Electronic Supplementary Material (ESI) for Polymer Chemistry.

Effect of aggregation behavior on photovoltaic performances in benzodithiophene-thiazolothiazole-based wide band-gap conjugated polymers with side chain position changes

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Contents

1. Instruments.

^1H NMR and ^{13}C NMR spectra were measured in deuterated solvents on a Bruker AVANCE 300 MHz NMR spectrometer at room temperature. Thermo gravimetric analysis (TGA) measurements were carried out on TGA-2050 Thermogravimetry Analyze. Elemental analysis of polymers was performed by a FLASH EA1112 elemental analyzer. Molecular weight and polydispersity (*Đ*) of both polymers were estimated by high temperature (145 °C) gel permeation chromatography (GPC) method by using monodispersed polystyrene as standard and *o*-dichlorobenzene as eluent. The current density-voltage (*J*−*V*) measurements were performed via the solar simulator (SS-F5-3A, Enlitech) along with AM 1.5G spectra whose intensity was calibrated by the certified standard silicon solar cell (SRC-2020, Enlitech) at 100 mW/cm^2. The EQE spectrum was measured through the Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd., Taiwan). Silicon diode was used as reference cell in both *J-V* and EQE.

2. Measurements

Optical characterizations: UV-vis absorption spectra of polymers in solution and in s films were measured on a Hitachi U-3100 UV−vis spectrophotometer. The film samples were spin-coated onto quartz plates (1×1 cm^2). The optical bandgaps of both polymers were calculated according to the absorption onset of the films.

Cyclic Voltammetry (CV): The electrochemical cyclic voltammetry was measured on a CH1650D electrochemical workstation in a three-electrode cell in anhydrous acetonitrile solvents solution of Bu_4NPF_6 (0.1 M) with a scan rate of 50 mV/s at room temperature under argon. A Ag/Ag$^+$ wire, A platinum wire, and a glassy carbon electrode were used as the reference electrode counter electrode, and working electrode, respectively. The potential of Ag/Ag$^+$ reference electrode was calibrated by using ferrocene/ferroncenium (Fc/Fc$^+$) as the redox couple.

Polymer solar cells fabrication and testing: All devices were fabricated with the conventional device architecture of ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)

(PEDOT:PSS)/BHJ/PFN-Br/Al. Pre-patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 10−15 ohm/square was cleaned sequential sonication in deionized water, acetone and isopropanol twice for 15 min. Then it was transferred to oven and dried at 150 °C for 15 min. After ultraviolet-ozone treatment for 20 min, the 10 nm layer of PEDOT:PSS (Heraeus Materials, 4083) was spin-coated on ITO. The substrates were annealed for 15 min at 150 °C, and transferred to the nitrogen-filled glovebox. The active layer materials were prepared according to the description under corresponding Table S1-S6. Finally, PFN-Br was spin-coated (3000rpm, 30s) onto the active layer as the cathode buffer layer, and the whole device was completed by vacuum evaporating Al metal electrodes (100 nm) to acquire an area of 4 mm^2 cell.

Carrier mobility measurement: The carrier mobility of the blend films were measured using the SCLC method, with the hole-only and electron-only device architecture of ITO/PEDOT:PSS/BHJ/Au and ITO/ZnO/BHJ/Al, respectively.

GIWAXS Characterization: GIWAXS measurements were performed by using a XEUSS SAXS/WAXS system. Samples were prepared on Si substrates using blend solutions identical to those devices used. The wavelength of the X-ray beam is 1.54 Å, and the incident angle was 0.2°. Scattered X-rays were detected by using a Dectris Pilatus 300 K photon counting detector. The crystal coherence length (CCL) was obtained using the Scherrer equation.

AFM characterizations: All film samples were prepared using spin-coating onto ITO/PEDOT:PSS substrates. The measurements were carried out by a Nanoscope V (Vecco) IN tapping mode.

Density functional theory (DFT) calculation: The molecular modeling calculations were conducted using the Gaussian 09 program based on the density functional theory method using B3LYP/6-31G (d, p) level.

3. Synthetic detail

Synthesis of 3-(2-hexyl-decyl)-thiophen (1)

To a suspension of magnesium turnings (2.83 g, 66.2 mmol) and a catalytic of iodine in anhydrous tetrahydrofuran (20 mL) was slowly added dropwise 2-hexyldecyl bromide (20 g, 65.5 mmol) at 80

^{o}C under Argon. The resulting mixture was refluxed for 2 before being cooled to room temperature. The gray solution was transferred into a 100 mL of two neck flask, which included a solution of 3-bromothiophene (9.0 g, 55.2 mmol) and dichloro(1,3-bis(diphenylphosphino)propane)nickel (Ni(dppp)Cl_2, 0.59 g, 1.1 mmol) in anhydrous tetrahydrofuran (30 mL). The resulting solution was heated to reflux overnight under Argon. After cooling to room temperature, the reaction was quenched with water (10 mL). The mixture was extracted with dichloromethane (3 x 50 mL). The combined organic phase was dried using $MgSO_4$ and concentrated to afford yellow oil, which was purified by column chromatography on silica gel eluting with petroleum ether to yield the compound **1** (colorless oil, 9.3 g, 55%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.21 (*m* 1H), 6.89 (*br*, 2H), 2.54 (*d*, J = 9 Hz, 2H), 1.57 (*br*, 1H), 1.25 (*br*, 24H), 0.86 (*m*, 6H); ^{13} C NMR (75 MHz, $CDCl_3$) δ (ppm) 142.05, 128.95, 124.90, 120.78, 39.11, 34.88, 33.51, 32.08, 30.17, 29.85, 29.79, 29.50, 26.78, 26.76, 22.85, 14.27; MS (EI) m/z: Calcd for $C_{20}H_{36}S$: 308; Found 308.

Synthesis of 2-Bromo-3-(2-hexyl-decyl)-thiophene (2)

NBS (1.48 g, 8.34 mmol) was added to a solution of compound **1** (2.71 g, 8.78 mmol) in 30 mL tetrahydrofuran at 0 °C under Argon. The reaction mixture was then allowed to warm up to ambient temperature and stirred for 2 h under dark. After removing the solvent under reduce pressure, the crude product was purified by column chromatography on silica gel eluting with petroleum ether to afford compound **2** (colorless oil, 3.03 g, 89%,). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.17 (*d*, J = 6 Hz, 1H), 6.75 (*d*, J = 6 Hz, 1H), 2.48 (*d*, J = 6 Hz, 2H), 1.65 (*br*, 1H), 1.26 (*br*, 24H), 0.86 (*t*, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 141.32, 128.96, 125.05, 109.55, 38.68, 34.16, 33.49, 32.07, 32.04, 30.15, 29.83, 29.76, 29.49, 26.67, 26.65, 22.84, 14.29; MS (EI) m/z: Calcd for $C_{21}H_{35}BrS$: 386; Found 386.

Synthesis of 3-(2-Hexyl-decyl)-thiophene-2-carbaldehyde (3)

Compound **2** (4.67 g, 12.05 mmol) was dissolved into 30 mL of dry tetrahydrofuran. The mixture was cooled to -78 °C. A solution of n-BuLi (1.6 M, 7.53 mL) was added slowly over 10 min. After stirring 1 h, the 3.32 of mL DMF was added to the mixture at this temperature. The reaction was warmed to room temperature over 1 h. The resulting mixture was poured into water and extracted with dichloromethane. The organic layers were combined, dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by column chromatography on silica gel eluting with dichloromethane/petroleum ether (2/1, v/v) to obtain compound **3**. (colorless oil, 3.7 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 10.02 (*s*, 1H), 7.61 (*d*, *J* = 6 Hz, 1H), 6.95 (*d*, *J* = 6 Hz, 1H), 2.86 (*d*, *J* = 6 Hz, 2H), 1.66 (*br*, 1H), 1.23 (*br*, 24H), 0.84 (*t*, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 182.45, 152.26, 138.46, 134.25, 131.31, 40.30, 33.48, 33.29, 31.99, 31.92, 30.01, 29.68, 29.66, 29.40, 26.65, 26.62, 22.77, 22.74, 14.21, 14.18; MS (EI) m/z: Calcd for $C_{21}H_{36}OS$: 336; Found 336.

Synthesis of 2,5-Bis-[3-(2-hexyl-decyl)-thiophen-2-yl]-thiazolo[5,4-*d*]thiazole (4)

A solution of compound **3** (3.7 g, 10.99 mmol) and dithiooxamide (0.529 g, 4.4 mmol) in 50 mL DMF was heated to 150 °C for overnight under Argon. The resulting mixture was cooled to room temperature, and then poured into water. The mixture was extracted with dichloromethane. The organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel eluting with dichloromethane/petroleum ether (1/6, v/v) to yield compound **4**. (yellow solid, 1.12g, 34%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.34 (*d*, *J* = 4.5 Hz, 2H), 6.94 (*d*, *J* = 6 Hz, 2H), 2.91 (*d*, *J* = 9 Hz, 4H), 1.81 (*br*, 2H), 1.23 (*br*, 48H), 0.84 (*t*, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 162.86, 150.08, 142.57, 132.38, 131.70, 127.17, 38.78, 34.92, 33.58, 32.05, 32.03, 30.19, 29.86, 29.76, 29.49, 26.54, 26.53, 22.83, 14.27; MS (MALDI) [+H] m/z: Calcd for $C_{44}H_{70}N_2S_4$: 754.4; Found 755.2.

