

Supporting information

N-type Conjugated Electrolytes Cathode Interlayer with Thickness-insensitivity for Highly Efficient Organic Solar Cells

Guodong Xu^{a,b}, Liang Gao^{c,d}, Haitao Xu^b, Liqiang Huang^a, Yuanpeng Xie^a, Xiaofang Cheng^a, Yongfang Li^{c,d}, Lie Chen^{*a,b} and Yiwang Chen^{*a,b}

^aCollege of Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

^bJiangxi Provincial Key Laboratory of New Energy Chemistry/Institute of Polymers, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

^cCAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

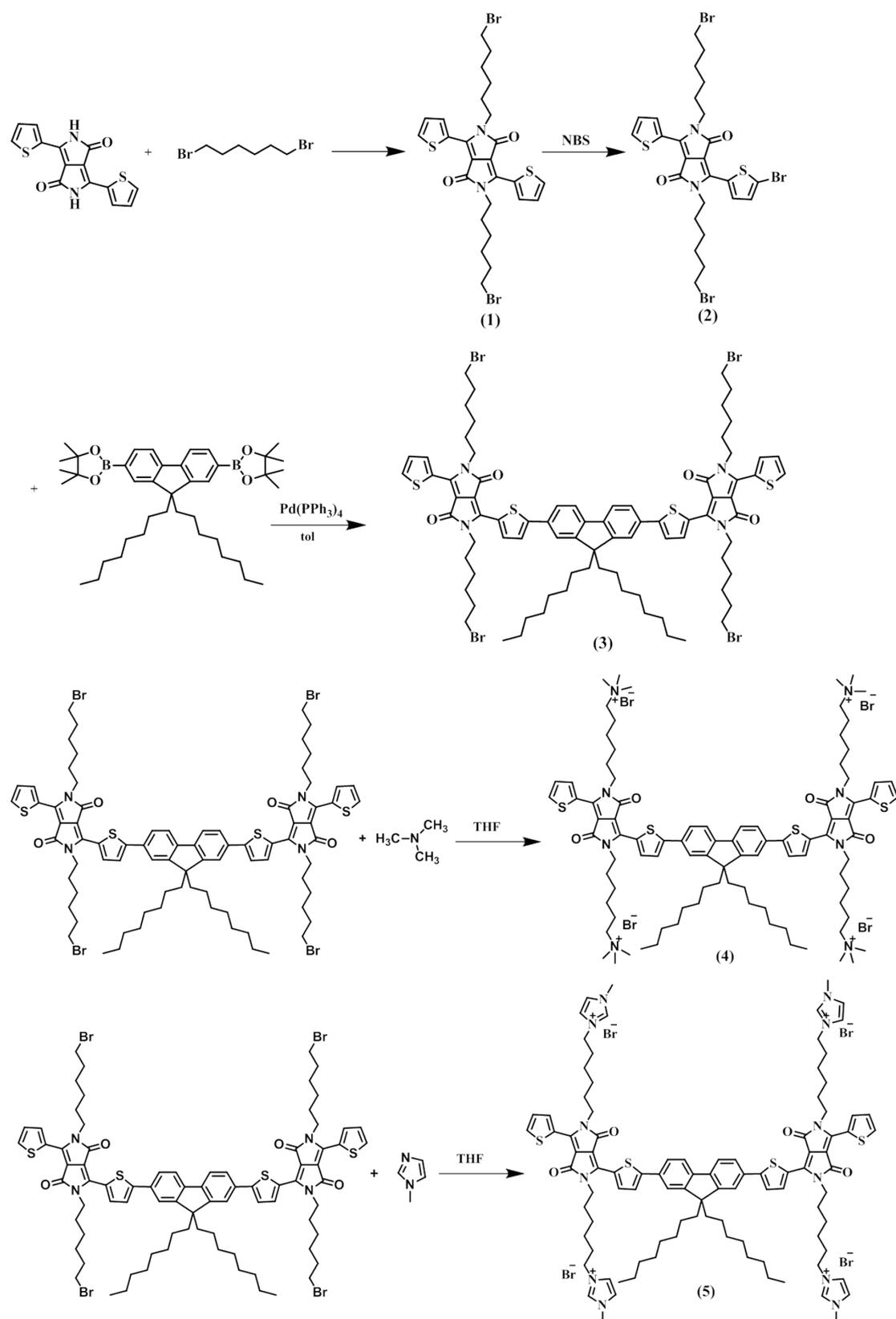
^dUniversity of Chinese Academy of Sciences, Beijing 100049, China

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

Author contributions. G. Xu and L. Gao contributed equally to this work.

Experimental Part

Materials: 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione(DPP), 1,6-dibromohexane,2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane);N-bromosuccinimide(NBS),tetrakis(triphenylphosphine)palladium(0)(Pd(PPh₃)₄),and other materials were purchase from Alfa or Aldrich, Some solvents were distilled before use (tetrahydrofuran (THF) from sodium), PTB7 (M_w=147000 PS standard, PDI=1.6) ,PTB7-Th (M_w=152000 PS standard, PDI=1.7) p-DTS-(FBTTH₂)₂,PC₇₁BM, molybdenum oxide (MoO₃) and Al (99.998%) were purchased from Nano-C and Rieke Metals, Inc. Indium tin oxide (ITO) was purchased from Delta Technologies Limited.



Scheme S1. Synthetic routes for FDPP₂-N and FDPP₂-M.

