

Supporting Information

Furan Containing Diketopyrrolopyrrole Copolymers: Synthesis, Characterization, Organic Field Effect Transistor Performance and Photovoltaic Properties

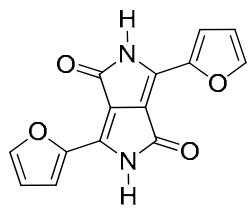
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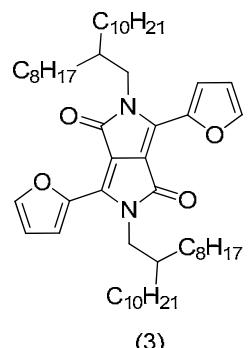
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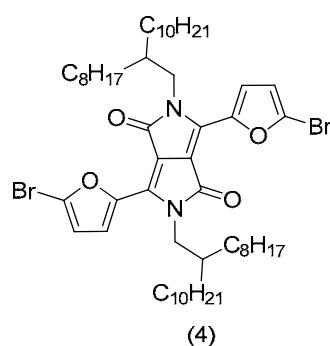
Synthesis of 3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (2): To a three-neck flask containing 2-methyl-1-butanol (60 mL) was added sodium (3.45 g, 0.15 mol) under argon. The mixture was heated to 90 °C and FeCl₃ (50 mg) was added. After sodium disappeared, the solution was cooled to 85 °C. 2-Furonitrile (9.31 g, 0.10 mol) was added to the reaction mixture, followed by drop-wise addition of diisopropyl succinate (8.1 g, 0.04 mol) in 2-methyl-1-butanol (5 mL) over 1 h at 85 °C. When the addition was completed, the mixture was stirred for additional 2 h at this temperature. The reaction mixture was then cooled to 50 °C, diluted with methanol (50 mL), and then slowly neutralized with glacial acetic acid (~15 mL) and refluxed for 15 min. The reaction mixture was cooled down to room temperature and filtered. The solid was washed respectively with hot methanol and de-ionized (DI) water several times, and dried in vacuo at 50 °C. A dark red solid was obtained. Yield: 6.54 g (61.0%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 11.17 (s, 2H), 8.04 (d, *J* = 1.3 Hz, 2H), 7.65 (d, *J* = 3.4 Hz, 2H), 6.83 (dd, *J* = 1.3 Hz, 3.4 Hz, 2H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 107.57, 113.71, 116.79, 131.27, 143.75, 146.91, 161.71.



(3)

Synthesis of 2,5-bis(2-octyl-1-dodecyl)-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3): To a dry 250 ml three-neck round bottom flask were added **1** (3.0 g. 11.18 mmol), anhydrous K₂CO₃ (4.63 g, 33.54 mmol), and anhydrous *N*, *N*-dimethylformamide (DMF) (250

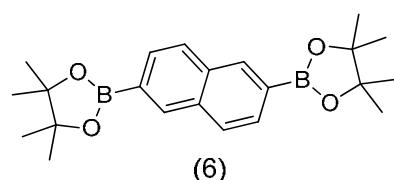
ml). The mixture was heated to 120°C under argon for 1h. 2-Octyl-1-dodecylbromide (12.12 g, 33.54 mmol) was then added drop-wise, and the reaction mixture was further stirred overnight at 130°C. The reaction mixture was allowed to cool down to room temperature and poured into water (500 mL) and stirred for 30 min. The product was extracted with chloroform, washed with DI water, and dried over anhydrous MgSO₄. Removal of the solvent afforded the crude product which was further purified using column chromatography on silica gel (a mixture of hexane and chloroform as eluent) to give the product as a red solid (4.5g, 48%). M.p. (DSC): 110.5 °C. ¹H NMR (400 MHz, CDCl₃): δ 0.86 (t, J = 6.4 Hz, 12 H), 1.15 -1.40 (m, 64 H), 1.79 (s, 2 H), 4.01 (m, 4 H), 6.68 (dd, J = 1.4 Hz, 1.6 Hz, 2 H), 7.59 (s, 2 H), 8.32(d, J = 3.6 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ 160.89, 146.25, 132.82, 126.16, 122.17, 115.48, 106.36, 46.65, 38.80, 31.90, 31.87, 31.48, 30.09, 29.62, 29.61, 29.54, 29.49, 29.32, 29.27, 26.48, 22.65, 22.63, 14.05. MS (MALDI-TOF, *m/z*): calcd. for C₅₄H₈₈N₂O₄, 828.67; found, 828.53 (M).



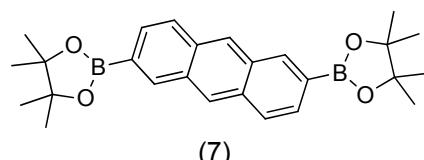
(4)

Synthesis of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-octyl-1-dodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (4): To a 100 mL three neck flask equipped with a stirring bar, a condenser, and a dropping funnel were charged with **2** (4.5 g, 5.42 mmol) and chloroform (40 mL). Bromine (Br₂) (0.55 mL, 10.84 mmol) in chloroform (20 mL) was then added to the flask at room temperature through the dropping funnel. The mixture was stirred at room temperature overnight, then slowly poured to an aqueous solution of sodium thiosulfate and stirred for additional 30 min. The product was extracted with chloroform, then washed with DI water, and dried over anhydrous MgSO₄. Removal of the solvent afforded the crude product which was further purified using column chromatography on silica gel (a mixture of hexane and chloroform as eluent) to give the product as a dark red solid (3.08g, 58%). M.p. (DSC): 105.0 °C.

¹H NMR (400 MHz, CDCl₃): δ 0.85 (t, J = 6.2 Hz, 12 H), 1.10-1.40 (m, 64 H), 1.76 (s, 2 H), 3.96 (d, J = 6.7 Hz, 4 H), 6.59 (d, J = 3.4 Hz, 2 H), 8.27 (d, J = 3.4 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃): δ 160.87, 146.23, 132.78, 126.13, 122.14, 115.45, 106.34, 46.63, 38.78, 31.87, 31.84, 31.47, 30.07, 29.59, 29.52, 29.46, 29.29, 29.24, 26.46, 22.62, 14.02. MS (MALDI-TOF, *m/z*): calcd. for C₅₄H₈₆Br₂N₂O₄, 984.50; found, 986.38 (M+2).



