

Supporting Information

High-Performance Vinyl-Flanked Diketopyrrolopyrrole-Selenophene Polymer Semiconductors with Branching, Linear and Cyclic Alkyl Side Chains

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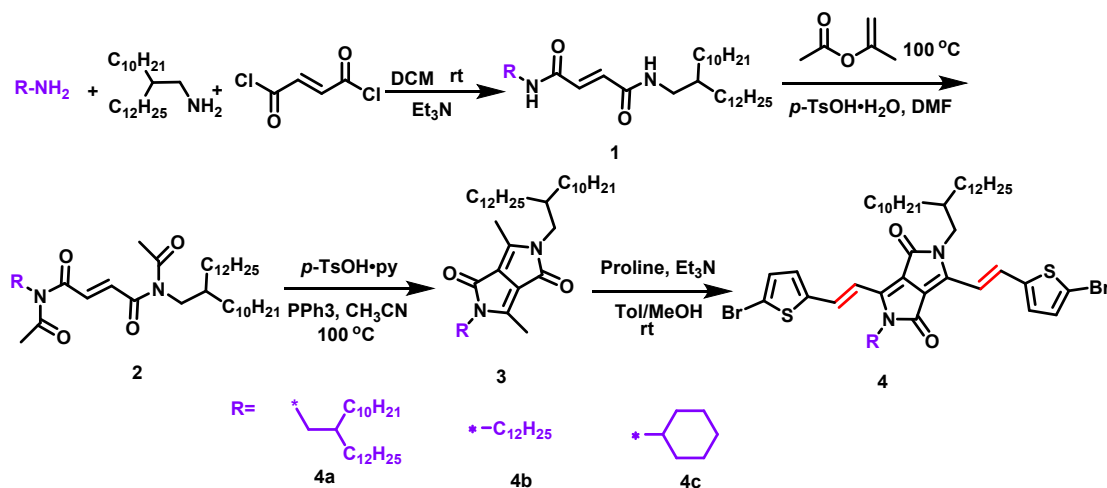
1. Materials and characterization techniques

All reagents and starting materials were purchased from commercial suppliers and used without further purification unless otherwise specified.

^1H NMR and ^{13}C NMR spectra were recorded on AVANCE III 400 MHz, AVANCE III 500 MHz and Bruker NEO 600 WB spectrometers. High-resolution mass spectral (HRMS) data were collected on either 9.4T Solarix Mass instrument or APEX II Mass instrument. Elemental analyses (EA) were performed on a Carlo-Erba-1106 instrument. Gel permeation chromatography (GPC) was performed on Agilent PL-GPC 220 instrument using *o*-dichlorobenzene as an eluent (1.0 mL/min) at 140 °C. Polystyrene was utilized as the calibration standard and 1,2,4-trichlorobenzene as eluent (the flow rate was 1.0 mL/min). Thermogravimetric analysis (TGA) analysis was carried on a PerkinElmer TGA 8000 Thermogravimetric Analyzer instrument under N_2 at a heating rate of 10 °C/min from 50 °C to 600 °C. Differential scanning calorimetry (DSC) analysis was performed on Netzsch STA 449C under N_2 at a rate of 10 °C/min from 50 °C to 300 °C. UV-vis-NIR absorption spectra were collected on a HITACHI UH4150 UV-vis spectrophotometer. Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using a glassy carbon as the working electrode, Pt as the counter electrode, and Ag/AgCl (saturated KCl) as the reference electrode on a computer-controlled CHI660C instruments at ambient temperature; *n*-Bu₄NPF₆ (0.1 M in acetonitrile) was used as the supporting electrolyte. For calibration, the redox potential of ferrocene/ferrocenium (Fc/Fc^+) was measured under the same conditions. HOMO and LUMO energies of these conjugated polymers were estimated with the following equations: $\text{HOMO} = -(E_{\text{ox}}^{\text{onset}} + 4.8) \text{ eV}$, $\text{LUMO} = -(E_{\text{red}}^{\text{onset}} + 4.8) \text{ eV}$. Atomic-force microscopy images of thin films of polymers were taken by using a Digital Instruments Nanoscope V atomic force microscope operated in tapping mode with a Nanoscope V instrument in air. The GIWAXS measurements were conducted on a Xenocs-SAXS/WAXS system with an X-ray wavelength of 1.5418 Å; all thin films were irradiated at a fixed angle of 0.2°. All thin films for Grazing Incidence Wide Angle X-Ray Scattering (GIWAXS) measurements were prepared on *n*-octadecyltrichlorosilane (OTS) treated Si/SiO₂ substrates, and the OTS treatment

process was the same as that for the fabrication of FET devices. The FET device performances were evaluated on a Keithley 4200 SCS semiconductor parameter analyzer.

2. Synthesis and characterization



Scheme S1 Synthetic routes of monomers **4a-c** according to previous reports^{S1-2}.

General procedure for the synthesis of compounds **1a-1c**

A 250 mL two-round-bottom flask equipped with a magnetic stir bar was charged with alkylamine, dichloromethane and triethylamine. The mixture was degassed and charged with nitrogen for three times. Then, fumaryl chloride mixed with dichloromethane was slowly added to the mixture at 0 °C (ice-water bath). After completely dropping, the mixture was warmed to room temperature and stirred overnight. Then, H₂O was added to quench the reaction and extracted with dichloromethane for three times and washed with H₂O for three times. The organic phase was separated and dried over Na₂SO₄. After removing the solvent, a large amount of precipitate was generated and filtered off. The precipitate was washed with MeOH. The residue was collected and dried under vacuum to afford the corresponding compounds **1a-1c**, which was directly used for the next step without further purification.

1a: 2-decyltetradecan-1-amine (23 g, 65.2 mmol), dichloromethane (150 mL), triethylamine (0.5 mL) and fumaryl chloride (5 g, 32.6 mmol) mixed with 50 mL dichloromethane were used. Compound **1a** was obtained as a light-green solid for the

next step (19.2 g) in 74.9% yield.

1b: 2-decyltetradecan-1-amine (11.5 g, 32.6 mmol), dodecylamine (6.03 g, 32.6 mmol), dichloromethane (150 mL), triethylamine (0.5 mL) and fumaryl chloride (5 g, 32.6 mmol) mixed with 50 mL dichloromethane were used. Compound **1b** was obtained as a light-green solid for the next step (16.2 g) in 80.2% yield.

1c: 2-decyltetradecan-1-amine (6.198 g, 19.6 mmol), cyclohexylamine (1.9 g, 19.2 mmol), dichloromethane (100 mL), triethylamine (0.5 mL) and fumaryl chloride (3 g, 19.6 mmol) mixed with 20 mL dichloromethane were used. Compound **1c** was obtained as a light-green solid for the next step (6.75 g) in 64.7% yield.

General procedure for the synthesis of compounds 2a-2c

A 250 mL two-round-bottom flask equipped with a magnetic stir bar was charged with **1** and isopropenyl acetate. The mixture was degassed and charged with nitrogen for three times. Then, *p*-toluenesulfonic acid monohydrate dissolved in DMF was added and the mixture was heated at 90 °C overnight. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure and the crude product was then purified by flash column chromatography on silica gel by using dichloromethane as eluent to give product **2**, which was directly used for the next step.

2a: compound **1a** (6 g, 7.6 mmol), isopropenyl acetate (150 mL), and *p*-toluenesulfonic acid monohydrate (500 mg, 2.63 mmol) in 20 mL DMF were used. Compound **2a** was obtained as a brown oily liquid (3.9 g).

2b: compound **1b** (16 g, the mixture of three components), isopropenyl acetate (200 mL), and *p*-toluenesulfonic acid monohydrate (2.0 g, 10.5 mmol) in 30 mL DMF were used. Compound **2b** was obtained as a brown oily liquid (8.6 g, the mixture of three products).

2c: compound **1c** (6.3 g, the mixture of three components), isopropenyl acetate (120 mL), and *p*-toluenesulfonic acid monohydrate (600 mg, 3.1 mmol) in 20 mL DMF were used. Compound **2c** was obtained as a brown oily liquid (6.35 g, the mixture of three products).

General procedure for the synthesis of compounds 3a-3c

A 250 mL round-bottom flask equipped with a magnetic stir bar was charged with **2**, PPh₃ and pyridinium *p*-toluenesulfonate in acetonitrile. The mixture was degassed and charged with nitrogen for three times and stirred at 100 °C for 12h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel by using dichloromethane as eluent to give product **3**, which was directly used for the next step.

3a: compound **2a** (2.5 g, 2.78 mmol), PPh₃ (1.08 g, 4.12 mmol), pyridinium *p*-toluenesulfonate (1 g, 4.0 mmol) and acetonitrile (100 mL) were used. Compound **3a** was obtained as a light-green oily liquid (521 mg) in 34.2% yield.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 3.67 (d, *J* = 7.4 Hz, 2H), 2.42 (s, 3H), 1.68-1.65 (m, 1H), 1.32-1.25 (m, 40H), 0.88 (t, *J* = 6.7 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 173.6, 168.1, 134.3, 48.7, 38.1, 31.9, 31.5, 31.4, 30.0, 29.7, 29.7, 29.7, 29.6, 29.6, 29.3, 26.4, 25.9, 22.7, 14.1. HRMS (MALDI-TOF) *m/z*: [M]⁺ calcd for C₅₆H₁₀₄N₂O₂ 836.8092; Found 836.8090.

3b: compound **2b** (4.6 g, the mixture of three products), PPh₃ (1.76 g, 6.69 mmol), pyridinium *p*-toluenesulfonate (562 mg, 2.2 mmol) and acetonitrile (100 mL) were used. Compound **3b** was obtained as a light-green oily liquid (1.2 g) in 27.4% yield.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 3.50 (t, *J* = 7.5 Hz, 2H), 3.38 (d, *J* = 7.4 Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 1.72-1.64 (m, 1H), 1.55-1.53 (m, 2H), 1.31-1.25 (m, 58), 0.88 (t, *J* = 6.7 Hz, 9H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 162.6, 162.3, 146.3, 145.8, 108.5, 108.4, 44.6, 40.2, 38.1, 31.9, 31.6, 30.0, 29.8, 29.7, 29.7, 29.6, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 26.9, 26.6, 22.7, 14.1, 13.0, 12.7. HRMS (MALDI-TOF) *m/z*: [M]⁺ calcd for C₄₄H₈₀N₂O₂ 668.6214; Found 668.6218.

3c: compound **2c** (6.35 g, the mixture of three products), PPh₃ (4 g, 15.2 mmol), pyridinium *p*-toluenesulfonate (1.236 g, 4.92 mmol) and acetonitrile (150 mL) were used. Compound **3c** was obtained as a light-green oily liquid (2.2 g, impure) in 29.9% yield.

HRMS (MALDI-TOF) *m/z*: [M]⁺ calcd for C₃₈H₆₆N₂O₂ 582.5119; Found 582.5127.

General procedure for the synthesis of compounds 4a-4c

A 50 mL Schlenk tube equipped with a magnetic stir bar was charged with **3**, 5-bromothiophene-2-carbaldehyde, *L*-proline and triethylamine in toluene/MeOH. The mixture was degassed and charged with nitrogen for three times and stirred at room temperature overnight. Then, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel by using petroleum/dichloromethane (3:1~1:1, v/v) as eluent to give product **4**.

4a: 3a (1.0 g, 1.2 mmol), 5-Bromothiophene-2-carbaldehyde (570 mg, 2.98 mmol), *L*-proline (300 mg, 2.64 mmol), triethylamine (0.7 mL, 5.15 mmol) and toluene/MeOH (7.0 mL/2.0 mL) were used. Compound **4a** was obtained as a purple solid (822 mg) in 58.1% yield

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.87 (d, *J* = 15.4 Hz, 2H), 7.09 (d, *J* = 3.9 Hz, 2H), 7.02 (d, *J* = 3.9 Hz, 2H), 6.51 (d, *J* = 15.4 Hz, 2H), 3.64 (d, *J* = 7.2 Hz, 4H), 1.80-1.66 (m, 2H), 1.33-1.24 (m, 80H), 0.89-0.85 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 161.6, 144.1, 143.9, 134.5, 131.6, 131.3, 115.7, 113.5, 109.7, 44.9, 38.8, 31.9, 31.7, 30.0, 29.9, 29.7, 29.7, 29.4, 26.8, 22.7, 14.1. HRMS (MALDI-TOF) *m/z*: [M]⁺ calcd for C₆₆H₁₀₆Br₂N₂O₂S₂ 1180.6056; Found 1180.6068. Elemental Anal. Calcd for C₆₆H₁₀₆Br₂N₂O₂S₂: C, 66.98; H, 9.03; N, 2.37; S, 5.42; Found: C, 66.90; H, 9.03; N, 2.33; S, 5.23.

