Electronic Supplementary Information

Donor-Acceptor Conjugated Polymers Based on Two-Dimensional Thiophene Derivatives for Bulk Heterojunction Solar Cells

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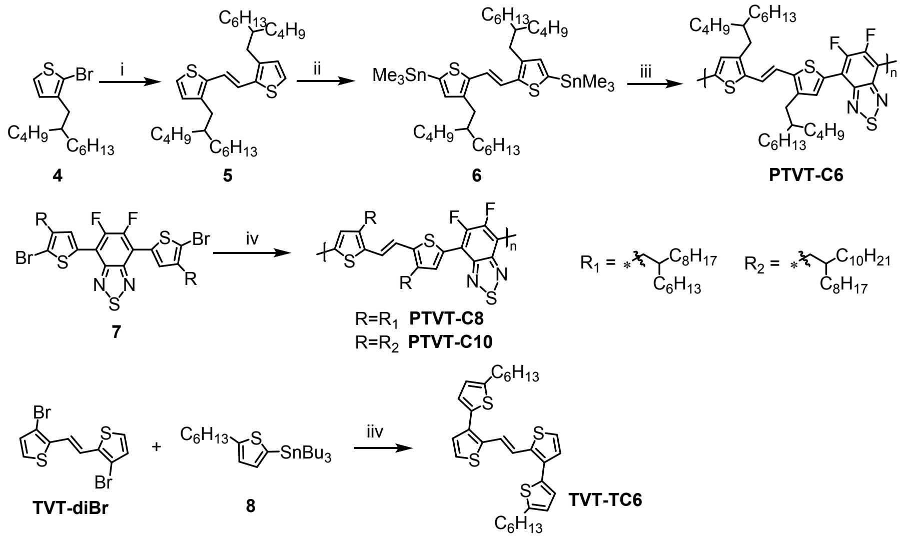
Materials and Methods. Tetrahydrofuran (THF), N,N-dimethylformamide (DMF), toluene, acetonitrile, diphenyl ether (DPE) were dried and distilled before use. $PC_{71}BM$ was purchased from American Dye Source. Inc. (ADS). Anhydrous *o*-xylene, *o*-dichlorobenzene (*o*-DCB) and chlorobenzene (CB) were purchased from Sigma-Aldrich. 2-Bromo-3-(2-butyloctyl)thiophene (**4**), 4,7-bis(5-bromo-4-alkylthiophen-2-yl)-5,6-difluoro-benzo[*c*][1,2,5]thiadiazole (**7**) and tributyl(5-hexylthiophen-2-yl)stannane (**8**) were synthesized according to previous literatures.[1-4] Other materials and reagents were purchased and used as received. ^1H NMR and ^{13}C NMR solution spectra were recorded on a Bruker AV 400 MHz spectrometer with chloroform-*d* ($CDCl_3$, tetramethylsilane (TMS) as an internal standard) or 1,1,2,2-tetrachlororoethane-d_2 as solvent. Elemental analysis was carried out on a FlashEA1112 elemental analyzer. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were measured on a Bruker/AutoflexIII Smartbean MALDI mass spectrometer with 2-[(2*E*)-3-(4-t-buthylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) as the matrix in a reflection mode. Single crystal analysis was conducted on Bruker SMART APEX CCD X-Ray Single Crystal diffractometer at 293 K with graphite-monochromated Mo Kα as X-ray sourse (λ = 0.71073 Å). High-temperature gel permeation chromatography (GPC) was performed on a PL-GPC 220 system by using 1,2,4-trichlorobenzene as eluent and polystyrene as standard at 150 ^oC. UV-Vis absorption spectra were recorded on a Shimadzu UV3600 UV-vis-NIR spectrometer. Film cyclic voltammetry (CV) measurements were carried out on a CHI660a electrochemical workstation using saturated calomel electrode (SEC) as reference electrode, platinum wire as counter electrode and glassy carbon electrode (diameter of 1 cm) as working electrode. NBu_4PF_6 (0.1 M) in distilled acetonitrile was used as electrolyte. TGA was carried out at a heating rate of 10 °C min^{-1} under nitrogen flow on a PerkinElmer TGA7. DSC was performed on a PerkinElmer DSC 7 with a heating/cooling rate of ±10 °C min^{-1} under nitrogen flow. Density functional theory (DFT, B3LYP/6-31G (d)) calculation was performed to calculate the frontier molecular orbitals. Atomic force microscopy (AFM) measurements were carried out in tapping mode on a SPA400HV instrument with a SPI 3800 controller (Seiko Instruments). Transmission electron microscopy (TEM) images were recorded on a JEM-1011 transmission electron microscope with accelerating voltage of 100 KV and camera length of 160 cm. Two-dimensional grazing-incidence wide angle X-ray scattering (GIWAXS) was measured at Shanghai Synchrotron Radiation Facility (SSRF) on beam line BL14B1 ($\lambda = 0.0689$ nm) with a MarCCD area detector at incidence angle of 0.16°.

Fabrication and characterization of OFET and SCLC devices. Bottom gate/top contact (BG/TC) OFET devices were fabricated on *n*-octadecyltrimethoxysilane (ODMS) modified Si/SiO_2 (300 nm, $C_i = 10$ nF/cm^2) substrates,[5] and the polymer film was prepared by spin casting an *o*-xylene solution (8 mg/mL) at 60 °C. Gold (40 nm) was deposited under vacuum as the source and drain electrodes. Post-annealing of films was done in glove box. The channel W(width) /L(length) is 3000/100. The characterization of OFETs was performed with two Keithley 236 source/drain in ambient environment.

Hole-only devices with a structure of ITO/PEDOT:PSS (40 nm)/polymer/MoO_3 (10 nm)/Al (100 nm) were fabricated as the reference.[5] The devices were measured using Keithley 236 source meter in the dark at ambient. The hole mobilities were calculated by fitting the dark current using the Mott–Gurney relationship: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$.[6-8]

Fabrication and characterization of PSC devices. PSC devices with a structure of ITO/ PEDOT:PSS (40 nm)/polymer:$PC_{71}BM$ (~ 100 nm) /LiF (1 nm)/Al (100 nm) were fabricated with *o*-xylene as solvent. Fabrication procedure was identical to that in our previous report.[9] The active layer was prepared by spin-casting polymer:$PC_{71}BM$ solution in *o*-xylene (8 mg/mL for the polymer) at 60 °C in a glove box. The active area of devices is 12 mm^2. Keithley 236 source meter (the light power 100 mA/cm^2, AM 1.5 G) was used to measure *J*-V curves in a glove box. EQE curves were detected on a QE-R3011IPCE measurement system (Enli Technology Co. Ltd).

Scheme S1. Synthetic Routes to Polymers PTVT-C6, PTVT-C8 and PTVT-C10.



Reagents and conditions: i) (*E*)-1,2-bis(tributylstannyl)ethene, $Pd_2(dba)_3$, $P(o\text{-tol})_3$, toulene, 110 °C; ii) *n*-BuLi, THF, -78 °C; $Sn(Me)_3Cl$, r.t.; iii) 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole, $Pd_2(dba)_3$, $P(o\text{-tol})_3$, toulene, 110 °C; iv) (*E*)-1,2-bis(tributylstannyl)ethene, $Pd_2(dba)_3$, $P(o\text{-tol})_3$, toulene, 110 °C. iiv) $Pd(PPh_3)_4$, DMF, 100 °C.

(E)-1,2-Bis(3-(2-butyloctyl)thiophen-2-yl)ethene (**5**). 2-Bromo-3-(2-butyloctyl)thiophene (**4**, 900 mg, 2.72 mmol), (*E*)-1,2-bis(tributylstannyl)ethene (823 mg, 1.36 mmol) , $Pd_2(dba)_3$ (44.0 mg, 1.8 mol% with respect to **4**), $P(o\text{-tol})_3$ (121 mg, 15 mol% to **4**) anhydrous toluene (30 mL) were added into a Schlenk tube. The mixture was heated up to 110 °C for 24 h in dark. The cooled mixture was poured into saturated KF aqueous solution and extracted by petroleum ether (PE). The organic extracts were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed, and the purification was conducted by column chromatography on silica gel with PE as eluent to afford **5** (0.51 g, 70%) as a pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.06 (d, J = 5.2 Hz, 2H), 6.99 (s, 2H), 6.81 (d, J = 4.8 Hz, 2H), 2.59 (d, J = 6.9 Hz, 4H), 1.60 (m, 2H), 1.20-1.28 (m, 32H), 0.84-0.90 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 140.0, 137.1, 130.6, 122.3, 119.7, 39.8, 33.6, 33.3, 33.2, 32.1, 29.9, 29.1, 26.8, 23.2, 22.8, 14.3. MALDI-TOF MS: calcd. for $C_{34}H_{56}S_2$: 528.4; Found. 528.4.

(E)-1,2-Bis(3-(2-butyloctyl)-5-(trimethylstannyl)thiophen-2-yl)ethene (**6**). *n*-BuLi (2.5 mol L^{-1} in hexane, 0.66 mL, 1.65 mol) was added dropwise to a solution of **5** (396 mg, 749 μmol) in anhydrous THF (10 mL) at -78 ^{o}C. The mixture was allowed to warm to 0 ^{o}C and stirred for 2 h followed by the addition of trimethyltin chloride (328 mg, 1.65 mmol). The reaction mixture was stirred overnight at room temperature. Then saturated KF aqueous solution was added. The resulting mixture was stirred for 30 min and extracted with PE. The organic extracts were washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to yield **6** as yellow oil, which was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.99 (s, 2H), 6.86 (s, 2H), 2.57 (d, J = 8.0 Hz, 4H), 1.60 (m, 2H), 1.26-1.35 (m, 32H), 0.84-0.90 (m, 12H), 0.36 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 142.9, 140.9, 139.0, 134.9, 119.7, 39.9, 33.7, 33.4, 33.0, 32.1, 29.9, 29.1, 26.8, 23.3, 22.9, 14.3, -8.2.

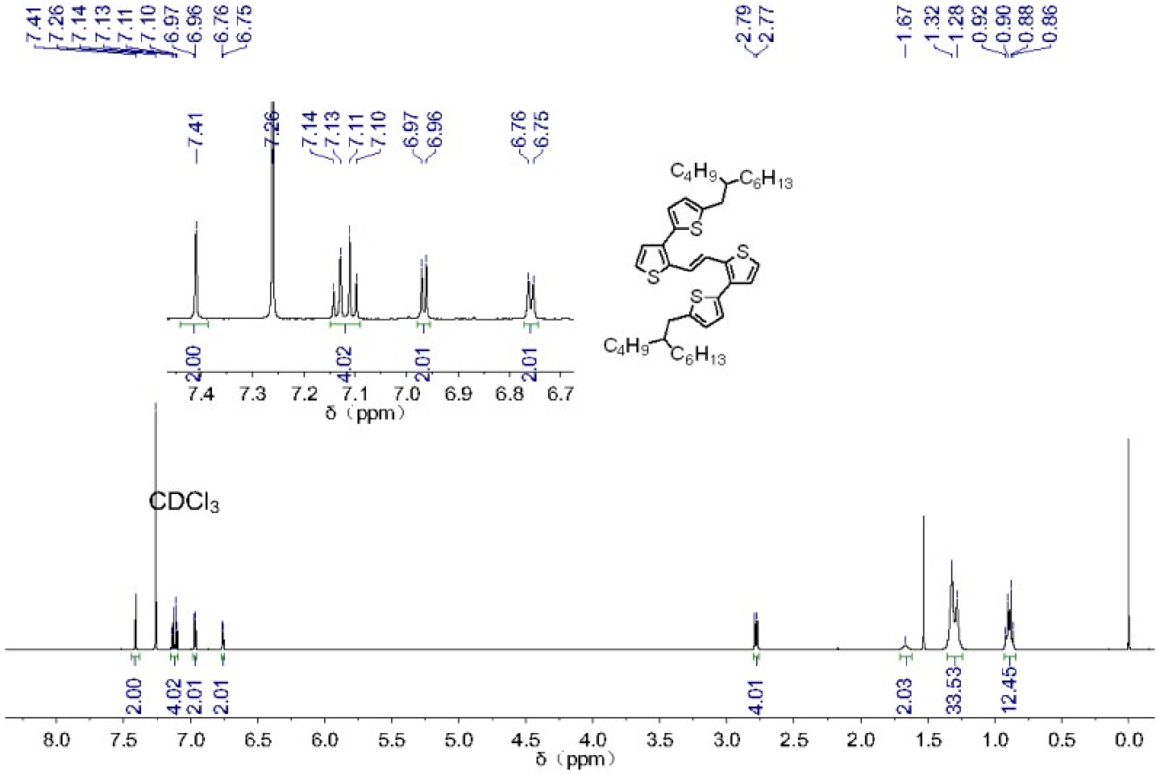
PTVT-C6. The compound **6** (280 mg, 328 μmol), 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5] thiadiazole (106 mg, 321 μmol), $Pd_2(dba)_3$ (6.00 mg, 2 mol% with respect to **5**), P(*o*-tol)$_3$ (16.0 mg, 16 mol% with respect to **6**) and anhydrous toluene (32 mL) were added into a 100 mL Schlenk tube. The mixture was heated to 110 ^{o}C for 48 h in dark. Then 2-bromothiophene (1 mL, 10.3 mmol) was added and the reaction was continued for another 12 h. After being cooled to room temperature, the mixture was added dropwise into methanol. The precipitates were collected by filtration and purified by Soxhlet extraction with ethanol, acetone and hexane. The remained solid was collected (for **PTVT-C8** and **PTVT-C10** the remained solid was dissolved in 30 mL *o*-DCB and precipitated into methanol once more). The **PTVT-C6** was obtained as a black solid in a yield of 77% (184.0 mg) after vacuum drying. Anal. Calcd: C, 68.72; H, 8.07, N, 4.01, S, 13.76%. Found: C, 67.81, H, 7.68, N, 3.99, S, 13.60%.

***PTVT-C8*. PTVT-C8** (273 mg, 84%) was obtained as a black solid from **7a** (364 mg, 386 μmol) and (*E*)-1,2-bis(tributylstannyl)ethene (239 mg, 394 μmol) following the procedure for the synthesis of **PTVT-C6**. Anal. Calcd: C, 71.06; H, 8.95, N, 3.45, S, 11.86%. Found: C, 69.96; H, 8.60, N, 3.32, S, 11.60%.

