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Increased conjugated backbone twisting to improve Carbonylated-Functionalized Polymers Photovoltaic Performance

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EXPERIMENTAL SECTION

Instruments.

^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated solvents on a Bruker DPX 300 or 400. Molecular weight and polydispersity (PDI) of both polymers were estimated by high temperature (145 °C) gel permeation chromatography (GPC) method by using monodispersed polystyrene as standard using o-dichlorobenzene as eluent. Thermogravimetric analysis (TGA) measurement was performed on TGA-2050 Thermogravimetry Analyze. Elemental analysis was performed on an instrument of Flash EA1112. 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/cm2. The EQE spectrum was measured through the Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd., Taiwan).

Measurements

Cyclic Voltammetry (CV): CV was carried out on a computer-controlled GSTAT12 in a threeelectrode 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 Pt wire, a silver wire, and a glassy carbon electrode were used as the counter electrode, reference electrode and working electrode, respectively. The Fc/Fc^+ redox couple was used as an external standard.

Optical characterizations: UV-vis absorption spectra were carried out using a Hitachi U-3100 UV−vis spectrophotometer. The film samples were spin-coated onto quartz plates (1×1 cm^2).

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

X-ray Diffraction（XRD）: Films X-ray diffraction were measured on a theta-theta Philips PW 1820 Kristalloflex diffractometer with a graphite-monochromized Cu-Kα X-ray beam (Cu Kα, λ = 1.5418 Å) hitting the film deposited as described in each case. The diffraction patterns were recorded in the 2θ range from 2^o to 30^o.

Synthetic details: All chemicals and reagents were used as received from commercial sources without further purification. Intermediates 1-(2-bromothiophen-3-yl)-3-ethylheptan-1-one (**1**)[1], 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene (**2**)[2] and 1,1'-(5,5''-dibromo-[2,2':5',2''-terthiophene]-3,3''-diyl)bis(3-ethylheptan-1-one) (**6**)[3] were synthesized according to the literatures.

1,1'-(thieno[3,2-b]thiophene-2,5-diylbis(thiophene-2,3-diyl))bis(3-ethylheptan-1-one) (3)

Compound **1** (2.5 g, 8.2 mmol), compound **2** (1.7 g, 3.7 mmol) and $Pd(PPh_3)_4$ (46.2 mg, 0.04 mmol) were dissolved in 30 mL of anhydrous toluene under argon. The resulting solution was stirred at 100 °C for 16 h. The solvent was removed to afford a dark-red oil, which was purified by column chromatography with dichloromethane: petroleum ether (1:2) as eluent to give 1.9 g (light red solid, 85%) of compound **3**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.61(s, 2H), 7.39 (d, J = 4.0 Hz, 2H), 7.28 (d, J = 4.0 Hz, 2H), 2.72 (d, J = 12.0 Hz, 4H), 1.96 (m, 2H), 1.32-1.19 (m, 16H), 0.84-0.79 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 197.96, 140.86, 140.81, 138.17, 136.72, 129.48, 125.10, 121.31, 46.93, 36.04, 33.28, 28.98, 26.52, 23.08, 14.20, 10.99. HRMS (MALDI) C32H40O2S4: m/z calc. 584.1906, found 584.1900.

5,5'-dibromo-1,1'-([2,2':5',2''-terthiophene]-3,3''-diyl)bis(3-ethylheptan-1-one) (4)

Compound **3** (1.8 g, 3.1 mmol) was dissolved in 15 mL of chloroform at room temperature. NBS (1.2 g, 6.78 mmol) was carefully added into the solution in small batches under dark. The mixture was stirred for 24 h. After removing the solvent under reduced pressure, the residue was purified by column chromatography with dichloromethane: petroleum ether (1:3) as eluent to give monomer **4** as a red solid (2.0 g, 89 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.56 (s, 2H), 7.34 (s, 2H), 2.66 (d, J = 12.0 Hz, 4H), 1.94 (m, 2H), 1.29-1.19 (m, 16H), 0.83-0.79 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 196.43, 141.85, 141.02, 138.41, 135.83, 131.82, 121.65, 112.24, 46.80, 35.88, 33.23, 28.95, 26.49, 23.05, 14.18, 10.97. HRMS (MALDI) C32H37Br2O2S4 [-H]: m/z calcd.739.0049, found 739.0045.