Synthesis of 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxabrolan-2-yl)naphthalene (6): 2,6-Dibromo-naphthalene (3.00 g, 10.49 mmol), bis(pinacolato)diboron (6.45 g, 25.18 mmol), PdCl₂(dpff) (1.85 g, 2.40 mmol), and potassium acetate (KOAc) (6.15 g, 61.52 mmol) were added in Schlenk flask and kept under vacuum for 10 min. Under an argon flow anhydrous 1, 4-dioxane (40 mL) was added to above mixture and the mixture was stirred at room temperature for 30 min before it was heated at 80 °C and stirred for 20 h. The resulting mixture was quenched by adding water and extracted with ethyl acetate (100 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, and filtered. After removing the solvent, a dark red solid was obtained, which was purified by silica gel chromatography by using 3 % ethyl acetate in hexane as eluent to give the title compound (**4**) as a white solid (2.5 g, 62 %). ¹H NMR (400 MHz, CDCl₃): δ 8.35 (s, 2H), 7.85-7.84 (dd, 4H), 1.39 (s, 24H). ¹³C NMR (100 MHz, CDCl₃): δ 136.39, 134.73, 130.75, 128.08, 84.36, 25.32. MS (MALDI-TOF) *m/z* 380.23 (M). calcd. for C₂₂H₃₀B₂O₄ = 380.12.



Chemical Formula: C₂₆H₃₂B₂O₄
Exact Mass: 430.25
Molecular Weight: 430.15

Synthesis of 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxabrolan-2-yl)anthracene (7): 2,6-Dibromo-anthracene (2.00 g, 6.46 mmol), bis(pinacolato)diboron (4.16 g, 16.16 mmol), PdCl₂(dpff)

(0.164 g, 26.38 mmol), and potassium acetate (KOAc) (2.5 g, 26.38 mmol) were added in Schlenk flask and kept under vacuum for 10 min. Under an argon flow anhydrous 1, 4-dioxane (40 mL) was added to above mixture and the mixture was stirred at room temperature for 30 min before it was heated at 80 °C and stirred for 20 h. The resulting mixture was quenched by adding water and extracted with ethyl acetate (100 mL). The combined organic layers were washed with brine, dried over MgSO₄, and filtered. After removing the solvent, a dark red solid was obtained, which was purified by silica gel chromatography by using 5 % ethyl acetate in hexane as eluent to give the title compound (**4**) as yellow solid (2.0 g, 71 %). ¹H NMR (400 MHz, CDCl₃): δ 8.55 (s, 2H), 8.44 (s, 2H), 8.01 (dd, 2H), 7.76 (dd, 2H), 1.39 (s, 24H). ¹³C NMR (100 MHz, CDCl₃): δ 137.68, 133.12, 132.23, 129.50, 127.80, 127.54, 84.38, 25.34. MS (MALDI-TOF) m/z 430.20 (M). calcd. for C₂₂H₃₀B₂O₄ = 430.15.

