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Electronic Supplementary Information

Evaluation of (*E*)-1,2-di(furan-2-yl)ethene as building unit in diketopyrrolopyrrole alternative copolymers for transistors

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Experimental

Materials and General Characterization

All the chemicals used for synthesis were purchased from Sigma-Aldrich and Fisher Scientific without further purification unless elsewhere mentioned. Tetrahydrofuran (THF) and toluene were freshly distilled over benzophenone/sodium ketyl. 11-(Bromomethyl)tricosane[1, 2] and 3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione[3] were synthesized according to the reported literature.

NMR measurements: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer at 25 ^{o}C. The sample was dissolved in $CDCl_3$. The chemical shift was reported in ppm on the δ scale relative to the $CHCl_3$ peak. The multiplicity was explained as: s=single, d=doublet, t=triplet, q=quartet, dd=doublet of doublets, br=broad and m=multiplet.

Single Crystal Structure: Single crystal structure was obtained from Bruker Kappa D8 Quest CMOS diffractometer equipped with an Oxford Cryostreams cooler. The sample was irradiated by Mo-Kα (λ=0.71073 Å) x-rays at room temperature. The structure was refined using software *SHELXL2014/7*.

Size Exclusion Chromatography measurements: The molecular weight of the polymer was measured at 30 ^{o}C by SEC on a Viscotec VE 3580 system equipped with CLM3009 columns, connected to a UV detector using 254 nm laser. The HPLC grade THF was used as eluent and the calibration was carried out using polystyrene standards.

Thermal Gravimetric Analyses and Differential Scanning Calorimetry measurements: TGA and DSC spectra were recorded on a Mettler Toledo TGA/DSC-1 system with a heating rate of 10 K/min and cooling rate of -10 K/min under nitrogen flow.

UV-visible Absorption measurements: The UV-vis absorption was recorded with an Agilent 8453 UV-VIS spectrometer. The UV-vis absorption of the molecules in chloroform was conducted in 1 cm cuvettes and the film was carried out by spin-coating the molecular solution on glass microscope slides.

Cyclic Voltammetry measurements: CV measurements were carried out on BAS CV-50W voltammetric analyzer with platinum disk, platinum wire and Ag/Ag$^+$ used as working electrode, auxiliary electrode, and reference electrode, respectively. 0.1 M of electrochemical grade tetrabutylammonium hexafluorophosphate in acetonitrile was chosen as the electrolytic solution. CV was calibrated by Ferrocene/ferrocenium (Fc/Fc$^+$), which was used as an internal reference, and the $E_{1/2}$ of the redox couple was found at 0.09V vs. Ag/Ag$^+$.

Tapping Mode Atomic Force Microscopy measurement: TMAFM was performed on the OFET devices using a Nanoscope IV Multimode Veeco, equipped with a vertical engage scanner. The TMAFM images were acquired using Si cantilever with resonance frequency of 320 KHz and spring constant of 42 N/m. The images were collected in 3 by 3 μm size with scan frequency of 1 Hz at 355 mV drive amplitude.

Grazing Incidence X-ray Diffraction measurement: GIXD investigation was carried out on a Rigaku SmartLab XRD facility. The sample was irradiated by Cu-Kα (λ=1.54 Å) x-rays at incident angle of 0.5^o. The data was collect at 0.05^o intervals, at rate of 3 degree/min from 1^o to 30^o. The samples were prepared on an OTS treated SiO_2 surface following the same conditions as for the OFET devices.

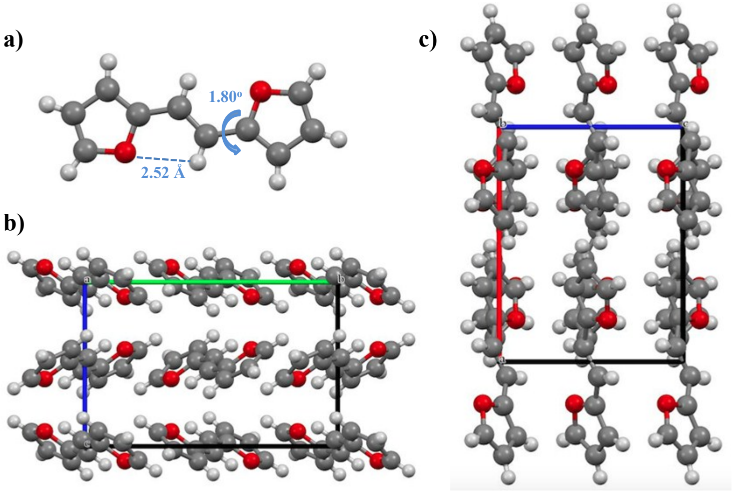


Figure S1. (a) Crystal structure of (*E*)-1,2-di(furan-2-yl)ethene and molecular stacking viewed along the (b) a axis and (c) b axis. Red ball represents oxygen atom.

The crystal structure for (E)-1,2-di(furan-2-yl)ethene (compound **1** in **Scheme S1**) was determined using low temperature (T=90 K) data collected on a 0.24 x 0.06 x 0.06 mm^3 crystal with a Bruker Kappa D8 Quest single crystal X-ray diffractometer. This diffractometer has a Mo Kα Incoatec microfocus source (IμS), Oxford Cryosystems 700 series cryostream, and CMOS Photon 100 detector. Datasets were integrated and scaled / corrected for absorption (multi-scan method) using Bruker SAINT and SADABS. Systematic absences were evaluated for space group determination with Bruker XPREP. Preliminary starting models and structure refinement were carried out with SHELXT2014/5 (intrinsic phasing method)[4] and SHELXL2014/7.[5] Crystal structure representations are shown in **Figure S1**.

Crystal data for (E)-1,2-di(furan-2-yl)ethene: $C_{10}H_8O_2$, M = 160.16, orthorhombic, a = 9.490(3) Å, b = 11.322(4) Å, c = 7.377(4) Å, V = 792.6(6) Å^3, T = 90(2) K, space group *Pbcn*, Z = 4, μ(MoKα) = 0.09 mm^{-1}, 7653 reflections measured, 1224 independent reflections (R_{int} = 0.064). The final R_1 values were 0.062 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.114 ($I > 2\sigma(I)$). The final R_1 values were 0.099 (all data). The final $wR(F^2)$ values were 0.126 (all data). The goodness of fit on F^2 was 1.07. Crystallization solvent = Hexane, **CCDC 1555680**.

Additional crystallographic details (atomic coordinates, displacement parameters, bond lengths, and bond angles) are included toward the end of this Supplementary Information file.

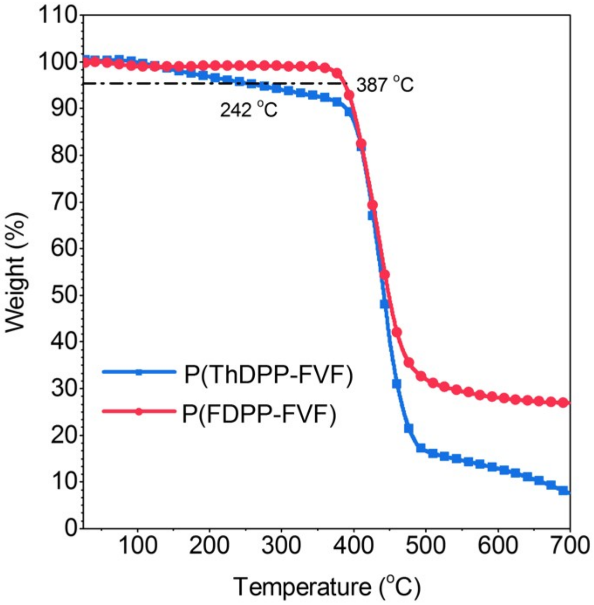


Figure S2. TGA thermograms of P(FDPP-FVF) and P(ThDPP-FVF).

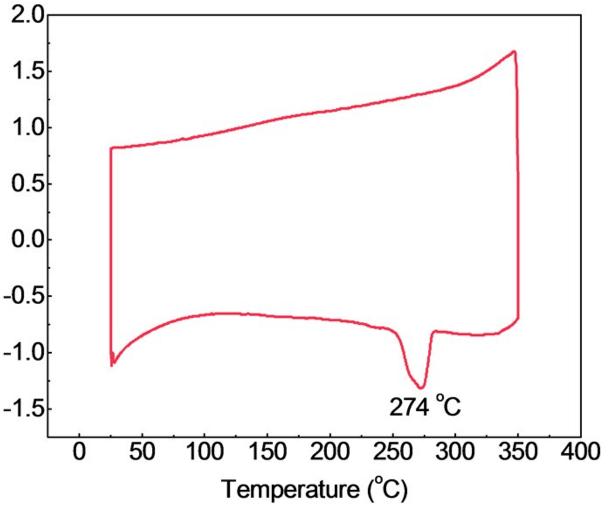


Figure S3. DSC curves of P(FDPP-FVF).