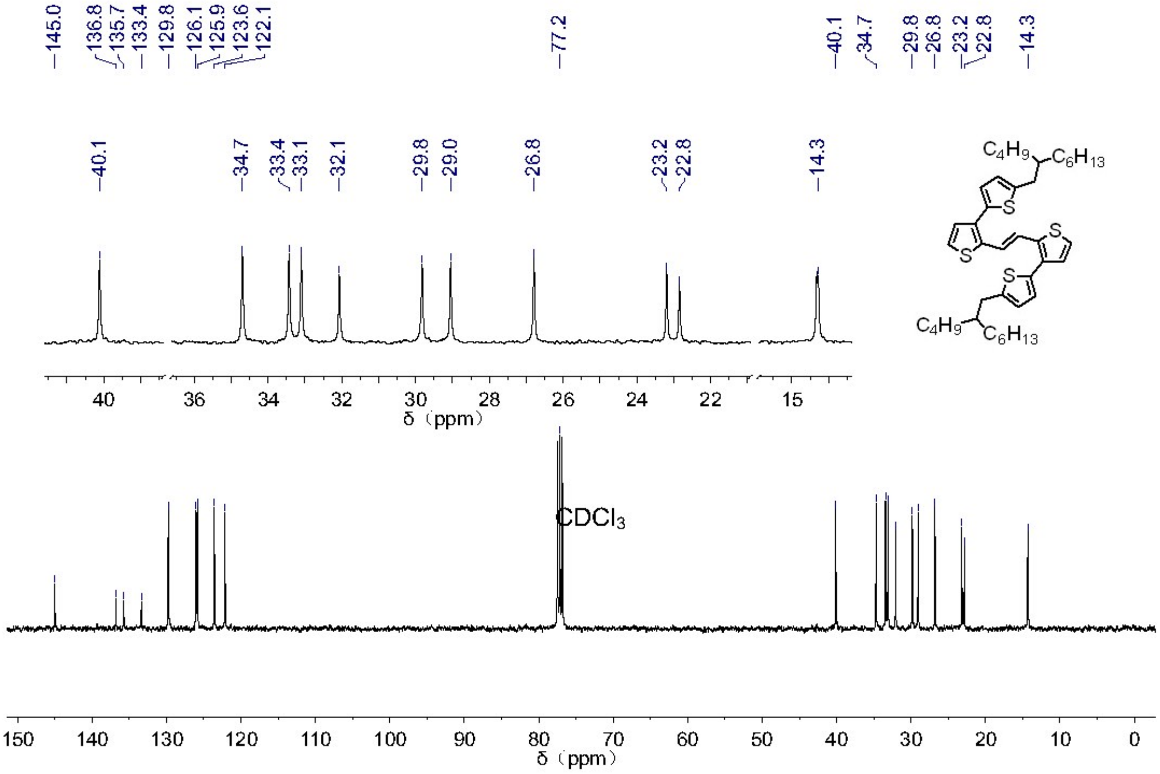
PTVT-C10. **PTVT-C10** (281 mg, 78%) was obtained as a black solid from **7b** (400 mg, 379 μmol) and (*E*)-1,2-bis(tributylstannyl)ethene (234 mg, 387 μmol) as the procedure for the synthesis of **PTVT-C6**. Anal. Calcd: C, 72.83; H, 9.60, N, 3.03, S, 10.42%. Found: C, 71.96; H, 9.28, N, 2.92, S, 10.31%.

(E)-1,2-Bis(5-hexyl-[2,3'-bithiophen]-2'-yl)ethene (***TVT-TC6***). Compound **TVT-TC6** (175 mg, 90%) as yellow block crystals was obtained from TVT-diBr (130 mg, 0.371 mmol) and **8** (425 mg, 0.928 mmol) following the procedure for the synthesis of **2a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.39 (s, 2H), 7.09-7.14 (m, 4H), 6.95 (d, J = 3.2 Hz, 2H), 6.78 (d, J = 3.2 Hz, 2H), 2.84 (t, J = 8 Hz 4H), 1.72 (m, 4H), 1.33-1.45 (m, 12H), 0.89-0.92 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 146.5, 136.8, 135.5, 133.4, 129.8, 126.2, 124.8, 123.6, 122.1, 31.8, 30.3, 29.0, 22.7, 14.2. MALDI-TOF MS: calcd. for $C_{30}H_{36}S_4$: 524.2; Found. 524.2. Anal. Calcd: C, 68.65; H, 6.91, S, 24.44%. Found: C, 68.61, H, 6，92, S, 24.42%. CCDC numbers: 1504784. The supplementary crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

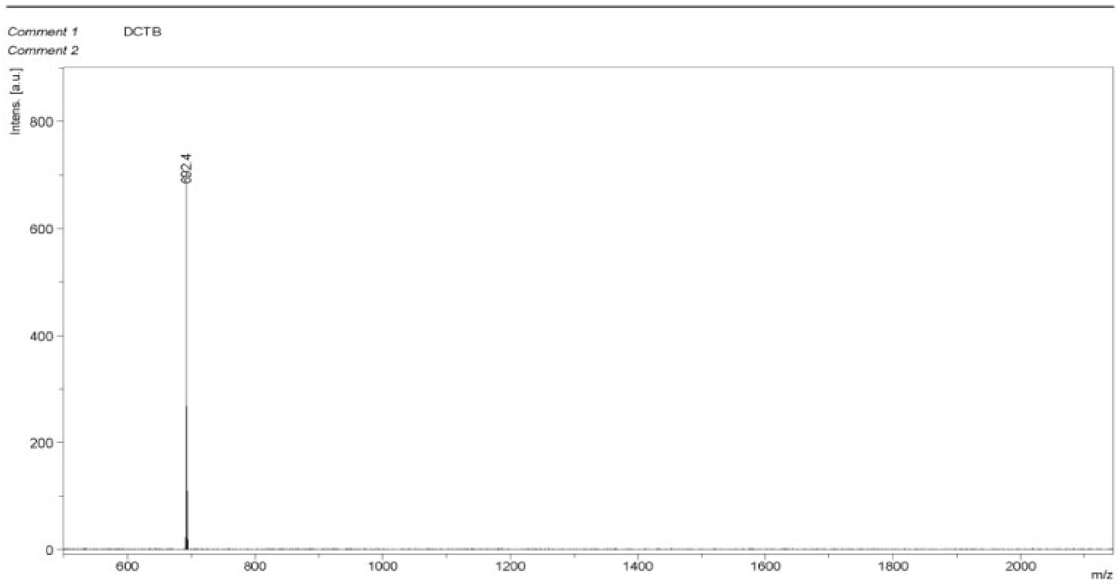
^{1}H NMR spectrum of compound **2a**.



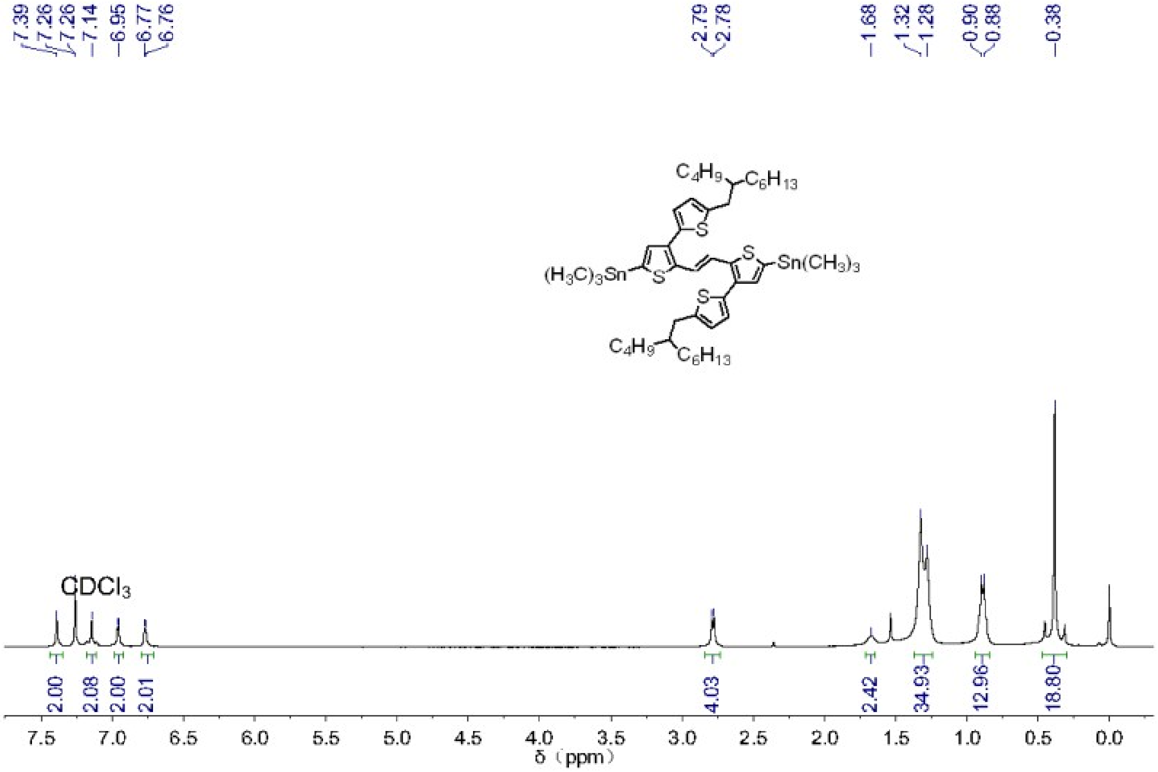
^{13}C NMR spectrum of compound **2a**.



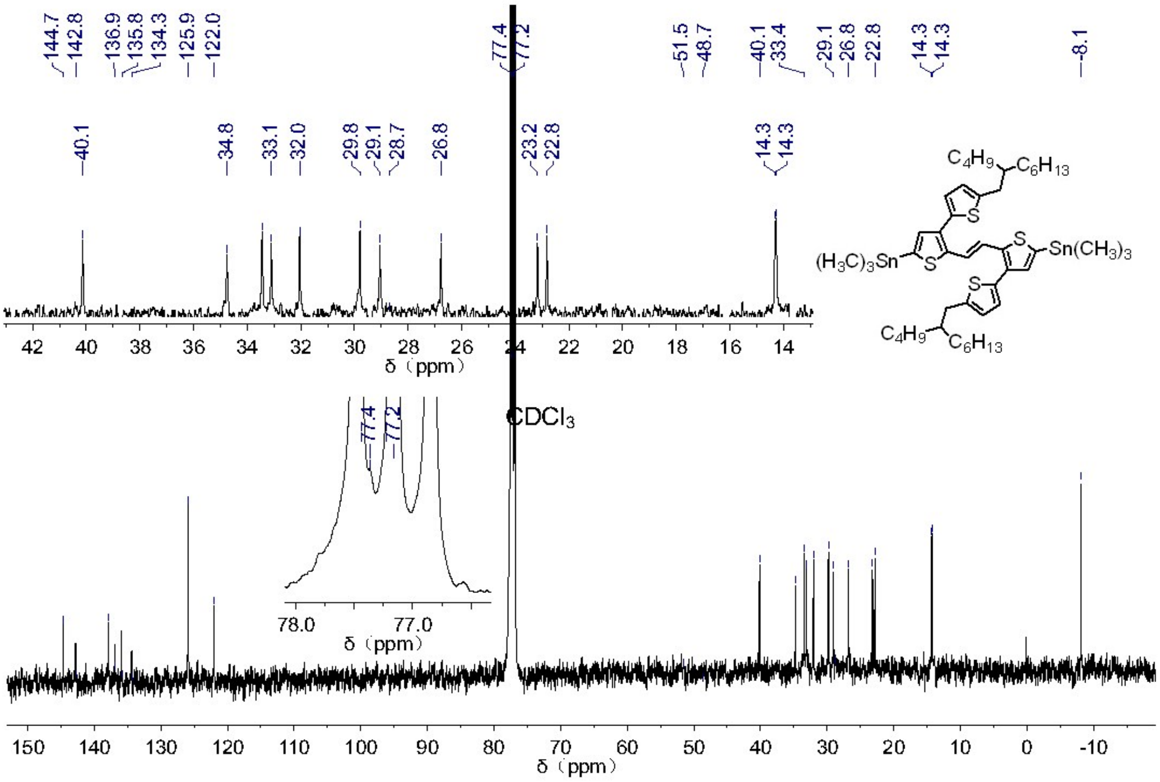
MALDI-TOF mass spectrum of compound **2a**.



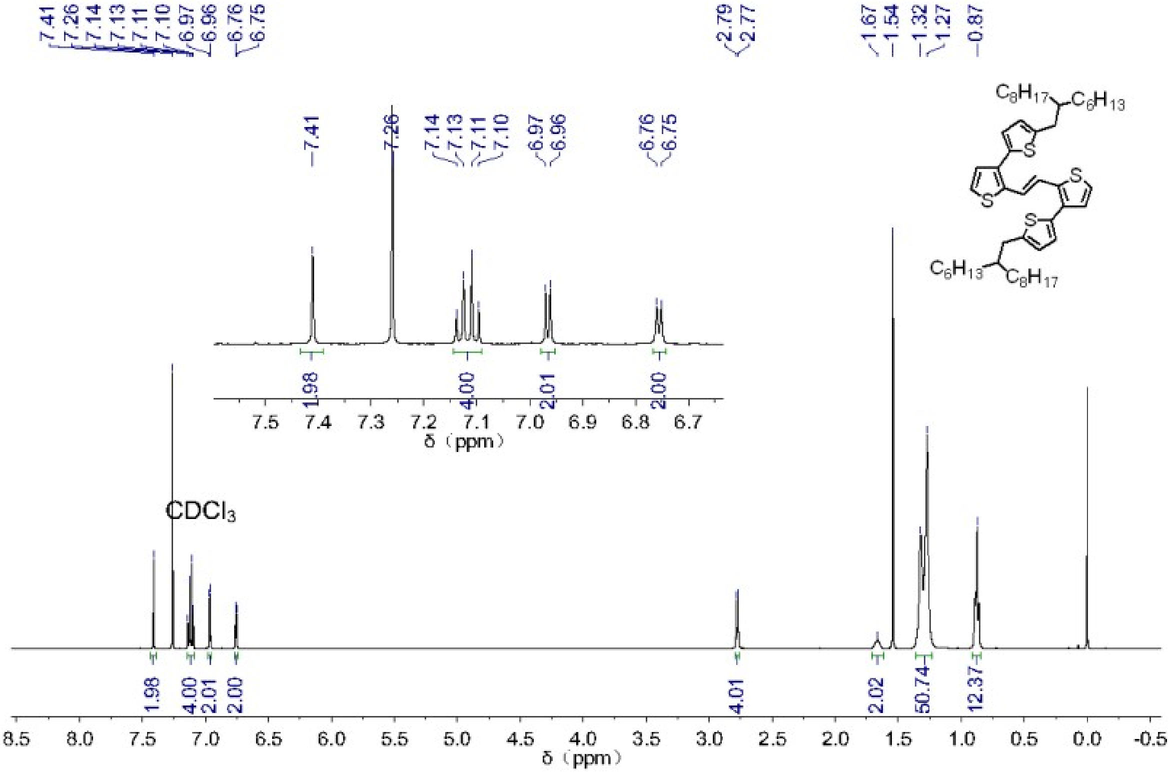
^{1}H NMR spectrum of compound **3a**.



