A Thienothiophene-Based Cation Treatment Allows Semitransparent Perovskite Solar Cells with Improved Efficiency and Stability

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Perovskite surface treatment with additives has been reported to improve charge extraction, stability, and/or surface passivation. In this study, treatment of a 3D perovskite ($(FAPbI_3)_{1-x}(MAPbBr_3)_x$) layer with a thienothiophene-based organic cation (TTMAI), synthesized in this work, is investigated. Detailed analyses reveal that a 2D (n = 1) or quasi-2D layer does not form on the PbI₂rich surface 3D perovskite. TTMAI-treated 3D perovskite solar cells (PSCs) fabricated in this study show improved fill factors, providing an increase in their power conversion efficiencies (PCEs) from 17% to over 20%. It is demonstrated that the enhancement is due to better hole extraction by drift-diffusion simulations. Furthermore, thanks to the hydrophobic nature of the TTMAI, PSC maintains 82% of its initial PCE under 15% humidity for over 380 h (the reference retains 38%). Additionally, semitransparent cells are demonstrated reaching 17.9% PCE with treated 3D perovskite, which is one of the highest reported efficiencies for double cationic 3D perovskites. Moreover, the semitransparent 3D PSC (TTMAI-treated) maintains 87% of its initial efficiency for six weeks (>1000 h) when kept in the dark at room temperature. These results clearly show that this study fills a critical void in perovskite research where highly efficient and stable semitransparent perovskite solar cells are scarce.

such as high absorption coefficient, long charge carrier diffusion length, and low exciton binding energy.^[1–5] Although PSCs demonstrate PCEs comparable to crystal silicon solar cells (over 25%^[6]), their insufficient operational stability due to a wide range of decomposition patterns related to moisture,^[7] oxygen,^[8] UV-light,^[9] and heat^[10] hinders their upscaled development for commercialization. 2D perovskites with a wide variety of organic cations have been shown to improve stability.^[11] However, their efficiencies are still far behind their 3D counterparts due to their poor charge separation, low transport between large-cation-separated perovskite layers, high exciton binding energy, and large bandgap.^[12-14] The modification of 3D perovskites with a 2D counterpart (3D/2D) in solar cells has been investigated to increase stability without compromising efficiency. A wide variety of organic ammonium salts with different structures have been used to fabricate 3D/2D

1. Introduction

Hybrid perovskite solar cells (PSCs) have attracted great attention due to their outstanding optical and electrical properties,

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cells.^[15–20] The formation of the 2D layer on 3D perovskite upon treatment with a large cation is most commonly characterized by the existence of a low angle (<10°) peak in X-ray diffraction (XRD).^[21,22] Recent studies revealed that 2D perovskite

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Dr. I. Yildiz The Central Laboratory Middle East Technical University Ankara 06800, Turkey formation was not observed with the addition of certain cations or aromatic/aliphatic amines; nevertheless, these treatments can still drastically improve the performance of the resulting devices.^[23–26] Recently, researchers have turned their attention to molecules containing chalcogens, especially sulfur,^[27,28] which provide high polarizability and strong intermolecular interactions, thus improving charge transport properties.^[29]

Here, we theorized that the treatment of 3D perovskite with a large sulfur-containing cation that is fused and highly conjugated should significantly improve hole transport properties due to strong π - π and intermolecular sulfur-sulfur interactions.^[30-32] These types of fused, large cations have not been employed in the treatment of 3D perovskites, and the structural characteristics of the formed layer and its effect on the performance of the resulting devices have not been investigated. In addition to high efficiencies and stabilities, semitransparent perovskite solar cells (ST-PSCs) are also of great interest due to the wide range of applications, including power-generating windows on buildings or automobiles, flexible wearable electronics, and tandem structured cells.^[33,34] ST-PSCs are typically fabricated by replacing the opaque metal back-contact with a sputtered transparent conductive oxide (TCO),^[35] such as indium-doped tin oxide (ITO), indium-doped zinc oxide, and others. A suitable transition metal oxide is required to protect the underlying perovskite or organic transport layers from any damage that may occur during the magnetron sputtering of the TCO layer.^[36,37] For this purpose, molybdenum oxide (MoO_x) is a widely used buffer layer; however, MoO_x-containing solar cells have notorious stability issues, which hinder their use in commercial applications.[38-40]

Herein, a fused thiophene derivative, thieno[3,2-*b*]thiophen-2-ylmethanaminium iodide (Scheme S1, Supporting Information) (TTMAI), was successfully synthesized and employed as