Synthesis of 2,5-Bis-[5-bromo-3-(2-hexyl-decyl)-thiophen-2-yl]-thiazolo[5,4-*d*]thiazole (5)

NBS (0.52 g, 2.91 mmol) was added to a solution of compound **4** (1.0 g, 1.32 mmol) in 30 mL tetrahydrofuran at 0 °C. The reaction mixture was then allowed to warm up slowly to ambient temperature and stirred in the dark for overnight. After removing the solvent, the crude product was purified by column chromatography on silica gel eluting with dichloromethane/petroleum ether (1/8, v/v) to afford monomer **5** (yellow solid, 1.10 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.90 (*s*, 2H), 2.82 (*d*, *J* = 6 Hz, 4H), 1.76 (*br*, 2H), 1.24 (*br*, 48H), 0.85 (*t*, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 160.57, 150.08, 142.93, 134.20, 133.98, 115.38, 39.16, 38.74, 35.07, 33.52, 33.49, 32.05, 32.01, 30.13, 29.81, 29.74, 29.47, 26.50, 22.83, 14.27; MS (MALDI) [+] m/z: Calcd for $C_{44}H_{68}Br_2N_2S_4$: 913.1; Found 913.3.

Synthesis of 4-(2-Hexyl-decyl)-thiophene-2-carbaldehyde (6)

To a solution of compound **1** (3.0 g, 9.27 mmol) in 30 mL of dry tetrahydrofuran, LDA (2 M in diethyl ether, 5.35 mL) was added slowly at -78 °C. After stirring one hour at this temperature, 3.57 mL dry DMF was added one portion. The reaction mixture was then allowed to warm up slowly to ambient temperature for 2 h. The mixture was poured into water and extracted with dichloromethane. The organic layers were combined, dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by column chromatography on silica gel eluting with dichloromethane/petroleum ether (2/1, v/v) to afford compound **6** (colorless oil, 2.98 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 9.88 (*s*, 1H), 7.57 (*s*, 1H), 7.34 (*s*, 1H), 2.56 (*d*, J = 6 Hz, 2H), 1.62 (*br*, 1H), 1.25 (*br*, 24H), 0.85 (*t*, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 183.12, 143.69, 143.61, 137.78, 131.35, 39.09, 34.75, 33.35, 32.03, 31.99, 30.08, 29.75, 29.72, 29.44, 26.72, 26.70, 22.81, 22.79, 14.24; MS (EI) m/z: Calcd for $C_{21}H_{36}OS$: 336; Found 336.

Synthesis of 2,5-Bis-[4-(2-hexyl-decyl)-thiophen-2-yl]-thiazolo[5,4-*d*]thiazole (7)

A solution of compound **6** (1.8 g, 5.35 mmol) and dithiooxamide (0.29 g, 2.43 mmol) in 50 mL DMF was heated to 150 °C and stirred overnight. The resulting mixture was cooled to room temperature, and then poured into water and extracted with dichloromethane. The organic phase was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by column chromatography on silica gel eluting with dichloromethane/petroleum ether (1/6, v/v) to afford compound **7** (yellow oil, 0.82 g, 45%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.37 (*s*, 2H), 7.02 (*s*, 2H), 2.54 (*d*, J = 6 Hz, 4H), 1.62 (*br*, 2H), 1.26 (*br*, 48H), 0.86 (*t*, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 162.88, 149.76, 143.49, 137.06, 128.63, 124.51, 39.03, 35.09, 33.40, 32.05, 32.03, 30.14, 29.85, 29.81, 29.76, 29.48, 26.72, 26.69, 22.83, 14.27; MS (MALDI) [+H] m/z: Calcd for $C_{44}H_{70}N_2S_4$: 754.4; Found 755.1.

Synthesis of 2,5-Bis-[5-bromo-4-(2-hexyl-decyl)-thiophen-2-yl]-thiazolo[5,4-*d*]thiazole (8)

NBS (0.48 g, 2.68 mmol) was added to a solution of compound **7** (0.92 g, 1.22 mmol) in 30 mL tetrahydrofuran at 0 °C. The reaction mixture was then allowed to warm up slowly to ambient temperature and stirred in the dark for overnight. After removing the solvent, the crude product was purified by column chromatography on silica gel eluting with dichloromethane/petroleum ether (1/8, v/v) to afford monomer **8** (yellow solid, 1.05 g, 924%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ (ppm) 7.24 (*s,* 2H), 2.51 (*d*, *J* = 6 Hz, 4H), 1.71 (*br*, 2H), 1.27 (*br*, 48H), 0.87 (*br*, 12H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ (ppm) 162.33, 150.40, 143.56, 137.25, 128.46, 114.33, 39.10, 34.82, 33.90, 33.88, 32.50, 32.46, 30.54, 30.23, 30.17, 29.91, 27.06, 27.05, 23.27, 14.46; MS (MALDI) [+] m/z: Calcd for $C_{44}H_{68}Br_2N_2S_4$: 913.1; Found 913.0.

Synthesis of PBTz-1

Compound **9** (0.2 mmol) and monomer **5** (0.2 mmol) were dissolved in anhydrous chlorobenzene (7 mL) in a microwave vial and deoxygenated with Argon for 10 min. $Pd(PPh_3)_4$ (23 mg, 0.02 mmol) was then added under Argon. The resulting mixture was heated under microwave irradiation at 135 °C for 3.5 h, after which it was allowed to cool to room temperature. Then the polymer was precipitated from methanol. The precipitated was further purified by column chromatography using chlorobenzene as the eluent to obtain red solid (224 mg, 82%). Molecular weight by GPC (145 °C): M_n = 21.9 kg mol^{-1}, $Đ$ = 2.75. Elemental analysis: Calcd. for C78H108F2N2S8: C 68.47, H 7.96, N 2.05; found: C 67.61, H 7.75, N 2.05.

Synthesis of PBTz-2

Compound **9** (0.2 mmol), monomer **8** (0.2 mmol) and anhydrous chlorobenzene (7 mL) were placed in a 50 mL two-neck flask. The mixture was purged with argon for 5 min, and then 11.0 mg of tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) and 14.6 mg of tri(o-tolyl)phosphine (P(o-tolyl$_{)3}$) were added. Then the mixture was heated to 100 °C for 3 h. The target polymer was precipitated from methanol. The precipitated was further purified by column chromatography using chlorobenzene as the eluent to obtain red solid (230 mg, 84%). Molecular weight by GPC (145 °C): M_n = 24.9 kg mol^{-1}, $Đ$ = 2.52. Elemental analysis: Calcd. for C78H108F2N2S8: C 68.47, H 7.96, N 2.05; found: C 68.39, H 7.75, N 1.99.

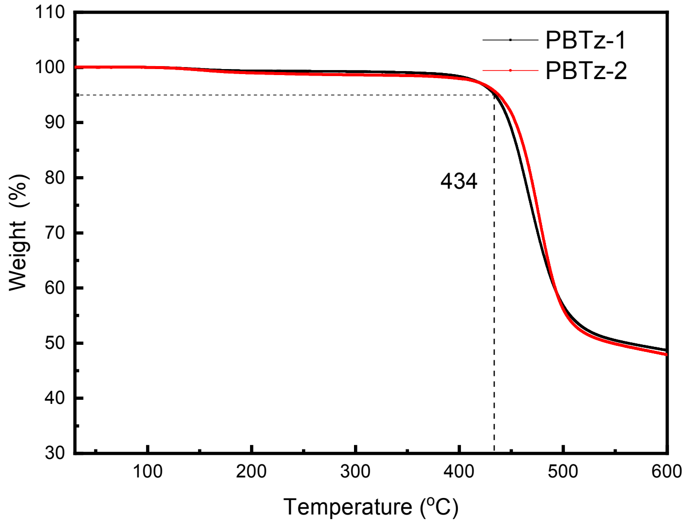

Figure S1. TGA curves of polymers **PBTz-1** and **PBTz-2** at a heating rate of 10 ºC min^{-1} under nitrogen.

