Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for

Impact of New Skeletal Isomerization in Polymer Semiconductors

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Contents

1. Experimental Section

1.1 Materials and characterization

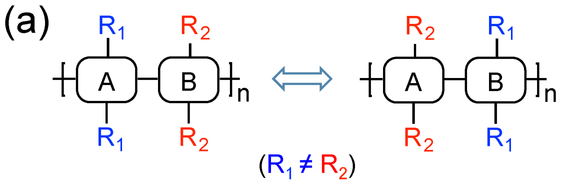
All chemicals and reagents were purchased from commercial sources and used without further purification unless otherwise noted. Thieno[3,2-*b*]thiophene, 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene and 2,5-bis(trimethylstannyl)thiophene was purchased from Derthon optoelectronic materials science technology Co LTD. Tributyl(thieno[3,2-*b*]thiophen-2-yl)stannane[1], tributyl(thiophen-2-yl)stannane[2] and 3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione[3] were synthesized using the literature procedure. All the reactions were conducted under nitrogen atmosphere.

The molecular modeling calculation was performed with the Gaussian 09 program using the density functional theory with B3LYP/6-31G(d) basis set. Nuclear magnetic resonance (NMR) spectra were measured on a Bruker AVANCE III 500 MHz NMR or Bruker AVANCE III 400 MHz NMR spectrometer. Thermogravimetric analyses (TGA) were recorded on a Simultaneous Thermal Analyser instrument (STA449C/449F5) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Differential scanning calorimetry (DSC) analyses were performed in a nitrogen atmosphere using a Perkin Elmer Pyris 1 instrument. Fourier transform infrared (FT-IR) spectroscopy implemented through Nicolet is550 of Thermo Fisher. Gel permeation chromatography (GPC) were conducted on a Waters 1515 liquid chromatography instrument using chloroform as eluent with polystyrene as standards and then carried out on a ShimadzuSIL-20A liquid chromatography instrument using 1,2,4-trichlorobenzene (TCB) as eluent at 150 ^{o}C with polystyrenes as standards. UV-vis spectra were recorded on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. Elemental analyses (EA) were measured on a Vario EL cube elementary analysis apparatus. Cyclic voltammentry (CV) measurements were carried out on a CHI 600 electrochemical analyzer with a three-electrode cell in a deoxygenated anhydrous acetonitrile solution of tetra-*n*-butylammonium-hexafluorophosphate (0.1 M) under nitrogen atmosphere. A platinum disk electrode, platinum-wire, and Ag/AgCl electrode were used as a working electrode, a counter electrode, and a reference electrode, respectively, with the polymer thin film for evaluation coated on the surface of platinum disk electrode. The CV curves were calibrated usingferrocene/ferrocenium (Fc/Fc$^+$) redox couple as an external standard, which was measured under the same condition before and after the measurement of samples. The surface morphology of polymers was obtained by a Bruker Multimode V atomic force microscopy (AFM). Grazing incidence wide-angle X-ray scattering (GIWAXS) experiments were done at BL14B1 beamline at Shanghai Synchrotron Radiation Facility. Electrical measurements of the OFET devices were performed in air (R_H = 40%, 25 ^oC) by a semiconductor parameter analyzer (Keithley 4200).

1.2 Device fabrication and characterization

The top-contact bottom-gate OFETs were fabricated on a heavily *p*-doped Si with a dielectric layer of 100 nm SiO_2. The silicon substrates were ulatrasonicated in acetone and isopropanol for 10 min respectively, and then dried with nitrogen. After that, the substrates were treated by a monolayer of (octadecyl)trichlorosilane (OTS) and rinsed with toluene and isopropanol to modify the SiO_2 dielectric surface. Subsequently, the polymers **P(DPPT-TT)** and **P(DPPTT-T),** dissolving in chlorobenzene (5 mg/mL) respectively, were spin-coated on the substrate with 1000 rpm for 60 s (or then annealed at 135 °C for 10 min) to be used as channel layer. Drain and source electrodes were deposited by thermal evaporation through a shadow mask with channel length and width defined as 30 μm and 100 μm, respectively. The field-effect mobility was calculated in the saturation regime by using the equation $I_{DS} = (\mu W C_i/2L)(V_G - V_T)^2$, where I_{DS} is the drain-source current, μ is the field-effect mobility, W is the channel width, L is the channel length, C_i is the capacitance per unit area of the gate dielectric layer, V_G is the gate voltage, and V_T is threshold voltage.

1.3 Literature overview of representative isomeric polymers for OFETs.



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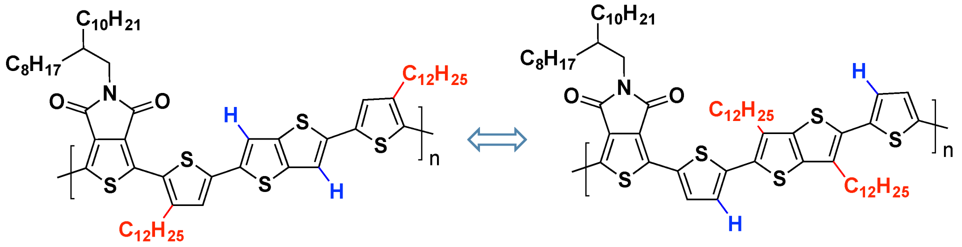
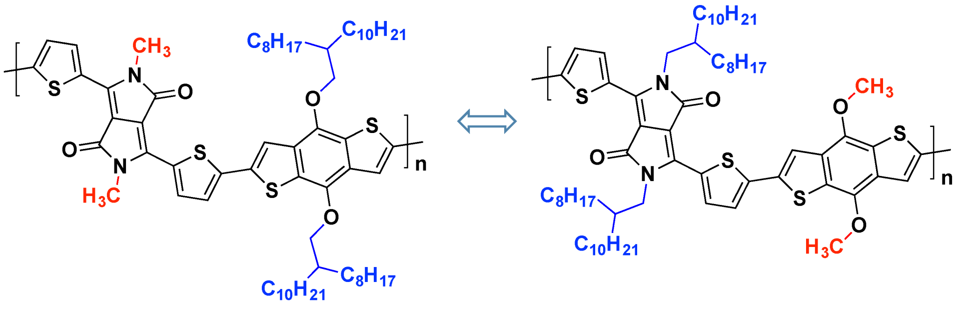


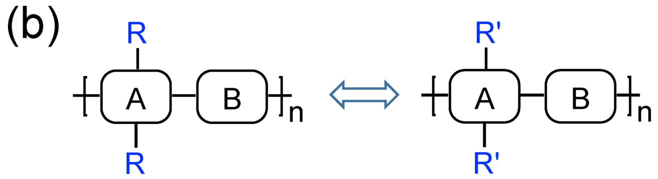
μ_h: 0.75 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10$^{4-5}$　　**μ_h: 1.29 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10$^{6-7}$**

***Macromolecules*, 2013, 46, 3887–3894.**



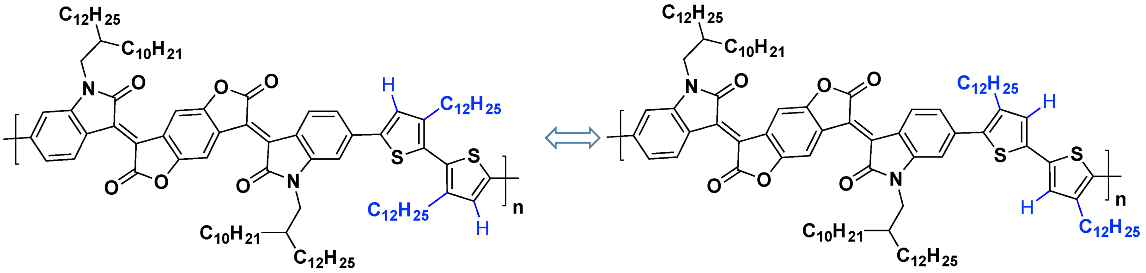
μ_h: 0.003 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10^{5}　　**μ_h: 0.29 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10^{7}**

***Polym. Chem.*, 2015, 6, 5369−5375.**



(isomeric units: R and R')

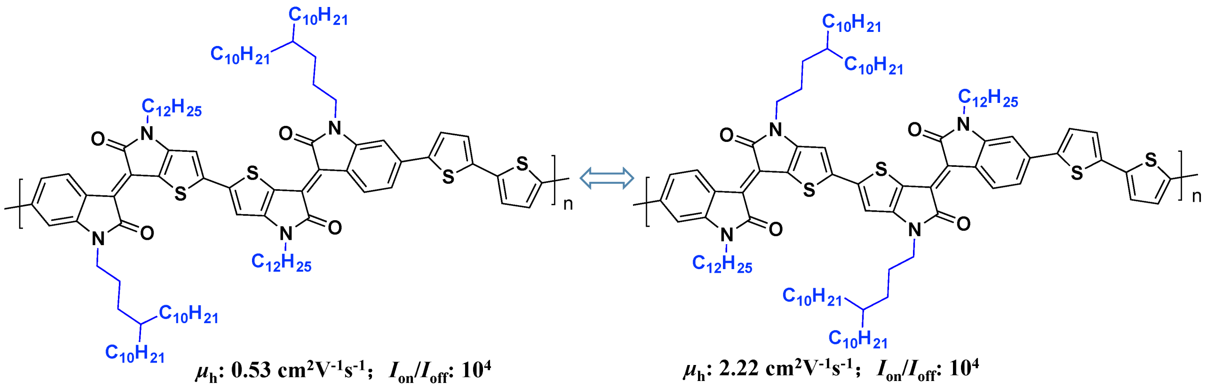
e.g.



μ_h: 0.37 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 22
μ_e: 1.23 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 17

μ_h: 0.17 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 56
μ_e: 0.70 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 30

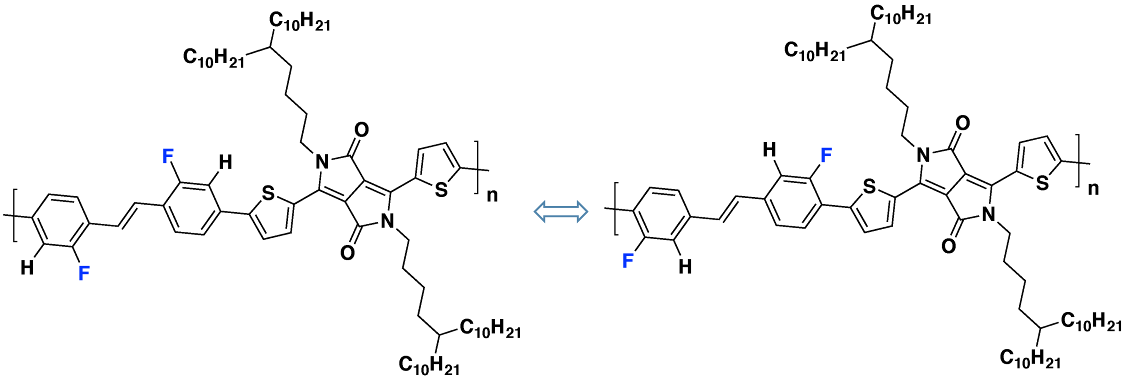
***J. Mater. Chem.C.*, 2016, 4, 6391−6400.**



μ_h: 0.53 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10^4

μ_h: 2.22 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10^4

***Macromolecules* 2018, 51, 8486−8492.**



μ_h: 1.48 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: $10^{6\text{-}7}$

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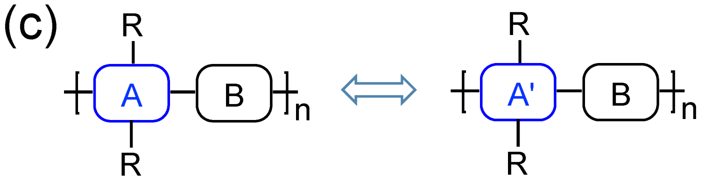
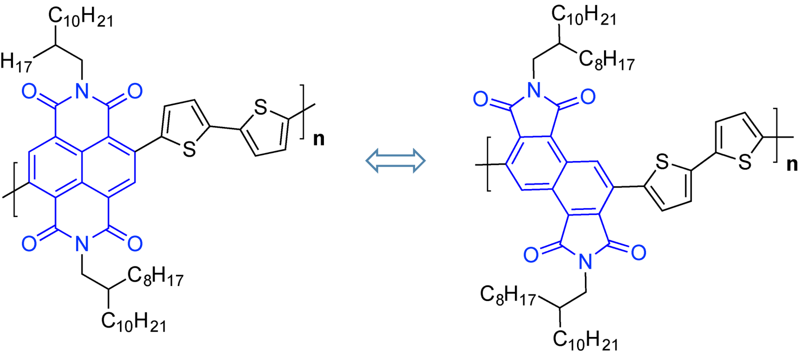
***Macromolecules* 2016, 49, 2582−2591.**



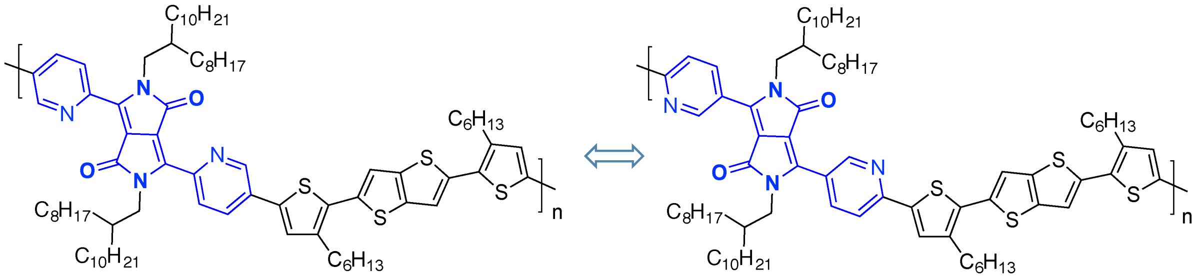
(isomeric units: A and A')

e.g.



