Supporting Information

Influence of heteroatoms on photovoltaic performance of donor-acceptor copolymers based on 2,6-di(thiophen-2-yl)benzo[1,2-b:4,5-b']difurans and diketopyrrolopyrrole.

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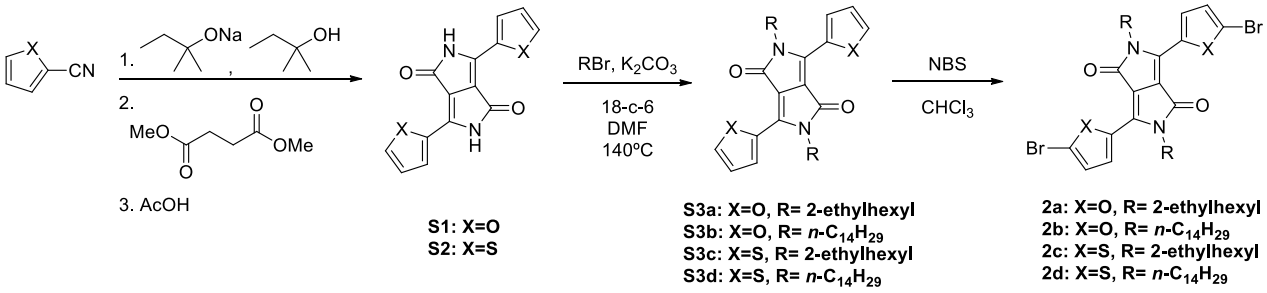
Table of Contents

Synthetic Procedures



Scheme S1. Synthesis of diketopyrrolopyrole monomers.

3,6-Di(furan-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (S1). Sodium metal (4.94 g, 218 mmol) was added portion-wise to *tert*-amyl alcohol and the solution was stirred overnight at 120°C. Furan-2-carbonitrile (20.0 g, 269 mmol) was then added to the hot alkoxide solution followed by the dropwise addition of a solution of dimethyl succinate (11.7 mL, 89 mmol) in 80 mL of *tert*-amyl alcohol. After complete addition of the dimethyl succinate solution, the mixture was allowed to stir at reflux overnight. The reaction mixture was then allowed to cool to 60°C, quenched with 40 mL of acetic acid, and allowed to stir at reflux for an additional hour. The resulting suspension was then filtered and the solid washed with hot methanol and water three times and dried *in vacuo*, affording a dark solid (21.8 g, 91%). Compound **S1** was used in the next step without further purification.

3,6-Di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (S2). The title compound was prepared in a similar manner to **S1** using sodium metal (3.85 g, 173 mmol), thiophene-2-carbonitrile (19.0 mL, 204 mmol) and dimethyl succinate (54 mmol, 0.67 M in *tert*-amyl alcohol) to afford a dark solid (15.1 g, 93%). Compound **S2** was used in the next step without further purification.

General alkylation procedure of DPP cores. The DPP core **S1** or **S2**, K_2CO_3 (4.3 equiv), and catalytic 18-crown-6 were dissolved in DMF under argon and stirred at 130°C for 1h. Alkyl bromide (3.7 equiv) was then added dropwise and the reaction mixture was stirred for 48h. The reaction mixture was then cooled to room temperature and dilute with water. Chloroform was added to the mixture and the layers were separated. The aqueous layer was extracted with chloroform. The combined organic layers were washed with water, dried over sodium sulfate and the solvent removed *in vacuo*. The crude product was purified by flash chromatography on silica, using either chloroform or 1:1 chloroform/hexanes as the eluent to give pure alkylated product.

2,5-bis(2-ethylhexyl)-3,6-di(2-furanyl)-pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (S3a). The title compound was synthesized according to the general alkylation procedure for DPP cores from 2.50 g (9.3 mmol) **S1** and 2-ethylhexyl bromide and purified by flash chromatography on silica using as the 1:1 chloroform/hexanes as the eluent to afford 2.75 g (5.6 mmol) of a tacky red solid in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 3.6, 0.7 Hz, 2H), 7.61 (dd, *J* = 1.7, 0.7 Hz, 2H), 6.69 (dd, *J* = 3.7, 1.7 Hz, 2H), 4.04 (dd, *J* = 7.4, 1.1 Hz, 4H), 1.83 – 1.67 (m, 2H), 1.42 – 1.19 (m, 16H), 0.98 – 0.78 (m, 6H).

3,6-di(2-furanyl)--2,5-ditetradecylpyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (S3b). The title compound was synthesized according to the general alkylation procedure for DPP cores from 3.42 g (13.2 mmol) **S1** and 1-bromotetradecane and purified by flash chromatography on silica using as the 1:1 chloroform/hexanes as the eluent to afford 3.75 g (5.7 mmol) of a tacky red solid in 43% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 3.7, 0.7 Hz, 2H), 7.63 (dd, *J* = 1.7, 0.7 Hz, 2H), 6.70 (dd, *J* = 3.7, 1.7 Hz, 2H), 4.13 – 4.08 (m, 4H), 1.83 – 1.58 (m, 4H), 1.43 – 1.18 (m, 44H), 0.88 (t, *J* = 7.1 Hz, 6H).

2,5-Bis(2-ethylhexyl)-3,6-di(2-thienyl)-pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (S3c). The title compound was synthesized according to the general alkylation procedure for DPP cores from 3.00 g (10.0 mmol) **S2** and 2-ethylhexyl bromide and purified by flash chromatography on silica using chloroform as the eluent to afford 2.29 g (4.3 mmol) of a tacky purple solid in 43% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ

8.89 (dd, *J* = 3.9, 1.2 Hz, 2H), 7.61 (dd, *J* = 5.0, 1.1 Hz, 2H), 7.25 – 7.23 (m, 2H), 4.04 (m, 4H), 1.83 – 1.67 (m, 2H), 1.42 – 1.19 (m, 16H), 0.98 – 0.83 (m, 6H).

