

Supplementary Information

Achieving High Performance Organic Solar Cells with a Closer π - π Distance in Branched Alkyl-chain Acceptors

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General Methods

Instruments. ^1H NMR spectra were recorded on a Bruker AV 400 MHz spectrometer in CHCl_3 with tetramethylsilane (TMS) as an internal standard. To determine the HOMO and LUMO levels of the polymers, cyclic voltammetry (CV) measurements were performed on a CHI660E potentiostat/galvanostat (Shanghai Chenhua Instrumental Co. Ltd. China), in a solution in MeCN of 0.1 mol/L tetrabutylammonium hexafluorophosphate ($[\text{n-Bu}_4\text{N}]^+ [\text{PF}_6]^-$) at a potential scan rate of 100 mV/s with an Ag/Ag^+ reference electrode and a platinum wire counter electrode under an argon atmosphere. Solution and film UV-Vis absorption spectra were recorded on a Shimadzu UV3600 spectrometer. The films were spin-coated from the solutions of the acceptors at a concentration of 10 mg/mL in chlorobenzene on a quartz substrate at 1000 rpm for 30 sec. The solution UV-Vis absorption spectra were measured in the CHCl_3 solution of the acceptors at a concentration of 1.0×10^{-5} M. Thermogravimetric analysis (TGA) plots were measured with a Discovery series instrument under a nitrogen atmosphere at heating and cooling rates of 10 $^\circ\text{C}/\text{min}$. Different scanning calorimetry (DSC) measurements were performed on a Discovery series thermal analyzer at a scanning rate of 10 $^\circ\text{C}/\text{min}$ in a nitrogen atmosphere. Atom force microscopy (AFM) images were taken on a NanoScopeIIIa controller (Veeco Metrology Group/Digital Instruments, Santa Barbara, CA), using built-in software (version V6.13R1) to capture images. Transmission electron microscopy (TEM) images were acquired using a HITACHI H-7650 electron microscope operating at an acceleration voltage of 100 kV.

Single crystal growth. Depending on the solubility of the materials in different solvents, we chose the slow diffusion method to achieve the growth of single crystals. About 5 mg of each acceptor material was weighed and dissolved in 5 mL of good solvent (e.g. chloroform, DCM), then 15 mL of poor solvent (e.g. ethanol, methanol) was slowly added to the container. The container is sealed and left to stand for 15 days protected from light to obtain a single crystal at the bottom of the container.

Fabrication and characterization of OSCs. The fabrication and measurement methods of OSCs devices are as follows: After a thorough cleaning of the indium-tin oxide (ITO)-coated glass substrate with detergent, deionized water, acetone and isopropanol followed by ultrasonication for 15 min each and being subsequently dried in an oven at 80 °C. The ITO glass substrates were treated with UV-ozone for 15 min and then the PEDOT: PSS were spin-coated onto the ITO substrates. The total concentration of the PBDB-TF:Acceptors (1:1.2) blend solution for spin-coating was 9 mg/mL with chlorobenzene as the processing solvent. The blend was stirred at room temperature (rt) in the glove box overnight. The active layer was spin-coated at 3000 rpm for 30 sec to obtain the blend film. PDINO-solution (1 mg/mL in EtOH) was then spin-coated as interface and a 100 nm Ag layer were subsequently evaporated through a 0.045 cm² shadow mask to define the active area of the devices. The integrated device structure is ITO/PEDOT:PSS/ PBDB-TF: Acceptors/PDINO/Ag. A solar simulator (Enlitech. Inc) with an AM 1.5 G filter was used as a light source to produce an intensity of 100 mW/cm² for the illumination of the photovoltaic cells. The light intensity was calibrated by a 2 cm × 2 cm calibrated silicon solar cell with KG-5 visible color filter.

A shadow mask was placed onto the devices in order to define the photoactive area accurately.

Steady-state current-voltage (J-V) curves were measured by a Keithley 2400 source-measurement unit under AM 1.5 G spectrum from a solar simulator (Enlitech. Inc) calibrated by a silicon reference cell (Hamamatsu S1133 color, with KG-5 visible filter). The relationship of J_{SC} to the light intensity were determined by steady-state current-voltage measurements, the light intensity was modulated by neutral density filters (NDF) with different values of optical density (OD). The external quantum efficiency (EQE) was measured by a solar cell–photodetector responsibility measurement system (Enlitech. Inc).

