

Supporting information

Synthesis of Thiophene-Containing Conjugated Polymers from 2,5-Thiophenebis(boronic ester)s by Suzuki Polycondensation

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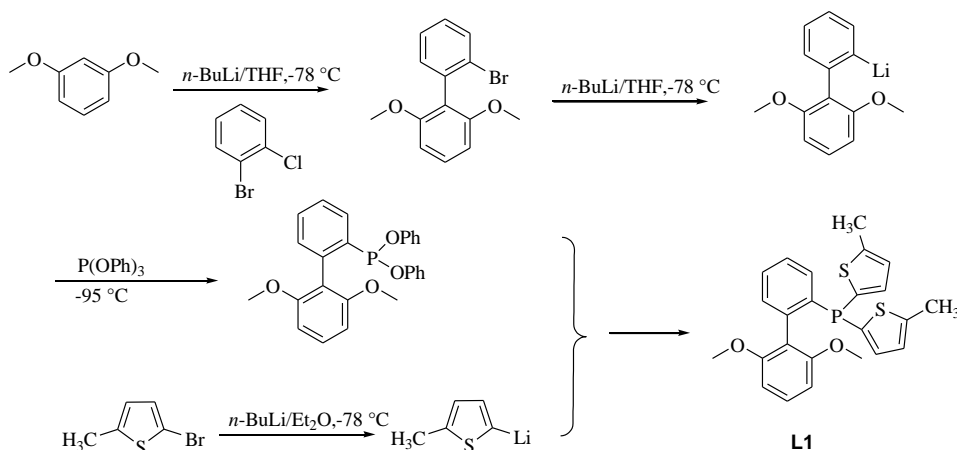
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Materials and Instruments

All chemicals were purchased from commercial suppliers and used without purification. Solvents were dried according to standard procedures. The catalyst precursor Pd(PPh₃)₄, Pd(PTh₃)₃ was prepared according to the literature^[1] and stored in a Schlenk tube under nitrogen. 3-hexylthiophen,^[2] 2,5-dibromo-3-hexyl thiophene,^[3] monomer G4^[4] were prepared according to literature procedure. All reactions were performed under an atmosphere of nitrogen and monitored by TLC with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200-300 mesh). ¹H, ¹³C and ³¹P NMR spectra were recorded on a Bruker DM 300 or AV 400 or AV 500 or AV 600 spectrometer in CDCl₃ or C₆D₆. The gel permeation chromatography (GPC) measurements were performed on a Waters chromatography connected to a Water 410 differential refractometer with THF as an eluent. Elemental analysis was performed on a Flash EA 1112 analyzer.

Synthesis of 2-bis(5-methylthiophen-2-yl)phosphino-2',6'-dimethoxybiphenyl



Scheme S1. Synthesis of Ligand **1**

To a cold (-78 °C), stirred solution of 2-bromo-5-methylthiophene (0.49 g, 5 mmol, 5 equiv) in dry Et₂O (60 mL) was added *n*-BuLi (2 mL, 2.5 M solution in hexanes, 5 mmol, 5 equiv) dropwise via syringe over 3 min. The reaction mixture was allowed to warm to room temperature and then stirred for 2h. The mixture was recooled to -78 °C and neat diphenyl 2-(2',6'-dimethoxybiphenyl)phosphonite (0.43 g, 1 mmol 1.0 equiv) was added in one portion and then stirred under this temperature for 2 h, The reaction mixture was allowed to warm to room temperature. Methanol (0.25 mL) was added via syringe and the resulting mixture was concentrated under reduced pressure at ambient temperature (10-20 °C). After removal of the solvent, the residue was purified by column chromatography on silica gel with petroleum ether (30-60 °C)/THF (10/1) as the eluent. The solvent was concentrated under reduced pressure at ambient temperature (10-20 °C) to afford **L1** (0.15 g, 35 %) as a white solid. ¹H NMR (400 MHz, C₆D₆) δ: 7.90 (ddd, 1H), 7.38 (ddd, 1H), 7.21 (td, 1H), 7.18 (t, 1H), 7.15 (td, 1H), 7.05 (dd, 2H), 6.45 (dd, 2H), 6.38 (d, 2H), 3.21 (s, 6H), 2.08 (s, 6H). ¹³C NMR (100MHz, C₆D₆) δ: 158.5, 145.9, 140.9, 140.6, 139.8, 139.7, 138.1, 137.8, 135.7, 135.4, 132.8, 131.8, 131.7, 129.2, 128.9, 127.9, 127.8, 126.3, 126.2, 119.5, 119.4, 103.9, 55.0, 15.2. ³¹P NMR (121.4 MHz, C₆D₆) δ: 38.0. MS (EI): m/z (%) 439 (M⁺). Anal. Calcd for C₂₄H₂₃PSO₂: C, 65.73, H, 5.29. Found: C, 65.55, H, 5.33.

Synthesis of 2-bromo-2',6'-dimethoxybiphenyl^[5]

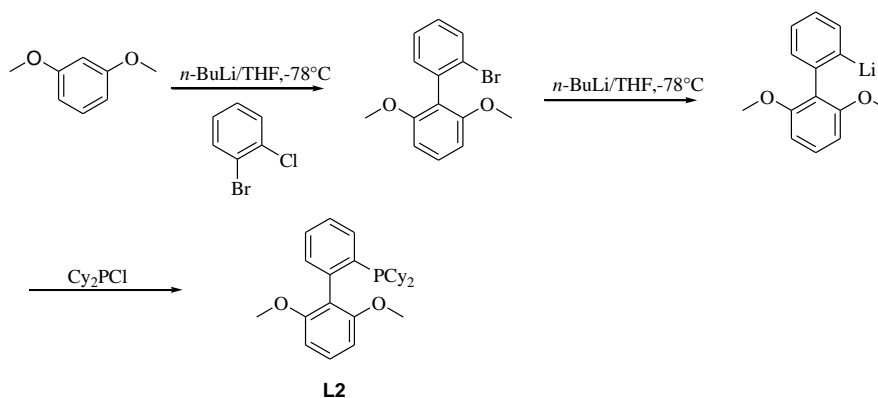
To a cold (0 °C), stirred solution of 1,3-dimethoxybenzene (4 mL, 30.6 mmol, 1.2 equiv) in dry THF (60 mL) was added *n*-BuLi (12.4 mL, 2.5 M solution in hexanes, 30.6 mmol, 1.2 equiv) dropwise via syringe over 5 min. The reaction mixture was allowed to warm to room temperature and then stirred for 5 h. The mixture was re-cooled to 0 °C and neat 2-bromochlorobenzene (3 mL, 25.6 mmol, 1.0 equiv) was added dropwise via syringe over 15 min, then stirred at room temperature over night. Methanol (0.25 mL) was added via syringe and the resulting mixture was concentrated under reduced pressure. Diethyl ether (50 mL) and water (50 mL) was added. The layers were separated and the aqueous phase was extracted with diethyl ether (2 x 25 mL). The combined organic extracts were washed with brine (1 x 20 mL), dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to provide a yellow solid. The crude product was recrystallized from methanol to afford the title compound (6.27 g , 84 %) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ: 7.67 (dd, 1H), 7.34-7.39 (m, 2H), 7.19-7.26 (m, 2H), 6.67 (d, 2H), 3.76 (s, 6H). The spectra were in agreement with those described in the literature.

Synthesis of diphenyl 2-(2',6'-dimethoxybiphenyl)phosphonite^[6]

To a cold (-78 °C), stirred solution of 2-Bromo-2',6'-dimethoxybiphenyl (2.93 g, 10 mmol, 1 equiv) in dry THF (100 mL) was added *n*-BuLi (4.4 mL, 2.5 M solution in hexanes, 11 mmol, 1.1 equiv) dropwise via syringe over 5 min. The resulting suspension was stirred for another 20 min. To the mixture, re-cooled to -95 °C, was added neat P(OPh)₃ (2.48 mL, 9.5 mmol, 0.95 equiv) in THF dropwise via syringe with vigorous stirring to avoid precipitation. The reaction mixture was allowed to warm to room temperature. The reaction was complete after the suspension became a clear solution. H₂O (1 mL) was added via syringe and the resulting mixture was concentrated

under reduced pressure. To the residue diethyl ether (50 mL) and water (50 mL) was added. The layers were separated and the aqueous phase was extracted with diethyl ether (2 x 25 mL). The combined organic extracts were washed with brine (1 x 20 mL), dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to provide a pale yellow solid. The crude product was recrystallized from acetone to afford the title compound (2.63 g, 61 % yield) as a white solid. ¹H NMR (400 MHz, C₆D₆) δ: 8.33 (ddd, 1H), 7.39 (ddd, 1H), 7.29 (td, 1H), 7.22 (td, 1H), 7.16 (t, 1H), 7.02 (d, 4H), 6.95 (t, 4H), 6.78 (t, 2H), 6.37 (d, 2H), 3.20 (s, 6H). ¹³C NMR (100MHz, C₆D₆) δ: 158.61, 156.26, 156.19, 140.34, 140.19, 139.37, 139.01, 131.67, 131.62, 130.82, 129.74, 129.60, 129.55, 127.98, 127.37, 123.20, 120.31, 120.22, 118.05, 117.97, 104.10, 55.22. ³¹P NMR (121.4 MHz, C₆D₆) δ:156.4. Anal. Calcd for C₂₆H₂₃PO₄: C, 72.55. H, 5.39. Found: C, 72.37. H, 5.43. The spectra were in agreement with those described in the literature.

Synthesis of 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl^[5]



Scheme S2. Synthesis of Ligand 2

To a cold (-78 °C), stirred solution of 2-bromo-2',6'-dimethoxybiphenyl (5.28 g, 18 mmol, 1 equiv) in dry THF (100 mL) was added *n*-BuLi (8 mL, 2.5 M solution in hexanes, 20 mmol, 1.1 equiv) dropwise via syringe over 5 min. The resulting mixture was stirred at -78 °C (periodic swirling of the reaction flask by hand was required) as stirring with a magnetic stirrer became

difficult for 30 min. Unpurified chlorodicyclohexylphosphine was then added via syringe. The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h and then allowed to slowly warm to room temperature. The resulting mixture was filtered through a pad of flash silica gel topped with a layer of celite, eluting with ethyl acetate (400 mL). The filtrate was concentrated under reduced pressure to provide a yellow solid. Recrystallization from acetone provided 800 mg of product as white solid. ^1H NMR (400 MHz, CDCl_3) δ : 7.58 (d, 1H), 7.40 (t, 1H), 7.34 (t, 1H), 7.32 (t, 1H), 7.18 (dd, 1H), 6.59 (d, 2H), 3.68 (s, 6H), 1.76 (t, 2H), 1.61-1.70 (m, 10H), 1.05-1.26 (m, 10H). ^{13}C NMR (100 MHz, CDCl_3) δ : 157.6, 142.9, 136.2, 136.1, 132.5, 131.1, 129.0, 128.4, 126.3, 120.1, 103.3, 55.4, 34.2, 34.1, 30.2, 30.1, 29.3, 29.2, 27.7, 27.6, 27.5, 26.7. The spectra were in agreement with those described in the literature.

Synthesis of Using Unpurified Chlorodicyclohexylphosphine^[7]

An dried 250 mL flask was capped with a rubber septum, filled with nitrogen, and then charged with PCl_3 (1.75 mL, 20 mmol) and diethyl ether (60 mL). The solution was cooled to $-40\text{ }^{\circ}\text{C}$ and cyclohexylmagnesium chloride (40 mmol) in diethyl ether [prepared from cyclohexylchloride] (11.8 mL, 0.1 mol) and magnesium turnings (2.64 g, 0.11 mol) in diethyl ether (30 mL) was added dropwise over 15 min. During the addition, a white solid (MgCl_2) precipitated. The mixture was warmed to $0\text{ }^{\circ}\text{C}$ over 2 h, and the solid material was removed with a Schlenk filter and washed with diethyl ether (5 mL) under nitrogen atmosphere. The filtrate and washing were combined and used directly in the reaction described below.

General Procedure A: Pd-Catalyzed ($\text{Pd}_2(\text{dba})_3+1$) Suzuki-Miyaura Coupling of Aryl

Halides with 2-thiopheneboronic Ester or 2,5-thiophenebis(boronic ester)s

A mixture of aryl halides, 2-thiopheneboronic ester or 2,5-thiophenebis(boronic ester)s, THF (16

mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ and **L1** was carefully degassed and charged with nitrogen. The reaction mixture was stirred and refluxed for 40-48 h. Et₂O was then added, the organic layer was separated and dried over Na₂SO₄. The crude product was chromatographically purified on silica gel eluting with petroleum ether (60-90 °C)/acetate ester to provide the title compound.