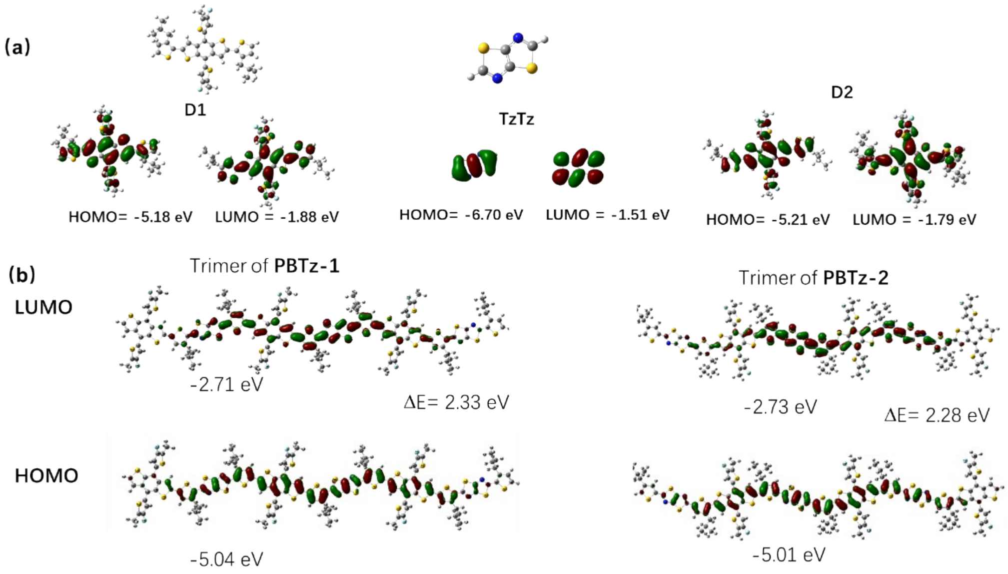

Figure S2. (a) The HOMO and LUMO of donor parts (D1 and D2) and TzTz unit in both polymers (b) LUMO (top) and HOMO (bottom) distributions for the minimum energy conformations of trimers of **PBTz-1** and **PBTz-2**, with methyl and isobutyl substituents, optimized with Gaussian at the B3LYP/6-31G(d, p) level.

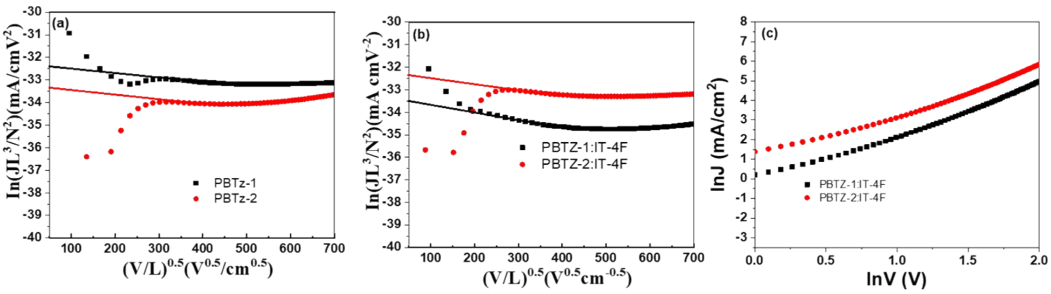

Figure S3. Plots for the calculation of hole mobility of both polymer from (a) hole-only devices, hole and electron mobilities of **PBTz-1**:IT-4F and **PBTz-**2:IT-4F obtained from the (b) hole-only and (c) electron-only devices.

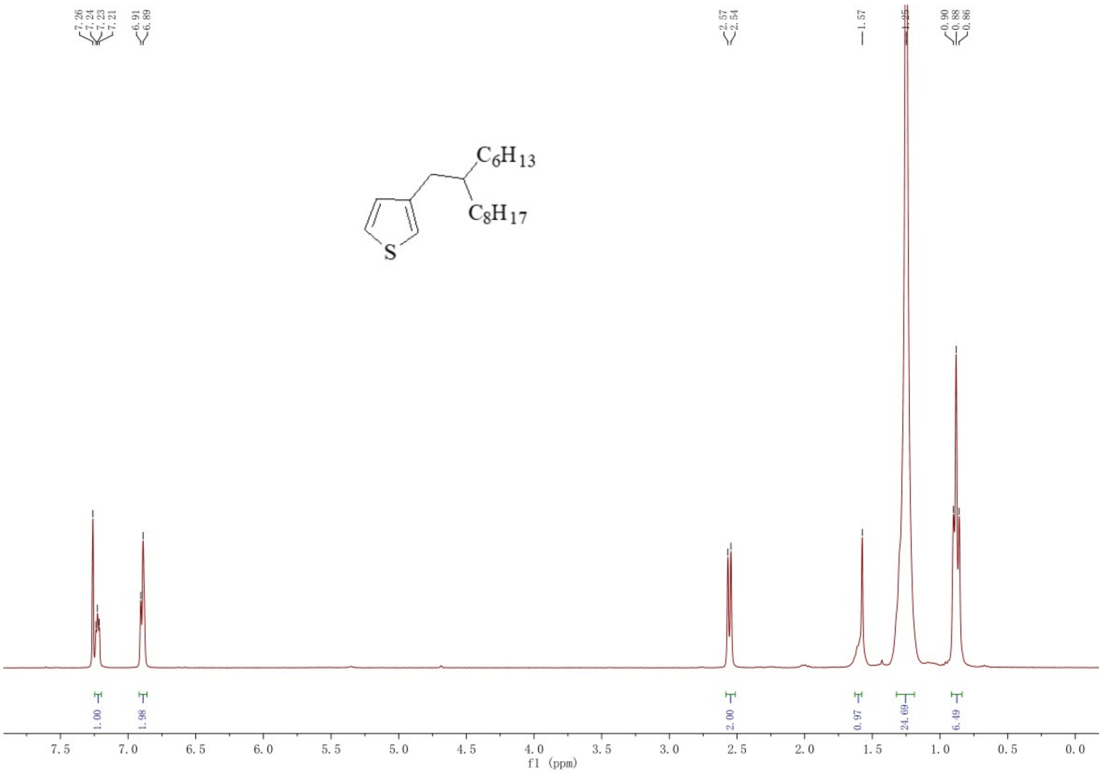

Figure S4. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

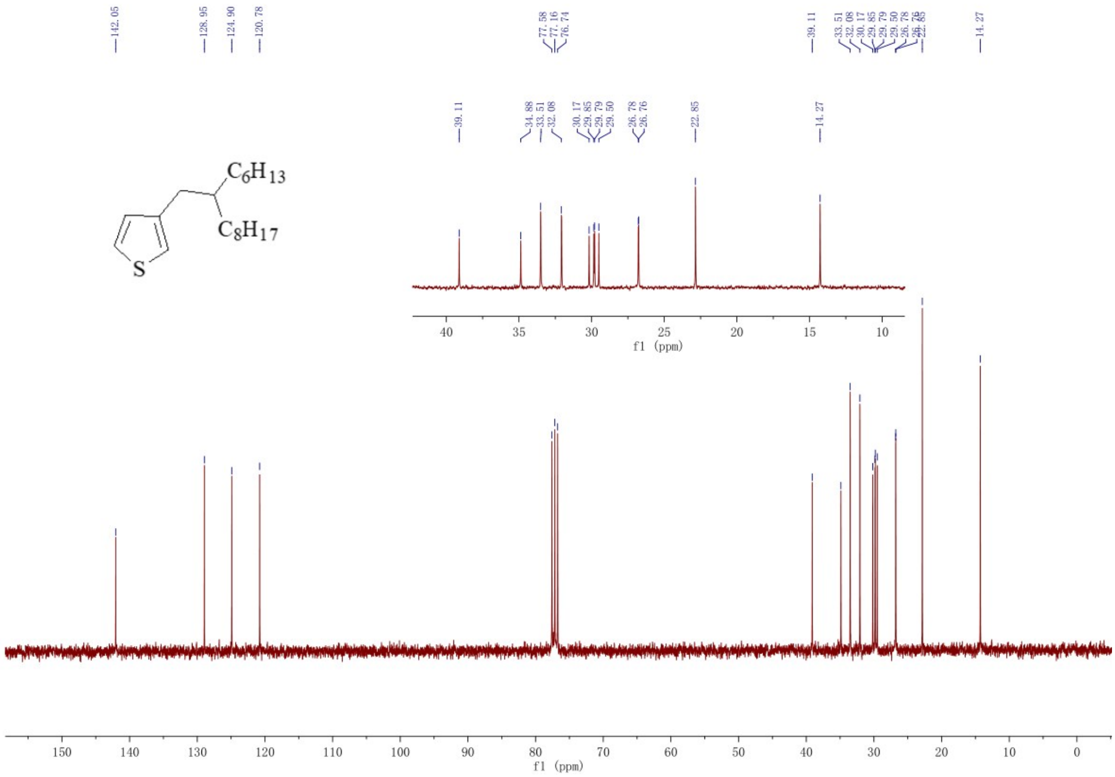

Figure S5. ^{13}C NMR spectrum of compound **1** in CDCl$_3$.

