

A Near-Infrared Non-Fullerene Electron Acceptor for High Performance Polymer Solar Cells

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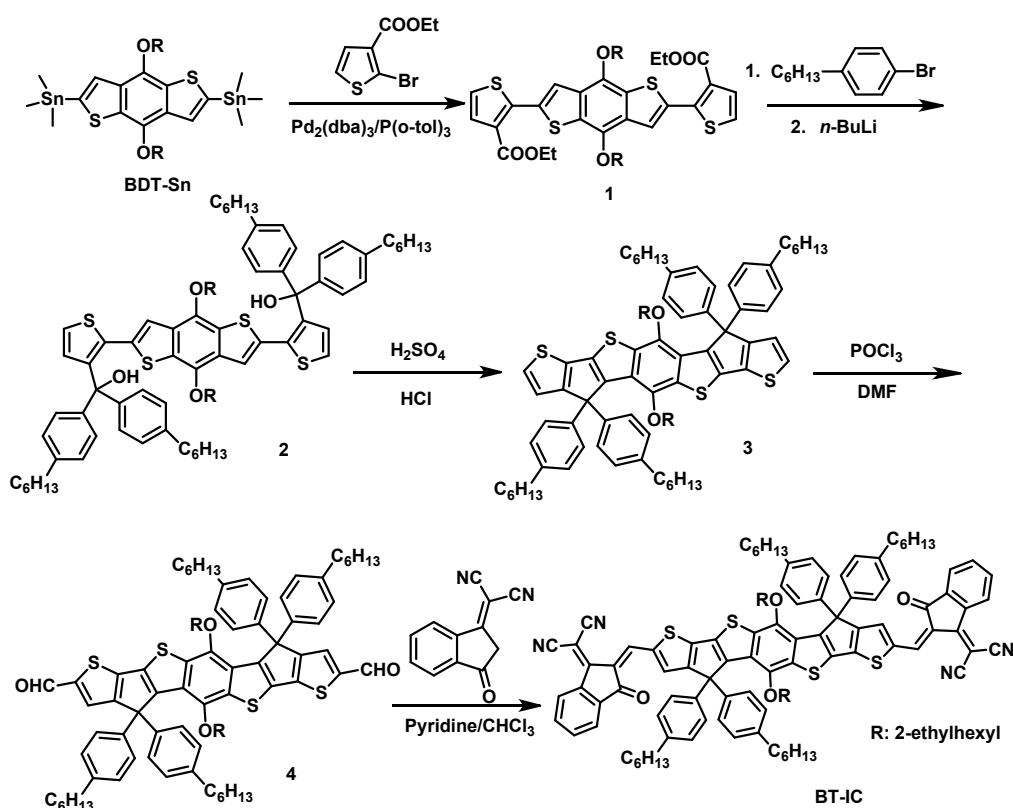
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Materials and Characterization:

All starting materials and reagents were purchased from commercial sources and used without further purification unless otherwise specified. All solvents were dehydrated and syringes, which were used to transfer reagents or solvents, were purged with Nitrogen prior to use. 2,6-Bis(trimethyltin)-4,8-bis (2-ethylhexyloxy)benzo[1,2-b:4,5-b'] dithiophene was used as received. Ethyl 2-bromothiophene-3-carboxylate were synthesized according to previously reported methods¹. The donor polymer J61 and J71 was used as received².



Scheme S1. The synthetic route for BT-IC.

Synthesis of Compound 1.

The BDT-Sn (1.54 g, 2.0 mmol) was dissolved in toluene (10 mL)/DMF (1 mL) and the ethyl 2-bromothiophene-3-carboxylate (1.18 g, 5.0 mmol) was then added. The mixture was deoxygenated by bubbling nitrogen gas through it for 30 minutes and then $\text{Pd}_2(\text{dba})_3$ (15 mg, 0.8 mol%) and $\text{P}(\text{o-tol})_3$ (29 mg, 4.8 mol%) were added. The resulted mixture was heated in a microwave reactor at 120 °C for 5 min, 150 °C for 3 h. After cooling to room

temperature, the resulted mixture was extracted with DCM. The organic phase was collected and dried over anhydrous Na_2SO_4 . Then, the solvent was evaporated and the crude product was purified on a silica gel chromatography using 1:1 (DCM: hexane) as the eluent. Evaporation of the solvent yielded the product as a yellow solid (1.37 g, 91%). ^1H NMR (400 MHz, CDCl_3 , δ): 7.82 (s, 2H), 7.55 (d, $J = 4.0$ Hz, 2H), 7.30 (d, $J = 4.0$ Hz, 2H), 4.34 (q, $J = 8.0$ Hz, 4H), 4.22 (d, $J = 8.0$ Hz, 4H), 1.82 (m, 2H), 1.61-1.33 (m, 16H), 1.31 (t, $J = 8.0$ Hz, 6H), 1.03 (t, $J = 8.0$ Hz, 6H), 0.94 (t, $J = 8.0$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 162.5, 143.9, 141.8, 133.3, 131.5, 130.3, 130.0, 129.0, 124.6, 121.9, 75.8, 60.4, 40.2, 30.0, 28.7, 23.4, 22.6, 13.7, 13.6, 10.8. MS (MALDI) m/z : M^+ , 754.267

Synthesis of Compound 3.

1-bromo-4-hexylbenzene (1.9 g, 8.0 mmol) was dissolved in anhydrous THF (50 mL) and placed under nitrogen atmosphere. The solution was cooled to -78 °C and stirred while 2.4 M *n*-butyllithium in hexane (3.3 mL, 8.0 mmol) was added dropwise. The mixture was stirred for 1 h at -78 °C, and then a solution of compound 1 (1.1 g, 1.5 mmol) in THF (30 mL) was added dropwise. The reaction was warmed to room temperature and stirred overnight, and then poured into water and extracted with DCM (3×50 mL). The organic extracts were combined and dried over anhydrous Na_2SO_4 . After removal of the solvent, the crude product was charged into three-neck flask. Acetic acid (50 mL) and concentrated HCl (0.5 mL) were added and the mixture was refluxed for 4 h. Then the mixture was poured into water, extracted with hexane. The resulted crude compound was purified by silica gel chromatography using a mixture of hexane/DCM (10:1) as the eluent to give a light yellow solid (710 mg, 63%). ^1H NMR (600 MHz, CDCl_3 , δ): 7.31 (m, 8H), 7.14 (d, $J = 6.0$ Hz, 2H), 7.01 (m, 8H), 6.86 (d, $J = 6.0$ Hz, 2H), 3.47 (d, $J = 6.0$ Hz, 4H), 2.53 (t, $J = 6.0$ Hz, 8H), 1.60-1.53 (m, 2H), 1.35-1.29 (m, 48H), 0.86 (m, 24H). ^{13}C NMR (125 MHz, CDCl_3 , δ): 163.3, 150.2, 144.7, 141.1, 137.8, 137.5, 134.5, 134.2, 128.6, 127.8, 127.1, 126.8, 123.2, 76.3, 63.6, 39.3, 35.5, 31.7, 31.2, 29.7, 29.2, 28.8, 23.4, 22.8, 22.6, 14.1, 10.9. MS (MALDI) m/z : M^+ , 1274.757.

Synthesis of Compound 4.

In a dry three neck round-bottomed flask, compound 3 (1.3 g, 1.0 mmol) was dissolved in DMF (50 mL) and placed under nitrogen atmosphere. The solution was cooled to 0 °C and stirred while phosphorus oxychloride in DCM (1.0 mL, 10.5 mmol) was added dropwise. The mixture was stirred for 1 h at 25 °C, and then stirred for 5 h at 105 °C. After the reaction, the mixture was cooled to room temperature and poured into ice water.

1 M NaOH solution was added and extracted with DCM, The resulted crude compound was purified by silica gel column using a mixture of hexane/DCM (3:2) as the eluent to give an orange solid (1.0 g, 75%). ¹H NMR (600 MHz, CDCl₃, δ): 9.73 (s, 2H), 7.49 (s, 2H), 7.31 (m, 8H), 7.06 (m, 8H), 3.49 (d, *J* = 6.0 Hz, 4H), 2.55 (t, *J* = 6.0 Hz, 8H), 1.60-1.53 (m, 2H), 1.35-1.29 (m, 48H), 0.86 (m, 24H). ¹³C NMR (125 MHz, CDCl₃, δ): 182.6, 163.5, 154.6, 145.6, 145.3, 144.6, 141.9, 137.3, 136.3, 135.1, 131.4, 128.5, 128.2, 127.7, 76.7, 64.0, 39.3, 35.5, 31.7, 31.2, 29.6, 29.2, 28.8, 23.3, 22.8, 22.6, 14.1, 10.9.

