

Supporting Information for

Structural regulation of thiophene-fused benzotriazole as a “ π -bridge” for A- π -D- π -A type acceptor:P3HT-based OSCs to achieve high efficiency

Jiacheng Wang,^a Guilong Cai,^c Boyu Jia,^b Heng Lu,^b Xinhui Lu,^{*c} Xiaowei Zhan^{*b} and Xingguo Chen^{*a}

^aHubei Key Laboratory on Organic and Polymeric Opto-electronic Materials, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China. Email: xgchen@whu.edu.cn

^bDepartment of Materials Science and Engineering, College of Engineering, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Peking University, Beijing 100871, China. Email: xwzhan@pku.edu.cn

^cDepartment of Physics, Chinese University of Hong Kong, New Territories 999077, Hong Kong, China. E-mail: xhlu@phy.cuhk.edu.hk

Instruments and measurements

^1H -NMR and ^{13}C -NMR were measured on a Bruker AVANCE III HD 400MHz. ESI-MS analysis was determined on a Finnigan-LCQ advantage mass spectrometer. MALDI-TOF analysis was performed on an Applied Biosystems 4700 proteomics Analyzer 155 mass spectrometer. The thermogravimetric analysis (TGA) was performed on TA thermal analyzer (model Q600 SDT) under a nitrogen flow at a heating rate of $10^\circ\text{C min}^{-1}$. The thickness of active layer was measured on a Bruker DektakXT profilometer. Elemental analyses were carried out on a 73 CARLOERBA-1106 microelemental analyzer. The electrochemical Cyclic Voltammetry (CV) was conducted on a CHI voltammetric analyzer with glassy carbon disk, Pt wire and Ag/Ag^+ electrode as working electrode, counter electrode and reference electrode respectively in a 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. The UV-vis absorption spectra of the materials were measured by a Varian Cary 5000 UV-vis-NIR spectrophotometer. Atomic force microscope (AFM) images were measured on Multimode 8 scanning probe microscopy (Bruker Daltonics Inc., United States) in the tapping mode in order to investigate the nanoscale morphology of the blends. The transmission electron microscopy (TEM) characterization was carried out on a JEM-2100 transmission electron microscope operated at 200 kV.

Fabrication and characterization of organic solar cells

Organic solar cells were fabricated with the structure: ITO/ZnO/active layer/ MoO_3 /Ag. The indium tin oxide (ITO) glass (sheet resistance = $10 \Omega \text{ sq}^{-1}$) was pre-cleaned in an ultrasonic bath of deionized water, acetone and isopropanol. ZnO layer (*ca.* 30 nm) was spin-coated onto the ITO glass from ZnO precursor solution (100 mg $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 0.02 mL ethanolamine dissolved in 1 mL 2-methoxyethanol), and baked at 200°C for 30 min. A chloroform solution of P3HT:acceptor (15 mg mL^{-1} in total) was spin-coated on ZnO layer to form a photoactive layer. The MoO_3 layer (*ca.* 5 nm) and Ag (100 nm) were successively evaporated onto the surface of the photoactive layer under vacuum (*ca.* 10^{-5}Pa). The active area of the device was 4.0 mm^2 , defined under an optical microscope. The J - V curve was measured using a computer-controlled B2912A Precision Source/Measure Unit (Agilent Technologies). An XES-70S1 (SAN-EI Electric Co., Ltd.) solar simulator (AAA grade, $70 \times 70 \text{ mm}^2$ photobeam size) coupled with AM 1.5G solar spectrum filters was used as the light source, and

the optical power at the sample was 100 mW cm^{-2} . A $2 \times 2 \text{ cm}^2$ monocrystalline silicon reference cell (SRC-1000-TC-QZ) was purchased from VLSI Standards Inc. The EQE spectra were measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell.

Mobility measurements

Hole-only and electron-only diodes were fabricated using the architectures: ITO/PEDOT:PSS/P3HT:acceptor/Au for holes and ITO/ZnO/P3HT:acceptor/Al or ITO/ZnO/acceptor/Al for electrons. Mobilities were extracted by fitting the current density–voltage curves using space-charge-limited current (SCLC) method. The J - V curves of the devices were plotted as $\ln(Jd^3/V^2)$ versus $(V/d)^{0.5}$ using the equation $\ln(Jd^3/V^2) \cong 0.89(1/E_0)^{0.5}(V/d)^{0.5} + \ln(9\epsilon_0\epsilon_r\mu/8)$, where J is the current density, d is the film thickness of active layer, μ is the hole or electron mobility, ϵ_r is the relative dielectric constant of the transport medium, ϵ_0 is the permittivity of free space ($8.85 \times 10^{-12} \text{ F m}^{-1}$), $V = V_{\text{appl}} - V_{\text{bi}}$, where V_{appl} is the applied voltage to the device, and V_{bi} is the built-in voltage due to the difference in work function of the two electrodes (for hole-only diodes, V_{bi} is 0.2 V; for electron-only diodes, V_{bi} is 0 V).

Synthesis

Unless stated otherwise, solvents and chemicals were obtained commercially and were used without further purification. Compound **1** was prepared following literature procedure.^[1]

Synthesis of compound **2**

Compound **1** (3.74 g, 10 mmol) and lithium hydroxide monohydrate (4.20 g, 100 mmol) were dissolved in a mixture of THF/H₂O (10:1, 200 mL in total), heated and stirred for 4h at 50°C. After the reaction, it was cooled to room temperature, dilute hydrochloric acid was added to make the solution acidic. The solvent was removed under vacuum to give compound **2** as a white solid (2.94 g, 85%). ¹H-NMR (400 MHz, CDCl₃, δ ppm): 8.32 (s, 1H), 8.23 (s, 1H), 4.73 (d, $J=7.2\text{Hz}$, 2H), 2.90 (s, 3H), 2.31 (m, 1H), 1.37 (m, 8H), 0.90 (m, 6H). ¹³C-NMR (100MHz, CDCl₃, δ ppm): 167.55, 144.02, 143.26, 139.01, 138.35, 133.74, 133.21, 121.41, 112.04, 60.73, 40.56, 30.44, 28.40, 23.84, 22.89, 15.79, 14.02, 10.47. EI-MS: Calcd. For [C₁₈H₂₃N₃O₂S]⁺: 345.15; Found: 345.37.

Synthesis of compound 3

Compound **2** (1.73g, 5mmol), silver acetate (835mg, 5mmol) and K_2CO_3 (690mg, 5mmol) were added into a Schlenk flask. The flask was purged by argon for 3 times and then N-Methyl pyrrolidone (30ml) was added. The mixture was refluxed for 24h at 150°C. After reaction, the mixture was poured into ice water to cool and then extracted with ethyl acetate. The organic phase was collected and dried over anhydrous sodium sulfate. The solvent was removed under vacuum. The solvent was removed under vacuum and the crude product was purified by column chromatography over silica gel with petroleum/ethyl acetate mixtures as the eluent to give compound **3** as a colorless oil (1.21g, 80%). 1H -NMR (400 MHz, $CDCl_3$, δ ppm): 8.13 (s, 1H), 7.42 (d, $J=5.6$ Hz, 1H), 7.35 (d, $J=5.6$ Hz, 1H), 4.69 (d, $J=7.2$ Hz, 2H), 2.89 (s, 3H), 2.30 (m, 1H), 1.36 (m, 8H), 0.93 (m, 6H). ^{13}C -NMR (100MHz, $CDCl_3$, δ ppm): 143.25, 142.84, 139.63, 137.64, 127.84, 124.27, 120.65, 108.22, 60.50, 40.51, 30.44, 28.40, 23.84, 22.90, 15.95, 14.02, 10.48. EI-MS: Calcd. For $[C_{17}H_{23}N_3S]^+$: 301.16; Found:301.55.

Synthesis of compound 4

Compound **3** (603mg, 2mmol) was dissolved and stirred in $CHCl_3$ (20mL) under ice bath conditions, then Br_2 (320 mg, 2mmol) diluted 10 times was added dropwise. TLC was used to monitor the reaction progress. When the reaction is complete, the mixture was poured into saturated sodium sulfite aqueous solution and extracted with CH_2Cl_2 , then the organic layer was dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum and the crude product was purified by column chromatography over silica gel with petroleum/ethyl acetate mixtures as the eluent to give **4** as a light blue oil (450mg, 60%). 1H -NMR (400 MHz, $CDCl_3$, δ ppm): 7.52 (s, 1H), 7.52 (s, 1H), 4.72 (d, $J=7.6$ Hz, 2H), 2.84(s, 3H), 2.34(s, 1H), 1.37(m, 8H), 0.93(m, 6H). ^{13}C -NMR (100MHz, $CDCl_3$, δ ppm): 142.68, 142.53, 138.98, 137.84, 129.21, 123.85, 120.28, 99.95, 60.86, 40.36, 30.29, 28.27, 23.76, 22.89, 15.69, 14.01, 10.42. EI-MS: Calcd. For $[C_{17}H_{22}BrN_3S]^+$: 379.07; Found:379.42.