4b: 3b (500 mg, 0.75 mmol), 5-Bromothiophene-2-carbaldehyde (357 mg, 1.87 mmol), *L*-proline (190 mg, 1.65 mmol), triethylamine (0.42 mL, 3.0 mmol) and toluene/MeOH (3.75 mL/1.5 mL) were used. Compound **4b** was obtained as a purple solid (365 mg) in 48.1% yield

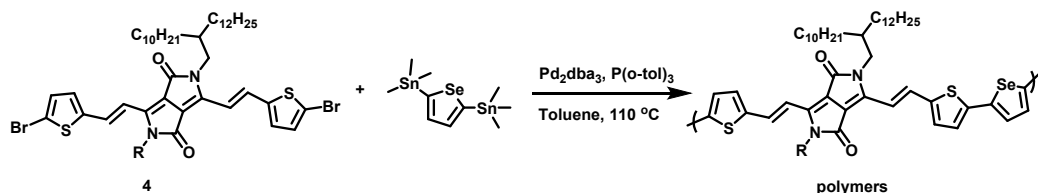
¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.88 (d, *J* = 15.4 Hz, 2H), 7.10 (d, *J* = 3.9 Hz, 1H), 7.08 (d, *J* = 3.9 Hz, 1H), 7.03 (d, *J* = 3.9 Hz, 2H), 6.50 (d, *J* = 15.4, 1H), 6.48 (d, *J* = 15.4, 1H), 3.75 (t, *J* = 7.5 Hz, 2H), 3.64 (d, *J* = 7.3 Hz, 2H), 1.71-1.62 (m, 3H), 1.41-1.16 (m, 58H), 0.87 (t, *J* = 6.7 Hz, 9H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 161.6, 161.2, 144.0, 143.9, 143.5, 134.7, 134.5, 131.6, 131.3, 131.3, 115.8, 113.5, 113.1, 109.7, 109.7, 44.9, 40.7, 38.8, 31.9, 31.7, 30.0, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 26.9, 26.8, 22.7, 14.1. HRMS (MALDI-TOF) *m/z*: [M]⁺ calcd for C₅₄H₈₂Br₂N₂O₂S₂ 1012.4178; Found 1012.4188. Elemental Anal. Calcd for

C₅₄H₈₂Br₂N₂O₂S₂: C, 63.89; H, 8.14; N, 2.76; S, 6.32; Found: C, 63.83; H, 8.16; N, 2.74; S, 6.10

4c: **3c** (600 mg, 1.03 mmol), 5-Bromothiophene-2-carbaldehyde (492 mg, 2.57 mmol), *L*-proline (260 mg, 2.26 mmol), triethylamine (0.57 mL, 4.12 mmol) and toluene/MeOH (5.0 mL/2.0 mL) were used. Compound **4c** was obtained as a purple solid (293 mg) in 30.7% yield.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.94 (d, *J* = 15.4, 1H), 8.92 (d, *J* = 15.2, 1H), 7.11-7.03 (m, 4H), 6.75 (d, *J* = 15.2 Hz, 1H), 6.51 (d, *J* = 15.4 Hz, 1H), 4.16 (br, 1H), 3.64 (d, *J* = 7.3 Hz, 2H), 2.22-2.02 (m, 2H), 1.95-1.86 (m, 4H), 1.79-1.71 (m, 2H), 1.48-1.11 (m, 44H), 0.94-0.85 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 161.6, 150.3, 144.1, 144.1, 143.8, 134.4, 134.3, 131.6, 131.2, 131.1, 115.7, 115.5, 114.1, 113.5, 110.0, 44.9, 38.8, 31.9, 31.6, 31.4, 30.0, 29.7, 29.7, 29.4, 26.7, 26.4, 25.5, 22.7, 14.1. HRMS (MALDI-TOF) *m/z*: [M]⁺ calcd for C₄₈H₆₈Br₂N₂O₂S₂ 926.3083; Found 926.3091. Elemental Anal. Calcd for C₄₈H₆₈Br₂N₂O₂S₂: C, 62.06; H, 7.38; N, 3.02; S, 6.90; Found: C, 61.98; H, 7.37; N, 2.99; S, 6.71.

General procedure for synthesis of PDPPTSe, PDPPTSe12 and PDPPTSeCyH



Scheme S2 Synthetic route for PDPPTSe, PDPPTSe12 and PDPPTSeCyH

To a 50 mL Schlenk tube equipped with a magnetic stir bar was charged with monomer **4**, 2,5-bis(trimethylstannyl)selenophene, Pd₂dba₃ and tri(*o*-tolyl)phosphine were added. Before redistilled toluene was injected, the mixture was degassed and charged with nitrogen for three times. Then through a freeze-pump-thaw cycle, the tube was charged with nitrogen for three times again. The reaction mixture was stirred at 110 °C for 16 h. After cooling to room temperature, the mixture was poured into CH₃OH and filtered. Then, the polymer was purified by Soxhlet extraction with various solvents (CH₃OH, acetone, and hexane sequentially) to remove the existing oligomers

and other impurities. Last, the chloroform fraction was collected. After removal of solvents, the sample was dried under vacuum at 50 °C for 12 h.

PDPPTSe: compound **4a** (118.2 mg, 0.1 mmol), 2,5-bis(trimethylstannyl)selenophene (45.7 mg, 0.1 mmol), Pd₂dba₃ (2.7 mg, 3 μmol), tri(o-tolyl)phosphine (3.6 mg, 0.012 mmol) and toluene (5 mL) were used. **PDPPTSe** was obtained as a dark solid (78 mg) in 67.6% yield.

¹H NMR (500 MHz, C₂D₂Cl₄, 373 K) δ (ppm) 8.82-8.67 (br, 2H), 7.30-7.19 (br, 2H), 7.07-6.96 (br, 4H), 6.57-6.47 (br, 2H), 3.59 (d, *J* = 9.6 Hz, 4H), 1.72 (br, 2H), 1.33-1.18 (m, 80H), 0.81-0.78 (m, 12H). Solid state ¹³C NMR (151 MHz, 298 K) δ (ppm) 161.7, 142.6, 141.9, 131.5, 126.0, 113.8, 110.9, 32., 29.9, 23.4, 14.7. *M_n* = 13.29 kg/mol, *M_w* = 26.17 kg/mol, PDI = 1.96. Anal. calcd for (C₇₂H₁₁₄N₂O₂S₂Se)_n: C, 73.11; H, 9.72; N, 2.37; S, 5.42; found: C, 72.60; H, 9.39; N, 2.44; S, 5.39.

PDPPTSe12: compound **4b** (101.4 mg, 0.1 mmol), 2,5-bis(trimethylstannyl)selenophene (45.7 mg, 0.1 mmol), Pd₂dba₃ (2.7 mg, 3 μmol), tri(o-tolyl)phosphine (3.6 mg, 0.012 mmol) and toluene (5 mL) were used. **PDPPTSe12** was obtained as a dark solid (70 mg) in 71.0% yield.

¹H NMR NMR (500 MHz, C₂D₂Cl₄, 373 K) δ (ppm) 8.78 (br, 2H), 7.18-6.97 (m, 6H), 6.53-6.50 (br, 2H), 3.69-3.58 (br, 4H), 1.63 (br, 3H), 1.34-1.06 (m, 58H), 0.81-0.78 (m, 9H). Solid state ¹³C NMR (151 MHz, 298 K) δ (ppm) 161.3, 142.5, 132.5, 126.0, 113.8, 111.7, 40.6, 32.7, 30.5, 23.5, 14.8. *M_n* = 24.00 kg/mol, *M_w* = 73.67 kg/mol, PDI = 3.06. Anal. calcd for (C₆₀H₉₀N₂O₂S₂Se)_n: C, 71.04; H, 8.94; N, 2.76; S, 6.32; found: C, 69.80; H, 8.48; N, 2.80; S, 6.26.

PDPPTSeCyH: compound **4c** (92.8 mg, 0.1 mmol), 2,5-bis(trimethylstannyl)selenophene (45.7 mg, 0.1 mmol), Pd₂dba₃ (2.7 mg, 3 μmol), tri(o-tolyl)phosphine (3.6 mg, 0.012 mmol) and toluene (5 mL) were used. **PDPPTSeCyH** was obtained as a dark solid (73 mg) in 81.1% yield.

¹H NMR (500 MHz, C₂D₂Cl₄, 373 K) δ (ppm) 8.82-8.67 (br, 2H), 7.27-6.78 (br, 6H), 6.61 (br, 2H), 4.11 (br, 1H), 3.60-3.58 (br, 2H), 2.09 (br, 2H), 1.98-1.88 (br, 4H), 1.72 (br, 2H), 1.6-0.83 (m, 43H), 0.79 (s, 6H). Solid state ¹³C NMR (151 MHz, 298 K) δ (ppm) 161.1, 142.5, 132.6, 125.7, 111.7, 55.5, 42.1, 40.1, 31.9, 30.7, 27.6, 23.5, 14.8.

$M_n = 14.89$ kg/mol, $M_w = 41.57$ kg/mol, PDI = 2.79. Anal. calcd for $(C_{54}H_{76}N_2O_2S_2Se)_n$:
C, 69.87; H, 8.25; N, 3.02; S, 6.91; found: C, 68.74; H, 7.65; N, 3.03; S, 6.85.

3. Thermogravimetric analysis (TGA) analysis

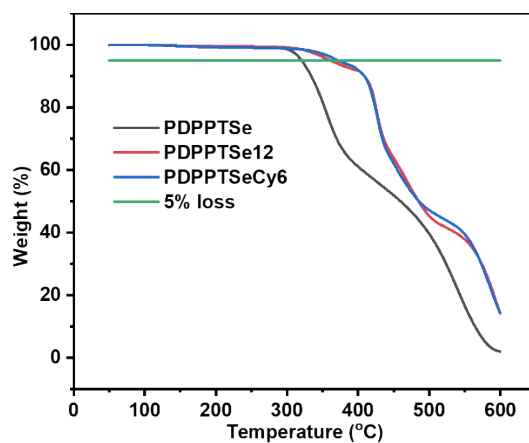


Figure S1. TGA curves of **PDPPTSe**, **PDPPTSe12** and **PDPPTSeCyH**; heating rate: 10 °C/min from 50 °C to 600 °C under nitrogen atmosphere.

4. Differential scanning calorimetry (DSC) analysis

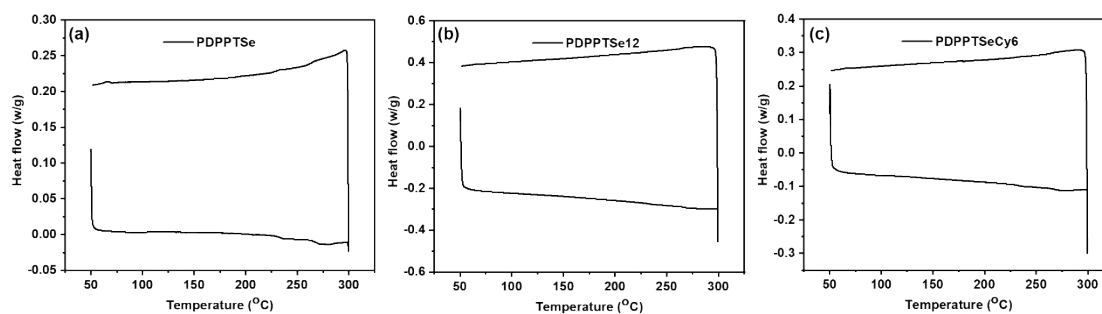


Figure S2. DSC heating and cooling traces at a scanning speed of 10 °C/min from 50 to 300 °C under nitrogen: (a) **PDPPTSe**; (b) **PDPPTSe12**; (c) **PDPPTSeCyH**. No obvious phase transitions were observed.

5. Gel permeation chromatography (GPC) results

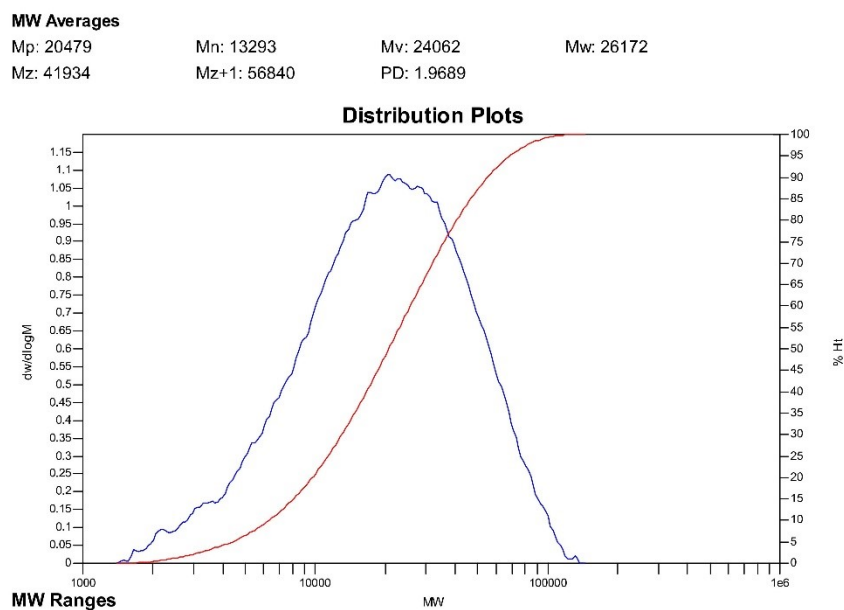


Figure S3 Molecular weight distribution plots of **PDPPTSe** (1,2,4-trichlorobenzene, 140 °C)

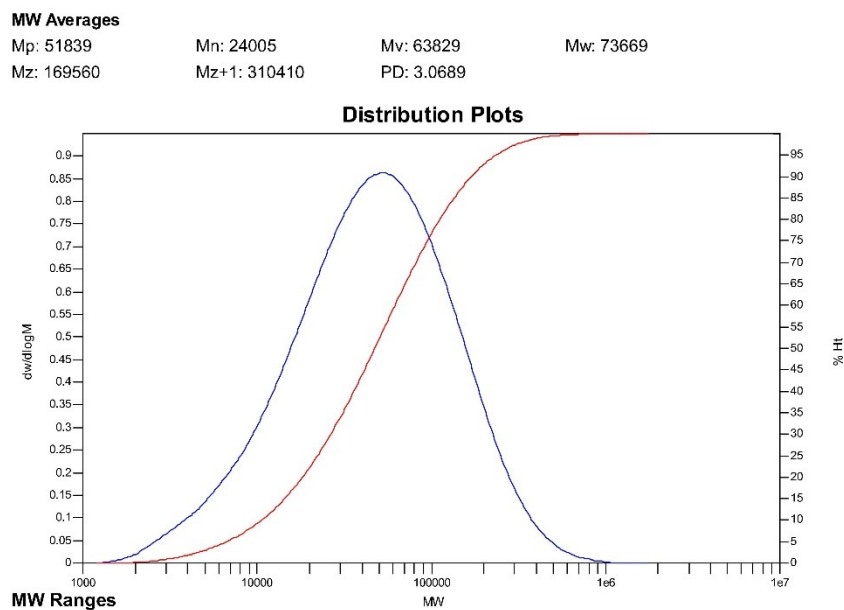


Figure S4 Molecular weight distribution plots of **PDPPTSe12** (1,2,4-trichlorobenzene, 140 °C)