General Procedure B: Pd-Catalyzed (Pd(PPh₃)₄) Suzuki-Miyaura Coupling of Aryl Halides with 2-thiopheneboronic Ester

A mixture of aryl halides, 2-thiopheneboronic ester, THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd(PPh₃)₄ was carefully degassed and charged with nitrogen. The reaction mixture was stirred and refluxed for 40-48 h. Et₂O was then added, and the organic layer was separated and dried over Na₂SO₄. The crude product was chromatographically purified on silica gel eluting with petroleum ether (60-90 °C)/acetate ester to provide the title compound.

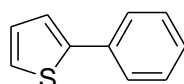
General Procedure C: Pd-Catalyzed (Pd(PTh₃)₃) Suzuki-Miyaura Coupling of Aryl Halides with 2-thiopheneboronic Ester

A mixture of aryl halides, 2-thiopheneboronic ester, THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd(PTh₃)₃ was carefully degassed and charged with nitrogen. The reaction mixture was stirred and refluxed for 40-48 h. Et₂O was then added, and the organic layer was separated and dried over Na₂SO₄. The crude product was chromatographically purified on silica gel eluting with petroleum ether (60-90 °C)/acetate ester to provide the title compound.

General Procedure D: Pd-Catalyzed (Pd₂(dba)₃ +L2) Suzuki-Miyaura Coupling of Aryl Halides with 2-thiopheneboronic Ester or 2,5-thiophenebis(boronic ester)s

A mixture of aryl halides, 2-thiopheneboronic ester or 2,5-thiophenebis(boronic ester)s, THF (16

mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ and **L2** was carefully degassed and charged with nitrogen. The reaction mixture was stirred and refluxed for 40-48 h. Et₂O was then added, the organic layer was separated and dried over Na₂SO₄. The crude product was chromatographically purified on silica gel eluting with petroleum ether (60-90 °C)/acetate ester to provide the title compound.



2-phenylthiophene (3a) (Table 1, Entry 1)

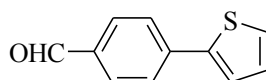
Following general procedure **A**, a mixture of bromobenzene (0.157 g, 1 mmol), 2-thiopheneboronic ester (0.21 g, 1 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (2 mg, 0.4 mo% Pd) and **L1** (5 mg, 1.2 mol%) was carefully degassed and charged with nitrogen. The reaction mixture was stirred and refluxed for 40-48 h. Et₂O was then added, the organic layer was separated and dried over Na₂SO₄. The crude product was chromatographically purified on silica gel eluting with petroleum ether (60-90 °C) to provide the title compound as a white solid (0.15 g, 94 %). ¹H NMR (400 MHz, CDCl₃) δ: 7.61 (d, 2H), 7.38 (t, 2H), 7.31 (d, 1H), 7.25-7.30 (m, 2H), 7.08 (dd, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 144.4, 134.4, 128.9, 128.0, 126.0, 124.8, 123.1. Anal. Calcd for C₁₀H₈S: C, 74.96, H, 5.03. Found: C, 75.22, H, 5.29.

Following general procedure **B**, bromobenzene (0.156 g, 1 mmol, 1 equiv), 2-thiopheneboronic ester (0.21 g, 1 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd(PPh₃)₄ (10 mg, 1 mol % Pd) were used, the product (0.13 g, 84 %) was obtained.

Following general procedure **C**, bromobenzene (0.15 g, 1 mmol, 1 equiv), 2-thiopheneboronic ester (0.21 g, 1 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol),

Pd(PTh₃)₃ (10 mg, 1 mol % Pd) were used, the product (<1 %) was observed.

Following general procedure **D**, bromobenzene (0.1547 g, 1 mmol, 1 equiv), 2-thiopheneboronic ester (0.21 g, 1 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (5 mg, 1 mol % Pd) and **L2** (12 mg, 3 mol %) were used, the product (0.14 g, 88 %) was obtained.



4-(thiophene-2-yl)benzaldehyde (**3b**) (Table 1, Entry 2)

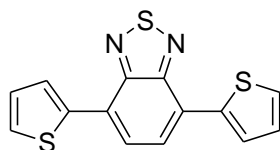
Following general procedure **A**, a mixture of 4-bromobenzaldehyde (0.13 g, 0.71 mmol, 1 equiv), 2-thiopheneboronic ester (0.15 g, 0.71 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (3 mg, 1 mol % Pd) and **L1** (8 mg, 3 mol %) was carefully degassed and charged with nitrogen. The reaction mixture was stirred and refluxed for 40-48 h. Et₂O was then added, the organic layer was separated and dried over Na₂SO₄. The crude product was chromatographically purified on silica gel eluting with petroleum ether (60-90 °C)/ acetate ester (10/1) to provide the title compound as a white solid (0.12 g, 93 %). ¹H NMR (400 MHz, CDCl₃) δ: 10.00 (s, 1H), 7.89 (d, 2H), 7.77 (d, 2H), 7.47 (dd, 1H), 7.39 (dd, 1H), 7.13 (dd, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 191.5, 18142.7, 140.1, 135.1, 130.5, 128.5, 126.9, 126.0, 125.0. Anal. Calcd for C₁₁H₈OS: C, 70.18, H, 4.28. Found: C, 70.13, H, 4.28.

Following general procedure **B**, 4-bromobenzaldehyde (0.13 g, 0.71 mmol, 1 equiv), 2-thiopheneboronic ester (0.15 g, 0.71 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd(PPh₃)₄ (8 mg, 1 mol % Pd) were used, the product (0.11 g, 84 %) was obtained.

Following general procedure **C**, 4-bromobenzaldehyde (0.13 g, 0.71 mmol), 2-thiopheneboronic ester (0.15 g, 0.71 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol),

$\text{Pd}(\text{PTh}_3)_3$ (7 mg, 1 mol % Pd) were used, the product (<1 %) was observed.

Following general procedure **D**, 4-bromobenzaldehyde (0.13 g, 0.71 mmol), 2-thiopheneboronic ester (0.15 g, 0.71 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO_3 (0.35 g, 4 mmol), $\text{Pd}_2(\text{dba})_3$ (5 mg, 1 mol % Pd) and **L2** (10 mg, 3 mol %) were used, the product (0.12 g, 89 %) was obtained.



4,7-di(thiophene-2-yl)benzo[1,2,5]thiadiazole (3c) (Table 1, Entry 3)

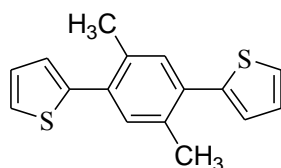
Following general procedure **A**, a mixture of 4,7-dibromobenzo[1,2,5]thiadiazole (0.14 g, 0.48 mmol, 1 equiv), 2-thiopheneboronic ester (0.21 g, 1 mmol, 2.08 equiv), THF (16 mL), water (4 mL), NaHCO_3 (0.35 g, 4 mmol), $\text{Pd}_2(\text{dba})_3$ (2 mg, 0.4 mol% Pd correspond to the quantity of 2-thiopheneboronic ester) and **L1** (5 mg, 1.2 mol %) was carefully degassed and charged with nitrogen. The reaction mixture was stirred and refluxed for 40-48 h. Et_2O was then added, the organic layer was separated and dried over Na_2SO_4 . The crude product was chromatographically purified on silica gel eluting with petroleum ether (60-90 °C)/ CH_2Cl_2 (8/1) to provide the title compound as a red solid (0.136 g, 95 %). ^1H NMR (400 MHz, CDCl_3) δ : 8.12 (d, 2H), 7.88 (s, 2H), 7.46 (d, 2H), 7.22 (t, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 152.8, 139.6, 128.2, 127.7, 127.0, 126.2, 125.9. Anal. Calcd for $\text{C}_{14}\text{H}_8\text{N}_2\text{S}_3$: C, 55.97, H, 2.68, N, 9.32. Found: C, 55.99, H, 2.62, N, 9.03.

Following general procedure **B**, 4,7-dibromobenzo[1,2,5]thiadiazole (0.14 g, 0.48 mmol, 1 equiv), 2-thiopheneboronic ester (0.21 g, 1 mmol, 2.1 equiv), THF (16 mL), water (4 mL), NaHCO_3 (0.35

g, 4 mmol), Pd(PPh₃)₄ (11 mg, 1 mol % Pd correspond to the quantity of 2-thiopheneboronic ester) were used, the product (0.11 g, 78 %) was obtained.

Following general procedure **C**, 4,7-dibromobenzo[1,2,5]thiadiazole (0.14 g, 0.48 mmol, 1equiv), 2-thiopheneboronic ester (0.21 g, 1 mmol, 2.1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd(PTh₃)₃ (10 mg, 1 mol % Pd correspond to the quantity of 2-thiopheneboronic ester) were used, the product (<1 %) was observed.

Following general procedure **D**, 4,7-dibromobenzo[1,2,5]thiadiazole (0.14 g, 0.48 mmol, 1 equiv), 2-thiopheneboronic ester (0.21 g, 1 mmol, 2.1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (5 mg, 1 mol % Pd correspond to the quantity of 2-thiopheneboronic ester) and **L2** (11 mg, 3 mol %) were used, the product (0.14 g, 95 %) was obtained.



2-(2,5-dimethyl-4-(thiophene-2-yl)phenyl)thiophene (3d) (Table 1, Entry 4)

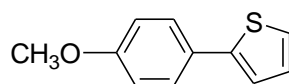
Following general procedure **A**, 1,4-dibromo-2,5-dimethylbenzene (0.132 g, 0.5 mmol, 1.0 equiv), 2-thiopheneboronic ester (0.21 g, 1 mmol, 2 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (5 mg, 1 mol % Pd correspond to the quantity of 2-thiopheneboronic ester) and **L1** (12 mg, 3 mol %) was carefully degassed and charged with nitrogen. The reaction mixture was stirred and refluxed for 40-48 h. Et₂O was then added, the organic layer was separated and dried over Na₂SO₄. The crude product was chromatographically purified on silica gel eluting with petroleum ether (60-90 °C)/ acetate ester (15/1) to provide the title compound as a white solid (0.12 g, 87 %). ¹H NMR (400 MHz, CDCl₃) δ: 7.34-7.36 (m, 2H), 7.33 (s, 2H), 7.10-7.12 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ: 142.7, 133.5, 133.4, 132.7, 127.1, 126.4, 125.2, 20.6. Anal. Calcd

for C₁₆H₁₄S₂: C, 71.07, H, 5.22. Found: C, 71.01, H, 5.25.

Following general procedure **B**, 1,4-dibromo-2,5-dimethylbenzene (0.165 g, 0.6 mmol, 1 equiv), 2-thiopheneboronic ester (0.26 g, 1.24 mmol, 2.1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd(PPh₃)₄ (11 mg, 1 mol % Pd correspond to the quantity of 2-thiopheneboronic ester) were used, the product (0.11 g, 67 %) was obtained.

Following general procedure **C**, 1,4-dibromo-2,5-dimethylbenzene (0.14 g, 0.5 mmol), 2-thiopheneboronic ester (0.22 g, 1.0 mmol, 2.1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd(PTh₃)₃ (10 mg, 1 mol % Pd correspond to the quantity of 2-thiopheneboronic ester) were used, the product (<1 %) was observed.

Following general procedure **D**, 1,4-dibromo-2,5-dimethylbenzene (0.13 g, 0.49 mmol), 2-thiopheneboronic ester (0.21 g, 1.0 mmol, 2.1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (5 mg, 1 mol % Pd correspond to the quantity of 2-thiopheneboronic ester) and **L2** (12 mg, 3 mol %) were used, the product (0.11 g, 83 %) was obtained.



2-(4-methoxyphenyl)thiophene (3e) (Table 1, Entry 5)

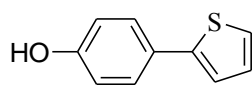
Following general procedure **A**, 1-bromo-4-methoxybenzene (0.154 g, 0.71 mmol, 1.0 equiv), 2-thiopheneboronic ester (0.15 g, 0.71 mmol, 1.0 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (3 mg, 1 mol % Pd) and **L1** (8 mg, 3 mol %) was carefully degassed and charged with nitrogen. The reaction mixture was stirred and refluxed for 40-48 h. Et₂O was then added, the organic layer was separated and dried over Na₂SO₄. The crude product was chromatographically purified on silica gel eluting with petroleum ether (60-90 °C)/acetate ester

(15/1) to provide the title compound as a white solid (0.12 g, 90 %). ^1H NMR (400 MHz, CDCl_3) δ : 7.54 (d, 2H), 7.20 (td, 2H), 7.05 (dd, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 159.1, 127.9, 127.3, 127.2, 123.8, 122.1, 114.2, 55.3. Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{SO}$: C, 69.44, H, 5.30. Found: C, 69.25, H, 5.32.

Following general procedure **B**, 1-bromo-4-methoxybenzene (0.165 g, 0.7 mmol, 1 equiv), 2-thiopheneboronic ester (0.16 g, 0.76 mmol, 1.1 equiv), THF (16 mL), water (4 mL), NaHCO_3 (0.35 g, 4 mmol), $\text{Pd}(\text{PPh}_3)_4$ (8 mg, 1 mol % Pd) were used, the product (0.10 g, 72 %) was obtained.

