

Supporting Information

Ultra-Narrow Bandgap Derived from Thienoisindigo Polymers: Structural Influence on Reducing Bandgap and Self-Organization

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Contents of Supporting Information:

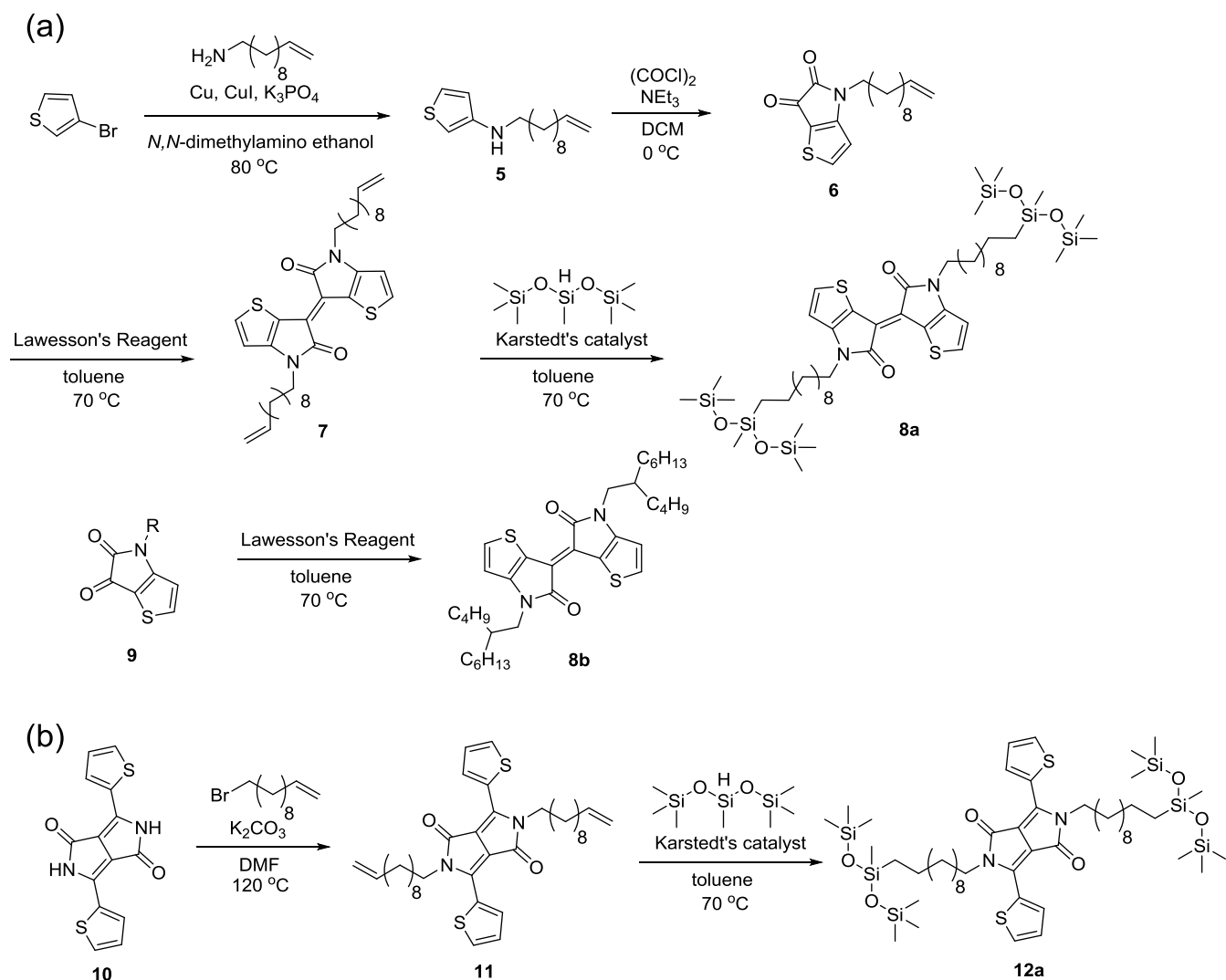
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I. General

All the chemicals and solvents were of reagent grade purchased from Tokyo Kasei Chemical Industries, Wako Pure Chemical Industries, and Aldrich and used without further purification. All reactions were carried out under an argon atmosphere. ^1H and ^{13}C NMR spectra were recorded using a JEOL JNM-AL300 spectrometer (300 MHz) in deuterated chloroform at 298 K and tetramethylsilane was used as the internal standard. Mass spectrograms were recorded on a Shimadzu QP-5000 (EI-MS) or a Shimadzu MALDI-AXIMA time of flight mass spectrometer (MALDI-TOF) operated in the linear mode. Number-average molecular weights (M_n) and polydispersity indices (PDI) were measured by gel-permeation chromatography (GPC) with GL Sciences PU 713, UV 702, CO 705, AD 430 using chloroform and a polystyrene (PS) standard at room temperature. Density Functional Theory (DFT) calculations were performed using the Gaussian 09 program based on the B3LYP/6-31G(d,p).¹ Internal rotation potentials were calculated at each 5 degrees rotation of single bond connecting monomer units using the Gaussian 09 program based on the B3LYP/6-31G(d,p). FT-Raman spectra were measured using JASCO NRS-5100 with laser wavelength 532.26 nm on drop-casted or spin-coated polymer thin-films. Elemental analyses were performed at Center for Advanced Materials Analysis, Tokyo Institute of Technology.

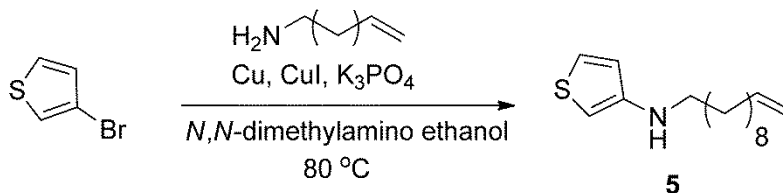
II. Material Synthesis

Compounds **9**, **10**, **12b** and **3b** were prepared according to the previous reports.^{2,3}



Scheme S1. Synthesis of (a) TII unit with siloxane or branched alkyl chains and (b) TDPP unit with siloxane chains.

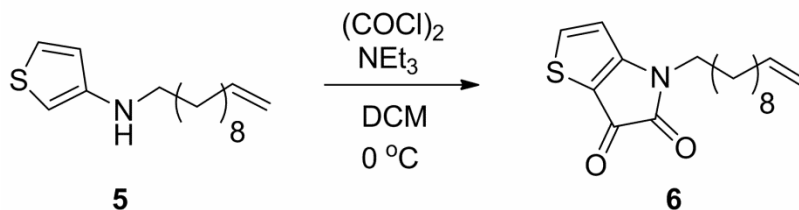
N-(undecen-10-en-1-yl)-thiophen-3-amine (**5**)



3-Bromothiophene (7.71 g, 47.3 mmol), undecen-10-en-1-amine (12.0 g, 70.8 mmol), copper (0.150 g, 2.37 mmol), and copper (I) iodide (0.45 g, 2.37 mmol) were suspended in *N,N*-dimethylamino ethanol (30 mL) under an argon atmosphere. The resulting mixture was heated at 80 °C for 48 h. After cooling to room temperature, the reaction mixture was filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography,

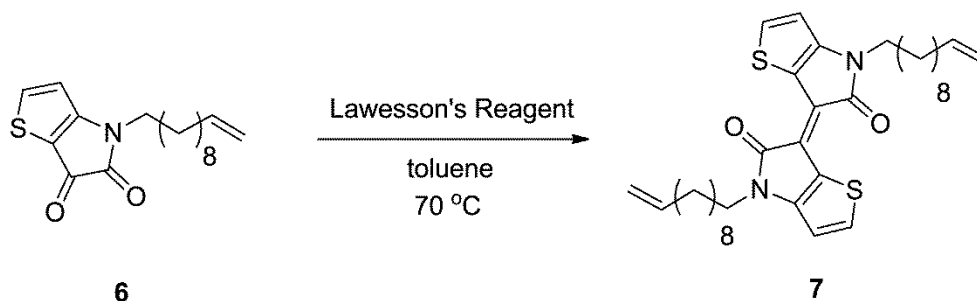
eluting with (CH₂Cl₂) to provide 8.11 g (69%) as a brown oil. This compound was slightly unstable and was used for the next step immediately. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 7.11 (dd, *J* = 5.1, 2.7 Hz, 1H), 6.57 (dd, *J* = 4.2, 1.5 Hz, 1H), 5.91 (dd, *J* = 3.0, 1.5 Hz, 1H), 5.87-5.74 (m, 1H), 5.02-4.90 (m, 2H), 3.52 (bs, 1H), 3.03 (t, *J* = 7.2 Hz, 2H), 2.07-2.00 (m, 4H), 1.64-1.54 (m, 2H), 1.39-1.29 (m, 10H). ¹³C NMR (75 MHz, CDCl₃, 25 °C): 149.04, 139.30, 125.10, 120.01, 114.29, 95.23, 46.37, 33.80, 29.60, 29.54, 29.46, 29.12, 28.91, 27.20. MS(EI) *m/z*: 251 [M]⁺.