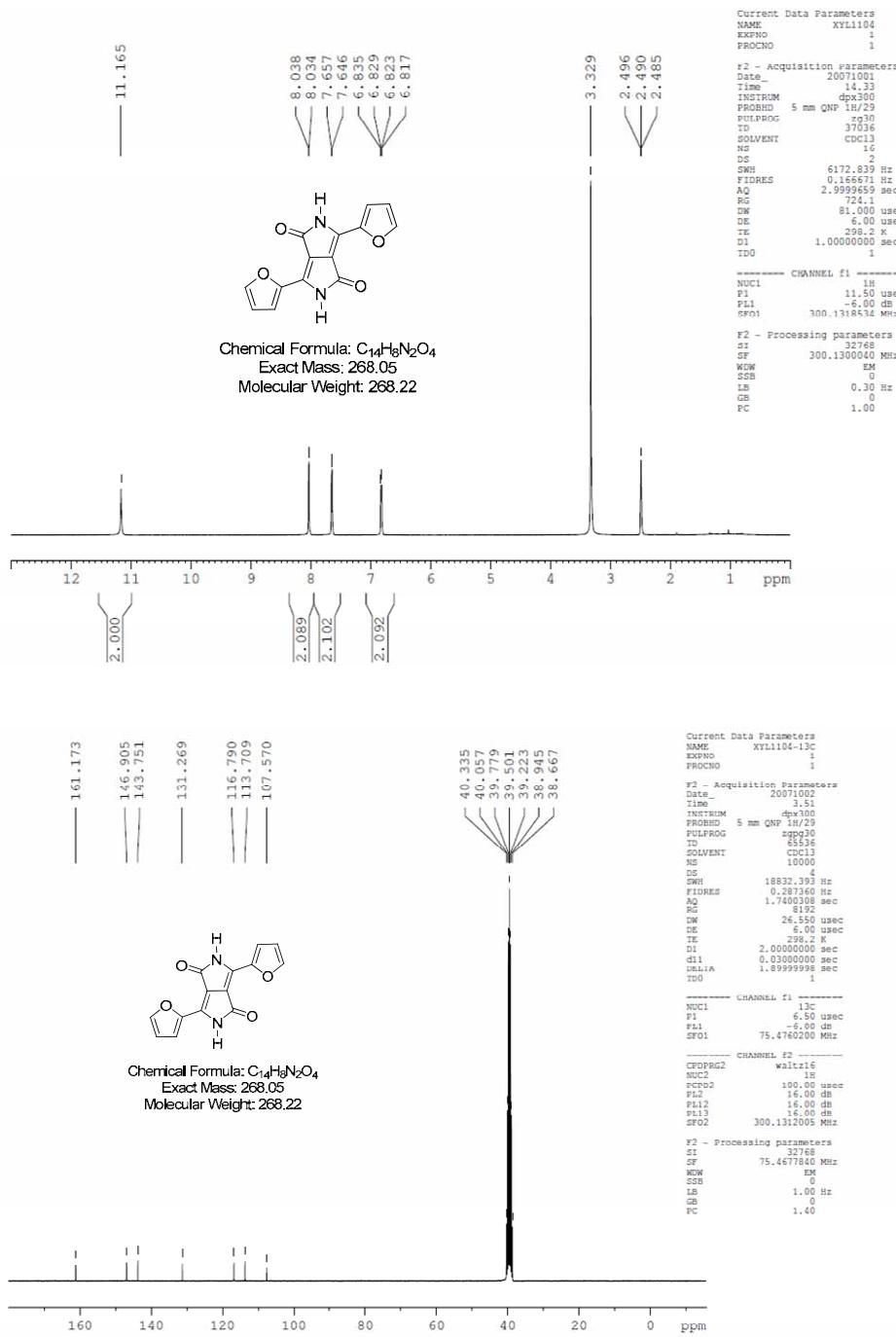


Figure S1. ¹H NMR and ¹³C spectra of 3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**2**) in DMSO-*d*₆.

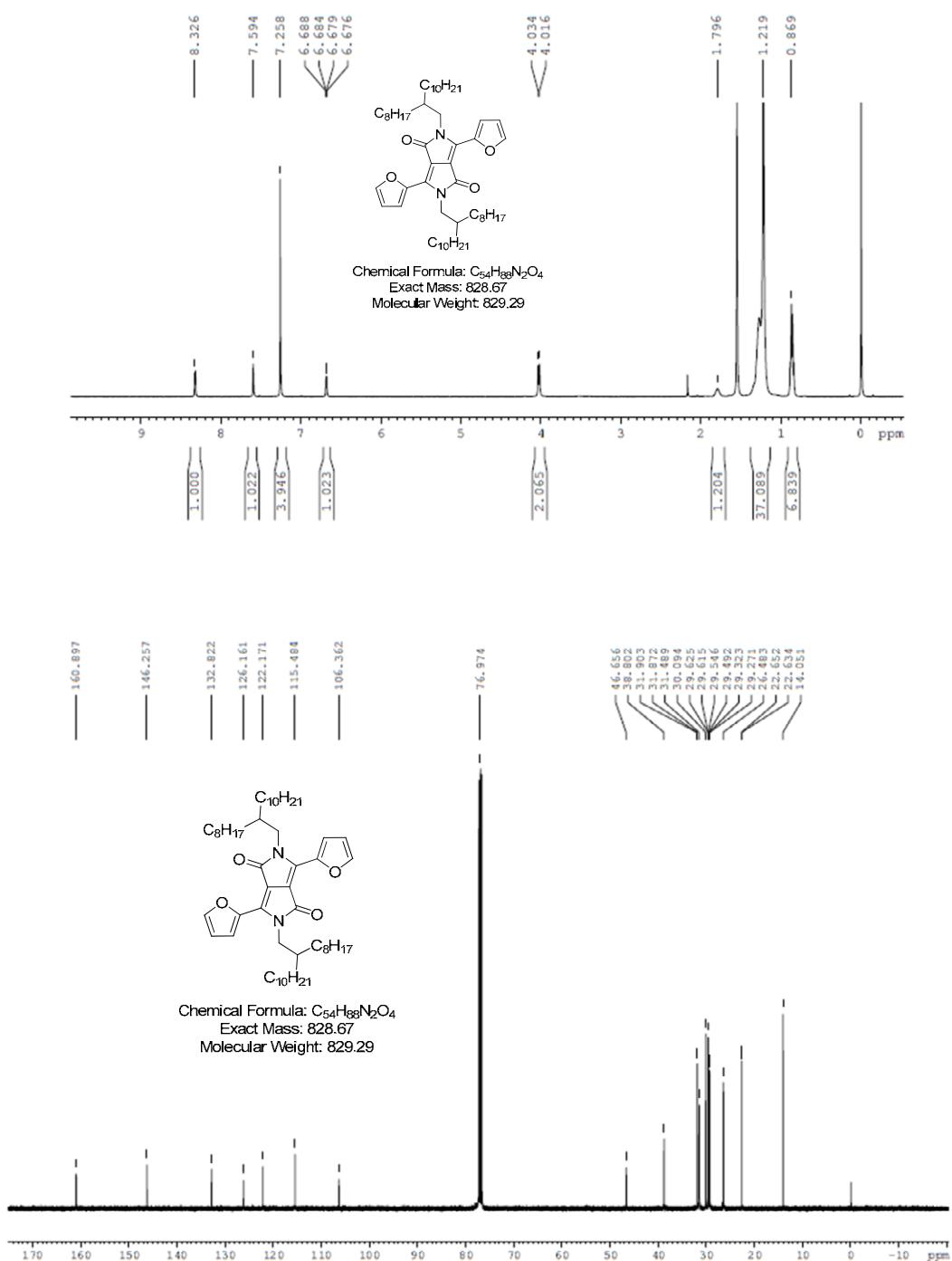


Figure S2. ^1H NMR and ^{13}C spectrum spectra of 2,5-bis(2-octyl-1-dodecyl)-3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**3**) in CDCl_3 .

