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Supporting information

Halogen Substitution of Perinone Based Cathode Interfacial Materials for High-Efficiency Inverted Perovskite Solar Cells

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1. Experimental

1.1. Materials.

Unless otherwise stated, all chemicals were purchased from Aladdin, Energy Chemical and Sinopharm Chemical Reagent Co., Ltd. 2,6-Dibromo-1,4,5,8-naphthalenetetracarboxylic dianhydride were purchased from Derthon Co., Ltd. Cesium iodide (CsI), formamidinium iodide (FAI), methylammonium chloride (MACl), lead iodide (PbI_2), lead bromide ($PbBr_2$) and methylammonium bromide (MABr) were purchased from Advanced Election Technology Co., Ltd (China). [2-(3,6-Dimethoxy-9H-carbazol-9-yl)ethyl] phosphonic acid (MeO-2PACz) was purchased from TCI (Japan). The solvents, including dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and chlorobenzene (CB) were purchased from Sigma-Aldrich.

1.2. Synthesis.

1-Bromo-3,5-bis((2-ethylhexyl)oxy)benzene (1):

5-Bromobenzene-1,3-diol (5.00 g, 26.4 mmol), potassium carbonate (34.54 g, 250.0 mmol) and sodium iodide (496 mg, 2.6 mmol) were mixed in anhydrous acetonitrile (200 mL) for a while, and then 2-ethylhexyl bromide (14.48 g, 75.0 mmol) was added and the reaction mixture was stirred at 90 ^{o}C for 12 h under argon. After cooling to room temperature, the solvent was removed under reduced pressure to obtain crude product. The product was then purified by column chromatography on silica gel using pertroleum ether (PE) as eluent afforded a colorless oil (10.00 g, 92%) ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 6.64 (s, 2 H), 6.37 (s, 1 H), 3.76-3.81 (m, 4 H), 1.66-1.73 (m, 2 H), 1.39-1.45 (m, 4 H), 1.30-1.32 (m, 12 H), 0.83-0.90 (m, 12 H).

(3,5-Bis((2-ethylhexyl)oxy)phenyl)tributylstannane (2):

Compound **1** (4.13 g, 10.0 mmol) was dissolved in degassed anhydrous tetrahydrofuran (100 mL) under argon atmosphere, and n-butyl lithium solution (5 mL, 12.0 mmol, 2.4 M) was added dropwise at -78 ^{o}C. After stirring for 1 h, tributyltin chloride (3.90 g, 12.0 mmol) was added and the reaction mixture was stirred at room temperature for another 8 h, and then deionized water was added to quench the reaction. After extracting by PE for three time, the organic phase was dried over Na_2SO_4. Subsequently, the solvent was removed with rotary evaporator, and 7.80 g of colorless oil was obtained without further purification. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 6.60 (s, 2 H), 6.42 (s, 1 H), 3.82-3.87 (m, 4 H), 1.72-1.77 (m, 2 H), 1.44-1.52 (m, 12 H), 1.32-1.38 (m, 16 H), 1.06-1.08 (m, 6 H), 0.92-0.95 (m, 21 H)

Tetrabutyl 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylate (3):

2,6-Dibromo-1,4,5,8-naphthalenetetracarboxylic dianhydride (2.13 g, 6.4 mmol) and n-butyl alcohol (2.87 g, 38.7 mmol) were dissolved in anhydrous acetonitrile under argon atmosphere. And then 1,8-diazabicyclo[5.4.0]undecane-7-ene (5.89 g, 38.7 mmol) was added into the mixture. After stirring at room temperature for 0.5 h, 1-bromobutane (5.30 g, 38.7 mmol) was added and refluxed overnight. The pH of the solution was adjusted to neutral with dilute hydrochloric acid. After extracting by dichloromethane (DCM) for three time, the organic phase was dried over Na_2SO_4. Subsequently, the solvent was removed under reduced pressure to obtain crude product. The product was then further purified by column chromatography on silica gel using DCM:PE (1:1) as eluent to afford a yellow solid (2.60 g, 70%). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 8.05 (s, 2 H), 4.30-4.32 (t, 8 H), 1.75-1.80 (m, 8 H), 1.44-1.52 (m, 8 H), 0.96-1.00 (m, 12 H).

