Supplementary Information (SI) for Polymer Chemistry.

Metal-Free Multicomponent Polymerization to Access Polythiophenes from Elemental Sulfur, Dialdehydes, and Imides

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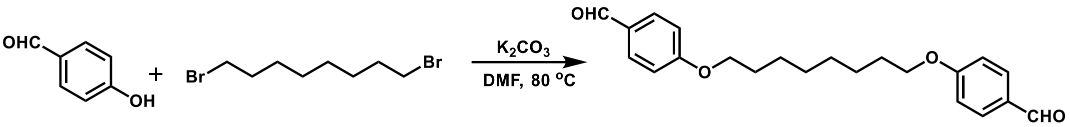
1. Materials

4,4'-Biphenyldicarboxaldehyde (Energy Chemical, 97%), succinic anhydride (aladdin, 99%), hexylamine (aladdin, 99%), 4-heptylamine (aladdin, 99%), isopropylamine(aladdin, 98%), potassium carbonate (Tianjin Bodi Chemical Co., 99%), ammonium persulphate(Tianjin Damao Chemical Co., 99%), 4-hydroxybenzaldehyde (Energy Chemical, 99%), potassium hydroxide (Tianjin Damao Chemical Co., 85%), tetraethylene glycol (Energy Chemical, 99%), 1,8-dibromooctane (Macklin, 99%), ammonium chloride (Tianjin Guangfu Fine Chemical Co., 99.5%), pyridinium chlorochromateand (PCC, aladdin, 99%), 1,8-octanediol ((Leyan, 99%), succinimide (Macklin, 98%), sodium tetrachloridopalladate(II) (Aladdin, 98%) and vinyl acetate (Macklin, 98%) were used without further purification. All the solvents including 1,4-dioxane, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), methyl *tert*-butyl ether(MTBE), ethyl acetate (EA), petroleum ether (PE), methanol (MeOH) and ethanol (EtOH) were dried using a column packed with 4 Å molecular sieves before use.

2. Instruments

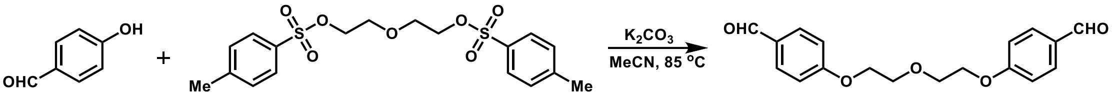
^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker AVANCE II 400 NMR or 500 NMR spectrometer with $CDCl_3$ or d_6-DMSO as the solvent and tetramethylsilane (TMS; $\delta=0$ ppm) as an internal standard at room temperature. The number-average molecular weight (M_n), weight-average molecular weight (M_w) and poly-dispersities ($Đ$) of the polymers were determined using a gel permeation chromatography (GPC) system equipped with an isocratic pump (model 515, Waters Corporation) (mobile phase: DMF; standard: PMMA) and refractive index detector. Absolute molecular weight was determined by GPC in DMF using a MALLS detector. UV-vis absorption spectra were recorded on a Lambda 1050+. Thermal gravimetric analysis was performed using Q500 analyzer at the heating rate of 10 $°C\cdot min^{-1}$. DSC analysis was performed using Q20 differential scanning calorimeter at a rate of 10 $°C\cdot min^{-1}$. Cyclic voltammetry was conducted on a BioLogic VMP3 electrochemical workstation using sample film coated on glassy carbon as the working electrode, Pt wire as the counter electrode, and platinum plate electrode as the reference electrode, in a 0.1 M tetrabutylammonium tetrafluoroborate acetonitrile solution and ferrocene/ferrocenium (Fe/Fe^+) couple was used as an internal reference. FT-IR spectra were tested with Thermo Nicolet Nexus 470 spectrometer. Elemental analysis using vario EL cube.

3. Synthesis of 1b-1f, 2a-2d, S1(1/2a/3)



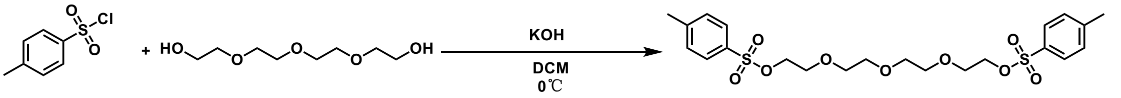
Scheme S1. Synthesis of **1b**.

4-Hydroxybenzaldehyde (10 mmol, 1.22 g) and potassium carbonate (10 mmol, 1.38 g) were added into a solution of 1,8-dibromooctane (5 mmol, 1.36 g) in 8 mL of DMF. After stirring under nitrogen for 12 h at 80 °C, and the resulting solution was poured into 50 mL of water. The precipitant was collected and recrystallized from EtOH, obtaining **1b** as a white solid in 86% yield (1.51 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 2H), 7.83 (d, *J* = 8.0 Hz, 4H), 7.00 (d, *J* = 8.0 Hz, 4H), 4.08-4.04 (m, 4H), 1.92-1.75 (m, 4H), 1.49- 1.42 (m, 8H).



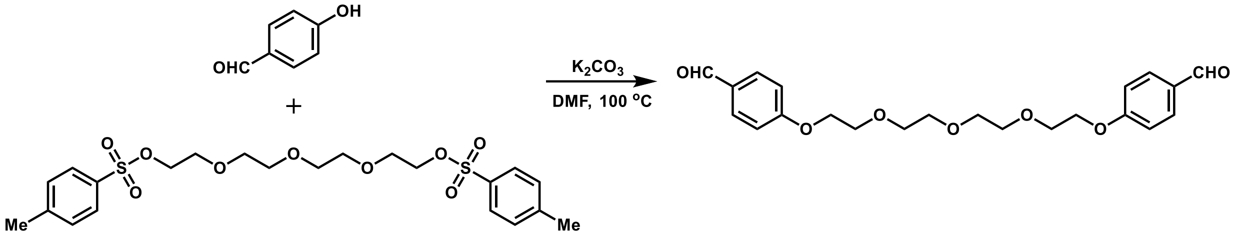
Scheme S2. Synthesis of **1d**.

4-Hydroxybenzaldehyde (8.7 mmol, 1.06 g) and potassium carbonate (35 mmol, 4.83 g) were added into a solution of oxybis(ethane-2,1-diyl)bis(4-methylbenzenesulfonate) (3 mmol, 1.25 g) in 25 mL of MeCN. The mixture was heated at 85 °C for 15 h under N_2 atmosphere. The solution was then poured into a water-ice mixture (50 mL) and vigorously stirred, filtered, washed with an ethanol-ice mixture (25 mL) and washed with EA (25 mL). The solid was dried in vacuo at 60 °C to afford **1d** as a white solid in 89% yield (0.78 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 2H), 7.83 (d, *J* = 8.0 Hz, 4H), 7.03 (d, *J* = 8.0 Hz, 4H),4.26-4.22 (m, 4H), 3.99-3.95 (m, 4H).



Scheme S3. Synthesis of **1e'**.

Excess potassium hydroxide (32 mmol, 1.80 g) was added portion-wise to a cool (0 °C) solution of tetraethylene glycol (4 mmol, 0.7 mL) and *p*-toluenesulfonyl chloride (8 mmol, 1.53 g) in dichloromethane (DCM, 16 mL). The reaction mixture was stirred for 3 h at 0 °C. Water (16 mL) was then added and the aqueous phase was extracted with DCM (3×15 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure to afford pure product **1e'** as a white solid in 90% yield (1.81 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 4H), 7.34 (d, *J* = 8.5 Hz, 4H), 4.20-4.15 (m, 4H), 3.70-3.66 (m, 4H), 3.58-3.54 (m, 8H), 2.44 (s, 6H).

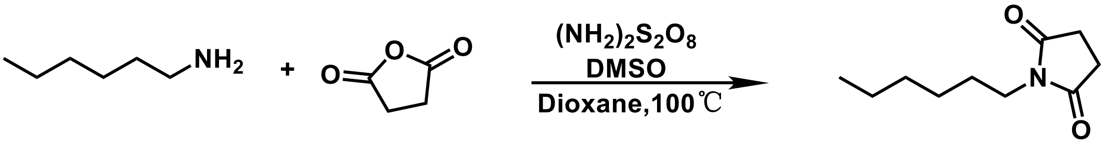


Scheme S4. Synthesis of **1e**.

To a solution of 4-hydroxybenzaldehyde (7.2 mmol, 0.88 g) in 10 mL of DMF was added anhydrous potassium carbonate (7.2 mmol, 0.99 g) and **1e'** (3.6 mmol, 1.8 g). The reaction mixture was stirred under reflux for about 16 h, and the resulting solution was partially concentrated under reduced pressure and poured into 50 mL of water. The precipitant was collected and recrystallized from MeOH, obtaining **1e** as an ivory solid in 88% yield (1.27 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 2H), 7.83 (d, *J* = 8.0 Hz, 4H), 7.02 (d, *J* = 8.1 Hz, 4H), 4.22-4.18 (m, 4H), 3.89-3.86 (m, 4H), 3.75-3.70 (m, 8H).

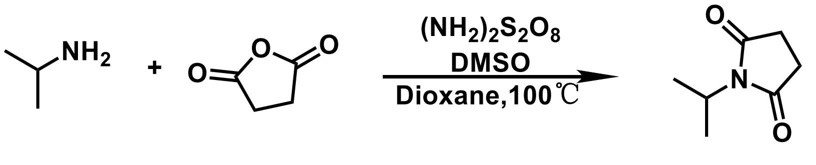
Scheme S5. Synthesis of **1f**.

A mixture of 1,8-octanediol (73.1 mg, 5.0 mmol) and PCC (2.44 g, 11.0 mmol) in DCM (15 mL) was stirred at room temperature for 5 h. The reaction mixture was quenched with saturated NH_4Cl (20 mL), and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and evaporated under vacuo. The crude product was purified by column chromatography using a PE:EA = 1:1 eluent and evaporated under vacuo to obtain **1f** as a colorless transparent liquid in 36% yield (257 mg);^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (s, 2H), 2.44 (t, *J* = 7.3 Hz, 4H), 1.67-1.61 (m, 4H), 1.38-1.34 (m, 4H).



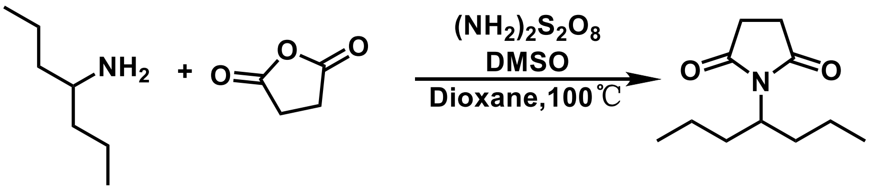
Scheme S6. Synthesis of **2a**.

In two-necked round bottom flask equipped with water condenser, solution of hexylamine (60.8mg, 0.46 mmol) and succinic anhydride (51.03 mg, 0.51 mmol) in dioxane were stirred at room temperature for 10 min under open flask. Then ammonium peroxodisulphate (211.86 mg, 0.93 mmol) and DMSO (72.66 mg, 0.93 mmol) were added to reaction mixture at room temperature, then heated to 100°C and allowed stirring in open air atmosphere for 7 h. Reaction mixture was filtered through cotton plug and dioxane was removed in vacuo. Crude product dissolved in EA and washed with dil.HCl, sat.$NaHCO_3$ and brine. Organic layer dried over anhydrous Na_2SO_4, solvent removed under vacuo, obtaining **2a** as yellow oil (97 mg, 99% Yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.49-3.47 (m, 2H), 2.69 (s, 4H), 1.56-1.52 (m, 2H), 1.29-1.24 (m, 6H), 0.88-0.84 (m, 3H).



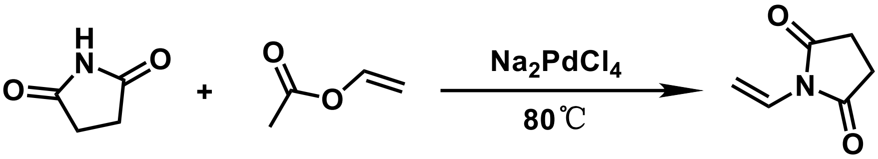
Scheme S7. Synthesis of **2b**.

In two-necked round bottom flask equipped with water condenser, solution of isopropylamine (39.5mg, 0.46 mmol) and succinic anhydride (51.03 mg, 0.51 mmol) in dioxane were stirred at room temperature for 10 min under open flask. Then ammonium peroxodisulphate (211.86 mg, 0.93 mmol) and DMSO (72.66 mg, 0.93 mmol) were added to reaction mixture at room temperature, then heated to 100 °C and allowed stirring in open air atmosphere for 7 h. Reaction mixture was filtered through cotton plug and dioxane was removed in vacuo. Crude product dissolved in EA and washed with dil.HCl, sat.$NaHCO_3$ and brine. Organic layer dried over anhydrous Na_2SO_4, solvent removed under vacuo, obtaining **2b** as dark brown solid (107 mg, yield: 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.39-4.36 (m, 1H), 2.63 (s, 4H), 1.37 (d, *J* = 2.0 Hz, 6H).



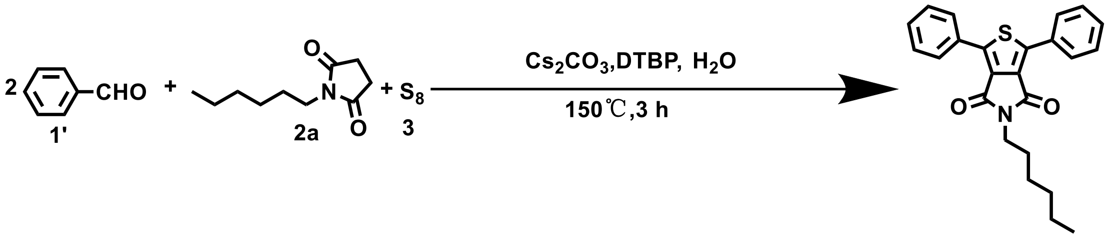
Scheme S8. Synthesis of **2c**.

