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Supporting Information

Dynamical Evolution of the 2D/3D Interface: A Hidden Driver behind Perovskite Solar Cell Instability

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Materials and Methods

Synthesis of thiophene-based cations

A desired concentrated aqueous solution of HI (1.1 eq) was added dropwise to a stirred 1.0 mol/L ethanol solution of the corresponding thiophenealkylamine (1.0 eq) at 0°C. The mixture was allowed to gradually reach room temperature and then it was poured into an excess of diethyl ether (Et_2O). The formed precipitate was collected and washed thoroughly with Et_2O. The salts were recrystallized from EtOH-Et_2O mixtures, providing with crystalline solids (yields ≈70 %).

Preparation of 2D/3D perovskite films and device fabrication

FTO-coated glass (Nippon sheet glass)[1] was chemically etched using zinc powder and HCl solution, followed by cleaning using Hellmanex, water, acetone, and 2-propanol. A 30 nm thick compact TiO_2 layer as electron transporting layer was deposited by spray pyrolysis using a titanium diisopropoxide bis(acetylacetonate) solution (Sigma-Aldrich) diluted in 2-propanol (1:15 v/v) at 450 °C. On top of the compact layer, a 100 nm thick mesoporous layer of TiO_2 was deposited by spin coating TiO_2 paste (GreatCellSolar, 30NR-D) diluted in ethanol (1:8 w/v) at 5000 rpm for 20 s followed by heating at 125 °C for 10 min and sintering at 500 °C for 20 min. A thin layer of passivating tin oxide of ≈20 nm was spin-coated by using tin (IV) chloride (Acros) solution (12 μL diluted in 988 μL water) at 3000 rpm for 30 s, followed by annealing at 100 °C for 10 min and 190 °C for 1 h. The prepared substrates were treated with UV-ozone for 15 min before perovskite deposition. A 1.3 mol/L $[(FAPbI_3)_{0.87}(MAPbBr_3)_{0.13}]_{0.92}(CsPbI_3)_{0.08}$ perovskite solution with excess PbI_2 (PbI_2:FAI = 1.05:1) was prepared by mixing FAI (GreatCellSolar), MABr (GreatCellSolar), CsI (ABCR),

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[1] Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

PbI_2 (TCI), and $PbBr_2$ (TCI) in DMF and DMSO (0.78:0.22 v/v). For the 2D perovskite n=1 (R_2PbI_4, R is the corresponding thiophene alkylammonium cation), the perovskite precursor solution was prepared by dissolving thiophene alkylammonium cation and PbI_2 with the molar ratio of 2:1 in mixed solvent of DMF and DMSO (0.78:0.22 v/v). For the quasi 2D perovskite n=2 ($R_2MAPb_2I_7$), the perovskite precursor solution was prepared by dissolving thiophene alkylammonium cation, methylammonium iodide (MAI, GreatCellSolar), and PbI_2 with the molar ratio of 2:1:2 in mixed solvent of DMF and DMSO (0.78:0.22 v/v). The prepared perovskite precursor was then spin-coated on the prepared at 2000 rpm for 12 s and 5000 rpm for 30 s. Chlorobenzene was added as an anti-solvent at 15 s before the end of spin coating process. The films were subsequently annealed at 100 °C for 60 min. After cooling down to room temperature, 0.06 mol/L of thiophene alkyl ammonium iodide cations in 2-propanol was spin-coated dynamically by adding the solution during spinning at 4000 rpm for 30 s, followed by annealing at 100 °C for 6 min. Spiro OMeTAD was used as the hole-transporting materials (HTM). The HTM layer was prepared by dissolving 78.2 mg spiro-OMeTAD (Merck) in 1 mL chlorobenzene doped with 31.28 μL of 4-tert-butylpyridine (Sigma-Aldrich), 18.57 μL of Li-bis (trifluoromethanesulphonyl) imide (Aldrich) from the stock solution (196 mg in 379 μL acetonitrile), 13.69 μL of FK 209 Co(III) TFSI (GreatCellSolar) from the stock solution (99 mg in 263 μL acetonitrile). The doped spiro-OMeTAD solution was then deposited by spin-coating at 4000 rpm for 30 s. Finally, a 70 nm-thick gold counter electrode was thermally evaporated on top of HTM layer.

Film Characterization

UV-VIS Absorption

The absorption spectra of the perovskite thin films were recorded with using an ultraviolet, visible, near-infrared spectrophotometer (PerkinElmer Lambda 950S).

Photoluminescence

Photoluminescence spectra of the perovskite thin films were measured and recorded using Fluorolog3-22 spectrofluorometer. The spectra were recorded upon excitation at 450 nm. For the 2D/3D films, the emissions were measured from both front side (2D perovskite side) and back side (3D perovskite side) of the film.

X-ray Diffraction (XRD)

XRD measurements were performed at room temperature with Bruker D8 Advance diffractometer and non-monochromated Cu radiation. For the 2D-3D films, the XRD patterns were obtained using grazing incident diffraction (GID) geometry with Bruker D8 Discover diffractometer and non-monochromated Cu radiation at the incident angle of 2.0°. In situ X-ray diffraction was performed at 50°C in ambient atmosphere and using a custom-made high-temperature cell (temperature stability +/- 1 K), in Bragg Brentano geometry, with a Bruker D8 Discover diffractometer and non-monochromated Cu radiation. The data acquisition time for the entire pattern between 2 and 16° 2θ was approx. 15 minutes, in order to allow for comparison from PL experiments.

Scanning Electron Microscopy (SEM)

Cross-section and top surface SEM images were recorded by in-lens detector of FEI Teneo scanning electron microscope at high tension of 3 kV and 5 kV.

Grazing incidence wide angle X-ray scattering (GIWAXS) measurements

GIWAXS measurements were carried out in reflection geometry at the CMS beamline of the National Synchrotron Light Source II (NSLS II), a U.S. Department of Energy (DOE) office of the Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory. Samples were measured at a detector distance of 0.153 m using X-ray wavelength of 1.24 Å, at 0.16° angle of incidence with respect to the substrate plane. Scattering intensity was detected by a PILATUS 300K detector. Nika[2] software package was used to sector average the 2D GIWAXS images. Data plotting was done in Igor Pro (Wavemetrics, Inc., Lake Oswego, OR, USA).

Device characterization

The current density–voltage (J–V) curves were measured under 1 sun illumination (AM 1.5G) by xenon lamp solar simulator (450 W, Oriel Sol3A, AAA class). The J-V measurements were carried out under ambient condition and room temperature. The light intensity was calibrated to 1 sun by using a Si reference equipped with an IR-cutoff (KG5) filter. An external voltage bias was applied and the current responses were measured at the same time using a digital source meter (Keithley 2400). An active area of 0.16 cm^2 was determined by a metal mask with aperture of 0.16 cm^2. The J-V curves were scanned with the rate of 50 mV s^{-1} without any preconditioning, such as light soaking or pre-biasing for a long time. For the light intensity dependent measurement, the J-V characteristics were obtained using a VeraSol LED solar simulator (Newport) under various light intensity. External quantum efficiency (EQE) measurement was carried out by using IQE200B (Oriel).

