

Supporting Information

Benzo[1,2-*d*:4,5-*d'*]bisthiazole-based wide-bandgap copolymer semiconductor for efficient fullerene-free organic solar cells with a small energy loss of 0.50 eV

Nai-Yu Chen, Qihui Yue, Wenrui Liu, Hao-Li Zhang* and Xiaozhang Zhu*

Experimental Section

Materials and General Methods:

All reactions involving air- or moisture-sensitive compounds were carried out in a dry reaction vessel under a positive pressure of nitrogen. Unless stated otherwise, starting materials were obtained from Adamas, Aldrich, or J&K and were used without further purification. Anhydrous THF and toluene were distilled over Na/benzophenone prior to use. Anhydrous DMF was distilled over CaH₂ prior to use. Compounds **1**¹, **4**², **5**³ and polymer **PTZ1** were prepared according to published procedures. ¹H and ¹³C NMR spectra were measured with Bruker Fourier 300, Bruker Avance 400, or Bruker Avance 600 spectrometers. Chemical shifts for hydrogens are reported in parts per million (ppm, scale) downfield from tetramethylsilane and are referenced to the residual protons in the NMR solvent (CDCl₃: 7.26). ¹³C NMR spectra were recorded at 100 MHz. Chemical shifts for carbons are reported in parts per million (ppm, scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent (CDCl₃: 77.2). The data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances, br = broad), coupling constant in hertz (Hz), and integration. MALDI measurements were performed with a MALDI-FT 9.4 T, Bruker solariX, or MALDI-TOF MS Bruker Autoflex III. Elemental analyses were performed with a Flash EA 1112 Series from ThermoQuest. UV-vis was recorded with Jasco V-570 spectrometers. Cyclic voltammetry (CV) was performed with a CHI620D potentiostat. All measurements were carried out in a one-compartment cell under a nitrogen atmosphere, equipped with a glassy-carbon electrode, a platinum counter-electrode, and an Ag/Ag⁺ reference

electrode with a scan rate of 100 mV s^{-1} . The supporting electrolyte was a 0.1 mol/L dichloromethane solution of tetrabutylammonium perchlorate (TBAP). All potentials were corrected against Fc/Fc^+ . CV was measured with a scan rate of 100 mV s^{-1} . Thermogravimetric analysis (TGA) was performed with a Shimadzu DTG 60 instrument at a heating rate of 10 C min^{-1} under a nitrogen atmosphere with runs recorded from room temperature to $500 \text{ }^\circ\text{C}$.

Device Fabrication:

Device fabrication: Devices were fabricated with a conventional structure of ITO/PEDOT:PSS/active layer/PDINO/Al. ITO-coated glass substrates ($15 \text{ } \Omega \text{ sq}^{-1}$) were cleaned by sequential ultrasonication in soap deionized water, deionized water, acetone, and isopropanol. The washed substrates were further treated with oxygen plasma for 20 min to eliminate any remaining organic component. A thin layer (ca. 30 nm) of PEDOT:PSS was first spin-coated on the ITO substrates at 3,000 r.p.m. and baked at $150 \text{ }^\circ\text{C}$ for 30 min in air. The substrates were then transferred into a nitrogen-filled glovebox. Subsequently, the active layer was spin-coated on the PEDOT:PSS layer from a chloroform solution of 9 mg ml^{-1} **BBTA/PZT1** and 9 mg ml^{-1} **ZITI-2Br** at various spin rates. The resulting film thickness was measured via a surface profilometer (Dektak XT, Bruker). Here, thermal annealing (TA) was used to optimize the blend morphology and promote device performance. Then, 1 mg ml^{-1} PDINO in methanol was spin-coated on the active layer. At the final stage, aluminum (100 nm) was thermally evaporated onto the active layer as the top electrode. Shadow masks were used to define the OSC active area (0.05 cm^2) of the devices.

Device Characterization:

The current density–voltage (J – V) characteristics of photovoltaic devices were measured under N_2 using a Keithley 2400 source meter. A 300 W xenon arc solar simulator (Oriel) with an AM 1.5 global filter operated at 100 mW cm^{-2} was used to simulate the AM 1.5G solar irradiation. The illumination intensity was corrected by using a silicon photodiode with a protective KG5 filter calibrated by the National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE) was performed using certified IPCE equipment from Enlitech, Taiwan.

Mobility Characterization:

Space charge-limited currents were tested in electron-only devices with a configuration of ITO/ZnO/active layer/PFN/Al and hole-only devices with a configuration of ITO/PEDOT:PSS/active layer/MoO₃/Ag. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC current with field dependent mobility, which is described as

$$J = \frac{9\varepsilon_0\varepsilon_r\mu_0V^2}{8L^3} \quad (1)$$

Where J is the current, μ_0 is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, V is the effective voltage, and L is the thickness of the active layer. From the plots of $J^{0.5}$ vs V , hole and electron mobilities can be deduced.

Synthetic part

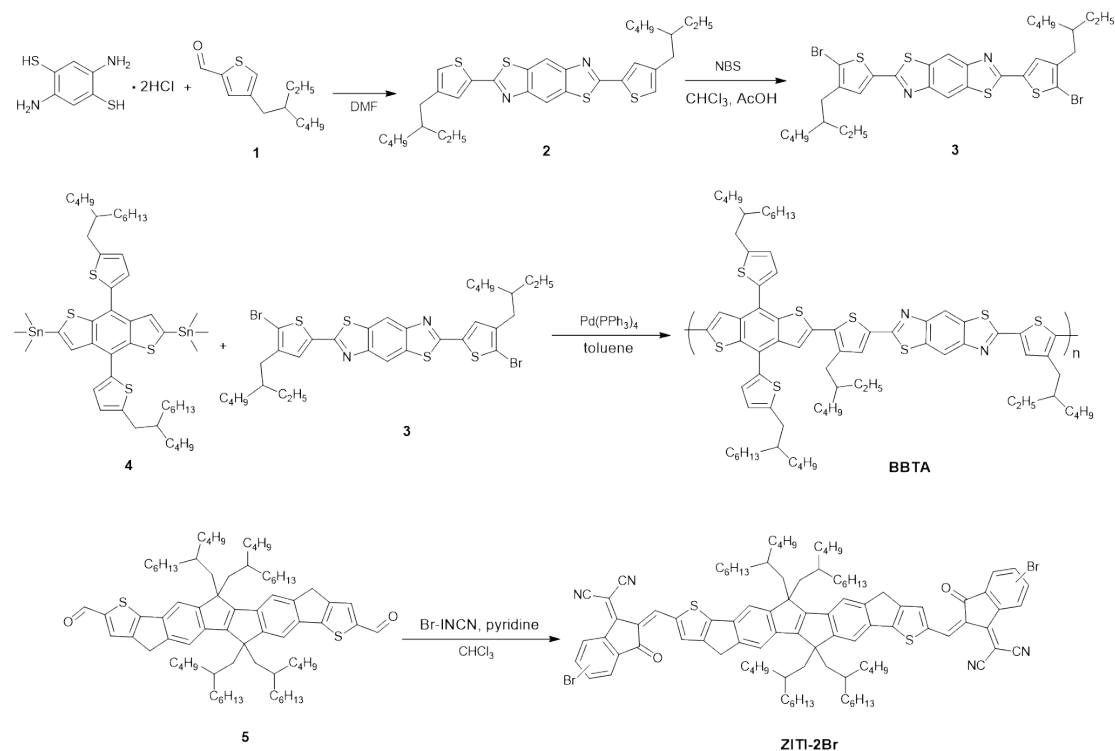


Fig. S1. Synthesis routes of **BBTa** and **ZITI-2Br**.

2,6-bis(4-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*d*:4,5-*d'*]bisthiazole (2).

