Supporting Information for

Structural Influence of Dichalcogenopheno-1,3,4-chalcogenodiazole Comonomer on Optoelectronic Properties of Diketopyrrolopyrrole-based Conjugated Polymers

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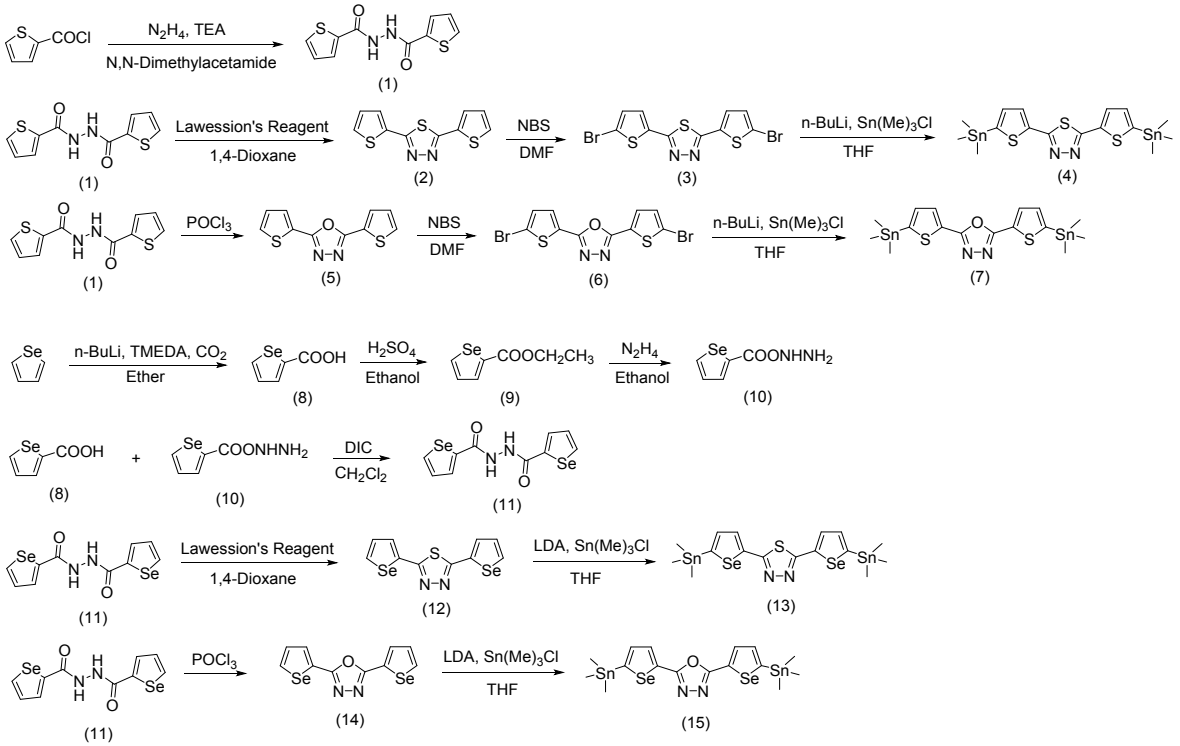
Materials

All chemicals were purchased from Aldrich, Alpha, TCI: n-Butylitium, , Lawessons's Reaent and NBS were used without further purification. 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(7-decylnonadecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione was synthesized via published literature procedures.[S1]



Scheme S1. Synthesis of monomers

Synthesis

Synthesis of N'-(thiophene-2-carbonyl)thiophene-2-carbohydrazine (1) [S2-S3]

A mixture of thiophene-2-carbonyl chloride (10 g, 68.2 mmol) and N,N-dimethylacetamide (100 mL) was cooled to 0 ^{o}C, and hydrazine hydrate (2 g, 54.5 mmol) was slowly added into it. After the addition, the reaction mixture was allowed to attain the room temperature and then it was stirred for 3 h. Resulting solution was poured into the ice-cold water, and corresponding hydrazine was precipitated out. The precipitate was filtered and washed with water and cold methanol, and white solid product was obtained. Yield: 6.19 g (79%), ^{1}H NMR (300 MHz, DMSO): δ (ppm) = 10.56 (s, 2 H), 7.87 (t, 4 H), 7.22 (t, 2 H), ^{13}C NMR (300 MHz, DMSO): δ (ppm) = 160.9, 137.2, 131.8, 129.1, 128.2., HRMS (EI+): m/z: 252.0025.

Synthesis of 2,5-di(thiophen-2-yl)-1,3,4-thiadiazole (2) [S2-S3]

A mixture of compound 1 (5.00 g, 19.81 mmol) and Lawesson's Reagent (16.03 g, 39.36 mmol) was stirred in refluxing 1,4-dioxane for 24 h, a light brown product precipitated during the reaction. After the reaction, precipitate was collected by filteration and washed with 1N NaOH to remove excess of Lawesson's Reagent and then with water. The crude product was purified by silica gel chromatography (dichloromethane) and crystallized by petroleum ether to needle shape crystal. Yield: 4.06 g, (82%), ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.58 (m, 2 H), 7.52 (m, 2 H), 7.16 (m, 2 H).

Synthesis of 2,5-bis(5-bromothiophen-2-yl)-1,3,4-thiadiazole (3) S2-S3

NBS (8.5 g, 47.93 mmol) was added in portions to a solution of the compound 2 (3.0 g, 11.98 mmol) in DMF (100 mL) in dark and stirred for 12 h at room temperature. After the reaction completion, the reaction mixture was partitioned between water and ether. The organic layer was extracted, dried over $MgSO_4$, and evaporated under reduced pressure to obtain yellow solid. Yield: 4.3 g (88%), ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.30 (d, 2 H), 7.12 (d, 2 H).

Synthesis of 2,5-bis(5-(trimethylstannyl)thiophen-2-yl)-1,3,4-thiadiazole (4) S2-S3

Compound 3 (1.0 g, 2.45 mmol) was dissolved in 50 mL of anhydrous THF in a nitrogen atmosphere, and cooled to -78 ^{o}C. 2.5 M n-Butyl lithium (2.15 mL, 5.39 mmol) was added to the resulting mixture, which was stirred for 30 min. Then, the mixture was warmed to room temperature, stirred at room temperature for 1 h, and cooled again to -78 ^{o}C. Then, trimethyltin chloride (5.39 mL, in 1 M hexane solution, 5.39 mmol) was added to the resulting reaction mixture, which was stirred for 10 min then warmed to room temperature. After solvent removed, the reaction mixture was recrystallized from methanol. Yield: 0.77 g (55%), ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.66 (d, 2 H), 7.21 (d, 2 H), 0.44 (m, 18 H).

Synthesis of 2,5-di(thiophen-2-yl)-1,3,4-oxadiazole (5) S2-S3

A mixture of compound 1 (5.0 g, 19.81 mmol) and $POCl_3$ (150 mL) were introduced into a flask equipped with magnetic stirrer, and refluxed for 6 h. After cooling to room temperature, the reaction mixture was poured into an ice-water mixture, and the resulting precipitate was filtered, washed several times with water and dried. Yield: 3.62 g (78%), ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.84 (d, 2 H), 7.60 (d, 2 H), 7.22 (t, 2 H), ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) = 160.5, 130.4, 130.0, 128.3, 125.1

Synthesis of 2,5-bis(5-bromothiophen-2-yl)-1,3,4-oxadiazole (6) S2-S3

NBS (10.63 g, 59.72 mmol) was added in portions to a solution of the compound 5 (3.5 g, 14.93 mmol) in DMF (200 mL) in dark and stirred for 12 h at room temperature. After the reaction completion, the reaction mixture was partitioned between water and ether. The organic layer was extracted, dried over $MgSO_4$, and evaporated under reduced pressure to obtain yellow solid. Yield: 4.9 g (84%), ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.56(d, 2H), 7.17 (d, 2H), ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) = 159.3, 131.4, 130.3, 126.2, 118.6., HRMS (EI+): m/z: 389.8123.

