

Supporting Information

Conductive Fullerene Surfactants via Anion Doping as Cathode Interlayers for Efficient Organic and Perovskite Solar Cells

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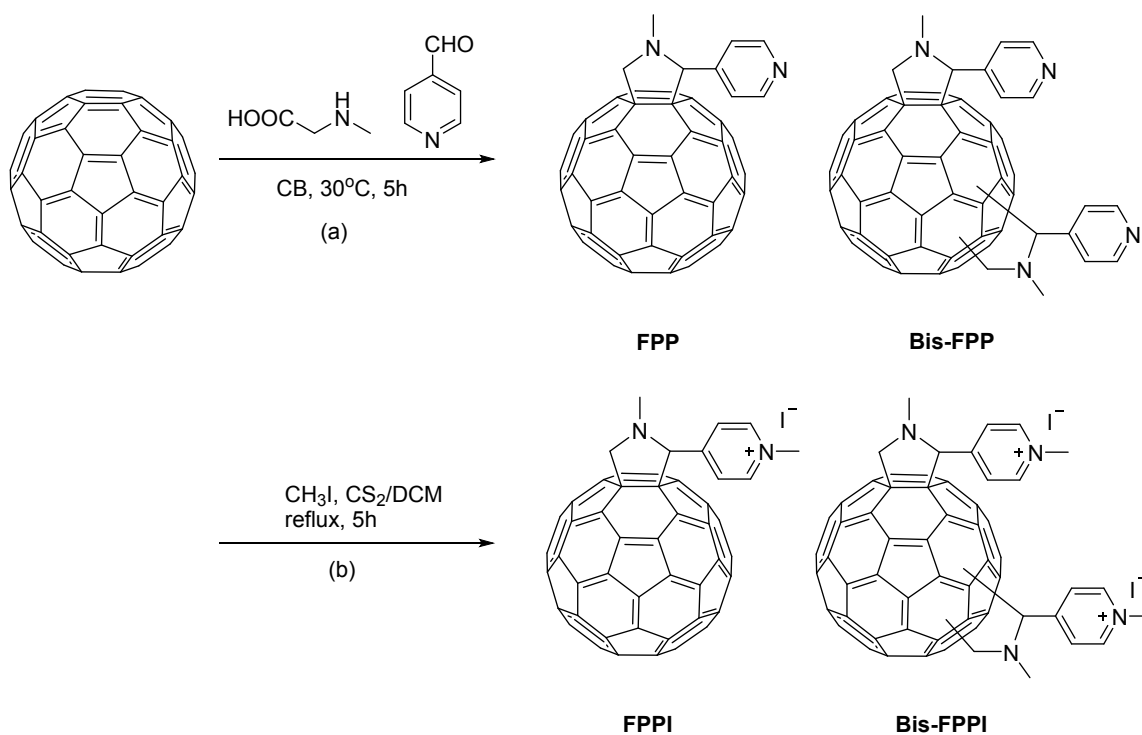
1. Experimental Procedures

1.1 General Information.

Instrument. ¹H NMR spectra were characterized by a Bruker Advance III 400 (400 MHz) nuclear magnetic resonance (NMR) spectroscope. MALDI-TOF MS spectra were measured on a Walters Maldi Q-TOF Premier mass spectrometry. UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Cyclic voltammetry (CV) was done on a CHI600A electrochemical workstation with Pt disk, Pt plate, and standard calomel electrode (SCE) as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 M Bu₄NPF₆ CH₂Cl₂ solution. The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene-ferrocenium (Fc/Fc⁺) redox couple (5.1 eV below the vacuum level). Ultraviolet photoelectron spectrometer (UPS) measurements were conducted on an ESCALAB 250Xi (Thermo) system with a bias voltage of -9.8 eV. Topographic and phase images of the ETL films were obtained on a VeecoMultiMode atomic force microscopy (AFM) in the tapping mode, and the scanning rate for a 2 μm × 2 μm image size was 1.5 Hz.

Materials. All reagents and solvents, unless otherwise specified, were purchased from Aladdin, Aldrich, Energy Chemical, J&K Scientific Ltd and TANFENG. and were used without further purification. Donors and acceptors were purchased from Solarmer Energy, Inc.

