

Supplementary Information

Conjugated Polyelectrolytes as Promising Hole Transport Materials for Inverted Perovskite Solar Cells: Effect of Ionic Groups

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1. Synthesis of hole transport materials

Materials: 9H-Fluorene, *o*-phenylenediamine, lead(II) iodide (PbI₂) and hydroiodic acid (HI) were purchased from Alfa Aesar. Thiophene and methylamine (MA) were purchased from ACROS. PEDOT:PSS, PC₆₁BM, PEI branched, silver and indium tin oxide (ITO) were obtained from Uni-Region, Solenne BV, Aldrich Chemical Co., Gredmann, and w Buwon Act Co., respectively. Anhydrous chlorobenzene (CB), tetrahydrofuran (THF), dimethyl formamide (DMF) and methanol were purchased from Sigma-Aldrich, Merck, ACROS; normal CB, THF, chloroform, dichloromethane (DCM) and other solvents were purchased from Echo Chemicals Co. and Mallinckrodt Pharmaceuticals. The synthetic routes toward the target CPEs are shown in Scheme S1.

1.1. Synthesis of 2,7-dibromo-9H-fluorene (1)¹

A 250 mL one-necked flask equipped with a magnetic stirrer bar and a dropping funnel was loaded with 9H-fluorene (5.00 g, 30.10 mmol) and CHCl₃ (100 mL). The solution was stirred while bromine (3.87 mL, 75.20 mmol) in CHCl₃ (5.0 mL) was added dropwise. The solution was stirred at

room temperature for 12 h in the dark. After the reaction was finished, the solid was filtered and washed with CHCl_3 (70 mL). The product was re-crystallized from CHCl_3 , and a white solid was obtained with 95% yield (9.17g.). ^1H NMR (400 MHz, CDCl_3): δ 7.686 (s, 2H), δ 7.610-7.630 (d, 2H), δ 7.512-7.537 (d, 2H), δ 3.886 (s, 2H), ^{13}C NMR (100 MHz, CDCl_3): δ 144.70, δ 139.61, δ 128.22, δ 121.10, δ 120.85, δ 36.47.

1.2. Synthesis of 2,7-dibromo-9,9-bis(3-bromopropyl)-9H-fluorene (2)

Compound 1 (2.00 g, 6.17 mmol) was added to a mixture of aqueous sodium hydroxide (10M, 25 mL) and tetrabutylammonium bromide (0.398 g, 1.23 mmol) at 70 °C under nitrogen. After 20 min, 1,3-dibromopropane (3.15 mL, 30.86 mmol, liquid) was added *via* a syringe. The mixture was then cooled to room temperature after stirring continuously for 1 h. The solution was extracted with dichloromethane, and the organic layer was collected after being washed successively with water, aqueous HCl (1 M), water, and brine, and then dried over MgSO_4 . After removal of the solvent by reduced pressure and the excess 1,3-dibromopropane by distillation, the residue was purified by silica gel column chromatography using hexane and dichloromethane (8:1) as the eluent. A white solid was obtained with 60% yield (1.85 g, 2.88 mmol). ^1H NMR (400 MHz, CDCl_3): δ 7.506-7.570 (m, 6H), δ 3.141-3.174 (t, 4H), δ 2.143-2.183 (m, 4H), δ 1.122-1.195 (m, 4H), ^{13}C NMR (100 MHz, CDCl_3): δ 150.60, δ 138.87, δ 130.88, δ 126.09, δ 121.88, δ 121.37, δ 54.40, δ 38.416, δ 33.51, δ 26.87.

1.3. Synthesis of 9,9-bis(3-azidopropyl)-2,7-dibromo-9H-fluorene (3)

A 250 mL one-necked flask equipped with a magnetic stirrer bar was loaded with compound 2 (1.56 g, 2.76 mmol), sodium azide (0.0.601 g, 9.25 mmol), and DMSO (50 mL). The mixture was stirred at 70 °C for 12h. After the reaction was finished, the solution was extracted with diethyl ether (100 mL), and the organic layers were collected after being washed with water and brine, then dried over MgSO_4 . The solvent was removed under reduced pressure. A pale-yellow solid was obtained with 95% yield (1.31 g, 2.65 mmol). ^1H NMR (400 MHz, CDCl_3): δ 7.497-7.579 (m, 6H), δ 3.041-

3.074 (t, 4H), δ 2.097-2.056 (m, 4H), δ 0.878-0.936 (m, 4H) ^{13}C NMR (100 MHz, CDCl_3): δ 150.63, δ 138.958, δ 130.88, δ 125.99, δ 121.92, δ 121.39, δ 54.67, δ 51.21, δ 37.00, δ 23.27.

1.4. Synthesis of di-*tert*-butyl((2,7-dibromo-9H-fluorene-9,9-diyl) bis(propane- 3,1-diyl))-dicarbamate (4)²

Compound 3 (1.30 g, 2.65 mmol) was added to a mixture of THF (40 mL) and water (5 mL) in a 250 mL one-necked flask equipped with a magnetic stirrer bar. Triphenyl phosphine (1.60 g, 6.10 mmol) was added to the solution and the mixture was stirred at 25 °C for 12h. Then, di-*tert*-butyl dicarbonate (1.33 g, 6.10 mmol) dissolved in THF (45 mL) was added into the mixture and stirred at 25 °C for 12h. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using dichloromethane and methanol (50:1) as the eluent. A white solid was obtained with 90% yield (1.47 g, 2.39 mmol). ^1H NMR (400 MHz, CDCl_3): δ 7.451-7.548 (m, 6H), δ 4.285 (br, 2H), δ 2.903 (m, 4H), δ 1.964-2.006 (m, 4H), δ 1.413 (s, 18H), δ 0.729-0.806 (m, 4H) ^{13}C NMR (100 MHz, CDCl_3): δ 155.69, δ 151.22, δ 138.94, δ 130.60, δ 125.97, δ 121.75, δ 121.23, δ 79.06, δ 54.82, δ 40.30, δ 37.07, δ 28.28, δ 24.42.