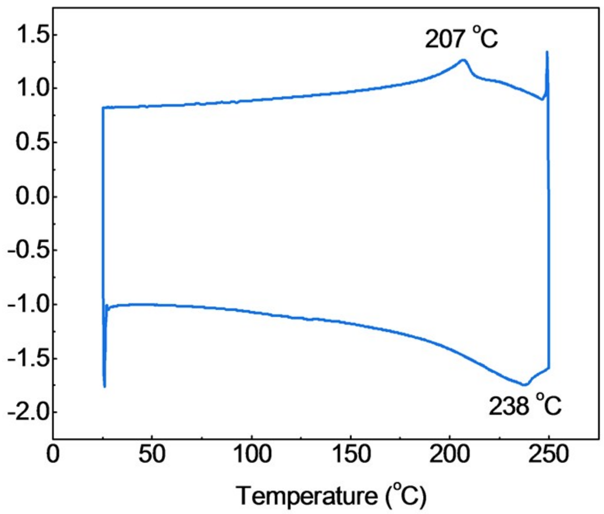


Figure S4. DSC curves of P(ThDPP-FVF).

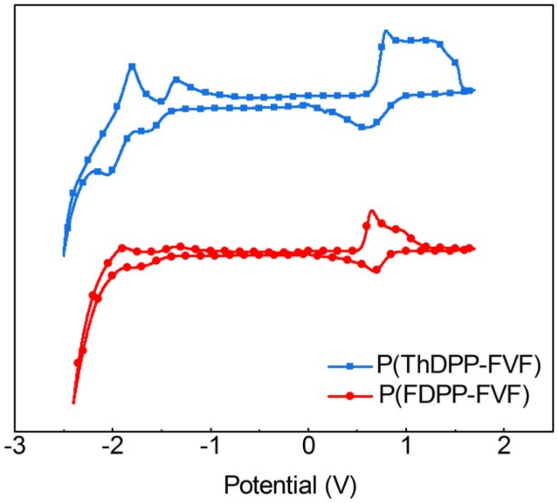


Figure S5. Cyclic voltammetry spectrum of P(FDPP-FVF) and P(ThDPP-FVF).

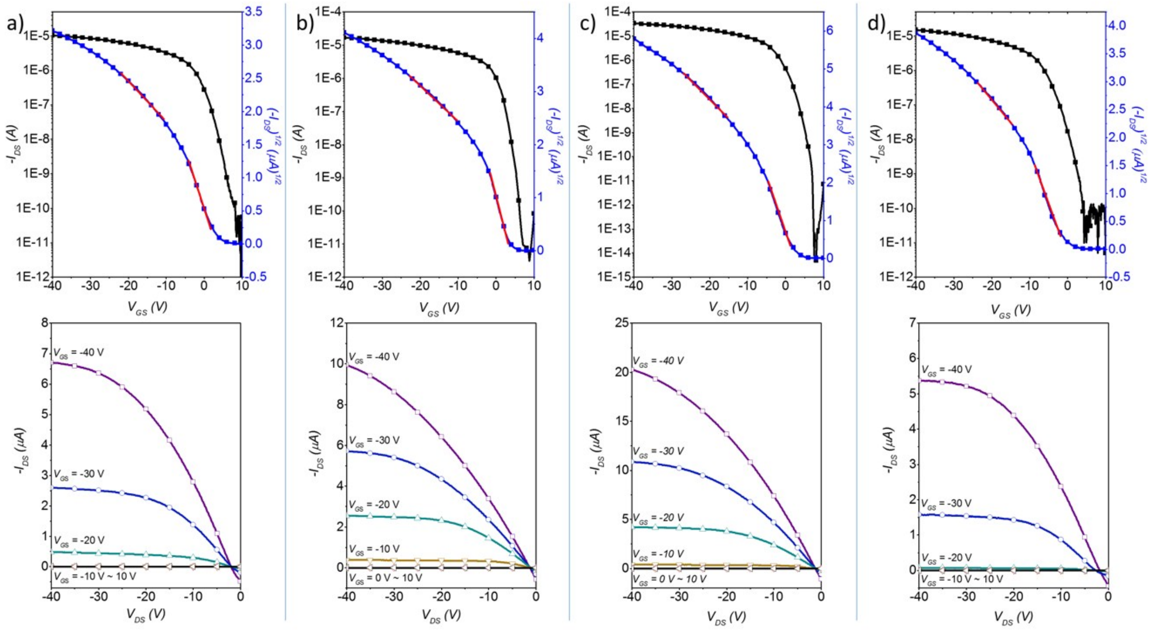


Figure S6. Transfer curve (top, V_{DS} = -40 V) and output curve of OFET devices based on P(FDPP-FVF) without annealing (a), annealed at 100 °C for 5 minutes (b), annealed at 150 °C for 5 minutes (c), and annealed at 200 °C for 5 minutes (d).

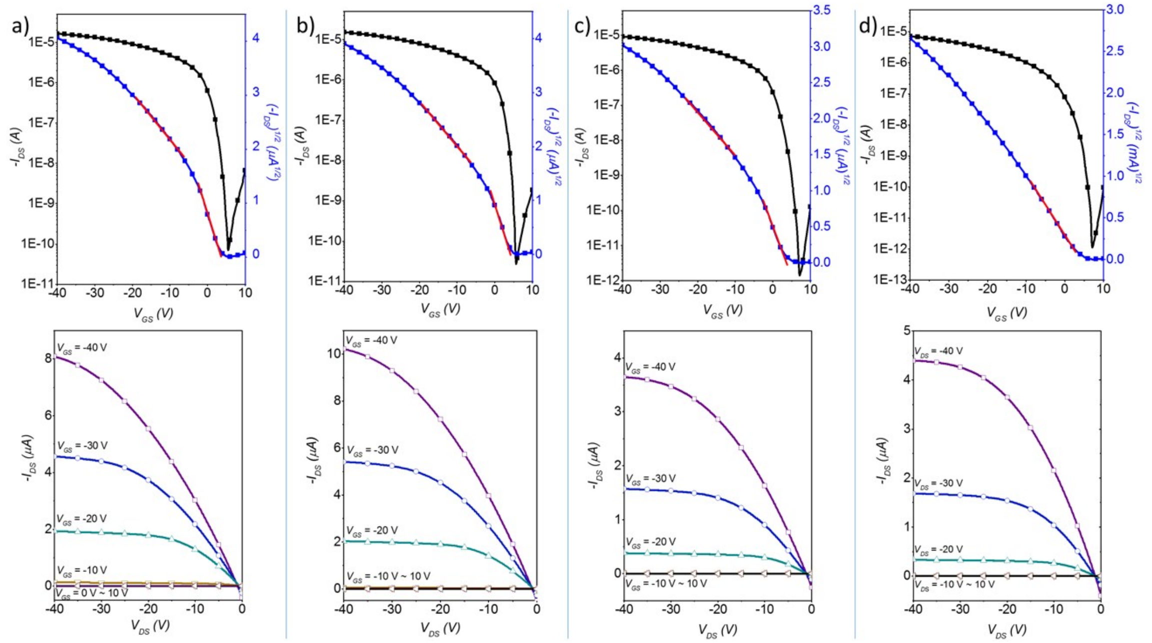
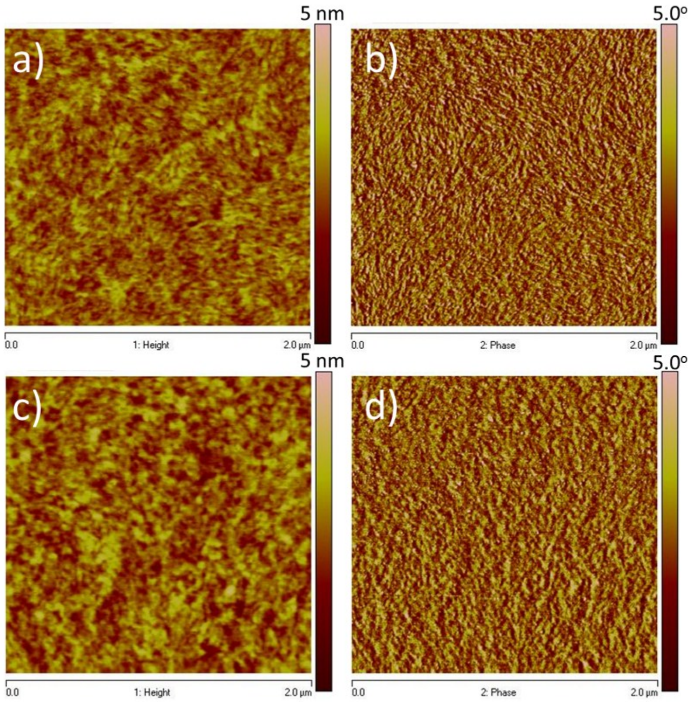
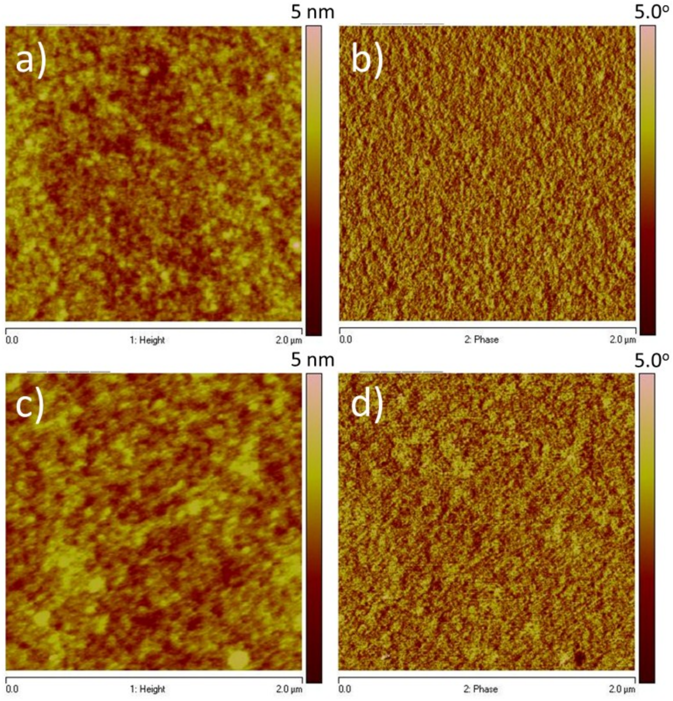