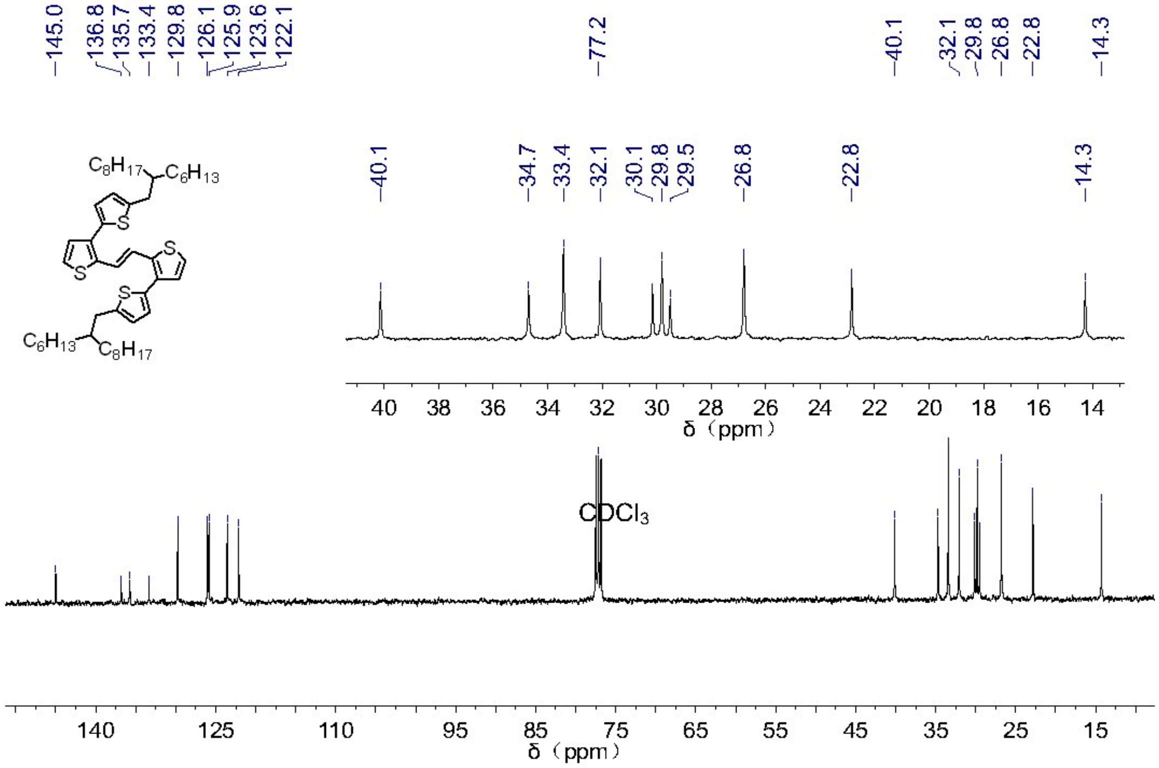
^{13}C NMR spectrum of compound **3a**.



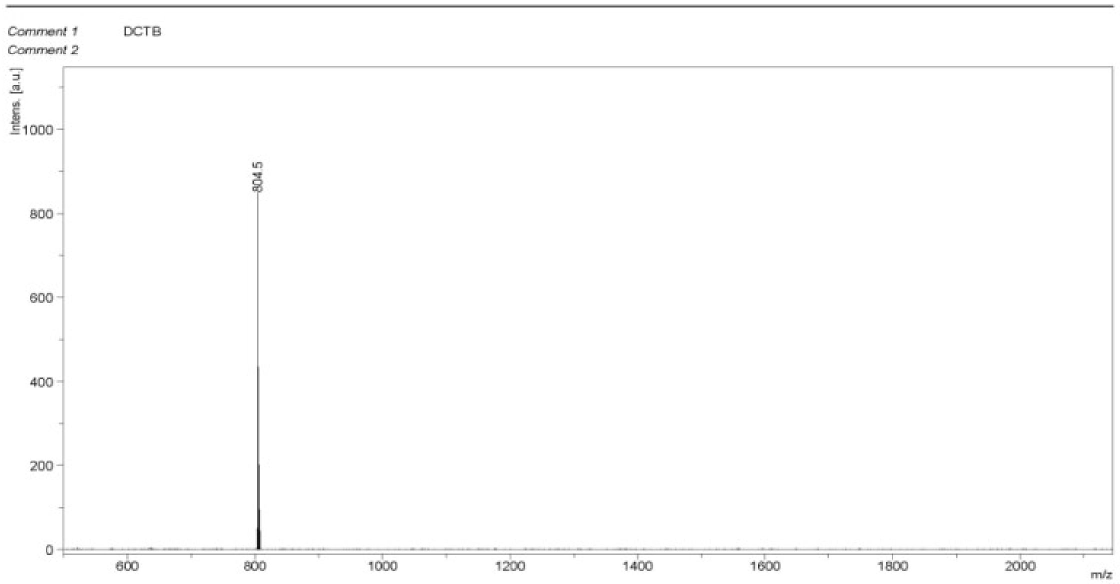
^{1}H NMR spectrum of compound **2b**.



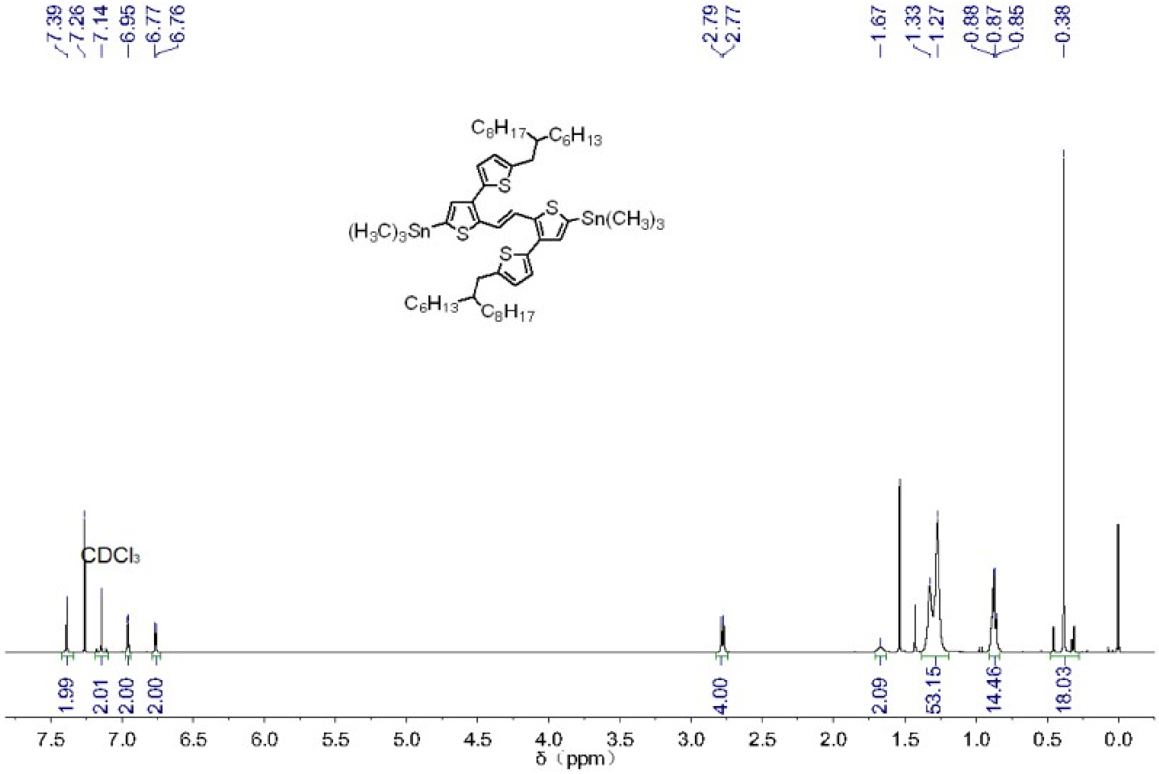
^{13}C NMR spectrum of compound **2b**.



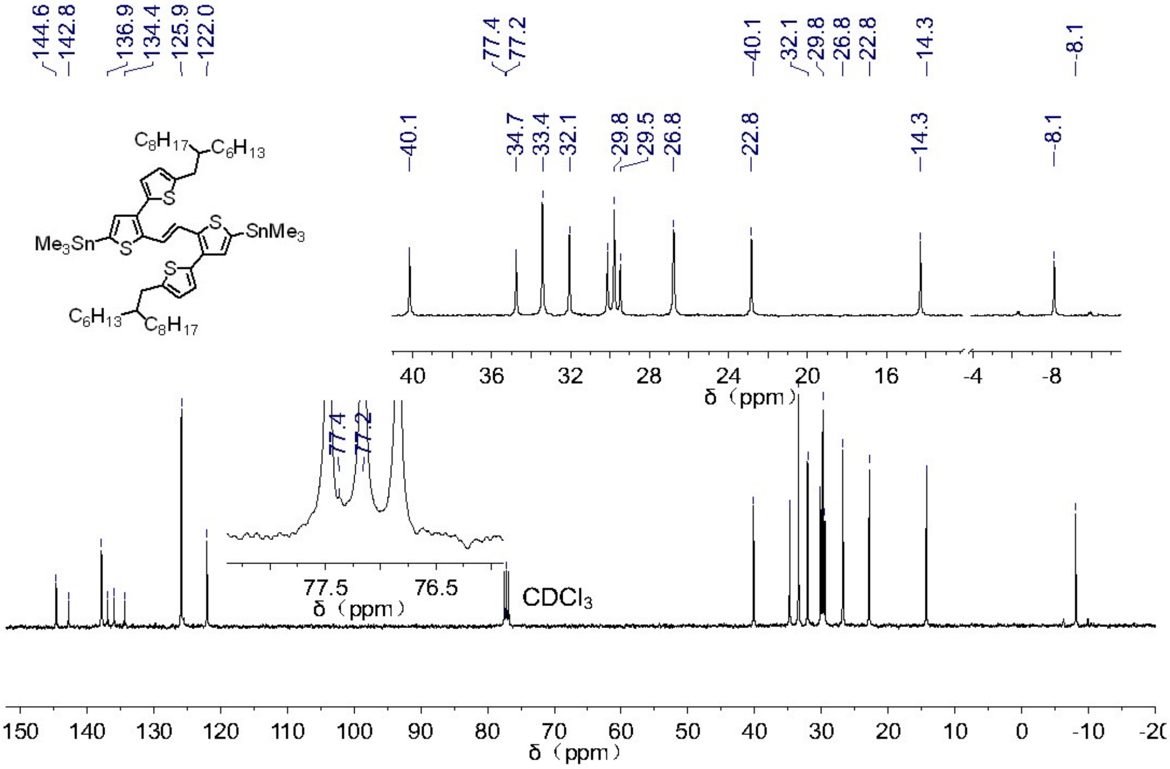
MALDI-TOF mass spectrum of compound **2b**.



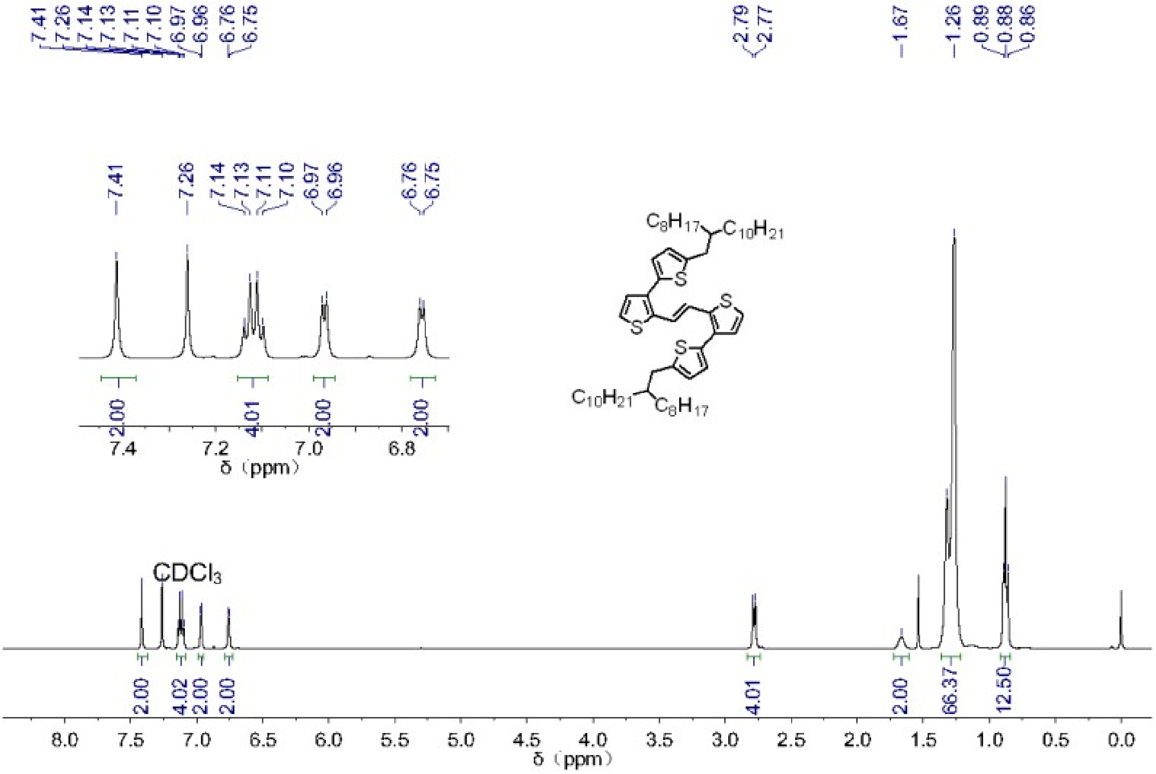
^{1}H NMR spectrum of compound **3b**.