Synthesis of the SMEs

The synthesis of 2,5-bis(6-bromohexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-

c]pyrrole-1,4(2H,5H)-dione(1). At 250mL flask, solution of 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (1.0g, 3.3mmol, 1equiv) in acetonitrile (CH₃CN) (40mL). Then, the hexamethylenedibromide (13g, 52.8mmol, 16 equiv) and cesium carbonate (6.5g, 19.8mmol, 6equiv) were added. After reacted at 90°C for 12h under nitrogen atmosphere, the solution cooled to room temperature. The solution was poured into brine and extracted twice with dichloromethane, which was combined and dried over sodium sulfate. The solvent was removed by vacuum evaporation. And the crude product was further purified by column chromatography on silica with dichloromethane as eluent, yielding compound (1) (0.8g, Yield, 65%). ¹H-NMR (CDCl₃, 400MHz): d (ppm) 8.89 (d, 2H), 7.70 (d, 2H), 7.30 (t, 2H), 4.08 (t, 4H), 3.42 (t, 4H), 1.92-0.8 (m, 16H).

The synthesis of 2,5-bis(6-bromohexyl)-3-(5-bromothiophen-2-yl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (2). Compound (1) (0.468g, 0.6mmol) were solution into dichloromethane (15mL) in a dry 100mL flask. Then, N-bromosuccinimide (NBS, 0.6mmol) (0.230g) was added stirred in room temperature under nitrogen protection with avoid light processing, which reacted about 8 h. Subsequently, the solution was added into brine and extracted three times with chloroform. The organic phase dried over sodium sulfate and removed the solvent by vacuum evaporation. The further purification was accomplished by column chromatography on silica with dichloromethane: petroleum ether = 2:1 (v:v) to afford with dark red solid (0.29g, 52%). ¹H-NMR (CDCl₃, 400 MHz): d (ppm) 8.91 (d, 1H), 8.65 (d, 1H), 7.71 (t, 1H), 7.31 (d, 1H), 7.28 (d, 1H), 1.92-0.8 (m, 16H).

The synthesis of 6,6'-(5,5'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(thiophene-5,2-diyl))bis(2,5-bis(6-bromohexyl)-3-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione(3). Compound (2) and 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.06g, 0.1mmol), Pd(PPh₃)₄ (10mg,) were added into 100mL Schlenk flask and degassed for 30 min with nitrogen. Then, anhydrous

toluene(10mL) and K_2CO_3 (2M, 3mL) were added, which stirred at 110°C for 36 h. The mixture was then cooled to room temperature. Chloroform was added into the solution for extraction. The combined organic layer was washed with brine and water in three times. Then, it dried over anhydrous $MgSO_4$. The solvent was removed and crude product was purified using chromatography on silica gel with dichloromethane: hexanes = 2:1(v:v), to give the desired product compound(3)(0.1g, Yield, 60%). 1H -

NMR($CDCl_3$, 400MHz):d(ppm)8.94(d,2H), 7.71(d,2H), 7.68(d,4H), 7.63(t,2H), 7.55(d,2H), 7.28(t,2H), 7.23(d,2H), 7.33-7.17(m,4H), 2.16-0.7(m,56H), 0.64(d,6H).

The synthesis of 6,6'-(5,5'-(9,9-dioctyl-9H-fluorene-2,7diyl)bis(thiophene-5,2-diyl))-bis[(6-(N,N,N-trimethyl-ammonium)hexyl]-3-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione) (4). Compound (3) (0.1g) was dissolved into THF(10mL) in a 50 mL flask. Then, the condensed trimethylamine (5.0 mL) was added slowly at 0 °C. Subsequently, the mixture was allowed to warm up to room temperature gradually. The precipitate was dissolved the amount of methanol. And then, an extra 5 mL of trimethylamine was added slowly at 0 °C. The resulting mixture was stirred for 24 h at room temperature. The black purple precipitate was collected by filtration and the precipitate was washed with diethyl ether several times. The desired product was dried in vacuum oven to give a black purple solid(0.09g, Yield, 87%). 1H -NMR(CD_3OD , 400MHz):d(ppm)8.94(d,2H), 7.71(d,2H), 7.68(d,4H), 7.63(t,2H), 7.55(d,2H), 7.28(t,2H), 7.23(d,2H), 7.33-7.17(m,4H), 3.10(s,36H), 2.16-0.7(m,56H), 0.64(d,6H). ^{13}C -NMR(DMSO, 400MHz) 165.13, 142.63, 141.06, 136.61, 128.92, 127.12, 113.61, 54.8, 45.42, 43.91, 36.82, 31.11, 30.10, 29.66, 27.31, 26.81, 24.43, 19.22, 14.11.

The synthesis of 6,6'-(5,5'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(thiophene-5,2-diyl))-bis[(2,5-bis(6-Methylimidazole)hexyl]-3-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione(5). Compound(3)(0.1g) was dissolved into THF(10mL) in a 50 mL flask. Then, N-methylimidazole (0.5mL) was slowly added stirred at 55°C for 8h, and the black purple precipitate was collected by filtration. The precipitate was washed with diethyl ether several times, then the desired product was dried in vacuum oven to give a black purple solid(0.092g, Yield, 89%). ¹H-NMR(CD₃OD, 400MHz): d(ppm) 8.94(d, 2H), 8.82(s, 4H), 7.88(d, 4H), 7.81(d, 4H), 7.71(d, 2H), 7.68(d, 4H), 7.63(t, 2H), 7.55(d, 2H), 7.28(t, 2H), 7.23(d, 2H), 7.33-7.17(m, 4H), 3.9(s, 12H), 2.16-0.7(m, 56H), 0.64(d, 6H). ¹³C-NMR (DMSO, 400 MHz) 165.13, 142.63, 141.06, 136.61, 137.03, 128.92, 127.12, 123.00, 122.83, 113.61, 45.42, 43.91, 37.11, 36.82, 31.11, 30.10, 29.66, 27.31, 26.81, 24.43, 19.22, 14.11.

