Supporting Information

Low Bandgap Poly(thienylenemethine) Derivatives Bearing Side Chain Terarylene Moieties

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Contents

1. Experimental Section

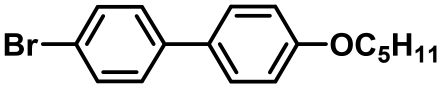
Materials 4-Bromo-4′-hydroxybiphenyl and tributyltinchloride, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were purchased from Aldrich and used without further purification. 1-Bromopentane, 1-bromodocosane, *N*-bromosuccinimide (NBS), and 2,2′-bithiophene were purchased from Tokyo Chemical Industry and used without further purification. Tetrahydrofuran (THF), acetonitrile (ACN), and diethyl ether, toluene, 1,4-dioxane, and dimethylformamide (DMF) were purified by the fractional or vacuum distillation, dried, and distilled immediately before use. Thiophene was vacuum-distilled before use.

Instruments All ^{1}H NMR and ^{13}C NMR spectra were measured with an EX-400 spectrometer. $CDCl_3$ was used as the deuterated solvent, and trimethylsilane (TMS) was used as an internal standard. Elemental analysis was measured using a Perkin-Elmer 2400CHN elemental analyzer. Infrared spectroscopic measurements were carried out with a JASCO FT-IR 550 spectrometer using the KBr method**.** The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Shodex A-80M column and a JASCO HPLC 870-UV detector with THF used as solvent during measurements. The instrument was calibrated with a polystyrene standard. Thermal behaviour of polymers was investigated in a heating run at a heating rate of 10 °C min^{-1} in flowing nitrogen gas, using thermogravimetry-differential thermal analysis (TG-DTA) apparatus (DTG-60, Shimadzu) with alumina pan. UV-vis-NIR absorption was recorded on a JASCO V-570 spectrometer. Cyclic voltammetry was investigated with an AUTOLAB PGSTAT12 potentiostat instrument by using an ITO working electrode, a platinum wire counter electrode and a Ag/AgCl reference electrode. The film thickness was measured using Nikon Digimicro digital length measuring system with DIGIMICRO MH-15M, DIGIMICRO STAND MS-5C, and DIGITAL READOUT UC-101. The electrical resistance of polymer films was measured at room temperature using a high resistivity meter, Hiresta UX with a MCP-HT800 USR probe (Mitsubishi Chemical Analytech). X-ray diffraction (XRD) measurements were performed with a Rigaku ultra X18 diffractometer. XRD patterns were recorded with an X-ray generator with Ni filtered CuKα radiation (40 kV/300 mA: λ = 1.54 Å) and a flat-plate camera (RINT2500, Rigaku). Films were cast on the ITO glass with a spin coater (Opticoat MS-A150, MIKASA Corp.). Film thickness was measured by atomic force microscopy (AFM) with an Asylum Technology MFP-3D-SA in the AC mode. The ITO glass consists of a 1 mm thick ITO layer on glass (10 Ω/cm^2, Furuuchi Chemical Corp.). 0.1 M tetra-*n*-butylammonium perchrolate (TBAP) was used as an electrolyte.

2. Synthesis of side chain moieties

- Synthesis of terphenylaldehyde

4-bromo-4′-pentyloxy-1,1′-biphenyl (1)

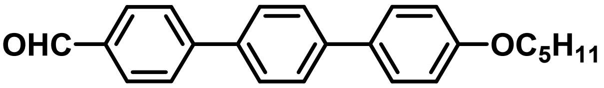


(1)

A mixture of 4-bromo-4’-hydroxybiphenyl (3.0 g, 12 mmol), 1-bromopentane (3.6 g, 24 mmol), potassium carbonate (1.66g, 12 mmol) and acetone (60 mL) was refluxed for 24 h. The solvent was removed under reduced pressure, and the obtained residue was extracted with chloroform, washed with water and dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the crude product was passed through a column chromatograph with chloroform, and purified by recrystallisation with hexane and chloroform. A white solid of **1** (1.99 g) was obtained (Yield: 53%). Anal., calcd for

$C_{17}H_{19}BrO$: C, 63.96 %; H, 6.00 %; Br, 25.03 %; O, 5.01 %, Found: C, 63.68 %; H, 5.86 %; O, 5.16 %. ^{1}H-NMR ($CDCl_3$, 400MHz, δ from TMS, ppm) δ = 7.53–7.51 (d, 2H, Ph*H*), 7.48–7.46 (d, 2H, Ph*H*), 7.42–7.40 (d, 2H, Ph*H*), 7.00–6.95 (d, 2H, Ph*H*), 4.01–3.98 (t, 2H, –O–C*H₂*–), 1.81 (m, 2H, –C*H₂*–), 1.42 (m, 4H, –C*H₂*–), 0.94 (t, 3H, –C*H₃*).

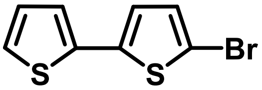
4″-pentyloxy-(1,1′:4′,1″-terphenyl)-4-carbaldehyde (abbreviated as terphenylaldehyde)



(terphenylaldehyde)

A mixture of 4-formylphenyl boronic acid (0.54 g, 3.6 mmol), compound **1** (0.958 g, 3 mmol), sodium hydrogen carbonate (0.76 g, 9 mmol), tetrakis(triphenylphosphine) palladium (0.057 g, 0.030 mmol), THF (15 mL) and water (15 mL) were refluxed for 24 h. The solvent was removed under reduced pressure, and the obtained residue was extracted with chloroform, washed with water and dried over anhydrous sodium sulfate. The crude product was passed through a column chromatograph with chloroform, and purified by recrystallisation with hexane and chloroform. White coloured compound, terphenylaldehyde (0.60 g) was obtained. (Yield: 58 %) Anal., calcd for $C_{24}H_{24}O_2$: C, 83.69 %; H, 7.02 %; O, 9.29 %, Found: C, 82.57 %; H, 6.90 %; O, 10.72 %. ^{1}H NMR ($CDCl_3$, 400 MHz, δ from TMS, ppm) δ = 10.06 (s, 1H, –C*H*O), 7.95–7.97 (d, 2H, Ph*H*), 7.79–7.81 (d, 2H, Ph*H*), 7.71–7.66 (m, 4H, Ph*H*), 7.00–6.98 (s, 2H, Ph*H*), 4.03–3.99 (t, 2H, –O–C*H₂*–), 1.84–1.81 (t, 2H, –C*H₂*–), 1.47–1.40 (m, 4H, –C*H₂*–), 0.93–0.97 (t, 3H, –C*H₃*). ^{13}C NMR ($CDCl_3$, 100MHz, δ from TMS, ppm) δ = 191.7, 159.0, 146.7, 141.0, 137.8, 135.2, 132.4, 130.2, 128.0, 127.2, 114.9, 68.1, 29.0, 28.3, 22.7, 14.1.

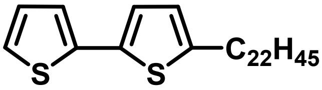
5-bromo-2,2′-bithiophene (2)



(2)

2,2′-Bithiophene (5.5 g, 33 mmol) was dissolved in dry DMF (50 mL) under argon atmosphere, and N-bromosuccinimide (NBS) (5.78 g, 33 mmol) in DMF (50 mL) was added dropwise to the solution at the room temperature. After stirred for 4h, the reaction solution was washed with water and extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate. The crude product was passed through a column chromatograph with chloroform / hexane (1:1), and purified by recrystallisation with hexane and chloroform. A white solid of **2** (5.77 g) was obtained (Yield: 71.4 %). ^{1}H NMR (CDCl$_3$, 400 MHz, δ from TMS, ppm) δ = 7.21 (d, 1H, Th*H*), 7.09 (d, 1H, Th*H*), 6.98 (d, 1H, Th*H*), 6.95 (d, 1H, Th*H*), 6.90 (d, 1H, Th*H*).

