

Supporting Information

Binary and ternary single junction polymer solar cells-based D-A copolymer with a low-lying HOMO energy level and two nonfullerene acceptors

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Experimental Part

Instruments

¹H NMR spectra were obtained on an Agilent 600 MHz DD2 nuclear magnetic resonance (NMR) spectrometer, using CDCl₃ as solvent at the resonance frequency of 600 MHz at room temperature. UV-vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. The molecular weight of polymers was determined by wafers 1515 gel permeation chromatography using 1,2,4-trichlorobenzene as eluent at 60°C and polystyrene as a standard. The thermal characteristics of the polymers were investigated using thermogravimetric analysis (TGA) on a "Perkin Elmer-7" and differential scanning calorimetry (DSC-3) "Mettler-Toledo, Switzerland" at rapid heating of 10°C/min in argon. Oxidation and reduction potentials of the compounds were determined by cyclic voltammetry (CV) experiments on a computer-controlled potentiostat "Autolab type III" at a scan rate of 50 mV s⁻¹. A platinum working electrode, Ag/AgNO₃ (0.1 M in anhydrous acetonitrile), and a platinum wire were used as the working electrode, reference electrode and counter electrode, respectively, in a nitrogen-saturated tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) solution (0.1 M in anhydrous acetonitrile). Assuming the absolute energy level of Fc/Fc⁺ to be

-4.43 eV versus the vacuum level, thus the HOMO and LUMO energy levels were obtained from the equation of $E_{\text{HOMO}}/E_{\text{LUMO}} = -(E_{\text{ox}}/E_{\text{red}} + 4.43)$ (eV), where oxidation/reduction onset potential ($E_{\text{ox}}/E_{\text{red}}$) were determined from the position at which the current raised initially from the baseline.

Materials

All of the reagents and chemicals were purchased from Aldrich, Across and TCI and used without further purification. Toluene was dried and purified by fractional distillation over sodium/benzophenone under argon. The M1 and M2 were synthesized according to the literature procedures.

The synthesis of copolymer P(DTB-BDD):

Mixture M1 (0.4122g, 0.5 mmol) M3 (0.3834g, 0.5 mmol) and palladium catalyst $\text{Pd}(\text{Ph}_3\text{P})_4$ (0.027g) was polymerized for 48h to give P132a (0.47g, yield 86%). Elem. Anal. Calcd for $(\text{C}_{66}\text{H}_{86}\text{O}_2\text{S}_6)$: C, 71.82; H, 7.85; S, 17.43. Found: C, 71.40; H, 7.77; S, 17.03%. ^1H NMR (CDCl_3 , 400 MHz, δ / ppm): 7.92-7.33 (br, 2H), 7.23-6.00 (br, 4H), 3.79-2.20 (br, 8H), 1.87-0.72 (br, m, 72H). $M_n=32.3$ kDa and $\text{PDI}=1.96$.

Device fabrication and characterization

The polymer solar cells were fabricated with a conventional device structure ITO/PEDOT:PSS/P(DTB-BDD):Y6 or DBTBT-IC/PFN/Al. The ITO glass substrates were cleaned sequentially under sonication with detergent, deionized water, acetone and isopropyl alcohol and then dried at 70° C in the vacuum oven. A PEDOT:PSS (~40 nm) was spun cast on ITO substrates and dried at 120° C for 15 min. The BHJ active layer solutions were prepared in chloroform with different weight ratios between the P(DTB-BDD) and Y6 or DBTBT-IC and then stirred on a hot plate at 40° C for overnight to ensure the complete dissolution. The total concentration the is same for all the solutions, i.e., 16 mg/mL. Active layers were spin-cast from the blend solutions on the top of PEDOT:PSS at room temperature at a spinning speed of 1500 rpm. In order to prepare the ternary PSCs, the weight ratio between two acceptors, i.e. DBTBT-IC and Y6 is varied and the weight ratio of P(DTB-BDD) is kept constant and the total concentration same (16 mg/mL) as for binary PSCs. The optimized weight ratio active layers were subjected to the solvent vapor annealing via exposing the thin films to THF vapors for different times and then dried at room temperature. A 10 nm PFN cathode interfacial layer was than spin-cast from PFN methanol solution at a concentration of 0.5mg/ml at 2000 rpm for 30 s. After that the samples were transferred to the vacuum chamber. At a vacuum level

of 10^{-5} Torr, Finally, an aluminum (Al) electrode of thickness of about 100 nm was thermally deposited as the top electrode through a shadow mask. The active area of all the devices is 16 mm^2 . The J-V characteristics were measured on a computer-controlled leveled Keithley 2400 source meter under 1 sun, AM1.5 G illumination came from a solar simulator and light intensity was 100 mW/cm^2 . The EQE spectra measurements were performed on an EQE measurement system (Bentham Make).