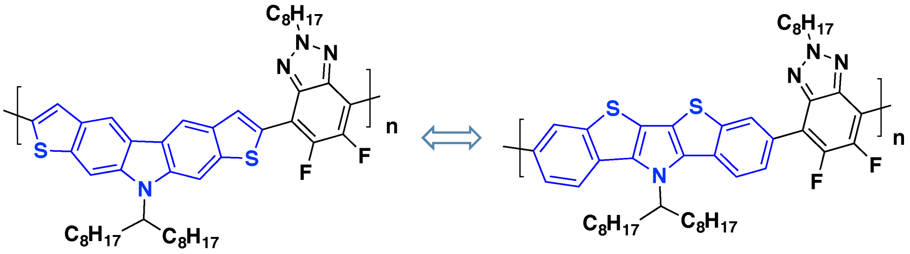
μ_e: 0.85 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10$^{6\text{-}7$ **μ_h: 0.30 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10^4**

***Nature* 2009, 457, 679−687.**
***Macromolecules* 2013, 46, 7705−7714.**



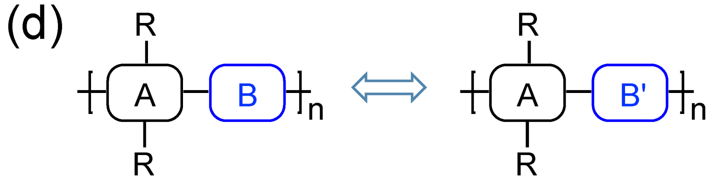
μ_e: 0.35 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10$^{4\text{-}5}$ **μ_h: 3.7×10^{-4} cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10$^{2\text{-}3}$**

***J. Mater. Chem. C*, 2016, 4, 2470−2479.**



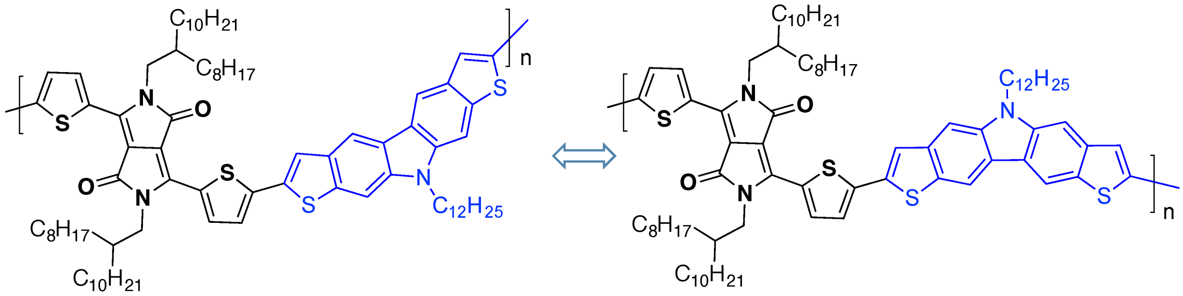
μ_h: 8.31×10^{-4} cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10^4 **μ_h: 0.03 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10^5**

***ACS Appl. Mater. Interfaces*, 2018, 10, 6471−6483**



(isomeric units: B and B')

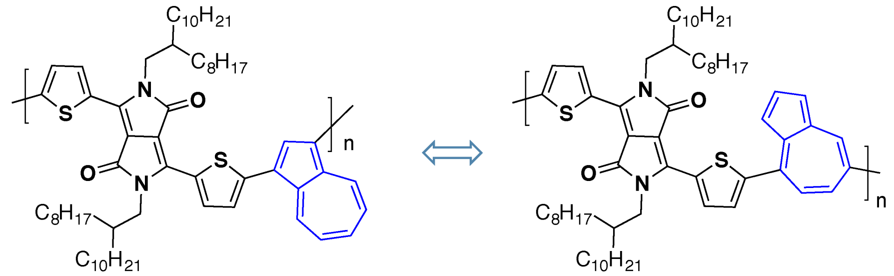
e.g.



μ_e: 6.7×10^{-3} cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10^4

μ_h: 1.36 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10^5

Macromolecules, 2012, 45, 8621−8627.

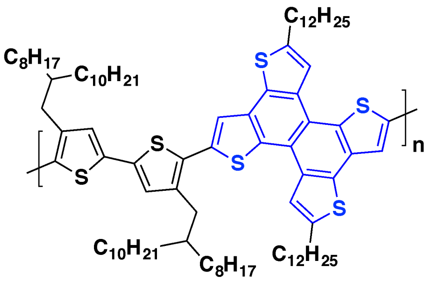


μ_e: 0.97 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: $10^{4\text{-}5}$

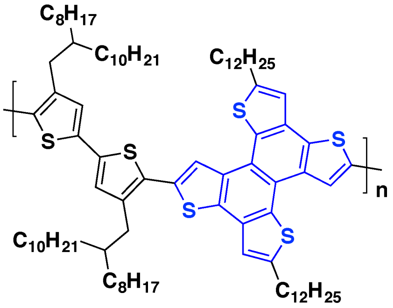
μ_h: 0.062 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10^3

μ_e: 0.021 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: $10^{1\text{-}2}$

Macromolecules, 2015, 48, 2039−2047.



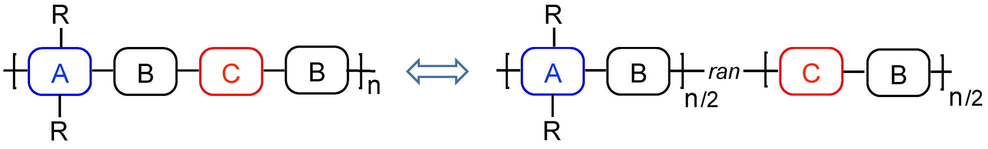
μ_h: 0.0126 cm^{2}V^{-1}s^{-1}



μ_h: 2.4×10^{-4} cm^{2}V^{-1}s^{-1}

Org. Lett., 2016, 18, 368−371

(e)



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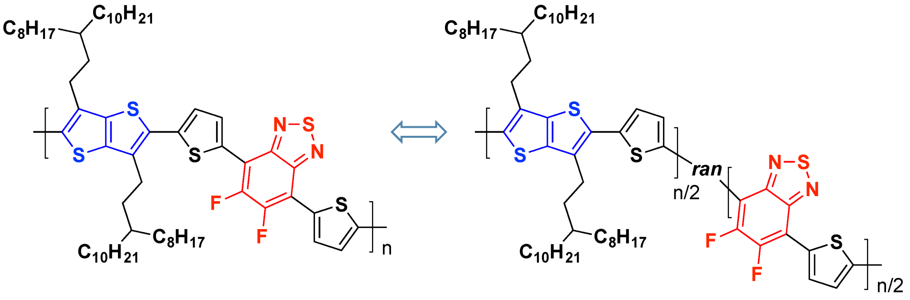
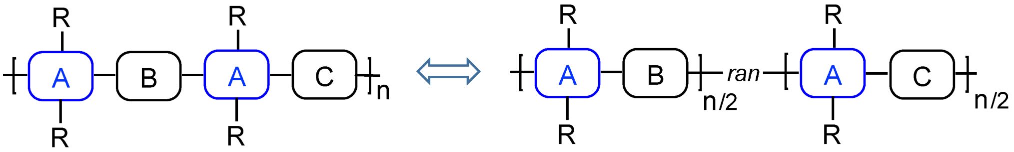


μ_e: 0.061 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10^5 **μ_h: 0.030 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10^5**

***Macromolecules*, 2016, 49, 2541−2548.**

(f)



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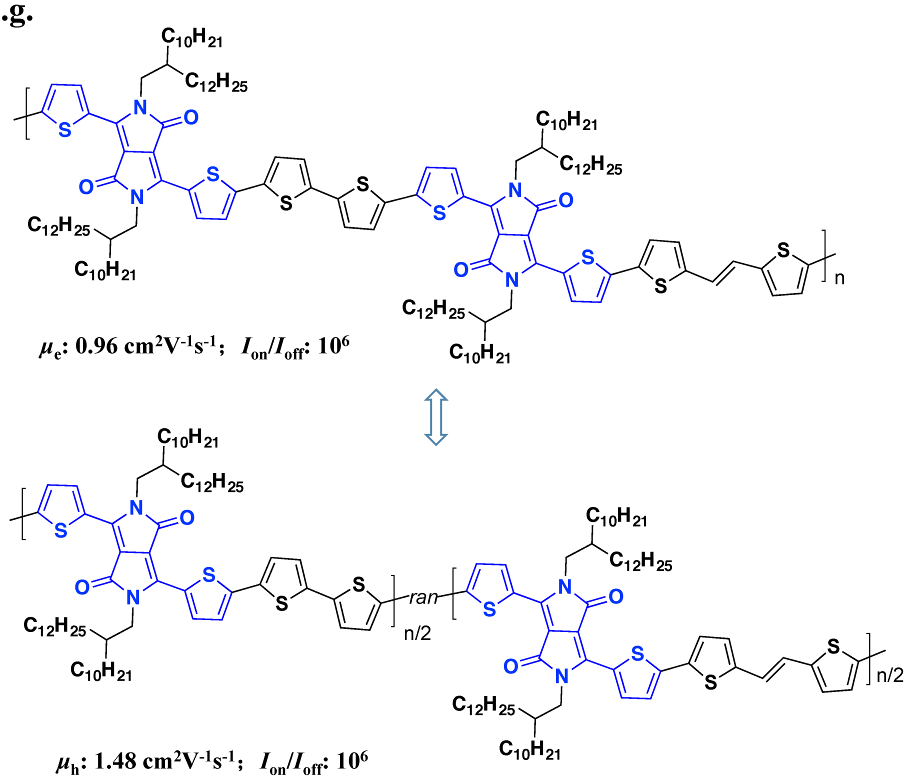
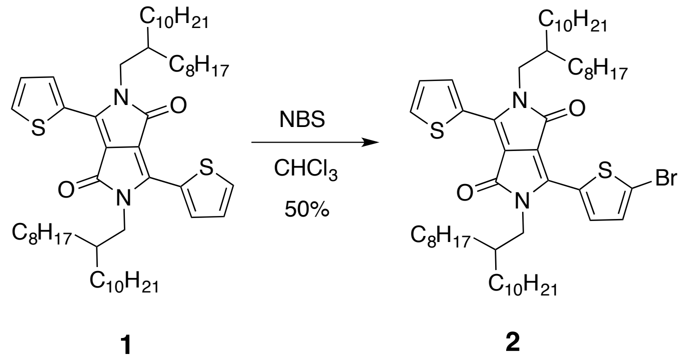


