Electronic Supplementary Information

Benzo[1,2-*b*:4,5-*b*']difuran and Furan Substituted Diketopyrrolopyrrole Alternating Copolymer for Organic Photovoltaics with High Fill Factor

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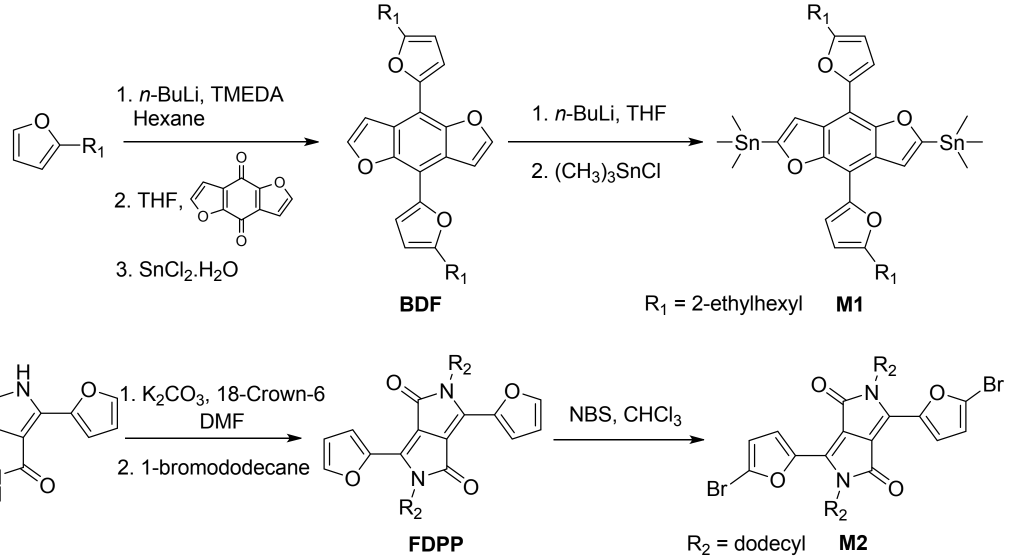


Scheme S1. Synthetic procedure of M1 and M2

1. Detailed Synthetic Procedure

1.1 Synthesis of 2-(2-ethylhexyl)furan

Furan (2.00 g, 29.38 mmol) was mixed with 100 mL THF in a three neck flask under nitrogen. The reaction mixture was cooled down to -78°C before 12.3 mL *n*-butyllithium (2.5 M in THF) was added dropwise to solution. After stirring for 2 hours, 2-ethylhexyl bromide (5.95g, 30.85 mmol) was injected in one portion and the reaction mixture was warmed to room temperature and then refluxed overnight. The reaction was quenched in DI water and extracted with hexane three times. The combined organic layer was then dried over anhydrous magnesium sulfate. After removing the solvent, the crude product was purified by silica gel column chromatography using hexane as eluent. Colorless oil was acquired as product. (Yield: 2.9 g, 55%) ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 7.29 (d, 1H), 6.27 (d, 1H), 5.97 (d, 1H), 2.55 (d, 2H), 1.63 (m, 1H), 1.28 (m, 8H), 0.87 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 155.65, 140.64, 110.00, 105.73, 38.71, 32.72, 32.01, 28.89, 25.91, 23.00, 14.11, 10.85.

1.2 Synthesis of 4,8-bis(5-(2-ethylhexyl)furan-2-yl)benzo[1,2-*b*:4,5-*b*']difuran (BDF)

2-(2-ethylhexyl)furan (562.5 mg, 3.12 mmol) was mixed with 30 mL hexane in a three neck flask under nitrogen. The reaction mixture was kept at -5°C while 1.37 mL *n*-butyllithium (2.5 M in THF) and tetramethylethylenediamine (398.8 mg, 3.43 mmol) were added. After 2 hours, the solution was diluted by adding 20 mL THF before benzo[1,2-*b*:4,5-*b*']difuran-4,8-dione (300 mg, 1.60 mmol) was added in one portion. The mixture was kept at -5°C for another 15 minutes before heating to reflux. Tin chloride dihydrate (1.87 g, 8.29 mmol) dissolved in 10% hydrochloric acid was injected in one portion after 2 hours of refluxing. The reaction was continued for another 3 hours before quenching in DI water. The mixture was extracted using hexane 3 times and the combined organic layer was dried over anhydrous magnesium sulfate. After removing the solvent, the crude product was purified by silica gel column chromatography using hexane as eluent. Light yellow solid was acquired as the product. (Yield: 350 mg, 42%) ^{1}H NMR (CDCl$_3$, 500 MHz), δ: 7.77 (d, 2H), 7.54 (d, 2H), 7.24 (d, 2H), 6.24 (d, 2H), 2.75 (d, 4H), 1.79 (m, 2H), 1.36 (m, 16H), 0.90 (m, 12H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ: 155.51, 148.15, 147.34, 145.16, 121.30, 111.57, 108.66, 108.18, 106.04, 39.08, 32.89, 32.27, 29.02, 26.06, 23.05, 14.15, 11.04.

1.3 Synthesis of (4,8-bis(5-(2-ethylhexyl)furan-2-yl)benzo[1,2-*b*:4,5-*b*']difuran-2,6-diyl)bis(trimethylstannane) (M1)

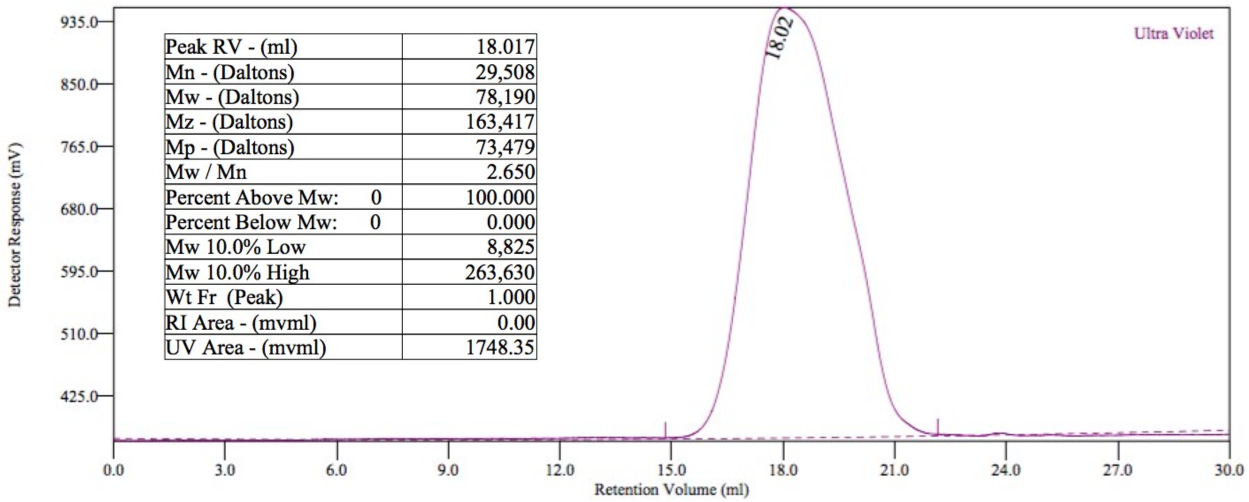
BDF (130 mg, 0.25 mmol) was dissolved in 50 mL THF in a three neck flask under nitrogen. 0.6 mL *n*-butyllithium (2.5 M in THF) was slowly added at -5°C. The reaction was kept for 2 hours at -5°C before 1.76 mL trimethyltin chloride (1 M in hexane) was injected in one portion. After keeping the reaction at room temperature for an additional 3 hours, the reaction mixture was quenched in DI water. The mixture was extracted using hexane by 3 times and the combined organic layer was dried over anhydrous magnesium sulfate. After removing the solvent, the yellow sticky product was used for polymerization without further purification. (Yield: 195 mg, 93%) ^{1}H NMR (CDCl$_3$, 500 MHz), δ: 7.68 (s, 2H), 7.20 (d, 2H), 6.24 (d, 2H), 2.77 (d, 4H), 1.79 (t, 2H), 1.37 (m, 16H), 0.97 (t, 6H), 0.89 (t, 6H), 0.47 (s, 18H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ: 165.42, 155.05, 151.01, 149.02, 121.62, 118.97, 111.02, 108.58, 104.54, 39.14, 32.95, 32.19, 29.14, 26.10, 22.99, 14.18, 11.16, -9.06

1.4 Synthesis of 2,5-didodecyl-3,6-di(furan-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (FDPP)

3,6-di(furan-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (800 mg, 2.98 mmol), potassium carbonate (1.85 g, 13.42 mmol) and 20 mg 18-crown-6 were dissolved in 20 mL DMF. The reaction was kept at 120°C for 3 hours and then 1-bromododecane (2.97 g, 11.92 mmol) was added. The reaction mixture was kept at refluxing for 12 hours before quenching in DI water. The mixture was extracted using methylene chloride 3 times and combined organic layer was dried over anhydrous magnesium sulfate. After removing the solvent, the crude product was purified by silica gel column chromatography using a mixture of hexane and methylene chloride as the eluent (hexane: methylene chloride=1: 1). A pink solid was obtained as the product. (Yield: 685 mg, 38%) ^{1}H NMR (CDCl$_3$, 500 MHz), δ: 8.30 (d, 2H), 7.63 (s, 2H), 6.69 (d, 2H), 4.10 (t, 4H), 1.67 (m, 4H), 1.27 (m, 36H), 0.87 (t, 6H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ: 160.88, 145.14, 144.69, 133.67, 120.10, 113.45, 106.46, 42.43, 31.92, 30.22, 29.65, 29.63, 29.60, 29.53, 29.35, 29.30, 26.86, 22.69, 14.12.

