

Supporting Information

Achieving Efficient and Stabilized Organic Solar Cells by Precisely Controlling the Proportion of Copolymerized Units in Electron-rich Polymers

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1. Experimental Section

Materials and Methods.

Monomer 2H-BDT was purchased from Zhengzhou Alfa Chemical., Ltd, **2Sn-BDT**, **2Br-BDD** and **2Sn-BDD** was purchased from Solarmer Materials Inc., and those monomers are used without further purification. Chloroform, Al (99.999%) was purchased from Alfa, or Aldrich and used without further purification. Indium-tin oxide (ITO) glass was purchased from Delta Technologies Limited, whereas PEDOT:PSS (Baytron PA14083) was obtained from Bayer Inc. The **2Br-BDT** was synthesized as shown in **Scheme S1**.

The ^1H NMR spectra were recorded in deuterated solvents on a Bruker ADVANCE 400 NMR Spectrometer. ^1H NMR chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer TGA 7 instrument for thermal analysis at a heating rate of 10 °C/min under nitrogen. Number-average (M_n) and polydispersity index (PDI) were determined with Waters Breeze gel permeation chromatography (GPC) with in 1,2,4-Trichlorobenzene.

Optical characterizations

UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. All film samples were spin-cast on ITO substrates. Solution UV-Vis absorption spectra at elevated temperatures also were collected on a Perkin Elmer Lambda 750 Spectrophotometer. The temperature of the cuvette was controlled with a Perkin Elmer PTP 6+6 Peltier System, which is supplied by a Perkin Elmer PCB 1500 Water Peltier System. Before each measurement, the system was held for at least 10 min at the target temperature to reach thermal equilibrium.

Electrochemical characterizations.

Cyclic voltammetry (CV) was performed by a Zahner IM6e electrochemical workstation, using Ag/AgCl as the reference electrode, a Pt plate as the counter

electrode, and a glassy carbon as the working electrode. Polymers were drop-cast onto the electrode from CHCl_3 solutions to form thin films. 0.1 mol/L tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the supporting electrolyte.

AFM and TEM characterizations.

The specimen for AFM measurements was prepared using the same procedures those for fabricating devices but without MoO_3/Ag on top of the active layer. The specimen for TEM measurement was prepared by spin casting the blend solution on ITO/PEDOT:PSS substrate, then floating the film on a water surface, and transferring to TEM grids.

Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) Characterization:

GIWAXS measurements were performed at beamline 7.3.3^[1] at the Advanced Light Source. Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.16° , selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 1M photon counting detector.

Hole and electron mobility measurements.

The device of ITO/PEDOT:PSS/active layer/ MoO_3/Ag and ITO/ ZnO /active layer/Au was employed to fabricate the hole-only and electron-only diodes, respectively. The carrier mobilities were measured using the space-charge-limited-current (SCLC) model, which is described by:

$$J = 9\epsilon_0\epsilon_r u V^2 / 8L^3$$

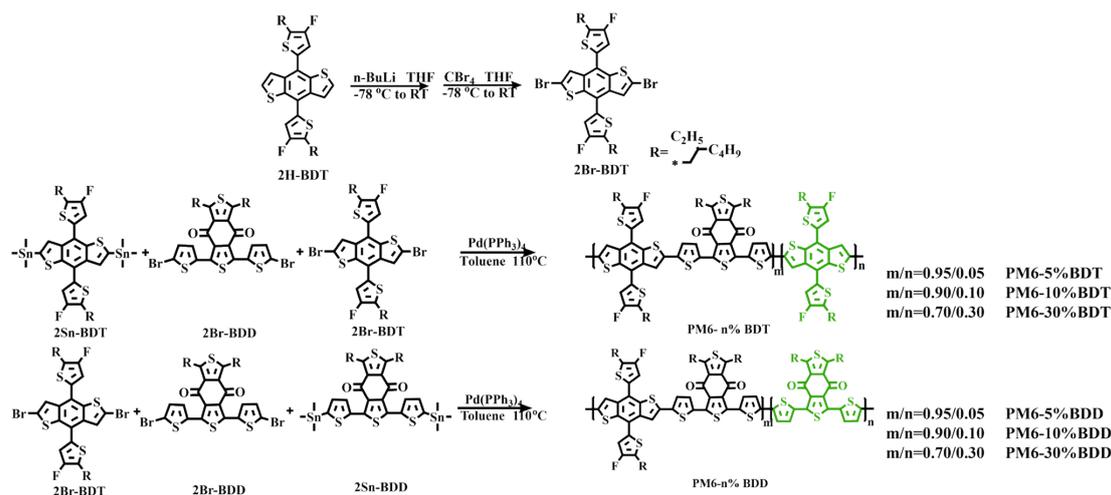
where J is the current density, L is the film thickness of active layer, ϵ_0 is the permittivity of free space ($8.85 \times 10^{-12} \text{F m}^{-1}$), ϵ_r is the relative dielectric constant of the transport medium, u is the hole or electron mobility, V is the internal voltage in the device and $V = V_{\text{appl}} - V_r - V_{bi}$, where V_{appl} is the applied voltage to the device, V_r is the voltage drop due to contact resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.^[2-4] The hole-mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