μ_e: 0.96 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10^6

μ_h: 1.48 cm^{2}V^{-1}s^{-1}; I_{on}/I_{off}: 10^6

***ACS Appl. Mater. Interfaces*, 2015, 49, 28303−28310.**

1.4 Synthesis of monomers and polymers

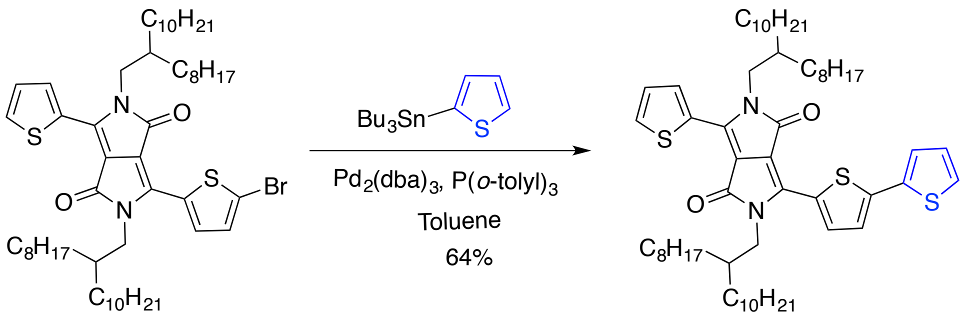


*3-(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo-[3,4-c]pyrrole-1,4-dione(**2**).*

A solution of *N*-bromosuccinimide (NBS) (0.35 g, 1.97 mmol) in chloroform (150 mL) was added dropwise to a stirred solution of 2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione(**1**) (1.7 g, 1.97 mmol) in chloroform (50 mL) which was cooled in an ice-water bath. The reaction mixture was stirred until the reaction was complete (TLC; 8 h) and then poured into ice water. The mixture was then extracted with dichloromethane. The organic layer was washed with water and brine. It was dried with anhydrous sodium sulfate. After removing solvent, the crude product was purified by flash column chromatography on silica gel (dichloromethane/petroleum ether = 1/3, V/V) to afford the titled compound (0.98 g, 50%) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (t, *J* = 4.0 Hz, 1H), 8.60 (d, *J* = 4.0 Hz, 1H), 7.63 (t, *J* = 4.0 Hz, 1H), 7.27-7.21 (m, 2H), 4.00 (d, *J* = 4.0 Hz, 2H), 3.93 (d, *J* = 8.0 Hz, 2H), 1.58 (s, 4H), 1.90-1.89 (m, 2H), 1.36-1.15 (m, 60H), 0.84-0.89 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.64, 161.47, 140.88, 138.93, 135.52, 135.05, 131.40, 131.26, 130.78, 129.76, 128.47, 118.57, 108.14, 107.78, 46.28, 37.77, 31.94, 31.90, 31.17, 30.01, 29.65, 29.59, 29.57, 29.52, 29.51, 29.38, 29.31, 26.19, 22.71, 22.69, 14.15.



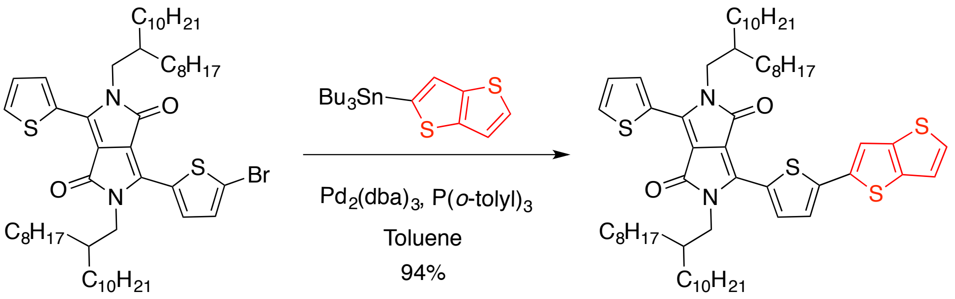
2 **3**

*3-([2,2'-bithiophen]-5-yl)-2,5-bis(2-octyldodecyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo-[3,4-c]pyrrole-1,4-dione(**3**).*

A mixture of 3-(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione(**2**) (1.1 g, 1.17 mmol), 2-trimethylstannylthiophene (0.67 g, 1.8 mmol), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (53.5 mg, 0.058 mmol) and tri(*o*-tolyl)phosphine (P(*o*-tolyl)$_3$) (35.6 mg, 0.117 mmol) in anhydrous toluene (10 mL) in a Schlenk tube was subjected to three cycles of evacuation and admission of nitrogen and subsequently stirred at 100 °C for 12 h. The reaction mixture was allowed to cool to room temperature. Solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel with dichloromethane as eluent to afford the titled compound (0.70 g, 64%) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.97-8.80 (m, 2H), 7.61 (d, J = 5.6 Hz, 1H), 7.35-7.27 (m, 3H), 7.25 (d, J = 3.4 Hz, 1H), 7.08 (dd, J = 5.1, 3.7 Hz, 1H), 4.03 (d, J = 7.7 Hz, 4H), 1.93 (s, 2H), 1.57 (s, 4H), 1.42-1.20 (m, 60H), 1.00-0.70 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.78, 161.63, 142.78, 140.04, 139.92, 136.72, 136.23, 135.15, 130.37, 129.93, 128.41, 128.26, 128.06, 126.24, 125.15, 124.75, 108.15, 108.12, 46.27, 37.93, 37.76, 31.95, 31.91, 31.33, 31.19, 30.07, 30.04, 29.67, 29.64, 29.58, 29.53, 29.39, 29.33, 22.71, 22.69, 14.15.



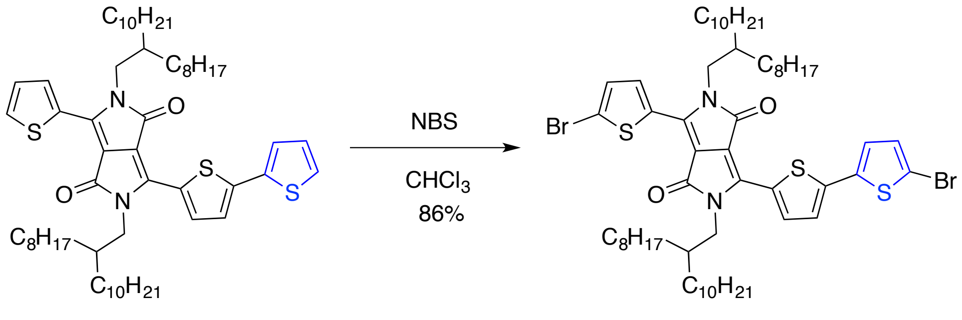
2 **4**

*2,5-bis(2-octyldodecyl)-3-(5-(thieno[3,2-b]thiophen-2-yl)thiophen-2-yl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione(**4**).*

A mixture of 3-(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (**2**) (0.5 g, 0.53 mmol), tributyl(thieno[3,2-*b*]thiophen-2-yl)stannane (0.68 g, 1.6 mmol), $Pd_2(dba)_3$ (34.3 mg, 0.0265 mmol) and P(*o*-tolyl)$_3$ (16.1 mg, 0.053 mmol) in anhydrous toluene (10 mL) in a Schlenk tube was subjected to three cycles of evacuation and admission of nitrogen and subsequently stirred at 100 °C for 12 h. The reaction mixture was allowed to cool to room temperature. Solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel with dichloromethane as eluent to afford the titled compound (0.50 g, 94%) as a purple solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.90 (d, *J* = 4.1 Hz, 2H), 7.67 (d, *J* = 4.0 Hz, 1H), 7.54 (s, 1H), 7.47 (d, *J* = 4.6 Hz, 1H), 7.38 (d, *J* = 3.8 Hz, 1H), 7.34-7.20 (m, 2H), 4.02 (dd, *J* = 7.7, 3.7 Hz, 4H), 1.92 (d, *J* = 34.0 Hz, 2H), 1.55 (s, 4H), 1.43-1.15 (m, 60H), 0.99-0.73 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.64, 140.05, 139.82, 136.62, 135.14, 130.40, 128.45, 128.39, 124.80, 119.49, 117.15, 108.30, 46.30, 37.95, 37.76, 31.92, 31.89, 31.35, 31.22, 30.06, 30.01, 29.65, 29.57, 29.50, 29.36, 29.31, 29.29, 26.36, 26.23, 22.68, 22.66, 14.10.



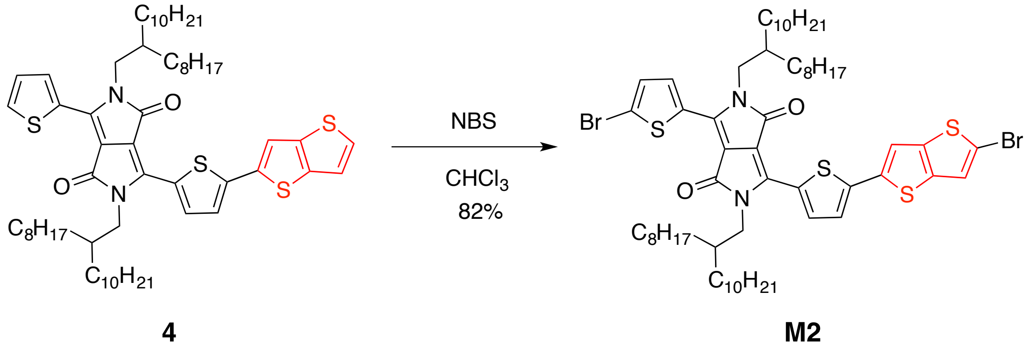
3 **M1**

*3-(5'-bromo-[2,2'-bithiophen]-5-yl)-6-(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione(**M1**).*

A solution of NBS (0.35 g, 1.97 mmol) in chloroform (50 mL) was added dropwise to a stirred solution of 3-([2,2'-bithiophen]-5-yl)-2,5-bis(2-octyldodecyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione(**3**) (0.075 g, 0.53 mmol) in chloroform (50 mL) which was cooled in an ice-water bath. The reaction mixture was stirred until the reaction was complete (TLC; 8 h) and then poured into ice water. The mixture was then extracted with dichloromethane. The organic layer was washed with water and brine. It was dried with anhydrous sodium sulfate. After removing solvent, the crude product was purified by flash column chromatography on silica gel (dichloromethane/petroleum ether = 1/4, V/V) to afford the titled compound (0.50 g, 86%) as a purple solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (d, *J* = 3.8 Hz, 1H), 8.62 (d, *J* = 4.0 Hz, 1H), 7.23 (dd, *J* = 11.2, 4.1 Hz, 2H), 7.11 -6.99 (m, 2H), 3.97 (dd, *J* = 29.1, 7.7 Hz, 4H), 1.90 (dd, *J* = 16.3, 9.6 Hz, 2H), 1.56 (s, 4H), 1.39-1.07 (m, 60H), 0.86 (qd, *J* = 7.0, 1.9 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.51, 161.29, 141.62, 139.99, 138.67, 137.57, 136.71, 135.11, 131.35, 131.25, 131.07, 128.29, 125.15, 124.82, 118.65, 113.24, 108.24, 108.17, 46.28, 37.89, 37.75, 31.93, 31.89, 31.28, 31.16, 30.04, 30.00, 29.66, 29.57, 29.52, 29.38, 29.32, 29.31, 26.32, 26.18, 22.70, 22.68, 14.13.