Device Fabrication

(1) The device structure was ITO/PEDOT:PSS/PTB7-Th:PC₇₁BM/with ETL/Al. A glass substrate with a pre-patterned ITO (sheet resistance = 15 Ω sq⁻¹) was first ultrasonicated in acetone, detergent, deionized water and isopropanol in turn, and then modified by air plasma treatment for 3 min. After filtration through a 0.45 μm filter, PEDOT:PSS (Bay PVP AI4083, Bayer AG) was spin-coated at 5000 rpm for 60 s to form a thickness of 30 nm thin layer on the cleaned ITO substrate, and baked on a hot plate at 140 °C for about 20 min. The PTB7-Th:PC₇₁BM (1:1.5 w/w) was dissolved in chlorobenzene with 3% (vol %) 1,8-diodooctane (DIO), mixed in solution with total concentration of 25 mg mL⁻¹, spin-coated onto the interfacial layer at 1000 rpm for 2 min. The PFN solution (0.2 mg/mL) was spin-coated on the active layer at 5000 rpm for 60 s, the FDPP₂-M and FDPP₂-N dissolved in Methanol (1 mg/mL) was directly spin-coating on the active layer at 3000 to 5000 rpm for 60s, then the aluminium cathode was thermal evaporation over interface layer under a high vacuum chamber (7 × 10⁻⁴ Pa) to accomplish the device fabrication.

(2) The device structure was ITO/ZnO/ETL/PTB7-Th:p-DTS-(FBTTH₂)₂:PC₇₁BM

/MoO₃/Ag. A glass substrate with a pre-patterned ITO (sheet resistance =15 Ω sq⁻¹) was ultrasonicated in acetone, detergent, deionized water and isopropanol in turn, and then modified by air plasma treatment for 3 min. After spin-coating ZnO with 4000rpm, 1min. and baked on a hot plate at 205 °C for about 60 min. and the two SMEs (0.5 mg/mL in methyl alcohol) spin-coating with 3000 rpm 1 min, and baked on a hot plate at 140 °C for about 10 min, and the ternary blend system (PTB7-Th(85):p-DTS-(FBTTH₂)₂(15):PC₇₁BM(110)) was dissolved in chlorobenzene with 3% (vol %)1,8-diiodooctane(DIO),(total concentration is 27 mg/mL) with 800 rpm for 1 min for active materials. Then the molybdenum trioxide (7 nm) and argentum cathode (90 nm) was successively thermal evaporation over interface layer under a high vacuum chamber (7×10⁻⁴ Pa) to accomplish the device fabrication. and p-DTS-(FBTTH₂)₂:PC₇₁BM : The active layers were spun at 1750 rpm from a Solution of p-DTS(FBTTh₂)₂ :PC₇₁BM at a weight ratio of 3:2 and an overall concentration of 35 mg mL⁻¹. The solution was heated for 15 min at 90 °C prior to casting. The obtained films were allowed to dry for 30 min and were then heated to 70 °C for 10 min under an inert atmosphere to drive off residual solvent. Then, a specific binary solvent containing mostly MeOH with a trace of CN was dropped onto the active layer surface for a 15 second wetting treatment and spinning at 3600 rpm. 7 nm of MoO₃ was deposited using sequential thermal evaporation, followed by 90 nm of Ag.

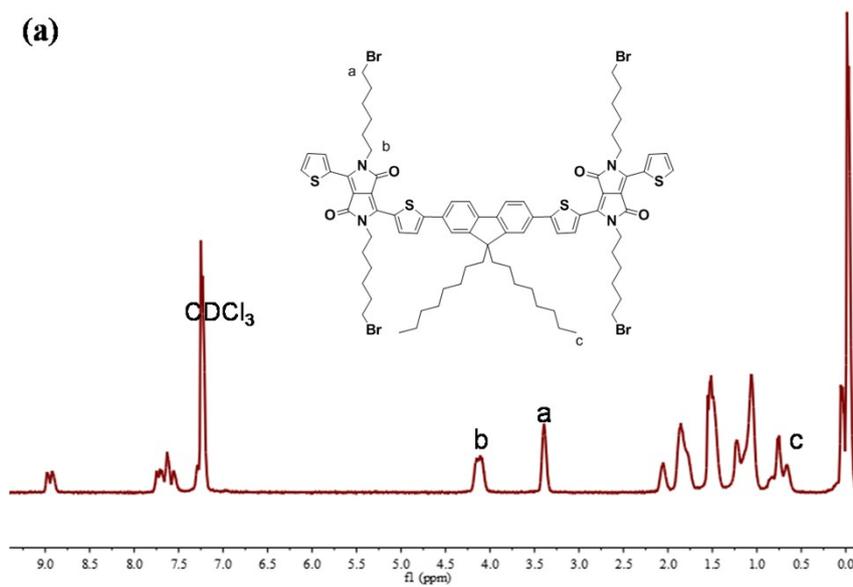
(3) The device structure was ITO/PEDOT:PSS/J51:ITIC/ETL/Al and ITO/PEDOT:PSS/J61:ITIC/ETL/Al A glass substrate with a pre-patterned ITO (sheet resistance =15 Ω sq⁻¹) was first ultrasonicated in acetone, detergent, deionized water and isopropanol in turn, and then modified by air plasma treatment for 3 min. After filtration through a 0.45 μm filter, PEDOT:PSS (Bay PVPAI4083, Bayer AG) was spin-coated at 5000 rpm for 60 s to form a thickness of 30 nm thin layer on the cleaned ITO substrate, and baked on a hot plate at 140 °C for about 20 min. The J51:ITIC or J61:ITIC (1:1 w/w) was dissolved in chloroform, mixed in solution with total concentration of 18mg mL⁻¹, spin-coated onto the interfacial layer at 2800 rpm for 1 min. and then annealing for 1min. The FDPP₂-M and FDPP₂-N dissolved in Methanol (1 and 0.5 mg/mL) was directly spin-coating on the active layer at 3000 to

