Enhancement of 3D/2D Perovskite Solar Cells using an F4TCNQ Molecular Additive

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ABSTRACT

Recent developments in hybrid organic-inorganic lead-halide perovskite solar cells (PSCs) have shown that use of a 2-dimensional (2D) perovskite capping layer on a 3D perovskite absorber layer (3D/2D PSCs) results in substantially improved environmental stability of the devices. However, in these 3D/2D PSC structures the poor charge transporting properties through the 2D layer hinders device performance, particularly for thicker 2D layers. Here, we report a facile method that overcomes some of the inherent challenges in using such 2D capping layers through the introduction of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) as a molecular additive into the 2D layer. It is found that this additive undergoes partial charge transfer with the perovskite layer to provide a passivation effect, which also modifies the crystalline domain sizes of the 2D perovskite. PSCs incorporating a F4TCNQ-modified 2D capping layer grown in-situ on top of the 3D Cs/MA/FA mixed-cation perovskite absorber layer display modified interfacial characteristics that yield improved charge extraction and reduced charge recombination compared with 3D/2D PSCs comprising an unmodified 2D capping layer. This modification results in 3D/2D PSCs for which the maximum power conversion efficiency is increased to more than 20% compared with 18.2% for unmodified 2D capping layers.
INTRODUCTION

Metal-halide perovskites have become one of the most promising materials for high-performance photovoltaic devices due to their unique optoelectronic properties, such as strong light harvesting capability,\(^1\) long charge carrier diffusion lengths and mobilities,\(^2\) and narrow photoluminescence (PL) bands with high PL quantum yield.\(^3\) Owing to these advantages, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has improved rapidly from 3.8% to more than 25% in less than ten years.\(^4,\)\(^5\) These record efficiencies are now on par with those of silicon-based solar cells, and come with major advantages in terms of ease of processing and lower cost, at an equivalent manufacturing scale.\(^4,\)\(^6\) However, the underlying problems of metal-halide perovskites in terms of their instability towards moisture and difficulty in controlling crystallisation during solution-processing are hindering the further development of PSC technology.\(^7,\)\(^8\)

Significant research effort has been focused on improving the PSC performance by means of configuration design,\(^1,\)\(^9,\)\(^10\) material optimization,\(^11-13\) interface engineering\(^14,\)\(^15\) and encapsulation techniques.\(^16\) Among these approaches, lowering the spatial dimensionality of the perovskite from 3D to 2D by using non-volatile and longer chain organic cations has been reported widely as a promising strategy to simultaneously reduce interfacial defects and improve stability of PSCs.\(^17,\)\(^18\) Incorporation of these types of cations induces the formation of layered structures having the general chemical form (RNH\(_3\))\(_2\)A\(_n-1\)B\(_n\)X\(_{3n+1}\) (n=1,2,3,4…∞),\(^19\) where A\(_n-1\)B\(_n\)X\(_{3n+1}\) is the perovskite layer, RNH\(_3^+\) is a large aliphatic or aromatic alkylammonium spacer cation that isolates the perovskite layers, and n is an integer that represents the number of perovskite layers.\(^20,\)\(^21\) In general, structures having smaller values of n are considered to be 2D or quasi-2D perovskites, with 3D-like perovskite structure developing with increasing values of n. The existence of the larger spacer cations in the 2D sheet structures makes them more hydrophobic than their 3D analogues, facilitating an
improved environmental stability, which is conducive to their commercialization. However, the PCE of 2D PSCs is limited due to their high exciton binding energies and poor charge transport properties.

In response, hybrid 3D/2D perovskite bilayers have emerged as a promising PSC configuration, with the 3D perovskite dominating the optical absorption and charge transport characteristics and a very thin 2D perovskite capping layer acting to passivate surface defects and protect the 3D perovskite from moisture. However, solution processed 2D perovskite films possess undesired orientation or crystallization of the 2D perovskite domains, which results in charge accumulation at the 3D/2D perovskite and perovskite/hole transport material (HTM) interfaces. Most development efforts towards addressing these issues within 3D/2D PSCs have focused on the introduction of new 2D perovskite hydrophobic cations or improving undesired orientation or crystallization of the 2D perovskite during film formation process. For example, alkali cations, such as K+ and Rb+, have been shown to induce preferential orientation and higher crystallinity of the 2D perovskite capping layer, which have enhanced its charge transport properties. An alternative potential approach, which has been widely applied to 3D perovskites, is the use of molecular additives that enable control of properties, such as electrical doping and grain orientation. To the best of our knowledge, the use of such a molecular additive strategy to passivate the interface between 3D/2D perovskite layers and 2D perovskite domains has not been reported.