In a Schlenk flask equipped with a magnetic stirrer were placed 4-(2-ethylhexyl)thiophene-2-carbaldehyde (1, 718 mg, 3.2 mmol, 2.0 eq.), 2,5-

diaminobenzene-1,4-dithiol bis-hydrochloride (392.3 mg, 1.6 mmol, 1.0 eq.) and anhydrous *N,N*-dimethylformamide (16 mL, 0.1M). The resulting solution was refluxed at 160°C and stirred for 1 day. Then, it was cooled at room temperature and the precipitate was collected by filtration, washed with ethanol and hexane to obtain 243 mg of benzobisthiazole **2** as a flaky yellowish solid (0.42 mmol, 26% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.42 (s, 1H), 7.49 (s, 1H), 7.11 (s, 1H), 2.59 (d, J = 6.9 Hz, 2H), 1.42 – 1.17 (m, 9H), 0.91 (dd, J = 9.3, 5.5 Hz, 7H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 162.35, 151.68, 143.38, 136.55, 134.17, 130.68, 125.56, 114.76, 40.31, 34.45, 32.41, 28.85, 25.58, 23.01, 14.12, 10.82. HRMS (MALDI-TOF) calcd for C₃₂H₄₁N₂S₄ [M+1]⁺: 581.2147, found, 581.2144.

2,6-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*d*:4,5-*d'*]bisthiazole (3).

In a Schlenk flask equipped with a magnetic stirrer, 2,6-bis(4-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*d*:4,5-*d'*]bisthiazole (**2**, 464.7 mg, 0.8 mmol, 1.0 eq.) and *N*-bromosuccinimide (356 mg, 2 mmol, 2.5 eq.) were dissolved in a 20mL glacial acetic acid/CHCl₃ = 1 : 1.2 mixture solvent. The resulting reaction mixture was shielded from light and stirred overnight at room temperature. The precipitate was collected by filtration, washed with water, ethanol and hexane, and then dried to afford 508.2 mg of dibromide **3** as a yellowish solid (0.69 mmol, 86% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.40 (s, 1H), 7.33 (s, 1H), 2.55 (d, J = 7.2 Hz, 2H), 1.66 (d, J = 6.0 Hz, 1H), 1.35 (dd, J = 14.5, 7.3 Hz, 9H), 0.96 – 0.84 (m, 7H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 161.30, 151.63, 142.80, 136.31, 134.11, 129.93, 115.30, 114.91, 39.94, 33.85, 32.43, 28.75, 25.67, 23.02, 14.11, 10.82. HRMS (MALDI-TOF) calcd for C₃₂H₃₉Br₂N₂S₄ [M+1]⁺: 737.0357, found, 737.0361.

Polymer BBTA.

In a 15 mL pressure tube, (4,8-bis(5-(2-butyloctyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) **4** (123.2 mg, 0.12 mmol) and 2,6-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*d*:4,5-*d'*]bisthiazole **3** (89.5 mg, 0.12 mmol) were dissolved in 4 mL toluene. After being purged with argon for 20 min, 6.4

mg (4.6 mol%) of Pd(PPh₃)₄ was added into the tube as the catalyst, and then the reaction mixture was purged with argon for another 30 min. The reaction mixture was stirred and heated to reflux (110°C) for 12 h under an argon atmosphere. When the reaction mixture was cooled down to room temperature, the polymer was precipitated by addition of methanol, collected by filtration and then subjected to Soxhlet extraction with methanol, hexane, and chloroform in the end. The polymer was recovered as a scarlet solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum. The yield was 95%. GPC: M_w = 35.27 K; M_n = 16.24 K; PDI = 2.17.

Compound **ZITI-2Br**.

Br-INCN (73.7 mg, 0.27 mmol) and compound **5** (50 mg, 0.045 mmol) were added to a solvent mixture of chloroform (10 mL) and pyridine (5 drops). The reaction was placed in an oil bath at 75 °C and was stirred for 18 hours. The mixture was directly purified on a silica-gel column chromatography using chloroform as eluent to give 49 mg of **ZITI-2Br** as reddish brown solid (0.03 mmol, 66% yield). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.98 (s, 2H), 8.81 (s, 1H), 8.54 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 1.5 Hz, 1H), 7.91 (s, 2H), 7.85 (dd, J = 8.1, 4.0 Hz, 2H), 7.82 – 7.76 (m, 3H), 7.75 (s, 1H), 7.56 (s, 2H), 3.88 (s, 5H), 2.13 (s, 9H), 1.16 – 0.51 (m, 111H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 187.33, 186.91, 164.86, 159.85, 159.26, 158.87, 156.87, 148.31, 142.49, 141.31, 140.05, 139.81, 139.50, 138.01, 138.14, 138.01, 137.47, 137.14, 135.49, 134.40, 129.90, 129.33, 128.10, 126.66, 126.35, 124.50, 120.10, 117.18, 116.78, 114.76, 68.62, 68.09, 54.08, 42.84, 35.09, 34.81, 34.53, 34.02, 33.93, 33.63, 31.88, 29.73, 28.32, 27.61, 26.03, 25.10, 23.05, 22.68, 14.18, 13.67. HRMS (MALDI-TOF): calcd for C₁₀₀H₁₁₉Br₂N₄O₂S₂ [M+1]⁺: 1629.7136, found, 1629.7127; Anal. Calcd for C₁₀₀H₁₁₈Br₂N₄O₂S₂ (%): C, 73.6; H, 7.29; N, 3.43; found: C, 72.90; H, 7.62; N, 3.30.

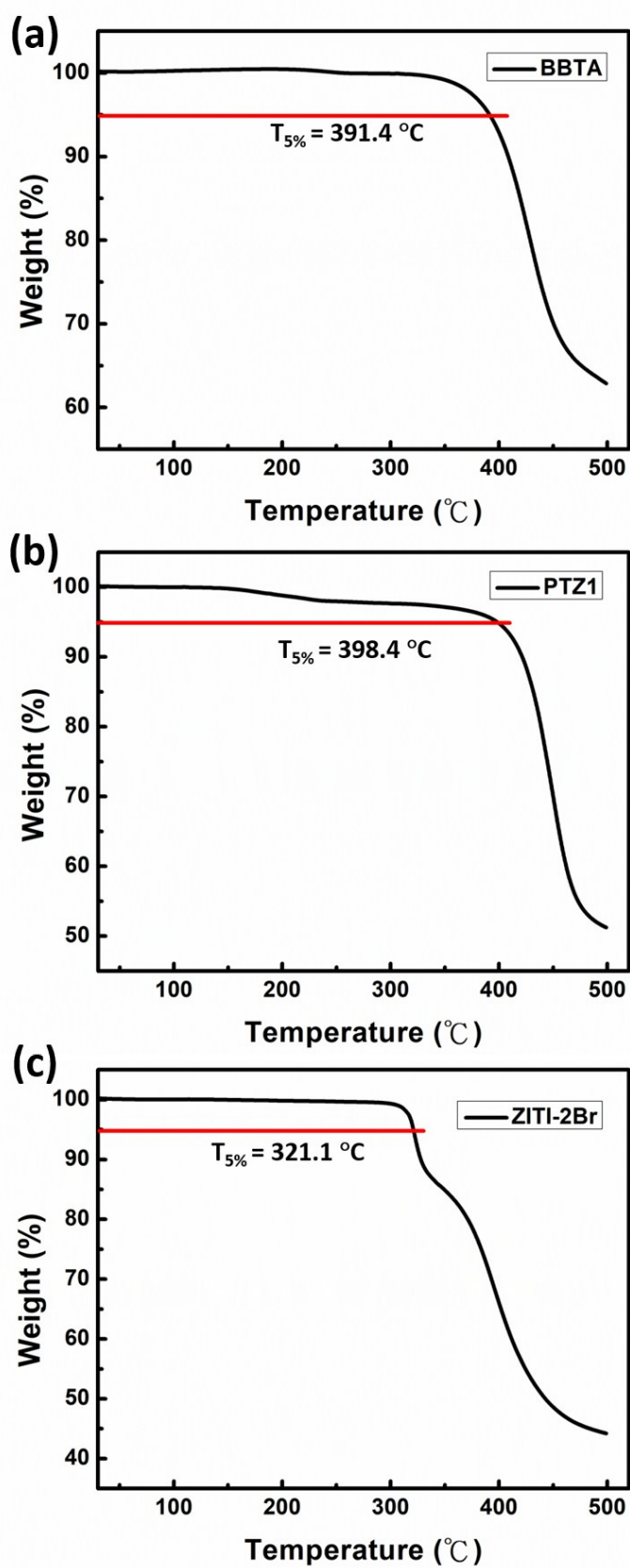


Fig. S2. Thermal gravimetric analysis (TGA) curve of (a) **BBTA**; (b) **PTZ1** and (c) **ZITI-2Br**.

