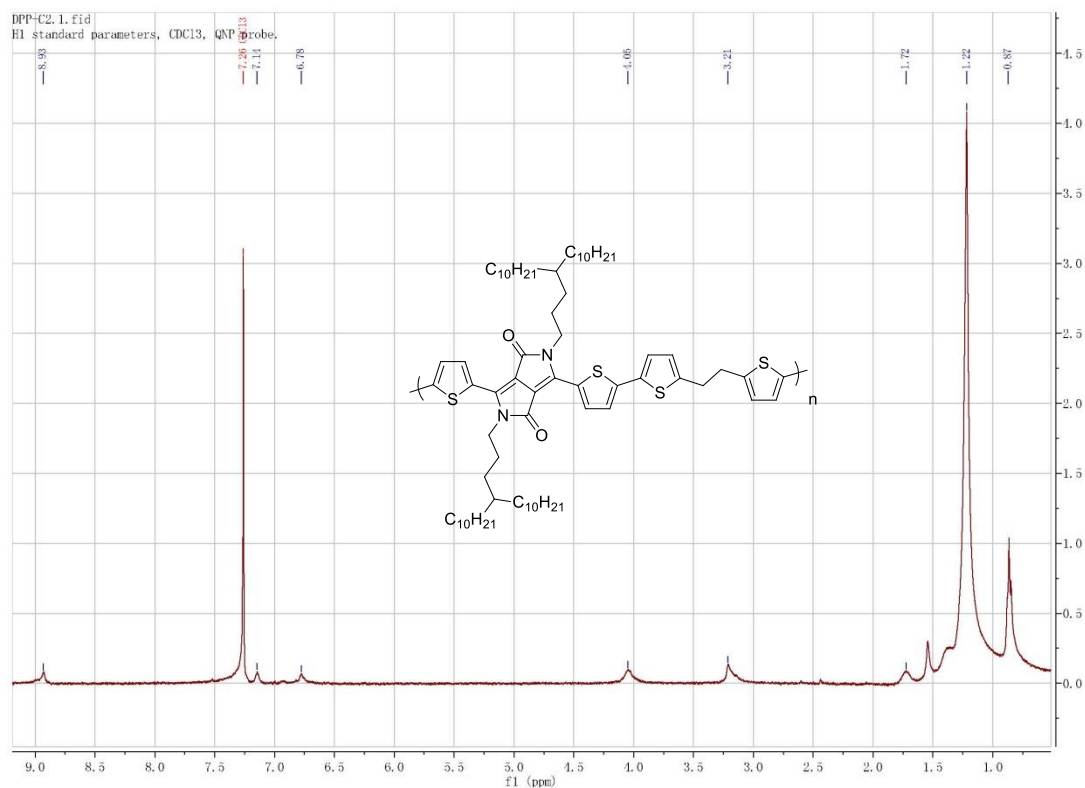
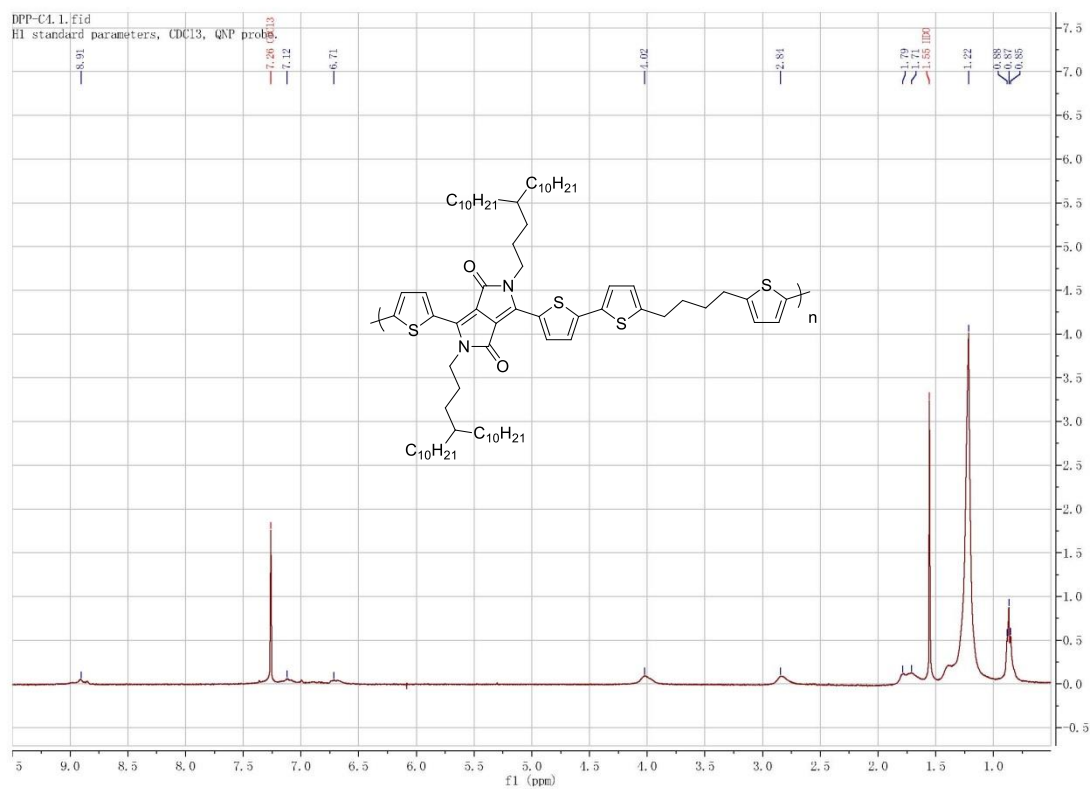


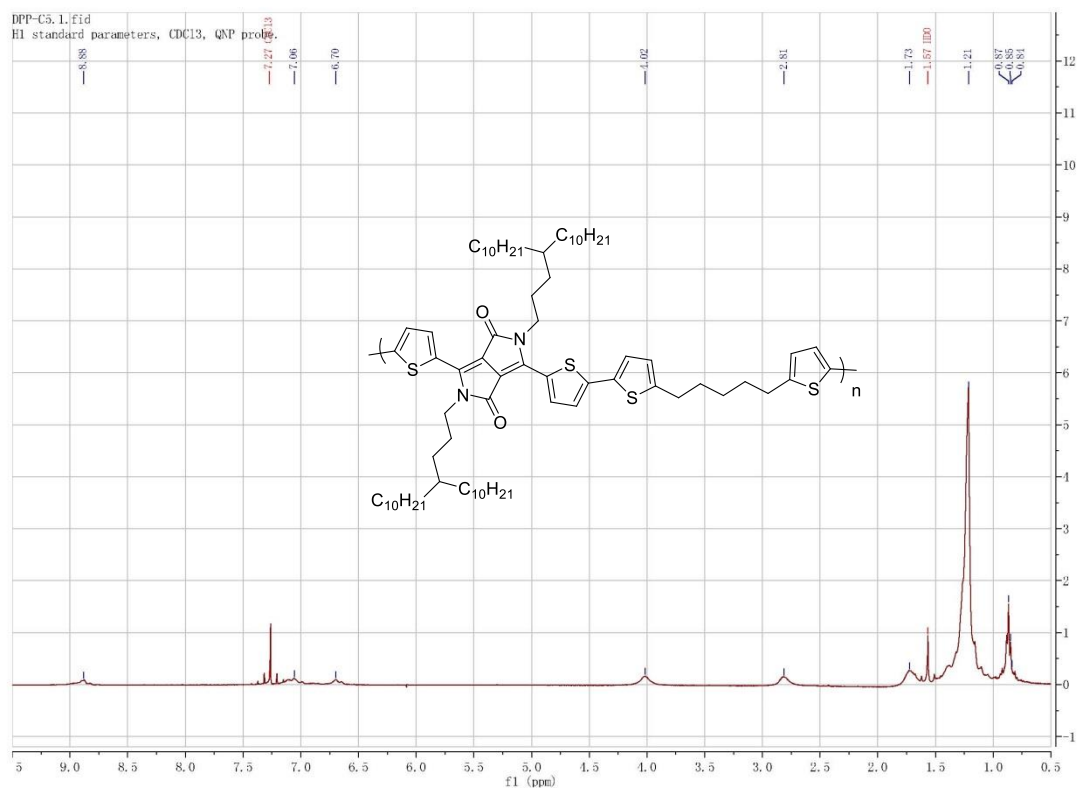
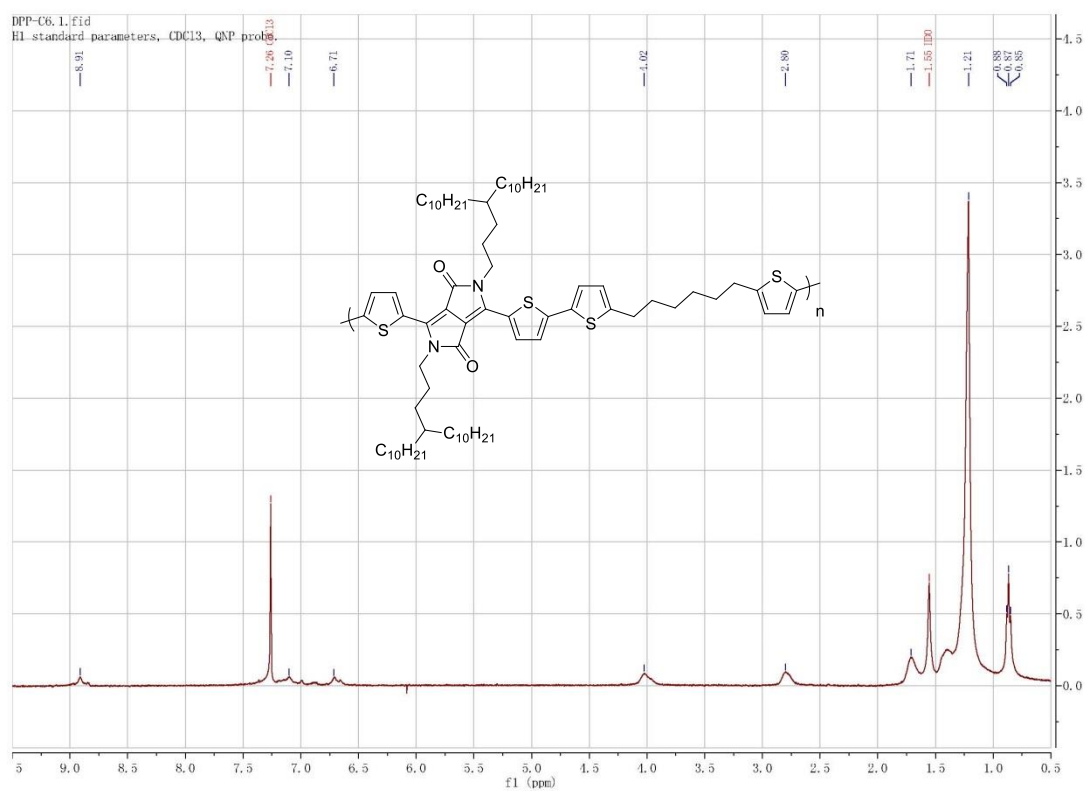