Figure S7. Transfer curve (top, V_{DS} = -40 V) and output curve of OFET devices based on P(ThDPP-FVF) without annealing (a), annealed at 100 °C for 5 minutes (b), annealed at 150 °C for 5 minutes (c), and annealed at 200 °C for 5 minutes (d).



Fiugre S8. Tapping mode AFM height (a, c) and phase images (b, d) of P(FDPP-FVF) without annealing (a, b) and annealed at 150 ^{o}C for 5 minutes (c, d)



Fiugre S9. Tapping mode AFM height (a, c) and phase images (b, d) of P(ThDPP-FVF) without annealing (a, b) and annealed at 100 ^{o}C for 5 minutes (c, d)

Detailed Synthetic Procedure

*Synthesis of (E)-1,2-di(furan-2-yl)ethene (**FVF**)*

In a three-neck round bottom flask, $TiCl_4$ (11.83 g, 62.4 mmol) was added dropwise to a stirred solution of furfural (5.00 g, 52.0 mmol) in THF over 30 minutes at -10 ^oC. After another 30 minutes, Zn powder (8.17 g, 125.0 mmol) was added to solution in small portions over 30 minutes. The mixture was kept at -10 ^oC for an hour before warming up to room temperature and then refluxed for 3 hours. Ice cold water was used to quench the reaction and the precipitated solid was collected by filtration. The solid was dissolved in methylene chloride and the insoluble inorganic compound was removed. After removing the solvent, the crude product was purified by silica gel chromatography using hexane as eluent to give light yellow solid as the final product (1.8 g, 42%). ^1H NMR (500 MHz, $CDCl_3$): 7.38 (d, 2H), 6.81 (s, 2H), 6.41 (dd, 2H), 6.32 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 152.99, 142.12, 114.96, 111.73, 108.77.

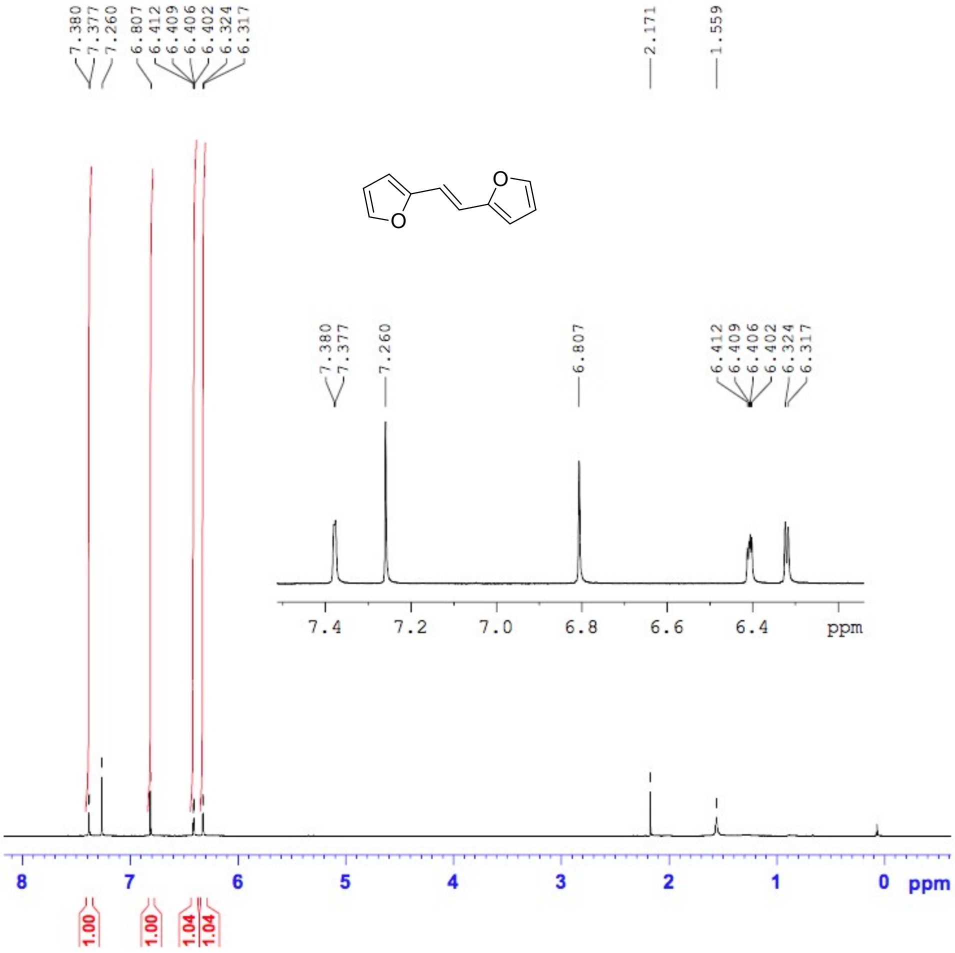


Figure S10. ^{1}H NMR spectrum of (E)-1,2-di(furan-2-yl)ethane.

