# Alkylammonium bis(trifluoromethylsulfonyl)imide as a dopant in the hole-transporting layer for efficient and stable perovskite solar cells

Youngwoong Kim[a, †], Geunjin Kim[a, †], Eun Young Park[a], Chan Su Moon[a], Seung Joo Lee[a], Jason J. Yoo[a], Seongsik Nam[a, b], Jino Im[c], Seong Sik Shin[a, b], Nam Joong Jeon[a, *], and Jangwon Seo[a, d, *]

[a]Division of Advanced Materials, Korea Research Institute of Chemical Technology (KRICT), Daejeon 34114, Republic of Korea

[b]SKKU Advanced Institute of Nanotechnology (SAINT) and Department of Nanoengineering, Sungkyunkwan University, Suwon 16419, Republic of Korea

[c]Chemical Data-Driven Research Center, Korea Research Institute of Chemical Technology (KRICT), Daejeon 34114, Republic of Korea

[d]Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

[†]Y. Kim and G. Kim contributed equally to this work.

Email: njjeon@krict.re.kr, jwseo@kaist.ac.kr

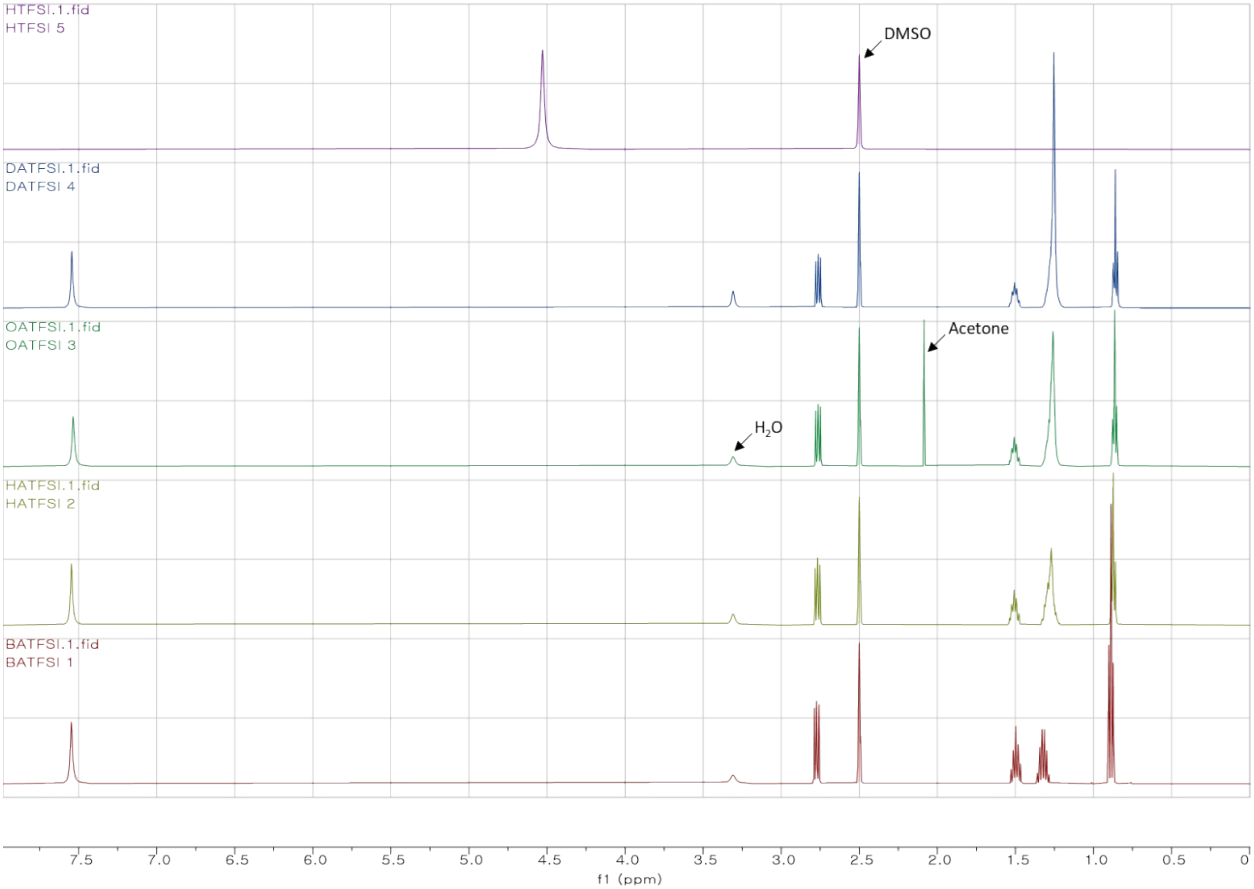



**Fig. S1.** $^{1}$H NMR spectrum of ionic liquid dopants

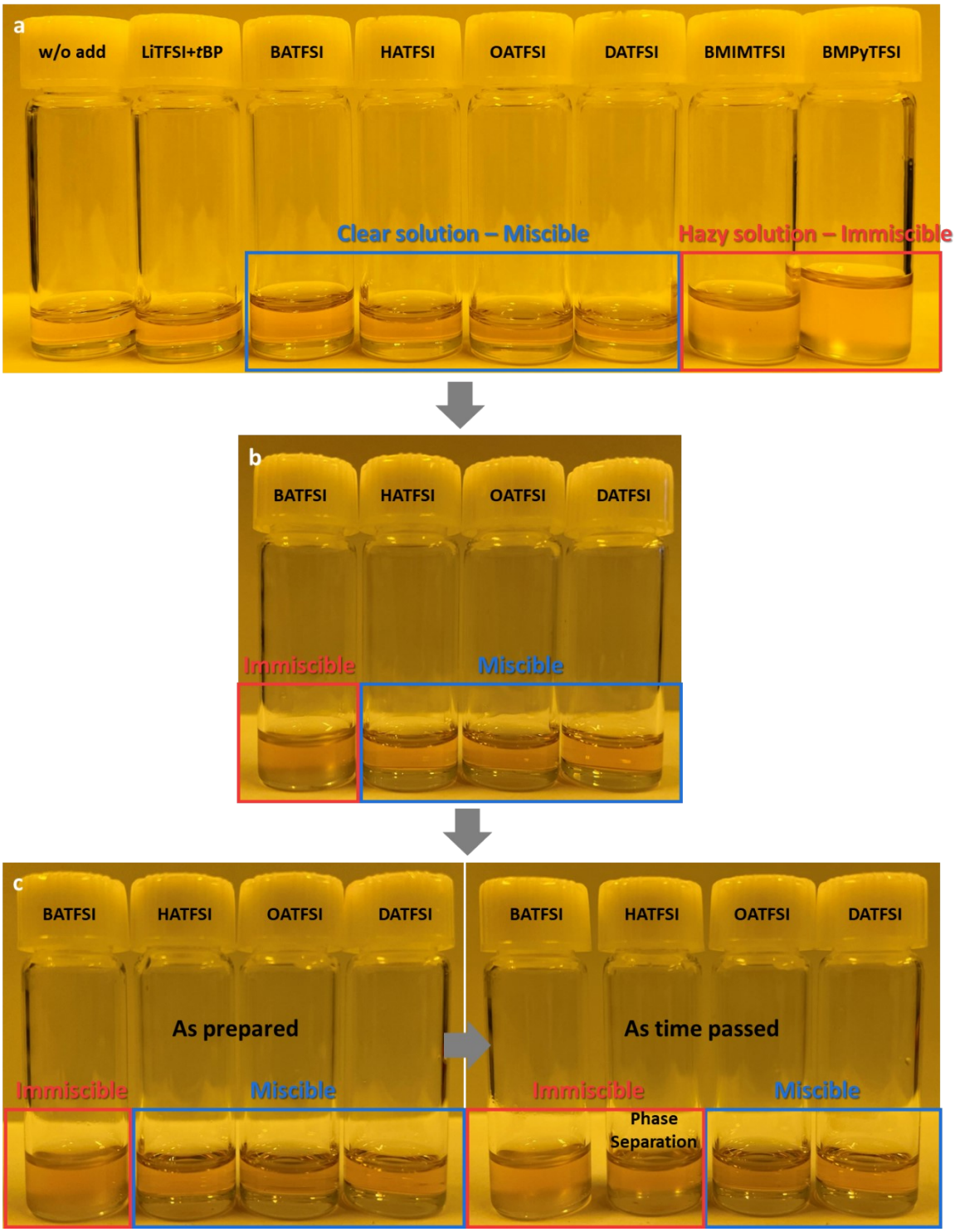



**Fig. S2.** Photographs of PTAA solutions (a) without dopant or with LiTFSI+*t*BP and 9.75 mM of IL dopants, (b) 24.37 mM of IL dopants, and (c) 80.41 mM of IL dopants

| Dopant concentration (mM)[a] | BATFSI | HATFSI | OATFSI | DATFSI |
|---|---|---|---|---|
| 9.75 | O | O | O | O |
| 24.37 | X | O | O | O |
| 60.92 | X | O | O | O |
| 80.41 | X | X | O | O |
| 121.84 | X | X | O | O |
| 243.67 | X | X | O | O |
| 304.59 | X | X | X | X |

**Table S1**. Miscibility test of alkylammonium TFSIs in PTAA solutions

[a)]The solutions are also containing PTAA at 10mg $ml^{-1}$.