Synthesis of 2,5-bis(5-(trimethylstannyl)thiophen-2-yl)-1,3,4-oxadiazole (7) S2-S3

Compound 6 (1.0 g, 2.55 mmol) was dissolved in 50 mL of anhydrous THF in a nitrogen atmosphere, and cooled to -78 ^{o}C. 2.5 M n-Butyl lithium (2.24 mL, 5.61 mmol) was added to the resulting mixture, which was stirred for 30 min. Then, the mixture was warmed to room temperature, stirred at room temperature for 1 h, and cooled again to -78 ^{o}C. Then, trimethyltin chloride (5.61 mL, in 1 M hexane solution, 5.61 mmol) was added to the resulting reaction mixture, which was stirred for 10 min then warmed again to room temperature. After solvent removed, the reaction mixture was recrystallized from methanol. Yield: 0.74 g (52%), ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.90 (d, 2 H), 7.26 (d, 2 H), 0.46 (m, 18 H).

Synthesis of selenophene-2-carboxylic acid (8)

Selenophene (20 g, 152.63 mmol) in diethyl ether (150 mL) was added N,N,N',N'-tetramethylethylenediamine (25.5 mL, 170.0 mmol) and then n-Butyllithium (61.12 mL, 2.5

M in hexane, 152.8 mmol) was added dropwise at room temperature. The mixture was heated at 50 °C for 1.5 h and cooled at -78 °C, crushed solid carbon dioxide (40 g, 909.1 mmol) was added. The reaction mixture was allowed to return to room temperature and stirred for 2 h. The solution was quenched by addition of 10% KOH solution (300 mL). The aqueous layer was acidified to pH 3 with c-HCl, and then extracted by diethyl ether. The organic solution was dried over anhydrous magnesium sulfate and the solvent was removed. Yield: 25.2 g (crude product), ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.46 (br, 1 H), 8.41 (d, 1 H), 8.17 (d, 1 H), 7.41 (t, 1 H).), ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) = 168.5, 140.4, 138.3, 137.8, 130.7., HRMS (EI+): m/z: 175.9379.

Synthesis of ethyl selenophene-2-carboxylate (9)

Compound 8 (8.00 g, 45.70 mmol) was dissolved into ethanol (80 mL) under the nitrogen atmosphere. Sulfuric acid (32.00 mL, 594.1 mmol) was added dropwise for 30 min to mixture at room temperature. The reaction mixture was stirred at 80 °C for 5 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with diethyl ether. The organic solution was dried over anhydrous magnesium sulfate and evaporated. After the removal of the solvent, the crude product was purified by column chromatography on silica gel using the solvent of hexane/ethyl acetate (4:1). Yield: 7.46 g (80.4%), ^{1}H NMR (300 MHz, DMSO): δ (ppm) = 8.57 (d, 1 H), 8.01 (d, 1 H), 7.44 (t, 1 H), 4.26 (m, 2 H), 1.28 (m, 3 H).

Synthesis of selenophene-2-carbohydrazide (10)

In a 500 mL dried flask, compound 9 (7.40 g, 36.44 mmol) was dissolved in ethanol (75 mL) and then added 50~60% hydrazine hydrate (9.15 mL, 291.5 mmol). The mixture was stirred for 20 h at 85 °C. After cooling to room temperature, the solvent was removed by evaporation and then obtained yellow solid. And the resulting precipitate was filtered with a glass filter, and washed several times with hexane and dried. Yield: 6.0 g (crude product), ^{1}H NMR (300 MHz, DMSO): δ (ppm) = 9.75 (br, 1 H), 8.37 (d, 1 H), 7.88 (d, 1 H), 7.36 (t, 1 H), 4.43 (br, 2 H), ^{13}C NMR (300MHz, DMSO): δ (ppm) = 162.8, 145.4, 136.9, 130.8, 129.9.

Synthesis of N'-(selenophene-2-carbonyl)selenophene-2-carbohydrazide (11)

Compound 8 (6.20 g, 35.42 mmol) and compound 10 (5.15 g, 27.25 mmol) were dissolved in dichloromethane (250 mL) under the nitrogen atmosphere. Subsequently, N,N'-diisopropylcarbodiimide (DIC, 6.24 mL, 35.42 mmol) was injected into the solution and the reaction was stirred for 3 h at room temperature. The mixture was filtered with a glass filter, and washed with dichloromethane. Yield: 7.10 g (75%), ^{1}H NMR (300 MHz, DMSO): δ (ppm) = 10.52 (s, 2 H), 8.50 (d, 2 H), 8.07 (d, 2 H), 7.46 (t, 2 H), ^{13}C NMR (300 MHz, DMSO): δ (ppm) = 162.1, 143.7, 138.1, 131.2, 130.6., HRMS (EI+): m/z: 347.8918.

Synthesis of 2,5-di(selenophen-2-yl)-1,3,4-thiadiazole (12)

A mixture of compound 11 (4.0 g, 11.56 mmol) and Lawesson's reagent (9.35 g, 23.12 mmol) in 1,4-dioxane (75 mL) was refluxed at 110 °C overnight. The mixture was cooled to room temperature, poured onto 10% aqueous NaOH, and extracted with ethyl acetate. The organic solution was dried over anhydrous magnesium sulfate. After the removal of the solvent, the residue was purified by column chromatography on silica gel using solvent of hexane/ethyl acetate (4:1). Yield: 2.60 g (65%), ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.20 (d, 2 H), 7.72 (d, 2 H), 7.39 (t, 2 H), ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) = 163.1, 137.1, 135.1, 132.1, 130.4., HRMS (EI+): m/z: 345.8583.

Synthesis of 2,5-bis(5-(trimethylstannyl)selenophen-2-yl)-1,3,4-thiadiazole (13)

In a 100 mL dried flask, compound 12 (1.0 g, 2.91 mmol) was dissolved in THF (55 mL). Lithium diisopropylamide (7.28 mL, 1.0 M in THF/hexanes, 7.28 mmol) was added dropwise for 30 min at -78 °C. The mixture was stirred for 1.5 h at -78 °C. Trimethyltin chloride (7.28 mL, 1.0 M in THF, 7.28 mmol) was added and warmed to room temperature. The mixture was stirred for 5h. The reaction mixture was extracted with diethyl ether and dried over anhydrous magnesium sulfate. After the removal of the solvent, the crude product was purified by recrystallization from ethyl acetate and methanol. Yield: 1.32g (68%), ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.79(d, 2H), 7.52(d, 2H), 0.44(m, 18H), ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) = 162.8, 152.2, 141.8, 138.3, 132.9, -7.67.