Following general procedure **C**, 1-bromo-4-methoxybenzene (0.16 g, 0.7 mmol), 2-thiopheneboronic ester (0.16 g, 0.7 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO_3 (0.35 g, 4 mmol), $\text{Pd}(\text{PTh}_3)_3$ (7 mg, 1 mol % Pd) were used, the product (<1 %) was observed.

Following general procedure **D**, 1-bromo-4-methoxybenzene (0.154 g, 0.7 mmol), 2-thiopheneboronic ester (0.15 g, 0.7 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO_3 (0.35 g, 4 mmol), $\text{Pd}_2(\text{dba})_3$ (5 mg, 1 mol % Pd) and **L2** (12 mg, 3 mol %) were used, the product (0.101 g, 75 %) was obtained.



4-(thiophene-2-yl)phenol (**3f**) (Table 1, Entry 6)

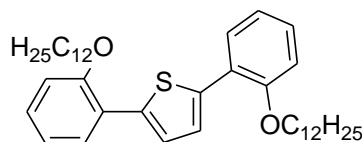
Following general procedure **A**, 4-bromophenol (0.124 g, 0.71 mmol, 1.0 equiv), 2-thiopheneboronic ester (0.15 g, 0.71 mmol, 1 equiv), THF (16 mL), water (4 mL), K_2CO_3 (0.56 g, 4 mmol), $\text{Pd}_2(\text{dba})_3$ (3 mg, 1 mol % Pd) and **L1** (8 mg, 3 mol %) was carefully degassed and charged with nitrogen. The reaction mixture was stirred and refluxed for 40-48 h. Et_2O was then added, the organic layer was separated and dried over Na_2SO_4 . The crude product was

chromatographically purified on silica gel eluting with petroleum ether (60-90 °C)/ acetate ester (8/1) to provide the title compound as a white solid (0.12 g, 93 %). ¹H NMR (400 MHz, CDCl₃) δ: 7.50 (d, 2H), 7.22 (d, 1H), 7.20 (d, 1H), 7.05 (dd, 1H), 6.85 (d, 2H), 4.77 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 155.0, 144.2, 127.9, 127.6, 127.4, 123.9, 122.1, 115.7. Anal. Calcd for C₁₀H₈SO: C, 68.15, H, 4.58. Found: C, 68.01, H, 4.56.

Following general procedure **B**, 4-bromobenzaldehyde (0.13 g, 0.71 mmol, 1 equiv), 2-thiopheneboronic ester (0.15 g, 0.71 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd(PPh₃)₄ (8 mg, 1 mol % Pd) were used, the product (0.11 g, 87 %) was obtained.

Following general procedure **C**, 4-bromobenzaldehyde (0.13 g, 0.71 mmol, 1 equiv), 2-thiopheneboronic ester (0.15 g, 0.71 mmol, 1.1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd(PTh₃)₃ (7 mg, 1 mol % Pd) were used, the product (<1 %) was observed.

Following general procedure **D**, 4-bromobenzaldehyde (0.124 g, 0.71 mmol, 1 equiv), 2-thiopheneboronic ester (0.15 g, 0.71 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (3 mg, 1 mol % Pd) and **L2** (8 mg, 3 mol %) were used, the product (0.10 g, 80 %) was obtained.

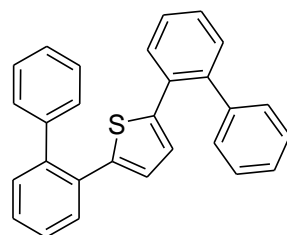


2,5-bis(2-dodecyloxy)phenylthiophene (**3g**) (Table 1, Entry 7)

Following general procedure **A**, a mixture of 1-bromo-2-(dodecyloxy)benzene (0.224 g, 0.66 mmol, 2.0 equiv), 2,5-thiophenebis(boronic ester)s (0.110 g, 0.33 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (3 mg, 2 mol % Pd) correspond to the quantity

of 2,5-thiophenebis(boronic ester)s) and **L1** (8 mg, 6 mol %) was carefully degassed and charged with nitrogen. The reaction mixture was stirred and refluxed for 48 h. Et₂O was then added, the organic layer was separated and dried over Na₂SO₄. The crude product was chromatographically purified on silica gel eluting with petroleum ether (60-90 °C)/ acetate ester (15/1) to provide the title compound as a yellow solid (0.17 g, 87 %). ¹H NMR (500 MHz, CDCl₃) δ: 7.68 (d, 2H), 7.52 (s, 2H), 7.20 (t, 2H), 6.96 (t, 2H), 6.95 (d, 2H), 4.07 (t, 4H), 1.87-1.94 (m, 4H), 1.49-1.56(m, 4H), 1.24-1.36 (m, 32), 0.87 (t, 6H); ¹³C NMR (125 MHz, CDCl₃) δ: 155.2, 139.3, 128.2, 128.0, 125.5, 123.7, 120.7, 112.4, 68.8, 31.9, 29.67, 29.64, 29.48, 29.38, 29.33, 26.3, 22.7, 14.1. Anal. Calcd for C₄₀H₆₀SO₂: C, 79.41, H, 10.00. Found: C, 79.14, H, 9.88.

Following general procedure **D**, a mixture of 1-bromo-2-(dodecyloxy)benzene (0.147 g, 0.42 mmol, 2.0 equiv), 2,5-thiophenebis(boronic ester)s (0.0723 g, 0.21 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (3 mg, 2 mol % Pd correspond to the quantity of 2,5-thiophenebis(boronic ester)s) and **L2** (7 mg, 6 mol %) was used, the product (56 mg, 38 %) was obtained.



2,5-bis[(1,1'-biphenyl)-2-yl] thiophene (3h) (Table 1, Entry 8)

Following general procedure **A**, a mixture of 2-Bromobiphenyl (0.193 g, 0.83 mmol, 2.0 equiv), 2,5-thiophenebis(boronic ester)s (0.139 g, 0.414 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (3 mg, 1.4 mol % Pd correspond to the quantity of

2,5-thiophenebis(boronic ester)s) and **L1** (7 mg, 4 mol %) was carefully degassed and charged with nitrogen. The reaction mixture was stirred and refluxed for 48 h. Et₂O was then added, the organic layer was separated and dried over Na₂SO₄. The crude product was chromatographically purified on silica gel eluting with petroleum ether (60-90 °C)/ acetate ester (15/1) to provide the title compound as a yellow solid (0.14 g, 89 %). ¹H NMR (500 MHz, CDCl₃) δ: 7.37-7.39 (m, 2H), 7.25-7.26 (m, 6H), 7.19-7.22 (m, 6H), 7.13-7.16 (m, 4H), 6.29(s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ:141.99, 140.36, 139.70, 132.03, 129.69, 129.24, 128.56, 126.90, 126.61, 126.39, 126.08, 125.88. Anal. Calcd for C₂₈H₂₀S: C, 86.56, H, 5.19. Found: C, 86.30, H, 5.28.

Following general procedure **D**, a mixture of 2-Bromobiphenyl (0.145 g, 0.62 mmol, 2.0 equiv), 2,5-thiophenebis(boronic ester)s (0.104 g, 0.31 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (3 mg, 2 mol % Pd correspond to the quantity of 2,5-thiophenebis(boronic ester)s) and **L2** (8 mg, 6 mol %) was used, the product (53 mg, 28 %) was obtained.

Synthesis of the monomer and the polymer

1,4-dibromo-2,5-bis(dodecyloxy)benzene (**M1a**)

A mixture of 2,5-dibromobenzene-1,4-diol (1.34 g, 5 mmol, 1 equiv), 1-bromododecane (2.74 g, 11 mmol, 2.2 equiv) and K₂CO₃ (2.76 g, 20 mmol, 4 equiv) in 150 mL butanone was carefully degassed and charged with nitrogen. The reaction mixture was stirred at refluxing for one day. Ethyl acetate and H₂O was then added, the organic layer was separated and dried over Na₂SO₄. After the removal of the solvent, the crude product was chromatographically purified on silica gel eluting with petroleum ether (60-90 °C)/acetate ester (15/1) to provide the title compound 1,4-dibromo-2,5-bis(dodecyloxy)benzene as a White solid (2.78 g, 92 %). ¹H NMR (400 MHz,

CDCl_3) δ : 7.08 (s, 2H), 3.94 (t, 4H), 1.76-1.83 (m, 4H), 1.44-1.51(m, 4H), 1.26-1.32 (m, 32H), 0.88 (t, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 150.08, 118.49, 111.14, 70.32, 31.91, 29.64, 29.63, 29.56, 29.53, 29.34, 29.28, 29.11, 25.92, 22.68, 14.11. The spectra were in agreement with those described in the literature.

1,4-bis(2-hexyldecyloxy)-2,5-dibromobenzene (M1b)

A mixture of 2,5-dibromobenzene-1,4-diol (1.50 g, 5.60 mmol, 1 equiv) , 7-(bromomethyl)pentadecan (5.18 g, 17 mmol, 3 equiv) and K_2CO_3 (3.04 g, 22 mmol, 4 equiv) in 150 mL butanone was carefully degassed and charged with nitrogen. The reaction mixture was stirred at refluxing for 2 days. Ethyl acetate and H_2O was then added, the organic layer was separated and dried over Na_2SO_4 . After the removal of the solvent, the crude product was chromatographically purified on silica gel eluting with petroleum ether (60-90 °C)/acetate ester (15/1) to provide the title compound 1,4-bis(2-hexyldecyloxy)-2,5-dibromobenzene as an oil (2.78 g, 76 %). ^1H NMR (400 MHz, CDCl_3) δ : 7.07 (s, 2H), 3.81 (d, 4H), 1.78-1.81 (m, 2H), 1.28-1.49(m, 48H), 0.87-0.90 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ : 151.1, 119.1, 112.0, 73.9, 38.9, 32.8, 32.7, 32.2, 30.9, 30.6, 30.5, 30.2, 27.7, 27.6, 23.6, 15.0. The spectra were in agreement with those described in the literature.

2,5-thiophenebis(boronic ester)s (M2)

At -78°C , stirred 2,5-dibromo-thiophene (5.2 g, 21 mmol, 1equiv) in THF (150 mL), *n*-BuLi (2.5 M, 22 mL, 2.4 equiv) was added dropwise via syringe, the mixture was kept stirring for 2-3 h at the same temperature and then $\text{B}(\text{O-}i\text{-Pr})_3$ (27 mL, 5equiv) was added, the reaction was allowed to warm the room temperature. Ether and H_2O was then added, the organic layer was separated and dried over Na_2SO_4 . The crude product was chromatographically purified on silica gel eluting with

petroleum ether (60-90 °C)/acetate ester (3/1) to provide the compound 2,5-thiophenediboronic acid as a white solid. The solid and 2, 3-dimethylbutane-2, 3-diol (5.01 g, 2 equiv) were resolved in CH₂Cl₂, the reaction mixture stirred at 30-40 °C for 2 h. After the removal of the solvent, The crude product was chromatographically purified on silica gel eluting with petroleum ether (60-90 °C)/acetate ester (10/1) to provide the title compound 2,5-thiophenebis(boronic ester)s in the total yield of 68 % (4.8 g) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ: 7.66 (s, 2H), 1.34 (s, 24H). The spectra were in agreement with those described in the literature.

Monomer: 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene (M3)

A mixture of 2,7-dibromofluorene (9.72 g, 30mmol, 1 equiv) and *t*-BuOK (7.4 g, 66 mmol, 2.2 equiv) in 100 mL THF was carefully degassed and charged with nitrogen. 3-(bromomethyl)heptane (12.74 g, 66 mmol, 2.2 equiv) was added via syringe .The reaction mixture was stirred at room temperature for 3 days. Ethyl acetate and H₂O was then added, the organic layer was separated and dried over Na₂SO₄. After the removal of the solvent, the residue was recrystallised in the mixture of ethyl acetate and petroleum ether. White solid was obtained in the yield of 88 % (14.5 g). ¹H NMR (400 MHz, CDCl₃) δ: 7.44-7.53 (m, 6H), 1.93 (d, 4H), 0.45-0.91 (m, 30H). The spectra were in agreement with those described in the literature.

