

Quasi-three-dimensional self-doped conjugated polyelectrolytes based on a triphenylamine skeleton for non-fullerene organic solar cells

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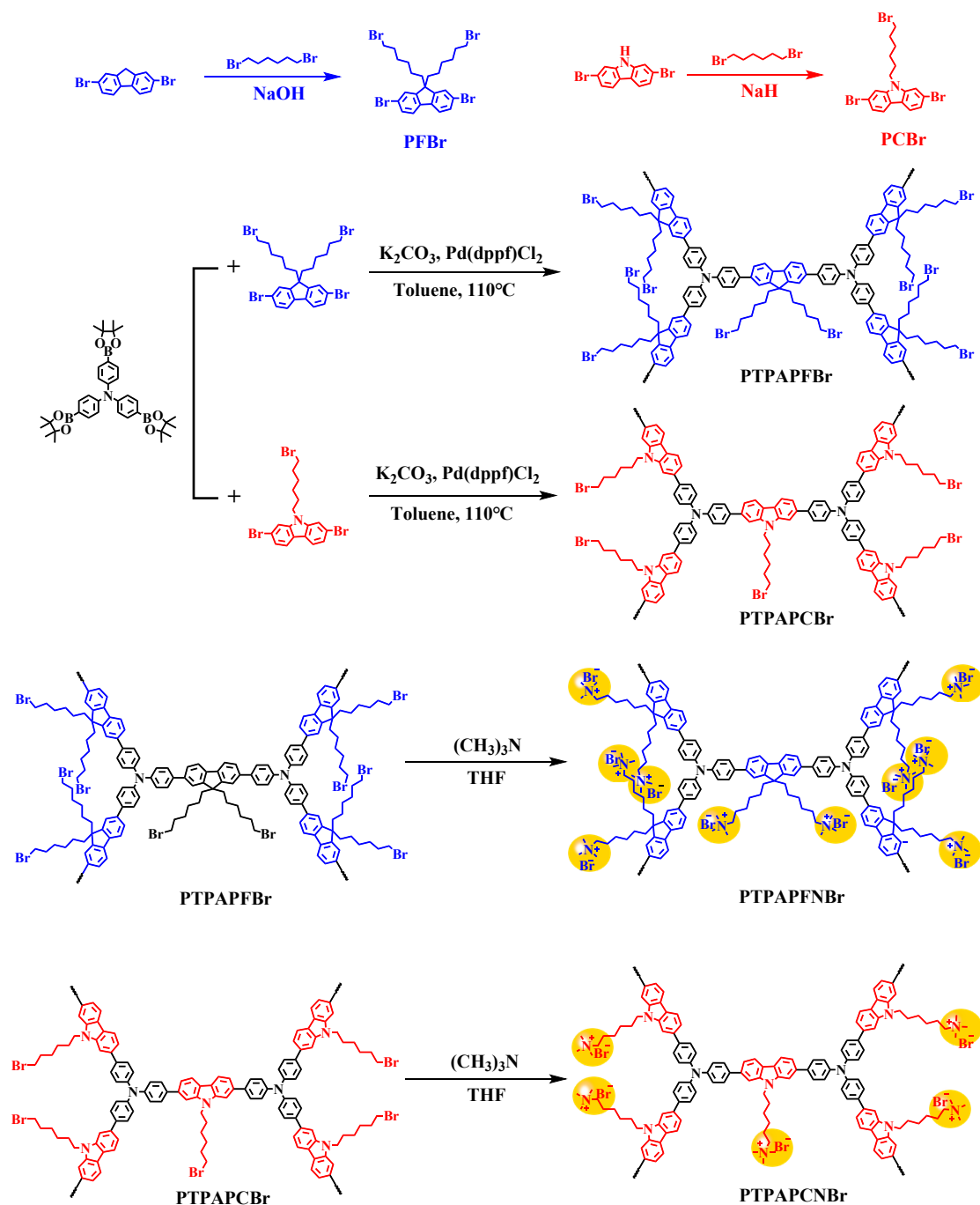
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1. Experimental Section

Materials:

