

Supporting Information

Steric hindrance driven passivating cations for stable perovskite
solar cells with an efficiency over 24%

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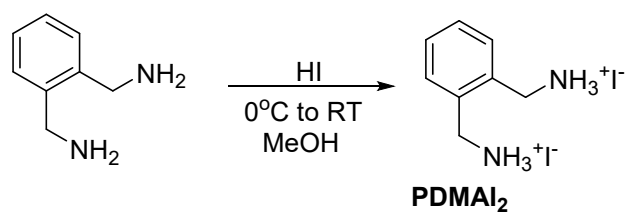
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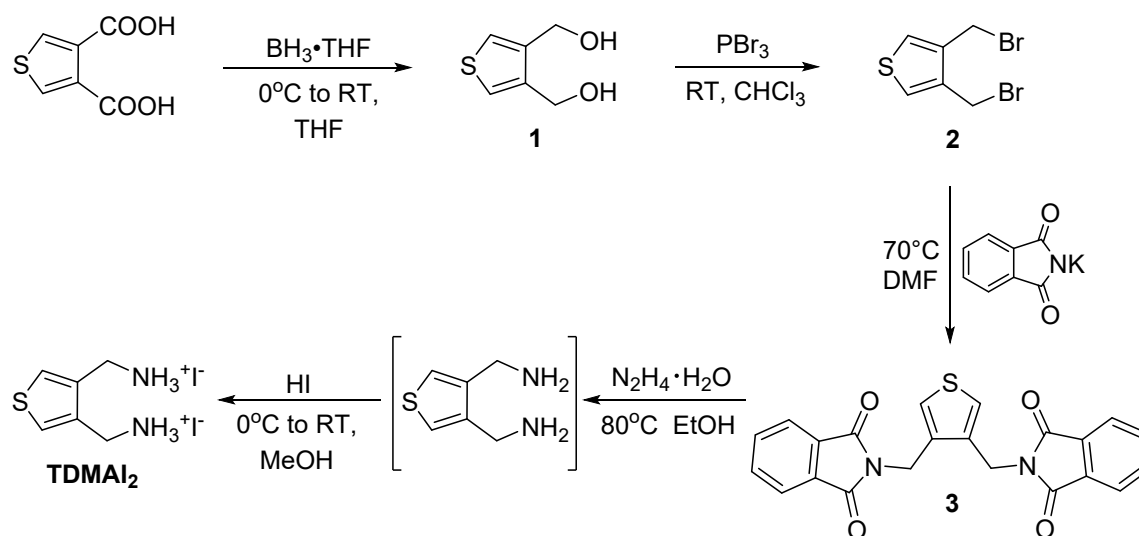
Synthesis

Chemicals required for the synthesis were purchased from Sigma-Aldrich and TCI Europe and used as received without additional purification. ^1H NMR spectra were recorded at 400 MHz on a Bruker Avance III spectrometer with a 5 mm double resonance broad band BBO z-gradient room temperature probe, ^{13}C NMR spectra were collected using the same instrument at 101 MHz. The chemical shifts, expressed in ppm, were relative to tetramethylsilane (TMS). All the NMR experiments were performed at 25 °C. Reactions were monitored by thin-layer chromatography on ALUGRAM SIL G/UV254 plates and developed with UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å, Aldrich) was used for column chromatography. Elemental analysis was performed with an Exeter Analytical CE-440 elemental analyser, Model 440 C/H/N/. MS were recorded on Waters SQ Detector 2 Spectrometer using electrospray ionization (ESI) technique.



1,2-Phenylenedimethanamonium iodide (PDMAI₂)

1,2-Phenylenedimethanamine (0.5 g, 3.67 mmol) was dissolved in MeOH (20 mL), and a reaction flask was placed in an ice bath. HI (57 %, 1 mL, 8 mmol) was added dropwise under argon atmosphere. The flask was covered with foil to avoid light exposure and stirred for 24 hours at RT. Afterwards, reaction mixture was distilled, and the obtained crude was dissolved in CH₃OH and precipitated into 20-fold excess of Et₂O. The product was filtered, washed with Et₂O to yield 1.29 g of greyish powder (90%). ^1H NMR (400 MHz, DMSO-*d*₆) δ 8.08 (s, 6H), 7.53 (s, 4H), 4.17 (s, 4H). ^{13}C NMR (101 MHz, DMSO) δ 132.71, 130.15, 129.03. Elemental analysis calcd %: C 24.51%, H 3.60%, N 7.15%; found C 24.31 %, H 3.71%, N 7.09%. C₈H₁₄I₂N₂[M⁺] exact mass = 391.925, MS (ESI) = 390.85.



Thiophene-3,4-diyldimethanol (1)

Thiophene-3,4-dicarboxylic acid (6.8 g, 40 mmol) was dissolved in 54 mL THF and cooled down to 0 °C, 0.1 M $\text{BH}_3 \cdot \text{THF}$ solution in THF (104 mL, 104 mmol) was added dropwise. After stirring for 24 h at room temperature, the mixture was cooled down to 0 °C and quenched with dropwise addition of 1:1 (v:v) THF:water solution (50 mL). Resulting mixture was extracted with EtOAc (3 x 50 mL). Combined organic extracts were dried over anhydrous Na_2SO_4 and filtered, the solvent was evaporated *in vacuo* and the crude product was chromatographed on silica gel using 30% acetone in hexane to give **1** as white powder. Yield 3.4 g (59%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.26 (s, 2H), 5.06 (s, 2H), 4.46 (s, 4H). ^{13}C NMR (101 MHz, DMSO) δ 141.71, 122.25, 58.09. Elemental analysis calcd %: C 49.98%, H 5.59%; found C 50.21%, H 5.73%.