Herein, we describe the use of 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) as a molecular additive to alleviate the charge-transport limitations of the 2D perovskite capping layer in hybrid 3D/2D PSCs. F4TCNQ is a fluorinated molecular p-type dopant and a strong electron acceptor that is used widely for doping conjugated polymers to enhance their electrical conductivity. Moreover, its use as a 3D perovskite surface modifier has been studied, showing that it effectively passivates the surface states through
supramolecular interactions between the F4TCNQ and the surface halide ions. In the present work, we investigate the role of F4TCNQ as a molecular additive in the 2D perovskite capping layer and its influence on charge extraction, recombination and device performance within 3D/2D hybrid PSCs. We find that through this approach the PCEs of the resulting devices is significantly improved from 18.1% to over 20%. Importantly, the introduction of F4TCNQ also renders high performance of hybrid 3D/2D PSCs with improved moisture stability, which provides a feasible strategy to achieve PSCs with high PCE and stability simultaneously.

RESULTS AND DISCUSSION

Hybrid 3D/2D-architecture perovskite films were fabricated via in-situ crystallization of 2D perovskite on a pre-formed mixed-cation 3D perovskite film comprising caesium, formamidinium (FA) and methylammonium (MA). A 5 mg mL⁻¹ solution of n-butylammonium iodide (BAI) in isopropanol (IPA) was spin-cast onto a Cs₀.₀₅FA₀.₇₉MA₀.₁₆PbI₂.₄₉Br₀.₅₁ 3D perovskite film (Figure 1A). The 3D perovskite film was formulated to contain a stoichiometric excess of PbI₂ of around 5 mol %. The surface of the 3D perovskite subsequently converts to a BA₂(FA/MA/Cs)ₙ₋₁Pbₙ(I/Br)ₙ₊₁ 2D capping layer after BAI is introduced. The F4TCNQ additive was introduced into the 2D capping solution prior to spin-casting onto the 3D layer. Here we use the notation 2DF# to denote the weight percentage of F4TCNQ relative to BAI in the 2D capping solution, e.g. 2DF5 corresponds to an IPA solution containing 0.25 mg mL⁻¹ F4TCNQ and 5 mg mL⁻¹ BAI.

The top-view scanning electron microscope (SEM) images (Figure 1B) show the morphologies of 3D, 3D/2D, 3D/2DF5 and 3D/2DF10 perovskite films, respectively. A clear change in the surface morphology of the 3D perovskite film is observed when the 2D perovskite capping layer is formed, with the grain boundaries becoming indistinct and the appearance of a secondary surface layer emerging. These changes are ascribed to the reconstruction of the
perovskite on the surface during the formation of the 2D perovskite.\textsuperscript{24} The addition of 5\% w/w F4TCNQ into the BAI solution (i.e. 2DF5) results in no further change to this surface morphology, while evidence of both aggregation of the additive on the surface as well as pin-holes are seen upon further increase in F4TCNQ for 2DF10 (Figure 1B and S1).

X-ray diffraction (XRD) measurements in Figure 2A confirm the existence of the 2D layer through the emergence of new scattering peaks at 9.04° and 13.5°, which are characteristic of the (040) and (060) planes of a 2D perovskite (n =2).\textsuperscript{22} These are accompanied by the reduction of the PbI\textsubscript{2} peak at 12.7°. This suggests that the formation of the 2D perovskite capping layer arises from the conversion of residual PbI\textsubscript{2} at the surface of the 3D perovskite film. A more detailed structural comparison across 3D, 3D/2D and 3D/2DF films can be deduced from their 2D grazing-incidence wide-angle x-ray scattering (GIWAXS) patterns (see Figure S2) and the corresponding azimuthally-integrated intensity versus q curves in Figure 2B. The characteristic peaks of 2D perovskite at 6.4 nm\textsuperscript{-1} and 9.6 nm\textsuperscript{-1} appear in all 3D/2D perovskite films, indicating the formation of 2D perovskite, while the crystal orientation is not significantly altered by the F4TCNQ additive. In addition, it is clear that within experimental error the characteristic peaks of 2D and 3D perovskites are not shifted by the introduction of F4TCNQ. This indicates that the molecule does not intercalate into the 2D or the 3D perovskite crystalline domains, respectively. However, the full width at half maxima (FWHM) of the 2D perovskite peaks is slightly broadened with increasing concentration of F4TCNQ in the 2D perovskite layer, which indicates that the F4TCNQ reduces the 2D perovskite domain size.