1.5. Synthesis of 3,3'-(2,7-dibromo-9H-fluorene-9,9-diyl) bis (*N,N,N*-trimethyl propan-1-ammonium) bromide (5)³

A 100 mL one-necked flask equipped with a magnetic stirrer bar and a dropping funnel was loaded with compound 3 (0.50 g, 0.883 mmol) and THF (40 mL). The solution was added dropwise with 45 wt % trimethylamine (1.0 mL) in THF (5.0 mL) under stirring. The solution was stirred at room temperature for 12 h. After the reaction was finished, the solution was extracted with chloroform and water, and the aqueous layers were collected. The solvent was removed under reduced pressure and the residue was washed with acetone (70 mL). A white solid was obtained with 95% yield (0.573 g, 0.839 mmol, solid). ^1H NMR (400 MHz, D_2O): δ 7.714-7.746 (m, 4H), δ 7.592-7.596 (d, 2H), δ 2.942-2.985 (m, 4H), δ 2.723 (s, 18H), δ 2.073-2.112 (m, 4H), δ 0.879-0.960 (m, 4H) ^{13}C NMR (100 MHz, D_2O): δ 149.91, δ 139.14, δ 131.29, δ 126.55, δ 121.92, δ 121.66, δ 66.00, δ 54.41, δ 52.41, δ 34.93, δ 17.24.

1.6. Synthesis of potassium 3,3'-(2,7-dibromo-9H-fluorene-9,9-diyl)bis(propane- 1-sulfonate) (6)⁴

Compound 1 (0.75 g, 2.31 mmol) was added to a mixture of aqueous sodium hydroxide (10M, 25 mL) and tetrabutylammonium bromide (0.040 g, 0.120 mmol) at 25 °C under nitrogen. After 10 min, 1,3-dibromopropane (3.15 mL, 30.86 mmol) was added *via* syringe and stirred for 4 h. After the reaction was finished, the mixture was poured into an acetone bath (250 mL). The yellow precipitate was collected by filtration, and the product was recrystallized from water. A white solid was obtained with 42% yield (0.61 g, 0.97 mmol, solid). ¹H NMR (400 MHz, D₂O): δ 7.669-7.673 (d 2H), δ 7.632-7.653 (d 2H), δ 7.505-7.529 (d 2H), δ 2.509-2.548 (t 4H), δ 2.098-2.139 (m 4H), δ 0.921-1.000 (m 4H) ¹³C NMR (100 MHz, D₂O): δ 151.06, δ 138.99, δ 130.57, δ 126.47, δ 121.51, δ 121.24, δ 54.87, δ 50.88, δ 37.61, δ 18.84.

1.7. Synthesis of tributyl(thiophen-2-yl)stannane (7)

A 250 mL one-necked flask equipped with a magnetic stirrer bar and a dropping funnel was loaded with thiophene (5.00 g, 59.4 mmol) and anhydrous THF (100 mL) and cooled to -78°C in an acetone bath under nitrogen protection, followed by the addition of a *n*-butyllithium/hexane solution (2.5 M, 23.77 mL, 59.4 mmol) dropwise. After stirring for another 1.5h at the same temperature, *n*-tributyltin chloride (19.34 mL, 71.31 mmol) was added slowly and stirred for 1.5h. The reaction mixture was warmed to room temperature and kept stirring overnight. After the reaction was finished, the mixture was quenched with 50 mL water and extracted with hexane. The organic layers were collected after being washed with water, brine and then dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by distillation, and the second portion was collected. A colorless liquid was obtained with 80% yield (17.7 g, 47.5 mmol, liquid). ¹H NMR (400 MHz, CDCl₃): δ 7.672-7.686 (m, 1H), δ 7.292-7.303 (m, 1H), δ 7.220-7.230 (m, 1H), δ 1.60-1.65 (m, 6H), δ 1.38-1.41 (m, 6H), δ 1.0-1.2 (m, 6H), δ 1.0-1.2 (m, 6H), δ 0.85-0.95 (t, 9H) ¹³C NMR (100 MHz, CDCl₃): δ 135.06, δ 130.46, δ 127.71, δ 28.85, δ 27.15, δ 13.55, δ 10.70.

1.8. Synthesis of benzo[c][1,2,5]thiadiazole (8)

o-Phenylenediamine (3.25 g, 30.1 mmol) was added to a mixture of dichloromethane (150 mL, liquid) and triethylamine (18.0 mL, 130.0 mmol) in a 250 mL two-necked flask equipped with a magnetic stirrer bar, a cooling system, and a dropping funnel. The equipment was cooled in an ice bath, and thionyl chloride (7.00 mL, 96.0 mmol) was added dropwise under stirring. After stirring for an additional 10 min at the same temperature, the mixture was removed from the ice bath and heated to reflux for 12h. After the reaction was finished, the solution was extracted with dichloromethane. The organic layers were collected after being washed with water and brine, and then dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using hexane and ethyl acetate (5:1) as the solvent. A white solid was obtained with 96.8 % yield (3.96 g, 29.1 mmol). ¹H NMR (400 MHz, CDCl₃): δ 7.996-8.031 (m, 2H), δ 7.575-7.621 (m, 2H) ¹³C NMR (100 MHz, CDCl₃): δ 154.70, δ 129.21, δ 121.46.