PSCs Fabrication

The traditional devices were fabricated in the configuration of ITO/PEDOT:PSS/active layer/PDINO/Al. ITO-coated glass was cleaned by ultrasonic agitation in acetone, detergent, deionized water, and isopropanol sequentially followed by plasma treatment for 3 min. Then the PEDOT:PSS (Baytron PVP 4083) was spin-cast on the ITO glass at 4000 rpm for 40 s and annealed at 150 °C for 10 min in air. The devices were transferred into a glovebox filled with N₂. Active layer solutions (polymer:Y6 weight ratio is 1:1.2) were prepared in CF. The total active layer solution concentration is 16 mg ml⁻¹. The active layer solution was stirred for 8 h at 45 °C, then the active layers were spin coated from the polymer:Y6 solution on the substrates at 3000 rpm for 45 s after the solution cool down to room temperature. The blend films were annealed at 100 °C for 10 min. Finally, the PDINO dissolved in methanol with a concentration of 1 mg/ml was spin-coated on top of active layer. The device fabrication was finished by depositing 100 nm Al in vacuum chamber of 10⁻⁷ Torr. Typical cells have devices area of 4.00 mm², which is defined by a metal mask with an aperture aligned with the device area.

PSCs Characterization

The I-V characteristic curves were recorded in a Keithley 2400 source unit under a simulated solar irradiance (solar simulator from Newport Inc.) A certified silicon diode, which can be traced back to NREL, is used to calibrate the illumination intensity to 1 sun (100 mW/cm²). A neutral filter is used to study the light intensity dependent device performance. EQE spectra were measured in an assembled setup including a stable light source, light chopper, monochromator, and lock-in amplifier.



Scheme S1. The synthetic routes of the 2Br-BDT and random polymers.

Synthetic procedures of 2Br-BDT and the polymers

2,6-dibromo-4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (2Br-BDT):

The synthetic procedures of 2Br-BDT referred to the previous literatures^[5], and the details as following: **2H-BDT** (500 mg, 0.813 mmol, 1.0 equiv) and anhydrous THF (15 mL) were added to a 100 mL flask equipped with a magnetic stirrer and then transferred to a glove box protected with N₂ and cooled to -78 °C. n-BuLi in hexanes ([2.5] M, 0.813 ml, 2.03 mmol, 2.5 equiv) was added dropwise, and the reaction was stirred for 1 h, then gradually warm to room temperature and keep stirring for 1.5 h. The reaction went from yellow to light green to a blue-green fluorescent color. CBr₄ ([1.25] M, 1.626 ml, 2.03 mmol, 2.5 equiv) was added dropwise after the reaction was cooled to -78 °C, then the reaction was warmed to room temperature and keep stirring overnight. Solvent was then removed under reduced pressure, and the product was diluted in ether, washed with H₂O, dried over anhydrous MgSO₄, and concentrated under vacuum. Purification by column chromatography (hexanes) and recrystallization from isopropanol yielded **2Br-BDT** (500 mg, 79.6%) as a yellow-orange solid. ¹H NMR (400 MHz, CDCl₃) δ 7.57 (s, 2H), 7.06 (s, 2H), 2.77 (d, J = 6.7 Hz, 4H), 1.46-1.23 (m, 16H), 0.94 (dd, J = 13.0, 5.6 Hz, 12H).

PM6-5%BDT:

(4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-

diyl)bis(trimethylstannane) (**2Sn-BDT**) (94.05 mg, 0.1 mmol), 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione (**2Br-BDD**) (72.84 mg, 0.095 mmol) and **2Br-BDT** (3.865 mg, 0.005 mmol) were added to a reaction vial equipped with a magnetic stirrer. The vial was then transferred to a glove box protected with N₂ where Pd(PPh₃)₄ (9.25 mg, 8 μmol) and anhydrous toluene (10 mL) were added. The reaction mixture was then sealed and heated at 110 °C for 30 h. The mixture cooled to room temperature and precipitated with 100 ml methanol. The crude polymer then soxhlet extracted with methanol, acetone, hexane, and chloroform until the extract was colorless. The chloroform solution was concentrated and precipitated in methanol. The precipitate was filtered and dried in vacuo to get the polymer **PM6-5% BDT** as dark solid 95 mg, $M_n = 53.9$ kDa, PDI= 1.54.