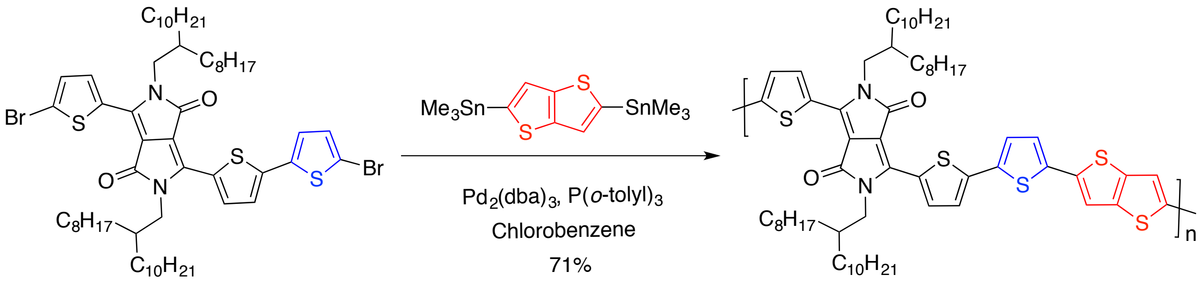


*3-(5-(5-bromothieno[3,2-b]thiophen-2-yl)thiophen-2-yl)-6-(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione(**M2**).*

A solution of NBS (0.24 g, 1.33 mmol) in chloroform (50 mL) was added dropwise to a stirred solution of 2,5-bis(2-octyldodecyl)-3-(5-(thieno[3,2-*b*]thiophen-2-yl)thiophen-2-yl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione(**4**) (0.52 g, 0.53 mmol) in chloroform (50 mL) which was cooled in an ice-water bath. The reaction mixture was stirred until the reaction was complete (TLC; 12 h) and then poured into ice water. The mixture was then extracted with dichloromethane. The organic layer was washed with water and brine. It was dried with anhydrous sodium sulfate. After removing solvent, the crude product was purified by flash column chromatography on silica gel (dichloromethane/petroleum ether = 1/4, V/V) to afford the titled compound (0.19 g, 82%) as a purple solid.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.90 (d, *J* = 4.4 Hz, 1H), 8.59 (d, *J* = 2.6 Hz, 1H), 7.43 (d, *J* = 2.5 Hz, 1H), 7.39-7.34 (m, 1H), 7.29 (s, 1H), 7.25 (d, *J* = 3.5 Hz, 1H), 3.96 (dd, *J* = 36.3, 7.6 Hz, 4H), 2.05-1.73 (m, 2H), 1.55 (d, *J* = 1.0 Hz, 4H), 1.42-1.10 (m, 60H), 0.94-0.75 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.52, 161.25, 142.56, 140.20, 139.94, 138.56, 138.02, 137.16, 136.85, 135.07, 131.35, 131.30, 128.44, 124.90, 122.16, 118.61, 116.58, 114.92, 108.30, 108.17, 46.35, 37.95, 37.79, 31.94, 31.91, 31.33, 31.21, 30.07, 30.01, 29.65, 29.58, 29.52, 29.38, 29.32, 29.31, 26.36, 26.22, 22.70, 22.68, 14.12.



M1 **P(DPPT-TT)**

*Polymer **P(DPPT-TT)**.*

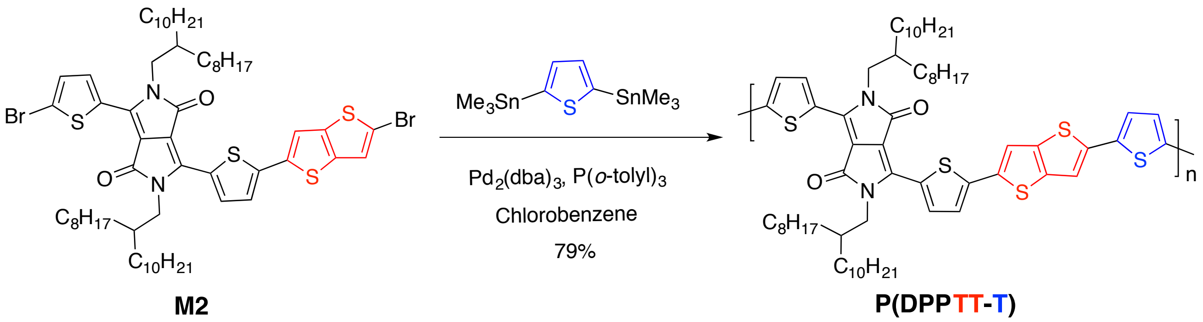
A mixture of **M1** (188.7 mg, 0.2 mmol), 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (93.2 mg, 0.20 mmol), $Pd_2(dba)_3$ (3.7 mg, 0.004 mmol), P(*o*-tolyl)$_3$ (4.9 mg, 0.016 mmol) in anhydrous chlorobenzene (6 mL) in a Schlenk tube was subjected to three cycles of evacuation and admission of nitrogen and subsequently stirred at 100 °C for 48 h. After polymerization, the reaction mixture was allowed to cool to room temperature and poured into stirring methanol to precipitate the crude product. The precipitate was collected by filtration and was further purified by sequential Soxhlet extractions with dried methanol, petroleum ether and toluene each for 24 h. The residue after Soxhlet extractions was then extracted with dried chloroform. The chloroform solution was reprecipitated with methanol. The solid was collected and then dried to obtain the title polymer. (Blue solid with a metallic luster, 154 mg, 71%).

^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d2, 80 ^{o}C) δ 8.94 (br, 2H), 6.85-7.75 (m, 6H), 4.11 (br, 4H), 2.07 (m, 2H), 1.22-1.45 (m, 64H), 0.96 (br, 12H).

Anal. Calcd for $C_{64}H_{90}N_2O_2S_5$: C, 71.19; H, 8.40; N, 2.59 , Found: C, 71.51; H, 7.86; N, 2.47.

GPC (chloroform, 25 ^{o}C): M_n = 53.9 kDa, M_w = 215 kDa, PDI = 3.98.

GPC (TCB, 150 ^{o}C): M_n = 22.5 kDa, M_w = 52.1 kDa, PDI = 2.32.



*Polymer **P(DPPTT-T)**.*

A mixture of **M2** (199.9 mg, 0.2 mmol), 2,5-bis(trimethylstannyl)thiophene (82.0 mg, 0.20 mmol), $Pd_2(dba)_3$ (3.7 mg, 0.004 mmol), P(*o*-tolyl)$_3$ (4.9 mg, 0.016 mmol) in anhydrous chlorobenzene (6 mL) in a Schlenk tube was subjected to three cycles of evacuation and admission of nitrogen and subsequently stirred at 100 °C for 48 h. After polymerization, the reaction mixture was allowed to cool to room temperature and poured into stirring methanol to precipitate the crude product. The precipitate was collected by filtration and was further purified by sequential Soxhlet extractions with dried methanol, petroleum ether and toluene each for 24 h. The residue after Soxhlet extractions was then extracted with dried chloroform. The chloroform solution was reprecipitated with methanol. The solid was collected and then dried to obtain the title polymer. (Blue solid with a metallic luster, 195 mg, 79%).

^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d2, 80 ^{o}C) δ 8.91 (br, 2H), 6.85-7.75 (m, 6H), 4.11 (br, 4H), 2.07 (m, 2H), 1.22-1.45 (m, 64H), 0.95 (br, 12H).

Anal. Calcd for $C_{64}H_{90}N_2O_2S_5$: C, 71.19; H, 8.40; N, 2.59, Found: C, 71.46; H, 7.93; N, 2.45.

GPC (chloroform, 25 ^{o}C): M_n = 66.2 kDa, M_w = 251 kDa, PDI = 3.80.

GPC (TCB, 150 ^{o}C): M_n = 27.0 kDa, M_w = 61.5 kDa, PDI = 2.28.

2. Figures in Supporting Information

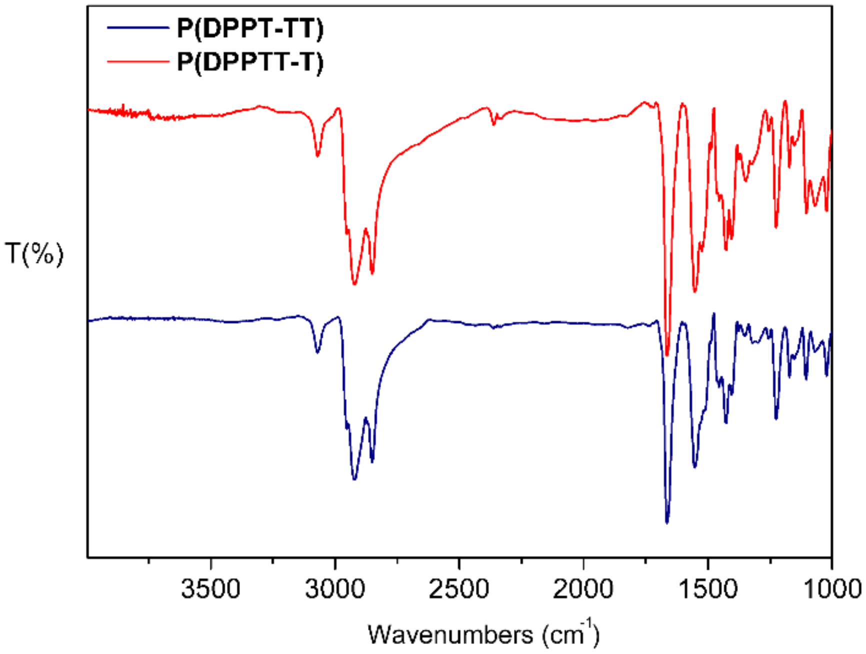


Figure S1. FT-IR spectrum of polymers **P(DPPT-TT)** and **P(DPPTT-T)**

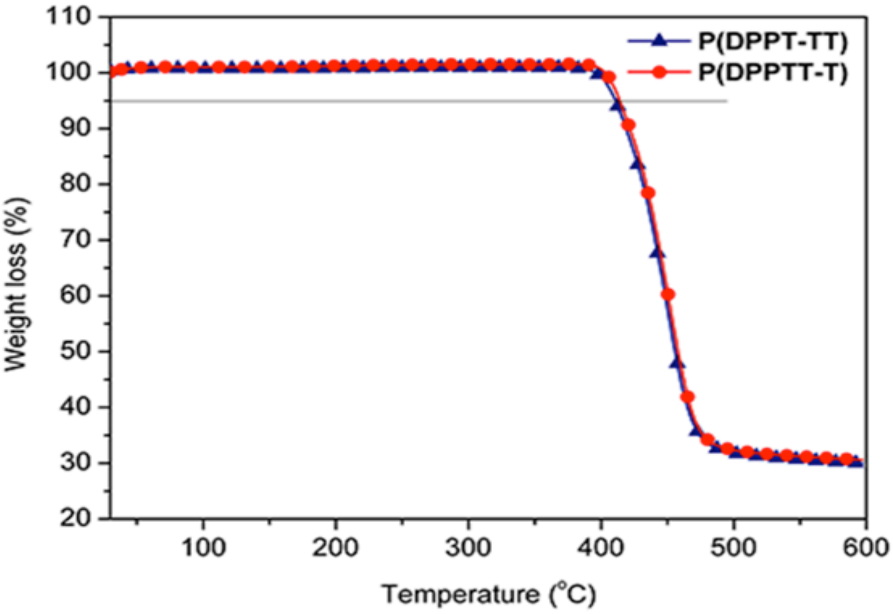


Figure S2. TGA plots of polymers **P(DPPT-TT)** and **P(DPPTT-T)** at a heating rate of 10 °C min^{-1} under nitrogen atmosphere