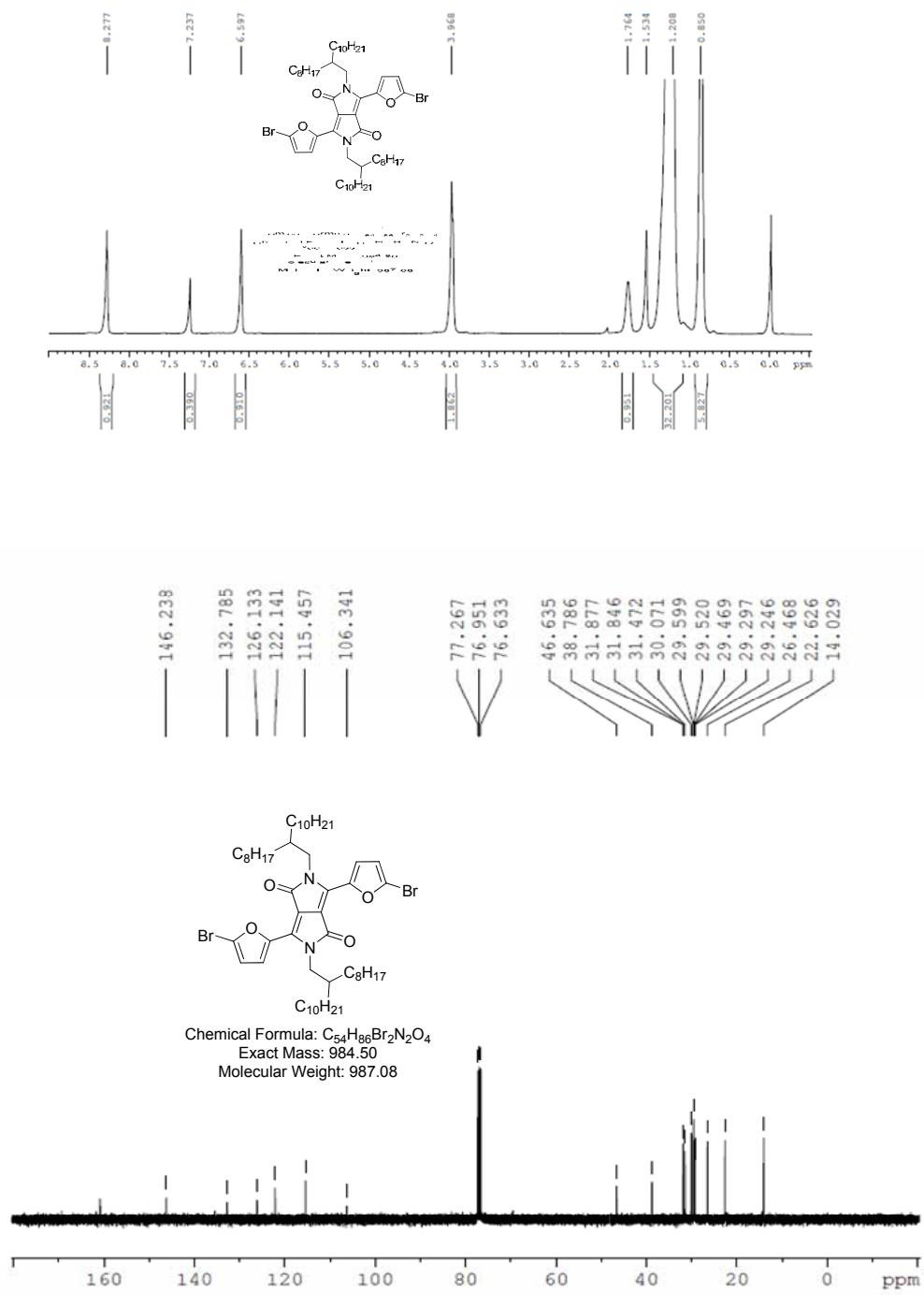


Figure S3. ^1H NMR and ^{13}C spectrum of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-octyl-1-dodecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione in CDCl_3 (**4**).

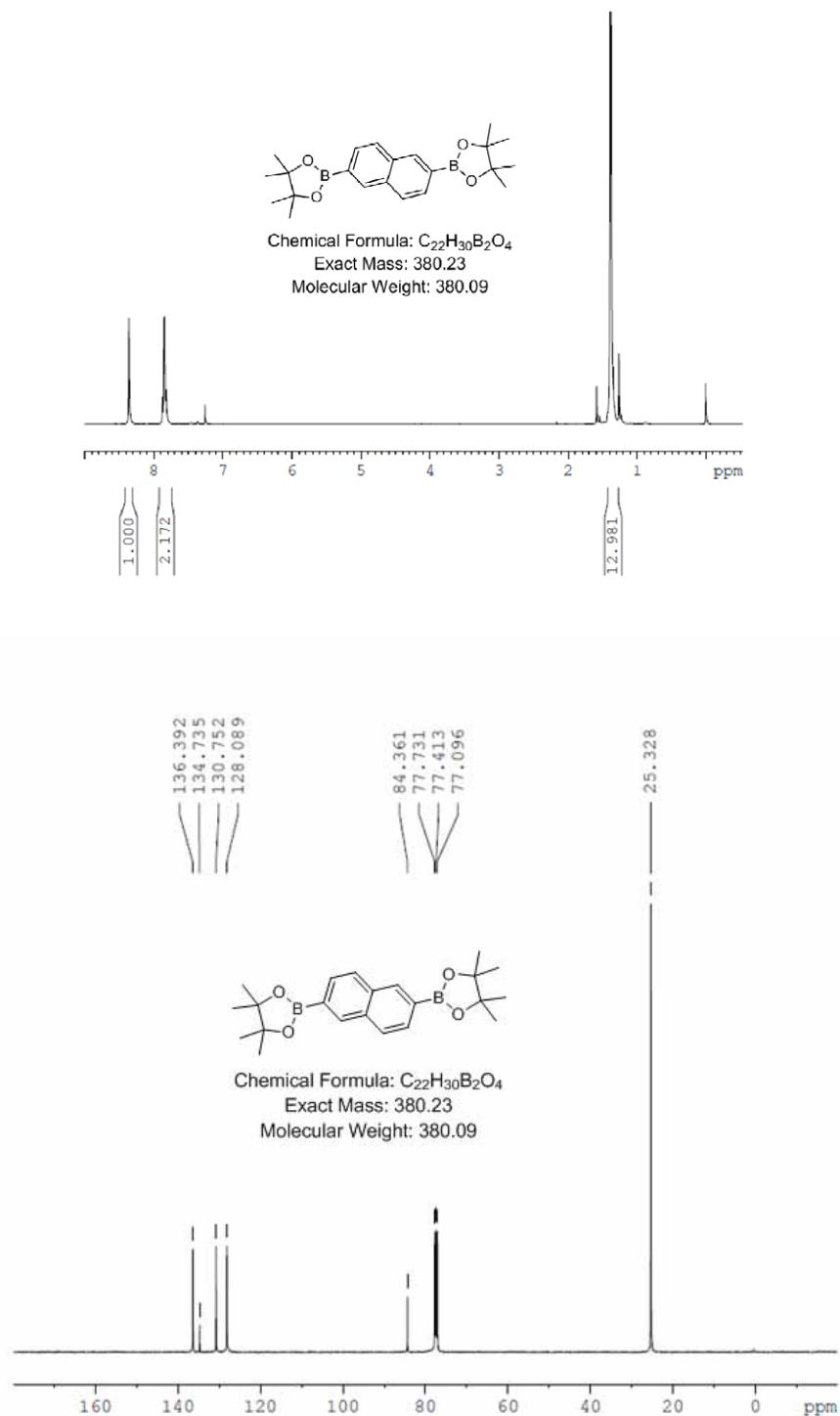


Figure S4. ^1H NMR and ^{13}C spectrum of 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxabolan-2-yl)naphthalene in CDCl₃.