PM6-10% BDT and PM6-30% BDT:

PM6-10% BDT and PM6-30% BDT were prepared by similar procedures with PM6-5% BDT, with different amount of 2Br-BDT unit. The number-average molecular weight (M_n) and polydispersity index (PDI) of PM6-10% BDT and PM6-30% BDT were 44.3 kDa, 40.1 kDa, and 1.62, 1.69, respectively.

PM6-5% BDD:

1,3-bis(2-ethylhexyl)-5,7-bis(5-(trimethylstannyl)thiophen-2-yl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione (**2Sn-BDD**) (93.46 mg, 0.1 mmol), 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione (**2Br-BDD**) (3.83 mg, 0.005 mmol) and **2Br-BDT** (73.41 mg, 0.95 mmol) were added to a reaction vial equipped with a magnetic stirrer. The vial was then transferred to a glove box protected with N₂ where Pd(PPh₃)₄ (9.25 mg, 8 μmol) and anhydrous toluene (10 mL) were added. The reaction mixture was then sealed and heated at 110 °C for 30 h. The mixture cooled to room temperature and precipitated with 100 ml methanol. The crude polymer then soxhlet extracted with methanol, acetone, hexane, and chloroform until the extract was colorless. The chloroform solution was concentrated and precipitated in methanol. The precipitate was filtered

and dried in vacuo to get the polymer **PM6-5% BDD** as dark solid 94 mg, $M_n = 43.6$ kDa, PDI= 1.96.

PM6-10% BDD and PM6-30% BDD:

PM6-10% BDD and PM6-30% BDD were prepared by similar procedures with PM6-5% BDT, with different amount of 2Br-BDD unit. The number-average molecular weight (M_n) and polydispersity index (PDI) of PM6-10% BDD and PM6-30% BDD were 51.5 kDa, 55.8 kDa, and 1.82, 1.91, respectively.

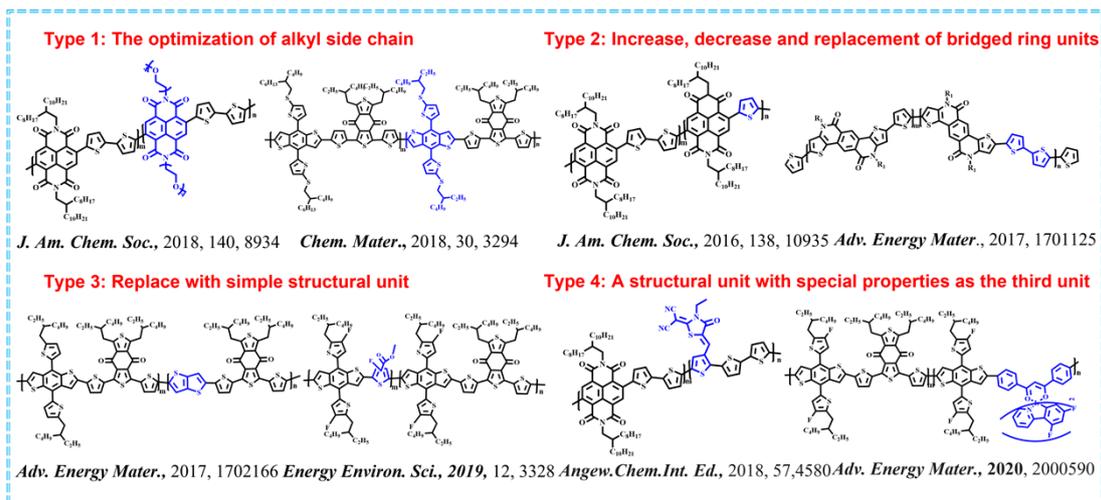


Figure S1. Four categories of the third unit in previous literatures.

