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Self-assembled Diblock Conjugated Polyelectrolytes as Electron Transport Layers for Organic Photovoltaics

Dan Zhou[a,b], Jinliang Liu[a], Lie Chen*[a], Haitao Xu[a,b], Xiaofang Cheng[a], Fangying Wu[a], Yiwang Chen[a]

[a]College of Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

[b]Key Laboratory of Jiangxi Province for Persistent Pollutants, Control and Resources Recycle, Nanchang Hangkong University, 696 Fenghe South Avenue, Nanchang 330063, China

Corresponding author. Tel.: +86 791 83968703; fax: +86 791 83969561. E-mail: chenlie@ncu.edu.cn (L. Chen).

EXPERIMENTAL SECTION

Materials:

3-Thiophenemethanol, N-bromosuccinimide (NBS), 2-(2-(2-methoxyethoxy)ethoxy)ethanol, 1,6-dibromohexane, tetrabutylammonium bromide, 2,7-dibromofluorene, [1,3-bis(diphenylphosphino) propane]-dichloronickel（Ⅱ）N-methylimidazole, trimethylamine in THF solution (ca. 13% in Tetrahydrofuran, ca. 2 mol/L), 2,7-dibromo-9H-carbazole, hydride sodium, $Zn(CH_3COO)_2 \cdot 2H_2O$, $NH_2CH_2CH_2OH$ and $CH_3OCH_2CH_2OH$ were purchased from Alfa, Aldrich or TCI. MoO_3 (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) and [6,6]-phenyl-C_{60}-butyric acid methyl ester ($PC_{61}BM$, 99.5% purity) 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

The P3HT/$PC_{61}BM$ devices were manufactured with the structure of Glass/ZnO/CPEs/active layer/MoO_3/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 ZnO precursor solution which was prepared by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 99.9%, 0.5 g) and ethanolamine ($NH_2CH_2CH_2OH$, 99.5%, 128 μL) in 2-methoxyethanol ($CH_3OCH_2CH_2OH$, 99.8%, 5 mL) under vigorous stirring for 12 h was coated onto the cleaned ITO substrates at a spin speed of 4000 rpm for 1 min, and annealed at 220 °C for 1 h. Then, the diblock CPEs (0.5 mg/mL dissolved in methanol) solutions were spin-coated onto ZnO 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/$PC_{61}BM$ (1:0.8 w/w), a blend solution of 10 mg of P3HT and 8 mg of $P_{61}CBM$ 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 MoO_3 (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 effective area of each cell was 0.04 cm^2. The current−voltage (*J*−V) curve was measured by a Keithley 2400 Source Meter under simulated solar light (100 mW/cm^2, AM 1.5 G, Abet Solar Simulator Sun 2000).

Synthesis

The detailed synthetic procedure of the target dibolck polymers are displayed in **Scheme S1**. 3-Thiophenemethanol reacted with N-bromosuccinimide to afford compound **1**. Compound **2** was obtained between the etherification of compound **1** and 1, 6-dibromohexane. Compound **4** was synthesized by the substitution reaction of 2,7-dibromofluorene with compound **3** which was obtained from the reaction of 2-(2-(2-methoxyethoxy)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 **4** and **2**. 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. Compound **5** was prepared by the reaction of 2,7-dibromo-9H-carbazole and 1,6-dibromohexane. Diblock polymer **PF$_{\mathbf{EO}}$-*b*-PCBr** was prepared by the Kumada Catalyst Transfer Coupling polymerization between compounds **4** and **5**. The final step to the target diblock polyelectrolyte **PF$_{\mathbf{EO}}$-*b*-PCNBr** was synthesized by quaternization of the alkyl bromide side groups of the diblock **PF$_{\mathbf{EO}}$-*b*-PTBr** with an excess of trimethylamine in tetrahydrofuran (THF) solutions.

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

3-Thiophenemethanol (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. ^{1}H NMR (400 MHz, $CDCl_3$), (ppm): 7.01 (s, 2H), 4.56 (s, 2H), 1.66 (s, 1H).