6000 rpm for 60s, then aluminium cathode was thermal evaporation over interface layer under a high vacuum chamber (7×10^{-4} Pa) to accomplish the device fabrication. Electron-only devices were fabricated similar to the PSCs with a structure of ITO/ZnO/PTB7-Th: PC₇₁BM/ ETL/Al. The thickness of films was measured using a Dektak 6 M surface profilometer. The effective device area of one cell was 0.04cm². The I–V characterization of the devices were measured by a Keithley 2400 Source Meter under simulated solar light (100 mW/cm², AM 1.5 G, Abet Solar Simulator Sun2000). The EQE values measuring system (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp), the monochromatic light from a xenon lamp. A solar simulator was used as the light source, and the light intensity was monitored by using a standard Si solar cell. All characterization processes were conducted in the air.

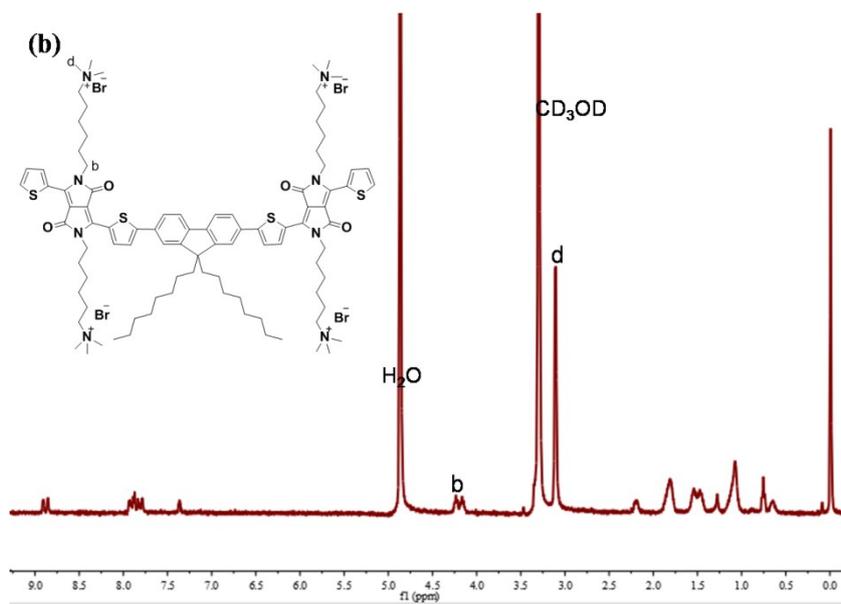
CV measurements were carried out on a CHI660 potentiostat/galvanostat electrochemical work station at a scan rate of 20 mVs⁻¹, with a platinum wire as counter electrode and a silver/silver chloride (Ag/AgCl) as reference electrode in a 0.1 mol L⁻¹ solution of tetrabutylammonium perchlorate (n-Bu₄NClO₄) in anhydrous and nitrogen-saturated acetonitrile (CH₃CN). A platinum plate coated on a thin film of the studied the two small molecule electrolyte was used as the work electrode. The HOMO and LUMO energy level were calculated by the empirical formula: HOMO=[E_{ox}+ 4.4] (-q) (eV J⁻¹), LUMO = [E_{red} + 4.4] (-q) (eV J⁻¹).

The E_{ox} and E_{red} is the analyte oxidation onset and reduction onset, q is the elementary charge(1.6022×10^{-19} C), and eV J⁻¹ represents the conversion constant(6.2415×10^{18} eV J⁻¹) from joules to electron volts.

