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Electronic Supplementary Information

An Effective Strategy of Controlling Morphology for High-Performance

Non-Fullerene Polymer Solar Cells with No Post-Treatment: Employ Bare

Rigid Aryl Rings as Lever Arms in New Asymmetry Benzodithiophene

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1. Materials and Methods

All reagents and starting materials were obtained commercially as analytical grade and used directly without any purification. Toluene and THF were distilled over sodium/benzophenone and calcium hydride under N2 prior to use. 2-bromo-5-((2decyltetradecyl)thio)thiophene¹, 1-bromo-4-(hexyloxy)benzene² and 1-bromo-4-(hexylthio)benzene³ were synthesized as reported in the literature. ¹H NMR and ¹³C NMR spectra were taken on a Bruker AVANCE-III 600 Spectrometer. Thermal gravimetric analysis (TGA) measurement was performed on STA-409 at a heating rate of 10 °C min⁻¹. UV-Vis absorption spectrum was measured with a Hitachi U-4100 spectrophotometer. The organic molecule films on quartz used for absorption spectral measurement were prepared by spincoating their chlorobenzene solutions. Cyclic voltammetry (CV) was performed using a CHI660D electrochemical workstation with a glassy carbon working electrode, a saturated calomel reference electrode (SCE) and a platinum wire counter electrode at a scan rate of 100 mV s⁻¹. Tetrabutylammonium phosphorus hexafluoride (Bu₄NPF₆, 0.1 M) in acetonitrile was used as the supporting electrolyte. Polymer film was prepared by drop-casting onto the glassy carbon working electrode from chlorobenzene solution and dried before measurements. The redox potential of the Fc/Fc⁺ internal reference is 0.39 V vs. SCE. The highest occupied molecular orbit (HOMO) was determined by calculating the empirical formulas⁴ of E_{HOMO} = $e(E_{ox} + 4.8 - E_{1/2}(Fc/Fc^+))$, where E_{ox} was the onset oxidation potential. The lowest unoccupied molecular orbit (LUMO) energy levels calculated from the equation of $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{g}^{\text{opt}}$, where E_{g}^{opt} was the optical band gap. Density functional theory (DFT) calculations were carried out by the Gaussian 09 program suite at the B3LYP/6-31G(d,p) level.⁵ Transmission electron microscopy (TEM) images were acquired using a HITACHI H-7650 electron microscope operating at an acceleration voltage of 100 kV.

2. Device Fabrication and Testing

Photovoltaic devices were fabricated on pre-patterned indium tin oxide (ITO) coated glass substrates with a layered structure of ITO/PEDOT:PSS/active layer/PFN-Br (5 nm)/Al (100 nm). The ITO coated glass substrates were cleaned sequentially with detergent, de-ionized water, acetone and isopropanol, followed by drying with N₂ flow. And then, oxygen plasma treatment was made for 20 min, then spin-coated with PEDOT:PSS at 5000 rpm, and dried under argon for 20 min at 120 °C. Subsequently, the active layer was spin-coated from different blend weight ratios of donor and acceptor in chlorobenzene solution with or without CN solvent on the ITO/PEDOT:PSS substrate, then spin-coated with PFN-Br at 2000 rpm. The thickness of the active layer was controlled by changing the spin speed during the spincoating process and measured using Veeco Dektak 150 surface profiler in our laboratory. Finally, aluminum (100 nm) was thermally evaporated at a vacuum of $\sim 2 \times 10^{-4}$ Pa on top of PFN-Br. The effective area of the device was measured to be 0.1 cm². The current densityvoltage (J-V) characteristics were measured with a Keithley 2420 source measurement unit under simulated 100 mW cm⁻² (AM 1.5 G) irradiation from a Newport solar simulator. Light intensity was calibrated with a standard silicon solar cell. The external quantum efficiencies (EQE) of solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system. Hole mobility and electron mobility were measured using the space charge limited current (SCLC) model, using a device configuration of ITO/PEDOT:PSS/active layer/Au and ITO/ZnO/active layer/PFN-Br/Al, respectively, and fitting the results to a space charge limited form, where the SCLC was described by:

$J = (9/8)\varepsilon\mu(V^2/L^3)$

where ε was the static dielectric constant of the medium and μ was the carrier mobility, V was the voltage drop across the device ($V = V_{appl} - V_{bi} - V_{rs}$, where V_{appl} was the applied voltage to the device, V_{bi} was the built-in voltage due to the difference in work function of the two electrodes, and V_{rs} was the voltage drop due to series resistance across the electrodes), and Lwas the active layer thickness.

3. Synthesis and Characterization



Scheme S1. Synthetic routes of polymer donors.

