

Supporting Information

Regulation of microstructure and charge transport properties of cyclopentadiene-based conjugated polymers via side-chain engineering

Jianeng Ma,¹ Qiao He,² Zhongyuan Xue,³ Hou Lon Sou,² Yang Han,⁴ Hongliang Zhong,³ Agostino Pietrangelo,⁵ Martin Heeney,^{2, *} and Zhuping Fei^{1, *}

¹ Institute of Molecular Plus, Key Laboratory of Organic Integrated Circuits, Ministry of Education & Tianjin Key Laboratory of Molecular Optoelectronic Science, Department of Chemistry, Tianjin University, Tianjin 300072, China

² Department of Chemistry and Centre for Processable Electronics, Imperial College London, W12 0BZ, UK

³ School of Chemistry and Chemical Engineering, Shanghai Key Lab of Electrical Insulation and Thermal Aging, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

⁴ School of Materials Science and Engineering and Tianjin Key Laboratory of Molecular Optoelectronic Science, Tianjin University, Tianjin 300350, China

⁵ Present address: ExxonMobil Technology and Engineering Company, Annandale, New Jersey 08801, United States

Instruments and experimental conditions:

All reactions were carried out in oven-dried glassware under Ar using solvents and reagents as commercially supplied, unless otherwise stated. Preparative GPC utilized a Shimadzu recycling GPC system running in hexane at 40°C, using Agilent PLgel 10µm 50A or MIXED-D column, DGU-20A3 Degasser, LC-20A Pump, CTO-20A Column Oven and SPD-20A UV Detector. The ¹H spectrum was recorded on a Bruker AV-400 (400 MHz), using the residual solvent resonance of CDCl₃ and is given in ppm. Number-average (M_n) and weight-average (M_w) molecular weight were determined by Agilent Technologies 1200 series GPC running in chlorobenzene at 80 °C, using two

PL mixed B columns in series, and calibrated against narrow polydispersity poly(styrene) standards. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Bruker ultrafleXtreme MALDI-TOF analyzer. Anthracene (or 2,5-dihydroxybenzoic acid) and myoglobin were used as the matrix and calibration internal standard respectively. Differential scanning calorimetry (DSC) was carried out on a DSC214 Polyma at a ± 10 °C/min heating/cooling rate under N₂. UV-vis-NIR absorption spectra were obtained by Shimadzu UV3600-plus spectrometer. Variable temperature measurements were performed using a water-heated cell holder. Photo Electron Spectroscopy in Air (PESA) measurements was recorded with a Riken Keiki AC-2 PESA spectrometer with a power setting of 10 nW and a power number of 0.5. Samples for PESA were prepared on glass substrates by spin-coating method. The thermogravimetric analysis (TGA) was conducted on a TG 209F3 thermogravimetric analyzer with a heating rate of 10 °C/min at a nitrogen flow. Grazing-incidence wide-angle x-ray scattering (GIWAXS) characterizations were carried out at the beamline 14B1 of Shanghai Synchrotron Radiation Facility (SSRF).

OFET (organic field effect transistor) device fabrication.

The solutions of PDPPCp-C4-OD, PDPPCp-C7-OD, and PDPPCp-C7-HO were prepared by dissolving the polymer in chlorobenzene at a concentration of 10 mg/ml, respectively. Transistors were prepared by first thermally evaporating Au (40 nm) onto glass substrates through a shadow mask to form bottom source/drain (S/D) electrodes. Then CuSCN was dissolved in diethyl sulfide at a concentration of 5 mg/mL and spin cast onto the substrates with pre-patterned Au electrodes at 5000 rpm for 60s. The obtained CuSCN thin film was annealed at 100 °C for 30 min under nitrogen. Polymer was then spin coated at 1000 rpm for 60 s on top of the substrates with CuSCN treated bottom electrodes to give films of 60-70 nm thickness. The obtained films were then thermally annealed at 120 or 200 °C for 30 min under nitrogen. A layer of 900-nm CYTOP (Asahi Glass) dielectric was then deposited on top of the polymer layer by spin coating at 2000 rpm for 60 s followed by an annealing step at 100 °C for 30 min. The

transistor structure was then completed by thermally evaporating 50 nm Al gate electrodes through a shadow mask, resulting in the bottom contact, top contact architecture. The channel width and length of the final transistors were 1000 μm and 30 or 40 μm , respectively. Transistor characterization was carried out under dinitrogen using a Keithley 4200 parameter analyzer. Linear mobility was calculated according to the equation below:

$$\mu_{\text{lin}} = \frac{L}{WC_i V_D} \left(\frac{\partial I_{D \text{ lin}}}{\partial V_G} \right)$$

And saturation mobility was extracted from the slope of $I_D^{1/2}$ vs. V_G :

$$\mu_{\text{sat}} = \frac{2L}{WC_i} \left(\frac{\partial \sqrt{I_{D \text{ sat}}}}{\partial V_G} \right)^2$$

EXPERIMENTAL SECTION

General: All reactions were carried out in oven-dried glassware under Ar. All solvents and reagents were commercially supplied unless otherwise stated. 5,5-dimethylcyclopenta-1,3-diene-1,4-diyl bis(trifluoromethanesulfonate)¹, 7-(iodomethyl)pentadecane² and 9-(4-iodobutyl)nonadecane³ were synthesised by the reported methods.

Synthesis

7-(but-3-en-1-yl)pentadecane (2)

Allylmagnesium chloride (42 mL, 71.4 mmol, 1.7 M in THF) was added into a solution of 7-(iodomethyl)pentadecane (**1**) (25.0 g, 71.4 mmol) in dry THF (100 mL) dropwise at room temperature under argon atmosphere. The resulting mixture was refluxed for 24 hours. The solvent was evaporated under reduced pressure, filtered over silica (eluent: hexane) and concentrated to yield a colorless oil **2** (18.3 g, 96%). ¹H NMR (400 MHz, CDCl₃): δ [ppm] 5.87-5.77 (m, 1H), 5.02-4.91 (m, 2H), 2.05-2.00 (m, 2H), 1.32 – 1.24 (m, 27H), 0.90-0.83 (t, $J = 6.7$ Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 139.61, 113.87, 36.95, 33.54, 31.94, 31.09, 30.14, 29.80-29.38(overlapping carbons), 26.62-26.60 (XXXverlapping carbons), 22.71, 14.11. HRMS (EI)⁺ calculated for C₁₉H₃₈: 266.2974. Found: 266.2983.