the large cation for surface treatment of a 3D perovskite film. Structural characterizations revealed that TTMAI forms a 2D perovskite structure ((TTMA)₂PbI₄, n = 1) when coated at lower concentrations (1.5 mg mL⁻¹) and covers the surface in the salt form at higher concentrations (TTMAI-treated 3D perovskite, TT3DP). Significant PCE improvement (from 17% to over 20%) was achieved with TTMAI-treated samples, and the reason for the enhancement was shown to be related to better hole extraction properties by drift-diffusion (DD) simulations using solar cell capacitance simulator (SCAPS).^[41,42] We demonstrated that the capping layer significantly enhances stability even though all solar cells fabricated in this work contain a MoO_x layer. TT3DP-based PSC retained 82% of its initial PCE, while the reference solar cell maintained only 38% of it for 384 h at a relative humidity below 15%. Since we achieved exceptional stability with MoO_x-containing solar cells, we also fabricated ST-PSCs with TTMAI-treated perovskite (ST-TT3DP) with an efficiency of 17.9% PCE, one of the highest efficiencies among ST-PSCs fabricated with formamidinium methylammonium (FAMA)-based perovskites.^[43-49] The TTMAI treatment also enhanced the stability of ST-TT3DP significantly where after six weeks (>1000 h), the ST-TT3DP retained 87% of its initial efficiency, while the reference solar cell maintained only 69% of it. Considering the efficiency and stability aspects together, the results in this work constitute one of the best-performing ST-PSCs in the literature (Table S1, Supporting Information).

2. Results and Discussion

The corresponding ammonium iodide salt, TTMAI, was synthesized (**Figure 1**a) starting from commercially available thieno[3,2-*b*]thiophene-2-carbonitrile in two steps with



Figure 1. a) Schematics of the thieno[3,2-*b*]thiophen-2-ylmethanaminium iodide (TTMAI) structure and illustration of the solar cell architecture used in this study. b) XPS spectra of 3D perovskite and TTMAI-treated perovskite. c) Top-view SEM image of the 3D perovskite and TTMAI-treated perovskite. d) GIXRD pattern of the reference 3D perovskite, TTMAI-coated glass, TTMA₂PbI₄, and perovskite treated with TTMAI (TT3DP). * and * represent diffraction peaks of PbI₂ and 3D perovskite, respectively.

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78% overall yield (Figure S1, Supporting Information). Solar cells were fabricated by glass/ITO/SnO₂/perovskite/2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD)/MoO_x/Au architecture as shown in Figure 1a. As the absorber layer, 3D FAMA was used, and TTMAI in isopropyl alcohol (IPA) was coated on the reference 3D FAMA perovskite to form the TT3DP structure.

TT3DP surface contains sulfur, revealing the existence of the organic capping layer on the 3D film according to X-ray photoelectron spectroscopy (XPS) (Figure 1b). Moreover, angleresolved X-ray photon spectroscopy (ARXPS) measured at 20°, 45°, and 70° (Figure S2, Supporting Information) displayed that S 2s peak position does not change with take-off angle, indicating the oxidation state of sulfur is uniform near the surface (up to about 8 nm). Additionally, no metallic Pb was found on the perovskite surface, which was prepared and transferred to the XPS chamber in the inert atmosphere (Figure S3, Supporting Information). Scanning electron microscopy (SEM) top-view images revealed that the surface morphology (i.e., the grain boundaries mostly vanished) of the 3D film upon treatment with TTMAI is significantly altered (Figure 1c), indicating the formation of a new layer.^[50] In addition, Atomic force microscopy (AFM) images showed that the TTMAI treatment slightly reduces the roughness of the 3D surface (Figure S4, Supporting Information), which is consistent with the SEM images.

The grazing incidence X-ray diffraction (GIXRD) showed a peak below 10°, which is commonly attributed to the formation of a 2D perovskite layer.^[51–53] The observed peak at 5.10° for TTMAI-treated 3D perovskite (Figure 1d) was initially assigned to TTMA₂PbI₄ 2D perovskite (n = 1). To support our claim, 2D perovskite (n = 1) was formed by coating TTMAI and PbI₂ (2:1) on SnO₂, and GIXRD analysis was performed, which revealed a peak at 5.60° (Figure 1d). Due to the large variation in the GIXRD peak, the formation of 2D perovskite with n = 1 was excluded. Next, several thin films were prepared from solutions of TTMAI, MAI, and PbI₂ (2:12) and TTMAI,

methylammonium bromide (MABr), formamidinium iodide (FAI), and PbI₂ (for various ratios, see the Supporting Information) on SnO₂ followed by annealing to address the possible formation of quasi-2D perovskites with or without incorporation of Br and FA ions. Yet, none of these films displayed a GIXRD peak around 5.10°. Finally, GIXRD for the TTMAI (coated on glass) was recorded, and a diffraction peak at 5.10° was observed, which is consistent with the GIXRD peak of the capping layer at 5.10° (Figure 1d). In addition, compared to the 3D perovskite film, almost no change was observed in the full width half maximum (FWHM) of the perovskite (100) peak for TT3DP, indicating that TTMAI did not incorporate into the 3D bulk (Table S2 and Figure S6, Supporting Information). GIXRD studies were performed to see the effect of TTMAI concentration on the surface of the perovskite film. The results showed that at 1.5 mg mL⁻¹ concentration, a diffraction peak at 5.60° was observed (Figure S7, Supporting Information), consistent with the 2D perovskite structure with n = 1 (5.60°) as shown in Figure 1d. However, at higher concentrations, this peak disappears, and a new peak at 5.10° appear, which correlates with the TTMAI diffraction peak at 5.10° (Figure S7, Supporting Information). The curious observation of the 2D perovskite peak disappearance at higher TTMAI concentrations stays unresolved at the moment and will be investigated in detail.