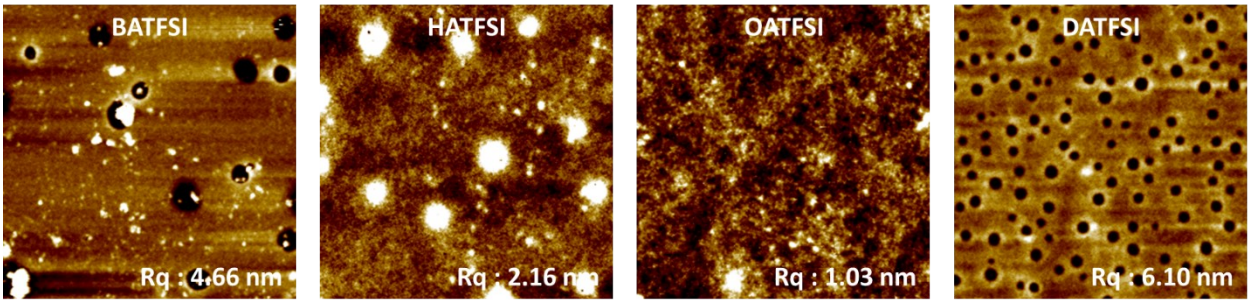



**Fig. S3.** AFM images (5 μm × 5 μm) of PTAA containing the same concentration of alkylammonium TFSI dopants with different alkyl chain lengths

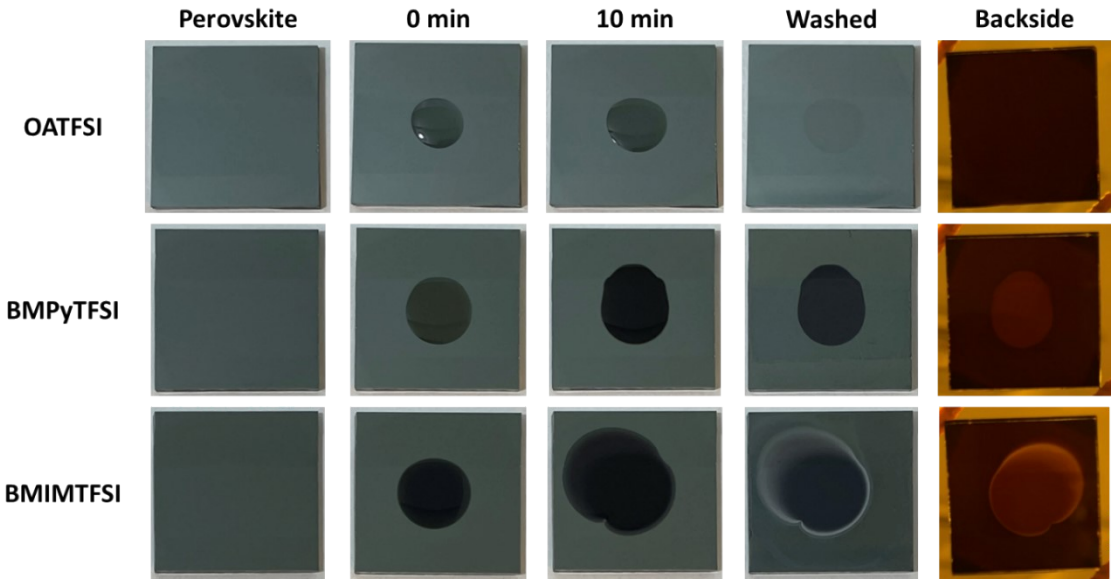



**Fig. S4.** Photographs of perovskite layers with droplets of OATFSI, BMPyTFSI, and BMIMTFSI

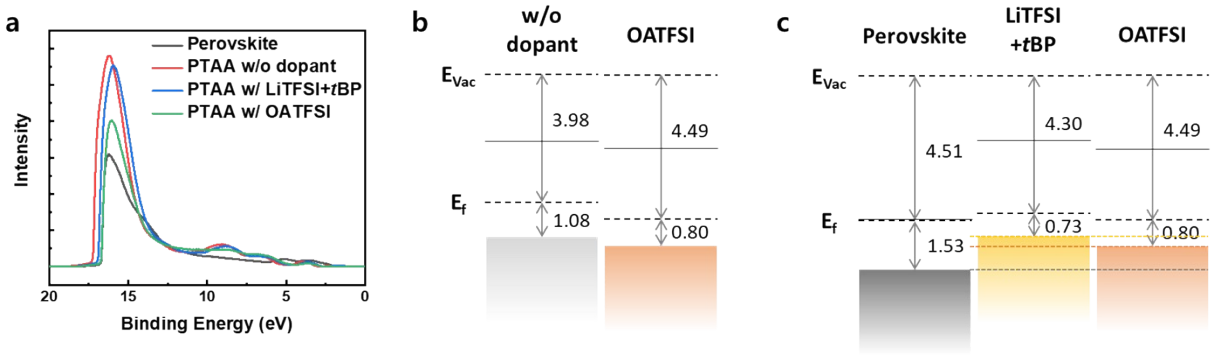



**Fig. S5.** (a) UPS spectra for perovskite, PTAA with or without various dopants, (b) change of energy level for PTAA in present/absence of OATFSI, and (c) energy level alignments of perovskite and PTAA with LiTFSI+*t*BP or OATFSI.

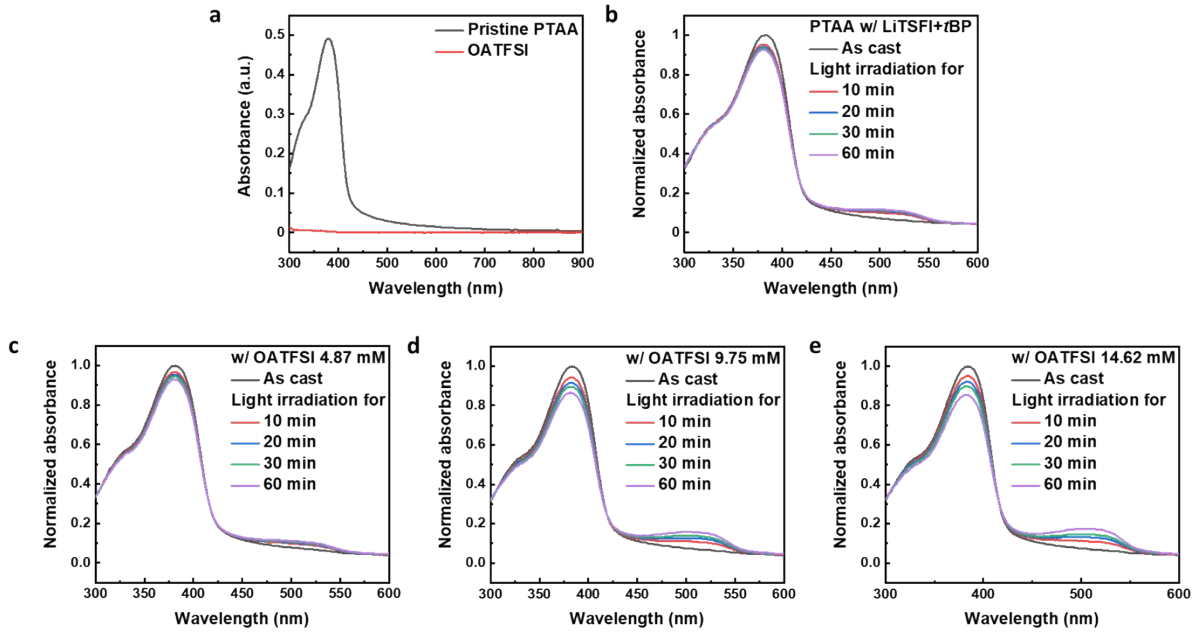



**Fig. S6.** UV-vis spectra of (a) pristine PTAA in film state (prepared from 10 mg $ml^{-1}$ of PTAA solution in toluene) and pristine OATFSI in solution state (9.75 mM of OATFSI in toluene) and change of UV-Vis absorption spectra for (b) PTAA film with LiTFSI+*t*BP and (c-e) PTAA films with various dopant concentrations of OATFSI under illumination