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[2] J. Ilavsky, Nika: software for two-dimensional data reduction. J. Appl. Crystallogr. **45**, 324-328 (2012).

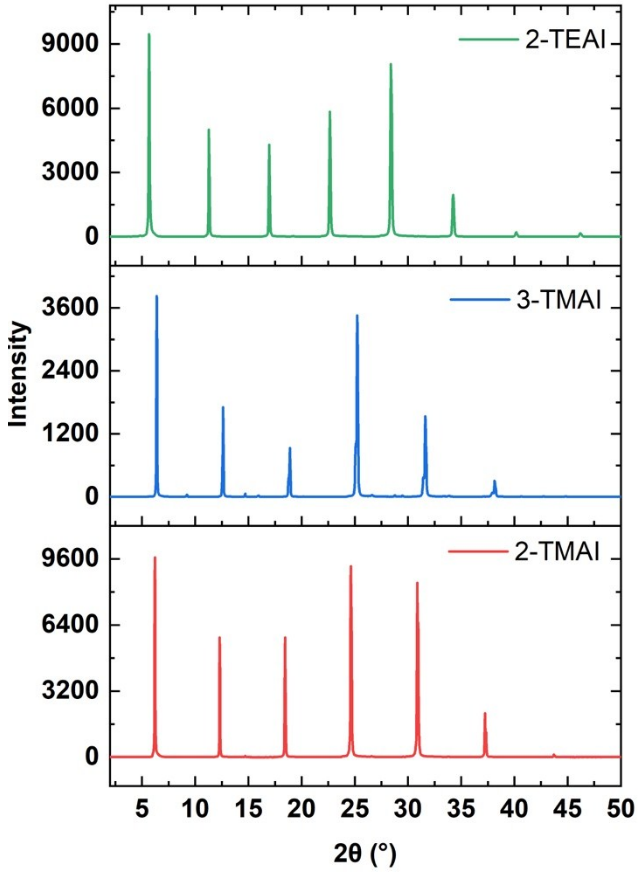


Figure S1. XRD patterns of pure 2D perovskite films with n=1 employing 2-TMAI, 3-TMAI and 2-TEAI cations.

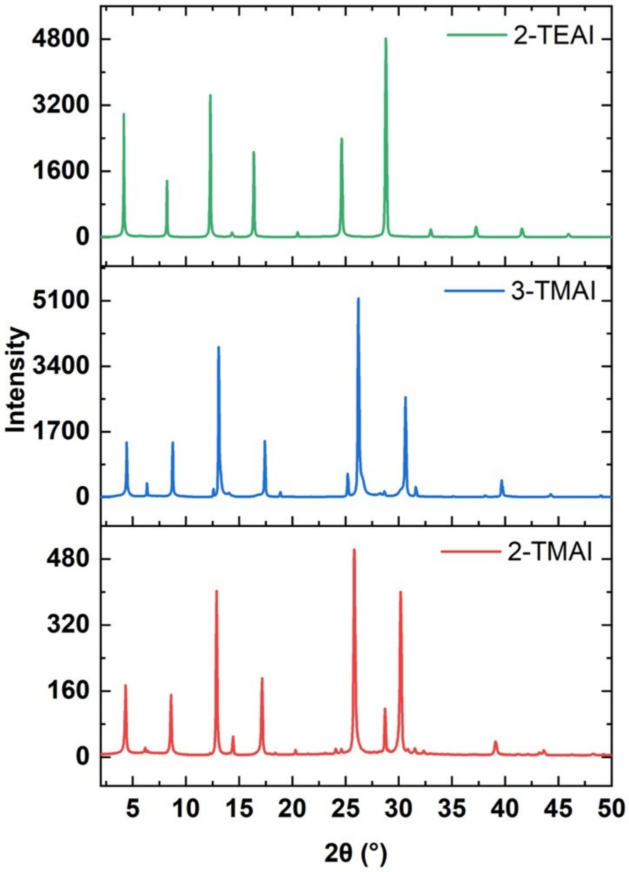


Figure S2. XRD patterns of quasi-2D perovskite films with n=2 employing 2-TMAI, 3-TMAI and 2-TEAI cations using MA as small cation.

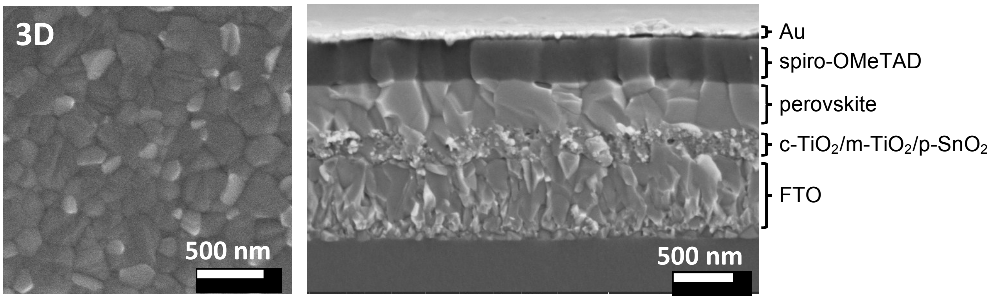


Figure S3. Scanning electron microscopy images of the top view (left) of the perovskite film and cross-section (right) of the 3D control device.

Table S1. Optimization of the 2D layer thickness on the 3D PSCs by varying 2-TMAI concentration showed over 15 devices fabricated in the same batch.

Concentration	**Voc (V)**	**Jsc (mA cm^{-2})**	**FF**	**PCE (%)**
0.05 M	1.07 ± 0.02	23.8 ± 0.3	0.77 ± 0.01	19.6 ± 0.4
0.06 M	1.11 ± 0.03	23.7 ± 0.2	0.76 ± 0.01	19.8 ± 0.2
0.07 M	1.07 ± 0.01	22.8 ± 0.3	0.70 ± 0.02	17.0 ± 0.2

Table S2. Statistics of the photovoltaics parameters of 3D control and 2D/3D PSCs based on 2-TMAI, 3-TMAI, and 2-TEAI over 86 devices measured at their peak performance time.