Monomer: 3-hexyl-thienylene-2,5-diboronic ester (M4)

At -78°C, stirred 2,5-dibromo-3-hexylthiophene (1.05g, 3.2 mmol, 1equiv) in THF (150 mL), *n*-BuLi (2.5 M, 3.1 mL, 2.4 equiv) was added dropwise via syringe, the mixture was kept stirring for 2-3 h at the same temperature and then B(O-*i*-Pr)₃ (3.7 mL, 5 equiv) was added, the reaction was allowed to warm the room temperature. Ether and H₂O was then added, the organic layer was separated and dried over Na₂SO₄. The crude product was chromatographically purified on silica

gel eluting with petroleum ether (60-90 °C)/acetate ester (3/1) to provide the compound 3-hexyl-2,5-thiophenediboronic acid as a white solid. The solid and 2,3-dimethylbutane-2,3-diol were resolved in CH₂Cl₂, the reaction mixture stirred at 30-40 °C for 2 h. After the removal of the solvent, The crude product was chromatographically purified on silica gel eluting with petroleum ether (60-90 °C)/acetate ester (10/1) to provide the title compound 3-hexyl-2,5-thiophenebis(boronic ester)s in the total yield of 25 % (0.33 g) as an oil. ¹H NMR (400 MHz, C₆D₆) δ: 7.93 (s, 1H), 3.13 (t, 2H), 1.65-1.73 (m, 2H), 1.33-1.40 (m, 2H), 1.24-1.28 (m, 4H), 1.06 (s, 24H), 0.87 (t, 3H). ¹³C NMR (100 MHz, CDCl₃) δ: 155.3, 139.8, 84.2, 83.8, 32.0, 31.9, 30.1, 29.2, 25.0, 22.8, 14.3. Anal. Calcd for C₂₂H₃₈B₂SO₄: C, 62.88, H, 9.11. Found: C, 63.57, H, 9.10.

General Procedure for the Polycondensation:

Polymer: A mixture of fluorene halide or aryl halide, 2,5-thiophenebis(boronic ester)s or 3-hexyl-2,5-thiophenebis(boronic ester)s, THF, water, NaHCO₃, catalyst was carefully degassed and charged with nitrogen. The reaction mixture was stirred and refluxed for 3 days. THF was then added, the organic layer was separated and dried over Na₂SO₄. After the removal the solvent, the residue was dissolved in a minimum amount of THF and precipitated into methanol. The former precipitate was collected by filtration to give the polymers.

P1a as red solid. See general procedure for SPC. ¹H NMR (400 MHz, CDCl₃) δ: 7.54 (s, 2H), 7.33(s, 2H), 4.10(d, 4H), 1.93(m, 4H), 1.26-1.54(m, 36H), 0.87(t, 6H). ¹³C NMR (150 MHz, CDCl₃) δ: 150.07, 139.30, 126.69, 122.95, 112.81, 70.30, 38.37, 31.92, 29.11-29.66 (m), 25.93, 22.69, 14.12. Anal. Calcd for (C₃₄H₅₄O₂S)_n: C, 77.51, H, 10.33. Found C, 76.78, H, 9.23

P1b as red oil. See general procedure for SPC. ¹H NMR (400 MHz, CDCl₃) δ: 7.60(s, 2H), 7.33(s,

2H), 4.03(d, 4H), 1.93(m, 2H), 1.27-1.63(m, 48H), 0.85(t, 12H). ^{13}C NMR (150 MHz, CDCl_3) δ : 149.64, 139.05, 125.97, 122.81, 112.13, 71.76, 38.37, 31.91-29.38 (m), 27.01-26.88(m), 22.68, 14.10. Anal. Calcd for $(\text{C}_{42}\text{H}_{70}\text{O}_2\text{S})_n$: C, 78.94, H, 11.04. Found: C, 75.15, 10.54.

P2 as green solid. See general procedure for SPC. ^1H NMR (400 MHz, CDCl_3) δ : 7.68-7.87 (m, 2H), 7.62 (s, 2H), 7.48(d, 2H), 7.25(s, 1H), 0.51-2.68 (br, 47H). ^{13}C NMR (150 MHz, CDCl_3) δ : 151.5, 151.1, 142.8, 140.3, 139.6, 138.0, 132.9, 128.1, 125.4, 124.9, 124.5, 121.0, 119.9, 119.7, 55.1, 44.94, 34.8, 33.8, 31.8, 31.2, 29.4, 28.4, 28.2, 27.2, 27.0, 22.8, 22.8, 14.1, 10.4. Anal. Calcd for $(\text{C}_{39}\text{H}_{54}\text{S})_n$: C, 84.11, H, 10.14. Found: C, 80.48, H, 9.45.

Polymer P3

A mixture of 2,7-dibromo-9,9-dioctyldibenzosilole (287 mg, 0.51 mmol), 2,5-thiophenebis(boronic ester)s (173 mg, 0.51 mmol) and Aliquat336 (42 mg) was degassed with N_2 before 3.5 ml of toluene was added. Then, $\text{Pd}(\text{PPh}_3)_4$ (8 mg) and 2M aqueous sodium carbonate solution (1.0 ml), which had been degassed for 1 h, was added under N_2 . The mixture was stirred vigorously, and heated at reflux for 2 days. The highly viscous reaction mixture was next poured into boiling acetone (8 mL), precipitating a green polymer. The polymer was collected by filtration and washed with acetone, methanol, water, and dried in vacuum. The polymer was next dissolved in trichlorobenzene and reprecipitated with 100 mL methanol two times to give 153 mg of final pure green polymer (62%). ^1H NMR (500 MHz, CDCl_3) δ : 7.41-7.73 (8H, broad), 0.86-1.41(34H, m).

PG4 A mixture of monomer **G4** (1061.9 mg, 0.30 mmol), 2,5-thiophenebis(boronic ester)s (100.82 mg, 0.30 mmol), THF (50 mL), water (10 mL), NaHCO_3 (1.0 g), $\text{Pd}_2(\text{dba})_3$ (3 mg, 2 mol Pd %) and **L1** or **L2** (8 mg, 6 mol %) was carefully degassed and charged with nitrogen. The

reaction mixture was stirred and refluxed for 3 days. THF was then added, and the organic layer was separated and dried over Na_2SO_4 . After the removal the solvent, the residue was dissolved in a minimum amount of THF and precipitated into methanol. The former faint yellow precipitate was collected by filtration to give the polymers ($\text{Pd}_2(\text{dba})_3$ + **L1**, 999 mg, 96 %; $\text{Pd}_2(\text{dba})_3$ + **L2**, 985 mg, 95%). ^1H NMR (500 MHz, CDCl_3) δ : 7.19(br, 84H), 6.49(br, 28H), 6.38(br, 14H), 6.16(br, 3H), 4.66-4.74(br, 62H), 2.19(br, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ : 159.9, 139.2, 136.7, 128.4, 127.8, 127.5, 106.2, 101.4, 69.8. Anal. Calcd for $(\text{C}_{228}\text{H}_{194}\text{O}_{31}\text{S})_n$: C, 79.10, H, 5.65. Found C, 78.59, H, 5.62.

Table 2, Entry 1: 1,4-dibromo-2,5-bis(dodecyloxy)benzene (0.181 g, 0.3 mmol, 1 equiv), 2,5-thiophenebis(boronic ester)s (0.101 g, 0.3 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO_3 (0.35 g, 4 mmol), $\text{Pd}_2(\text{dba})_3$ (3 mg, 2 mol % Pd) and **L1** (8 mg, 6 mol %) were used, the product (0.145 g, 92 %) was obtained.

Table 2, Entry 2: 1,4-dibromo-2,5-bis(dodecyloxy)benzene (0.181 g, 0.3 mmol, 1 equiv), 2,5-thiophenebis(boronic ester)s (0.101 g, 0.3 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO_3 (0.35 g, 4 mmol), $\text{Pd}_2(\text{dba})_3$ (3 mg, 2 mol % Pd) and **L2** (7 mg, 6 mol %) were used, the product (0.12 g, 76 %) was obtained.

Table 2, Entry 3: 1,4-dibromo-2,5-bis(dodecyloxy)benzene (0.181 g, 0.3 mmol, 1 equiv), 2,5-thiophenebis(boronic ester)s (0.101 g, 0.3 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO_3 (0.35 g, 4 mmol), $\text{Pd}(\text{PPh}_3)_4$ (7 mg, 2 mol % Pd) were used, the product (0.097 g, 61 %) was obtained.

Table 2, Entry 4: 1,4-dibromo-2,5-bis(dodecyloxy)benzene (0.181 g, 0.3 mmol, 1 equiv), 2,5-thiophenebis(boronic ester)s (0.101 g, 0.30 mmol, 1 equiv), THF (16 mL), water (4 mL),

NaHCO₃ (0.35 g, 4 mmol), Pd(PTh₃)₃ (10 mg, 3 mol % Pd) were used, no polymer was obtained.

Table 2, Entry 5: 1,4-bis(2-hexyldecyloxy)-2,5-dibromobenzene (**8**) (0.20 g, 0.28 mmol, 1 equiv), 2,5-thiophenebis(boronic ester)s (0.094 g, 0.28 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (3 mg, 2 mol % Pd) and **L1** (8 mg, 6 mol %) were used, the product (0.17g, 89 %) was obtained.

Table 2, Entry 6: 1,4-bis(2-hexyldecyloxy)-2,5-dibromobenzene (0.182 g, 0.25 mmol, 1 equiv), 2,5-thiophenebis(boronic ester)s (0.086 g, 0.25 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (3 mg, 2 mol % Pd) and **L2** (7 mg, 6 mol %) were used, the product (0.13 g, 75 %) was obtained.

Table 2, Entry 7: 1,4-bis(2-hexyldecyloxy)-2,5-dibromobenzene (0.19 g, 0.26 mmol, 1 equiv), 2,5-thiophenebis(boronic ester)s (0.091 g, 0.26 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd(PPh₃)₄ (7 mg, 2 mol % Pd) were used, the product (0.095 g, 54 %) was obtained.

Table 2, Entry 8: 1,4-bis(2-hexyldecyloxy)-2,5-dibromobenzene (0.17 g, 0.24 mmol, 1 equiv), 2,5-thiophenebis(boronic ester)s (0.08 g, 0.24 mmol, 1 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd(PTh₃)₃ (10 mg, 4 mol % Pd) were used, no polymer was obtained.

Table 2, Entry 9: 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene (0.15 g, 0.28 mmol, 1 equiv), 3-hexyl-thienylene-2,5-diboronic ester (0.12 g, 0.28 mmol, 1.01 equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (3 mg, 2 mol % Pd) and **L1** (7 mg, 6 mol %) were used, the product (0.156 g, 98 %) was obtained.

Table 2, Entry 10: 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene (0.18 g, 0.33 mmol, 1 equiv), 3-hexyl-thienylene-2,5-diboronic ester (0.14 g, 0.33 mmol, 1 equiv), THF (16 mL), water (4 mL),

NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (3 mg, 2 mol % Pd) and **L2** (8 mg, 6 mol %) were used, the product (0.11 g, 68 %) was obtained.

Table 2, Entry 11: 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene (0.18 g, 0.32 mmol, 1 equiv), 3-hexyl-thienylene-2,5-diboronic ester (0.14 g, 0.32 mmol, 1equiv), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd(PPh₃)₄ (8 mg, 2 mol % Pd) were used, the product (0.152 g, 89 %) was obtained.

Table 2, Entry 12: 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene (0.15 g, 0.274 mmol, 1 equiv), 3-hexyl-thienylene-2,5-diboronic ester (0.116 g, 0.274 mmol, 1 equiv), THF (16 mL) water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd(PTh₃)₃ (10 mg, 4 mol % Pd) were used, no polymer was obtained.

Table 2, Entry 13: 2,7-dibromo-9,9-dioctyldibenzosilole (156.6mg, 0.28mmol), 2,5-thiophenebis(boronic ester)s (93.3mg, 0.28mmol), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), and Pd(PPh₃)₄ (8 mg) were used. **P3** (86.4 mg, 64 %) was obtained.

Table 2, Entry 14: 2,7-dibromo-9,9-dioctyldibenzosilole (292.6 mg, 0.52 mmol), 2,5-thiophenebis(boronic ester)s (174.8 mg, 0.52 mmol), THF (16 mL), water (4 mL), NaHCO₃ (0.35 g, 4 mmol), Pd₂(dba)₃ (2 mg), and **L1** (6 mg) were used. **P3** (135 mg, 70 %) was obtained.

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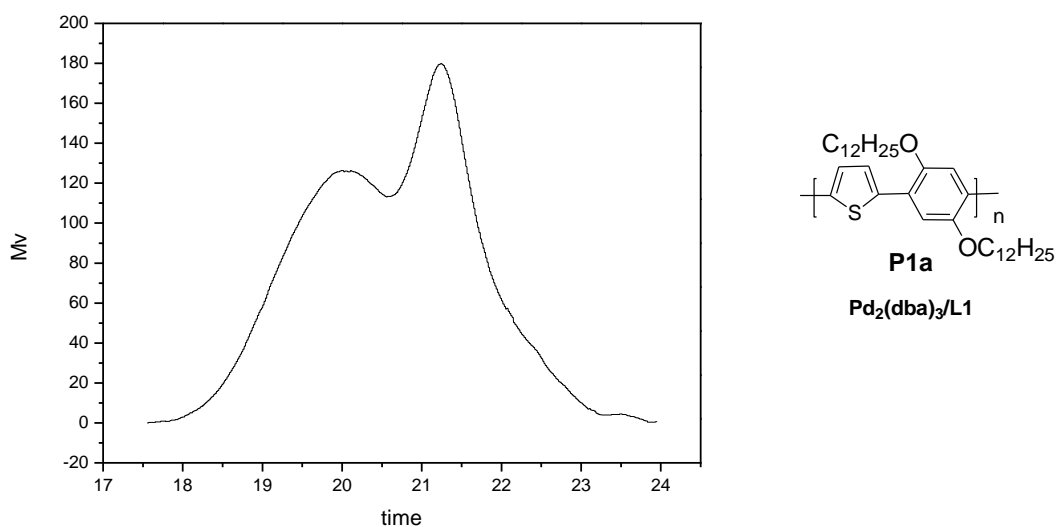


Figure S1. GPC elution curve of polymer **P1a** prepared by using $\text{Pd}_2(\text{dba})_3/\text{L1}$ as the catalyst precursors.