(a)



(b)



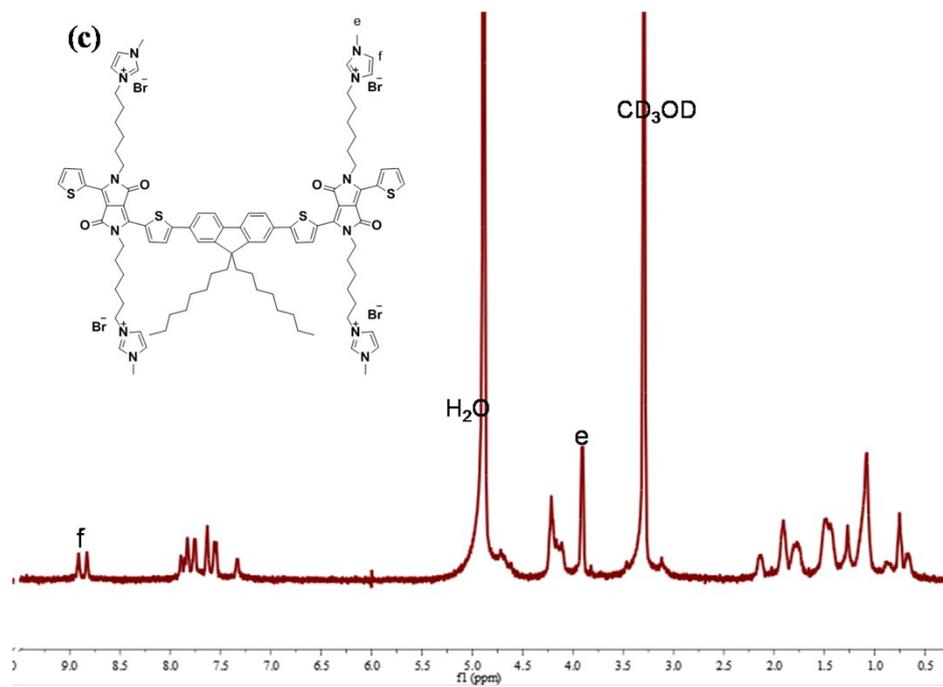


Figure S1 (a) ¹H NMR spectra of FDPP₂ in CDCl₃. (b) ¹H NMR spectra of FDPP₂-N in CD₃OD. (c) ¹H NMR spectra of FDPP₂-M in CD₃OD.

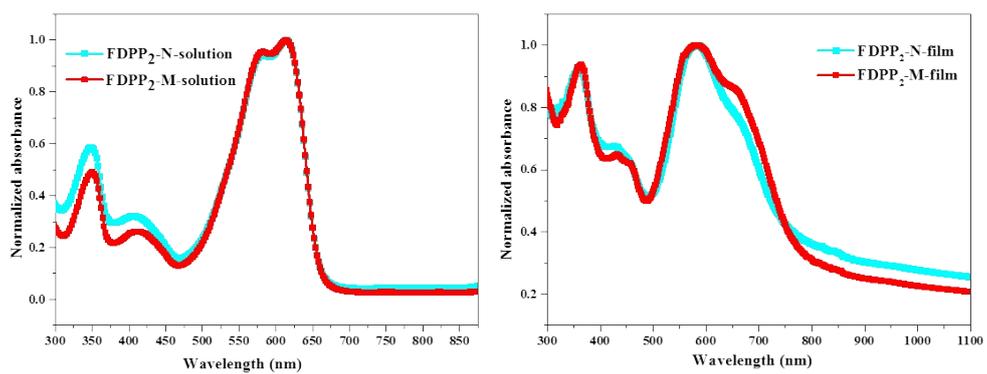


Figure S2. The UV spectra of FDPP₂-N and FDPP₂-M in solution and in film.

(a)

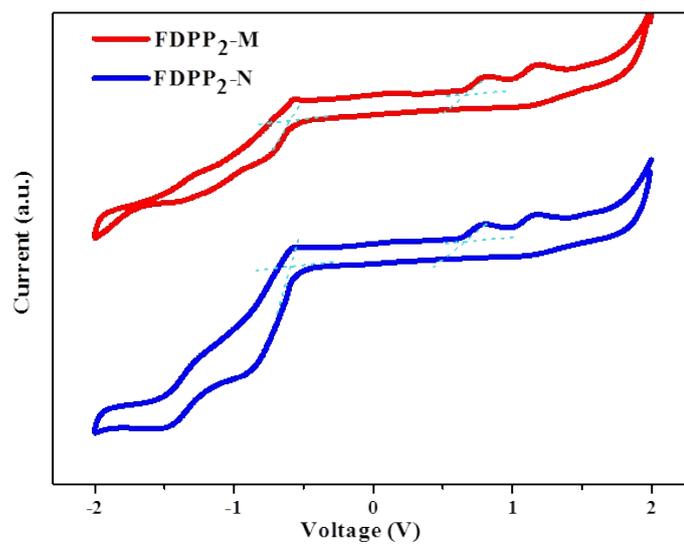


Figure S3. (a) Cyclic voltammogram of FDPP₂-N and FDPP₂-M film in an acetonitrile solution of 0.1M Bu₄NPF₆ with a Pt electrode and an Ag/AgCl reference of electrode at a scan rate of 50mV S⁻¹.

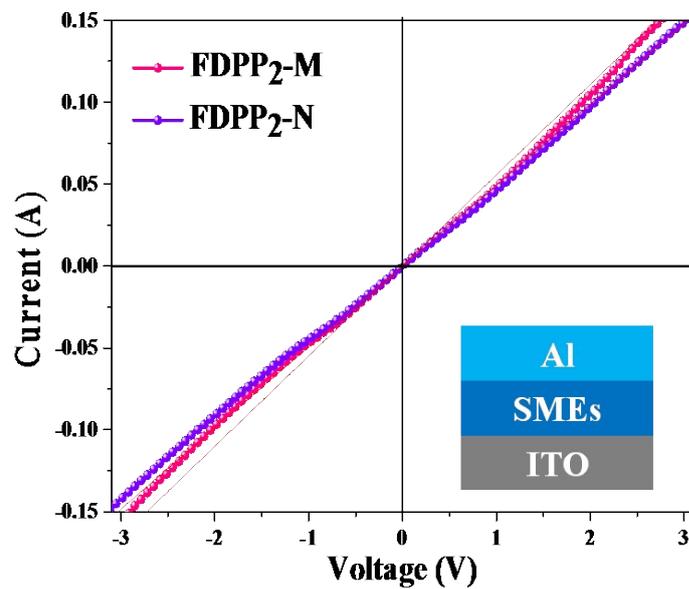


Figure S4. I-V curves for electron-only transfer devices ITO/SMEs/Al.