Using the simplified Scherrer equation, \( D = \frac{2\pi K}{\Delta q} \),\textsuperscript{34} where D refers to the mean size of the domains, K is a shape factor (typically 0.8−1, here we use 1) and \( \Delta q \) is the FWHM, the domain sizes of the 2D, 2DF5 and 2DF10 perovskites can be estimated to be 23.3 nm, 18.5 nm and 17.0 nm, respectively.
To correlate these structural changes to the underlying chemical nature of the F4TCNQ, grazing-angle reflectance Fourier-transform infrared spectra (GA-FTIR) of pristine F4TCNQ, 3D/2D, 3D/2DF5, and 3D/2D10 perovskite films (Figure S3) were measured to probe the charge state of F4TCNQ in the modified perovskite. The primary cyano-vibrational stretch mode of pristine F4TCNQ at 2227 cm\(^{-1}\) changes to a pair of peaks at 2217 cm\(^{-1}\) and 2195 cm\(^{-1}\) when F4TCNQ is introduced into the 3D/2D perovskite films. This is indicative of charge transfer arising to induce an anionic F4TCNQ species within the resulting films.\(^{32}\) Notably, the 3D/2DF10 film shows stronger FTIR absorption peaks with the same absorption peak positions as for the 3D/2DF5 film. This suggests that the same anionic state of the F4TCNQ exists in both films. The magnitude of the IR absorption band shift is indicative of a partial charge-transfer mechanism, as has been previously observed for the interaction of F4TCNQ with organic molecules.\(^{35, 36}\) As we have no evidence for intercalation of F4TCNQ into the 2D or 3D structure has been observed, this result implies the presence of chemically adsorbed species at the interface between the 2D perovskite domains and the 3D surface. Accordingly, a higher concentration of F4TCNQ introduced into a 2D capping layer would naturally result in a reduction of the 2D domain size itself, as is observed.

Ultraviolet-visible (UV-Vis) absorption measurements of a pristine 3D perovskite film and 3D/2D perovskite bilayers, both with and without F4TCNQ additive, are shown in Figure 3A. These measurements were made using substantially thinner 3D perovskites layers than those typically used in devices (0.2 mol L\(^{-1}\) precursor solution \(c.f.\) 1.32 mol L\(^{-1}\) precursor solution for devices) to amplify the absorption by the 2D perovskite capping layer relative to that of the 3D perovskite films (\(c.f.\) Figure S4). The absorption band centred at \(~550\) nm and a Tauc-derived bandgap of \(~2.3\) eV, are consistent with the formation of an \(n = 2\) 2D perovskite capping layer.\(^{37}\) This absorption peak shows a negligible shift upon the introduction of F4TCNQ, implying no change in bandgap. In addition, the optical bandgap of the 3D perovskite for pristine 3D, 3D/2D
and 3D/2DF5 perovskite films were calculated to be 1.55 eV, indicating the energy band structure of the 3D perovskite is not altered by the 2D perovskite capping layer.

To further probe the optical properties of these perovskite layers, steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements were conducted. The PL peak of the 3D perovskite layer is located at ~762 nm, with a negligible emission shift being detected upon addition of the 2D capping layers, both with and without F4TCNQ (Figure S5). TRPL measurements were conducted to examine the charge transport and defect passivation effects of the 2D capping layer on the 3D perovskite films (Figure 3B). These clearly show multi-component decay characteristics, with contributions from both short and long recombination lifetimes. To quantify these characteristics, the PL decay curves were fitted using the following bi-exponential decay function, with the best-fit parameter values summarized in Table S1:

\[ Y = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) + y_0 \]  

where \( A_n \) and \( \tau_n \) are the best-fit amplitudes and PL decay times, respectively. Under the low excitation fluence used here, the slight deviation from exponentiality seen in the PL decay curve of the pristine 3D perovskite film is attributed mainly to PL quenching by trap-assisted recombination associated with defects at the surface and in the bulk of the perovskite layer.\(^{38}\) The lifetime of the longer-lived PL component is extended from 2.9 \( \mu \)s for the pristine 3D perovskite film to more than 3.2 \( \mu \)s for all of the 3D/2D perovskite bilayer films, which appears independent of F4TCNQ modification of the 2D perovskite layer. This indicates that the 2D perovskite capping layer, either with or without F4TCNQ modification, reduces the rate of non-radiative recombination in the 3D perovskite layer, presumably as a result of passivation of the 3D perovskite surface defects at the 3D/2D perovskite interface. This builds on the work by Song et al. who showed that F4TCNQ passivates the surface of neat 3D perovskites.\(^{51}\)
Meanwhile, the proportion of the shorter-lived component that decays within 0.3 μs after excitation, increases concomitantly with increasing amount of F4TCNQ in the 2D perovskite layer. Given that the fast decay component in the TRPL of perovskites in the presence of a charge-transporting layer is typically associated with charge transfer,\textsuperscript{38, 39} we attribute this observed trend to an enhanced rate of charge transfer between the 3D perovskite and the 2D perovskite capping layers with increasing F4TCNQ content.