1.9. Synthesis of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (9)

Compound 8 (10.0 g, 73.5 mmol) was added to a solvent of hydrobromic acid (50.0 mL, 48 wt%, aqueous) in a 250 mL two-necked flask equipped with a magnetic stirrer bar, a cooling system, and a dropping funnel. The reaction system was cooled in an ice bath, and thionyl chloride (7.00 mL, 96.0 mmol) was added dropwise under stirring. After stirring for an additional 10 min at the same temperature, it was moved out from the ice bath and heated to reflux for 6 h. After the reaction was finished, the solid was filtered and washed with CHCl₃ (70 mL). The product was re-crystallized from CHCl₃. A white solid was obtained with 80% yield (9.17 g, 28.60 mmol). ¹H NMR (400 MHz, CDCl₃): δ 7.749 (s, 2H) ¹³C NMR (100 MHz, CDCl₃): δ 152.89, δ 132.27, δ 113.83.

1.10. Synthesis of 4,7-di(thiophen-2-yl) benzo[*c*][1,2,5]thiadiazole (10)

A 30 mL microwave bottle equipped with a magnetic stirrer bar was loaded with compound 7 (0.50 g, 0.883 mmol) and compound 9 (0.50 g, 0.883 mmol). Tetrakis(triphenylphosphine) palladium (0) (Pd(PPh₃)₄) (10 mg) and toluene (15 mL) were added as catalyst and solvent, respectively, and sealed with a Teflon cap before being put in the microwave machine. The reaction was conducted at 210 °C, held for 1 h, and then cooled to room temperature. After the reaction was finished, the

mixture was moved to a 100 mL one-necked flask and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using hexane and dichloromethane (5:1) as the eluent. A red solid was obtained with 70 % yield (0.629 g, 2.09 mmol, solid). ¹H NMR (400 MHz, CDCl₃): δ 8.142-8.154 (d, 2H), δ 7.905 (s, 2H), δ 7.479-7.495 (t, 2H), δ 7.231-7.253 (d, 2H) ¹³C NMR (100 MHz, CDCl₃): δ 152.53, δ 139.26, δ 127.91, δ 127.41, δ 126.70, δ 125.89, δ 125.66.

1.11. Synthesis of 4,7-bis(5-(trimethylstannyl) thiophen-2-yl) benzo[c] [1,2,5] thiadiazole (11)

A 250 mL one-necked flask equipped with a magnetic stirrer bar and a dropping funnel was loaded with 2,2,6,6-tetramethylpiperidine (0.846 g, 5.99 mmol) and anhydrous THF (100 mL), cooled to -78°C in an acetone bath under nitrogen protection and then added with a n-Butyllithium/hexane solution (2.5 M, 2.40 mL, 5.99 mmol) dropwise. After stirring for another 0.5 h at the same temperature, the reaction mixture was warmed to room temperature and continued stirring for 1h. The mixture was cooled again to -78°C and compound 10 (0.60 g, 1.99 mmol) was added slowly and stirred for 2h. A trimethyltin chloride/THF solution (1 M, 4.99 mL, 4.99 mmol) was added slowly and stirred for 1h at the same temperature. Finally, the mixture was removed from the acetone bath to room temperature and stirred overnight. After the reaction was finished, the mixture was quenched with 50 mL water and extracted with dichloromethane. The organic layers were collected after being washed with water and brine, and then dried over MgSO₄. The solvent was removed under reduced pressure, and the residue was recrystallized from acetone. A red solid was obtained with 50 % yield (0.623 g, 0.995 mmol, solid). ¹H NMR (400 MHz, CDCl₃): δ 8.206-8.214 (d, 2H), δ 7.897 (s, 2H), δ 7.318-7.327 (d, 2H) ¹³C NMR (100 MHz, CDCl₃): δ 152.59, δ 144.96, δ 140.17, δ 136.0, δ 128.30, δ 125.73, δ -8.251.

1.12. Synthesis of polymers

1.12.1. Synthesis of BF-Boc

Compound 4 (85.4 mg, 0.125 mmol) and compound 11 (78.3 mg, 0.125 mmol) were weighed into a 10 mL bottle. Pd(PPh₃)₄ (4.3 mg, 0.00375 mmol) was added as a catalyst under nitrogen in a

glove box and sealed with a Teflon cap. Then, anhydrous toluene (2.5 mL) was added *via* syringe. The polymerization was carried out at 95°C for 24h under nitrogen protection. The raw product was precipitated into methanol and purified by Soxhlet extractions using methanol, acetone, hexane, and dichloromethane as solvents to remove the low molecular weight polymer. Finally, the highest molecular weight was collected from chloroform (GPC-THF system: $M_w = 23.6$ kDa, $M_n = 15.5$ kDa and PDI = 1.52) and a purple solid was obtained with 45% yield (45.4 mg, solid). ^1H NMR (400 MHz, DMSO- d_6): δ FT-IR (KBr): NH band at 3400 cm^{-1} and C=O band at 1706 cm^{-1} .

1.12.2. Synthesis of BF-NH₃

BF-Boc (40 mg) was dissolved in chloroform (40 mL) in a 100 mL one-necked flask. Trifluoroacetate acid (5 mL) was then added and stirred at 25°C. After one hour, hydrobromic acid (5 mL, 48 wt%, aqueous) was added and stirred at 25°C for an additional 2h. After the reaction was finished, the solvent was removed under reduced pressure and a few drops of water and acetone was added several times to remove acid and by-product. A purple solid was obtained with 90 % yield (34.2 mg, solid). FT-IR (KBr): NH (NH_3^+Br^-) band at 3438 cm^{-1} and 1656 cm^{-1} .

1.12.3. Synthesis of BF-NMe₃

Compound 5 (205.3 mg, 0.30 mmol) and compound 11 (187.8 mg, 0.30 mmol) were weighed into a 10 mL bottle. Pd(PPh₃)₄ (17.3 mg, 0.015 mmol) was added as a catalyst under nitrogen in a glove box and sealed with a Teflon cap. Then, anhydrous *N, N*-dimethylformamide (2.0 mL) was added *via* syringe. The polymerization was carried out at 95°C for 48h under nitrogen protection. The raw product was precipitated into water and purified by Soxhlet extractions using water and acetone as solvents to remove the low molecular weight polymer. Finally, the highest molecular weight was collected from methanol (GPC-DMF system: $M_w = 15.6$ kDa, $M_n = 10.4$ kDa and PDI = 1.50) and a purple solid was obtained with 80 % yield (45.4 mg, solid).

