Supporting Information

Dithienylbenzodiimide: a New Electron-Deficient Unit for n-Type Polymer Semiconductors

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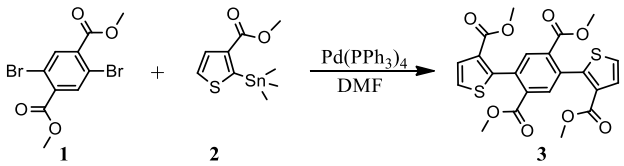
1. Experimental Section

1.1. Materials and Synthesis

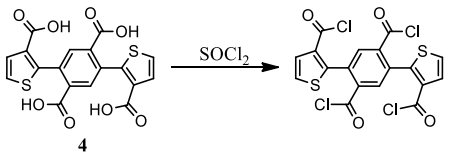
All the chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. Anhydrous THF, ether, and toluene were distilled from Na/benzophenone under argon, whereas anhydrous dichloromethane was distilled from calcium hydride. Unless otherwise stated, all reactions were carried out under inert atmosphere using standard Schlenk line techniques. The synthetic route of the monomer and polymers were displayed in Scheme 1. The detailed synthetic procedures of compounds were demonstrated as follows:



Synthesis of dimethyl 2,5-bis(3-(methoxycarbonyl)thiophen-2-yl)terephthalate **(3):** Compound **1** (351 g, 1 mmol), **2** (915 mg, 3 mmol)**,** $Pd(PPh_3)_4$ (100 mg), and DMF (15 mL) were added to an air-free reaction tube under nitrogen atmosphere. The reaction tube was heated to 150 °C for 4 h under microwave irradiation. After cooling to room temperature, the DMF was evaporated under a reduced pressure. 100 mL methanol was added to the round bottom flask and then filtrated. The solid was washed with water (30 mL) and methanol (30 mL) to give compound **3** as gray solid (210 mg, yield 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.03 (s, 2H), 7.56 (d, J = 5.3 Hz, 2H), 7.37 (d, J = 5.3 Hz, 2H), 3.73 (s, 6H), 3.70 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 165.92, 163.19, 147.94, 134.72, 133.40, 133.31, 129.44, 128.99, 124.70, 52.35, 51.59.

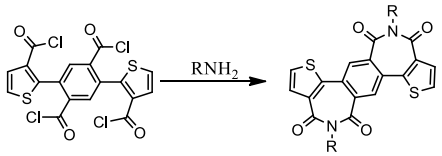
3 4

***Synthesis of 2,5-bis(3-carboxythiophen-2-yl)terephthalic acid* (4):** Compound **3** (474 mg, 1 mmol), KOH (118 mg, 3 mmol)**,** H_2O (15 mL) and THF (15 mL) were added to a round bottom flask. The reaction mixture was heated to 70 °C and stirred overnight. After cooling to room temperature, the THF was evaporated under a reduced pressure. The aqueous solution was cooled to 0 °C, and then 2 mL hydrochloric acid was added. The product **4** was obtained by filtration and then washed by water (30 mL) as white solid (410 mg, yield 98%). The product was pure enough without any further purification for the next step reaction.^{1}H NMR (500 MHz, DMSO) δ (ppm): 12.61 (s, 4H), 7.80 (s, 2H), 7.65 (d, *J* = 5.3 Hz, 2H), 7.44 (d, *J* = 5.3 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) δ (ppm): 167.04, 163.96, 147.63, 134.64, 134.35, 133.09, 130.83, 129.65, 125.98.



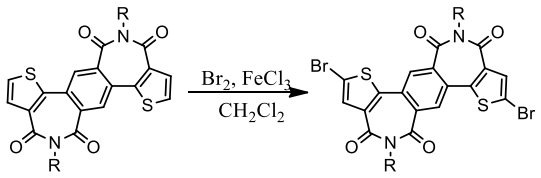
4 5

***Synthesis of 2,5-bis(3-(chlorocarbonyl)thiophen-2-yl)terephthaloyl dichloride (5)*:** Compound **4** (418 mg, 1 mmol) and $SOCl_2$ (15 mL) were added to a round bottom flask in nitrogen atmosphere and then heated to 80 °C overnight. The excess $SOCl_2$ was removed by evaporation. The crude product of **5** was directly used in the next step without any further purification.



5 6

The general synthesis of TBDI (6): To a round bottom flask with dry compound **5** was added 2 eq RNH_2 in nitrogen atmosphere. The reaction mixture was carefully sealed and then heated to 150 °C for 4 h. After cooling to room temperature, the dark residue was dissolved in $CHCl_3$ (2 mL) and then purified by silica gel column chromatography with $CHCl_3$/petroleum ether (1:4) as eluent. The compound **6** was obtained as pale yellow solid. **6a** (yield: 40%) ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.35 (s, 2H), 7.63 (d, *J* = 5.2 Hz, 2H), 7.41 (d, *J* = 5.2 Hz, 2H), 4.19 (d, *J* = 7.2 Hz, 4H), 1.95 (s, 2H), 1.29-1.24 (m, 80H), 0.92-0.84 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.24 , 161.69, 142.29, 135.24, 135.03, 134.71, 132.16, 128.68, 114.26, 51.12, 36.87, 31.95, 31.53, 30.17, 29.81, 29.49, 29.39, 26.26, 22.72, 14.16. HRMS (MALDI+) Calcd for: $C_{66}H_{104}N_2O_4S_2$ (M^+): 1053.7510, found: 1053.7528.

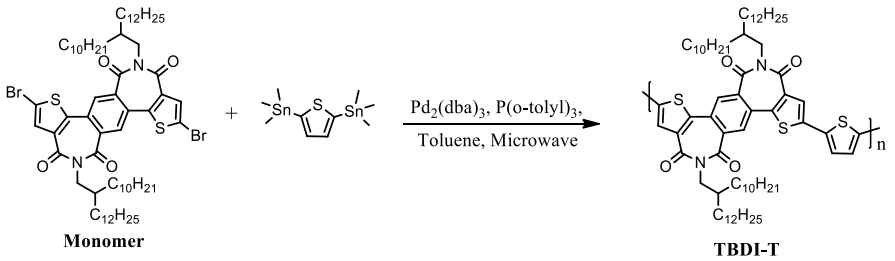


6 **Monomer**

Synthesis of monomers: To a solution of compound **6** (1 eq) in CH_2Cl_2 was added a catalytic amount of $FeCl_3$ and Br_2 (2.2 eq). And then, the reaction mixture was heated to 55 °C for 24 h. After cooling to room temperature, the reaction mixture was poured to water and extracted by CH_2Cl_2. The combined organic layer was dried by anhydrous Na_2SO_4 and then filtrated. The organic solution was evaporated under a reduced pressure. The yellow residue was dissolved in $CHCl_3$ (2 mL) and then

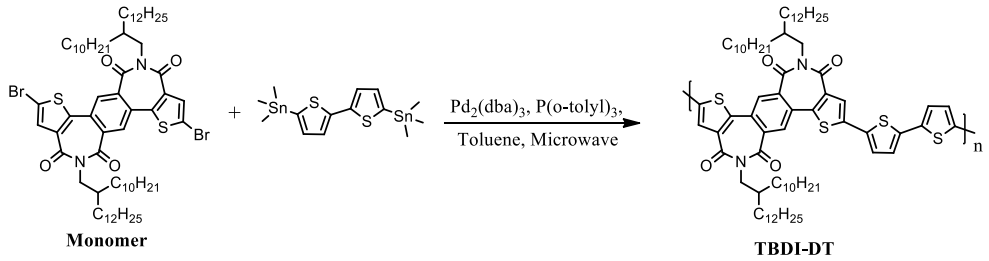
purified by silica gel column chromatography with $CHCl_3$/petroleum ether (1:4) as eluent. The compound **6** was obtained as pale yellow solid in high yield over 90%. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.21 (s, 2H), 7.59 (s, 2H), 4.16 (d, J = 7.3 Hz, 4H), 1.91 (s, 2H), 1.37 - 1.26 (m, 80H), 0.91 - 0.88 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 168.24, 161.69, 142.29, 135.24, 135.03, 134.71, 132.16, 128.68, 114.26, 51.12, 36.87, 31.95, 31.94, 31.53, 30.17, 29.73, 29.68, 29.67, 29.40, 29.39, 26.26, 22.72, 14.16. HRMS ($MALDI^+$) Calcd for: $C_{66}H_{103}O_4N_2Br_2S_2$ (M^+): 1211.5700, found: 1211.5714.

The general synthesis of TBDI-based polymers: Two monomers (0.1 mmol each), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, 2mg), and tris(*o*-tolyl)phosphine (P(*o*-tolyl)$_3$, 5 mg) were added to a glass tube. After the tube was subjected to 3 pump/purge cycles with argon, anhydrous toluene (3 mL) was added via syringe. The tube was sealed under argon flow and then stirred at 140 ºC for 3 h under microwave irradiation. Then, 0.1 mL of 2-(tributylstanny)thiophene was added and the mixture was stirred under microwave irradiation at 140 ºC for 0.5 h. Finally, 0.2 mL of 2-bromothiophene was added and the reaction mixture was stirred at 140 ºC for another 0.5 h. After cooling to room temperature, the reaction mixture was slowly dripped into 100 mL of methanol (containing 2 mL 12 N hydrochloric acid) under vigorous stirring. The solid was collected and Soxhlet-extracted with methanol, acetone, hexane, dichloromethane and chloroform. The chloroform part was concentrated and dripped into methanol. The product polymer was collected and dried.



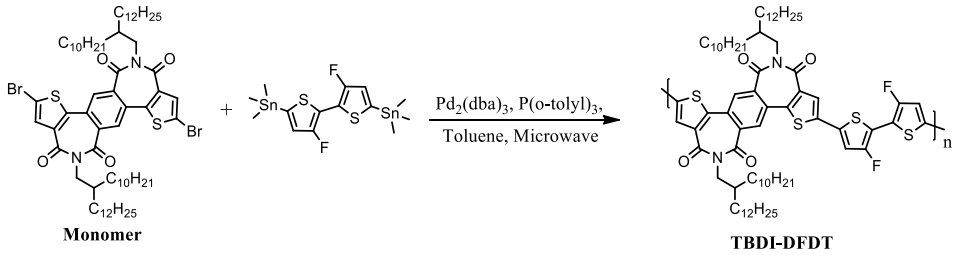
Monomer TBDI-T

TBDI-T: The polymer was obtained as a red solid (104 mg, yield: 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (br), 7.63 (br), 4.62 (br), 1.99 (br), 1.36 (br), 0.96(br). Anal. Calcd for $C_{70}H_{104}N_2O_4S_3$ (%): C, 74.15; H, 9.25; N, 2.47; O, 5.64; S, 8.48. Found (%): C, 73.96; H, 9.33; N, 2.43; S, 8.56.



Monomer TBDI-DT

TBDI-DT: The polymer was obtained as a purple solid (111 mg, yield: 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (br), 7.54 (br), 4.43 (br), 1.64-1.38 (br,), 0.96(br). Anal. Calcd for $C_{74}H_{106}N_2O_4S_4$ (%): C, 73.10; H, 8.79; N, 2.30; O, 5.26; S, 10.55. Found (%): C, 71.2; H, 8.72; N, 2.18; S, 10.15.



Monomer TBDI-DFDT

TBDI-T: The polymer was obtained as a red solid (102 mg, yield: 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (br), 7.73 (br), 4.45 (br), 1.63-1.35 (br,), 0.94(br).. Anal. Calcd for $C_{74}H_{104}F_2N_2O_4S_4$ (%): C, 71.00; H, 8.37; F, 3.04; N, 2.24; O, 5.11; S, 10.25. Found (%): C, 70.65; H, 8.49; N, 2.19; S, 10.24.