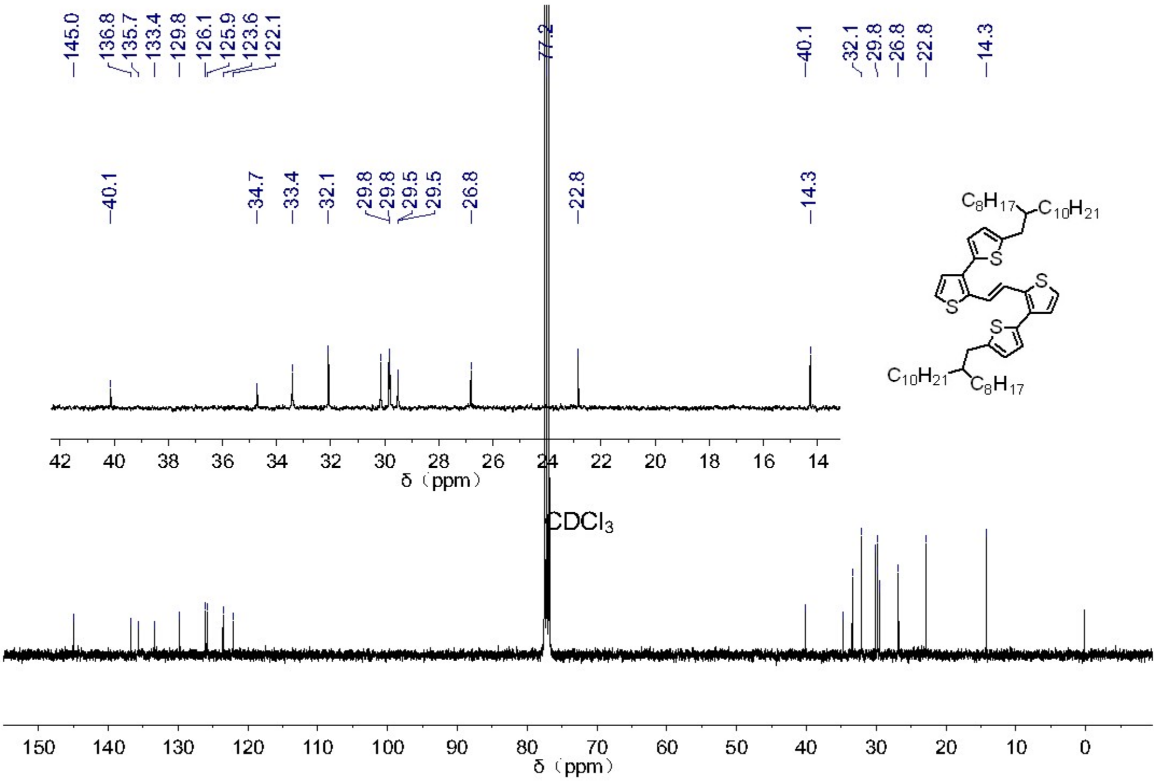
^{13}C NMR spectrum of compound **3b**.



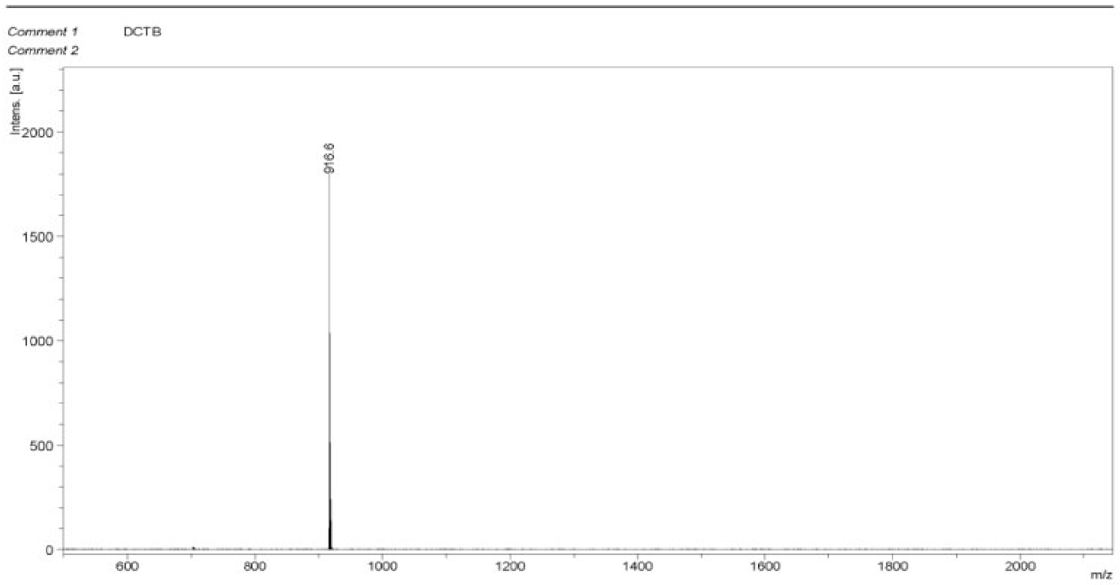
^{1}H NMR spectrum of compound **2c**.



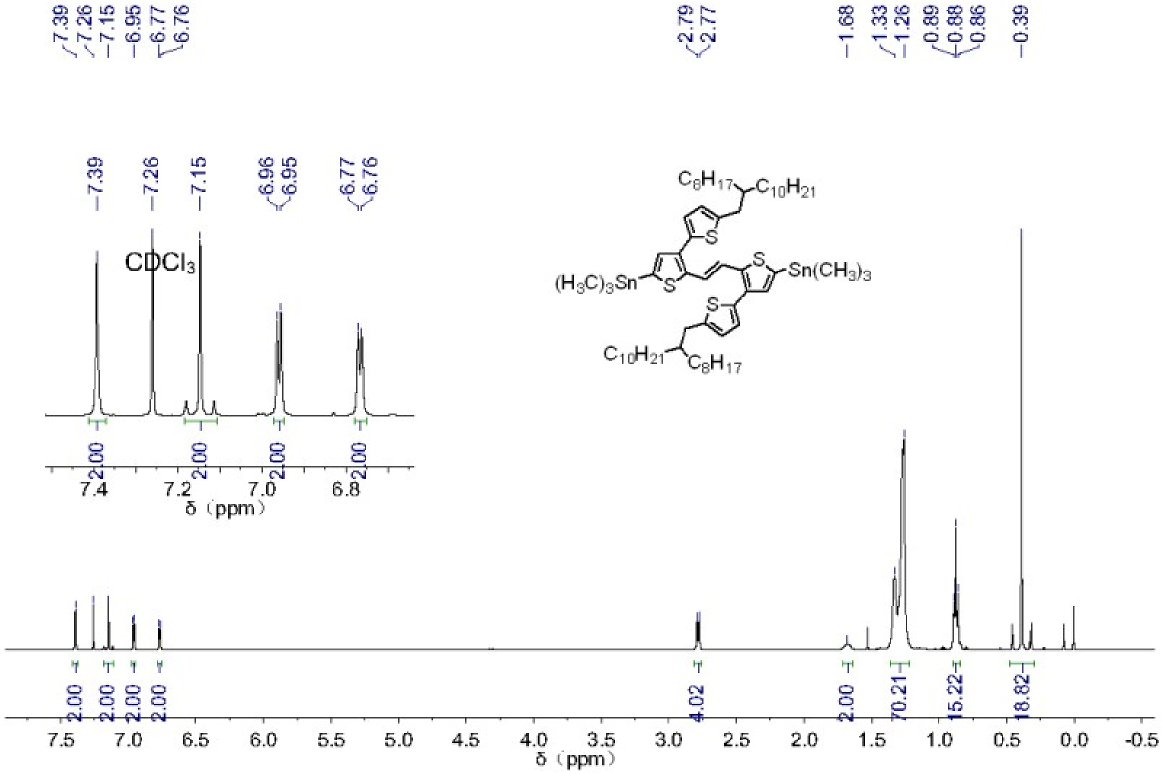
^{13}C NMR spectrum of compound **2c**.



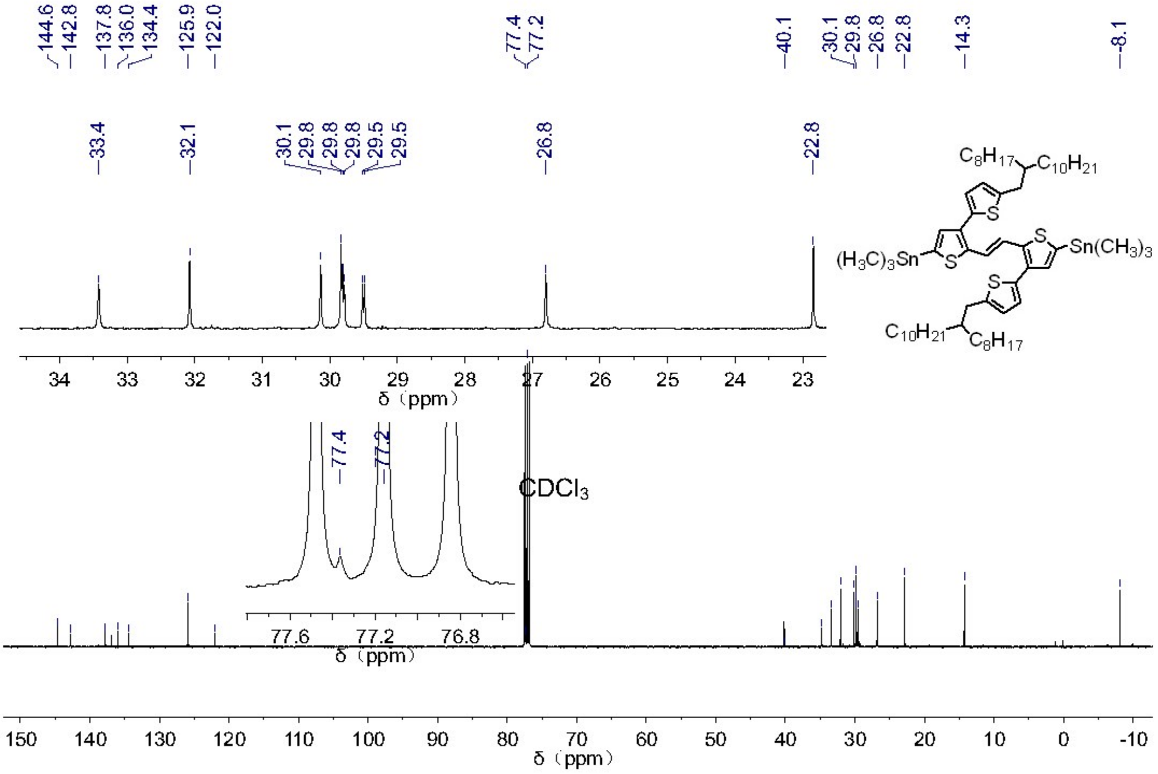
MALDI-TOF mass spectrum of compound **2c**.



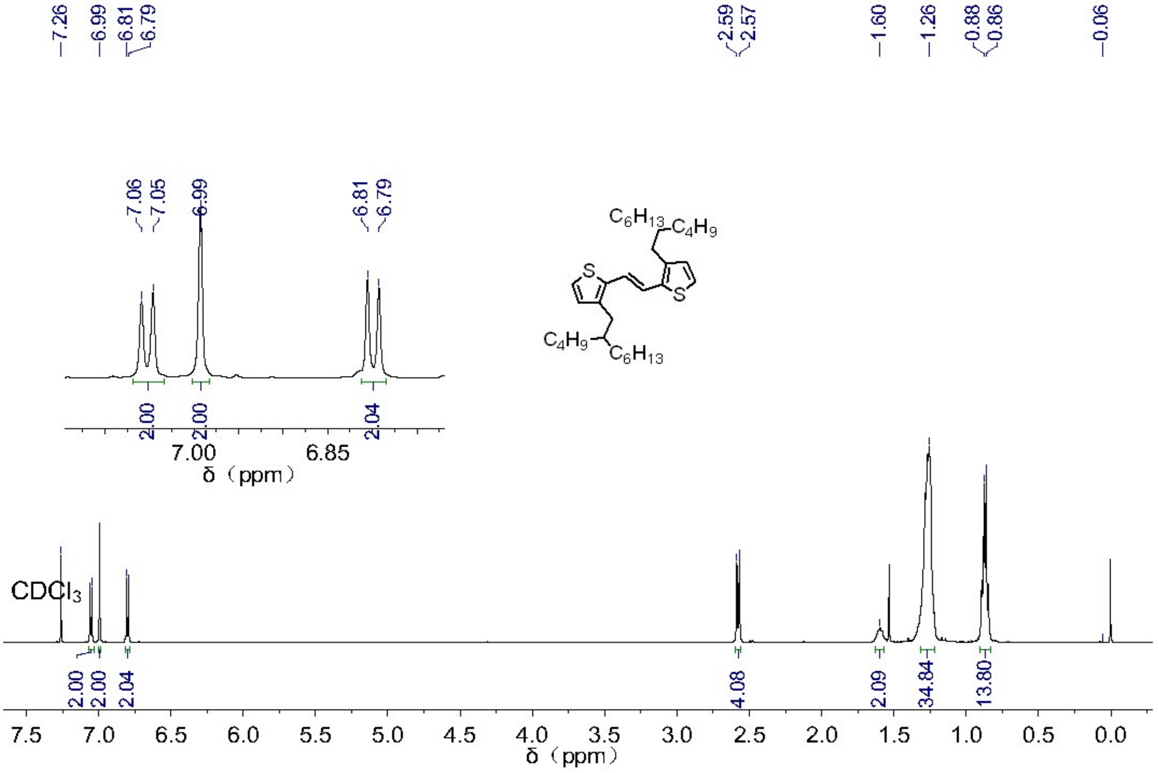
^{1}H NMR spectrum of compound **3c**.