5-hexyltridecan-1-ol (3)

Borane (33.8 mL, 33.8 mmol, 1 M in THF) was added into a solution of **2** (18.0 g, 67.6 mmol) in dry THF (100 mL) under argon atmosphere at 0 °C. After stirring for 2 hours at room temperature, water (10 mL) and NaOH (29 mL, 87.0 mmol, 3M in water) were added dropwise. After 1.5 hours, H₂O₂ (29 mL, 284.0 mmol, 30 %) was added dropwise into the solution at 0°C and reacted for 2 hours. Saturated NaCl solution (100 mL) was added, and extracted with ether (3 × 100 mL). The organics was concentrated under reduced pressure, filtered over silica (eluent: hexane followed by DCM), concentrated to yield a colorless oil **3** (15.7 g, 82%). ¹H NMR (400 MHz, CDCl₃): δ [ppm] 3.64 (t, *J* = 6.6 Hz, 2H), 1.58-1.51 (m, 2H), 1.35-1.18 (m, 29H), 0.88 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 63.15, 37.43, 33.65, 33.54, 33.31, 31.94, 30.15-29.37(overlapping carbons), 26.71-26.68 (overlapping carbons), 22.90, 22.70, 14.11. HRMS (EI)[M-OH] calculated for C₁₉H₃₉: 267.3053. Found: 267.3060.

7-(4-iodobutyl)pentadecane (4)

NIS (12.4 g, 55.0 mmol) was added to a solution of **3** (15.5g, 55.0 mmol) and triphenylphosphine (14.4 g, 55.0 mmol) in DCM (200 mL) at 0 °C in portions in the absence of light. The reaction was stirred overnight at room temperature, quenched with saturated sodium sulfite solution (50 mL) and washed with water, and extracted with DCM (3 × 50 mL). The organic layer was dried (MgSO₄), filtered and evaporated under reduced pressure. The residue was filtered over silica (eluent: hexane) and concentrated to allow **4** as a colorless oil. (20.0 g, 92%). ¹H NMR (400 MHz, CDCl₃): δ [ppm] 3.19 (t, *J* = 7.0 Hz, 2H), 1.84-1.77 (m, 2H), 1.40-1.22 (m, 29H), 0.88 (t, *J* = 6.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 37.26, 34.01, 33.73, 33.60, 32.53, 31.94, 30.13-29.37(overlapping carbons), 27.65, 26.67-26.65 (overlapping carbons), 22.70, 14.12. HRMS (EI)+calculated for C₁₉H₃₉I: 394.2097. Found: 394.2085.

8-hexylhexadec-1-ene (5)

Allylmagnesium chloride (28.6 mL, 48.7 mmol, 1.7 M in THF) was added into a solution of **4** (19.2 g, 48.7 mmol) in dry THF (100 mL) dropwise at room temperature

under argon atmosphere. The resulting mixture was refluxed for 24 hours. The solvent was evaporated under reduced pressure, filtered over silica (eluent: hexane) and concentrated to yield a colorless oil **5** (14.2 g, 95%). ¹H NMR (400 MHz, CDCl₃): δ [ppm] 5.85-5.77 (m, 1H), 5.02-4.92 (m, 2H), 2.07-2.02 (m, 2H), 1.40 – 1.22 (m, 33H), 0.88 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 139.27, 114.07, 37.41, 33.85, 33.71, 33.66, 31.97-31.95 (overlapping carbons), 30.17-29.00 (overlapping carbons), 26.71-26.55 (overlapping carbons), 22.70, 14.11. HRMS (EI)+ calculated for C₂₂H₄₄: 308.3443. Found: 308.3450.

8-hexylhexadecan-1-ol (6)

Borane (24.3 mL, 24.3 mmol, 1 M in THF) was added into a solution of **2** (15.0 g, 48.7 mmol) in dry THF (100 mL) under argon atmosphere at 0 °C. After stirring for 2 hours at room temperature, water (10 mL) and NaOH (21.0 mL, 63.0 mmol, 3M in water) were added in dropwise. After 1.5 hours, H₂O₂ (21.0 mL, 205.7 mmol, 30 %) was added dropwise into the solution at 0°C and reacted for 2 hours. Saturated NaCl solution (100 mL) was added, and extracted with ether (3 × 100 mL). The organics was concentrated under reduced pressure, filtered over silica (eluent: hexane followed by DCM), concentrated to yield a colorless oil **3** (14.7 g, 93%). ¹H NMR (400 MHz, CDCl₃): δ [ppm] 3.64 (t, *J* = 6.6 Hz, 2H), 1.60-1.53 (m, 2H), 1.39-1.18 (m, 35H), 0.88 (t, *J* = 6.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 63.11, 37.42, 33.71, 32.84, 31.96-31.94 (overlapping carbons), 30.16-29.38(overlapping carbons), 26.71-25.78 (overlapping carbons), 22.71, 14.11. HRMS (ES-TOF)[M+MeCN] calculated for C₂₀H₅₀NO: 368.3892. Found: 368.3891.

7-(4-iodobutyl)pentadecane (C7-HO-I, 7)

NIS (10.1 g, 45.1 mmol) was added to a solution of **6** (14.7 g, 45.1 mmol) and triphenylphosphine (11.8 g, 45.1 mmol) in DCM (200 mL) at 0 °C in portions in the absence of light. The reaction was stirred overnight at room temperature, quenched with saturated sodium sulfite solution (50 mL) and washed with water, and extracted with DCM (3 × 50 mL). The organic layer was dried (MgSO₄), filtered and evaporated under

reduced pressure. The residue was filtered over silica (eluent: hexane) and concentrated to afford **7** as a colorless oil. (18.0 g, 92%). ¹H NMR (400 MHz, CDCl₃): δ [ppm] 3.19 (t, *J* = 7.0 Hz, 2H), 1.86-1.79 (m, 2H), 1.40-1.22 (m, 35H), 0.88 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 37.41, 33.71-33.61 (overlapping carbons), 31.97-31.95 (overlapping carbons), 30.54, 30.17-29.38 (overlapping carbons), 28.58, 26.72-26.60 (overlap carbons), 22.71, 14.13. HRMS (EI)[M-I] calculated for C₂₂H₄₅: 309.3521. Found: 309.3516.

