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Supporting Information

Interface-Induced Face-on Orientation of Active Layer by Self-assembled

Diblock Conjugated Polyelectrolytes for Efficient Organic Photovoltaic Cells

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EXPERIMENTAL SECTION

Materials:

N-bromosuccinimide 3-Thiophenemethanol, (NBS), 2-(2-(2methoxyethoxy)ethoxy)ethanol, 1,6-dibromohexane, tetrabutylammonium bromide, 2,7-dibromofluorene, [1,3-bis(diphenylphosphino) propane]-dichloronickel (II) Nmethylimidazole and trimethylamine in THF solution (ca. 13% in Tetrahydrofuran, ca. 2 mol/L) were purchased from Alfa, Aldrich or TCI. MoO₃ (99.99%), Ag (99.99%), poly(3-hexylthiophene) (P3HT, Mw=48300 g mol-1, 2.0-2.4 polydispersity, regiogegular: head-to-tail, 99% purity), [2,6'-4,8-di(5poly ethylhexylthienyl)benzo[1,2-b;3,3-b] dithiophene] [3-fluoro-2](2-ethyl hexyl)carbonyl]thieno[3,4-*b*]thiophenediyl]] (PTB7-Th), [6,6]-phenyl-C₆₀-butyric acid methyl ester (PC₆₁BM, 99.5% purity) and [6,6]-phenyl-C₇₀-butyric acid methyl ester (PC₇₁BM) were purchased from Alfa and used without further purification. Indium-tin oxide (ITO) glass was purchased from Delta Technologies Limited. Tetrahydrofuran (THF) was dried over sodium.

Device Fabrication

P3HT/PC₆₁BM The devices were manufactured with the structure of Glass/ITO/CPEs/active layer/MoO₃/Ag. The conductive ITO substrates were sequentially cleaned with ultrasonication in acetone, detergent, deionized water, and isopropanol. After the ITO substrates were dried by nitrogen purging and treated the surface with UV ozone for15 min, the diblock CPEs (0.5 mg/mL dissolved in methanol) solutions were spin-coated onto the cleaned ITO substrates at 4000 r/min for 1 min under air atmosphere. And the interface layer was annealed at 150 °C for 10 min. The active layer P3HT/PC₆₁BM (1:0.8 w/w), a blend solution of 10 mg of P3HT and 8 mg of P₆₁CBM dissolved in 0.5 mL o-dichlorobenzene solution with a concentration of 20 mg mL⁻¹ and was prepared and by spin-casted at 800 rpm for 30 s. And then the film was dried in the glove box for 2 hours, subsequently annealed at 150 °C for 10 min in a nitrogen-atmosphere glove box. Subsequently, the anode buffer layer MoO₃ (7 nm) and Ag (90 nm) electrode were deposited on the active layer by thermal evaporation under a vacuum chamber to accomplish the device fabrication. The PTB7-Th/PC71BM system (1:1.5 by weight), a blend solution of 6 mg of PTB7-Th and 9 mg of PC71BM dissolved in 0.582 mL chlorobenzene solution and were spin-coated from a chlorobenzene solution with 3 vol % 1,8-diiodooctane as cosolvent at a speed of 1000 rpm/min for 2 min with the structure of Glass/ITO/ZnO/CPEs/PTB7-Th/PC71BM/MoO3/Ag. Finally, 70Å MoO3 and a 900 Å Ag electrode were sequentially deposited by thermal evaporation. The effective area of each cell was 0.04 cm². The current-voltage (J-V) curve was measured by a Keithley 2400 Source Meter under simulated solar light (100 mW/cm², AM 1.5 G, Abet Solar Simulator Sun 2000).

Synthesis

The detailed synthetic routes of the target dibolck polymers are displayed in **Scheme S1**. 3-Thiophenemethanol reacted with N-bromosuccinimide to afford compound 1. Compound 2 was prepared by the etherification of compound 1 and 1, 6dibromohexane. Compound **4** was synthesized by the substitution reaction of 2,7dibromofluorene with compound **3** which was obtained from the reaction of 2-(2-(2methoxyethoxy)ethoxy)ethanol and 4-methylbenzene-1-sulfonyl chloride. Diblock polymer PF_{EO} -*b*-PTBr was first prepared by the Kumada Catalyst Transfer Coupling polymerization between compounds **2** and **4**. The ionized diblock polymer PF_{EO} -*b*-PTNBr was obtained through a quantitative quaternization for the diblock PF_{EO} -*b*-PTBr with an excess of trimethylamine in tetrahydrofuran (THF) solutions under -78 °C with liquid nitrogen. The final step to the target diblock polyelectrolyte PF_{EO} -*b*-PTImBr was a polymer-analogous quaternization of the alkyl bromide side groups with N-methylimidazole.