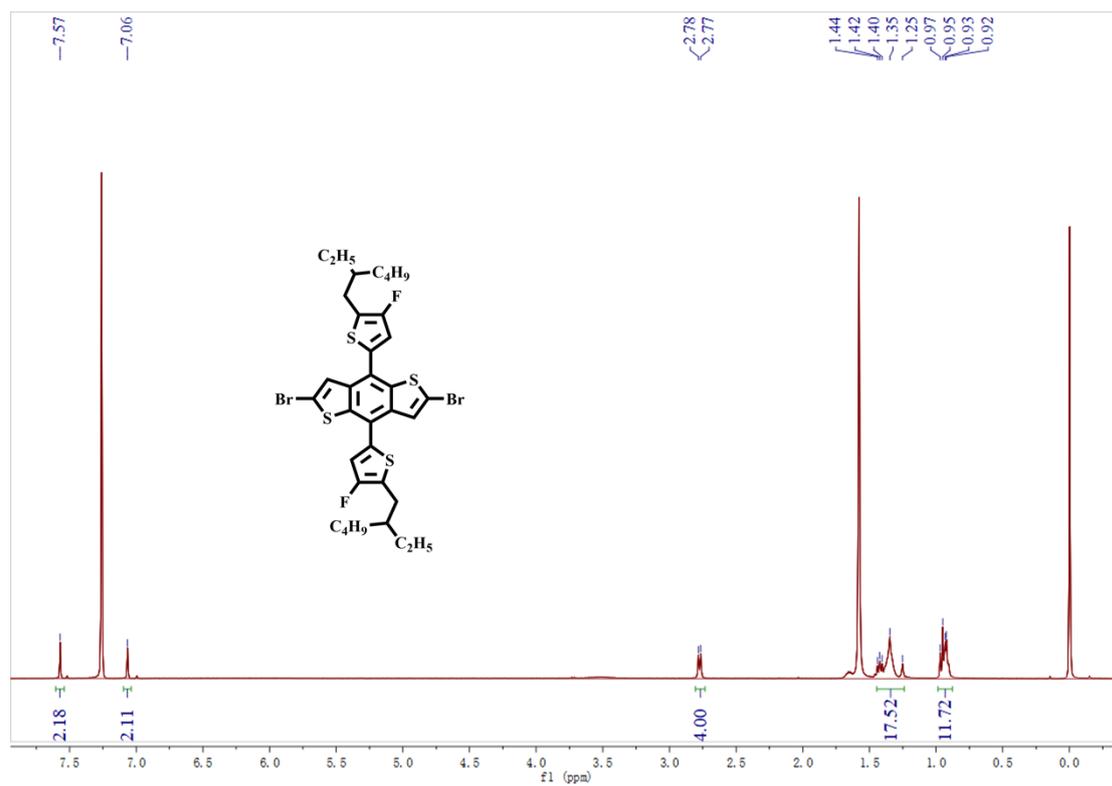


Figure S2. ¹H NMR spectra of *2Br-BDT* in CDCl₃.

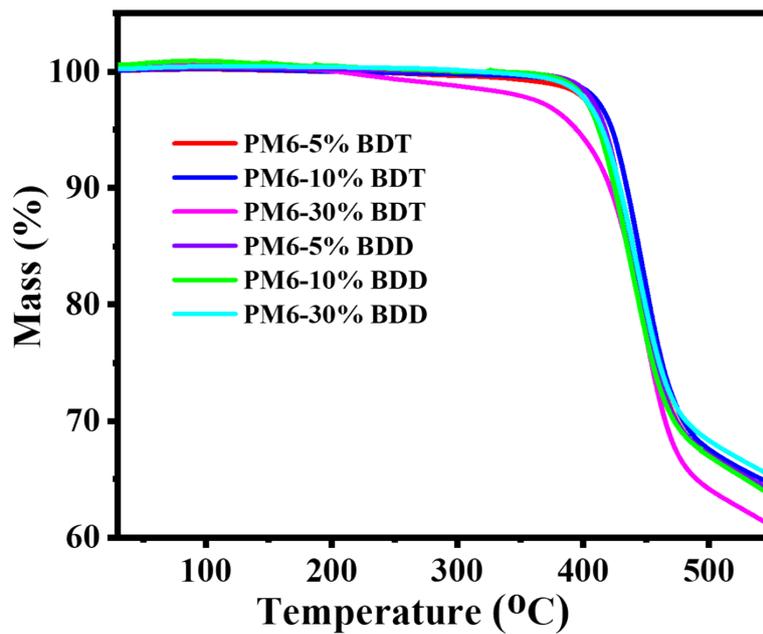


Figure S3. Thermogravimetric analysis (TGA) plot of polymers with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