4-(undecen-10-en-1-yl)-4*H*-thieno[3,2-*b*]pyrrole-5,6-dione (6)



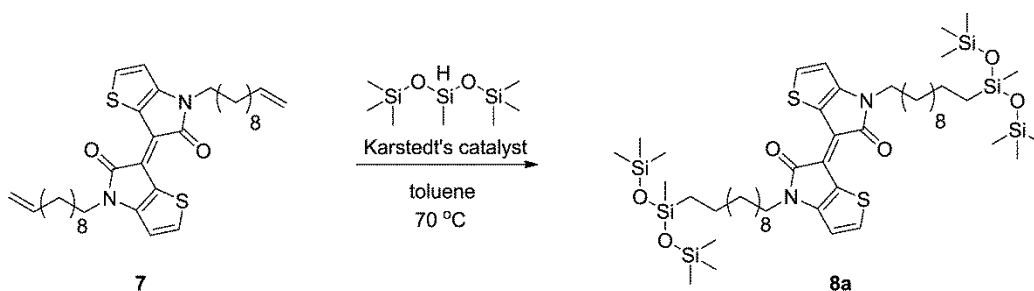
To a solution of oxalyl chloride (5.46 g, 43.0 mmol) diluted in anhydrous dichloromethane (20 mL) cooled at 0 °C under an argon atmosphere, a solution of compound **5** (8.10 g, 32.3 mmol) diluted in anhydrous dichloromethane (10 mL) was added dropwise over 20 min. After 30 min, triethylamine (14.5 g, 143.6 mmol) was added dropwise over 20 min. The resulting mixture was allowed to warm to room temperature. After stirring for 12 h at room temperature, the mixture was filtered and evaporated under reduced pressure. The residue was purified by silica gel chromatography, eluting with (CH₂Cl₂) to provide 5.72 g (58%) as a red solid. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 8.01 (d, *J* = 4.8 Hz, 1H), 6.79 (d, *J* = 5.1 Hz, 1H), 5.84-5.70 (m, 1H), 4.99-4.87 (m, 2H), 3.63 (t, *J* = 7.2 Hz, 2H), 2.03-1.96 (m, 2H), 1.69-1.60 (m, 2H), 1.30-1.24 (m, 13H). ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ 173.26, 165.42, 161.69, 144.25, 139.30, 114.28, 113.18, 111.10, 42.13, 33.75, 29.35, 29.31, 29.10, 29.01, 28.84, 28.14, 26.72. MS(EI) *m/z*: 305 [M]⁺. Elemental Anal. Calcd. for C₁₇H₂₃NO₂S: C, 66.85; H, 7.59; N, 4.59; S, 10.50; found: C, 66.48; H, 7.70; N, 4.54; S, 10.61.

(*E*)-4,4'- di(undec-10-en-1-yl)-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'(4*H*,4'*H*)-diones (7).



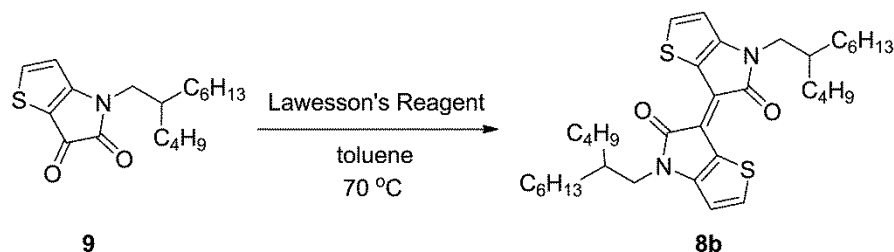
Compound **6** (1.00 g, 3.27 mmol) and Lawesson's Reagent (1.32 g, 3.27 mmol) dissolved in anhydrous toluene (20 mL) under an argon atmosphere. The resulting mixture was heated to 60 °C and stirred for 2 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. The residue was purified by silica gel chromatography, eluting with (CH₂Cl₂ : hexane = 2 : 3) to provide 0.43 g (45%) as dark purple solid. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 7.53 (d, *J* = 5.1 Hz, 2H), 6.81 (d, *J* = 5.1 Hz, 2H), 5.86-5.73 (m, 2H), 5.01-4.90 (m, 4H), 3.80 (t, *J* = 7.2 Hz, 4H), 2.05-1.98 (m, 4H), 1.77-1.67 (m, 4H), 1.34-1.26 (m, 26H). ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ 171.28, 151.48, 139.46, 134.60, 114.32, 111.38, 41.87, 33.86, 29.48, 29.43, 29.31, 29.13, 28.95, 28.65, 26.96. MS (MALDI-TOF) *m/z*: 578.21 [M]⁺. Elemental Anal. Calcd. for C₃₄H₄₆N₂O₂S₂: C, 70.54; H, 8.01; N, 4.84; found: C, 70.19; H, 8.05; N, 4.80.

(*E*)-4,4'-bis(11-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)undecyl)-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'(4*H*,4'*H*)-dione (8a**)**



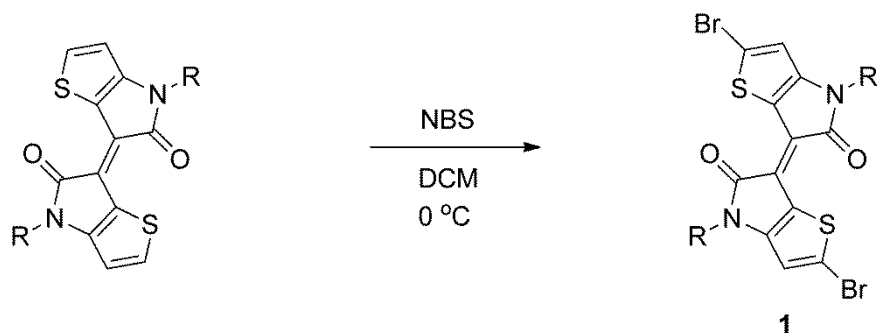
To a solution of compound **7** (0.52 g, 0.90 mmol) dissolved in anhydrous toluene (20 mL) under an argon atmosphere, 1,1,1,3,5,5,5-heptamethyltrisiloxane (0.80 g, 3.60 mmol) was added, followed by the addition of a drop (10 μL) of Karstedt's catalyst (platinum-divinyltetramethyl-siloxane complex in xylene). The resulting mixture was heated to 60 °C until complete consumption of compound **7**, which was monitored by TLC. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography, eluting with (CH₂Cl₂ : hexane = 2 : 3) to provide 0.44 g (48%) as a dark purple oil. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 7.47 (d, *J* = 5.1 Hz, 2H), 6.76 (d, *J* = 5.4 Hz, 2H), 3.77 (t, *J* = 7.2 Hz, 4H), 1.78-1.65 (m, 4H), 1.31-1.24 (m, 32H), 0.46-0.41 (m, 4H), 0.08 (bs, 36H), -0.01 (s, 6H). ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ 171.09, 151.35, 134.44, 121.14, 114.31, 111.22, 41.77, 33.23, 29.61, 29.55, 29.52, 29.35, 29.32, 26.94, 23.06, 17.59, 1.83, -0.29. MS (MALDI-TOF) *m/z*: 1022.85 [M]⁺. Elemental Anal. Calcd. for C₄₈H₉₀N₂O₆S₂Si₆: C, 56.31; H, 8.86; N, 2.74; S, 6.26; found: C, 56.52; H, 8.55; N, 2.74; S, 6.36.

(*E*)-4,4'-di(2-butyl-octyl)-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'(4*H*,4'*H*)-dione (8b**)**



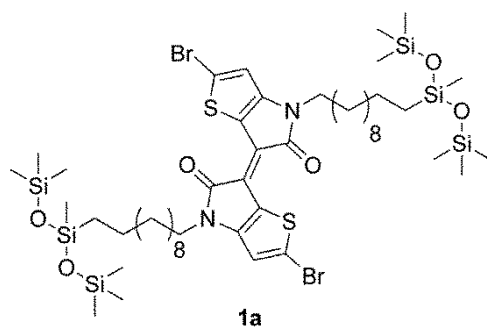
Compound **8b** was synthesized from **9** (3.03 g, 9.43 mmol) with the same procedure for **7**.² Purification by silica gel chromatography (CH_2Cl_2 : hexane = 1 : 1) provided 0.89 g (31%) as a dark purple solid. ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 7.51 (d, J = 5.1 Hz, 2H), 6.77 (d, J = 5.4 Hz, 2H), 3.68 (d, J = 7.5 Hz, 4H), 1.89 (m, 2H), 1.31-1.23 (m, 32H), 0.89-0.82 (m, 12H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ 171.56, 151.76, 134.43, 121.21, 114.39, 111.51, 46.17, 37.19, 31.83, 31.49, 31.20, 29.67, 28.67, 26.42, 23.06, 22.66, 14.10, 14.07. MS (MALDI-TOF) m/z : 610.27 [M]⁺. Elemental Anal. Calcd. for $\text{C}_{36}\text{H}_{54}\text{N}_2\text{O}_2\text{S}_2$: C, 70.77; H, 8.91; N, 4.59; S, 10.59; found: C, 70.84; H, 9.28; N, 4.57; S, 10.31.