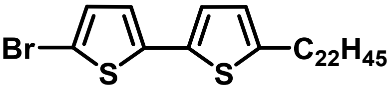
5-dcosanyl -2,2′-bithiophene (3)



(3)

Under argon atmosphere, compound **2** (1.2 g, 4 mmol) was dissolved in dry THF (30 mL) and the solution was cooled to −78 °C. Keeping this temperature constant, the solution of *n*-BuLi (3.06 mL, 1.6 mol/L) in hexane was added dropwise and stirred for 1h. Then, 1-bromodocosane (1.89 g, 4 mmol) was added dropwise to the reaction solution at the same temperature. After stirred for 12h, the reaction mixture was washed with water and extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate. The crude product was passed through a column chromatograph with chloroform / hexane (1:1), and purified by recrystallisation with hexane and chloroform. A white solid of **3** (1.184 g) was obtained (Yield: 62.3 %). ^{1}H NMR ($CDCl_3$, 400 MHz, δ from TMS, ppm) δ = 7.22 (m, 2H, Th*H*), 7.11 (d, 2H, Th*H*), 6.65 (m, 1H, Th*H*), 2.77 (t, 2H, $-CH_2-$), 1.67 (m, 2H, $-CH_2-$), 1.35 (m, 38H, $-CH_2-$), 0.89 (t, 3H, $-CH_3$).

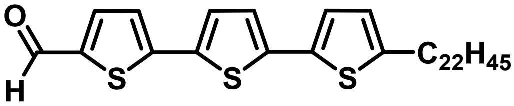
5-bromo-5′-docosanyl-2,2′-bithiophene (4)



(4)

Compound **3** (1.8 g, 3.8 mmol) was dissolved in dry DMF (10 mL) under argon atmosphere, and *N*-bromosuccinimide (NBS) (0.67 g, 3.8 mmol) in DMF (10 mL) was added dropwise to the solution at room temperature. After stirred for 4h, the reaction solution was washed with water and extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate. The crude product was passed through a column chromatograph with chloroform / hexane (1:1), and purified by recrystallisation with hexane and chloroform. A white solid of **4** (1.67 g) was obtained (Yield: 79.4 %). ^{1}H NMR ($CDCl_3$, 400 MHz, δ from TMS, ppm) δ = 6.93 (d, 1H, Th*H*), 6.91 (d, 1H, Th*H*), 6.82 (d, 1H, Th*H*), 6.67 (d, 1H, Th*H*), 2.77 (t, 2H, $-CH_2-$), 1.67 (m, 2H, $-CH_2-$), 1.35 (m, 38H, $-CH_2-$), 0.89 (t, 3H, $-CH_3$).

5″-docosanyl-(2,2′:5′, 2″-terthiophene)-5-carbaldehyde (terthienylaldehyde)

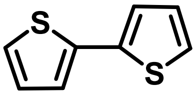


(terthienylaldehyde)

Under argon atmosphere, 2-formylthiophene boronic acid (0.704 g, 4.5 mmol), compound **4** (2.5 g, 4.5 mmol), and Pd(XPhos) catalyst[1] (0.075 g, 0.095 mmol) were dissolved in THF (80 mL). A solution of K_3PO_4 (0.206 g, 0.97 mmol) in water (80 mL) was added dropwise to the solution. After stirring for 5h, the solvent was removed under reduced pressure and the obtained residue was extracted with chloroform, washed with water and dried over anhydrous sodium sulfate. The crude product was passed through a column chromatograph with chloroform and hexane respectively, and purified by recrystallisation with hexane and chloroform. A yellow solid of terthienylaldehyde (0.646 g) was obtained (Yield: 60.1 %). ^{1}H NMR ($CDCl_3$, 400 MHz, δ from TMS, ppm) δ = 9.88 (s, 1H, Th*H*), 7.68 (d, 1H, Th*H*), 7.25 (d, 1H, Th*H*), 7.20 (d, 1H, Th*H*), 7.05 (m, 2H, Th*H*), 6.72 (d, 1H, Th*H*), 2.77 (t, 2H, $-CH_2-$), 1.66 (m, 2H, $-CH_2-$), 1.34 (m, 38H, $-CH_2-$), 0.89 (t, 3H, $-CH_3$).

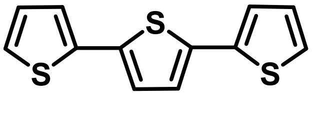
3. Synthesis of main chain moieties

2,2′-bithiophene

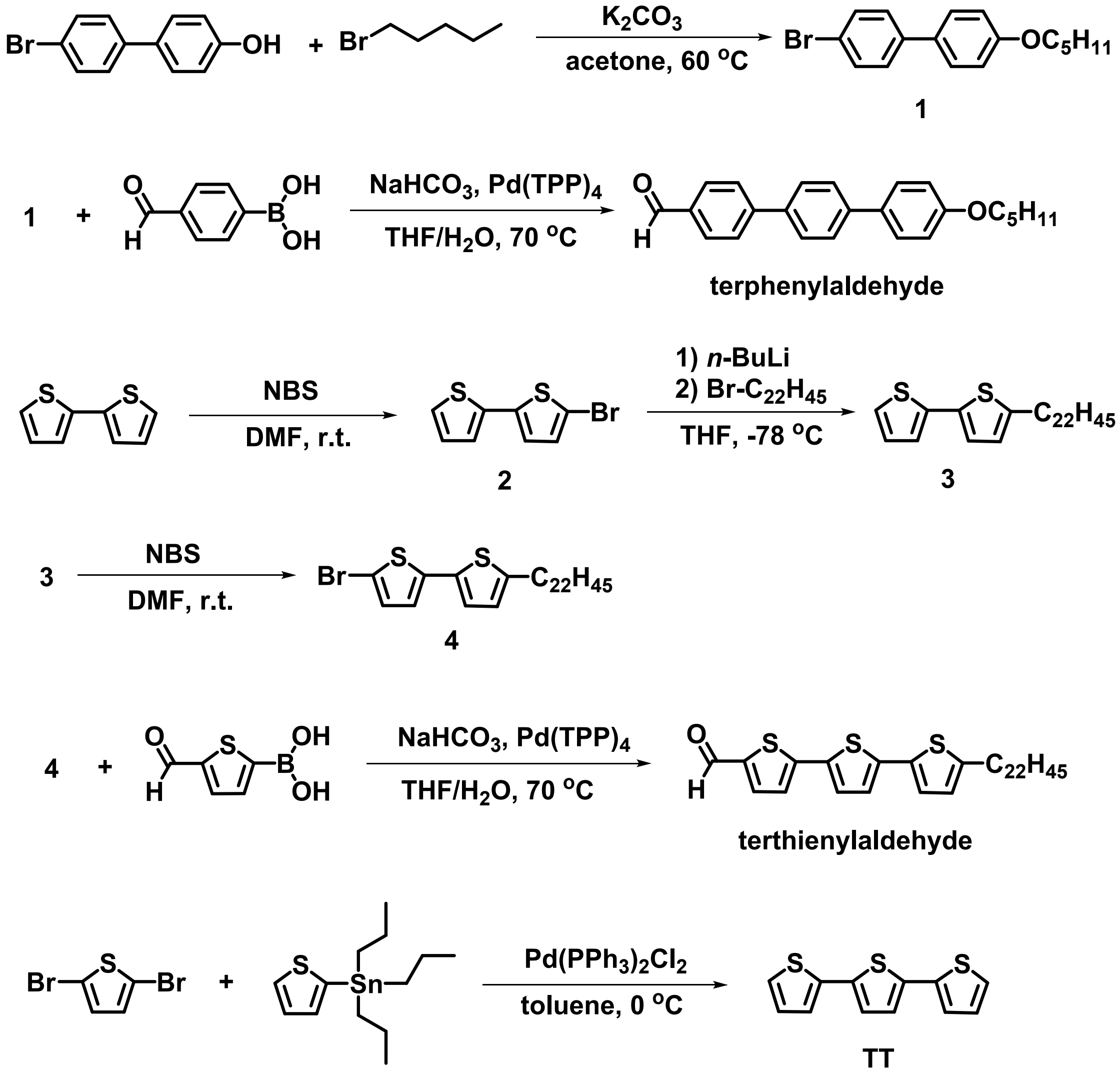


Bithiophene was purchased from Tokyo Chemical Industry and was used directly for synthesis of polymers.