1.5 Synthesis of 3,6-bis(5-bromofuran-2-yl)-2,5-didodecylpyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (M2)

FDPP (180 mg, 0.30 mmol) was dissolved in 30 mL chloroform under argon and protected from light. *N*-bromosuccinimide (116 mg, 0.65 mmol) was added to the solution in portions at 0°C. The progress of the reaction was monitored by thin-layer chromatography. The reaction was quenched by pouring the solution to DI water and the mixture was extracted using chloroform 3 times. The combined organic layer was dried over anhydrous magnesium sulfate. After removing the solvent, the crude product was purified by column chromatography with chloroform as eluent. Purple solid was achieved as the product. (Yield: 135 mg, 60%) ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 8.25 (d, 2H), 6.63 (d, 2H), 4.04 (t, 4H), 1.68 (m, 4H), 1.24 (m, 36H), 0.87 (t, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 160.53, 146.18, 132.52, 126.42, 122.11, 115.52, 106.29, 42.51, 31.93, 30.21, 29.65, 29.60, 29.58, 29.37, 29.28, 26.87, 22.70, 14.13.



Peak RV - (ml)	18.017
Mn - (Daltons)	29,508
Mw - (Daltons)	78,190
Mz - (Daltons)	163,417
Mp - (Daltons)	73,479
Mw / Mn	2.650
Percent Above Mw: 0	100.000
Percent Below Mw: 0	0.000
Mw 10.0% Low	8,825
Mw 10.0% High	263,630
Wt Fr (Peak)	1.000
RI Area - (mvml)	0.00
UV Area - (mvml)	1748.35

Figure S1. Size exclusion chromatography results of P(BDF-FDPP)

Table S1. Percentage of DIO in blend [P(BDF-FDPP): PC$_{71}$BM = 1: 2]

	J_{sc}(mA/cm^2)	V_{oc}(V)	FF	PCE(%)	Thickness
0%	1.45 ± 0.06 (1.51)	0.73 ± 0.01 (0.74)	0.66 ± 0.03 (0.64)	0.66 ± 0.03 (0.71)	95.5
1%	4.25 ± 0.37 (4.69)	0.69 ± 0.01 (0.69)	0.69 ± 0.01 (0.70)	2.01 ± 0.18 (2.26)	117.2
2%	8.33 ± 0.27 (8.69)	0.68 ± 0.01 (0.68)	0.71 ± 0.01 (0.72)	4.06 ± 0.09 (4.17)	111.5
3%	9.02 ± 0.07 (9.10)	0.67 ± 0.01 (0.67)	0.71 ± 0.01 (0.72)	4.29 ± 0.04 (4.34)	110.9
4%	8.60 ± 0.18 (8.67)	0.67 ± 0.01 (0.68)	0.71 ± 0.01 (0.72)	4.10 ± 0.08 (4.23)	115.2

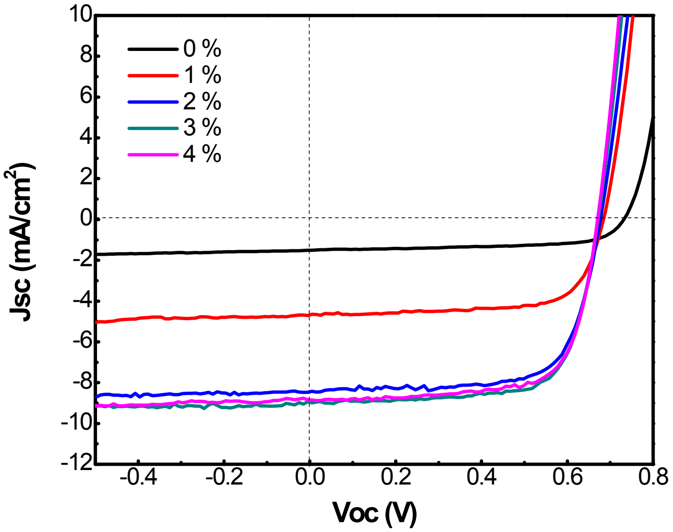


Figure S2. *J-V* curve of photovoltaic devices fabricated from different percentage of DIO.

[P(BDF-FDPP): $PC_{71}BM$ = 1: 2]

Table S2. Different weight ratio with 3% DIO added

	J_{sc}(mA/cm^2)	V_{oc}(V)	FF	PCE(%)	Thickness
1: 1.0	7.31 ± 0.26 (7.62)	0.68 ± 0.01 (0.68)	0.66 ± 0.01 (0.68)	3.25 ± 0.10 (3.36)	109.2
1: 1.5	8.82 ± 0.25 (9.05)	0.67 ± 0.01 (0.67)	0.71 ± 0.01 (0.71)	4.16 ± 0.14 (4.29)	113.5
1: 2.0	9.02 ± 0.07 (9.10)	0.67 ± 0.01 (0.67)	0.71 ± 0.01 (0.72)	4.29 ± 0.04 (4.34)	110.9
1: 2.5	8.19 ± 0.11 (8.28)	0.67 ± 0.01 (0.68)	0.69 ± 0.01 (0.70)	3.83 ± 0.02 (3.85)	115.4
1: 3.0	7.41 ± 0.08 (7.59)	0.68 ± 0.01 (0.68)	0.68 ± 0.01 (0.70)	3.47 ± 0.05 (3.56)	106.1

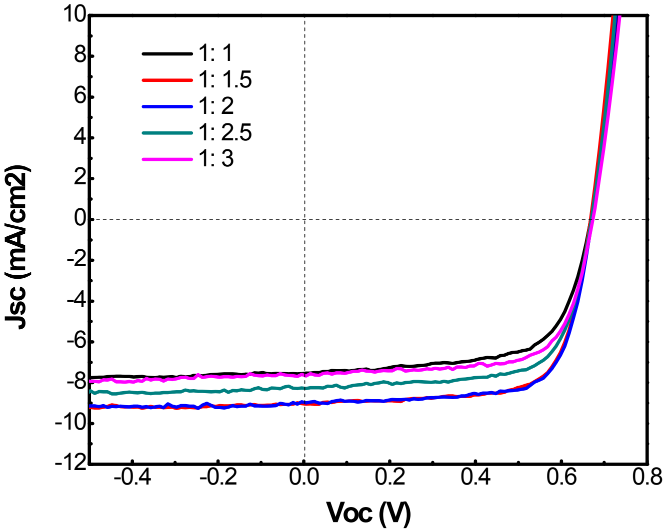


Figure S3. *J-V* curve of photovoltaic devices fabricated from different weight ratios.

Table S3. Percentage of DPE in blend [P(BDF-FDPP): $PC_{71}BM$ = 1: 2]

	Jsc(mA/cm^2)	Voc(V)	FF	PCE(%)	Thickness
1%	3.63 ± 0.11 (3.76)	0.69 ± 0.01 (0.70)	0.63 ± 0.01 (0.63)	1.58 ± 0.05 (1.64)	120.1
3%	9.78 ± 0.18 (9.91)	0.66 ± 0.01 (0.66)	0.70 ± 0.01 (0.70)	4.53 ± 0.09 (4.60)	119.4
4%	11.18 ± 0.40 (11.52)	0.67 ± 0.01 (0.67)	0.72 ± 0.01 (0.73)	5.40 ± 0.16 (5.55)	114.5
5%	11.17 ± 0.16 (11.37)	0.67 ± 0.01 (0.67)	0.71 ± 0.01 (0.72)	5.29 ± 0.16 (5.50)	112.0
6%	10.93 ± 0.21 (11.18)	0.67 ± 0.01 (0.67)	0.71 ± 0.01 (0.72)	5.14 ± 0.11 (5.23)	113.7
7%	10.58 ± 0.21 (10.80)	0.66 ± 0.01 (0.66)	0.69 ± 0.01 (0.70)	4.83 ± 0.05 (4.88)	112.5

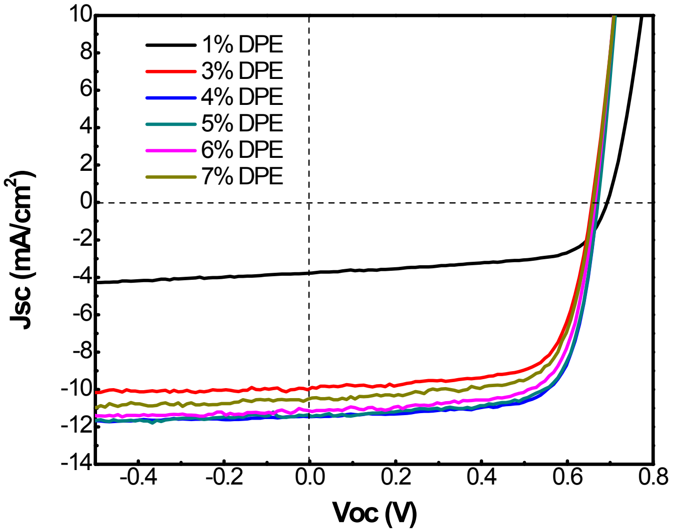


Figure S4. *J-V* curve of photovoltaic devices fabricated from different percentage of DPE.