1.12.4. Synthesis of BF-SO₃

Compound 6 (180.7 mg, 0.280 mmol) and compound 11 (175.6 mg, 0.280 mmol) were weighed into a 10 mL bottle. Pd(PPh₃)₄ (9.7 mg, 0.0084 mmol) was added as a catalyst under nitrogen in a

glove box and sealed with a Teflon cap. Then, anhydrous N, N-dimethylformamide (2.0 mL) was added *via* syringe. The polymerization was carried out at 95°C for 48h under nitrogen protection. The raw product was precipitated into methanol and purified by Soxhlet extractions using methanol, acetone, hexane, and dichloromethane as solvents to remove the low molecular weight polymer. Finally, the highest molecular weight was collected from chloroform (GPC-DMF system: $M_w = 15.1$ kDa, $M_n = 12.3$ kDa and PDI = 1.20) and a purple solid was obtained with 49.2 % yield (108.5 mg, solid).

2. Synthesis of methylammonium iodide

57% hydroiodic acid was weighed in a one-necked flask equipped with a magnetic stirrer bar and a dropping funnel at 0°C under nitrogen. Methylamine dissolved in ethanol was added dropwise to the hydroiodic acid solution. After 2 hr, the solvent was removed under reduced pressure. The yellow solid was washed several times with diethyl ether, recrystallized from diethyl ether/methanol to form a white solid and then dried under reduced pressure.

3. Device Fabrication and Instrument

3.1. Device fabrication:

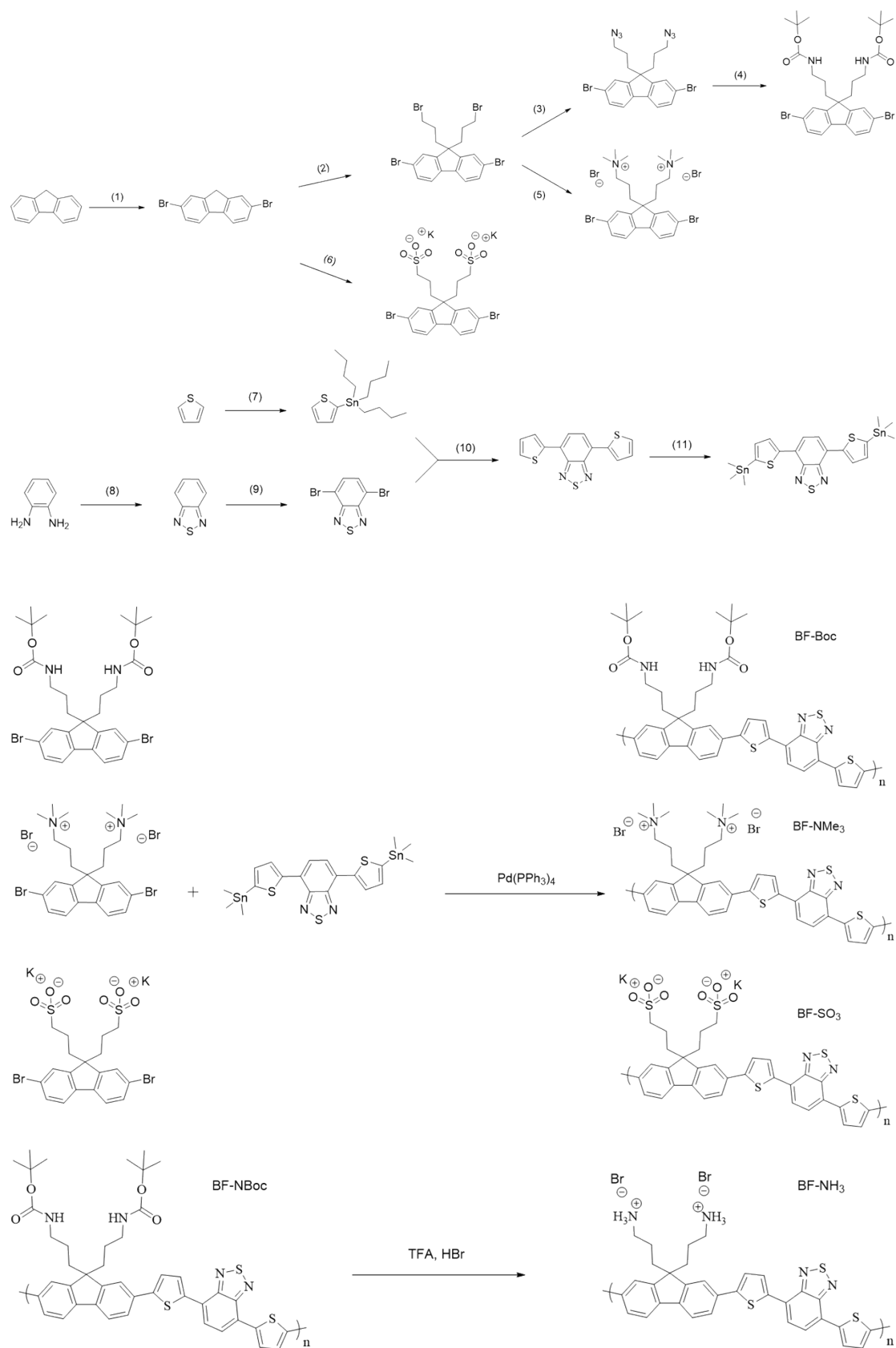
ITO ($15 \text{ ohm square}^{-1}$)-coated glass substrates were cleaned with deionized water, acetone, and isopropanol in an ultrasonic bath for 10 min, followed by ozone treatment for 10 min. BF-NH₃, BF-SO₃ solution (1 mg mL^{-1} in DMF), and BF-NM₃ solution (1 mg mL^{-1} in 2-methoxyethanol) were filtered through a $0.25 \mu\text{m}$ polytetrafluoroethylene (PTFE) filter, then spin-coated onto the ITO substrate at 4000 rpm for 40 sec. Poly(3,4-ethylenedioxythiophene): polystyrenesulfonated (PODET:PSS) was filtered through a $0.25 \mu\text{m}$ polyvinylidene fluoride (PVDF) filter, then spin-coated onto the ITO substrate at 3500 rpm for 40 s. These four HTMs coated ITO substrates were then annealed at 140 °C for 10 min on a hot plate. Perovskite precursor was prepared by mixing PbI₂, MAI and DMSO (1:1:2 by molar ratio) in a solvent of DMF (45 wt % of solution) and filtered through a $0.25 \mu\text{m}$ polytetrafluoroethylene (PTFE) filter. The perovskite solution was spin-coated in a glovebox at 6000 rpm for 25 s. Anti-solvent (diethyl ether, 3 mL) was dropped onto the spinning