Synthesis of 2,5-di(selenophen-2-yl)-1,3,4-oxadiazole (14)

Compound 11 (3.0 g, 8.67 mmol) was dissolved in $POCl_3$ (30 mL) and then stirred at 100 °C for 16 h. The mixture was poured into ice water (300 mL) and neutralized by sodium hydroxide, and then extracted with ethyl acetate. The organic solution was dried over anhydrous magnesium sulfate and evaporated. After the removal of the solvent, the crude product was purified by column chromatography on silica gel using the solvent of hexane/ethyl acetate (4:1). Yield: 1.91 g (67%), ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.28 (d, 2 H), 8.03 (d, 2 H), 7.45 (t, 2 H), ^{13}C NMR (300MHz, $CDCl_3$): δ (ppm) = 162.0, 136.0, 132.1, 130.5, 129.0., HRMS (EI+): m/z: 329.8814.

Synthesis of 2,5-bis(5-(trimethylstannyl)selenophen-2-yl)-1,3,4-oxadiazole (15)

Compound 14 (1.0 g, 3.05 mmol) was dissolved in THF (55 mL). Lithium diisopropylamide (7.63 mL, 1.0 M in THF/hexanes, 7.63 mmol) was added dropwise for 30 min at -78 °C. The mixture was stirred for 1.5 h. Trimethyltin chloride (7.63 mL, 1.0 M in THF, 7.63 mmol) was added and warmed to room temperature. The mixture was stirred for 5 h. The reaction mixture was extracted with diethyl ether and dried over anhydrous magnesium sulfate. After the removal of the solvent, the crude product was purified by recrystallization from ethyl acetate and methanol. Yield: 1.37 g (69%), ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.09 (d, 2 H), 7.57 (d, 2 H), 0.45 (m, 18 H), ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) = 162.2, 153.5, 138.5, 133.8, 132.9, -7.63.

Polymerization of Poly(2,5-bis(7-decylnonadecyl)-3-(5-methylthiophen-2-yl)-6-(5'-(5-(5-methylthiophen-2-yl)-1,3,4-oxadiazol-2-yl)-[2,2'-bithiophen]-5-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione) (PDPP-T-Odz)

The polymer was prepared using a palladium-catalyzed Stille coupling reaction. In a Schlenk flask 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(7-decylnonadecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.3000 g, 0.2359 mmol) and compound 7 (0.1321 g, 0.2359 mmol) were dissolved in dry chlorobenzene (7.5 mL). After degassing under nitrogen for 30 min. $Pd_2(dba)_3$ (2.00 mg, 0.0236 mmol) and P(*o*-tol)$_3$ (2.1 mg, 0.0071 mmol) were added to the mixture, which was then stirred for 48 h at 110 °C. 2-(Tributylstannyl)thiophene were injected sequentially into the reaction mixture for end-capping; the solution was stirred for 6 h after each addition. The polymer was precipitated in methanol. The crude polymer was collected by filtration and purified by soxhlet extraction with methanol, acetone, hexane, toluene, and chloroform, successively. The PDPP-T-Odz was obtained by precipitation of the chloroform solution into methanol. Yield: 0.25 g (80%),

Polymerization of Poly(2,5-bis(7-decylnonadecyl)-3-(5-methylthiophen-2-yl)-6-(5'-(5-(5-methylthiophen-2-yl)-1,3,4-thiadiazol-2-yl)-[2,2'-bithiophen]-5-yl)-2,5-dihydropyrrolo[3,4-

c]pyrrole-1,4-dione) (PDPP-T-Tdz)

The polymer was prepared using a palladium-catalyzed Stille coupling reaction. In a Schlenk flask 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(7-decylnonadecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.3000 g, 0.2359 mmol) and compound 4 (0.1358 g, 0.2359 mmol) were dissolved in dry chlorobenzene (7.5 mL). After degassing under nitrogen for 30 min. $Pd_2(dba)_3$ (2.00 mg, 0.0236 mmol) and P(*o*-tol)$_3$ (2.1 mg, 0.0071 mmol) were added to the mixture, which was then stirred for 48 h at 110 °C. 2-(Tributylstannyl)thiophene were injected sequentially into the reaction mixture for end-capping; the solution was stirred for 6 h after each addition. The polymer was precipitated in methanol. The crude polymer was collected by filtration and purified by soxhlet extraction with methanol, acetone, hexane, toluene, and chloroform, successively. The PDPP-T-Tdz was obtained by precipitation of the chloroform solution into methanol. Yield: 0.22 g (71%)

Polymerization of Poly(2,5-bis(7-decylnonadecyl)-3-(5-(5-(5-(5-methylselenophen-2-yl)-1,3,4-oxadiazol-2-yl)selenophen-2-yl)thiophen-2-yl)-6-(5-methylthiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione) (PDPP-Se-Odz)

In a Schlenk flask 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(7-decylnonadecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.3000 g, 0.2332 mmol) and compound 15 (0.1524 g, 0.2332 mmol) were dissolved in dry chlorobenzene (7.5 mL) and degassed with nitrogen for 30 min. $Pd_2(dba)_3$ (2.00 mg, 0.0020 mmol) and P(*o*-tol)$_3$ (2.10 mg, 0.0070 mmol) were added to the mixture, and then the mixture was stirred at 110 °C for 48 h. Afterwards, 2-(tributylstannyl)thiophene (0.1 mL) was added to the mixture for end-capping, and then stirred for 6 h. The reaction mixture was precipitated into a mixture of methanol (300 mL) and 0.2 M HCl (20 mL). The crude polymer was collected by filtration and purified by soxhlet extraction with methanol, hexane, toluene, and chloroform successively. The PDPP-Se-Odz was obtained by precipitation of the chloroform solution into methanol. Yield: 0.26 g (83%)

Polymerization of Poly(2,5-bis(7-decylnonadecyl)-3-(5-(5-(5-(5-methylselenophen-2-yl)-1,3,4-thiadiazol-2-yl)selenophen-2-yl)thiophen-2-yl)-6-(5-methylthiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione) (PDPP-Se-Tdz)

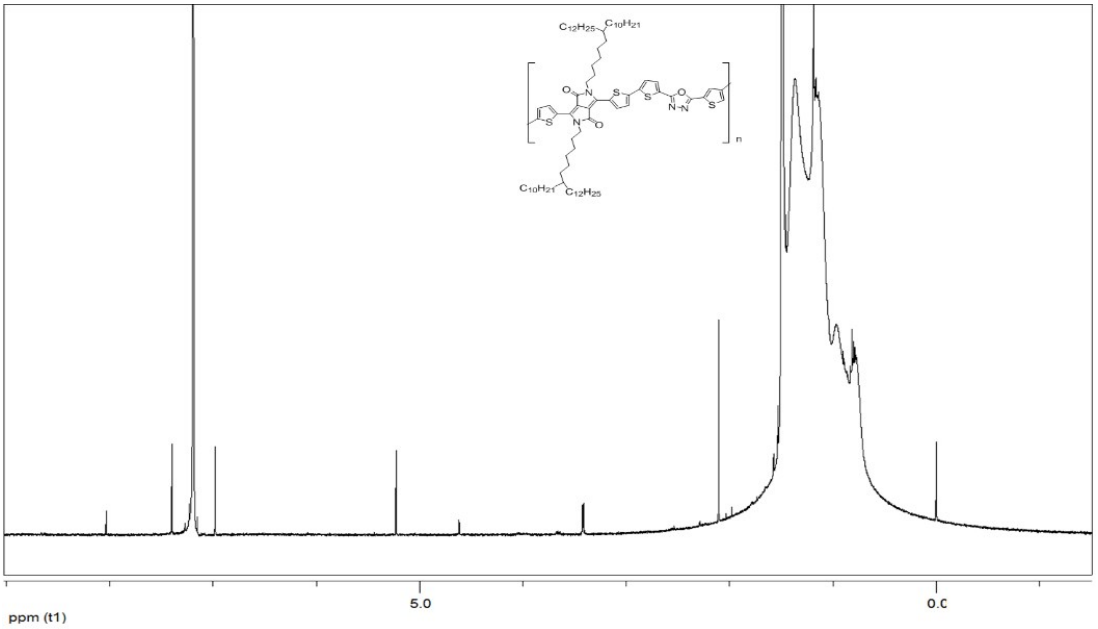
In a Schlenk flask 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(7-decylnonadecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.2000 g, 0.1554 mmol) and compound 13 (0.1041 g, 0.1554 mmol) were dissolved in dry chlorobenzene (5 mL) and degassed with nitrogen for 30 min. $Pd_2(dba)_3$ (1.40 mg, 0.0016 mmol) and P(*o*-tol)$_3$ (1.40 mg, 0.0047 mmol) were added to the mixture, and then the mixture was stirred at 110 °C for 48 h. Afterwards, 2-(tributylstannyl)thiophene (0.1 mL) was added to the mixture for end-capping, and then stirred for 6 h. The reaction mixture was precipitated into a mixture of methanol (300 mL) and 0.2 M HCl (20 mL). The crude polymer was collected by filtration and purified by soxhlet extraction with methanol, hexane, toluene, and chloroform, successively. The PDPP-Se-Tdz was obtained by precipitation of the chloroform solution into methanol. Yield: 0.21 g (90%)