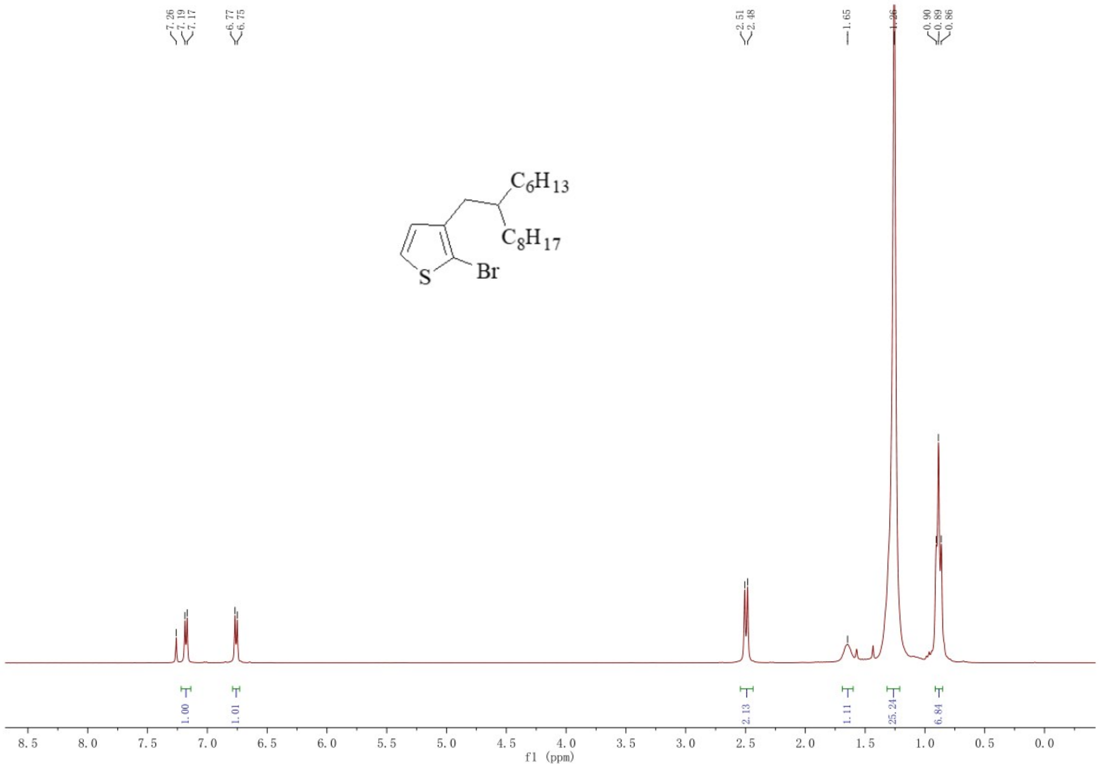

Figure S6. ^{1}H NMR spectrum of compound **2** in CDCl$_3$.

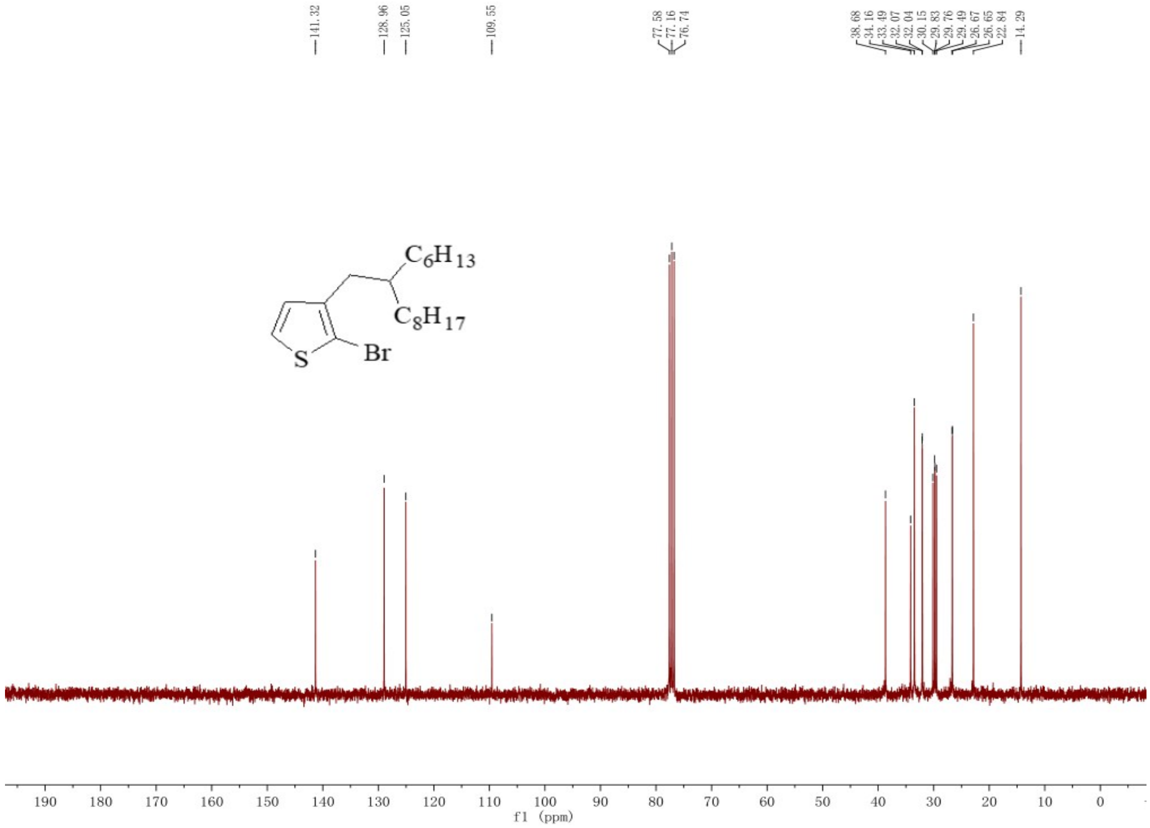

Figure S7. ^{13}C NMR spectrum of compound **2** in CDCl$_3$.

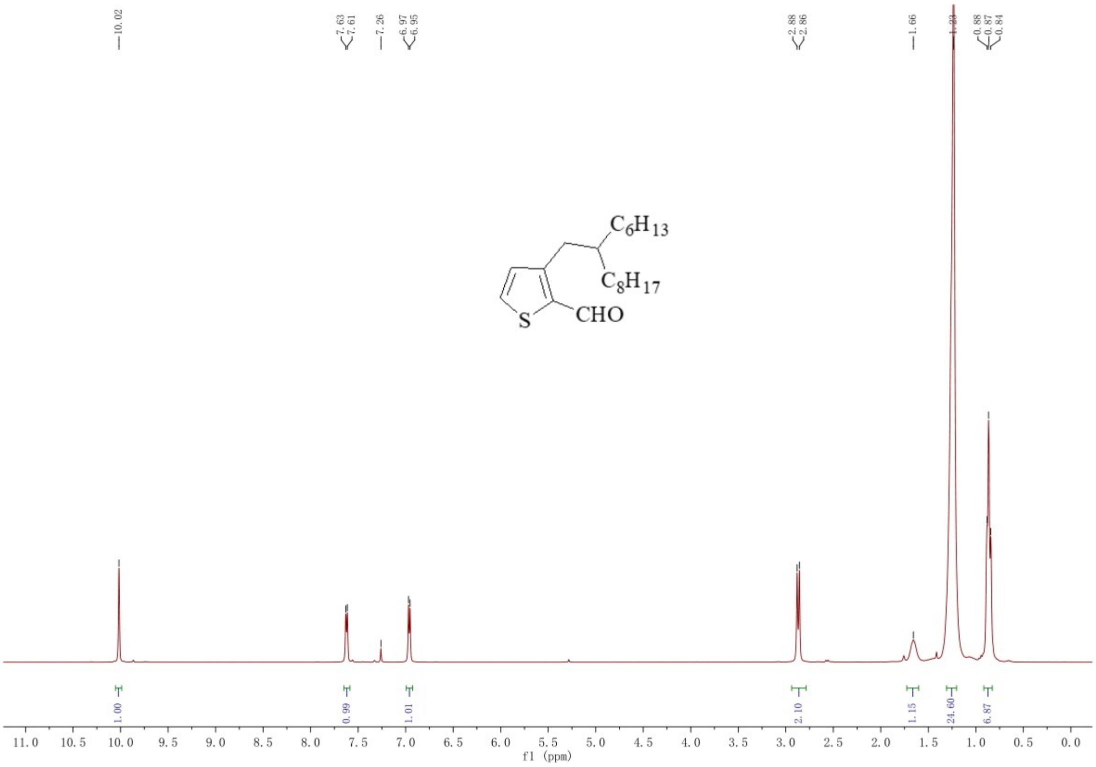

Figure S8. ^{1}H NMR spectrum of compound **3** in CDCl$_3$.