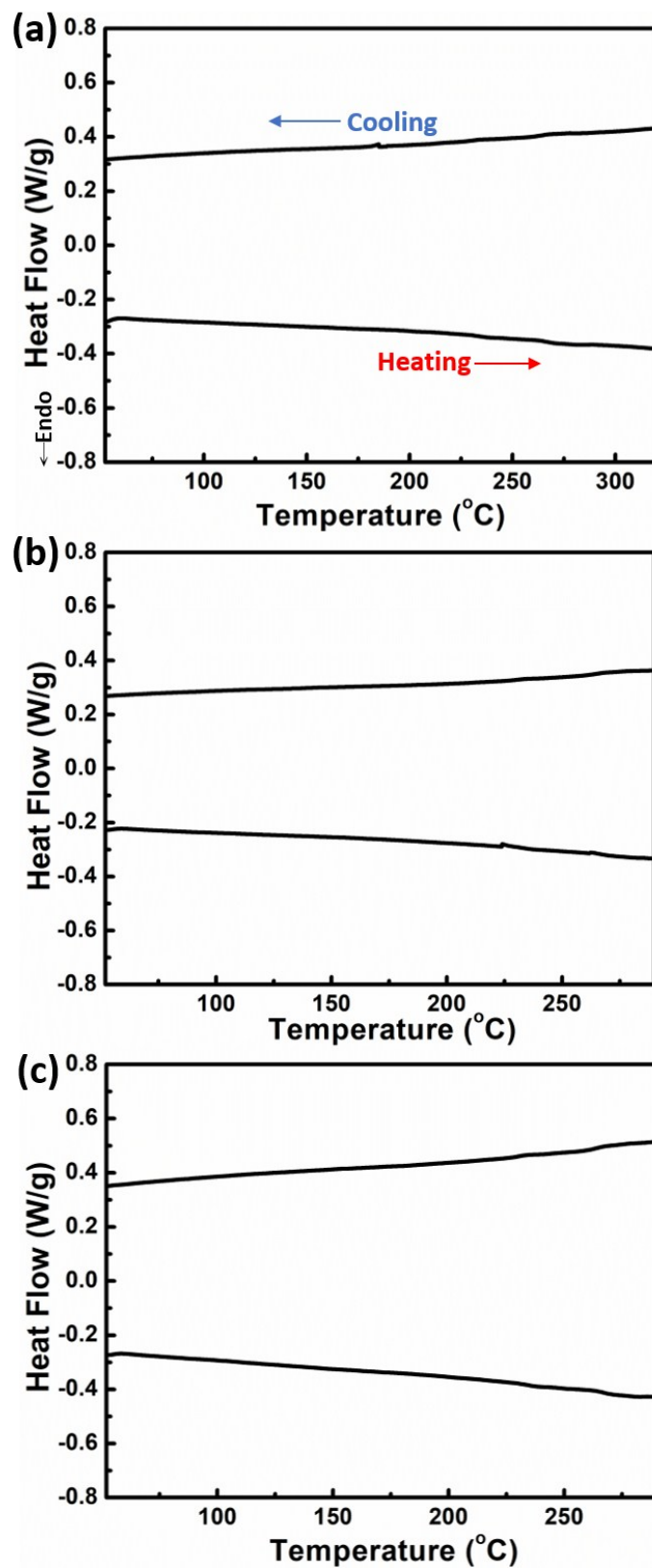


Fig. S3. Differential scanning calorimetry (DSC) curve of (a) **BBTA**; (b) **PTZ1** and (c) **ZITI-2Br**.

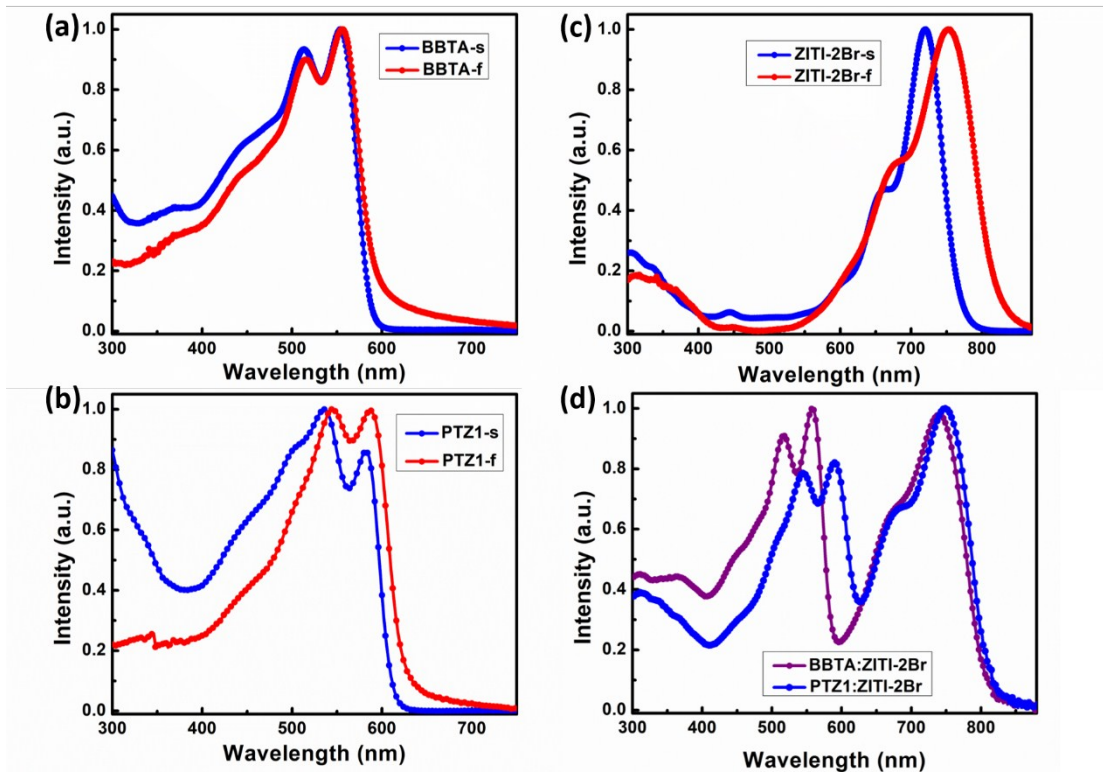


Fig. S4. UV-vis absorption spectra of (a) BBTA; (b) PTZ1 and (c) ZITI-2Br in chloroform solution and thin film (d) BBA:ZITI-2Br, PTZ1:ZITI-2Br active layers film