**Table S2**. Electrical property of pristine PTAA film, PTAA film with LiTFSI+*t*BP, and PTAA films with various dopant concentrations of OATFSI

| Dopant | Conductivity (S $cm^{-1}$) |
|---|---|
| **w/o additive** | $1.41\times10^{-7}$ |
| **LiTFSI+*t*BP** | $2.99\times10^{-5}$ |
| **OATFSI 4.87 mM** | $3.28\times10^{-5}$ |
| **OATFSI 9.75 mM** | $1.06\times10^{-4}$ |
| **OATFSI 14.62 mM** | $1.22\times10^{-4}$ |

| Dopant Concentration[a] | Scan Direction | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | FF | PCE$_{max}$(%) (PCE$_{avg}$(%)) | *R*s (Ω·cm$^2$) | *R*sh (kΩ·cm$^2$) |
|---|---|---|---|---|---|---|---|
| **0 mM** | Rev. | 0.884 | 25.29 | 0.335 | 7.50 (7.12) | 984.71 | 16.57 |
| | Fwd. | 0.836 | 25.09 | 0.256 | 5.36 (5.16) | 1210.00 | 1.22 |
| **2.44 mM** | Rev. | 0.985 | 25.82 | 0.796 | 20.24 (20.14) | 33.04 | 27.07 |
| | Fwd. | 0.928 | 25.84 | 0.685 | 16.43 (16.34) | 69.32 | 68.17 |
| **4.87 mM** | Rev. | 0.997 | 25.41 | 0.803 | 20.34 (20.20) | 31.59 | 28.02 |
| | Fwd. | 0.952 | 25.39 | 0.715 | 17.27 (17.32) | 61.03 | 33.77 |
| **7.31 mM** | Rev. | 0.997 | 25.53 | 0.810 | 20.63 (20.35) | 27.75 | 3410.00 |
| | Fwd. | 0.962 | 25.48 | 0.748 | 18.33 (17.99) | 43.07 | 117.4 |
| **9.75 mM** | Rev. | 1.028 | 25.60 | 0.822 | 21.63 (21.31) | 23.20 | 725.32 |
| | Fwd. | 0.993 | 25.55 | 0.775 | 19.65 (19.49) | 33.79 | 294.01 |
| **12.18 mM** | Rev. | 1.030 | 25.61 | 0.818 | 21.57 (21.07) | 24.21 | 21.32 |
| | Fwd. | 0.997 | 25.61 | 0.777 | 19.84 (19.32) | 33.42 | 39.96 |
| **14.62 mM** | Rev. | 1.036 | 25.17 | 0.793 | 20.69 (20.03) | 25.28 | 39.96 |
| | Fwd. | 0.948 | 25.08 | 0.723 | 17.19 (16.63) | 44.57 | 32.50 |

**Table S3**. Photovoltaic properties of PSCs using different dopant concentrations of OATFSI

[a)]Devices were fabricated without surface treatment on mp-$TiO_2$

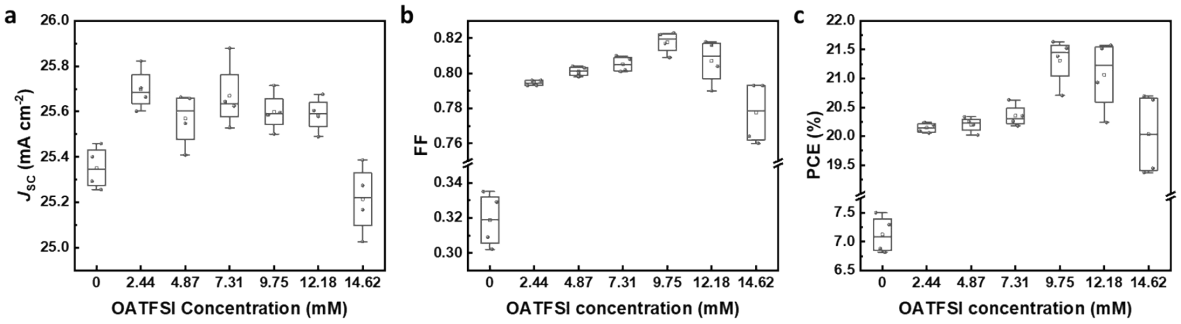



**Fig. S7.** (a) $J_{SC}$, (b) FF, and (c) PCE statistics in box-and-whisker plots (center line: median, box limits: upper and lower quartiles, whiskers: 1.5× interquartile range, points: outliers) of PSCs using different dopant concentrations of OATFSI

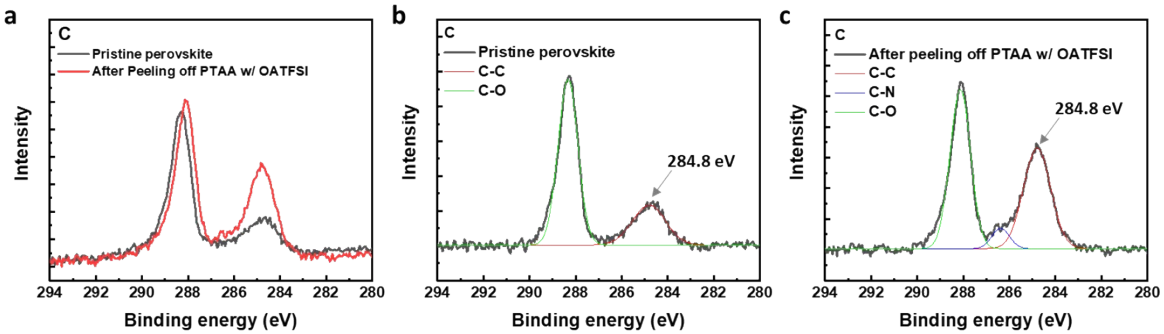



**Fig. S8.** XPS spectra of (a) pristine perovskite layer and perovskite layer after peeling off PTAA film using 9.75 mM of OATFSI with (b-c) the detailed fitting curves

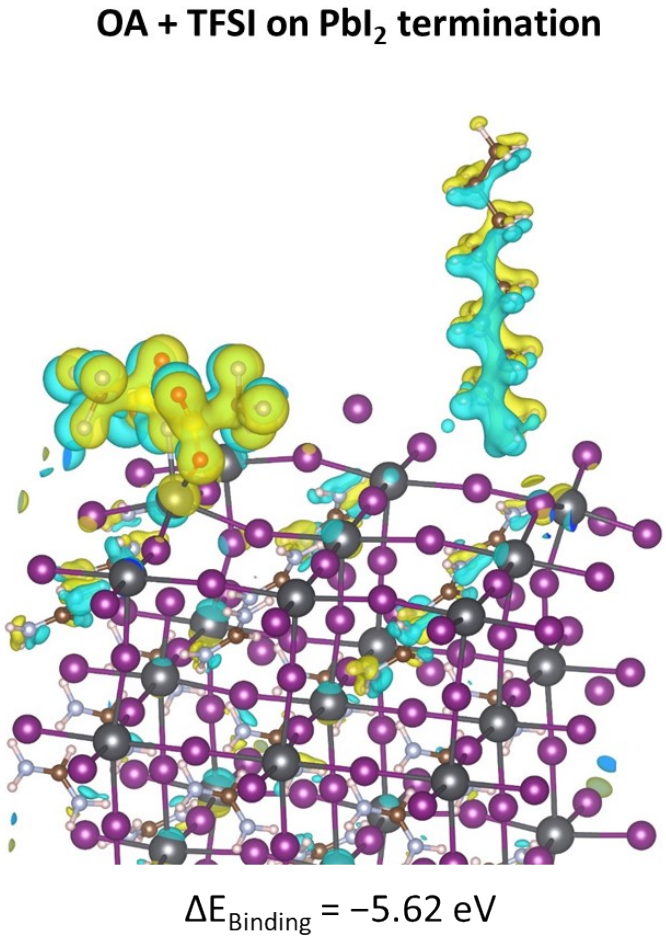



**Fig. S9.** DFT calculation for interaction between the OATFSI and perovskite

| OATFSI Concentration[a] | Surface Treatment | Scan Direction | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | FF | $PCE_{max}$(%) ($PCE_{avg}$(%)) |
|---|---|---|---|---|---|---|
| **4.87 mM** | X | Rev. | 1.007 | 25.11 | 0.816 | 20.62 (20.00) |
| | | Fwd. | 0.981 | 25.12 | 0.785 | 19.34 (18.68) |
| **9.75 mM** | X | Rev. | 1.073 | 25.00 | 0.833 | 22.37 (21.93) |
| | | Fwd. | 1.022 | 24.97 | 0.801 | 20.44 (20.02) |
| **4.87 mM** | O | Rev. | 1.036 | 25.01 | 0.822 | 21.31 (20.93) |
| | | Fwd. | 0.999 | 24.95 | 0.796 | 19.85 (19.43) |
| **9.75 mM** | O | Rev. | 1.087 | 24.89 | 0.839 | 22.70 (22.25) |
| | | Fwd. | 1.034 | 24.83 | 0.796 | 20.42 (20.10) |