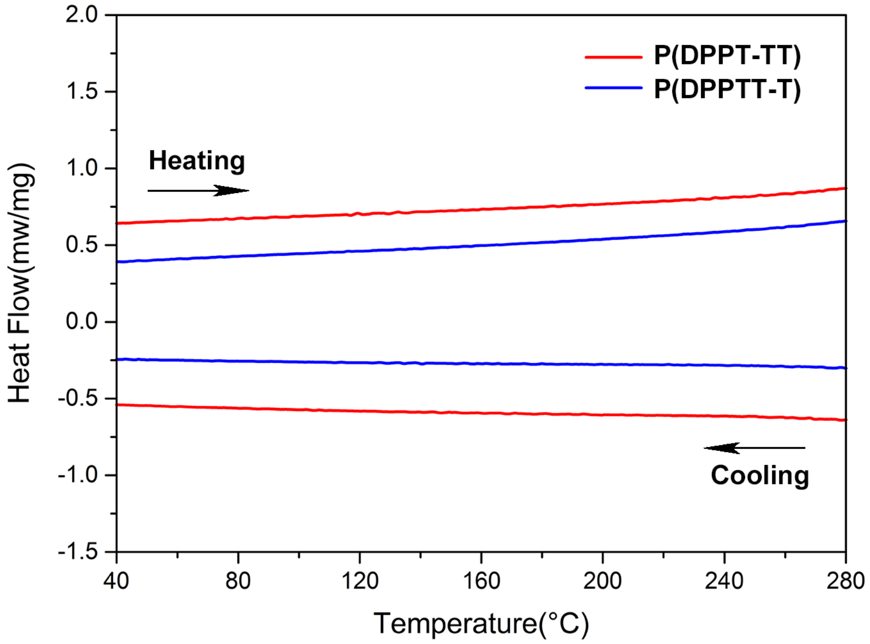
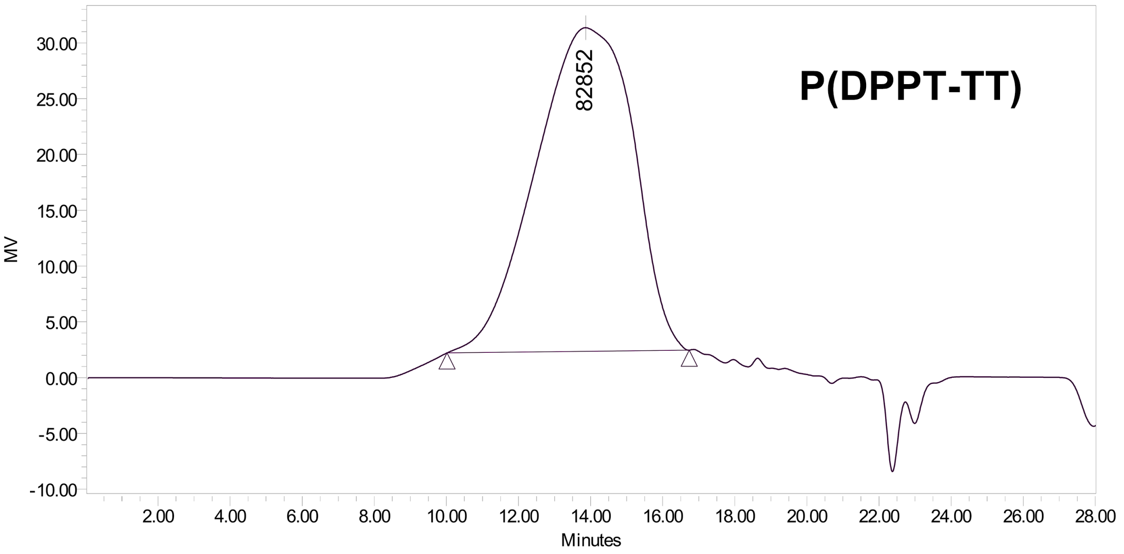
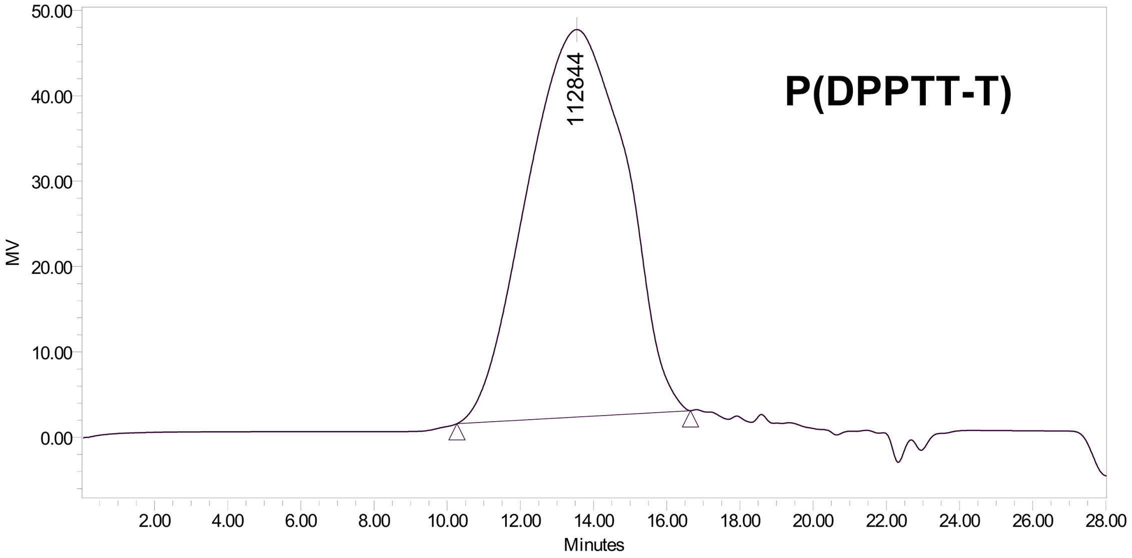


Figure S3. DSC thermograms of first cooling and second heating scan of polymers at temperature ramp of 10 ^{o}C/min under nitrogen atmosphere.



Broad Unknown Modified Universal Peak Table

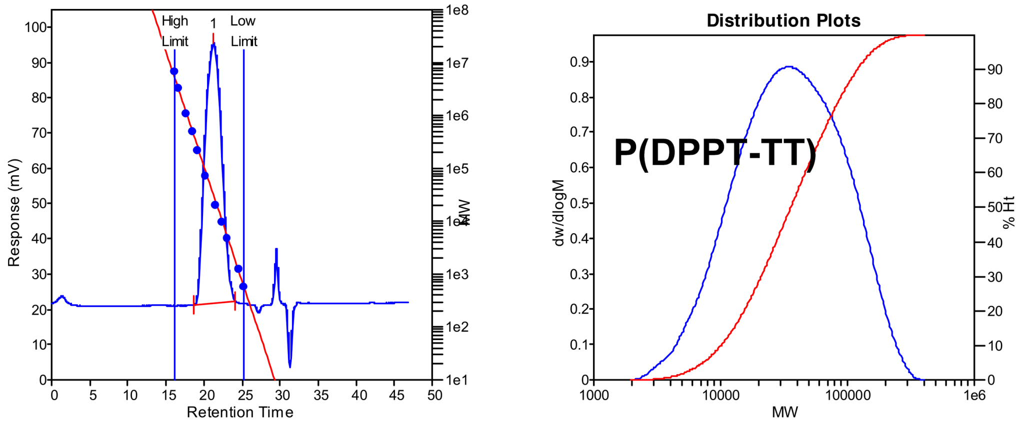
	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						53905	214609	82852	1228797	3703460	3.981283	5.725743



Broad Unknown Modified Universal Peak Table

	Distribution Name	Mv (Daltons)	K (dl/g)	alpha	Intrinsic Viscosity (dl/g)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw
1						66172	251512	112844	955083	2152018	3.800908	3.797363

Figure S4. GPC test result of polymer samples ($CHCl_3$ as eluent, r.t.).

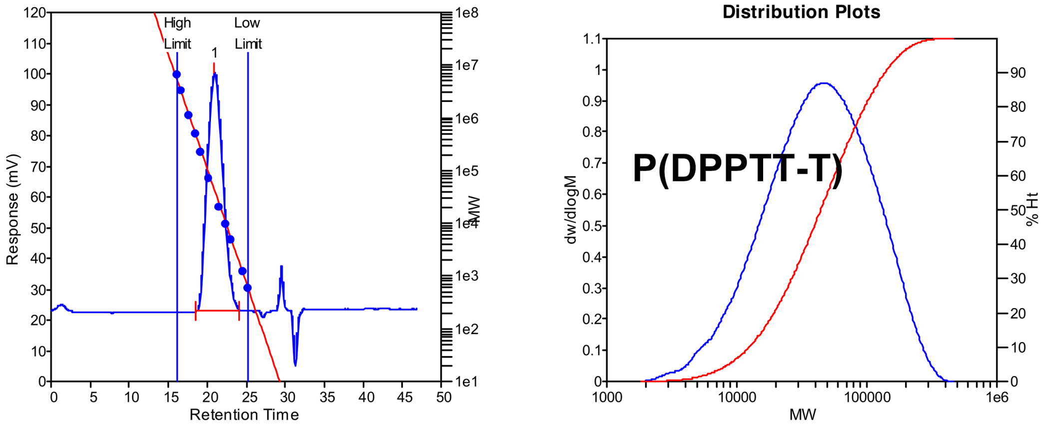


MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	34202	22465	52148	97645	142218	46034	2.3213

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		18.70	21.17	24.02	73.854	100	11545.5	100



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	46152	27032	61506	110697	159708	54764	2.2753

Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		18.57	20.87	24.10	77.6682	100	11216.5	100

Figure S5. GPC test result of polymer samples (TCB as eluent, 150°C).

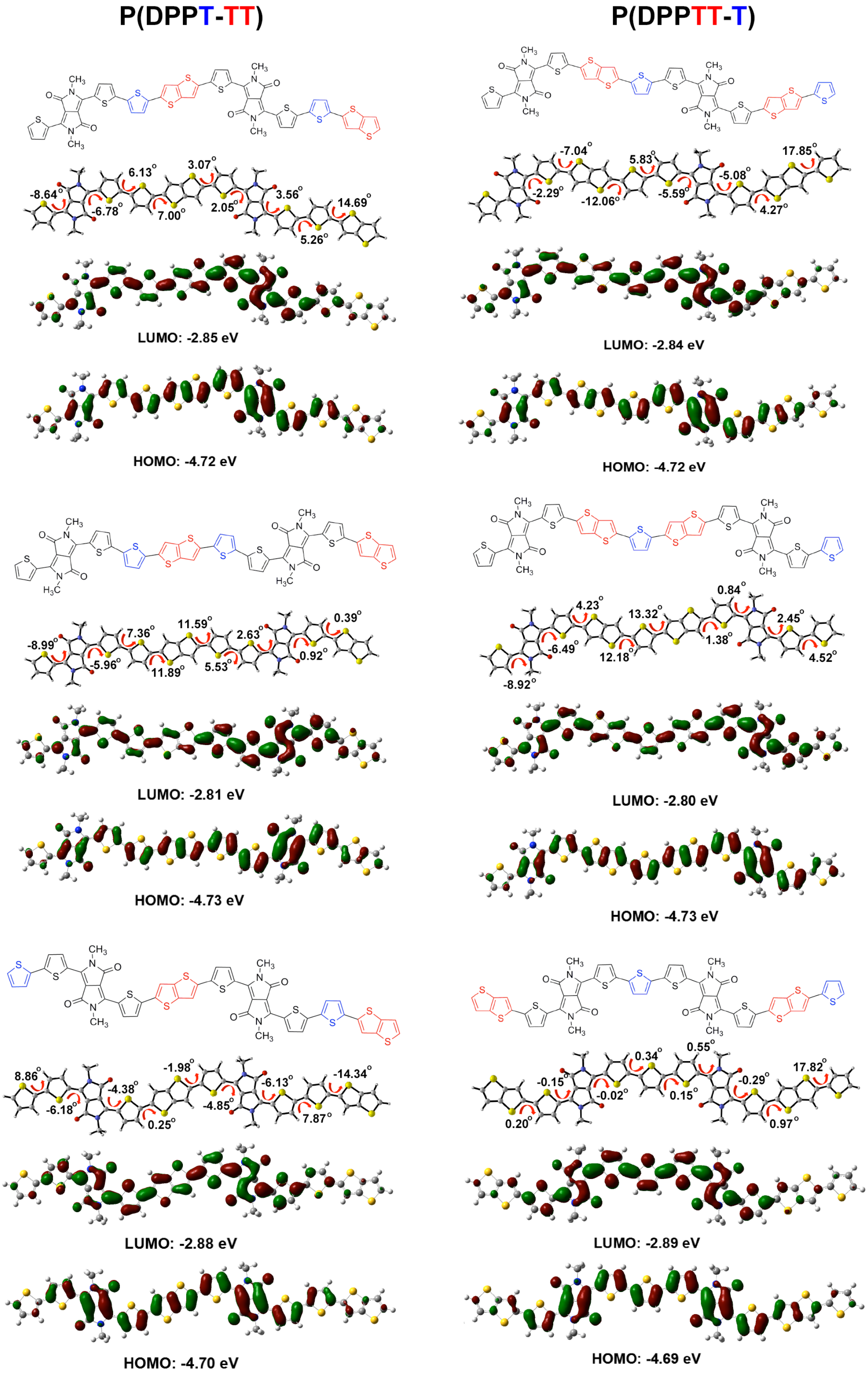


Figure S6. Model molecules and the corresponding optimized geometries and their simulated FMO energy levels and electron density distributions