References

S1. I. Kang, H.-J. Yun, D. S, Chung, S.-K. Kwon, Y.-H. Kim, *J. Am. Chem. Soc.* **2013**, *135*, 14896.

S2. H. Chen, Z. Liu, Z. Zhao, L. Zheng, S. Tan, Z. Yin, C. Zhu, Y. Liu, *ACS. Appl. Mater. Interfaces* **2016**, *8*, 33051

S3. E. Kurach, K. Kotwica, J. Zapala, M. Knor, R. Nowakowski, D. Djurado, P. Toman, J. Pfleger, M. Zagorska, A. Pron, *J. Phys. Chem. C*. **2013**, *117*, 15316.



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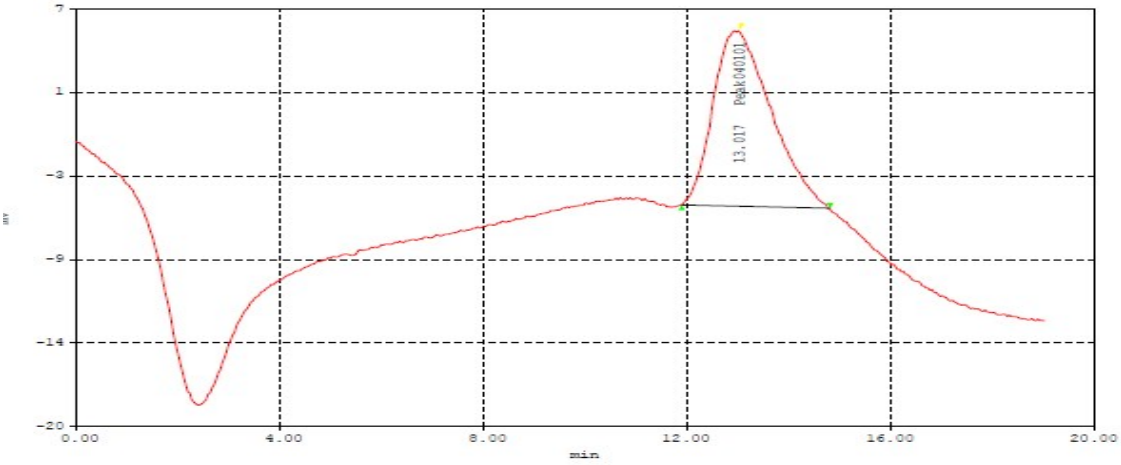

정 량 정 보

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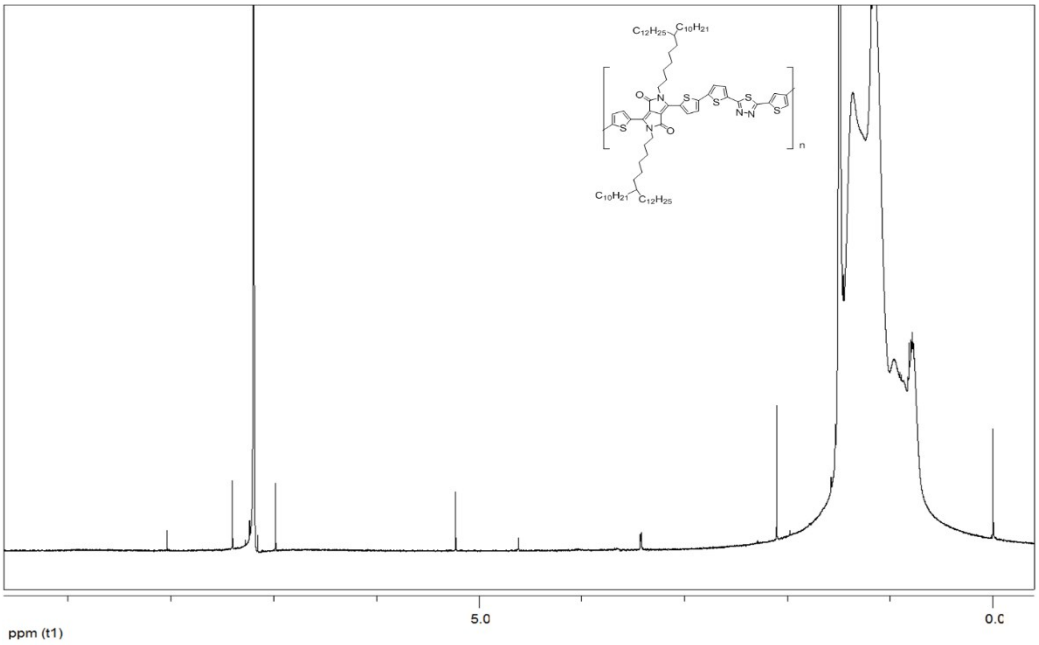
Figure S1. ^{1}H NMR spectrum and GPC chromatogram of PDPP-T-Odz.



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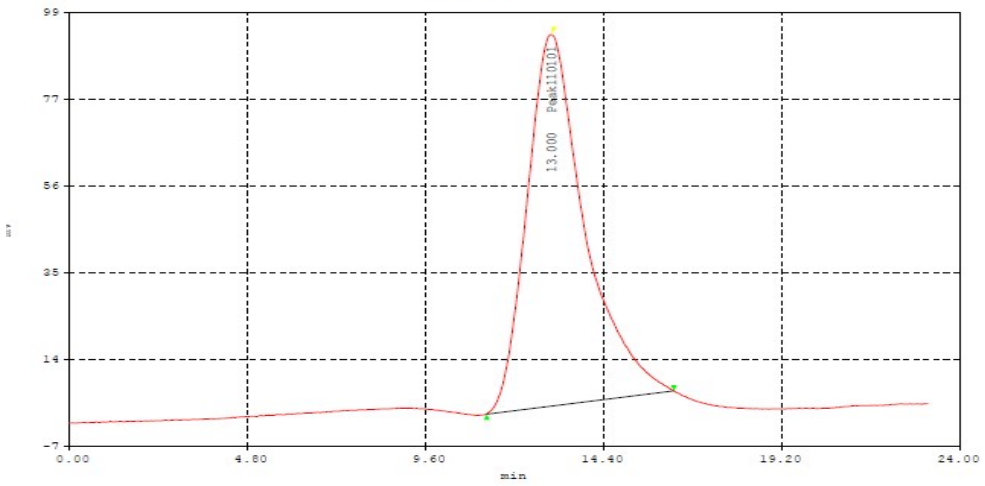