Synthesis of compound 5

Compound **4** (760mg, 2mmol), N-Bromo-succinimide (NBS, 890mg, 5mmol) and dibenzoyl peroxide (BPO, 120mg, 0.5mmol) were added to a 250 mL single-necked flask, and 50 mL of chlorobenzene was used as a solvent to dissolve, and the reaction was heated and stirred at 80 °C for 12 h. After the reaction is over, the mixture was poured into saturated sodium sulfite aqueous solution

and extracted with CHCl_3 , then the organic layer was dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum and the crude product was purified by column chromatography over silica gel with petroleum/ethyl acetate mixtures as the eluent to give **5** as a light yellow solid (394mg, 50%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ ppm): 11.04 (s, 1H), 7.72 (d, $J=5.6\text{Hz}$, 1H), 7.62 (d, $J=5.6\text{Hz}$, 1H), 4.80 (d, $J=7.2\text{Hz}$, 2H), 2.36 (m, 1H), 1.38 (m, 8H), 0.92 (m, 6H). $^{13}\text{C-NMR}$ (100MHz, CDCl_3 , δ ppm): 187.16, 143.26, 142.77, 140.54, 139.75, 133.23, 122.23, 116.01, 112.84, 61.11, 40.52, 30.36, 28.30, 23.82, 22.87, 14.01, 10.44. EI-MS: Calcd. For $[\text{C}_{17}\text{H}_{20}\text{BrN}_3\text{OS}]^+$: 393.05; Found: 393.28.

Synthesis of compound 7

Compound **5** (100mg, 0.25mmol), compound **6** (104mg, 0.1mmol), and $\text{Pd}(\text{PPh}_3)_4$ (5.8mg, 0.005mmol) were added into a Schlenk flask under argon atmosphere. The flask was purged by argon for 3 times and then anhydrous toluene was added. The mixture was refluxed for 2 days at 110°C . After cooling to room temperature, the solvent was removed under vacuum and the crude product was purified by column chromatography over silica gel with petroleum/ CH_2Cl_2 mixtures as the eluent to give compound **7** as a purple solid (108mg, 80%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ ppm): 11.06 (s, 2H), 8.15 (d, $J=6.0\text{Hz}$, 2H), 8.06 (s, 2H), 7.72 (d, $J=6.0\text{Hz}$, 2H), 7.49 (s, 2H), 4.85 (d, $J=6.8\text{Hz}$, 4H), 2.36 (m, 2H), 2.15 (m, 4H), 1.99 (m, 4H), 1.55-0.75 (br, 88H). $^{13}\text{C-NMR}$ (100MHz, CDCl_3 , δ ppm): 186.69, 156.18, 154.16, 146.52, 143.90, 141.89, 141.37, 138.63, 136.26, 136.22, 131.69, 127.13, 126.50, 122.41, 114.91, 114.04, 60.46, 54.31, 40.60, 39.18, 31.85, 30.59, 30.13, 29.42, 29.31, 28.46, 24.53, 24.03, 22.99, 22.63, 14.11, 14.09, 10.61. MS (MALDI-TOF): calculated for $\text{C}_{82}\text{H}_{112}\text{N}_6\text{O}_2\text{S}_4$, 1340.77; found: 1340.79.

Synthesis of acceptor JC14

Compound **7** (134mg, 0.1mmol), 3-ethyl-2-(1,1-dicyanomethylene)rhodanine (193mg, 1.0mmol) and ammonium acetate (154mg, 2.0mmol) were dissolved in $\text{CH}_3\text{COOH}/\text{CHCl}_3$ (1:4, 50mL), then the mixture was refluxed overnight under argon atmosphere. After cooling to room temperature, the mixture was poured into methanol and filtered with methanol for several times until the filtrate has no obvious color. The residue was purified by column chromatography over silica gel with CH_2Cl_2 as the eluent to give **JC14** as a blue solid (152mg, 90%). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ ppm): 8.42 (s, 2H), 8.15 (d, $J=6.0\text{Hz}$, 2H), 8.04 (s, 2H), 7.59 (d, $J=6.0\text{Hz}$, 2H), 7.48 (s, 2H), 4.84 (d, $J=6.8\text{Hz}$, 4H), 4.34

(d, $J=7.2\text{Hz}$, 4H), 2.44 (m, 2H), 2.15 (m, 4H), 1.98 (m, 4H), 1.55-1.10 (br, 64H), 1.03 (m, 12H), 0.91 (m, 6H), 0.80 (m, 12H). ^{13}C -NMR (100MHz, CDCl_3 , δ ppm): 167.21, 166.98, 156.35, 154.25, 146.56, 146.42, 141.69, 140.49, 138.80, 136.29, 135.59, 129.59, 127.63, 126.13, 124.77, 124.43, 119.06, 114.03, 113.52, 113.35, 112.89, 60.77, 54.55, 54.32, 40.66, 40.53, 39.17, 31.85, 30.66, 30.12, 29.43, 29.31, 28.41, 24.53, 24.12, 23.04, 22.63, 14.22, 14.12, 14.09, 10.66. MS (MALDI-TOF): calculated for $\text{C}_{98}\text{H}_{122}\text{N}_{12}\text{O}_2\text{S}_6$, 1691.82; found: 1691.91. Anal. calcd for $\text{C}_{98}\text{H}_{122}\text{N}_{12}\text{O}_2\text{S}_6$ (%): C, 69.55; H, 7.27; N, 9.93. Found(%): C, 69.84; H, 7.41; N, 10.02.

Table S1. The parameters of P3HT:JC14 based devices (D:A = 1:0.6) with different annealing temperature for 5 min.

		Temperature (°C)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
P3HT:JC14		/	0.843	4.84	33.2	1.36
		90	0.728	12.24	60.0	4.63
		110	0.726	12.54	54.1	4.92
		120	0.769	12.44	58.3	5.57
		140	0.746	8.53	54.0	3.44
		160	0.709	5.10	50.4	1.82

Table S2. The parameters of P3HT:JC14 based devices (D:A = 1:0.6) with different solvent additives.

		Additives (v/v)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
P3HT:JC14	1:0.6	0.5% CN	0.767	9.39	54.9	3.96
		0.5%DPE	0.719	12.75	61.0	5.60
		0.5% <i>o</i> -DCB	0.794	5.28	54.0	2.26
		1%TMB	0.752	6.89	46.8	2.42
		0.25%DIO	0.766	14.62	59.2	6.63
		0.4%DIO	0.767	15.30	62.2	7.29
		0.5%DIO	0.759	16.04	63.4	7.72
		0.6%DIO	0.763	15.93	60.0	7.30
		0.8%DIO	0.745	13.66	66.3	6.74
		1%DIO	0.749	14.04	65.4	6.88

Table S3. The parameters of P3HT:JC14 based devices with different D/A ratios.

Device	Additives (v/v)	D:A (w/w)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
P3HT:JC14	0.5%DIO	1:1	0.748	14.24	63.5	6.76
		1:0.8	0.754	16.02	62.2	7.51
		1:0.6	0.759	16.04	63.4	7.72
		1:0.5	0.767	12.61	63.2	6.11

Table S4. The parameters of P3HT:JC14 based devices with different solvents.

Device	D:A (w/w)	solvents	Additives (v/v)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
P3HT:JC14 4	1:0.6	CF	/	0.843	4.84	33.2	1.36
			0.5%DIO	0.759	16.04	63.4	7.72
		CB	/	0.795	7.04	52.2	2.92
			0.5%DIO	0.772	10.55	57.5	4.69
		<i>o</i> -DCB	/	0.779	4.83	56.6	2.13
			0.5%DIO	0.711	4.03	56.9	1.63
		THF	0.5%DIO	0.765	10.36	50.3	3.98

Table S5. Carrier transport properties of acceptor neat films and optimized P3HT:acceptor blended films.

Acceptor	$\mu_e^{a)}$ (cm ² V ⁻¹ s ⁻¹)	$\mu_h^{b)}$ (cm ² V ⁻¹ s ⁻¹)	$\mu_e^{b)}$ (cm ² V ⁻¹ s ⁻¹)	μ_h/μ_e
JC2	4.10×10^{-4}	5.55×10^{-5}	2.49×10^{-5}	2.23
JC14	2.75×10^{-4}	7.49×10^{-5}	4.55×10^{-5}	1.65

^{a)}Acceptor neat films; ^{b)}optimized P3HT:JC2 or P3HT:JC14 blended films.

Table S6. Calculated GIWAXS characteristics in the IP direction.