Synthesis of ThsBDTPh

To a mixture of magnesium turnings (0.33 g, 18 mmol) and a grain of I₂ in dry THF (10 mL) was added dropwise 2-bromo-5-((2-decyltetradecyl)thio)thiophene (6.38 g, 12 mmol) in THF (10 mL) at a rate sufficient to maintain reflux under nitrogen. After addition, the reflux was maintained for 1.5 h. The Grignard reagent was then added dropwise to a solution of 4,8-dihydrobenzo[1,2-*b*:4,5-*b*']dithiophen-4,8-dione (2.20 g, 10 mmol) in toluene (100 mL) under an ice-water bath and the mixture was stirred for 5 h at room temperature under nitrogen. Then, the other prepared Grignard reagent of bromobenzene (20 mmol, 1 M in THF) was added dropwise to the mixture down to room temperature, $SnCl_2 \cdot 2H_2O$ (9.03 g, 40 mmol) in 10% aqueous HCl (20 mL) was added, and the mixture was stirred for another 3 h at 50 °C. The mixture was poured into ice water and extracted with diethyl ether. The organic phase was dried over Na₂SO₄. After removing the solvent under vacuum, residue was purified by

silica column chromatography with petroleum ether to give compound ThsBDTPh as light yellow oil (3.73 g, 52%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.68-7.65 (m, 2H), 7.62 (d, *J*=5.7 Hz, 1H), 7.56-7.53 (m, 2H), 7.50-7.46 (m, 1H), 7.43 (d, *J*=5.7 Hz, 1H), 7.39 (d, *J*=5.7 Hz, 1H), 7.32 (d, *J*=3.6 Hz, 1H), 7.28 (d, *J*=5.7 Hz, 1H), 7.21 (d, *J*=3.6 Hz, 1H), 2.93 (d, *J*=6.2 Hz, 2H), 1.72-1.67 (m, 1H), 1.49-1.43 (m, 2H), 1.41-1.36 (m, 2H), 1.32-1.21 (m, 36H), 0.88-0.85 (m, 6H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 142.52, 139.04, 138.92, 138.24, 137.31, 136.47, 136.17, 132.56, 131.22, 129.33, 128.84, 128.30, 128.17, 127.82, 127.31, 123.04, 122.94, 122.86, 44.00, 37.83, 32.93, 31.93, 29.93, 29.70, 29.67, 29.37, 26.57, 22.69, 14.13.

Synthesis of ThsBDTNaPh

ThsBDTNaPh was synthesized as light yellow solid (4.98 g, 65%) according to the method of ThsBDTPh described above. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.16 (s, 1H), 8.02 (d, *J*=8.4 Hz, 1H), 7.96-7.93 (m, 1H), 7.92-7.89 (m, 1H), 7.78-7.76 (m, 1H), 7.65 (d, *J*=5.7 Hz, 1H), 7.58-7.54 (m, 2H), 7.44 (d, *J*=5.7 Hz, 1H), 7.41 (d, *J*=5.7 Hz, 1H), 7.35 (d, *J*=3.6 Hz, 1H), 7.32 (d, *J*=5.6 Hz, 1H), 7.22 (d, *J*=3.6 Hz, 1H), 2.94 (d, *J*=6.2 Hz, 2H), 1.72-1.68 (m, 1H), 1.50-1.45 (m, 2H), 1.41-1.37 (m, 2H), 1.32-1.23 (m, 36H), 0.88-0.85 (m, 6H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 142.52, 138.98, 138.50, 137.37, 136.55, 136.53, 136.37, 133.51, 133.11, 132.58, 131.09, 128.57, 128.48, 128.27, 128.22, 127.90, 127.87, 127.49, 127.25, 126.52, 126.49, 123.10, 123.00, 122.95, 44.01, 37.85, 32.94, 31.93, 29.94, 29.71, 29.67, 29.37, 26.92, 26.58, 22.70, 14.13.

Synthesis of ThsBDTPhPh

ThsBDTPhPh was synthesized as light yellow solid (4.76 g, 60%) according to the method of ThsBDTPh described above. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.77-7.72 (m, 4H), 7.70-7.67 (m, 2H), 7.63 (d, *J*=5.7 Hz, 1H), 7.48-7.45 (m, 2H), 7.42 (d, *J*=5.7 Hz, 1H), 7.39-7.34 (m, 3H), 7.32 (d, *J*=3.6 Hz, 1H), 7.20 (d, *J*=3.4 Hz, 1H), 2.93 (d, *J*=6.2 Hz, 2H), 1.72-1.68 (m, 1H), 1.49-1.44 (m, 2H), 1.41-1.36 (m, 2H), 1.32-1.22 (m, 36H), 0.88-0.85 (m, 6H).

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¹³C NMR (151 MHz, CDCl₃): δ (ppm) 142.50, 141.02, 140.56, 138.97, 138.21, 137.96,
137.36, 136.51, 136.17, 132.54, 130.81, 129.75, 128.86, 128.18, 127.79, 127.52, 127.49,
127.38, 127.10, 123.07, 122.96, 122.92, 43.98, 37.83, 32.93, 31.93, 29.93, 29.71, 29.67, 29.37,
26.91, 26.57, 22.70, 14.13.