Tetrabutyl 2-(3,5-bis((2-ethylhexyl)oxy)phenyl)-6-(3-((3-ethylheptyl)oxy)-5-((2-ethylhexyl)oxy)phenyl)naphthalene-1,4,5,8-tetracarboxylate (4):

Compound **2** (5.46 g, 8.7 mmol), tetrakis(triphenylphosphine)palladium (168 mg, 0.1 mmol), and **3** (2.00 g, 2.9 mmol) were mixed in 50 mL anhydrous toluene under argon atmosphere. After refluxing for 24 h, 50 mL deionized water was added to quench the reaction. After extracting by DCM for three time, the organic phase was dried over Na_2SO_4. Subsequently, the solvent was removed under reduced pressure to obtain crude product. The product was then further purified by column chromatography on silica gel using DCM:PE (1:2) as eluent to afford a yellow oil (1.81 g, 78%). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 7.93 (s, 2 H), 6.48 (s, 6 H), 4.26-4.29 (t, 4 H), 3.94-3.97 (t, 4 H), 3.79-3.85 (m, 8 H), 1.73-1.78 (m, 4 H), 1.41-1,52 (m, 16 H), 1.30-1.38 (m, 32 H), 1.02-

1.1 (m, 6 H), 0.83-0.98 (m, 24 H), 0.78-0.8 (t, 6 H).

4-(3,5-bis((2-ethylhexyl)oxy)phenyl)-9-(3-((2-ethylhexyl)oxy)-5-(heptan-3-yloxy)phenyl)isochromeno[6,5,4-def]isochromene-1,3,6,8-tetraone (5):

Compound **4** (4.67 g, 3.9 mmol) and potassium hydroxide (8.96 g, 160.0 mmol) was dissolved in 100 mL methyl alcohol and stirred in 85 ^{o}C for 24 h. After cooling down to room temperature, dilute hydrochloric acid was added to adjust the pH to 7, resulting in a yellow precipitate. The precipitation was dried in a vacuum drying oven for 4 h, and then dissolved with acetic acid. After stirred in acetic acid at 110 ℃ for another 24 h, the solvent was removed under reduced pressure to obtain crude product. The product was then further purified by column chromatography on silica gel using DCM:PE (1:1) as eluent to afford a red solid (2.98 g, 83%). ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 8.79 (s, 2 H), 6.61 (s, 2 H), 6.52 (s, 4 H), 3.84-3,90 (m, 8 H), 1.72-1.76 (m, 4 H), 1.42-1.48 (m, 8 H), 1.30-1.37 (m, 24 H), 0.87-0.95 (m, 24 H).

7,16-bis(3,5-bis((2-ethylhexyl)oxy)phenyl)-2,3,11,12-tetrafluorobenzo[lmn]benzo[4,5]imidazo[2,1-b]benzo[4,5]imidazo[2,1-i][3,8]phenanthroline-8,17-dione (NX-F):

Compound **5** (1.30 g,1.4 mmol), 4,5-difluorobenzene-1,2-diamine (600 mg, 4.2 mmol), $SnCl_2 \cdot 2H_2O$ (32 mg, 0.1 mmol) and $Zn(AcO)_2 \cdot 2H_2O$ (31 mg, 0.1 mg) was dissolved in 50 mL propionic acid under argon atmosphere. After refluxing for 24 h, 50 mL deionized water was added to quench the reaction. And then the organic phase was dried over Na_2SO_4 after extracting by DCM for three times. Subsequently, the solvent was removed under reduced pressure to obtain crude product. The product was then further purified by column chromatography on silica gel using DCM:PE (2:3) as eluent to afford a red isomer mixed solid (718 mg, 63%).