2,7-Dibromofluorene, 2,7-Dibromocarbazole, Tetrabutylammonium bromide, 1,6-Dibromohexane, 4-(Tetramethyl-1,3,2-dioxaborolan-2-yl)-N, N-bis-[4-(tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl] were purchased from Macklin. Trimethylamine is purchased from TCI. Pd(dppf)Cl₂ and sodium hydride (NaH) were purchased from Sigma-Aldrich. NaOH and potassium carbonate (K₂CO₃) were purchased from Sinopharm chemical reagent co., Ltd. All these ingredients were used as received without any further purification. Tetrahydrofuran (THF), toluene and other chemicals were obtained from Shanghai Reagent Co., Ltd. and used as received. poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thiophen-2-yl)-benzo[1,2-b:4,5-b']dithiophene))-*alt*-(5,5-(1',3'-di-2-thienyl-5',7'-bis(2-ethylhexyl)benzo[1',2'-c:4',5'-c']dithiophene-4,8-dione))] (PBDB-T-2F) and 3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6,7-difluoro)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-

dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (IT-4F) were purchased from Solarmer Materials, Inc. Molybdenum oxide (MoO_3) were purchased from Rieke Metals, Inc. Indium-tin oxide (ITO) glass was obtained from Delta Technologies Limited. The synthetic routes toward the target hyperbranched CPEs are shown in Scheme S1.



Scheme S1. Synthetic routes for PTPAPFNBr and PTPAPCNBr.

1.1 Synthesis of PTPAPFNBBr

Synthesis of 2,7-dibromo-9,9-bis-(6-bromo-hexyl)-9H-fluorene (PFBr)

2,7-dibromo-9,9-bis-(6-bromo-hexyl)-9H-fluorene was synthesized according to method from the reported literature.^[1] Briefly, 2,7-dibromofluorene (2.00 g, 6.21 mmol) and a phase transfer catalyst tetrabutylammonium bromide (TBAB) (0.04 g) were added to a 100 mL flask. The flask was purged with nitrogen for approximately 10 min and 1,6-dibromohexane (12 mL, 1.584 g/mL) and NaOH (12 g, 50 wt%) were injected into the flask. Then, the solution was heated with stirring in an oil bath maintained at 85 °C for 6 hours. When the reaction is completed, the mixture was poured into water and extracted with chloroform, the solvent was removed under vacuum. The resulting solid was washed with salt water for several times and dried over magnesium sulfate (MgSO₄). Ultimately, the crude product was purified by column chromatography by using dichloromethane: petroleum ether = 1:2 (v/v) as eluent. The white solid was obtained with the yield of 68%. ¹H NMR (400 MHz, CDCl₃) δ(ppm): 7.54-7.52 (d, 2H), 7.48-7.45 (d, 2H), 7.44(s, 2H), 3.31-3.28 (t, 4H), 1.95-1.90 (t, 4H), 1.71-1.64 (t, 4H), 1.24-1.17(t, 4H), 1.12-1.05 (t, 4H), 0.63-0.55 (t, 4H).

Synthesis of PTPAPFNBBr

2,7-dibromo-9,9-bis-(6-bromo-hexyl)-9H-fluorene (0.487 g, 0.75 mmol), tris-[4-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-phenyl]-amine (0.31 g, 0.5 mmol) K₂CO₃ (138 mg), 27.3 mg Pd(dppf)Cl₂ and a few drops of TBAB were dissolved in 15 mL of deoxidized toluene: water (2:1), then the mixture was flushed with nitrogen for 10 minutes. After that, the reaction mixture was refluxed at 110 °C for 30 minutes. Subsequently, the solution was poured into 500 mL methanol under vigorous stirring. The precipitate was filtered off and purified by precipitation in methanol, followed by Soxhlet extraction using methanol, acetone, and chloroform.