Devices were fabricated to measure hole and electron mobility by using the space-charge-limited current (SCLC) method. The device structure used for hole and electron only devices are ITO/ PEDOT:PSS/active layer/Au and ITO/Al/active layer/Al, respectively. The mobility was determined by fitting the dark current to the model of a single-carrier SCLC, which is described by the equation $J = (9/8)\epsilon_0\epsilon_r\mu((V^2)/(d^3))$, where J is current, μ 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 layers, and V is the effective voltage is estimated as $V = V_a - V_{bi}$, where V_a and V_{bi} are the applied voltage and built-in potential.

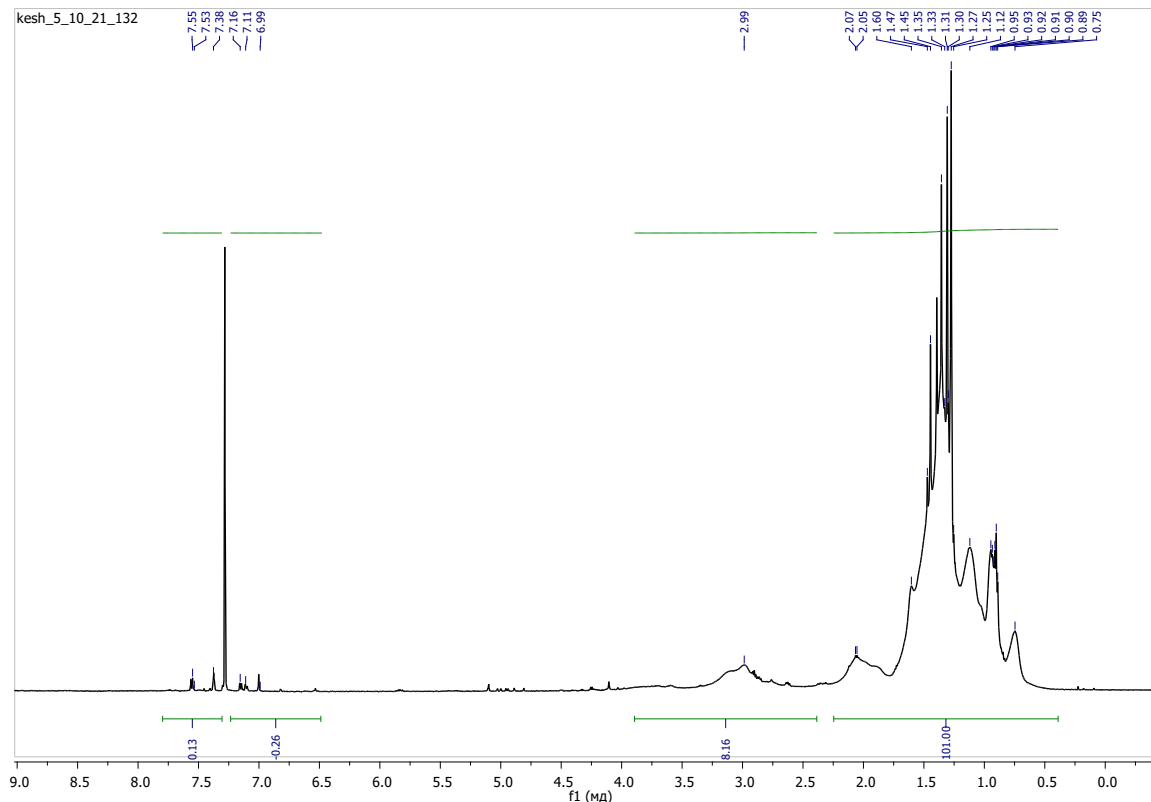


Figure S1. $^1\text{H-NMR}$ spectrum of polymer P(DTB-BDD) in CDCl_3

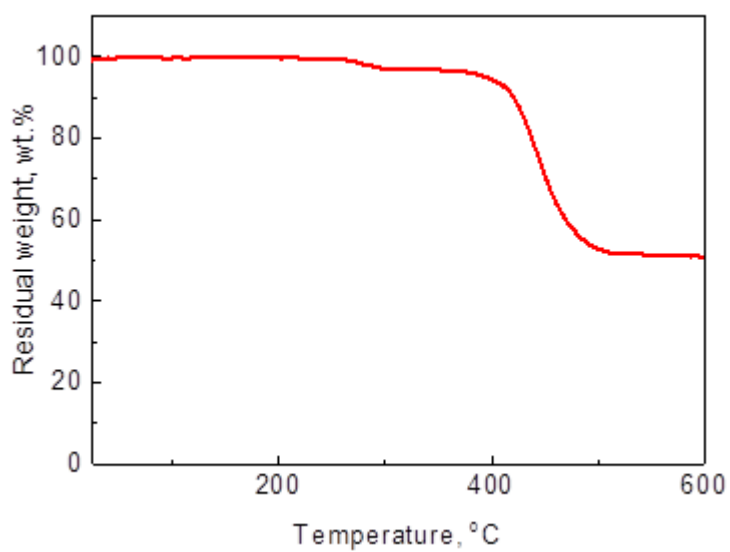


Figure S2. TGA thermogram of copolymer **P(DTB-BDD)** with a heating rate of 10°C/min

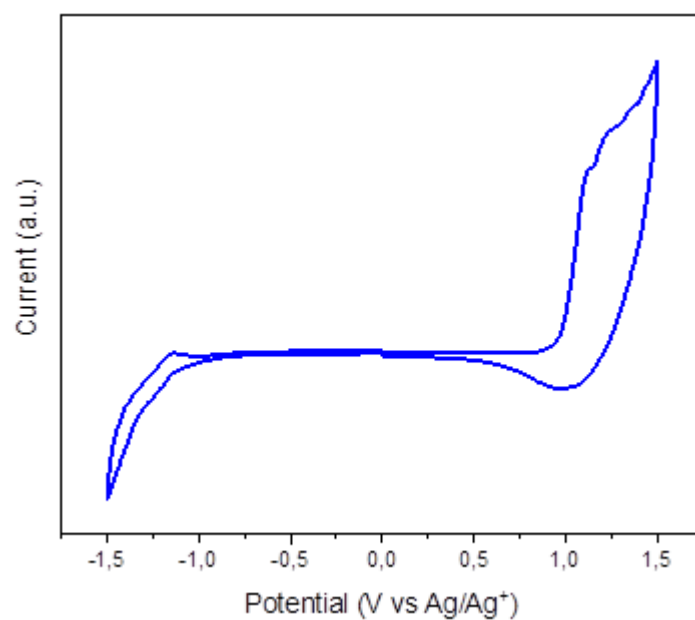


Figure S3. Cyclic voltammograms of the **P(DTB-BDD)** film in 0.1M Bu₄NPF₆ in CH₃CN solution (scan rate 60 mV/s)