2,5-Ditetradecyl-3,6-di(2-thienyl)-pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (S3d). The title compound was synthesized according to the general alkylation procedure for DPP cores from 0.30 g (1.0 mmol) **S2** and 1-bromotetradecane and purified by flash chromatography on silica using chloroform as the eluent to afford 0.18 g (0.26 mmol) of a tacky purple solid in 26% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.89 (dd, *J* = 3.9, 1.2 Hz, 2H), 7.61 (dd, *J* = 5.0, 1.1 Hz, 2H), 7.25 – 7.23 (m, 2H), 4.13 – 4.08 (m, 4H), 1.83 – 1.58 (m, 4H), 1.43 – 1.18 (m, 44H), 0.88 (t, *J* = 7.1 Hz, 6H).

General bromination procedure of DPP cores. Alkylated-DPP was dissolved in chloroform, placed under an argon atmosphere and protected from light. The reaction mixture was then cooled to 0°C and NBS (2.4 equiv) was added portion-wise over 5 minutes. The reaction mixture was warmed to room temperature and stirred for 48h before being quenched with methanol. The solution was then washed with water and the organic layer was dried with sodium sulfate before being concentrated *in vacuo*. The crude product was then purified by flash chromatography on silica, using chloroform as eluent to give pure product.

3,6-Bis(5-bromofuran-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (2a). The title compound was synthesized according to the general bromination procedure of DPP cores from 1.66 g (1.66 g, 3.4 mmol) **S3a** to afford 1.31 g (1.8 mmol) of a dark red solid in 60% yield, (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 3.7 Hz, 2H), 6.62 (d, *J* = 3.7 Hz, 2H), 3.99 (dd, *J* = 7.4, 2.7 Hz, 4H), 1.77 – 1.68 (m, 2H), 1.42 – 1.20 (m, 16H), 0.96 – 0.83 (m, 12H).

3,6-Bis(5-bromofuran-2-yl)-2,5-ditetradecylpyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (2b). The title compound was synthesized according to the general bromination procedure of DPP cores from 1.50 g (2.28 mmol) **S3a** to afford 0.80 g (1.0 mmol) of a dark red solid in 40% yield, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (d, *J* = 3.7 Hz, 2H), 6.63 (d, *J* = 3.7 Hz, 2H), 4.05 (dd, *J* = 8.6, 6.7 Hz, 4H), 1.85 – 1.60 (m, 4H), 1.35 – 1.21 (m, 44H), 0.88 (t, *J* = 7.0 Hz, 6H).

3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (2c). The title compound was synthesized according to the general bromination procedure of DPP cores from 824 mg (1.6 mmol) **S3a** to afford 203 mg (0.3 mmol) of a dark purple solid in 19% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.2 Hz, 2H), 7.16 (d, *J* = 4.2 Hz, 2H), 3.92 – 3.78 (m, 4H), 1.83 – 1.71 (m, 2H), 1.37 – 1.02 (m, 16H), 0.92 – 0.72 (m, 12H).

3,6-Bis(5-bromothiophen-2-yl)-2,5-ditetradecylpyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (2d). The title compound was synthesized according to the general bromination procedure of DPP cores from 536 mg (0.8 mmol) **S3a** to afford 154 mg (0.2 mmol) of a dark purple solid in 25% yield, ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.2 Hz, 2H), 7.24 (d, *J* = 4.2 Hz, 2H), 4.12 – 3.80 (m, 4H), 1.85 – 1.60 (m, 4H), 1.41 – 1.04 (m, 44H), 0.88 (t, *J* = 6.4 Hz, 6H).