Synthesis of dibromo thienoisindigo monomers(1)



(*E*)-2,2'-dibromo-4,4'-bis(11-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)undecyl)-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'(4*H*,4'*H*)-dione (**1a**)

Compound **8a** (0.30 g, 0.29 mmol) was dissolved in anhydrous dichloromethane (20 mL) under argon atmosphere. The flask was shielded from light and *N*-bromosuccinimide (0.11 g, 0.65 mmol) was added over 10min at 0 °C. The resulting mixture was stirred for 2h at 0 °C. The reaction was quenched with 100 mL of saturated NH_4Cl water and extracted with CH_2Cl_2 three

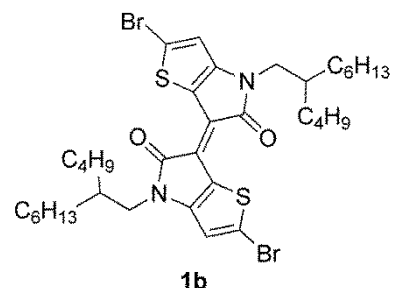


times. The organic layer was washed with water twice and then dried with MgSO_4 . After the removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography, eluting with (CH_2Cl_2 : hexane = 2 : 3) to provide 0.19 g (56%) as a dark purple solid. ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 6.83 (s,

2H), 3.73 (t, $J = 7.5$ Hz, 4H), 1.70-1.66 (m, 4H), 1.31-1.25 (m, 32H), 0.46-0.41 (m, 4H), 0.08 (bs, 36H), -0.01 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ 170.39, 150.11, 123.42, 119.93, 115.03, 114.84, 41.96, 33.32, 29.68, 29.63, 29.59, 29.43, 29.34, 28.66, 26.96, 23.13, 17.68, 1.90, -0.23. MS (MALDI-TOF) m/z : 1178.17 $[\text{M}]^+$. Elemental Anal. Calcd. for $\text{C}_{48}\text{H}_{88}\text{Br}_2\text{N}_2\text{O}_6\text{S}_2\text{Si}_6$: C, 48.79; H, 7.51; N, 2.37; S, 5.43; found: C, 48.63; H, 7.68; N, 2.31; S, 5.50.

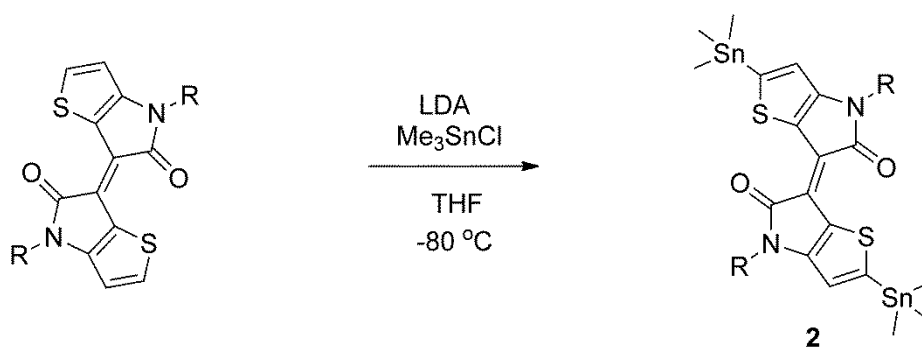
(E)-2,2'-dibromo-4,4'-bis(2-butyloctyl)-[6,6'-bithieno[3,2-b]pyrrolylidene]-5,5'-(4H,4'H)-dione (1b)

Compound **8b** (0.30 g, 0.49 mmol) was synthesized with the same procedure for **1a**. Purification by silica gel chromatography (CH_2Cl_2 : hexane = 2 : 3) provided 0.30 g (80%) as a dark purple solid. ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 6.82 (s, 2H), 3.63 (d, $J = 7.5\text{Hz}$, 4H), 1.88-1.77 (m, 2H), 1.29-1.24 (m, 32H), 0.95-0.83 (m, 12H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ 170.58, 150.38,



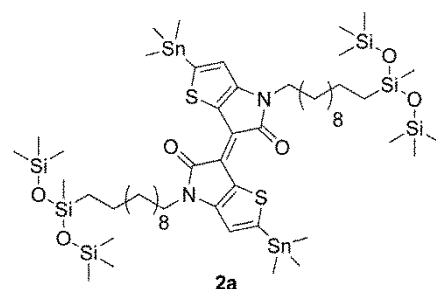
123.25, 119.78, 115.13, 114.83, 46.24, 37.28, 31.84, 31.42, 31.16, 29.69, 28.66, 26.37, 23.09, 22.69, 14.12, 14.09. MS (MALDI-TOF) m/z : 766.54 $[\text{M}]^+$. Elemental Anal. Calcd. for $\text{C}_{36}\text{H}_{52}\text{Br}_2\text{N}_2\text{O}_2\text{S}_2$: C, 56.25; H, 6.82; N, 3.64; S, 8.34; found: C, 56.58; H, 7.08; N, 3.56; S, 8.33.

Synthesis of di(trimethylstannyl) thienoisindigo monomers (2)



(E)-4,4'-bis(11-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)undecyl)-2,2'-bis(trimethylstannyl)-[6,6'-bithieno[3,2-b]pyrrolylidene]-5,5'-(4H,4'H)-dione (2a)

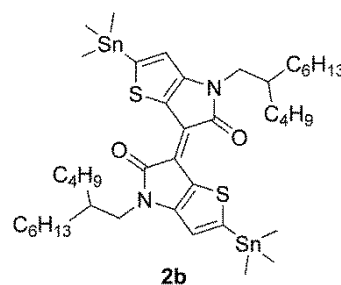
To a solution of freshly prepared excess LDA (lithium diisopropylamide) (5.00 mL, 2.00 mmol) in dry THF-hexane solution cooled at -80 °C under an argon atmosphere, compound **8a** (0.25 g, 0.25 mmol) dissolved in 10 mL of dry THF was added over 20 min. The



resulting mixture was stirred for 1 h at -80 °C. The mixture was again cooled to -100 °C and trimethyltin chloride (0.60 g, 3.00 mmol) in dry THF solution was added rapidly. The mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with 100 mL of saturated brine and extracted with Et₂O three times. The organic layer was washed with brine twice and then dried with MgSO₄. After the removal of the solvent under reduced pressure, the residue was washed with 100 mL of methanol to provide 0.22 g (64%) as a dark purple solid. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 6.83 (s, 2H), 3.80 (t, *J* = 6.9 Hz), 1.79-1.68 (m, 4H), 1.40-1.25 (m, 32H), 0.90-0.82 (m, 4H), 0.43 (s, 18H), 0.08 (s, 36H), -0.01 (s, 6H). ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ 172.01, 152.66, 151.18, 120.23, 117.86, 117.76, 41.94, 29.72, 29.65, 29.46, 29.43, 23.13, 17.68, 1.90, -0.24, -8.08. MS (MALDI-TOF) *m/z*: 1350.90 [M]⁺. Elemental Anal. Calcd. for C₅₄H₁₀₆N₂O₆S₂Si₆Sn₂: C, 48.06; H, 7.92; N, 2.08; S, 4.75; found: C, 47.82; H, 8.22; N, 1.98; S, 4.79.

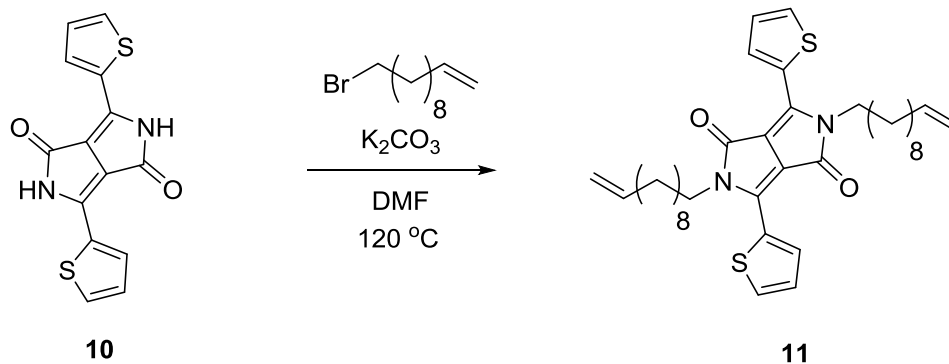
(*E*)-4,4'-bis(2-butyloctyl)-2,2'-bis(trimethylstannyl)-[6,6'-bithieno[3,2-*b*]pyrrolylidene]-5,5'(4*H*,4'*H*)-dione (2b)

Compound **2b** was synthesized from **8b** (0.30 g, 0.49 mmol) with the same procedure for **2a** to afford 0.27 g (63%) as a dark purple solid. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 6.79 (s, 2H), 3.69 (d, *J* = 6.9 Hz, 4H), 1.96-1.86 (m, 2H), 1.31-1.24 (m, 32H), 0.87-0.82 (m, 12H), 0.40 (s, 18H). ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ 172.29, 152.96, 150.94, 120.50, 120.24, 118.01, 46.21, 37.13, 31.87, 31.41, 31.18,



29.71, 28.66, 26.35, 23.11, 22.71, 14.13, -8.13. MS (MALDI-TOF) *m/z*: 938.27 [M]⁺. Elemental Anal. Calcd. for C₄₂H₇₀N₂O₂S₂Sn₂: C, 53.86; H, 7.53; N, 2.99; S, 6.85; found: C, 53.68; H, 7.86; N, 3.01; S, 6.67.