In two-necked round bottom flask equipped with water condenser, solution of 4-heptylamine (68.2mg, 0.46 mmol) and succinic anhydride (51.03 mg, 0.51 mmol) in dioxane were stirred at room temperature for 10 min under open flask. Then ammonium peroxodisulphate (211.86 mg, 0.93 mmol) and DMSO (72.66 mg, 0.93 mmol) were added to reaction mixture at room temperature, then heated to 100°C and allowed stirring in open air atmosphere for 7 h. Reaction mixture was filtered through cotton plug and dioxane was removed in vacuo. Crude product dissolved in EA and washed with dil.HCl, sat.$NaHCO_3$ and brine. Organic layer dried over anhydrous Na_2SO_4, solvent removed under vacuo obtaining **2c** as dark brown solid (107 mg, yield: 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09-4.07 (m, 1H), 2.64 (s, 4H), 1.98-1.94 (m, 2H), 1.59-1.56 (m, 2H), 1.24-1.20 (m, 4H), 0.89-0.84 (m, 6H).



Scheme S9. Synthesis of **2d**.

Succinimide (10.1 mmol, 1.00 g) and sodium tetrachloridopalladate(II) (0.202 mmol, 59.0 mg) were added into vinyl acetate (270 mmol, 25.0 mL) . The reaction mixture was stirred for 72 h at 80 °C. Reaction mixture was filtered through sintered glass funnel, washed with sat.$NaHCO_3$ and brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure to afford crude product. The crude product was purified by column chromatography using a PE:EA = 3:1 eluent and evaporated under vacuo again to obtain **2d** as a pale yellow solid in 82% yield (1.03 g); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.72 (dd, J = 16.4, 9.9 Hz, 1H), 6.11 (d, J = 16.4 Hz, 1H), 5.09 (d, J = 9.8 Hz, 1H), 2.75 (s, 4H).

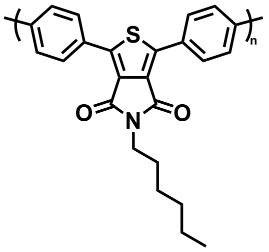


Scheme S10. Synthesis of **S1**(1'/2a/3).

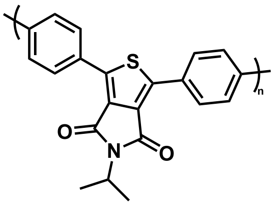
Benzaldehyde **1'** (0.16 mmol), cyclic imide **2a** (0.8 mmol), elemental sulfur (0.12 mmol), cesium carbonate (0.4 mmol), *tert*-butyl peroxide (0.16 mmol) and deionized water (1.0 mmol) were dissolved in a mixed solvent of DMF (2 mL). The reaction was carried out at 150 ° C for 2 h and cooled to room temperature. After cooling to room temperature, the reaction was diluted with EA (15 mL) and washed with saturated salt water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 for three times. The combined organic layer was dried over sodium sulfate and the volatiles were removed under reduced pressure. The crude product was purified by silica gel chromatography (eluent: PE) to afford the product S1(1'/2a/3) as a yellow oil with the yield of 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 4H), 7.55-7.45 (m, 6H), 3.72-3.70 (m, 2H), 1.73-1.71 (m, 2H), 1.38-1.35 (m, 6H), 0.94-0.91 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0, 145.0, 130.6, 130.5, 130.2, 129.0, 128.2, 38.7, 31.4, 28.4, 26.6, 22.5, 14.0.

4. General procedure for MCP method

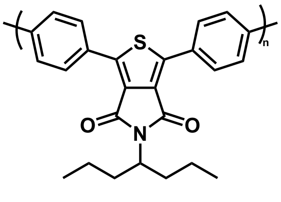
The MCP reaction were carried out as mentioned below using **1a**, **2a** and **3** for the synthesis of **P1** as a typical example. 4,4-Biphenyldialdehyde **1a** (0.8 mmol), cyclic imide **2a** (0.8 mmol), elemental sulfur (0.12 mmol), cesium carbonate (0.4 mmol), di-*tert*-butyl peroxide (0.16 mmol) and water (1.0 mmol) were added into a mixed solvent of DMF (2 mL). The reaction was carried out at 150°C for 6 h and cooled to room temperature. The reactant was precipitated in MTBE, and the precipitate was collected by centrifugation. The precipitate was redissolved with DMF, which was precipitated in the MTBE again. The above process was repeated three times. The precipitate was washed twice with MTBE. The product was dried to constant weight in a vacuum drying oven.



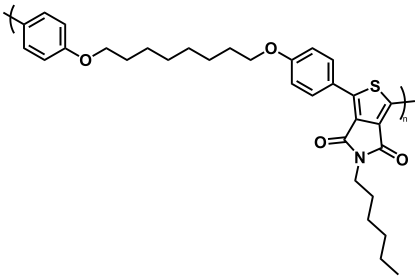
P1(1a/2a/3): yield: 83%, black solid, M_w=22900 g/mol, M_w/M_n=1.48, ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.50 (8H), 3.09 (2H), 1.18-0.79 (11H). ^{13}C NMR (101 MHz, d_6-DMSO) δ161.8, 145.8, 141.9, 138.3, 135.5, 130.6, 127.5, 31.2, 29.2, 27.4, 26.3, 22.4, 14.3.



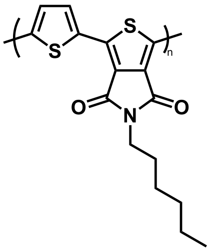
P2(1a/2b/3): yield: 81%, brown solid, M_w=12900 g/mol, M_w/M_n=1.32, ^{1}H NMR (400 MHz, d_6-DMSO): δ 8.34-7.07 (8H), 4.25 (1H), 1.68-0.57 (6H). ^{13}C NMR (101 MHz, d_6-DMSO) δ151.9, 139.9, 130.6, 130.0, 128.9, 127.5, 125.6, 124.8, 22.9, 22.6, 22.2, 20.9, 19.5.



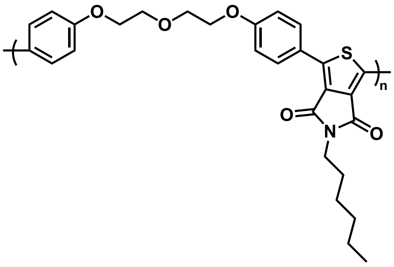
P3(1a/2c/3): yield: 80%, brown solid, M_w=24800 g/mol, M_w/M_n=1.40, ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.62 (8H), 4.25 (1H), 1.47-0.60 (14H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 161.8, 145.9, 135.7, 130.7, 127.7, 127.6, 33.5, 19.6, 14.4, 14.0.



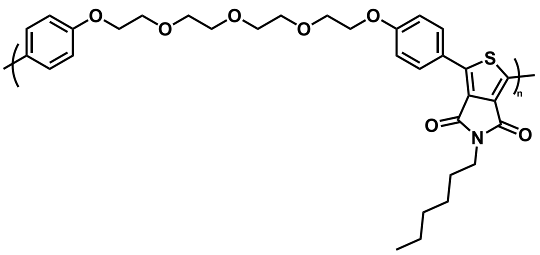
P4(1b/2a/3): yield: 85%, brown solid, M_w=17800 g/mol, M_w/M_n=1.36, ^{1}H NMR (400 MHz, d_6-DMSO): δ 8.37-6.53 (8H), 4.25-3.70 (4H), 3.31-2.83 (2H), 1.71 (4H), 1.58-0.93 (16H), 0.83 (3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 160.2, 145.4, 132.3, 131.8, 130.0, 128.7, 115.4, 114.6, 112.0, 68.5, 67.9, 31.5, 30.5, 29.2, 28.0, 27.4, 25.9, 22.4, 14.3.



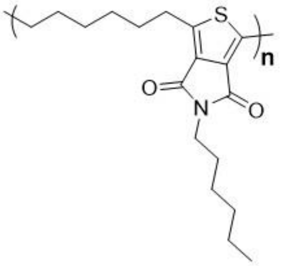
P5(1c/2a/3): yield: 88%, brown solid, M_w=8600 g/mol, M_w/M_n=1.20, ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.08 (2H), 3.21-3.08 (2H), 1.42-0.85 (11H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 184.0, 165.3, 163.0, 31.2, 29.9, 29.3, 26.4, 22.4, 14.3.



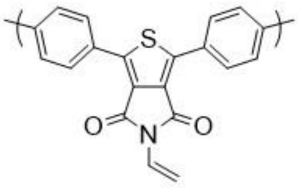
P6(1d/2a/3): yield: 86%, brown solid, M_w=15200 g/mol, M_w/M_n=1.26, ^{1}H NMR (400 MHz, d_6-DMSO): δ 8.64-6.29 (8H), 4.64-3.48 (8H), 3.32-2.95 (2H), 1.82-1.54 (2H), 1.36-1.06 (6H), 0.89-0.47 (3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 165.32, 132.25, 131.74, 130.15, 129.74, 69.49, 68.15, 67.49, 31.46, 27.39, 26.38, 26.21, 22.43, 14.37.



P7(1e/2a/3): yield: 80%, brown solid, M_w=19100 g/mol, M_w/M_n =1.35, ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.07-6.65 (8H), 4.19-3.95 (4H), 3.74-3.67 (4H), 3.56-3.50 (8H), 3.05-3.01 (2H), 1.48-0.82 (11H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 162.8, 145.6, 132.3, 130.9, 130.1, 130.1, 70.3, 69.2, 68.2, 36.2, 31.5, 31.4, 31.2, 31.2, 27.3, 26.6, 22.5, 14.4.



P8(1f/2a/3): yield: 73%, black solid, M_w=5800 g/mol, M_w/M_n =1.07, ^{1}H NMR (400 MHz, d_6-DMSO): δ 2.92-2.71 (2H), 2.35-1.95 (4H), 1.81-0.70 (19H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 162.8, 130.6, 130.1, 127.5, 37.0, 36.3, 35.3, 33.3, 31.2, 28.4.



P9(1a/2d/3): yield: 64%, brown solid, M_w=7600 g/mol, M_w/M_n =1.12, ^{1}H NMR (400 MHz, d_6-DMSO): δ 8.50-6.93 (11H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 184.0, 165.3, 163.0, 31.2, 29.9, 29.3, 26.4, 22.4, 14.3.

5. Screening of polymerization conditions

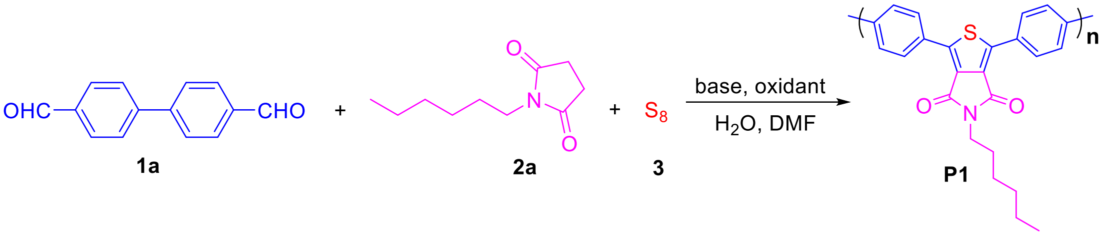


Table S1. Effect of Solvent on the MCP of 1a, 2a and 3 [a].

Entry	Solvent	Yield (%)	M_n [b] (g/mol)	M_w [b] (g/mol)	$Đ$ [b]
1	DMF	83	15400	22900	1.48
2	DMF : *n*-hexane (v:v = 2:1)	44	13500	21000	1.56
3	DMSO	28	9300	9800	1.05

[a] Conditions: The reaction was carried out in solution with opening in the air for 6 h. [1a]:[2a]:[3]:[Cs_2CO_3]:[DTBP]:[H_2O] = 1:1:0.15:0.5:0.2:1.25.

[b] M_n, M_w and $Đ$ were determined by GPC in DMF with PMMA standards.

Table S2. Effect of Temperature on the MCP of 1a, 2a and 3 [a].

Entry	*T*（°C）	Yield (%)	M_n [b] (g/mol)	M_w [b] (g/mol)	$Đ$ [b]
1	70	7	-	-	-
2	110	10	-	-	-
3	130	56	7900	9100	1.16
4	150	83	15400	22900	1.48

[a] Conditions: The reaction was carried out in DMF solution with opening in the air for 6 h. [1a]:[2a]:[3]:[Cs_2CO_3]:[DTBP]:[H_2O] = 1:1:0.15:0.5:0.2:1.25.

[b] M_n, M_w and $Đ$ were determined by GPC in DMF with PMMA standards.

Table S3. Effect of Monomer Concentration on the MCP of 1a, 2a and 3 [a].

Entry	[1a] (M)	Yield (%)	M_n [b] (g/mol)	M_w [b] (g/mol)	$Đ$ [b]
1	0.3	56	13300	19400	1.46
2	0.4	83	15400	22900	1.48
3	0.5	52	17800	25900	1.46
4	0.6	59	13800	19600	1.42
5 [c]	0.8	-	-	-	-

[a] Conditions: The reaction was carried out in DMF solution at 150 °C with opening in the air for 6 h. [1a] = X M, [2a] = 0.4 M, [3] = 0.06 M, [Cs_2CO_3] = 0.2 M, [DTBP] = 0.08 M, [H_2O] = 0.5 M.

[b] M_n, M_w and $Đ$ were determined by GPC in DMF with PMMA standards.

[c] Formation of gel and the polymers cannot be dissolved.

Table S4. Effect of Base on the MCP of 1a, 2a and 3 [a].

Entry	base	Yield (%)	M_n [b] (g/mol)	M_w [b](g/mol)	$Đ$ [b]
1	Cs_2CO_3	83	15400	22900	1.48
2	K_2CO_3	34	6700	7200	1.09
3	NaOH	-	-	-	-
4	Et_3N	-	-	-	-
5	DBU	-	-	-	-

[a] Conditions: The reaction was carried out in DMF solution at 150 °C with opening in air for 6 h (in the sealed tube). [1a] = 0.4 M, [2a] = 0.4 M, [3] = 0.06 M, [base] = 0.2 M, [DTBP] = 0.08 M, [H_2O] = 0.5 M.

[b] M_n, M_w and $Đ$ were determined by GPC in DMF with PMMA standards.

Table S5. Effect of the Equivalent of Cs_2CO_3 on the MCP of 1a, 2a and 3 [a].

Entry	Cs_2CO_3 (equiv)	Yield (%)	M_n ^{b} (g/mol)	M_w ^{b}(g/mol)	$Đ^b$
1	0.375	66	14300	19200	1.35
2	0.5	83	15400	22900	1.48
3	0.6	68	20800	27400	1.32
4	0.7	63	17600	28300	1.61

[a] Conditions: The reaction was carried out in DMF solution at 150 °C with opening in air for 6 h. [1a]:[2a]:[3]:[Cs_2CO_3]:[DTBP]:[H_2O] = 1:1:0.15:X:0.2:1.25.