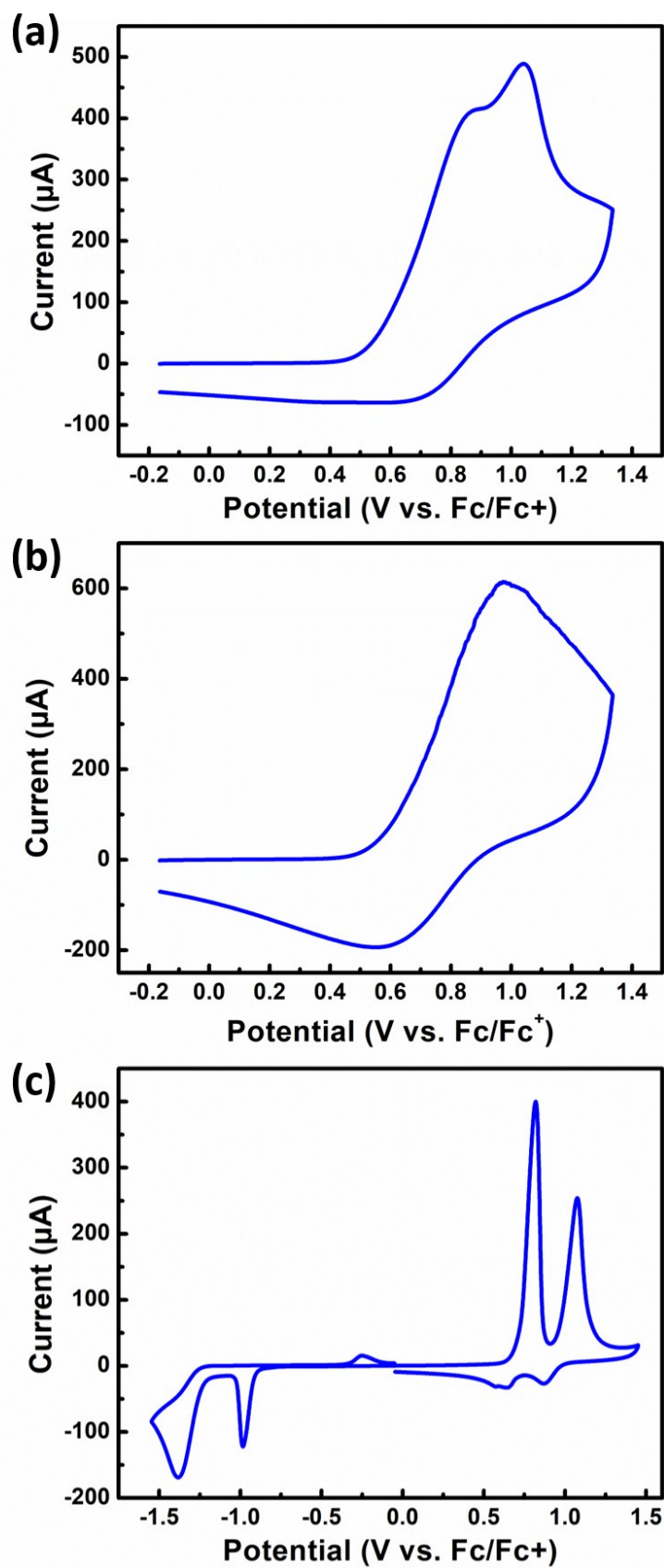


Fig. S5. Cyclic voltammogram of (a) **BBT_a**; (b) **PTZ1** and (c) **ZITI-2Br** film in diluted CH₃CN solution with a scan rate of 100 mV s⁻¹.

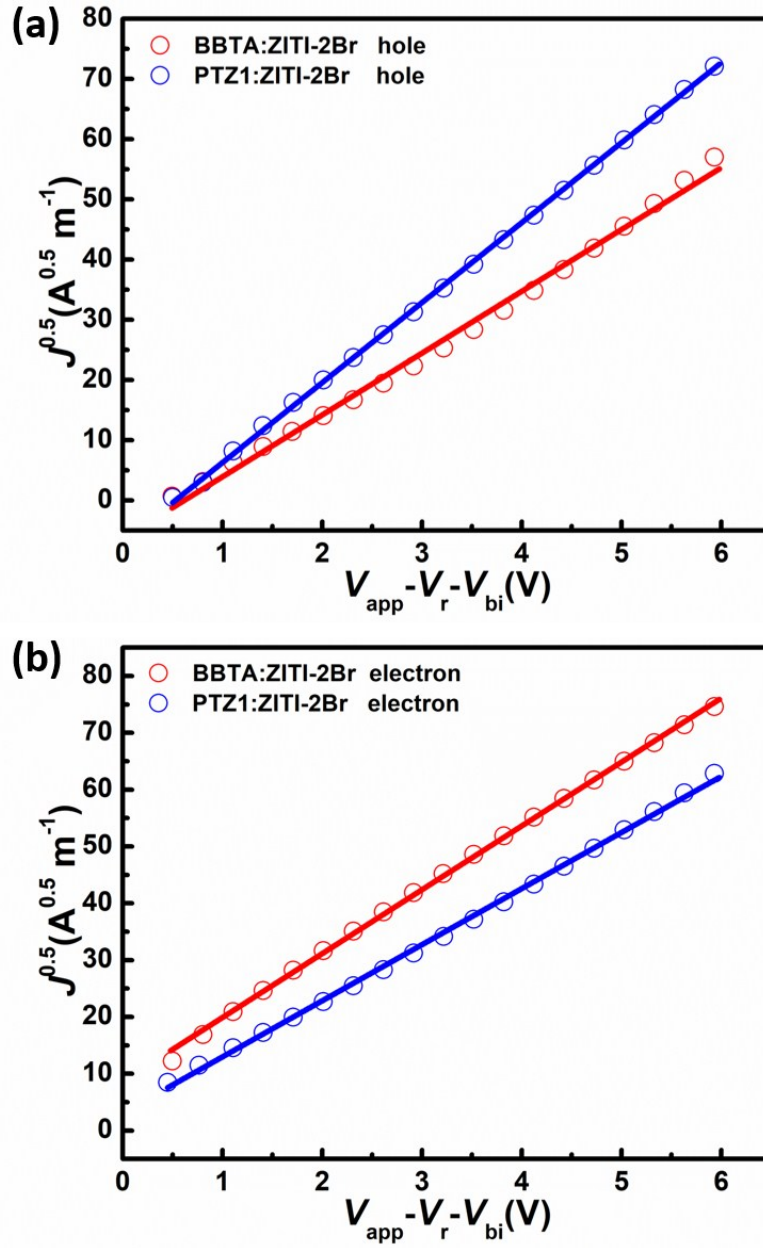


Fig. S6. $J^{0.5}$ - V curves for the (a) hole-only and (b) electron-only devices based on **BBTA:ZITI-2Br** and **PTZ1:ZITI-2Br** (1:1, w/w) with thermal annealing at 110°C for 10 min.

Table S1. The device performance parameters for the OPVs based on **BBTA:ZITI-2Br** with different D/A ratios and thermal annealing for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm⁻².

D : A	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
1 : 0.5	0.99	15.93	53.44	8.43(8.37±0.04)
1 : 0.8	0.99	17.15	59.29	10.01(9.92±0.09)
1 : 1	1.00	17.63	63.10	11.08(10.99±0.12)

1 : 1.2	0.99	17.70	62.23	10.76(10.65±0.11)
1 : 1.5	0.94	14.90	52.72	8.18(8.04±0.13)

Table S2. The device performance parameters for the OPVs based on **BBTA:ZITI-2Br** at 1:1 weight ratio with thermal annealing for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm⁻².

Treatment	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
As-cast	1.02	14.82	53.78	8.14(8.04±0.07)
90°C	1.01	16.67	61.79	10.27(10.15±0.11)
110°C	1.00	17.63	63.10	11.08(10.99±0.12)
130°C	0.97	17.54	61.92	10.56(10.40±0.12)

Table S3. Effect of the active layer thickness on the device performance parameters for the OPVs based on **BBTA:ZITI-2Br** at 1:1 weight ratio with thermal annealing at 110°C for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm⁻².

Thickness (nm)	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
85	0.99	17.14	63.41	10.74(10.61±0.12)
100	1.00	17.63	63.10	11.08(10.99±0.12)
120	0.99	18.00	59.43	10.57(10.41±0.11)

Table S4. The device performance parameters for the OPVs based on **PTZ1:ZITI-2Br** with different D/A ratios and thermal annealing for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm⁻².