2,2′:5′,2″-terthiophene



Under argon atmosphere, a solution of 2,5-Dibromo-thiophene (4.11 g, 17 mmol) in dry toluene (150 mL) was added at 0 °C to 2-tributylstannylthiophene (6.35 g, 17 mmol). A catalyst of dichlorobis(triphenylphosphine) palladium(Ⅱ) [$Pd(PPh_3)Cl_2$] (0.105 g, 0.15 mmol) was added. The reaction mixture was stirred for 8h under an argon atmosphere. After evaporation of the solvent, the residue was thoroughly washed with water and chloroform. The organic layer was dried over anhydrous anhydrous sodium sulfate. The crude product was passed through a column chromatograph with chloroform containing triethylamine, and purified by recrystallisation with hexane and chloroform. A yellow solid of terthiophene (3.73 g) was obtained (Yield: 31.5%). ^{1}H NMR ($CDCl_3$, 400MHz, δ from TMS, ppm) δ = 7.24–7.21 (m, 4H, Th*H*), 7.18–7.01 (m, 4H, Th*H*).



Scheme S1. Synthetic routes of terphenylaldehyde, terthienylenealdehyde, and terthiophene.

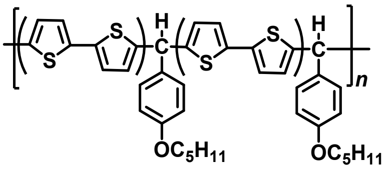
4. Synthesis of catalyst

Pd (XPhos) catalyst

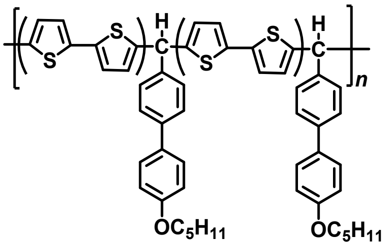
The Pd catalyst was synthesised using Xphos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) ligand according to the method described in the following reference: T. Kinzel, Y. Zhang, S. L. Buchwald, *J. Am. Chem. Soc.*, 2010, **132**, 14073-14075.

Table S1. Polymerisation results of the benzonoidal polymers with phenylene moieties at side chains

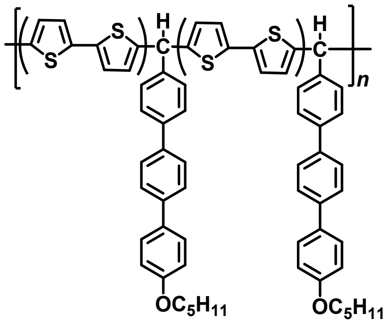
Polymer	M_n	M_w	M_w/M_n	D.P.[a] (T.U.)[b]	Yield (%)
Poly-2PB-1	3,100	4,800	1.54	9 (18)	3
Poly-2PB-2	7,100	26,300	3.73	17(34)	26
Poly-2PB-3	5,100	7,400	1.45	10 (20)	34



Poly-2PB-1



Poly-2PB-2



Poly-2PB-3

a) D.P.: Degree of polymerisation

b) T.U.: Number of thienylene unit

※ Polymerisation conditions

Acid agent: H_2SO_4,

Solvent: 1,4-dioxane,

Polymerisation temperature: 80 °C

Polymerisation time: 24 hr.

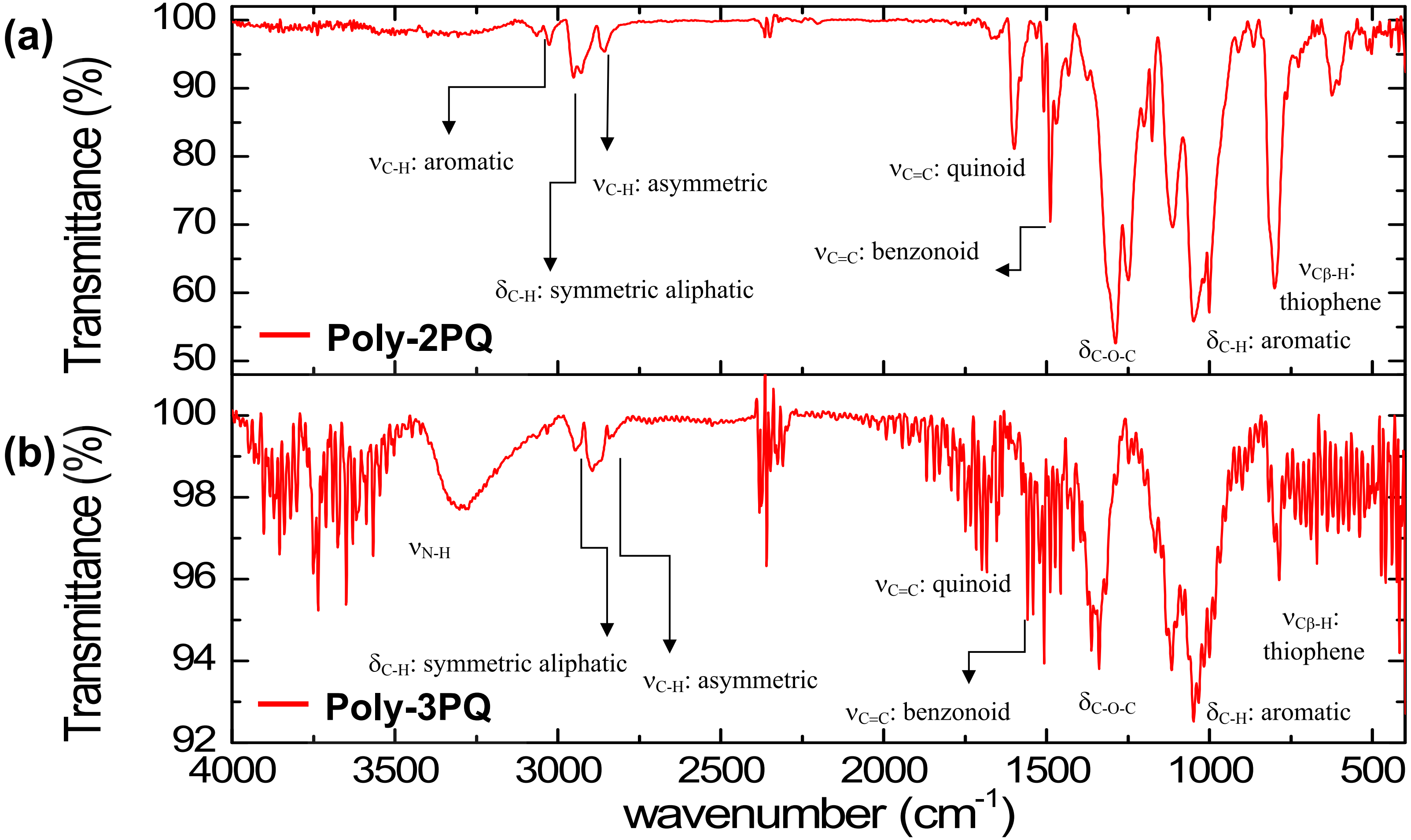


Figure S1. IR spectra of (a)**Poly-2PQ** and (b) **Poly-3PQ** in KBr disk.