	Voc (V)	**Jsc (mA cm^{-2})**	**FF**	**PCE (%)**
2-TMAI	1.09 ± 0.02	23.8 ± 0.3	0.75 ± 0.01	19.3 ± 0.4
3-TMAI	1.13 ± 0.01	23.4 ± 0.1	0.76 ± 0.01	20.0 ± 0.5
2-TEAI	1.11 ± 0.00	23.2 ± 0.2	0.70 ± 0.01	18.1 ± 0.5
3D	1.09 ± 0.02	23.8 ± 0.3	0.78 ± 0.01	20.3 ± 0.5

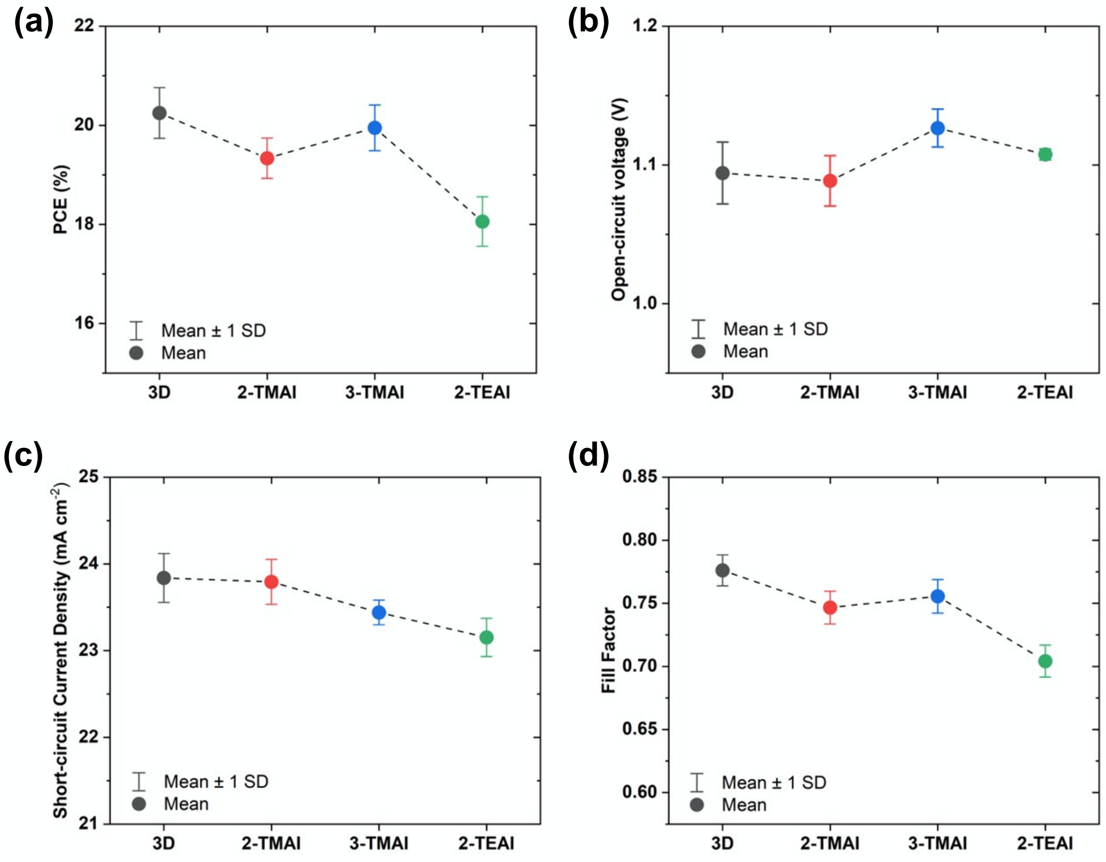


Figure S4. Statistics of the photovoltaics parameters with standard deviation bars (SD) of 3D control and 2D/3D PSCs based on 2-TMAI, 3-TMAI, and 2-TEAI PSCs over 86 devices measured at their peak performance time: (a) power conversion efficiency, (b) open-circuit voltage, (c) short-circuit current density, and (d) fill factor. Color code is as in Figure 2.

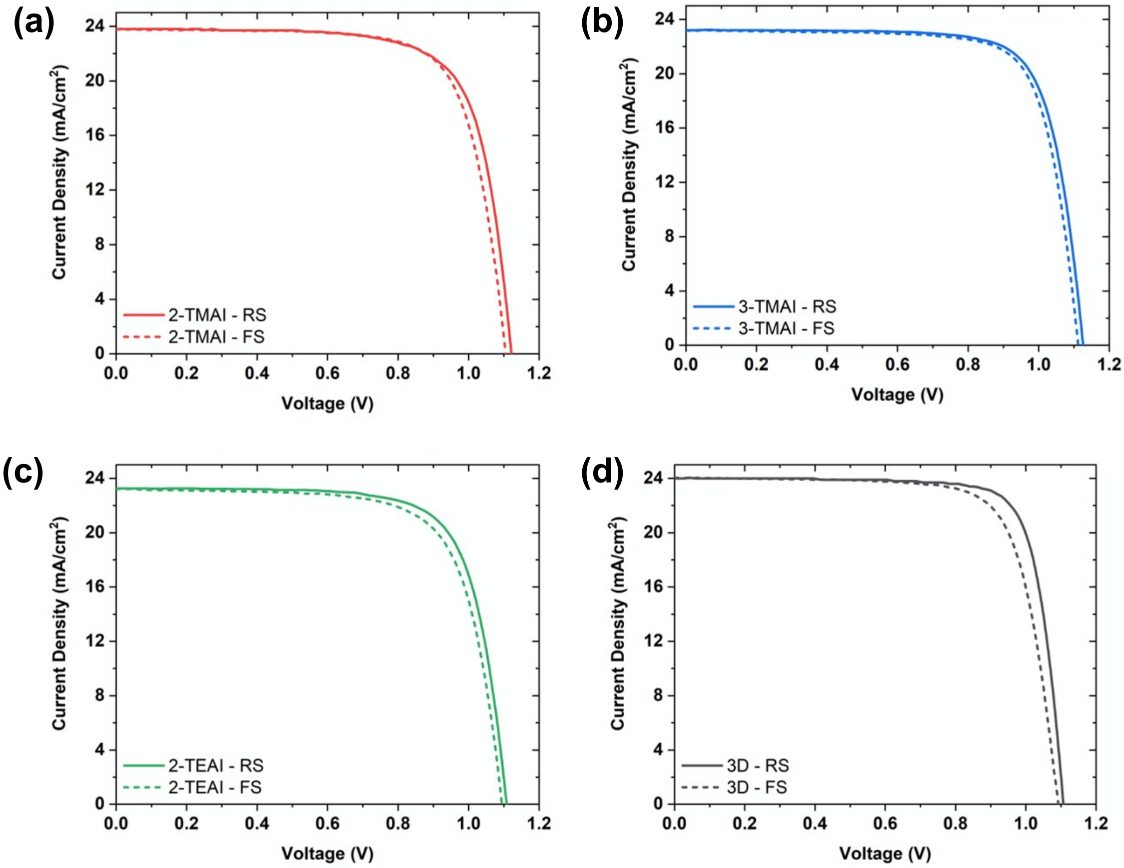


Figure S5. Hysteresis measurement between reverse scan (RS) and forward scan (FS) of 2D/3D PSCs employing (a) 2-TMAI, (b) 3-TMAI, (c) 2-TEAI, and (d) 3D control measured at their peak performance time.