[b] M_n, M_w and $Đ$ were determined by GPC in DMF with PMMA standards.

Table S6. Effect of the Equivalent of H_2O on the MCP of 1a, 2a and 3 [a].

Entry	H_2O (equiv)	Yield (%)	M_n ^{b} (g/mol)	M_w ^{b} (g/mol)	$Đ$ ^{b}
1	0	-	-	-	-
2	0.75	31	-	-	-
3	1.0	67	13800	19400	1.41
4	1.2	83	15400	22900	1.48
5	2	12	-	-	-

[a] Conditions: The reaction was carried out in DMF solution at 150 °C with opening in air for 6h. [1a]:[2a]:[3]:[Cs_2CO_3]:[DTBP]:[H_2O] = 1:1:0.15:0.5:0.2:X.

[b] M_n, M_w and $Đ$ were determined by GPC in DMF with PMMA standards.

Table S7. Effect of the Equivalent of S_8 on the MCP of 1a, 2a and 3 [a].

Entry	S_8 (equiv)	Yield (%)	M_n ^{b} (g/mol)	M_w ^{b}(g/mol)	$Đ^b$

1	0.125	81	14000	20900	1.50
2	0.15	83	15400	22900	1.48
3	0.175	78	16500	23800	1.46

[a] Conditions: The reaction was carried out in DMF solution at 150 °C with opening in air for 6 h. [1a]:[2a]:[3]:[Cs_2CO_3]:[DTBP]:[H_2O] = 1:1:X:0.5:0.2:1.25.

[b] M_n, M_w and *Đ* were determined by GPC in DMF with PMMA standards.

Table S8. Effect of Oxidant on the MCP of 1a, 2a and 3 [a].

Entry	oxidant	Yield (%)	M_n [b] (g/mol)	M_w [b] (g/mol)	*Đ* [b]
1	-	-	-	-	-
2	DTBP	83	15400	22900	1.48
3	TBHP	-	-	-	-
4	TEMPO	-	-	-	-
5	H_2O_2	30	7100	8100	1.14
6	$(NH_4)_2S_2O_8$	-	-	-	-
7	$KMnO_4$	-	-	-	-

[a] Conditions: The reaction was carried out in DMF solution at 150 °C with opening in air for 6 h. [1a]:[2a]:[3]:[Cs_2CO_3]:[oxidant]:[H_2O] = 1:1:0.15:0.5:0.2:1.25.

[b] M_n, M_w and *Đ* were determined by GPC in DMF with PMMA standards.

6. Characterization of polymers

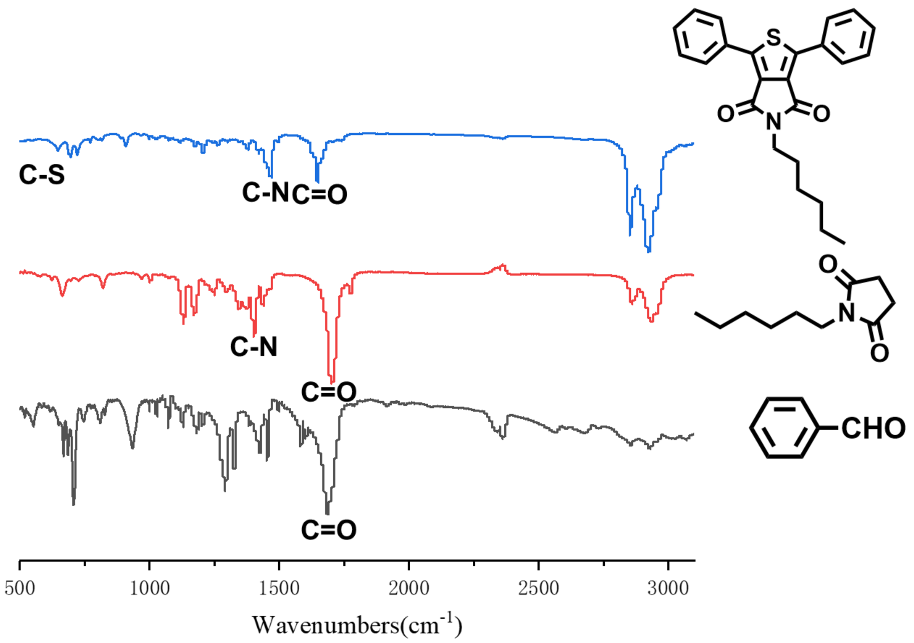


Figure S1. FT-IR spectra for the comparison of **S1**, **2a** and benzaldehyde **1'**.

Table S9. TGA-Derived Thermal Stability Parameters of **P1-P9**.

Polymer	Temperature at 5% weight loss (℃)	Peak decomposition temperature (℃)	Char Yield (%)
P1	289	470	42
P2	187	454	52
P3	257	452	42
P4	201	408	37
P5	93	366	30
P6	329	427	31
P7	183	385	54
P8	216	420	25
P9	205	432	63

[a] Conditions: Heating rate = 10°C min^{-1}, nitrogen atmosphere.

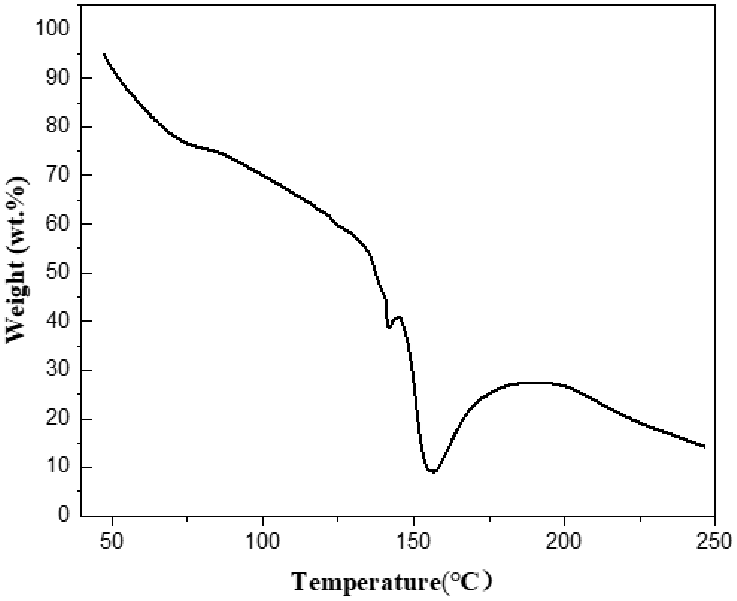


Figure S2. DSC curve of **P1** with a heating rate of 10°C min^{-1}.

Table S10. Elemental analysis characterization of **P1**.

P1	Weight (mg)	S area	S (%)
Experimental	2.1340	787	3.179
Theoretical		-	8.275

Table S11. Electrochemical properties of **P1** and **P5**.

Polymer	E_{ox}^{onset}(eV)	HOMO(eV) [a]	LUMO(eV) [b]
P1	0.59	-5.21	-3.37
P5	0.82	-5.44	-3.92

[a] The HOMO is calculated from the oxidation onsets (E_{ox}^{onset})

[b] $E_{LUMO} = E_{HOMO} + Eg^{opt}$

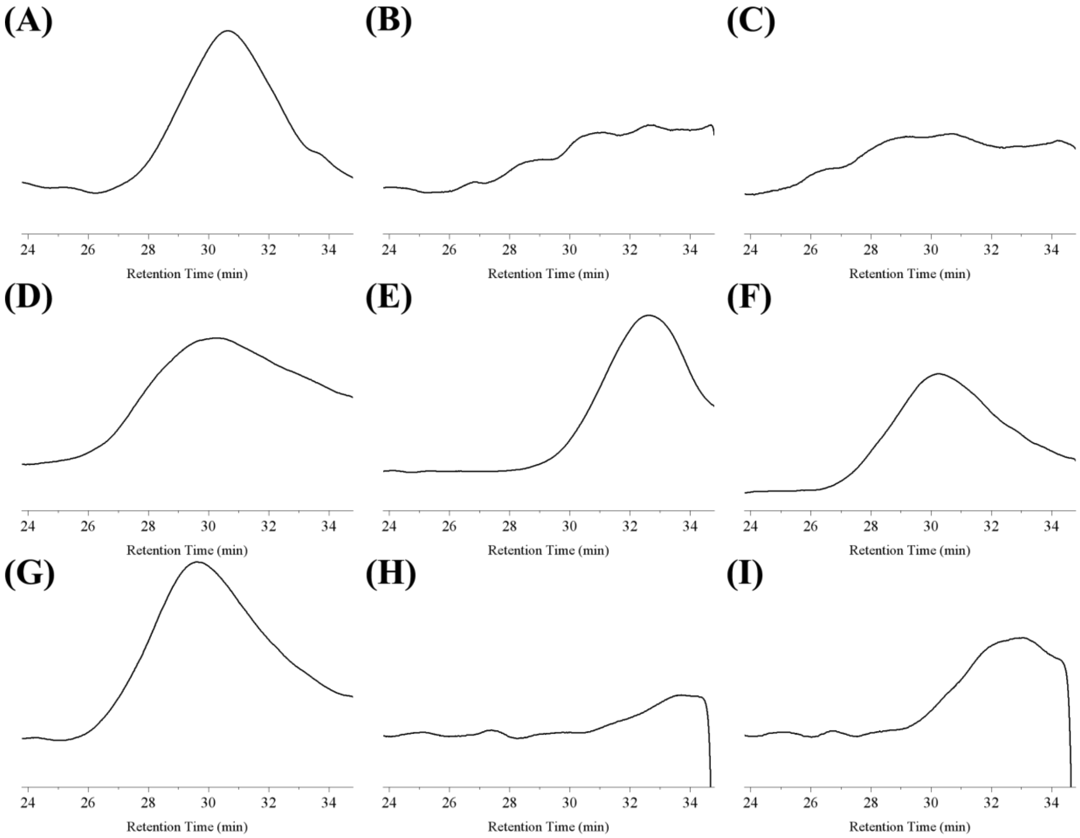


Figure S3. GPC traces of **P1-P9**. **P1** (A), **P2** (B), **P3** (C), **P4** (D), **P5** (E), **P6** (F), **P7** (G), **P8** (H) and **P9** (I).

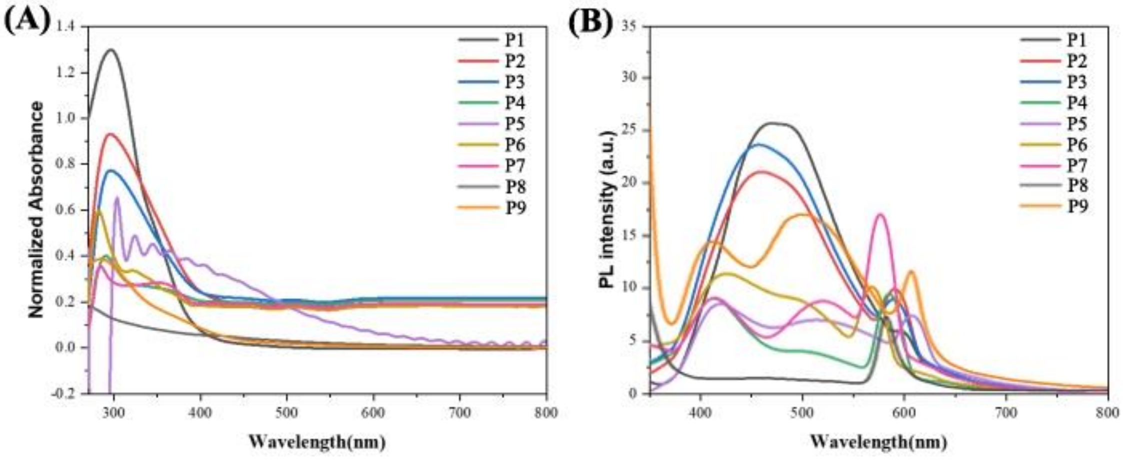


Figure S4. (A) UV-vis absorption spectra of **P1-P9**. Concentration: 2.15×10^{-2} mg/L. (B) Photoluminescence (PL) spectra of **P1-P9** in DMF. Concentration: 2.15×10^{-2} mg/L. Excitation wavelengths: 298 nm for **P1**, 294 nm for **P2**, 294 nm for **P3**, 290 nm for **P4**, 302 nm for **P5**, 282 nm for **P6**, 286 nm for **P7**, 270 nm for **P8** and 285 nm for **P9.**

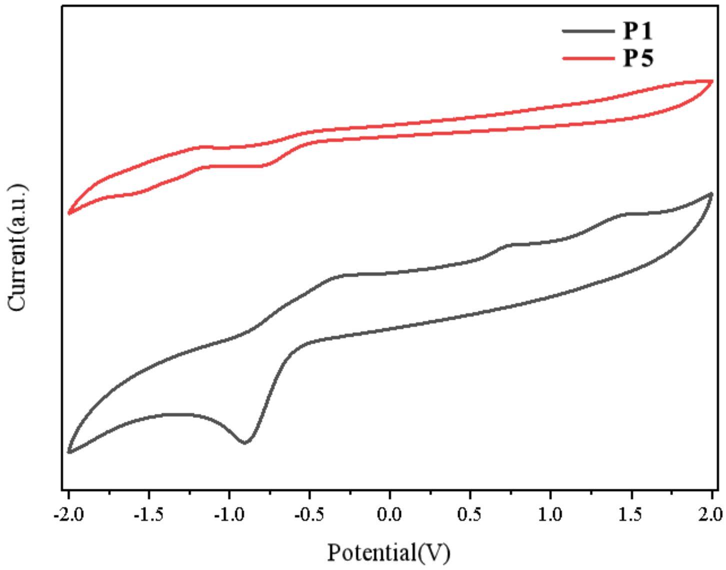


Figure S5. Cyclic voltammogram (CV) of **P1** and **P5** film on a glassy carbon electrode in CH_3CN with 0.1 mol L^{-1} $^{n}Bu_4NBF_4$.