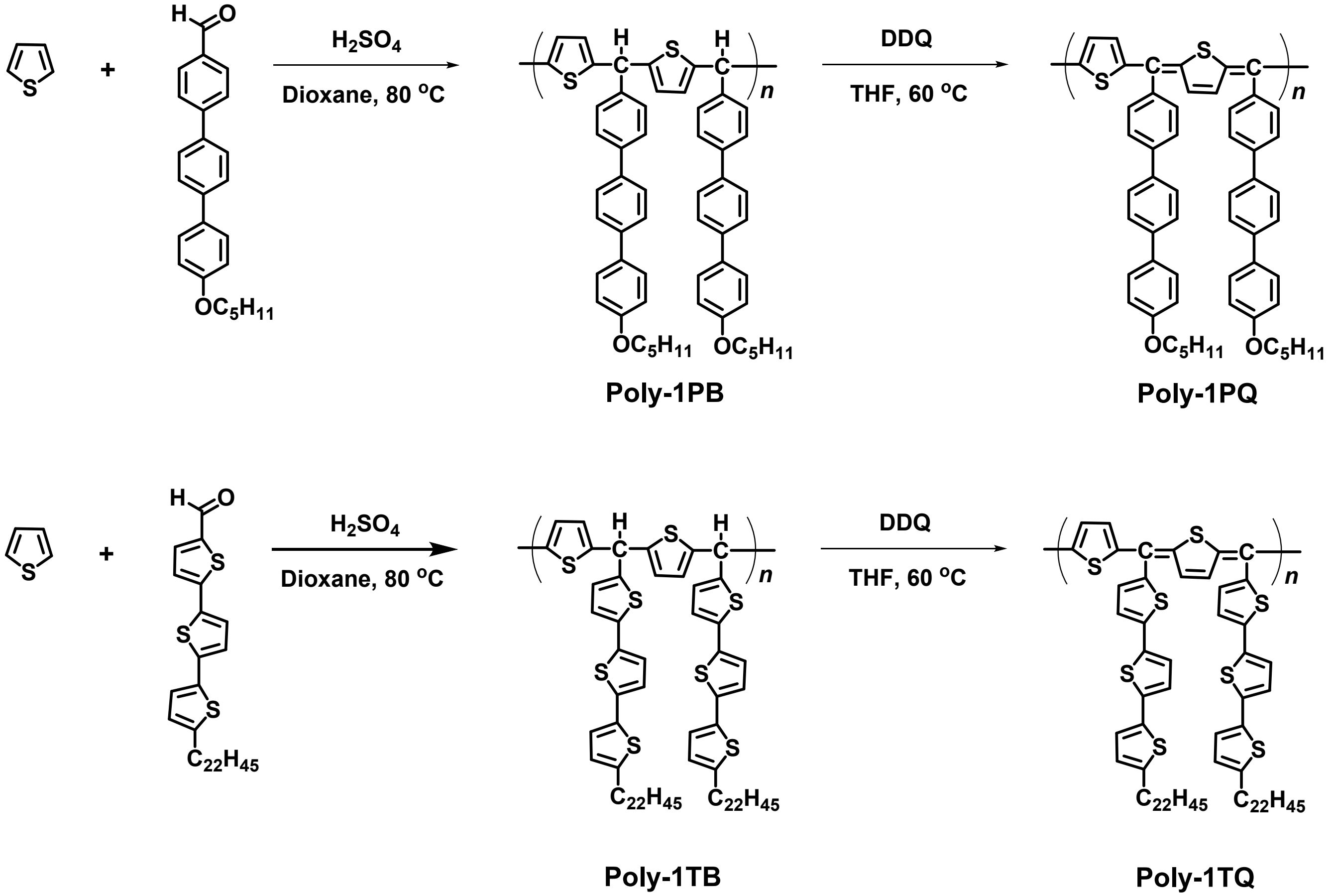
5. Poly(thienylenemethine) derivatives

Poly-1PB. A mixture of thiophene (0.13 g, 1.5 mmol), terphenylaldehyde (0.603 g, 1.75 mmol), 4 mL of 1,4-dioxane, and 0.05 mL (0.5 mmol) of 96 % sulfuric acid was prepared. The reaction temperature was kept constant at 80 °C for 24 h. A dark blue product was reprecipitated in 500 mL of methanol, redissolved in THF, and reprecipitated in methanol. Subsequently, the black product was reprecipitated in 500 mL of a mixture of acetone and methanol, redissolved in $CHCl_3$, reprecipitated, filtered in acetone, and dried under vacuum. A dark red polymer (0.205 g) was obtained (Yield: 34 %). $M_w = 2{,}900$ $M_w/M_n = 1.35$ (GPC, PS calibration). ^{1}H NMR ($CDCl_3$, 400MHz, δ from TMS, ppm) δ = 7.68–7.00 (br, 32H, Ph*H* and Th*H*), 4.00 (br, 4H, $-OCH_2-$), 1.82 (br, 4H, $-CH_2-$), 1.20–0.93 (br, 18H, $-CH_2-$ and $-CH_3$).

Poly-1PQ. A mixture of 0.025 g of **Poly-1PB**, 0.014 g (0.061 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and 1 mL of dry THF was prepared. The reaction temperature was maintained at 60 °C for 24 h. A dark blue product was recovered in 200 mL of stirring methanol, dissolved in THF, and reprecipitated in methanol. Subsequently, the black product was reprecipitated in 500 mL of a mixture of acetone and methanol, redissolved in $CHCl_3$, reprecipitated, filtered in acetone, and dried under vacuum. A dark red polymer (0.010 g) was obtained (Yield: 20 %). ^{1}H NMR ($CDCl_3$, 400MHz, δ from TMS, ppm) δ = 7.59–7.16 (br, 24H, Ph*H* and 4H, Th*H*), 4.0 (br, 4H, $-OCH_2-$), 1.90–0.93 (br, 18H, $-CH_2-$and $-CH_3$).

Poly-1TB. A mixture of thiophene (0.11 g, 0.1 mmol), terthienylaldehyde (0.68 g, 0.12 mmol), 1 mL of 1,4-dioxane, and 0.024 mL (0.45 mmol) of 96 % sulfuric acid was prepared. The reaction temperature was kept constant at 80 °C for 24 h. A dark blue product was reprecipitated in 500 mL of methanol, redissolved in THF, and reprecipitated in methanol. Subsequently, the black product was reprecipitated in 500 mL of a mixture of acetone and methanol, redissolved in $CHCl_3$, reprecipitated, filtered in acetone, and dried under vacuum. A dark red polymer (0.038 g) was obtained (Yield: 58 %). M_w = 2,100 M_w/M_n = 1.2 (GPC, PS calibration). ^1H NMR ($CDCl_3$, 400MHz, δ from TMS, ppm) δ = 7.65 (br, 2H, Th*H*), 7.49 (br, 2H, Th*H*), 7.11–6.88 (br, 12H, Th*H*), 5.98 (br, 1.9H, methine *H*), 2.49 (br, 4H, $-CH_2-$), 1.54–1.08 (br, 80H, $-CH_2-$), 0.86 (br, 6H, $-CH_3$).

Poly-1TQ. A mixture of 0.027 g of **Poly-1TB**, 0.0105 g (0.047 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and 1 mL of dry THF was prepared. The reaction temperature was maintained at 60 °C for 24 h. A dark blue product was recovered in 200 mL of stirring methanol, dissolved in THF, and reprecipitated in methanol. Subsequently, the black product was reprecipitated in 500 mL of a mixture of acetone and methanol, redissolved in $CHCl_3$, reprecipitated, filtered in acetone, and dried under vacuum. A dark red polymer (0.0137 g) was obtained (Yield: 23.1%). ^1H NMR ($CDCl_3$, 400MHz, δ from TMS, ppm) δ = 7.66 (br, 4H, Th*H*), 7.11–6.88 (br, 12H, Th*H*), 2.49 (br, 4H, $-CH_2-$), 1.62–1.26 (br, 80H, $-CH_2-$), 0.88 (br, 6H, $-CH_3$).



Poly-1PB

Poly-1PQ

Poly-1TB

Poly-1TQ

Scheme S2. Synthetic routes of **Poly-1PB**, **Poly-1PQ**, **Poly-1TB** and **Poly-1TQ**.