Synthesis of 3-(((6'-bromohexyl)oxy)methyl)-2,5-dibromo-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 50wt% 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%).^{1}H NMR (400 MHz, $CDCl_3$), (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-methoxyethoxy)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 $MgSO_4$ 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, $CDCl_3$), (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’-(2’-methoxyethoxy)ethoxy)ethyl)-2,7-dibromo - 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-methoxyethoxy)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 $MgSO_4$. 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, $CDCl_3$), (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’-methoxyethoxy)ethoxy)ethyl)-2,7-fluorene)]-*block*-poly[3-(((6’-bromohexyl)oxy)methyl)-2,5-thiophene] **PF_{EO}-*b*-PTBr diblock polymer**

9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-2,7-dibromo-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 A solution. 3-(((6-bromohexyl)oxy)methyl) 2,5-dibromo-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 (Et_2O) was added to A solution and (0.80 mL, 2.4 mmol) 3 M magnesium bromide in diethyl ether (Et_2O) 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; 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 ^{1}H NMR, the final obtained precise ration between the two blocks polyfluorene and polythiophene is 1:2. ^{1}H NMR (400 MHz, $CDCl_3$), (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). ^{13}C NMR (100 MHz, $CDCl_3$), (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%. ^{1}H NMR (400 MHz, CD_3OD-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). ^{13}C 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 9-(6-bromohexyl)-2,7-dibromo-carbazole (5).

2,7-Dibromo-carbazole (3.25 g, 10mmol) and hydride sodium (1.8 g, 75.0 mmol) were stirred in acetone (40 mL) at 0 °C. The solution was stirred for 1h. Then excess 1,6-dibromohexane (9.76 g, 40 mmol) was added in one portion, and the mixture was stirred at room temperature overnight. After the completion of the reaction, the reaction mixture was poured into water and extracted with ethyl acetate. The combined organic phases were washed with water followed by dried over magnesium sulfate ($MgSO_4$). After the solvent was removed, the residue was recrystallized from hexane and purified by column chromatography ethyl acetate /petroleum ether to provide a white solid (3.92 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$), (ppm): 7.93-7.84 (d, 2H, J=3.6 Hz), 7.52 (s, 2H), 7.37-7.27 (d, 2H, J=4.0 Hz), 4.27-4.15 (t, 2H, J=2.4 Hz), 3.42-3.32 (t, 2H, J=2.2 Hz), 1.92-1.77 (m, 4H), 1.59-1.44 (m, 2H), 1.43-1.32 (m, 2H).

Poly[(9,9-bis(2'-(2'-(2'-methoxyethoxy)ethoxy)ethyl)-2,7-fluorene)]-*block*-poly[9-(6-bromohexyl)-2,7-carbazole] $\mathbf{PF_{EO}}$-*b*-PCBr diblock polymer

9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-2,7-dibromo-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 A solution. 9-(6-bromohexyl)-2,7-dibromo-carbazole (0.97 g, 2.0 mmol) and THF (12 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 (0.4 mL, 1.2 mmol) was added to A solution and 0.8 mL 3 M magnesium bromide 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, and 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 dark green solid. According to the ^{1}H NMR, the final obtained precise ration between the two blocks polyfluorene and polycarbazole is 1:2. ^{1}H NMR (400 MHz, $CDCl_3$), (ppm): 7.94-7.13 (m, 18H), 4.29-4.20 (t, 4H, *J*=1.8 Hz), 3.75-3.42 (m, 16H), 3.34 (s, 6H), 3.24-3.15 (t, 4H, *J*=1.8 Hz), 2.82-2.71 (t, 4H, *J*=2.2 Hz), 2.38-2.27 (t, 4H, *J*=2.2 Hz), 1.92-1.83 (m, 8H), 1.66-1.49 (m, 8H). M_n(11 800), M_w (14 800) and M_w/M_n=1.25.