Film	q (\AA^{-1})	d-spacing (\AA)	FWHM (\AA^{-1})	CCL (\AA)
P3HT	0.371	16.9	0.071	79.6
JC2	0.325	19.3	0.064	88.4
JC14	0.317	19.8	0.057	99.2
P3HT/JC2 (as-cast)	0.340	18.5	0.083	68.1
P3HT/JC14 (as-cast)	0.374	16.8	0.111	50.9
P3HT/JC2 (optimized)	0.330	19.0	0.093	60.8
P3HT/JC14 (optimized)	0.308	20.4	0.048	117.8
	0.371	16.9	0.077	73.4

Table S7. Calculated GIWAXS characteristics in the OOP direction.

Film	q (\AA^{-1})	d-spacing (\AA)	FWHM (\AA^{-1})	CCL(\AA)
P3HT	0.378	16.6	0.084	80.8
	1.652	16.9	0.138	41.0
JC2	0.345	18.2	0.063	89.8
	1.80	3.49	0.108	52.4
JC14	0.328	19.2	0.046	122.9
P3HT/JC2 (as-cast)	0.389	16.2	0.087	65.0
	1.668	3.77	0.237	23.9
P3HT/JC14 (as-cast)	0.380	16.5	0.089	63.5
	1.720	3.65	0.189	29.9
P3HT/JC2 (optimized)	0.382	16.4	0.082	69.0
P3HT/JC14 (optimized)	0.382	16.4	0.077	73.4

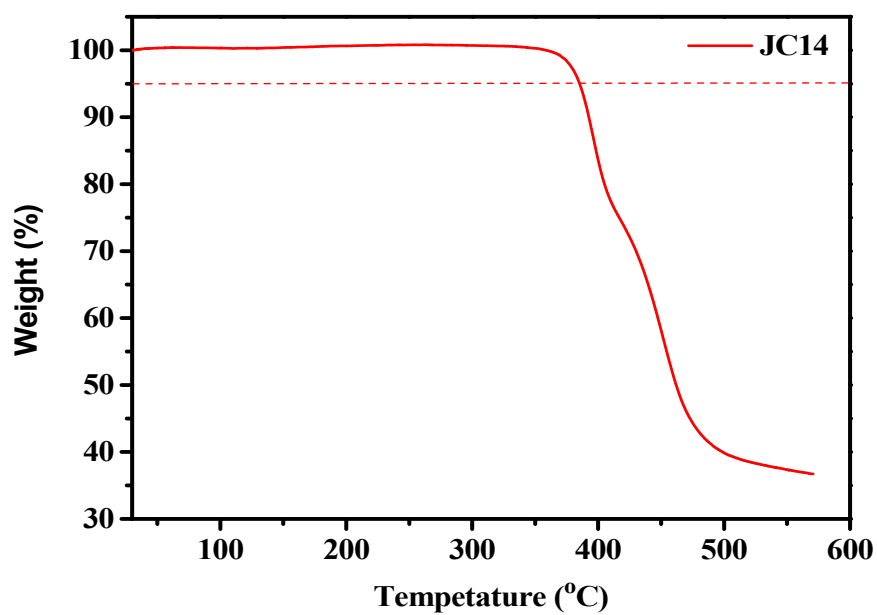


Figure S1. The TGA curves of JC14.

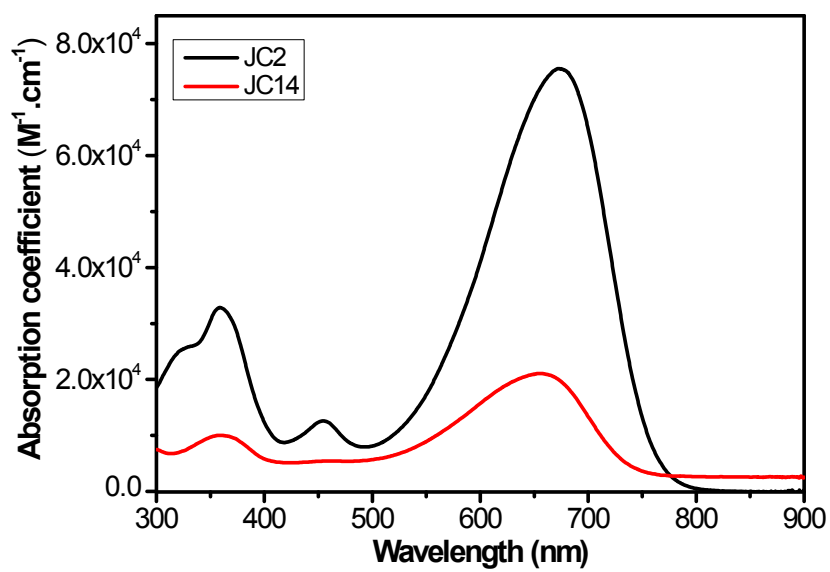


Figure S2. The UV-vis absorption spectra of JC2 and JC14 in the solution.

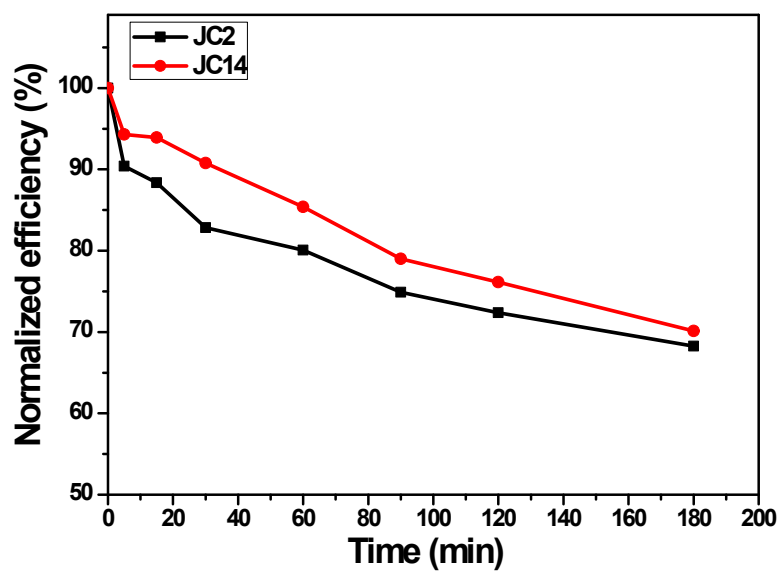


Figure S3. Photo-stability test of the JC2-based and JC14-based OPV devices.

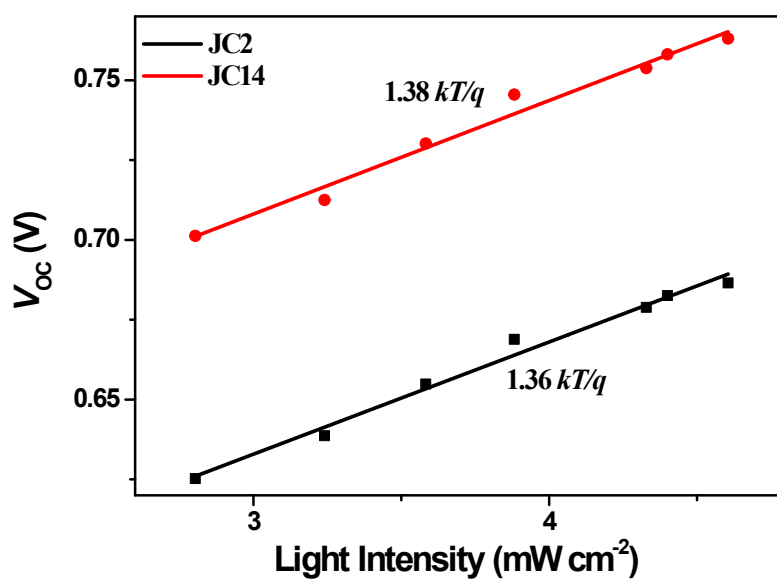


Figure S4. V_{OC} versus light intensity under illumination.