[P(BDF-FDPP): $PC_{71}BM$ = 1: 2]

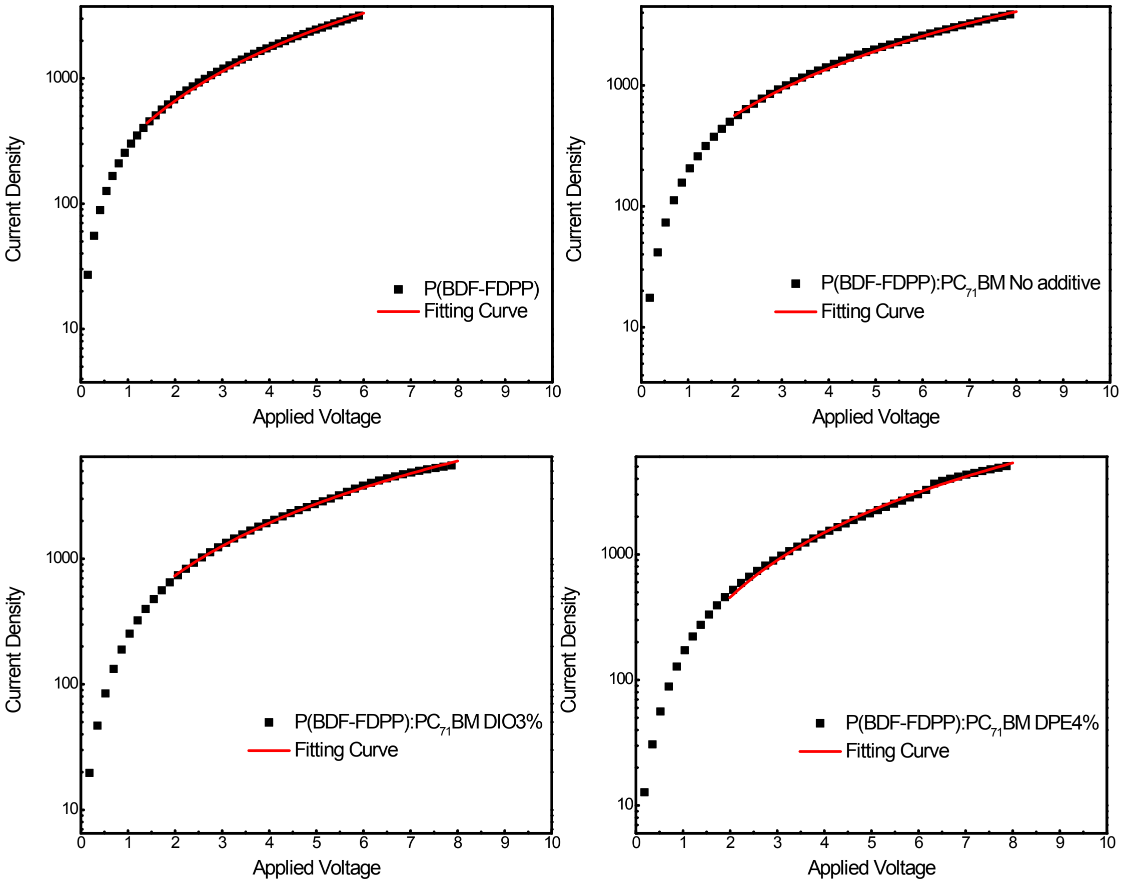


Figure S5. Hole mobility measured from Schottky diode under different conditions

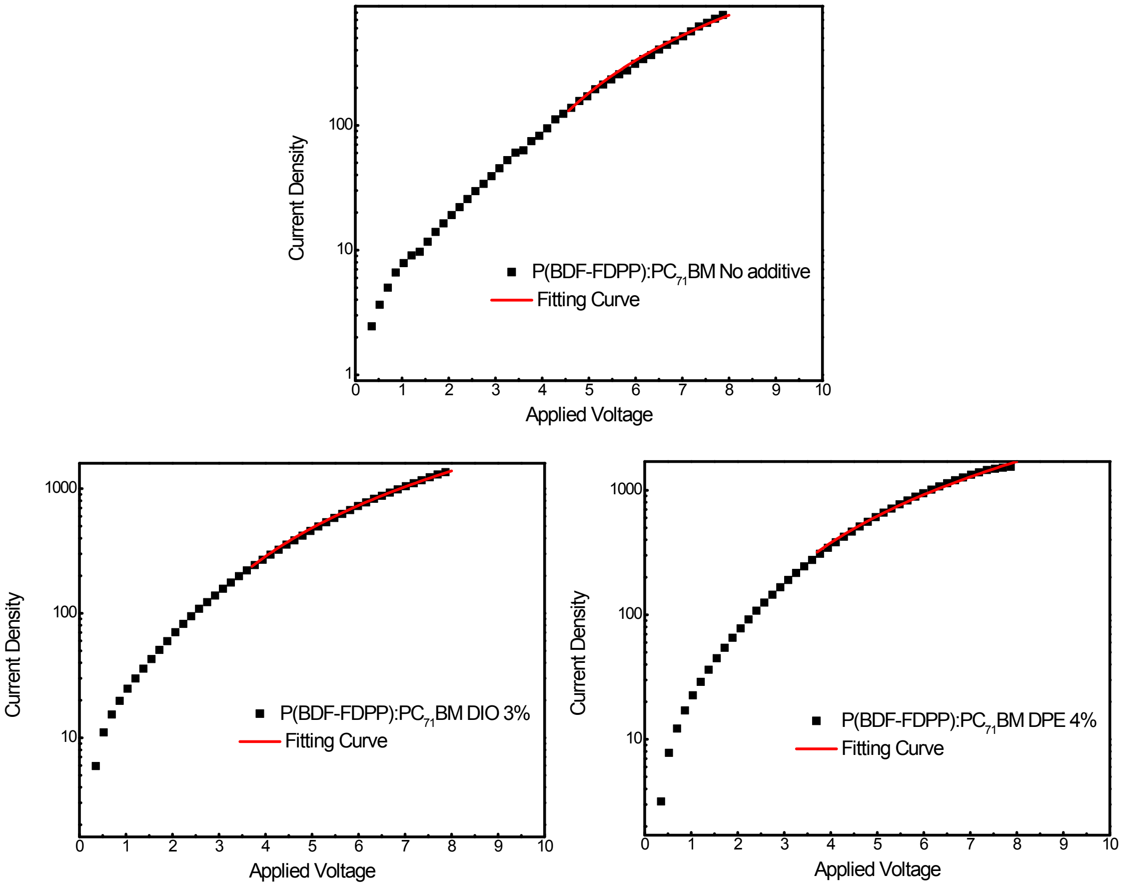


Figure S6. Electron mobility measured from Schottky diode under different conditions

Atomic Force Microscopy (AFM) Sample Preparation

The samples were prepared under a dry nitrogen environment in a glovebox. The 2 × 2 cm silicon wafers with native oxide were cleaned with hexanes, acetone and isopropanol then dried under nitrogen; followed by UV/Ozone treatment at 120 °C for 45 minutes (Novascan PSD-UVT). The wafers were then placed under vacuum (10 mTorr) for 90 min. 1 mg/mL CB solutions were prepared for thick films and a 0.1 mg/mL CB solution for ultra-thin films. Solutions were then heated to 50 °C in glass vials for 30 minutes, filtered through a 0.22 mm PTFE syringe filter using a glass syringe, and re-heated for 10 minutes prior to dropcasting hot solutions onto the wafers placed inside a petri dish. The films were dried overnight in an inert environment prior to measurement in AFM tapping mode.

AFM imaging conditions:

The as-obtained films were imaged with a Bruker Dimension V hybrid AFM in tapping mode. Tapping mode tips Bruker MPP-11220-10 with a spring constant of 40 N/m, a resonance frequency of 300 kHz, tuned at 15% off resonance, with a drive amplitude of 10 mV at a scan rate of 0.5 Hz for soft tapping mode conditions of the ultra-thin film. The thick film was measured using the same tip with a drive amplitude of 30 mV at a scan rate of 1 Hz. Image resolution for a 2 × 2 μm image was 1024 pixels/line × 1024 lines.

Additional AFM Profiles

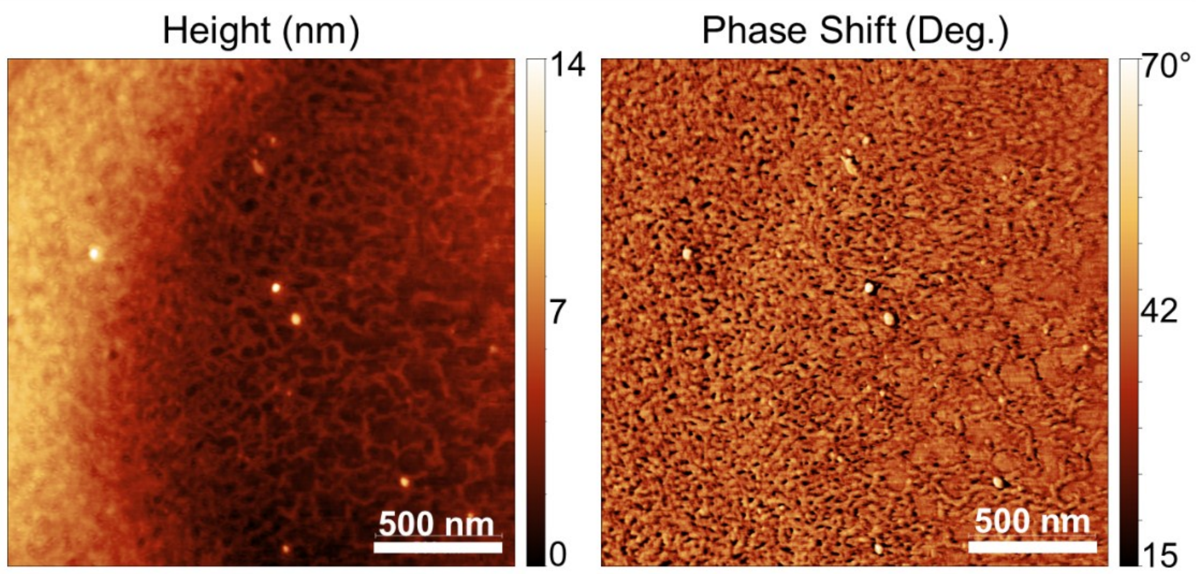


Figure S7. Tapping mode AFM of ultra-thin film of P(BDF-FDPP).