Synthesis of BT-IC.

1,1-dicyanamethylene-3-indanone (194mg, 1.0 mmol) was added into the mixture of compound 4 (400 mg, 0.3 mmol) in anhydrous chloroform with pyridine (1 mL), the reaction was deoxygenated with nitrogen for 30 min and then refluxed for 10 h . After cooling to room temperature, the solution was poured into methanol and the precipitate was filtered off. Then it was extracted with DCM and washed with water. The crude product was purified by silica gel column using a mixture of hexane/DCM (3:2) as the eluent to give a purple solid (378 mg, 85%). ¹H NMR (400 MHz, CDCl₃, δ): 8.78 (s, 2H), 8.64 (m, 2H), 7.87 (m, 2H), 7.69 (m, 4H), 7.47 (s, 2H), 7.31 (m, 8H), 7.08 (m, 8H), 3.48 (t, *J* = 4.0 Hz, 4H), 2.57 (t, *J* = 8.0 Hz, 8H), 1.60-1.53 (m, 2H), 1.35-1.29 (m, 48H), 0.96 (t, *J* = 8.0 Hz, 6H), 0.86 (m, 18H). ¹³C NMR (100 MHz, CDCl₃, δ): 188.1, 164.0, 159.8, 156.7, 153.4, 145.7, 141.7, 140.2, 139.4, 138.2, 138.0, 137.7, 136.3, 135.4, 134.5, 133.8, 128.0, 127.8, 124.8, 123.1, 120.8, 114.3, 67.9, 63.5, 38.9, 35.1, 31.2, 30.8, 29.2, 29.1, 28.7, 28.3, 22.8, 22.2, 22.1, 13.7, 13.6, 10.3. MS (MALDI) *m/z*: M⁺, 1683.722.

General measurement:

UV-Vis spectra were measured using a Perkin-Elmer Lambda-9 spectrophotometer. The ¹H and ¹³C NMR spectra were collected on a Bruker AV400 and 600 spectrometer in deuterated chloroform solution with TMS as reference. Time of Flight MS - MALDI (TOF) MS were performed on a Bruker Autoflex II / Compass 1.0 from Department of Materials Science and Engineering in Soochow University. Differential scanning calorimetry (DSC) was performed using a TA DSC 2010 unit under nitrogen at a heating rate of 10 °C/min from room temperature to 300 °C. Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of 10 °C/min from room temperature to 800 °C under nitrogen. Cyclic voltammetry of polymer film was conducted in acetonitrile with 0.1 M of tetrabutylammonium hexafluorophosphate using

a scan rate of 100 mV s⁻¹. ITO, Ag/AgCl and Pt mesh were used as working electrode, reference electrode and counter electrode, respectively. Atomic force microscopy (AFM) images of the interfacial films were obtained using a Veeco Multimode V instrument. TEM images was recorded on a Tecnai G2 F20 S-TWIN instrument at 200 kV accelerating voltage. Ultraviolet photoelectron spectroscopy was performed on Kratos AXIS ULTRA DLD instrument with UV light source is not monochromatic He I (21.22 eV). Grazing incidence x-ray diffraction (GIXD) characterization of BT-IC was performed at beamline 7.3.3, Advanced Light Source (ALS), Lawrence Berkeley National Lab (LBNL). X-ray energy was 10 keV and operated in top off mode. The scattering intensity was recorded on a 2D image plate (Pilatus 1M) with a pixel size of 172 μm (981 × 1043 pixels). The samples were ~10 mm long in the direction of the beam path, and the detector was located at a distance of 300 mm from the sample center (distance calibrated by AgB reference). The incidence angle was chosen to be 0.16° (above critical angle) for GIXD measurement. OPV samples were prepared on PEDOT:PSS covered Si wafers in a similar manner to the OPV devices. RSoXS was performed at beamline 11.0.1.2 Lawrence Berkeley National Lab. Thin films was flowed and transferred onto Si₃N₄ substrate and experiment was done in transition mode. The steady-state photoluminescence spectra and time resolved photoluminescence were measured by utilizing Edinburgh luminescence spectrometer (FS 920) and a single photon counting spectrometer (Life Spec II from Edinburgh instruments). The microwave-assisted Stille reaction was working on a CEM DISCOVER instrument.

Device Fabrication and Characterization:

The PSCs were fabricated in the configuration of ITO/PEDOT:PSS/J61 or J71:BT-IC/PDINO/Al. ITO-coated glass substrates were cleaned sequentially with deionized water, acetone, ethanol, and isopropanol under sonication for 10 min each and then treated by oxygen plasma for 15 min to generate the hydrophilic surface. The filtered PEDOT:PSS solution (Baytron P VP AI 4083 from H. C. Starck) was spin-coated onto the cleaned ITO substrates at 2000 rpm, followed by baking at 150 °C for 15 min in air. Subsequently, the substrates were transferred into a N₂-filled glove box for spin-coating of the photoactive layer. The active layer (ca. 130 nm) was then spin-coated from the blend solutions (total

concentration 16 mg mL⁻¹), which were prepared at 25 °C in chloroform. The mixed solutions were spin-coated on the top of the PEDOT:PSS layer at 1500 rpm for 90 s, followed by thermal annealing at 120 °C for 10 min. Methanol solution of PDINO with a concentration of 1.5 mg/mL was then spin-coated on the photoactive layer at 3000 rpm for 30 s to afford a thickness of ca. 10 nm. Finally, Al top electrode was deposited onto the PDINO buffer layer by thermal evaporation at a pressure of 5.0×10⁻⁵ Pa. The deposition rate and film thickness were monitored with a quartz crystal sensor. Shadow masks were used to define the active area (4.7 mm²) of the devices.

The current density-voltage (*J-V*) characteristics were measured using a Keithley 2450 Source-Measure Unit. Oriel Sol3A Class AAA Solar Simulator (model, Newport 94023A) with a 450 W xenon lamp and an air mass (AM) 1.5 filter was used as a light source. The light intensity was calibrated to 100 mW cm⁻² by a Newport Oriel 91150V reference cell. The EQE was measured with a solar cell spectral response measurement system (Enli Technology Co., Ltd., QE-R3011). The light intensity was calibrated using a single-crystal Si photovoltaic cell as a standard.

Space Charge Limited Current (SCLC) characterization:

Hole and electron mobility were measured using the space charge limited current (SCLC) method. ITO/PEDOT:PSS/ J61:BT-IC/Au for hole-only devices and ITO/ZnO/ J61:BT-IC /PDINO/Al for electron-only devices. The SCLC mobilities were calculated by MOTT-Gurney equation:

$$J = \frac{9\epsilon_r\epsilon_0\mu V^2}{8L^3}$$

Where *J* is the current density, ϵ_r is the relative dielectric constant of active layer material usually 2-4 for organic semiconductor, herein we use a relative dielectric constant of 4, ϵ_0 is the permittivity of empty space, μ is the mobility of hole or electron and *L* is the thickness of the active layer, *V* is the internal voltage in the device. As shown in Figure S8, S9&S10, the hole and electron mobilities of J61 : BT-IC (1:1,w/w) are estimated as 6.15×10⁻⁴ and 4.59×10⁻⁴ cm² V⁻¹ s⁻¹ respectively, corresponding to nearly balanced charge transport ($\mu_h/\mu_e = 1.3$).

Transient Absorption Characterization:

Transient absorption data were collected using transient absorption spectroscopy setup. This setup consists of the spectrometer (Ultrafast Helios system) and amplified Ti:Sapphire Laser. The output of amplified Ti:Sapphire Laser provides 800 nm fundamental pulses at 1kHz repetition rate which were splitted into two optical beams to generate pump and probe pulses. One fundamental beam was used to generate pump beam using an optical parametric amplifier (OPA) system (Coherent Opera Solo). A white light/NIR probe was generated by focusing another fundamental beam into a flint glass. Pump and probe beams were focused on a sample and probe light was collected by a charge-coupled device CCD device. The spectral detection region is 0.8 eV to 2.6 eV. The thin film samples were encapsulated using UV curable glue before measurement. The instrument response function (IRF) was ~ 100 fs FWHM. The samples were excited with the excitation energy 1.62 eV (765 nm) for acceptor excitation and 2.25 eV (550 nm) for donor excitation. The fractional change in transmission was detected in the probe range 0.8-2.6 eV at several time delays.

