Supplementary Information for

Conjugated Zwitterionic Polyelectrolytes-Based Interface Modification Materials for High Performance Polymer Optoelectronic Devices

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Experimental

Instruments and measurements. ^{1}H NMR spectra were recorded on a Bruker-300 operating at 300 MHz in deuterated solvents at 298 K. Chemical shifts were reported as δ values (ppm) with respect to an internal tetramethylsilane (TMS) standard. Number-average (M_n), weight-average molecular weights (M_w) and polydispersity index (PDI) of polymers were determined by gel permeation chromatography (GPC) using a series of mono-disperse polystyrene as standards in chloroform (with 0.25 v/v% triethylamine) on a Water system at room temperature. UV-vis absorption spectra were recorded on an HP 8453 spectrophotometer. Photoluminescent (PL) spectra were recorded on a Jobin Yvon Fluorolog-3 spectrophotometer. Cyclic voltammetry (CV) was performed on a CHI600A electrochemical workstation with a platinum working electrode and a Pt wire counter electrode at a scan rate of 50 mV s^{-1} against a Ag/Ag^{+} (0.1 M of $AgNO_3$ in acetonitrile) reference electrode with a argon-saturated anhydrous solution of 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile. The polymer films for electrochemical measurements were coated from the polymer dilute solution.

Materials. M1,[1] M2,[2] M3,[3] M4[4] and M5[5] were prepared according to the reported procedures. All starting chemicals, unless otherwise specified, were purchased from Alfa Aesar or Sigma-Aldrich and used as received. Solvents were purified by normal procedure before use. The other materials were common commercial level and used as received.

General procedure of copolymerization by Suzuki coupling. The equimolecular amount of diboronic ester monomer and dibromide monomer(s), and $Pd(PPh_3)_4$ (～1 mol%) were dissolved in a mixture of degassed toluene and degassed 20% aqueous tetraethylammonium hydroxide in a 25 mL two-necked round-bottomed flask under argon. The solution was flushed with argon for 15 min. The mixture was vigorously stirred at 90-95 °C under an argon atmosphere. After 24 hours, phenylboronic acid solution (0.5 equiv) was injected to the reaction and then 3 hours later, bromobenzene (0.5 mL) was added and the reaction was further refluxed for 3 hours to complete end-capping reaction. After cooling to room temperature, the mixture was poured into methanol. The precipitated crude material was collected by filtration through a funnel. After washing with acetone for 24 hour in a Soxhlet apparatus to remove oligomers and catalyst residues, the resulting polymer was dissolved in chloroform. The solution was filtered with a 0.45 μm PTFE filter, concentrated and precipitated from methanol to yield the neutral precursor polymer.

Poly[(9,9-bis(*N*,*N*-dimethylamino)-propyl)-2,7-fluorene)-*alt*-*N*-phenyl-4,4'-diphenylamine)] (PFN-TPA). Monomer M1 (0.5 mmol) and monomer M2 (0.5 mmol) were used in this copolymerization. Yield: 238 mg, 83%. ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm): 7.76-7.39 (d, J = 7.6 Hz, 2H, fluorene ring), 7.60-7.57 (d, J = 9.1 Hz, 8H, fluorene ring, triphenylamine ring), 7.34-7.32 (m, 2H, triphenylamine ring), 7.23 (m, 5H, triphenylamine ring), 7.10-7.08 (m, 2H, triphenylamine ring), 2.17-2.07 (br, 20H, $-CH_2N$, $-NCH_3$, H-alkyl), 0.93-0.85 (m, 4H, H-alkyl). GPC (chloroform, polystyrene standard): M_n = 5.3 kg mol^{-1}, PDI = 1.8.

Poly[(9,9-bis(*N*,*N*-dimethylamino)-propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN). Monomer M3 (1 mmol) and monomer M2 (1 mmol) were used in this copolymerization. Yield: 650 mg, 90%. ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm): 7.85-7.82 (m, 4H, fluorene ring), 7.71-7.65 (m, 8H, fluorene ring), 2.06 (br, 24H, $-CH_2N$, $-NCH_3$, H-alkyl), 1.14 (br, 24H, H-alkyl), 0.83-0.79 (m, 10H, H-alkyl). GPC (chloroform, polystyrene standard): M_n = 44.5 kg mol^{-1}, PDI = 2.3.