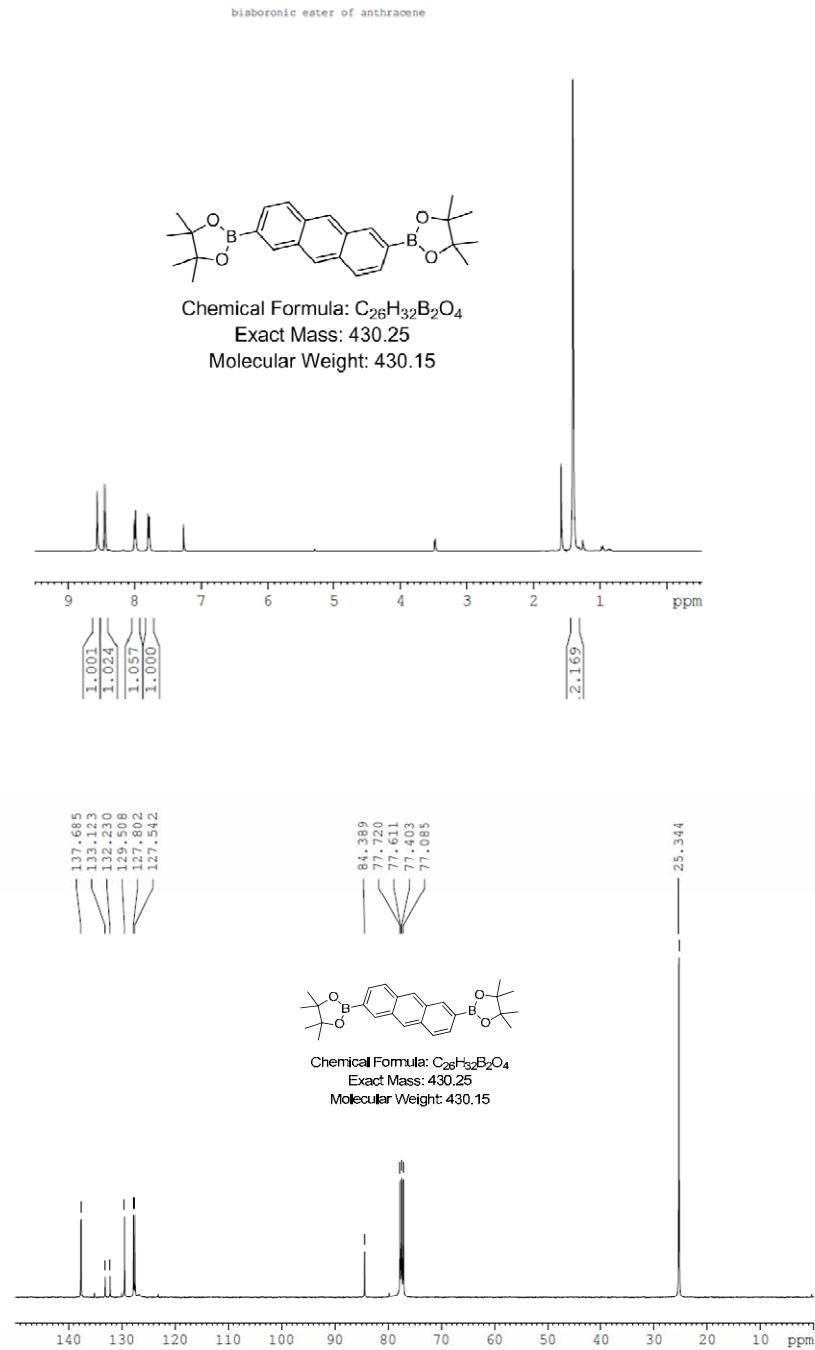
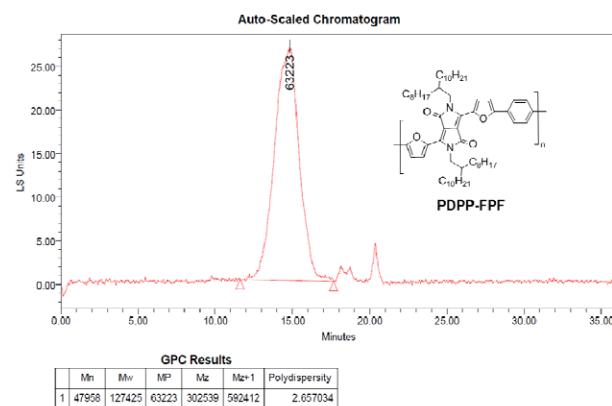
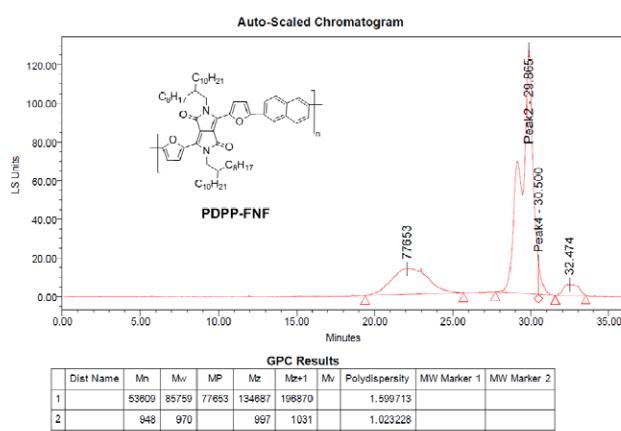


Figure S5. 1H NMR and ^{13}C spectrum of 2,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxabolan-2-yl)anthracene in $CDCl_3$.