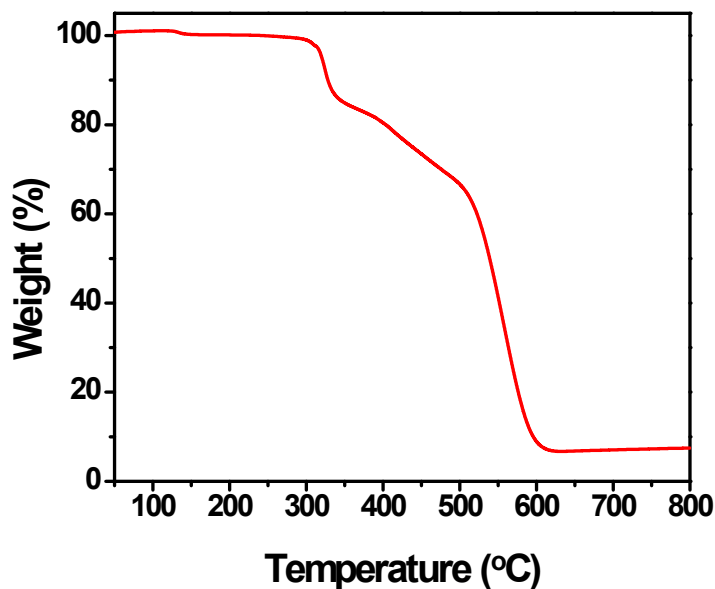


Figure S1. TGA curve of BT-IC with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under an inert atmosphere.

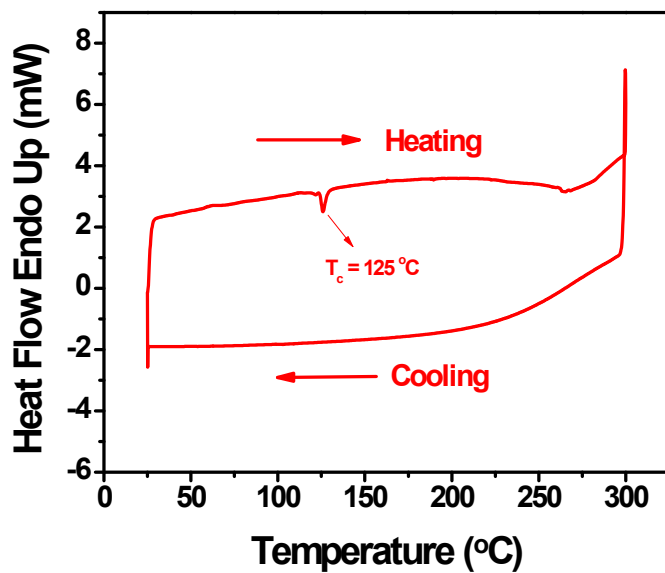


Figure S2. DSC curve of BT-IC with a heating rate of $10^\circ\text{C min}^{-1}$ under an inert atmosphere.

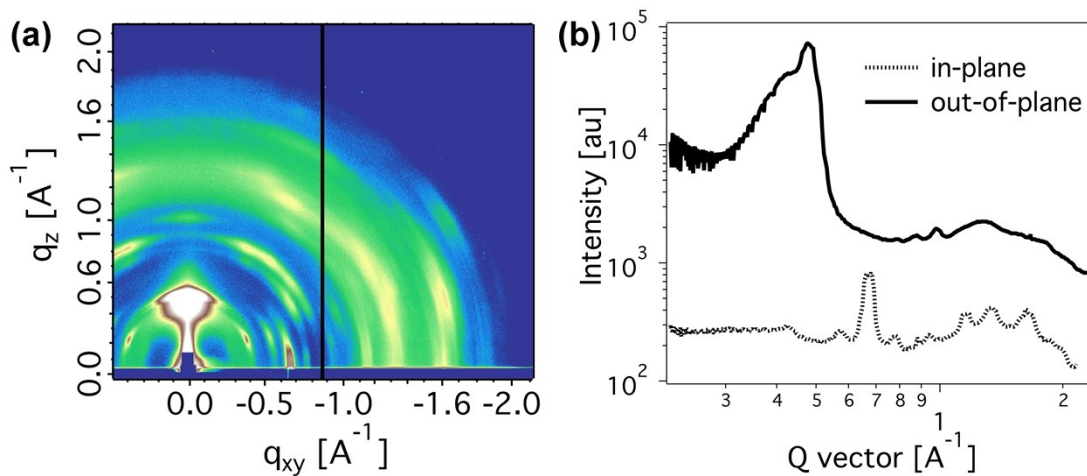


Figure S3. (a) 2D GIXD diffraction images of BT-IC as cast films; (b) In-plane (dotted line) and out-of-plane (solid line) X-ray scattering profiles extracted from the 2D GIXD images.

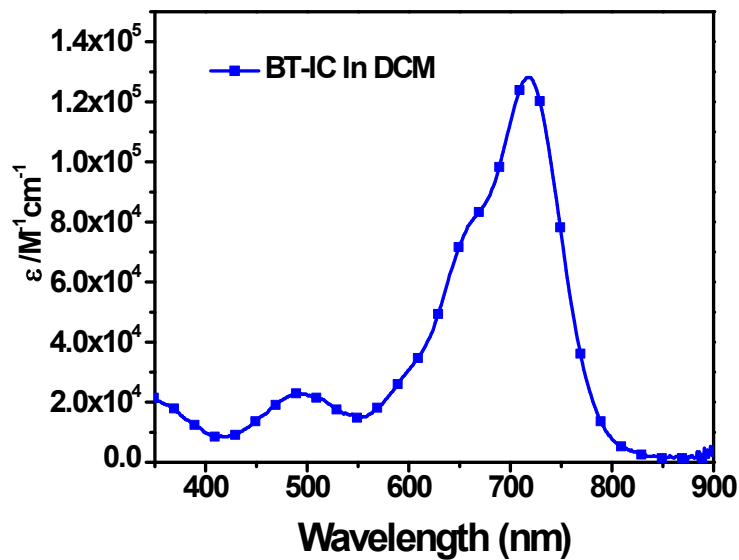


Figure S4. UV-vis absorption spectrum of BT-IC in DCM.

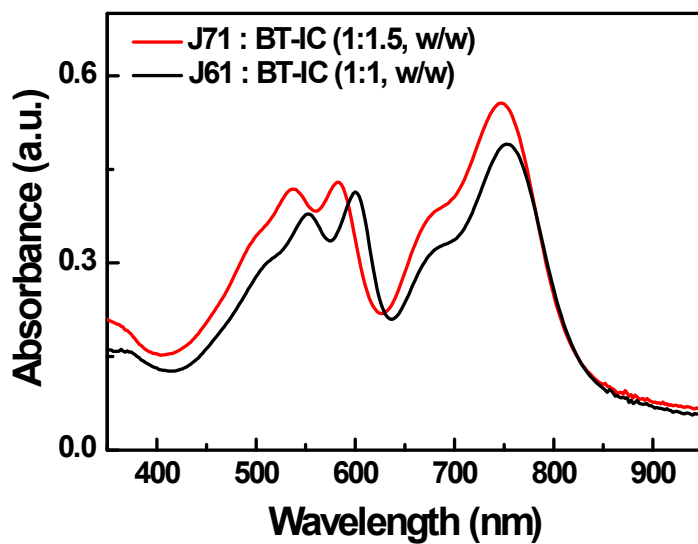


Figure S5. UV-vis absorption spectra of J71:BT-IC and J61:BT-IC blend films.

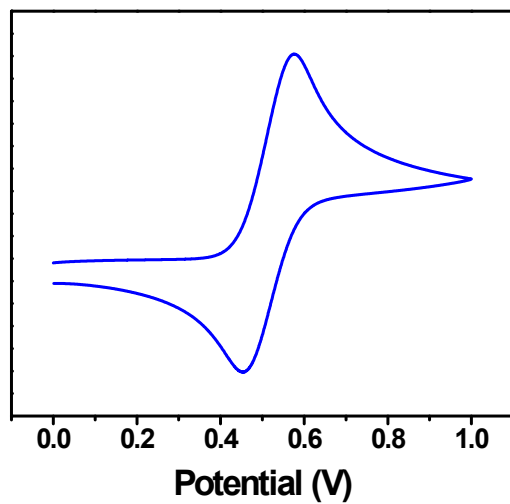


Figure S6. The cyclic voltammetry curve of ferrocene in $\text{CH}_3\text{CN} / 0.1 \text{ M } [\text{nBu}_4\text{N}]^+[\text{PF}_6]^-$ at 100 mV s^{-1} , the horizontal scale refers to the Ag/AgCl electrode.