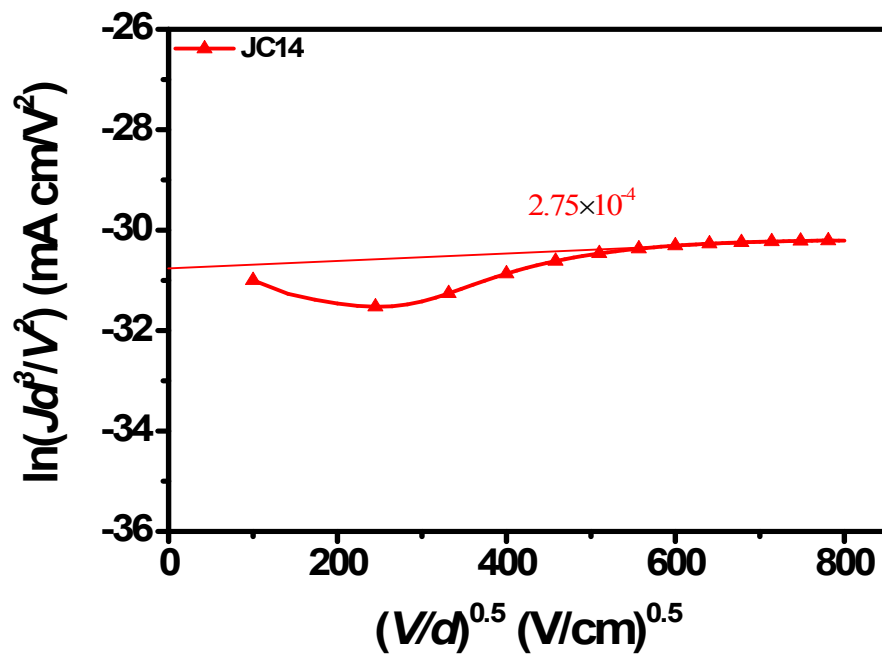


Figure S5. J - V characteristics in dark for electron-only device based on pure acceptor JC14.

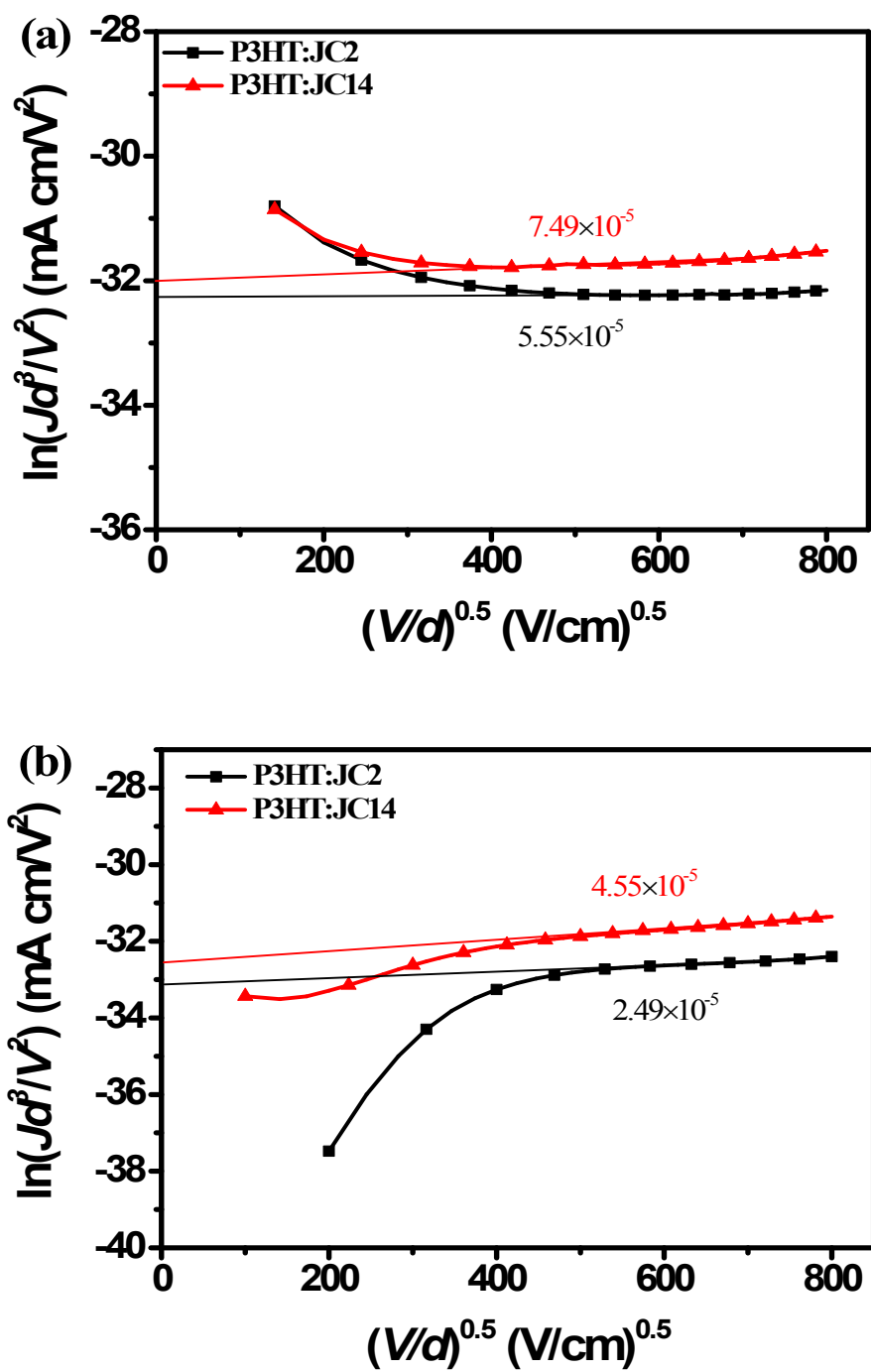


Figure S6. J - V characteristics in dark for a) hole-only and b) electron-only devices based on optimized P3HT:JC2 and P3HT:JC14.

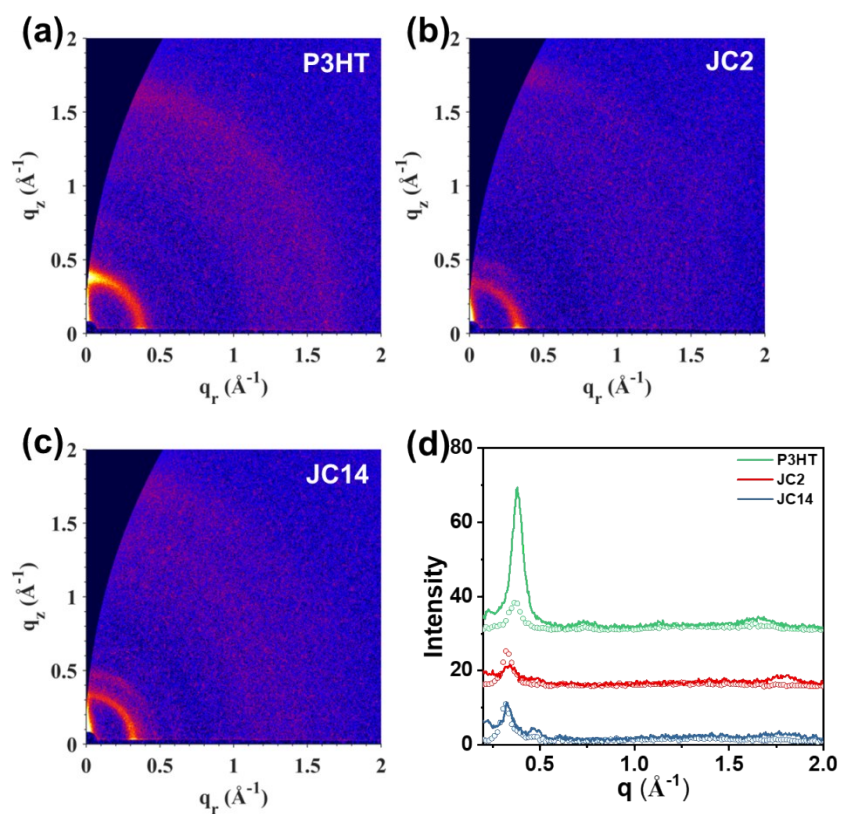


Figure S7. 2D GIWAXS patterns of (a) P3HT, (b) JC2 and (c) JC14 pure films; (d) the corresponding intensity profiles along the in-plane (dotted line) and out-of-plane (solid line) directions.