D : A	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
1 : 0.5	0.94	15.15	60.04	8.53(8.46±0.05)
1 : 0.8	0.94	15.73	65.21	9.64(9.55±0.13)
1 : 1	0.94	16.82	62.45	9.86(9.68±0.08)
1 : 1.2	0.94	16.98	58.20	9.24(9.16±0.10)
1 : 1.5	0.93	15.20	53.69	7.69(7.61±0.09)

Table S5. The device performance parameters for the OPVs based on **PTZ1:ZITI-2Br** at 1:1 weight ratio with thermal annealing for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm⁻².

Treatment	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
As-cast	0.96	15.53	57.31	8.54(8.39±0.14)
70°C	0.95	16.13	60.00	9.19(9.10±0.08)
90°C	0.94	16.82	62.45	9.86(9.68±0.08)

110°C	0.92	15.18	60.73	8.51(8.41±0.16)
-------	------	-------	-------	-----------------

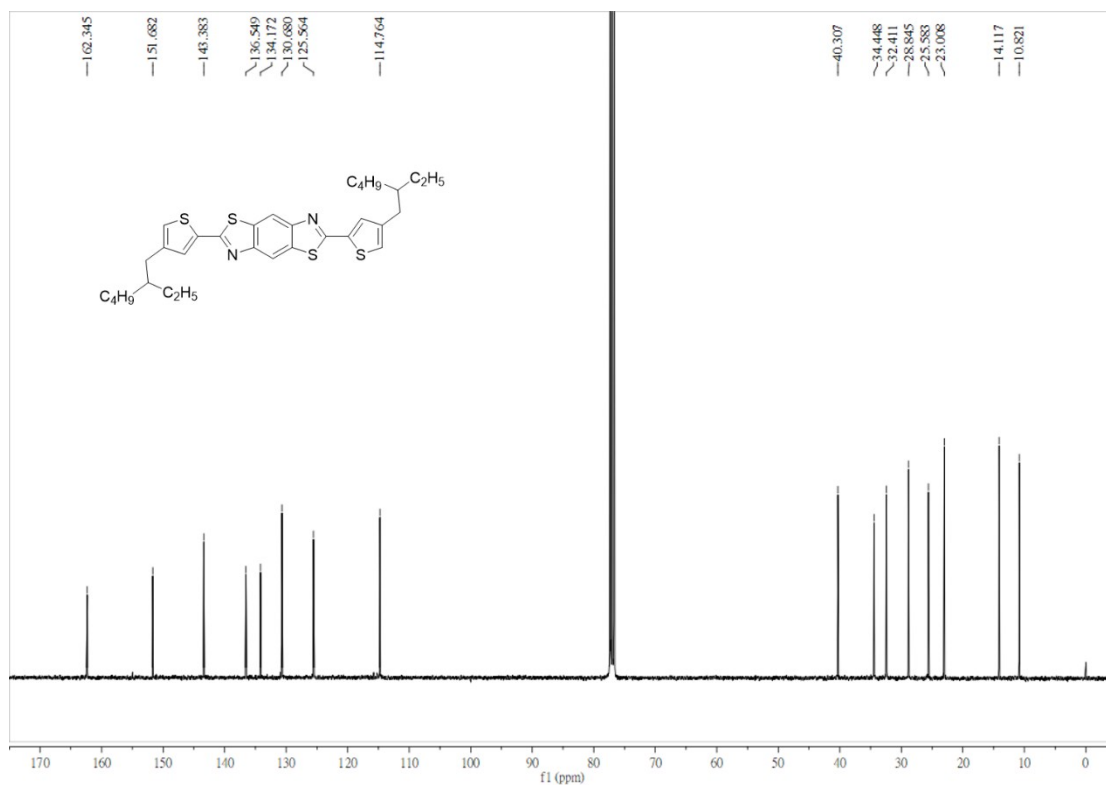
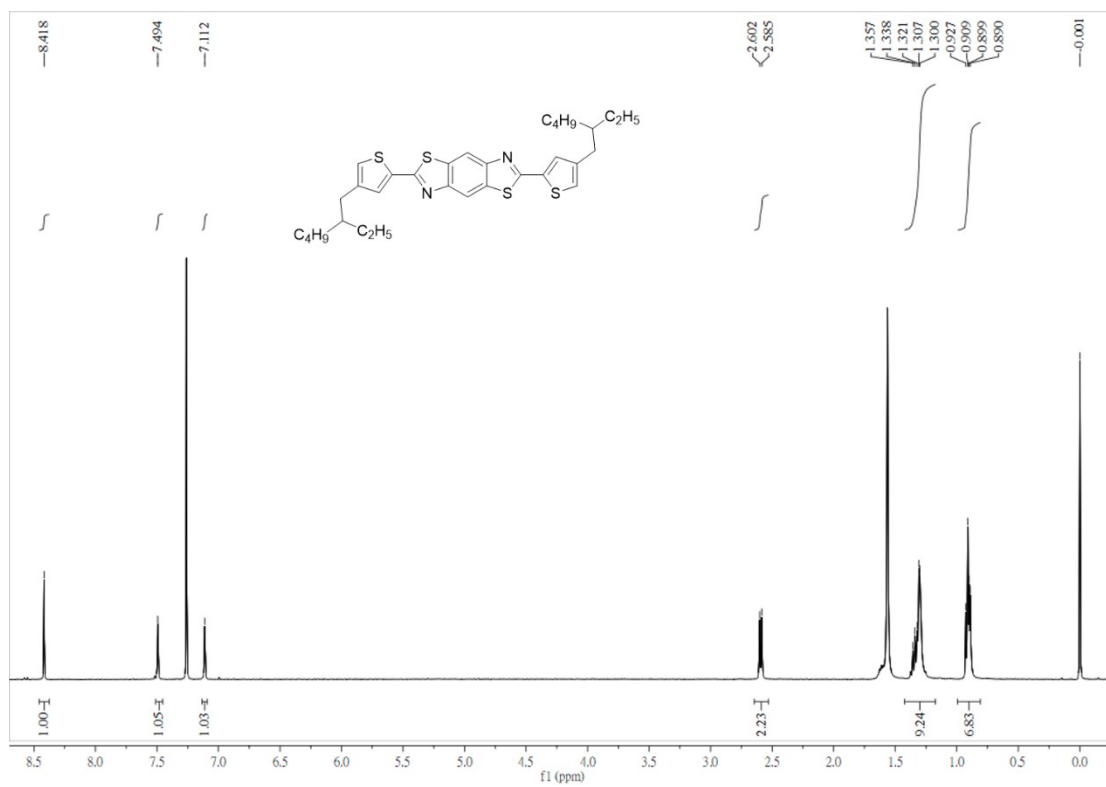
Table S6. Effect of the active layer thickness on the device performance parameters for the OPVs based on **PTZ1:ZITI-2Br** at 1:1 weight ratio with thermal annealing at 90°C for 10 minutes, under the irradiation of AM 1.5G, 100 mW cm⁻².