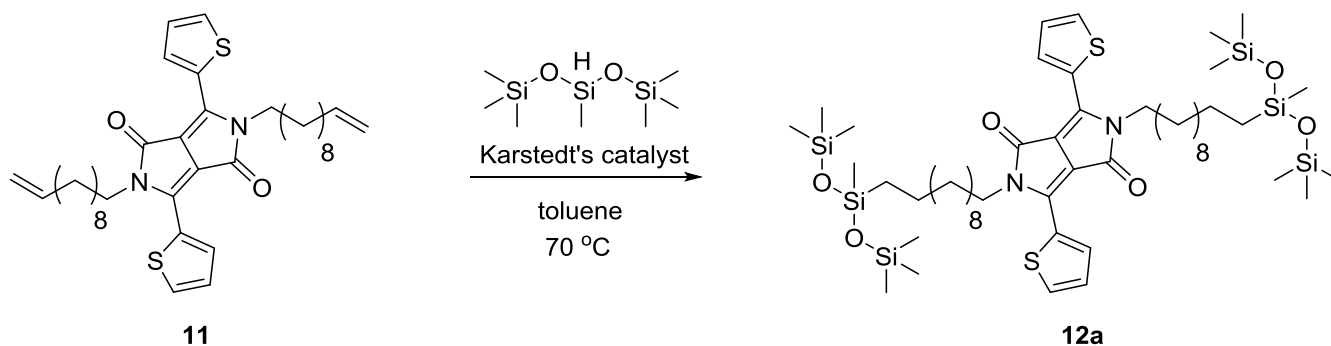
2,5-bis(undecen-10-en-1-yl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (11)



Compound **10**³ (2.00 g, 6.67 mmol), potassium carbonate (2.03 g, 14.7 mmol), and 11-bromo-1-undecene (3.42 g, 14.7 mmol) were suspended in anhydrous DMF (20 mL) under an argon atmosphere. The resulting mixture was heated to 120 °C and stirred overnight. After cooling to room temperature, the solvent was evaporated under reduced

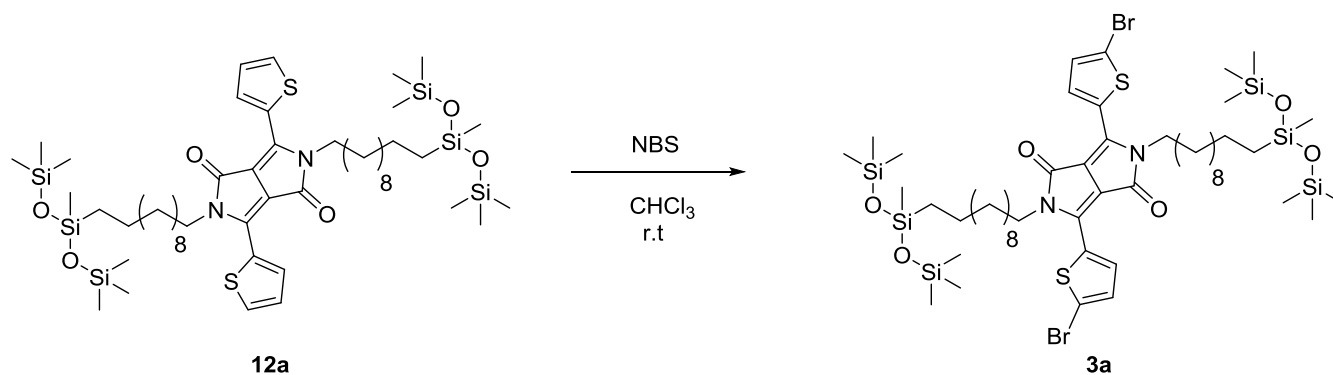
pressure. The residue was purified by silica gel chromatography, eluting with (CH₂Cl₂ : hexane = 1 : 1) to provide 1.85 g (46%) as a dark purple solid. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 8.93 (dd, *J* = 4.2, 1.5 Hz, 2H), 7.63 (dd, *J* = 5.1, 1.2 Hz, 2H), 7.28 (dd, *J* = 5.1, 3.9 Hz, 2H), 5.87-5.74 (m, 2H), 5.02-4.90 (m, 4H), 4.06 (t, *J* = 7.8 Hz, 4H), 2.06-1.99 (m, 4H), 1.79-1.69 (m, 4H), 1.43-1.27 (m, 24H). ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ 161.61, 140.23, 139.44, 135.49, 130.87, 129.99, 128.82, 114.31, 107.85, 42.28, 33.86, 30.00, 29.50, 29.43, 29.26, 29.13, 28.96, 26.90. MS (MALDI-TOF) *m/z*: 604.28 [M]⁺. Elemental Anal. Calcd. for C₃₆H₄₈N₂O₂S₂: C, 71.48; H, 8.00; N, 4.63; found: C, 71.61; H, 8.13; N, 4.70.

2,5-bis(11-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)undecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (12a)



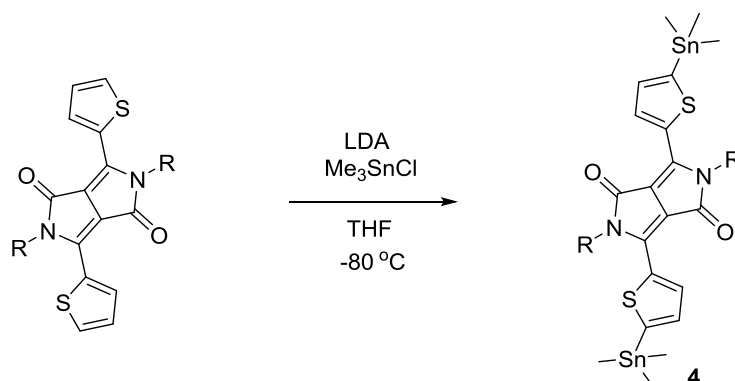
Compound **12a** was synthesized from **11** (1.45 g, 2.39 mmol) with the same procedure for **8a**. Purification by silica gel chromatography (CH₂Cl₂ : hexane = 2 : 3) provided 1.18 g (47%) as a dark purple solid. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 8.93 (dd, *J* = 3.6, 0.9 Hz, 2H), 7.61 (dd, *J* = 4.8, 1.2 Hz, 2H), 7.25 (dd, *J* = 5.4, 4.2 Hz, 2H), 4.04 (t, *J* = 7.8 Hz, 4H), 1.78-1.68 (m, 4H), 1.41-1.25 (m, 32H), 0.47-0.42 (m, 4H), 0.08 (s, 36H), -0.01 (s, 6H). ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ 161.50, 140.13, 135.49, 130.77, 129.97, 128.75, 107.80, 42.25, 33.29, 30.00, 29.65, 29.61, 29.41, 29.31, 26.93, 23.10, 17.64, 1.87, -0.26. MS (MALDI-TOF) *m/z*: 1049.14 [M+H]⁺. Elemental Anal. Calcd. for C₅₀H₉₂N₂O₆S₂Si₆: C, 57.20; H, 8.83; N, 2.67; found: C, 56.90; H, 9.13; N, 2.65.

3,6-bis(5-bromothiophen-2-yl)-2,5-bis(11-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)undecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (3a)



Compound **12a** (0.30 g, 0.29 mmol) was dissolved in anhydrous chloroform (20 mL) under argon atmosphere. The flask was shielded from light and *N*-bromosuccinimide (0.11 g, 0.65 mmol) was added over 10 min at room temperature. The resulting mixture was stirred overnight. The reaction was quenched with 100 mL of saturated NH_4Cl water and extracted with CH_2Cl_2 three times. The organic layer was washed with water twice and then dried with MgSO_4 . After the removal of the solvent under reduced pressure, the residue was purified by silica gel chromatography, eluting with (CH_2Cl_2 : hexane = 2 : 3) to provide 0.24 g (70%) as a dark purple solid. ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 8.68 (d, J = 4.2 Hz, 2H), 7.23 (d, J = 4.2 Hz, 2H), 3.97 (t, J = 8.4 Hz, 4H), 1.75-1.66 (m, 4H), 1.42-1.26 (m, 32H), 0.46-0.42 (m, 4H), 0.08 (s, 36H), -0.01 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ 161.30, 139.23, 135.61, 131.88, 131.36, 119.37, 107.97, 42.38, 33.35, 30.09, 29.69, 29.66, 29.60, 29.46, 29.31, 26.92, 23.15, 17.69, 1.90, -0.23. MS (MALDI-TOF) m/z : 1204.18 $[\text{M}]^+$. Elemental Anal. Calcd. for $\text{C}_{50}\text{H}_{90}\text{Br}_2\text{N}_2\text{O}_6\text{S}_2\text{Si}_6$: C, 49.73; H, 7.51; N, 2.32; S, 5.31; found: C, 50.00; H, 7.69; N, 2.27; S, 5.31.