3,4-Bis(bromomethyl)thiophene (2)

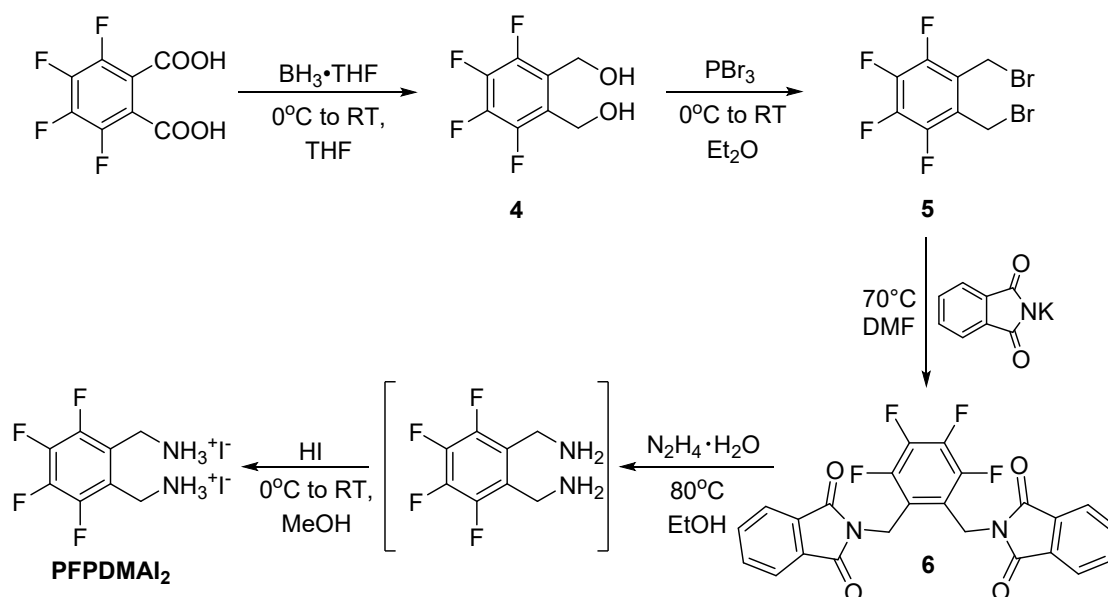
1 (2.9 g, 19.4 mmol) was dissolved in dry chloroform (450 mL) and PBr_3 (5.6 mL, 52.9 mmol) was slowly added dropwise at room temperature. After 1 h, the reaction was quenched with water (50 mL). Resulting mixture was extracted with chloroform (3 x 50 mL). Combined organic extracts were dried over anhydrous Na_2SO_4 and filtered, the solvent was evaporated *in vacuo* and the crude product was chromatographed on silica gel using hexane to give **2** as yellowish oil. Yield 5.1 g (94%). ^1H NMR (400 MHz, CDCl_3-d) δ 7.35 (s, 2H), 4.63 (s, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 136.62, 127.31, 25.69.

2,2'-(Thiophene-3,4-diyldis(methylene))bis(isoindoline-1,3-dione) (3)

2 (2.5 g, 9 mmol) and potassium phthalimide (6.85 g, 37 mmol) were dissolved in DMF (50 mL). After heating at 70 °C for 18 h, water (40 mL) was added to the reaction mixture and formed white precipitate was filtered and washed with water to yield 3.4 g of **3** (94%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.89 (d, *J* = 10,9 Hz, 8H), 7.31 (s, 2H), 4.86 (s, 4H). ¹³C NMR (101 MHz, DMSO) δ 167.69, 135.09, 134.56, 131.70, 123.27, 35.33. Elemental analysis calcd %: C 65.66%, H 3.51%, N 6.96%; found C 65.4%, H 3.6%, N 7.05%. C₂₂H₁₄N₂O₄SNa [M⁺] exact mass = 425.047, MS (ESI) = 425.07.

Thiophene-3,4-diylidimethanamonium iodide (TDMAI₂)

Compound **3** (1.8 g, 4.47 mmol) was dissolved in EtOH (50 mL) and hydrazine monohydrate (0.67 mL, 13 mmol) was added to the solution. After heating at 80 °C for 3 h, the reaction mixture is cooled down to room temperature and formed phthalhydrazide side product is separated by filtration. Next, the filtrate is distilled, and the obtained crude was used for the next step without further purification. The amine (0.6 g, 4.22 mmol) was dissolved in MeOH (30 mL) and a reaction flask was placed in an ice bath. HI (57 %, 1.22 mL, 9.28 mmol) was added dropwise under argon atmosphere. The flask was covered with foil to avoid light exposure and stirred for 24 hours at RT. Afterwards, reaction mixture was filtered, and the filtrate distilled. The obtained crude was dissolved in CH₃OH and precipitated into 20-fold excess of Et₂O. The product was filtered, washed with Et₂O to yield 1.47 g of yellowish powder (88%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.05 (s, 6H), 7.64 (s, 2H), 4.07 (q, *J* = 5,7 Hz, 4H). ¹³C NMR (101 MHz, DMSO) δ 133.31, 126.91, 35.77. Elemental analysis calcd %: C 18.1%, H 3.04%, N 7.04%; found C 18.27%, H 3.09%, N 6.89%. C₆H₁₂I₂N₂S[M⁺] exact mass = 397.881, MS (ESI) = 396.89.