Synthesis of 2,5-dibromo-3-thiophenemethanol (1).

3-Thiophenemethanol (1) (2.5 g, 22.0 mmol) was dissolved in dried THF (60 mL) in a dried 250 mL round bottom flask. Then, NBS (7.9 g, 44.0 mmol) was added in several portions to the reaction mixture (over 2 h) and the reaction mixture was kept in dark place and stirred at room temperature overnight. The residual NBS was removed through a plug of Cealite. And the THF was removed by rotary evaporation. The product was extracted with diethyl ether (200 mL), washed with 1M sodium hydroxide solution and water. The organic layer was concentrated and the product was purified by column chromatography with hexane:ethyl acetate 3:1 (v:v) to yield the desired product (80% yield) as a light yellow solid. ¹H NMR (400 MHz, CDCl₃), (ppm): 7.01 (s, 2H), 4.56 (s, 2H), 1.66 (s, 1H).

Synthesis of 3-(((6'-bromohexyl)oxy)methyl)-2,5-thiophene (2).

Under the protection of nitrogen, 2,5-dibromo-3-thiophenemethanol(1.5 g, 5.5 mmol), 1,6-dibromohexane(12.0 g, 49.6 mmol), tetrabutylammonium bromide (0.1 g, 0.3 mmol) and 50 wt% sodium hydroxide solution(10 mL) were added in 250 mL nitrogen bottom flask. The reaction mixture was stirred at 80 °C overnight under an argon atmosphere. After cooling to room temperature, the organic layer was extracted with dichloromethane (100 mL) and water, and then dried over anhydrous MgSO₄. The residue was purified by column chromatography with1:3 (v/v) ethyl acetate

/petroleum ether as the eluent to give the final compound as a colorless liquid (1.39 g, 88%). ¹H NMR (400 MHz, CDCl₃), (ppm): 6.97 (s, 2H), 4.35 (s, 2H), 3.48-3.43 (t,2H), 3.39-3.33 (t, 2H), 1.89-1.80 (m, 2H), 1.63-1.56 (t, 2H), 1.49-1.31 (m, 4H).

Synthesis of 2-(2-(2-methoxy)ethoxy)ethyl-4-methylbenzenesulfonate (3).

2-(2-(2-methoxyethoxy)ethoxy)ethanol(8.2 g, 50.0 mmol) and 4-methylbenzene-1-sulfonyl chloridel(10.5 g, 55.1 mmol) were dissoved in THF (120 mL) in a dried 250 mL round bottom flask and cooled to 0 °C in an ice bath. A solution of NaOH (10.0 g) in 50 mL water was added to the reaction mixture. The mixture was gradually warmed to room temperature and stirred overnight. The solution was washed with aqueous sodium hydrogen carbonate and extracted with dichloromethane and washed with water, dried over MgSO₄ and filtered, and the solvent was evaporated. The crude product was purified by silica chromatography 1:1 (v/v) ethyl acetate/petroleum ether to give a colorless liquid (90 %). ¹H NMR (400 MHz, CDCl₃), (ppm): 7.76 (d, 2H), 7.29 (d, 2H), 4.13 (t, 2H), 3.65-3.50 (m, 10H), 3.33 (s, 3H), 2.42 (s, 3H).

Synthesis of 9,9-bis(2'-(2'-methoxyethoxy)ethoxy)ethyl)-2,7-fluorene (4).

In a 250 mL round bottom flask, 2,7-dibromofluorene (5.0 g, 15.5 mmol) was dissolved in dried THF solution (80 mL). Sodium hydride (1.5 g, 60 mmol) was slowly added to the stirred THF solution at room temperature under nitrogen atmosphere. The mixture was refluxed at 85 °C for 4h. Compound 3 2-(2-(2-methoxy)ethoxy)ethyl)-4-methylbenzenesulfonate (11.8 g, 37 mmol) in 15 mL of dry THF was added dropwise to the refluxed solution. The mixture was allowed to reflux overnight, then cooled to room temperature, poured into distill water, and extracted with dichloromethane three times. The organic layer was combined and washed with saturated NaCl solution and distilled water (1 × 100 mL), dried over MgSO₄. The solvent was removed by reduced pressure rotary evaporation. Crude product was further purified by column chromatography ethyl acetate /petroleum ether to provide a 5.0 g light yellow solid in 53 % yield. ¹H NMR (400 MHz, CDCl₃), (ppm): 7.62-7.42 (m, 6H), 3.52-3.48 (m, 8H), 3.37 (t, 4H), 3.34 (s, 6H), 3.19 (t, 4H), 2.77 (t, 4H), 2.33 (t, 4H).