Synthesis of PTPAPFNBBr

A condensed trimethylamine (3 mL) was added dropwise to a solution of 0.05 g PTPAPFNBBr in THF (10 mL) under -78 °C. The reacted mixture was allowed to warm to room temperature and stirred for 24 h. Then, an extra trimethylamine (2 mL) was

added after the mixture was cooled to below zero and the mixture was stirred for 24 h at room temperature and this process was repeated for three days. After the reaction was over, the solvents were evaporated under reduced pressure. The resulting polymer was dissolved in methanol and precipitated into diethyl ether. The precipitated polymer was filtered and purified by reprecipitation with methanol and diethyl ether several times. The final product was 0.020g (36%) by drying under vacuum. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 7.82-7.39 (m, 12H), 7.26 (d, 6H), 3.26 (s, 4H), 1.92 (m, 16H), 1.34-0.53 (m, 36H).

1.2 Synthesis of PTPAPCBr

Synthesis of 2,7-dibromo-9-(6-bromohexyl)-carbazole (PCBr)

2,7-Dibromo-9-(6-bromohexyl)-carbazole was synthesized according to literature procedure.^[2] 2,7-dibromocarbazole (1.32 g, 4.09 mmol) and NaH (0.20 g, 8.2 mmol) were dissolved in THF (20 mL) at a dry 100 mL flask and sealed under a nitrogen atmosphere. The reaction mixture was stirred at 60 °C for 1 h and then 1,6-dibromohexane (3.00 g, 12.3 mmol) in 50 mL anhydrous THF was added. The reaction mixture was refluxed for 18 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the oil phase was extracted with dichloromethane (100 mL), washed successively with water, and then dried over anhydrous MgSO_4 . The residue was purified by column chromatography with 1:5 (v/v) dichloromethane/petroleum ether as the eluent to give the title compound as a white solid (1.11 g, 56%). ^1H NMR (400 MHz, CDCl_3), δ (ppm): 7.90-7.88 (d, 2H), 7.52 (s, 2H), 7.35-7.33 (d, 2H), 4.23-4.19 (t, 2H), 3.39-3.36 (t, 2H), 1.86 (m, 4H), 1.52 (m, 2H), 1.38 (m, 2H).

Synthesis of PTPAPCBr

2,7-Dibromo-9,9-bis-(6-bromohexyl)-carbazole (0.487 g, 0.75 mmol), tris-[4-(4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan-2-yl)-phenyl]-amine (0.31 g, 0.5 mmol) potassium carbonate K_2CO_3 (138 mg), 27.3 mg $\text{Pd}(\text{dppf})\text{Cl}_2$ and a few drops of TBAB were dissolved in 15 mL of deoxidized toluene: water (2:1) at a dry 100 mL flask, then the mixture was flushed with nitrogen for 10 minutes. The reaction mixture was

refluxed at 100 °C for 30 minutes. Subsequently, the solution was poured into 500 mL methanol under vigorous stirring. The precipitate was filtered off and purified by precipitation in methanol followed by Soxhlet extraction using methanol, acetone, and chloroform.

Synthesis of PTPAPCNBr

A condensed trimethylamine (3 mL) was added slowly into a solution of 0.05 g PTPAPCNBr in THF (20 mL) under -78 °C. The react mixture was allowed to warm to the ambient temperature and stirred for 24 h. Then, an extra trimethylamine (2 mL) was added after the mixture was cooled to below zero and the mixture was stirred for 24 h at room temperature and repeat it for three days. After the reaction was over, the solvents were evaporated under reduced pressure. The resulting polymer was dissolved in methanol and precipitated into diethyl ether. The precipitated polymer was filtered and purified by reprecipitation with methanol and diethyl ether for several times. The final product was 0.014 g (27%) by drying under vacuum. ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.20-7.38 (m, 12H), 7.33-6.83 (m, 6H), 4.32 (d, 4H), 3.34 (s, 4H), 1.70 (m, 20H), 1.15-0.62 (m, 20H).

Figure S1. The ^1H NMR of the intermediate (a) PFBr, (b) PCBr, (c) PTPAPFNBr and (d) PTPAPCNBr.

2. Characterization

The nuclear magnetic resonance (NMR) spectra were collected on an Agilent Technologies 400 NMR spectrometer with deuterated dichloromethane, methanol as the solvent and with tetramethylsilane ($\delta=0$) as the internal standard. The ultraviolet-visible (UV-vis) spectra of samples were recorded on Hitachi UV-3010 spectrophotometer diffuse. The current density-voltage (J - V) characteristics were measured using Keithley 2400 Source Meter in the dark and under 100 mW cm^{-2} simulated AM 1.5 G irradiation (Abet Solar Simulator Sun 2000). EQE measurements were utilized by using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source. PL spectra were recorded on a FLS920 spectrofluorimeter (Edinburgh Instruments) by using a 150W, Ozone-free xenon arc lamp.