3D perovskite films were first treated with 2.0 mg mL⁻¹ of TTMAI (IPA), a commonly employed concentration for large cations, at 500, 1000, and 5000 rpm, to find the ideal spin-coating conditions for TTMAI, and 1000 rpm was found to be the optimum (Figure S8, Supporting Information), (Table S3, Supporting Information). To further optimize the 2D layer, the 3D perovskite films were treated with four different concentrations (1.5, 2.0, 2.5, and 3.0 mg mL⁻¹) of TTMAI. The fill factor (FF) was improved significantly in addition to slight enhancements in open-circuit voltage (V_{OC}) and short-circuit current (J_{SC}) with increased TTMAI concentration, as shown in **Figure 2a**–c. The highest PCE of TT3DP and reference PSCs



Figure 2. a) V_{OC} , b) J_{SC} , c) FF, and d) PCE statistics of reference solar cells and solar cells treated with different concentrations of TTMAI. e) J-V curves and f) EQE spectra of the champion solar cells with different concentrations of TTMAI. The highest PCEs of the champion solar cells with different concentrations of TTMAI are given in panel (e).

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Figure 3. a) Absorption spectra and b) PL spectra of the reference and TT3DP films. c) Nyquist plot of the reference and TT3DP solar cells.

were obtained as 20.16% ($V_{OC} = 1.11$ V, $J_{SC} = 22.47$ mA cm⁻², and FF = 80.52%) and 17.11% ($V_{OC} = 1.09$ V, $J_{SC} = 21.30$ mA cm⁻², and FF = 73.78%), respectively (Figure 2e). Although the treatment with 3.0 mg mL⁻¹ TTMAI concentration resulted in the highest average PCE (Figure 2d), a turbid solution was attained at this concentration compared to others (Figure S9, Supporting Information). Therefore, all studies were conducted with 2.5 mg mL⁻¹ concentration, in which the highest PCE was achieved as 19.30% ($V_{OC} = 1.10$ V, $J_{SC} = 21.91$ mA cm⁻², and FF = 80.27%). It should be noted that a high reproducibility was obtained for all 3D and TT3DP PSCs (over 20 devices) (Figure S10, Supporting Information).

The integrated J_{SC} results calculated by integrating the external quantum efficiency (EQE) spectra (Table S4, Supporting Information) are consistent with those obtained from the *J*–*V* measurements. EQE studies revealed that the layer thicknesses chosen for the fabrication of solar cells benefit from constructive interferences in the 3D perovskite layer, as revealed by the high EQE around 750 nm.^[54]

It was also demonstrated that the TTMAI treatment at all concentrations improves the hysteresis index (HI) of the resulting devices (Table S4, Supporting Information). To further clarify the origin of the improvement in TT3DP samples, we measured J-V curves of 3D and TT3DP solar cells for the fast to slow scan rates of 400, 200, 40, and 13 mV s⁻¹ to determine the effect of the TTMAI treatment on the degree of hysteresis (Table S5 and Figure S11, Supporting Information). A lower hysteresis in J-V curves of the TT3DP solar cell indicates well-stabilized slow response processes. This observation is likely to be a consequence of the reduction in capacitive charge accumulation caused by the decrease in density of mobile ionic species at the perovskite interface.^[55]

The TTMAI layer is transparent and 2D perovskite (n = 1) has a high band gap (Figure S12, Supporting Information); hence they did not contribute to the absorption spectra of the TT3DP PSC (**Figure 3**a) as expected, which is consistent with the EQE spectra shown in Figure 2f. A decrease in photoluminescence (PL) intensity upon TTMAI addition was observed (Figure 3b), indicating better charge carrier extraction or a higher surface recombination rate (i.e., increased surface recombination velocity). Impedance measurements at the open-circuit condition under moderate illumination of 0.1 suns were performed on reference and TT3DP solar cells, and impedance spectra are displayed via Nyquist plots as in Figure 3c. As the opencircuit—where carrier generation is compensated exactly by the recombination, and there is no net carrier transport—is maintained, the resulting high-frequency impedance response can be readily analyzed in connection with recombination processes. In this regard, the shrinkage of the high-frequency semicircle upon insertion of the TTMAI layer, compared to the reference (Figure 3c), indicates faster recombination since the recombination resistance is reduced, which is consistent with the PL results. As a result, in the absence of notable J_{SC} and V_{OC} increase, we associate the PL quenching observed in the TT3DP samples with better hole transport, consistent with the notably enhanced fill factors (Figure 2c).^[56] However, unlike most 2D-perovskite layers, neither the surface recombination nor the trap density was reduced as there is only a slight increase in V_{OC} .