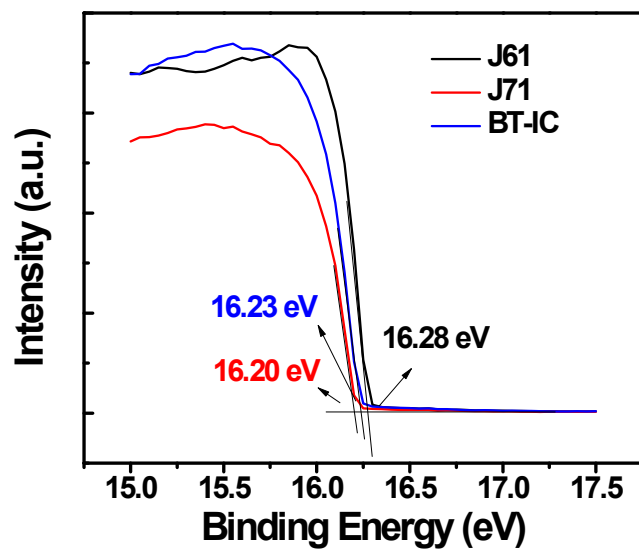


Figure S7. Ultraviolet photoelectron spectroscopy data of neat J61, J71 and BT-IC films.

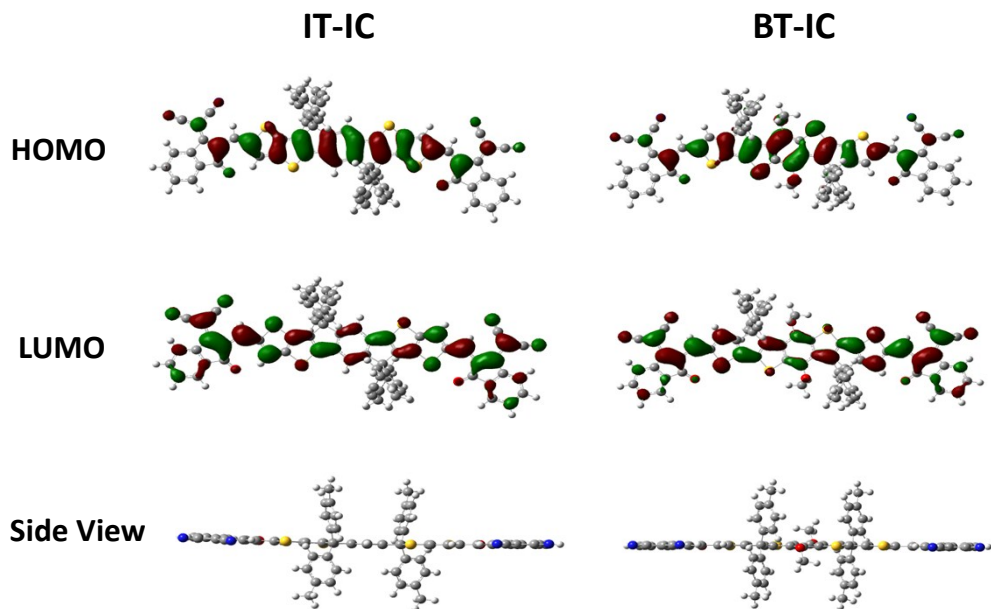


Figure S8. Molecular geometries and HOMO/LUMO wave functions of the IT-IC and BT-IC.

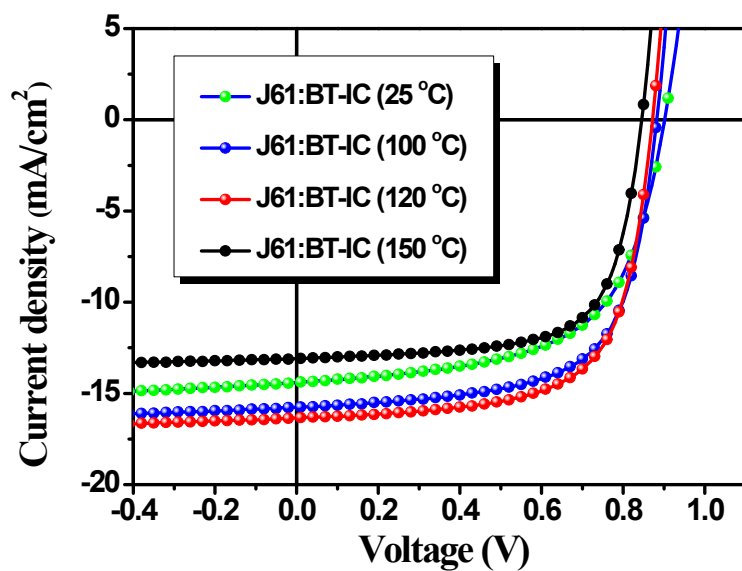


Figure S9. The J - V characteristics of the PSCs based on J61 and BT-IC (blend ratio of 1:1, w/w) at different annealing temperature.

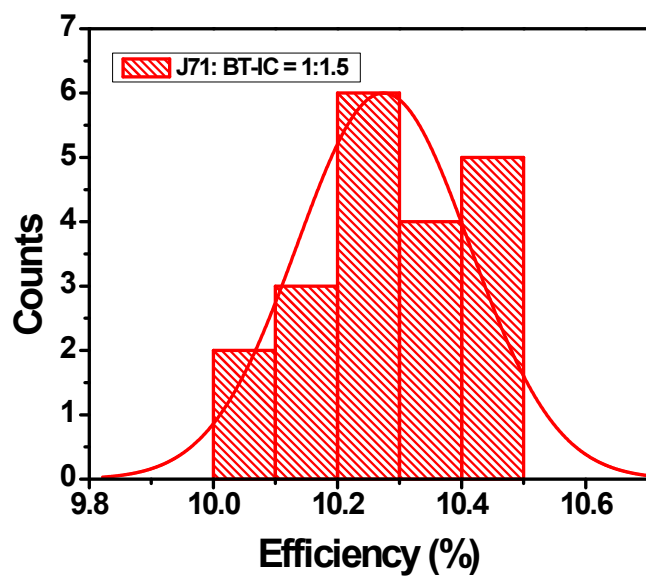
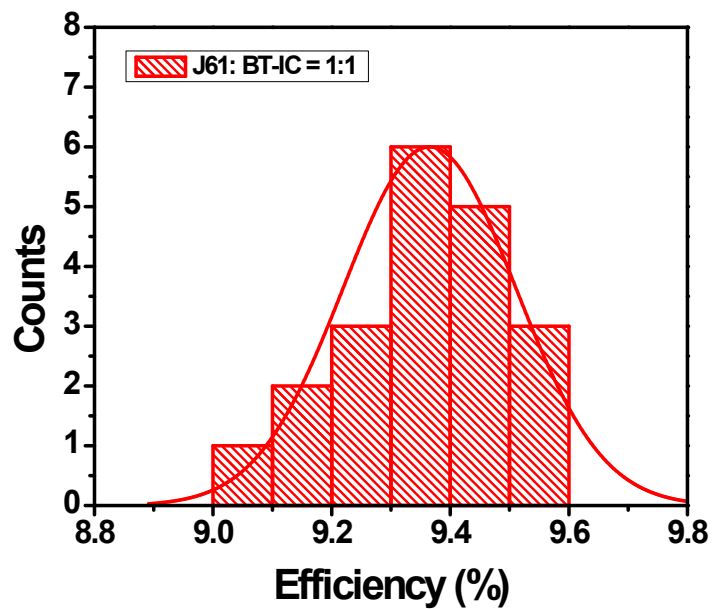


Figure S10. Statistical histogram of PCEs of PSCs based on J61: BT-IC (1:1, w/w) and J71: BT-IC (1:1.5, w/w) fabricated with chloroform solution followed by thermal annealing at 120 °C for 10 min.