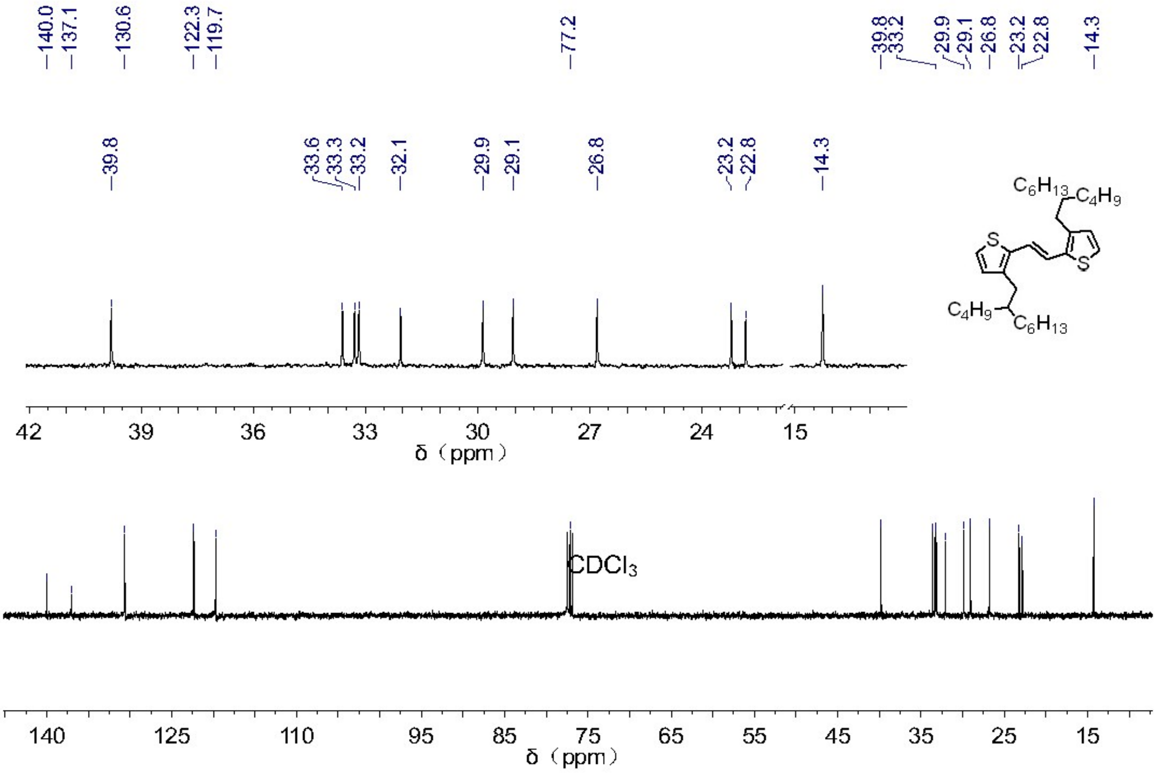
^{13}C NMR spectrum of compound **3c**.



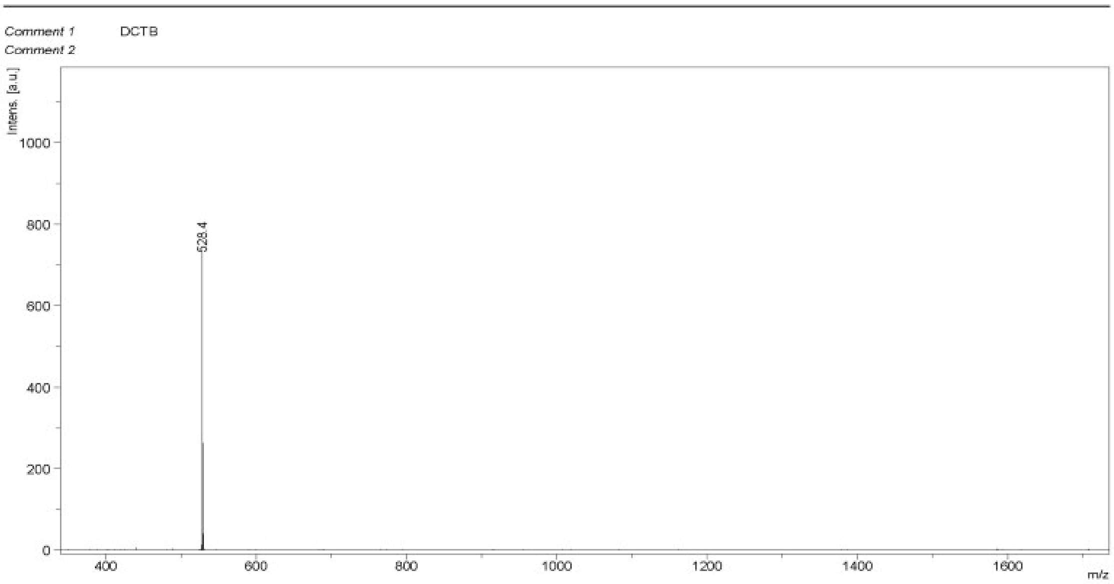
^{1}H NMR spectrum of compound **5**.



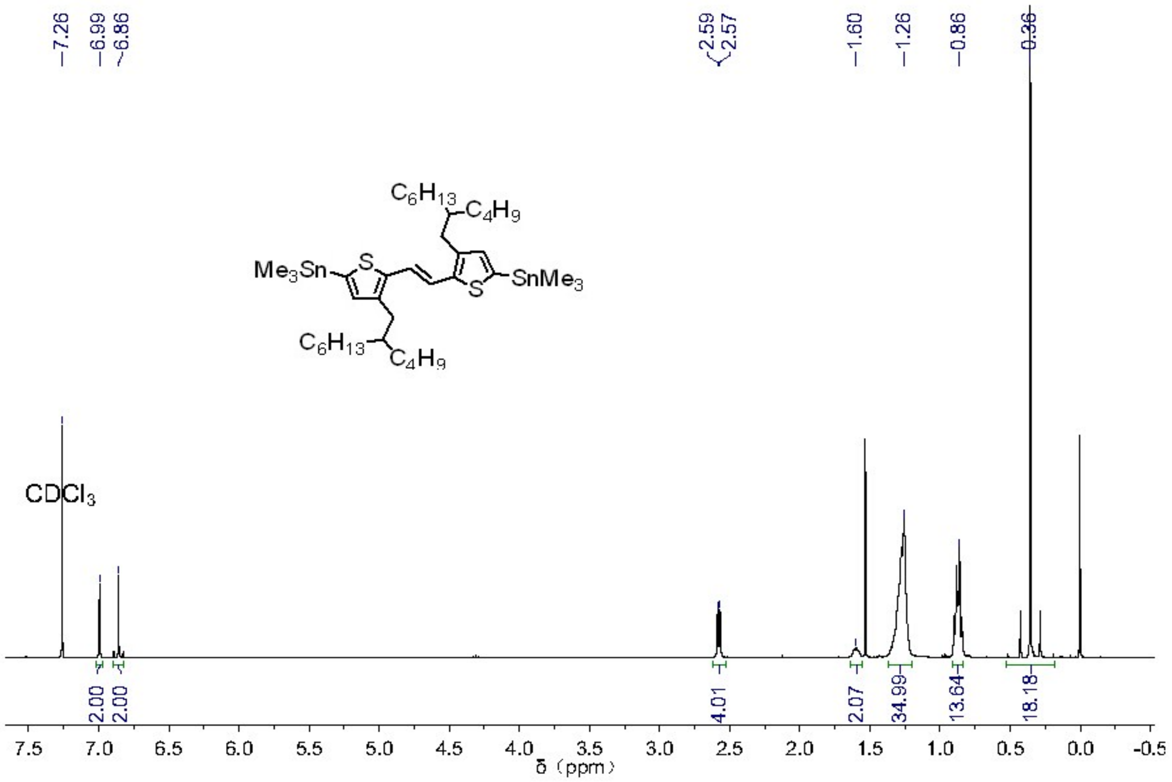
^{13}C NMR spectrum of compound **5**.



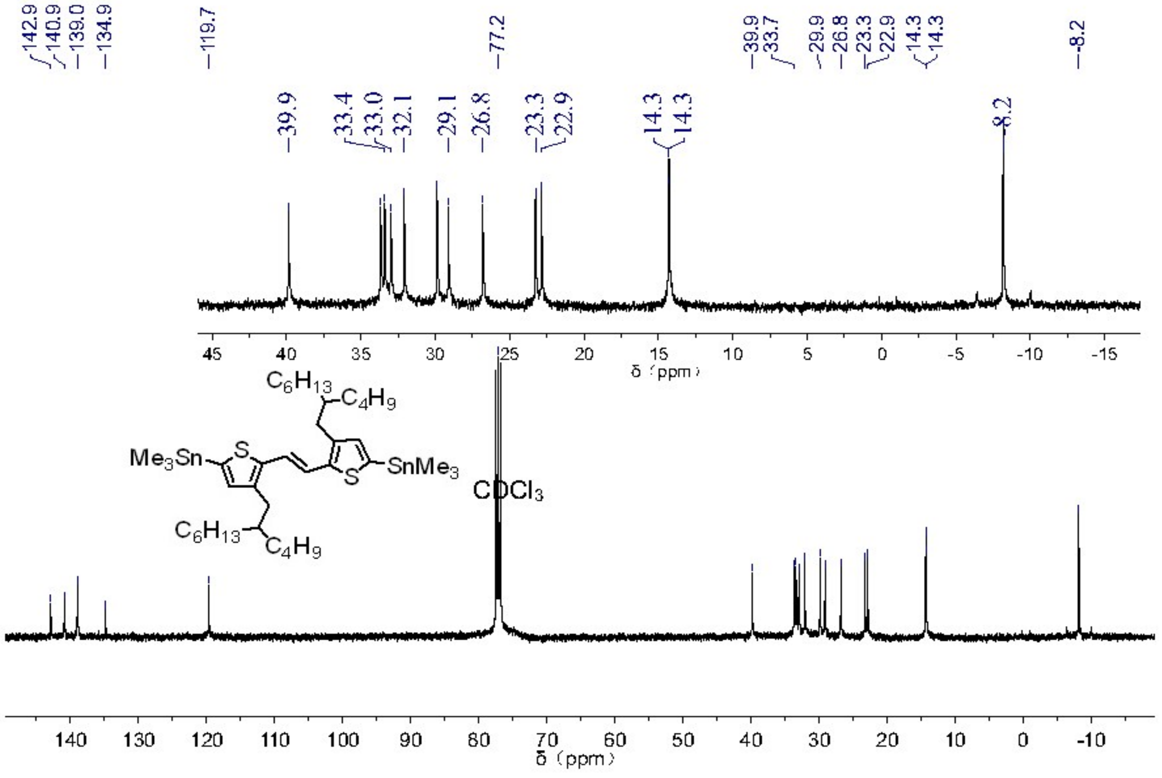
MALDI-TOF mass spectrum of compound **5**.



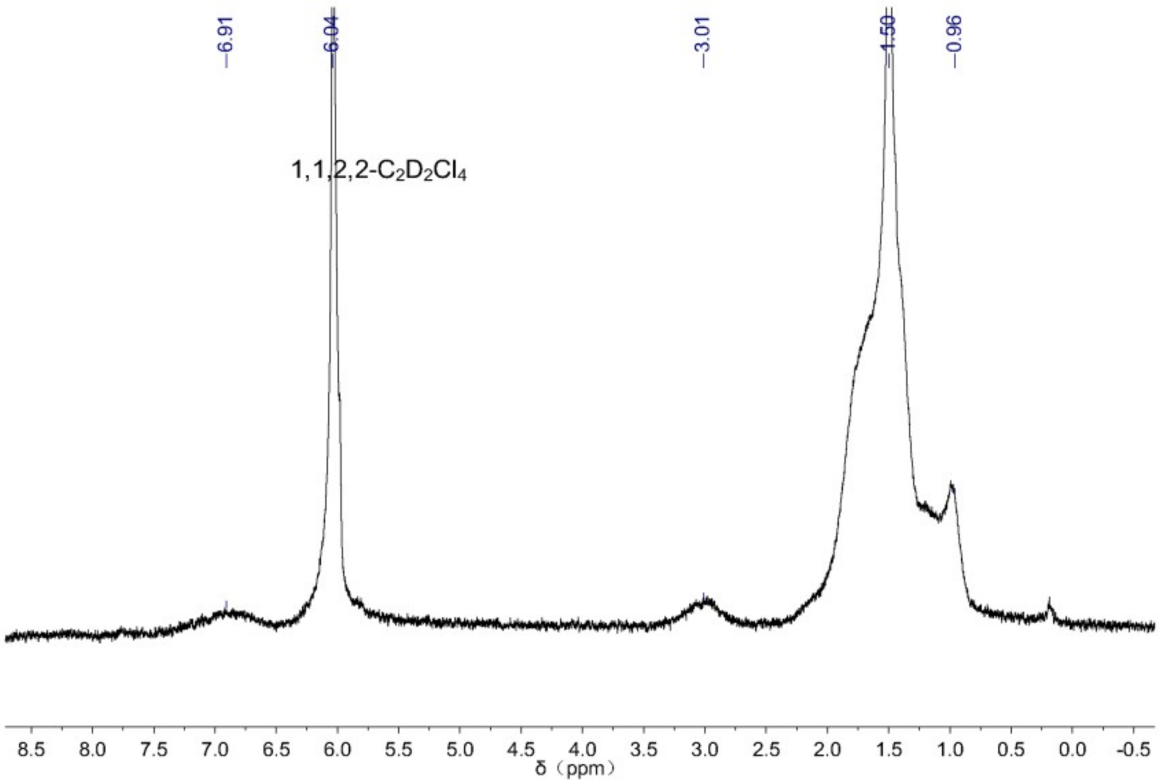
^{1}H NMR spectrum of compound **6**.



^{13}C NMR spectrum of compound **6**.



^{1}H NMR spectrum of **PTVT-T8** at 110 ^{o}C.