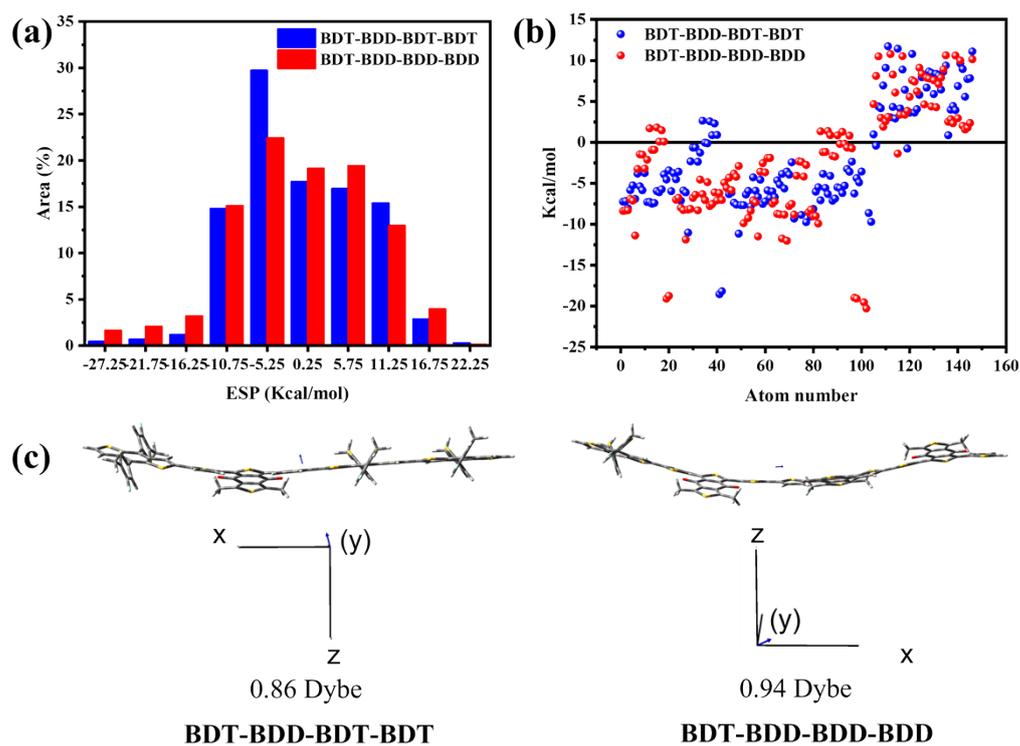


Figure S4. (a) ESP area distributions of the molecules; (b) Averaged ESP values of the atoms; (c) The results of the dipole moment simulation in the structures of BDT-BDD-BDT-BDT and BDT-BDD-BDD-BDD.

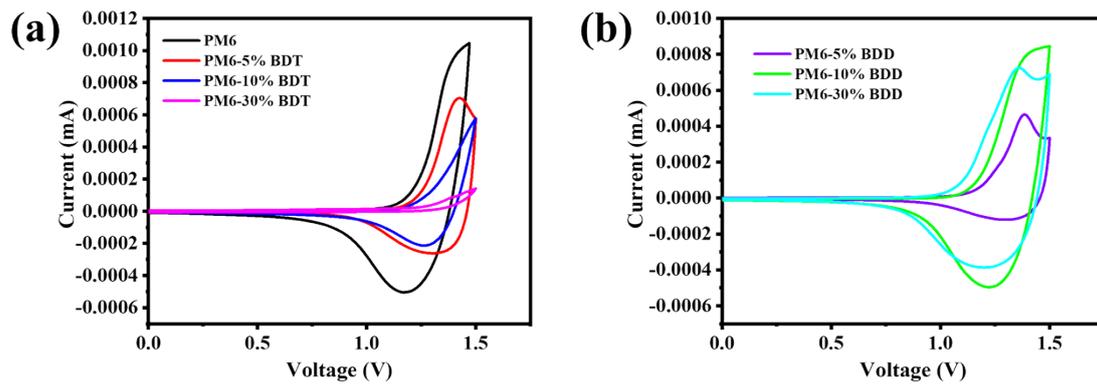


Figure S5. Cyclic voltammograms of the polymers.