Synthesis of PBTCO-TT

(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (**5**, 0.3 mmol), monomer **4**, chlorobenzene (7 mL) were placed in a 50 mL two-neck flask with a condenser. The mixture was protected by blowing a stream of argon for 10 min. Afterwards, the $Pd(PPh_3)_4$ (0.03 mmol, 36.7 mg) was added. The mixture was heated to 115 ^oC for 20 h. After cooling to room temperature, the reaction mixture was poured into vigorously stirred methanol (100 mL). The polymer was filtered and subjected to Soxhlet extraction with methanol, acetone, hexane and chloroform. The chloroform fraction was collected and dried in vacuum to afford dark-red solid (278 mg, 80 %). Molecular weight by GPC (145 ^oC): M_n = 18.7 kg mol^{-1}, $Đ$ = 2.0. Elemental analysis: Calcd. for C64H78O4S7: C 67.70, H 6.93; found: C 67.65, H 6.93.

Synthesis of PBTCO-T

Monomer **5** (0.3 mmol), monomer **6**, chlorobenzene (7 mL) were placed in a 50 mL two-neck flask with a condenser. The mixture was protected by blowing a stream of argon for 10 min. Afterwards, the $Pd(PPh_3)_4$ (0.03 mmol, 36.7 mg) was added. The mixture was heated to 120 ^oC for 24 h. After cooling to room temperature, the reaction mixture was poured into vigorously stirred methanol (100 mL). The polymer was filtered and subjected to Soxhlet extraction with methanol, acetone, hexane and chloroform. The chloroform fraction was collected and dried in vacuum to afford dark-red solid (275 mg, 83 %). Molecular weight by GPC (145 °C): M_n = 18.6 kg mol^{-1}, $Đ$ = 2.1. Elemental analysis: Calcd. for C64H78O4S7: C 67.70, H 6.93; found: C 67.65, H 6.93.

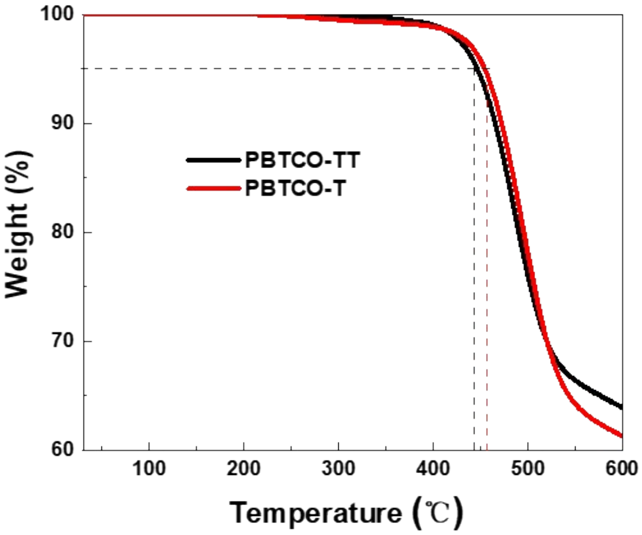


Figure S1. TGA curves for **PBTCO-TT** and **PBTCO-T** measured under a nitrogen atmosphere at a heating rate of 10 °C/min.

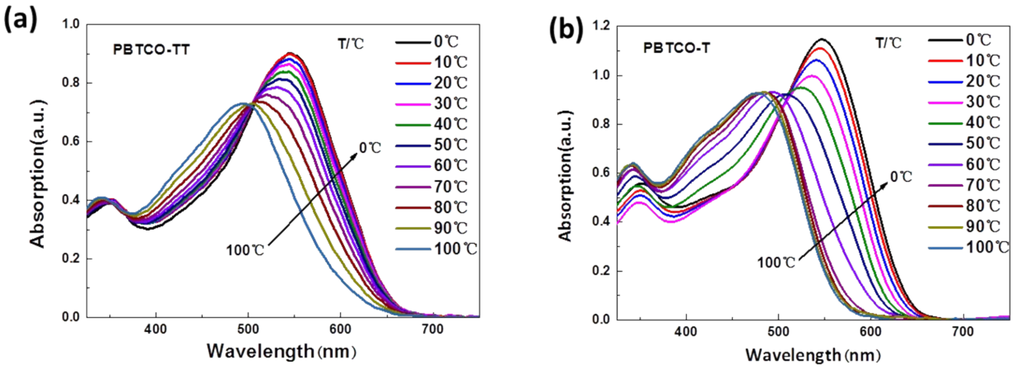


Figure S2. The temperature-dependent absorption spectra of (a) **PBTCO-TT** and (b) **PBTCO-T** in chlorobenzene.