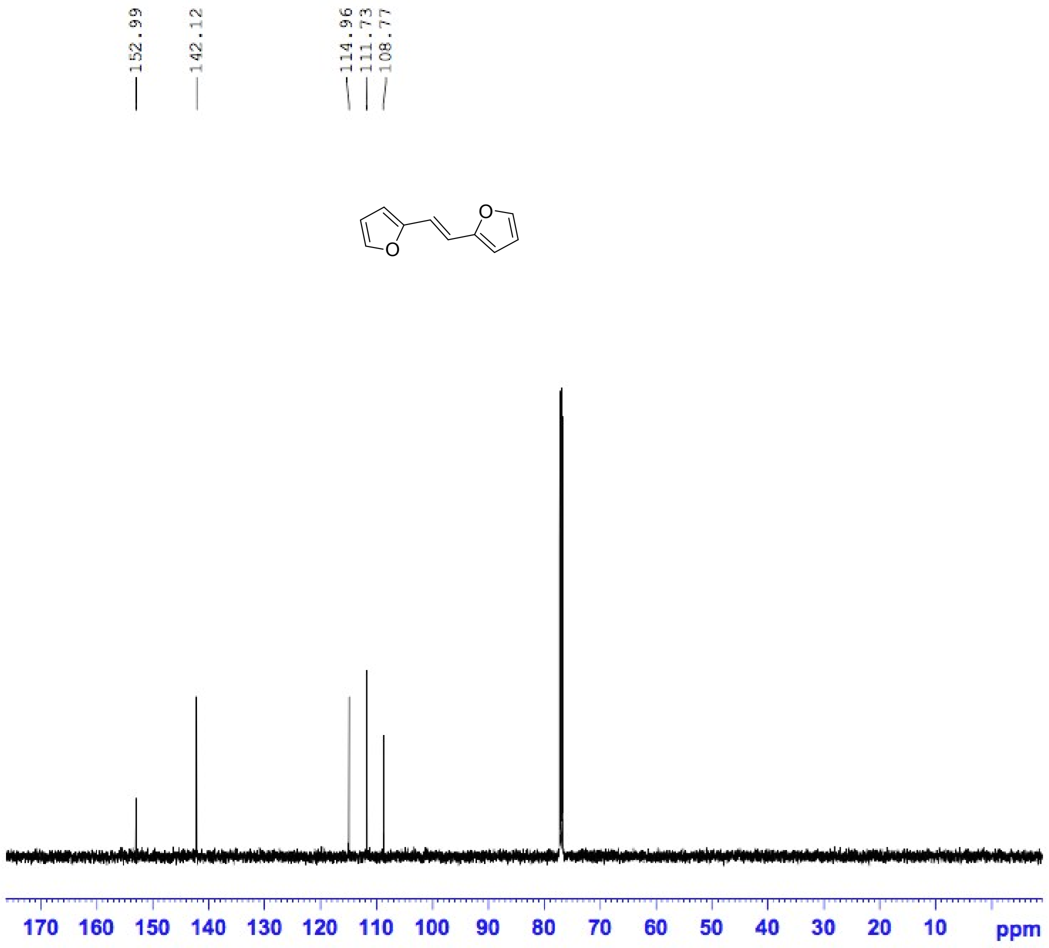


Figure S11. ^{13}C NMR spectrum of (E)-1,2-di(furan-2-yl)ethane

Synthesis of (E)-1,2-bis(5-(trimethylstannyl)furan-2-yl)ethene ***(FVF-Sn)***

To a solution of (E)-1,2-di(furan-2-yl)ethene (0.30 g, 1.87 mmol) in 30 mL dry THF and 20 mL dry hexane, tetramethylethylenediamine (0.48 g, 4.11 mmol) was added and the solution was cooled to -78 ^{o}C. *n*-Butyllithium (2.00 mL in hexane, 4.49 mmol) was added slowly to the solution and the reaction was kept at -78 ^{o}C for an hour. Trimethyltin chloride (5.61 mL, 5.61 mmol) was then added at -78 ^{o}C and the mixture was allowed to warm to room temperature. After two hours, the reaction mixture was quenched in deionized water and the product was extracted with hexane three times. The combined organic layers were dried over anhydrous magnesium sulfate. After removing the solvent, the crude product was purified by recrystallization from ethanol (554 mg, 61%). ^{1}H NMR (500 MHz, CDCl$_3$): 6.87 (s, 2H), 6.58 (d, 2H), 6.34 (d, 2H), 0.35 (s, 18H).

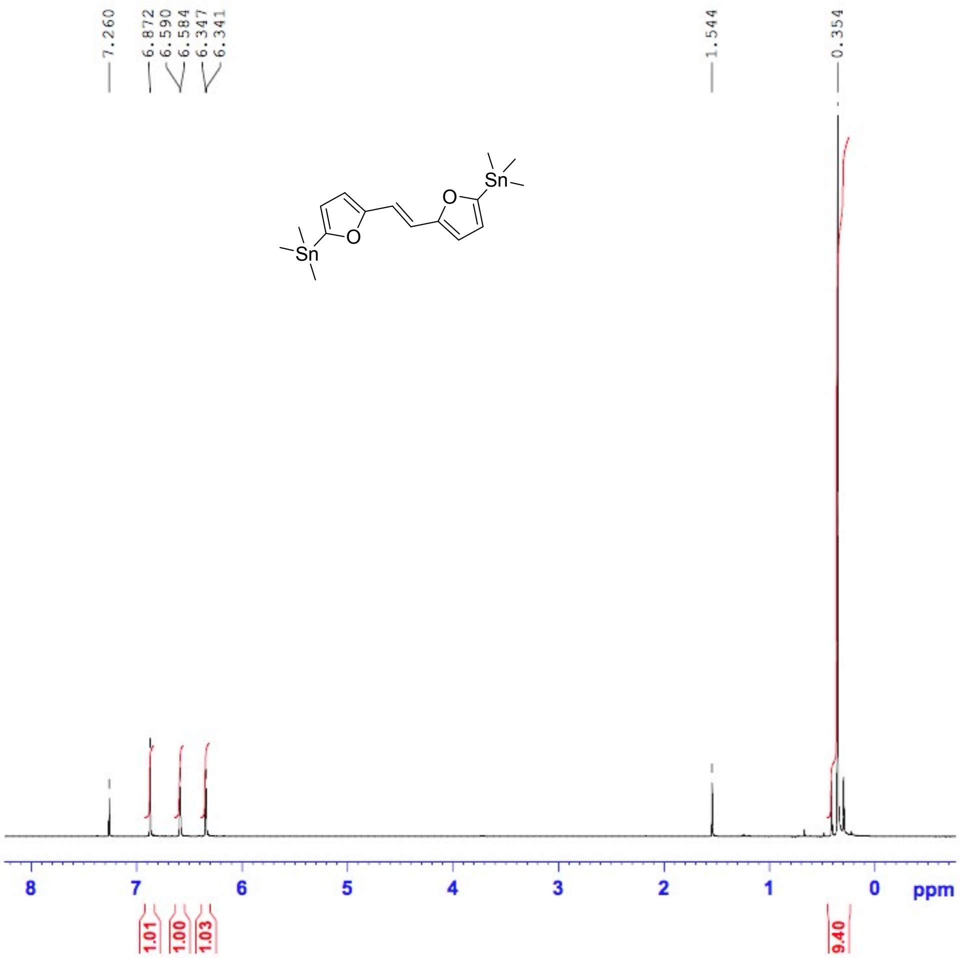


Figure S12. ^{1}H NMR spectrum of (E)-1,2-bis(5-(trimethylstannyl)furan-2-yl)ethane.

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

The crude product 3,6-di(furan-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione[3] (1.20 g, 4.47 mmol) and potassium carbonate (2.04g, 14.76 mmol) were placed in a three-neck flask under nitrogen. DMF (15 mL) was added and the reaction mixture was heated at 120 °C for 6 hours before 11-(bromomethyl)tricosane (5.60 g, 13.41 mmol) was added in one portion. The reaction mixture was stirred at 100°C for 12 hours before quenching into water and extracted with chloroform three times. The organic layers were dried over magnesium sulfate and the solvent was removed. The crude product was purified by using silica gel chromatography with methylene chloride and hexane (3:7) as eluent to give a dark red solid as the pure product. (1.56 mg, 37%) ^{1}H NMR (500 MHz, $CDCl_3$): 8.32 (d, 2H), 7.60 (d, 2H), 6.68 (dd, 2H), 4.02 (d, 4H), 1.80 (m, 2H), 1.26 (m, 80H), 0.87 (t, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): 161.26, 144.81, 144.69, 133.95, 120.18, 113.47, 106.48, 46.56, 38.53, 31.94, 31.93, 31.51, 30.03, 29.70, 29.67, 29.65, 29.63, 29.37, 29.36, 26.52, 22.70, 14.13.