MW Averages

Mp: 29548

Mn: 14898

Mv: 36126

Mw: 41575

Mz: 96710

Mz+1: 188822

PD: 2.7906

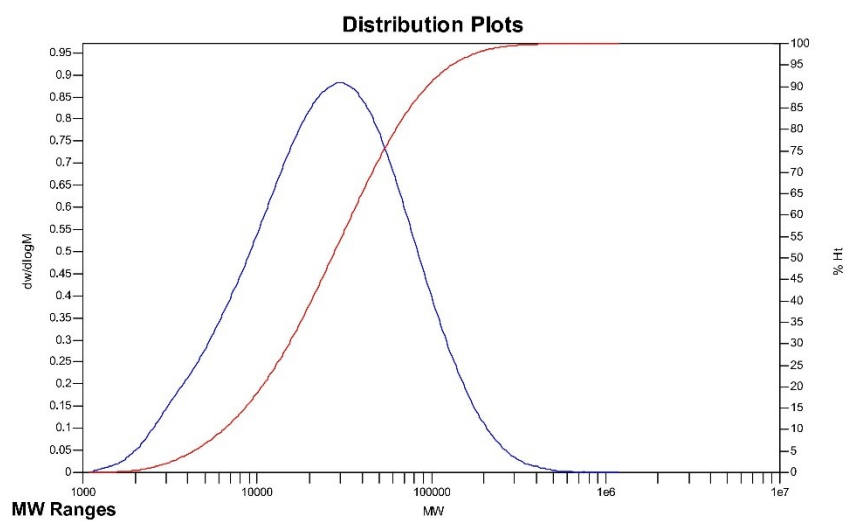


Figure S5 Molecular weight distribution plots of **PDPPTSeCyH** (1,2,4-trichlorobenzene, 140 °C)

6. UV-vis absorption spectra of thin films.

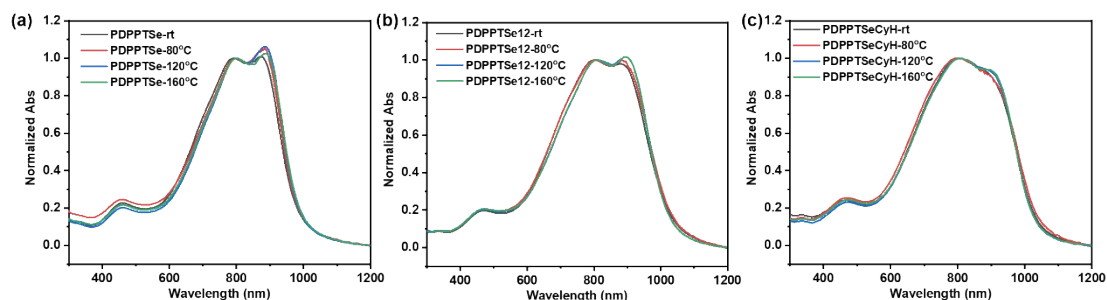


Figure S6 The absorption spectra of thin films before and after annealing at 80 °C, 120 °C and 160 °C for 10 minutes under air atmosphere: (a) **PDPPTSe**; (b) **PDPPTSe12**; (c) **PDPPTSeCyH**.

7. Cyclic voltammograms

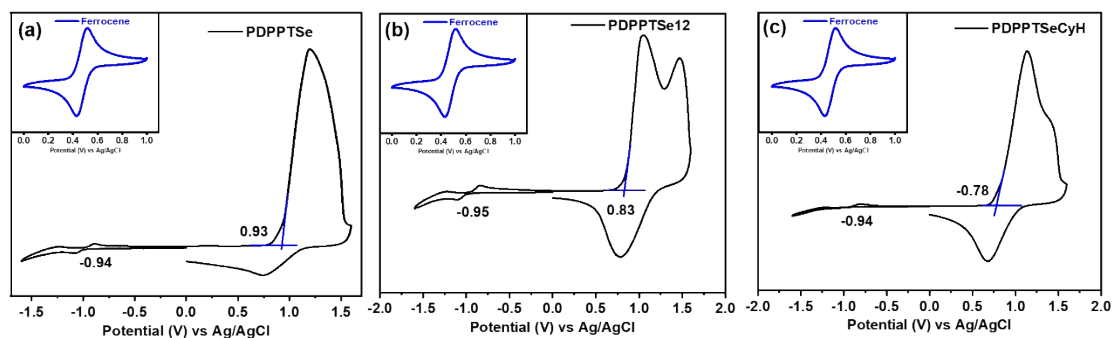


Figure S7. Cyclic voltammograms of **ferrocene** (inset), **PDPPTSe** (a), **PDPPTSe12** (b) and **PDPPTSeCyH** (c) (in the form of thin films) at a scan rate of 100 mVs⁻¹. A glassy carbon electrode was used as the working electrode, Pt as the counter electrode and Ag/AgCl (saturated KCl) as the reference electrode; *n*-Bu₄NPF₆ (0.1 M) in CH₃CN as the supporting electrolyte. For calibration, the redox potential of ferrocene/ferrocenium (Fc/Fc⁺) was measured under the same conditions.

8. OFET device fabrication and measurements

Fabrication of Bottom-gate bottom-contact (BGBC) devices

A heavily doped n-type Si wafer with a dry oxidized SiO₂ layer of 300 nm and a capacitance of 11.0 nF cm⁻² was employed as the gate electrode and dielectric layer. The drain-source (D-S) gold contacts were fabricated by photo-lithography. The substrates were first cleaned by sonication in acetone and water for 5 min, and immersed in Piranha solution (7:3 mixture of sulfuric acid and 30% hydrogen peroxide) for 30 min. The substrates were further rinsed with deionized water and isopropyl alcohol for three times and they were blow-dried with nitrogen. Then, the substrate was processed by UV ozone for about 10 min. After that, the substrates were placed into a petri dish, and one drop of *n*-octadecyltrichlorosilane (OTS) was dropped into the middle of petri dish. The system was stored under vacuum at 120 °C for 4 h to form an OTS self-assembled monolayer. After the substrate surfaces were modified with OTS, they were washed with *n*-hexane, CHCl₃ and isopropyl alcohol sequentially. Next, thin films of PDPPTSe, PDPPTSe12 and PDPPTSeCyH were prepared by spin-coating of their CHCl₃ solutions (5.0 mg/mL, 10 μL) onto the modified substrates at 3000 rpm for 60 s. The annealing process was performed in an air atmosphere for 10 min at 80 °C, 120 °C and 160 °C. The transfer and output curves of FETs were measured at room temperature in an air atmosphere using a Keithley 4200 SCS semiconductor parameter analyzer. The charge mobility of the OFETs in the saturation region was extracted from the following equation:

$$I_{DS} = \mu C_i (V_{GS} - V_{Th})^2 W/2L$$

Where I_{DS} is the current collected by the drain electrode; L and W are the channel length and width, respectively; μ is the mobility of the device; C_i is the capacitance per unit area of the gate dielectric layer (11.0 nF/cm²); V_{GS} is the gate voltage, and V_{Th} is the threshold voltage, respectively. The V_{Th} of the device was obtained by extrapolating the $(I_{DS,sat})^{1/2}$ vs. V_{GS} plot to $I_{DS} = 0$

Fabrication of top-gate bottom-contact (BGBC) devices

A heavily doped n-type Si wafer with a dry oxidized SiO₂ layer of 300 nm was used as substrate and the substrate was modified with OTS following the above procedures. The thin films of **PDPPTSe**, **PDPPTSe12** and **PDPPTSeCyH** were prepared by spin-coating of their CHCl₃ solutions (5.0 mg/mL, 10 μL) onto the modified substrates at 3000 rpm for 60 s. Then, the film was annealed at 120 °C for 10 minutes. Cytop solution was spin-coated on the surface of the polymer layer at 2000 rpm for 60 s to give a Cytop thin film and then annealed at 100 °C for 20 minutes in a nitrogen box. The capacitance of the Cytop film was ca. 2.1 nF cm⁻².^{S3} After that, the aluminum gate electrode (~100 nm) was deposited on the dielectric layer by a vacuum deposition method. The transfer and output curves of the TGBC devices were measured at room temperature in an air atmosphere using a Keithley 4200 SCS semiconductor parameter analyzer.

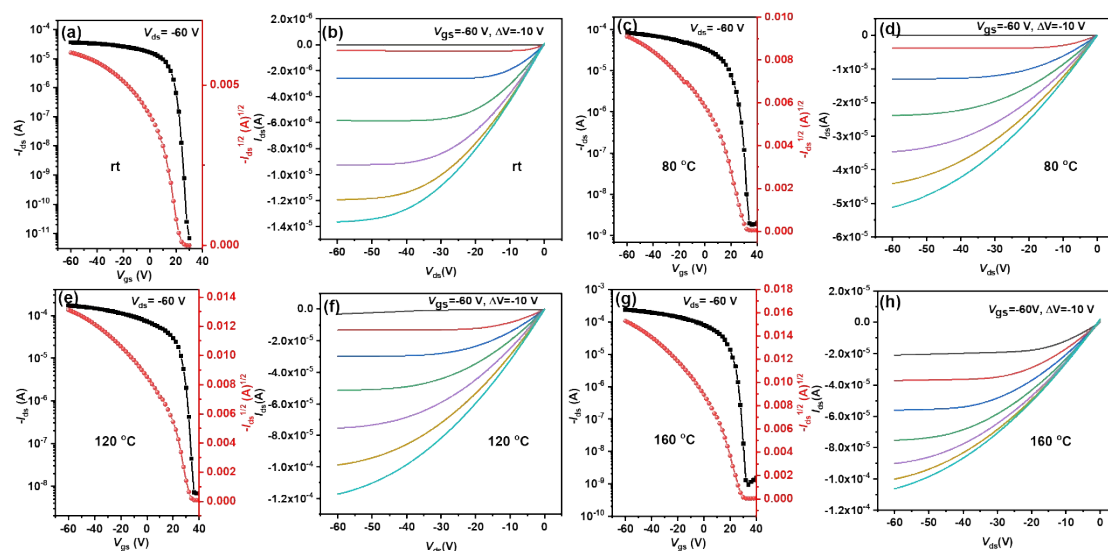


Figure S8 Typical transfer (a, c, e, g) and output (b, d, f, h) curves of BGBC FETs devices with the film of **PDPPTSe** before (a, b) and after annealing at 80 °C (c, d), 120 °C (e, f) and 160 °C (g, h).

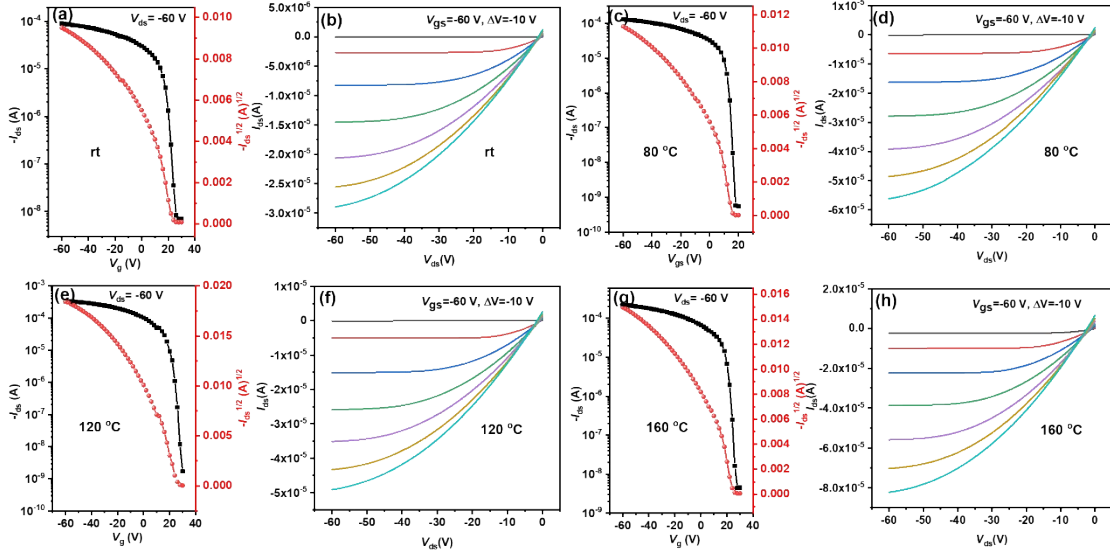


Figure S9 Typical transfer (a, c, e, g) and output (b, d, f, h) curves of BGBC FETs devices with the film of **PDPPTSe12** before (a, b) and after annealing at 80 °C (c, d), 120 °C (e, f) and 160 °C (g, h).