Poly[(9,9-bis(2'-(2'-(2'-methoxy)ethoxy)ethoxy)ethyl)-2,7-fluorene)]-*block*-poly[3-(((6'-bromohexyl)oxy)methyl)-2,5-thiophene] \mathbf{PF}_{EO} -**b**-**PTBr diblock polymer**

2,7-dibromo-9,9-bis(2-(2-(2-methoxy)ethoxy)ethoxy)ethyl)-fluorene (0.614 g, 1.0 mmol) and THF (6 mL) were added to a 100mL flask equipped with a condenser and nitrogen inlet. marked as А solution. 2,5-dibromo-3-(((6bromohexyl)oxy)methyl)thiophene (0.86 g, 2.0 mmol) and THF (20 mL) were added to another 100 mL flask equipped with a condenser and nitrogen inlet, marked as B solution. A 3M solution of magnesium bromide (0.40 mL, 1.2 mmol) in diethyl ether (Et2O) was added to A solution and (0.80 mL, 2.4 mmol) 3 M magnesium bromide in diethyl ether (Et2O) was added to B solution, then all reactions were refluxed for 2 h. The A flask was cooled to room temperature, and [1,3-bis(diphenylphosphino) propane]-dichloronickel (II) (12 mg, 2.25×10-5 mol) was added through a tee. The reaction mixture was stirred at reflux temperature until dark color was observed. About 10 min later, a solution was prepared typically to 99% conversion, then B solution was added by a tee to the flask (A solution). The solution was reacted at 80 °C for 3 days. Finally, the mixture was precipitated into hexane. The polymer was filtered and purified by sequential soxhlet extractions using methanol, hexane and chloroform respectively. The chloroform fraction was dried to yield the desired diblock copolymer as a light yellow solid. According to the 1H NMR, the final obtained precise ration between the two blocks polyfluorene and polythiophene is 1:2. ¹H NMR (400 MHz, CDCl₃), (ppm): 7.73-7.46 (m, 6H), 6.98 (s, 2H), 4.35 (s, 4H), 3.51-3.48 (m, 12H), 3.38-3.11 (m, 18H), 2.77 (t, 4H, J=6.4 Hz), 2.32 (t, 4H, J=6.4 Hz), 1.75-1.46 (m, 8H), 1.40-1.20 (m, 8H). ¹³C NMR (100 MHz, CDCl₃), (ppm): 150.89, 139.8, 138.41, 131.76, 129.62, 126.66, 124.83, 121.61, 121.19, 77.31, 71.85, 70.43, 70.03, 66.75, 59.00, 51.87, 39.47, 34.12, 32.67, 31.89, 30.29, 29.16, 24.83. M_n $(13700), M_w(16600), M_w/M_n=1.21.$

Synthesis of PF_{EO} -*b*-PTNBr diblock polymer

Under -78 °C, 100 mg PF_{EO} -*b*-PTBr was dissolved in 30 mL THF. An excess of trimethylamine in THF solution (ca. 13% in Tetrahydrofuran, ca. 2 mol/L) (9.0 mL)

was added to the solution. The mixture was stirred for 5 days at room temperature. Once some precipitates were formed, and some methanol was added to dissolve them, and additional 2 mL of trimethylamine in THF solution (ca. 13% in Tetrahydrofuran, ca. 2 mol/L) was added every day. The solution was evaporated and the residue was redissolved in methanol. The ionic polymer was precipitated from ether and purified by a dialysis bag. The diblock polymer was dried in vacuum overnight and obtained as orange yellow powder. The yield was as high as 91%. ¹H NMR (400 MHz, CD₃OD-*d*₄), (ppm): 7.78-7.42 (m, 6H), 6.98 (s, 2H), 4.35 (s, 4H), 3.66-3.49 (m, 12H), 3.48-3.36 (m,18H), 3.22-3.06 (s,18H), 2.87-2.73 (t, 4H, *J*=2.8 Hz), 2.44-2.30(t, 4H, *J*=2.8 Hz), 1.95-1.46 (m, 8H), 1.43-1.23 (m, 8H). ¹³C NMR (100 MHz, DMSO-*d*₆), (ppm): 150.93, 138.96, 137.89, 131.82, 129.34, 125.13, 124.03, 121.65, 121.03, 71.96, 70.53, 70.02, 66.32, 58.72, 51.32, 32.73, 31.83, 30.38, 29.26, 24.59.