(Perfluoro-1,2-phenylene)dimethanol (4)

Perfluoro phthalic acid (4.2 g, 17.7 mmol) was dissolved in 40 mL THF and cooled down to 0 °C, 0.1 M $\text{BH}_3 \cdot \text{THF}$ solution in THF (53 mL, 53 mmol) was added dropwise. After stirring for 24 h at room temperature, the mixture was cooled down to 0 °C and quenched with dropwise addition of 1:1 (v:v) THF:water solution (50 mL). Resulting mixture was extracted with DCM (3 x 50 mL). Combined organic extracts were dried over anhydrous Na_2SO_4 and filtered, the solvent was evaporated *in vacuo* and the crude product was chromatographed on silica gel using 20% acetone in hexane to give **4** as yellowish oil. Yield 2.42 g (65%). ^1H NMR (400 MHz, CDCl_3 -*d*) δ 4.82 (s, 4H), 2.88 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.09, 144.64, 141.54, 139.07, 123.59, 54.99. Elemental analysis calcd %: C 45.73%, H 2.88%; found C 45.49%, H 2.81%. $\text{C}_8\text{H}_6\text{F}_4\text{O}_2[\text{M}^+]$ exact mass = 210.03, MS (ESI) = 208.92.

1,2-Bis(bromomethyl)-3,4,5,6-tetrafluorobenzene (5)

Compound **4** (2 g, 9.5 mmol) was dissolved in dry diethyl ether (55 mL) and PBr_3 (2.71 mL, 28.5 mmol) was slowly added dropwise at 0 °C. After stirring 3 h at room temperature, the reaction was quenched with water (30 mL). Resulting mixture was extracted with EtOAc (3 x 50 mL). Combined organic extracts were dried over anhydrous Na_2SO_4 and filtered, the solvent was evaporated *in vacuo* and the crude product was chromatographed on silica gel using hexane to give

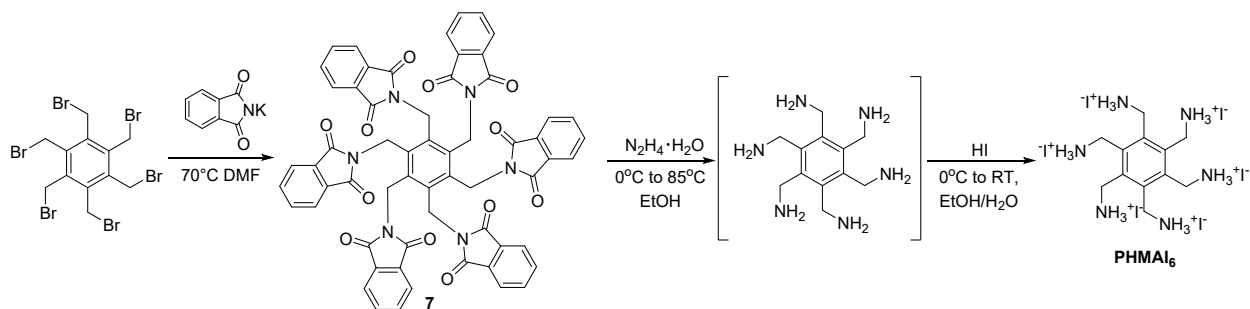
5 as yellowish oil. Yield 2.32 g (73%). ¹H NMR (400 MHz, CDCl₃-*d*) δ 4.61 (s, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 147.48, 145.07, 142.15, 139.65, 121.16, 19.10.

2,2'-((Perfluoro-1,2-phenylene)bis(methylene))bis(isoindoline-1,3-dione) (6)

5 (1 g, 3 mmol) and potassium phthalimide (2.22 g, 12 mmol) were dissolved in DMF (20 mL). After heating at 70 °C for 18 h, water (50 mL) was added to the reaction mixture and formed white precipitate was filtered and washed with water to yield 1.18 g of **6** (85%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.82 (s, 8H), 5.07 (s, 4H). ¹³C NMR (101 MHz, DMSO) δ 167.32, 134.56, 131.46, 123.17, 32.40. Elemental analysis calcd %: C 61.55%, H 2.58%, N 5.98%; found C 61.64%, H 2.69%, N 6.1%. C₂₄H₁₂F₄N₂O₄Na[M⁺] exact mass = 491.053, MS (ESI) = 491.07.

(Perfluoro-1,2-phenylene)dimethanaminium iodide (PFPDMAI₂)

Compound **6** (0.6 g, 1.27 mmol) was dissolved in EtOH (20 mL) and hydrazine monohydrate (0.19 mL, 3.83 mmol) was added to the solution. After heating at 80 °C for 2 h, the reaction mixture is cooled down to room temperature and formed phthalhydrazide side product is separated by filtration. Next, the filtrate is distilled, and the obtained crude was used for the next step without further purification. The amine (0.2 g, 0.9 mmol) was dissolved in MeOH (10 mL) and a reaction flask was placed in an ice bath. HI (57 %, 0.28 mL, 2.13 mmol) was added dropwise under argon atmosphere. The flask was covered with foil to avoid light exposure and stirred for 24 hours at RT. Afterwards, reaction mixture was distilled. The obtained crude was dissolved in CH₃OH and precipitated into 20-fold excess of Et₂O. The product was filtered, washed with Et₂O to yield 0.4 g of white powder (89%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.13 (s, 6H), 4.25 (s, 4H). ¹³C NMR (101 MHz, DMSO) δ 147.52, 145.01, 141.27, 138.79, 118.61, 32.64. Elemental analysis calcd %: C 20.71%, H 2.17%, N 6.04%; found C 20.41%, H 2.28%, N 6.19%. C₈H₁₀F₄I₂N₂[M⁺] exact mass = 463.887, MS (ESI) = 462.96.