7. NMR Spectra

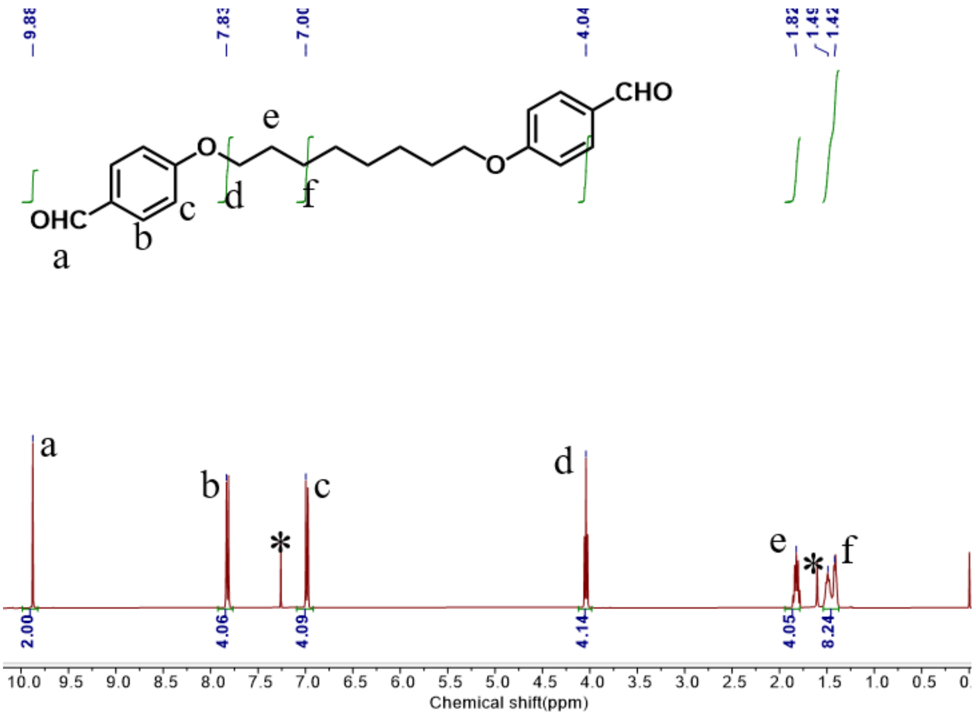


Figure S6. ^{1}H NMR spectrum of **1b** in $CDCl_3$. The solvent peaks are marked with asterisks.

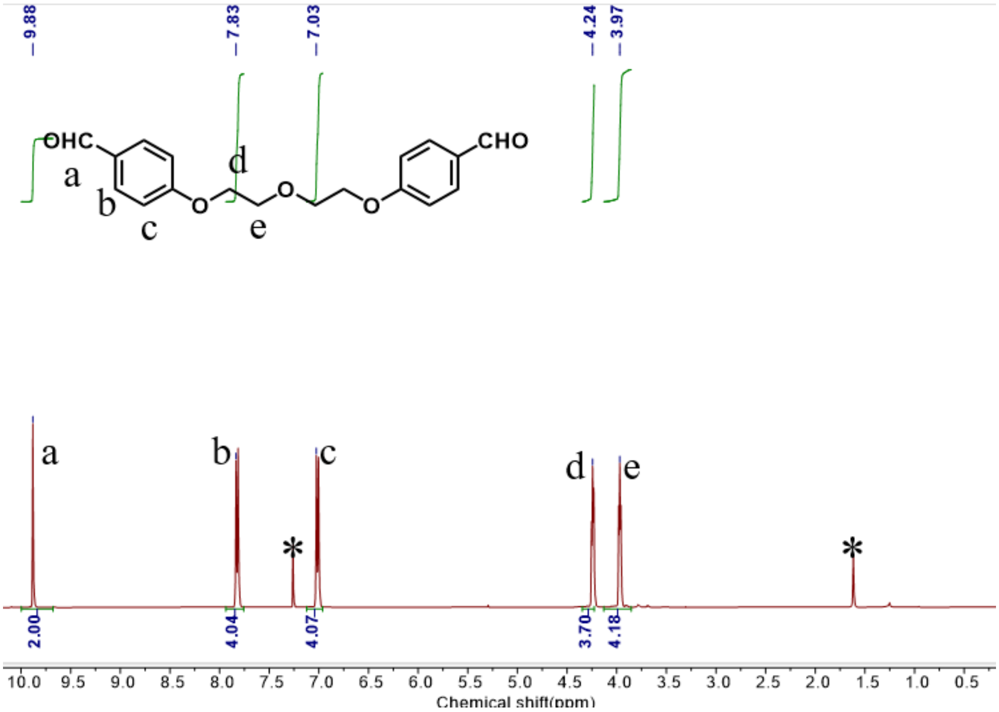


Figure S7. ^{1}H NMR spectrum of **1d** in $CDCl_3$. The solvent peaks are marked with asterisks.

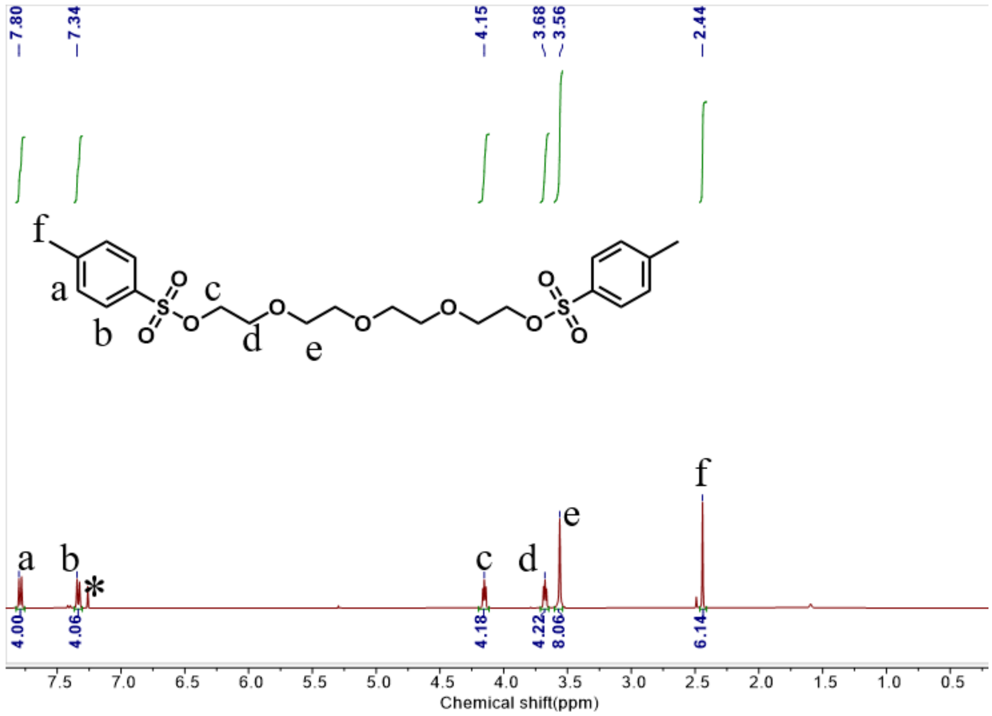


Figure S8. ^{1}H NMR spectrum of **1e'** in CDCl$_3$. The solvent peaks are marked with asterisks.

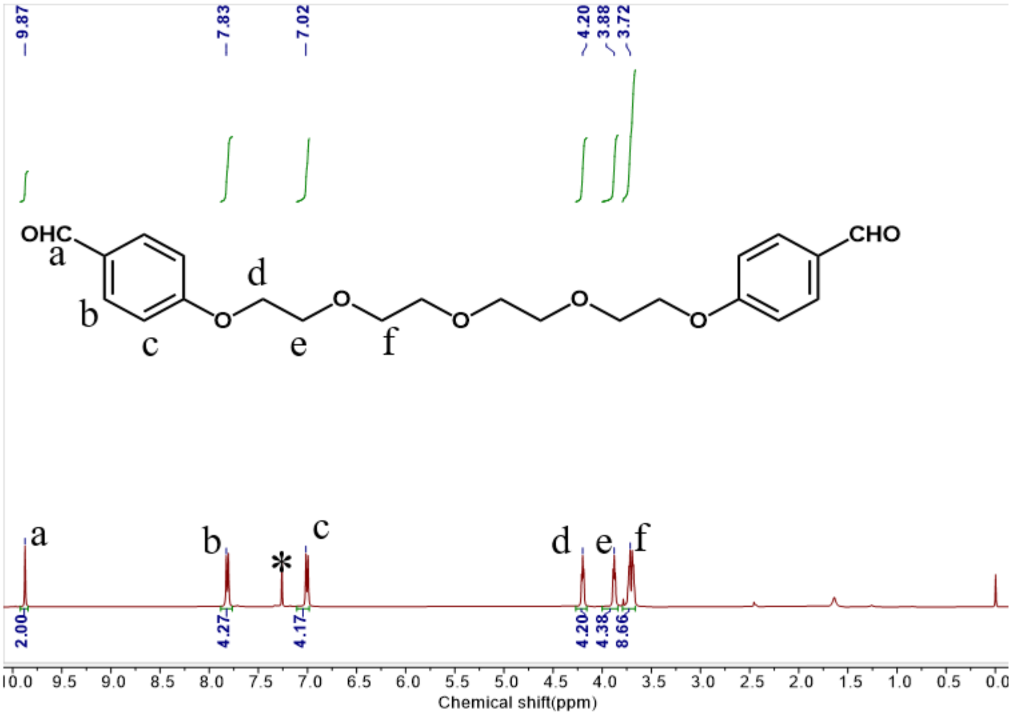


Figure S9. ^{1}H NMR spectrum of **1e** in CDCl$_3$. The solvent peaks are marked with asterisks.

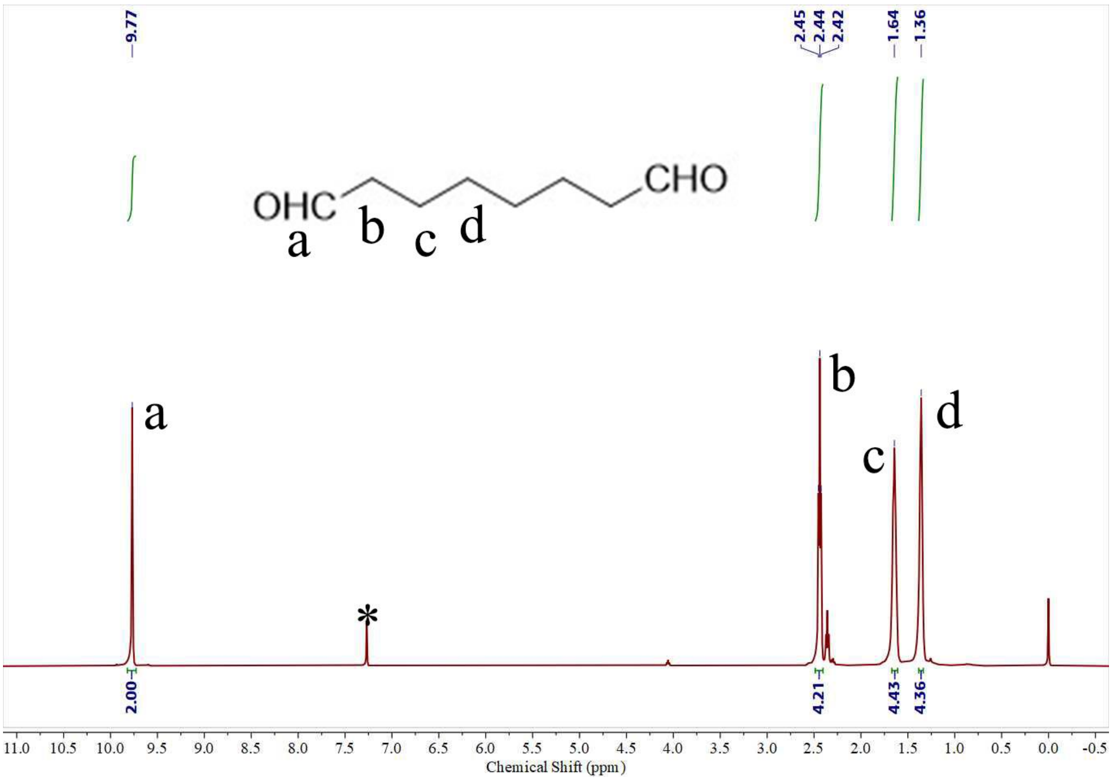


Figure S10. ^{1}H NMR spectrum of **1f** in $CDCl_3$. The solvent peaks are marked with asterisks.

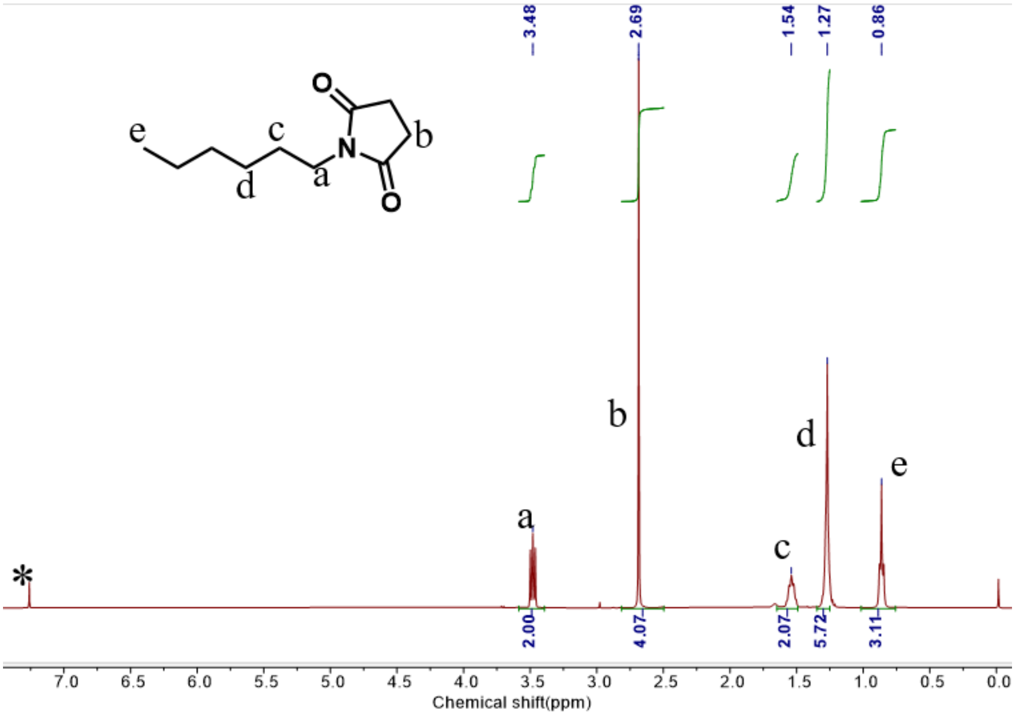


Figure S11. ^{1}H NMR spectrum of **2a** in $CDCl_3$. The solvent peaks are marked with asterisks.