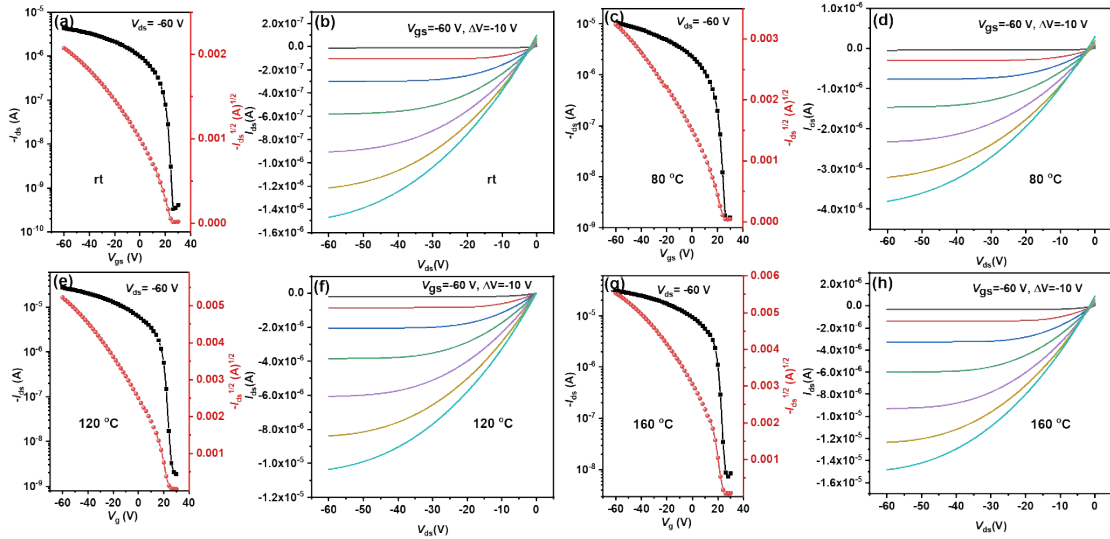


Figure S10 Typical transfer (a, c, e, g) and output (b, d, f, h) curves of BGBC FETs devices with the film of **PDPPTSeCyH** before (a, b) and after annealing at 80 °C (c, d), 120 °C (e, f) and 160 °C (g, h).

Table S1 The OFETs performance of BGBC devices based on the polymer film before and after annealing at 80 °C, 120 °C and 160 °C.

Compounds	PDPPTSe			PDPPTSe12			PDPPTSeCyH		
	μ (max/ave) ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	V_{th} (V)	$I_{\text{on/off}}$	μ (max/ave) ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	V_{th} (V)	$I_{\text{on/off}}$	μ (max/ave) ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	V_{th} (V)	$I_{\text{on/off}}$
rt	0.57/0.39	28~34	$>10^5$	1.67/0.98	22~26	$>10^5$	0.04/0.02	22~29	$10^3\sim 10^4$
80 °C	1.29/0.77	27~33	$10^4\sim 10^5$	3.58/2.85	13~17	$>10^5$	0.07/0.05	21~26	$10^3\sim 10^4$
120 °C	4.20/2.30	28~34	$10^4\sim 10^5$	6.62/4.15	13~16	$>10^5$	0.26/0.23	22~26	$10^4\sim 10^5$
160 °C	3.49/1.74	27~36	$10^4\sim 10^5$	3.54/2.94	16~25	$>10^5$	0.51/0.44	20~24	$10^3\sim 10^4$

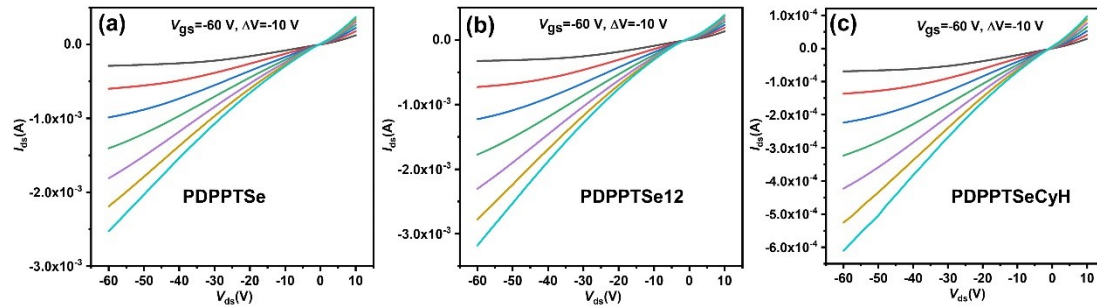


Figure S11 The typical output curves of PDPPTSe (a), PDPPTSe12 (b) and PDPPTSeCyH (c) with thermal annealing at 120 °C based on the TGBC devices.

Table S2 The OFETs performance of TGBC devices based on the polymer thin films after thermal annealing at 120 °C.

Properties	PDPPTSe	PDPPTSe12	PDPPTSeCyH
μ (max/ave) ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	3.50(2.21)	6.76(4.77)	0.83(0.54)
V_{th} (V)	15~27	15~19	22~31
$I_{\text{on/off}}$	$10^4\sim 10^5$	$10^3\sim 10^4$	$10^3\sim 10^4$
Reliability factor	85.4%	71.1%	79.0%

Table S3 The average mobility of two-batch devices. The average mobility was calculated based on over 5 devices.

Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Devices	PDPPTSe	PDPPTSe12	PDPPTSeCyH
First batch	BGBC	2.3	4.15	0.23
	TGBC	2.21	4.77	0.54
Second batch	BGBC	2.47	4.02	0.21
	TGBC	2.19	4.2	0.43

Table S4 The semiconducting properties of the representative DPP-selenophene copolymers.

Polymers	Mobility (cm ² V ⁻¹ s ⁻¹)		Device structure	Reference
	Hole	Electron		
PSeDPPDTT	0.23		TGBC	<i>J. Mater. Chem.</i> , 2012 , 22, 12817-12823
PSeDPP	1.62	0.14	TGBC	<i>J. Mater. Chem.</i> , 2012 , 22, 2120-2128
PTDPPSe-Si	3.97	2.2	BGTC	<i>J. Am. Chem. Soc.</i> 2012 , 134, 20713–20721
P(DPP-alt-DTBS ₂ Se)	1.5		BGTC	<i>J. Am. Chem. Soc.</i> 2011 , 133, 10364–10367
PDPPSSS	5		BGTC	<i>Chem. Commun.</i> , 2013 , 49, 7132-7134
PDPPDTSE	4.97		BGBC	<i>Adv. Mater.</i> 2013 , 25, 524-528
P-29-DPPDTSE	12		BGTC	<i>J. Am. Chem. Soc.</i> 2013 , 135, 14896–14899
PDPPSe	1.35			
PDPPSe-10	8.1		BGBC	<i>Chem. Mater.</i> 2018 , 30, 3090-3100
PDPPSe-12	9.4			
PSeFDFT	0.31	0.21		
PSeDPPFT	0.14	0.05	TGBC	<i>Chin. J. Chem.</i> 2020 , 38, 1075–1080
PSDPP-SVS	5.23			
PSDPP-SVS	4.15		BGBC	<i>Polym. Chem.</i> , 2015 , 6, 1777–1785
PSDPP-BT	1.79			
PSPP-BS	2.08			
PSeDPPBT	0.46	0.84	TGBC	<i>Adv. Mater.</i> , 2012 , 24, 1558
PDPPTSe	3.5			
PDPPTSe12	6.76		TGBC	This work
PDPPTSeCyH	0.83			

9. Atomic-force microscope (AFM) images

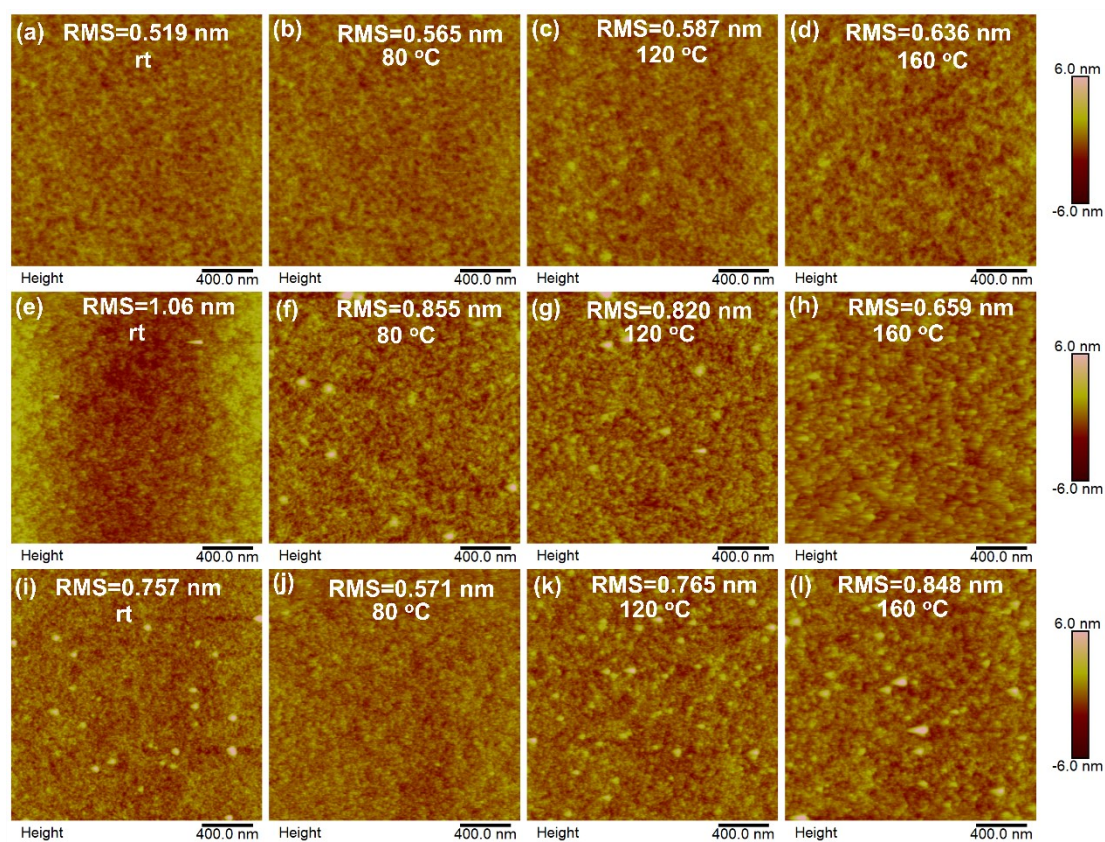


Figure S12 AFM images of **PDPPTSe** (a-d), **PDPPTSe12** (e-h) and **PDPPTSeCyH** (i-l) before and after thermal annealing at 80 °C, 120 °C and 160 °C for 10 minutes.

10. ^1H NMR, ^{13}C NMR and HRMS spectra

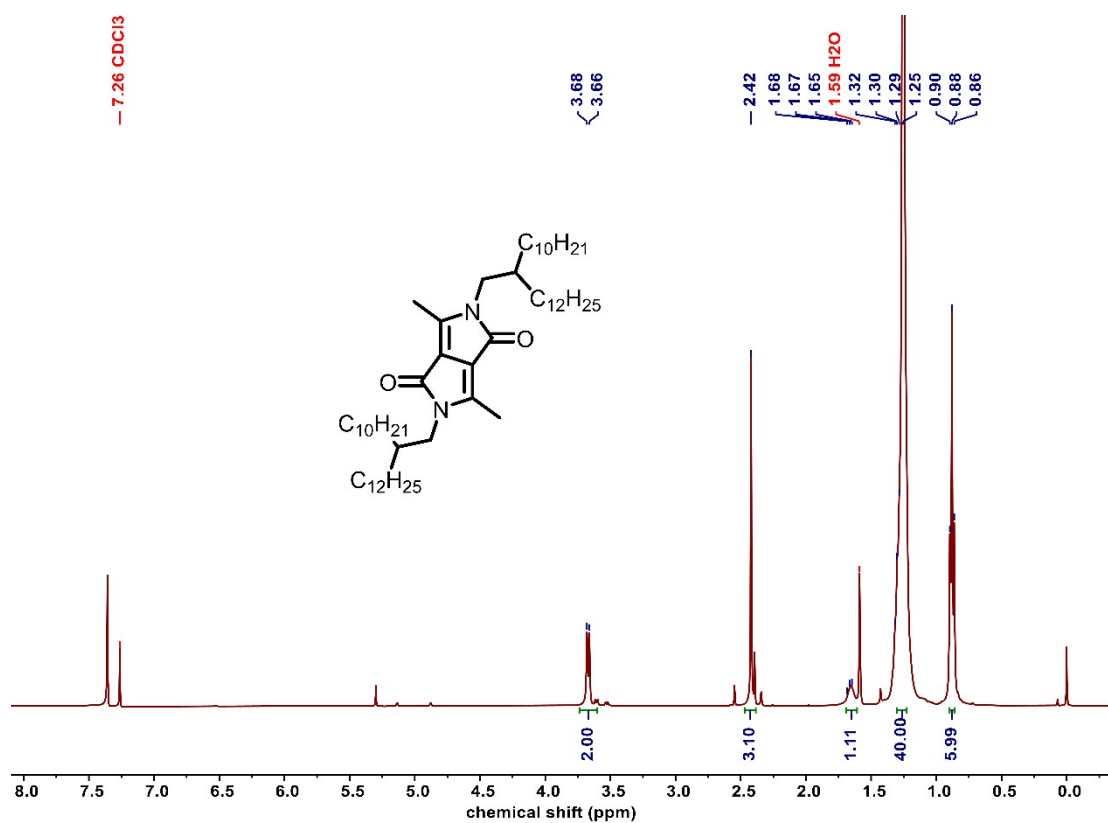


Figure S13 ^1H NMR spectrum of compound **3a** (400 MHz, CDCl_3 , 298 K)