2,2',2'',2''',2''''-(Benzene-1,2,3,4,5,6-hexaylhexakis(methylene))hexakis(isoindoline-1,3-dione) (7)

1,2,3,4,5,6-Hexakis(bromomethyl)benzene (2 g, 3 mmol) and potassium phthalimide (5.56 g, 30 mmol) were dissolved in DMF (80 mL). After heating at 70 °C for 18 h, water (100 mL) was added to the reaction mixture and formed white precipitate was filtered and washed with water to yield 2.76 g of **6** (89%). Spectral data is in agreement with the values reported elsewhere.^[1]

Benzene-1,2,3,4,5,6-hexaylhexamethanamonium iodide (PHMAI₆)

To the suspension of compound **7** (1.5 g) in EtOH (50 mL), hydrazine monohydrate (0.625 mL, 12.5 mmol) was added. After heating at 85 °C for 48 h, reaction mixture is cooled down to room temperature and formed phthalhydrazide side product is separated by filtration. Next, the filtrate is distilled, and the obtained crude was used for the next step without further purification. The obtained amine was dissolved in EtOH (50 mL) and a reaction flask was placed in an ice bath. 1 N HI aq. (20 mL) was added, and insoluble solid was separated by filtration and the filtrate was distilled. The obtained crude was dissolved in water and precipitated into 20-fold excess of MeOH. The product was filtered, washed with EtOH to yield 0.5 g of white powder (49%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.13 (s, 18H), 4.38 (s, 12H). ¹³C NMR (101 MHz, DMSO) δ 136.95, 37.07. Elemental analysis calcd %: C 14.13%, H 2.97%, N 8.24%; found C 13.97%, H 3.19%, N 7.88%. C₁₂H₃₀I₆N₆[M⁺] exact mass = 1019.680, MS (ESI) = 1019.22.

Materials for PSCs fabrication

Titanium diisopropoxide bis(acetylacetonate) (TAA), 4-*tert*-butylpyridine (*t*-BP), tin(IV) chloride pentahydrate (SnCl₄), bis(trifluoromethane) sulfonamide lithium salt (Li-TFSI), and FK209

[tris(2-(1*H*-pyrazol-1-yl)-4-*tert*-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl) imide)], chlorobenzene, dimethylsulphoxide (DMSO), dimethylformamide (DMF) and isopropanol (IPA) were supplied from Sigma-Aldrich. Mesoporous TiO₂ (30-NRT), FAI, MAI, PbBr₂ and MACl were purchased from GreatCell Solar. PbI₂ were purchased from TCI. Spiro-OMeTAD was purchased from Merck. All of the purchased chemicals were used as received without further purification.

Device fabrication

The chemically etched FTO glass (Nippon Sheet Glass) was cleaned with a detergent solution, deionized water, acetone, and isopropanol. For the compact TiO₂ (c-TiO₂) layer, TAA solution in ethanol (1.2 mL of TAA in 20 mL of anhydrous isopropanol) was sprayed at 450°C, and further heating for 1 h at 450°C was done. Mesoporous TiO₂ paste was diluted with ethanol with a ratio of 1:10 and coated on top of the c-TiO₂ substrate at a speed of 3000 rpm for 20 s and finally heated at 500°C for 20 min. The tin oxide layer was formed by dissolving SnCl₄ in deionized water at a concentration of 12 µL/mL and spin-coated on the mesoporous TiO₂ layer at a speed of 3000 rpm for 20 s, and finally heated at 190°C for 60 min. Next, the perovskite solutions (the ratio of PbI₂, MAI, FAI, PbBr₂ was 1: 0.16: 0.84: 0.11, the molar of PbI₂ was 1.38 mmol/mL, the MACl was 0.305 mmol/mL which added to the perovskite solution. The solvent was composed of DMSO and DMF (1:4) and was successively spin-coated on the substrates at 1000 rpm for 10 s and 5000 rpm for 30 s, respectively. 200 µL of chlorobenzene was dropped over 10 s at 5000 rpm. The perovskite films were annealed at 150 °C for 10 min. The synthetic 2D cations salts (dissolved in IPA) were spin-coating at 4000 rpm for 20 s and followed heating the films 10 min under 100°C. The HTM solution was prepared by dissolving 80 mg of Spiro-OMeTAD (Merck) in 1 mL of chlorobenzene. As additives, 19 µL of Li-TFSI from the stock solution (520 mg in 1 mL of acetonitrile), 14 µL of FK209 (375 mg in 1 mL of acetonitrile), and 32 µL of *t*-BP were added. The HTM layers were formed by spin-coating the solution at 4000 rpm for 20 s and followed by the deposition of the 70 nm-thick Au electrode. All the preparative work to deposit perovskite and Spiro-OMeTAD was carried out in an N₂ filled glove box.

Devices and films Characterization

The film morphology was investigated by using a high-resolution scanning electron microscope (SEM) (Merlin, Zeiss) equipped with a GEMINI II column and a Schottky Field Emission gun. Images were acquired with an In-Lens Secondary Electron Detector. For the PL measurements, samples were excited with a 408 nm pulsed laser (MDL 300, PicoQuant) with $40 \mu\text{m cm}^2$ pulse energy density. Current-voltage characteristics were recorded by applying an external potential bias to the cell while recording the generated photocurrent with a digital source meter (Keithley Model 2400). The light source was a 450 W Xenon lamp (Oriol) equipped with a SchottK113 Tempax sunlight filter (Prazisions Glas & Optik GmbH) to match the emission spectrum of the lamp to the AM1.5G standard. Before each measurement, the exact light intensity was determined using a calibrated Si reference diode equipped with an infrared cutoff filter (KG3, Schott). The cells were masked with an active area of 0.09 cm^2 . IPCE spectra were recorded as a function of wavelength under a constant white light bias of 10 mW cm^2 supplied by an array of white light-emitting diodes. The excitation beam from a 300 W xenon lamp (ILC Technology) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd) and chopped at 2 Hz. The signal was recorded using a Model SR830 DSP Lock-In Amplifier (Stanford Research Systems). XRD was performed using a D8 Advance diffractometer (Bruker AXS) model.