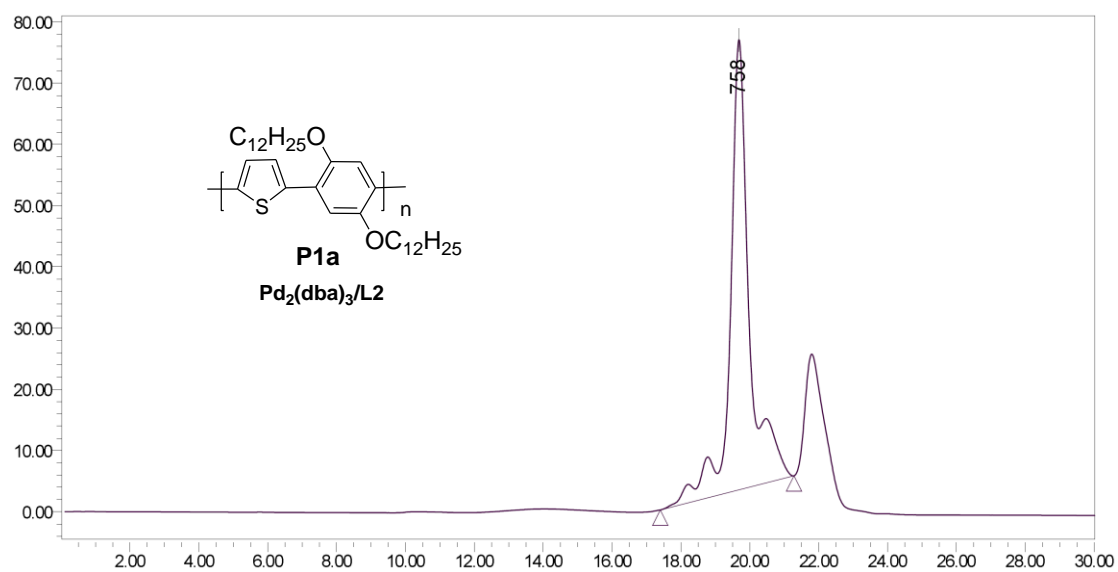


Figure S2. GPC elution curve of polymer **P1a** prepared by using $\text{Pd}_2(\text{dba})_3/\text{L2}$ as the catalyst precursors. (The large peak with a retention time of about 22 Min is the solvent peak.)

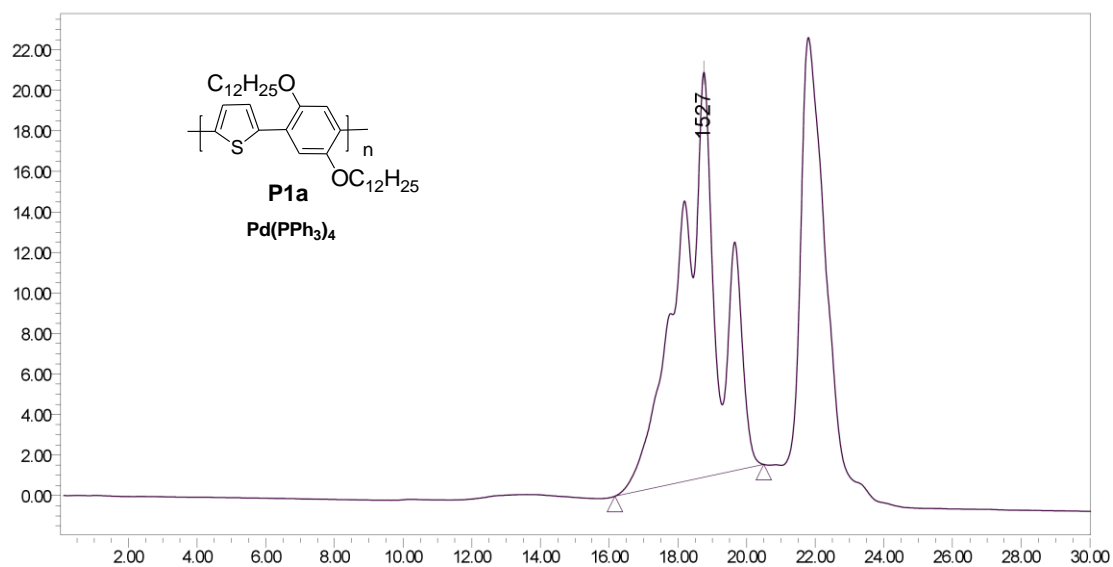


Figure S3. GPC elution curve of polymer **P1a** prepared by using $\text{Pd}(\text{PPh}_3)_4$ as the catalyst precursor. (The large peak with a retention time of about 22 Min is the solvent peak.)

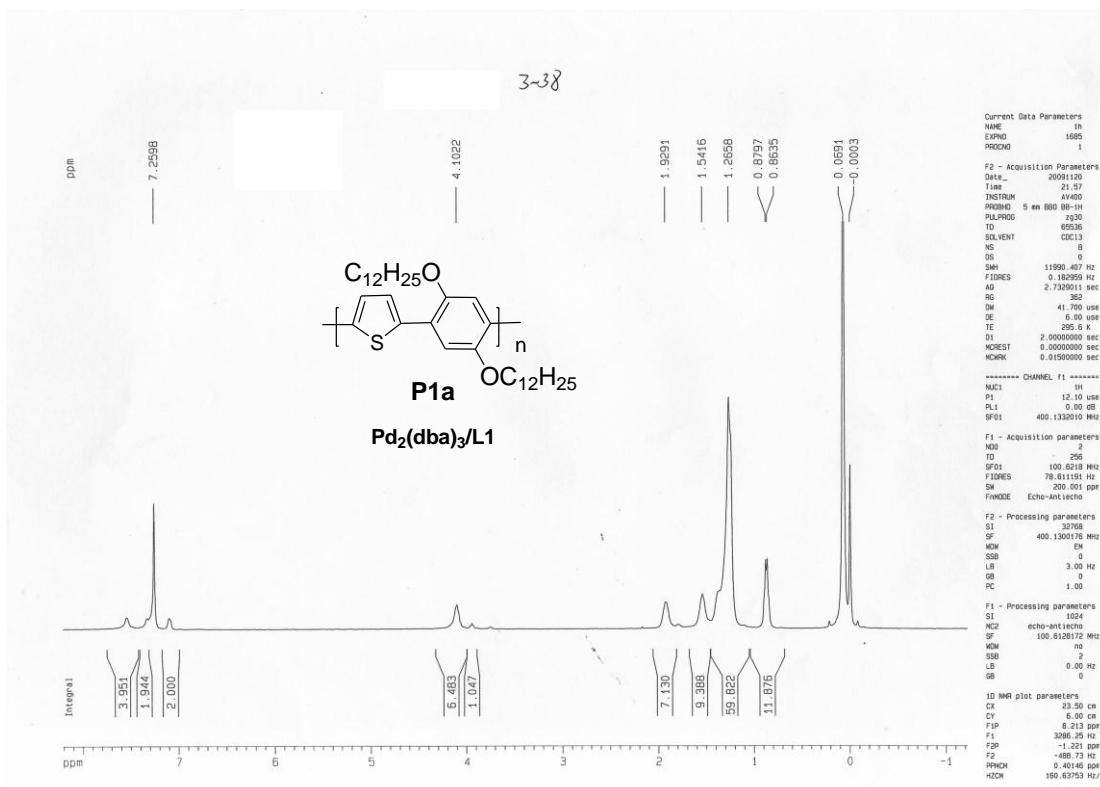


Figure S4. ^1H NMR spectrum of polymer **P1a** prepared by using $\text{Pd}_2(\text{dba})_3/\text{L1}$ as the catalyst precursors.

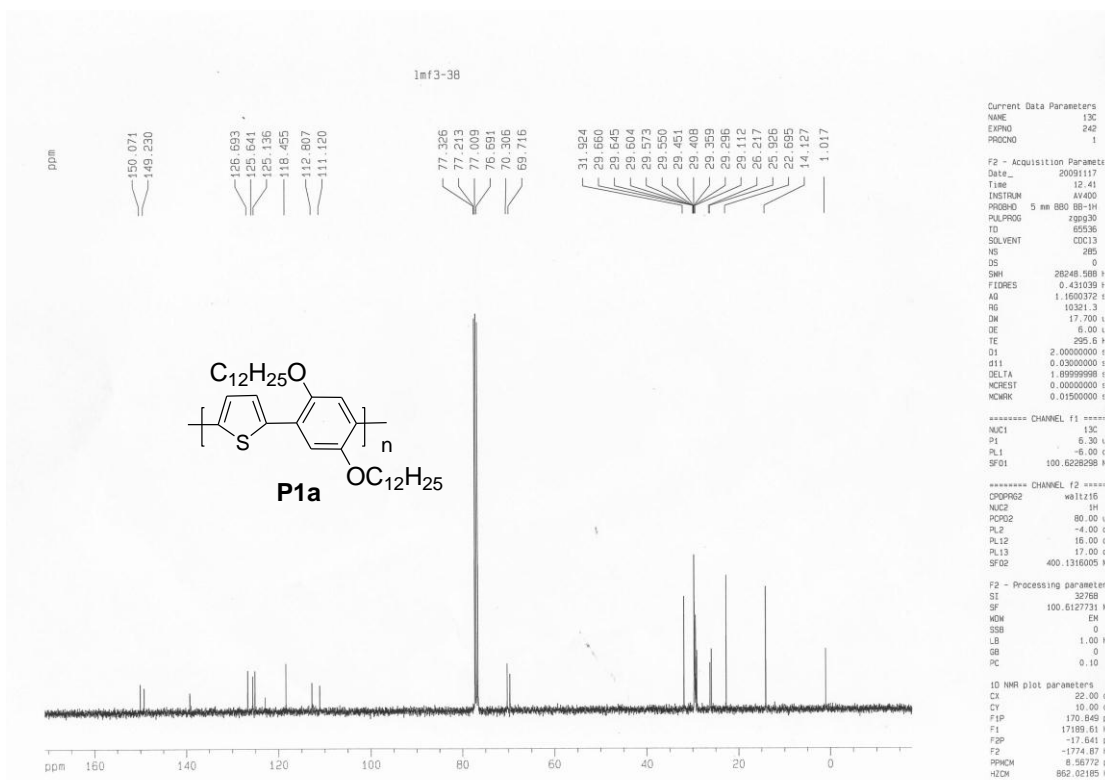


Figure S5. ^{13}C NMR spectrum of polymer **P1a** prepared by using $Pd_2(dba)_3/L1$ as the catalyst precursors.

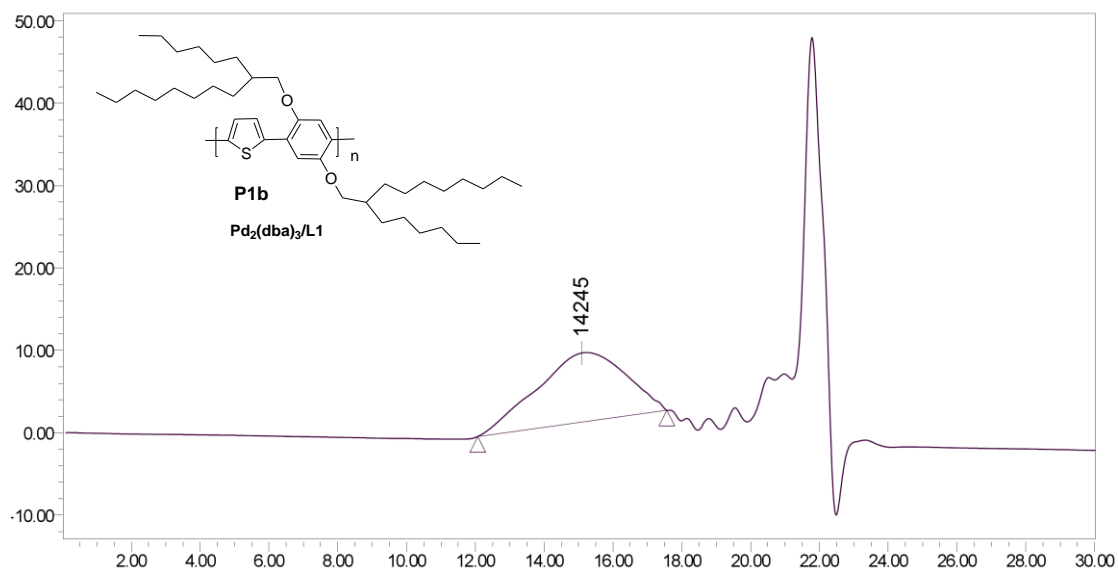


Figure S6. GPC elution curve of polymer **P1b** prepared by using $Pd_2(dba)_3/L1$ as the catalyst precursors. (The large peak with a retention time of about 22 Min is the solvent peak.)