The ionization energy of the TTMAI film was measured as 5.36 eV by ultraviolet photoelectron spectroscopy (UPS) (Figure 4a). An illustration of the energy band alignment of 3D perovskite, 2D perovskite, Spiro-OMeTAD, and Au is also demonstrated in Figure 4a. The I-V characteristics of PSC with and without the TTMAI layer are computed, and obtained results are compared with measurements in Figure 4b. First, simulation input parameters of the reference solar cell are determined from measured I-V curves. For this, solar cell parameters (i.e., series and shunt resistances) are fitted to obtain the maximum overlap between the simulated curves and experimental results. Then, using the deduced parameters (Table S6, Supporting Information), the TTMAI layer is introduced between perovskite and Spiro-OMeTAD. It should be noted that the input parameters of the TT3DP are defined in the light of the spectroscopic ellipsometry (Figures S13 and S14, Supporting Information) and UPS measurements. As shown in Figure 4b, simulation and experimental results are in good agreement in both cell structures. Next, to elucidate the effect of the interface recombination for both cell configurations (reference and TT3DP), the surface recombination velocities (SRVs) at the perovskite/Spiro-OMeTAD and perovskite/TTMAI interfaces are varied. Simulated PCEs as a function of SRV values are presented in Figure 4c, along with experimentally obtained values marked with teal (the reference) and purple (TT3DP) dots. The PCE drop with increased SRV of the TT3DP is substantially lower than that of the reference solar cell. Similar trends are observed with V_{OC} (Figure 4d), I_{SC} (Figure 4e), and FF (Figure 4f). Although it is observed that the perovskite/TTMAI has relatively higher SRVs compared to the reference structure (in line with the reduction in PL intensity and the shrinkage of semicircles in impedance spectroscopy), higher PCEs (especially FFs) are obtained for the TT3DP thanks to favorable band alignment and larger hole mobility of the TTMAI layer compared to Spiro-OMeTAD alone. Figure 4c shows that an







Figure 4. a) UPS spectrum of the TTMAI film and linear fits to determine the work function and valence band maximum (V.B.M.). A schematic showing valence band levels of reference, TTMAI, Spiro-OMeTAD, and gold is given in the inset of panel (a). b) J-V results obtained with measurement (solid line) and simulations (dotted line) of the reference (teal) and TTMAI (purple) configurations. c) PCE, d) V_{OC} , e) J_{SC} , and f) FF simulations as a function of surface recombination velocity for 3D (teal) and TT3DP (purple) PSCs.

efficiency above 21% can be achieved with enhanced surface passivation using the same perovskite.

The steady-state PCE versus time of the reference and TT3DP unencapsulated solar cells were performed under continuous illumination (i.e., light soaking) by recording the current density at the maximum power point voltage at room temperature and under 25% relative humidity (**Figure 5**a). While PCE

dropped from 17.3% to 15.8% for the reference solar cell, the TT3DP cell remained almost intact (18.5% \rightarrow 18.02%) at the end of the 1000 s, demonstrating its superior photostability. To further assess the stability of our devices, we performed long-term stability tests. The reference and TT3DP solar cells were kept in a dark environment and under <15% relative humidity for 384 h with intermittent measurements. It was



Figure 5. a) PCEs of the reference and TT3DP PSCs measured under continuous light at ambient conditions (i.e., room temperature and 25% relative humidity). b) Normalized PCEs of the reference and TT3DP PSCs at room temperature and <15% humidity. c) Contact angle images of the reference (3D only) and TT3DP perovskite using water droplets.







Figure 6. a) J-V curves of the champion reference and TT3DP ST-PSCs. V_{OC} , J_{SC} , FF, and PCE values are provided in panel (a). b) Normalized PCE of the reference and TT3DP ST-PSCs kept under the dark at room temperature with <15% relative humidity for six weeks. The measurements are performed at room temperature. Inset: Photograph of a TT3DP ST-PSC.

shown that the reference PSC maintained only 38% of its initial efficiency whereas, TT3DP PSC retained 82% of its initial PCE (Figure 5b). It is important to highlight here that these TT3DP solar cells are the first examples of unencapsulated double cationic perovskite solar cells with MoO_x buffer layer that showed significant stability (over 350 h).^[57] It was envisioned that the increased stability was partly due to the more hydrophobic character of the TTMAI layer, and to support our claim, the increased hydrophobicity in TT3DP perovskites was demonstrated with contact angle studies using water droplets in Figure 5c (3D: 70.2°, TT3DP: 84.4°).

Last, due to enhanced stabilities achieved with MoO_x-containing opaque solar cells, we turned our attention to the fabrication of semitransparent perovskite solar cells with glass/ ITO/SnO₂/perovskite/Spiro-OMeTAD/MoO_x/ITO configuration. PCE of 16.16% ($V_{OC} = 1.04 \text{ V}$, $J_{SC} = 20.85 \text{ mA cm}^{-2}$, and FF = 74.73%) (Figure 6a) and PCE of 17.90% (V_{OC} = 1.06 V, J_{SC} = 21.74 mA cm⁻², and FF = 77.44%), which is the highest PCE obtained for FAMA perovskites, were achieved by the reference and TT3DP structured PSCs, respectively. Integrated JSC values from the EQE spectra were consistent with the short-circuit current density obtained from the *I*-V measurements (Figure S15, Supporting Information). Stability measurements of the 3D and TT3DP ST-PSCs were performed at ambient conditions upon storing them below 15% relative humidity at dark. After six weeks, the reference solar cell only maintained 69% of its initial PCE, while the TT3DP ST-PSC retained 87% (Figure 6b).