Synthesis of ThsBDTPhR

ThsBDTPhR was synthesized as light yellow oil (4.97 g, 62%) according to the method of ThsBDTPh described above. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.61 (d, *J*=5.7 Hz, 1H), 7.58 (d, *J*=8.0 Hz, 2H), 7.43 (d, *J*=5.7 Hz, 1H), 7.38 (d, *J*=5.7 Hz, 1H), 7.35 (d, *J*=8.0 Hz, 2H), 7.33-7.30 (m, 2H), 7.20 (d, *J*=3.6 Hz, 1H), 2.92 (d, *J*=6.2 Hz, 2H), 2.72 (t, *J*=8.4Hz, 2H), 1.74-1.67 (m, 3H), 1.46-1.36 (m, 8H), 1.30-1.21 (m, 38H), 0.92 (t, *J*=7.0 Hz, 3H), 0.88-0.85 (m, 6H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 143.13, 142.64, 138.92, 138.26, 137.21, 136.47, 136.26, 136.21, 132.58, 131.39, 129.15, 128.81, 128.13, 127.80, 127.08, 123.15, 123.03, 122.63, 44.01, 37.83, 35.91, 32.94, 31.93, 31.78, 31.37, 29.93, 29.70, 29.67, 29.37, 29.15, 26.92, 26.57, 22.70, 22.65, 14.13.

Synthesis of ThsBDTPhOR

ThsBDTPhOR was synthesized as yellow oil (4.50 g, 55%) according to the method of ThsBDTPh described above. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.62 (d, *J*=5.7 Hz, 1H), 7.59 (d, *J*=8.4 Hz, 2H), 7.44 (d, *J*=5.7 Hz, 1H), 7.39 (d, *J*=5.6 Hz, 1H), 7.33-7.30 (m, 2H), 7.20 (d, *J*=3.5 Hz, 1H), 7.07 (d, *J*=8.4 Hz, 2H), 4.06 (t, *J*=6.5 Hz, 2H), 2.93 (d, *J*=6.1 Hz, 2H), 1.87-1.82 (m, 2H), 1.72-1.67 (m, 1H), 1.46-1.36 (m, 8H), 1.31-1.23 (m, 38H), 0.94 (t, *J*=6.6 Hz, 3H), 0.88-0.85 (m, 6H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 159.18, 142.69, 138.94, 138.44, 137.20, 136.47, 136.33, 132.61, 131.18, 131.15, 130.51, 128.14, 127.83, 127.09, 123.11, 122.53, 114.76, 68.13, 44.04, 37.86, 32.96, 31.96, 31.66, 29.96, 29.73, 29.69, 29.39, 29.34, 26.95, 26.60, 25.84, 22.72, 22.68, 14.15, 14.10.

Synthesis of ThsBDTPhSR

ThsBDTPhSR was synthesized as yellow solid (4.17 g, 50%) according to the method of

ThsBDTPh described above. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.62 (d, *J*=5.6 Hz, 1H), 7.59 (d, *J*=8.1 Hz, 2H), 7.47 (d, *J*=8.1 Hz, 2H), 7.44 (d, *J*=5.6 Hz, 1H), 7.41 (d, *J*=5.6 Hz, 1H), 7.32 (d, *J*=3.5 Hz, 1H), 7.30 (d, *J*=5.6 Hz, 1H), 7.21 (d, *J*=3.4 Hz, 1H), 3.03 (t, *J*=7.4 Hz, 2H), 2.93 (d, *J*=6.1 Hz, 2H), 1.78-1.73 (m, 2H), 1.71-1.67 (m, 1H), 1.45-1.34 (m, 8H), 1.29-1.23 (m, 38H), 0.92 (t, *J*=6.6 Hz, 3H), 0.88-0.85 (m, 6H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 142.50, 138.98, 138.20, 137.81, 137.36, 136.52, 136.16, 136.07, 132.59, 130.67, 129.76, 128.33, 128.21, 127.82, 127.42, 123.12, 122.91, 44.03, 37.86, 33.16, 32.95, 31.94, 31.41, 29.94, 29.72, 29.68, 29.38, 28.64, 26.94, 26.59, 22.71, 22.59, 14.14, 14.07.

Synthesis of ThsBDTPh-Sn

To a solution of compound ThsBDTPh (1.79 g, 2.5 mmol) in THF (60 mL) at -78 °C was added dropwise *n*-BuLi (3.90 mL, 6.25 mmol, 1.6 M in hexane) under nitrogen. The mixture was stirred at -78 °C for 1 h and then warmed to room temperature for 0.5 h. After cooling back to -78 °C again, trimethyltin chloride (6.75 mL, 6.75 mmol, 1 M in hexane) was added in one portion. The mixture was brought to room temperature and stirred overnight. Water was subsequently added to the reaction mixture and extracted by diethyl ether. The combined organic extracts were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was washed by ethanol two times. Compound ThsBDTPh-Sn was obtained as yellow oil (2.03 g, 78%). ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.73-7.69 (m, 3H), 7.58-7.54 (m, 2H), 7.49-7.46 (m, 1H), 7.37 (d, *J*=3.6 Hz, 1H), 7.34 (s, 1H), 7.23 (d, *J*=3.6 Hz, 1H), 2.95 (d, *J*=6.3 Hz, 2H), 1.75-1.70 (m, 1H), 1.52-1.45 (m, 2H), 1.43-1.37 (m, 2H), 1.34-1.21 (m, 36H), 0.88-0.84 (m, 6H), 0.43-0.32 (m, 18H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 143.50, 143.27, 142.91, 142.73, 142.25, 139.83, 137.39, 137.12, 136.89, 132.65, 130.82, 130.72, 129.71, 129.55, 128.86, 128.14, 121.32, 58.52, 32.03, 32.02, 30.03, 29.79, 29.76, 29.75, 29.74, 29.47, 29.46, 26.63, 22.80, 18.54, 14.25, -8.24.