Poly[(9,9-bis(*N*,*N*-dimethylamino)-propyl)-2,7-fluorene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PFN-BT). Monomer M4 (0.50 mmol) and monomer M5 (0.50 mmol) were used in this copolymerization. Yield: 196 mg, 84%. ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm): 8.10-8.03 (m, 4H, benzothiadiazole ring, fluorene ring), 7.98-7.89 (m, 4H, fluorene ring), 2.20-2.06 (br, 20H, -CH_2N, -NCH_3, H-alkyl), 1.28-1.22 (m, 4H, H-alkyl). GPC (chloroform, polystyrene standard): M_n = 10.5 kg mol^{-1}, PDI = 2.5.

General procedure of quaternization. 1,4-Butane sultone (800 mg) was added to a solution of neutral precursor polymer (100 mg) in chloroform. The mixture was refluxed with stirring under an argon atmosphere. Once some precipitates appeared, some methanol was added to dissolve them. After 5 days, the solvent was removed under reduced pressure, and the crude product was dissolved in methanol. The solution was filtered with a 0.45μm PTFE filter, concentrated and precipitated from ethyl acetate, and dried in a vacuum oven to yield the target zwitterionic polymers.

Poly[(9,9-bis((*N*-(4-sulfonate-1-butyl)-*N*,*N*-dimethylammonium)-propyl)-2,7-fluorene)-*alt*-*N*-phenyl-4,4'-diphenylamine)] (PFNSO-TPA). The polymer was derived from PFN-TPA by the above-mentioned procedure. Yield: 105 mg, 71% ^{1}H NMR (CD_3OD, 300 MHz), δ (ppm): 7.80-7.65 (m, 6H), 7.45 (br, 6H), 7.31-7.09 (m, 7H), 3.10 (br, 4H, -$CH_2SO_3^-$), 2.89-2.81 (br, 12H, -NCH_3), 2.63-2.47 (m, 8H, -CH_2N), 1.87-1.81 (m, 4H, H-alkyl), 1.67-1.62 (m, 8H, H-alkyl), 0.87-0.84 (m, 4H, H-alkyl).

Poly[(9,9-bis((*N*-(4-sulfonate-1-butyl)-*N*,*N*-dimethylammonium)-propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFNSO). The polymer was derived from PFN by the above-mentioned procedure. Yield: 121 mg, 88%. ^{1}H NMR (CD_3OD, 300 MHz), δ (ppm): 8.02-7.84 (m, 12H, fluorine ring), 3.10 (br, 4H, -$CH_2SO_3^-$), 2.89-2.86 (m, 12H, -NCH_3), 2.69 (br, 8H, -CH_2N), 1.92-1.82 (m, 8H, H-alkyl), 1.76-1.67 (m, 8H, H-alkyl), 1.15 (m, 24H, H-alkyl), 0.93-0.85 (m, 10H, H-alkyl).

Poly[(9,9-bis((*N*-(4-sulfonate-1-butyl)-*N*,*N*-dimethylammonium)-propyl)-2,7-fluo

rene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PFNSO-BT). The polymer was derived from PFN-BT by the above-mentioned procedure. Yield: 115 mg, 73%. ^{1}H NMR (CD_3OD, 300 MHz), δ (ppm): 8.30-8.00 (br, 8H, benzothiadiazole ring, fluorine ring), 3.19 (br, 4H, $-CH_2SO_3^-$), 2.99-2.82 (m, 12H, $-NCH_3$), 2.76-2.73 (m, 8H, $-CH_2N$), 1.92-1.84 (m, 4H, H-alkyl), 1.69-1.64 (m, 8H, H-alkyl), 0.88-0.86 (m, 4H, H-alkyl).

Device fabrication and characterization. For the PSC devices, a thickness of 40 nm PEDOT:PSS (Baytron P4083, BayerAG) layer was spin-coated on a pre-cleaned ITO substrate and dried by baking at 200 °C for 10 min to remove residual water. Then, 90 nm PTB7/$PC_{61}BM$ (1/1.5, w/w) layer was spin-coated onto PEDOT:PSS from chlorobenzene solution. The WSCP layers were spin-coated onto active layer from methanol solution with the thickness of 5 nm. After dried in high vacuum for 2 h to absolutely remove methanol, a 80 nm thick aluminium was thermally deposited as cathode through a shadow mask (defined active area of 0.16 cm^2) in a chamber with a base pressure $<3\times10^{-4}$ Pa.