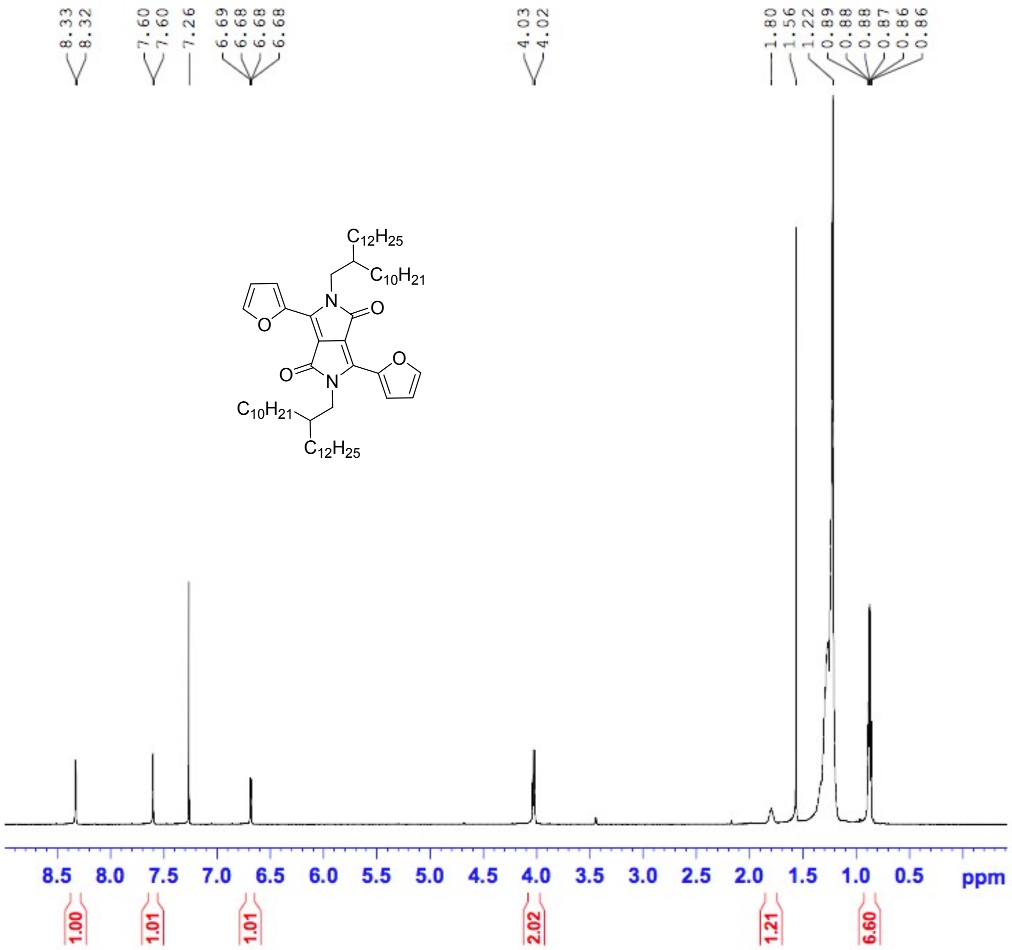


Figure S13. ^{1}H NMR of spectrum of 2,5-bis(2-decyltetradecyl)-3,6-di(furan-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione.

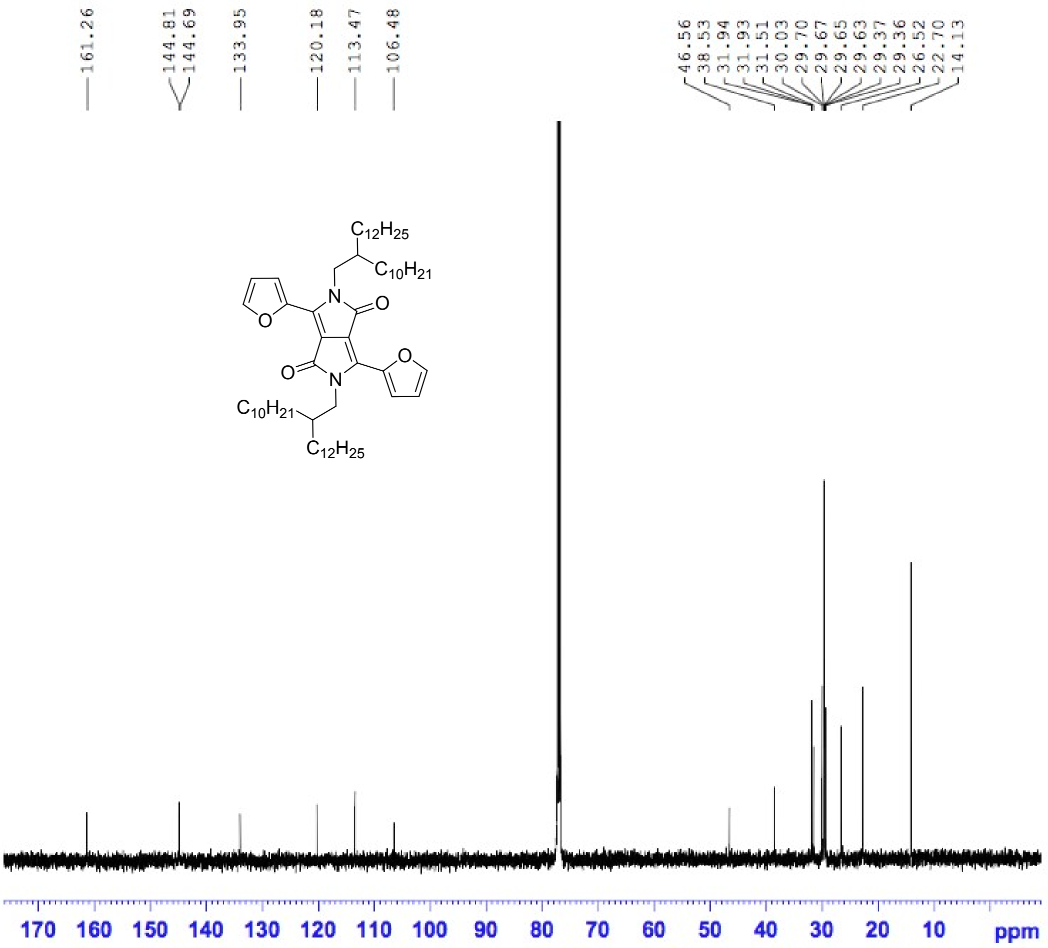


Figure S14. ^{13}C NMR spectra of 2,5-bis(2-decyltetradecyl)-3,6-di(furan-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione.

*Synthesis of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**FDPP-Br**)*

2,5-Bis(2-decyltetradecyl)-3,6-di(furan-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (300 mg, 0.32 mmol) was dissolved in 50 mL chloroform under nitrogen. N-bromosuccinimide (125 mg, 0.70 mmol) was added to reaction gradually over 5 minutes in 3 small portions at 0 °C. The reaction was stirred at room temperature in the dark for 4 hours. After 4 hours, the reaction was poured into water and extracted with chloroform three times. The organic layer was dried over anhydrous magnesium sulfate and solvent was removed after drying. The crude product was purified by silica gel chromatography using chloroform as eluent to give a purple solid. (215 mg, 62%) ^{1}H NMR

(500 MHz, $CDCl_3$): 8.29 (d, 2H), 6.62 (d, 2H), 3.98 (d, 4H), 1.78 (m, 2H), 1.26 (m, 80H), 0.87 (t, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): 160.92, 146.23, 132.81, 126.23, 122.24, 115.52, 106.31, 46.62, 38.83, 31.94, 31.47, 30.14, 29.72, 29.71, 29.67, 29.60, 29.38, 26.51, 22.71, 14.13.

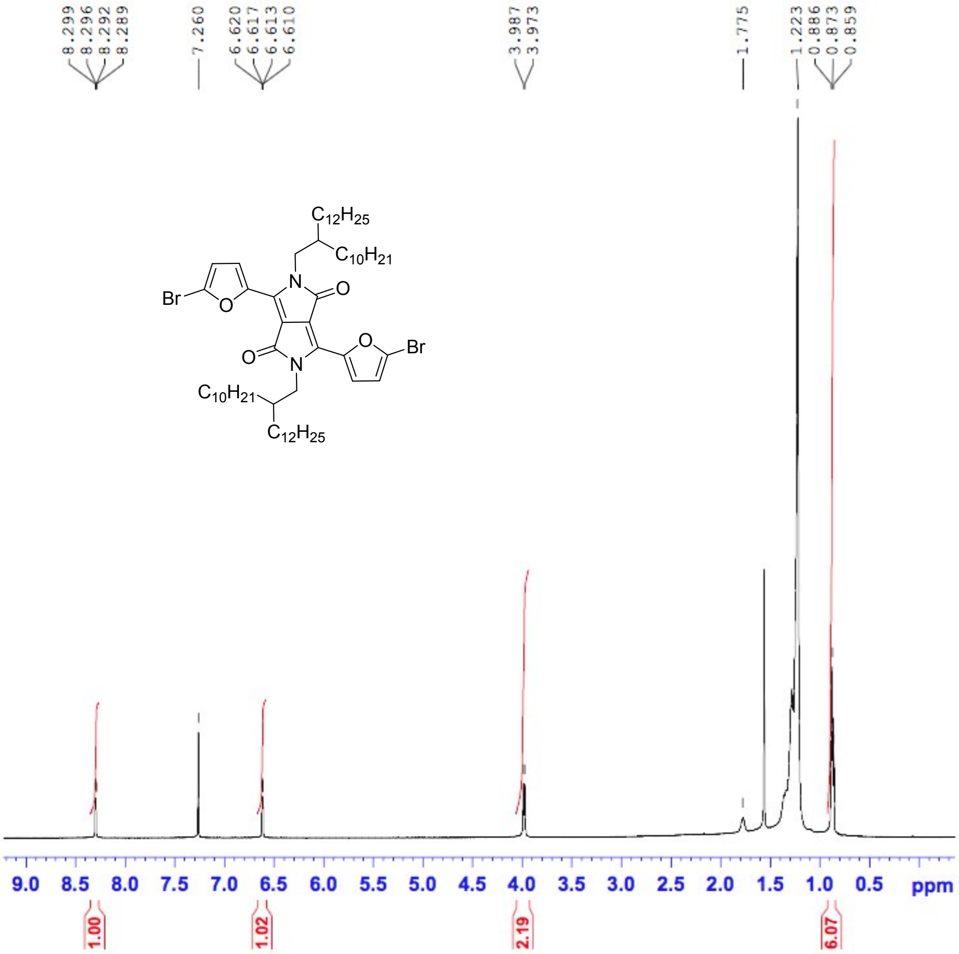


Figure S15. ^1H NMR spectrum of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione

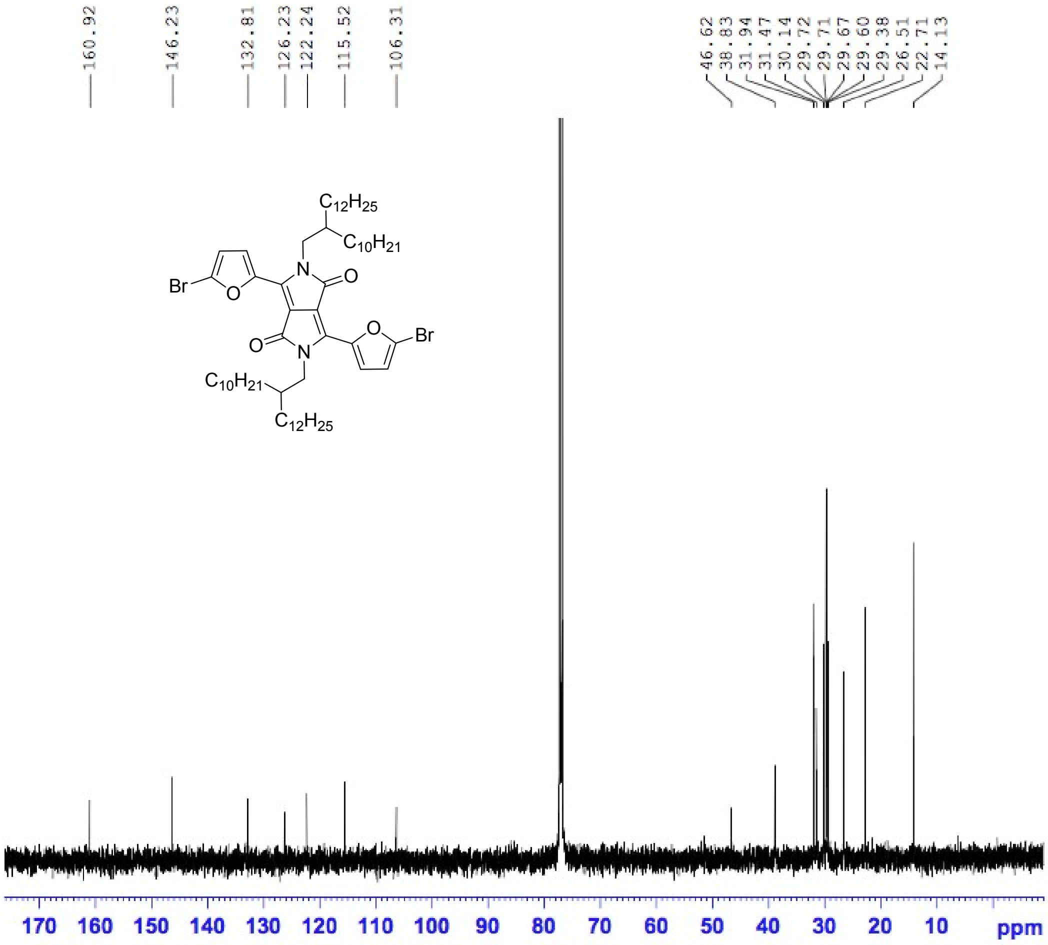


Figure S16. ^{13}C NMR spectrum of 3,6-bis(5-bromofuran-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione.

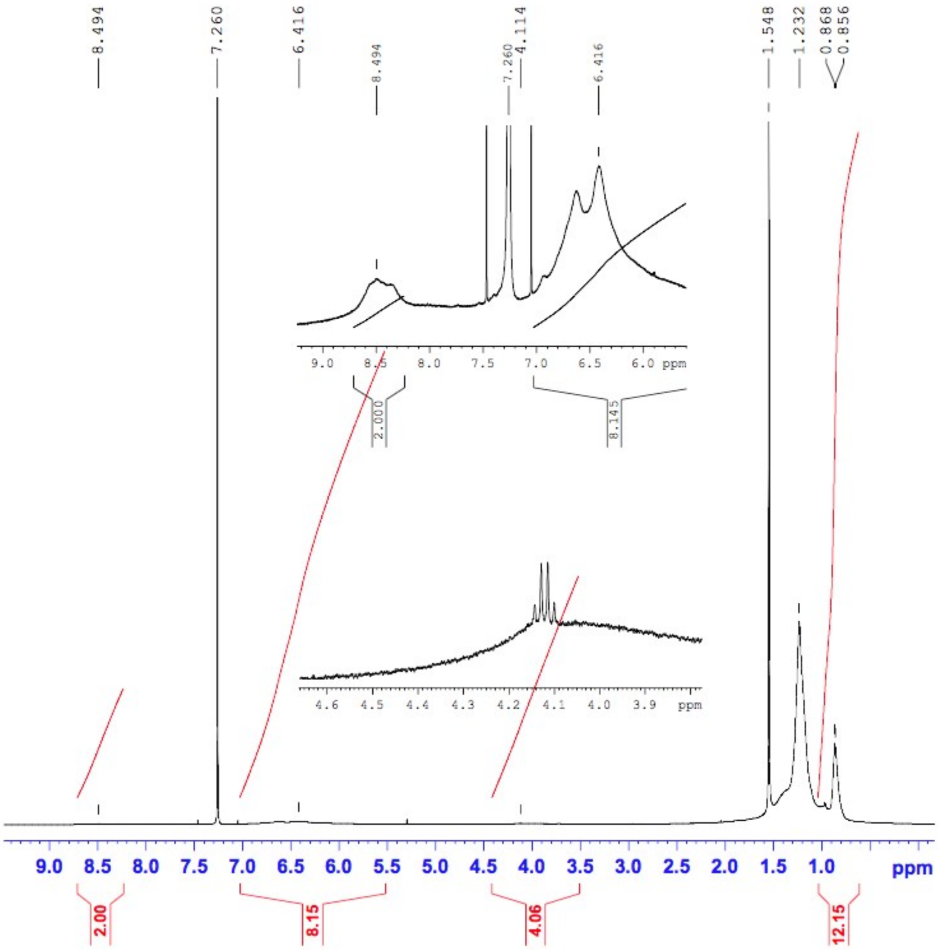


Figure S17. ^{1}H NMR spectrum of P(FDPP-FVF).

*Synthesis of 2,5-bis(2-decyltetradecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**ThDPP**)*

Similar procedure and post processing in FDPP were applied. 3,6-Di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (743 mg, 2.47 mmol), 11-(bromomethyl)tricosane (2.58 g, 6.18 mmol), potassium carbonate (1.13 g, 8.15 mmol) and 15 mL DMF were used. Dark red solid was obtained as the pure product. (1.56 mg, 37%) ^{1}H NMR (500 MHz, $CDCl_3$): 8.86 (d, 2H), 7.61 (d, 2H), 7.27 (dd, 2H), 4.02 (d, 4H), 1.90 (m, 2H), 1.26 (m, 80H), 0.87 (t, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): 161.77, 140.44, 135.22, 130.45, 129.86, 128.40, 107.96, 46.23, 37.75, 31.95, 31.93, 31.20, 30.03, 29.71, 29.66, 29.64, 29.57, 29.37, 26.23, 22.71, 14.13.