Synthesis of ThsBDTNaPh-Sn

ThsBDTNaPh-Sn was synthesized as offwhite solid (2.05 g, 75%) according to the method

of ThsBDTPh-Sn described above. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.19 (s, 1H), 8.05 (d, *J*=8.4 Hz, 1H), 7.98 -7.94 (m, 2H), 7.81-7.79 (m, 1H), 7.71 (s, 1H), 7.59-7.55 (m, 2H), 7.39 (d, *J*=3.6 Hz, 1H), 7.35 (s, 1H), 7.24 (s, 1H), 2.96 (d, *J*=6.3 Hz, 2H), 1.76-1.70 (m, 1H), 1.50-1.45 (m, 2H), 1.43-1.38 (m, 2H), 1.32-1.22 (m, 36H), 0.88-0.85 (m, 6H), 0.42-0.31 (m, 18H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 143.37, 143.20, 142.96, 142.87, 142.44, 137.33, 137.26, 137.22, 136.82, 133.56, 133.03, 132.56, 130.77, 130.62, 129.48, 128.45, 128.34, 128.09, 127.87, 127.56, 126.37, 121.34, 44.09, 37.82, 32.92, 31.92, 29.94, 29.69, 29.66, 29.65, 29.64, 29.36, 26.53, 22.69, 14.13, -8.32, -8.34.

Synthesis of ThsBDTPhPh-Sn

ThsBDTPhPh-Sn was synthesized as offwhite solid (1.96 g, 70%) according to the method of ThsBDTPh-Sn described above. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.83-7.78 (m, 4H), 7.76-7.73 (m, 2H), 7.69 (s, 1H), 7.52-7.49 (m, 2H), 7.43-7.38 (m, 2H), 7.37 (d, *J*=3.6 Hz, 1H), 7.23 (d, *J*=3.6 Hz, 1H), 2.95 (d, *J*=6.2 Hz, 2H), 1.75-1.70 (m, 1H), 1.51-1.45 (m, 2H), 1.43-1.37 (m, 2H), 1.32-1.22 (m, 36H), 0.88-0.85 (m, 6H), 0.44-0.33 (m, 18H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 143.35, 143.25, 142.85, 142.58, 142.33, 140.76, 140.71, 138.68, 137.34, 137.03, 136.81, 132.55, 130.78, 130.65, 129.88, 129.22, 128.87, 128.09, 127.47, 127.16, 121.30, 44.09, 37.83, 32.92, 31.93, 31.92, 29.95, 29.69, 29.66, 29.65, 29.64, 29.36, 26.53, 22.69, 14.13, -8.30, -8.32.

Synthesis of ThsBDTPhR-Sn

ThsBDTPhR-Sn was synthesized as yellow oil (2.54 g, 75%) according to the method of ThsBDTPh-Sn described above. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.68 (s, 1H), 7.61 (d, *J*=7.6 Hz, 2H), 7.39-7.35 (m, 4H), 7.22 (d, *J*=3.4 Hz, 1H), 2.95 (d, *J*=6.2 Hz, 2H), 2.4 (t, *J*=7.8 Hz, 2H), 1.76-1.71 (m, 3H), 1.46-1.35 (m, 8H), 1.29-1.23 (m, 38H), 0.92 (t, *J*=6.2 Hz, 3H), 0.88-0.85 (m, 6H), 0.42-0.33 (m, 18H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 143.48, 143.17, 142.82, 142.75, 142.64, 141.85, 137.27, 137.05, 136.91, 136.67, 132.55, 130.84, 130.73, 129.77, 129.25, 128.73, 128.01, 121.00, 67.96, 44.08, 37.81, 35.95, 32.92, 31.93,

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31.77, 31.31, 29.94, 29.69, 29.66, 29.65, 29.63, 29.36, 29.22, 26.52, 25.61, 22.69, 22.65, 14.13, -8.33, -8.35.

Synthesis of ThsBDTPhOR-Sn

ThsBDTPhOR-Sn was synthesized as yellow oil (2.33 g, 68%) according to the method of ThsBDTPh-Sn described above. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.68 (s, 1H), 7.62 (d, *J*=8.1 Hz, 2H), 7.38-7.32 (m, 2H), 7.22 (d, *J*=2.9 Hz, 1H), 7.09 (d, *J*= 8.1Hz, 2H), 4.07 (t, *J*=6.3 Hz, 2H), 2.94 (d, *J*=6.0 Hz, 2H), 1.88-1.84 (m, 2H), 1.75-1.69 (m, 1H), 1.51-1.37 (m, 8H), 1.30-1.22 (m, 38H), 0.94 (t, *J*=6.1 Hz, 3H), 0.89-0.84 (m, 6H), 0.42-0.33 (m, 18H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 158.97, 143.50, 143.15, 142.76, 141.84, 137.25, 137.16, 136.64, 132.55, 131.80, 130.82, 130.78, 130.57, 129.53, 127.99, 120.87, 114.63, 68.05, 67.97, 44.08, 37.81, 32.92, 31.93, 31.92, 31.65, 29.94, 29.69, 29.65, 29.63, 29.36, 26.52, 25.84, 25.62, 22.69, 22.66, 14.13, 14.08, -8.34, -8.35.