For the PLED devices, a thickness of 40 nm PEDOT:PSS (Baytron P4083, BayerAG) layer was spin-coated on a pre-cleaned ITO substrate and dried by baking at 200 °C for 10 min to remove residual water. Then, 90 nm EML (P-PPV or F8BT) was spin-casted onto PEDOT:PSS from *p*-xylene solution. The WSCPs were spin-coated on top of EML from methanol solutions as cathode interlayer with the thickness of 5 nm. After dried in high vacuum for 2 hours to absolutely remove methanol, a 80 nm thick aluminium was thermally deposited as cathode through a shadow mask (defined active area of 0.19 cm^2) in a chamber with a base pressure

$<3\times10^{-4}$ Pa.

The cathode thickness was monitored upon deposition by using a crystal thickness monitor (Sycon). Ellipsometer (Auto SE Spectroscopic Ellipsometer, HORIBA Jobin Yvon) was used to determine the thickness of the polymer films. Device fabrication was carried out in an N_2 atmosphere dry-box (Vacuum Atmosphere Co.). PCEs were measured under an AM1.5G solar simulator (Oriel model 91192). The power of the sun simulation was calibrated as a value of 100 mW cm^{-2} before the testing using a standard silicon solar cell. Electroluminescence (EL) spectra were recorded on an Instaspec 4 CCD spectrophotometer (Oriel Co.). J–V–L data was collected using a Keithley 236 source meter and a calibrated silicon photodiode in the N_2 atmosphere dry-box. After typical encapsulation of the devices with UV epoxy and cover glass, the devices were taken out from dry-box and the external EL quantum efficiencies (QE_{ext}) were obtained by measuring the total light output in all directions in an integrating sphere (IS-080, Labsphere). The theoretical J_{sc} were obtained by integrating the external quantum efficiency (EQE) curves.

The surface morphologies of the PTB7:$PC_{71}BM$ films upon the incorporation of WSCPs were tracked by atomic force microscopy (AFM) on a Digital Instrument DI Multimode Nanoscope IIIa under tapping mode. The films in AFM measurements were prepared identical to those in real PSC devices.

Carrier Mobility Measurement: Single carrier devices were fabricated to measure the hole and electron mobility using space charge limited current (SCLC) method. The structure of hole-only device is ITO/PEDOT:PSS/active layer/interlayer/MoO_3/Al while structure of electron-only device is ITO/Al/active layer/interlayer/Ca/Al. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the equation: $J = \frac{9}{8}\varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3}$, where J is the current density, μ is the zero-filed 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 layer, and V is the effective voltage. The effective voltage can be obtained by subtracting the build-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}), $V=V_{appl}-V_{bi}-V_s$. The charge mobility can be calculated from slope of the $J^{1/2}\sim V$ curves.

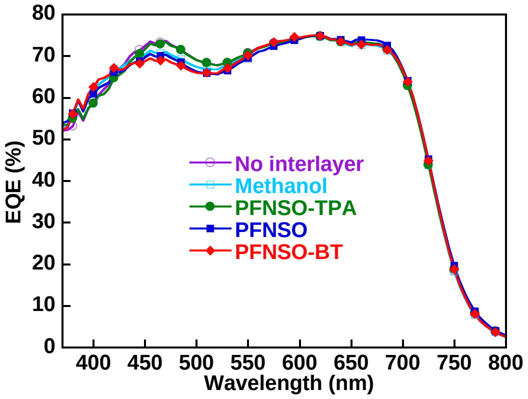

Figure S1. External quantum efficiency (EQE) spectra of the PSCs with different interlayer or without interlayer. (Device configuration ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/interlayer/Al).