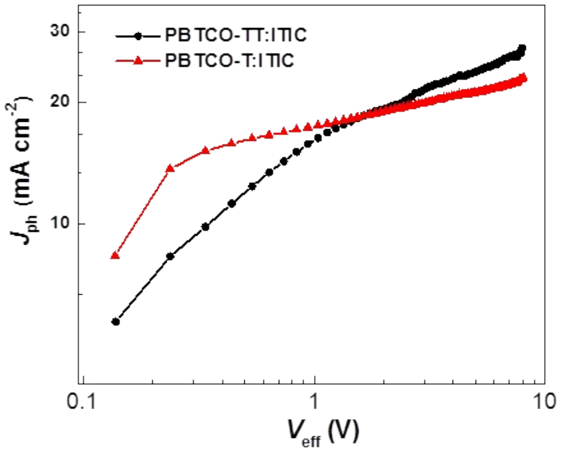


Figure S3. The J_{ph} plotted with respect to effective bias curves of the optimized **PBTCO-TT**: ITIC and **PBTCO-T**: ITIC-based devices.

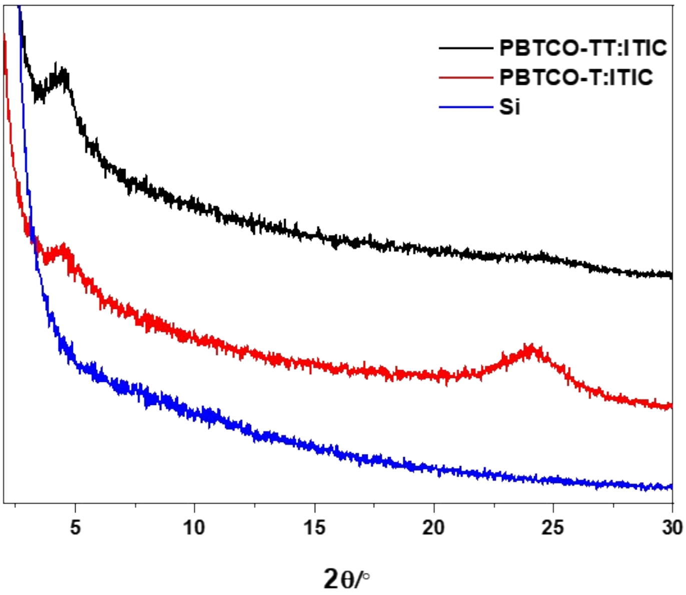


Figure S4. The x-ray diffraction profiles of **PBTCO-TT**: ITIC and **PBTCO-T**: ITIC films.