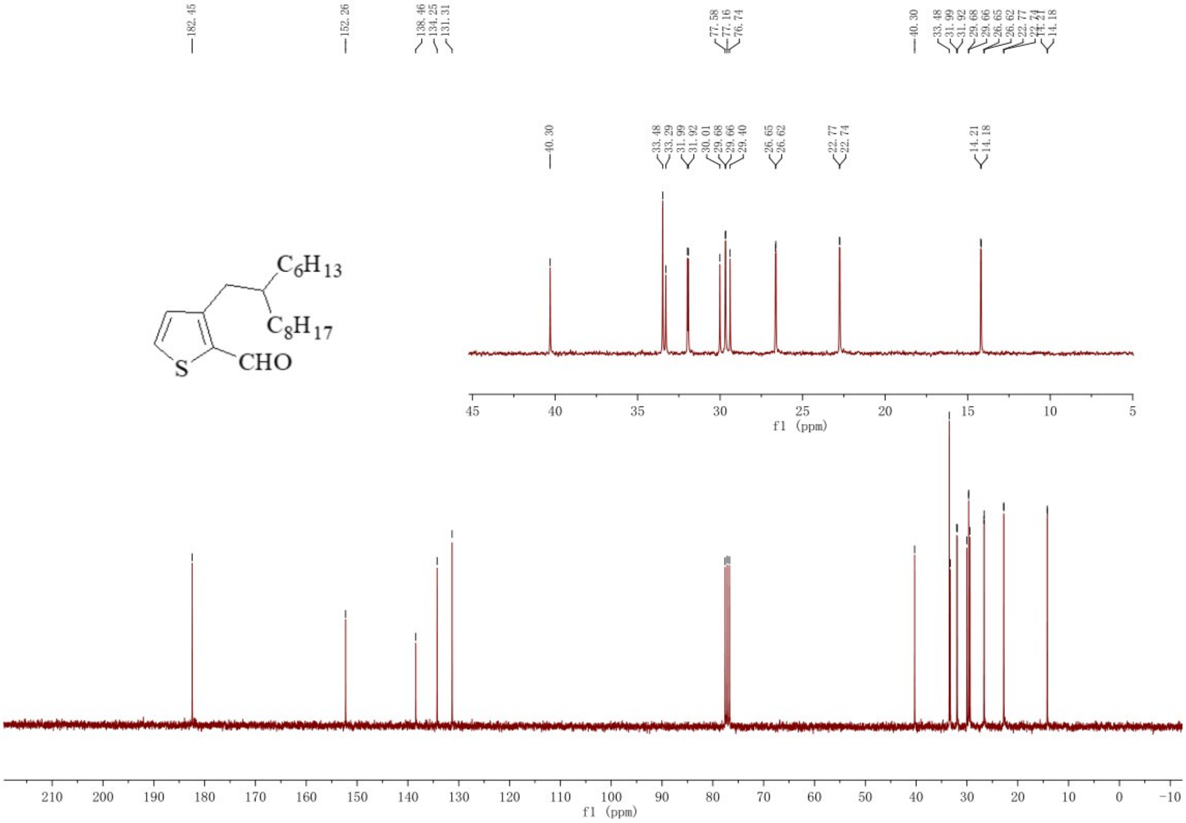

Figure S9. ^{13}C NMR spectrum of compound **3** in CDCl$_3$.

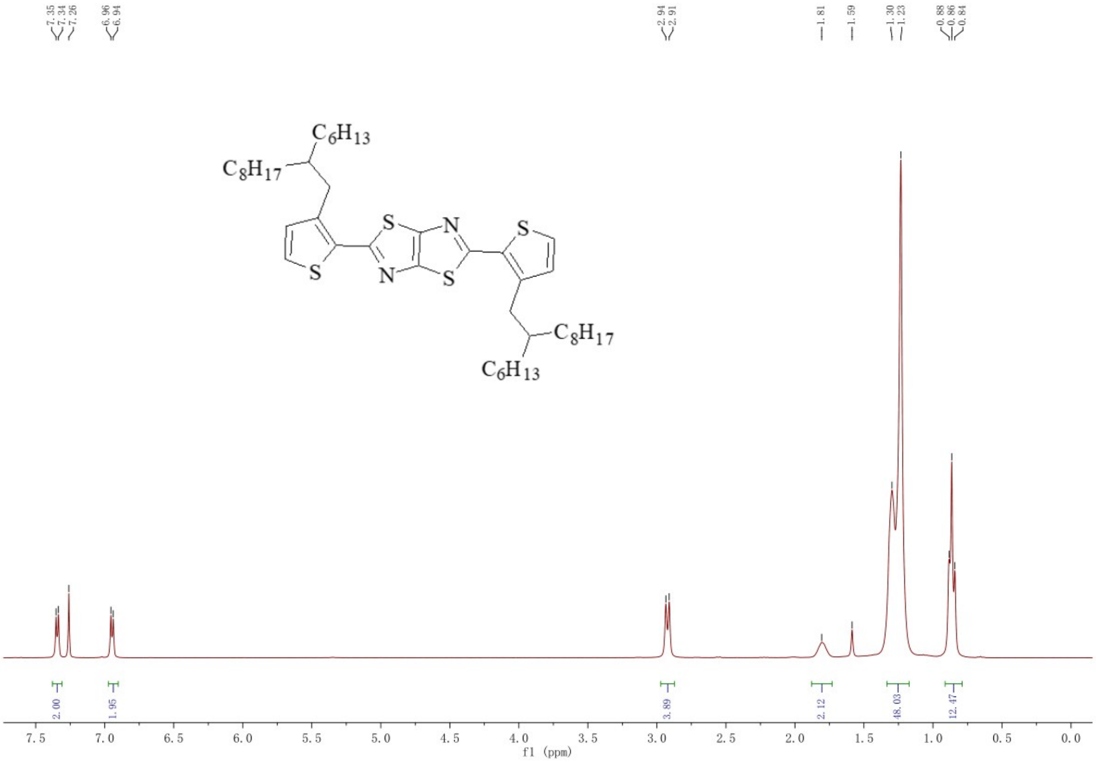

Figure S10. ^{1}H NMR spectrum of compound **4** in CDCl$_3$.