9-(hept-6-en-1-yl)nonadecane (9)

Allylmagnesium chloride (18.7 mL, 31.8 mmol, 1.7 M in THF) was added into a solution of 9-(4-iodobutyl)nonadecane (**8**) (14.3 g, 31.8 mmol) in dry THF (100 mL) dropwise at room temperature under argon atmosphere. The mixture was reacted under reflux for 24 hours. The solvent was evaporated under reduced pressure, filtered over silica (eluent: hexane) and concentrated to yield a colorless oil **9** (11.8 g, 97%). ¹H NMR (400 MHz, CDCl₃): δ [ppm] 5.90-5.75 (m, 1H), 5.05-4.93 (m, 2H), 2.12-2.01 (m, 2H), 1.32 – 1.24 (m, 41H), 0.88 (t, 6H). ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 139.27, 114.07, 110.00, 37.39, 33.70, 31.94, 29.3 – 30.1 (overlapping carbons), 26.70, 22.70, 14.12. MS (EI+): *m/z* : 364 (M⁺).

8-octyloctadecan-1-ol (10)

Borane (15.0 mL, 15.0 mmol, 1 M in THF) was added into a solution of **9** (11.0 g, 30.1 mmol) in dry THF (100 mL) under argon atmosphere at 0 °C. After stirring for 2 hours at room temperature, water (10 mL) and NaOH (13.0 mL, 39.0 mmol, 3M in water) were added in dropwise. After 1.5 hours, H₂O₂ (13.0 mL, 127.3 mmol, 30 %) was added dropwise into the solution at 0°C and reacted for 2 hours. Saturated NaCl solution (100 mL) was added, and extracted with ether (3 × 100 mL). The organics was concentrated under reduced pressure, filtered over silica (eluent: hexane followed by DCM), concentrated to yield a colorless oil **10** (8.3 g, 74%). ¹H NMR (400 MHz, CDCl₃): δ [ppm] 3.67 (t, *J* = 6.6 Hz, 2H), 1.61-1.57 (m, 2H), 1.37-1.21 (m, 43H), 0.88 (t, *J* = 6.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 68.20, 63.08, 39.42, 37.41, 33.70,

32.84, 31.94, 29.38 – 30.1 (overlapping carbons), 26.71, 26.67, 25.83, 25.79, 23.47, 22.70, 14.12. MS (EI+): m/z : 381 (M^+).

9-(7-iodoheptyl)nonadecane (C7-OD-I, 11)

NIS (6.8 g, 21.0 mmol) was added to a solution of **10** (8.0 g, 21.0 mmol) and triphenylphosphine (5.5 g, 21.0 mmol) in DCM (200 mL) at 0 °C in portions in the absence of light. The reaction was stirred overnight at room temperature, quenched with saturated sodium sulfite solution (50 mL) and washed with water, and extracted with DCM (3 × 50 mL). The organic layer was dried ($MgSO_4$), filtered and evaporated under reduced pressure. The residue was filtered over silica (eluent: hexane) and concentrated to allow **11** as a colorless oil. (8.8 g, 85%). 1H NMR (400 MHz, $CDCl_3$): δ [ppm] 3.21 (t, $J = 7.0$ Hz, 2H), 1.86-1.79 (m, 2H), 1.37-1.24 (m, 43H), 0.88 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ [ppm] 37.39, 33.69, 33.65, 33.61, 31.95, 29.3 – 30.1 (overlap carbons), 28.59, 26.72, 26.60, 26.55, 22.71, 22.63, 14.14. MS (EI+): m/z : 492 (M^+).

General synthetic procedures of compound 13~15

The corresponding alkyl iodide chain was added dropwise to a mixture of 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **12**, dry potassium carbonate and 18-crown-6 in dry DMF (120 mL) at 80 °C and stirred overnight. The mixture was poured into water (200 mL) and extracted with $CHCl_3$ (3 × 150 mL), the combined organic layer was washed with water (3 × 200 mL) and dried ($MgSO_4$), filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography to afford the corresponding compound **13~15**.

2,5-bis(5-octylpentadecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (13)

The following compounds were used: **8** (9.0 g, 20.0 mmol), 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **12** (2.0 g, 6.7 mmol), dry potassium carbonate (2.8 g, 20.0 mmol), and 18-crown-6 (25 mg). The crude product was purified by flash chromatography (hexane/ $CHCl_3$: 2/1) to afford a dark red solid **13** (4.0 g, 63%). 1H NMR ($CDCl_3$, 400MHz), δ [ppm] 8.96 (d, $J = 3.8$ Hz, 2H), 7.66 (d, $J = 4.8$ Hz, 2H),

7.31 (t, $J = 4.8$ Hz, 2H), 4.07 (t, $J = 7.7$ Hz, 4H), 1.78-1.72 (m, 4H), 1.42-1.21 (m, 74H), 0.89-0.86 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] 161.35, 140.01, 135.25, 130.61, 129.80, 128.60, 107.71, 42.29, 37.32, 33.58, 33.30, 31.94, 29.38 – 30.37 (overlapping carbons), 26.68, 24.07, 22.70, 14.13. MS (MALDI-TOF): 946 (M^+).

2,5-bis(8-octyloctadecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (14)

The following compounds were used: **11** (8.0 g, 16.2 mmol), 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **12** (1.6 g, 5.4 mmol), dry potassium carbonate (2.2 g, 16.2 mmol), and 18-crown-6 (25 mg). The crude product was purified by flash chromatography (hexane/ CHCl_3 : 2/1) to afford a dark red solid **14** (3.5 g, 65%). ^1H NMR (CDCl_3 , 400MHz), δ [ppm] 8.95 (d, $J = 3.8$ Hz, 2H), 7.65 (d, $J = 4.8$ Hz, 2H), 7.30 (t, $J = 4.8$ Hz, 2H), 4.07 (t, $J = 7.8$ Hz, 4H), 1.78-1.73 (m, 4H), 1.37-1.21 (m, 86H), 0.89-0.85 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] 161.35, 140.00, 135.26, 130.61, 129.80, 128.60, 109.98, 107.70, 77.34, 77.22, 77.02, 76.70, 42.25, 37.41, 33.69, 31.94, 31.90, 29.38 – 30.2 (overlapping carbons), 29.33, 29.03, 26.94, 26.71, 26.66, 22.71, 14.13. MS (MALDI-TOF): 1029 (M^+).