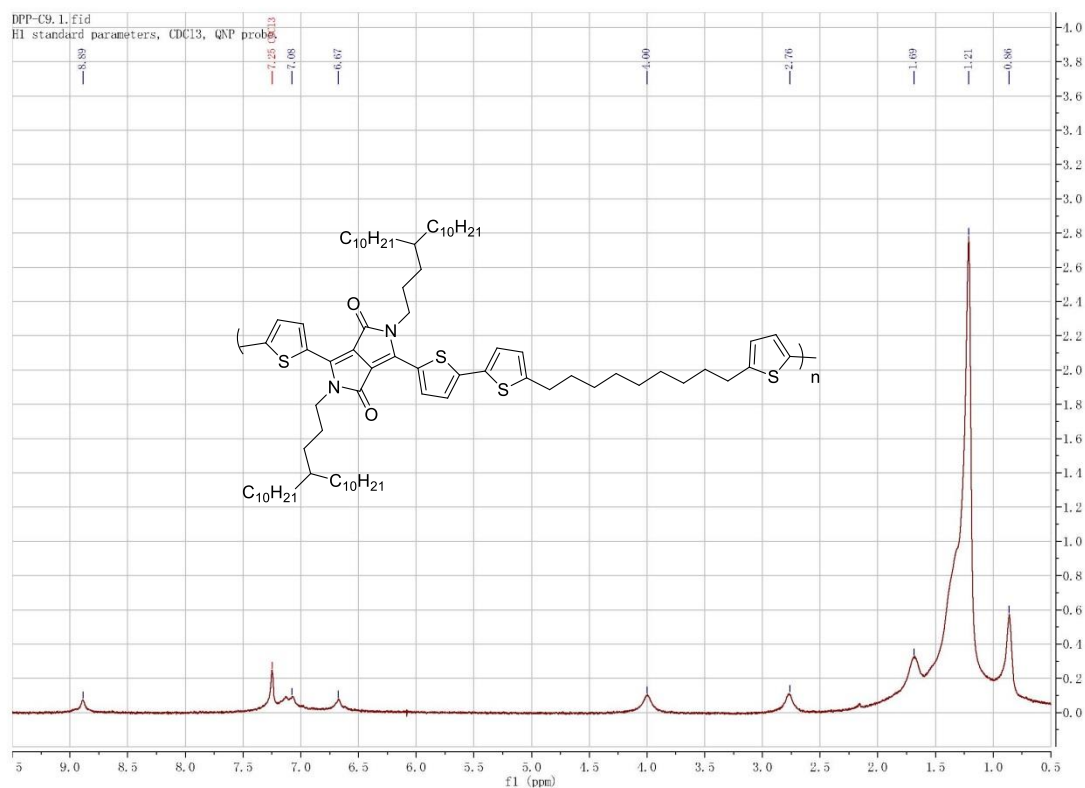
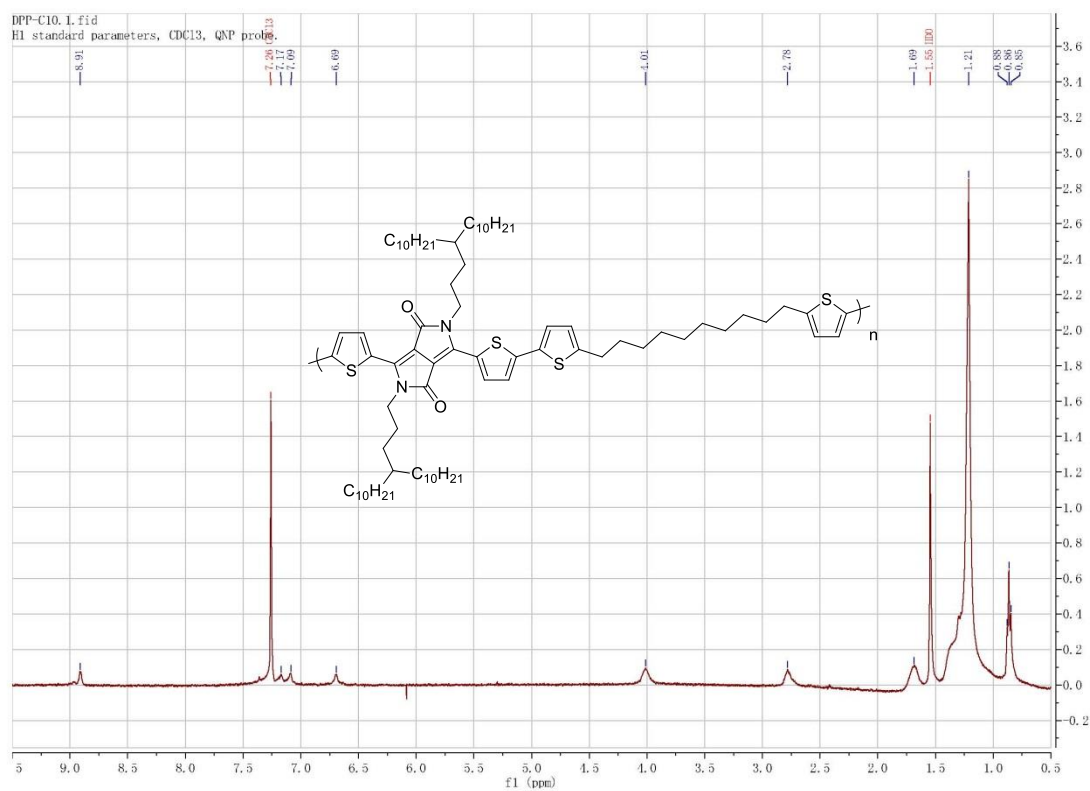




Figure S1 ^1H and ^{13}C NMR Spectra of the CBS monomers.







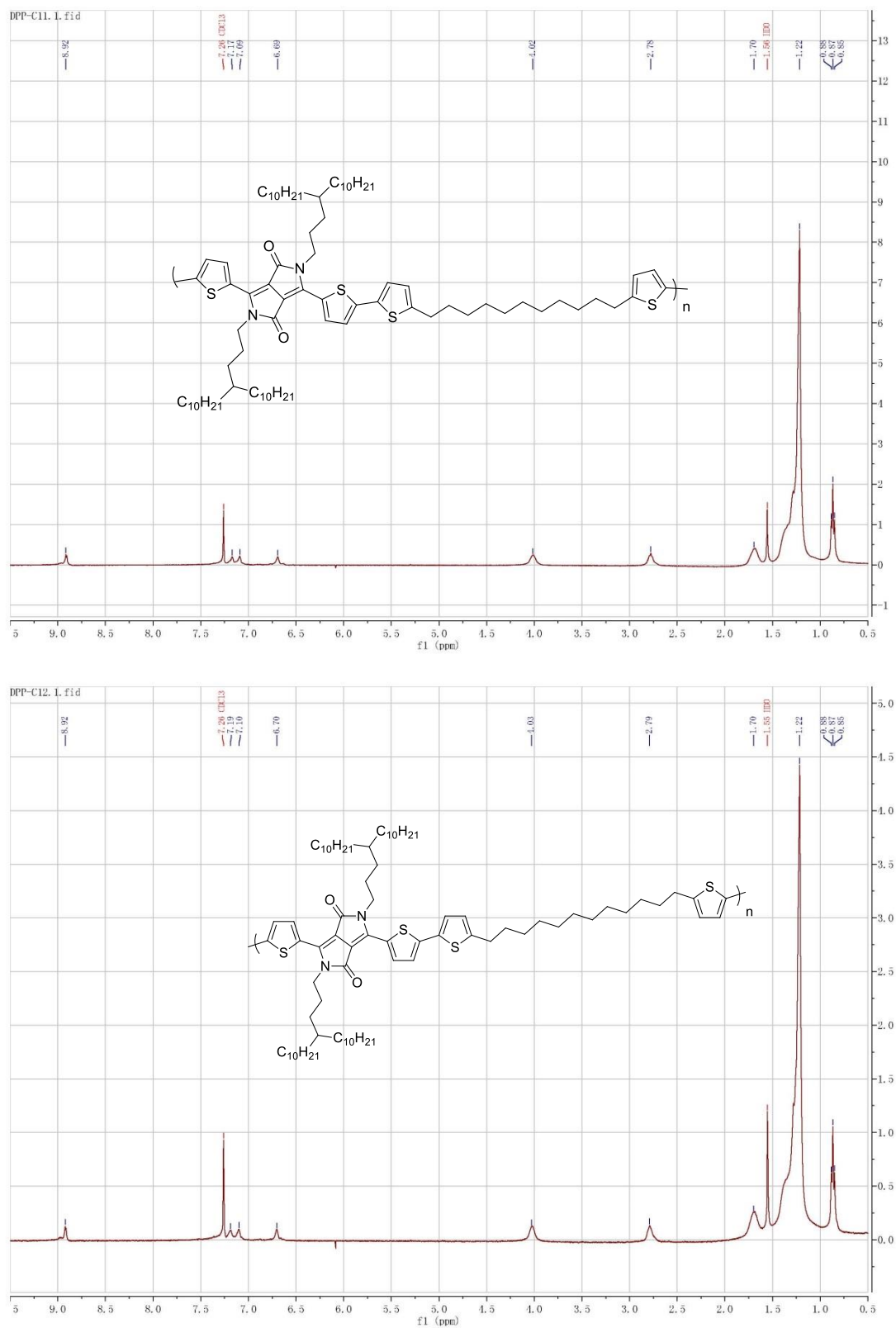


Figure S2 ^1H NMR Spectra of the CBS polymers.

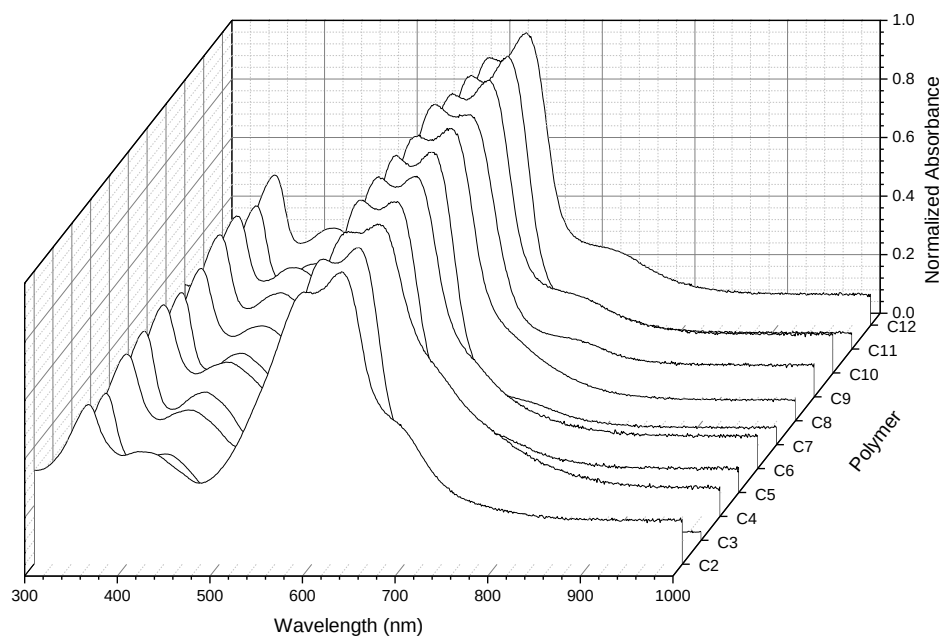


Figure S3 UV-vis-NIR spectra of the **CBS** polymers, DPP-Cm ($m = 2$ to 12), in chloroform solutions.

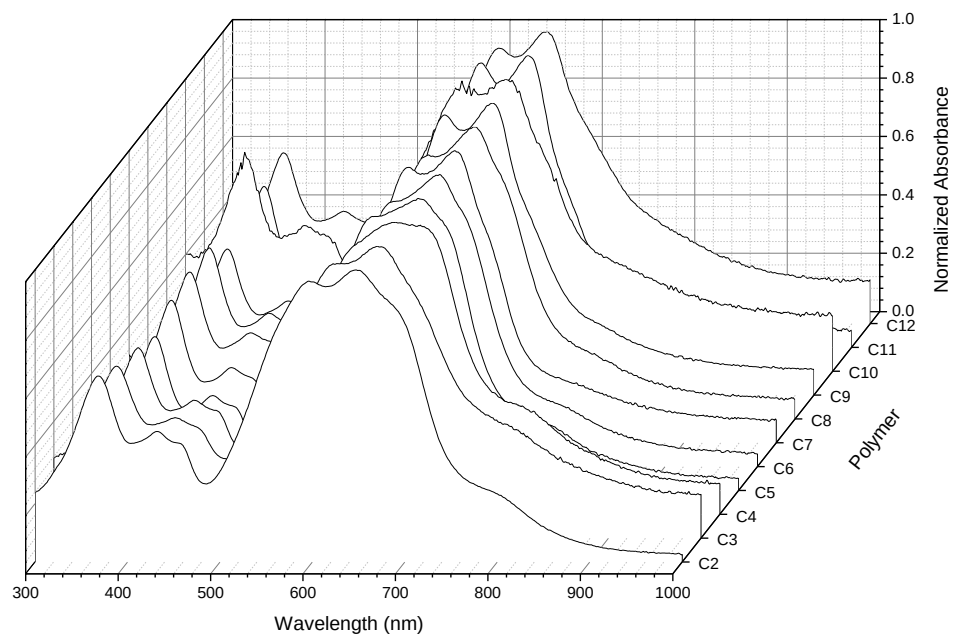


Figure S4 UV-vis-NIR spectra of the **CBS** polymers, DPP-Cm ($m = 2$ to 12), as thin films.