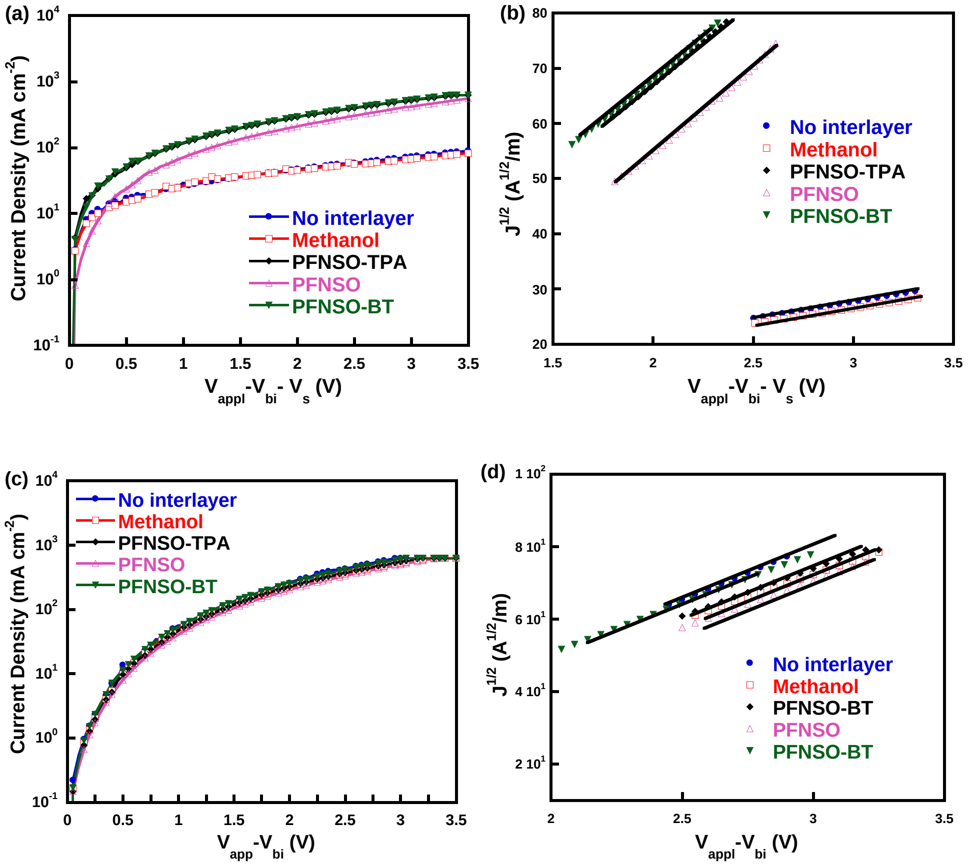

Figure S2. (a) *J-V* plots and (b) $J^{1/2}$-*V* of hole-only devices with the structures ITO/PEDOT:PSS/PTB7:PC$_{71}$BM/interlayer (100 nm)/MoO$_3$/Al; (c) *J-V* plots and (d) $J^{1/2}$-*V* of electron-only devices with the structures ITO/Al/ PTB7:PC$_{71}$BM/interlayer (100 nm)/Ca/Al. The solid lines represent the fitting curves.

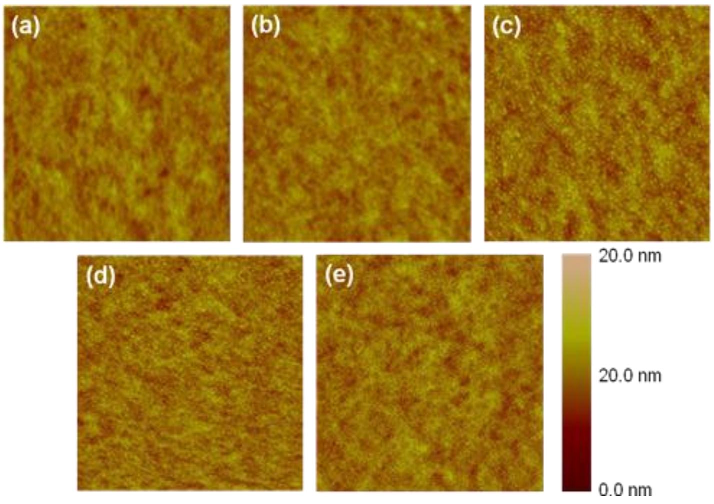

Figure S3. Surface topographic AFM images (size: 5 μm ×5 μm) of (a) the control PTB7:$PC_{71}BM$ layer, (b) the PTB7:$PC_{71}BM$ layer after rinsing with methanol, (c) after deposition of PFNSO-TPA on top of PTB7:$PC_{71}BM$ layer, (d) after deposition of PFNSO on top of PTB7:$PC_{71}BM$ layer, and (e) after the deposition of PFNSO-BT on top of PTB7:$PC_{71}BM$ layer.

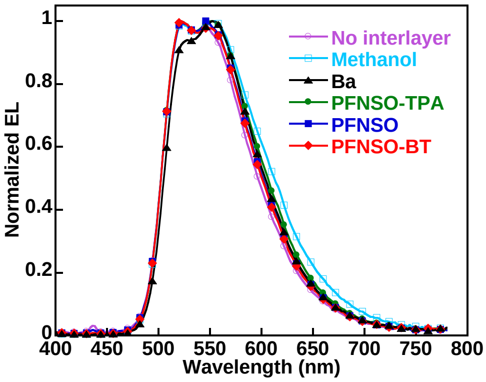

Figure S4. EL spectra of the PLEDs with and without cathode interlayer. (Device configuration: ITO/PEDOT:PSS/P-PPV/interlayer/Al).

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