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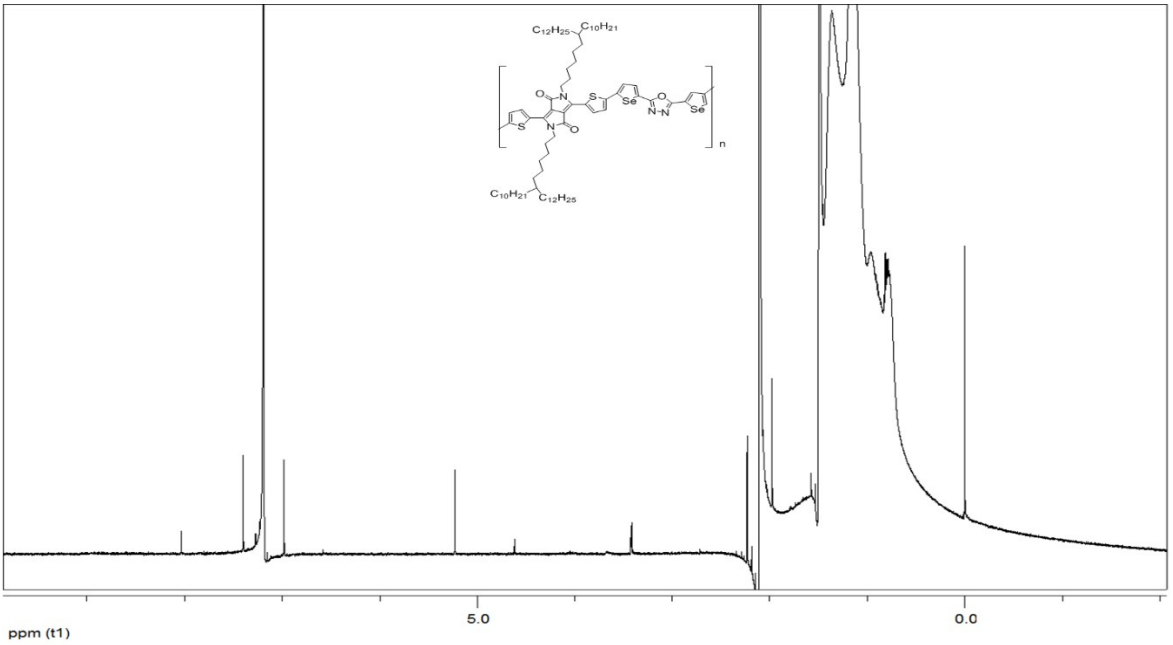
Figure S2. ^{1}H NMR spectrum and GPC chromatogram of PDPP-T-Tdz.



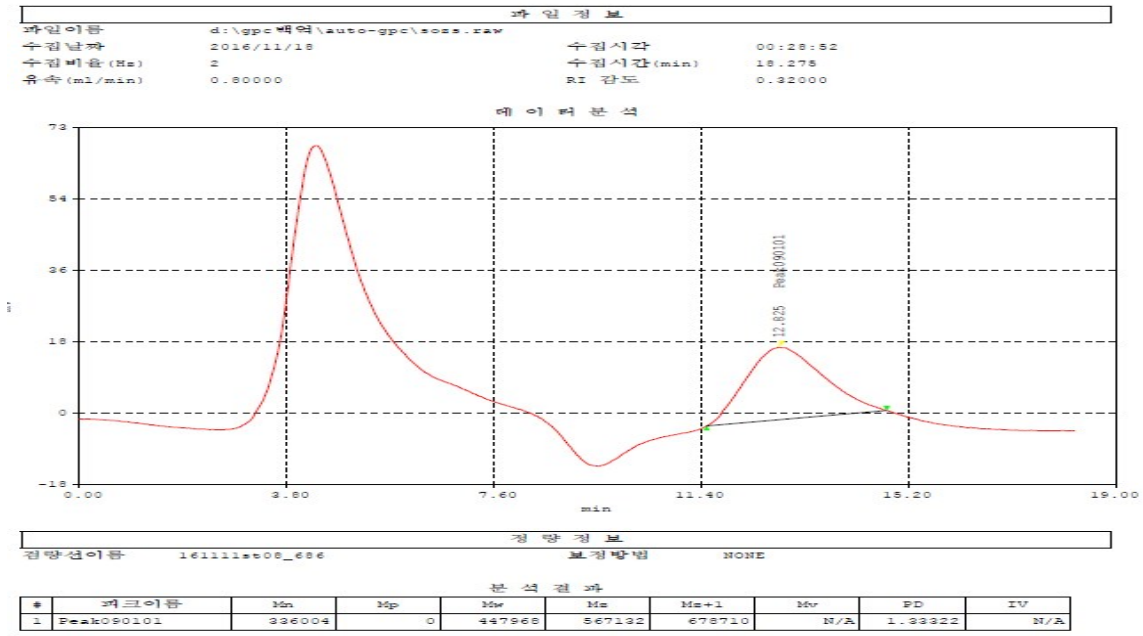
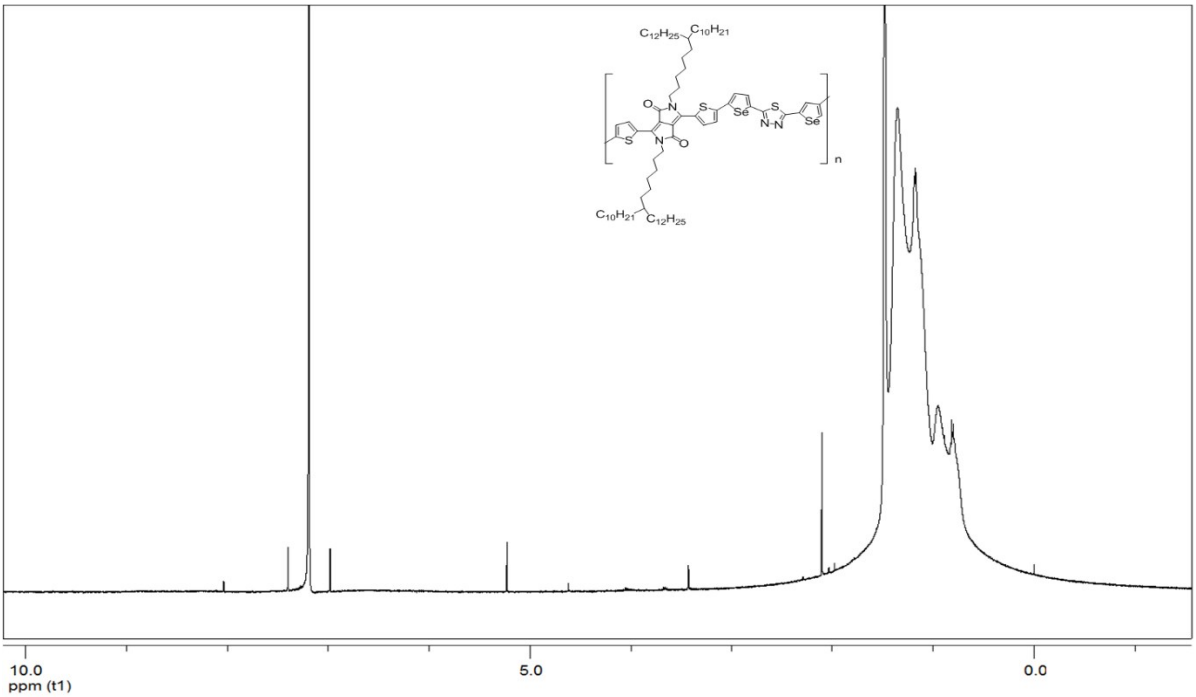


Figure S3. ^{1}H NMR spectrum and GPC chromatogram of PDPP-Se-Odz.