**Table S4**. Photovoltaic properties of PSCs before/after surface treatment using OATFSI

[a)]Devices were fabricated with surface treatments on mp-$TiO_2$ using strontium bis(trifluoromethylsulfonyl)imide. Similar to surface treatments using salt materials on ETLs, surface treatment using strontium bis(trifluoromethylsulfonyl)imide was used to improve the performance of PSCs.[1-4]

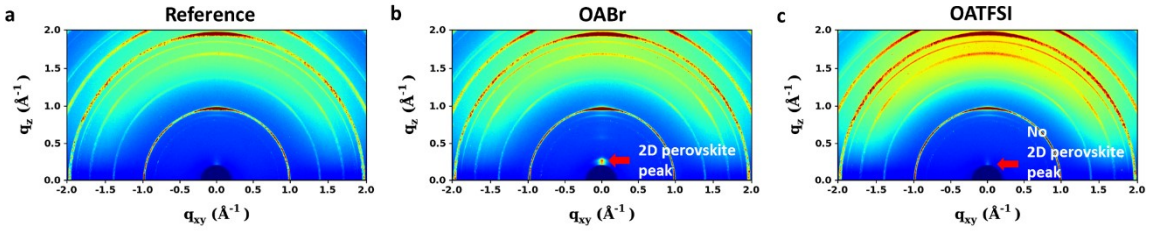



**Fig. S10.** GIWAXS patterns of (a) pristine perovskite, (b) octylammonium bromide (OABr)-treated perovskite, and (c) octylammonium TFSI (OATFSI)-treated perovskite. To obtain surface crystalline profile for the corresponding samples, the incidence angle of the X-ray beam was set to 0.10°

| | Sample 1 decay time (μs) | Sample 2 decay time (μs) | Sample 3 decay time (μs) | Average decay time (μs) |
|---|---|---|---|---|
| Pristine perovskite on quartz | 6.1 | 5.3 | - | 5.7 |
| Perovskite w/ OATFSI surface treatment | 9.7 | 10.0 | - | 9.8 |
| PTAA w/ OATFSI 4.87 mM[a] | 13.2 | 11.9 | 13.6 | 12.9 |
| PTAA w/ OATFSI 9.75 mM[a] | 27.7 | 30.9 | 30.0 | 29.5 |
| PTAA w/ LiTFSI+*t*BP[a] | 10.3 | 10.3 | 11.3 | 10.6 |

**Table S5**. Summary of long component of lifetime extracting from TCSPC curves

[a)]Perovskite layers were not treated with OATFSI

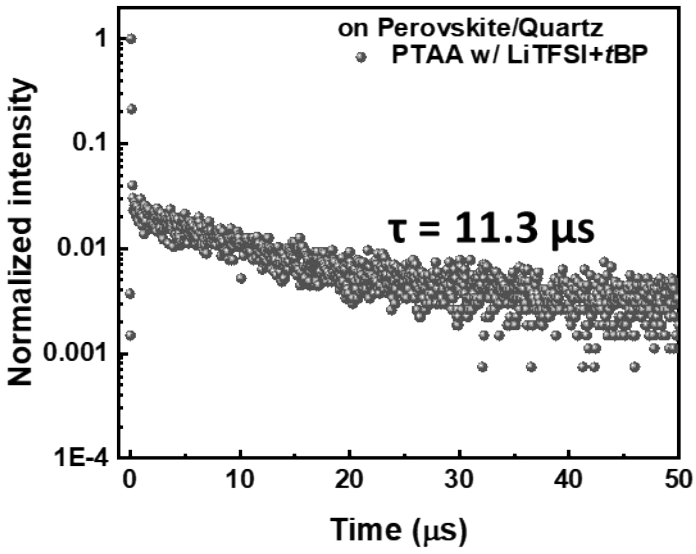
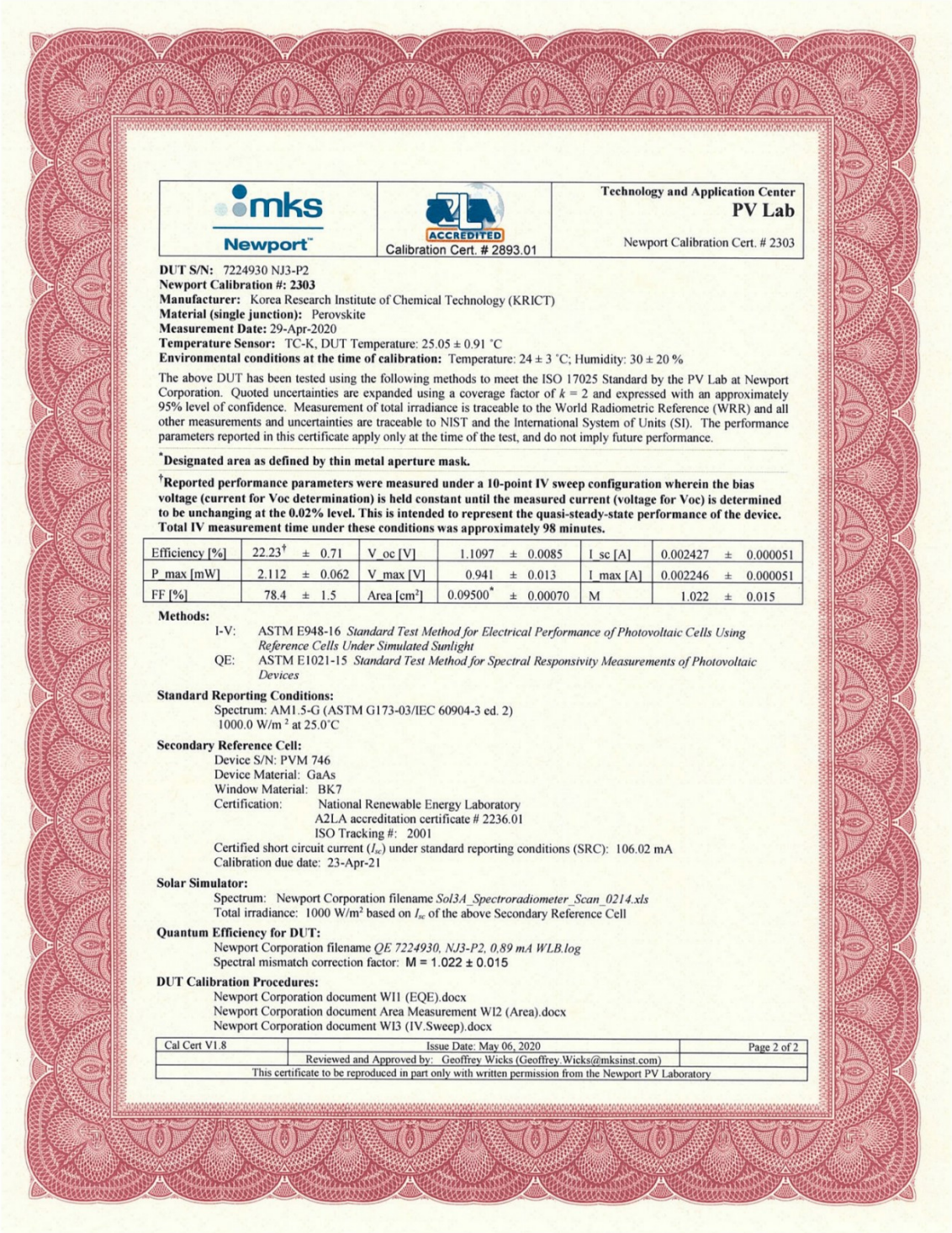



**Fig. S11.** PL transients of perovskite covered by PTAA with LiTFSI+*t*BP



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**Technology and Application Center**
**PV Lab**
Newport Calibration Cert. # 2303

**DUT S/N:** 7224930 NJ3-P2
**Newport Calibration #: 2303**
**Manufacturer:** Korea Research Institute of Chemical Technology (KRICT)
**Material (single junction):** Perovskite
**Measurement Date:** 29-Apr-2020
**Temperature Sensor:** TC-K, DUT Temperature: 25.05 ± 0.91 °C
**Environmental conditions at the time of calibration:** Temperature: 24 ± 3 °C; Humidity: 30 ± 20 %

The above DUT has been tested using the following methods to meet the ISO 17025 Standard by the PV Lab at Newport Corporation. Quoted uncertainties are expanded using a coverage factor of $k = 2$ and expressed with an approximately 95% level of confidence. Measurement of total irradiance is traceable to the World Radiometric Reference (WRR) and all other measurements and uncertainties are traceable to NIST and the International System of Units (SI). The performance parameters reported in this certificate apply only at the time of the test, and do not imply future performance.