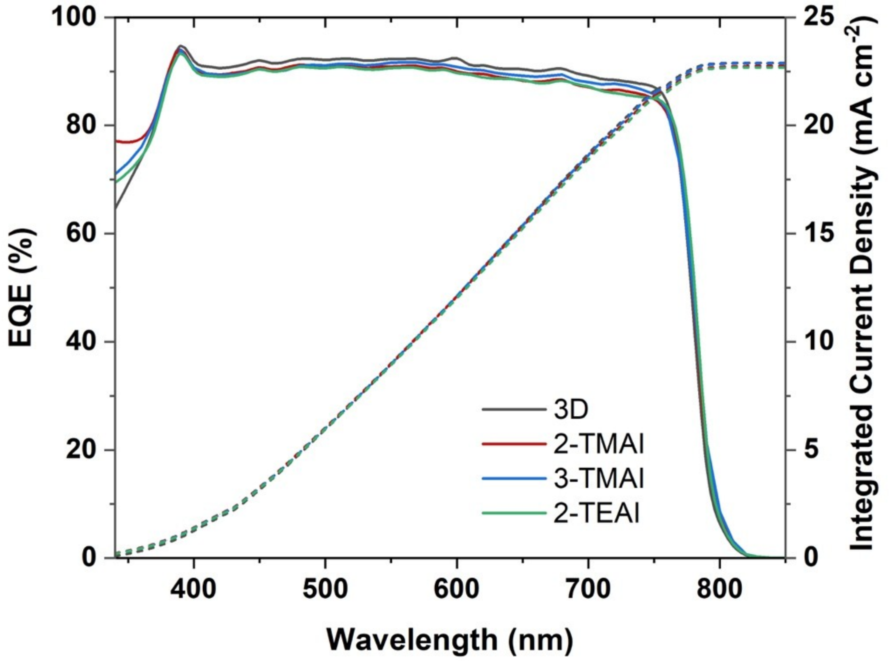


Figure S6. External quantum efficiency (EQE) of 2D/3D PSCs based on 2-TMAI, 3-TMAI, 2-TEAI, and 3D control measured at their peak performance time.

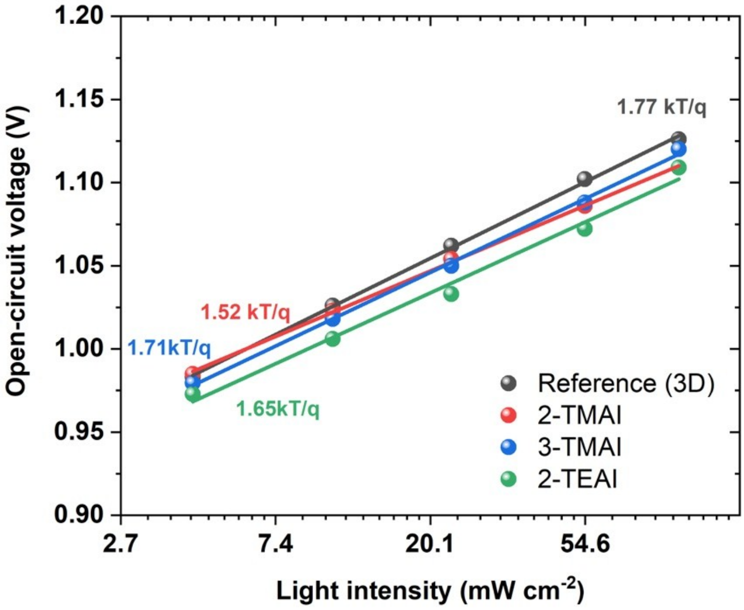


Figure S7. Open-circuit voltage (V_{oc}) vs light intensity plot of 2D/3D PSC employing 2-TMAI, 3-TMAI, 2-TEAI, and 3D control on semi natural logarithmic scale.

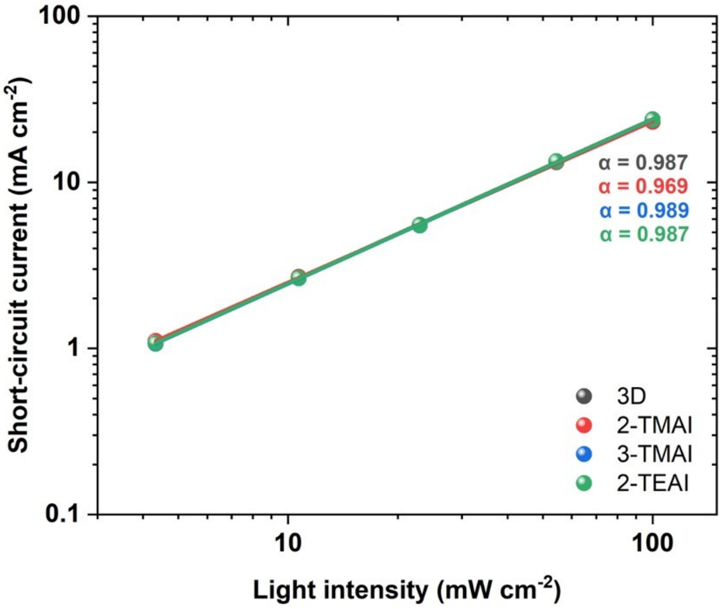


Figure S8. Short-circuit current density (J_{sc}) vs light intensity plot of 2D/3D PSC employing 2-TMAI, 3-TMAI, 2-TEAI, and 3D control on double logarithmic scale.