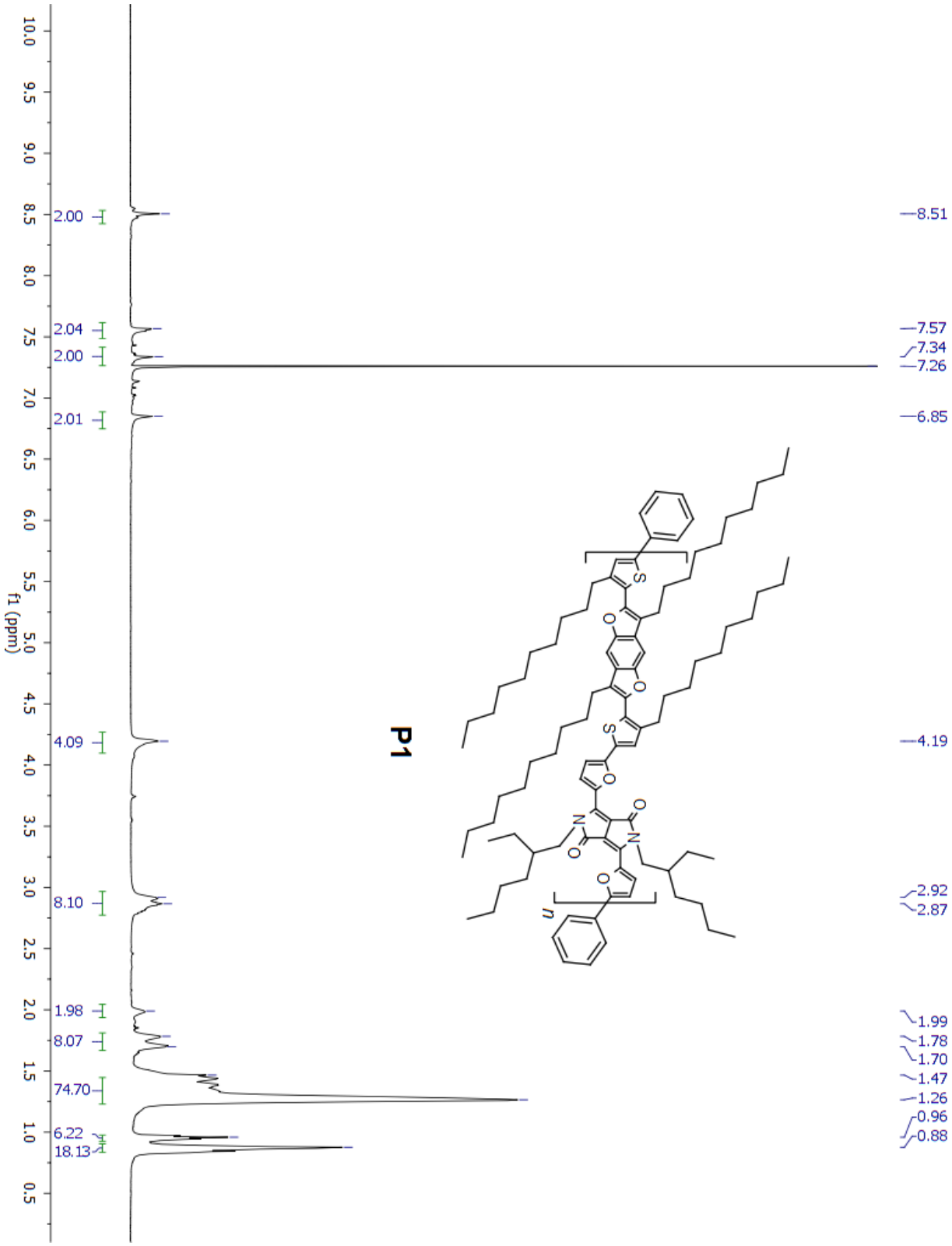


Figure S1. ^{1}H NMR of **P1**

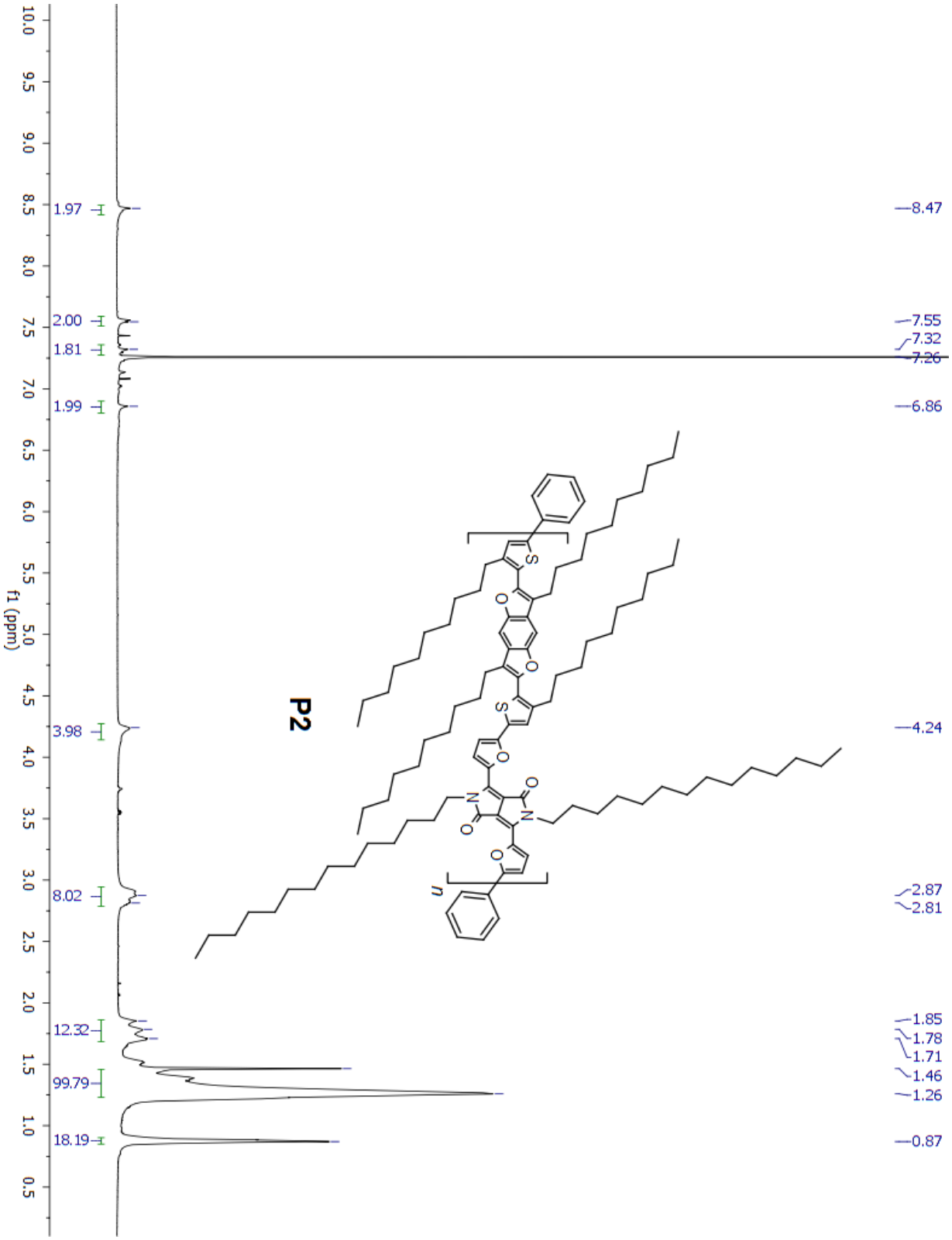