Synthesis of PF$_{EO}$-*b*-PCNBr diblock polymer

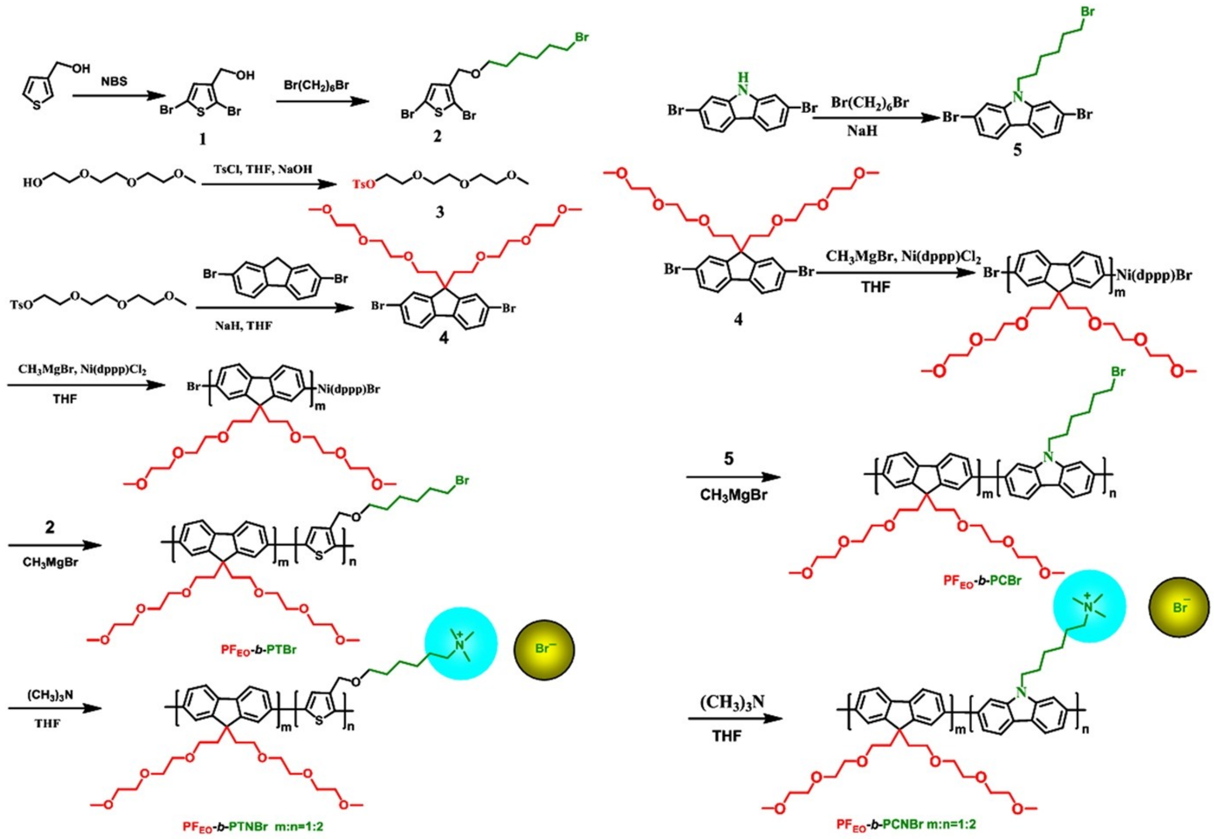
Under -78 °C, 100 mg PF$_{EO}$-b-PCBr was dissolved in 30 mL THF. An excess of trimethylamine (9.0 mL) in THF solution (ca. 13% in Tetrahydrofuran, ca. 2 mol/L) was added to the solution. The mixture was stirred for 5 days at room temperature. Once some precipitates were formed, and some methanol was added to dissolve them, and additional 2 mL of trimethylamine solution was added every day. The solution was evaporated and the residue was redissolved in methanol. The ionic polymer was precipitated from ether and a dark green powder resulted as a yield 90%. ^{1}H NMR (400 MHz, CD_3OD-d_4), (ppm): 7.86-7.08 (m, 18H), 4.29-4.20 (t, 4H, *J*=2.8 Hz), 3.65-3.37 (m, 16H), 3.36-3.08 (m,28H), 2.86-2.69 (t, 4H, *J*=2.8 Hz), 2.45-2.26(t, 4H, *J*=2.8 Hz), 1.92-1.83 (m, 8H), 1.66-1.53 (m, 8H). ^{13}C NMR (100 MHz, DMSO-d_6), (ppm): 153.02, 138.80, 138.62, 130.32, 126.14, 121.21, 121.10, 109.82, 99.21, 71.62, 70.41, 59.12, 58.52, 55.32, 29.41, 27.52,27.36,27.03, 26.82, 25.13.

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. The XPS of N 1s and O 1s in **figure 3** are deconvoluted according to the professional XPS-peak-differentation-imitating analysis software XPSPEAK41 with fixed full width at half maximum(FWHM). 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×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

$$-\mathrm{HOMO} = h\nu-(\mathrm{Ecutoff} - \mathrm{Eonset})$$

Where hν is the incident photon energy, hν= 21.22 eV. E_{cutoff} is defined as the high binding energy cutoff; E_{onset} is the HOMO energy onset, generally referred to as the low binding energy onset. TEM images were recorded using a JEOL-2100F transmission electron microscope and an internal charge-coupled device (CCD) camera. Current-voltage (*J*-V) characteristics were recorded using Keithley 2400 Source Meter in the dark under 100 mW/cm^2 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.