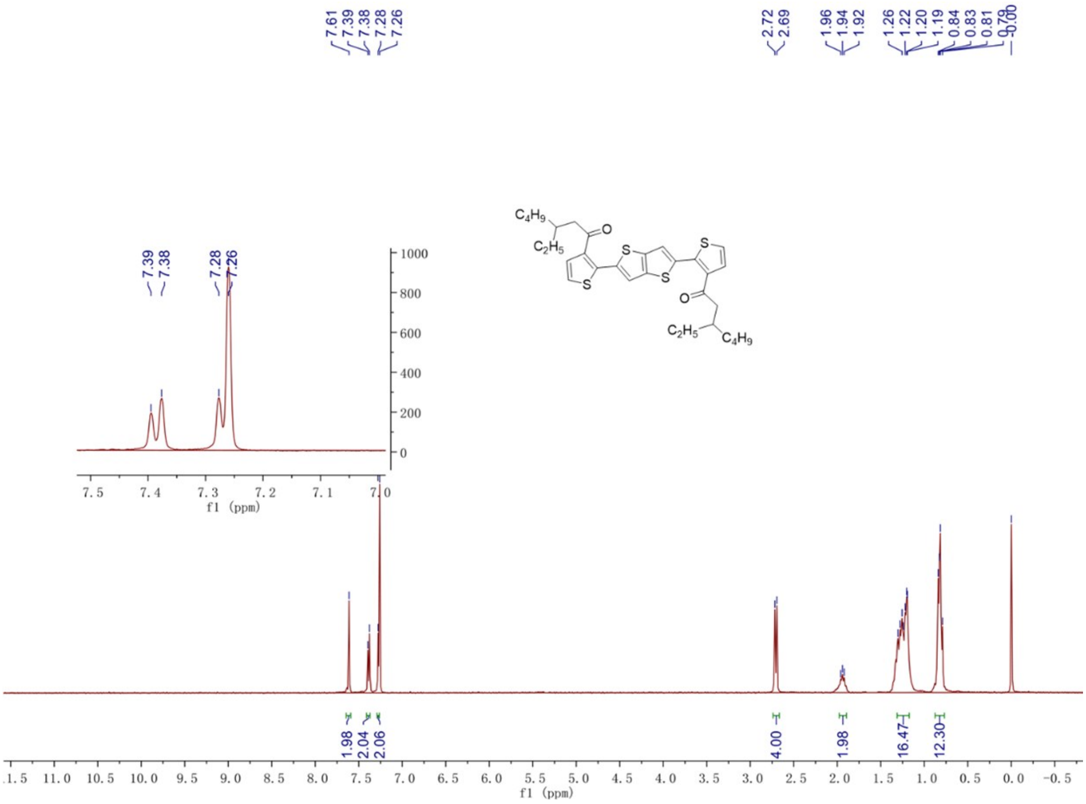


Figure S5. The ^{1}H-NMR of compound **3** in the $CDCl_3$.

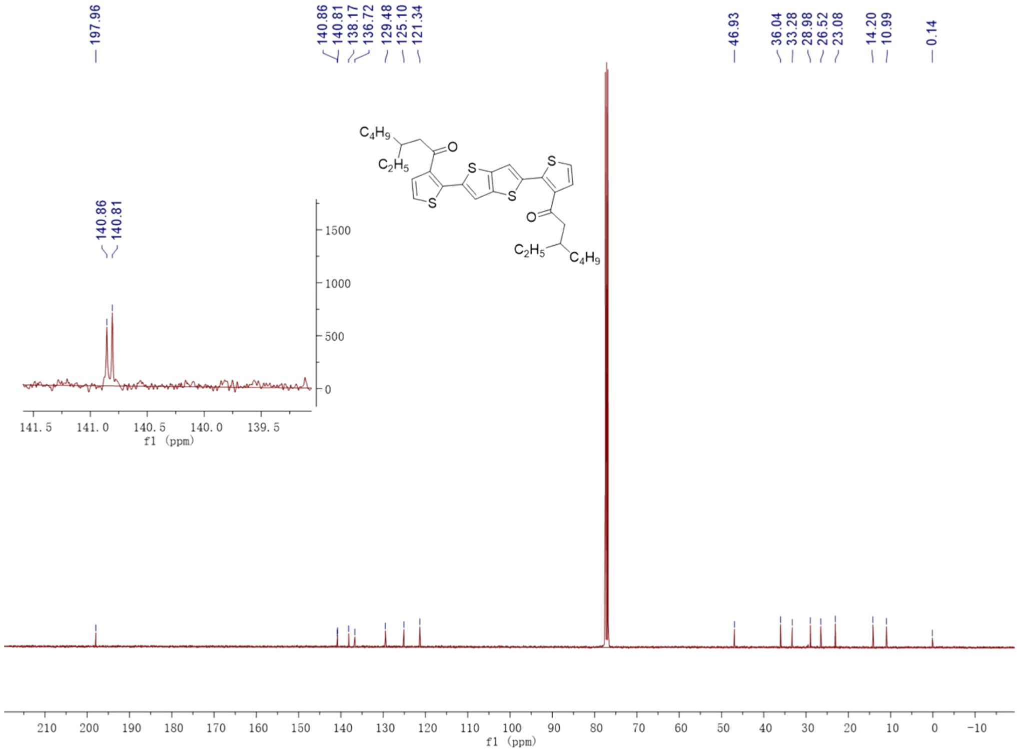


Figure S6. The ^{13}C-NMR of compound **3** in the $CDCl_3$.