3. Conclusion

A significant increase in PCEs (from 17% to 20%) was achieved, mainly through improved FF, by deposition of thienothiophene-based salt (TTMAI) on double cationic perovskite. It was demonstrated that the enhanced FF is due to better hole extraction using impedance spectroscopy, ultraviolet photoelectron spectroscopy, and drift-diffusion modeling. In addition to improvement in PCE, the hydrophobic nature of the lowdimensional perovskite layer enabled improved stability. The unencapsulated TT3DP perovskite solar cell maintained 82% of its initial efficiency (stored in the dark and below 15% relative humidity), while the reference solar cell maintained only 38% after 384 h. Moreover, semitransparent perovskite solar cells were realized by utilizing evaporated MoO_x and sputtered ITO with one of the highest reported PCEs (17.9%) for the FAMA-based solar cells. The TT3DP ST-PSC maintained 87% of its initial efficiency over six weeks (>1000 h). The results in this work constitute one of the best performing semitransparent perovskite solar cells in the literature when the efficiency and stability aspects are taken into consideration.

4. Experimental Section

Materials: SnO₂ colloid solution (tin (IV) oxide, 15% in H₂O colloidal dispersion) was purchased from Alfa Aesar. FAI and MABr were purchased from Greatcell Solar. Lead iodide (PbI2) was purchased from Tokyo Chemical Company (TCI). MACI was purchased from Lumtec. IPA, Spiro-OMeTAD, molybdenum trioxide (MoO₃), bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI), 4-tertbutylpyridine (TBP), and chlorobenzene (CB) were provided from Sigma-Aldrich. Dimethylformamide (99.9%) (DMF) and dimethyl sulfoxide (99.9%) (DMSO) were purchased from Acros Organics. Solution for 2D perovskite (n = 1) film was prepared by dissolving TTMAI and PbI₂ (2:1) in the DMF:DMSO (95:5) (v:v) mixture. The precursor solution was coated at 3000 rpm, 30 s, and annealed at 100 °C for 10 min. Precursor solutions for FA and/or MABr incorporated quasi-2D perovskites were prepared by dissolving TTMAI, MAI, PbI₂ (2:1:2), TTMAI, FAI, PbI₂ (2:1:2), TTMAI, MABr, PbI₂ (2:1:2), and TTMAI:MABr:FAI:PbI₂ (2:0.5:0.5:2) in DMF:DMSO (95:5) (v:v) mixture. All solutions were coated at 3000 rpm, 30 s, and followed by thermal annealing at 100 °C for 10 min.

Solar Cell Fabrication: The glass substrates coated with ITO (13 ohms sq^-1) were etched with zinc powder and 3 $\ensuremath{\mathsf{M}}$ HCl. Then, ITO samples were washed with Hellmanex, deionized (DI) water, acetone, and IPA for 10 min, respectively. The cleaning procedure was followed by the UV-ozone treatment of substrates for 10 min. The diluted SnO₂ solution (2.14% in deionized water) was coated on the cleaned substrates at 4000 rpm, for 30 s, and annealed at 150 °C for 30 min. After cooling, the samples were treated with UV-ozone for 10 min and transferred into the N2-filled glovebox. PbI2 solution was prepared by dissolving 1.3 M in DMF:DMSO (95:5) (v/v) mixture. To prepare the FAMA solution, FAI:MACI:MABr (60:6:6 mg) was dissolved in 1 mL of IPA and stirred. The coating was performed by a sequential method. First, the PbI_2 solution was coated at 1500 rpm and annealed at 70 °C for 1 min. After cooling the substrates, the FAMA precursor solution was coated at 1500 rpm, 30 s, and annealed at 150 °C for 15 min. Different concentrations of TTMAI salt were dissolved in 1 mL of IPA and coated

at 1000 rpm, 30 s, followed by thermal annealing at 100 °C for 5 min. For the preparation of Spiro-OMeTAD solution, 72.3 mg Spiro-OMeTAD was dissolved in 1 mL chlorobenzene and 17.5 μ L Li-TFSI (520 mg mL⁻¹ in acetonitrile), 28.8 μ L TBP was added in it. The solution was coated at 3000 rpm, 20 s. Finally, 20 nm MoO₃ and 60 nm gold were evaporated on the substrates under a high vacuum consecutively. Fabrication of the ST-PSCs was identical to those of opaque solar cells up to the back-contact deposition. ITO bottom electrode was deposited by magnetron sputtering, which was carried out at a power density of 2.2 W cm⁻² with a deposition pressure of 2 mTorr. Last, to lower the sheet resistance of ITO film (30 ohms sq⁻¹), a 60 nm of current-collecting gold film was deposited by thermal evaporation.