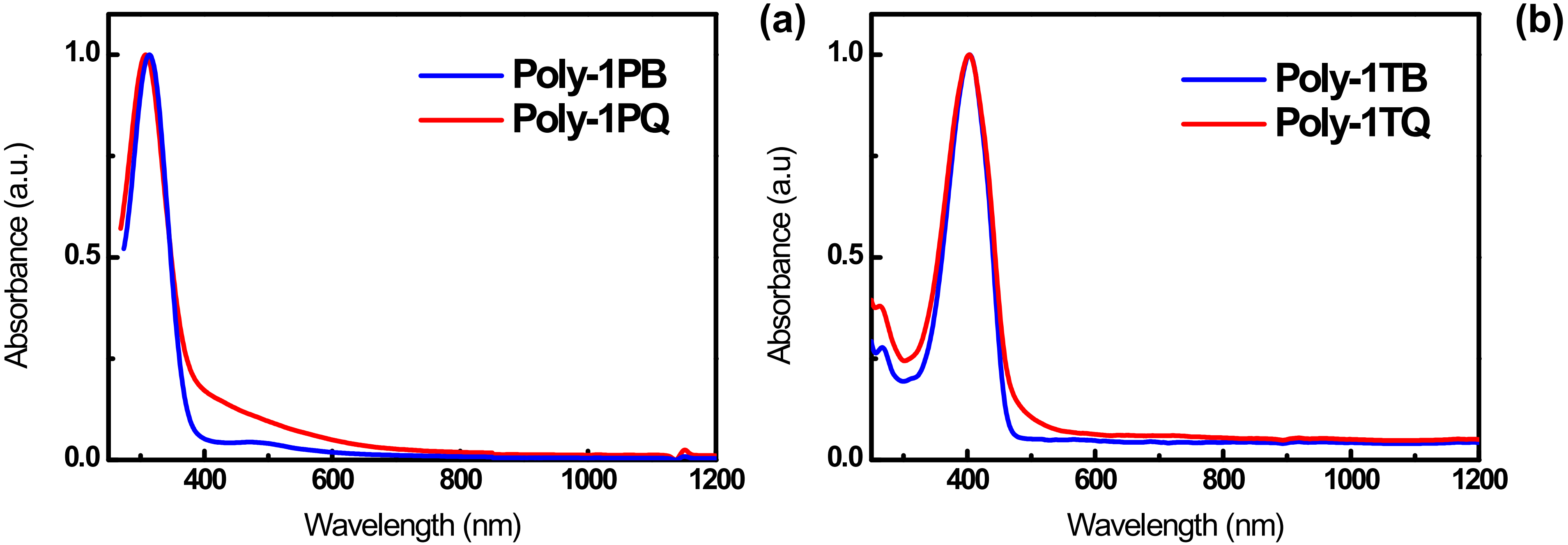


Figure S2. UV-vis-NIR absorption spectra of benzonoidal and quinoidal structures of the (a) **Poly-1P** and (b) **Poly-1T** in $CHCl_3$. Blue and red lines indicate the benzonoidal polymer and quinoidal polymers, respectively.

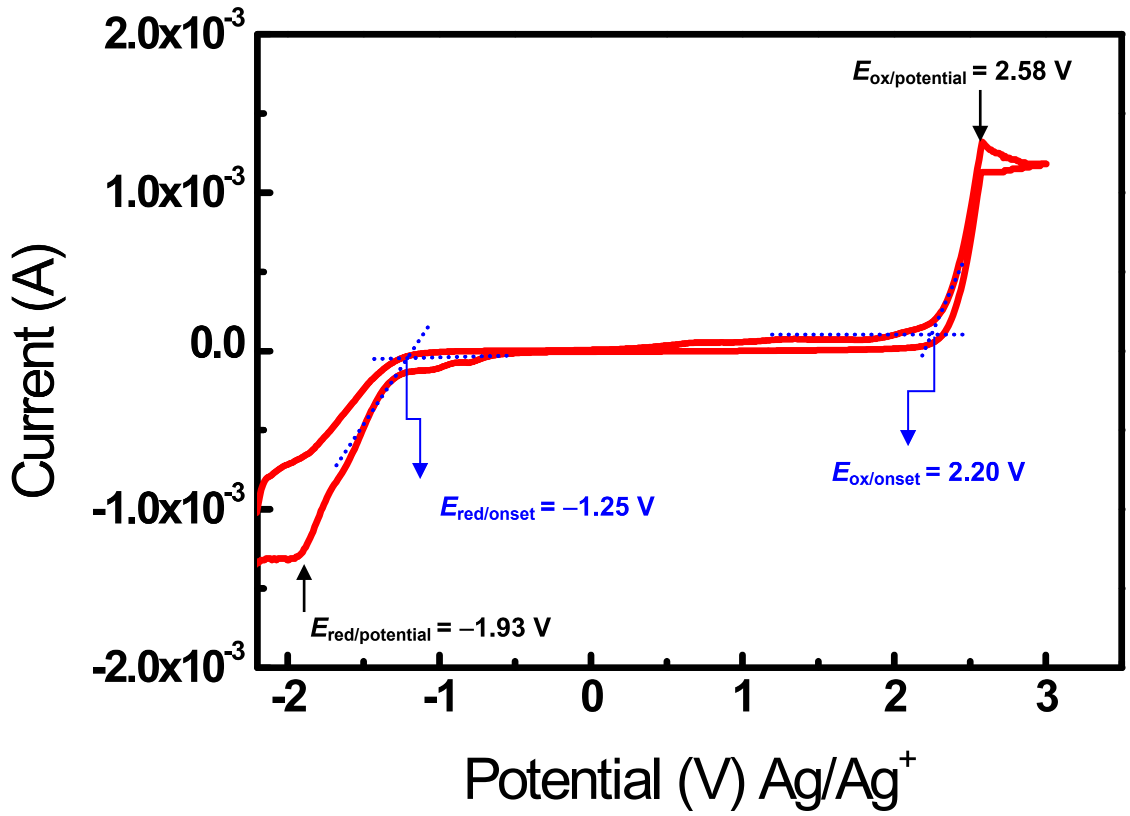


Figure S3. Cyclic voltammogram of **Poly-1PQ** films on a platinum electrode in acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP) measured with a scan rate of 10 mV/sec.

6. Poly(hexyl-thienylenemethine) and poly(hexyl-bithienylenemethine) derivatives

6-1. Synthesis of 3,4′-dihexyl-2,2′-bithiophene (2HT)

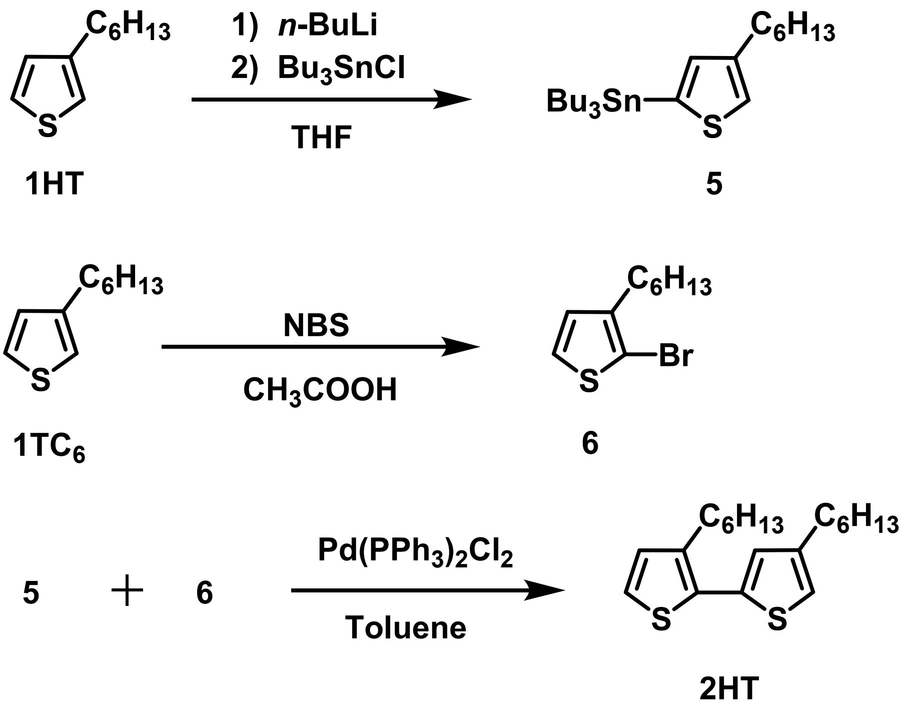
2-Tributylstannyl-4-hexylthhiophene (5).

Under argon atmosphere, 3-hexylthiophene (4.40 g, 26.1 mmol) was dissolved in dry THF (60 mL) and the solution was cooled to −78 °C. Keeping this temperature, the solution of *n*-BuLi (16.34 mL, 26 mmol, 1.6 mol /L) in hexane was added dropwise and stirred for 1h. Then, tributyltinchloride (8.51 g, 26 mmol) was added dropwise to the reaction solution at the same temperature. After stirred for 12h, the reaction mixture was washed with water and extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate. The crude product was passed through a column chromatograph with chloroform. A clear oil (3.32 g) was obtained (Yield: 52.4%). ^{1}H NMR ($CDCl_3$, 400MHz, δ from TMS, ppm) δ= 7.22 (s, 1H, Th*H*), 6.96 (s, 1H, Th*H*), 2.65 (t, 2H, $-CH_2-$), 1.61 (m, 12H, $-CH_2-$), 1.54 (m, 12H, $-CH_2-$), 1.27 (t, 2H, $-CH_2-$), 0.88 (m, 12H, $-CH_3$).