2,5-bis(8-hexylhexadecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (15)

The following compounds were used: **7** (7.7 g, 17.6 mmol), 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **12** (1.8 g, 6.0 mmol), dry potassium carbonate (2.4 g, 17.6 mmol), and 18-crown-6 (20 mg). The crude product was purified by flash chromatography (hexane/ CHCl_3 : from 3/1 to 2/1) to afford a dark red solid **15** (3.2 g, 58%). ^1H NMR (CDCl_3 , 400MHz), δ [ppm] 8.94 (d, $J = 3.9$ Hz, 2H), 7.63 (d, $J = 4.8$ Hz, 2H), 7.28 (t, $J = 4.8$ Hz, 2H), 4.07 (t, $J = 7.7$ Hz, 4H), 1.78-1.71 (m, 4H), 1.42-1.21 (m, 70H), 0.89-0.86 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ [ppm] 161.37, 140.02, 135.26, 130.62, 129.81, 128.60, 107.72, 42.25, 33.70, 31.96, 31.94, 30.17-29.32 (overlap carbons), 26.94, 26.71, 26.68, 22.72, 14.13. MS (MALDI-TOF): 917 (M^+).

General synthetic procedures of compound 16~18

n-Butyllithium was added into a solution of diisopropylamine in THF (9 mL) at -25 °C

and stirred for 0.5 hours. The freshly prepared LDA was added dropwise into a mixture of the corresponding DPP-based compounds and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in dry THF (30 mL) under argon at -25 °C. The mixture was slowly warmed to RT and stirred for another 1.5 h. HCl (5 mL, 1 M) was added and extracted with DCM (3 x 40 mL), dried (MgSO₄), and concentrated under reduced pressure. The crude mixture was purified by gel permeation chromatography to yield the corresponding compound **16~18**.

2,5-bis(5-octylpentadecyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (16)

The following compounds were used: *n*-butyllithium (1.0 mL, 2.5 mmol, 2.5 M in hexane), diisopropylamine (0.5 mL, 3.2 mmol), **13** (1.0 g, 1.1 mmol), and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.7 mL, 3.2 mmol). The crude mixture was purified by gel permeation chromatography (eluent: hexane, 40 °C) to yield a dark purple solid **16** (0.76 g, 58 %). ¹H NMR (CDCl₃, 400MHz), δ [ppm] 9.03 (d, *J* = 3.9 Hz, 2H), 7.75 (d, *J* = 3.9 Hz, 2H), 4.14 (t, *J* = 7.6 Hz, 4H), 1.78-1.69 (m, 4H), 1.41-1.20 (m, 98H), 0.89-0.86 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 161.39, 140.05, 137.95, 136.30, 135.62, 108.53, 84.64, 42.21, 37.41, 33.70, 31.94, 30.17-29.38 (overlapping carbons), 26.98-26.95 (overlapping carbons), 24.79, 22.71, 14.13. MS (MALDI-TOF): 1197 (M⁺).

2,5-bis(8-octyloctadecyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (17)

The following compounds were used: *n*-butyllithium (1.0 mL, 2.5 mmol, 2.5 M in hexane), diisopropylamine (0.5 mL, 3.2 mmol), **14** (1.0 g, 1.0 mmol), and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.7 mL, 3.2 mmol). The crude mixture was purified by gel permeation chromatography (eluent: hexane, 40 °C) to yield a dark purple solid **17** (0.81 g, 63 %). ¹H NMR (CDCl₃, 400MHz), δ [ppm] 9.04 (d, *J* = 3.9 Hz, 2H), 7.75 (d, *J* = 3.9 Hz, 2H), 4.14 (t, *J* = 7.6 Hz, 4H), 1.78-1.69 (m, 4H), 1.41-1.21 (m, 110H), 0.90-0.86 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 161.39, 140.05, 137.97, 136.30, 135.62, 108.53, 84.65, 42.20, 37.41, 33.70, 31.94, 30.17-29.38 (overlapping carbons), 26.98-26.91 (overlapping carbons), 24.79, 22.71,

14.13. MS (MALDI-TOF): 1283 (M⁺).

2,5-bis(8-hexylhexadecyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (18)

The following compounds were used: *n*-butyllithium (0.9 mL, 2.3 mmol, 2.5 M in hexane), diisopropylamine (0.5 mL, 3.2 mmol), **15** (0.7 g, 0.76 mmol), and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.7 mL, 3.2 mmol). The crude mixture was purified by gel permeation chromatography (eluent: hexane, 40 °C) to yield a dark purple solid **18** (0.72 g, 81 %). ¹H NMR (CDCl₃, 400MHz), δ [ppm] 9.01 (d, *J* = 3.9 Hz, 2H), 7.73 (d, *J* = 3.9 Hz, 2H), 4.11 (t, *J* = 7.6 Hz, 4H), 1.75-1.71 (m, 4H), 1.41-1.20 (m, 94H), 0.89-0.86 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 161.39, 140.05, 137.95, 136.30, 135.62, 108.53, 84.64, 42.21, 37.41, 33.70, 31.94, 30.17-29.38 (overlapping carbons), 26.97, 26.70, 26.67, 24.79, 22.71, 14.12. MS (MALDI-TOF): 1169 (M⁺).