DFT calculations

The DFT calculations are performed by using the CASTEP package codes.^[2] The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional is employed as the density functional.^[3] The self-consistent field (SCF) convergence criterion of $5 \times 10^{-6} \text{ eV/atom}$ was adopted to the geometry optimization and electronic computation, and the total energy convergence tolerance and force tolerance were set to be $1 \times 10^{-4} \text{ eV/atom}$, $5 \times 10^{-2} \text{ eV \AA}^{-1}$, respectively. The cutoff energy was set as 580 eV and the Monkhorst-Pack k-point mesh is $2 \times 2 \times 1$.

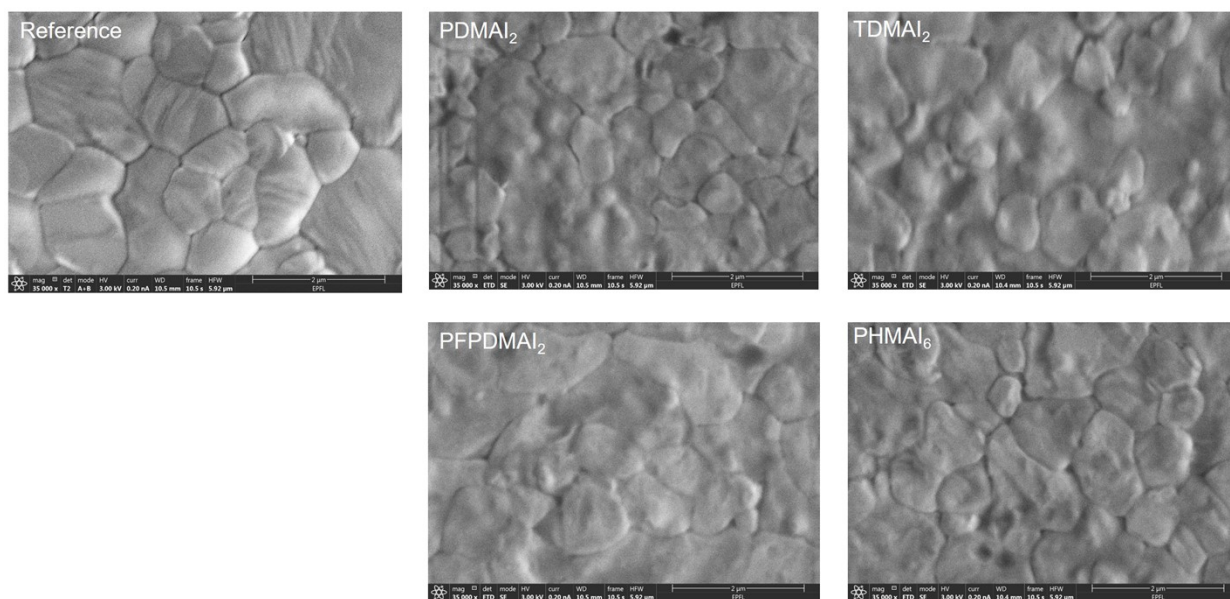


Figure S1. The surface SEM of perovskite films with or without the passivation salt modification.

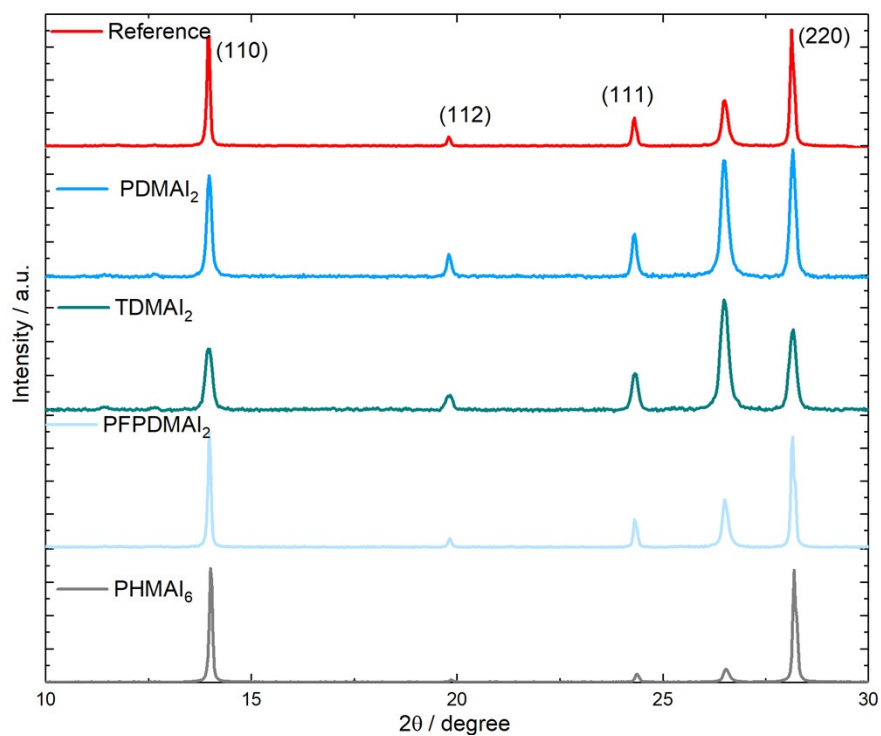


Figure S2. The compared XRD of the perovskite films with or without the passivation salt modification.