1.2 Synthesis of Intermediates and fullerene ETMs¹⁻³



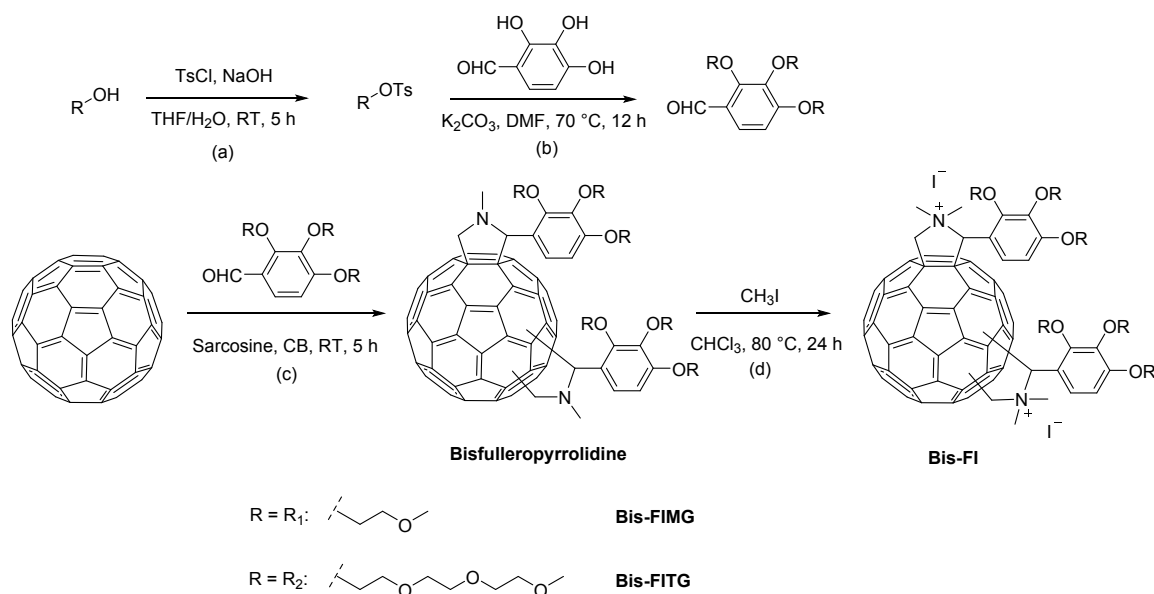
Scheme. S1. Synthetic routes of FPPI and Bis-FPPI. (a) Sarcosine, 4-pyridinecarboxaldehyde, CB, 30 °C, 5h, Ar. Yield FPP 32% and Bis-FPP 18%. (b) CH₃I, CS₂, reflux, 5h, Yield FPPI 70%; CH₃I, DCM, reflux, 5h, Yield Bis-FPPI 62%.

Fullropyrrolidine pyridine (FPP) and Bis-fullropyrrolidine pyridine (Bis-FPP). Fullerene C₆₀ 731 mg (1.01 mmol, 1 eq), 4-pyridinecarboxaldehyde 163 mg (1.52 mmol, 1.5 eq) and sarcosine 360 mg (4.04 mmol, 4 eq) were added into 100 ml clean and dry three-necked flask, and 50 ml dichlorobenzene (DCB) used as solvent was also added into the flask. Then DCB was bubbled with argon gas (Ar) 0.5 hour. After bubbling, the mixture was heated to 110 °C for 5 hours. After cooled down, the solution mixture was directly poured into silica-gel column chromatography, then eluted with toluene until unreacted C₆₀ (150 mg, 0.208 mmol, 20%) was recovered. After that, column chromatography was eluted with the eluent (toluene: ethyl acetate = 5: 1, v/v). Yield: FPP (280 mg, 0.328 mmol, 32%, and 41% based on the consumed C₆₀), Bis-FPP (180 mg, 0.182 mmol, 18%, and 23% based on the consumed C₆₀). FPP: ¹H NMR (400 MHz, CDCl₃) δ 8.70 (d, J = 5.1 Hz, 2H), 7.80 (s, 2H), 5.01 (d, J = 9.5 Hz, 1H), 4.95 (s, 1H), 4.30 (d, J = 9.5 Hz, 1H), 2.82 (s, 3H). C₆₈H₁₀N₂, Exact Mass = 854.08, MS (MALDI-TOF) = 853.718. Bis-FPP (mixture of bis-adduct regioisomers): ¹H NMR (600 MHz, CDCl₃) δ 9.03 – 8.26 (m, 2H), 8.08 – 7.31 (m, 2H), 5.08 – 3.56 (m, 3H), 3.01 – 2.18 (m, 3H). C₇₆H₂₀N₄, Exact Mass = 988.17, MS (MALDI-TOF) = 987.254.

Fullropyrrolidine pyridinium iodide (FPPI). FPP (110 mg, 0.129 mmol, 1 eq) was dissolved with 20 ml carbon disulfide (CS₂) in 100 ml flask, and Methyl iodide (183 mg, 1.29 mmol, 10 eq) in dichloromethane (DCM) was dropped into the solution, and then heated to gentle reflux for 5 hours. After cooling down, the mixture was directly poured into a funnel for filtration, and washed with 50 ml CS₂ and 50 ml MeOH. The residue was collected and dried, achieved FPPI 90 mg (0.090 mmol, yield 70%). ¹H NMR (400 MHz, DMSO) δ 9.05 (d, J = 6.6 Hz, 2H), 8.59 (d, J = 6.7 Hz, 2H), 5.55 (s, 1H), 5.16 (d, J = 9.8 Hz, 1H), 4.44 (d, J = 9.9 Hz, 1H), 4.35 (s, 3H), 2.76 (s, 3H); ¹³C NMR (100 MHz, DMSO) δ 42.55, 42.61, 42.67, 55.52, 126.99, 127.26, 135.76, 136.02, 136.39, 136.61, 137.10, 137.43, 137.83, 138.06, 138.56, 138.82, 139.03, 139.49, 139.67, 139.84, 140.16, 140.68, 141.48, 141.75, 142.06, 142.33, 142.96, 143.46, 143.61, 143.84, 143.94, 144.17, 144.40,

144.88, 145.16, 145.28, 145.97, 146.29, 146.79, 147.76, 147.98, 148.99, 149.54, 149.78, 149.98, 150.55, 150.83, 150.93, 151.62, 151.80, 152.64, 152.78, 152.89, 153.19, 154.43, 154.55, 155.24, 155.58, 155.71, 156.42, 156.69. $C_{69}H_{13}IN_2$, Exact Mass = 996.01, MS (MALDI-TOF) $[C_{69}H_{13}N_2-I]^+ = 871.940$.