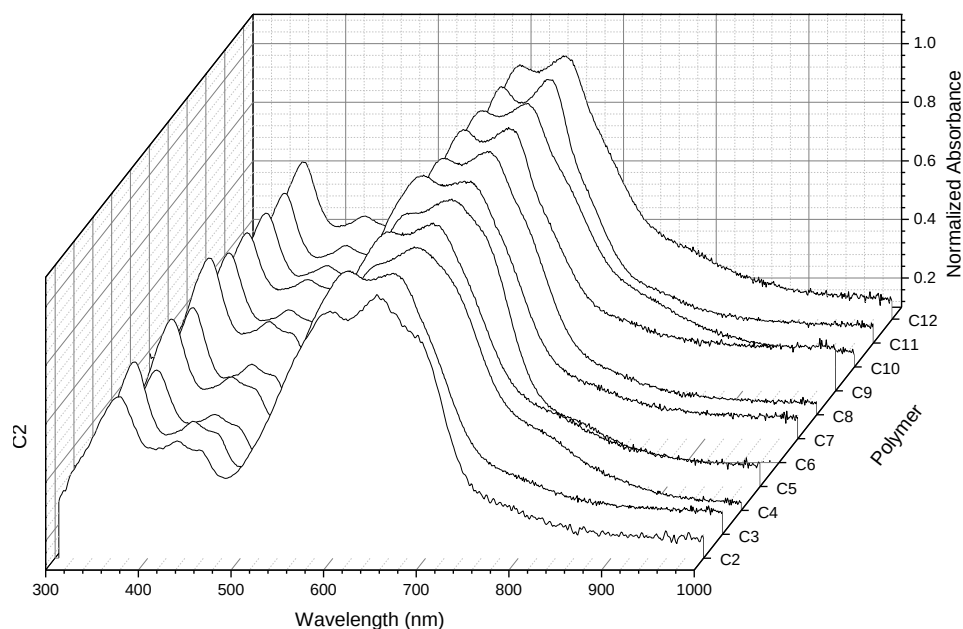


Figure S5 UV-Vis-NIR spectra of the *c*-SPBs with 2 wt% DPP-C0 as thin films.

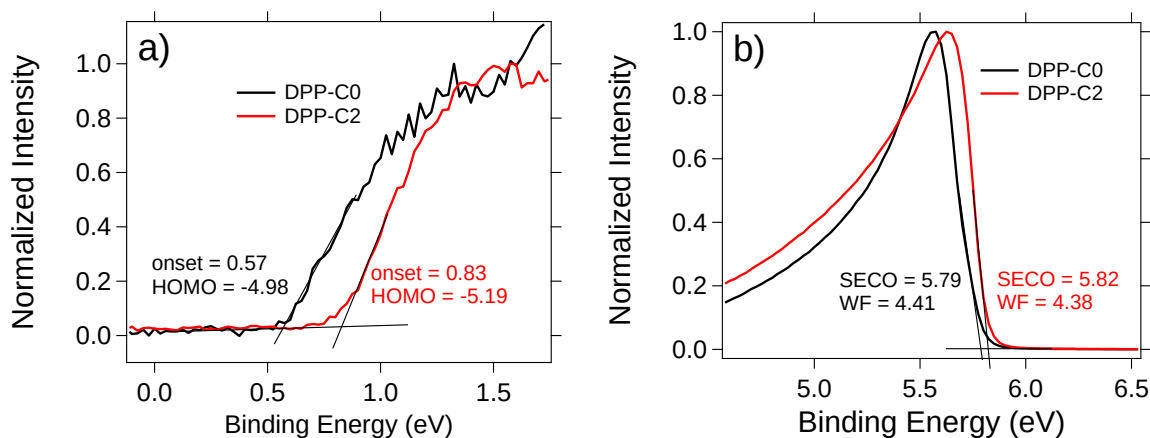


Figure S6. HOMO onset (a) and secondary electron cut-off (b) regions for DPP-C0 and DPP-C2 vs. the Fermi energy. The HOMO energies vs. vacuum are indicated in (a) and the work functions (WF) are indicated in (b). The WF was found by subtracting the secondary electron cut-off (SECO) energy from the source energy (10.20 eV).

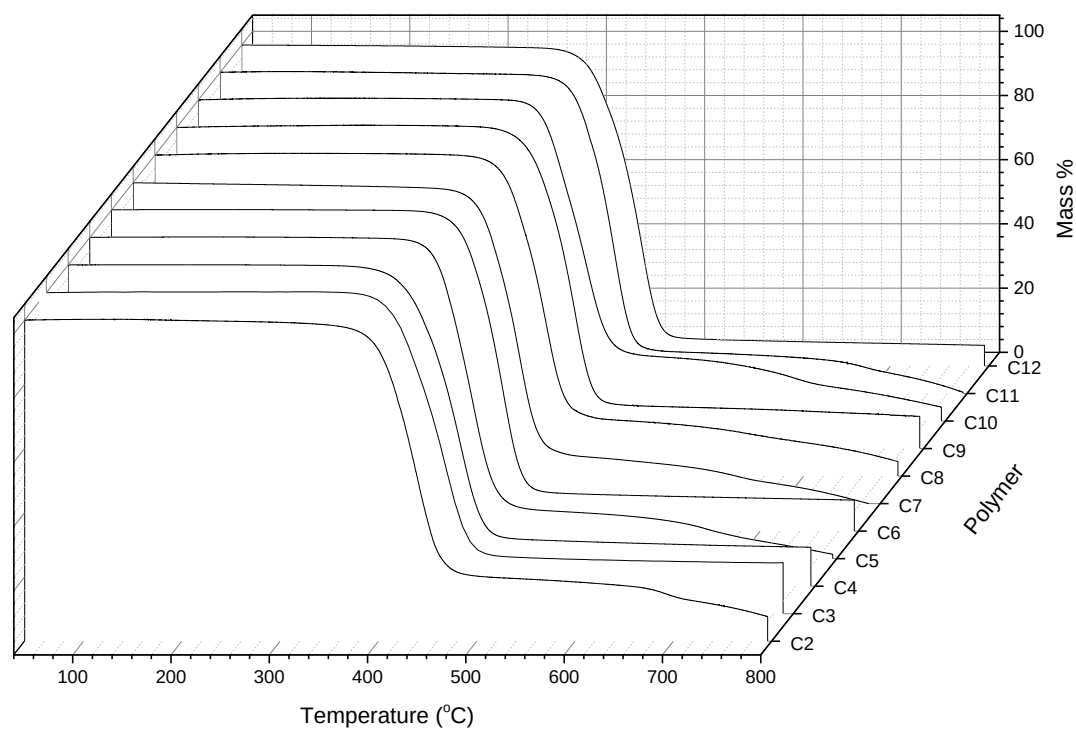
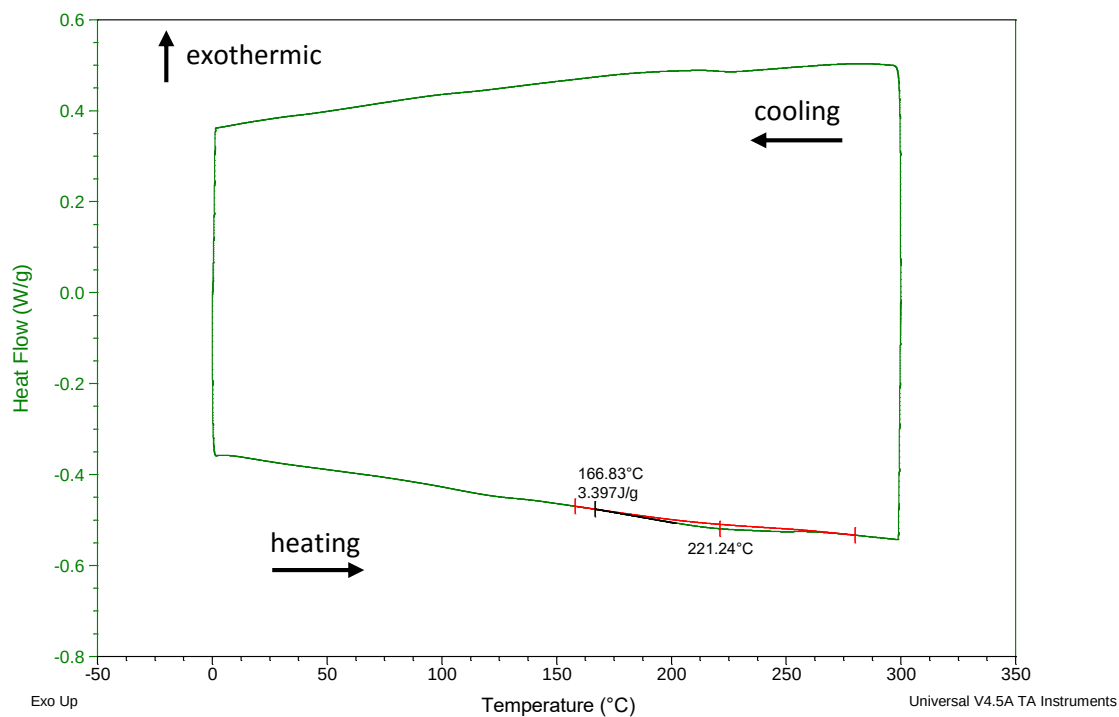


Figure S7 Thermogravimetric analysis (TGA) curves of DPP polymers (10 °C/min under nitrogen atmosphere).

Sample: DPP-C2
Size: 5.5000 mg
Method: DPP-Standard

DSC

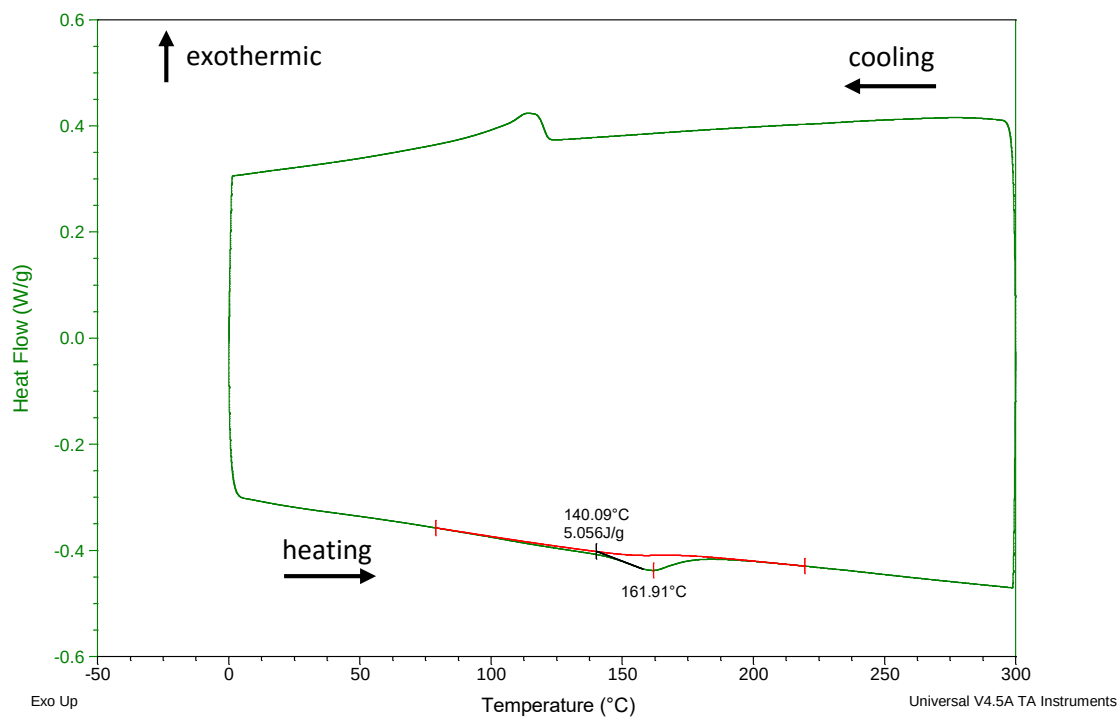
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Instrument: DSC Q2000 V24.11 Build 124