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 8.80-8.93 (t, 2 H), 8.25-8.36 (m, 2 H), 7.36-7.65 (m, 2 H), 6.64-6.7 (t, 4 H), 6.58-6.70 (d, 2 H), 3.86-3.92 (m, 8 H), 1.72-1.78 (m, 4 H),1.40-1.51(m, 16 H), 1.29-1.33 (m, 16H), 0.88-0.97 (m, 24 H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ = 160.0, 158.0, 150.6 149.0, 148.1, 144.0, 141.3, 139.5, 136.8, 126.6, 123.8, 123.0, 108.8, 107.5, 104.5, 104.3 101.7, 70.8, 39.4, 30.5, 29.1, 23.9, 23.1, 14.1, 11.1. TOF-MS: Exact Mass for $C_{70}H_{81}F_4N_4O_6$ $[M+H]^+$: 1149.6014; found: 1149.6156

7,16-bis(3,5-bis((2-ethylhexyl)oxy)phenyl)-2,3,11,12-tetrachlorobenzo[lmn]benzo[4,5]imidazo[2,1-b]benzo[4,5]imidazo[2,1-i][3,8]phenanthroline-8,17-dione (NX-Cl):

Compound **5** (0.65 g, 0.7 mmol), 4,5-dichlorobenzene-1,2-diamine (300 mg, 2.1 mmol), $SnCl_2{\cdot}2H_2O$ (16 mg, 0.1 mmol) and $Zn(AcO)_2{\cdot}2H_2O$ (15 mg, 0.1 mg) was dissolved in 30 mL propionic acid under argon atmosphere. After refluxing for 24 h, 50 mL deionized water was added to quencher the reaction. And then the organic phase was dried over Na_2SO_4 after extracting by DCM for three time. Subsequently, the solvent was removed under reduced pressure to obtain crude product. The product was then further purified by column chromatography on silica gel using DCM:PE (1:1) as eluent to afford a red isomer mixed solid (576 mg, 68%).

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ = 8.88-8.92 (d, 2 H), 8.57-8.60 (d, 2 H), 7.68-7.92 (d, 2 H), 6.66 (s, 4 H), 6.61 (d, 2 H), 3.85-3.92 (m, 8 H), 1.72-1.78 (m, 4 H),1.38-1.58 (m, 16 H), 1.27-1.36 (m, 16H), 0.88-0.97 (m, 24 H). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ = 160.7, 158.6, 149.9, 148.5 148.2, 144.6, 141.2, 136.4, 131.9, 126.7, 122.8, 122.2, 117,1, 107.3, 106.2, 101.8, 101.2, 70.8, 39.4, 30.5, 29.1, 23.9, 23.1, 14.1, 11.1. TOF-MS: Exact Mass for $C_{70}H_{81}Cl_4N_4O_6$ $[M+H]^+$: 1215.4802; found: 1215.4858

1.3. Measurements

^1H NMR and ^{13}C NMR spectra were measured on Bruker 600 MHz NMR spectrometer, and tetramethyl silane (TMS) was used as the internal reference. Time-of-flight mass spectrometer (4600 LC-Q-TOF) was used to measure the molecule weight. UV-vis absorption spectra were measured via ultraviolet spectrophotometer (723S, Lengguang Tech Limited Company). Thermogravimetric analysis (TGA) was measured by thermogravimetric analyzer (TG 209 F1, Netzsch). The energy levels were measured by cyclic voltammetry (CV) using an electrochemical workstation (CHI660D) with a three-electrode system. The electrolyte was oxygen-free acetonitrile solution containing 0.1 M tetra-n-butylammonium hexafluorophosphate, Ag/AgCl was used as the reference electrode and Pt wire was used as the counter electrode. Ferrocene/ferrocenium (Fc/Fc^+) was used as the internal standard whose redox potential was 0.38 V vs. Ag/AgCl. And the $E_{LUMO} = -(E_{red} + 4.42)$ (eV), the $E_{HOMO} = E_{LUMO} - E_g$. The stead PL and TRPL were measured via fluorescence spectrophotometer (FL3-111, HORIBA). The AFM and SEM were test in atomic force microscope (3100 SPM, Vecco) and scanning electron microscope (Verios G4 UC, Thermo scientific). EIS and Mott-Schottky Line were measured by Controlled Intensity Modulation Photochemical Spectrometer (Zennium pro PP212, Zahner). Contact angles were measured by contact angle goniometer (DCAT21, Ningbo Jinmao).