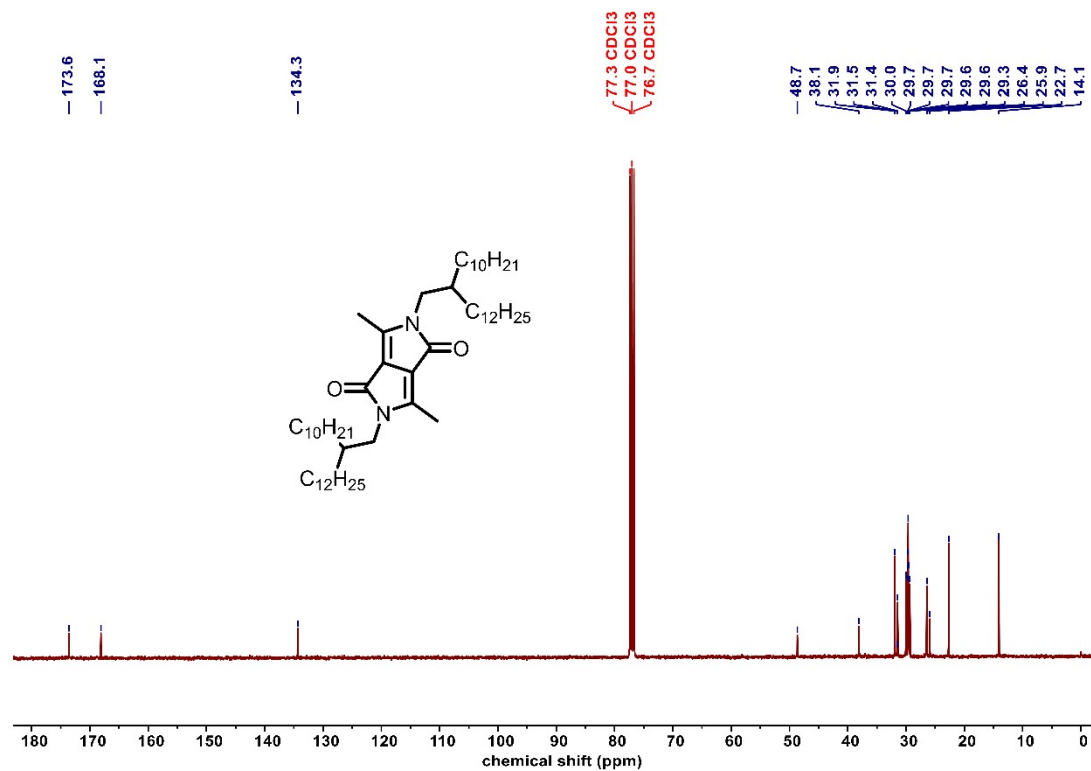


Figure S14 ^{13}C NMR spectrum of compound **3a** (101 MHz, CDCl_3 , 298 K)

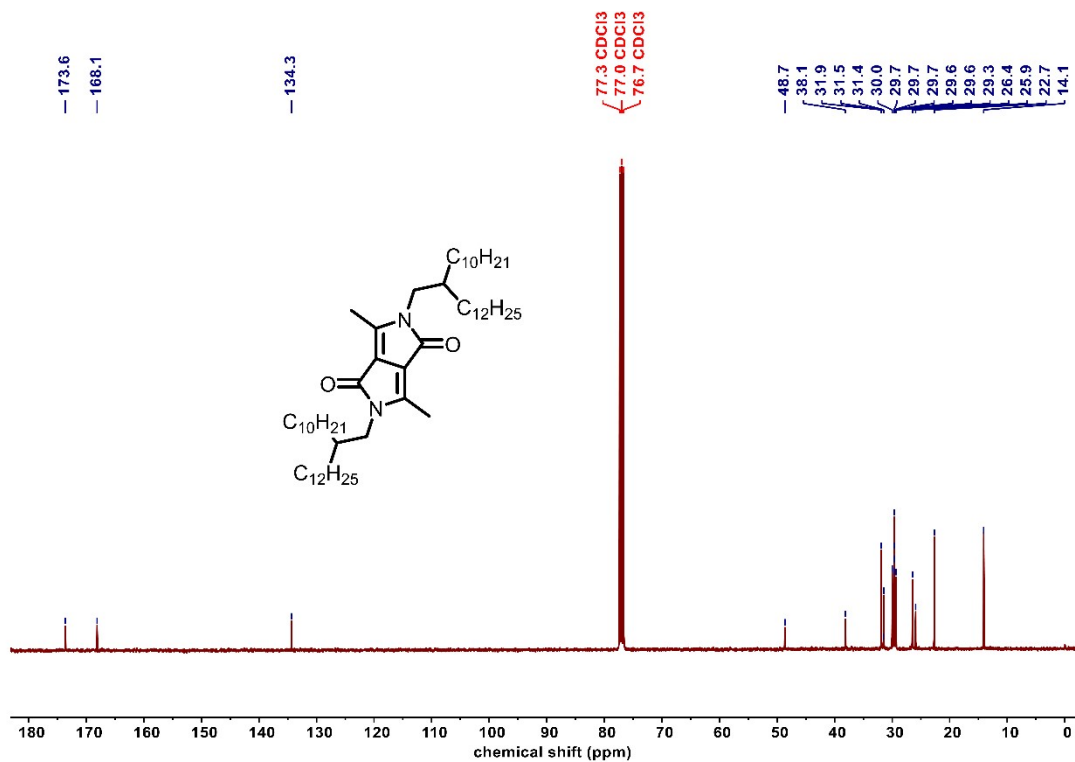


Figure S15 1H NMR spectrum of compound **3b** (400 MHz, $CDCl_3$, 298 K)

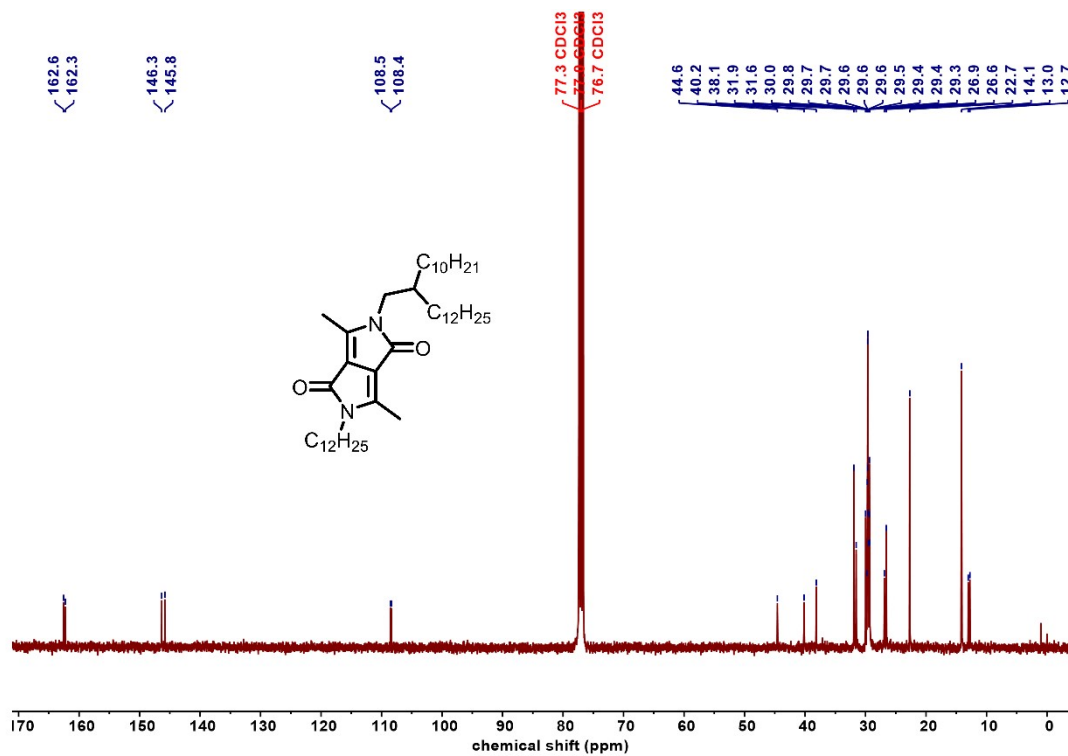


Figure S16 ^{13}C NMR spectrum of compound **3b** (101 MHz, $CDCl_3$, 298 K)

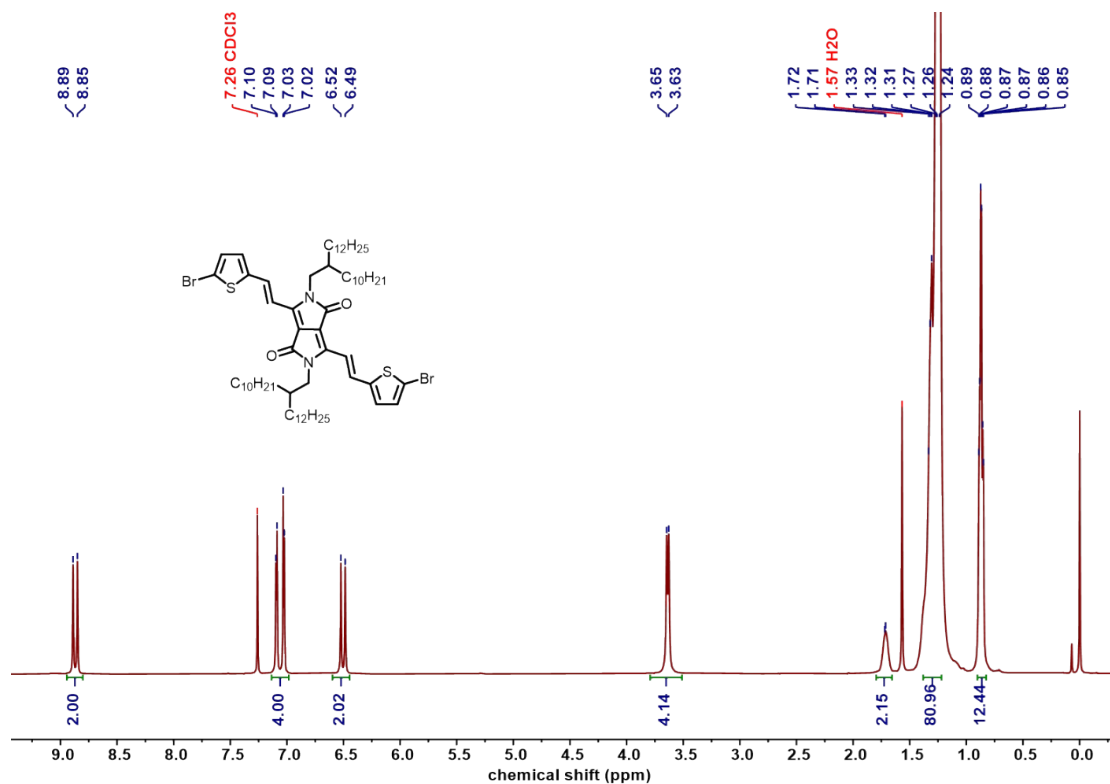


Figure S17 ¹H NMR spectrum of compound 4a (400 MHz, CDCl₃, 298 K)

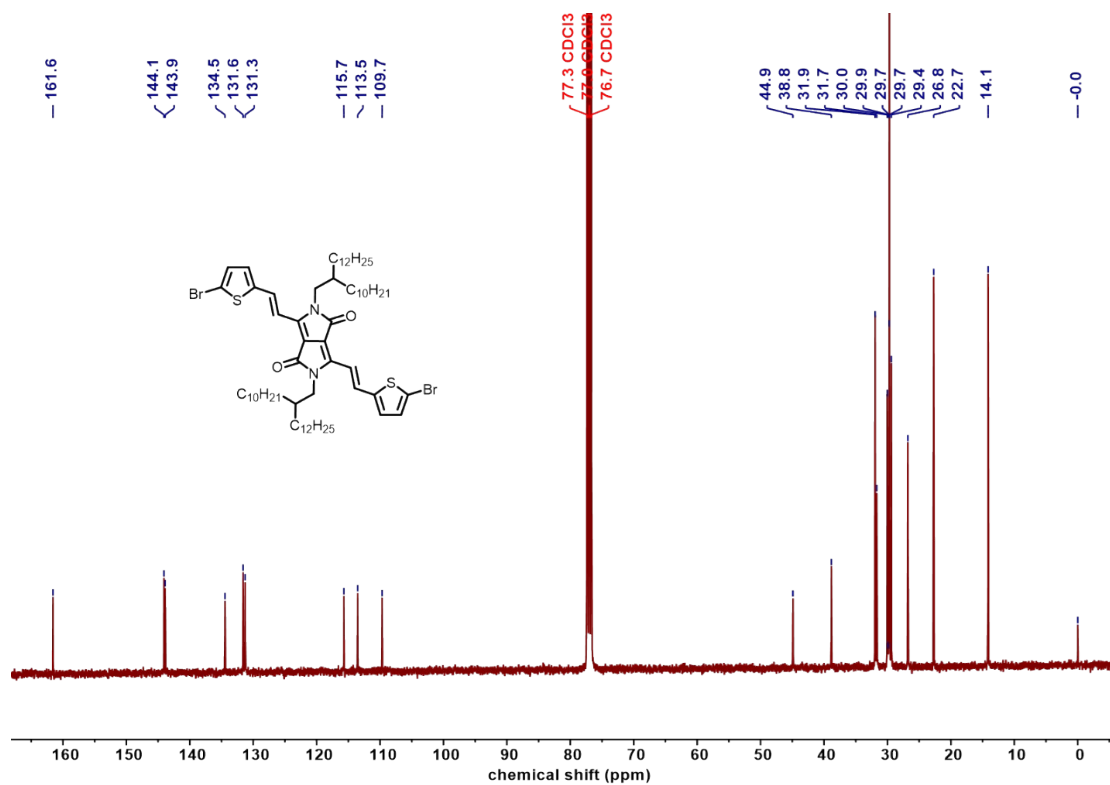


Figure S18 ¹³C NMR spectrum of compound 4a (101 MHz, CDCl₃, 298 K)