Having shown that the use of F4TCNQ as an additive within 2D capping layers on 3D perovskites results in changes to the structural, optical and interfacial properties of the system, we investigated the impacts of these changes on PSCs. As shown in Figure 4A, the solar cell architecture consisted of fluorine-doped tin oxide (FTO)/TiO\textsubscript{2}/m-TiO\textsubscript{2}/3D perovskite (with or without 2D perovskite capping layer)/Spiro-OMeTAD/Au configuration. The corresponding energy levels of the individual materials are included in Figure 4B,\textsuperscript{40} with the perovskite levels determined from their measured ionization energies (IE) using photoelectron spectroscopy (PESA) in air, see Figure S6, and their optical bandgap.\textsuperscript{40, 41}

Figure 4C, D show the current-voltage (J-V) characteristics and steady-state PCEs of the PSC devices, respectively. The 3D PSC shows \( J_{sc} = 21.3 \) mA cm\(^{-2} \), \( V_{oc} = 1.10 \) V, FF = 74.4\% and PCE= 17.5\% under a reverse-bias scan from 1.2 V to -0.1 V, with the corresponding steady-state PCE stabilising at 17.4\% within 300 s. Coating of a pristine 2D perovskite layer on top of the 3D perovskite film improves the PCE to 18.2\%, due to the enhancement in \( V_{oc} \) (1.11 V) and FF (76.6\%). The improvement of the \( V_{oc} \) and FF is attributed to a reduced non-radiative recombination loss at the interface between the perovskite layer and charge extraction layers.\textsuperscript{42}

This trend is further supported by the larger dark-current onset voltage for devices with perovskites comprising the 2D capping layer. Meanwhile, the introduction on an optimal 5\% w/w F4TCNQ sample (3D/2DF5), causes the \( J_{sc} \), \( V_{oc} \) and PCE of the PSC to be dramatically improved to 22.8 mA cm\(^{-2} \), 1.16 V and 20.1\%, respectively. Notably, these devices also exhibit
the lowest the series resistance ($R_s$) and highest shunt resistance values across the various 3D and 3D/2D systems. Forward and reverse scan J-V curves of these optimised devices, which exhibit negligible hysteresis, as well as incident-photons-to-current efficiency (IPCE) results of 3D/2D and 3D/2DF5 PSCs, are shown in Figure S7. Notably, the devices comprising 3D/2DF10 hybrid perovskite films exhibit slightly lower PCEs compared with 3D/2DF5 PSC. This is attributed to the accumulation of F4TCNQ additives on the perovskite film surface and/or structural variations of the 2D capping layer at the higher F4TCNQ concentrations, as discussed earlier. The distribution of device parameters are shown in Figure 4E-H and also summarized in Table 1. The average $J_{sc}$, $V_{oc}$, FF and PCE of 3D/2DF5 devices are 22.3 mA cm$^{-2}$, 1.15 V, 75.5% and 19.4%, respectively, with good reproducibility. These parameters are significantly better than those of 3D/2D PSCs without F4TCNQ additives at 21.4 mA cm$^{-2}$, 1.11 V, 75.1% and 17.3%, respectively.