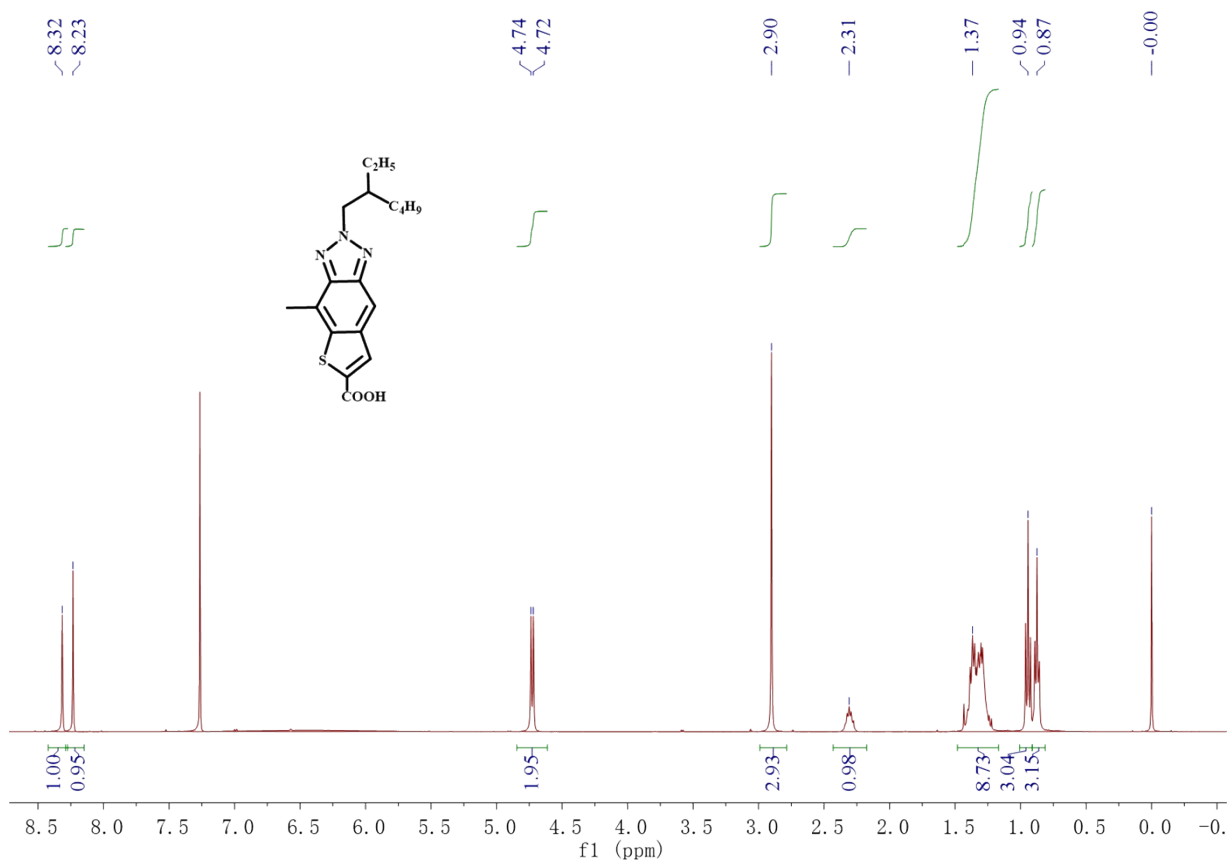


Figure S8. ^1H NMR spectrum of compound 2.

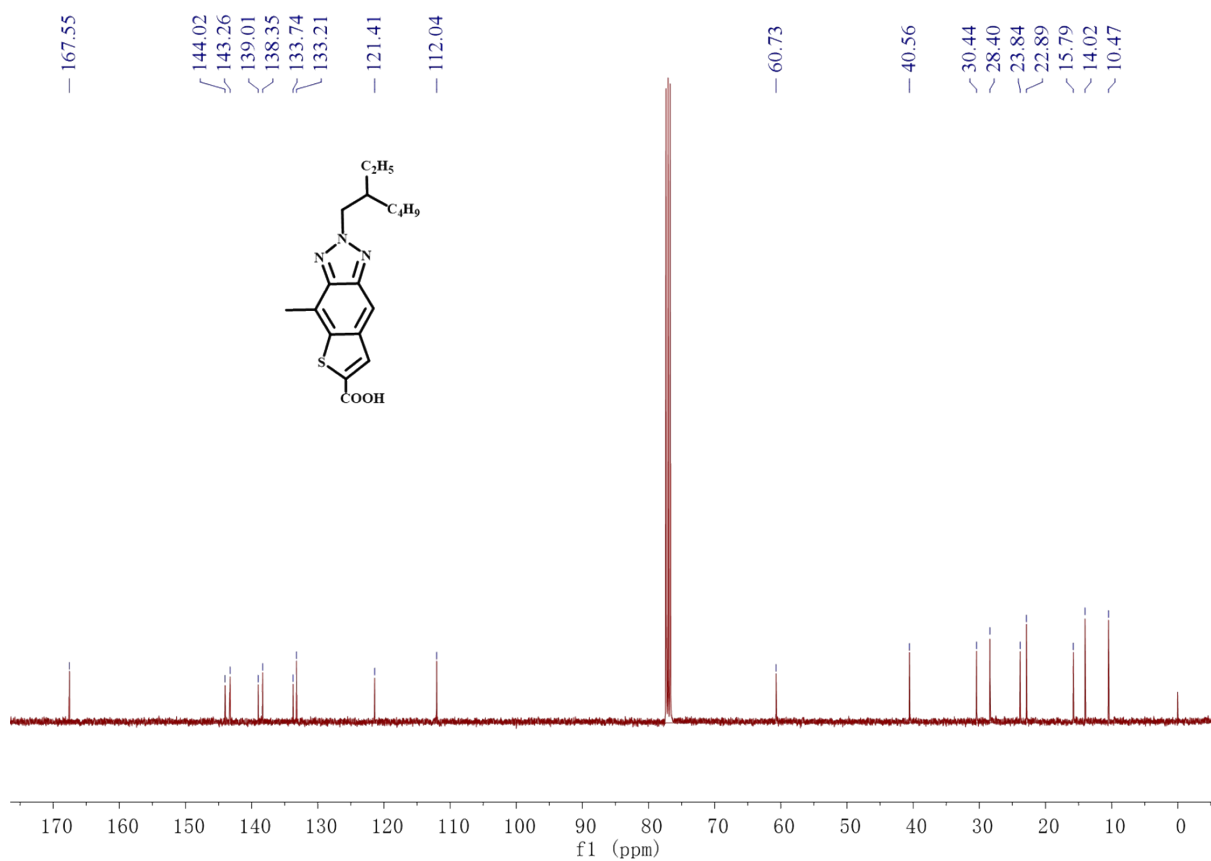


Figure S9. ^{13}C NMR spectrum of compound 2.

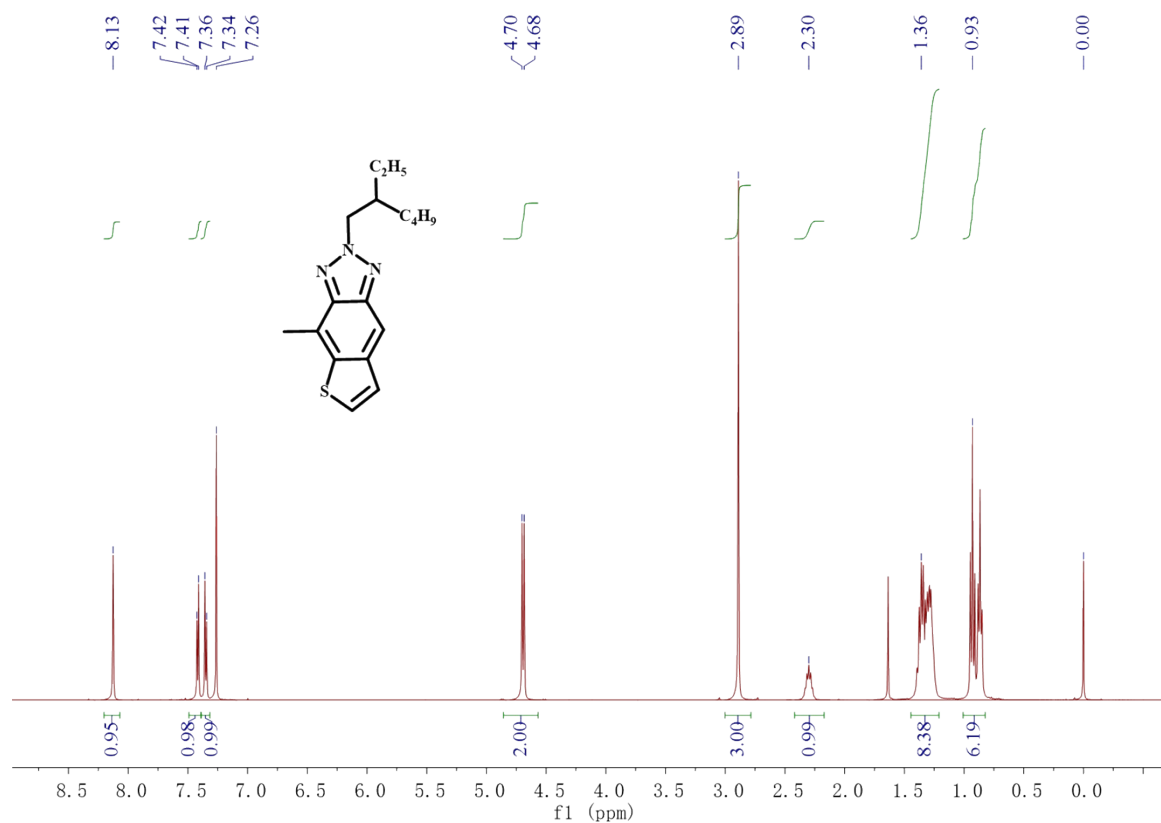


Figure S10. ¹H NMR spectrum of compound 3.