Sample: DPP-C3
Size: 8.2000 mg
Method: DPP-Standard

DSC

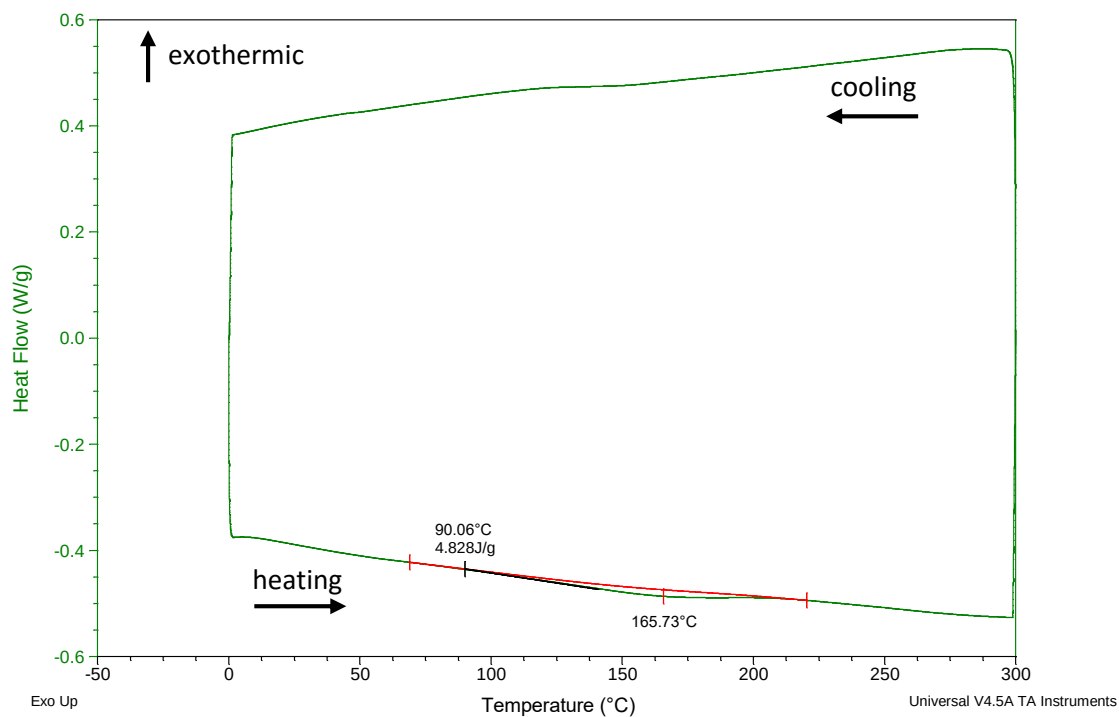
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Sample: DPP-C4
Size: 5.2000 mg
Method: DPP-Standard

DSC

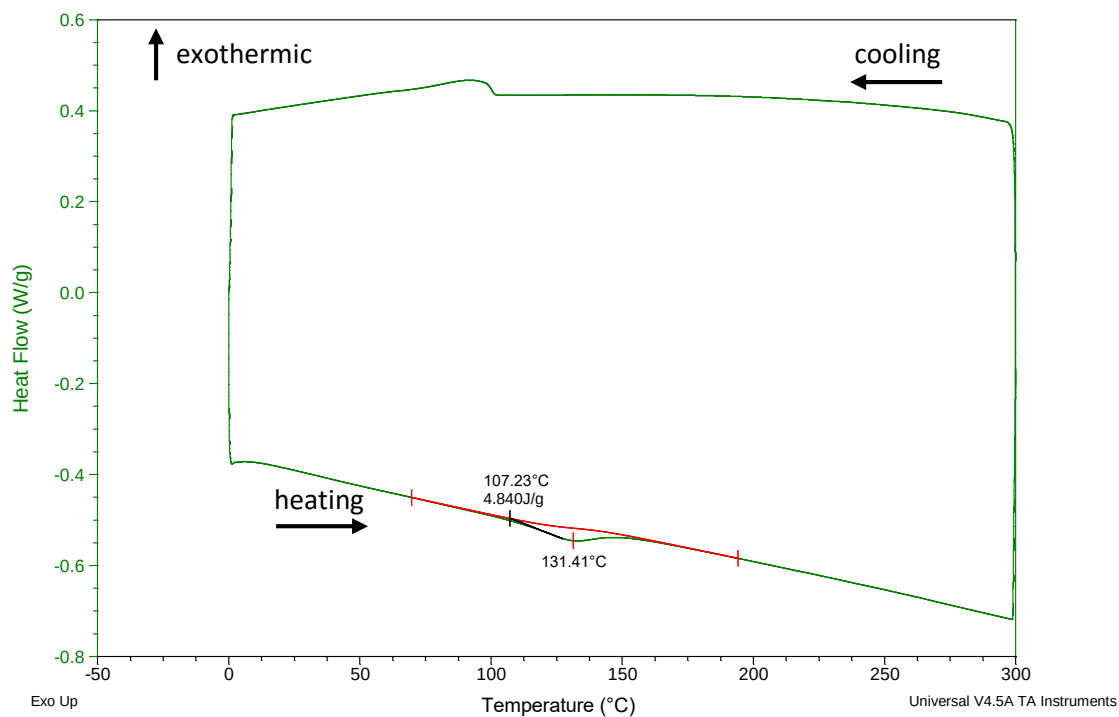
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Sample: DPP-C5
Size: 5.0000 mg
Method: DPP-Standard

DSC

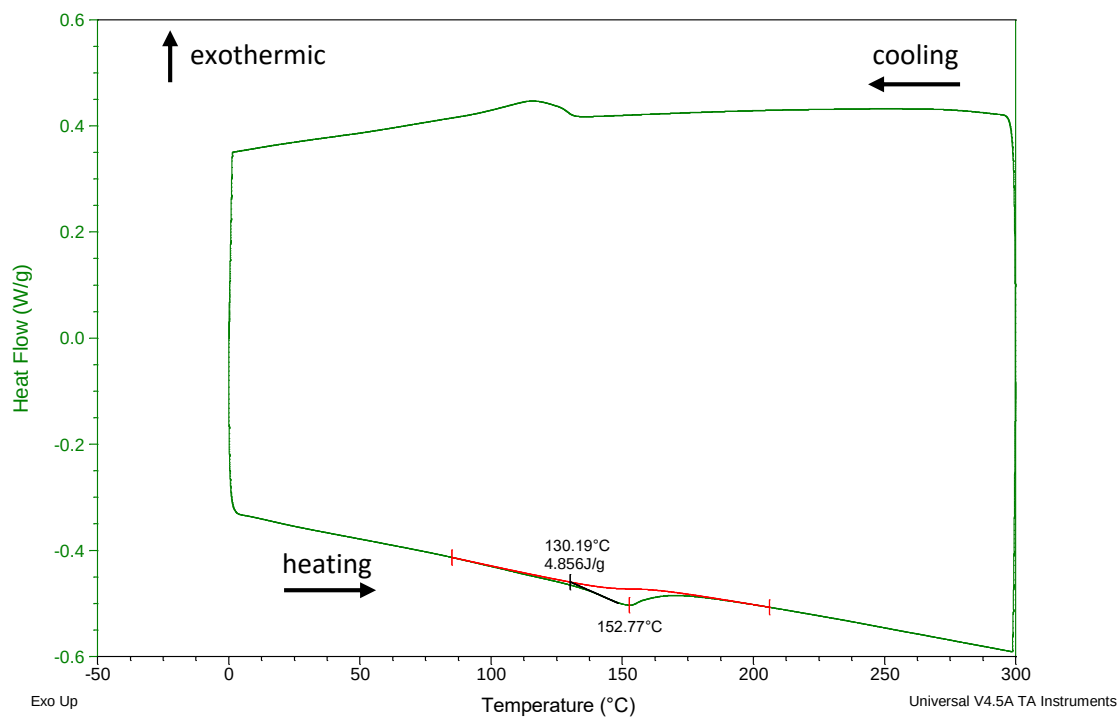
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Sample: DPP-C6
Size: 8.4000 mg
Method: DPP-Standard

DSC

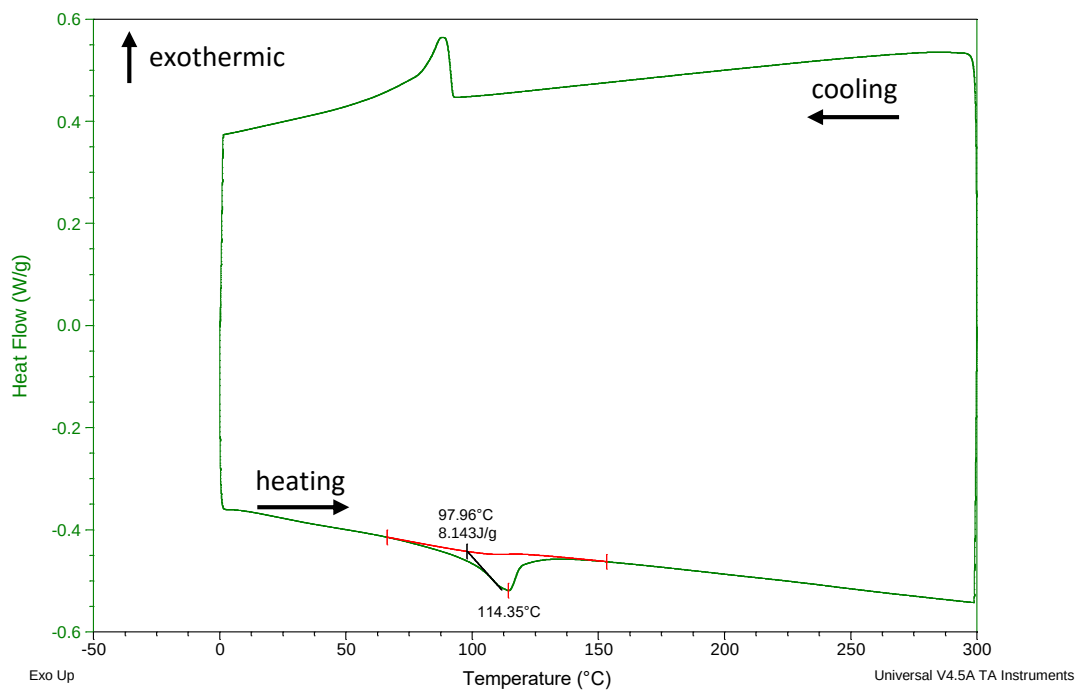
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Sample: DPP-C7
Size: 5.6000 mg
Method: DPP-Standard

DSC

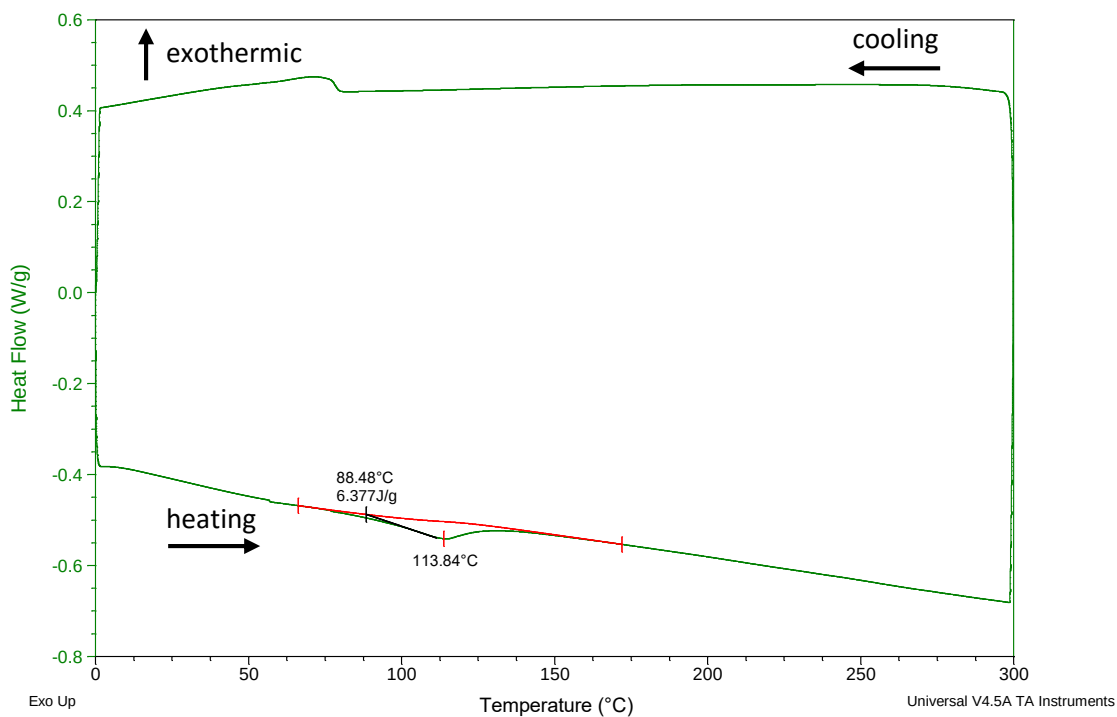
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Sample: DPP-C8
Size: 5.0000 mg
Method: DPP-Standard