To better understand the underlying differences that the 2D perovskite and F4TCNQ have on the PSC characteristics, charge-carrier dynamics were investigated using the transient photocurrent (TPC) technique. For these measurements, the devices were illuminated using a 200 µs square pulse of 525 nm LED light. By conducting TPC measurements at different light intensities, the turn-on and turn-off dynamics and charge trapping and de-trapping characteristics inside the device could be probed. Figure 5 shows the normalized TPC responses of the PCS devices at short circuit condition, with the raw TPC responses of these devices being included in Figure S8 of the supplementary information. The results show that the PSCs with 3D and 3D/2D architectures possess a rapid photocurrent component and a much slower secondary process with a rise time in the 100’s µs range. The introduction of the F4TCNQ additive into the 2D capping layer causes a dramatic enhancement of these slower rise-time dynamics to <20 µs at 20 mW cm$^{-2}$. This indicates enhanced charge extraction dynamics for these devices.
The existence of the slower rise time process in TPC measurements is suggestive of an imbalance between the charge carrier collection efficiencies and/or the presence of traps.\textsuperscript{45} We have shown that the 3D structure is unaffected by the inclusion of F4TCNQ in the 2D perovskite layer and that long-lived charge carriers exist in these devices. As such, it can be inferred that the origin of any differences in the rise-time dynamics arise due to the trapping of charges at the 3D/2D interface and/or the charge extraction through the 2D layer, rather than the bulk of the device. It is worth noting that the TPC risetime of the 3D/2D device is slower compared to the 3D or 3D/2DF5 devices. This is direct evidence of retarded charge extraction through the pristine 2D layer.\textsuperscript{46} We also observe a reduction in the risetime of the F4TCNQ-containing 2D layer devices at lower light intensities (Figure S8). This suggests that shallow traps in these devices do exist, but are readily filled under low-light conditions. For completeness we note that excessive F4TCNQ in the 3D/2DF10 device leads to an overshoot in the turn-on of TPC curves (Figure S9). This may be ascribed to the redistribution of the internal electric field in the device due to trapping of charges by aggregated F4TCNQ, which would suppress charge extraction between the 3D and 2DF10 perovskite layers.\textsuperscript{45} Such a finding is consistent with the performance decrease of 3D/2DF10 devices.

Meanwhile, the turn-off dynamics of the TPC curves consist of an initial fast decay component, which originates from the collection of free charge carriers, and a long-lived photocurrent tail corresponding to the collection of slower mobile carriers (see Figure 5D). The pristine 2D perovskite capping layer exhibits an enhanced proportion of the long carriers (beyond $\sim 250$ $\mu$s) compared to both the 3D and modified 2D interfaces. This can be ascribed to hole accumulation at the 3D/2D interface. Thus, although the charge recombination at the 3D perovskite surface has been reduced due to passivation by the 2D perovskite capping layer, charge collection from the perovskite to the Spiro-OMeTAD/Au electrode is restricted by the neat 2D capping layer. It is also clear that the fast decay component is accelerated following
the introduction of the modified and unmodified 2D perovskite layers, with the magnitude of this fast decay component being increased upon F4TCNQ addition. This indicates that the modified 2D perovskite capping layer improves hole extraction from the perovskite, likely due to a better passivated interface between the 3D and 2D perovskites, as well as more efficient transport through the 2D layer. These results are in agreement with those from TRPL measurements which suggested a passivation of the 3D surface by the 2D perovskite and a further enhanced hole transfer from the 3D to the 2D perovskite upon F4TCNQ addition.

The recombination and charge-transfer dynamics were further investigated by using impedance spectroscopy measurements under 1-sun illumination at various applied voltages near open circuit conditions (Figure S10, Table S2-4). These measurements yield the total recombination resistance ($R_{\text{rec}}$) in the device, which is related directly to the recombination at the interface of the perovskite. The experimental results show that for voltages greater than 0.8 V (i.e. beyond the device maximum power-point), the $R_{\text{rec}}$ value decreases exponentially with increasing applied voltage, indicating a dominant (non-radiative) bimolecular recombination process in this voltage regime. Of the samples studied here, the 3D/2DF5 PSC showed larger recombination resistance values as compared to those fabricated with either pristine 3D or 3D/2D perovskites. This is indicative of a suppression to the interfacial recombination process by the F4TCNQ additive. The observed results are consistent with the PSC device characteristics, where the introduction of the 2D perovskite capping layer and F4TCNQ additive improves the $V_{\text{oc}}$.

Based on the above observations, we schematically depict the proposed charge collection mechanisms across the different PCSs studied here in Figure 6. For the pristine 3D perovskite (Figure 6A), trap states at the interface with spiro-OMeTAD result in charge recombination losses (Figure 6B). Application of a thin 2D perovskite capping layer grown in-situ (Figure 6C) passivates the 3D perovskite surface, while concurrently inducing shallow traps within the
2D and/or at the 3D/2D interface. These shallow traps are active near the short-circuit conditions of these devices, hindering the achievable $J_{sc}$. Near open-circuit conditions, the presence of the 2D layer helps in the suppression of non-radiative recombination channels, as observed from impedance measurements. As a result, devices fabricated using 3D/2D perovskites exhibit an enhanced $V_{oc}$ compared to their 3D counterparts. Meanwhile, when F4TCNQ is introduced as an additive during the processing of the 2D layer, it simultaneously passivates the 3D perovskite surface and the 2D domains (Figure 6E and 6F). This results in improved charge transfer and charge extraction efficiency of the 3D/2DF5 devices, which yield higher overall PSC performance characteristics.