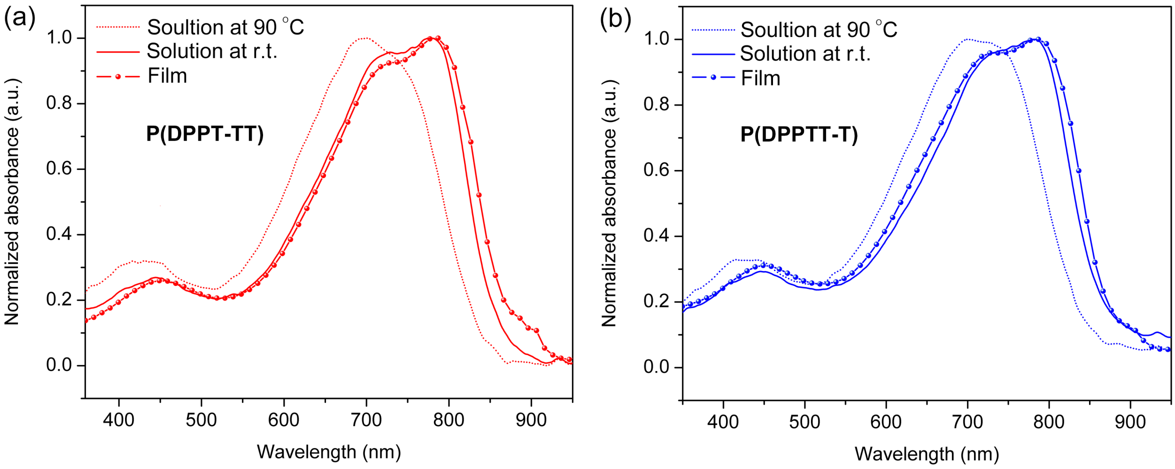


Figure S7. Normalized UV-vis-NIR absorption spectra of polymers: (a) **P(DPPT-TT)** and (b) **P(DPPTT-T)**.

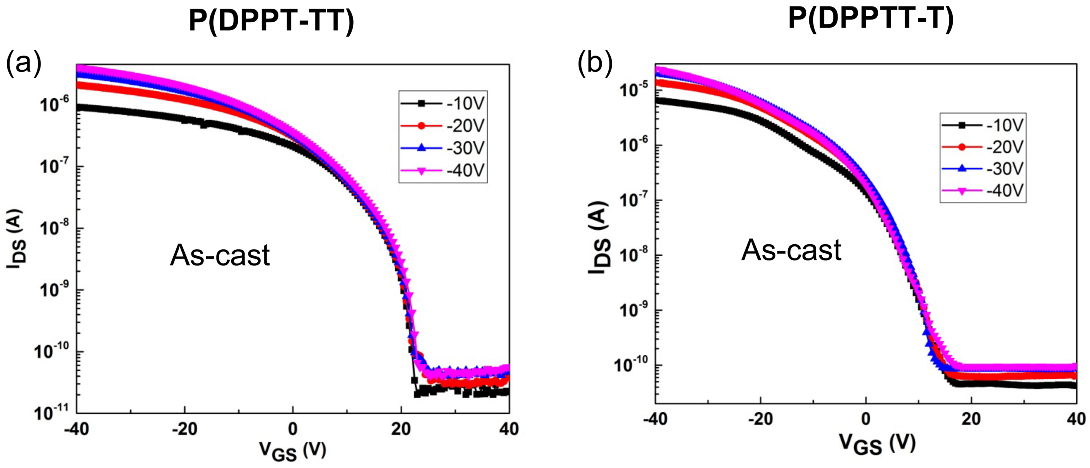


Figure S8. Transfer curves of OFET based on as-cast films: (a) **P(DPPT-TT)** and (b) **P(DPPTT-T)**.

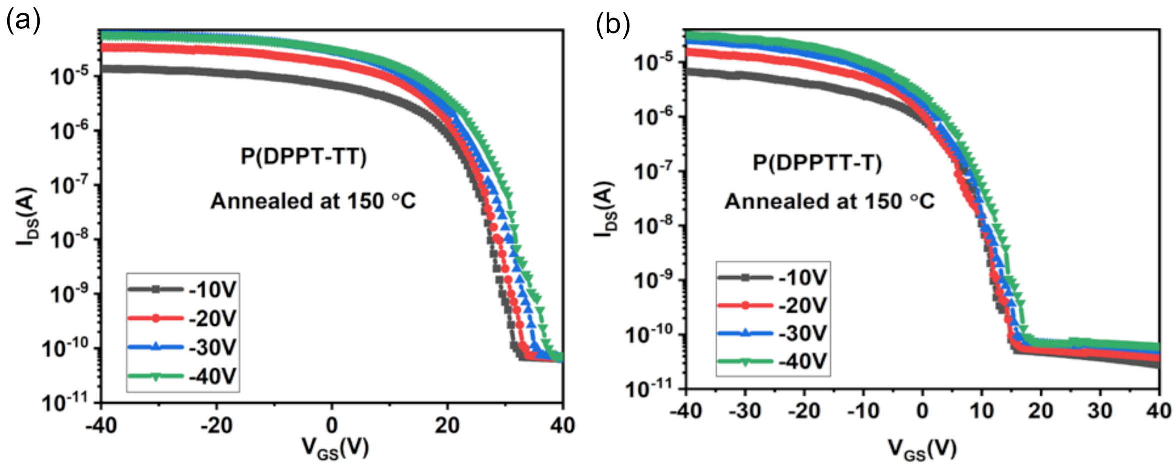


Figure S9. Transfer curves of OFET based on 150 ^{o}C-annealed films: (a) **P(DPPT-TT)** and (b) **P(DPPTT-T)**.

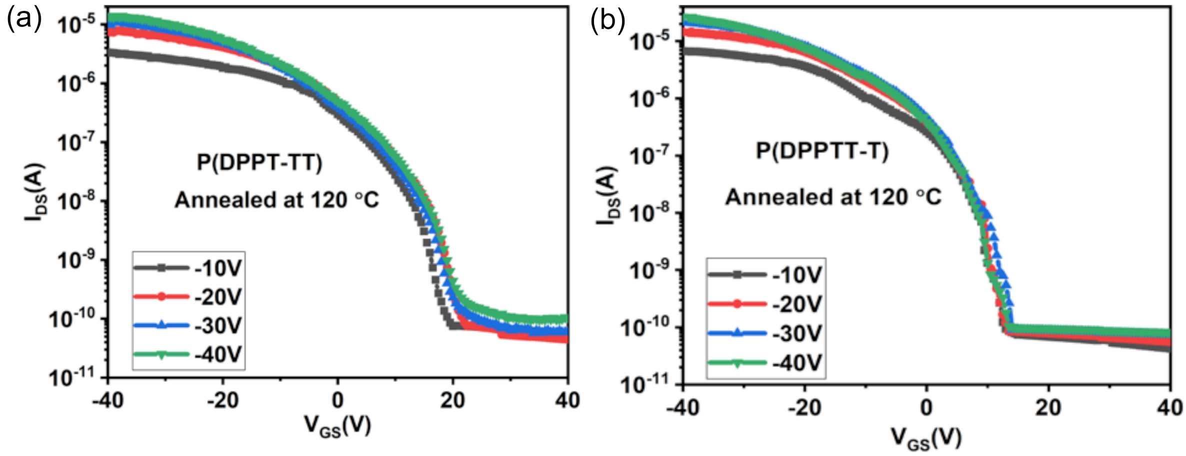


Figure S10. Transfer curves of OFET based on 120 ^{o}C-annealed films: (a) **P(DPPT-TT)** and (b) **P(DPPTT-T)**.

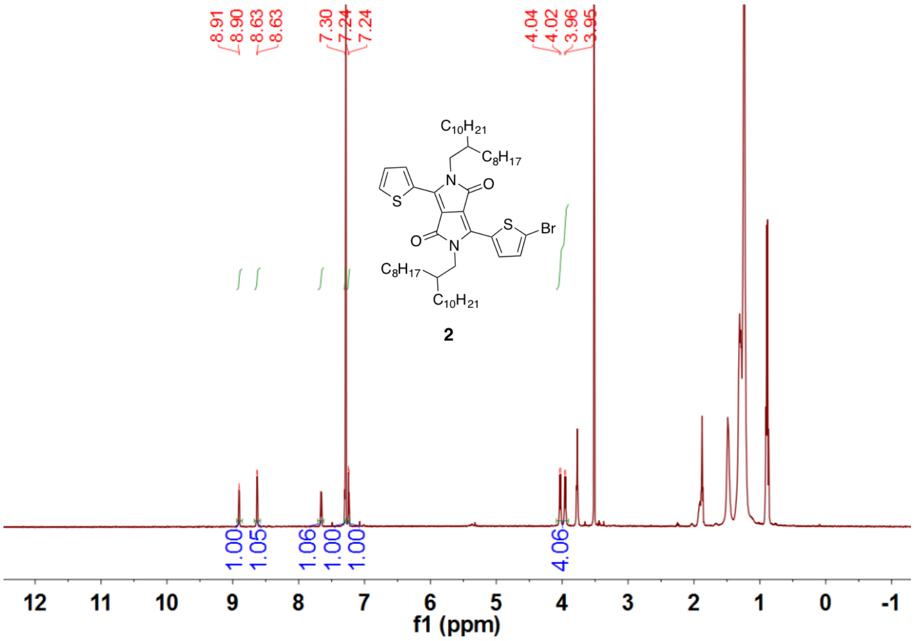


Figure S11. ^{1}H NMR spectrum of **2** (500 MHz, $CDCl_3$, r.t.)

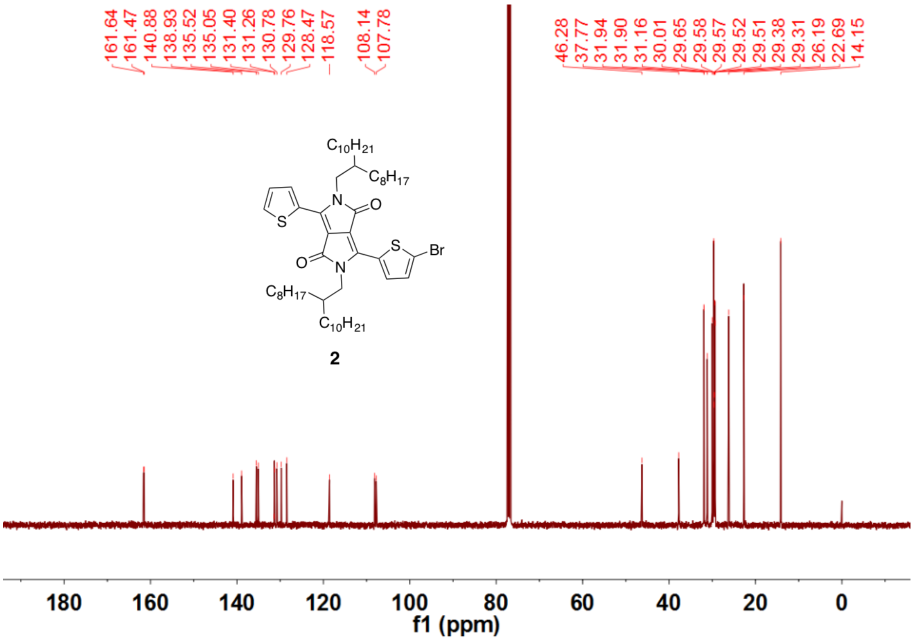


Figure S12. ^{13}C NMR spectrum of **2** (101 MHz, $CDCl_3$, r.t.)