Bis-fulleropyrrolidine pyridinium iodide (Bis-FPPI) (mixture of bis-adduct regioisomers). Bis-FPP (82 mg, 0.083 mmol, 1 eq) was dissolved with 20 ml dichloromethane (DCM) in 100 ml flask, and Methyl iodide (600 mg, 4.23 mmol, 50 eq) in dichloromethane (DCM) was dropped into the solution, and then heated to gentle reflux for 5 hours. After cooling down, the mixture was directly poured into a funnel for filtration, and washed with 100 ml DCM and 50 ml MeOH. The residue was collected and dried, achieved Bis-FPPI (65 mg, 0.051 mmol, yield 62%). 1H NMR (500 MHz, DMSO) δ 9.45 – 8.75 (m, 2H), 8.75 – 7.97 (m, 2H), 5.77 – 3.72 (m, 6H), 2.73 – 2.28 (m, 3H); ^{13}C NMR (125 MHz, DMSO) δ 42.57, 42.61, 42.65 – 42.68, 55.82 – 56.44, 126.93 – 127.08, 127.12 – 127.26, 135.84, 136.02, 136.37, 136.60, 137.00, 137.43, 137.81, 138.16, 138.56, 138.84, 139.07, 139.39, 139.64, 139.82, 140.16, 140.68, 141.38, 141.72, 142.03, 142.33, 142.98, 143.46, 143.61, 143.86, 143.93, 144.17, 144.28, 144.40, 144.88, 144.96, 145.06, 145.16, 145.24, 145.95, 146.29, 146.51, 146.79, 147.75, 147.98, 148.42, 148.99, 149.53, 149.67, 149.78 – 149.98, 150.45, 150.82 – 150.95, 151.61 – 151.68, 151.82, 152.68, 152.74 – 152.79, 152.89, 153.09, 154.42, 154.55, 155.22 – 155.54, 155.72, 156.40, 156.56, 156.67. $C_{78}H_{13}I_2N_2$, Exact Mass = 1272.02, MS (MALDI-TOF) $[C_{69}H_{13}N_2-2I]^+ = 1114.904$.



Scheme S2. Synthetic routes of Bis-FIMG and Bis-FITG. (a) TsCl, NaOH, THF/H₂O, RT (25 °C), 12 h. Yield R1-OTs 60%; Yield R2-OTs ~100%. (b) 2,3,4-trihydroxybenzaldehyde, K₂CO₃, DMF, 70 °C, 12 h, Ar. Yield MG-CHO 84%; Yield TG-CHO 70%. (c) MG-CHO/TG-CHO, Sarcosine, CB, 120 °C, 5h, Ar. Yield Bis-FMG 90%; Yield Bis-FTG 90%. (d) CH₃I, CHCl₃, 80 °C, 24 h, Ar. Yield Bis-FIMG (quantitative) and Bis-FITG (quantitative).

2-methoxyethyl 4-methylbenzenesulfonate (R₁-OTs). 2-methoxyethan-1-ol (R₁-OH) (5 g, 65.7 mmol, 1.2 eq) and sodium hydroxide (NaOH) (3.3 g, 82.1 mmol, 1.5 eq) were dissolved in the mixed solvents of 50 ml H₂O and 50 ml tetrahydrofuran (THF). Then 4-methylbenzenesulfonyl chloride (TsCl) (10.4 g, 54.8 mmol, 1.0 eq) was dissolved in 150 ml THF and it was dropped into R₁-OH solution

through constant pressure drop funnel in 0.5 hours. After droplet, the reaction lasted 12 hours at room temperature (RT). The solvent THF was evaporated, and then dichloromethane (DCM) and saturated salt solution were used for extraction. The organic phase was dried by anhydrous sodium sulfate, after evaporating the solvent, achieved colorless oil R₁-OTs. Yield: R₁-OTs (7.5 g, 32.6 mmol, 60% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.16 (t, J = 9.2 Hz, 2H), 3.58 (t, J = 9.2 Hz, 2H), 3.31 (s, 3H), 2.45 (s, 3H). C₁₀H₁₄O₄S, Exact Mass = 230.06.

2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (R₂-OTs). 2-(2-(2-methoxyethoxy)ethoxy)ethan-1-ol (R₂-OH) (4.99 g, 30.3 mmol, 1 eq) and NaOH (1.82 g, 45.6 mmol, 1.5 eq) were dissolved in the solvent of 100 ml THF and 50 ml H₂O. Then TsCl (6.37 g, 33.4 mmol, 1.1 eq) was dissolved in 100 ml THF and it was dropped into R₂-OH solution through constant pressure drop funnel in 0.5 hours. After droplet, the reaction lasted 12 hours at room temperature (RT). And the post treatment was the same as R₁-OTs. Yield: colorless oil R₂-OTs (9.67 g, 30.3 mmol, ~100% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.16 (t, J = 9.6 Hz, 2H), 3.69 (t, J = 10.0 Hz, 2H), 3.64 – 3.56 (m, 6H), 3.53 (dd, J = 5.7, 3.3 Hz, 2H), 3.37 (s, 3H), 2.45 (s, 3H). C₁₄H₂₂O₆S, Exact Mass = 318.11.