In addition to maximising efficiency, a key to the future prospects of PSCs is overcoming their operational instability. To this end, here we have measured the stability of the 3D, 3D/2D and 3D/2DF5 PSCs of unsealed devices for 30 days at room temperature and high humidity (~ 60% RH) conditions (Figure 7A). Moreover, in the inset photographs in Figure 7A we also show the changes in the bare perovskite films exposed to these same testing conditions. It is found that high humidity leads to fast degradation of perovskites, with the PSC of the 3D device degrading to 47% of its original PCE during the test period. This degradation is mainly reflected in a reduced $J_{sc}$ and FF (see Figure S11). The photographs of the 3D perovskite film exhibit changes from a brown to yellow colour, which reflects a decomposition from perovskite to PbI$_2$. In comparison, the 2D perovskite layer dramatically improves the PSC stability to 80% of the original PCE after the 30 days, with the F4TCNQ-modified 2D perovskite layer further improving this stability factor to 85%. Photographs of the 2D-capped perovskite films show that, while becoming slightly more opaque, their dark brown colour remains intact after the test period. This is clear evidence that these films are more resistant to moisture than 3D perovskites alone. To further support our claim, we conducted XRD measurement of various perovskite films stored under comparable environmental conditions to that mentioned above.
(see Figure 7BC). Based on the ratio of PbI₂ and 3D perovskite scattering peaks after 30 days of storage, it is evident that the ambient stability of the perovskite films follows $3D < 3D/2D < 3D/2DF5$. This confirms that the observed device PCE trends are fundamentally related to the modified structural stability of the perovskite films.

The origins of this moisture-resistance have been probed through contact angle measurements between water droplets and these perovskite films (see Figure S12). Compared with the neat 3D perovskite, the pristine 2D perovskite capping layer increases its contact angle from 42.5° to 51.8°, likely owing to the hydrophobic properties of the BA⁺ cation forming the 2D structure.²⁴ Addition of the fluorine-terminated F4TCNQ further increases the contact angle to 56.6°. This slightly improved hydrophobicity may be the origin of the slightly enhanced stability under the high humidity environment.⁸

CONCLUSION

In this study we have developed a unique and facile interfacial engineering approach that has enabled the performance and stability of 3D/2D perovskite solar cells to be improved. The molecular additive F4TCNQ was used to modify the 2D perovskite capping layer without altering the 3D perovskite crystal properties. The strong electron-acceptor characteristic of F4TCNQ enabled it to undergo partial charge transfer with the perovskite, which stabilised the surface to reduce the degree of interfacial non-radiative recombination and improved charge extraction characteristics from the bulk perovskite to the 2D perovskite layer. These enhancements resulted in PSCs with 2D perovskite capping layers modified with F4TCNQ exhibiting device efficiencies of $>20\%$, which represents a relative increase compared to neat 3D and 3D/2D perovskite structures by 13% and 10%, respectively. In addition to the improvements device efficiency, the long-term stability of PSCs with F4TCNQ was also enhanced. It is envisaged that the universal nature of this additive approach lends itself to be
adopted in other perovskite-based optoelectronics, where achieving high efficiency and maximising stability are also paramount.

EXPERIMENTAL SECTION

Materials. FTO coated glass was purchased from Latech Scientific Supply; BAI, formamidinium iodide (FAI), methylammonium bromide (MABr) and TiO$_2$ nanoparticle paste (NR30) were purchased from Greatcell Solar; lead iodide (PbI$_2$) and lead bromide (PbBr$_2$) were purchased from Alfa Aesar; F4TCNQ and 2,2’;7,7’-Tetrakis[N,N-di(4-methoxyphenyl)amino]9,9’-spirobifluorene (Spiro-OMeTAD) were purchased from Lumtech; all other chemicals were purchased from Sigma-Aldrich. All chemicals were used as received without any further purification.