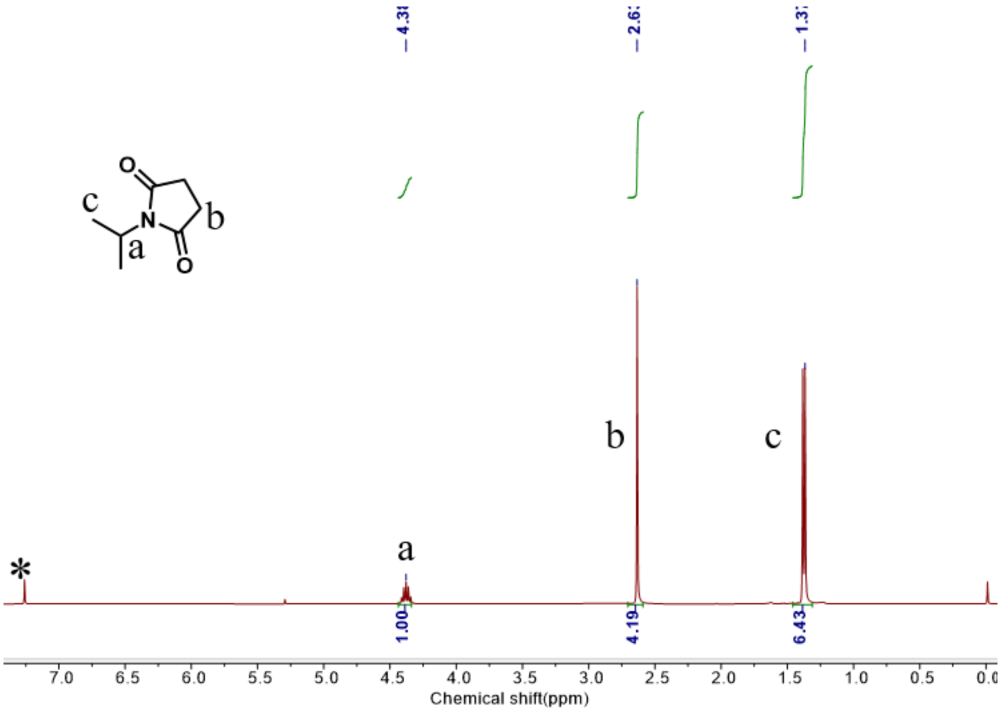


Figure S12. ^{1}H NMR spectrum of **2b** in $CDCl_3$. The solvent peaks are marked with asterisks.

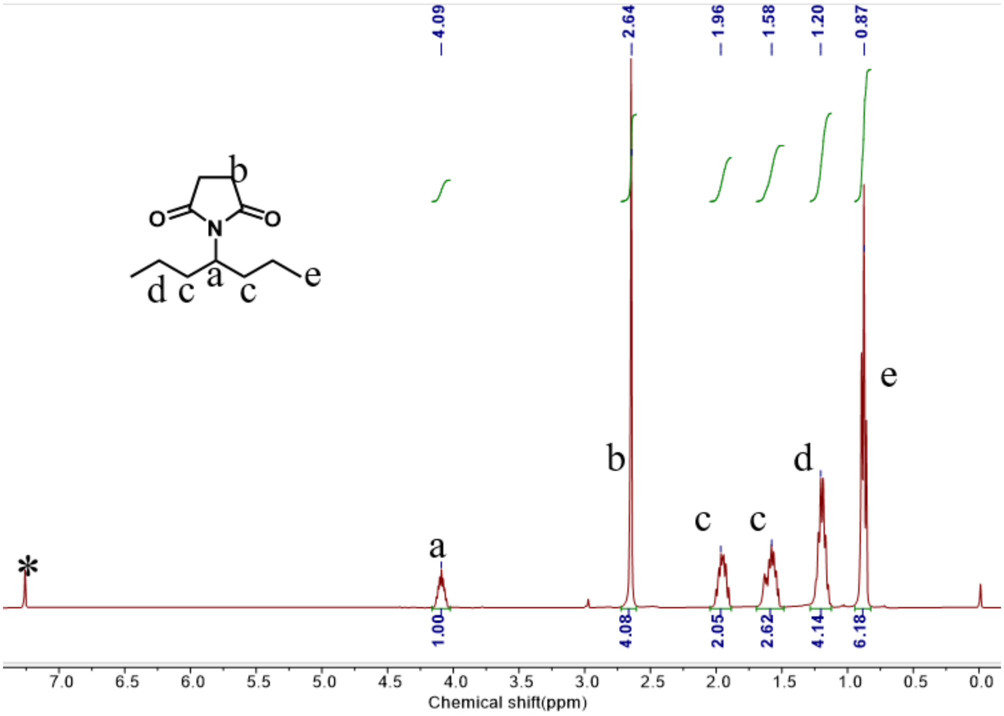


Figure S13. ^{1}H NMR spectrum of **2c** in $CDCl_3$. The solvent peaks are marked with asterisks.

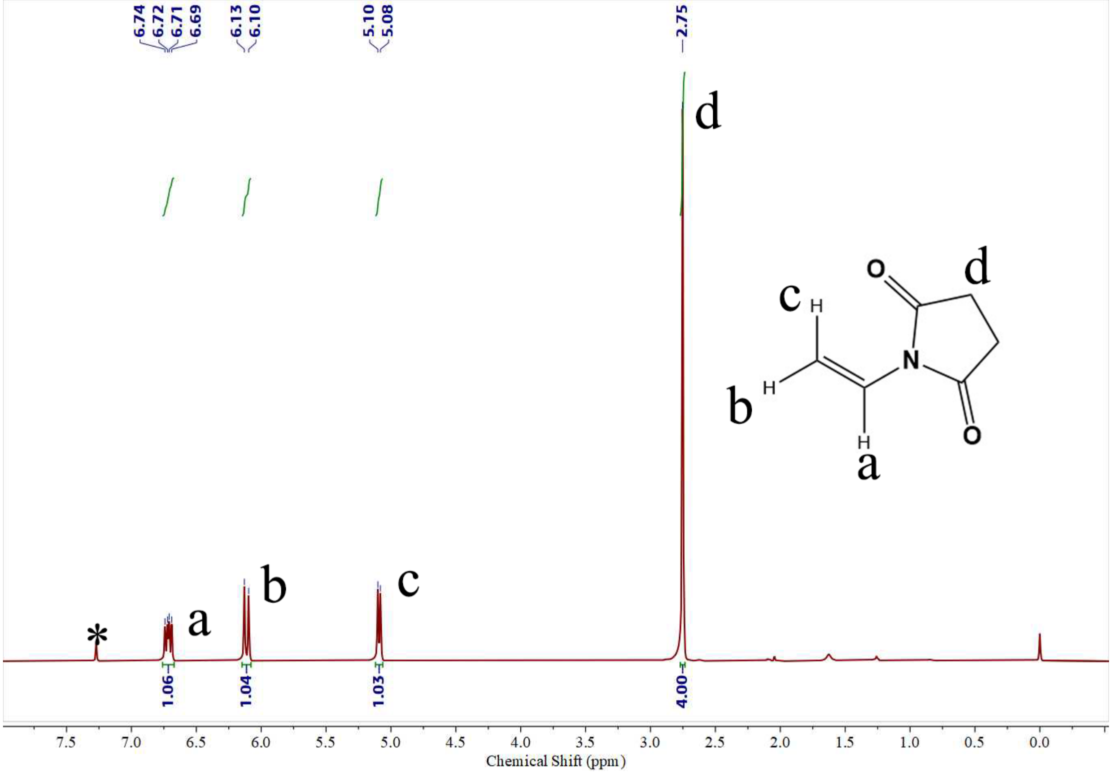


Figure S14. ^{1}H NMR spectrum of **2d** in CDCl$_3$. The solvent peaks are marked with asterisks.

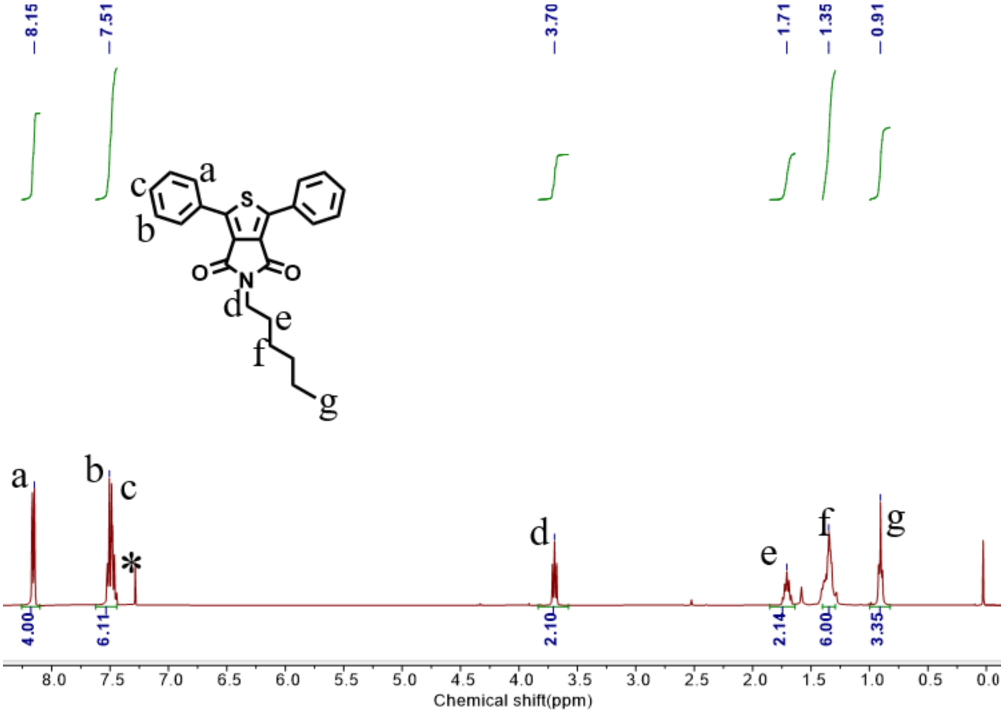


Figure S15. ^{1}H NMR spectrum of **S1**(1'/2a/3) in CDCl$_3$. The solvent peaks are marked with asterisks.

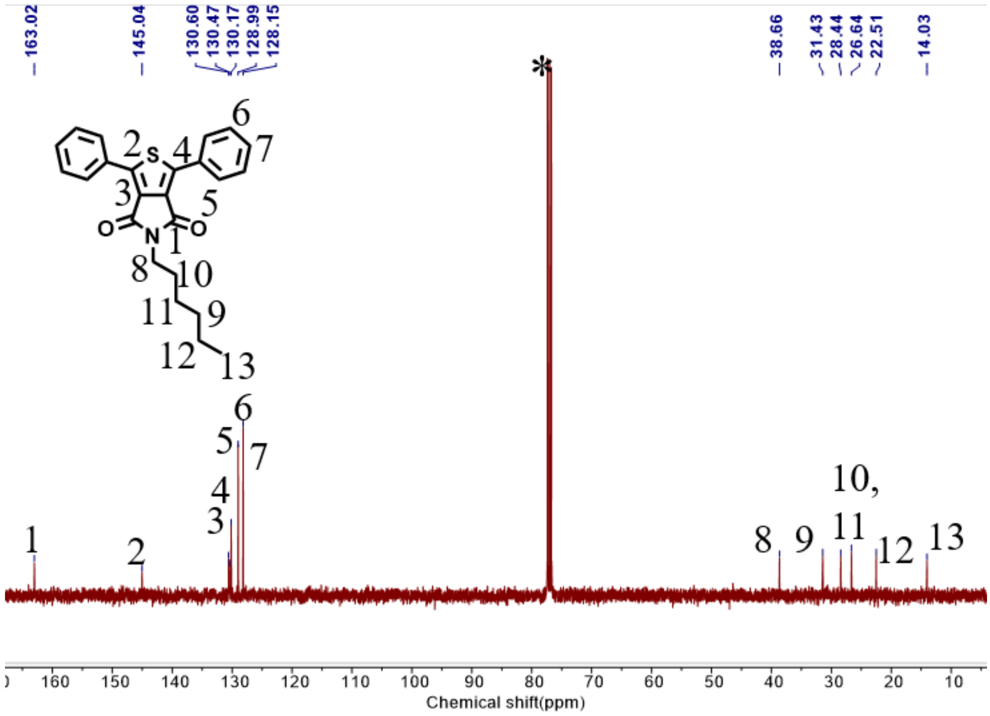


Figure S16. ^{13}C NMR spectrum of **S1**(1'/2a/3) in $CDCl_3$. The solvent peaks are marked with asterisks.

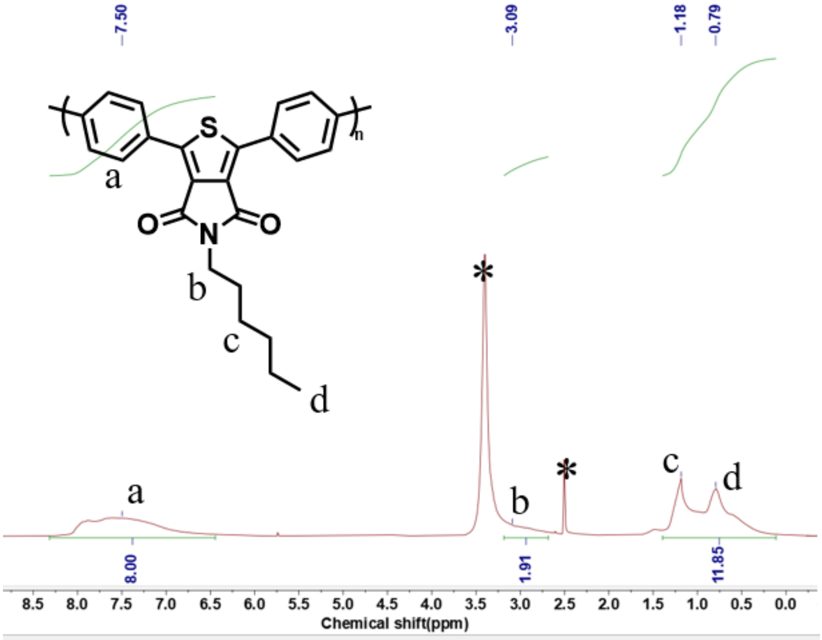


Figure S17. ^{1}H NMR spectrum of **P1**(1a/2a/3) in d_6-DMSO. The solvent peaks are marked with asterisks.