General Procedure of Suzuki Polymerization for PDPPCp-C4-OD, PDPPCp-C7-OD and PDPPCp-C7-HO

5,5-Dimethylcyclopenta-1,3-diene-1,4-diyl bis(trifluoromethanesulfonate), the corresponding diboron monomer, Pd(*dba*)₂, and P(Cy)₃ were added into an over-dried 20 mL high pressure microwave reactor tube. The tube was sealed and flushed with Ar, then degassed toluene (3 mL), THF (3 mL) and degassed aqueous 4.4 M KF (0.4 mL) were added. The mixture was thoroughly degassed under Ar, and then the argon inlet was removed. Then reaction was stirred at RT until gelation (around 0.5 h). Additional degassed toluene (6 mL) was added and the mixture was heated to 90 °C and stirred for 3 days. The mixture was precipitated in methanol (100 mL) and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane and chloroform. The chloroform solution was concentrated in *vacuo* and re-precipitated into methanol. Vacuum filtration followed by drying under vacuum afforded the corresponding polymers.

Poly{2,5-bis(5-octylpentadecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-alt-5,5-dimethylcyclopenta-1,3-dien-1,4-diyl}(PDPPCp-C4-OD)

The following compounds were used: 5,5-dimethylcyclopenta-1,3-diene-1,4-diyl

bis(trifluoromethanesulfonate) (99 mg, 0.25 mmol), **16** (303 mg, 0.25 mmol), Pd(dba)₂ (15 mg, 0.025 mmol), and P(Cy)₃ (28 mg, 0.10 mmol). The crude polymer was purified by Soxhlet apparatus with methanol, acetone, hexane and chloroform. The chloroform solution was concentrated in *vacuo* and re-precipitated into methanol. Vacuum filtration followed by drying under vacuum afforded **PDPPCp-C4-OD** as a dark-green solid (240 mg, yield: 60%). ¹H NMR (CDCl₃, 400MHz, 50 °C), δ (ppm): 9.01 (broad, 2H), 7.39 (broad, 2H), 6.98 (broad, 2H), 4.15 (broad, 4H), 1.81 (broad, 4H), 1.45 (broad, 6H), 1.37-1.23 (broad, 74H), 0.88 (broad, 12H). GPC: Mn = 108 kDa, Đ = 2.3.

Poly{2,5-bis(8-octyloctadecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-alt-5,5-dimethylcycopenta-1,3-dien-1,4-diyl}(PDPPCp-C7-OD)

The following compounds were used: 5,5-dimethylcyclopenta-1,3-diene-1,4-diyl bis(trifluoromethanesulfonate) (59 mg, 0.15 mmol), **17** (192 mg, 0.15 mmol), Pd(dba)₂ (8 mg, 0.014 mmol), and P(Cy)₃ (17 mg, 0.060 mmol). The crude polymer was purified by Soxhlet apparatus with methanol, acetone, hexane and chloroform. The chloroform solution was concentrated in *vacuo* and re-precipitated into methanol. Vacuum filtration followed by drying under vacuum afforded **PDPPCp-C7-OD** as a dark-green solid (117 mg, yield: 70%). ¹H NMR (CDCl₃, 400MHz, 50 °C), δ (ppm): 9.00 (broad, 2H), 7.40 (broad, 2H), 6.98 (broad, 2H), 4.14 (broad, 4H), 1.79 (broad, 2H), 1.45 (broad, 6H), 1.37-1.23 (broad, 86H), 0.88 (broad, 12H). GPC: Mn = 103 kDa, Đ = 1.8.

Poly{2,5-bis(8-hexylhexadecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-alt-5,5-dimethylcycopenta-1,3-dien-1,4-diyl}(PDPPCp-C7-HO)

The following compounds were used: 5,5-dimethylcyclopenta-1,3-diene-1,4-diyl bis(trifluoromethanesulfonate) (114 mg, 0.29 mmol), **18** (341 mg, 0.29 mmol), Pd(dba)₂ (14 mg, 0.024 mmol), and P(Cy)₃ (27 mg, 0.095 mmol). The crude polymer was purified by Soxhlet apparatus with methanol, acetone, hexane and chloroform. The chloroform solution was concentrated in *vacuo* and re-precipitated into methanol. Vacuum filtration followed by drying under vacuum afforded **PDPPCp-C7-HO** as a dark-green solid (210 mg, yield: 71%). ¹H NMR (CDCl₃, 400MHz, 50 °C), δ (ppm): 9.05 (broad, 2H), 7.39 (broad, 2H), 7.01 (broad, 2H), 4.05 (broad, 4H), 2.00 (broad, 2H), 1.64 (broad, 6H), 1.37-1.23 (broad, 64H), 0.84 (broad, 12H). GPC: Mn = 106 kDa,

D = 1.9.

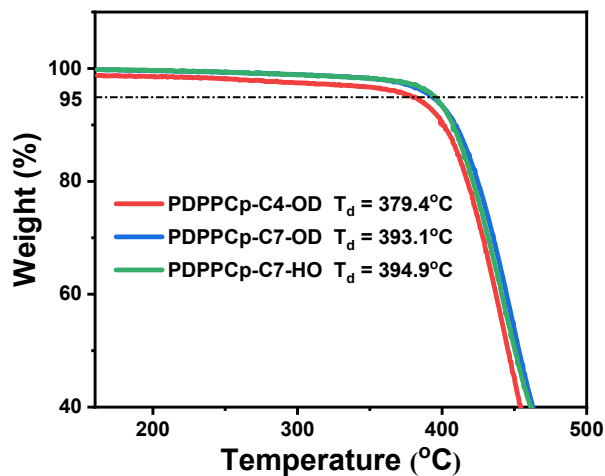


Figure S1. TGA curves of PDPPCp-C4-OD, PDPPCp-C7-OD and PDPPCp-C7-HO under N_2 .