***Designated area as defined by thin metal aperture mask.**

**†Reported performance parameters were measured under a 10-point IV sweep configuration wherein the bias voltage (current for Voc determination) is held constant until the measured current (voltage for Voc) is determined to be unchanging at the 0.02% level. This is intended to represent the quasi-steady-state performance of the device. Total IV measurement time under these conditions was approximately 98 minutes.**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Efficiency [%] | 22.23† | ± | 0.71 | V_oc [V] | 1.1097 | ± | 0.0085 | I_sc [A] | 0.002427 | ± | 0.000051 |
| P_max [mW] | 2.112 | ± | 0.062 | V_max [V] | 0.941 | ± | 0.013 | I_max [A] | 0.002246 | ± | 0.000051 |
| FF [%] | 78.4 | ± | 1.5 | Area [cm²] | 0.09500* | ± | 0.00070 | M | 1.022 | ± | 0.015 |

**Methods:**
I-V: ASTM E948-16 *Standard Test Method for Electrical Performance of Photovoltaic Cells Using Reference Cells Under Simulated Sunlight*
QE: ASTM E1021-15 *Standard Test Method for Spectral Responsivity Measurements of Photovoltaic Devices*

**Standard Reporting Conditions:**
Spectrum: AM1.5-G (ASTM G173-03/IEC 60904-3 ed. 2)
1000.0 W/m² at 25.0°C

**Secondary Reference Cell:**
Device S/N: PVM 746
Device Material: GaAs
Window Material: BK7
Certification: National Renewable Energy Laboratory
A2LA accreditation certificate # 2236.01
ISO Tracking #: 2001
Certified short circuit current ($I_{sc}$) under standard reporting conditions (SRC): 106.02 mA
Calibration due date: 23-Apr-21

**Solar Simulator:**
Spectrum: Newport Corporation filename *Sol3A_Spectroradiometer_Scan_0214.xls*
Total irradiance: 1000 W/m² based on $I_{sc}$ of the above Secondary Reference Cell

**Quantum Efficiency for DUT:**
Newport Corporation filename *QE 7224930, NJ3-P2, 0.89 mA WLB.log*
Spectral mismatch correction factor: M = 1.022 ± 0.015

**DUT Calibration Procedures:**
Newport Corporation document WI1 (EQE).docx
Newport Corporation document Area Measurement WI2 (Area).docx
Newport Corporation document WI3 (IV.Sweep).docx




**Fig. S12. (Continued on next page)** Certification of OATFSI-based PSC exhibiting QSS PCE of 22.23%

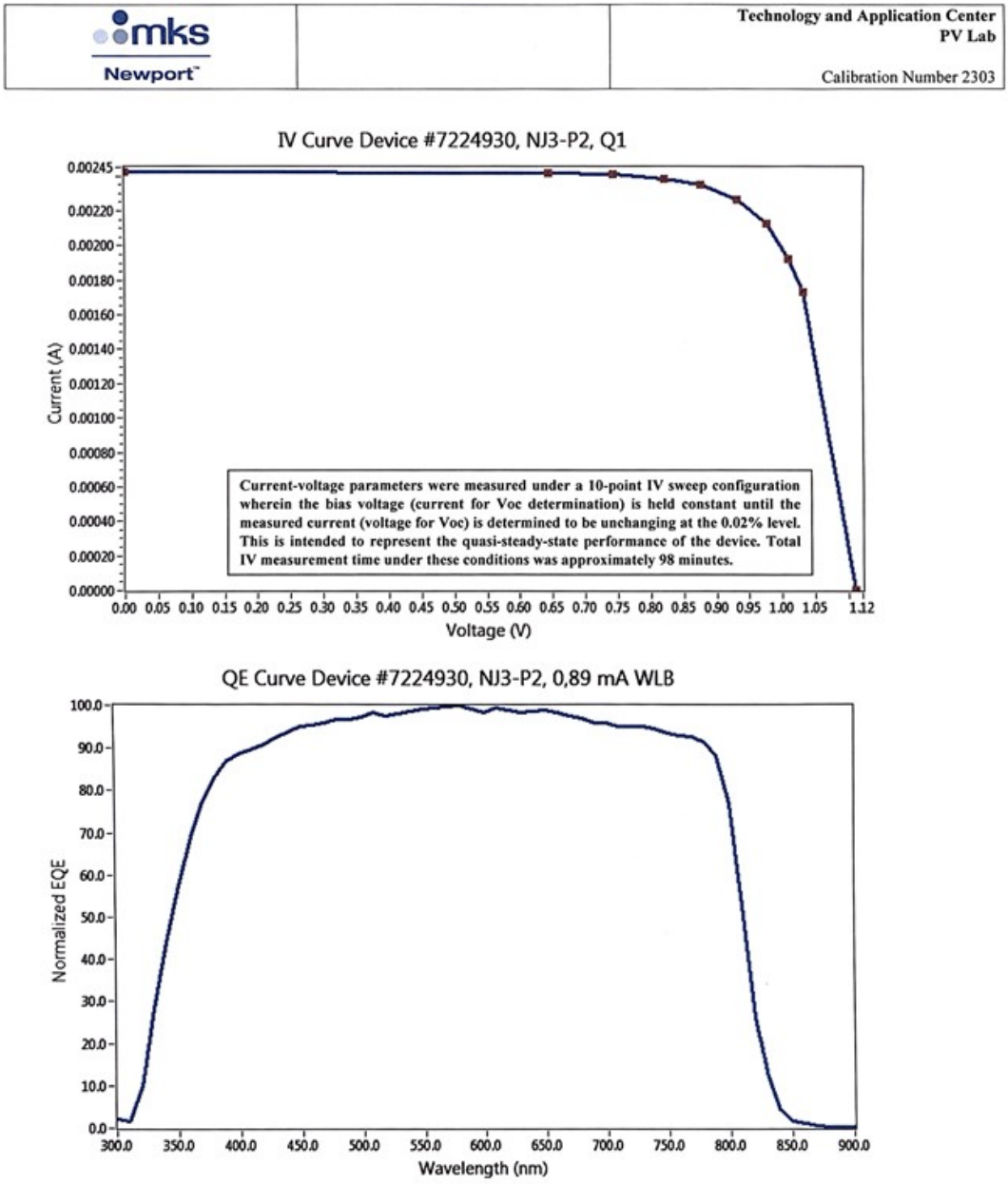



**Fig. S12. (Continued on next page)** Certification of OATFSI-based PSC exhibiting QSS PCE of 22.23%

**Table S6**. Summary of the certified performances (with PCE of over 22%) for PTAA-based PSCs reported to date

| No. | Structure | Measurement Method | Certified PCE (%) | dopant | Reference |
|---|---|---|---|---|---|
| This work | n-i-p | **QSS measurement** | 22.2 | OATFSI | - |
| 1 | n-i-p | **Reverse/Forward measurement** | 22.1 | LiTFSI+*t*BP | *Science* **2017**, 356, 1376-1379 |
| 2 | n-i-p | **Reverse/Forward measurement** | 23.9 | F4TCNQ+LiHFDF | *Science* **2022**, 377, 1227-1232 |
| 3 | p-i-n | **QSS measurement** | 22.3 | X | *Nat. Energy* **2020**, 5, 131-140 |
| 4 | p-i-n | **Reverse/Forward measurement** | 22.8 | X | *J. Am. Chem. Soc.* **2020**, 142, 20134-20142 |
| 5 | p-i-n | **Reverse/Forward measurement** | 24.3 | X | *Science* **2022**, 376, 416-420 |