Thickness (nm)	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
85	0.93	15.41	64.49	9.24(9.17±0.08)
100	0.94	16.82	62.45	9.86(9.68±0.08)
120	0.94	16.91	60.01	9.44(9.35±0.09)

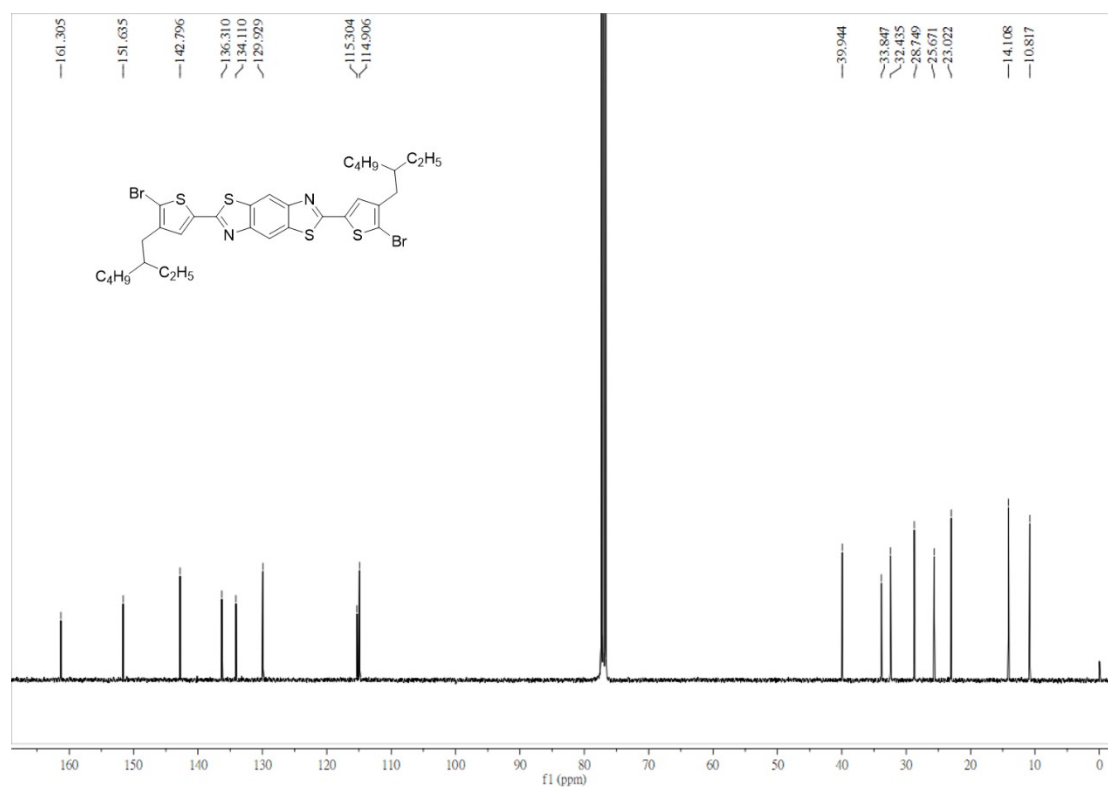
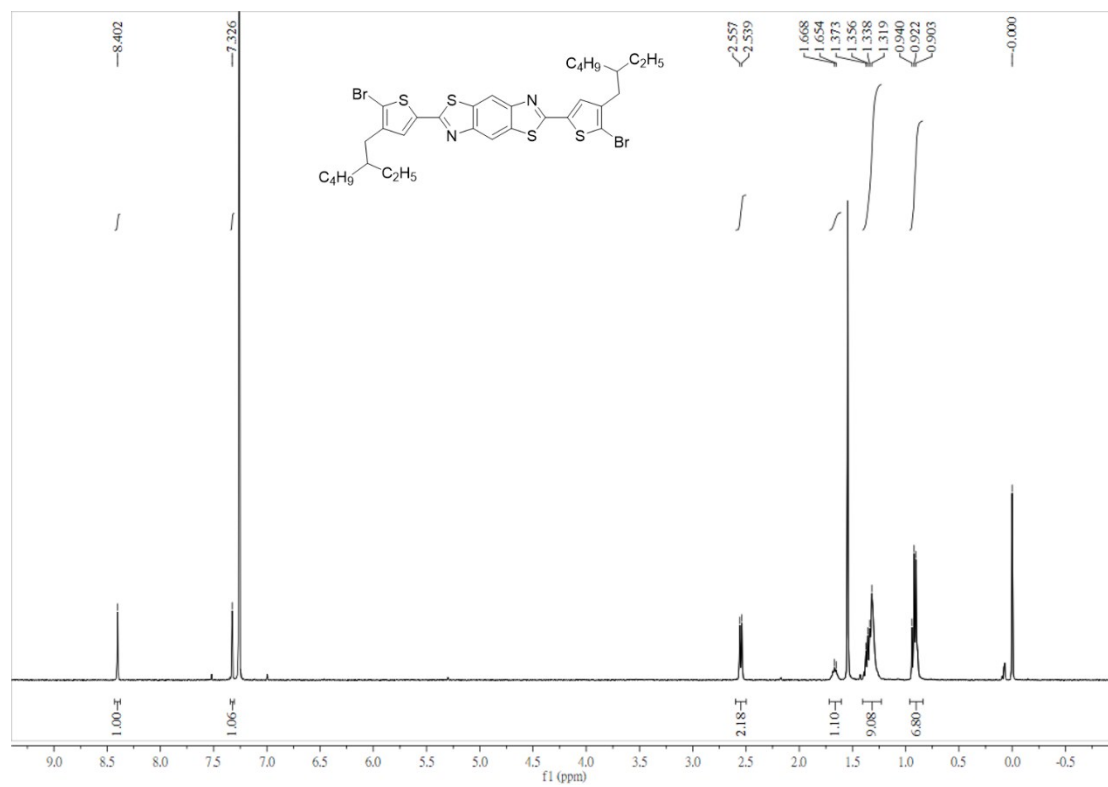
Table S7. The device performance parameters for the OPVs based on **BBTA:PC₇₁BM** at 1:2.5 weight ratio with different treatments, *o*-DCB as solvent, under the irradiation of AM 1.5G, 100 mW cm⁻².

Treatment	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
As-cast	0.87	6.93	57.42	3.46(3.38±0.11)
90°C	0.88	7.51	57.71	3.81(3.71±0.07)
110°C	0.87	6.96	58.93	3.59(3.51±0.09)
0.5% DIO	1.00	6.04	59.53	3.58(3.50±0.05)
2.5% DIO	0.99	8.06	63.34	5.04(4.97±0.07)