GIWAXS Post-Processing

GIWAXS 2D pixel array images were post processed using Mathematica Software (Wolfram Research, Inc.). The scattering wavevector transfer components q_x, q_y and q_z were treated elastically to derive q|| and q⊥ functions as described in literature.[1] Diffuse scattering outside of the Ewald sphere was depicted as a missing wedge, thereby any 2D-GIWAXS patterns were representative of the satisfied Bragg diffraction condition. 2D images were normalized by the exposure time and the invariant. All images and profiles were blank subtracted at the appropriate incidence angle using a blank correction factor (BCF, scales the blank appropriately), Table S4, to eliminate the scattering from the substrate.

Table S4. GIWAXS Parameters for Blank Subtraction and Normalization

Sample **P(BDF-FDPP)**	Incidence Angle (°)	Exposure Time (sec)	Blank Correction Factor (BCF)	Invariant
P(BDF-FDPP) Homopolymer	0.15	5	1.22	1350.60
Polymer : $PC_{71}BM$ (1: 2) No Additive	0.09	5	1.45	1188.32
Polymer : $PC_{71}BM$ (1: 2) 3% DIO	0.16	5	1.01	1083.03
Polymer : $PC_{71}BM$ (1: 2) 4% DPE	0.15	3	0.90	1152.68

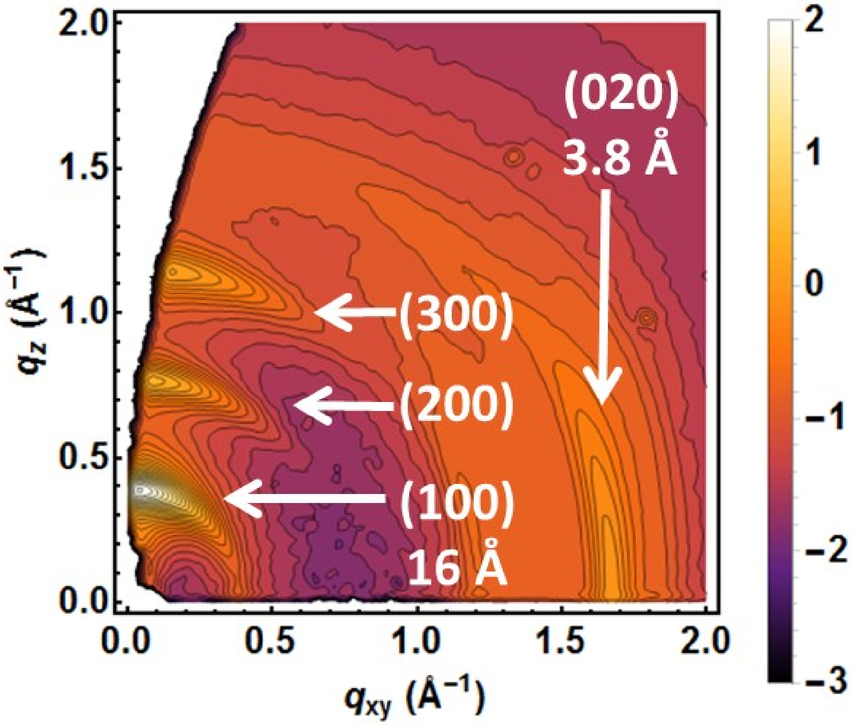


Figure S8. GIWAXS 2D pattern of rr-P3HT (Mn = 38,200, Đ = 1.12) were blank subtracted (BCF: 1.116) and normalized by exposure time (5 sec.), incident angle (0.14°) and the invariant (1127.17) with Log scale intensities represented by the scale bar. Image accounts for diffuse scattering by representing the Ewald sphere as a missing wedge.

AFM Images used for Height Profile Analysis

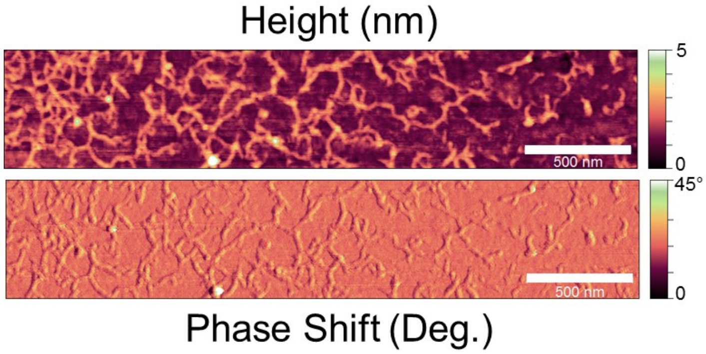


Figure S9. Tapping mode AFM image of ultra-thin film of P(BDF-FDPP) used for height profile analysis. (159 lines × 1020 pixels/line). Each line profile was baseline corrected prior to analysis using Mathematica software (Wolfram Research, Inc.). Peak values were tabulated and normalized by the total area to determine the statistical height distribution of the image, shown in Figure 9 a.

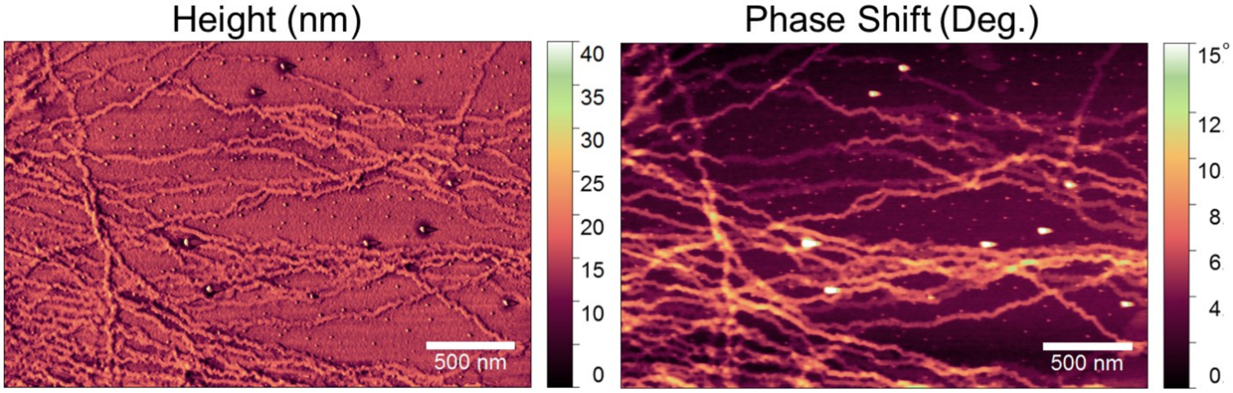


Figure S10. Tapping mode AFM image of "ultra-thin" film of rr-P3HT used for height profile analysis (508 lines × 776 pixels/line). Each line profile was baseline corrected prior to analysis using Mathematica software (Wolfram Research, Inc.). Peak values were tabulated and normalized by the total area to determine the statistical height distribution of the image, shown in Figure 9 b.