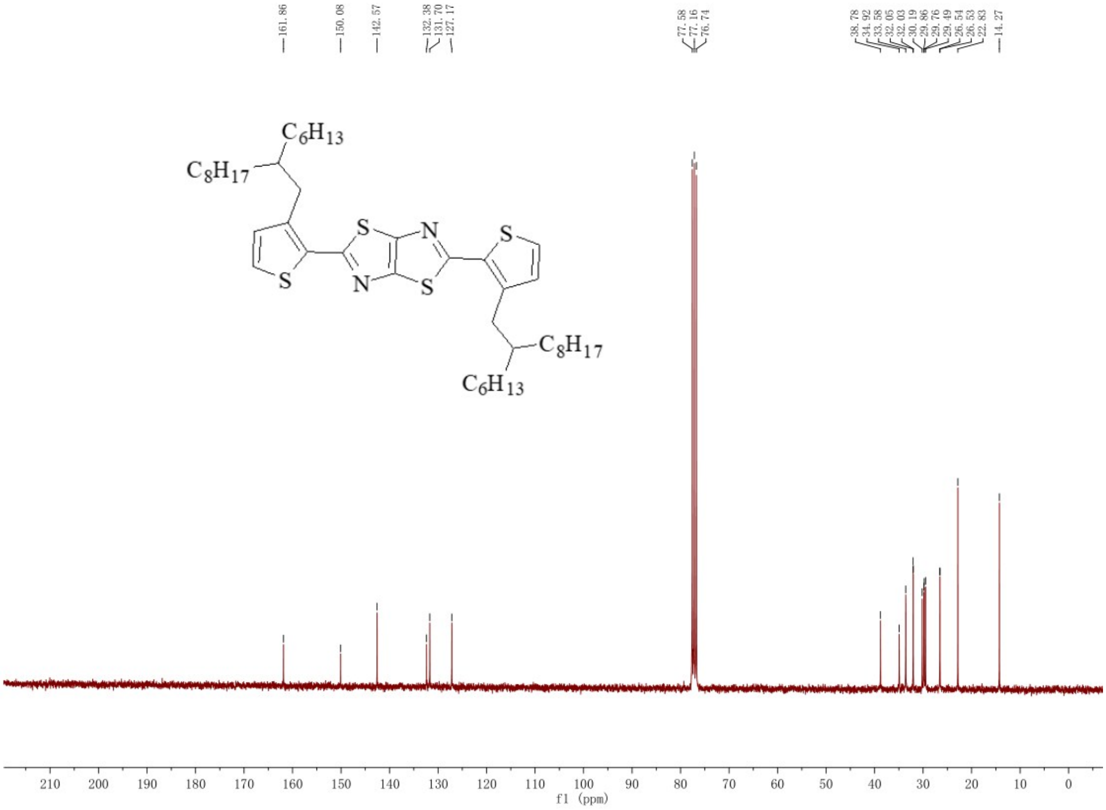

Figure S11. ^{13}C NMR spectrum of compound **4** in $CDCl_3$

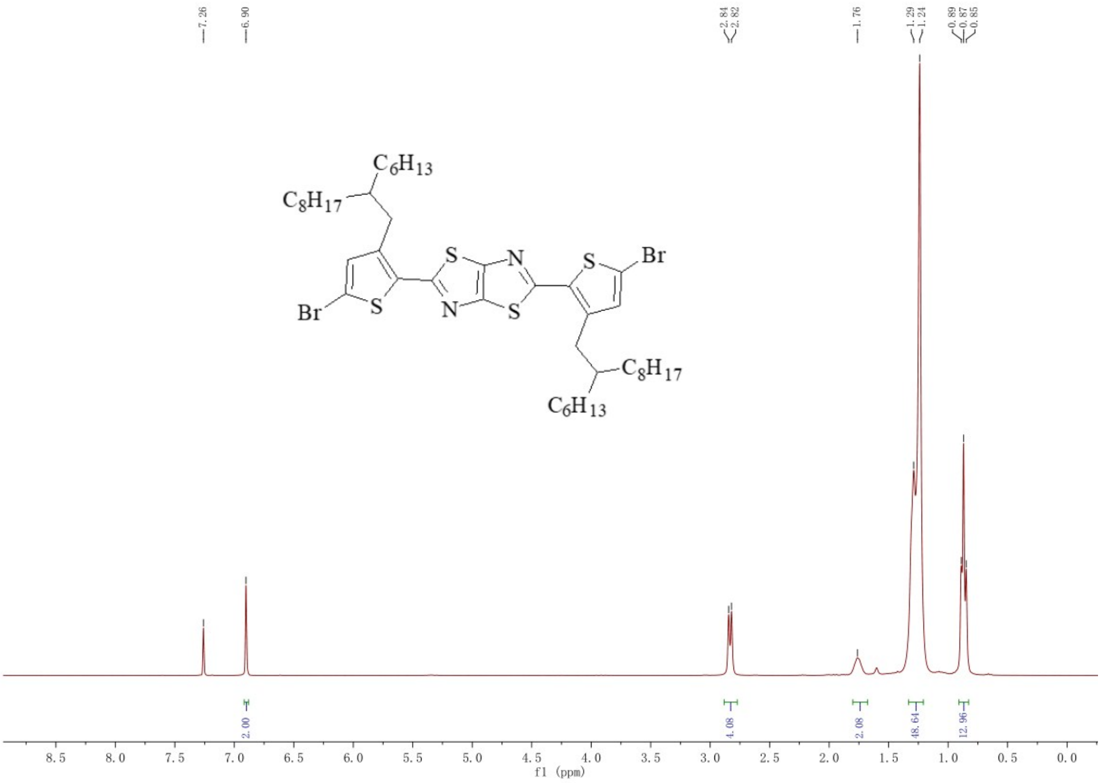

Figure S12. ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

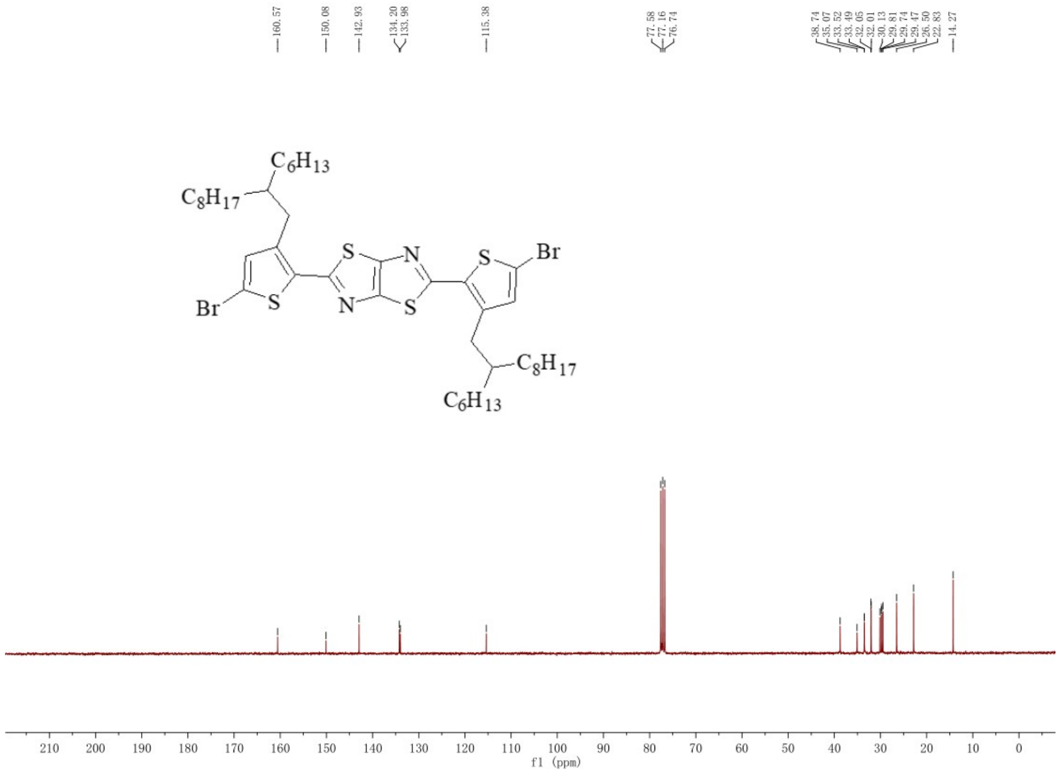

Figure S13. ^{13}C NMR spectrum of compound **5** in $CDCl_3$.

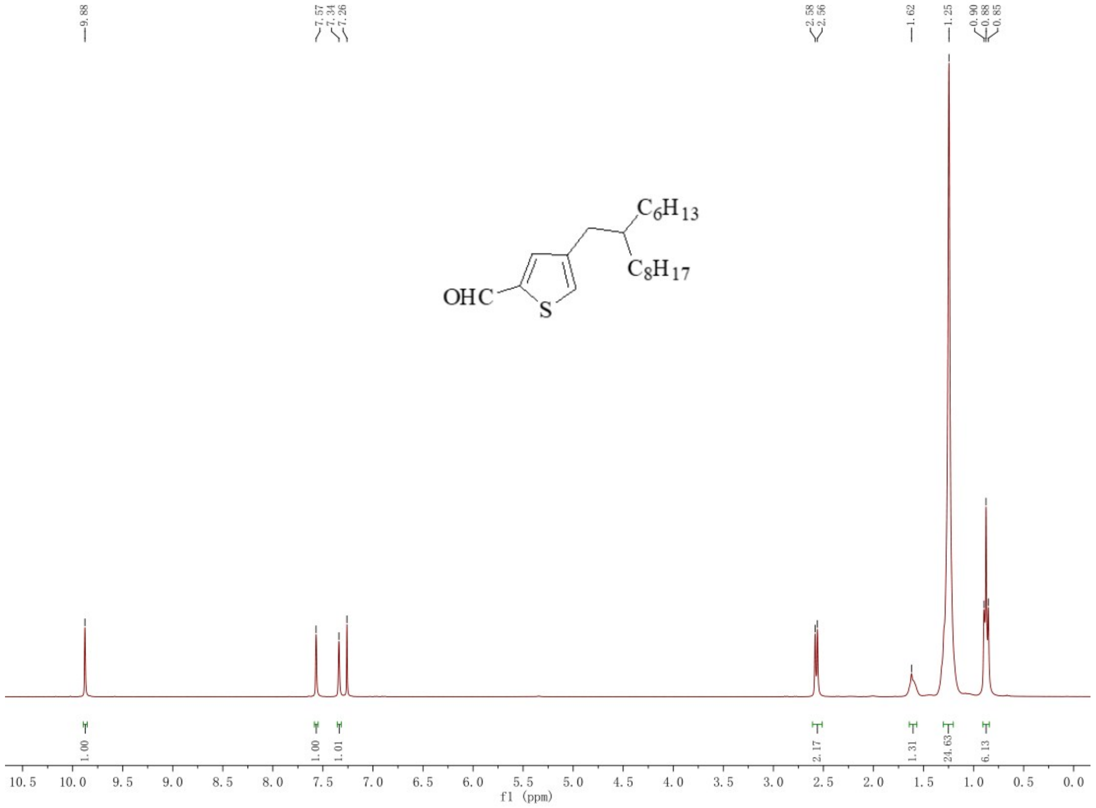

Figure S14. ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

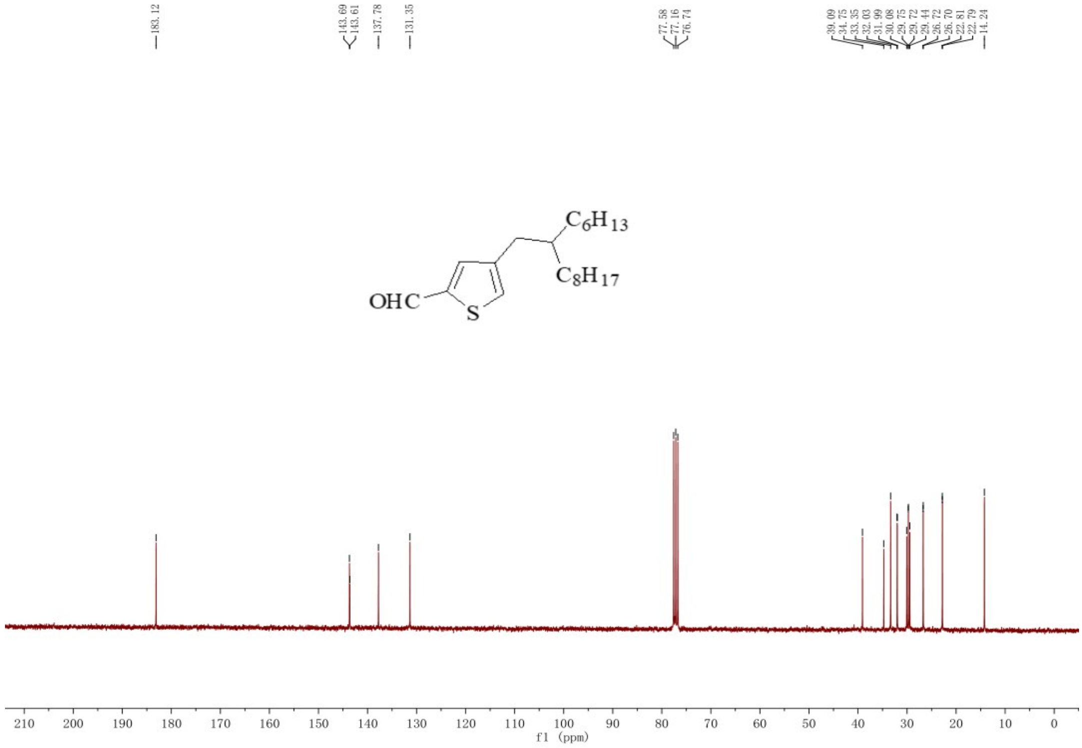

Figure S15. ^{13}C NMR spectrum of compound **6** in $CDCl_3$.