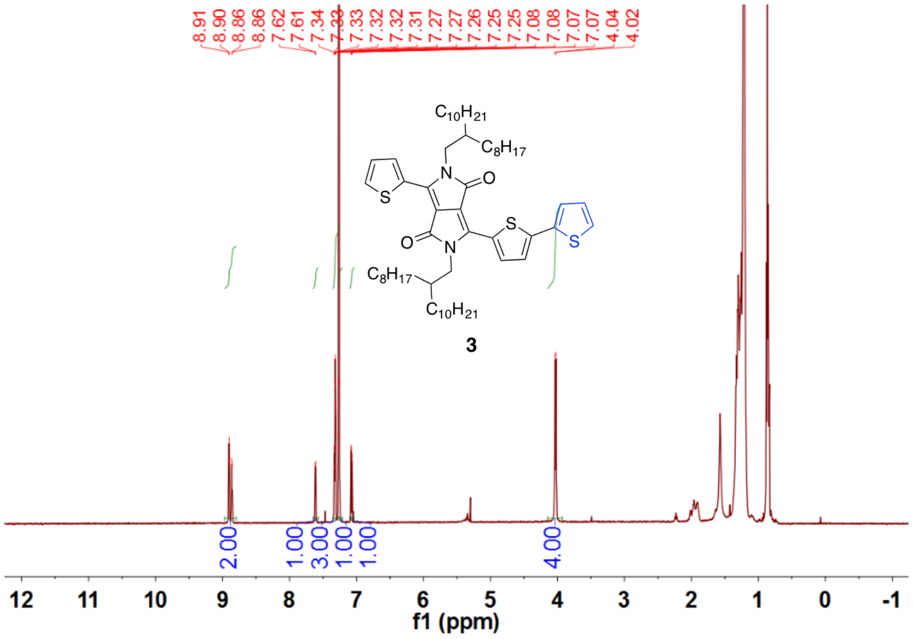


Figure S13. ^{1}H NMR spectrum of **3** (500 MHz, $CDCl_3$, r.t.)

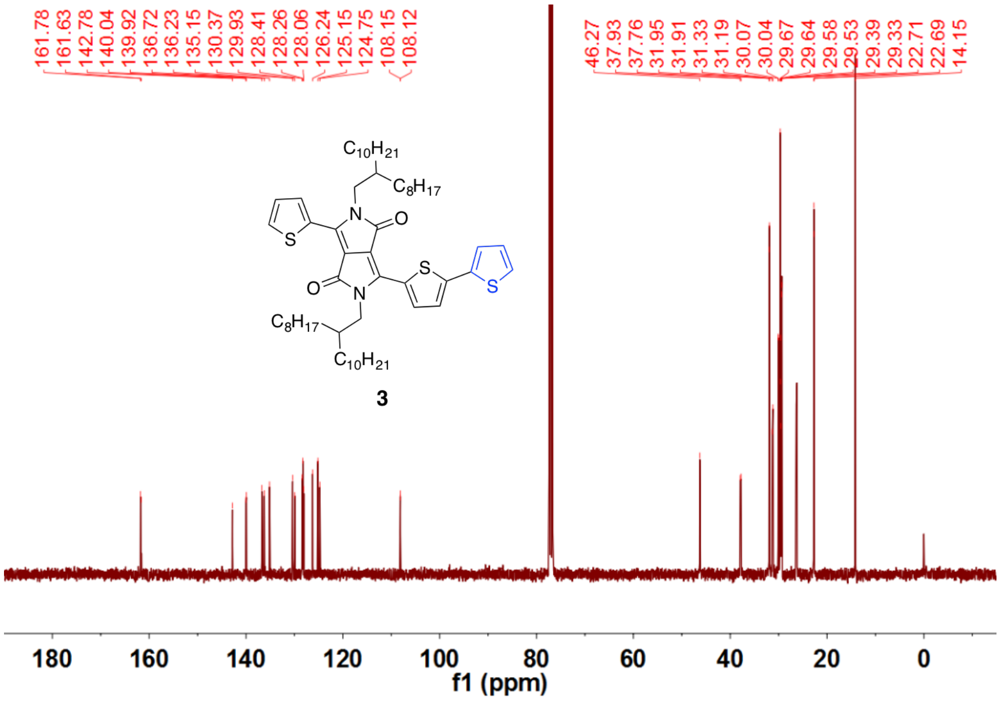


Figure S14. ^{13}C NMR spectrum of **3** (101 MHz, $CDCl_3$, r.t.)

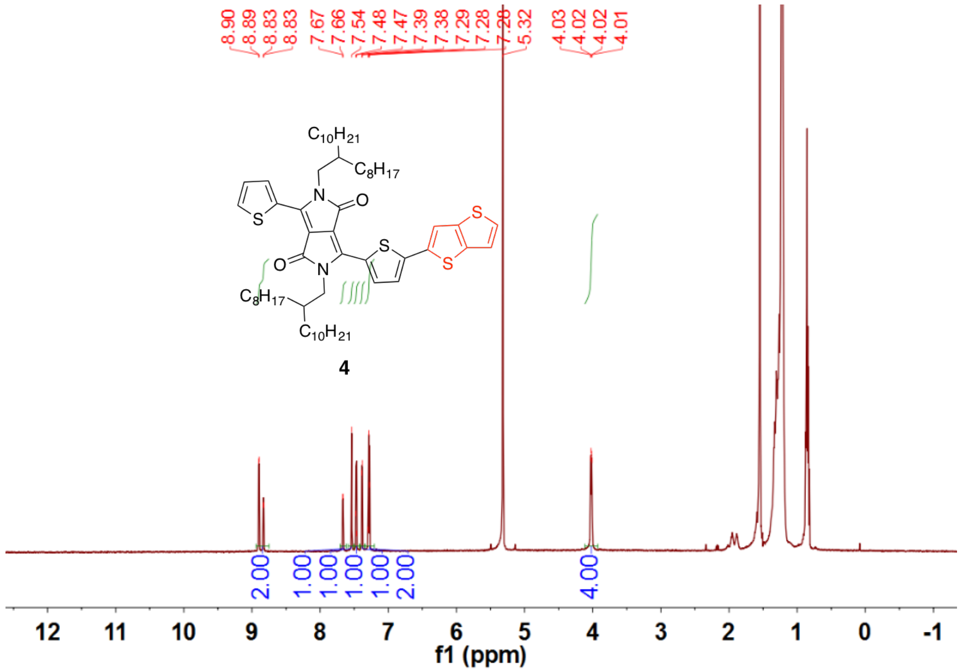


Figure S15. ^{1}H NMR spectrum of **4** (500 MHz, CD_2Cl_2, r.t.)

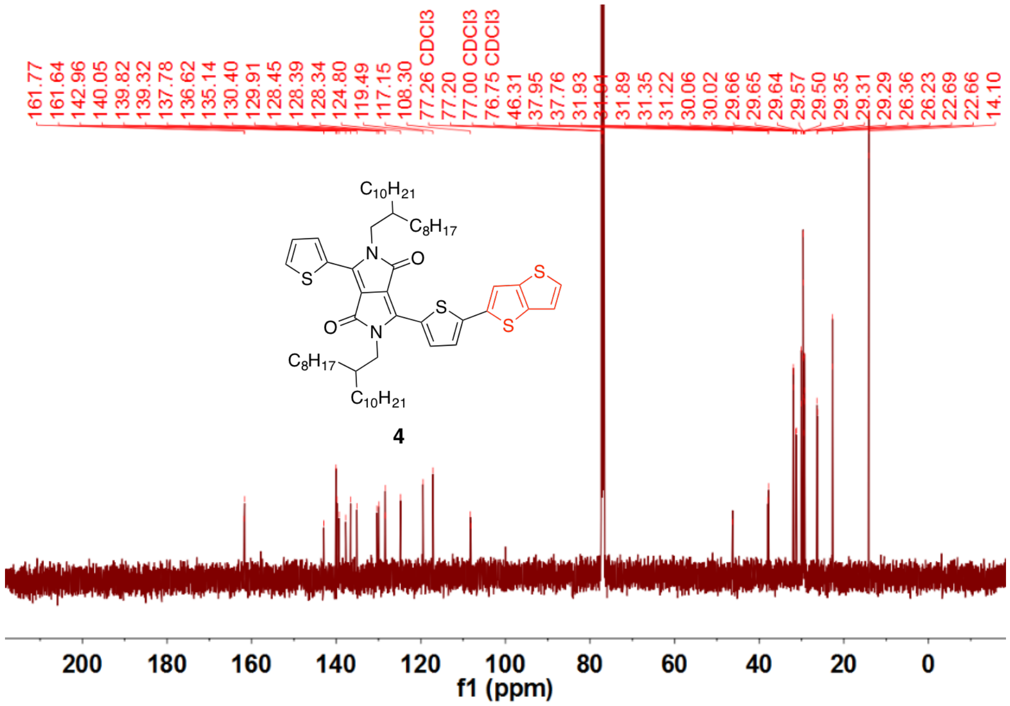


Figure S16. ^{13}C NMR spectrum of **4** (126 MHz, $CDCl_3$, r.t.)

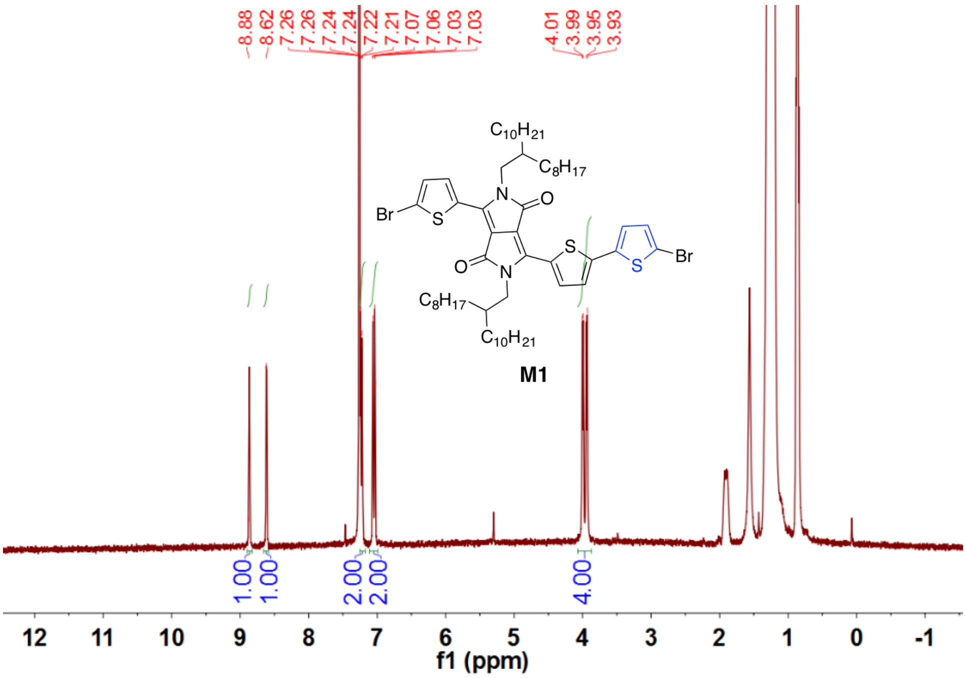


Figure S17. ^{1}H NMR spectrum of **M1** (500 MHz, $CDCl_3$, r.t.)

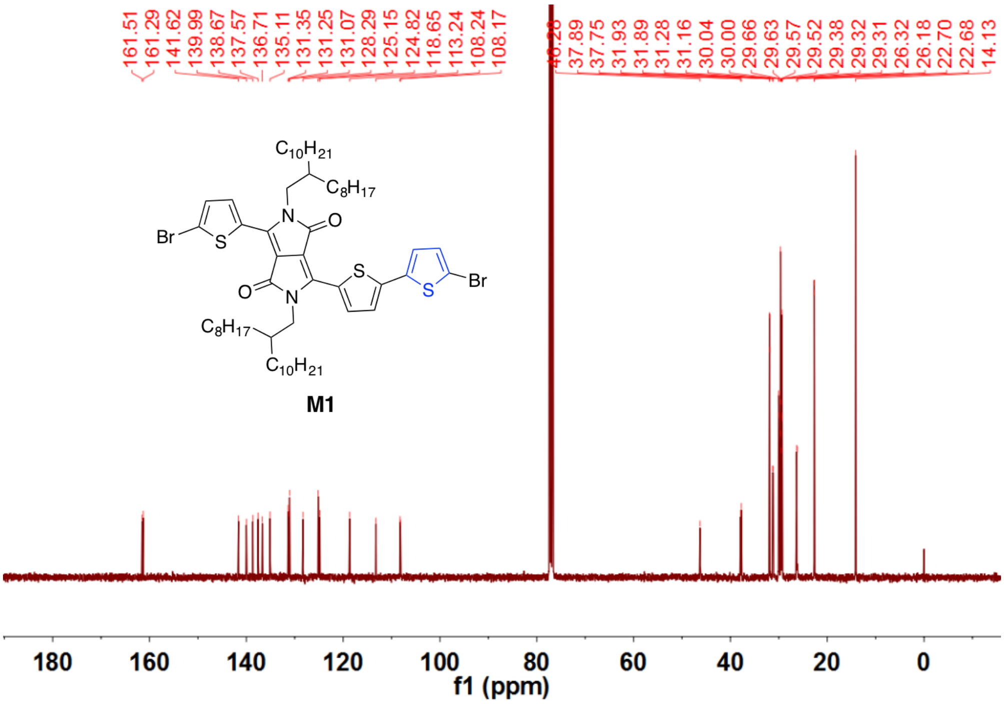


Figure S18. ^{13}C NMR spectrum of **M1** (101 MHz, $CDCl_3$, r.t.)