2. Materials Characterization

^{1}H and ^{13}C spectra were recorded on a Bruker Ascend 400 MHz spectrometer. HR-MS measurements were performed on a Bruker APEX II FT-ICRMS spectrometer. Elemental analyses (EA) of monomer and polymers were performed on Vario EL Cube at Shenzhen University (Shenzhen, Guangdong). Polymer molecular weights were measured on Polymer Laboratories GPC-PL220 high temperature GPC/SEC system at 150 ºC vs polystyrene standards using trichlorobenzene as eluent. Differential scanning calorimetry (DSC) curves were recorded on a differential scanning calorimetry with heating rate of 10 ºC/min in nitrogen atmosphere. Thermogravimetric analysis (TGA) curves were recorded on a Mettler, STARe TA Instrument. UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Cyclic voltammetry (CV) measurements were carried out using a CHI760E voltammetric analyzer with 0.1 M tetra-*n*-butyl-ammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile as supporting electrolyte. A platinum disk, platinum wire and silver wire were employed as working electrode, counter electrode and reference electrode, respectively. Polymer films were drop-coated from chloroform solutions on a Pt working electrode. The scan rate was 100 mV/s. And Fc/Fc^{+} was used as internal reference for all measurements. AFM measurements of pure polymer films were performed by using a Dimension Icon Scanning Probe Microscope (Asylum Research, MFP-3D-Stand Alone) in tapping mode.

3. Device Fabrication and Characterization

Bottom-gate/top-contact (BGTC) thin film transistor was fabricated in order to investigate the mobility of TBDI-based polymers. P-doped silicons with 200 nm SiO_2 substrate were sonicated in acetone and isopropanol followed by SC-1 cleaning, which is made up of 100 mL H_2O, 20 mL ammonium hydroxide, and 20 mL hydrogen peroxide at the temperature of 120 ^oC. 3 mM octadecyltrimethoxysilane (OTS) solution with trichloroethylene (TCE) solvent was spin-coated after UV-ozone and plasma treatment. Exposing the substrates in ammonium vapor for 15 h, and treating them in toluene, isopropanol, and deionized water subsequently, the contact angles on these substrates are 108°-110°. The polymer layer was spin coated from 3 mg/mL CF solution onto the substrate at 3000 rmp, which was subjected to thermal annealing at various temperatures of 250 ^oC, 220 ^oC, and 190 ^oC for 10 minutes, and then cooled to room temperature. The device without annealing was also fabricated. Finally, 40 nm Au was evaporated on the top of substrate as source-drain electrodes. The mobilities of thin-film transistors were extracted from saturated region based on the equation:

$$I_{SD} = \frac{WC_i}{2L}\mu(V_G - V_T)^2$$

W is the width of channel (1000μm); L is the length of channel (100μm); I_{DS} is the source−drain saturation current; C_i is the capacitance per unit area of the insulator; μ is the mobility; V_G the gate voltage; and V_{th} the threshold voltage.

4. DFT Calculation of Molecular Orbitals.

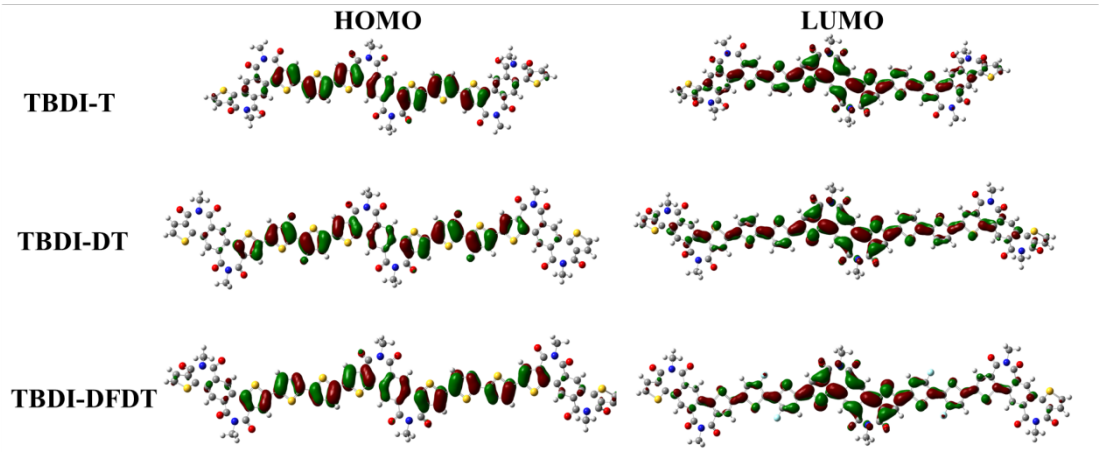


Figure S1. Calculated molecular orbitals of TBDI-based polymers.

5. Molecular Weight and TGA Data of TBDI-based Polymers.

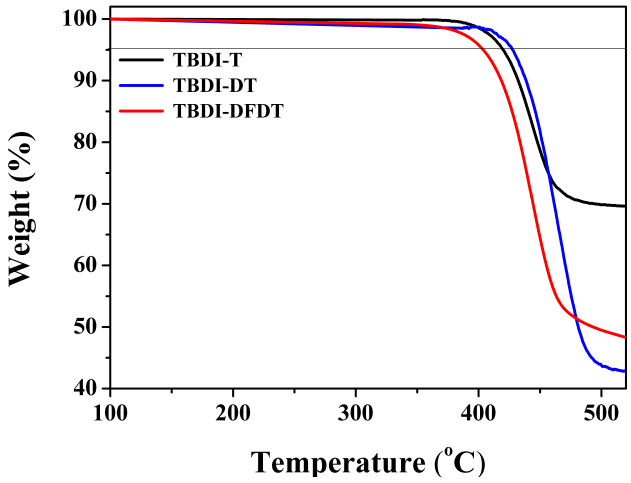


Figure S2. The TGA curves of TBDI-based polymers.

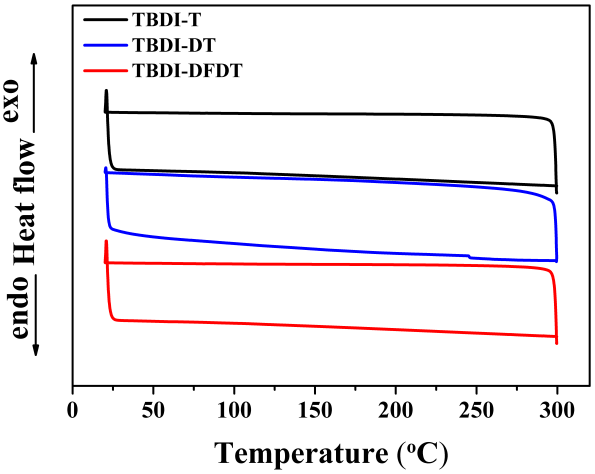


Figure S3. The DSC curves of TBDI-based polymers.

Table S1. The molecular weight and TGA data of TBDI-based polymers.

Polymers	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI	T_d (°C)
TBDI-T	41	90	2.19	420
TBDI-DT	69	207	3.0	426
TBDI-DFDT	75	336	4.48	402

6. Temperature Dependent UV Absorption of TBDI-Based Polymers.

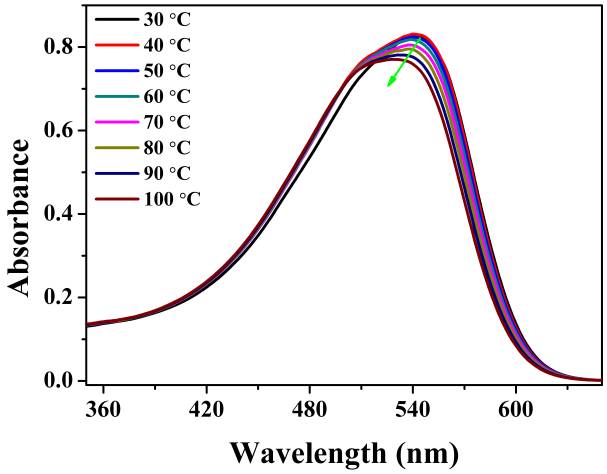


Figure S4. The UV absorption spectra of polymer TBDI-T in *o*-DCB solution (1 x 10^{-5} M) at various temperatures.

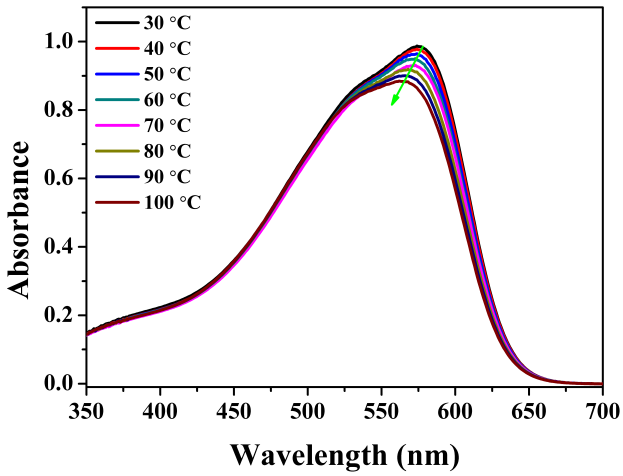


Figure S5. The UV absorption spectra of polymer TBDI-DT in *o*-DCB solution (1 x 10^{-5} M) at various temperatures.

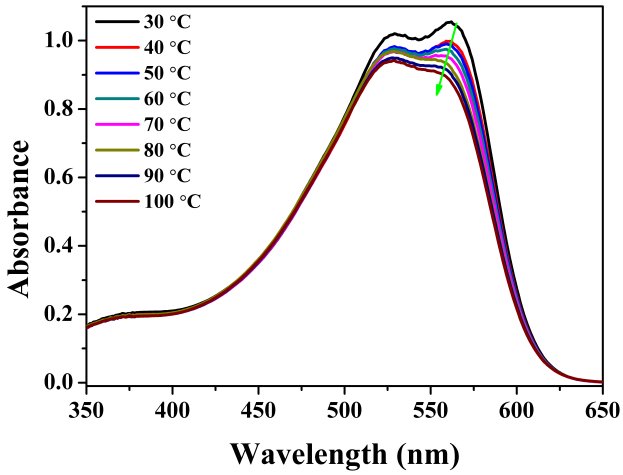


Figure S6. The UV absorption spectra of polymer TBDI-DFDT in *o*-DCB solution (1 x 10^{-5} M) at various temperatures.

7. Organic Thin-Film Transistor Performance Data of TBDI-based Polymer Semiconductors

Table S2. Summary of important transistor operating characteristics

Polymers	Annealing Temp (°C)	n-channel operation				p-channel operation			
		$\mu_{lin\ max}$ ($cm^2V^{-1}s^{-1}$)	$\mu_{sat\ max}$ ($cm^2V^{-1}s^{-1}$)	V_{Th} [b] (V)	I_{on}/I_{off}	$\mu_{lin\ max}$ ($cm^2V^{-1}s^{-1}$)	$\mu_{sat\ max}$ ($cm^2V^{-1}s^{-1}$)	V_{Th} [b] (V)	I_{on}/I_{of}
TBDI-T	25	0.0073	0.031	47	10^4				
	190	0.0057	0.021	32	10^3				
	220	0.021	0.051	48	10^4				
	250	0.040	0.110	36	10^4				
TBDI-DT	25	0.017	0.092	65	10^4	0.0040	0.0052	24	10^4
	190	0.052	0.153	55	10^3	0.0076	0.012	38	10^3
	220	0.098	0.155	63	10^3	0.015	0.034	43	10^4
	250	0.074	0.103	57	10^3	0.011	0.019	44	10^3
TBDI-DFDT	25	0.0216	0.096	57	10^5				
	25[a]	0.0188	0.0191	29	10^4				
	190	0.043	0.133	40	10^6				
	190[a]	0.107	0.125	18	10^5				
	220	0.064	0.324	48	10^6				
	220[a]	0.145	0.165	20	10^5				
	250	0.085	0.400	49	10^5				
	250[a]	0.187	0.337	22	10^7				

[a] Al was used as source/drain electrodes. [b] The average threshold voltage (V_T) are calculated from the saturation regimes.