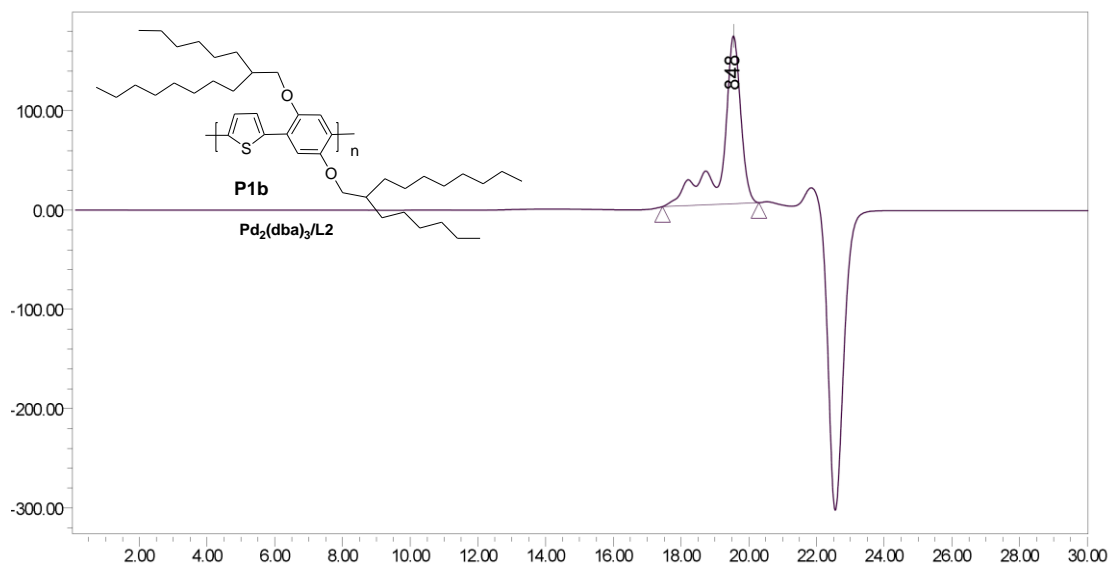


Figure S7. GPC elution curve of polymer **P1b** prepared by using $\text{Pd}_2(\text{dba})_3/\text{L2}$ as the catalyst precursors.

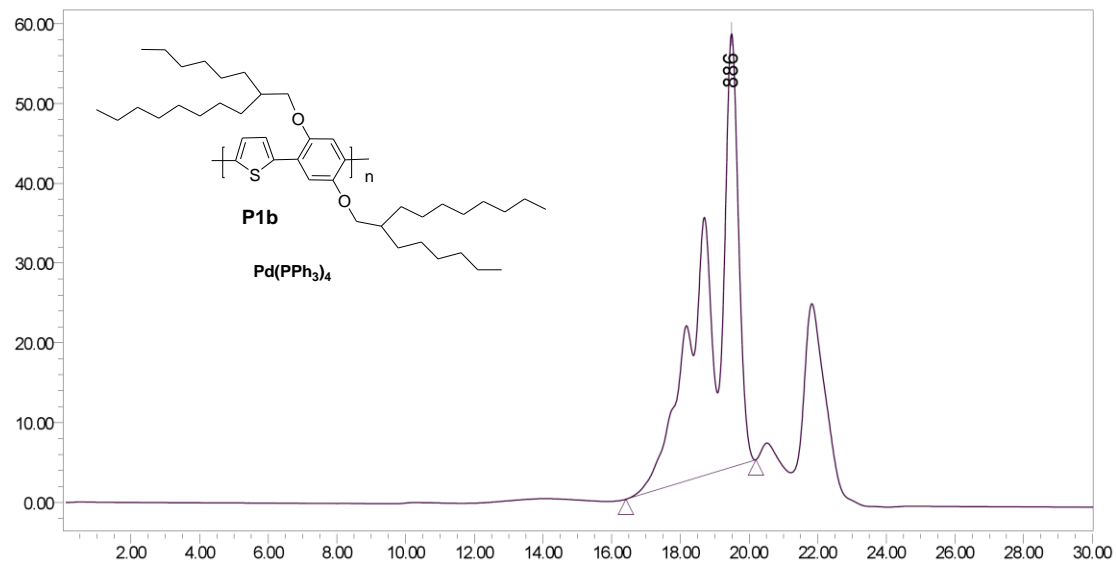


Figure S8. GPC elution curve of polymer **P1b** prepared by using $\text{Pd}(\text{PPh}_3)_4$ as the catalyst precursor.
(The large peak with a retention time of about 22 Min is the solvent peak.)

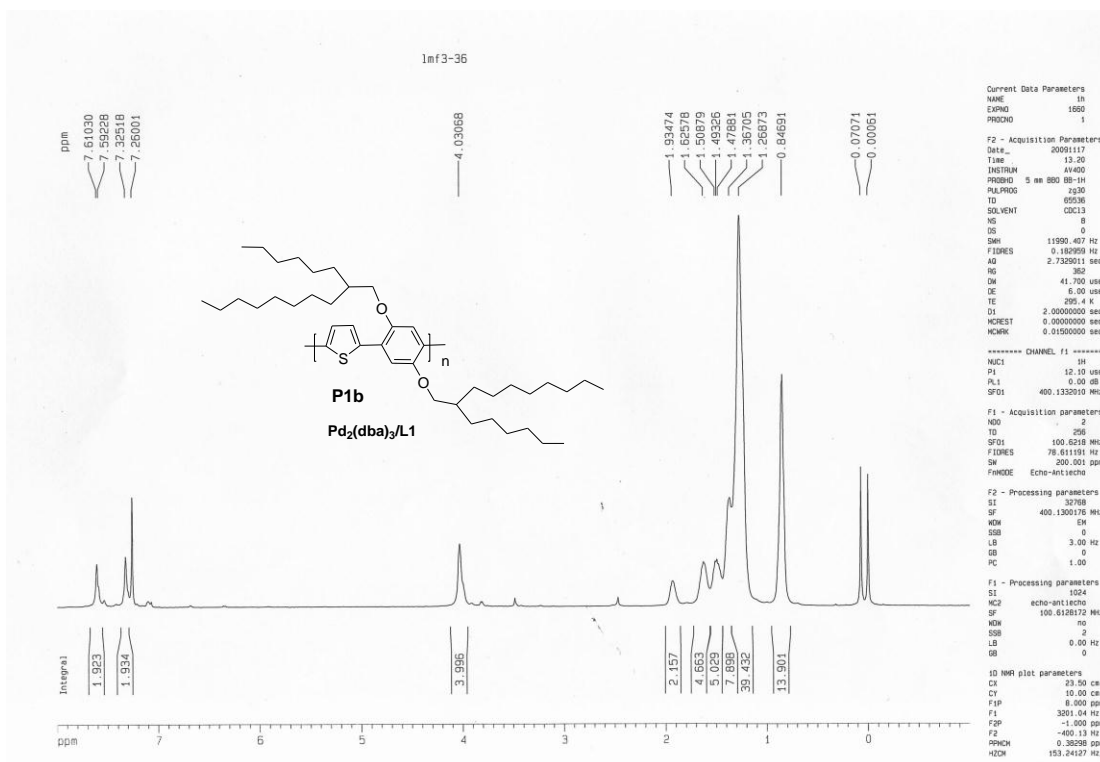


Figure S9. ¹H NMR spectrum of polymer **P1b** prepared by using $\text{Pd}_2(\text{dba})_3/\text{L1}$ as the catalyst precursors.

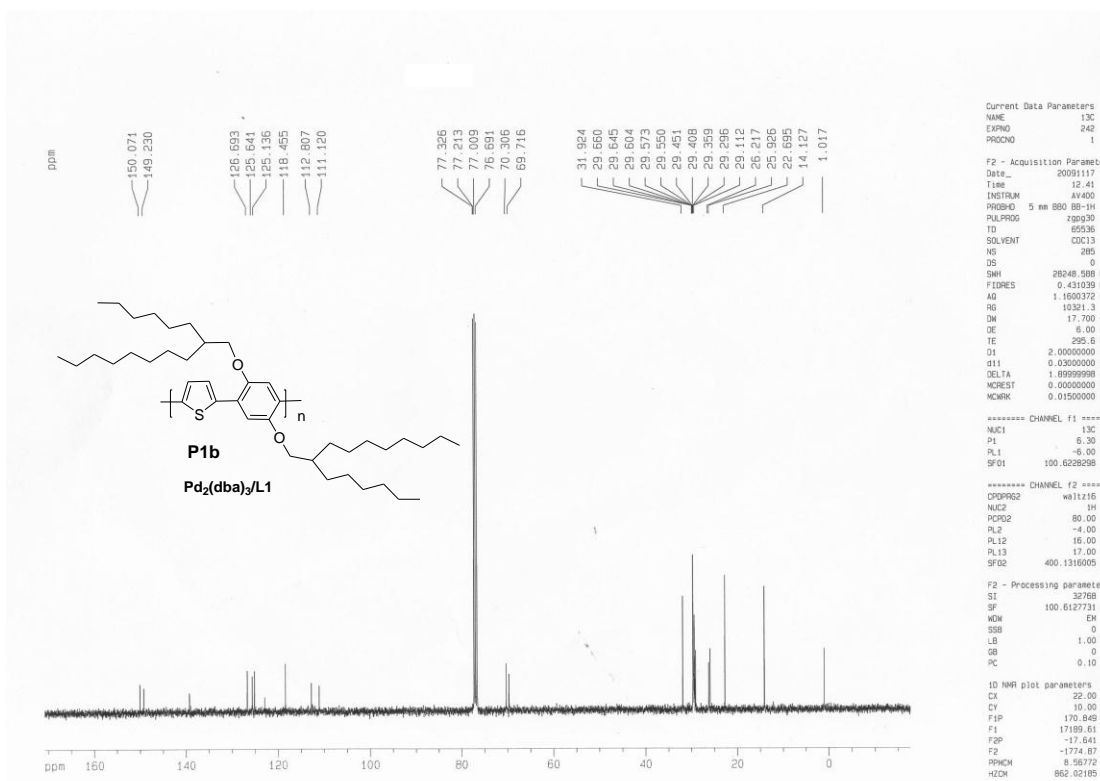


Figure S10. ¹³C NMR spectrum of polymer **P1b** prepared by using $\text{Pd}_2(\text{dba})_3/\text{L1}$ as the catalyst precursors.

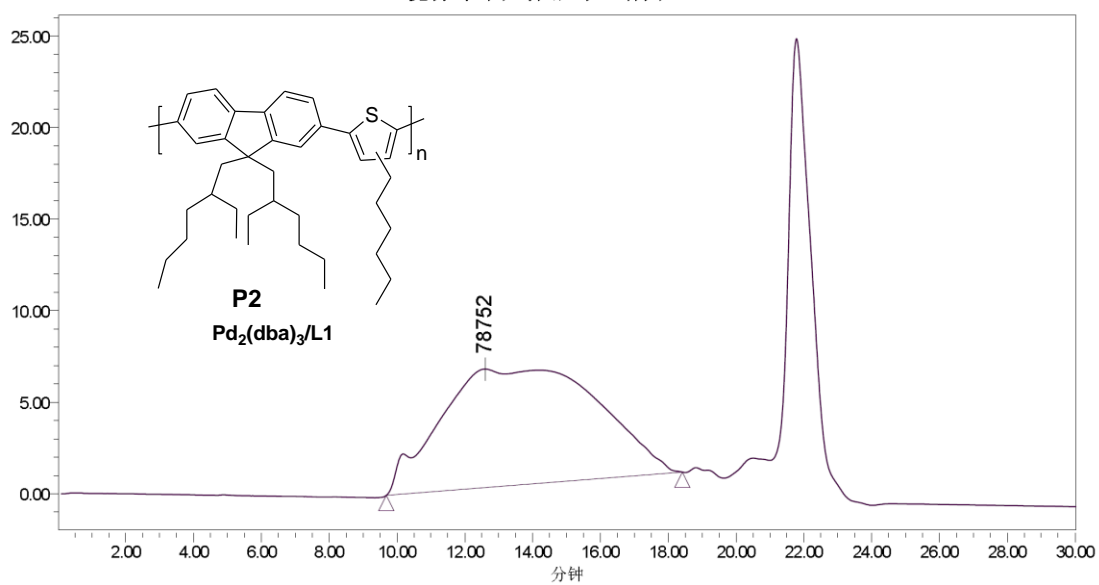


Figure S11. GPC elution curve of **P2** prepared by using $\text{Pd}_2(\text{dba})_3/\text{L1}$ as the catalyst precursors.