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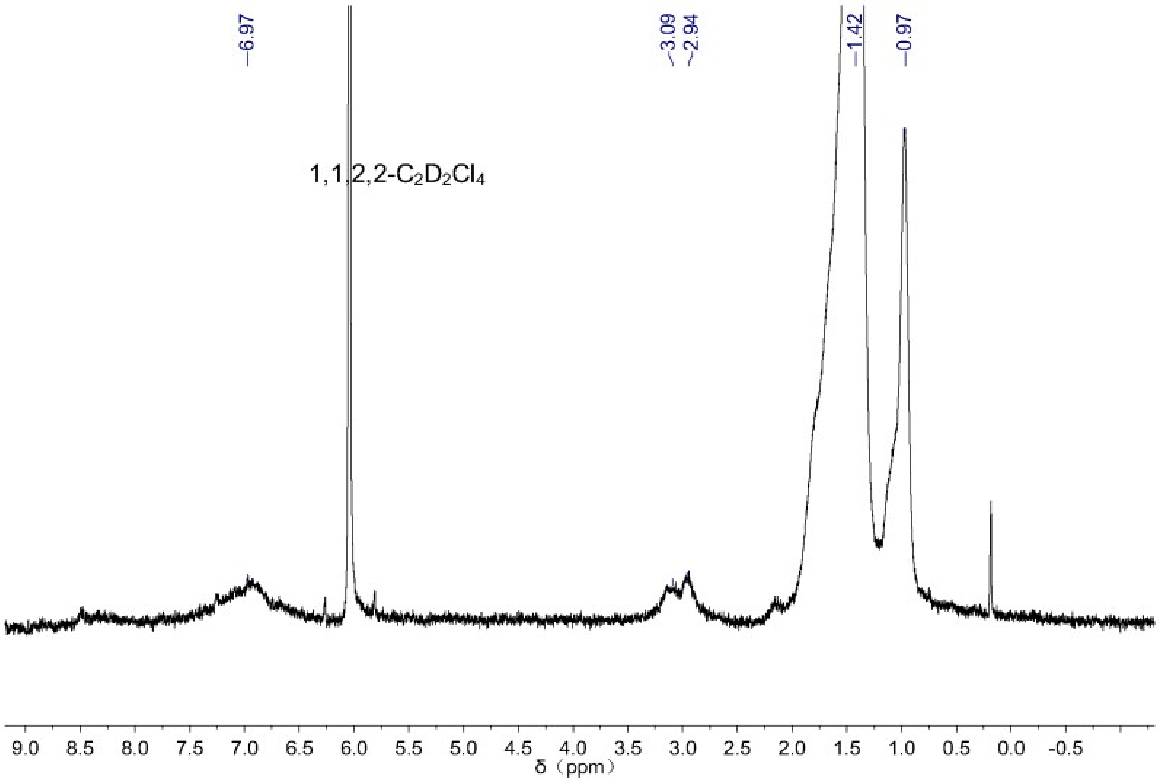
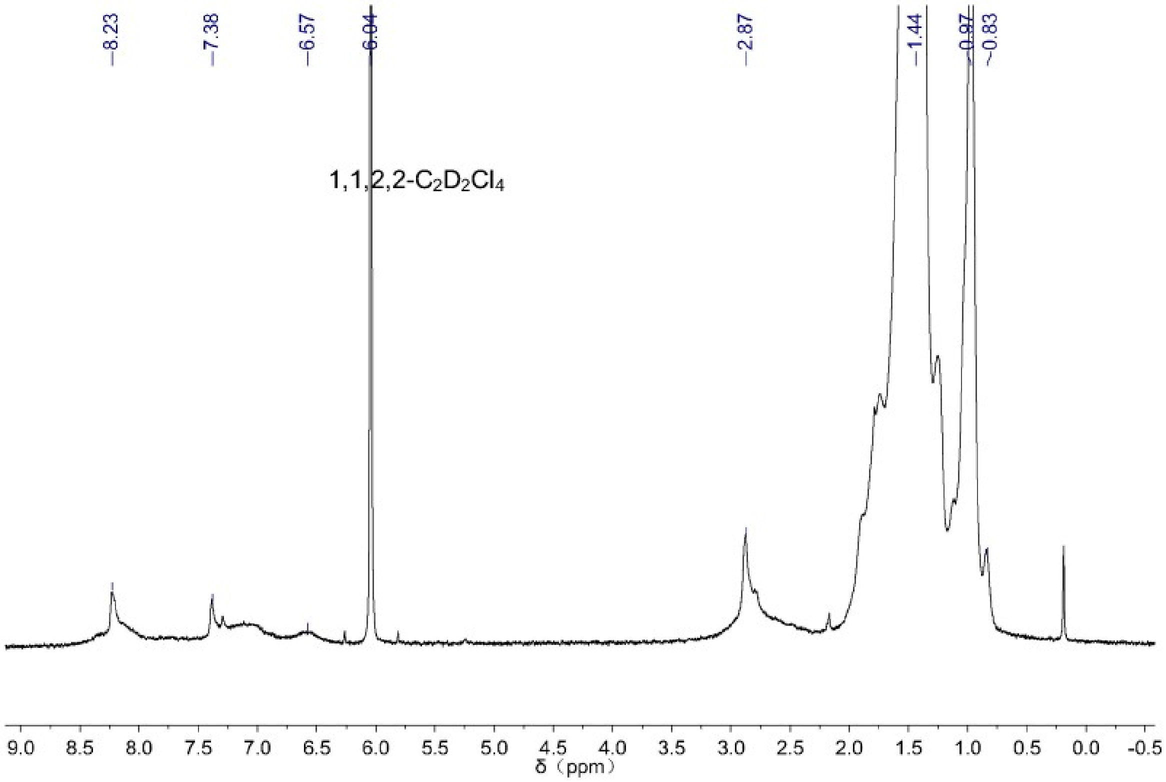


^{1}H NMR spectrum of **PTVT-C8** at 110 ^{o}C.



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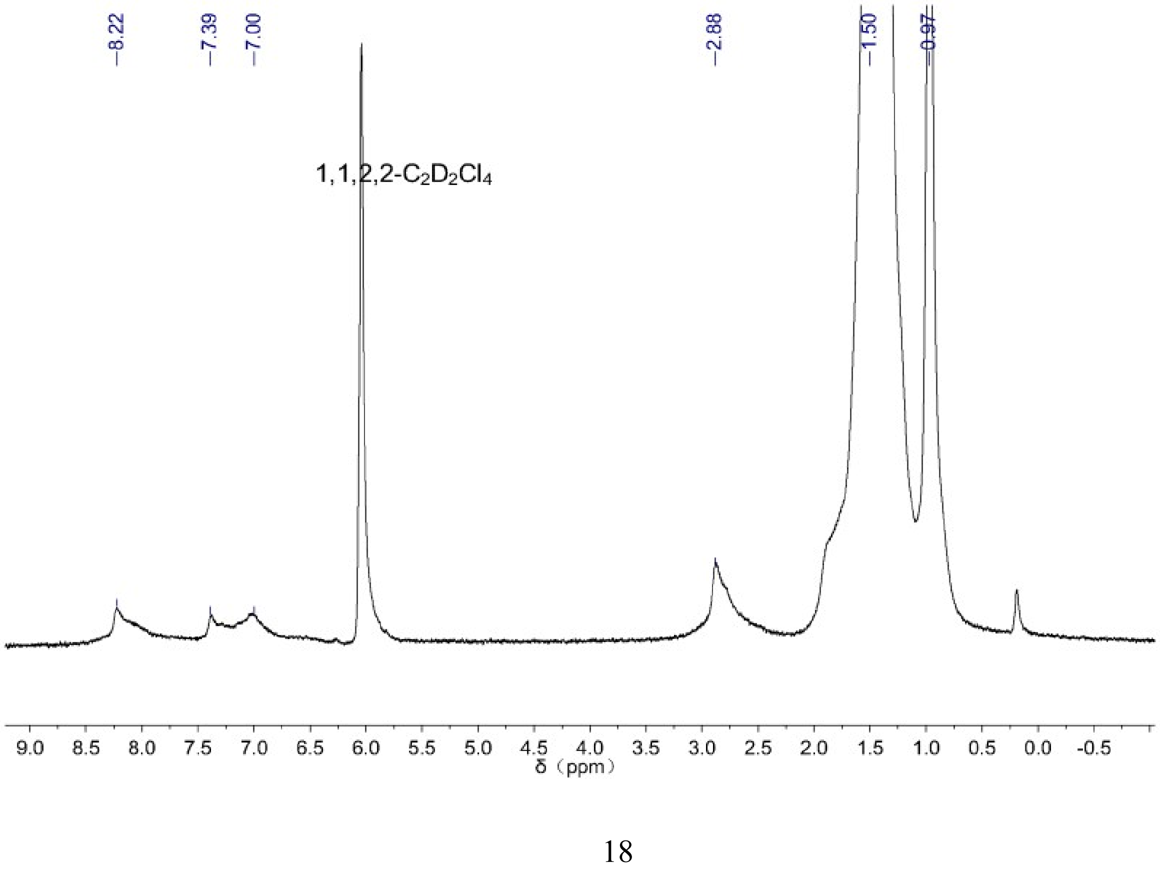
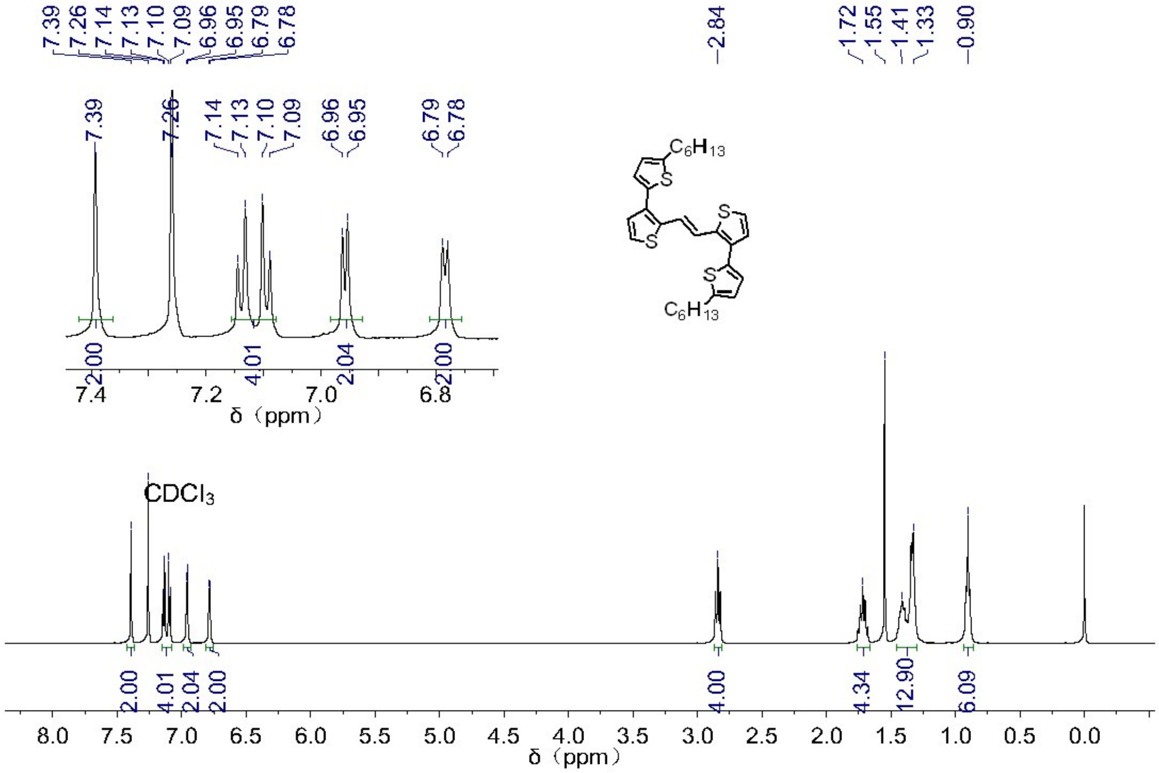
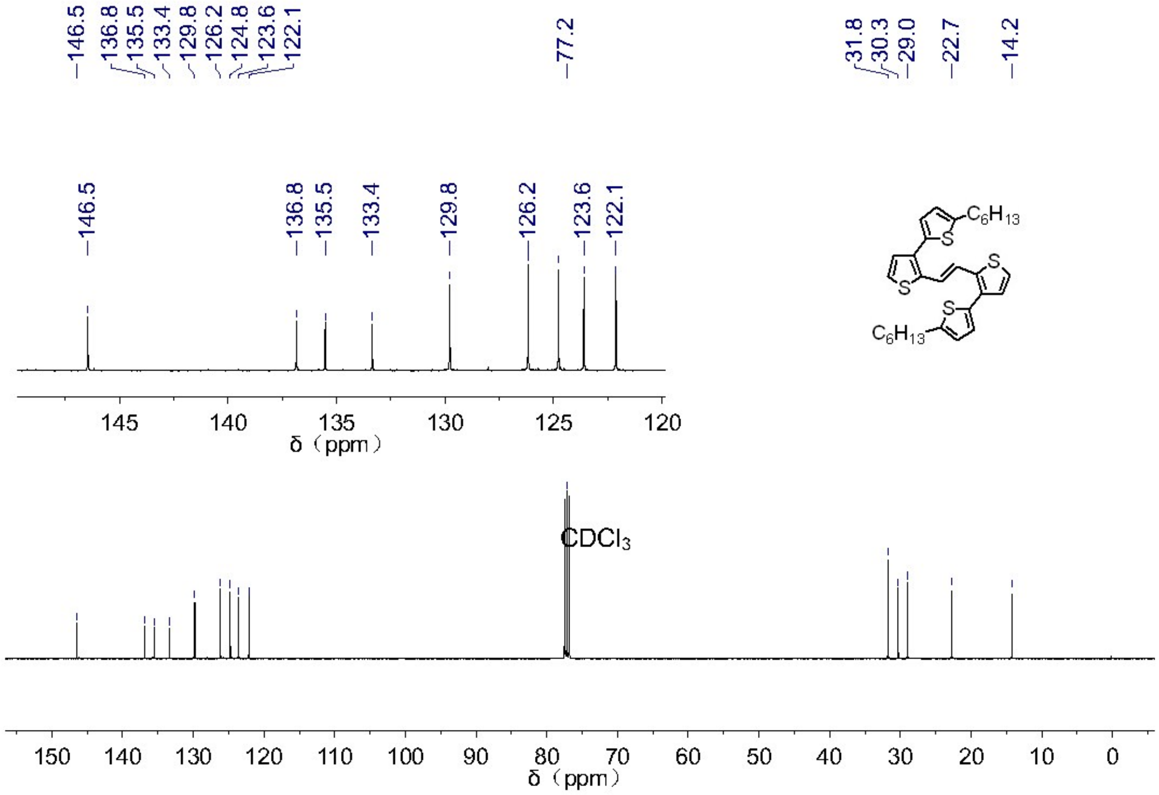


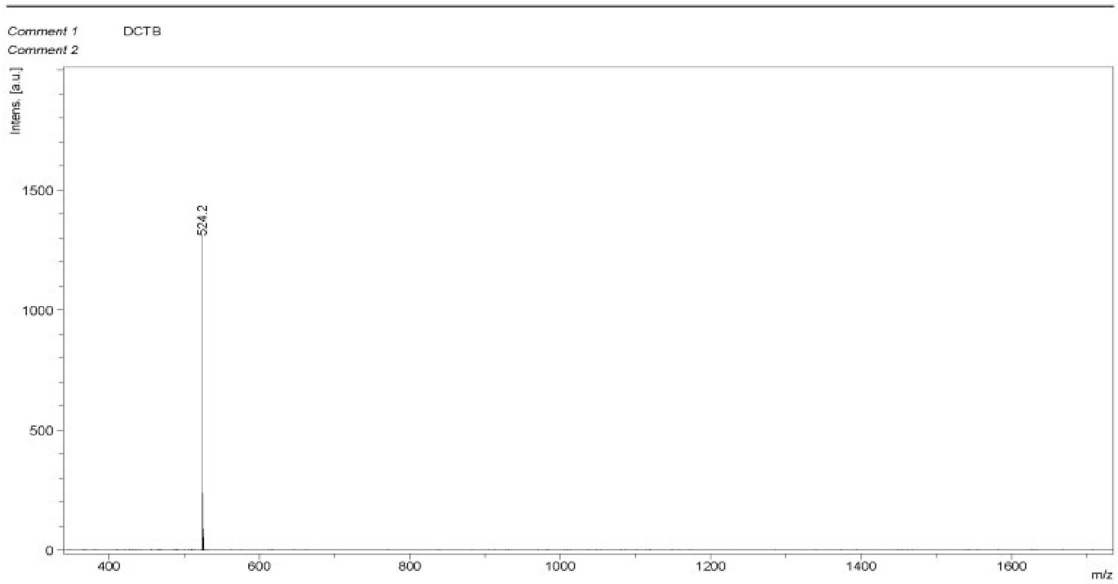
^{1}H NMR spectrum of compound **TVT-TC6**.