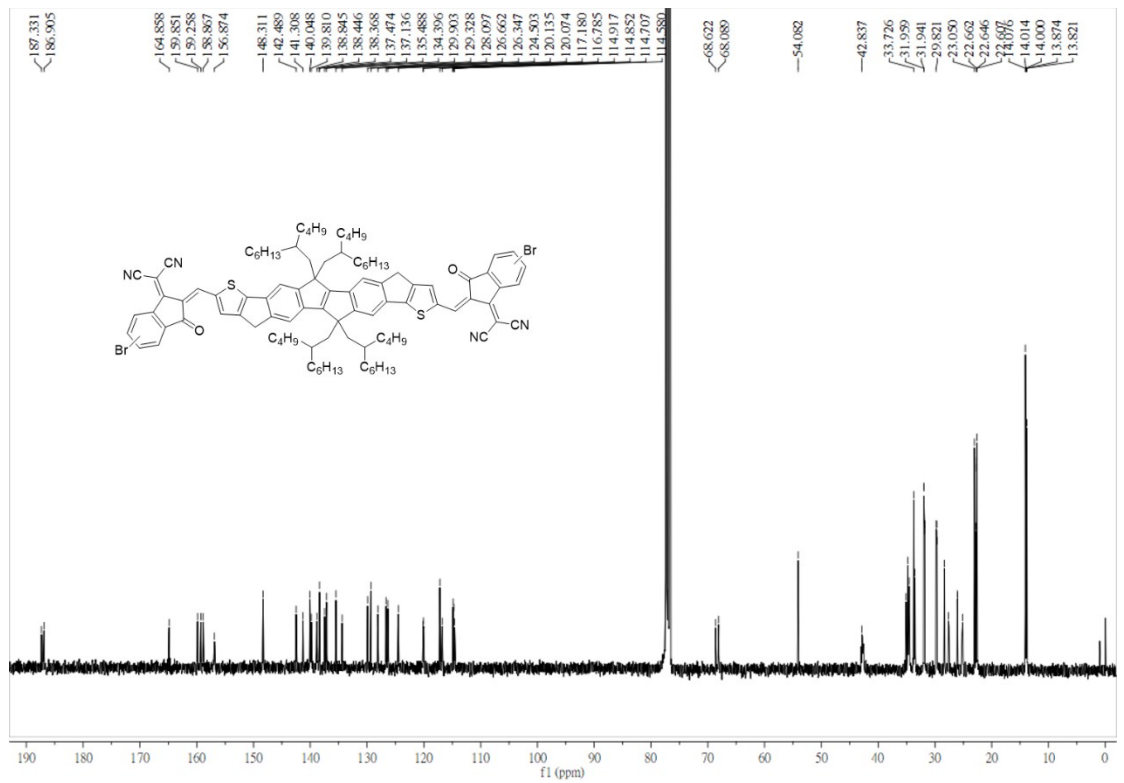
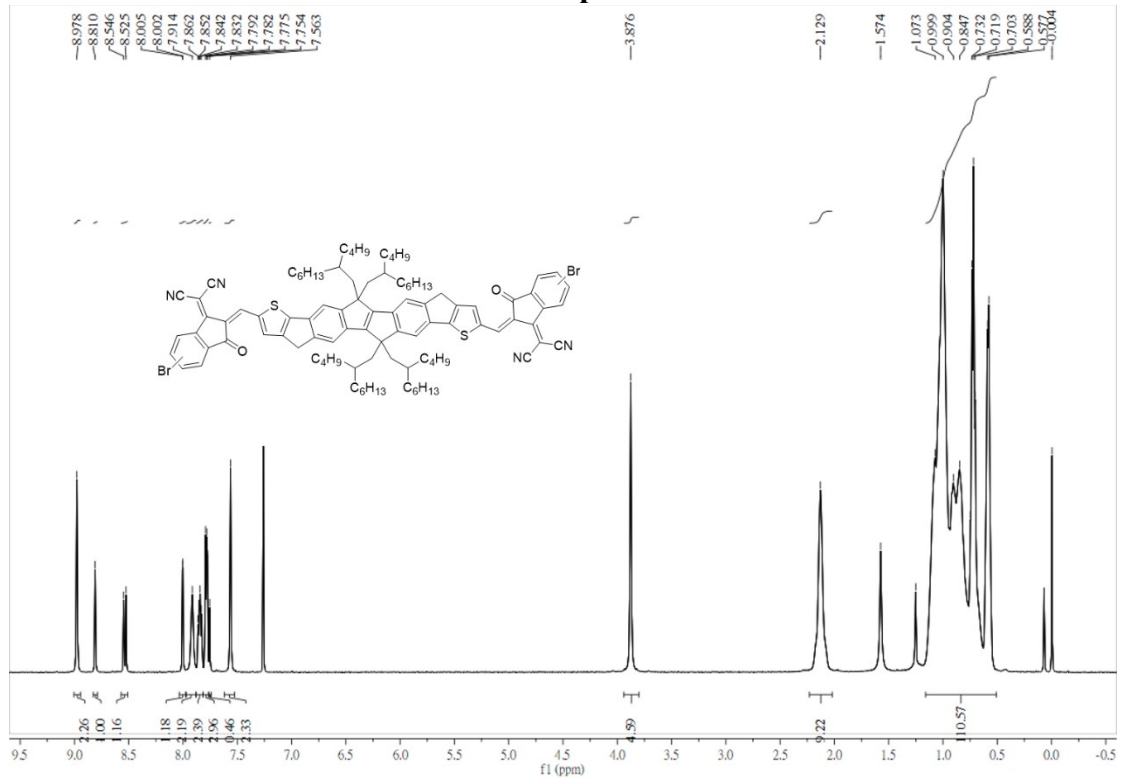
**^1H NMR and ^{13}C NMR spectrum of
2,6-bis(4-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-d:4,5-d']bisthiazole (2).**



^1H NMR and ^{13}C NMR spectrum of 2,6-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-d:4,5-d']bisthiazole (3).



¹HNMR and ¹³CNMR spectrum of ZITI-2Br



MALDI, BBTA, 20180904

Analysis Info

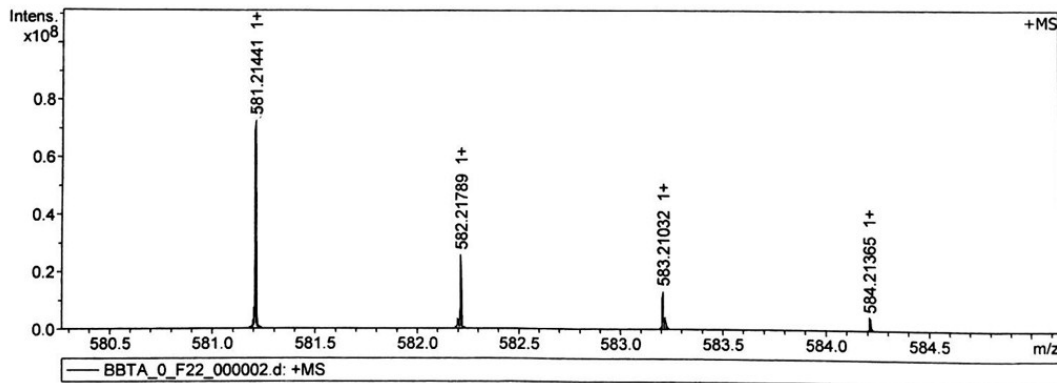
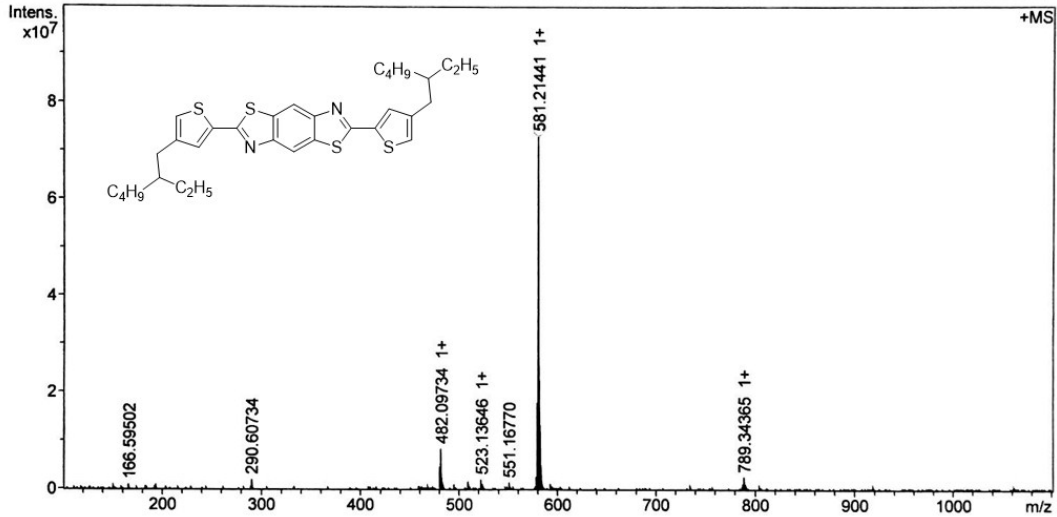
Analysis Name D:\Data\MALDI\2018\0904\BBTA_0_F22_000002.d
 Method MALDI_P_100-3000
 Sample Name MURU-N-ESI
 Comment

Acquisition Date 9/4/2018 6:14:33 PM

Operator
 Instrument solariX

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	2	Calibration Date	Tue Sep 4 06:11:15 2018
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	101.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	1100.0 m/z	Laser Power	32.8 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
581.214407	1	C ₃₂ H ₄₁ N ₂ S ₄	100.00	581.214710	-0.5	0.9	34.0	13.5	even	ok