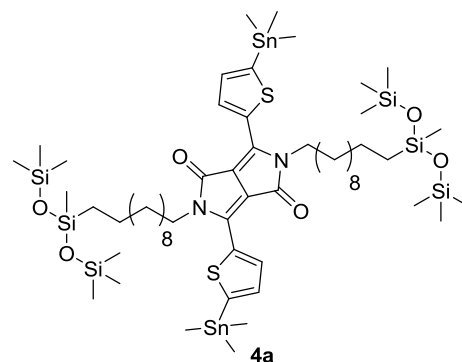
Synthesis of di(trimethylstannyl) thienyl diketopyrrolopyrrole monomers (**4**)



2,5-bis(11-(1,1,1,3,5,5,5-heptamethyltrisiloxan-3-yl)undecyl)-3,6-bis(5-(trimethylstannyl)thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**4a**)

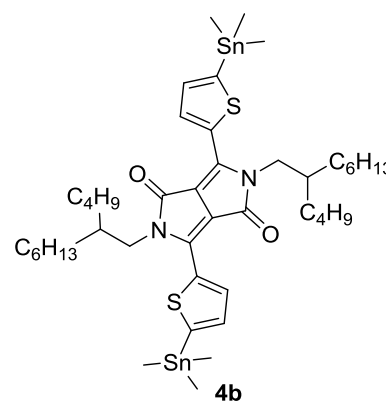
Compound **4a** was synthesized from **12a** (0.20 g, 0.19 mmol) with the same procedure for **2a** to afford 0.16 g (61%) as a dark purple oil. ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 8.98 (d, J = 3.6 Hz, 2H), 7.34 (d, J = 3.6 Hz, 2H), 4.09 (t,

$J = 8.4$ Hz, 4H), 1.80-1.70 (m, 4H), 1.43-1.26 (m, 32H), 0.88-0.83 (m, 4H), 0.44 (s, 18H), 0.08 (s, 36H), -0.01 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ 161.72, 146.44, 139.68, 136.58, 136.04, 135.51, 107.22, 42.28, 33.34, 29.99, 29.72, 29.68, 29.66, 29.46, 29.35, 26.98, 23.13, 17.68, 1.89, -0.25, -8.03. MS (MALDI-TOF) m/z : 1376.69 $[\text{M}]^+$. Elemental Anal. Calcd. for $\text{C}_{56}\text{H}_{108}\text{N}_2\text{O}_6\text{S}_2\text{Si}_6\text{Sn}_2$: C, 48.90; H, 7.91; N, 2.04; found: C, 49.02; H, 8.24; N, 2.00.



2,5-bis(2-butyloctyl)-3,6-bis(5-(trimethylstannyl)thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**4b**)

Compound **4b** was synthesized from **12**³ (0.27 g, 0.42 mmol) with the same procedure for **2a** to afford 0.38 g (93%) as a dark purple solid. ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 8.96 (d, $J = 3.6$ Hz, 2H), 7.32 (d, $J = 3.6$ Hz, 2H), 4.04 (d, $J = 7.8$ Hz, 4H), 1.95-1.85 (m, 2H), 1.28-1.20 (m, 32H), 0.86-0.81 (m, 12H), 0.43 (s, 18H). ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): δ 162.17, 146.08, 140.12, 136.38, 136.15, 135.55, 107.46, 46.21, 37.93, 32.98, 31.88, 31.43, 29.80, 28.70, 27.74, 26.44, 23.17, 22.69, 14.14, -8.06. MS (MALDI-TOF) m/z : 964.88 $[\text{M}]^+$.



Elemental Anal. Calcd. for $\text{C}_{44}\text{H}_{72}\text{N}_2\text{O}_2\text{S}_2\text{Si}_6$: C, 54.90; H, 7.54; N, 2.91; found: C, 55.56; H, 7.97; N, 2.72.

Polymer synthesis via Stille polycondensation (P1-P6).

PTII-Si11 (P1a)

A flask was charged with **1a** (115.4 mg, 0.15 mmol), **2a** (141.4 mg, 0.15 mmol), tris(dibenzylideneacetone)dipalladium(0) (1.38 mg, 0.0015 mmol), tri(*o*-tolyl)phosphine (3.67 mg, 0.012 mmol), anhydrous toluene (5 mL) and a stirring bar under argon atmosphere. The mixture was heated to 110 °C and allowed to stir for 48 h. After the completion, the mixture was cooled to room temperature and dropped into 200 mL of methanol. The obtained solid was collected by filtration and subjected to sequential Soxhlet extraction with methanol (1 d) and acetone (1 d) to remove the low molecular weight fractions of the materials. The residue was extracted with hexane, dropped into 200 mL of methanol and collected by filtration, yielding 76.6 mg (63%) as a dark green solid. Solubility in chloroform is 12.8 mg/mL. ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ 7.26-7.24 (br, 2H), 4.03-3.34 (br, 4H), 1.81-1.64 (br, 4H), 1.48-1.05 (br, 32H), 0.52-0.36 (br, 4H), 0.19-(-0.02) (br, 42H). Elemental Anal. Calcd. for $\text{C}_{48}\text{H}_{90}\text{N}_2\text{O}_6\text{S}_2\text{Si}_6$: C, 56.31; H, 8.86; N, 2.74; S, 6.26; found: C, 56.16; H, 9.33; N, 2.62; S, 6.06.

PTII-BO (P1b)

Compound **P1b** was synthesized from **1b** (115.4 mg, 0.15 mmol) and **2b** (141.4 mg, 0.15 mmol) with the same procedure for **P1a**. The crude polymer was purified by Soxhlet extraction with methanol (1 d), acetone (1 d) and hexane (1 d) to remove the low molecular weight fractions of the materials. The residue was extracted with chloroform, dropped into 200 mL of methanol and collected by filtration, yielding 52.1 mg (28%) as a dark green solid. Solubility in chloroform is 11.8 mg/mL. $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25 °C): δ 7.24-7.20 (br, 2H), 4.21-3.25 (br, 4H), 2.16-1.76 (br, 2H), 1.48-1.07 (br, 32H), 1.03-0.67 (br, 12H). Elemental Anal. Calcd. for $\text{C}_{36}\text{H}_{54}\text{N}_2\text{O}_2\text{S}_2$: C, 70.77; H, 8.91; N, 4.59; S, 10.50; found: C, 70.46; H, 9.12; N, 4.50; S, 10.69.

P(TII-TDPP)-Si11 (P2a)

Compound **P2a** was synthesized from **2a** (100.1 mg, 0.073 mmol) and **3a** (85.7 mg, 0.073 mmol) with the same procedure for **P1a**. The crude polymer was purified by Soxhlet extraction with methanol (1 d) and acetone (1 d) to remove the low molecular weight fractions of the materials. The residue was extracted with hexane, dropped into 200 mL of methanol and collected by filtration, yielding 124.0 mg (82%) as a dark green solid. Solubility in chloroform is 12.2 mg/mL. $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25 °C): δ 9.16-8.90 (br, 2H), 7.25-7.24 (br, 4H), 4.07-3.37 (br, 8H), 1.86-1.64 (br, 8H), 1.45-1.09 (br, 64H), 0.56-0.34 (br, 8H), 0.18-(-0.01) (br, 84H). Elemental Anal. Calcd. for $\text{C}_{98}\text{H}_{180}\text{N}_4\text{O}_{12}\text{S}_4\text{Si}_{12}$: C, 56.81; H, 8.76; N, 2.70; S, 6.19; found: C, 56.61; H, 9.15; N, 2.66; S, 6.03.