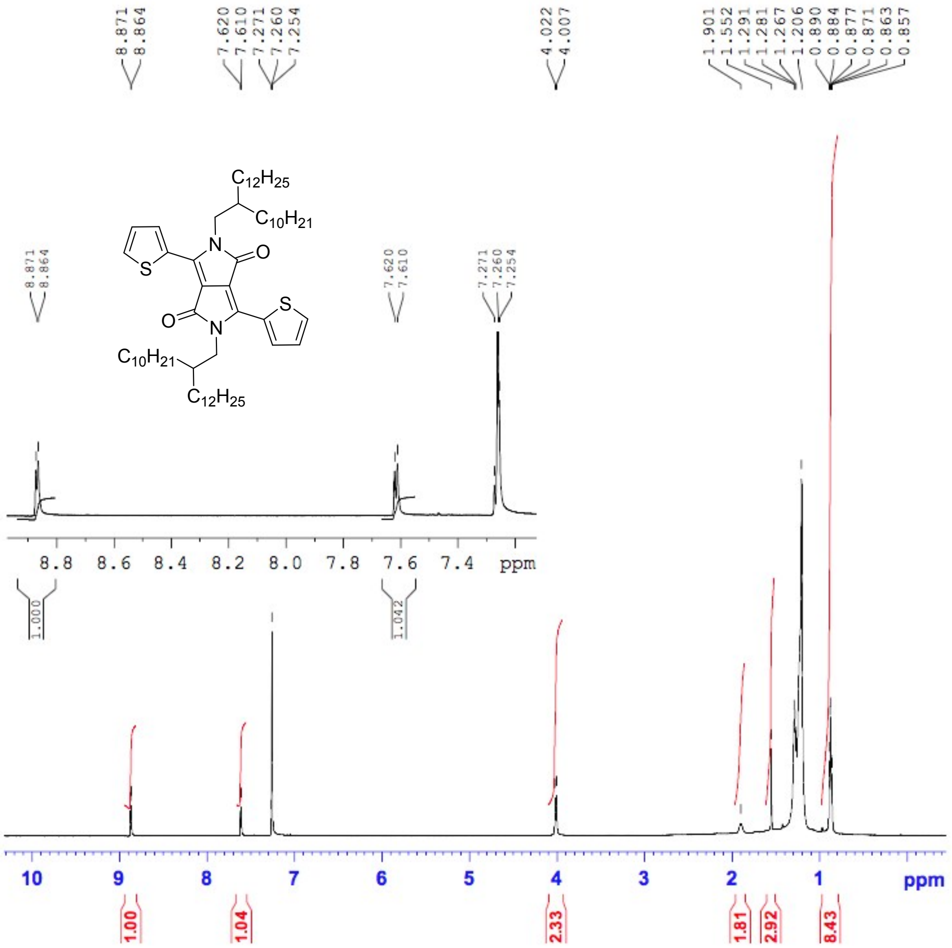


Figure S18. ^{1}H NMR spectrum of 2,5-bis(2-decyltetradecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione

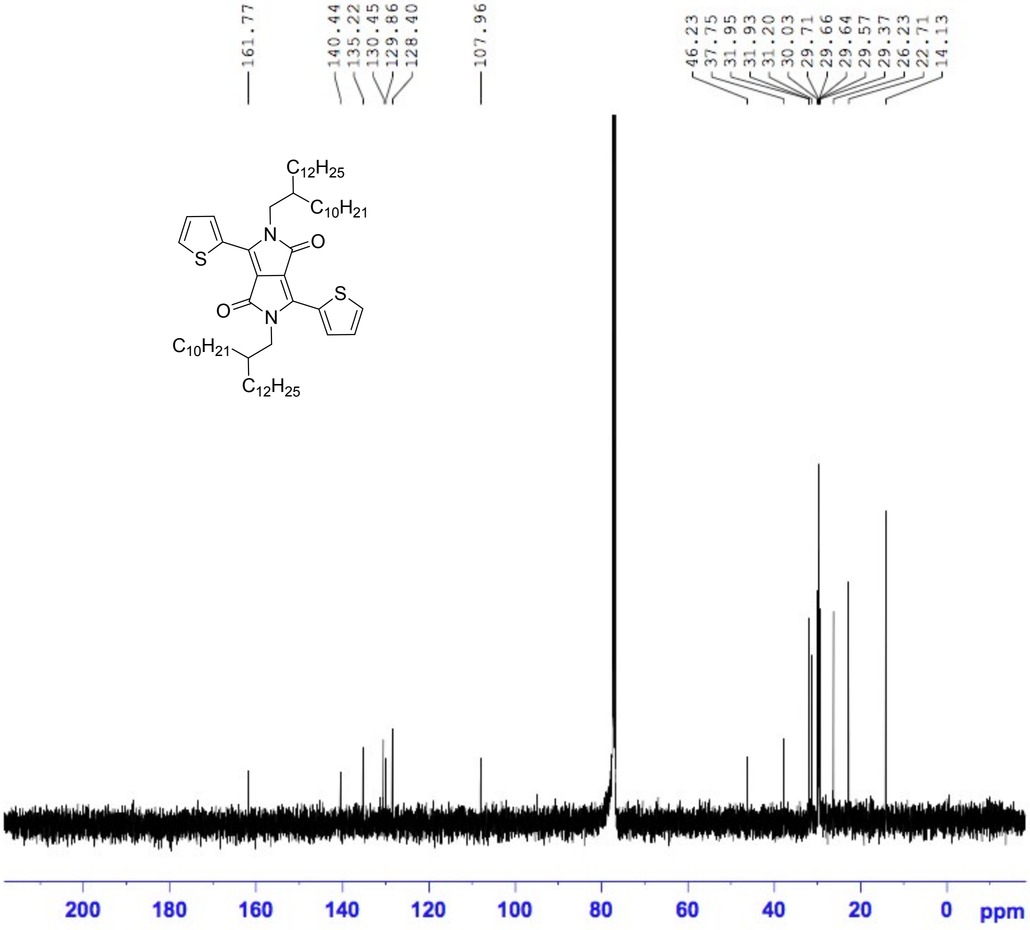


Figure S19. ^{13}C NMR spectrum of 2,5-bis(2-decyltetradecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione

*Synthesis of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**ThDPP-Br**)*

Similar procedure and post processing in FDPP-Br were applied. 2,5-Bis(2-decyltetradecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (300 mg, 0.31 mmol), N-bromosuccinimide (120 mg, 0.68 mmol), and 50 mL Chloroform were used. Purple solid was obtained as pure product. (313 mg, 90%) ^{1}H NMR (500 MHz, $CDCl_3$): 8.62 (d, 2H), 7.21 (d, 2H), 3.91 (d, 4H), 1.87 (m, 2H), 1.21 (m, 80H), 0.87 (t, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): 161.42, 139.42, 135.33, 131.45, 131.18, 118.97, 108.04, 46.36, 37.78, 31.94, 31.19, 30.00, 29.72, 29.71, 29.69, 29.66, 29.58, 29.39, 29.38, 26.20, 22.71, 14.14.

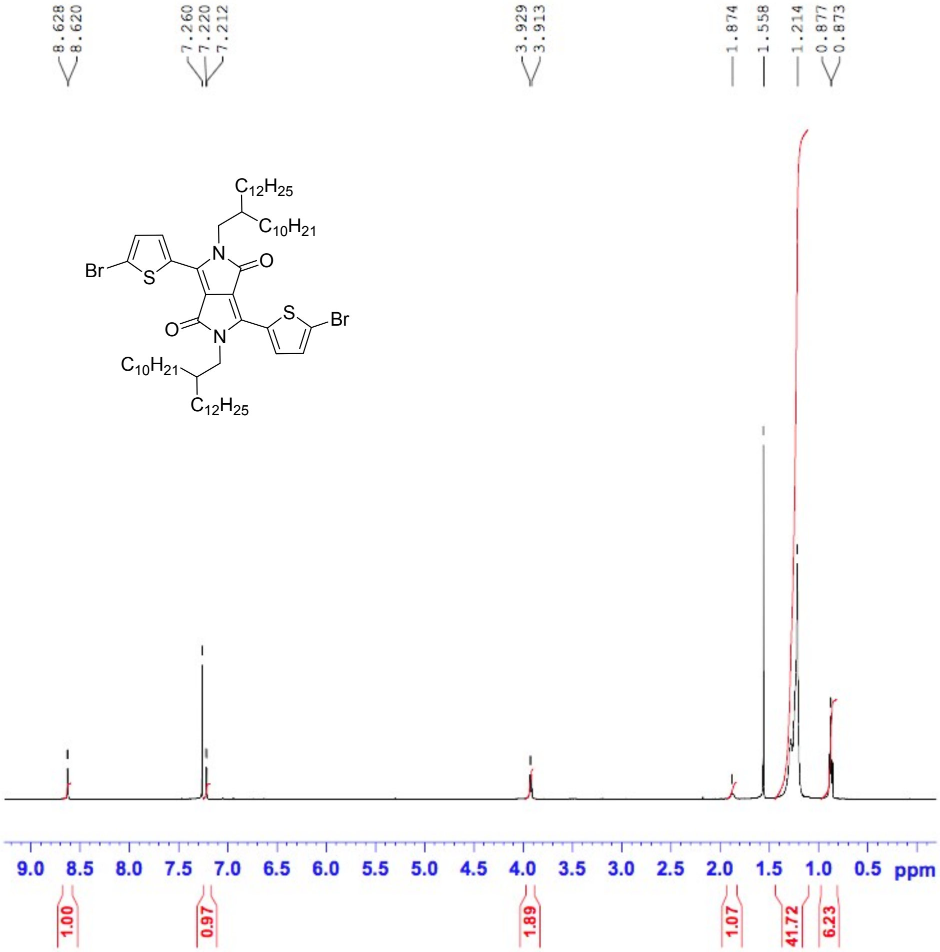


Figure S20. ^{1}H NMR spectrum of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione

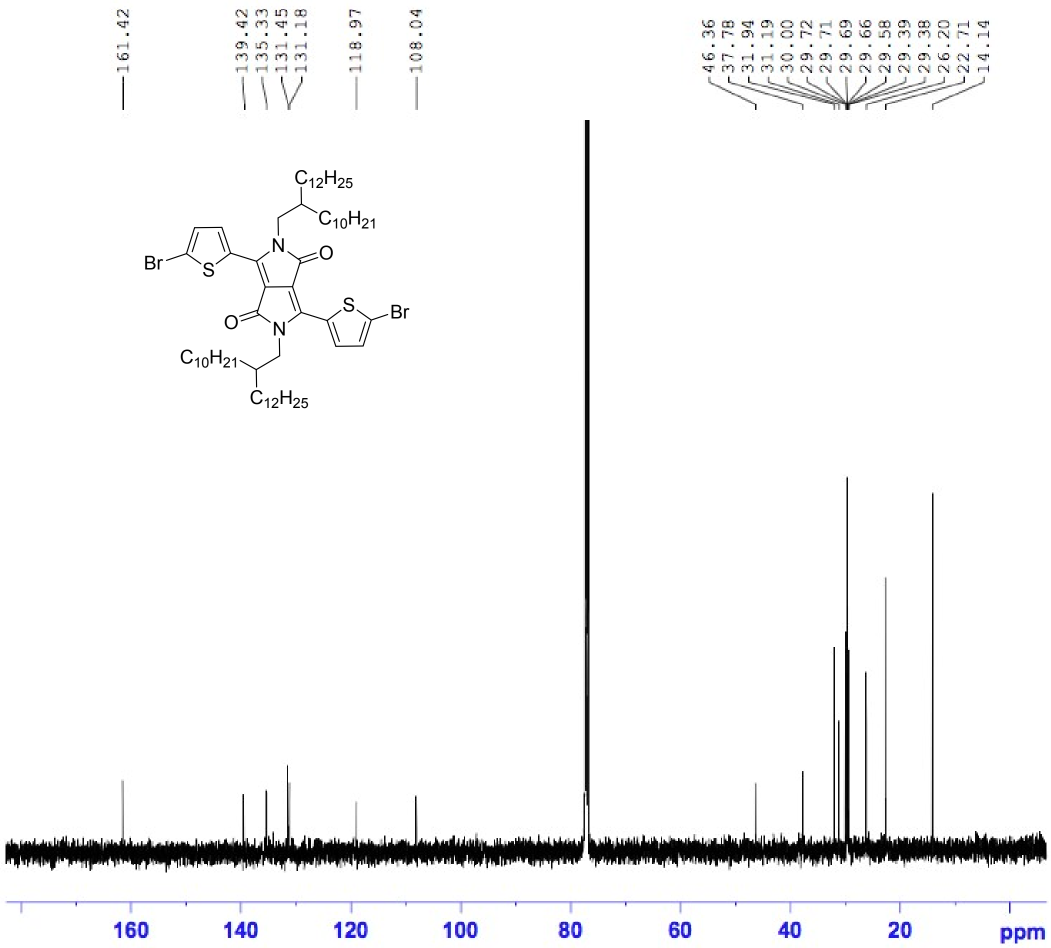


Figure S21. ^{13}C NMR spectrum of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione

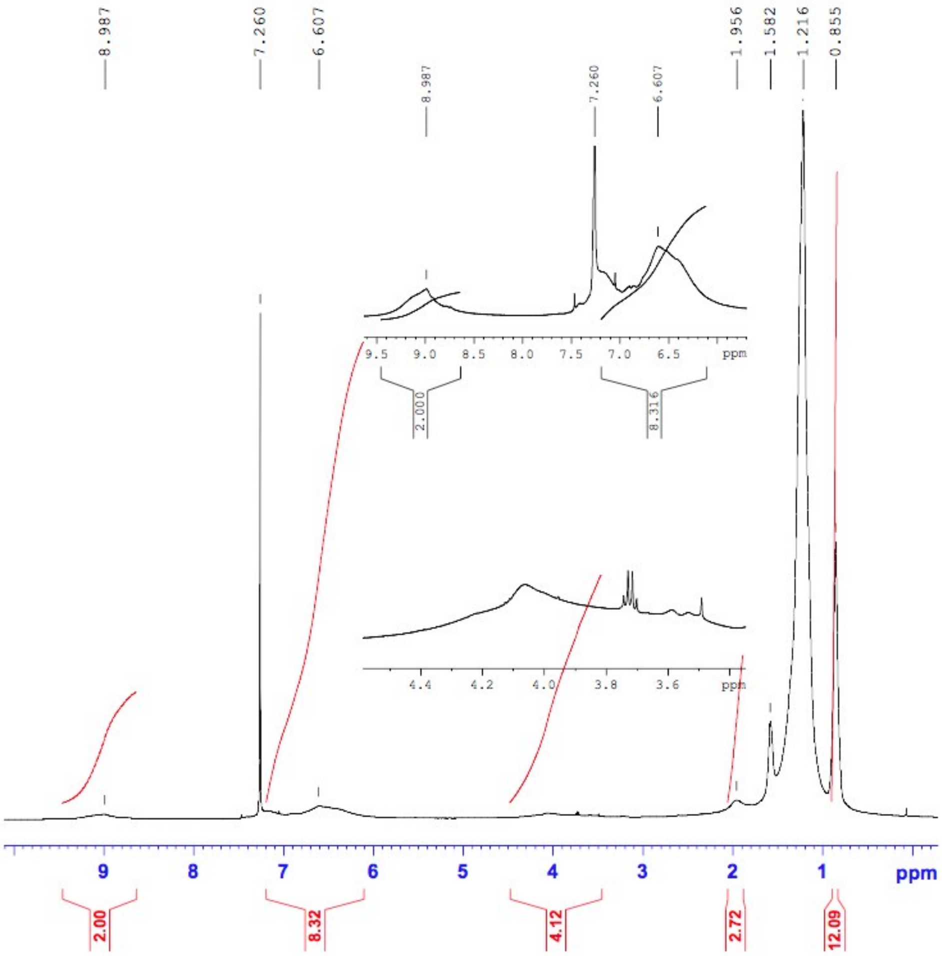
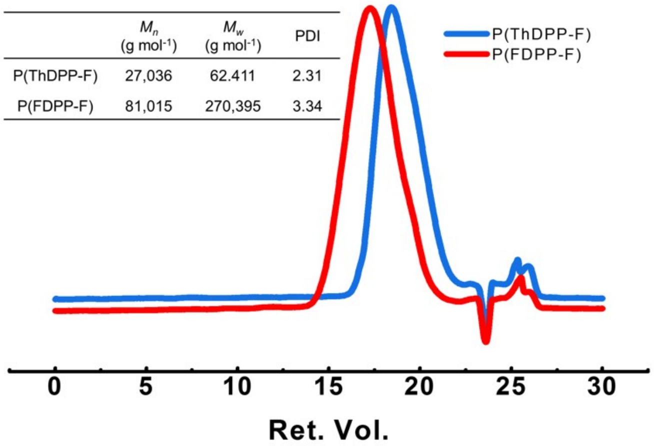


Figure S22. ^{1}H NMR spectrum of P(FDPP-FVF).



	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI
P(ThDPP-F)	27,036	62.411	2.31
P(FDPP-F)	81,015	270,395	3.34

Figure S23. Size exclusion chromatography results of P(FDPP-FVF) and P(ThDPP-FVF).

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