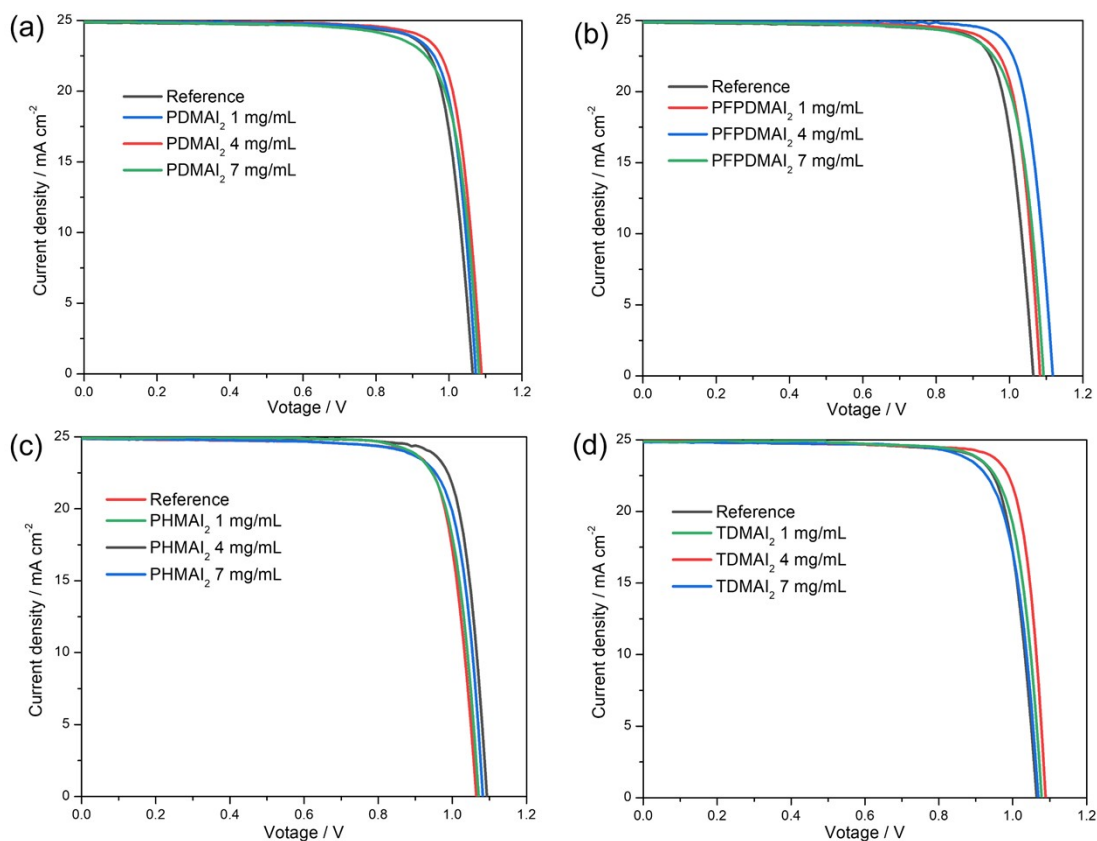


Figure S3. The J - V curves of PSCs based on synthesized passivating salts using different concentrations.

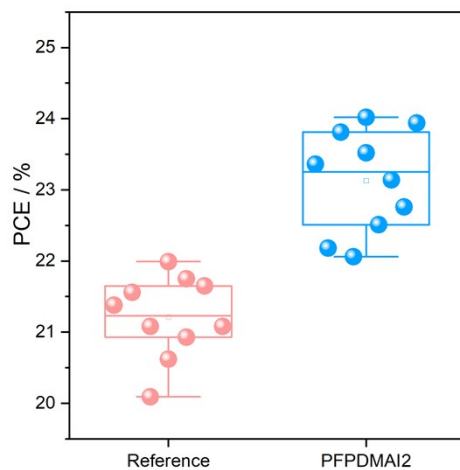


Figure S4. The statistical efficiency of reference PSCs and **PFPDMAI₂**-passivated.

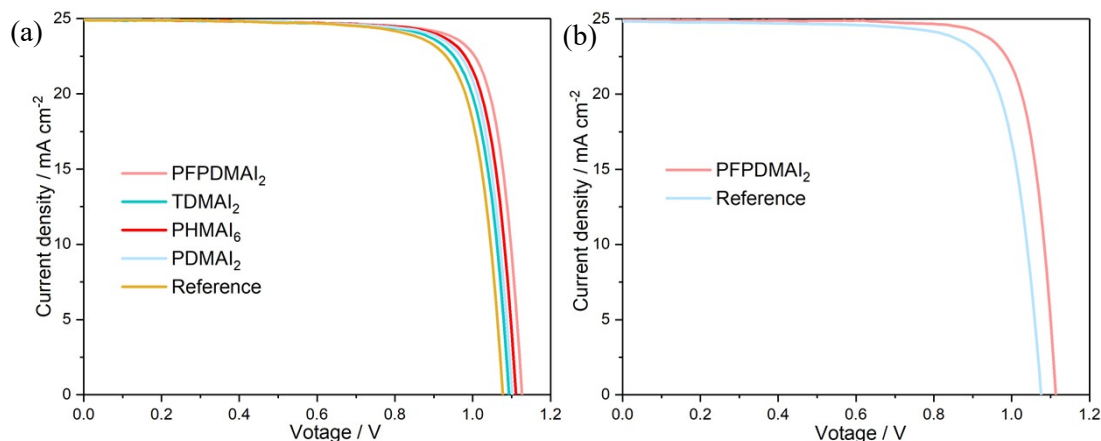


Figure S5. (a) The J - V curves of PSCs based on various passivating cations for the maximum power point tracking (MPPT) stability measurements; (b) The J - V curves of PSCs with/without the **PFPDMAI₂** cation passivation for the air stability measurements.