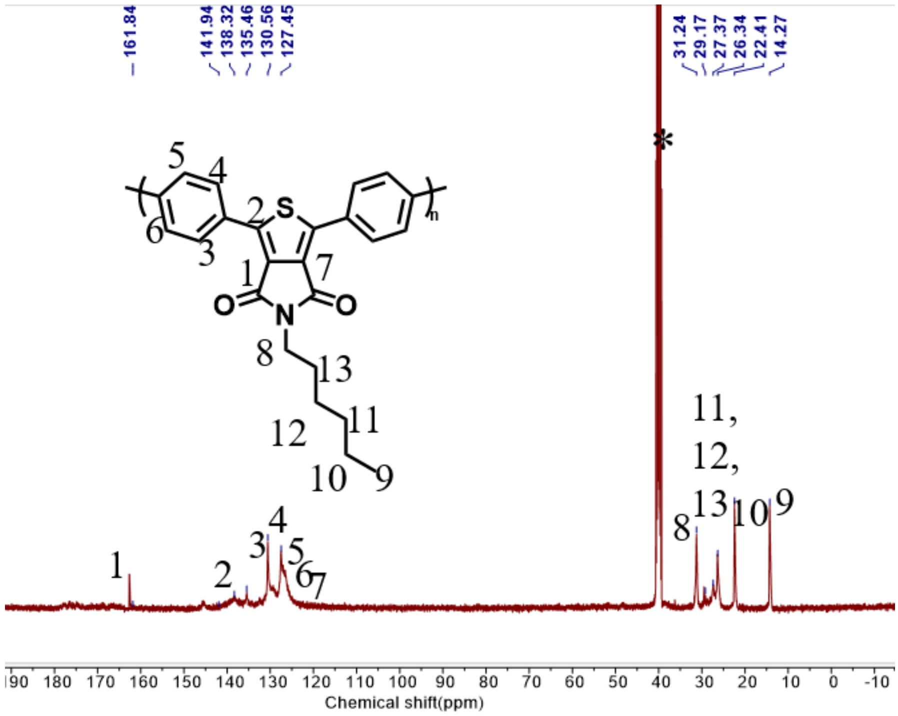


Figure S18. ^{13}C NMR spectrum of **P1**(1a/2a/3) in d_6-DMSO. The solvent peaks are marked with asterisks.

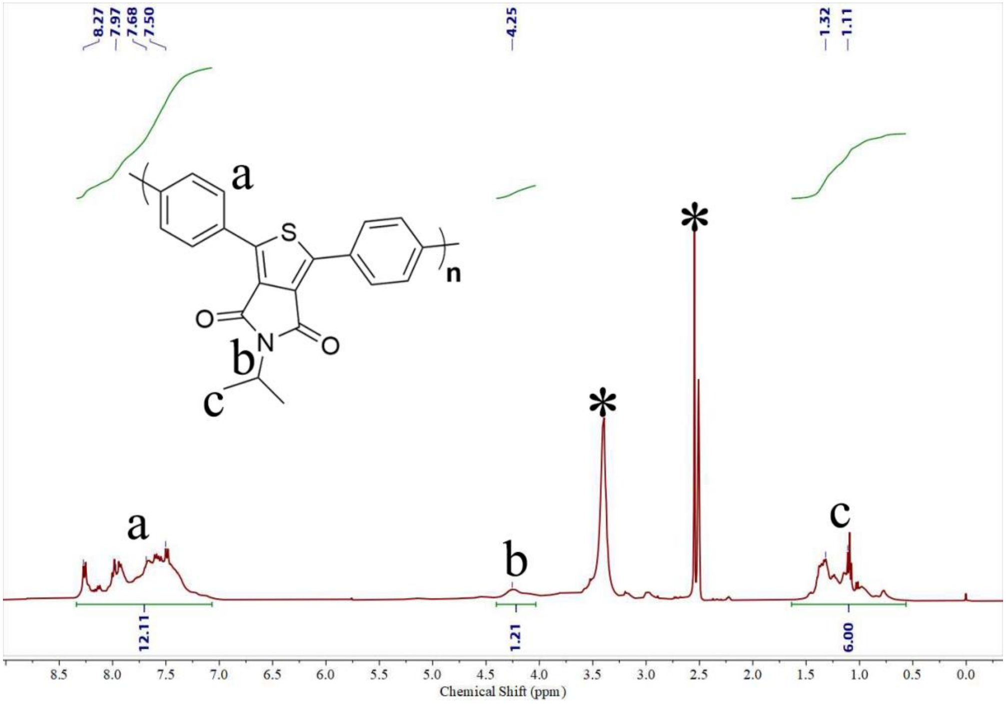


Figure S19. ^{1}H NMR spectrum of **P2**(1a/2b/3) in d_6-DMSO. The solvent peaks are marked with asterisks.

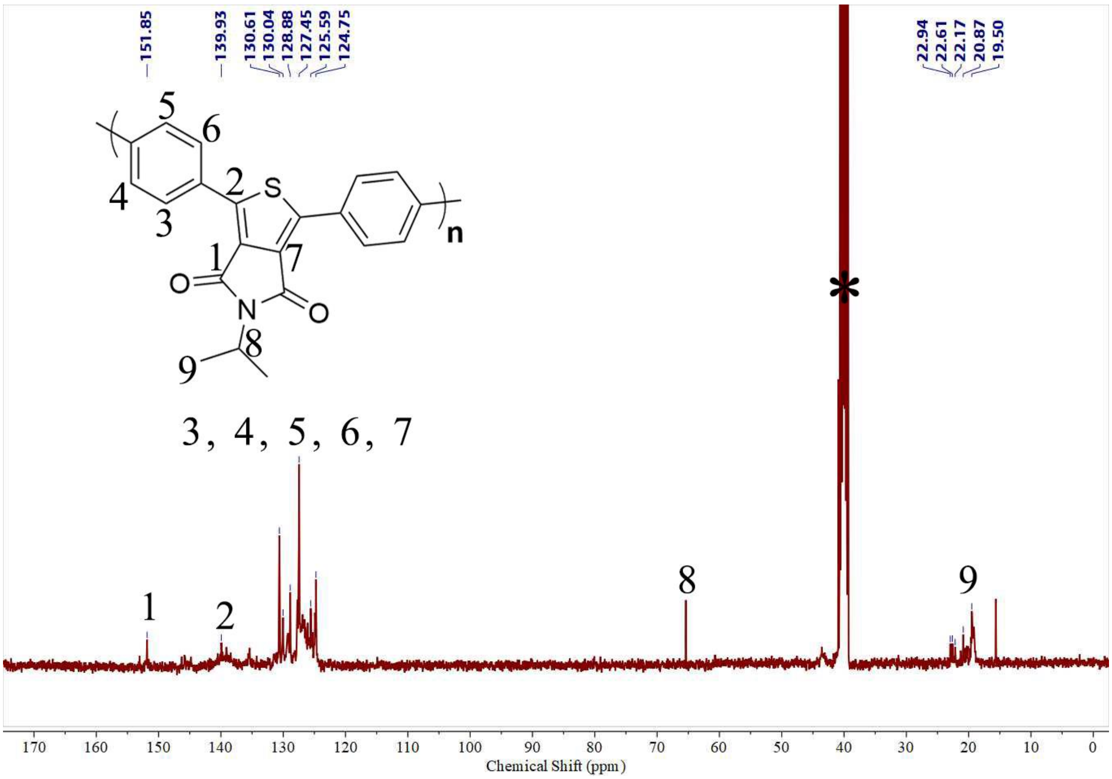


Figure S20. ^{13}C NMR spectrum of **P2**(1a/2a/3) in d_6-DMSO. The solvent peaks are marked with asterisks.

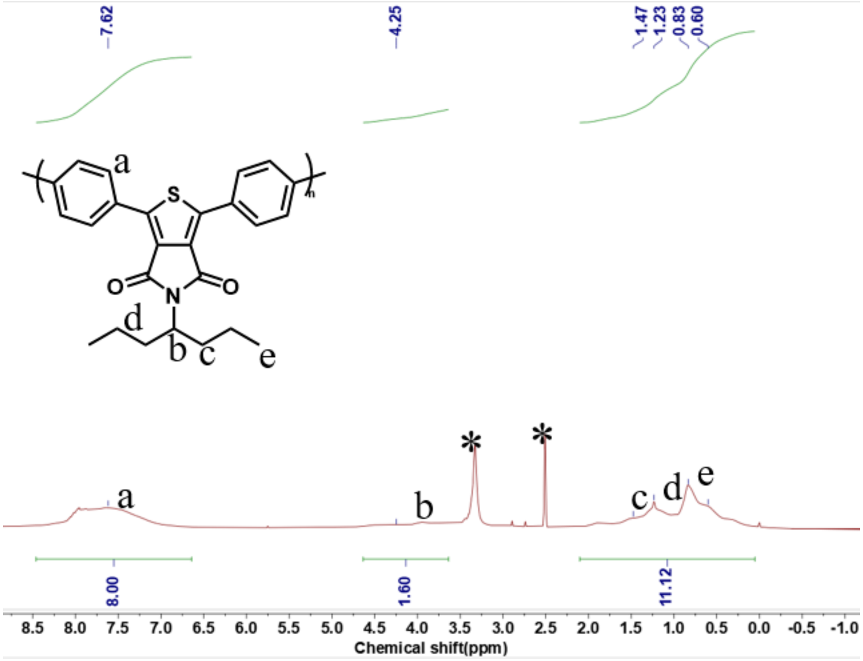


Figure S21. ^{1}H NMR spectrum of **P3**(1a/2c/3) in d_6-DMSO. The solvent peaks are marked with asterisks.

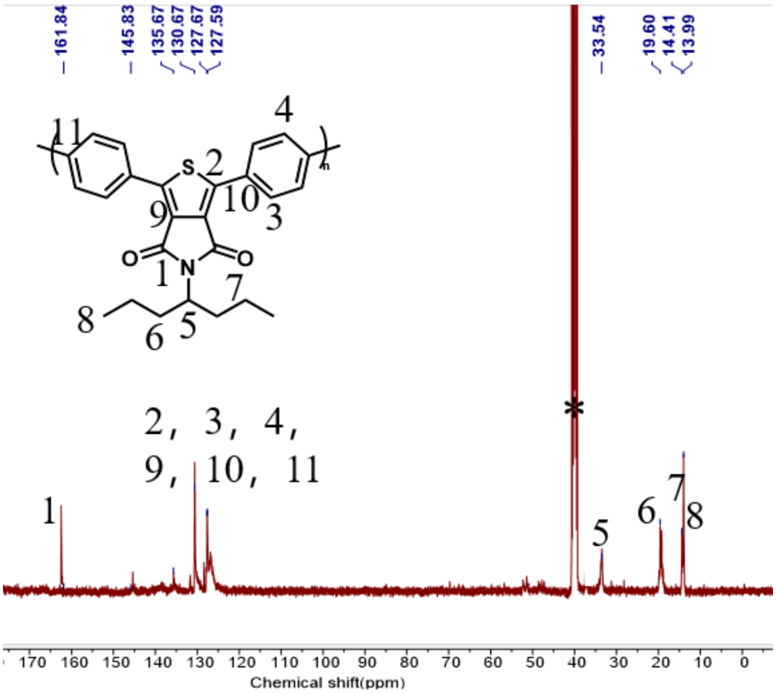


Figure S22. ^{13}C NMR spectrum of **P3**(1a/2c/3) in d_6-DMSO. The solvent peaks are marked with asterisks.

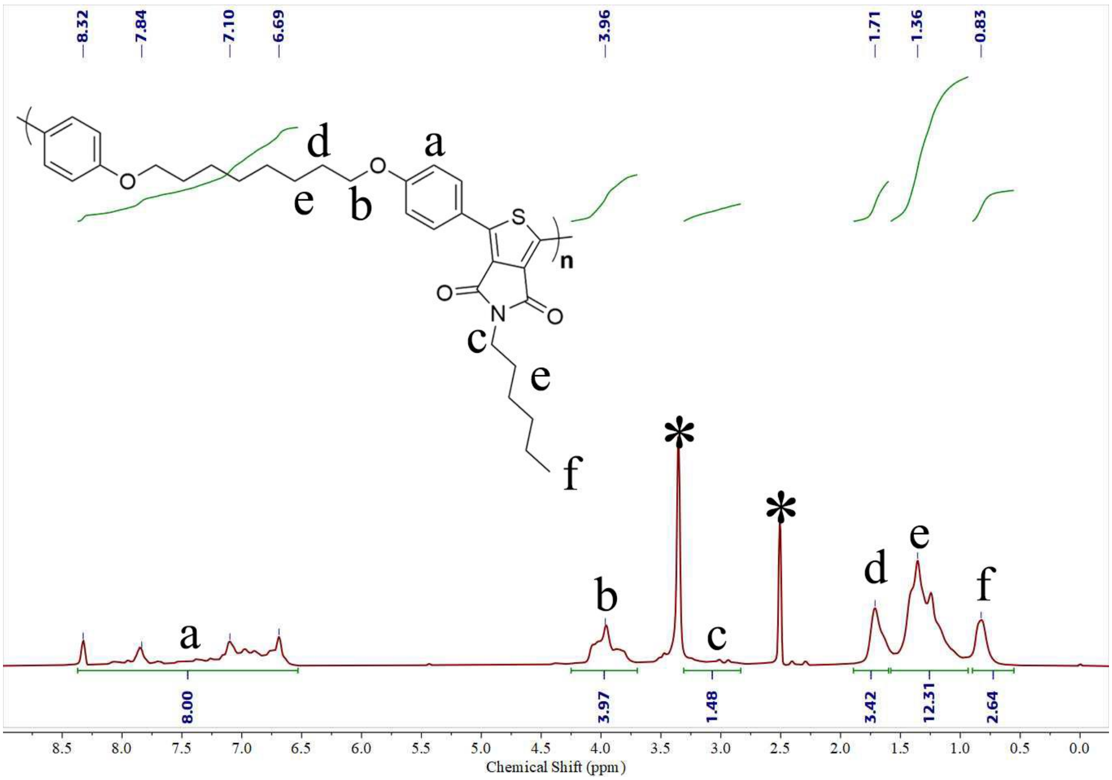


Figure S23. ^{1}H NMR spectrum of **P4**(1b/2a/3) in d_6-DMSO. The solvent peaks are marked with asterisks.