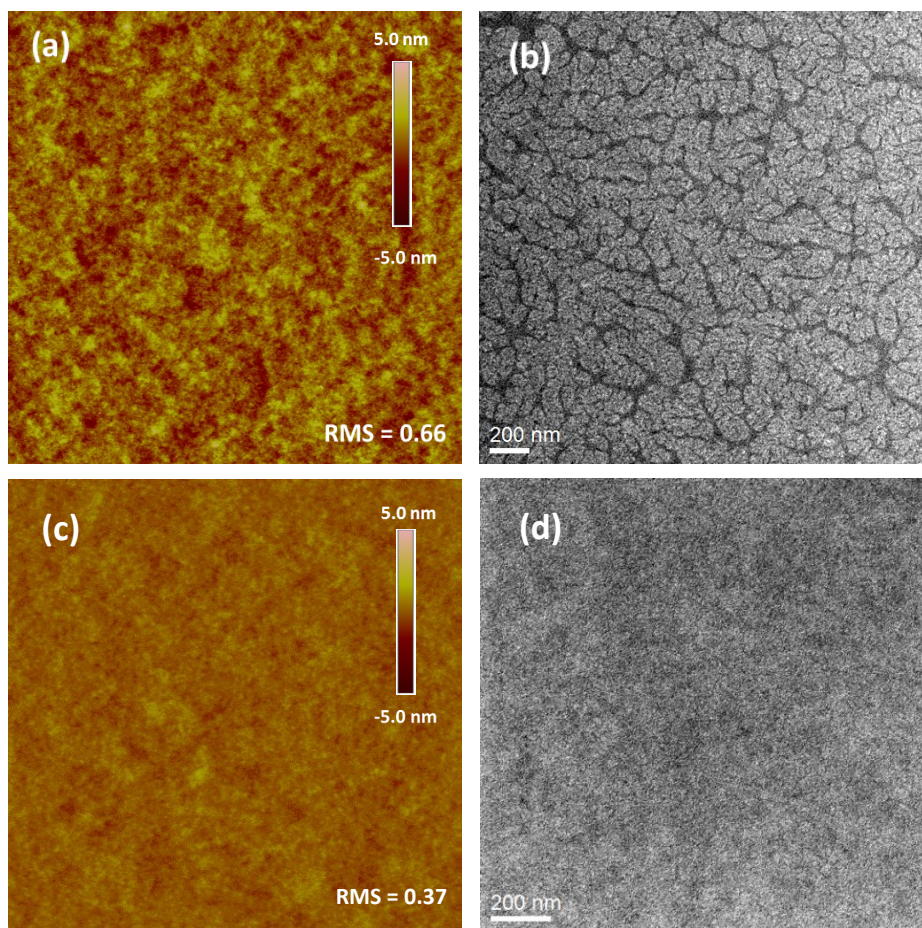


Figure S11. (a) AFM topographic image ($5 \times 5 \mu\text{m}$) and (b) TEM image of J61:BT-IC (1:1, w/w) and J71:BT-IC (1:1.5, w/w) blend films cast from chloroform solution.

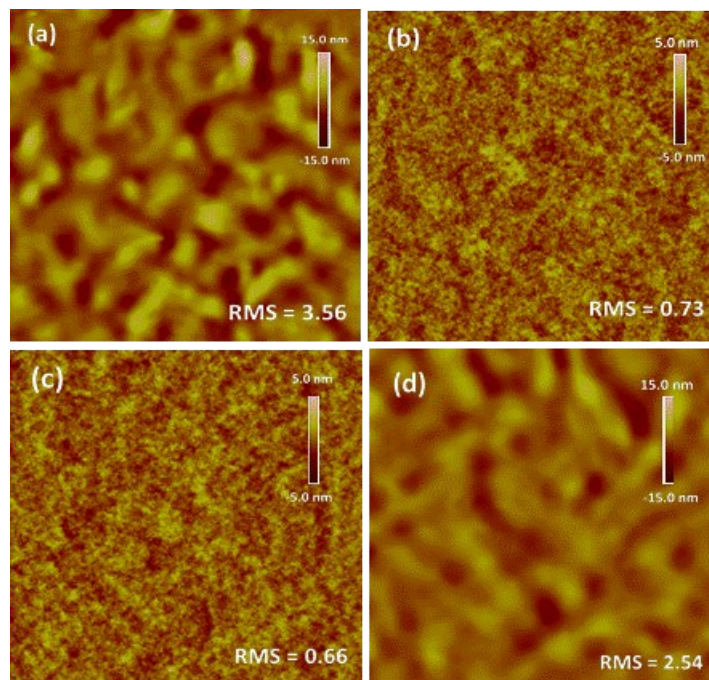


Figure S12. AFM topography images ($5 \times 5 \mu\text{m}$) of J61:BT-IC (1 : 1 w/w) blend films from CF at the annealing temperature of 25°C(a), 100°C(b), 120°C(c) and 150°C(d).

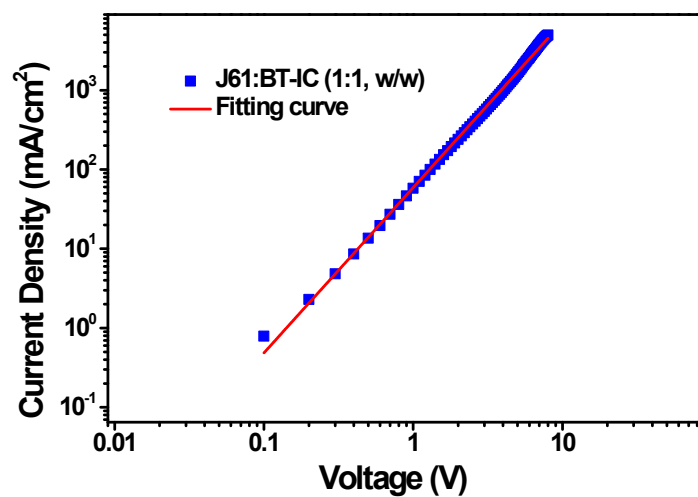


Figure S13. J - V plots for electron-only devices based on J61:BT-IC (1:1, w/w) blended films.

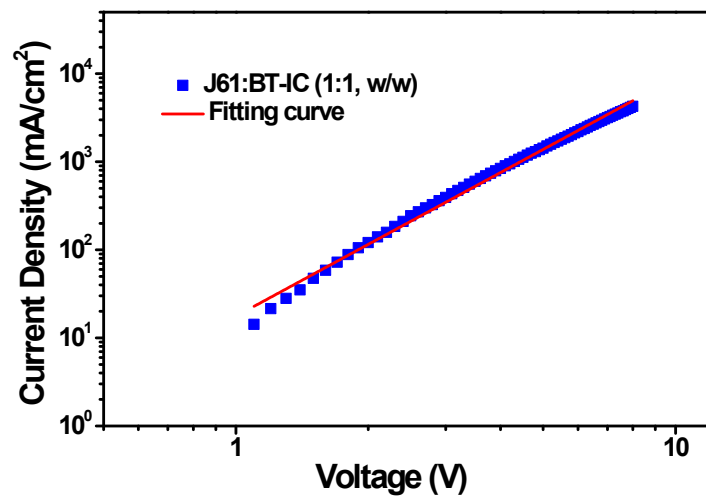


Figure S14. J - V plots for hole-only devices based on J61:BT-IC (1:1, w/w) blended films.

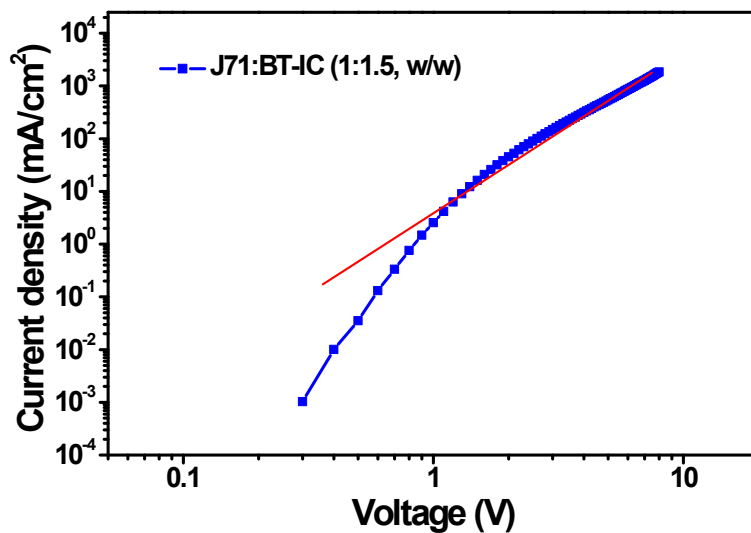


Figure S15. J - V plots for hole-only devices based on J71:BT-IC (1:1.5, w/w) blended films.