Synthesis of ThsBDTPhSR-Sn

ThsBDTPhSR-Sn was synthesized as yellow solid (2.57 g, 74%) according to the method of ThsBDTPh-Sn described above. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 7.67 (s, 1H), 7.62 (d, *J*=7.9 Hz, 2H), 7.48 (d, *J*=7.9 Hz, 2H), 7.35 (d, *J*=3.2 Hz, 1H), 7.33 (s, 1H), 7.22 (d, *J*=3.4 Hz, 1H), 3.05 (t, *J*=7.3 Hz, 2H), 2.95 (d, *J*=5.9 Hz, 2H), 1.78 -1.70 (m, 3H), 1.47-1.34 (m, 8H), 1.29-1.23 m, 38H), 0.92 (t, *J*= 6.6 Hz, 3H), 0.88-0.85 (m, 6H), 0.42-0.33 (m, 18H). ¹³C NMR (151 MHz, CDCl₃): δ (ppm) 143.33, 143.20, 142.80, 142.52, 142.30, 137.42, 137.30, 136.98, 136.79, 136.72, 132.53, 130.76, 130.55, 129.86, 129.02, 128.18, 128.05, 121.23, 67.97, 44.07, 37.81, 33.12, 32.91, 31.92, 31.40, 29.93, 29.69, 29.65, 29.64, 29.63, 29.35, 29.12, 28.64, 26.52, 25.61, 22.69, 22.57, 14.13, 14.06, -8.32, -8.34.

Synthesis of PBDTTAZ-Ph

To a 25 mL flask, compound ThsBDTPh-Sn (146.0 mg, 0.14 mmol), 4,7-bis(5bromothiophen-2-yl)-5,6-difluoro-2-(2-hexyldodecyl)-2*H*-benzo[*d*][1,2,3]triazole (98.2 mg, 0.14 mmol) and Pd(PPh₃)₄ (8.1 mg, 0.007 mmol) were added under nitrogen. After the addition of toluene (5 mL), the mixture was heated to 110 °C and maintained at the same temperature for 6 h. After cooling to room temperature, the mixture was poured into methanol. The precipitates were collected and purified by column chromatography over silica using chlorobenzene as the eluant. Then, the solution was poured into methanol again. The product was collected and dried overnight under vacuum at 40 °C with the yield 63% for PBDTTAZ-Ph as dark solid. GPC: M_n =43.5 KDa, PDI=1.63. T_d =343 °C.

Synthesis of PBDTTAZ-NaPh

PBDTTAZ-NaPh was synthesized as dark solid with a yield of 58% according to the method of PBDTTAZ-Ph described above. GPC: M_n =48.7 KDa, PDI=2.01. T_d =341 °C.

Synthesis of PBDTTAZ-PhPh

PBDTTAZ-PhPh was synthesized as dark solid with a yield of 54% according to the method of PBDTTAZ-Ph described above. GPC: M_n =50.2 KDa, PDI=1.96. T_d =337 °C.

Synthesis of PBDTTAZPh-R

PBDTTAZPh-R was synthesized as dark solid with a yield of 50% according to the method of PBDTTAZ-Ph described above. GPC: M_n =34.5 KDa, PDI=2.56. T_d =345 °C.

Synthesis of PBDTTAZPh-OR

PBDTTAZPh-OR was synthesized as dark solid with a yield of 55% according to the method of PBDTTAZ-Ph described above. GPC: M_n =53.6 KDa, PDI=1.73. T_d =352 °C.

Synthesis of PBDTTAZPh-SR

PBDTTAZPh-SR was synthesized as dark solid with a yield of 58% according to the method of PBDTTAZ-Ph described above. GPC: M_n =58.1 KDa, PDI=2.32. T_d =342 °C.

4. TGA, UV-Vis, CV and DFT Measurements and Basic Properties



Fig. S1. Thermogravimertic analysis (TGA) of the polymers.



Fig. S2. Absorption spectra in chlorobenzene solution at room temperature. (a) PBDTTAZ-Ph, PBDTTAZ-NaPh and PBDTTAZ-PhPh; (b) PBDTTAZPh-R, PBDTTAZPh-OR and

PBDTTAZPh-SR.



Fig. S3. Electrochemical cyclic voltammetry curves. (a) PBDTTAZ-Ph, PBDTTAZ-NaPh and

PBDTTAZ-PhPh; (b) PBDTTAZPh-R, PBDTTAZPh-OR and PBDTTAZPh-SR.