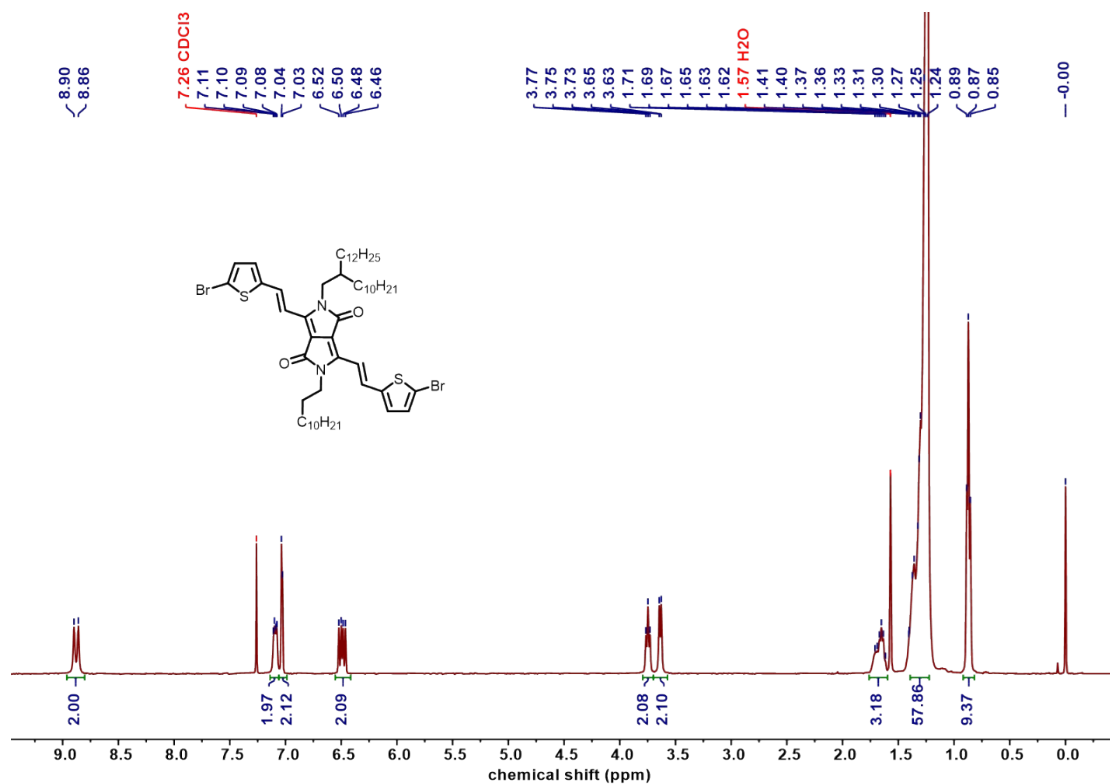


Figure S19 ¹H NMR spectrum of compound **4b** (400 MHz, CDCl₃, 298 K)

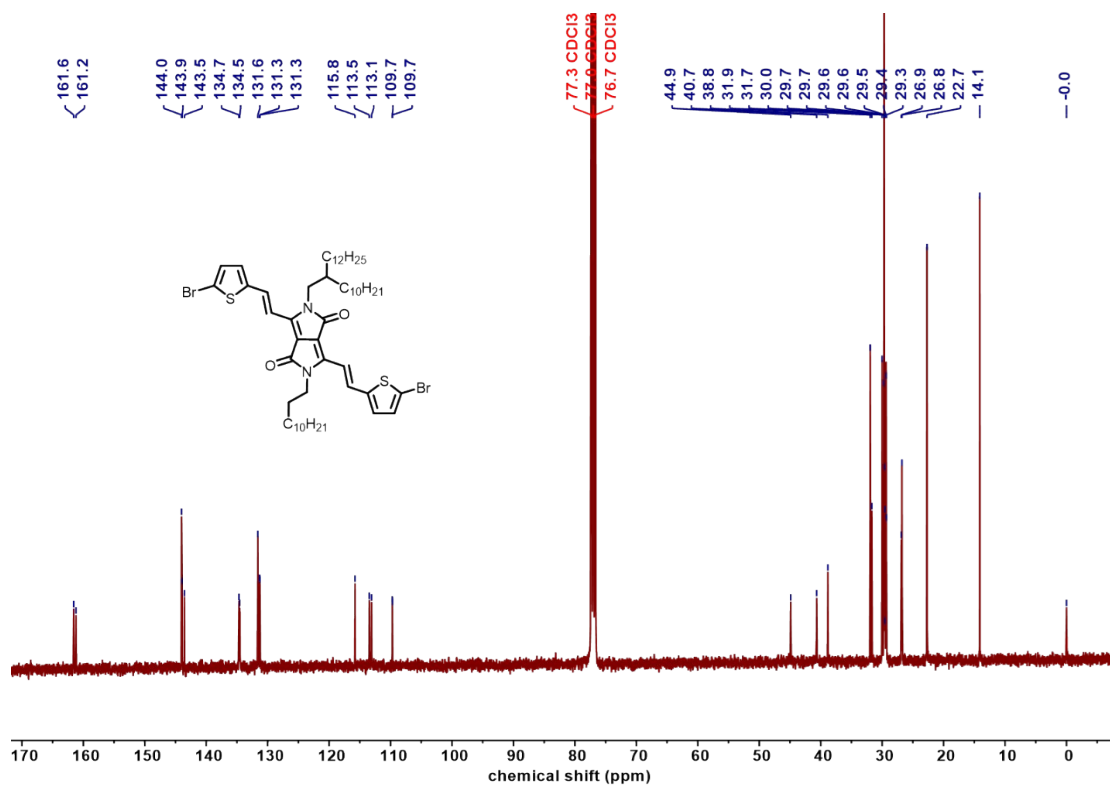


Figure S20 ¹³C NMR spectrum of compound **4b** (101 MHz, CDCl₃, 298 K)

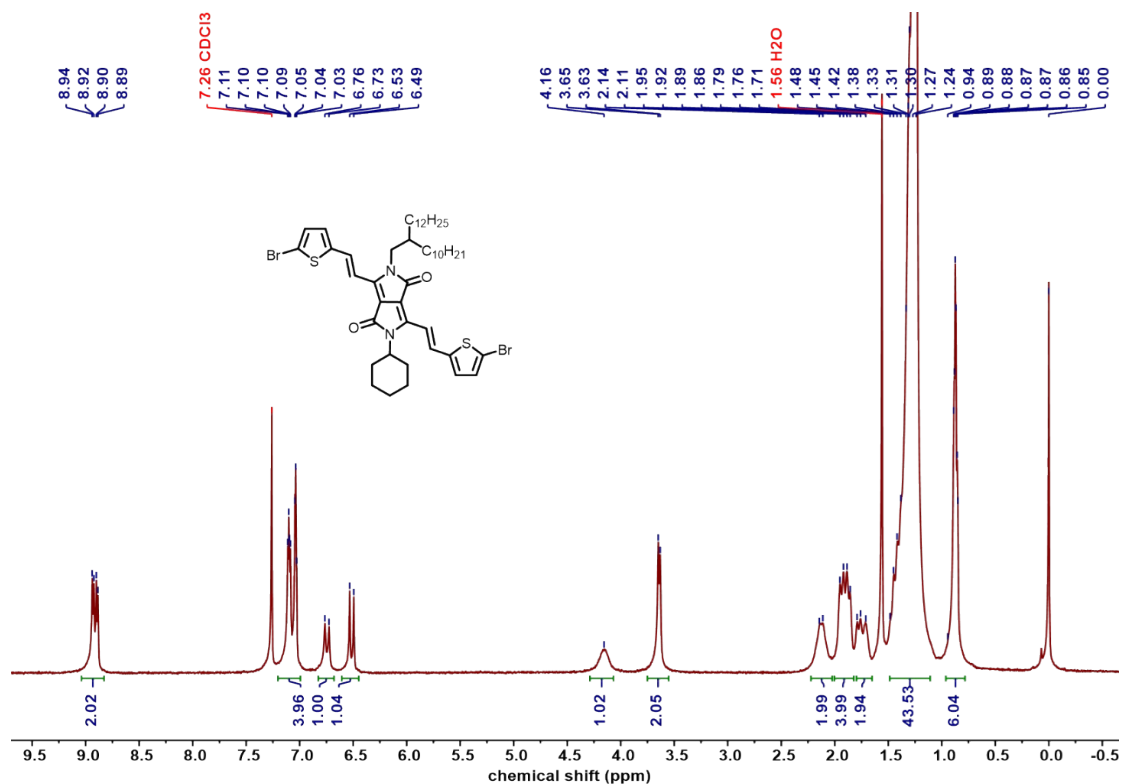


Figure S21 ^1H NMR spectrum of compound **4c** (400 MHz, CDCl₃, 298 K)

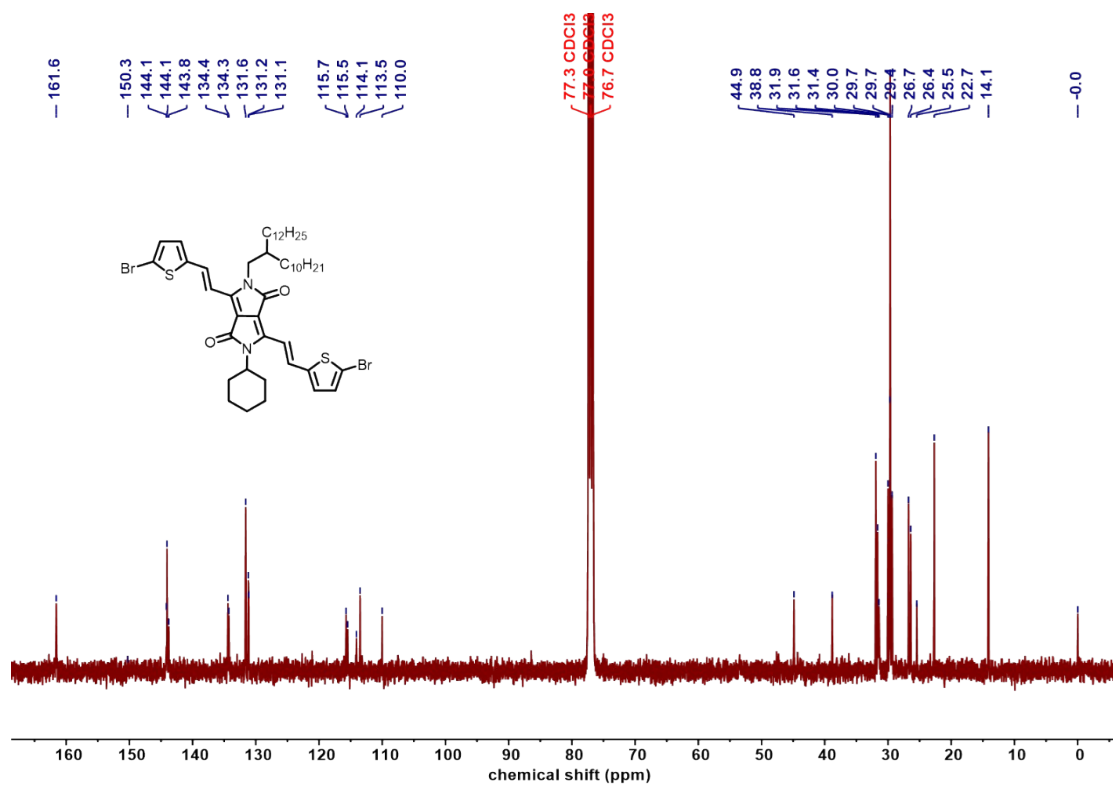


Figure S22 ^{13}C NMR spectrum of compound **4c** (101 MHz, CDCl₃, 298 K)