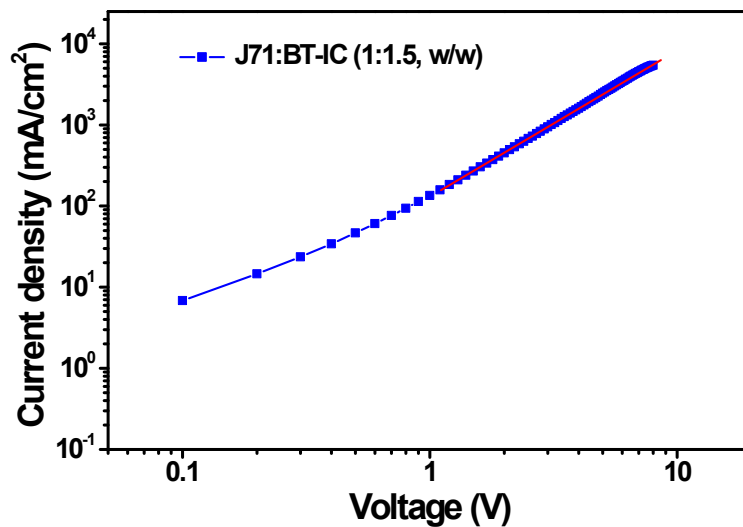


Figure S16. J - V plots for electron-only devices based on J71:BT-IC (1:1.5, w/w) blended films.

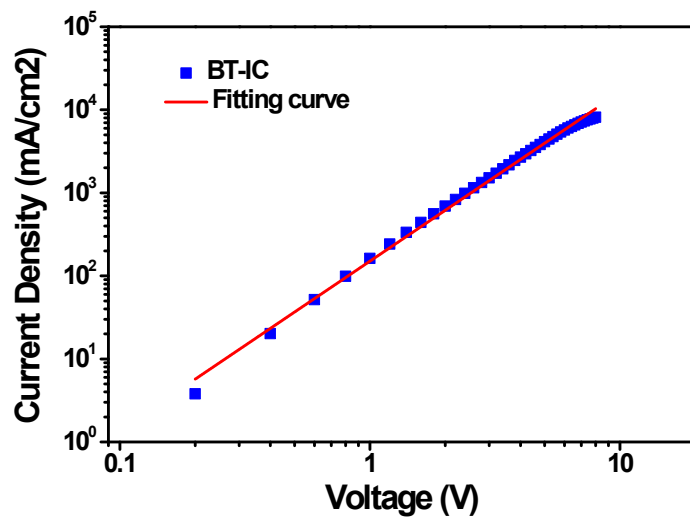


Figure S17. J - V plots for electron-only device based on BT-IC films.

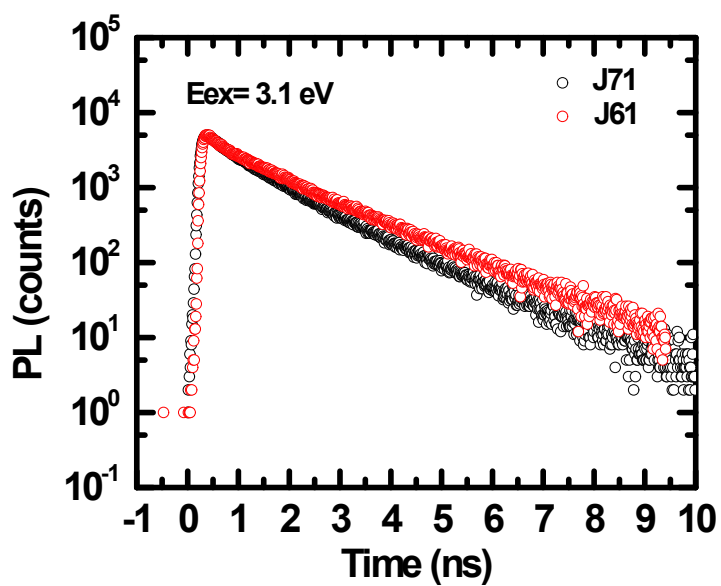


Figure S18. Time-resolved fluorescence of neat J61 and J71 in thin film.

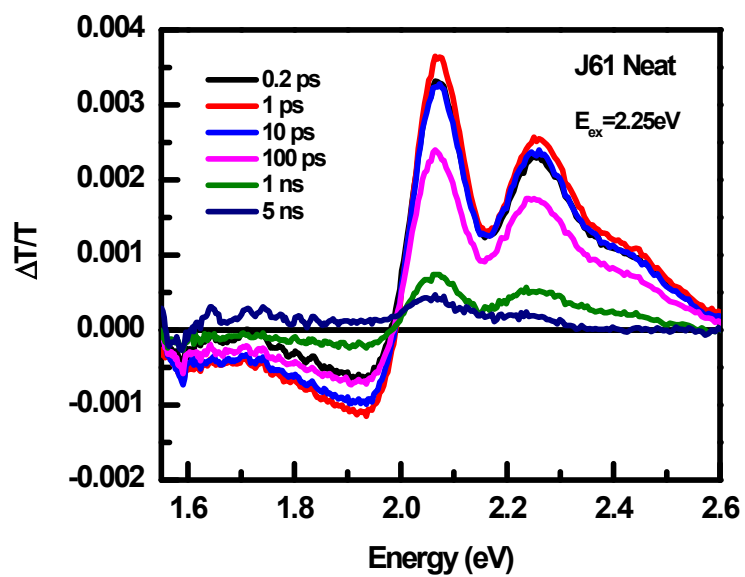


Figure S19. Transient absorption spectra of neat donor J61 at 2.25 eV excitation.

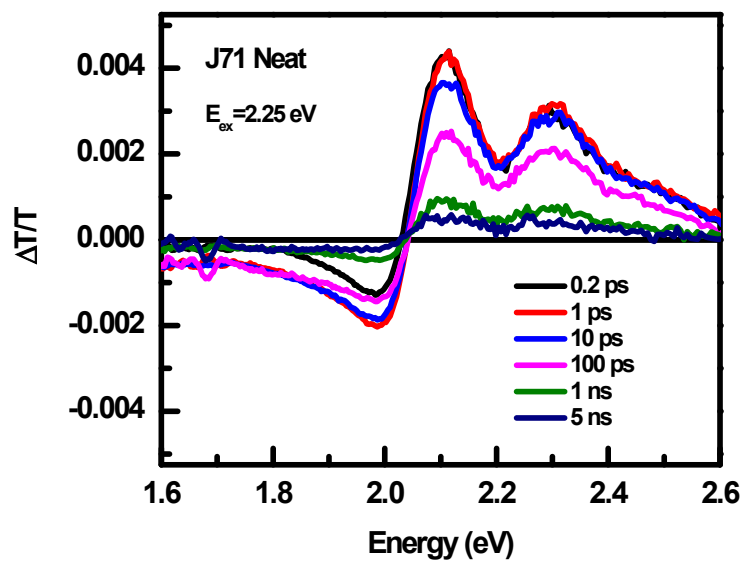


Figure S20. Transient absorption spectra of neat donor J71 at 2.25 eV excitation.

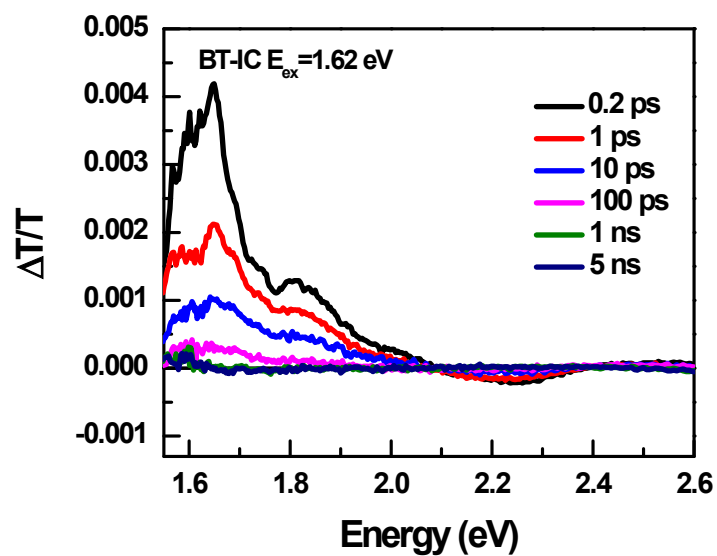


Figure S21. Transient absorption spectra of neat acceptor BT-IC at 1.62 eV excitation.