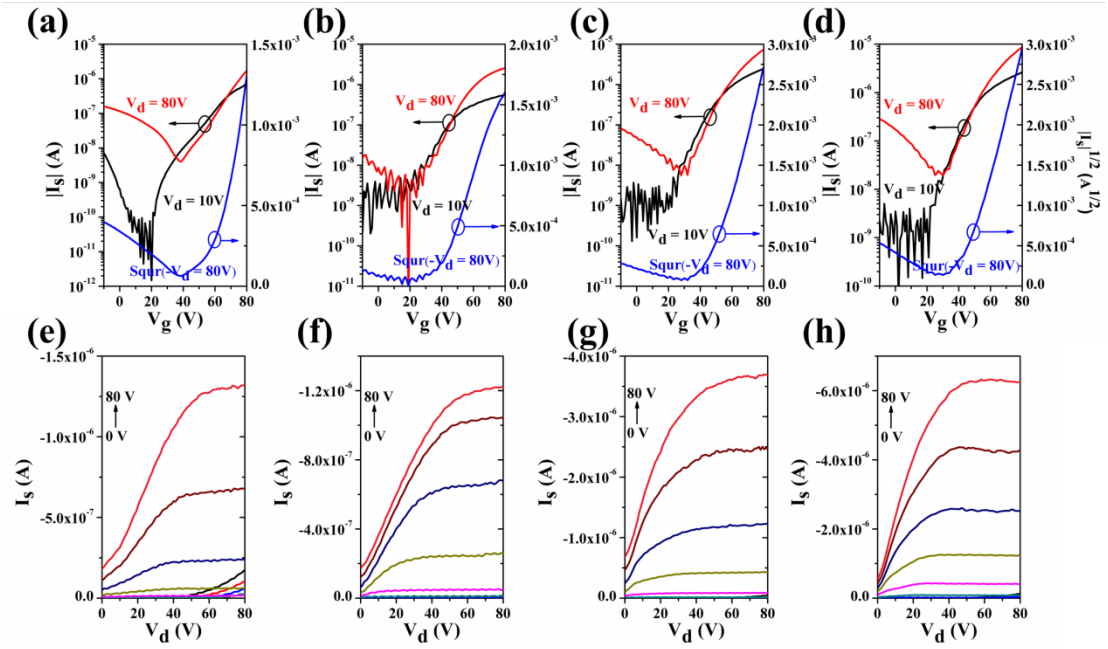


Figure S7. Typical n-channel transfer (top) and output (down) characteristics of TBDI-T based OTFTs annealed at various temperature, (a, e): 25 ^{o}C; (b, f): 190 ^{o}C; (c, g): 220 ^{o}C; (d, h): 250 ^{o}C.

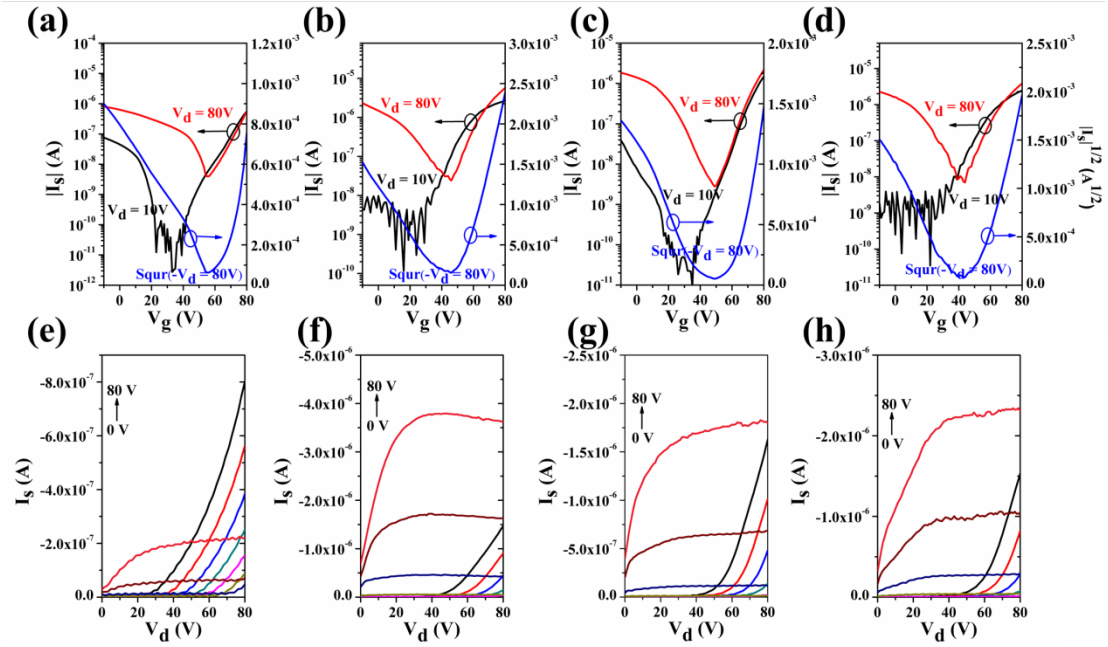


Figure S8. Typical n-channel transfer (top) and output (down) characteristics of TBDI-DT based OFET device annealed at various temperature, (a, e): 25 ^{o}C; (b, f): 190 ^{o}C; (c, g): 220 ^{o}C; (d, h): 250 ^{o}C.

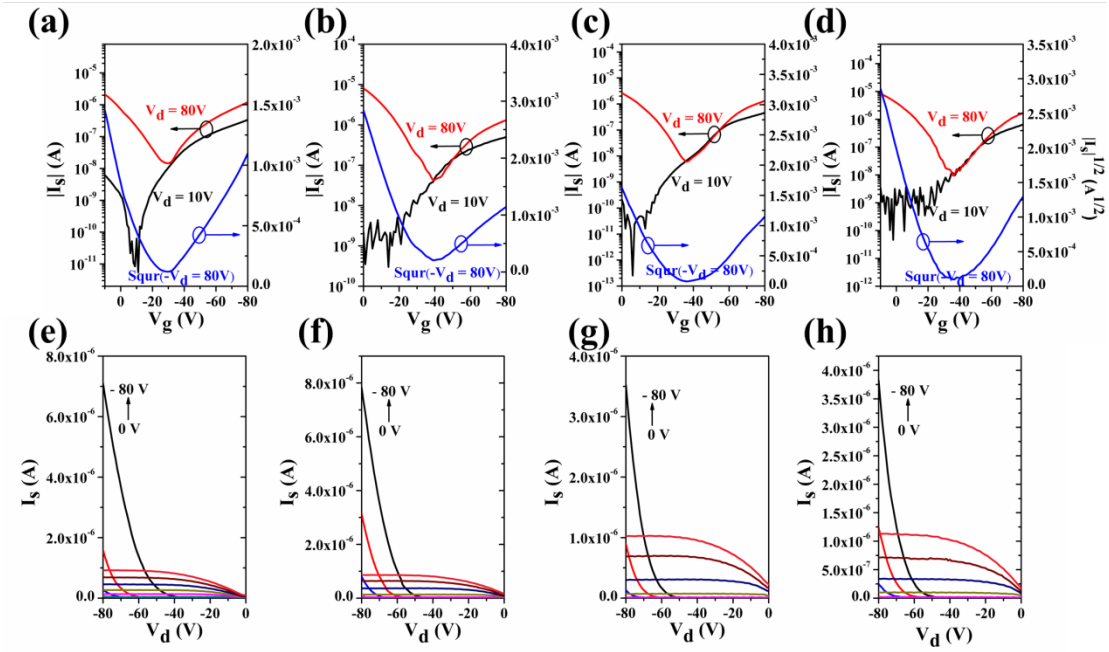


Figure S9. Typical p-channel transfer (top) and output (down) characteristics of TBDI-DT based OTFT device annealed at various temperature, (a, e): 25 ^{o}C; (b, f): 190 ^{o}C; (c, g): 220 ^{o}C; (d, h): 250 ^{o}C.

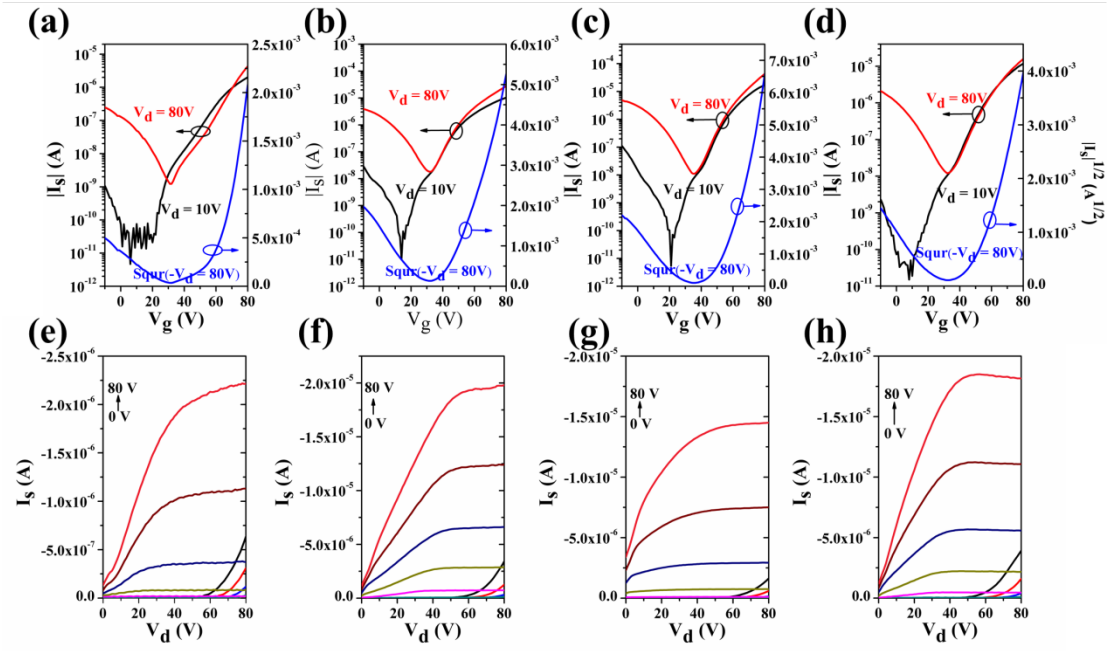


Figure S10. Typical n-channel transfer (top) and output (down) characteristics of TBDI-DFDT based OTFT device annealed at various temperature, (a, e): 25 ^{o}C; (b, f): 190 ^{o}C; (c, g): 220 ^{o}C; (d, h): 250 ^{o}C.

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8. AFM Image of As-Cast Polymer Films.

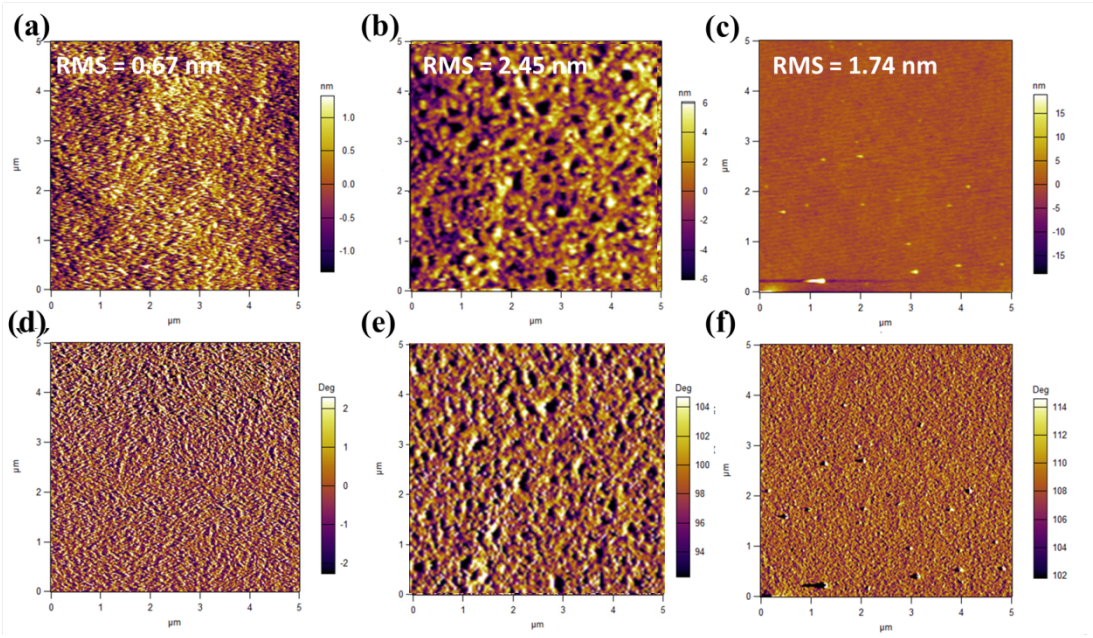

Figure S11. AFM height and corresponding phase images (5 × 5μm) of TBDI-T (a, d); TBDI-DT (b, e) and TBDI-DFDT (c, f) as-cats films.