2,3,4-tris(2-methoxyethoxy)benzaldehyde (MG-CHO). 2,3,4-trihydroxybenzaldehyde (1.25 g, 8.11 mmol, 1 eq), potassium carbonate (K₂CO₃) (10.1 g, 73 mmol, 9 eq) and 30 ml anhydrous dimethylformide (DMF) were added into 250 ml three-necked flask, after 30 minutes stirring, the solution was heated to 70 °C. R₁-OTs (6.16 g, 26.8 mmol, 3.3 eq) in 15 ml DMF was added into the flask, lasting 12 hours at 70 °C. It was extracted by water and ethyl acetate (EtOAc) and washed by salt solution 5 times. After evaporation of the solvent, the residue was subjected to chromatograph purification on a silica gel column, and the eluent was EtOAc and methol (v: v = 5: 1). Yield: faint yellow oil MG-CHO (2.25 g, 6.85 mmol, 84% yield). ¹H NMR (400 MHz, CDCl₃) δ 10.32 (s, 1H), 7.59 (d, J = 8.8 Hz, 1H), 6.75 (d, J = 8.8 Hz, 1H), 4.52 – 4.30 (m, 2H), 4.25 – 4.20 (m, 2H), 4.19 – 4.16 (m, 2H), 3.82 – 3.77 (m, 2H), 3.74 – 3.70 (m, 2H), 3.45 (s, 3H), 3.44 (s, 3H), 3.39 (s, 3H). C₁₆H₂₄O₇, Exact Mass = 328.15.

2,3,4-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzaldehyde (TG-CHO). 2,3,4-trihydroxybenzaldehyde (440 mg, 2.86 mmol, 1 eq), K₂CO₃ (3.55 g, 25.7 mmol, 9 eq) and 20 ml anhydrous dimethylformide (DMF) were added into 100 ml three-necked flask, after 30 minutes stirring, the solution was heated to 70 °C. R₂-OTs (3 g, 9.42 mmol, 3.3 eq) in 10 ml DMF was added into the flask, lasting 12 hours at 70 °C. It was extracted by water and EtOAc and washed by brine solution 5 times. After evaporation of the solvent, the residue was subjected to chromatograph purification on a silica gel column, and the eluent was EtOAc and methol (v: v = 5: 1). Yield: faint yellow oil TG-CHO (1.2 g, 2.02 mmol, 70% yield). ¹H NMR (400 MHz, CDCl₃) δ 10.33 (s, 1H), 7.57 (d, J = 8.8 Hz, 1H), 6.74 (d, J = 8.8 Hz, 1H), 4.54 – 4.39 (m, 2H), 4.30 – 4.11 (m, 4H), 3.94 – 3.85 (m, 2H), 3.84 – 3.77 (m, 6H), 3.77 – 3.68 (m, 16H), 3.68 – 3.60 (m, 6H), 3.59 – 3.50 (m, 9H). C₂₈H₄₈O₁₃, Exact Mass = 392.31.

Bisfulleropyrrolidine tris(methoxyethoxy)phenyl (Bis-FMG) (mixture of bis-adduct regioisomers). MG-CHO (1.22 g, 3.72 mmol, 3 eq), fullerene C₆₀ (893 mg, 1.24 mmol, 1 eq) and sarcosine (447 mg, 4.34 mmol, 3.5 eq) were dissolved in 100 ml chlorobenzene (CB), bubbled with argon gas 0.5 hour. After bubbling, the mixture was heated to reflux for 5 hours. After evaporation of the solvent, the residue was subjected to chromatograph purification on a silica gel column. Elution with toluene gave little unchanged C₆₀. Bisadducts consisting mixture of regioisomers was then collected with EtOAc eluent, and no mono adduct was collected. Yield: brown solid Bis-FMG (1.6 g,

1.12 mmol, 90% yield). ^1H NMR (600 MHz, CDCl_3) δ 8.10 – 7.34, 7.11 – 6.43, 5.86 – 3.17, 3.00 – 2.42 (m, NCH_3), 1.80 – 0.71. $\text{C}_{96}\text{H}_{58}\text{N}_2\text{O}_{12}$, Exact Mass = 1430.40.

Bisfulleropyrrolidine tris(methoxytriglycol)phenyl (Bis-FTG) (mixture of bis-adduct regioisomers). TG-CHO (0.6 g, 1.01 mmol, 3 eq), fullerene C_{60} (243 mg, 0.34 mmol, 1 eq) and sarcosine (120 mg, 1.16 mmol, 3.5 eq) were dissolved in 80 ml chlorobenzene (CB), bubbled with argon gas 0.5 hour. After bubbling, the mixture was heated to reflux for 5 hours. After evaporation of the solvent, the residue was subjected to chromatograph purification on a silica gel column. Elution with toluene and EtOAc gave little unchanged C_{60} and residue M2. Bisadducts consisting mixture of regioisomers was then collected with EtOAc: MeOH (v: v = 5:1) eluent, and no mono adduct was collected. Yield: viscous liquid Bis-FTG 600 mg (0.31 mmol, 90% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.08 – 7.31, 7.20 – 6.43, 5.78 – 5.33, 5.30 – 3.44, 3.41 – 3.25, 2.97 – 2.08 (m, NCH_3), 1.73 – 0.74. $\text{C}_{120}\text{H}_{106}\text{N}_2\text{O}_{24}$, Exact Mass = 1958.71.