1.4. Device fabrication

The glass/ITO substrates (2×2 cm^2, Rs≤15 Ω sq^{-1}, and transmittance ≥86%) were sequentially cleaned by sonication with detergent, distilled water, acetone, and IPA for 20 min. Then the cleaned substrates were treated in O_2 plasma for 15 min. Afterwards, 60 μL MeO-2PACz solution (0.5 mg/mL in ethanol) was spin-coated onto the ITO substrate at 3000 rpm for 30 s, then annealing at 100 °C for 10 min in N_2-filled glove box. For perovskite precursor preparation, 3.8 mg MABr, 12.9 mg $PbBr_2$, 15.0 mg MACl, 22.5mg CsI, 227.0 mg FAI and 720.0 mg PbI_2 were dissolved in 1 mL DMF: DMSO (6:1, v/v) mixed solvent and stirred for 2 h. For perovskite films fabrication, 100 μL perovskite precursor was spin-coated on the as-prepared substrates with MeO-2PACz at 5000 rpm for 30 s, and 150 μL CB was dropped onto the center at 13 s before the end of spin-coated. After waiting for 1 minute when the perovskite film to become darker, the substrates were transferred to the hotplate and annealed at 120 ^{o}C for 20 min. After cooling down to room temperature, 50 μL NX-F or NX-Cl solution (0.5-5 mg/mL in CB) were spin-coated at 3000 rpm for 30 s. Finally, 25 nm C_{60}, 6 nm BCP and 100 nm silver electrode were thermally evaporated respectively, under high vacuum (< 3×10^{-4} Pa). The active area of all devices was 0.09 cm^{-2}.

The electron-only devices with structure of ITO/SnO_2/perovskite/CIMs/C_{60}/Ag were fabricated as follows: First, SnO_2 (15% in H_2O colloidal dispersion) was diluted to 5% using deionized water and then sonicated for 20 min. Soon after, the solution was spun cast onto the O_2 plasma treated substrates at 3000 rpm for 30 s, then annealed at 150 °C for 30 min in air. The remaining layers were fabricated as above.

The electron-only devices with structure of ITO/ZnO_2/CIMs/Ca/Al were fabricated as follows: The 1.5 M ZnO precursor solution was spin-coated on the O_2 plasma treated substrates at 4000 rpm for 30 s and then annealed at 250 °C for 30 min. After the films were cooled down, NX-F and NX-Cl solution (10 mg mL^{-1}, CB) were spin-coated at 1500 rpm for 30 s without additional annealing. Finally, Ca (20 nm) and Al (100 nm) films were evaporated on top of the active layer as the electrode.

1.5. Device characterization

The current density-voltage characteristics was measured via Keithley 2400 source meter under the illumination of AM 1.5G (100 mW cm^{-2}), which calibrated by Sol3A class AAA solar simulator (Newport, model 94023A, 2×2 in.). The external quantum efficiency (EQE) was conducted by EQE system (Enlitech, QE-R310).

The trap density was studied with the structure of ITO/SnO_2/Perovskite/ETL/C_{60}/Ag and depicted by using equation (Eq S1):

$$N_{traps} = \frac{2\varepsilon_0 \varepsilon_r V_{TEF}}{eL^2} \qquad (1)$$

where e was the elemental charge, V_{TFL} was the onset voltage of the trap-filled limit region, and L was the thickness of perovskite.