(a)



(b)



(c)

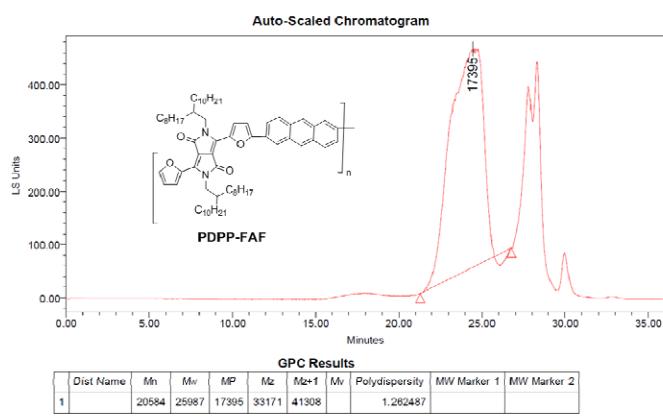
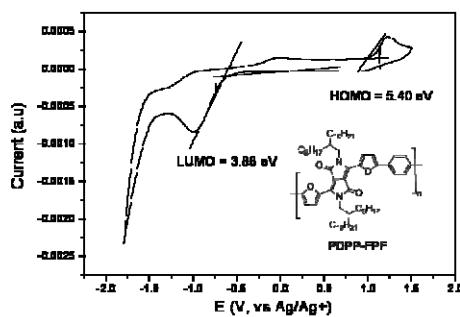
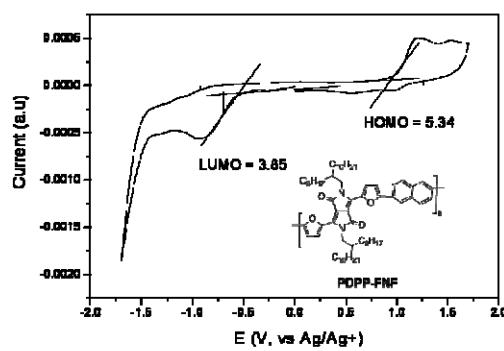


Figure S6. GPC elution curve and molecular weights of (a) PDPP-FPF, (b) PDPP-FNF and (c) PDPP-FAF respectively using THF as eluent and PMMA as standards at a column temperature of 40°C.

(a)



(b)



(c)

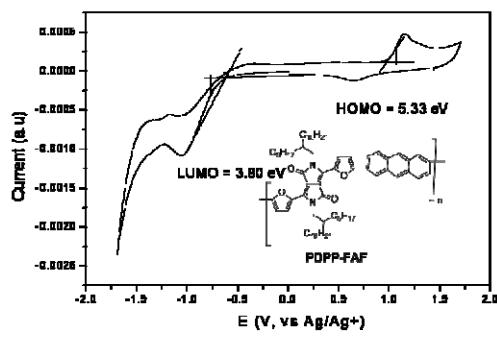
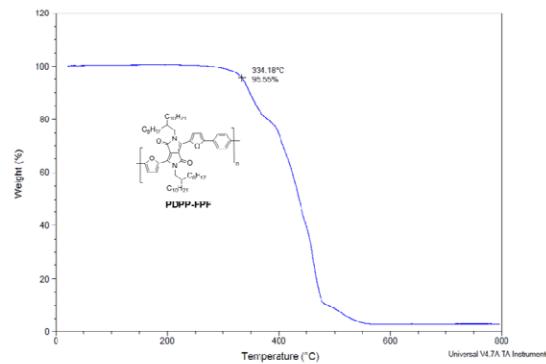
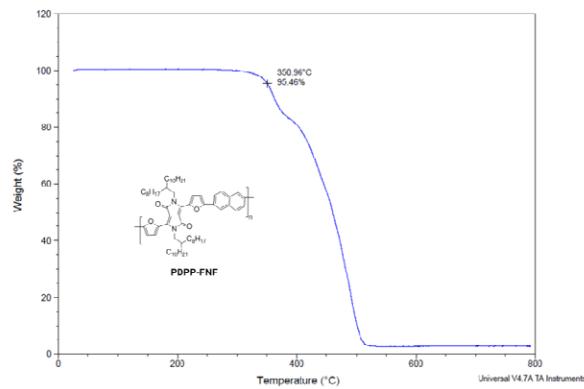


Figure S7. Cyclic voltamograms showing the cathodic and anodic cycles of (a) **PDPP-FPF**, (b) **PDPP-FNF** and (c) **PDPP-FAF** spin coated polymers respectively on working electrode at a scan rate 50 mVs⁻¹ in acetonitrile. The electrolyte was 0.1 M TBAPF₆.

(a)



(b)



(c)