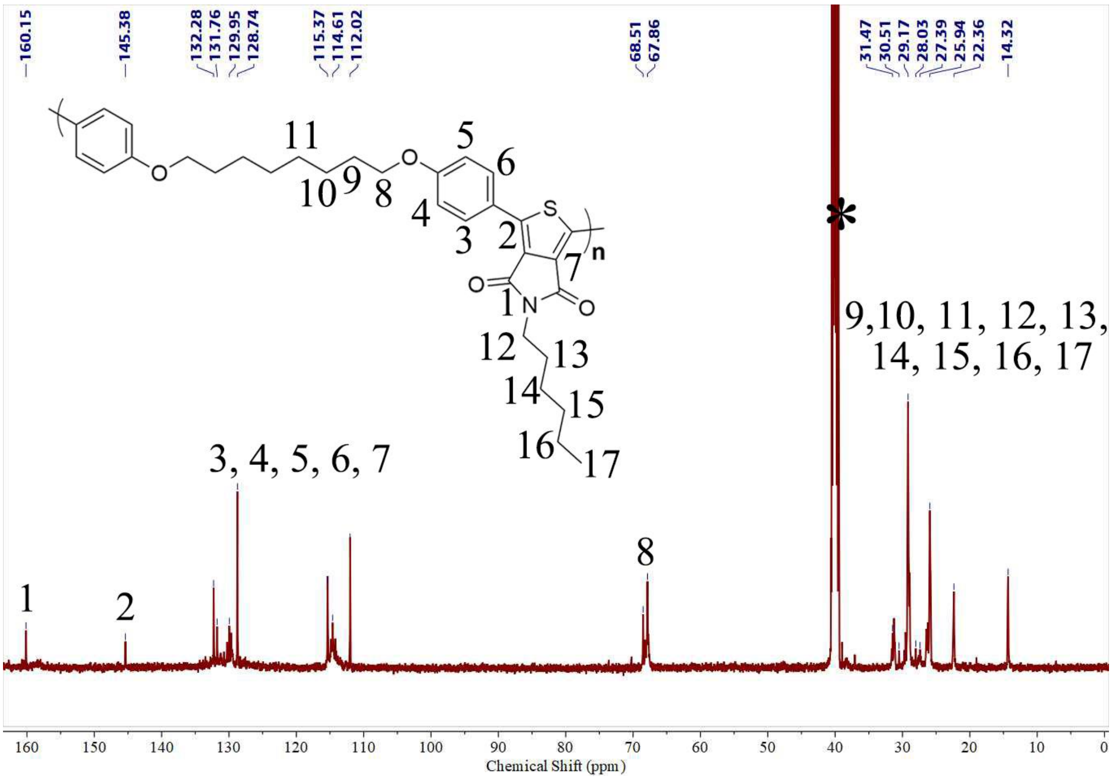


Figure S24. ^{13}C NMR spectrum of **P4**(1b/2a/3) in d_6-DMSO. The solvent peaks are marked with asterisks.

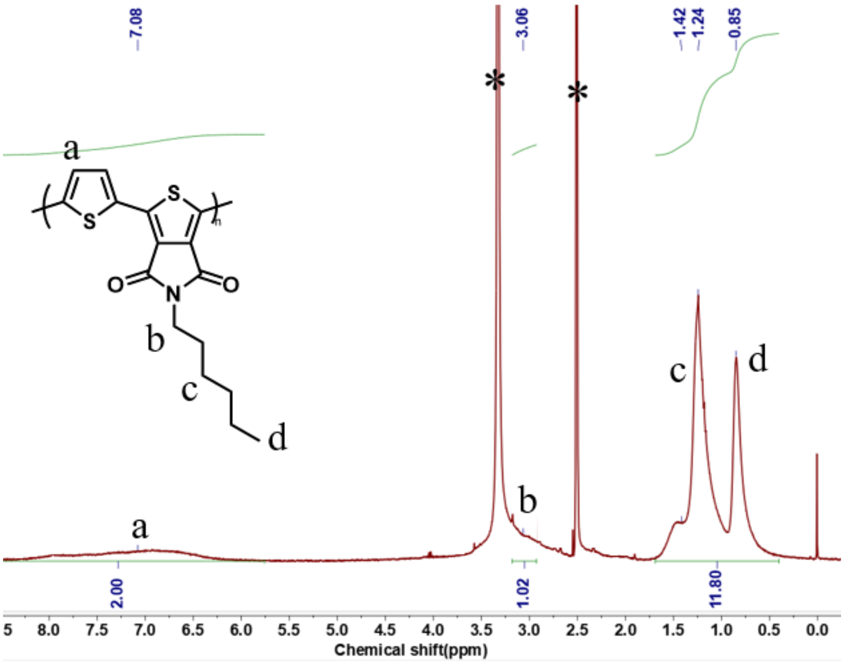


Figure S25. ^{1}H NMR spectrum of **P5**(1c/2a/3) in d_6-DMSO. The solvent peaks are marked with asterisks.

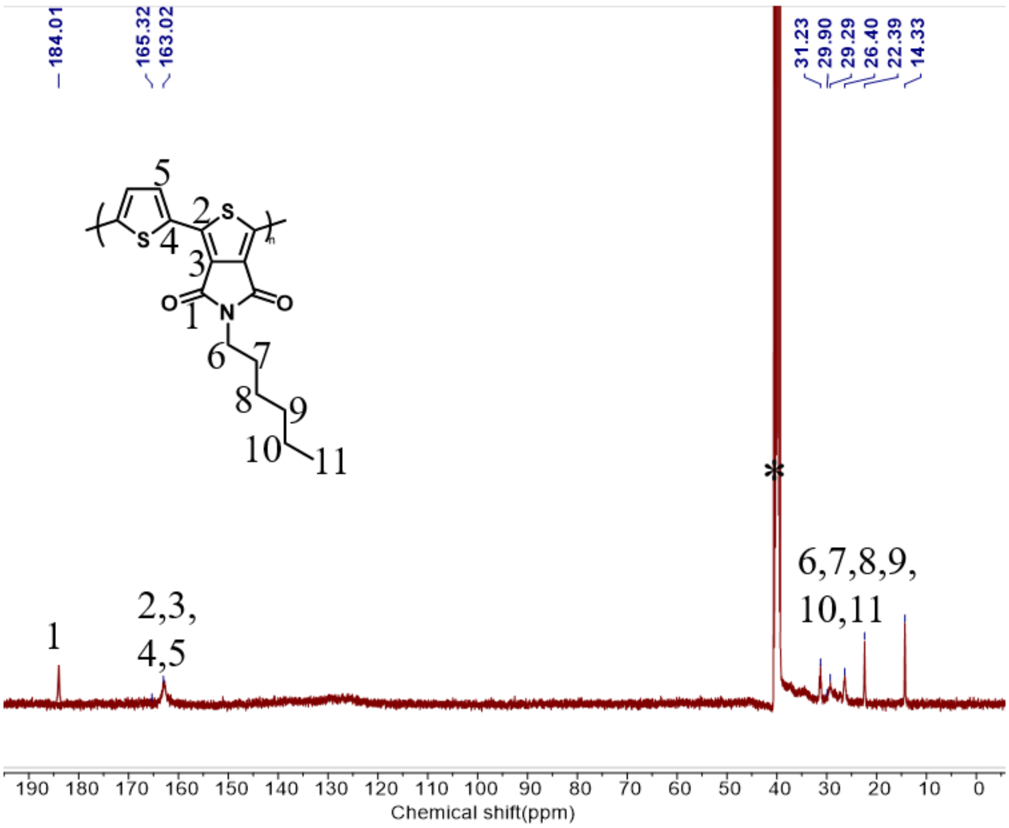


Figure S26. ^{13}C NMR spectrum of **P5**(1c/2a/3) in d_6-DMSO. The solvent peaks are marked with asterisks.

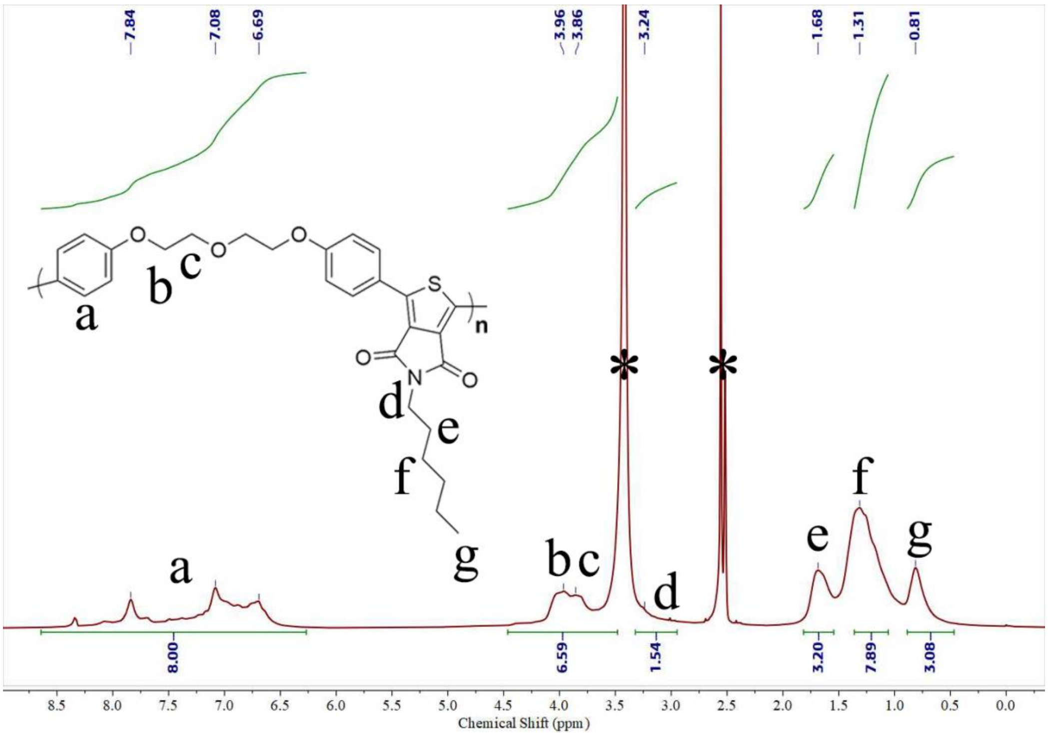


Figure S27. ^{1}H NMR spectrum of **P6**(1d/2a/3) in d_6-DMSO. The solvent peaks are marked with

asterisks.

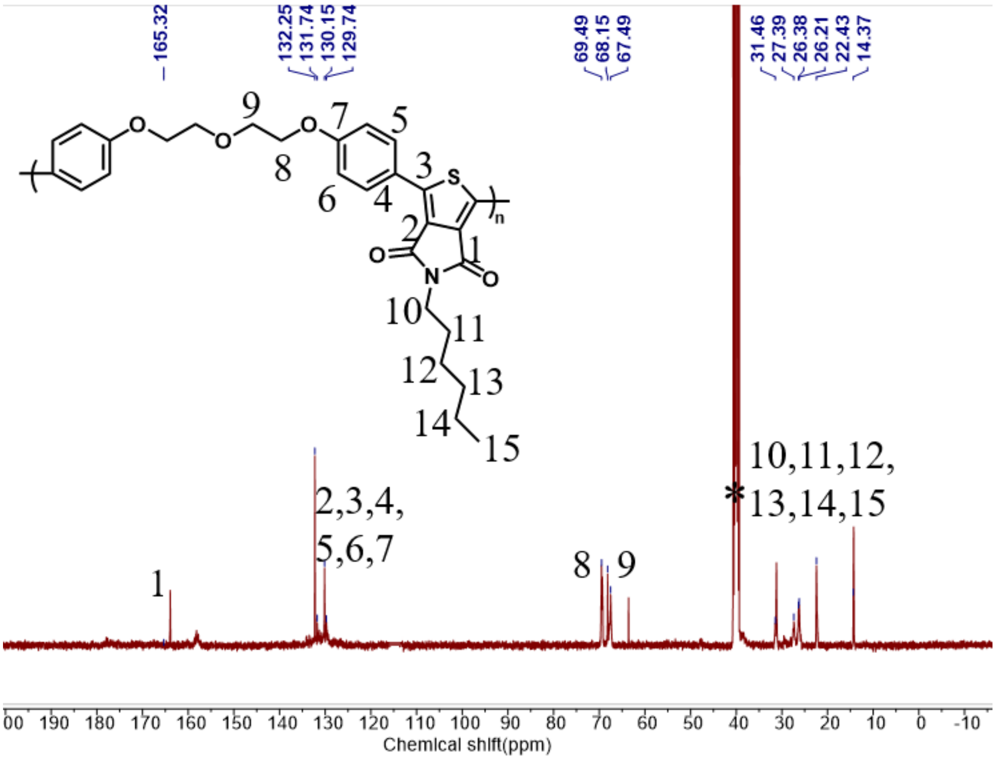


Figure S28. ^{13}C NMR spectrum of **P6**(1d/2a/3) in d_6-DMSO. The solvent peaks are marked with asterisks.

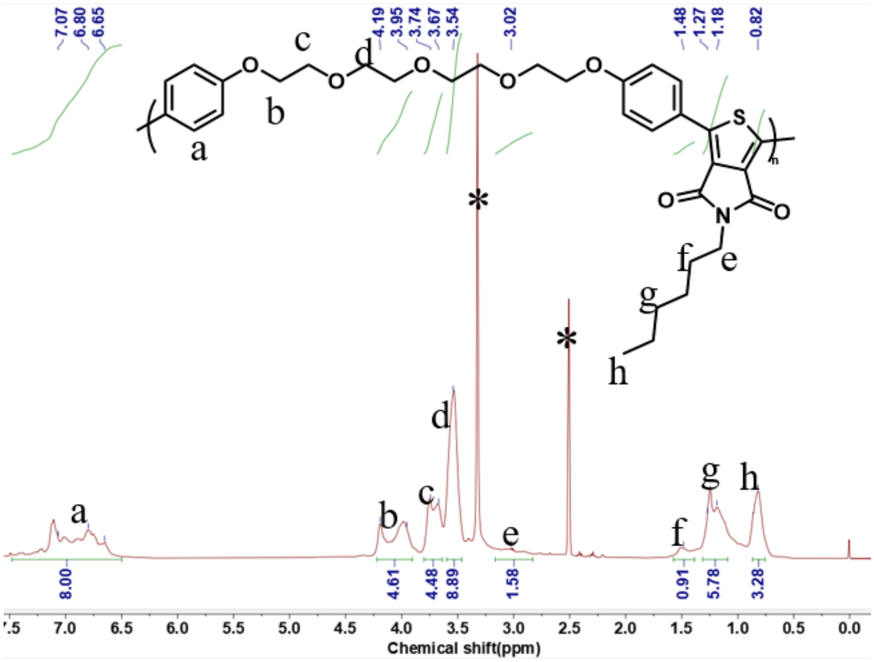


Figure S29. ^{1}H NMR spectrum of **P7**(1e/2a/3) in d_6-DMSO. The solvent peaks are marked with

asterisks.