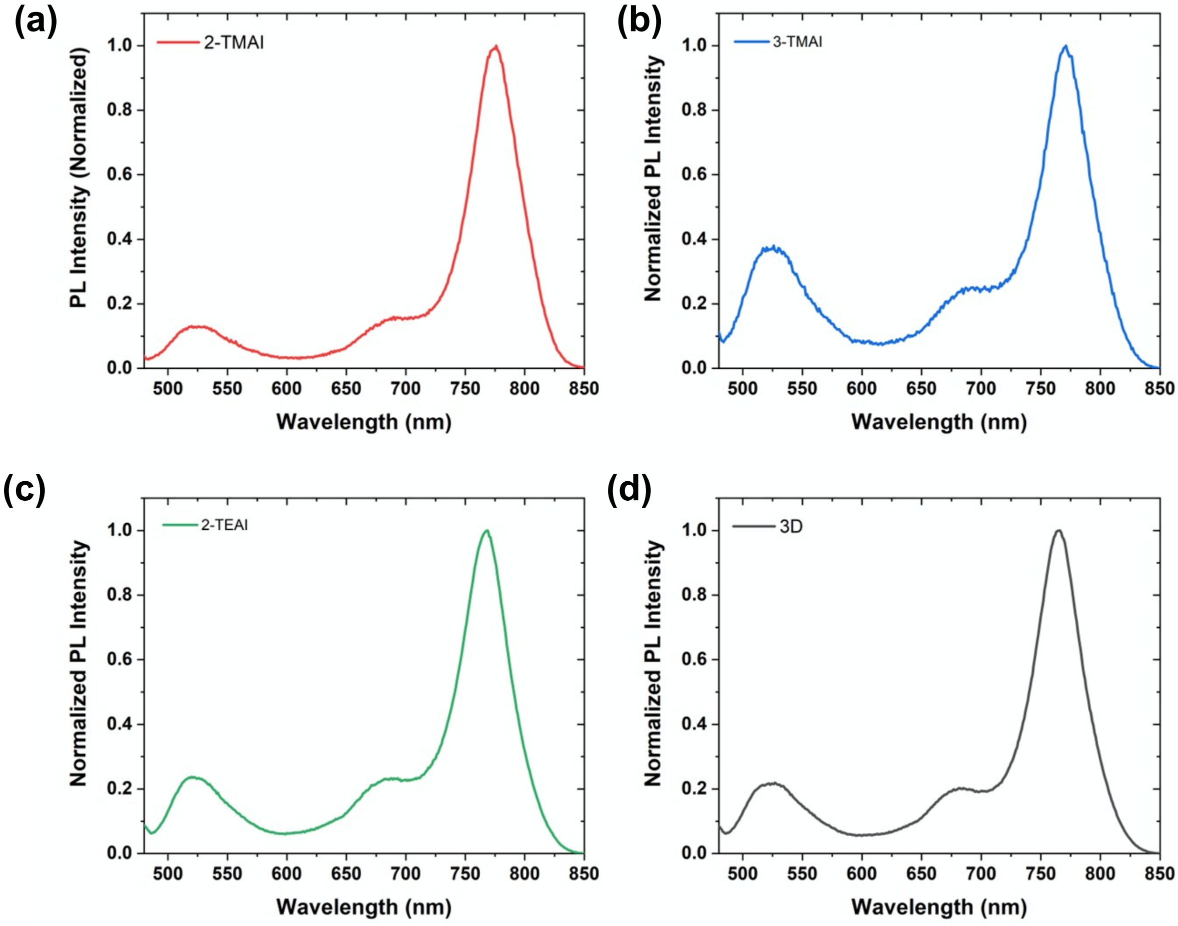


Figure S9. Photoluminescence spectra of 2D/3D films employing (a) 2-TMAI, (b) 3-TMAI, (c) 2-TEAI, and (d) 3D control upon back side excitation exciting at 450 nm.

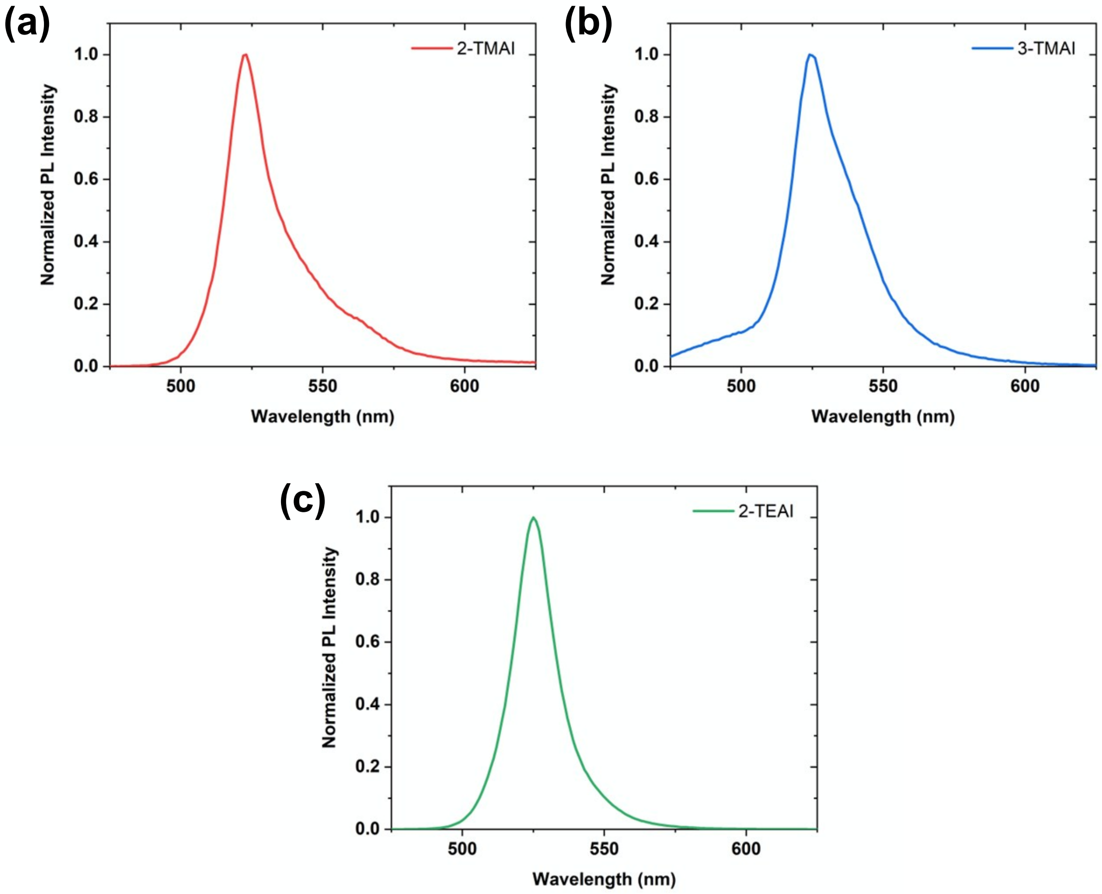


Figure S10. Photoluminescence spectra of 2D perovskite films with n=1 employing (a) 2-TMAI, (b) 3-TMAI, and (c) 2-TEAI exciting at 450 nm.