2.1 UPS/XPS measurement

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. XPS studies were performed on a Thermo-VG Scientific ESCALAB 250 photoelectron spectrometer using a monochromated AlK α (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. Solutions were dissolved at a concentration of 0.1% wt. in methanol for PTPAPFNBr/PTPAPCNBr. The solutions were spun cast on top of pre-cleaned ITO substrates with a thickness about 10 nm. Atomic force microscopic (AFM) images were measured on a nanoscope III A (Digital Instruments) scanning probe microscope using the tapping mode. The thicknesses of the films are measured on a profilometer (Bruker Countor GT K).

2.2 Cyclic voltammetry measurements

The cyclic voltammetry (CV) was performed on a CHI660C potentiostat equipped with electrochemical analysis system software and standard three-electrode configuration under an argon atmosphere at room time and a scan rate of 50 mV/s. Glassy carbon, platinum wire, and Ag/AgCl electrode were used as working electrode, counter electrode, and reference electrode in a 0.1 mol/L n-Bu $_4$ NPF $_6$ -acetonitrile solution, respectively.

2.3 Work function measurements

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 ($\Delta\Phi = e \times \text{VCPD}$), where e is the electron charge between the probe and the sample. The work functions values 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 100 points are measured over the scan area of 1.2 mm \times 1.2 mm for each sample.

Specifically, to measure the work function of Al and PTPAPFNBr/Al, Al layer was thermally deposited on the bare glass under the vacuum condition. Then, the PTPAPFNBr (1 mg/mL) layer was spin-coated on the Al layer with a rotate speed of

800 r/min. Subsequently, the work function of Al was measured with the glass deposited by Al, and the work function of PTPAPFNBr/Al was measured using the glass deposited with Al and PTPAPFNBr. The work function of PTPAPCNBr/Al was characterized under the similar condition with PTPAPFNBr/Al.

2.4 The Electron paramagnetic resonance (EPR) analysis.

Samples were prepared by drop casting solutions onto 2 cm by 2 cm quartz microscope cover slides. The samples were cleaved into approximately 3 mm-wide pieces; the most uniform and rectangular pieces were saved as the final samples. Samples were then transferred into a dry glovebox with a nitrogen atmosphere. All samples were then inserted into 4 mm-diameter quartz EPR tubes. These tubes were sealed with plastic caps and Teflon tape inside the glovebox. They were then transferred outside of the glovebox and their EPR spectra were measured within two hours.

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

To characterize the carrier mobility of modified device, electron-only devices were fabricated. The electron-only devices used a diode configuration of glass /ITO/ZnO/PBDB-T-2F:IT-4F/PTPAPFNBr/Al, the carrier mobility was measured using the SCLC model at low voltage which is described by MOTT-Gurney equation (S1):

$$J=9\varepsilon_0\varepsilon_r\mu V^2/8L^3 \quad (S1)$$

Where ε_0 is the permittivity of free space ($8.85 \times 10^{-12} \text{ F}\cdot\text{m}^{-1}$), ε_r is the dielectric constant of PBDB-T-2F or IT-4F, μ is the mobility of an electron, V is the applied voltage, and L is the film thickness. The thickness of the BHJ blend for SCLC measurement was about 100 nm.

2.6 The electrical conductivity measurement

The electrical conductivity was tested by space charge limited current method using an ITO/interface layer (17 nm) /Ag (100 nm) structure.

According to the following formula, we calculate the electrical conductivity:

$$R = \frac{1}{G} \quad (S2)$$

$$\rho = \frac{RS}{L} \quad (\text{S3})$$

$$\kappa = \frac{1}{\rho} \quad (\text{S4})$$

Here, R is resistance, G is slope of the I - V curve, ρ is the resistivity and κ is the electrical conductivity. Obviously, a higher slope results in a larger electrical conductivity.