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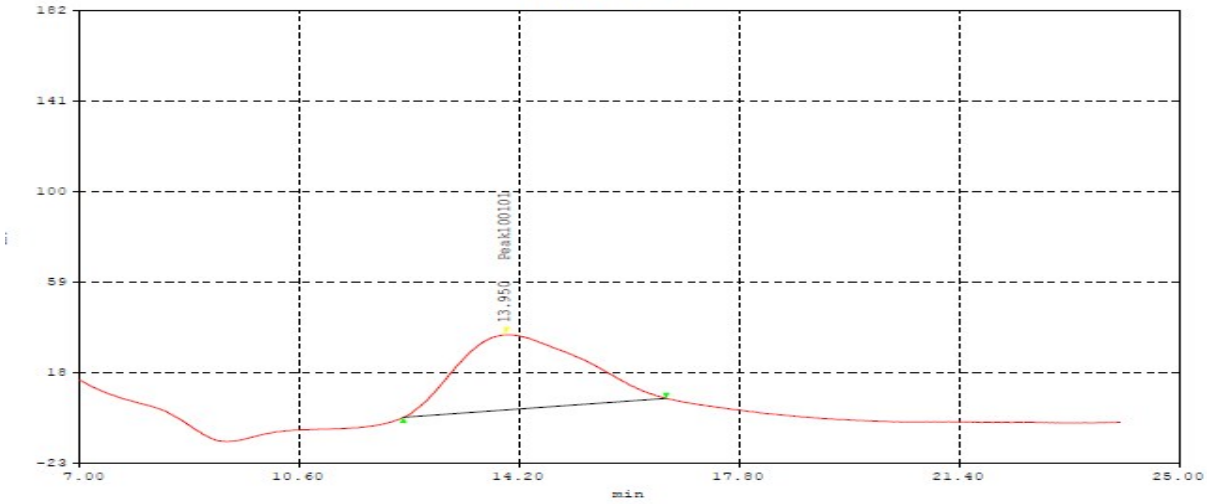
유속(ml/min)	0.80000	RI 감도	0.32000

데 이 터 분 석



정 량 정 보

검량선이름	161111st08_686	보정방법	NONE

분 석 결 과

#	피크이름	Mn	Mp	Mw	Mz	Mz+1	Mv	PD	IV
1	Peak100101	97522	170584	164125	245080	318924	N/A	1.68295	N/A

Figure S4. ^{1}H NMR spectrum and GPC chromatogram of PDPP-Se-Tdz..

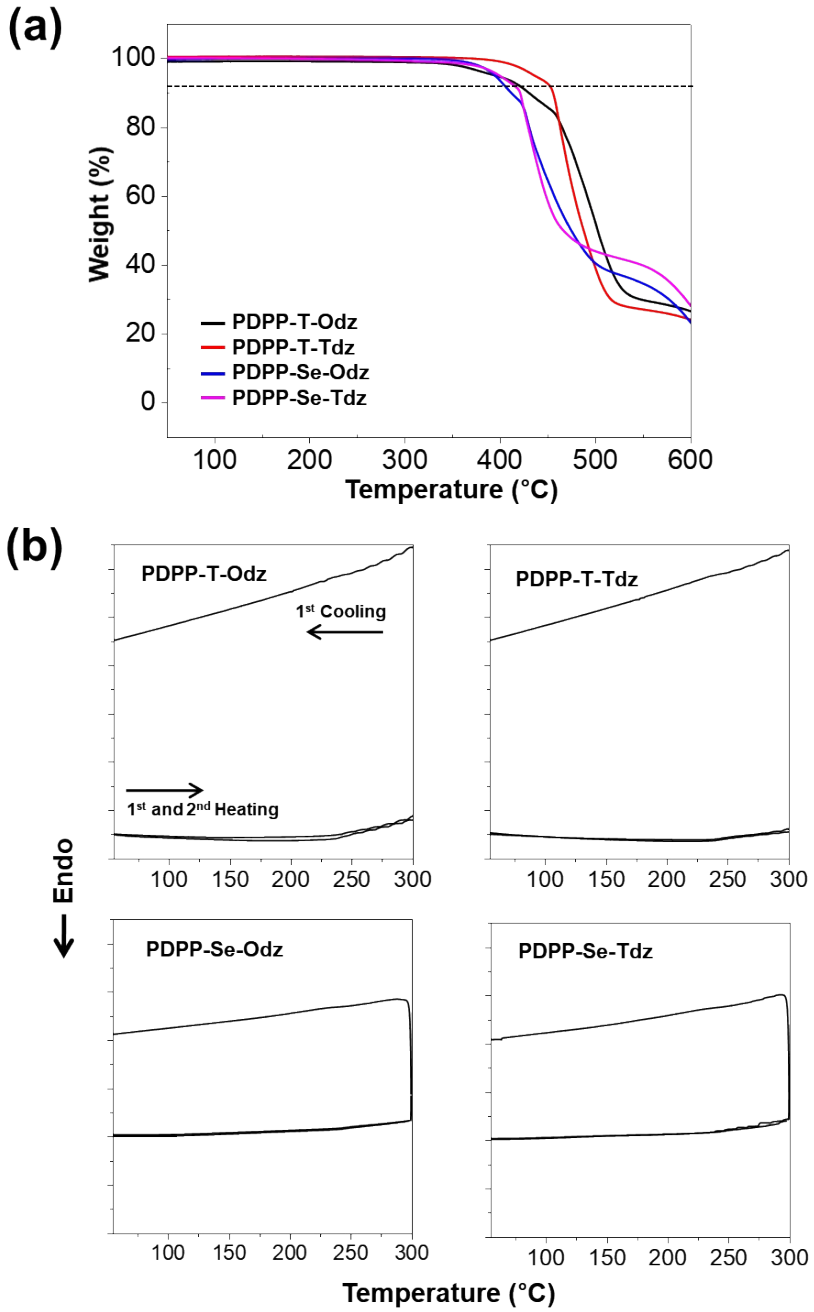


Figure S5. (a) Thermogravimetric analysis (TGA) plots and (b) differential scanning calorimetry (DSC) thermogram of the polymers in a N_2 atmosphere at a scan rate of 10 °C min^{-1}.