Scheme S1. Synthetic route to **PF$_{EO}$-*b*-PCNBr** and **PF$_{EO}$-*b*-PTNBr** diblock polymers.

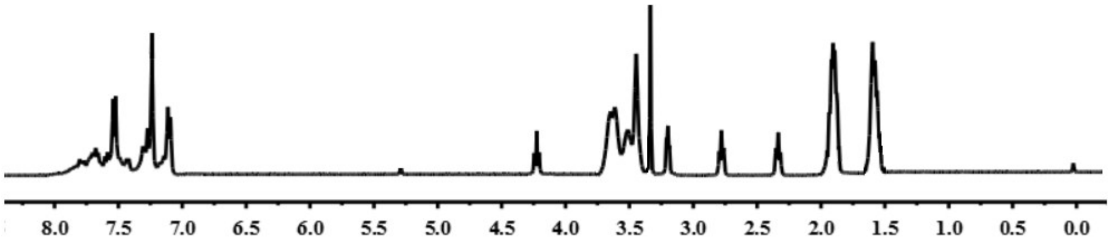


Figure S1. The ^{1}H NMR spectrum of the diblock polymer PF$_{EO}$-*b*-PCBr recorded in deuterated chloroform solution.

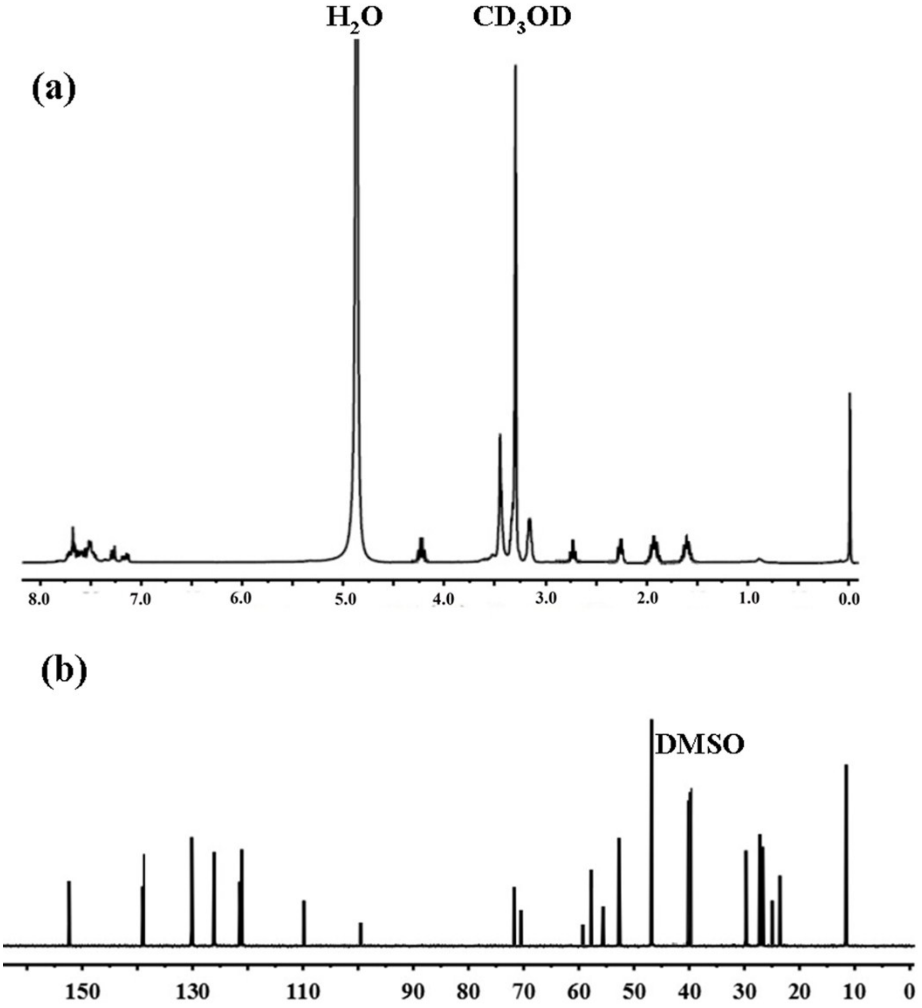


Figure S2. The ^{1}H NMR (a) spectrum of the diblock polymer **PF$_{EO}$-*b*-PCNBr** recorded in deuterated methanol solution and ^{13}C NMR (b) spectrum of the diblock polymer **PF$_{EO}$-*b*-PCNBr** recorded in deuterated DMSO solution.