2.7 Electrochemical impedance spectroscopy (EIS) measurement

The EIS spectra were measured with a frequency range of 20 Hz to 1 MHz under dark conditions at the illumination of AM 1.5G, 100 mW cm⁻². A bias voltage equal to V_{oc} was applied to vanish the total current.

3. Fabrication of NOSCs

The conventional NOSCs were manufactured with the structure of glass/ITO/PEDOT: PSS/PBDB-T-2F:IT-4F/PTPAPFNBr/Al. Solution of PEDOT: PSS spined on beforehand cleaned ITO electrodes at a speed of 4000 r/min for 1 minute. Then, baking PEDOT: PSS films at 150 °C for 20 min. To prepare PBDB-T-2F:IT-4F chlorobenzene mixture (1:1 wt/wt), the total concentration of that was 20 mg/mL, the solution was stirred for a few hours to make it completely dissolved. The mixed solution was spun coating on the PEDOT: PSS layer, the thickness of the active layer was about 100 nm. The PTPAPFNBr (1 mg/mL) was spin-coated on the active layer at a speed of 4000 r/min (this method corresponding to a thickness of 11 nm of PTPAPFNBr). The PTPAPFNBr films with different thicknesses were spin-coated with a series of speed gradients. The thicknesses were measured using a Dektak 6 M surface profilometer. Finally, under the condition of vacuum, the Al layer was thermally deposited on the surface of PTPAPFNBr layer. The device of glass/ITO/PEDOT: PSS/PBDB-T-2F:IT-4F/PTPAPCNBr/Al structure was prepared under the similar condition of glass/ITO/PEDOT: PSS/PBDB-T-2F:IT-4F/PTPAPFNBr/Al.

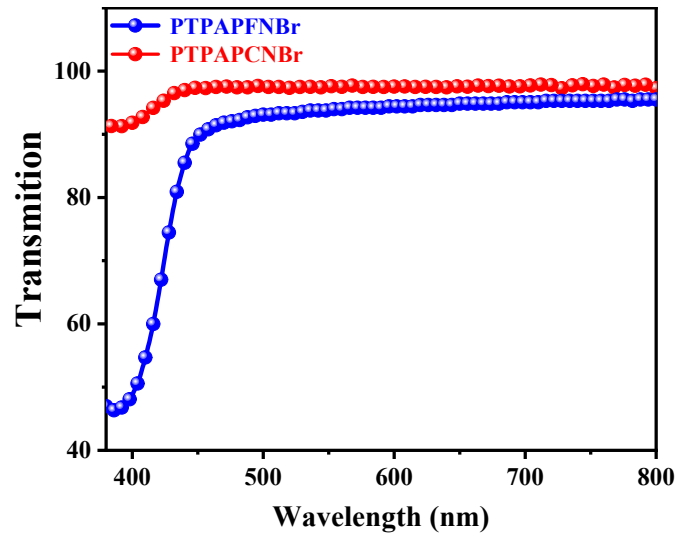


Figure S2. Transmission spectra of PTPAPFNBr and PTPAPCNBr.

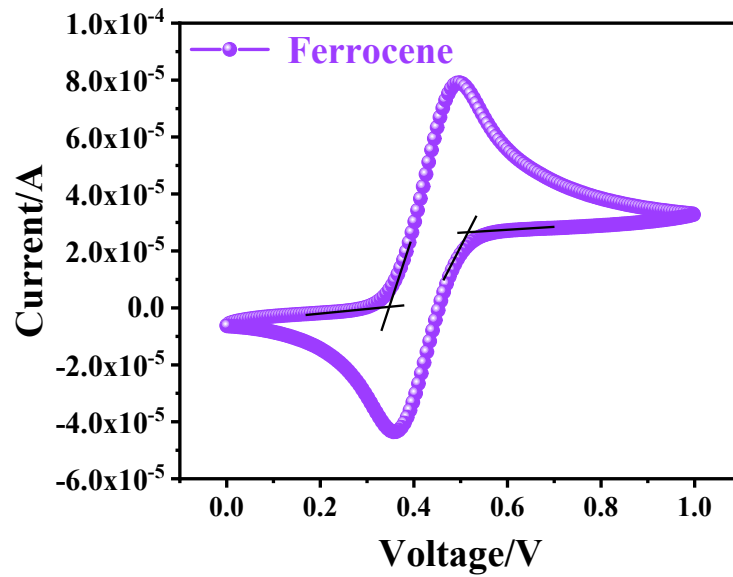


Figure S3. Cyclic voltammogram of Ferrocene versus Ag/Ag⁺.