DSC

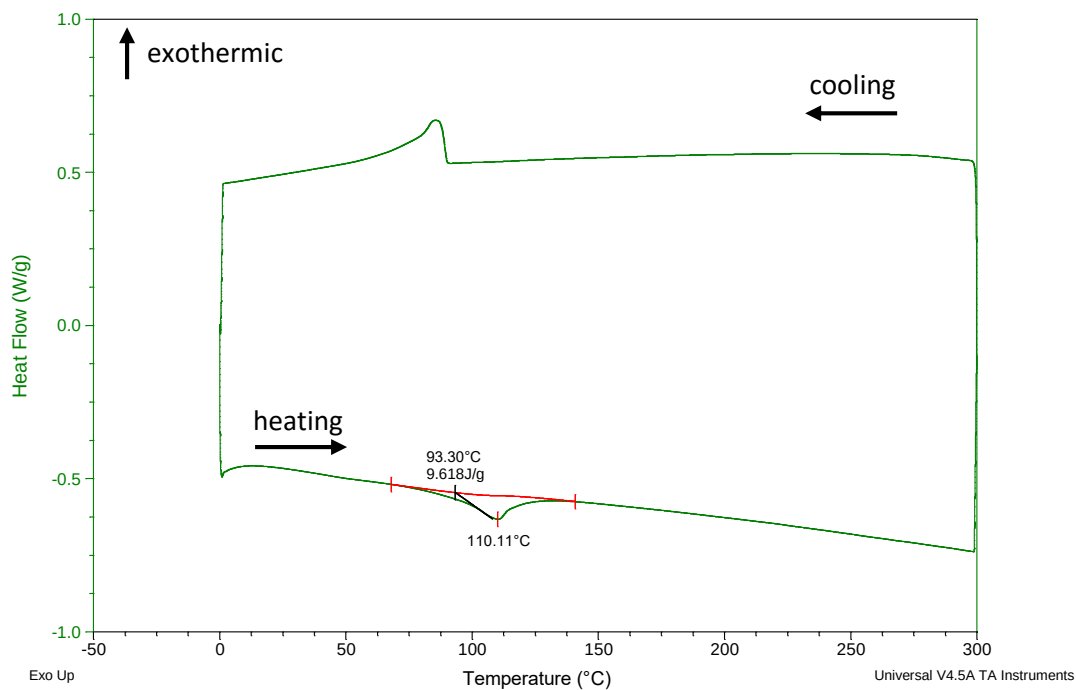
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Sample: DPP-C9
Size: 3.1000 mg
Method: DPP-Standard

DSC

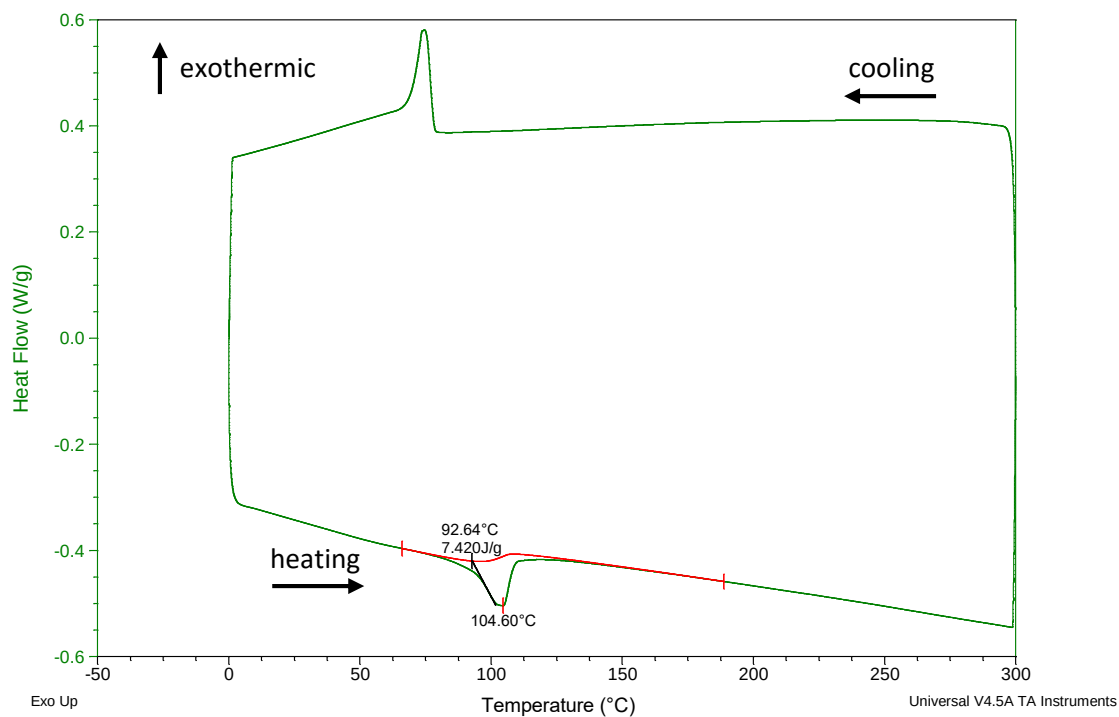
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Sample: DPP-C10
Size: 8.1000 mg
Method: DPP-Standard

DSC

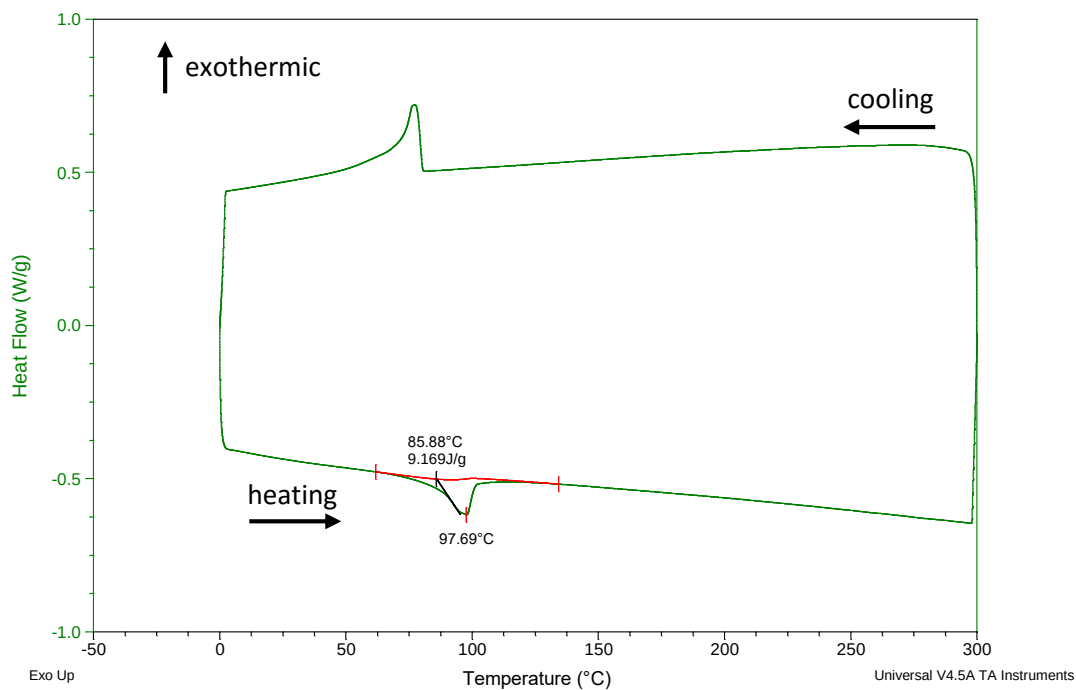
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Sample: DPP-C11
Size: 3.9000 mg
Method: DPP-Standard

DSC

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Instrument: DSC Q2000 V24.11 Build 124



Sample: DPP-C12
Size: 7.6000 mg
Method: DPP-Standard

DSC

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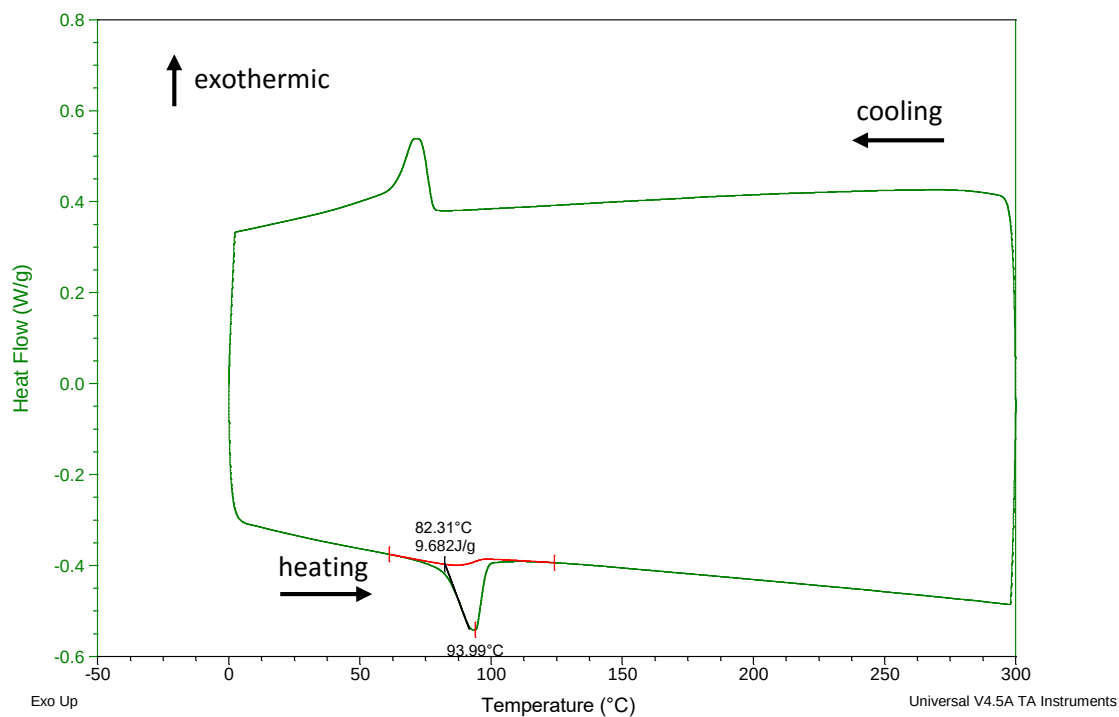


Figure S8 Differential scanning calorimetry (DSC) curves of the DPP polymers.

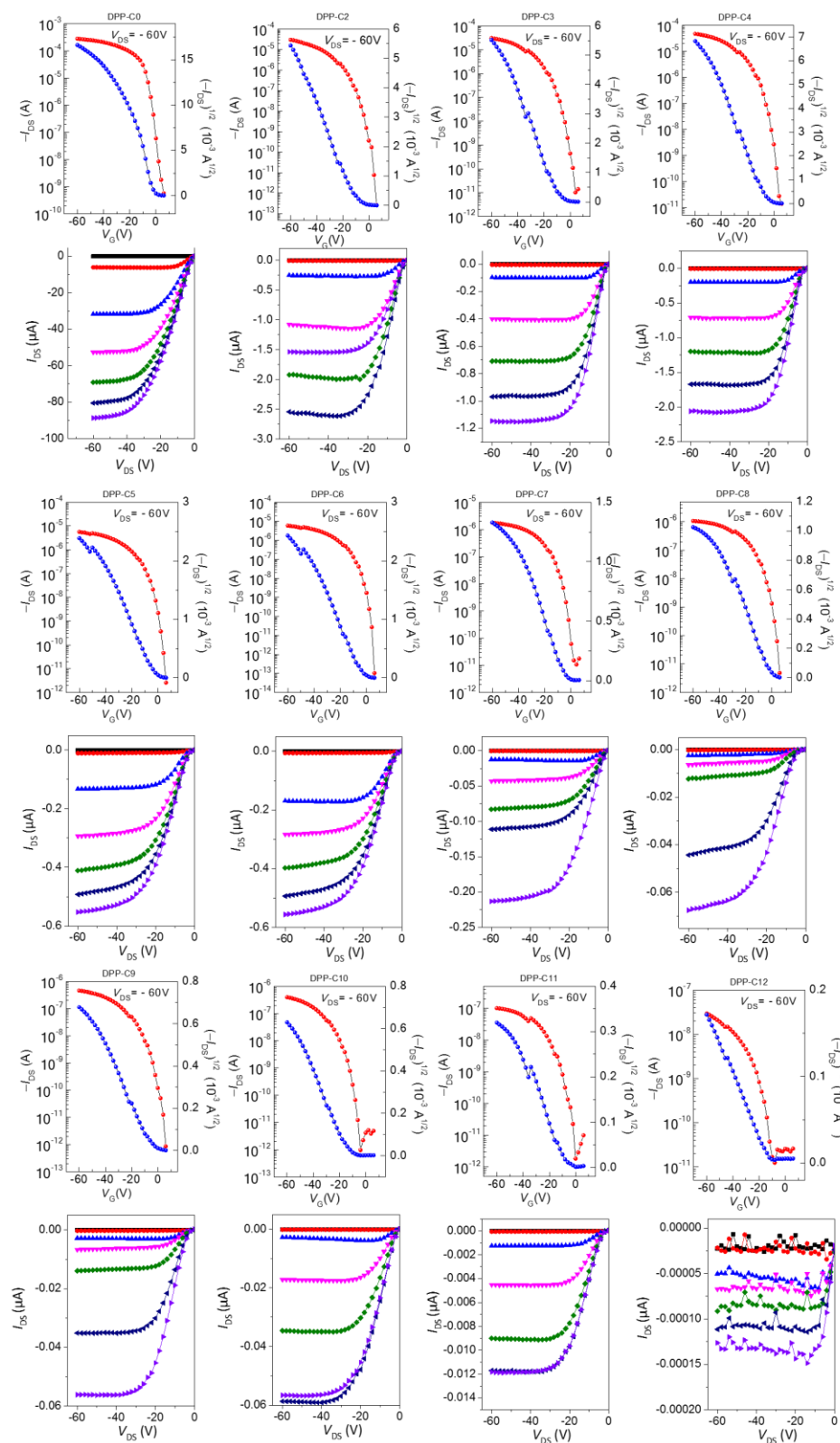


Figure S9 Transfer and output characteristics of pure DPP-C0 to DPP-C12 OFETs fabricated by spin coating. The V_G was set from 0 V to -60 V in steps of -10 V for all output testing.