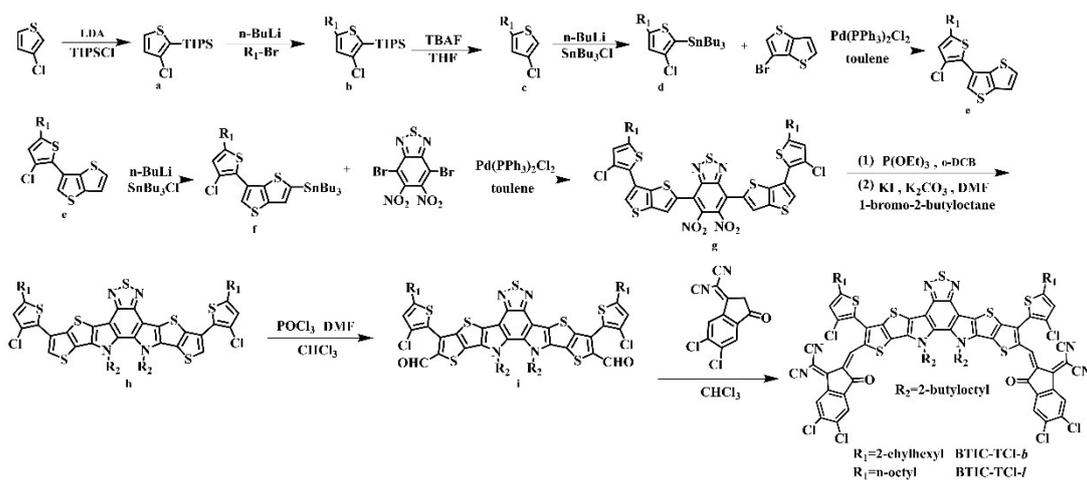
Fabrication of electron-only and hole-only devices. Electron-only devices were fabricated with the device structure of ITO/ZnO/PBDB-TF:acceptors/PDINO/Ag, while the hole-only devices were fabricated with the device structure of ITO/PEDOT:PSS/PBDB-TF:acceptors/MoO₃/ Ag. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC, ^{1,2} which is described by the equation:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_h \frac{V^2}{d^3} \quad (1)$$

where J is the current, μ_h is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage.

Materials and Synthesis

All chemicals, unless otherwise specified, were purchased from commercial resources and used as received.



Scheme S1. The synthetic routes to **BTIC-4Cl-b** and **BTIC-4Cl-l**

Synthesis of a: A solution of lithium diisopropylamide (LDA) (25.3 mL, 50.6 mmol) was added dropwise under an argon atmosphere to a solution of 3-chlorothiophene (6 g, 50.6 mmol) in THF (100 mL) at $-78\text{ }^\circ\text{C}$. After stirring for 2 h at this temperature, triisopropylsilyl chloride (10.73 g, 55.66 mmol) was added dropwise. The reaction mixture was gradually warmed to rt then stirred overnight. The mixture was quenched with a saturated aqueous solution of NH_4Cl , and extracted with DCM. The organic layers were dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified through silica column chromatography using hexane as the eluent to afford a colorless liquid product (**a**). (14.6 g, 96.4%) ^1H NMR (400 MHz, CDCl_3) δ : 7.53 (d, 1H), 7.06 (d, 1H), 1.50 (m, 3H), 1.14 (d, 18H).

Synthesis of b: *n*-Butyllithium (2.4 M, 13.8 mL, 33.17 mmol) or (2.4 M, 12.7 mL,

30.55 mmol) was added dropwise under an argon atmosphere to a solution of compound **a** (7.6g, 25.46 mmol)/ (7g, 25.46 mmol) in THF (100 mL) at -78 °C was added. After stirring for 2 h at this temperature, 3-(bromomethyl)heptane (6.6 g, 34.55 mmol) or 1-bromooctane (6.3 g, 31.82 mmol) was added dropwise. The reaction mixture was gradually warmed to rt then stirred overnight. The mixture was quenched with water, and extracted with hexane. The organic layers were dried by anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The crude product was purified through silica column chromatography using hexane as the eluent to afford a colorless liquid product (**b**). (10.5 g, 91%)/ (9.8 g, 91%). ¹H NMR (400 MHz, CDCl₃) δ: 6.73 (s, 1H), 2.75 (t, 2H), 1.68 (m, 1H), 1.55 (m, 2H), 1.49 (m, 3H), 1.30-1.32 (m, 6H), 1.13 (d, 18H), 0.88 (t, 6H) for R₁=2-ethylhexyl. ¹H NMR (400 MHz, CDCl₃) δ: 6.73 (s, 1H), 2.75 (t, 2H), 1.66 (m, 2H), 1.49 (m, 3H), 1.30-1.32 (m, 10H), 1.13 (d, 18H), 0.88 (t, 3H) for R₁=n-octyl.