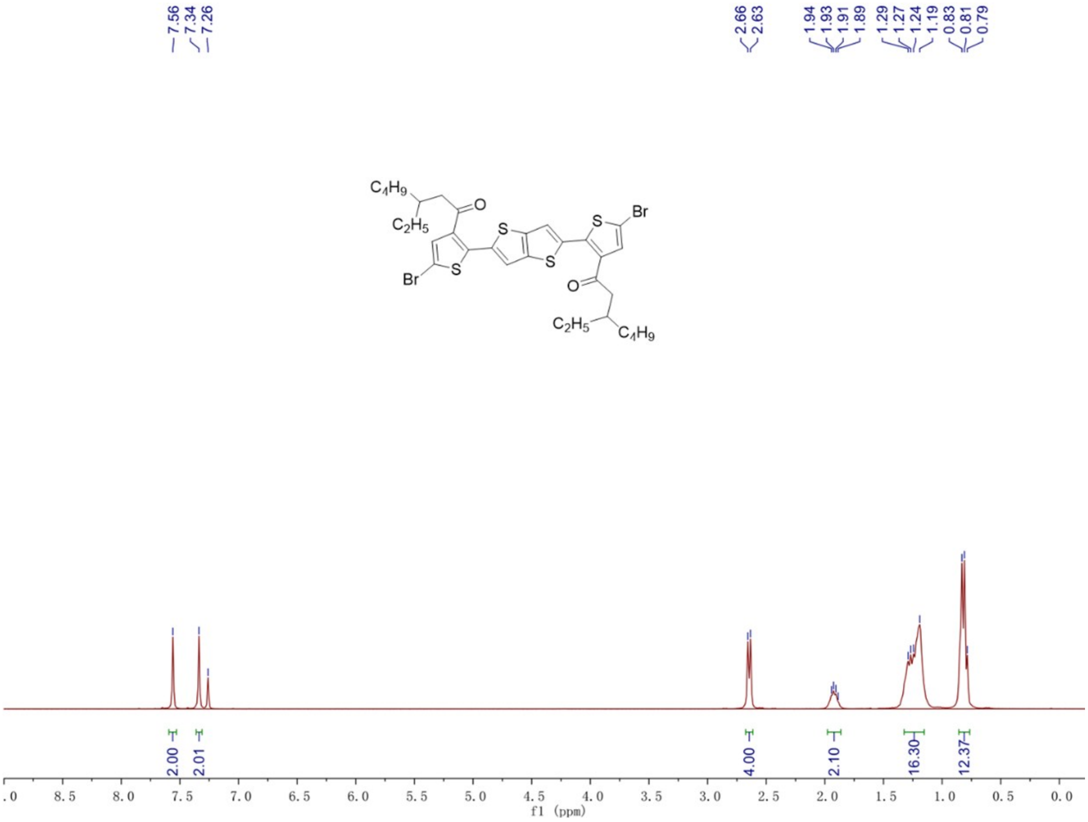


Figure S7. The ^{1}H-NMR of compound **4** in the $CDCl_3$.