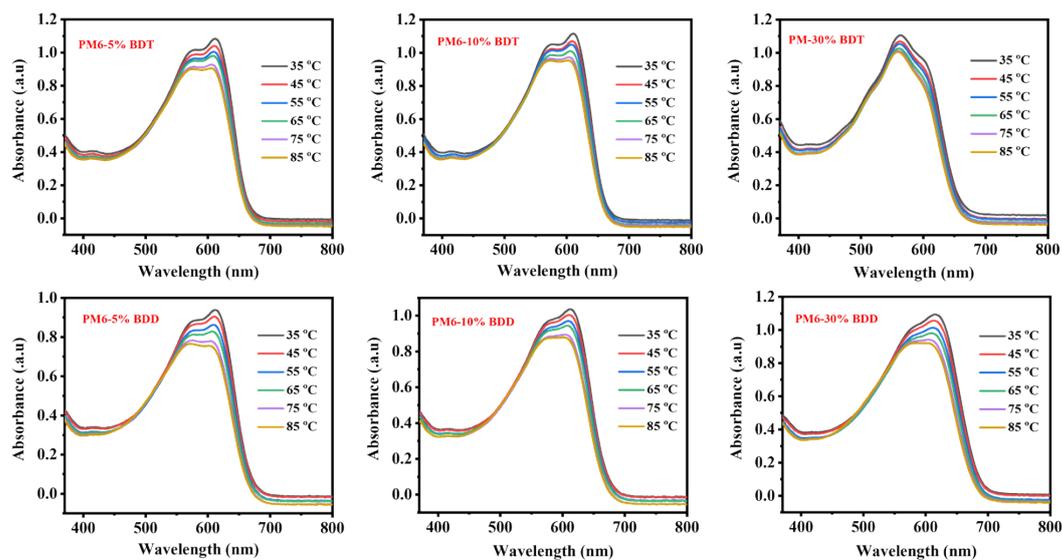


Figure S6. Temperature-dependent UV–vis absorption spectra of random polymers (0.02 mg/mL in CB solution).

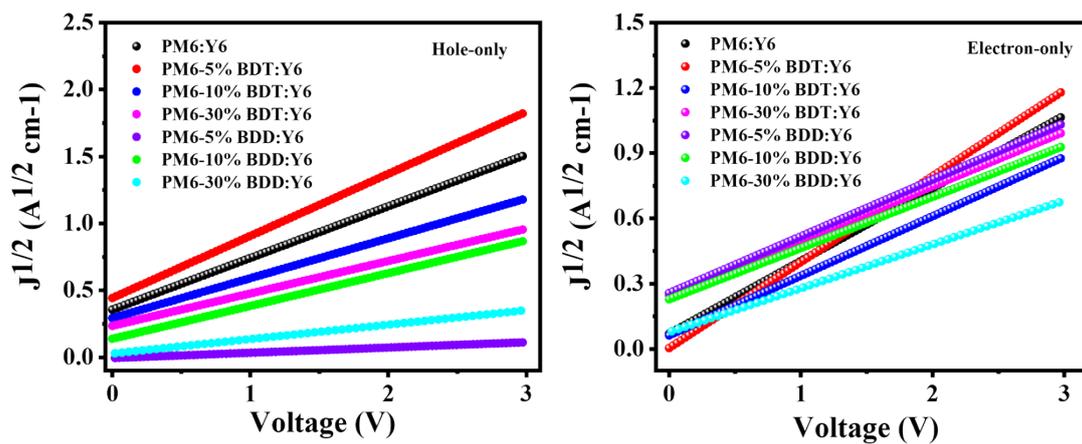


Figure S7. (a) $J^{0.5}-V$ plots of hole-only devices with a structure of ITO/PEDOT:PSS/polymer:Y6/MoO₃/Al and (b) $J^{0.5}-V$ plots of electron-only devices with a structure of ITO/ZnO/polymer:Y6/PDINO/Ag.

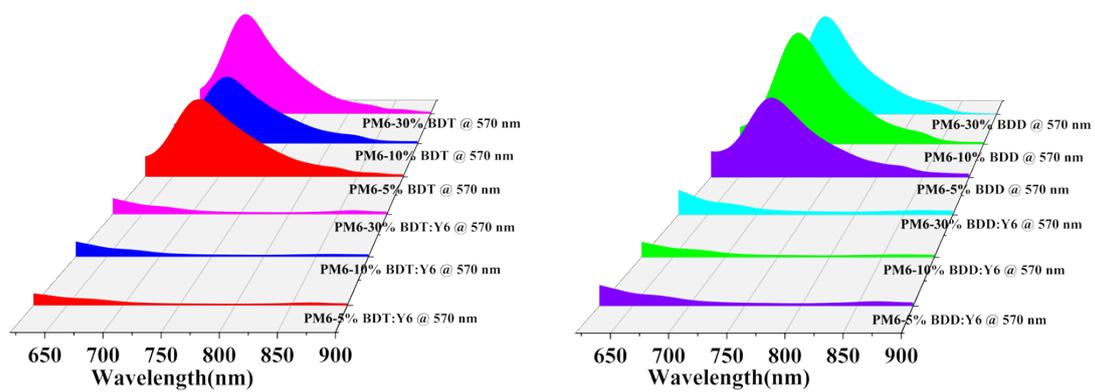


Figure S8. PL spectra obtained from the polymer films and polymer:Y6 blend films, excitation at 570 nm.