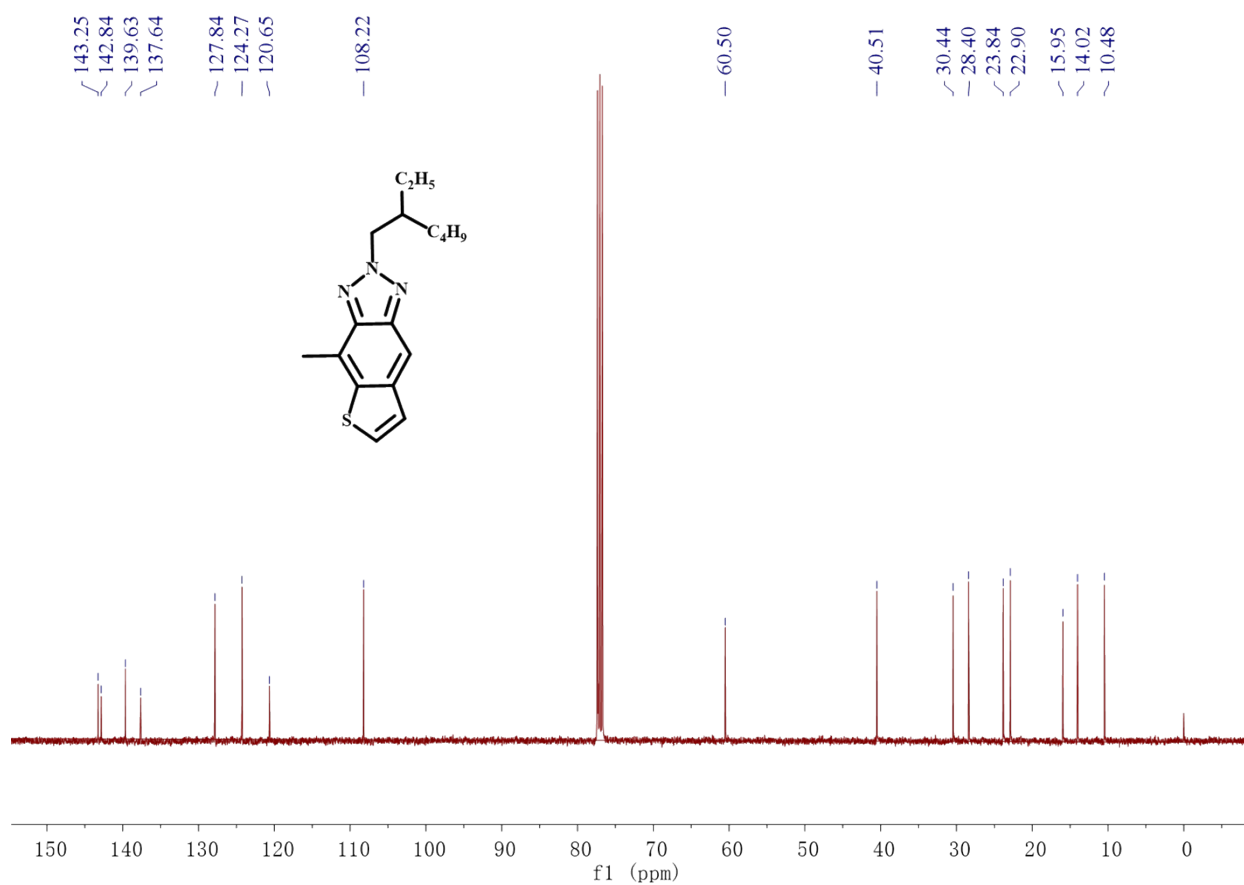


Figure S11. ¹³C NMR spectrum of compound 3.

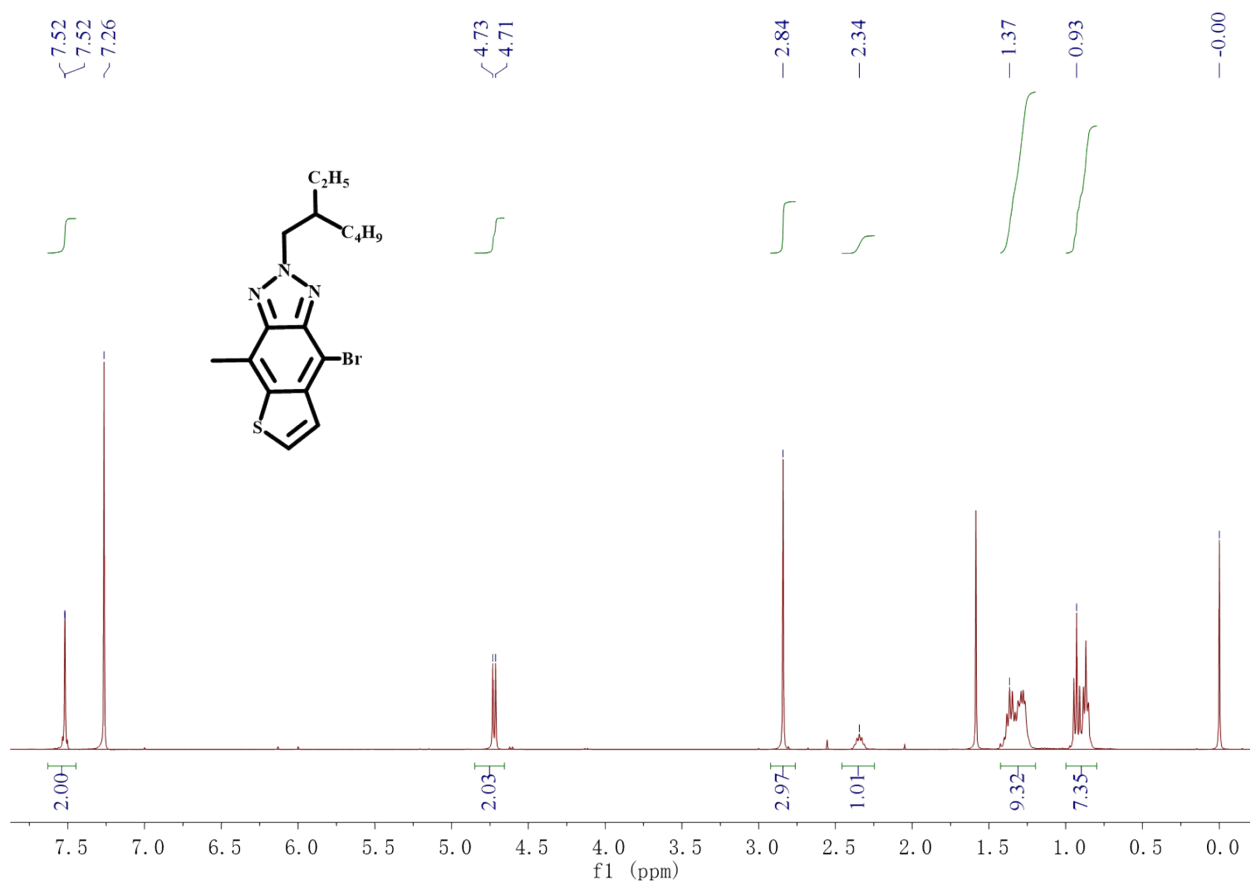


Figure S12. ¹H NMR spectrum of compound 4.