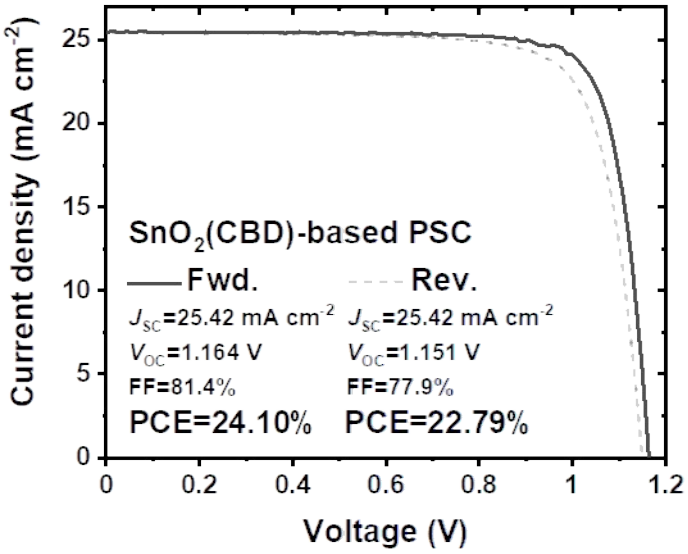



**Fig. S13.** *J*–*V* curve for CBD $SnO_2$-based PSC

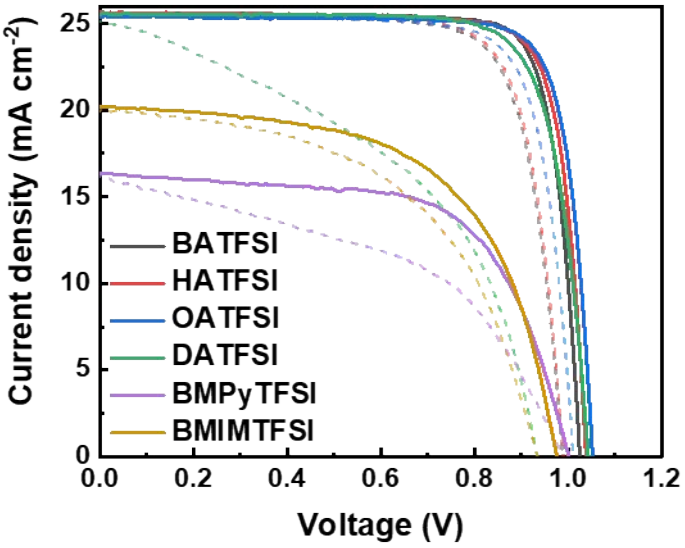



**Fig. S14.** *J*–*V* curves of PSCs using the same concentration of alkylammonium TFSIs with different alkyl chain lengths and commercial ionic liquid dopants

**Table S7.** Photovoltaic properties of PSCs using the same concentration of alkylammonium TFSIs with different alkyl chain lengths and commercial ionic liquid dopants

| Dopant[a] | Scan Direction | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | FF | $PCE_{max}$ (%) ($PCE_{avg}$ (%)) |
|---|---|---|---|---|---|
| **BATFSI** | Rev. | 1.026 | 25.63 | 0.821 | 21.59 (21.10) |
| | Fwd. | 0.991 | 25.59 | 0.768 | 19.47 (18.51) |
| **HATFSI** | Rev. | 1.039 | 25.65 | 0.814 | 21.69 (21.27) |
| | Fwd. | 0.993 | 25.57 | 0.775 | 19.67 (19.33) |
| **OATFSI** | Rev. | 1.052 | 25.41 | 0.819 | 21.91 (21.38) |
| | Fwd. | 1.013 | 25.43 | 0.785 | 20.24 (19.54) |
| **DATFSI** | Rev. | 1.043 | 25.56 | 0.784 | 20.90 (20.00) |
| | Fwd. | 0.936 | 25.11 | 0.462 | 10.85 (11.57) |
| **BMPyTFSI** | Rev. | 1.002 | 16.34 | 0.640 | 10.47 (6.62) |
| | Fwd. | 0.994 | 16.18 | 0.471 | 7.57 (3.64) |
| **BMIMTFSI** | Rev. | 0.976 | 20.17 | 0.592 | 11.66 (9.52) |
| | Fwd. | 0.937 | 19.94 | 0.530 | 9.90 (7.90) |

[a]Devices were fabricated with surface treatments on mp-$TiO_2$ using strontium bis(trifluoromethylsulfonyl)imide.

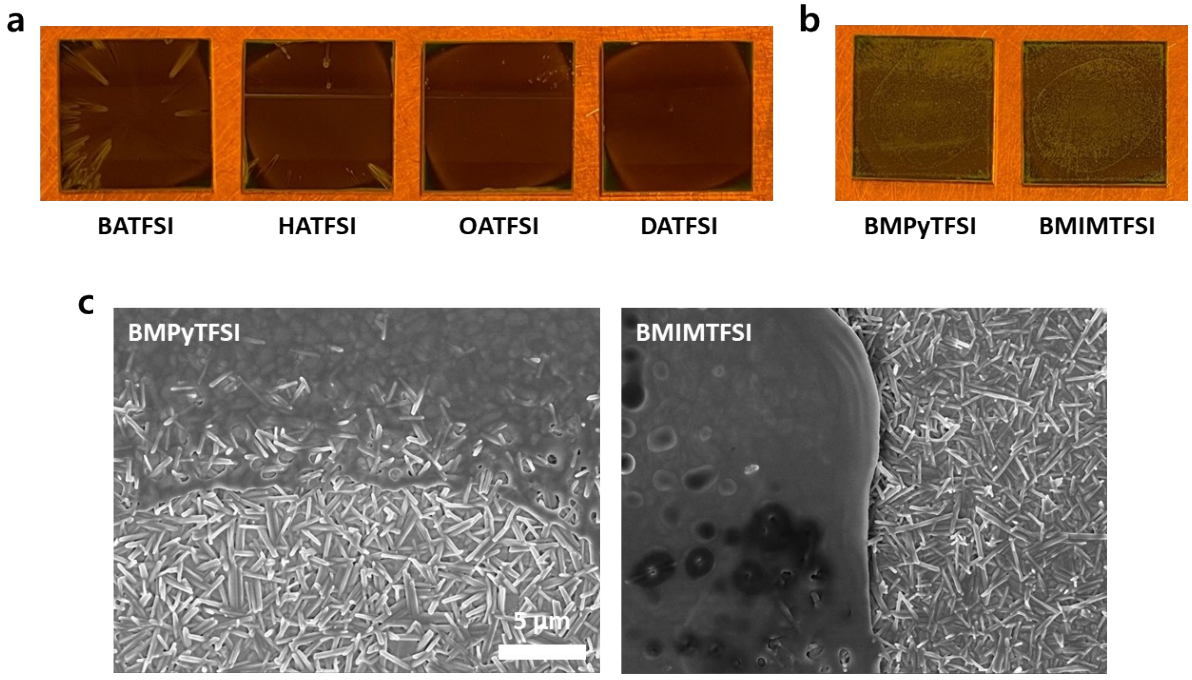



**Fig. S15.** Photographs of (a) HTLs containing alkylammonium TFSIs with different alkyl chain lengths and (b) HTLs containing commercial ionic liquid dopants on the perovskite layers; (c) SEM images of HTLs containing commercial ionic liquid dopants on the perovskite layers

