Supporting information

Anionic Conjugated Polyelectrolyte-Wetting Property with the Emission Layer and Free Ion Migration When Serves as Cathode Interface Layer in Polymer Light Emitting Diodes (PLEDs)

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The Supporting information includes:

Experimental section

Device fabrication

Experimental

The synthetic routes toward the target polymers were outlined in **Scheme1**. The monomers 2,7-dibromo-9,9-bis(4'-sulfonatobutyl)fluorene disodium (3) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (4) were synthesized according to the literatures.[1-3]

Synthesis of 2,7-dibromo-9,9-bis(2-(2-ethoxyethoxy)ethyl) fluorene:

1-Bromo-2-(2-ethoxyethoxy)ethane (4.1 g, 21 mmol) was added to the mixture of 2,7-dibromofluorene (3.2 g, 10 mol), tetrabutyl ammonium bromide (TBAB) (0.30 g, 0.90 mmol), 40 ml of toluene and 20 ml aqueous NaOH (50%). After heated at 80 °C for 16 h, the reaction mixture was cooled to room temperature and the resulting solution was extracted with chloroform (3×50 ml). Then the combined organic fractions were washed with water, dilute hydrochloric acid, and brine. After dried over anhydrous magnesium sulfate, the crude product was purified by chromatography on silica gel with eluent (ethylacetate/hexane=2/7) to obtain a white solid product (4.2 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 2H), 7.45-7.51 (m, 4H), 3.39-3.44 (m, 4H), 3.31-3.34 (t, 4H), 3.18-3.20 (t, 4H), 2.77-2.81 (t, 4H), 2.32-2.36 (t, 4H) , 1.12-1.16 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.91, 138.45, 130.66, 126.73, 121.67, 121.19, 70.13, 69.65, 66.77, 66.62, 51.86, 39.47, 15.06. MS m/z (APCI) : 556.1 (M^+).

Synthesis of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(2-(2-ethoxy ethoxy)ethyl)fluorene:

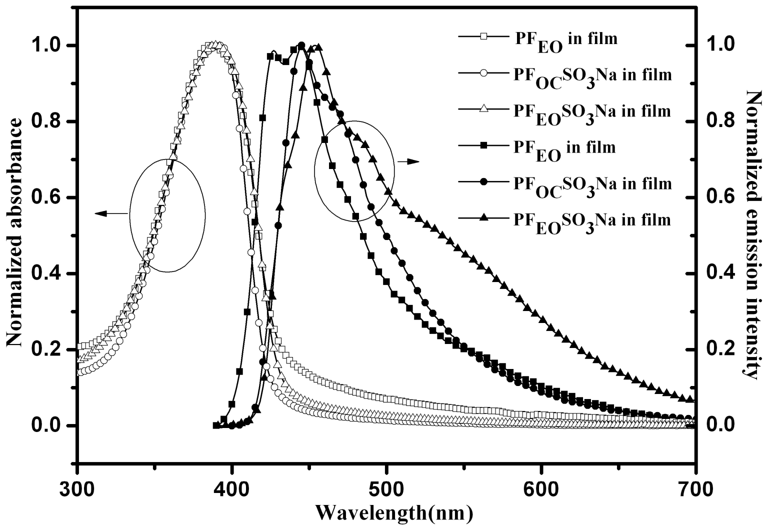
To a solution of 2,7-dibromo-9,9-bis(2-(2-ethoxyethoxy)ethyl)fluorene (1.1 g, 2.0 mmol) in anhydrous THF(30 mL), n-butyllithium (2 mL, 2.5M in hexane)was added in dropwise at -78 °C under N_2. Then the mixture was stirred at -78 °C for another 30 min, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.89 g, 4.8 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirred for another 24 h. After poured into water and extracted with chloroform, the combined organic layers were washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the crude produce was purified by chromatography with eluent (ethylacetate/hexane=1/2) to get final product as a white solid (0.52 g, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 2H), 7.67-7.82 (m, 4H), 3.38-4.34 (m, 4H), 3.32-3.34 (t, 4H), 3.15-3.18 (t, 4H), 2.66-2.77 (m, 4H), 2.39-2.48 (m, 4H), 1.39 (s, 24H), 1.11-1.35 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.52, 143.11, 134.02, 129.29, 119.53, 83.85, 70.03, 69.70, 66.91, 66.57, 50.98, 39.51, 24.96, 15.09. MS m/z (APCI) : 650.5 (M^+).