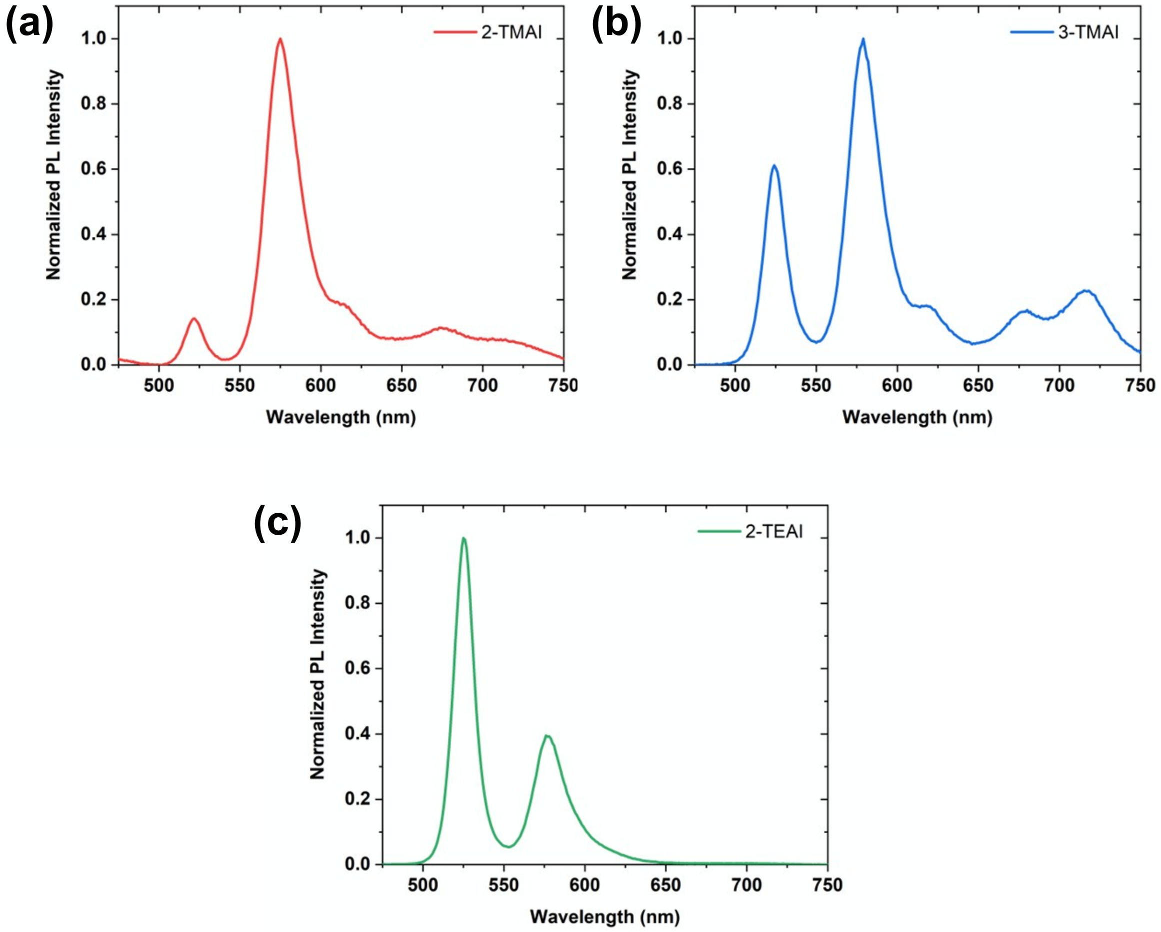


Figure S11. Photoluminescence spectra of quasi-2D perovskite films with n=2 employing (a) 2-TMAI, (b) 3-TMAI, and (c) 2-TEAI using MA as small cation exciting at 450 nm.

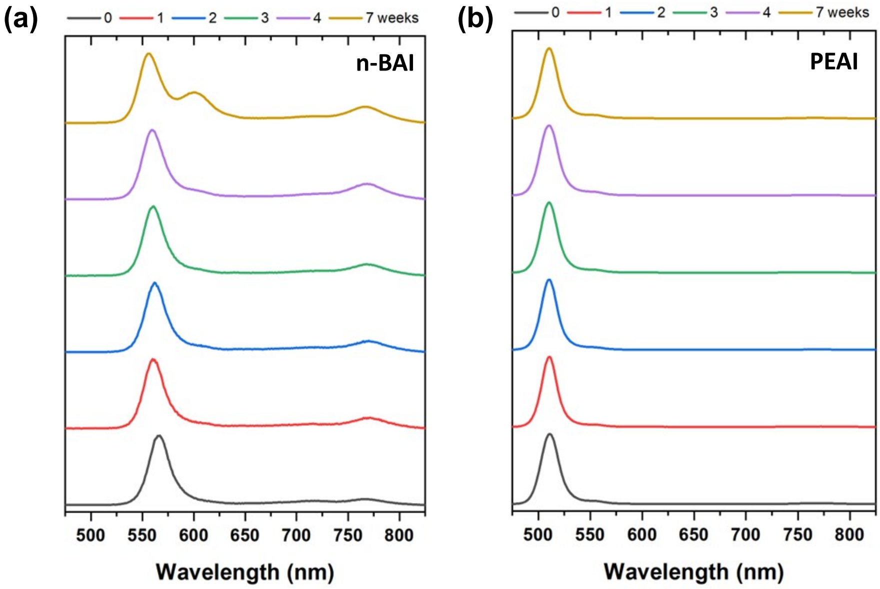


Figure S12. PL spectra of 2D/3D perovskite employing n-BAI and PEAI as the large organic cations upon aging in dark and dry environment (RH <10%).

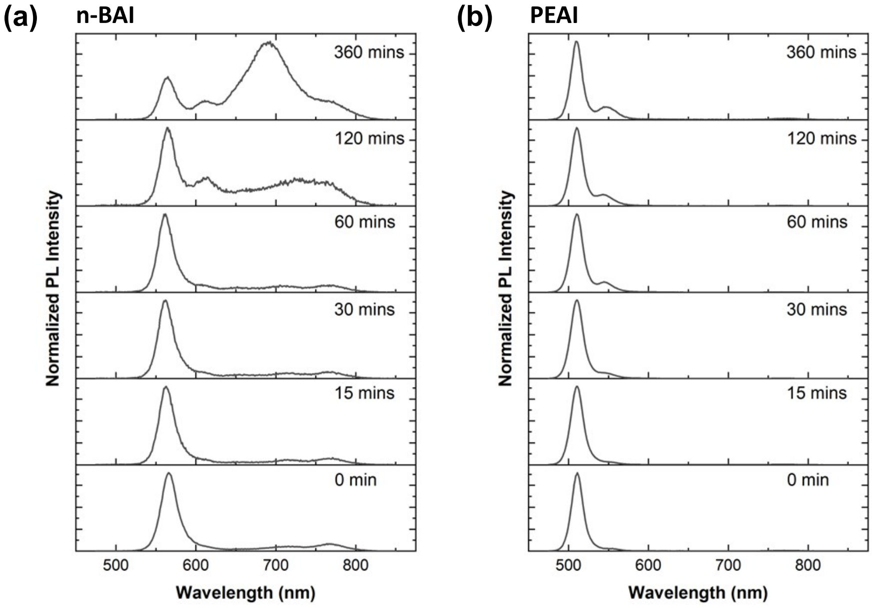
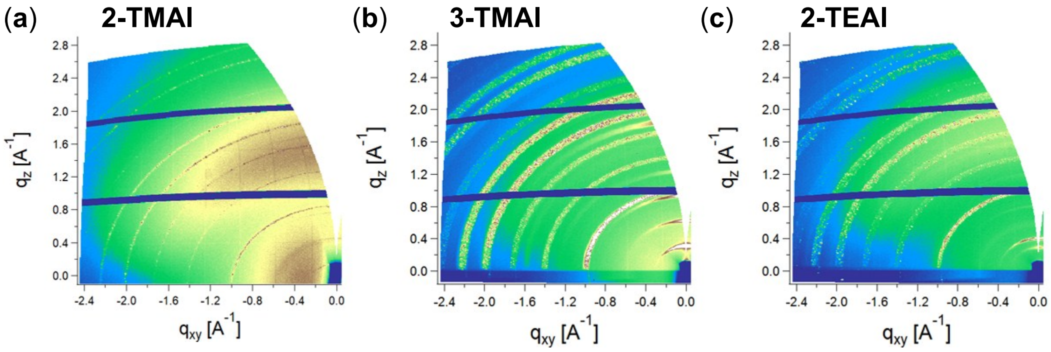
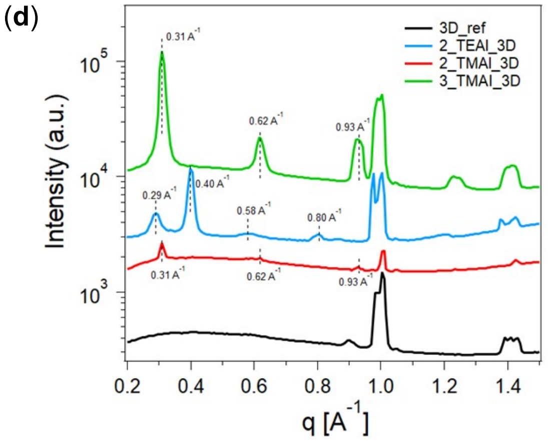