Fabrication of PSC Devices. FTO coated glass substrates were cleaned using a three-stage sonication process in hellmanex, water and ethanol. The dense TiO$_2$ blocking layer was formed by an ultrasonic spray pyrolysis of a Ti(acac)$_2$OiPr$_2$ solution at 500 °C, as we reported previously.$^{53}$ For the mesoporous layer, a commercial 30 nm TiO$_2$ nanoparticle paste (NR30) was diluted in ethanol (1:6 vol) prior to spin-coating on the dense TiO$_2$ blocking layer at 4000 rpm for 20 s in air and then annealed at 500 °C for 30 mins. Then the following processes were carried out in a N$_2$ filled glovebox. Deposition of the perovskite layer was carried out by a modified method to that reported in literature.$^{54}$ Typically, C$_{30.08}$FA$_{0.79}$MA$_{0.16}$PbI$_{2.49}$Br$_{0.51}$ precursor solution (1.32 M) was prepared by dissolving FAI (1 M), PbI$_2$ (1.1 M), MABr (0.2 M) and PbBr$_2$ (0.22 M), CsI (0.065 M) in anhydrous DMF:DMSO=4:1(vol.). The perovskite films were deposited onto the TiO$_2$ mesoporous substrates with a two-step spin coating procedure. The first step involved 1000 rpm for 5 s with an acceleration of 200 rpm s$^{-1}$. The second step was conducted at 6000 rpm for 20 s with a ramp-up of 1000 rpm s$^{-1}$. Chlorobenzene (200 µL) was deposited on the spinning substrate during the second spin-coating step at 5 s
before the end of the procedure. The substrates were then immediately transferred to a hotplate and heated at 110 °C for 50 min. To grow the 2D perovskite layer, a 5 mg mL\(^{-1}\) (or ~25 mM) BAI in isopropanol (IPA) solution with various concentration of F4TCNQ was prepared then stirred for 24h prior to use. The solution was spin-cast on ready-made 3D perovskite substrates using dynamic spinning at 6000 rpm for 20s and then annealed at 100 °C for 10 min. Subsequently, a ready-prepared Spiro-OMeTAD solution with additives (FK 209 Co(III) PF6 salt, Lithium bis(trifluoromethanesulfonyl)imide and 4-tert-Butylpyridine) was spin-coated on the perovskite layers at 3000 rpm for 30s as widely reported.\(^{54}\) Finally, the films were placed under a vacuum of 2 ×10\(^{-6}\) Pa, then 80 nm thick Au films were evaporated using an evaporation rate of 2 Å s\(^{-1}\) as the top electrode. Devices were covered by aluminium foil and stored in a dry-box for 2 days before testing.

**Characterization.** Absorption spectra were characterized by a Perkin Elmer Lambda 950 UV/VIS/NIR spectrophotometer. Top-view morphology were characterized by the FEI Magellan scanning electron microscope. X-ray powder diffraction (XRD) patterns were recorded using a D2 phaser X-ray diffractometer with Cu Kα radiation. Grazing angle FTIR (GA-FTIR) spectra were recorded with Spectrum 100 FTIR spectrometer.

The GIXRD measurements were conducted at the SAXS/WAXS beamline of the Australian Synchrotron. 12 keV photons, with a grazing incidence angle of 0.13°, were used and recorded on a Pilatus 1 m detector placed ≈24 cm from the sample position. Steady-state photoluminescence measurements were performed using a Fluoromax4 Spectro fluorometer. Samples were illuminated using a 465.8 nm excitation source. Slit widths were set to 1.2 nm and the samples were excited for a duration of 1 μs. Transient photoluminescence decay measurements were performed using an Edinburgh Instruments Ltd. FLSP920 time correlated single-photon counting spectrometer equipped with a 465.8 nm pulsed diode laser excitation source (EPL-475, Edinburgh Instruments Ltd.) operating at 50 kHz, with ~100 ps pulse width.
and a peak laser excitation density of ~0.2 nJ cm$^{-2}$. Luminescence was collected using a grating monochromator. Samples were prepared on 1cm ×1cm glass microscope slides without encapsulation. Both excitation and luminescence collection were performed on the perovskite side.

The J–V curve characteristics of completed solar cell devices were recorded using a Keithley 2400 Source Meter. The devices were illuminated using a Xenon lamp source (100 mW cm$^{-2}$) provided by an Oriel solar simulator with an AM1.5G filter. A non-reflective mask with an aperture of 0.16 cm$^2$ was used to keep the irradiation area constant.

Incident photon to current conversion efficiency (IPCE) spectra were recorded using a Keithley 2400 Source Meter under 300 W xenon lamp irradiation with an Oriel Corner-stone 260¼ m monochromator. The monochromatic photon flux was quantified through a calibrated silicon cell. For open-circuit voltage decay measurements, devices were illuminated with a 630 nm LED source with a switch-off response time of ≈20 µs. Voltage transients measured using an NI-DAQMX USB-6212 data acquisition card.