Synthesis of PF_{EO}*:*

2,7-Dibromo-9,9-bis(2-(2-ethoxyethoxy)ethyl)fluorene (1) (0.278 g, 0.50 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(2-(2-ethoxyethoxy)ethyl) fluorene (2) (0.325 g, 0.50 mmol), Na_2CO_3 (1.08 g, 10 mmol) and $Pd(OAC)_2$ (27.6 mg, 1mol%) were added into flask under nitrogen, then 5 ml of oxygen-free distilled water and 8 ml of oxygen-free THF were injected into the mixture. After vigorously stirred at 80 °C for 120 h, the solvent was removed and the crude product was extracted on Soxhlet apparatus with hexane, toluene and methanol. The methanol fraction was kept as the final product (96.8 mg, 45%) after remove the solvent under vacuum. GPC: Mn=5.4 kDa; Mw/Mn=1.7. ^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.12 (m, 2H), 7.97-7.99 (m, 2H), 7.87-7.89 (m, 2H), 3.31-3.32 (m,4H), 3.23-3.25 (m, 4H), 2.98-3.00 (m, 4H), 2.60 (m, 4H), 2.05-2.07 (m, 4H), 1.02-1.05 (m, 6H).

Synthesis of $PF_{OC}SO_3Na$ *and* $PF_{EO}SO_3Na$*:*

The synthesis process was similar to that of PF_{EO}. After stirring at 80°C for 120h, the mixture was dialyzed for one week in distilled water using a membrane to cut off the compounds with molecular weight less than 8,000. After the water was removed under vacuum, the crude product was extracted on Soxhlet apparatus with hexane, toluene and methanol. The solvent of methanol fraction was removed under reduced pressure to get the final product. For $PF_{OC}SO_3Na$, ^{1}H NMR (400 MHz, CD_3OD): δ 7.69-7.88 (m, 12H), 2.58-2.62 (m, 4H), 2.21 (m, 8H), 1.68 (m, 4 H), 1.13 (m, 20H), 0.79-0.81(m, 14H). For $PF_{EO}SO_3Na$, ^{1}H NMR (400 MHz, CD_3OD): δ 7.78-7.88 (m, 12H), 3.25-3.38 (m, 12H), 2.98 (m, 4H), 2.61 (m, 8H), 2.29 (m, 4H), 1.67 (m, 4H), 1.04-1.08 (m, 6H), 0.82 (m, 4H).



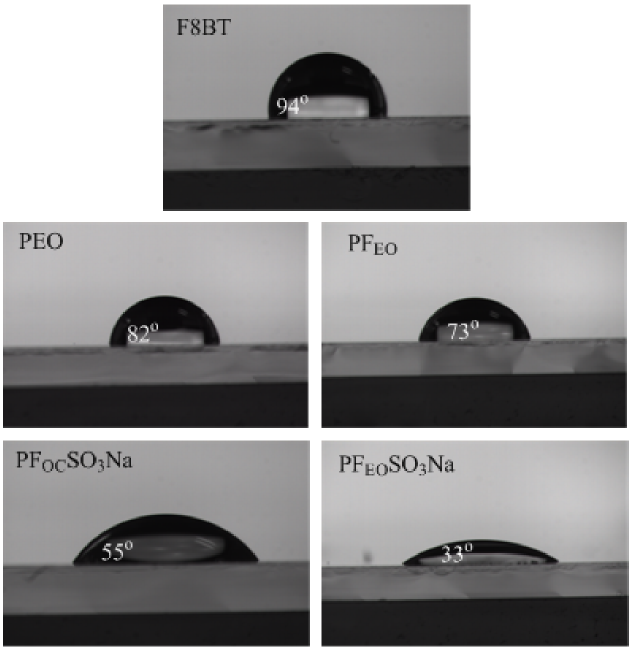
Fugure S1. Normalized UV-Vis aborption spectra and Photoluminescence spectra of those CPEs in solid film

Table S1. UV-Vis Absorption, Photoluminescence and Electrochemical properties of the polymers (in solid films).

polymers	λ_{absmax} (nm)	optical band gap[a] (eV)	E_{oxide} (V)	HOMO (eV)	LUMO [b] (eV)	λ_{PLmax} (nm)
PF_{EO}	386	2.86	0.85	5.51	2.65	427, 443
$PF_{OC}SO_3Na$	392	2.91	0.83	5.49	2.58	445, 466
$PF_{EO}SO_3Na$	389	2.86	0.95	5.61	2.75	454, 477

[a] Determined from absorption onset, [b] calculated from optical band gap.