Figure S2. ^{1}H NMR of **P2**

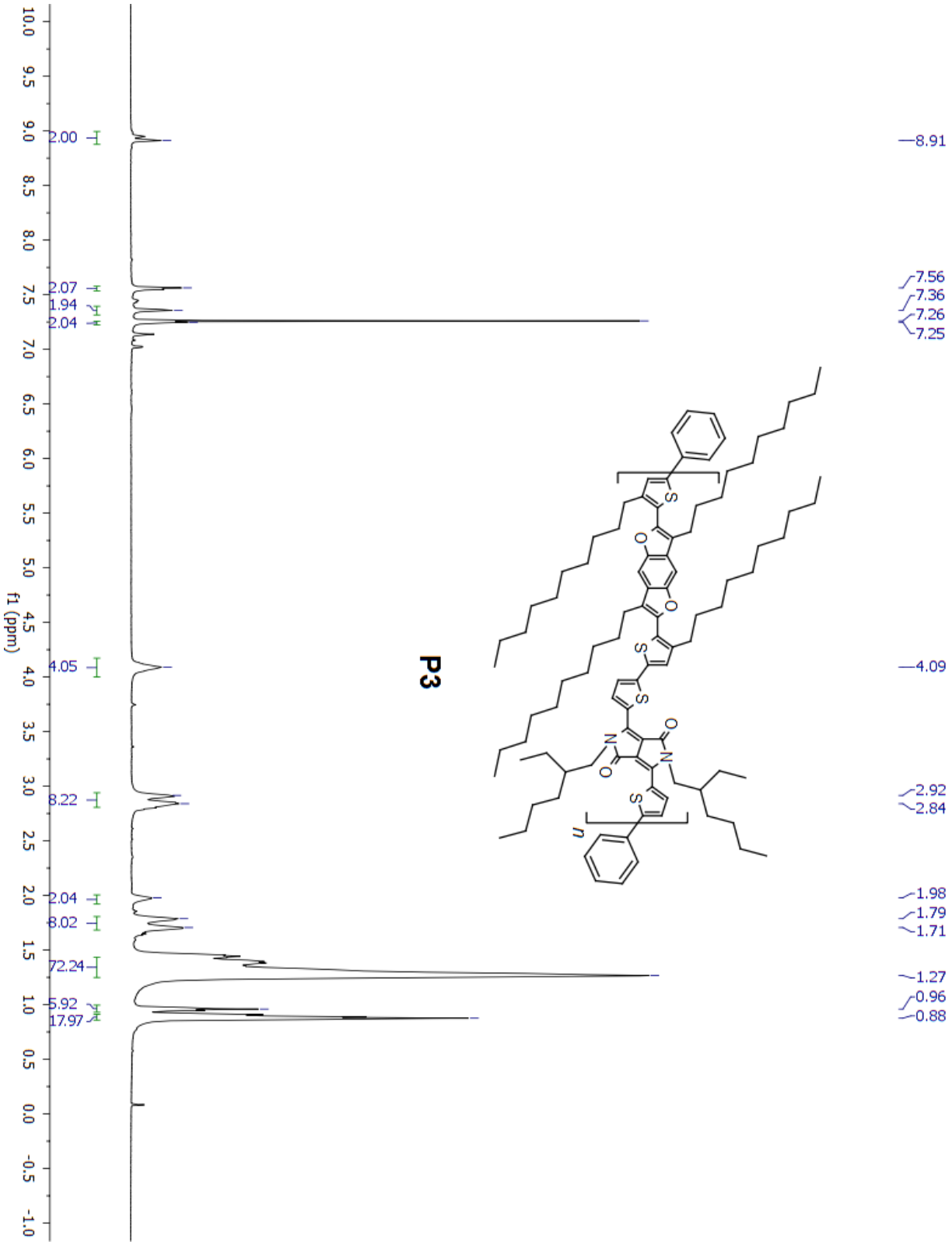


Figure S3. ^{1}H NMR of **P3**

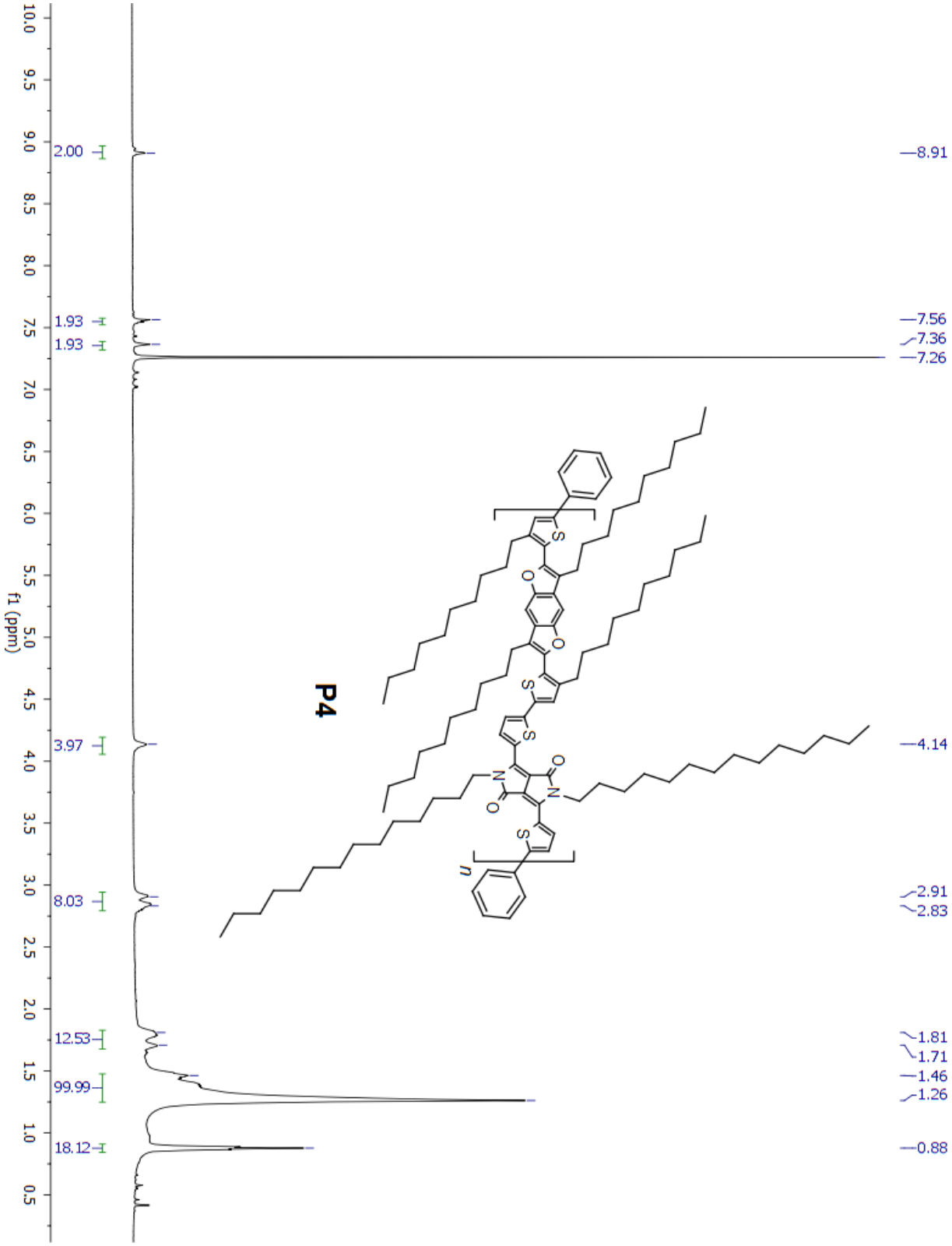