Solar Cell Characterization: The J-V characterizations of all solar cells were measured by Keithley 2400 under a solar simulator (Pico G2V LED Solar Simulator) at AM1.5G with 100 mW $\rm cm^{-2}$ illumination intensity with a scan rate of 100 mV s^{-1} . For defining the active area of the metal bottom-contact cells, laser-cut silicon shadow masks with 3 mm² rectangular openings, and for the semitransparent cells, the shadow masks with 3.14 mm² circular openings were used. EQE, reflection (R), and transmission (T) measurements were done by a PV characterization system equipped with a BaSO4-covered integrating sphere (Bentham Instruments, PVE300). Absorption (A) spectra of the films were then calculated using A = 1 - R - T. Impedance measurements were performed using MFIA Impedance Analyzer (Zurich Instruments) in the frequency range from 10 Hz to 1 MHz with an oscillation peak amplitude of 15 mV. The cell was operated under the open-circuit condition at all times using a DC blocking capacitor connected to the signal output of the impedance analyzer while the true oscillation voltage across the cell was sensed via 4-terminal measurement mode. The cells were illuminated with a 625 nm red LED (Thorlabs M625L4), which was calibrated by the short-circuit photocurrent of a sample cell, corresponding to an equivalent of 0.1 suns AM1.5G.

Film Characterization: SEM measurements were operated at 30.00 kV with a resolution of 1.2 nm (QUANTA 400F Field Emission). AFM measurements were carried out by Park System, PSIA XE100. GIXRD patterns were obtained (Rigaku Ultima-IV X-Ray diffractometer) with Cu K α radiation at 30 kV and 40 mA operation conditions and a grazing angle of 0.5° at a scan rate of 2° min $^{-1}$ XPS, ARXPS, and UPS experiments were carried out (Physical Electronics (PHI), VersaProbe 5000) under high vacuum with a base pressure of 1×10^{-9} mbar. X-ray energy of 23.4 W, pass energy of 58.70 eV, energy step of 0.1 eV, and X-ray spot size of 100 μ m were used for all three angles (20°, 45°, and 70°) for the ARXPS measurement. The He discharge lamp (21.22 eV) was used as the light source in UPS measurements. The positions of the valence band maxima were determined using linear extrapolation of the leading edge of the valence band emissions, and work function was determined from the linear extrapolation with the baseline of the secondary electron onset. Photoluminescence spectroscopy measurements (Horiba Jobin Yvon, Fluorolog 3) were done from the glass side with an excitation wavelength at 495 nm (the films were coated on the glass substrates). Contact angle measurements were conducted using a tensiometer (the Attension Theta Lite), and water was used as the solvent.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

Keywords

hole extraction, novel organic capping layers, semitransparent perovskite solar cells, stability, surface-treated perovskite solar cells

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Supporting Information

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A Thienothiophene-Based Cation Treatment Allows Semitransparent Perovskite Solar Cells with Improved Efficiency and Stability

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1.Experimental Details

1.1. Synthesis



Figure S1. Synthesis of TTMAI.

Thieno[3,2-b]thiophen-2-ylmethanamine (2): The synthesis of the target compound performed according to the literature.^[1] The commercially available was thienothiophene carbonitrile (1) (0.50 g, 3.03 mmol) was dissolved in dry THF (10 mL) in a reaction flask under an argon atmosphere. In another reaction flask, LiAIH₄ (0.345 q, 9.09 mmol) was dissolved in dry THF (10 mL). The LiAIH₄ solution was added dropwise to the reaction flask containing starting material at 0 °C. After the addition, the solution was heated to 50 °C and stirred for 24 hours. The reaction cooled down to 0 °C, and the reaction mixture was diluted with diethyl ether (10 mL). Distilled water (5mL), 5% NaOH solution (10 mL), and MgSO₄ were added at 0°C. The reaction was warmed to room temperature and stirred for 30 minutes. The resultant mixture was filtered and washed with diethyl ether (100 mL). The collected filtrates were concentrated under low pressure to yield the title compound as a white solid (0.503 g, 98% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, J = 5.2 Hz, 1H), 7.15 (d, J = 5.2 Hz, 1H), 7.03 (s, 1H), 4.04 (s, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 149.01, 137.63, 137.02, 125.08, 118.58, 114.86, 41.44 ppm.

Thieno[3,2-b]thiophen-2-ylmethanaminium iodide (TTMAI): The synthesis of the target compound was performed according to the literature with small modifications.^[1] Thieno[3,2-b]thiophene-2-methylamine (**2**) (0.20 g, 1.18 mmol) was dissolved in ethanol (10 mL). HI (0.2 mL) was added to this solution at 0 °C, and the mixture was stirred for 3 hours. The excess solvent was evaporated under low pressure to give a dark brown solid, which was recrystallized from diethyl ether. The material was further washed with excess diethyl ether and dried to give the title compound as a cream-colored solid (0.16 g, 80% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.23 (s, 3H), 7.73 (d, *J* = 5.3 Hz, 1H), 7.56 (s, 1H), 7.47 (d, *J* = 5.2 Hz, 1H), 3.37 (s, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 139.93, 138.36, 137.58, 129.37, 122.16, 120.39, 38.34.

2. Material Characterization

Table S1. Solar cell parameters and stability information of the best performing (i.e., PCE>17%) semitransparent perovskite cells reported in the literature and this work. N₂ and air storage environments of solar cells are denoted as * and +, respectively.