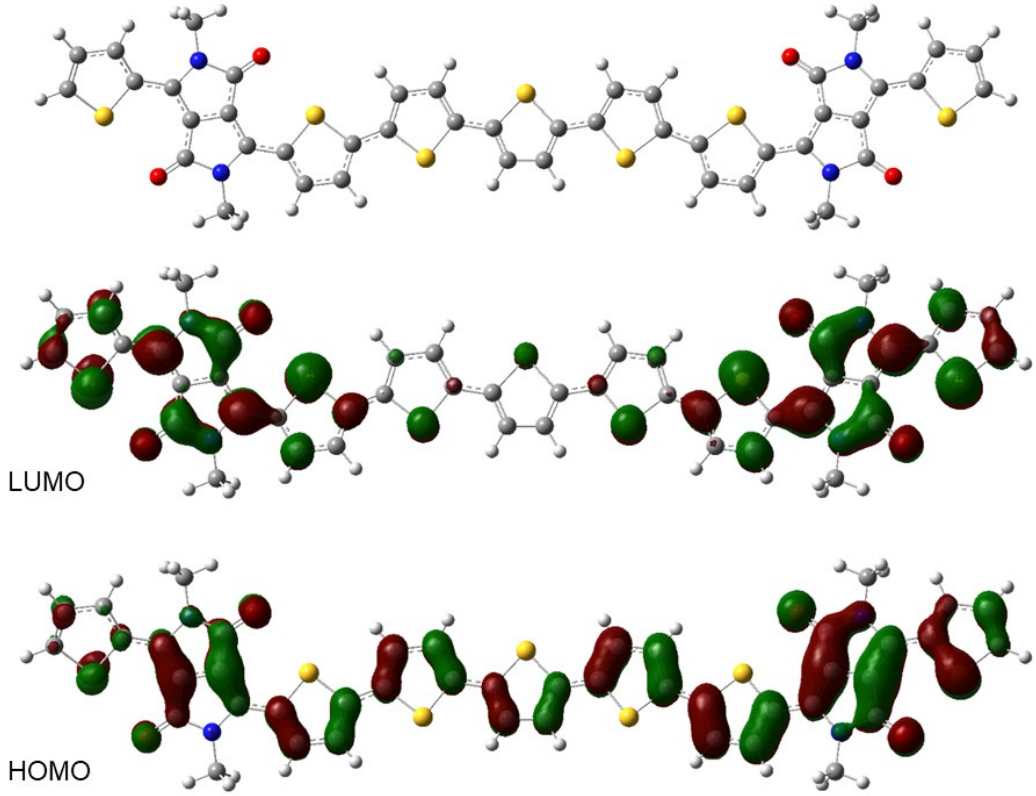


Figure S6. Energy minimized structure of of PDPP-5T and its frontier orbitals (B3LYP/6-31G*).

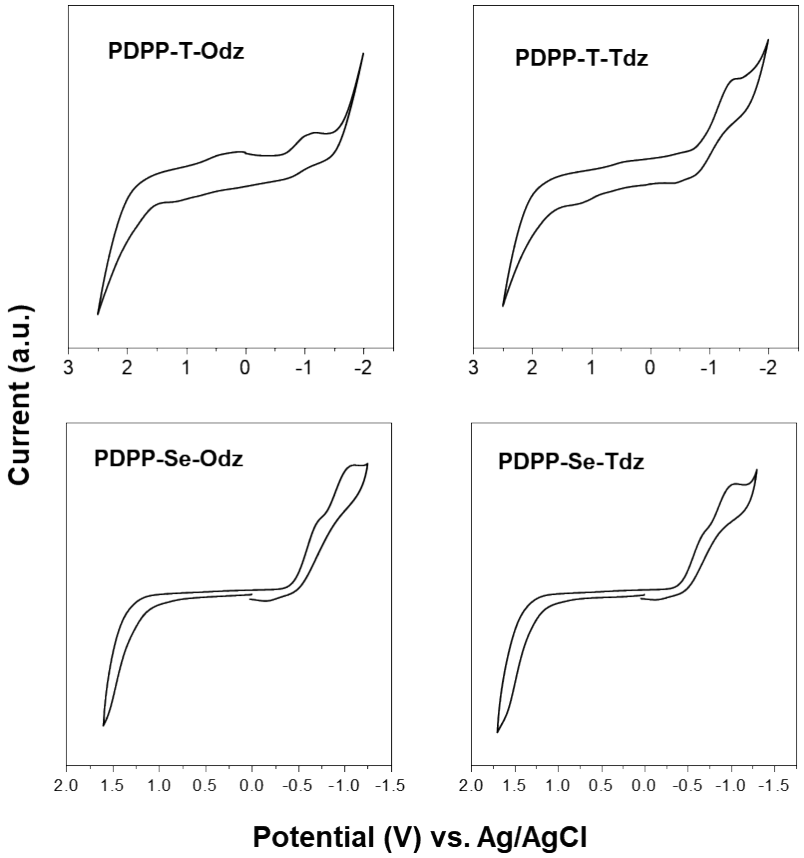


Figure S7. Cyclic voltammograms of the polymers.

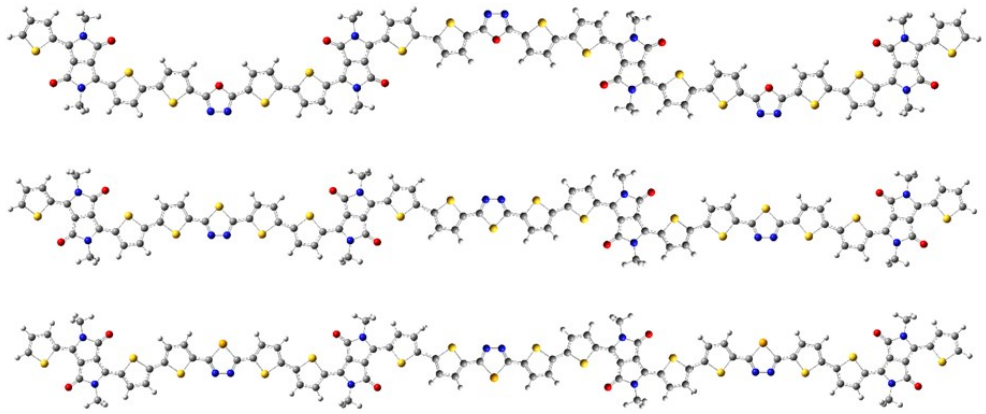


Figure S8. Quatamer structures of PDPP-T-Odz (top), PDPP-T-Tdz (middle), and PDPP-T-Sdz (bottom) polymers, which shows the different degree of chain curvatures.