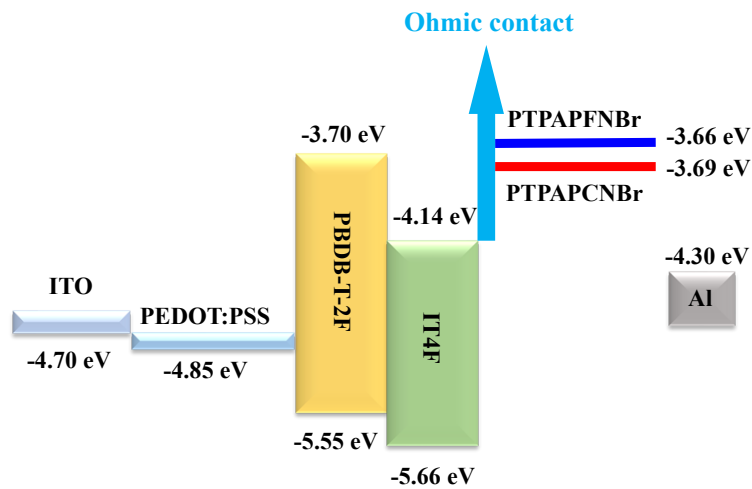


Figure S4. Schematic energy-level diagram of the device.

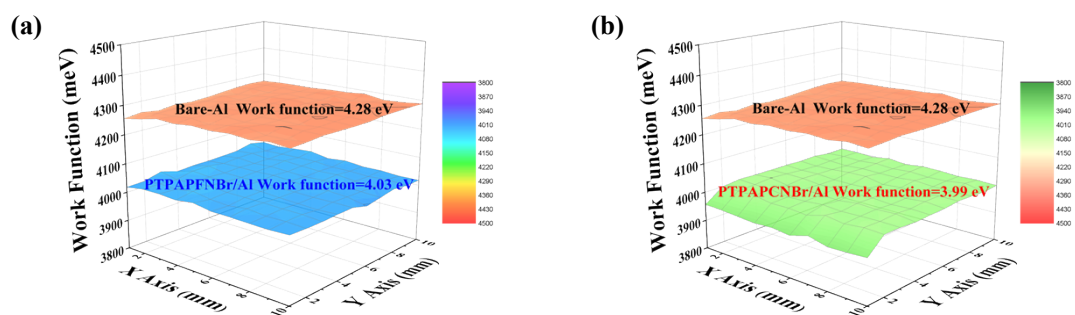


Figure S5. WF images from matrix of (a) the Al and PTPAPFNBr/Al, and (b) Al and PTPAPCNBr/Al.

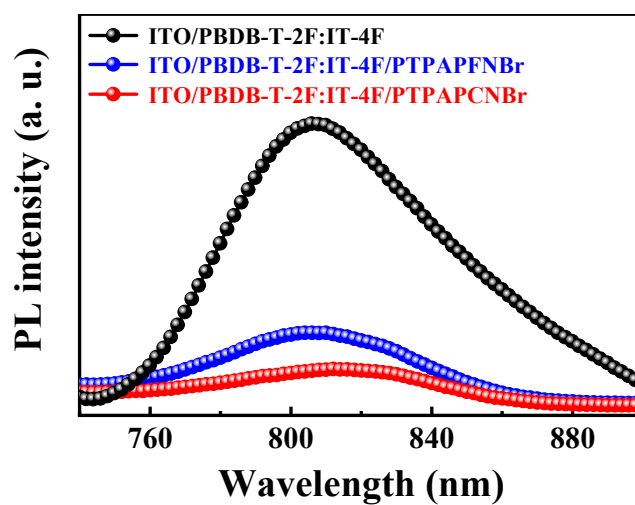


Figure S6. Photoluminescence spectra of the active layer based on different ETLs.