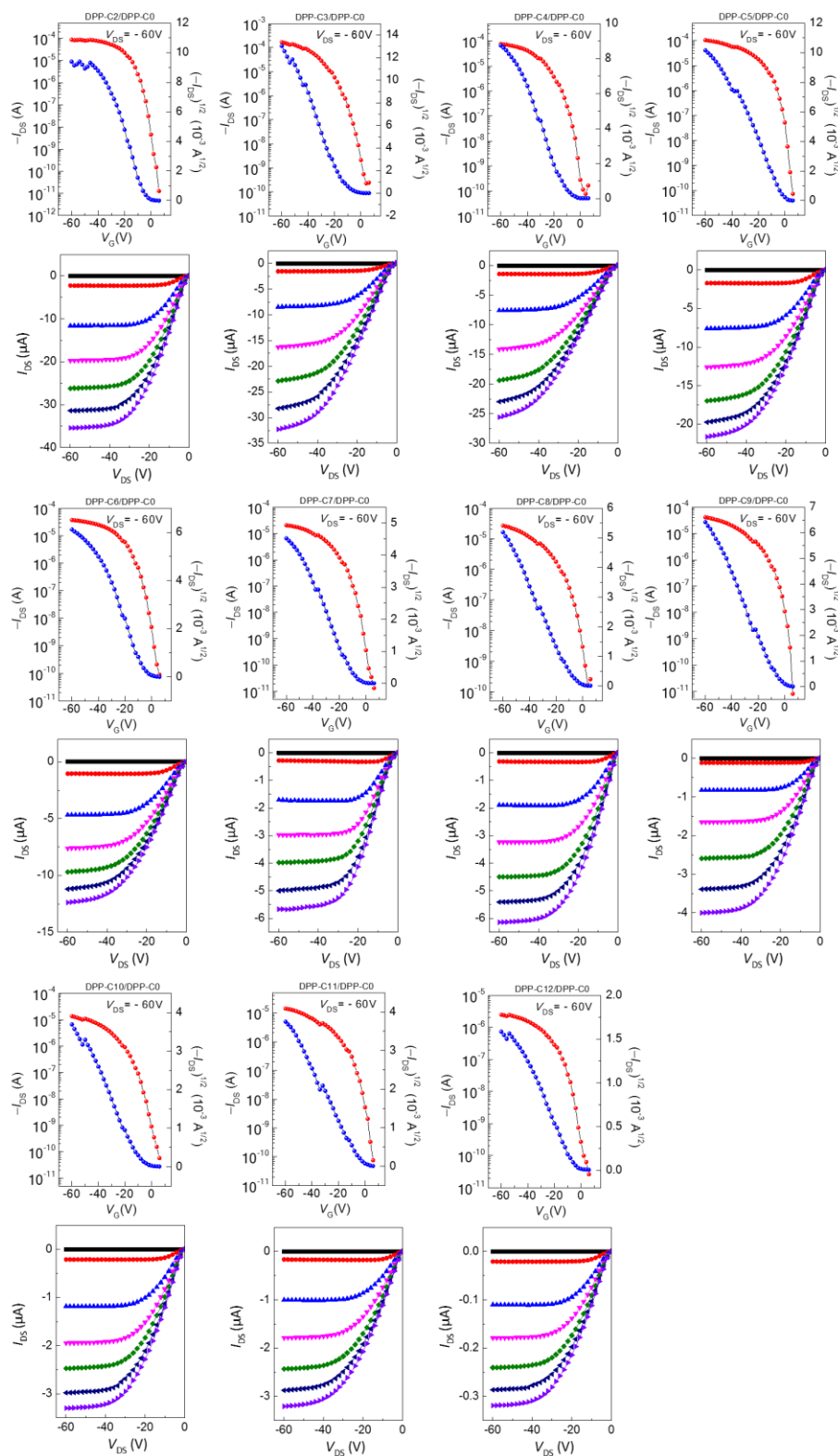


Figure S10 Transfer and output characteristics of *c*-SPB OFETs fabricated by spin coating. The V_G was set from 0 V to -60 V in steps of -10 V for all output testing.

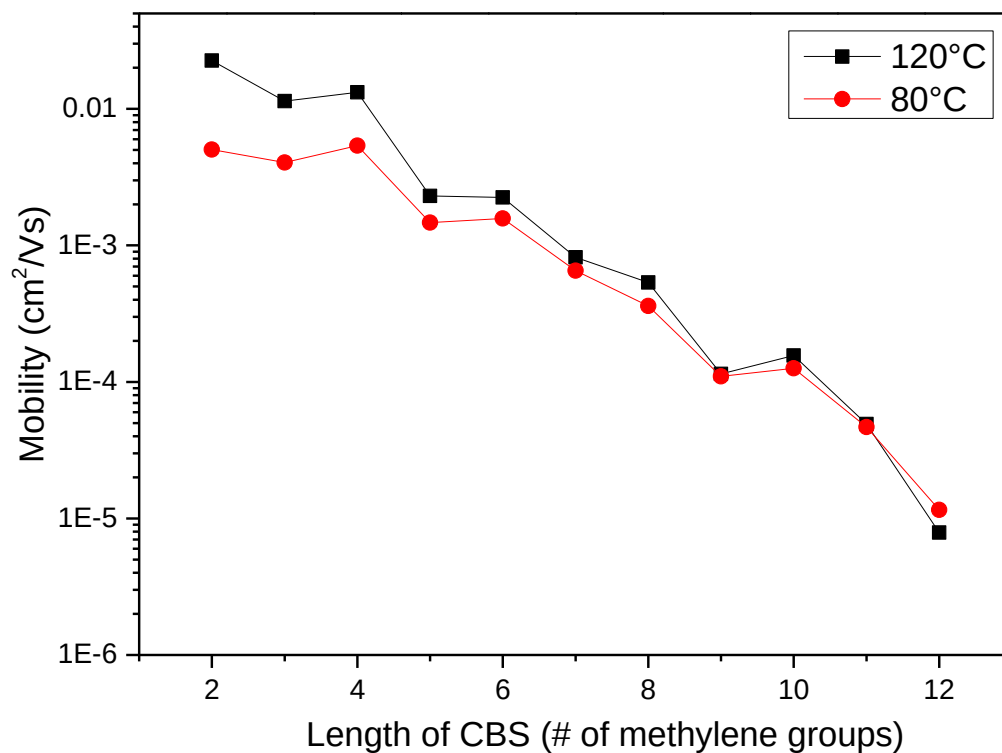


Figure S11 Charge carrier mobility of pure polymers as a function of number of methylene groups in CBSs after annealed at 120 and 80 °C.

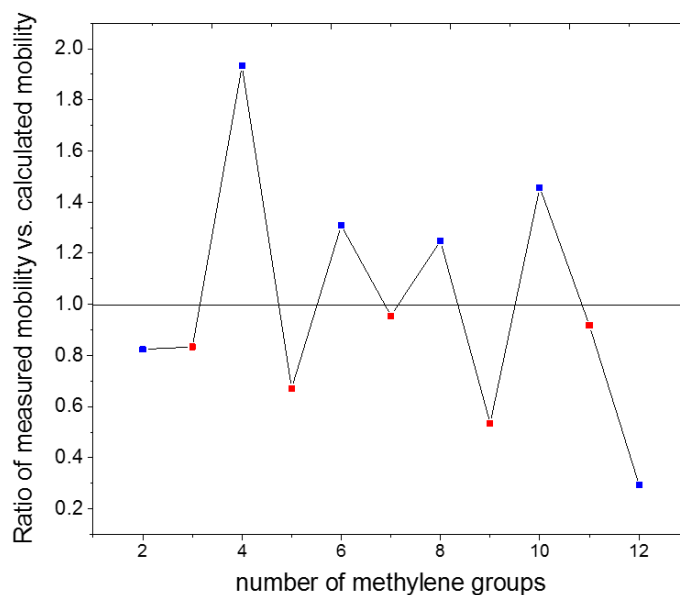


Figure S12 Ratios between measured charge carrier mobilities vs exponential fit values of pure polymers as a function of number of methylene groups in CBSs.

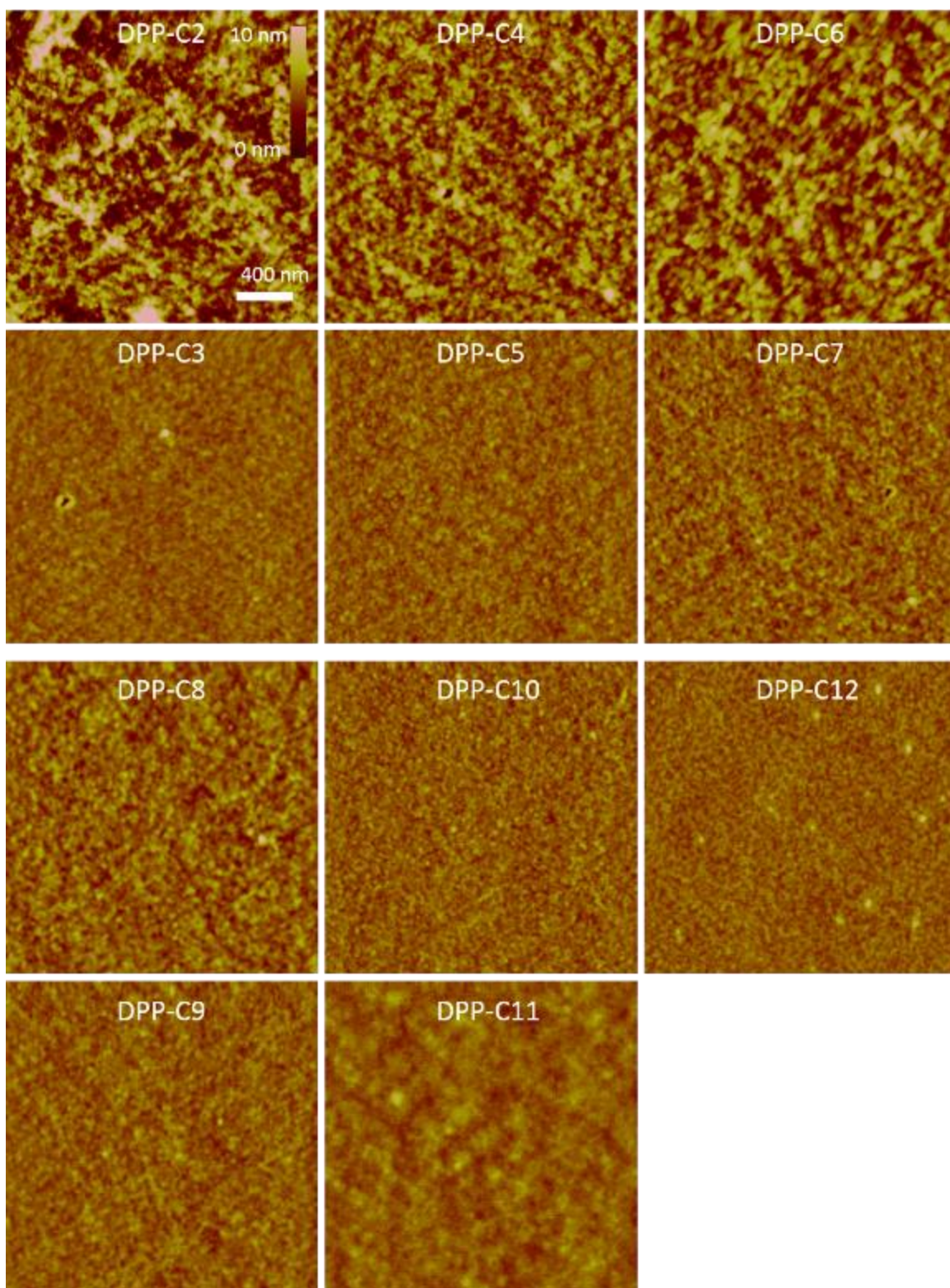


Figure S13 AFM images of pure polymer thin films. The polymer thin films were fabricated by spin coating on OTS modified Si/SiO₂ substrates. The films were tested as cast.