2-Bromo-3-hexylthiophene (6). Under argon atmosphere, 3-hexylthiophene (0.72 g, 4.27 mmol) was dissolved in acetic acid (50 mL) and the solution was cooled to 0 °C. Keeping this temperature, *N*-bromosuccinimide (NBS) (0.76 g, 4.27 mmol) in acetic acid was added dropwise. (It is difficult to dissolve NBS in acetic acid. Therefore, by warming the solution a little, it enabled to dissolve NBS in acetic acid). Since then the temperature of the solution was raised up to room temperature. After stirred for 5h, the reaction mixture was washed with water and extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate. The crude product was passed through a column chromatograph with chloroform, and purifying by recrystallisation with hexane and chloroform. A yellow oil (0.59 g) was obtained (Yield: 55.9 %). ^{1}H NMR ($CDCl_3$, 400MHz, δ from TMS, ppm) δ =

7.18–7.17 (d, 1H, Th*H*), 6.80–6.78 (d, 1H, Th*H*), 2.58–2.53 (t, 2H, –CH_2–), 1.31 (m, 8H, –CH_2–) 0.88 (t, 3H, –CH_3). ^{13}C NMR ($CDCl_3$, 100MHz, δ from TMS, ppm) δ = 142.0, 128.2, 125.1, 108.8, 31.6, 29.7, 29.5, 28.9, 14.1. MS (MALDI-TOF, m/z): Calc. for 246.0078, Found: 246.0078.

3,4′-Dihexyl-2,2′-bithiophene (2HT). 2-Tributylstannyl-4-hexylthhiophene (1.09 g, 2.38 mmol) and 2-bromo-3hexylthiophene were dissolved in toluene (35 mL) under argon atmosphere and a little of tetrakis (triphenylphosphine) palladium (0) [$Pd(PPh_3)_2Cl_2$] was added to the solution at room temperature. After stirred for 8h, the reaction mixture was washed with water and extracted with chloroform. The organic layer was dried over anhydrous sodium sulfate. The crude product was passed through a column chromatogram with chloroform containing triethyl amine. A yellow liquid (0.714 g) was obtained (Yield: 89.6 %). Anal., calcd for $C_{20}H_{30}S_2$: C, 71.80 %; H, 9.04 %; S, 19.17 %. Found: C, 57.77 %; H, 7.50 %; S, 15.52 %. ^{1}H NMR ($CDCl_3$, 400MHz, δ from TMS, ppm) δ= 7.21 (t, 1H, Th*H*), 7.18 (d, 2H, Th*H*), 6.91 (t, 2H, Th*H*), 6.77 (d, 2H Th*H*), 2.61 (t, 2H, –CH_2–), 2.55 (t, 2H, –CH_2–), 1.52 (m, 4H, –CH_2–), 1.45 (m, 2H, –CH_2–), 1.30 (m, 8H, –CH_2–), 0.88 (m, 6H, –CH_3). ^{13}C NMR ($CDCl_3$, 100MHz, δ from TMS, ppm) δ = 160.43, 132.38, 131.77, 118.74, 111.19, 35.93, 31.71, 29.11, 25.33, 22.58, 19.99, 14.05.



Scheme S3. Synthetic routes of **2HT**.

6-2. Synthesis of Poly-1HT and Poly-2HT

Poly-1HTB. The mixture was for polymerisation was prepared with **1HT** (0.0229 g, 0.136 mmol), terthienylaldehyde (0.0047 g, 0.136 mmol), 0.50 ml of *p*-dioxane, and 0.024 mL (0.45 mmol) of 96 % sulfuric acid. The reaction temperature was kept at 80 °C for 24 h.

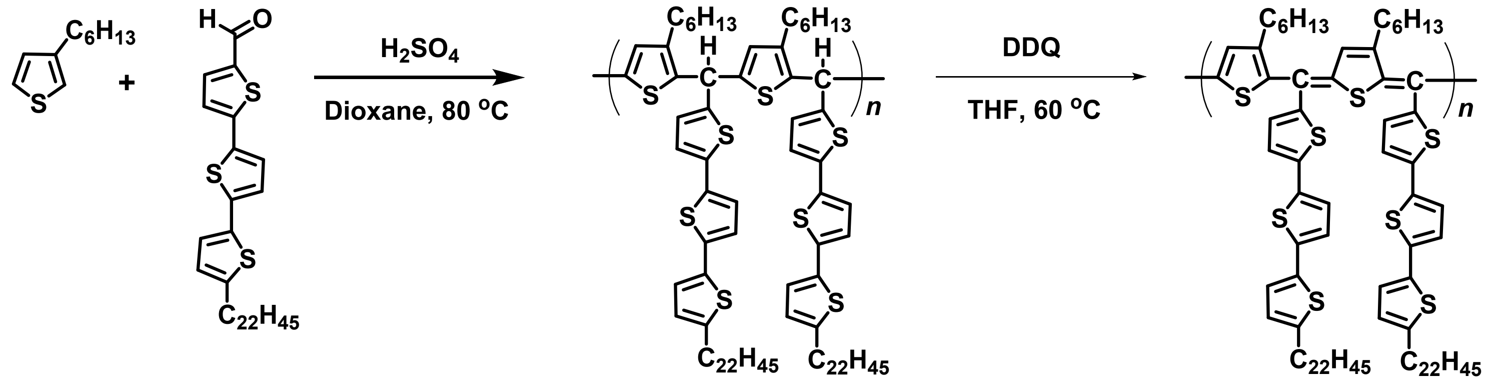
A black product was recovered in 500 mL of stirring methanol, redissolved in THF, recovered in methanol. In addition, a black product was recovered in 500 mL of stirring acetone, redissolved in $CHCl_3$, recovered in acetone and dried in a vacuum. A black polymer (0.050 g) was obtained (Yield: 50 %). M_w = 1,100 M_w/M_n = 1.03 (GPC, PS calibration). ^1H NMR ($CDCl_3$, 400MHz, δ from TMS, ppm) δ = 7.70 (br, 2H, Th*H*), 7.30–7.05 (br, 12H, Th*H*), 6.02 (br, 1.8H, methine *H*), 2.52 (br, 8H, $-CH_2-$), 1.61 (br, 8H, $-CH_2-$), 1.46–1.15

(br, 88H, $-CH_2-$), 0.91 (br, 12H, $-CH_3$).

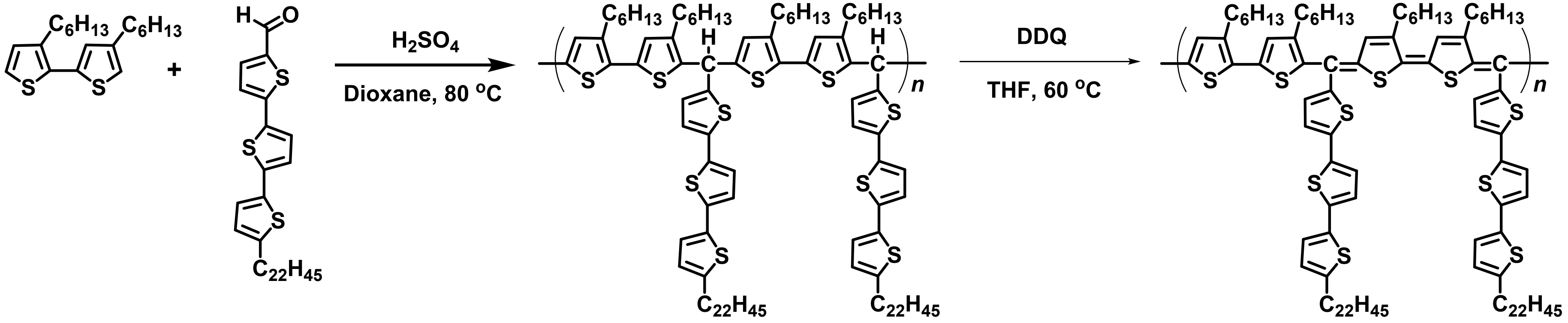
Poly-1HTQ. The mixture was prepared with 0.042 g of **Poly-1HTB**, 0.014 g (0.057 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and 1 mL of anhydrous THF. The reaction temperature was maintained at 60 °C for 24 h. A black product was recovered in 200 mL of stirring methanol, dissolved in $CHCl_3$, recovered in methanol. In addition, a black product was recovered in 500 mL of stirring acetone, redissolved in THF, recovered in acetone and dried in a vacuum. A black polymer (0.014 g) was obtained (Yield: 33.4%). ^1H NMR ($CDCl_3$, 400MHz, δ from TMS, ppm) δ = 7.69 (br, 2H, ThH), 7.32–7.04 (br, 12H, ThH), 2.52 (br, 8H, $-CH_2-$), 1.62 (br, 8H, $-CH_2-$), 1.45–1.14 (br, 88H, $-CH_2-$), 0.91 (br, 12H, $-CH_3$). IR (KBr, cm^{-1}): 2929, 2899 (ν_{CH2}, ν_{CH3}), 1683, 1541 ($\nu_{C=C\ quinoid}$), 1508 ($\nu_{C=C\ benzonoid}$), 888, 799, 698 (δ_{C-H}).