Synthesis of PF_{EO}-b-PTImBr diblock polymer

Under nitrogen, a large excess of 1-methylimidazole (800 mg, 9.76 mmol), dried THF (60 mL) and PF_{EO}-*b*-PTBr (100 mg) were added to a 250 mL three-neck flask. The reaction mixture was stirred at room temperature for 2 hours. And then the solution was gradually warmed to 85 °C and refluxed for 3 days. The mixture was subsequently cooled to room temperature, and the crude product was obtained by filtration. Then, the filter residue was redissolved in methanol (10 mL). After filtration to remove some insoluble material the solvents were removed by a rotary evaporator. The obtained product was further purified by dialysis against methanol using a dialysis membrane with a cut-off of 2000 g/mol. The polymer was isolated by removing methanol under reduced pressure rotary evaporator, and dried under vacuum to yield 85 mg (85 %) of **PF**_{EO}-*b*-**PTImBr** as a jacinth solid. ¹H NMR (400 MHz, CD₃OD-*d*₄), (ppm): 8.53 (s, 2H), 7.96-7.15 (m, 10H), 6.98 (s, 2H), 4.35 (s, 4H), 4.15-4.00 (t, 4H, *J*=3.0 Hz), 3.85 (s, 6H), 3.79-3.67 (m, 8H), 3.58-3.39 (m, 18H), 2.98-2.87 (t, 4H, *J*=2.2 Hz), 2.35-2.21(t, 4H, *J*=2.8 Hz), 1.75-1.33 (m, 8H), 1.29-1.14 (m, 8H). ¹³C NMR (100 MHz, DMSO-*d*₆), (ppm): 150.76, 138.83, 137.89, 136.03, 130.53,

129.04, 125.63, 125.03, 123.0, 122.8, 121.65, 121.03, 71.78, 70.44, 70.02, 66.73, 58.72, 51.52, 31.83, 30.38, 29.26, 24.57.

Characterizations

The nuclear magnetic resonance (NMR) spectra were measured on a Bruker ARX 400 NMR spectrometer with deuterated chloroform, deuterated methanol and deuterated DMSO as the solvent and with tetramethylsilane (δ =0) as the internal standard. The molecular weights and dispersity index (M_w/M_n) were determined by size exclusion chromatograms (SEC) on a Waters system, which was equipped with a Waters 2515 HPLC pump and Waters 2707 Plus Autosampler equipped with Waters 2414 refractive index detector and two Waters Styragel high-resolution column (HT3, HT4: effective molecular weight range 500-30000, 5000-600000, respectively). Tetrahydrofuran (HPLC grade) (flow rate of 1.0 mL/min) was used as eluent. Ultraviolet-visible (UV) spectra and optical transmittance spectra of the samples were recorded on a Hitachi UV-3010 spectrophotometer. XPS studies were performed on a Thermo-VG Scientific ESCALAB 250 photoelectron spectrometer using a monochromated AlKa (1,486.6 eV) X-ray source. All recorded peaks were corrected for electrostatic effects by setting the C-C component of the C 1s peak to 284.8 eV. The base pressure in the XPS analysis chamber was 2×10^{-9} mbar. Atomic force microscopic (AFM) images were measured on a nanoscope III A (Digital Instruments) scanning probe microscope using the tapping mode. The work functions of the modified cathode were investigated using a Kelvin probe (KP 6500 Digital Kelvin probe, McAllister Technical Services. Co.,Ltd.), which can detect the contact potential difference (VCPD) and the work function difference ($\Delta \Phi = e \times VCPD$), where e is the electron charge between the probe and the sample. The Kelvin probe microscopy (KPM) shown in the figures are obtained by subtracting the pristine values from the work function of Au probe tip, which is 5.1 eV. The total 225 points are measured over the scan area of 1.5 mm ×1.5 mm for each sample. The work function value was the average value of 144 points. X-ray diffraction (XRD) studies of the samples were carried out using a Bruker D8 Focus X-ray diffractometer operating at 30 kV and 20 mA with a copper target (λ =1.54 Å) and at a scanning rate of 2° min⁻¹.The UPS measurements were carried out in a Thermo-VG Scientific ESCALAB 250 using a He I (21.22 eV) discharge lamp. A bias of -8.0 V was applied to the samples for separation of the sample and the secondary edge for the analyzer. The HOMO energies are determined by