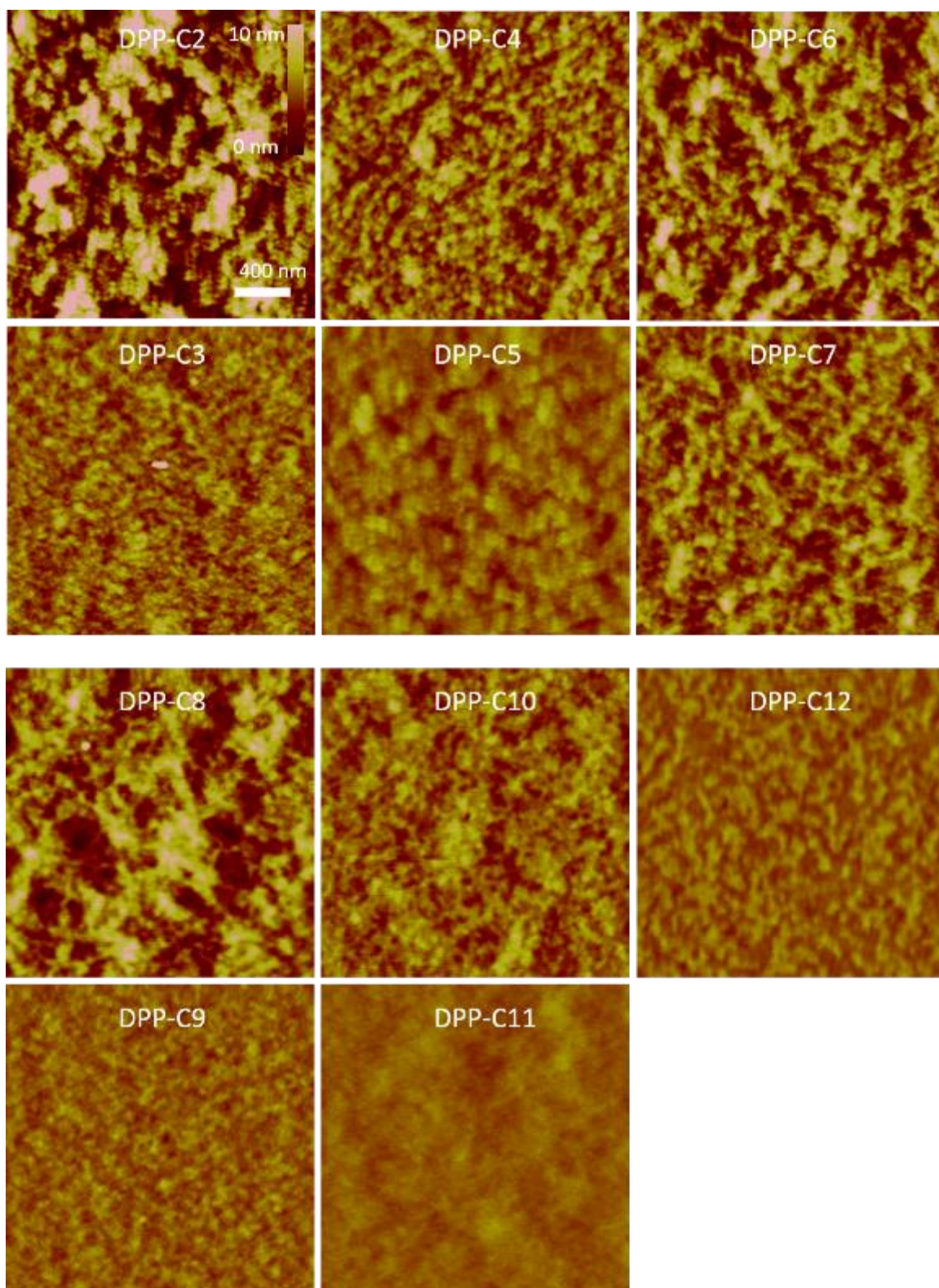


Figure S14 AFM images of polymer thin films. The polymer thin films were fabricated by spin coating on OTS modified Si/SiO₂ substrates. The films were annealed at 80 °C before tested.

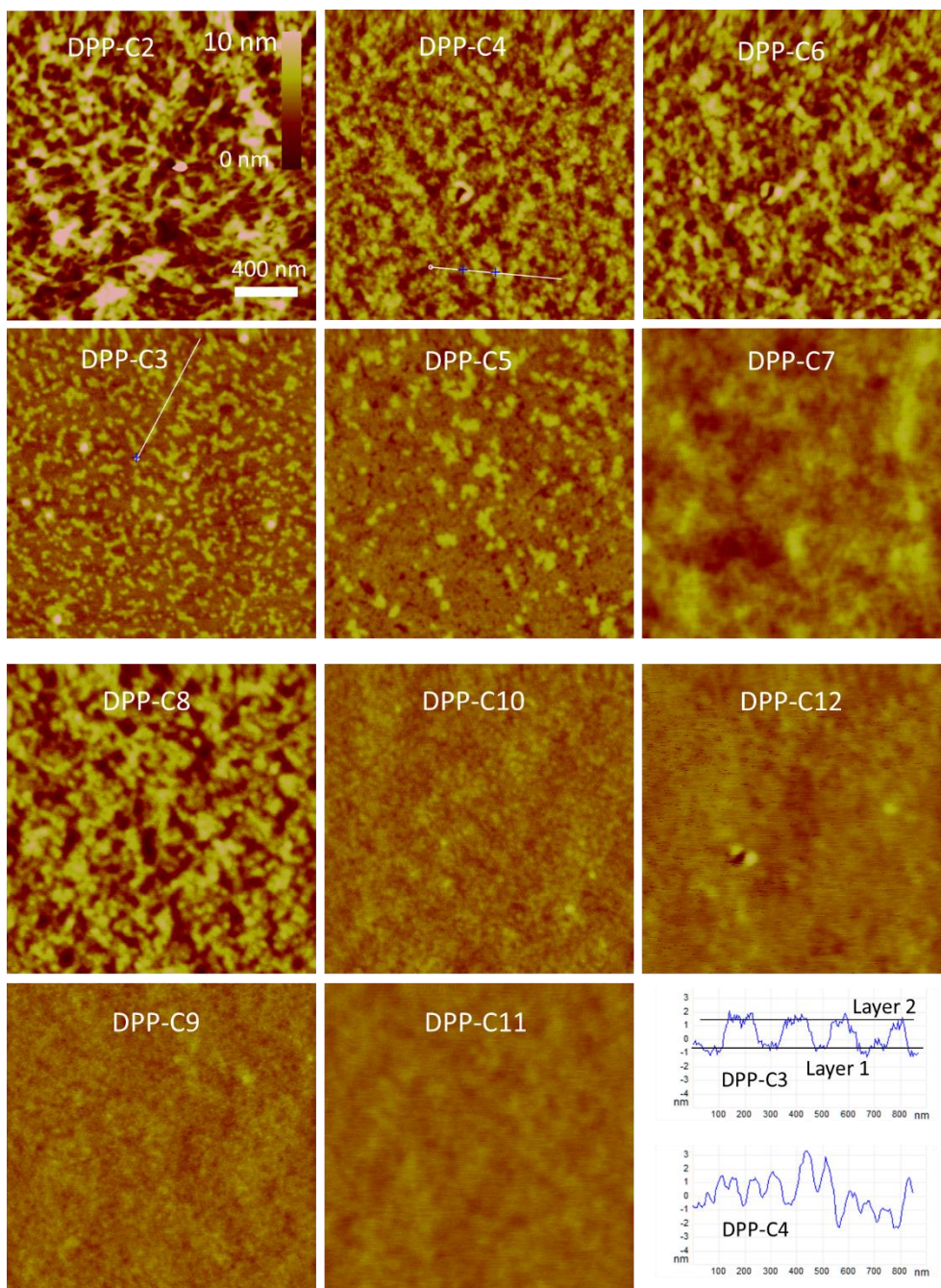


Figure S15 AFM images of polymer thin films. The polymer thin films were fabricated by spin coating on OTS modified Si/SiO₂ substrates. The films were annealed at 120 °C before tested.

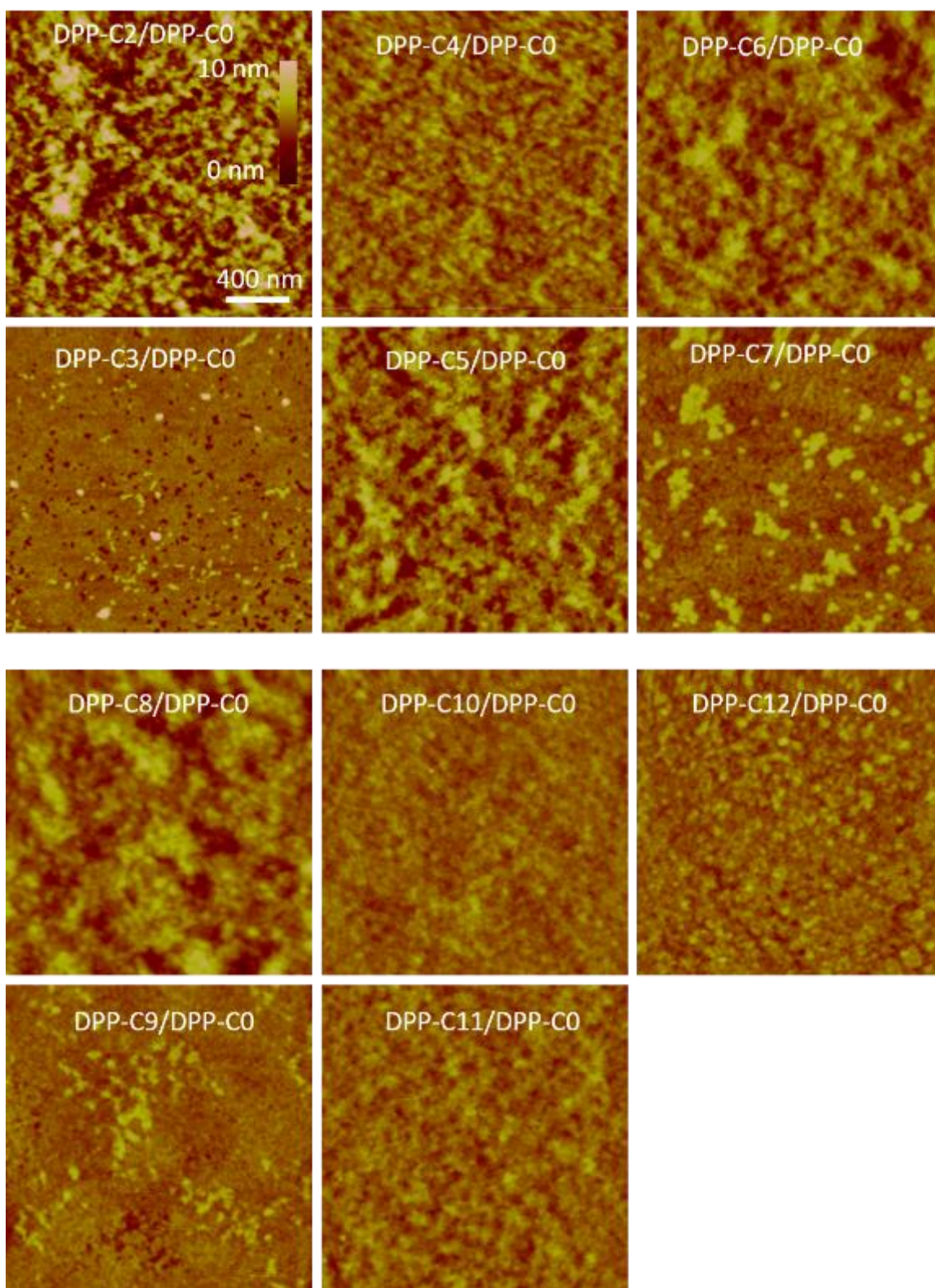


Figure S16 AFM images of c-SPB thin films. The polymer thin films were fabricated by spin coating on OTS modified Si/SiO₂ substrates. The films were annealed at 120 °C before tested. The ratio of DPP-C0 is 2 wt% for all the films.