Poly-2HTB. The mixture was prepared with **2HT** (0.0455 g, 0.136 mmol), terthienylaldehyde (0.08 g, 0.136 mmol), 0.50 ml of *p*-dioxane, and 0.024 mL (0.45 mmol) of 96 % sulfuric acid. The reaction temperature was kept at 80 °C for 24 h. A black product was recovered in 500 mL of stirring methanol, redissolved in THF, recovered in methanol. In addition, a black product was recovered in 500 mL of stirring acetone, redissolved in $CHCl_3$, recovered in acetone and dried in a vacuum. A black polymer (0.090 g) was obtained (Yield: 70 %). M_w = 1,800 M_w/M_n = 1.20 (GPC, PS calibration). ^1H NMR ($CDCl_3$, 400MHz, δ from TMS, ppm) δ = 7.63 (br, 4H, ThH), 7.20–6.88 (br, 12H, ThH), 5.99 (br, 0.62H, methine H), 2.57 (br, 12H, $-CH_2-$), 1.66 (br, 12H, $-CH_2-$), 1.41-1.08(br, 100H, $-CH_2-$), 0.87 (br, 18H, $-CH_3$).

Poly-2HTQ. The mixture was prepared with 0.0085 g of **Poly-2HTB**, 0.0024 g (0.0011 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and 1 mL of anhydrous THF. The reaction temperature was maintained at 60 °C for 24 h. A black product was recovered in 200 mL of stirring methanol, dissolved in $CHCl_3$, recovered in methanol. In addition, a black product was recovered in 500 mL of stirring acetone, redissolved in THF, recovered in acetone and dried in a vacuum. A black polymer (0.0019 g) was obtained (Yield: 23%). ^{1}H NMR ($CDCl_3$, 400MHz, δ from TMS, ppm) δ = 7.61–7.48 (br, 4H, Th*H*), 7.20–6.88 (br, 12H, Th*H*), 2.57 (br, 12H, $-CH_2-$), 1.66 (br, 12H, $-CH_2-$), 1.40–1.08 (br, 100H, $-CH_2-$), 0.87 (br, 18H, $-CH_3$). IR (KBr, cm^{-1}): 2949, 2894 (ν_{CH2}, ν_{CH3}), 1683, 1541 ($\nu_{C=C\ quinoid}$), 1508 ($\nu_{C=C\ benzonoid}$), 824, 795, 707 (δ_{C-H}).



Poly-1HTB **Poly-1HTQ**



Poly-2HTB **Poly-2HTQ**

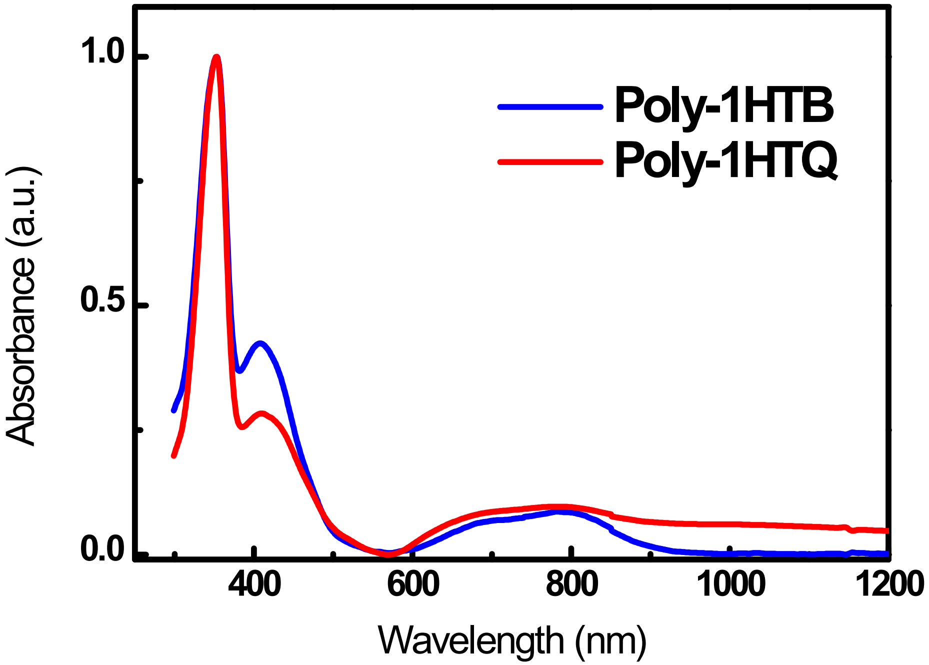
Scheme S4. Synthetic routes of **Poly-1HTB**, **Poly-1HTQ**, **Poly-2HTB**, and **Poly-2HTQ**.

Table S2. GPC data and optical bandgaps of **Poly-1PQ**, **Poly-1TQ**, **Poly-1HTQ**, and **Poly-2HTQ**

Polymer	M_n	M_w	$M_{w/}\ M_n$	D.P.[a] (T.U.)[b]	λ_{max} (nm)	λ_{onset} (nm)	Optical bandgap (eV)
Poly-1PQ	2,200	2,900	1.35	5 (5)	470	550	2.25
Poly-1TQ	2,100	2,500	1.20	3 (3)	850	1,400	0.89
Poly-1HTQ	1,100	1,200	1.03	2 (2)	800	980	1.24
Poly-2HTQ	1,800	3,000	1.20	2 (4)	750	1,200	1.04

[a] D.P.: Degree of polymerisation

[b] T.U.: Number of thienylene unit


Poly-1HTB
Poly-1HTQ
Absorbance (a.u.)
1.0
0.5
0.0
400
600
800
1000
1200
Wavelength (nm)

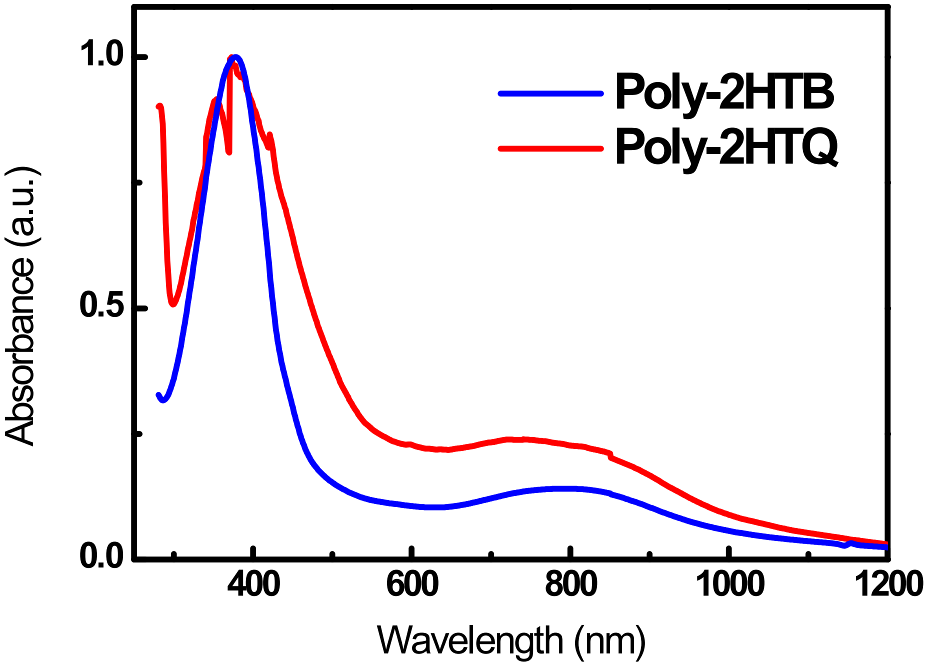

Poly-2HTB
Poly-2HTQ
Absorbance (a.u.)
1.0
0.5
0.0
400
600
800
1000
1200
Wavelength (nm)

Figure S4. UV-vis-NIR absorption spectra of benzonoidal and quinoidal structures of (a) **Poly-1HT** and (b) **Poly-2HT** in $CHCl_3$. Blue and red lines indicate the benzonoidal and quinoidal polymers, respectively.