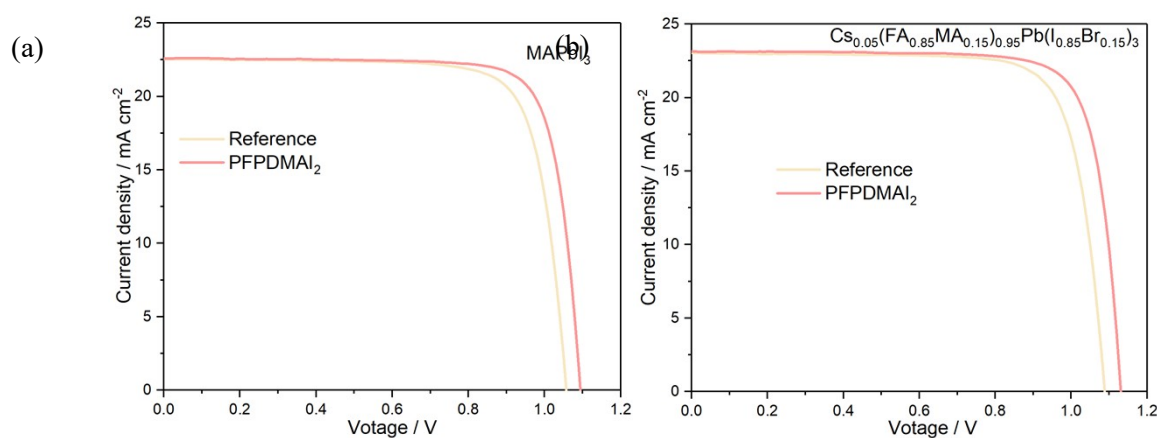


Figure S6. (a) The J - V curves of PSCs with/without the **PFPDMAI₂** cation passivation for the MAPbI₃ perovskite; (b) The J - V curves of PSCs with/without the **PFPDMAI₂** cation passivation for the Cs_{0.05}(FA_{0.85}MA_{0.15})_{0.95}Pb(I_{0.85}Br_{0.15})₃ perovskite.

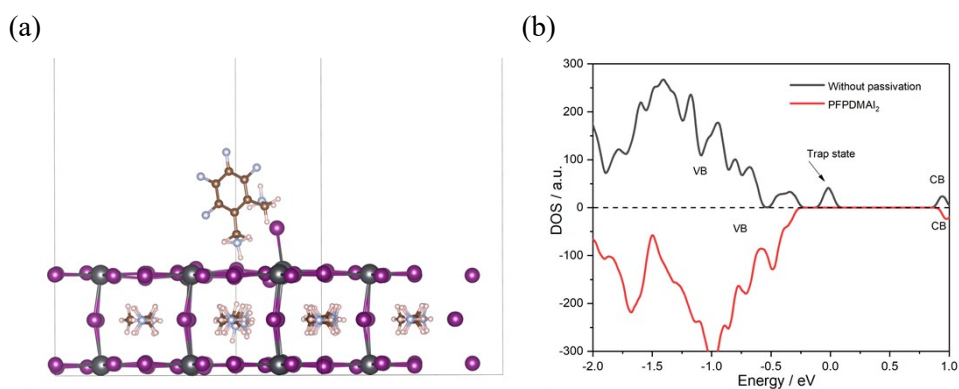


Figure S7. (a) the optimized geometry of PFPDMAI_2 cation interacted with the PbI_3^- anti-defects of perovskite surface; (b) the DOS of defected perovskite surface with/without the PFPDMAI_2 passivation.

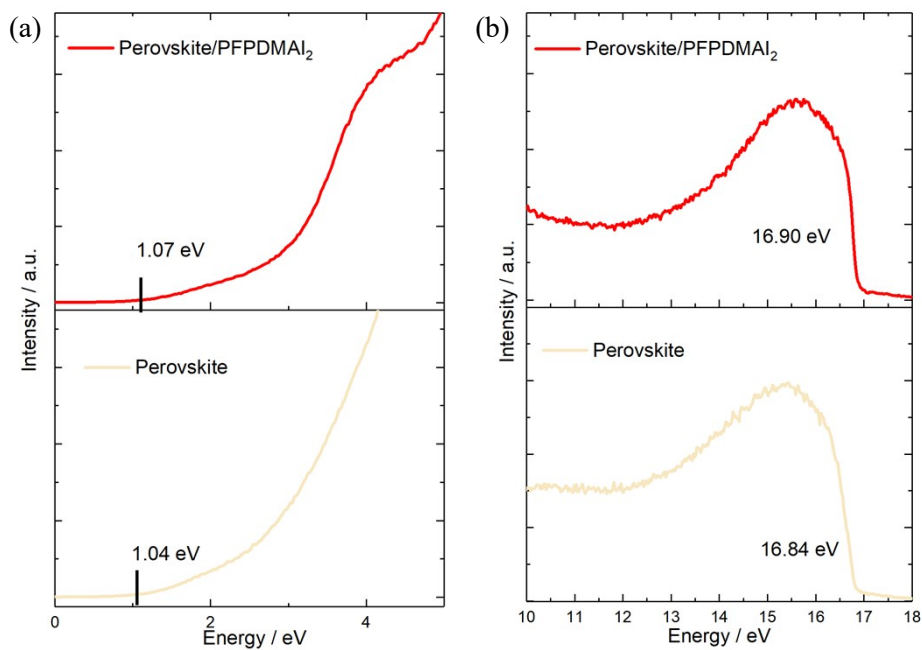


Figure S8. The onset (a) and cutoff (b) energy region of UPS based on perovskite and perovskite/ PFPDMAI_2 films.