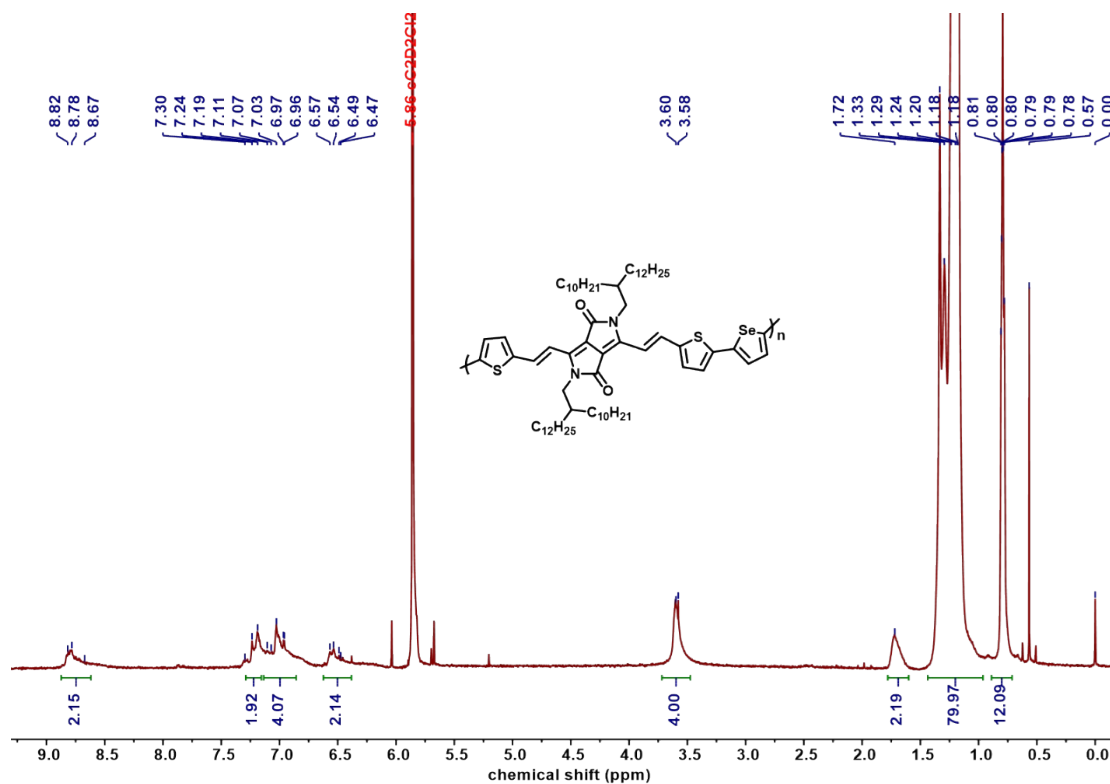


Figure S23 ^1H NMR spectrum of PDPPTSe (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K)

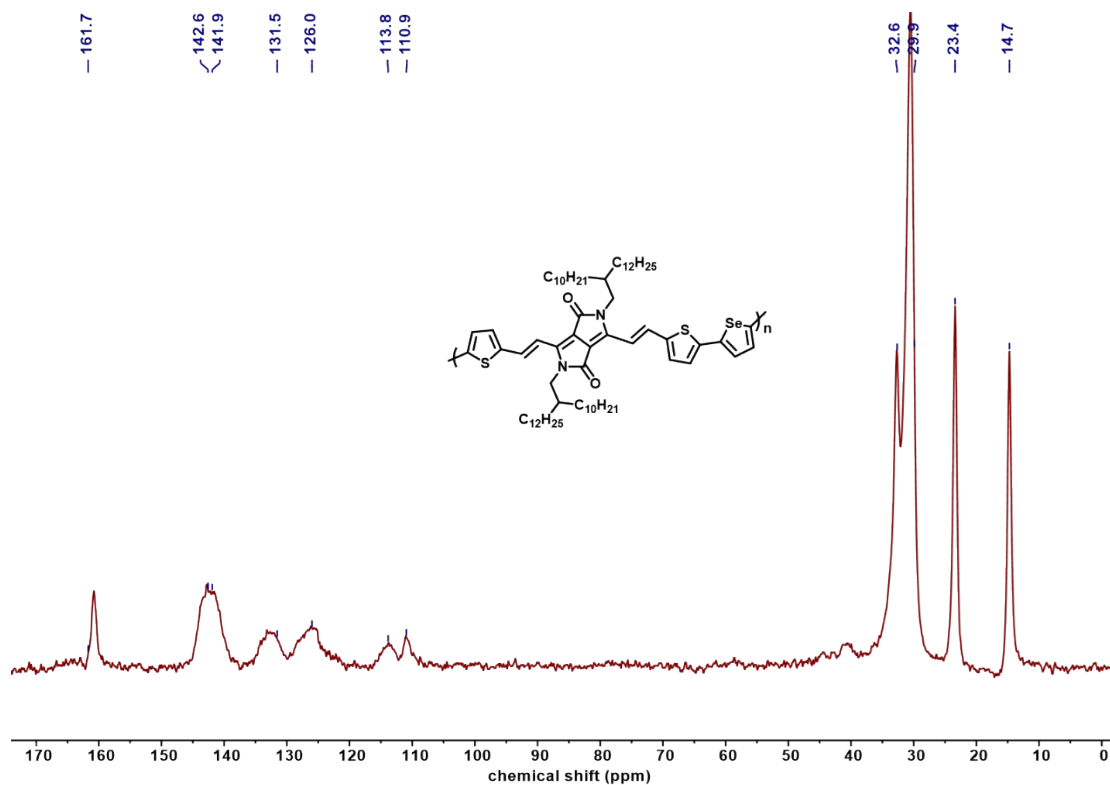


Figure S24 Solid state ^{13}C NMR spectrum of PDPPTSe (151 MHz, 298 K)

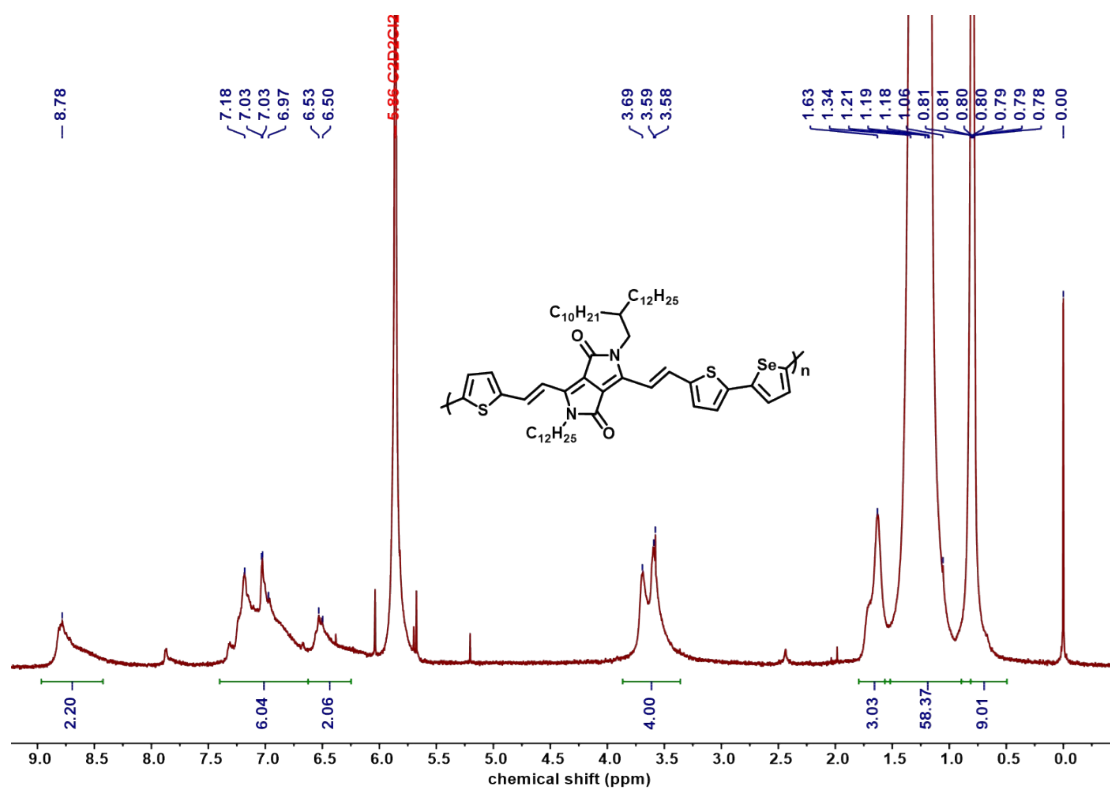


Figure S25 ^1H NMR spectrum of **PDPPTSe12** (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K)

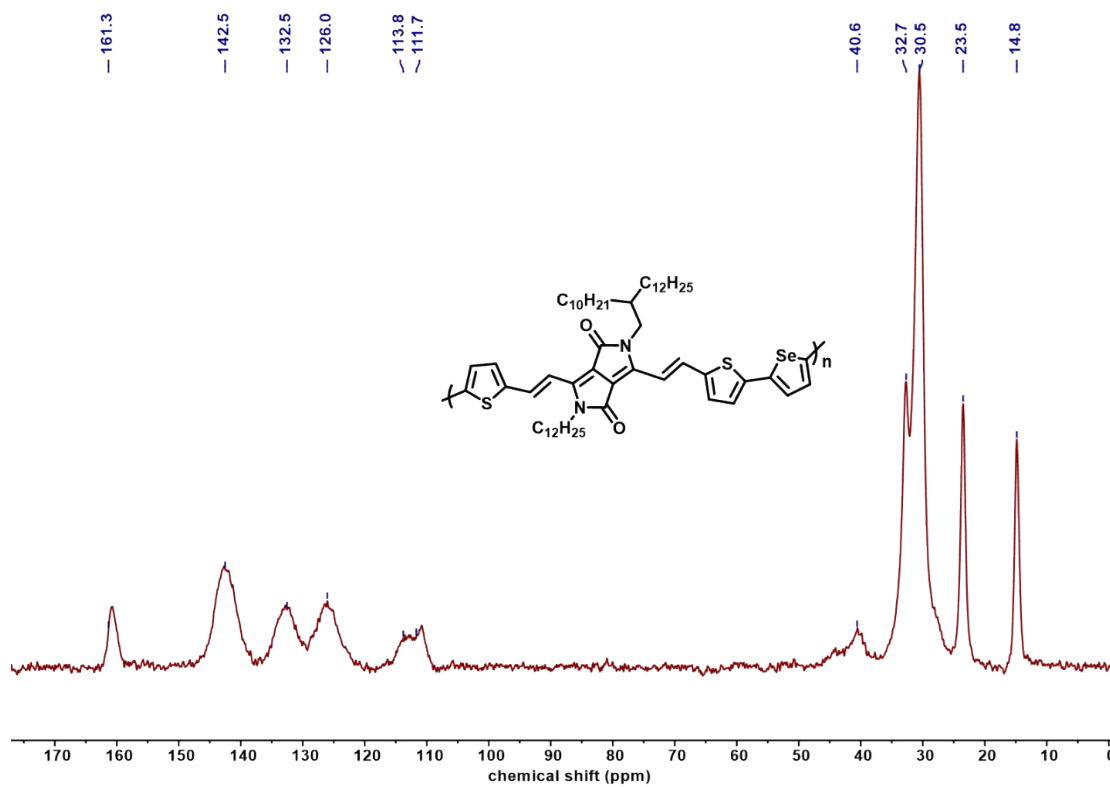


Figure S26 Solid state ^{13}C NMR spectrum of **PDPPTSe12** (151 MHz, 298 K)

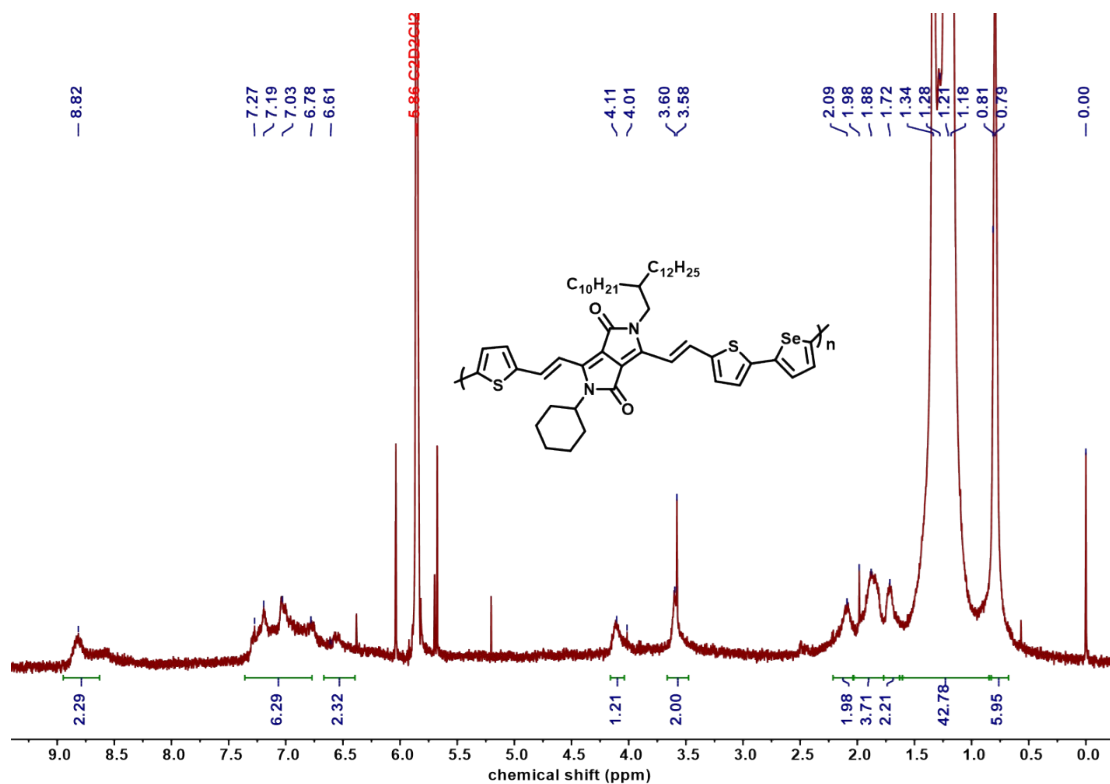


Figure S27 ^1H NMR spectrum of PDPPTSeCyH (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K)