Synthesis of c: Tetrabutylammonium fluoride (TBAF) (29.3 mL, 29.3 mmol) or (27.3 mL, 27.3 mmol) was added dropwise to a solution of compound **b** (10.5 g, 29.3 mmol) or (9.8 g, 27.3 mmol) in THF (100 mL) at 0 °C. The reaction mixture was stirred for 20 min at 0 °C, then the mixture was poured into water and extracted with hexane. The organic layers were dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified through silica column chromatography using hexane as the eluent to afford a colorless liquid product **c** (5 g, 95%)/(4.8 g, 96%). ¹H NMR (400 MHz, CDCl₃) δ: 6.87 (s, 1H), 6.64 (m, 1H), 2.75 (t, 2H), 1.68 (m, 1H), 1.55 (m, 2H), 1.49 (m, 3H), 1.30-1.32 (m, 6H), 1.13 (d, 18H), 0.88

(t, 6H) for R₁=2-ethylhexyl. δ : 6.87 (d, 1H), 6.64 (m, 1H), 2.75 (t, 2H), 1.64 (m, 2H), 1.30-1.33 (m 10H), 0.88 (t, 3H) for R₁= n-octyl.

Synthesis of d: *n*-Butyllithium (2.4 M, 11.5 mL, 27.17 mmol) or (2.4 M, 11.00 mL, 26.00 mmol) was added dropwise at -78 °C under argon atmosphere to a solution of compound **c** (5 g, 21.73 mmol) or (4.8 g, 20.88mmol) in THF (100 mL), After stirring at the same temperature for 1.5 h, tributyltin chloride(7.4 g, 27.17 mmol)/ (7.1g, 26.00 mmol) was added to the mixture at -78 °C, and the mixture was gradually warmed to rt. After stirring overnight, the mixture was quenched with water and extracted with hexane. The organic layer was dried with anhydrous MgSO₄. Removed the solvent under reduced pressure and gave the crude compound (**d**). Without any further purification, the product was used into the following reaction.

Synthesis of e: 3-bromothiено[3,2-b] thiophene (2 g, 9.36 mmol) or (3.5 g, 16.16 mmol), compound **d** (7.3 g, 14.04 mmol) or (12 g, 24.24), and Pd(PPh₃)₂Cl₂ (100 mg) were dissolved in toluene (100 mL) and stirred at 120 °C overnight under an argon atmosphere. The solvent was removed under vacuum after the reaction mixture was cooled to rt and then concentrated under reduced pressure. The crude product was purified through silica column chromatography using hexane as the eluent to afford a colorless liquid product **e** (2.45 g, 78.7%)/(2 g, 64.3%). ¹H NMR (400 MHz, CDCl₃) δ : 7.89 (d, 1H), 7.43 (dd, 1H), 7.30 (d, 1H), 6.71 (s 1H), 2.75 (m, 2H), 1.73-1.65 (m, 5H), 1.37-1.32 (m, 4H), 0.90 (t, 6H), for R₁=2-ethylhexyl. ¹H NMR (400 MHz, CDCl₃) δ : 7.87 (dd, 1H), 7.44 (d, 1H), 7.30 (d, 1H), 6.72 (s 1H), 2.79 (t, 2H), 1.68 (m, 2H), 1.37-1.27 (m, 10H), 0.90 (t, 3H), for R₁= n-octyl.

Synthesis of f: LDA (2M, 3.4 mL, 6.64 mmol)/ (2M, 2.7 mL, 5.42 mmol) was added dropwise at -78 °C under argon atmosphere to a solution of compound **e** (2.45 g, 6.64 mmol) or (2 g, 5.42 mmol) in THF (100 mL). After stirring at the same temperature for 1.5 h, tributyltin chloride (1.89 g, 6.97 mmol)/ (1.54 g, 5.69 mmol) was added to the mixture at -78 °C, and the mixture was gradually warmed to rt. After stirring overnight, the mixture was quenched with water and extracted with hexane. The organic layer was dried with anhydrous MgSO₄. Removing the solvent under reduced pressure gave the crude compound (**f**). Without any further purification, the product was used in the following reaction.

Synthesis of g: Compound **f** (5.5 g, 8.36 mmol)/ (4.4 g, 6.69 mmol), 4,7-dibromo-5,6-dini-tribenzo-[c][1,2,5] thiadiazole (1.46 g, 3.8 mmol) or (1.16 g, 3.04 mmol), and Pd(PPh₃)₂Cl₂ (100 mg) were dissolved in toluene (100 mL) and stirred at 85 °C overnight under an argon atmosphere. The solvent was removed under vacuum after the reaction mixture was cooled to rt and then concentrated under reduced pressure. The crude product was purified by chromatography on a silica gel column eluting with hexane/DCM (4:1, v/v). which yielded a red powder as product **g**. (3.6 g, 74.2%)/(3.2 g, 49.5%) ¹H NMR (400 MHz, CDCl₃) δ: 8.01 (s, 2H), 7.73 (s, 2H), 6.74 (s, 2H), 2.76 (t, 4H) 1.63 (m, 2H), 1.32-1.37 (m, 16H), 0.92 (t, 6H). R₁=2-ethylhexyl. ¹H NMR (400 MHz, CDCl₃) δ: 8.01 (s, 2H), 7.73 (s, 2H), 6.75 (s, 2H), 2.81 (t, 4H) 1.70-1.74 (m, 4H), 1.32-1.37 (m, 20H), 0.92 (t, 6H) for R₁= n-octyl.