9. GIWAXS images of As-Cast Polymer Films.

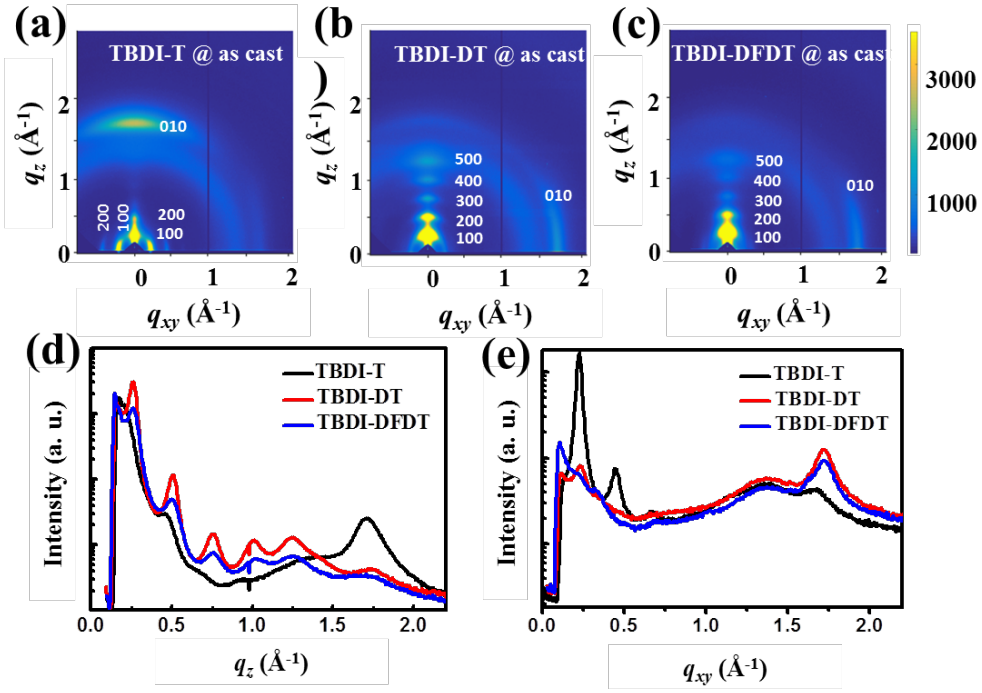

Figure S12. GIWAXS images of TBDI-T (a) TBDI-DT (b) TBDI-DFDT (c) and the corresponding linecuts of the TBDI-based polymer films in out-of-plane (d) in-plane (e). The films were casted on silicon substrate at room temperature.

Table S3. *d*-Spacings and crystalline correlation lengths (calculated via Scherrer analysis) for TBDI-based polymers as cast films.

Blend film	d-spacing (Å)		Correlation length (nm)	
	(100)	(010)	(100)	(010)
TBDI-T (face-on)	29.9	3.7	8.1	4.4
TBDI-T (edge-on)	27.7		19.4	
TBDI-DT (face-on)	24.1		15.4	
TBDI-DT (edge-on)		3.6		5.8
TBDI-DFDT (face-on)	24.3		8.4	
TBDI-DFDT (edge-on)		3.6		5.1

10. ^{1}H NMR, ^{13}C NMR, and HR-MS of Compounds.

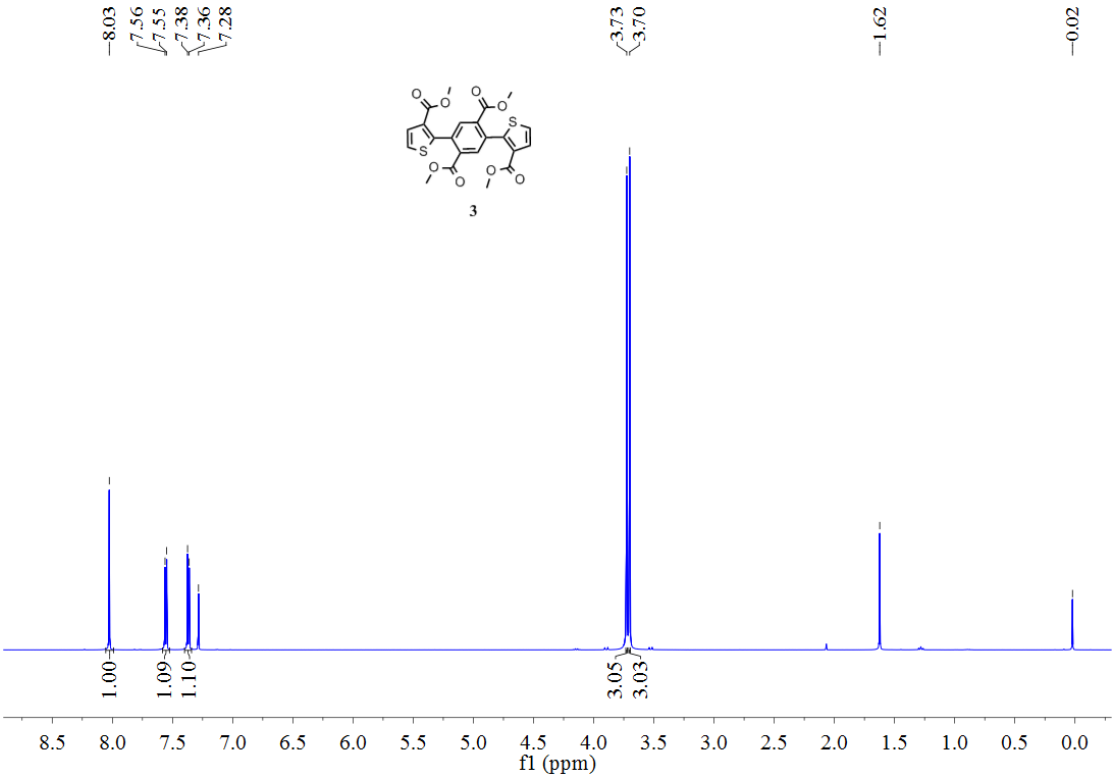

Figure S13. The ^{1}H NMR of compound **3**.

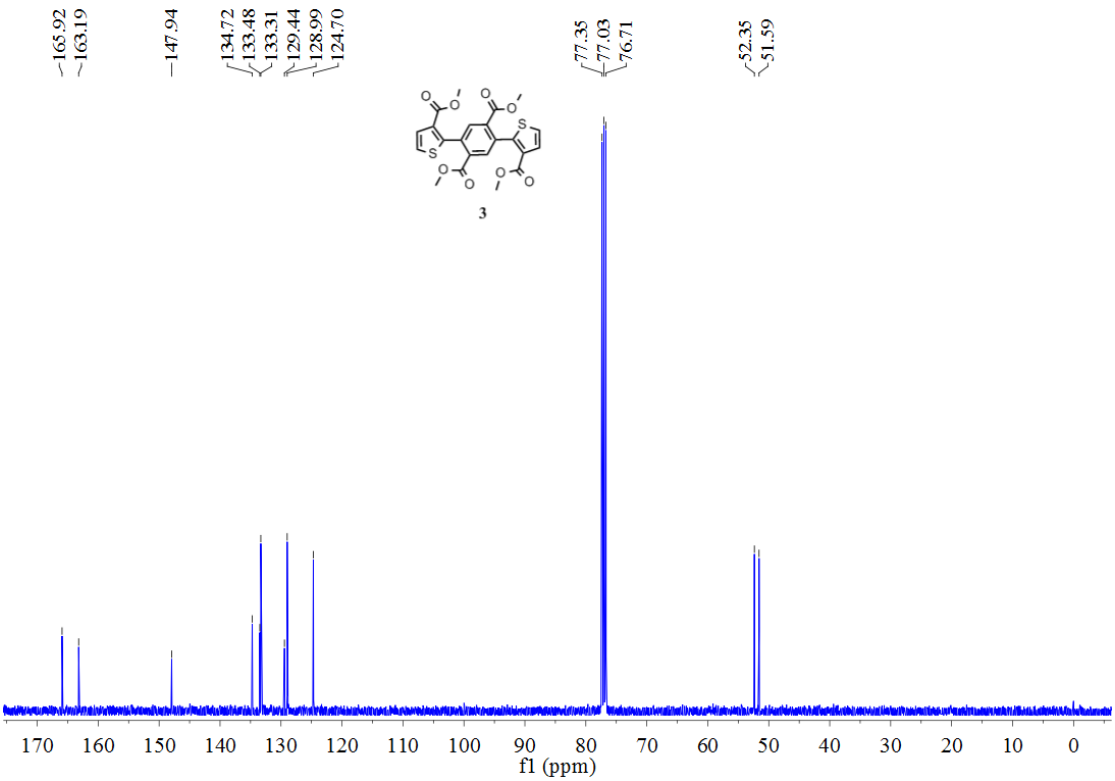

Figure S14. The ^{13}C NMR of compound **3**.

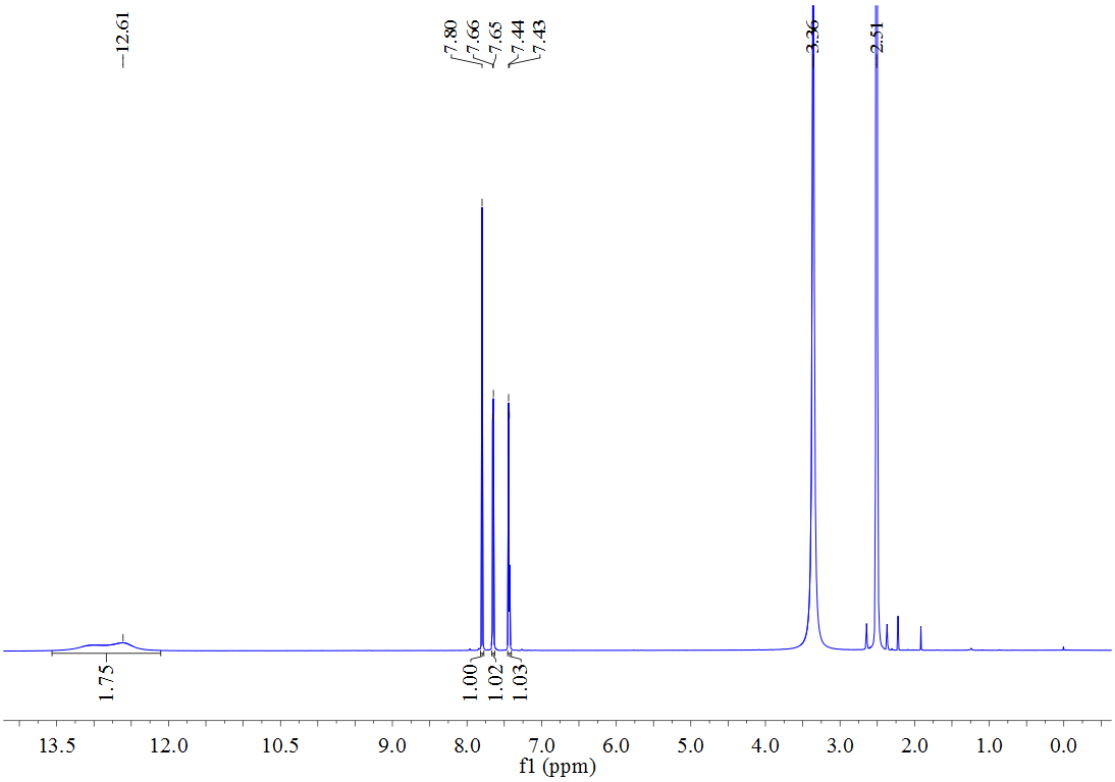

Figure S15. The ^{1}H NMR of compound **4**.