P(TII-TDPP)-BO (P2b)

Compound **P2b** was synthesized from **3b**³ (123.8 mg, 0.16 mmol) and **2b** (150.1 mg, 0.16 mmol) with the same procedure for **P1a**. The crude polymer was purified by Soxhlet extraction with methanol (1 d), acetone (1 d) and hexane (1 d) to remove the low molecular weight fractions of the materials. The residue was extracted with chloroform, dropped into 200 mL of methanol and collected by filtration, yielding 101.9 mg (52%) as a dark green solid. Solubility in chloroform is 12.8 mg/mL. $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25 °C): δ 9.20-8.99 (br, 2H), 6.98-6.57 (br, 4H), 4.36-3.39 (br, 8H), 2.05-1.84 (br, 8H), 1.49-0.65 (br, 84H). Elemental Anal. Calcd. for $\text{C}_{74}\text{H}_{108}\text{N}_4\text{O}_4\text{S}_4$: C, 71.34; H, 8.74; N, 4.50; S, 10.29; found: C, 71.14; H, 9.07; N, 4.39; S, 10.25.

PTDPP-Si11 (P3a)

Compound **P3a** was synthesized from **3a** (83.6 mg, 0.069 mmol) and **4a** (95.5 mg, 0.069 mmol) with the same

procedure for **P1a**. The crude polymer was purified by Soxhlet extraction with methanol (1 d), acetone (1 d) and hexane (1 d) to remove the low molecular weight fractions of the materials. The residue was extracted with chloroform, dropped into 200 mL of methanol and collected by filtration, yielding 67.0 mg (46%) as a dark green solid. Solubility in chloroform is 11.1 mg/mL. $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25 °C): δ 9.25-8.94 (br, 2H), 7.25-7.24 (br, 2H), 4.26-3.54 (br, 4H), 1.82-1.69 (br, 4H), 1.41-1.07 (br, 32H), 0.49-0.39 (br, 4H), 0.20-(-0.02) (br, 42H). Elemental Anal. Calcd. for $\text{C}_{50}\text{H}_{92}\text{N}_2\text{O}_6\text{S}_2\text{Si}_6$: C, 57.20; H, 8.83; N, 2.67; S, 6.11; found: C, 56.95; H, 9.21; N, 2.67; S, 5.99.

PTDPP-BO (P3b)

Compound **P3b** was synthesized from **3b**³ (97.5 mg, 0.12 mmol) and **4b** (118.7 mg, 0.12 mmol) with the same procedure for **P1a**. The crude polymer was purified by Soxhlet extraction with methanol (1 d), acetone (1 d) and hexane (1 d) to remove the low molecular weight fractions of the materials. The residue was extracted with chloroform, dropped into 200 mL of methanol and collected by filtration, yielding 41.9 mg (27%) as a dark green solid. Solubility in chloroform is 13.5 mg/mL. $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25 °C): δ 9.31-9.14 (br, 2H), 7.17-7.03 (br, 2H), 4.37-4.02 (br, 4H), 2.02-1.84 (br, 2H), 1.49-0.65 (br, 44H). Elemental Anal. Calcd. for $\text{C}_{38}\text{H}_{56}\text{N}_2\text{O}_2\text{S}_2$: C, 71.65; H, 8.86; N, 4.40; S, 10.07; found: C, 71.79; H, 9.01; N, 4.36; S, 9.83.

III. Thermal properties

Thermal gravimetric analyses (TGA) were performed using a RIGAKU Thermo plus EVO TG8120 thermal analyzer at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under a N_2 atmosphere.

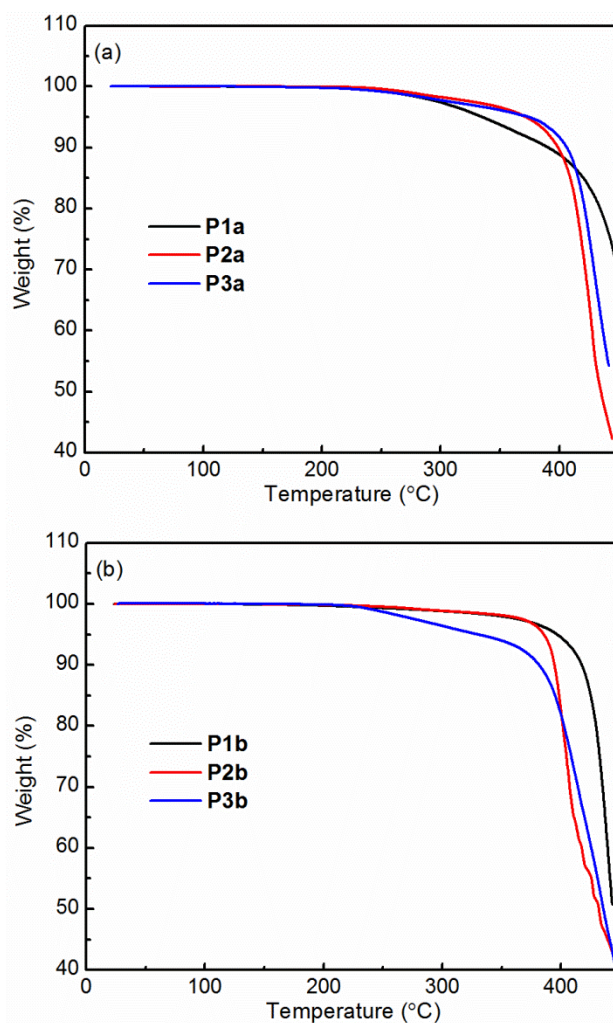


Figure S1. TGA curves of (a) **P1a-P3a** and (b) **P1b-P3b** at the heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 atmosphere.

IV. Optical and redox properties

UV-Vis-NIR absorption spectra of a dilute solution and a spin-coated thin film of the present compounds were collected on a Jasco Corporation V-670 UV-VIS-NIR Spectrophotometer. The optical energy gaps E_g^{opt} were estimated from the low-energy band edge of the absorption spectra of thin films.

Cyclic voltammetry (CV) was carried out on an ALS/CH Instruments Electrochemical Analyzer Model 700C. The measurement was performed in dehydrated acetonitrile solution containing 0.1 M *n*-Bu₄NPF₆ as a supporting electrolyte using a glassy carbon working electrode, a platinum counter electrode, and an Ag/AgNO₃ electrode as a reference electrode at a scan rate of 100 mV s⁻¹. The films of the prepared polymers were formed on a glassy carbon working electrode, and we prepared fresh polymer films at each measurement. To verify the reproducibility of profiles, the scans were recorded several times in argon saturated acetonitrile solution for eliminating external factors, and the obtained potentials are averaged. From the onset oxidation and reduction potentials $E_{\text{ox, onset}}$ and $E_{\text{red, onset}}$, the HOMO and LUMO levels were estimated by assuming the ferrocene/ferrocenium energy level to be -4.8 eV under the vacuum level.

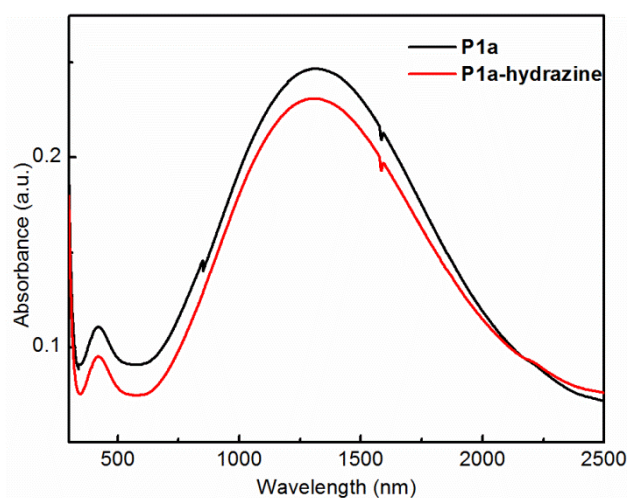


Figure S2. UV-Vis-NIR absorption spectra of thin film of **P1a** before and after dipping into ~5% hydrazine/ACN solution for 90 seconds.⁴