Figure S13. PL spectra of 2D/3D perovskite employing n-BAI and PEAI as the large organic cations upon heating at 50°C.





Sample	**n**	**Peak positions (Å^{-1})**
2-TEAI	1	0.40, 0.80
	2	0.29, 0.58
2-TMAI	2	0.31, 0.62, 0.93
3-TMAI	2	0.31, 0.62, 0.93

Figure S14. GIWAXS patterns of aged 2D/3D films employing (a) 2-TMAI, (b) 3-TMAI, and (c) 2-TEAI cations. (d) Sector average (90 to 125)° for data in (a)-(c), indicating principle features of the 2D layer. Table: Summary of the *n* number based on the GIWAXS patterns.

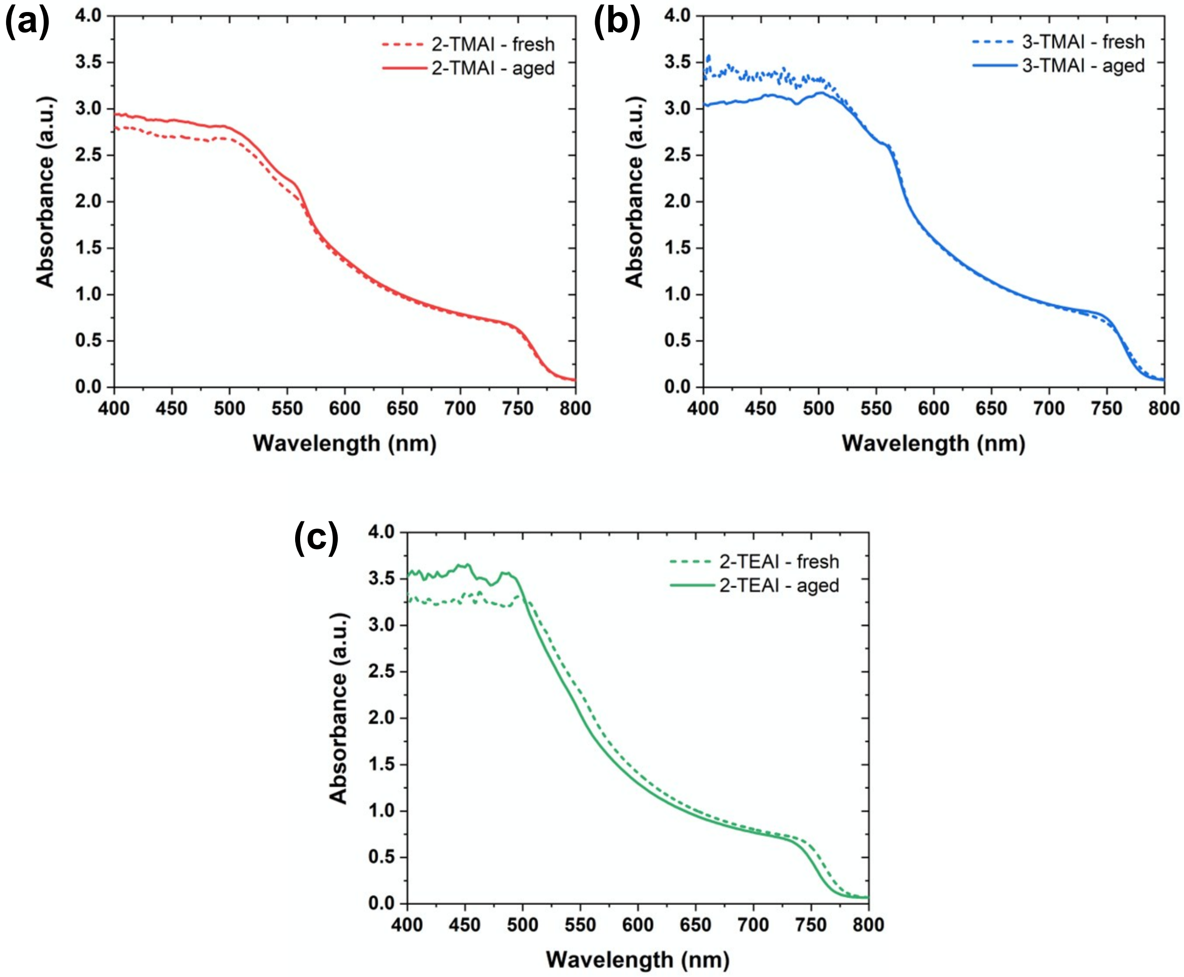


Figure S15. Absorption spectra of fresh and aged (stored in the dark and dry environment for 4 months) 2D/3D films employing (a) 2-TMAI, (b) 3-TMAI, and (c) 2-TEAI cations.