$$-HOMO = hv-(Ecutoff - Eonset)$$

where hv is the incident photon energy, hv = 21.22 eV. E_{cutoff} is defined as the high binding energy cutoff, Eonset is the HOMO energy onset, generally referred to as the low binding energy onset. The GIXRD profiles were obtained by using a Bruker D8 Discover reflector with an X-ray generation power of 40 kV tube voltage and 40 mA tube current. The measurements were obtained in a scanning interval of 20 between 2° and 30°. TEM images were recorded using a JEOL-2100F transmission electron microscope and an internal charge-coupled device (CCD) camera. Fluorescence measurement for fluorescence probe of the polymers was carried out on a Hitachi F-7000 PC spectrofluorophotometer with a xenon lamp as the light source. The 176 mg pyrene (80 mg/mL) dissolved in 2 mL chlorobenzene and 0.2 mL diblock CPEs (0.5 mg/mL in CH₃OH solution) was added in the above pyrene solution. The diblock CPEs doped pyrene solution was spin-coated on ITO substrate at 4000 r/min to obtain the solid film. The fluorescence probe was measured by the solid film from 200 to 800 nm wavelength on a Hitachi F-7000 PC spectrofluorophotometer with a xenon lamp as the light source. The electron paramagnetic resonance (EPR) was carried out by JES-FA200. Current-voltage (J-V) characteristics were recorded using Keithley 2400 Source Meter in the dark and under 100 mW/cm² simulated AM 1.5 G irradiation (Abet Solar Simulator Sun 2000). The concentration and the rotate speed of the diblock CPEs in UPS and KPM characterizations are consistent with those in the solar cell devices, the concentration of the diblock CPE is 0.5 mg/mL, and the rotate speed is 4000 r/min.

Space-charge-limited-current (SCLC) mobility measurement

In order to explore the electron transfer characteristic of diblock CPEs ETL, the electron only device with the structure of $ITO/CPEs/P3HT:PC_{61}BM/A1$ were investigated by the space charge limited current (SCLC) method according to the Mott–Gurney equation.

$$J=(9/8) \ \mu \ \varepsilon_0 \ \varepsilon_r (V^2/L^3)$$

where *J* is the current density, W μ is the charge carrier mobility, ε_0 is the permittivity of free space (8.85 × 10⁻¹²F m⁻¹), ε_r is the dielectric constant of P3HT or PC61BM (assumed to 3), *V* is the applied voltage, and *L* is the film thickness. The thickness of the active layer for SCLC measurement is approximate 120 nm. EQE were detected under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp), and the calibration of the incident light was performed with a monocrystalline silicon diode. The active area of the device the device is 0.04 cm².



Scheme S1. Synthesis of PF_{EO} -*b*-PTNBr and PF_{EO} -*b*-PTImBr diblock polymers.



(a)

Figure S1. The ¹H NMR (a) and ¹³C NMR (b) spectra of the diblock polymer PF_{EO} -*b*-PTBr recorded in deuterated chloroform solution.



Figure S2. The ¹H NMR (a) spectrum of the diblock polymer PF_{EO} -*b*-PTNBr recorded in deuterated methanol solution and ¹³C NMR (b) spectrum of the diblock polymer PF_{EO} -*b*-PTNBr recorded in deuterated DMSO solution.



Figure S3. The ¹H NMR (a) spectrum of the diblock polymer PF_{EO} -*b*-PTImBr recorded in deuterated methanol solution and ¹³C NMR (b) spectrum of the diblock polymer PF_{EO} -*b*-PTImBr recorded in deuterated DMSO solution.



Figure S4. Size exclusion chromatograms (SEC) of the 1st block synthesized (polyfluorene) PF_{EO} (red) and its respective block copolymer PF_{EO} -*b*-PTBr (blue), PF_{EO} ($M_n = 6.96$ kDa, $M_w/M_n = 1.13$), PF_{EO} -*b*-PTBr ($M_n = 13.7$ kDa, $M_w/M_n = 1.21$).