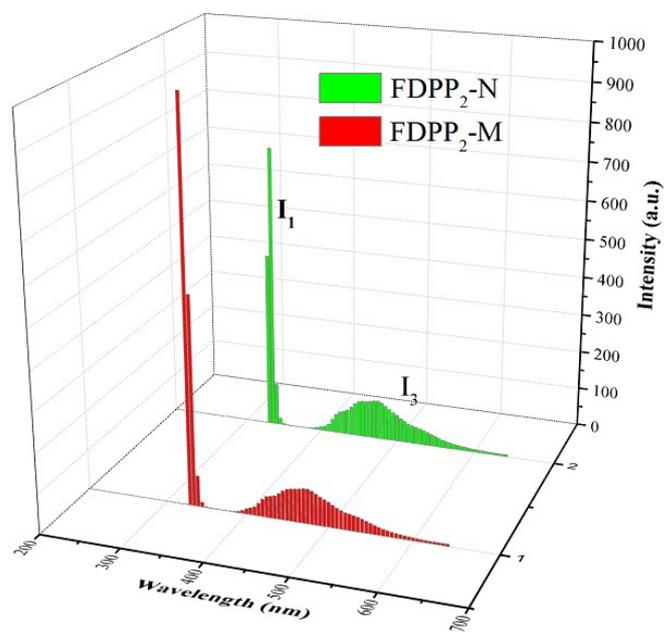


Figure S5. Fluorescence spectra of pyrene in FDPP₂-N and FDPP₂-M film.
(excitation wavelength: 329 nm)

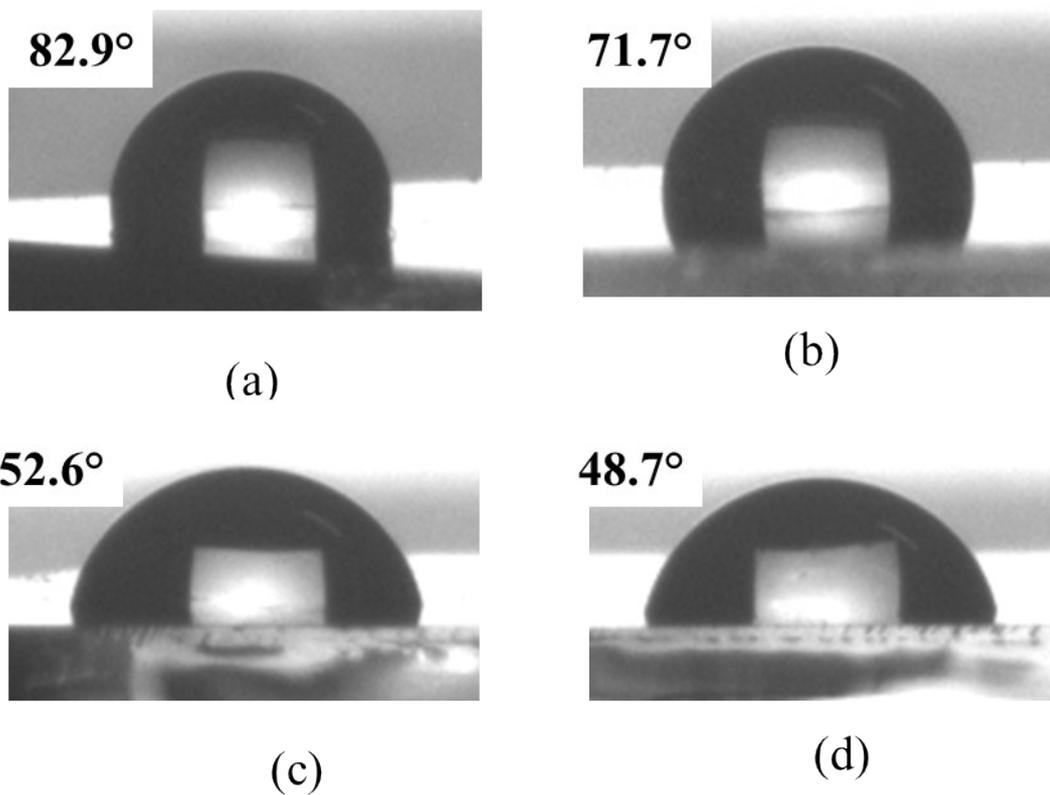


Figure S6. The contact angles of various interfacial materials spin-coated on the PTB7-Th:PC₇₁BM. (a) at cast; (b) PFN; (c) FDPP₂-N; (d) FDPP₂-M .