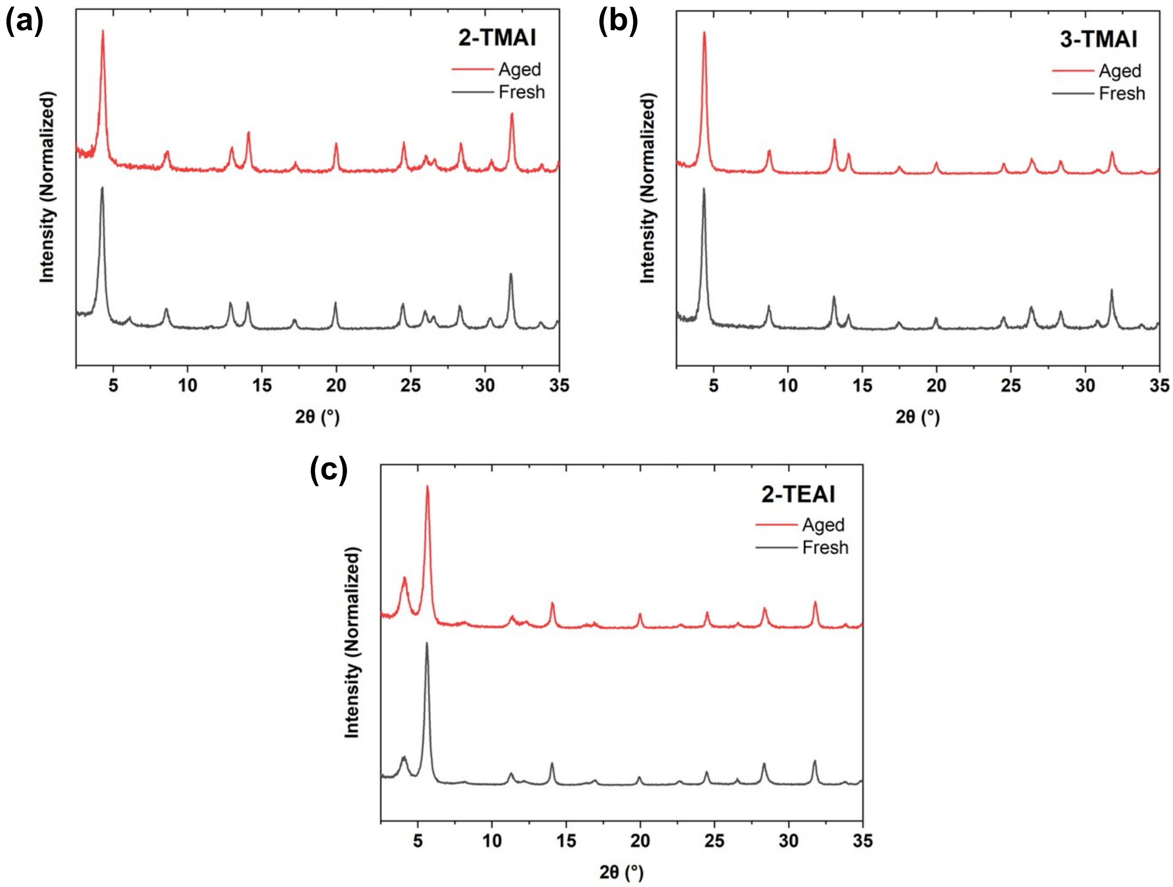


Figure S16. XRD patterns of fresh and aged (stored in the dark and dry environment for 4 months) 2D/3D films employing (a) 2-TMAI, (b) 3-TMAI, and (c) 2-TEAI cations recorded at incident angle of 2°.

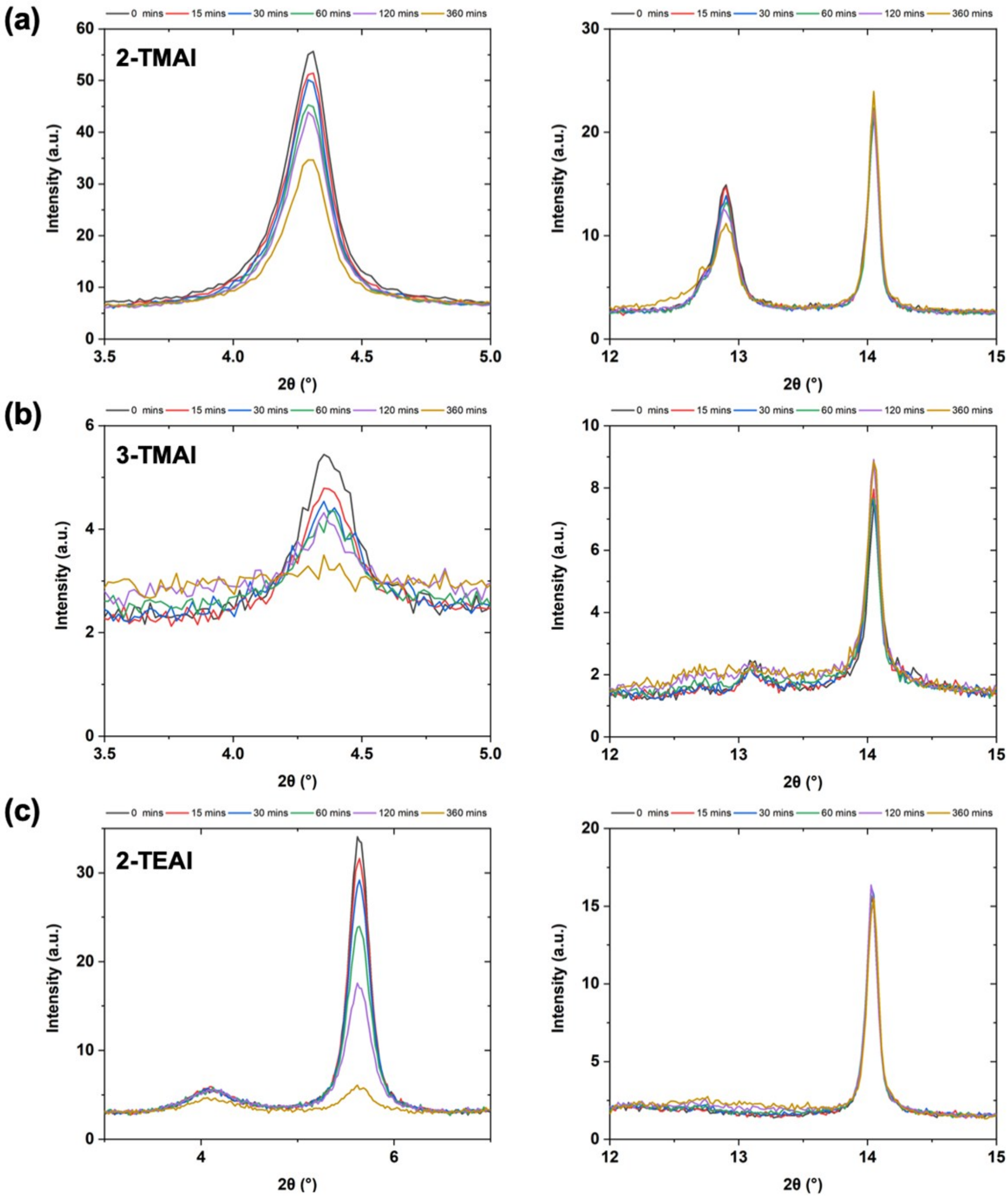


Figure S17. In-situ XRD measurement of 2D/3D perovskite films employing 2-TMAI, 3-TMAI, and 2-TEAI upon thermal aging at 50°C