Bisfulleropyrrolidinium tris(methoxyethoxy)phenyl iodide (Bis-FIMG) (mixture of bis-adduct regioisomers). Bis-FMG 400 mg (0.28 mmol) in chloroform (5 mL) and MeI (3 mL) in a screw-topped Schlenk tube under Ar. Reaction mixture lasted at 80 °C in dark condition for 12 h. After evaporation of the solvent, the product was dissolve in chloroform and precipitated with ethyl ether. After washed with ethyl ether, black solid Bis-FIMG was obtained in quantitative yield. ^1H NMR (400 MHz, CDCl_3) δ 8.07 – 7.40, 7.20 – 6.49, 5.64 – 4.87, 4.87 – 4.02, 4.02 – 3.57 (m, NCH_3), 3.57 – 3.01, 1.72 – 0.75; ^{13}C NMR (100 MHz, CDCl_3) δ 54.71 – 55.04, 55.96 – 56.44, 61.34 – 61.48, 61.60 – 61.83, 63.97 – 65.26, 65.81 – 66.40, 68.01 – 69.01, 70.72 – 71.36, 72.99 – 73.55, 74.84 – 76.84, 77.10 – 77.49, 78.21 – 78.55, 125.94 – 126.08, 126.36 – 126.84, 126.98 – 127.02, 127.23 – 127.28, 135.66, 135.94, 136.16, 136.37, 136.62, 137.02, 137.45, 137.80, 138.26, 138.54, 138.88, 139.03, 139.49, 139.64, 139.80, 140.16, 140.45, 141.31, 141.82, 142.05, 142.34, 142.98, 143.48, 143.65, 143.87, 143.98, 144.17, 144.28, 144.49, 144.86, 144.93, 145.16, 145.24, 145.95, 146.32, 146.54, 146.82, 147.74, 147.97, 148.44, 148.95, 149.57, 149.62, 149.74 – 149.88, 150.80 – 150.94, 151.65 – 151.72, 151.81, 152.26, 152.63, 152.72 – 152.89, 152.94, 153.12, 154.32, 154.55, 155.46, 155.74, 156.45, 156.66, 156.69. $\text{C}_{98}\text{H}_{64}\text{I}_2\text{N}_2\text{O}_{12}$, Exact Mass = 1714.25, MS (MALDI-TOF) $[\text{C}_{98}\text{H}_{64}\text{N}_2\text{O}_{12}-2\text{I}]^+ = 1587.039$.

Bisfulleropyrrolidinium tris(methoxytriglycol)phenyl iodide (Bis-FITG) (mixture of bis-adduct regioisomers). Bis-FTG 185 mg (0.094 mmol) in chloroform (4 mL) and MeI (3 mL) in a screw-topped Schlenk tube under Ar. Reaction mixture lasted at 80 °C in dark condition for 12 h. After evaporation of the solvent, the product was dissolve in chloroform and precipitated with ethyl ether. After washed with ethyl ether, black solid Bis-FITG was obtained in quantitative yield. ^1H NMR (400 MHz, CDCl_3) δ 8.12 – 7.31, 7.18 – 6.27, 5.86 – 4.89, 4.84 – 4.43, 4.40 – 4.05 (m, NCH_3), 4.00 – 3.47, 3.45 – 3.42, 3.42 – 3.09, 1.80 – 0.71; ^{13}C NMR (100 MHz, CDCl_3) δ 54.80 – 55.45, 55.39 – 56.86, 61.30 – 61.46, 61.50 – 61.60, 61.64 – 61.75, 61.76 – 61.83, 63.50 – 63.97, 65.26 – 66.23, 68.00 – 69.03, 70.72 – 71.04, 71.06 – 71.42, 72.67 – 74.16, 74.68 – 75.24, 76.22 – 76.62, 77.10 – 77.25, 77.49 – 77.60, 77.63 – 77.83, 78.21 – 78.48, 78.56 – 78.75, 125.52 – 125.89, 126.10 – 126.33, 126.59 – 127.06, 127.15 – 127.46, 136.13, 136.47, 136.65, 137.12, 137.40, 137.80, 138.26, 138.42, 138.59, 138.85, 139.17, 139.35, 139.63, 139.85, 140.06, 140.45, 140.68, 141.48, 141.72, 142.97, 143.43, 143.65, 143.86, 143.96, 144.27, 144.44, 144.85, 144.94, 145.16, 145.26, 145.44, 145.68, 145.95, 146.27, 146.79, 147.75 – 147.98, 148.45, 148.94, 149.50, 149.64, 149.77 – 149.95, 150.55, 150.83 – 150.98, 151.21, 151.61, 151.83, 152.68, 152.76 – 152.85, 152.92, 153.19, 154.44, 154.65, 155.12 – 155.37, 155.78, 156.42, 156.50, 156.58. $\text{C}_{122}\text{H}_{112}\text{I}_2\text{N}_2\text{O}_{24}$, Exact Mass = 2242.57, MS (MALDI-TOF) $[\text{C}_{122}\text{H}_{112}\text{N}_2\text{O}_{24}-2\text{I}]^+ = 2115.067$.