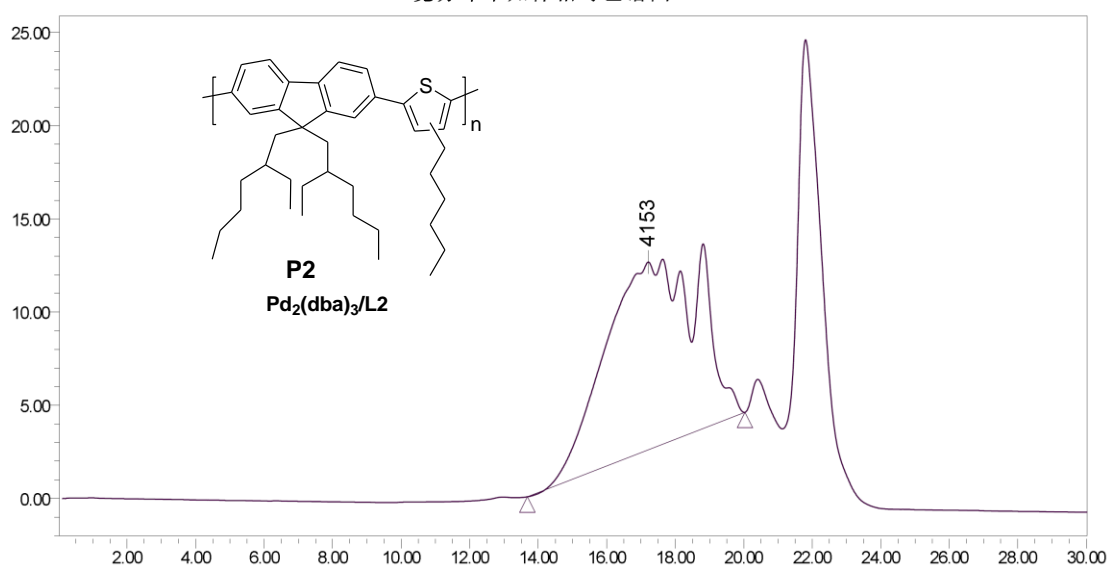


Figure S12. GPC elution curve of **P2** prepared by using $\text{Pd}_2(\text{dba})_3/\text{L2}$ as the catalyst precursors.

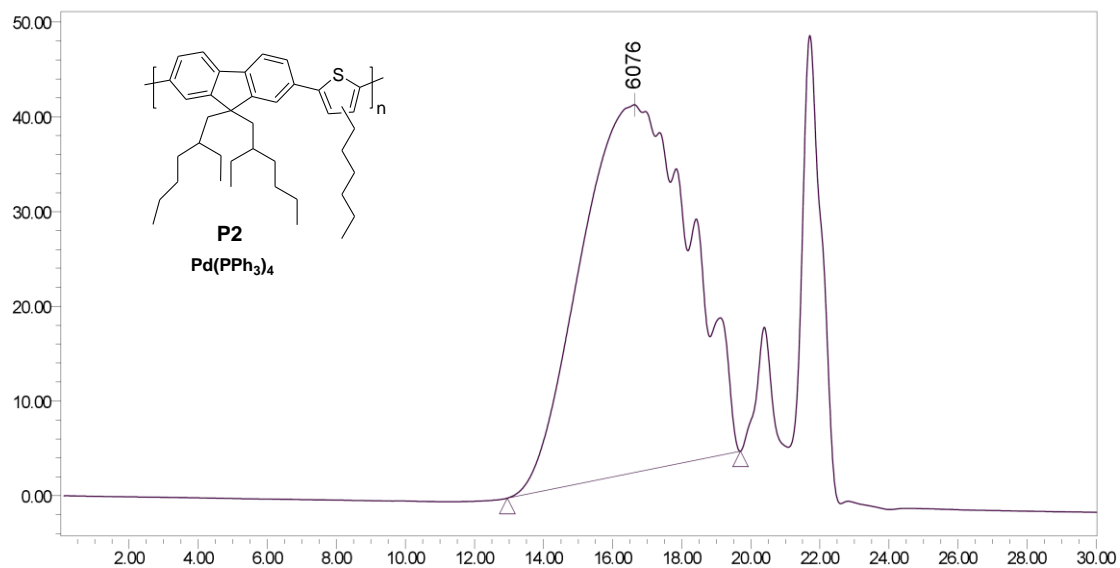


Figure S13. GPC elution curve of **P2** prepared by using $\text{Pd}(\text{PPh}_3)_4$ as the catalyst precursor.

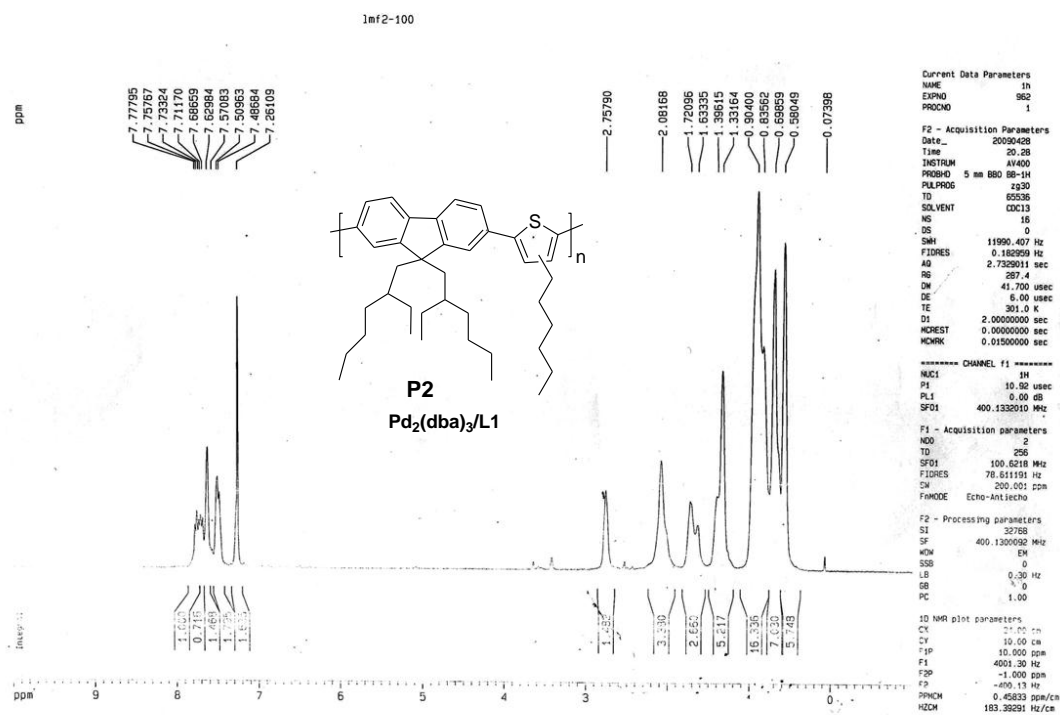


Figure S14. ^1H NMR spectrum of polymer **P2** prepared by using $\text{Pd}_2(\text{dba})_3/\text{L1}$ as the catalyst precursors.

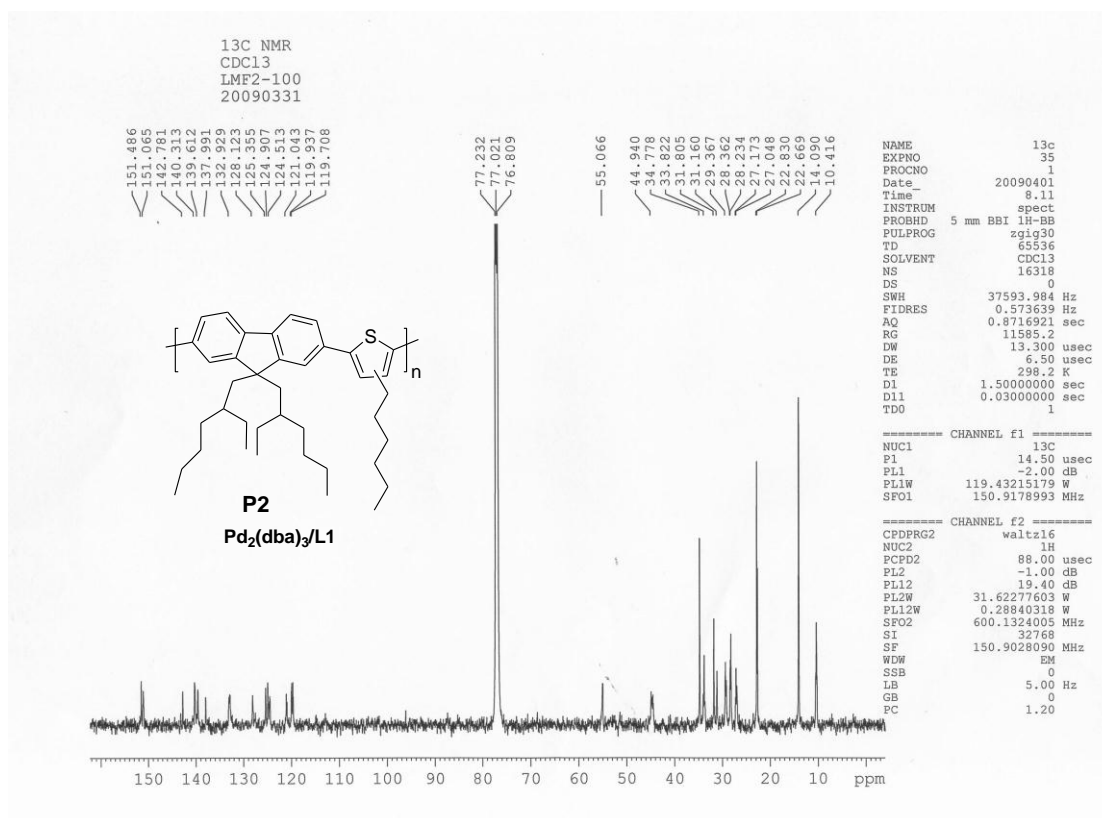


Figure S15. ¹³C NMR spectrum of polymer **P2** prepared by using Pd₂(dba)₃/L1 as the catalyst precursors.

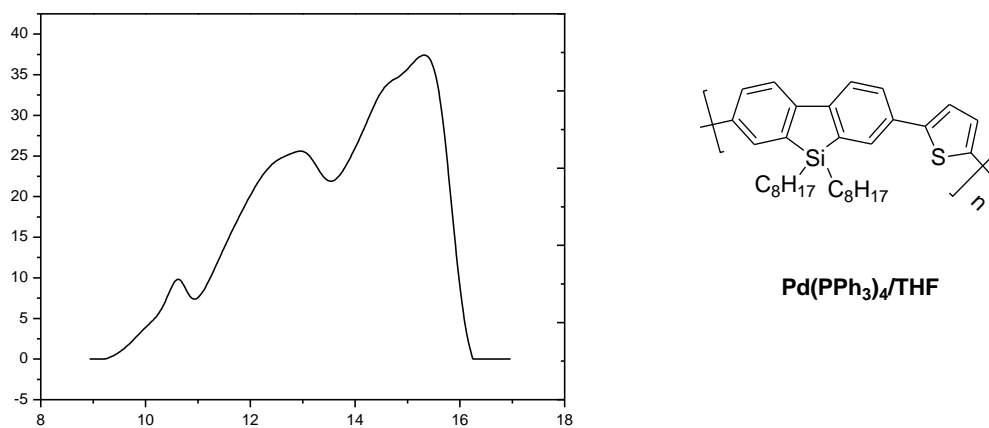


Figure S16. GPC elution curve of **P3** prepared by using Pd(PPh₃)₄ as the catalyst precursor.

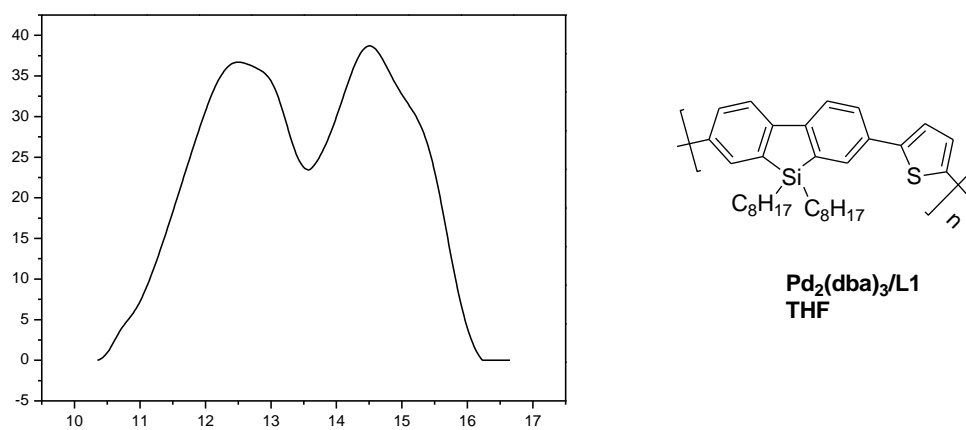


Figure S17. GPC elution curve of **P3** prepared by using Pd₂(dba)₃/L1 as the catalyst precursors.