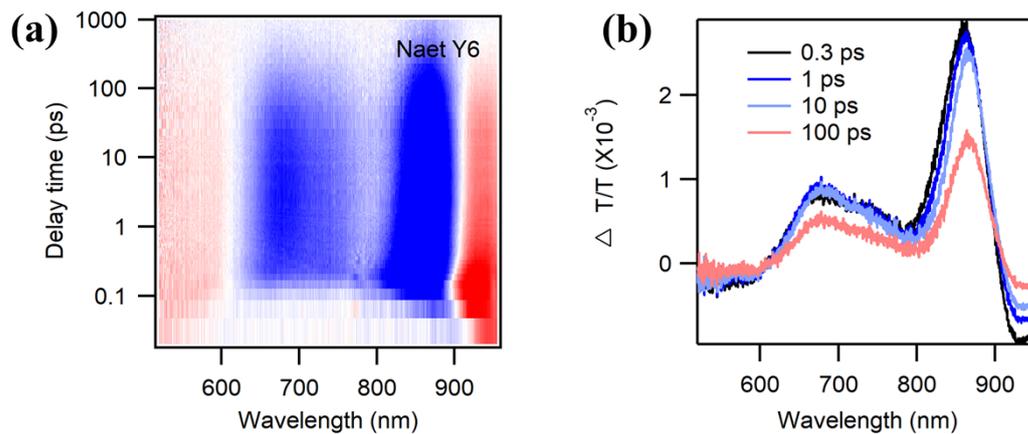


Figure S9. (a) 2D color plot of fs TA spectra of neat Y6 blend films under 750 nm excitation. (b) Representative fs TA spectra of neat Y6 at indicated delay times.

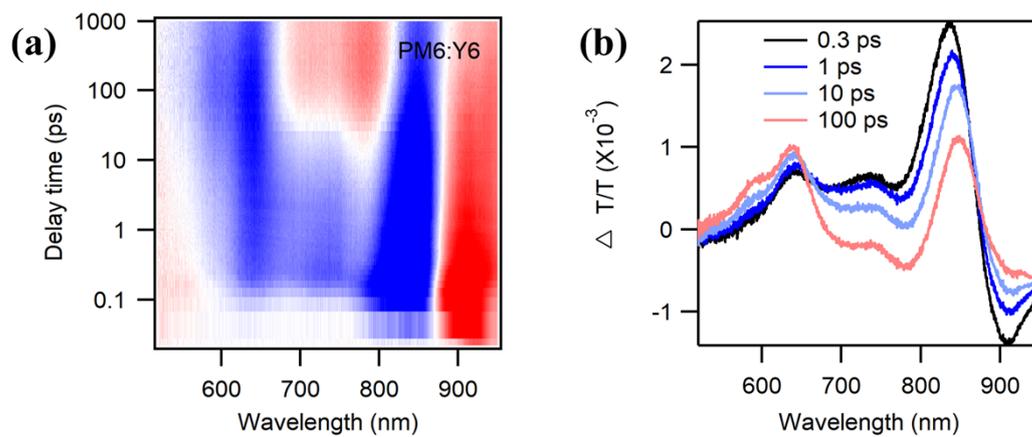


Figure S10. (a) 2D color plot of fs TA spectra of PM6:Y6 blend films under 750 nm excitation. b) Representative fs TA spectra of PM6:Y6 at indicated delay times.