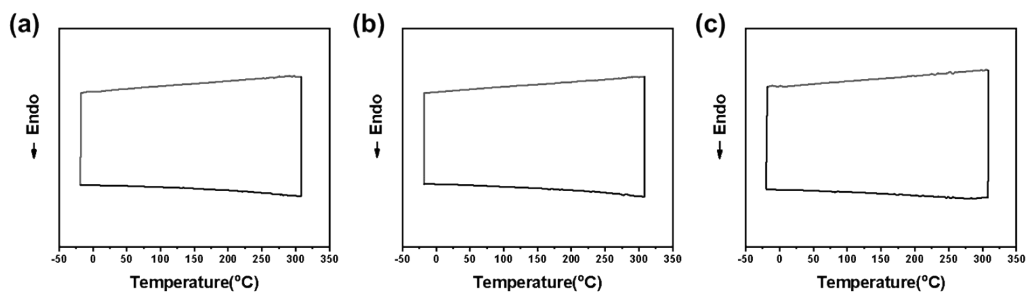


Figure S2. DSC curves of PDPPCp-C4-OD (a), PDPPCp-C7-OD (b) and PDPPCp-C7-HO (c)

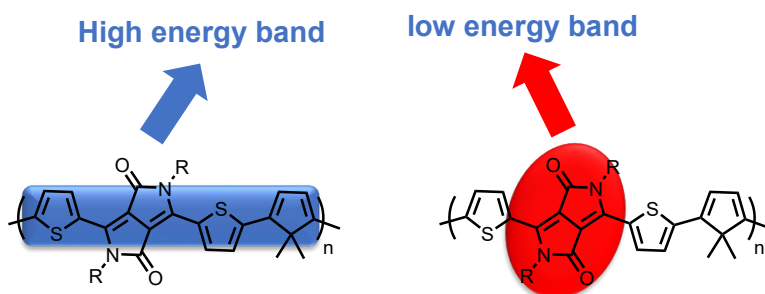


Figure S3. An illustration of the possible electronic transition of PDPPCp polymer series.

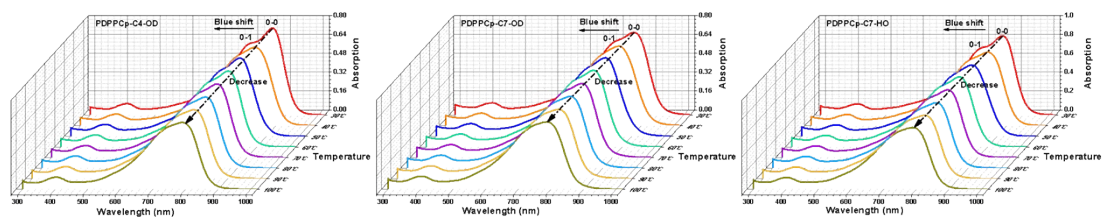


Figure S4. Temperature dependent UV-vis-NIR absorption spectra of PDPPCp-C4-OD, PDPPCp-C7-OD and PDPPCp-C7-HO (a, b, c) in CB solution (10^{-5} M).

Table S1. Ratio of peak intensities of 0-0 and 0-1 in the Temperature dependent UV-vis-NIR absorption spectra of the polymers in CB solution (10^{-5} M).

| Temperature (°C) | Absorption intensity ratios of 0-0/0-1 | | |
|------------------|--|--------------|--------------|
| | PDPPCp-C4-OD | PDPPCp-C7-OD | PDPPCp-C7-HO |
| 30 | 1.295 | 1.232 | 1.257 |
| 40 | 1.211 | 1.186 | 1.185 |
| 50 | 1.207 | 1.183 | 1.176 |
| 60 | 1.193 | 1.153 | 1.154 |
| 70 | 1.154 | 1.115 | 1.117 |
| 80 | 1.117 | 1.089 | 1.089 |
| 90 | 1.092 | 1.071 | 1.074 |
| 100 | 1.078 | 1.061 | 1.063 |

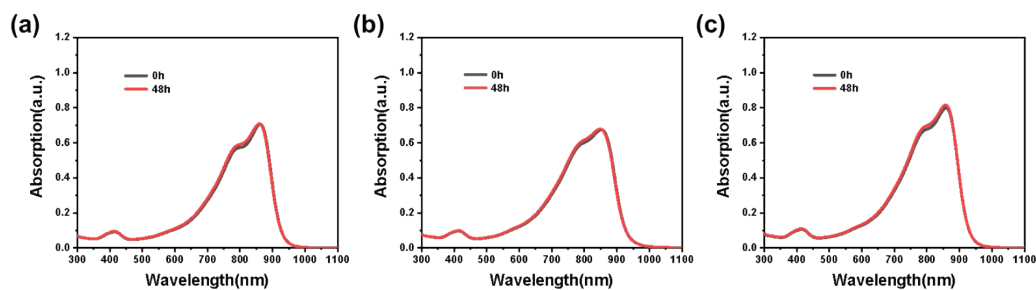


Figure S5. UV-vis-NIR absorption spectra of PDPPCp-C4-OD (a), PDPPCp-C7-OD (b) and PDPPCp-C7-HO (c) in CB solution before and after exposure to ambient conditions for 48 h.

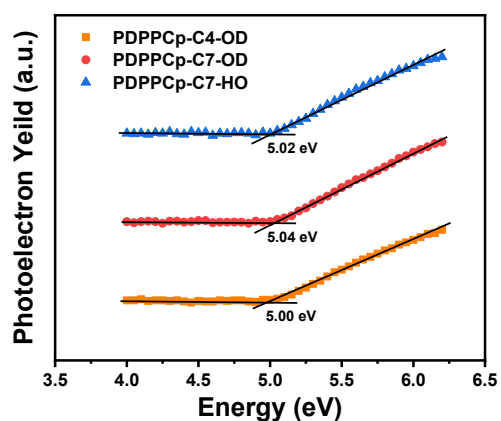


Figure S6. Photoelectron spectroscopy in air (PESA) spectra of polymers.