Figure S4. ^{1}H NMR of **P4**

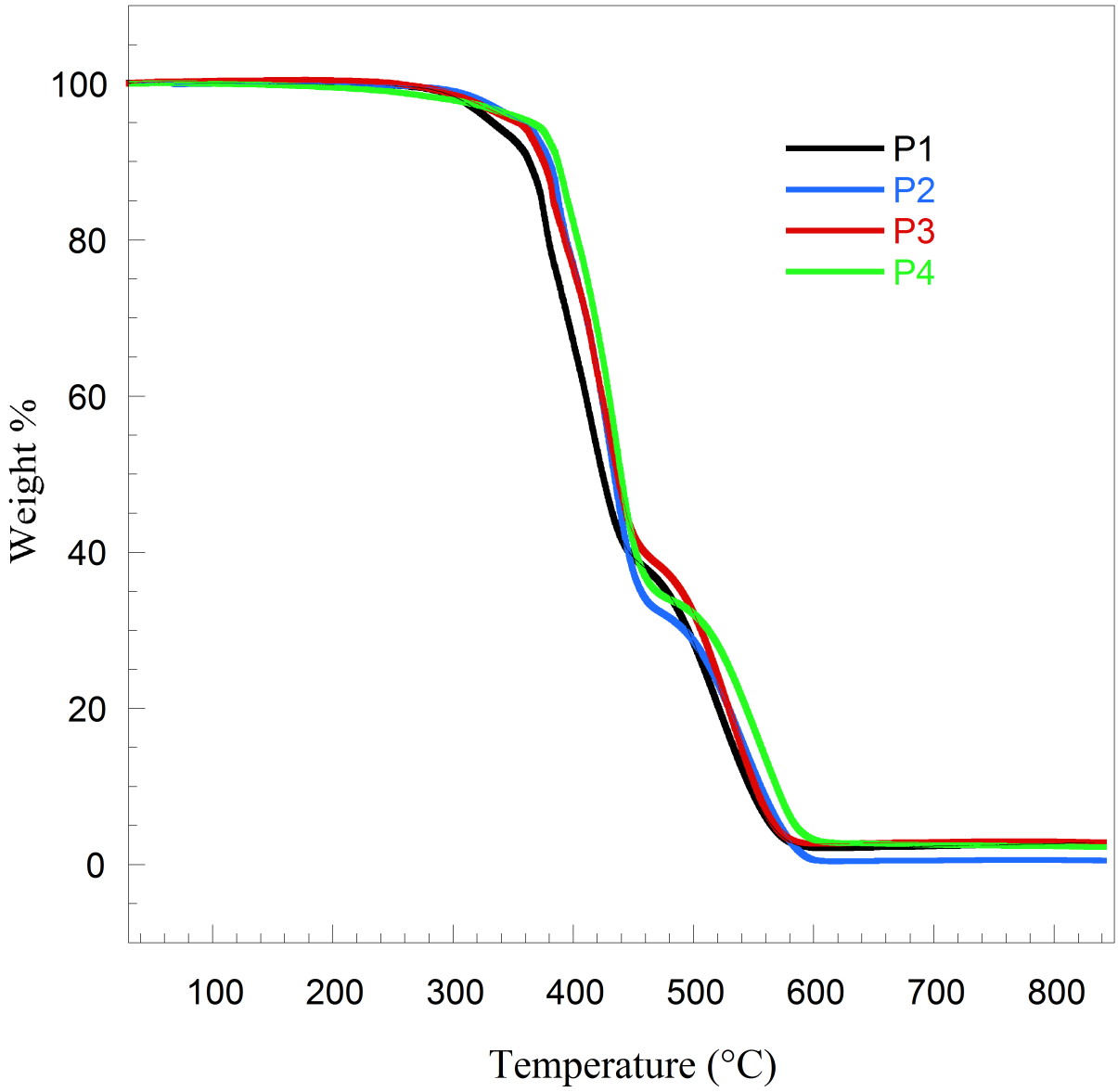


Figure S5. Thermal Gravometric Analysis of **P1-P4**.