Device Structure	Voc (V)	J _{sc} (mA/c m²)	FF (%)	PCE (%)	Active Area (mm ²)	Stability	Ref.
Glass/ITO/SnO 2/Cs 0.05FA 0.95Pbl3/Spiro- OMeTAD/Cr/Au/MgF2	1.14	21.9	79.7	19.8	100	Storage in dark⁺ for 60 days Retained PCE: ~80%	[2]
Glass/IZrO/SnO₂/ Cs₀₀₅FA₀.в₁MA₀.₁4Pbl₂.₅₅Br₀.4₅ /Spiro- OMeTAD/MoO₄/IZO/MgF₂/Ag	1.12	22.3	77.7	19.4	4.90	MPPT under continuous illumination* for 100h Retained PCE: 75%	[3]
FTO/bl-TiO₂/m-TiO₂/(FAPbl₃)₁. ₂(MAPbBr₃)₂/PTAA/WO₄/NbOℊ -AR/ITO/Au fingers	1.02	23.5	78.8	18.9	7.00	MPPT under continuous illumination ⁺ for 100h Retained PCE: 90%	[4]
Glass/ITO/TiO₂/MAPbl₃/Spiro -OMeTAD/MoO₃/Au/MoO₃	1.16	19.8	79.9	18.3	9.60	Storage in the dark⁺ for 172 h Retained PCE: 95%	[5]
ITO/C ₆₀ /MAPbl₃- _x Br _x /Spiro- OMeTAD/MoO₃/Au/MoO₃	1.07	22.4	73.0	17.5	7.57	N/A	[6]
Quartz/ITO/c-TiO2/ <i>m</i> - TiO2/Rb _{0.05} Cs _{0.095} MA _{0.1425} FA _{0.71} 25Pbl2Br / <i>n</i> -BABr/Spiro- OMeTAD/MoO ₂ /IZO	1.21	18.0	78.9	17.1	21.0	MPPT under continuous illumination* for over 100h Retained PCE: 94%	[7]
ITO/NiO _x /4-bromobenzoin acid/ Perovskite /LiF/C60/SnO _x /IZO	1.15	19.99	78.7	18.04	103	MPP: 40 °C 500 h Thermal: 85 °C ~1000h	[8]
ITO/CuSCN/CH₃NH₃Pbl₃/PC₀₀ BM / <i>np-</i> ZnO:Al nps. /AgNW	1.10	21.00	74.1	17.1	100	N/A	[9]
ITO/SnO₂/(FAPbl₃)₁. x(MAPbBr₃)x/TTMAI/Spiro- OMeTAD/MoOx/ITO	1.06	21.7	77.4	17.9	3.14	Storage in the dark⁺ for 1000 h, Retained PCE: 87%	This work



Figure S2. Normalized ARXPS spectra for Pb 4f and S 2s signals of the TT3DP film at different take-off angles.



Figure S3. Image of the XPS holder used to transfer perovskite samples from the glovebox to the XPS chamber.



Figure S4. AFM topography images of the reference and TT3DP films. The root-square mean value for the reference sample was calculated as 27.6 nm and for the TT3DP sample as 26.6 nm, respectively.

Table S2. d spacing, full width at half maximum (FWHM), and crystallite size parameters obtained from the GIXRD measurements for the reference, TT3DP, and TTMAI films.

Samples	d spacing of the 2D layer (Å)	d spacing of the TTMAI layer (Å)	d spacing of the <100> 3D- perovskite (Å)	FWHM of the <100> 3D- perovskite (°)	Crystallite Size 3D- Perovskite (nm)
Reference	-	-	6.27	0.344	24.3
TT3DP	-	17.33	6.26	0.353	23.7
2D (n=1)	15.52	-	-	-	-
TTMAI	-	17.33	-	-	-



Figure S5. GIXRD patterns of quasi 2D perovskite films prepared from solutions **A** (TTMAI, MAI, Pbl₂ | 2:1:2), **B** (TTMAI, MABr, Pbl₂ | 2:1:2) **C** (TTMAI, MABr, FAI, Pbl₂ | 2:0.5:0.5:2) and **D** (TTMAI, FAI, Pbl₂ | 2:1:2) letters denote the various composition the of perovskites. The dotted line denotes the position of the diffraction peak of TTMAI on the 3D perovskite (**TT3DP**).



Figure S6. GIXRD pattern of the TT3DP film at different grazing angles. Inset: Schematics of information depth versus incidence angle of TTMAI-coated 3D perovskite.



Figure S7. GIXRD patterns of 3D perovskite film treated with different concentrations of TTMAI.



Figure S8. (a) V_{OC} , (b) J_{SC} , (c) FF, and (d) PCE statistics of reference solar cells and solar cells treated with different spin speeds of TTMAI. e) J-V curves of the champion solar cells. f) EQE spectra of the champion PSCs. J_{SC} values calculated by integrating EQE spectra are given in (f).