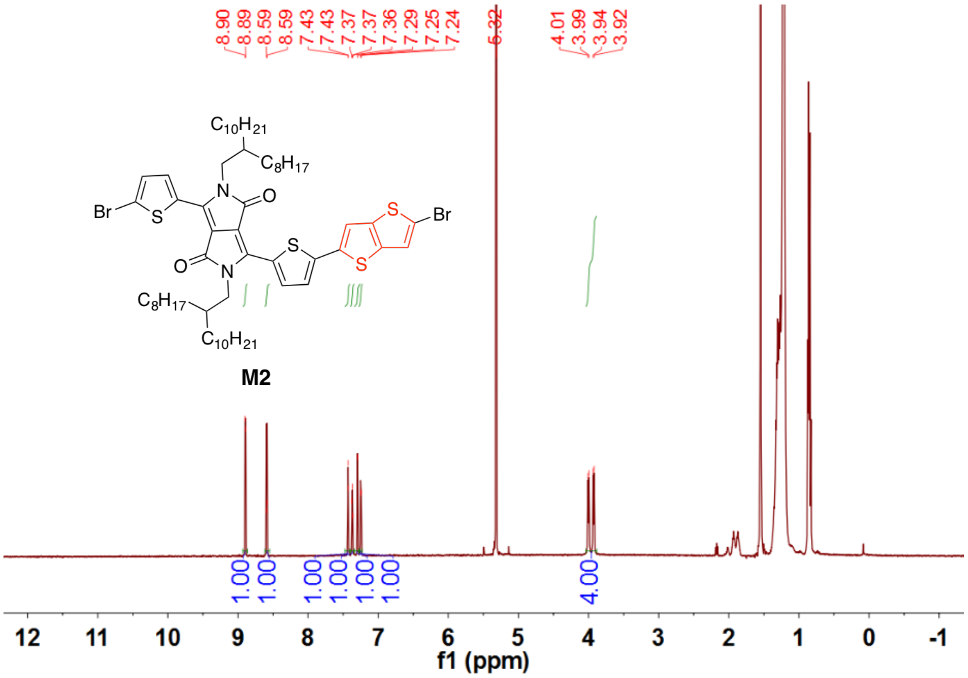


Figure S19. ^{1}H NMR spectrum of **M2** (500 MHz, CD_2Cl_2, r.t.)

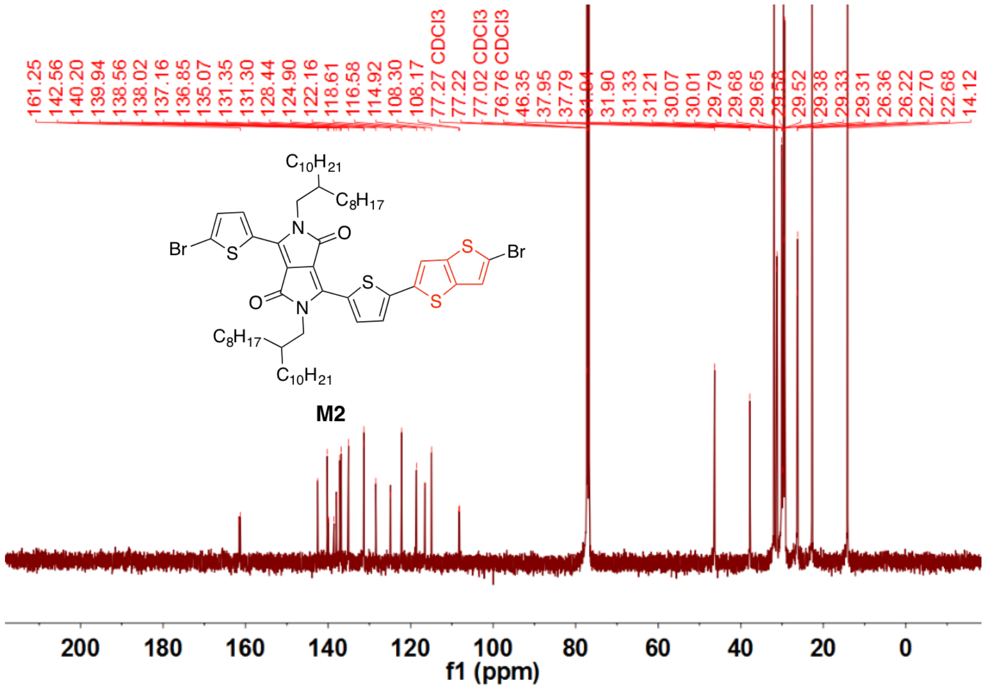


Figure S20. ^{13}C NMR spectrum of **M2** (126 MHz, $CDCl_3$, r.t.)

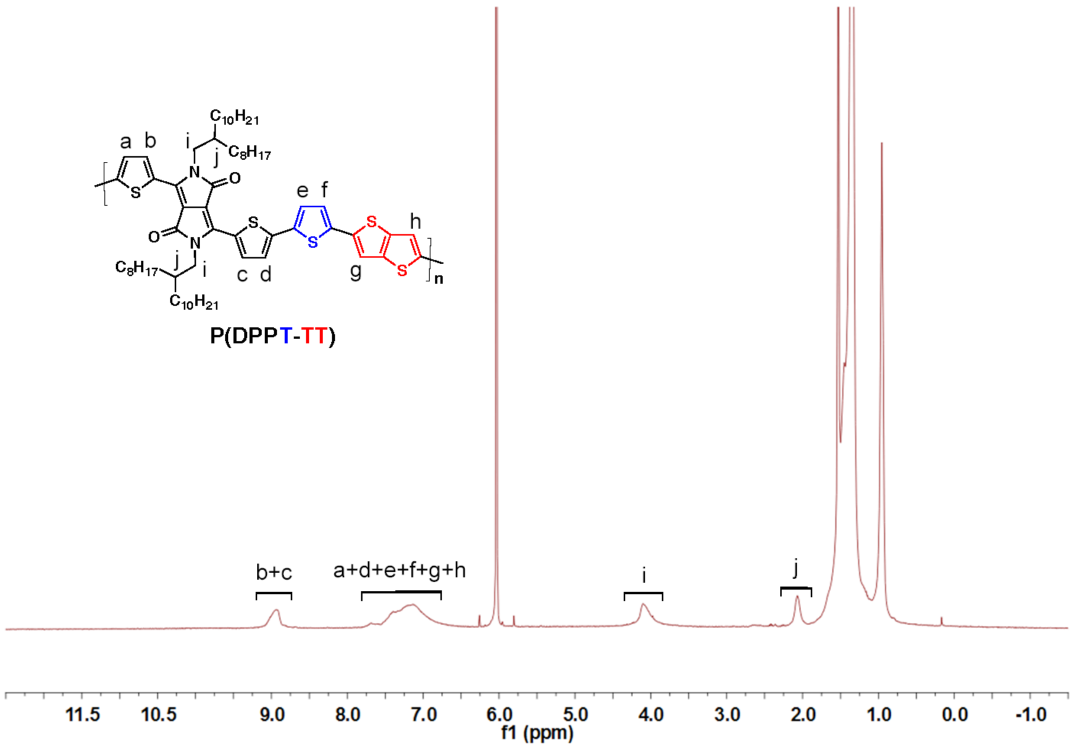


Figure S21 ^{1}H NMR spectrum of polymer **P(DPPT-TT)** (400 MHz, 1,1,2,2-tetrachloroethane-d2, 80 °C)

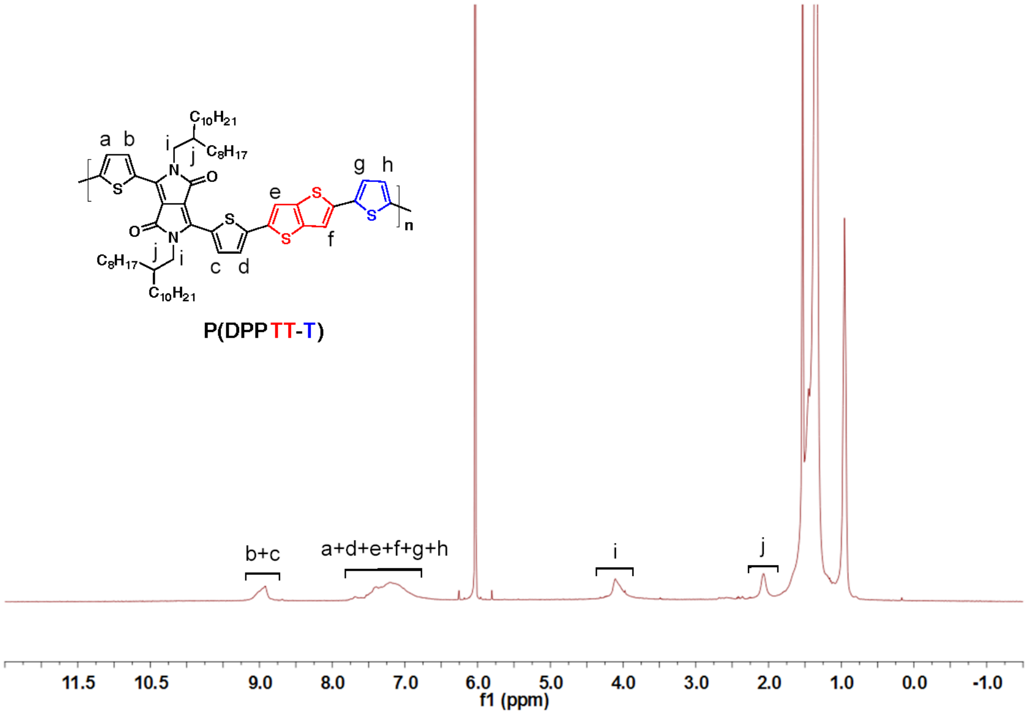


Figure S22. ^{1}H NMR spectrum of polymer **P(DPPTT-T)** (400 MHz, 1,1,2,2-tetrachloroethane-d2, 80 °C)

3. Tables in Supporting Information

Table S1 Performance parameters of OFET based on 150 °C-annealed and 120 °C-annealed thin films of polymers

Polymer	Annealing temperature (°C)	Mobility ($cm^2V^{-1}s^{-1}$)	I_{on}/I_{off}	V_T (V)
P(DPPT-TT)	150	0.70±0.05	$(2.3\pm0.30)\times10^5$	30±0.50
	120	0.68±0.10	$(2.0\pm0.30)\times10^5$	28±0.40
P(DPPTT-T)	150	2.0±0.20	$(5.0\pm0.30)\times10^5$	5±0.50
	120	1.2±0.15	$(3.5\pm0.30)\times10^5$	4±0.40

Table S2 The GIWAXS test data of new polymers

Polymer	(100)	(010)	π-π stacking distance
P(DPPT-TT)	3.42 nm^{-1}	17.6 nm^{-1}	3.57 Å
P(DPPTT-T)	3.43 nm^{-1}	17.8 nm^{-1}	3.52 Å

4. References

(1) K. Kawabata, M. Takeguchi, H. Goto, *Macromolecules*, 2013, **46**, 2078-2091.

(2) D. Y. Wang, C. Wang, M. Uchiyama, *J. Am. Chem. Soc.* 2015, **137**, 10488-10491.

(3) Y. Li, P. Sonar, S. P. Singh, M. S. Soh, M. van Meurs, J. Tan, *J. Am. Chem. Soc.*, 2011, **133**, 2198-2204.