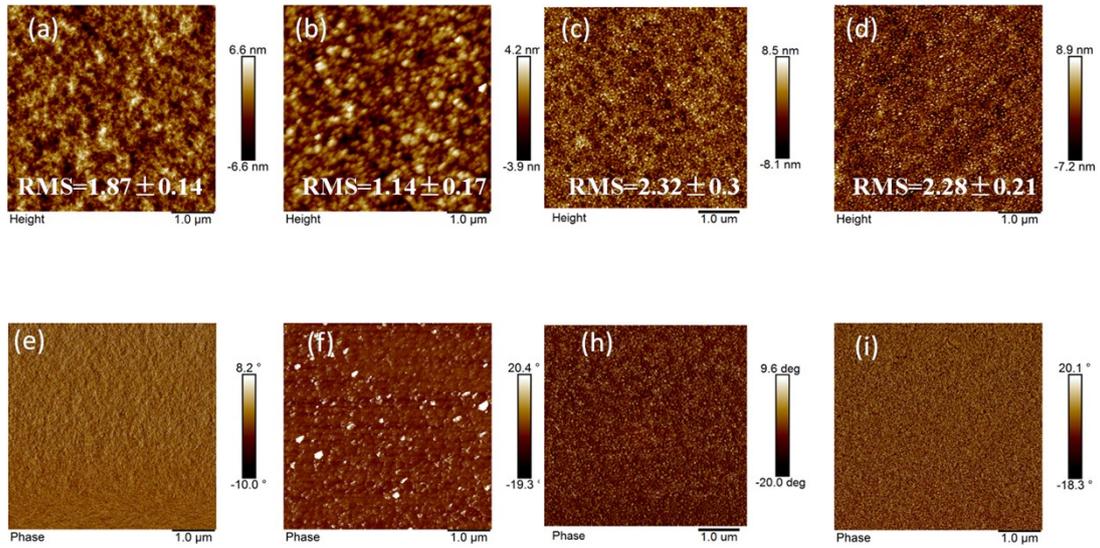


Figure S7. a-d) AFM height images and e-i) phase images of different electrolytes spin-coated on PTB7-Th:PC₇₁BM surface. a,e) as cast; b,f) PFN; c,h) FDPP₂-N; d,i) FDPP₂-M. Image size: 5×5 μm², respectively.

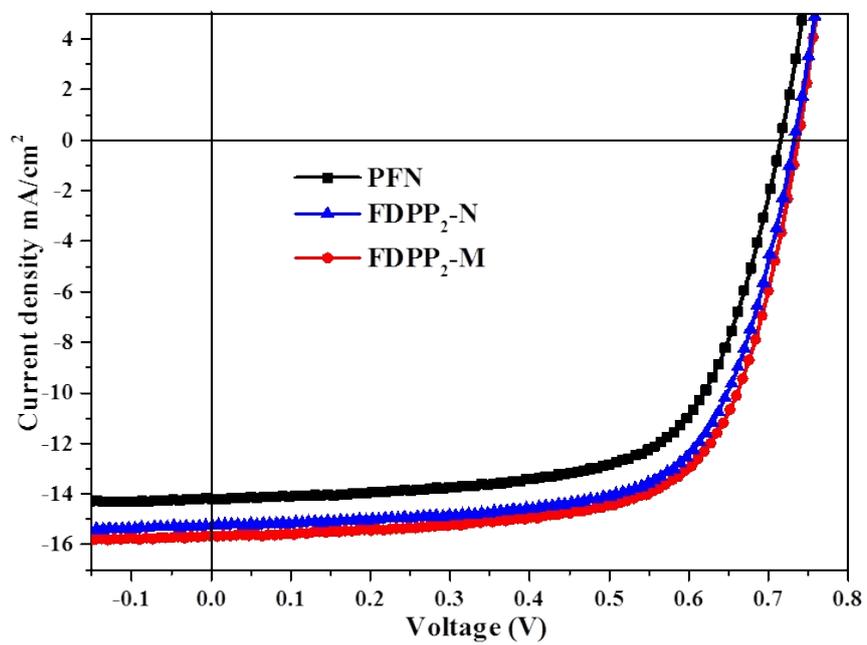


Figure S8. J - V curves of the PSCs devices ITO/PEDOT:PSS/PTB7:PC₇₁BM/ETL/Al with various ETLs.