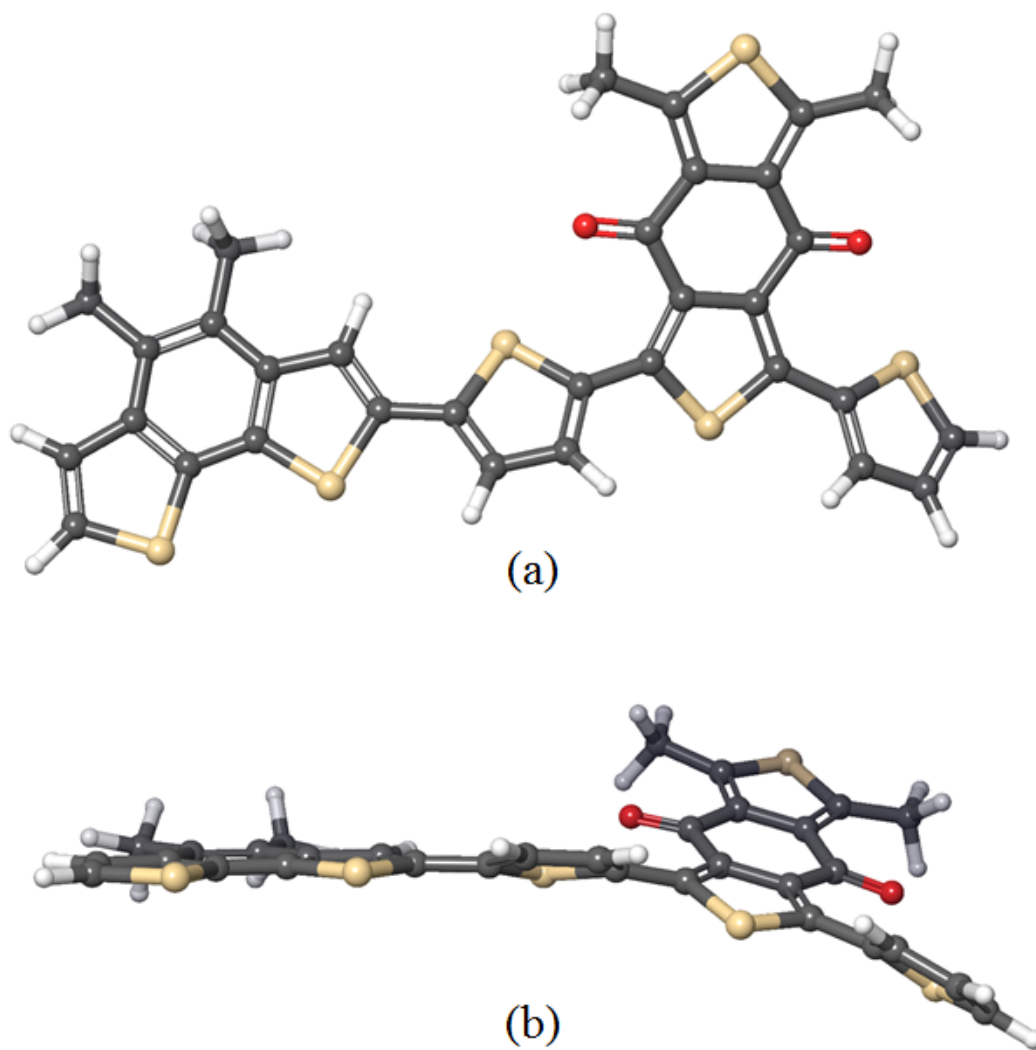


Figure S4 (a) Front and (b) side of **P(DTB-BDD)**

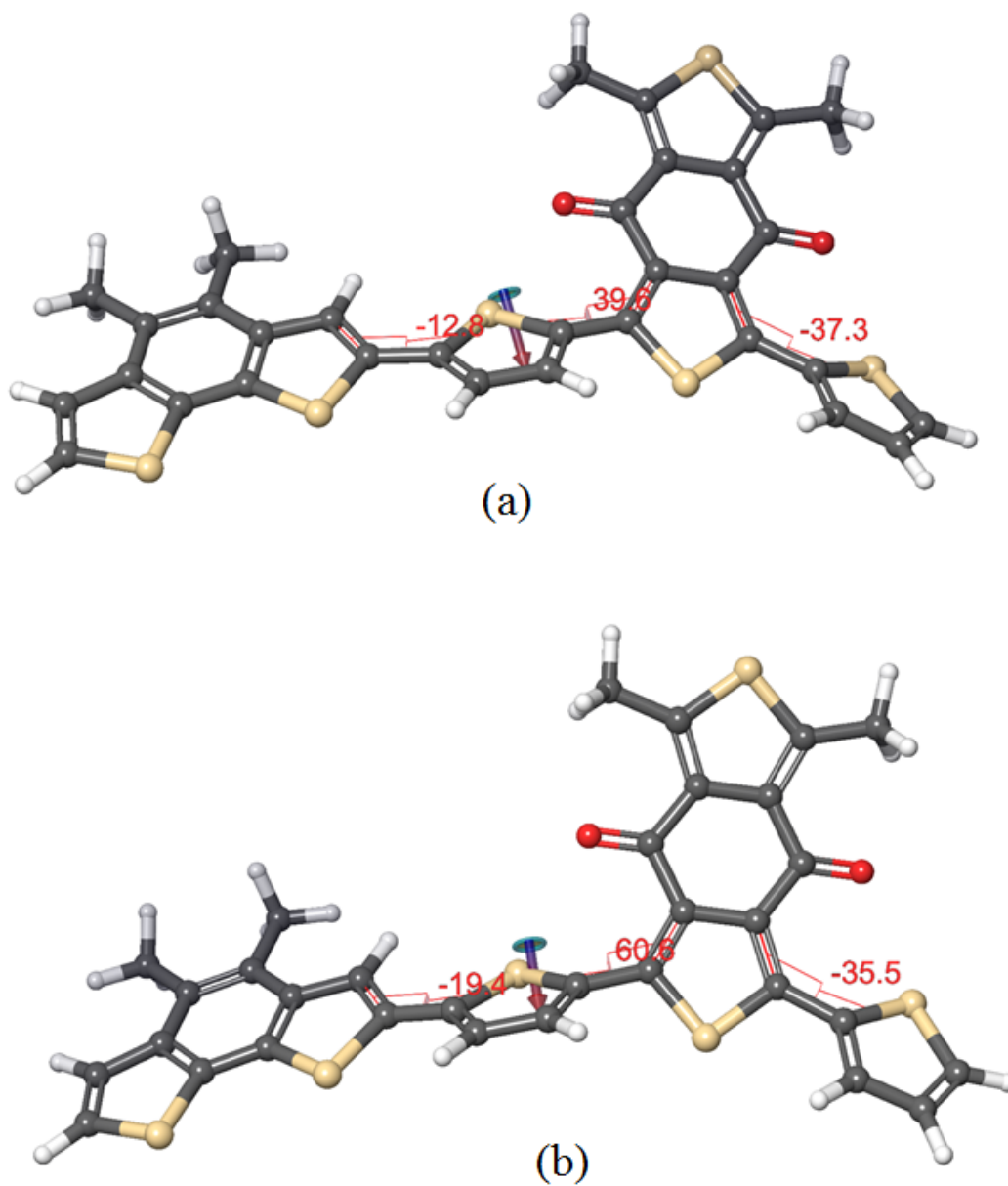


Figure S5a. Model of monomer unit **P(DTB-BDD)**. (a) Equilibrium geometry (b) transition state optimized