Devices		Voc (V)	J _{sc} (mA/cm ²)	FF (%)	PCE %
	Average	1.08 ± 0.01	22.05 ± 0.44	67.30 ±	16.03 ± 0.77
Reference	Highest	1.07	22.65	3.12	17.34
				71.48	
	Average	1.07 ± 0.01	21.96 ± 0.66	75.46 ±	17.75 ± 0.79
TTMAI, 500 rpm				1.45	
	Highest	1.08	22.47		19.15
				78.92	
	Average	1.08 ± 0.02	22.51 ± 0.47	74.29 ±	18.00 ± 1.27
TTMAI, 1000 rpm				3.40	
	Highest	1.11	22.80		19.37
				76.20	
	Average	1.09 ± 0.01	22.52 ± 0.49	72.66 ±	17.81 ± 0.71
TTMAI, 5000 rpm				2.63	
	Highest	1.10	23.11		18.72
				73.83	

Table S3. Average and the champion device parameters of the reference cell and cells coated with TTMAI at different spin rates.



Figure S9. Images of the solutions of TTMAI in IPA with different concentrations (From left to right: 3.0 mg/mL, 2.5 mg/mL, and 2.0 mg/mL).



Figure S10. Scattering graph of the reference and TT3DP solar cells (out of 20 devices). Solid curves are to guide the eye.

HI of the PSCs were calculated by the following equation (equation 1), and the results were given in Table S4 and Table S5.

$$HI = \frac{PCE_{RS} - PCE_{FS}}{PCE_{RS}}$$
(S1)

Table S4. Integrated J_{SC} values of reference cells and devices containing TTMAI layer with different concentrations obtained from external quantum efficiency spectra. Hysteresis Index (%) results of the TMMAI layer with different concentrations.

Samples	Integrated J _{sc} values (mA/cm ²)	Hysteresis (HI, %)
Reference	22.01	12.43
1.5 mg/mL	22.25	6.63
2.0 mg/mL	21.81	5.87
2.5 mg/mL	21.86	7.44
3.0 mg/mL	21.83	7.60

Table S5. Hysteresis Index (%) calculations of the reference and the champion TT3DP perovskite solar cells at different scan rates.

Devices / Scan Rates (mV/s)	400	200	40	13	
Reference	10.03 ±2.53	2.89 ± 2.97	2.50 ± 1.44	5.59 ± 3.54	
TT3DP	6.73 ± 5.42	3.17 ± 0.33	2.44 ± 0.78	1.81 ±1.04	



Figure S11. Hysteresis index vs. scan rate for the reference and TT3DP solar cells.



Figure S12. Transmission spectra of TTMAI and TTMA₂PbI₄ (2D perovskite, n=1).



Figure S13. Measured and fitted tan ψ and cos Δ spectra of materials used in this study, including ITO on Glass (a, b), SnO₂/ITO/Glass (c, d), 3D perovskite (e, f), and TTMAI (g, h).

Table S6. Simulation input parameters. All thicknesses are obtained from either ellipsometry or SEM. Electron affinity of TTMAI was measured by UPS, Energy bandgap of perovskite and TTMAI were obtained from absorption spectra. The other parameters are adapted from the literature used for theoretical performance analysis.^[10–20]

Properties	Unit	Device Layers						
		ΙΤΟ	SnO ₂	Perovskite	TTMAI	Spiro-OMeTAD		
Thickness	nm	150*	17*	700*	8*	170*		
Energy band gap	eV	3.72	3.24 ^[10]	1.55 ^{‡, §}	4.03*	2.91 ^[11,12]		
Electron Affinity Energy	eV	4.70 ^[10]	4.30 ^[10]	3.89 ^[13]	1.33 ^{*,†}	2.20 ^[11,12]		
VB effective density of states	1/cm ³	1.0x10 ^{19[10]}	4.0 x10 ^{18[10]}	2.0 x10 ^{19[11]}	1.0 x10 ²⁰	2.2 x10 ^{18[11]}		
CB effective density of states	1/cm ³	1.0 x10 ^{19[10]}	1.0 x10 ^{18[10]}	2.0 x10 ^{18[11]}	1.0 x10 ¹⁹	2.2 x10 ^{18[11]}		
Dielectric Permittivity		3.3 ^[10]	10.0 ^[14]	9.40	2.16*	3.0 ^[11,15-18]		
Acceptor Concentration	1/cm ³	-	-	1.3 x10 ^{16[11]}	1.0 x10 ¹⁵	1.3 x10 ^{18[19]}		
Donor Concentration	1/cm ³	5.0 x10 ^{20*}	1.0 x10 ^{20[10]}	1.3 x10 ^{16[11]}	_	-		
Hole Mobility	cm ² /V.s	0.025 ^[10]	0.025 ^[10]	2 ^[11]	1	1.0 x10 ^{-4[20]}		
Electron Mobility	cm ² /V.s	25 ^[10]	1 ^[10]	2 ^[11]	1	1.0 x10 ^{-4[20]}		

*, †, ‡, and § indicated values obtained/adapted by the spectroscopic ellipsometry, UPS, absorption, and PL measurements, respectively.



Figure S14. Refractive index (solid lines) and extinction coefficient (dashed lines) spectra of materials used in this study extracted from the spectroscopic ellipsometry measurements.



Figure S15. EQE spectra of the reference and TT3DP ST-PSCs



Figure S16. ¹H-NMR Spectrum of Compound 2.



Figure S17. ¹³C-NMR Spectrum of Compound 2.







Figure S19. ¹³C-NMR Spectrum of TTMAI.

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