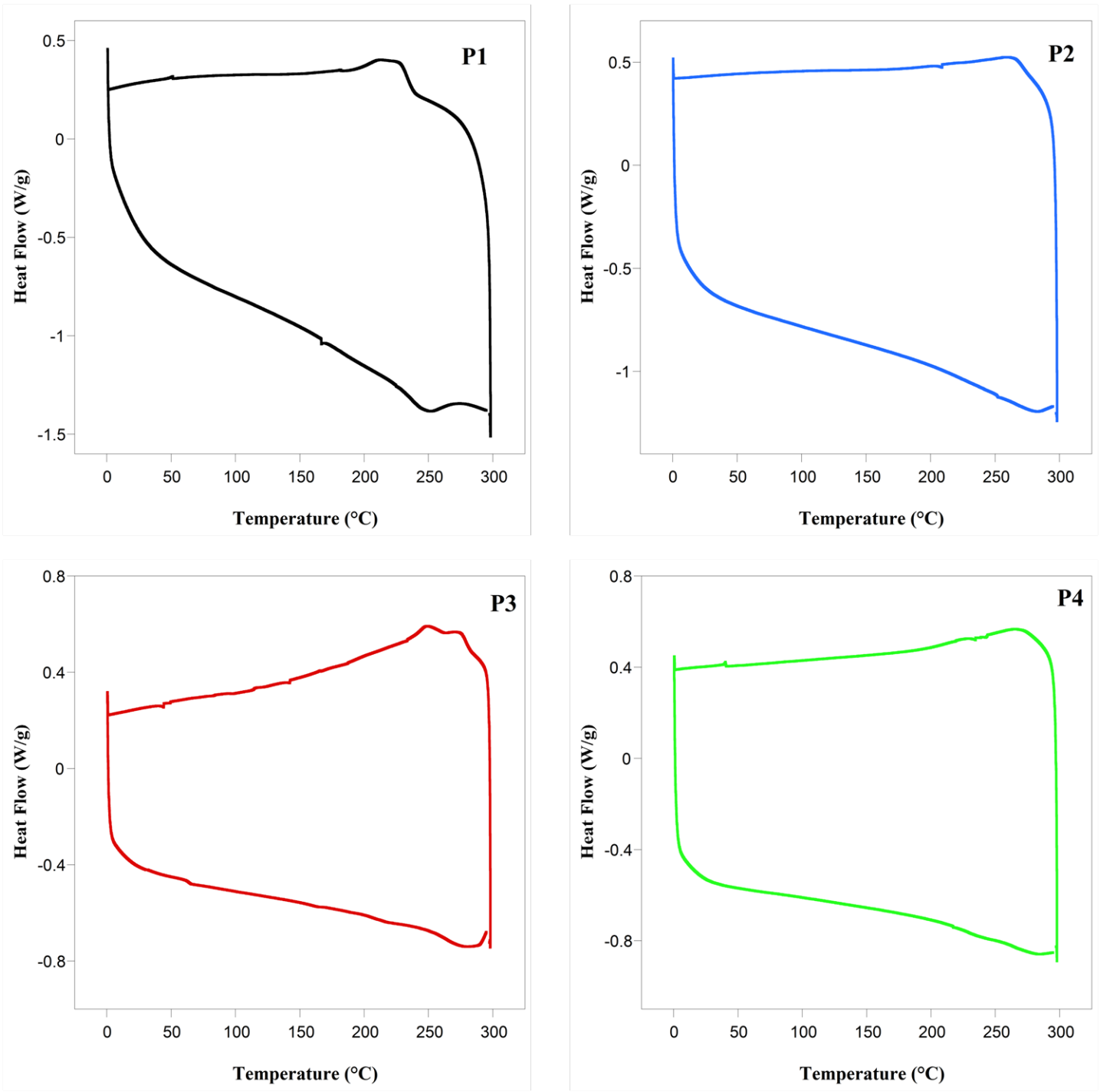


Figure S6. Differential scanning calorimetery (DSC) plots of **P1-P4**.