substrate at the 6th sec during the spin-coating step. The films were then successively annealed at 65 °C for 4 min and 100 °C for 1h. After the substrate was cooled to room temperature, [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM) in chlorobenzene (25 mg/ mL) filtered through a 0.25 μm PTFE filter as an electron-transporting layer was then spin-coated atop the devices at 1000 rpm for 60 s inside a glovebox. After set aside for 45 min, PEI was spin-coated on the device at 4000 rpm for 40 min, and then the substrate was transferred to a vacuum chamber. 100 nm Ag was deposited by thermal evaporation using a metal shadow mask. The device area was 0.16 cm².

3.2. Measurements and characterization

¹H and ¹³C NMR spectra were recorded using a Bruker 400 MHz spectrometer. FT-IR data were measured using a JASCO FT/IR-480 Plus IR spectrometer. UV-vis absorption spectra were recorded using a JASCO V-670 UV-vis spectrometer. The surface morphology of the ITO/HTL and ITO/HTL/perovskite films was investigated by a Hitachi S-4800 SEM. The XRD patterns of perovskite were recorded on a diffractometer (Bruker D8) equipped with Cu-Kα radiation ($\lambda = 1.5418 \text{ \AA}$). The energy levels (HOMO and work function) of each layer components were acquired using photo-electron spectroscopy in air (Riken Keiki Surface Analyzer model AC-2). AFM measurements were performed in air using a Park XE-100 instrument at the NTNU Precision Analysis and Material Research Center, Taiwan.

Photovoltaic performance measurements of PSC were conducted under full sunlight (100 mW/cm²) using a water-based IR filter and AM 1.5 filter equipped 1000 W ozone-free Xenon lamp (Newport Corporation). The illumination intensity was calibrated using a standard Si reference cell. The $J-V$ characteristics were recorded using a computer-controlled Keithley 2400 source measurement. The external quantum efficiency (EQE) spectra were estimated using the cell response at different wavelengths from 300 nm to 800 nm, where the solar spectrum mismatch was corrected using a calibrated silicon reference cell.



Scheme S1 Synthetic routes for conjugated polyelectrolytes (BF-NMe₃, BF-SO₃, and BF-NH₃).

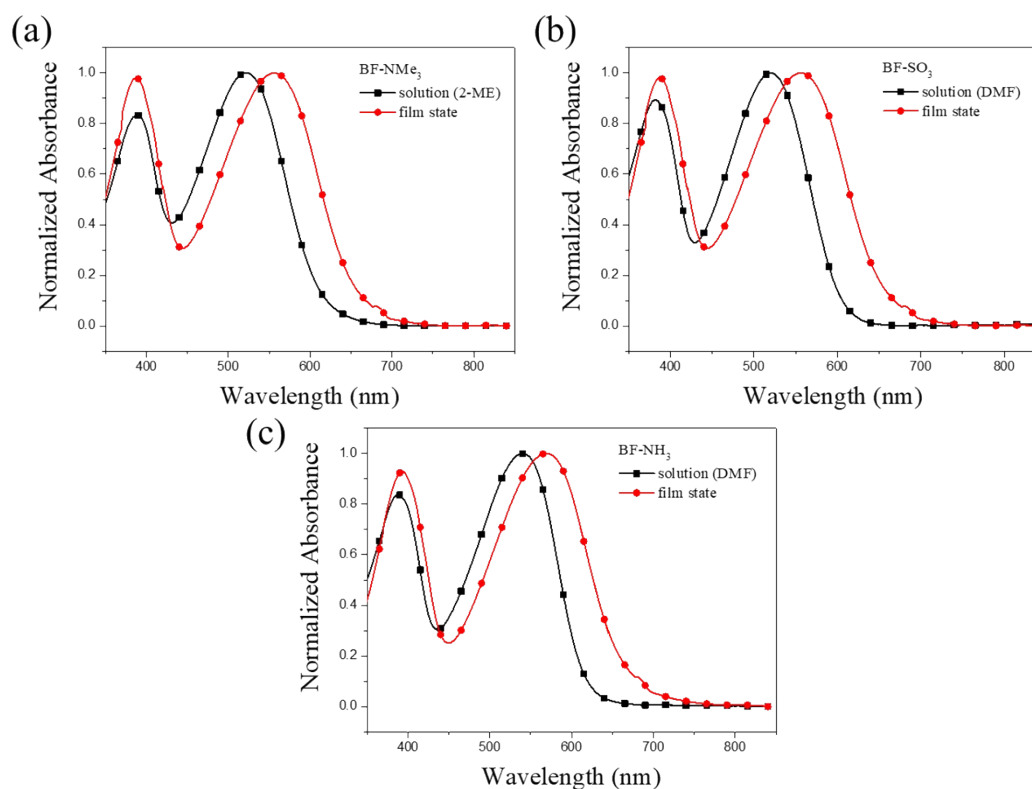


Fig. S1 Normalized UV-Vis absorption spectra of (a) BF-NMe₃, (b) BF-SO₃, and (c) BF-NH₃ in solution (0.1 mg mL⁻¹) and in solid film.