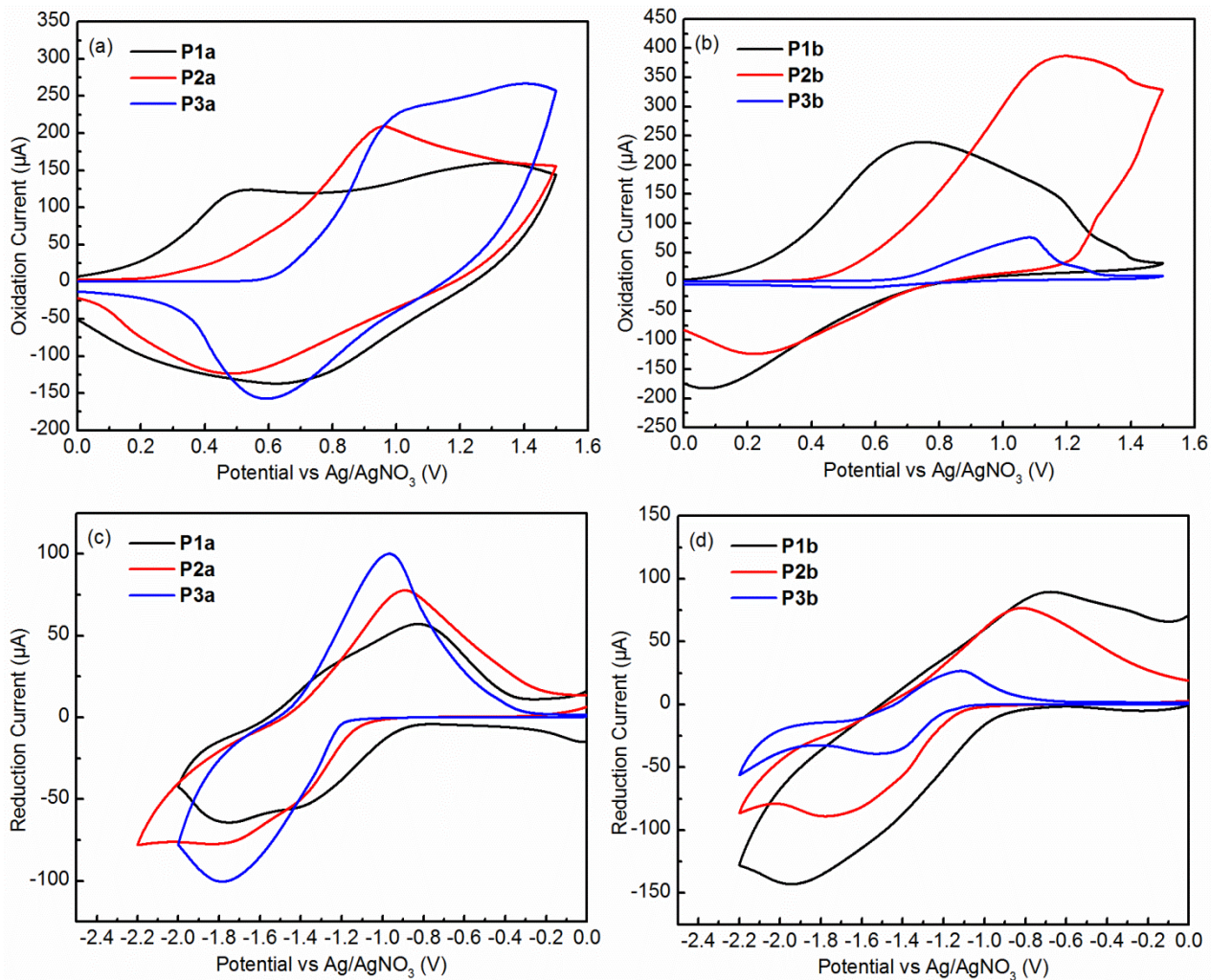


Figure S3. Electrochemical properties on films of **P1a-P3b** spin-coated from chloroform solutions: (a) and (b) for oxidation waves and (c) and (d) for reduction waves.

V. Fabrication and Characterization of Organic Field-Effect Transistors

A 300 nm thermally grown SiO₂ on a highly doped silicon wafer (capacitance (C_i) = 11.5 nF cm⁻²) were cleaned in a piranha solution (70% H₂SO₄ + 30% H₂O₂) for 15 min, and then washed with distilled water. The SiO₂ dielectric surface was modified with an octadecyltrimethoxysilane (OTMS) self-assembled monolayer by spin-coating from 3.0 mM OTMS solution at 3000 rpm in 1,2-dichloroethane and then exposed to an ammonia atmosphere for 20 h⁵. The OTMS modified SiO₂ substrates were washed with anhydrous toluene. The active layer was formed by spin-coating from a 3~4 mg/mL polymer solution at 1000 rpm in chloroform, and annealed at 150 °C, 200 °C and 250 °C for 1 h in an argon-filled glove box. Finally, the source and drain electrodes were formed by vapor deposition of Au (50 nm). The standard channel lengths (L) and widths (W) are 50-200 μm and 1000 μm, respectively. The OFET properties were measured with a Keithley 4200 semiconductor parameter analyzer under vacuum condition. The field-effect mobility (μ) and threshold voltage (V_{th}) were calculated in the saturation region using an equation, $I_{DS} = \mu(WC_i/2L)(V_G - V_{th})^2$, where I_{DS} and V_G are the drain current and the gate voltages, respectively. The field-effect mobility (μ) in the linear regime were calculated using an equation, $g_m = (\partial I_D / \partial V_G) = (\mu W C_i / L) V_D$. The electrical conductivity was measured by a Keithley 4200 semiconductor parameter analyzer under vacuum condition with a two-probe method. Atomic force microscopic (AFM) images were obtained by an SII Nanonavi SPA400 scanning probe microscope with an SII SI-DF40 cantilever. Two-dimensional grazing incidence wide-angle X-ray scattering (GIWAXS) patterns were obtained at SPring-8 on beamline BL46XU. The samples were irradiated at a fixed incident angle on the order of 0.10 ° and the GIWAXS patterns were recorded with a 2-D image detector (PILATUS 300K). The wavelength of the X-ray beam was 0.1 nm (energy of 12.39 KeV) and the camera length was 173.8 mm.

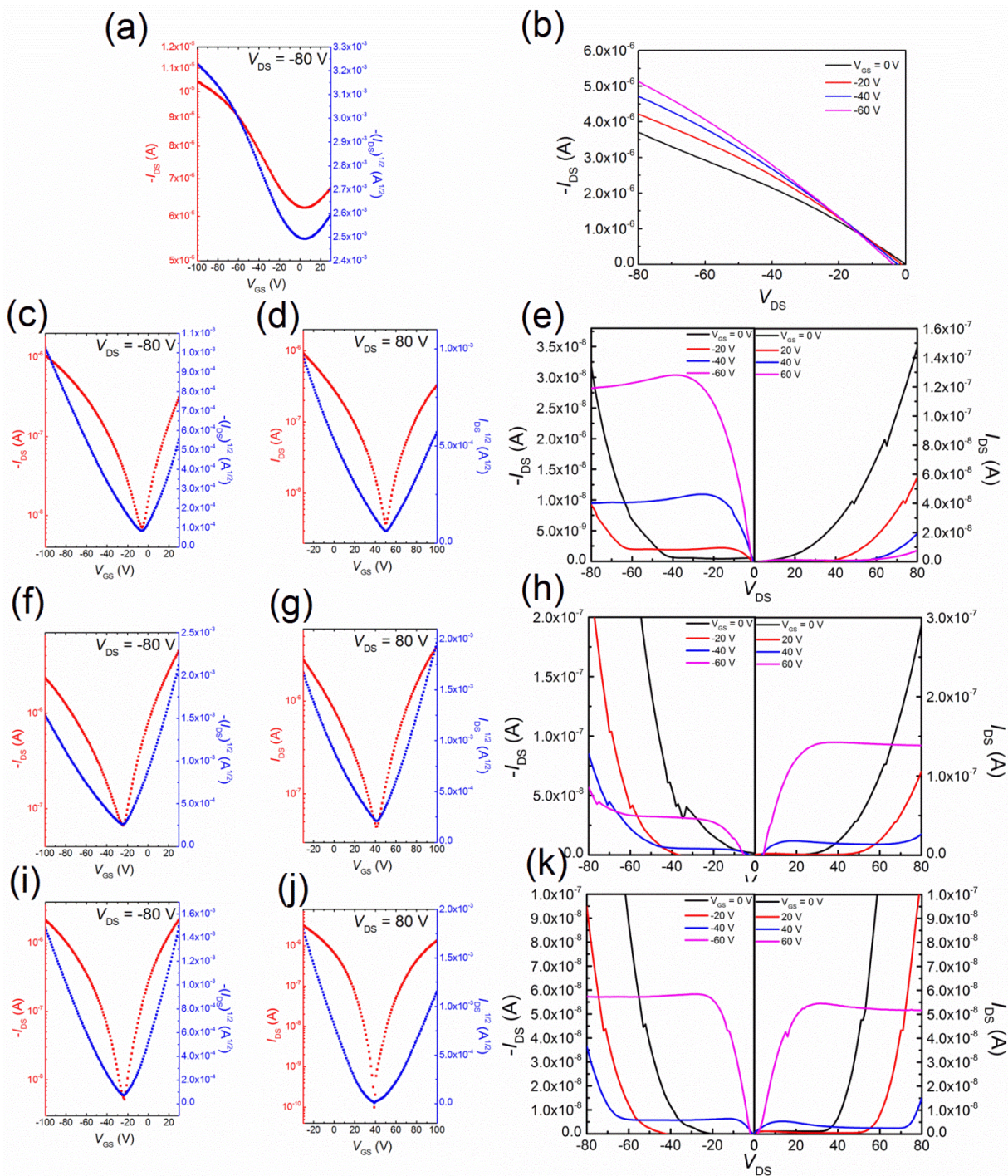


Figure S4. (a) transfer curve, (b) output curve of **P1b**, (c) p-type, (d) n-type transfer curves, (e) output curve of **P2a**, (f) p-type, (g) n-type transfer curves, (h) output curve of **P2b**, (i) p-type, (j) n-type transfer curves, and (k) output curve of **P3b**.