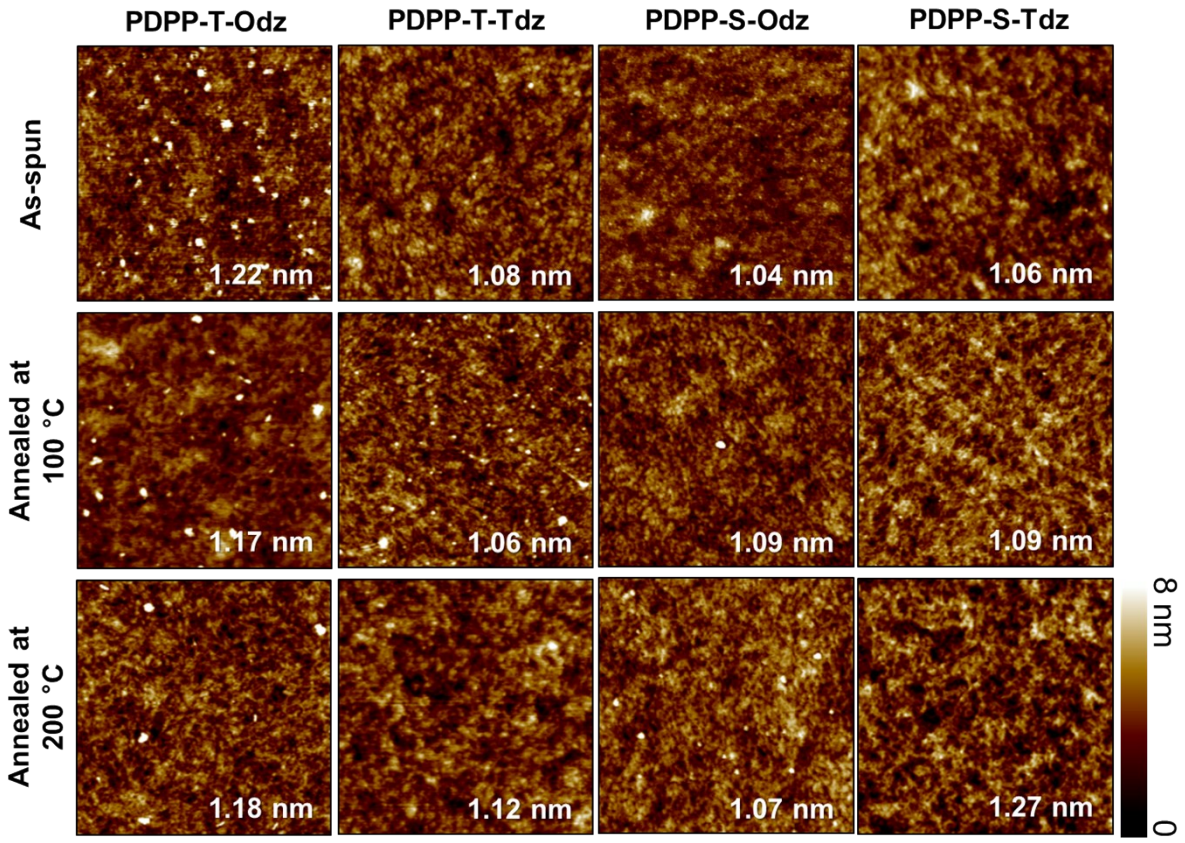


Figure S9. AFM height images of the polymer thin films as-spun and annealed.

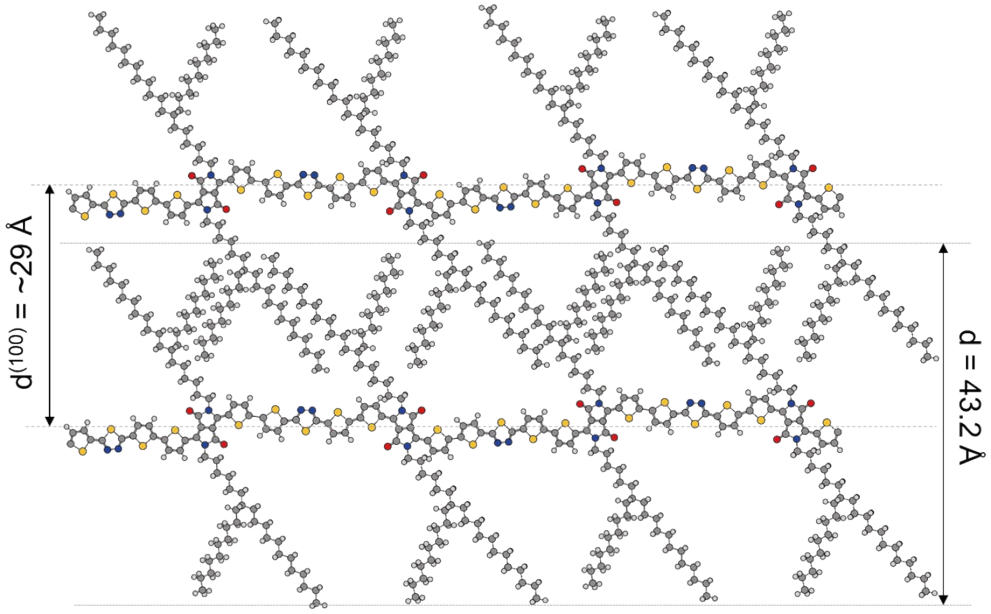


Figure S10. The proposed solid-state structure of PDPP-TzVTz, where the theoretical values were obtained from the DFT-simulated structure (B3LYP 6-31G*) and the experimental value was evaluated from the 2D GIXD result.

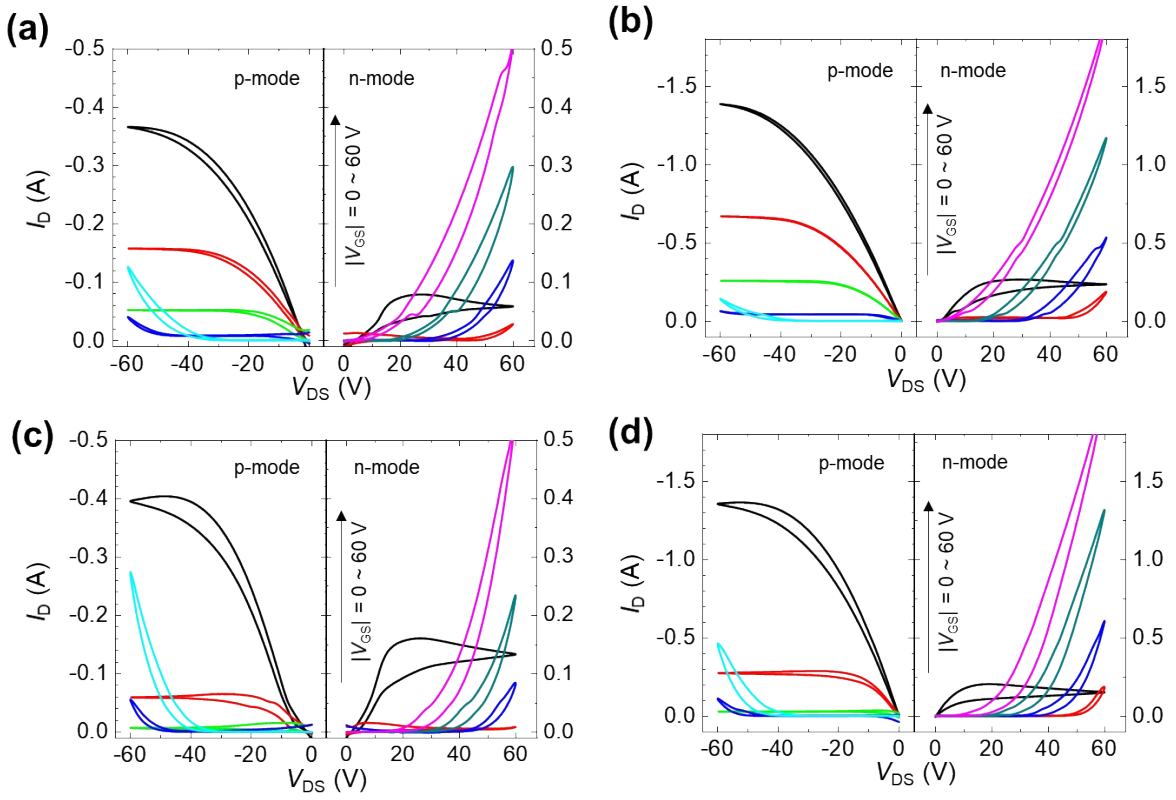


Figure S11. Output characteristics of the PFET devices at the optimized annealing temperature: (a) PDPP-T-Odz, (b) PDPP-T-Tdz, (c) PDPP-Se-Tdz, and (d) PDPP-Se-Odz.