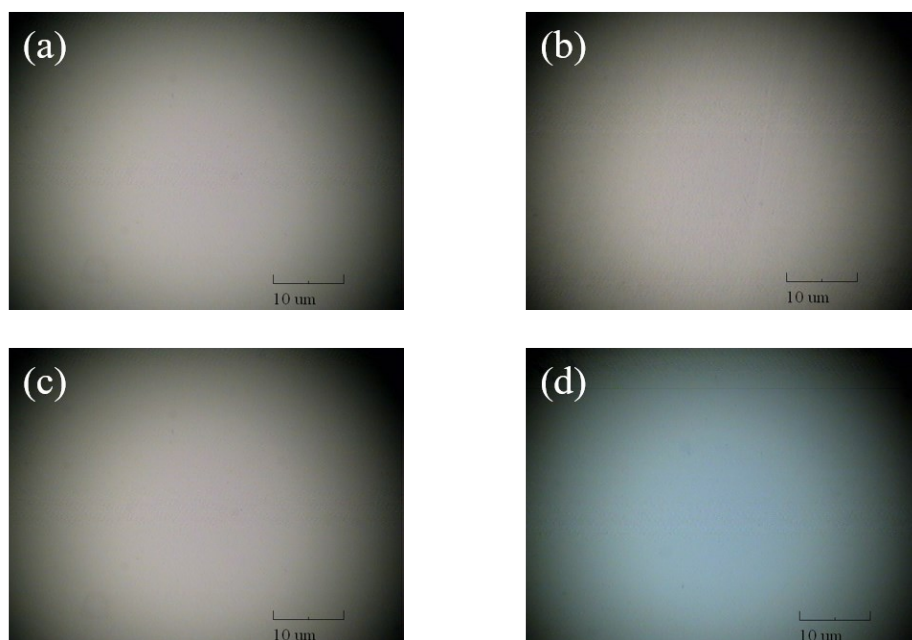


Fig. S2 Optical microscopy images of (a) BF-NMe₃, (b) BF-SO₃, (c) BF-NH₃ and (d) PEDOT:PSS films on a ITO/Glass substrate.

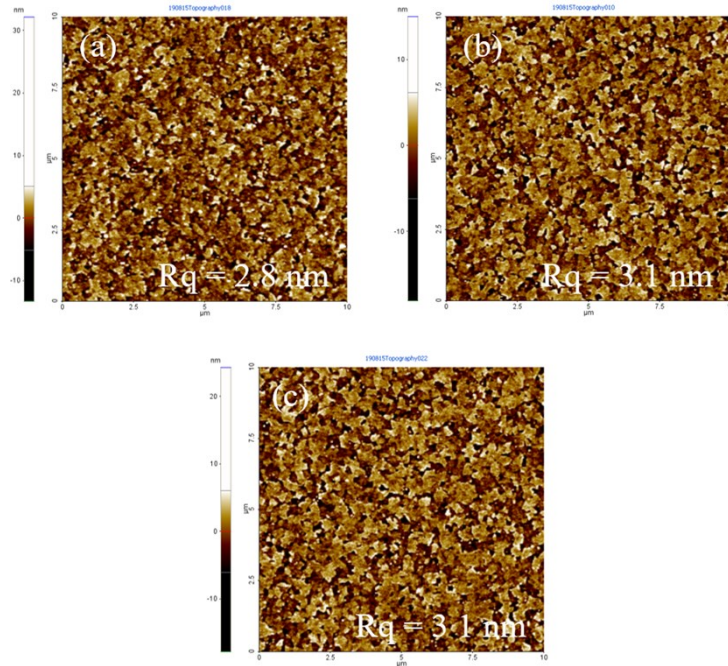


Fig. S3 AFM images of (a) BF-NMe₃, (b) BF-SO₃ and (c) BF-NH₃ films. The respective roughness values (Rq) are 2.8 nm, 3.1 nm, and 3.1 nm. The range of AFM images is 10 μ m.