Table S1. OFET performance of **P1a-P3b**.

polymer	T_a^a [°C]	<i>p</i> -channel			<i>n</i> -channel		
		$\mu_{h,avg} (\mu_{h,max})$ [cm ² V ⁻¹ s ⁻¹]	V_{th} [V]	I_{on}/I_{off}	$\mu_{e,avg} (\mu_{e,max})$ [cm ² V ⁻¹ s ⁻¹]	V_{th} [V]	I_{on}/I_{off}
P1a^b	150	2.6×10^{-2} (2.8×10^{-2})		10^1			
	200	1.9×10^{-2} (2.2×10^{-2})	N.A	10^1		N.A	
	250	6.3×10^{-2} (7.8×10^{-2})		10^1			
P1b^b	150	8.1×10^{-3} (8.9×10^{-3})		10^1			
	200	7.4×10^{-3} (8.2×10^{-3})	N.A	10^1		N.A	
	250	5.8×10^{-3} (6.0×10^{-3})		10^1			
P2a^c	150	1.6×10^{-3} (1.9×10^{-3})	-15.5	10^3	1.2×10^{-3} (1.5×10^{-3})	51.9	10^3
	200	1.9×10^{-3} (2.2×10^{-3})	-12.3	10^4	8.8×10^{-4} (1.1×10^{-3})	55.5	10^2
	250	1.2×10^{-3} (1.9×10^{-3})	-11.2	10^3	2.6×10^{-4} (4.5×10^{-4})	62.7	10^2
P2b^c	150	4.7×10^{-3} (5.5×10^{-3})	-4.6	10^2	9.1×10^{-3} (1.2×10^{-2})	37.3	10^3
	200	6.3×10^{-3} (9.7×10^{-3})	-11.7	10^2	2.3×10^{-2} (2.7×10^{-2})	46.8	10^3
	250	3.1×10^{-3} (3.6×10^{-3})	-13.6	10^2	6.4×10^{-3} (8.7×10^{-3})	55.9	10^3
P3a^c	150	4.7×10^{-2} (6.0×10^{-2})	-13.8	10^4	4.4×10^{-2} (5.1×10^{-2})	40.4	10^4
	200	6.5×10^{-2} (6.8×10^{-2})	-35.3	10^4	6.5×10^{-2} (7.4×10^{-2})	22.3	10^4
	250	9.0×10^{-2} (1.1×10^{-1})	-25.5	10^4	8.1×10^{-2} (1.2×10^{-1})	36.2	10^4
P3b^c	150	6.7×10^{-3} (8.4×10^{-3})	-24.4	10^4	8.1×10^{-3} (9.5×10^{-3})	28.8	10^4
	200	8.9×10^{-3} (1.0×10^{-2})	-25.0	10^4	1.2×10^{-2} (1.4×10^{-2})	42.6	10^4
	250	6.6×10^{-3} (8.6×10^{-3})	-27.5	10^4	1.8×10^{-2} (2.7×10^{-2})	50.7	10^4

^a Anneal temperatures. ^b Calculated from this equation : $g_m = (\partial I_D / \partial V_G) = (\mu WC_i / L) V_D$ ($L = 50\text{-}200 \mu\text{m}$, $W = 1000 \mu\text{m}$ and $V_D = -80 \text{ V}$). ^c Calculated from this equation : $I_{DS} = \mu(WC_i / 2L)(V_G - V_{th})^2$.

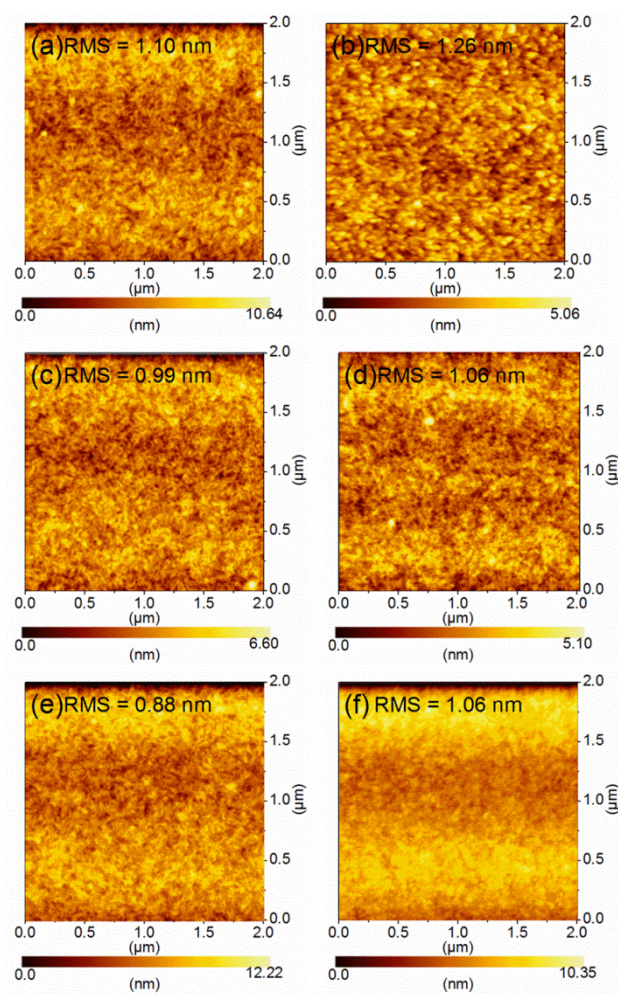


Figure S5. AFM images of (a)**P1a**, (b)**P1b**, (c)**P2a**, (d)**P2b**, (e)**P3a** and (f)**P3b** annealed at 200 °C

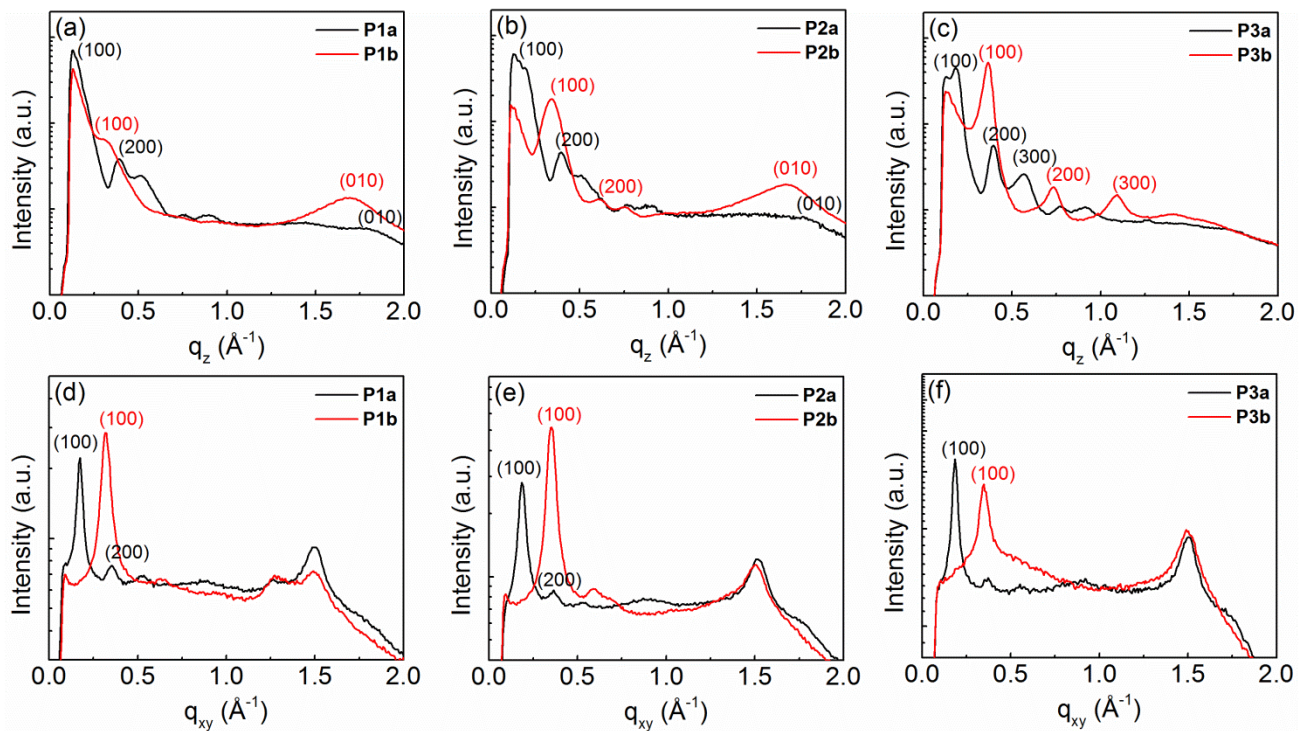


Figure S6. GIWAXS diffraction profiles: (a), (b) and (c) for out-of-plane and (d), (e) and (f) for in-plane GIWAXS

patterns of **P1a**, **P1b**, **P2a**, **P2b**, **P3a**, and **P3b**.

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