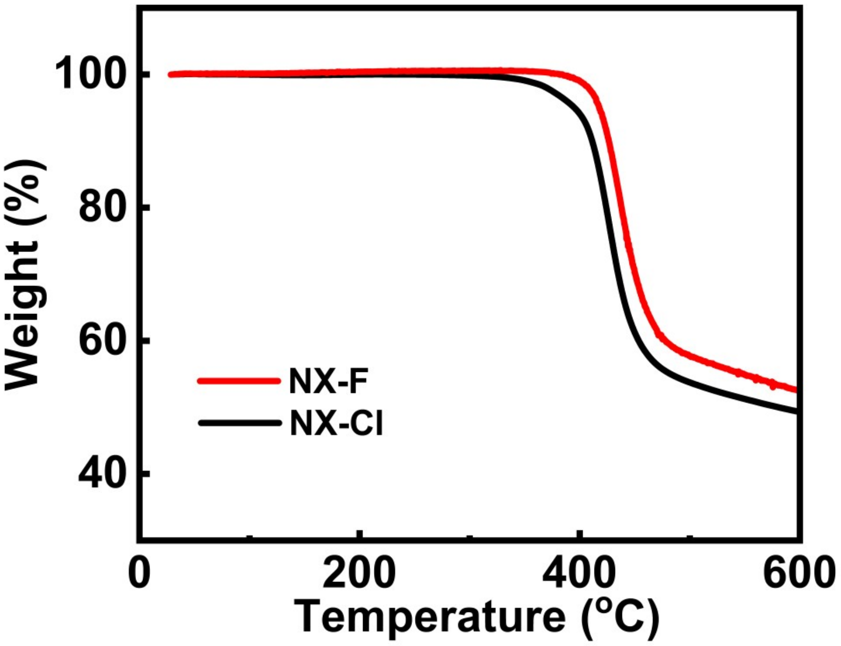

Fig. S1. TGA of NX-F and NX-Cl

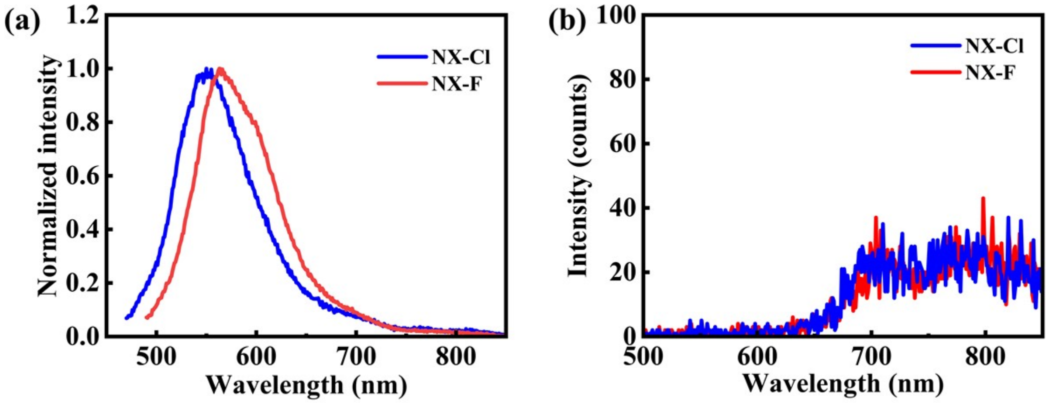

Fig. S2. (a) PL (b) phosphorescence spectra of NX-F and NX-Cl solution.