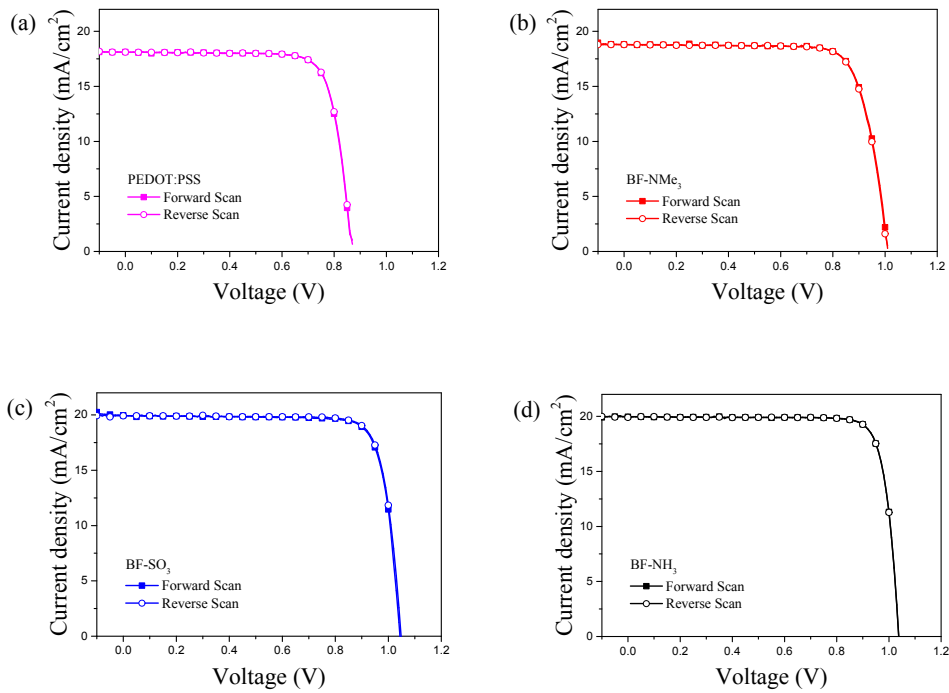


Fig. S4 Forward and Reverse scanned J - V curves of the PSCs using (a) PEDOT:PSS, (b) BF-NMe₃, (c) BF-SO₃ and (d) BF-NH₃ as the hole transport material.

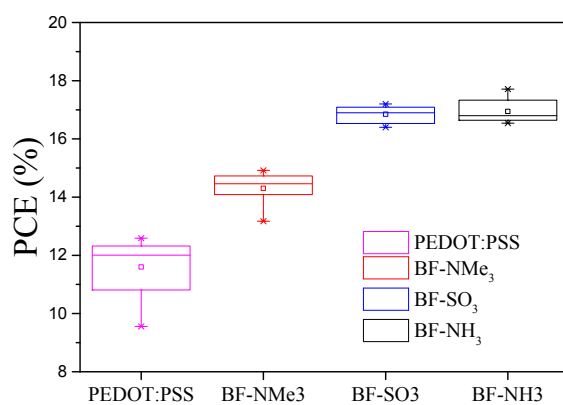


Fig. S5 Statistic distribution of PCE for PSCs using PEDOT:PSS, BF-NMe₃, BF-SO₃ and BF-NH₃ as the hole transport material.

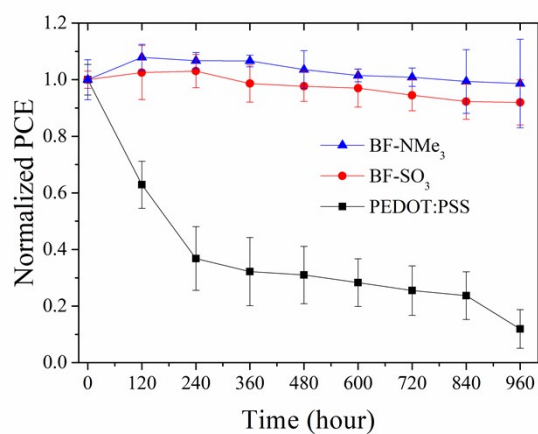


Fig. S6 Plots of PCE as a function of time. The devices are unencapsulated and stored in a chamber maintained at 25 ± 2 °C and relative humidity of 25 ± 10 %.

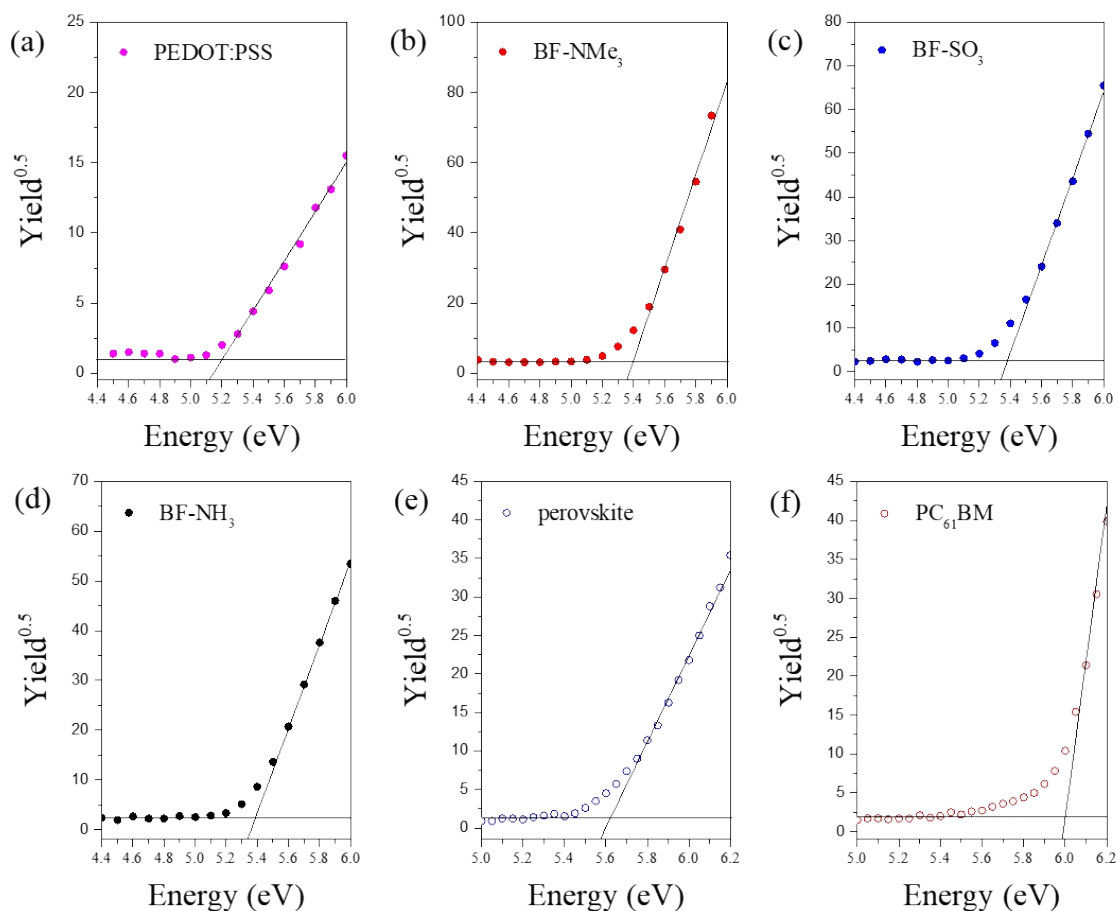


Fig. S7 Photo-electron spectroscopy in air (PESA) spectra of (a) PEDOT:PSS, (b) BF-NMe₃, (c) BF-SO₃, (d) BF-NH₃, (e) perovskite (MAPbI₃) and (f) PC₆₁BM. Solid lines show fitted base and trend lines. Measurements extracted from ionization energies are shown in Table S1.