by DFT/ ω B97X-D3(BJ)/6-31G(d,p)++. Torsional angles and dipole moment.

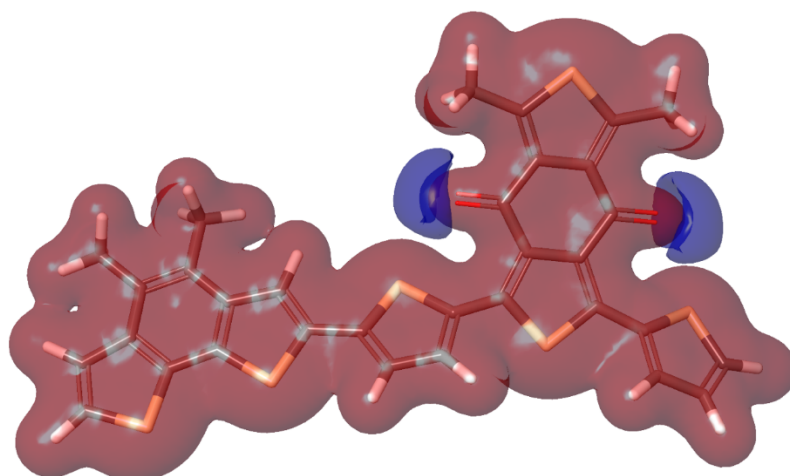


Figure S6. Electrostatic potential surface for the model **P(DTB-BDD)**. Calculation by method TD-DFT / M11-L / def2-SVPD.