Synthesis of h: Compound **g** (3.6 g, 6.2 mmol)/ (3.2 g, 3.3 mmol) and triethyl phosphite 10 ml were dissolved in the 1,2-dichlorobenzene (*o*-DCB, 50 mL) under an argon

atmosphere. The mixture was stirred at 180 °C overnight. After cooling to rt., the solvent was removed under reduced pressure, which gave an orange solid. The orange intermediate was transferred to a round-bottomed flask. Potassium carbonate (2.4 g, 17.4 mmol)/ (1.05 g, 7.62 mmol), potassium iodide (240 mg, 1.79 mmol)/ (105 g, 0.78 mmol), 1-bromo-2-butyloctane (1.6 g, 6.4 mmol)/ (700 mg, 2.8 mmol) and DMF (50 mL) were added and the mixture was deoxygenated with argon for 15 min. The mixture was stirred at 80 °C for 15 h under an argon atmosphere. After removing the solvent from the filtrate, the residue was extracted with DCM. The organic layers were combined and dried over anhydrous MgSO₄. Compound **h** was obtained by column chromatography on silica gel using hexane/DCM (8:1, v/v) as the eluent to give an orange solid (1.1 g, 56.8%)/ (1.0 g, 62.7%) ¹H NMR (400 MHz, CDCl₃) δ: 7.94 (s, 2H), 6.77 (s, 2H), 4.66 (d, 4H), 2.80 (t, 4H), 2.09 (m, 2H), 1.68 (m, 4H), 1.35-1.42(m, 16H), 0.84-1.01 (m, 40H), 0.58-0.67 (m, 24H) for R₁=2-ethylhexyl. ¹H NMR (400 MHz, CDCl₃) δ: 7.92 (s, 2H), 6.79 (s, 2H), 4.65 (d, 4H), 2.85 (t, 4H), 2.10 (m, 2H), 1.84 (m, 4H), 1.35-1.42(m, 12H), 0.84-1.01 (m, 36H), 0.58-0.67 (m, 18H) for R₁= n-octyl.

Synthesis of i: To a flask containing anhydrous DMF (5 mL)/ (5 mL), phosphorus oxychloride (1 mL)/ (1 mL) was added at 0 °C, the mixture was then stirred for 1 h. A solution of compound **h** (1.1 g, 0.818 mmol)/ (1.0 g, 0.744 mmol) in CHCl₃ (50 mL) or (50 mL) was added to the mixture dropwise. After stirring for another 20 min at 0 °C the mixture was heated to 50 °C and reacted overnight. The mixture was poured into water to quench the reaction and extracted with DCM several times. The organic layer was washed with water, dried by anhydrous MgSO₄. Removing the solvent and the

crude product was purified by column chromatography in a silica gel column, eluting with hexane/DCM (2:1, v/v) to give an orange solid compound **i** (1.1 g, 94%)/(1.0 g, 85.5%). ¹H NMR (400 MHz, CDCl₃) δ: 9.99 (s, 2H) 6.86 (s, 2H), 4.67 (d, 4H), 2.81 (t, 4H), 2.08 (m, 2H), 1.68 (m, 2H), 1.42-1.36 (m, 22H), 0.97-0.92 (m, 40H), 0.60-0.71 (m, 24H) for R₁=2-ethylhexyl. ¹H NMR (400 MHz, CDCl₃) δ: 9.99 (s, 2H) 6.88 (s, 2H), 4.65 (d, 4H), 2.88 (t, 4H), 2.07 (m, 2H), 1.77 (m, 6H), 1.32-1.46 (m, 30H), 0.85-1.02 (m, 44H), 0.60-0.71 (m, 20H) for R₁= n-octyl.