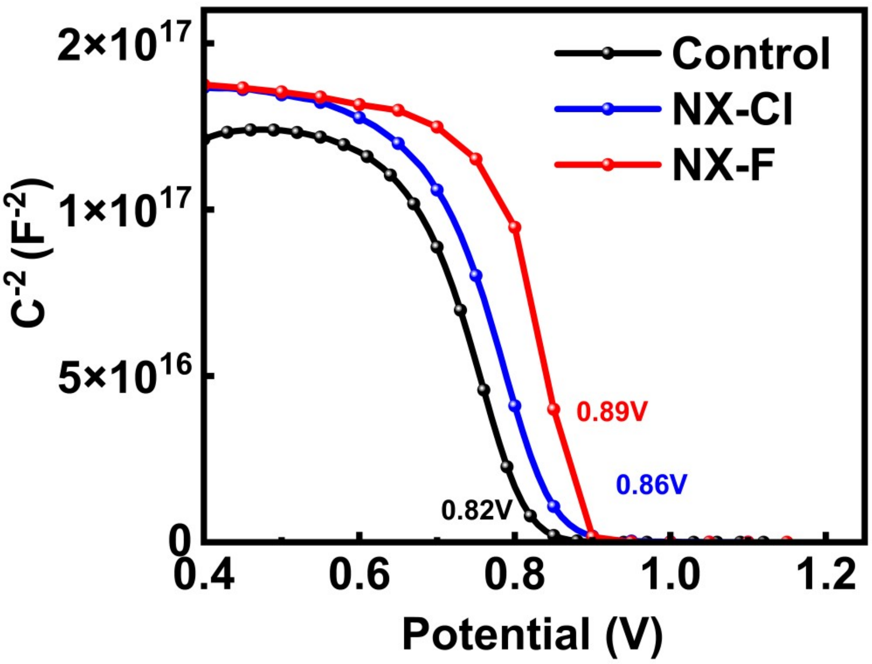

Fig. S3. The Mott-Schottky plots of the PSCs with and without CIM.

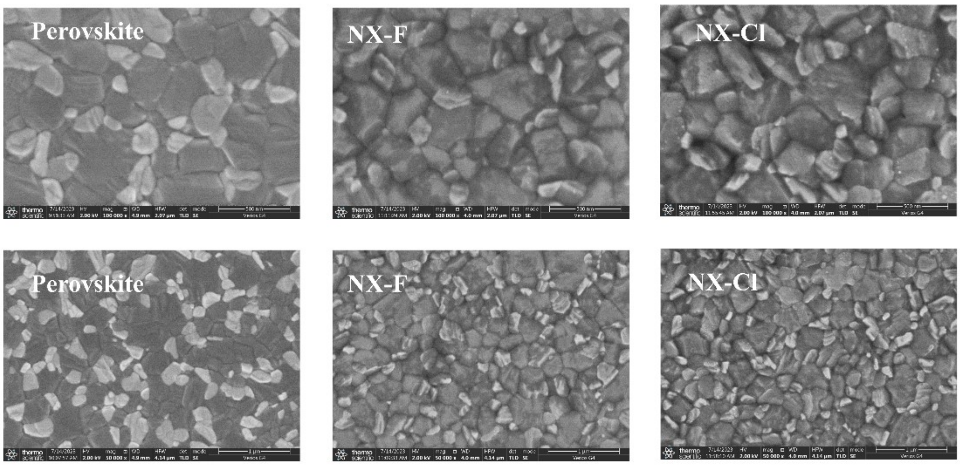

Fig. S4. The top-viewing SEM image of the pure perovskite film, perovskite/NX-F film and perovskite/NX-Cl film.