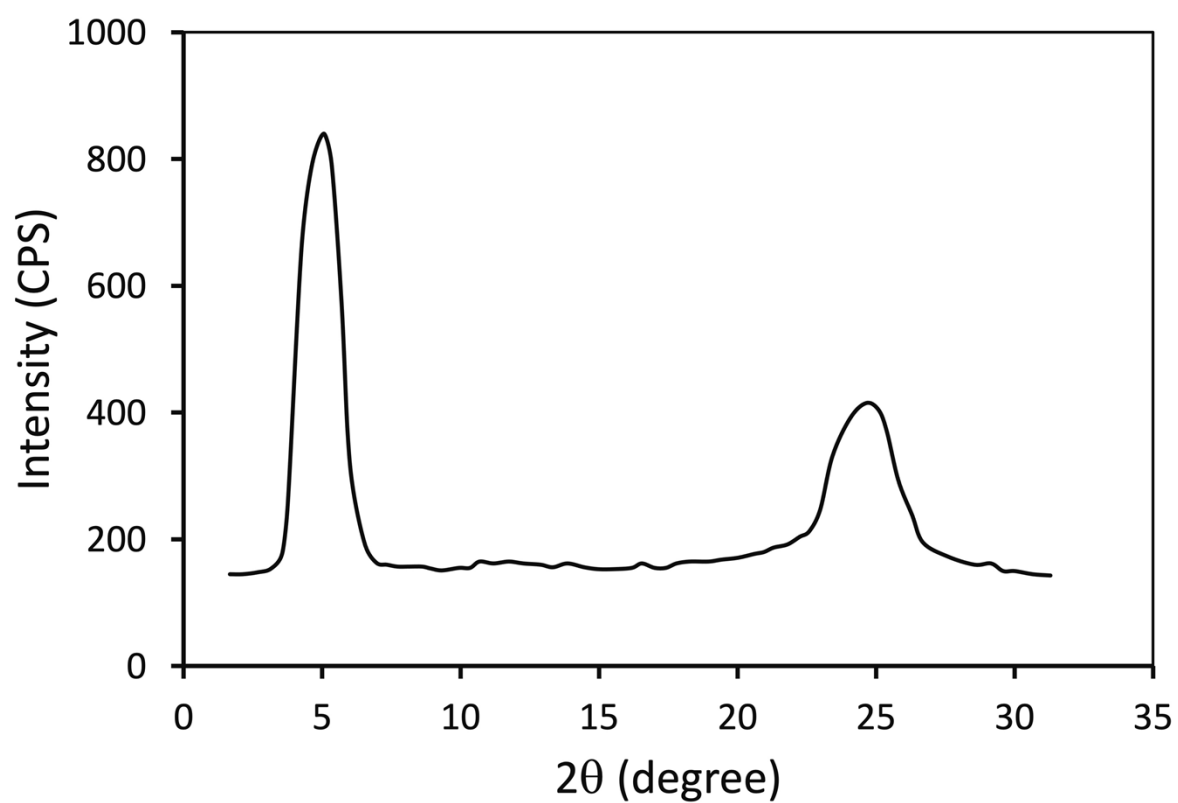


Figure S7. XRD pattern of pristine **P(DTB-BDD)** film

Table S1 Photovoltaic parameters of PSCs based on **P(DTB-BDD):Y6** with different weight ratio between **P(DTB-BDD)** and Y6 processed from chloroform solution

P(DTB-BDD):Y6	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
1:0.4	14.37	0.86	0.51	6.30
1:0.8	16.12	0.87	0.53	7.43
1:1.2	18.48	0.85	0.56	8.80
1:1.4	17.74	0.86	0.54	8.24

Table S2. Photovoltaic parameters of PSCs based on **P(DTB-BDD):DBTBT-IC** with different weight ratios between **P(DTB-BDD)** and DBTBT-IC processed from chloroform solution

P(DTB-BDD):DBTBT-IC	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
1:0.4	13.61	1.07	0.55	8.00
1:0.8	14.96	1.08	0.56	11.47
1:1.2	15.67	1.07	0.58	9.72
1:1.4	14.09	1.07	0.56	8.44

Table S3 Photovoltaic parameters of PSCs based on the ternary active layer with different weight ratios between DBTBT-IC and Y6 processed from chloroform solution

DBTBT-IC:Y6	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
0.1:1.1	18.97	0.96	0.62	11.29
0.3:0.9	20.05	0.97	0.65	12.64
0.4:0.8	19.13	0.98	0.63	11.81