1.3 Optoelectronic Characterization

Inverted Device Fabrication: Polymer solar cells were fabricated on glass substrates commercially pre-coated with a layer of indium tin oxide (ITO) with the inverted structure of ITO/ETL/PBDB-T: ITIC/MoO₃/Ag. Prior to fabrication, the substrates were cleaned using detergent, deionized water, acetone and isopropanol consecutively for every 15 min, and then treated in an ultraviolet ozone generator for 15 min. A thin layer ETL of ZnO was spin-coated onto clean ITO-coated glass substrates at 3500 rpm for 60 s and then annealed at 170 °C for 20 min, then the substrates were transferred to a glovebox. FPPI and Bis-FPPI can be dissolved into DMF of 5 mg/ml. And the FPPI/Bis-FPPI solutions were prepared by mixing with PFN-Br (0.5 mg/ml in methanol) with different volume ratios accordingly (1:0, 5:1, 1:1, 1:5 and 0:1). And then, the ETLs were spin coated into ITO substrates in glovebox. The mixture of PBDB-T: ITIC in chlorobenzene (20 mg/ml, 1:1, w/w, 0.5% DIO) was then spin-coated on the ETLs at 2500 rpm. Then the BHJ layers were annealed at 100 °C for 10 min under nitrogen atmosphere. After annealing, hole transporting layer MoO₃ (4 nm) was deposited on the active layers. Finally, silver (100 nm) was thermally evaporated through shadow masks.

Conventional Device Fabrication: The Bis-FIMG and Bis-FITG solutions in methanol were stirred overnight to spin-coating in glovebox at 2000 rpm. The ITO substrates were cleaned by ultrasonication in acetone for 30 min, followed by manual scrubbing with detergent and deionized water, then sonication in deionized water, isopropanol and ethyl alcohol for 30 min respectively. The substrates were blown dry under a nitrogen stream and immediately make ultraviolet and ozone pretreatments for 5 min. A 40 nm thick layer of PEDOT: PSS was spin-coated onto each substrate and subsequently annealed in oven at 140 °C for 20 min. The mixture of PBDB-T: ITIC in chlorobenzene (20 mg/ml, 1:1, w/w) was then spin-coated on the PEDOT: PSS layers at 2500 rpm, and then ETL solutions were spin-coated on the BHJ layer subsequently. Then the BHJ layer and ETL layer annealed at 120 °C for 10 min under nitrogen atmosphere to obtain a film thickness of approximately 100 nm. Finally, silver (100 nm) was thermally evaporated onto the ETLs through shadow masks.

Perovskite Device Fabrication: The ITO coated substrates were cleaned sequentially in detergent (2% vol Hellmenex), deionized water, acetone, and isopropanol ultrasonic bath for 15 min, respectively. After then, the substrates were dried in nitrogen flow and cleaned by UV-Ozone treatment for 20 min before using. NiO_x substrate was prepared by spin coating precursor solution (Nickel (II) nitrate hexahydrate: Ethylenediamine = 1M: 1M in ethylene glycol) on ITO glass and annealed at 300 °C for 1h, detail information could be found in other report.⁴ MAI and PbI₂ were mixed by 1:1 molar ratio in DMF and NMP (4:1) mixture with the concentration of 1.4 M. Before spin-coating the perovskite layer, the precursor solution and NiO_x substrate were heated at 70 °C. The spin-coating process was 1000 rpm for 10 s, and 4000 rpm for 30 s, and started initially after dropping the heated precursor to the heated substrate, after that 50 µl toluene was dropped at around 15 s during the second procedure, followed by annealing at 100 °C for 2 min. PCBM solution (10 mg/ml in CB) was spin-coated on perovskite at 2000 rpm for 30 s; buffer materials (dissolved in Ethanol) were spin-coated at 3000 rpm for 30 s, followed by deposited 100 nm Ag in vacuum chamber under high vacuum of 5x10⁻⁴ Pa. The device area is 0.115 cm², which is defined by the cross section of Ag and ITO.

Solar Cell Characterization: The current density-voltage (J - V) characteristic curves were recorded on the Keithley source unit under AM 1.5G 1 sun intensity illumination (100 mW cm^{-2}) by a solar simulation from Enli Technology, and the light intensity was calibrated with a standard photovoltaic reference cell. The EQE spectrum was measured using a QE-R Model of Enli Technology.

Schottky-Junction Device Fabrication and Characterization: Around 60 nm thick ETLs were spin-coated on clean ITO glass, and then deposited 100 nm Ag in vacuum chamber under high vacuum of 5×10^{-4} Pa. The J - V curves were carried out on the Keithley source unit in dark and illuminated conditions.

AFM Samples Fabrication and Characterization: The samples (ETLs on ITO glass) were fabricated same with operating conditions. Topographic and phase images of the ETL films were obtained on a VeecoMultiMode AFM in the tapping mode, and the scanning rate for a $2 \mu\text{m} \times 2 \mu\text{m}$ image size was 1.5 Hz.