Synthesis of BTIC-4Cl-*b* and BTIC-4Cl-*l*: Under an argon atmosphere, compound **i** (110 mg, 0.09 mmol) or (110 mg, 0.09 mmol) and 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (94.7 mg, 0.36 mmol) or (94.7 mg, 0.36 mmol) were dissolved in THF (20 mL)/(20 mL). Then pyridine (1 mL)/(1 mL) was added to the mixture. After stirring at 60 °C overnight, the mixture was cooled to rt, the solution was concentrated under reduced pressure, poured into MeOH and filtered. The residue was purified in a silica gel column using hexane/DCM (1:1, v/v) as the eluent and obtained compound **BTIC-4Cl-*b* and BTIC-4Cl-*l*** as a blue solid (145 mg, 94%)/ (138 mg, 89%). ¹H NMR (400 MHz, CDCl₃) δ: 8.97 (s, 2H), 8.80 (s, 2H), 7.99 (s, 2H), 6.92 (s, 2H), 4.79 (m, 4H), 2.84 (t, 4H), 2.14 (m, 2H), 1.68 (m, 2H), 1.35-1.49 (m, 20H), 0.90-1.01 (m, 40H), 0.63-0.73 (m, 24H) for R₁=2-ethylhexyl. ¹H NMR (400 MHz, CDCl₃) δ: 8.95 (s, 2H), 8.79 (s, 2H), 7.98 (s, 2H), 6.94 (s, 2H), 4.79 (m, 4H), 2.90 (t, 4H), 2.15 (m, 2H), 1.74-1.81 (m, 6H), 1.35-1.49 (m, 22H), 0.90-1.01 (m, 42H), 0.63-0.73 (m, 18H) for R₁= n-octyl.

Figures and Tables

Table S1 Photovoltaic performance based on J_{cal} of two OSC devices.

Active layer	V_{OC} [V]	J_{cal} [mA cm ⁻²]	FF [%]	PCE [%]
PBDB-TF: BTIC-TCl-<i>b</i>	0.88	23.59	75.78	15.73
PBDB-TF: BTIC-TCl-<i>l</i>	0.88	23.33	73.62	15.11

Table S2 Photovoltaic performance based on two 1 cm² OSC devices.

Active layer	V_{OC} [V]	J_{SC} [mA cm ⁻²]	J_{cal} [mA cm ⁻²]	FF [%]	PCE [%]
PBDB-TF:BTIC-TCl-<i>b</i>	0.87	22.92	22.14	66.92	13.36
PBDB-TF:BTIC-TCl-<i>l</i>	0.87	22.48	21.76	64.40	12.58

Table S3. The detailed parameters of 2D-GIWAX profiles.

Active layer	(010) peak				(100) peak			
	q (Å ⁻¹)	^a Distance (Å)	FWHM (Å ⁻¹)	^b CCL (Å)	q (Å ⁻¹)	^a Distance (Å)	FWHM (Å ⁻¹)	^b CCL (Å)
PBDB-TF: BTIC-TCl-<i>b</i>	1.76	3.55	0.327	17.28	0.30	20.9	0.162	34.89
PBDB-TF: BTIC-TCl-<i>l</i>	1.75	3.59	0.331	17.06	0.31	20.26	0.181	31.23

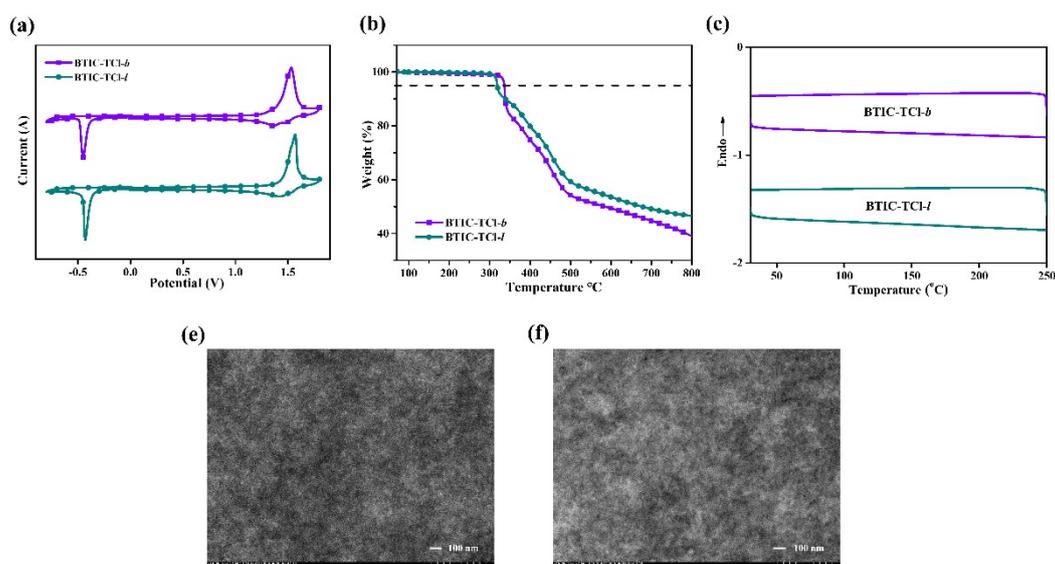


Figure S1. (a) Cyclic voltammograms of **BTIC-TCl-*b*** and **BTIC-TCl-*I*** in DCM with $(n\text{-Bu})_4\text{NPF}_6$ (0.1 M) as the supporting electrolyte, Pt wire as the counter electrode, and Ag/Ag^+ as the reference electrode. (b) Thermogravimetric analysis (TGA) results and (c) Differential scanning calorimetry (DSC) results of **BTIC-TCl-*b*** and **BTIC-TCl-*I***. TEM images of **BTIC-TCl-*b*** (e) and **BTIC-TCl-*I*** (f) -based devices.