The electrochemical measurements were performed in a solution of Bu_4NPF_6 (0.1 M) in acetonitrile at a scan rate of 25 mV/s under the protection of N_2. A glassy carbon electrode coated with a thin polymer film was used as the working electrode, a Pt wire was used as the counter electrode, an Ag/Ag^+ electrode was used as the reference electrode, ferrocene was used as an interior label compound to correct the reference electrode.

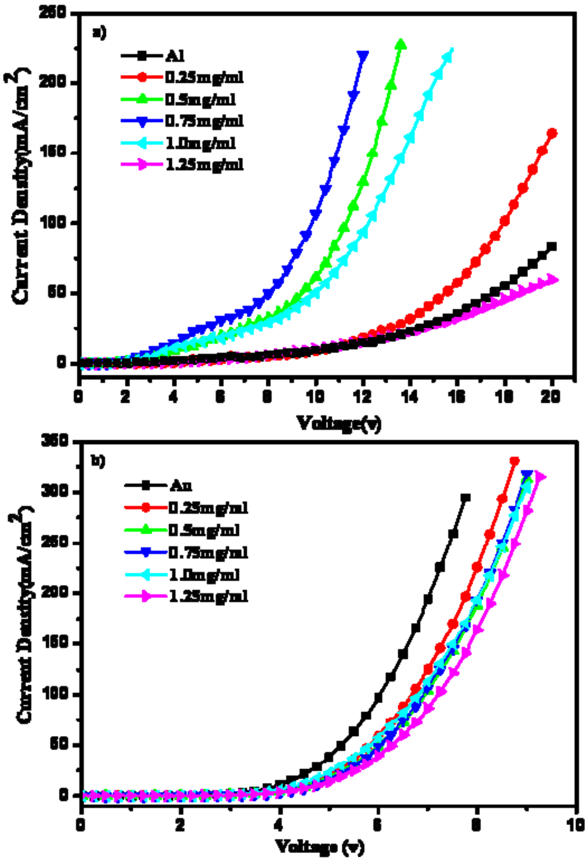


Fugure S2: Contact angle images of different CPEs on F8BT coated substrate

The above pictures show the contact angle images of the different CPEs coated F8BT on substrates. As shown in Fug.S2, the contact angle decreased from PEO to PFEOSO3Na, which means that the wetting property increased. Especially, when PFEOSO3Na was spin coated above F8BT, this thin film obviously changed the surface property from hydrophobicity to hydrophilcity.

Devide fabrication and characteristic: The fabrication process followed a standard procedure. PEDOT:PSS (Bayton P4083, Bayer AG) was spin-coated on a pre-cleaned ITO glass and dried in an oven at 120 °C for 30 min. Subsequently, about 100 nm F8BT emissive layer was spin-coated from 10 mg/mL toluene solution at 1500 rpm. The CPE layer was spin-coated from the methanol solution at 4000 rpm to give the interface layer. Then a 150 nm thick capping layer of Al was deposited through mask (defined active area of 0.09 cm^2) in a chamber at pressure of 4×10^{-4} Pa. For comparison, the devices without interfacial layers were also fabricated using the same procedures, which is identical to those for devices with interfacial layer. The thickness of Al was monitored upon deposition by using a crystal thickness monitor. And the thicknesses of the PEDOT:PSS and F8BT were estimated by Surface Profiler (Veeco dektak 150). For the thicknesses of CPEs and the surface morphologies were measured by the atomic force microscopy (Veeco dimension 3100) using tapping mode. J-V-L data were measured with a diode array rapid scan system using a PhotoResearch PR655 spectrophotometer and a computer-controlled, programmable, direct current (DC) source.

As shown in Fig.S3 (a), the electron-only device with Al only shows low current density even at high operation voltage. The reason is the existence of a big electron injection barrier between F8BT and Al interface. However, the electron-only devices with appropriate amount of $PF_{EO}SO_3Na$ as the cathode modification layer exhibit much higher current density, which means the $PF_{EO}SO_3Na$ layer can promote electron injection. For the hole-only devices, 10nm MoO_3 layer were used as a buffer layer between F8BT and Au cathode to block the electron injection for the CPEs could promote electron injection from high work function metal.[4, 5] The current densities of the hole-only device with different amount of $PF_{EO}SO_3Na$ are much lower than those of Au cathode only device at the same operation voltage, indicating that $PF_{EO}SO_3Na$ layer could also block holes, as shown in Fig.S3 (b).