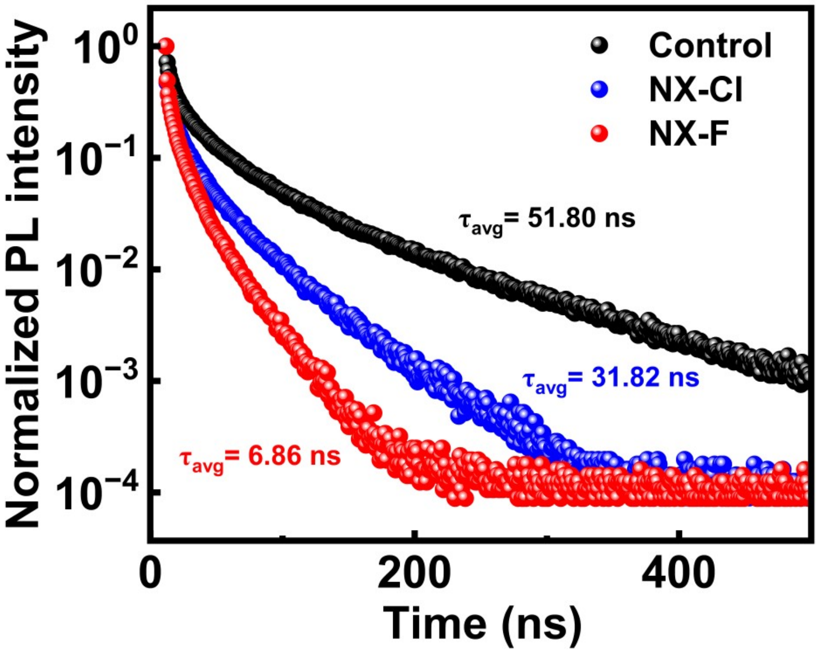

Fig. S5. The TRPL spectra of pure perovskite film, perovskite/NX-F film and perovskite/NX-Cl film.

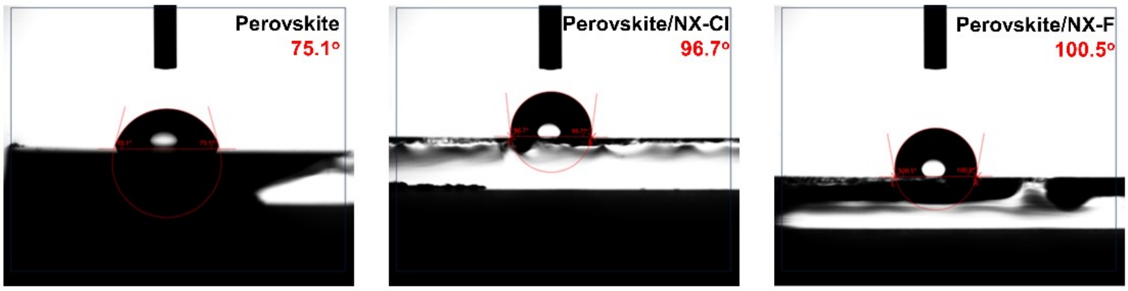

Fig. S6. The water contact angle image of perovskite covered with different CIMs.