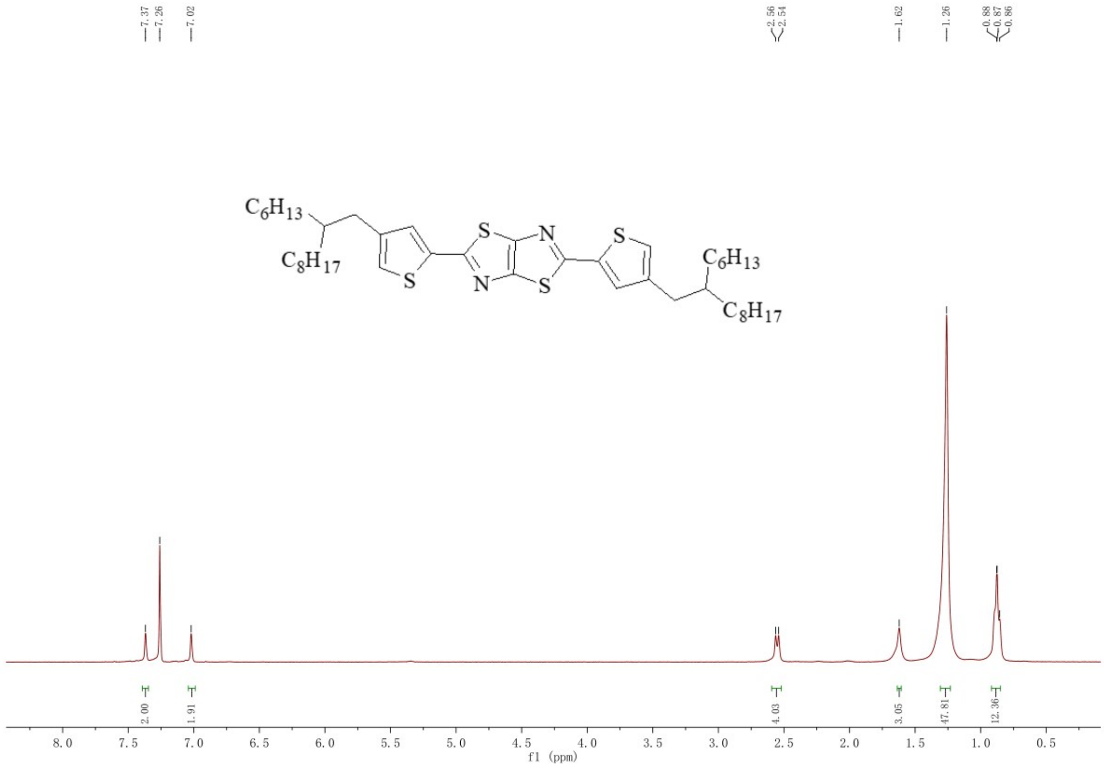

Figure S16. ^{1}H NMR spectrum of compound **7** in $CDCl_3$.

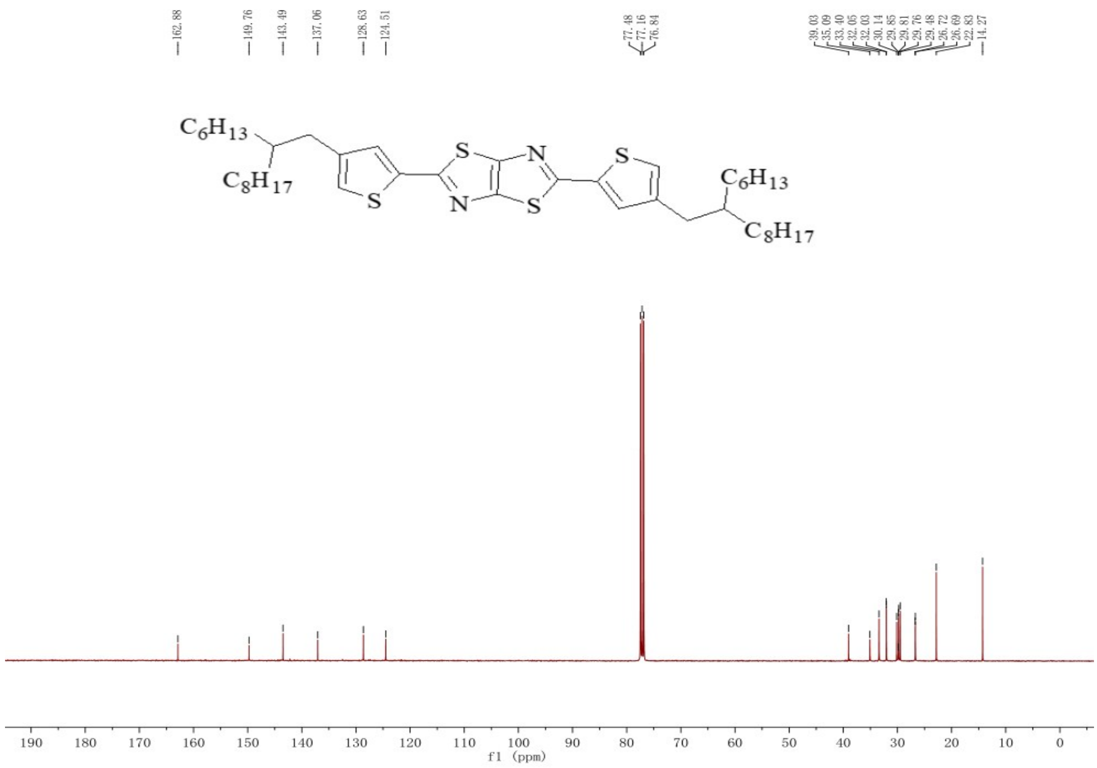

Figure S17. ^{13}C NMR spectrum of compound **7** in $CDCl_3$.

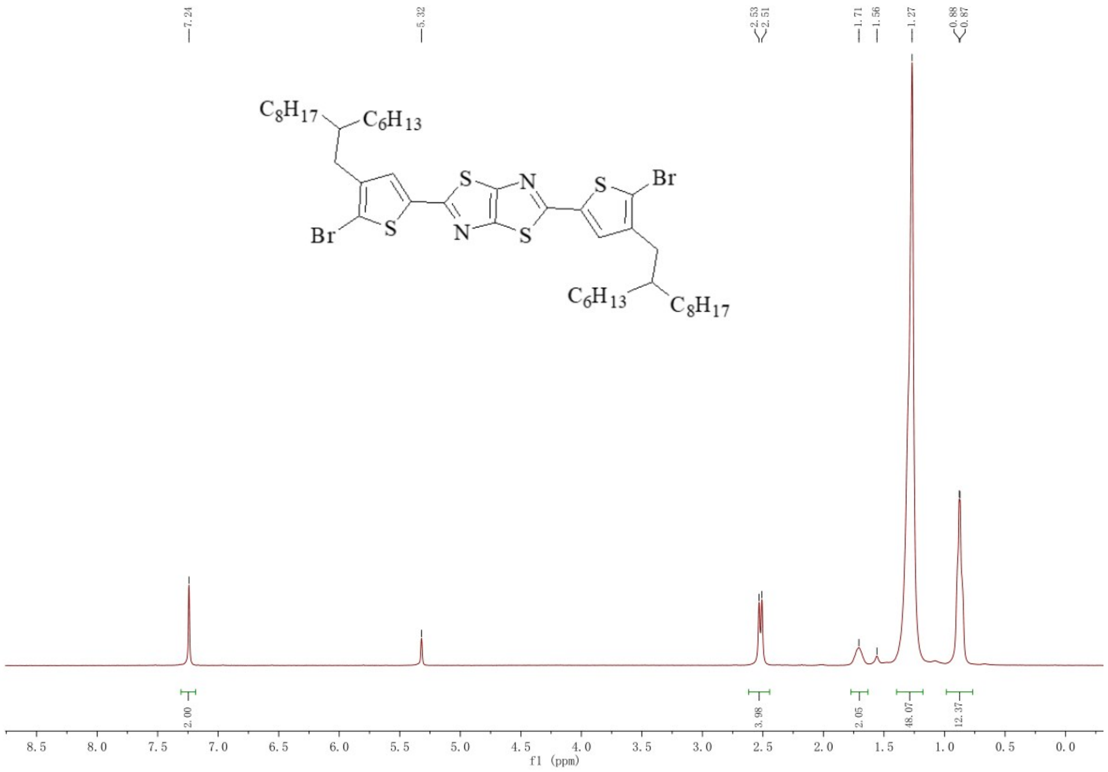

Figure S18. ^{1}H NMR spectrum of compound **8** in CD_2Cl_2.