UPS measurements: The UPS samples were fabricated in the experimental operating conditions. ETL materials were spin-coated on ITO glass. Ultraviolet photoemission spectrometer (UPS) measurements were conducted on an ESCALAB 250Xi (Thermo) system with a bias voltage of -9.8 eV in the ultra-high vacuum system. He I (21.2 eV) excitation lines from a helium plasma discharge lamp were employed for the UPS measurements. The instrumental resolution was 0.05 eV for UPS.

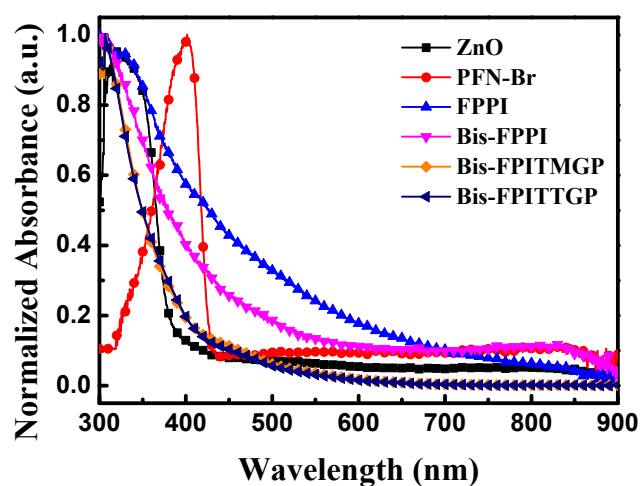


Fig. S1. Absorption spectra of ETM films atop of ITO glass substrates.

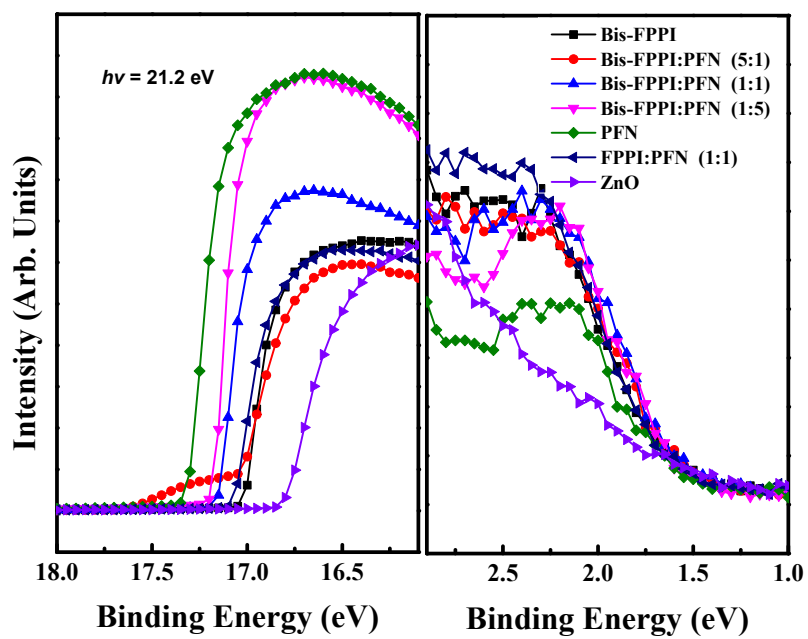


Fig. S2. UPS spectra of different ETLs covered on the ITO/glass surface, UPS He I spectra yield the valence band region of the plain surfaces, $h\nu = 21.2$ eV.

Table S1. Work function of different ETL covered on the ITO/glass surface.

ETL	Work Function (eV)
Bis-FPPI	4.22
Bis-FPPI:PFN-Br 5:1	4.17
Bis-FPPI:PFN-Br 1:1	4.07
Bis-FPPI:PFN-Br 1:5	4.03
PFN-Br	3.90
FPPI:PFN-Br 1:1	4.17
ZnO	4.43

Table S2. Photovoltaic performances based on different thickness of Bis-FPPI: PFN-Br ETLs under AM 1.5G Illumination (100 mW/cm²)

Thickness (nm)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE (%)
15	0.86	18.09	0.65	10.05
25	0.86	18.28	0.64	9.99
40	0.85	17.09	0.69	10.01
60	0.86	17.00	0.69	9.98
80	0.86	15.72	0.72	9.79

Table S3. Photovoltaic performances based on different thickness of Bis-FIMG ETLs under AM 1.5G Illumination (100 mW/cm²)

Thickness (nm)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE (%)
10	0.90	16.17	0.72	10.50
15	0.91	15.96	0.72	10.42
20	0.91	15.99	0.72	10.45
25	0.90	17.03	0.70	10.76
30	0.91	16.57	0.72	10.82
35	0.90	16.03	0.73	10.58
40	0.91	16.06	0.71	10.33
50	0.91	15.57	0.72	10.23

Table S4. Photovoltaic performances of perovskite solar cells applying Bis-FIMG and Bis-FITG as buffer layer under AM 1.5G Illumination (100 mW/cm²)

Buffer Layer	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE (%)
BCP	1.07	22.30	0.789	18.80
Bis-FIMG	1.08	22.92	0.795	19.31
Bis-FITG	1.07	22.15	0.804	19.01