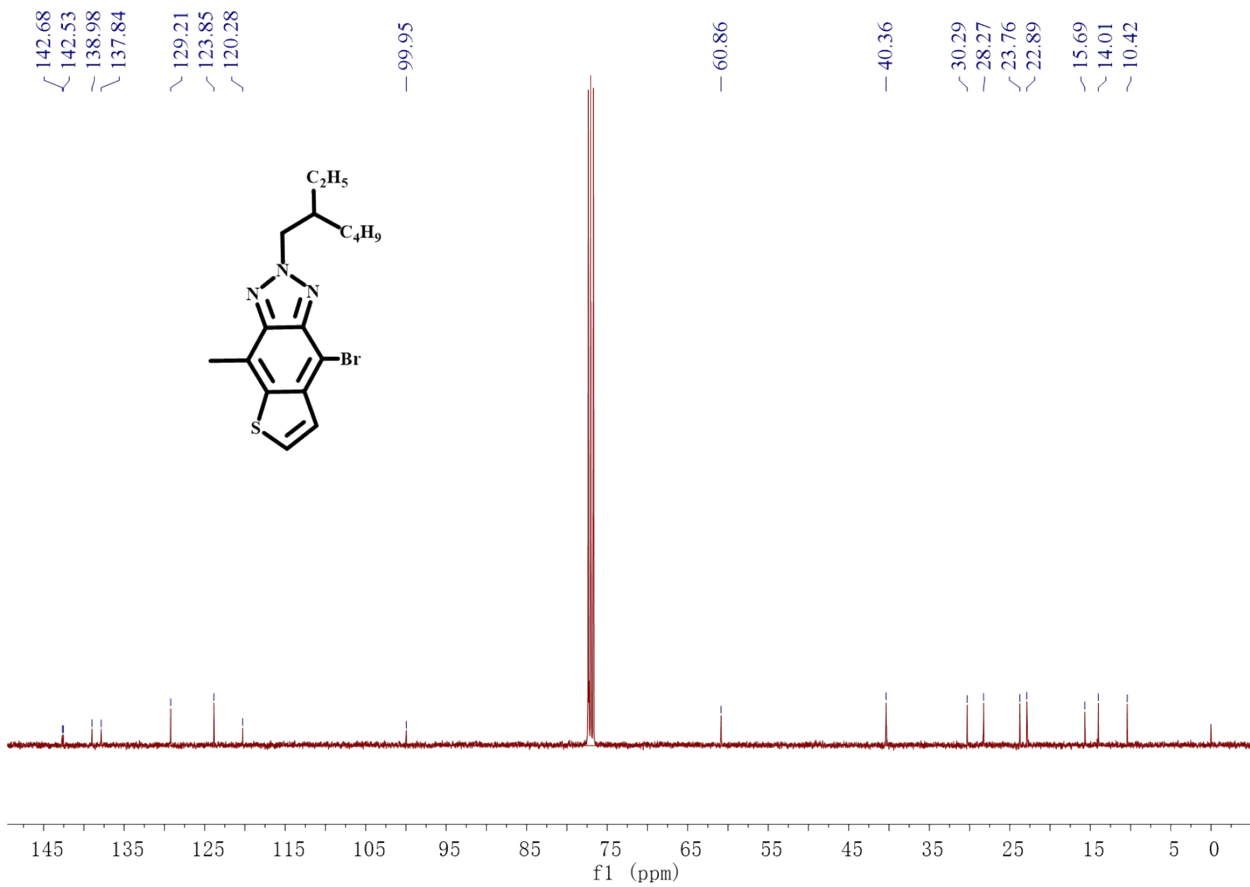


Figure S13. ¹³C NMR spectrum of compound 4.

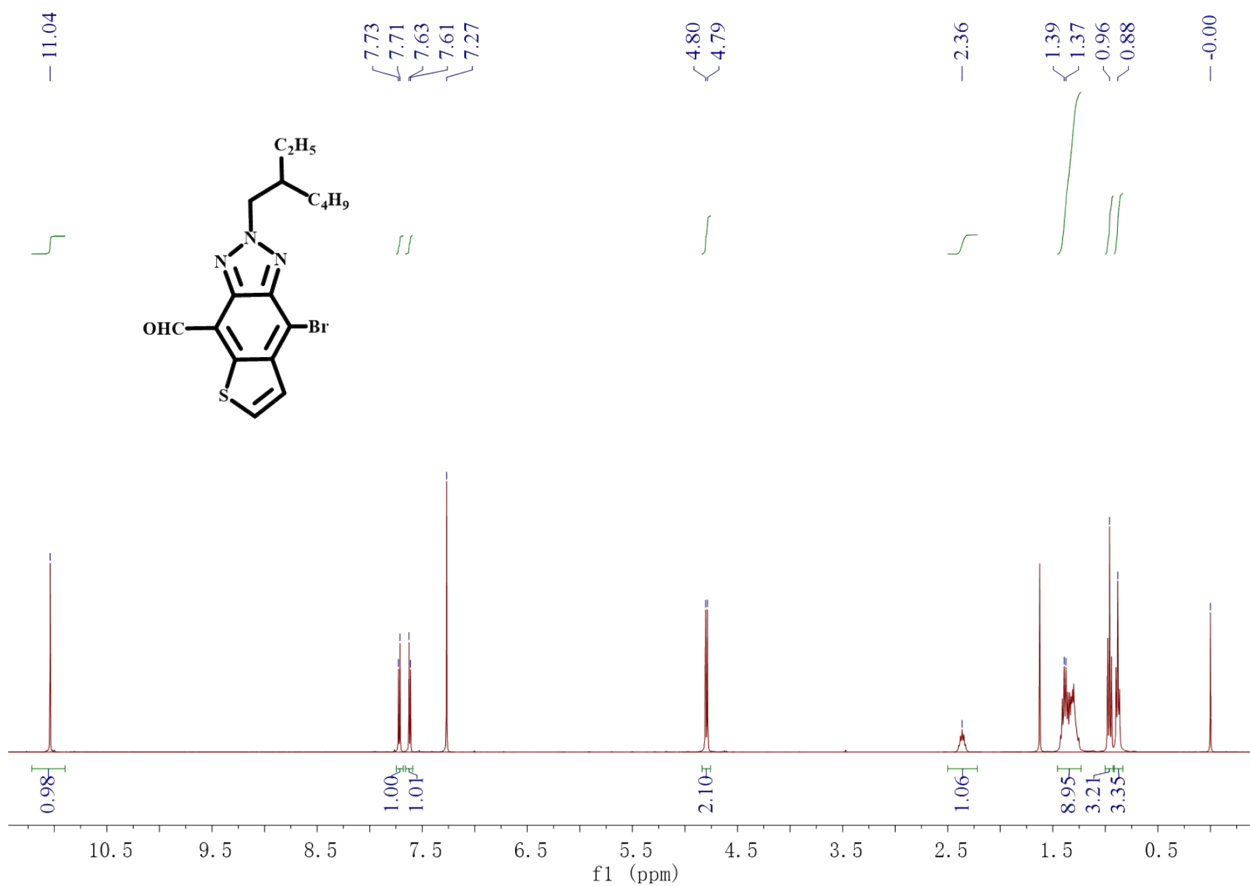


Figure S14. ^1H NMR spectrum of compound 5.

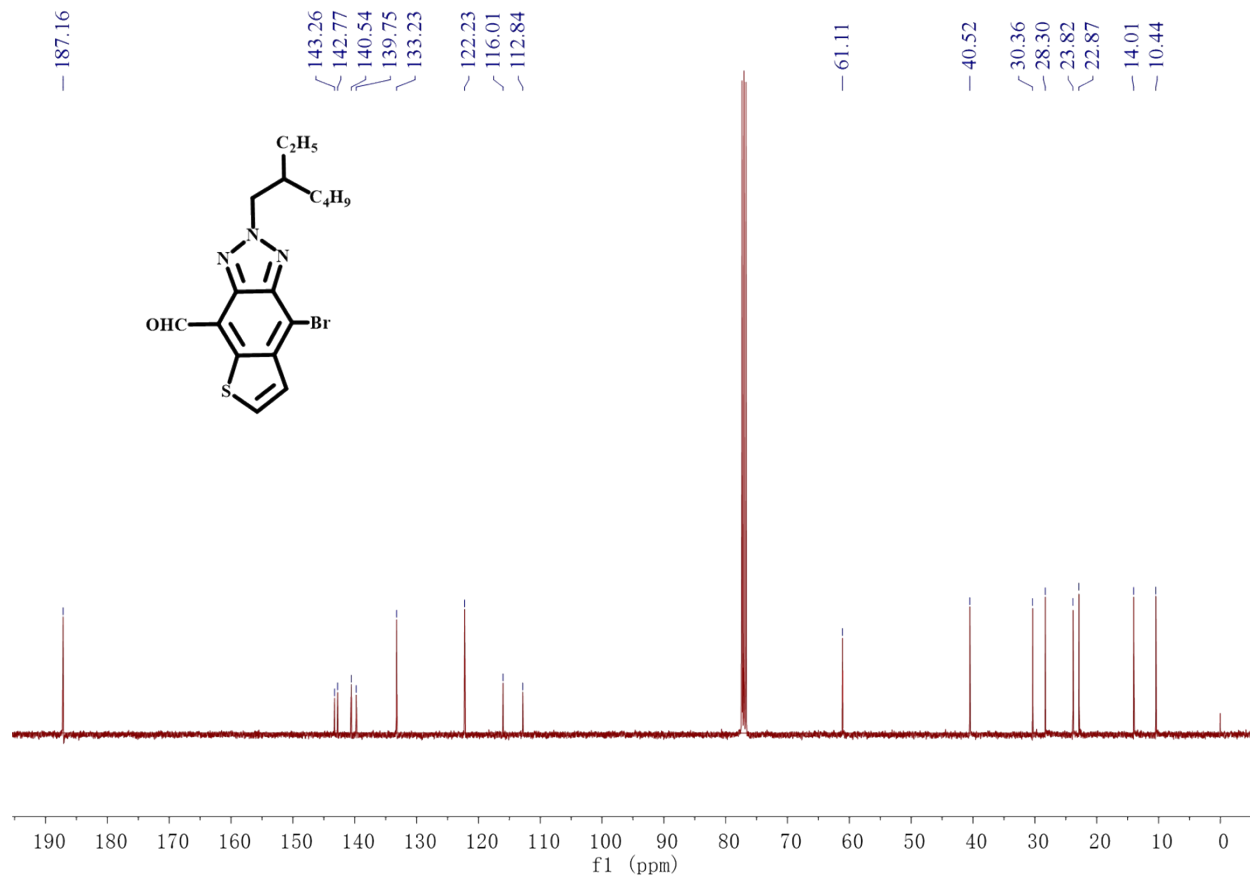


Figure S15. ^{13}C NMR spectrum of compound 5.