^{13}C NMR spectrum of compound **TVT-TC6**.



MALDI-TOF mass spectrum of compound **TVT-TC6**.



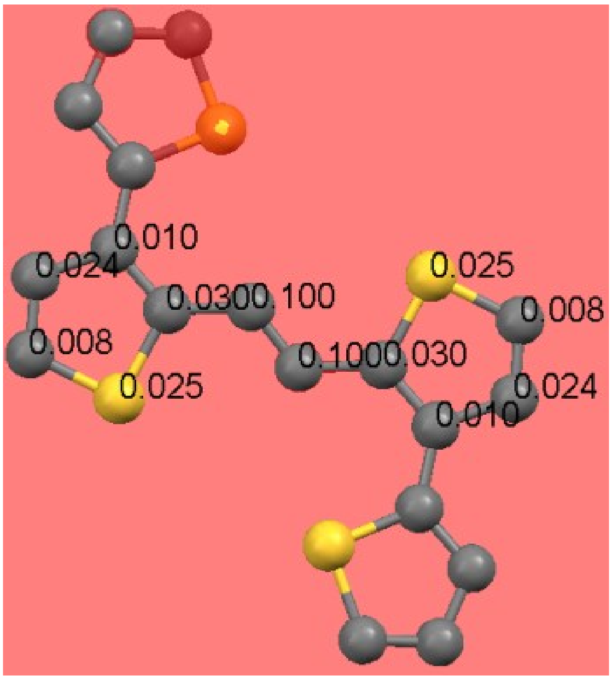


Figure S1. Single crystal structure of **TVT-TC6**. Red plane is the TVT backbone plane. Black number is the distance (Å) from the atom to the TVT plane.

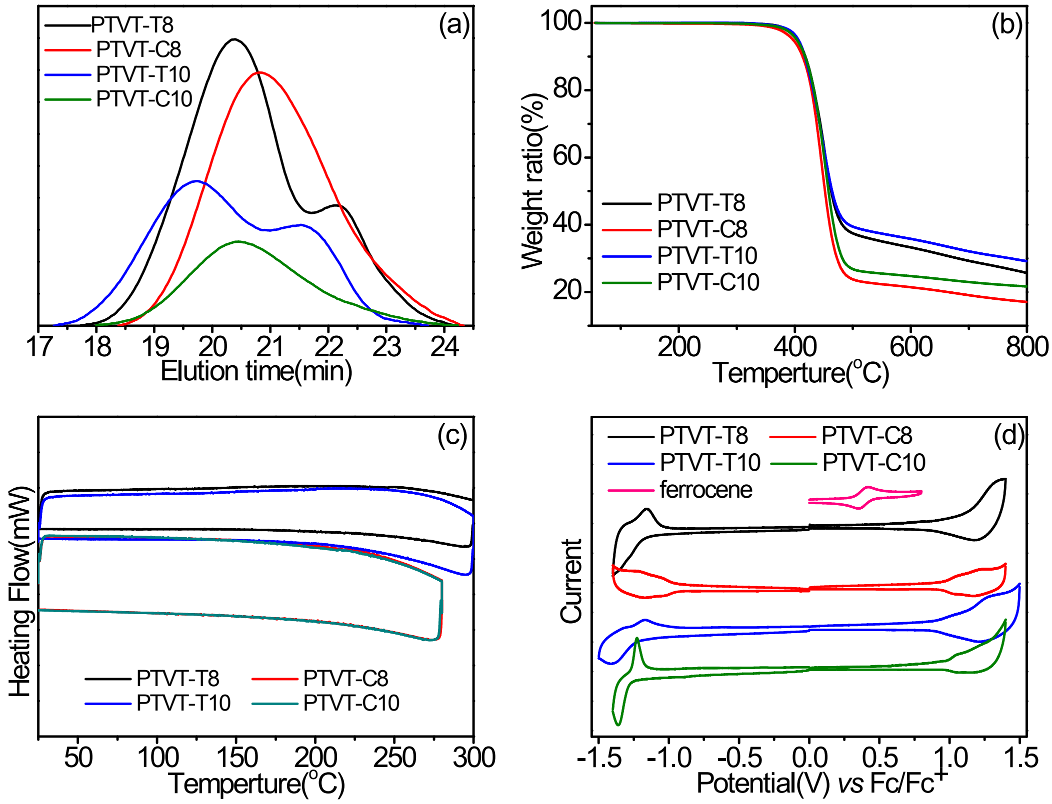


Figure S2. GPC (a), TGA (b), DSC (c) and film CV (d) curves of the polymers.

Table S1. Molecular Weights and Decomposition Temperatures (T_d) of the Polymers.

polymer	M_n (kDa)	M_w (kDa)	Đ	T_d (°C)
PTVT-T8	38	98	2.6	404
PTVT-C8	30	66	2.2	396
PTVT-T10	50	143	2.9	405
PTVT-C10	39	91	2.3	404

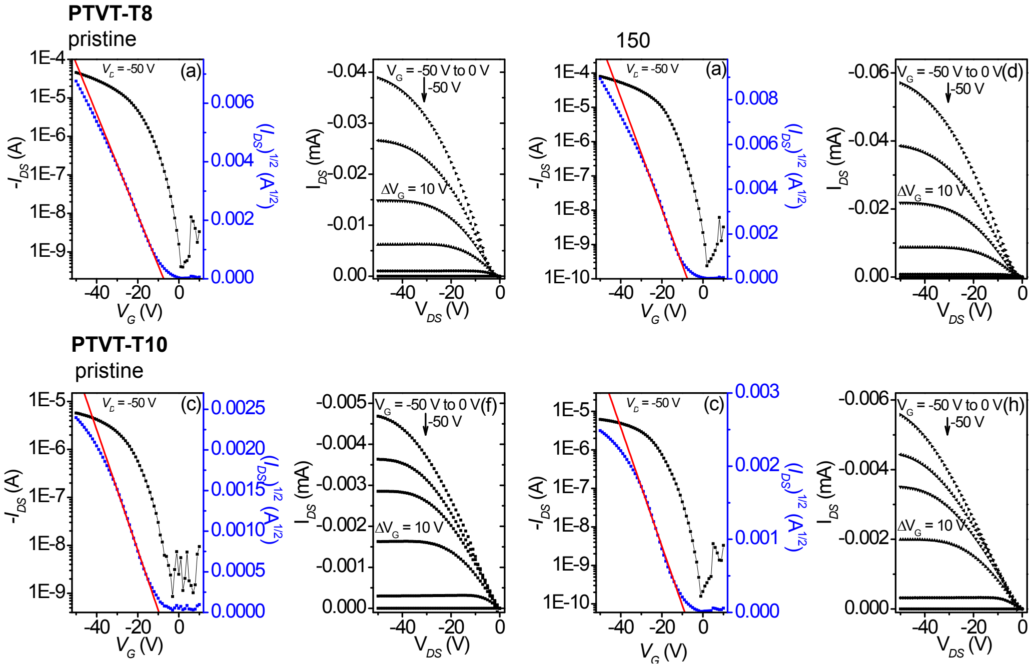


Figure S3. Transfer (a, c, e, g) and output (b, d, f, h) characteristics of OFETs based on **PTVT-T8** (a, b, c, d), **PTVT-T10** (e, f, g, h). The active layer was spin-coated on substrates at 60 °C. Left: without thermal annealing; right: with thermal annealing.

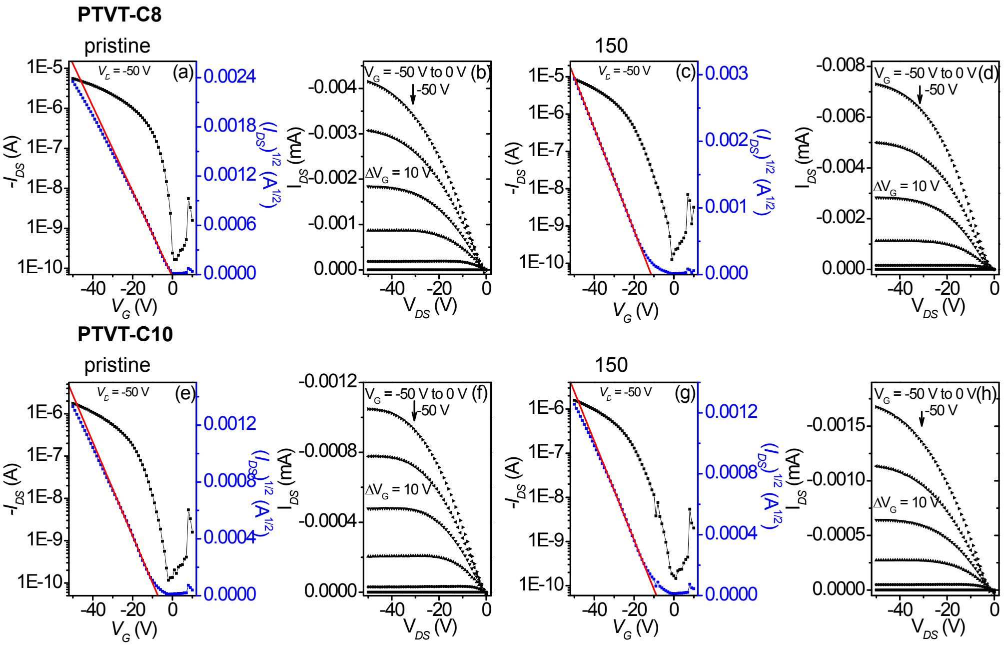


Figure S4. Transfer (a, c, e, g) and output (b, d, f, h) characteristics of OFETs based on **PTVT-C8** (a, b, c, d), **PTVT-C10** (e, f, g, h). The active layer was spin-coated on substrates at 60 °C. Left: without thermal annealing; right: with thermal annealing.

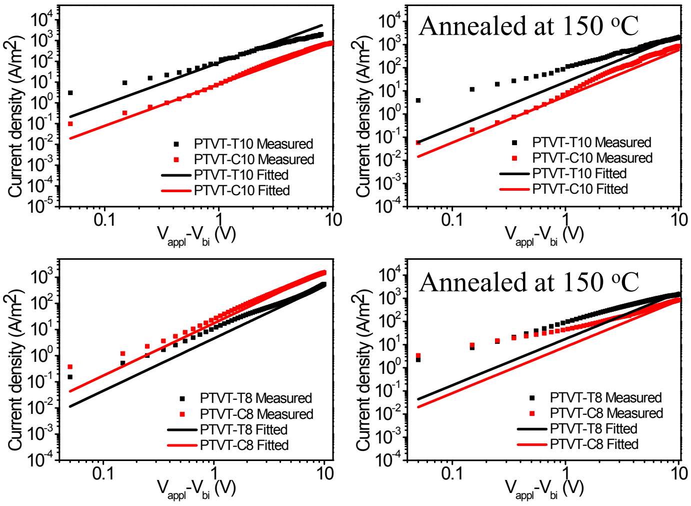


Figure S5. *J-V* characteristics of hole-only devices of the polymers. Lines represent the fitting results using a model of single-carrier space-charge-limited current with field-dependent mobility. The active layer was spin-coated on substrates at the same conditions with OFET processing.

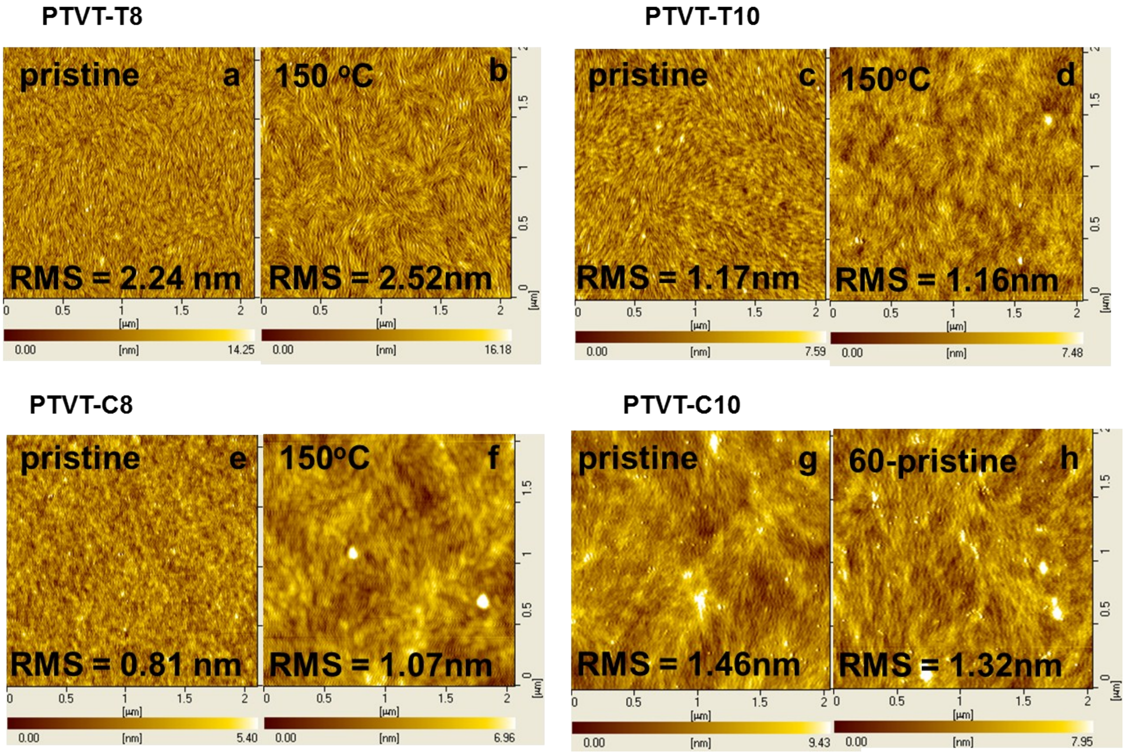


Figure S6. Film AFM height images of **PTVT-T8** (a, b), **PTVT-T10** (c, d), **PTVT-C8** (e, f) and **PTVT-C8** (g, h,). The active layer was spin-coated on substrates at 60 °C and thermal annealing was done at 150 °C for 15 min.