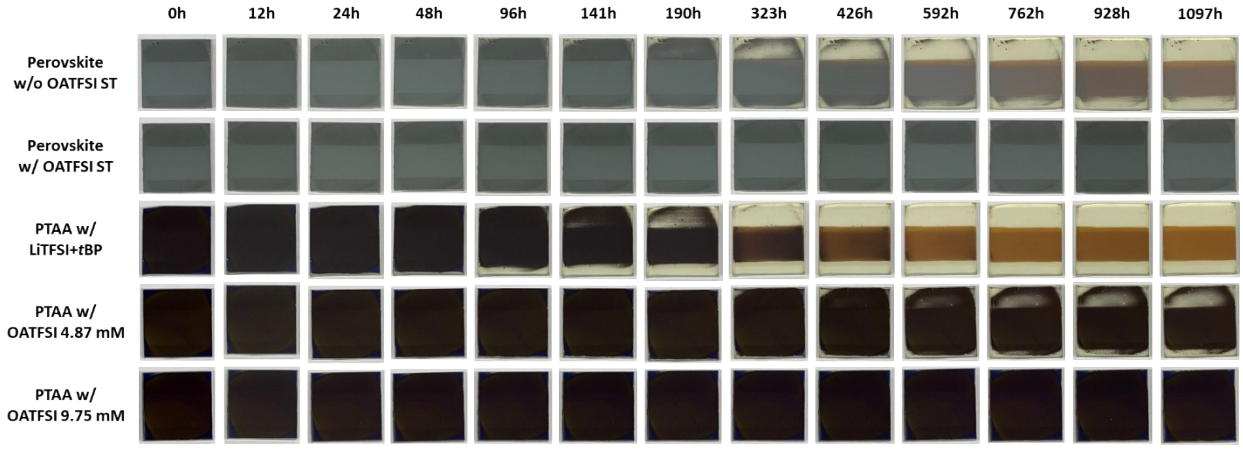



**Fig. S16.** Photographs of changes for perovskite films with and without surface treatment using OATFSI and perovskite films covered by PTAAs doped by OATFSI and LiTFSI+*t*BP at 40~55% RH

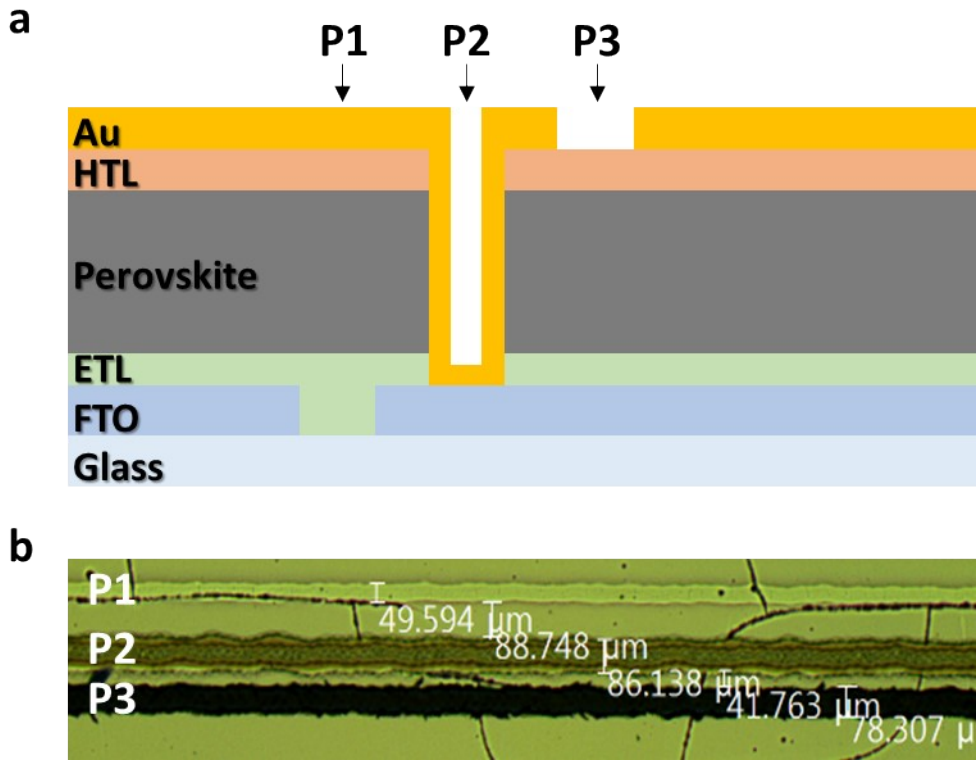
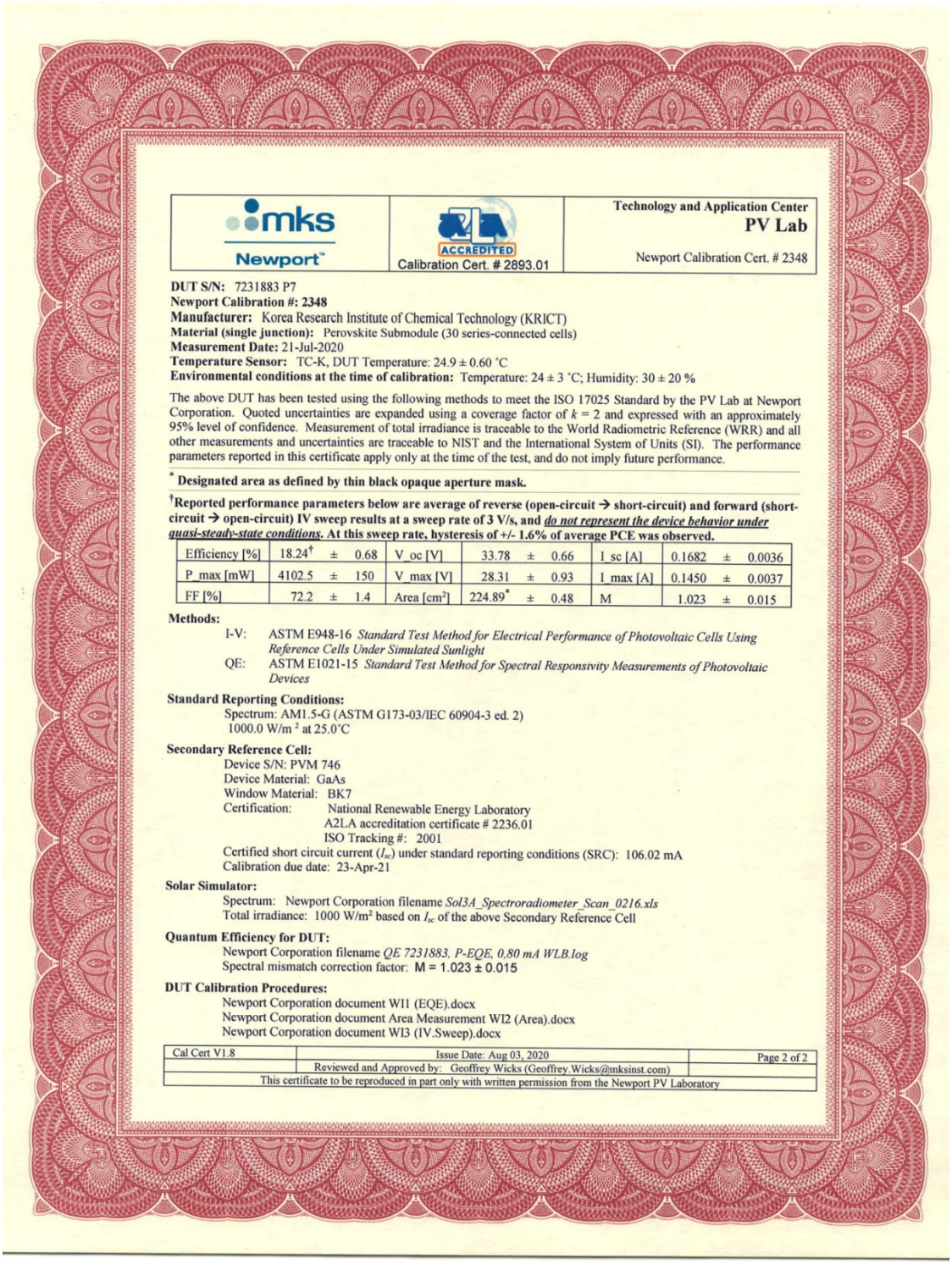



**Fig. S17.** (a) Schematic and (b) optical microscope image of P1, P2, and P3 interconnection lines of the module



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Technology and Application Center
**PV Lab**
Newport Calibration Cert. # 2348

**DUT S/N:** 7231883 P7
**Newport Calibration #: 2348**
**Manufacturer:** Korea Research Institute of Chemical Technology (KRICT)
**Material (single junction):** Perovskite Submodule (30 series-connected cells)
**Measurement Date:** 21-Jul-2020
**Temperature Sensor:** TC-K, DUT Temperature: 24.9 ± 0.60 °C
**Environmental conditions at the time of calibration:** Temperature: 24 ± 3 °C; Humidity: 30 ± 20 %

The above DUT has been tested using the following methods to meet the ISO 17025 Standard by the PV Lab at Newport Corporation. Quoted uncertainties are expanded using a coverage factor of $k = 2$ and expressed with an approximately 95% level of confidence. Measurement of total irradiance is traceable to the World Radiometric Reference (WRR) and all other measurements and uncertainties are traceable to NIST and the International System of Units (SI). The performance parameters reported in this certificate apply only at the time of the test, and do not imply future performance.