Fugure S3. a) Current density (*J*) *versus* Voltage (*V*) characteristics of the electron-only devices about $PF_{EO}SO_3Na$ with different concentration.(Device configuration: ITO/Al/F8BT/$PF_{EO}SO_3Na$/Al); b) Current density (*J*) *versus* Voltage (*V*) characteristics of the hole-only devices about $PF_{EO}SO_3Na$ with different concentration.(Device configuration: ITO/PEDOT:PSS/F8BT/MoO_3/$PF_{EO}SO_3Na$/Au)

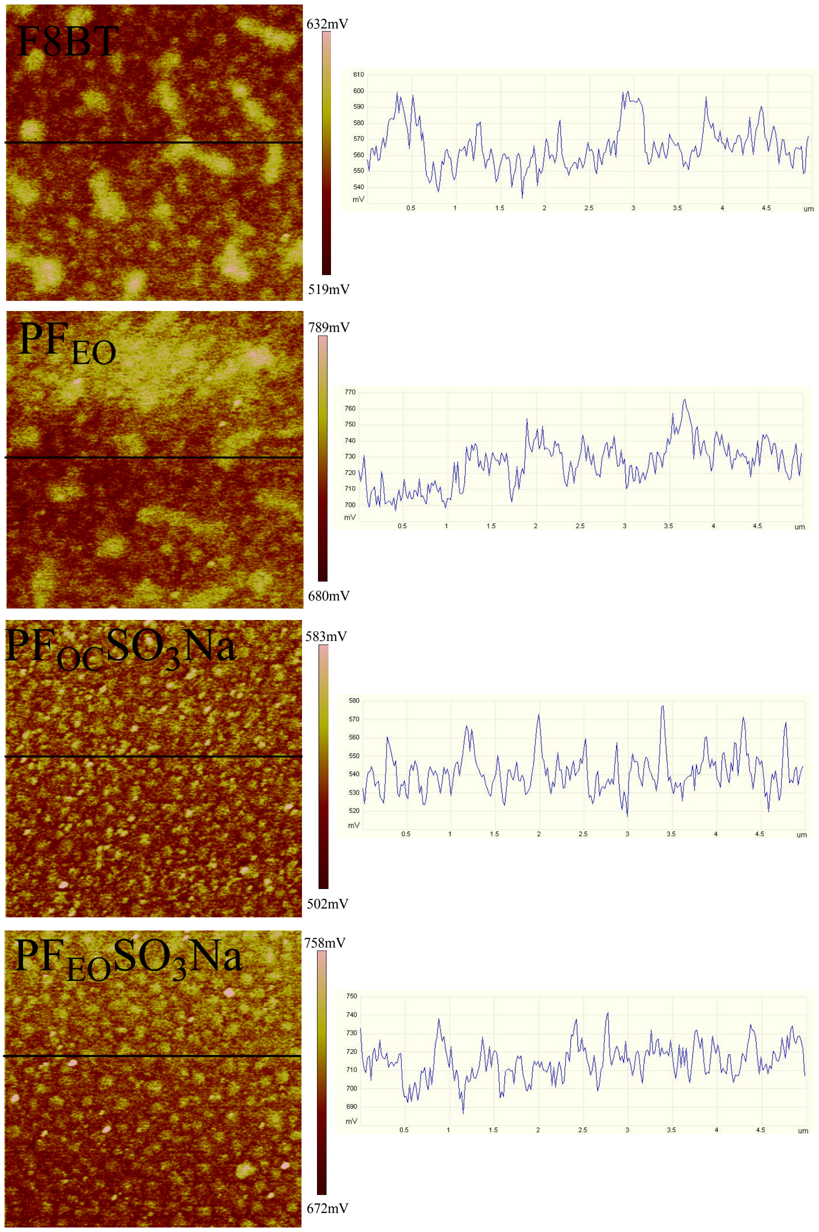


Figure S4: Surface potential images of different CPEs on F8BT coated substrate

Reference

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