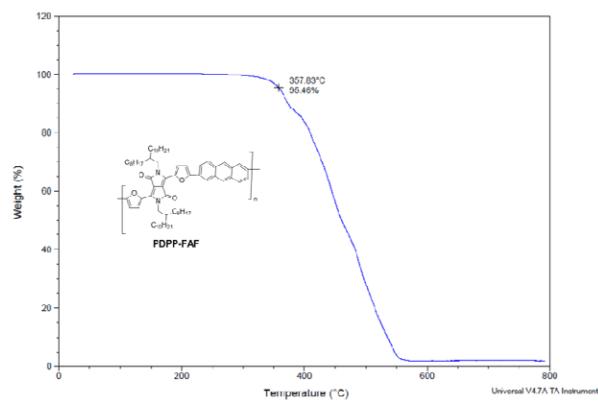
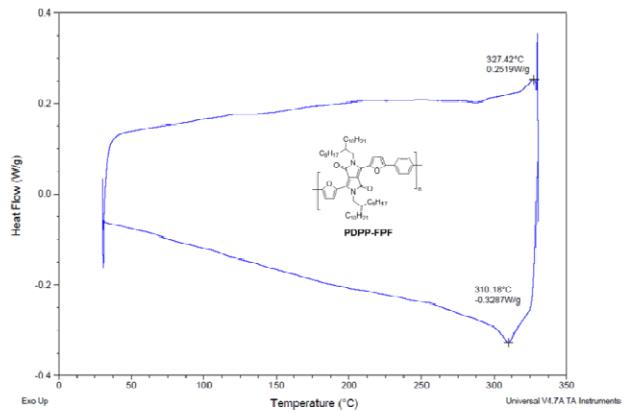
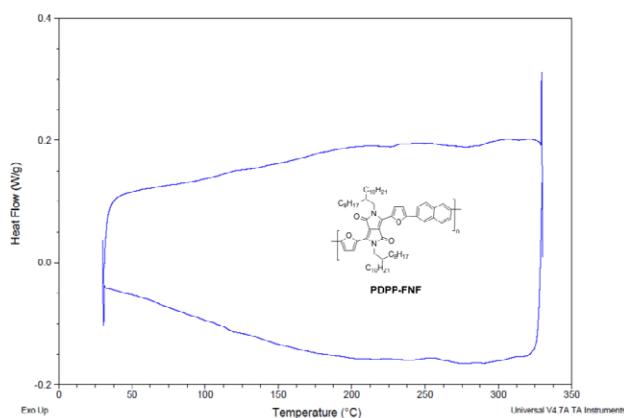


Figure S8. Thermogravimetric analysis (TGA) curves of (a) PDPP-FPF, (b) PDPP-FNF and (c) PDPP-FAF respectively.

(a)



(b)



(c)

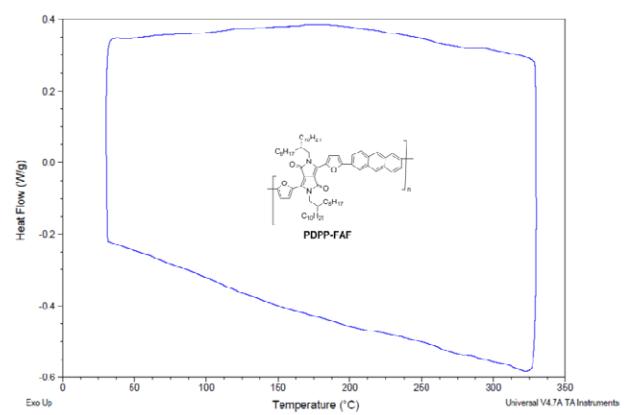


Figure S9. Differential scanning calorimetry (DSC) graphs of (a) PDPP-FPF, (b) PDPP-FNF and (c) PDPP-FAF respectively.

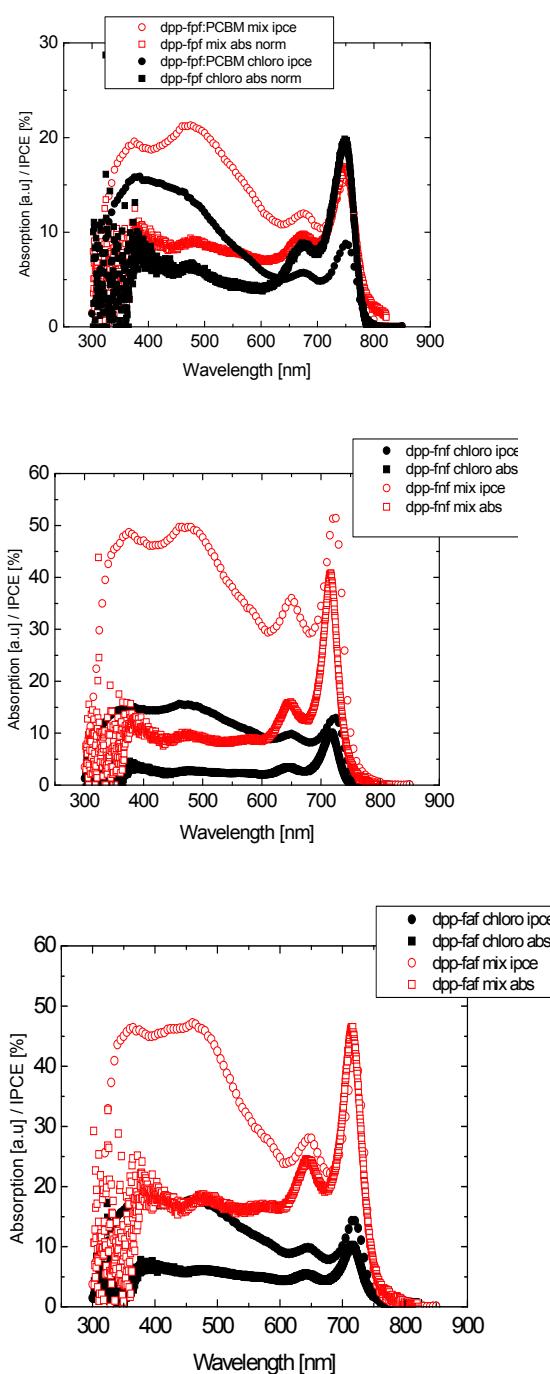


Fig. S10 (a) IPCE spectra of **PDPP-FPF**, **PDPP-FNF** and **PDPP-FAF** copolymer devices, as blended with [70]PCBM in a 1:2 ratio.