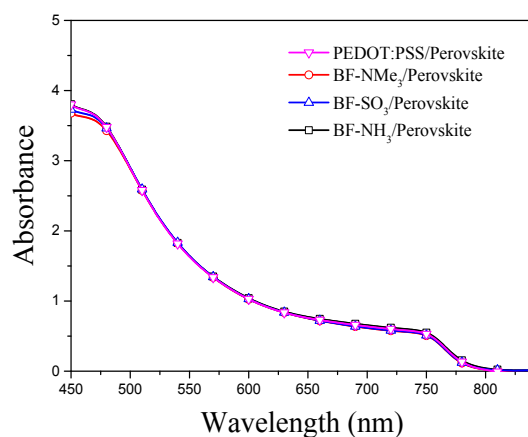


Fig. S8 UV-vis absorption spectra of HTMs/ MAPbI₃.

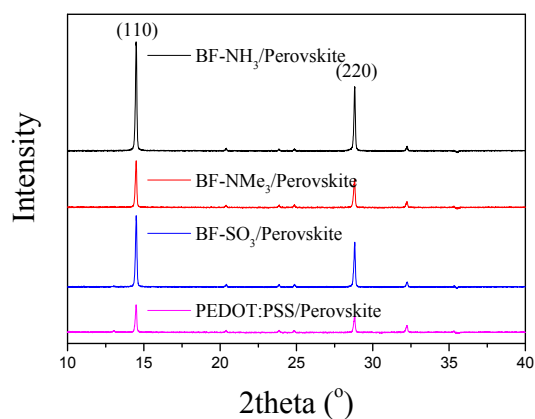


Fig. S9 XRD patterns of perovskite films grown from different substrates of ITO/ HTMs.

Table S1. Molecular weight characteristics, optical properties, and energy levels of the relevant compounds.

Compound	M_w/M_n (kDa) ^a	PDI	λ_{abs} solution/ film (nm)	HOMO ^b (eV)	E_g (eV) ^c
BF-NMe ₃	15.6/ 10.4	1.50	385, 521/ 387, 557	-5.40	1.88
BF-SO ₃	15.1/ 12.3	1.20	385, 521/ 387, 557	-5.40	1.88
BF-NH ₃	23.6/ 15.5	1.52	388, 524/ 393, 560	-5.39	1.86
PEDOT: PSS	-	-	-	-5.20	-
Perovskite	-	-	-	-5.62	-
PC ₆₁ BM	-	-	-	-6.00	-

^a M_w , M_n and PDI of BF-NH₃ were determined from BF-Boc by a GPC-THF system, and BF-NMe₃ and BF-SO₃ by a GPC-DMF system.

^bThe HOMO levels of these compounds coated on ITO were determined by PESA.

^cThe bandgap, E_g , was derived from the onset of the corresponding absorption spectrum.

Table S2 Photovoltaic performance of PSCs based on various CPEs as the hole transport materials, which were prepared from the corresponding solutions at different concentrations.

HTM	Conc. (mg/ mL)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
BF-NMe₃	0.5	1.00 ± 0.02	18.30 ± 0.56	76.37 ± 2.27	13.95 ± 0.83
	1.0	1.00 ± 0.01	18.71 ± 0.25	78.14 ± 0.88	14.65 ± 0.19
	1.5	0.98 ± 0.02	18.11 ± 0.69	77.51 ± 1.70	13.71 ± 0.84
	2.0	0.97 ± 0.03	18.28 ± 0.33	74.90 ± 5.09	13.33 ± 1.20
BF-SO₃	0.5	0.98 ± 0.06	18.33 ± 0.87	77.60 ± 2.62	13.93 ± 1.48
	1.0	1.04 ± 0.02	19.97 ± 0.27	80.92 ± 0.95	16.85 ± 0.30
	1.5	1.05 ± 0.01	19.20 ± 0.61	75.67 ± 1.79	15.25 ± 0.39
	2.0	0.98 ± 0.04	18.24 ± 0.5	77.56 ± 4.09	13.88 ± 0.80
BF-NH₃	0.5	0.73 ± 0.03	18.49 ± 0.27	77.27 ± 1.86	10.40 ± 0.60
	1.0	1.04 ± 0.03	20.13 ± 0.32	80.82 ± 1.43	16.94 ± 0.40
	1.5	1.00 ± 0.02	19.87 ± 0.43	79.76 ± 1.62	15.80 ± 0.45
	2.0	0.98 ± 0.03	19.95 ± 0.32	79.33 ± 2.70	15.52 ± 0.66

Table S3 The parameters τ_1 and τ_2 of biexponential decay fitting for the TRPL results

HTM	τ_1		τ_2	
	Lifetime (ns)	Content (%)	Lifetime (ns)	Content (%)
PEDOT: PSS	1.54	42.80	4.46	57.20
BF-NMe₃	2.05	58.99	7.37	41.01
BF-SO₃	2.20	59.10	11.31	40.90
BF-NH₃	2.19	59.05	11.29	40.95

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