^{1}H and ^{13}C NMR

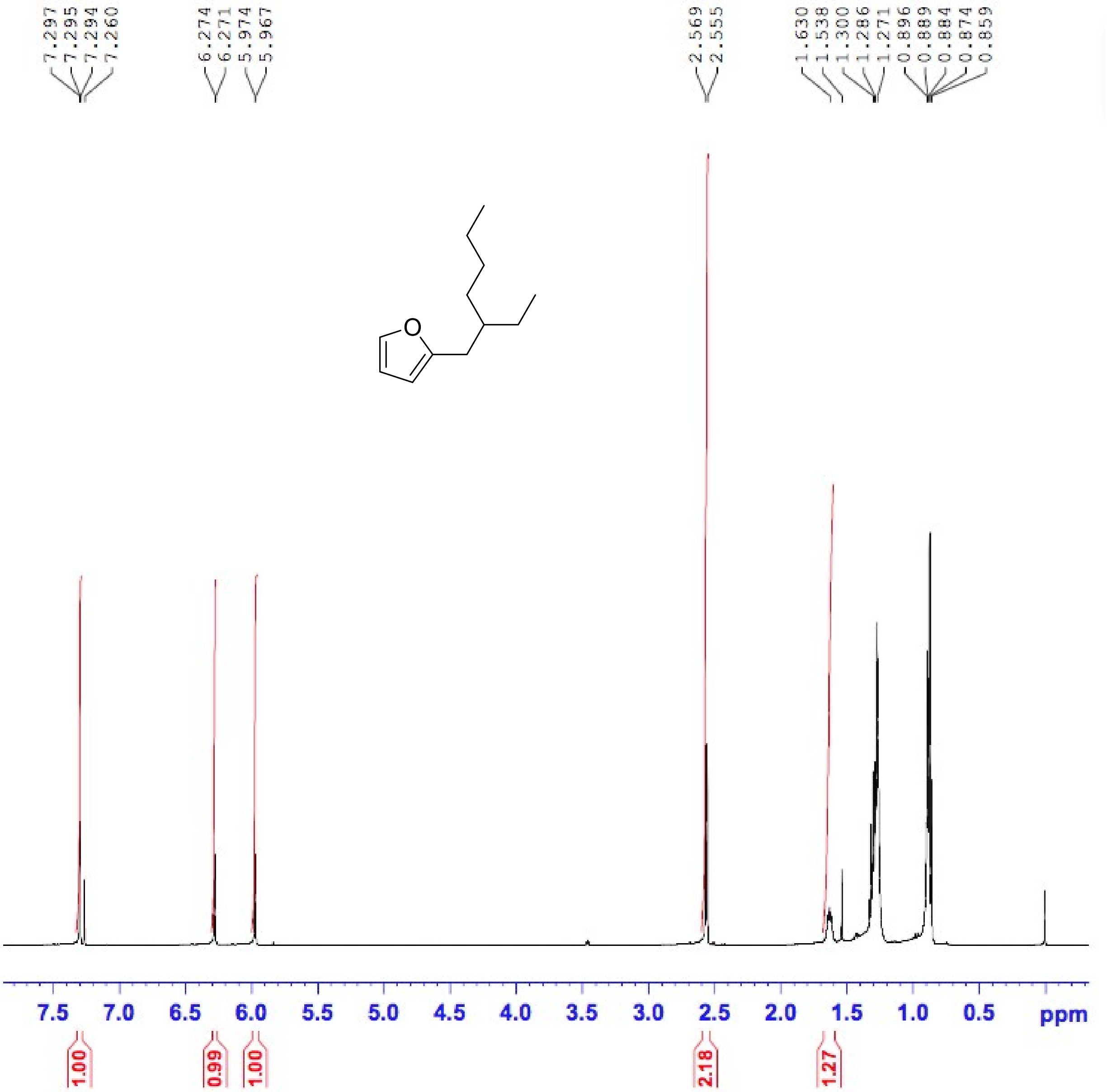


Figure S11. ^{1}H NMR of 2-(2-ethylhexyl)furan

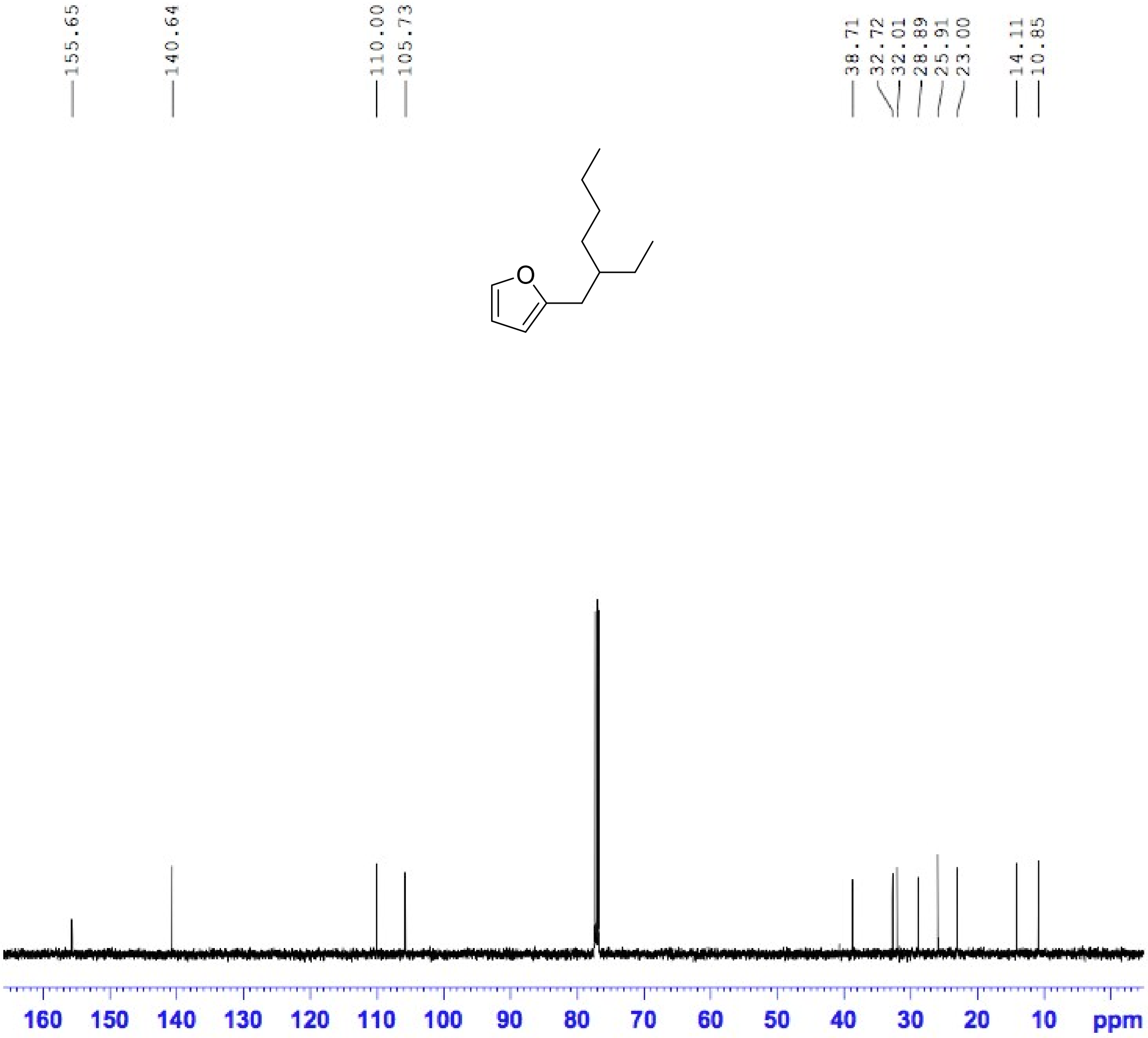


Figure S12. ^{13}C NMR of 2-(2-ethylhexyl)furan

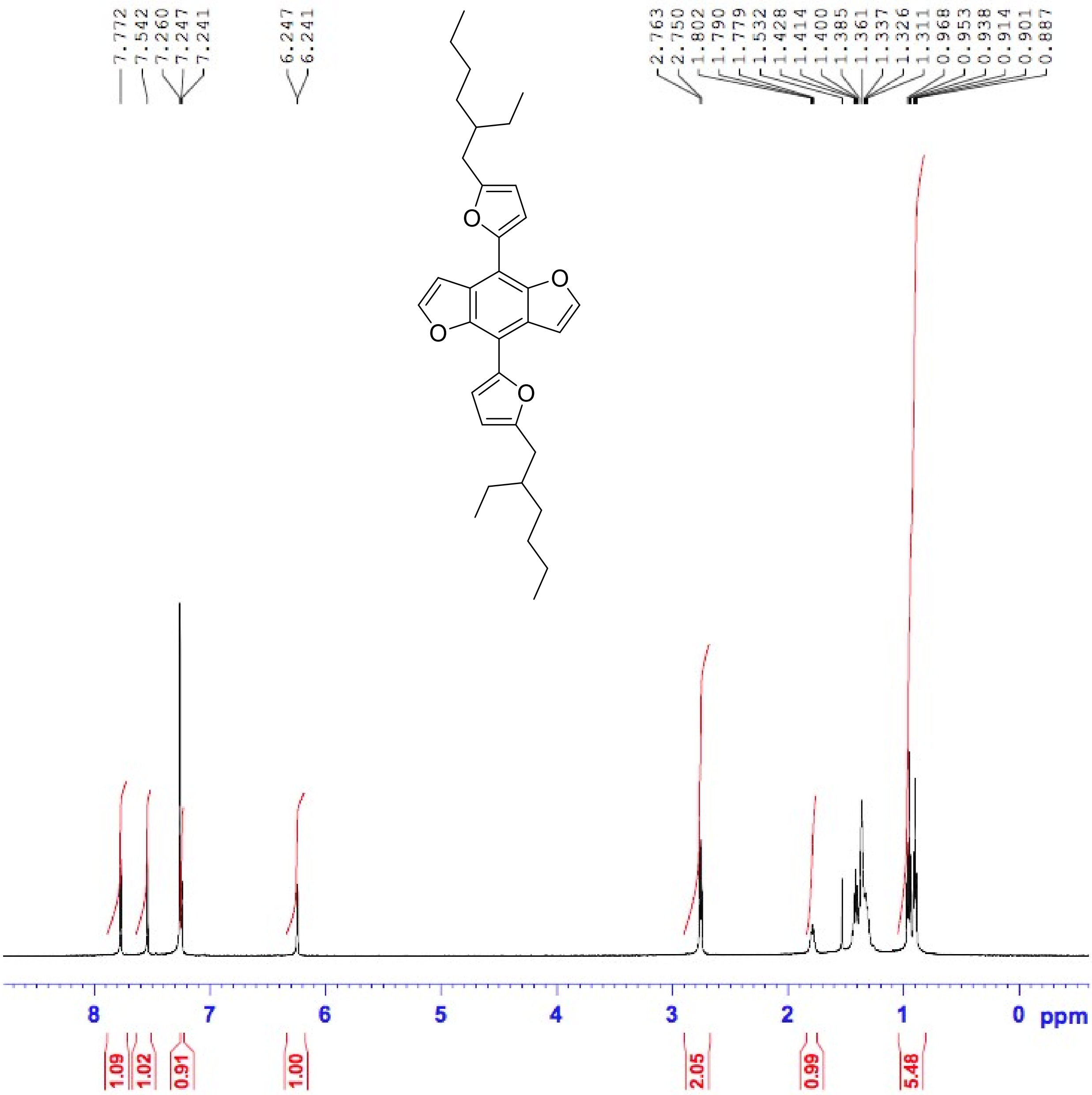


Figure S13. ^{1}H NMR of 4,8-bis(5-(2-ethylhexyl)furan-2-yl)benzo[1,2-*b*:4,5-*b*']difuran (BDF)