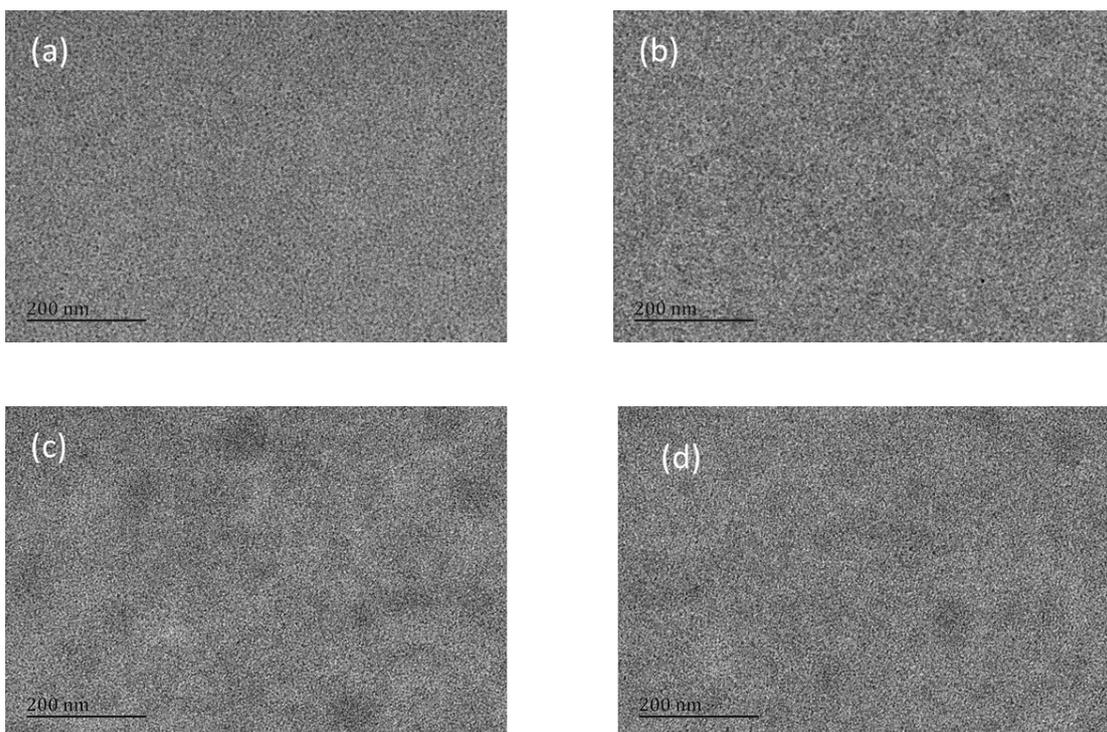


Figure S9. Transmission electron microscope (TEM) images of various electrolytes spin-coated on PTB7-Th:PC₇₁BM surface (a) as cast, (b) PFN, (c) FDPP₂-N, (d) FDPP₂-M.

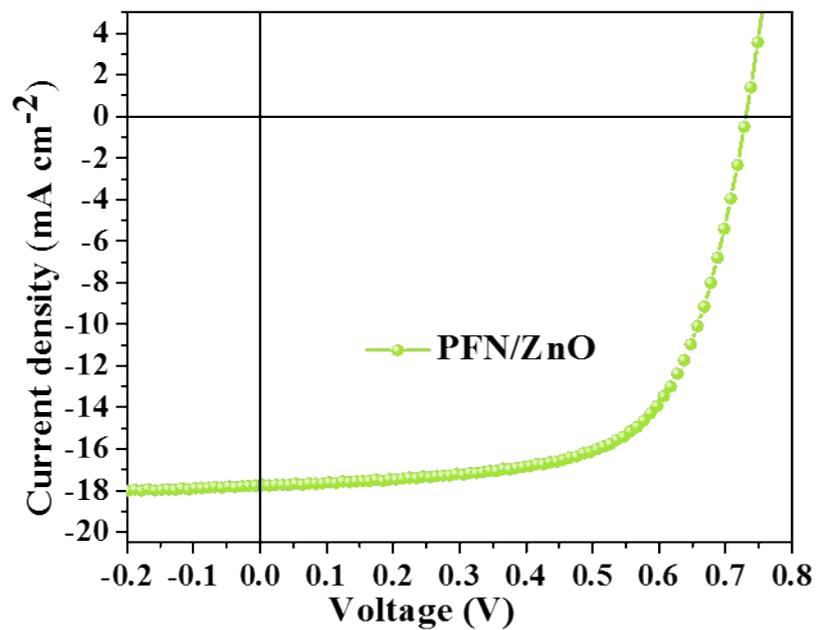


Figure S10. *J-V* curves of the PSCs devices ITO/ZnO/PFN/PTB7-Th:p-DTS-(FBT TH₂)₂:PC₇₁BM/MoO₃/Ag .

Table S1. Cyclic voltammogram of FDPP₂-N and FDPP₂-M film in an acetonitrile solution of 0.1M Bu₄NPF₆ with a P_t electrode and an Ag/AgCl reference of electrode at a scan rate of 50mV S⁻¹.

Compound	LUMO	HOMO	E _g ^{cv}	E _g ^{opt}
FDPP ₂ -N	-3.78eV	-5.13eV	1.35eV	1.54eV
FDPP ₂ -M	-3.80eV	-5.10eV	1.30eV	1.52eV

Table S2. Fluorescence spectra of pyrene in FDPP₂-N and FDPP₂-M film. (excitation wavelength: 329 nm)

	FDPP ₂ -N	FDPP ₂ -M
I ₁	734.5	997.9
I ₃	101.7	88.14
I ₁ /I ₃	7.22	11.32

Table S3. *J-V* curves of the PSCs devices of ITO/PEDOT:PSS/PTB7:PC₇₁BM/ETLs/Al with various ETLs under the illumination of AM 1.5G, 100 mW cm⁻².

ETL	V _{oc} (V)	J _{sc} (mAcm ⁻²)	FF(%)	PCE(%)
PFN	0.720±0.005	14.69±0.08	66.9±0.5	7.05±0.13 (7.18)
FDPP ₂ -N	0.732±0.004	15.22±0.14	67.4±0.6	7.51±0.15 (7.66)
FDPP ₂ -M	0.736±0.006	15.67±0.17	67.3±0.8	7.76±0.17 (7.93)

Table S4. *J-V* curves of the PSCs devices ITO/ZnO/PFN/PTB7-Th:p-DTS-(FBT TH₂)₂:PC₇₁BM/MoO₃/Ag . Under the illumination of AM 1.5G, 100 mW cm⁻².

ETL	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE (%)
PFN/ZnO	18.17	0.742	67.8	9.14