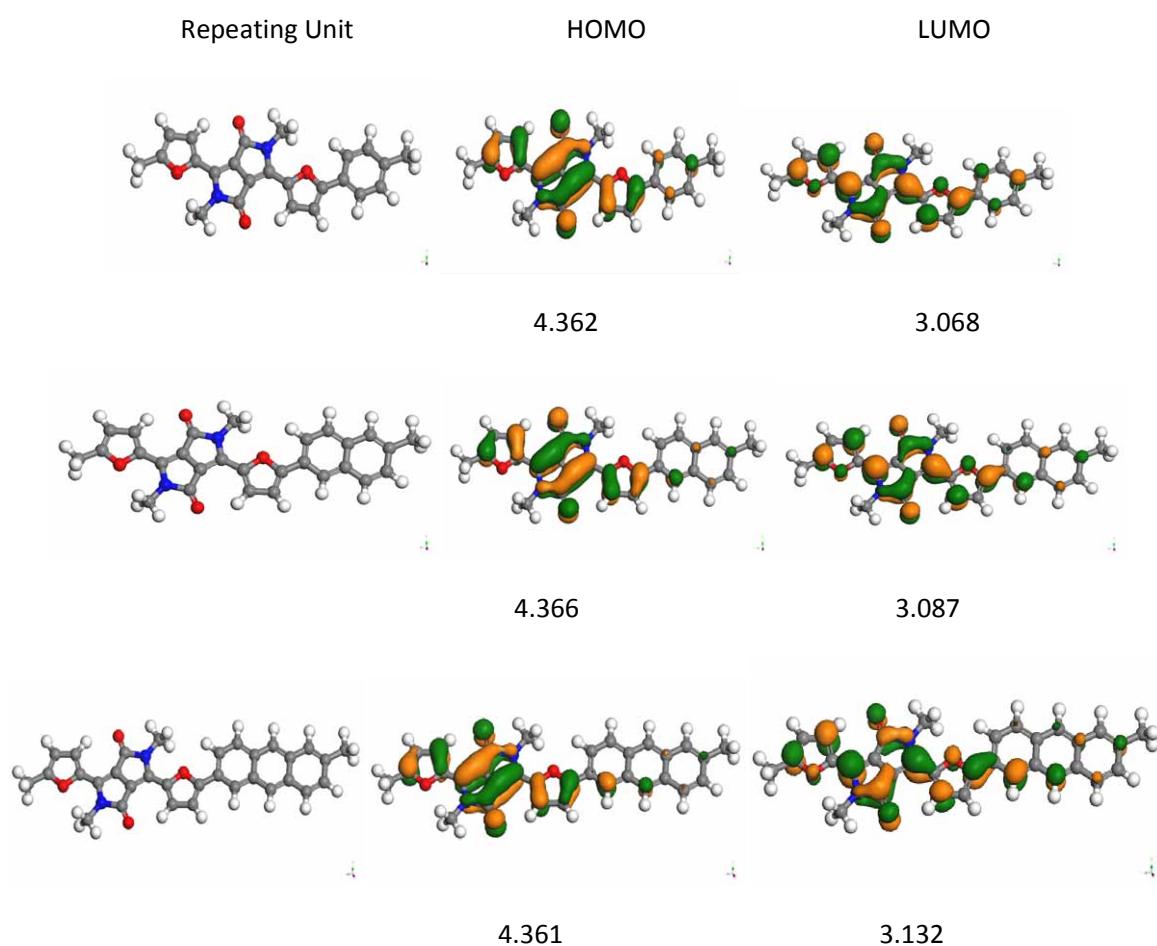


Figure S11. The electron density isocontours of HOMO and LUMO of representative repeating unit of the **PDPP-FPF**, **PDPP-FNF** and **PDPP-FAF** polymers respectively using GGA-PW91/dnp- DMol³ software.

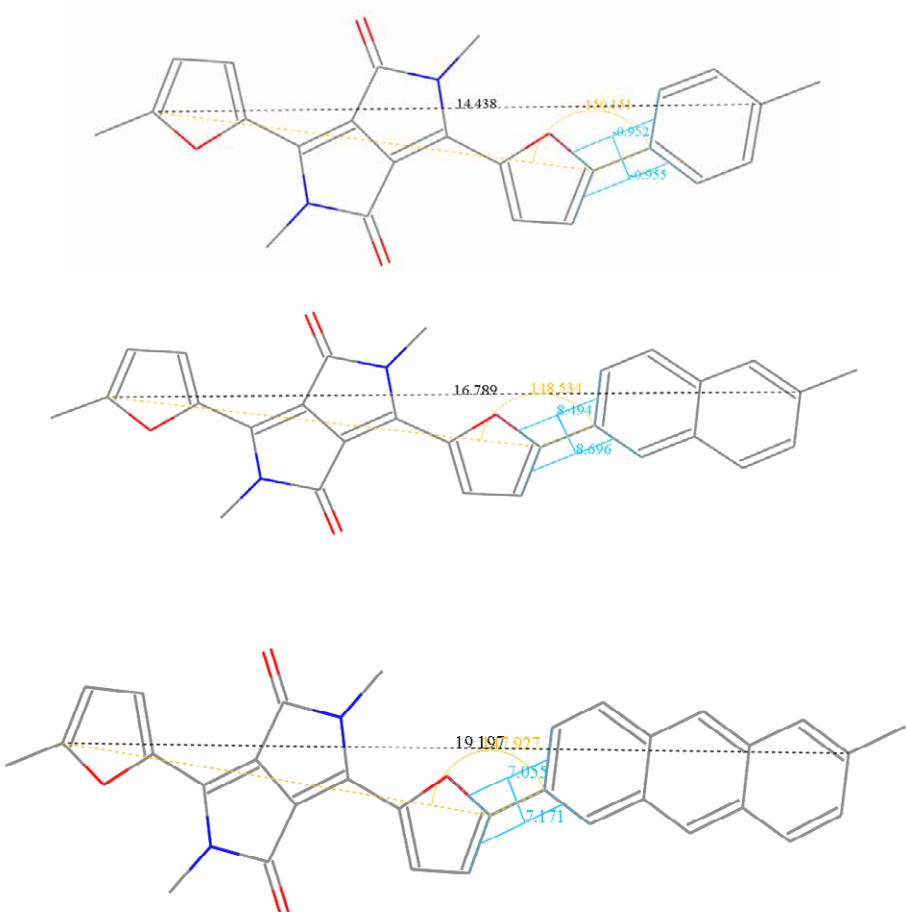


Figure S12. Dihedral angles between furan DPP and phenylene, naphthalene and the total length of the repeating units of **PDPP-FPF**, **PDPP-FNF** and **PDPP-FAF** polymers respectively calculated at the level of theory GGA-PW91/dnp using DMol³ software.