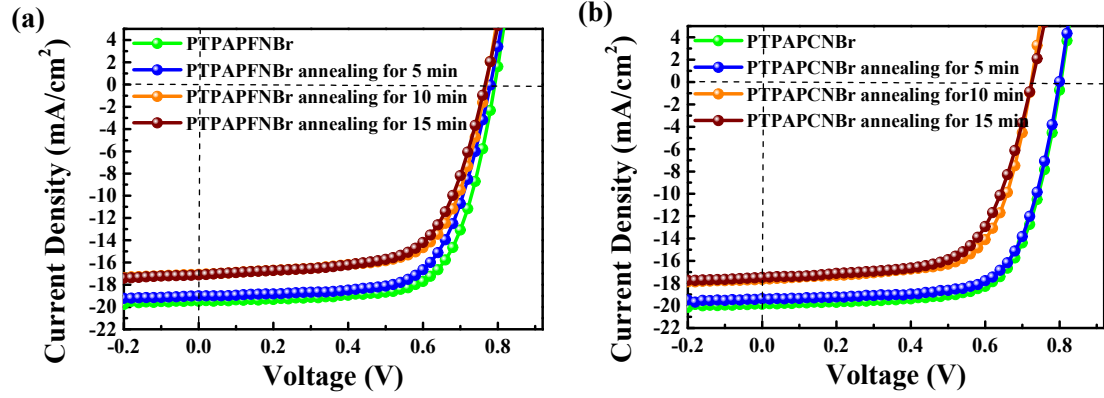
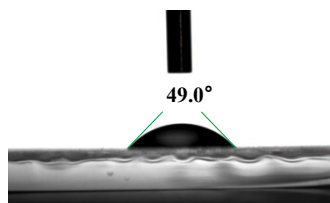


Figure S7. J - V measurement OSCs based on PBDB-T-2F:IT-4F with (a) PTPAPFNBr and (b) PTPAPCNBr as ETLs under different annealing times.

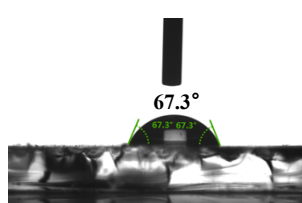
Table S1. Photovoltaic data of traditional devices with PTPAPFNBr and PTPAPCNBr as ETL under different annealing time.

Annealing time	ETL	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
0	PTPAPFNBr	0.79	19.48	69.25	10.68
	PTPAPCNBr	0.80	19.88	69.77	11.14
5 min	PTPAPFNBr	0.78	19.00	67.39	9.99
	PTPAPCNBr	0.80	19.38	69.75	10.81
10 min	PTPAPFNBr	0.77	17.15	68.09	8.99
	PTPAPCNBr	0.72	17.64	67.36	8.61
15 min	PTPAPFNBr	0.77	17.11	65.10	8.53
	PTPAPCNBr	0.73	17.47	64.62	8.20

(a) Bare ITO



(b) ITO/PTPAPFNBr



(c) ITO/PTPAPCNBr

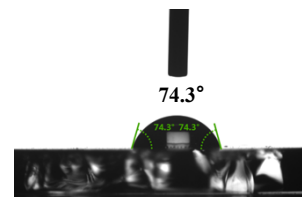


Figure S8. The contact angles of (a) ITO, (b) ITO/PTPAPFNBr, and (c) ITO/PTPAPCNBr.

Reference

- [1] Liu H, Hu L, Wu F, et al. Polyfluorene electrolytes interfacial layer for efficient polymer solar cells: controllably interfacial dipoles by regulation of polar groups[J]. ACS applied materials & interfaces, 2016, 8(15): 9821-9828.
- [2] Xu X, Cai W, Chen J, et al. Conjugated polyelectrolytes and neutral polymers with poly (2, 7-carbazole) backbone: Synthesis, characterization, and photovoltaic application[J]. Journal of Polymer Science Part A: Polymer Chemistry, 2011, 49(5): 1263-1272.