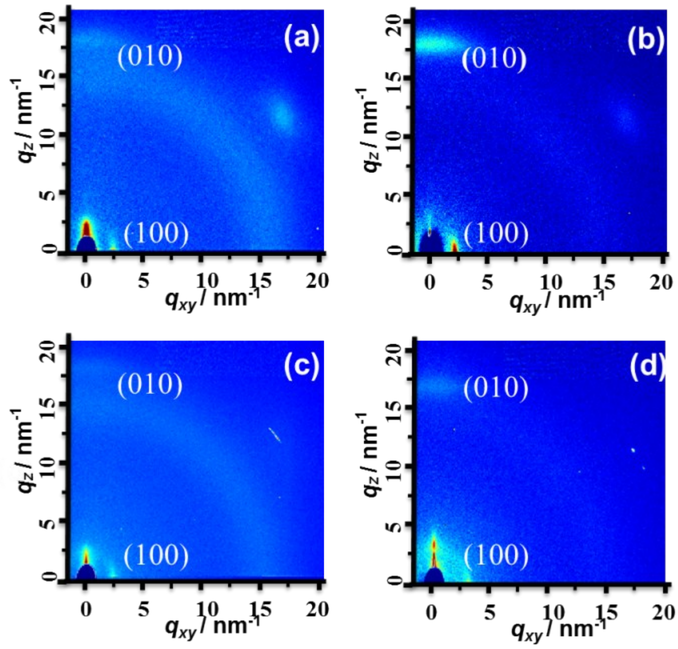


Figure S7. Two-dimensional (2D) GIWAXS patterns of the pristine films of **PTVT-T8** (a), **PTVT-T10** (b), **PTVT-C8** (c) and **PTVT-C10** (d). The films were prepared by spin-casting on ODMS modified Si/SiO_2 substrates at 60 °C.

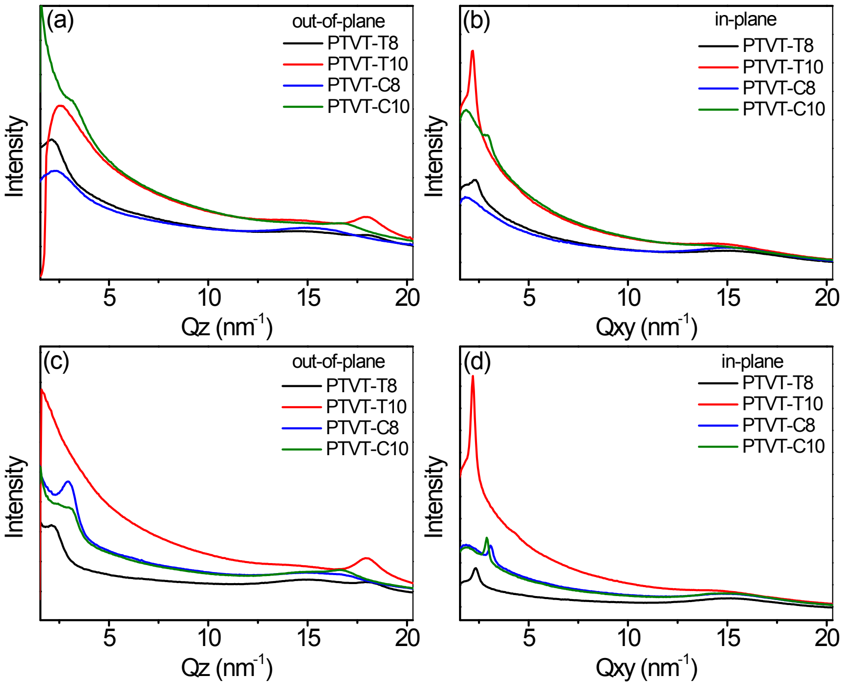


Figure S8. Out-of-plane (a, c) and in-plane (b, d) profiles of GIWAXS patterns of the pristine (a, b) and annealed (c, d) polymer films. The films were prepared by spin-casting on ODMS modified Si/SiO_2 substrate at 60 °C.

Table S2. Photovoltaic Parameters of PSC Devices Based on **PTVT-T8** with *o*-xylene as Solvent, and DPE and HPN as Additives.

PTVT-T8:PC$_{71}$BM (wt/wt%)	DPE (v/v %)	HPN (w/w %)	V$_{OC}$ (V)	J_{SC} (mA cm^{-2})	J_{SC} (mA cm^{-2})^{a}	FF	PCE^{b} (%)
1：1.5	0	0	0.76	3.25	3.30	0.55	1.36(1.30)
1：1.5	1	0	0.74	5.20	5.31	0.60	2.31(2.24)
1：1.5	3	0	0.72	12.26	12.53	0.51	4.50(4.46)
1：1.5	5	0	0.71	12.60	13.07	0.48	4.29(3.93)
1：1	3	0	0.73	12.88	13.28	0.58	5.45(5.19)
1：1.5	3	0	0.72	12.86	13.18	0.61	5.64(5.54)
1：2	3	0	0.72	12.03	12.35	0.60	5.19(5.04)
1：2.5	3	0	0.71	10.67	10.81	0.65	4.92(4.60)
1：3	3	0	0.70	10.23	10.01	0.63	4.49(4.29)
1：1.5	3	4	0.73	13.67	13.84	0.68	6.79(6.31)
1：1.5	3	8	0.73	13.80	13.97	0.65	6.55(6.13)
1：1.5	3	12	0.72	13.61	13.84	0.66	6.47(5.99)

[a]The values were calculated from EQE. [b]The values in parentheses are average from 8 devices.

Table S3. Photovoltaic Parameters of PSC Devices Based on **PTVT-T8** with *o*-DCB and CB as Solvents.

PTVT-T8:PC$_{71}$BM (wt/wt%)	solvent	DPE (v/v%)	V$_{OC}$ (V)	J_{SC} (mA cm^{-2})	J_{SC} (mA cm^{-2})^{a}	FF	PCE^{b} [%]
1:1.5	*o*-DCB	0	0.73	10.04	10.05	0.54	3.99(3.42)
		1	0.73	11.42	12.06	0.51	4.22(4.17)
		3	0.72	10.99	11.59	0.50	3.93(3.83)
		5	0.74	11.23	10.72	0.38	3.05(2.65)
	CB	0	0.71	7.28	6.93	0.56	2.88(2.61)
		1	0.70	11.34	11.79	0.56	4.55(4.37)
		3	0.72	13.31	14.13	0.53	5.09(4.84)
		5	0.72	12.80	14.07	0.57	5.29(5.03)

[a]The values were calculated from EQE; [b]The values in parentheses are average from 4 devices.

Table S4. Photovoltaic Parameters of PSC Devices Based on **PTVT-T8** with *o*-xylene as Solvent and Methylnaphthalene as Additive.

PTVT-T8 /PC$_{71}$BM (wt/wt%)	MN (v/v %)	V_{OC} (V)	J_{SC} (mA cm^{-2})	J_{SC} (mA cm^{-2})^{a}	FF	PCE^{b} (%)
1：1.5	0	0.76	3.25	3.30	0.55	1.36(1.30)
1：1.5	1	0.75	6.19	6.29	0.58	2.69(2.53)
1：1.5	3	0.74	10.20	10.37	0.53	4.00(3.83)
1：1.5	5	0.74	11.16	11.34	0.54	4.46(4.32)
1：1.5	7	0.75	11.58	11.77	0.50	4.34(4.27)

[a]The values were calculated from EQE; [b]The values in parentheses are average from 4 devices.

Table S5. Photovoltaic Parameters of PSC Devices Based on **PTVT-T8** with Thermal Annealing at Different Temperatures for 10 min.

PTVT-T8:PC$_{71}$BM (wt/wt%)	Annealing temp.(^{o}C)	DPE (v/v%)	HPN (wt%)	V_{OC} (V)	J_{SC} (mA cm^{-2})	J_{SC} (mA cm^{-2})^{a}	FF	PCE^{b} [%]
1:1.5	NO	3	4	0.72	13.47	13.51	0.67	6.50(6.46)
	100	3	4	0.76	11.79	12.27	0.63	5.64(5.53)
	125	3	4	0.76	12.03	12.49	0.63	5.76(5.71)
	150	3	4	0.76	11.53	11.88	0.62	5.43(5.23)

Table S6. Photovoltaic Parameters of PSC Devices Based on **PTVT-C8** with *o*-xylene as Solvent.

PTVT-C8 :$PC_{71}BM$ (wt/wt%)	DPE (v/v %)	HPN (w/w %)	V_{OC} (V)	J_{SC} (mA cm^{-2})	J_{SC} (mA cm^{-2})[a]	FF	PCE (%)[b]
1：1.5	0	0	0.76	0.84	0.85	0.57	0.36(0.35)
1：1.5	1	0	0.76	3.20	3.11	0.56	1.36(1.31)
1：1.5	3	0	0.75	6.75	6.53	0.53	2.68(2.59)
1：1.5	5	0	0.73	9.16	8.96	0.51	3.41(3.18)
1：1.5	7	0	0.73	9.11	8.91	0.43	2.89(2.86)
1：1	5	0	0.75	8.72	9.01	0.52	3.40(3.28)
1：1.5	5	0	0.74	8.91	9.23	0.53	3.49(3.32)
1：2	5	0	0.74	9.26	9.33	0.52	3.60(3.43)
1：2.5	5	0	0.74	9.18	9.30	0.58	3.94(3.77)
1：3	5	0	0.74	8.64	8.93	0.58	3.70(3.60)
1：2.5	5	2	0.72	6.60	6.63	0.56	2.66(2.60)
1：2.5	5	4	0.72	7.28	7.29	0.58	3.04(2.96)
1：2.5	5	8	0.72	6.29	6.19	0.57	2.58(2.54)
1：2.5	5	12	0.73	5.85	5.87	0.54	2.31(2.03)

[a)]The values were calculated from EQE; [b)]The values in parentheses are average from 8 devices

Table S7. Photovoltaic Parameters of PSC Devices Based on **PTVT-T10** with *o*-Xylene as Solvent.

PTVT-T10 :$PC_{71}BM$ (wt/wt%)	DPE (v/v %)	HPN (w/w %)	V_{OC} (V)	J_{SC} (mA cm^{-2})	J_{SC} (mA cm^{-2})[a]	FF	PCE (%)[b]
1：1.5	0	0	0.80	1.63	1.63	0.62	0.81(0.80)
1：1.5	1	0	0.78	8.45	8.76	0.65	4.30(4.16)
1：1.5	3	0	0.77	11.20	11.34	0.58	5.00(4.90)
1：1.5	5	0	0.76	10.95	11.18	0.46	3.82(3.80)
1：1	3	0	0.76	8.92	9.41	0.58	3.92(3.59)
1：1.5	3	0	0.76	11.17	11.21	0.57	4.83(4.55)
1：2	3	0	0.74	9.42	9.55	0.59	4.11(4.04)
1：2.5	3	0	0.75	9.34	9.34	0.61	4.30(4.21)
1：3	3	0	0.76	7.41	7.18	0.60	3.36(3.00)
1：1.5	3	4	0.75	10.04	10.23	0.70	5.27(5.11)
1：1.5	3	8	0.74	11.06	11.17	0.69	5.65(5.35)
1：1.5	3	12	0.74	10.89	11.10	0.70	5.64(5.22)

[a)]The values were calculated from EQE; [b)]The values in parentheses are average from 8 devices.

Table S8. Photovoltaic Parameters of PSC Devices Based on **PTVT-C10** with *o*-Xylene as Solvent.

PTVT-C10 :$PC_{71}BM$ (wt/wt%)	DPE (v/v %)	HPN (w/w %)	V_{OC} (V)	J_{SC} (mA cm^{-2})	J_{SC} (mA cm^{-2})^{a}	FF	PCE (%)^{b}
1：1.5	0	0	0.75	0.55	0.63	0.23	0.093(0.061)
1：1.5	1	0	0.75	1.66	1.61	0.57	0.71(0.67)
1：1.5	3	0	0.73	2.87	2.79	0.47	0.99(0.98)
1：1.5	5	0	0.75	5.53	4.33	0.45	1.53(1.41)
1：1.5	7	0	0.73	4.28	4.16	0.45	1.41(1.38)
1：1.5	5	0	0.75	4.42	4.58	0.47	1.56(1.39)
1：2	5	0	0.75	3.83	3.72	0.51	1.47(1.38)
1：2.5	5	0	0.74	2.88	2.91	0.58	1.24(1.22)
1：3	5	0	0.76	2.76	2.66	0.56	1.18(1.14)
1：1.5	5	4	0.74	3.59	3.54	0.48	1.27(1.10)
1：1.5	5	8	0.74	4.30	4.08	0.50	1.59(1.46)
1：1.5	5	12	0.75	4.15	4.00	0.55	1.70(1.57)

$^{a)}$The values were calculated from EQE; $^{b)}$The values in parentheses are average from 8 devices.

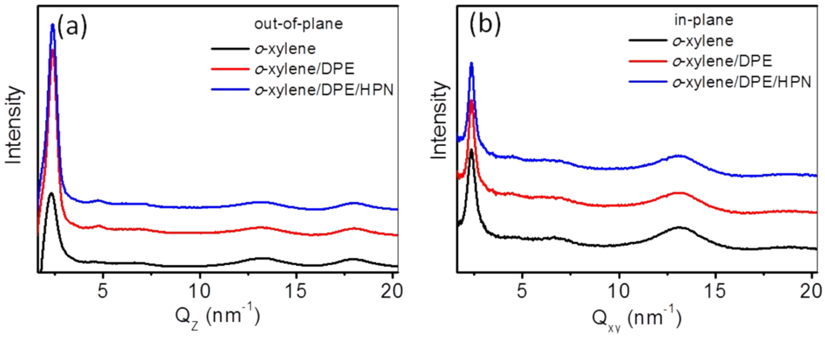


Figure S9. Out-of-plane (a) and in-plane (b) profiles of GIWAXS patterns of **PTVT-T8**:$PC_{71}BM$ blend films with different additives.

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