Fig. S4. Calculated HOMO and LUMO energy levels of the polymers. (a) PBDTTAZ-Ph, PBDTTAZ-NaPh and PBDTTAZ-PhPh; (b) PBDTTAZPh-R, PBDTTAZPh-OR and PBDTTAZPh-SR.

			T	Solu	ution		Film		LIONO			
Polymer	_М (KDa)	PDI	7 _d (°C)	$\frac{\lambda_{max}}{(nm)}$	λ _{onset} (nm)	λ _{max} (nm)	λ _{onset} (nm)	E _g ^{opt[a]} (eV)	(eV)	(eV)	(eV)	(eV)
PBDTTAZ-Ph	43.5	1.63	343	546	625	546	635	1.95	-5.44	-3.49	-5.06	-2.30
PBDTTAZ- NaPh	48.7	2.01	341	548	625	550	635	1.95	-5.44	-3.49	-5.05	-2.30
PBDTTAZ- PhPh	50.2	1.96	337	546	625	550	635	1.95	-5.44	-3.49	-5.05	-2.29
PBDTTAZPh-R	34.5	2.56	345	536	621	543	633	1.96	-5.42	-3.46	-5.03	-2.29
PBDTTAZPh- OR	53.6	1.73	352	540	622	545	636	1.95	-5.40	-3.45	-5.00	-2.27
PBDTTAZPh- SR	58.1	2.32	342	537	621	545	633	1.96	-5.42	-3.46	-5.03	-2.29

Table S1. Basic characteristics of the materials.

[a] Calculated from the absorption onset. [b] Measured by cyclic voltammetry. [c] Calculated

from HOMO energy levels and optical band gaps. [d] Calculated by DFT.

5. Detailed Optimized Device Parameters

Table S2. Photovoltaic parameters based on the active layers with different D/A rati	ios
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Polymer/Acceptor D/A (w/w)		V _{oc} ^a (V)	J _{SC} ^a (mA cm ⁻²)	FFª	PCEª (%)	
	1:1	0.914(0.906±0.010)	15.02(14.78±0.33)	0.675(0.669±0.010)	9.27(9.12±0.13)	
PBDTTAZ- Ph/ITIC	1:1.3	0.919(0.915±0.006)	17.86(17.46±0.43)	0.649(0.638±0.011)	10.65(10.34±0.26)	
	1:1.5	0.908(0.901±0.008)	18.01(17.86±0.20)	0.624(0.607±0.017)	10.20(10.03±0.17)	
	1:1	0.935(0.921±0.015)	17.25(16.85±0.43)	0.685(0.676±0.012)	11.05(10.75±0.28)	
PBDTTAZ- NaPh/ITIC	1:1.3	0.936(0.928±0.009)	18.21(18.06±0.21)	0.678(0.673±0.007)	11.56(11.36±0.16)	
	1:1.5	0.928(0.915±0.013)	18.23(17.96±0.29)	0.629(0.621±0.008)	10.64(10.41±0.19)	
	1:1	0.921(0.914±0.010)	16.01(15.71±0.42)	0.621(0.618±0.005)	9.16(8.97±0.16)	
PBDTTAZ- PhPh/ITIC	1:1.3	0.926(0.921±0.007)	16.67(16.32±0.36)	0.604(0.588±0.015)	9.32(9.03±0.23)	
	1:1.5	0.914(0.905±0.009)	16.82(16.71±0.19)	0.597(0.586±0.012)	9.18(8.96±0.29)	
	1:1	0.921(0.912±0.011)	7.01(6.75±0.38)	0.358(0.352±0.009)	2.31(2.16±0.13)	
PBDTTAZPh- R/ITIC	1:1.3	0.934(0.925±0.012)	7.19(6.85±0.36)	0.422(0.410±0.013)	2.83(2.51±0.30)	
	1:1.5	0.928(0.924±0.006)	8.16(7.82±0.34)	0.363(0.351±0.016)	2.75(2.45±0.34)	
	1:1	0.898(0.893±0.008)	13.44(13.26±0.24)	0.535(0.527±0.012)	6.46(6.28±0.15)	
PBDTTAZPh- OR/ITIC	1:1.3	0.893(0.881±0.014)	14.53(14.37±0.18)	0.534(0.529±0.008)	6.93(6.76±0.13)	
	1:1.5	0.884(0.875±0.011)	13.02(12.86±0.16)	0.554(0.542±0.014)	6.38(6.10±0.27)	
	1:1	0.925(0.918±0.008)	10.58(10.23±0.35)	0.416(0.408±0.011)	4.07(3.83±0.18)	
PBDTTAZPh- SR/ITIC	1:1.3	0.916(0.910±0.006)	11.25(11.01±0.29)	0.406(0.402±0.006)	4.18(4.02±0.013)	
	1:1.5	0.909(0.902±0.011)	11.38(11.06±0.40)	0.400(0.389±0.013)	4.14(3.89±0.23)	

^a Data were provided in optimal (statistical) results based on 15 devices for each case.