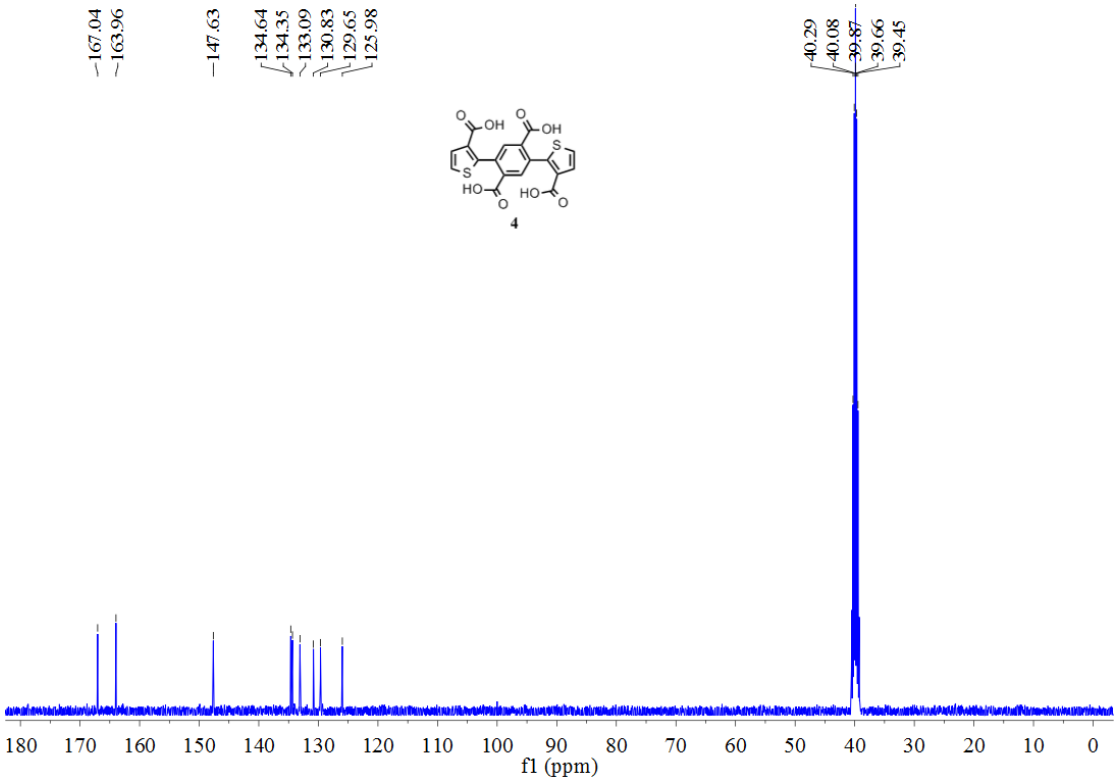

Figure S16. The ^{13}C NMR of compound **4**.

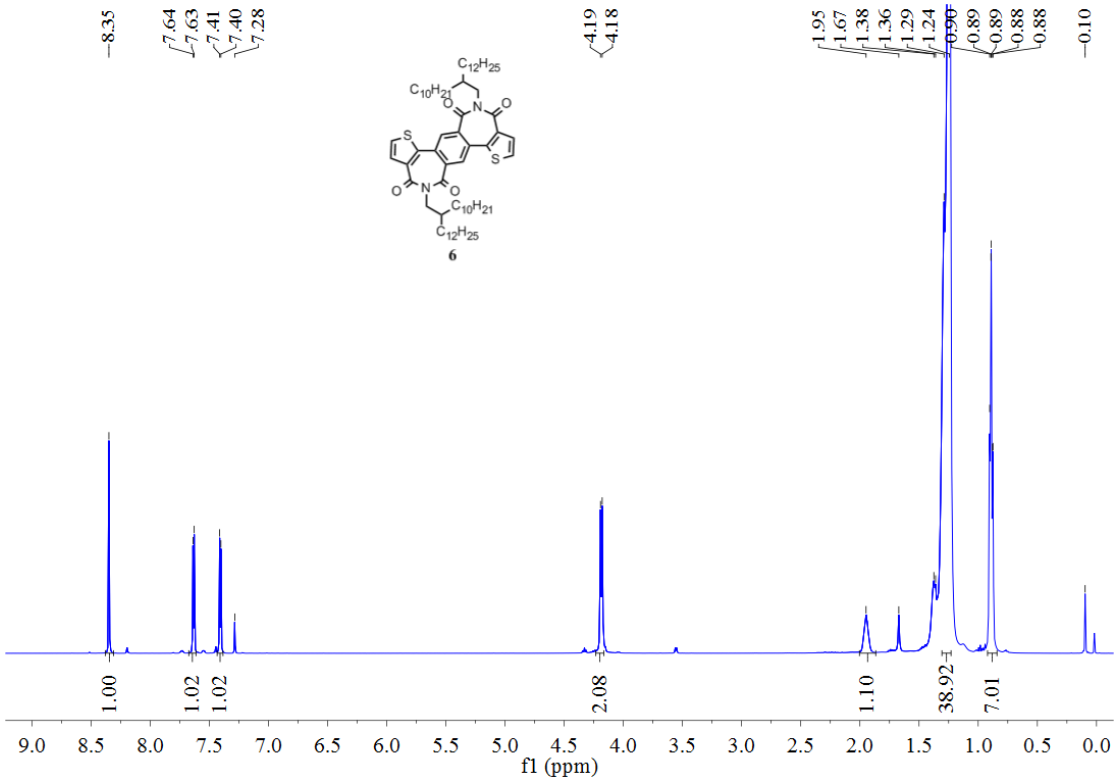

Figure S17. The ^{1}H NMR of compound **6**.

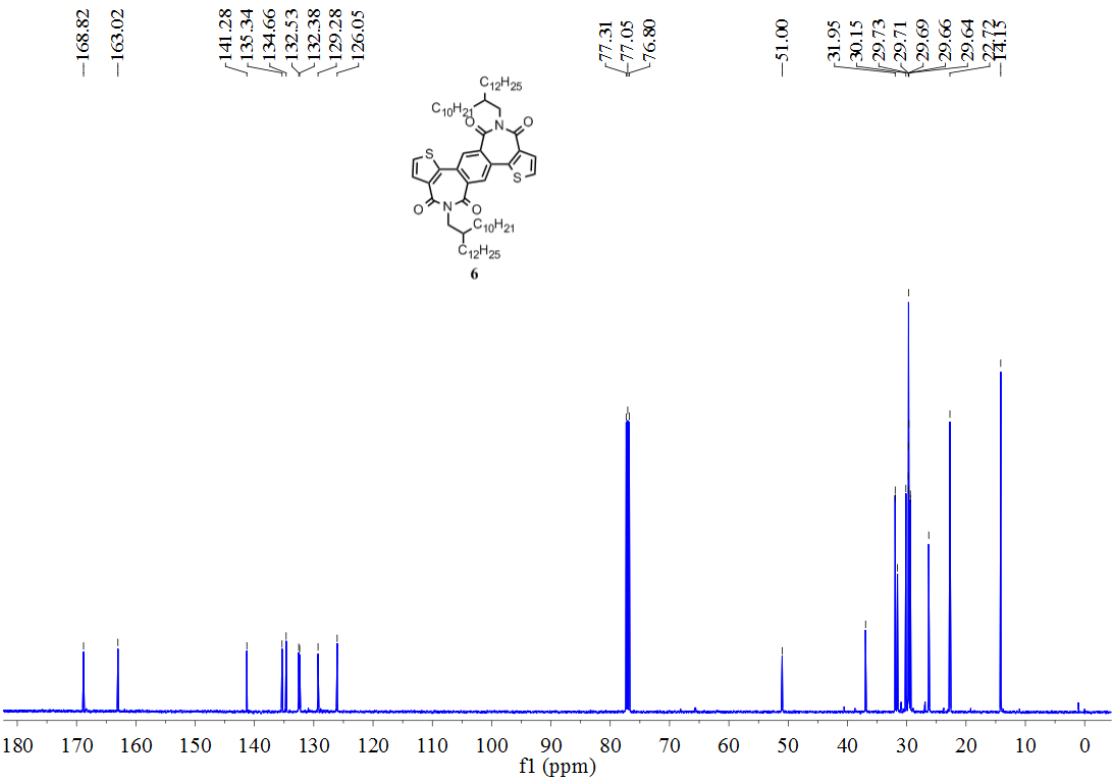

Figure S18. The ^{13}C NMR of compound **6**.

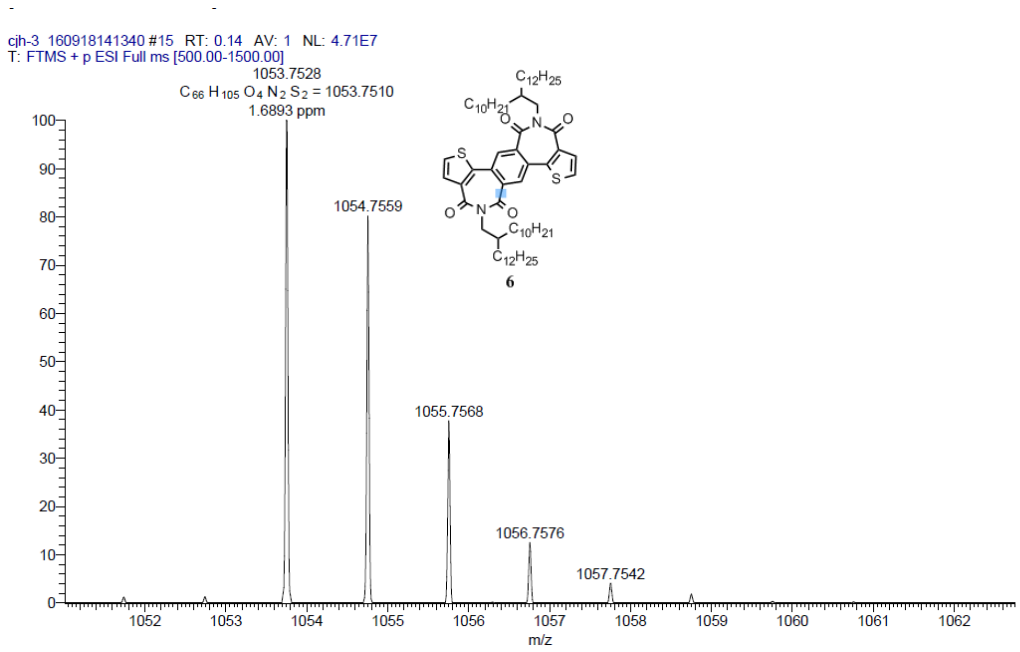

Figure S19. The HRMS of compound **6**.