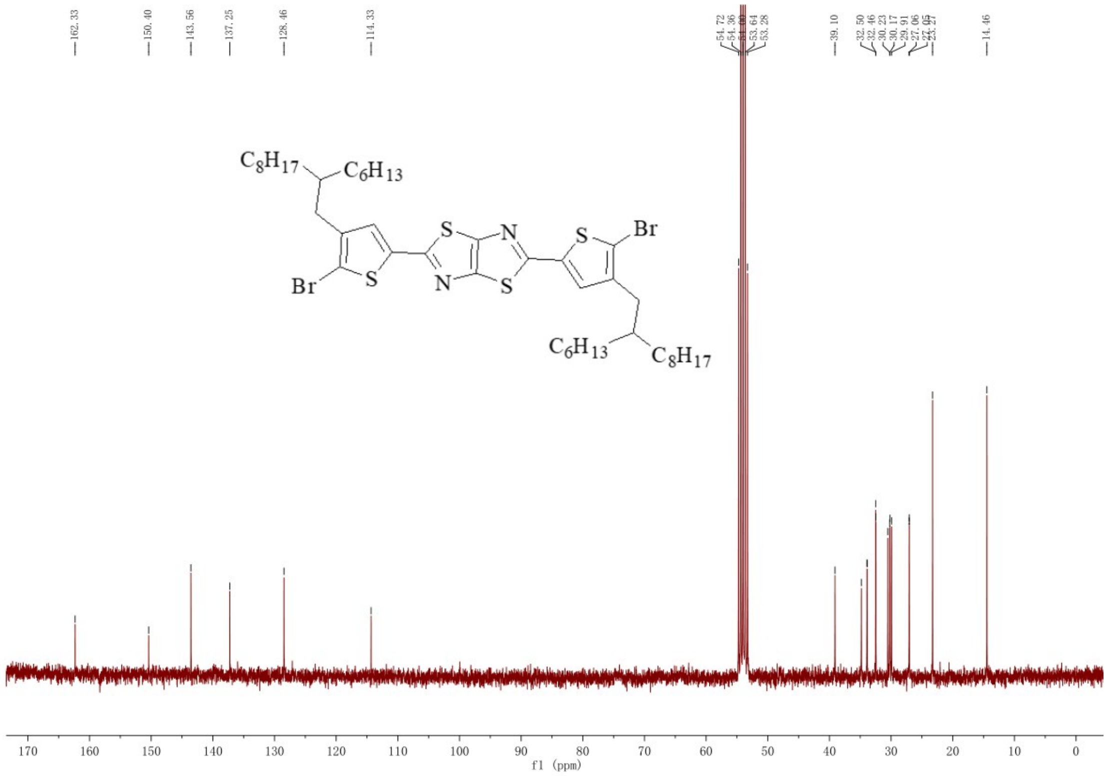

Figure S19. ^{13}C NMR spectrum of compound **8** in CD_2Cl_2.

Table S1. Summary of photovoltaic parameters for the best PCE of the **PBTz-1**:IT-4F-based PSCs with different D:A weight ratios (w/w) under simulated AM 1.5 G (100 mW cm^{-2}) illumination.[(a)]

D:A ratio	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	*PCE* (%)
1.5:1	0.96	7.69	54.20	4.01
1:1	0.96	9.37	54.60	4.91
1:1.5	0.95	8.28	58.62	4.63

(a) **PBTz-1**:IT-4F were dissolved in chlorobenzene solution with a concentration of 10 mg mL^{-1}. The solution was heated to 60 °C until total dissolution. The resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1400-1600 r.m.p. Subsequently, the active layer was annealed at 100 °C for 10 min.

Table S2. Summary of photovoltaic parameters for the best PCE of the **PBTz-1**:IT-4F-based PSCs with different DIO ratio (v/v) under simulated AM 1.5 G (100 mW cm^{-2}) illumination. [(a)]

DIO ratio	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	*PCE* (%)
0	0.96	9.37	54.60	4.91
0.5%	0.94	11.08	58.97	6.14
1%	0.90	10.31	60.60	5.63
2%	0.91	9.05	54.79	4.52

[(a)] **PBTz-1**:IT-4F (1:1 w/w) were dissolved in chlorobenzene solution with a concentration of 10 mg mL^{-1}. The solution was heated to 60 °C until total dissolution. The DIO was added into above solution. After 30 min, the resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1400-1600 r.m.p. Subsequently, the active layer was annealed at 100 °C for 10 min.

Table S3. Summary of photovoltaic parameters for the best PCE of the **PBTz-1**:IT-4F-based PSCs with different annealing temperature under simulated AM 1.5 G (100 mW cm−2) illumination. [(a)]

Annealing temperature (°C)	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	*PCE* (%)
80	0.95	10.81	58.04	5.95
100	0.94	11.08	58.97	6.14
120	0.93	11.12	58.92	6.11
140	0.92	10.58	57.08	5.55
160	0.90	11.05	55.13	5.46

[(a)] **PBTz-1**:IT-4 (1:1 w/w) were dissolved in chlorobenzene solution with a concentration of 10 mg mL^{-1}. The solution was heated to 60 °C until total dissolution. The 0.5% DIO was added into above solution. After 30 min, the resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1500 r.m.p. Subsequently, the active layer was annealed at 80-160 °C for 10 min.

Table S4. Summary of photovoltaic parameters for the best PCE of the **PBTz-2**:IT-4F-based PSCs with different D:A weight ratios (w/w) under simulated AM 1.5 G (100 mW cm^{-2}) illumination.$^{(a)}$

D:A ratio	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	*PCE* (%)
1.5:1	0.96	14.35	68.56	9.52
1:1	0.96	17.88	61.39	10.54
1:1.5	0.95	17.13	55.09	8.99

(a) **PBTz-2**:IT-4F were dissolved in chlorobenzene solution with a concentration of 8 mg mL^{-1}. The solution was heated to 60 ^{o}C until total dissolution. The resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1300-1500 r.m.p. Subsequently, the active layer was annealed at 100 ^{o}C for 10 min.

Table S5. Summary of photovoltaic parameters for the best PCE of the **PBTz-2**:IT-4F-based PSCs with different DIO ratio (v/v) under simulated AM 1.5 G (100 mW cm^{-2}) illumination. $^{(a)}$

DIO ratio	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	*PCE* (%)
0	0.96	17.88	61.39	10.54
0.5%	0.92	19.66	68.82	12.36
1%	0.90	14.66	53.65	7.11
2%	0.89	19.51	53.73	9.31

(a) **PBTz-2**:IT-4F (1:1 w/w) were dissolved in chlorobenzene solution with a concentration of 10 mg mL^{-1}. The solution was heated to 60 ^{o}C until total dissolution. The DIO was added into above solution. After 30 min, the resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1300-1500 r.m.p. Subsequently, the active layer was annealed at 100 ^{o}C for 10 min.

Table S6. Summary of photovoltaic parameters for the best PCE of the **PBTz-2**:IT-4F-based PSCs with different annealing temperature under simulated AM 1.5 G (100 mW cm^{-2}) illumination. [(a)]

Annealing temperature (°C)	V_{OC} (V)	J_{SC} (mA cm^{-2})	*FF* (%)	*PCE* (%)
80	0.92	18.25	66.46	11.20
100	0.92	19.66	68.82	12.36
120	0.91	18.74	63.57	10.80
140	0.90	19.00	56.91	10.40
160	0.89	18.74	58.06	9.71

(a) **PBTz-2**:IT-4F (1:1 w/w) were dissolved in chlorobenzene solution with a concentration of 10 mg mL^{-1}. The solution was heated to 60 °C until total dissolution. The 0.5% DIO was added into above solution. After 30 min, the resulting solution was spin-coated onto PEDOT:PSS modified ITO in succession. The thickness (around 90 nm) of film was controlled the spin-coating speed at 1400 r.m.p. Subsequently, the active layer was annealed at 80-160 °C for 10 min.

Table S7. Hole and electron mobilities for pure and blended films.

Materials	Hole mobilities (cm^2 V^{-1} s^{-1})	Electron mobilities (cm^2 V^{-1} s^{-1})	Hole/Electron
PBTz-1	3.47×10^{-5}		
PBTz-2	1.28×10^{-5}		
PBTz-1:IT-4F	1.05×10^{-5}	3.89×10^{-6}	2.70
PBTz-2:IT-4F	3.14×10^{-5}	2.89×10^{-5}	1.09