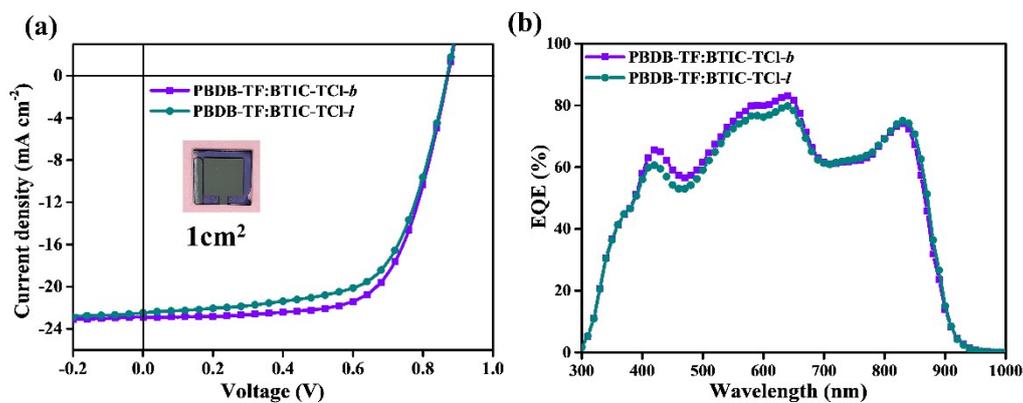


Figure S2 (a) J - V curves and (b) EQE curves of 1 cm^2 devices based on **BTIC-TCl-*b*** and **BTIC-TCl-*I***.

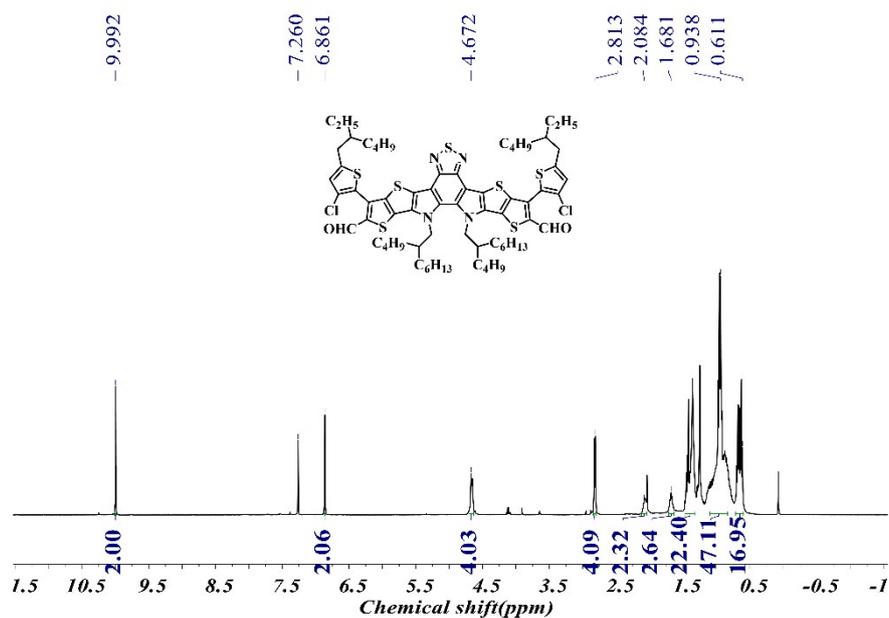


Figure S3. ^1H NMR of compound **i** ($R_1=2$ -ethylhexyl) in CDCl_3 .