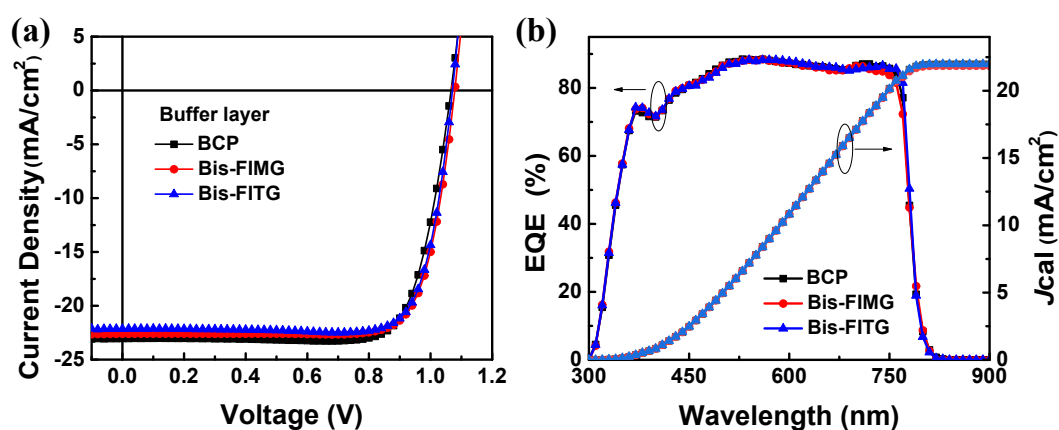


Fig. S3. (a) *J-V* curves and (b) EQE spectra of devices based on BCP, Bis-FIMG and Bis-FITG as buffer layers. (c) and (d) *J-V* curves of devices based on Bis-FIMG and Bis-FITG at varied concentrations.

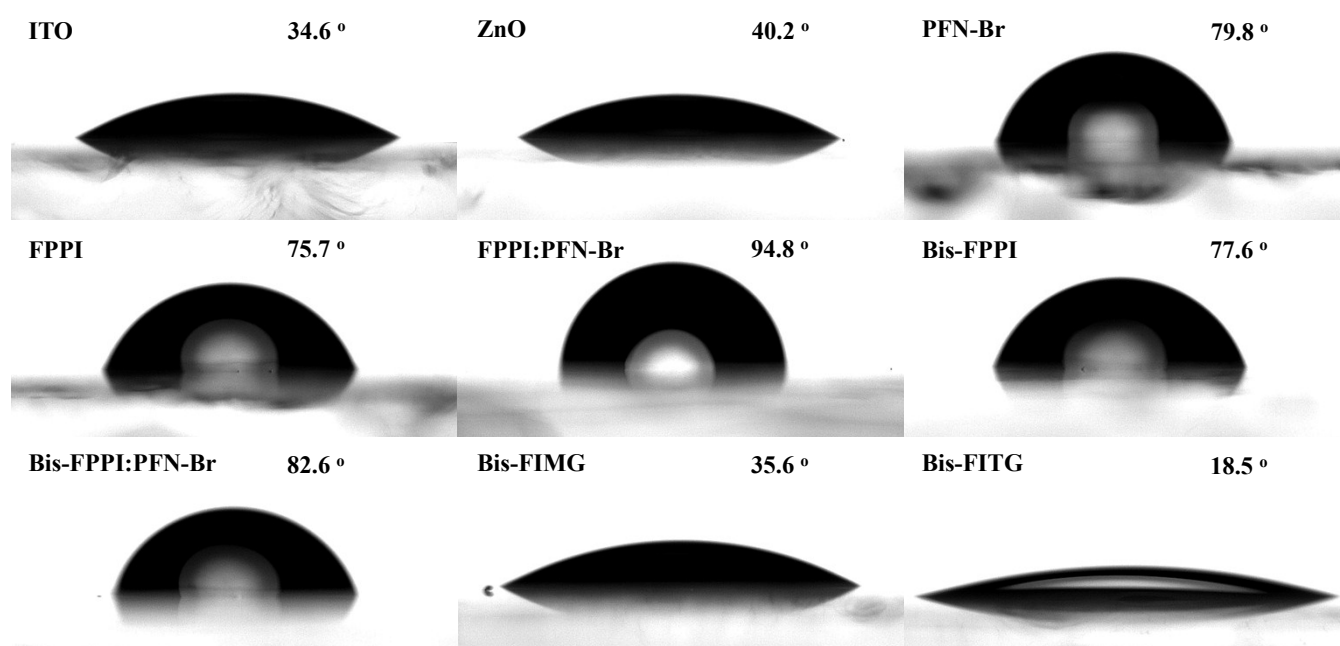


Fig. S4. Water contact angles on ITO, ZnO, PFN-Br, FPPI, FPPI: PFN-Br, Bis-FPPI, Bis-FPPI: PFN-Br, Bis-FIMG and Bis-FITG are 34.6°, 40.2°, 79.8°, 75.7°, 94.8°, 77.6°, 82.6°, 35.6° and 18.5°, respectively.

Table S5. Photovoltaic performances of perovskite solar cells applying FPPI and FPPI: PFN-Br as ETLs under AM 1.5G Illumination (100 mW/cm²)

ETL	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
FPPI	0.69	14.91	0.47	4.89
FPPI: PFN-Br	0.77	14.32	0.50	5.52

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