Impedance spectroscopy measurements were performed under 1 sun illumination using a white LED powered by a PP210 potentiostat. A Zahner Zennium electrochemical workstation ECW IM6 was used as a frequency response analyser.

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SUPPORTING INFORMATION

Fitting parameters of PL decay, SEM images with EDX mapping, GIWAXS patterns, GA-FTIR spectra, UV-Vis spectra, steady-state PL spectra, PESA spectra and contact angle images of perovskite films; J-V curves, IPCE spectra, raw TPC curves and impedance Nyquist plots with fitting parameters of devices; device parameters of stability testing; contact angle characterisation of perovskite films

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Figure 1 (A) The schematic of 3D/2D/F4TCNQ perovskite deposition. (B) Top-view SEM images of 3D, 3D/2D, 3D/2DF5 and 3D/2DF10 perovskite films.

Figure 2 (A) XRD results and (B) azimuthally-integrated GIWAXS of 3D, 3D/2D, 3D/2DF5 and 3D/2DF10 perovskite films.
**Figure 3** (A) UV-vis absorption and (B) TRPL spectra of 3D, 3D/2D and 3D/2D (with 1%, 5% and 10% F4TCNQ) perovskite films on glass slides. For TRPL measurements, excitation and PL detection was from the perovskite-coated side. Excitation wavelength = 466 nm; emission wavelength = 765 nm.
Figure 4 (A) Schematics of the solar cell device architecture and (B) corresponding energy level landscape. (C) J-V curves of PSCs measured under light and dark conditions, with (D) showing the steady-state PCE characterization. (E-H) Summarized solar cell parameters of 20 individual PSC devices with 3D, 3D/2D and 3D/2DF (1%, 5% and 10%) films.
Figure 5 Normalized photocurrent decay curves of PSCs with (A) 3D, (B) 3D/2D and (C) 3D/2DF5 perovskite films. (D) The semi-log TPC decay profiles of PSCs at 5.7 mW cm$^{-2}$. 
Figure 6 Schematic depiction of the electrical pathways and the corresponding interfacial structure of PSCs with 3D (A, B), 3D/2D (C, D) and 3D/2DF (E, F) perovskite films, respectively.
Figure 7 (A) Stability of unencapsulated devices with 3D, 3D/2D and 3D/2DF5 perovskite films under dark ambient environment with ~60% humidity for 30 days. The photo insets correspond to the initial (3D, 2D, 2DF5) and final perovskite (3D’, 2D’, 2DF5’) films. (B) XRD patterns of 3D’, 2D’ and 2DF5’, with (C) showing the intensity ratio of the PbI₂ and perovskite scattering peaks.
Table 1. Summarized parameters of PSCs corresponding to Figure 3. $R_{sh}$ and $R_s$ are obtained from the slopes of J-V curves at zero and over open circuit potential.

<table>
<thead>
<tr>
<th>Devices</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$R_{sh}$ (Ω cm$^2$)</th>
</tr>
</thead>
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<tr>
<td>3D</td>
<td>21.3 $^a$ (20.8±0.81)</td>
<td>1.10 (1.06±0.04)</td>
<td>74.4</td>
<td>17.5</td>
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<tr>
<td>3D/2D</td>
<td>21.4 (20.8±0.8)</td>
<td>1.11 (1.11±0.03)</td>
<td>76.6</td>
<td>18.2</td>
<td>5.01</td>
<td>1869</td>
</tr>
<tr>
<td>3D/2DF1</td>
<td>21.3 (21.4±0.6)</td>
<td>1.15 (1.11±0.05)</td>
<td>76.1</td>
<td>18.8</td>
<td>3.72</td>
<td>2160</td>
</tr>
<tr>
<td>3D/2DF5</td>
<td>22.8 (22.3±0.5)</td>
<td>1.16 (1.15±0.02)</td>
<td>76.0</td>
<td>20.1</td>
<td>3.70</td>
<td>2937</td>
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<tr>
<td>3D/2DF10</td>
<td>21.8 (21.3±0.7)</td>
<td>1.15 (1.14±0.02)</td>
<td>76.6</td>
<td>19.3</td>
<td>4.11</td>
<td>1486</td>
</tr>
</tbody>
</table>

$^a$ Parameters of the best device in each architecture.

$^b$ Mean values with standard deviation are calculated from the values obtained for 20 independent devices.