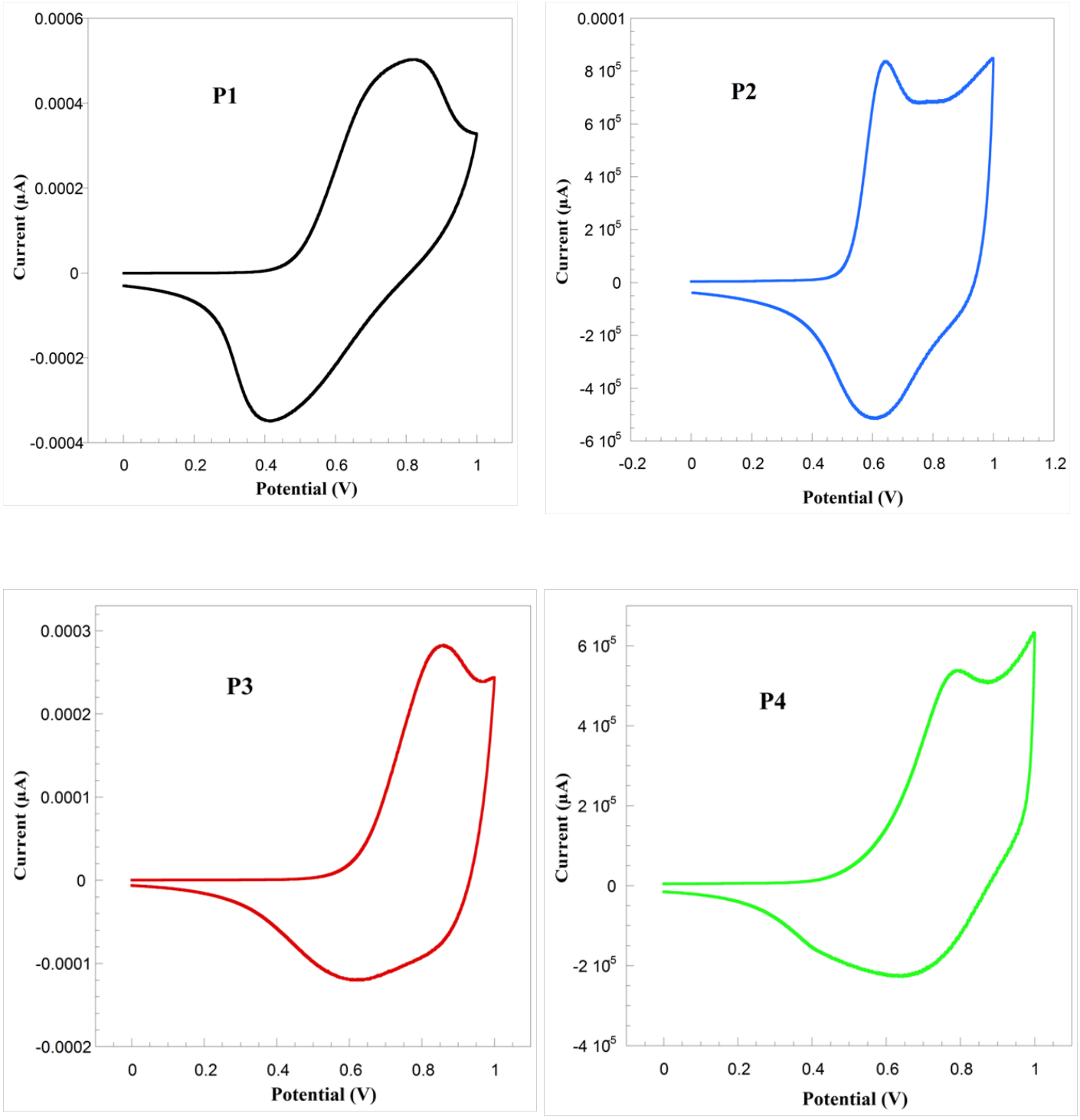


Figure S7. Cyclic voltammetry traces for oxidation cycles of **P1-P4**.