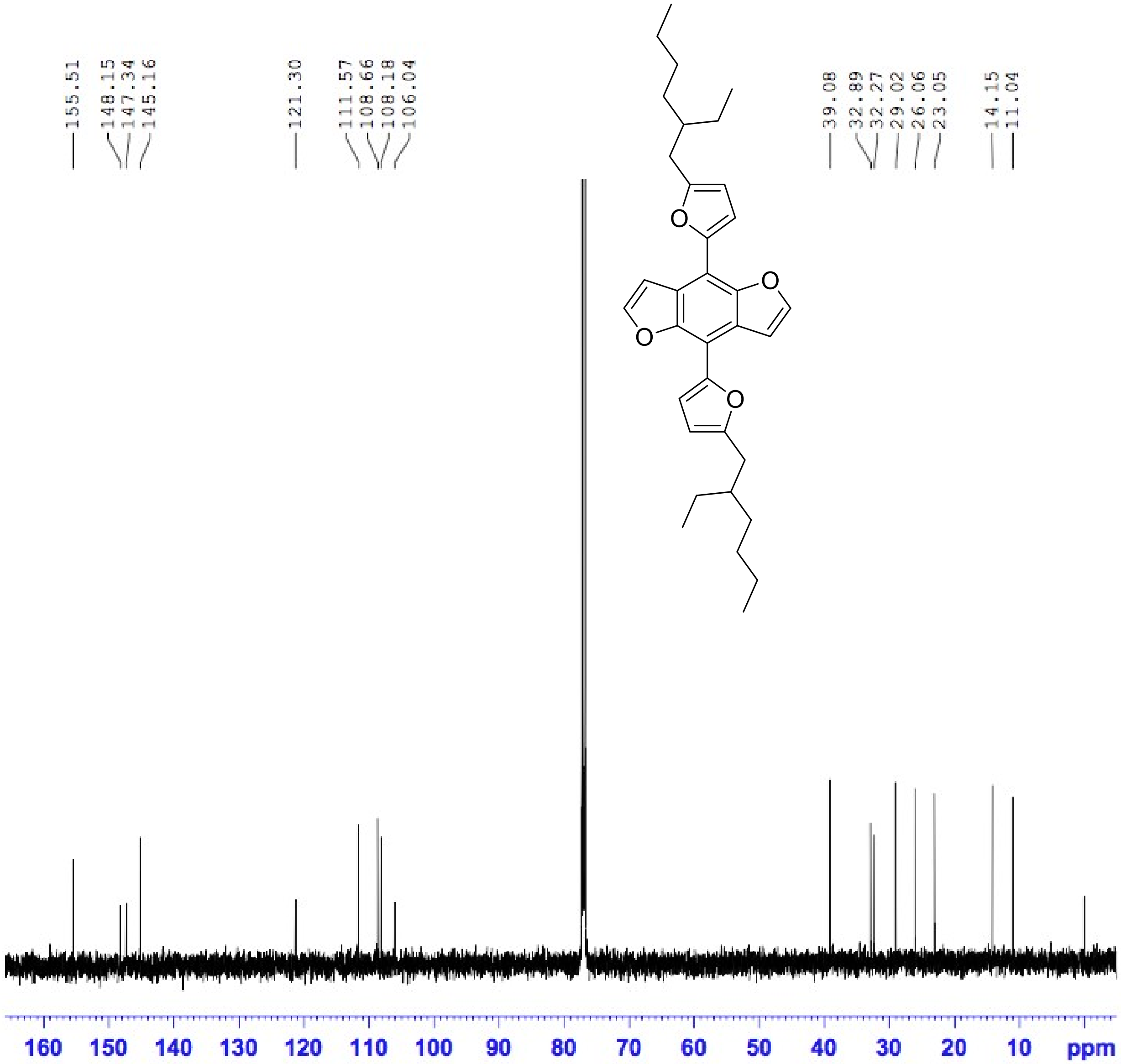


Figure S14. ^{13}C NMR of 4,8-bis(5-(2-ethylhexyl)furan-2-yl)benzo[1,2-*b*:4,5-*b*']difuran (BDF)

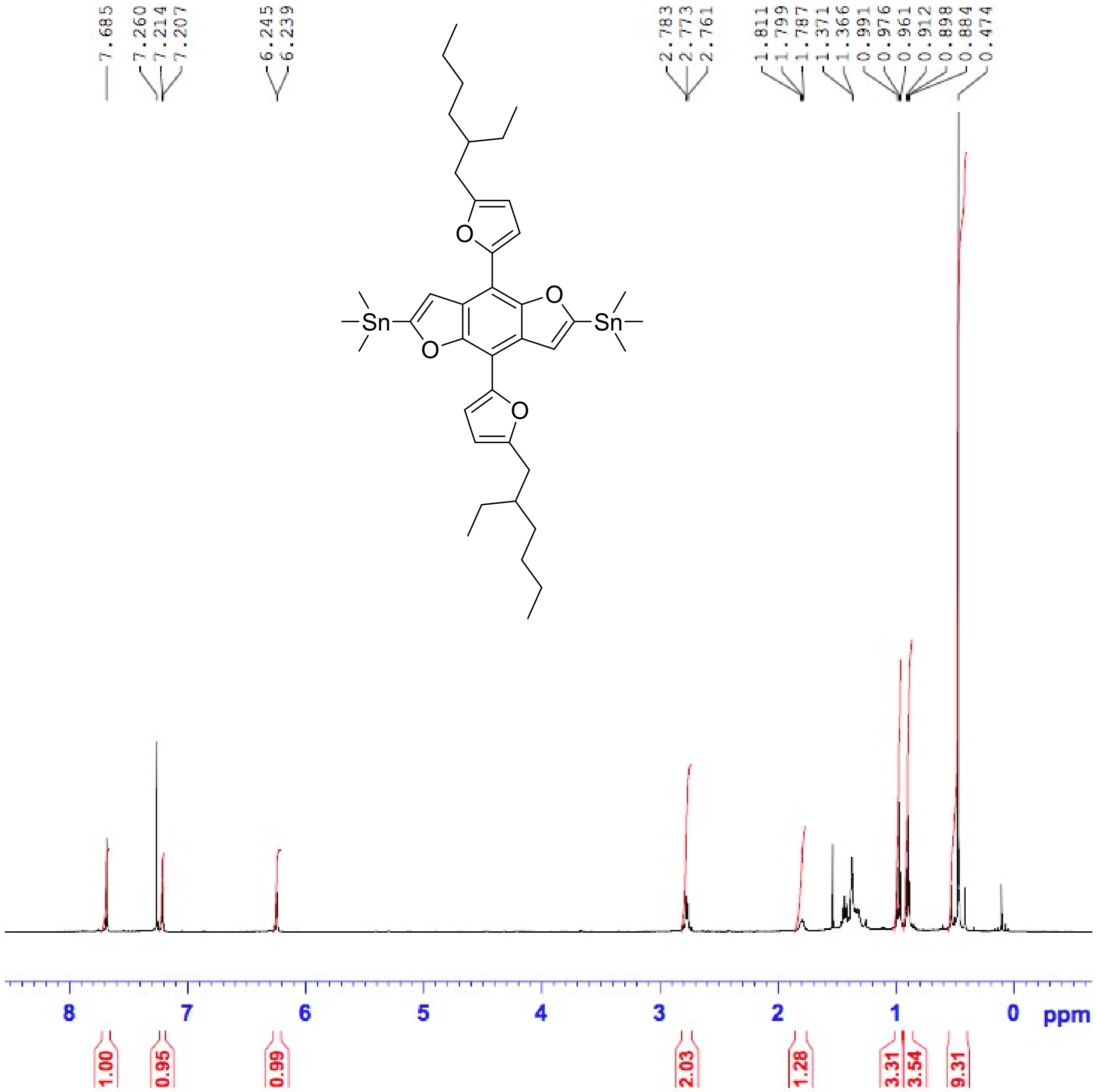


Figure S15. ^{1}H NMR of (4,8-bis(5-(2-ethylhexyl)furan-2-yl)benzo[1,2-*b*:4,5-*b*']difuran-2,6-diyl)bis(trimethylstannane) (M1)