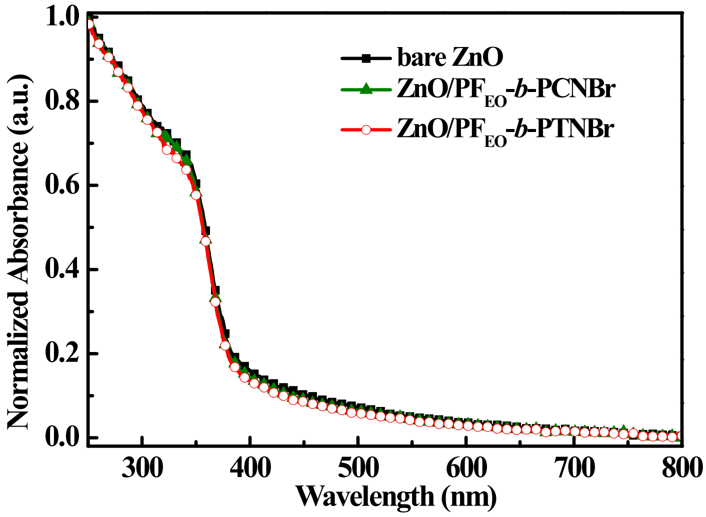


Figure S3. Normalized UV-vis absorption spectra of bare ZnO, ZnO/**PF$_{EO}$-*b*-PCNBr**, and ZnO/**PF$_{EO}$-*b*-PTNBr** ETLs.

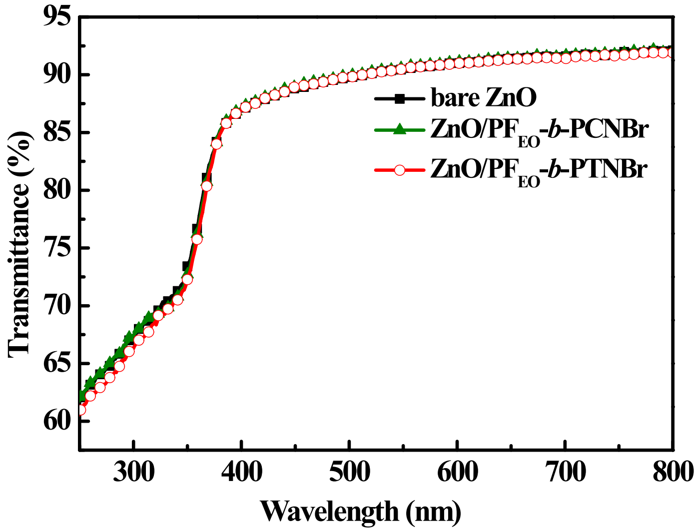


Figure S4. Optical transmittance spectra of the bare ZnO, ZnO/**PF$_{EO}$-*b*-PCNBr**, and ZnO/**PF$_{EO}$-*b*-PTNBr** ETLs.

Table S1. Energy Levels of the electron transport layers (ETLs).

ETLs	E_{cutoff} (eV)[a]	E_{oneset} (eV)[b]	HOMO (eV)[c]	LUMO (eV)[d]	E_g^{opt} (eV)
ZnO	14.46	1.07	-7.83	-4.55	3.28
ZnO/**PF$_{EO}$-*b*-PCNBr**	15.11	1.21	-7.32	-4.04	3.28
ZnO/**PF$_{EO}$-*b*-PTNBr**	15.18	1.05	-7.09	-3.81	3.28

[a] The high binding-energy cutoff. [b] The onset relative to the Fermi level (E_F) of Au (at 0 eV), where the E_F was determined from the Au substrate. [c] Calculated according to -HOMO = hν− (Ecutoff−Eoneset), where hν is the incident photon energy, hν = 21.22 eV. [d] Calculated from the HOMO level and optical band gap obtained from UV−vis absorption spectra.