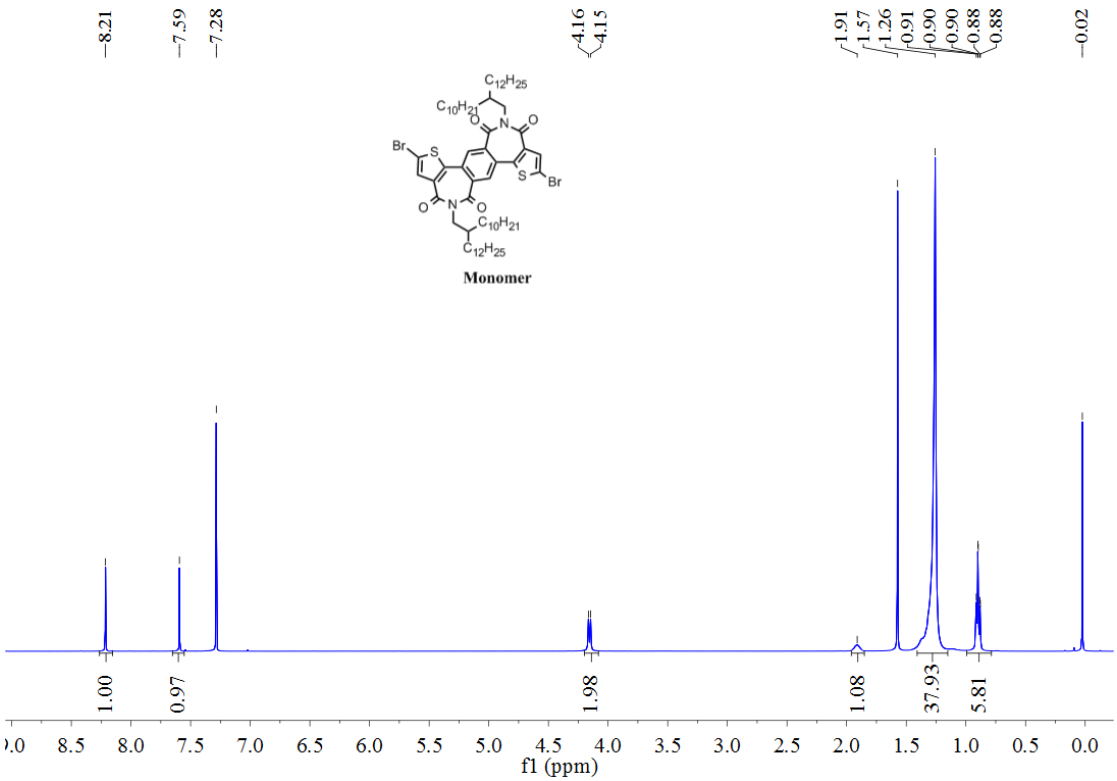

Figure S20. The ^{1}H NMR of compound **monomer.**

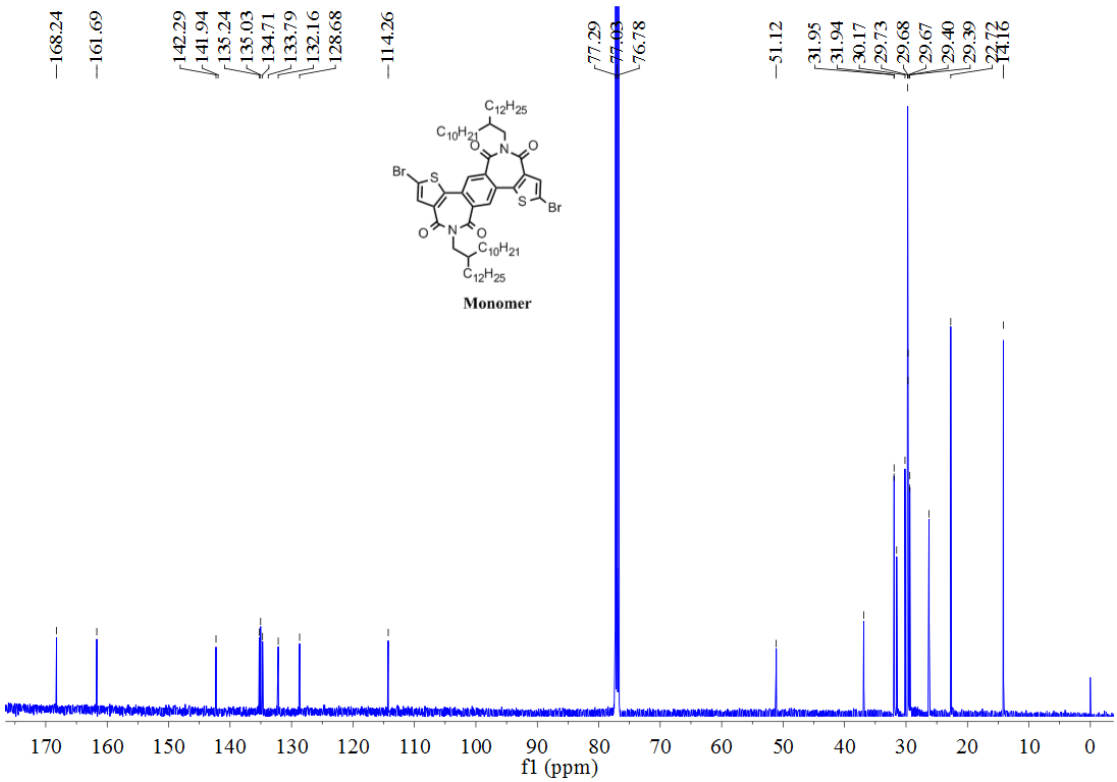

Figure S21. The ^{13}C NMR of compound **monomer.**

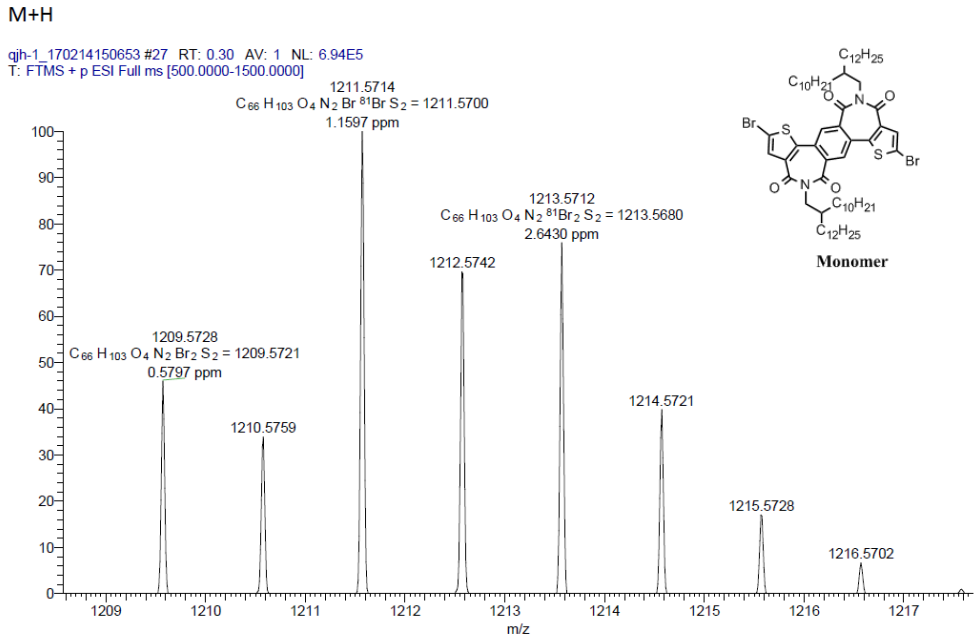

Figure S22. The HRMS of compound **monomer**.

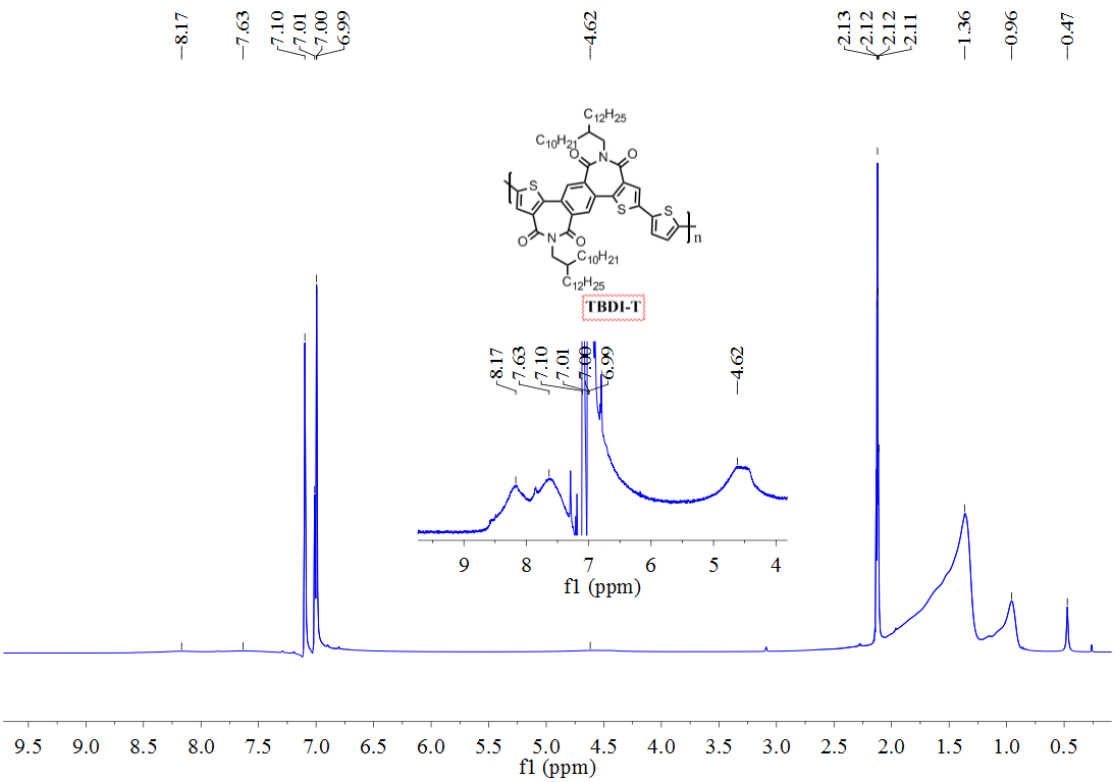

Figure S23. The ^{1}H NMR of polymer **TBDI-T**.

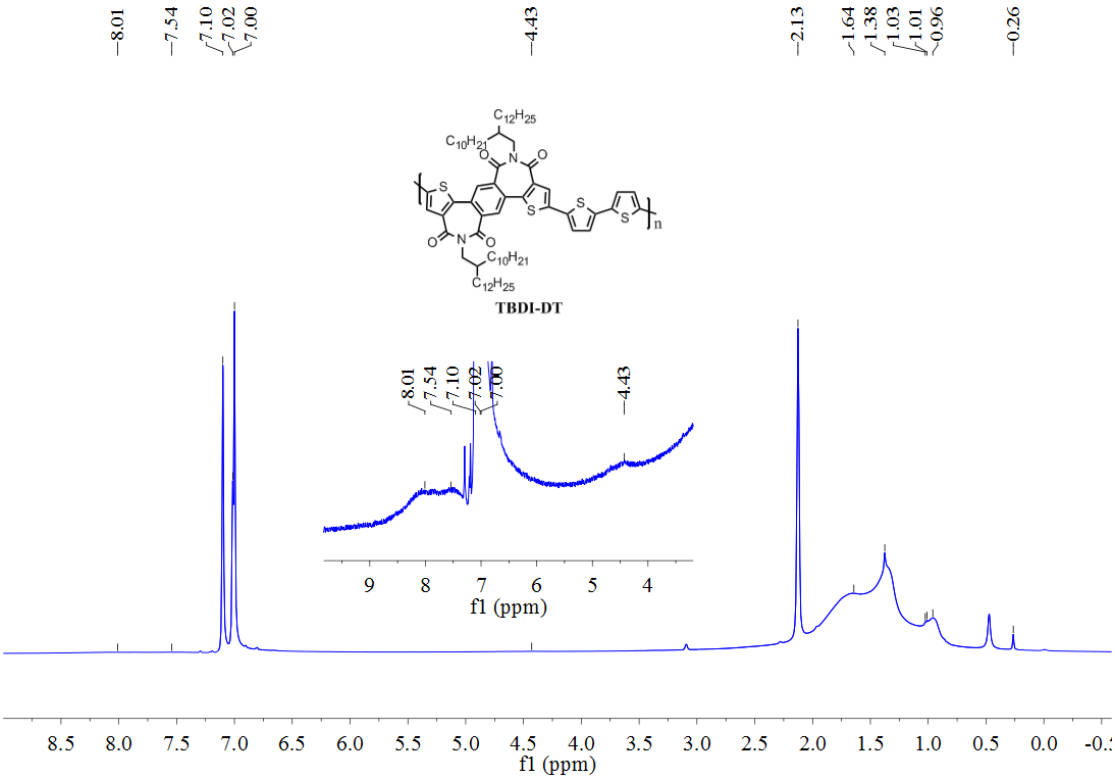

Figure S24. The ^{1}H NMR of polymer **TBDI-DT**.