Table S3. Photovoltaic parameters based on the active layers with different thermal annealing

Polymer/Acceptor	D/A (w/w)	Thermal annealing (°C)ª	V _{oc} ^b (V)	J _{SC^b} (mA cm ⁻²)	FF ^b	PCE⁵ (%)	
		60	0.917(0.912±0.006)	17.59(17.37±0.33)	0.634(0.627±0.011)	10.23(10.08±0.13)	
		80	0.915(0.907±0.011)	17.89(17.56±0.41)	0.631(0.626±0.008)	10.33(10.13±0.18)	
PBDTTAZ- Ph/ITIC	1:1.3	100	0.913(0.906±0.007)	17.52(17.26±0.38)	0.631(0.627±0.005)	10.09(9.86±0.20)	
		120	0.905(0.896±0.013)	17.80(17.46±0.43)	0.633(0.621±0.016)	10.20(10.03±0.14)	
		140	0.900(0.892±0.009)	17.61(17.41±0.33)	0.642(0.632±0.014)	10.18(9.97±0.21)	
		60	0.933(0.926±0.009)	18.39(18.12±0.31)	0.664(0.656±0.010)	11.39(11.12±0.25)	
		80	0.927(0.918±0.009)	18.13(17.95±0.28)	0.663(0.651±0.015)	11.14(10.98±0.15)	
PBDTTAZ- NaPh/ITIC	1:1.3	100	0.923(0.916±0.010)	18.25(17.98±0.36)	0.653(0.648±0.006)	11.00(10.75±0.23)	
		120	0.920(0.915±0.007)	18.19(17.87±0.32)	0.650(0.642±0.011)	10.88(10.52±0.29)	
		140	0.916(0.910±0.006)	18.06(17.69±0.40)	0.664(0.657±0.009)	10.98(10.67±0.24)	
	1:1.3	60	0.926(0.917±0.009)	16.51(16.36±0.19)	0.607(0.601±0.012)	9.28(9.12±0.12)	
		80	0.918(0.910±0.009)	16.55(16.38±0.23)	0.600(0.592±0.009)	9.12(9.01±0.10)	
PBDTTAZ- PhPh/ITIC		100	0.918(0.911±0.008)	16.62(16.46±0.22)	0.590(0.571±0.019)	9.00(8.78±0.20)	
		120	0.916(0.907±0.011)	16.59(16.32±0.37)	0.587(0.581±0.010)	8.92(8.71±0.18)	
		140	0.915(0.908±0.009)	16.71(16.42±0.36)	0.593(0.585±0.009)	9.07(8.74±0.29)	
	1:1.3	60	0.937(0.922±0.016)	7.86(7.49±0.37)	0.379(0.369±0.012)	2.79(2.65±0.13)	
		80	0.935(0.921±0.014)	8.72(8.51±0.21)	0.358(0.350±0.008)	2.92(2.74±0.18)	
PBDTTAZPh- R/ITIC		100	0.931(0.920±0.011)	9.04(8.88±0.19)	0.385(0.371±0.017)	3.24(3.02±0.11)	
		120	0.921(0.914±0.008)	10.43(10.25±0.23)	0.398(0.390±0.009)	3.83(3.61±0.13)	
		140	0.922(0.913±0.010)	9.12(8.92±0.28)	0.356(0.346±0.010)	2.99(2.87±0.10)	
	1:1.3	60	0.889(0.886±0.005)	15.62(15.46±0.31)	0.504(0.492±0.015)	7.00(6.72±0.26)	
		80	0.887(0.879±0.008)	15.71(15.59±0.23)	0.565(0.559±0.007)	7.87(7.70±0.16)	
PBDTTAZPh- OR/ITIC		100	0.888(0.874±0.014)	16.31(15.98±0.39)	0.576(0.568±0.013)	8.34(7.94±0.26)	
		120	0.880(0.869±0.013)	15.96(15.70±0.34)	0.548(0.541±0.008)	7.70(7.52±0.17)	
		140	0.873(0.868±0.006)	16.01(15.78±0.35)	0.527(0.519±0.011)	7.37(7.12±0.21)	
PBDTTAZPh- SR/ITIC		60	0.924(0.913±0.012)	13.22(12.97±0.28)	0.413(0.403±0.014)	5.04(4.80±0.19)	
		80	0.923(0.915±0.008)	14.89(14.62±0.30)	0.403(0.396±0.009)	5.54(5.35±0.13)	
	1:1.3	100	0.913(0.908±0.006)	13.98(13.61±0.43)	0.400(0.390±0.011)	5.11(4.88±0.30)	
		120	0.907(0.901±0.007)	13.31(13.06±0.27)	0.390(0.378±0.016)	4.71(4.52±0.16)	
		140	0.889(0.881±0.010)	12.62(12.35±0.39)	0.371(0.359±0.013)	4.16(3.96±0.17)	

temperature.

^a The blend films were thermally annealed for 10 mins. ^b Data were provided in optimal

(statistical) results based on 15 devices for each case.