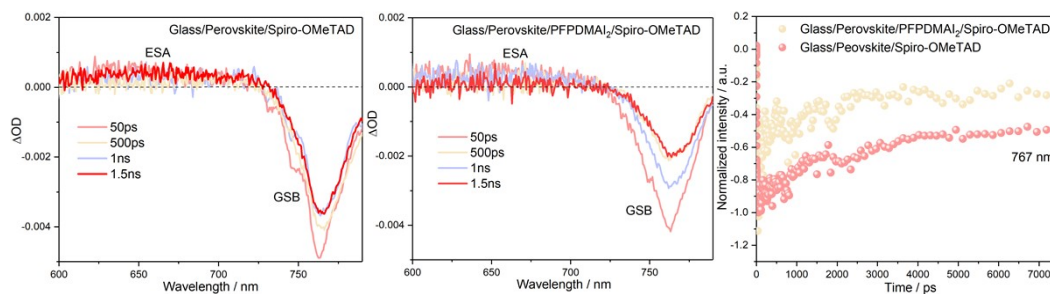


Figure S9. (a) Transient absorption spectra of Glass/Perovskite/Spiro-OMeTAD film in a range of 50-1500 ps; (b) transient absorption spectra of Glass/Perovskite/**PFPDMAI₂**/Spiro-OMeTAD film in a range of 1-5000 ps; (c) normalized kinetic traces for photobleaching probed at 767 nm based on Glass/Perovskite/Spiro-OMeTAD and Glass/Perovskite/**PFPDMAI₂**/Spiro-OMeTAD films

Table S1. The detailed photovoltaic parameters of PSCs passivated with or without **PFPDMAI₂**.

ID	scan direction	J_{SC} , [mA cm ⁻²]	V_{OC} , [V]	FF	PCE, [%]
PFPDMAI₂	R	24.99	1.154	83.3	24.02
	F	25.02	1.137	82.3	23.41
Reference	R	24.93	1.093	80.7	21.99
	F	24.98	1.069	79.4	21.20

Table S2. The detailed photovoltaic parameters of PSCs with or without the passivation salt modification under the various concentrations.

Devices	Concentrations [mg/mL]	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF /%	PCE [%]
Reference		24.86	1.063	80.2	21.19
PHMAI₆	1	24.91	1.07	80.5	21.45
PHMAI₆	4	24.97	1.093	81.5	22.24
PHMAI₆	7	24.88	1.081	80.2	21.57
PDMAI₂	1	24.91	1.074	80.5	21.53
PDMAI₂	4	24.94	1.089	81.0	21.99
PDMAI₂	7	24.88	1.081	78.4	21.08
PFPDMAI₂	1	24.92	1.082	80.8	21.78
PFPDMAI₂	4	24.98	1.117	81.3	22.68
PFPDMAI₂	7	24.89	1.093	79.2	21.54
TDMAI₂	1	24.89	1.078	80.2	21.51
TDMAI₂	4	24.92	1.088	81.1	21.98
TDMAI₂	7	24.83	1.069	79.3	21.04

Table S3. Fitting parameters of *bi*-exponential decay function in TRPL of Glass/Perovskite with or without the **PFPDMAI₂** modification.

Films	Fraction A ₁	τ_1 (ns)	Fraction A ₂	τ_2 (ns)	Average decay time τ (ns) ^a
FTO/Perovskite	75.2%	18.7	24.8%	177.7	139.3
FTO/Perovskite/ PFPDMAI₂	70.3%	27.5	29.7%	321.7	272.3

^a Average decay time is calculated according to the equation: $\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.

Table S4. The detailed photovoltaic parameters of PSCs based various passivating cations for the maximum power point tracking (MPPT) stability measurements.

Devices	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF /%	PCE [%]
Reference	24.90	1.076	78.3	20.97
PHMAI₆	24.94	1.112	79.8	22.13
PDMAI₂	24.95	1.101	79.1	21.73
TDMAI₂	24.90	1.092	78.6	21.37
PFPDMAI₂	24.93	1.126	80.3	22.54

Table S5. The detailed photovoltaic parameters of PSCs with/without the **PFPDMAI₂** cation passivation for the air stability measurements.

Devices	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF /%	PCE [%]
Reference	24.83	1.074	77.6	20.69
PFPDMAI₂	24.93	1.114	80	22.21

Table S6. The detailed photovoltaic parameters of PSCs with/without the **PFPDMAI₂** cation passivation for the MAPbI₃ perovskite

Devices	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF /%	PCE [%]
Reference	22.54	1.057	77.8	18.53
PFPDMAI₂	22.59	1.094	80.1	19.79

Table S7. The detailed photovoltaic parameters of PSCs with/without the **PFPDMAI₂** cation passivation for the $\text{Cs}_{0.05}(\text{FA}_{0.85}\text{MA}_{0.15})_{0.95}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3$ perovskite

Devices	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF [%]	PCE [%]
Reference	23.03	1.088	78	19.54
PFPDMAI₂	23.13	1.131	79.6	20.73

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