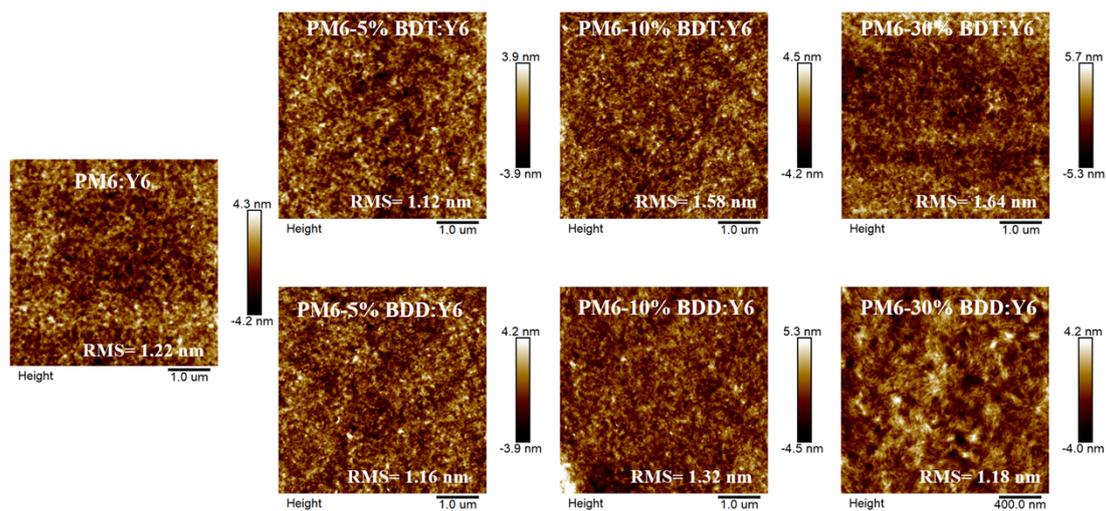


Figure S11. AFM height images of polymer:Y6 blend films prepared from CF.

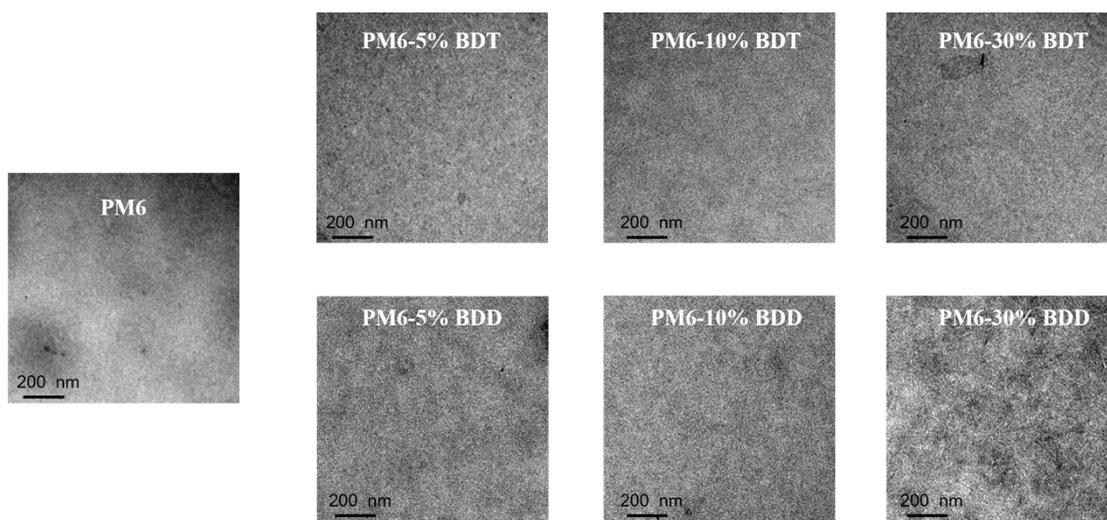


Figure S12. TEM images of polymer:Y6 blend films prepared from CF.

Table S1. The simulation calculation of dipole moment in the structure of BDT-BDD-BDT-BDT and BDT-BDD-BDD-BDD.

Molecular structure	X (Dybe)	Y (Dybe)	Z (Dybe)	Total (Dybe)
BDT-BDD-BDT-BDT	0.1369	-0.2805	-0.8189	0.8769
BDT-BDD-BDD-BDD	0.6700	0.6502	0.1256	0.9420

Table S2. Hole transfer kinetics in Polymer:Y6 blends.

blend film	A ₁	τ_1 (ps)	A ₂	τ_2 (ps)
PM6:Y6	0.593	0.148	0.407	16.7
PM6-5% BDT:Y6	0.585	0.152	0.415	17.8
PM6-5% BDD:Y6	0.533	0.149	0.467	21.6

References:

- [1] Q. Xie, X. Liao, L. Chen, M. Zhang, K. Gao, B. Huang, H. Xu, F. Liu, A. K. Y. Jen, Y. Chen, *Nano Energy*, 2019, **61**, 228-235.
- [2] H. C. Chen, C. W. Lai, I. C. Wu, H. R. Pan, I. Chen, P. Wen, Y. K. Peng, C. L. Liu, C. h. Chen, P. T. Chou, *Adv. Mater.*, 2011, **23**, 5451-5455.
- [3] Y. J. Cheng, C. H. Hsieh, P. J. Li, C. S. Hsu, *Adv. Funct. Mater.*, 2011, **21**, 1723-1732.
- [4] Y. Liu, X. Wan, F. Wang, J. Zhou, G. Long, J. Tian, Y. Chen, *Adv. Mater.*, 2011, **23**, 5387-5391.
- [5] P. D. Homyak, J. Tinkham, P. M. Lahti, E. B. Coughlin, *Macromolecules*, 2013, **46**, 8873-8881.