Figure S5. Normalized UV-vis absorption spectra of the diblock polymers in solid films spincoated on ITO.



Figure S6. Optical transmittance spectra of the bare ITO, ITO/**PF**_{EO}-*b*-**PTNBr** and ITO/**PF**_{EO}-*b*-**PTImBr** films.



Figure S7. Effective work functions graph from Kelvin Probe of the bare ITO, ITO/PF_{EO}-*b*-PTNBr and ITO/PF_{EO}-*b*-PTImBr ETLs.



Figure S8. Atomic force microscopy (AFM) tapping mode height images (left) and phase image (right) of the surface of (a, b) **PF**_{EO}-*b*-**PTNBr**, (c, d) **PF**_{EO}-*b*-**PTImBr**.



Figure S9. Transmission electron microscopy images of (a) PF_{EO} -*b*-PTNBr and (b) PF_{EO} -*b*-PTImBr films.



Figure S10. Atomic force microscopy tapping mode height images of the surface of (a) ITO/P3HT:PC₆₁BM, (b) **PF**_{E0}-*b*-**PTNBr**/P3HT:PC₆₁BM, and (c) **PF**_{E0}-*b*-**TImBr**/P3HT:PC₆₁BM films.



Figure S11. Atomic force microscopy tapping mode three-dimensional image of the surface of (a) bare ITO, (b) PF_{EO}-b-PTNBr, (c) PF_{EO}-b-PTImBr, (d) ITO/P3HT:PC₆₁BM, (e) PF_{EO}-b-PTNBr/P3HT:PCBM, and (f) PF_{EO}-b-TImBr/P3HT:PC₆₁BM films.



Figure S12. The dark current of the inverted PSCs based on PTB7-Th:PC₇₁BM.

Pvrene/PF _{EO} - <i>b</i> -PTImBr	Start (nm)	Apex (nm)	End (nm)	Height (Data)
	201.2	275 4	250.2	7773
11	201.2	323.4	559.2	1213
I_2	359.2	445.8	453.4	436.4
I_3	453.4	466.2	631.6	446.8
I_4	631.6	650.4	736	495.1
I_5	736	893.8	898.8	8.003
Pyrene/PF _{EO} - <i>b</i> -PTNBr	Start (nm)	Apex (nm)	End (nm)	Height (Data)
I ₁	201.2	325	350.8	6344
I_2	350.8	442.8	451.6	382
I_3	451.6	467	629.4	427.4
I_4	629.4	649.8	735.6	451.2
I_5	735.6	887.8	898.8	8.44
pyrene	Start (nm)	Apex (nm)	End (nm)	Height (Data)
I ₁	201.2	325.2	349.6	5533
I_2	349.6	444.6	453.6	425.9
I_3	453.6	466.2	635.6	432.8
I_4	635.6	651.2	723.8	570.6
I_5	736	893.8	898.8	8.003

Table S1. Principal vibronic bands in pyrene monomer and PF_{EO} -*b*-PTNBr/PF_{EO}-*b*-PTImBr doped pyrene of fluorescence spectra.

ETLs	Active layers	$V_{ m oc}({ m V})$	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
ZnO	PTB7-Th:PC71BM	0.775 ± 0.002	16.460 ± 0.286	63.1±1.15	$8.1^{a}(8.2)^{b}$
PFN	PTB7-Th:PC71BM	0.790 ^c	16.350 ^c	65.7 ^c	8.42 ± 0.06 ^c
PFNBr	PTB7-Th:PC71BM	0.800 ± 0.010 ^c	16.620 ± 0.310 ^c	63.0 ± 3.00 ^c	8.38 ± 0.22 ^c

Table S2. Device parameters of the PSCs with different electron transport layers (ETLs) and PTB7-Th:PC₇₁BM under the illumination of AM 1.5G, 100 mW cm⁻².

^{*a*}The average values for photovoltaic solar cell parameters of each device are obtained from 20 devices, and the \pm refer to the standard deviation. ^{*b*}Values in parentheses represent the best power conversion efficiency (PCE). ^{*c*} The data from references 23-24 published and commonly used PFN and PFNBr ETLs based devices for comparison with the diblock CPEs **PF**_{EO}-*b*-**PTNBr** and **PF**_{EO}-*b*-**PTImBr** ETLs.