Table S4. Photovoltaic parameters based on the active layers with different additive (CN)

Polymer/Acceptor	D/A (w/w)	Additive CN (v%)	V _{OC} ^a (V)	J _{SC} ^a (mA cm ⁻²)	FF ^a	PCE ^a (%)
PBDTTAZ- Ph/ITIC	1:1.3	0.25	0.915(0.906±0.013)	16.98(16.66±0.38)	0.630(0.621±0.013)	9.79(9.38±0.28)
		0.5	0.913(0.906±0.009)	17.35(17.01±0.39)	0.619(0.608±0.014)	9.81(9.40±0.32)
		1	0.914(0.905±0.012)	17.65(17.36±0.31)	0.622(0.615±0.009)	10.03(9.87±0.15)
		1.5	0.907(0.895±0.013)	16.21(16.02±0.26)	0.603(0.596±0.011)	8.87(8.58±025)
		0.25	0.932(0.928±0.006)	17.22(17.02±0.24)	0.650(0.642±0.009)	10.43(10.19±0.21)
PBDTTAZ-	1:1.3	0.5	0.929(0.922±0.009)	18.15(17.91±0.29)	0.641(0.638±0.005)	10.81(10.54±0.22)
NaPh/ITIC		1	0.905(0.901±0.006)	18.02(17.79±0.27)	0.549(0.540±0.010)	8.95(8.70±0.19)
		1.5	0.879(0.872±0.007)	16.59(16.32±0.30)	0.479(0.471±0.013)	6.99(6.71±0.19)
PBDTTAZ- PhPh/ITIC	1:1.3	0.25	0.923(0.913±0.011)	16.32(16.05±0.33)	0.578(0.572±0.008)	8.71(8.42±0.27)
		0.5	0.920(0.908±0.013)	16.78(16.51±0.35)	0.571(0.565±0.007)	8.81(8.51±0.26)
		1	0.913(0.906±0.008)	15.91(15.55±0.39)	0.554(0.541±0.015)	8.05(7.76±0.20)
		1.5	0.900(0.896±0.009)	15.63(15.46±0.21)	0.482(0.471±0.014)	6.78(6.52±0.25)
PBDTTAZPh- R/ITIC	1:1.3	0.25	0.932(0.923±0.012)	7.23(6.94±0.33)	0.376(0.372±0.006)	2.53(2.28±0.21)
		0.5	0.926(0.922±0.006)	9.85(9.71±0.19)	0.387(0.378±0.016)	3.53(3.39±0.12)
		1	0.919(0.911±0.013)	8.93(8.78±0.20)	0.307(0.296±0.011)	2.52(2.39±0.13)
		1.5	0.907(0.901±0.008)	9.75(9.63±0.18)	0.237(0.232±0.007)	2.10(2.02±0.08)
PBDTTAZPh- OR/ITIC	1:1.3	0.25	0.898(0.896±0.007)	15.74(15.48±0.26)	0.535(0.531±0.005)	7.56(7.35±0.17)
		0.5	0.896(0.891±0.007)	15.98(15.71±0.29)	0.564(0.559±0.008)	8.08(7.83±0.23)
		1	0.887(0.879±0.012)	15.53(15.38±0.17)	0.508(0.501±0.012)	7.00(6.71±0.26)
		1.5	0.883(0.868±0.016)	15.42(15.19±0.25)	0.495(0.492±0.006)	6.74(6.50±0.17)
PBDTTAZPh- SR/ITIC	1:1.3	0.25	0.924(0.920±0.007)	14.66(14.44±0.26)	0.397(0.391±0.008)	5.38(5.20±0.16)
		0.5	0.917(0.911±0.009)	14.92(14.75±0.19)	0.394(0.389±0.007)	5.39(5.23±0.11)
		1	0.915(0.908±0.010)	15.24(14.96±0.28)	0.439(0.429±0.011)	6.12(5.76±0.31)
		1.5	0.912(0.901±0.016)	14.35(14.03±0.36)	0.389(0.381±0.013)	5.09(4.82±0.27)

volume fraction.

^a Data were provided in optimal (statistical) results based on 15 devices for each case.

6. Hole Mobility and Electron Mobility Measurement



Fig. S5. SCLC curves for hole-only based on optimized devices. (a) PBDTTAZ-Ph/ITIC; (b) PBDTTAZ-NaPh/ITIC; (c) PBDTTAZ-PhPh/ITIC; (d) PBDTTAZPh-R/ITIC with thermal annealing at 120 °C; (e) PBDTTAZPh-OR/ITIC with thermal annealing at 100 °C; (f) PBDTTAZPh-SR/ITIC with 1% CN. (The symbols are experimental data for transport of hole, and the red lines are fitted according to the space-charge-limited-current model. The thicknesses of the active layers were about 100 nm.).



Fig. S6. SCLC curves for electron-only based on optimized devices. (a) PBDTTAZ-Ph/ITIC; (b) PBDTTAZ-NaPh/ITIC; (c) PBDTTAZ-PhPh/ITIC; (d) PBDTTAZPh-R/ITIC with thermal annealing at 120 °C; (e) PBDTTAZPh-OR/ITIC with thermal annealing at 100 °C; (f) PBDTTAZPh-SR/ITIC with 1% CN. (The symbols are experimental data for transport of electron, and the red lines are fitted according to the space-charge-limited-current model. The thicknesses of the active layers were about 100 nm.).

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