7. Hole mobility measurements

Charge carrier mobility in blend films was evaluated by the space charge limited current (SCLC) method. The hole-only device with the same active layer thickness as actual devices was fabricated by constructing **ITO** / **PEDOT–PSS** / active polymer–**PCBM** (1:1) / Au structure (Figure S4). The electrodes were then modified by a spin cast layer of **PEDOT–PSS** (Clevios P VP. AI 4083 HC-Starck filtered through a 0.45 μm membrane just prior use). The spin casting was achieved on ITO glass with a thickness of about 40 nm, and the electrode was then dried by heating at 120–150 °C for 15 min. The polymer and **PCBM** were blended and dissolved in chlorobenzene, followed by forming the active polymer layer with a thickness of about 130 nm and drying at a given temperature. Au film with thickness of 100 nm was prepared with by a vacuum deposition. This procedure was adjusted to maintain the deposition rate less than 0.01 nm/sec. The hole mobility was evaluated by fitting the dark *J*-*V* curve of the hole-only device to the SCLC (space charge limited current) model at low voltages, in which the current density (*J*) is given by

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu_h \frac{V^2}{L^3}$$

Here, ε_0 is a dielectric constant of free space, ε_r is a dielectric constant of the polymer and is assumed to be approximate 3 for conjugated polymers, μ_h is a hole mobility, V is a voltage drop across the device, and L is a film thickness of the active layer.

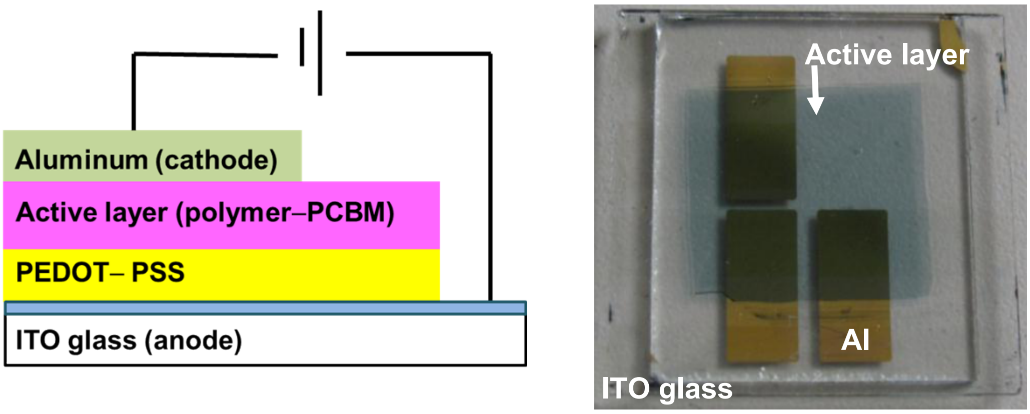
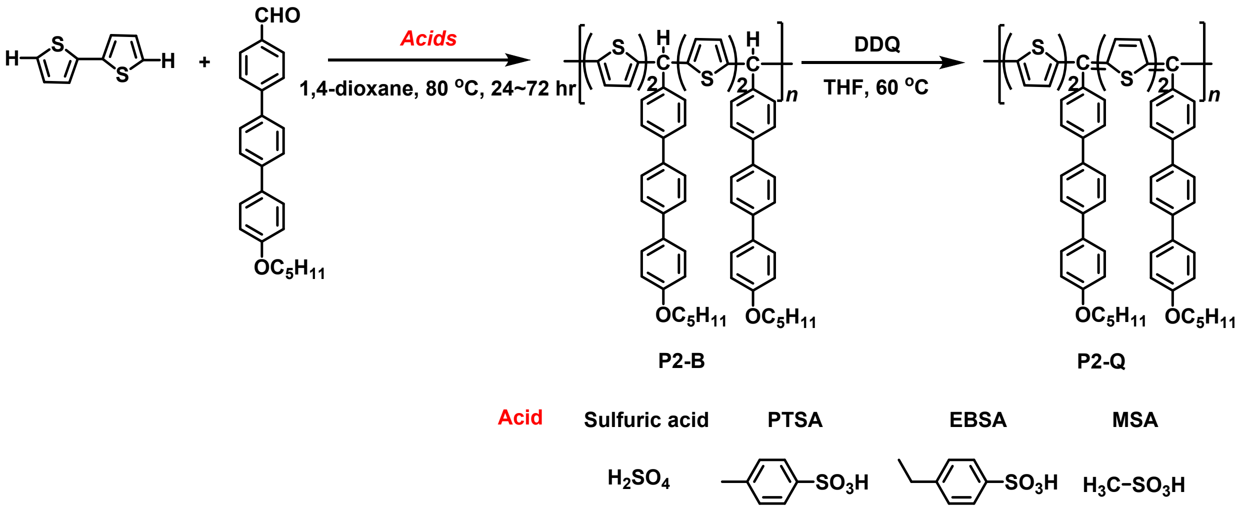


Figure S5. Schematic diagram and photo of the polymer solar cell with a layered structure consisting of ITO/**PEDOT–PSS**/active layer [**Poly-2PQ–PCBM** (1:1 wt%)]/aluminium. Here, ITO is indium tinoxide, **PEDOT** is poly(3,4-ethylenedioxythiophene), **PSS** is poly(styrenesulfonic acid), and **PCBM** is [6,6]-phenyl-C_{61}-butyric acid methyl ester. **PEDOT–PSS** is used as a hole-conducting buffer.

8. Polymerizations using several types of acidic catalysts



Scheme S5. Synthetic routes for synthesis of benzonoidal (**Poly-2PB**) and quinoidal (**Poly-2PQ**) polymers. The polymerization conditions were improved by using several types of sulphonic acids and also polymerization time.

Table S3. Polymerization results of **Poly-2PB** by using alkyl and aryl sulphonic acids as catalysts

Entry	Polymerization Time (hr)	Acidic catalyst [a]	M_n	M_w	M_w/M_n	D.P. [b]	T.U. [c]
1	24	H_2SO_4	5,700	8,900	1.57	11	22
2	24	PTSA	5,900	9,400	1.59	12	24
3	24	EBSA	3,800	5,200	1.36	8	16
4	24	MSA	4,000	5,500	1.39	8	16
5	48	H_2SO_4	6,700	12,000	1.78	14	28
6	48	PTSA	3,100	4,100	1.33	6	12
7	48	EBSA	4,800	7,300	1.51	10	20
8	48	MSA	5,400	8,900	1.64	11	22
9	72	H_2SO_4	6,300	10,300	1.65	13	26
10	72	PTSA	7,800	14,500	1.86	16	32
11	72	EBSA	8,200	16,100	1.96	17	34
12	72	MSA	7,300	14,300	1.95	15	30

a) MSA : methane sulphonic acid

PTSA : para-toluene sulphonic acid

EBSA : 4-ethylbenzene sulphonic acid

b) D.P.: Degree of polymerization

c) T.U.: Number of thienylene unit

9. Electrical conductivity

Electrical conductivity of polymer cast film can be evaluated using the following equation:

$$\sigma = \frac{1}{\rho} = \frac{L}{RA} = \frac{L}{RDW} = \frac{1}{RD}$$

where σ is the conductivity, ρ is the resistivity, R is the electrical resistance of the film, L is the length of the film, A is the cross-sectional area, W is the width, and D is the thickness.