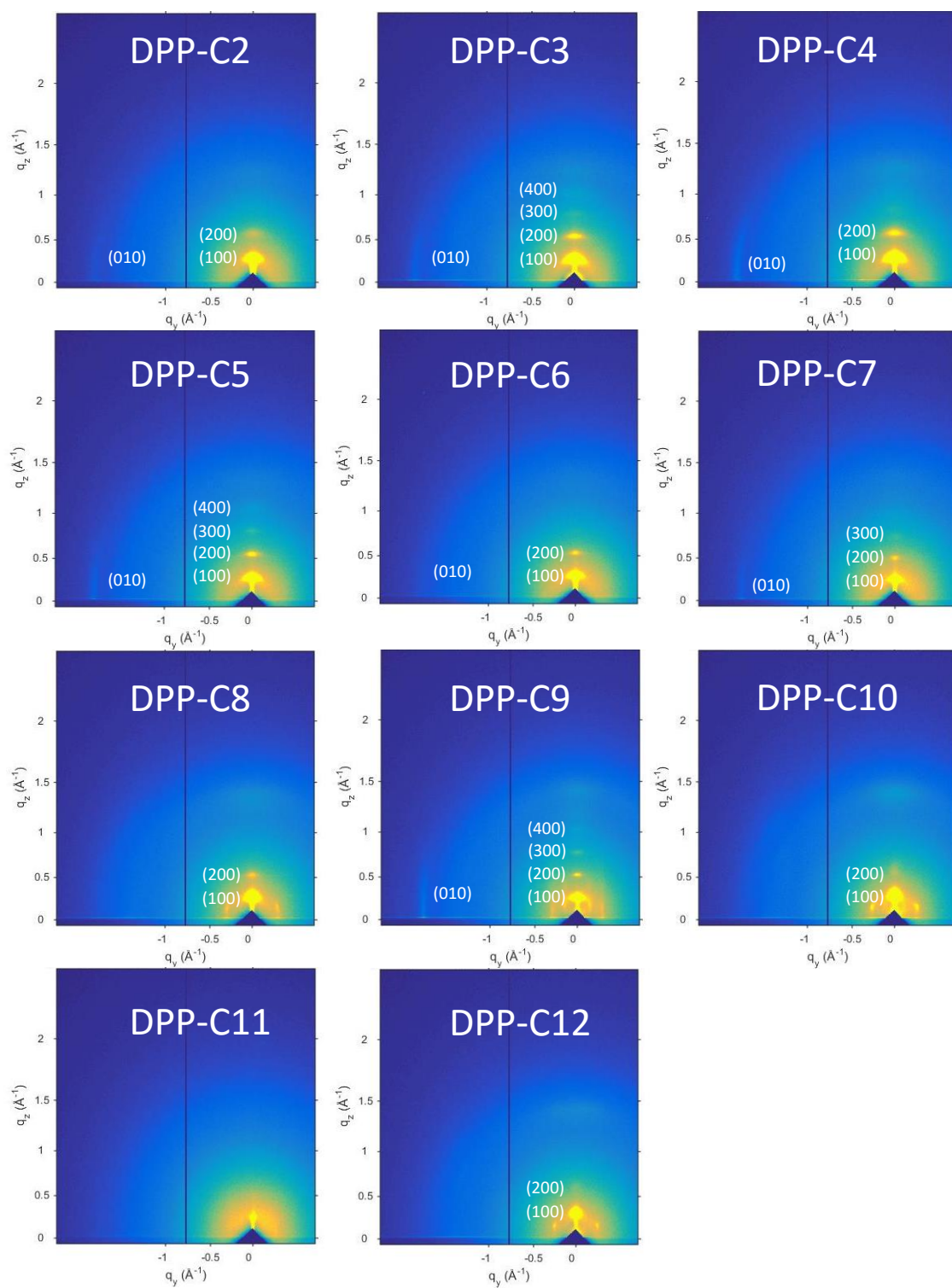


Figure S17 GIXRD images pure polymer DPP-Cm

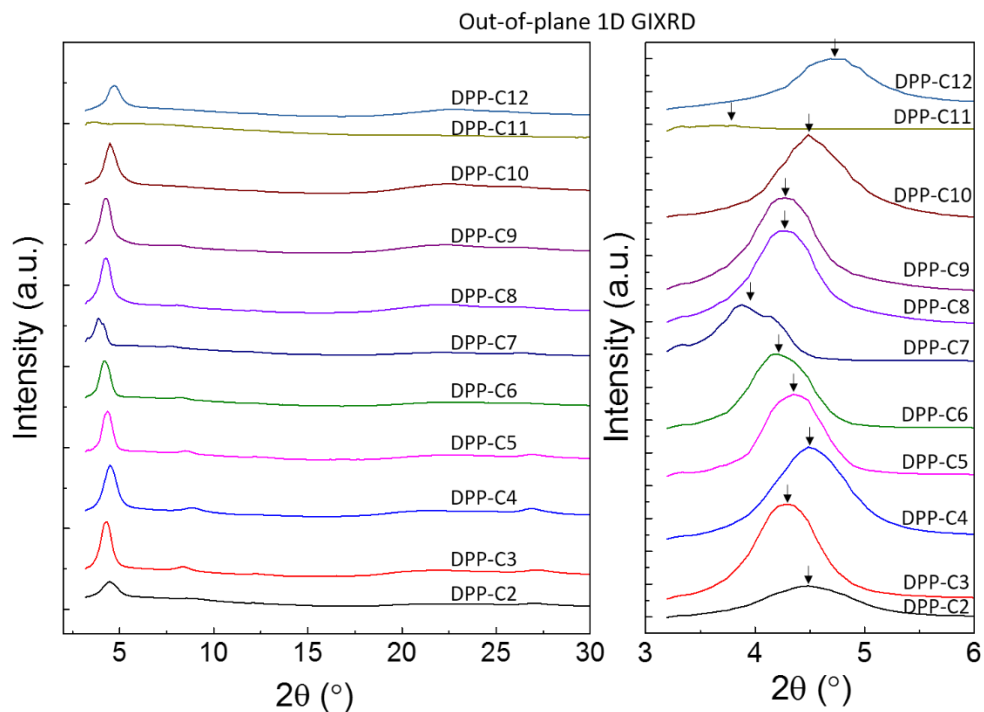


Figure S18 (a), Out-of-plane direction 1D-GIXRD. (b) shows the detail information of (100) peaks.

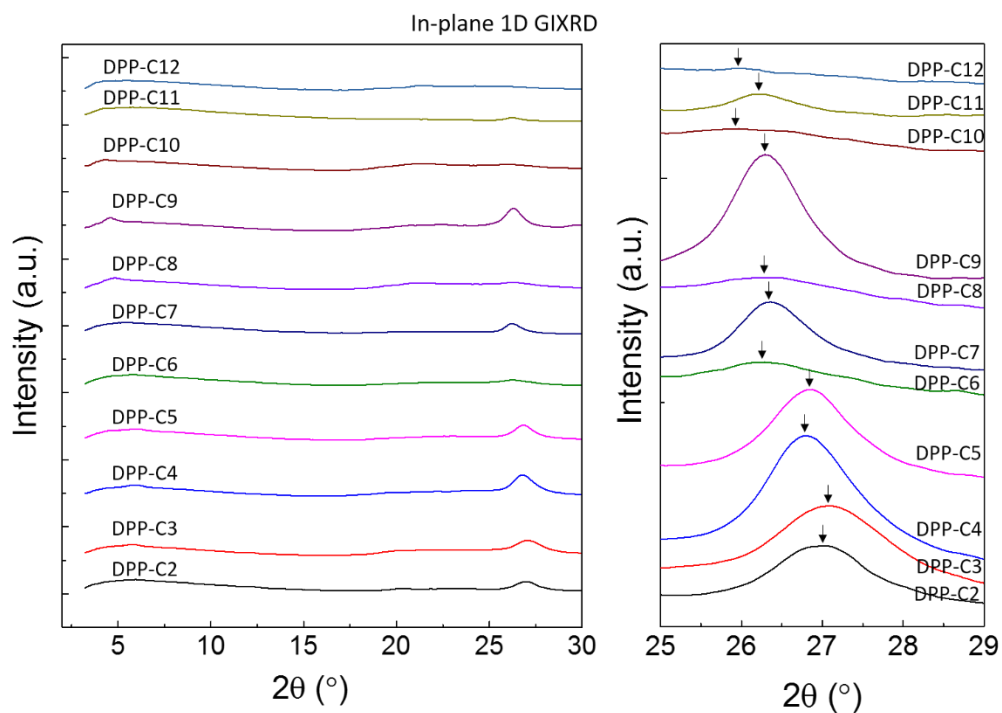


Figure S19 (a), In-plane direction 1D-GIXRD. (b) shows the detail information of (010) peak.

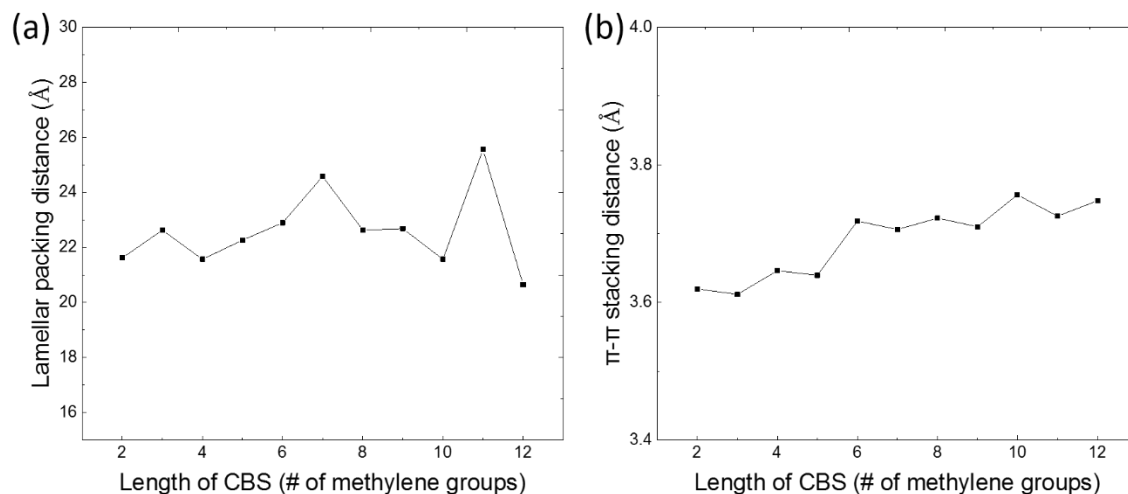


Figure S20 Lamellar packing (a) and π - π stacking (b) distances as a function of the number of methylene units in the CBSs. Results are calculated from 2D-GIXRD experiment.

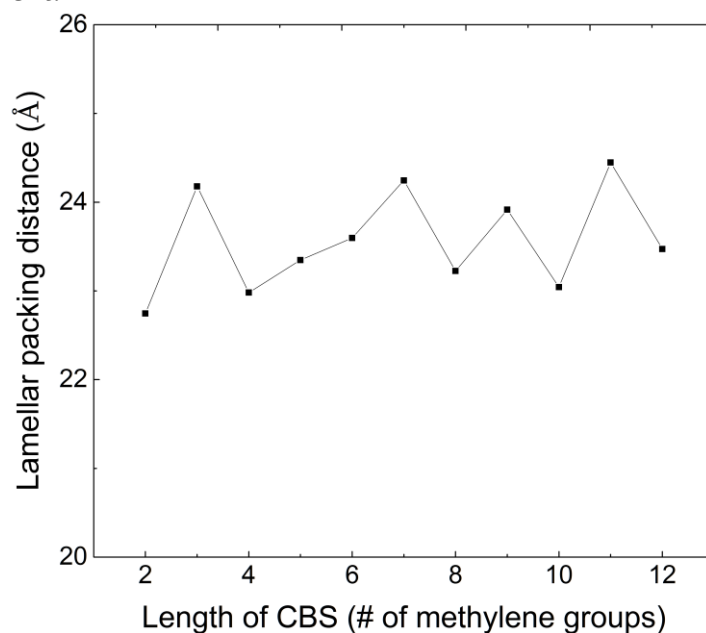


Figure S21 Lamellar packing distances as a function of the number of methylene units in the CBSs. Results are calculated from 1D regular XRD experiment.