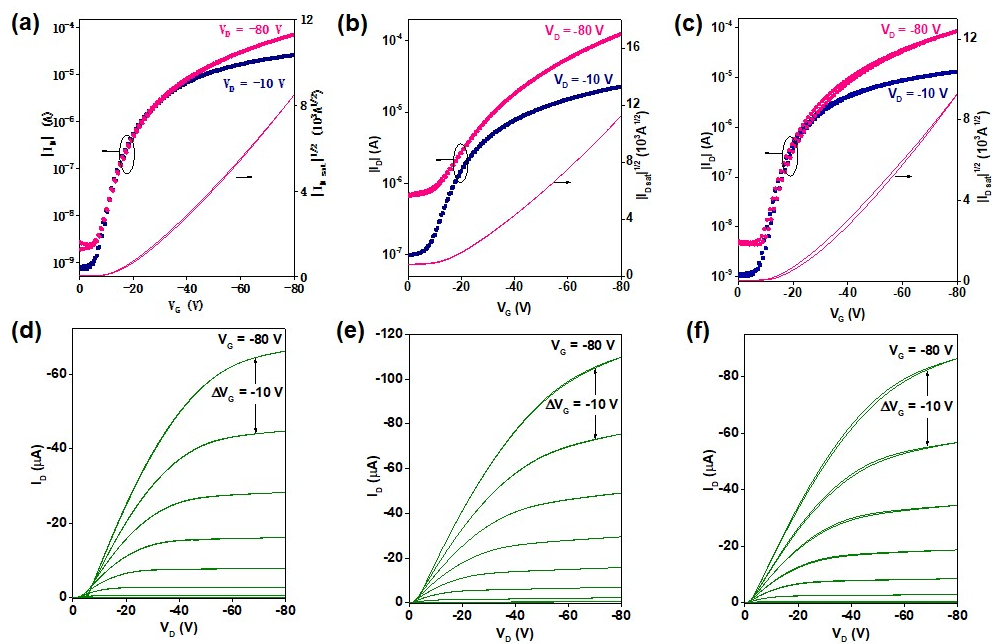


Figure S7. Typical transfer and output characteristics of PDPPCp-C4-OD (a, d), PDPPCp-C7-OD (b, e) and PDPPCp-C7-HO (c, f) based BG/TC configuration OFETs devices with annealed at 120 °C.

Table S2. OFET devices performance of PDPPCp-C4-OD, PDPPCp-C7-OD and PDPPCp-C7-HO in bottom gate, top contact devices with annealed at 120 °C.

| Polymer | μ_{lin} average ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) | μ_{sat} average ($\mu_{\text{sat max}}$) ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) | V_{Th} (V) | $I_{\text{on}}/I_{\text{off}}$ |
|--------------|--|---|---------------------|--------------------------------|
| PDPPCp-C4-OD | 0.64 ± 0.041 | 0.70 ± 0.026 (0.72) | -24.7 ± 0.7 | $10^3 \sim 10^4$ |
| PDPPCp-C7-OD | 0.39 ± 0.032 | 0.93 ± 0.019 (0.96) | -20.3 ± 0.8 | $10^2 \sim 10^3$ |
| PDPPCp-C7-HO | 0.23 ± 0.041 | 0.85 ± 0.17 (1.1) | -28.0 ± 1.7 | $10^4 \sim 10^5$ |

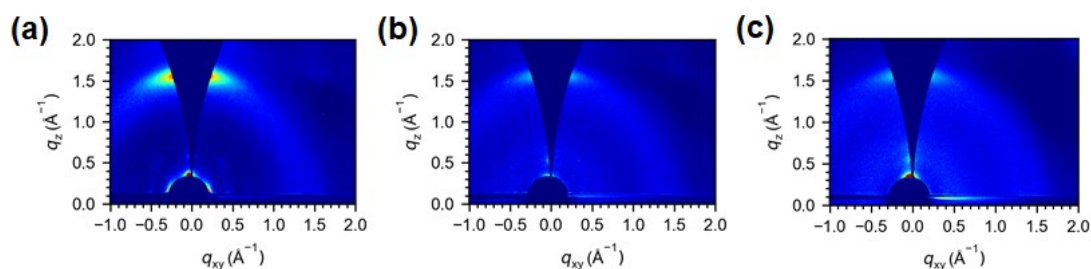


Figure S8. Two-dimensional GIWAXS images of PDPPCp-C4-OD, PDPPCp-C7-OD and PDPPCp-C7-HO films annealed at 120°C (d, e, f), respectively

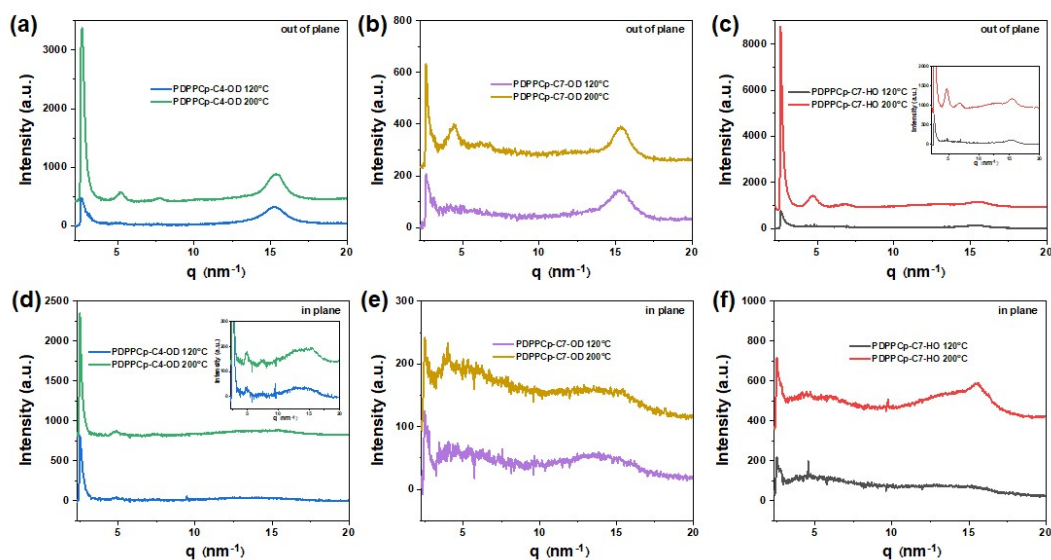


Figure S9. 1D plots in the out-of-plane direction of PDPPCp-C4-OD (a), PDPPCp-C7-OD (b) and PDPPCp-C7-HO (c) with annealing at 120°C and 200°C; 1D plots in the in-plane direction of PDPPCp-C4-OD (d), PDPPCp-C7-OD (e) and PDPPCp-C7-HO (f) with annealing at 120°C and 200°C