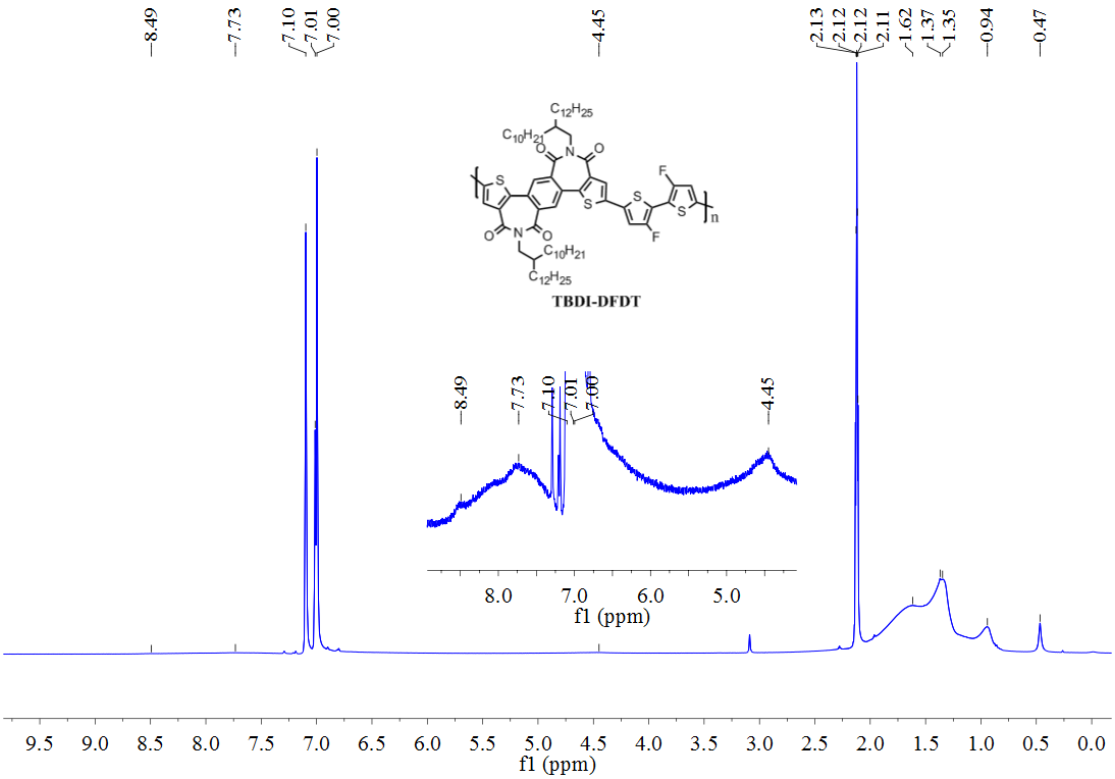

Figure S25. The ^{1}H NMR of polymer **TBDI-DFDT**.

11. Single Crystal Data of TBDI.

Crystal data

CHNOS	V = 2431.6 (19) Å^3
M_r = 75.09	Z = 31
	F(000) = 1178
a = 9.639 (5) Å	D_x = 1.590 Mg m^{-3}
b = 11.745 (5) Å	Mo $K\alpha$ radiation, λ = 0.71073 Å
c = 22.285 (8) Å	μ = 0.76 mm^{-1}
α = 76.86 (5)°	T = 566 K
β = 81.81 (3)°	
γ = 88.16 (4)°	

Data collection

Radiation source: fine-focus sealed tube	R_{int} = 0.223
graphite	θ_{max} = 25.3°, θ_{min} = 1.8°
33023 measured reflections	h = -11→11
8500 independent reflections	k = -13→12
4245 reflections with $I > 2\sigma(I)$	l = -26→25

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.160	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.463	$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.26	$(\Delta/\sigma)_{max}$ = 1.161
8500 reflections	$\Delta\rangle_{max}$ = 0.96 e Å^{-3}
569 parameters	$\Delta\rangle_{min}$ = -0.48 e Å^{-3}
0 restraints	Extinction correction: *SHELXL*, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant	Extinction coefficient: 0.000 (5)

direct methods	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.87135 (14)	0.40554 (16)	0.05560 (8)	0.1013 (6)
O1	1.5469 (4)	0.4170 (4)	-0.15945 (19)	0.1076 (13)
S2	1.65663 (16)	0.15713 (16)	0.01673 (8)	0.1033 (6)
O5	0.7430 (4)	0.6971 (4)	-0.10621 (19)	0.1043 (13)
S3	0.93603 (16)	0.35335 (16)	-0.11067 (8)	0.1044 (7)
C3	0.6396 (5)	0.5256 (6)	-0.0147 (3)	0.0879 (15)
C4	0.5534 (5)	0.5774 (5)	-0.0576 (3)	0.0866 (15)
C5	0.5935 (6)	0.4488 (5)	0.0428 (3)	0.0853 (14)
C6	0.6258 (6)	0.6633 (6)	-0.1113 (3)	0.0967 (17)
N1	1.3977 (5)	0.3903 (5)	-0.2249 (2)	0.0999 (15)
N3	0.5800 (5)	0.7034 (4)	-0.1690 (2)	0.0931 (14)
N2	1.1987 (5)	-0.0006 (4)	0.1099 (2)	0.0929 (13)

C10	1.1546 (6)	0.2134 (6)	-0.0375 (3)	0.0943 (16)
C11	1.2363 (6)	0.1550 (5)	0.0060 (3)	0.0922 (16)
C12	0.6957 (5)	0.3987 (5)	0.0833 (3)	0.0900 (16)
C13	1.3844 (5)	0.1711 (5)	-0.0073 (3)	0.0885 (15)
O2	1.2634 (5)	0.3701 (5)	-0.2974 (3)	0.1352 (17)
C15	1.4382 (5)	0.2437 (5)	-0.0655 (3)	0.0937 (16)
C16	0.9174 (7)	0.3466 (6)	0.1278 (3)	0.1012 (18)
C17	1.4354 (6)	0.3764 (6)	-0.1652 (3)	0.0995 (18)
C18	1.3556 (6)	0.2999 (5)	-0.1093 (3)	0.0898 (15)
C19	1.2068 (6)	0.2820 (6)	-0.0948 (3)	0.0910 (16)
C20	1.1365 (6)	0.3733 (6)	-0.2020 (3)	0.1005 (18)
O6	0.4516 (5)	0.6964 (5)	-0.2443 (3)	0.1270 (16)
C22	1.1521 (7)	0.0850 (8)	0.0622 (3)	0.122 (2)
C23	1.4839 (6)	0.1171 (5)	0.0364 (3)	0.0906 (15)
C24	1.0839 (7)	-0.0690 (6)	0.1520 (3)	0.112 (2)
O3	1.0264 (5)	0.0949 (8)	0.0654 (3)	0.209 (4)
C26	1.1090 (6)	0.3377 (5)	-0.1369 (3)	0.0911 (16)
C27	0.6747 (6)	0.3502 (5)	0.1474 (3)	0.0866 (15)
C28	0.4524 (6)	0.6793 (5)	-0.1881 (3)	0.0954 (16)
C29	0.8053 (7)	0.3187 (6)	0.1720 (3)	0.1055 (18)
C30	0.8954 (7)	0.4036 (7)	-0.1857 (4)	0.112 (2)
C31	1.0086 (8)	0.4098 (7)	-0.2291 (3)	0.115 (2)
C32	1.2642 (7)	0.3734 (6)	-0.2423 (3)	0.1052 (18)
C33	1.0142 (7)	-0.0142 (6)	0.2019 (3)	0.114 (2)
C34	1.4590 (6)	0.0427 (6)	0.0938 (3)	0.1013 (18)
C35	0.7821 (8)	0.7042 (7)	-0.2519 (3)	0.121 (2)
C36	0.8774 (8)	-0.0730 (7)	0.2345 (4)	0.122 (2)
C37	1.6978 (7)	0.0725 (7)	0.0849 (4)	0.113 (2)
C38	1.5834 (6)	0.0182 (6)	0.1207 (3)	0.110 (2)
C39	0.6834 (7)	0.7761 (7)	-0.2179 (3)	0.115 (2)
C40	1.5110 (7)	0.4355 (7)	-0.2768 (3)	0.120 (2)
C41	1.6059 (8)	0.3365 (8)	-0.2929 (4)	0.133 (3)

C42	1.3362 (7)	-0.0182 (7)	0.1274 (4)	0.120 (2)
C43	0.7959 (9)	-0.0114 (8)	0.2808 (5)	0.153 (3)
C44	1.7286 (9)	0.3875 (10)	-0.3414 (4)	0.146 (3)
O4	1.3422 (6)	-0.0909 (8)	0.1721 (4)	0.224 (5)
C46	0.9960 (10)	0.7078 (10)	-0.3340 (4)	0.160 (3)
C47	0.6569 (9)	-0.0691 (10)	0.3097 (4)	0.152 (3)
C48	0.8944 (9)	0.7781 (8)	-0.2983 (4)	0.140 (3)
C49	0.5760 (11)	0.0011 (11)	0.3550 (5)	0.172 (4)
C50	1.8355 (11)	0.2900 (12)	-0.3572 (5)	0.182 (4)
C51	0.4337 (15)	-0.0507 (14)	0.3806 (7)	0.226 (6)
C52	1.212 (2)	0.685 (3)	-0.4099 (10)	0.325 (15)
C53	1.1095 (14)	0.7718 (13)	-0.3778 (6)	0.218 (6)
C54	1.9562 (11)	0.3409 (16)	-0.4072 (6)	0.221 (6)
C55	2.0500 (16)	0.249 (2)	-0.4230 (8)	0.287 (10)
C56	0.3513 (19)	0.017 (3)	0.4245 (11)	0.320 (11)
C57	2.181 (3)	0.328 (3)	-0.492 (2)	0.38 (2)
C58	1.401 (3)	0.615 (3)	-0.4604 (12)	0.343 (13)
C59	1.314 (3)	0.700 (3)	-0.426 (2)	0.41 (2)
C60	2.201 (6)	0.238 (4)	-0.483 (3)	0.60 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0655 (9)	0.1178 (14)	0.1243 (12)	0.0026 (8)	-0.0167 (8)	-0.0329 (9)
O1	0.083 (3)	0.114 (3)	0.125 (3)	-0.011 (2)	-0.016 (2)	-0.024 (2)
S2	0.0692 (9)	0.1089 (13)	0.1323 (13)	-0.0003 (8)	-0.0194 (8)	-0.0245 (9)
O5	0.075 (2)	0.123 (3)	0.117 (3)	-0.018 (2)	-0.016 (2)	-0.026 (2)
S3	0.0729 (9)	0.1100 (13)	0.1360 (13)	0.0082 (8)	-0.0226 (8)	-0.0358 (10)
C3	0.063 (3)	0.106 (4)	0.098 (3)	0.000 (3)	-0.018 (3)	-0.027 (3)
C4	0.059 (3)	0.099 (4)	0.103 (4)	-0.003 (3)	-0.007 (3)	-0.028 (3)
C5	0.067 (3)	0.092 (4)	0.102 (4)	-0.005 (3)	-0.015 (2)	-0.028 (3)
C6	0.069 (3)	0.099 (4)	0.128 (5)	-0.004 (3)	-0.014 (3)	-0.038 (3)
N1	0.082 (3)	0.117 (4)	0.098 (3)	-0.016 (3)	-0.008 (2)	-0.020 (3)