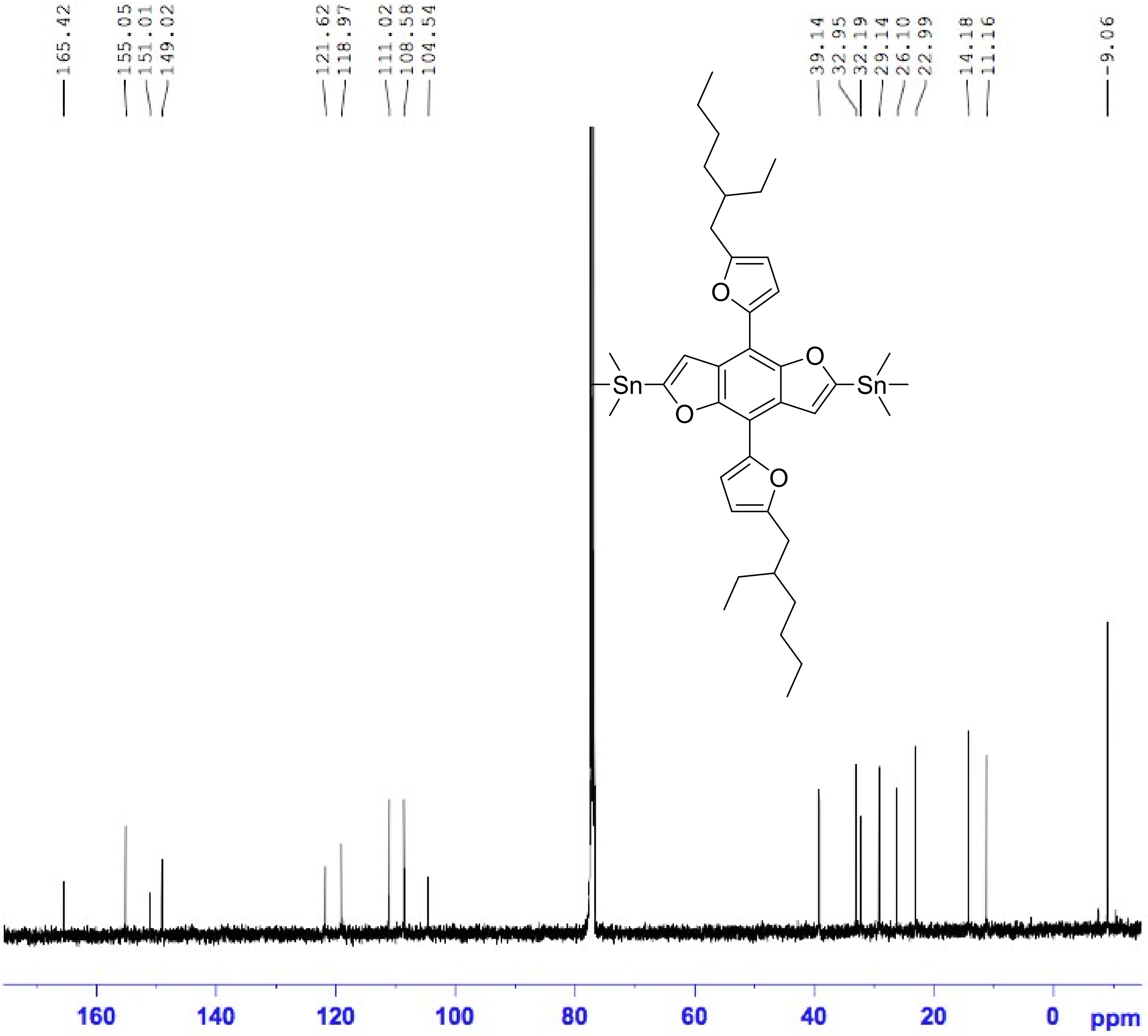


Figure S16. ^{13}C NMR of (4,8-bis(5-(2-ethylhexyl)furan-2-yl)benzo[1,2-*b*:4,5-*b*']difuran-2,6-diyl)bis(trimethylstannane) (M1)

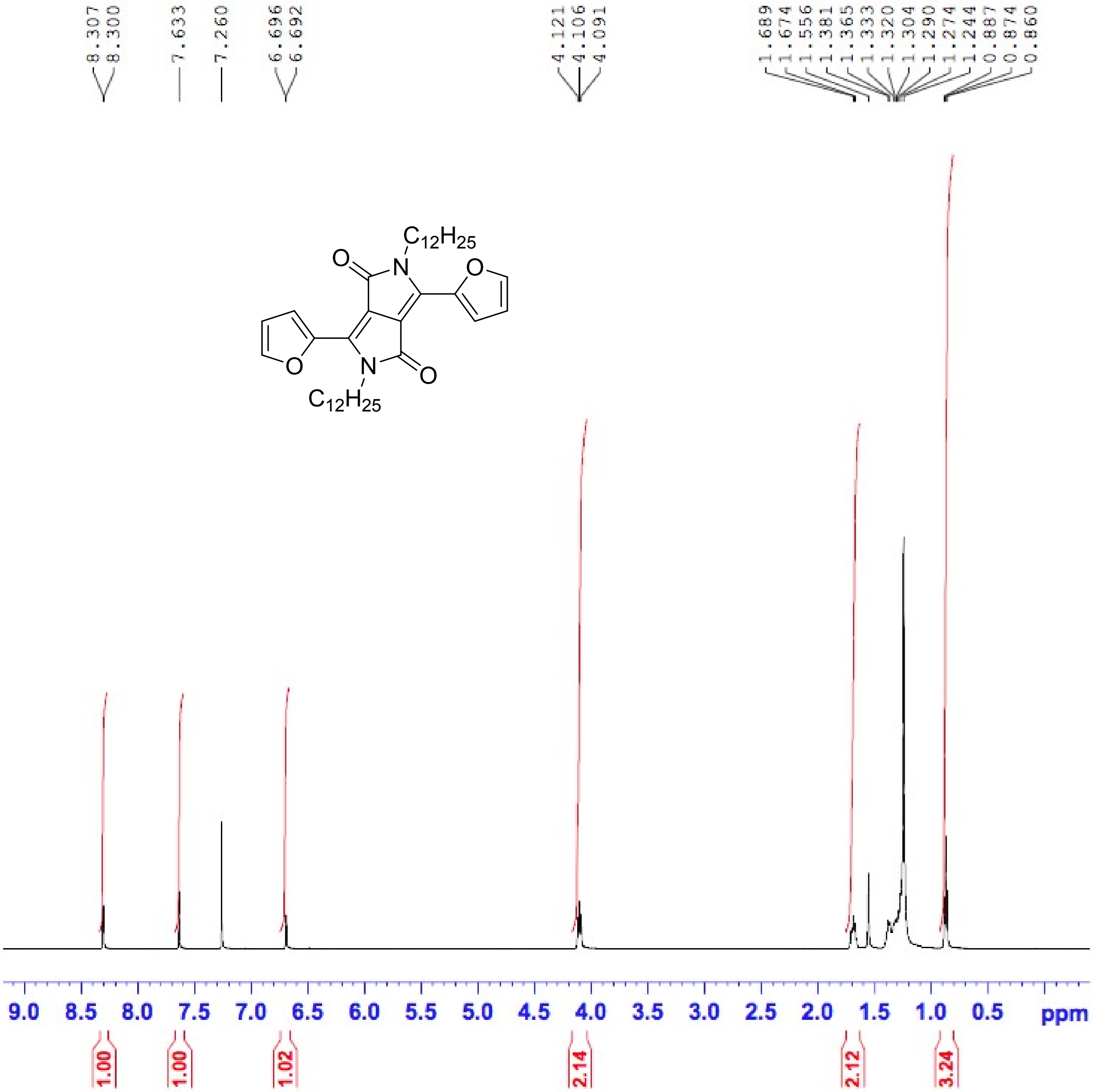


Figure S17. ^{1}H NMR of 2,5-didodecyl-3,6-di(furan-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (FDPP)