Table S3. Data summary of GIWAXS patterns of PDPPCp-C4-OD, PDPPCp-C7-OD and PDPPCp-C7-HO with annealing at 120°C in the out-of-plane direction

| Polymer | OOP π - π | | | | OOP lamellar | | | |
|--------------|-------------------------|--------------------|----------------------------|---------------------|-------------------------|--------------------|----------------------------|---------------------|
| | q (\AA^{-1}) | d (\AA) | FWHM (\AA^{-1}) | CL (\AA) | q (\AA^{-1}) | d (\AA) | FWHM (\AA^{-1}) | CL (\AA) |
| PDPPCp-C4-OD | 1.53 | 4.11 | 0.142 | 44.3 | 0.265 | 23.70 | 0.044 | 141.6 |
| PDPPCp-C7-OD | 1.53 | 4.10 | 0.138 | 45.4 | 0.252 | 24.92 | 0.039 | 163.1 |
| PDPPCp-C7-HO | 1.54 | 4.09 | 0.170 | 36.9 | 0.261 | 24.06 | 0.040 | 156.4 |

Table S4. Data summary of GIWAXS patterns of PDPPCp-C4-OD, PDPPCp-C7-OD and PDPPCp-C7-HO with annealing at 120°C in the in-plane direction.

| Polymer | IP π - π | | | | IP lamellar | | | |
|--------------|-------------------------|--------------------|----------------------------|---------------------|-------------------------|--------------------|----------------------------|---------------------|
| | q (\AA^{-1}) | d (\AA) | FWHM (\AA^{-1}) | CL (\AA) | q (\AA^{-1}) | d (\AA) | FWHM (\AA^{-1}) | CL (\AA) |
| PDPPCp-C4-OD | | | — | | 0.266 | 23.61 | 0.023 | 273.0 |
| PDPPCp-C7-OD | | | — | | 0.254 | 24.72 | 0.038 | 163.6 |
| PDPPCp-C7-HO | | | — | | 0.262 | 23.97 | 0.028 | 220.6 |

Table S5. Data summary of GIWAXS patterns of PDPPCp-C4-OD, PDPPCp-C7-OD and PDPPCp-C7-HO with annealing at 200°C in the out-of-plane direction.

| Polymer | OOP π - π | | | | OOP lamellar | | | |
|--------------|-------------------------|--------------------|----------------------------|---------------------|-------------------------|--------------------|----------------------------|---------------------|
| | q (\AA^{-1}) | d (\AA) | FWHM (\AA^{-1}) | CL (\AA) | q (\AA^{-1}) | d (\AA) | FWHM (\AA^{-1}) | CL (\AA) |
| PDPPCp-C4-OD | 1.53 | 4.09 | 0.120 | 52.3 | 0.27 | 23.61 | 0.022 | 281.4 |
| PDPPCp-C7-OD | 1.54 | 4.09 | 0.117 | 53.7 | 0.25 | 25.12 | 0.027 | 235.8 |
| PDPPCp-C7-HO | 1.55 | 4.05 | 0.137 | 45.8 | 0.26 | 24.25 | 0.019 | 331.2 |

Table S6. Data summary of GIWAXS patterns of PDPPCp-C4-OD, PDPPCp-C7-OD and PDPPCp-C7-HO with annealing at 200 °C in the in-plane direction.

| Polymer | IP π - π | | | | IP lamellar | | | |
|--------------|-------------------------|--------------------|----------------------------|---------------------|-------------------------|--------------------|----------------------------|---------------------|
| | q (\AA^{-1}) | d (\AA) | FWHM (\AA^{-1}) | CL (\AA) | q (\AA^{-1}) | d (\AA) | FWHM (\AA^{-1}) | CL (\AA) |
| PDPPCp-C4-OD | | | — | | 0.258 | 24.34 | 0.017 | 371.9 |
| PDPPCp-C7-OD | | | — | | 0.241 | 26.06 | 0.033 | 189.1 |
| PDPPCp-C7-HO | 1.56 | 4.03 | 0.121 | 51.8 | 0.250 | 25.12 | 0.019 | 335.8 |

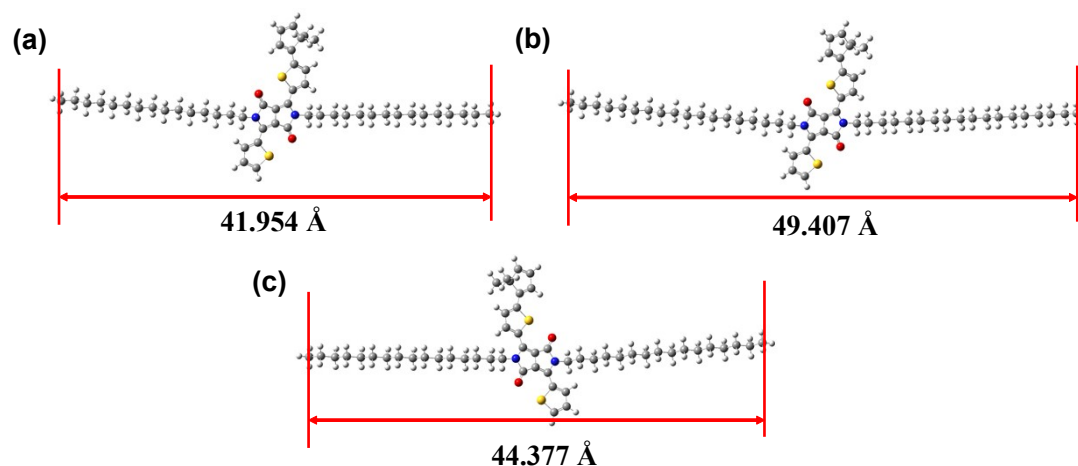


Figure S10. Lamellar distance of PDPPCp-C4-OD (a), PDPPCp-C7-OD (b), and PDPPCp-C7-HO (c) for fully extended alkyls according to DFT calculation.

Reference :

- 1 L. Chen, S. M. Mahmoud, X. Yin, R. A. Lalancette and A. Pietrangelo, *Org. Lett.*, 2013, **15**, 5970–5973.
- 2 J. Burdyńska, Y. Li, A. V. Aggarwal, S. Höger, S. S. Sheiko and K. Matyjaszewski, *J. Am. Chem. Soc.*, 2014, **136**, 12762–12770.
- 3 G. J. N. Wang, F. Molina-Lopez, H. Zhang, J. Xu, H. C. Wu, J. Lopez, L. Shaw, J. Mun, Q. Zhang, S. Wang, A. Ehrlich and Z. Bao, *Macromolecules*, 2018, **51**, 4976–4985.