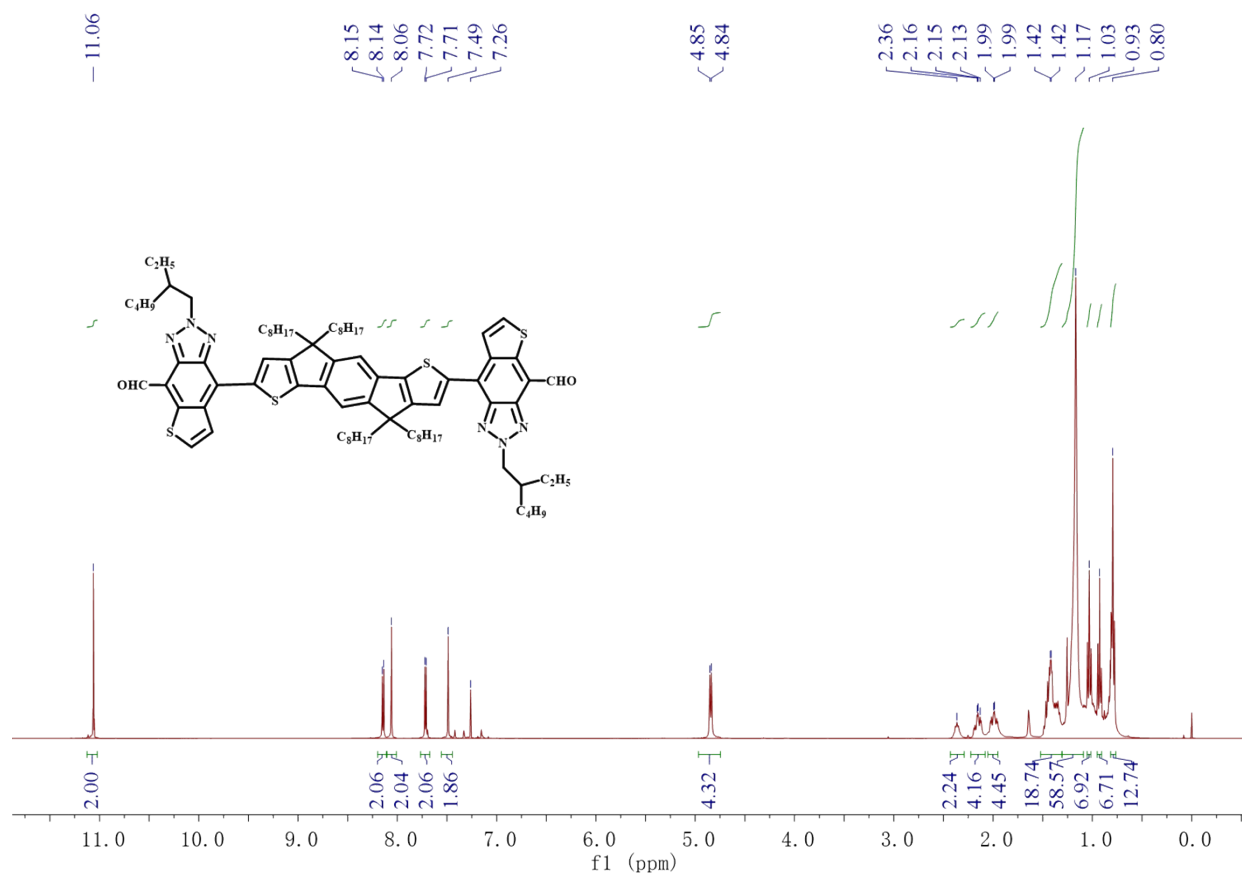


Figure S16. ¹H NMR spectrum of compound 7.

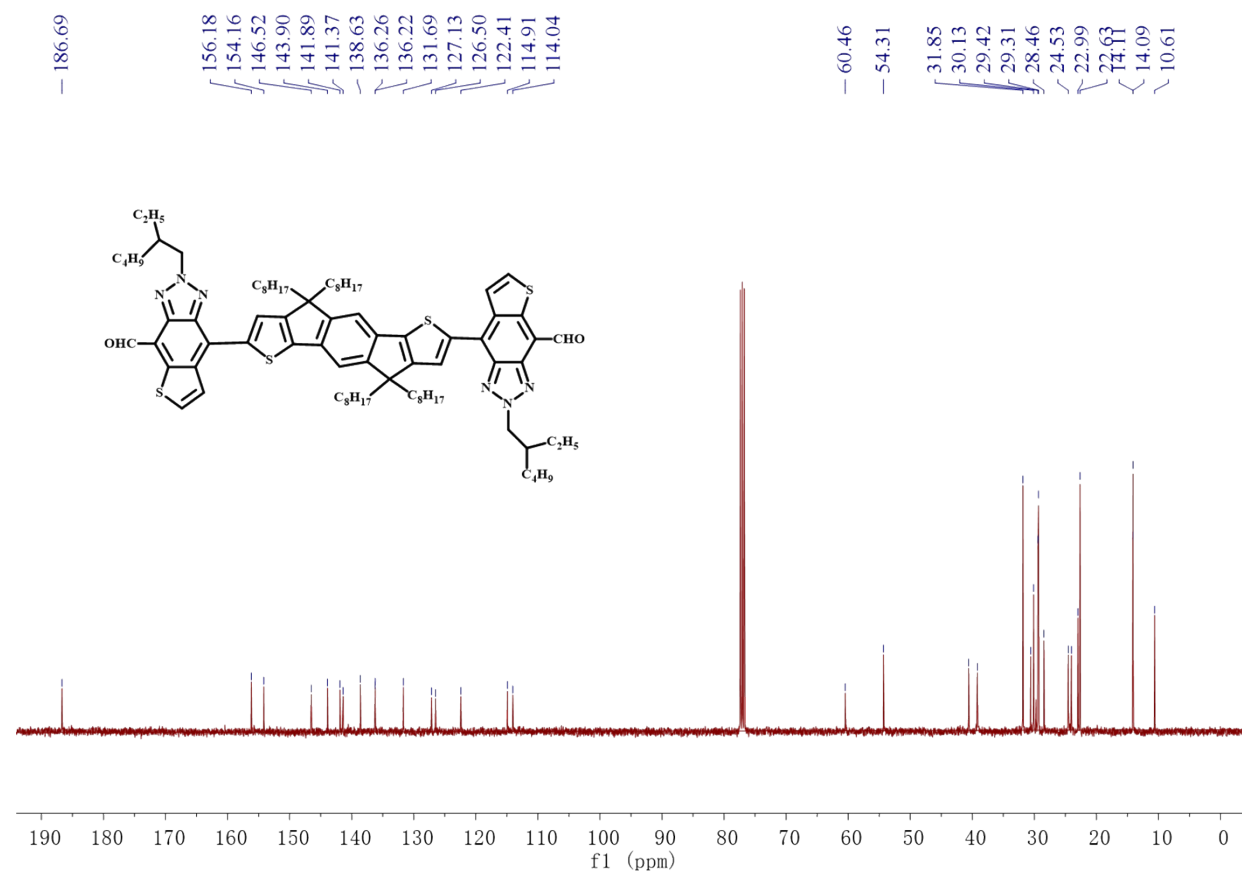


Figure S17. ¹³C NMR spectrum of compound 7.

Reference

1. J. Wang, T. Li, X. Wang, Y. Xiao, C. Zhong, J. Wang, K. Liu, X. Lu, X. Zhan and X. Chen, Enhancing the JSC of P3HT-based OSCs via a thiophene-fused aromatic heterocycle as a “ π -Bridge” for A- π -D- π -A-type acceptors, *ACS Appl. Mater. Interfaces* **2019**, *11*, 26005-26016.