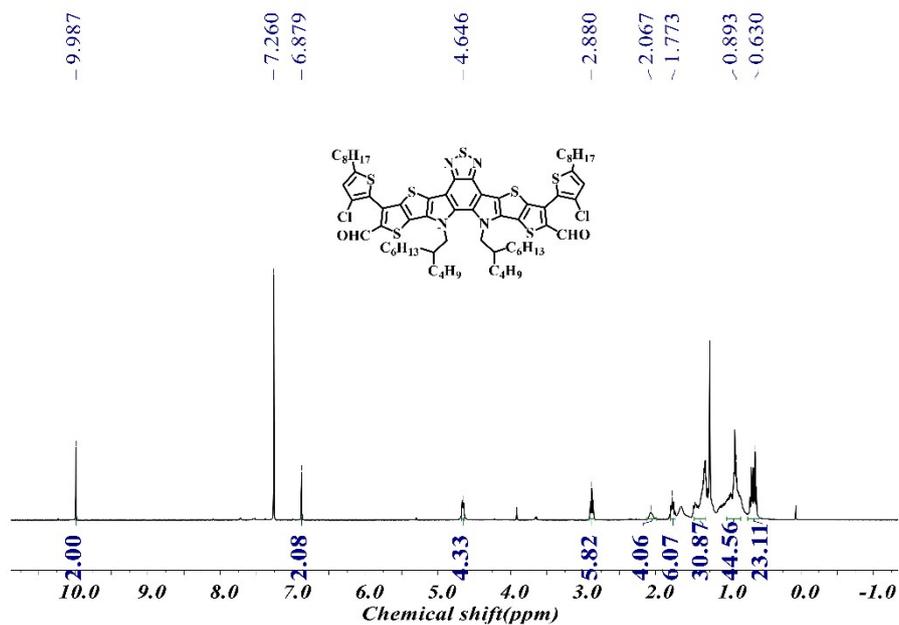


Figure S4. ^1H NMR of compound **i** ($R_1= n$ -octyl) in CDCl_3 .

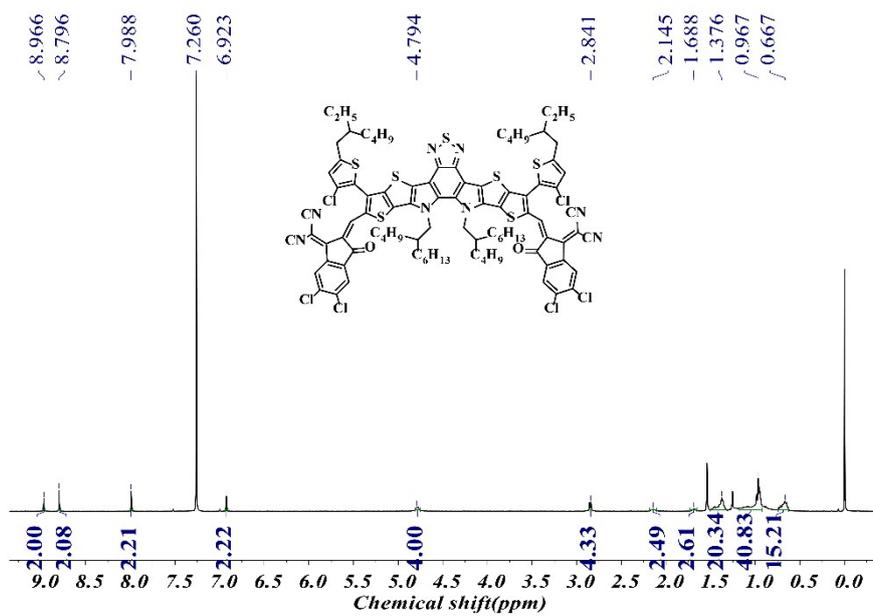


Figure S5. ^1H NMR of compound **BTIC-TCl-b** in CDCl_3 .

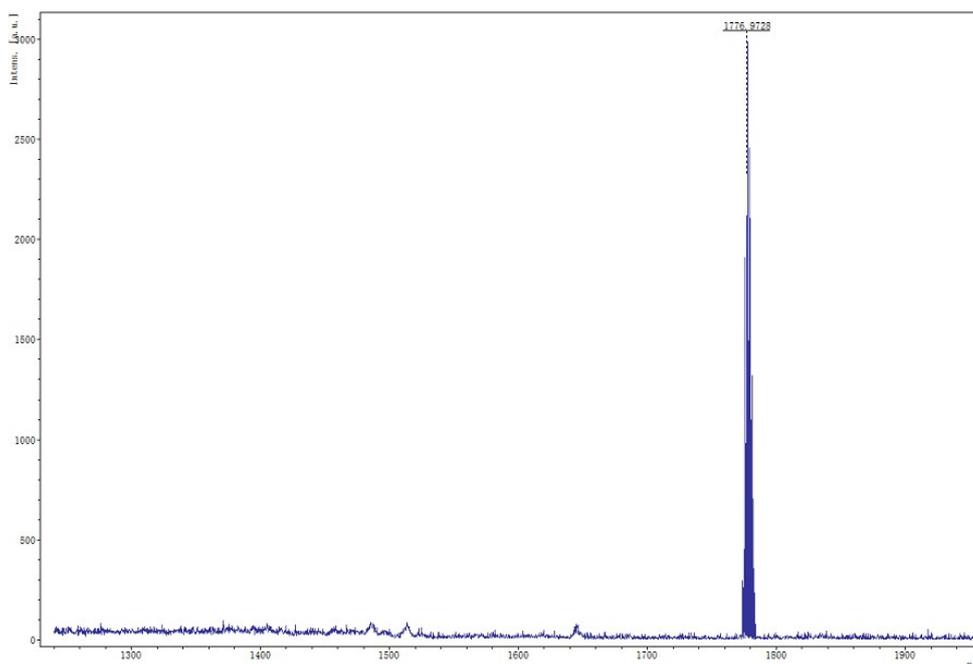


Figure S6. MALDI-TOF-MS of compound **BTIC-TCl-b**.