*** Designated area as defined by thin black opaque aperture mask.**

**† Reported performance parameters below are average of reverse (open-circuit → short-circuit) and forward (short-circuit → open-circuit) IV sweep results at a sweep rate of 3 V/s, and *do not represent the device behavior under quasi-steady-state conditions*. At this sweep rate, hysteresis of +/- 1.6% of average PCE was observed.**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Efficiency [%] | 18.24† | ± | 0.68 | V_oc [V] | 33.78 | ± | 0.66 | I_sc [A] | 0.1682 | ± | 0.0036 |
| P_max [mW] | 4102.5 | ± | 150 | V_max [V] | 28.31 | ± | 0.93 | I_max [A] | 0.1450 | ± | 0.0037 |
| FF [%] | 72.2 | ± | 1.4 | Area [cm²] | 224.89* | ± | 0.48 | M | 1.023 | ± | 0.015 |

**Methods:**

I-V: ASTM E948-16 *Standard Test Method for Electrical Performance of Photovoltaic Cells Using Reference Cells Under Simulated Sunlight*
QE: ASTM E1021-15 *Standard Test Method for Spectral Responsivity Measurements of Photovoltaic Devices*

**Standard Reporting Conditions:**

Spectrum: AM1.5-G (ASTM G173-03/IEC 60904-3 ed. 2)
1000.0 W/m ² at 25.0°C

**Secondary Reference Cell:**

Device S/N: PVM 746
Device Material: GaAs
Window Material: BK7
Certification: National Renewable Energy Laboratory
A2LA accreditation certificate # 2236.01
ISO Tracking #: 2001
Certified short circuit current ($I_{sc}$) under standard reporting conditions (SRC): 106.02 mA
Calibration due date: 23-Apr-21

**Solar Simulator:**

Spectrum: Newport Corporation filename *Sol3A_Spectroradiometer_Scan_0216.xls*
Total irradiance: 1000 W/m² based on $I_{sc}$ of the above Secondary Reference Cell

**Quantum Efficiency for DUT:**

Newport Corporation filename *QE 7231883, P-EQE, 0.80 mA WLB.log*
Spectral mismatch correction factor: M = 1.023 ± 0.015

**DUT Calibration Procedures:**

Newport Corporation document WI1 (EQE).docx
Newport Corporation document Area Measurement WI2 (Area).docx
Newport Corporation document WI3 (IV.Sweep).docx




**Fig. S18.** Certification of OATFSI-based perovskite module exhibiting PCE of 18.24%

**Table S8**. Photovoltaic parameters of the perovskite modules using OATFSI

| No. | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF (%) | PCE in aperture area (225 cm$^2$) (%) |
|---|---|---|---|---|
| 1 | 0.72 | 31.4 | 77.8 | 17.6 |
| 2 | 0.69 | 31.3 | 74.5 | 16.2 |
| 3 | 0.70 | 30.9 | 69.3 | 15.0 |
| 4 | 0.70 | 31.4 | 72.0 | 15.7 |
| 5 | 0.67 | 30.8 | 77.0 | 16.1 |
| 6 | 0.72 | 31.9 | 76.2 | 17.5 |
| 7 | 0.69 | 31.3 | 75.2 | 16.2 |
| 8 | 0.71 | 32.6 | 78.2 | 18.2 |
| 9 | 0.69 | 30.6 | 73.4 | 15.5 |
| 10 | 0.72 | 32.6 | 79.7 | 18.6 |
| 11 | 0.71 | 31.0 | 74.1 | 16.2 |
| 12 | 0.72 | 31.2 | 77.0 | 17.0 |
| 13 | 0.72 | 30.9 | 74.6 | 16.7 |
| 14 | 0.68 | 30.5 | 72.1 | 15.0 |
| 15 | 0.73 | 33.0 | 80.0 | 19.2 |
| 16 | 0.70 | 32.7 | 76.1 | 17.5 |
| 17 | 0.73 | 32.7 | 73.2 | 17.6 |
| 18 | 0.75 | 32.1 | 76.8 | 18.4 |
| 19 | 0.71 | 32.3 | 79.9 | 18.3 |
| 20 | 0.72 | 32.3 | 78.2 | 18.2 |
| 21 | 0.71 | 32.2 | 80.0 | 18.4 |
| 22 | 0.71 | 32.8 | 79.7 | 18.7 |
| 23 | 0.71 | 33.2 | 82.0 | 19.4 |
| 24 | 0.71 | 31.1 | 77.4 | 17.2 |
| Average | 0.7105±0.0174 | 31.83±0.84 | 76.46±3.11 | 17.30±1.30 |

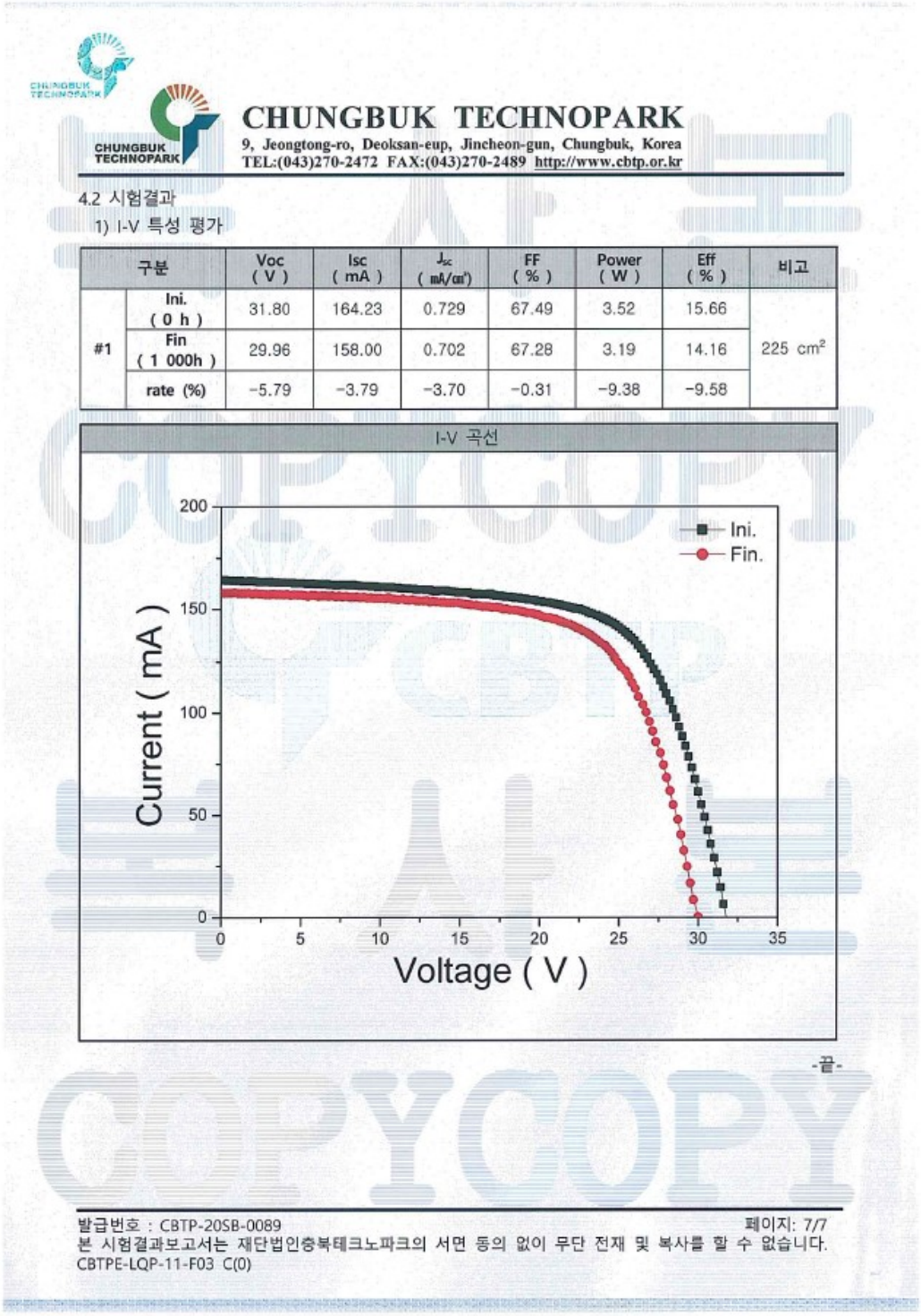


**Fig. S19.** Result of outsourcing damp heat test for OATFSI-based perovskite module before and after 1000 h

**Supplemental references**


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