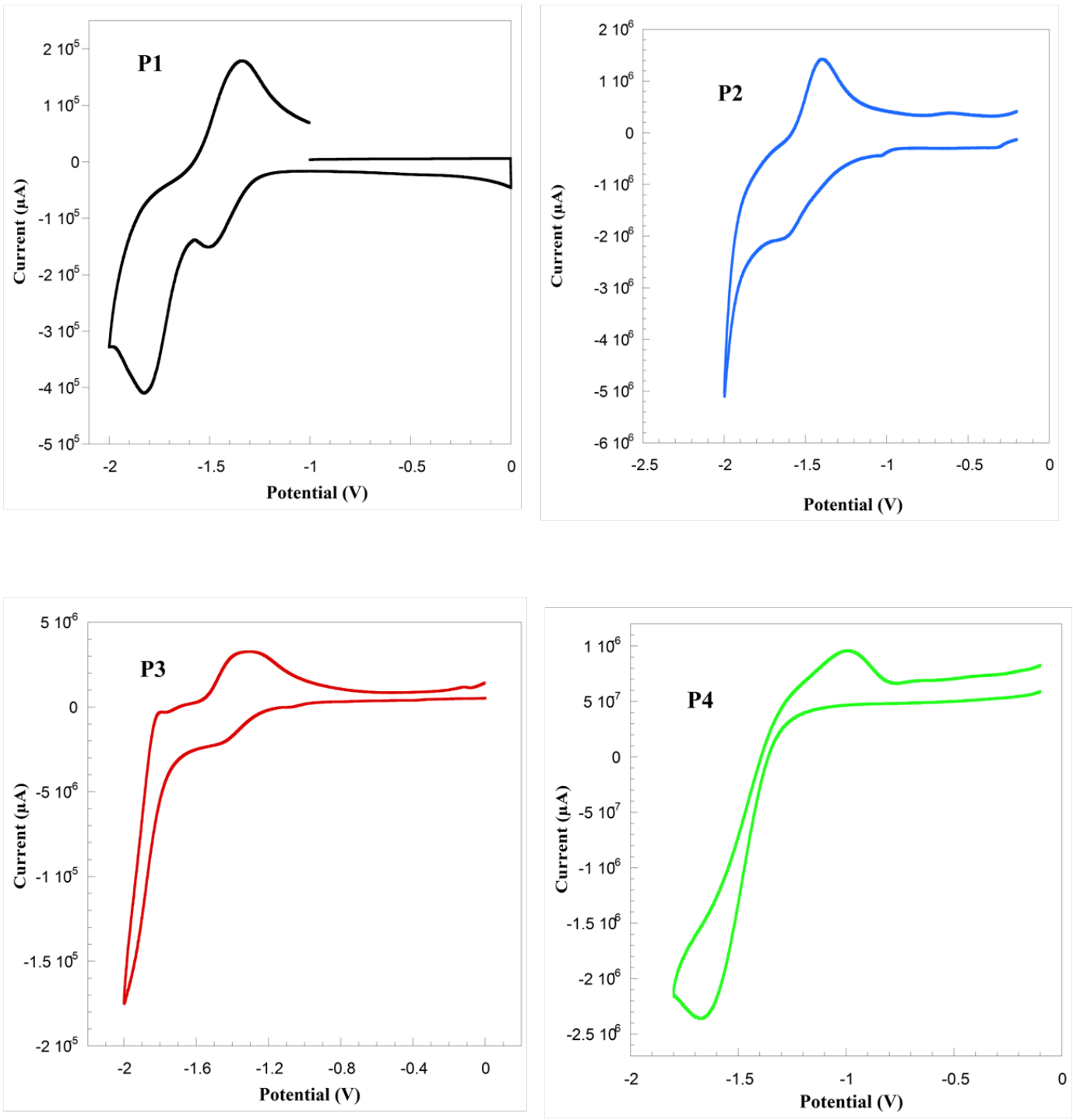


Figure S8. Cyclic voltammetry traces for reduction cycles of **P1-P4**.

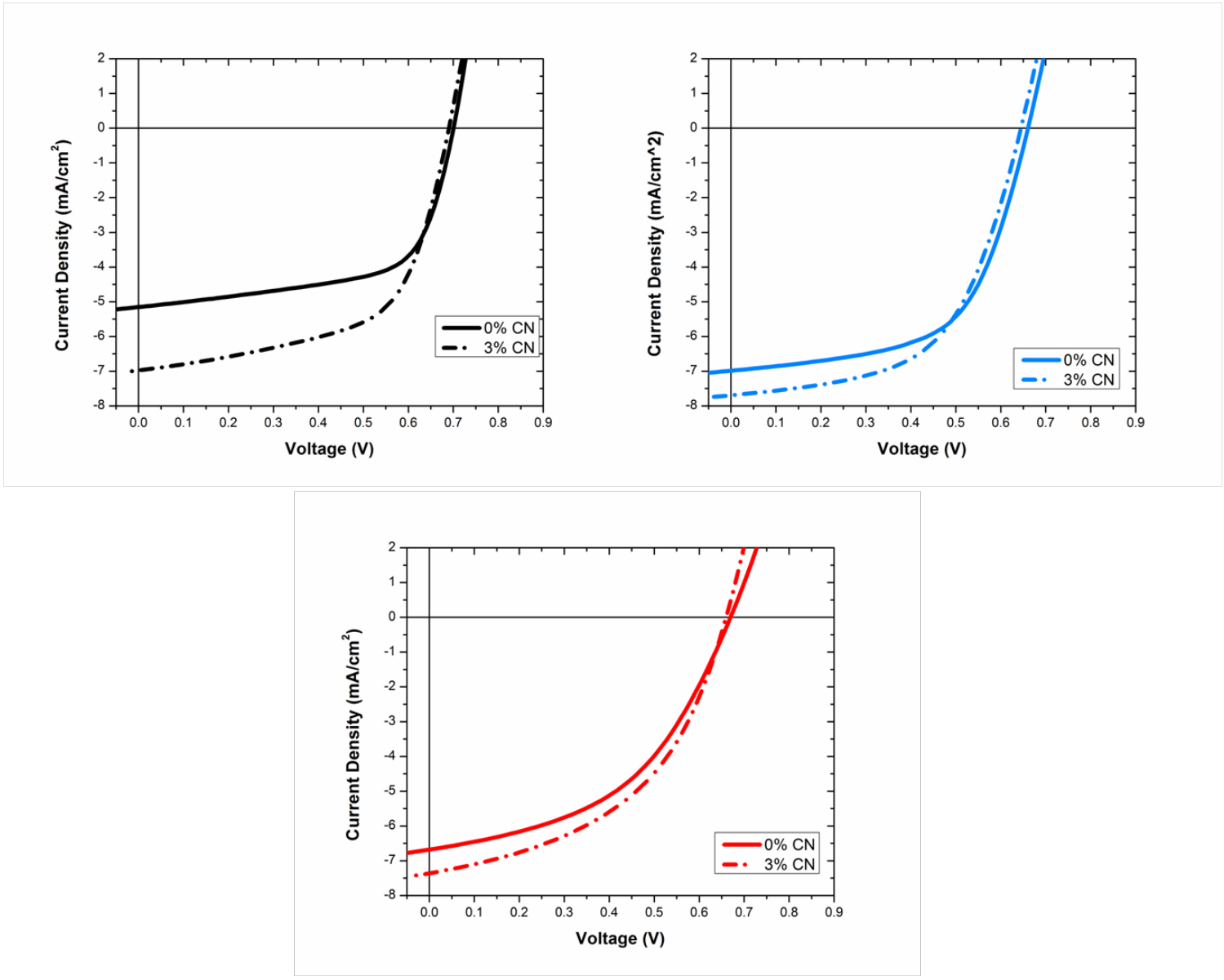


Figure S9. Current-voltage characteristics for polymer OPVs of **P1** (black), **P2** (blue), and **P3** (red) processed with and without 3% chloronapthalene.