MALDI, BBTAO, 20180607

Analysis Info

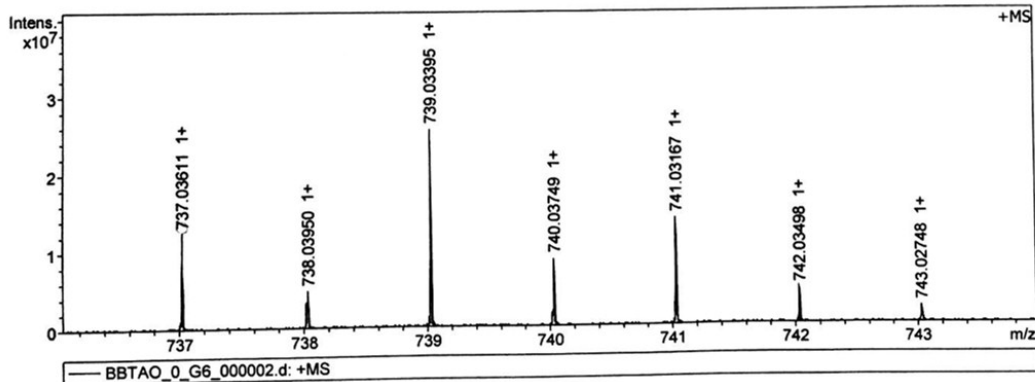
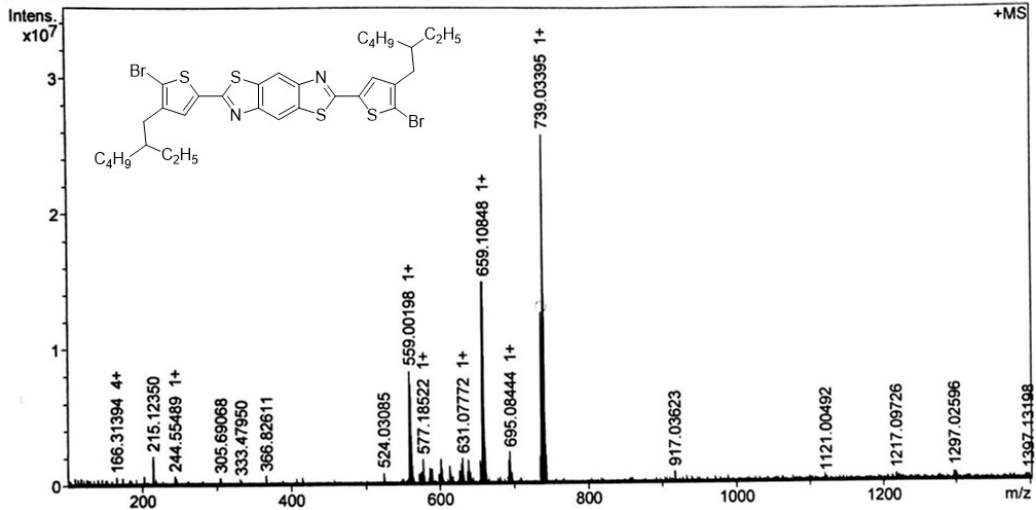
Analysis Name D:\Data\MALDI\2018\0608\BBTAO_0_G6_000002.d
 Method MALDI_P_100-3000
 Sample Name MURU-N-ESI
 Comment

Acquisition Date 6/8/2018 4:08:02 PM

Operator
 Instrument solariX

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	3	Calibration Date	Fri Jun 8 03:38:07 2018
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2097152
Broadband Low Mass	101.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	1400.0 m/z	Laser Power	24.4 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
737.036106	1	C ₃₂ H ₃₉ Br ₂ N ₂ S ₄	100.00	737.035734	0.5	-0.3	52.0	13.5	even	ok

MALDI,ZITI-BR,20180711

Analysis Info

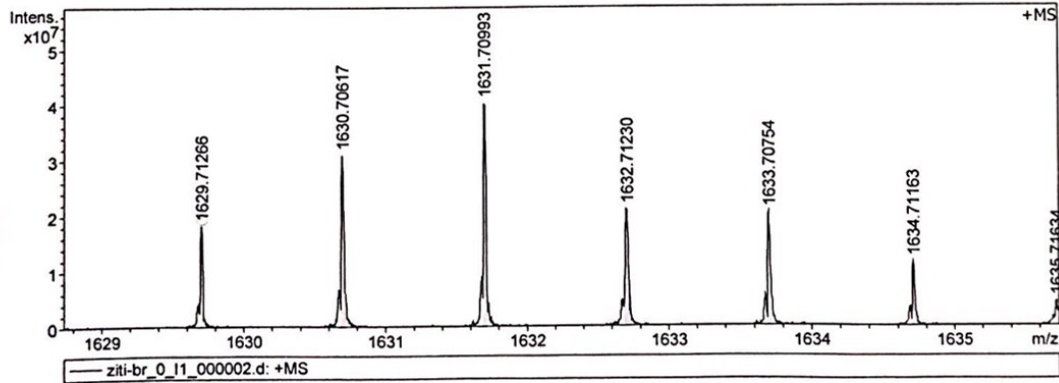
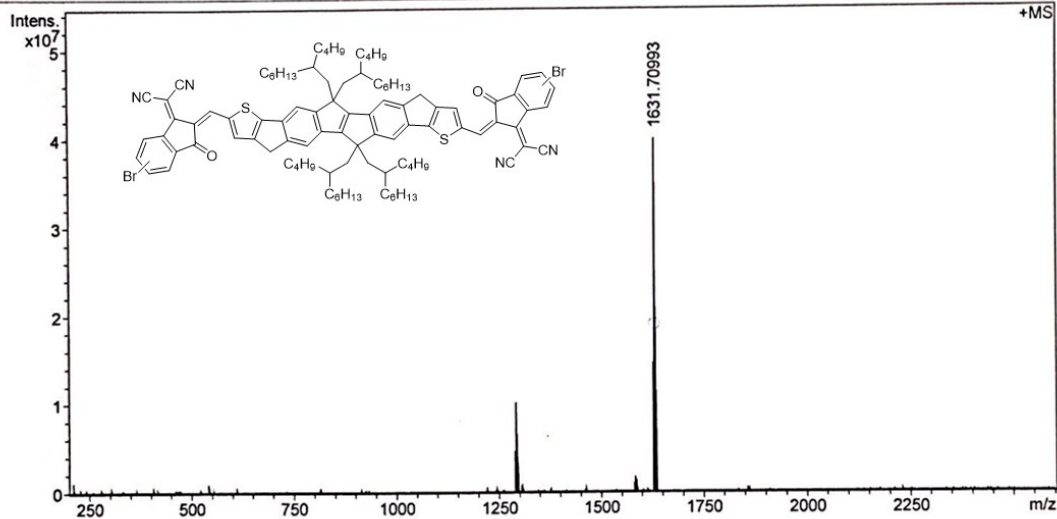
Analysis Name D:\Data\MALDI\2018\0711\ziti-br_0_11_000002.d
 Method MALDI_P_100-3000
 Sample Name MURU-N-ESI
 Comment

Acquisition Date 7/11/2018 6:03:56 PM

Operator
 Instrument solariX

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	2	Calibration Date	Wed Jul 11 06:03:43
Polarity	Positive	No. of Cell Fills	1	Data Acquisition Size	2098152
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	4194304
Broadband High Mass	2600.0 m/z	Laser Power	29.2 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]	mSigma	rdb	e ⁻ Conf	N-Rule
1629.712656	1	C ₁₀₀ H ₁₁₉ Br ₂ N ₄ O ₂ S ₂	100.00	1629.713572	0.6	252.6	42.5	even	ok

References

- 1 S. Wen, W. Chen, M. Fan, L. Duan, M. Qiu, M. Sun, L. Han and R. Yang, *J. Mater. Chem. A*, 2016, **4**, 18174.
- 2 J. Lee, J. Kim, B. Moon, H. G. Kim, M. Kim, J. Shin, H. Hwang, and K. Cho. *Macromolecules*, 2015, **48**, 1723.
- 3 W. Liu, J. Zhang, Z. Zhou, D. Zhang, Y. Zhang, S. Xu and X. Zhu, *Adv. Mater.*, 2018, **30**, 1800403.