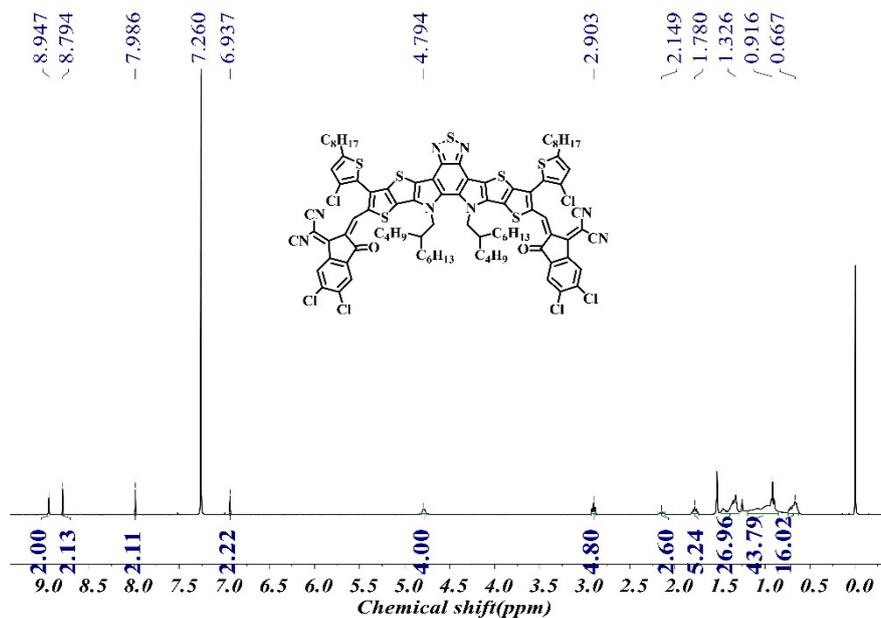


Figure S7. ^1H NMR of compound BTIC-TCI-I in CDCl_3 .

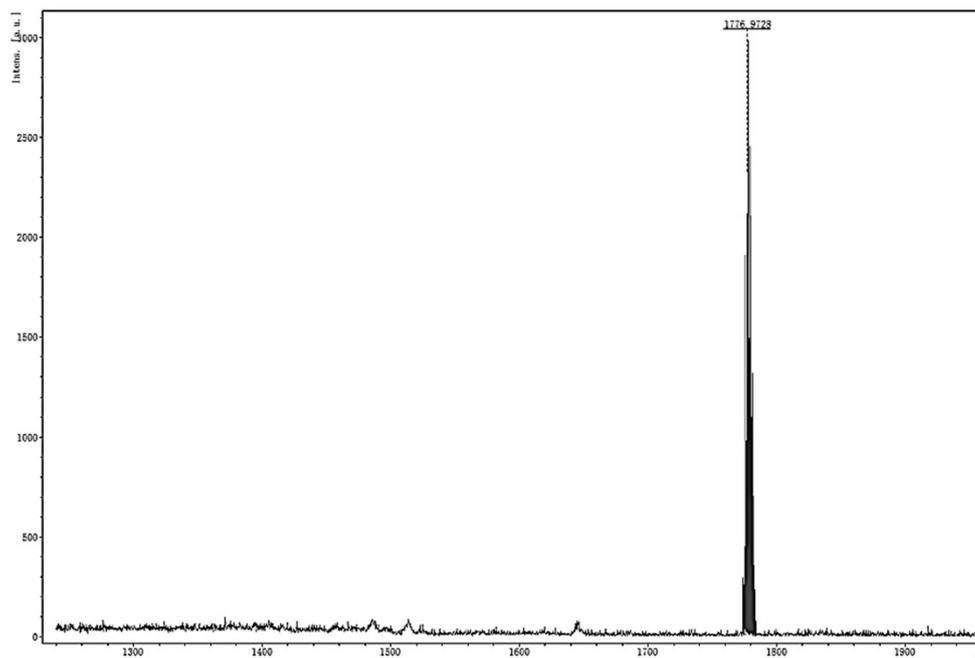


Figure S8. MALDI-TOF-MS of compound BTIC-TCI-I.

References

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