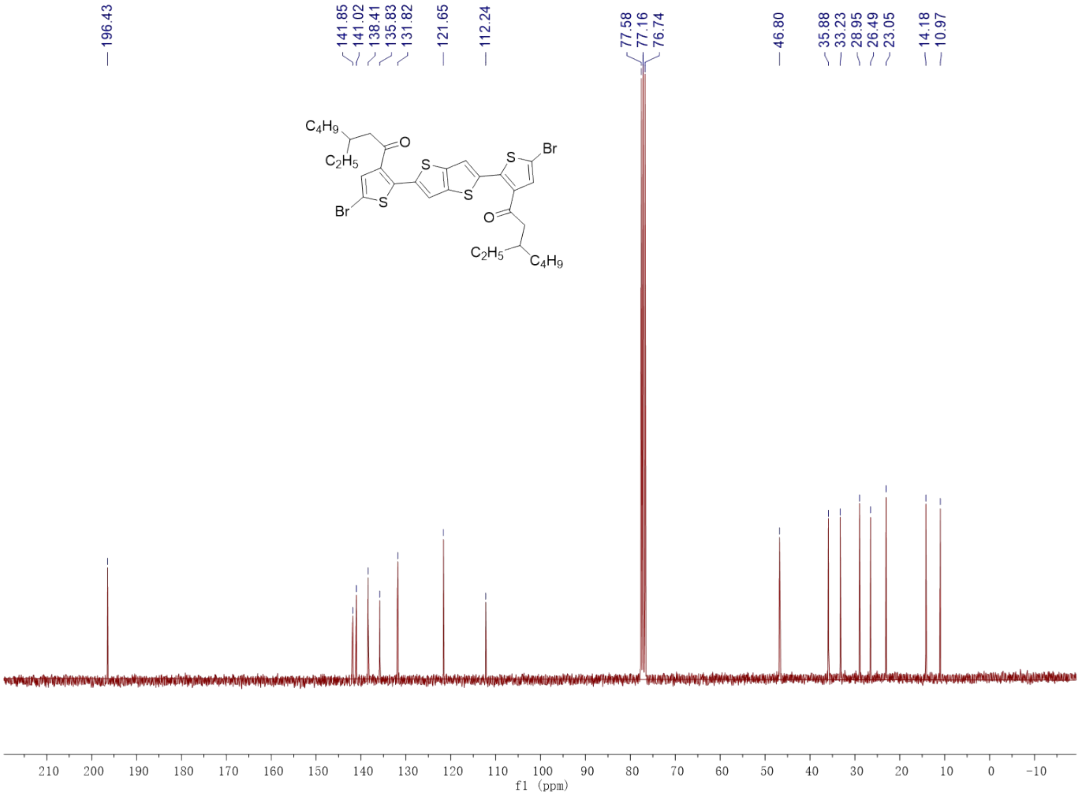
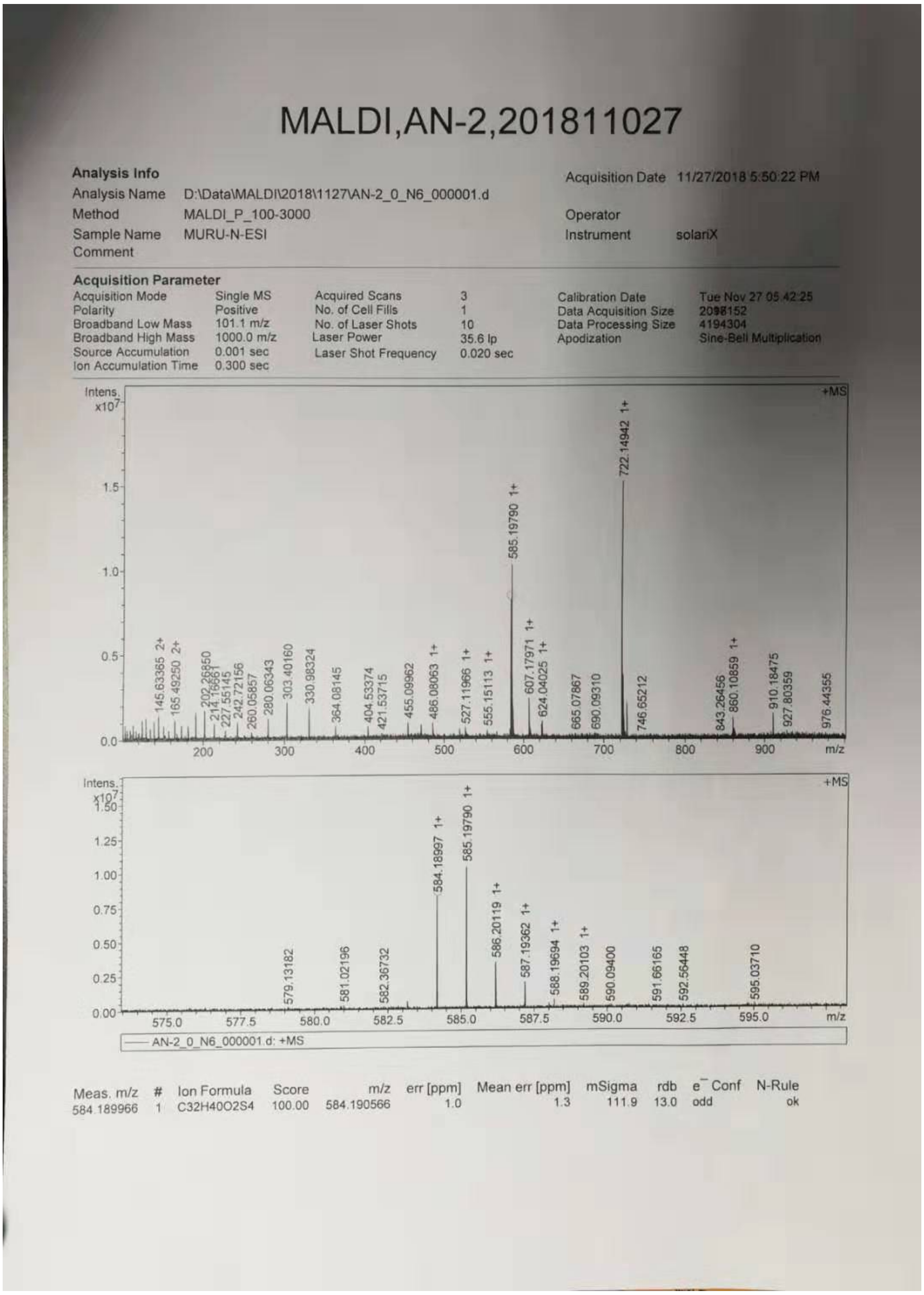


Figure S8. The ^{13}C-NMR of compound **4** in the $CDCl_3$.