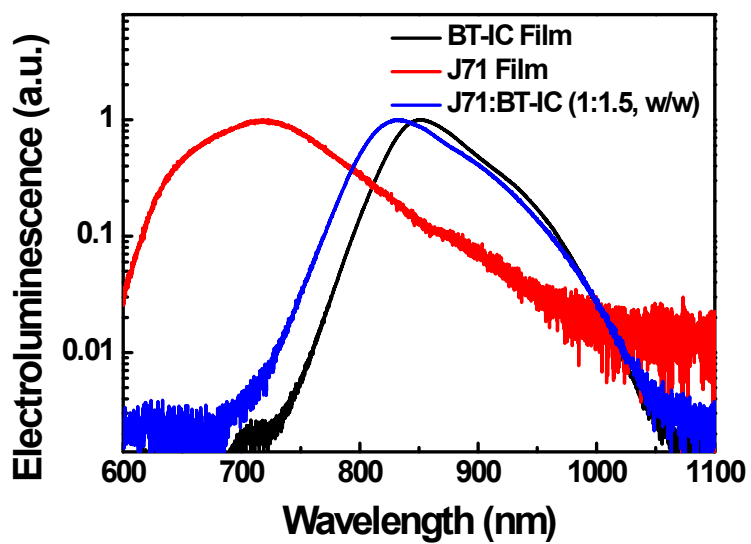


Figure S22. EL spectra of the J71 and BT-IC neat film and J71:BT-IC blend film.

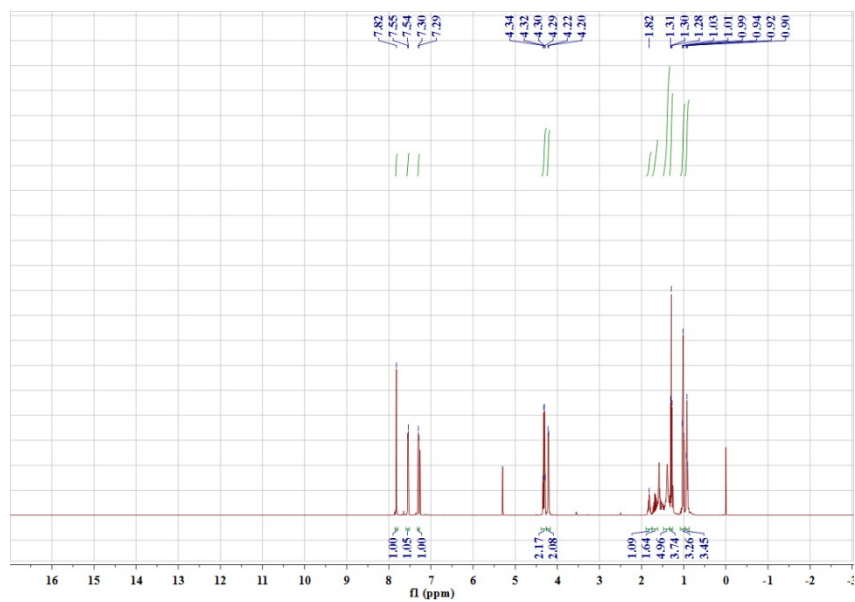


Figure S23. The ^1H NMR spectrum of Compound 1, conducted in Chloroform-*d*.

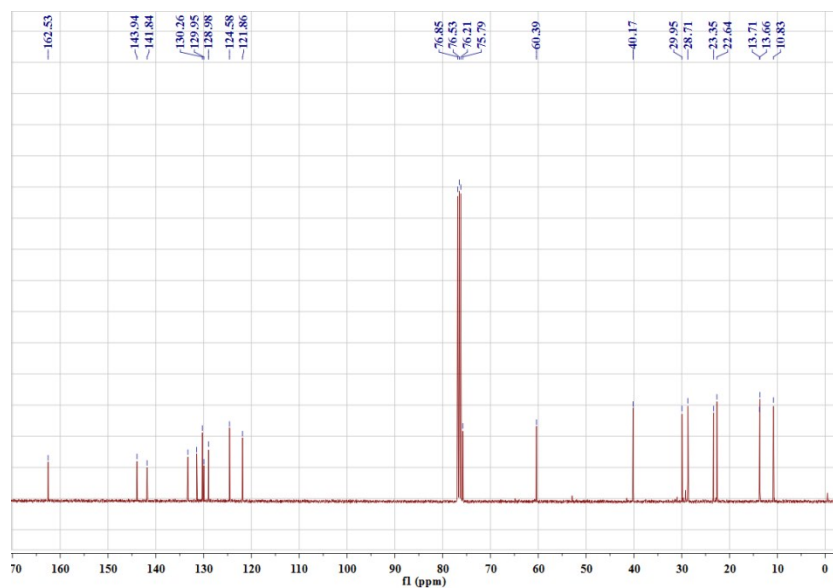


Figure S24. The ^{13}C NMR spectrum of Compound 1, conducted in Chloroform-*d*.

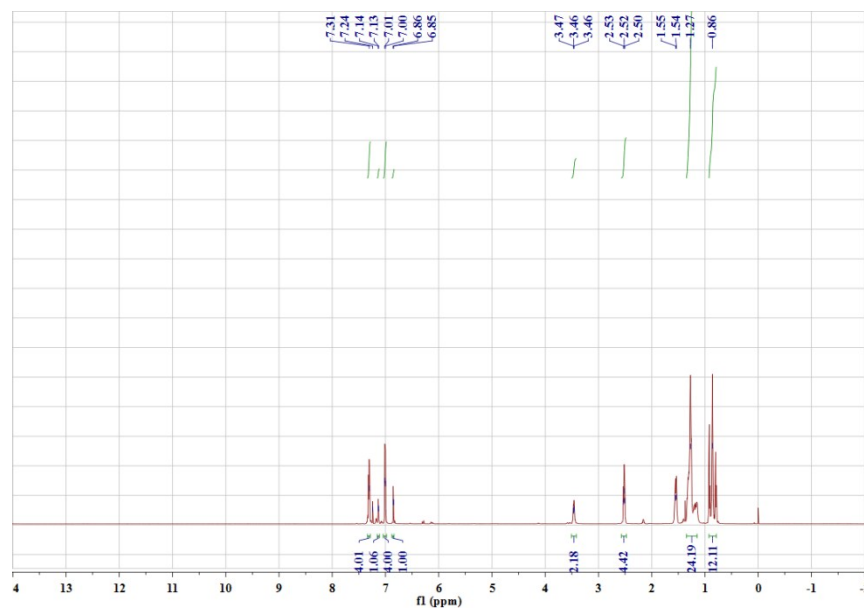


Figure S25. The ^1H NMR spectrum of Compound 3, conducted in Chloroform-*d*.

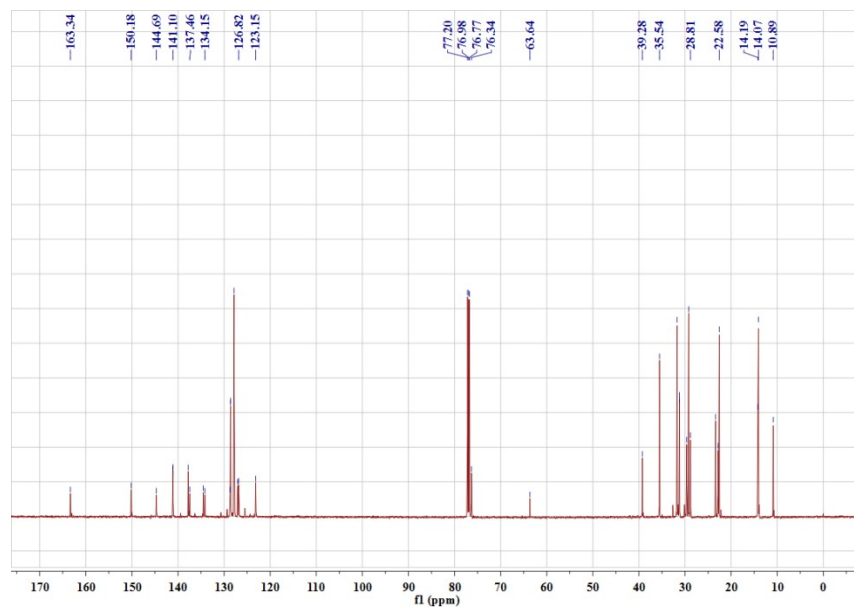


Figure S26. The ^{13}C NMR spectrum of Compound 3, conducted in Chloroform-*d*.