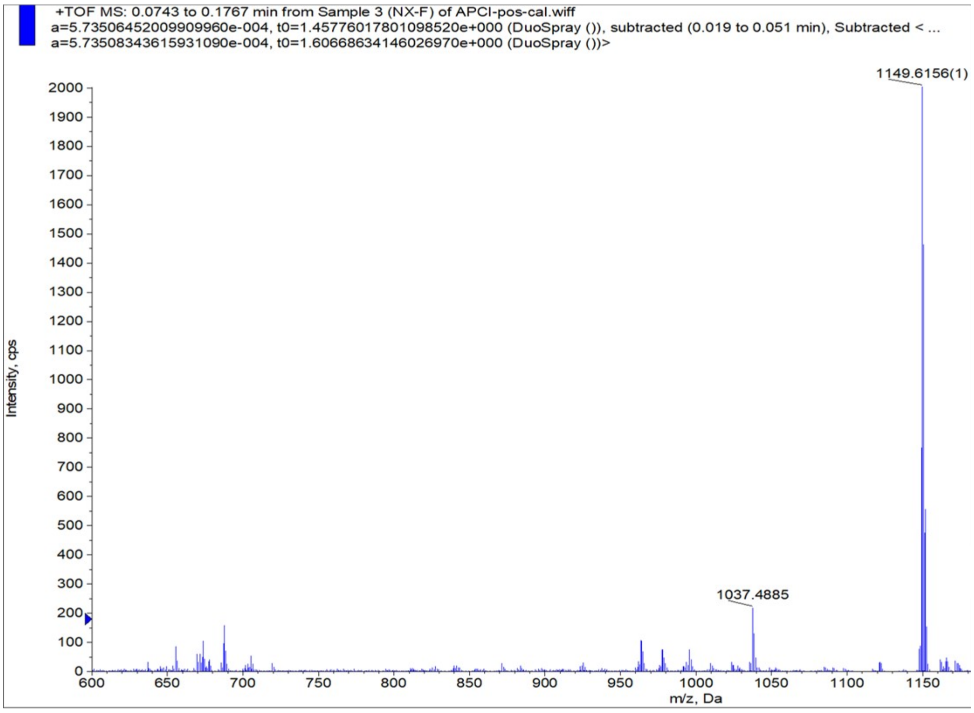

Fig. S7. TOF-MS spectra of NX-F.

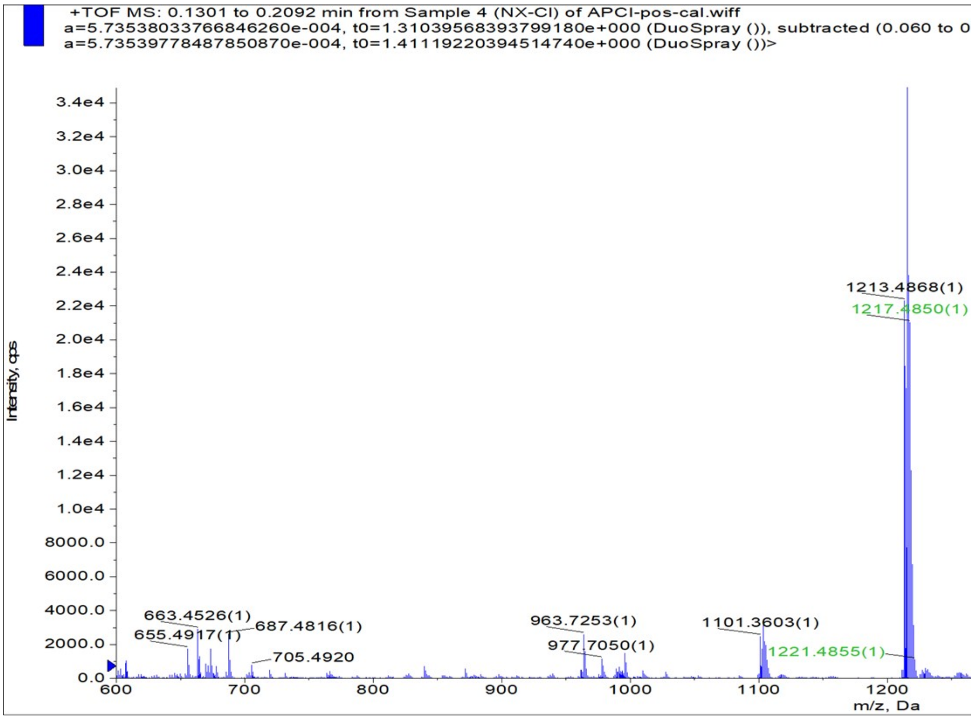

Fig. S8. TOF-MS spectra of NX-Cl.

Table S1. Concentration optimization of NX-F devices.

Concentration (mg/mL)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
0.5	1.109	23.32	79.11	20.46
1.0	1.128	23.50	79.88	21.18
3.0	1.095	23.75	73.13	19.02
5.0	1.087	24.28	63.36	16.72

Table S2. Concentration optimization of NX-Cl devices.

Concentration (mg/mL)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE(%)
0.5	1.108	22.92	78.97	20.06
1.0	1.117	22.91	79.12	20.25
3.0	1.084	23.00	70.81	17.66
5.0	1.073	23.10	65.53	16.20