MALDI,AN-2,201811027

Analysis Info

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Method MALDI_P_100-3000
Sample Name MURU-N-ESI
Comment
Acquisition Date 11/27/2018 5:50:22 PM
Operator
Instrument solariX

Acquisition Parameter

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Broadband High Mass 1000.0 m/z
Source Accumulation 0.001 sec
Ion Accumulation Time 0.300 sec
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No. of Laser Shots 10
Laser Power 35.6 lp
Laser Shot Frequency 0.020 sec
Calibration Date Tue Nov 27 05:42:25
Data Acquisition Size 2098152
Data Processing Size 4194304
Apodization Sine-Bell Multiplication

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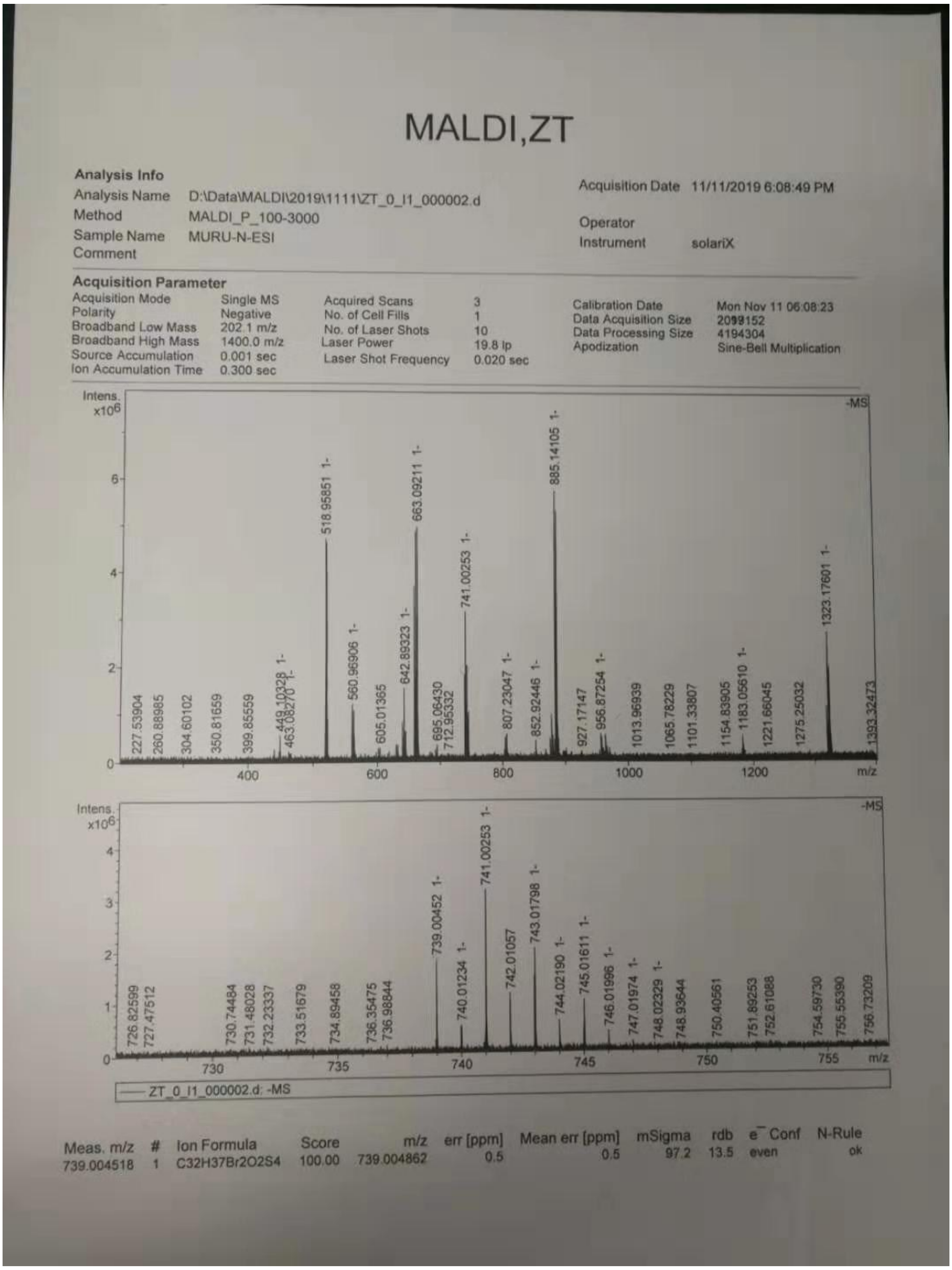
Figure S9. The HRMS of compound **3**.