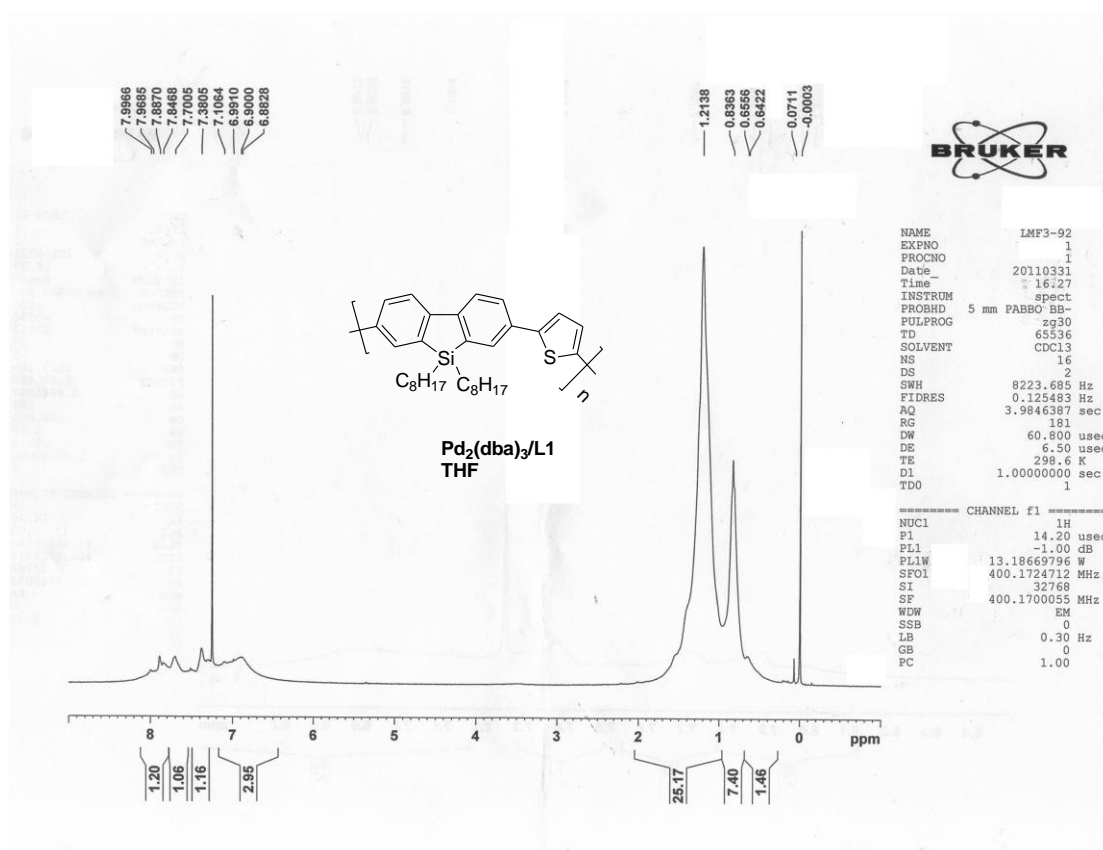


Figure S18. ¹H NMR spectrum of polymer **P3** prepared by using Pd₂(dba)₃/L1 as the catalyst precursors.

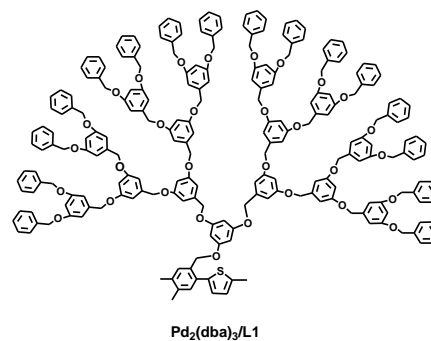
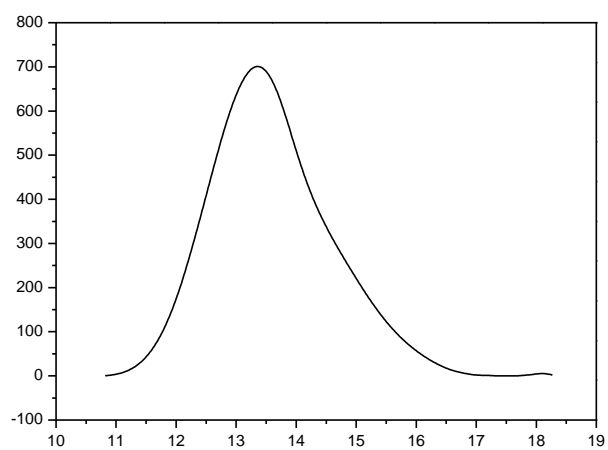


Figure S19. GPC elution curve of the fourth generation dendronized polymer prepared by using $\text{Pd}_2(\text{dba})_3/\text{L1}$ as the catalyst precursors.

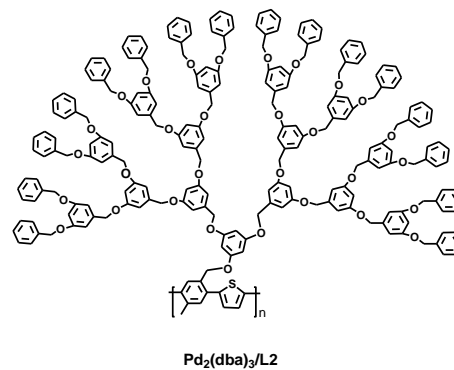
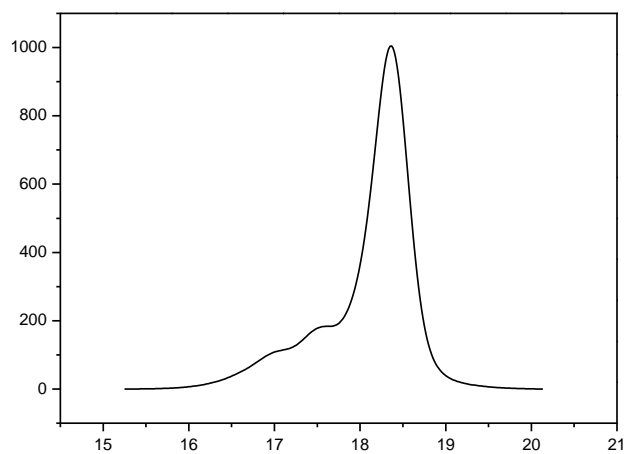


Figure S20. GPC elution curve of the fourth generation dendronized polymer prepared by using $\text{Pd}_2(\text{dba})_3/\text{L2}$ as the catalyst precursors.

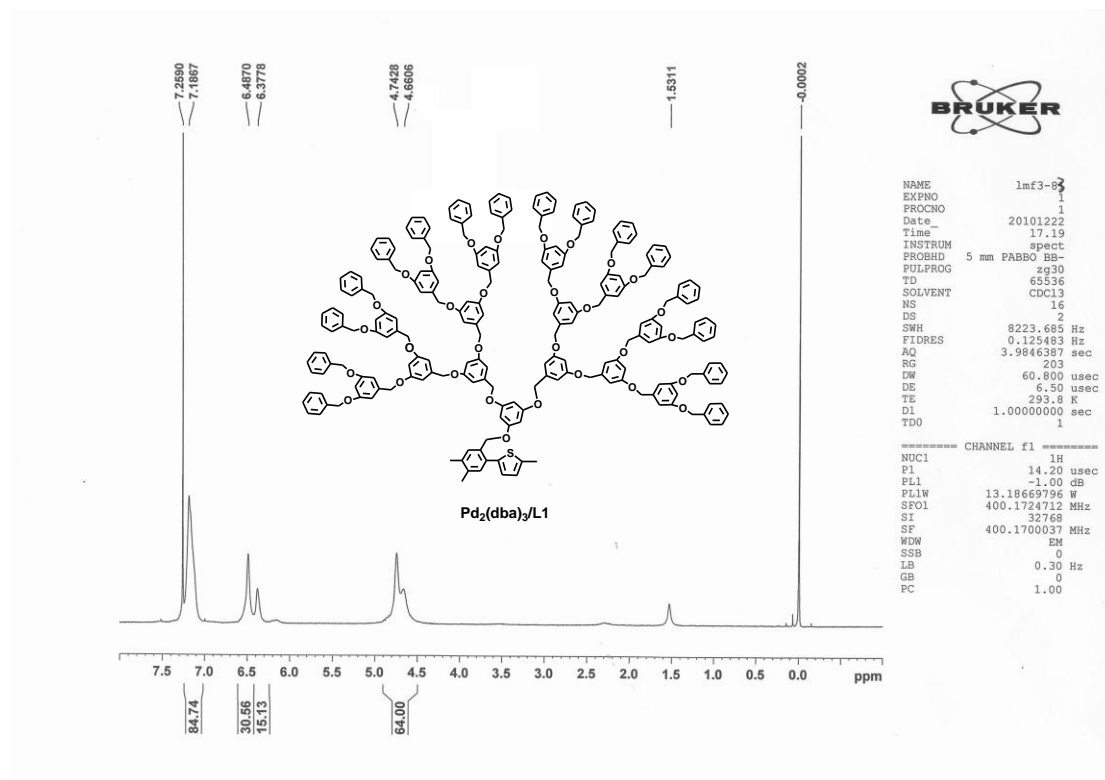


Figure S21. ¹H NMR spectrum of the fourth generation dendronized polymer prepared by using Pd₂(dba)₃/L1 as the catalyst precursors.

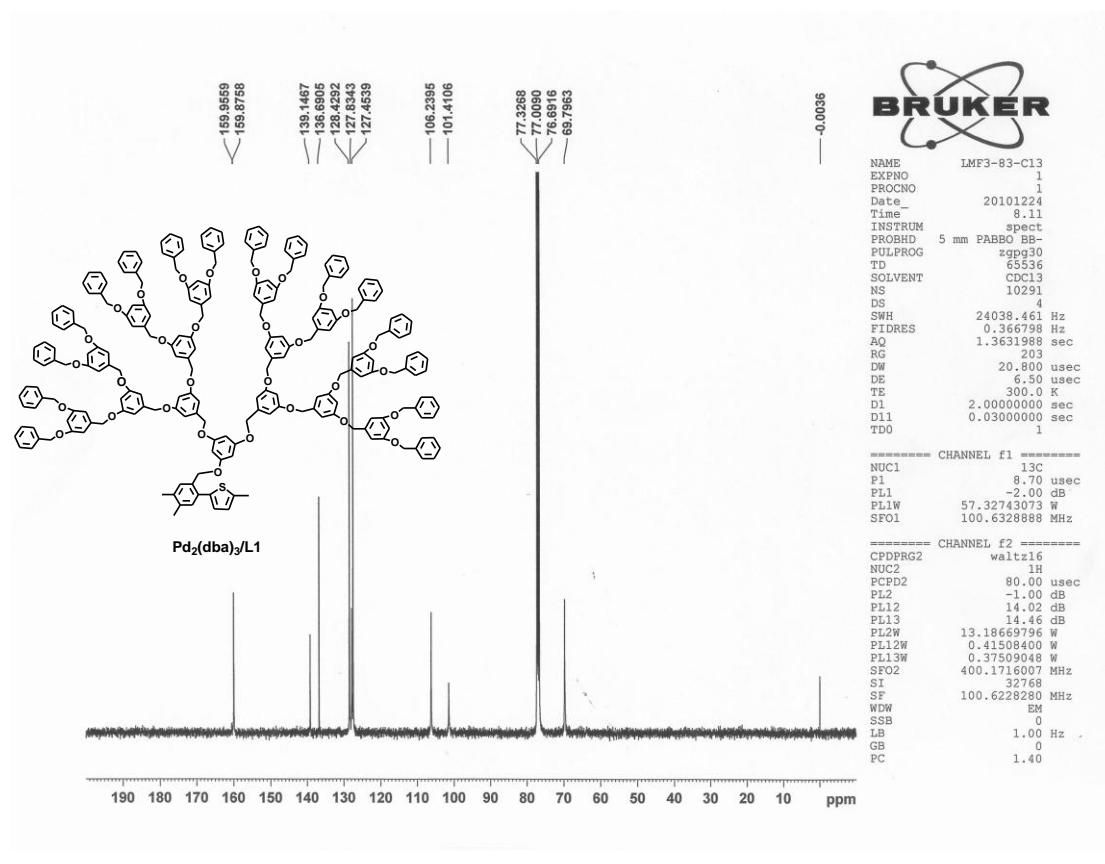


Figure S22. ¹³C NMR spectrum of the fourth generation dendronized polymer prepared by using Pd₂(dba)₃/L1 as the catalyst precursors.