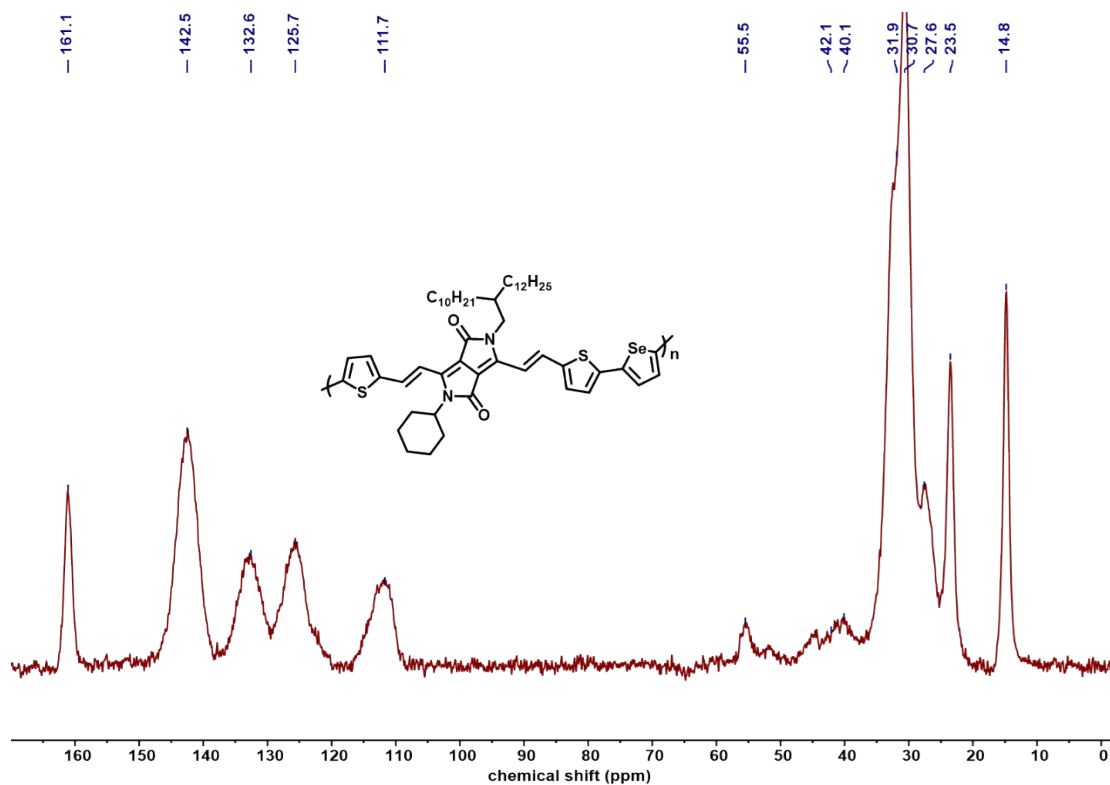
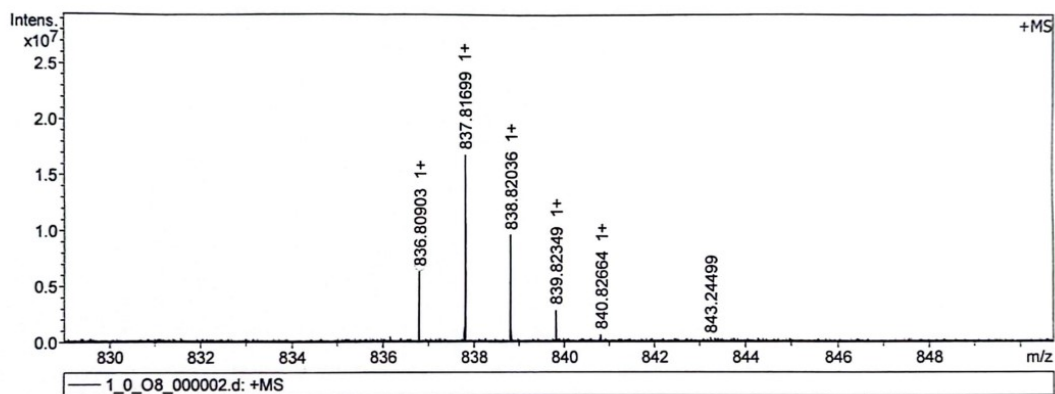
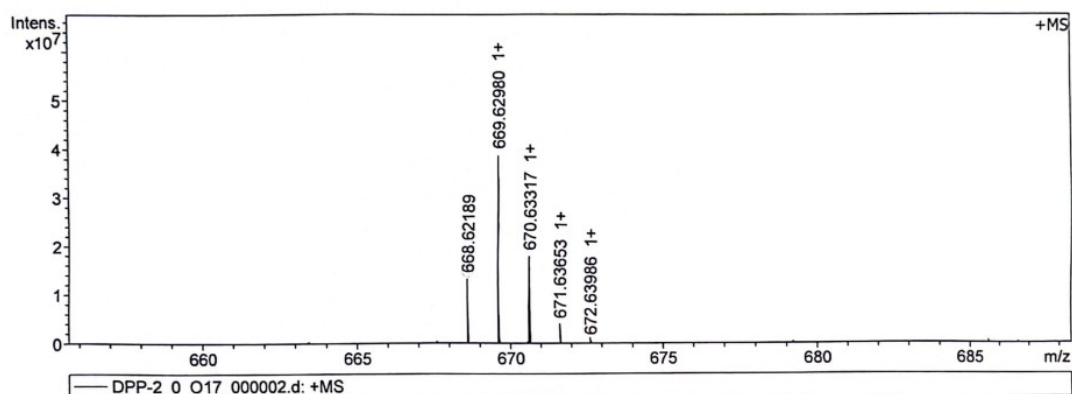


Figure S28 Solid state ^{13}C NMR spectrum of PDPPTSeCyH (151 MHz, 298 K)



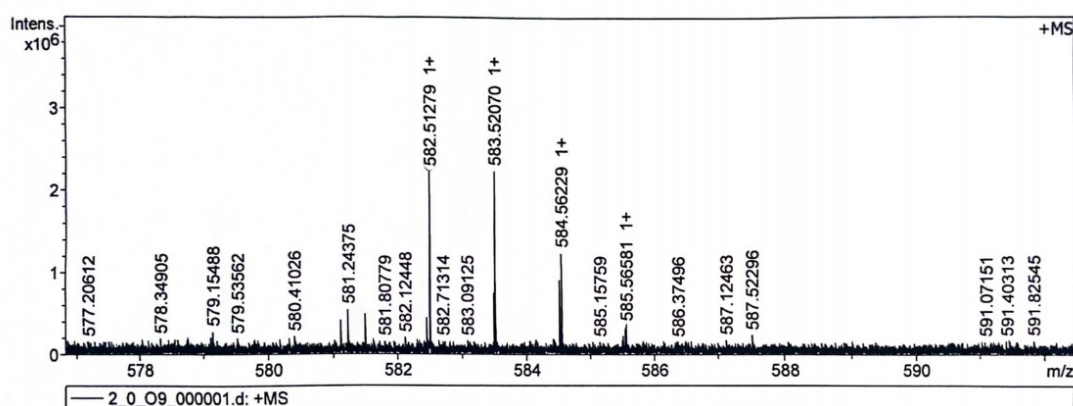
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
836.809031	1	C ₅₆ H ₁₀₄ N ₂ O ₂	100.00	836.809232	0.2	0.8	24.8	6.0	odd	ok

Figure S29 HRMS (MALDI-TOF) of compound 3a



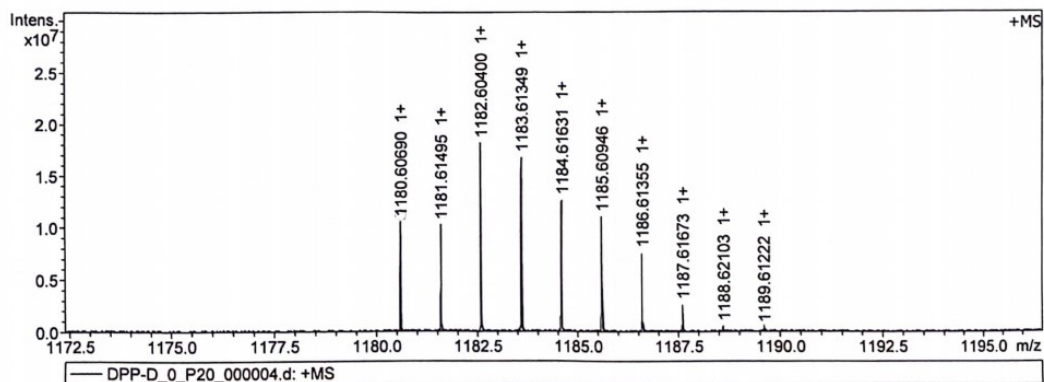
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
668.621894	1	C ₄₄ H ₈₀ N ₂ O ₂	100.00	668.621431	-0.7	-0.3	55.9	6.0	odd	ok

Figure S30 HRMS (MALDI-TOF) of compound 3b



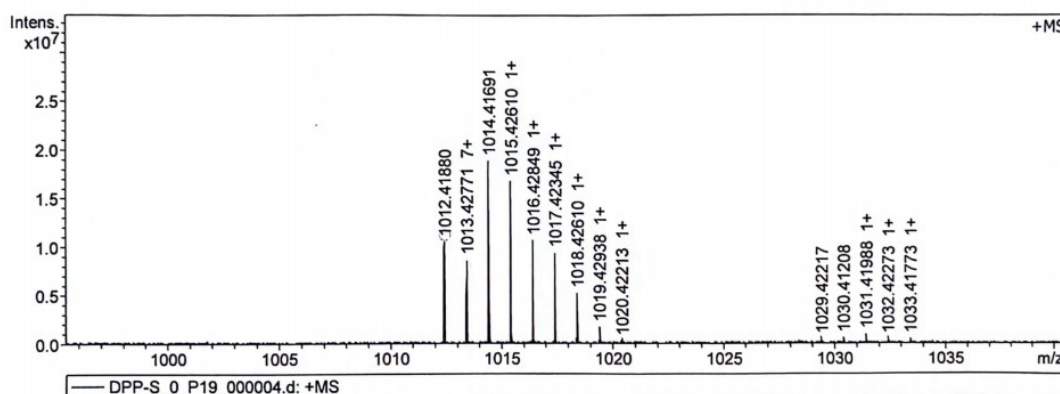
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
582.512786	1	C ₃₈ H ₆₆ N ₂ O ₂	100.00	582.511881	-1.6	-1.3	70.5	7.0	odd	ok

Figure S31 HRMS (MALDI-TOF) of compound 3c



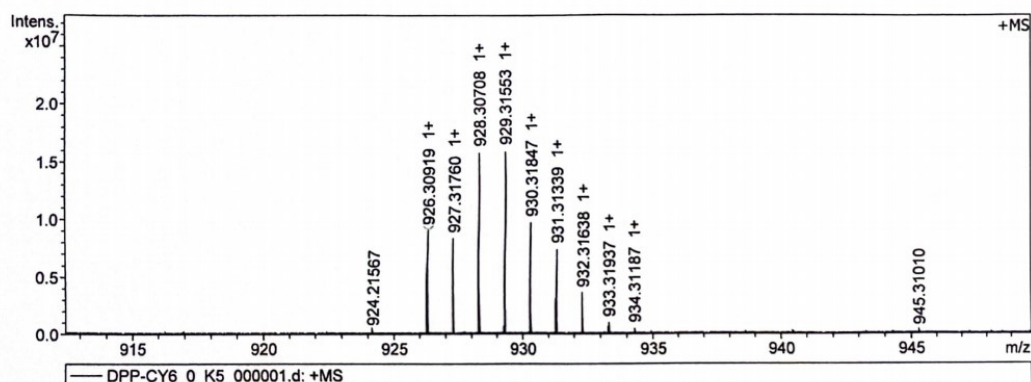
Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
1180.606896	1	C ₆₆ H ₁₀₆ Br ₂ N ₂ O ₂ S ₂	100.00	1180.605698	1.0	-2.0	161.8	14.0	odd	ok

Figure S32 HRMS (MALDI-TOF) of compound 4a



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
1012.418800	1	C ₅₄ H ₈₂ Br ₂ N ₂ O ₂ S ₂	100.00	1012.417897	-0.9	0.2	96.5	14.0	odd	ok

Figure S33 HRMS (MALDI-TOF) of compound 4b



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e ⁻ Conf	N-Rule
926.309192	1	C ₄₈ H ₆₈ Br ₂ N ₂ O ₂ S ₂	100.00	926.308347	0.9	0.2	73.4	15.0	odd	ok

Figure S34 HRMS (MALDI-TOF) of compound 4c

11. Reference

- S1. Feng, D.; Barton, G.; Scott, C. N., Synthesis of 2,5-Dibutyl-3,6-dimethyl-1H,2H,4H,5H-pyrrolo[3,4-c]pyrrole-1,4-dione: A Diketopyrrolopyrrole Scaffold for the Formation of Alkenyldiketopyrrolopyrrole Compounds. *Org. Lett.* **2019**, *21* (7), 1973-1978.
- S2. Wahalathantrige Don, R.; Das, P.; Ma, Z.; Kuruppu, U. M.; Feng, D.; Shook, B.; Gangishetty, M. K.; Stefan, M. C.; Pradhan, N. R.; Scott, C. N., Vinyl-Flanked Diketopyrrolopyrrole Polymer/MoS₂ Hybrid for Donor–Acceptor Semiconductor Photodetection. *Chem. Mater.* **2023**, *35* (12), 4691-4704.
- S3. Hamilton, R.; Smith, J.; Ogier, S.; Heeney, M.; Anthony, J. E.; McCulloch, I.; Veres, J.; Bradley, D. D. C.; Anthopoulos, T. D., High-Performance Polymer-Small Molecule Blend Organic Transistors. *Adv. Mater.* **2009**, *21* (10-11), 1166-1171.