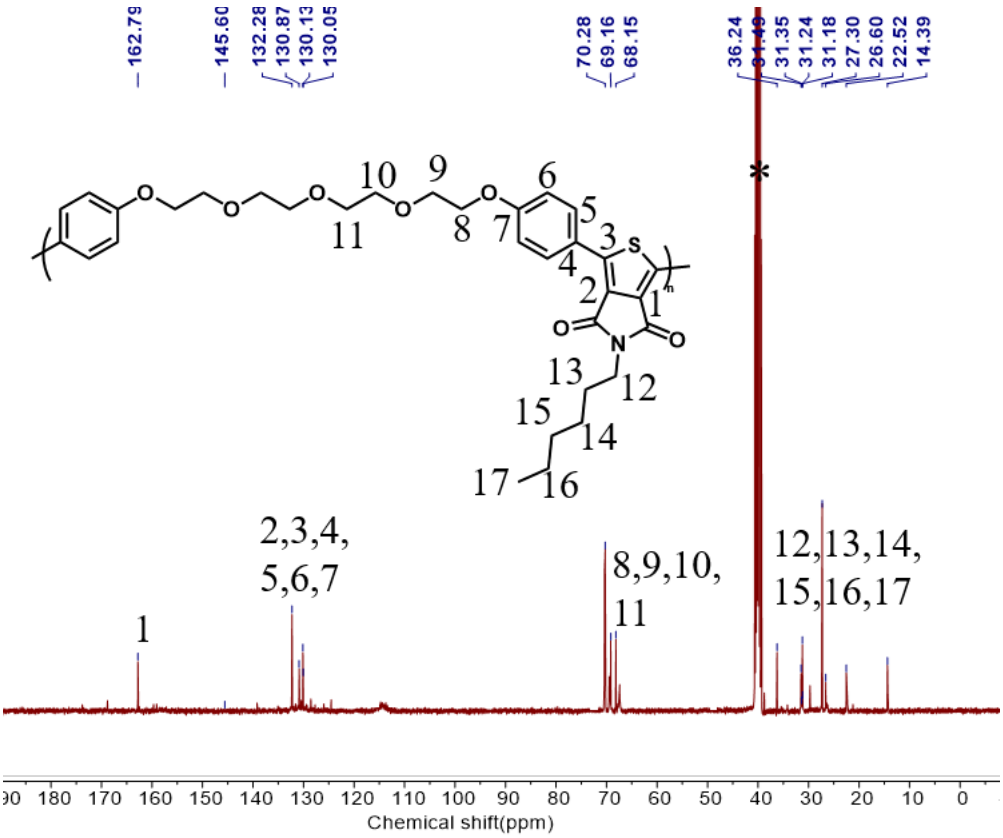


Figure S30. ^{13}C NMR spectrum of **P7**(1e/2a/3) in *d*$_6$-DMSO. The solvent peaks are marked with asterisks.

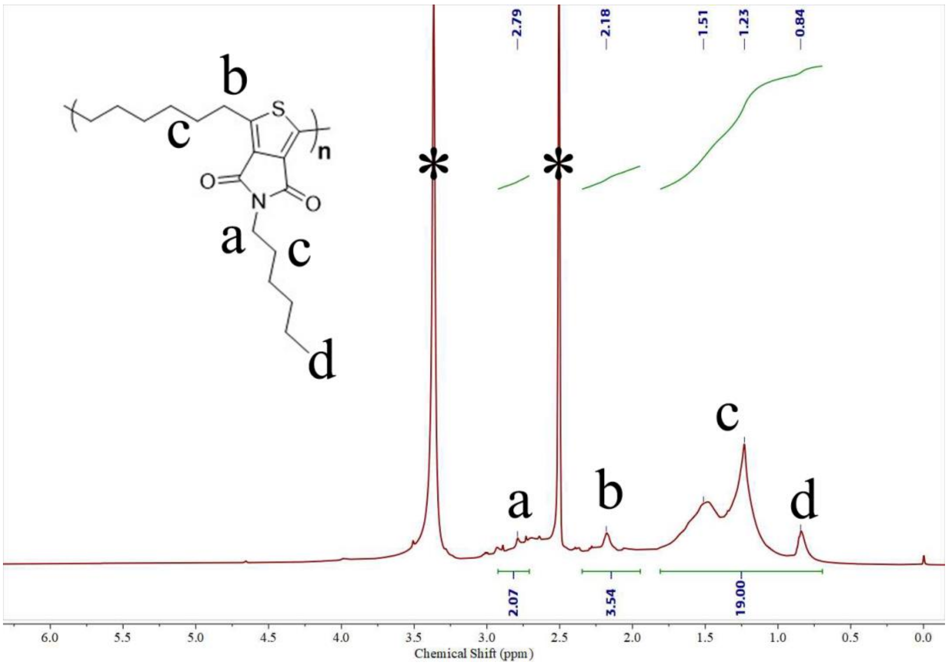


Figure S31. ^{1}H NMR spectrum of **P8**(1f/2a/3) in *d*$_6$-DMSO. The solvent peaks are marked with

asterisks.

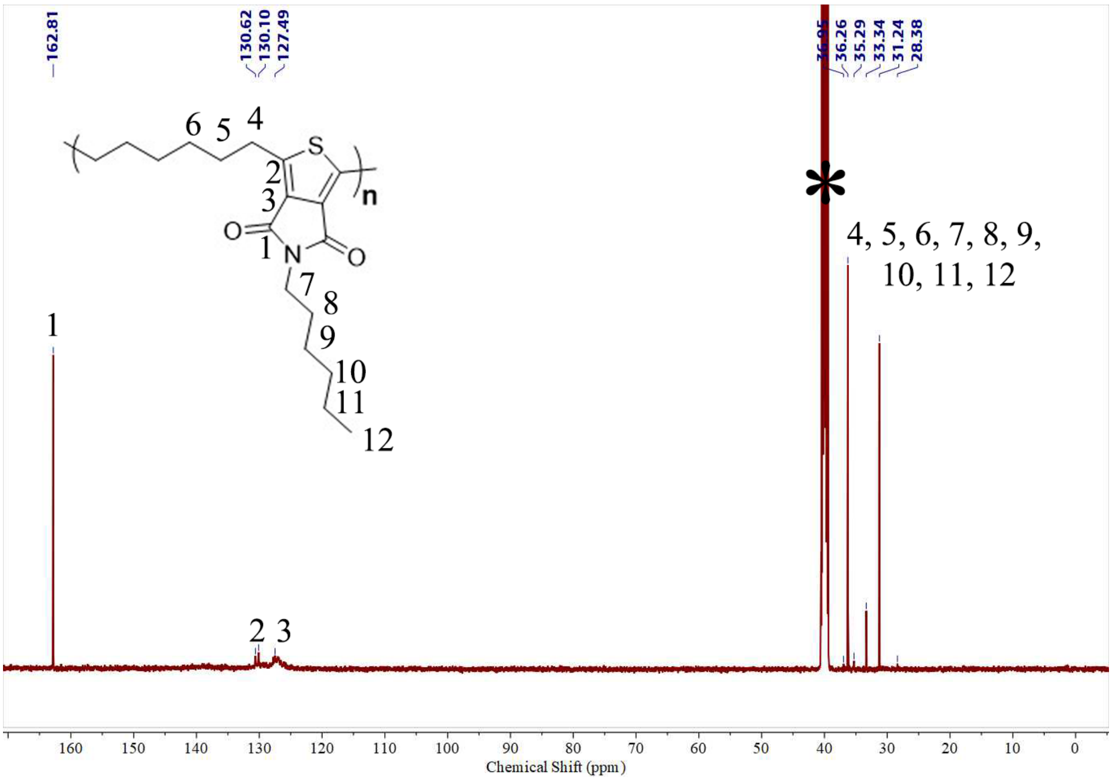


Figure S32. ^{13}C NMR spectrum of **P8**(1f/2a/3) in d_6-DMSO. The solvent peaks are marked with asterisks.

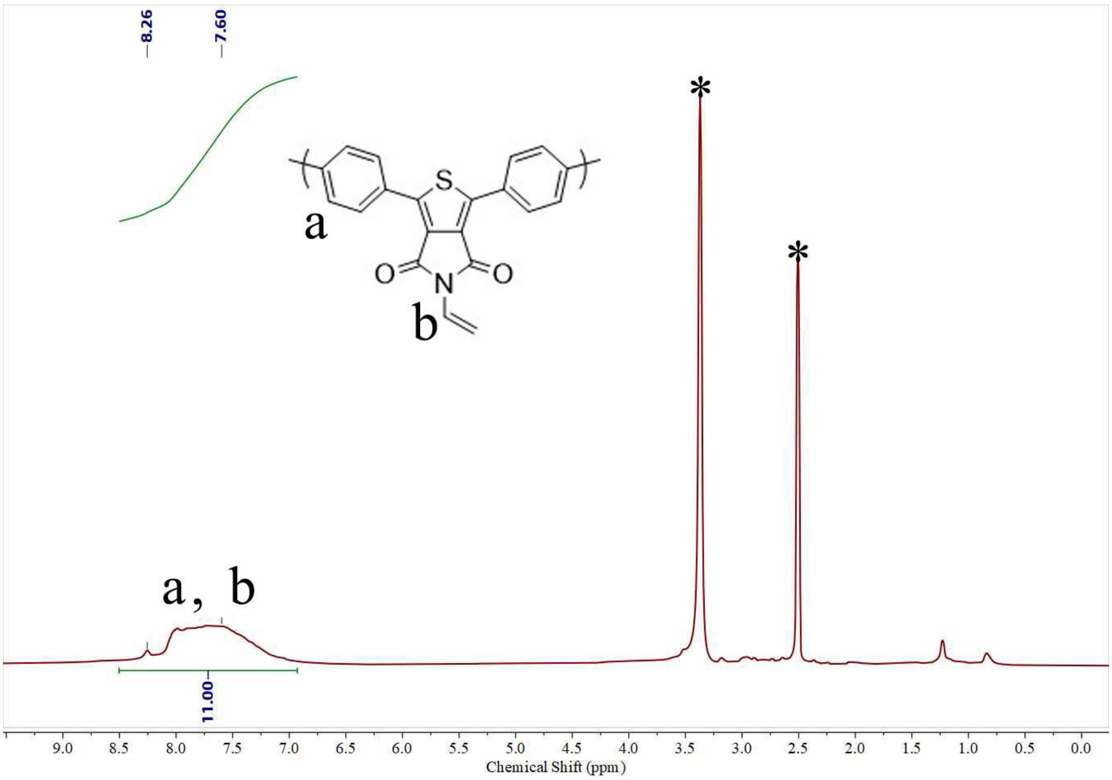


Figure S33. ^{1}H NMR spectrum of **P9**(1a/2d/3) in d_6-DMSO. The solvent peaks are marked with

asterisks.

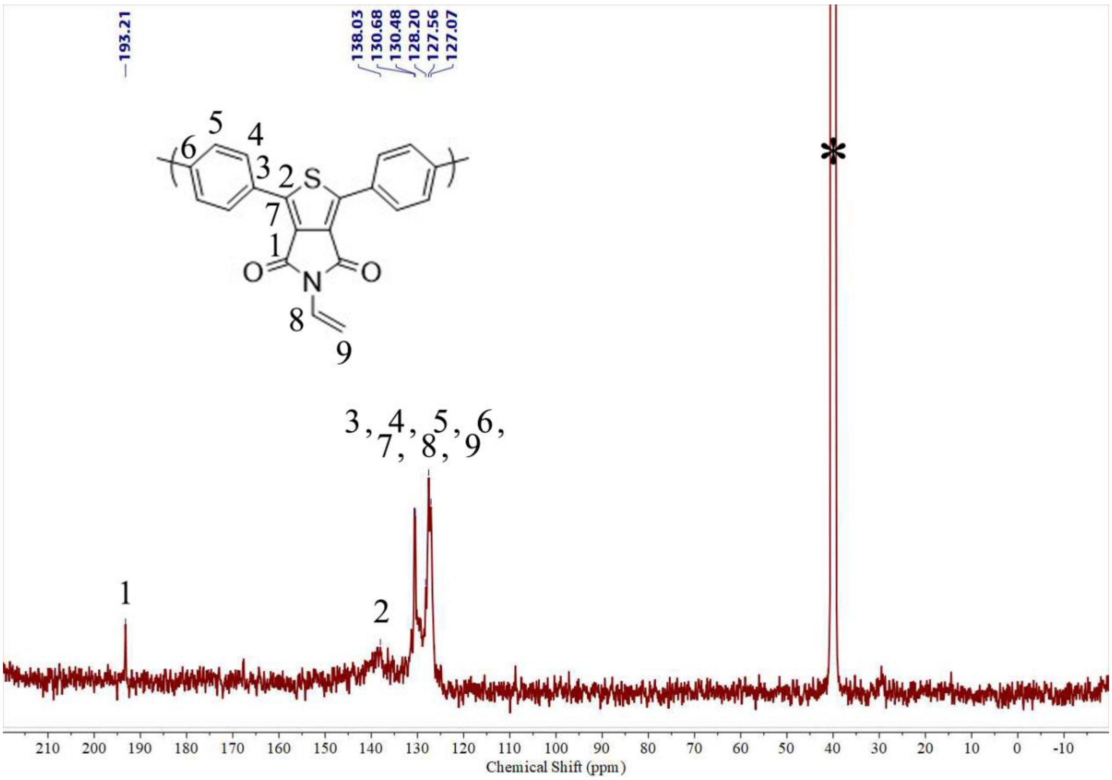


Figure S34. ^{13}C NMR spectrum of **P9**(1a/2d/3) in *d_6*-DMSO. The solvent peaks are marked with asterisks.