N3	0.071 (3)	0.105 (4)	0.100 (3)	-0.004 (2)	-0.018 (2)	-0.014 (2)
N2	0.082 (3)	0.089 (3)	0.105 (3)	0.003 (2)	-0.015 (2)	-0.017 (2)
C10	0.066 (3)	0.101 (4)	0.114 (4)	-0.004 (3)	-0.010 (3)	-0.020 (3)
C11	0.065 (3)	0.095 (4)	0.117 (4)	-0.002 (3)	-0.011 (3)	-0.025 (3)
C12	0.062 (3)	0.083 (4)	0.127 (5)	-0.006 (3)	-0.010 (3)	-0.029 (3)
C13	0.070 (3)	0.098 (4)	0.095 (3)	0.004 (3)	-0.005 (3)	-0.022 (3)
O2	0.116 (4)	0.162 (5)	0.132 (4)	-0.014 (3)	-0.018 (3)	-0.041 (3)
C15	0.061 (3)	0.095 (4)	0.132 (4)	0.005 (3)	-0.023 (3)	-0.035 (3)
C16	0.080 (4)	0.102 (4)	0.126 (4)	0.001 (3)	-0.032 (3)	-0.024 (3)
C17	0.074 (3)	0.093 (4)	0.131 (5)	0.005 (3)	-0.013 (3)	-0.024 (3)
C18	0.066 (3)	0.098 (4)	0.110 (4)	-0.005 (3)	-0.013 (3)	-0.032 (3)
C19	0.071 (3)	0.105 (4)	0.106 (4)	0.006 (3)	-0.026 (3)	-0.034 (3)
C20	0.077 (3)	0.101 (4)	0.124 (5)	-0.003 (3)	-0.022 (3)	-0.021 (3)
O6	0.102 (3)	0.146 (4)	0.133 (4)	-0.012 (3)	-0.020 (3)	-0.027 (3)
C22	0.077 (4)	0.160 (7)	0.125 (5)	-0.013 (4)	-0.016 (4)	-0.020 (5)
C23	0.073 (3)	0.094 (4)	0.111 (4)	0.007 (3)	-0.017 (3)	-0.033 (3)
C24	0.096 (4)	0.085 (4)	0.143 (5)	-0.015 (3)	0.019 (4)	-0.019 (3)
O3	0.065 (3)	0.320 (10)	0.182 (5)	-0.020 (4)	-0.023 (3)	0.074 (6)
C26	0.071 (3)	0.088 (4)	0.124 (5)	-0.007 (3)	-0.018 (3)	-0.040 (3)
C27	0.072 (3)	0.086 (4)	0.107 (4)	0.007 (3)	-0.020 (3)	-0.029 (3)
C28	0.096 (4)	0.103 (4)	0.085 (4)	0.005 (3)	-0.009 (3)	-0.021 (3)
C29	0.081 (4)	0.105 (5)	0.131 (5)	0.013 (3)	-0.025 (3)	-0.023 (3)
C30	0.087 (4)	0.115 (5)	0.141 (5)	-0.006 (4)	-0.028 (4)	-0.034 (4)
C31	0.091 (4)	0.120 (5)	0.136 (5)	0.008 (4)	-0.043 (4)	-0.021 (4)
C32	0.094 (4)	0.117 (5)	0.111 (5)	-0.005 (3)	-0.022 (3)	-0.033 (4)
C33	0.103 (4)	0.106 (5)	0.126 (5)	-0.018 (4)	0.008 (4)	-0.025 (4)
C34	0.074 (3)	0.106 (4)	0.120 (4)	0.001 (3)	-0.007 (3)	-0.019 (4)
C35	0.113 (5)	0.123 (6)	0.128 (5)	-0.015 (4)	0.008 (4)	-0.041 (4)
C36	0.104 (5)	0.116 (5)	0.143 (5)	-0.009 (4)	-0.006 (4)	-0.029 (4)
C37	0.078 (4)	0.121 (5)	0.145 (5)	0.008 (4)	-0.030 (4)	-0.035 (4)
C38	0.074 (4)	0.116 (5)	0.144 (5)	0.020 (3)	-0.030 (3)	-0.034 (4)
C39	0.095 (4)	0.119 (5)	0.117 (4)	0.002 (4)	-0.008 (3)	-0.006 (4)

C40	0.104 (5)	0.139 (6)	0.109 (4)	0.010 (4)	0.001 (3)	-0.024 (4)
C41	0.099 (5)	0.161 (7)	0.140 (5)	0.001 (5)	0.002 (4)	-0.048 (5)
C42	0.099 (5)	0.121 (6)	0.124 (5)	0.017 (4)	-0.004 (4)	-0.007 (4)
C43	0.123 (6)	0.135 (7)	0.189 (7)	-0.011 (5)	0.038 (5)	-0.046 (6)
C44	0.108 (5)	0.200 (9)	0.127 (5)	0.005 (6)	0.001 (4)	-0.044 (5)
O4	0.105 (4)	0.269 (9)	0.217 (6)	-0.011 (5)	-0.015 (4)	0.109 (7)
C46	0.126 (6)	0.194 (10)	0.159 (7)	-0.030 (6)	0.035 (5)	-0.067 (6)
C47	0.109 (5)	0.177 (9)	0.158 (6)	-0.010 (5)	0.022 (5)	-0.035 (6)
C48	0.122 (6)	0.148 (7)	0.139 (5)	-0.032 (5)	0.033 (4)	-0.032 (5)
C49	0.138 (7)	0.174 (9)	0.192 (8)	-0.001 (7)	0.008 (6)	-0.036 (7)
C50	0.120 (7)	0.226 (13)	0.198 (9)	-0.002 (7)	0.019 (6)	-0.069 (8)
C51	0.177 (10)	0.239 (15)	0.242 (13)	-0.042 (10)	0.084 (10)	-0.076 (11)
C52	0.181 (15)	0.46 (4)	0.268 (17)	-0.042 (19)	0.117 (15)	-0.034 (19)
C53	0.184 (10)	0.229 (13)	0.230 (12)	-0.061 (9)	0.085 (9)	-0.093 (10)
C54	0.123 (7)	0.36 (2)	0.197 (9)	-0.001 (9)	0.037 (6)	-0.125 (11)
C55	0.158 (11)	0.42 (3)	0.260 (15)	0.067 (14)	0.049 (10)	-0.089 (16)
C56	0.187 (15)	0.43 (3)	0.32 (2)	0.011 (17)	0.028 (14)	-0.09 (2)
C57	0.23 (2)	0.26 (3)	0.59 (5)	0.03 (2)	0.11 (3)	-0.09 (3)
C58	0.31 (2)	0.36 (3)	0.33 (2)	0.17 (2)	0.001 (18)	-0.09 (2)
C59	0.26 (3)	0.31 (3)	0.69 (7)	0.07 (2)	-0.02 (3)	-0.23 (4)
C60	0.58 (8)	0.26 (4)	1.00 (12)	0.06 (4)	-0.24 (7)	-0.12 (6)

Geometric parameters (Å, º)

S1—C16	1.715 (7)	C20—C32	1.416 (9)
S1—C12	1.715 (6)	C20—C26	1.404 (9)
O1—C17	1.224 (7)	C20—C31	1.458 (9)
S2—C37	1.708 (7)	O6—C28	1.224 (7)
S2—C23	1.713 (6)	C22—O3	1.207 (8)
O5—C6	1.237 (7)	C23—C34	1.370 (9)
S3—C26	1.705 (6)	C24—C33	1.479 (10)
S3—C30	1.739 (7)	C27—C28^{i}	1.418 (8)
C3—C4	1.380 (8)	C27—C29	1.448 (8)

C3—C5	1.411 (8)	C28—C27^{i}	1.418 (8)
C4—C5^{i}	1.434 (7)	C30—C31	1.342 (10)
C4—C6	1.481 (9)	C33—C36	1.517 (9)
C5—C4^{i}	1.434 (7)	C34—C38	1.410 (8)
C5—C12	1.452 (8)	C34—C42	1.426 (9)
C6—N3	1.394 (8)	C35—C39	1.493 (11)
N1—C17	1.403 (8)	C35—C48	1.525 (10)
N1—C32	1.427 (8)	C36—C43	1.508 (12)
N1—C40	1.486 (8)	C37—C38	1.349 (10)
N3—C28	1.414 (8)	C40—C41	1.532 (12)
N3—C39	1.494 (8)	C41—C44	1.521 (11)
N2—C22	1.402 (9)	C42—O4	1.162 (8)
N2—C42	1.429 (9)	C43—C47	1.511 (12)
N2—C24	1.472 (7)	C44—C50	1.582 (16)
C10—C11	1.382 (9)	C46—C53	1.459 (13)
C10—C19	1.382 (9)	C46—C48	1.517 (13)
C11—C13	1.426 (7)	C47—C49	1.555 (16)
C11—C22	1.478 (9)	C49—C51	1.500 (15)
C12—C27	1.400 (9)	C50—C54	1.525 (15)
C13—C15	1.417 (8)	C51—C56	1.52 (3)
C13—C23	1.489 (8)	C52—C59	1.00 (3)
O2—C32	1.240 (8)	C52—C53	1.61 (3)
C15—C18	1.385 (8)	C54—C55	1.46 (2)
C16—C29	1.349 (9)	C55—C57	1.92 (4)
C17—C18	1.488 (8)	C57—C60	1.05 (4)
C18—C19	1.436 (8)	C58—C59	1.54 (3)
C19—C26	1.460 (8)		
C16—S1—C12	92.8 (3)	N2—C22—C11	128.2 (6)
C37—S2—C23	91.5 (3)	C34—C23—C13	130.0 (5)
C26—S3—C30	92.4 (3)	C34—C23—S2	112.0 (4)
C4—C3—C5	124.7 (5)	C13—C23—S2	117.9 (4)

C3—C4—C5^{i}	117.6 (5)	C33—C24—N2	115.4 (5)
C3—C4—C6	113.9 (5)	C20—C26—C19	126.9 (6)
C5^{i}—C4—C6	128.2 (5)	C20—C26—S3	111.4 (4)
C3—C5—C4^{i}	117.7 (5)	C19—C26—S3	121.4 (5)
C3—C5—C12	119.1 (5)	C12—C27—C28^{i}	129.4 (5)
C4^{i}—C5—C12	123.2 (5)	C12—C27—C29	112.3 (5)
O5—C6—N3	116.3 (5)	C28^{i}—C27—C29	118.1 (5)
O5—C6—C4	117.2 (6)	O6—C28—N3	116.1 (5)
N3—C6—C4	126.3 (5)	O6—C28—C27^{i}	119.2 (6)
C17—N1—C32	128.8 (5)	N3—C28—C27^{i}	124.4 (5)
C17—N1—C40	114.8 (5)	C16—C29—C27	112.0 (6)
C32—N1—C40	116.2 (5)	C31—C30—S3	112.3 (5)
C6—N3—C28	128.8 (5)	C30—C31—C20	112.5 (6)
C6—N3—C39	115.1 (5)	O2—C32—C20	120.3 (6)
C28—N3—C39	116.0 (5)	O2—C32—N1	116.1 (6)
C22—N2—C42	128.9 (5)	C20—C32—N1	123.3 (6)
C22—N2—C24	113.3 (5)	C24—C33—C36	113.4 (6)
C42—N2—C24	117.2 (5)	C23—C34—C38	111.1 (6)
C11—C10—C19	124.5 (5)	C23—C34—C42	132.1 (6)
C10—C11—C13	118.2 (5)	C38—C34—C42	116.6 (6)
C10—C11—C22	112.7 (5)	C39—C35—C48	112.5 (7)
C13—C11—C22	129.1 (5)	C43—C36—C33	114.7 (7)
C27—C12—C5	128.9 (5)	C38—C37—S2	111.4 (5)
C27—C12—S1	110.3 (4)	C37—C38—C34	114.0 (6)
C5—C12—S1	120.5 (5)	N3—C39—C35	112.7 (6)
C15—C13—C11	117.4 (5)	N1—C40—C41	111.3 (6)
C15—C13—C23	118.8 (5)	C44—C41—C40	109.6 (8)
C11—C13—C23	123.8 (5)	O4—C42—C34	120.9 (7)
C18—C15—C13	123.9 (5)	O4—C42—N2	113.9 (7)
C29—C16—S1	112.6 (5)	C34—C42—N2	125.1 (6)
O1—C17—N1	119.1 (5)	C47—C43—C36	113.0 (8)
O1—C17—C18	117.9 (6)	C41—C44—C50	112.1 (9)

N1—C17—C18	122.4 (5)	C53—C46—C48	117.1 (10)
C15—C18—C19	117.6 (5)	C43—C47—C49	110.3 (9)
C15—C18—C17	114.0 (5)	C35—C48—C46	113.8 (7)
C19—C18—C17	128.3 (5)	C51—C49—C47	110.9 (11)
C10—C19—C18	118.2 (5)	C54—C50—C44	112.0 (11)
C10—C19—C26	119.1 (5)	C49—C51—C56	112.1 (15)
C18—C19—C26	122.6 (5)	C59—C52—C53	126 (3)
C32—C20—C26	129.7 (6)	C46—C53—C52	111.4 (13)
C32—C20—C31	118.8 (6)	C50—C54—C55	111.0 (15)
C26—C20—C31	111.4 (6)	C54—C55—C57	104.4 (17)
O3—C22—N2	114.9 (6)	C60—C57—C55	70 (5)
O3—C22—C11	116.7 (6)	C52—C59—C58	122 (4)

Symmetry code: (i) -*x*+1, -*y*+1, -*z*.