MALDI,ZT

Analysis Info

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Sample Name	MURU-N-ESI	Instrument	solariX
Comment			

Acquisition Parameter

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Broadband High Mass	1400.0 m/z	Laser Power	19.8 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
739.004518	1	C32H37Br2O2S4	100.00	739.004862	0.5	0.5	97.2	13.5	even	ok

Figure S9. The HRMS of compound **4**.

Table S1. Summary of photovoltaic parameters for the best PCE of **PBTCO-TT**: ITIC-based devices with different D: A weight ratios (w/w).

D:A ratio	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
1.5:1	0.863	12.09	41.30	4.31
1:1	0.863	13.02	43.32	4.88
1:1.5	0.875	11.79	45.02	4.62

Note: **PBTCO-TT**: ITIC were dissolved in chlorobenzene solution with a concentration of 10 mg mL^{-1}. The solution was heated to 50 °C until total dissolution. The resulting solution was spin-coated onto PEDOT: PSS modified ITO in succession. The thickness (around 100 nm) of film was controlled the spin-coating speed at 1500-2000 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 **PBTCO-TT**: ITIC-based devices with different DIO ratios.

DIO ratio	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
0	0.865	13.02	43.32	4.88
0.5%	0.881	13.01	46.31	5.31
1%	0.865	13.16	41.22	4.69

Note: **PBTCO-TT**: ITIC (1:1 w/w) were dissolved in chlorobenzene solution with a concentration of 10 mg mL^{-1}. The solution was heated to 50 °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 100 nm) of film was controlled the spin-coating speed at 1500-2000 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 **PBTCO-TT**: ITIC -based devices with different annealing temperatures.

Annealing temperature (°C)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
80	0.884	13.05	41.54	4.79
100	0.881	13.01	46.31	5.31
120	0.882	12.98	42.24	4.84
140	0.882	12.15	42.56	4.56
160	0.881	11.97	42.82	4.52

Note: **PBTCO-TT**: ITIC (1:1 w/w) were dissolved in chlorobenzene solution with a concentration of 10 mg mL^{-1}. The solution was heated to 50 °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 100 nm) of film was controlled the spin-coating speed at 1500-2000 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 **PBTCO-T**:ITIC-based devices with different D:A weight ratios (w/w).

D:A ratio	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
1.5:1	0.960	15.92	62.26	9.52
1:1	0.960	16.46	63.52	10.03
1:1.5	0.961	15.72	60.66	9.17

Note: **PBTCO-T**: ITIC were dissolved in chlorobenzene solution with a concentration of 10 mg mL^{-1}. The solution was heated to 50 °C until total dissolution. The resulting solution was spin-coated onto PEDOT: PSS modified ITO in succession. The thickness (around 100 nm) of film was controlled the spin-coating speed at 1500-2000 r.m.p. Subsequently, the active layer was annealed at 100 °C for 10 min.

Table S5. Summary of photovoltaic parameters for the best PCE of **PBTCO-T**:ITIC- based devices with different DIO ratios.

DIO ratio	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
0	0.960	16.46	63.52	10.03
0.5%	0.959	16.21	66.89	10.40
1%	0.970	16.23	55.91	8.80
2%	0.990	12.80	46.16	5.85

Note: **PBTCO-T**: ITIC (1:1 w/w) were dissolved in chlorobenzene solution with a concentration of 10 mg mL^{-1}. The solution was heated to 50 ^{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 100 nm) of film was controlled the spin-coating speed at 1500-2000 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 **PBTCO-T**:ITIC -based devices with different annealing temperatures.

Annealing temperature (^{o}C)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
80	0.961	16.94	62.87	10.23
100	0.959	16.21	66.89	10.40
120	0.957	16.51	64.12	10.13
140	0.956	15.62	64.53	9.64
160	0.955	15.52	65.27	9.67

Note: **PBTCO-T**: ITIC (1:1 w/w) were dissolved in chlorobenzene solution with a concentration of 10 mg mL^{-1}. The solution was heated to 50 ^{o}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 100 nm) of film was controlled the spin-coating speed at 1500-2000 r.m.p. Subsequently, the active layer was annealed at 80-160 ^{o}C for 10 min.

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