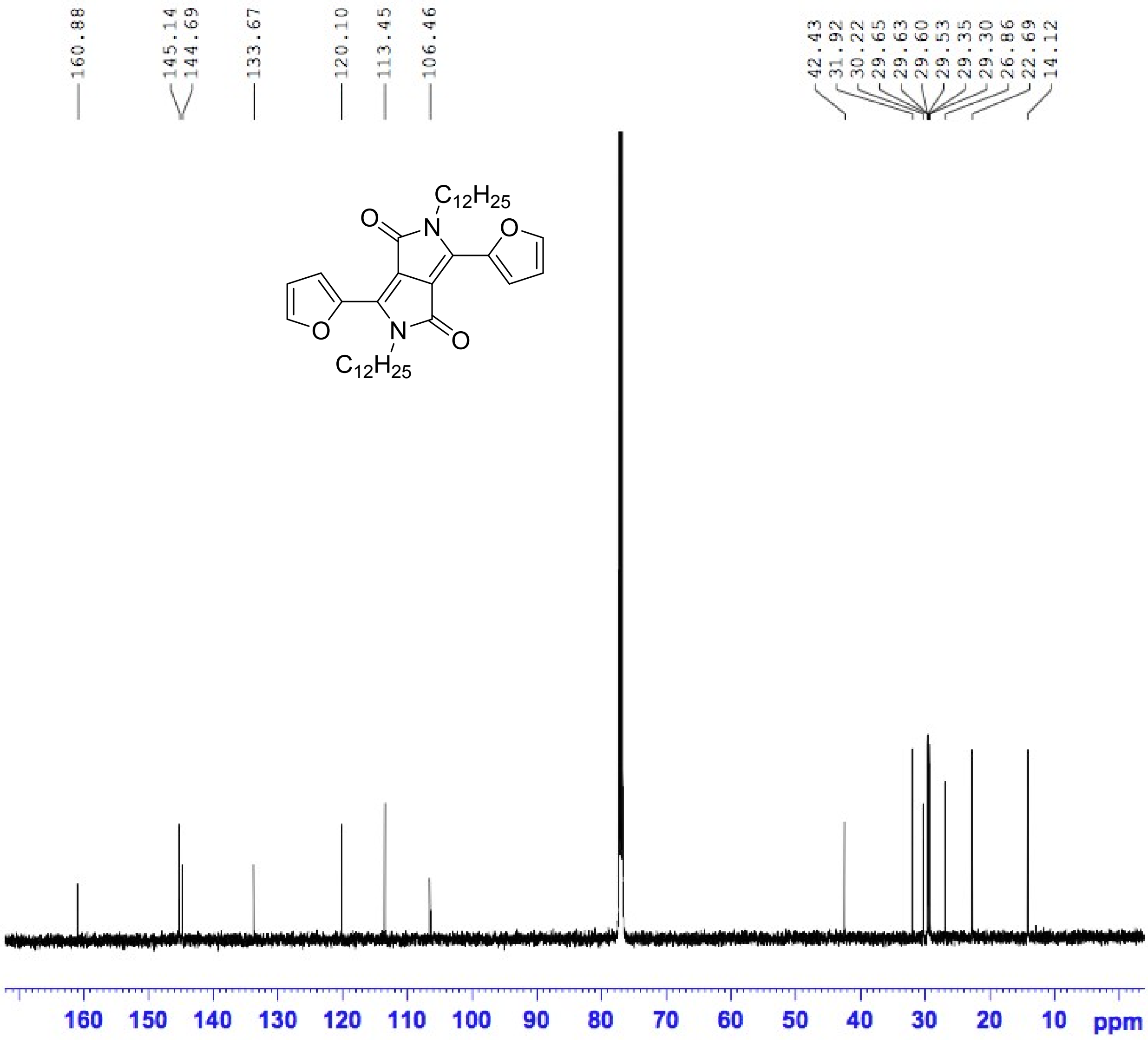


Figure S18. ^{13}C NMR of 2,5-didodecyl-3,6-di(furan-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (FDPP)

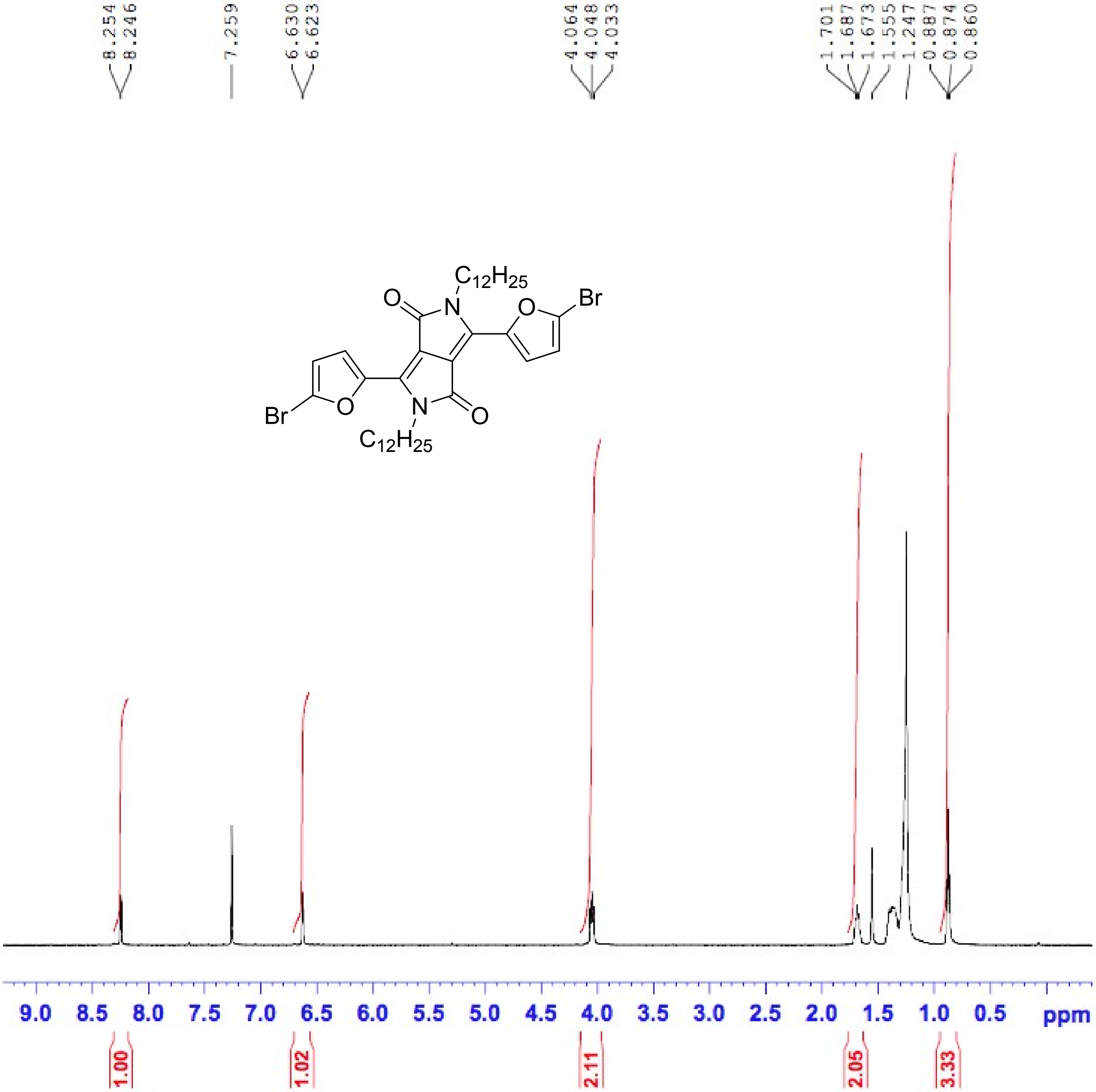


Figure S19. ^{1}H NMR of 3,6-bis(5-bromofuran-2-yl)-2,5-didodecylpyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (M2)

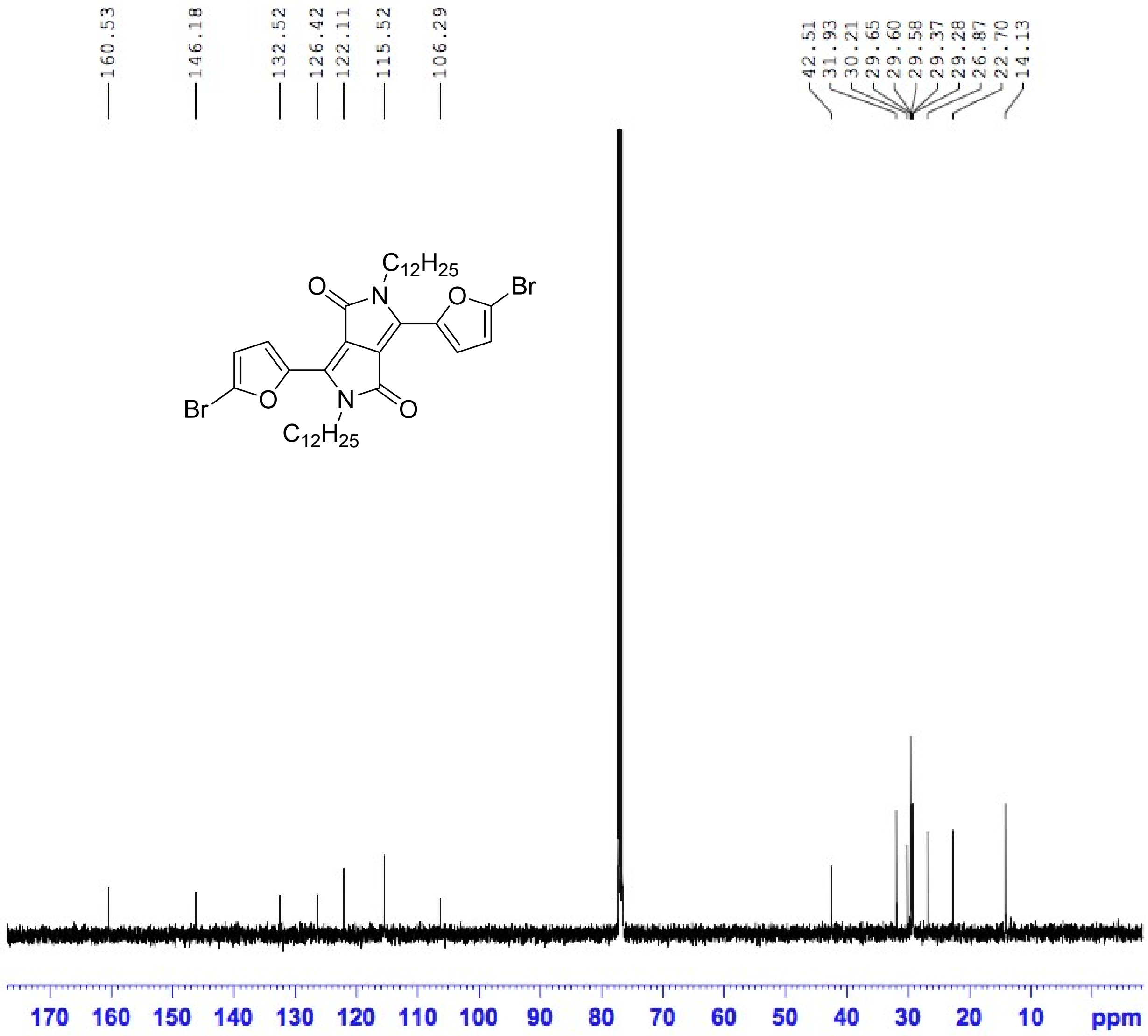


Figure S20. ^{13}C NMR of 3,6-bis(5-bromofuran-2-yl)-2,5-didodecylpyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (M2)

References:

1. Renaud, G.; Lazzari, R.; Leroy, F., Probing Surface and Interface Morphology with Grazing Incidence Small Angle X-Ray Scattering. *Surf. Sci. Rep* **2009,** 4, 255.