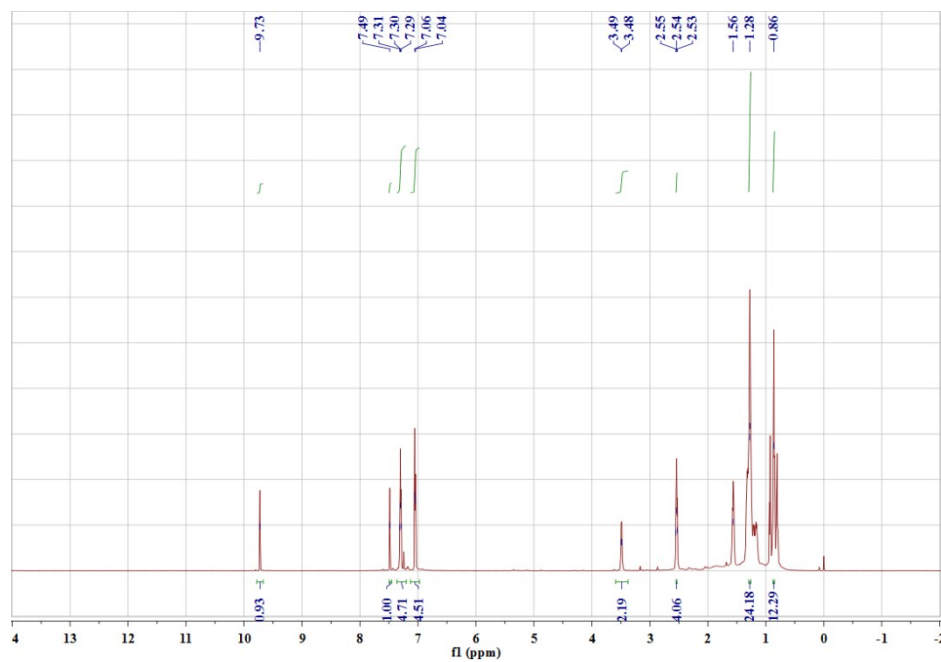


Figure S27. The ^1H NMR spectrum of Compound 4, conducted in Chloroform-*d*.

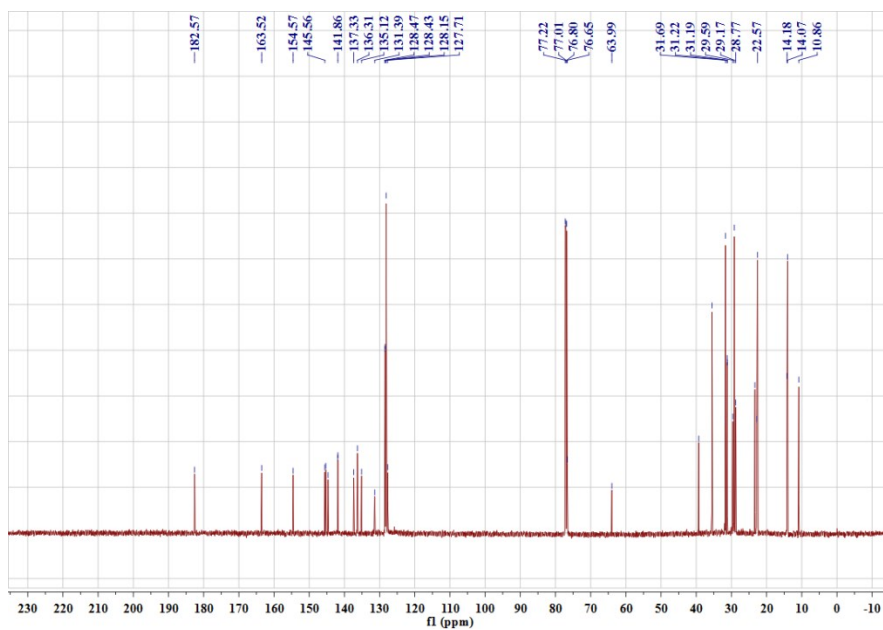


Figure S28. The ^{13}C NMR spectrum of Compound 4, conducted in Chloroform-*d*.

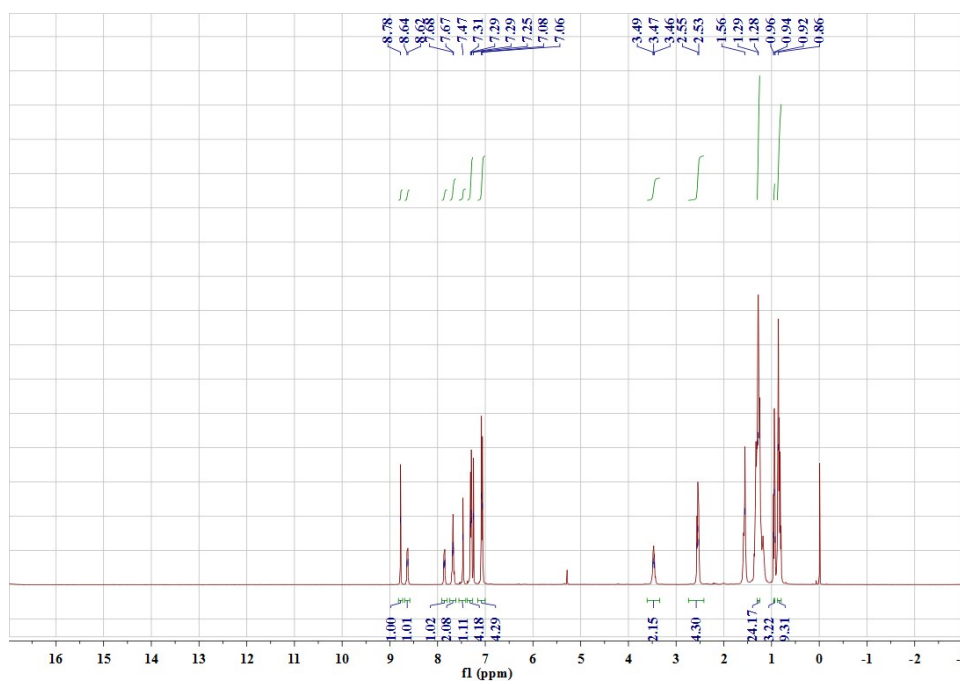


Figure S29. The ^1H NMR spectrum of BT-IC, conducted in Chloroform-*d*.

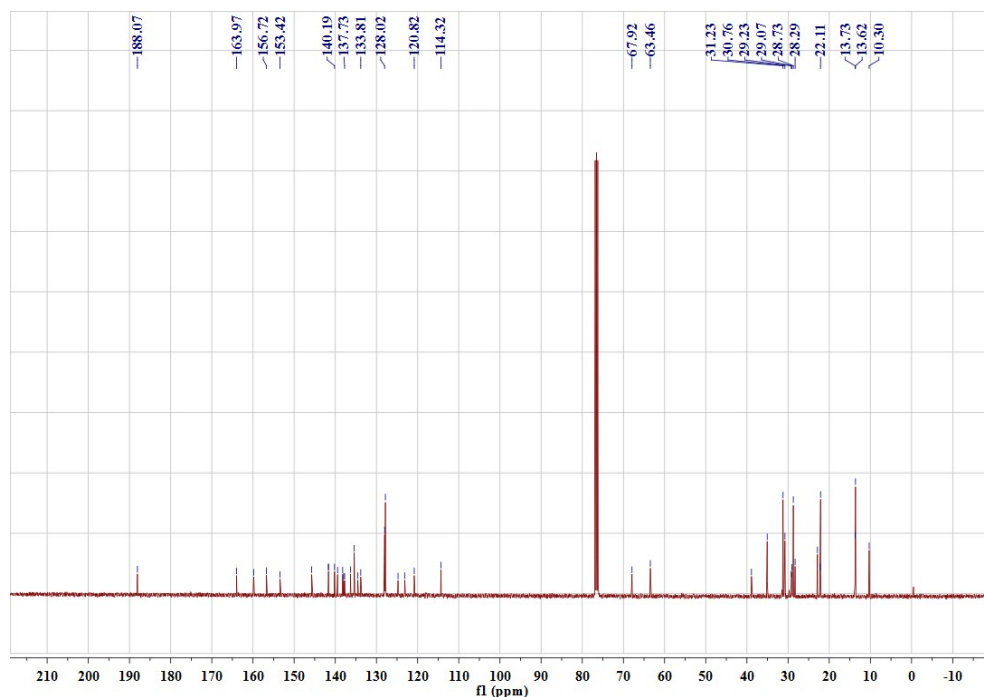


Figure S30. The ^{13}C NMR spectrum of BT-IC, conducted in Chloroform-*d*.

Table S1. Photovoltaic parameters of the PSCs based on J61 as a donor and BT-IC, as an acceptor with different annealing temperature under the illumination of AM 1.5G, 100 mW cm^{-2} .

Temperatur e ($^{\circ}\text{C}$)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE_{ave} ^{a,b} (%)	PCE_{max} ^a (%)
25	0.90	14.41	60.6	7.51	7.88
100	0.88	16.10	65.4	8.92	9.22
120	0.87	16.35	67.1	9.37	9.56
150	0.85	13.10	68.8	7.30	7.61

^a the device fabricate with CF without additive; ^b the reported values are average PCEs from 20 devices.

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